

Synthesis and Physical Properties of High Entropy Oxide Ceramics

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DEDICATION

I dedicate this to my husband, Cordell. I look forward to the life we will build together.

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ABSTRACT

Utilizing entropy as the driving force for stabilizing oxide materials offers a path for the discovery of innovative compounds with unique structure-property relations. The multi-cation approach inherent to high entropy oxides (HEOs) is expected to allow for the tailoring of physical properties that meet the requirements of potential applications. However, the intrinsic disorder and highly localized chemical environments of HEOs bring along new challenges. In order to shed light on the complexities associated multi-cation oxides, we have initiated a systematic study of polycrystalline HEO samples across multiple crystal systems. This work expands the multi-component concept to new compositions and crystal systems and investigates kinetic, magnetic, and elastic properties of materials across multiple crystal systems, including spinel, perovskite, and Ruddlesden-Popper multi-component materials. It contributes to a better understanding of (1) the mechanism of phase formation in HEOs, (2) the effect of various synthesis methods, and (3) the effect of cation disorder on the physical properties.

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CHAPTER ONE

INTRODUCTION AND BACKGROUND INFORMATION

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Selected portions from this paper have been stated in this section. The introduction, material design, compilation of literature studies, magnetic, mechanical, thermal expansion, and concluding remarks sections were written by Brianna L. Musicó as well as the assemblage, editing, and organization of the contributors’ written sections. The entropy section was written by Easo George; the correlated electron section by Thomas Zac Ward; local structure and prediction models section written by Katharine Page; and the ionic conductivity, thermoelectric, and ferroelectric sections written by Dustin Gilbert. David Mandrus and Veerle Keppens were advisors involved in the editing and revision of the paper and Jiaqiang Yan as an advisor.

1.1. Overview of high entropy oxides (HEOs)

This section provides background on the field of disordered materials and introduce the specific class of HEOs that this dissertation work investigates. “High entropy” became a commonplace term in materials research ever since a new method of alloy design was proposed in 2004, relying on the combination of multiple elements in equimolar ratios [1][2]. This was the start of a new research focus, called High Entropy Alloys (HEAs) that is still active and growing. HEAs attracted interest because of the possibility that a solid solution of five or more elements could be stabilized due to high mixing entropy. The exceptional mechanical properties achieved by the multicomponent approach has dominated HEA research in the field of structural materials [3]. More recently, HEAs have expanded to include studies of electronic, ionic, magnetic, thermal, and superconducting properties [4] [5] [6]. Reports on the unique properties achieved with HEAs motivated the exploration of compositional complexity as an approach to materials design [7]. The field of multi-component materials was expanded in 2015 to include High Entropy Oxides [8], and was followed by High Entropy Metal Diborides [9], High Entropy Carbides [10], High Entropy Sulfides [11], High Entropy Fluorides [12], and High Entropy Alumino Silicides [13] as depicted in Figure 1-1. Metal oxides are attractive for applications [14], and multicomponent design could expand the available compositional space, providing greater flexibility to meet the demands of today’s advanced materials. HEOs also show great promise for applications in energy storage and catalysis. The electrochemical application of HEOs, including the high Li-ion conductivity and Li-storage capabilities of rocksalt-HEOs for use in battery applications, have shown promise and has been highlighted by Sarkar et al. in a research news article [15].

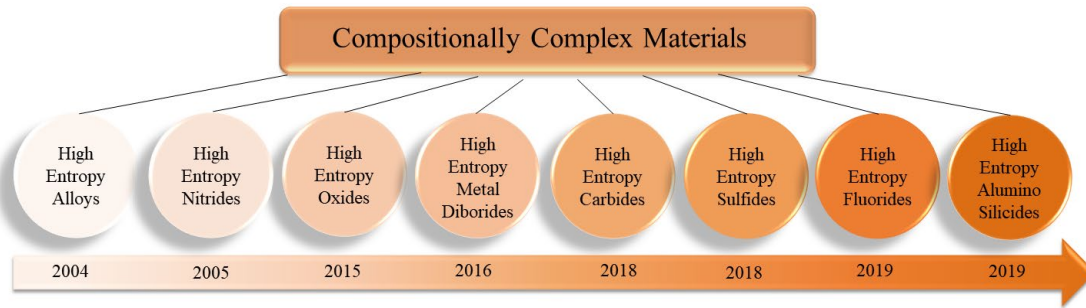


Figure 1-1 Timeline for the development of different classes of compositionally complex materials.

1.2. Entropy and Materials Design

Entropy is not the whole story

In HEAs it was initially proposed that the increased ΔS_{conf} of near-equiatomic alloys with 5 or more elements may favor the formation of solid solution phases over competing intermetallic compounds [7]. However, experiments showed that configurational entropy is generally not able to override the competing driving forces, such as enthalpy, which also contribute to phase stability [16]. For example, the equiatomic alloy CoCrFeMnNi is known to solidify as a single-phase solid solution [2]. Since the change in ideal configurational entropy (mixing entropy) of an equiatomic alloy is given by $R \ln n$, where R is the gas constant and n the number of elements in the alloy, its value for the CoCrFeMnNi alloy is $1.61 R$. This value will not change when individual elements are replaced one at a time to produce new alloys as long as n does not change. Thus, it is $1.61 R$ also in CoCrFeMnCu (where Cu replaces Ni in the original alloy). Otto, et al. [16] showed that every new alloy thus created (CoCrFeMnCu, CoMoFeMnNi, TiCrFeMnNi, etc.) rather than being a single-phase solid solution, phase-separated into multiple metallic and intermetallic phases after 3-day anneals at high temperatures. Therefore, although in the CoCrFeMnNi alloy entropic effects were stronger than enthalpic effects (at sufficiently high temperatures), in the other derivative alloys, enthalpic effects won out (at comparable temperatures). Even in the CoCrFeMnNi alloy, at lower temperatures ($<800^\circ\text{C}$), the single-phase solid solution decomposes into multiple metallic and intermetallic phases [17], consistent with the decreasing influence of entropy with decreasing temperature.

Recent work by Rost, et al. [8] has demonstrated analogous behavior in oxide mixtures. When they mixed five binary oxides (MgO, CoO, CuO, NiO, and ZnO) in equimolar proportions and heated the mixture in the $850\text{-}900^\circ\text{C}$ temperature range, a single-phase quinary HEO, $(\text{Mg}_{0.2}\text{Co}_{0.2}\text{Cu}_{0.2}\text{Ni}_{0.2}\text{Zn}_{0.2})\text{O}$, with the rocksalt structure was observed to form, which separated into a two-phase mixture (rocksalt and tenorite) at lower temperatures. The phase transformation from single-phase to two-phase and back was reversible with temperature, similar to that observed in the CrMnFeCoNi alloy [18], indicative of the increased/decreased contribution of configurational entropy at high/low temperatures. The authors attributed the increased configurational entropy of the HEO to the random distribution of cations on the cation sublattice sites, which was confirmed by extended X-ray absorption fine structure. Nevertheless, the formation of a single-phase quinary HEO is fascinating because its individual components (binary oxides) do not show complete solid solubility with each other. They also have different crystal structures: MgO, NiO and CoO have the rocksalt structure, CuO has the tenorite structure, and ZnO has the wurtzite structure. This is reminiscent of the CrMnFeCoNi HEA in which Ni, Fe and Co (the latter two only at elevated temperatures) have the face-centered cubic structure, Cr has the body-centered cubic structure, and Mn the complex A12 crystal structure; yet when mixed together the result is a single-phase solid solution with the face-centered cubic crystal structure. In both cases, the formation enthalpy of competing phases appears to be low enough that it can be overcome by configurational entropy at elevated temperatures. Additional work has been done on this rocksalt to investigate the effect that grain size has on controlling the phase spectrum behavior [19]. As in the rocksalt system, a reversible multi-to-single phase transition was observed in later HEO perovskite work on $(\text{Gd}_{0.2}\text{La}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Y}_{0.2})\text{MnO}_3$ indicating entropy stabilized behavior along with information supporting that the 10-cationic system

$(\text{Gd}_{0.2}\text{La}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Y}_{0.2})(\text{Co}_{0.2}\text{Cr}_{0.2}\text{Fe}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.2})\text{O}_3$ is also most likely entropy stabilized, extending the concept of entropy stabilization to multicomponent perovskites [20]. Work on a five-component fluorite $(\text{Ce}_{0.2}\text{Zr}_{0.2}\text{Hf}_{0.2}\text{Sn}_{0.2}\text{Ti}_{0.2})\text{O}_2$ also showed a reversible multi-phase to single phase transition indicating entropy stabilization of the compound [21]. An interesting aspect of the formation of these perovskites is the stabilization of the lower symmetry orthorhombic phase, whereas the rocksalt [8] and fluorite type [22] had a preference to maintain a high symmetry structure, which suggests an enthalpy contribution to octahedral tilt Jahn-Teller type distortion making an adaptation to the cubic phase energetically costly [20]. While the nominal work in this field showed the rocksalt $(\text{Mg}_{0.2}\text{Ni}_{0.2}\text{Co}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2})\text{O}$ composition to be truly entropy stabilized, this has not been verified for many of the other compositions in literature. The recent review of the electrochemical applications of HEOs points out that entropy stabilization may be contributing to not just phase stability, but to the functional properties as well, as shown in reversible de/lithiation behavior of the rocksalt based HEOs [15]. The differentiation between compositionally complex materials that are truly entropy stabilized versus multicomponent solid solutions is imperative as research in this area continues to progress.

There are also key differences that are worth noting. For example, in the rocksalt HEO mentioned earlier, removal of *any one* of the components (binary oxides) from the quinary mixture to produce a quaternary mixture results in the loss of the single-phase rocksalt structure and decomposition into multiphase structures [8]. This is consistent with the notion that a decrease in the configurational entropy (quinary to quaternary) decreases the stability of the solid solution. In contrast, removal of several of the components (elements) from the quinary HEA CrMnFeCoNi (Mn, Cr, and Fe) to form quaternaries (FeNiCoCr, FeNiCoMn, and NiCoCrMn) retains the single-phase solid solution state [23]. The lower configurational entropy of the metallic quaternaries presumably is sufficient to overcome the enthalpy of competing intermetallic phases whereas that of the oxide quaternaries is insufficient to overcome the enthalpy of competing oxide phases. Another difference is that, in some perovskite, spinel, and fluorite HEOs, when certain cation species are switched out for others based on ionic radii, not all compositions stabilize as a single phase [24]–[27]. Additionally, rare earth oxides crystallizing in the fluorite CaF_2 type structure with 5 elements on the rare-earth site form a single phase only with the addition of cerium, showing evidence of cerium as a stabilizer in this case [22]. This is reminiscent of the HEA results [16] discussed earlier.

Materials design is challenging given that entropy is but one factor contributing to phase stability of ceramic compounds. In some cases, if the system's configurational entropy is large enough it can be a stabilizing factor, as was shown in the seminal HEO work [8]. In general, the picture is much more complicated, and it is necessary to take into account variables such as the charge states and the ionic radii of the individual cations. Understanding the underlying reasons behind compositional effects on phase stability and distinguishing entropy-stabilized material systems versus solid-solutions is an important area for future investigation.

Selection criteria and synthesis

The initial HEO work of Rost, et al. showed that even in cases where i) the component binary oxides do not exhibit uniform crystal structure, electronegativity or cation coordination, and ii) the pairs of binary oxides do not exhibit extensive mutual solubility, it may be possible to obtain single-phase solid solutions if the entire collection is isovalent [8]. In later studies, the initial

oxidation state of the starting materials has not proven to be a primary factor in the formation of the desired phase, as equilibrium can be reached at high temperatures with oxygen loss and preserved upon quenching [28]. This aliovalent substitution widens the possibilities for compositional variation and in turn properties and applications. The synthesis of $(\text{Co,Cr,Fe,Mn,Ni})_3\text{O}_4$ shows the expansion into other crystal structures with the creation of a single phase HEO with either spinel or rocksalt structure by means of varying the oxygen partial pressure [29]. This manipulation of synthesis method was not something that was seen or able to be used in HEA systems, but should be considered with other oxide synthesis methods as the broader range of structures available in oxides, as shown by the timeline in Figure 1-2, which opens up possibilities to maximize the potential of this new materials class.

In summary:

- Evidence supports that high configurational entropy of mixing is a contributing factor to the formation of a single-phase solid solution, but not exclusively.
- Work on rare earth HEOs shows evidence that particular element additions can be a stabilizing factor [30].
- Minimization of Gibbs free energy to achieve single phase stability benefits from configurational entropy maximization via the mixing of many diverse element species.
- For the case of oxides, it has been stated that there should be appropriately diverse structures, coordination, and cationic radii to directly test whether entropy is a dominant factor in stabilizing solid solutions.

1.3.Literature review of HEO materials and properties

An extensive literature review has been performed and is summarized in the appendix by Table 17 which lists the crystal structure, composition, synthesis method, and material properties investigated. This survey was done as research was performed not only to be up to date with the field, but to understand what has been achieved so that this work could apply the multicomponent concept to new compositions and crystal systems.

1.4.Magnetism

A magnetic moment, m , is the torque experienced by a material when in a given applied magnetic field, H . The magnetic field's units are Oersted, Oe , in cgs units, or ampere per meter, A/m , in SI units. The magnetization, M , is defined as the magnetic moment per unit volume, as shown in Equation 1. In the case of nonuniform sample shape or powder measurement, the magnetization is reported by unit mass and is often seen in literature and in this work in emu/g where emu stands for electromagnetic unit and is the cgs unit for magnetic moment. The shape of the magnetization curve as a function of temperature gives indication of the magnetic character as well as indicating any magnetic transition points.

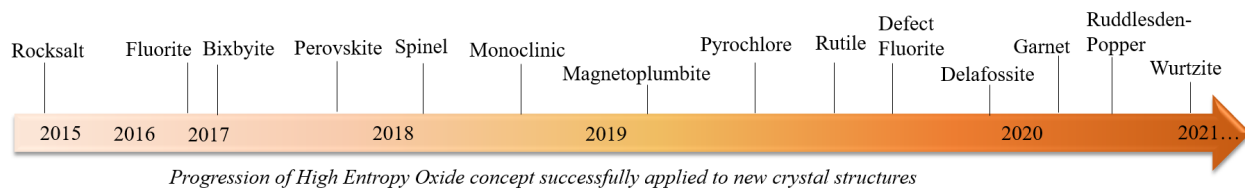


Figure 1-2 Timeline representing the expansion of high entropy oxides to other crystal systems since their realization with the rocksalt structure.

$$\text{Equation 1: } M = \frac{m}{V} \frac{\text{emu}}{\text{cm}^3} \text{ or } M = \frac{m}{\text{mass}} \frac{\text{emu}}{g}$$

The magnetic properties of a material are further defined by how these quantities vary with the applied magnetic field. The magnetic susceptibility, χ , is the ratio of magnetization to magnetic field and is given by Equation 2 and can be reported per unit volume or per unit mass with the cgs units shown whereas it is dimensionless in SI units. The susceptibility is an indicator of how responsive a material is to an applied magnetic field.

$$\text{Equation 2: } \chi = \frac{M}{H} \frac{\text{emu}}{\text{cm}^3 \text{Oe}} \text{ or } \frac{\text{emu}}{g \text{Oe}}$$

Magnetic classifications

Diamagnetic materials exclude magnetic field from their interior and cause a repulsive force resulting in magnetization in the opposite direction of the field. In *paramagnets* and *antiferromagnets* the overall magnetization is zero due to their dipole ordering, which is random in the case of paramagnets and antiparallel in the case of antiferromagnets. The magnetic dipole moments in *ferromagnets* line up in the same direction. *Ferrimagnets* have antiparallel dipole ordering, similar to that of antiferromagnetic, however the magnitude of the dipole moments are different, which leads to a net overall magnetic moment. Schematics for these orderings and the resulting magnetic behavior is summarized in Table 1.

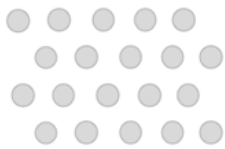
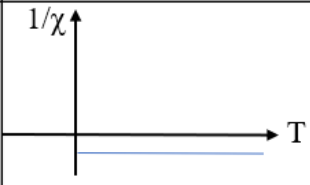
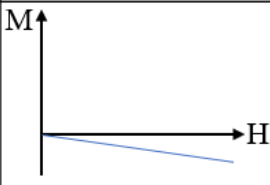
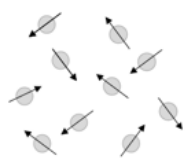
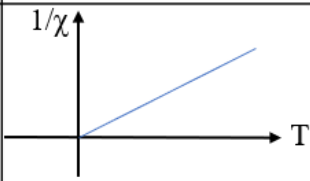
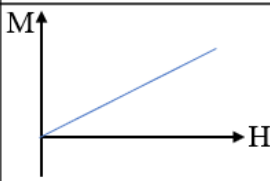
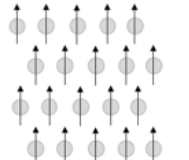
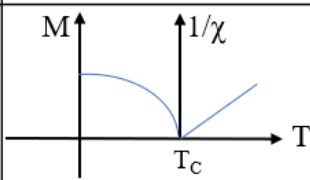
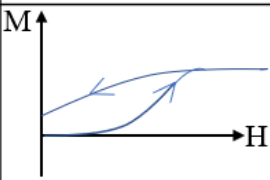
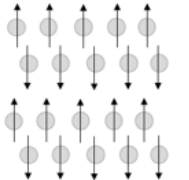
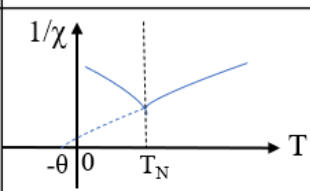
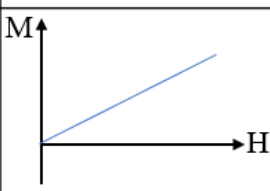
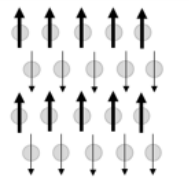
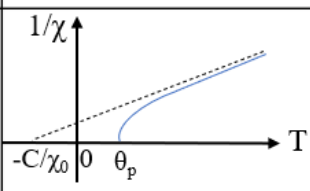
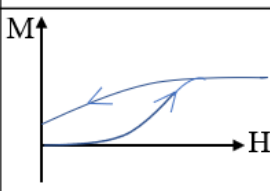
The shape of the magnetization or susceptibility plot as a function of temperature gives an indication of the magnetic character as well as showing any magnetic transition points. In ferromagnets, dipole ordering is no longer observed above their Curie temperature, T_C . Other magnetic transition points for antiferromagnetic materials can be identified from inflection points in the magnetization with temperature at the Néel temperature, T_N .

From the hysteresis loops, the graphs of M versus H , the saturation point and coercivity can be determined.

Magnetism in oxide materials

Magnetism in oxide materials is generally governed by indirect interactions such as Superexchange, double exchange, and Ruderman–Kittel–Kasuya–Yosida (RKKY) interactions and are influenced by the local environment. Superexchange is a short-range interaction and, depending on the geometrical characteristics of the bond and the electronic configuration of the two coupled transition metal ions, this can be either an antiferromagnetic or ferromagnetic interaction. It is highly dependent on the metal-oxygen-metal (M-O-M) bond angle and orbitals involved, given by the schematic in Figure 1-3 (a), where two magnetic cations interact via the intervening ion, in the case of the materials studied here this is oxygen. In double exchange, an electron has moved between the neighboring metal ions, retaining its spin as shown in Figure 1-3 (b). This is typically between ions with differing oxidation states. The ability to delocalize reduces the kinetic energy and can lead to ferromagnetic alignment of neighboring ions. If no hopping occurs, this can be antiferromagnetic. RKKY is an itinerant exchange that happens in rare earths, where the inner d or f shell electrons are localized and exchange is mediated by (non-magnetic) conduction electrons as shown in Figure 1-3 (c) and is a long-range interaction.

Table 1 Summary of types of magnetism and their typical magnetic behavior with schematics for dipole ordering, inverse susceptibility with temperature, and magnetization with magnetic field.

Type of Magnetism	Magnetic Behavior		
	Dipole Ordering	With Temperature	With Field
Diamagnetic			
Paramagnetic			
Ferromagnetic			
Antiferromagnetic			
Ferrimagnetic			

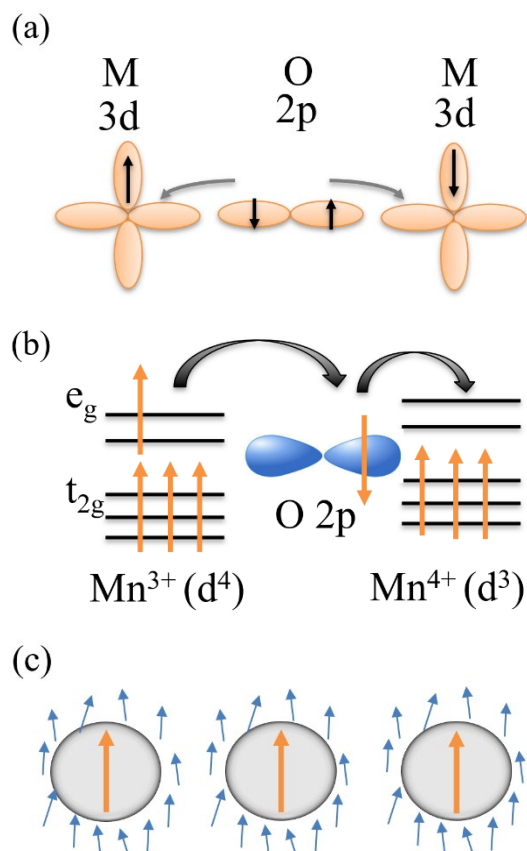


Figure 1-3 Schematics representing the interactions in (a) Superexchange, (b) double exchange and (c) RKKY interactions in magnetic materials.

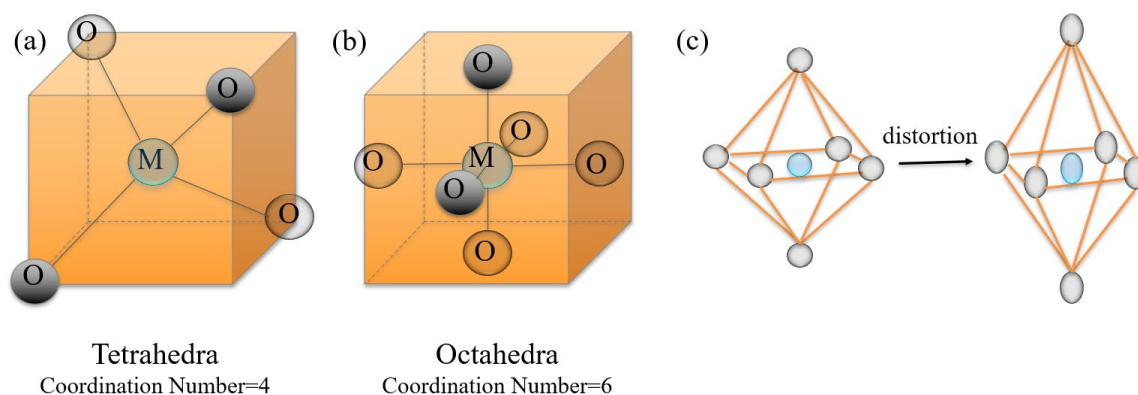


Figure 1-4 Representative (a) tetrahedra and (b) octahedra for a metal cation surrounded by oxygen anions and (c) octahedral distortion.

In a disordered material there is a variation in element constituents and bond angles and multi-valent states could be expected, so many of these interactions can come into play. In oxides, where the physical behavior is strongly correlated to stereochemistry and electronic structure, the poly-cation approach creates a unique platform to tailor the interplay of extreme structural and chemical disorder to realize unprecedented functionalities. Depending on the crystal structure and the site that disorder is applied to, the interactions, and cations' contribution to the magnetic character are affected. A representation for octahedral and tetrahedral coordination is shown in Figure 1-4 (a) and (b). The multi-component approach makes these interesting as any type of structural changes, such as lattice distortion or tilting of octahedra shown in Figure 1-4 (c), have often shown a decisive impact on material properties.

First Order Reversal Curve Analysis

The First Order Reversal Curve (FORC) method is a useful technique for determining separate and collective effects of multiphase magnetic systems. It is applied to understand various hysteretic behaviors and distinguish the different magnetic signals in multiphase systems as well as investigate subtle magnetic features caused by interaction between multiple magnetic phases. The Preisach model is a mathematical model where hysteresis can be described by operators called hysterons and characterized by two parameters: the coercivity field, H_C , and the bias field, H_U . The magnetization switches down at a reversal field, H_R , given by Equation 3 and switches back up for a certain external applied field given by Equation 4 as shown on the labeled plot in Figure 1-5.

Equation 3: $H_R = -(H_C + H_U)$

Equation 4: $H = (H_C - H_U)$

The difference in magnetization between the applied field and reversal field is directly proportional to the amount of hysterons that switched back up. This kind of minor hysteresis is called FORC and Figure 1-6 shows the collection of FORC measurements. Information about all the hysterons in the system is the FORC distribution and is given by Equation 5.

Equation 5: $\rho_{FORC} = -\frac{1}{2} \frac{\partial^2 M(H, H_R)}{\partial H \partial H_R}$

Characterization of the reversible processes can be done through the calculation of a reversibility indicator, η , given by Equation 6 where a value of $\eta=0$ corresponds to a completely irreversible process and $\eta=1$ to a fully reversible process.

Equation 6: $\eta(H = H_R) = \frac{\chi_{FORC}(H=H_R)}{\chi_{hyst}(H=H_R)}$

Information about both the irreversible and reversible portions can be put into graphical representation for a FORC diagram, shown in Figure 1-7, with a change in coordinates such that $H_C = \frac{H-H_R}{2}$ and $H_U = -\frac{H+H_R}{2}$. In the classical Preisach model approach, the H_C and H_U cross sections of the FORC distribution directly yield the coercivity and interaction field distributions. From the FORC distribution width and positions relative to the axes, information about the magnetic character can be inferred.

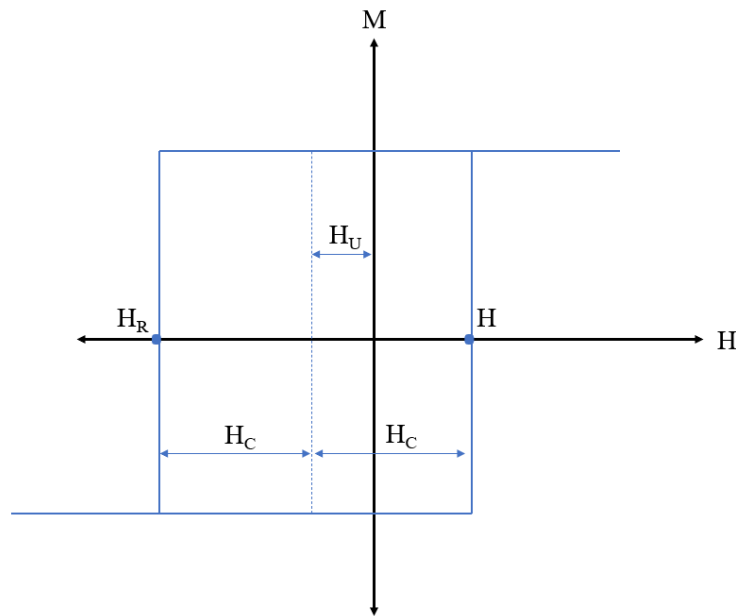


Figure 1-5 magnetization with magnetic field showing the bias, coercivity and reversal fields.

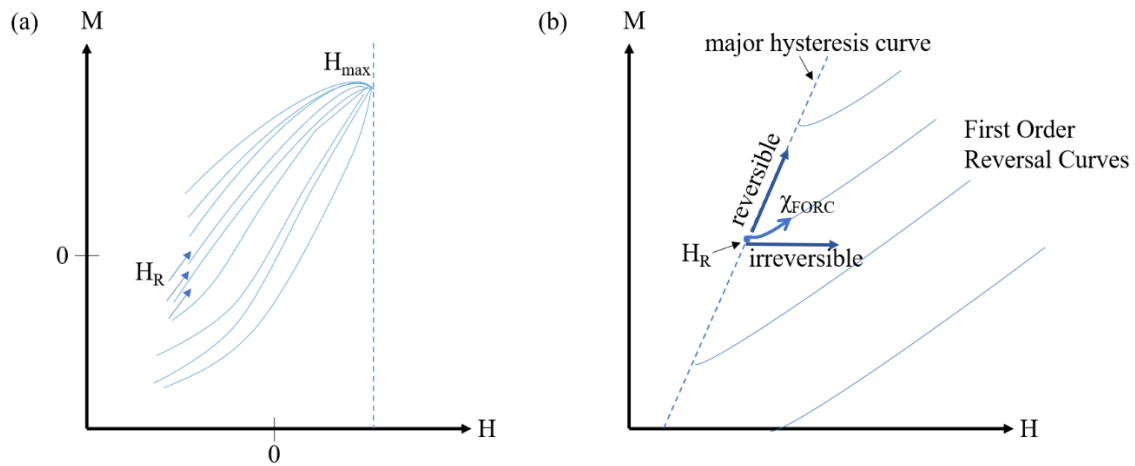


Figure 1-6 Representative figures (a) showing the measurement of first order reversal curves and (b) with only four curves shown.

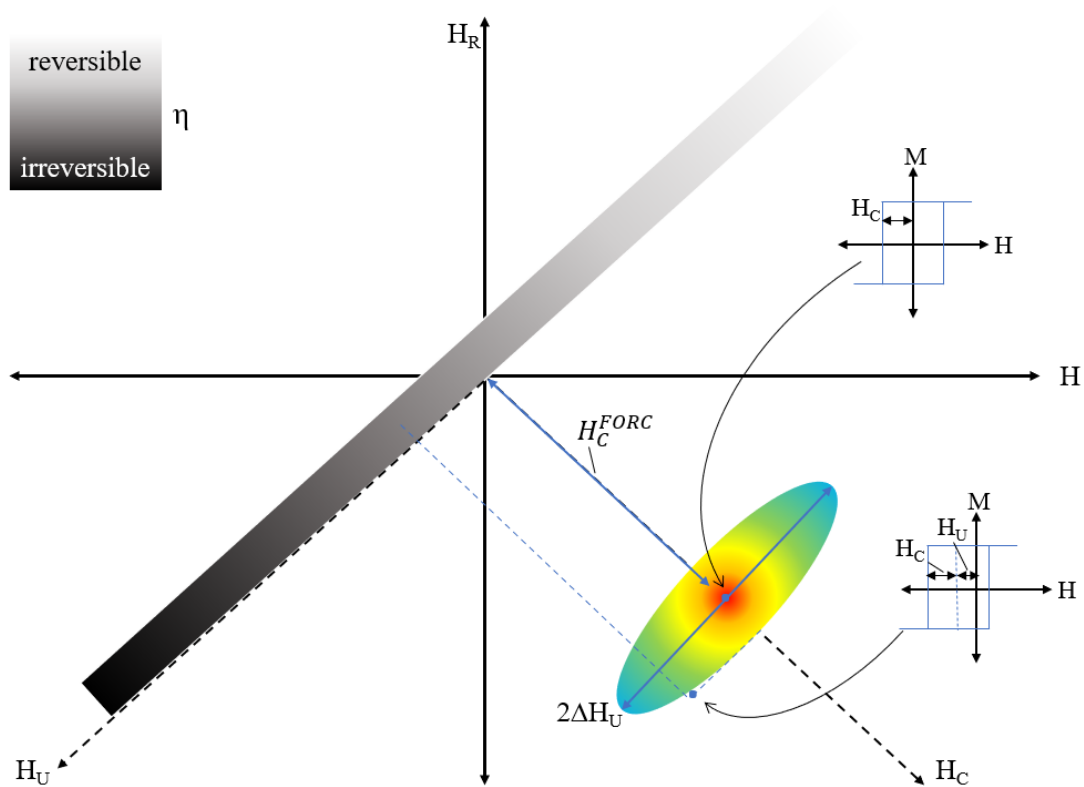


Figure 1-7 graphical representation of a FORC diagram with axes transformation and labels.

1.5.Kinetic theory

A version of text from this section is to be published in a textbook chapter “Experimental Characterization of High Entropy Oxides with In-situ High Temperature X-Ray Diffraction Techniques” by Brianna L. Musicó, Cordell J. Delzer, John R. Salasin, Michael R. Koehler, and Claudia J. Rawn in the textbook:

Brechtl, J., Liaw, P.K. (2021). Fundamental Studies of High Entropy Materials. Manuscript in preparation for publication by Springer.

Selected portions from this chapter have been stated in this section. The introduction and background were written by Brianna L. Musicó and Claudia J. Rawn. Experiments were performed by Brianna L. Musicó and Michael R. Koehler. Background knowledge for experiment set up and design provided by John R. Salasin. Data analysis performed by Brianna L. Musicó and Cordell J. Delzer. Discussion and prospects written by Brianna L. Musicó and reviewed by Claudia J. Rawn.

Kinetic Transformation Mechanisms

The commonly used reaction models in solid-state kinetics can be divided based on mechanistic assumptions into nucleation, geometrical contraction, diffusion, or reaction-order models. In phase boundary controlled processes a surface nucleation occurs rapidly at the surface towards the center as given by Figure 1-8 (a). In diffusion controlled reactions, a transport process is dominating as given by Figure 1-8 (b). The nucleation and growth models, or Avrami models, have described crystallization, transition, decomposition, hydration, and absorption [31]. In nucleation, a nucleation site acts as a reactive point in the lattice, given by Figure 1-8 (c).

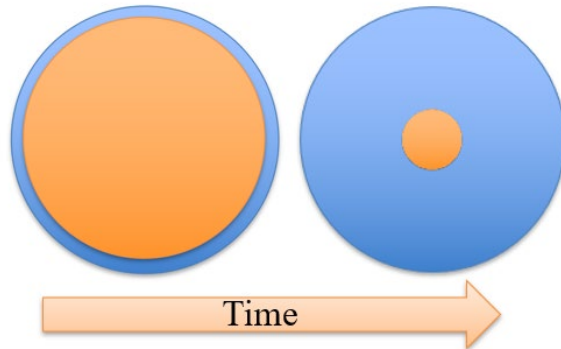
Kinetic Transformation Investigation

The focus of this section is to provide the necessary background needed for understanding data analysis performed from high temperature X-ray powder diffraction to study the formation or transformation of high entropy materials. Kinetic transformations can be investigated by determining the reacted fraction, α as a function of time using a variety of characterization methods. From X-ray powder diffraction data, α can be calculated by either analyzing the integrated peak area (A) if limited diffraction maxima are available or the phase fraction (wt%) if determined through Rietveld refinement, as shown in Equation 7.

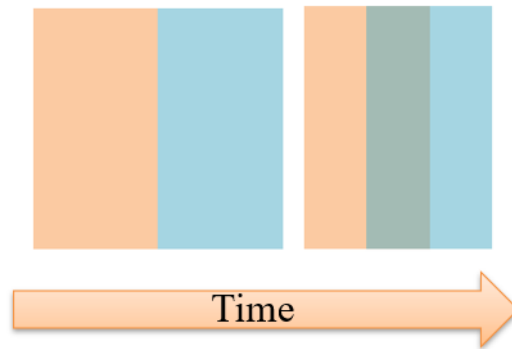
$$\text{Equation 7: } \alpha = \frac{A_{\text{observed}}}{A_{\text{max}}} = \frac{Wt\%_{\text{observed}}}{Wt\%_{\text{max}}}$$

The Johnson-Mehl-Avrami-Kolmogorov (JMAK) model, often known as simply the Avrami equation, shown in Equation 2 relates the reacted fraction to the reaction time (t), rate constant (k) with units of time^{-1} , and a constant (n) that depends on the reaction mechanism. These JMAK mechanisms are denoted in later figures as An , where n represents the reaction mechanism included in Equation 8, Equation 9, and Equation 10.

(a) Phase Boundary Controlled



(b) Diffusion Controlled



(c) Random Nucleation and Growth

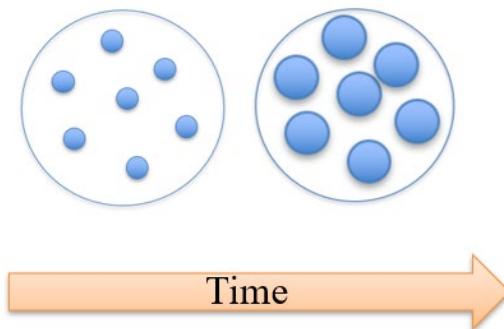


Figure 1-8 Schematics for the common kinetic transformation mechanisms.

Equation 8: $\alpha = 1 - \exp(-kt)^n$

Rearranging Equation 8 to solve for kt results in Equation 9 below.

Equation 9: $-\ln(\alpha - 1)]^{1/n} = kt$

The JMAK model describes homogeneous random nucleation and growth. Substituting various values of α into the equation above yields a sigmoidal curve with three distinct stages corresponding to slow growth when homogenous random nucleation initially occurs, faster growth during the second stage of nuclei growth, and a return to slower growth due to nuclei impingement as the reacted fraction α approaches 100%.

Mathematically manipulating Equation 9 gives the form of Equation 10,

Equation 10: $-\ln \ln(1 - \alpha) = n \ln k + n \ln t$

where $-\ln \ln(1 - \alpha)$ can be plotted against $\ln t$ for a line with a slope of n and a y-intercept of k for an isothermal experiment. When several isothermal curves collected on a compound are plotted and are parallel but displaced from each other, the reaction mechanism n (from the slope) is the same for each curve but the rate constant k (from the intercept) is different.

The Arrhenius equation, Equation 11,

Equation 11: $k = A \exp\left(\frac{-E_a}{RT}\right)$

relates the rate constant to the activation energy, E_a . Other information used in the equation includes the gas constant (R) and the absolute temperature (T). A is the pre-exponential factor and is constant for each reaction. Once k is determined at each temperature from the isothermal experiments described above, E_a can be determined from the slope ($-E_a/R$) that results when plotting $\ln k$ vs $1/T$ (K).

The JMAK model is useful when describing (1) a single step nucleation and growth from a solution or wet chemistry synthesis where reactants are well mixed and diffusion lengths are short or (2) for certain material systems a reaction where a solid decomposes at higher temperatures to form a different solid and a gas (e.g., $\text{BaCO}_3 \rightarrow \text{BaO} + \text{CO}_2(\text{g})$) [32]. However, other kinetic models are also important when studying solid-state synthesis techniques, not only for comparisons but for insights into the reactions occurring during the synthesis. The shape of the fraction transformed vs. time (α vs. t) curve guides the choice of a potential kinetic model. When data are collected isothermally, the α vs. t curve for the JMAK model, as discussed above, results in a sigmoidal shape. However, for the solid-state reaction models in which the amount transformed proceeds quickly at low t and then slowly approaches the 100% conversion limit, a geometric contraction

(R) or diffusion controlled (D) deceleration model should be considered. In a review paper, Khawam and Flanagan [31] present these models along with acceleratory and linear models and provide an in-depth discussion.

For reactions occurring based on geometric contraction (R), initial nucleation occurs rapidly on the surface of the particle, and the rate of conversion is controlled by the resulting reaction interface as it progresses toward the center of the particle. The model used will depend on the shape of the particle, and Khawam and Flanagan derived the equations relating the transformed fraction to the rate constant and time for constricted area (R2), described as a cylindrical particle, and for constricted volume (R3), described as a spherical or cubic particle; these are given in Equation 12 and Equation 13, respectively.

$$\text{Equation 12: } 1 - (1 - \alpha)^{1/2} = k_o t$$

$$\text{Equation 13: } 1 - (1 - \alpha)^{1/3} = k_o t$$

In the derivation of these equations, the initial radius of the particle (r_0) and the radius at any time (r) are considered, and $k_o = k/r_0$.

For equations based on diffusion controlled (D) reactions, the interfacial reaction product that forms between the initial phase(s) and the resultant phase after the reaction is an important factor. Considered in the derivation of the diffusion-controlled reactions are the molecular weight, density, and thickness of the reactant and product layers, the molecular weight of the second reactant, the diffusion coefficient, and the concentration gradient. Using these factors, Khawam and Flanagan present the derivations to arrive at the diffusion-controlled reactions for the 1-D (infinite flat plate, D1), 2-D (cylindrical, D2), and 3-D (spherical, D3) geometries given in Equation 14, Equation 15, and Equation 16, respectively.

$$\text{Equation 14: } \alpha^2 = kt$$

$$\text{Equation 15: } ((1 - \alpha) \ln(1 - \alpha) + \alpha) = kt$$

$$\text{Equation 16: } (1 - (1 - \alpha)^{1/3})^2 = kt$$

The above discussion examining the α vs. t curves focuses on isothermal data collection, but experiments for obtaining α can also be conducted as a function of temperature (T), resulting in an α vs. T curve. For evaluating these non-isothermal data, “master plots” are often used. In Gotor et al. [33], a method of creating master plots is presented. Equation 9 and its progressions were

previously presented in the review by Khawam and Flanagan as $g(\alpha) = kt$, where $g(\alpha)$ is the integral of the reaction model defined by Equation 17.

Equation 17: $g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)}$

Taking the reciprocal of the derivative of $g(\alpha)$ results in the equation $f(\alpha)$. $f(\alpha)/f(\alpha)_{0.5}$, where $f(\alpha)_{0.5}$ is the value when $\alpha = 0.5$ or 50% of the material has been transformed, is then used to generate the master plots presented by Gotor et al. [22] and recreated in Figure 1-9 (a). These were calculated using the algebraic expressions given in Figure 1-10. As the plot progressions show, some of these kinetic mechanisms are hard to distinguish and sometimes even overlap, especially in the case of $f(\alpha)g(\alpha)/f(0.5)g(0.5)$ given in Figure 1-9 (d). This is a drawback in using non-isothermal data since some behaviors can no longer be discerned.

Using the data for the master plot depicted in Figure 1-9 (d), a plot of the theoretical α as a function of time since crystallization can be generated by applying an area normalized integral of the $f(\alpha)g(\alpha)/f(0.5)g(0.5)$ data set for each kinetic model, the result of which is given in Figure 1-10. In this study we are not considering order-based models.

1.6. Background on reported crystal structures

As a variety of compositions were synthesized and studied in this work, an understanding of the various crystal structures is critical to understanding the role disorder and composition variation have on the material properties. This section will provide crystallographic background and is divided into sections for the three structures investigated: spinel, perovskite, and Ruddlesden-Popper.

Spinel

The spinel structure belongs to space group Fd-3m and has a complex unit cell consisting of 32-anions and 24-cations. The face centered cubic arrangement of the anions lead to octahedral (B) and tetrahedral (A) crystallographic sites for the cations, as shown by the representative unit cell in Figure 1-11. Only 1/8 of the tetrahedral and 1/2 of the octahedral sites generated by the anion arrangement are occupied. The structure's distribution can be described by $(A_{1-x}B_x)[A_{x/2}B_{1-x/2}]_2O_4$ where the parentheses denote the tetrahedral site and the brackets denote the octahedral site. Where $x = 0$ corresponds to a normal spinel distribution, $x = 1$ to an inverse, and $x = 2/3$ to a completely random solution. In the normal spinel $MgAl_2O_4$, the larger Mg^{2+} cation occupies the tetrahedral A site, while both smaller Al^{3+} ions occupy the octahedral sites so that it is of the form $(Mg^{2+})[Al^{3+}Al^{3+}]O_4$. In 2-3 type spinels, such as those reported here, the larger ion typically occupies the tetrahedral site, resulting in the normal spinel configuration as described for $MgAl_2O_4$ [34], [35].

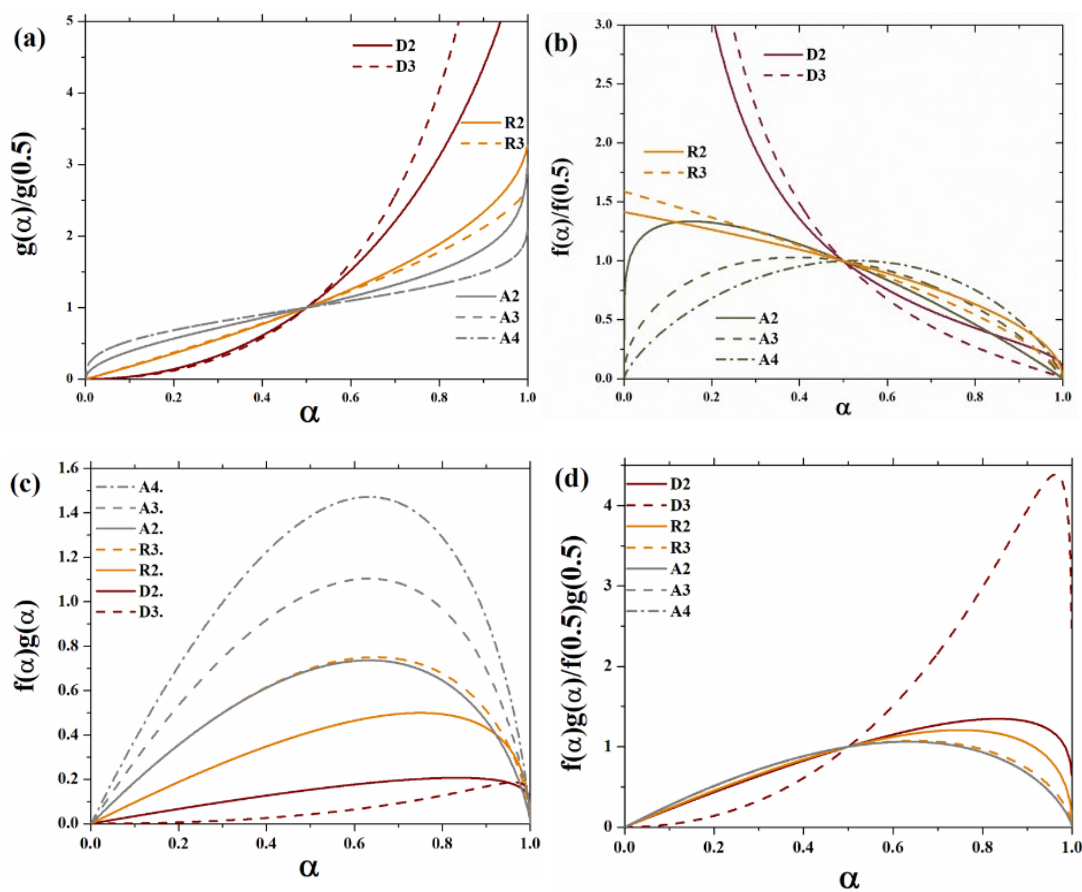


Figure 1-9 The theoretical master plots (a) in integral form representing, (b) in differential form, (c) in differential-integral form, and (d) curves in differential-integral form all as a function of α for the different kinetic models.

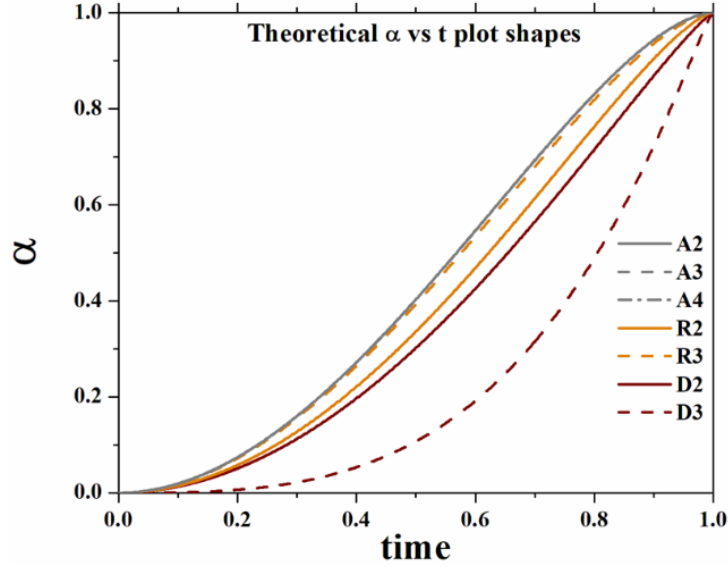


Figure 1-10 The theoretical shape of degree of crystallization, α , with time as calculated from performing an area normalized integral of the $f(\alpha)g(\alpha)/f(0.5)g(0.5)$ data set for each kinetic model.

Table 2 Summary of select models for solid state kinetic transformations and their algebraic expressions for the $f(\alpha)$ and $g(\alpha)$ functions adapted from Gotor and Khawam.

Kinetic Mechanism	symbol	$f(\alpha)$	$g(\alpha)$
Phase boundary controlled reaction (2D)	R2	$(1 - \alpha)^{1/2}$	$2[1 - (1 - \alpha)^{1/2}]$
Phase boundary controlled reaction (3D)	R3	$(1 - \alpha)^{2/3}$	$3[1 - (1 - \alpha)^{1/3}]$
Random nucleation and growth (Johnson-Mahl-Avrami equation, JMAK model)	An	$n(1 - \alpha)[- \ln(1 - \alpha)]^{1-1/n}$	$[- \ln(1 - \alpha)]^{1/n}$
2D diffusion	D2	$\frac{1}{[- \ln(1 - \alpha)]}$	$(1 - \alpha) \ln(1 - \alpha) + \alpha$
3D diffusion (Jander equation)	D3	$\frac{3(1 - \alpha)^{2/3}}{2[(1 - \alpha)^{1/3}]}$	$[1 - (1 - \alpha)^{1/3}]^2$

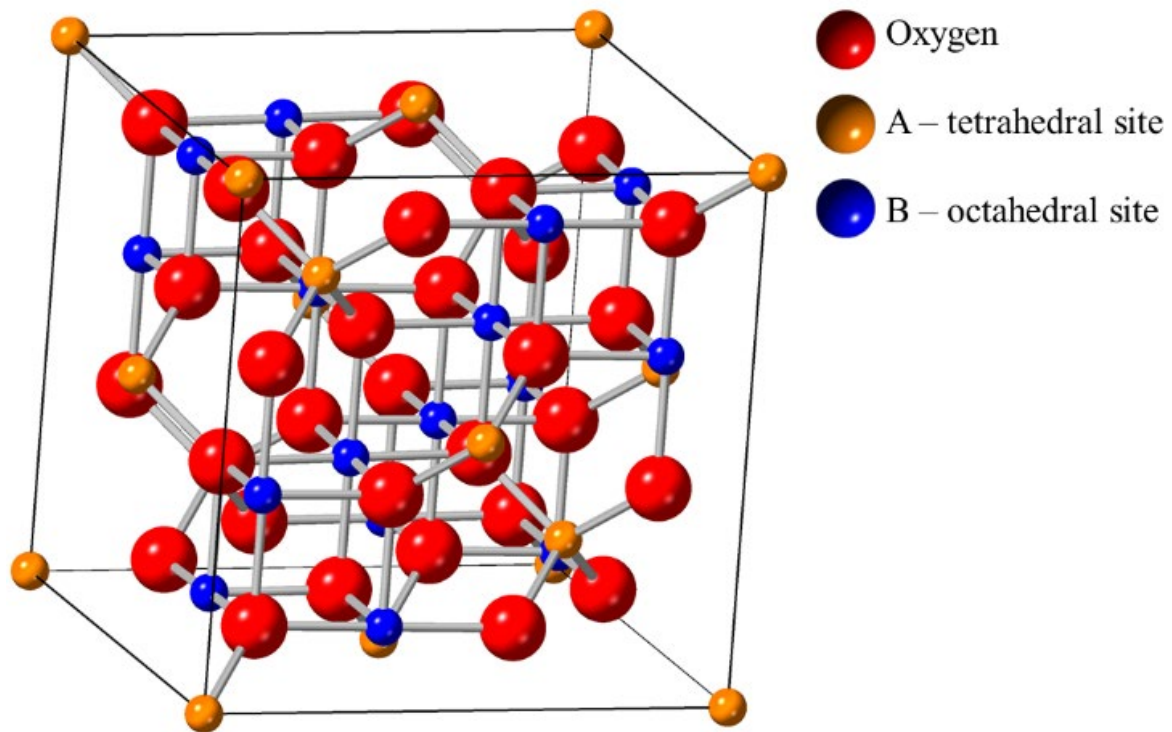


Figure 1-11 Representative unit cell of the spinel structure with labeled atoms sites.

