

CRYSTAL GROWTH OF HIGH-ENTROPY OXIDES

A Dissertation Presented for the
Doctor of Philosophy
Degree
The University of Tennessee, Knoxville

Matheus Pianassola
December 2022

Copyright © 2022 by Matheus Pianassola.
All rights reserved.

DEDICATION

To my family and close friends who have supported and encouraged me.

ACKNOWLEDGEMENTS

I would like to express my gratitude to my advisor Dr. Mariya Zhuravleva, Dr. Charles Melcher, and Dr. Luis Stand for mentoring me through my graduate school journey with their motivation and support. Thank you to my Ph.D. dissertation committee for their time and valuable suggestions, Dr. Mariya Zhuravleva, Dr. Charles Melcher, Dr. Veerle Keppens, Dr. Bryan Chakoumakos, and Dr. Jake McMurray. A special thanks to Mrs. Merry Koschan for patiently investing time in helping me develop my scientific communication skills and also for her important contribution to my research.

I would like to acknowledge the funding sources for their support. This work is supported by the National Science Foundation under the award DMR-1846935. I also acknowledge the financial support of Siemens Healthineers for their contributions to the Scintillation Materials Research Center. I am also thankful to the Center for Materials Processing for supporting the undergraduate students who worked on this project.

I would like to thank our collaborators from Oak Ridge National Lab (ORNL), Dr. Joerg C. Neuefeind, Dr. Jake McMurray, and Dr. Can Agca, for their support with melting point measurements and *in-situ* high-temperature neutron diffraction measurements. I'm also thankful to Dr. Bryan Chakoumakos, also from ORNL, for collaborating with single-crystal diffraction data collection and structure refinement. I also would like to thank Dr. Chris Benmore from Argonne National Lab (ANL) for collaborating with *in-situ* high-temperature X-ray diffraction measurements at the Advanced Photon Source (APS).

I would like to thank Dr. Michael Koehler for his assistance with powder X-ray diffraction measurements performed at the IIAM Diffraction Facility. I also would like to thank Dr. Molly McCanta and Dr. Allan Patchen for collaborating with the electron probe microanalysis measurements performed at the Electron Microprobe Laboratory in the Earth and Planetary Sciences Department - UTK.

I am fortunate to have had the undergraduate students Madeline Loveday, Marlena Alexander, and Joshua Safin working closely on this project. This work would not have been possible without their assistance. Some of the data presented here were collected by graduate students Kaden Anderson and Rebecca Lalk; thank you to both of them! I would like to thank the SMRC students who made my graduate school experience go more smoothly, Dr. Matt Loyd, Dr. Camera Foster, Dr. Josh Smith, Dr. Cordell Delzer, Eleanor Comer, Kaycee Gass, Daniel Rutstrom, Kim Pestovich, Kaden Anderson, Rebecca Lalk, Kate Joshi, Sarah Longworth, and Nathan Gillespie.

ABSTRACT

This dissertation advances the field of crystal growth of emerging high-entropy oxides with great potential for novel structural and functional properties. The high-temperature structural stability of high-entropy rare-earth (RE) sesquioxides (RE_2O_3) upon cooling from the melt was studied for the first time to inform crystal growth experiments. While high-entropy oxides are mainly synthesized as polycrystalline ceramics, this work demonstrates their practical crystal growth for further exploration. The micro-pulling-down (mPD) crystal growth of high-entropy RE sesquioxides (RE_2O_3), aluminates ($\text{RE}_3\text{Al}_5\text{O}_{12}$, REAlO_3 , and $\text{RE}_4\text{Al}_2\text{O}_9$), and perovskites ($\text{RE}'\text{RE}''\text{O}_3$) was demonstrated. Additionally, the scalable Czochralski (Cz) growth of aluminate crystals was explored. Compositions were formulated taking into consideration the type of RE and the average ionic radius (AIR) of the high-entropy compound. The correlation between phase formation and AIR is demonstrated as a first step towards developing a predictive capability for more complex compositions. The potential for the success of high-entropy scintillators was evaluated by growing and assessing the scintillation properties mPD Ce-doped garnet crystals.

The structural evolution of high-entropy oxides upon cooling from the melt was assessed via *in-situ* high-temperature neutron and X-ray diffraction on aerodynamically levitated samples. Melting point temperatures were determined via the cooling traces method. The effect of composition on phase formation was evaluated via powder and single-crystal X-ray diffraction (XRD). The microstructure and composition of crystal defects were evaluated with scanning electron microscopy and energy dispersive spectroscopy (SEM/EDS). The elemental distribution in the single crystals was determined via electron microprobe analysis (EPMA). The luminescence properties assessed for complex garnet scintillators include radioluminescence, photoluminescence, light yield, and afterglow.

The demonstration of the crystal growth of high-entropy oxides in this dissertation opens the door to further discovery and development of highly complex crystals. This work will inspire the investigation and unlock the full potential of such complex materials since the availability of single crystals will allow the assessment of unique properties that cannot be replicated in polycrystals. The field of aluminate optical crystals may benefit the most from the results presented in this dissertation since their high-entropy analogous crystals were the most promising in terms of optical quality and phase purity.

TABLE OF CONTENTS

CHAPTER ONE: INTRODUCTION	1
The technological and scientific significance of crystal growth	2
Growth of compositionally complex oxide crystals	2
Goals of this dissertation	4
Specific objectives	4
Original contributions to the field of materials science and crystal growth	5
Justification for crystal growth methods	5
The micro-pulling-down (mPD) crystal growth method	5
The Czochralski (Cz) crystal growth method	7
High-entropy oxide materials	10
High-entropy rare-earth sesquioxides	12
High-entropy rare-earth aluminates	15
Rare-earth perovskites	18
Crystal growth of high-entropy oxides	18
CHAPTER TWO: EFFECTS OF COMPOSITION ON MELTING POINT AND PHASE FORMATION OF HIGH-ENTROPY SESQUIOXIDES	21
Abstract	22
Introduction	22
Methods	23
Composition formulation	23
Sample preparation	25
Melting point qualitative evaluation	25
Phase composition analysis	25
Results and discussions	25
Qualitative evaluation of melting point	25
Effects of composition on phase formation	27
Conclusion	29
CHAPTER THREE: TUNING THE MELTING POINT AND PHASE STABILITY OF RARE-EARTH OXIDES TO FACILITATE THEIR CRYSTAL GROWTH FROM THE MELT	31
Abstract	32
Introduction	32
Methods	35
Composition formulation	35
Powder synthesis	35
Bead synthesis	35
Room-temperature X-ray diffraction	35
In-situ high-temperature neutron diffraction	35
Differential scanning calorimetry	36
Crystal growth	36
Electron probe microanalysis	37
Melting point measurements	37
Results and discussions	38

Structure of as-prepared samples	38
High-temperature structural stability upon cooling from the melt.....	40
Evaluation of phase stability in the range of 30–1300°C	42
Crystal growth	44
Melting temperatures in the (Lu,Y,Gd,Nd,La) ₂ O ₃ system.....	44
Elemental distribution profiles in the grown crystals	46
Conclusion	46
CHAPTER FOUR: IN-SITU HIGH-TEMPERATURE STRUCTURAL ANALYSIS OF HIGH-ENTROPY RARE-EARTH SESQUIOXIDES.....	49
Abstract.....	50
Introduction.....	50
Methods	52
Composition formulation	52
Powder synthesis	52
Room-temperature powder X-ray diffraction	52
Preparation of spherical bead samples	52
Structural evolution analysis with in-situ high-temperature X-ray diffraction	54
Results and discussion	54
Structure of the as-prepared powders	54
Structure of the as-prepared bead samples	56
Phase evolution upon cooling from the melt	56
Thermal expansion coefficient obtained from refined unit cell parameters ..	62
Conclusion	67
CHAPTER FIVE: CRYSTAL GROWTH AND ELEMENTAL HOMOGENEITY OF THE MULTICOMPONENT RARE-EARTH GARNET	
(Lu _{1/6} Y _{1/6} Ho _{1/6} Dy _{1/6} Tb _{1/6} Gd _{1/6}) ₃ Al ₅ O ₁₂	68
Abstract.....	69
Introduction.....	69
Methods	71
Starting materials	71
Crystal growth	71
Density measurements	72
Powder X-ray diffraction	72
Single-crystal X-ray diffraction	72
Electron Microprobe Analysis.....	74
Results and discussion	74
Grown crystals	74
Crystal Structure	74
Radial Distribution	77
Axial distribution	83
Conclusion	85
CHAPTER SIX: EFFECTS OF COMPOSITION AND GROWTH PARAMETERS ON PHASE FORMATION IN MULTICOMPONENT ALUMINUM GARNET CRYSTALS.....	86

Abstract.....	87
Introduction.....	87
Methods	89
Compositions	89
Starting materials	89
Crystal growth	91
Optical microscopy	91
Scanning electron microscopy and energy dispersive spectroscopy.....	91
Powder X-ray diffraction	91
Single-crystal X-ray diffraction	91
Electron microprobe analysis	92
Results and discussion	92
Grown crystals	92
Phase formation and crystal structure	94
Radial elemental distribution	103
Inclusions on the outer surface of crystals	105
Conclusion	107
CHAPTER SEVEN: CRYSTAL GROWTH AND PHASE FORMATION OF HIGH-ENTROPY RARE-EARTH ALUMINUM PEROVSKITES.....	110
Abstract.....	111
Introduction.....	111
Methods	112
Composition formulation	112
Crystal growth	114
Powder X-ray diffraction	114
Single crystal X-ray diffraction.....	116
Scanning electron microscopy and energy dispersive spectroscopy.....	116
Results and discussion	116
Grown crystals	116
Phase formation and crystal structure	118
Radial elemental distribution in single-phase crystals	125
Distribution and composition of secondary phases	125
Conclusion	129
CHAPTER EIGHT: CRYSTAL GROWTH AND PHASE FORMATION OF HIGH-ENTROPY MONOCLINIC ALUMINATES.....	131
Abstract.....	132
Introduction.....	132
Methods	133
Composition formulation	133
Crystal growth	135
Powder X-ray diffraction	135
Annealing experiments	135
Electron probe microanalysis	135
Results and discussion	137

Grown crystals	137
Crystal structure via powder X-ray diffraction.....	137
Dark surface features in crystals 2 and 4.....	140
Conclusion	144
CHAPTER NINE : CRYSTAL GROWTH AND PHASE COMPOSITION OF RARE-EARTH PEROVSKITES	145
Abstract.....	146
Introduction.....	146
Methods	149
Composition formulation	149
Crystal growth	149
Powder X-ray diffraction	149
Scanning electron microscopy and energy dispersive spectroscopy	150
Electron Microprobe Analysis.....	150
Radioluminescence measurements	150
Annealing study.....	150
Results	150
Grown crystals	150
Powder X-ray diffraction	152
Inclusions: microstructure and elemental composition	152
Elemental distribution in La(Lu,Yb,Tm,Er,Y)O ₃ :Ce.....	155
Radioluminescence	155
Conclusion	161
CHAPTER TEN: CZOCHRALSKI GROWTH AND CHARACTERIZATION OF THE MULTICOMPONENT GARNET (Lu _{1/4} Yb _{1/4} Y _{1/4} Gd _{1/4}) ₃ Al ₅ O ₁₂	162
Abstract.....	163
Introduction.....	163
Methods	165
Materials and crystal growth	165
Optical microscopy	166
Optical transmission	166
Powder X-ray diffraction	166
Single-crystal X-ray diffraction	166
Electron probe microanalysis	168
Scanning electron microscopy and energy dispersive spectroscopy	168
Results and discussion	168
Grown crystal and macroscopic defects	168
Crystal structure	170
Elemental distribution	174
Inclusions: microstructure and elemental composition	178
Conclusion	181
CHAPTER ELEVEN: SCINTILLATION PROPERTIES OF CE-DOPED (Lu,Y,Tb,Gd) ₃ Al ₅ O ₁₂ MICRO-PULLING-DOWN CRYSTALS	183
Abstract.....	184

Introduction.....	184
Methods	185
Composition formulation	185
Crystal growth	186
Sample preparation	186
Absorbance	186
Radioluminescence	186
Photoluminescence	186
Light yield.....	187
Afterglow.....	187
Results	187
Grown crystals	187
Absorbance	189
Photoluminescence	189
Radioluminescence	189
Light yield.....	193
Afterglow.....	193
Conclusion	193
CHAPTER TWELVE: CONCLUSION.....	196
Structural stability and melting point of high-entropy oxides.....	197
Crystal growth of RE-based oxides.....	197
The potential of high-entropy garnet scintillators	197
Future investigation.....	198
High-entropy sesquioxides RE_2O_3	198
High-entropy aluminates $\text{RE}_3\text{Al}_5\text{O}_{12}$, REAlO_3 , and $\text{RE}_4\text{Al}_2\text{O}_9$	198
High-entropy RE perovskites $\text{RE}'\text{RE}''\text{O}_3$	199
REFERENCES	200
VITA	230

LIST OF TABLES

Table 2.1 - High-entropy RE ₂ O ₃ compositions with respective average ionic radii.	24
Table 2.2 - Chemical composition, average ionic radius, and phase composition of high-entropy rare-earth sesquioxides.	30
Table 3.1 - List of trivalent rare-earth cations and their respective ionic radius ..	34
Table 3.2 - List of high-entropy RE sesquioxides compositions and their respective average ionic radius.....	34
Table 4.1 - List of RE ³⁺ cations, their respective ionic radius, and the average ionic radius.....	53
Table 4.2 - Coefficients of thermal expansion (CTE) for each lattice axis of the B- or H-type unit cells for compositions 1 and 2	65
Table 5.1 - A list of crystals grown with respective pulling rates and molten zone depths.....	73
Table 5.2 - Single-crystal X-ray diffraction data collection and refinement parameters.....	78
Table 5.3 - Fractional atomic coordinates and equivalent isotropic displacement parameters.....	79
Table 6.1 - List of compositions with respective stoichiometric coefficients for each RE element.....	90
Table 6.2 - Phase composition obtained from Rietveld refinement	99
Table 6.3 - Single-crystal X-ray diffraction data collection and refinement parameters.....	101
Table 6.4 - Fractional atomic coordinates and equivalent isotropic displacement parameters.....	102
Table 6.5 - EDS elemental composition of crystal J	108
Table 7.1 - List of RE ³⁺ cations ordered from small to large ionic radius [124] and crystal structure [227] of the respective single-RE REAlO ₃ compounds.	113
Table 7.2 - List of compositions and the respective number of REs that form each of the four structures.....	115
Table 7.3 - Lattice parameters and phase fraction of crystals A-F obtained via Rietveld structure refinement	121
Table 7.4 - Single-crystal X-ray diffraction data collection and refinement parameters.....	126
Table 7.5 - Fractional atomic coordinates and equivalent isotropic displacement parameters.....	127
Table 7.6 - Elemental composition of crystal F (Lu,Nd,Pr,Ce,La)AlO ₃	130
Table 8.1 - List of rare-earth cations and their respective ionic radius [124].	134
Table 8.2 - List of high-entropy RE ₄ Al ₂ O ₉ compositions	136
Table 8.3 - EPMA elemental composition data for crystal 2.	142
Table 9.1 - Elemental composition of crystal La(Lu,Yb,Tm,Er,Y)O ₃	157
Table 10.1 - (Lu _{1/4} Yb _{1/4} Y _{1/4} Gd _{1/4}) ₃ Al ₅ O ₁₂ Czochralski crystal portions and respective dimensions.	167

Table 10.2 - Singe-crystal X-ray diffraction data collection and refinement parameters.....	175
Table 10.3 - Fractional atomic coordinates and equivalent isotropic displacement parameters.....	176
Table 10.4 - EDS elemental composition results for areas 1-6	180

LIST OF FIGURES

Figure 1.1 - KDN Dai-Ichi Kiden micro-pulling-down growth station	6
Figure 1.2 - Schematic representation of the mPD crystal growth setup	8
Figure 1.3 - Schematic representation of the bottom of the Ir crucible	8
Figure 1.4 - Cyberstar Oxypuller 05-03 Czochralski growth station	9
Figure 1.5 - Schematic representation of the Cz crystal growth setup.	9
Figure 1.6 - Schematic representation of the Cz melt reservoir	11
Figure 1.7. Schematic representation of the field of compositionally complex oxides [41].	11
Figure 1.8 - Polymorphic transformation of the lanthanide sesquioxides.....	13
Figure 1.9 - Schematic representation of the unit cell of RE_2O_3	14
Figure 1.10 - Sesquioxide crystals grown by the mPD method.....	14
Figure 1.11 - Reported high-entropy sesquioxide samples.....	16
Figure 1.12 - Schematic representation of the unit cell of RE aluminates.	16
Figure 1.13 - Aluminate crystals grown by the mPD method.	19
Figure 1.14 - Schematic representation of the $\text{RE}'\text{RE}''\text{O}_3$ orthorhombic unit cell.	19
Figure 2.1 - Melting point of single-RE RE_2O_3 as a function of RE atomic number [56].	24
Figure 2.2 - Photos of samples a-d after the crystal growth attempt.	26
Figure 2.3 – Photos of samples 1-6 after growth experiments.	28
Figure 2.4 - Room-temperature powder XRD patterns	28
Figure 3.1 - Schematic diagram of polymorphic transformations for single-RE RE_2O_3	39
Figure 3.2 – Room temperature powder XRD patterns.	39
Figure 3.3 - In-situ high-temperature neutron diffraction data and Rietveld refinement results.....	41
Figure 3.4 - The lattice parameter of the C-type structure	43
Figure 3.5 - Differential scanning calorimetry (DSC) curves were measured on as-prepared bead samples in air.	43
Figure 3.6 - Photos of samples 1, 2, and 3 after the growth attempt.	45
Figure 3.7 - Measured melting points of compositions from the system of composition 3 ($\text{Lu}, \text{Y}, \text{Gd}, \text{Nd}, \text{La}$) $_2\text{O}_3$	45
Figure 3.8 - EPMA radial concentration profiles of the seed end (left) and the tail end (right) of crystal 2.	47
Figure 3.9 - EPMA radial concentration profiles of the seed end (left) and the tail end (right) of crystal 3.	47
Figure 4.1 - Room-temperature powder XRD patterns of the as-prepared powders.	55
Figure 4.2 - Schematic diagram of polymorphic transformations for single-RE RE_2O_3 as a function of temperature and RE ionic radius.....	57
Figure 4.3 - Room-temperature synchrotron X-ray diffraction patterns and Rietveld refinement results	58
Figure 4.4 - <i>In-situ</i> high-temperature X-ray diffraction patterns of 1 ($\text{Lu}, \text{Y}, \text{Ho}, \text{Nd}, \text{La}$) $_2\text{O}_3$	59

Figure 4.5 - Schematic representation of phase transitions observed upon cooling from the melt	59
Figure 4.6 - <i>In-situ</i> high-temperature X-ray diffraction patterns of 2 (Lu,Y, Ho,Nd,La) ₂ O ₃	61
Figure 4.7 - Lattice parameters of the B-type (a) and H-type (b) structures of 1 (Lu,Y, Ho,Nd,La) ₂ O ₃	63
Figure 4.8 - Lattice parameters of the B-type (a) and H-type (b) structures of 2 (Gd,Eu,Sm,Nd,La) ₂ O ₃	66
Figure 5.1 - Single crystals of (Lu _{1/6} Y _{1/6} Ho _{1/6} Dy _{1/6} Tb _{1/6} Gd _{1/6}) ₃ Al ₅ O ₁₂	75
Figure 5.2 - Images of the molten zone monitored in real-time	75
Figure 5.3 – Powder XRD patterns of (Lu _{1/6} Y _{1/6} Ho _{1/6} Dy _{1/6} Tb _{1/6} Gd _{1/6}) ₃ Al ₅ O ₁₂ single-crystals	76
Figure 5.4 - The literature values of the lattice parameters of single-REAG	79
Figure 5.5 - EPMA radial elemental profiles of the 005-300 crystal	80
Figure 5.6 - EPMA radial concentration profiles	82
Figure 5.7 - Comparison of EPMA radial concentration profiles	84
Figure 6.1 - Photos of crystals grown from raw powders;	93
Figure 6.2 - Optical microscope images of 1-mm-thick radial sections	95
Figure 6.3 - a) Crystals grown from pre-synthesized powders;	96
Figure 6.4 - Powder XRD patterns of crystals grown from raw powders	97
Figure 6.5 - Powder XRD patterns of crystals H-J grown from pre-synthesized powders	100
Figure 6.6 - EPMA radial concentration profiles of crystals A (a) and J (b)	104
Figure 6.7 - SEM images of crystals C (a and c) and J (b and d)	106
Figure 7.1 - Photos of Ø3 mm cylindrical crystals.	117
Figure 7.2 - a) Powder XRD patterns of (a) crystals A and B	119
Figure 7.3 - Lattice parameters of orthorhombic single-RE REAlO ₃ (squares) from the literature	120
Figure 7.4 - Powder XRD patterns of (a) crystal C, an orthorhombic YAlO ₃ and an orthorhombic GdAlO ₃ reference patterns;	122
Figure 7.5 - Powder XRD patterns of (a) crystal F, an orthorhombic YAlO ₃ , an orthorhombic GdAlO ₃ , and a rhombohedral NdAlO ₃ reference patterns; (b) crystal G, a rhombohedral NdAlO ₃ , and an orthorhombic YAlO ₃ reference patterns	124
Figure 7.5 - Radial concentration profiles obtained with EPMA	128
Figure 7.6 – SEM images of a cross-sectional sample from crystal G (Lu,Nd,Pr,Ce,La)AlO ₃	128
Figure 8.1 - Photo of the high-entropy RE ₄ Al ₂ O ₉ crystals.	138
Figure 8.2 - Photo of the growing crystal 2 (Lu,Yb,Y,Tb,Gd) ₄ Al ₂ O ₉	138
Figure 8.3 - Powder XRD patterns of crystals 1-5	139
Figure 8.4 - Lattice parameters of crystals 1-5	141
Figure 8.5 - Micrograph of crystal 2 obtained via back-scattered electron imaging	142
Figure 8.6 - Samples from crystals 2 and 4	143

Figure 9.1 - Phase diagram of the $\text{La}_2\text{O}_3\text{-Yb}_2\text{O}_3$ system.	148
Figure 9.2 - Photos of the as-grown, undoped (Sm,Nd,Pr,Ce,La) LuO_3 (left) and La(Lu,Yb,Tm,Er,Y) O_3 (right) crystals.	151
Figure 9.3 - La(Lu,Yb,Tm,Er,Y) O_3 crystals doped with Ce (left), Pr (center), and Tb (right).	153
Figure 9.4 - Polished cross-sectional samples of La(Lu,Yb,Tm,Er,Y) O_3 crystals.	153
Figure 9.5 - a) Powder XRD pattern of (Sm,Nd,Pr,Ce,La) LuO_3	154
Figure 9.6 - SEM image of the La(Lu,Yb,Tm,Er,Y) O_3 crystal.....	156
Figure 9.7 – Radial elemental composition profiles of the La(Lu,Yb,Tm,Er,Y) $\text{O}_3\text{:Ce}$ crystal.	158
Figure 9.8 – Radioluminescence of the as-grown undoped and Ce-, Pr-, and Tb- doped La(Lu,Yb,Tm,Er,Y) O_3 crystals.	159
Figure 9.9 - Radioluminescence of the undoped and Ce-, Pr-, and Tb-doped La(Lu,Yb,Tm,Er,Y) O_3 crystals after oxidizing annealing.	159
Figure 9.10 - Radioluminescence of the undoped and Ce-, Pr-, and Tb-doped La(Lu,Yb,Tm,Er,Y) O_3 crystals.....	160
Figure 10.1 - Schematic representation of the $(\text{Lu}_{1/4}\text{Yb}_{1/4}\text{Y}_{1/4}\text{Gd}_{1/4})_3\text{Al}_5\text{O}_{12}$ crystal	167
Figure 10.2 - a) As-grown $(\text{Lu}_{1/4}\text{Yb}_{1/4}\text{Y}_{1/4}\text{Gd}_{1/4})_3\text{Al}_5\text{O}_{12}$ boule;	169
Figure 10.3 - Optical microscope images of internal defects in samples a) C1, b) C2, and c) C3.	171
Figure 10.4 - Optical image of inclusions in sample C3.....	171
Figure 10.5 - Optical transmission spectra.	172
Figure 10.6 - a) Powder XRD patterns of samples S, C1, C2, C3, C4, and T... ..	173
Figure 10.7 - EPMA radial concentration profiles of samples C1 (left), C2 (center), and C3(right).	177
Figure 10.8 - SEM image of an inclusion with a eutectic microstructure in sample C3.....	179
Figure 11.1 - Photo of cross-sectional samples of the crystals	188
Figure 11.2 - Absorbance spectra of crystals with Ce at 0 and 2 at%.	190
Figure 11.3 - Photoluminescence excitation (black) and emission (blue and red) monitored for Ce^{3+}	191
Figure 11.4 - a) Photoluminescence emission and excitation of the undoped crystal	192
Figure 11.5 - Radioluminescence spectra of undoped and Ce-doped crystals.	192
Figure 11.6 - Pulse height spectra of the $(\text{Lu,Y,Tb,Gd})_3\text{Al}_5\text{O}_{12}\text{:Ce}$ crystals.	194
Figure 11.7 - Afterglow profiles of $(\text{Lu,Y,Tb,Gd})_3\text{Al}_5\text{O}_{12}\text{:Ce}$ crystals.....	194

CHAPTER ONE: INTRODUCTION

The technological and scientific significance of crystal growth

Bulk single crystals are an important group of materials in practical applications and their synthesis via crystal growth is of great technological importance. Due to their continuous and highly ordered structure, single crystals possess unique electrical, optical, mechanical, and magnetic properties that cannot be replicated in polycrystals. A few examples of applications of single crystals include semiconductors, optical materials, hard materials for mechanical components, piezoelectric materials, magnetic materials, and gems [1]. The most relevant crystal growth methods include growth from the melt via the Czochralski, Bridgman-Stockbarger, and zone melting techniques; growth from solution via flux growth and hydrothermal growth techniques; growth from the vapor (more commonly applied to thin films) via chemical vapor transport and physical vapor transport methods [2].

Crystal growth plays a crucial role in the development of novel materials for scientific progress and economic growth. The search for improved materials is driven by the fact that “virtually every technology is materials-limited” [3]. Therefore technological progress depends on the discovery of enhanced materials. In the materials development process, the availability of single crystals allows the complete elucidation of properties and the achievement of full functionality. Many properties of crystalline materials depend on the direction in which a measurement is taken. Thus, the growth of single crystals is crucial for the measurement of such properties since polycrystalline samples provide only an average value as the directional dependence is masked. Another benefit of single crystals is the absence of grain boundaries since they contribute to electrical resistivity and act as light scattering centers, for instance [1].

Crystal growth is also an instrumental tool to support and validate computer modeling studies for the development of new complex materials. In the past few decades, significant progress was observed in the field of materials modeling and design via computational approaches [4]. The fundamental and functional properties of novel materials have been explored employing classical and quantum models. By now, the development of novel complex materials relies on computational modeling as an essential and promising pillar of materials science research. In the development of a novel material, the growth and the full characterization of a single crystal play an important role in informing a model. Since single crystals allow the assessment of properties that are unavailable in polycrystalline samples, crystal growth becomes essential for the validation and further improvement of a model [3].

Growth of compositionally complex oxide crystals

Compositionally complex oxides have been investigated in an effort to improve the existing materials and discover novel properties and applications.

Such oxides have multiple elements fractionally occupying the cation sublattices. In 2015, a report on the discovery of single-phase high-entropy oxides with five cations in equiatomic amounts demonstrated that highly complex compounds can be synthesized. This discovery has opened the door to the exploration of various polycrystalline complex oxides and materials with attractive properties have been identified. A few properties of high-entropy oxides include superionic conductivity [5], high dielectric constant [6], electrical and thermal conductivities [7], [8], reversible energy storage [9], magnetic [10]–[12], phosphorescence [13], and lasing properties [14].

At this early stage of development, the growth of bulk high-entropy oxide crystals is significantly limited and their full potential as bulk single crystals is not widely explored. Research on optical bulk crystals traditionally explores admixing no more than three cations to improve scintillation and lasing properties in aluminate crystals such as $(\text{Lu}, \text{Y}, \text{Gd})_3\text{Al}_5\text{O}_{12}$ [15]–[20] and $(\text{Lu}, \text{Gd})\text{AlO}_3$ [21]–[25]. A few complex laser borate crystals have also been reported with no more than three admixed cations such as in $(\text{La}, \text{Gd}, \text{Sc})_4(\text{BO}_3)_4$ [26]–[29]. These complex aluminates and borates were grown via directional solidification via the micro-pulling-down and Czochralski methods. The field of growth of thin films pioneered the exploration of high-entropy oxides in the single-crystal form. Structural, electronic, and magnetic properties have been explored in thin films of several compositions [7], [10], [11], [30]–[34]. The growth of high entropy pyrochlores such as $(\text{Yb}, \text{Tm}, \text{Lu}, \text{Ho}, \text{Er})_2\text{Ti}_2\text{O}_7$ was also recently demonstrated via directional solidification via the floating zone method [35], [36]. These novel complex pyrochlores were grown for the assessment of magnetic properties.

The growth of crystals from other complex compositional systems remains unexplored as well as the effects of composition and growth parameters on the structure and elemental distribution in single crystals. Therefore, two main research areas should still be explored. First, the effects of composition on phase formation and structural behavior of polycrystalline high-entropy oxides should be determined at a wide range of temperatures up to the melting point. This will inform the second research area by providing a deeper understanding of the phase transitions that complex oxides undergo when subjected to growth via directional solidification. In the second research area, the practical aspect of growing complex oxide crystals should be demonstrated using both laboratory-scale and scalable growth techniques. The use of both types of growth scales will allow for fast compositional screening and the evaluation of the scalability of the growth of complex crystals, respectively. Subsequential structural, compositional, and functional characterization of the grown crystals should then support the proof of concept and validate which growth parameters and compositions are best suitable for the growth of high-quality crystals.

Goals of this dissertation

This dissertation aims to advance the field of crystal growth of highly complex oxides by demonstrating the practical aspect of the growth of rare-earth-based oxides. The interest in such oxides is due to their potential application as optical materials as discussed later in this Introduction. Polycrystalline samples are prepared via a wet chemistry route and the effects of composition on their structural behavior are studied. Single crystals are grown via the laboratory-scale micro-pulling-down (mPD) method and the scalable Czochralski (Cz) method. The effects of composition and growth parameters on phase formation and elemental distribution of single crystals are studied. The scintillation properties of Ce-doped high-entropy crystals are also demonstrated.

Specific objectives

1) Determine how composition affects the structural behavior of polycrystalline high-entropy sesquioxides RE_2O_3 upon cooling from the melt. Here, RE represents an equiatomic mixture of five rare-earth elements.

2) Demonstrate the practical aspect of growing high-entropy crystals from the following systems using the mPD method.

a) High-entropy RE sesquioxides – RE_2O_3

b) High-entropy RE aluminates

i) Garnet – $\text{RE}_3\text{Al}_5\text{O}_{12}$

ii) Perovskite – REAlO_3

iii) Monoclinic – $\text{RE}_4\text{Al}_2\text{O}_9$

c) High-entropy RE perovskites – $\text{RE}'\text{RE}''\text{O}_3$

3) Demonstrate the scalability of the growth of high-entropy garnet ($\text{RE}_3\text{Al}_5\text{O}_{12}$) and perovskite (REAlO_3) aluminate crystals using the Cz method.

4) Determine how composition and average ionic radius affects phase formation and elemental distribution in the crystals.

5) Demonstrate the potential of Ce-doped high-entropy garnet crystals ($\text{RE}_3\text{Al}_5\text{O}_{12}$) as scintillators by growing and assessing the scintillation properties of mPD crystals.

Original contributions to the field of materials science and crystal growth

A list of original research efforts included in this dissertation is below.

- For the first time, the structural characterization of high-entropy oxides upon cooling from the melt is investigated using *in-situ* diffraction techniques on levitated samples. The effects of composition on melting point and polymorphic behavior are determined.
- The crystal growth of high-entropy RE sesquioxide, aluminates, and perovskites is demonstrated for the first time. Additionally, the effect of composition and mPD growth parameters on phase formation and elemental distribution is explored.
- The Cz technique is used for the first time to demonstrate the scalability of the growth of high-entropy oxides.
- The scintillation properties of a promising complex garnet scintillator containing four RE host elements are evaluated for the first time.

Justification for crystal growth methods

The **micro-pulling-down** (mPD) crystal growth method was chosen because it is an optimal technique for materials discovery and development [37]. This is because only a small amount of expensive raw materials (~1 g) is necessary to grow miniature single crystals. Additionally, the mPD method allows for relatively high growth rates (up to 20 mm/min), which is ideal for high throughput in composition screening studies.

The **Czochralski** (Cz) crystal growth method was chosen because it is a scalable method used in industry to grow functional materials such as semiconductors and optical crystals [38]. By using this technique, the scalability of the growth of high-entropy oxides can be tested, which will provide insight into their potential for large-scale production.

The micro-pulling-down (mPD) crystal growth method

The mPD method is a directional solidification technique that allows the growth of miniature crystals (~ 3 mm in diameter) with relatively fast pulling rates (up to 20 mm/min), which is ideal for materials development [37]. A photo of the mPD growth station installed at the Scintillation Materials Research Center (SMRC) at the University of Tennessee, Knoxville (UTK) is shown in Figure 1.1. As indicated in the figure, the main components of the setup are the growth chamber, the control panel, and the radiofrequency (RF) generator.



Figure 1.1 - KDN Dai-Ichi Kiden micro-pulling-down growth station installed at the SMRC-UTK. The numbers in the image indicate 1 - the growth chamber, 2 - the control panel, and 3 - the RF generator model TR-02001 operated at 26 kVA.

A schematic representation of the mPD growth setup is shown in Figure 1.2. Precursor powders of ~1-2 g are placed into small Ir or Re crucibles. Typical crucible geometries are 16 mm in diameter, with a cylindrical die/shaper of 3mm diameter and a capillary microchannel of 0.5 mm diameter at the bottom. The crucible is inductively heated to melt the precursor material.

Growth is initiated by touching the bottom outlet of the capillary channel with a seed and using the seed to pull down the melt. Seeds are usually made of previously grown crystals or an Ir pin when a crystal seed is not available. Controlled solidification of the melt is achieved by a thermal gradient maintained by an Ir after-heater placed at the bottom of the crucible. A molten zone is formed between the bottom of the crucible die and the solid-liquid interface. The melt is fed into the molten zone through the capillary channel and gravity prohibits the transport of melt upward back into the crucible. Therefore, rejected species cannot accumulate in the melt reservoir and segregate toward the outer surface of the molten zone. This results in a radial composition gradient in the crystal.

In the molten zone, buoyancy-driven melt convection is negligible due to the small volume of the molten zone (<300 μm in thickness) and Marangoni convection is the dominant mechanism for melt flow. Marangoni flow lines are shown in Figure 1.3. Marangoni melt flow appears close to the surface of the melt and originates from a gradient of surface tension. Surface tension decreases with increasing temperature, so Marangoni melt flow occurs from a “colder” to a “hotter” surface [37]. In the mPD molten zone, the bottom of the crucible die is hotter than the solid-liquid interface. Therefore, close to the surface of the melt, the melt flows toward the crucible.

The Czochralski (Cz) crystal growth method

The Cz method is also a directional solidification crystal growth method for larger crystals than the mPD method [38]. The typical growth period for research purposes is a few weeks and this method is commercially used for scalable growth. A photo of the Cz growth station installed at the SMRC-UTK is shown in Figure 1.4. As indicated in the figure, the main components of the setup are the growth chamber, the controller, and the radiofrequency (RF) generator.

A schematic representation of the Cz growth setup is shown in Figure 1.5. Iridium crucibles are used and their typical dimensions are ~ $\varnothing$ 60 mm and 60 mm in height. Precursor powder of ~700 g is placed into the crucible, which is inductively heated to melt the charge. Growth is initiated by touching the top surface of the melt with a rotating seed and slowly translating the seed upward. As the seed is slowly pulled out of the melt, the material solidifies and a crystal grows on the seed. Typical translation and rotation rates are 1 mm/h and 11 rpm.

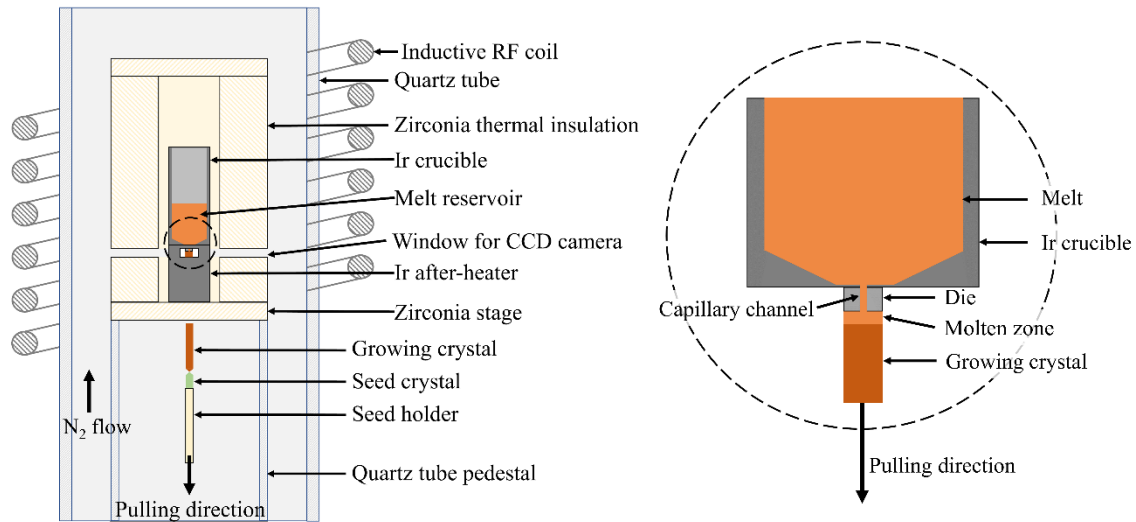


Figure 1.2 - Schematic representation of the mPD crystal growth setup (left). The circled region is shown in more detail on the right; the after-heater is omitted for simplicity [39]. The diameter of the crucible and die are 16 mm and 3 mm, respectively.

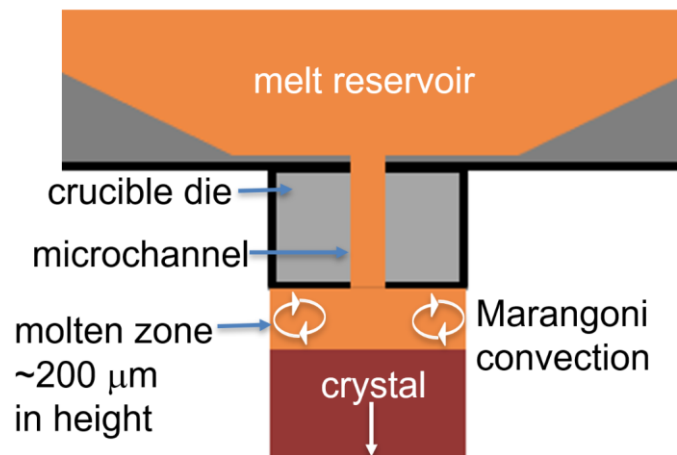


Figure 1.3 - Schematic representation of the bottom of the Ir crucible with the Marangoni convection flow lines indicated as white, curved arrows. The diameter of the crucible and die are 16 mm and 3 mm, respectively.

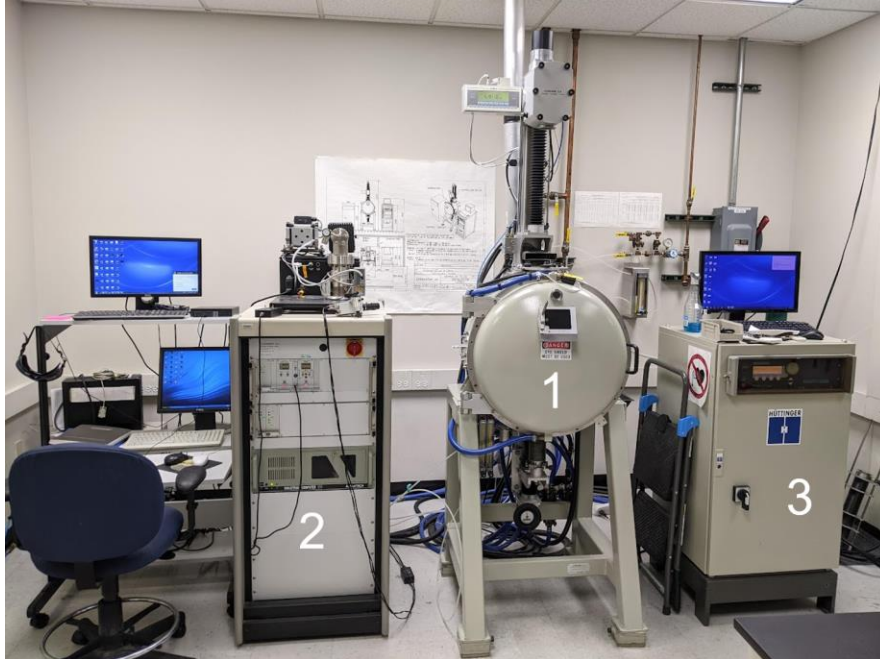


Figure 1.4 - Cyberstar Oxypuller 05-03 Czocharalski growth station installed at the SMRC-UTK. The numbers in the image indicate 1 - the growth chamber, 2 - the controller, and 3 - the Huttinger RF generator.

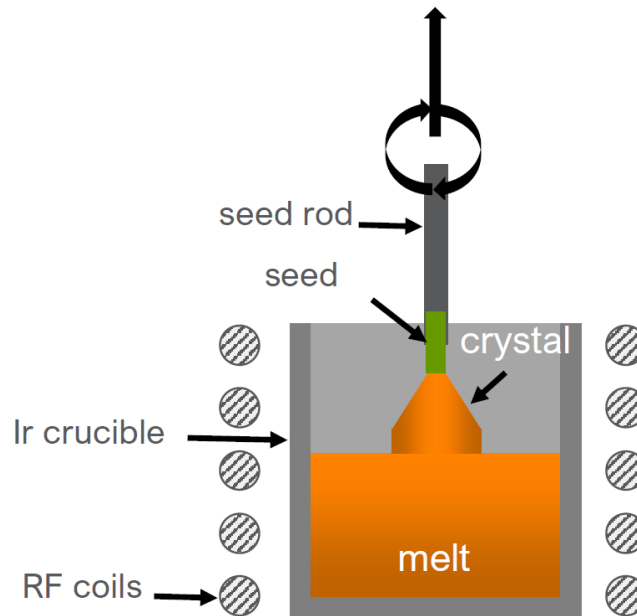


Figure 1.5 - Schematic representation of the Cz crystal growth setup.

Compared to the mPD method, the solid-liquid interface is in contact with a relatively larger volume of melt. Rejected species may stay in the melt reservoir, which results in an axial composition gradient in Cz crystals. Melt flow near the growth interface results from buoyancy-driven convection, Marangoni flow, and rotational forced convection [38]. A schematic representation of the melt flow in a Cz is shown in Figure 1.6. Buoyancy-driven convection is generated from a density gradient in the melt that results from a temperature gradient. Since the crucible is the source of heat, the melt at the bottom of the crucible is “hotter” and less dense than the melt close to the surface of the liquid. The Marangoni flow takes place close to the surface of the melt and its nature is discussed in the previous section. Finally, the rotational forced convection results from the rotation of the seed and the growing crystal. By adding this forced convection in the melt, better mixing is achieved close to the growth interface which favors a homogeneous elemental distribution in the crystal [38].

High-entropy oxide materials

High-entropy oxides are an emerging type of material with promising properties [40]. As seen in Figure 1.7, high-entropy oxides belong to a broader class of materials often called “compositionally complex oxides” [41]. This class of oxides includes the medium-entropy oxides that contain three or four cations in equiatomic amounts or mixtures of more cations in non-equiatomic amounts. Medium-entropy oxides have a configurational entropy S_{conf} in the range of $1 \leq S_{\text{conf}} \leq 1.5$ R/mol, where R is the universal gas constant. The high-entropy oxides contain five or more cations in equiatomic amounts and their configurational entropy is $S_{\text{conf}} > 1.5$ R/mol. Some compositionally complex oxides can be classified as “entropy-stabilized”, which refers to the formation of single phase that is stabilized by their medium- or high-entropy nature.

The investigation into complex oxides began as an effort to apply to ceramics the compositional concept of high-entropy alloys. In high-entropy alloys, five or more principal elements form a single-phase solid solution [42]. This multicomponent compositional design differs from that of traditional alloys, which are typically composed of one principal element and small amounts of alloying elements. Some high-entropy alloys have exceptional hardness [43], [44], tensile strength [45], [46], electrical resistivity [47], [48], superconductivity [49], [50], and magnetic properties [51], [52]. Inspired by the functionality of high-entropy alloys, the exploration of multicomponent oxides has revealed compounds with attractive superionic conductivity [5], high dielectric constant [6], electrical and thermal conductivities [7], [8], reversible energy storage [9], magnetic [10]–[12], phosphorescence [13], and lasing properties [14].

An entropy-driven phase stabilization has been identified in both high-entropy alloys and oxides [42], [53]. In these materials, the configurational entropy ΔS_{conf} is maximized by having n elements (usually, $n \geq 5$) in close to equiatomic

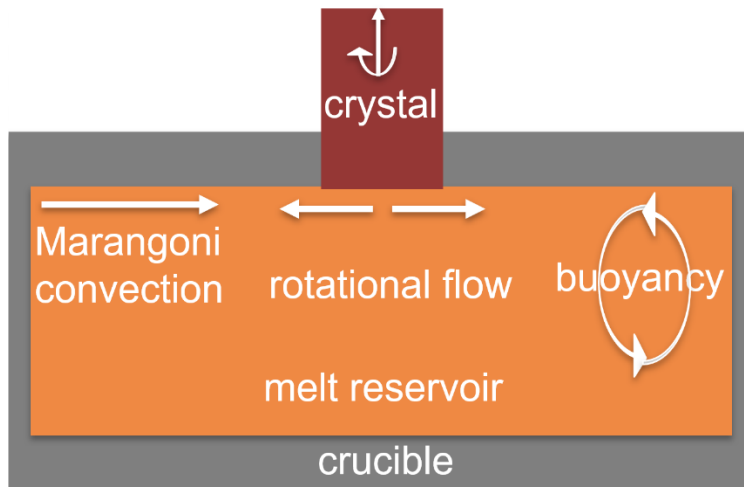


Figure 1.6 - Schematic representation of the Cz melt reservoir with Marangoni, rotational, and buoyancy melt flow lines.

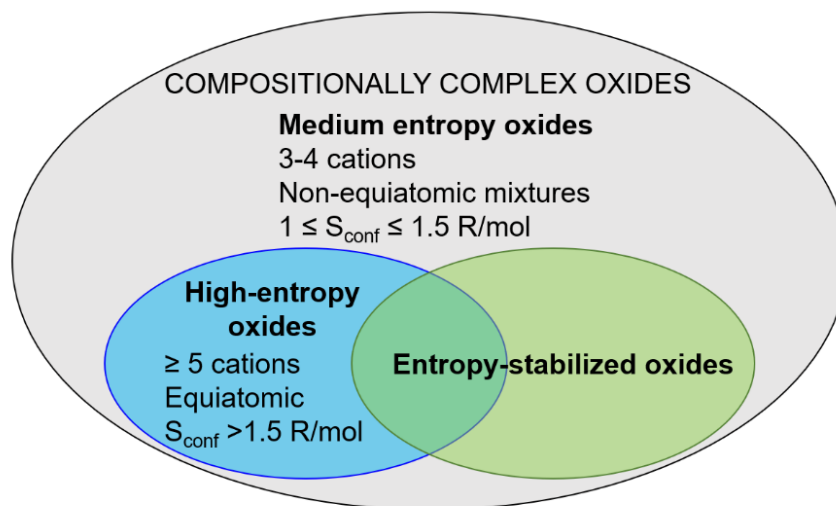


Figure 1.7. Schematic representation of the field of compositionally complex oxides [41].

amounts. Equations 1 and 2 show how ΔS_{conf} is maximized by equiatomic compositions, where x_i is the molar concentration of the i^{th} element and R is the gas constant. The maximization of ΔS_{conf} increases the entropy of mixing ΔS_{mix} , which minimizes the Gibbs free energy of mixing ΔG_{mix} at high temperatures T , as shown in Equation 3. Therefore, at high temperatures, a single phase is thermodynamically favored over a mixture of phases [42]. To maintain entropy-stabilized single phases at room temperature, high-entropy materials are usually quenched, which consists of rapid cooling from synthesis temperatures [42], [53].

$$\Delta S_{conf} = -R \sum_{i=1}^n x_i \ln x_i \quad \text{Equation 1}$$

$$\Delta S_{conf} = -R \left(\frac{1}{n} \ln \frac{1}{n} + \frac{1}{n} \ln \frac{1}{n} + \dots + \frac{1}{n} \ln \frac{1}{n} \right) = R \ln n \quad \text{Equation 2}$$

$$\Delta G_{mix} = \Delta H_{mix} - T \Delta S_{mix} \quad \text{Equation 3}$$

High-entropy rare-earth sesquioxides

The refractory and polymorphic nature of single-RE sesquioxides presents a challenge for crystal growth by directional solidification. All of the single-RE sesquioxide compounds melt above 2200°C [54], which surpasses the operating temperature of traditional iridium crucibles (2100°C)[55]. Additionally, solid-solid polymorphic phase transitions lead to cracking and hinder the growth of single crystals. Single-RE sesquioxides solidify from the melt with either an X (cubic, $Im\bar{3}m$) or H (hexagonal, $P6_3/mmc$) structure. Upon cooling, solid-solid phase transitions take place and below 2000°C three polymorphs are observed, the A (trigonal, space group $P\bar{3}m1$), B (monoclinic, $C2/m$), and C (cubic, $Ia\bar{3}$) structures [56]. A phase diagram of the polymorphic transformations in RE sesquioxides is seen in Figure 1.8. Schematic representations of the RE_2O_3 unit cells are shown in Figure 1.9. The high-entropy compositional approach may be promising to minimize the melting point and prevent polymorphic transitions by constraining a single entropy-stabilized phase [57].

To the best of our knowledge, high-entropy sesquioxides have only been synthesized as polycrystalline ceramics; however, crystal growth of one-cation sesquioxides has been reported. Doped Lu_2O_3 , Y_2O_3 , and Sc_2O_3 crystals have been investigated for lasing or scintillation applications. Due to the refractory nature of the sesquioxides, crucibles with a high melting temperature and chemical stability are necessary. Rhenium crucibles satisfy these requirements and are commonly used as a melt reservoir for the growth of sesquioxides. The directional solidification growth methods applied to grow Lu_2O_3 , Y_2O_3 , or Sc_2O_3 include mPD [58]–[61], Cz [62], [63], edge-defined film-fed [64], Nacken-Kyropoulos [65], Bridgman [66], and heat exchanger [67]–[69]. Figure 1.10 shows photos of

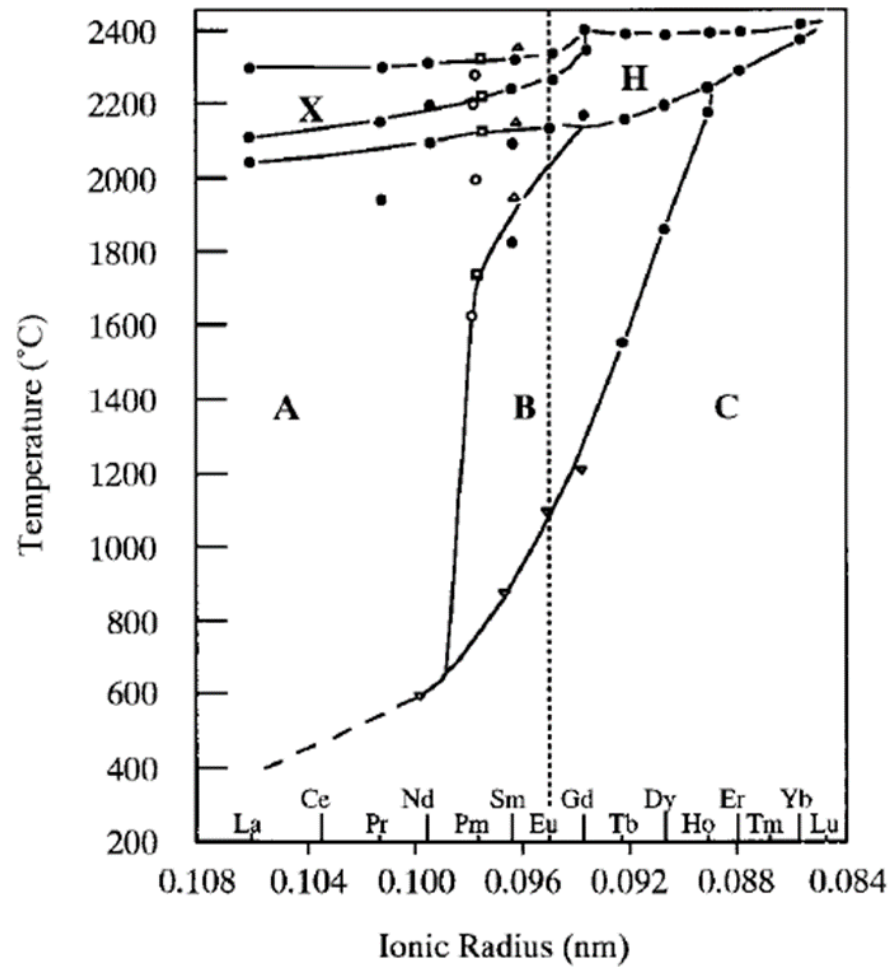


Figure 1.8 - Polymorphic transformation of the lanthanide sesquioxides. A – hexagonal, B – monoclinic, C – cubic, X – cubic, H – hexagonal [56]

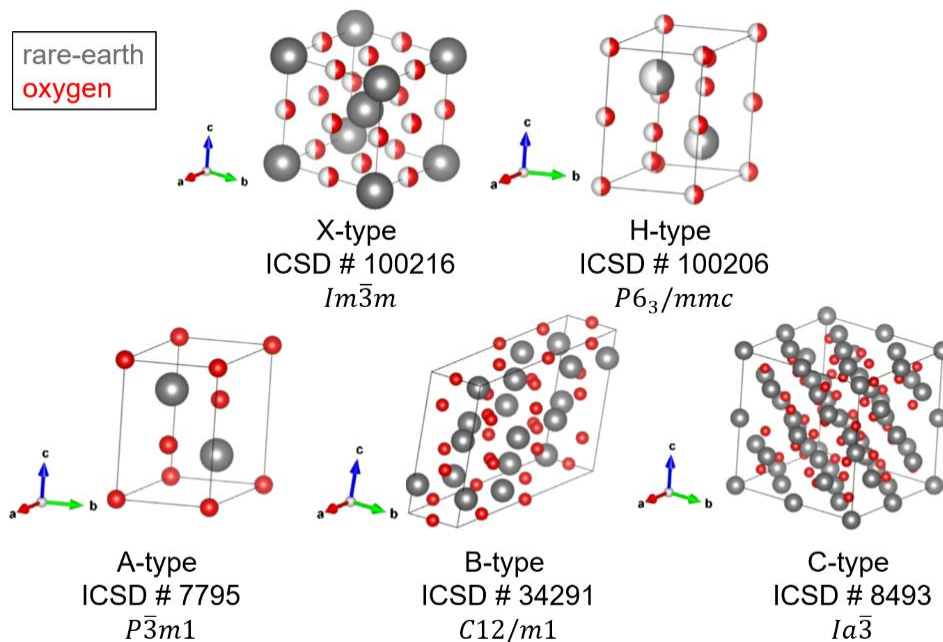


Figure 1.9 - Schematic representation of the unit cell of RE_2O_3 . Unit cells were generated with VESTA using Crystallographic Information Files (CIF) from the Inorganic Crystal Structure Database (ICSD). Half-filled spheres represent fractionally occupied lattice sites.



Figure 1.10 - Sesquioxide crystals grown by the mPD method. a) $Yb:Y_2O_3$ grown by the mPD method [58]. b) $Er:Lu_2O_3$ grown by the edge-defined film-fed method [64]. c) $Yb:Lu_2O_3$ grown by the heat exchanger method [69].

sesquioxide crystals grown by the mPD (a), edge-defined film-fed (b), and heat exchanger (c) methods.

In one of the pioneering reports on high-entropy oxides, Djenadic *et al.* [70] studied how the composition affected phase formation in high-entropy RE oxides of the system (Ce,Gd,La,Nd,Pr,Sm,Y)₂O₃. Commas in chemical formulas indicate equiatomic amounts of the REs; Y and Sc are referred to as REs for simplicity. Powders were produced via nebulized spray pyrolysis and the presence of Ce was identified as essential to the formation of a single fluorite phase. A picture of the (Ce,Gd,La,Pr,Sm,Y)₂O₃ sample is seen in Figure 1.11.a.

Pianassola *et al.* [71] also explored the system (Ce,Gd,La,Nd,Pr,Sm,Y)₂O₃ by producing ceramics via solid-state reaction. They demonstrated that compounds without Ce can be stabilized as single cubic bixbyite or monoclinic phases even when using slow cooling rates. Also, structures formed at initial synthesis may be converted to different ones by annealing in different atmospheres. A picture of the (Gd,La,Nd,Sm,Y)₂O₃ sample is seen in Figure 1.11.b.

Tseng *et al.* [57] reported on a single-phase high-entropy RE sesquioxide that does not contain Ce and does not undergo phase transitions after annealing followed by slow cooling. A (Gd,Tb,Dy,Ho,Er)₂O₃ ceramic was produced as a single cubic bixbyite phase by a wet chemistry method and the phase stabilization was attributed to the small cationic radii difference between the five RE elements, which was within 5%.

Zhang *et al.* [13] reported on a high-entropy (Lu,Y,Yb,Gd,Dy)₂O₃ transparent ceramic prepared via solid-state reaction, seen in Figure 1.11.c. High density and optical transparency were achieved. The authors demonstrated that complex oxides can be obtained as a highly transparent ceramic and explored the potential application as a multi-wavelength emission phosphor.

Ushakov *et al.* [72] performed thermal analysis on five-component sesquioxides and identified high-temperature phase transitions characteristic of one-RE sesquioxides. Samples of the system (La,Sm,Dy,Er,Nd,Gd,Y)₂O₃ were prepared via a wet chemistry method and had a single bixbyite phase. After laser melting followed by quenching, the samples had a single monoclinic phase. They found that the melting temperature of the multicomponent compound is higher than the constituent one-RE sesquioxides.

High-entropy rare-earth aluminates

In the RE₂O₃-Al₂O₃ systems, where RE represents a rare-earth element or Y, three compounds are formed with a garnet RE₃Al₅O₁₂, perovskite REAlO₃, or monoclinic RE₄Al₂O₉ structure [73], [74]. Schematic representations of the unit cells are shown in Figure 1.12. The garnet structure is cubic (space group *Ia $\bar{3}d$*)

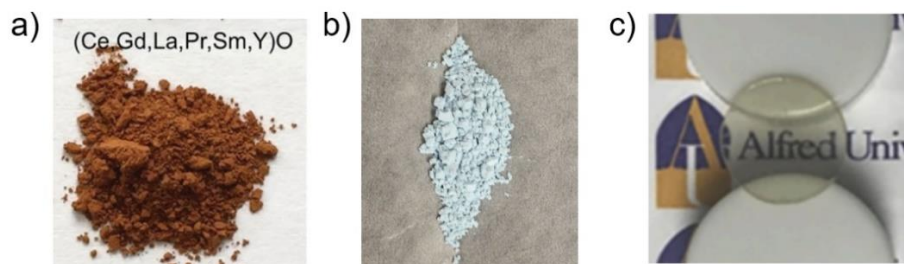


Figure 1.11 - Reported high-entropy sesquioxide samples. a) Single cubic phase $(\text{Ce,Gd,La,Pr,Sm,Y})_2\text{O}_3$ powder reported by Djenadic et al. [70] Single monoclinic phase $(\text{Gd,La,Nd,Sm,Y})_2\text{O}_3$ prepared by Pianassola et al. [71] c) $(\text{Lu,Y,Yb,Gd,Dy})_2\text{O}_3$ transparent ceramic prepared by Zhang et al. [13]

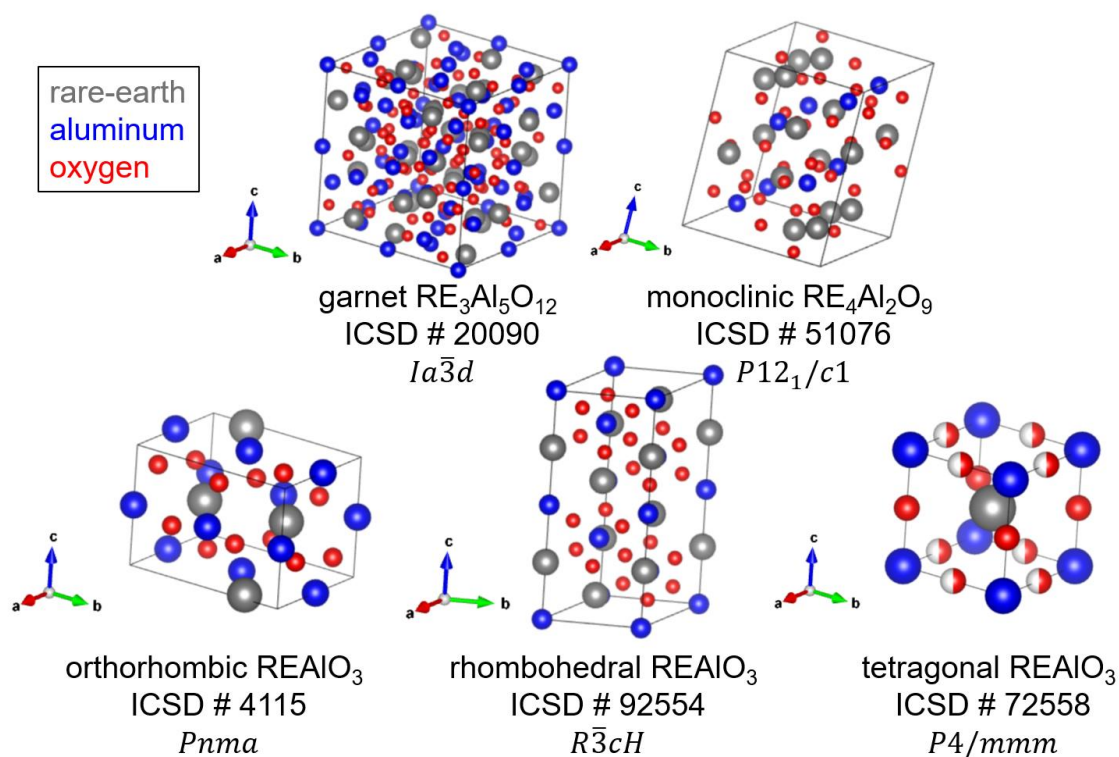


Figure 1.12 - Schematic representation of the unit cell of RE aluminates. Unit cells were generated with VESTA using Crystallographic Information Files (CIF) from the Inorganic Crystal Structure Database (ICSD). Half-filled spheres represent fractionally occupied lattice sites.

and is only thermodynamically stable for small RE = Eu-Lu. Garnets formed by RE = Eu-Tb melt incongruently, while those formed by RE = Dy-Lu melt congruently. The perovskite aluminates are orthorhombic ($Pnma$) for RE = Sm-Lu, rhombohedral ($R\bar{3}cH$) for RE = La, Pr, and Nd, and tetragonal ($P4/mmm$) for RE = Ce. All REs form thermodynamically stable perovskites and only Yb^{3+} and Lu^{3+} form incongruently melting perovskites. The monoclinic aluminates ($P12_1/c1$) are thermodynamically stable for RE = Pr-Lu. Monoclinic aluminates formed RE = Pm-Lu melt congruently. Melt congruency is essential for crystal growth by directional solidification so that the growing crystal has the same composition as the melt and no solid-solid phase transitions take place upon cooling.

Composition exploration of RE aluminate crystals reveals that multicomponent compositions may have attractive scintillation and lasing performance. The mPD method is usually used to rapidly identify optimized compositions. Crystals of various compositions can be readily available for characterization due to the relatively short time needed to grow crystals. Crystal properties are usually optimized by admixing two or three elements in the RE or Al sites [15]–[17], [24], [75]–[77]. Admixing multiple elements in the RE site might lead to further improvement of functional properties, which motivates the development of high-entropy aluminate crystals.

There are only a few reports on high-entropy RE aluminates. Zhao *et al.* [78] prepared a five-component perovskite powder (Y,Nd,Sm,Eu,Er)AlO₃ by a co-precipitation method. They reported promising thermal and environmental barrier properties for oxide/oxide composites. Chen *et al.* [79] reported on the thermal barrier properties of a five-component garnet ceramic (Y,Yb,Lu,Eu,Er)₃Al₅O₁₂ prepared by solid-state reaction. Zhao *et al.* prepared a high-entropy monoclinic aluminate (Nd,Sm,Eu,Y,Yb)₄Al₂O₉ and assessed its potential application as an environmental barrier coating [80].

Although most RE aluminum monoclinic compounds melt congruently, a high-temperature solid-solid phase transition hinders their growth via directional solidification. Differential calorimetry studies revealed that aluminum monoclinic compounds containing Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, or Y undergo phase transitions in the temperature range of 1000–1400°C [81], [82]. Dilatometry measurements indicate a volume expansion of the monoclinic unit cell upon cooling. Due to the lattice strain related to the phase transition, crystals grown by directional solidification become polycrystalline upon cooling.

Rare-earth aluminum garnet and perovskite crystals are widely grown by the Cz and mPD methods, while the growth of monoclinic crystals is not common. Cz aluminum garnet crystals containing Dy, Ho, Tm, Yb, Lu, and Y have been reported [83]–[87] as well as mPD crystals containing Yb, Lu, and Y [88]–[90]. One-RE aluminum perovskites of most of the REs have been successfully grown by the Cz method [91], [92], [101], [102], [93]–[100], while only aluminum perovskites of

La, Pr, Nd, Lu, and Y have been grown by the mPD method [77], [103]–[106]. Only a few reports demonstrate the growth of monoclinic crystals, including the Cz-grown $\text{Lu}_4\text{Al}_2\text{O}_9$ [107], and mPD-grown $\text{Y}_4\text{Al}_2\text{O}_9$ [108] and $\text{Lu}_2\text{Y}_2\text{Al}_2\text{O}_9$ [109]. Figure 1.13 shows photos of mPD-grown garnet (a), perovskite (b), and monoclinic (c) samples. The three samples have a well-controlled cylindrical shape; the garnet and perovskite crystals are transparent while the monoclinic sample is polycrystalline, which is likely due to the solid-solid phase transition discussed in the previous paragraph.

Rare-earth perovskites

In binary systems containing two RE sesquioxides $\text{RE}'_2\text{O}_3$ - $\text{RE}''_2\text{O}_3$, a RE perovskite compound $\text{RE}'\text{RE}''\text{O}_3$ can be formed when the difference in ionic radius of the RE^{3+} elements is greater than 0.20 Å [110]. In the general formula, RE'^{3+} has a larger ionic radius than RE''^{3+} . Rare-earth perovskites have an orthorhombic structure (space group *Pnma*); a schematic representation of the unit cell is in Figure 1.14. In the literature, RE perovskites are also referred to as “double oxides” [111] or “interlanthanide perovskites” [112]. The reported RE perovskites include LaRO_3 , where $R = \text{Lu, Yb, Tm, Er, Y, Ho, or Dy}$; CeXO_3 , where $X = \text{Lu, Yb, or Tm}$; PrZO_3 , where $Z = \text{Lu or Yb}$; and NdLuO_3 [112]–[114]. These compounds melt incongruently and first crystallize as an X-type sesquioxide when cooling from the melt [115]. A few reports demonstrate the growth of LaLuO_3 and similar compounds via the Czochralski [111], [113], [114], and flux growth methods [116]. These reports focus on the luminescence and structural properties of the crystals. Although not widely explored, this compositional system is attractive for scintillation applications due to its intrinsic high density and effective atomic number. These fundamental properties result in high stopping power for ionizing radiation, which increases the radiation detection efficiency of scintillators [114], [117]. Compositional engineering in complex $\text{RE}'\text{RE}''\text{O}_3$ crystals may result in attractive fundamental and functional properties. However, no high-entropy RE perovskites have been reported to the best of our knowledge.

Crystal growth of high-entropy oxides

It is important to consider the practical aspect of crystal growth when evaluating high-entropy oxides for applications such as lasing and scintillation. To date, there are only a few reports on the crystal growth of multicomponent oxides. The investigation of multicomponent crystals initially focused on thin films [7], [11], [30]–[32], [34], [118]. More recently, directional solidification methods have been applied to grow multicomponent oxides as bulk crystals. Reports focused on the floating zone growth of a RE pyrochlore $(\text{Yb}_{0.2}\text{Tb}_{0.2}\text{Gd}_{0.2}\text{Dy}_{0.2}\text{Er}_{0.2})_2\text{Ti}_2\text{O}_7$ [35] and the Cz growth of a calcium oxyborate $\text{Yb}_{0.19}\text{Y}_{0.34}\text{Lu}_{0.12}\text{Gd}_{0.35}\text{Ca}_4\text{O}(\text{BO}_3)_3$ [28].

The field of crystal growth of complex oxides is relatively new and knowledge gaps are still to be addressed. All reports on crystal growth of

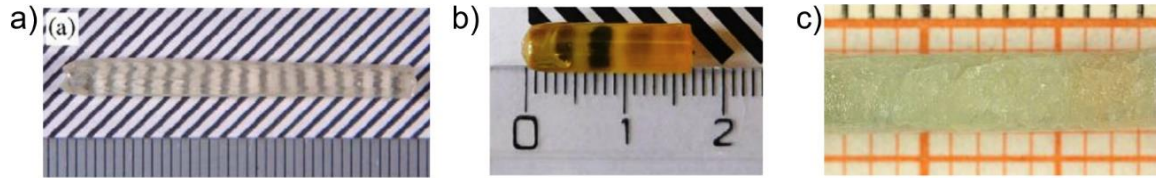


Figure 1.13 - Aluminate crystals grown by the mPD method. a) $\text{Pr}:\text{Y}_3\text{Al}_5\text{O}_{12}$ [89], $\text{Ce}:\text{LaAlO}_3$ [103], and $\text{Pr}:\text{Lu}_2\text{Y}_2\text{Al}_4\text{O}_9$ crystals [109].

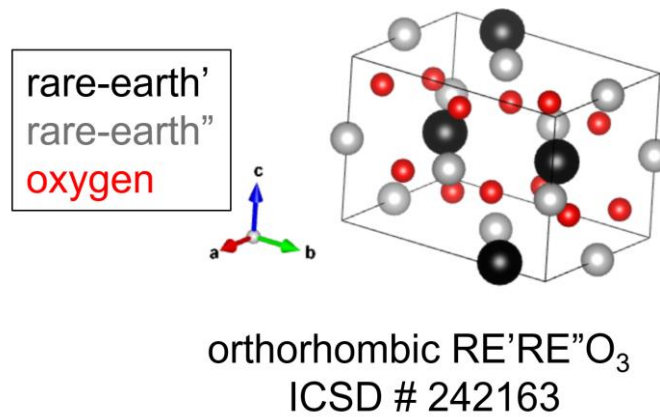


Figure 1.14 - Schematic representation of the $\text{RE}'\text{RE}''\text{O}_3$ orthorhombic unit cell.

multicomponent oxides focus on specific compositions and do not extensively explore various composition and growth parameters. To advance the knowledge in this field, it is important to determine how composition and growth parameters affect melt behavior, phase formation, optical quality, and elemental distribution of complex crystals.

**CHAPTER TWO:
EFFECTS OF COMPOSITION ON MELTING POINT AND PHASE
FORMATION OF HIGH-ENTROPY SESQUIOXIDES**

A version of this chapter was presented by Matheus Pianassola as an oral presentation.

M. Pianassola, J. Safin, C. Agca, J. W. McMurray, C. L. Melcher, and M. Zhuravleva, “Crystal growth and phase composition of high-entropy rare-earth sesquioxides”. Oral presentation delivered at the Materials Research Society Spring Meeting, Honolulu – HI, May 2022.

This chapter is the written version of the original oral presentation.

Abstract

In this chapter, a correlation between composition, T_m , and phase formation of high-entropy sesquioxides is established. Five-component equiatomic compositions were formulated using the average ionic radius AIR as a parameter to select RE species. Pre-reacted precursor powders were produced via a wet chemistry method. The powders were loaded into a micro-pulling-down iridium-rhenium crucible. The crucible was inductively heated to its maximum operating temperature. The crucible capillary channel was probed with an iridium pin (seed) to visually determine whether or not the material melted by observing the presence of melt. For the compositions that melted, the molten material was pulled down and crystals were grown. Lanthanum is identified as a key element for the minimization of the melting point. Three crystal structures were identified in the samples after the growth experiments, cubic, orthorhombic, and monoclinic. Samples with a smaller RE average ionic radius (AIR) have a single cubic phase, while samples with a larger AIR have a single monoclinic phase. Mixtures of phases were identified for samples with intermediate AIR.