This is the case for three of the individual spinels of one of the multicomponent compositions studied, MgAl_2O_4 , CoAl_2O_4 , and ZnAl_2O_4 , whereas NiAl_2O_4 takes on a largely inverse spinel configuration [36] and CuAl_2O_4 [37] has a disordered structure with tendency towards some degree of inversion. In the case of an inverse spinel such as NiFe_2O_4 , the occupational preference is such that the cation distribution is $(\text{Fe}^{3+})[\text{Ni}^{2+}\text{Fe}^{3+}]\text{O}_4$. Preferential site occupancies for the cation species based off charge [38], [39] is provided in Figure 1-12 for reference, but the effect of the complexity of the compositions studied in this work should be considered.

The expected ordering for iron and chromium-based HEO spinel compositions studied in this work are presented in Table 3. The magnetic behavior in spinel materials is largely dependent on the cation species occupying the A and B sites. Typically an antiferromagnetic interaction between the A and B sites in normal ferrites determines the magnetic ordering, but is dependent on the cations as non-magnetic constituents, such as zinc, would lead to paramagnetic character. As mentioned, the complexity of these compositions and the spinel structure could lead to deviation from the expected ordering and unique magnetic behavior to arise, something that is reported in Magnetic Properties- Spinel.

Cubic and Orthorhombic Perovskites

Oxide perovskites are of the form ABO_3 where the larger ion typically occupies the 12-fold occupancy A site while the smaller cations occupy the corner octahedral sites. The Goldschmidt tolerance factor, t , is an indicator of the degree of distortion within the material and is given by: $t = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)}$ where r_A , r_B , and r_O are the radii of the A cation, B cation and oxygen anion, respectively. For $t > 1$ a hexagonal or tetragonal structure is expected, while for $0.9 < t < 1$ a cubic structure is expected, and for $0.71 < t < 0.9$ an orthorhombic or rhombohedral structure is expected. However, in high entropy oxide materials it has been shown that a Goldschmidt tolerance factor near 1 may be necessary (but not sufficient) to obtain a single phase perovskite [25]. This is an interesting result and something to consider when studying multi-component perovskite materials. Representative unit cells for cubic (space group Pm-3m) and orthorhombic (space group Pbnm) perovskite crystal structures are shown in Figure 1-13.

Ruddlesden-Popper Series

The Ruddlesden Popper (RP) series is generally of the form $A_{n+1}B_nX_{3n+1}$, where A and B are cations, X is an anion, and n is the number of the layers of octahedra in the perovskite-like stack. Typically, A is an alkali, alkaline metal, or rare earth (RE) metal ion; and B is a transition metal located inside anionic octahedra, pyramids, or squares [40]. The tetragonal T-structure, shown in Figure 1-14 (a), is typically formed for $\text{RE}=\text{La}$ while the T'-structure, Figure 1-14 (b), can be expected for traditional RP $n=1$ cuprate compositions of Pr through Gd. The RP phase A_2BO_4 , having the K_2NiF_4 structure with space group $I4/mmm$, has been extensively studied [41] because of its dielectric, superconducting, and magnetic properties. Composition, oxygen stoichiometry, and electron/hole doping are known to impact the functional properties in RP oxides with the Nd_2CuO_4 type T'-structure [42]–[44], but the effect of cation-site disorder has yet to be investigated and could be an area for continued study.

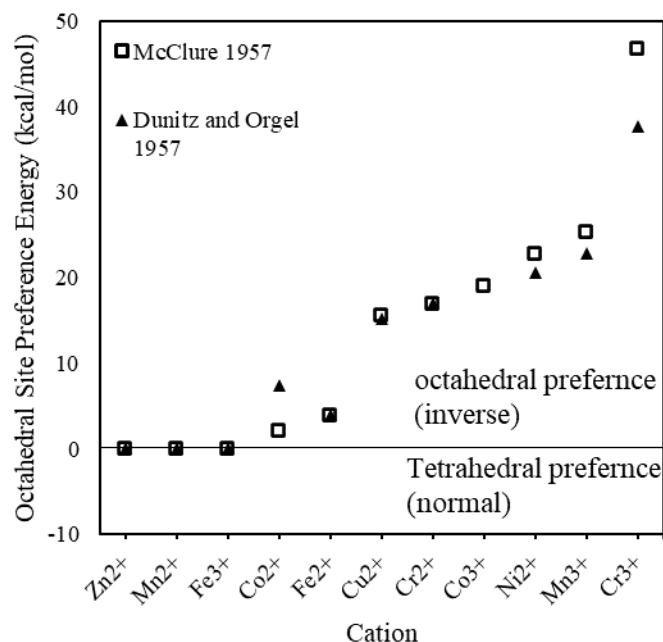


Figure 1-12 Plot of site occupancy preferences for transition metal cation species based on energy values taken from Dunitz and McClure.

Table 3 Expected ordering of Fe and Cr based HEO spinel compositions from site preference energies of constituents.

Composition	Expected Ordering: ()=Tetrahedra []=octahedra
$(\text{Mg}_{0.2}\text{Ni}_{0.2}\text{Co}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2})\text{Cr}_2\text{O}_4$	$(\text{Zn}_{0.2}^{2+}\text{Co}_{0.2}^{2+}\text{Mg}_{0.2}^{2+}\text{Cu}_{0.2}^{2+}\text{Ni}_{0.2}^{2+})[\text{Cr}_1^{3+}\text{Cr}_1^{3+}]\text{O}_4$
$(\text{Mg}_{0.2}\text{Ni}_{0.2}\text{Co}_{0.2}\text{Cu}_{0.2}\text{Fe}_{0.2})\text{Cr}_2\text{O}_4$	$(\text{Co}_{0.2}^{2+}\text{Mg}_{0.2}^{2+}\text{Cu}_{0.2}^{2+}\text{Ni}_{0.2}^{2+}\text{Fe}_{0.2}^{2+})[\text{Cr}_1^{3+}\text{Cr}_1^{3+}]\text{O}_4$
$(\text{Ni}_{0.2}\text{Co}_{0.2}\text{Cr}_{0.2}\text{Fe}_{0.2}\text{Mn}_{0.2})_3\text{O}_4$	?
$(\text{Mg}_{0.2}\text{Ni}_{0.2}\text{Co}_{0.2}\text{Cu}_{0.2}\text{Fe}_{0.2})\text{Fe}_2\text{O}_4$	$(\text{Fe}_1^{3+})[\text{Fe}_1^{3+}\text{Ni}_{0.2}^{2+}\text{Cu}_{0.2}^{2+}\text{Fe}_{0.2}^{2+}\text{Mg}_{0.2}^{2+}\text{Co}_{0.2}^{2+}]\text{O}_4$
$(\text{Mg}_{0.2}\text{Ni}_{0.2}\text{Co}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2})\text{Fe}_2\text{O}_4$	$(\text{Fe}_{0.8}^{3+}\text{Zn}_{0.2}^{2+})[\text{Fe}_{1.2}^{3+}\text{Ni}_{0.2}^{2+}\text{Cu}_{0.2}^{2+}\text{Mg}_{0.2}^{2+}\text{Co}_{0.2}^{2+}]\text{O}_4$
$(\text{Mg}_{0.2}\text{Ni}_{0.2}\text{Co}_{0.2}\text{Cu}_{0.2}\text{Mn}_{0.2})\text{Fe}_2\text{O}_4$	$(\text{Fe}_{0.8}^{3+}\text{Mn}_{0.2}^{2+})[\text{Fe}_{1.2}^{3+}\text{Ni}_{0.2}^{2+}\text{Cu}_{0.2}^{2+}\text{Mg}_{0.2}^{2+}\text{Co}_{0.2}^{2+}]\text{O}_4$
$(\text{Ni}_{0.2}\text{Co}_{0.2}\text{Cu}_{0.2}\text{Fe}_{0.2}\text{Mn}_{0.2})\text{Fe}_2\text{O}_4$	$(\text{Fe}_{0.8}^{3+}\text{Mn}_{0.2}^{2+})[\text{Fe}_{1.2}^{3+}\text{Ni}_{0.2}^{2+}\text{Cu}_{0.2}^{2+}\text{Fe}_{0.2}^{2+}\text{Co}_{0.2}^{2+}]\text{O}_4$

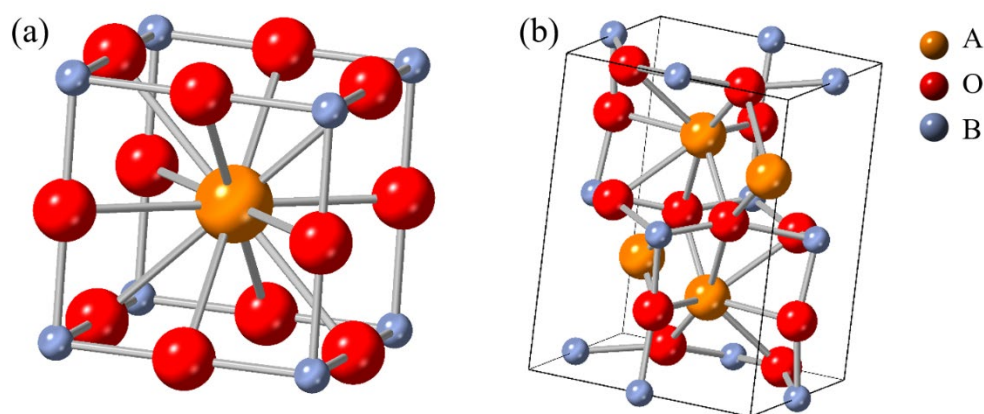


Figure 1-13 Representative unit cells for (a) cubic and (b) orthorhombic perovskites.

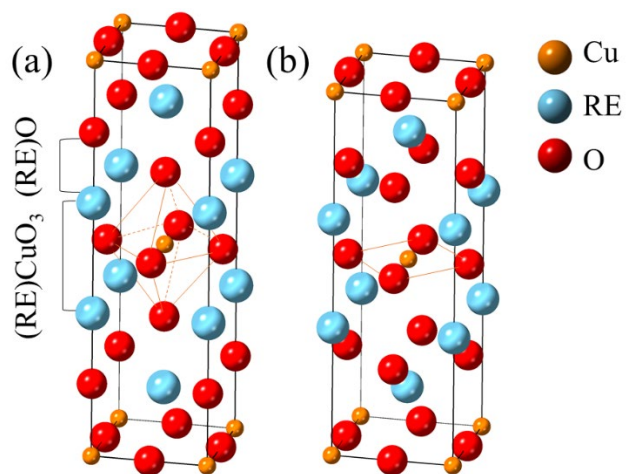


Figure 1-14 The (a) T-structure and (b) T'-structure of $(RE)_2CuO_4$ rare earth (RE) cuprates with the (RE)CuO₃ and (RE)O layers labeled.

The ability to manipulate the configurational complexity within the 2D planes could lead to a new approach towards identifying and realizing desirable functionalities. Hole-doped copper perovskite materials are well known for their high- T_C superconducting behavior. In its undoped state, the parent compound is an antiferromagnetic Mott insulator, with superconductivity emerging from the CuO_2 planes being doped with charge carriers [44]. The joint phase diagram for the T-structure and T'-structure is given in Figure 1-15 from [45]. As mentioned previously, the T-structure is formed for La_2CuO_4 which is hole doping with strontium. Nd_2CuO_4 , forming the T'-structure, is electron doped with cerium.

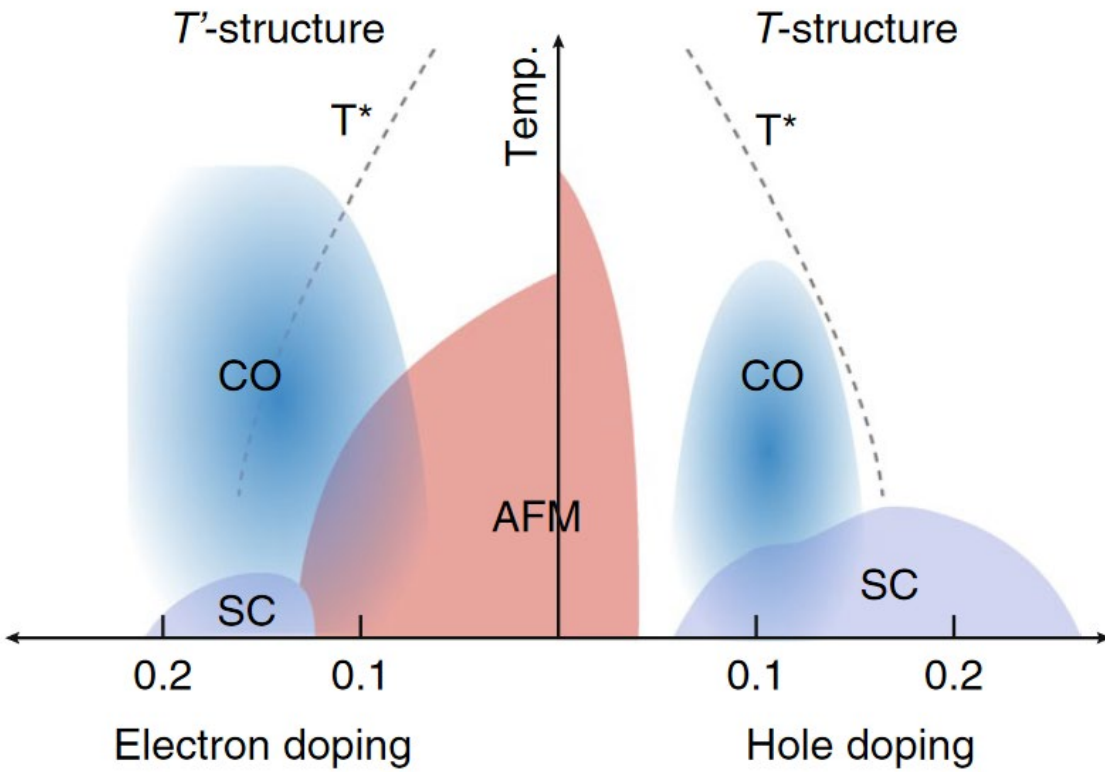


Figure 1-15 Doping–temperature phase diagram of cuprates, with superconducting (SC), antiferromagnetic (AFM), charge ordering (CO), and pseudogap (T^*) regions highlighted from [45].

CHAPTER TWO

MATERIALS AND METHODS

This chapter details the methods utilized for the synthesis and characterization of the investigated multicomponent oxide materials.

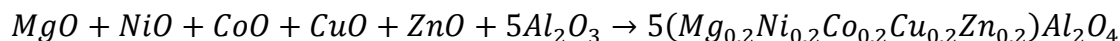
2.1. Material synthesis

The investigated elemental combinations were chosen primarily on the basis of cation radius compatibility. See Appendix Table 18 for information from the table of Shannon Radii [46].

Solid State Reaction Method

The solid-state reaction method is common in ceramic synthesis. It is a diffusion-driven process that involves individual metal oxides or carbonates being combined in stoichiometric amounts and heated to high temperature to achieve a thermodynamically favorable state. The time required for full reaction and the development of a stoichiometric phase can be hours to days of time and often requires multiple reprocessing steps to get a stoichiometric and homogenous phase. The solid-state reaction method is a relatively straightforward synthesis method with minimal equipment requirements but is slow and offers limited control over the resultant material microstructure. Ensuring homogeneity becomes more problematic with multiple metal oxide constituent in the mixture, as is the case for high entropy oxides. In all the materials synthesized, metal oxides were used as the starting materials for reactions similar to that shown for $(Mg_{0.2}Ni_{0.2}Co_{0.2}Cu_{0.2}Zn_{0.2})Al_2O_4$ in the reaction in Equation 18.

Equation 18:



For the solid-state synthesized samples made in these studies, precursor powders of individual metal oxides were used. Prior to being weighed to stoichiometric amounts, the individual oxides were dried overnight to remove any moisture. This is a very important step as water content in the metal oxides would negatively impact the stoichiometry of the end compound. The rare earth oxides were dried at 900 °C while the other metal oxides were dried in a warming oven. The higher temperature drying for the rare earth oxides is necessary due to their stronger binding with water. Small 5-gram batches of each composition were ball milled in a SPEX 8000M Mixer/Mill. Through the process of making these samples, it was found that mixing in polypropylene containers was necessary as tungsten carbide and zirconia cannisters led to contamination of the samples, with zirconia particles segregating at the grain boundaries. Samples were then pressed into ½-inch pellets using a die and Carver Uniaxial Press under 3 metric tons of force. These pellet samples were then placed into a muffle furnace using alumina boats and sintered in air. If single phase was not achieved upon initial heat treatment, the samples were ground, repressed, and heat treated again. This was done up to three times to achieve a single phase. These steps are summarized in the process diagram in Figure 2-1.

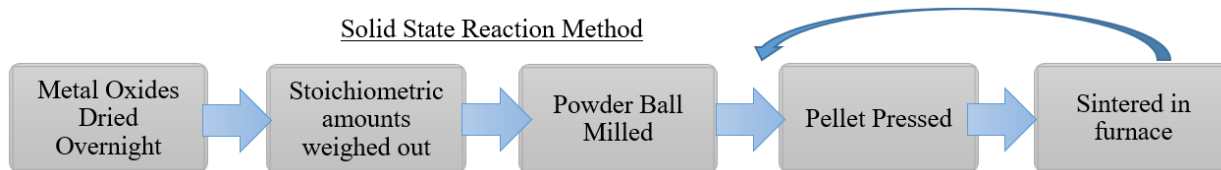


Figure 2-1 processing diagram for the solid-state method.

Polymeric Steric Entrapment Method

The polymeric steric entrapment (PSE) synthesis method is a wet chemistry technique that can be described as a polymer assisted sol gel where the cations are thoroughly mixed and held close together by polymer chains [47], [48]. Using long chain polymers, in these studies polyvinyl alcohol (PVA), ensures a high degree of mixing and a homogenous distribution of the cation species. As the ions are physically entrapped in a polymeric network within the solution, this inhibits elemental segregation or precipitation. For non-water soluble salts, ethylene glycol (EG) can be used as the polymerization agent as it is a solvent in wet chemistry methods when a water soluble form of a material is not available. In our studies, some form of the metal salt, whether nitrate, acetate or chloride, could be used that was water soluble. In addition to the type of solvent, other factors that can be varied include: the degree of polymerization, the cation to organics ratio, the solution pH, and the calcination and crystallization temperatures and times. Changing these parameters can affect the resultant particle size and size distribution, morphology, and microstructure. Because obtaining a homogeneously distributed single- phase material was the main priority for the work performed in these studies, the effects of such variable changes on the powder properties was not investigated but does present an avenue for future studies.

An example calculation process for the production of $(\text{Mg}_{0.2}\text{Ni}_{0.2}\text{Co}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2})\text{Al}_2\text{O}_4$, termed XAlO, with the PSE method is presented in the following steps. The total cation valence is calculated from the cation charges multiplied by the mol per formula unit of the cation in the final desired compound as shown in Table 4. This is then used to calculate the amount of PVA, $\text{CH}_2\text{CH}(\text{OH})$, needed for the batch based on the batch size and mol ratio of the total cation valence to the valences of the OH- functional groups in the PVA, as shown in Equation 19.

Equation 19:

$$(5 \text{ g XAlO}) \left(\frac{1 \text{ mol XAlO}}{172.13 \text{ g XAlO}} \right) \left(\frac{8 \text{ mol charges}}{1 \text{ mol XAlO}} \right) \left(\frac{1 \text{ mol PVA}}{4 \text{ mol charges}} \right) \left(\frac{44.05 \text{ g PVA}}{1 \text{ mol PVA}} \right) = 2.55 \text{ g PVA}$$

In all syntheses, a 4:1 cation to PVA ratio was used. A 5wt.% PVA solution with deionized (DI) water is then produced by mixing the PVA and water in a beaker on a hot plate at 60°C. While there will be additional water in the final solution, this is approximately how much is needed for completely dissolving the PVA before it is added to the nitrate solution.

Stoichiometric amounts of the metal nitrates are calculated and weighed out and then dissolved into DI water in a beaker on hot plate at 60 °C while continuously stirring. The nitrate salts are in complete solution once the mixture is transparent. Note: if the mixture is not transparent after thorough stirring has been done, nitric acid can be slowly dropped into the beaker to aid dissolution and is stopped once a cloudy to clear transition in the solution is reached. Once both mixtures are completely into solution, the stir bar is removed from the PVA solution and the contents of the beaker is slowly poured into the nitrate solution while it is stirring. Mixing is continued until the solution is clear indicating the nitrates and PVA has fully dissociated. Once good mixing is achieved, the temperature of the solution in the beaker is increased to 100°C. allowing the water to evaporate.

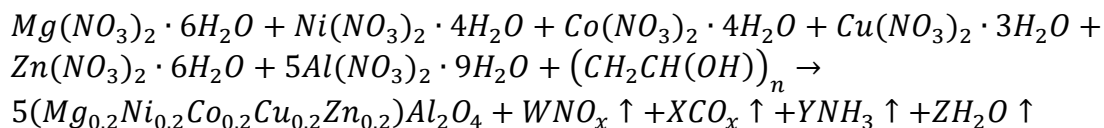
Table 4 Precursor material for $(\text{Mg}_{0.2}\text{Ni}_{0.2}\text{Co}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2})\text{Al}_2\text{O}_4$ synthesis with PSE.

<u>Precursor</u>	<u>Cation Charge</u>	<u>Mol per formula unit</u>
$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	2	0.2
$\text{Ni}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	2	0.2
$\text{Co}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	2	0.2
$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$	2	0.2
$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	2	0.2
$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	3	2
Total cation valence:		8

This step can take several hours. After the water has been driven off, the beaker is placed in a drying oven overnight. The next day the resultant foam powder is scraped out of the beaker, lightly ground using a mortar and pestle, and placed into a crucible. In preparation for the calcining process, this crucible is covered with two layers of aluminum foil with holes poked into them in alternating locations. As the calcining step is exothermic, these alternating layers allow for gases to exit while preventing any powder from escaping. In addition, a slow furnace ramp rate of 1°C/minute is used for the calcining step to also reduce powder activity.

Equation 20 shows the stoichiometric equation for producing $(Mg_{0.2}Ni_{0.2}Co_{0.2}Cu_{0.2}Zn_{0.2})Al_2O_4$ with the PSE method. As some steps involved produce gases, the water reduction, drying, and calcining steps should all be performed in a fume hood.

Equation 20:



The calcined powder is then pressed into a pellet and crystallized at a crystallization temperature, typically for 1 hour, with a 5 °C/min ramp rate before being furnace cooled. The described steps for the PSE synthesis process which results in a homogenous distribution of chemical species and in material with small particle size, are summarized in the processing diagram in Figure 2-2.

The advantages of this technique are its low heating temperatures, improved mixing, low cost, and ease of scalability.

A summary of all the multicomponent compositions produced, whether they were successful in producing a single-phase material, their resultant crystal structure, and the processing method and conditions utilized are summarized in Table 2.5.

Hot Uniaxial Pressing

In order to obtain high-density samples for resonant ultrasound spectroscopy measurement, PSE synthesized spinel powders were hot-pressed using a uniaxial hot press procured from OXY-GON industries (Model No. FR210-25T-A-200-04T). Single phase powder was loaded into a 13 mm diameter grafoil-lined graphite die, as shown in Figure 2-3, and hot pressed for 1 hour at 67 MPa under vacuum or flowing Ar depending on sample composition. Flowing Argon was necessary for the multicomponent composition, as hot pressing under vacuum resulted in the vaporization of some of the transition metal constituents. After hot pressing, the samples were air annealed in a muffle furnace for 2 hours at the hot-pressing temperature to reduce residual stress and remove the carbon from the sample surface. The density of the hot-pressed pellets after annealing was measured by the Archimedes method using a Mettler-Toledo XS64 scale with density kit. Table 6 summarizes the heating conditions and achieved densities.

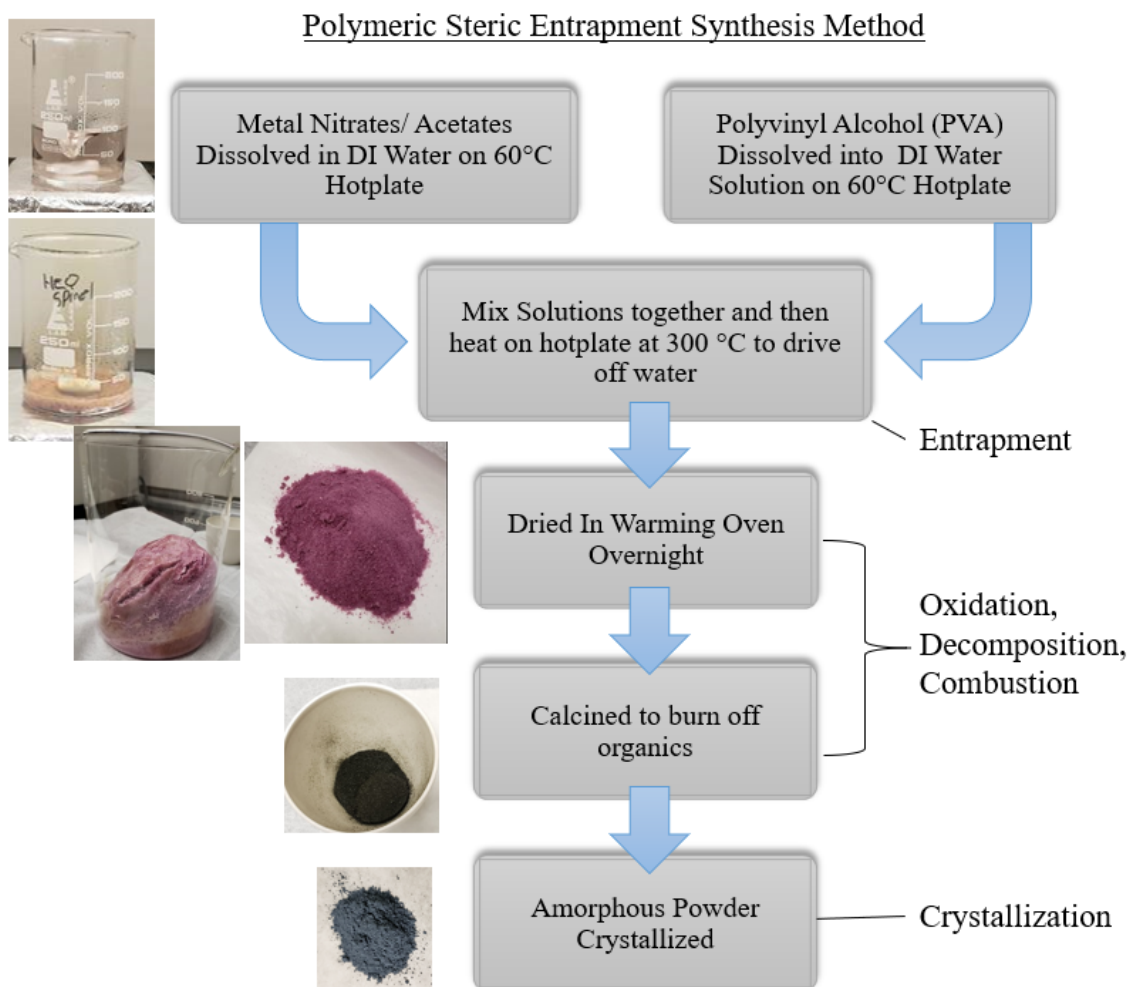


Figure 2-2 processing diagram with steps and pictures for the polymeric steric entrapment method.

Table 2.5. Summary of all material compositions synthesized, heat treatments used, whether single phase was achieved, and their crystal structure and space group.

Composition	Solid State reaction method	Polymeric steric entrapment (PSE)	Single phase?	Crystal Structure and Space Group
$(\text{Mg}_{0.2}\text{Ni}_{0.2}\text{Co}_{0.2}\text{Cu}_{0.2}\text{Fe}_{0.2})\text{Fe}_2\text{O}_4$	1250°C 10 hrs 5°C/min ramp, furnace cooled	-	Yes, SSS	Spinel: Fd-3m
$(\text{Mg}_{0.2}\text{Ni}_{0.2}\text{Co}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2})\text{Fe}_2\text{O}_4$	1250°C 10 hrs 5°C/min ramp, furnace cooled	-	Yes, SSS	Spinel: Fd-3m
$(\text{Mg}_{0.2}\text{Ni}_{0.2}\text{Co}_{0.2}\text{Cu}_{0.2}\text{Mn}_{0.2})\text{Fe}_2\text{O}_4$	Calcine 950°C for 10 hrs then 1250°C 10 hrs 5°C/min ramp, furnace cooled	-	Yes, SSS	Spinel: Fd-3m
$(\text{Ni}_{0.2}\text{Co}_{0.2}\text{Cu}_{0.2}\text{Fe}_{0.2}\text{Mn}_{0.2})\text{Fe}_2\text{O}_4$	1250°C 10 hrs 5°C/min ramp, furnace cooled	-	Yes, SSS	Spinel: Fd-3m
$(\text{Ni}_{0.2}\text{Co}_{0.2}\text{Cr}_{0.2}\text{Fe}_{0.2}\text{Mn}_{0.2})_3\text{O}_4$	1250°C 10 hrs 5°C/min ramp, furnace cooled	-	Yes, SSS	Spinel: Fd-3m
$(\text{Ni}_{0.2}\text{Co}_{0.2}\text{Cu}_{0.2}\text{Fe}_{0.2}\text{Mn}_{0.2})_3\text{O}_4$	1250°C 10 hrs 5°C/min ramp, furnace cooled	-	No, SSS	Multiphase
$(\text{Mg}_{0.2}\text{Ni}_{0.2}\text{Co}_{0.2}\text{Cu}_{0.2}\text{Fe}_{0.2})_3\text{O}_4$	1250°C 10 hrs 5°C/min ramp, furnace cooled	-	No, SSS	Multiphase
$(\text{Mg}_{0.2}\text{Ni}_{0.2}\text{Co}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2})\text{Al}_2\text{O}_4$	1600°C 10 hrs 5°C/min ramp, furnace cooled	Calcine: 300°C 2.5 h 1°C/min Crystallize: 550°C, 1 h, 5°C/min, FC	Yes, SSS, PSE	Spinel: Fd-3m
$(\text{Mg}_{1/6}\text{Ni}_{1/6}\text{Co}_{1/6}\text{Cu}_{1/6}\text{Zn}_{1/6}\text{Al}_{1/6})_3\text{O}_4$	-	Calcine: 300°C 2.5 h 1°C/min Crystallize: 550°C, 900°C, 1 h, 5°C/min, FC	No	Mixed phase: spinel and rocksalt
$(\text{Mg}_{0.2}\text{Ni}_{0.2}\text{Co}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2})\text{Cr}_2\text{O}_4$	1250°C 10 hrs 5°C/min ramp, furnace cooled	-	Yes, SSS	Spinel: Fd-3m
$(\text{Mg}_{0.2}\text{Ni}_{0.2}\text{Co}_{0.2}\text{Cu}_{0.2}\text{Fe}_{0.2})\text{Cr}_2\text{O}_4$	1250°C 10 hrs 5°C/min ramp, furnace cooled	-	Yes, SSS	Spinel: Fd-3m
$(\text{Mg}_{0.2}\text{Ni}_{0.2}\text{Co}_{0.2}\text{Cu}_{0.2}\text{Mn}_{0.2})\text{Cr}_2\text{O}_4$	1250°C 10 hrs 5°C/min ramp, furnace cooled	-	Yes, SSS	Spinel: Fd-3m
$(\text{Ni}_{0.2}\text{Co}_{0.2}\text{Cu}_{0.2}\text{Fe}_{0.2}\text{Mn}_{0.2})\text{Cr}_2\text{O}_4$	1250°C 10 hrs 5°C/min ramp, furnace cooled	-	No, SSS	-

Table 2.5 continued

Composition	Solid State reaction method	Polymeric steric entrapment (PSE)	Single phase?	Crystal Structure and Space Group
$\text{Ba}(\text{Zr}_{0.2}\text{Hf}_{0.2}\text{Sn}_{0.2}\text{Ti}_{0.2}\text{Nb}_{0.2})\text{O}_3$	1400°C 10 hrs, 5°C/min ramp, furnace cooled	-	Yes, SSS	Perovskite: Pm-3m
$\text{Ba}(\text{Zr}_{0.2}\text{Hf}_{0.2}\text{Sn}_{0.2}\text{Ti}_{0.2}\text{Nb}_{0.2})\text{O}_3 + .5\text{at}\% \text{ Ce}$ $\text{Ba}(\text{Zr}_{0.2}\text{Hf}_{0.2}\text{Sn}_{0.2}\text{Ti}_{0.2}\text{Nb}_{0.2})\text{O}_3 + 1\text{at}\% \text{ Ce}$	1300°C 10 hrs 2X 5°C/min ramp, 270 min cool 1300°C to 300°C then furnace cool	-	Yes, SSS	Perovskite: Pm-3m
$\text{Sr}(\text{Zr}_{0.2}\text{Hf}_{0.2}\text{Sn}_{0.2}\text{Ti}_{0.2}\text{Nb}_{0.2})\text{O}_3$	1500°C 10 hrs 5°C/min ramp, furnace cooled	-	Yes, SSS	Perovskite: Pm-3m
$\text{Sr}(\text{Zr}_{0.2}\text{Hf}_{0.2}\text{Sn}_{0.2}\text{Ti}_{0.2}\text{Nb}_{0.2})\text{O}_3 + 0.5\text{at}\% \text{ Ce}$ $\text{Sr}(\text{Zr}_{0.2}\text{Hf}_{0.2}\text{Sn}_{0.2}\text{Ti}_{0.2}\text{Nb}_{0.2})\text{O}_3 + 1\text{at}\% \text{ Ce}$ $\text{Sr}(\text{Zr}_{0.2}\text{Hf}_{0.2}\text{Sn}_{0.2}\text{Ti}_{0.2}\text{Nb}_{0.2})\text{O}_3 + 1\text{at}\% \text{ Eu}$	1500°C 10 hrs 5°C/min ramp, furnace cooled	-	Yes, SSS	Perovskite: Pm-3m
$\text{Sr}(\text{Zr}_{0.2}\text{Hf}_{0.2}\text{Sn}_{0.2}\text{Ti}_{0.2}\text{Mn}_{0.2})\text{O}_3$	1500°C 10 hrs 5°C/min ramp, furnace cooled	-	Yes, SSS	Perovskite: Pm-3m
$\text{La}(\text{Co}_{0.2}\text{Cr}_{0.2}\text{Fe}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.2})\text{O}_3$	1200°C 10 hrs 5°C/min ramp, furnace cooled 2X 1200°C 10 hrs 5°C/min ramp, 1200°C to 300°C 4 hr cool, then furnace off	-	Yes, SSS	Perovskite: Pbm̄n
$\text{Bi}(\text{Co}_{0.2}\text{Cr}_{0.2}\text{Fe}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.2})\text{O}_3$	700°C 5 hr, 5°C/min ramp, furnace cooled	Calcine: 550°C 2.5 hrs ramp 1°C/min Crystallize: 700°C 1 hr 1°C/min ramp, furnace cooled	Nearly, SSS, PSE	Tetragonal $\text{Bi}_{14}\text{CrO}_{24}$ (I4/m) slight unknown secondary phase
$(\text{Gd}_{0.2}\text{La}_{0.2}\text{Sm}_{0.2}\text{Nd}_{0.2}\text{Y}_{0.2})\text{MnO}_3$	950°C 10 hrs, 1250°C 10 hrs	-	Yes, SSS	Perovskite: Pbm̄n
$(\text{Gd}_{0.2}\text{La}_{0.2}\text{Sm}_{0.2}\text{Nd}_{0.2}\text{Y}_{0.2})\text{NiO}_3$	1250°C 10 hrs	-	No, SSS	Multiphase matches literature [20]
$(\text{Gd}_{0.2}\text{La}_{0.2}\text{Sm}_{0.2}\text{Nd}_{0.2}\text{Y}_{0.2})\text{AlO}_3$	1500°C 10 hrs	-	Yes, SSS	Perovskite: Pm-3m
$(\text{Gd}_{0.2}\text{La}_{0.2}\text{Sm}_{0.2}\text{Nd}_{0.2}\text{Y}_{0.2})(\text{Co}_{0.2}\text{Cr}_{0.2}\text{Fe}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.2})\text{O}_3$	950°C 10 hrs 1250°C 10 hrs 5°C/min ramp, furnace cool Also tried 1400°C 20 hr	-	No	Perovskite (Pbm̄n) with remnant metal oxide phase

Table 2.5 continued

Composition	Solid State reaction method	Polymeric steric entrapment (PSE)	Single phase?	Crystal Structure and Space Group
$(\text{La}_{0.2}\text{Y}_{0.2}\text{Ce}_{0.2}\text{Pr}_{0.2}\text{Nd}_{0.2})\text{MnO}_3$	1200°C 10 hrs 5°C/min ramp, furnace cool 2X 1200°C 10 hrs 5°C/min ramp, 1200°C-300°C 4 hr cool, furnace off	-	No	Mixed phase: perovskite and fluorite
$(\text{La}_{0.2}\text{Y}_{0.2}\text{Ce}_{0.2}\text{Pr}_{0.2}\text{Nd}_{0.2})(\text{Co}_{0.2}\text{Cr}_{0.2}\text{Fe}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.2})\text{O}_3$	1200°C 10 hrs 5°C/min ramp, furnace cool 2X 1200°C 10 hrs 5°C/min ramp, 1200-300°C 4 hr cool, furnace off	-	No	Mixed phase: perovskite and fluorite
$(\text{La}_{0.2}\text{Pr}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2})_2\text{CuO}_4$	1000°C 12 hr, 5 °C/min ramp furnace cooled	Calcine: 550°C 2.5 hr 1°C/min Crystallize: 900°C 1 hr, 5°C/min, FC	Yes, SSS, PSE	RP n=1: I 4/m m m
$(\text{La}_{0.2}\text{Nd}_{0.2}\text{Gd}_{0.2}\text{Tb}_{0.2}\text{Dy}_{0.2})_2\text{CuO}_4$	1000°C 12 h, 5 °C/min ramp furnace cooled	Calcine: 550°C 2.5 h 1°C/min Crystallize: 900°C 1 h, 5°C/min, FC	Yes, SSS, PSE	RP n=1: I 4/m m m
$(\text{La}_{0.36}\text{Pr}_{0.36}\text{Nd}_{0.36}\text{Sm}_{0.36}\text{Eu}_{0.36}\text{Sr}_{0.2})\text{CuO}_4$	1170°C 24 hrs 5°C/min ramp, air quench	-	SSS yes, but slightly melted/ vaporized	RP n=1: I 4/m m m
$(\text{La}_{0.2}\text{Pr}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2}\text{Gd}_{0.2}\text{Tb}_{0.2}\text{Dy}_{0.2}\text{Ho}_{0.2}\text{Sr}_{0.2})\text{CuO}_4$	1100°C 15 hrs 5°C/min, furnace cooled	Calcine: 550°C 2.5 h 1°C/min Crystallize: 900°C 1 h, 5°C/min, FC	SSS no, PSE no	-
$(\text{La}_{0.37}\text{Pr}_{0.37}\text{Nd}_{0.37}\text{Sm}_{0.37}\text{Eu}_{0.37}\text{Ce}_{0.15})\text{CuO}_4$	-	Calcine: 550°C 2.5 h 1°C/min Crystallize: 900°C 1 h, 5°C/min, FC	PSE nearly	RP n=1: I 4/m m m with small secondary
$(\text{Gd}_{0.2}\text{La}_{0.2}\text{Y}_{0.2}\text{Tb}_{0.2}\text{Sm}_{0.2})_3(\text{Al}_5\text{O}_{12}+1\text{at}\%\text{Ce})$	-	Calcine: 550°C 2.5 h 1°C/min Crystallize: 1050°C 1 hr	PSE yes	Garnet

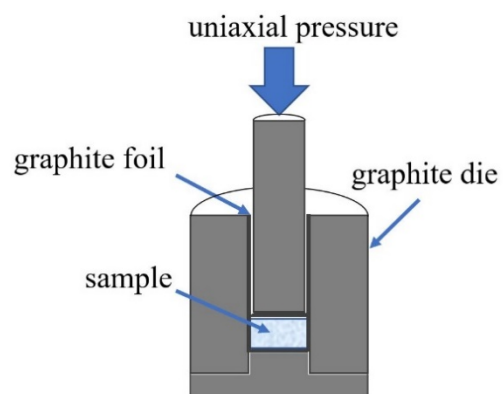


Figure 2-3 Visual representation of the cross-section of a loaded graphite die used for hot uniaxial pressing.

Table 6 Summary of hot-pressing conditions and resultant densities for single phase samples for the investigated spinel compositions.

Sample	Archimedes Density	% Theoretical Density	Hot pressing conditions
MgAl ₂ O ₄	3.1664 g/cm ³	88%	1100°C, flowing argon
MgAl ₂ O ₄	3.5187 g/cm ³	98%	1400°C, vacuum
(Mg _{1/5} Ni _{1/5} Co _{1/5} Cu _{1/5} Zn _{1/5})Al ₂ O ₄	3.9973 g/cm ³	93%	1100°C, flowing argon

2.2.X-ray Diffraction Techniques

All x-ray diffraction experiments were conducted using a Malvern PANalytical Empyrean diffractometer with a Cu-source and a PIXcel^{3d} area detector. X-ray diffraction was used to verify phase formation and identify the crystal structure(s) of the synthesized materials. High temperature X-ray diffraction (HTXRD) measurements were performed with an Anton Paar HTK 1200N high temperature furnace and allowed for a study of the phase formation and thermal stability of a few selected HEO materials.

Kinetic Studies: This experimental setup provided both a stable and controlled environmental chamber that, coupled with rapid data collection on heating, can capture both dynamic and static phase transformations. When collecting diffraction data, the compromise between intensity and resolution are weighed and decisions made for data collection parameters. For in-situ measurements data can be collected as quickly as 30 seconds. However, rapid data collection sacrifices data quality and sample quality (including disorder effects, apparent in HEO's) make such a rapid data collection ill advised. The time required for data collection for each unique sample is therefore evaluated when such in-situ experiments are performed. For kinetic studies, in order to gain information on the phase formation mechanisms within the HEO materials data were collected in a 2θ range of $28-38^\circ$ with a 0.026° step size. Four-minute scans were performed continuously while ramping from 25°C to the dwell temperature, at a heating rate of $1.7^\circ\text{C}/\text{min}$. For isothermal experiments, the temperature was held at the dwell temperature for several hours while continually collecting.

Thermal stability: Samples' thermal stability and lattice expansion with temperature were also investigated with HTXRD techniques. Full range $10-90^\circ$ 2θ scans were performed when the sample reached each set temperature. Using Rietveld refinement techniques with the GSASII package [49], lattice parameters can be determined and plotted as a function of temperature to determine the thermal expansion behavior. In addition, the collected diffraction spectra enable phase stability analysis at high temperatures.

2.3.Scanning electron microscopy

Microscopy of the sample was performed using a ZEISS EVO scanning electron microscope (SEM) with Bruker xFlash 6130 energy dispersive X-ray spectrometer (EDXS). SEM images were used to gain information about the microstructure and grain sizes of polycrystalline samples and to examine powder morphology. EDXS elemental mapping was performed on the bulk samples to determine elemental homogeneity after processing and was a useful tool for identifying segregation or inhomogeneities.

2.4.Thermal Analysis

Thermal analysis methods can be complementary to in-situ HTXRD techniques. Simultaneous Thermogravimetric Analyzer (TGA) & Differential Scanning Calorimeter (DSC) was performed on some samples to better select processing temperatures and to compare between the solid state and polymeric steric entrapment synthesis routes. While these measurements are informative, they do not give any crystallographic information about the phases formed. Other measurements need

to be performed to understand the phase formations indicated by the features seen in DSC/TGA. TGA and DSC measurements were performed on powders using a TA Instruments DSC SDT Q600 while increasing the temperature with a 5°C/minute rate. For solid state synthesized powders, material was taken after ball milling to be measured. For PSE synthesized material some powder was taken after the drying oven step to better understand the necessary calcination temperature. As material measured at this point will go through organic burn off, it is recommended that only a small amount of material is measured and that disposable alumina pans with lids are used to hold the sample and prevent contamination of the chamber. Some powders were also measured after the calcining step in PSE synthesis, this was for samples where only the crystallization points were of interest and being compared.

2.5.Magnetometry

Magnetization and Hysteresis

High-temperature magnetometry measurements from 300–850 K were performed using a Quantum Design VersaLab with vibrating sample magnetometer (VSM), while low-temperature measurements 3–300 K were performed with a Quantum Design Magnetic Property Measurement System (MPMS) with VSM. The low-temperature magnetization sequence was performed in the following method on rounded pieces from polycrystalline pellets [50]. For the zero-field-cooled (ZFC) measurement the sample was cooled in zero field from room temperature. Once the lowest temperature is reached, the magnetic field is applied and the magnetization is measured as a function of temperature while warming. The field-cool-cooling (FC) curve is then obtained from measuring the magnetization while cooling to low temperature in the same field. With the same field still applied the field-cooled-warming (FW) curve is obtained from measuring magnetization while warming. The material's magnetic moment was measured both as a function of temperature and as a function of applied magnetic field.

First order reversal curve

First order reversal curve (FORC) measurements were performed in a Quantum Design Dynacool Physical Property Measurement System (PPMS). A FORC is measured by progressively saturating a sample in field, then decreasing the field, reversing the field and sweeping it back to the saturation field in a series of regular field sweeps.

2.6.Resonant Ultrasound Spectroscopy

In a RUS experiment, the mechanical resonances of a freely vibrating solid of known shape are measured, and an iteration procedure is used to “match” the measured lines with a calculated spectrum. The latter is based on the sample's known mass and dimensions, and an “educated guess” of its elastic moduli. [51], [52]. In a typical RUS experimental set-up, a specimen is lightly held between an exciting and receiving piezoelectric transducer as shown in the schematic on the left in Figure 2-4 A frequency generator produces an electromagnetic wave that is sent to one transducer, which is then converted into a mechanical wave that excites the sample. The sample's response is collected and converted to an electrical signal at the second transducer. The frequency

is swept, typically between 100kHz and 2 MHz, and the sample's response is recorded, as shown with a representative spectrum collected on hot pressed MgAl_2O_4 (right portion of Figure 2-4). Large responses are detected when the frequency corresponds to sample's eigenfrequency. The resonance position in terms of frequency value is dependent on the sample's dimensions, density, and elastic moduli.

While other methods exist for determining a material's elastic properties, the main advantages of RUS, other than being non-destructive, are its high precision and sensitivity. For polycrystalline samples, a successful RUS experiment will yield the longitudinal and shear modulus, which allows determination of Young's modulus and bulk modulus for easy comparison with reported literature values.

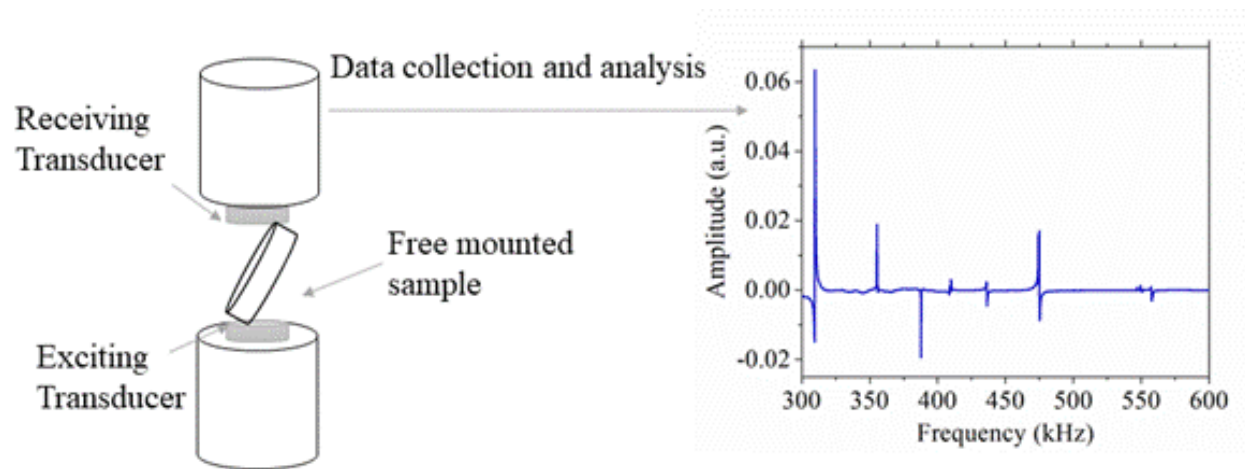


Figure 2-4 Visual schematic of resonant ultrasound spectroscopy measurement and resultant spectra.

CHAPTER THREE

MATERIAL CHARACTERIZATION RESULTS AND DISCUSSION

A version of this chapter's sections *Iron and Chromium based spinels*, *Ferritic spinels: high temperature magnetic behavior*, *Ferritic spinels: low temperature magnetic behavior*, *Chromium based spinels: low temperature magnetic behavior*, and *Valence information* was originally published by Brianna L. Musicó, Quinton Wright, Thomas Zac Ward, Alexander Grutter, Elke Arenholz, Dustin Gilbert, David Mandrus, and Veerle Keppens. A portion of the results and discussion portions from this paper have been stated in this section.

B. Musicó, Q. Wright, T. Z. Ward, A. Grutter, E. Arenholz, D. Gilbert, D. Mandrus, and V. Keppens: Tunable magnetic ordering through cation selection in entropic spinel oxides. *Phys. Rev. Mater.* 3(10), 104416 (2019).

Samples were synthesized by Brianna L. Musicó and Quinton Wright. Magnetic measurements were performed by Brianna L. Musicó. X-ray absorption spectroscopy with x-ray magnetic linear dichroism performed by Dustin Gilbert at Advanced Light Source (ALS) on Beamline 4.0.2 with the help of Alexander Grutter and Elke Arenholz. Alexander Grutter, Dustin Gilbert, David Mandrus, Veerle Keppens, Thomas Zac Ward, and Brianna L. Musicó all contributed to the result discussion. The final compilation, editing, and organization of findings done by Brianna L. Musicó.

A version of this chapter's section *Aluminate spinels* and *Resonant ultrasound spectroscopy results* is to be published by Brianna L. Musicó, Joshua P. Smith, Quinton Wright, Kurt Sickafus, David G. Mandrus, and Veerle Keppens. A portion of the results and discussion portions from this paper have been stated in this section.

"Synthesis, mechanical properties, and high temperature stability of multicomponent spinel oxide" has been submitted to the journal *MRS Communications*.

Samples were synthesized by Brianna Musicó with the assistance of Quinton Wright and Joshua Smith. Phase stability and elastic property measurement and analysis was performed by Brianna Musicó. Work was advised by Veerle Keppens, David Mandrus, and Kurt Sickafus.

A version of this chapter's sections *Ruddlesden-Popper* and *Magnetic Properties- Ruddlesden-Popper cuprates* has been accepted for publication by Brianna L. Musicó, Quinton Wright, Cordell Delzer, T. Zac Ward, Claudia J. Rawn, David G. Mandrus, and Veerle Keppens.

B. L. Musicó, Q. Wright, C. Delzer, T. Z. Ward, C. J. Rawn, D. G. Mandrus, and V. Keppens: Synthesis method comparison of compositionally complex rare-earth based Ruddlesden-Popper $n=1$ T' -type cuprates. *J. Am. Ceram. Soc. Jace.* 17750 (2021).

A version of this chapter, sections 3.1 and 4.3, is to be published in a textbook chapter "Experimental Characterization of High Entropy Oxides with In-situ High Temperature X-Ray Diffraction Techniques" by Brianna L. Musicó, Cordell J. Delzer, John R. Salasin, Michael R. Koehler, and Claudia J. Rawn in the textbook:

Brechtl, J., Liaw, P.K. (2021). *Fundamental Studies of High Entropy Materials*. Manuscript in preparation for publication by Springer.

Selected portions from this chapter have been stated in this section. The introduction and background was written by Brianna L. Musicó and Claudia J. Rawn. Sample synthesis was performed by Brianna L. Musicó. Diffraction experiments were performed by Brianna L. Musicó and Michael R. Koehler. Background knowledge for experiment set up and design provided by John R. Salasin. Data analysis performed by Brianna L. Musicó and Cordell J. Delzer. Discussion and prospects written by Brianna L. Musicó and reviewed by Claudia J. Rawn.

3.1. Single Phase verification and elemental homogeneity

Iron and Chromium based spinels

Eleven compositions have been studied and their processing temperatures are summarized in Table 7, while processing conditions have been detailed in Table 2.5. Samples were synthesized from precursor powders of MgO, NiO, CoO, CuO, ZnO, MnO₂, Fe₂O₃, Al₂O₃, Cr₂O₃ of at least 99.95% purity. Single-phase purity was confirmed for eight compositions with X-ray diffraction spectra that align with the spinel *Fd-3m* structure as shown in Figure 3-1. A few of the single phase materials' XRD spectra were refined using GSASII and Table 8 shows the lattice parameters and refinement parameters for the fits [46], [49], [53]. The (Mn_{0.2}Fe_{0.2}Co_{0.2}Ni_{0.2}Cu_{0.2})₃O₄ and (Mn_{0.2}Fe_{0.2}Co_{0.2}Ni_{0.2}Cu_{0.2})Cr₂O₄ compositions had remnant metal oxide phase present. The (Mg_{0.2}Fe_{0.2}Co_{0.2}Ni_{0.2}Cu_{0.2})₃O₄ composition pellet had surface irregularities and did not achieve a single phase.

Energy Dispersive X-Ray Spectroscopy (EDXS) mapping, Figure 3-2, Figure 3-3, and Figure 3-4, shows that the sample possesses a homogenous elemental distribution with no tendency towards segregation. SEM micrographs of (Mg_{0.2}Fe_{0.2}Co_{0.2}Ni_{0.2}Cu_{0.2})Cr₂O₄ and (Mg_{0.2}Co_{0.2}Ni_{0.2}Cu_{0.2}Zn_{0.2})Fe₂O₄ pellets are shown in Figure 3-5 (b) and (c), respectively. These images show that these samples have substantial differences in microstructure, with the Fe-based spinel having large, highly-interconnected grains, while the Cr-based oxides have a much finer grain structure.

Aluminate spinels

Pictures of the crystallized PSE synthesized powders of each composition are given in Figure 3-6. Synthesis of (Mg_{1/6}Ni_{1/6}Co_{1/6}Cu_{1/6}Zn_{1/6}Al_{1/6})₃O₄ was attempted, but a single phase was not achieved. Initial heat treatment at 550°C resulted in a weak crystalline signature, and additional treatment at 900°C for 1 hour resulted in a mixture of spinel and rocksalt phases. In 2-3 type spinels, such as those reported here, the larger ion typically occupies the tetrahedral site, resulting in the normal spinel configuration as described for MgAl₂O₄ [34], [35]. This is the case for three of the individual spinels of this multicomponent composition, MgAl₂O₄, CoAl₂O₄, and ZnAl₂O₄, whereas NiAl₂O₄ takes on a largely inverse spinel configuration [36] and CuAl₂O₄ [37] has a disordered structure with tendency towards some degree of inversion.

Table 7 Summary of the iron and chromium-based HEO spinel compositions synthesized and investigated in this study.

Name	Composition	Single Phase
F1	$(\text{Mg}_{0.2}\text{Fe}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2})\text{Fe}_2\text{O}_4$	Yes
F3	$(\text{Mg}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2})\text{Fe}_2\text{O}_4$	Yes
F4	$(\text{Mg}_{0.2}\text{Mn}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2})\text{Fe}_2\text{O}_4$	Yes
F5	$(\text{Mn}_{0.2}\text{Fe}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2})\text{Fe}_2\text{O}_4$	Yes
F6	$(\text{Cr}_{0.2}\text{Mn}_{0.2}\text{Fe}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2})_3\text{O}_4$	Yes
F7	$(\text{Mn}_{0.2}\text{Fe}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2})_3\text{O}_4$	No
F8	$(\text{Mg}_{0.2}\text{Fe}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2})_3\text{O}_4$	No
S1	$(\text{Mg}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2})\text{Al}_2\text{O}_4$	Yes
C1	$(\text{Mg}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2})\text{Cr}_2\text{O}_4$	Yes
C2	$(\text{Mg}_{0.2}\text{Fe}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2})\text{Cr}_2\text{O}_4$	Yes
C3	$(\text{Mg}_{0.2}\text{Mn}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2})\text{Cr}_2\text{O}_4$	Yes
C4	$(\text{Mn}_{0.2}\text{Fe}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2})\text{Cr}_2\text{O}_4$	No

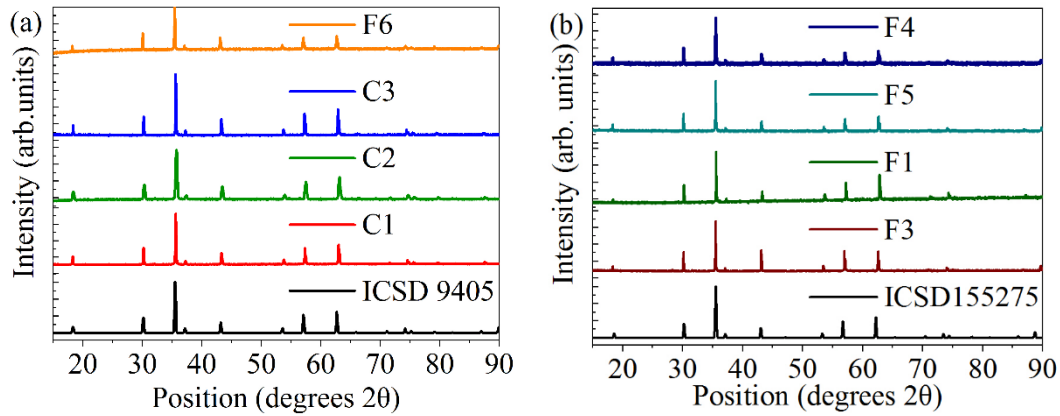


Figure 3-1 X-ray diffraction for single phase HEO spinel compositions that are (a) chromium base with ICSD 9405 NiCrMnO₄ d, (b) iron based with ICSD 155275 MnFe₂O₄.

Table 8 Lattice parameter and Rietveld refinement results for a few HEO spinel compositions successfully synthesized in this study.

Name	Composition	Lattice Parameter (Å)	Refinement Parameters		
			wR	R	GOF
F1	(Mg _{0.2} Fe _{0.2} Co _{0.2} Ni _{0.2} Cu _{0.2})Fe ₂ O ₄	8.380550 esds: 0.000278	2.96%	2.21%	1.15
F3	(Mg _{0.2} Co _{0.2} Ni _{0.2} Cu _{0.2} Zn _{0.2})Fe ₂ O ₄	8.406226 esds: 0.00247	2.89%	2.26%	1.13
C1	(Mg _{0.2} Co _{0.2} Ni _{0.2} Cu _{0.2} Zn _{0.2})Cr ₂ O ₄	8.314964 esds: 6.6E-7	7.03%	4.86%	1.58
C2	(Mg _{0.2} Mn _{0.2} Co _{0.2} Ni _{0.2} Cu _{0.2})Cr ₂ O ₄	8.344590 esds: 0.000296	6.35%	4.21%	1.62

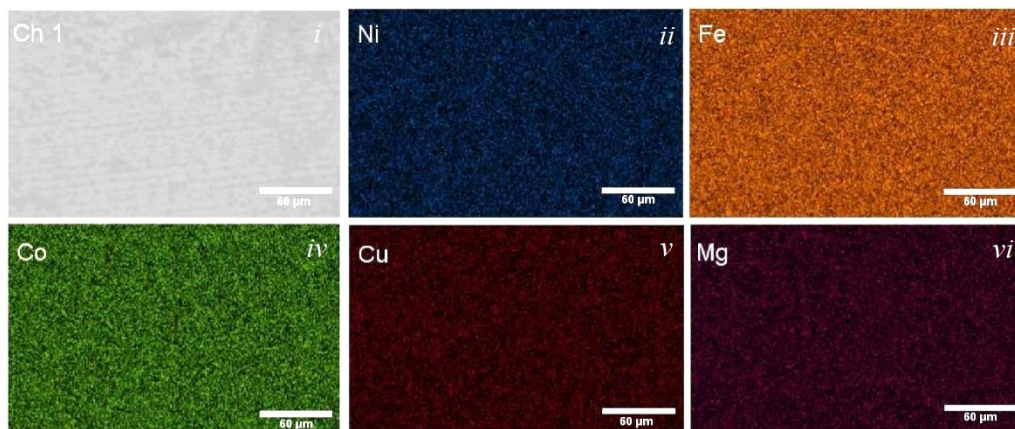


Figure 3-2 SEM image of a polished (Mg_{0.2}Fe_{0.2}Co_{0.2}Ni_{0.2}Cu_{0.2})Fe₂O₄ pellet and EDXS elemental mapping of the ii Ni, iii Fe, iv Co, v Cu, and vi Mg distributions. The scale bar indicates 60 microns.

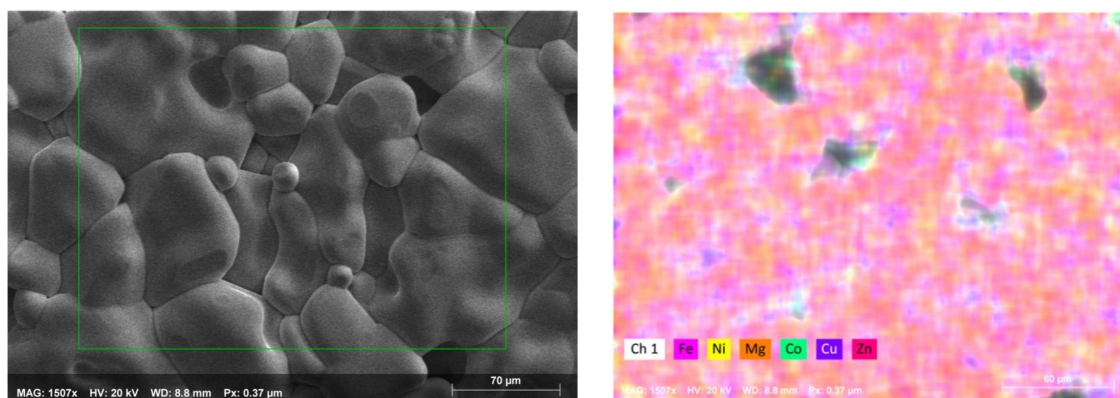


Figure 3-3 SEM and EDXS color mapping of $(\text{Mg}_{0.2}\text{Co}_{0.2} \text{Ni}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2})\text{Fe}_2\text{O}_4$ polycrystalline pellet sintered at 1250°C for 10 hours in air.

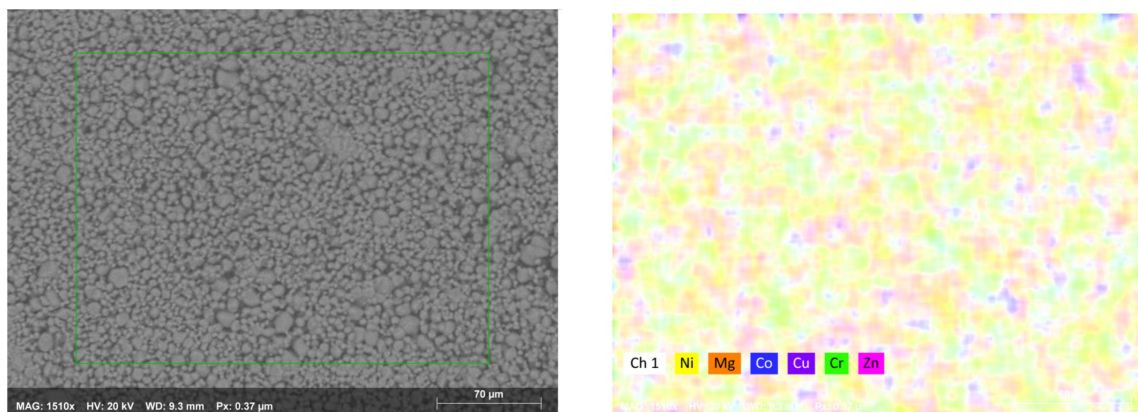


Figure 3-4 SEM and EDXS color mapping of $(\text{Mg}_{0.2}\text{Co}_{0.2} \text{Ni}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2})\text{Cr}_2\text{O}_4$ polycrystalline pellet sintered at 1250°C for 10 hours in air.

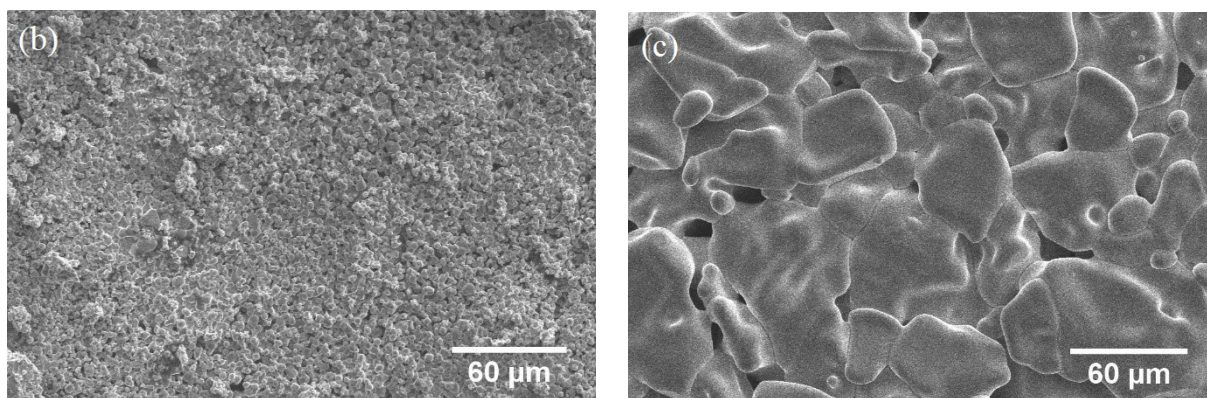


Figure 3-5 (b) SEM image of $(\text{Mg}_{0.2}\text{Fe}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2})\text{Cr}_2\text{O}_4$ pellet and (c) SEM image of $(\text{Mg}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2})\text{Fe}_2\text{O}_4$ pellet that was sintered, ground, pressed and re-sintered.

The disordered structure of CuAl_2O_4 is attributed to Jahn-Teller effects of the Cu-cations, and has also been reported in HEO rocksalt ($\text{Mg}_{0.2}\text{Ni}_{0.2}\text{Co}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}$)O [54], [55]. A combination of these factors could be contributing to the inability to obtain a single phase ($\text{Mg}_{1/6}\text{Ni}_{1/6}\text{Co}_{1/6}\text{Cu}_{1/6}\text{Zn}_{1/6}\text{Al}_{1/6}$) $_3\text{O}_4$ and indicates that the entropy within the system was not sufficient to stabilize a single-phase material. X-ray diffraction (XRD) of the ($\text{Mg}_{1/6}\text{Ni}_{1/6}\text{Co}_{1/6}\text{Cu}_{1/6}\text{Zn}_{1/6}\text{Al}_{1/6}$) $_3\text{O}_4$ multiphase material is provided in Figure 3-7 showing a mixture of rocksalt and spinel phases. The XRD spectra for the single phase pellets after hot pressing and annealing is shown in Figure 3-8 (a). The (113) crystallographic reflection on the XRD pattern is the primary peak and is the sum of the form factors for both the A-site and B-site. The strong intensity of the (220) reflection is indicative of multiple cation species occupying the tetrahedral positions as it is only dependent on A-site contributions. In contrast, the (222) is just B-site dependent and is weaker in the disordered ($\text{Mg}_{1/5}\text{Ni}_{1/5}\text{Co}_{1/5}\text{Cu}_{1/5}\text{Zn}_{1/5}$) Al_2O_4 than the traditional MgAl_2O_4 . In addition, the lack in intensity for the (111) reflection in ($\text{Mg}_{1/5}\text{Ni}_{1/5}\text{Co}_{1/5}\text{Cu}_{1/5}\text{Zn}_{1/5}$) Al_2O_4 indicates a high degree of inversion within the structure as it scales as a difference between the form factors for the A- and B-sites. Due to the number of constituents, determining the degree of inversion and site-occupancies for the material is complex, but these findings indicate that ($\text{Mg}_{1/5}\text{Ni}_{1/5}\text{Co}_{1/5}\text{Cu}_{1/5}\text{Zn}_{1/5}$) Al_2O_4 does not follow a normal ordering with predominant aluminum occupancy of the octahedral sites. The Williamson-Hall (W-H) method [56] is used for analysis of the crystallite size, D , of the hot pressed pellets using the XRD data and the results are shown in Figure 3-8 (b) and (c). Using the relation in Equation 21 where FWHM = peak full width at half maximum, θ = peak position, K = Scherrer constant = 0.94, λ = x-ray wavelength = 1.54 Å, and ε = strain, the crystallite size can be determined from the y-intercept while the slope from the linear fit corresponds to the strain.

$$\text{Equation 21: } \text{FWHM} \cdot \cos\theta = \frac{K \cdot \lambda}{D} + 4 \cdot \varepsilon \cdot \sin\theta$$

From Figure 3-8, it is clear that the multicomponent spinel has a higher strain value than that of the MgAl_2O_4 . The crystallite sizes determined from the W-H method are provided along with unit cell information determined from Rietveld refinements using GSASII [49] of the XRD data in Table 9. Scanning electron microscopy (SEM) with energy dispersive x-ray spectroscopy (EDXS) was utilized in order to investigate the ($\text{Mg}_{1/5}\text{Ni}_{1/5}\text{Co}_{1/5}\text{Cu}_{1/5}\text{Zn}_{1/5}$) Al_2O_4 pellet after hot pressing and confirm the sample maintained a homogenous elemental distribution as shown in Figure 3-9. No elemental segregation was detected and the EDXS results in combination with the single-phase confirmation from XRD verify the sample's uniformity.

Ruddlesden-Popper

Ruddlesden-Popper (RP) cuprate HEOs were synthesized via both solid state (SSR) and polymeric steric entrapment (PSE) methods. Powder X-ray diffraction is used to determine the phase(s) present in sample. Figure 3-10 (a) shows the powder diffraction pattern for the two SSR samples. A detailed view of the 20-35° 2θ range in Figure 3-10 (b) shows evidence of a minor amount of secondary phase in SSR ($\text{La}_{0.2}\text{Nd}_{0.2}\text{Gd}_{0.2}\text{Tb}_{0.2}\text{Dy}_{0.2}$) $_2\text{CuO}_4$. The low intensity of these impurity phase peaks, along with the number of starting constituents, makes quantifying a specific phase fraction becomes problematic, but they are likely due to remnant rare earth oxide as Figure 3-11 shows.

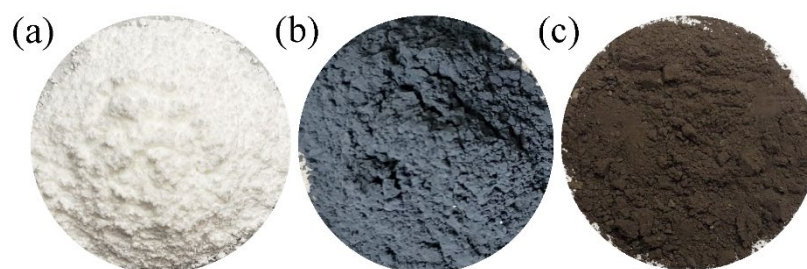


Figure 3-6 Images of the crystallized PSE synthesized powders of (a) MgAl_2O_4 , (b) $(\text{Mg}_{1/5}\text{Ni}_{1/5}\text{Co}_{1/5}\text{Cu}_{1/5}\text{Zn}_{1/5})\text{Al}_2\text{O}_4$, and (c) $(\text{Mg}_{1/6}\text{Ni}_{1/6}\text{Co}_{1/6}\text{Cu}_{1/6}\text{Zn}_{1/6}\text{Al}_{1/6})_3\text{O}_4$.

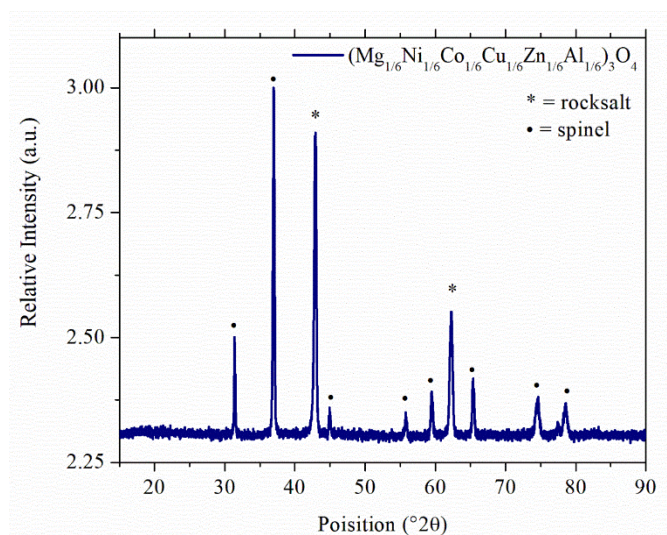


Figure 3-7 X-ray diffraction spectra of $(\text{Mg}_{1/6}\text{Ni}_{1/6}\text{Co}_{1/6}\text{Cu}_{1/6}\text{Zn}_{1/6}\text{Al}_{1/6})_3\text{O}_4$ crystallized at 900°C showing rocksalt and spinel phases.

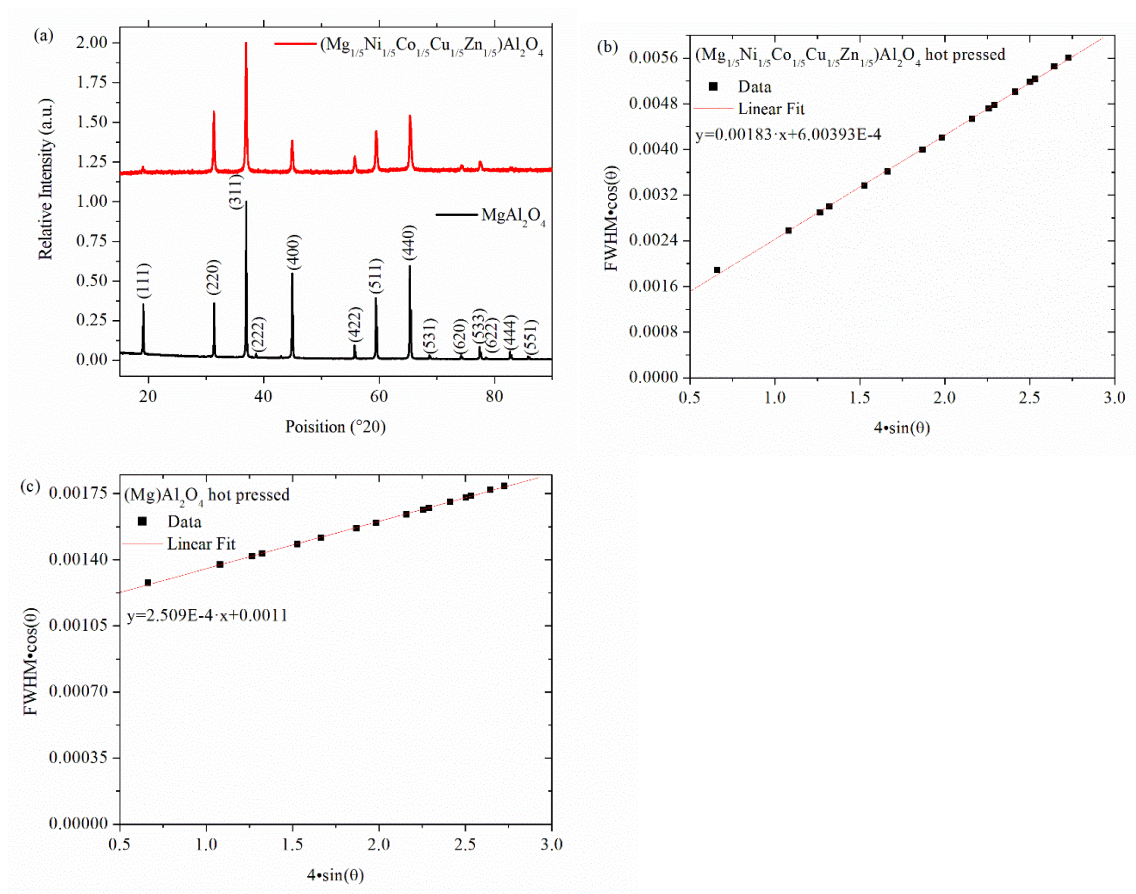


Figure 3-8 (a) X-ray diffraction patterns for hot pressed the single phase hot pressed samples and plots from Williamson-Hall analysis for (b) $(\text{Mg}_{1/5}\text{Ni}_{1/5}\text{Co}_{1/5}\text{Cu}_{1/5}\text{Zn}_{1/5})\text{Al}_2\text{O}_4$ and (c) MgAl_2O_4 .

Table 9 Crystallographic information for the pellets determined from Rietveld refinement and W-H methods of x-ray diffraction data taken on the samples after hot pressing and air annealing.

Sample	Lattice Parameter (Å)	Unit Cell Volume (Å ³)	Crystallite size (nm)
MgAl ₂ O ₄	8.0842(8)	528.3(1)	131.6
(Mg _{1/5} Ni _{1/5} Co _{1/5} Cu _{1/5} Zn _{1/5})Al ₂ O ₄	8.0726(9)	526.0(1)	240.9

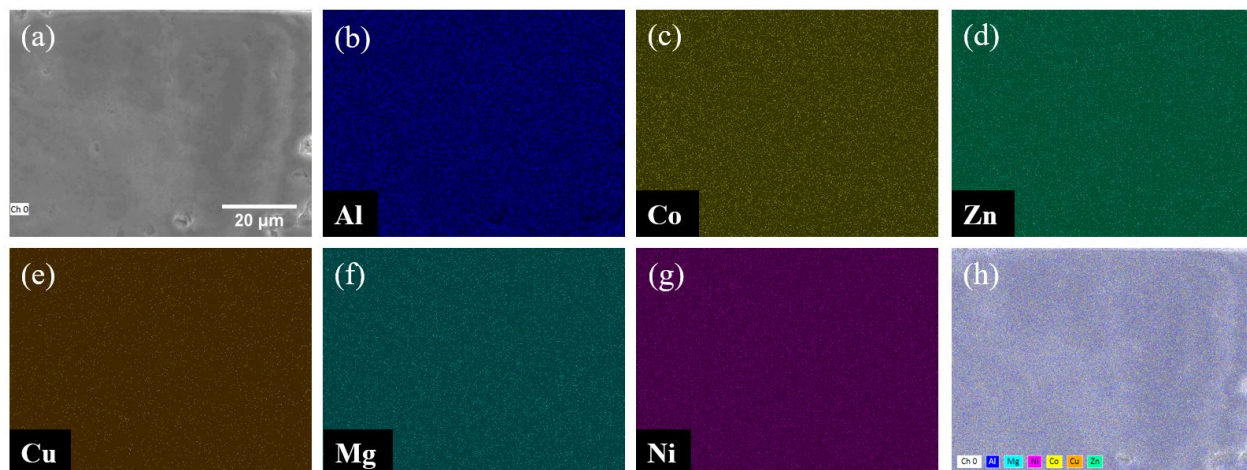


Figure 3-9 Polished pellet surface of (Mg_{1/5}Ni_{1/5}Co_{1/5}Cu_{1/5}Zn_{1/5})Al₂O₄ after hot pressing (a) SEM image and EDXS elemental mapping of the (b) Al, (c) Co, (d) Zn, (e) Cu, (f) Mg, (g) Ni, and (h) combined element distributions. The scale bar indicates 20 microns.

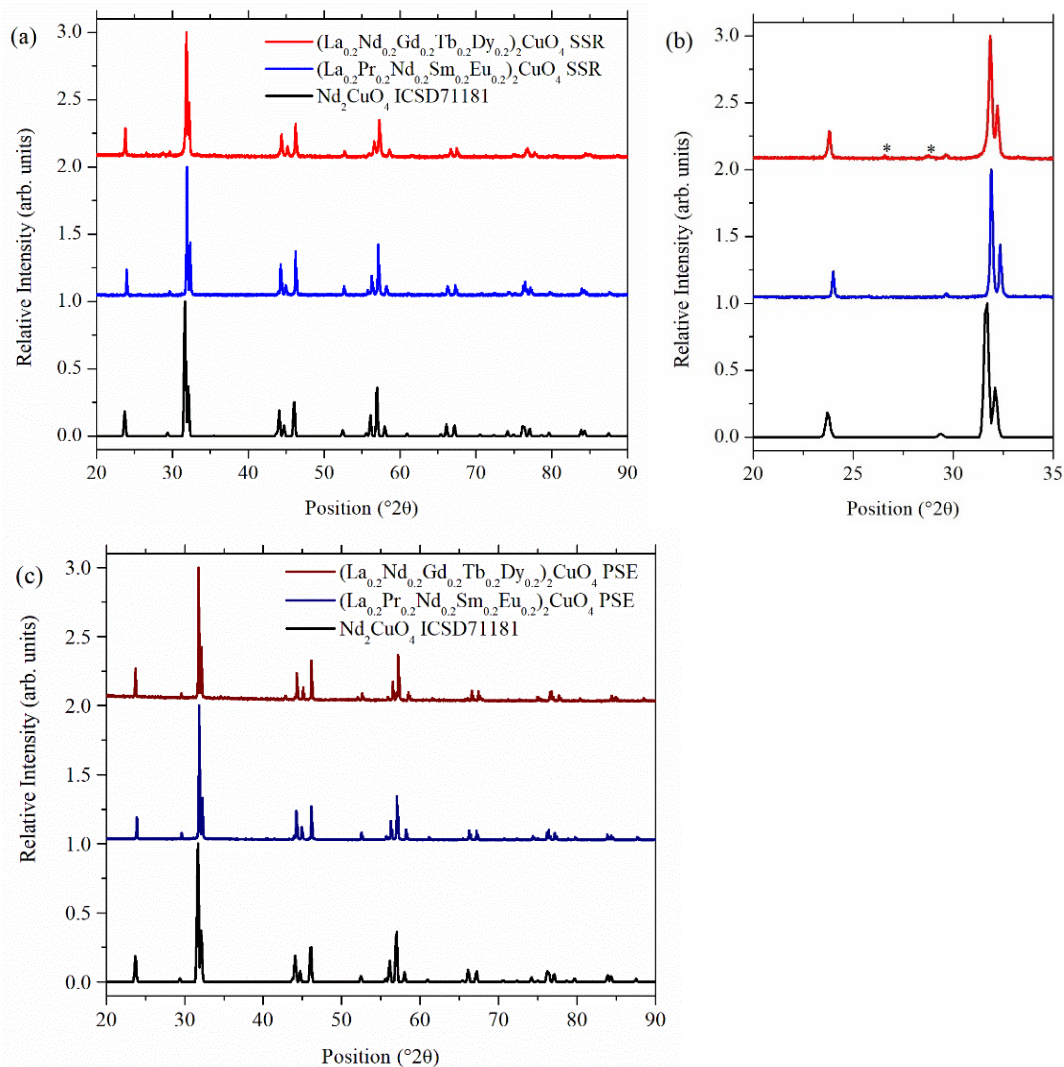


Figure 3-10 X-ray diffraction data for the HEO cuprate compositions made using (a) solid state reaction, with (b) showing a detailed view of the 20-35 $^{\circ}$ 2θ region, and (c) polymeric steric entrapment with ICSD 71181 Nd_2CuO_4 reference pattern showing I4/mmm structure

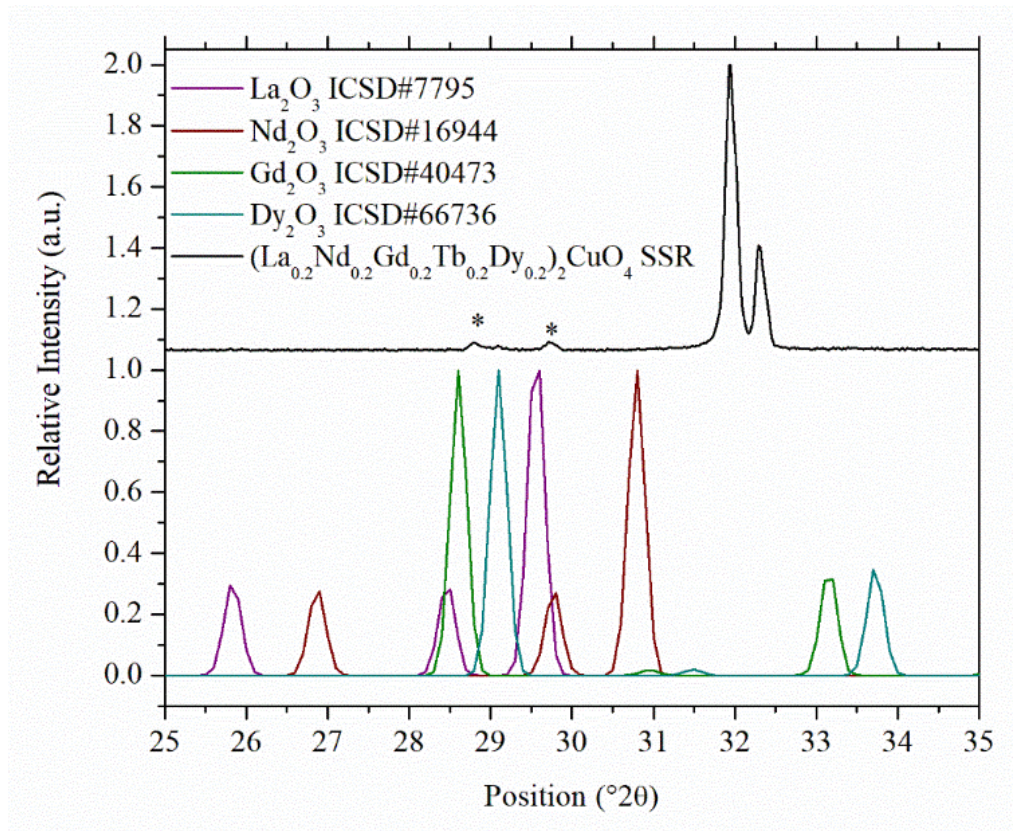


Figure 3-11 Powder X-ray diffraction data for SSR synthesized $(La_{0.2}Nd_{0.2}Gd_{0.2}Tb_{0.2}Dy_{0.2})_2CuO_4$ along with reference patterns for individual La_2O_3 , Nd_2O_3 , Gd_2O_3 and Dy_2O_3 rare-earth oxides.

The diffraction patterns of the PSE synthesized samples are shown in Figure 3-10 (c) and display no evidence of a secondary phase. The data were analyzed using the Rietveld method with the GSASII [19] software package. Refined lattice parameters and unit cell volumes are reported in Table 10. The refined lattice parameters and volumes determined from the data collected on samples synthesized via PSE have slightly larger unit cells than those synthesized via SSR. The average ionic radii [46] for the disordered A-site in both compounds falls within the existence range for oxide RP phases given by $1.6R_B < R_A < 1.24R_B + 0.9\text{\AA}$. For $(\text{La}_{0.2}\text{Nd}_{0.2}\text{Gd}_{0.2}\text{Tb}_{0.2}\text{Dy}_{0.2})_2\text{CuO}_4$, the average cation radius for the A-site is $R_A = 1.1328\text{\AA}$; and for $(\text{La}_{0.2}\text{Pr}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2})_2\text{CuO}_4$, $R_A = 1.162\text{\AA}$. Both of these R_A values fall within the RP phase existence range, as shown by values in Table 11. With these ionic radii the ability to achieve a single RP phase is not unexpected, but the application of disorder to the structure offers opportunity for further property investigation, compositional variation, and doping studies.

Scanning electron microscopy (SEM) with energy dispersive x-ray spectroscopy (EDXS) elemental mapping is used to investigate the microstructure and gain information on the distribution of the elemental constituents in the multicomponent oxide. Analysis of $(\text{La}_{0.2}\text{Pr}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2})_2\text{CuO}_4$ given in Figure 3-12 (a) shows elemental segregation in the SSR sample with clustering evident for the rare earth cations. This is especially distinct in the Pr, Nd, Sm, and La elemental maps. Given this inhomogeneity, it is not surprising to see evidence of secondary phases in the XRD (Figure 3-10 (a) and (b)). For SSR sample $(\text{La}_{0.2}\text{Nd}_{0.2}\text{Gd}_{0.2}\text{Tb}_{0.2}\text{Dy}_{0.2})_2\text{CuO}_4$, Figure 3-13 (a) shows slight segregation for the rare earth elements, most notably for Tb, Dy, and Gd. The PSE sample EDXS in Figure 3-12 (b) and Figure 3-13 (b), however, demonstrates homogenous distribution of all the cation species, corroborating the single phase result determined by XRD.

Doped ruddlesden popper cuprates

For the doping trials, the $(\text{La}_{0.2}\text{Pr}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2})_2\text{CuO}_4$ composition was selected as it achieved a single phase with solid state synthesis as discussed in the previous section. Initial doping trials were performed by adding strontium to the rare earth site composition resulting in a $(\text{La}_{0.36}\text{Pr}_{0.36}\text{Nd}_{0.36}\text{Sm}_{0.36}\text{Eu}_{0.36}\text{Sr}_{0.2})\text{CuO}_4$ material. The 0.2 Sr content is within the superconducting region of $(\text{La}, \text{Sr})_2\text{CuO}_4$ as shown in the phase diagram in Figure 1-15. The resultant x-ray diffraction pattern for different heating conditions for $(\text{La}_{0.36}\text{Pr}_{0.36}\text{Nd}_{0.36}\text{Sm}_{0.36}\text{Eu}_{0.36}\text{Sr}_{0.2})\text{CuO}_4$ is shown in Figure 3-14. The secondary phases seen in the samples with the lower temperature heat treatments were not identified. What appeared to be nearly a single phase was achieved by heating to 1170°C for 24 hours and air quenching by removing the sample boat from the furnace and placing it onto a piece of alumina. Unfortunately, the sample had melted into the sample boat. This was unexpected as 1170°C was below the melting point of the metal oxides in the material. Assuming that having equal amounts on the disordered site would help to stabilize the structure, a $(\text{La}_{0.2}\text{Pr}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2}\text{Gd}_{0.2}\text{Tb}_{0.2}\text{Dy}_{0.2}\text{Ho}_{0.2}\text{Sr}_{0.2})\text{CuO}_4$ composition was made via the solid state reaction method. Heating trials were carried out, as shown by the XRD spectra in Figure 3-15, but a single phase was not achieved for any of the samples.

Table 10 Summary of refined lattice parameters of RP cuprates by synthesis method and composition.

Composition	Solid State (SSR)	Polymeric Steric Entrapment (PSE)
	Cell Parameters	Cell Parameters
(La_{0.2}Nd_{0.2}Gd_{0.2}Tb_{0.2}Dy_{0.2})₂CuO₄	$a = 3.917(1) \text{ \AA}$	$a = 3.920(1) \text{ \AA}$
	$c = 12.016(4) \text{ \AA}$	$c = 12.025(3) \text{ \AA}$
	Volume = 184.4(1) $\text{\AA}^3$	volume: 184.8(1) $\text{\AA}^3$
(La_{0.2}Pr_{0.2}Nd_{0.2}Sm_{0.2}Eu_{0.2})₂CuO₄	$a = 3.941(1) \text{ \AA}$	$a = 3.9507(8) \text{ \AA}$
	$c = 12.155(7) \text{ \AA}$	$c = 12.1504(7) \text{ \AA}$
	Volume = 188.8(1) $\text{\AA}^3$	Volume = 189.65(8) $\text{\AA}^3$

Table 11 Summary of starting cations with their expected charge state, coordination number, and radii. Coordination number and cation radius reported are taken from the Table of Shannon Ionic Radii.

A-Site	(La_{0.2}Nd_{0.2}Gd_{0.2}Tb_{0.2}Dy_{0.2})₂CuO₄			(La_{0.2}Pr_{0.2}Nd_{0.2}Sm_{0.2}Eu_{0.2})₂CuO₄		
	Cation	coordination number	Ionic Radii ($\text{\AA}$)	Cation	coordination number	Ionic Radii ($\text{\AA}$)
	La ³⁺	IX	1.216	La ³⁺	IX	1.216
	Nd ³⁺	IX	1.163	Pr ³⁺	IX	1.179
	Gd ³⁺	IX	1.107	Nd ³⁺	IX	1.163
	Tb ³⁺	IX	1.095	Sm ³⁺	IX	1.132
	Dy ³⁺	IX	1.083	Eu ³⁺	IX	1.12
	R _A avg:		1.1328	R _A avg:		1.162
	Cu ²⁺	IV	0.57	Cu ²⁺	IV	0.57

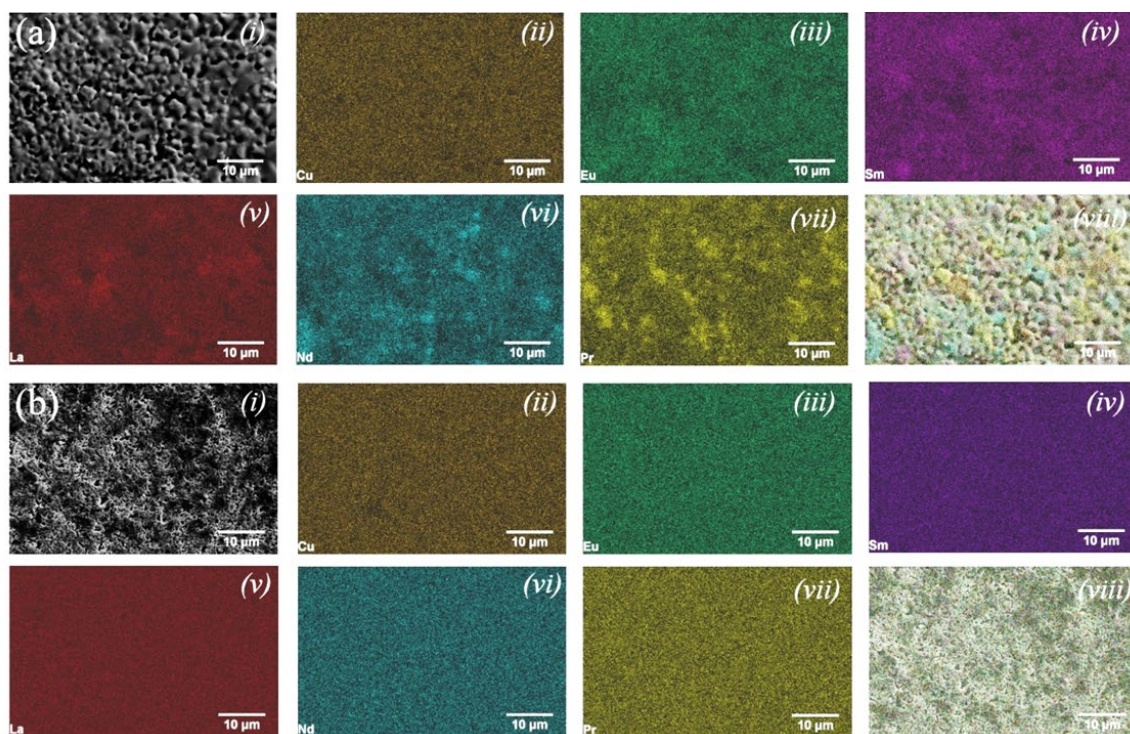


Figure 3-12 $(\text{La}_{0.2}\text{Pr}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2})_2\text{CuO}_4$ (i) SEM image and EDXS elemental mapping of the (ii) Cu, (iii) Eu, (iv) Sm, (v) La, (vi) Nd, (vii) Pr, and (viii) combined element distributions in (a) SSR synthesized and (b) a PSE synthesized pellet.

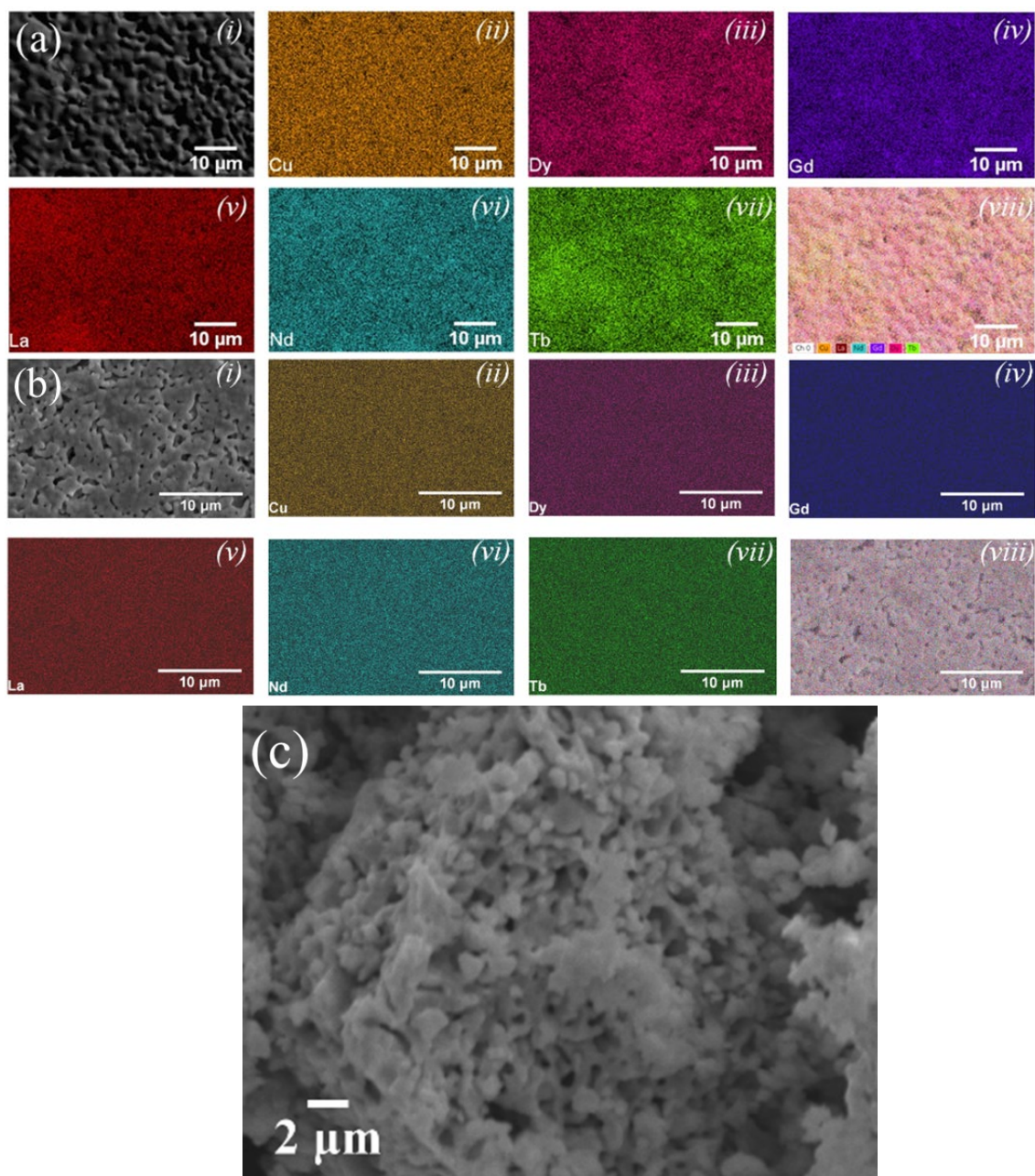


Figure 3-13 $(\text{La}_{0.2}\text{Nd}_{0.2}\text{Gd}_{0.2}\text{Tb}_{0.2}\text{Dy}_{0.2})_2\text{CuO}_4$ (i) SEM image and EDXS mapping of the (ii) Cu, (iii) Dy, (iv) Gd, (v) La, (vi) Nd, (vii) Tb, and (viii) combined element distributions in (a) SSR synthesized pellet and (b) PSE synthesized pellet. (c) PSE powder.

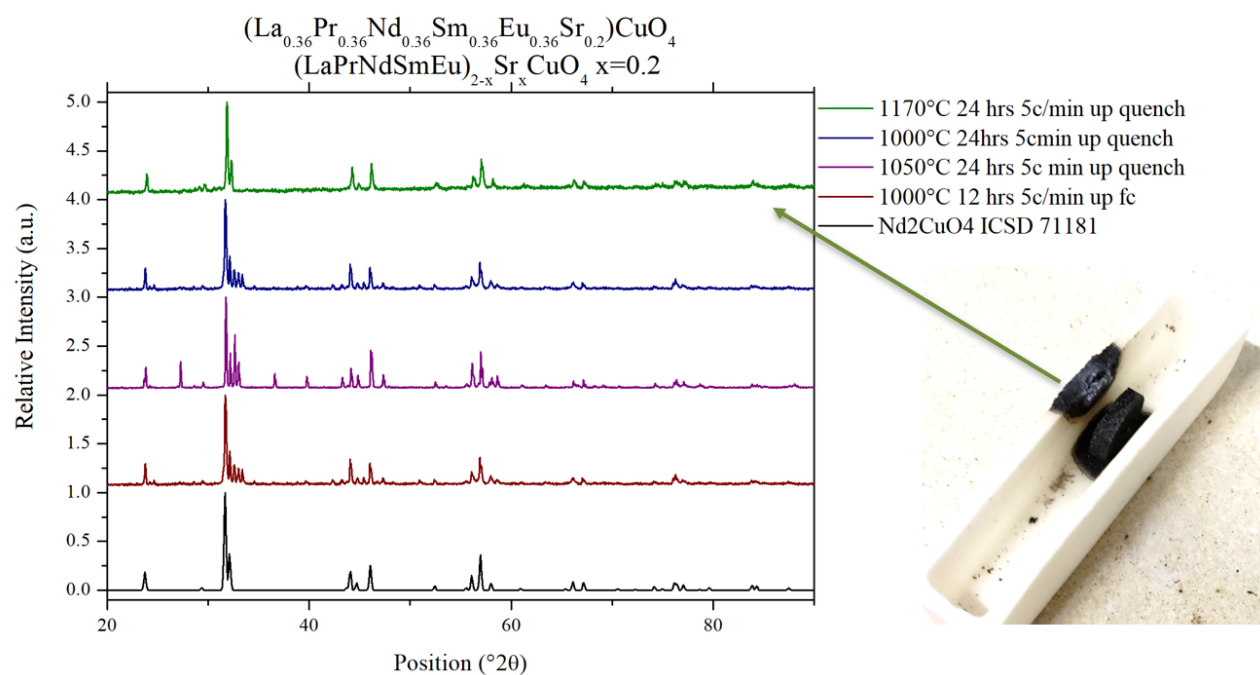


Figure 3-14 XRD spectra for different solid state synthesis attempts of $(\text{La}_{0.36}\text{Pr}_{0.36}\text{Nd}_{0.36}\text{Sm}_{0.36}\text{Eu}_{0.36}\text{Sr}_{0.2})\text{CuO}_4$.