Introduction

Rare-earth sesquioxides (RE_2O_3) are attractive host materials for scintillation and lasing applications [69], [119]–[123]. Due to the similarity in ionic radii, rare-earth luminescent activators such as Yb^{3+} and Nd^{3+} can be easily accommodated into the crystal lattice of RE_2O_3 , which allows their use as functional, luminescent materials [124]. Additionally, the high radiation stopping power and density [119]–[121] and the low thermal conductivity of RE_2O_3 [69], [122], [123] are desirable properties for scintillation and laser materials, respectively. For such luminescent applications, the light collection is crucial transparent single-crystals are preferred over polycrystalline materials. However, RE_2O_3 are not widely explored as in the single crystal form due to some of their fundamental characteristics, which are discussed in the next paragraph.

The crystal growth of RE sesquioxides via directional solidification is hindered by two basic properties, 1) their refractory nature and 2) the solid-solid phase transitions that take place upon cooling from the melt [56]. First, as shown

in Figure 2.1, the melting point (T_m) of the single-RE RE_2O_3 is above 2200°C, which limits the availability of compatible crucible materials for crystal growth. Iridium crucibles are commonly used in traditional growth techniques such as the Cz method. However, its maximum operating temperature is ~2100°C, therefore, they cannot be used to grow RE_2O_3 crystals [54]. Rhenium crucibles are compatible with RE_2O_3 crystals, but their high hardness makes crucible fabrication difficult and expensive [61], [125]. Second, the polymorphic behavior of RE_2O_3 results in solid-solid phase transitions upon cooling from the melt, as shown in Figure 1.6. Consequently, a crystal grown via directional solidification would crack due to the stresses related to the polymorphic transitions, which leads to the growth of polycrystalline samples rather than single crystals.

Such limitations to the crystal growth of RE_2O_3 inspire the exploration of the high-entropy compositional design [53] to determine how composition affects both the T_m and phase formation in high-entropy sesquioxides. In this Chapter, we formulate complex compounds based on the ionic radius of RE^{3+} cations, since the polymorphic phase transitions depend on the RE ionic radii (Figure 1.6)[56]. The T_m is qualitatively assessed based on whether a sample melts at the highest operating temperature of an iridium-rhenium crucible in an mPD growth station. Phase composition is assessed after growth attempts using powder X-ray diffraction and Rietveld structure refinement.

Methods

Composition formulation

To qualitatively evaluate the T_m of five-component rare-earth sesquioxides, two initial compositions were formulated taking into account the ionic radius range of the rare-earths selected (RE^{3+} , coordination number VIII [124]). Composition a) $(Lu, Y, Dy, Tb, Gd)_2O_3$ has a relatively shorter rare-earth ionic radius range of 0.977 - 1.053 Å, while composition b) $(Lu, Y, Gd, Nd, La)_2O_3$ has a wider ionic radius range of 0.977 - 1.160 Å. Commas represent equiatomic amounts. To identify a possible element responsible for lowering the T_m in composition b), two additional compositions were prepared by removing REs from composition b). In composition c) $(Lu_{1/4}Y_{1/4}Gd_{1/4}La_{1/4})_2O_3$ Nd was removed and in composition d) $(Lu_{1/3}Y_{1/3}Gd_{1/3})_2O_3$ Nd and La were removed.

After identifying La as a key element for lowering the T_m of high-entropy RE_2O_3 , six additional compounds were formulated to determine the effect of composition on phase formation. The ionic radii of the trivalent RE elements were kept as a parameter for composition formulation. The compositions include five small REs (Lu, Yb, Er, Ho, and Dy), three medium-size REs (Gd, Eu, and Sm), and two large REs (Nd and La). A list of the compositions and their average ionic radius (AIR) is seen in Table 2.1. The compositions are labeled from 1 to 6 and have a decreasing AIR from 1 to 6 in the range of 0.875-0.982 Å [7]. Lanthanum

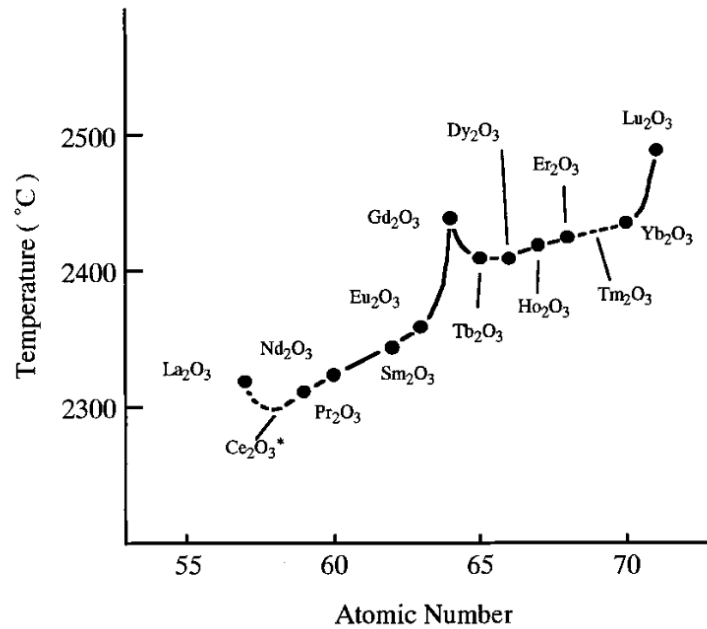


Figure 2.1 - Melting point of single-RE RE₂O₃ as a function of RE atomic number [56].

Table 2.1 - High-entropy RE₂O₃ compositions with respective average ionic radii. Compositions a-d were formulated to identify a key element for minimizing the T_m and compositions 1-6 were formulated to explore the effects of composition on phase formation.

ID	Composition	Average ionic radius CN VI (Å) [124]
<i>Compounds to identify a key element for minimizing the T_m:</i>		
a	(Lu _{1/5} Y _{1/5} Dy _{1/5} Tb _{1/5} Gd _{1/5}) ₂ O ₃	0.902
b	(Lu _{1/5} Y _{1/5} Gd _{1/5} Nd _{1/5} La _{1/5}) ₂ O ₃	0.947
c	(Lu _{1/4} Y _{1/4} Gd _{1/4} La _{1/4}) ₂ O ₃	0.935
d	(Lu _{1/3} Y _{1/3} Gd _{1/3}) ₂ O ₃	0.893
<i>Compounds to determine the effects of composition on phase formation:</i>		
1	(Gd _{1/5} Eu _{1/5} Sm _{1/5} Nd _{1/5} La _{1/5}) ₂ O ₃	0.982
2	(Er _{1/5} Y _{1/5} Eu _{1/5} Sm _{1/5} Nd _{1/5}) ₂ O ₃	0.936
3	(Ho _{1/5} Dy _{1/5} Gd _{1/5} Eu _{1/5} Sm _{1/5}) ₂ O ₃	0.931
4	(Lu _{1/5} Yb _{1/5} Er _{1/5} Nd _{1/5} La _{1/5}) ₂ O ₃	0.929
5	(Lu _{1/5} Yb _{1/5} Er _{1/5} Ho _{1/5} Nd _{1/5}) ₂ O ₃	0.895
6	(Lu _{1/5} Yb _{1/5} Er _{1/5} Y _{1/5} Ho _{1/5}) ₂ O ₃	0.875

was only added to compositions 1 and 4 to verify its importance in the minimization of the T_m . The effect of the AIR on phase formation is evaluated before and after the growth experiments. The AIR is expected to affect the phase formation because the RE ionic radius determines the polymorphs formed in single-RE sesquioxides.

Sample preparation

Powders were synthesized via a wet chemistry method using nitrates as the source of cations. The precursor powder was crystallized at 900°C for 1h in air.

Melting point qualitative evaluation

To qualitatively evaluate the melting point of compounds a-d (Table 2.1), precursor powders were loaded into the micro-pulling-down iridium-rhenium crucible and the crucible was inductively heated at maximum operating power (~2100°C). We qualitatively determine whether the precursors melted in two ways:

1) This first strategy relies upon the real-time visualization of the crucible die by using a CCD camera. When the charged crucible is subjected to the maximum inductive heating power, an iridium seed probes the bottom opening of the crucible capillary channel. If molten material is observed, then the material melted and growth is initiated by pulling the seed down. In case no molten material is observed on the seed, we probe the capillary again after 1 h at the maximum operating temperature.

2) In case we do not observe molten material when the crucible is at high temperatures, we cool the crucible to room temperature and observe the appearance of the charged material. A charge that has been melted will have a flat surface and will homogeneously cover the internal bottom section of the crucible.

Phase composition analysis

To determine the crystal structure of the samples before and after the growth attempt, powder X-ray diffraction patterns were obtained at room temperature using a Panalytical Empyrean diffractometer in the Bragg-Brentano geometry using a Cu K α X-ray source at 45 kV and 40 mA. Rietveld refinements were performed using General Structure Analysis System II software (GSASII).

Results and discussions

Qualitative evaluation of melting point

Lanthanum may be a key element for minimizing the T_m of high-entropy RE₂O₃. Photos of the samples after the growth attempt are shown in Figure 2.2.

a)
 $(\text{Lu}_{1/5}\text{Y}_{1/5}\text{Dy}_{1/5}\text{Tb}_{1/5}\text{Gd}_{1/5})_2\text{O}_3$



b)
 $(\text{Lu}_{1/5}\text{Y}_{1/5}\text{Gd}_{1/5}\text{Nd}_{1/5}\text{La}_{1/5})_2\text{O}_3$



c)
 $(\text{Lu}_{1/4}\text{Y}_{1/4}\text{Gd}_{1/4}\text{La}_{1/4})_2\text{O}_3$



d)
 $(\text{Lu}_{1/3}\text{Y}_{1/3}\text{Gd}_{1/3})_2\text{O}_3$



Figure 2.2 - Photos of samples a-d after the crystal growth attempt. Compositions are given in the figure. Compounds did not melt for compositions a) and d) and top view of the $\varnothing$ 16 mm iridium-rhenium crucible with solid material inside is shown. Compounds melted for compositions b) and c) and the grown sample is shown.

Composition a) did not melt and a solid pellet is seen inside the crucible in Figure 2.2.a. On the other hand, composition b) melted and the sample could be grown as presented in Figure 2.2.b. To identify a possible element responsible for lowering the T_m in composition b, compositions c and d were evaluated. Compared to composition b, Nd is removed in composition c and the compound still melts and can be grown; the grown sample is shown in Figure 2.2.c. However, in composition d Nd and La are removed and the compound does not melt; a solid material is shown inside the crucible in Figure 2.2.d. This indicates that La may play an important role in lowering the melting point of rare-earth sesquioxides, which allows the crystal growth from the melt by the micro-pulling down method. The inconsistency in color in both grown samples may be related to the loss of high vapor pressure elements. An in-depth structural evaluation of composition b is presented in Chapter Three and Chapter Four.

From compositions 1-6 listed in Table 2.1, samples containing La could be grown by the micro-pulling-down method, which further indicates that La is a key element that minimizes the T_m of high-entropy sesquioxides. A picture of either a grown crystal or the top view of the crucible after the growth attempt is shown for each composition in Figure 2.3. Samples of compositions 1 and 4 contain La and have the lowest T_m in this set of samples since they melted and could be grown; the grown crystals are shown in Figure 2.3. The crystal of composition 1 has poor diameter control because the melt was not sufficiently overheated, even with the crucible was at its maximum operating temperature. Samples of compositions 2, 3, 5, and 6 could not be grown and a picture of the remaining material in the crucible is shown for each sample in Figure 2.3. Both samples 2 and 5 look like they softened but did not melt completely, while samples 3 and 6 remained solid during the growth attempt. These results confirm the role of La in minimizing the T_m of high-entropy sesquioxides, allowing their crystal growth from the melt.

Effects of composition on phase formation

To determine how composition affects phase formation, the structure of compounds 1-6 was analyzed by collecting room-temperature powder XRD patterns using two sample conditions, 1) the as-prepared powders and 2) after the growth attempt using the samples shown in Figure 2.3. The expected structures are the ones reported as the room-temperature polymorphs of single-RE sesquioxides. Small REs form a cubic sesquioxide (space group $Ia\bar{3}$), medium-sized REs form a monoclinic sesquioxide ($C2/m$), and large REs form a trigonal sesquioxide ($P\bar{3}m1$) [56]. Additionally, mixtures of large La^{3+} and Nd^{3+} with smaller Lu^{3+} , Yb^{3+} , Tm^{3+} , Er^{3+} , Y^{3+} , Ho^{3+} , and Dy^{3+} may form an orthorhombic perovskite structure ($Pnma$) of the type $LaLuO_3$ [113].

As-prepared powders have a single cubic phase and, therefore, composition and the AIR do not affect phase formation. The XRD peaks of each sample match those of a cubic Y_2O_3 reference pattern, as seen in Figure 2.4.a.

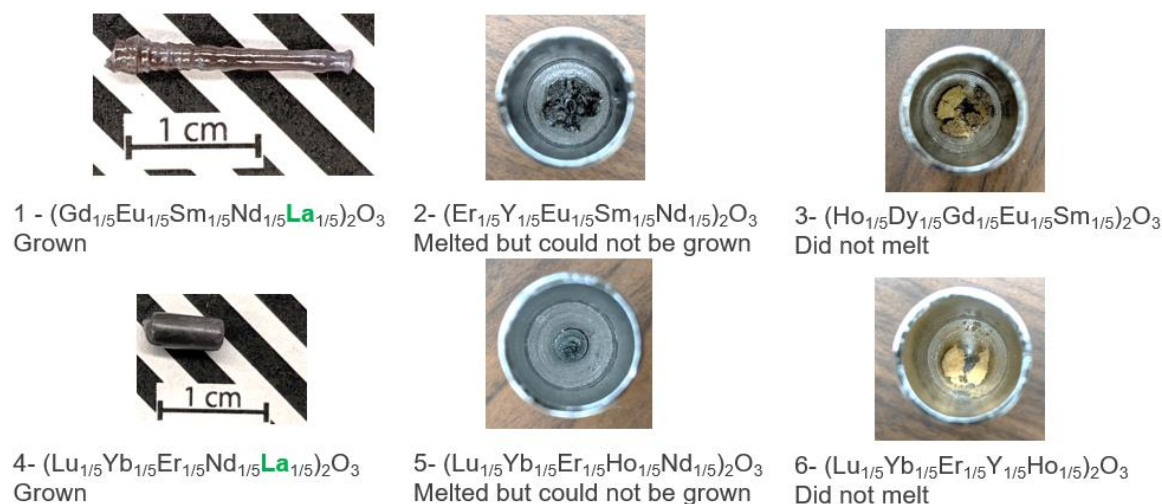


Figure 2.3 – Photos of samples 1-6 after growth experiments. Crystals of compositions 1 and 4 contain La and could be grown due to a relatively low T_m . For compositions 2, 3, 5, and 6, a top view of the iridium-rhenium crucible shows the material remaining after the growth attempt.

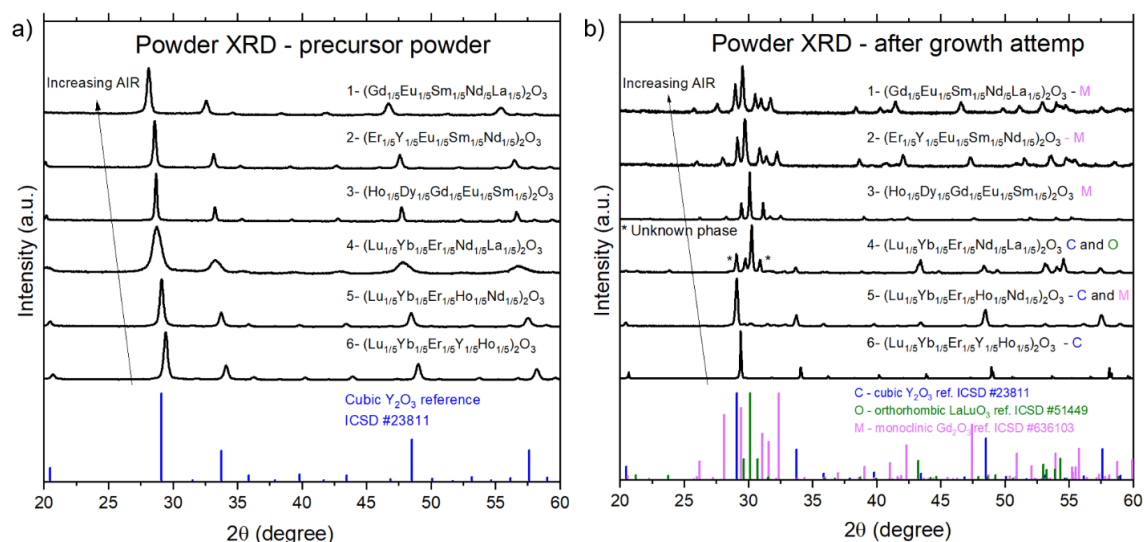


Figure 2.4 - Room-temperature powder XRD patterns of as-prepared powders (a) and samples after growth experiments (b). As-prepared samples are a single cubic phase. After growth experiments, three structures are observed, cubic, orthorhombic, and monoclinic.

Sample 4 has broader peaks than those observed for the other samples. This results from a pronounced lattice microstrain in sample 4, which contains the three smallest REs (Lu^{3+} , Yb^{3+} , and Er^{3+}) and the two largest REs (Nd^{3+} and La^{3+}) included in this study. In fact, Rietveld refinement indicates that the unitless isotropic microstrain parameter of sample 4 (46,645) is greater than the ones observed for the other samples (in the range of 7,578-17,564).

After growth experiments, three structures were observed, monoclinic, orthorhombic, and cubic; both the AIR and the type of elements in each composition affect phase formation. Powder XRD patterns of each sample and reference patterns are shown in Figure 2.4.b. Phase compositions obtained from Rietveld refinement are listed in Table 2.2. In this study, samples 1, 2, and 3 have the three largest AIR and formed single a monoclinic structure after the growth experiment. Sample 4 is a mixture of the three smallest REs (Lu^{3+} , Yb^{3+} , and Er^{3+}) and the two largest REs (Nd^{3+} and La^{3+}); this sample formed a mixture of a cubic and an orthorhombic phase. The cubic phase is typical for small RE, while the orthorhombic phase appears due to a mixture of the largest and smallest REs. Sample 5 is a mixture of four small and one large (Nd^{3+}) RE; this sample formed a mixture of a primary cubic phase with a secondary monoclinic phase that is likely induced by Nd^{3+} . Sample 6 has the smallest AIR and contains only small REs; this sample formed a single cubic phase.

Conclusion

Lanthanum contributes to decreasing the melting temperature of high-entropy sesquioxide compounds. Having 20 mol% of La in such refractory oxides decreases their melting point and enables their crystal growth by the micro-pulling-down method. A correlation between composition, T_m , and phase formation of high-entropy sesquioxides was established. Three crystal structures were identified in the samples after the growth experiments, cubic, orthorhombic, and monoclinic. Samples with a smaller RE average ionic radius (AIR) have a single cubic phase, while samples with a larger AIR have a single monoclinic phase. Mixtures of phases were identified for samples with intermediate AIR.

Table 2.2 - Chemical composition, average ionic radius, and phase composition of high-entropy rare-earth sesquioxides.

Composition	Average ionic radius CN VI (Å) [124]	Phase composition after growth attempt (wt%)		
		M	C	O
1 - (Gd _{1/5} Eu _{1/5} Sm _{1/5} Nd _{1/5} La _{1/5}) ₂ O ₃	0.982	100	-	-
2 - (Er _{1/5} Y _{1/5} Eu _{1/5} Sm _{1/5} Nd _{1/5}) ₂ O ₃	0.936	100	-	-
3 - (Ho _{1/5} Dy _{1/5} Gd _{1/5} Eu _{1/5} Sm _{1/5}) ₂ O ₃	0.931	100	-	-
4 - (Lu _{1/5} Yb _{1/5} Er _{1/5} Nd _{1/5} La _{1/5}) ₂ O ₃	0.929	-	31	69
5 - (Lu _{1/5} Yb _{1/5} Er _{1/5} Ho _{1/5} Nd _{1/5}) ₂ O ₃	0.895	29	71	-
6 - (Lu _{1/5} Yb _{1/5} Er _{1/5} Y _{1/5} Ho _{1/5}) ₂ O ₃	0.875	-	100	-

Phases: M- monoclinic, C - cubic, O - orthorhombic

**CHAPTER THREE:
TUNING THE MELTING POINT AND PHASE STABILITY OF
RARE-EARTH OXIDES TO FACILITATE THEIR CRYSTAL
GROWTH FROM THE MELT**

A version of this chapter was published by Matheus Pianassola and colleagues:

M. Pianassola *et al.*, “Tuning the melting point and phase stability of rare-earth oxides to facilitate their crystal growth from the melt,” *J. Adv. Ceram.*, vol. 11, no. 9, pp. 1479–1490, 2022, doi: <https://doi.org/10.1007/s40145-022-0625-z>.

This chapter is the reformatted version of the original work submitted to the referenced journal. A portion of the experimental section was reworded.

Abstract

The challenge of growing rare-earth (RE) sesquioxide crystals can be overcome by tailoring their structural stability and melting point via composition engineering. This work contributes to the advancement of the field of crystal growth of high-entropy oxides. A compound with only small REs (Lu,Y,Ho,Yb,Er)₂O₃ maintains a cubic C-type structure upon cooling from the melt, as observed via in-situ high-temperature neutron diffraction on aerodynamically levitated samples. On the other hand, a compound with a mixture of small and large REs (Lu,Y,Ho,Nd,La)₂O₃ crystallizes as a mixture of a primary C-type phase with an unstable secondary phase. Crystals of compositions (Lu,Y,Ho,Nd,La)₂O₃ and (Lu,Y,Gd,Nd,La)₂O₃ were grown by the micro-pulling-down (mPD) method with a single monoclinic B-type phase, while a powder of (Lu,Y,Ho,Yb,Er)₂O₃ did not melt at the maximum operating temperature of an iridium–rhenium crucible. The minimization of the melting point of the two grown crystals is attributed to the mismatch in cation sizes. The electron probe microanalysis reveals that the general element segregation behavior in the crystals depends on the composition.

Introduction

After decades of development and application of crystal growth techniques, the growth of single crystals of rare-earth (RE) oxides via directional solidification is still a challenge. Since the mid-1950s, semiconductors and oxides have been grown by pulling single crystals from the melt via the Czochralski method [126], [127]. The success of the growth depends on certain material requirements including (1) a melting point (T_m) compatible with available crucibles and (2) structural stability upon cooling. Compounds that melt above the maximum operating temperature of the widely used iridium crucibles ($\sim 2100^\circ\text{C}$) [55] are challenging to grow due to the lack of other practical crucible material. Additionally, crystals that present phase transitions upon cooling have poor structural quality due to the severe cracking that results from the lattice expansion and/or contraction.

Rare-earth sesquioxides (RE₂O₃) do not meet those two requirements and because of this, their potential as laser and scintillator crystals has not been fully investigated. All of the RE₂O₃ compounds melt above 2200°C [54], which

surpasses the operating temperature of iridium crucibles. Rhenium crucibles can be used to grow RE_2O_3 crystals, but their high hardness makes crucible fabrication difficult and expensive [61], [125]. Upon cooling from the melt, most RE_2O_3 compounds undergo polymorphic transitions and five phases can be observed as a function of temperature and RE ionic radius [56]. Despite not being widely explored in the single-crystal form, RE_2O_3 compounds are attractive as host crystals for high-power lasers due to their low thermal conductivity [69], [122], [123], and as high radiation stopping power scintillators due to their high density [119]–[121]. In both applications, the host RE ion can be easily substituted by an optical activator such as Yb^{3+} .

The field of RE_2O_3 crystal growth may benefit from the high-entropy compositional concept as the T_m and structural stability can potentially be tuned via composition engineering. An unusual compositional concept introduced by high-entropy alloys [128]–[130] has recently fostered the development of functional high-entropy oxides containing five or more elements in nearly equiatomic amounts [53]. Composition engineering is known to reveal attractive properties in relatively simple compounds [131], [132]; the combinatorial possibilities are widely expanded in high-entropy materials, which may allow the tuning of fundamental properties. This inspires an investigation to verify whether the high-entropy compositional design approach can minimize the T_m and suppress polymorphic transitions in RE_2O_3 , thus enabling their crystal growth from the melt. To date, reports on the T_m and structural stability of high-entropy RE sesquioxides are limited to polycrystalline ceramics, and bulk single crystal growth has not yet been demonstrated [57], [70]–[72].

In this work, the minimization of the T_m and practical aspect of crystal growth of high-entropy RE_2O_3 is demonstrated for the first time. We design three high-entropy RE sesquioxides containing Lu, Yb, Er, Y, Ho, Gd, Nd, and La. The RE^{3+} ionic radius (Table 3.1) was chosen as a formulation criterion to study the effect of cation size mismatch on the T_m and phase stability. Composition 1 $(\text{Lu}, \text{Y}, \text{Ho}, \text{Yb}, \text{Er})_2\text{O}_3$ contains only small REs, while composition 2 $(\text{Lu}, \text{Y}, \text{Ho}, \text{Nd}, \text{La})_2\text{O}_3$ and composition 3 $(\text{Lu}, \text{Y}, \text{Gd}, \text{Nd}, \text{La})_2\text{O}_3$ are a mixture of small and large REs. The average ionic radius (AIR) of each composition is listed in Table 3.2. The structure of the as-prepared samples was evaluated via the powder X-ray diffraction (XRD). Structural stability is evaluated via the in-situ high-temperature neutron diffraction and differential scanning calorimetry (DSC). Crystals were grown from the melt by the micro-pulling-down (mPD) method [37] using an iridium–rhenium 90–10 wt% alloy crucible. The mPD method is ideally suited for this study due to the relatively small amounts of expensive starting materials (~1 g) and faster growth rates that can be achieved compared to scalable techniques such as the Czochralski method [37]. The minimization of the T_m in composition 3 is demonstrated via the cooling trace method [133].

Table 3.1 - List of trivalent rare-earth cations and their respective ionic radius for coordination number VI [124].

RE cation	Lu ³⁺	Yb ³⁺	Er ³⁺	Y ³⁺	Ho ³⁺	Gd ³⁺	Nd ³⁺	La ³⁺
Ionic radius for CN VI (Å) [124]	0.848	0.858	0.881	0.892	0.894	0.938	0.995	1.061

Table 3.2 - List of high-entropy RE sesquioxides compositions and their respective average ionic radius (AIR) for coordination number VI [124].

Composition ID	Chemical formula	Average ionic radius (AIR) for CN VI (Å) [26]	Subjected to neutron diffraction?	Grown from the melt?
1	(Lu,Y,Ho,Yb,Er) ₂ O ₃	0.875	Yes	No
2	(Lu,Y,Ho,Nd,La) ₂ O ₃	0.938	Yes	Yes
3	(Lu,Y,Gd,Nd,La) ₂ O ₃	0.947	No	Yes

Methods

Composition formulation

To study the effect of the mismatch in cation size in high-entropy RE sesquioxides on melting point, phase formation, and structural stability, eight REs from a wide range of ionic radii were selected. The ionic radius of each trivalent RE cation is listed in Table 3.1. Six REs were selected from the smaller end of that range, Lu, Yb, Er, Y, Ho, and Gd, and two REs from the larger end, Nd and La. Three compositions with equiatomic amounts of REs were formulated, one with only small REs (Lu,Y,Ho,Yb,Er)₂O₃ (commas indicate equiatomic amounts) and two with a mixture of small and large REs, (Lu,Y,Ho,Nd,La)₂O₃ and (Lu,Y,Gd,Nd,La)₂O₃.

Powder synthesis

Powders were synthesized via a wet chemistry method using nitrates as the source of cations. The precursor powder was crystallized at 900°C for 1h in air.

Bead synthesis

Bead samples were prepared for aerodynamic levitation to allow a containerless sample environment for *in-situ* high-temperature neutron diffraction experiments. The procedure described in this section was performed at the Spallation Neutron Source at Oak Ridge National Laboratory (ORNL). Powders were melted in a copper hearth using a 400-W continuous-wave CO₂ laser for heating. The samples were rapidly cooled by turning off the laser resulting in 2–3 mm diameter spherical bead samples.

Room-temperature X-ray diffraction

To determine the crystal structure of the as-prepared powders and the bead samples, powder XRD patterns were obtained at room temperature using a Panalytical Empyrean diffractometer in the Bragg–Brentano geometry using a Cu K α X-ray source at 45 kV and 40 mA. Rietveld refinements were performed using General Structure Analysis System II (GSASII) software.

In-situ high-temperature neutron diffraction

To evaluate phase transitions upon cooling from the melt and in the temperature range of 1000–2500°C, the time-of-flight (TOF) neutron diffraction patterns were collected using the Nanoscale-Ordered Materials Diffractometer (NOMAD) at the Spallation Neutron Source at ORNL [134]. An aerodynamic levitator, a 400-W continuous-wave CO₂ laser, and a single wavelength (0.9 μ m) optical pyrometer (Chino Inc.) were used to provide a containerless environment and enable data collection at elevated temperatures [135]–[137]. Two

compositions were selected for neutron diffraction experiments, composition 1 (Lu,Y,Ho,Yb,Er)₂O₃ and composition 2 (Lu,Y,Ho,Nd,La)₂O₃. Bead samples with ~2 mm in diameter were levitated using high-purity Ar gas in an Ar-filled chamber. The sample temperature was varied by adjusting the CO₂ laser power. The empty conical nozzle levitator and a Si bead were measured at room temperature for normalization and correction of all patterns.

Initially, the samples were melted on the levitator, and then the laser power was slowly decreased to solidify the sample. 5-min scans were performed to determine whether the sample was molten or crystallized. After finding the solidification point, 2-h scans were performed at constant temperatures in the range of 1000–2500°C with a cooling rate of ~20 °C/min between scans. The standard deviation of the temperature measurements was smaller than 30°C for all scans. Powder-like diffraction patterns were collected by ensuring the random rotation of the bead samples, which was achieved by controlling the Ar gas flow through the aerodynamic nozzle levitator. The best signal-to-noise ratio was observed for the 65° scattering bank of the NOMAD instrument, which was used for structure refinement. Rietveld refinement was performed using GSASII software in the range of 3.3 – 18.4 ms TOF.

Differential scanning calorimetry

To identify any phase transitions in the 30–1300°C temperature range, the DSC curves were obtained for the as-prepared bead samples. The samples were ground in a mortar and placed in alumina crucibles. A Labsys EVO instrument was used to obtain the DSC curves with a heating and cooling rate of 5 °C /min.

Crystal growth

Crystals were grown using the mPD method, which is optimal for material development due to the small amount of material necessary (~1 g) to evaluate the growability of novel compounds. A KDN mPD furnace (Dai-Ichi Kiden, Japan) equipped with a radio frequency (RF) generator model TR-02001 operated at 26 kVA was used. The mPD growth method and setup were previously described in detail [39]. A 16-mm diameter iridium–rhenium alloy crucible (20 wt% Re) with a 3-mm diameter die and a 0.5-mm diameter capillary channel was used to grow cylindrical crystals. The as-prepared powder samples were placed in the crucible, which was heated inductively to melt the samples. An iridium pin was used as a seed to initiate the growth. The crucible temperature cannot be assessed during growth since the crucible is held within alumina insulation tubes. However, the RF power used during all growth experiments is the same as the one used to previously grow Lu₂SiO₅ crystals from the same crucible in the same growth setup. Therefore, the maximum crucible temperature in this work is estimated to be slightly above 2150°C, which is the melting point of Lu₂SiO₅.

Electron probe microanalysis

A 1-mm thick cross-section sample was cut from the seed end and tail end of the crystals. The samples were embedded in epoxy and then polished for the elemental composition analysis. Concentration profiles were obtained by using a CAMECA SX100 Electron Microprobe operated at a voltage of 15 kV and a current of 30 nA. Images were acquired by high-speed backscattered electron detectors. Compositional information was obtained by detecting characteristic X-rays with wavelength-dispersive spectrometers. Radial concentration profiles were obtained by collecting data in 100- μm steps. The probe point size was 1 μm , and the excitation area diameter was in the 2–3 μm range.

Melting point measurements

The cooling trace method was used for the determination of liquidus temperatures in the $(\text{Lu}, \text{Y}, \text{Gd}, \text{Nd}, \text{La})_2\text{O}_3$ system and consists in melting samples and recording their temperature upon cooling. A temperature peak during cooling indicates the recalescence phenomenon, and the peak maximum is assigned as the sample liquidus temperature [133]. Optical pyrometers are commonly used to measure such high temperatures, and the spectral emissivity of the sample should be known for accurate measurements. The spectral emissivity of multi-RE samples was calculated as a weighted average of the spectral emissivities of the single-RE sesquioxides formed by the constituent REs. The following experiments were performed at the Spallation Neutron Source at ORNL. To obtain the spectral emissivity of the constituent sesquioxides, powders of Lu_2O_3 , Y_2O_3 , Gd_2O_3 , Nd_2O_3 , and La_2O_3 of at least 99.99% purity were individually melted in a copper hearth to form 2–3 mm diameter spherical beads; a 400-W continuous wave CO_2 laser was used for heating. The bead samples were placed on an aerodynamic levitator and levitated using a 80% Ar–20% O_2 gas mixture to obtain a containerless sample environment and avoid any possible reactions with crucible material. The samples were then heated using the CO_2 laser and melted under levitation. Their spectral emissivity was determined using their reported melting temperatures in Refs. [138]–[141].

To determine the effect of the number of REs on the liquidus temperature in the compositional $(\text{Lu}, \text{Y}, \text{Gd}, \text{Nd}, \text{La})_2\text{O}_3$ system, powder of three compounds were prepared, $(\text{Lu}, \text{Y}, \text{Gd})_2\text{O}_3$, $(\text{Lu}, \text{Y}, \text{Gd}, \text{Nd})_2\text{O}_3$, and $(\text{Lu}, \text{Y}, \text{Gd}, \text{Nd}, \text{La})_2\text{O}_3$. As described for the single-RE powders, the three multi-RE samples were prepared as 2–3 mm diameter beads and placed on an aerodynamic levitator. The samples were then heated using the CO_2 laser and melted under levitation. After a 5-s dwell at the molten state, the heating laser was shut off. The temperature profile was recorded using a single wavelength (0.9 μm) optical pyrometer (Chino Inc.) with a data acquisition rate of 25 Hz and an operating temperature range of 600–3000°C. The temperature was corrected by Wien's law [142]. This procedure was repeated at least six times for each sample.

Results and discussions

Structure of as-prepared samples

Synthesis temperature and AIR are known to affect phase formation in high-entropy RE sesquioxides[57], [71], and therefore samples of compositions 1, 2, and 3 were prepared with two distinct thermal histories for structural evaluation. Samples referred to as “powders” were crystallized at 900°C, and cooled slowly. Samples referred to as “beads” are 2–3 mm diameter spheres made by melting powders in a copper hearth with a CO₂ laser as a heat source; the beads were rapidly cooled from the melt by turning off the laser. Phase formation in these samples may follow the polymorphic behavior of single-RE sesquioxides. As seen in Figure 3.1, five polymorphs are formed as a function of temperature and ionic radius of single-RE sesquioxides [56]. This diagram of polymorphic transformations will be used to correlate synthesis temperature, AIR, and phase formation of powders and bead samples.

Although Figure 3.1 has been traditionally adopted to study RE₂O₃ [56], [143], [144], a few considerations should be mentioned. First, some data points used to construct the diagram are controversial. For instance, a few authors report on Yb₂O₃ with the H-type structure [54], while some publications indicate that Yb₂O₃ maintains the C-type structure until its melting [145], [146]. Second, an additional phase is formed when two REs with a difference in ionic radii of at least 0.20 Å are mixed in equal amounts. Compounds such as LaLuO₃ have an orthorhombic perovskite structure (space group Pnma) [110], [113], [114] and are not predicted in Figure 3.1 since they are not single-RE RE₂O₃.

A single cubic C-type phase (space group Ia-3) was identified for powders of compositions 1, 2, and 3, as indicated by the powder XRD patterns in Fig. 3.2(a). In fact, the C-type phase could be predicted in Fig. 3.1. The AIR of compositions 1, 2, and 3 (indicated in Figure 3.1) lie in the C-type region at the synthesis temperature of powders, 900°C. Both compositions 2 and 3 have large La³⁺ and Nd³⁺ ions that do not form the C-type structure in La₂O₃ and Nd₂O₃. This may lead to a lattice distortion, which would explain the higher degree of crystallinity seen as sharper XRD reflection peaks of the powders of composition 1 compared to compositions 2 and 3 (Figure 3.2.a).

In the bead samples, composition 1 is also a single C-type phase, while both compositions 2 and 3 have a single monoclinic B-type phase (space group C2/m), as seen in Figure 3.2.b. The beads are expected to retain high-temperature structures at room temperature since they were rapidly cooled from the melt. Therefore, composition 1 may not undergo phase transitions in a large range of temperatures since both the powders and the bead of composition 1 are a single C-type phase. On the other hand, compositions 2 and 3 undergo a phase transformation from the low-temperature C-type phase to the high-temperature B-

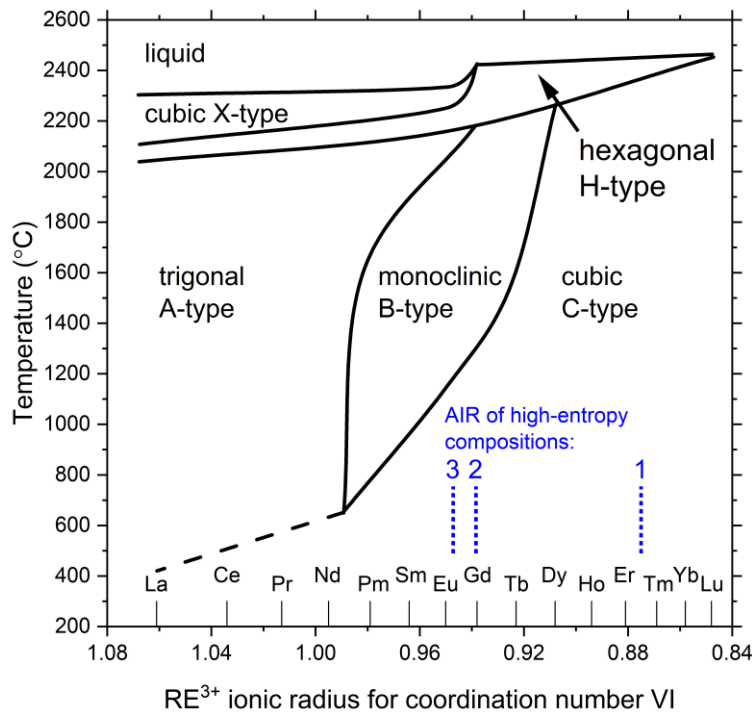


Figure 3.1 - Schematic diagram of polymorphic transformations for single-RE RE_2O_3 as a function of temperature and RE ionic radius for coordination number VI [56], [124]. The relative horizontal position of the AIR of the high-entropy compositions 1 (Lu,Y,Ho,Yb,Er) $_2\text{O}_3$, 2 (Lu,Y,Ho,Nd,La) $_2\text{O}_3$, and 3 (Lu,Y,Gd,Nd,La) $_2\text{O}_3$ are indicated as vertical dashed lines.

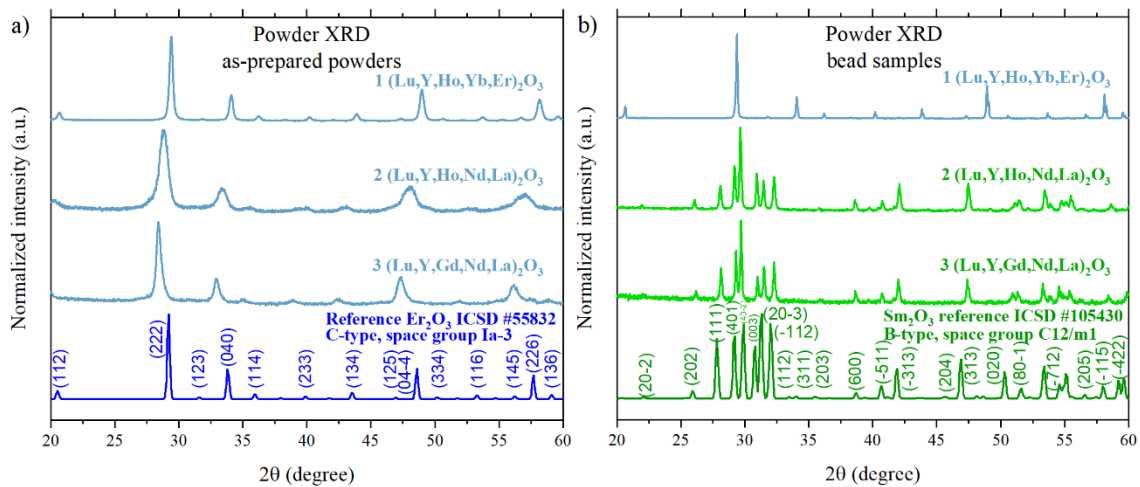


Figure 3.2 – Room temperature powder XRD patterns. a, As-prepared powders have a single C-type phase; a reference reflection pattern of Er_2O_3 is shown for comparison. b, The bead sample of composition 1 maintains the single C-type phase, while the beads of compositions 2 and 3 are a single B-type phase; a reference pattern of Sm_2O_3 is shown for comparison.

type phase. This C- to B-type phase transition follows the trend of polymorphic behavior in single-RE sesquioxides, as observed by the relative position of the AIR of compositions 2 and 3 in Figure 3.1.

Composition 1 is a promising candidate for crystal growth since the single C-type structure is observed after slow cooling from 900°C and after fast cooling from the melt. Compositions 2 and 3 may also be promising, as they could potentially retain a B-type structure when cooled slowly from the melt after crystal growth. To further evaluate the structural stability of the high-entropy RE sesquioxide compounds proposed here, high-temperature structural characterization is necessary.

High-temperature structural stability upon cooling from the melt

To evaluate the structural stability upon cooling from the melt, beads of compositions 1 (Lu,Y,Ho,Yb,Er)₂O₃ and 2 (Lu,Y,Ho,Nd,La)₂O₃ were subjected to *in-situ* high-temperature neutron diffraction using the NOMAD instrument at ORNL. Composition 3 (Lu,Y,Gd,Nd,La)₂O₃ is not included here because Gd has a large neutron absorption cross-section [147] which makes the data quality poor. A containerless sample environment was achieved by using a conical nozzle levitator in an Ar atmosphere and a CO₂ laser for heating. This unique experimental setup allowed extremely high temperatures (~2500°C) to be achieved without the need for refractory sample holders. To investigate the structure of the beads, a room-temperature pattern was initially acquired. The beads were then melted at 2550–2600°C; the molten state was confirmed by collecting a diffraction pattern and ensuring the absence of reflection peaks. The beads were then cooled slowly (20 °C/min) to obtain diffraction patterns at fixed temperatures in the range of 1000–2500°C.

The bead of composition 1 (Lu,Y,Ho,Yb,Er)₂O₃ is a single C-type phase at room temperature (before heating) and in the 1000–2500°C temperature range. The room-temperature C-type structure agrees with the powder XRD results in Fig. 2(b). Diffraction patterns obtained at 2456 ± 16, 1640 ± 19, and 1114 ± 17 °C are seen in Figure 3.3.a; a single C-type phase was confirmed via Rietveld refinement. The stability of the C-type structure upon cooling from the melt makes composition 1 a promising candidate for the growth of high-quality crystals. A combination of REs of similar, small ionic radii in composition 1 may have constrained the lattice into a single C-type phase over a wide temperature range [57]. Therefore, selecting REs of similar ionic radii may be essential to suppress polymorphic transformations in high-entropy RE sesquioxides.

The structure of the bead of composition 2 (Lu,Y, Ho,Nd,La)₂O₃ could not be determined at room temperature by neutron diffraction due to the low signal-to-noise ratio of the data. The pattern obtained at room temperature before heating resembles the expected one for the monoclinic structure identified via the XRD in

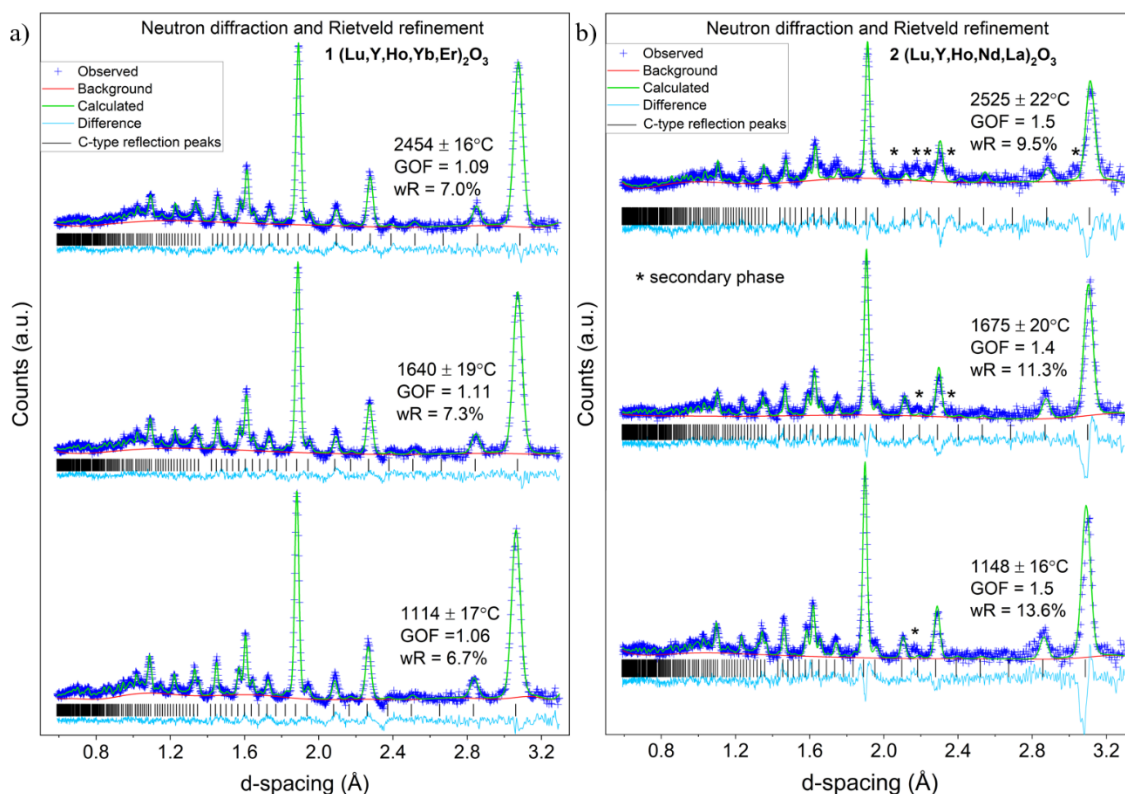


Figure 3.3 - In-situ high-temperature neutron diffraction data and Rietveld refinement results for beads of composition 1 (Lu,Y,Ho,Yb,Er)₂O₃ (a) and 2 (Lu,Y,Ho,Nd,La)₂O₃ (b). Sample temperature is indicated in each pattern. The bead of composition 1 is a single C-type phase and the bead of composition 2 is a mixture of a primary C-type phase with an unknown secondary phase.

Figure 3.2.b. However, Rietveld structure refinement using neutron diffraction data was inconclusive. To better use the beam-time, high-temperature measurements were prioritized.

A mixture of a primary C-type phase with an unknown secondary phase was observed for a bead of composition 2 in the $\sim 1000\text{--}2500^\circ\text{C}$ temperature range. Patterns collected at 2525 ± 22 , 1675 ± 20 , and $1148 \pm 16^\circ\text{C}$ are shown in Figure 3.3.b. During Rietveld refinement, the secondary phase peaks indicated in Figure 3.3.b could not be matched with any of the expected phases in Figure 3.1 or with the orthorhombic perovskite structure typical of LaLuO_3 . This may suggest a suboxide structure. This bead sample lost $\sim 2/3$ of its mass during the measurements due to evaporation; this is likely due to the fact that Nd_2O_3 and La_2O_3 have the highest vapor pressures among all single-RE sesquioxides [47]. The resulting composition fluctuation may explain the variation in the number and intensity of the secondary peaks with decreasing temperature, as seen in Figure 3.3.b.

For a composition that tends to evaporate at temperatures close to their T_m , the mass loss is expected to be pronounced for the bead samples due to their large specific surface area. The relative mass loss is expected to be less pronounced for melt reservoirs used in crystal growth due to the larger volume of material. Therefore, composition 2 is not discarded for crystal growth experiments, since the effects of evaporation on phase composition may be distinct from those observed for the bead samples during the high-temperature neutron diffraction experiments.

In general, the refined lattice parameter of the C type structure in the bead of composition 1 is smaller than that of composition 2, as seen in Figure 3.4. This is expected since the AIR of composition 1 ($0.875\text{ \AA}$) is smaller than that of composition 2 ($0.938\text{ \AA}$). Additionally, the lattice parameter of composition 1 increases linearly with temperature ($R^2 = 0.99$), while the lattice parameter of the bead of composition 2 also increases with temperature, but with a significant deviation from linearity ($R^2 = 0.95$). This may result from both composition fluctuation in the bead of composition 2 due to sample evaporation and a possible cation exchange between the C-type phase and the secondary phase [37].

Evaluation of phase stability in the range of $30\text{--}1300^\circ\text{C}$

To identify possible low-temperature phase transitions in the as-prepared bead samples, DSC curves were obtained in Figure 3.5. The initial structure of the beads was C-type for composition 1 and B-type for compositions 2 and 3 (Figure 3.2.b). No endothermic or exothermic peaks were identified in the DSC curves, which indicates that none of the bead samples undergo phase transitions in the $30\text{--}1300^\circ\text{C}$ temperature range. Therefore, all the three compositions are attractive for crystal growth experiments.

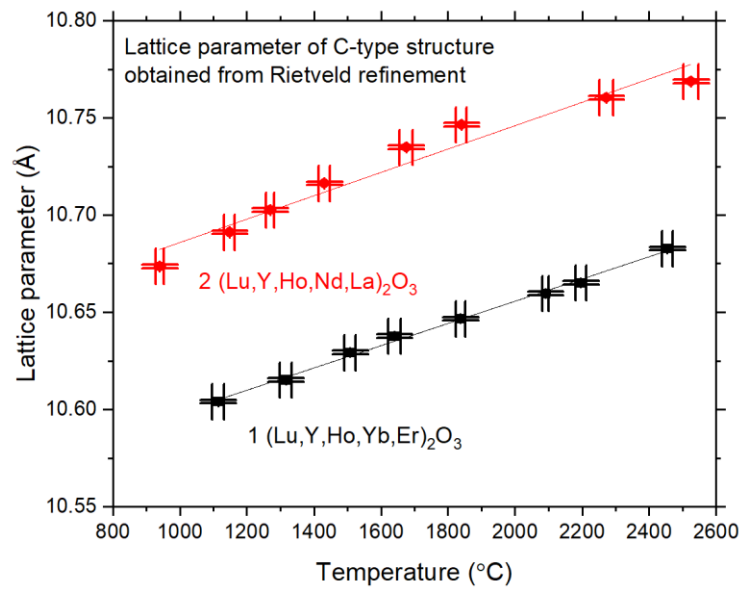


Figure 3.4 - The lattice parameter of the C-type structure was obtained via Rietveld structure refinement from neutron diffraction data collected for beads of compositions 1 and 2. In general, the bead of composition 2 (AIR = 0.938 Å) has a larger lattice parameter than the bead of composition 1 (AIR = 0.875 Å) due to its larger AIR. Linear regression fits are shown for each data set.

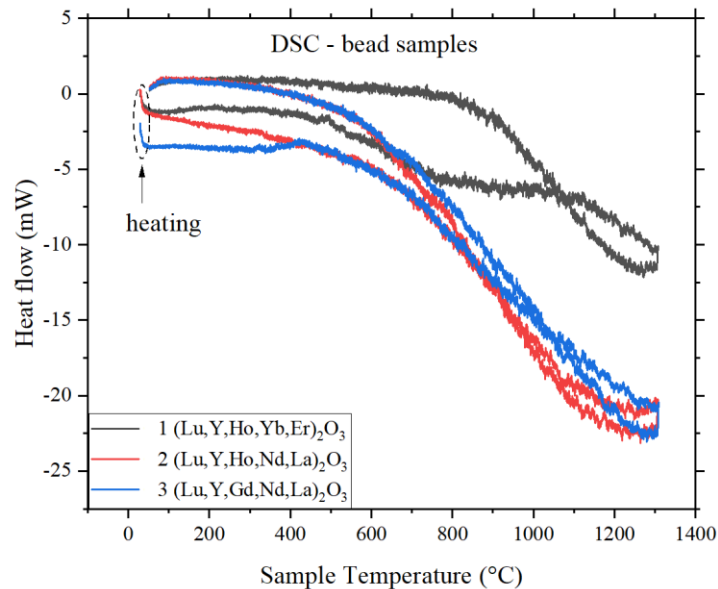


Figure 3.5 - Differential scanning calorimetry (DSC) curves were measured on as-prepared bead samples in air. Temperature range of 30°C - 1300°C, heating and cooling rate are 5°C/min.

Crystal growth

Crystals of compositions 2 (Lu,Y,Ho,Nd,La)₂O₃ and 3 (Lu,Y,Gd,Nd,La)₂O₃ were grown by the mPD method using an iridium–rhenium 90–10 wt% alloy crucible, which demonstrates the practical aspect of growing high-entropy RE sesquioxides crystals with a T_m minimized via composition engineering. Hereafter these crystals are referred to as “crystal 2” and “crystal 3”. The powder of composition 1 (Lu,Y,Ho,Yb,Er)₂O₃ did not melt at the crucible’s maximum operating temperature. This indicates that compositions 2 and 3 have lower T_m than 1 and the mixture of small and large REs in compositions 2 and 3 may favor the minimization of the T_m .

Figure 3.6.a shows the top view of the crucible with the sintered powders of composition 1 after the growth attempt. Figure 3.6.b and Figure 3.6.c show the grown crystals 2 and 3, respectively. The seed end and tail end of the crystals are indicated in Figure 3.6 and correspond to the first and last portion to be solidified, respectively. Intense sample evaporation was observed during the growth of crystals 2 and 3, which may compromise the composition homogeneity of the crystal. The powder XRD data of the samples after the growth experiments are similar to those of the bead samples in Figure 3.2.b and indicate a single C-type phase for the sintered powders of composition 1 and a single B-type phase for both crystals 2 and 3.

Melting temperatures in the (Lu,Y,Gd,Nd,La)₂O₃ system

We hypothesize that the larger number of REs in a sesquioxide, the lower the T_m . The T_m can be described as the ratio between the enthalpy of fusion ΔH_{fus} and the entropy of fusion ΔS_{fus} thus $T_m = \Delta H_{fus} / \Delta S_{fus}$. By increasing the number of REs in a compound, the ΔS_{fus} is expected to increase, minimizing the T_m . To verify that, the T_m of the multi-RE sesquioxides (Lu,Y,Gd)₂O₃, (Lu,Y,Gd,Nd)₂O₃, and (Lu,Y,Gd,Nd,La)₂O₃ were measured via the cooling trace method [133]. The measured T_m of the multi-RE samples are significantly lower than those of single-RE sesquioxides formed by the constituent REs as seen in Figure 3.7. Additionally, as the nominal number of REs increases, the T_m decreases, which results from an increasing ΔS_{fus} . The sample of composition 3 (Lu,Y,Gd,Nd,La)₂O₃ melts below 2200°C, which allowed the crystal growth of this compound as discussed in the “Crystal growth” section of this chapter. This minimization of T_m with an increasing number of REs may be composition-dependent since a (La,Sm,Dy,Er,Nd)₂O₃ sample has been reported with a higher melting point than its constituent oxides [72]. This unexpected increase in T_m was attributed to a nonideal mixing in the solid and/or the liquid phases, and therefore the effects of complex compositions and local ordering on the T_m need to be further investigated.



Figure 3.6 - Photos of samples 1, 2, and 3 after the growth attempt. a, Top view of the iridium-rhenium crucible with sintered powder of composition 1 that did not melt at the maximum operating temperature of the crucible. b, Crystal of composition 2. c, Crystal of composition 3.

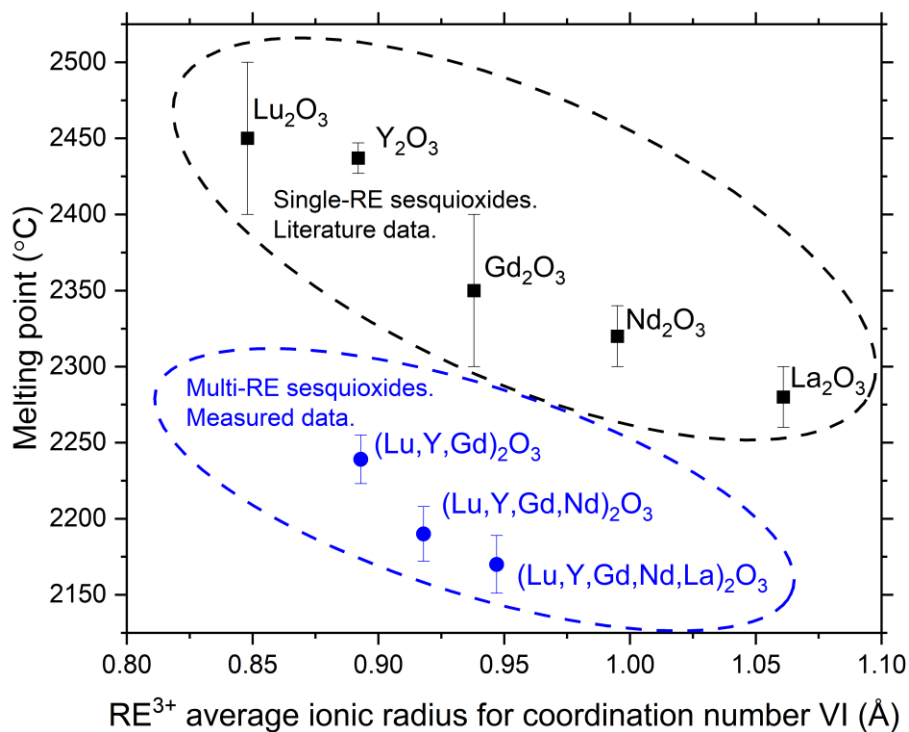


Figure 3.7 - Measured melting points of compositions from the system of composition 3 $(\text{Lu}, \text{Y}, \text{Gd}, \text{Nd}, \text{La})_2\text{O}_3$ (blue circles) are lower than the melting points of Lu_2O_3 [138], Y_2O_3 [141], Gd_2O_3 [140], Nd_2O_3 [138], and La_2O_3 [141] obtained from the literature (black squares).

Elemental distribution profiles in the grown crystals

To evaluate the elemental distributions in the crystals, radial concentration profiles were obtained via electron probe microanalysis (EPMA) on thin disks cut from the grown crystals and are shown in Figure 3.8. On the tail end of crystal 2 (Lu,Y,Ho,Nd,La)₂O₃ (Figure 3.8, left), the concentration data are more continuous than those of the seed end (Figure 3.8, right) because the melt flow at the solidification front may not have been completely equilibrated at the beginning of the growth. The fact that the relative concentration of Lu is higher than that of the other elements may be related to the composition fluctuation resulting from the significant sample evaporation during growth.

The elemental segregation in the mPD crystals is evaluated by the shape of the radial concentration profile. Flat profiles indicate a segregation coefficient $k \approx 1$, downwardly curved profiles indicate $k < 1$ (which results from the rejection of the element by the growing crystal), and upwardly curved profiles indicate $k > 1$ (which results from the preferential incorporation) [37], [39]. In Figure 3.8, Lu and Nd have close-to-flat profiles and do not segregate significantly; Y and Ho have upwardly curved profiles and are preferentially incorporated; and La has a downwardly curved profile and is rejected.

Although compositions 2 (Lu,Y,Ho,Nd,La)₂O₃ and 3 (Lu,Y,Gd,Nd,La)₂O₃ are similar, Lu is rejected by crystal 3 but not by crystal 2. The EPMA concentration profiles of crystal 3 are shown in Figure 3.9, in which Lu has downwardly curved profiles. Similar to crystal 2, Nd has a flat profile in crystal 3, Y and Gd (which substitute Ho in crystal 2) have upwardly curved profiles, and La has a downwardly curved profile. The lower La concentration on the tail end of crystal 3 may indicate the gradual evaporation of La, such that the melt was depleted in La toward the end of the growth. Further studies on growth parameters such as pulling rate may result in crystals with a more homogeneous elemental distribution [39]. Additionally, adding a small percentage of oxygen to the growth atmosphere may prevent sample evaporation and favor composition homogeneity [148].

Conclusion

Composition engineering is the key to designing structurally stable high-entropy RE sesquioxides. Mixing only small REs in composition 1 (Lu,Y,Ho,Yb,Er)₂O₃ led to a stable C-type phase, which was formed upon crystallization of melt and was preserved upon cooling. Therefore, cations with similar ionic radii may favor the structural stability of these sesquioxides. Mixing small and large REs in composition 2 (Lu,Y,Ho,Nd,La)₂O₃ led to the formation of a primary C-type phase with an unstable secondary phase upon cooling from the melt. Therefore, cations with a wide range of ionic radii may hinder the structural stability of high-entropy RE sesquioxides. Structural analysis at temperatures around the melting point of high-entropy RE sesquioxides was possible due to a

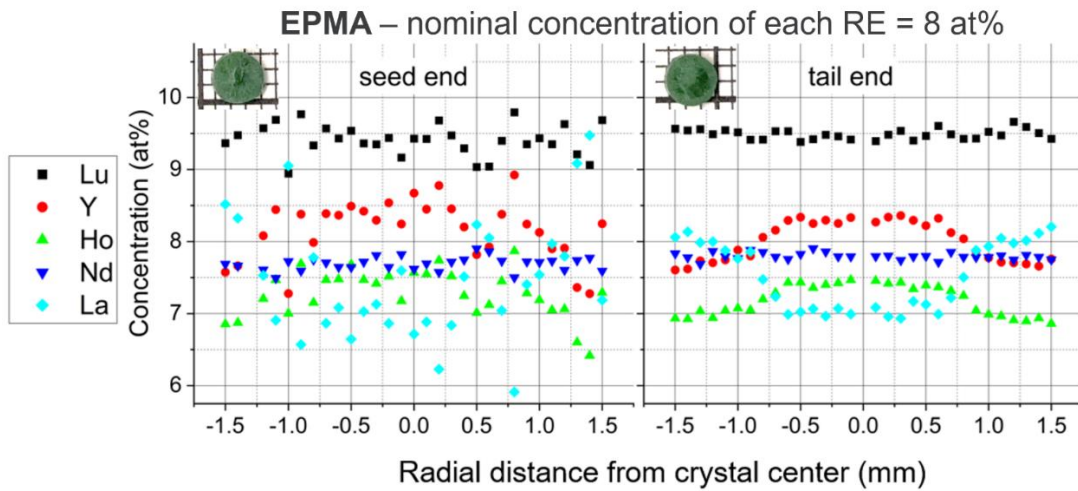


Figure 3.8 - EPMA radial concentration profiles of the seed end (left) and the tail end (right) of crystal 2. The legend on the left applies to both graphs. On the vertical axis, -1.5 mm and 1.5 mm correspond to the last measurement toward the outer surface of the crystal; zero correspond to the center of the crystal.

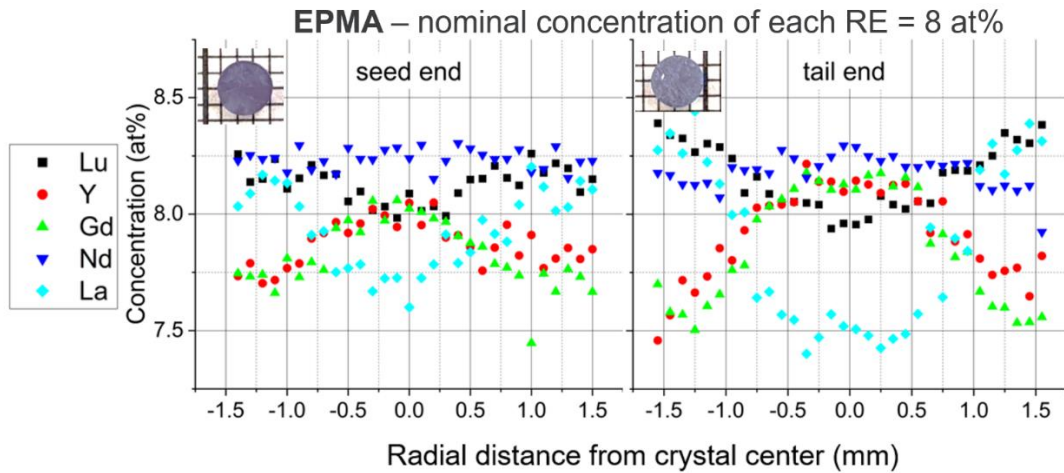


Figure 3.9 - EPMA radial concentration profiles of the seed end (left) and the tail end (right) of crystal 3. The legend on the left applies to both graphs. On the vertical axis, -1.5 mm and 1.5 mm correspond to the last measurement toward the outer surface of the crystal; zero correspond to the center of the crystal.

unique containerless sample environment achieved via aerodynamic levitation of bead samples. This experimental setup was essential to acquire the in-situ high-temperature neutron diffraction patterns using the NOMAD instrument at ORNL.

Melting points of high-entropy RE sesquioxides are affected by the composition. While the powder of composition 1 did not melt at the maximum operating temperature of an iridium–rhenium crucible, those of compositions 2 and 3 (Lu,Y,Ho,Nd,La)₂O₃ did melt and could be grown by the mPD method. This indicates that compounds with a significant mismatch in cation sizes such as compositions 2 and 3 may melt at lower temperatures than compounds with a more limited range of cation sizes such as composition 1.

Further investigation into growth parameters such as pulling rate and growth atmosphere may lead to high-entropy RE sesquioxide crystals with better optical quality and composition homogeneity. Additionally, doping these crystals with optically active REs such as Ce³⁺, Pr³⁺, and Yb³⁺ may reveal attractive luminescent properties for scintillation and laser applications.

**CHAPTER FOUR:
IN-SITU HIGH-TEMPERATURE STRUCTURAL ANALYSIS OF
HIGH-ENTROPY RARE-EARTH SESQUIOXIDES**

A version of this chapter was published by Matheus Pianassola and colleagues:

M. Pianassola *et al.*, “In-situ high-temperature structural analysis of high-entropy rare-earth sesquioxides,” Chem. Mater., Under review.

This chapter is the reformatted version of the original work submitted to the referenced journal.

Abstract

High-entropy rare-earth (RE) sesquioxides (RE_2O_3) containing five cations in equimolar amounts have been investigated for a variety of applications, but little is known about their polymorphic behavior and coefficient of thermal expansion. Here, we evaluate the effect of the average ionic radius (AIR) on the polymorphism of high-entropy RE_2O_3 . Powder samples of compositions 1 ($\text{Lu,Y,Ho,Nd,La}_2\text{O}_3$) (AIR = 0.938 Å) and 2 ($\text{Gd,Eu,Sm,Nd,La}_2\text{O}_3$) (AIR = 0.982 Å) were synthesized via a wet chemical method and bead samples were prepared for aerodynamic levitation by melting the powders in a copper hearth. Structural transitions were monitored upon cooling from the melt to 1000°C via *in-situ* X-ray diffraction on aerodynamically levitated samples. The phase evolution was liquid, hexagonal H-type, and monoclinic B-type for composition 1; and liquid, cubic X-type, H-type, and B-type for composition 2. Based on their AIR, the general polymorphic transformations of the high-entropy RE_2O_3 follow the trend of single-RE RE_2O_3 , but the transition temperatures differ from those of single-RE RE_2O_3 . The CTE of the B-type phase of compositions 1 and 2 are similar to those of Gd_2O_3 and previously published high-entropy RE_2O_3 .

Introduction

Rare-earth (RE) sesquioxides (RE_2O_3) are of great technological importance due to their unique fundamental properties[149]. Typically, the oxides formed by the trivalent lanthanides from La^{3+} to Lu^{3+} and the rare-earth-like Y^{3+} and Sc^{3+} cations are referred to as rare-earth sesquioxides. Some of the RE_2O_3 offer high quantum yield, attractive biocompatibility, high thermal and chemical stability, and resistance to phase transformation upon irradiation, which makes them suitable for optical[150], biomedical[151], electronic[152], and nuclear materials[146], [153].

Most of the RE_2O_3 undergo polymorphic transitions[54], which should be considered when designing such materials for specific applications. Three polymorphs are observed below 2000°C. Sesquioxides from La_2O_3 to Nd_2O_3 are stable with a trigonal structure (A-type, space group $P\bar{3}m1$); sesquioxides from Sm_2O_3 to Gd_2O_3 are stable with a monoclinic (B-type, $C2/m$) or a cubic structure (C-type, $Ia\bar{3}$); Y_2O_3 , Sc_2O_3 , and sesquioxides from Tb_2O_3 to Lu_2O_3 are stable with a C-type structure. Above 2000°C, RE_2O_3 transform into a high-temperature hexagonal (H-type, $P6_3/mmc$) and cubic structure (X-type, $Im\bar{3}m$)[54], [56]. An

additional orthorhombic perovskite (*Pnma*) structure is observed in LaLuO₃ and compounds with a similar difference in cationic radii[110], [113].

Mixing five or more REs in equiatomic amounts has been proven to result in single-phase RE₂O₃ with potential functional applications. Inspired by the compositional design of high-entropy oxides[40], [53], pioneering work on multicomponent RE oxides indicates the surprising stability of a single-phase up to 1500°C[70], [71]. Such structural stability and the variety of high-entropy RE₂O₃ compounds that can be synthesized[57], [72], [154]–[156] open the door to the discovery of functional properties that may surpass the performance of single-RE oxides. A few properties reported for high-entropy RE oxides include multi-wavelength luminescence emission[13], photocatalytic activity[157], electrical conductivity[158], [159], and environmental barrier coating[160].

Only a few studies focus on the polymorphic transformations and thermal expansion of high-entropy RE₂O₃ at elevated temperatures. Such knowledge is relevant for applications and synthesis methods that involve refractory temperatures such as environmental barrier coating and crystal growth from the melt, respectively. A single C-type phase was reported for (Gd,Tb,Dy,Ho,Er)₂O₃ up to 1650°C[57]. However, one might expect a transition to H- and/or X-type phases around 2000°C as in the case of single-RE RE₂O₃. In fact, another report demonstrates the transition sequence B-, H-, X-type in the range 1900°-2400°C for (La,Sm,Dy,Er,X)₂O₃ where X is either Nd, Gd, or Y[72]. The reported coefficient of thermal expansion (CTE) of these compounds is similar to that of Gd₂O₃[161]. However, it is not clear yet how composition affects the polymorphic behavior and thermal expansion of high-entropy RE₂O₃.

Since the polymorphism of single-RE RE₂O₃ is dictated by the RE³⁺ ionic radius[56], the average ionic radius (AIR) of complex compositions may play an important role in their structural stability. We previously demonstrated that a composition with only small REs maintains a cubic structure upon cooling from the melt to room temperature[162]. In this work, we formulate two compositions based on the ionic radius of the constituent cations. Composition 1 (Lu,Y,Ho,Nd,La)₂O₃ has mixed small (Lu³⁺, Y³⁺, and Ho³⁺) and large cations (Nd³⁺ and La³⁺), while composition 2 (Gd,Eu,Sm,Nd,La)₂O₃ has mixed medium (Gd³⁺, Eu³⁺, and Sm³⁺) and large cations. The structural evolution of both compounds is analyzed upon cooling from the melt via *in-situ* high-temperature X-ray diffraction in the range of 1000°C - 2450°C. A unique sample aerodynamic levitation capability allowed data collection at extreme temperatures (>2400°C) in a containerless sample environment.

Methods

Composition formulation

To study the effect of AIR on the polymorphic behavior of high-entropy RE_2O_3 , two five-component equiatomic compositions were formulated. The criterion to select RE elements was their ionic radii. Composition 1 ($\text{Lu}, \text{Y}, \text{Ho}, \text{Nd}, \text{La}$) $_2\text{O}_3$ contains a mixture of small (Lu^{3+} , Y^{3+} , and Ho^{3+}) and large REs (Nd^{3+} and La^{3+}) REs and composition 2 ($\text{Gd}, \text{Eu}, \text{Sm}, \text{Nd}, \text{La}$) $_2\text{O}_3$ contains a mixture of medium (Gd^{3+} , Eu^{3+} , and Sm^{3+}) and large REs; commas indicate equiatomic amounts. Table 4.1

Table 4.1 is a list of the REs and their respective ionic radius; the AIR of compositions 1 and 2 are included for comparison. The AIR of composition 1 is the same as the ionic radius of Gd^{3+} , while the AIR of composition 2 is close to that of Pm^{3+} (0.979 Å), although Pm was not included in any of the two formulations[124].