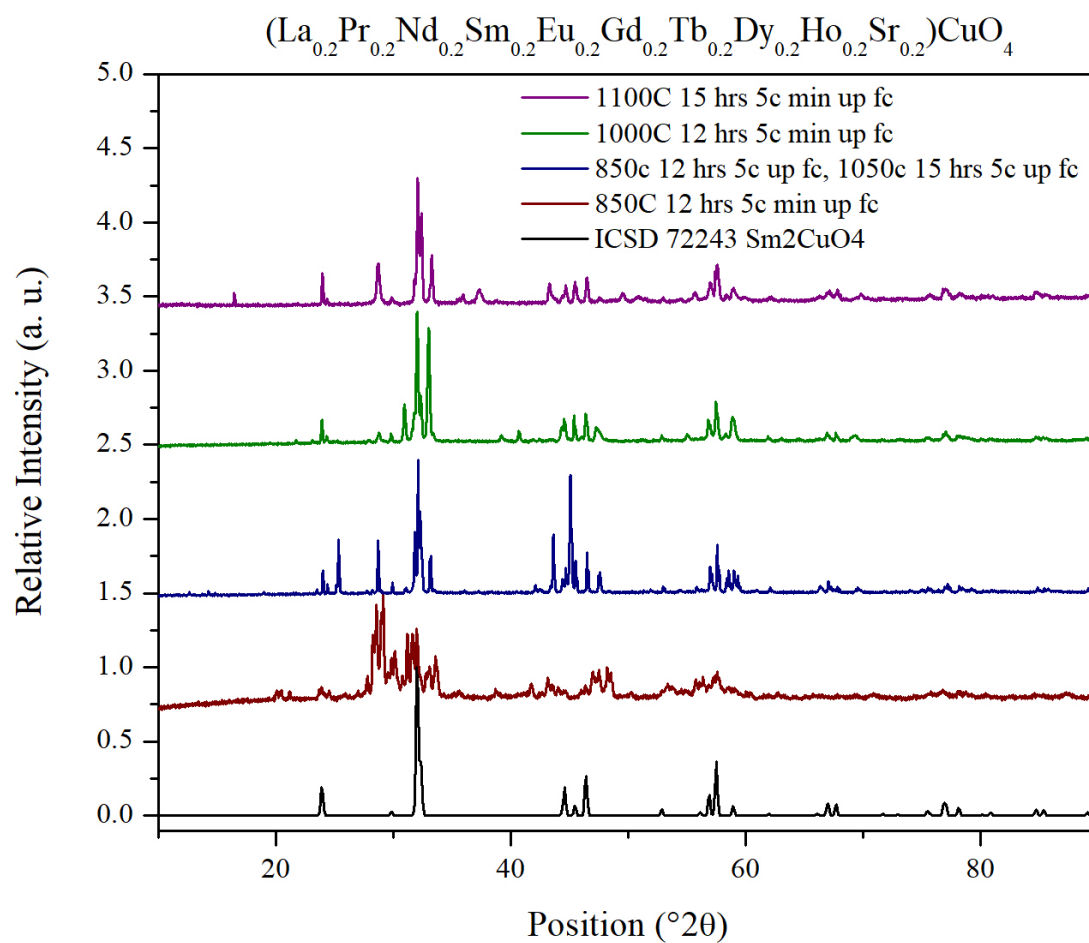


Figure 3-15 XRD spectra for different solid state synthesis attempts of $(\text{La}_{0.2}\text{Pr}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2}\text{Gd}_{0.2}\text{Tb}_{0.2}\text{Dy}_{0.2}\text{Ho}_{0.2}\text{Sr}_{0.2})\text{CuO}_4$.

After the synthesized HEO cuprate compositions were studied more carefully and literature was reviewed, we realized that electron doping should have been the pursued path as the materials took on the T'-structure. Following successful PSE synthesis of undoped cuprates, a Ce doped composition was made via steric entrapment. A cerium content of 0.15, rather than 0.2, was selected as it is near the middle of the superconducting dome. $(\text{La}_{0.37}\text{Pr}_{0.37}\text{Nd}_{0.37}\text{Sm}_{0.37}\text{Eu}_{0.37}\text{Ce}_{0.15})\text{CuO}_4$ was made via PSE with calcination at 550°C and a near single phase achieved after crystallizing at 900°C for 1 hour, as shown in Figure 3-16.

3.2.Magnetic Properties- Spinel

Ferritic spinels: high temperature magnetic behavior

This section focuses on the effect of multicomponent composition on the magnetic properties. Ferrite spinels with a structure $(\text{X}^{2+})(\text{Fe}^{3+})_2\text{O}_4$, typically have the B-site ions antiferromagnetically coupled with no net magnetization, while the unpaired electrons on the A-site ion order collinear relative to the B-site ions. This interaction between A-site and B-site cations gives rise to Neel Ferrimagnetism, and the net magnetization is sensitive to the cation distribution over the sites. The A-site ion, having no canceling partner, contributes to the observed magnetism of the ferrite. Introducing highly disordered A-site occupancy will naturally setup a local distribution in the magnetization. Complicating this picture is the change in occupancy of the A-site ions when substituting the Fe^{3+} ions causing an imbalance in the antiferromagnetism, generating an additional magnetic moment. This is known to occur when the A-site ion is small, as is the case for the elements Mg and Zn. The filled s and d-shells of Mg and Zn means they do not contribute to the magnetism, maximizing the asymmetry, but also causing a reduction in the Néel Temperature, T_N . Indeed, the HEOs incorporating both Zn and Mg show the largest moment and have the lowest T_N relative to the other HEOs, as shown in Figure 3-17 (a). The ferrites with only Mg show the next-largest saturation moment and a higher T_N , where T_N is the high temperature ferrimagnetic to paramagnetic transition temperature. Finally, the ferrite without either Mg or Zn has the smallest moment, but also a lower T_N .

This indicates some site preference trends are maintained. These results emphasize the crucial role played by the antiferromagnetic ordering on the B-site, in that even fractional substitution causes significant changes in T_N . This sentiment is further emphasized in the HEO without a preferred B-site occupancy, which shows a significantly suppressed T_N and magnetic moment.

The room temperature magnetization for each of the HEOs is presented in Figure 3-17 (b). These measurements show a narrow coercivity for each of the samples, with saturation fields of >4 kOe (1 kOe = 0.1 T). The hysteretic behavior confirms the ferrimagnetic behavior expected for these materials. The large saturation field may indicate local regions that are mutually antiferromagnetically coupled or possess large magnetocrystalline anisotropy.

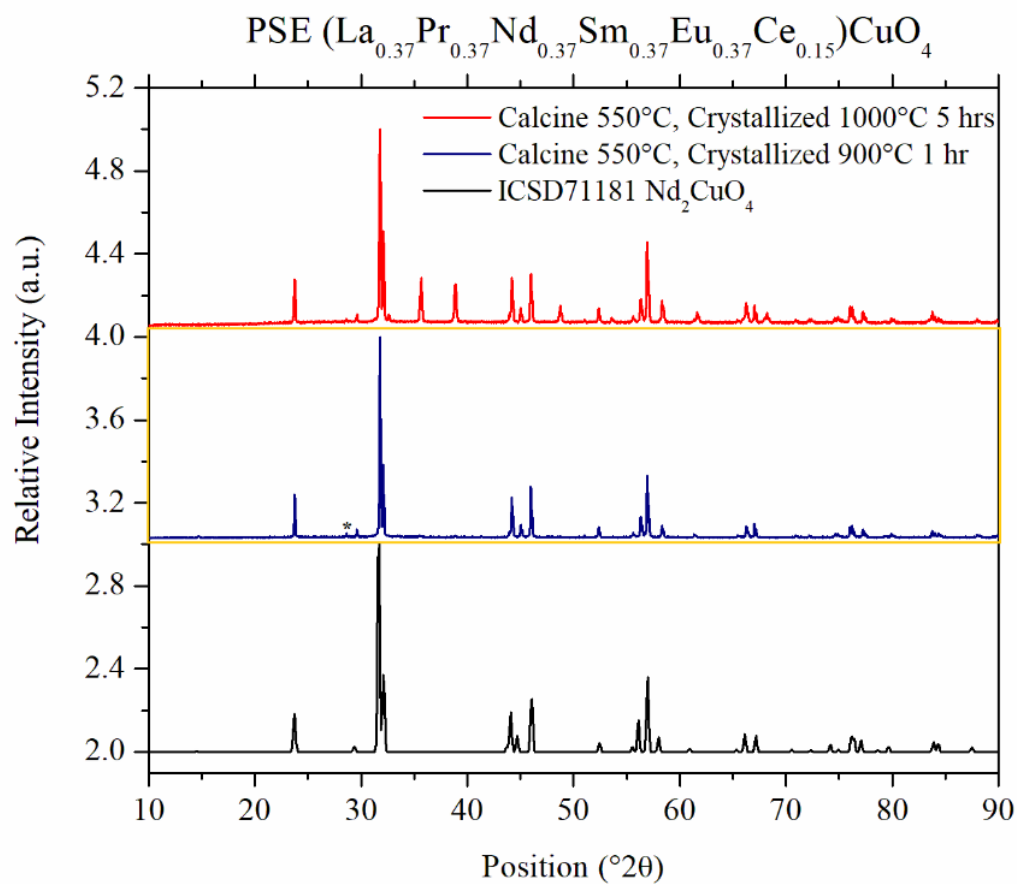


Figure 3-16 XRD spectra for PSE synthesized ($\text{La}_{0.37}\text{Pr}_{0.37}\text{Nd}_{0.37}\text{Sm}_{0.37}\text{Eu}_{0.37}\text{Ce}_{0.15}$) CuO_4 .

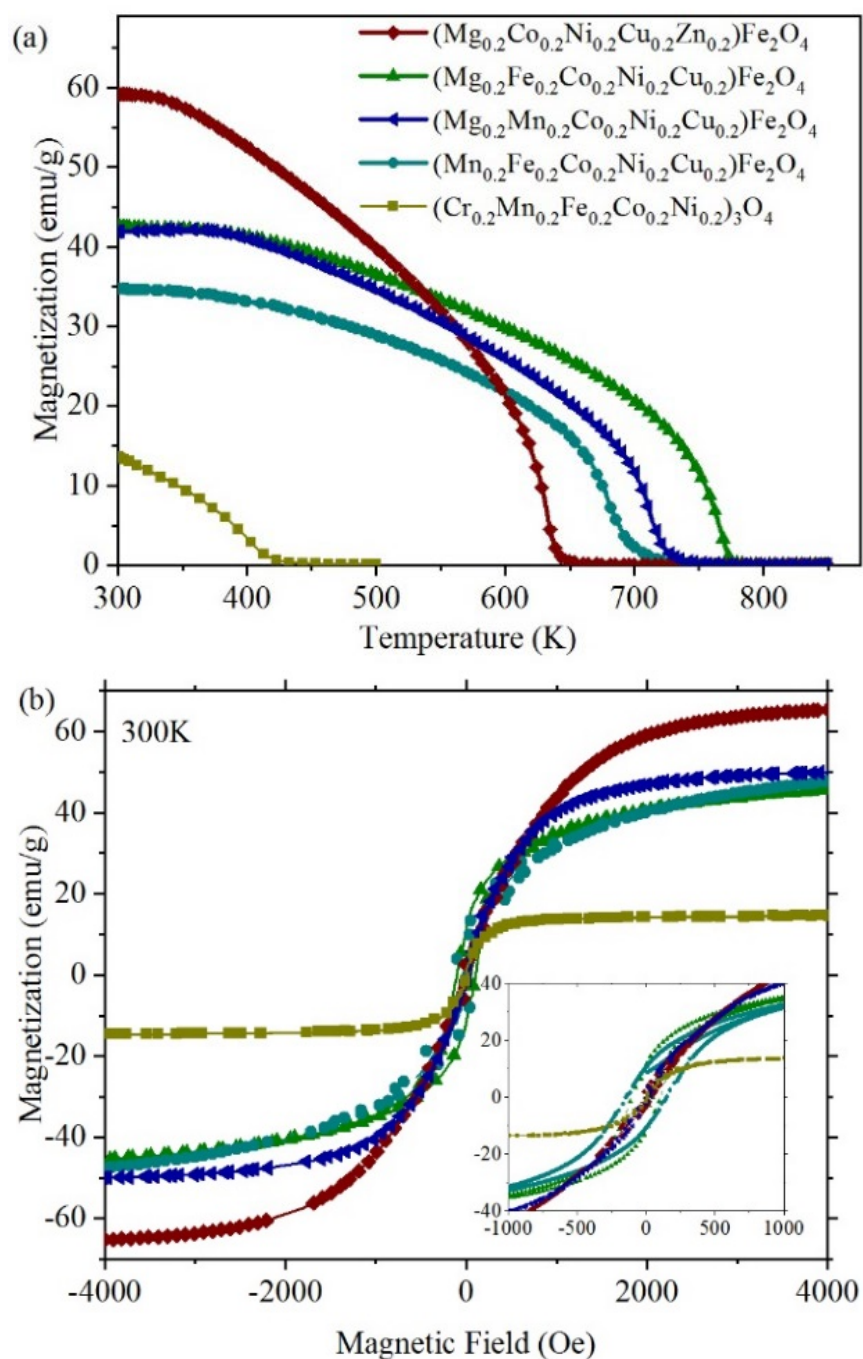


Figure 3-17 (a) Field cooled magnetization of ferritic HEO spinels from 300 K – 850 K with applied field of 1000 Oe and (b) magnetization as a function of applied field at 300 K with inset showing hysteretic behavior ($1 \text{ emu} = 10^{-3} \text{ Am}^2$). The legend applies to both.

Ferritic spinels: low temperature magnetic behavior

Magnetometry measurements performed on $(\text{Cr}_{0.2}\text{Mn}_{0.2}\text{Fe}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2})_3\text{O}_4$ are shown in Figure 3-18. The ZFC plot shows a series of inflections, potentially indicating the onset of ordering of various regions within the sample. The direct exchange interaction, which exists only between two neighboring atoms, is intrinsically localized. Specifically, statistical fluctuations may cause regions to be particularly rich in a specific element at a local level, resulting in a localized variation in T_N . Alternatively, local atomic regions particularly rich in Cr or Mn may possess an antiferromagnetic to ferromagnetic transition, resulting from their negative exchange coupling with the other constituent elements. This hypothesis is further supported by the FC and FW plots in Figure 3-18 (a) which show a peak at 230 K, where the magnetization is in-fact decreasing with decreasing temperature, and by the small magnetization in this sample shown in Figure 3-17 (a). Magnetic hysteresis loops were also measured and show an increase in coercivity with decreasing temperature – as would be expected for thermally activated reversal. However, the scale of the coercivity's thermal dependence is notable for a bulk material, increasing from 20 Oe at 300 K to 197 Oe at 50 K. This is likely a consequence of the large site-specific T_N , resulting from the compositional distribution.

Figure 3-19 shows the low temperature magnetization of two ferrite-based HEO spinels, $(\text{Mg}_{0.2}\text{Mn}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2})\text{Fe}_2\text{O}_4$ and $(\text{Mg}_{0.2}\text{Fe}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2})\text{Fe}_2\text{O}_4$, revealing interesting magnetic behavior with (i) the FW data dipping below the FC plot, and (ii) a reduction in magnetization with decreasing temperature. Inset plots are provided to emphasize the cross-over and hysteresis in the FC and FW plots. This again could be due to an antiferromagnetic coupling between neighboring elemental components. These minority phases may be frozen upon cooling, and persist upon warming, exhibiting a thermal hysteresis, and explaining the crossover.

Chromium based spinels: low temperature magnetic behavior

While the ferrite spinels show features typical of ferro – or ferri – magnetic behavior, the chrome-based spinels are notably different. The ZFC magnetization versus temperature for the chromates, shown in Figure 3-21, increases from low temperatures and approaches a maximum before decreasing upon further increasing temperatures. This feature is well known and associated with superparamagnetic behavior, with the maximum called the blocking temperature (T_B) [57]. Superparamagnetism arises due to the magnetic interaction volume and anisotropy being smaller than the thermal fluctuations. Thus, the presence of a blocking temperature indicates that the magnetic regions within the sample are small and relatively isolated. Assuming that the magnetic anisotropy is similar to that of conventional ferrite spinels ($18.7 \times 10^{-3} \text{ J/m}^3$), the diameter of the magnetic regions can be estimated as $\approx 7.3 \text{ nm}$ [58]. The FC data shows an increase in the magnetization with increasing field, which is not typical for superparamagnetic materials, but simply indicates that there may be some residual regions with antiferromagnetic ordering at room temperature. The magnetization curves in Figure 3-21 (a), (b), and (c) show slight dips approaching T_B as well as different character at the antiferromagnetic onset approaching T_N . There is also a field dependence seen in the magnetization curves. This could be explained by ferromagnetic contributions to the lattice.

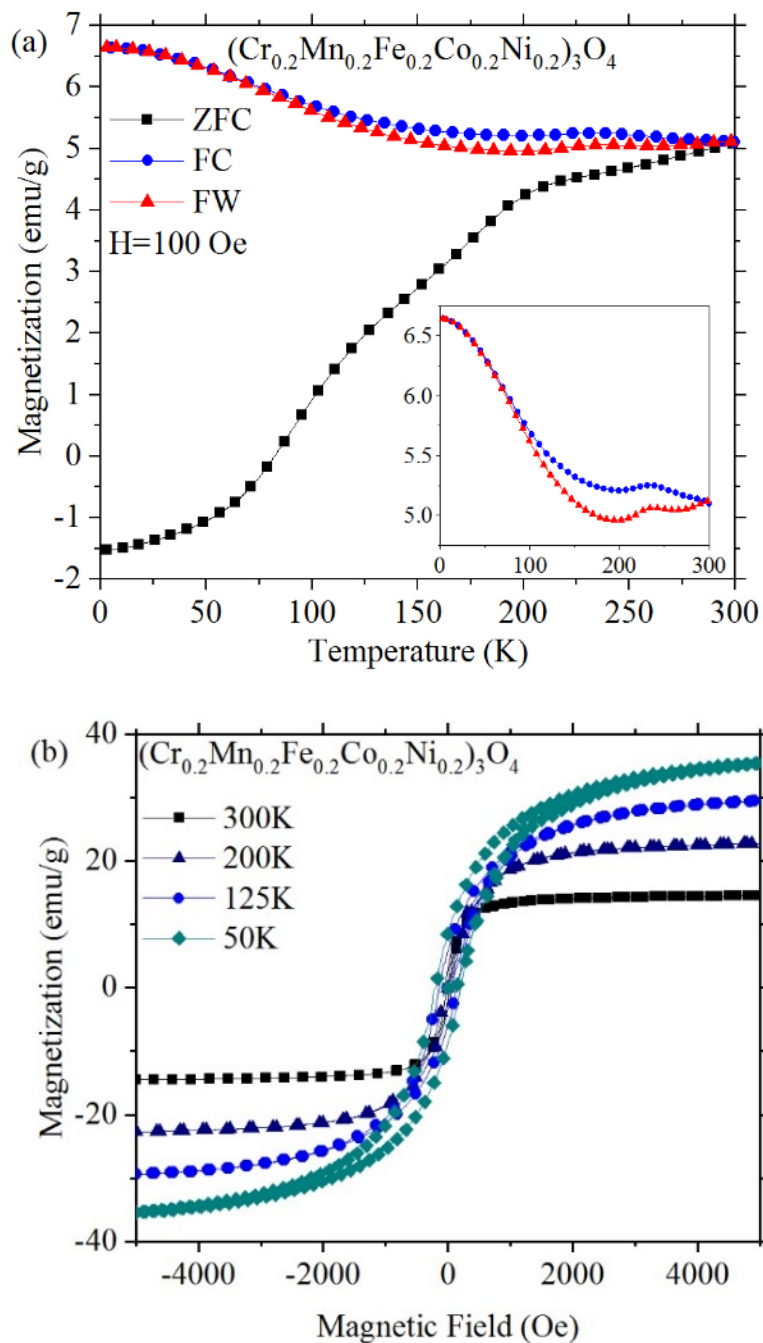


Figure 3-18 DC magnetization for $(\text{Cr}_{0.2}\text{Mn}_{0.2}\text{Fe}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2})_3\text{O}_4$ (a) with temperature from 3 K - 300 K showing the ZFC, FC, and FW plots with applied field of 100 Oe; and (b) magnetic hysteresis loops measured at 300K, 200K, 125K, and 50K.

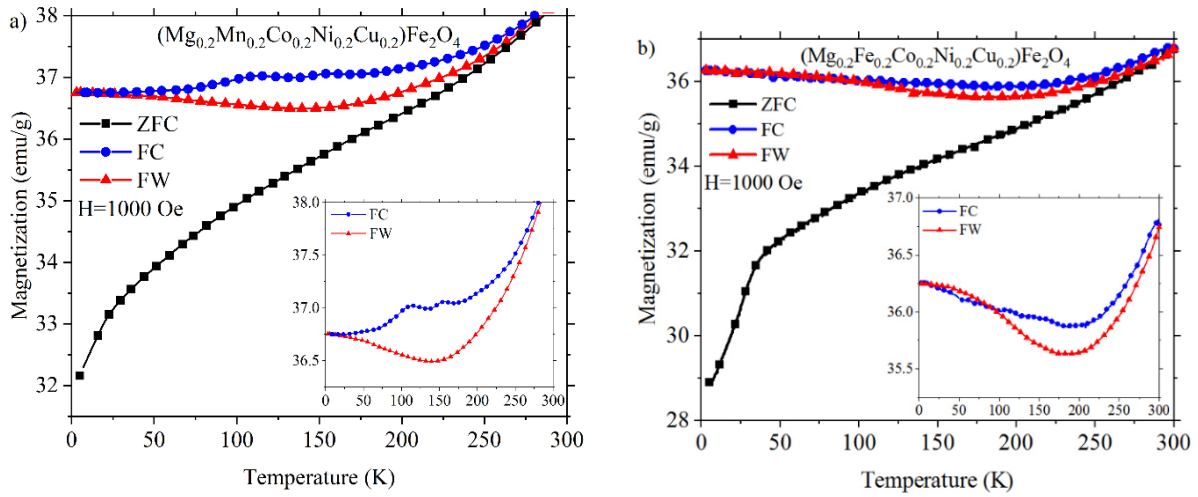


Figure 3-19 DC magnetization as a function of temperature from 3 K – 300 K showing the ZFC, FC, and FW measured at 1000 Oe, for (a) $(\text{Mg}_{0.2}\text{Mn}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2})\text{Fe}_2\text{O}_4$ and (b) $(\text{Mg}_{0.2}\text{Fe}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2})\text{Fe}_2\text{O}_4$.

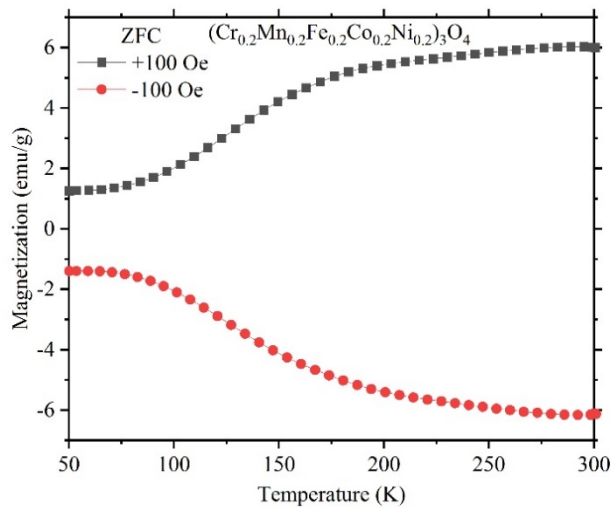


Figure 3-20 Zero-Field Cooled Magnetization vs Temperature of $(\text{Cr}_{0.2}\text{Mn}_{0.2}\text{Fe}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2})_3\text{O}_4$ in both a positive field (+100 Oe) and negative field (-100 Oe) performed on a Quantum Design VersaLab with VSM.

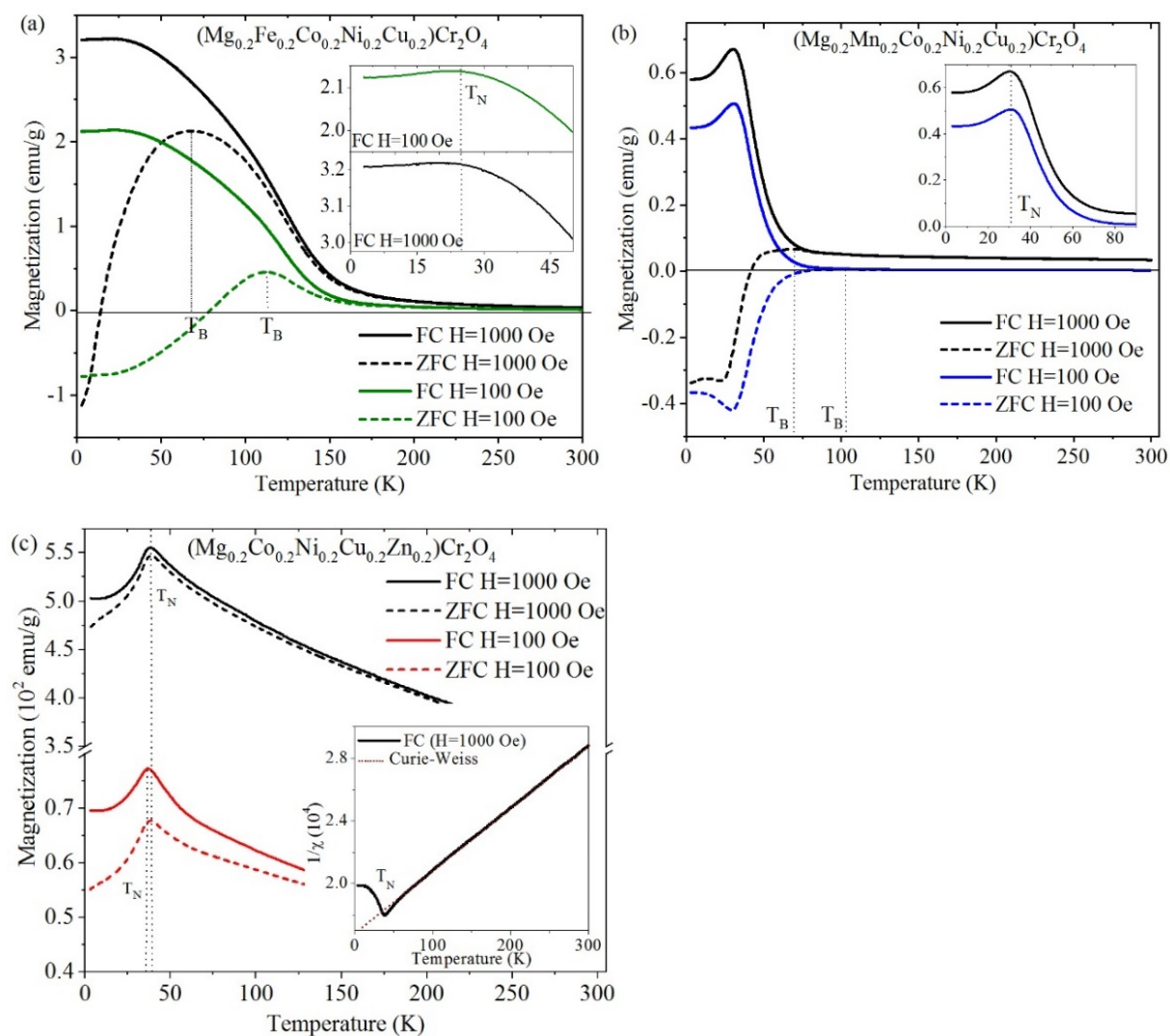


Figure 3-21 Low temperature DC magnetization from 3 K – 300 K under 100 Oe and 1000 Oe for (a) $(\text{Mg}_{0.2}\text{Fe}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2})\text{Cr}_2\text{O}_4$, (b) $(\text{Mg}_{0.2}\text{Mn}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2})\text{Cr}_2\text{O}_4$ and (c) $(\text{Mg}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2})\text{Cr}_2\text{O}_4$.

This was noted as a possible factor in the recent HEO perovskite magnetic investigation where small ferromagnetic contributions are distinguished amidst predominantly antiferromagnetic behavior possibly due to small ferromagnetic clusters or configurations within the antiferromagnetic matrix [10]. In a disordered material, especially ones such as these with multiple magnetic constituents, homogeneity at the atomic level is not assumed. Local variations could give rise to small ferromagnetic clusters, small pockets of slightly differently ordered spins within a larger overall ordering. Ferrimagnetic contributions are further supported by the mirror-like symmetry in the FC- ZFC behavior in $(\text{Mg}_{0.2}\text{Mn}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2})\text{Cr}_2\text{O}_4$ shown in Figure 3-21 (b) as this symmetry is typical for materials containing a ferromagnetic component [59]. The inverse susceptibility of $(\text{Mg}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2})\text{Cr}_2\text{O}_4$ shown in the inset of Figure 3-21 (c) shows more classical Curie-Weiss-like behavior, with low-temperature antiferromagnetic ordering at $T_N = 36$ K. The blocking temperatures can be identified at 100 Oe and 1000 Oe to be ≈ 38.1 K and ≈ 39 K for $(\text{Mg}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2})\text{Cr}_2\text{O}_4$, ≈ 69 K and ≈ 112.2 K for $(\text{Mg}_{0.2}\text{Fe}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2})\text{Cr}_2\text{O}_4$, and ≈ 102.2 K and ≈ 69 K for $(\text{Mg}_{0.2}\text{Mn}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2})\text{Cr}_2\text{O}_4$, respectively.

Magnetization versus magnetic field for $(\text{Mg}_{0.2}\text{Fe}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2})\text{Cr}_2\text{O}_4$ and $(\text{Mg}_{0.2}\text{Mn}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2})\text{Cr}_2\text{O}_4$ was measured using a Quantum Design Physical Property Measurement System (PPMS) DynaCool with VSM. Hysteresis of $(\text{Mg}_{0.2}\text{Fe}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2})\text{Cr}_2\text{O}_4$ is shown in Figure 3-22 and has a saturation field of ~ 5 T at 30 K with the coercive force increasing towards 1.9 K, but without any changes in the saturation behavior. $(\text{Mg}_{0.2}\text{Mn}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2})\text{Cr}_2\text{O}_4$, shows a lack of saturation even at 9 T fields. In Figure 3-23 an exchange bias is seen increasingly at lower temperature. Increasing coercivity with decrease in temperature is indicative of thermally activated reversal and was expected. However, at lower temperature the coercivity diverges and narrows as depicted by the behavior at 1.9 K. Figure 3-23 shows no decrease in the magnetic saturation even though it was expected to occur in correlation with the coercivity divergence. These behaviors could indicate more complex changes in the ordering at the transitions identified in Figure 3-21.

Exchange coupling as well as small localized antiferromagnetic contributions and antiferromagnetic stability could be contributing to an increase in coercivity. In a recent study on $(\text{Mg}_{0.25(1-x)}\text{Co}_x\text{Ni}_{0.25(1-x)}\text{Cu}_{0.25(1-x)}\text{Zn}_{0.25(1-x)})\text{O}$ heterostructures with changes in Co concentration, anisotropic magnetic exchange and the presence of a critical blocking temperature was observed, indicating antiferromagnetic order with composition changes tuning the disorder, exchange field and magnetic anisotropy [60]. Magnetization with magnetic field plots for $(\text{Mg}_{0.2}\text{Ni}_{0.2}\text{Co}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2})\text{Cr}_2\text{O}_4$, $(\text{Mg}_{0.2}\text{Mn}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2})\text{Fe}_2\text{O}_4$ and $(\text{Mg}_{0.2}\text{Fe}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2})\text{Fe}_2\text{O}_4$ are provided in Figure 3-24 and Figure 3-25 [53].

Valence information

The measurements presented in the above sections have captured the bulk features of a system with extremely localized chemical and likely magnetic disorder. To fingerprint the magnetic ordering and chemical environment of each of the constituent elements, X-ray absorption spectroscopy (XAS) and X-ray magnetic linear dichroism (XMLD) were used. An example case, measuring the Cr and Fe L_3 and L_2 edges of $(\text{Mg}_{0.2}\text{Fe}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2})\text{Cr}_2\text{O}_4$ at 20 K and 300 K, is shown in Figure 3-26.

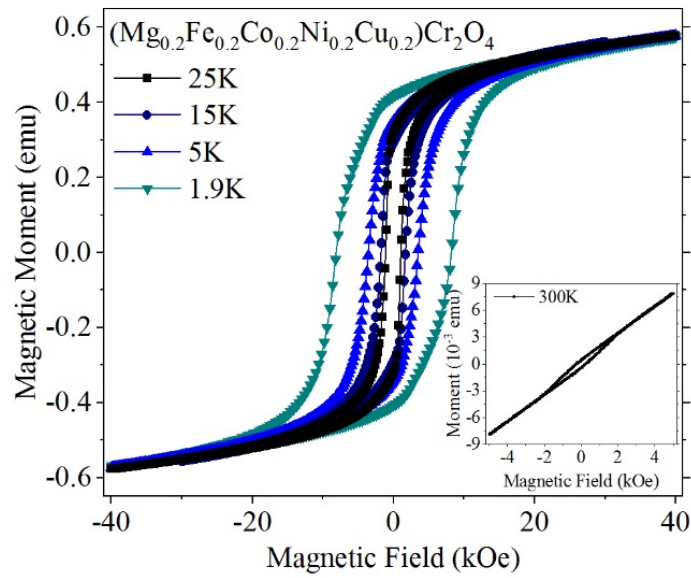


Figure 3-22 The hysteresis plots at 25 K, 15 K, 5 K and 1.9 K for $(\text{Mg}_{0.2}\text{Fe}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2})\text{Cr}_2\text{O}_4$ with inset showing behavior at 300 K.

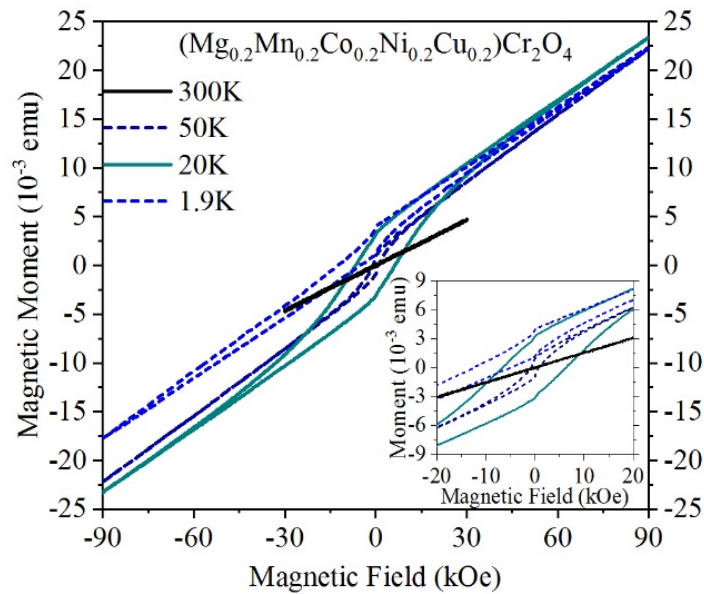


Figure 3-23 Magnetization with Field of $(\text{Mg}_{0.2}\text{Mn}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2})\text{Cr}_2\text{O}_4$ at 300 K, 50 K, 20 K, and 1.9 K with inset better showing hysteresis.

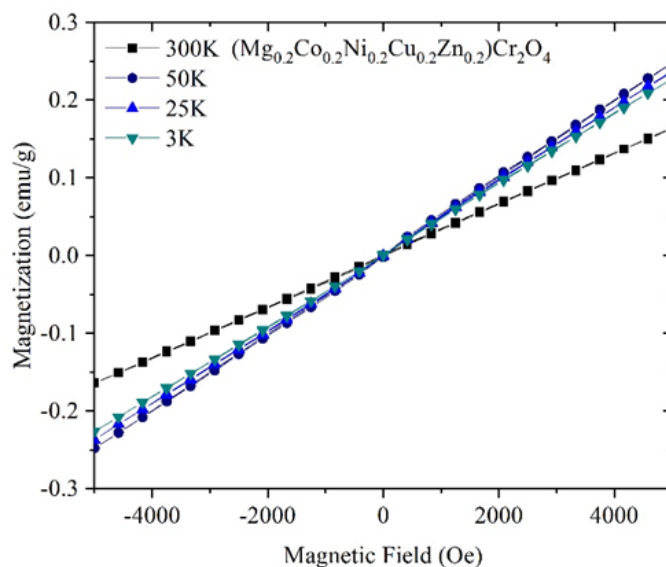


Figure 3-24 The magnetization with magnetic field behavior at 300K, 50K, 25K and 3K for $(\text{Mg}_{0.2}\text{Ni}_{0.2}\text{Co}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2})\text{Cr}_2\text{O}_4$.

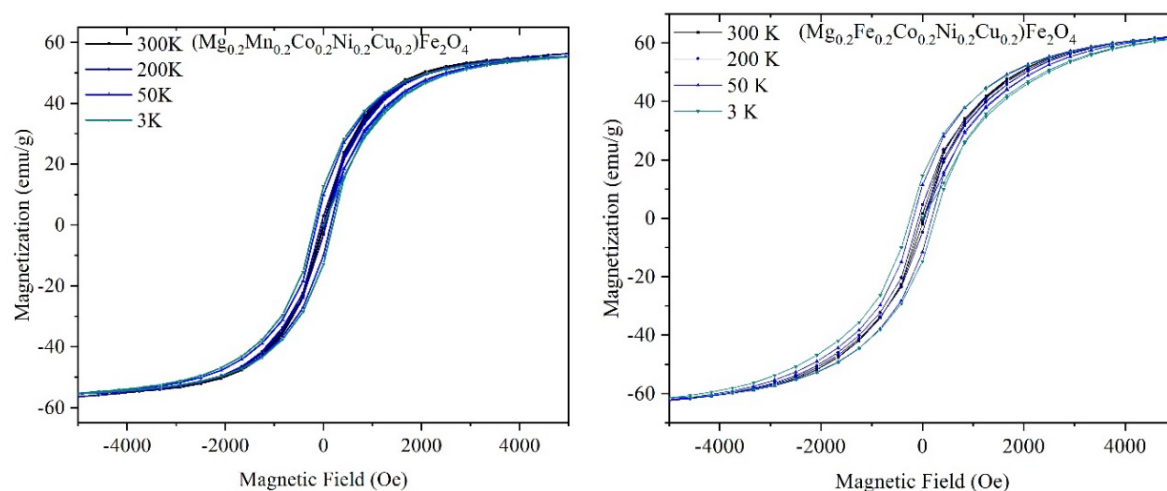


Figure 3-25 The magnetization with magnetic field behavior at 300K, 50K, 25K and 3K for (left) $(\text{Mg}_{0.2}\text{Mn}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2})\text{Fe}_2\text{O}_4$ and (right) $(\text{Mg}_{0.2}\text{Fe}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2})\text{Fe}_2\text{O}_4$ showing slight hysteresis.

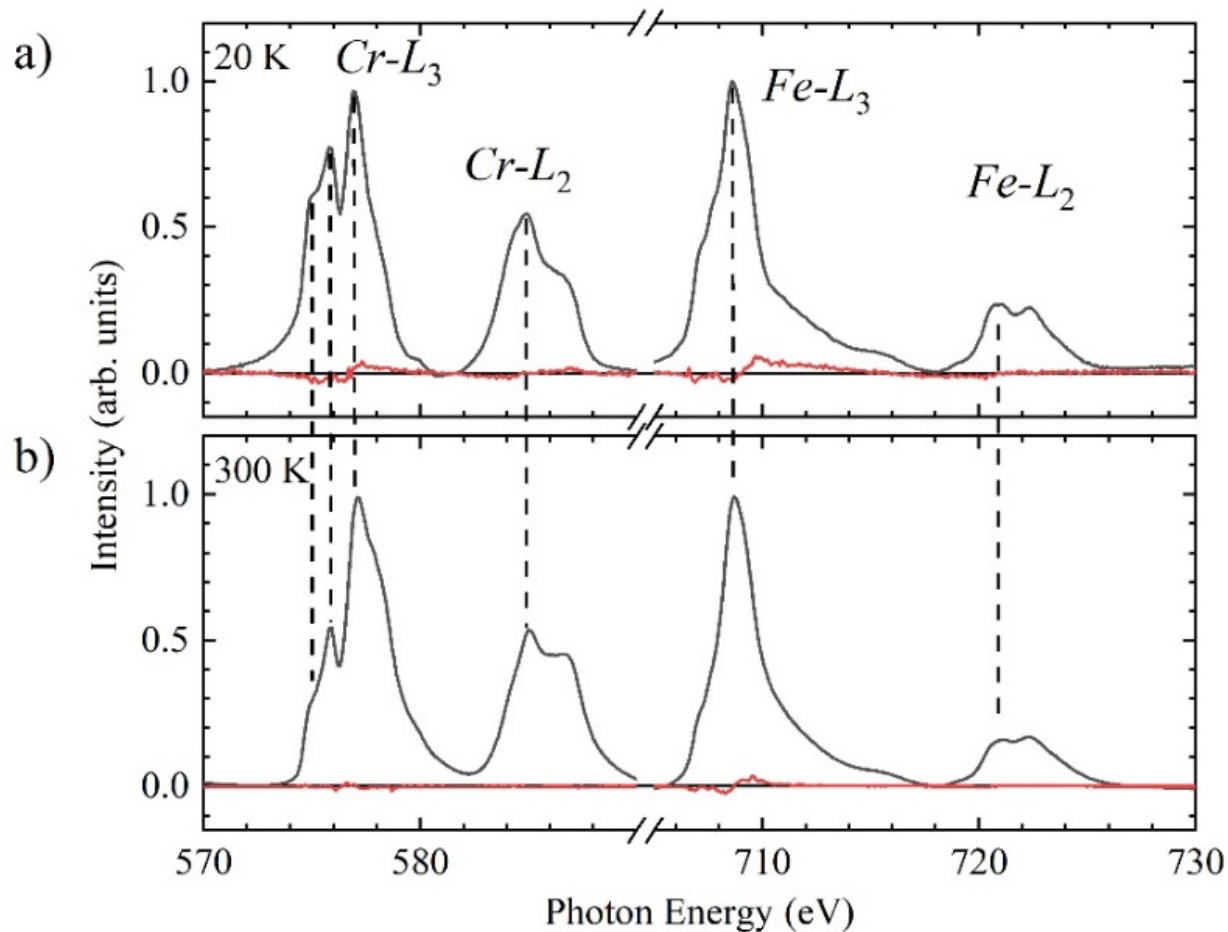


Figure 3-26 Cr and Fe X-ray absorption spectroscopy (XAS) spectra with X-ray magnetic linear dichroism (XMLD) signal given by red line at (a) 300 K, and (b) 20 K for polycrystalline $(\text{Mg}_{0.2}\text{Fe}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2})\text{Cr}_2\text{O}_4$.

At 20 K (Figure 3-26 (a)) the Cr XMLD signal is weak, but shows a clear positive/negative inflection, strongly suggesting that the Cr is antiferromagnetically coupled – as expected on the octahedral B-site. Increasing the temperature to 300 K, the XMLD signal disappears, indicating that the B-site ion is no-longer antiferromagnetically coupled. This is consistent with the magnetization data discussed above, which show magnetic transitions at 23 K and 146 K. XMLD measurements were also performed on the Fe element and show antiferromagnetic ordering to at-least room temperature. This may indicate Fe substitution for Cr on the B-site in this composition. The XMLD signal can also arise due to orbital polarization, in this case induced by symmetry breaking at the surface, however, we would not expect a strong temperature dependence of this effect, which is observed here. This supports that the origin of the XMLD is antiferromagnetic ordering. XMLD measurements performed on the ferrites confirmed the antiferromagnetic ordering on the B-site at 20 K and 300 K for both of the tested samples, $(\text{Mg}_{0.2}\text{Mn}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2})\text{Fe}_2\text{O}_4$, and $(\text{Mn}_{0.2}\text{Fe}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2})\text{Fe}_2\text{O}_4$.

Valence information is determined from the XAS measurement for $(\text{Mg}_{0.2}\text{Fe}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2})\text{Cr}_2\text{O}_4$, indicating an unexpected mixed state, with $\text{Cr}^{3+}/\text{Cr}^{4+}$. Interestingly, the Cr valence *increases* with temperature, starting at $\text{Cr}^{3.55+}$ at 20 K, and increasing to $\text{Cr}^{3.65+}$ at 300 K; error on the valence is ± 0.03 , as determined by the weighting necessary to reduce the quality of the fit by one standard deviation. The valence increase can be qualitatively inferred from the XAS spectra, Figure 9. Specifically, between 20 K and 300 K the features on the low-energy side of the L_3 peak are suppressed, while a new shoulder emerges on the high-energy side. The XAS of the Fe in the $(\text{Mg}_{0.2}\text{Fe}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2})\text{Cr}_2\text{O}_4$ shows a mixed $\text{Fe}^{2+}/\text{Fe}^{3+}$ state, and a decrease in valence (from $\text{Fe}^{2.29+}$ to $\text{Fe}^{2.15+}$) with increasing temperatures, with the decrease in the Fe valence complementing the increase in the Cr. This shows that the chromium valence increases towards $4+$ with temperature while the iron valence decreased towards $2+$ with increasing temperature. Chromium containing spinel oxides are expected to possess a mixed $\text{Cr}^{2+}/\text{Cr}^{3+}$ state, so the presence of Cr^{4+} is unique [35], [61]. In spinels where $A=2+$ and $B=3+$ (2,3 spinels) there is a preference for the larger ion to occupy the tetrahedral site, while in 2-4 spinels ($A=4+$ and $B=2+$) the opposite holds true with larger ions preferring the octahedral site [35].

XAS and XMLD of the Fe and Mn ions in $(\text{Mg}_{0.2}\text{Mn}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2})\text{Fe}_2\text{O}_4$ was also measured (not shown). These measurements confirm the expected mixed $\text{Fe}^{3+}/\text{Fe}^{2+}$ and mixed $\text{Mn}^{3+}/\text{Mn}^{2+}$ valence. At 20K the valences are found to be $\text{Fe}^{2.96+}$ and $\text{Mn}^{2.11+}$, the XMLD showing antiferromagnetic ordering in the Fe and seemingly no magnetic ordering in the Mn. Increasing the temperature to 77 K and 300 K increases the Mn valence to $\text{Mn}^{2.25+}$ and $\text{Mn}^{2.42+}$ and decreases the Fe valence to $\text{Fe}^{2.81+}$ and $\text{Fe}^{2.43+}$, respectively. The larger $\text{Fe}^{2.96+}$ valence at low-temperature is partly expected at lower temperatures to help stabilize the d^5 configuration, but more importantly due to the $2+$ preference of the Mn, Ni and Co cations. These coupled changes in valence are similar to the chromate case and illustrate a balancing of the electrons in the system. The XMLD measurements shows strong antiferromagnetic ordering in the Fe site at 20 K and 77 K, but only weak, noise-level XMLD signal at 300 K; the Mn XMLD shows no antiferromagnetic ordering at any temperature. A similar trend was seen in $(\text{Mn}_{0.2}\text{Fe}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2})\text{Fe}_2\text{O}_4$ with the Fe valence decreasing with increasing temperature with antiferromagnetic ordering at low temperature and no discernable antiferromagnetic ordering at room temperature. The valence information for these three samples is summarized in Table 12 [53].

Table 12 Summary of valence information determined from the X-Ray Absorption spectra of samples measured at ALS.

	(Mg_{0.2}Mn_{0.2}Co_{0.2}Ni_{0.2}Cu_{0.2})Fe₂O₄		(Mn_{0.2}Fe_{0.2}Co_{0.2}Ni_{0.2}Cu_{0.2})Fe₂O₄		(Mg_{0.2}Fe_{0.2}Co_{0.2}Ni_{0.2}Cu_{0.2})Cr₂O₄	
	<u>Mn</u>	<u>Fe</u>	<u>Mn</u>	<u>Fe</u>	<u>Cr</u>	<u>Fe</u>
20K	Mn ^{2.11+} 11% Mn ³⁺ , 79%Mn ²⁺ nonmagnetic	Fe ^{2.96+} 96% Fe ³⁺ , 4%Fe ²⁺ AFM		Fe ^{2.93+} 93% Fe ³⁺ , 7%Fe ²⁺ AFM	Cr ^{3.55+} 44%Cr ³⁺ , 56% Cr ⁴⁺ AFM	Fe ^{2.29+} 29% Fe ³⁺ , 71%Fe ²⁺ AFM
77K	Mn ^{2.25+} 25% Mn ³⁺ , 75%Mn ²⁺ Nonmagnetic	Fe ^{2.81+} 81% Fe ³⁺ , 19%Fe ²⁺ AFM				
300K	Mn ^{2.42+} 42% Mn ³⁺ , 58%Mn ²⁺ nonmagnetic	Fe ^{2.43+} 43% Fe ³⁺ , 67%Fe ²⁺ Not AFM	Mn ^{2.89+} 89% Mn ³⁺ , 11%Mn ²⁺ Difficult to discern but looks like very weak AFM	Fe ^{2.86+} 86% Fe ³⁺ , 14%Fe ²⁺ AFM at RT	Cr ^{3.65+} 35%Cr ³⁺ , 65% Cr ⁴⁺ Appears magnetic	Fe ^{2.15+} 15% Fe ³⁺ , 85%Fe ²⁺ non AFM

Valence changes in spinel systems often tie to lattice inversion and site occupancy changes with temperature. As these compositions are novel, the mechanism of valence change with temperature is not yet clear but could be due to electron delocalization.

Chromium based spinels First Order Reversal Curve

Based on the low temperature magnetic behavior seen in the chromium-based HEO spinels, additional characterization with a Dynacool PPMS were performed. The first composition further studied was $(\text{Mg}_{0.2}\text{Fe}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2})\text{Cr}_2\text{O}_4$ because of its low temperature hysteresis discussed in Figure 3-22. The major loop coercivity was diverging approaching $T=0$ K, but the magnetic saturation is not increasing. This potentially indicates that it is not a true ferromagnetic to antiferromagnetic transition, but that it may be a different region within the sample undergoing antiferromagnetic ordering. The magnetic moment with magnetic field first order reversal curve (FORC) measurements are shown in Figure 3-27 at 15 K, 5 K, and 1.9 K. The FORCs were measured where the coercivity was increasing from Figure 3-22. The FORC diagrams are then shown in Figure 3-28. At 15 K there is a single feature oriented along the H_C axis. This indicates that the magnetic elements are reversing in a relatively isolated fashion, and that there is no bias and thus no long range order or enough anisotropy to pin the magnetic moments. This is probably why there is a large coercive distribution. Since the feature is on the H_C axis, the width of the feature is the distribution of intrinsic coercivity within the sample. From 15 K to 5 K, the feature shifts but has a similar coercive distribution. Then going from 5 K down to 1.9 K, the entire distribution collapses to a single point. As the temperature is decreased, the feature moves along the H_C axis, which could be due to thermally activated reversal, but at the lowest temperature collapses to a single point that is still along the H_C axis and is an interesting and atypical progression.