Powder synthesis

Powders were synthesized via a wet chemistry method using nitrates as the source of cations. The precursor powder was crystallized at 900°C for 1h in air.

Room-temperature powder X-ray diffraction

To determine the structure of the as-prepared powders, the samples were subjected to room-temperature powder X-ray diffraction (XRD). A Panalytical Empyrean diffractometer was used in the Bragg-Brentano geometry. X-rays were generated from a Cu K α source operated at 45 kV and 40 mA. The General Structure Analysis System II software (GSAS-II) was used to perform Rietveld structure refinements[163].

Preparation of spherical bead samples

Spherical samples were prepared with a favorable sample geometry for aerodynamic levitation during the *in-situ* high-temperature diffraction experiments described in section 2.5. Herein, such samples are referred to as beads. The following procedures were performed at the Spallation Neutron Source at Oak Ridge National Laboratory (ORNL). Powder samples were melted in a copper hearth to prepare 2-3 mm diameter beads. A 400-W continuous-wave CO_2 laser was used to heat and melt the powders. The melt was rapidly cooled by turning off the laser so that the samples maintained a spherical shape.

Table 4.1 - List of RE³⁺ cations, their respective ionic radius, and the average ionic radius (AIR) of the high-entropy compositions 1 and 2 for coordination number VI[124]. Commas in sample compositions indicate equiatomic amounts.

	RE ³⁺ cations								
	Lu ³⁺	Y ³⁺	Ho ³⁺	Gd ³⁺	Eu ³⁺	Sm ³⁺	Pm ³⁺	Nd ³⁺	La
Ionic radius (Å)	0.848	0.892	0.894	0.938	0.950	0.964	0.979	0.995	1.061
	Sample ID and composition								
	1 (Lu,Y,Ho,Nd,La) ₂ O ₃					2 (Gd,Eu,Sm,Nd,La) ₂ O ₃			
AIR (Å)	0.938					0.982			

Structural evolution analysis with in-situ high-temperature X-ray diffraction

The polymorphic behavior of both 1 (Lu,Y,Ho,Nd,La)₂O₃ and 2 (Gd,Eu,Sm,Nd,La)₂O₃ was studied via *in-situ* high-temperature synchrotron-generated X-ray diffraction at the Advanced Photon Source (APS), beamline 6-ID-D, at Argonne National Laboratory (ANL). To achieve elevated temperatures (>2400°C) without concern with sample holder stability and reactivity, a containerless sample environment was adopted by using an aerodynamic conical nozzle levitator system[137]. Bead samples were placed on the levitator nozzle and ultra-high purity Ar gas was used to levitate the samples. The vertical position of the levitator was adjusted with respect to the X-ray beam to provide diffraction from the top part of the sample. Monochromatic synchrotron radiation (0.124035 Å) was used to obtain diffraction patterns in the Debye-Scherrer geometry. An amorphous-silicon 2D X-ray detector was used and the sample-to-detector distance was ~1241 mm. Room-temperature diffraction from a LaB₆ standard sample was obtained to calibrate the detector distance and tilt.

To heat the samples, a Synrad Firestar i401 400 Watt continuous-wave carbon dioxide laser (10.6 μm) was focused on the top of the beads. A Chino IR-CAS near-infrared optical pyrometer was used to record the sample temperature, which was estimated using Wien's law. The emissivity of the samples was set to 0.92, which is a typical value for oxides[164]. Both laser and X-ray beams were co-incident on the top few hundred microns of the sample. The experimental setup used in this work has been previously described [165]–[167]. The mass change of the bead samples after the data collection was lower than 1.3 wt%.

Diffraction patterns were collected upon cooling the samples from the melt. A room-temperature pattern was initially collected and then the samples were melted. The FIT2D software was used for real-time visualization of the diffraction patterns and the molten state was determined when the diffraction lines were no longer seen and a typical pattern from a liquid sample was observed[168]. Diffraction patterns were obtained at constant temperatures every 50°C down to 1000°C; the cooling rate between temperature steps was ~20 °C/min. FIT2D was used to refine instrumental parameters and integrate the 2D diffraction images into 1D patterns. GSAS II was used for Rietveld structure refinement.

Results and discussion

Structure of the as-prepared powders

A single C-type phase was observed for as-prepared powders of compositions 1 and 2. As seen in Figure 4.1, the room-temperature powder XRD patterns of both samples match well with a reference pattern of C-type Er₂O₃. At 900°C, which is the highest temperature to which powders were heated during the synthesis, the expected structure of compositions 1 and 2 should be the C- and B-

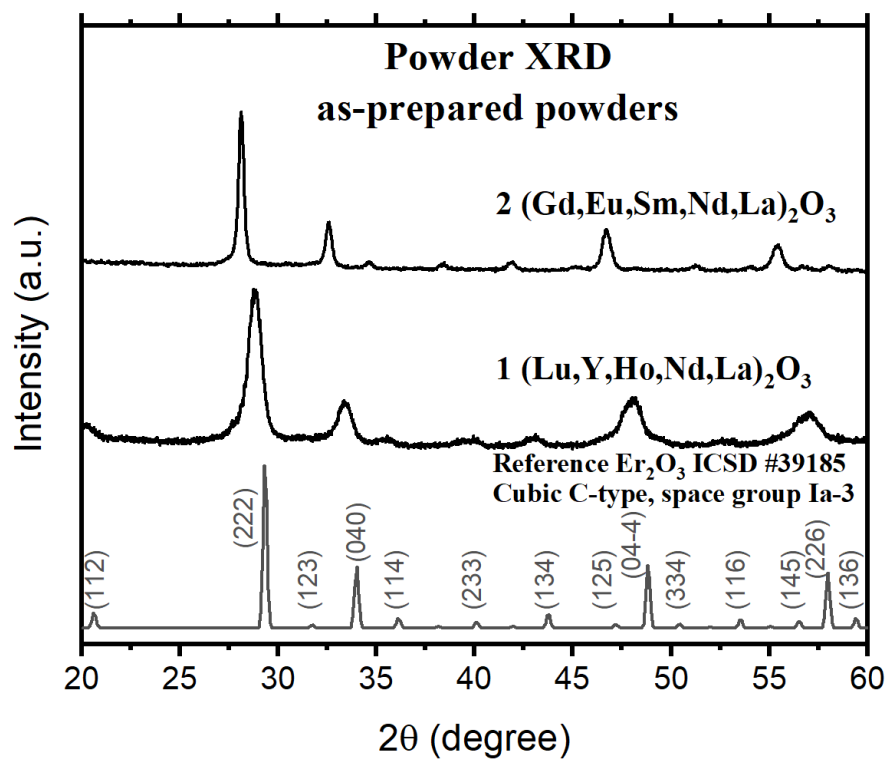


Figure 4.1 - Room-temperature powder XRD patterns of the as-prepared powders. Samples of compositions 1 and 2 have a single C-type phase. A reference pattern of C-type Er₂O₃ (ICSD # 39185) is included for comparison.

type, respectively, considering their AIR in the schematic diagram of polymorphic transformations seen in Figure 4.2. Considering that the C- to B-type transition is irreversible in single-RE RE₂O₃[54], composition 2 may have this transition above 900°C for composition 2, which is surprising since the transition occurs at 700°C for Pm₂O₃[169]. This indicates that the complex nature of composition 2 favors the C-type structure over a wide range of temperatures compared to single-RE RE₂O₃ of similar AIR. Significant variations in phase transition temperatures of high-entropy RE₂O₃ compared to single-RE RE₂O₃ have been previously reported[72]. Therefore, polymorphic transition temperatures of high-entropy RE₂O₃ cannot be predicted by the diagram of polymorphic transformations of single-RE RE₂O₃.

The powder of composition 1 has a more intense lattice strain and a smaller unit cell volume than composition 2. In Figure 4.1, the more pronounced peak broadening observed for composition 1 indicates a more intense lattice strain. This is expected since composition 1 combines small and large RE³⁺ and this disparity in ionic radii induces lattice strain. The refined lattice parameters of compositions 1 and 2 are 10.7313 Å and 10.9950 Å, respectively. Therefore, composition 2 has a larger C-type unit cell, which is expected since composition 2 is composed of larger REs as seen in Table 4.1.

Structure of the as-prepared bead samples

A single monoclinic B-type structure was observed for the as-prepared beads of composition 1 (Lu,Y,Ho,Nd,La)₂O₃ and 2 (Gd,Eu,Sm,Nd,La)₂O₃, indicating a phase transition from the C-type phase seen in the powders. Room-temperature synchrotron X-ray diffraction patterns of the as-prepared beads were obtained on the conical nozzle levitator setup prior to the high-temperature experiments. Figure 4.3 includes those patterns with Rietveld refinement results. The patterns of both samples were well fitted with calculated patterns of a single monoclinic phase. As seen by the lattice parameters listed in Figure 4.3, the bead of composition 1 has a smaller unit cell volume (434.996 Å³) than that of composition 2 (456.632 Å³), which is expected considering their AIR listed in Table 4.1. Since the beads were prepared by melting the powders with a C-type phase, there is a phase transition from C- to B-type for both compositions 1 and 2. In this work, high-temperature phase transitions are determined using the bead samples, therefore the C- to B-type transition temperature is not investigated.

Phase evolution upon cooling from the melt

Phase evolution of 1 (Lu,Y,Ho,Nd,La)₂O₃

As the bead of composition 1 was cooled from the melt, X-ray diffraction patterns corresponding to liquid, single H-type phase, and single B-type phase were observed as seen in Figure 4.4. A schematic representation of the phase evolution is shown in Figure 4.5, left. The sample of composition 1 solidified at

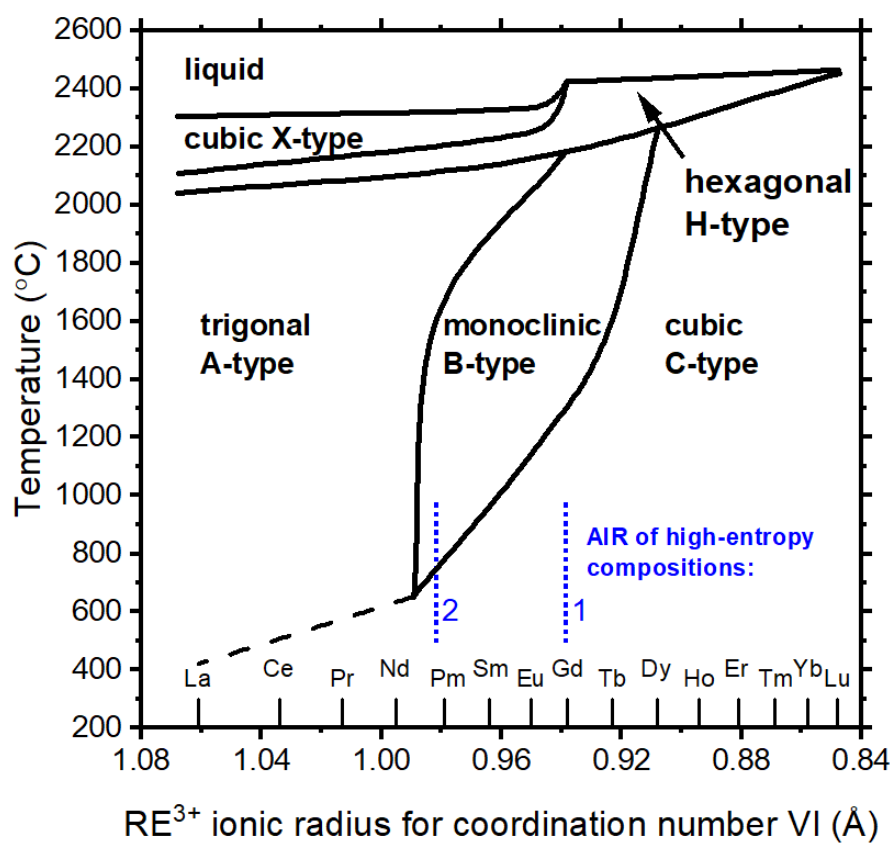


Figure 4.2 - Schematic diagram of polymorphic transformations for single-RE RE_2O_3 as a function of temperature and RE ionic radius for coordination number VI. Vertical dashed lines indicate the relative horizontal position of the AIR of compositions 1 (Lu, Y, Ho, Nd, La) $_2\text{O}_3$ and 2 (Gd, Eu, Sm, Nd, La) $_2\text{O}_3$.

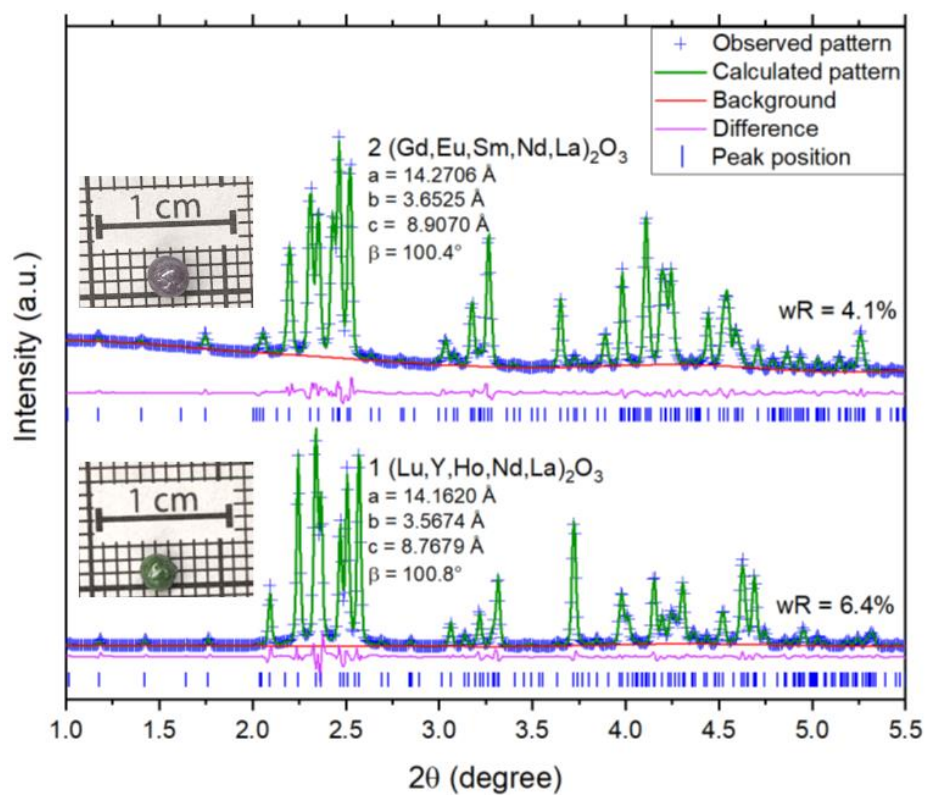


Figure 4.3 - Room-temperature synchrotron X-ray diffraction patterns and Rietveld refinement results of the as-prepared beads of compositions 1 $(\text{Lu, Y, Ho, Nd, La})_2\text{O}_3$ and 2 $(\text{Gd, Eu, Sm, Nd, La})_2\text{O}_3$. Both compounds have a single B-type phase. The lattice parameters of the monoclinic unit cell are listed in the figure.

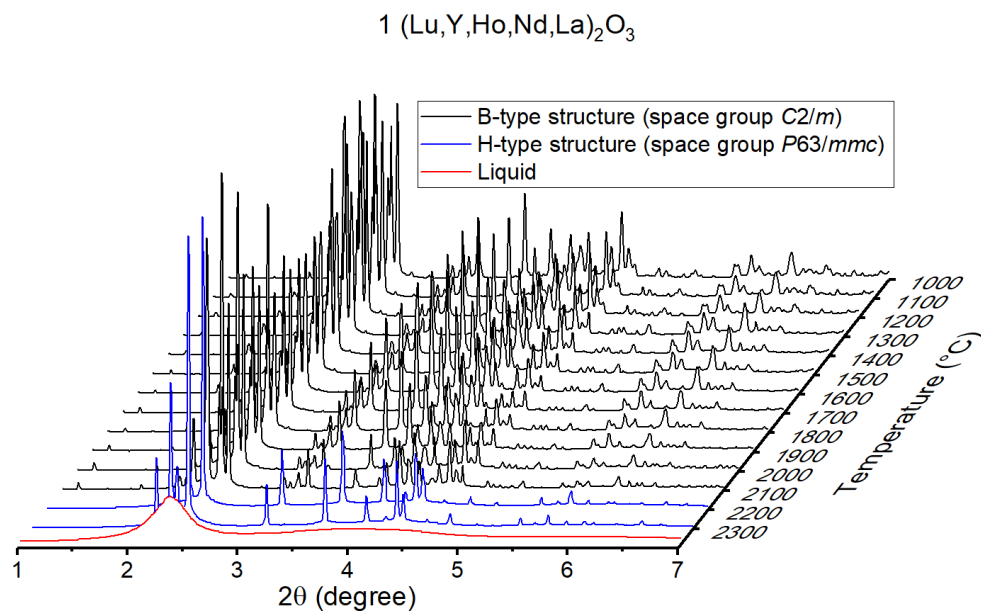


Figure 4.4 - *In-situ* high-temperature X-ray diffraction patterns of 1 (Lu,Y,Ho,Nd,La)₂O₃. The transitions observed upon cooling from the melt are liquid to H-type (~2350°C) and H-type to B-type (~2150°C).

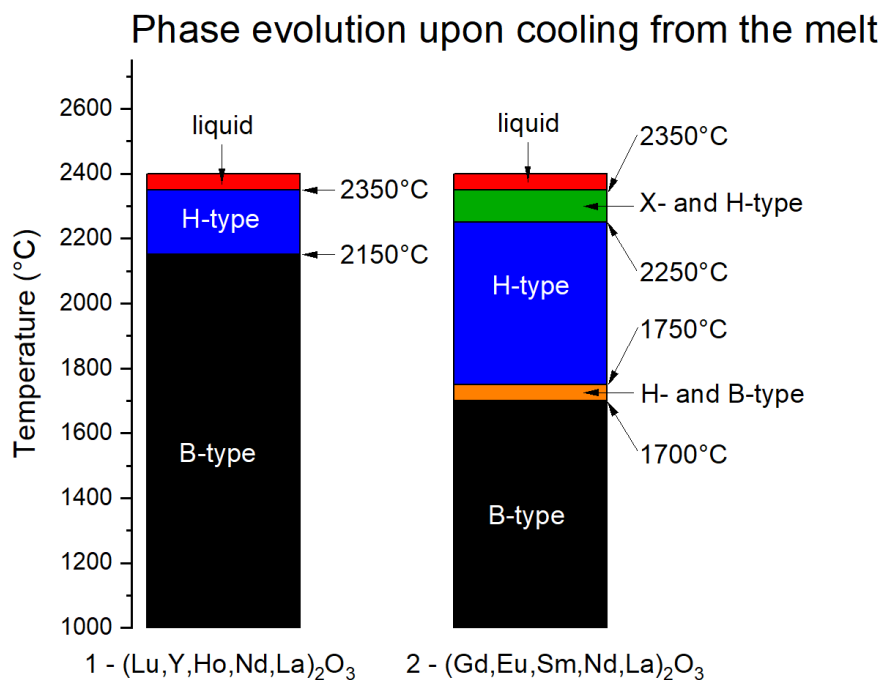


Figure 4.5 - Schematic representation of phase transitions observed upon cooling from the melt for compositions 1 (left) and 2 (right).

~2350°C with a single H-type structure. A transition from single H-type to single B-type structure occurred at ~2150°C; the B-type phase was stable upon cooling to 1000°C. These polymorphic transformations are expected according to the position of the AIR of composition 1 in the diagram of polymorphic transformations in Figure 4.2. None of the diffraction patterns indicated a mixture of phases for composition 1. The transition temperatures listed here correspond to the temperature at which a diffraction pattern indicated a different crystal structure than the immediately preceding collected pattern. Exact phase transition temperatures may lie within the 50°C temperature step between measurements.

Both the melting and B- to H-type transition temperatures of composition 1 are close to the smaller end of the temperature range previously reported for Gd_2O_3 . Composition 1 is compared to Gd_2O_3 because its AIR is the same as the ionic radius of Gd^{3+} , Table 4.1. The melting point of Gd_2O_3 is reported in the range of 2392°C - 2445°C [141], [143], [170]–[173] while composition 1 solidifies ~2350°C. This is in agreement with previous work that demonstrated that the melting point of RE_2O_3 can be suppressed in high-entropy compositions with similar AIR [162]. The B- to H-type transition temperature of Gd_2O_3 is reported in the range of 2170°C - 2195°C [170], [173] while composition 1 had this transition at ~2150°C, which is close to the lower end of this range. Therefore, the polymorphic behavior of single- RE_2O_3 can be used to predict the type of phase transformations that may occur in high-entropy RE_2O_3 .

Phase evolution of 2 (Gd,Eu,Sm,Nd,La)₂O₃

As the bead of composition 2 was cooled from the melt, X-ray diffraction patterns corresponding to liquid, a mixture of X- and H-type, single H-type, a mixture of H- and B-type, and single H-type structures were observed as seen in Figure 4.6. A schematic representation of the phase evolution is shown in Figure 4.5, right. The sample of composition 2 solidified ~2350°C and a mixture of H- and X-type structures was observed at ~2350°C and ~2300°C; the relative amounts of the H-type phase were 57 and 95 wt%, respectively. This indicates that the cubic X-type phase is stable in a relatively short temperature range and the H-type phase is preferentially formed at temperatures close to the melting point. A single H-type phase was observed from 2250°C to 1800°C. The H- to B-type transition was observed at 1750°C with a mixture of both phases (81 wt% H-type). Upon further cooling, a single B-type phase was observed from 1700°C to 1000°C.

The observed polymorphic transformations of composition 2 are slightly different than the ones predicted in the diagram of polymorphic transformations in Figure 4.2 for the respective AIR. Since the AIR of composition 2 is close to that of Pm^{3+} , the polymorphism of a single RE Pm_2O_3 will be considered to compare to composition 2. The melting point of Pm_2O_3 (X-type to liquid) was reported as 2320°C [143], [169] while composition 2 solidifies at ~2350°C. The X- to H-type

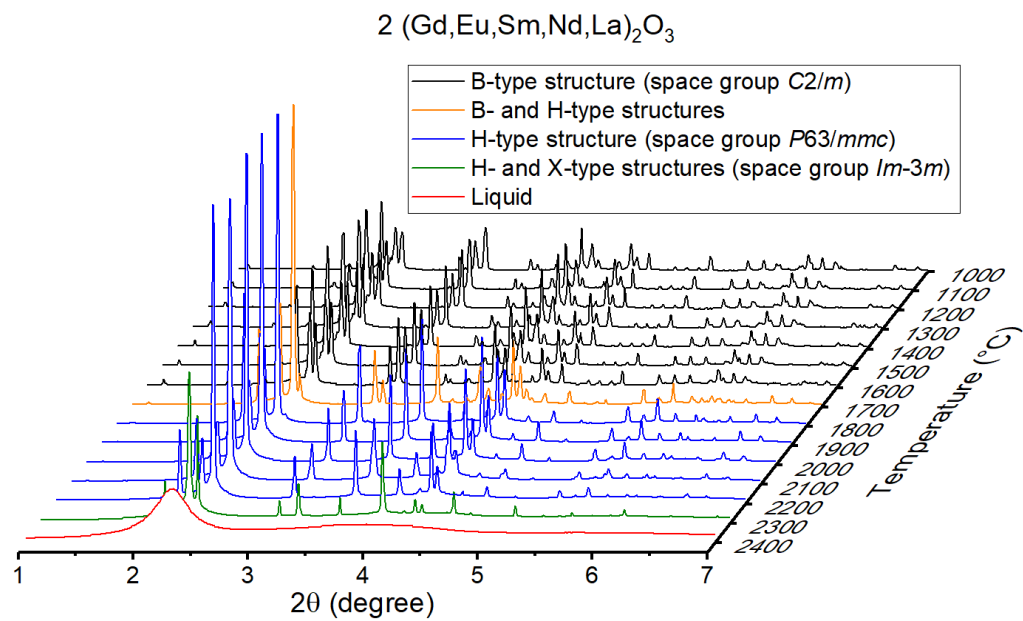


Figure 4.6 - *In-situ* high-temperature X-ray diffraction patterns of $2 (\text{Lu, Y, Ho, Nd, La})_2\text{O}_3$. The transitions observed upon cooling from the melt are liquid to a mixture of H- and X-type ($\sim 2350^{\circ}\text{C}$), a single H-type (2250°C), a mixture of B- and H-type (1750°C), and a single B-type structure (1700°C).

transition of Pm_2O_3 was reported as 2225°C [143], [169], indicating that the temperature range of stability of the X-type structure is larger for Pm_2O_3 ($\sim 100^\circ\text{C}$) than composition 2, for which a single X-type phase was not observed. Additionally, the H- to A-type transition was reported for Pm_2O_3 in the range of 2117°C - 2135°C [143], [169], but was not observed for composition 2. Finally, the A- to B-type transition of Pm_2O_3 was reported in the range of 1600°C - 1740°C [169], [174], while the H- to B-type transition was observed at 1750°C which is close to the smaller end of the reported range. Once again, the polymorphic behavior of a high-entropy RE_2O_3 could not be accurately predicted by the polymorphism of a single-RE RE_2O_3 with a similar AIR.

In general, the polymorphic nature of both compositions 1 and 2 as a function of their AIR is in agreement with the polymorphism of single-RE RE_2O_3 as seen in Figure 4.2 and Figure 4.5. Upon cooling from the melt, the transition sequence for the smaller-AIR composition 1 was liquid, H-type, and B-type structure, while for the larger-AIR composition 2 the sequence was liquid, X-type, H-type, and B-type. Additionally, the transition to a B-type phase was at a much lower temperature for composition 2 (1700°C) than for composition 1 (2150°C). It is important to note that the specific transition temperatures of compositions 1 and 2 could not be predicted by the diagram in Figure 4.2. Also, composition 2 did not form the A-type phase indicated in that diagram.

Thermal expansion coefficient obtained from refined unit cell parameters

Thermal expansion of 1 (Lu,Y,Ho,Nd,La) $_2\text{O}_3$

Structure refinement results indicate the expansion of the B- and H-type unit cell with temperature for composition 1. Figure 4.7.a includes the lattice parameters a , b , c , and β of the B-type unit cell. The parameter β corresponds to the angle formed between the a - and c - axis, which varied less than 1% in the entire temperature range in which the B-type phase was observed. Figure 4.7.b includes the lattice parameters a , and c of the H-type unit cell. A relatively low goodness-of-fit R^2 (84.4%) was obtained for the linear regression of the H-type lattice parameter c , because only four data points are available for the H-type cell. Refined lattice parameters can be used to determine the high-temperature coefficient of thermal expansion (CTE). The CTE α is determined as

$$\alpha = \left(\frac{dl}{dT} \right) \frac{1}{l_0}$$

Equation 1

where l is the lattice parameter and T is temperature. The differential expression dl/dT was taken as the slope of the linear regression applied to the lattice parameter data (Figure 4.7.a). Additionally, l_0 was taken as the refined lattice parameter at the lowest temperature that a given crystal structure was observed

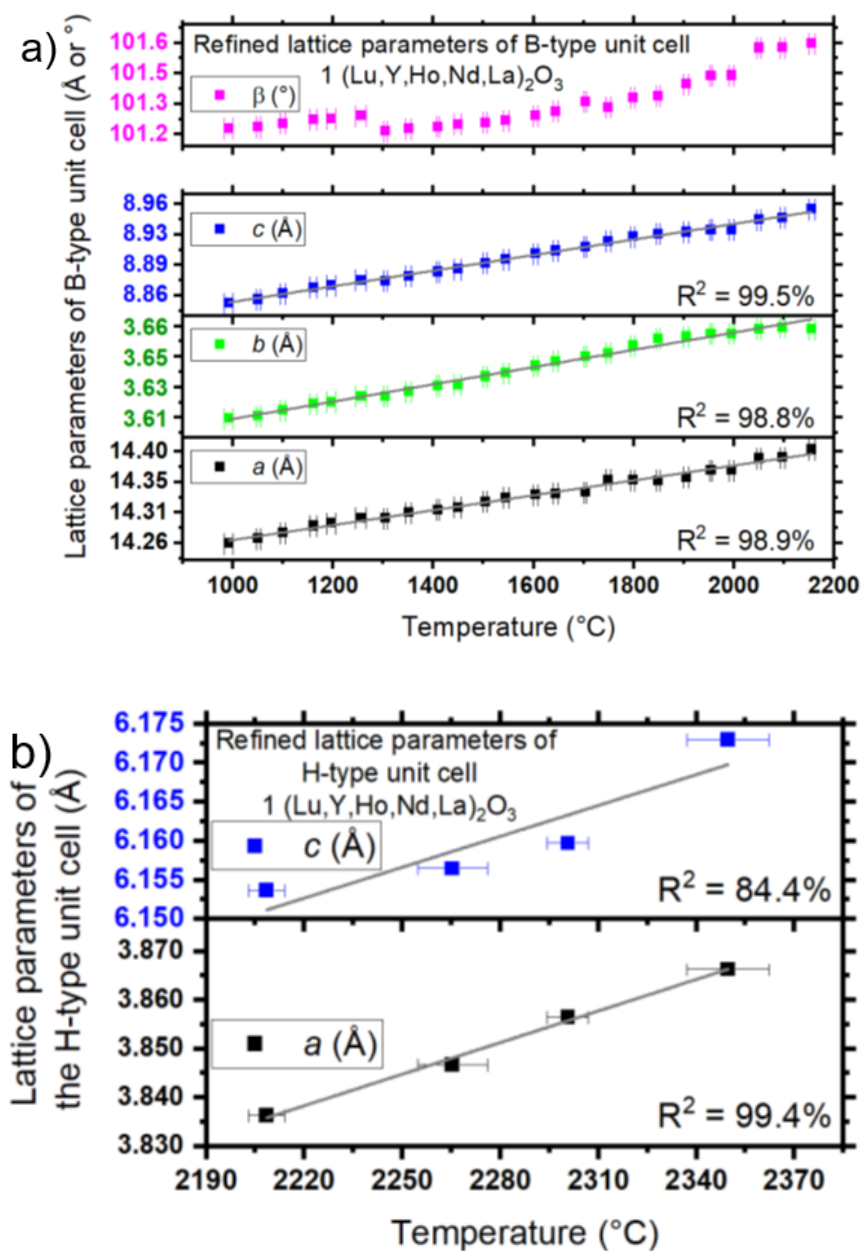


Figure 4.7 - Lattice parameters of the B-type (a) and H-type (b) structures of 1 (Lu,Y,Ho,Nd,La)₂O₃. Values were obtained from structure refinement using in-situ high-temperature X-ray diffraction data. Gray lines are linear regression fits and their respective goodness-of-fit R^2 is included in the images.

during the high-temperature experiments. The CTE values of the B-type phase of composition 1 are listed in Table 4.2.

Composition 1 has CTE values similar to those of Gd_2O_3 and previously published high-entropy RE_2O_3 . Sawbridge and Waterman[161] reported the CTE of B-type Gd_2O_3 in the range of 20°C - 900°C and Ushakov *et al.*[72] reported the CTE of B-type $(\text{La,Sm,Dy,Er,X})_2\text{O}_3$, where X is either Nd, Gd, or Y from room temperature to ~1950°C. The reported values are in Table 4.2; the $(\text{La,Sm,Dy,Er,X})_2\text{O}_3$ compounds had similar CTE and only one set of values was listed. The similarity in the CTE values of composition 1, Gd_2O_3 , and $(\text{La,Sm,Dy,Er,X})_2\text{O}_3$ indicates that complex compositions do not largely affect the thermal expansion of RE_2O_3 . It was not possible to accurately calculate the CTE of the H-type structure for composition 1 because of its narrow temperature range of stability and the resulting small number of data points seen in Figure 4.7.b.

Thermal expansion of 2 (Gd,Eu,Sm,Nd,La)₂O₃

Structure refinement results indicate the expansion of the B- and H-type unit cell with temperature for composition 2. Figure 4.8.a includes the lattice parameters a , b , c , and β of the B-type unit cell. The angle β varied less than 1% in the entire temperature range in which the B-type phase was observed. At 1750°C, a mixture of B- and H-type phases was observed. At this temperature, the lattice parameters a and c of the B-type unit cell lie below the linear trend seen for the values obtained at lower temperatures. This indicates that the B-type cell is richer in smaller REs than the H-type cell at 1750°C. A similar observation is seen at ~2300°C and 2350°C in Figure 4.8.a. At those temperatures, there is a mixture of H- and X-type phases and the H-type phase is richer in smaller REs than the X-type phase. Such deviation from linearity for lattice parameter values at phase transition temperatures is a common phenomenon[175]–[177]. The X-type phase was observed in only two diffraction patterns and its lattice parameter increased from 4.37397 Å at ~2300°C to 4.3807 Å at ~2350°C.

For composition 2, the CTE values of the H-type phase are significantly larger than those of the B-type phase as seen in Table 4.2. The B-type phase has CTE values similar to those of composition 1, which suggests that the type of REs in a high-entropy sesquioxide does not largely affect the CTE. A relatively large number of lattice parameter data points allowed the calculation of the CTE values of the H-type phase of composition 2 seen in Table 4.2. To the best of our knowledge, the CTE of H-type single-RE or high-entropy RE_2O_3 has not been previously reported. The CTE of the hexagonal YbFeO_3 (same space group as the B-type structure, $C2/m$) along the c -axis was reported as $\sim 30 \times 10^{-6}/\text{K}$ [178], which is similar to the calculated value for composition 2 seen in Table 4.2. The CTE calculations reported here did not include the lattice parameters corresponding to temperatures at which a mixture of phases was observed (1750°C, 2300°C, and

Table 4.2 - Coefficients of thermal expansion (CTE) for each lattice axis of the B- or H-type unit cells for compositions 1 and 2 as well as literature values for B-type Gd_2O_3 and $(\text{La},\text{Sm},\text{Dy},\text{Er},\text{X})_2\text{O}_3$, X = Nd, Gd, or Y. Anisotropic factor (A) values are included.

Sample	Phase	Temperature range (°C)	CTE α ($\times 10^{-6}/\text{K}$)			A ($\times 10^{-6}/\text{K}$)
			α_a (a-axis)	α_b (b-axis)	α_c (c-axis)	
1 $(\text{Lu},\text{Y},\text{Ho},\text{Nd},\text{La})_2\text{O}_3$	B-type	1000 – 2150	7.8 ± 0.2	13.4 ± 0.3	10.5 ± 0.2	11
2 $(\text{Gd},\text{Eu},\text{Sm},\text{Nd},\text{La})_2\text{O}_3$	B-type	1000 – 1700	9.0 ± 0.3	18.8 ± 0.3	13.2 ± 0.2	19
	H-type	1800 – 2250	41 ± 3	-	32 ± 1	18
Gd_2O_3 from [161]	B-type	20 – 900	9.7 ± 0.2	15.4 ± 0.4	13.9 ± 0.2	11
$(\text{La},\text{Sm},\text{Dy},\text{Er},\text{X})_2\text{O}_3$, X = Nd, Gd, or Y from [72]	B-type	25 – ~1950	7.8 ± 0.7	16 ± 2	12 ± 5	16

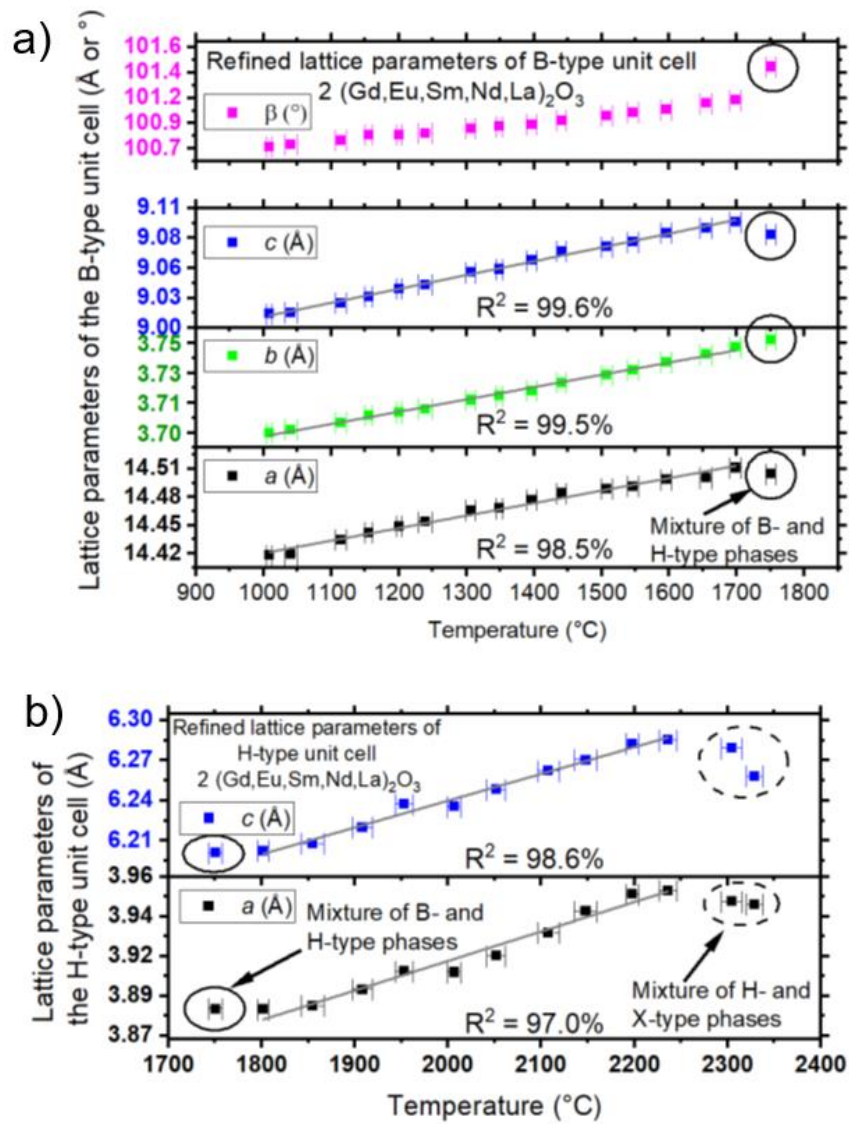


Figure 4.8 - Lattice parameters of the B-type (a) and H-type (b) structures of $2(\text{Gd,Eu,Sm,Nd,La})_2\text{O}_3$. Values were obtained from Refined structure refinement using the in-situ high-temperature X-ray diffraction data. Gray lines are linear regression fittings and their respective goodness-of-fit R^2 is included in the images.

2350°C).

Composition 2 has a higher degree of expansion anisotropy than composition 1 and is less favorable for high-temperature applications and synthesis methods. The anisotropic factor A is given by $A = |\alpha_a - \alpha_b| + |\alpha_a - \alpha_c| + |\alpha_b - \alpha_c|$ and is listed in Table 4.2. High A values for composition 2 indicate a greater disparity in the CTE along the unit cell axes, which makes it more likely to fracture if subjected to high-temperature applications under cycling conditions. Additionally, materials with high A values are more challenging to grow as single crystals via directional solidification. As the crystal cools, twinning and cracking may result from the expansion anisotropy and are more likely to occur for materials with high A values [179], [180].

Conclusion

The polymorphic structures formed in high-entropy RE_2O_3 are dictated by their AIR and follow the general trend of single-RE RE_2O_3 . Upon cooling from the melt to 1000°C, the phase evolution observed for composition 1 ($\text{Lu,Y,Ho,Nd,La})_2\text{O}_3$ was liquid, H-type, and B-type. The AIR of composition 1 is equal to that of Gd^{3+} and its polymorphic behavior is similar to that of Gd_2O_3 , and the transition temperatures are lower for the high-entropy compound. The phase evolution observed for composition 2 ($\text{Gd,Eu,Sm,Nd,La})_2\text{O}_3$ was liquid, X-type, H-type, and B-type. The AIR of composition 1 is close to that of Pm^{3+} and its polymorphic behavior is similar to that of Pm_2O_3 , except for the H- to A-type transition that was not detected for composition 2. Additionally, the X-type phase is stable in a much shorter temperature range for composition 2 than Pm_2O_3 .

Complex compositions do not largely affect the CTE of the B-type phase; the CTE of the H-type phase was reported for the first time and is considerably larger than that of the B-type phase. Both compositions 1 and 2 have CTE values that are similar to those of Gd_2O_3 and previously published high-entropy RE_2O_3 . The CTE of the B-type phase is α_a , α_b , and α_c equal to 7.8, 13.4, and $10.5 \times 10^{-6}/\text{K}$ for composition 1, and 9.0, 18.8, and $13.2 \times 10^{-6}/\text{K}$ for composition 2, respectively. For the first time, we report the CTE values of the H-type phase of a RE_2O_3 , which are significantly larger than those of the B-type phase. Composition 2 has α_a and α_c equal to 41 and $32 \times 10^{-6}/\text{K}$, respectively.

Future investigation of high-temperature applications and synthesis methods for high-entropy RE_2O_3 can benefit from the polymorphism and thermal expansion results reported here. Novel compounds could be tailored as a function of AIR to prioritize a specific structure over a desired temperature range or to adjust transition temperatures. Additionally, rare-earth combinations other than the ones reported here may result in compounds with surprisingly different polymorphic and thermal expansion behaviors, which inspires further investigation.

CHAPTER FIVE:
CRYSTAL GROWTH AND ELEMENTAL HOMOGENEITY OF THE
MULTICOMPONENT RARE-EARTH GARNET
(Lu_{1/6}Y_{1/6}Ho_{1/6}Dy_{1/6}Tb_{1/6}Gd_{1/6})₃Al₅O₁₂

A version of this chapter was published by Matheus Pianassola and colleagues:

M. Pianassola, M. Loveday, B. C. Chakoumakos, M. Koschan, C. L. Melcher, and M. Zhuravleva, "Crystal Growth and Elemental Homogeneity of the Multicomponent Rare-Earth Garnet $(\text{Lu}_{1/6}\text{Y}_{1/6}\text{Ho}_{1/6}\text{Dy}_{1/6}\text{Tb}_{1/6}\text{Gd}_{1/6})_3\text{Al}_5\text{O}_{12}$," *Cryst. Growth Des.*, vol. 20, no. 10, pp. 6769–6776, Oct. 2020, doi: 10.1021/acs.cgd.0c00887.

This chapter is the reformatted version of the original work submitted to the referenced journal. No additional changes to the content of the original article were done other than formatting to conform to the dissertation format.

Abstract

High-entropy aluminum garnets were grown as bulk single crystals using the micro-pulling-down method, taking the synthesis of complex ceramics a step further from the conventional preparation of polycrystalline materials. We studied the effects of growth parameters on the elemental distribution in high optical quality crystals of $(\text{Lu}_{1/6}\text{Y}_{1/6}\text{Ho}_{1/6}\text{Dy}_{1/6}\text{Tb}_{1/6}\text{Gd}_{1/6})_3\text{Al}_5\text{O}_{12}$ containing six cations (yttrium and rare-earths) taken in equimolar amounts. A single garnet structure was confirmed by powder X-ray diffraction. Electron microprobe measurements were obtained to correlate the radial distribution of rare-earth elements with pulling rates and molten zone height. The nature of the elemental distribution in the radial direction was associated with ionic radius: smaller rare-earths concentrated in the center of the crystal while larger rare-earths segregated toward the outer edge of the cylindrical crystal. Faster pulling rates led to flattening of the concentration profiles toward the nominal concentration, promoting a more homogeneous radial elemental distribution, while varying the molten zone height did not have a significant effect. The demonstrated success with crystal growth enables practical availability of single crystals of multicomponent aluminum garnets for further discovery of new phenomena and applications.

Introduction

Commercial rare-earth aluminum garnet (REAG) crystals usually have one or two types of rare-earths (RE); however, recent studies on high-entropy ceramics suggest that mixing five or more elements in equimolar amounts may enhance functional properties [40]. REAG crystals are widely used and investigated for luminescent applications. Typical compositions include $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Nd}$ and $\text{Lu}_3\text{Al}_5\text{O}_{12}:\text{Pr}$ used as a lasing medium and a scintillator, respectively [86], [87]. The general formula of a REAG is $\text{RE}_3\text{Al}_5\text{O}_{12}$, where RE is a rare-earth element. In the cubic garnet structure, the RE occupies a dodecahedral crystallographic site, while Al occupies tetrahedral and octahedral sites. Due to the geometry of the dodecahedral site, only REs smaller than Gd^{3+} can form an aluminum garnet without disrupting the Al-O framework [181]. Small amounts of larger cations such

as Nd^{3+} and Pr^{3+} can be added into REAG as dopants without major lattice distortions. The functional performance of REAG crystals is commonly explored by admixing 2 or 3 elements in the RE or Al sites [15]–[20]. Although the interesting compositional design of high-entropy oxides has been applied to many compounds [40], high-entropy REAG single crystals with multiple principal REs have not yet been reported. High-entropy oxides are single-phase materials that contain 5 or more principal cations and have a configurational entropy ΔS_{conf} higher than $1.5R$ (where R is the universal gas constant). ΔS_{conf} is maximized by having equimolar amounts of cations, which then minimizes the Gibbs free energy of mixing, favoring the thermodynamic stabilization of a single phase with multiple cations [130].

Following the general trend of high-entropy metallic alloys,[130] the possibility of obtaining exceptional functional properties has inspired the investigation of high-entropy oxides [40], [53]. A few RE-based high-entropy polycrystalline ceramics have been reported including sesquioxide [70], [71], silicate [182], [183], zirconate [79], phosphate [184], aluminum perovskite [78], and aluminum garnet [79] structures. In previous reports, the availability of high-entropy oxides was restricted to the synthesis methods for ceramics or thin films [11]. To consider highly complex REAG compositions as prospective host materials for applications such as lasing and scintillation, high optical quality single crystals need to be synthesized to enable the characterization of luminescence properties such as optical transmittance and light yield. To the best of our knowledge, bulk single-crystal high-entropy oxide materials have not yet been synthesized.

In this work, the crystal growth of high optical quality highentropy aluminum garnet $(\text{Lu}_{1/6}\text{Y}_{1/6}\text{Ho}_{1/6}\text{Dy}_{1/6}\text{Tb}_{1/6}\text{Gd}_{1/6})_3\text{Al}_5\text{O}_{12}$ was demonstrated, and distribution of the six REs was investigated. For simplicity we refer to yttrium as one of the REs in this multicomponent garnet. These six REs were selected for this study due to their wide range of RE^{3+} ionic radii, 0.097–1.06 Å [124]. Most studies into the elemental homogeneity of micro-pulling-down crystals focus on the distribution of small dopant concentrations [185]–[188] or solid solutions with a smaller number of constituents [189]. Here we used electron microprobe analysis to investigate the distribution of the six principal REs in a highly complex aluminum garnet crystal.

Single-crystal growth of the one-component garnets formed by each of these six RE and their structural stability have been reported. While $\text{Lu}_3\text{Al}_5\text{O}_{12}$, $\text{Y}_3\text{Al}_5\text{O}_{12}$, $\text{Ho}_3\text{Al}_5\text{O}_{12}$, and $\text{Dy}_3\text{Al}_5\text{O}_{12}$ single crystals can be produced from the melt with relative ease [83], [86], [190], [191], the crystal growth of $\text{Gd}_3\text{Al}_5\text{O}_{12}$ or $\text{Tb}_3\text{Al}_5\text{O}_{12}$ is a challenge, since both compounds melt incongruently [73], [181], [192]–[194]. Despite this challenge, we grew $(\text{Lu}_{1/6}\text{Y}_{1/6}\text{Ho}_{1/6}\text{Dy}_{1/6}\text{Tb}_{1/6}\text{Gd}_{1/6})_3\text{Al}_5\text{O}_{12}$ crystals from a stoichiometric melt. This success expands the compositional space of REAG toward areas with higher configurational entropy and enables the practical availability of single crystals for the investigation of fundamental and functional properties. Although the crystals studied in this work satisfy the definition of a high-entropy oxide [40], here we refrain from referring to them as entropy-

stabilized materials, since the precise mechanism of phase stabilization is still unknown.

Methods

Starting materials

In preparation for the crystal-growth experiments, the following powder materials were dried at 800°C for 5 h in air: Lu_2O_3 (Yarmouth Materials, 99.999%), Y_2O_3 (Yarmouth Materials, 99.999%), Ho_2O_3 (Alfa Aesar, 99.99%), Dy_2O_3 (Alfa Aesar, 99.99%), Tb_4O_7 (Alfa Aesar, 99.9%), Gd_2O_3 (American Elements, 99.999%), and Al_2O_3 (Yarmouth Materials, 99.99%). One-gram stoichiometric mixtures of the dried powders were mixed by manual agitation in 4 mL glass vials.

Crystal growth

Five cylindrical single crystals were grown using a KDN Dai-Ichi Kiden micro-pulling-down furnace equipped with an RF generator model TR-02001 operated at 26 kVA. A schematic representation of the furnace setup is shown in Figure 1.2, which is similar to previously reported work [37]. A $\varnothing 16$ mm iridium crucible with a $\varnothing 3$ mm die and a $\varnothing 0.5$ mm capillary channel was used as a melt reservoir. Growth was initiated by touching the outlet of the capillary channel with a Czochralski-grown $\text{Lu}_3\text{Al}_5\text{O}_{12}$ crystal seed. Crystal growth proceeds by continuous lowering of the seed, which leads to a controlled solidification of the melt. An appropriate temperature gradient is maintained by use of an Ir after-heater immediately below the crucible. An appropriate temperature gradient is judged by the visual observation of the stable shape and height of the molten zone. The melt is supplied to the molten zone through the crucible capillary.

A charge-coupled device (CCD) camera was focused on the bottom of the crucible die to allow real-time visualization of seeding and monitoring of the molten zone. The shape and height of the molten zone affect the shape of the crystal, its structural quality, the mass exchange in the molten zone, and, consequently, the spatial distribution of the elements in the grown crystal [37]. Oxidation of the crucible and the deposition of possible volatiles on the lower portion of the outer quartz tube were prevented by use of a growth atmosphere composed of flowing nitrogen. The RF generator power was ramped over a period of 2 h to achieve the melting point, which was visually determined by probing the capillary with the seed and observing the presence of molten material.

Five crystals were grown with differing molten zone heights and pulling rates, chosen to study the effect of these parameters on the elemental distribution both radially and axially throughout the crystal. Crystal growth was initiated ~ 10 min after melting with an initial pulling rate of 0.05 mm/min. One crystal was grown with a molten zone height of ~ 100 μm and pulling rate of 0.05 mm/min throughout

the entire growth process. Four crystals were grown with a molten zone height of $\sim 300\ \mu\text{m}$; after these crystals reached the full 3 mm diameter, the pulling rate was either kept at 0.05 mm/min or gradually increased. For the crystal pulled at 0.10 mm/min, the target pulling rate was achieved at 1.8 mm from the seed end; similarly, the crystals pulled at 0.15 and 0.20 mm/min reached the target pulling rate at 2.4 and 3.2 mm from the seed end, respectively. The fluctuation of the molten zone height was visually estimated to be in the range of 25–50 μm . The melt temperature is directly proportional to the visible molten zone height, which was controlled by manually adjusting the RF generator power. A stable molten zone is essential for growth stability and crystal diameter control. After the growth was finished, the RF generator power ramp-down was conducted over a period of 4 h. A small amount of material remained at the bottom of the crucible after all growth experiments. A list of crystals studied and their respective pulling rates and molten zone heights is in Table 5.1.

Density measurements

The crystal density was measured by the Archimedes principle method using a Sartorius YDK 01 Density Determination Kit with a Sartorius CP324 S balance. Deionized water at room temperature was used as the immersion liquid.

Powder X-ray diffraction

To identify the crystalline phase, each crystal was cut in half longitudinally, and one of the halves was ground in a mortar for room-temperature powder X-ray diffraction (XRD). Patterns were obtained with a Panalytical Empyrean diffractometer in the Bragg–Brentano geometry using a Cu K α X-ray source at 45 kV and 40 mA. Phase analysis and lattice parameters were evaluated via Rietveld refinements with the General Structure Analysis System II software (GSASII). A goodness-of-fit value smaller than 1.60 was achieved for all refinements.

Single-crystal X-ray diffraction

Two crystal fragments ($\sim 0.001\ \text{mm}^3$) were cut from the center and outer surface of the crystal 005–100. The fragments were suspended in the mineral oil of a plastic loop attached to a copper pin/goniometer. Single-crystal diffraction data were collected at 260 K using a Rigaku XtaLAB PRO diffractometer with graphite monochromated Mo K α radiation ($\lambda = 0.710\ 73\ \text{\AA}$, 50 kV, and 40 mA) equipped with a Rigaku HyPix6000HE detector and an Oxford N-HeliX cryocooler. Peak indexing and integration were done using the Rigaku Oxford Diffraction CrysAlisPro software.³⁶ An empirical absorption correction was applied using the SCALE3 ABSPACK algorithm as implemented CrysAlisPro. The SHELXL-2013 and WinGX software packages were used for data processing and structure refinement [195], [196]. The structure refinements were made with oxygen atompositional coordinates, anisotropic atomic displacement parameters, an

Table 5.1 - A list of crystals grown with respective pulling rates and molten zone depths. The naming convention used is “pulling rate - molten zone height”.

Crystal	Pulling rate (mm/min)	Molten zone height (μm)
005-100	0.05	~100
005-300	0.05	~300
010-300	0.10	~300
015-300	0.15	~300
020-300	0.20	~300

extinction parameter, and the scale factor.

Electron Microprobe Analysis

A longitudinal half of each crystal was embedded in epoxy for the elemental composition analysis of crystal cross sections by electron probe microanalysis (EPMA) with a CAMECA SX100 Electron Microprobe. The instrument is equipped with high-speed backscattered electron (BSE) detectors and four wavelength-dispersive spectrometers (WDS). Images were obtained by detecting the backscattered electrons, and compositional information was acquired by detecting characteristic X-rays by WDS. The instrumental voltage and current were 15 kV and 30 nA, respectively. The probe point size was 1 μm , and the excitation area diameter was in the 2–3 μm range. Radial distribution profiles were obtained by collecting data at 100 μm steps; multiple profiles were spaced 2.5 mm apart.

Results and discussion

Grown crystals

All five 3 mm diameter crystals grown are yellow and crack-free, except the crystal pulled at 0.20 mm/min, which has a small crack close to the seed end as indicated in Figure 5.1 by a white dashed oval. The formation of this crack was visually observed in real time and started propagating when the crystal was still being pulled at 0.05 mm/min; therefore, the crack formation is not correlated with the faster pulling rate. The different pulling rates and molten zone heights used did not affect the visually observable quality of the crystals. Images of the molten zone of crystals 005–100 and 005–300 are shown in Figure 5.2 for comparison of the monitored molten zone height. The crystal density measured by the Archimedes method is 5.95 g/cm³.

Crystal Structure

Powder XRD

The $(\text{Lu}_{1/6}\text{Y}_{1/6}\text{Ho}_{1/6}\text{Dy}_{1/6}\text{Tb}_{1/6}\text{Gd}_{1/6})_3\text{Al}_5\text{O}_{12}$ crystals have a single garnet phase, as confirmed by the powder XRD patterns in Figure 5.3; reference YAG reflection peaks [197] are also plotted for comparison. Assuming a homogeneous mixture of the six REs throughout the whole crystal, one would expect the lattice parameter of the multicomponent composition to be close to the average taken from the lattice parameters of the corresponding one-component REAG, namely, LuAG [198], YAG [198], HoAG [191], DyAG [199], TbAG [200], and GdAG [198].

Figure 5.4 includes the literature values of the lattice parameters of single-REAG as a function of rare-earth ionic radius for the 3+ oxidation state and

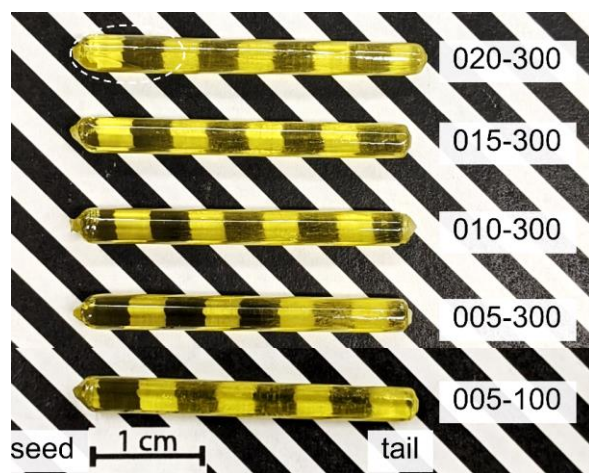


Figure 5.1 - Single crystals of $(\text{Lu}_{1/6}\text{Y}_{1/6}\text{Ho}_{1/6}\text{Dy}_{1/6}\text{Tb}_{1/6}\text{Gd}_{1/6})_3\text{Al}_5\text{O}_{12}$ were grown with varying growth parameters, see Table 5.1. All crystals are cylinders with 3 mm in diameter. A white dashed oval indicates the area with a crack in the crystal pulled at 0.20 mm/min.

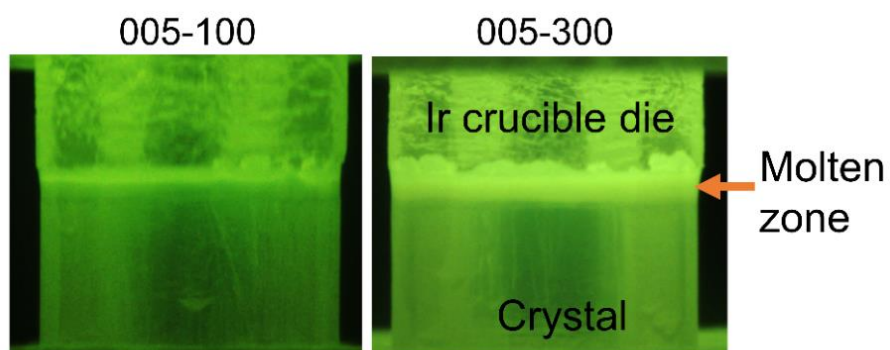


Figure 5.2 - Images of the molten zone monitored in real-time for the crystals 005-100 (left) and 000-300 (right).

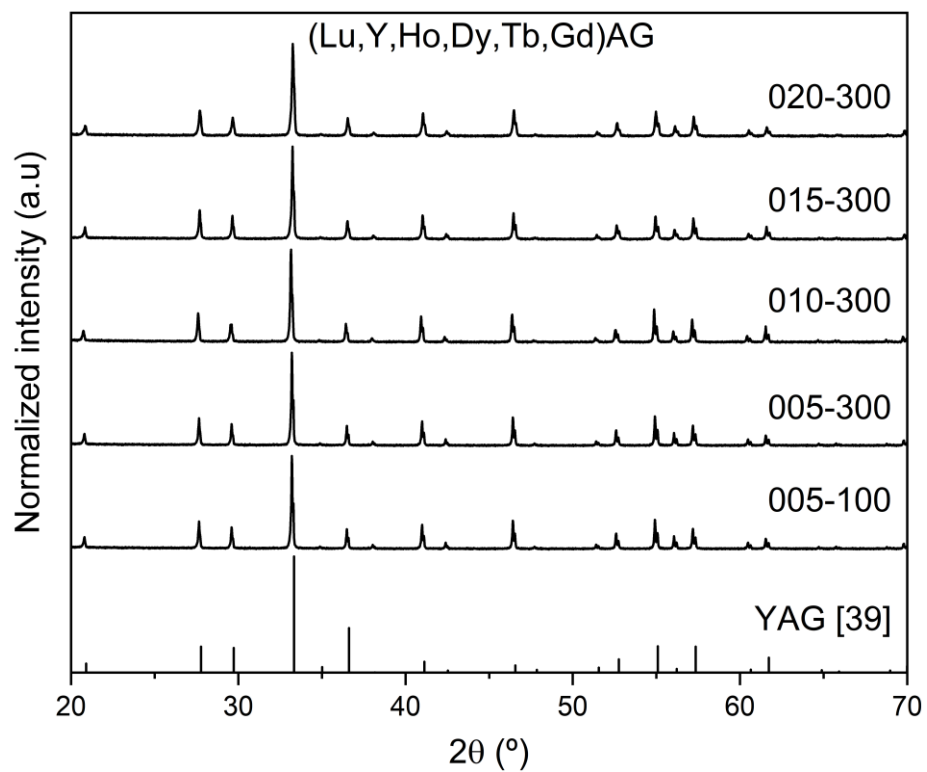


Figure 5.3 – Powder XRD patterns of $(\text{Lu}_{1/6}\text{Y}_{1/6}\text{Ho}_{1/6}\text{Dy}_{1/6}\text{Tb}_{1/6}\text{Gd}_{1/6})_3\text{Al}_5\text{O}_{12}$ single-crystals indicate a single garnet phase. YAG reflection peaks are plotted for comparison [197].

coordination number VIII [124] (black circles). The lattice parameter of $(\text{Lu}_{1/6}\text{Y}_{1/6}\text{Ho}_{1/6}\text{Dy}_{1/6}\text{Tb}_{1/6}\text{Gd}_{1/6})_3\text{Al}_5\text{O}_{12}$ obtained from Rietveld refinement, 12.033(7) Å, is also plotted as a function of the calculated average ionic radius of the six REs, which is 1.023 Å (blue square). This lattice parameter is nearly identical to the calculated average value of the lattice parameters of the single-REAG, which is 12.025 Å. This indicates that the lattice parameter of a multicomponent garnet can be predicted based on the composition and ionic radius.

Single-crystal XRD

The single-crystal X-ray diffraction refinement parameters are given in the Supporting Information in Table 5.2. The number of elements on the RE site in $(\text{Lu}_{1/6}\text{Y}_{1/6}\text{Ho}_{1/6}\text{Dy}_{1/6}\text{Tb}_{1/6}\text{Gd}_{1/6})_3\text{Al}_5\text{O}_{12}$ makes site occupation refinements underdetermined, so the RE site occupation was held fixed at the nominal composition. The fractional atomic coordinates and equivalent isotropic displacement parameters are in Table 5.3. The oxygen coordinate is the same for both the center and edge samples of the boule, whereas the cell size is significantly different. The larger cell size for the edge sample implies that the RE elements with a smaller ionic radius are reduced somewhat relative to the larger REs, and the RE–O bond lengths are slightly longer, as would be expected, as seen in Table 5.2. The X-ray patterns showed no obvious diffuse scattering, which suggests no short-range clustering of the REs.

Radial Distribution

Relationship between ionic radii and the general shape of concentration profiles

EPMA results reveal a nonuniform radial elemental distribution, with some elements at a higher concentration in the center of the crystal, while other elements are at a higher concentration near the outer surface of the cylindrical crystal. As shown in Figure 5.4, the average ionic radius of the six REs in $(\text{Lu}_{1/6}\text{Y}_{1/6}\text{Ho}_{1/6}\text{Dy}_{1/6}\text{Tb}_{1/6}\text{Gd}_{1/6})_3\text{Al}_5\text{O}_{12}$ can be used to divide them into two groups: Group 1, which is comprised of the REs that are smaller than 1.023 Å, namely, Lu, Y, and Ho, and Group 2, which is comprised of the REs that are larger than that value, namely, Dy, Tb, and Gd. Figure 5.5 shows radial elemental profiles for the six REs measured at various distances from the seed end of the crystal 005–300. There is a clear correlation between the elemental distribution profiles and the RE ionic radius. On the one hand, the smaller elements of Group 1 concentrate in the center of the crystal and are preferentially incorporated into the crystal lattice as shown by their upwardly curved concentration profiles in Figure 5.5. On the other hand, the larger elements of Group 2 have downwardly curved profiles and therefore were rejected toward the outer surface of the crystal. Similar trends were observed for all crystals, which support the observation of a larger unit cell at the outer edge of the crystal in single-crystal XRD, as seen in Table 5.1. These results

Table 5.2 - Single-crystal X-ray diffraction data collection and refinement parameters.

Sample	005-100 center	005-100 outer surface
Formula	RE ₃ Al ₅ O ₁₂	RE ₃ Al ₅ O ₁₂
T (K)	260(1)	260(1)
Crystal system	cubic	cubic
space group	<i>Ia</i> $\bar{3}$ <i>d</i>	<i>Ia</i> $\bar{3}$ <i>d</i>
a (Å)	12.0346(1)	12.0423(2)
V (Å³)	1743.01(1)	1746.36(1)
Z	8	8
D_{calc} (mgm⁻³)	5.93	5.92
μ (Mo Kα) (mm⁻¹)	26.017	25.972
F(000)	2776	2776
Crystal size (mm)	0.15×0.1×0.05	0.2×0.15×0.05
θ range for data collection	4.2-33.1	4.2-30.4
Index ranges	-18 ≤ <i>h</i> ≤ 18 -18 ≤ <i>k</i> ≤ 18 -18 ≤ <i>l</i> ≤ 18	-13 ≤ <i>h</i> ≤ 17 -17 ≤ <i>k</i> ≤ 16 -17 ≤ <i>l</i> ≤ 17
No. reflections collected (equivalents agreement)	6940(0.036)	5835(0.068)
No. unique reflections collected with <i>F</i>_o > 4σ <i>F</i>_o 	284	228
No. of variables	18	18
<i>R</i>_F	0.015	0.018
<i>R</i>_{wF}	0.036	0.044
Goodness of fit	1.439	1.329
largest diff. peak and hole (eÅ⁻³)	0.98, -0.65	0.91, -0.61
Scale factor	0.0882(8)	0.100(1)
Extinction coefficient	0.0069(2)	0.0012(1)
^{IV}Al-O (Å)	1.771(2) × 4	1.773(3) × 4
^{VI}Al-O (Å)	1.933(2) × 6	1.932(3) × 6
^{VIII}Ln-O (Å)	2.314(2) × 4 2.442(2) × 4	2.316(3) × 4 2.445(3) × 4

Table 5.3 - Fractional atomic coordinates and equivalent isotropic displacement parameters for high-entropy garnet samples from 005-100 center ($a = 12.0346(1) \text{ \AA}$) and 005-100 edge ($a = 12.0423(2) \text{ \AA}$), space group $la\bar{3}d$. For the purposes of the structural refinements, RE was fixed as Sm, which has the closest atomic number to the average of Lu, Y, Ho, Dy, Tb, and Gd.

Atom	Site	Symmetry	x	y	z	$U_{eq} (\text{\AA}^2)$
<i>005-100 center</i>						
Al1	16a	$\bar{3}$	0	0	0	0.0018(3)
Al2	24d	$\bar{4}$	3/8	0	1/4	0.0028(3)
RE	24c	222	1/8	0	1/4	0.0025(1)
O	96h	1	0.1007(1)	0.1991(1)	0.2806(1)	0.0026(3)
<i>005-100 outer edge</i>						
Al1	16a	$\bar{3}$	0	0	0	0.0047(5)
Al2	24d	$\bar{4}$	3/8	0	1/4	0.0051(5)
RE	24c	222	1/8	0	1/4	0.0042(1)
O	96h	1	0.1010(2)	0.1993(2)	0.2806(2)	0.0041(4)

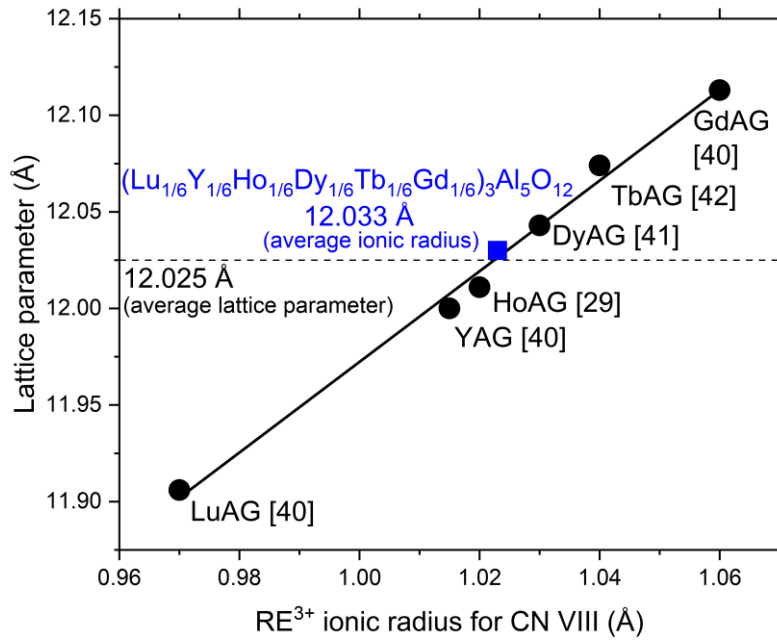


Figure 5.4 - The literature values of the lattice parameters of single-REAG(referenced in the figure) as a function of rare-earth ionic radius for the 3+ oxidation state and coordination number VIII [124] (black circles). The experimentally obtained lattice parameter of $(\text{Lu}_{1/6}\text{Y}_{1/6}\text{Ho}_{1/6}\text{Dy}_{1/6}\text{Tb}_{1/6}\text{Gd}_{1/6})_3\text{Al}_5\text{O}_{12}$ (12.033 Å) is nearly identical to the calculated average value of the lattice parameters of the single-REAG (12.025 Å). The ionic radius of the RE ions in $(\text{Lu}_{1/6}\text{Y}_{1/6}\text{Ho}_{1/6}\text{Dy}_{1/6}\text{Tb}_{1/6}\text{Gd}_{1/6})_3\text{Al}_5\text{O}_{12}$ is plotted as the average of the six REs (blue square).

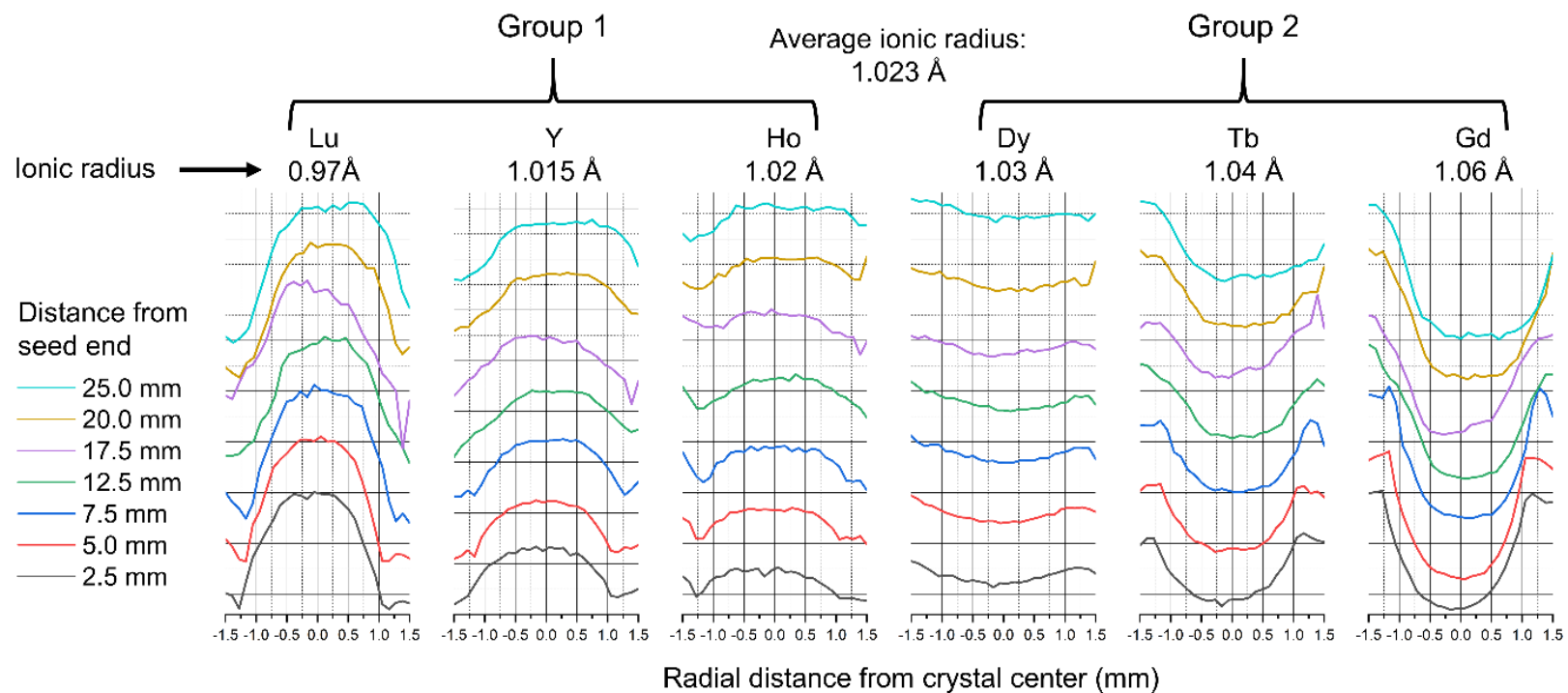


Figure 5.5 - EPMA radial elemental profiles of the 005-300 crystal are plotted to compare their general shape; these are stacked in order to show various areas across the length of the crystal. REs with an ionic radius smaller than the average 1.023 Å have an upwardly curved profile, while larger REs have a downwardly curved profile. Note that the degree of curvature is proportional to the difference between the ionic radius and the average. On the horizontal axis, zero represents the center of the crystal, while -1.5 or +1.5 mm represent the last measurement toward the outer surface of the crystal.

indicate that elements in Group 1 have segregation coefficients $k > 1$ and are readily incorporated into the crystal lattice, while elements of Group 2 have a $k < 1$ and are rejected from the growth interface. Considering the average RE ionic radius as the size of the hosting site for the RE elements, our observations are consistent with the fact that ions smaller than the substituted element have a $k > 1$, while larger constituents have a $k < 1$ [201].