This could perhaps be indicative of the domains all grouping and changing together. This pinning all together is indicative of antiferromagnetic character since it is at a non-zero value for the coercive field. This shows that the magnetization appears to reverse in a single event, and that the sample is strongly coupled. As discussed previously and seen in Figure 3-23, replacing Fe with Mn causes magnetic turn over to occur at higher temperatures and fields, but again without any decrease in the magnetic saturation. Most interestingly in $(\text{Mg}_{0.2}\text{Mn}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2})\text{Cr}_2\text{O}_4$, the coercivity diverges at the lowest temperatures in the high field, which is unusual in a cubic material. This bias is atypical in combination with the lack of decrease in saturation and could be due to the small ferromagnetic regions surrounded by a predominately antiferromagnetic matrix, something proposed earlier. The FORC diagram measurement performed on $(\text{Mg}_{0.2}\text{Mn}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2})\text{Cr}_2\text{O}_4$ in Figure 3-29 again show a feature along the H_C axis that is longer in length, indicating a larger intrinsic coercivity distribution. Because of the saturation field divergence in this sample, additional measurements at lower temperatures could not be performed. The results from the FORC diagrams support the proposed theory of isolated ferromagnetic regions, or clusters.

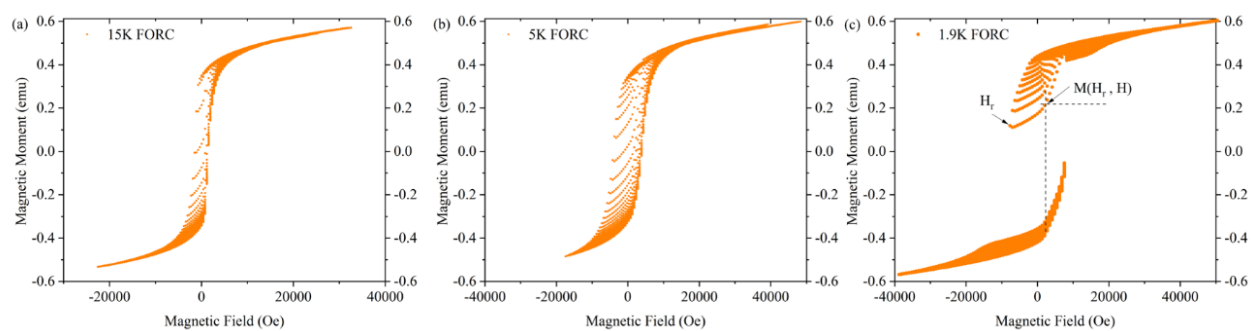


Figure 3-27 Raw FORC data for $(\text{Mg}_{0.2}\text{Fe}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2})\text{Cr}_2\text{O}_4$ polycrystalline powder at (a) 15K, (b) 5K and (c) 1.9K.

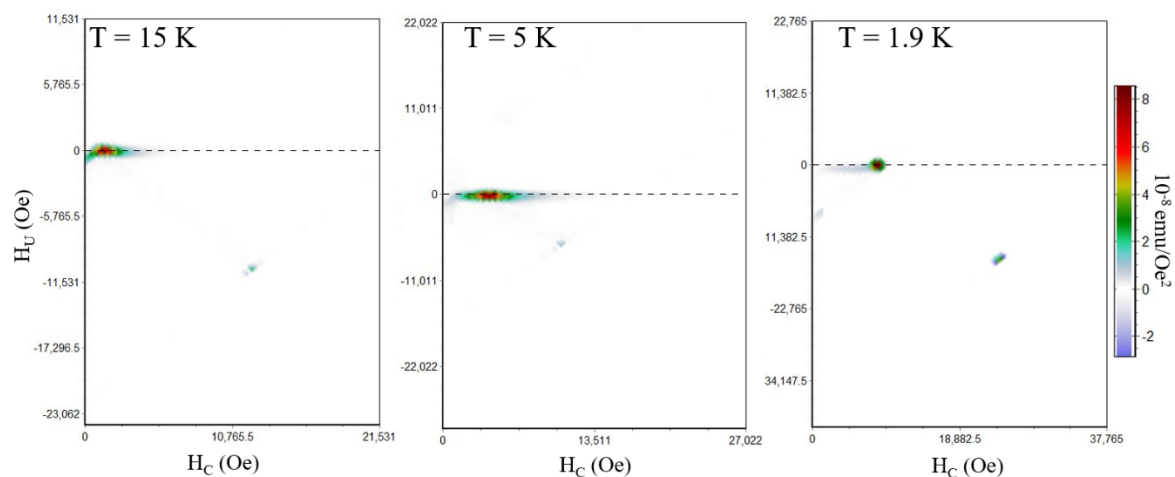


Figure 3-28 First Order Reversal Curve (FORC) diagrams of $(\text{Mg}_{0.2}\text{Fe}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2})\text{Cr}_2\text{O}_4$ polycrystalline powder measured with DynaCool PPMS at (a) 15K, (b) 5K and (c) 1.9K.

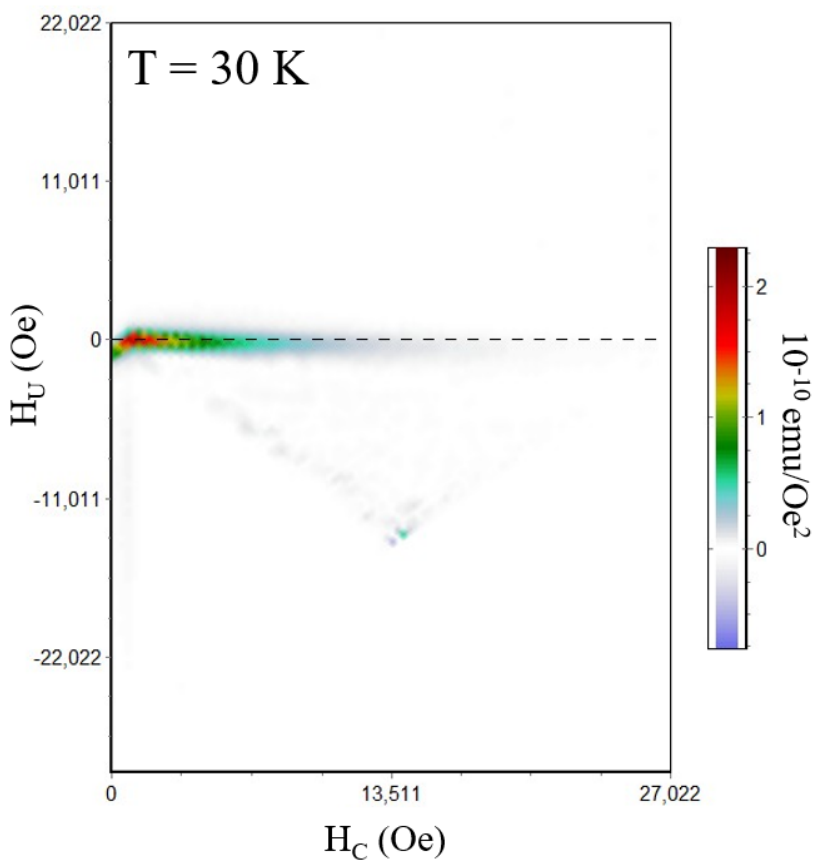


Figure 3-29 First Order Reversal Curve (FORC) diagrams of $(\text{Mg}_{0.2}\text{Mn}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2})\text{Cr}_2\text{O}_4$ polycrystalline powder.

3.3. Magnetic Properties- Ruddlesden-Popper cuprates

Magnetic properties are measured using a magnetic property measurement system (MPMS3) in the 300 K-3 K temperature range. The inverse susceptibility, $1/\chi$, with temperature for PSE synthesized $(\text{La}_{0.2}\text{Nd}_{0.2}\text{Gd}_{0.2}\text{Tb}_{0.2}\text{Dy}_{0.2})_2\text{CuO}_4$ and SSR and PSE $(\text{La}_{0.2}\text{Pr}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2})_2\text{CuO}_4$ are shown in Figure 3-30 (a) and (b), respectively. The ferrimagnetic Curie point, θ_f , is the intersection of the experimental data with the x-axis and is the point at which the susceptibility diverges and spontaneous magnetization occurs. The Curie-Weiss law, given by Equation 22, where C is the Curie constant is denoted by the dashed lines on the plot. The x-axis intersection, $-C/\chi_0$, allows determination of the Curie-Weiss constant and the values for these are reported on the plots.

Equation 22:
$$\chi = \frac{C}{T + (\frac{C}{\chi_0})}$$

From the linear portion of the Curie-Weiss fit, the values for the effective magnetic moments, μ_{eff} , are determined for the two PSE samples using Equation 23 where k_B = Boltzmann's constant and N_A = Avogadro's number.

Equation 23:
$$\mu_{\text{eff}} = \sqrt{\frac{3k_B C}{N_A}} \approx 2.84\sqrt{C}$$

These are reported in Table 13 along with values from literature for single rare earth ion 2-1-4 type cuprates and those of the individual rare earth ions for comparison. The negative value for the intersections of the Curie-Weiss fit in conjunction with the shape of the data indicate that both compositions exhibit ferrimagnetic behavior at low temperatures. Both PSE and SSR samples of polycrystalline $(\text{La}_{0.2}\text{Pr}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2})_2\text{CuO}_4$ were measured and despite the elemental inhomogeneity seen in the EDXS mapping, the magnetic properties do not seem to have been affected. The magnetization with temperature for zero field cooled (ZFC) and field cooled (FC) data show paramagnetic behavior and are provided in Figure 3-31 along with the hysteresis behavior M vs H Figure 3-32. The magnetometry indicates low temperature ferrimagnetic behavior, and despite the elemental inhomogeneity seen in the solid state synthesized $(\text{La}_{0.2}\text{Pr}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2})_2\text{CuO}_4$ the magnetic character was not impacted.

3.4. Thermal Analysis

Spinel

The DSC/TGA measurement results on $(\text{Mg}_{1/5}\text{Ni}_{1/5}\text{Co}_{1/5}\text{Cu}_{1/5}\text{Zn}_{1/5})\text{Al}_2\text{O}_4$ are shown, where mass loss corresponds to the TGA and heat flow to the DSC portions of the experiment, respectively. After the materials had been dried overnight, a small amount of the entrapped foam powder was measured.

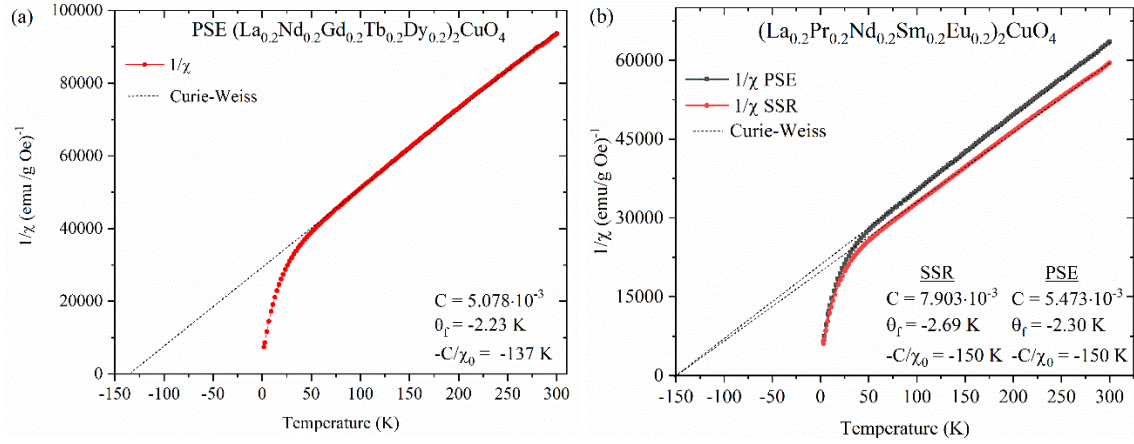


Figure 3-30 Inverse susceptibility with temperature and Curie-Weiss fits (dashed lines) for (a) PSE $(\text{La}_{0.2}\text{Nd}_{0.2}\text{Gd}_{0.2}\text{Tb}_{0.2}\text{Dy}_{0.2})_2\text{CuO}_4$ and (b) SSR and PSE $(\text{La}_{0.2}\text{Pr}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2})_2\text{CuO}_4$.

Table 13 Summary of magnetic properties of PSE synthesized HEO cuprates and those of polycrystalline traditional rare-earth RP cuprate compositions from literature.

Composition	Curie-Weiss effective moment (μ_B)	Structure	Rare-earth ion effective moment [62]
$(\text{La}_{0.2}\text{Nd}_{0.2}\text{Gd}_{0.2}\text{Tb}_{0.2}\text{Dy}_{0.2})_2\text{CuO}_4$	0.210	T'-structure	-
$(\text{La}_{0.2}\text{Pr}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2})_2\text{CuO}_4$	0.202	T'-structure	-
Sm_2CuO_4	0.5 [44]	T'-structure	1.5
Eu_2CuO_4	0 [44]	T'-structure	3.4
Gd_2CuO_4	7.8 [44]	T'-structure	8.0
Nd_2CuO_4	1.23 [44]	T'-structure	3.5
Pr_2CuO_4	0.08 [44]	T'-structure	3.5
Tb_2CuO_4 poly	9.62 [63]	T'-structure	9.5
La_2CuO_4 poly	0.48 [64]	T-structure	0

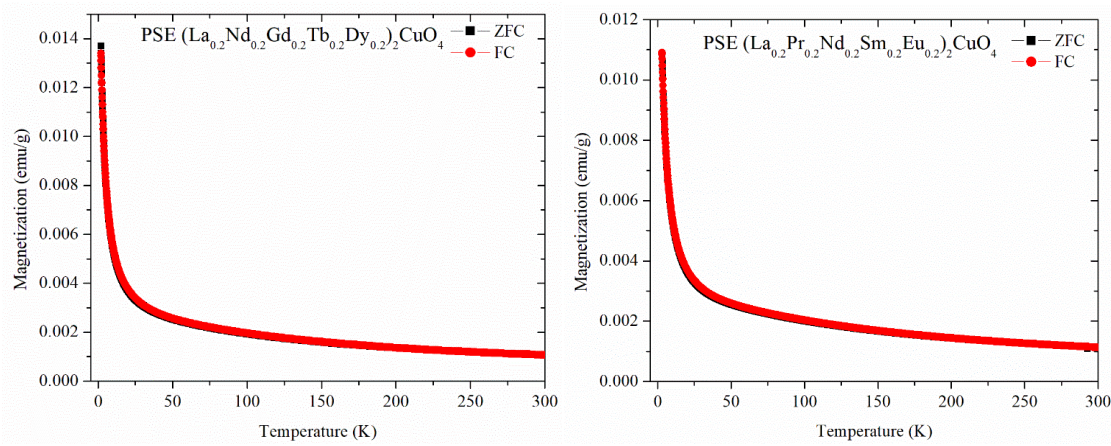


Figure 3-31 Magnetization versus temperature measured from 300 K-3 K in both the field cooled (FC) and zero-field cooled (ZFC) methods with an applied field of 100 Oe for (left) $(\text{La}_{0.2}\text{Nd}_{0.2}\text{Gd}_{0.2}\text{Tb}_{0.2}\text{Dy}_{0.2})_2\text{CuO}_4$ and (right) $(\text{La}_{0.2}\text{Pr}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2})_2\text{CuO}_4$.

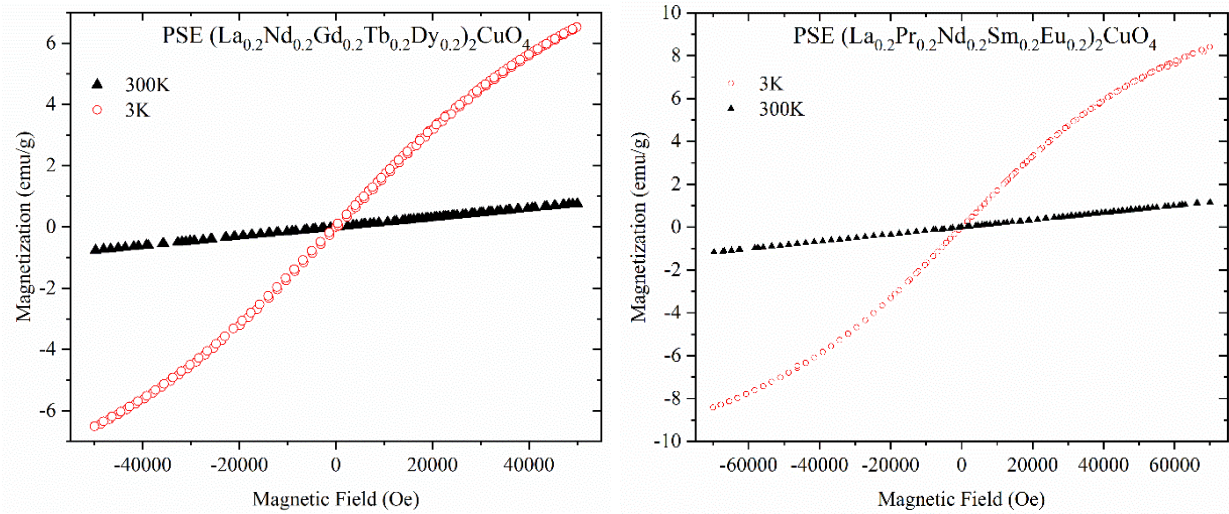


Figure 3-32 Magnetization versus magnetic field measurements at 3 K and 300 K for (left) $(\text{La}_{0.2}\text{Nd}_{0.2}\text{Gd}_{0.2}\text{Tb}_{0.2}\text{Dy}_{0.2})_2\text{CuO}_4$ and (right) $(\text{La}_{0.2}\text{Pr}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2})_2\text{CuO}_4$.

In Figure 3-33 the dashed line denotes a broad peak occurring at 260°C which corresponds to the organic burn off and was the reasoning behind the selected 300°C calcination temperature for the PSE synthesized powders. The dotted line marks a second exothermic peak in the DSC at 330°C which signifies the onset of crystallization. A crystallization temperature of 550°C was determined for this material as it is past the crystallization point and at a point where mass loss has stopped. The DSC/TGA measurement results on $(\text{Cr}_{0.2}\text{Mn}_{0.2}\text{Fe}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2})_3\text{O}_4$ PSE powder after drying and before calcining are shown in Figure 3-34. There is a slight endotherm and corresponding dip in the mass loss before 100°C that is most likely due to moisture loss. The only other notable features are a small exotherm followed by a sharp endothermic peak right before 300°C. This is believed to correspond to the removal of organics and other volatiles followed by the onset of crystallization. The thermal analysis of these PSE synthesized precursor powder of HEO spinel compositions explain the low temperatures at which crystalline powders can be obtained by the polymeric steric entrapment synthesis method.

Ruddlesden-Popper Cuprates

Simultaneous DSC/TGA was performed on the solid state reaction (SSR) samples (after the powders had been ball milled) and on the PSE samples (after the calcining step) and the plotted results are provided in Figure 3-35 (a)-(d). Measurements were performed while increasing the temperature with a 5°C/minute rate. For both PSE samples, the mass loss begins to level out above 850°C. For the $(\text{La}_{0.2}\text{Nd}_{0.2}\text{Gd}_{0.2}\text{Tb}_{0.2}\text{Dy}_{0.2})_2\text{CuO}_4$ sample there is also a slight inflection in the heat flow occurring at this point. From this result, the 900°C crystallization temperature was chosen for PSE synthesizes samples. The DSC portion of the measurements for these samples is atypical and constitutes of a single broad exothermic peak. Both SSR samples show exothermic crystallization peaks in the DSC measurement near 1100°C, with the inflections prior to this temperature being attributed to moisture removal from the rare-earth oxides. While the starting oxides were all dried immediately prior to being weighed stoichiometrically, the powder was not dried again after ball milling before the DSC/TGA was performed and moisture had been reabsorbed.

3.1. Thermal Stability

The thermal phase-stability of a few spinel and perovskite HEO compositions was studied using in-situ HTXRD. The initial thought for these studies was to look for atypical thermal expansion behavior, where the interactions from the crystalline and magnetic lattices and the disorder within the system could cause interesting effects. As the peak position and lattice parameter are inversely proportional, a shift in the Bragg peaks to a lower position in 2θ indicates lattice expansion. As described below, this is what was seen in the samples upon heating and is typical thermal expansion behavior.

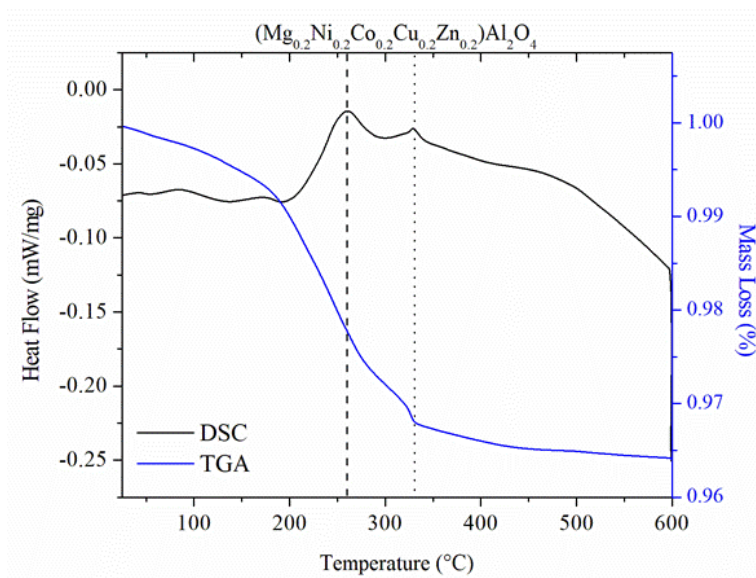


Figure 3-33 Simultaneous DSC/TGA measurement from 25°C to 600°C of $(\text{Mg}_{0.2}\text{Ni}_{0.2}\text{Co}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2})\text{Al}_2\text{O}_4$ powder before calcining.

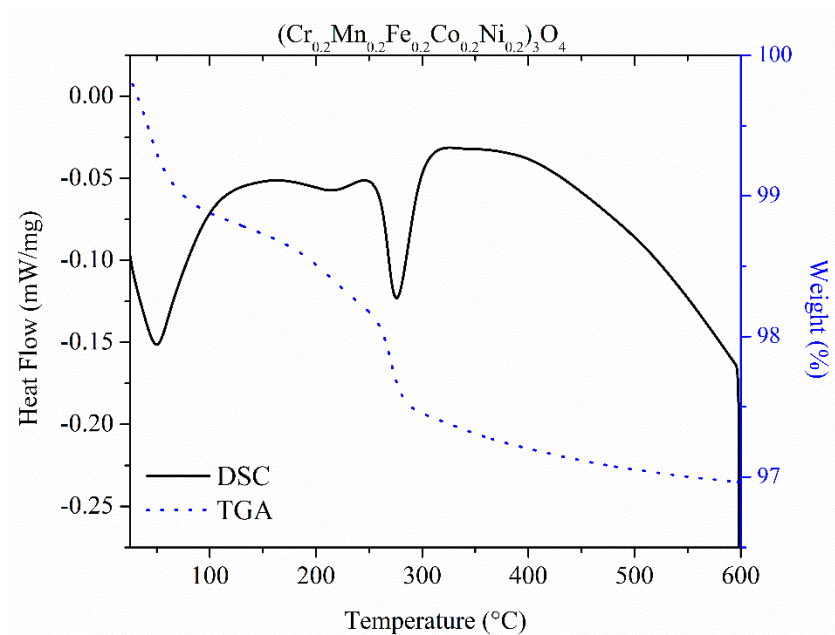


Figure 3-34 Simultaneous DSC/TGA measurement from 25°C to 600°C of $(\text{Cr}_{0.2}\text{Mn}_{0.2}\text{Fe}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2})_3\text{O}_4$ powder before calcining.

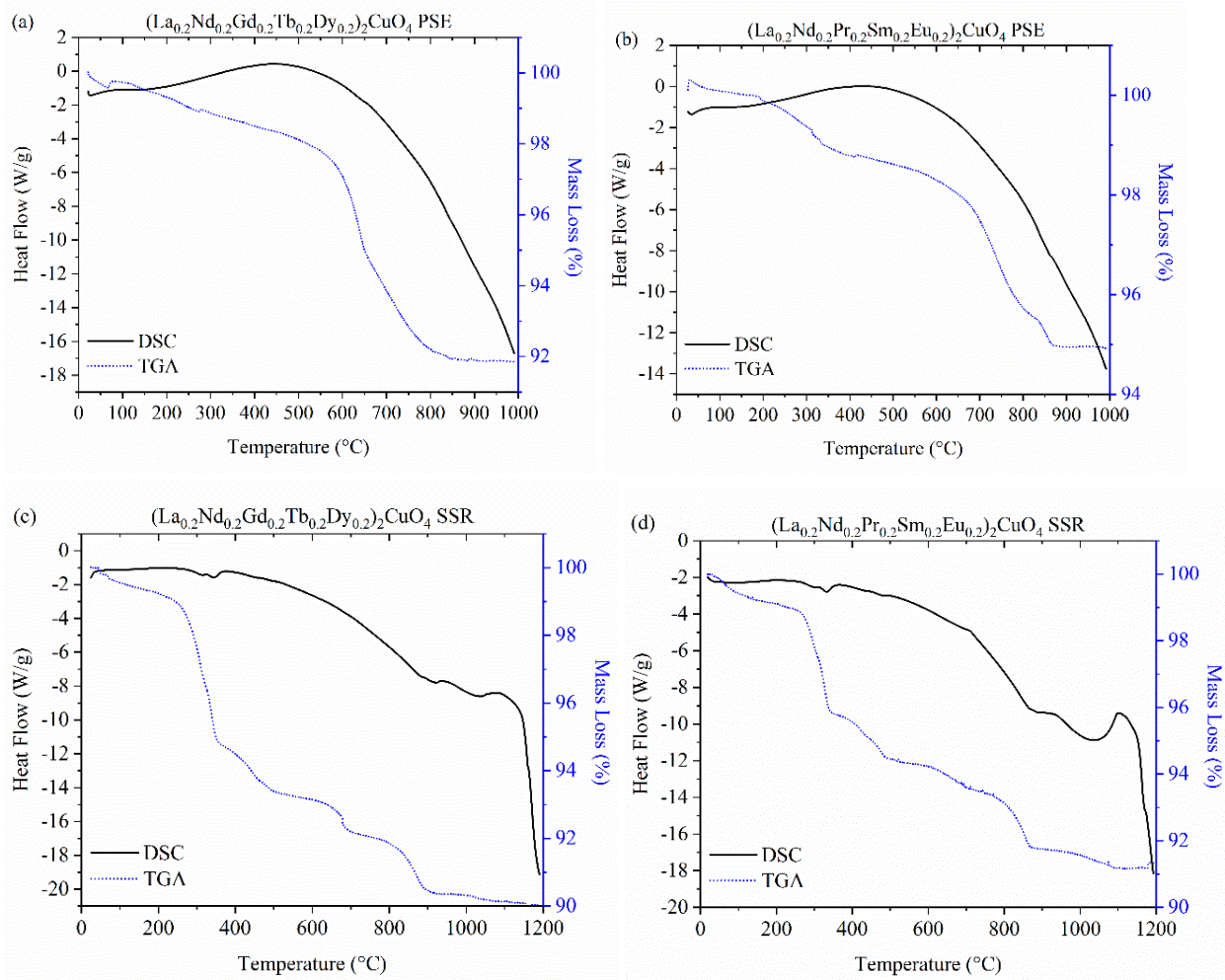


Figure 3-35 Simultaneous DSC/TGA measurements of PSE (a) $(\text{La}_{0.2}\text{Nd}_{0.2}\text{Gd}_{0.2}\text{Tb}_{0.2}\text{Dy}_{0.2})_2\text{CuO}_4$ and (b) $(\text{La}_{0.2}\text{Pr}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2})_2\text{CuO}_4$ powder after calcining and post ball milled SSR (c) $(\text{La}_{0.2}\text{Nd}_{0.2}\text{Gd}_{0.2}\text{Tb}_{0.2}\text{Dy}_{0.2})_2\text{CuO}_4$ and (d) $(\text{La}_{0.2}\text{Pr}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2})_2\text{CuO}_4$ powder.

Spinel

In-situ HTXRD of solid state synthesized $(\text{Mg}_{0.2}\text{Ni}_{0.2}\text{Co}_{0.2}\text{Cu}_{0.2}\text{Fe}_{0.2})\text{Cr}_2\text{O}_4$ was measured on a single phase polycrystalline pellet that had been synthesized with the solid state method. It was measured from 25°C to 1200°C, starting at 25°C and then at 100°C, 200°C, 300°C, 600°C, 900°C and 1200°C and is given in Figure 3-36. This showed that the material maintained a single phase spinel structure through the full temperature range.

The thermal expansion and high temperature phase stability of PSE synthesized $(\text{Mg}_{1/5}\text{Ni}_{1/5}\text{Co}_{1/5}\text{Cu}_{1/5}\text{Zn}_{1/5})\text{Al}_2\text{O}_4$ were investigated using in-situ high temperature x-ray diffraction (HTXRD) techniques. A pellet of crystallized powder was uniaxially pressed and placed on the sample stage for measurement of the full $10\text{-}90^\circ 2\theta$ range from 25°C to 300°C in increments of 25°C and at 600°C, 900°C, and 1200°C. The data are shown in the waterfall plot in Figure 3-37 (a), with the inset showing the peak position shift with temperature for the primary (311) reflection. The material exhibited excellent thermal stability, maintaining a single-phase spinel structure. From sequential Rietveld refinements of the HTXRD data with GSASII [49], the lattice parameters were determined and plotted as a function of temperature in Figure 3-37 (b). The data was fit with a third order polynomial function: $a = 8.07879 + 5.25792 \cdot 10^{-5} \cdot T + 3.55107 \cdot 10^{-8} \cdot T^2 - 1.5866 \cdot 10^{-11} \cdot T^3$, where a is the lattice parameter and T the temperature in degrees Celsius.

Perovskites

The $\text{Sr}(\text{Zr}_{0.2}\text{Sn}_{0.2}\text{Ti}_{0.2}\text{Hf}_{0.2}\text{Mn}_{0.2})\text{O}_3$ composition has a cubic perovskite structure (space group Pm-3m) whereas $(\text{Gd}_{0.2}\text{La}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Y}_{0.2})\text{AlO}_3$ and $(\text{Gd}_{0.2}\text{La}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Y}_{0.2})\text{MnO}_3$ are both orthorhombic perovskites (space group Pbnm). The cubic $\text{Sr}(\text{Zr}_{0.2}\text{Sn}_{0.2}\text{Ti}_{0.2}\text{Hf}_{0.2}\text{Mn}_{0.2})\text{O}_3$ shown in Figure 3-38 exhibited excellent phase stability up to 1200°C. The $(\text{Gd}_{0.2}\text{La}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Y}_{0.2})\text{AlO}_3$ shown in Figure 3-39 exhibited peak broadening behavior that could be indicative of splitting and secondary orthorhombic phase developing. The $(\text{Gd}_{0.2}\text{La}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Y}_{0.2})\text{MnO}_3$ shown in Figure 3-40 had secondary peaks of a different structure appear at elevated temperature. This was an interesting comparison between a composition with non-magnetic Al compared to a composition with magnetic Mn as the B- site constituent. This shows the phase stability to have some dependence on composition. However, the primary peak's shift to a lower position $^\circ 2\theta$ for both compositions is similar.

3.1.Kinetic Analysis

This section goes through the kinetic analysis on in-situ high temperature x-rya diffraction data for the two synthesis methods described in 2.1 Material synthesis for two different spinel compositions and one Ruddlesden-Popper composition. This builds off of the material introduced in 1.5 Kinetic theory to identify the mechanisms involved through the described data analysis methods.

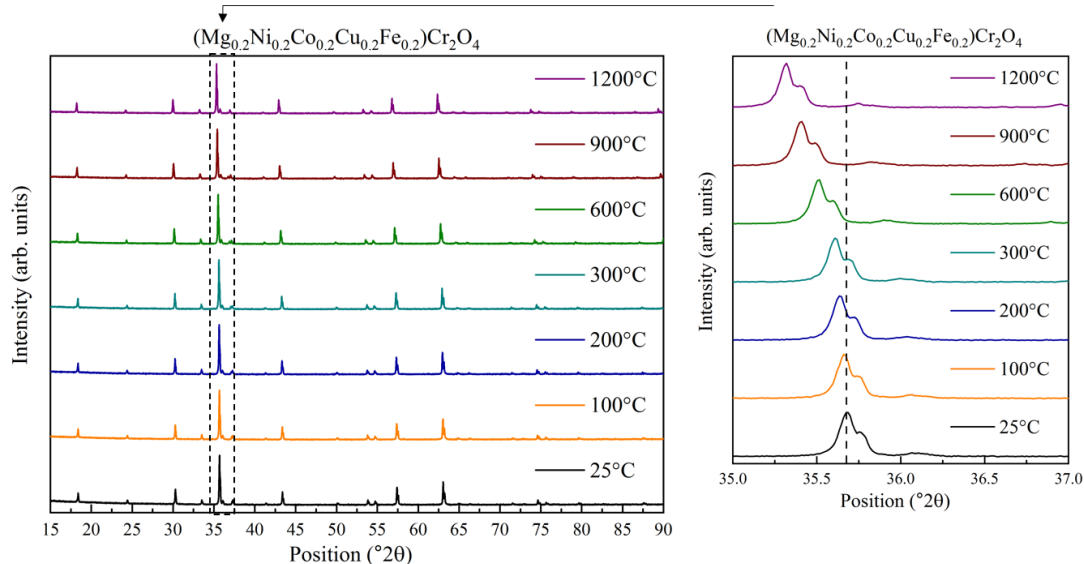


Figure 3-36 HTXRD spectra of $(\text{Mg}_{0.2}\text{Ni}_{0.2}\text{Co}_{0.2}\text{Cu}_{0.2}\text{Fe}_{0.2})\text{Cr}_2\text{O}_4$.

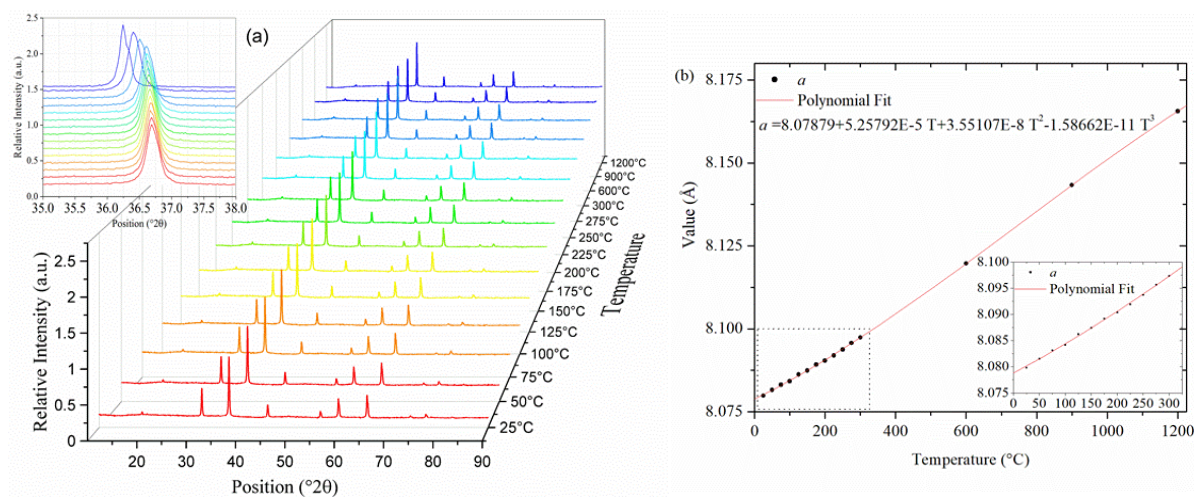


Figure 3-37 (a) X-ray Diffraction data as a function of temperature with inset showing the peak position shift for the primary (311) reflection and (b) the lattice parameter with temperature with polynomial fit for $(\text{Mg}_{1/5}\text{Ni}_{1/5}\text{Co}_{1/5}\text{Cu}_{1/5}\text{Zn}_{1/5})\text{Al}_2\text{O}_4$.

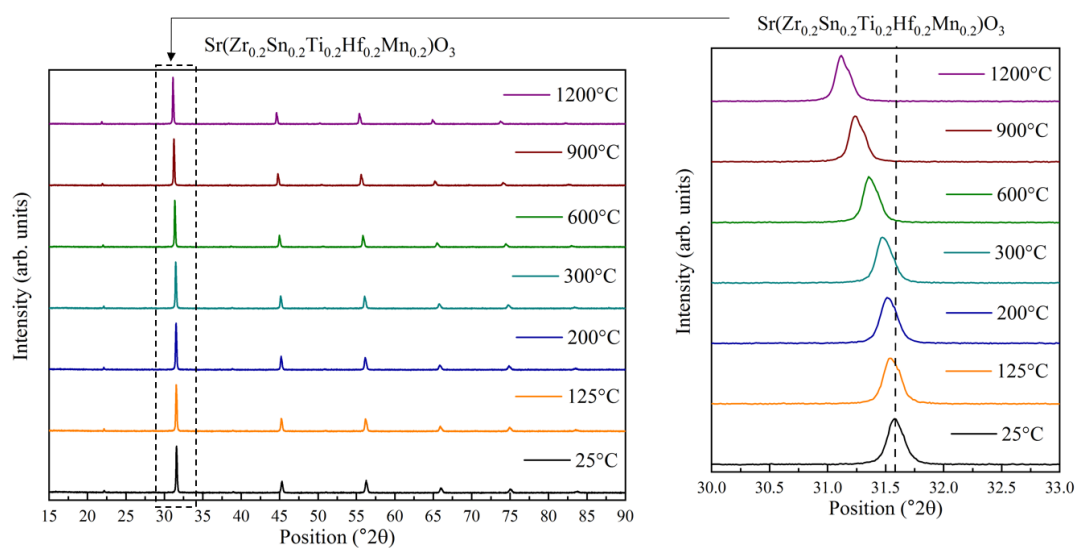


Figure 3-38 HTXRD spectra of $\text{Sr}(\text{Zr}_{0.2}\text{Sn}_{0.2}\text{Ti}_{0.2}\text{Hf}_{0.2}\text{Mn}_{0.2})\text{O}_3$.

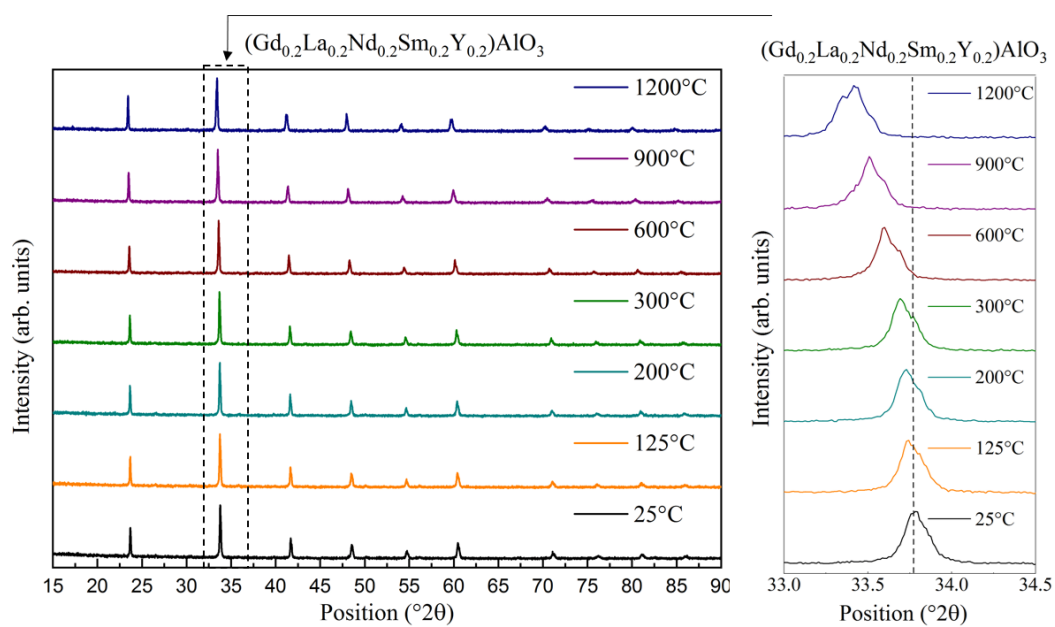


Figure 3-39 HTXRD spectra of $(\text{Gd}_{0.2}\text{La}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Y}_{0.2})\text{AlO}_3$.

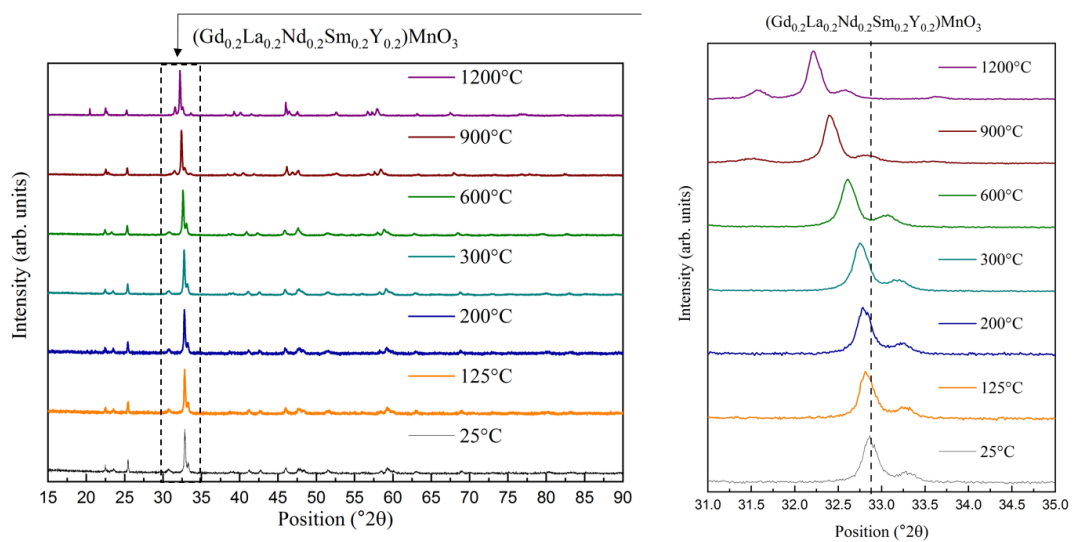


Figure 3-40 HTXRD spectra of $(\text{Gd}_{0.2}\text{La}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Y}_{0.2})\text{MnO}_3$.

In-situ HTXRD results: Spinel

In our study an HEO spinel composition $(\text{Mg}_{0.2}\text{Ni}_{0.2}\text{Co}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2})\text{Al}_2\text{O}_4$ [24] is synthesized via the solid-state synthesis method and polymeric steric entrapment (PSE) in order to investigate and contrast the kinetic behavior. An additional HEO spinel composition, $(\text{Co}_{0.2}\text{Cr}_{0.2}\text{Fe}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.2})_3\text{O}_4$, made via solid-state synthesis was also studied. In an ideal situation, isothermal data would be used, resulting in fewer variables and making the subsequent kinetic analysis easier. However, in this type of in-situ data collection and analysis it should be expected that multiple data sets will be required to capture the necessary data for optimum evaluation. Often, with both solid-state and wet chemistry synthesis methods, the exact crystallization point is unknown unless other thermogravimetric or other temperature dependent measurements have been conducted. Even then, discerning the exact temperature at which to dwell to capture the phase's crystallization can require multiple attempts. This is shown by the two ramping experiments for which data were collected on solid-state synthesized $(\text{Co}_{0.2}\text{Cr}_{0.2}\text{Fe}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.2})_3\text{O}_4$ and shown in Figure 3-41 as heatmaps.

Figure 3-41 (a) shows the initial experiment where the data were collected on ramping to 1200 °C before dwelling at that temperature. The lower portion of these plots shows the data collected while ramping to the desired temperature and the upper portion of these plots shows data collected at the dwelling temperature (isothermal). During both the ramping and isothermal experiments, the data were recorded continuously. Figure 3-41 (a) indicates that during the ramping experiment, crystallization of the spinel phase occurred at approximately 800°C and prior to the dwell temperatures. This is denoted by the appearance of the marked (022), (113) and (222) reflections. Figure 3-41 (b) shows a subsequent experiment where the data were collected on ramping to 850°C, followed by a dwell. Even at this significantly lower temperature, the material crystallized prior to the dwell temperature, and there was not enough of a change in the degree of crystallinity, α , to determine kinetic information from these isothermal data. This illustrates a case where using non-isothermal data and master plots is valuable.

Isothermal experiments were performed on the PSE synthesized $(\text{Mg}_{0.2}\text{Ni}_{0.2}\text{Co}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2})\text{Al}_2\text{O}_4$, and the results are shown in Figure 3-42. A maximum ramp rate was used to reach the target temperature before dwelling for two hours. In the case of the 400 °C experiment it took 8 minutes to reach temperature and start data collection; for the 600 °C experiment it took 10 minutes to reach temperature and start data collection. As seen in the plot, the samples showed evidence of initial crystallinity early in the experiments even with such fast ramping rates. While data were continually collected during the two-hour dwell, only the last scan of the dwell is plotted. This indicates that there was not a considerable change in peak intensity for the isothermal experiments, especially when compared to the change between initial and final measurement during the ramping experiment. This slight change in peak area was not enough to gain significant information about the kinetic behavior from the isothermal runs. The rapid crystalline formation was unexpected, and without further experimentation cannot be attributed to the disordered nature of the material, to a feature unique to this specific system and/or synthesis method, or to other factors.

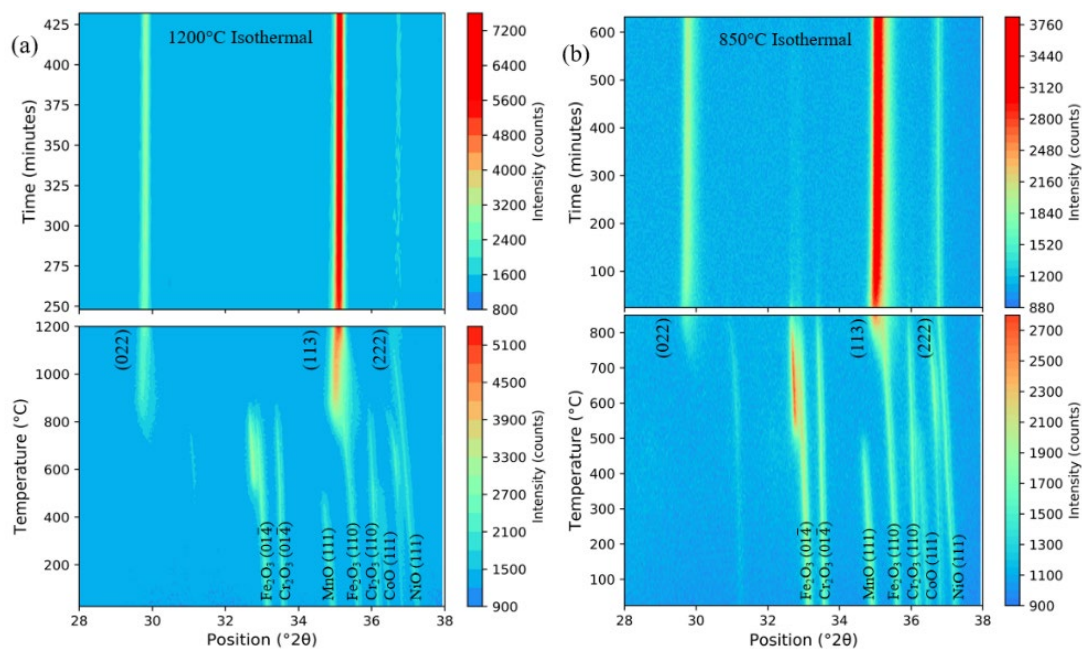


Figure 3-41 Heatmaps (temperature (°C) vs position (°2θ) and the intensity is shown in color) of the in-situ HTXRD data collected on solid-state synthesized $(\text{Co}_{0.2}\text{Cr}_{0.2}\text{Fe}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.2})_3\text{O}_4$ with both ramping experiments (lower) and subsequent dwell experiment (upper).

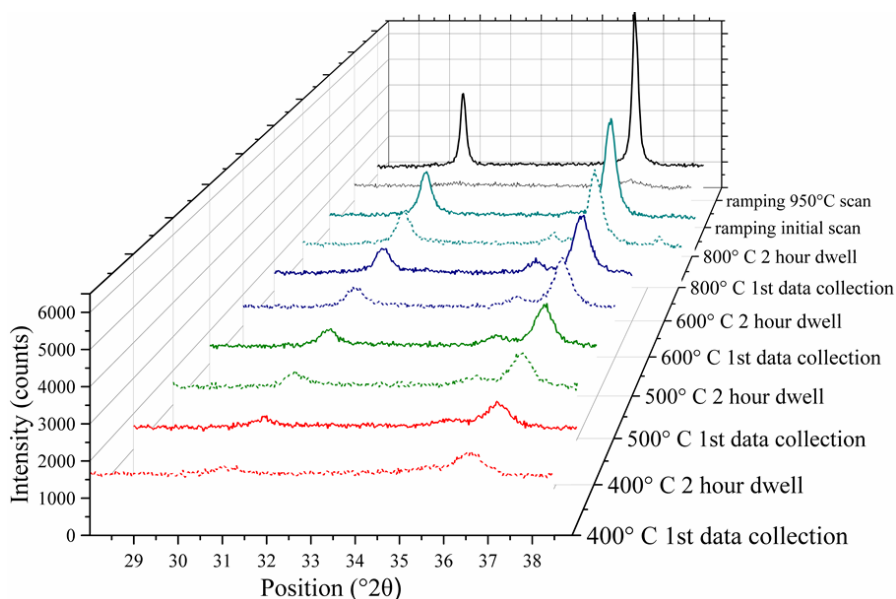


Figure 3-42 X-ray diffraction data for the initial and final scans of isothermal measurements of PSE synthesized $(\text{Mg}_{0.2}\text{Ni}_{0.2}\text{Co}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2})\text{Al}_2\text{O}_4$ samples measured at varying temperature compared to data collected at 950°C during a ramping temperature dependent run.

Isothermal data analysis is not only easier for interpreting kinetic behavior but is also required to determine information such as the activation energy. Although not obtainable from the experimental data collected in this work, the steps for this determination are described. The Avrami behavior is the first step and can be given by the following modified equations:

$$\text{Equation 24: } \alpha = 1 - e^{-(k_a t)^n}$$

$$\text{Equation 25: } \ln[-\ln(1 - \alpha)] = n \ln k_a + n \ln t$$

where α is still the fraction transformed, k_a is the rate constant, and n is the reaction mechanism [65]. Note that Equation 25 was previously seen in a slightly different form but is restated here for convenience. The rate constant is dependent on the growth and nucleation and is thus susceptible to temperature. The value of n gives information on the dimensionality of crystalline transformation and whether it is lineal, plate-like, or polyhedral [66]. The information learned from the value of n can tie into the dimensionality of the behavior followed when further kinetic calculation is performed and plotted over the master plot. When $\ln[-\ln(1 - \alpha)]$ is plotted versus $\ln t$, the slope is n and the y-intercept is $n \ln k_a$. An Arrhenius plot can then be made by plotting $\ln k_a$ versus $1/T$ and the activation energy E_a determined from the linear slope, where the slope is E_a/R and R is the gas constant. Note that this requires the collection of isothermal data at multiple temperatures in order to generate a sufficient Arrhenius plot from the information learned from the Avrami plot. This E_a can then be used as a comparative value for different regions of kinetic trends [67], or for subsequent calculations.