Our observations of the radial distribution of the REs in $(\text{Lu}_{1/6}\text{Y}_{1/6}\text{Ho}_{1/6}\text{Dy}_{1/6}\text{Tb}_{1/6}\text{Gd}_{1/6})_3\text{Al}_5\text{O}_{12}$ are consistent with previous reports on radial dopant distribution in micro-pullingdown crystals. Dopants that are smaller than the substituted host element usually concentrate in the center of the crystal, while larger dopants segregate toward the outer surface. This has been observed in fiber crystals of Cr- or Ga-doped Al_2O_3 , Cr- or Tb-doped $\text{Gd}_3\text{Ga}_5\text{O}_{12}$, and Yb-doped $\text{Y}_3\text{Al}_5\text{O}_{12}$ [185]. Dopant distribution profiles follow the same trend in the bulk crystals of Cr-, Nd-, Yb-, or Ce-doped $\text{Y}_3\text{Al}_5\text{O}_{12}$ [186], Nd-, Ho-, Er-, or Tm-doped $\text{Lu}_3\text{Al}_5\text{O}_{12}$ [187], and Pr-doped YAlO_3 [202] and Y_2SiO_5 [203]. Similarly, in $(\text{Lu}_{1/6}\text{Y}_{1/6}\text{Ho}_{1/6}\text{Dy}_{1/6}\text{Tb}_{1/6}\text{Gd}_{1/6})_3\text{Al}_5\text{O}_{12}$ RE that are smaller than the average ionic radius concentrate in the center of the crystal, while larger RE segregate toward the outer surface.

Effect of the pulling rate on elemental distribution

To investigate whether the pulling rate affects the radial elemental distribution, profiles were compared for crystals grown at different pulling rates in Figure 5.6. Two EPMA radial profiles are shown for each crystal. These were spaced widely apart along the growth axis, one close to the seed end and one close to the tail end. In the $\text{RE}_3\text{Al}_5\text{O}_{12}$ stoichiometry, the nominal atomic concentration of each RE element is 2.5 atom %. Faster pulling rates resulted in greater uniformity, promoting a flattening of the radial distribution profiles toward the nominal concentration. The radial profiles of the crystal pulled at 0.20 mm/min (020–300) are closer to 2.5 atom % than the profiles of the crystal pulled at 0.05 mm/min (005– 300). With increasing pulling rates, there is a more intense melt flow from the crucible and a faster solidification rate, which limits the radial element diffusion and segregation. This explains the flattening of the distribution profiles in 020–300.

In general, REs with an ionic radius closer to the average RE radius in $(\text{Lu}_{1/6}\text{Y}_{1/6}\text{Ho}_{1/6}\text{Dy}_{1/6}\text{Tb}_{1/6}\text{Gd}_{1/6})_3\text{Al}_5\text{O}_{12}$ have profiles closer to 2.5 atom %, as shown in Figure 5.6. However, overall concentrations of Lu and Gd deviate significantly from the nominal value in all crystals; Lu is in excess, while Gd is deficient. A small amount of material did remain in the crucible capillary after growths were completed; if this remaining material is deficient in Lu and rich in Gd, it would explain the concentration deviation. It was not possible to verify the chemical composition of the remaining material, because it could not be removed from the

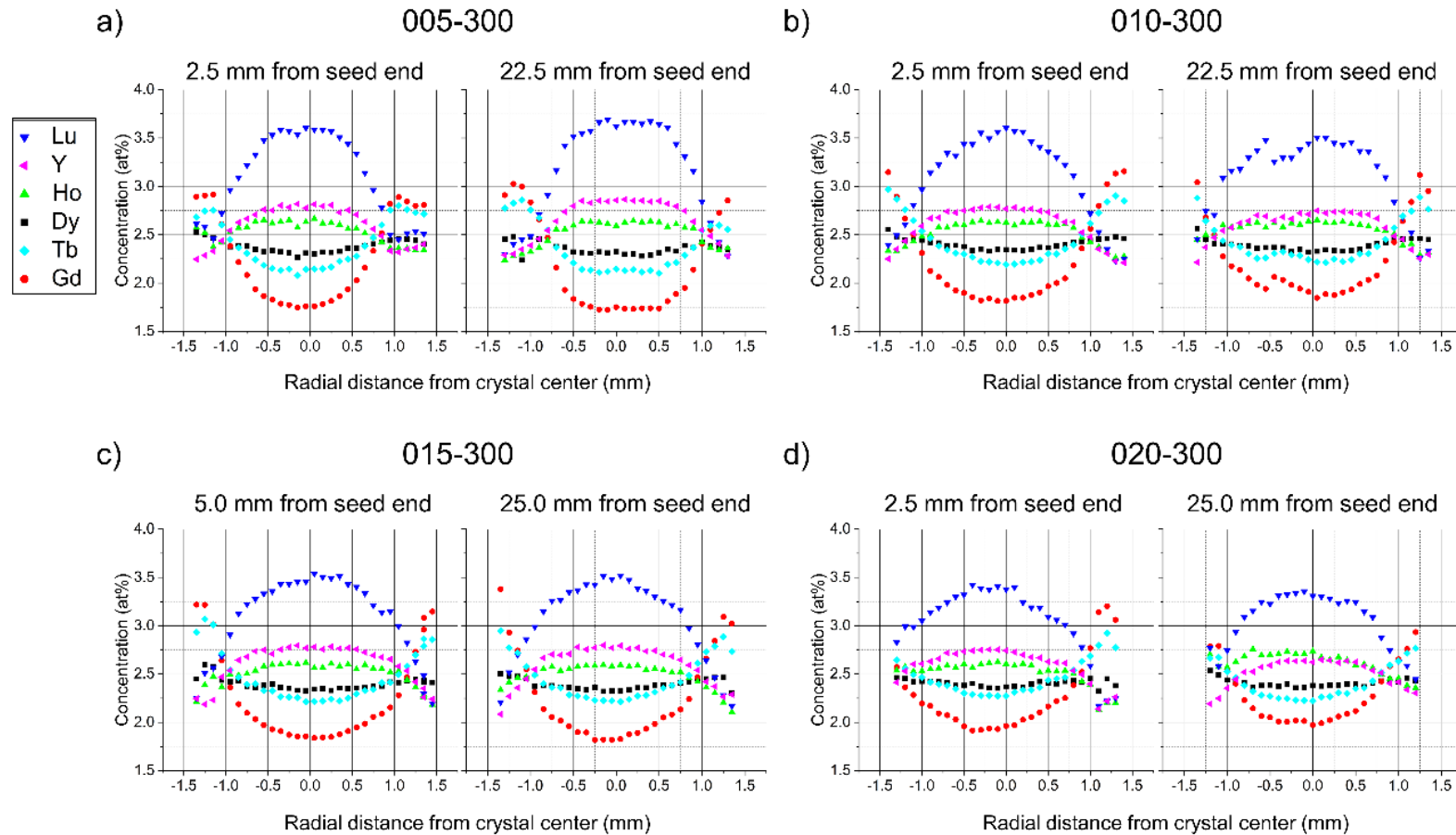


Figure 5.6 - EPMA radial concentration profiles were measured at different ends of the crystals 005-300 (a), 010-300 (b), 015-300 (c), and 020-300 (d) that were grown with the same height of the molten zone, but at different pulling rates. The legend by item (a) applies to all graphs. RE elemental profiles are closer to the nominal 2.5 at% in crystals pulled at a faster rate. On the horizontal axis, zero represents the center of the crystal, while -1.5 or +1.5 mm represent the last measurement toward the outer surface of the crystal.

crucible for analysis. A more likely explanation is that Lu concentrations might have been slightly overestimated due to extra counts from other RE in the EPMA measurements, specifically Dy, since their spectral lines overlap. Gadolinium, however, is the largest RE and would, therefore, have segregated farther toward the outer surface of the crystal outside the boundaries of the EPMA measurement. The deviation of the Lu and Gd concentrations is improved with the more intense melt flow and faster solidification rates that accompany faster pulling rates, consistent with limited diffusion and segregation.

Most of the individual elemental profiles in the eight plots in Figure 5.6 are radially symmetric with respect to the crystal vertical axis. One exception is the crystal 020–300, in which the profiles at 2.5 mm from the seed end are asymmetric. Similar asymmetry in dopant distribution profiles has been reported by others [186], [188]. Although not shown in this manuscript, once a distance of 12.5 mm from the seed was achieved, the profiles of all REs in 020–300 became symmetric. Therefore, the initial asymmetry in RE radial distribution may be attributed to a delay in reaching stable conditions due to stepwise increases in the pulling rate required to achieve the target rate.

Axial distribution

The axial elemental distribution was quite uniform as to be expected in many materials grown by the micro-pulling-down method [37]. We compare the two concentration profiles shown for each one of the four crystals: left versus right plots for each part of Figure 5.6.a–d. One of the two profiles was measured at either 2.5 or 5.0 mm distant from the seed end, representing the portion of each crystal that crystallized first; the other profile was measured at either 22.5 or 25.0 mm distant from the seed end, representing the portion of the crystal that crystallized near the end of growth. Comparing the two plots in Figure 5.6.a, clearly the overall content of the six REs did not vary significantly along the length of the crystals. The same general trend is observed for the other crystals in Figure 5.6.b–d.

The EPMA radial profiles of the crystals 005–300 and 005–100, grown at the same pulling rate of 0.05 mm/min but with a different molten zone of 300 or 100 μm , respectively, are shown in Figure 5.7. There is no significant variation in the shape of the profile curves for all six cations. Closer to the outer edge of the crystals, the concentrations are closer to nominal in the crystal that was grown with a thicker molten zone, 005–300. This can be attributed to an enhanced mixing due to a more pronounced Marangoni flow close to the free surface of the melt, which is expected for thicker molten zones [37], [204].

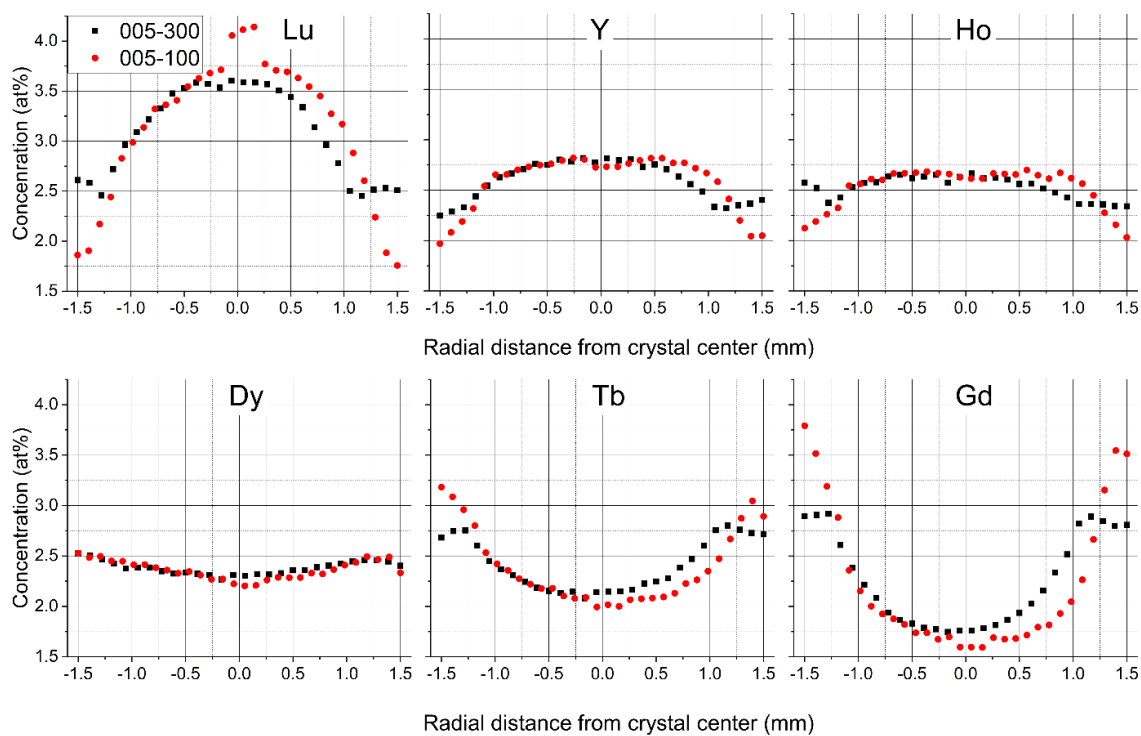


Figure 5.7 - Comparison of EPMA radial concentration profiles for the crystals 005-300 (black squares) and 005-100 (red circles), both grown at 0.05 mm/min with a molten zone of 300 μm or 100 μm , respectively. Measurements were obtained at 2.5 mm from the seed end for both crystals. The RE stoichiometric concentration is 2.5 at%.

Conclusion

For the first time we demonstrated successful crystal growth of the complex high-entropy aluminum garnet $(\text{Lu}_{1/6}\text{Y}_{1/6}\text{Ho}_{1/6}\text{Dy}_{1/6}\text{Tb}_{1/6}\text{Gd}_{1/6})_3\text{Al}_5\text{O}_{12}$ using the micro-pulling-down method. These crystals are readily grown with excellent reproducibility in terms of molten zone height, diameter control, surface transparency, and optical quality. All crystals grown had a single-phase garnet structure with a space group $\text{Ia}\bar{3}\text{d}$ and a relatively homogeneous axial composition. We established that radial distribution of elements in the crystals is associated with their ionic radii. Smaller REs concentrate in the center of the crystal, while larger elements segregate toward the outer surface. Faster pulling rates were found to have a favorable effect on flattening the radial nonuniformity.

Further investigation into high-entropy aluminum garnets may reveal attractive functional properties in this and similar systems, as previously demonstrated in other high-entropy oxides. This may be of particular value for applications that require crystals with high optical quality, such as lasing and scintillation. The crystalline environment strongly affects structural and functional properties; therefore, a homogeneous elemental distribution is required to design a material with a desired performance. Understanding of the mechanism for incorporation of principal elements in a multicomponent crystal lattice leads to selection of the most suitable crystal growth technique for larger-size crystals for commercial applications.

**CHAPTER SIX:
EFFECTS OF COMPOSITION AND GROWTH PARAMETERS ON
PHASE FORMATION IN MULTICOMPONENT ALUMINUM
GARNET CRYSTALS**

A version of this chapter was published by Matheus Pianassola and colleagues:

M. Pianassola, M. Alexander, B. Chakoumakos, M. Koschan, C. Melcher, and M. Zhuravleva, "Effects of composition and growth parameters on phase formation in multicomponent aluminum garnet crystals," *Acta Crystallogr. B. Struct. Sci. Cryst. Eng. Mater.*, vol. 78, pp. 476–484, Jun. 2022, doi: 10.1107/S2052520622002967/TQ5001SUP2.PDF.

This chapter is the reformatted version of the original work submitted to the referenced journal. A portion of the experimental section was reworded.

Abstract

The effects of composition on the phase formation of multicomponent garnet crystals grown via directional solidification by the micro-pulling-down method are studied. A relatively wide range of rare-earth (RE) average ionic radii (AIR) is explored by formulating ten compositions from the system (Lu,Y,Ho,Dy,Tb,Gd)₃Al₅O₁₂. Crystals were grown at either 0.05 or 0.20 mm/min. The hypothesis is that multicomponent compounds with large AIR will form secondary phases as the single-RE aluminum garnets formed by larger Tb³⁺ or Gd³⁺; this will result in crystals of poor optical quality. Crystals with large AIR have a central opaque region in optical microscopy images, which is responsible for their reduced transparency compared to crystals with small AIR. Slow pulling rates suppress the formation of the opaque region in crystals with intermediate AIR. Powder and single-crystal X-ray diffraction and electron probe microanalysis results indicate that the opaque region is a perovskite phase. Scanning electron microscopy and energy dispersive spectroscopy measurements reveal eutectic inclusions at the outer surface of the crystals. The concentration of the eutectic inclusions increases with increasing AIR.

Introduction

A surprising phase stabilization and attractive functional properties have been reported for oxides containing five cations that fractionally occupy the same crystallographic site [40], [53]. Such complex compositions are usually called 'high-entropy' or 'multicomponent' [70], [71], [205], [206]. Admixing two or three elements in garnet crystals has been shown to improve scintillation properties [15], [17], [75], [207]. Therefore, multicomponent crystals could lead to further improvement in performance for radiation detection in medical imaging and homeland security applications. To date, only two multicomponent aluminum garnet compounds have been reported with five or more rare-earth (RE) elements, one synthesized as a polycrystalline ceramic [208] and one as a single crystal [39]. Further study on composition design and crystal growth of garnets containing multiple REs is needed to establish a correlation between composition and phase

formation, and to guide future investigation into fundamental and functional properties in single crystals.

The phase stabilization of multicomponent oxides has been attributed to an entropy-driven mechanism [53], but the composition and synthesis method can also affect phase formation in polycrystalline samples [70], [71]. In the case of crystals grown via directional solidification, the formation of a single phase also depends on melt congruency and elemental segregation. While there are several publications on multicomponent oxide thin films [7], [10], [211]–[213], [11], [30]–[34], [209], [210], only a few reports demonstrate the growth and phase formation in multicomponent oxide bulk crystals [26], [28], [35], [39], [214]. We previously demonstrated the growth of a six-component aluminum garnet ($\text{Lu}_{1/6}\text{Y}_{1/6}\text{Ho}_{1/6}\text{Dy}_{1/6}\text{Tb}_{1/6}\text{Gd}_{1/6}\text{Al}_5\text{O}_{12}$) that melted congruently, formed a single phase, and was grown with excellent optical quality and reproducibility [39]. That work focused on only one composition with RE elements in equiatomic amounts; here Y is referred to as an RE element for simplicity. The effect of non-equiatomic compositions on phase formation in multicomponent garnets remains unexplored.

The correlation between RE^{3+} ionic radius and fundamental properties of one-RE aluminum garnets suggests that the Average Ionic Radius (AIR) of REs in multicomponent crystals may affect phase formation. In the garnet structure, RE^{3+} occupy dodecahedral crystallographic sites and have coordination number (CN) VIII, while Al^{3+} ions occupy tetrahedral and octahedral sites with CN IV and VI, respectively. Due to the small size of the dodecahedral site, only Gd^{3+} and REs smaller than Gd^{3+} form thermodynamically stable single-RE garnets [73]. For the same reason, smaller REs are preferentially incorporated in multicomponent crystals grown from the melt [39]. Smaller REs also form congruently melting garnets, while larger Tb^{3+} and Gd^{3+} form garnets that melt incongruently. Additionally, as the RE^{3+} ionic radius increases, the composition of the eutectic formed between single-RE $\text{RE}_3\text{Al}_5\text{O}_{12}$ (garnet stoichiometry) and Al_2O_3 is closer to the garnet stoichiometry [73], [215].

In this work, we determine the effects of composition and AIR on the formation of a single phase in garnet crystals grown by pulling from the melt. In single-RE aluminum garnets there is a transition from congruent to incongruent melting between $\text{Dy}_3\text{Al}_5\text{O}_{12}$ and $\text{Tb}_3\text{Al}_5\text{O}_{12}$. Therefore, we expect multicomponent compositions with an AIR equal to or smaller than that of Dy^{3+} (1.030 Å for CN VIII [124]) to melt congruently and solidify into a single garnet phase, while we expect compositions with an AIR approaching that of Tb^{3+} (1.040 Å for CN VIII [124]) to melt incongruently and form detrimental secondary phases during solidification. We expand on our previously explored multicomponent garnet system ($\text{Lu}_{1/6}\text{Y}_{1/6}\text{Ho}_{1/6}\text{Dy}_{1/6}\text{Tb}_{1/6}\text{Gd}_{1/6}\text{Al}_5\text{O}_{12}$) (AIR = 1.023 Å) and formulate ten nonequiatomic compositions using the same five RE elements and Y, with an AIR in the range 1.021–1.040 Å. Here we design the AIR by varying the relative fractional occupation of the dodecahedral crystallographic site by Lu, Y, Ho, and

Dy. The fractions of REs that form incongruent single-RE aluminum garnet (Tb and Gd) are kept constant at 1/4. We also investigate the effect of elemental segregation on phase formation.

We used the micro-pulling-down method (mPD) to grow the crystals. This method is ideally suited for this study due to its ability to produce compositionally homogenous crystals with minimal axial elemental gradient [37]. Additional advantages of the mPD method include the use of relatively small amounts of expensive raw materials (1 g per crystal) and faster pulling rates (0.05–20 mm/min) compared to scalable growth methods, such as the Czochralski technique.

Methods

Compositions

Our approach to study the effects of AIR of REs on phase formation of garnet crystals involves formulating multicomponent compounds with various AIR. We designed ten compositions within the $(\text{Lu}, \text{Y}, \text{Ho}, \text{Dy}, \text{Tb}, \text{Gd})_3\text{Al}_5\text{O}_{12}$ system by varying the relative atomic fractional occupation of the dodecahedral crystallographic site by Lu, Y, Ho, and Dy. The fractions of Tb and Gd, which form incongruent melting single-RE aluminum garnets, were held constant at 1/4 each; therefore, 50 at% of the REs in all compositions form incongruent single-RE aluminum garnets. The ionic radii of Lu^{3+} , Y^{3+} , Ho^{3+} , Dy^{3+} , Tb^{3+} , and Gd^{3+} for coordination number VIII are 0.970, 1.015, 1.020, 1.030, 1.040, and 1.060 Å, respectively [124]. A list of compositions with the stoichiometric coefficient of each RE element and Y and the respective AIR of REs is shown in Table 6.1 in order of increasing the AIR.

Starting materials

To study the effect of the type of precursor powder on phase formation, we used two types of precursor powders, namely, raw and pre-synthesized. Raw powders were mixtures of raw oxides, while pre-synthesized powders were single-phase multicomponent garnet powders.

Raw precursor powder

To prepare raw precursor powders, the following powder oxides of at least 99.99% purity were dried at 800 °C for 8 h in air and mixed in stoichiometric ratios: Lu_2O_3 , Y_2O_3 , Ho_2O_3 , Dy_2O_3 , Tb_2O_3 , Gd_2O_3 and Al_2O_3 .

Pre-synthesized precursor powder

Powders were synthesized via a wet chemistry method using nitrates as the source of cations. The precursor powder was crystallized at 900°C for 1h in air.

Table 6.1 - List of compositions with respective stoichiometric coefficients for each RE element and Y and resulting AIR of REs in order of increasing AIR [124].

Composition ID	Fraction of REs and Y in (Lu,Y,Ho,Dy,Tb,Gd) ₃ Al ₅ O ₁₂						AIR of REs and Y (Å)	RE with closest ionic radius	Type of precursor powder
	Lu	Y	Ho	Dy	Tb	Gd			
A	1/4	1/4	-	-	1/4	1/4	1.021	Ho ³⁺	R
B	1/4	-	1/4	-	1/4	1/4	1.023	Ho ³⁺	R
C	1/4	-	-	1/4	1/4	1/4	1.025	Ho ³⁺	R
D	1/6	1/6	1/6	-	1/4	1/4	1.026	Dy ³⁺	R
E	1/6	-	1/6	1/6	1/4	1/4	1.028	Dy ³⁺	R
F	1/8	-	1/4	1/8	1/4	1/4	1.030	Dy ³⁺	R
G	-	1/2	-	-	1/4	1/4	1.033	Dy ³⁺	R
H	-	-	1/2	-	1/4	1/4	1.035	Dy ³⁺	R and P
I	-	-	1/4	1/4	1/4	1/4	1.038	Tb ³⁺	R and P
J	-	-	-	1/2	1/4	1/4	1.040	Tb ³⁺	R and P

“-” - Element not included in the composition. “R” - raw precursor powder (mixture of sesquioxides), “P” - pre-synthesized precursor powder (multicomponent aluminum garnet)

Crystal growth

Cylindrical crystals of 3 mm diameter were grown by the mPD method using a KDN Dai-Ichi Kiden furnace with an RF generator model TR-02001 operated at 26 kVA. A Ø16 mm iridium crucible with a Ø3 mm die and a Ø0.5 mm capillary channel was used as a melt reservoir. A Czochralski-grown $\text{Lu}_3\text{Al}_5\text{O}_{12}$ crystal was used as seed to initiate the growth. Two 1 g crystals of each composition listed in Table 6.1 were grown from raw precursor powders, one at 0.05 mm/min (slow pulling rate) and the other at 0.20 mm/min (fast pulling rate), to study the effect of pulling rate on crystal quality. One 0.3–0.5 g crystal of compositions H, I, and J was grown from pre-synthesized powder at 0.05 mm/min to study the effect of the type of precursor powder on phase formation. A molten-zone height of 200 mm was maintained for all growth experiments by adjusting the power of the RF generator. A previous publication includes details about the mPD method and the crystal growth set-up used [39].

Optical microscopy

To evaluate the optical quality of the crystals, a 1 mm-thick cross sectional sample was cut from each crystal. The samples were cut 2 mm apart from the seed end. After polishing the samples, a Leica MC170 HD microscope camera was used to obtain optical images.

Scanning electron microscopy and energy dispersive spectroscopy

The samples used for optical microscopy were also imaged using a Zeiss EVO MA15 Scanning Electron Microscope (SEM). The SEM instrument is equipped with a Bruker xFlash 6130 Energy Dispersive X-ray Spectrometer (EDS), which was used to analyze the elemental composition of inclusions.

Powder X-ray diffraction

Phase identification was conducted by acquiring powder X-ray diffraction (PXRD) patterns of all crystals. Crystals were cut into three cylindrical sections of equal lengths, and the middle section was used for phase analysis. A PANalytical Empyrean diffractometer was used to obtain diffraction patterns. The instrument operates in the Bragg–Brentano geometry using a Cu K X-ray source at 45 kV and 40 mA. Unit-cell parameter and phase composition were obtained via Rietveld refinements with the General Structure Analysis System II software (GSASII). A goodness-of-fit value smaller than 1.60 was achieved for all refinements.

Single-crystal X-ray diffraction

To identify differences in the crystal structure in the center and the surface of the crystals, samples cut from the center and outer surface of selected crystals were analyzed using single crystal XRD. These samples were cut 2 mm away from

the seed end. Two crystals grown from raw precursor powders were selected, i.e., crystal C grown at 0.20 mm/min and crystal I grown at 0.05 mm/min. The former was selected from a group of transparent crystals and the latter from a group of crystals that are transparent in the outer surface and have a central opaque region.

A Rigaku XtaLAB PRO diffractometer was used to collect single-crystal diffraction data at 270 K using a Rigaku HyPix6000HE detector and an Oxford N-HeliX cryocooler and graphite-monochromated Mo K radiation ($\lambda = 0.71073 \text{ \AA}$, 50 kV and 40 mA). The Rigaku Oxford Diffraction CrysAlis PRO software was used for peak indexing and integration [216]. An empirical absorption correction was applied using the SCALE3 ABSPACK algorithm, as implemented in CrysAlis PRO. The SHELXL2013 [195] and WinGX [196] software packages were used for data processing and structure refinement. The structure refinements were made with O-atom positional coordinates, anisotropic atomic displacement parameters, an extinction parameter, and the scale factor.

Electron microprobe analysis

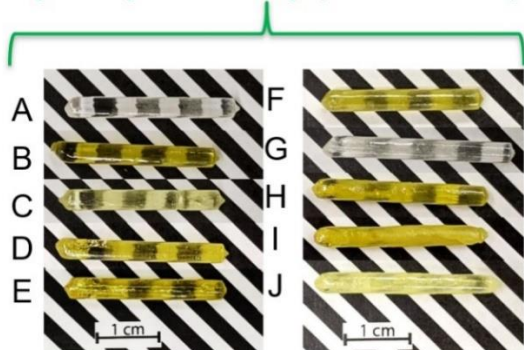
The radial elemental distribution in selected crystals was investigated by Electron Probe Micro Analysis (EPMA). Radial sections of 1 mm thickness were cut 2 mm away from the seed end of crystals of compositions A and J, that were grown at 0.05 mm/min. The samples were embedded in epoxy and a CAMECA SX100 Electron Microprobe was used for elemental composition analysis. The instrument is equipped with high-speed Back-Scattered Electron (BSE) detectors and four Wavelength-Dispersive Spectrometers (WDS). Images were obtained by detecting the back-scattered electrons and compositional information was acquired by detecting characteristic X-rays by WDS. The instrumental voltage and current were 15 kV and 30 nA, respectively. The probe point size was 1 mm and the diameter of the excitation area was in the range 2–3 mm. Radial elemental distribution profiles were obtained by collecting data at 100 μm steps.

Results and discussion

Grown crystals

Higher optical quality was obtained for crystals grown using slower pulling rates and for compositions with smaller AIR. In Figure 6.1, crystals of compositions A–J grown from raw powders are grouped according to their respective pulling rate. In general, crystals pulled slowly (0.05 mm/min) are more transparent than crystals pulled fast (0.20 mm/min). Additionally, within each group, crystals of compositions with smaller AIR (A–E) are more transparent than those of compositions with larger AIR (F–J). Cracking may contribute to the reduced transparency of the crystals with larger AIR and fast pulling rate. The surface roughness of crystals pulled fast may be related to a more pronounced thermal

Crystals pulled *slowly* (0.05 mm/min)



Crystals pulled *fast* (0.20 mm/min)

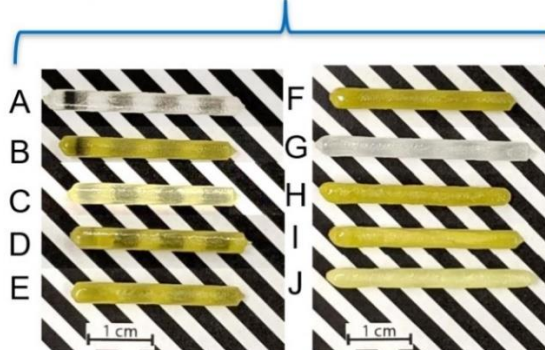


Figure 6.1 - Photos of crystals grown from raw powders; crystal IDs A-J correspond to the compositions listed in Table 6.1. The yellow color seen in most crystals comes from Ho and/or Dy. Slower pulling rates and compositions with smaller AIR lead to better optical quality.

etching due to the relatively higher temperatures necessary to maintain a stable molten zone for growth at high pulling rates using the mPD method.

Optical microscope images revealed that a central opaque region occurs in crystals with large AIR and grown using fast pulling rates. 1 mm-thick cross sections of crystals grown from raw precursor powders are shown in Figure 6.2. For crystals pulled slowly, crystals A–G are transparent, while crystals H–J (larger AIR) have a central opaque region. On the other hand, for crystals pulled fast, crystals A–D are transparent throughout, and crystals E–J (larger AIR) have a central opaque region. This opaque region explains the reduced transparency of crystals with large AIR as seen in Figure 6.1. Additionally, all crystals have small dark inclusions close to their outer surface, which are more pronounced for crystals pulled fast. A correlation of the opaque central regions with phase formation is discussed in following sections in this Chapters; we also discuss the nature of the small dark inclusions later in this Chapter.

To investigate whether the nature of the precursor powder affects the formation of the central opaque region, crystals of composition H–J were also grown from raw powders using a slow pulling rate (0.05 mm/min). These three compositions are the only ones that formed a central opaque region in crystals grown from raw powder and pulled slowly (Figure 6.2). As shown in Figure 6.3.a, the transparency of crystals H and I improved compared to the crystals grown from raw powders and pulled slowly (Figure 6.1). However, the transparency of crystals H and I in Figure 6.3.a is still inferior to that of crystals with smaller AIR (A–E) grown from raw powders (Figure 6.1). The transparency of crystal J in Figure 6.3.a is similar to that of crystal J grown from raw powder and pulled slowly (Figure 6.1). Optical images of 1 mm sections of the crystals grown from raw materials are shown in Figure 6.3.b. Crystals H and I are transparent across the entire diameter, while crystal J has a central opaque region. A comparison of crystals H–J grown from pre-synthesized powders (Figure 6.3) with crystals of the same composition grown from raw powders (Figure 6.2) indicates that starting with pre-synthesized powders prevents the formation of an opaque phase for compositions H and I, but not for J, which has the largest AIR in this study.

Phase formation and crystal structure

Powder X-ray diffraction (PXRD)

The majority of the crystals grown from raw powders formed the desired single garnet phase, even though the nominal compositions have 50% of the dodecahedral sites occupied by Tb and Gd (25% each), which form incongruent melting $\text{Tb}_3\text{Al}_5\text{O}_{12}$ and $\text{Gd}_3\text{Al}_5\text{O}_{12}$ [73]. The PXRD patterns of crystals grown slowly are shown in Figure 6.4.a; reference patterns of $\text{Tb}_3\text{Al}_5\text{O}_{12}$ [217] and TbAlO_3 [218] are included for comparison. These patterns indicate a single garnet phase with space group $Ia\bar{3}d$ ($\text{Tb}_3\text{Al}_5\text{O}_{12}$, ICSD #33602) for compositions A–H (smaller AIR),

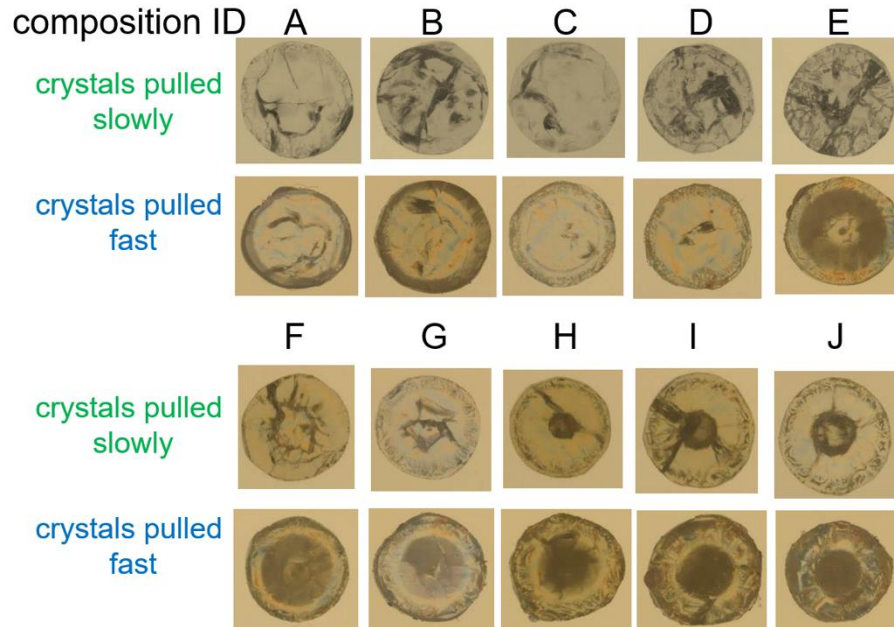


Figure 6.2 - Optical microscope images of 1-mm-thick radial sections cut 2 mm away from the seed end of crystals. Composition ID and pulling rates are indicated in the figure. A central opaque region is present in crystals H-J, which were pulled slowly, and crystals E-J, which were pulled fast.

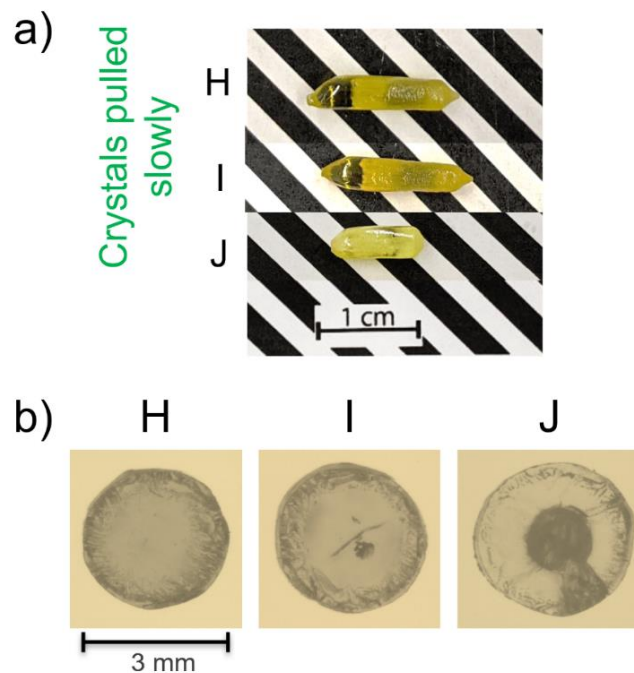


Figure 6.3 - a) Crystals grown from pre-synthesized powders; crystal IDs H-J correspond to the compositions listed in Table 1. b) Optical microscope images of 1-mm-thick radial sections cut 2 mm away from the seed end of crystals grown from pre-synthesized powders. Composition IDs are indicated in the figure.

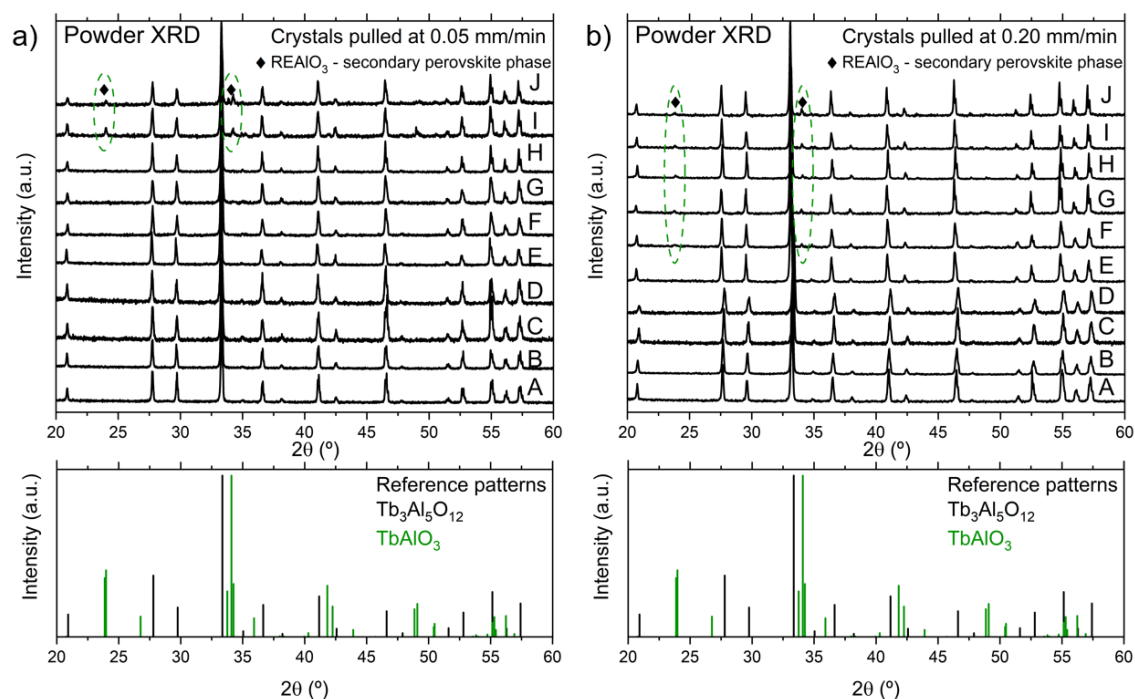


Figure 6.4 - Powder XRD patterns of crystals grown from raw powders and pulled slowly (a) and fast (b). Reference patterns for Tb₃Al₅O₁₂ (ICSD # 33602) and TbAlO₃ (ICSD # 84422) are presented at the bottom for comparison. Crystals A-H pulled slowly and crystals A-E pulled fast have a single garnet phase. Reflection peaks of secondary perovskite phases are indicated by a dashed oval.

while compositions I–J (larger AIR) have a secondary perovskite phase with space group Pbnm (TbAlO₃, ICSD #84422). On the other hand, the PXRD patterns of crystals grown fast indicate a single garnet phase for compositions A–E (smaller AIR), while compositions F–J (larger AIR) have a secondary perovskite phase, as seen in Figure 6.4.b. Therefore, a single phase can be obtained for melt-grown crystals having relatively large amounts of large REs, such as Tb and Gd, but the AIR should be maintained below 1.038 Å°, which here corresponds to the composition I (Table 6.1).

Table 6.2 is a list of phase compositions obtained from Rietveld refinement for all crystals grown from raw precursor powders. The amount of perovskite phase does not exceed 20 wt% and its presence may be related to the central opaque area seen in crystals with large AIR (Figure 6.2), which is discussed using single-crystal XRD data and EPMA later in this Chapter.

As the AIR of multicomponent garnets increases, the tendency to melt incongruently may also increase, as in the case of single-RE RE₃Al₅O₁₂ [73]. Compounds with large AIR may melt incongruently, which explains the crystallization of a mixture of garnet and perovskite phases. Interestingly, crystals of compositions F–H form a single garnet phase when pulled slowly but have a secondary perovskite phase when pulled fast. This indicates that for those compositions a slow growth rate may favor the incorporation of relatively large REs into the small dodecahedral site of the garnet phase. On the other hand, faster pulling rates lead to the formation of a secondary orthorhombic perovskite structure, which has larger dodecahedral sites that easily accommodate large RE elements [181].

Crystals H and I grown from pre-synthesized powders formed the desired single garnet phase, while crystal J has a secondary perovskite phase, as seen in the PXRD patterns in Figure 6.5. This indicates that using pre-synthesized powders prevents the formation of a perovskite phase in composition I, but not in J, which has the largest AIR in this study. The phase fraction of the primary garnet structure in crystal J is 85 wt%, which was obtained via Rietveld refinement. This phase fraction of crystal J grown from pre-synthesized powder is slightly smaller than that of crystal J grown from raw powder (88 wt%; Table 6.2).

Single-crystal XRD

To compare the structure of the center and surface of the crystals, single-crystal XRD data were collected and analyzed for crystals C and I grown from raw precursor powder at 0.20 and 0.05 mm/min. The supporting information contains the single-crystal X-ray diffraction refinement parameters in Table 6.3 and the fractional atomic coordinates and equivalent isotropic displacement parameters in Table 6.4. Crystal C is a single garnet phase (space group Ia-3d) and the lattice parameter is larger in the outer surface [12.0703 (3) Å] than in the center [12.0516

Table 6.2 - Phase composition obtained from Rietveld refinement for crystals of compositions A-J pulled slowly (0.05 mm/min) and fast (0.20 mm/min).

		Phase composition (wt%)									
Crystal composition ID		A	B	C	D	E	F	G	H	I	J
Crystals pulled slowly	<i>Garnet</i>	100	100	100	100	100	100	100	100	88	90
	<i>Perovskite</i>	-	-	-	-	-	-	-	-	12	10
Crystals pulled fast	<i>Garnet</i>	100	100	100	100	100	87	88	81	91	88
	<i>Perovskite</i>	-	-	-	-	-	13	12	19	9	12

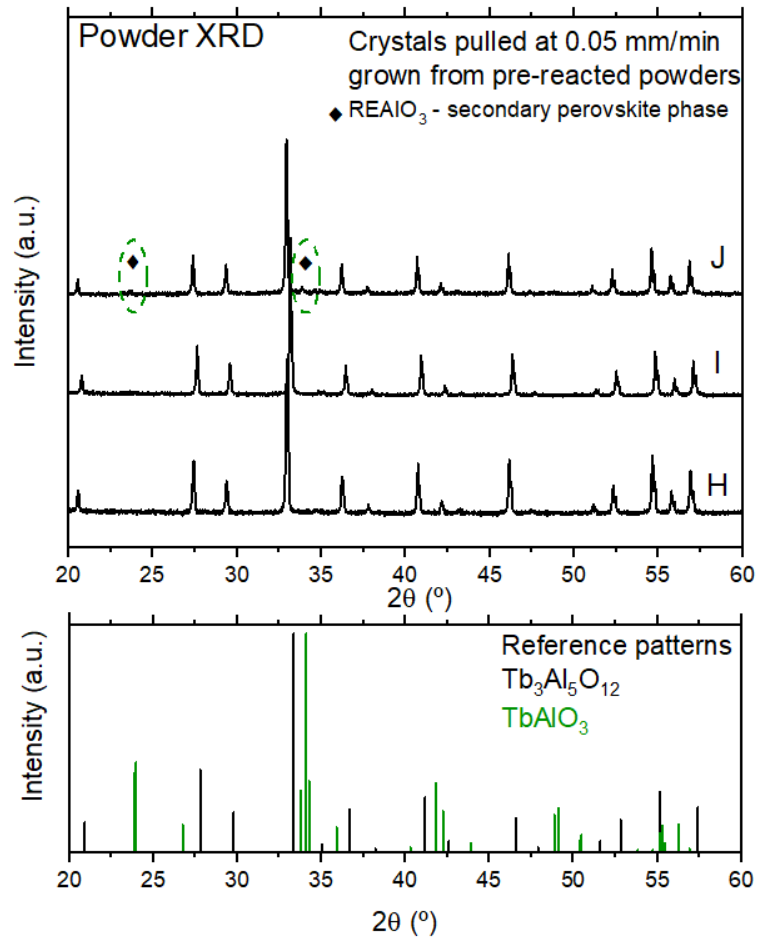


Figure 6.5 - Powder XRD patterns of crystals H-J grown from pre-synthesized powders and pulled slowly. Reference patterns for Tb₃Al₅O₁₂ (ICSD # 33602) and TbAlO₃ (ICSD # 84422) are presented at the bottom for comparison. Crystals H-I have a single garnet phase. Reflection peaks of secondary perovskite phases are indicated by a dashed oval.

Table 6.3 - Single-crystal X-ray diffraction data collection and refinement parameters for crystals C and I grown from unreacted precursor powders at 0.20 and 0.05 mm/min, respectively.

Sample	C (outer edge)	C (center)	I (outer edge)
Formula	RE ₃ Al ₅ O ₁₂	RE ₃ Al ₅ O ₁₂	RE ₃ Al ₅ O ₁₂
T (K)	270(1)	270(1)	270(1)
Crystal system	cubic	cubic	Cubic
space group	<i>la$\bar{3}$d</i>	<i>la$\bar{3}$d</i>	<i>la$\bar{3}$d</i>
a (Å)	12.0703(3)	12.0516(4)	12.0892(2)
v (Å³)	1758.54(8)	1750.38(9)	1766.81(2)
Z	8	8	8
D_{calc} (mgm⁻³)	6.173	6.202	4.877
μ (Mo Kα) (mm⁻¹)	26.93	26.93	16.91
F(000)	2884	2884	2336
Crystal size (mm)	0.2 x 0.2 x 0.05	0.2 x 0.2 x 0.04	0.2 x 0.1 x 0.06
θ range for data collection	3.36-32.54	2.34-31.84	3.37-31.39
Index ranges	-15 ≤ h ≤ 9 -9 ≤ k ≤ 16 -16 ≤ l ≤ 6	-5 ≤ h ≤ 16 -3 ≤ k ≤ 15 -10 ≤ l ≤ 11	-7 ≤ h ≤ 17 -17 ≤ k ≤ 9 -14 ≤ l ≤ 13
No. reflections collected (equivalents agreement)	2310(0.02)	4776 (0.19)	2180 (0.02)
No. unique reflections collected with F_o > 4σ F_o 	183	179	225
No. of variables	18	18	18
R_F	0.014	0.054	0.014
R_{wF}	0.029	0.164	0.029
Goodness of fit	1.44	1.20	1.36
Largest diff. peak and hole (eÅ⁻³)	0.63, -0.66	2.47, -2.48	0.47, -0.46
Scale factor	0.139(5)	0.068(1)	0.1258(1)
Extinction coefficient	0.0005(3)	0.003(7)	0.0003(2)
^{IV}Al-O (Å)	1.773(3) x 4	1.783(7) x 4	1.776(2) x 4
^{VI}Al-O (Å)	1.936(3) x 6	1.933(7) x 6	1.936(2) x 6
^{VIII}Ln-O (Å)	2.319(3) x 4	2.315(6) x 4	2.327(2) x 4
	2.457(3) x 4	2.436(6) x 4	2.461(2) x 4

Table 6.4 - Fractional atomic coordinates and equivalent isotropic displacement parameters for (RE)₃Al₅O₁₂ crystals C and I grown from unreacted precursor powders at 0.20 and 0.05 mm/min, respectively.

Atom	Site	Symmetry	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} (Å ²)
<i>C (outer edge)</i>						
Al1	16a	$\bar{3}$	0	0	0	0.0028(4)
Al2	24d	$\bar{4}$	3/8	0	1/4	0.0030(5)
RE*	24c	222	1/8	0	1/4	0.0034(1)
O	96h	1	0.1007(2)	0.1997(2)	0.2807(2)	0.0027(5)
<i>C (center)</i>						
Al1	16a	$\bar{3}$	0	0	0	0.014(2)
Al2	24d	$\bar{4}$	3/8	0	1/4	0.014(2)
RE*	24c	222	1/8	0	1/4	0.0156(9)
O	96h	1	0.1011(6)	0.1984(5)	0.2800(5)	0.016(1)
<i>I (outer edge)</i>						
Al1	16a	$\bar{3}$	0	0	0	0.0033(3)
Al2	24d	$\bar{4}$	3/8	0	1/4	0.0037(4)
RE**	24c	222	1/8	0	1/4	0.0038(1)
O	96h	1	0.1011(2)	0.1998(2)	0.2809(2)	0.0037(4)

* RE = fixed composition Lu_{1/4}Dy_{1/4}Tb_{1/4}Gd_{1/4}

** RE = fixed composition Ho_{1/4}Dy_{1/4}Tb_{1/4}Gd_{1/4}

(4) Å], as seen in Table 6.3 . This indicates a segregation of larger REs to the outer surface of the crystals, which is discussed later in this Chapter and has been observed previously in multicomponent aluminum garnet crystals grown via the mPD method [39]. The outer surface of crystal I is also a single garnet phase (space group Ia3d) and has a larger unit-cell parameter [12.0892 (2) Å] than that of crystal C, which is expected since the AIR of composition I is larger than that of composition C (Table 6.1). The diffraction pattern obtained for the center of crystal I is typical of a perovskite structure, which could not be confidently refined because the particular distortion is uncertain. The quality of the data was poor, possibly due to chemical inhomogeneity, twinning, and the presence of multiple misaligned grains, which would explain the opacity of the central region of the crystal as shown in Figure 6.2.

Radial elemental distribution

To understand how AIR affects radial elemental profiles, EPMA data were collected for crystals A and J pulled slowly. Crystal A has the smallest AIR in this study and is transparent, while crystal J has the largest AIR and has a central opaque region (Table 6.1 and Figure 6.2). A microscope image and the EPMA results of crystal A ($\text{Lu}_{1/4}\text{Y}_{1/4}\text{Tb}_{1/4}\text{Gd}_{1/4}\text{Al}_5\text{O}_{12}$) are shown in Figure 6.6.a; the RE and Y concentration profiles are continuous and located in the vicinity of the nominal concentration (3.75 at%). Additionally, smaller elements (Lu and Y) have downwardly curved profiles (higher concentrations in the center of the crystal), while larger elements (Tb and Gd) have upwardly curved profiles (higher concentrations in the outer surface of the crystal). This is typical of multicomponent aluminum garnet crystals and indicates the preferential incorporation of smaller REs into the small dodecahedral crystallographic sites of the garnet structure. The rejected larger REs cannot accumulate in the crucible since mPD crystals are grown without direct contact with the melt reservoir. Therefore, the larger REs segregate toward the outer surface of the crystal [37], [39].

A microscope image and the EPMA results of sample J ($\text{Dy}_{1/4}\text{Tb}_{1/4}\text{Gd}_{1/4}\text{Al}_5\text{O}_{12}$) are shown in Figure 6.6.b. The RE and Y concentration profiles are discontinuous with a sharp increase in the center of the crystal. Closer to the outer surface of the crystal (from 1.5 to 0.6 mm and 0.5 to 1.4 mm), the profiles are located in the vicinity of the nominal concentration (7.5 at% for Dy and 3.75 at% for Tb and Gd). On the other hand, in the center of the crystal, all RE and Y have concentrations that are higher than the nominal, suggesting that the opaque and transparent regions are different phases.

The ratio between the sum of the concentrations of REs and Al obtained via EPMA can be used to confirm the phases that are present in the clear and opaque regions of the crystals. If we consider stoichiometric multicomponent aluminates, the nominal ratio should be 0.6 for garnet ($\text{RE}_3\text{Al}_5\text{O}_{12}$) and 1.0 for perovskite (REAlO_3). The experimental ratio was calculated for each EPMA data

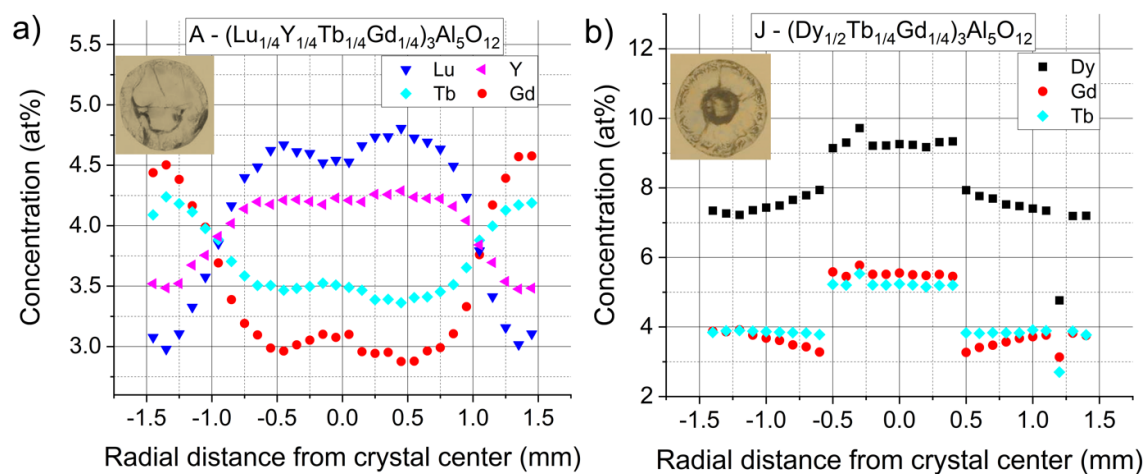


Figure 6.6 - EPMA radial concentration profiles of crystals A (a) and J (b) grown from raw powders and pulled slowly. Measurements were done on 1-mm-thick radial sections cut 2 mm away from the seed end. In composition A the nominal concentration is 3.75 at% for all REs. In composition J, the nominal concentration is 7.5 at% for Dy and 3.75 at% for Tb and Gd.

point shown in Figure 6.6 to explain the discontinuity in elemental profiles. The average of this ratio for crystal A is 0.62 ± 0.003 , indicating a garnet phase for all data points. On the outer surface of crystal J (from 1.5 to 0.6 mm and 0.5 to 1.4 mm; Figure 6.6), the average of this ratio is 0.6 ± 0.05 , indicating a garnet phase. In the center of crystal J, the average of this ratio is 1.0 ± 0.04 , indicating a perovskite phase; therefore, the central opaque region is caused by perovskite inclusions, which confirms the results from singlecrystal XRD.

The formation of the perovskite phase only in the center of crystal J may be due to a higher melt temperature in the center of the molten zone [204] and may result in Al_2O_3 inclusions. At high temperatures, melts with a nominal garnet stoichiometry preferentially crystallize into a relatively simple orthorhombic perovskite structure rather than the more complex garnet structure [219].

A smaller amount of Al is consumed to form the perovskite (REAlO_3) phase than the garnet ($\text{RE}_3\text{Al}_5\text{O}_{12}$) phase and, therefore, after formation of the perovskite phase in the center, excess Al^{3+} remaining in the molten zone is accumulated near the periphery. According to our observations using a CCD camera, the growth interface was convex toward the melt. The shape of the interface leads to a radial crystal growth and segregation of excess Al^{3+} toward the outer surface of the crystal, inducing the formation of Al_2O_3 inclusions, as observed previously in $\text{Tb}_3\text{Al}_5\text{O}_{12}$ crystals [193]. Alumina inclusions are discussed later in this Chapter. The convex shape of the solid–liquid interface may have been favored by the high crystallization temperature of the perovskite structure in the center of the crystal compared to the garnet structure near the outer surface. This difference in crystallization temperature is typical of the single-RE RE_2O_3 – Al_2O_3 systems formed by the REs in composition J, namely Dy, Tb, and Gd [73].

Inclusions on the outer surface of crystals

To investigate the morphology and composition of the inclusions seen on the outer surface of the crystals (Figure 6.2), SEM images and EDS data were acquired from 1 mm-thick cross-sectional samples. Figure 6.7.a and Figure 6.7.b are SEM images of crystals C and J pulled fast, respectively; dark veins are close to the outer surface of the crystals and crystal J has a higher concentration of them. Similar dark inclusions are in crystals G–J pulled slowly and C–J pulled fast, and their concentration increases with increasing AIR (from C to J). Higher magnification images of crystals C and J shown in Figure 6.7.c and Figure 6.7.d, respectively, reveal that these dark veins are composed of entangled and interpenetrating lighter and darker phases, which is typical of a eutectic microstructure [220]. Alumina and eutectic inclusions near the outer surface of the crystals have been reported previously for mPD-grown single-RE garnets and have been attributed to incongruent melting in $\text{La}:\text{Lu}_3\text{Al}_5\text{O}_{12}$ [221] and a convex solid–liquid growth interface in $\text{Tb}_3\text{Al}_5\text{O}_{12}$ [193].

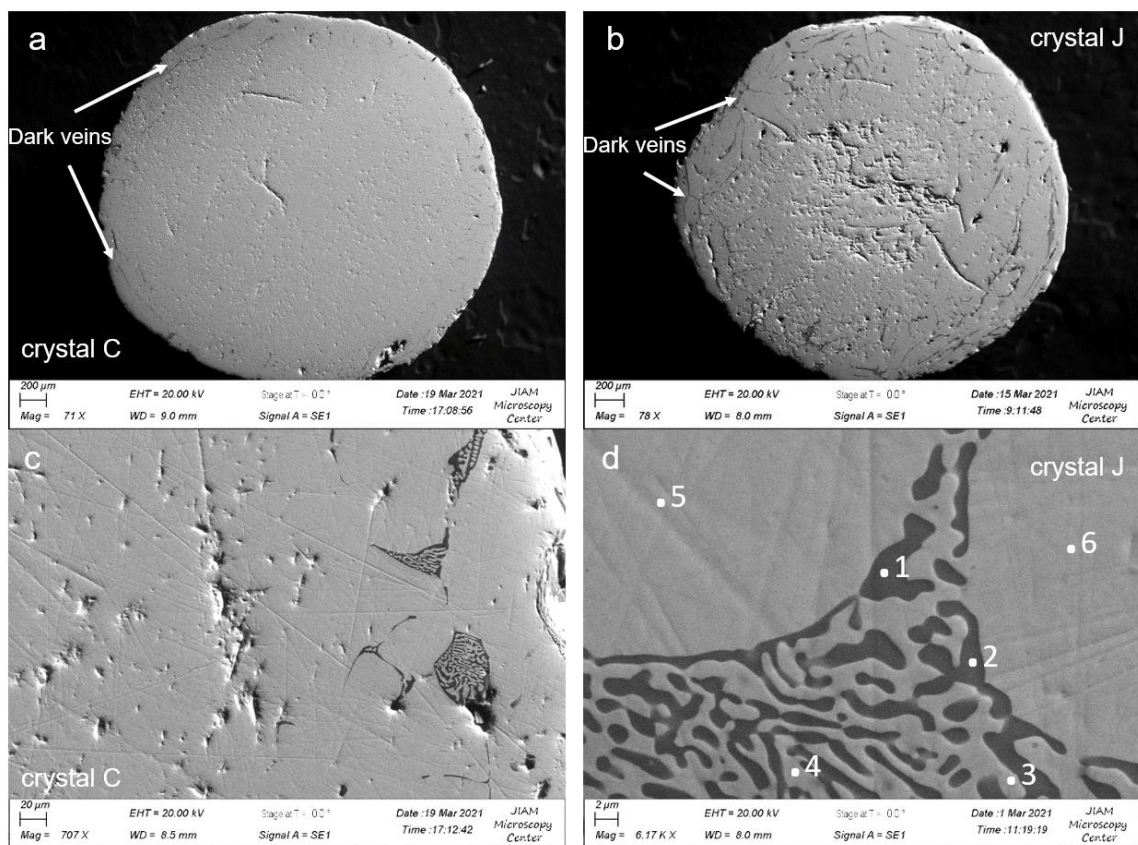


Figure 6.7 - SEM images of crystals C (a and c) and J (b and d) grown from raw powders and pulled fast (0.20 mm/min). EDS data obtained for points 1-6 in (d) are seen in Table 6.5.

To assess the elemental composition of the inclusions, EDS data were collected from the six points indicated in Figure 6.7.d and are presented in Table 6.3. Darker areas in the inclusions (points 1 and 2) have lower concentrations of REs (Dy, Tb, and Gd) and are richer in Al, which indicates a secondary alumina phase that was below the detection limits of XRD techniques. Lighter areas in the inclusions (points 3 and 4) have relatively higher concentrations of REs than the dark areas, but still significantly lower than the nominal concentration; lighter areas are also rich in Al. On the other hand, outside of the inclusion (points 5 and 6), the concentration of REs and Al, and the measured stoichiometry, are closer to nominal.

The formation of eutectic inclusions may be related to composition. A larger AIR may induce the formation of eutectic inclusions since their concentration increases in compositions C to J. In the phase diagrams of single-RE $\text{RE}_2\text{O}_3\text{--Al}_2\text{O}_3$ systems, the position of the eutectic point between the single-RE garnet $\text{RE}_3\text{Al}_5\text{O}_{12}$ and Al_2O_3 is closer to the garnet stoichiometry as the RE ionic radius increases [73], [215]. Therefore, the probability of forming eutectic inclusions during directional solidification increases for compositions with larger AIR and for regions in the crystal where larger elements are concentrated, such as the outer surface (Figure 6.6.a). Additionally, the crystallization of a perovskite phase in the center of the crystal (discussed previously in this Chapter) results in the rejection of Al^{3+} since the relative amount of Al in perovskites (REAlO_3) is lower than in garnets ($\text{RE}_3\text{Al}_5\text{O}_{12}$). This would lead to a molten zone rich in Al, which can shift the melt stoichiometry toward the eutectic composition.

Conclusion

We established a relation between the AIR of Y and RE elements and phase formation in multicomponent aluminum garnet crystals by growing and evaluating the phase composition of micro-pulling-down crystals of the system $(\text{Lu,Y,Ho,Dy,Tb,Gd})_3\text{Al}_5\text{O}_{12}$. To determine this relation, ten compositions were formulated to obtain compounds within a relatively large range of AIR. In general, compositions with small AIR and slow pulling rates favor the formation of a single garnet phase. A central opaque region is formed in crystals with large AIR and has been attributed to a secondary perovskite phase. Additionally, a larger concentration of eutectic inclusions is formed at the outer surface of crystals with larger AIR.

Most crystals melted congruently and formed a single phase, even though 50% of the garnet dodecahedral sites were occupied by Tb^{3+} and Gd^{3+} (25% each), which form incongruent melting single-RE aluminum garnets. Although relatively large quantities of large Tb and Gd do not result in incongruent melting, large AIR induces the formation of secondary perovskite and eutectic phases. Future exploration of the fundamental and functional properties of multicomponent garnet crystals could include compositions with Tb and Gd in relatively large

Table 6.5 - EDS elemental composition of crystal J grown fast for areas 1-6 shown in the SEM image in Figure 7.d.

		EDS elemental composition (at%), error < 0.001 at%					
Area	Points from Figure 7.d <i>Nominal composition</i>	Dy	Tb	Gd	Al	O	Stoichiometry
		7.5	3.75	3.75	25.00	60.00	$RE_3Al_5O_{12}$
Darker area in the inclusion	1	1.63	0.87	0.91	46.06	50.53	$RE_{0.7}Al_{9.2}O_{10.1}$
	2	1.60	0.87	0.93	46.27	50.33	$RE_{0.7}Al_{9.3}O_{10.1}$
Lighter area in the inclusion	3	5.42	3.15	3.44	36.24	51.75	$RE_{2.4}Al_{7.2}O_{10.4}$
	4	4.54	2.79	3.30	37.80	51.57	$RE_{2.1}Al_{7.6}O_{10.3}$
Outside the inclusion	5	7.70	3.90	3.80	31.60	53.00	$RE_{3.1}Al_{6.3}O_{10.6}$
	6	7.35	3.99	4.16	32.37	52.13	$RE_{3.1}Al_{6.5}O_{10.4}$

concentrations without inducing secondary phases, as long as the AIR is maintained lower than 1.038 Å, which here corresponds to the composition I.

**CHAPTER SEVEN:
CRYSTAL GROWTH AND PHASE FORMATION OF HIGH-
ENTROPY RARE-EARTH ALUMINUM PEROVSKITES**

A version of this chapter was submitted for publication in a peer-reviewed journal by Matheus Pianassola and colleagues:

M. Pianassola, B. Chakoumakos, C. Melcher, and M. Zhuravleva, "Crystal growth and phase formation of high-entropy rare-earth aluminum perovskites," *Cryst. Growth Des.*, Under review.

This chapter is the reformatted version of the original work submitted to the referenced journal.

Abstract

We demonstrate for the first time the crystal growth of high-entropy rare-earth (RE) aluminum perovskites (REAlO_3) using the micro-pulling-down method to inform future exploration of functional crystals. To determine how composition affects phase formation, we formulate equiatomic compositions containing five REs from the following list: Lu, Yb, Tm, Er, Y, Ho, Dy, Tb, Gd, Eu, Sm, Nd, Pr, Ce, La. To test whether combinations of REs with similar ionic radii may favor a single phase, compositions containing REs with consecutive or non-consecutive ionic radius values were formulated. Powder and single-crystal X-ray diffraction indicate that crystals containing only REs with similar ionic radii that form orthorhombic single-RE REAlO_3 are a single phase. Crystals containing REs with dissimilar ionic radii or mixtures of REs that form orthorhombic, rhombohedral, and tetragonal single-RE REAlO_3 are a mixture of phases. The elemental distribution in single-phase crystals analyzed via electron probe microanalysis confirms no evidence of preferential incorporation of any of the constituent REs. The distribution and composition of secondary phases were analyzed via scanning electron microscopy and energy dispersive spectroscopy; secondary phases were seen as a small region in the center of the crystals with branching features closer to the outer surface.

Introduction

Pioneering reports on bulk high-entropy oxide single crystals have motivated further studies on the growth of complex crystals from various compositional systems [27], [35], [39]. The interest in such crystals originates from the enhanced properties seen in polycrystalline high-entropy oxides, such as reversible energy storage, low thermal conductivity for environmental barriers, and high thermal stability [40], [53]. In those oxides, admixing five or more cations in equiatomic amounts leads to an entropy-driven phase stabilization and a synergistic effect on functional properties [40]. Demonstrations of the growth of highly complex oxides crystals have been limited to a few rare-earth-based compositional systems including aluminum garnets [39], [214], [222], titanates [35], [36], borates [26], [27], calcium borates [28], [29], and sesquioxides [123]. The practical aspect of the growth of crystals from other high-entropy compositional

systems remains unexplored.

The field of crystal growth of high-entropy rare-earth (RE) aluminates attracts attention due to the possibility of maximizing the luminescence properties of analogous low-entropy crystals. Single-RE aluminum garnet ($\text{RE}_3\text{Al}_5\text{O}_{12}$) and perovskite (REAlO_3) crystals formed by Lu, Y, and Gd are commercially used for scintillation and lasing applications [86], [87], [223], [224]. Several studies have proven that the performance of garnet crystals can be improved by admixing two or three REs [15], [16], [18], [225]. This motivated studies on the practical aspect of crystal growth of high-entropy garnets [39], [214]. Similar admixing studies on aluminum perovskites are limited [21]–[25] and high-entropy perovskites have been only produced as polycrystalline ceramics [78]. Therefore, this study aims to demonstrate the growth of complex perovskites and leverage the future development of functional, complex perovskite crystals.

The correlation between the RE^{3+} ionic radius and the crystal structure of REAlO_3 compounds is summarized in Table 7.1. Here, Y is referred to as a RE element for simplicity. Smaller cations from Lu^{3+} to Sm^{3+} form an orthorhombic REAlO_3 structure with $Pnma$ space group where RE^{3+} cations have a coordination number (CN) VIII [226]–[228]. Such REAlO_3 are often reported with $Pbnm$ space group, which is equivalent to the $Pnma$ space group and is described by a permutation of its a , b , c axes [229]–[232]. The larger Nd^{3+} , Pr^{3+} , and La^{3+} form a rhombohedral REAlO_3 structure with $R\bar{3}ch$ space group where RE^{3+} cations have a CN XII [233]. Although Ce^{3+} has an ionic radius similar to that of Pr^{3+} and La^{3+} , CeAlO_3 has a tetragonal structure with $P4/mmm$ space group where RE^{3+} cations have a CN XII [234].

In this work, we demonstrate the crystal growth of high-entropy RE aluminum perovskites and correlate their composition and phase formation. We focus on seven REAlO_3 compositions containing five REs in equiatomic amounts to fractionally occupy the rare-earth cation sublattice. Our composition formulation is based on the premise that REs with similar ionic radii may favor the formation of single-phase high-entropy oxides [57]. Compositions containing REs with consecutive or non-consecutive ionic radius values were formulated to test that premise. Crystals were grown via directional solidification by the micro-pulling-down (mPD) method. This growth technique is optimal for materials development due to the small amount of material needed (~1 g) and the fast pulling rates that can be achieved (up to 20 mm/min) [37].

Methods

Composition formulation

High-entropy REAlO_3 compounds were formulated with five REs mixed in equiatomic amounts to study how phase formation is affected by two composition

Table 7.1 - List of RE³⁺ cations ordered from small to large ionic radius [124] and crystal structure [226] of the respective single-RE REAlO₃ compounds.

RE ³⁺ cation	RE ³⁺ ionic radius for CN VI (Å)	REAlO ₃ unit cell geometry and space group
Lu ³⁺	0.848	orthorhombic (<i>Pnma</i>)
Yb ³⁺	0.858	orthorhombic (<i>Pnma</i>)
Tm ³⁺	0.869	orthorhombic (<i>Pnma</i>)
Er ³⁺	0.881	orthorhombic (<i>Pnma</i>)
Y ³⁺	0.892	orthorhombic (<i>Pnma</i>)
Ho ³⁺	0.894	orthorhombic (<i>Pnma</i>)
Dy ³⁺	0.908	orthorhombic (<i>Pnma</i>)
Tb ³⁺	0.923	orthorhombic (<i>Pnma</i>)
Gd ³⁺	0.938	orthorhombic (<i>Pnma</i>)
Eu ³⁺	0.950	orthorhombic (<i>Pnma</i>)
Sm ³⁺	0.964	orthorhombic (<i>Pnma</i>)
Nd ³⁺	0.995	rhombohedral (<i>R</i> $\bar{3}$ <i>c</i>)
Pr ³⁺	1.013	rhombohedral (<i>R</i> $\bar{3}$ <i>c</i>)
Ce ³⁺	1.034	tetragonal (<i>P4/mmm</i>)
La ³⁺	1.061	rhombohedral (<i>R</i> $\bar{3}$ <i>c</i>)

parameters: 1) the similarity in their ionic radii and 2) the type of REs in terms of the structure of the respective single-RE REAlO₃. Table 7.2 is a list of the compositions studied with the respective ID, the number of REs that form each of the three structures observed in single-RE REAlO₃, and the average ionic radius (AIR). Previous work demonstrated that REs with similar ionic radii may favor the formation of a single phase in high-entropy oxides [57]. To test that concept and study the effect of the similarity of the RE³⁺ ionic radii on phase formation, compositions A, B, D, and E have only REs with consecutive ionic radius values in Table 7.1, while compositions C, F and G have REs with non-consecutive ionic radius values. To study the effect of the type of REs on phase formation, compositions A-D have only REs that form orthorhombic single-RE REAlO₃, while compositions E-G have mixtures of REs that form an orthorhombic, rhombohedral, and tetragonal single-RE REAlO₃.

Crystal growth

Cylindrical Ø 3 mm crystals were grown by the mPD method [37] using a KDN Dai-Ichi Kiden furnace with an RF generator model TR-02001 operated at 26 kVA. The starting powders were Lu₂O₃, Yb₂O₃, Tm₂O₃, Er₂O₃, Y₂O₃, Ho₂O₃, Dy₂O₃, Tb₂O₃, Gd₂O₃, Eu₂O₃, Sm₂O₃, Nd₂O₃, Pr₂O₃, CeO₂, La₂O₃, and Al₂O₃ of at least 99.99% purity. The powders were dried at 800°C for 8 h in air, mixed in stoichiometric ratios, and placed in a Ø16 mm iridium crucible with a Ø3 mm die and a Ø0.5 mm capillary channel. The crucible was inductively heated to melt the powders and two types of seed material were used to initiate the growth. An orthorhombic YAlO₃ seed oriented in the [001] direction was used for crystals A, B, C, D, and F. An orthorhombic structure was expected for those crystals since most of the constituent REs form an orthorhombic single-RE REAlO₃ (Table 7.2). An iridium pin was used for crystals E and G. A rhombohedral structure was expected for those crystals since most of the constituent REs form a rhombohedral single-RE REAlO₃ (Table 7.2); however, a rhombohedral crystal seed was not available. All crystals were grown with a pulling rate of 0.05 mm/min. Details about the mPD growth method and the crystal growth setup used here can be found in a previous publication [39].

Powder X-ray diffraction

All crystals were subjected to phase analysis by acquiring room-temperature powder X-ray diffraction (XRD) patterns, which were used for Rietveld structure refinement. Crystals were cut into three cylindrical sections of equal lengths, and the middle section was ground in a mortar and used for phase analysis. Diffraction patterns were collected with a Panalytical Empyrean diffractometer in the Bragg-Brentano geometry using a Cu K α X-ray source at 45 kV and 40 mA. Lattice parameter and phase composition were obtained via Rietveld refinements with the General Structure Analysis System II software (GSASII).

Table 7.2 - List of compositions and the respective number of REs that form each of the four structures seen in single-RE REAlO₃ (O – orthorhombic, R – rhombohedral, T – tetragonal); crystallographic space groups are in parenthesis. Commas in the compositions represent equiatomic amounts of REs. Average ionic radii (AIR) for coordination number VI are listed [124].

ID	Composition	REs with consecutive ionic radius values in Table 7.1?	Number of REs that form each of the three structures observed in single-RE REAlO ₃			AIR (Å)
			O (<i>Pnma</i>)	R (<i>R</i> $\bar{3}$ <i>c</i>)	T (<i>P4/mmm</i>)	
A	(Yb,Tm,Er,Y,Ho)AlO ₃	Yes	5	0	0	0.879
B	(Y,Ho,Dy,Tb,Gd)AlO ₃	Yes	5	0	0	0.911
C	(Lu,Er,Y,Gd,Sm)AlO ₃	No	5	0	0	0.905
D	(Dy,Tb,Gd,Eu,Sm)AlO ₃	Yes	5	0	0	0.937
E	(Sm,Nd,Pr,Ce,La)AlO ₃	Yes	1	3	1	1.013
F	(Lu,Yb,Y,Gd,La)AlO ₃	No	4	1	0	0.919
G	(Lu,Nd,Pr,Ce,La)AlO ₃	No	1	3	1	0.990

Single crystal X-ray diffraction

Crystals that were phase pure according to powder XRD results were subjected to single crystal XRD for further assessment of the crystal structure. A Rigaku XtaLAB PRO diffractometer equipped with a Rigaku HyPix-6000HE detector and an Oxford N-HeliX cryocooler was used to collect single-crystal diffraction data at room temperature. Graphite monochromated Mo K α radiation was used ($\lambda = 0.71073$ Å, 50 kV and 40 mA). Peak indexing and integration were performed using the Rigaku Oxford Diffraction CrysAlisPro software [216]. An empirical absorption correction was applied using the SCALE3 ABSPACK algorithm as implemented in CrysAlisPro. The SHELXL-2013 and WinGX software packages were used for data processing and structure refinement. The structure refinements were made with oxygen atom positional coordinates, isotropic atomic displacement parameters, an extinction parameter, and the scale factor.

Scanning electron microscopy and energy dispersive spectroscopy

To evaluate the microstructure of the crystals, 1-mm thick cross-sectional samples were cut, polished, and imaged with a Zeiss EVO MA15 Scanning Electron Microscope (SEM). The elemental composition of the samples was analyzed with a Bruker xFlash 6130 Energy Dispersive X-Ray Spectrometer (EDS), which was mounted in the SEM sample chamber.

Results and discussion

Grown crystals

Crystals containing only REs with consecutive ionic radius values and that form orthorhombic single-RE REAlO₃ (crystals A, B, and D) are transparent. As seen in Figure 7.1, crystals A and B are crack-free and transparent, while crystal D is heavily cracked with a transparent section on the seed-end (left side of the photo). Crystal D was transparent during growth and cracked upon cooling, which is a common issue in orthorhombic REAlO₃ crystals due to their anisotropic coefficients of thermal expansion [179], [180]. Cracking in composition D may be avoided by growing crystals with a longer neck and shoulder section to prevent seed defects from propagating into the crystal. The orange color in those crystals comes from Ho³⁺, Dy³⁺, and Sm³⁺.

Crystals that contain REs with non-consecutive ionic radius values or mixtures of REs that form an orthorhombic, rhombohedral, and tetragonal single-RE REAlO₃ are opaque (crystals C, E, F, and G). These crystals were opaque during growth, which may indicate a mixture of phases as discussed in the next section. Crystal C is orange due to Sm³⁺, while crystals E and G are dark green due to Pr³⁺.

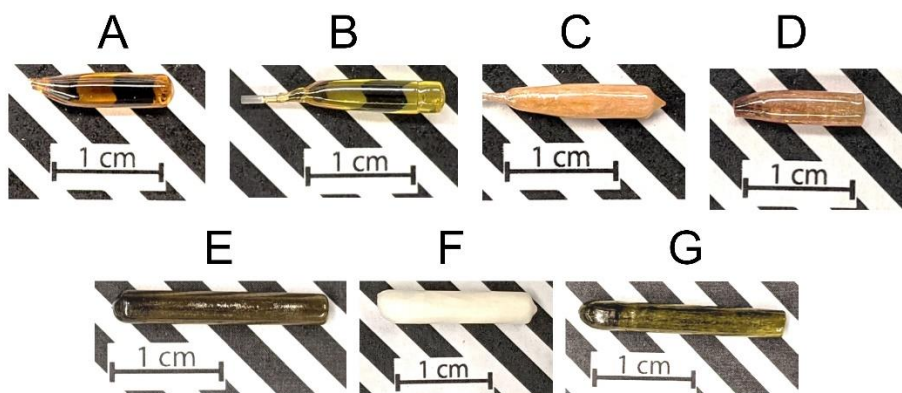


Figure 7.1 - Photos of $\varnothing 3$ mm cylindrical crystals. Crystal IDs A-G corresponds to the compositions listed in Table 7.2. Crystals A, B, and D are transparent and crystals C, E, F, and G are opaque. The seed- and the tail-end of the crystals are on the left and right sides of the photos, respectively. A piece of the YAlO_3 seed is seen on the seed-end of crystal B.

Phase formation and crystal structure

Powder XRD

Crystals A, B, and D are a single orthorhombic phase, which may have been favored by mixtures of REs that have similar ionic radii and form orthorhombic single-RE REAlO₃ (Table 7.2). Powder XRD patterns of crystals A and B have reflection peaks that match those of an orthorhombic YAlO₃ reference pattern as seen in Figure 7.2.a. A powder XRD pattern is shown in Figure 7.2.b and indicates that the reflection peaks of crystal D match those of an orthorhombic GdAlO₃ reference pattern. These reference patterns were chosen due to the similarity of their RE³⁺ ionic radius and the AIR of compositions A, B, and D (Table 7.1 and Table 7.2).

The lattice parameters of crystals A, B, and D follow the general trend of single-RE REAlO₃ with respect to the RE³⁺ average ionic radius, as seen in Figure 7.3. The refined lattice parameters are shown in Table 7.3. In general, with an increasing RE³⁺ ionic radius, the unit cell volume of single-RE REAlO₃ increases with the *b* and *c* axes while the *a* axis decreases. This trend is also observed for the high-entropy crystals A, B, and D. Additionally, the lattice parameters of crystals A, B, and D are similar to those of ErAlO₃, DyAlO₃, and GdAlO₃, respectively. Trivalent Er, Dy³⁺, and Gd³⁺ have ionic radius values close to the AIR of A, B, and D, respectively. This indicates that lattice parameters of high-entropy perovskites vary consistently with their AIR.

The successful growth of crystals A, B, and D demonstrates the practical aspect of growing phase-pure high-entropy REAlO₃ crystals. These crystals contain REs with consecutive ionic radius values as listed in Table 7.1; additionally, all constituent REs form orthorhombic single-RE REAlO₃. In the next paragraphs, we discuss how phase formation is affected by mixing REs that have non-consecutive ionic radii or that form single-RE REAlO₃ with an orthorhombic, rhombohedral, and tetragonal structure.

Crystal C is a mixture of two orthorhombic structures and the weight fraction of the primary and secondary phases are 90 wt% and 10 wt% respectively; this mixture may have been induced by the dissimilarity in the ionic radius of the constituent REs. A powder XRD pattern of crystal C is shown in Figure 7.4.a with reference patterns of orthorhombic YAlO₃ and orthorhombic GdAlO₃. Similar to the single-phase crystals A, B, and D, crystal C only has REs that form orthorhombic single-RE REAlO₃. However, the single-phase crystals A, B, and D have REs with consecutive ionic radii values, while the REs in crystal C have non-consecutive ionic radii values. Therefore, the formation of two orthorhombic phases may have resulted from the dissimilarity in the size of RE cations in crystal C. The unit cell volume of the primary and secondary orthorhombic unit cells are 202.724 Å³ and 209.274 Å³, which indicates that the larger REs such as Gd³⁺ and Sm³⁺ are

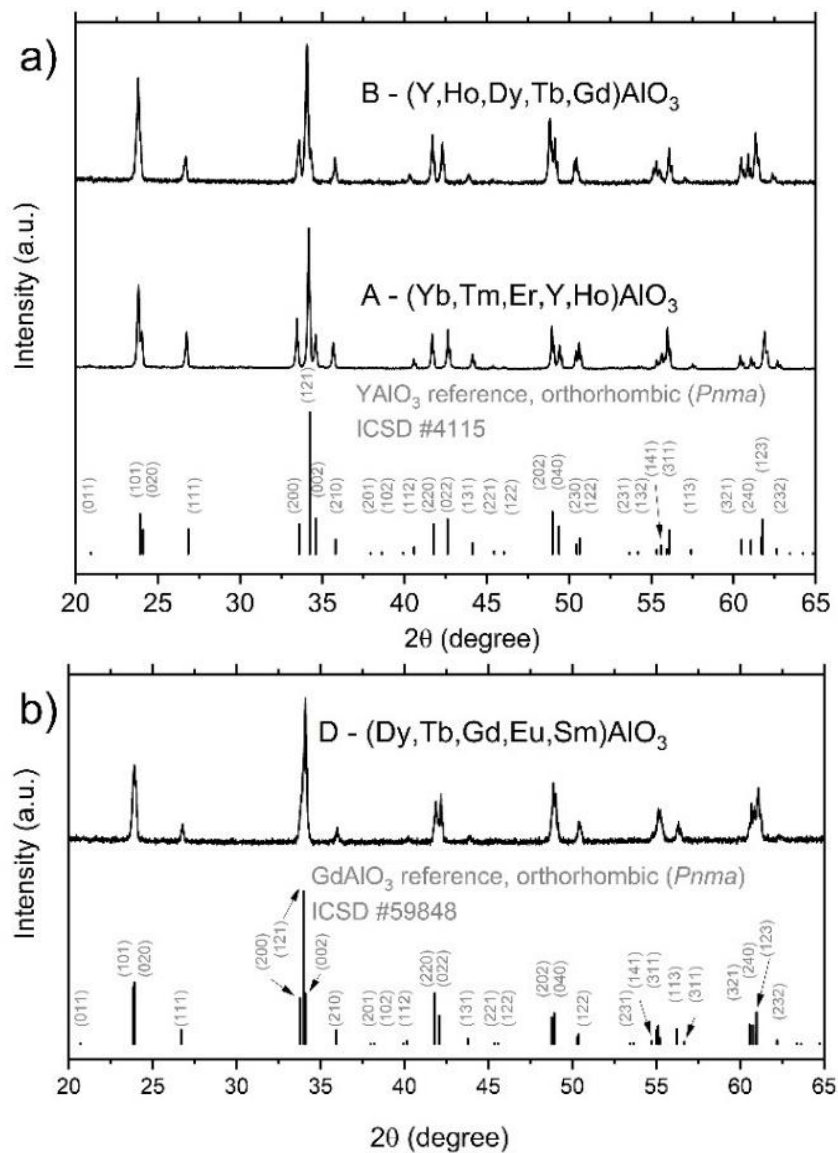


Figure 7.2 - a) Powder XRD patterns of (a) crystals A and B and an orthorhombic YAlO₃ reference pattern; (b) crystal D and an orthorhombic GdAlO₃ reference pattern. The ICSD reference numbers are listed in the figures.

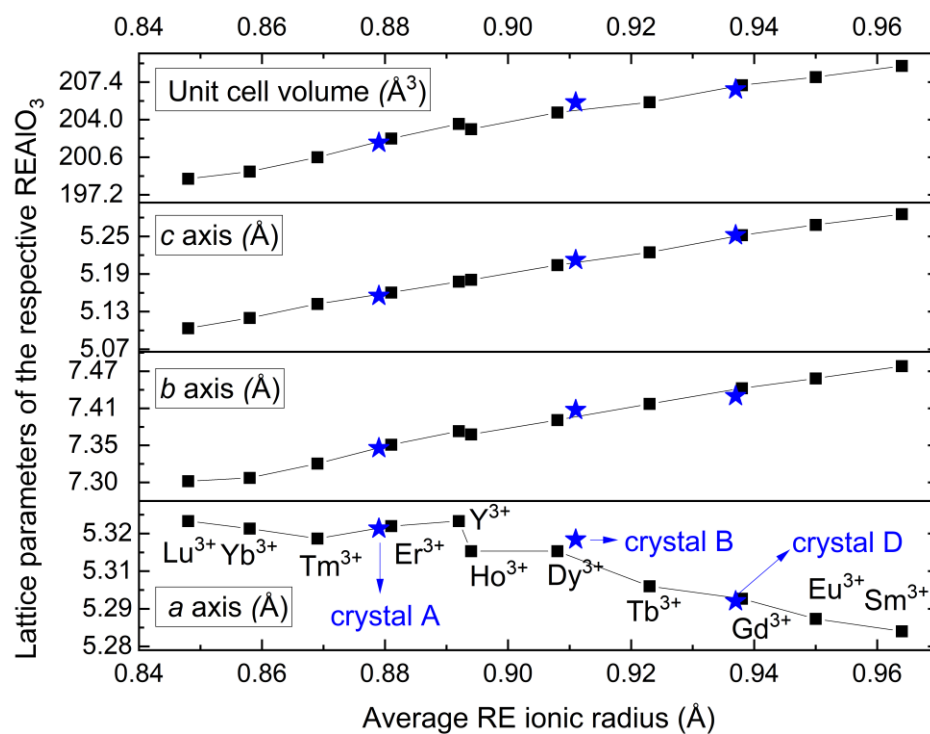


Figure 7.3 - Lattice parameters of orthorhombic single-RE REAlO₃ (squares) from the literature [215], [226] and those of the high-entropy crystals A, B, and D (stars) obtained via powder XRD data and Rietveld refinement (Table 7.3). The labels in the bottom graph apply to all graphs.

Table 7.3 - Lattice parameters and phase fraction of crystals A-F obtained via Rietveld structure refinement using powder XRD data. The acronyms PP and SP stand for “primary phase” and “secondary phase”, respectively.

		Refined unit cell lattice parameters (<i>a</i> , <i>b</i> , and <i>c</i> in Å) and phase fraction (PF in wt%) of each structure.														
Sample ID	Composition	Orthorhombic PP (<i>Pnma</i>)				Orthorhombic SP (<i>Pnma</i>)				Rhombohedral (<i>R</i> $\bar{3}$ <i>c</i>)			Tetragonal (<i>P4/mmm</i>)			
		<i>a</i>	<i>b</i>	<i>c</i>	PF	<i>a</i>	<i>b</i>	<i>c</i>	PF	<i>a</i>	<i>c</i>	PF	<i>a</i>	<i>c</i>	PF	
A	(Yb,Tm,Er,Y,Ho)AlO ₃	5.327(0)	7.348(9)	5.157(8)	100	-	-	-	-	-	-	-	-	-	-	
B	(Y,Ho,Dy,Tb,Gd)AlO ₃	5.322(6)	7.407(4)	5.214(0)	100	-	-	-	-	-	-	-	-	-	-	
C	(Lu,Er,Y,Gd,Sm)AlO ₃	5.301(9)	7.375(3)	5.184(3)	90	5.299(9)	7.463(5)	5.290(7)	10	-	-	-	-	-	-	
D	(Dy,Tb,Gd,Eu,Sm)AlO ₃	5.298(0)	7.428(8)	5.253(0)	100		-	-	-	-	-	-	-	-	-	
E	(Sm,Nd,Pr,Ce,La)AlO ₃	-	-	-	-	-	-	-	-	5.332(2)	12.963(4)	86	3.753(7)	3.761(3)	14	
F	(Lu,Yb,Y,Gd,La)AlO ₃	5.322(3)	7.378(2)	5.180(2)	45	5.315(5)	7.409(7)	5.220(9)	38	5.331(5)	12.992(1)	17	-	-	-	
G	(Lu,Nd,Pr,Ce,La)AlO ₃	5.327(3)	7.336(8)	5.141(9)	39	-		-	-	5.327(2)	13.016(3)	61	-	-	-	

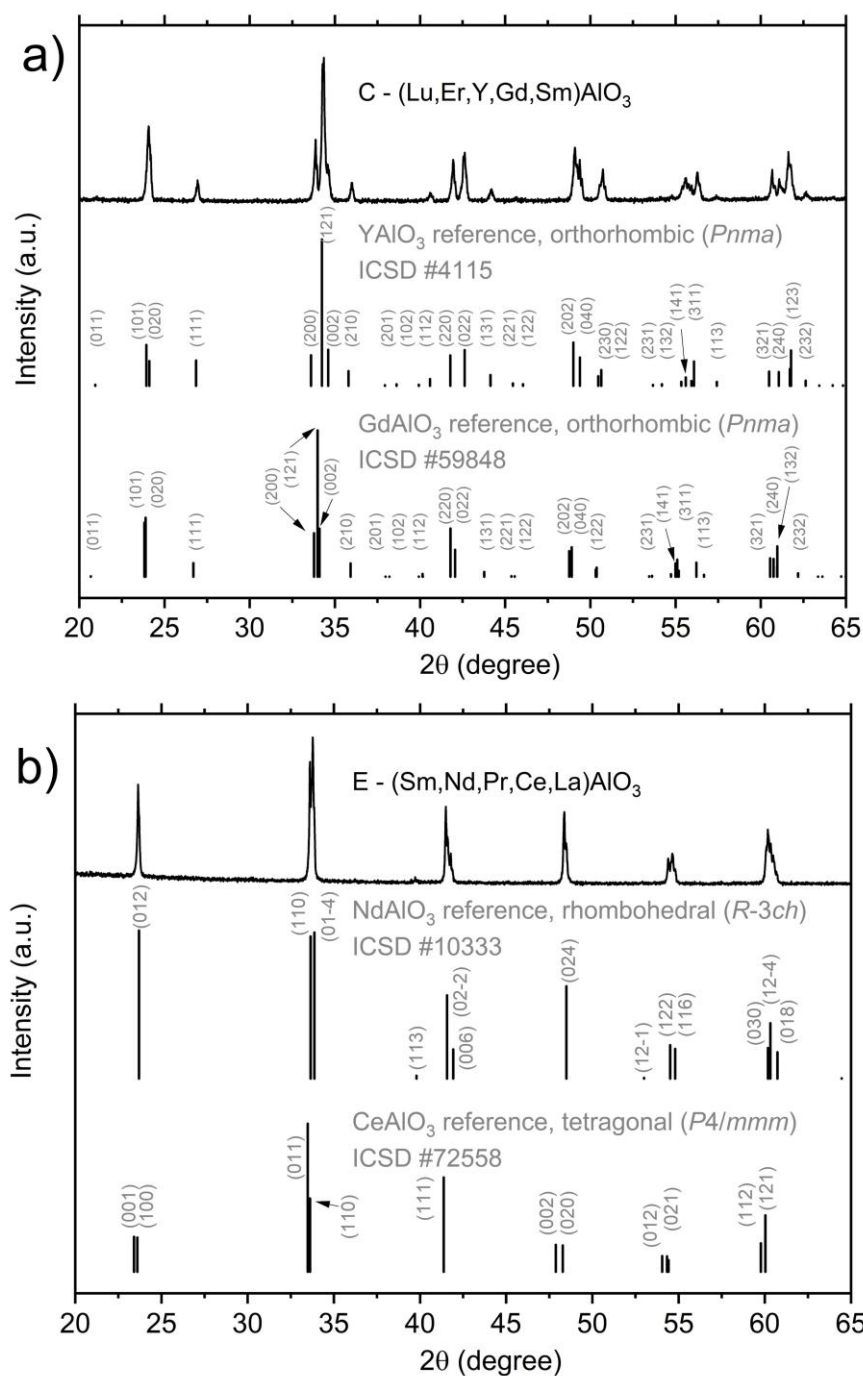


Figure 7.4 - Powder XRD patterns of (a) crystal C, an orthorhombic YAlO_3 and an orthorhombic GdAlO_3 reference patterns; (b) crystal E, a rhombohedral NdAlO_3 , and a tetragonal NdAlO_3 reference patterns.

concentrated in the secondary phase.

Crystals E is a mixture of rhombohedral (86 wt%) and tetragonal (14 wt%) phases although the constituent REs have consecutive ionic radius values; this mixture may have resulted from combinations of REs that form orthorhombic, rhombohedral, or tetragonal single-RE REAlO₃ (Table 7.2). A powder XRD pattern of crystal E is shown in Figure 7.4.b with reference patterns of rhombohedral NdAlO₃ and tetragonal CeAlO₃. Most of the REs in crystal E form rhombohedral single-RE REAlO₃ (Table 7.2), which explains a larger weight fraction of the rhombohedral phase. Since no orthorhombic phases were observed, Sm³⁺ was likely incorporated in the rhombohedral or tetragonal phases, although SmAlO₃ is orthorhombic (Table 7.1). The AIR of composition E is close to the ionic radius of Pr³⁺ and PrAlO₃ is rhombohedral (Table 7.1 and Table 7.2). Therefore, the AIR of E may have favored the formation of a primary rhombohedral structure.

Crystal F is a mixture of a primary orthorhombic (45 wt%), a secondary orthorhombic (38 wt%), and rhombohedral (17 wt%) structures, which may have resulted from a mixture of REs that form different structures in single-RE REAlO₃ (Table 7.3). A powder XRD pattern of crystal F is shown in Figure 7.5.a with reference patterns of orthorhombic YAlO₃, orthorhombic GdAlO₃, and rhombohedral NdAlO₃. Four of the five REs in composition F form orthorhombic single-RE REAlO₃, which explains the larger weight fraction of orthorhombic phases. As a result, having four REs that form the same structure in single-RE REAlO₃ and only one RE that forms a different structure is enough to induce a mixture of phases. The AIR of composition F is close to the ionic radius of Tb³⁺ and TbAlO₃ is orthorhombic. Therefore, the AIR of F may have favored the formation of the dominant orthorhombic structures.

Crystal G is a mixture of orthorhombic (39 wt%) and rhombohedral (61 wt%) structures, which may also have resulted from a mixture of REs that form different structures in single-RE REAlO₃ (Table 7.2). A powder XRD pattern of crystal G is shown in Figure 7.5.b with reference patterns of orthorhombic YAlO₃ and rhombohedral NdAlO₃. Three of the five REs in composition G form rhombohedral single-RE REAlO₃, which explains the larger weight fraction of the rhombohedral phase. The AIR of composition F is close to the ionic radius of Nd³⁺ and NdAlO₃ is rhombohedral. Therefore, the AIR of G may have favored the formation of the dominant phase.

The high-entropy nature of crystals C, E, F, and G does not stabilize a single phase and the structures formed depend on the type of REs in each composition. Combinations of REs with dissimilar ionic radius values and combinations of REs that form an orthorhombic, rhombohedral, and tetragonal single-RE REAlO₃ hinder the formation of single-phases. Such combinations should be avoided to design phase-pure high-entropy REAlO₃ crystals.

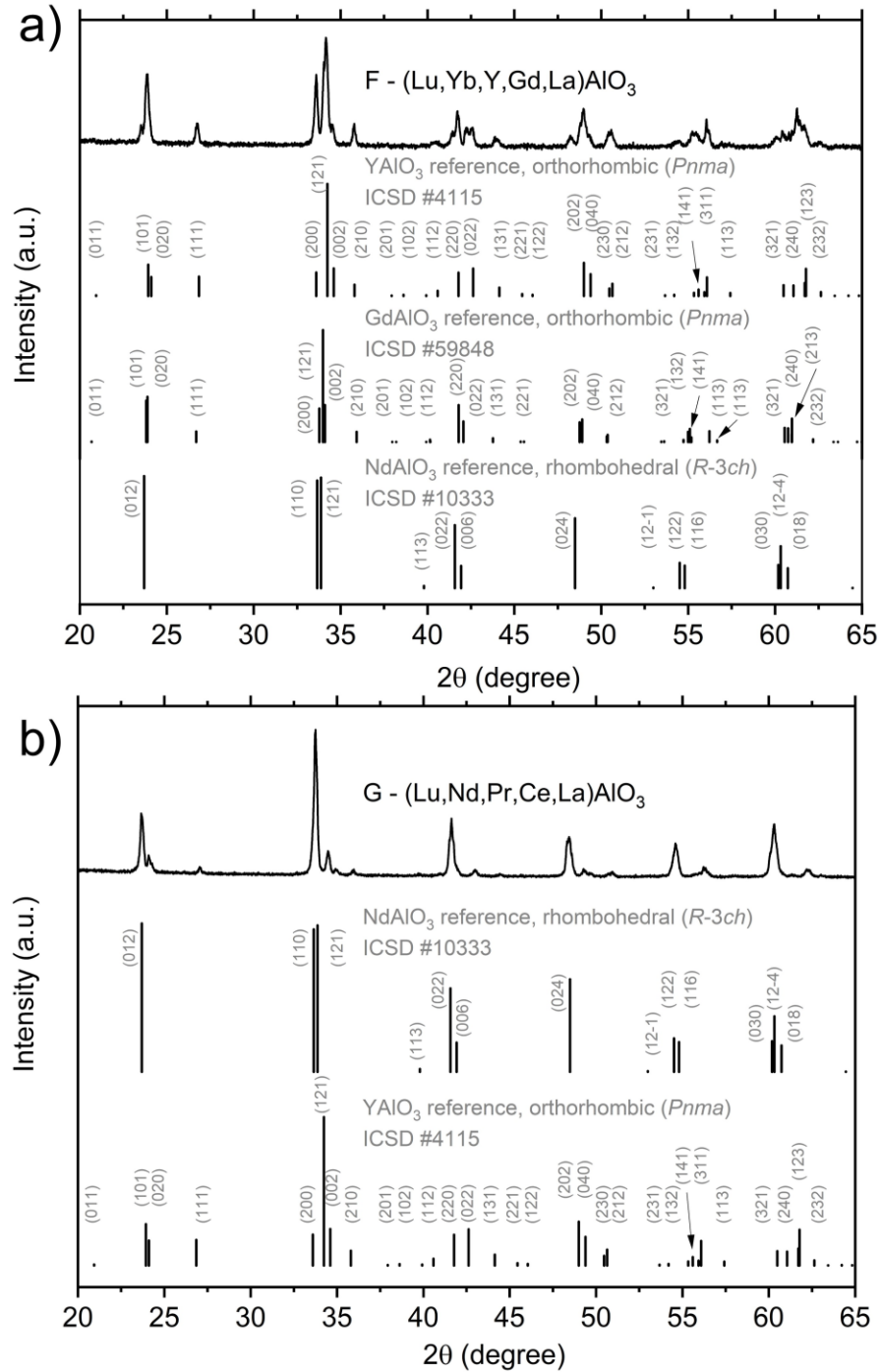


Figure 7.5 - Powder XRD patterns of (a) crystal F, an orthorhombic YAIO_3 , an orthorhombic GdAlO_3 , and a rhombohedral NdAlO_3 reference patterns; (b) crystal G, a rhombohedral NdAlO_3 , and an orthorhombic YAIO_3 reference patterns.

Single crystal XRD

Single crystal XRD results confirm a single orthorhombic *Pnma* structure in crystals A and B. These two crystals were selected for further structural investigation because they were a single phase according to powder XRD and did not crack during the growth. The RE site occupation was held fixed at the nominal composition since the number of elements on the RE site makes site occupation refinements underdetermined. No short-range clustering of the REs was observed since the diffraction patterns indicated no obvious diffuse scattering. The refinement parameters from single-crystal X-ray diffraction are given in Table 7.4. Fractional atomic coordinates and isotropic displacement parameters are listed in Table 7.5. The refined lattice parameters are like those obtained via refinement from powder XRD data in Figure 7.3. Therefore, single crystal XRD data confirms a smaller unit cell volume for crystal A compared to B, although the lattice parameter *a* of crystal A is slightly larger than that of B.

Radial elemental distribution in single-phase crystals

According to EPMA radial concentration profiles, there is no clear evidence of preferential incorporation of any REs in crystals A and B. In general, mPD crystals are compositionally homogeneous along the growth axis, elemental segregation and preferential incorporation may be seen in cross-sectional elemental distribution profiles [37], [39]. Radial concentration profiles of crystals A and B are seen in Figure 7.5.a and Figure 7.5.b; the nominal concentration of each RE is 4 at%. These crystals were selected for elemental distribution studies because they are phase pure and not cracked. In crystal A, the elemental profiles are close to nominal concentration and close to horizontal from -1.1 to 1.1 mm. Discontinuities close to the outer edge of the crystal (-1.5 to -1.2 mm and 1.2 to 1.5 mm) may result from better mixing of the melt achieved by the Marangoni melt flow that occurs close to the outer surface of the melt in the molten zone. In crystal B, the distribution profiles are close to horizontal along the whole diameter of the crystal. Since the elemental distribution profiles are close to horizontal along most of the crystal diameter, none of the RE species is preferentially incorporated into the crystals. This is in contrast with previously published high-entropy aluminum garnet mPD crystals ($\text{RE}_3\text{Al}_5\text{O}_{12}$) in which the preferential incorporation of smaller REs was evident by significantly curved profiles [39], [222].

Distribution and composition of secondary phases

Crystal G ($\text{Lu,Nd,Pr,Ce,La}\text{AlO}_3$) has a Lu-rich secondary phase in a matrix with a composition that is closer to the nominal stoichiometry. Crystal G is the focus of this section since its SEM images have more phase separation features than the other crystals with multiple phases (crystals C, E, and F Table 7.3). An SEM image of a cross-sectional sample is seen in Figure 7.6.a and reveals a lighter area in the center with branching structures closer to the outer surface of the crystal. To

Table 7.4 - Single-crystal X-ray diffraction data collection and refinement parameters for crystal A (Yb,Tm,Er,Y,Ho)AlO₃ and crystal B (Y,Ho,Dy,Tb,Gd)AlO₃.

Sample	Crystal A	Crystal B
Formula	REAlO ₃	REAlO ₃
<i>T</i> (K)	294(2)	295.6(2)
Crystal system	orthorhombic	cubic
space group	<i>Pnma</i>	<i>Pnma</i>
<i>a</i> (Å)	5.3241(3)	5.3077(2)
<i>b</i> (Å)	7.3429(5)	7.3863(3)
<i>c</i> (Å)	5.1536(2)	5.1994(2)
<i>V</i> (Å ³)	201.48(2)	203.84(2)
<i>Z</i>	1	1
<i>D</i> _{calc} (mgm ⁻³)	7.50	7.22
μ (Mo K α) (mm ⁻¹)	40.156	34.354
<i>F</i> (000)	398	389
Crystal size (mm)	0.1×0.075×0.01	0.1×0.075×0.02
θ range for data collection	4.83 - 28.27	4.2-30.4
Index ranges	-7 ≤ <i>h</i> ≤ 7 -9 ≤ <i>k</i> ≤ 9 -6 ≤ <i>l</i> ≤ 6	-13 ≤ <i>h</i> ≤ 17 -17 ≤ <i>k</i> ≤ 16 -17 ≤ <i>l</i> ≤ 17
No. reflections collected (equivalents agreement)	2074 (0.065)	3920(0.082)
No. unique reflections collected with $ F_o > 4\sigma F_o $	264	244
No. of variables	13	13
<i>R</i> _F	0.033	0.029
<i>R</i> _{wF}	0.072	0.064
Goodness of fit	1.492	1.234
largest diff. peak and hole (eÅ ⁻³)	5.05, -3.03	1.90, -2.02
Scale factor	0.5026(8)	0.5221(9)
Extinction coefficient	0.1130(8)	0.0624(9)
^{VI} Al-O (Å)	1.894(2) × 2 1.911(4) × 2 1.918(4) × 2	1.894(2) × 2 1.903(3) × 2 1.916(3) × 2
^{VIII} Ln-O (Å)	2.233(7) × 1 2.261(4) × 2 2.300(6) × 1 2.458(4) × 2 2.564(4) × 2	2.270(6) × 1 2.290(4) × 2 2.354(5) × 1 2.487(3) × 2 2.586(3) × 2

Table 7.5 - Fractional atomic coordinates and equivalent isotropic displacement parameters* for high-entropy perovskites crystals A (Yb,Tm,Er,Y,Ho)AlO₃ and B (Y,Ho,Dy,Tb,Gd)AlO₃. Space group *Pnma*.

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} (Å ²)
A (Yb,Tm,Er,Y,Ho)AlO ₃					
RE	4 <i>c</i>	0.4443(4)	0.25	-0.0127(6)	0.0048(4)
Al	4 <i>b</i>	0	0.5	0	0.0048(7)
O1	4 <i>c</i>	0.0234(1)	0.25	0.0873(1)	0.0065(1)
O2	8 <i>d</i>	0.2042(7)	0.4541(6)	0.7021(8)	0.0057(9)
B (Y,Ho,Dy,Tb,Gd)AlO ₃					
RE	4 <i>c</i>	0.4531(4)	0.25	-0.0101(6)	0.0051(3)
Al	4 <i>b</i>	0	0.5	0	0.0039(6)
O1	4 <i>c</i>	0.0183(9)	0.25	0.0786(1)	0.0062(1)
O2	8 <i>d</i>	0.2082(6)	0.4575(5)	0.7082(6)	0.0059(8)

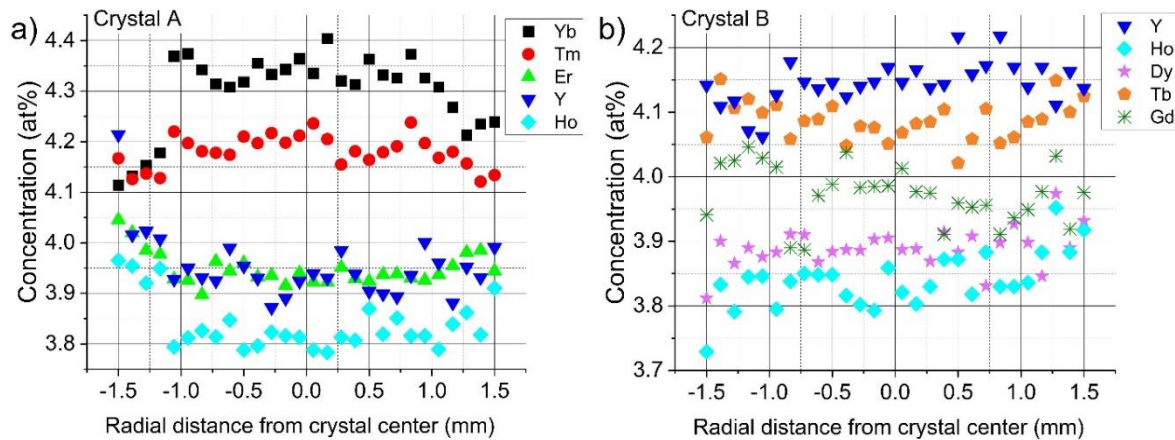


Figure 7.5 - Radial concentration profiles obtained with EPMA for crystals a) A (Yb,Tm,Er,Y,Ho)AlO₃ and b) B (Y,Ho,Dy,Tb,Gd)AlO₃. The nominal concentration of each RE is 4 at%.

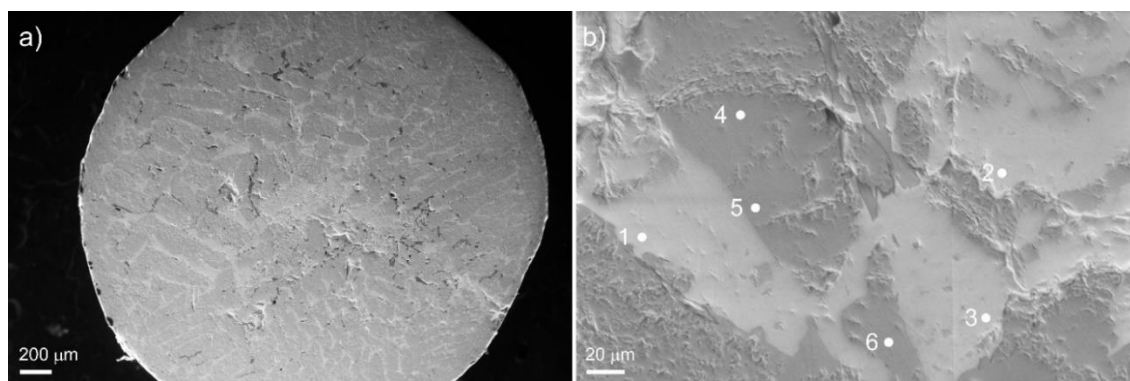


Figure 7.6 – SEM images of a cross-sectional sample from crystal G (Lu,Nd,Pr,Ce,La)AlO₃ using low (a) and high (b) magnification. The elemental composition was analyzed via EDS for the points identified with numbers in (b); EDS results are presented in Table 7.6.

assess the elemental composition of both the lighter areas and the darker matrix, EDS data were collected from the six points shown in Figure 7.6.b and are presented in Table 7.6. The lighter areas (points 1-3) are Lu-rich and are likely to have the orthorhombic structure that is typical of LuAlO_3 (Table 7.1) and was observed in crystal G (Table 7.3). The darker matrix (points 4-6) has a composition that is closer to stoichiometric but is also slightly rich in Lu; the matrix is likely to have the primary rhombohedral phase observed in crystal F (Table 7.3). Although Al-rich inclusions have been previously reported for LaAlO_3 mPD crystals [235], here the general ratio of RE to Al concentrations is close to stoichiometric for all points assessed. This indicates no significant deviation from the nominal REAlO_3 perovskite stoichiometry.

Conclusion

High-entropy REAlO_3 single crystals can be grown via directional solidification and phase formation depends on the composition. Here we reported the practical aspect of growing five-component equiatomic REAlO_3 via the micro-pulling-down method and determined the effects of composition on phase formation. Crystals containing only REs with similar ionic radii and that form orthorhombic single-RE REAlO_3 are a single orthorhombic phase. On the other hand, crystals containing a combination of REs with dissimilar ionic radii or that form an orthorhombic, rhombohedral, and tetragonal single-RE REAlO_3 are a mixture of phases. In single crystal samples, there is no evidence of preferential incorporation of any of the REs into the crystal. In multiphase crystals, the secondary phase is concentrated in the center of the crystal with a branching structure closer to the outer edge.

Demonstrations of the crystal growth of high-entropy oxides encourage the exploration of potential functional properties in highly complex single crystals. The findings reported here may be leveraged for future studies on compositionally complex perovskite crystals. High-entropy versions of the traditional host crystals YAlO_3 and LuAlO_3 may reveal attractive luminescence properties for scintillation and lasing applications. To develop such materials, future efforts should focus on compositions containing only REs with similar ionic radii and that form orthorhombic single-RE REAlO_3 so that single-phase crystals can be produced with high optical quality.

Table 7.6 - Elemental composition of crystal F (Lu,Nd,Pr,Ce,La)AlO₃ for areas 1-6 shown in the SEM image in Figure 7.6.b.

EDS elemental composition (at%), error < 0.001 at%									
Area	Points from Figure 5.b	Lu	Nd	Pr	Ce	La	Al	O	Stoichiometry
<i>Nominal composition</i>		<i>4</i>	<i>4</i>	<i>4</i>	<i>4</i>	<i>4</i>	<i>20</i>	<i>60</i>	<i>RE_{1.0}Al_{1.1}O_{10.1}</i>
Lighter area	1	20.2	2.1	2.4	2.6	2.6	31.4	38.7	RE _{1.0} Al _{1.1} O _{10.1}
	2	20.1	1.7	1.9	2.0	1.8	33.9	38.6	RE _{1.0} Al _{1.2} O _{10.1}
	3	20.1	1.9	2.1	2.2	2.3	33.0	38.4	RE _{1.0} Al _{1.2} O _{10.4}
Darker area	4	6.5	4.4	5.5	6.2	4.2	33.7	39.5	RE _{1.0} Al _{1.3} O _{10.3}
	5	6.1	4.5	5.3	6.1	6.4	32.7	38.9	RE _{1.0} Al _{1.2} O _{10.6}
	6	6.9	4.3	5.0	5.8	6.0	32.6	39.4	RE _{1.0} Al _{1.2} O _{10.4}

**CHAPTER EIGHT:
CRYSTAL GROWTH AND PHASE FORMATION OF HIGH-
ENTROPY MONOCLINIC ALUMINATES**

A version of this chapter is in preparation for publication in a peer-reviewed journal by Matheus Pianassola and colleagues:

M. Pianassola, M. Loveday, C. Melcher, and M. Zhuravleva, "Crystal growth and phase formation of high-entropy rare-earth monoclinic aluminates," In preparation.

Abstract

For the first time, high-entropy rare-earth monoclinic aluminate crystals were grown via directional solidification. Five high-entropy compositions were formulated with a general formula $\text{RE}_4\text{Al}_2\text{O}_9$, where RE is an equiatomic mixture of five rare-earth elements. To study the effects of rare-earth average ionic radius on phase formation, five combinations of rare-earth elements were formulated based on their ionic radii. The rare-earth elements included were Lu, Yb, Er, Y, Ho, Dy, Tb, Gd, Eu, Sm, Nd, and La. Powder X-ray diffraction and Rietveld structure refinement indicated that all crystals were a single monoclinic phase and the average ionic radius does not affect phase purity. The refined lattice parameters increase consistently with the average ionic radius. Electron probe microanalysis reveals Al-rich inclusions on the surface of the crystals. Crystals containing Tb had dark surface features that could be seen by the naked eye. After reducing annealing, a lighter color was observed for these crystals. This indicates that the dark features may originate from Tb^{4+} , whose oxides have a characteristic dark color.

Introduction

Rare-earth (RE) aluminate single crystals have been extensively investigated for luminescence applications [86], [223]. In general, three compounds are formed in the $\text{RE}_2\text{O}_3\text{-Al}_2\text{O}_3$ systems. Garnets, perovskites, and monoclinic aluminates are formed with the general formula $\text{RE}_3\text{Al}_5\text{O}_{12}$, REAlO_3 , and $\text{RE}_4\text{Al}_2\text{O}_9$, respectively [73]. Among those three compounds, garnet and perovskite aluminates such as $\text{Lu}_3\text{Al}_5\text{O}_{12}$ and YAlO_3 have been commercialized as host crystals for scintillation and laser applications [86], [87]. The exploration and practical application of monoclinic aluminate crystals remain relatively limited. All REs and Y form thermodynamically stable $\text{RE}_4\text{Al}_2\text{O}_9$ (space group $\text{P2}_1/\text{c}$), except for Nd, Pr, Ce, and La [73].

A high-temperature phase transition hinders the growth of monoclinic aluminate single crystals via directional solidification. Differential calorimetry studies revealed that single-RE monoclinic aluminates containing Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, or Y undergo a lattice expansion upon cooling in the temperature range of 1000-1400°C [81], [82]. Due to the lattice strain related to the phase transition, crystals grown by directional solidification become polycrystalline at room temperature. Since the growth of high optical quality crystals via directional solidification is not practical, the functional and fundamental

properties of such single crystals are not widely investigated.

Recent reports have focused on the luminescent and thermal properties of polycrystalline monoclinic aluminates. A few functional properties investigated include scintillation [236], [237], lasing [238], phosphorescence [239], [240], down-conversion of the solar spectrum [241], and thermal environmental barrier [242]. These properties were evaluated using ceramic or powder samples produced either via ceramic synthesis routes or directional solidification.

The effects of the high-entropy compositional approach on the optical quality of monoclinic aluminate crystals have not yet been evaluated. Such a compositional approach is inspired by the high-entropy alloys [42] and consists of admixing five or more cations in equiatomic amounts to fractionally occupy cation sublattices. An entropy-driven phase stabilization has been reported for this type of complex oxide and synergistic effects on functional properties have been observed [40], [53]. To the best of our knowledge, only one high-entropy monoclinic aluminate has been reported. A (Nd,Sm,Eu,Y,Yb)₄Al₂O₉ polycrystalline ceramic (commas represent equiatomic amounts) was evaluated for environmental barrier applications [80].

The high-entropy compositional approach could be instrumental to prevent the phase transition in monoclinic aluminates. A suppression of polymorphic transitions in RE sesquioxides has been previously attributed to the high-entropy compositional approach [57], [162]. This inspires the investigation of the crystal growth of high-entropy monoclinic aluminates as the typical lattice expansion upon cooling may be suppressed in such complex compounds.

In this work, we evaluate the phase formation and optical quality of monoclinic aluminates containing five REs, including Lu, Yb, Er, Y, Ho, Dy, Tb, Gd, Eu, Sm, Nd, and La. Our composition formulation strategy uses the rare-earth average ionic radius as a parameter to evaluate its effects on phase formation and optical quality. Crystals are grown via directional solidification via the micro-pulling-down method, which is ideal for materials development due to the small amount of precursor material necessary (~ 1 g) and the fast growth rates that can be achieved (up to 20 mm/min) [37].

Methods

Composition formulation

To study the potential effect of the average ionic radius (AIR) on the phase formation of high-entropy RE₄Al₂O₉, the ionic radius of the RE³⁺ cations was used as a composition formulation parameter. Table 8.1 is a list of the REs included in the compositions and their respective ionic radius for coordination number VI. Five high-entropy RE₄Al₂O₉ compounds were formulated containing five REs in

Table 8.1 - List of rare-earth cations and their respective ionic radius [124].

RE³⁺ cation	RE³⁺ ionic radius for CN VI (Å)
Lu ³⁺	0.848
Yb ³⁺	0.858
Er ³⁺	0.881
Y ³⁺	0.892
Ho ³⁺	0.894
Dy ³⁺	0.908
Tb ³⁺	0.923
Gd ³⁺	0.938
Eu ³⁺	0.950
Sm ³⁺	0.964
Nd ³⁺	0.995
La ³⁺	1.061

equiatomic amounts. The five compositions, their respective ID and average ionic radius (AIR) are listed in Table 8.2. The AIR values increase consistently from composition 1 to 5. Composition 1 has only small REs (Lu-Ho); composition 2 has a mixture of small and medium REs (Tb and Gd); composition 3 has a mixture of small, medium, and large REs (Sm and Nd); compositions 4 and 5 have a mixture of medium and large REs.

Crystal growth

The micro-pulling-down method [37] was used to grow cylindrical $\varnothing$ 3 mm crystals. A KDN Dai-Ichi Kiden growth station was used with an RF generator model TR-02001 operated at 26 kVA. A $\varnothing$ 16 mm iridium crucible with a $\varnothing$ 3 mm die and a $\varnothing$ 0.5 mm capillary channel was used as a melt reservoir. The starting materials were Lu_2O_3 , Yb_2O_3 , Er_2O_3 , Y_2O_3 , Ho_2O_3 , Dy_2O_3 , Tb_2O_3 , Gd_2O_3 , Eu_2O_3 , Sm_2O_3 , Nd_2O_3 , La_2O_3 , and Al_2O_3 powders of at least 99.99% purity. The powders were dried at 800°C for 8 h in air, mixed in stoichiometric ratios, and placed in the crucible. The crucible was inductively heated to melt the powders. An iridium pin was used as a seed to initiate the growth by touching the bottom outlet of the crucible capillary channel and pulling down the melt. All crystals were grown with a pulling rate of 0.10 mm/min. Details about the mPD growth method and the crystal growth setup used here can be found in a previous publication [39].

Powder X-ray diffraction

Phase analysis was performed by acquiring room-temperature powder X-ray diffraction (XRD) patterns for each crystal. The middle section of each crystal was cut and ground in a mortar. A Panalytical Empyrean diffractometer was used to collect diffraction patterns in the Bragg-Brentano geometry using a Cu K α X-ray source at 45 kV and 40 mA. The patterns were used to determine the phase composition and lattice parameters via Rietveld structure refinements, which were performed with the General Structure Analysis System II software (GSASII).

Annealing experiments

To study the effects of reducing annealing on surface features, crystals were annealed in a flowing atmosphere of 2% H_2 in bulk N_2 at 1300°C for 8 h. Subsequently, the same samples were subjected to oxidizing annealing in air at 1300°C for 8 h. A tubular CM High Temperature Furnace model 1630-12 was used for these experiments.

Electron probe microanalysis

To evaluate the microstructure and composition of the crystals, small fragments ($<1 \text{ mm}^3$) of the crystals were embedded in epoxy and polished. The samples were then subjected to imaging and composition analysis via electron

Table 8.2 - List of high-entropy RE₄Al₂O₉ compositions, their ID, and respective average ionic radius (AIR) [124].

ID	Composition	AIR (Å)
1	(Lu,Yb,Er,Y,Ho) ₄ Al ₂ O ₉	0.845
2	(Lu,Yb,Y,Tb,Gd) ₄ Al ₂ O ₉	0.892
3	(Yb,Y,Gd,Sm,Nd) ₄ Al ₂ O ₉	0.929
4	(Dy,Tb,Gd,Eu,Sm) ₄ Al ₂ O ₉	0.937
5	(Er,Dy,Gd,Sm,La) ₄ Al ₂ O ₉	0.950

probe microanalysis (EPMA) with a CAMECA SX100 Electron Microprobe operated at 15 kV and 30 nA. The instrument is equipped with high-speed backscattered electron (BSE) detectors and four wavelength-dispersive spectrometers (WDS). The probe point size was 1 μm , and the excitation area diameter was in the 2–3 μm range.

Results and discussion

Grown crystals

All crystals were grown with a good diameter control. A photo of the crystals is in Figure 8.1. Crystals 1 and 4 are yellow due to Ho^{3+} , Dy^{3+} , and Sm^{3+} . Crystal 2 was expected to be white, but dark brown features are seen on its surface, which also appears on crystal 4. Such features will be discussed later in this Chapter. Crystal 3 is purple due to Nd^{3+} . Crystal 5 has a salmon color due to pink Er^{3+} and yellow Sm^{3+} cations.

All crystals were transparent during growth and polycrystalline after cooling to room temperature. A picture obtained during the growth of crystal 2 is seen in Figure 8.2. The darker central region in the growing crystal indicates translucency as the camera captures the dark background through the crystal. Similar indications of translucency were observed during the growth of all crystals. Cracks in crystal 2 are indicated by white ovals in Figure 8.2. All five crystals likely undergo the typical lattice expansion upon cooling since they were transparent during growth but polycrystalline at room temperature (Figure 8.1). Such lattice expansion would result in residual stresses in the crystals, which would lead to cracking and polycrystallinity.

Crystal structure via powder X-ray diffraction

Crystals 1-5 are a single monoclinic phase (space group $P2_1/c$) according to powder XRD and Rietveld structure refinement, and their AIR does not affect phase formation. Diffraction patterns of the five crystals are seen in Figure 8.3. Reference patterns of $\text{Lu}_4\text{Al}_2\text{O}_9$ and $\text{Sm}_4\text{Al}_2\text{O}_9$ are also included to compare the reflection peaks of single-RE $\text{RE}_4\text{Al}_2\text{O}_9$ formed by smaller (Lu^{3+}) and larger RE^{3+} (Sm^{3+}). The reference patterns indicate that the diffraction peaks shift to smaller two-theta values for larger REs due to an enlargement of the unit cell. Additionally, the relative position of the peaks also varies RE^{3+} size. As indicated in Figure 8.3, around 30° , the order of the reflection peaks for $\text{Lu}_4\text{Al}_2\text{O}_9$ going from small to large two-theta is (22-1), (023), (032), (211), and (-213). For $\text{Sm}_4\text{Al}_2\text{O}_9$ the order of these peaks is (22-1), (211), (032), (023), and (-213). The relative distance between these peaks also varies. This explains why the collected patterns look different around 30° as the AIR increases from crystal 1-5.

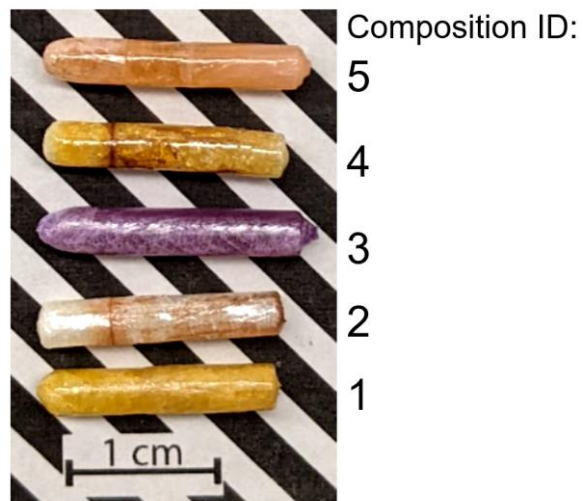


Figure 8.1 - Photo of the high-entropy $\text{RE}_4\text{Al}_2\text{O}_9$ crystals. Composition ID is indicated in the figure and refer to the composition in Table 8.2. Crystals are 3 mm in diameter and were grown with good shape control. All crystals were polycrystalline at room temperature.

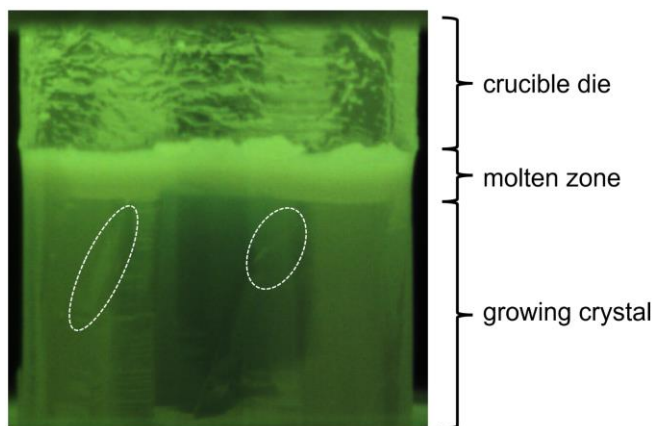


Figure 8.2 - Photo of the growing crystal 2 $(\text{Lu,Yb,Y,Tb,Gd})_4\text{Al}_2\text{O}_9$ obtained during the growth. The iridium crucible die, molten zone, and growing crystal are indicated in the figure. In the growing crystal, cracks are indicated by white ovals. The darker central region in the crystal indicates translucency as the camera captures the darker background through the crystal.

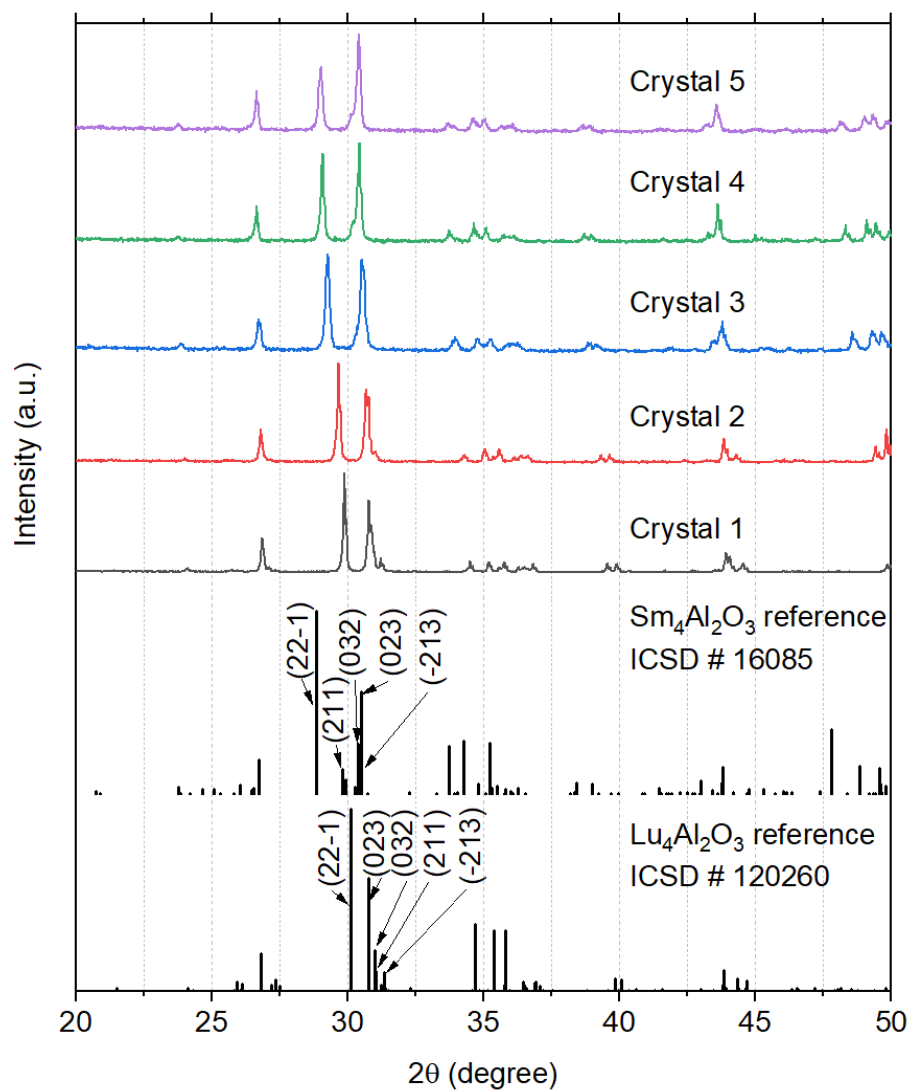


Figure 8.3 - Powder XRD patterns of crystals 1-5 and reference patterns of Lu₄Al₂O₉ and Sm₄Al₂O₉ (space group $P2_1/c$). Crystal ID and compositions are seen in Table 8.2.

Rietveld refinement results indicate that the lattice parameter values of crystals 1-5 increase consistently with their AIR. As seen in Figure 8.4, the three lattice parameters (a , b , and c) increase close to linearly with increasing lattice parameters from crystal 1 to 5. The β angle between the a - and c -axis also increases with the AIR, as shown in Figure 8.4. Consequently, the unit cell volume also increases, and the values obtained from the refinement are shown in Figure 8.4. This consistent variation of lattice parameters with AIR has been previously observed in high-entropy garnet aluminate crystals grown by the micro-pulling-down method [222].

Dark surface features in crystals 2 and 4

To determine the nature of the dark surface features in crystals 2 and 4, EPMA data were collected and indicated aluminum-rich inclusions on the outer surface of crystal 2. In general, the composition characterization of the crystals was challenging due to their brittleness, which hindered appropriate sample preparation such as cutting and polishing. A back-scattered electron image of a surface fragment of crystal 2 is shown in Figure 8.5. Dark inclusions are seen in a brighter matrix; the measured composition of points 1-4 indicated in Figure 8.5 is presented in Table 8.3. The dark inclusions (points 3 and 4) are richer in aluminum compared to the matrix (points 1 and 2). Similar Al-rich inclusions were previously seen on the surface of micro-pulling-down RE garnet aluminates [221], [222]. In back-scattered electron imaging, the higher the atomic number of the atoms probed, the brighter the image. This explains why the matrix in Figure 8.5 is brighter than the Al-rich inclusions since the concentration of REs (higher atomic numbers) is relatively higher in the matrix.

It is not clear whether the inclusions seen in Figure 8.5 correspond to the dark surface features of crystal 2. Aluminum-rich inclusions observed by the naked eye would not be dark. This is because Al_2O_3 is white and the mixture of the trivalent constituent REs in this composition would result in a light yellow color. Therefore, it is likely that the dark features on the crystal surface result from tetravalent REs such as Tb^{4+} , whose oxides are dark. In this case, such features would not be distinguishable in back-scattered electron imaging because the image contrast arises from gradients of atomic numbers [243], not oxidation states. Therefore, further investigation is needed to determine the nature of the dark surface features seen in crystals 2 and 4.

The dark surface features may be related to composition and the presence of Tb^{4+} . Both crystals 2 and 4 are the only ones containing Tb in their composition (see Table 8.2). Among all the REs included in this study (Table 8.1), only Tb commonly assumes the 4+ oxidation state, which leads to a characteristic dark color. To test this proposed explanation, fragments from the tail end of crystal 2 and the seed end of crystal 4 were subjected to reducing annealing to check for color changes. As shown in Figure 8.6, a lighter color is seen on the surface of the

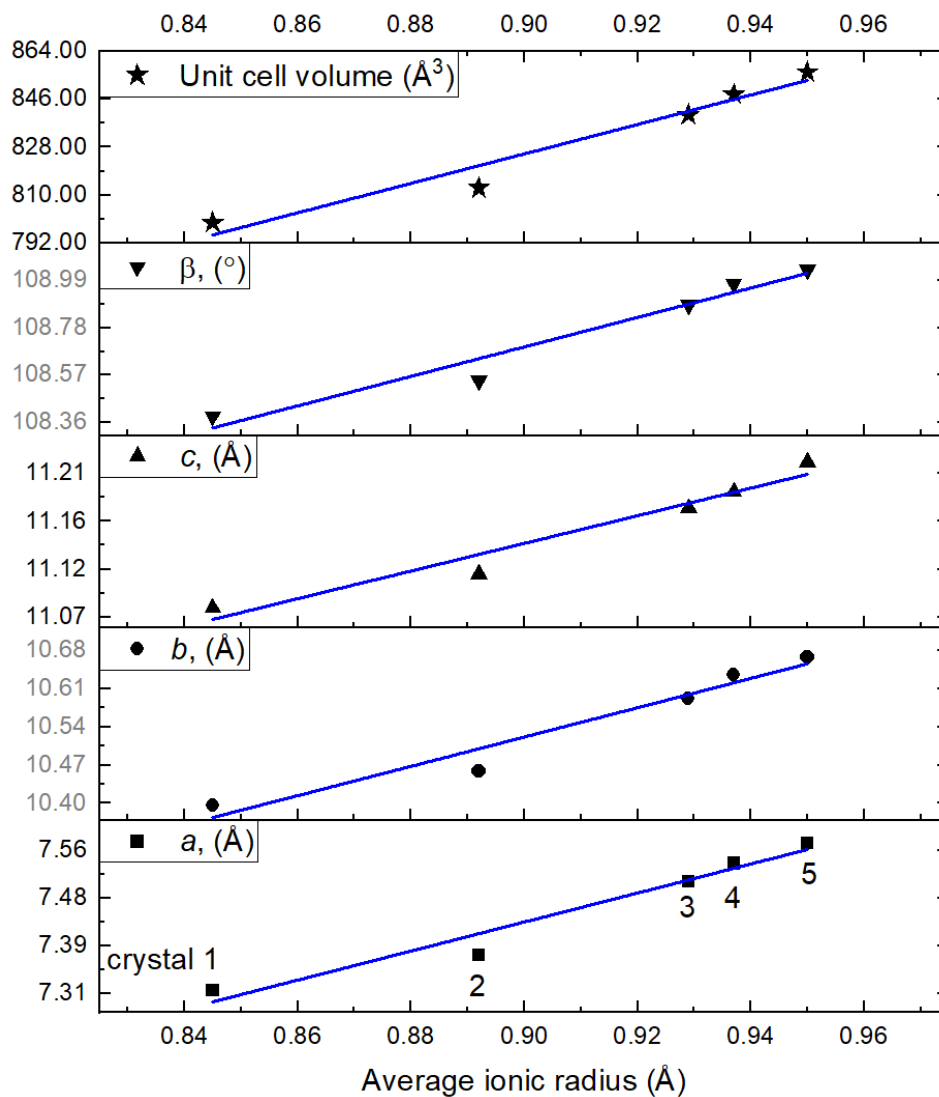


Figure 8.4 - Lattice parameters of crystals 1-5 obtained with powder XRD and Rietveld refinement. The crystal ID at the bottom graph applies for all graphs and compositions are listed in Table 8.2. Linear regression lines are shown for each data set ($R^2=94\%$ for all regressions).

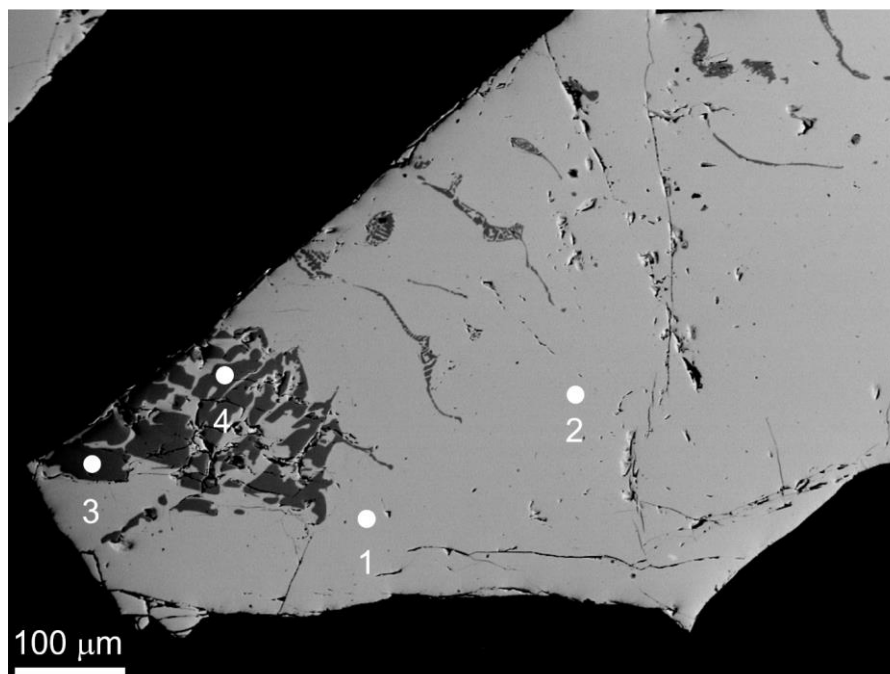


Figure 8.5 - Micrograph of crystal 2 obtained via back-scattered electron imaging using an EPMA instrument. The chemical composition of points 1-4 is presented in Table 8.3.

Table 8.3 - EPMA elemental composition data for crystal 2. Points 1-4 correspond to the areas indicated in Figure 8.5.

EPMA elemental composition (at%), error < 0.001 at%									
Area	Points from Figure 8.5	Lu	Yb	Y	Tb	Gd	Al	O	Stoichiometry
<i>Nominal composition</i>									
		5.3	5.3	5.3	5.3	5.3	13.3	60	$RE_4Al_2O_9$
Lighter	1	5.8	6.5	5.3	5.9	5.1	11.3	60.1	$RE_{4.1}Al_{1.6}O_{8.6}$
matrix	2	5.9	6.4	5.0	5.8	5.8	11.0	60.1	$RE_{4.1}Al_{1.6}O_{8.6}$
Darker	3	3.5	4.0	3.4	5.0	5.4	18.8	59.9	$RE_{3.0}Al_{2.7}O_{8.6}$
areas	4	3.0	3.6	3.3	5.3	5.9	18.9	60.0	$RE_{3.0}Al_{2.7}O_{8.6}$

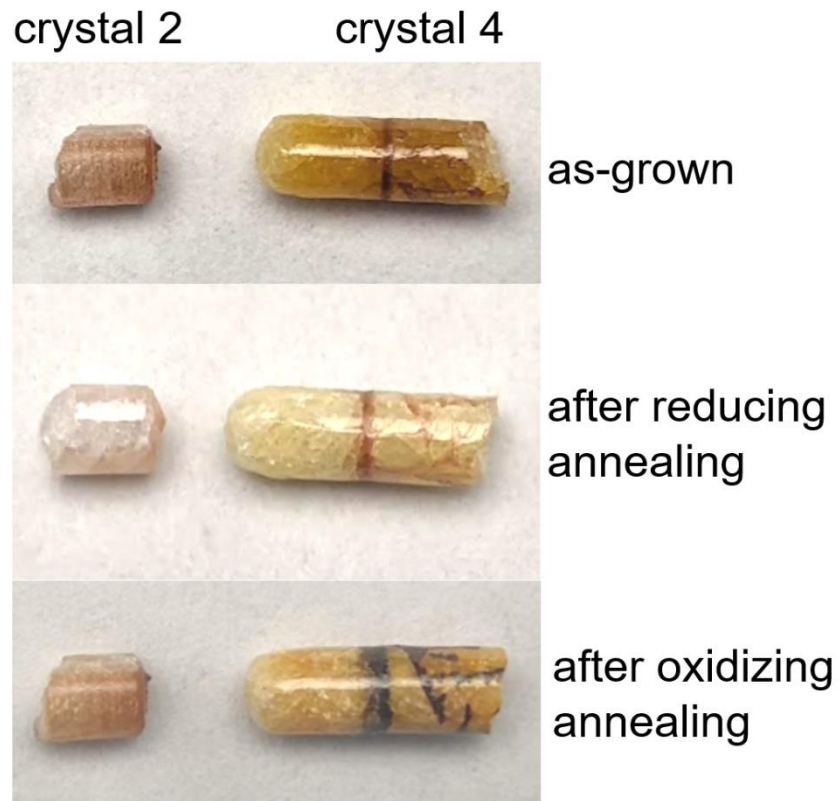


Figure 8.6 - Samples from crystals 2 and 4 in the as-grown condition and after reducing and subsequent oxidizing annealing. The sample from crystal 2 is from the tail end, while the sample from crystal 4 is from the seed end. Crystals are 3 mm in diameter.

crystals after the reducing annealing. The same samples were subsequently subjected to oxidizing annealing. The surface features became darker after the oxidizing annealing. This supports the proposed explanation for the nature of the dark surface features as a fraction of the tetravalent cations may have been reduced during the first annealing leading to lighter surface color. A fraction of the Tb^{3+} ions may have oxidized during the second annealing, leading to darker surface features.

Tetravalent Tb may have originated from the raw materials or the oxidation of Tb^{3+} during growth. The source of Tb in this study is Tb_2O_3 , in which Tb is nominally in the 3+ oxidation state; however, the raw powder may have contained some amount of Tb^{4+} as a result of the spontaneous oxidation of the powder stored in air. Additionally, Tb^{3+} may have been converted into Tb^{4+} during growth although the growth atmosphere is inert. This is because crystals 2 and 4 contain Yb and Eu, respectively, which can assume the 2+ oxidation state. Therefore, redox reactions could have happened during the growth. These reactions would be $\text{Tb}^{3+} \rightarrow \text{Tb}^{4+} + \text{e}^-$ and $\text{Yb}^{3+} + \text{e}^- \rightarrow \text{Yb}^{2+}$ or $\text{Eu}^{3+} + \text{e}^- \rightarrow \text{Eu}^{2+}$. Such redox reactions have been previously observed in oxide materials [244], [245].

Conclusion

For the first time, high-entropy monoclinic aluminate crystals were grown via directional solidification. Compositions containing a combination of five REs in equiatomic amounts were formulated to determine the effects of AIR on phase formation. All the grown crystals successfully formed a single monoclinic phase. All crystals were transparent during growth and polycrystalline at room temperature, which is likely due to a lattice expansion upon cooling that is typical of one-RE monoclinic aluminates. Dark surface features in Tb-containing crystals may be related to the presence of Tb^{4+} ions in the compounds.

Future investigation into high-entropy monoclinic aluminate crystals may reveal a combination of REs that may suppress the lattice expansion upon cooling from the melt. In such studies, the formulation of compositions with REs that generally present the tetravalent oxidation state could be avoided to prevent the formation of dark surface features. Additionally, this work inspires the investigation of functional properties in high-entropy polycrystalline samples since single-phase compounds were successfully produced with a variety of RE combinations.

**CHAPTER NINE :
CRYSTAL GROWTH AND PHASE COMPOSITION OF
RARE-EARTH PEROVSKITES**

A version of this chapter is in preparation for publication in a peer-reviewed journal by Matheus Pianassola and colleagues:

M. Pianassola, C. Melcher, and M. Zhuravleva, "Crystal growth and phase composition of $\text{La}(\text{Lu}, \text{Yb}, \text{Tm}, \text{Er}, \text{Y})\text{O}_3$ and $(\text{Sm}, \text{Nd}, \text{Pr}, \text{Ce}, \text{La})\text{LuO}_3$," In preparation.