Determining kinetic behavior from time and temperature dependent data

The master plots, described in 1.5 Kinetic theory, can be used for analyzing both isothermal and non-isothermal using the methods described by the following series of equations which are further explained in the work by Gotor et al. [33]. The amount transformed, α , can be determined from the experimental data and used in the relationship shown in Equation 26.

$$\text{Equation 26: } \frac{d\alpha/d\theta}{d\alpha/d\theta_{\alpha=0.5}} = \frac{d\alpha/dt}{d\alpha/dt_{\alpha=0.5}} \frac{\exp(\frac{E}{RT})}{\exp(E/RT_{0.5})}$$

The generalized time is used to determine the kinetic rate equation at infinite temperature, given in Equation 27, where θ denotes the reaction time taken to obtain a given α at infinite temperature.

$$\text{Equation 27: } \theta = \int_0^t \exp\left(-\frac{E}{RT}\right) dt = \frac{E}{\beta R} \int_x^\infty \frac{\exp(-x)}{x^2} dx = \frac{E}{\beta R} p(x)$$

Using the expansion given in Equation 27, where $x=E/RT$ and β is the linear heating rate, the function $p(x)$ is defined in an open form using Equation 28 and Equation 29 in order to obtain the value of $\theta/\theta_{0.5}$ given by Equation 30.

Equation 28: $p(x) = \frac{e^{-x}}{x} \pi(x)$

Equation 29: $\pi(x) = \frac{x^3 + 18x^2 + 86x + 96}{x^4 + 20x^3 + 120x^2 + 240x + 120}$

Equation 30: $\frac{\theta}{\theta_{0.5}} = \frac{p(x)}{p(x_{0.5})}$

As shown in the previous equations, the activation energy E is required for determining the reaction mechanism from linear non-isothermal data. This interdependence of the kinetic model with these parameters is a drawback and explains why, as mentioned earlier, isothermal data is ideal for further analysis as well as necessary to obtain the actual value for E . In the case of this study it was found that while the exact value could not be experimentally determined or calculated for these systems, it was not vital. Changing the order of magnitude of the value used did not cause any significant alteration, and the kinetic behavior that the data best followed did not shift.

The experimental data can then be analyzed by plotting $\frac{\theta(\frac{d\alpha}{d\theta})}{\theta_{0.5}(\frac{d\alpha}{d\theta})_{\alpha=0.5}}$ as a function of α over the master plot given by Figure 1-9 (d). An example of this analysis is provided using the ramping data collected up to 1200 °C on the solid-state synthesized $(\text{Co}_{0.2}\text{Cr}_{0.2}\text{Fe}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.2})_3\text{O}_4$. The previously collected data (Figure 3-41 (a)) is shown again in Figure 3-43 (a) with the formation and crystallization of the desired phase denoted by the red dashed outline. It is preferable to utilize the highest intensity peak in this analysis, however, as in the example presented here, this is not always the best option. It would be difficult to separate the characteristic peaks belonging to the transformed phase from characteristic peaks indicative of the precursor or untransformed phase(s). Two examples of this difficulty can be found in Figure 3-43 (a), namely the close spatial relation of the transformed (222) peak to the precursor NiO (111) peak and of the transformed (113) peak to the precursor Fe_2O_3 (110) peak. In laboratory XRD experiments, compromises are often made between data collection time, intensity, and resolution. Minimizing data collection time is vital for kinetic investigations of rapidly-changing systems, maximizing intensity helps reduce noise and ensure an accurate modeling of the peaks, and maximizing resolution helps in the differentiation of peaks located at similar values of 2θ . If we were to optimize resolution in this example to avoid the problems of spatial resolution outlined above, data collection time and intensity would need to be sacrificed, which would create new difficulties. Fortunately, the (022) peak was not spatially obscured within the transformation range by precursor peaks for the solid state synthesized $(\text{Co}_{0.2}\text{Cr}_{0.2}\text{Fe}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.2})_3\text{O}_4$ and $(\text{Mg}_{0.2}\text{Ni}_{0.2}\text{Co}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2})\text{Al}_2\text{O}_4$ samples, so the need to optimize resolution to the detriment of data collection time and intensity could be avoided by selecting this peak for analysis. Using the (022) reflection for SSS $(\text{Co}_{0.2}\text{Cr}_{0.2}\text{Fe}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.2})_3\text{O}_4$, $\frac{\theta(\frac{d\alpha}{d\theta})}{\theta_{0.5}(\frac{d\alpha}{d\theta})_{\alpha=0.5}}$ is calculated and plotted over the $f(\alpha)g(\alpha)/f(0.5)g(0.5)$ master plot and given in Figure 3-43 (b). This shows a distribution following either the An or Rn mechanism and does not appear to be diffusion controlled.

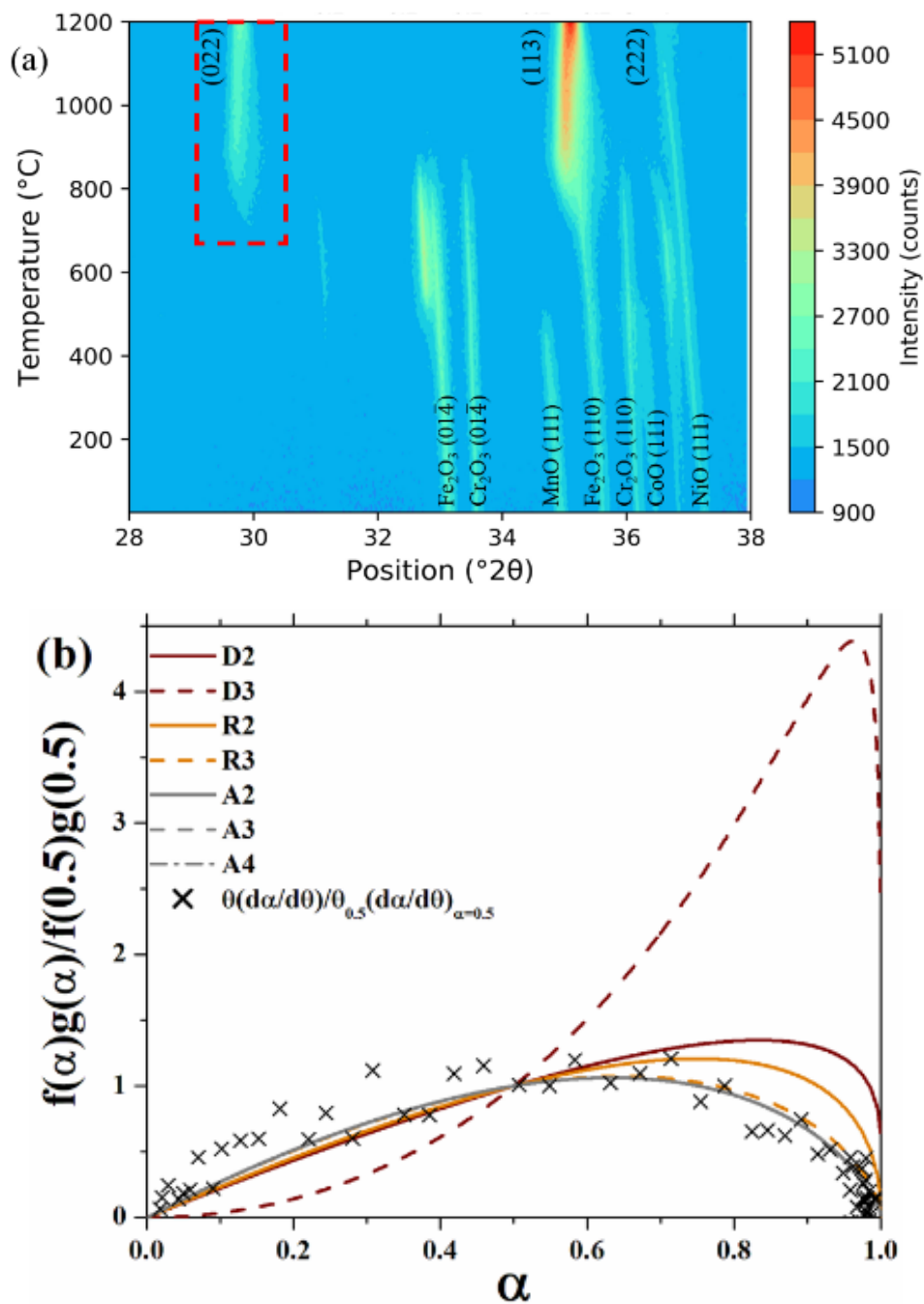


Figure 3-43 (a) The heatmap of the in-situ HTXRD data collection performed on solid-state synthesized $(\text{Co}_{0.2}\text{Cr}_{0.2}\text{Fe}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.2})_3\text{O}_4$. The red dashed box outlines the peak used for the calculations plotted on (b).

Comparison of synthesis method

The in-situ HTXRD data collection and analysis techniques described above can be utilized to compare the phase transformation behavior for different synthesis methods. Figure 3-45 illustrates an example of this in (a) and (b) for $(\text{Mg}_{0.2}\text{Ni}_{0.2}\text{Co}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2})\text{Al}_2\text{O}_4$ made via solid state reaction synthesis (SSS) and polymeric steric entrapment (PSE), respectively. The data is plotted in the $28\text{--}38^\circ 2\theta$ range as a heat map with the polymeric steric entrapment precursor material plot starting at 250°C since the material was previously heat treated up to this temperature in calcining. In the SSS $(\text{Mg}_{0.2}\text{Ni}_{0.2}\text{Co}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2})\text{Al}_2\text{O}_4$ sample, similar to the SSS $(\text{Co}_{0.2}\text{Cr}_{0.2}\text{Fe}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.2})_3\text{O}_4$ discussed above, the individual metal oxides transform into a single-phase solid solution spinel. This phase transformation initiates around 1000°C , whereas the crystallization of the PSE sample from an amorphous state begins to appear at a significantly lower temperature, near 500°C . Another notable variance is the peak shape of the (022) and (113) reflections. There is an increase in the peak broadening for the PSE sample when compared to that of the SSS $(\text{Mg}_{0.2}\text{Ni}_{0.2}\text{Co}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2})\text{Al}_2\text{O}_4$. This could be indicative of a higher degree of positional species disorder since the PSE method has the advantage of forming a more homogenous distribution of cations. However, there are several factors that can contribute to peak broadening. These include disorder, micro strains (which can result from different size cations in different places), crystallite size variation, and a distribution in lattice parameters. To better understand the contributions to the peak shapes, as shown in Figure 3-44, Rietveld refinements were performed using GSAS-II [49] using room temperature XRD scans of both PSE and SSS samples in the $10\text{--}90^\circ 2\theta$ range. The lattice parameters from refinement results were $a=8.079(5)\text{ \AA}$ for PSE and $a=8.059(1)\text{ \AA}$ for SSS. Crystallite size is estimated from the refined spectra using the Scherrer equation given in Equation 31:

$$\text{Equation 31: } D = \frac{K\lambda}{FWHM \cos(\theta)}$$

where: D = crystallite size, K = Scherrer constant = 0.94 for spherical crystallites with cubic symmetry, λ = wavelength of x-rays = $1.54051\text{ \AA}$ for Cu- α source, FWHM = full width at half maximum in 2θ , and θ = Bragg angle.

The crystallite sizes from the most intense peak, (113), are found to be 53.77 nm for polymeric steric entrapment synthesized powder and 139.03 nm for solid state powder. The average crystallite sizes for the entire $10\text{--}90^\circ 2\theta$ spectra are 55.52 nm and 101.79 nm for PSE and SSS, respectively. There is a considerable difference in crystallite size between the two synthesis methods, and while the smaller value for PSE is to be expected, this large difference can be a contributing factor to the difference seen in peak shape. The peak position in 2θ along with the full width at half maximum (FWHM) values for each are listed on the plots.

The degree of crystallinity, α , versus temperature for the (113) reflection of the PSE synthesized material given in Figure 3-45 (d) shows a classic sigmoidal shape. As seen in Figure 1-10, this is indicative of a JMAK (An) or geometric contraction (R) type behavior.

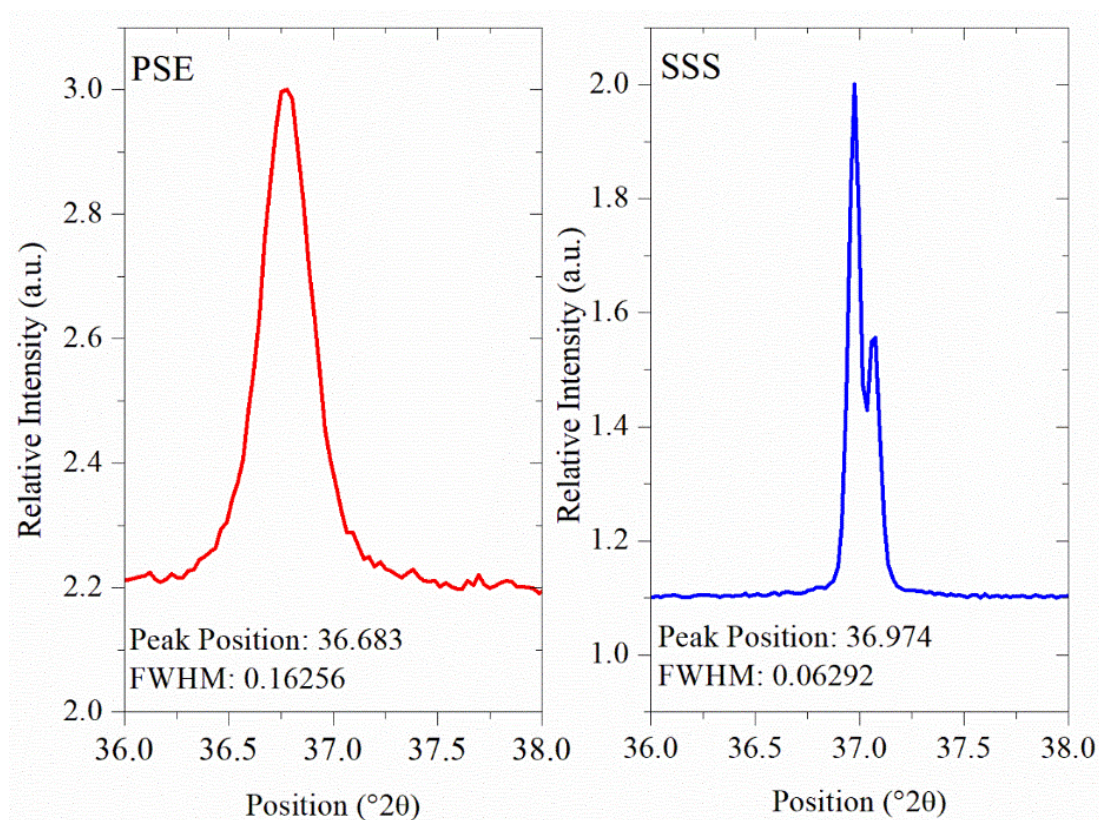


Figure 3-44 Room temperature x-ray diffraction spectra comparing of the (113) reflection for (left) polymeric steric entrapment synthesized and (right) solid state synthesized $(\text{Mg}_{0.2}\text{Ni}_{0.2}\text{Co}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2})\text{Al}_2\text{O}_4$ showing the difference in peak shape.

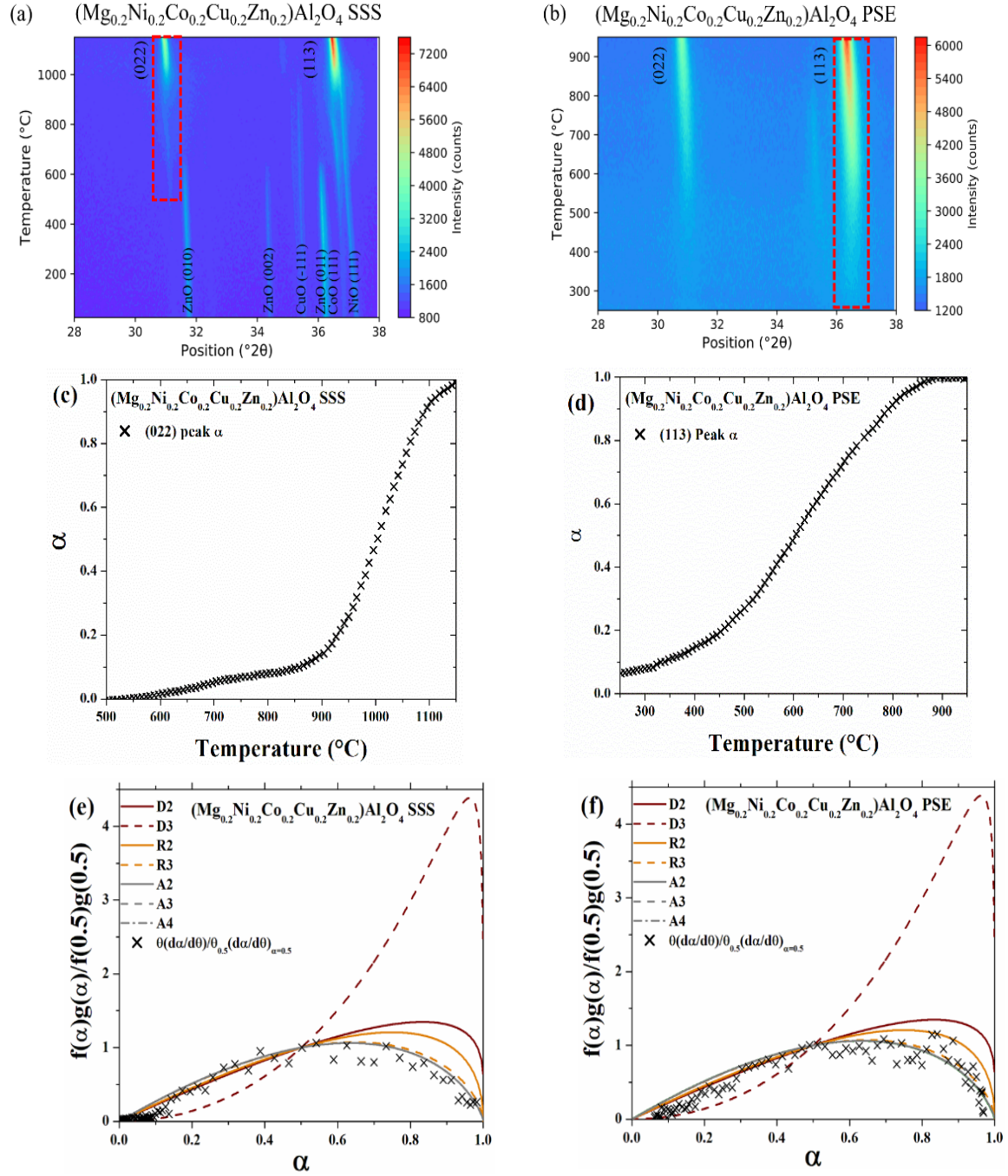


Figure 3-45 The heatmaps of the in-situ HTXRD samples made via (a) SSS and (b) PSE. Red dashed box outlines the peak used for the α with temperature plotted in (c) and (d) as well as the calculations from the experimental data over the master plot in (e) and (f).

This is further confirmed by the calculation of $\frac{\theta(\frac{d\alpha}{d\theta})}{\theta_{0.5}(\frac{d\alpha}{d\theta})_{\alpha=0.5}}$ plotted in (f) which shows a distribution following the An and Rn mechanism on the $f(\alpha)g(\alpha)/f(0.5)g(0.5)$ master plot. The SSS sample analysis from the (222) reflection has a different shape to the α plot given in Figure 3-45 (c). As corroborated by the overlay on the master plot in Figure 3-45 (e), this is suggestive of initially being diffusion controlled, but then switching to a JMAK or geometric contraction kinetic mechanism.

In general, higher temperatures promote diffusion, but the spontaneity of the switch to JMAK or R-type seen here is not yet well understood. Following the changes seen in Figure 3-45 (a), (c), and (e), the ZnO reflection disappears during the diffusion period, while it is not until after the CuO reflection begins to decrease in intensity that the JMAK or R-type behavior starts. This could be indicative of the diffusion limited into JMAK as the thermodynamics change being kinetically favorable. Typically, solid state reaction synthesis is diffusion controlled and wet-chemistry based methods such as sol-gel synthesis and PSE are JMAK controlled and therefore have lower crystallization temperatures. This difference in crystallization temperature is seen from the XRD phase analysis when comparing synthesis methods, but when looking at the kinetic analysis other differences can also be gleaned. While, as mentioned above, diffusion controlled kinetic mechanisms would be expected for solid state reaction synthesis, the behavior seen for solid state synthesized $(\text{Co}_{0.2}\text{Cr}_{0.2}\text{Fe}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.2})_3\text{O}_4$ in Figure 3-43 indicates a JMAK type mechanism. For the SSS $(\text{Mg}_{0.2}\text{Ni}_{0.2}\text{Co}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2})\text{Al}_2\text{O}_4$, this is not entirely the case as it initially follows diffusion controlled behavior. There is also a lower transition temperature at which the spinel phase forms for $(\text{Co}_{0.2}\text{Cr}_{0.2}\text{Fe}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.2})_3\text{O}_4$ when compared to the SSS $(\text{Mg}_{0.2}\text{Ni}_{0.2}\text{Co}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2})\text{Al}_2\text{O}_4$. As they have different compositions and arguably different degrees of disorder, the exact contributions to these differences, whether it be kinetic mechanism, composition dependent, entropic contribution, or a mixture of these, cannot be ascertained. This does, however, provide an interesting avenue for thought and further study as the high entropy material field continues to be explored, and the experimental techniques and analysis provided in this work provide one such method for investigation.

In-situ HTXRD results: Ruddlesden Popper

After successful application of this analysis method on the spinel systems, similar measurements were conducted for the HEO cuprate $(\text{La}_{0.2}\text{Nd}_{0.2}\text{Gd}_{0.2}\text{Tb}_{0.2}\text{Dy}_{0.2})_2\text{CuO}_4$ made via the PSE method in order to better understand the phase formation. Polymeric steric entrapment powder of $(\text{La}_{0.2}\text{Nd}_{0.2}\text{Gd}_{0.2}\text{Tb}_{0.2}\text{Dy}_{0.2})_2\text{CuO}_4$ that had been calcined at 550 °C was pressed into a half inch pellet and placed on the furnace stage for *in-situ* HTXRD data collection allowing the study of phase transformations and data collection for time-dependent kinetics calculations. The data is plotted as a heat map in Figure 3-46, showing the transformation from amorphous to crystalline with the Miller indices of the RP crystallographic reflections labeled at the top of the plot. The onset of crystallization from the HTXRD data observed around 850°C, is in agreement with the DSC/TGA data on the PSE samples in Figure 3-35. Due to the rapid onset of crystallization, as seen with the spinels, isothermally collected data did not have a large enough variation in the range of α to allow for meaningful kinetic analysis.

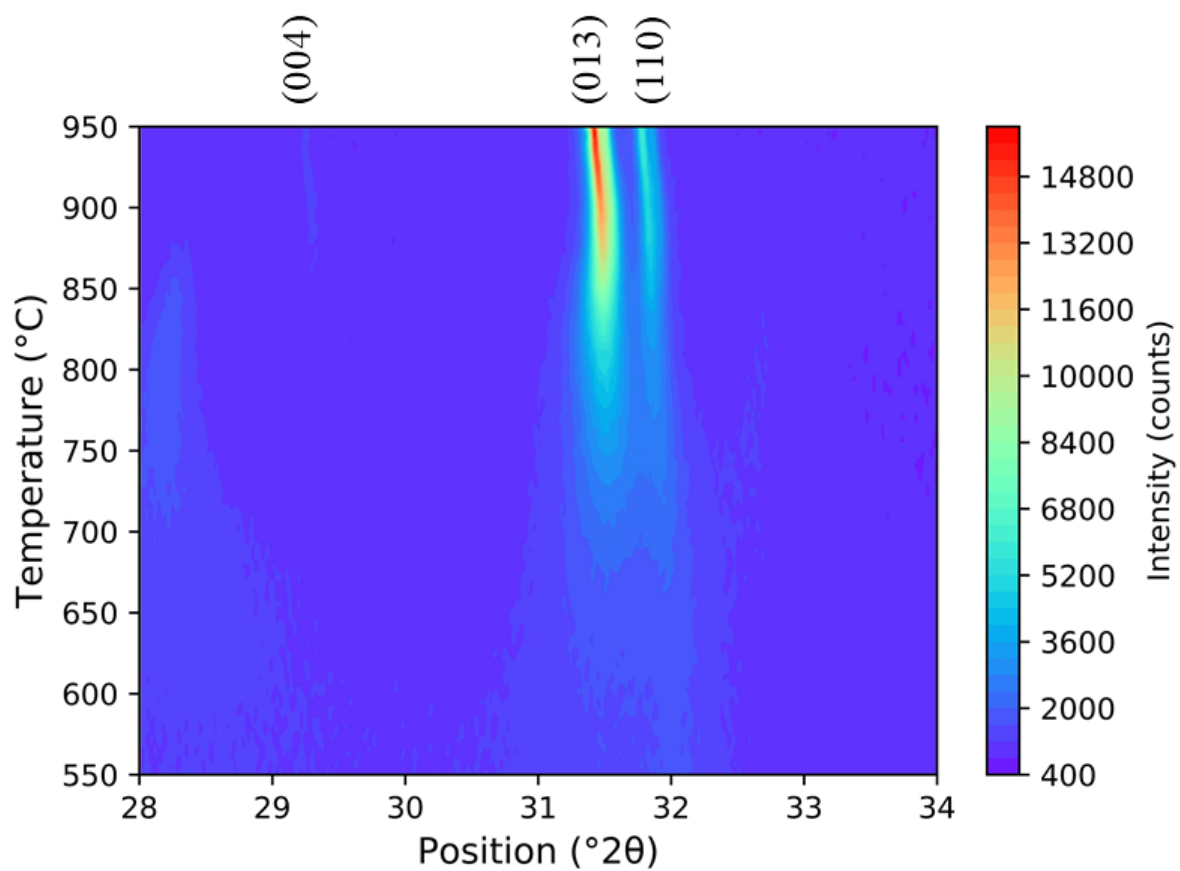


Figure 3-46 In-situ HTXRD of $(\text{La}_{0.2}\text{Nd}_{0.2}\text{Gd}_{0.2}\text{Tb}_{0.2}\text{Dy}_{0.2})_2\text{CuO}_4$ showing peak evolution of homogeneous PSE reactants upon heating.

Two-dimensional and three-dimensional phase boundary-controlled reactions are denoted by $R2$ and $R3$, respectively, while diffusion-controlled behavior is given by $D2$ for two-dimensional and $D3$ for three-dimensional diffusion. The results in Figure 3-47 (b) show the experimental data to follow the behavior for JMAK or phase boundary-controlled reaction rather than diffusion-controlled mechanisms. This is not unexpected: wet chemistry methods such as sol-gel and PSE are expected to follow a random nucleation and growth model, and the sigmoidal shape of the α vs T plot indicates that crystallization occurs through a nucleation and growth mechanism. The lack of diffusion behavior also corroborates the homogeneity and high level of mixing that has been attributed to the PSE synthesis technique.

3.1. Resonant ultrasound spectroscopy results

Using the RUS set-up, the free-body resonances were measured for polycrystalline $(\text{Mg}_{0.2}\text{Ni}_{0.2}\text{Co}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2})\text{Al}_2\text{O}_4$ and MgAl_2O_4 , allowing the determination of the elastic shear and longitudinal moduli. Table 14 and Table 15 show the RUS output file and Table 16 lists the values of the elastic moduli. Literature values are also reported for individual aluminate spinels for comparison. The moduli determined for the hot pressed MgAl_2O_4 are in excellent agreement with those in literature. The moduli for $(\text{Mg}_{1/5}\text{Ni}_{1/5}\text{Co}_{1/5}\text{Cu}_{1/5}\text{Zn}_{1/5})\text{Al}_2\text{O}_4$ are lower than the values for those of individual spinels. In contrast, the Young's modulus for a disordered monoclinic rare-earth silicate $(\text{Y}_{1/4}\text{Ho}_{1/4}\text{Er}_{1/4}\text{Yb}_{1/4})_2\text{SiO}_5$ was found to exceed the value predicted by the rule of mixtures [68]. An expansive study performed on different entropic pyrochlore oxides, where a size disorder parameter was introduced and described as a useful predictor, the material system showed medium-entropy ceramics to outperform their high entropy counterparts in terms of Young's modulus and modulus to thermal conductivity ratio [69]. This is an intriguing result as it indicates that the mechanical properties of multicomponent materials are not straightforward to predict.

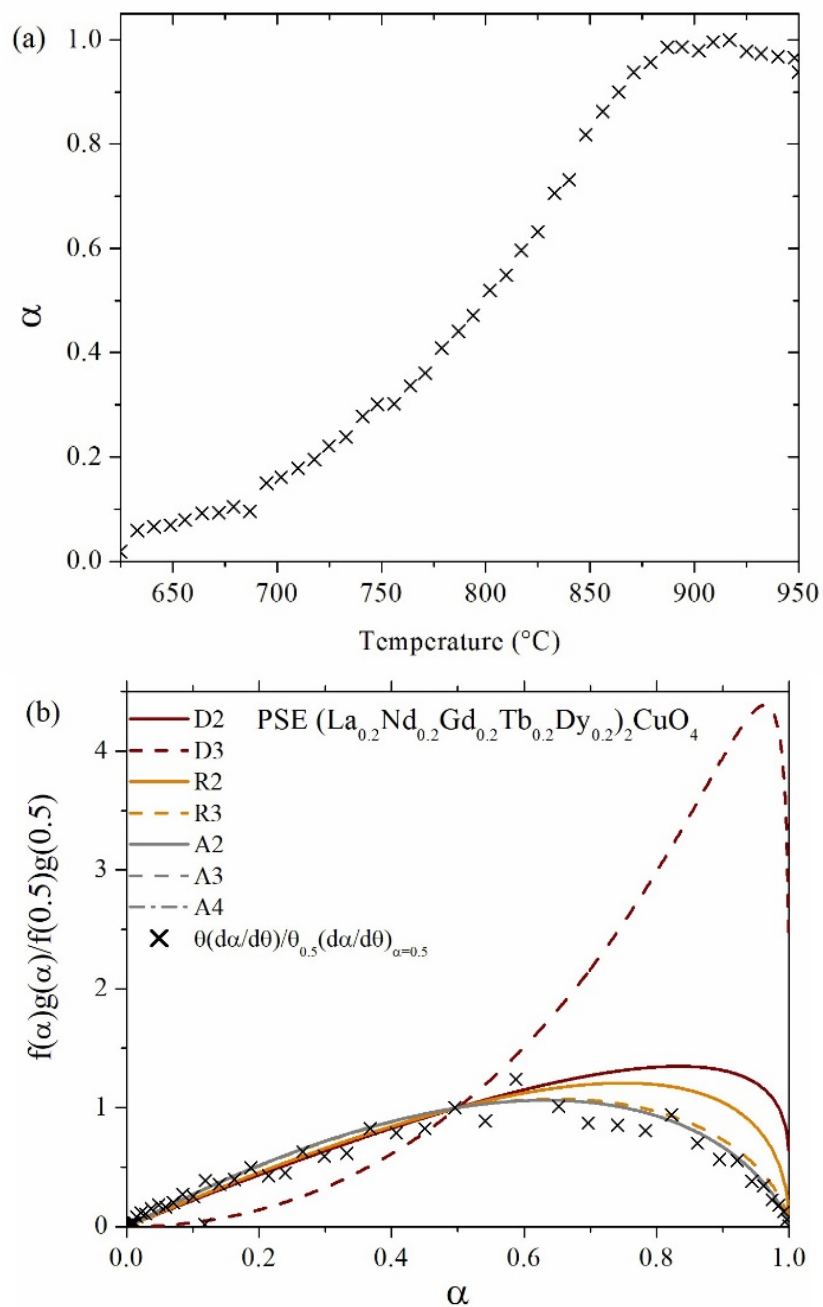


Figure 3-47 (a) Quantitative phase determination, α , as a function of temperature of homogeneous PSE reactants and (b) the subsequent calculation from experimental data given over masterplot.

Table 14 RUS fit results for $(\text{Mg}_{0.2}\text{Ni}_{0.2}\text{Co}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2})\text{Al}_2\text{O}_3$ hot pressed pellet.

resonance	f_{measured}	f_{fitted}	%error	c11 dependence	c44 dependence
1	0.265534	0.264185	-0.51	0	1
2	0.291939	0.292812	0.3	0.24	0.76
3	0.329593	0.327375	-0.67	0.23	0.77
4	0.464095	0.464176	0.02	0.2	0.8
5	0.495586	0.496011	0.09	0.06	0.94
6	0.513997	0.514939	0.18	0.03	0.97
7	0.52734	0.527821	0.09	0.11	0.89
8	0.624956	0.622268	-0.43	0.01	0.99
9	0.643355	0.644335	0.15	0.28	0.72
10	0.678071	0.673385	-0.69	0.06	0.94
11	0.697086	0.696091	-0.14	0.23	0.77
12	0.702722	0.701327	-0.2	0.14	0.86
13	0.726866	0.724518	-0.32	0.14	0.86
14	0.728734	0.729917	0.16	0.05	0.95
15	0.734158	0.733459	-0.1	0.08	0.92
16	0.740877	0.741011	0.02	0.06	0.94
17	0.775673	0.780433	0.61	0.09	0.91
18	0.778328	0.780828	0.32	0.03	0.97
19	0.781542	0.784586	0.39	0.08	0.92
20	0.788478	0.786354	-0.27	0.18	0.82
21	0.801587	0.80206	0.06	0.13	0.87
22	0.830273	0.830546	0.03	0.19	0.81
23	0.854682	0.855357	0.08	0.07	0.93
24	0.885993	0.887539	0.17	0.03	0.97
25	0.923474	0.929234	0.62	0.16	0.84
rms error	0.3388%				
C11	240.6	GPa			
C44	79.6	GPa			
Bulk modulus	134.5	GPa			
Young's modulus	200	GPa			

Table 15 RUS fit results for MgAl₂O₄ hot pressed pellet.

resonance	f_{measured}	f_{fitted}	%error	c11 dependence	c44 dependence
1	0.135855	0.135542	-0.23	0.05	0.95
2	0.136664	0.135542	-0.82	0.05	0.95
3	0.210564	0.210167	-0.19	0.57	0.43
4	0.268987	0.27018	0.44	0.06	0.94
5	0.270417	0.27018	-0.09	0.06	0.94
6	0.309189	0.308351	-0.27	0.01	0.99
7	0.309887	0.308351	-0.5	0.01	0.99
8	0.355295	0.355622	0.09	0.18	0.82
9	0.355877	0.355622	-0.07	0.18	0.82
10	0.387813	0.387501	-0.08	0.39	0.61
11	0.387813	0.387501	-0.08	0.39	0.61
12	0.40893	0.41138	0.6	0.06	0.94
13	0.40981	0.411382	0.38	0.06	0.94
14	0.436253	0.435625	-0.14	0.64	0.36
15	0.474203	0.47281	-0.29	0.02	0.98
16	0.47484	0.47281	-0.43	0.02	0.98
17	0.54698	0.549852	0.53	0.19	0.81
18	0.549483	0.549852	0.07	0.19	0.81
19	0.551112	0.554155	0.55	0.05	0.95
20	0.551112	0.554155	0.55	0.05	0.95
21	0.557625	0.558614	0.18	0.3	0.7
22	0.558489	0.558621	0.02	0.3	0.7
23	0.602677	0.603255	0.1	0.32	0.68
24	0.616904	0.61474	-0.35	0.04	0.96
rms error	0.3630%				
C11	316.4	GPa			
C44	101.5	GPa			
Bulk modulus	180.9	GPa			
Young's modulus	257	GPa			

Table 16 Summary of elastic properties from RUS fit results for the hot-pressed samples along with those of traditional spinel compositions from literature. All values are reported in units of GPa.

Composition	Longitudinal Modulus	Shear Modulus	Bulk Modulus	Young's Modulus	Ref.
MgAl₂O₄	316	102	181	257	This work
(Mg_{1/5}Ni_{1/5}Co_{1/5}Cu_{1/5}Zn_{1/5})Al₂O₄	241	80	135	200	This work
MgAl₂O₄ Resonance method on hot pressed polycrystal	305	104	166	258	[70]
NiAl₂O₄ Monte-Carlo estimate at 1000K					
Normal ordering	-	-	165	-	[71]
Inverse ordering	-	-	180	-	
CoAl₂O₄					
Vienna ab initio Simulation Package	-	-	197	-	[72]
Resonant sphere technique on polycrystals	-	-	-	283	[73]
CuAl₂O₄ statistical-learning-based prediction with density functional theory	242	64	157	169	[74], [75]
ZnAl₂O₄					
Vienna ab initio Simulation Package	272	100	189	254	[76]
Cambridge Serial Total Energy Package	270	104	184	263	[76]
Ultrasonic measurement	290	146	202	353	[77]
First principles calculation	316	148	218	362	[78]

CHAPTER FOUR

CONCLUDING REMARKS

We report a systematic study of several multi-component oxide materials, contributing to a better understanding of the effects of composition and synthesis on the material's homogeneity, phase formation, and physical properties. The sections below summarize the findings.

4.1. HEO Material Synthesis

Several methods for the successful synthesis of a variety of HEO compositions across multiple crystallographic systems were developed. While an iterative process of grinding, repressing, and firing samples synthesized using solid state reaction routinely leads to a single phase sample, the polymeric steric entrapment method proved to be especially advantageous when considering compositionally complex materials. It achieves a single phase on the first heat treatment, which shows efficiency from a time, energy, and cost perspective, and results in samples with superior homogeneity. Despite cation compatibility, some compositions could not be synthesized as a single phase material. This inability could be due to factors such as site occupancy preferences, local distortions, and other entropy effects.

4.2. Magnetism in multicomponent spinels

A family of new HEO materials are synthesized, and bulk structural and magnetic properties are reported, showing low temperature antiferromagnetic ordering in some ferritic and in all chromium based spinels and high temperature ferrimagnetic transition in ferritic HEO spinels. Blocking temperatures are found for $(\text{Mg}_{0.2}\text{Fe}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2})\text{Cr}_2\text{O}_4$, $(\text{Mg}_{0.2}\text{Mn}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2})\text{Cr}_2\text{O}_4$ and $(\text{Mg}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2})\text{Cr}_2\text{O}_4$. While the exact mechanism for the observed magnetic behavior is not yet understood, a few theories with supporting literature are explored. Field cooled and field warmed hysteresis behavior is seen in $(\text{Mg}_{0.2}\text{Mn}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2})\text{Fe}_2\text{O}_4$, $(\text{Mg}_{0.2}\text{Fe}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2})\text{Fe}_2\text{O}_4$ and $(\text{Cr}_{0.2}\text{Mn}_{0.2}\text{Fe}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2})_3\text{O}_4$. X-Ray Absorption measurements showed valence trends with temperature for $(\text{Cr}_{0.2}\text{Mn}_{0.2}\text{Fe}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2})_3\text{O}_4$, $(\text{Mg}_{0.2}\text{Mn}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2})\text{Fe}_2\text{O}_4$ as well as the presence of Cr^{4+} in $(\text{Mg}_{0.2}\text{Fe}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2})\text{Cr}_2\text{O}_4$, along with indications of some degree of low temperature antiferromagnetic ordering in all three compositions. While the multitude of magnetic species leads to a complex magnetic structure that is difficult to solve, entropic systems offer an avenue for tuning of magnetic properties. But prior to tailoring this new HEO material class for functional applications, further studies of the local structure are needed to develop a fundamental understanding.

4.3. In-situ HTXRD techniques and kinetic studies

In-situ HTXRD data collection and analysis is utilized for real-time characterization of the crystalline evolution and high temperature stability in high entropy oxide systems. Using non-isothermal data collection, $(\text{Co}_{0.2}\text{Cr}_{0.2}\text{Fe}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.2})_3\text{O}_4$, $(\text{Mg}_{0.2}\text{Ni}_{0.2}\text{Co}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2})\text{Al}_2\text{O}_4$, and $(\text{La}_{0.2}\text{Nd}_{0.2}\text{Gd}_{0.2}\text{Tb}_{0.2}\text{Dy}_{0.2})_2\text{CuO}_4$ are studied with the aim of determining the kinetic mechanisms exhibited in spinel phase formation. Results suggest that the SSS $(\text{Co}_{0.2}\text{Cr}_{0.2}\text{Fe}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.2})_3\text{O}_4$, PSE $(\text{Mg}_{0.2}\text{Ni}_{0.2}\text{Co}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2})\text{Al}_2\text{O}_4$, and PSE $(\text{La}_{0.2}\text{Nd}_{0.2}\text{Gd}_{0.2}\text{Tb}_{0.2}\text{Dy}_{0.2})_2\text{CuO}_4$ were not

diffusion controlled and instead followed a JMAK or geometric contraction type kinetic mechanism while SSS $((\text{Mg}_{0.2}\text{Ni}_{0.2}\text{Co}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2})\text{Al}_2\text{O}_4)$ showed evidence of initial diffusion type behavior that transitioned to JMAK or geometric contraction mechanisms as the crystallization progressed. The benefits of in-situ HTXRD techniques in revealing crystallographic information that can be tied to other thermal measurements along with difficulties in obtaining ideal experimental data sets were discussed. This technique provided an avenue for comparison between compositions and synthesis method. While additional experiments are required to fully understand phase formations in the materials described here, this work expands techniques used on traditional materials to high entropy systems and describes the theory behind the kinetics.

In-situ HTXRD experiments offer valuable insight in the formation of both high entropy and traditional materials. In-situ HTXRD data collected while heating allow for direct comparison between synthesis techniques concerning the phase evolution and formation temperatures. These results provide details for discerning differences and advantages of the synthesis methods and allowing the experimentalist to choose the optimum method. In addition, data analysis methods such as Rietveld refinement can allow information such as lattice parameter and crystallite size trends to be determined. This gives further understanding to what is contributing to the character of the peak and further identify differences that result from the synthesis method.

When used in conjunction with complementary thermal measurement techniques, in-situ HTXRD offers the ability to link features observed in the thermal data to crystallographic changes occurring within the material. This ability to capture data providing the formation of phase(s) in-situ can uncover unexpected information, including intermediate and/or metastable phases. In measurements taken on the solid-state synthesized $(\text{Co}_{0.2}\text{Cr}_{0.2}\text{Fe}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.2})_3\text{O}_4$ shown in Figure 3-41, there is an unidentified reflection that forms in the 500-800 °C temperature range around $33^\circ 2\theta$.

Several difficulties were encountered when applying the data collection and analysis technique described above to determine the formation kinetics of the two multi-component spinel systems:

- The disordered nature of high entropy materials results in peak-broadening and an increase of the background, which complicates the analysis where peak area and intensity are important factors.
- The phase transformations studied here occurred rapidly making it difficult to collect isothermal data for determination of the rate constant, reaction mechanism, and activation energy. Ideally, several isothermal data sets need to be collected for determining this information, but for the compositions synthesized with the PSE technique 100% conversion was achieved prior to reaching the isothermal dwell temperature.

4.4.Elastic properties of HEO spinel

The moduli of the synthesized MgAl_2O_4 are in good agreement with literature values while Young's modulus of $(\text{Mg}_{1/5}\text{Ni}_{1/5}\text{Co}_{1/5}\text{Cu}_{1/5}\text{Zn}_{1/5})\text{Al}_2\text{O}_4$ at 195 GPa is lower than those of the individual spinels in literature. This emphasizes the complex effects of disorder on material properties, especially in structures with the possibility of cation multi-site occupancy and structural inversion. This study shows the merit for future investigation into the effects of composition variation on the structure and subsequent properties for the development of new high strength ceramic materials.

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APPENDIX

Table 17 Summary of High Entropy Oxide compounds synthesized in literature, their crystal structure, synthesis method, their investigated properties/application and reference. ‘ES’ indicates that the study showed the composition to be entropy stabilized.

Crystal Structure	Compound(s)	Synthesis	Investigated Property or Application	Ref.
Rock salt (Fm-3m)	$(\text{Co}_{0.25}\text{Mg}_{0.25}\text{Ni}_{0.25}\text{Zn}_{0.25})\text{O}$ $(\text{Co}_{0.2}\text{Cu}_{0.2}\text{Mg}_{0.2}\text{Ni}_{0.2}\text{Zn}_{0.2})\text{O}$	nebulized spray pyrolysis, flame spray pyrolysis, reverse co- precipitation	Synthesis method for phase stability	[79]
Rock salt (Fm-3m)	$(\text{Mg}_{0.25(1-x)}\text{Co}_x\text{Cu}_{0.25(1-x)}\text{Ni}_{0.25(1-x)}\text{Zn}_{0.25(1-x)})\text{O}$ $x=0.2, 0.27, 0.33$	Pulsed Laser Deposition	Exchange bias	[80]
Rock salt (Fm-3m)	$(\text{Mg}_{0.2}\text{Co}_{0.2}\text{Cu}_{0.2}\text{Ni}_{0.2}\text{Zn}_{0.2})\text{O}$, ES	Solid state reaction	Entropy Stabilization Local Structure	[8] [54]
Rock salt (Fm-3m)	$(\text{Mg}_{0.2}\text{Co}_{0.2}\text{Cu}_{0.2}\text{Ni}_{0.2}\text{Zn}_{0.2})_{1-x}\text{Li}_x\text{O}$ $(\text{Mg}_{0.2}\text{Co}_{0.2}\text{Cu}_{0.2}\text{Ni}_{0.2}\text{Zn}_{0.2})_{1-2x}(\text{LiGa})_x\text{O}$ $(\text{Mg}_{0.2}\text{Co}_{0.2}\text{Cu}_{0.2}\text{Ni}_{0.2}\text{Zn}_{0.2})_{0.8}(\text{LiGa})_{0.2}\text{O}$	Solid state reaction	Dielectric properties	[28]
	$(\text{Mg}_{0.2}\text{Co}_{0.2}\text{Cu}_{0.2}\text{Ni}_{0.2}\text{Zn}_{0.2})_{1-x}\text{Li}_x\text{O}$			[81]
	$(\text{Mg}_{0.2}\text{Co}_{0.2}\text{Cu}_{0.2}\text{Ni}_{0.2}\text{Zn}_{0.2})_{1-x}\text{Na}_x\text{O}$ $(\text{Mg}_{0.2}\text{Co}_{0.2}\text{Cu}_{0.2}\text{Ni}_{0.2}\text{Zn}_{0.2})_{0.95}\text{K}_{0.5}\text{O}$			
Rocksalt (Fm-3m)	$(\text{Mg}_{0.2}\text{Co}_{0.2}\text{Cu}_{0.2}\text{Ni}_{0.2}\text{Zn}_{0.2})\text{O}$ $(\text{Mg}_{0.25}\text{Co}_{0.25}\text{Cu}_{0.25}\text{Ni}_{0.25})\text{O}$ $(\text{Mg}_{0.25}\text{Co}_{0.25}\text{Ni}_{0.25}\text{Zn}_{0.25})\text{O}$ $(\text{Mg}_{0.25}\text{Cu}_{0.25}\text{Ni}_{0.25}\text{Zn}_{0.25})\text{O}$	Nebulized Spray Pyrolysis	Reversible Energy Storage	[82]
Rocksalt (Fm-3m)	$(\text{Mg}_{0.2}\text{Co}_{0.2}\text{Cu}_{0.2}\text{Ni}_{0.2}\text{Zn}_{0.2})\text{O}$ PtMgCoCuNiZnO (0.3wt%Pt)	Physical Mixture and Co- precipitation	Catalysts with high- temperature stabilities	[83]
Rocksalt (Fm-3m)	$(\text{MgCoNiZn})_{1-x}\text{Cu}_x\text{O}$ $(x=0.13, 0.2, 0.26)$	N/A DFT studies	first-principles study	[84]
Rocksalt (Fm-3m)	$(\text{Mg}_{0.2}\text{Co}_{0.2}\text{Cu}_{0.2}\text{Ni}_{0.2}\text{Zn}_{0.2})\text{O}$	co-precipitation and hydrothermal synthesis	Density	[85]
Rocksalt (Fm-3m)	$(\text{Mg}_{0.2}\text{Co}_{0.2}\text{Cu}_{0.2}\text{Ni}_{0.2}\text{Zn}_{0.2})\text{O}$ $(\text{Mg}_x\text{Co}_x\text{Cu}_x\text{Ni}_x\text{Zn}_x\text{Sc}_x)\text{O}$, $x\sim 0.167$ $(\text{Mg}_x\text{Co}_x\text{Cu}_x\text{Ni}_x\text{Zn}_x\text{Li}_x)\text{O}$, $x\sim 0.167$	Solid state reaction, Pulsed Laser Deposition, DFT studies	DFT studies of lattice stability	[86]
Rocksalt (Fm-3m)	$(\text{Mg}_{0.2}\text{Co}_{0.2}\text{Cu}_{0.2}\text{Ni}_{0.2}\text{Zn}_{0.2})\text{O}$	Solid state reaction	Diffraction study of Jahn-Teller Distortion	[55]

Table 17 continued

Crystal Structure	Compound(s)	Synthesis	Investigated Property or Application	Ref.
Rocksalt (Fm-3m)	$(\text{Mg}_x\text{Co}_x\text{Cu}_x\text{Ni}_x\text{Zn}_x\text{Sc}_x)\text{O}$, $x \sim 0.167$	Pulsed Laser Deposition	Different growth conditions to modulate particle kinetic energy and plume reactivity	[87]
Rocksalt (Fm-3m)	$\text{Mg}_x\text{Ni}_x\text{Cu}_x\text{Co}_x\text{Zn}_x\text{O}$, $x = 0.2$ $\text{Mg}_x\text{Ni}_x\text{Cu}_x\text{Co}_x\text{Zn}_x\text{Sc}_x\text{O}$, $x = 0.167$ $\text{Mg}_x\text{Ni}_x\text{Cu}_x\text{Co}_x\text{Zn}_x\text{Sb}_x\text{O}$, $x = 0.167$ $\text{Mg}_x\text{Ni}_x\text{Cu}_x\text{Co}_x\text{Zn}_x\text{Sn}_x\text{O}$, $x = 0.167$ $\text{Mg}_x\text{Ni}_x\text{Cu}_x\text{Co}_x\text{Zn}_x\text{Cr}_x\text{O}$, $x = 0.167$ $\text{Mg}_x\text{Ni}_x\text{Cu}_x\text{Co}_x\text{Zn}_x\text{Ge}_x\text{O}$, $x = 0.167$	Pulsed Laser Deposition	Charge Induced Disorder controlled Thermal Conductivity	[88]
Rocksalt (Fm-3m)	$(\text{Mg}_{0.2}\text{Co}_{0.2}\text{Cu}_{0.2}\text{Ni}_{0.2}\text{Zn}_{0.2})\text{O}$	Solid state reaction	Reaction Sequence and Mechanical Properties	[89]
Rocksalt (Fm-3m)	$(\text{Co}_{0.2}\text{Cu}_{0.2}\text{Mg}_{0.2}\text{Ni}_{0.2}\text{Zn}_{0.2})\text{O}$ electrode material in full-cells with a $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathode	Nebulized Spray Pyrolysis	Lithium-ion battery applications	[90]
Rocksalt (Fm-3m)	$(\text{Mg}_{0.2}\text{Co}_{0.2}\text{Cu}_{0.2}\text{Ni}_{0.2}\text{Zn}_{0.2})\text{O}$	Solid state reaction	anode material for lithium ion batteries	[91]
Rocksalt (Fm-3m)	$(\text{Mg}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2})\text{O}$ $(\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Li}_{0.1}\text{Ga}_{0.1})\text{O}$ $(\text{Mg}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2}\text{Li}_{0.1}\text{Ga}_{0.1})\text{O}$ $(\text{Mg}_{0.19}\text{Co}_{0.19}\text{Ni}_{0.19}\text{Cu}_{0.19}\text{Zn}_{0.19}\text{Li}_{0.05})\text{O}$ $(\text{Mg}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Li}_{0.1}\text{Ga}_{0.1})\text{O}$ $(\text{Mg}_{0.2}\text{Co}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Li}_{0.1}\text{Ga}_{0.1})\text{O}$ $(\text{Mg}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Zn}_{0.2}\text{Li}_{0.1}\text{Ga}_{0.1})\text{O}$ $(\text{Mg}_{0.16}\text{Co}_{0.16}\text{Ni}_{0.16}\text{Cu}_{0.16}\text{Zn}_{0.16}\text{Li}_{0.10}\text{Fe}_{0.10})\text{O}$	Solid state reaction	Influence of Substitution on Magnetic Properties	[92]
Rocksalt (Fm-3m)	$(\text{Mg}_{0.2}\text{Co}_{0.2}\text{Cu}_{0.2}\text{Ni}_{0.2}\text{Zn}_{0.2})\text{O}$	Solid state reaction	Neutron Diffraction, Magnetic Structure and Properties	[93]
Rocksalt: Fm-3m Fluorite: Fm-3m Perovskite: Pbmnn	$(\text{Co}_{0.2}\text{Cu}_{0.2}\text{Mg}_{0.2}\text{Ni}_{0.2}\text{Zn}_{0.2})\text{O}$, $(\text{Ce}_{0.2}\text{La}_{0.2}\text{Pr}_{0.2}\text{Sm}_{0.2}\text{Y}_{0.2})\text{O}_{2-8}$, $(\text{Gd}_{0.2}\text{La}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Y}_{0.2})(\text{Co}_{0.2}\text{Cr}_{0.2}\text{Mn}_{0.2}\text{Fe}_{0.2}\text{Ni}_{0.2})\text{O}_3$	Nebulized Spray Pyrolysis	Homogeneity at the atomic scale	[94]
Rocksalt (Fm-3m)	$(\text{Al}_{0.31}\text{Cr}_{0.20}\text{Fe}_{0.14}\text{Ni}_{0.35})\text{O}$	radio frequency (RF) reactive magnetron sputtering	Effects of helium implantation on mechanical properties	[95]
Rocksalt (Fm-3m)	$(\text{MgCoNiCuZn})_{1-x}\text{Li}_x\text{O}$ ($x=0$ to 0.3)	Solid state reaction	charge compensation mechanisms	[96]
Rocksalt (Fm-3m)	$(\text{Li}_x(\text{Co}_{0.2}\text{Cu}_{0.2}\text{Mg}_{0.2}\text{Ni}_{0.2}\text{Zn}_{0.2})\text{OF}_x)$ $\text{Na}_y(\text{Co}_{0.2}\text{Cu}_{0.2}\text{Mg}_{0.2}\text{Ni}_{0.2}\text{Zn}_{0.2})\text{OCl}_y$	Solid state reaction	Energy storage: enhanced Li storage properties	[97]

Table 17 continued

Crystal Structure	Compound(s)	Synthesis	Investigated Property or Application	Ref.
Rocksalt (Fm-3m)	(NiMgCuZnCo)O 2 and 5 wt % Pt/Ru- (NiMgCuZnCo)O	Mechano-chemical synthesis	High temperature stability and catalytic ability	[98]
Rocksalt (Fm-3m)	Li/Mn doped (Mg _{0.2} Co _{0.2} Cu _{0.2} Ni _{0.2} Zn _{0.2})O	Solid state reaction	Thermal and compressive stability at high temperatures	[99]
Rocksalt (Fm-3m)	(Mg _{0.2} Co _{0.2} Cu _{0.2} Ni _{0.2} Zn _{0.2})O, ES	Solid state reaction with Conventional Sintering and Spark Plasma Sintering	Study of the effect of grain size on controlling the volume fractions of a secondary phase and entropic single-phase	[19]
spinel-rocksalt two-phase oxide system	(FeMgCoNi)O _x	Solid state reaction	Thermochemical water splitting at low temperatures	[100]
mesoporous structure and single rock salt phase	(CuNiFeCoMg)O _x -Al ₂ O ₃	Mechanochemical nonhydrolytic sol-gel method	mesoporous high-entropy metal oxide synthesis and superior SO ₂ -resisting performance in the catalytic oxidation of CO	[101]
Rocksalt (Fm-3m)	(Mg _{0.2} Co _{0.2} Cu _{0.2} Ni _{0.2} Zn _{0.2})O	mechanochemical synthesis	Microstructure and electrical conductivity with temperature	[102]
Rocksalt (Fm-3m)	(Mg _{0.2} Co _{0.2} Ni _{0.2} Cu _{0.2} Zn _{0.2})O	Solid state reaction and laser molecular beam epitaxy	Tunable pseudocapacitive contribution to achieve superior lithium-storage properties	[103]
Rocksalt (Fm-3m)	Mg _{0.25(1-x)} Co _{0.25(1-x)} Ni _{0.25(1-x)} Cu _x Zn _{0.25(1-x)} O (x=0.11,0.17,0.20,0.24,0.27) (Mg _{0.25(1-x)} Co _x Ni _{0.25(1-x)} Cu _{0.25(1-x)} Zn _{0.25(1-x)})O (x=0.20,0.27,0.33)	epitaxial films	Magnetic frustration control through tunable stereochemically driven disorder	[104]
Rocksalt (Fm-3m)	(Mg _{0.2} Co _{0.2} Ni _{0.2} Cu _{0.2} Zn _{0.2})O	Comparison of experimental values from [88] with molecular dynamics values and Bridgman equation	Influence of mass and charge disorder on the phonon thermal conductivity of entropy stabilized oxides determined by molecular dynamics simulations	[105]

Table 17 continued

Crystal Structure	Compound(s)	Synthesis	Investigated Property or Application	Ref.
Orthorhombic Perovskite (Pbnm)	$(\text{Gd}_{0.2}\text{La}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Y}_{0.2})\text{MnO}_3$, ES $(\text{Gd}_{0.2}\text{La}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Y}_{0.2})\text{FeO}_3$ $(\text{Gd}_{0.2}\text{La}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Y}_{0.2})\text{CrO}_3$ $(\text{Gd}_{0.2}\text{La}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Y}_{0.2})\text{CoO}_3$ $\text{Y}(\text{Co}_{0.2}\text{Cr}_{0.2}\text{Fe}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.2})\text{O}_3$ $\text{Sm}(\text{Co}_{0.2}\text{Cr}_{0.2}\text{Fe}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.2})\text{O}_3$ $\text{Nd}(\text{Co}_{0.2}\text{Cr}_{0.2}\text{Fe}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.2})\text{O}_3$ $\text{La}(\text{Co}_{0.2}\text{Cr}_{0.2}\text{Fe}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.2})\text{O}_3$ $\text{Gd}(\text{Co}_{0.2}\text{Cr}_{0.2}\text{Fe}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.2})\text{O}_3$ $(\text{Gd}_{0.2}\text{La}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Y}_{0.2})$ $(\text{Co}_{0.2}\text{Cr}_{0.2}\text{Fe}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.2})\text{O}_3$	Nebulized Spray Pyrolysis	Synthesis, phase stability with HTXRD	[20]
Orthorhombic Perovskite (Pbnm)	$\text{Gd}(\text{Co}_{0.2}\text{Cr}_{0.2}\text{Fe}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.2})\text{O}_3$, $\text{La}(\text{Co}_{0.2}\text{Cr}_{0.2}\text{Fe}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.2})\text{O}_3$, $\text{Nd}(\text{Co}_{0.2}\text{Cr}_{0.2}\text{Fe}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.2})\text{O}_3$, $\text{Sm}(\text{Co}_{0.2}\text{Cr}_{0.2}\text{Fe}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.2})\text{O}_3$, $\text{Y}(\text{Co}_{0.2}\text{Cr}_{0.2}\text{Fe}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.2})\text{O}_3$. $(\text{Gd}_{0.2}\text{La}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Y}_{0.2})$ $(\text{Co}_{0.2}\text{Cr}_{0.2}\text{Fe}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.2})\text{O}_3$	Nebulized Spray Pyrolysis	Magnetic and Mössbauer Characterization	[106]
Orthorhombic Perovskite (Pbnm)	$\text{La}(\text{Cr}_{0.2}\text{Mn}_{0.2}\text{Fe}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2})\text{O}_3$	solid-state synthesis and pulsed laser epitaxy	Strain mismatch, microstructure, atomic resolution and magnetic properties showing anisotropy	[107]
Perovskite Cubic (Pm-3m)	$\text{Sr}(\text{Zr}_{0.2}\text{Sn}_{0.2}\text{Ti}_{0.2}\text{Hf}_{0.2}\text{Mn}_{0.2})\text{O}_3$ $\text{Sr}(\text{Zr}_{0.2}\text{Sn}_{0.2}\text{Ti}_{0.2}\text{Hf}_{0.2}\text{Nb}_{0.2})\text{O}_3$ $\text{Ba}(\text{Zr}_{0.2}\text{Sn}_{0.2}\text{Ti}_{0.2}\text{Hf}_{0.2}\text{Ce}_{0.2})\text{O}_3$ $\text{Ba}(\text{Zr}_{0.2}\text{Sn}_{0.2}\text{Ti}_{0.2}\text{Hf}_{0.2}\text{Y}_{0.2})\text{O}_{3-x}$ $\text{Ba}(\text{Zr}_{0.2}\text{Sn}_{0.2}\text{Ti}_{0.2}\text{Hf}_{0.2}\text{Nb}_{0.2})\text{O}_3$ $(\text{Sr}_{0.5}\text{Ba}_{0.5})(\text{Zr}_{0.2}\text{Sn}_{0.2}\text{Ti}_{0.2}\text{Hf}_{0.2}\text{Nb}_{0.2})\text{O}_3$	Solid state reaction	Phase formation and stability	[25]
Perovskite Cubic (Pm-3m)	$\text{Ba}(\text{Zr}_{0.2}\text{Sn}_{0.2}\text{Ti}_{0.2}\text{Hf}_{0.2}\text{Nb}_{0.2})\text{O}_3$	Pulsed Laser Deposition	Thermal Conductivity	[108]
Perovskite Cubic (Pm-3m)	$\text{Sr}((\text{Zr}_{0.94}\text{Y}_{0.06})_{0.2}\text{Sn}_{0.2}\text{Ti}_{0.2}\text{Hf}_{0.2}\text{Mn}_{0.2})\text{O}_{3-x}$	Spark Plasma Sintering	Density	[109]
Perovskite Cubic (Pm-3m)	$\text{Ba}_{0.5}\text{Sr}_{0.5}(\text{Zr}_{0.4}\text{Hf}_{0.3}\text{Ti}_{0.3})\text{O}_3$ $\text{Ba}_{0.4}\text{Sr}_{0.4}\text{Bi}_{0.2}(\text{Zr}_{0.3}\text{Hf}_{0.3}\text{Ti}_{0.2}\text{Fe}_{0.2})\text{O}_3$ $\text{Ru}_{0.13}/\text{Ba}_{0.3}\text{Sr}_{0.3}\text{Bi}_{0.4}(\text{Zr}_{0.2}\text{Hf}_{0.2}\text{Ti}_{0.2}\text{Fe}_{0.27})\text{O}_3$	Sonochemical-Based Method	nanoparticle with good catalytic activity for CO	[110]

Table 17 continued

Crystal Structure	Compound(s)	Synthesis	Investigated Property or Application	Ref.
Orthorhombic Perovskite (Pbnm)	$(\text{La}_{0.2}\text{Pr}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2})\text{NiO}_3$	Pulsed Laser Deposition	Valence state, temperature dependent electrical transport measurements	[111]
Perovskite Cubic (Pm-3m)	$\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.2}\text{Sn}_{0.2}\text{Hf}_{0.2}\text{Me}_{0.2})\text{O}_3$ (Me=Y ³⁺ , Nb ⁵⁺ , Ta ⁵⁺ , V ⁵⁺ , Mo ⁶⁺ , W ⁶⁺)	Solid state reaction	Microstructure and dielectric properties	[112]
Perovskite Cubic (Pm-3m)	$(\text{Na}_{0.2}\text{Bi}_{0.2}\text{Ba}_{0.2}\text{Sr}_{0.2}\text{Ca}_{0.2})\text{TiO}_3$	Solid state reaction	Dielectric properties and electrocaloric effect	[113]
Cubic-Bixbyite	$(\text{Gd}_{0.4}\text{Tb}_{0.4}\text{Dy}_{0.4}\text{Ho}_{0.4}\text{Er}_{0.4})\text{O}_3$	polymeric steric entrapment	Synthesis and high temperature phase stability	[114]
Fluorite (Fm-3m)	$(\text{Hf}_{0.25}\text{Zr}_{0.25}\text{Ce}_{0.25})(\text{Y}_{0.25})\text{O}_{2-x}$ $(\text{Hf}_{0.25}\text{Zr}_{0.25}\text{Ce}_{0.25})(\text{Y}_{0.125}\text{Yb}_{0.125})\text{O}_2$ $(\text{Hf}_{0.25}\text{Zr}_{0.25}\text{Ce}_{0.25})(\text{Y}_{0.2}\text{Yb}_{0.2})\text{O}_{2-x}$ $(\text{Hf}_{0.25}\text{Zr}_{0.25}\text{Ce}_{0.25})(\text{Y}_{0.125}\text{Ca}_{0.125})\text{O}_{2-x}$ $(\text{Hf}_{0.25}\text{Zr}_{0.25}\text{Ce}_{0.25})(\text{Y}_{0.125}\text{Gd}_{0.125})\text{O}_2$ $(\text{Hf}_{0.2}\text{Zr}_{0.2}\text{Ce}_{0.2})(\text{Y}_{0.2}\text{Gd}_{0.2})\text{O}_{2-x}$ $(\text{Hf}_{0.25}\text{Zr}_{0.25}\text{Ce}_{0.25})(\text{Yb}_{0.125}\text{Gd}_{0.125})\text{O}_{2-x}$ $(\text{Hf}_{0.2}\text{Zr}_{0.2}\text{Ce}_{0.2})(\text{Yb}_{0.2}\text{Gd}_{0.2})\text{O}_{2-x}$	Ball mill, spark plasma sintering, annealing	lower thermal conductivities	[115]
Fluorite (Fm-3m)	$(\text{Ce}, \text{Gd}, \text{La}, \text{Nd}, \text{Pr}, \text{Sm}, \text{Y})\text{O}_{2-\delta}$ $(\text{Ce}, \text{La}, \text{Nd}, \text{Pr}, \text{Sm}, \text{Y})\text{O}_{2-\delta}$ $(\text{Ce}, \text{La}, \text{Pr}, \text{Sm}, \text{Y})\text{O}_{2-\delta}$ $(\text{Ce}, \text{La}, \text{Pr}, \text{Y})\text{O}_{2-\delta}$ $(\text{Ce}, \text{La}, \text{Pr}, \text{Sm})\text{O}_{2-\delta}$ $(\text{Ce}, \text{La}, \text{Pr})\text{O}_{2-\delta}$ $(\text{Ce}, \text{Pr})\text{O}_{2-\delta}$	Nebulized spray pyrolysis (NSP)	optical properties	[30]
Bixbyite (Ia-3)	$(\text{Ce}, \text{Gd}, \text{La}, \text{Nd}, \text{Pr}, \text{Sm}, \text{Y})\text{O}_{2-\delta}$ $(\text{Ce}, \text{La}, \text{Nd}, \text{Pr}, \text{Sm}, \text{Y})\text{O}_{2-\delta}$ $(\text{Ce}, \text{La}, \text{Pr}, \text{Sm}, \text{Y})\text{O}_{2-\delta}$	Post NSP, Calcination		
Fluorite (Fm-3m)	$(\text{Ce}_{0.2}\text{Zr}_{0.2}\text{Hf}_{0.2}\text{Sn}_{0.2}\text{Ti}_{0.2})\text{O}_2$, ES	Solid state reaction	Thermal conductivity, entropy stabilization	[21]
Fluorite (Fm-3m)	$(\text{Sc}_{0.2}\text{Ce}_{0.2}\text{Pr}_{0.2}\text{Gd}_{0.2}\text{Ho}_{0.2})_2\text{O}_{3\pm\delta}$	precipitation	Synthesis, structure and surface morphology of HEO nanoparticles	[116]

Table 17 continued

Crystal Structure	Compound(s)	Synthesis	Investigated Property or Application	Ref.
Fluorite (Fm-3m)	$(\text{Gd}_{0.2}\text{La}_{0.2}\text{Y}_{0.2}\text{Hf}_{0.2}\text{Zr}_{0.2})\text{O}_2$ $(\text{Gd}_{0.2}\text{La}_{0.2}\text{Ce}_{0.2}\text{Hf}_{0.2}\text{Zr}_{0.2})\text{O}_2$	chemical co-precipitation followed by peptization in acidic medium under mild conditions	Confirmation of synthesis of single phase nanoparticles	[117]
Fluorite (Fm-3m)	$(\text{Ce}_{0.2}\text{La}_{0.2}\text{Pr}_{0.2}\text{Sm}_{0.2}\text{Y}_{0.2})\text{O}_{2-\delta}$	Nebulized Spray Pyrolysis	pressure-induced continuous tuning of lattice distortion (bond angles) and band gap, pressure induced amorphization and partial recovery upon decompression, forming glass–nanoceramic composite HEO	[118]
Fluorite (Fm-3m)	$(\text{La,Pr})\text{O}_{2-\delta}$ $(\text{La,Pr,Y})\text{O}_{2-\delta}$ $(\text{Ce,L a,Pr})\text{O}_{2-\delta}$ $(\text{Ce,Gd,L a,Pr})\text{O}_{2-\delta}$ $(\text{Ce,L a,Nd,Pr})\text{O}_{2-\delta}$ $(\text{Ce,L a,Pr,Sm})\text{O}_{2-\delta}$ $(\text{Ce,L a,Pr,Y})\text{O}_{2-\delta}$			
Bixbyite (Ia-3)	$(\text{Ce,Gd,L a})_2\text{O}_{3+\delta}$ $(\text{Ce,L a,Sm,Y})_2\text{O}_{3+\delta}$ $(\text{Ce,Gd,L a,Pr,Y})_2\text{O}_{3+\delta}$ $(\text{Ce,L a,Pr,Sm,Y})_2\text{O}_{3+\delta}$	Solid state reaction	Effect of composition, sintering temperature, sintering atmosphere and cooling rate on resulting crystal structure	[27]
Monoclinic (C2/m)	$(\text{Gd,L a,Sm})_2\text{O}_3$ $(\text{La,Nd,Y})_2\text{O}_3$ $(\text{Gd,L a,Nd,Sm})_2\text{O}_3$ $(\text{La,Nd,Sm,Y})_2\text{O}_3$ $(\text{Gd,L a,Sm,Y})_2\text{O}_3$ $(\text{Gd,L a,Nd,Sm,Y})_2\text{O}_3$ $(\text{Gd,L a,Pr,Y})_2\text{O}_3$ $(\text{La,Pr,Y})_2\text{O}_3$ $(\text{La,Gd,Nd,Pr,Sm,Y})_2\text{O}_3$			

Table 17 continued

Crystal Structure	Compound(s)	Synthesis	Investigated Property or Application	Ref.
Fluorite (Fm-3m)	$Zr_{0.852}Y_{0.148}O_{2-\delta}$	Solid state reaction	Phase stability, mechanical properties, and thermal conductivities showing increased cubic stability and reduced thermal conductivity while maintaining high modulus and hardness	[119]
	$Hf_{0.284}Zr_{0.284}Ce_{0.284}Y_{0.074}Yb_{0.074}O_{2-\delta}$			
	$Hf_{0.2}Zr_{0.2}Ce_{0.2}Y_{0.2}Yb_{0.2}O_{2-\delta}$			
	$Hf_{0.314}Zr_{0.314}Ce_{0.314}Y_{0.029}Ca_{0.029}O_{2-\delta}$			
	$Hf_{0.284}Zr_{0.284}Ce_{0.284}Y_{0.074}Ca_{0.074}O_{2-\delta}$			
	$Hf_{0.284}Zr_{0.284}Ce_{0.284}Y_{0.074}Gd_{0.074}O_{2-\delta}$			
Tetragonal	$Hf_{0.2}Zr_{0.2}Ce_{0.2}Y_{0.2}Gd_{0.2}O_{2-\delta}$	Solid state reaction	Synthesis Method	[29]
	$Hf_{0.314}Zr_{0.314}Ce_{0.314}Y_{0.029}Yb_{0.029}O_{2-\delta}$			
Spinel (Fd-3m)	$(Co_{0.2}Cr_{0.2}Fe_{0.2}Mn_{0.2}Ni_{0.2})_3O_4$	Solid state reaction	Lattice parameters, distortion. Magnetization versus Magnetic Field by powder size	[120]
Spinel (Fd-3m)	$(Co_{0.2}Cr_{0.2}Fe_{0.2}Mn_{0.2}Ni_{0.2})_3O_4$	Solution Combustion Synthesis	Magnetic properties	[121]
Spinel (Fd-3m)	$(Cr_{0.2}Fe_{0.2}Mn_{0.2}Ni_{0.2}Zn_{0.2})_3O_4$ $(Cr_{0.2}Fe_{0.2}Mn_{0.2}Co_{0.2}Zn_{0.2})_3O_4$ $(Cr_{0.2}Fe_{0.2}Mn_{0.2}Co_{0.2}Ni_{0.2})_3O_4$	glycine-nitrate solution combustion synthesis method	Magnetic properties as a function of temperature, charge state	[24]
Spinel (Fd-3m)	$(Mg_{0.2}Fe_{0.2}Co_{0.2}Ni_{0.2}Cu_{0.2})Fe_2O_4$ $(Mg_{0.2}Co_{0.2}Ni_{0.2}Cu_{0.2}Zn_{0.2})Fe_2O_4$ $(Mg_{0.2}Mn_{0.2}Co_{0.2}Ni_{0.2}Cu_{0.2})Fe_2O_4$ $(Mn_{0.2}Fe_{0.2}Co_{0.2}Ni_{0.2}Cu_{0.2})Fe_2O_4$ $(Cr_{0.2}Mn_{0.2}Fe_{0.2}Co_{0.2}Ni_{0.2})_3O_4$ $(Mg_{0.2}Co_{0.2}Ni_{0.2}Cu_{0.2}Zn_{0.2})Al_2O_4$ $(Mg_{0.2}Co_{0.2}Ni_{0.2}Cu_{0.2}Zn_{0.2})Cr_2O_4$ $(Mg_{0.2}Fe_{0.2}Co_{0.2}Ni_{0.2}Cu_{0.2})Cr_2O_4$ $(Mg_{0.2}Mn_{0.2}Co_{0.2}Ni_{0.2}Cu_{0.2})Cr_2O_4$	Solid state reaction	Seebeck coefficient and electrical conductivity as a function of temperature Phase contents depending on the composition and sintering temperature	[122]
Spinel (Fd-3m)	$(Co_{0.2}Cr_{0.2}Fe_{0.2}Mn_{0.2}Ni_{0.2})_3O_4$ $(Co_{0.2}Cr_{0.2}Fe_{0.2}Mg_{0.2}Mn_{0.2})_3O_4$ $(Cr_{0.2}Fe_{0.2}Mg_{0.2}Mn_{0.2}Ni_{0.2})_3O_4$	Solid state reaction	Low-temperature synthesis of small-sized nanoparticles for water oxidation	[123]
Spinel (Fd-3m)	$(Co_{0.2}Cu_{0.2}Fe_{0.2}Mn_{0.2}Ni_{0.2})_3O_4$	Solvothermal synthesis followed by annealing		

Table 17 continued

Crystal Structure	Compound(s)	Synthesis	Investigated Property or Application	Ref.
Spinel (Fd-3m)	$(\text{Zn}_{0.2}\text{Fe}_{0.2}\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cd}_{0.2})\text{Fe}_2\text{O}_4$	annealing of co-precipitated amorphous precursor	AC electrical conductivity and microwave absorption. Frequency and temperature dependence of dielectric permittivity and magnetic permeability.	[124]
Pyrochlore (Fd-3m)	$(\text{La}_{0.2}\text{Ce}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2})_2\text{Zr}_2\text{O}_7$	Coprecipitation method	Low thermal conductivity and slow grain growth for use as thermal barrier coating	[125]
Pyrochlore (Fd-3m)	$(\text{La}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2}\text{Gd}_{0.2})_2\text{Zr}_2\text{O}_7$ $(\text{Y}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2}\text{Gd}_{0.2})_2\text{Zr}_2\text{O}_7$ $(\text{La}_{0.2}\text{Y}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2}\text{Gd}_{0.2})_2\text{Zr}_2\text{O}_7$ $(\text{La}_{0.2}\text{Nd}_{0.2}\text{Y}_{0.2}\text{Eu}_{0.2}\text{Gd}_{0.2})_2\text{Zr}_2\text{O}_7$ $(\text{La}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Y}_{0.2}\text{Gd}_{0.2})_2\text{Zr}_2\text{O}_7$ $(\text{La}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2}\text{Y}_{0.2})_2\text{Zr}_2\text{O}_7$	Solid state reaction	low thermal conductivity for thermal barrier coating materials	[126]
Pyrochlore (Fd-3m)	$\text{Gd}_2\text{Zr}_2\text{O}_7$ $(\text{Gd}_{1/2}\text{Eu}_{1/2})_2\text{Zr}_2\text{O}_7$ $(\text{Gd}_{1/3}\text{Eu}_{1/3}\text{Sm}_{1/3})_2\text{Zr}_2\text{O}_7$ $(\text{Gd}_{1/4}\text{Eu}_{1/4}\text{Sm}_{1/4}\text{Nd}_{1/4})_2\text{Zr}_2\text{O}_7$ $(\text{Gd}_{1/5}\text{Eu}_{1/5}\text{Sm}_{1/5}\text{Nd}_{1/5}\text{La}_{1/5})_2\text{Zr}_2\text{O}_7$ $(\text{Gd}_{1/6}\text{Eu}_{1/6}\text{Sm}_{1/6}\text{Nd}_{1/6}\text{La}_{1/6}\text{Dy}_{1/6})_2\text{Zr}_2\text{O}_7$ $(\text{Gd}_{1/7}\text{Eu}_{1/7}\text{Sm}_{1/7}\text{Nd}_{1/7}\text{La}_{1/7}\text{Dy}_{1/7}\text{Ho}_{1/7})_2\text{Zr}_2\text{O}_7$	Solid state reaction	Synthesis and verified single phase and homogenous cation distribution	[127]
Pyrochlore	$\text{Sm}_2\text{Zr}_2\text{O}_7$ $\text{Lu}_2\text{Zr}_2\text{O}_7$	co-precipitation followed by solid-state reaction sintering	Thermal expansion, thermal conductivity, mechanical properties and phase stability for use as thermal barrier coating	[128]
Defect Fluorite	$(\text{Sm}_{1/3}\text{Eu}_{1/3}\text{Dy}_{1/3})_2\text{Zr}_2\text{O}_7$ $(\text{Sm}_{1/5}\text{Eu}_{1/5}\text{Tb}_{1/5}\text{Dy}_{1/5}\text{Lu}_{1/5})_2\text{Zr}_2\text{O}_7$	utilizing spark plasma sintering		
Mixed Pyrochlore and Defect Fluorite	$(\text{La}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Gd}_{0.2}\text{Yb}_{0.2})_2\text{Zr}_2\text{O}_7$	vacuum sintered using combustion synthesized nano-powder	In-line transmittance, Raman and UV-Vis spectra of transparent ceramic	[129]

Table 17 continued

Crystal Structure	Compound(s)	Synthesis	Investigated Property or Application	Ref.
Pyrochlore (Fd-3m)	$\text{La}_2(\text{Hf}_{1/2}\text{Zr}_{1/2})_2\text{O}_7$	Solid state reaction	Thermal conductivity and Young's modulus for use in thermal barrier coating applications. Thermal conductivity correlation with a size disorder parameter investigated as descriptor for thermally insulative material design.	[130]
	$\text{Sm}_2(\text{Sn}_{1/4}\text{Ti}_{1/4}\text{Hf}_{1/4}\text{Zr}_{1/4})_2\text{O}_7$			
	$\text{Gd}_2(\text{Sn}_{1/4}\text{Ti}_{1/4}\text{Hf}_{1/4}\text{Zr}_{1/4})_2\text{O}_7$			
	$(\text{Sm}_{1/2}\text{Gd}_{1/2})_2(\text{Ti}_{1/3}\text{Hf}_{1/3}\text{Zr}_{1/3})_2\text{O}_7$			
	$(\text{Eu}_{1/2}\text{Gd}_{1/2})_2(\text{Ti}_{1/3}\text{Hf}_{1/3}\text{Zr}_{1/3})_2\text{O}_7$			
	$(\text{La}_{1/2}\text{Pr}_{1/2})_2(\text{Sn}_{1/3}\text{Hf}_{1/3}\text{Zr}_{1/3})_2\text{O}_7$			
	$(\text{Eu}_{1/2}\text{Gd}_{1/2})_2(\text{Sn}_{1/3}\text{Hf}_{1/3}\text{Zr}_{1/3})_2\text{O}_7$			
	$(\text{La}_{1/3}\text{Pr}_{1/3}\text{Nd}_{1/3})_2(\text{Hf}_{1/2}\text{Zr}_{1/2})_2\text{O}_7$			
	$(\text{Sm}_{1/3}\text{Eu}_{1/3}\text{Gd}_{1/3})_2(\text{Hf}_{1/2}\text{Zr}_{1/2})_2\text{O}_7$			
	$(\text{Sm}_{1/3}\text{Eu}_{1/3}\text{Gd}_{1/3})_2(\text{Sn}_{1/3}\text{Hf}_{1/3}\text{Zr}_{1/3})_2\text{O}_7$			
	$(\text{Sm}_{1/3}\text{Eu}_{1/3}\text{Gd}_{1/3})_2(\text{Ti}_{1/4}\text{Sn}_{1/4}\text{Hf}_{1/4}\text{Zr}_{1/4})_2\text{O}_7$			
	$(\text{Sm}_{1/4}\text{Eu}_{1/4}\text{Gd}_{1/4}\text{Yb}_{1/4})_2(\text{Ti}_{1/4}\text{Sn}_{1/4}\text{Hf}_{1/4}\text{Zr}_{1/4})_2\text{O}_7$			
	$(\text{Sm}_{1/3}\text{Eu}_{1/3}\text{Gd}_{1/3})_2(\text{Ti}_{1/2}\text{Sn}_{1/6}\text{Hf}_{1/6}\text{Zr}_{1/6})_2\text{O}_7$			
	$(\text{Sm}_{1/3}\text{Eu}_{1/3}\text{Gd}_{1/3})_2(\text{Ti}_{3/4}\text{Sn}_{1/12}\text{Hf}_{1/12}\text{Zr}_{1/12})_2\text{O}_7$			
	$(\text{Sm}_{1/3}\text{Eu}_{1/3}\text{Gd}_{1/3})_2\text{Ti}_2\text{O}_7$			
	$(\text{Sm}_{1/4}\text{Eu}_{1/4}\text{Gd}_{1/4}\text{Yb}_{1/4})_2(\text{Ti}_{1/2}\text{Hf}_{1/4}\text{Zr}_{1/4})_2\text{O}_7$			
	$(\text{Sm}_{3/4}\text{Yb}_{1/4})_2(\text{Ti}_{1/2}\text{Zr}_{1/2})_2\text{O}_7$			
	$(\text{La}_{1/5}\text{Ce}_{1/5}\text{Nd}_{1/5}\text{Sm}_{1/5}\text{Eu}_{1/5})_2\text{Zr}_2\text{O}_7$			
	$(\text{La}_{1/7}\text{Ce}_{1/7}\text{Pr}_{1/7}\text{Nd}_{1/7}\text{Sm}_{1/7}\text{Eu}_{1/7}\text{Gd}_{1/7})_2(\text{Hf}_{1/2}\text{Zr}_{1/2})_2\text{O}_7$			
	$(\text{La}_{1/7}\text{Ce}_{1/7}\text{Pr}_{1/7}\text{Nd}_{1/7}\text{Sm}_{1/7}\text{Eu}_{1/7}\text{Gd}_{1/7})_2(\text{Sn}_{1/3}\text{Hf}_{1/3}\text{Zr}_{1/3})_2\text{O}_7$			
Nanotubes	$(\text{TaNbHfZrTi})\text{O}$	Anodizing HEA precursor	thermal stability	[131]
Monoclinic (C12/m1)	$(\text{Yb}_{0.2}\text{Y}_{0.2}\text{Lu}_{0.2}\text{Sc}_{0.2}\text{Gd}_{0.2})_2\text{Si}_2\text{O}_7$	Sol Gel Method	environmental barrier coating (EBC) for SiC-based composites	[132]
Monoclinic (C2/c)	$(\text{Y}_{1/4}\text{Ho}_{1/4}\text{Er}_{1/4}\text{Yb}_{1/4})_2\text{SiO}_5$	Ball mill, Hot press	Use as TEBC material: Young's modulus, thermal conductivity, thermal expansion, and high temperature water vapor resistance	[68]
Monoclinic (C12/m1)	$(\text{Yb}_{0.25}\text{Y}_{0.25}\text{Lu}_{0.25}\text{Er}_{0.25})_2\text{SiO}_5$	Solid state reaction	phase stability and anisotropy in thermal expansion	[133]
Amorphous glass spheres	$(\text{La, Ti, Nb, W, Zr})\text{O}$	containerless solidification: aerodynamic levitation	Hardness and optical properties	[134]

Table 17 continued

Crystal Structure	Compound(s)	Synthesis	Investigated Property or Application	Ref.
Magnetoplumbite (P63/mmc)	$(\text{Ba}_{0.7}\text{Sr}_{0.3})(\text{Fe}_{2.9}\text{Al}_{2.5}\text{Mn}_3\text{Ti}_1\text{Ni}_{2.9})\text{O}_{19}$	Solid state reaction	Microstructure, magnetization	[135]
	$(\text{Ba})(\text{Fe}_{5.9}\text{Ti}_{1.3}\text{Cr}_{1.2}\text{Co}_{1.3}\text{Ga}_{1.4}\text{In}_{0.9})\text{O}_{19}$			
	$(\text{Ba})(\text{Fe}_{5.3}\text{Ti}_{1.5}\text{Al}_{1.4}\text{Cr}_{1.9}\text{Mn}_{1.2}\text{Ni}_{0.7})\text{O}_{19}$			
	$(\text{Ba})(\text{Fe}_{7.2}\text{Ti}_{0.6}\text{Al}_{0.9}\text{Cr}_{0.7}\text{V}_{0.1}\text{Mn}_{0.3}\text{Co}_{0.3}\text{Ni}_{0.3}\text{Ga}_{0.6})\text{O}_{19}$			
	$(\text{Ba})(\text{Fe}_{1.4}\text{Ti}_{1.1}\text{Al}_{1.2}\text{Cr}_{1.2}\text{V}_{1.2}\text{Mn}_{1.5}\text{Co}_{1.5}\text{Ni}_{1.3}\text{Ga}_{1.1})\text{O}_{19}$			
	$(\text{Ba}_{0.5}\text{Sr}_{0.2}\text{La}_{0.2}\text{Ca}_{0.1})(\text{Fe}_{12})\text{O}_{19}$ $(\text{Ba}_{0.44}\text{Sr}_{0.33}\text{La}_{0.23})(\text{Fe}_{2.7}\text{Al}_{2.7}\text{Cr}_{2.7}\text{Ga}_{2.3}\text{In}_{1.3})\text{O}_{19}$			
Magnetoplumbite (P63/mmc)	$(\text{Ba}_1)(\text{Fe}_{5.83}\text{Al}_{1.19}\text{Ti}_{1.08}\text{Cr}_{1.12}\text{Cu}_{0.78}\text{Ga}_{1.03}\text{In}_{0.97})\text{O}_{19}$	Solid state reaction	Structure and magnetic properties with temperature	[136]
Rutile (P42/mmm)	$(\text{Al}_{0.19}\text{Cr}_{0.13}\text{Nb}_{0.19}\text{Ta}_{0.30}\text{Ti}_{0.19})\text{O}_2$	Reactive magnetron sputtering	Hardness and indentation moduli as a function of relative oxygen flow-rate	[137]
Non-crystalline films	FeCoNiO_x CrFeCoNiO_x AlFeCoNiO_x TiFeCoNiO_x	Arc melting, Physical Vapor Deposition	Microstructures and Electrical Resistivity	[138]
Mixed phase spinel, BCC, FCC nanoparticles	five elements (Ni, Fe, Co, Cr, and Al) and oxygen	sol-gel auto-combustion method and then used as the catalyst for the growth of CNTs by chemical vapor deposition technique	utilization of HEO nanoparticles as cost-effective catalyst for the growth of high yield carbon nanotubes for energy applications such as electrochemical capacitors	[139]
-	A case study with $\text{LaMnO}_{3\pm\delta}$	defect chemistry analysis and CALculation of PHase Diagram (CALPHAD) approach	Exploration of high entropy ceramics with computational thermodynamics	[140]
Review article	Review article	Review article	The emergent field of high entropy oxides: Design, prospects, challenges, and opportunities for tailoring material properties	[141]

Table 17 continued

Crystal Structure	Compound(s)	Synthesis	Investigated Property or Application	Ref.
Spinel (Fd-3m)	$\text{NiFe}_{1.9}(\text{Dy}_{0.02}\text{Er}_{0.02}\text{Gd}_{0.02}\text{Ho}_{0.02}\text{Tb}_{0.02})\text{O}_4$, $(\text{Co}_{0.2}\text{Cr}_{0.2}\text{Fe}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.2})\text{Fe}_2\text{O}_4$ and $(\text{Co}_{0.2}\text{Cr}_{0.2}\text{Fe}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.2})\text{Fe}_{1.9}(\text{Dy}_{0.02}\text{Er}_{0.02}\text{Gd}_{0.02}\text{Ho}_{0.02}\text{Tb}_{0.02})\text{O}_4$ ES	Sol-gel	Synthesis, Saturation magnetization (calculated and experimental values) and coercivity, calculation of configurational entropy of mixing	[142]
Rock salt (Fm-3m)	$(\text{Mg}_{0.2}\text{Co}_{0.2}\text{Cu}_{0.2}\text{Ni}_{0.2}\text{Zn}_{0.2})\text{O}$, ES	reaction assisted flash sintering at room temperature	feasibility of employing the reaction assisted flash sintering technique to fabricate ESOs	[143]
Rocksalt (Fm-3m) Spinel (Fd-3m) CaF_2 (Fm-3m) or CaF_2 (Ia-3)	$(\text{Co}_{0.2}\text{Cu}_{0.2}\text{Mg}_{0.2}\text{Ni}_{0.2}\text{Zn}_{0.2})\text{O}$ $(\text{Cr}_{0.2}\text{Fe}_{0.2}\text{Mn}_{0.2}\text{Mg}_{0.2}\text{Zn}_{0.2})_3\text{O}_4$ $(\text{Ce}_{0.2}\text{La}_{0.2}\text{Pr}_{0.2}\text{Sm}_{0.2}\text{Y}_{0.2})\text{O}_2$	solution combustion synthesis approach	nanocrystalline powders synthesis	[144]
Review article	Review article	Review article	Cation-disordered rocksalt transition metal oxides and oxyfluorides for high energy lithium-ion cathodes	[145]
Rock salt (Fm-3m)	$(\text{Co}_{0.2}\text{Cu}_{0.2}\text{Mg}_{0.2}\text{Ni}_{0.2}\text{Zn}_{0.2})\text{O}$ $\text{Li}(\text{Co}_{0.2}\text{Cu}_{0.2}\text{Mg}_{0.2}\text{Ni}_{0.2}\text{Zn}_{0.2})\text{OF}$	nebulized spray pyrolysis	report on side reactions leading to gas evolution in Li-ion cells	[146]
Rock salt (Fm-3m)	$(\text{Co}_{0.2}\text{Cu}_{0.2}\text{Mg}_{0.2}\text{Ni}_{0.2}\text{Zn}_{0.2})\text{O}$	Solution combustion and solid state syntheses	Experiments concurrent with molecular dynamics (MD) simulations show local stress fields around the cations played a critical role in stabilizing single phase	[147]
Fluorite (Fm-3m)	$(\text{Ce}_{0.2}\text{Zr}_{0.2}\text{Y}_{0.2}\text{Gd}_{0.2}\text{La}_{0.2})\text{O}_{2-\delta}$, ES	hydrothermal	reversible multiphase to a single-phase state. Composition and synthesis variation.	[148]
Delafossite Li_xMO_2 -type (R-3m)	$\text{Li}(\text{NiCoMnAlZn})_1\text{O}_2$ $\text{Li}(\text{NiCoMnAlFe})_1\text{O}_2$ $\text{Li}_{0.8}\text{Na}_{0.2}(\text{NiCoMnAlFe})_1\text{O}_2$	nebulized spray pyrolysis	Synthesis, potential cathode materials	[149]

Table 17 continued

Crystal Structure	Compound(s)	Synthesis	Investigated Property or Application	Ref.
Perovskite Cubic (Pm-3m)	$\text{Na}_{0.30}\text{K}_{0.07}\text{Ca}_{0.24}\text{La}_{0.18}\text{Ce}_{0.21}\text{TiO}_3$	Solid state reaction	Synthesis, dielectric properties	[150]
Orthorhombic Perovskite (Pbnm)	$(\text{Gd}_{0.2}\text{La}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Y}_{0.2})\text{CoO}_3$ $(\text{Gd}_{0.2}\text{La}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Y}_{0.2})\text{CrO}_3$ $(\text{Gd}_{0.2}\text{La}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Y}_{0.2})\text{FeO}_3$	nebulized spray pyrolysis	X-ray absorption near edge spectroscopy, magnetometry, and Mössbauer spectroscopy	[151]
Spinel (Fd-3m)	$(\text{Al}_{1/6}\text{Co}_{1/6}\text{Cr}_{1/6}\text{Fe}_{1/6}\text{Mn}_{1/6}\text{Ni}_{1/6})_3\text{O}_4$	facile solution combustion synthesis	Magnetic properties, long-range ferrimagnetic behavior	[152]
Review article	Review article	Review article	High-entropy ceramics (Nature Reviews Materials)	[153]
Rock salt (Fm-3m)	$(\text{Mg}_{0.2}\text{Co}_{0.2}\text{Cu}_{0.2}\text{Ni}_{0.2}\text{Zn}_{0.2})\text{O}$	Polymeric synthesis, reactive flash sintering	Synthesis variables	[154]
Review article	Review article	Review article	A step forward from high-entropy ceramics to compositionally complex ceramics: a new perspective	[155]
Rock salt (Fm-3m)	$(\text{Mg}_{0.2}\text{Co}_{0.2}\text{Cu}_{0.2}\text{Ni}_{0.2}\text{Zn}_{0.2})\text{O}$	flash assisted sintered	Synthesis variables	[156]
Orthorhombic Perovskite (Pbnm)	$(\text{Y}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2}\text{Er}_{0.2})\text{AlO}_3$	co-precipitation method	Thermal expansion, thermal conductivity, candidate environmental barrier coating material for	[157]
Multiphase composite	$(\text{Tm}_{0.2}\text{Y}_{0.2}\text{Dy}_{0.2}\text{Gd}_{0.2}\text{Tb}_{0.2})_3\text{Si}_2\text{C}_2$ $(\text{Tm}_{0.2}\text{Y}_{0.2}\text{Pr}_{0.2}\text{Gd}_{0.2}\text{Dy}_{0.2})_3\text{Si}_2\text{C}_2/(\text{Tm}_{0.2}\text{Y}_{0.2}\text{Pr}_{0.2}\text{Gd}_{0.2}\text{Dy}_{0.2})_2\text{O}_3$ $(\text{Tm}_{0.2}\text{Y}_{0.2}\text{Pr}_{0.2}\text{Gd}_{0.2}\text{Tb}_{0.2})_3\text{Si}_2\text{C}_2/(\text{Tm}_{0.2}\text{Y}_{0.2}\text{Pr}_{0.2}\text{Gd}_{0.2}\text{Tb}_{0.2})_2\text{O}_3$	Solid state reaction	Potential as electromagnetic wave absorbing materials	[158]
Fluorite (Fm-3m) or C-type bixbyite (Ia-3)	$(\text{Ce}_{0.2}\text{La}_{0.2}\text{Pr}_{0.2}\text{Sm}_{0.2}\text{Y}_{0.2})\text{O}_{2-\delta}$	reverse co-precipitation	reversible control of optical properties, heat treatment effects on bandgap energy, XANES, and bandgap tunability	[159]
Orthorhombic Perovskite (Pbnm)	$[(\text{Bi},\text{Na})_{1/5}(\text{La},\text{Li})_{1/5}(\text{Ce},\text{K})_{1/5}\text{Ca}_{1/5}\text{Sr}_{1/5}]\text{TiO}_3$	Solid state reaction	explored as anode material for lithium-ion batteries.	[160]
Spinel (Fd-3m)	$(\text{Mg}_{0.2}\text{Ti}_{0.2}\text{Zn}_{0.2}\text{Cu}_{0.2}\text{Fe}_{0.2})_3\text{O}_4$	Solid state reaction	anode material for lithium-ion batteries	[161]

Table 17 continued

Crystal Structure	Compound(s)	Synthesis	Investigated Property or Application	Ref.
Garnet	$(Y_{0.2}Yb_{0.2}Lu_{0.2}Eu_{0.2}Er_{0.2})_3Al_5O_{12}$	solid-state reaction method and spark plasma sintering	Thermal conductivity, thermal expansion coefficient for use as thermal barrier coating	[162]
Rock salt (Fm-3m) or Spinel (Fd-3m)	$Li_0(Ni_{0.15}Fe_{0.15}Mn_{0.15}Cr_{0.14}Co_{0.15})O_1$	nebulized spray pyrolysis	Redox behavior, spinel to rocksalt phase transformation with Li^+ addition. Potential for usage as negative and positive electrode materials in rechargeable lithium-ion batteries.	[163]
	$Li_{0.15}(Ni_{0.14}Fe_{0.14}Mn_{0.13}Cr_{0.13}Co_{0.14})O_1$			
	$Li_{0.25}(Ni_{0.12}Fe_{0.12}Mn_{0.12}Cr_{0.11}Co_{0.12})O_1$			
	$Li_{0.34}(Ni_{0.11}Fe_{0.11}Mn_{0.11}Cr_{0.10}Co_{0.11})O_1$			
	$Li_{0.41}(Ni_{0.10}Fe_{0.10}Mn_{0.10}Cr_{0.09}Co_{0.10})O_1$			
	$Li_{0.41}(Ni_{0.08}Fe_{0.08}Mn_{0.08}Cr_{0.08}Co_{0.08})O_1$			
	$Li_0(Ni_{0.14}Fe_{0.14}Mn_{0.14}Cr_{0.14}Mg_{0.14})O_1$			
	$Li_{0.15}(Ni_{0.14}Fe_{0.13}Mn_{0.13}Cr_{0.13}Mg_{0.14})O_1$			
	$Li_{0.25}(Ni_{0.12}Fe_{0.12}Mn_{0.12}Cr_{0.12}Mg_{0.12})O_1$			
	$Li_{0.35}(Ni_{0.11}Fe_{0.11}Mn_{0.11}Cr_{0.11}Mg_{0.11})O_1$			
Spinel (Fd-3m)	$Li_{0.39}(Ni_{0.10}Fe_{0.10}Mn_{0.10}Cr_{0.10}Mg_{0.10})O_1$	radio frequency reactive magnetron sputtering system and an ultra-high vacuum sintering furnace	effects of surface irradiation on the indirect irradiation region	[164]
	$Li_{0.44}(Ni_{0.08}Fe_{0.08}Mn_{0.08}Cr_{0.08}Mg_{0.08})O_1$			
Orthorhombic Perovskite (Pbnm)	$La(Cr_{0.2}Mn_{0.2}Fe_{0.2}Co_{0.2}Ni_{0.2})O_3$	pulsed laser epitaxy	Refined structure, first principles calculations, strain and crystal structure controlled orientation based on substrate	[165]
Perovskite Cubic (Pm-3m)	$Ba(Ti_{1/6}Sn_{1/6}Zr_{1/6}Hf_{1/6}Nb_{1/6}Ga_{1/6})O_3$	Solid state reaction	Reversible multiphase to single phase transition, dielectric properties	[166]

Table 17 continued

Crystal Structure	Compound(s)	Synthesis	Investigated Property or Application	Ref.
Rock salt (Fm-3m)	$(\text{Mg}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2})\text{O}$	Solid state reaction	magnetic order and the spin dynamic using muon spin relaxation and inelastic neutron scattering	[167]
Perovskite Cubic (Pm-3m)	$\text{Sr}(\text{Ti}_{0.2}\text{Y}_{0.2}\text{Zr}_{0.2}\text{Sn}_{0.2}\text{Hf}_{0.2})\text{O}_{3-x}$	Reactive flash sintering	Synthesis technique	[168]
Rock salt (Fm-3m)	$(\text{Mg}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2})\text{O}$	polymerized organic–inorganic synthesis, hot pressing	indentation modulus on grains showing a high degree of elastic isotropy, first principles calculations	[169]
Rock salt (Fm-3m)	$(\text{Mg}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2})\text{O}$	sol–gel	CO oxidation mechanisms, reversible oxidation/ reduction of Cu	[170]
Rock salt (Fm-3m)	$(\text{Mg}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2})\text{O}$ $(\text{Co}, \text{Ni}, \text{Mg}, \text{Cu}, \text{Zn})_{1-x}\text{Fe}_x\text{O}$	Reverse co-precipitation, flame spray pyrolysis, nebulized spray pyrolysis	Magnetic effects on crystalline lattice distortion with Fe addition and different synthesis methods	[171]
Rock salt (Fm-3m)	$(\text{MgCoNiZn})_{0.85}\text{Li}_{0.15}\text{O}$ $(\text{MgCoNiZn})_{0.75}\text{Li}_{0.25}\text{O}$ $(\text{MgCoNiZn})_{0.65}\text{Li}_{0.35}\text{O}$	Solid state reaction	Electrochemical properties for use as anode material for lithium-ion batteries	[172]
Rock salt (Fm-3m)	$(\text{Mo}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2})\text{O}$ $(\text{Co}_{0.25}\text{Ni}_{0.25}\text{Cu}_{0.25}\text{Zn}_{0.25})\text{O}$ $(\text{Mo}_{0.25}\text{Cu}_{0.25}\text{Zn}_{0.25}\text{Co}_{0.25})\text{O}$ $(\text{Mo}_{0.25}\text{Ni}_{0.25}\text{Zn}_{0.25}\text{Co}_{0.25})\text{O}$ $(\text{Mo}_{0.25}\text{Ni}_{0.25}\text{Cu}_{0.25}\text{Co}_{0.25})\text{O}$ $(\text{Mo}_{0.25}\text{Ni}_{0.25}\text{Cu}_{0.25}\text{Zn}_{0.25})\text{O}$	solid solution loading	application in oxidative desulfurization as function of composition, synthesis	[173]
Perovskite Cubic (Pm-3m)	$(\text{Bi}_{0.2}\text{Na}_{0.2}\text{K}_{0.2}\text{Ba}_{0.2}\text{Ca}_{0.2})\text{TiO}_3$	flash sintering	Dielectric and energy storage properties	[174]
Rock salt (Fm-3m)	$(\text{Mg}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2})\text{O}$	Theoretical comparison to experimental reports	Magnetic structure investigation with first principles and Monte Carlo simulations	[175]
Defect Fluorite	$\text{Ce}_{0.2}\text{Gd}_{0.2}\text{Hf}_{0.2}\text{La}_{0.2}\text{Zr}_{0.2}\text{O}_2$ with Eu^{3+} doping	co- precipitation	luminescent properties and local structural studies	[176]