Abstract

The micro-pulling-down growth of two high-entropy rare-earth perovskites of general formula $\text{RE}'\text{RE}''\text{O}_3$ was demonstrated to advance the field of crystal growth of complex oxides. The compositional disorder was introduced in each of the two cation sublattices by formulating two compositions, the $(\text{Sm}, \text{Nd}, \text{Pr}, \text{Ce}, \text{La})\text{LuO}_3$ crystal and the $\text{La}(\text{Lu}, \text{Yb}, \text{Tm}, \text{Er}, \text{Y})\text{O}_3$ crystal. The crystals were grown with good diameter control; the former crystal was opaque and the latter was transparent. Powder X-ray diffraction indicates that the former crystal is a mixture of orthorhombic perovskite and cubic fluorite, while the latter crystal is a primary orthorhombic perovskite phase with an unknown secondary phase. Lanthanum-rich inclusions were observed in the latter crystal via scanning electron microscopy and energy dispersive spectroscopy. There was no significant elemental segregation in the latter crystal according to electron probe microanalysis results. Three $\text{La}(\text{Lu}, \text{Yb}, \text{Tm}, \text{Er}, \text{Y})\text{O}_3$ crystals were grown with 0.5 at% of La being substituted with either Ce^{3+} , Pr^{3+} , or Tb^{3+} . These doped crystals have no light emission in radioluminescence in the as-grown condition as well as after oxidizing and reducing annealing.

Introduction

Rare-earth-based oxides are attractive host compounds for luminescent materials used in lasing and scintillation applications. Such oxides can easily accommodate rare-earth (RE) luminescent activators such as Ce^{3+} and Nd^{3+} since the RE cations have similar ionic radii [124]. A few compositional systems are vastly explored and commercially available including RE aluminates ($\text{RE}_3\text{Al}_5\text{O}_{12}$ [86] and REAlO_3 [22]) and RE silicates (RE_2SiO_5 [246]). Although not widely investigated, RE perovskites ($\text{RE}'\text{RE}''\text{O}_3$) have attractive properties as host compounds for scintillators. Their intrinsic high density and effective atomic number result in high stopping power for ionizing radiation, which increases the radiation detection efficiency of scintillators [114], [117]. In the literature, RE perovskites are also referred to as "double oxides" [111] or "interlanthanide perovskites" [112].

Rare-earth perovskites are formed by mixing two RE sesquioxides ($\text{RE}'_2\text{O}_3$ and $\text{RE}''_2\text{O}_3$) in equal amounts to form a $\text{RE}'\text{RE}''\text{O}_3$ stoichiometry. If the difference in RE ionic radius is larger than 0.20 Å, a perovskite structure (space group $Pnma$) is thermodynamically favorable [110]. In the general perovskite formula $\text{RE}'\text{RE}''\text{O}_3$, RE'^{3+} has a larger ionic radius than RE''^{3+} . A phase diagram of the La_2O_3 - Yb_2O_3 is

shown in Figure 9.1, where the perovskite phase (Per) is represented by a small area in the center of the diagram. A few RE perovskites have been reported, including LaRO_3 , where $R = \text{Lu, Yb, Tm, Er, Y, Ho, or Dy}$; CeXO_3 , where $X = \text{Lu, Yb, or Tm}$; PrZO_3 , where $Z = \text{Lu or Yb}$; and NdLuO_3 [112]–[114].

The incongruent melting of most of the RE perovskites hinders the growth of high-optical-quality crystals via directional solidification. As shown in Figure 9.1 for LaYO_3 , a RE perovskite first solidifies as a cubic X-type phase upon cooling from the melt. With decreasing temperature, these compounds then transform into the perovskite structure [115]. Such phase transition leads to the cracking of a crystal grown via directional solidification, which compromises its optical quality. Crystals with excellent optical quality are preferred for scintillation and lasing applications in which light collection is crucial.

The high-entropy compositional concept may be a strategy to suppress phase transitions in RE perovskites. This compositional concept consists in mixing five or more elements to fractionally occupy a cation sublattice [53]. The stabilization of a single phase and the suppression of polymorphic transitions have been previously reported for RE sesquioxides [57], [162]. Additionally, exceptional functional properties have been discovered in high-entropy oxides [40]. Such a combination of structural stability and unexpected functional properties inspires the application of the high-entropy compositional concept in RE perovskites.

The crystal growth from the melt and scintillation properties of RE perovskites have not been widely studied. A few publications include the growth of LaLuO_3 and similar compounds via the Czochralski [111], [113], [114], and flux growth methods [116]. Additionally, only a few reports focus on the luminescence properties of RE-doped RE perovskites and no scintillation characterization has been reported to the best of our knowledge [247], [248].

In this work, we demonstrate the crystal growth of high-entropy RE perovskites and evaluate their phase formation and scintillation properties. Concerning the general formula $\text{RE}'\text{RE}''\text{O}_3$, the high-entropy compositional concept was applied to both the RE' and the RE'' cation sublattices, and two compositions were formulated, $(\text{Sm}, \text{Nd}, \text{Pr}, \text{Ce}, \text{La})\text{LuO}_3$ and $\text{La}(\text{Lu}, \text{Yb}, \text{Tm}, \text{Er}, \text{Y})\text{O}_3$. Commas represent equiatomic amounts. Yttrium is referred to as a RE element for simplicity. Crystals were grown via the micro-pulling-down (mPD) method, which is an ideal technique for materials development since miniature crystals can be produced with a small quantity of expensive raw materials (~ 1 g). Additionally, fast growth rates (up to 20 mm/min) allow for rapid composition screening studies [37].

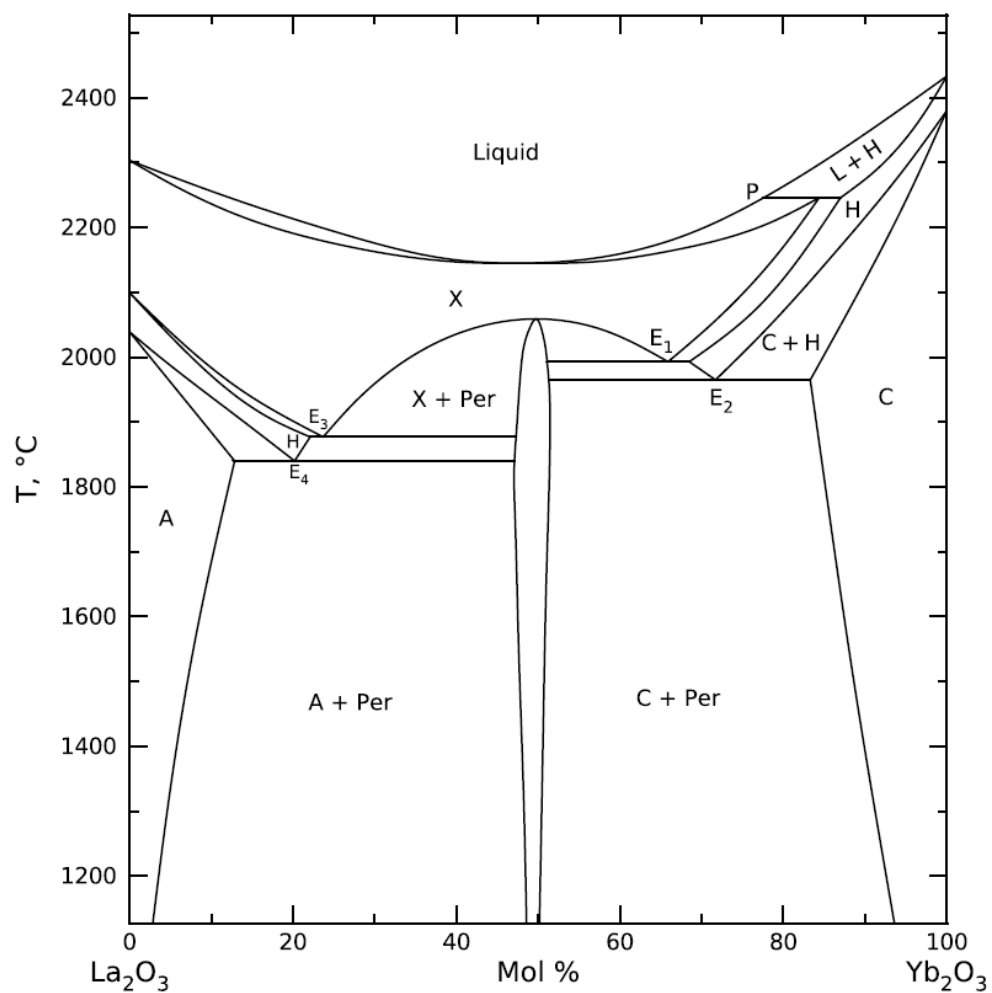


Figure 9.1 - Phase diagram of the La_2O_3 - Yb_2O_3 system. The LaYbO_3 perovskite phase (Per) is shown in the center of the diagram [115].

Methods

Composition formulation

To evaluate the phase formation in high-entropy RE'RE"O₃ with a compositional disorder in each of the RE sublattices, two compositions were formulated, (Sm,Nd,Pr,Ce,La)LuO₃ and La(Lu,Yb,Tm,Er,Y)O₃. Both compositions meet the criterion of difference in ionic radii between RE' and RE" of at least 0.2 Å. The average ionic radius of the disordered sublattices was taken into consideration to meet this criterion. Commas indicate equiatomic amounts. Since the difference in ionic radii between RE' and RE" is crucial to the formation of a perovskite structure, the five largest RE³⁺ cations were selected to occupy RE' sublattice in (Sm,Nd,Pr,Ce,La)LuO₃ while the smallest RE (Lu³⁺) occupies the RE" site. For the same reason, the largest RE³⁺ (La³⁺) was selected to occupy the RE' site in La(Lu,Yb,Tm,Er,Y)O₃ while the five smallest RE³⁺ cations were selected to occupy the RE" sublattice. Therefore, the ionic radius of the trivalent RE³⁺ cations was the parameter for composition formulation [124]. To assess the scintillation properties of Ce-, Pr-, and Tb-doped La(Lu,Yb,Tm,Er,Y)O₃, La³⁺ cations were substituted with each dopant at 0.5 at%, which resulted in three doped compositions, La(Lu,Yb,Tm,Er,Y)O₃:Ce, La(Lu,Yb,Tm,Er,Y)O₃:Pr, and La(Lu,Yb,Tm,Er,Y)O₃:Tb. These three dopants (Ce³⁺, Pr³⁺, and Tb³⁺) were selected because they are efficient luminescence activators.

Crystal growth

The mPD method was used to grow cylindrical Ø 3 mm crystals. A KDN Dai-Ichi Kiden furnace with an RF generator model TR-02001 operated at 26 kVA was used. The starting powders were Lu₂O₃, Yb₂O₃, Tm₂O₃, Er₂O₃, Y₂O₃, Sm₂O₃, Nd₂O₃, Pr₂O₃, CeO₂, and La₂O₃ of at least 99.99% purity. After drying at 800°C for 8 h in air, the powders were mixed in stoichiometric ratios. The mixtures were placed in a Ø16 mm iridium-rhenium (90%-10%) crucible with a Ø3 mm die and a Ø0.5 mm capillary channel. The crucible was inductively heated at its maximum operating temperature to melt the powders and an iridium pin was used to initiate the growth. All crystals were grown with a pulling rate of 0.10 mm/min. A previous publication includes a detailed description of the mPD growth method and the crystal growth setup used here [39].

Powder X-ray diffraction

The grown crystals were subjected to phase analysis by acquiring room-temperature powder X-ray diffraction (XRD) patterns. Crystals were ground in a mortar to obtain fine powders. Diffraction patterns were collected with a Panalytical Empyrean diffractometer in the Bragg-Brentano geometry using a Cu Kα X-ray source at 45 kV and 40 mA. Phase identification was performed using the HighScore XRD Analysis Software by Malvern Panalytical.

Scanning electron microscopy and energy dispersive spectroscopy

To evaluate the microstructure of the crystals, 1-mm thick cross-sectional samples were cut, polished, and imaged with a Zeiss EVO MA15 Scanning Electron Microscope (SEM). The elemental composition of the samples was analyzed with a Bruker xFlash 6130 Energy Dispersive X-Ray Spectrometer (EDS), which was mounted in the SEM sample chamber.

Electron Microprobe Analysis

A 1-mm thick cross-sectional sample of the $\text{La}(\text{Lu}, \text{Yb}, \text{Tm}, \text{Er}, \text{Y})\text{O}_3\text{:Ce}$ crystal was embedded in epoxy for the elemental composition analysis by electron probe microanalysis (EPMA) with a CAMECA SX100 Electron Microprobe. The instrument is equipped with high-speed backscattered electron (BSE) detectors and four wavelength-dispersive spectrometers (WDS). Images were obtained by detecting the backscattered electrons, and compositional information was acquired by detecting characteristic X-rays by WDS. The instrumental voltage and current were 15 kV and 30 nA, respectively. The probe point size was 1 μm , and the excitation area diameter was in the 2–3 μm range. A radial distribution profile was obtained by collecting data at 100 μm steps.

Radioluminescence measurements

The potential scintillation emission of the undoped and the Ce-, Pr-, and Tb-doped $\text{La}(\text{Lu}, \text{Yb}, \text{Tm}, \text{Er}, \text{Y})\text{O}_3$ crystals was analyzed via radioluminescence measurements. Samples from the doped and undoped crystals were cut and polished. The samples were 1-mm-thick cross-sections. Radioluminescence spectra were acquired in transmission mode in the range of 200 – 800 nm. A Cu target X-ray tube operated at 35 kV and 0.1 mA was used as the excitation source.

Annealing study

Samples of doped $\text{La}(\text{Lu}, \text{Yb}, \text{Tm}, \text{Er}, \text{Y})\text{O}_3$ crystals were annealed at 1200°C for 5 h in either air or 2% H_2 in bulk N_2 to study how annealing may affect the scintillation emission observed in radioluminescence.

Results

Grown crystals

Both the $(\text{Sm}, \text{Nd}, \text{Pr}, \text{Ce}, \text{La})\text{LuO}_3$ and $\text{La}(\text{Lu}, \text{Yb}, \text{Tm}, \text{Er}, \text{Y})\text{O}_3$ crystals could be grown with good diameter control and are shown in Figure 9.2. The dark color of the $(\text{Sm}, \text{Nd}, \text{Pr}, \text{Ce}, \text{La})\text{LuO}_3$ crystal likely originates from tetravalent Pr, since Pr_6O_{11} powder is black and is a mixture of Pr^{3+} and Pr^{4+} . Therefore, although the source of Pr was in the trivalent state in Pr_2O_3 , it is likely that Pr cations oxidize during the growth. This crystal fell from the seed after the growth and broke into

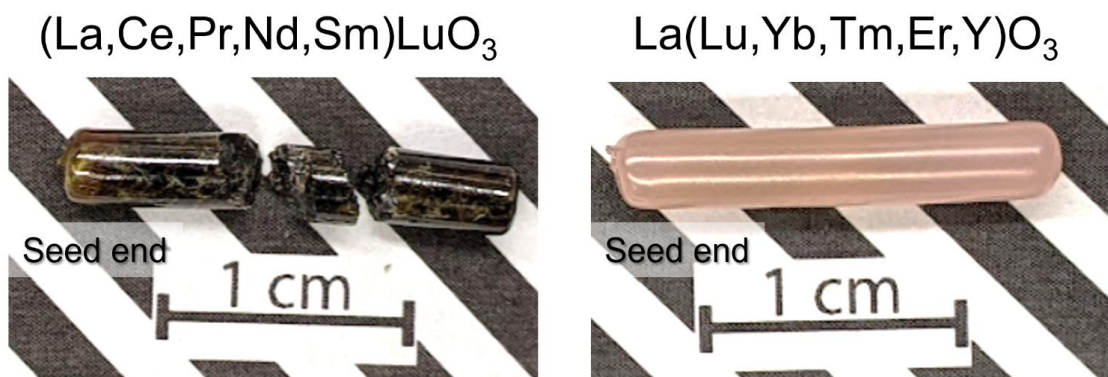


Figure 9.2 - Photos of the as-grown, undoped $(\text{Sm,Nd,Pr,Ce,La})\text{LuO}_3$ (left) and $\text{La}(\text{Lu,Yb,Tm,Er,Y})\text{O}_3$ (right) crystals.

three pieces. The light pinkish-orange color of $\text{La}(\text{Lu}, \text{Yb}, \text{Tm}, \text{Er}, \text{Y})\text{O}_3$ is likely from Er^{3+} since Er_2O_3 is pink.

The Ce-, Pr-, and Tb-doped $\text{La}(\text{Lu}, \text{Yb}, \text{Tm}, \text{Er}, \text{Y})\text{O}_3$ crystals were also grown with good diameter control as seen in Figure 9.3. The doped crystals are orange due to the mixture of pink from Er^{3+} and yellow/green from the trivalent dopants. The seed end of the crystals (left side in the photo) is polycrystalline while the tail end (right side in the photo) is transparent. Polished cross-sectional samples from the undoped and doped crystals are transparent as seen in Figure 9.4. Three sample conditions are shown in Figure 9.4, as-grown and after annealing in air (oxidizing atmosphere) or in 2% H_2 in bulk N_2 (reducing atmosphere). The Ce-doped sample becomes orange after reducing annealing due to the reduction of Ce^{4+} into Ce^{3+} . The Pr- and Tb-doped crystals become orange after oxidizing annealing due to the oxidation of both Pr^{3+} and Tb^{3+} into Pr^{4+} and Tb^{4+} , respectively. These tetravalent cations have a characteristic dark color, which may contribute to such color change.

Powder X-ray diffraction

A mixture of orthorhombic perovskite and cubic fluorite phases was identified for the $(\text{Sm}, \text{Nd}, \text{Pr}, \text{Ce}, \text{La})\text{LuO}_3$ crystal. A measured powder XRD pattern and reference patterns are seen in Figure 9.5.a. The orthorhombic perovskite phase is typical of RE perovskites and is expected for this crystal. The cubic fluorite structure is typical of oxides of tetravalent REs such as CeO_2 (ICSD # 24887) and Pr_6O_{11} (ICSD 28786). This is a further indication that Ce and Pr may be in their tetravalent oxidation state in this crystal. Therefore, including REs that can be oxidized to a 4+ state may be detrimental to the phase purity of high-entropy RE perovskites.

A primary orthorhombic perovskite phase was observed for the undoped and Ce-doped $\text{La}(\text{Lu}, \text{Yb}, \text{Tm}, \text{Er}, \text{Y})\text{O}_3$ crystals. A measured powder XRD pattern and a LaLuO_3 reference pattern are seen in Figure 9.5.b. Low-intensity peaks indicate an unknown secondary phase in both the doped and undoped crystals. Therefore, a perovskite phase is more effectively formed in the crystal with the compositional disorder in the RE" cation sublattice ($\text{La}(\text{Lu}, \text{Yb}, \text{Tm}, \text{Er}, \text{Y})\text{O}_3$) compared to the crystal with the disorder in the RE' sublattice ($(\text{Sm}, \text{Nd}, \text{Pr}, \text{Ce}, \text{La})\text{LuO}_3$). The absence of REs that can be oxidized to a tetravalent oxidation state in the former crystal is likely to have contributed to the formation of a primary perovskite phase.

Inclusions: microstructure and elemental composition

Lanthanum-rich inclusions were observed in the $\text{La}(\text{Lu}, \text{Yb}, \text{Tm}, \text{Er}, \text{Y})\text{O}_3$ crystal. This crystal was selected for SEM imaging and EDS compositional analysis because of its better optical quality and phase formation compared to

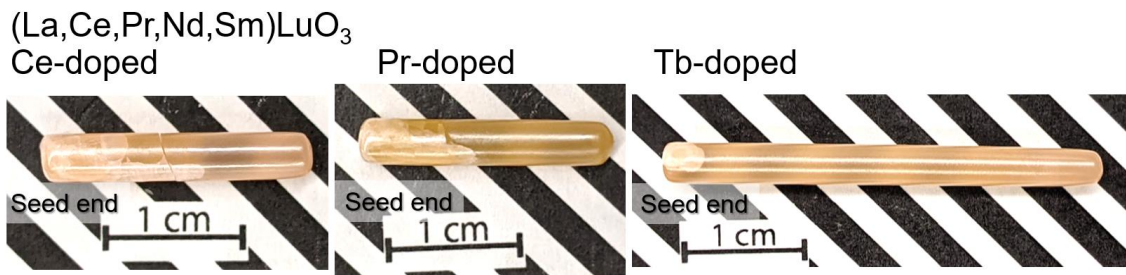


Figure 9.3 - La(Lu,Yb,Tm,Er,Y)O₃ crystals doped with Ce (left), Pr (center), and Tb (right). A longer Tb-doped sample was grown to obtain seeds for future growths.

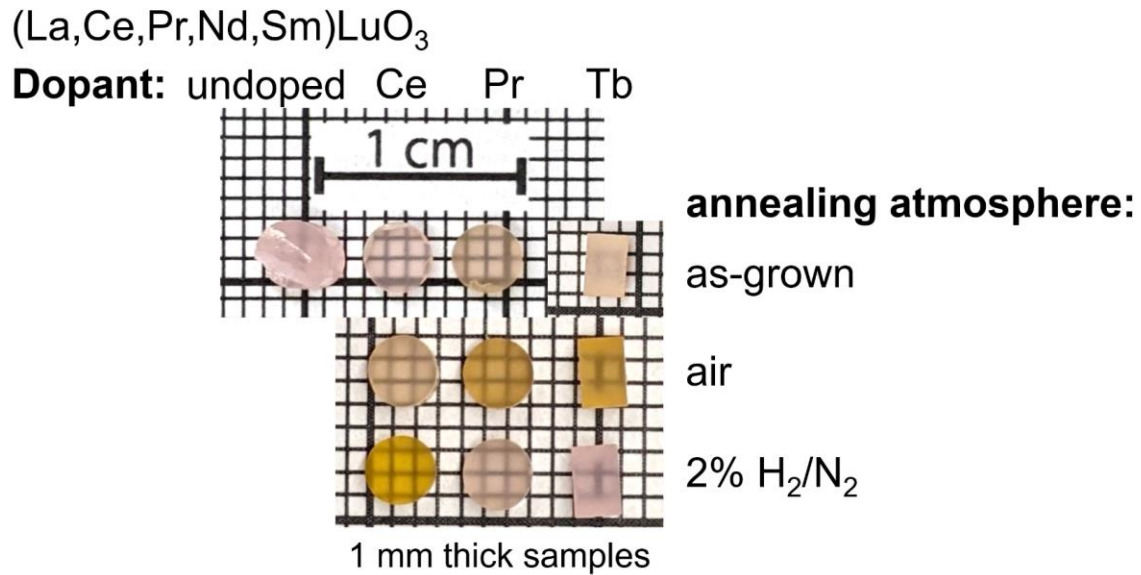


Figure 9.4 - Polished cross-sectional samples of La(Lu,Yb,Tm,Er,Y)O₃ crystals. The type of dopant and type of annealing atmosphere is indicated in the figure.

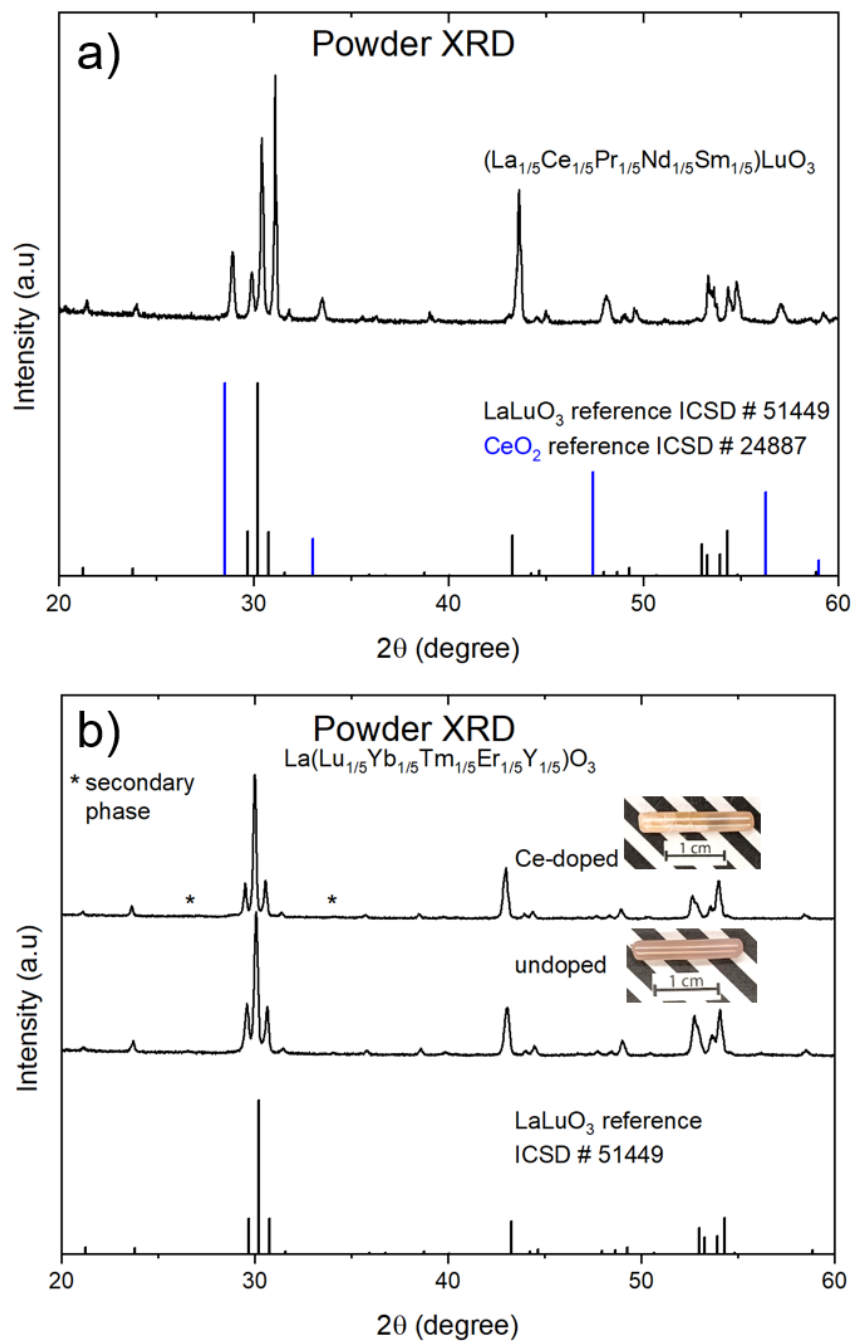


Figure 9.5 - a) Powder XRD pattern of (Sm,Nd,Pr,Ce,La)LuO₃ and reference patterns of LaLuO₃ (ICSD # 51449) and CeO₂ (ICSD # 24887). b) Powder XRD pattern of undoped and Ce-doped La(Lu,Yb,Tm,Er,Y)O₃ and a reference pattern of LaLuO₃ (ICSD # 51449).

the (Sm,Nd,Pr,Ce,La)LuO₃ crystal. As seen in Figure 9.6, SEM imaging reveals darker inclusions in a lighter matrix. Darker features in SEM images indicate elements with relatively low atomic numbers. Energy dispersive spectroscopy data were obtained from points 1-8 in Figure 9.6 and are shown in Table 9.1. Points 1-4 are in the inclusions while points 5-8 are in the matrix. The EDS data presented in Table 9.1 indicate that the inclusions are rich in La, which is a RE with a relatively low atomic number. The EDS data obtained from points 5-8 indicate that the matrix composition is closer to the nominal composition.

Elemental distribution in La(Lu,Yb,Tm,Er,Y)O₃:Ce

No significant macroscopic element segregation was observed in the La(Lu,Yb,Tm,Er,Y)O₃:Ce crystal according to composition analysis obtained via EPMA. In mPD crystals, the preferential incorporation of certain species is observed as downwardly curved radial elemental distribution profiles, while the rejection of elements is observed as upwardly curved profiles. In Figure 9.7.a, all REs are presented. If the sharp features are disregarded, the general radial distribution of La is relatively horizontal, which indicates no significant segregation. The sharp features may correspond to areas with La-rich inclusions as the ones seen in the previously discussed SEM/EDS results in Figure 9.6 and Table 9.1.

In Figure 9.7.b, the five REs that fractionally occupy the RE³⁺ sublattice are presented with no clear curvature trends in their radial profiles. This indicates no preferential incorporation of any of those five REs. In Figure 9.7.c, the Ce concentration profile is presented with shape features that occur at the same position as the ones seen in the La profile. This indicates that this crystal is likely to have inclusions that are rich in both La³⁺ and Ce³⁺, which is reasonable since those two cations have similar ionic radii and would easily substitute each other in the unknown secondary phase in the inclusions.

Radioluminescence

The undoped and the Ce-, Pr-, and Tb-doped La(Lu,Yb,Tm,Er,Y)O₃ crystals have no light emission under X-ray excitation. As seen in Figure 9.8, the radioluminescence spectra of the as-grown crystals exhibit low-intensity emission bands with a significantly low signal-to-noise ratio. Similar results were obtained for the doped crystals after the oxidizing and reducing annealing as observed in Figure 9.9 and Figure 9.10, respectively. The absence of significant light emission from the undoped and doped crystals leads to two observations, 1) the undoped La(Lu,Yb,Tm,Er,Y)O₃ crystal is not an intrinsic scintillator, and 2) Ce³⁺, Pr³⁺, and Tb³⁺ are not effective luminescent activators for scintillation purposes in the La(Lu,Yb,Tm,Er,Y)O₃ host lattice. The absence of Ce³⁺, Pr³⁺, and Tb³⁺ X-ray excited luminescence may be related to thermal quenching and a narrow bandgap. Further investigation into the composition of the host and the nature of the activator may identify potential high-entropy RE perovskite scintillators.

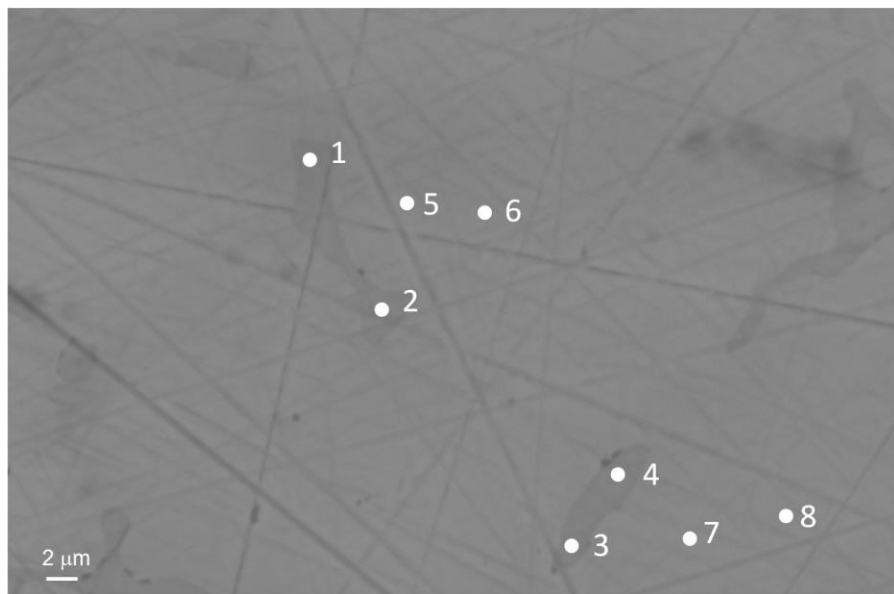


Figure 9.6 - SEM image of the La(Lu,Yb,Tm,Er,Y)O₃ crystal. EDS data obtained for points 1-8 and are seen in Table 9.1.

Table 9.1 - Elemental composition of crystal $\text{La}(\text{Lu}, \text{Yb}, \text{Tm}, \text{Er}, \text{Y})\text{O}_3$ for areas 1-8 shown in the SEM image in Figure 9.6.

		EDS elemental composition (at%), error < 0.001 at%						
Area	Points from Figure 9.6	La	Lu	Yb	Tm	Er	Y	O
	<i>Nominal composition</i>	20	4	4	4	4	20	60
Inclusions	1	34.7	2.6	2.9	3.3	3.8	4.5	48.2
	2	32.8	2.5	2.7	3.2	3.7	4.8	50.3
	3	35.1	2.4	2.6	3.0	3.5	4.0	49.4
	4	34.1	2.5	2.8	3.0	3.7	4.3	49.6
Matrix	5	24.5	5.3	5.4	5.1	5.0	5.8	48.9
	6	25.5	5.4	5.5	5.5	5.3	5.4	47.4
	7	25.7	5.7	5.5	5.3	5.2	5.5	47.1
	8	24.4	5.4	5.3	5.2	5.1	5.9	48.7

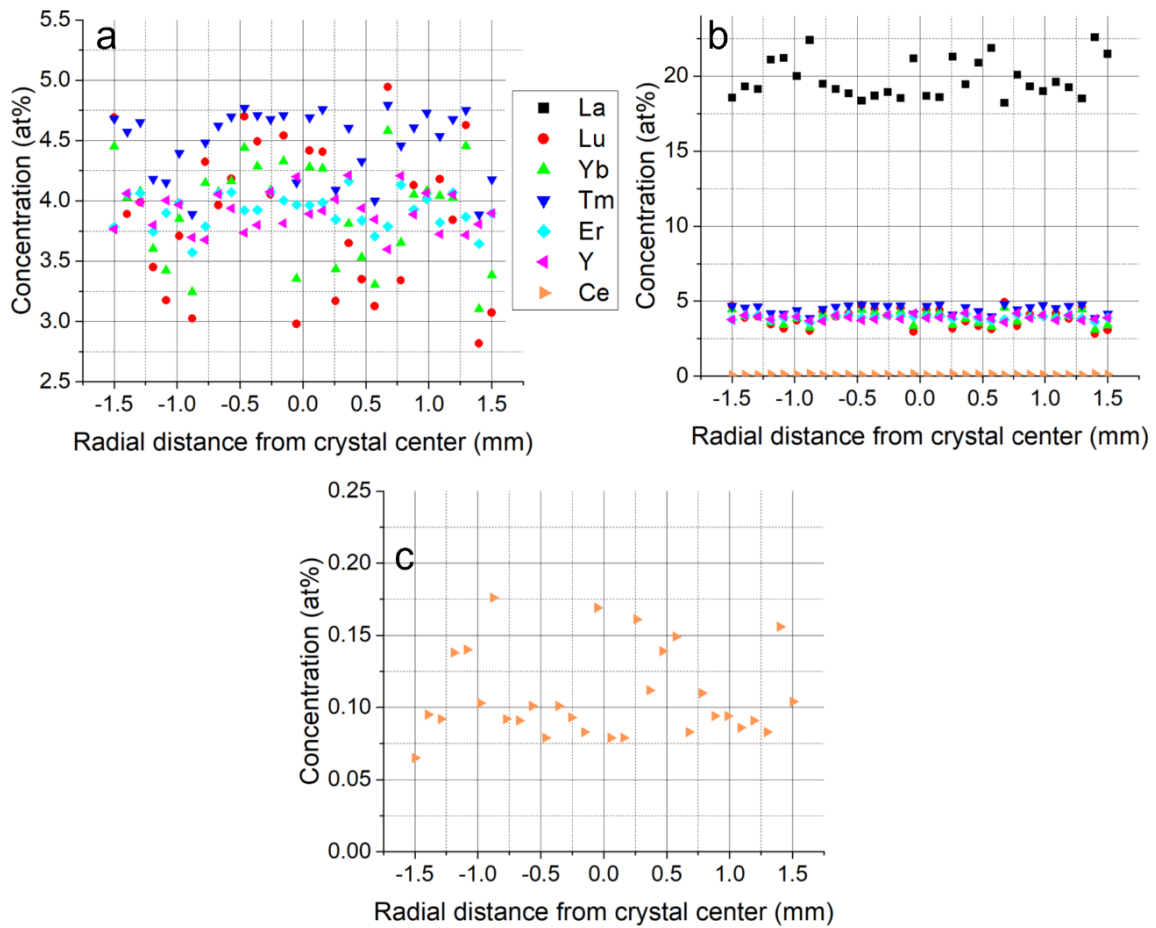


Figure 9.7 – Radial elemental composition profiles of the $\text{La}(\text{Lu}, \text{Yb}, \text{Tm}, \text{Er}, \text{Y})\text{O}_3:\text{Ce}$ crystal. The same data is presented using different vertical scales in items a), b), and c). a) All RE elements are presented, b) only the REs in the RE'' cation sublattice are presented; c) only the dopant Ce is presented. In the horizontal axis, zero corresponds to the center of the crystal and -1.5 mm and 1.5 mm correspond to the surface of the crystal. The legend by item a) also applies to items b) and c).

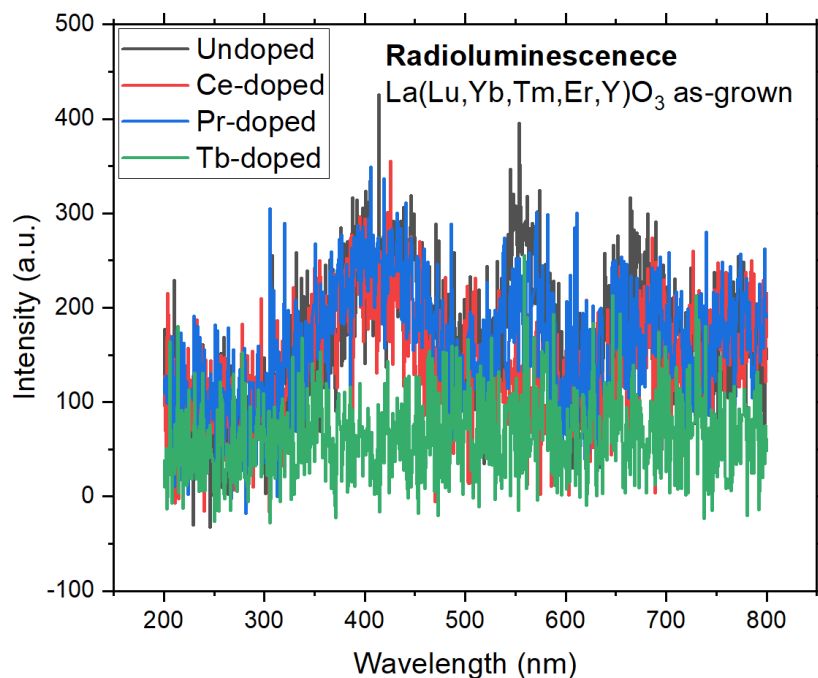


Figure 9.8 – Radioluminescence of the as-grown undoped and Ce-, Pr-, and Tb-doped La(Lu,Yb,Tm,Er,Y)O₃ crystals.

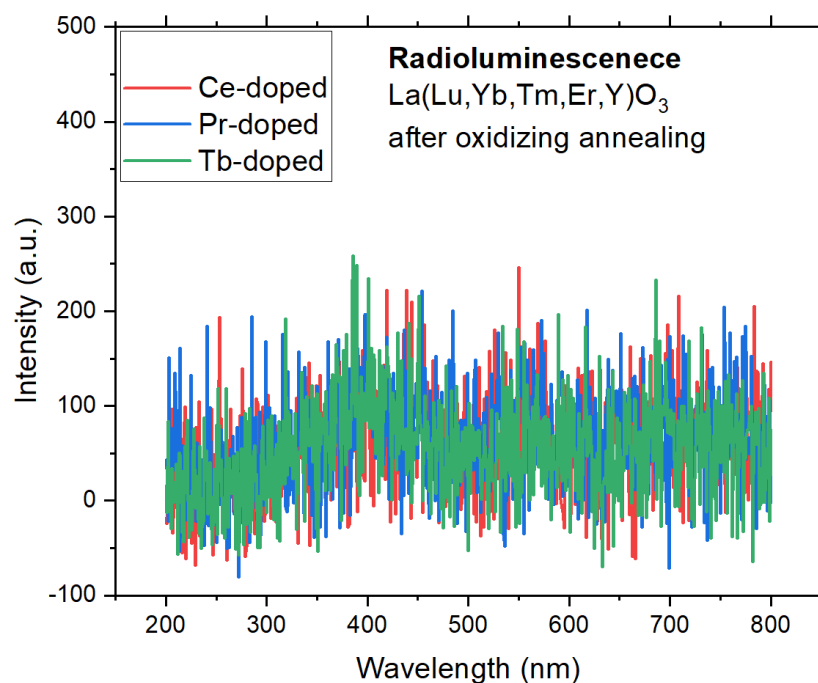


Figure 9.9 - Radioluminescence of the undoped and Ce-, Pr-, and Tb-doped La(Lu,Yb,Tm,Er,Y)O₃ crystals after oxidizing annealing.

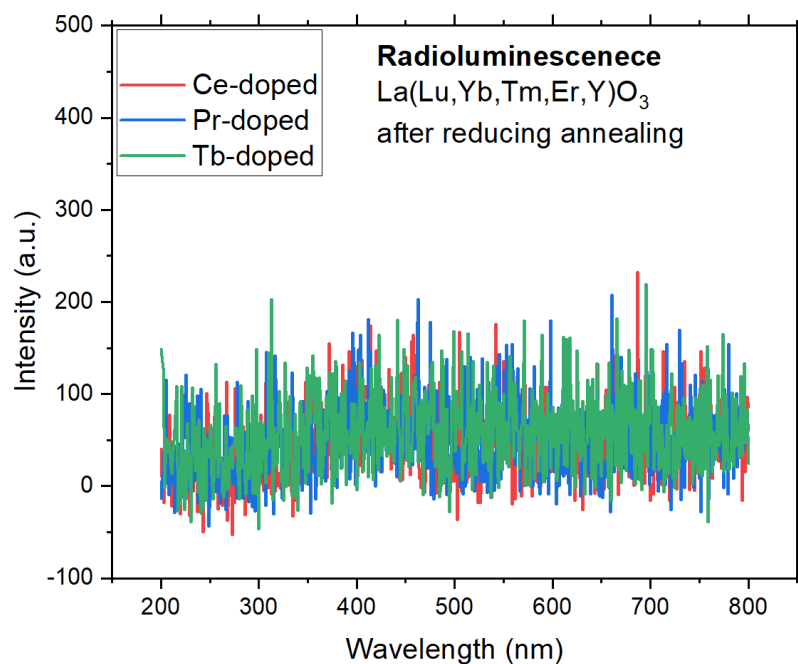


Figure 9.10 - Radioluminescence of the undoped and Ce-, Pr-, and Tb-doped $\text{La}(\text{Lu}, \text{Yb}, \text{Tm}, \text{Er}, \text{Y})\text{O}_3$ crystals after reducing annealing.

Conclusion

In this work, the growth of high-entropy RE perovskite crystals was demonstrated for the first time using. While (Sm,Nd,Pr,Ce,La)LuO₃ was a mixture of phases due to the presence of likely due to the presence of RE⁴⁺ cations, La(Lu,Yb,Tm,Er,Y)O₃ could be grown as a transparent crystal, which makes this composition attractive for the exploration of potential luminescence properties. No evident element segregation was observed in La(Lu,Yb,Tm,Er,Y)O₃. This indicates good compositional homogeneity which is desirable for functional luminescent materials such as laser and scintillators.

At this early stage of development, Ce-, Pr-, and Tb-doped La(Lu,Yb,Tm,Er,Y)O₃ crystals do not emit light when excited by X-rays. Future investigations could focus on photoluminescence and band-gap studies to determine the energy levels of the dopant and how the host composition affects the scintillation process in these crystals. Additional composition engineering focused on the lattice and dopant elements could then be instrumental in the potential development of a high-entropy RE perovskite scintillator.

**CHAPTER TEN:
CZOCHELSKI GROWTH AND CHARACTERIZATION OF THE
MULTICOMPONENT GARNET $(\text{Lu}_{1/4}\text{Yb}_{1/4}\text{Y}_{1/4}\text{Gd}_{1/4})_3\text{Al}_5\text{O}_{12}$**

A version of this chapter was published by Matheus Pianassola and colleagues:

M. Pianassola *et al.*, “Czochralski growth and characterization of the multicomponent garnet $(\text{Lu}_{1/4}\text{Yb}_{1/4}\text{Y}_{1/4}\text{Gd}_{1/4})_3\text{Al}_5\text{O}_{12}$,” *Phys. Rev. Mater.*, vol. 5, no. 8, p. 083401, Aug. 2021, doi: 10.1103/PhysRevMaterials.5.083401.

This chapter is the reformatted version of the original work submitted to the referenced journal. No additional changes to the content of the original article were done other than formatting to conform to the dissertation format.

Abstract

This work demonstrates the potential for practical scalable growth of complex garnets and evaluates the implications of a multicomponent composition in the optical quality and elemental distribution of a Czochralski-grown crystal. Our experimental approach was designed to elucidate the relation between a complex garnet composition $(\text{Lu}_{1/4}\text{Yb}_{1/4}\text{Y}_{1/4}\text{Gd}_{1/4})_3\text{Al}_5\text{O}_{12}$, crystal growth parameters, crystal structural, and elemental homogeneity. Our hypothesis is that combining multiple rare-earths (REs) that will fractionally occupy the dodecahedral site in the aluminum garnet structure will result in a stable, single garnet compound that can be grown by the Czochralski method. Single-crystal and powder X-ray diffraction indicated a single garnet phase with an increasing unit cell volume from seed to tail. In addition, we propose that the pattern of elemental segregation will be based on the deviation of the ionic radius of each constituent RE from the average RE ionic radius of the multicomponent garnet. Electron probe microanalysis revealed that ions that are smaller than that average (Lu^{3+} and Yb^{3+}) are preferentially incorporated in the crystal, while elements that are larger than that average (Gd^{3+}) are rejected. The ionic radius of Y^{3+} is close to that average and yttrium segregation was minimal. The concentrations of the four REs are closer to stoichiometric on the tail end of the boule. Scanning electron microscopy and energy dispersive X-ray spectroscopy analysis reveals Gd-rich inclusions with eutectic microstructures in the tail end of the boule.

Introduction

The surprising phase stabilization [53] and functional properties [40] of high-entropy oxide ceramics have inspired the investigation into crystal growth of complex oxides. Oxides containing five or more cations in equiatomic amounts can have an entropy-stabilized single phase [53]. This class of oxides meet the criteria for high configurational entropy ($\Delta S_{\text{conf}} \geq 1.5R$, where R is the gas constant [42]), but in some cases the stabilization of a single phase is not solely entropy-related [70], [71]. For this reason, the term “multicomponent oxide” is used to avoid implying an entropy-driven stabilization. In this current work, “multicomponent” indicates a composition with four or more types of cations that are expected to fractionally occupy the same crystallographic site. Interesting properties of

multicomponent oxides include superionic conductivity[6], phosphorescence[13], and lasing[14]. In an effort to study complex compositions in single crystal form, thin films have been produced [7], [10], [11], [30]–[34]. More recently, multicomponent oxides have also been reported as shaped crystals, grown by the micro-pulling-down (mPD) [39], floating zone [35], and Czochralski (Cz) [28] methods.

To date, only a few reports focus on multicomponent oxides grown by a scalable bulk growth method such as Cz growth [26]–[28], which is commercially used to grow bulk semiconductor, scintillator, and laser crystals [127]. These reports describe the Cz growth of borates containing three or more cations in close to equiatomic amounts. Although the chemical composition of borate crystals was found to be relatively homogeneous along the growth direction, Cz crystals of other compositions may exhibit element segregation. As an example, the preferential incorporation of smaller cations has been demonstrated in multicomponent rare-earth aluminum garnets grown by the mPD method [39].

The mPD method is advantageous for growing crystals of excellent quality and homogeneous composition. This crystal growth method is based on directionally solidifying the melt as it is pulled down from a small crucible through a capillary channel, which separates the growth interface from the bulk of the melt. A thin (< 1 mm thick) molten zone is located between the bottom of the crucible and the crystal. Rejected elements do not diffuse back into the crucible but segregate toward the periphery of the molten zone and are incorporated into the crystal. This results in radial composition gradients, while the axial elemental distribution is relatively homogeneous [37].

Significant differences in elemental distribution are expected between multicomponent garnets grown by the mPD and Cz methods, in that an axial composition gradient is expected for Cz-grown multicomponent crystals. Cz growth is based on directionally solidifying the melt by pulling the growing crystal upward out of the melt. There is no capillary channel, and the growing crystal is in contact with the bulk of the molten material. Rejected elements stay in the melt, leading to crystals with concentration gradients in the axial direction [201].

Additionally, the effects of melt flow on element incorporation are much more significant in Cz crystals due to the larger quantity of melt. In the Cz method, buoyancy-driven convection, Marangoni flow, and rotational (forced) convection affect the melt composition at the growth interface, impacting the radial element distribution [249]–[251]. In mPD growth, only the melt flows in the molten zone affect the composition at the growth interface; buoyancy-driven convection is negligible due to the small volume of melt, while Marangoni flow is dominant [37].

As the investigation of multicomponent aluminum garnets scales up from the mPD to the Cz technique, it is important to assess the implications of a

disordered cation sublattice on the compositional homogeneity and optical quality of a Cz crystal. Rare-earth (RE) aluminum garnet crystals have the general formula $\text{RE}_3\text{Al}_5\text{O}_{12}$ and are commercially produced for lasing and scintillation applications [86], [87]. Composition engineering has optimized functional properties by admixing up to three elements in the RE or Al sites [15], [17], [20], [207]. Adding more elements into the composition may result in improved performance, but elemental segregation and poor optical quality in a Cz crystal may lead to an inconsistency in properties along the boule.

Most studies of composition homogeneity of Cz crystals focus on investigating the segregation of a dopant element, because functional properties rely on its uniform distribution in the crystal [252]–[260]. Investigation of distribution of the primary constituent cations in crystals with complex compositions, which is the focus of this work, is of equal importance. Studies of the distribution of primary cations are limited to compositions in which no more than three elements compete for the same crystallographic site [26], [27], [261]–[267]. Here we demonstrate the Cz crystal growth and assess the extent of an axial concentration gradient, optical quality, and crystal structure of the four-component equiatomic aluminum garnet $(\text{Lu}_{1/4}\text{Yb}_{1/4}\text{Y}_{1/4}\text{Gd}_{1/4})_3\text{Al}_5\text{O}_{12}$. This compound is a medium entropy material with a $\Delta S_{\text{conf}} = 1.4R$ [42].

The composition contains four primary constituent RE elements that were selected from a relatively wide ionic radii range of 0.977 – 1.053 Å to investigate the dependence of element incorporation on cation size [268]. For simplicity, yttrium is referred to here as a RE element. Two REs lie at the shorter end of the range, Lu^{3+} (0.977 Å) and Yb^{3+} (0.985 Å), while Y^{3+} (1.019 Å) lies around the middle, and Gd^{3+} (1.053 Å) at the larger end of the range [268]. Small REs are expected to be more readily incorporated in garnet crystals since larger REs disrupt the Al–O framework [39], [181]. As larger REs are rejected by the growing crystal, they become enriched in the melt. Since the incorporation of ions in the crystal is proportional to their concentration in the melt, from the top to the bottom of the crystal the concentration of smaller REs is expected to decrease, while the concentration of larger REs is expected to increase. Consequently, the unit cell volume will expand, from the seed end to the tail end. This lattice misfit along the boule may cause lattice strain, which can result in defect formation due to internal stresses.

Methods

Materials and crystal growth

A $(\text{Lu}_{1/4}\text{Yb}_{1/4}\text{Y}_{1/4}\text{Gd}_{1/4})_3\text{Al}_5\text{O}_{12}$ crystal was grown by the Czochralski method using a Cyberstar Oxypuller 05-03 growth station. Powders of Lu_2O_3 , Yb_2O_3 , Y_2O_3 , Gd_2O_3 , and Al_2O_3 of at least 99.99% purity were mixed in stoichiometric quantities and the mixture was placed into an iridium crucible that is

60 mm in both height and diameter. The powder mixture was melted by inductively heating the crucible in a flowing nitrogen atmosphere with approximately 0.2 vol% of oxygen. Crystal growth was initiated on a $\text{Lu}_3\text{Al}_5\text{O}_{12}:\text{Ce}$ seed oriented in the $\langle 111 \rangle$ direction. The rotation and pulling rates were 11 rpm and 1 mm/h, respectively. Table 10.1 contains the crystal dimensions. A total of 525 g of material was pulled from the melt, which corresponds to 67% of the initial charge. After the active growth phase was finished, the crystal was gradually cooled over 48 h.

Five cross-sectional samples of the crystal were cut for characterization; each sample was 5 mm thick. Sample S was cut 5 mm below the seed in the neck region. Samples C1, C2, and C3 were cut from the cylindrical region and their respective original locations were 1 mm away from the shoulder, approximately the middle of the cylinder, and 1 mm away from the tail. Sample T was cut 5 mm away from the tip of the tail. A schematic representation of the crystal portions and the five cross-sectional samples is shown in Figure 10.1.

Optical microscopy

Half-diameter slices from samples C1, C2, and C3 were polished and inclusions were imaged with KEYENCE VHX-1000 and Zeiss Axio Observer A1 optical microscopes.

Optical transmission

Plates of 0.5 mm thickness cut from samples C1, C2, and C3 were polished for optical transmission measurements. A Varian Cary 5000 UV–VIS–IR spectrophotometer was used to acquire optical absorption spectra in the range of 200–800 nm.

Powder X-ray diffraction

A half-diameter slice from each of the five samples was ground in a mortar for phase analysis via powder X-ray diffraction (XRD). A Panalytical Empyrean diffractometer was used in the Bragg-Brentano geometry using a $\text{CuK}\alpha$ X-ray source ($\lambda_{\text{K}\alpha 1} = 1.540510 \text{ \AA}$, $\lambda_{\text{K}\alpha 2} = 1.544330 \text{ \AA}$) at 45 kV and 40 mA. Phase analysis and lattice parameter evaluation were done via Rietveld refinement using the General Structure Analysis System II software (GSASII).

Single-crystal X-ray diffraction

For further assessment of the crystal structure, single-crystal XRD data were obtained for samples C1, C2, and C3. A crystal portion was cut from the center of each sample. Sample dimensions are given in Table S-I in the Supplemental Material [269]. Each of the three portions was suspended in paratone oil on a plastic loop attached to a copper goniometer. A Rigaku XtaLAB

Table 10.1 - $(\text{Lu}_{1/4}\text{Yb}_{1/4}\text{Y}_{1/4}\text{Gd}_{1/4})_3\text{Al}_5\text{O}_{12}$ Czochralski crystal portions and respective dimensions.

Crystal portion	Dimension
Neck	20 mm length, 7 mm diameter
Shoulder	65 mm length, 44°
Cylinder	55 mm length, 30 mm diameter
Tail	55 mm length, 2 mm diameter

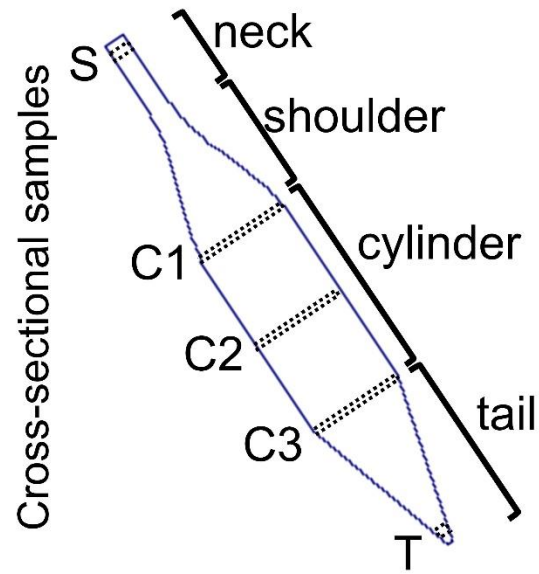


Figure 10.1 - Schematic representation of the $(\text{Lu}_{1/4}\text{Yb}_{1/4}\text{Y}_{1/4}\text{Gd}_{1/4})_3\text{Al}_5\text{O}_{12}$ crystal (blue). Crystal portions are named on the right side of the figure. Dotted lines indicate the regions from which the five cross-sectional samples were cut for characterization; sample IDs are shown on the left side of the image.

PRO diffractometer with graphite monochromated Mo K α radiation (50 kV, 40 mA, $\lambda = 0.71073 \text{ \AA}$) equipped with a Rigaku HyPix-6000HE detector and an Oxford N-HeliX cryocooler was used to collect single-crystal diffraction data at 250K. The Rigaku Oxford Diffraction CrysAlisPro software was used for peak indexing and integration [216]. The SCALE3 ABSPACK algorithm as implemented in CrysAlisPro was used to apply an empirical absorption correction. Data processing and structure refinement were performed using the SHELXL-2013 and WinGX software packages [195], [196]. The structure refinements were made with the scale factor, an extinction parameter, anisotropic atomic displacement parameters, and oxygen atom positional coordinates.

Electron probe microanalysis

To evaluate the elemental distribution in the crystal, samples C1, C2, and C3 were subjected to electron probe microanalysis (EPMA). A 2 mm-thick full-diameter slice was cut from each sample and embedded in epoxy. A CAMECA SX100 Electron Microprobe equipped with high-speed backscattered electron (BSE) detectors and 4 wavelength-dispersive spectrometers (WDS) was used at 15 kV and 30 nA. Images were acquired by detecting the backscattered electrons and compositional data were obtained from the characteristic X-rays by WDS. The probe point size was 1 μm and the diameter of the excitation area was in the 2 - 3 μm range. Data were collected in 1 mm steps to generate radial distribution profiles.

Scanning electron microscopy and energy dispersive spectroscopy

To investigate the morphology and elemental composition of inclusions, a small crystal fragment was cut from sample C3, which has a higher concentration of inclusions compared to samples C1 and C2. The fragment was polished to expose the inclusions to the surface. A Zeiss EVO MA15 Scanning Electron Microscope (SEM) equipped with a Bruker xFlash 6130 Energy Dispersive X-Ray Spectrometer (EDS) was used to image the inclusions and analyze their elemental composition.

Results and discussion

Grown crystal and macroscopic defects

A transparent $(\text{Lu}_{1/4}\text{Yb}_{1/4}\text{Y}_{1/4}\text{Gd}_{1/4})_3\text{Al}_5\text{O}_{12}$ crystal was grown, demonstrating the potential for practical Cz growth of complex multicomponent aluminum garnets. The melt behavior was typical for single RE aluminum garnets, with visible convective melt flow, indicating good mixing. As shown in Figure 10.2.a, the crystal has a well-controlled shape. The crystal surface is smooth on the seed end and rough on the tail end, as seen in Figure 10.2.b. The rough surface is due to thermal etching. The crystal was cooled inside the iridium crucible, which

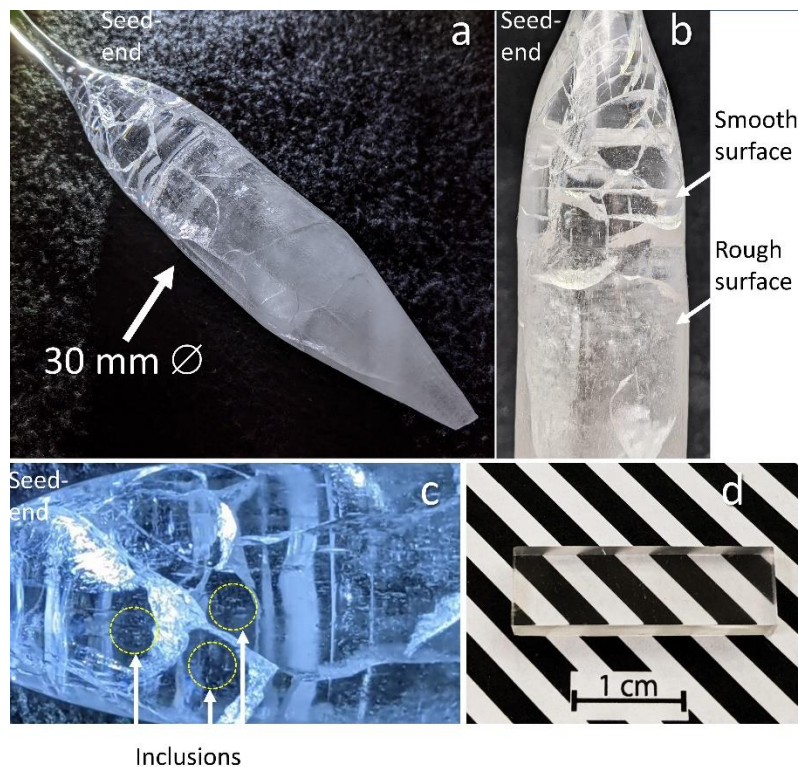


Figure 10.2 - a) As-grown $(\text{Lu}_{1/4}\text{Yb}_{1/4}\text{Y}_{1/4}\text{Gd}_{1/4})_3\text{Al}_5\text{O}_{12}$ boule; crystal is transparent and heavily cracked. b) In the cylindrical region, there is a clear transition from smooth to rough surface. c) Macroscopic inclusions in the shoulder region; similar inclusions were observed throughout the whole crystal. d) Polished pixel of 23 x 5 x 5 mm cut from sample C1.

explains a more pronounced thermal etching on the tail end.

Although the crystal is cracked and contains internal macroscopic defects, defect-free samples were obtained from the cylindrical region. Only a few cracks reach the center of the crystal, and they may originate from the lattice strain that results from the difference in ionic radii between the REs in the composition. Macroscopic inclusions can be observed by the naked eye, as seen in the shoulder section in Figure 10.2.c. Similar internal defects were observed throughout the whole crystal. Nevertheless, even at this early stage of development, samples with high optical quality could be obtained from the cylindrical portion of the boule; Figure 10.2.d shows a pixel cut from sample C1.

Samples C1, C2, and C3 contain inclusions and C3 also has cloud-like defects. Optical microscopy images of samples C1, C2, and C3 are presented in Figure 10.3.a, b, c, respectively. Samples C1 and C2 have lower concentrations of inclusions than C3. Also, cloud-like defects were observed in C3. Cloud-like defects may result from microcracks that formed due to a more pronounced lattice strain on the tail end of the crystal, which will be discussed later in this Chapter. An image of an inclusion in C3 is shown with higher magnification in Figure 10.4. A higher concentration of inclusions on the tail end is typical of defect-containing Cz-grown crystals [270]–[272]. This is due to a higher concentration of segregated species at the growth interface and a reduced convective melt flow due to a reduced depth of the melt.

Cloud-like defects and a higher concentration of inclusions are responsible for a diminished optical transmission on the tail end compared to the seed end. In Figure 10.5 the optical transmission spectra of samples C1, C2, and C3 are compared. In the 350-800 nm wavelength range, the optical transmittance of samples C1 and C2 are in the range of 68-76% and 63-65%, respectively. This transmittance range decreases to 38-42% for sample C3 due to the higher concentration of defects and inclusions. Gd^{3+} electronic transitions were observed at ~275 nm and ~310 nm and are indicated in Figure 10.5.

Crystal structure

Powder and single-crystal XRD measurements reveal that the $(Lu_{1/4}Yb_{1/4}Y_{1/4}Gd_{1/4})_3Al_5O_{12}$ crystal is a single garnet phase with a $Ia\bar{3}d$ space group. In Figure 10.6.a, the powder XRD patterns of samples S, C1, C2, C3, and T are compared to a reference pattern for $Er_3Al_5O_{12}$ [273]; the reflection peaks for the samples match well with the reference. The peak splitting is due to the overlap of $CuK\alpha_1$ and $CuK\alpha_2$ reflections. Among all RE elements, the ionic radius of Er^{3+} (1.004 Å) is the closest one to the average theoretical ionic radius of the REs in $(Lu_{1/4}Yb_{1/4}Y_{1/4}Gd_{1/4})_3Al_5O_{12}$, which is (1.009 Å) [268]. Rietveld refinement of powder XRD patterns reveals a single garnet phase and an increasing lattice parameter from seed to tail as shown in Figure 10.6.b. Refinement data for the

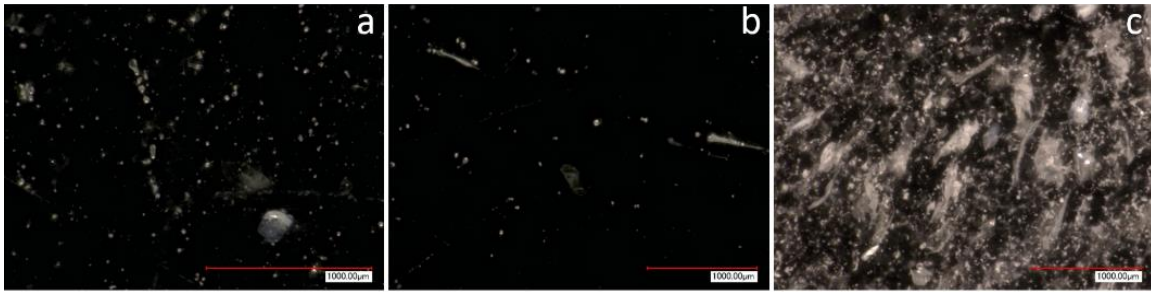


Figure 10.3 - Optical microscope images of internal defects in samples a) C1, b) C2, and c) C3. Sample C3 has cloud-like defects in addition to a higher concentration of inclusions compared to C1 and C2. Images obtained with a KEYENCE VHX-1000 microscope.



Figure 10.4 - Optical image of inclusions in sample C3. Image obtained with a Zeiss Axio Observer A1 microscope.

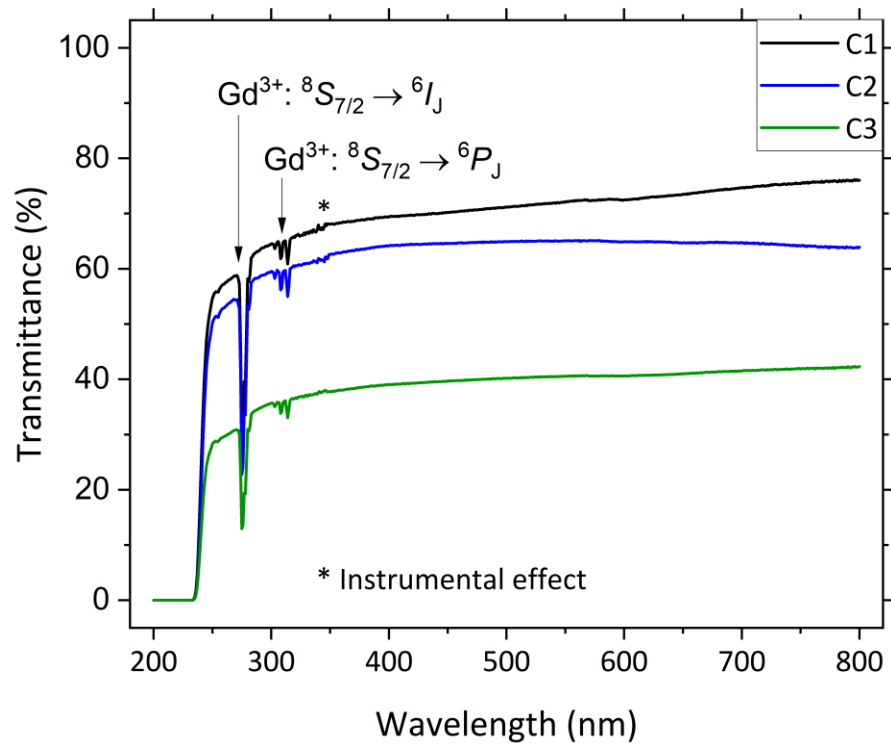


Figure 10.5 - Optical transmission spectra. The transmittance decreases from seed to tail end due to an increasing concentration of defects and inclusions.

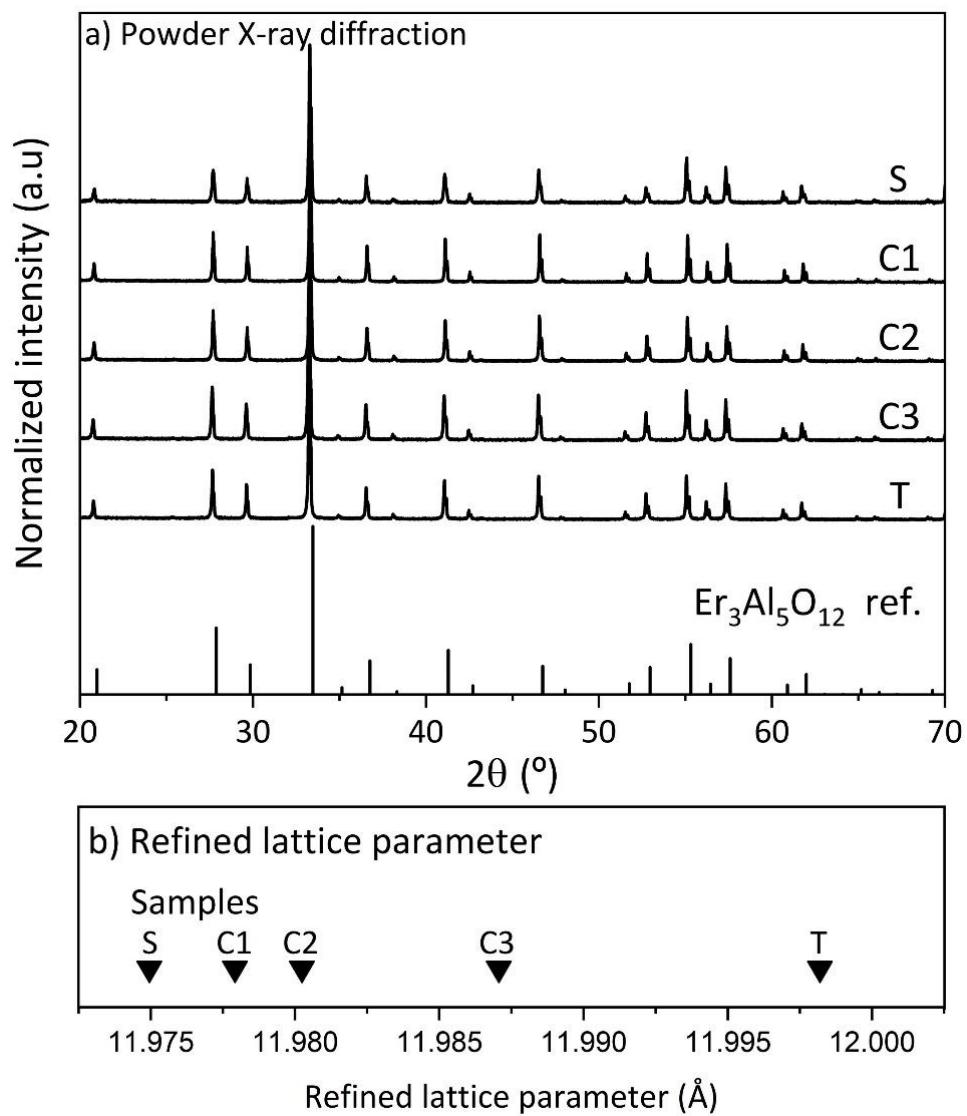


Figure 10.6 - a) Powder XRD patterns of samples S, C1, C2, C3, C4, and T indicate a single garnet phase. A reference pattern of $\text{Er}_3\text{Al}_5\text{O}_{12}$ [273] is plotted for comparison. b) Lattice parameter obtained via Rietveld refinement of powder XRD data for the five samples. Lattice parameter increases from seed to tail.

single-crystal XRD patterns of samples C1, C2, and C3 also indicate a single garnet phase and an increasing lattice parameter from seed to tail. Single-crystal XRD refinement parameters are in Table 10.2 and the fractional atomic coordinates and equivalent isotropic displacement parameters are in Table 10.3. No obvious diffuse scattering was observed in the X-ray patterns, which indicates no short-range clustering of REs.

The increasing lattice parameter from seed to tail indicates a gradient in crystal composition in the growth direction. This is due to the accumulation of larger REs in the melt as growth progressed. The incorporation of elements in the crystal is proportional to their concentration in the melt. Therefore, a higher concentration of the larger REs in the melt, which were rejected earlier in the growth process, led to a higher concentration of them toward the tail of the crystal. This can be confirmed by the fact that the difference in lattice parameter between consecutive samples is not monotonic, and becomes greater toward the tail of the crystal, as shown in Figure 10.6.b.

The higher concentration of larger elements on the tail end also results in a more pronounced lattice strain since large elements are geometrically disadvantaged in the RE aluminum garnet structure. Rietveld refinement of powder XRD data revealed an increase in the isotropic microstrain parameter from seed to tail end. The unitless microstrain peak broadening fraction of samples S, C1, C2, C3 and T are 562, 1038, 1044, 1055, and 1250, respectively. This explains the more intense cracking on the tail end.