Table 17 continued

Crystal Structure	Compound(s)	Synthesis	Investigated Property or Application	Ref.
CaF ₂ (Ia-3)	(Lu _{0.2} Y _{0.395} Gd _{0.2} Yb _{0.2} Tm _{0.005}) ₂ O ₃ with ZrO ₂ and La ₂ O ₃ as sintering additives	Solid state reaction, vacuum sintering	Transparent ceramic synthesis, transmittance	[177]
heterostructure of CeO ₂ phase and rocksalt	CuZnCeO _x -(Mg _{0.2} Co _{0.2} Ni _{0.2} Cu _{0.2} Zn _{0.2})O	Entropy-driven mechano-chemical process	CO oxidation catalyst CuCeO _x -HEO with a unique heterostructure	[178]
Rock salt (Fm-3m)	(Mg _{0.2} Co _{0.2} Ni _{0.2} Cu _{0.2} Zn _{0.2})O	anchoring–merging process	Holey lamellar HEO material with mesoporous structure as catalysis for oxidation of benzyl-alcohol	[179]
Ruddlesden-Popper T'-type	(La _{0.2} Pr _{0.2} Nd _{0.2} Sm _{0.2} Eu _{0.2}) ₂ CuO ₄	pulsed laser deposition	Role of heteroepitaxial strain in phase formation	[180]
Monoclinic (P21/c)	(Nd _{0.2} Sm _{0.2} Eu _{0.2} Y _{0.2} Yb _{0.2}) ₄ Al ₂ O ₉	co-precipitation method	high-temperature phase stability, thermal conductivity, thermal expansion	[181]
Perovskite Cubic (Pm-3m)	Ba(Mg _{0.2} Zn _{0.2} Ti _{0.2} W _{0.2} Mo _{0.2})O ₃ Ba(Zn _{0.2} Yb _{0.2} Y _{0.2} W _{0.2} Mo _{0.2})O ₃ Ba(Mg _{0.2} Zn _{0.2} Nb _{0.2} Ta _{0.2} W _{0.2})O ₃ Ba(Zn _{0.2} Yb _{0.2} Ti _{0.2} Nb _{0.2} W _{0.2})O ₃ Ba(Zn _{0.2} Yb _{0.2} Nb _{0.2} Ta _{0.2} Sb _{0.2})O ₃ Ba(Zn _{0.2} Ti _{0.2} Zr _{0.2} Hf _{0.2} W _{0.2})O ₃ Ba(Zn _{0.2} Ti _{0.2} Zr _{0.2} Nb _{0.2} Ta _{0.2})O ₃ Ba(Yb _{0.2} Y _{0.2} Ga _{0.2} Nb _{0.2} W _{0.2})O ₃ Ba(Yb _{0.2} Y _{0.2} Ti _{0.2} Zr _{0.2} W _{0.2})O ₃ Ba(Yb _{0.2} Y _{0.2} Ti _{0.2} Nb _{0.2} Ta _{0.2})O ₃ Ba(Yb _{0.2} Ti _{0.2} Zr _{0.2} Sn _{0.2} Nb _{0.2})O ₃ Ba(Ti _{0.2} Zr _{0.2} Hf _{0.2} Sn _{0.2} Ce _{0.2})O ₃	Solid state reaction	geometric compatibility in compositional selection, electrical properties, substituted cations with different valences	[182]
Review article	Review article	Review article	High entropy oxides: The role of entropy, enthalpy and synergy systematic trend in structure and properties as a function of substrate temperature during growth	[183]
Rock salt (Fm-3m)	(Mg _{0.2} Co _{0.2} Ni _{0.2} Cu _{0.2} Zn _{0.2})O	Pulsed laser deposition	Thermal expansion, phase stability, hardness, for candidate as thermal barrier coating	[184]
Defect Fluorite	(Y _{1/3} Yb _{1/3} Er _{1/3}) ₃ TaO ₇ (Y _{1/3} Yb _{1/3} Er _{1/3}) ₃ NbO ₇ (Sm _{1/6} Eu _{1/6} Y _{1/6} Yb _{1/6} Lu _{1/6} Er _{1/6}) ₃ (Nb _{1/2} Ta _{1/2})O ₇	Solid state reaction		[185]

Table 17 continued

Crystal Structure	Compound(s)	Synthesis	Investigated Property or Application	Ref.
Monoclinic (X1 P2 1 /c or X2 C2/c)	(Sc,Y,Dy,Er,Yb) ₂ SiO ₅	Spark plasma sintering, annealing	tailoring the thermal conductivity and thermal expansion for candidates as thermal and environmental barrier coatings	[186]
	(Dy,Er) ₂ SiO ₅			
	(Dy,Sc) ₂ SiO ₅			
	(Yb,Sc) ₂ SiO ₅			
	(Yb,Er) ₂ SiO ₅			
	Yb ₂ SiO ₅			
	Er ₂ SiO ₅			
	Dy ₂ SiO ₅			
	Y ₂ SiO ₅			
	Sc ₂ SiO ₅			
Spinel (Fd-3m)	(Fe _{0.2} Co _{0.2} Ni _{0.2} Cr _{0.2} Mn _{0.2}) ₃ O ₄	Solid state reaction	structural stability and superionic conductivity for use as anode for lithium-ion batteries	[187]
	AO type multicomponent	computational	method to estimate the phase formation of HEOs from first principles with Monte Carlo simulations to investigate the phase composition and local ionic segregation as a function of temperature	[188]
high-entropy layered hydroxide (HELH) 2D sheets	Mg ²⁺ , Al ³⁺ , Co ²⁺ , Ni ²⁺ , Zn ²⁺	co-precipitation method	Synthesis, thermal stability, and hydroxide ion conductivity	[189]
Rock salt (Fm-3m)	(Mg _{0.2} Co _{0.2} Ni _{0.2} Cu _{0.2} Zn _{0.2})O	Pulsed laser deposition	substrate temperature and deposition pressure effects on film texture and lattice parameter, electrical conductivity	[190]
γ-type Monoclinic (P21/c)	(Gd _{1/6} Tb _{1/6} Dy _{1/6} Tm _{1/6} Yb _{1/6} Lu _{1/6}) ₂ SiO ₇	Solid state reaction	Synthesis, thermal stability	[191]
CeBiOS ₂ type (P 4/n m m Z)	(La _{0.3} Ce _{0.3} Pr _{0.2} Nd _{0.1} Sm _{0.1})OBiS ₂ (La _{0.1} Ce _{0.3} Pr _{0.3} Nd _{0.2} Sm _{0.1})OBiS ₂ (La _{0.2} Ce _{0.2} Pr _{0.2} Nd _{0.2} Sm _{0.2})OBiS ₂ (La _{0.1} Ce _{0.3} Pr _{0.1} Nd _{0.2} Sm _{0.3})OBiS ₂	Single crystal growth using CsCl flux	Synthesis, valence states, superconducting transition temperatures and entropy effects on them	[192]

Table 17 continued

Crystal Structure	Compound(s)	Synthesis	Investigated Property or Application	Ref.
Fluorite (Fm-3m) or Bixbyite (Ia-3)	(Ce,Gd,Nd,Sm,Pr,Mo _x)O _{2-δ} and (Ce,Gd,Nd,Sm,Pr,Mo _x)O _{2-δ} , x = (0–0.5)	Solid state reaction	Composition effects on phase stabilization. Structural, microstructural and transport properties. Mo influence on oxygen vacancy concentration and charge state.	[193]
Tetragonal perovskite (I4/mcm)	(Ca,Sr,Ba)ZrO ₃ , ES	Solid state reaction	Synthesis, density, hardness, thermal conductivity, use as novel crucible material for the melting of titanium alloys.	[194]
Review/ perspective	Review/ perspective	Review/ perspective	Oxides and the high entropy regime: A new mix for engineering physical properties	[195]
Spinel (Fd-3m)	(Co _{0.2} Mg _{0.2} Mn _{0.2} Ni _{0.2} Zn _{0.2})(Al _{0.2} Co _{0.2} Cr _{0.2} Fe _{0.2} Mn _{0.2}) ₂ O ₄	Solid state reaction	Synthesis, homogeneity and inversion, XAS	[196]
β-type RE-disilcate	(Er _{0.25} Tm _{0.25} Yb _{0.25} Lu _{0.25}) ₂ Si ₂ O ₇	Solid state reaction	high temperature corrosion resistances, use as environmental barrier coating	[197]
Perovskite Cubic (Pm-3m)	Zn _{0.1} Ca _{0.1} Sr _{0.4} Ba _{0.4} ZrO ₃	Solid state reaction	Mechanical properties, thermal conductivity. potential as thermal barrier material. Non-equimolar multicomponent ceramics with targeted performances	[198]
NaSICON structure	Na ₃ Zr ₂ ([B,Al,Si,P,As,Sb,S,Se]O ₄) ₃	computational	Mathematical solution of accessible compositions	[199]
Pyrochlore (Fd-3m)	(La _{0.2} Nd _{0.2} Sm _{0.2} Eu _{0.2} Gd _{0.2}) ₂ Zr ₂ O ₇	atmospheric plasma spraying	double-ceramic-layer thermal barrier coating	[200]
Fluorite (Fm-3m)	(Pd _y CeZrHfTiLa)O _x	mechanochemical-assisted synthesis	Pd single-atom supports. CO oxidation activity, resistance to thermal and hydrothermal degradation	[201]

Table 17 continued

Crystal Structure	Compound(s)	Synthesis	Investigated Property or Application	Ref.
Rock salt (Fm-3m)	$(\text{Mg}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2})\text{O}$	nebulized spray pyrolysis	Lattice distortion and stability under pressure	[202]
Fluorite (Fm-3m)	$\text{Gd}_{0.2}\text{La}_{0.2}\text{Ce}_{0.2}\text{Hf}_{0.2}\text{Zr}_{0.2}\text{O}_2$ $\text{Gd}_{0.2}\text{La}_{0.2}\text{Y}_{0.2}\text{Hf}_{0.2}\text{Zr}_{0.2}\text{O}_2$	co-precipitation followed by peptization	photo-catalysts with excellent performance for natural sunlight driven degradation of Cr(VI) and methyleneblue dye.	[203]
BCC to amorphous with increases oxygen content	$(\text{NbMoTaWV})_{100-x}\text{O}_x$ ($x = 0-53.63$)	radio frequency magnetron sputtering	Effect of oxygen content on local structure, hardness, modulus, resistivity, and conduction mechanism	[204]
Review article	Review article	Review article	Toward expanding the realm of high entropy materials to platinum group metals: A review	[205]
SiC foam to support multiphase	$(\text{FeMgCoNi})\text{O}_{1.2}@\text{SiC}$	Sol-gel	thermal reduction and water splitting reactions are performed using equal-power microwave irradiation	[206]
Defect fluorite	$(\text{Dy}_{0.2}\text{Ho}_{0.2}\text{Er}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_3\text{NbO}_7$	Solid state reaction	High thermal coefficient, ultra-low thermal conductivity, use as thermal barrier coating	[207]
Fluorite	$(\text{Hf}_{0.314}\text{Zr}_{0.314}\text{Ce}_{0.314}\text{Y}_{0.029}\text{Yb}_{0.029})\text{O}_{2-\delta}$ $(\text{Hf}_{0.284}\text{Zr}_{0.284}\text{Ce}_{0.284}\text{Y}_{0.074}\text{Yb}_{0.074})\text{O}_{2-\delta}$ $(\text{Hf}_{0.2}\text{Zr}_{0.2}\text{Ce}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})\text{O}_{2-\delta}$	Solid state reaction	Sand corrosion, thermal expansion, and ablation properties	[208]
Garnet	$(\text{Lu}_{1/6}\text{Y}_{1/6}\text{Ho}_{1/6}\text{Dy}_{1/6}\text{Tb}_{1/6}\text{Gd}_{1/6})_3\text{Al}_5\text{O}_{12}$	Micro-pulling down bulk crystal growth	Effects of growth parameters on crystal quality	[209]
Nearly single phase fluorite	$\text{Ce}_{0.5}\text{Zn}_{0.1}\text{Co}_{0.1}\text{Mg}_{0.1}\text{Ni}_{0.1}\text{Cu}_{0.1}\text{O}_x$	Mechano-chemical synthesis	Synthesis and use as an ultra-stable catalyst in both thermal and hydrothermal conditions	[210]
Spinel (Fd-3m)	Ni-Co-Cr-Fe-Mn-O	wet-chemistry sol-gel strategy	Synthesis spherical mesoporous HEO for use as recyclable catalyst, or detection of DNA in complex systems	[211]

Table 17 continued

Crystal Structure	Compound(s)	Synthesis	Investigated Property or Application	Ref.
Rock salt (Fm-3m)	$(\text{Co}, \text{Mg}, \text{Ni}, \text{Zn})_x\text{Cu}_{1-x}\text{O}$	Solution combustion synthesis	Thermodynamic calculations and synthesis type and conditions	[212]
Perovskite Cubic (Pm-3m)	$\text{Ba}(\text{Zr}_{0.2}\text{Sn}_{0.2}\text{Ti}_{0.2}\text{Hf}_{0.2}\text{Ce}_{0.2})\text{O}_{3-\delta}$ $\text{Ba}(\text{Zr}_{0.2}\text{Sn}_{0.2}\text{Ti}_{0.2}\text{Hf}_{0.2}\text{Y}_{0.2})\text{O}_{3-\delta}$ $\text{Ba}(\text{Zr}_{1/7}\text{Sn}_{1/7}\text{Ti}_{1/7}\text{Hf}_{1/7}\text{Ce}_{1/7}\text{Nb}_{1/7}\text{Y}_{1/7})\text{O}_{3-\delta}$ $\text{Ba}(\text{Zr}_{0.15}\text{Sn}_{0.15}\text{Ti}_{0.15}\text{Hf}_{0.15}\text{Ce}_{0.15}\text{Nb}_{0.15}\text{Y}_{0.10})\text{O}_{3-\delta}$	Solid state reaction	proton conductivity investigated by studying water uptake and electrical conductivity in dry and wet air	[213]
Pyrochlore (Fd-3m)	$(\text{Yb}_{0.2}\text{Tb}_{0.2}\text{Gd}_{0.2}\text{Dy}_{0.2}\text{Er}_{0.2})_2\text{Ti}_2\text{O}_7$	Solid state reaction, floating zone growth	Synthesis, magnetic properties	[214]
Review article	Review article	Review article	Nano- HEO materials, synthesis strategies and catalytic applications	[215]
Spinel (Fd-3m)	$(\text{Co}_{0.2}\text{Cr}_{0.2}\text{Fe}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.2})_3\text{O}_4$	surfactant-assisted hydrothermal method	Nanoparticle synthesis and properties investigated for use as anode material in a lithium-ion battery	[216]
Rock salt (Fm-3m)	$(\text{Zn}_{0.2}\text{Ni}_{0.2}\text{Co}_{0.2}\text{Mn}_{0.2}\text{Cu}_{0.2})\text{O}$ $(\text{Zn}_{0.2}\text{Ni}_{0.2}\text{Co}_{0.2}\text{Mn}_{0.2}\text{Fe}_{0.2})\text{O}$ $(\text{Zn}_{0.17}\text{Ni}_{0.17}\text{Co}_{0.17}\text{Mn}_{0.17}\text{Fe}_{0.17}\text{Cu}_{0.17})\text{O}$ $(\text{Zn}_{0.14}\text{Ni}_{0.14}\text{Co}_{0.14}\text{Mn}_{0.14}\text{Fe}_{0.14}\text{Cu}_{0.14}\text{Mg}_{0.14})\text{O}$ $\text{Li}(\text{Zn}_{0.2}\text{Ni}_{0.2}\text{Co}_{0.2}\text{Mn}_{0.2}\text{Cu}_{0.2})\text{OF}$ $\text{Li}(\text{Zn}_{0.2}\text{Ni}_{0.2}\text{Co}_{0.2}\text{Mn}_{0.2}\text{Fe}_{0.2})\text{OF}$ $\text{Li}(\text{Zn}_{0.17}\text{Ni}_{0.17}\text{Co}_{0.17}\text{Mn}_{0.17}\text{Fe}_{0.17}\text{Cu}_{0.17})\text{OF}$ $\text{Li}(\text{Zn}_{0.14}\text{Ni}_{0.14}\text{Co}_{0.14}\text{Mn}_{0.14}\text{Fe}_{0.14}\text{Cu}_{0.14}\text{Mg}_{0.14})\text{OF}$	Mechanochemical synthesis	Synthesis approach, elemental homogeneity	[217]
Orthorhombic Perovskite (Pbnm)	$(\text{Gd}_{0.2}\text{Nd}_{0.2}\text{La}_{0.2}\text{Sm}_{0.2}\text{Y}_{0.2})\text{CoO}_3$	modified coprecipitation hydrothermal method	Structural and magnetic properties, Ab initio calculations of band gap, electronic transport properties	[218]
Rock salt (Fm-3m)	$(\text{Mg}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2})\text{O}$	Solid state reaction	Multivariate curve resolution analysis of operando XAS data for the investigation of the lithiation mechanisms	[219]

Table 17 continued

Crystal Structure	Compound(s)	Synthesis	Investigated Property or Application	Ref.
Hexagonal Perovskite (R-3cH)	$\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_{3-\delta}$ $\text{La}_{0.2}\text{Pr}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Sr}_{0.2}\text{MnO}_{3-\delta}$	sol-gel combustion method	potential cathode material that can suppress cation segregation for solid oxide fuel cell	[220]
Monoclinic (C2/ m)	$(\text{Y}_{0.1}\text{Yb}_{0.9})_2\text{Si}_2\text{O}_7$ $(\text{Y}_{0.5}\text{Yb}_{0.5})_2\text{Si}_2\text{O}_7$ $(\text{Y}_{0.2}\text{Yb}_{0.2}\text{Sc}_{0.2}\text{Gd}_{0.2}\text{Lu}_{0.2})_2\text{Si}_2\text{O}_7$	Spark plasma sintering	phase stability and low thermal conductivity candidates for thermal barrier coatings or ceramic matrix composites in gas turbine engines	[221]
rhombohedral perovskite	$\text{BiFe}_{1-5x}\text{Mo}_x\text{Ti}_x\text{Zr}_x\text{Ni}_x\text{Ce}_x\text{O}_3$ (x = 0.01, 0.02, 0.03)	Solid state reaction	effect of equimolecular quinary doping on the structural, morphological, optical, and magnetic properties	[222]
Fluorite	$(\text{Sm}_{0.2}\text{Eu}_{0.2}\text{Tb}_{0.2}\text{Dy}_{0.2}\text{Lu}_{0.2})_2\text{Ce}_2\text{O}_7$ $(\text{Sm}_{0.2}\text{Eu}_{0.2}\text{Tb}_{0.2}\text{Dy}_{0.2}\text{Lu}_{0.2})_2\text{ZrCeO}_7$	Solid state reaction	Phase stability, thermal expansion thermal conductivity, for thermal barrier coatings	[223]
Rhombohedral (R-3)	$(\text{Y}_{0.25}\text{Eu}_{0.25}\text{Gd}_{0.25}\text{Dy}_{0.25})_2\text{FeTaO}_7$	Solid state reaction	Thermal and mechanical properties for use as thermal barrier coating	[224]
Review article	Review article	Review article	Design and synthesis of chemically complex ceramics from the perspective of entropy	[225]
Rock salt (Fm-3m)	$\text{Li}_{1.3}\text{Mn}^{3+}_{0.4}\text{Ti}_{0.3}\text{O}_{1.7}\text{F}_{0.3}$ $\text{Li}_{1.3}\text{Mn}^{2+}_{0.2}\text{Mn}^{3+}_{0.2}\text{Ti}_{0.1}\text{Nb}_{0.2}\text{O}_{1.7}\text{F}_{0.3}$ $\text{Li}_{1.3}\text{Mn}^{2+}_{0.1}\text{Co}^{2+}_{0.1}\text{Mn}^{3+}_{0.1}\text{Cr}^{3+}_{0.1}\text{Ti}_{0.1}\text{Nb}_{0.2}\text{O}_{1.7}\text{F}_{0.3}$ $\text{Li}_{1.3}\text{Mn}^{2+}_{0.1}\text{Co}^{2+}_{0.05}\text{Mg}_{0.05}\text{Mn}^{3+}_{0.05}\text{Cr}^{3+}_{0.05}\text{Fe}^{3+}_{0.05}\text{Ga}_{0.05}\text{Ti}_{0.05}\text{Zr}_{0.05}\text{Nb}_{0.1}\text{Sb}_{0.05}\text{Ta}_{0.05}\text{O}_{1.7}\text{F}_{0.3}$	Solid state reaction	Improved performance in battery cathodes	[226]
Spinel (Fd-3m)	$(\text{Ni}_{0.2}\text{Co}_{0.2}\text{Mn}_{0.2}\text{Fe}_{0.2}\text{Ti}_{0.2})_3\text{O}_4$	Solid state reaction	Synchrotron studies for application as anode material for Li-ion batteries	[227]
Discussion article	Discussion article	Discussion article	Thermodynamics of high entropy oxides	[228]
Rock salt (Fm-3m)	$(\text{Mg}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2})\text{O}$	Solid state reaction	XAS study of HEO anode lithiation/delithiation cycle	[229]

Table 17 continued

Crystal Structure	Compound(s)	Synthesis	Investigated Property or Application	Ref.
Rock salt (Fm-3m)	$(\text{Mg}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2})\text{O}$	Computational	Simulating spin waves with linear spin-wave theory and supercell approximations	[230]
Cubic Perovskite (Pm-3m)	$\text{Sr}(\text{Ti}_{0.2}\text{Fe}_{0.2}\text{Mo}_{0.2}\text{Nb}_{0.2}\text{Cr}_{0.2})\text{O}_3$	Solid state reaction	Ultralow thermal conductivity	[231]
Spinel and multi-phase	$(\text{MgZnMnCoNi})\text{Ox}$ $(\text{CrFeMnCoNi})\text{Ox}$	combinatorial RF co-sputtering	Development of film library: High throughput analysis, film structure as a function of metallic elements	[232]
Rock salt (Fm-3m)	$(\text{Mg}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2})\text{O}$	Citrate gel auto-combustion method	Synthesis effects on phase purity, XANES, EXAFS	[233]
Rock salt (Fm-3m)	$(\text{Mg}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2})\text{O} + 1\text{wt}\% \text{ Au, Pd or Ru}$	Solid state reaction	Stabilization and CO oxidation capabilities	[234]
Tetragonal (P4mm)	$(\text{Pb}_{0.25}\text{Ba}_{0.25}\text{Sr}_{0.25}\text{Ca}_{0.25})\text{TiO}_3$	Solid state reaction	Relaxor-like ferroelectric with low loss	[235]
Pyrochlore Single and multi-phase	$(\text{La}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2}\text{Gd}_{0.2})_2\text{Zr}_2\text{O}_7$ $(\text{La}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Gd}_{0.2}\text{Yb}_{0.2})_2\text{Zr}_2\text{O}_7$ $(\text{La}_{0.2}\text{Nd}_{0.2}\text{Y}_{0.2}\text{Er}_{0.2}\text{Yb}_{0.2})_2\text{Zr}_2\text{O}_7$ $(\text{Dy}_{0.2}\text{Y}_{0.2}\text{Ho}_{0.2}\text{Er}_{0.2}\text{Yb}_{0.2})_2\text{Zr}_2\text{O}_7$	Solid state reaction	Glass-like thermal conductivity, hardness, thermal expansion, use as thermal barrier coating	[236]
Mixed phase monoclinic and orthorhombic perovskite	TiZrHfNbTaOx	mechanical alloying via the high-pressure torsion method	Low bandgap photocatalytic water splitting	[237]
Monoclinic (C12/m1), Rocksalt (Fm-3m), or Multiphase	$(\text{Co,Cu,Mg,Ni,Zn})\text{O}$ $(\text{Co,Cu,Mg,Na,Ni,Zn})\text{O}$ $(\text{Cu,Mg,Na,Zn})\text{O}$ $(\text{Cu,Mg,Na,Ni,Zn})\text{O}$ $(\text{Co,Mg,Na,Ni,Zn})\text{O}$ $(\text{Co,Cu,Na,Ni,Zn})\text{O}$ $(\text{Co,Cu,Mg,Na,Zn})\text{O}$ $(\text{Co,Cu,Mg,Na,Ni})\text{O}$	Reverse co-precipitation	Role of size, alio-/multi-valency and non-stoichiometry in the synthesis, FTIR, XPS, Raman, magnetic properties	[238]
Rock salt (Fm-3m) based	$(\text{Mg}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2})\text{O} + 1\%, 5\% \text{ Gd}$	polymeric solution method	Lattice effects from Gd addition	[239]

Table 17 continued

Crystal Structure	Compound(s)	Synthesis	Investigated Property or Application	Ref.
Rock salt (Fm-3m)	$\text{Li}_{1.3}\text{Mn}^{3+}_{0.4}\text{Ti}_{0.3}\text{O}_{1.7}\text{F}_{0.3}$ ($\text{Li}_{1.3}\text{Mn}^{2+}_{0.2}\text{Mn}^{3+}_{0.2}\text{Ti}_{0.1}\text{Nb}_{0.2}\text{O}_{1.7}$) $\text{F}_{0.3}$ ($\text{Li}_{1.3}\text{Mn}^{2+}_{0.1}\text{Co}^{2+}_{0.1}\text{Mn}^{3+}_{0.1}\text{Cr}^{3+}_{0.1}\text{Ti}_{0.1}\text{Nb}_{0.2}$) $\text{O}_{1.7}\text{F}_{0.3}$	Solid state reaction	short-range order, energy density and rate capability changes with composition for use as Li-ion cathode	[240]
Pyrochlore (Fd-3m)	($\text{La}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2}\text{Gd}_{0.2}$) $_2\text{Zr}_2\text{O}_7$	Reactive flash sintering	high density samples at low temperatures, effect of synthesis conditions on density and mechanical properties	[241]
Pyrochlore (Fd-3m)	(Sm,Yb) $_2\text{Ti}_2\text{O}_7$ (Sm,Yb,Gd) $_2\text{Ti}_2\text{O}_7$ (Sm,Yb,Gd,Er) $_2\text{Ti}_2\text{O}_7$ (Sm,Yb,Gd,Er,Dy) $_2\text{Ti}_2\text{O}_7$ ($\text{Sm}_{0.19}\text{Yb}_{0.19}\text{Gd}_{0.19}\text{Er}_{0.19}\text{Dy}_{0.19}\text{U}_{0.05}$) $_2\text{Ti}_2\text{O}_7$	Milled powders, spark plasma sintering	thermal conductivity, mechanical properties for materials design for nuclear applications	[242]
(P63/mmc) with slight impurity phase	$\text{Na}_{0.6}(\text{Ti}_{0.2}\text{Mn}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Ru}_{0.2})\text{O}_2$	Solid state reaction	Cathode design and structural changes with cycling for sodium ion batteries	[243]
Triclinic ZnMoO_4 -type (P-1)	($\text{Mg}_{0.25}\text{Ni}_{0.25}\text{Cu}_{0.25}\text{Zn}_{0.25}$) MoO_4 ($\text{Mg}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Fe}_{0.2}$) MoO_4	oxalate-based coprecipitation method	Synthesis, homogeneity, Raman, XPS	[244]
Rock salt (Fm-3m)	(($\text{Mg}_{1/3}\text{Co}_{1/3}\text{Ni}_{1/3}$) $_{1-x}\text{Zn}_x$)O $0.292 < x < 0.388$	Solid state reaction	Enthalpy of mixing correlation to ZnO concentration, predicted critical temperatures	[245]
Pyrochlore Orthorhombic (Imma)	$\text{Nd}_2(\text{Ta}_{0.2}\text{Sc}_{0.2}\text{Sn}_{0.2}\text{Hf}_{0.2}\text{Zr}_{0.2})_2\text{O}_7$ $\text{Nd}_2(\text{Ti}_{0.2}\text{Nb}_{0.2}\text{Sn}_{0.2}\text{Hf}_{0.2}\text{Zr}_{0.2})_2\text{O}_{7+x}$	Solid state reaction	Local structure PDF analysis, reverse monte carlo and ab initio molecular dynamic simulation	[246]
Perspective	Perspective	Perspective	Opportunities for High-Entropy Materials in Rechargeable Batteries	[247]
Pyrochlore or Defect Fluorite	Mixed fractions of: [($\text{Sm}_{0.25}\text{Eu}_{0.25}\text{Gd}_{0.25}\text{Yb}_{0.25}$) $_2(\text{Ti}_{0.5}\text{Hf}_{0.25}\text{Zr}_{0.25})_2\text{O}_7$] $_{1-x}$ [($\text{Sc}_{0.266}\text{Dy}_{0.248}\text{Tm}_{0.246}\text{Yb}_{0.240}$) $_3\text{NbO}_7$] $_x$ [($\text{Sc}_{0.333}\text{Dy}_{0.226}\text{Tm}_{0.224}\text{Yb}_{0.218}$) $_3\text{NbO}_7$] $_{0.5}$ [($\text{Y}_{0.266}\text{Dy}_{0.248}\text{Tm}_{0.246}\text{Yb}_{0.240}$) $_3\text{NbO}_7$] $_{0.5}$ $x = 0, 0.02, 0.1, 0.25, 0.5, 0.75, 0.9, 0.98, 1$	Solid state reaction	Order-disorder transition with composition change, thermal conductivity, young's modulus	[248]

Table 17 continued

Crystal Structure	Compound(s)	Synthesis	Investigated Property or Application	Ref.
Delafossite $\text{Na}_3\text{Ni}_2\text{SbO}_6$ - type (C2/m)	$\text{Na}_3\text{Ni}_2\text{SbO}_6$ $\text{Na}_3\text{Cu}_2\text{SbO}_6$ $\text{Na}_3(\text{CuNi})_2\text{SbO}_6$ $\text{Na}_3(\text{CuNiCo})_2\text{SbO}_6$ $\text{Na}_3(\text{CuNiCoFe})_2\text{SbO}_6$ $\text{Na}_3(\text{CuNiCoFeMn})_2\text{SbO}_6$	Solid state reaction	Synthesis, photocatalytic activity, optical band gap	[249]
Spinel (Fd-3m)	$(\text{Cr,Mn,Fe,Co,Ni})_3\text{O}_4$ $(\text{Cr,Mn,Fe,Co})_3\text{O}_4$ $(\text{Cr,Mn,Fe,Ni})_3\text{O}_4$	Solid state reaction	Structural and magnetic properties with VSM and Mossbauer	[250]
Cubic perovskite	$\text{Ba}(\text{Mg}_{0.2}\text{Zn}_{0.2}\text{Ti}_{0.2}\text{W}_{0.2}\text{Mo}_{0.2})\text{O}_3$ $\text{Ba}(\text{Zn}_{0.2}\text{Yb}_{0.2}\text{Y}_{0.2}\text{W}_{0.2}\text{Mo}_{0.2})\text{O}_3$ $\text{Ba}(\text{Mg}_{0.2}\text{Zn}_{0.2}\text{Nb}_{0.2}\text{Ta}_{0.2}\text{W}_{0.2})\text{O}_3$ $\text{Ba}(\text{Zn}_{0.2}\text{Yb}_{0.2}\text{Ti}_{0.2}\text{Nb}_{0.2}\text{W}_{0.2})\text{O}_3$ $\text{Ba}(\text{Zn}_{0.2}\text{Yb}_{0.2}\text{Nb}_{0.2}\text{Ta}_{0.2}\text{Sb}_{0.2})\text{O}_3$ $\text{Ba}(\text{Zn}_{0.2}\text{Ti}_{0.2}\text{Zr}_{0.2}\text{Hf}_{0.2}\text{W}_{0.2})\text{O}_3$ $\text{Ba}(\text{Zn}_{0.2}\text{Ti}_{0.2}\text{Zr}_{0.2}\text{Nb}_{0.2}\text{Ta}_{0.2})\text{O}_3$ $\text{Ba}(\text{Yb}_{0.2}\text{Y}_{0.2}\text{Ga}_{0.2}\text{Nb}_{0.2}\text{W}_{0.2})\text{O}_3$ $\text{Ba}(\text{Yb}_{0.2}\text{Y}_{0.2}\text{Ti}_{0.2}\text{Zr}_{0.2}\text{W}_{0.2})\text{O}_3$ $\text{Ba}(\text{Yb}_{0.2}\text{Y}_{0.2}\text{Ti}_{0.2}\text{Nb}_{0.2}\text{Ta}_{0.2})\text{O}_3$ $\text{Ba}(\text{Yb}_{0.2}\text{Ti}_{0.2}\text{Zr}_{0.2}\text{Sn}_{0.2}\text{Nb}_{0.2})\text{O}_3$ $\text{Ba}(\text{Ti}_{0.2}\text{Zr}_{0.2}\text{Hf}_{0.2}\text{Sn}_{0.2}\text{Ce}_{0.2})\text{O}_3$	Solid state reaction	Strategy for synthesis of single phase materials	[251]
Tetragonal (I4/mmm)	$\text{Bi}_2\text{V}_{1-x}(\text{Mg}_{0.25}\text{Cu}_{0.25}\text{Ni}_{0.25}\text{Zn}_{0.25})_x\text{O}_{5.5-3x/2-8}$.05 $\leq x \leq$ 0.40	Solid state reaction	Structural and electrical characterization	[252]
Aurivillius phase Orthorhombic (A21am)	$(\text{Ca}_{0.25}\text{Sr}_{0.25}\text{Ba}_{0.25}\text{Pb}_{0.25})\text{Bi}_2\text{Nb}_2\text{O}_9$ $(\text{Ca}_{0.2}\text{Sr}_{0.2}\text{Ba}_{0.2}\text{Pb}_{0.2}\text{Nd}_{0.1}\text{Na}_{0.1})\text{Bi}_2$ Nb_2O_9	Solid state reaction	Relaxor ferroelectric, domain configuration	[253]
Garnet (Ia-3d)	$(\text{Dy,Er,Gd,Ho,Y})_3\text{Fe}_5\text{O}_{12}$ $(\text{Dy,Gd,Ho,Sm,Y})_3\text{Fe}_5\text{O}_{12}$	modified Pechini method	Structure, transport properties, phase stability	[254]
Pyrochlore (Fd-3m)	$(\text{La}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Gd}_{0.2}\text{Yb}_{0.2})_2\text{Zr}_2\text{O}_7$	Solid state reaction, particle- stabilized foaming method	Comparison of synthesis methods, porosity, thermal conductivity	[255]
Rock salt (Fm-3m)	$(\text{Mg}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2})\text{O}$	microwave- assisted method	Nanoparticle synthesis for Li-ion battery applications	[256]

Table 17 continued

Crystal Structure	Compound(s)	Synthesis	Investigated Property or Application	Ref.
Pyrochlore and/or fluorite	Gd ₂ Ti ₂ O ₇	Solid state reaction	Investigation into size disorder and driving force for single phase formation	[257]
	Gd ₂ (Ti _{1/2} Zr _{1/2}) ₂ O ₇			
	Gd ₂ (Ti _{1/3} Zr _{1/3} Sn _{1/3}) ₂ O ₇			
	Gd ₂ (Ti _{1/4} Zr _{1/4} Sn _{1/4} Hf _{1/4}) ₂ O ₇			
	Gd ₂ (Ti _{1/5} Zr _{1/5} Sn _{1/5} Hf _{1/5} Ce _{1/5}) ₂ O ₇			
	Gd ₂ (Ti _{1/5} Zr _{1/5} Sn _{1/5} Hf _{1/5} Nb _{1/5}) ₂ O _{7.2}			
	(Eu _{1/2} Gd _{1/2}) ₂ Ti ₂ O ₇			
	(Eu _{1/2} Gd _{1/2}) ₂ (Ti _{1/2} Zr _{1/2}) ₂ O ₇			
	(Eu _{1/2} Gd _{1/2}) ₂ (Ti _{1/3} Zr _{1/3} Sn _{1/3}) ₂ O ₇			
	(Eu _{1/2} Gd _{1/2}) ₂ (Ti _{1/4} Zr _{1/4} Sn _{1/4} Hf _{1/4}) ₂ O ₇			
	(Sm _{1/3} Eu _{1/3} Gd _{1/3}) ₂ Ti ₂ O ₇			
	(Sm _{1/3} EuGd _{1/3}) ₂ (Ti _{1/2} Zr _{1/2}) ₂ O ₇			
	(Sm _{1/3} Eu _{1/3} Gd _{1/3}) ₂ (Ti _{1/3} Zr _{1/3} Sn _{1/3}) ₂ O ₇			
	(Sm _{1/3} Eu _{1/3} Gd _{1/3}) ₂ (Ti _{1/4} Zr _{1/4} Sn _{1/4} Hf _{1/4}) ₂ O ₇			
	(Nb _{1/4} Sm _{1/4} Eu _{1/4} Gd _{1/4}) ₂ Ti ₂ O ₇			
	(Nb _{1/4} Sm _{1/4} Eu _{1/4} Gd _{1/4}) ₂ (Ti _{1/2} Zr _{1/2}) ₂ O ₇			
	(Nb _{1/4} Sm _{1/4} Eu _{1/4} Gd _{1/4}) ₂ (Ti _{1/3} Zr _{1/3} Sn _{1/3}) ₂ O ₇			
	(Nb _{1/4} Sm _{1/4} Eu _{1/4} Gd _{1/4}) ₂ (Ti _{1/4} Zr _{1/4} Sn _{1/4} Hf _{1/4}) ₂ O ₇			
	(La _{1/5} Nd _{1/5} Sm _{1/5} Eu _{1/5} Gd _{1/5}) ₂ Ti ₂ O ₇			
	(La _{1/5} Nd _{1/5} Sm _{1/5} Eu _{1/5} Gd _{1/5}) ₂ (Ti _{1/2} Zr _{1/2}) ₂ O ₇			
	(La _{1/5} Nd _{1/5} Sm _{1/5} Eu _{1/5} Gd _{1/5}) ₂ (Ti _{1/3} Zr _{1/3} Sn _{1/3}) ₂ O ₇			
	(La _{1/5} Nd _{1/5} Sm _{1/5} Eu _{1/5} Gd _{1/5}) ₂ (Ti _{1/4} Zr _{1/4} Sn _{1/4} Hf _{1/4}) ₂ O ₇			
	(La _{1/6} Nd _{1/6} Sm _{1/6} Eu _{1/6} Gd _{1/6} Dy _{1/6}) ₂ Ti ₂ O ₇			
	(La _{1/6} Nd _{1/6} Sm _{1/6} Eu _{1/6} Gd _{1/6} Dy _{1/6}) ₂ (Ti _{1/2} Zr _{1/2}) ₂ O ₇			
	(La _{1/6} Nd _{1/6} Sm _{1/6} Eu _{1/6} Gd _{1/6} Dy _{1/6}) ₂ (Ti _{1/3} Zr _{1/3} Sn _{1/3}) ₂ O ₇			
	(La _{1/6} Nd _{1/6} Sm _{1/6} Eu _{1/6} Gd _{1/6} Dy _{1/6}) ₂ (Ti _{1/4} Zr _{1/4} Sn _{1/4} Hf _{1/4}) ₂ O ₇			
	(La _{1/7} Nd _{1/7} Sm _{1/7} Eu _{1/7} Gd _{1/7} Dy _{1/7} Ho _{1/7}) ₂ Ti ₂ O ₇			
	(La _{1/7} Nd _{1/7} Sm _{1/7} Eu _{1/7} Gd _{1/7} Dy _{1/7} Ho _{1/7}) ₂ (Ti _{1/2} Zr _{1/2}) ₂ O ₇			
	(La _{1/7} Nd _{1/7} Sm _{1/7} Eu _{1/7} Gd _{1/7} Dy _{1/7} Ho _{1/7}) ₂ (Ti _{1/3} Zr _{1/3} Sn _{1/3}) ₂ O ₇			
	(Gd _{1/7} Eu _{1/7} Sm _{1/7} Nd _{1/7} La _{1/7} Dy _{1/7} Ho _{1/7}) ₂ (Ti _{1/4} Zr _{1/4} Sn _{1/4} Hf _{1/4}) ₂ O ₇			
	(Nd _{1/5} Sm _{1/5} Gd _{1/5} Ho _{1/5} Er _{1/5}) ₂ Zr ₂ O ₇			
	(Sm _{1/5} Eu _{1/5} Gd _{1/5} Dy _{1/5} Er _{1/5}) ₂ Zr ₂ O ₇			
	(Sm _{1/5} Gd _{1/5} Dy _{1/5} Ho _{1/5} Er _{1/5}) ₂ Zr ₂ O ₇			
	(Sm _{1/5} Gd _{1/5} Ho _{1/5} Er _{1/5} Tm _{1/5}) ₂ Zr ₂ O ₇			
	(Eu _{1/5} Dy _{1/5} Ho _{1/5} Er _{1/5} Tm _{1/5}) ₂ Zr ₂ O ₇			
	(Gd _{1/5} Dy _{1/5} Ho _{1/5} Tm _{1/5} Yb _{1/5}) ₂ Zr ₂ O ₇			
	(Gd _{1/5} Ho _{1/5} Er _{1/5} Tm _{1/5} Lu _{1/5}) ₂ Zr ₂ O ₇			
	(Dy _{1/5} Er _{1/5} Tm _{1/5} Yb _{1/5} Lu _{1/5}) ₂ Zr ₂ O ₇			
Frontier article	Frontier article	Frontier article	Magnetic properties of high entropy oxides	[258]
Orthorhombic perovskite	(La _{0.2} Y _{0.2} Nd _{0.2} Gd _{0.2} Sr _{0.2})CrO ₃	Sol-gel	Effect of porosity on resistivity and thermal conductivity	[259]

Table 17 continued

Crystal Structure	Compound(s)	Synthesis	Investigated Property or Application	Ref.
Rocksalt, Fluorite, Spinel	$(\text{Zr,Ce,Hf,Ti,Mn,Co})\text{O}_{2-x}$	Solutions dried onto CNF films, dried and heated	nanoparticles design, synthesis, and structure and stability for catalytic methane combustion	[260]
	$(\text{Zr,Ce,Hf,Ti,La,Y})\text{O}_{2-x}$			
	$(\text{Zr,Ce})_{0.6}(\text{Mg,La,Y,Hf,Ti,Cr,Mn})_{0.3}\text{Pd}_{0.1}\text{O}_{2-x}$			
	$(\text{Zr,Ce})_{0.6}(\text{Mg,Hf,Ti,Cr,Mn,Fe,Cu})_{0.3}\text{Pd}_{0.1}\text{O}_{2-x}$			
	$(\text{Zr,Ce})_{0.66}(\text{Mg,La,Y,Hf,Ti,Cr,Mn})_{0.34}\text{O}_{2-x}$			
Y_2O_3 type cubic (Ia-3)	$(\text{Lu,Y,Yb,Gd,Dy})_2\text{O}_3$	Ball mill, vacuum sintering	Transparent ceramic for application as multi-wavelength emission phosphor transparent ceramics	[261]
Perovskite	$\text{Ba}(\text{Ti,Hf,Zr,Fe,Sn})\text{O}_3$ $\text{Ba}(\text{Hf,Zr,Fe,Sn})\text{O}_3$ $\text{Ba}(\text{Ti,Hf,Zr,Sn})\text{O}_3$	spin coating and hydrothermal synthesis	films on fluorine doped tin oxide substrates. Distortion, use in piezoelectric and ferroelectric applications	[262]
Pyrochlore	$\text{Y}_2(\text{TiZrHfMoV})_2\text{O}_7$	Reverse co-precipitation	Synthesis, phase, hardness, Young's moduli	[263]
Review article	Review article	Review article	The role of cation ordering and disordering on mass transport in complex oxides	[264]
Perovskite	$\text{Ba}(\text{Zr}_{0.2}\text{Sn}_{0.2}\text{Ti}_{0.2}\text{Hf}_{0.2}\text{Nb}_{0.2})\text{O}_3$	Sol-gel, spin coat	electronic structure and charge transport properties	[265]
Review article	Review article	Review article	High Entropy Oxides-Exploring a Paradigm of Promising Catalysts: A Review	[266]
Cubic Perovskite (Pm-3m)	$(\text{Ca}_{0.2}\text{Sr}_{0.2}\text{Ba}_{0.2}\text{Pb}_{0.2}\text{La}_{0.2})\text{TiO}_3$	Solid state reaction	Electrical and thermal transport properties for use as thermoelectric material	[267]
ZnO wurtzite	$(\text{Ba}_x\text{Sr}_x\text{Mn}_x\text{Fe}_x\text{Ni}_x)\text{Zn}_{1-5x}\text{O}$ where $x=0, 0.01, 0.02$, and 0.03	spray pyrolysis deposition	Structure, morphology, UV-Vis bandgap	[268]
Spinel (Fd-3m)	$(\text{Al}_{0.2}\text{CoCrFeMnNi})_{0.58}\text{O}_{4-\delta}$ $(\text{CoCrFeMnNi})_{0.6}\text{O}_{4-\delta}$	Solution combustion synthesis	Structural stability and cycling performance for anode material for li-ion batteries	[269]

Table 18 Summary of starting elemental oxide materials, their structure, possible charge state, radii and occupancy preference. Site preference is based off of the known energetic preference for the constituent and charge state. *HS =high spin, LS=low spin.

Starting Oxide	Crystal Structure	Charge State	Coordination Number	Cation radius (Å)	Ionic Radius (Å)	Cation Site preference
MgO	Rocksalt	Mg ²⁺	4 6	0.71 0.86	0.57 0.72	Tetrahedral
NiO	Rocksalt	Ni ²⁺	4 6	0.63 0.83	0.49 0.69	Octahedral
CoO	Rocksalt	Co ²⁺	4 HS 6 LS 6 HS	0.72 0.79 0.885	0.58 0.65 0.745	Tetrahedral
CuO	Monoclinic CuO	Cu ²⁺	4 6	0.71 0.87	0.57 0.73	Octahedral
ZnO	Wurtzite	Zn ²⁺	4 6	0.74 0.88	0.60 0.74	Tetrahedral
MnO ₂	Rutile	Mn ²⁺	4 HS	0.80	0.66	Tetrahedral
			6 LS	0.81	0.67	
			6 HS	0.97	0.83	
		Mn ³⁺	6 LS 6 HS	0.72 0.785	0.58 0.645	Octahedral
Fe ₂ O ₃	Corundum	Fe ²⁺	4 HS	0.77	0.63	Octahedral
			6 HS	0.92	0.78	
			6 LS	0.75	0.61	
		Fe ³⁺	4HS 6 HS 6 LS	0.63 0.785 0.69	0.49 0.645 0.55	Tetrahedral
Al ₂ O ₃	Corundum	Al ³⁺	4 6	0.53 0.675	0.39 0.535	Octahedral
Cr ₂ O ₃	Corundum	Cr ²⁺	6HS 6LS	0.94 0.87	0.8 0.73	-
		Cr ³⁺	6	0.755	0.615	Octahedral
		Cr ⁴⁺	4 6	0.55 0.69	0.41 0.55	Tetrahedral

Table 19 Summary of starting material compositions and purities for both solid state and polymeric steric entrapment methods.

Solid State Reaction			Polymeric Steric Entrapment		
CuO	Puratronic-Alfa Aesar	99.995%	Cu (NO ₃) ₂ hydrate	Alfa Aesar	99.999%
Dy ₂ O ₃	REacton-Alfa Aesar	99.9%	Dy (NO ₃) ₃ 5H ₂ O	Alfa Aesar	99.99%
Eu ₂ O ₃	REacton-Alfa Aesar	99.99%	Eu (NO ₃) ₃ 6H ₂ O	Acros Organics	99.9%
Gd ₂ O ₃	REacton-Alfa Aesar	99.9%	Gd (NO ₃) ₃ 6H ₂ O	Alfa Aesar	99.9%
La ₂ O ₃	Acros Organics	99.99%	La (NO ₃) ₃ 6H ₂ O	Alfa Aesar	99.99%
Nd ₂ O ₃	REacton-Alfa Aesar	99.9%	Nd (NO ₃) ₃ hydrate	Alfa Aesar	99.99%
Pr ₆ O ₁₁	REacton-Alfa Aesar	99.99%	Pr (NO ₃) ₃ 6H ₂ O	Strem Chemicals	99.9%
Sm ₂ O ₃	REacton-Alfa Aesar	99.9%	Sm (NO ₃) ₃ 6H ₂ O	Alfa Aesar	99.9%
Tb ₄ O ₇	REacton-Alfa Aesar	99.9%	Tb (NO ₃) ₃ 5H ₂ O	Aldrich	99.9%
NbO ₂	Alfa Aesar	99+%	Bi(NO ₃) ₃ 5H ₂ O	Acros Organics	98%
MgO	Alfa Aesar	99.95%	Mg (NO ₃) ₂ 6H ₂ O	Alfa Aesar	99.97%
NiO	Alfa Aesar	99.998%	Ni(NO ₃) ₂ 6H ₂ O	Alfa Aesar	99.9985%
CoO	Alfa Aesar	99.995%	Co(NO ₃) ₂ 6H ₂ O	Alfa Aesar	99.999%
ZnO	Puratronic-Alfa Aesar	99.9995%	Zn (NO ₃) ₂ 6H ₂ O	Acros organics	98%
MnO	Alfa Aesar	99.99%	Al(NO ₃) ₃ 9H ₂ O	Puratronic	99.999%
Al ₂ O ₃	Strem Chemicals	99.999%	Cr(NO ₃) ₃ 9H ₂ O	Alfa Aesar	99.99%
Cr ₂ O ₃	Puratronic-Alfa Aesar	99.97%	Fe (NO ₃) ₃ 9H ₂ O	Sigma aldrich	99.95%
Fe ₂ O ₃	Puratronic-Alfa Aesar	99.998%	Mn(CH ₃ COO) ₂ 4H ₂ O	Puratronic	99.999%
Y ₂ O ₃	REacton-Alfa Aesar	99.99%	Ho(NO ₃) ₃ 5H ₂ O	Alfa Aesar	99.9%
SrO	Strem Chemicals	99.9%	Ga(NO ₃) ₃ XH ₂ O	Alfa Aesar	99.9%
SnO ₂	Acros Organics	99.9%	Ce(NO ₃) ₃ 6H ₂ O	Alfa Aesar	99.99%
Nb ₂ O ₅	Puratronic-Alfa Aesar	99.9985%	Yb(NO ₃) ₃ 5H ₂ O	Strem Chemicals	99.9%
TiO ₂	Puratronic-Alfa Aesar	99.995%	Y(NO ₃) ₃ 6H ₂ O	Alfa Aesar	99.9%
ZrO ₂	Puratronic-Alfa Aesar	99.978%	Ni(CH ₃ COO) ₂ 4H ₂ O	Puratronic	99.999%
BaO	Alfa Aesar	99.5%	Al(NO ₃) ₃ 9H ₂ O	Acros Organics	99+%
HfO ₂	Alfa Aesar	99.95%	Poly(vinyl alcohol)	87-89% hydrolyzed	Sigma
Ho ₂ O ₃	REacton-Alfa Aesar	99.9%	Mw 13,000-23,000,		Aldrich
Bi ₂ O ₃	Puratronic-Alfa Aesar	99.999%			
CeO ₂	REacton-Alfa Aesar	99.9%			

VITA

Brianna Leigh Musicó was born in Nevada to the parents of Kevin and Lori Musicó. She is the first of three children with younger sister Madeline Marie and brother Vincenzo Joseph. She attended primary and secondary schools in Ohio and Texas and graduated High School from The John Cooper School in The Woodlands, Texas in 2012. She received her bachelor's degree in Materials Science and Engineering with an honors concentration from the University of Tennessee Knoxville in August of 2016. She received her master's degree in December 2018 and her PhD degree in May 2021, both in Materials Science and Engineering from the University of Tennessee Knoxville. Her dissertation is focused on the synthesis and application of disorder to multicomponent oxide systems and the effects of compositional variation and synthesis method on the material properties. Outside of her thesis project, she has collaborated with other scientists on multiple projects. These include resonant ultrasound spectroscopy studies on high entropy alloys and hybrid perovskites, providing bulk ceramic samples to collaborators at Oak Ridge National Laboratory for thin film growth of high entropy oxide compositions, and assisted with x-ray diffraction measurements on various materials. She has actively served as a mentor for many MSE undergraduate students doing research supported by the Center for Materials Processing (CMP) and served as the lab manager for the Dr. Keppens and Dr. Mandrus group labs.

Brianna will be continuing a career in scientific research and has accepted a postdoctoral research position at Los Alamos National Laboratory in New Mexico.