Elemental distribution

An axial composition gradient in $(\text{Lu}_{1/4}\text{Yb}_{1/4}\text{Y}_{1/4}\text{Gd}_{1/4})_3\text{Al}_5\text{O}_{12}$ indicates a rejection of larger REs by the growing crystal. In Figure 10.7, EPMA radial elemental profiles are shown for samples C1, C2, and C3. The nominal stoichiometric concentration of each RE element is 3.75 at% and the crystal composition is closer to stoichiometric in C3, which results in a more pronounced lattice strain on the tail end due to differences in RE^{3+} ionic radius. This results in the formation of microcracks which appear as the cloud like defects discussed later in this Chapter. A general trend in the elemental profiles of smaller Lu^{3+} and Yb^{3+} ions is observed across the three samples: both ions have similar, higher than nominal concentrations that decrease consistently from ~4.5 at% in C1 to ~4.0 at% in C3. All three samples have Y^{3+} ions in close to stoichiometric amounts; a consistent, slight increase in Y^{3+} concentration is observed from C1 through C3. All samples are depleted in larger Gd^{3+} ions; the concentration of Gd^{3+} increases consistently from ~2.25 at% in C1 to ~3.1 at% in C3. Based on the EPMA results, we conclude that larger ions are rejected by the growing crystal, as expected. This is consistent with the observed expansion in unit cell volume from seed to tail.

Table 10.2 - Single-crystal X-ray diffraction data collection and refinement parameters.

Sample	C1	C2	C3
Formula	RE ₃ Al ₅ O ₁₂	RE ₃ Al ₅ O ₁₂	RE ₃ Al ₅ O ₁₂
T (K)	250(1)	250(1)	250(1)
Crystal system	cubic	cubic	cubic
space group	<i>Ia$\bar{3}d$</i>	<i>Ia$\bar{3}d$</i>	<i>Ia$\bar{3}d$</i>
a (Å)	11.9885(2)	11.9974(2)	12.0046(1)
V (Å³)	1723.05(5)	1726.87(4)	1730.00(3)
Z	8	8	8
D_{calc} (mgm⁻³)	5.956	5.943	5.932
μ (Mo Kα) (mm⁻¹)	27.909	27.847	27.797
F(000)	2752	2752	2752
Crystal size (mm)	0.1×0.075×0.04	0.1×0.05×0.03	0.15×0.075×0.03
θ range for data collection	4.2-36.3	4.16-36.2	4.16-36.3
	-19 ≤ <i>h</i> ≤ 19	-10 ≤ <i>h</i> ≤ 17	-20 ≤ <i>h</i> ≤ 19
Index ranges	-19 ≤ <i>k</i> ≤ 19	-19 ≤ <i>k</i> ≤ 19	-19 ≤ <i>k</i> ≤ 20
	-16 ≤ <i>l</i> ≤ 19	-19 ≤ <i>l</i> ≤ 19	-17 ≤ <i>l</i> ≤ 19
No. reflections collected (equivalents agreement)	8192 (0.034)	8831 (0.026)	8177 (0.031)
No. unique reflections collected with $F_o > 4\sigma F_o$	353	353	355
No. of variables	18	18	18
R_F	0.017	0.014	0.018
R_{wF}	0.033	0.0289	0.034
Goodness of fit	1.439	1.440	1.466
largest diff. peak and hole (eÅ⁻³)	0.89, -0.88	0.584, -0.632	1.062, -0.564
Scale factor	0.1225(1)	0.1167(1)	0.1530(1)
Extinction coefficient	0.00097(4)	0.00023(2)	0.00148(5)
^{IV}Al-O (Å)	1.769(2) × 4	1.769(1) × 4	1.770(2) × 4
^{VI}Al-O (Å)	1.929(2) × 6	1.928(1) × 6	1.929(2) × 6
^{VIII}Ln-O (Å)	2.301(2) × 4	2.303(1) × 4	2.305(2) × 4
	2.425(2) × 4	2.430(1) × 4	2.431(2) × 4

Table 10.3 - Fractional atomic coordinates and equivalent isotropic displacement parameters for samples C1 ($a = 11.9885(2) \text{ \AA}$), C2 ($a = 11.9974(2) \text{ \AA}$) and C3 ($a = 12.0046(1) \text{ \AA}$), space group $1a\bar{3}d$.

Atom	Site	Symmetry	x	y	z	$U_{eq} (\text{\AA}^2)$
<i>Sample C1</i>						
Al1	16a	$\bar{3}$	0	0	0	0.0015(2)
Al2	24d	$\bar{4}$	3/8	0	1/4	0.0031(3)
RE*	24c	222	1/8	0	1/4	0.0024(1)
O	96h	1	0.1006(1)	0.1985(1)	0.2801(1)	0.0031(3)
<i>Sample C2</i>						
Al1	16a	$\bar{3}$	0	0	0	0.0036(3)
Al2	24d	$\bar{4}$	3/8	0	1/4	0.0051(5)
RE*	24c	222	1/8	0	1/4	0.0032(1)
O	96h	1	0.1007(2)	0.1988(2)	0.2802(2)	0.0038(1)
<i>Sample C3</i>						
Al1	16a	$\bar{3}$	0	0	0	0.0010(5)
Al2	24d	$\bar{4}$	3/8	0	1/4	0.0024(2)
RE*	24c	222	1/8	0	1/4	0.0021(1)
O	96h	1	0.1007(2)	0.1988(2)	0.2803(2)	0.0025(2)

* RE = fixed composition $(\text{Lu}_{1/4}\text{Yb}_{1/4}\text{Y}_{1/4}\text{Gd}_{1/4})_3\text{Al}_5\text{O}_{12}$

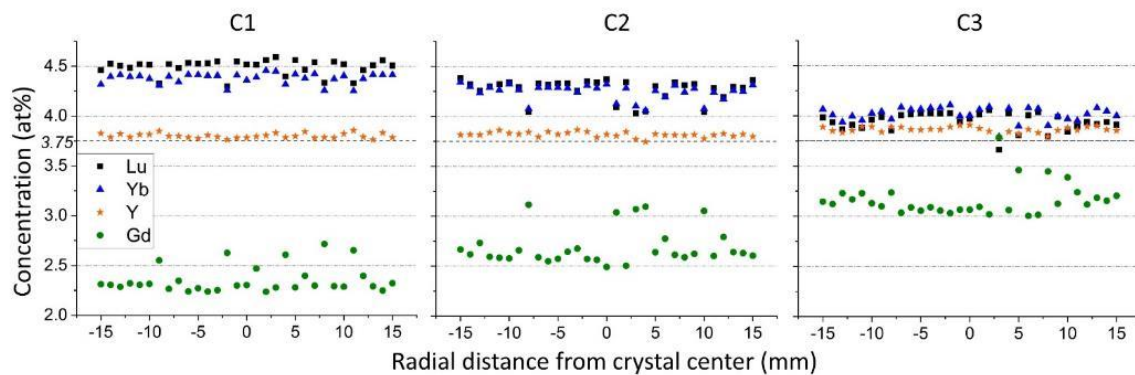


Figure 10.7 - EPMA radial concentration profiles of samples C1 (left), C2 (center), and C3(right). The legend on the left applies to all graphs. On the horizontal axis, zero represents the center of the crystal, while -15 or +15 mm represent the last measurement toward the outer surface of the cylindrical crystal. On the vertical axis, 3.75 at% indicate the nominal concentration of RE ions.

The rejection of Gd^{3+} primary constituent ions in $(\text{Lu}_{1/4}\text{Yb}_{1/4}\text{Y}_{1/4}\text{Gd}_{1/4})_3\text{Al}_5\text{O}_{12}$ is consistent with the rejection of dopants (typically used in small concentrations) that are larger than the substituted ion in garnet crystals [252]–[260]. Larger dopants have a segregation coefficient $k < 1$ and their concentration in the melt increases during the growth. As a result, the concentration of larger dopants increases in the crystal from seed to tail. Based on the EPMA results shown in Fig. 7, we can infer that in $(\text{Lu}_{1/4}\text{Yb}_{1/4}\text{Y}_{1/4}\text{Gd}_{1/4})_3\text{Al}_5\text{O}_{12}$ the segregation coefficient is $k > 1$ for both Lu^{3+} and Yb^{3+} , $k \approx 1$ for Y^{3+} , and $k < 1$ for Gd^{3+} .

As seen in Figure 10.7, in all samples the radial concentration profiles of Y^{3+} ions are relatively constant, while sharp variations are observed in the profiles of Lu^{3+} , Yb^{3+} , and Gd^{3+} . Local valleys in the concentration profiles of both Lu^{3+} and Yb^{3+} are observed; in general, the magnitude of these valleys is similar for both REs. These decreases in the concentration of Lu^{3+} and Yb^{3+} are correlated with a pronounced, sharp increase in the concentration of the larger Gd^{3+} . These sharp features may result from composition variations in the melt at the growth interface due to the accumulation of Gd ions. Therefore, when the melt at the solid/liquid interface is locally rich in Gd^{3+} , a relatively higher amount of Gd^{3+} is incorporated. This would explain the peaks in the concentration profiles of Gd^{3+} and the associated valleys for Lu^{3+} and Yb^{3+} .

The composition homogeneity of multicomponent Cz crystals may depend on the type of compositional system. While the multicomponent aluminum garnet $(\text{Lu}_{1/4}\text{Yb}_{1/4}\text{Y}_{1/4}\text{Gd}_{1/4})_3\text{Al}_5\text{O}_{12}$ has an axial composition gradient, multicomponent RE borate crystals have a homogeneous composition [26], [27], without any significant element segregation. Therefore, the axial composition gradient in multicomponent garnets may be characteristic of garnet crystals due to the rejection of larger elements by the crystal lattice.

Inclusions: microstructure and elemental composition

Inclusions such as the ones seen in Figure 10.4 have a eutectic microstructure and are rich in Gd. As seen in the SEM image of C3 in Figure 10.8, the inclusions have a typical eutectic microstructure composed of lighter and darker phases that are continuously entangled in a three-dimensional interpenetrating network [220]. Table 10.4 has the EDS data that were collected from the six points indicated in Figure 10.8 to assess the elemental composition outside and inside the inclusion. Outside the inclusion (points 1 and 2) the sample has similar amounts of Lu, Yb, Y, and is depleted in Gd. This is consistent with the EPMA results for sample C3 shown in Figure 10.7. On the other hand, lighter areas in the inclusion (points 3 and 4) are significantly richer in Gd. Therefore, the sharp features in Gd^{3+} concentration profile in Figure 10.7 may correspond to areas with these eutectic inclusions. Darker areas in the inclusion (points 5 and 6) have lower, close to equiatomic amounts of REs and are richer in Al, indicating a secondary

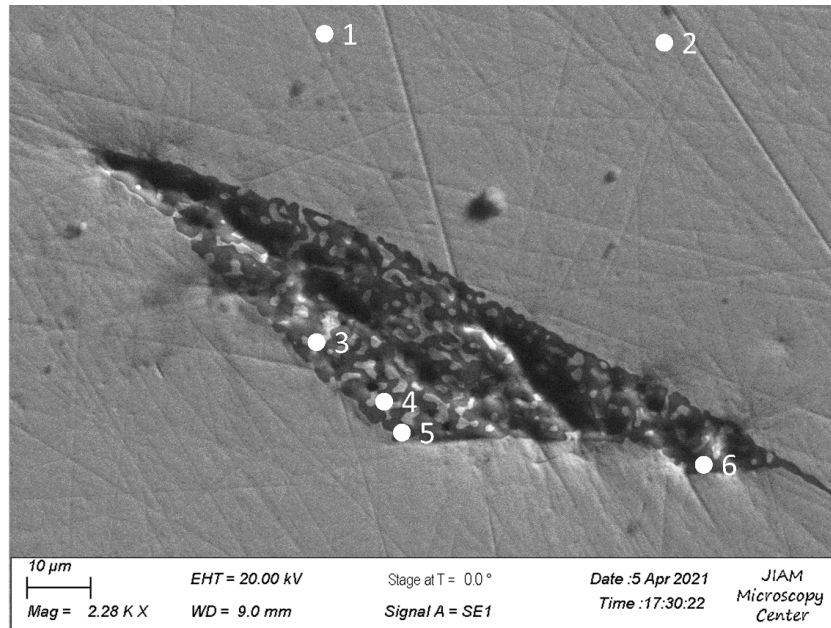


Figure 10.8 - SEM image of an inclusion with a eutectic microstructure in sample C3. Similar inclusions were observed in other areas of the sample. Table 10.4 has the EDS data collected for points 1-6 indicated in the image.

Table 10.4 - EDS elemental composition results for areas 1-6 shown in the SEM image in Figure 10.8. In the approximate stoichiometry of each area, the stoichiometric coefficient of “RE” represents the combined concentration of each RE.

Area	Point from Figure 10.8	EDS elemental composition (at%), error < 0.001 at%						Stoichiometry
		Lu	Yb	Y	Gd	Al	O	
	Nominal composition	3.75	3.75	3.75	3.75	3.75	3.75	RE ₃ Al ₅ O ₁₂
Outside the inclusion	1	4.28	4.11	4.44	3.43	28.67	55.07	RE _{3.3} Al _{5.7} O _{11.0}
	2	3.85	3.81	4.40	3.22	27.90	56.82	RE _{3.1} Al _{5.6} O _{11.4}
Lighter area in the inclusion	3	2.01	2.02	3.01	6.75	34.05	52.16	RE _{2.8} Al _{6.8} O _{10.4}
	4	1.96	2.06	2.96	6.88	31.60	54.54	RE _{2.8} Al _{6.3} O _{10.9}
Darker area in the inclusion	5	0.70	0.67	0.63	0.79	41.68	55.53	RE _{0.6} Al _{8.3} O _{11.1}
	6	0.68	0.67	0.64	1.00	38.67	58.34	RE _{0.6} Al _{7.7} O _{11.7}

alumina phase that could not be detected via powder or single-crystal XRD.

One possible explanation for the formation of eutectic inclusions would be clustering of Gd^{3+} at the growth interface, which could result in localized variations in melt composition. In the phase diagrams of one-RE $\text{RE}_2\text{O}_3\text{-Al}_2\text{O}_3$ systems, a trend can be observed in the position of the eutectic formed between the one-RE garnet $\text{RE}_3\text{Al}_5\text{O}_{12}$ and Al_2O_3 [73], [274]. The eutectic point is closer to the garnet stoichiometry as the ionic radius increases in the series of Lu, Yb, Y, and Gd; the position of the Al_2O_3 and $\text{Gd}_3\text{Al}_5\text{O}_{12}$ eutectic is the closest to the position of the garnet stoichiometry. In the case of multicomponent melts that are enriched in larger elements such as Gd, the probability of forming eutectic inclusions is increased.

To minimize the formation of defects in Cz-grown multicomponent garnets, growth parameters and composition could be optimized. A faster rotation rate is expected to intensify the forced melt convection and improve melt mixing and, therefore, elemental homogeneity in the growth interface. This effect would be more significant toward the end of the growth when the depth of the melt in the crucible is reduced, and buoyancy-driven convection is less pronounced [38]. Decreasing the relative amount of larger REs with respect to smaller RE in the nominal composition could minimize the formation of eutectic inclusions. In this case, the amount of REs would not be equiatomic. Additionally, off-stoichiometric melts have been shown to eliminate the formation of inclusions in garnet crystals [275]. In this case, the ratio of RE/Al could be slightly increased above the 3/5 stoichiometry.

Conclusion

A multicomponent garnet crystal $(\text{Lu}_{1/4}\text{Yb}_{1/4}\text{Y}_{1/4}\text{Gd}_{1/4})_3\text{Al}_5\text{O}_{12}$ was successfully grown by the Cz method with a well-controlled shape. The Cz-grown $(\text{Lu}_{1/4}\text{Yb}_{1/4}\text{Y}_{1/4}\text{Gd}_{1/4})_3\text{Al}_5\text{O}_{12}$ crystal is cracked and contains eutectic inclusions and cloud-like defects of unidentified nature. The crystal is a single garnet phase with increasing lattice parameters from seed to tail. Smaller REs have segregation coefficients $k > 1$ and are concentrated on the seed end, while larger REs have $k < 1$ and are concentrated in the tail end. Due to the variations in k among the REs, multicomponent garnets have an axial composition gradient of the primary constituent (or matrix) REs. This is analogous to the axial gradient in the dopant concentration seen in doped Cz-grown garnets.

We demonstrated the practical aspect of the scalable growth of complex garnet crystals, which had been previously reported only as miniature bulk crystals grown by the micro-pulling-down method. This opens a possibility of compositional engineering and growth of multicomponent garnets containing REs beyond the ones investigated here. Future work will focus on studying different combinations

of REs to investigate the correlation between ionic radii, segregation behavior, and incorporation of inclusions. Varying the range of RE ionic radii and deviating from equiatomic ratios may allow tuning of crystal structure and functional properties.

**CHAPTER ELEVEN:
SCINTILLATION PROPERTIES OF Ce-DOPED
(Lu,Y,Tb,Gd)₃Al₅O₁₂ MICRO-PULLING-DOWN CRYSTALS**

A version of this chapter is in preparation to be published by Matheus Pianassola and colleagues:

M. Pianassola *et al.*, “scintillation properties of Ce-doped (Lu,Y,Tb,Gd)₃Al₅O₁₂ micro-pulling-down crystals,” In preparation.

Abstract

For the first time, the scintillation properties of an equiatomic four-rare-earth aluminum garnet were explored. Three of the host cations, Lu³⁺, Y³⁺, and Gd³⁺, were selected due to their optical inactivity and Tb³⁺ was selected due to the well-known Tb-Ce energy transfer. Micro-pulling-down crystals of the system (Lu,Y,Tb,Gd)₃Al₅O₁₂:Ce were grown with Ce concentrations in the range of 0 - 8 at%. Radioluminescence spectra indicate a typical Ce³⁺ emission at 580 nm. Photoluminescence spectra indicate the typical Ce³⁺ 5d-4f transitions and the Tb-Ce energy transfer. The light yield is not affected by Ce concentrations in the range of 0.5 - 8 at% and was measured as 14,000 ph/MeV. The afterglow of (Lu,Y,Tb,Gd)₃Al₅O₁₂:Ce is significantly lower than that of Lu₃Al₅O₁₂:Ce and Y₃Al₅O₁₂:Ce. The (Lu,Y,Tb,Gd)₃Al₅O₁₂:Ce compositional system is a promising candidate to lead the development of high-entropy garnet scintillators.

Introduction

Rare-earth (RE) aluminum garnet scintillation crystals have been widely investigated and commercially applied in radiation detectors for medical imaging and homeland security purposes [86]. With a general formula RE₃Al₅O₁₂, RE³⁺ cations occupy dodecahedral sites in the cubic garnet crystallographic unit cell while Al³⁺ occupies both tetrahedral and octahedral sites. Luminescent activators such as Ce³⁺ and Pr³⁺ can easily substitute for the RE in the host lattice due to the similarity in ionic radius. This allows for the functionalization of the crystal as the dopant cations are essential for the emission of light through an efficient scintillation mechanism. Typical garnet scintillator compositions include Ce-doped Y₃Al₅O₁₂ (YAG:Ce) [276] and Pr-doped Lu₃Al₅O₁₂ (LuAG:Pr) [253].

Composition engineering efforts have revealed that admixing two cations in the sublattices of garnets can improve scintillation properties. Studies have focused on admixing elements to fractionally occupy the RE³⁺ and/or the Al³⁺ crystallographic sites [15]–[20]. Such investigations aimed to tailor the crystal bandgap and dopant energy levels. Compared to traditional garnet scintillators, those studies revealed that complex garnets can present improved scintillation properties such as higher light yield and faster scintillation decay time. In fact, the current brightest oxide scintillator, Gd₃Al₂Ga₃O₁₂:Ce (GGAG:Ce) was discovered in one of those studies [15].

The recent progress on the crystal growth of high-entropy oxides inspires the investigation of highly complex garnet scintillators. In such crystals, five or more cations are admixed to fractionally occupy cation sublattices. An entropy-driven phase stabilization has been reported for such complex oxides and improved functional properties in several compositional systems have been attributed to the disordered structure [40], [53]. The growth of high-entropy aluminum garnet crystals has been successfully demonstrated using the micro-pulling-down and the Czochralski methods [39], [214], [222]. Such demonstrations inspire the development of high-entropy garnet scintillators to assess the potential properties of highly disordered crystals.

In this work, we investigate the scintillation properties of $(\text{Lu}, \text{Y}, \text{Tb}, \text{Gd})_3\text{Al}_5\text{O}_{12}:\text{Ce}$ crystals with various Ce concentrations. Commas in the composition represent equiatomic ratios. The selection of the REs is based on their optical properties. The trivalent cations Lu^{3+} , Y^{3+} , and Gd^{3+} were selected because they are optically inactive and would not interact with Ce^{3+} luminescence [277]. Additionally, Tb^{3+} was selected because of the well-known Tb-Ce energy transfer, which could contribute to efficient recombination at Ce^{3+} centers [278]–[280]. Crystals with Ce concentrations in the range of 0–8 at% were grown by the micro-pulling-down (mPD) method, which is optimal for materials development due to the small amount of material needed ($\sim 1\text{g}$) and fast pulling rates (up to 20 mm/min) [37].

Methods

Composition formulation

An aluminum garnet composition with four REs in equiatomic amounts $(\text{Lu}, \text{Y}, \text{Tb}, \text{Gd})_3\text{Al}_5\text{O}_{12}:\text{Ce}$ was formulated to investigate the scintillation properties of complex crystals. Commas in the composition indicate equiatomic ratios. Lutetium, Y, and Gd were selected because they are optically inactive which is desired for host elements to prevent interactions with the dopant luminescence (Ce^{3+}). Terbium was also selected as a host element due to the widely investigated Tb-Ce energy transfer [278]–[280], which could assist the recombination of charge carriers to occur at Ce^{3+} centers rather than at other trapping centers. Seven cerium concentrations were studied, 0, 0.2, 0.5, 1, 2, 4, and 8 at%. Here, the Ce concentration represents the ratio of the RE crystallographic sites occupied by Ce. The remaining RE sites were occupied by an equiatomic mixture of the host REs. Therefore, compared to the undoped composition, in doped crystals the relative amounts of the Lu, Y, Tb, and Gd were equally decreased to accommodate the dopant.

Crystal growth

Cylindrical $\varnothing$ 3 mm crystals were grown by the mPD method using a KDN Dai-Ichi Kiden furnace with an RF generator model TR-02001 operated at 26 kVA. The starting powders were Lu_2O_3 , Y_2O_3 , Tb_2O_3 , Gd_2O_3 , Al_2O_3 , and CeO_2 of at least 99.99% purity. The powders were initially dried at 800°C for 8 h in air and then mixed in stoichiometric ratios. The powder mixtures were placed in a $\varnothing$ 16 mm iridium crucible with a $\varnothing$ 3 mm die and a $\varnothing$ 0.5 mm capillary channel. The crucible served as a melt reservoir and was inductively heated to melt the starting powders. A $\text{Lu}_3\text{Al}_5\text{O}_{12}:\text{Ce}$ crystal seed oriented in the (111) direction was used to initiate the growth. All crystals were grown with a pulling rate of 0.10 mm/min. Details about the mPD growth method and the crystal growth setup used here can be found in a previous publication [39].

Sample preparation

To assess luminescence properties, 1-mm-thick cross-sections were cut from each crystal and polished using polishing pads of 600, 800, and 1200 grit. The samples were not subjected to any further treatment and were characterized in the as-grown condition.

Absorbance

To identify the absorbance bands of both the dopant (Ce^{3+}) and host elements (Tb^{3+} and Gd^{3+}), absorbance spectra were obtained for samples with Ce at 0 and 2 at% with a Varian Cary 5000 UV–vis–NIR spectrophotometer in the 200–800 nm range at room temperature.

Radioluminescence

To identify the scintillation emission spectra, radioluminescence (or the X-ray excited luminescence) spectra were acquired under the X-ray excitation generated by a Cu-target X-ray tube operated at 35 kV and 0.1 mA. An ACTON SP-2155 monochromator was used and all measurements were performed at room temperature.

Photoluminescence

To identify the emission and excitation bands of the dopant (Ce^{3+}) and the possible Tb-Ce energy transfer, photoluminescence emission and excitation spectra were acquired at room temperature with a HORIBA Jobin Yvon Fluorolog-3 Spectrofluorometer using a 450 W continuous Xenon lamp as the excitation source.

Light yield

Pulse height spectra measurements were performed to obtain the absolute light yield of the crystals. Samples were coupled to a Hamamatsu R2059 photomultiplier tube (PMT) operated at 1.5 kV using optical grease. The samples and the PMT were covered with sheets of reflective Teflon. The samples were irradiated by a Cs-137 source. The signal processing chain used consisted of a Canberra 2005 preamplifier, an Ortec 672 amplifier set to a shaping time of 10 μ s, and a Tukan 8K multichannel analyzer. The absolute light yield was obtained by comparing the centroid of the 662 keV full energy photopeak to that of the single photoelectron (SPE). The quantum efficiency of the PMT at the emission wavelength of the crystals was taken into consideration.

Afterglow

Afterglow measurements were obtained at Radiation Monitoring Devices (RMD) in Watertown-MA using an in-house built experimental setup. Samples were irradiated by X-rays for 100 ms using an Electromed X-ray generator operated at 100 kVp, 200 mA. The sample emission was then recorded for 475 ms. Ten measurements were performed with a minute interval between measurements. The average of those measurements was taken. The samples doped with Ce at 0.5 and 2 at% were subjected to afterglow measurements. To compare the performance of the complex (Lu,Y,Tb,Gd)₃Al₅O₁₂:Ce crystals with single-RE, traditional scintillators, samples of previously grown mPD Lu₃Al₅O₁₂:Ce and Lu₃Al₅O₁₂:Ce crystals with Ce at 0.5 at 5% were prepared similarly and subjected to afterglow measurements.

Results

Grown crystals

All crystals were grown with good shape control and were transparent. Figure 11.1 is a photograph of the 1-mm-thick cross-sectional samples of all crystals under white and UV light; Ce concentrations are indicated in the figure. The undoped crystal is colorless and emits green light under UV excitation due to Tb³⁺ emission [281]. The Ce-doped crystals are yellow and their color becomes more intense with higher Ce concentrations. Their emission under UV is also yellow. In the doped crystals, an opaque layer around the surface of the samples becomes more significant with higher Ce concentrations. This opaque layer may result from eutectic inclusions previously seen in mPD high-entropy garnets containing a relatively high concentration of large REs such as Ce³⁺ [222].

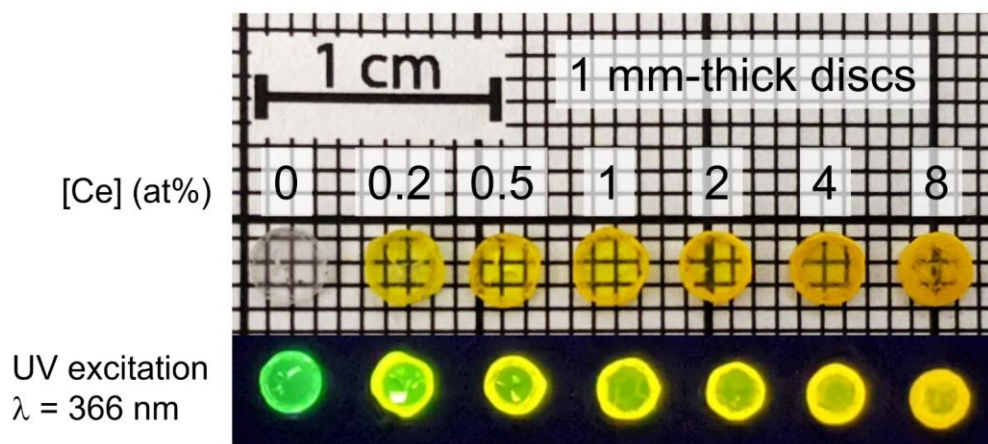


Figure 11.1 - Photo of cross-sectional samples of the crystals under white light (top) and UV excitation (bottom, $\lambda = 366 \text{ nm}$). Cerium concentration is indicated in the image.

Absorbance

Absorption bands of Ce^{3+} , Tb^{3+} , and Gd^{3+} could be identified in absorbance spectra of crystals with Ce at 0 and 2 at%, as seen in Figure 11.2. In the undoped crystal, characteristic Tb^{3+} 4f-4f absorption bands are seen around 375 nm, 325 nm, and below 300 nm as identified in Figure 11.2 [282]. A characteristic Gd^{3+} 4f-4f absorption is also expected at ~275 nm [283]. These absorption bands are also seen in the doped crystal as well as the characteristic Ce^{3+} 4f-5d₁ and 4f-5d₂ absorption bands at 456 nm and 338 nm, respectively [283]. This indicates the incorporation of the Ce^{3+} centers into the garnet structure since the absorption bands are at expected energy levels for the crystal field generated by an aluminum garnet host [284].

Photoluminescence

The characteristic Ce^{3+} and Tb^{3+} excitation and emission bands were observed in all doped crystals. Figure 11.3 contains the photoluminescence excitation and emission spectra monitored for Ce^{3+} transitions. In the undoped crystal (Ce at 0 at%), typical Tb^{3+} excitation is seen below 375 nm and emission bands are seen in the 450 - 650 nm range. For the doped samples, typical Ce^{3+} excitation and emission bands become more evident with increasing Ce concentrations. The 4f-5d₁ and 4f-5d₂ excitation bands appear at 450 nm and 340 nm, respectively, and the 5d-4f emission band appears with a maximum at 550 nm. This is an indication that the Ce^{3+} 4f and 5d energy levels are at expected relative positions within the band gap of a garnet scintillator [284].

Energy transfer from Tb^{3+} to Ce^{3+} has also been identified using photoluminescence. In Figure 11.4.a, the photoluminescence spectra of the undoped crystal are shown. The typical Tb^{3+} emission and excitation were monitored at 275 nm and 543 nm, respectively. In Figure 11.4.b, the emission spectra of the doped crystals are shown for Tb excitation monitored at 275 nm. Both the Tb^{3+} emission lines and the broad Ce^{3+} emission band are seen when Tb^{3+} centers are excited. The Ce^{3+} emission becomes more evident with an increasing Ce concentration. This indicates an energy transfer from Tb^{3+} to Ce^{3+} centers [278]–[280]. This is a desirable phenomenon since the recombination of charge carriers at Ce^{3+} centers results in faster and more efficient scintillation decay, which is a requirement for medical imaging applications [223], [285].

Radioluminescence

A typical Ce^{3+} emission band is seen overlapped with typical Tb^{3+} emissions in the radioluminescence of doped crystals. The spectra of both Ce-doped and undoped crystals are in Figure 11.5. In the undoped crystal, Tb^{3+} emission bands are in the range of 450 - 700 nm. In the doped crystals, broad Ce^{3+} emission overlaps with the Tb^{3+} emission bands. The Ce^{3+} emission becomes

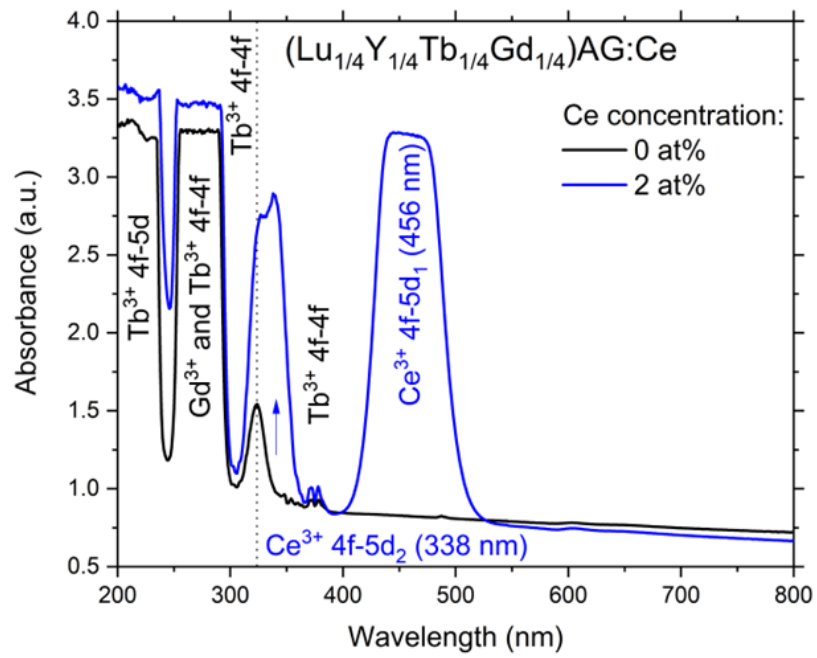


Figure 11.2 - Absorbance spectra of crystals with Ce at 0 and 2 at%. The Ce^{3+} , Tb^{3+} , and Gd^{3+} absorption bands are indicated in the figure.

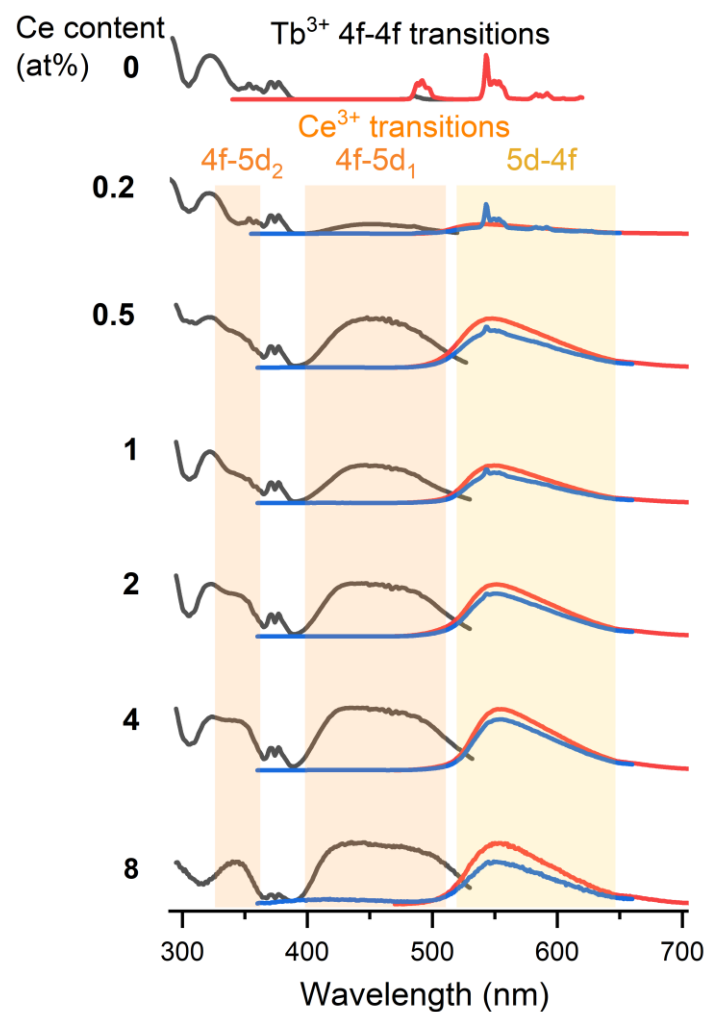


Figure 11.3 - Photoluminescence excitation (black) and emission (blue and red) monitored for Ce^{3+} .

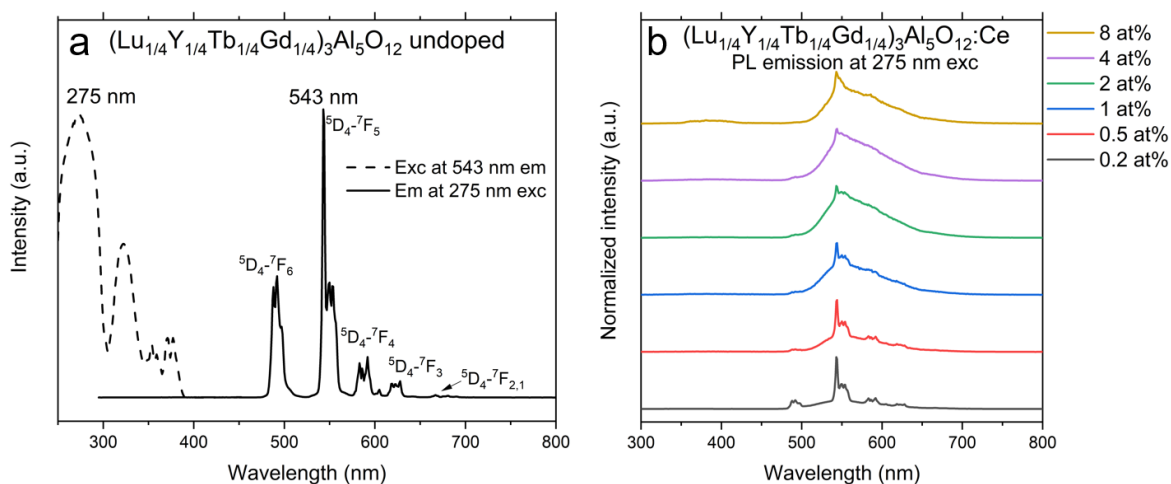


Figure 11.4 - a) Photoluminescence emission and excitation of the undoped crystal monitoring Tb^{3+} transitions. b) Photoluminescence emission of Ce-doped crystals using Tb^{3+} excitation at 275 nm.

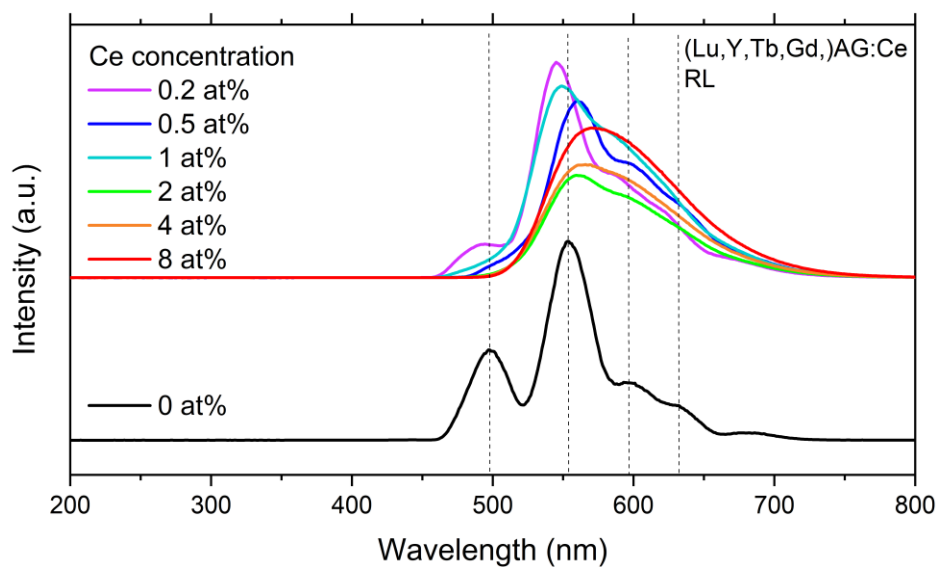


Figure 11.5 - Radioluminescence spectra of undoped and Ce-doped crystals. Typical Tb^{3+} 4f-4f emission bands are seen in the undoped crystal (bottom). Broad Ce^{3+} emission is seen in the doped crystals (top) and becomes more evident with increasing Ce concentration.

more pronounced with an increasing Ce concentration. For the sample with the highest Ce concentration (8 at%), the emission maximum is seen at ~580 nm. These results indicate that $(\text{Lu,Y,Tb,Gd})_3\text{Al}_5\text{O}_{12}:\text{Ce}$ is a promising scintillator compound since visible light is produced by irradiating the crystals with ionizing radiation (X-rays). Additionally, Ce^{3+} is a suitable luminescence activator for scintillation purposes since Ce^{3+} emission was observed in the doped samples.

Light yield

All the doped crystals with Ce in the range of 0.5 - 8 at% have light yields of 14,000 ph/MeV. The pulse height spectra of the Ce-doped crystals are shown in Figure 11.6. No photopeak was observed for the crystal with Ce at 0.2 at%. The photopeak for all other crystals is centered around channel number 550, which indicates that Ce concentration may not affect light yield in this compositional system. Taking into consideration this channel number, the quantum efficiency of the PMT, and the position of its SPE, the absolute light yield of the $(\text{Lu,Y,Tb,Gd})_3\text{Al}_5\text{O}_{12}:\text{Ce}$ crystals is 14,000 ph/MeV. This light yield is comparable to those of the first generation $\text{Lu}_3\text{Al}_5\text{O}_{12}:\text{Ce}$ (12,000 ph/MeV) [86] and $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}$ (20,300 ph/MeV) crystals [276]. Therefore, complex garnet crystals are promising candidates for the next generation of scintillators.

Afterglow

The complex $(\text{Lu,Y,Tb,Gd})_3\text{Al}_5\text{O}_{12}:\text{Ce}$ crystals have a less intense afterglow than the relatively simple $\text{Lu}_3\text{Al}_5\text{O}_{12}:\text{Ce}$ and $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}$ crystals. Afterglow profiles are shown in Figure 11.7. In the 100 ms time range, the afterglow profiles of both $(\text{Lu,Y,Tb,Gd})_3\text{Al}_5\text{O}_{12}:\text{Ce}$ crystals doped at 0.5 and 2 at% have a faster decay and a lower background intensity than the $\text{Lu}_3\text{Al}_5\text{O}_{12}:\text{Ce}$ and $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}$ crystals with Ce at 0.5 at%. Additionally, the complex crystal with Ce at 2 at% has a lower afterglow than the one with Ce at 0.5 at%, indicating that a higher dopant concentration might contribute to lowering the afterglow. This reveals an opportunity to develop low-afterglow garnet scintillators by designing complex compositions. Such scintillators would be of great interest for applications that require low afterglow such as medical imaging and X-ray radiography [246], [286].

Conclusion

At this early stage of development of high-entropy garnet scintillators, $(\text{Lu,Y,Tb,Gd})_3\text{Al}_5\text{O}_{12}:\text{Ce}$ is a promising compositional system. Crystals have an emission wavelength of ~580 nm, which is typical of aluminum garnet scintillators. Samples with various Ce concentrations have a light yield of 14,000 ph/MeV which is comparable to the emission of the traditional single-RE garnets $\text{Lu}_3\text{Al}_5\text{O}_{12}:\text{Ce}$ and $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}$. The light yield is not affected by Ce concentration in the range of 0.5 - 8 at%. Energy transfer from Tb^{3+} to Ce^{3+} was detected via

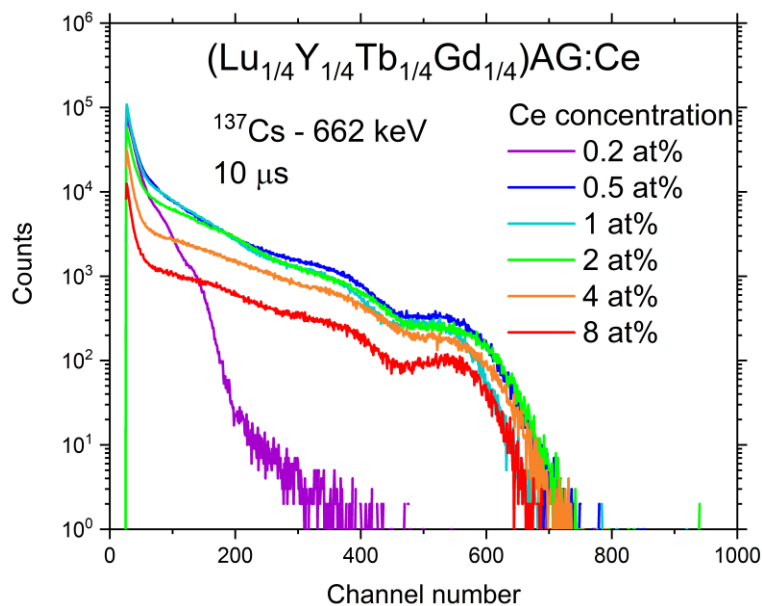


Figure 11.6 - Pulse height spectra of the $(\text{Lu}, \text{Y}, \text{Tb}, \text{Gd})_3\text{Al}_5\text{O}_{12}:\text{Ce}$ crystals.

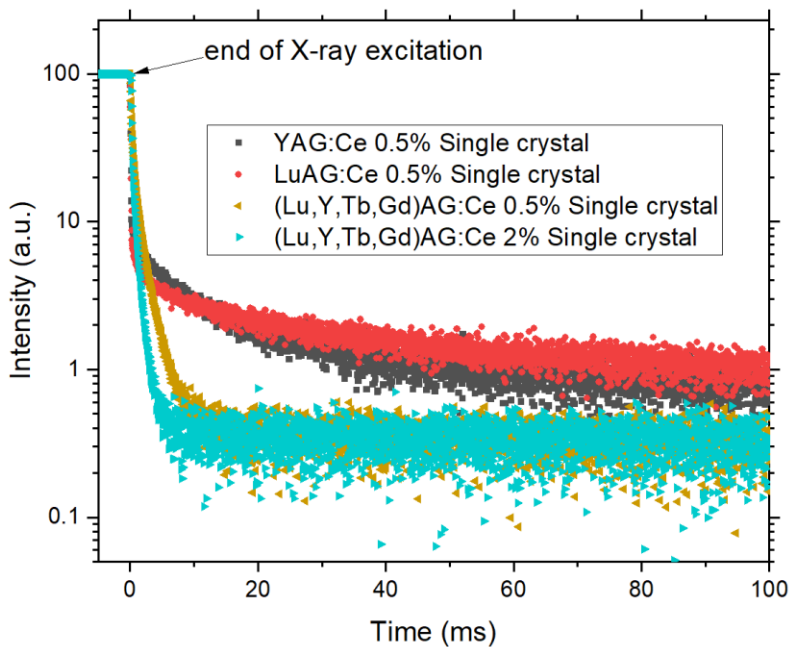


Figure 11.7 - Afterglow profiles of $(\text{Lu}, \text{Y}, \text{Tb}, \text{Gd})_3\text{Al}_5\text{O}_{12}:\text{Ce}$ crystals. Afterglow profiles of $\text{Lu}_3\text{Al}_5\text{O}_{12}:\text{Ce}$ and $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}$ is included for comparison.

photoluminescence, which may increase the probability of recombination of charge carriers at Ce^{3+} centers instead of at other charge-trapping defects. Surprisingly, the afterglow of the complex crystals is lower than those of single-RE garnets; higher Ce concentrations may further suppress the afterglow.

The field of complex garnet scintillators will benefit from this study as opportunities for future investigation arise. Further scintillation assessment is advisable to fully characterize the $(\text{Lu,Y,Tb,Gd})_3\text{Al}_5\text{O}_{12}:\text{Ce}$ scintillator and may reveal attractive properties. Such assessments include scintillation and photoluminescence decay, thermoluminescence, energy resolution, and radiation hardness. Oxidizing and reducing annealing may lead to improved scintillation properties as they may reduce the concentration of oxygen vacancies and convert possible Ce^{4+} cations into Ce^{3+} , respectively. Additionally, composition engineering studies may reveal improved performance in the $(\text{Lu,Y,Tb,Gd})_3\text{Al}_5\text{O}_{12}:\text{Ce}$ system. Although Lu, Y, Tb, and Gd have been identified as promising host elements for Ce-doped garnet crystals, their ideal relative amounts may differ from the equiatomic ratios explored here. Therefore, a systematic study should be done to optimize the host composition to obtain enhanced scintillation properties.

CHAPTER TWELVE: CONCLUSION

Structural stability and melting point of high-entropy oxides

In this dissertation, we investigated for the first time the structural behavior of high-entropy RE sesquioxides upon cooling from the melt. *In-situ* high-temperature neutron and X-ray diffraction were performed on aerodynamically levitated samples at ORNL and ANL, respectively. These specialized diffraction techniques allowed the in-depth analysis of liquid-solid and solid-solid phase transitions in highly complex oxides without the need for sample holders. The structural analysis resulting from these experiments offers a deeper understanding of the structural transitions that high-entropy sesquioxides undergo when subjected to crystal growth via directional solidification. Additionally, composition engineering studies were instrumental to revealing composition requirements for low melting points in this system. Lanthanum was identified as a key element for minimizing the melting points, which allowed the use of traditional iridium-rhenium crucibles as melt reservoirs for crystal growth experiments.

Crystal growth of RE-based oxides

For the first time, the growth of high-entropy RE sesquioxides, aluminates, and perovskites single crystals was demonstrated. The results presented here are significant progress in the field of crystal growth of complex oxides. Crystals were primarily grown via the mPD method. This crystal growth method allowed a high throughput in compositional screening studies due to the low amount of raw material needed and relatively fast growth rates. The effect of growth rate and molten zone height on phase formation and elemental distribution was determined. Additionally, the effects of average ionic radius and type of REs on phase formation and elemental distribution were assessed. Clear trends between phase formation, composition, and elemental distribution were established. Additionally, aluminate crystals were grown via the Cz method to assess the potential for scalability of the growth of high-entropy oxides. Single-phase garnet and perovskite aluminate crystals were grown via the Cz method, which is a significant indication that the growth of such complex crystals may be possible on large scale.

The potential of high-entropy garnet scintillators

In this work, the potential functional application of a high-entropy garnet crystal is demonstrated by evaluating the scintillation properties of a Ce-doped compound. Since garnet scintillators are traditionally improved by admixing no more than three REs, here we explored the scintillation properties of $(\text{Lu}, \text{Y}, \text{Tb}, \text{Gd})_3\text{Al}_5\text{O}_{12}:\text{Ce}$. A typical Ce^{3+} emission in garnet scintillators was observed at 580 nm under X-ray excitation. The light yield of 14,000 ph/MeV is comparable to those of the traditional single-RE garnets $\text{Lu}_3\text{Al}_5\text{O}_{12}:\text{Ce}$ and $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}$; the light yield is not affected by Ce concentration in the range of 0.5 – 8 at %. Surprisingly, the afterglow of the complex crystals is improved compared to the traditional $\text{Lu}_3\text{Al}_5\text{O}_{12}:\text{Ce}$ and $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}$, which is promising for applications

in X-ray radiography and medical imaging. These results inspire further investigation on highly complex garnet scintillators, since improved properties may be found by optimizing non-equiatomic compositions and exploring even more complex compounds.

Future investigation

This dissertation inspires the exploration of the crystal growth of high-entropy crystals from other oxide systems that were not addressed here. Therefore, demonstrations of the practical aspect of crystal growth of high-entropy oxides could be expanded beyond rare-earth-based sesquioxides, aluminates, and perovskites. The discovery and development of novel materials and functionalities in complex single crystals may open the door to scientific and technological progress in the next few decades. Additionally, the correlation between phase formation and AIR is a first step towards developing a predictive capability for more complex compositions.

Future experiments could explore reducing and slightly oxidizing growth atmospheres to investigate the effect of multiple charge states of some RE elements on phase formation. Elements that can present multiple charge states include Ce, Pr, Eu Tb, and Yb. Post-growth annealing can also be explored to determine the effects of the RE charge state on the phase stability of grown crystals. Additionally, X-Ray Photoelectron Spectroscopy (XPS) measurements may be instrumental in experimentally determining the cation oxidation state.

Specific suggestions for future work on crystals of the compositional systems that were included here are listed below.

High-entropy sesquioxides RE_2O_3

The next steps in the investigation of the growth of high-entropy sesquioxides should include further compositional engineering to find optimal compounds that will contain two characteristics: 1) reasonably low melting points to allow the use of iridium crucibles; and 2) the absence of polymorphic transitions. In this dissertation, compounds with La and a mixture of large, medium, and small REs satisfy characteristic 1, while compounds without La and with only smaller REs satisfy characteristic 2. Therefore, future work should focus on non-equiatomic compounds containing primarily small REs with a relatively low amount of La to minimize the melting point.

High-entropy aluminates $RE_3Al_5O_{12}$, $REAlO_3$, and $RE_4Al_2O_9$

Since the growth of high-entropy **garnet** and **perovskite** aluminate crystals with high optical quality was demonstrated here, a potential next step is to dope them with RE^{3+} luminescence activators such as Ce^{3+} , Pr^{3+} , and Yb^{3+} and

investigate luminescence properties. The scintillation and lasing performance of those crystals may surpass the ones of traditional low-entropy materials as a result of the synergistic effect in functional properties. Such improvement in properties has been previously reported for several high-entropy oxide materials and is attributed to the highly disordered cation sublattices.

In the case of **monoclinic** aluminates, further investigation is needed to identify the possible high-temperature phase transition that may be preventing the growth of single crystals. If the lattice expansion upon cooling that is typical of single-RE monoclinic aluminates is also present in high-entropy crystals, then further investigation is needed to suppress this transition. Since composition engineering was successfully applied to suppress the polymorphism in high-entropy sesquioxides, there is potential to obtain similar results in monoclinic aluminates. Different cation combinations than the ones included here and non-equiatomic compounds may result in structurally stable compounds.

High-entropy RE perovskites $RE'RE''O_3$

Since transparent high-entropy $RE'RE''O_3$ crystals were grown with the compositional disorder in the RE'' sublattice, a potential next step is to dope crystal with optical activators in either the RE' or RE'' sites. Activators that were not included in this dissertation such as Yb^{3+} , Eu^{3+} , and Nd^{3+} may result in attractive scintillation or lasing properties. Additionally, fewer cations or non-equiatomic mixtures may also result in better optical properties and suppress the formation of the La-rich inclusions seen in the crystal with the disorder in the RE'' sublattice.

REFERENCES

- [1] H. L. Bhat, *Introduction to Crystal Growth: Principles and Practice*, 1st ed. Boca Raton: CRC Press, 2014.
- [2] I. Milisavljevic and Y. Wu, "Current status of solid-state single crystal growth," *BMC Mater.*, vol. 2, no. 1, pp. 1–26, Jan. 2020, doi: 10.1186/S42833-020-0008-0.
- [3] P. Canfield, "Design, Discovery and Growth of Novel Materials For Basic Research: An Urgent U.S. Need Report on the DOE/BES Workshop: 'Future Directions of Design, Discovery and Growth of Single Crystals for Basic Research,'" US DOE Office of Science United States, Oct. 2003. doi: 10.2172/1278493.
- [4] S. G. Louie, Y. H. Chan, F. H. da Jornada, Z. Li, and D. Y. Qiu, "Discovering and understanding materials through computation," *Nat. Mater.*, vol. 20, no. 6, pp. 728–735, May 2021, doi: 10.1038/s41563-021-01015-1.
- [5] D. Bérardan, S. Franger, A. K. Meena, and N. Dragoë, "Room temperature lithium superionic conductivity in high entropy oxides," *J. Mater. Chem. A*, vol. 4, pp. 9536–9541, 2016, doi: 10.1039/c6ta03249d.
- [6] D. Bérardan, S. Franger, D. Dragoë, A. K. Meena, and N. Dragoë, "Colossal dielectric constant in high entropy oxides," *Phys. Status Solidi - Rapid Res. Lett.*, vol. 10, no. 4, pp. 328–333, 2016, doi: 10.1002/pssr.201600043.
- [7] J. L. Braun *et al.*, "Charge-Induced Disorder Controls the Thermal Conductivity of Entropy-Stabilized Oxides," *Adv. Mater.*, vol. 30, no. 51, pp. 1–8, Dec. 2018, doi: 10.1002/adma.201805004.
- [8] J. Gild *et al.*, "High-entropy fluorite oxides," *J. Eur. Ceram. Soc.*, vol. 38, no. 10, pp. 3578–3584, 2018, doi: 10.1016/j.jeurceramsoc.2018.04.010.
- [9] A. Sarkar *et al.*, "High entropy oxides for reversible energy storage," *Nat. Commun.*, vol. 9, pp. 1–9, 2018, doi: 10.1038/s41467-018-05774-5.
- [10] P. B. Meisenheimer, T. J. Kratofil, and J. T. Heron, "Giant enhancement of exchange coupling in entropy-stabilized oxide heterostructures," *Sci. Rep.*, vol. 7, no. 1, pp. 1–6, Dec. 2017, doi: 10.1038/s41598-017-13810-5.
- [11] Y. Sharma *et al.*, "Single-crystal high entropy perovskite oxide epitaxial films," *Phys. Rev. Mater.*, vol. 2, no. 6, p. 060404, Jun. 2018, doi: 10.1103/PhysRevMaterials.2.060404.
- [12] R. Witte *et al.*, "High entropy oxides: An emerging prospect for magnetic rare earth - transition metal perovskites," *Phys. Rev. Mater.*, vol. 3, no. 034406, pp. 1–8, 2019, doi: 10.1103/PhysRevMaterials.3.034406.

- [13] G. Zhang, I. Milisavljevic, K. Grzeszkiewicz, P. Stachowiak, D. Hreniak, and Y. Wu, "New optical ceramics: High-entropy sesquioxide X_2O_3 multi-wavelength emission phosphor transparent ceramics," *J. Eur. Ceram. Soc.*, vol. 41, no. 6, pp. 3621–3628, Jan. 2021, doi: 10.1016/j.jeurceramsoc.2021.01.027.
- [14] X. Chen and Y. Wu, "High-entropy transparent fluoride laser ceramics," *J. Am. Ceram. Soc.*, vol. 103, no. 2, pp. 750–756, Feb. 2020, doi: 10.1111/jace.16842.
- [15] K. Kamada *et al.*, "Scintillator-oriented combinatorial search in Ce-doped (Y,Gd) $3(Ga,Al) 5O_{12}$ multicomponent garnet compounds," *J. Phys. D. Appl. Phys.*, vol. 44, no. 50, pp. 505104–505112, Dec. 2011, doi: 10.1088/0022-3727/44/50/505104.
- [16] K. Kamada *et al.*, "Composition engineering in cerium-doped (Lu,Gd) $3(Ga,Al) 5O_{12}$ single-crystal scintillators," *Cryst. Growth Des.*, vol. 11, no. 10, pp. 4484–4490, Oct. 2011, doi: 10.1021/cg200694a.
- [17] P. Prusa, K. Kamada, M. Nikl, A. Yoshikawa, and J. A. Mares, "Light yield of (Lu, Y, Gd) $3Al_2Ga_3O_{12}$:Ce garnets," *Radiat. Meas.*, vol. 56, pp. 62–65, 2013, doi: 10.1016/j.radmeas.2013.01.055.
- [18] W. Chewpraditkul *et al.*, "Luminescence properties and scintillation response in Ce^{3+} -doped $Y_2Gd_1Al_5-xGa_xO_{12}$ ($x = 2, 3, 4$) single crystals," *J. Appl. Phys.*, vol. 116, no. 8, p. 083505, Aug. 2014, doi: 10.1063/1.4893675.
- [19] Y. Zorenko, V. Gorbenko, V. Savchyn, T. Zorenko, A. Fedorov, and O. Sidletskiy, "Development of scintillating screens based on the single crystalline films of Ce doped (Gd,Y) $3(Al,Ga,Sc)5O_{12}$ multi-component garnets," *J. Cryst. Growth*, vol. 401, pp. 532–536, Sep. 2014, doi: 10.1016/J.JCRYSGRO.2014.01.075.
- [20] W. Chewpraditkul *et al.*, "Optical and scintillation properties of Ce^{3+} -doped $YGd_2Al_5-xGa_xO_{12}$ ($x=2,3,4$) single crystal scintillators," *J. Lumin.*, vol. 169, pp. 43–50, Jan. 2016, doi: 10.1016/j.jlumin.2015.09.001.
- [21] G. Garton and B. M. Wanklyn, "The rare earth aluminates," *J. Cryst. Growth*, vol. 1, no. 3, pp. 164–166, Aug. 1967, doi: 10.1016/0022-0248(67)90028-0.
- [22] M. Pokorný *et al.*, "Gd-admixed (Lu,Gd) AlO_3 single crystals: breakthrough in heavy perovskite scintillators," *NPG Asia Mater.* 2021 131, vol. 13, no. 1, pp. 1–9, Oct. 2021, doi: 10.1038/s41427-021-00332-w.
- [23] W. Gieszczyk *et al.*, "Luminescent properties of undoped and Ce^{3+} doped crystals in Y_2O_3 Lu_2O_3 Al_2O_3 triple oxide system grown by micro-pulling-

down method,” *Opt. Mater. (Amst.)*, vol. 89, pp. 408–413, Mar. 2019, doi: 10.1016/J.OPTMAT.2019.01.023.

- [24] W. Gieszczyk *et al.*, “Luminescent properties of Tb and Eu activated $AxB_{1-x}AlO_3$ ($A = Y, Lu, Gd$; $B = Lu$; $x = 0, 0.5, 1$) mixed oxides crystals prepared by micro-pulling-down method,” *Radiat. Meas.*, vol. 126, p. 106140, Jul. 2019.
- [25] T. Horiai *et al.*, “Crystal growth and optical properties of Ce-doped (Y, Lu) AlO_3 single crystal,” *Jpn. J. Appl. Phys.*, vol. 61, no. 7, p. 072002, Jun. 2022, doi: 10.35848/1347-4065/AC7271.
- [26] M. Greculeasa *et al.*, “Bifunctional $LaxNdyGdzSc_{4-x-y-z}(BO_3)_4$ crystal: Czochralski growth, linear and nonlinear optical properties, and near-infrared laser emission performances,” *Opt. Laser Technol.*, vol. 131, p. 106433, Nov. 2020, doi: 10.1016/j.optlastec.2020.106433.
- [27] L. Gheorghe, F. Khaled, A. Achim, F. Voicu, P. Loiseau, and G. Aka, “Czochralski Growth and Characterization of Incongruent Melting $LaxGdyScz(BO_3)_4$ ($x + y + z = 4$) Nonlinear Optical Crystal,” *Cryst. Growth Des.*, vol. 16, no. 6, pp. 3473–3479, Jun. 2016, doi: 10.1021/acs.cgd.6b00446.
- [28] F. Liu *et al.*, “Crystal growth, structural characterization and laser operation of an $Yb_{0.19}Y_{0.34}Lu_{0.12}Gd_{0.35}Ca_4O(BO_3)_3$ mixed crystal,” *J. Cryst. Growth*, vol. 558, p. 126023, Mar. 2021, doi: 10.1016/j.jcrysgro.2020.126023.
- [29] W. Han, L. Dong, Y. Zhou, Y. Zhang, H. Xu, and J. Liu, “Spectroscopic properties and laser emission of $Yb_{0.05}Y_{0.20}La_{0.12}Gd_{0.63}Ca_4O(BO_3)_3$ mixed oxyborate crystal,” *Laser Phys. Lett.*, vol. 19, no. 5, p. 055802, Mar. 2022, doi: 10.1088/1612-202X/AC5B5B.
- [30] V. Jacobson, D. Diercks, B. To, A. Zakutayev, and G. Brennecke, “Thin film growth effects on electrical conductivity in entropy stabilized oxides,” *J. Eur. Ceram. Soc.*, vol. 41, no. 4, pp. 2617–2624, Apr. 2021, doi: 10.1016/j.jeurceramsoc.2020.12.021.
- [31] T. X. Nguyen *et al.*, “Exploring the First High-Entropy Thin Film Libraries: Composition Spread-Controlled Crystalline Structure,” *ACS Comb. Sci.*, vol. 22, no. 12, pp. 858–866, Dec. 2020, doi: 10.1021/acscombsci.0c00159.
- [32] S. Sivakumar, E. Zwier, P. B. Meisenheimer, and J. T. Heron, “Bulk and thin film synthesis of compositionally variant entropy-stabilized oxides,” *J. Vis. Exp.*, vol. 2018, no. 135, May 2018, doi: 10.3791/57746.

- [33] Y. Sharma *et al.*, “Magnetic Texture in Insulating Single Crystal High Entropy Oxide Spinel Films,” *ACS Appl. Mater. Interfaces*, vol. 13, pp. 17971–17977, 2021, doi: 10.1021/acsami.1c01344.
- [34] R. K. Patel *et al.*, “Epitaxial stabilization of ultra thin films of high entropy perovskite,” *Appl. Phys. Lett.*, vol. 116, no. 7, p. 71601, Feb. 2020, doi: 10.1063/1.5133710.
- [35] C. Kinsler-Fedon *et al.*, “Synthesis, characterization, and single-crystal growth of a high-entropy rare-earth pyrochlore oxide,” *Phys. Rev. Mater.*, vol. 4, no. 10, p. 104411, Oct. 2020, doi: 10.1103/PhysRevMaterials.4.104411.
- [36] C. Kinsler-Fedon *et al.*, “Effects of Au²⁺ irradiation induced damage in a high-entropy pyrochlore oxide single crystal,” *Scr. Mater.*, vol. 220, p. 114916, Nov. 2022, doi: 10.1016/J.SCRIPTAMAT.2022.114916.
- [37] T. Fukuda and V. I. Chani, *Shaped Crystals: Growth by the Micro-Pulling-Down Technique*. Berlin, Heidelberg: Springer Berlin Heidelberg, 2007.
- [38] B. R. Pamplin, *Crystal Growth*, 2nd ed. Elmsford: Pergamon Press, 1980.
- [39] M. Pianassola, M. Loveday, B. C. Chakoumakos, M. Koschan, C. L. Melcher, and M. Zhuravleva, “Crystal Growth and Elemental Homogeneity of the Multicomponent Rare-Earth Garnet (Lu_{1/6}Y_{1/6}Ho_{1/6}Dy_{1/6}Tb_{1/6}Gd_{1/6})₃Al₅O₁₂,” *Cryst. Growth Des.*, vol. 20, no. 10, pp. 6769–6776, Oct. 2020, doi: 10.1021/acs.cgd.0c00887.
- [40] B. L. Musicó *et al.*, “The emergent field of high entropy oxides: Design, prospects, challenges, and opportunities for tailoring material properties,” *APL Mater.*, vol. 8, no. 4, p. 040912, Apr. 2020, doi: 10.1063/5.0003149.
- [41] A. J. Wright, Q. Wang, C. Huang, A. Nieto, R. Chen, and J. Luo, “From high-entropy ceramics to compositionally-complex ceramics: A case study of fluorite oxides,” *J. Eur. Ceram. Soc.*, vol. 40, no. 5, pp. 2120–2129, 2020, doi: 10.1016/j.jeurceramsoc.2020.01.015.
- [42] B. S. Murty, J. W. Yeh, and S. Ranganathan, *High-Entropy Alloys*. Butterworth-Heinemann Elsevier, 2014.
- [43] S. Varalakshmi, M. Kamaraj, and B. S. Murty, “Formation and stability of equiatomic and nonequiatomic nanocrystalline CuNiCoZnAlTi high-entropy alloys by mechanical alloying,” *Metall. Mater. Trans. A Phys. Metall. Mater. Sci.*, vol. 41A, no. 10, pp. 2703–2709, 2010, doi: 10.1007/s11661-010-0344-x.

- [44] W. Chen, Z. Fu, S. Fang, Y. Wang, H. Xiao, and D. Zhu, "Processing, microstructure and properties of Al_{0.6}CoNiFeTi_{0.4} high entropy alloy with nanoscale twins," *Mater. Sci. Eng. A*, vol. 565, pp. 439–444, 2013, doi: 10.1016/j.msea.2012.12.072.
- [45] B. Gludovatz, A. Hohenwarter, D. Catoor, E. H. Chang, E. P. George, and R. O. Ritchie, "A fracture-resistant high-entropy alloy for cryogenic applications," *Science* (80-.), vol. 345, no. 6201, pp. 1153–1158, Sep. 2014, doi: 10.1126/SCIENCE.1254581.
- [46] A. Gali and E. P. George, "Tensile properties of high- and medium-entropy alloys," *Intermetallics*, vol. 39, pp. 74–78, 2013, doi: 10.1016/j.intermet.2013.03.018.
- [47] K. Jin and H. Bei, "Single-Phase Concentrated Solid-Solution Alloys: Bridging Intrinsic Transport Properties and Irradiation Resistance," *Front. Mater.*, vol. 5, no. April, pp. 1–11, 2018, doi: 10.3389/fmats.2018.00026.
- [48] Y.-F. Kao, S.-K. Chen, T.-J. Chen, P.-C. Chu, J.-W. Yeh, and S.-J. Lin, "Electrical, magnetic, and Hall properties of Al_xCoCrFeNi high-entropy alloys," *J. Alloys Compd.*, vol. 509, no. 5, pp. 1607–1614, 2011, doi: 10.1016/j.jallcom.2010.10.210.
- [49] P. Koželj *et al.*, "Discovery of a Superconducting High-Entropy Alloy," *Phys. Rev. Lett.*, vol. 113, no. 10, p. 107001, Sep. 2014, doi: 10.1103/PhysRevLett.113.107001.
- [50] S. Vrtnik *et al.*, "Superconductivity in thermally annealed Ta-Nb-Hf-Zr-Ti high-entropy alloys," *J. Alloys Compd.*, vol. 695, pp. 3530–3540, 2017, doi: 10.1016/j.jallcom.2016.11.417.
- [51] Y. Zhang, T. Zuo, Y. Cheng, and P. K. Liaw, "High-entropy alloys with high saturation magnetization, electrical resistivity, and malleability," *Sci. Rep.*, vol. 3, pp. 1–7, 2013, doi: 10.1038/srep01455.
- [52] A. J. Zaddach *et al.*, "Structure and magnetic properties of a multi-principal element Ni–Fe–Cr–Co–Zn–Mn alloy," *Intermetallics*, vol. 68, pp. 107–112, 2016, doi: 10.1016/j.intermet.2015.09.009.
- [53] C. M. Rost *et al.*, "Entropy-stabilized oxides," vol. 6, no. 1, pp. 1–8, Sep. 2015, doi: 10.1038/ncomms9485.
- [54] Y. Zhang and I. H. Jung, "Critical evaluation of thermodynamic properties of rare earth sesquioxides (RE = La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Sc and Y)," *Calphad*, vol. 58, pp. 169–203, Sep. 2017, doi: 10.1016/J.CALPHAD.2017.07.001.

- [55] A. Yoshikawa, M. Nikl, G. Boulon, and T. Fukuda, "Challenge and study for developing of novel single crystalline optical materials using micro-pulling-down method," *Opt. Mater. (Amst.)*, vol. 30, no. 1, pp. 6–10, Sep. 2007, doi: 10.1016/J.OPTMAT.2006.10.030.
- [56] G. Y. Adachi and N. Imanaka, "The binary rare earth oxides," *Chem. Rev.*, vol. 98, no. 4, pp. 1479–1514, 1998, doi: 10.1021/cr940055h.
- [57] K. P. Tseng, Q. Yang, S. J. McCormack, and W. M. Kriven, "High-entropy, phase-constrained, lanthanide sesquioxide," *J. Am. Ceram. Soc.*, vol. 103, no. 1, pp. 569–576, Jan. 2020, doi: 10.1111/jace.16689.
- [58] J. H. Mun, A. Novoselov, A. Yoshikawa, G. Boulon, and T. Fukuda, "Growth of Yb³⁺-doped Y₂O₃ single crystal rods by the micro-pulling-down method," *Mater. Res. Bull.*, vol. 40, no. 8, pp. 1235–1243, Aug. 2005, doi: 10.1016/j.materresbull.2005.04.040.
- [59] A. Novoselov, J. H. Mun, R. Simura, A. Yoshikawa, and T. Fukuda, "Micro-pulling-down: A viable approach to the crystal growth of refractory rare-earth sesquioxides," *Inorg. Mater.*, vol. 43, no. 7, pp. 729–734, Jul. 2007, doi: 10.1134/S0020168507070114.
- [60] R. Simura *et al.*, "Growth and spectroscopic properties of Yb³⁺-doped Sc₂O₃ crystals grown by the micro-pulling-down method," *Opt. Mater. (Amst.)*, vol. 30, no. 1, pp. 18–21, Sep. 2007, doi: 10.1016/j.optmat.2006.11.047.
- [61] A. Fukabori *et al.*, *Growth of Y₂O₃, Sc₂O₃ and Lu₂O₃ crystals by the micro-pulling-down method and their optical and scintillation characteristics*, vol. 318, no. 1. North-Holland, 2011, pp. 823–827.
- [62] L. Fornasiero, E. Mix, V. Peters, K. Petermann, and G. Huber, "New Oxide Crystals for Solid State Lasers," *Cryst. Res. Technol.*, vol. 34, no. 2, pp. 255–260, Feb. 1999, doi: 10.1002/(SICI)1521-4079(199902)34:2<255::AID-CRAT255>3.0.CO;2-U.
- [63] L. Fornasiero, E. Mix, V. Peters, K. Petermann, and G. Huber, "Czochralski growth and laser parameters of RE³⁺-doped Y₂O₃ and Sc₂O₃," *Ceram. Int.*, vol. 26, no. 6, pp. 589–592, Jul. 2000, doi: 10.1016/S0272-8842(99)00101-7.
- [64] Y. Yin *et al.*, "Controllable and directional growth of Er:Lu₂O₃ single crystals by the edge-defined film-fed technique," *CrystEngComm*, vol. 22, no. 39, pp. 6569–6573, Oct. 2020, doi: 10.1039/d0ce00855a.
- [65] P. Koopmann, R. Peters, K. Petermann, and G. Huber, "Crystal growth,

spectroscopy, and highly efficient laser operation of thulium-doped Lu₂O₃ around 2 μ m,” *Appl. Phys. B Lasers Opt.*, vol. 102, no. 1, pp. 19–24, Jan. 2011, doi: 10.1007/s00340-010-4361-7.

- [66] K. Petermann, L. Fornasiero, E. Mix, and V. Peters, “High melting sesquioxides: Crystal growth, spectroscopy, and laser experiments,” in *Optical Materials*, Feb. 2002, vol. 19, no. 1, pp. 67–71, doi: 10.1016/S0925-3467(01)00202-6.
- [67] V. Peters, A. Bolz, K. Petermann, and G. Huber, “Growth of high-melting sesquioxides by the heat exchanger method,” in *Journal of Crystal Growth*, Apr. 2002, vol. 237–239, no. 1-4 I, pp. 879–883, doi: 10.1016/S0022-0248(01)02054-1.
- [68] R. Peters, C. Kränkel, K. Petermann, and G. Huber, “Crystal growth by the heat exchanger method, spectroscopic characterization and laser operation of high-purity Yb:Lu₂O₃,” *J. Cryst. Growth*, vol. 310, no. 7–9, pp. 1934–1938, Apr. 2008, doi: 10.1016/j.jcrysgr.2007.10.078.
- [69] C. Krankel, “Rare-earth-doped sesquioxides for diode-pumped high-power lasers in the 1-, 2-, and 3- μ m spectral range,” *IEEE J. Sel. Top. Quantum Electron.*, vol. 21, no. 1, pp. 250–262, Jan. 2015, doi: 10.1109/JSTQE.2014.2346618.
- [70] R. Djenadic *et al.*, “Multicomponent equiatomic rare earth oxides,” *Mater. Res. Lett.*, vol. 5, no. 2, pp. 102–109, 2017, doi: 10.1080/21663831.2016.1220433.
- [71] M. Pianassola, M. Loveday, J. W. McMurray, M. Koschan, C. L. Melcher, and M. Zhuravleva, “Solid-state synthesis of multicomponent equiatomic rare-earth oxides,” *J. Am. Ceram. Soc.*, vol. 103, no. 4, pp. 2908–2918, Apr. 2020, doi: 10.1111/jace.16971.
- [72] S. V. Ushakov, S. Hayun, W. Gong, and A. Navrotsky, “Thermal Analysis of High Entropy Rare Earth Oxides,” *Mater. 2020, Vol. 13, Page 3141*, vol. 13, no. 14, p. 3141, Jul. 2020, doi: 10.3390/MA13143141.
- [73] P. Wu and A. D. Pelton, “Coupled thermodynamic-phase diagram assessment of the rare earth oxide-aluminium oxide binary systems,” *J. Alloys Compd.*, vol. 179, no. 1–2, pp. 259–287, Feb. 1992, doi: 10.1016/0925-8388(92)90227-Z.
- [74] H. Mao, M. Selleby, and O. Fabrichnaya, “Thermodynamic reassessment of the Y₂O₃-Al₂O₃-SiO₂ system and its subsystems,” *Calphad Comput. Coupling Phase Diagrams Thermochem.*, vol. 32, no. 2, pp. 399–412, Jun. 2008, doi: 10.1016/j.calphad.2008.03.003.

- [75] W. Chewpraditkul *et al.*, “Luminescence and scintillation characteristics of (GdxY3-x)Al2Ga3O12:Ce (x = 1,2,3) single crystals,” *Opt. Mater. (Amst)*, vol. 76, pp. 162–168, 2018, doi: 10.1016/j.optmat.2017.12.025.
- [76] A. Markovskiy, W. Gieszczyk, P. Bilski, A. Fedorov, T. Zorenko, and Y. Zorenko, “MPD growth of single crystals of Ce3+ doped Gd3-xLuxAl5-yGayO12 mixed garnets and their luminescent, scintillation and photoconversion properties,” *Mater. Sci. Eng. B Solid-State Mater. Adv. Technol.*, vol. 262, p. 114751, Dec. 2020, doi: 10.1016/j.mseb.2020.114751.
- [77] J. B. Shim *et al.*, “Growth and characterization of Yb3+-doped (Lu,Y)AlO3 fiber single crystals grown by the micro-pulling-down method,” *Japanese J. Appl. Physics, Part 1 Regul. Pap. Short Notes Rev. Pap.*, vol. 43, no. 11 A, pp. 7661–7664, Nov. 2004, doi: 10.1143/JJAP.43.7661.
- [78] Z. Zhao *et al.*, “High-entropy (Y0.2Nd0.2Sm0.2Eu0.2Er0.2)AlO3: A promising thermal/environmental barrier material for oxide/oxide composites,” *J. Mater. Sci. Technol.*, vol. 47, pp. 45–51, Jun. 2020, doi: 10.1016/j.jmst.2020.02.011.
- [79] H. Chen *et al.*, “High entropy (Y0.2Yb0.2Lu0.2Eu0.2Er0.2)3Al5O12: A novel high temperature stable thermal barrier material,” *Journal of Materials Science and Technology*, vol. 48. Chinese Society of Metals, pp. 57–62, Jul. 01, 2020, doi: 10.1016/j.jmst.2020.01.056.
- [80] Z. Zhao *et al.*, “High-entropy (Nd0.2Sm0.2Eu0.2Y0.2Yb0.2)4Al2O9 with good high temperature stability, low thermal conductivity, and anisotropic thermal expansivity,” *J. Adv. Ceram.*, vol. 9, no. 5, pp. 595–605, Oct. 2020, doi: 10.1007/S40145-020-0399-0.
- [81] H. Yamane, K. Ogawara, M. Omori, and T. Hirai, “Phase Transition of Rare-Earth Aluminates (RE4Al2O9) and Rare-Earth Gallates (RE4Ga2O9),” *J. Am. Ceram. Soc.*, vol. 78, no. 9, pp. 2385–2390, Sep. 1995, doi: 10.1111/j.1151-2916.1995.tb08673.x.
- [82] M. Gervais and A. Douy, “Solid phase transformation and melting of the compounds Ln4Al2O9 (Ln = Gd, Dy, Y),” *Mater. Sci. Eng. B*, vol. 38, no. 1–2, pp. 118–121, Mar. 1996, doi: 10.1016/0921-5107(95)01322-9.
- [83] Y. Miyazawa, M. Mori, and S. Honma, “Interface shape transitions in the Czochralski growth of Dy3Al5O12,” *J. Cryst. Growth*, vol. 43, no. 4, pp. 541–542, May 1978, doi: 10.1016/0022-0248(78)90357-3.
- [84] A. O. Ivanov *et al.*, “Generation of stimulated emission of holmium in the 2 micron region in aluminum holmium garnet crystals,” *KvanE*, vol. 2, pp. 186–188, 1975, Accessed: Mar. 16, 2021. [Online]. Available:

<https://ui.adsabs.harvard.edu/abs/1975KvanE...2..186I/abstract>.

- [85] K. Papagelis, G. Kanellis, T. Zorba, S. Ves, and G. A. Kourouklis, "Infrared lattice spectra of $\text{Tm}_3\text{Al}_5\text{O}_{12}$ and $\text{Yb}_3\text{Al}_5\text{O}_{12}$ single crystals," *J. Phys. Condens. Matter*, vol. 14, no. 4, pp. 915–923, Feb. 2002, doi: 10.1088/0953-8984/14/4/323.
- [86] M. Nikl *et al.*, "Development of LuAG-based scintillator crystals - A review," *Prog. Cryst. Growth Charact. Mater.*, vol. 59, no. 2, pp. 47–72, 2013, doi: 10.1016/j.pcrysgrow.2013.02.001.
- [87] A. Ikesue, Y. L. Aung, T. Taira, T. Kamimura, K. Yoshida, and G. L. Messing, "Progress in ceramic lasers," *Annu. Rev. Mater. Res.*, vol. 36, no. 3, pp. 397–429, 2006, doi: 10.1146/annurev.matsci.36.011205.152926.
- [88] V. I. Chani, A. Yoshikawa, H. Machida, and T. Fukuda, "(Tb,Yb) $3\text{Al}_5\text{O}_{12}$ garnet: Crystal-chemistry and fiber growth by micro-pulling-down technique," *Mater. Sci. Eng. B Solid-State Mater. Adv. Technol.*, vol. 75, no. 1, pp. 53–60, May 2000, doi: 10.1016/S0921-5107(00)00382-2.
- [89] H. Ogino, A. Yoshikawa, M. Nikl, A. Krasnikov, K. Kamada, and T. Fukuda, "Growth and scintillation properties of Pr-doped $\text{Lu}_3\text{Al}_5\text{O}_{12}$ crystals," in *Journal of Crystal Growth*, Jan. 2006, vol. 287, no. 2, pp. 335–338, doi: 10.1016/j.jcrysgro.2005.11.023.
- [90] J. Didierjean *et al.*, "High-power laser with Nd:YAG single-crystal fiber grown by the micro-pulling-down technique," *Opt. Lett.*, vol. 31, no. 23, p. 3468, Dec. 2006, doi: 10.1364/OL.31.003468.
- [91] Y. Zong, G. Zhao, J. Zhu, and J. Xu, "Growth and its spectroscopic properties of Sm:YAP crystal," *J. Cryst. Growth*, vol. 291, no. 2, pp. 468–471, Jun. 2006, doi: 10.1016/j.jcrysgro.2006.03.003.
- [92] H. Zhang *et al.*, "Structure, defects, and spectroscopic properties of a Yb, Ho, Pr:YAP laser crystal," *J. Alloys Compd.*, vol. 672, pp. 223–228, Jul. 2016, doi: 10.1016/j.jallcom.2016.02.060.
- [93] X. Zeng *et al.*, "Crystal growth and optical properties of LaAlO_3 and Ce-doped LaAlO_3 single crystals," *J. Cryst. Growth*, vol. 271, no. 1–2, pp. 319–324, Oct. 2004, doi: 10.1016/j.jcrysgro.2004.07.032.
- [94] P. Arhipov *et al.*, "Growth and characterization of large CeAlO_3 perovskite crystals," *J. Cryst. Growth*, vol. 430, pp. 116–121, Nov. 2015, doi: 10.1016/j.jcrysgro.2015.08.025.
- [95] S. Turczynski *et al.*, "Czochralski crystal growth, thermal conductivity, and

magnetic properties of $\text{Pr}_x\text{La}_{1-x}\text{AlO}_3$, where $x = 1, 0.75, 0.55, 0.40, 0$,” *Cryst. Growth Des.*, vol. 11, no. 4, pp. 1091–1097, Apr. 2011, doi: 10.1021/cg101273y.

- [96] Y. Miyazawa, H. Toshima, and S. Morita, “The growth of NdAlO_3 single crystals by Czochralski method,” *J. Cryst. Growth*, vol. 128, no. 1-4 PART 2, pp. 668–671, Mar. 1993, doi: 10.1016/S0022-0248(07)80021-2.
- [97] H. M. O'Bryan, P. K. Gallagher, G. W. Berkstresser, and C. D. Brandle, “Thermal analysis of rare earth gallates and aluminates,” *J. Mater. Res.*, vol. 5, no. 1, pp. 183–189, Jan. 1990, doi: 10.1557/JMR.1990.0183.
- [98] J. W. M. Verweij, M. T. Cohen-Adad, D. Bouttet, H. Lantesse, B. Moine, and C. Pédrini, “Luminescence properties of GdAlO_3 : Ce powders. Dependence on reduction conditions,” *Chem. Phys. Lett.*, vol. 239, no. 1–3, pp. 51–55, Jun. 1995, doi: 10.1016/0009-2614(95)00439-B.
- [99] M. Sekita, Y. Miyazawa, S. Morita, H. Sekiwa, and Y. Sato, “Strong Tb^{3+} emission of TbAlO_3 at room temperature,” *Appl. Phys. Lett.*, vol. 65, no. 19, pp. 2380–2382, Nov. 1994, doi: 10.1063/1.112682.
- [100] Y. Okano, T. Ikeya, K. Hoshikawa, and T. Fukuda, “Behavior of RAIO_3 ($R=\text{Ho, Er and Dy}$) during crystal growth by the Czochralski method,” *Journal of Crystal Growth*, vol. 131, no. 3–4. North-Holland, pp. 616–619, Aug. 01, 1993, doi: 10.1016/0022-0248(93)90215-I.
- [101] O. Buryy *et al.*, “Thermal changes of the crystal structure and the influence of thermo-chemical annealing on the optical properties of YbAlO_3 crystals,” *J. Phys. Condens. Matter*, vol. 22, no. 5, p. 055902, Jan. 2010, doi: 10.1088/0953-8984/22/5/055902.
- [102] W. Drozdowski, A. J. Wojtowicz, D. Wiśniewski, T. Łukasiewicz, and J. Kisielewski, “Scintillation properties of Pr-activated LuAlO_3 ,” in *Optical Materials*, Jan. 2006, vol. 28, no. 1–2, pp. 102–105, doi: 10.1016/j.optmat.2004.09.031.
- [103] J. Pejchal, J. Barta, T. Trojek, R. Kucerkova, A. Beitlerova, and M. Nikl, “Luminescence and scintillation properties of rare-earth-doped LaAlO_3 single crystals,” *Radiat. Meas.*, vol. 121, pp. 26–31, Feb. 2019, doi: 10.1016/j.radmeas.2018.11.010.
- [104] A. Novoselov, A. Yoshikawa, J. Pejchal, M. Nikl, and T. Fukuda, “Crystal growth and scintillation properties of Ce-doped PrAlO_3 ,” *Opt. Mater. (Amst.)*, vol. 30, no. 1, pp. 168–170, Sep. 2007, doi: 10.1016/j.optmat.2006.11.050.
- [105] A. Szysiak *et al.*, “The investigation of $\text{YAlO}_3\text{-NdAlO}_3$ system, synthesis and

characterization,” *J. Alloys Compd.*, vol. 509, no. 35, pp. 8615–8619, Sep. 2011, doi: 10.1016/j.jallcom.2011.06.049.

- [106] M. Zhuravleva, A. Novoselov, A. Yoshikawa, J. Pejchal, M. Nikl, and T. Fukuda, “Crystal growth and scintillation properties of Pr-doped YAlO₃,” *Opt. Mater. (Amst)*., vol. 30, no. 1, pp. 171–173, Sep. 2007, doi: 10.1016/j.optmat.2006.11.057.
- [107] S. Derenzo *et al.*, “Dense Ce³⁺-activated scintillator materials Synthesis and characterization of scintillators View project TOF PET View project DENSE Ce ³⁺-ACTIVATED SCINTILLATOR MATERIALS.” Accessed: Mar. 16, 2021. [Online]. Available: <https://www.researchgate.net/publication/268328770>.
- [108] W. Drozdowski, K. Brylew, M. Malinowski, and S. Turczyński, “Scintillation properties of μ pD-grown Y₄Al₂O₉:Pr (YAM:Pr) crystals,” *J. Alloys Compd.*, vol. 632, pp. 816–821, May 2015, doi: 10.1016/j.jallcom.2015.01.274.
- [109] W. Drozdowski *et al.*, “A preliminary assessment of Lu₂Y₂Al₂O₉:Pr (LuYAM:Pr) as a potential scintillator,” *Radiat. Meas.*, vol. 93, pp. 41–45, Oct. 2016, doi: 10.1016/j.radmeas.2016.06.009.
- [110] K. Ito, K. Tezuka, and Y. Hinatsu, “Preparation, Magnetic Susceptibility, and Specific Heat on Interlanthanide Perovskites ABO₃ (A=La–Nd, B=Dy–Lu),” *J. Solid State Chem.*, vol. 157, no. 1, pp. 173–179, Feb. 2001, doi: 10.1006/JSSC.2000.9071.
- [111] K. L. Ovanesyan, A. G. Petrosyan, G. O. Shirinyan, C. Pedrini, and L. Zhang, “Czochralski single crystal growth of Ce- and Pr-doped LaLuO₃ double oxide,” *J. Cryst. Growth*, vol. 198–199, no. PART I, pp. 497–500, Mar. 1999, doi: 10.1016/S0022-0248(98)01091-4.
- [112] U. Berndt, D. Maier, and C. Keller, “New AlIIIBIIIIO₃ interlanthanide perovskite compounds,” *J. Solid State Chem.*, vol. 13, no. 1–2, pp. 131–135, Feb. 1975, doi: 10.1016/0022-4596(75)90090-0.
- [113] K. L. Ovanesyan, A. G. Petrosyan, G. O. Shirinyan, C. Pedrini, and L. Zhang, “Single crystal growth and characterization of LaLuO₃,” *Opt. Mater. (Amst)*., vol. 10, no. 4, pp. 291–295, Sep. 1998, doi: 10.1016/S0925-3467(98)00008-1.
- [114] R. Uecker *et al.*, “Large-lattice-parameter perovskite single-crystal substrates,” *J. Cryst. Growth*, vol. 457, pp. 137–142, Jan. 2017, doi: 10.1016/J.JCRYSGRO.2016.03.014.
- [115] M. Ilatovskaia, S. Sun, I. Saenko, G. Savinykh, and O. Fabrichnaya,

“Experimental Investigation of Phase Relations in the ZrO₂-La₂O₃-Yb₂O₃ System,” *J. Phase Equilibria Diffus.*, vol. 41, no. 4, pp. 311–328, Aug. 2020, doi: 10.1007/S11669-020-00790-9/FIGURES/9.

- [116] M. Bharathy, A. H. Fox, S. J. Mugavero, and H. C. zur Loye, “Crystal growth of inter-lanthanide LaLn'O₃ (Ln' = Y, Ho–Lu) perovskites from hydroxide fluxes,” *Solid State Sci.*, vol. 11, no. 3, pp. 651–654, Mar. 2009, doi: 10.1016/J.SOLIDSTATESCIENCES.2008.10.005.
- [117] S. E. Derenzo, M. J. Weber, E. Bourret-Courchesne, and M. K. Klintenberg, “The quest for the ideal inorganic scintillator,” *Nucl. Instruments Methods Phys. Res. Sect. A Accel. Spectrometers, Detect. Assoc. Equip.*, vol. 505, no. 1–2, pp. 111–117, Jun. 2003, doi: 10.1016/S0168-9002(03)01031-3.
- [118] Y. Sharma *et al.*, “Magnetic anisotropy in single-crystal high-entropy perovskite oxide La(Cr_{0.2}Mn_{0.2}Fe_{0.2}Co_{0.2}Ni_{0.2})O₃ films,” *Phys. Rev. Mater.*, vol. 4, no. 1, p. 014404, Jan. 2020, doi: 10.1103/PhysRevMaterials.4.014404.
- [119] H. Rétot, S. Blahuta, A. Bessière, B. Viana, B. LaCourse, and E. Mattmann, “Improved scintillation time response in (Lu_{0.5}Gd_{0.5})₂O₃: Eu³⁺ compared with Lu₂O₃: Eu³⁺ transparent ceramics,” *J. Phys. D. Appl. Phys.*, vol. 44, no. 23, p. 235101, May 2011, doi: 10.1088/0022-3727/44/23/235101.
- [120] Y. Futami *et al.*, “Optical and scintillation properties of Sc₂O₃, Y₂O₃ and Lu₂O₃ transparent ceramics synthesized by SPS method,” *Radiat. Meas.*, vol. 55, pp. 136–140, Aug. 2013, doi: 10.1016/J.RADMEAS.2013.01.014.
- [121] T. Yanagida, Y. Fujimoto, H. Yagi, and T. Yanagitani, “Optical and scintillation properties of transparent ceramic Yb:Lu₂O₃ with different Yb concentrations,” *Opt. Mater. (Amst.)*, vol. 36, no. 6, pp. 1044–1048, Apr. 2014, doi: 10.1016/J.OPTMAT.2014.01.022.
- [122] K. Beil *et al.*, “Yb-doped mixed sesquioxides for ultrashort pulse generation in the thin disk laser setup,” *Appl. Phys. B* 2013 1131, vol. 113, no. 1, pp. 13–18, Apr. 2013, doi: 10.1007/S00340-013-5433-2.
- [123] C. Kränkel *et al.*, “Czochralski growth of mixed cubic sesquioxide crystals in the ternary system Lu₂O₃–Sc₂O₃–Y₂O₃,” *Acta Crystallogr.*, no. 4, pp. 550–558, Jul. 2021, doi: 10.1107/S2052520621005321.
- [124] R. D. Shannon and C. T. Prewitt, “Effective ionic radii in oxides and fluorides,” *Acta Crystallogr. Sect. B Struct. Crystallogr. Cryst. Chem.*, vol. 25, no. 5, pp. 925–946, May 1969, doi: 10.1107/s0567740869003220.
- [125] A. Fukabori, V. Chani, K. Kamada, and A. Yoshikawa, “Growth of Yb-doped

Y₂O₃, Sc₂O₃, and Lu₂O₃ single crystals by the micro-pulling-down technique and their optical and scintillation characterization,” *J. Cryst. Growth*, vol. 352, no. 1, pp. 124–128, Aug. 2012, doi: 10.1016/J.JCRYSGRO.2012.01.027.

- [126] R. Uecker, “The historical development of the Czochralski method,” *J. Cryst. Growth*, vol. 401, pp. 7–24, Sep. 2014, doi: 10.1016/J.JCRYSGRO.2013.11.095.
- [127] C. D. Brandle, “Czochralski growth of oxides,” *J. Cryst. Growth*, vol. 264, no. 4, pp. 593–604, Mar. 2004, doi: 10.1016/J.JCRYSGRO.2003.12.044.
- [128] B. Cantor, I. T. H. Chang, P. Knight, and A. J. B. Vincent, “Microstructural development in equiatomic multicomponent alloys,” *Mater. Sci. Eng. A*, vol. 375–377, pp. 213–218, Jul. 2004, doi: 10.1016/j.msea.2003.10.257.
- [129] J.-W. Yeh *et al.*, “Nanostructured High-Entropy Alloys with Multiple Principal Elements: Novel Alloy Design Concepts and Outcomes,” *Adv. Eng. Mater.*, vol. 6, no. 5, pp. 299–303, May 2004, doi: 10.1002/adem.200300567.
- [130] D. . Miracle and O. N. Senkov, “A critical review of high entropy alloys and related concepts,” *Acta Mater.*, vol. 122, no. October, pp. 448–511, 2017, doi: 10.1016/j.actamat.2016.08.081.
- [131] A. V. Trukhanov *et al.*, “Control of electromagnetic properties in substituted M-type hexagonal ferrites,” *J. Alloys Compd.*, vol. 754, pp. 247–256, Jul. 2018, doi: 10.1016/J.JALLCOM.2018.04.150.
- [132] A. V. Trukhanov, V. O. Turchenko, I. A. Bobrikov, S. V. Trukhanov, I. S. Kazakevich, and A. M. Balagurov, “Crystal structure and magnetic properties of the BaFe_{12–x}Al_xO₁₉ (x=0.1–1.2) solid solutions,” *J. Magn. Magn. Mater.*, vol. 393, pp. 253–259, Nov. 2015, doi: 10.1016/J.JMMM.2015.05.076.
- [133] C. Agca, J. C. Neuefeind, J. W. McMurray, R. Weber, and A. Navrotsky, “Melting temperature measurement of refractory oxide ceramics as a function of oxygen fugacity using containerless methods,” *J. Am. Ceram. Soc.*, vol. 103, no. 9, pp. 4867–4875, Sep. 2020, doi: 10.1111/JACE.17216.
- [134] J. Neuefeind, M. Feygenson, J. Carruth, R. Hoffmann, and K. K. Chipley, “The Nanoscale Ordered Materials Diffractometer NOMAD at the Spallation Neutron Source SNS,” *Nucl. Instruments Methods Phys. Res. Sect. B Beam Interact. with Mater. Atoms*, vol. 287, pp. 68–75, Sep. 2012, doi: 10.1016/J.NIMB.2012.05.037.
- [135] S. Calder *et al.*, “A suite-level review of the neutron powder diffraction instruments at Oak Ridge National Laboratory,” *Rev. Sci. Instrum.*, vol. 89,

no. 9, p. 092701, Sep. 2018, doi: 10.1063/1.5033906.

- [136] L. B. Skinner *et al.*, "Structure of Molten CaSiO_3 : Neutron Diffraction Isotope Substitution with Aerodynamic Levitation and Molecular Dynamics Study," *J. Phys. Chem. B*, vol. 116, no. 45, pp. 13439–13447, Nov. 2012, doi: 10.1021/JP3066019.
- [137] C. J. Benmore and J. K. R. Weber, "Aerodynamic levitation, supercooled liquids and glass formation," *Adv. Phys. X*, vol. 2, no. 3, pp. 717–736, May 2017, doi: 10.1080/23746149.2017.1357498.
- [138] V. P. Glushko, *Termicheskie Konstanty, Veshchestv (Thermal Constants of Substances)*. Moscow: VINITI, 1981.
- [139] R. J. Ackermann and E. G. Rauh, "The thermodynamic properties of substoichiometric yttrium sesquioxide," *J. Chem. Thermodyn.*, vol. 5, no. 3, pp. 331–340, May 1973, doi: 10.1016/S0021-9614(73)80021-7.
- [140] C. E. Curtis and J. R. Johnson, "Ceramic Properties of Samarium Oxide and Gadolinium Oxide; X-Ray Studies of Other Rare-Earth Oxides and Some Compounds," *J. Am. Ceram. Soc.*, vol. 40, no. 1, pp. 15–19, Jan. 1957, doi: 10.1111/J.1151-2916.1957.TB12541.X.
- [141] M. Foex and J. P. Traverse, "Investigations about crystalline transformation in rare earths sesquioxides at high temperature," *Rev. Int. des hautes Temp. des Refract*, vol. 3, pp. 429–453, 1966.
- [142] W. Wien, "On the division of energy in the emissionspectrum of a black body," *London, Edinburgh, Dublin Philos. Mag. J. Sci.*, vol. 43, pp. 214–220, 1897.
- [143] M. Zinkevich, "Thermodynamics of rare earth sesquioxides," *Prog. Mater. Sci.*, vol. 52, no. 4, pp. 597–647, May 2007, doi: 10.1016/J.PMATSCI.2006.09.002.
- [144] P. P. Fedorov, M. V. Nazarkin, and R. M. Zakalyukin, "On polymorphism and morphotropism of rare earth sesquioxides," *Crystallogr. Reports* 2002 472, vol. 47, no. 2, pp. 281–286, Mar. 2002, doi: 10.1134/1.1466504.
- [145] J. M. Badie, "Phases et transitions de phases à haute température dans les systèmes Sc_2O_3 - Ln_2O_3 (Ln = lanthanide et yttrium)," *Rev. Int. Hautes Temp.*, vol. 15, pp. 183–199, 1978.
- [146] A. Pavlik III, S. V. Ushakov, A. Navrotsky, C. J. Benmore, and R. J. K. Weber, "Structure and thermal expansion of Lu_2O_3 and Yb_2O_3 up to the melting points," *J. Nucl. Mater.*, vol. 495, pp. 385–391, Nov. 2017, doi:

10.1016/J.JNUCMAT.2017.08.031.

- [147] V. F. Sears, "Neutron scattering lengths and cross sections," *Neutron News*, vol. 3, no. 3, pp. 26–37, Jan. 1992, doi: 10.1080/10448639208218770.
- [148] Y. Tomm, P. Reiche, D. Klimm, and T. Fukuda, "Czochralski grown Ga₂O₃ crystals," *J. Cryst. Growth*, vol. 220, no. 4, pp. 510–514, Dec. 2000, doi: 10.1016/S0022-0248(00)00851-4.
- [149] G. Y. Adachi and N. Imanaka, *Binary Rare Earth Oxides*, vol. 98, no. 4. Springer Netherlands, 2004.
- [150] M. K. Hossain, S. Hossain, M. H. Ahmed, M. I. Khan, N. Haque, and G. A. Raihan, "A Review on Optical Applications, Prospects, and Challenges of Rare-Earth Oxides," *ACS Appl. Electron. Mater.*, vol. 3, no. 9, pp. 3715–3746, Sep. 2021, doi: 10.1021/ACSAELM.1C00682/ASSET/IMAGES/LARGE/EL1C00682_0019.JPEG.
- [151] M. K. Hossain, M. I. Khan, and A. El-Denglawey, "A review on biomedical applications, prospects, and challenges of rare earth oxides," *Appl. Mater. Today*, vol. 24, p. 101104, Sep. 2021, doi: 10.1016/J.APMT.2021.101104.
- [152] M. K. Hossain, M. H. Ahmed, M. I. Khan, M. S. Miah, and S. Hossain, "Recent Progress of Rare Earth Oxides for Sensor, Detector, and Electronic Device Applications: A Review," *ACS Appl. Electron. Mater.*, vol. 3, no. 10, pp. 4255–4283, Oct. 2021, doi: 10.1021/ACSAELM.1C00703/ASSET/IMAGES/LARGE/EL1C00703_0016.JPEG.
- [153] C. L. Tracy, M. Lang, F. Zhang, C. Trautmann, and R. C. Ewing, "Phase transformations in Ln₂O₃ materials irradiated with swift heavy ions," *Phys. Rev. B - Condens. Matter Mater. Phys.*, vol. 92, no. 17, p. 174101, Nov. 2015, doi: 10.1103/PHYSREVB.92.174101/FIGURES/12/MEDIUM.
- [154] B. Cheng *et al.*, "Pressure-induced tuning of lattice distortion in a high-entropy oxide," *Commun. Chem.*, vol. 2, no. 1, pp. 1–9, Sep. 2019, doi: 10.1038/s42004-019-0216-2.
- [155] T. Park *et al.*, "Effect of processing route on the crystal structure and physical properties of bixbyite high-entropy oxides," *J. Alloys Compd.*, vol. 893, p. 162108, Feb. 2022, doi: 10.1016/J.JALLCOM.2021.162108.
- [156] Y. Xing, W. Dan, Y. Fan, and X. Li, "Low temperature synthesis of high-entropy (Y_{0.2}Yb_{0.2}Sm_{0.2}Eu_{0.2}Er_{0.2})₂O₃ nanofibers by a novel electrospinning method," *J. Mater. Sci. Technol.*, vol. 103, pp. 215–220, Mar.

2022, doi: 10.1016/J.JMST.2021.06.057.

- [157] S. Nundy *et al.*, “Bandgap Engineering in Novel Fluorite-Type Rare Earth High-Entropy Oxides (RE-HEOs) with Computational and Experimental Validation for Photocatalytic Water Splitting Applications,” *Adv. Sustain. Syst.*, p. 2200067, 2022, doi: 10.1002/adsu.202200067.
- [158] J. Dąbrowa *et al.*, “Stabilizing fluorite structure in ceria-based high-entropy oxides: Influence of Mo addition on crystal structure and transport properties,” *J. Eur. Ceram. Soc.*, vol. 40, no. 15, pp. 5870–5881, Dec. 2020, doi: 10.1016/J.JEURCERAMSOC.2020.07.014.
- [159] M. N. Yapyrintsev, I. V. Sudzhanskaya, R. A. Lyubushkin, and E. N. Yapyrintseva, “Synthesis and electric transportation properties of high-entropy oxides based on cerium oxide,” *IOP Conf. Ser. Mater. Sci. Eng.*, vol. 1014, no. 1, p. 012059, Jan. 2021, doi: 10.1088/1757-899X/1014/1/012059.
- [160] Y. Sun *et al.*, “Preparation and properties of CMAS resistant bixbyite structured high-entropy oxides RE₂O₃ (RE = Sm, Eu, Er, Lu, Y, and Yb): Promising environmental barrier coating materials for Al₂O₃f/Al₂O₃ composites,” *J. Adv. Ceram.*, vol. 10, no. 3, pp. 596–613, Mar. 2021, doi: 10.1007/S40145-021-0461-6.
- [161] P. T. Sawbridge and N. A. Waterman, “On the thermal expansion and crystallography of cubic (C) and monoclinic (B) forms of Gd₂O₃ in the temperature range 20 to 900°C,” *J. Mater. Sci.* 1968 31, vol. 3, no. 1, pp. 15–18, Jan. 1968, doi: 10.1007/BF00550884.
- [162] M. Pianassola *et al.*, “Tuning the melting point and phase stability of rare-earth oxides facilitates their crystal growth from the melt,” *J. Adv. Ceram.*, vol. 11, no. 9, pp. 1479–1490, 2022, doi: <https://doi.org/10.1007/s40145-022-0625-z>.
- [163] B. H. Toby and R. B. Von Dreele, “GSAS-II: the genesis of a modern open-source all purpose crystallography software package,” *J. Appl. Crystallogr.*, vol. 46, no. 2, pp. 544–549, 2013, doi: 10.1107/S0021889813003531.
- [164] S. Krishnan, J. K. R. Weber, R. A. Schiffman, P. C. Nordine, and R. A. Reed, “Refractive Index of Liquid Aluminum Oxide at 0.6328 μm ,” *J. Am. Ceram. Soc.*, vol. 74, no. 4, pp. 881–883, Apr. 1991, doi: 10.1111/J.1151-2916.1991.TB06947.X.
- [165] R. Weber, S. K. Wilke, and C. J. Benmore, “Containerless Techniques for in-situ X-Ray Measurements on Materials in Extreme Conditions,” *J. Phys. Soc. Japan*, vol. 91, p. 091008, May 2022, doi: 10.7566/JPSJ.91.091008.

- [166] J. K. R. Weber, C. J. Benmore, G. Jennings, M. C. Wilding, and J. B. Parise, "Instrumentation for fast in-situ X-ray structure measurements on non-equilibrium liquids," *Nucl. Instruments Methods Phys. Res. Sect. A Accel. Spectrometers, Detect. Assoc. Equip.*, vol. 624, no. 3, pp. 728–730, Dec. 2010, doi: 10.1016/J.NIMA.2010.09.125.
- [167] J. K. R. Weber *et al.*, "Aerodynamic levitator for in situ x-ray structure measurements on high temperature and molten nuclear fuel materials," *Rev. Sci. Instrum.*, vol. 87, no. 7, p. 073902, Jul. 2016, doi: 10.1063/1.4955210.
- [168] A. P. Hammersley, "FIT2D: a multi-purpose data reduction, analysis and visualization program," *J. Appl. Crystallogr.*, vol. 49, no. 2, pp. 646–652, 2016, doi: 10.1107/S1600576716000455.
- [169] T. D. Chikalla, C. E. Mcneilly, and F. P. Roberts, "Polymorphic Modifications of Pm_2O_3 ," *J. Am. Ceram. Soc.*, vol. 55, no. 8, pp. 428–429, Aug. 1972, doi: 10.1111/J.1151-2916.1972.TB11329.X.
- [170] S. G. Tresvyatkii and A. W. Lopato, L M Schwetschenko, "Untersuchung Des, KAE Einflusses Hochschmelzender Oxide Der Elemente II. Gruppe Des Periodischen Systems. Auf Polymorphe Hochtem-Peratur-Umwandlungen von Oxiden Der Seltenerdelemente," *Colloq Intern Cent. Natl. Rech Sci. Paris*, vol. 205, pp. 247–253, 1971.
- [171] J. Coutures, A. Rouanet, R. Verges, and M. Foex, "Etude a haute température des systèmes formes par le sesquioxyde de lanthane et les sesquioxydes de lanthanides. I. Diagrammes de phases ($1400^\circ\text{C} < T < T$ Liquide)," *J. Solid State Chem.*, vol. 17, no. 1–2, pp. 171–182, Feb. 1976, doi: 10.1016/0022-4596(76)90218-8.
- [172] M. Mizuno, T. Yamada, and T. Noguchi, "Phase diagrams of the system $\text{Al}_2\text{O}_3\text{-Eu}_2\text{O}_3$ and $\text{Al}_2\text{O}_3\text{-Gd}_2\text{O}_3$ at high temperatures," *Yogyo Kyokai-Shi*, vol. 85, no. 11, pp. 543–548, 1977.
- [173] A. V. Shevthenko and L. M. Lopato, "DTA method applikation to the highest refractory oxide systems investigation," *Thermochim. Acta*, vol. 93, no. C, pp. 537–540, Sep. 1985, doi: 10.1016/0040-6031(85)85135-2.
- [174] F. Weigel and V. Scherer, "Chemistry of promethium. II. Polymorphism of promethium-(III) oxide," *Radiochim. Acta*, vol. 4, no. 4, pp. 197–202, 1965.
- [175] C. Agca *et al.*, "In Situ High-Temperature Synchrotron Diffraction Studies of $(\text{Fe,Cr,Al})_3\text{O}_4$ Spinel," *Inorg. Chem.*, vol. 59, no. 9, pp. 5949–5957, May 2020, doi: 10.1021/ACS.INORGCHEM.9B03726.
- [176] D. Reig-I-Plessis *et al.*, "Structural transition and orbital glass physics in

near-itinerant CoV_2O_4 ,” *Phys. Rev. B*, vol. 93, no. 1, p. 014437, Jan. 2016, doi: 10.1103/PHYSREVB.93.014437/FIGURES/5/MEDIUM.

- [177] M. Lepple *et al.*, “Thermochemistry and phase stability of the polymorphs of yttrium tantalate, YTaO_4 ,” *J. Eur. Ceram. Soc.*, vol. 41, no. 2, pp. 1629–1638, Feb. 2021, doi: 10.1016/J.JEURCERAMSOC.2020.10.039.
- [178] H. Iida *et al.*, “Ferroelectricity and Ferrimagnetism of Hexagonal YbFeO_3 Thin Films,” *J. Phys. Soc. Japan*, vol. 81, no. 2, p. 024719, Jan. 2012, doi: 10.1143/JPSJ.81.024719.
- [179] B. Cockayne, B. Lent, J. S. Abell, and I. R. Harris, “Cracking in yttrium orthoaluminate single crystals,” *J. Mater. Sci.*, vol. 8, pp. 871–875, 1973.
- [180] Y. Lu, J. Wang, Y. Yang, Y. Dai, B. Sun, and S. Li, “Czochralski growth of YAP crystal doped with high Tm concentration,” *J. Cryst. Growth*, vol. 292, no. 2, pp. 381–385, 2006.
- [181] J. G. Li and Y. Sakka, “Recent progress in advanced optical materials based on gadolinium aluminate garnet ($\text{Gd}_3\text{Al}_5\text{O}_{12}$),” *Science and Technology of Advanced Materials*, vol. 16, no. 1. Institute of Physics Publishing, p. 14902, Feb. 18, 2015, doi: 10.1088/1468-6996/16/1/014902.
- [182] X. Ren, Z. Tian, J. Zhang, and J. Wang, “Equiatomic quaternary $(\text{Y}_{1/4}\text{Ho}_{1/4}\text{Er}_{1/4}\text{Yb}_{1/4})_2\text{SiO}_5$ silicate: A perspective multifunctional thermal and environmental barrier coating material,” *Scr. Mater.*, vol. 168, pp. 47–50, Jul. 2019, doi: 10.1016/J.SCRIPTAMAT.2019.04.018.
- [183] H. Chen, H. Xiang, F. Z. Dai, J. Liu, and Y. Zhou, “High entropy $(\text{Yb}_{0.25}\text{Y}_{0.25}\text{Lu}_{0.25}\text{Er}_{0.25})_2\text{SiO}_5$ with strong anisotropy in thermal expansion,” *J. Mater. Sci. Technol.*, vol. 36, pp. 134–139, Jan. 2020, doi: 10.1016/J.JMST.2019.07.022.
- [184] Z. Zhao *et al.*, “ $(\text{La}_{0.2}\text{Ce}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2})\text{PO}_4$: A high-entropy rare-earth phosphate monazite ceramic with low thermal conductivity and good compatibility with Al_2O_3 ,” *J. Mater. Sci. Technol.*, vol. 35, no. 12, pp. 2892–2896, Dec. 2019, doi: 10.1016/J.JMST.2019.08.012.
- [185] D. Maier, D. Rhede, R. Bertram, D. Klimm, and R. Fornari, “Dopant segregations in oxide single-crystal fibers grown by the micro-pulling-down method,” *Opt. Mater. (Amst.)*, vol. 30, no. 1, pp. 11–14, Sep. 2007, doi: 10.1016/J.OPTMAT.2006.10.023.
- [186] R. Simura, A. Yoshikawa, and S. Uda, “The radial distribution of dopant (Cr, Nd, Yb, or Ce) in yttrium aluminum garnet ($\text{Y}_3\text{Al}_5\text{O}_{12}$) single crystals grown by the micro-pulling-down method,” *J. Cryst. Growth*, vol. 311, no. 23–24,

pp. 4763–4769, Dec. 2009, doi: 10.1016/J.JCRYSGRO.2009.07.012.

- [187] M. Sugiyama *et al.*, “Dopant segregation in rare earth doped lutetium aluminum garnet single crystals grown by the micro-pulling down method,” *J. Cryst. Growth*, vol. 352, no. 1, pp. 110–114, Aug. 2012, doi: 10.1016/J.JCRYSGRO.2011.12.039.
- [188] Y. Yokota *et al.*, “Improvement of dopant distribution in radial direction of single crystals grown by micro-pulling-down method,” *J. Cryst. Growth*, vol. 474, pp. 178–182, Sep. 2017, doi: 10.1016/J.JCRYSGRO.2016.11.119.
- [189] S. Uda, J. Kon, K. Shimamura, and T. Fukuda, “Analysis of Ge distribution in Si1 – xGe_x single crystal fibers by the micro-pulling down method,” *J. Cryst. Growth*, vol. 167, no. 1–2, pp. 64–73, Sep. 1996, doi: 10.1016/0022-0248(96)00237-0.
- [190] B. Cockayne, D. B. Gasson, D. Findlay, D. W. Goodwin, and R. A. Clay, “The growth and laser characteristics of yttrium-gadolinium-aluminium garnet single crystals,” *J. Phys. Chem. Solids*, vol. 29, no. 6, pp. 905–910, Jun. 1968, doi: 10.1016/0022-3697(68)90225-4.
- [191] A. O. Ivanov, I. V Mochalov, A. M. Tkachuk, V. A. Fedorov, and P. P. Feofilov, “Emission of $\lambda \approx 2 \mu$ stimulated radiation by holmium in aluminum holmium garnet crystals,” *Sov. J. Quantum Electron.*, vol. 5, no. 1, pp. 115–116, Jan. 1975, doi: 10.1070/QE1975V005N01ABEH010821.
- [192] S Ganschow, D Klimm, P Reiche, and R Uecker, “On the Crystallization of Terbium Aluminium Garnet,” *Cryst. Res. Technol.*, vol. 34, no. 5–6, pp. 615–619, 1999.
- [193] S. Ganschow, D. Klimm, B. M. Epelbaum, A. Yoshikawa, J. Doerschel, and T. Fukuda, *Growth conditions and composition of terbium aluminum garnet single crystals grown by the micro pulling down technique*, vol. 225, no. 2–4. North-Holland, 2001, pp. 454–457.
- [194] M. Geho, T. Sekijima, and T. Fujii, “Growth mechanism of incongruently melting terbium aluminum garnet (Tb₃Al₅O₁₂; TAG) single crystals by laser FZ method,” *J. Cryst. Growth*, vol. 275, no. 1–2, pp. e663–e667, Feb. 2005, doi: 10.1016/J.JCRYSGRO.2004.11.048.
- [195] G. M. Sheldrick, “A short history of SHELX,” *Acta Crystallogr., Sect. A Found. Crystallogr.*, vol. A64, pp. 112–122, 2008, doi: 10.1107/S0108767307043930.
- [196] L. J. Farrugia, “WinGX and ORTEP for Windows: an update,” *J. Appl. Cryst.*, vol. 45, pp. 849–854, 2012, doi: 10.1107/S0021889812029111.

- [197] A. Emiraliev, A. G. Kocharov, R. V Bakradze, U. Karimov, and Z. I. Ahmetzhanov, "The neutron diffraction redefinition of the coordinates of the atoms of oxygen in yttrio-aluminium garnet," *Kristallografiya*, vol. 21, pp. 211–213, 1976.
- [198] F. Euler and J. A. Bruce, "Oxygen coordinates of compounds with garnet structure," *Acta Crystallogr.*, vol. 19, no. 6, pp. 971–978, Dec. 1965, doi: 10.1107/S0365110X65004747.
- [199] H. Kimura, M. Sakamoto, T. Numazawa, M. Sato, and H. Maeda, "Crystal growth of large size Dy₃Al₅O₁₂ Garnet single crystals," *J. Cryst. Growth*, vol. 99, no. 1–4, pp. 850–853, Jan. 1990, doi: 10.1016/S0022-0248(08)80039-5.
- [200] G. A. Slack and D. W. Oliver, "Thermal Conductivity of Garnets and Phonon Scattering by Rare-Earth Ions," *Phys. Rev. B*, vol. 4, no. 2, p. 592, Jul. 1971, doi: 10.1103/PhysRevB.4.592.
- [201] C. D. Brandle, A. J. Valentino, and G. W. Berkstresser, "Czochralski growth of rare-earth orthosilicates (Ln₂SiO₅)," *J. Cryst. Growth*, vol. 79, no. 1–3, pp. 308–315, Dec. 1986, doi: 10.1016/0022-0248(86)90454-9.
- [202] M. Zhuravleva, A. Novoselov, A. Yoshikawa, J. Pejchal, M. Nikl, and T. Fukuda, "Scintillating properties of Pr-doped YAlO₃ single crystals grown by the micro-pulling-down method," *Inorg. Mater.*, vol. 43, no. 7, pp. 753–757, Jul. 2007, doi: 10.1134/S0020168507070163.
- [203] A. Novoselov *et al.*, "Crystal growth, optical and luminescence properties of Pr-doped Y₂SiO₅ single crystals," *Opt. Mater. (Amst.)*, vol. 29, no. 11, pp. 1381–1384, Jul. 2007, doi: 10.1016/J.OPTMAT.2006.04.017.
- [204] G. Samanta, A. Yeckel, P. Daggolu, H. Fang, E. D. Bourret-Courchesne, and J. J. Derby, "Analysis of limits for sapphire growth in a micro-pulling-down system," *J. Cryst. Growth*, vol. 335, no. 1, pp. 148–159, Nov. 2011, doi: 10.1016/J.JCRYSGRO.2011.09.015.
- [205] A. Karati, T. Parida, J. Gupta, H. K. Adigilli, P. H. Borse, and J. Joardar, "Band-gap engineering in novel delafossite-type multicomponent oxides for photocatalytic degradation of methylene blue," *Mater. Res. Bull.*, vol. 137, p. 111181, May 2021, doi: 10.1016/j.materresbull.2020.111181.
- [206] L. Sun *et al.*, "A multicomponent γ -type (Gd_{1/6}Tb_{1/6}Dy_{1/6}Tm_{1/6}Yb_{1/6}Lu_{1/6})₂Si₂O₇ disilicate with outstanding thermal stability," *Mater. Res. Lett.*, vol. 8, no. 11, pp. 424–430, Nov. 2020, doi: 10.1080/21663831.2020.1783007.

- [207] K. Kamada *et al.*, “Czochralski growth and scintillation properties of Ce:(Gd,Y,Lu)₃(Al,Ga)₄O₁₂ single crystals,” *IEEE Trans. Nucl. Sci.*, vol. 61, no. 1, pp. 293–296, 2014, doi: 10.1109/TNS.2013.2285613.
- [208] H. Chen *et al.*, “High entropy (Y_{0.2}Yb_{0.2}Lu_{0.2}Eu_{0.2}Er_{0.2})₃Al₅O₁₂: A novel high temperature stable thermal barrier material,” *J. Mater. Sci. Technol.*, vol. 48, pp. 57–62, Jul. 2020, doi: 10.1016/J.JMST.2020.01.056.
- [209] G. N. Kotsonis *et al.*, “Property and cation valence engineering in entropy-stabilized oxide thin films,” *Phys. Rev. Mater.*, vol. 4, no. 10, p. 100401, Oct. 2020, doi: 10.1103/PhysRevMaterials.4.100401.
- [210] G. N. Kotsonis, C. M. Rost, D. T. Harris, and J. P. Maria, “Epitaxial entropy-stabilized oxides: Growth of chemically diverse phases via kinetic bombardment,” *MRS Commun.*, vol. 8, no. 3, pp. 1371–1377, Sep. 2018, doi: 10.1557/mrc.2018.184.
- [211] Y. Liang, B. Luo, H. Dong, and D. Wang, “Electronic structure and transport properties of sol-gel-derived high-entropy Ba(Zr_{0.2}Sn_{0.2}Ti_{0.2}Hf_{0.2}Nb_{0.2})O₃ thin films,” *Ceram. Int.*, Apr. 2021, doi: 10.1016/j.ceramint.2021.04.026.
- [212] Y. W. Chen, J. J. Ruan, J. M. Ting, Y. H. Su, and K. S. Chang, “Solution-based fabrication of high-entropy Ba(Ti,Hf,Zr,Fe,Sn)O₃ films on fluorine-doped tin oxide substrates and their piezoelectric responses,” *Ceram. Int.*, vol. 47, no. 8, pp. 11451–11458, Apr. 2021, doi: 10.1016/j.ceramint.2020.12.272.
- [213] A. Kirnbauer, C. Spadt, C. M. Koller, S. Kolozsvári, and P. H. Mayrhofer, “High-entropy oxide thin films based on Al–Cr–Nb–Ta–Ti,” *Vacuum*, vol. 168, p. 108850, Oct. 2019, doi: 10.1016/j.vacuum.2019.108850.
- [214] M. Pianassola *et al.*, “Czochralski growth and characterization of the multicomponent garnet (Lu_{1/4}Yb_{1/4}Y_{1/4}Gd_{1/4})₃Al₅O₁₂,” *Phys. Rev. Mater.*, vol. 5, no. 8, p. 083401, Aug. 2021, doi: 10.1103/PhysRevMaterials.5.083401.
- [215] I. A. Bondar, L. N. Koroleva, and E. T. Bezruk, “Physicochemical properties of yttrium aluminates and gallates,” *Izv. Akad. Nauk SSSR, Neorg. Mater.*, vol. 20, no. 2, pp. 257–261, 1984.
- [216] Rigaku, *CrystalClear*. Tokyo, Japan: Rigaku Corporation, 2005.
- [217] J. Hammann, “Etude par diffraction de neutrons à 0,31°K de la structure antiferromagnétique des grenats d’aluminium–terbium et d’aluminium–holmium,” *Acta Crystallogr. Sect. B Struct. Crystallogr. Cryst. Chem.*, vol. 25,

no. 9, pp. 1853–1856, Sep. 1969, doi: 10.1107/s0567740869004833.

- [218] A. Bombik, B. Leśniewska, J. Mayer, and A. W. Pacyna, “Crystal structure of solid solutions $\text{REFe}_{1-x}(\text{Al or Ga})\text{O}_3$ ($\text{RE} = \text{Tb, Er, Tm}$) and the correlation between superexchange interaction $\text{Fe}^{+3}\text{-O-Fe}^{+3}$ linkage angles and Néel temperature,” *J. Magn. Magn. Mater.*, vol. 257, no. 2–3, pp. 206–219, Feb. 2003, doi: 10.1016/S0304-8853(02)01172-1.
- [219] I. A. Bondar and L. P. Mezentseva, “Single crystals of rare-earth oxides: Constitution and properties,” *Prog. Cryst. Growth Charact.*, vol. 16, no. C, pp. 81–141, Jan. 1988, doi: 10.1016/0146-3535(88)90016-0.
- [220] V. M. Orera and J. Llorca, “Directionally Solidified Eutectic Oxide Ceramics,” in *Encyclopedia of Materials: Science and Technology*, Elsevier, 2005, pp. 1–9.
- [221] K. Bartosiewicz *et al.*, “Effects of La doping on the crystal growth, phase stability and scintillation properties of $\text{Lu}_3\text{Al}_5\text{O}_{12}$ single crystals,” *Mater. Sci. Eng. B Solid-State Mater. Adv. Technol.*, vol. 261, p. 114677, Nov. 2020, doi: 10.1016/j.mseb.2020.114677.
- [222] M. Pianassola, M. Alexander, B. Chakoumakos, M. Koschan, C. Melcher, and M. Zhuravleva, “Effects of composition and growth parameters on phase formation in multicomponent aluminum garnet crystals,” *Acta Crystallogr. B. Struct. Sci. Cryst. Eng. Mater.*, vol. 78, pp. 476–484, Jun. 2022, doi: 10.1107/S2052520622002967/TQ5001SUP2.PDF.
- [223] M. Nikl, A. Yoshikawa, M. Nikl, and A. Yoshikawa, “Recent R&D Trends in Inorganic Single-Crystal Scintillator Materials for Radiation Detection,” *Adv. Opt. Mater.*, vol. 3, no. 4, pp. 463–481, Apr. 2015, doi: 10.1002/ADOM.201400571.
- [224] I. F. Elder and M. J. P. Payne, “YAP versus YAG as a diode-pumped host for thulium,” *Opt. Commun.*, vol. 148, no. 4–6, pp. 265–269, Mar. 1998, doi: 10.1016/S0030-4018(97)00714-1.
- [225] O. Sakthong *et al.*, “Luminescence and scintillation properties of Mo co-doped $\text{Y}_{0.8}\text{Gd}_{2.2}(\text{Al}_{5-x}\text{Ga}_x)\text{O}_{12}$: Ce multicomponent garnet crystals,” *Opt. Mater. (Amst.)*, vol. 122, p. 111783, Dec. 2021, doi: 10.1016/J.OPTMAT.2021.111783.
- [226] T. Shishido, S. Nojima, M. Tanaka, H. Horiuchi, and T. Fukuda, “Flux growth of perovskite-type RAIO_3 single crystals,” *J. Alloys Compd.*, vol. 227, no. 2, pp. 175–179, Sep. 1995, doi: 10.1016/0925-8388(95)01622-8.
- [227] R. Diehl and G. Brandt, “Crystal structure refinement of YAIO_3 , a promising

- laser material,” *Mater. Res. Bull.*, vol. 10, no. 2, pp. 85–90, Feb. 1975, doi: 10.1016/0025-5408(75)90125-7.
- [228] M. Mizuno, “Phase diagrams of the systems $\text{Al}_2\text{O}_3\text{-Ho}_2\text{O}_3$ and $\text{Al}_2\text{O}_3\text{-Er}_2\text{O}_3$ at high temperatures,” *Yogyo Kyokaishi*, vol. 87, no. 8, pp. 405–412, 1979.
- [229] L. Holmes, R. Sherwood, and L. G. Van Uitert, “Metamagnetism in TbAlO_3 ,” *J. Appl. Phys.*, vol. 39, no. 2, p. 1373, Nov. 2003, doi: 10.1063/1.1656310.
- [230] C. J. Shilpa *et al.*, “ $\text{GdAlO}_3\text{:Eu}^{3+}\text{:Bi}^{3+}$ nanophosphor: Synthesis and enhancement of red emission for WLEDs,” *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.*, vol. 133, pp. 550–558, Dec. 2014, doi: 10.1016/J.SAA.2014.05.082.
- [231] A. P. Sakhya, A. Dutta, S. Shannigrahi, and T. Sinha, “Electronic structure, optical dielectric constant and born effective charge of EuAlO_3 ,” *J. Phys. Chem. Solids*, vol. 88, pp. 1–7, Jan. 2016, doi: 10.1016/J.JPCS.2015.09.004.
- [232] S. Geller and V. B. Bala, “Crystallographic studies of perovskite-like compounds. II. Rare earth aluminates,” *Acta Crystallogr.*, vol. 9, no. 12, pp. 1019–1025, Dec. 1956, doi: 10.1107/S0365110X56002965.
- [233] H. Brusset, M. H. Gillier-Pandraud, and M. C. Saine, “Sur des gallates et aluminates mixtes de lanthanides,” *Mater. Res. Bull.*, vol. 10, no. 6, pp. 481–488, Jun. 1975, doi: 10.1016/0025-5408(75)90171-3.
- [234] M. Tanaka, T. Shishido, H. Horiuchi, N. Toyota, D. Shindo, and T. Fukuda, “Structure studies of CeAlO_3 ,” *J. Alloys Compd.*, vol. 192, no. 1–2, pp. 87–89, Feb. 1993, doi: 10.1016/0925-8388(93)90194-R.
- [235] J. Pejchal *et al.*, “Untangling the controversy on Ce^{3+} luminescence in LaAlO_3 crystals,” *Mater. Adv.*, vol. 3, no. 8, pp. 3500–3512, Apr. 2022, doi: 10.1039/D1MA01083B.
- [236] G. Okada *et al.*, “Characterizations of Ce-doped $\text{Y}_4\text{Al}_2\text{O}_9$ Crystals for Scintillator Applications,” *Sensors Mater.*, vol. 30, no. 7, pp. 1547–1554, 2018, doi: 10.18494/SAM.2018.1919.
- [237] W. Drozdowski, K. Brylew, M. Malinowski, and S. Turczyński, “Scintillation properties of μPD -grown $\text{Y}_4\text{Al}_2\text{O}_9\text{:Pr}$ (YAM:Pr) crystals,” *J. Alloys Compd.*, vol. 632, pp. 816–821, May 2015, doi: 10.1016/J.JALLCOM.2015.01.274.
- [238] M. Kaczkan, S. Turczyński, D. A. Pawlak, M. Wencka, and M. Malinowski, “Laser site-selective spectroscopy of Eu^{3+} ions doped $\text{Y}_4\text{Al}_2\text{O}_9$,” *Opt.*

Mater. (Amst)., vol. 58, pp. 412–417, Aug. 2016, doi: 10.1016/J.OPTMAT.2016.06.023.

- [239] Z. Boruc, B. Fetlinski, M. Kaczkan, S. Turczynski, D. Pawlak, and M. Malinowski, "Temperature and concentration quenching of Tb³⁺ emissions in Y₄Al₂O₉ crystals," *J. Alloys Compd.*, vol. 532, pp. 92–97, Aug. 2012, doi: 10.1016/J.JALLCOM.2012.04.017.
- [240] Y. shu Lian *et al.*, "Structural and fluorescence features of Dy³⁺:Y₄Al₂O₉ phosphors for yellow color emitting displays," *Vacuum*, vol. 173, p. 109165, Mar. 2020, doi: 10.1016/J.VACUUM.2020.109165.
- [241] B. Fetlinski, Z. Boruc, M. Kaczkan, S. Turczynski, D. Pawlak, and M. Malinowski, "Sensitisation of Pr³⁺ in Y₄Al₂O₉:Ce³⁺+Pr³⁺ system for down-conversion of solar spectrum," *J. Lumin.*, vol. 181, pp. 133–137, Jan. 2017, doi: 10.1016/J.JLUMIN.2016.09.008.
- [242] H. Xiang, Z. Feng, Z. Li, and Y. Zhou, "Crystal structure, mechanical and thermal properties of Yb₄Al₂O₉: A combination of experimental and theoretical investigations," *J. Eur. Ceram. Soc.*, vol. 37, no. 6, pp. 2491–2499, Jun. 2017, doi: 10.1016/J.JEURCERAMSOC.2017.02.016.
- [243] S. H. White, H. F. Shaw, and J. M. Huggett, "The use of back-scattered electron imaging for the petrographic study of sandstones and shales," *J. Sediment. Res.*, vol. 54, no. 2, pp. 487–494, Jun. 1984, doi: 10.1306/212F844F-2B24-11D7-8648000102C1865D.
- [244] H. Li *et al.*, "Enhancement of photocatalytic activity in Tb/Eu co-doped Bi₂MoO₆: the synergistic effect of Tb–Eu redox cycles," *RSC Adv.*, vol. 6, no. 53, pp. 48089–48098, May 2016, doi: 10.1039/C6RA08739F.
- [245] A. D. Sontakke, J. Ueda, Y. Katayama, Y. Zhuang, P. Dorenbos, and S. Tanabe, "Role of electron transfer in Ce³⁺ sensitized Yb³⁺ luminescence in borate glass," *J. Appl. Phys.*, vol. 117, no. 1, p. 013105, Jan. 2015, doi: 10.1063/1.4905317.
- [246] C. W. E. van Eijk, "Radiation detector developments in medical applications: inorganic scintillators in positron emission tomography," *Radiat. Prot. Dosimetry*, vol. 129, no. 1–3, pp. 13–21, Mar. 2008, doi: 10.1093/RPD/NCN043.
- [247] S. Nagashima, K. Ueda, and T. Omata, "Site-Dependent Tb³⁺ Luminescence by Energy Transfer from Ce³⁺ in Ce³⁺-Tb³⁺ Codoped LaLuO₃," *J. Phys. Chem. C*, vol. 126, no. 14, pp. 6499–6504, Apr. 2022, doi: 10.1021/ACS.JPCC.2C01074/ASSET/IMAGES/LARGE/JP2C01074_0007.JPEG.

- [248] K. Ueda, S. Tanaka, T. Yoshino, Y. Shimizu, and T. Honma, "Site-Selective Doping and Site-Sensitive Photoluminescence of Eu^{3+} and Tb^{3+} in Perovskite-Type LaLuO_3 ," *Inorg. Chem.*, vol. 58, no. 16, pp. 10890–10897, Aug. 2019, doi: 10.1021/ACS.INORGCHEM.9B01273/ASSET/IMAGES/LARGE/IC-2019-01273M_0007.JPEG.
- [249] J. R. Carruthers, "Radial Solute Segregation in Czochralski Growth," *J. Electrochem. Soc.*, vol. 114, no. 9, p. 959, Sep. 1967, doi: 10.1149/1.2426790.
- [250] A. D. W. Jones, "Hydrodynamics of Czochralski growth-A review of the effects of rotation and buoyancy force," *Prog. Cryst. Growth Charact.*, vol. 9, no. 1–2, pp. 139–168, Jan. 1984, doi: 10.1016/0146-3535(84)90099-6.
- [251] S. Abbasoglu and I. Sezai, "Three-dimensional modelling of melt flow and segregation during Czochralski growth of GexSi_{1-x} single crystals," *Int. J. Therm. Sci.*, vol. 46, no. 6, pp. 561–572, Jun. 2007, doi: 10.1016/j.ijthermalsci.2006.07.010.
- [252] R. R. Monchamp, "The distribution coefficient on neodymium and lutetium in Czochralski grown $\text{Y}_3\text{Al}_5\text{O}_{12}$," *J. Cryst. Growth*, vol. 11, no. 3, pp. 310–312, Dec. 1971, doi: 10.1016/0022-0248(71)90101-1.
- [253] H. Ogino, A. Yoshikawa, M. Nikl, K. Kamada, and T. Fukuda, "Scintillation characteristics of Pr-doped $\text{Lu}_3\text{Al}_5\text{O}_{12}$ single crystals," *J. Cryst. Growth*, vol. 292, no. 2, pp. 239–242, Jul. 2006.
- [254] H. Sato, K. Shimamura, V. Sudesh, M. Ito, H. Machida, and T. Fukuda, "Growth and characterization of Tm, Ho-codoped $\text{Lu}_3\text{Al}_5\text{O}_{12}$ single crystals by the Czochralski technique," *J. Cryst. Growth*, vol. 234, no. 2–3, pp. 463–468, Jan. 2002, doi: 10.1016/S0022-0248(01)01724-9.
- [255] Y. Kuwano, "Effective distribution coefficient of neodymium in $\text{Nd}:\text{Gd}_3\text{Ga}_5\text{O}_{12}$ crystals grown by the Czochralski method," *J. Cryst. Growth*, vol. 57, no. 2, pp. 353–361, Apr. 1982, doi: 10.1016/0022-0248(82)90491-2.
- [256] K. Kamada *et al.*, "2 inch diameter single crystal growth and scintillation properties of $\text{Ce}:\text{Gd}_3\text{Al}_2\text{Ga}_3\text{O}_{12}$," in *Journal of Crystal Growth*, Aug. 2012, vol. 352, no. 1, pp. 88–90, doi: 10.1016/j.jcrysgr.2011.11.085.
- [257] Z. Jia *et al.*, "Growth and properties of $\text{Nd}:(\text{LuGd}_{1-x})_3\text{Ga}_5\text{O}_{12}$ laser crystal by Czochralski method," *Opt. Mater. (Amst.)*, vol. 31, no. 2, pp. 346–349, Oct. 2008, doi: 10.1016/j.optmat.2008.05.008.

- [258] Z. Chen, L. Yang, Y. Hang, and X. Wang, "Preparation and characterization of highly transparent Ce³⁺ doped terbium gallium garnet single crystal," *Opt. Mater. (Amst)*, vol. 47, pp. 39–43, Sep. 2015, doi: 10.1016/j.optmat.2015.06.050.
- [259] Y. Kuwano, S. Saito, and U. Hase, "Crystal growth and optical properties of Nd: GGAG," *J. Cryst. Growth*, vol. 92, no. 1–2, pp. 17–22, Oct. 1988, doi: 10.1016/0022-0248(88)90427-7.
- [260] Q. Sai, D. Zhou, C. Xia, X. Xu, J. Di, and L. Wang, "Spectroscopic properties of Nd³⁺:Lu₃ScAl₄O₁₂ single crystal," *Laser Phys.*, vol. 23, no. 11, p. 115801, Nov. 2013, doi: 10.1088/1054-660X/23/11/115801.
- [261] I. Baumann, P. Rudolph, D. Krabe, and R. Schalge, "Orthoscopic investigation of the axial optical and compositional homogeneity of Czochralski grown LiNbO₃ crystals," *J. Cryst. Growth*, vol. 128, no. 1-4 PART 2, pp. 903–908, Mar. 1993, doi: 10.1016/S0022-0248(07)80067-4.
- [262] M. Kürten and J. Schilz, "Czochralski growth of SiGe_{1-x} single crystals," *J. Cryst. Growth*, vol. 139, no. 1–2, pp. 1–5, May 1994, doi: 10.1016/0022-0248(94)90021-3.
- [263] P. S. Dutta and A. G. Ostrogorsky, "Suppression of cracks in In_xGa_{1-x}Sb crystals through forced convection in the melt," *J. Cryst. Growth*, vol. 194, no. 1, pp. 1–7, Nov. 1998, doi: 10.1016/S0022-0248(98)00621-6.
- [264] I. Yonenaga, "Czochralski growth of GeSi bulk alloy crystals," *J. Cryst. Growth*, vol. 198–199, no. PART I, pp. 404–408, Mar. 1999, doi: 10.1016/S0022-0248(98)00992-0.
- [265] B. Bauer and P. Gille, "Crystal growth of al-rich complex metallic phases in the System Al-Cr-Fe using the czochralski method," *Zeitschrift für Anorg. und Allg. Chemie*, vol. 637, no. 13, pp. 2052–2058, Nov. 2011, doi: 10.1002/zaac.201100290.
- [266] K. Bader and P. Gille, "Single Crystal Growth of FeGa₃ and FeGa_{3-x}Gex from High-Temperature Solution Using the Czochralski Method," *Cryst. Res. Technol.*, vol. 55, no. 2, p. 1900067, Feb. 2020, doi: 10.1002/crat.201900067.
- [267] C. Gugushev *et al.*, "Czochralski growth and characterization of perovskite-type (La,Nd)(Lu,Sc)O₃ single crystals with a pseudocubic lattice parameter of about 4.09 Å," *J. Cryst. Growth*, vol. 536, p. 125526, Apr. 2020, doi: 10.1016/j.jcrysgro.2020.125526.
- [268] R. D. Shannon, "Revised effective ionic radii and systematic studies of

interatomic distances in halides and chalcogenides,” *Acta Crystallogr. Sect. A*, vol. 32, no. 5, pp. 751–767, Sep. 1976, doi: 10.1107/S0567739476001551.

- [269] D. N. Travessa, M. Pianassola, M. G. S. Carneiro, and M. Lieblich, “Effect of T6 treatment on the hardness of carbon nanotube reinforced AA6061 aluminium alloy matrix composites,” *Adv. Compos. Aerospace, Mar. L. Appl. II*, pp. 357–368, 2016, doi: 10.1007/978-3-319-48141-8_28.
- [270] C. Chen *et al.*, “Influence of melt convection on distribution of indium inclusions in liquid-encapsulated Czochralski-grown indium phosphide crystals,” *J. Mater. Sci. Mater. Electron.*, vol. 31, no. 22, pp. 20160–20167, Nov. 2020, doi: 10.1007/s10854-020-04537-7.
- [271] A. Yoshikawa, Y. Kagamitani, D. A. Pawlak, H. Sato, H. Machida, and T. Fukuda, “Czochralski growth of Tb₃Sc₂Al₃O₁₂ single crystal for Faraday rotator,” *Mater. Res. Bull.*, vol. 37, no. 1, pp. 1–10, Jan. 2002, doi: 10.1016/S0025-5408(01)00788-7.
- [272] L. C. Lim, L. K. Tan, and H. C. Zeng, “Bubble formation in Czochralski-grown lead molybdate crystals,” *J. Cryst. Growth*, vol. 167, no. 3–4, pp. 686–692, Oct. 1996, doi: 10.1016/0022-0248(96)00275-8.
- [273] T. S. Chernaya, L. A. Muradyan, A. A. Rusakov, A. A. Kaminskii, and V. I. Simonov, “Refinement and analysis of atomic structures of Er₃Al₅O₁₂ and (Y_{2.80}Er_{0.20})Al₅O₁₂,” *Kristallografiya*, vol. 30, pp. 72–75, 1985.
- [274] O. Fabrichnaya, H. J. Seifert, T. Ludwig, F. Aldinger, and A. Navrotsky, “The assessment of thermodynamic parameters in the Al₂O₃-Y₂O₃ system and phase relations in the Y-Al-O system,” *Scand. J. Metall.*, vol. 30, no. 3, pp. 175–183, Jun. 2001, doi: 10.1034/j.1600-0692.2001.300308.x.
- [275] C. D. Brandle, D. C. Miller, and J. W. Nielsen, “The elimination of defects in Czochralski grown rare-earth gallium garnets,” *J. Cryst. Growth*, vol. 12, no. 3, pp. 195–200, Mar. 1972, doi: 10.1016/0022-0248(72)90003-6.
- [276] M. Moszyński, T. Ludziejewski, D. Wolski, W. Klamra, and L. O. Norlin, “Properties of the YAG:Ce scintillator,” *Nucl. Instruments Methods Phys. Res. Sect. A Accel. Spectrometers, Detect. Assoc. Equip.*, vol. 345, no. 3, pp. 461–467, Jul. 1994, doi: 10.1016/0168-9002(94)90500-2.
- [277] I. Hernández and W. P. Gillin, “Organic Chromophores-Based Sensitization of NIR-Emitting Lanthanides: Toward Highly Efficient Halogenated Environments,” *Handb. Phys. Chem. Rare Earths*, vol. 47, pp. 1–100, Jan. 2015, doi: 10.1016/B978-0-444-63481-8.00269-4.

- [278] X. Liu, X. Wang, L. Ma, W. Shen, and Z. Wang, "Tb³⁺→Ce³⁺ energy transfer in Y₃Ga₅O₁₂:Ce³⁺,Tb³⁺ garnet," *J. Lumin.*, vol. 40–41, no. C, pp. 653–654, Feb. 1988, doi: 10.1016/0022-2313(88)90374-2.
- [279] A. A. Setlur, J. J. Shiang, and C. J. Vess, "Transition from long-range to short-range energy transfer through donor migration in garnet hosts," *J. Phys. Chem. C*, vol. 115, no. 8, pp. 3475–3480, Mar. 2011, doi: 10.1021/JP110520J/ASSET/IMAGES/JP-2010-10520J_M014.GIF.
- [280] K. Bartosiewicz *et al.*, "Luminescence and energy transfer processes in Ce³⁺ activated (Gd,Tb)₃Al₅O₁₂ single crystalline films," *J. Lumin.*, vol. 188, pp. 60–66, Aug. 2017, doi: 10.1016/J.JLUMIN.2017.04.010.
- [281] K. Ohno and T. Abe, "The Synthesis and Particle Growth Mechanism of Bright Green Phosphor YAG : Tb," *J. Electrochem. Soc.*, vol. 141, no. 5, pp. 1252–1254, May 1994, doi: 10.1149/1.2054905/XML.
- [282] Z. Xing *et al.*, "Photoluminescence and unique magnetoluminescence of transparent (Tb_{1-x}Y_x)₃Al₅O₁₂ ceramics," *Ceram. Int.*, vol. 46, no. 7, pp. 8971–8978, May 2020, doi: 10.1016/J.CERAMINT.2019.12.144.
- [283] C. Yang, G. Gu, X. Zhao, X. Liang, and W. Xiang, "The growth and luminescence properties of Y₃Al₅O₁₂:Ce³⁺ single crystal by doping Gd³⁺ for W-LEDs," *Mater. Lett.*, vol. 170, pp. 58–61, May 2016, doi: 10.1016/J.MATLET.2016.02.001.
- [284] J. Ueda and S. Tanabe, "(INVITED) Review of luminescent properties of Ce³⁺-doped garnet phosphors: New insight into the effect of crystal and electronic structure," *Opt. Mater. X*, vol. 1, p. 100018, Jan. 2019, doi: 10.1016/J.OMX.2019.100018.
- [285] P. Lecoq and M. Korznik, "Scintillator developments for high energy physics and medical imaging," pp. 1–5, Jan. 2003, doi: 10.1109/NSSMIC.1999.842439.
- [286] J. Glodo *et al.*, "New Developments in Scintillators for Security Applications," *Phys. Procedia*, vol. 90, pp. 285–290, Jan. 2017, doi: 10.1016/J.PHPRO.2017.09.012.

VITA

Matheus Pianassola was born in São José dos Campos, Brazil. In 2008 he received a full scholarship to study at Embraer High School, one of the best-ranked schools in Brazil. In that high school, he received the necessary support to pass the competitive entrance exams of four of the most prestigious public universities in Brazil. He pursued his bachelor's degree in Science and Technology at the Federal University of São Paulo, becoming a proud first-generation college student. In 2014, when he was 21 years old, he received a full scholarship from the Brazilian Science Without Borders mobility program and spent a year at the University of Tennessee where he took engineering classes and worked as an undergraduate researcher at the Scintillation Materials Research Center. Matheus received his second bachelor's degree in Materials Engineering in 2017 and moved back to Tennessee to pursue his PhD degree also in Materials Engineering at The University of Tennessee, Knoxville.