

**Mechanochemical and Combustion Syntheses of
Cerium-Doped Lutetium Oxyorthosilicate Powders
and Preliminary Studies into the Syntheses of
Optically-Active Beta-Germanium(IV) Oxide and
Alpha-Quartz Nanoparticles**

A Dissertation Presented for the
Doctor of Philosophy
Degree
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Dedication

I would like to dedicate this dissertation to my husband, J. Samuel Bailey. I could not have made it through this journey without your constant support, love, and unending faith in me. I would also like to dedicate this to my parents, John and Lisa Lassig, who encouraged me to always do what I love and what makes me happy. Throughout my life, you have led by example with your dedication, hard work, and compassion. I would not have made it this far without the three of you.

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Abstract

Lu₂SiO₅:Ce powders were produced using solvent-free mechanochemistry. The Burzio-Rojac model for the planetary ball mill was used to conduct a parametric study of this synthesis, investigating the effect of varying the powder mass, the vial and ball density, the number of balls, the diameter of the balls, and the rotation rate of the mill on reaction time. The influence of additives was researched with Zn possibly leading to increased reduction of Ce⁴⁺ to Ce³⁺ and with various solvents hindering or preventing Lu₂SiO₅:Ce production.

The solution and gel combustion syntheses of Lu₂SiO₅:Ce powders were executed using the fuels urea and hexamethylenetetramine both individually and as a mixture. The mixed-fuel solution combustion method successfully produced LSO:Ce powder with excellent replicability. This method produced LSO:Ce powders with a combination of the $P 1\ 2_1/c\ 1$ and $C 1\ 2/c\ 1$ space groups, which were compared to mechanochemically-produce LSO:Ce powders with $C 1\ 2/c\ 1$ symmetry.

Lu₂SiO₅:Ce powders produced by each method were sintered using either a microwave or a furnace. While furnace sintering increased intensity in their photoluminescence excitation and emission spectra, the intensity was decreased with microwave sintering. By furnace sintering the previously microwaved-sintered powder in air, it was determined that oxygen vacancies created during microwave sintering caused the loss of photoluminescence intensities.

Preliminary studies were conducted to synthesize optically-active α [alpha]-quartz nanoparticles using optically-active β [beta]-GeO₂ nanoparticles as a template. Templating optical activity in β [beta]-GeO₂ nanoparticles using L-lysine and (R)-(+)-1,2-diaminopropane as templating agents was attempted. No optical activity was observed in polarimetry and circular dichroism measurements, which was most likely due to insufficient capping agent adsorption. *Rac*- β [beta]-GeO₂ nanoparticles were used to attempt to template α [alpha]-quartz at room temperature as well as when heated in NaOH, NH₄OH, Ba(OH)₂, and CsOH solutions. α [alpha]-Quartz did not form in any powders although the silica may have dissolved during the heating.

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List of Abbreviations

Acac	Acetylacetone
α -SiO ₂	α -Quartz
BGO	Bismuth Germanate (Bi ₄ Ge ₃ O ₁₂)
Bij 30	Polyoxyethylene (23) Lauryl Ether
CCD	Charge Coupled Device
CD	Circular Dichroism
DAP	1,2-Diaminopropane
DAP-GeO ₂	β -GeO ₂ Produced in the Presence of 1,2-Diaminopropane
DMF	Dimethylformamide
DMSO	Dimethylsulfoxide
DLS	Dynamic Light Scattering
EDS	Energy-Dispersive X-Ray Spectroscopy
EDTA	Ethylenediaminetetraacetate
EG	Ethylene Glycol
FT	Fourier Transform
FTIR	Fourier Transform Infrared Spectroscopy
FWHM	Full Width Half Maximum
GC	Gel Combustion
GSO:Ce	Cerium-Doped Gadolinium Oxyorthosilicate (Gd ₂ SiO ₅ :Ce)
HIPing	Hot Isostatic Pressing
ICSD	Inorganic Crystal Structure Database
IR	Infrared
JIAM	Joint Institute for Advanced Materials
LAG	Liquid-Assisted Grinding
λ_{em}	Emission Wavelength
λ_{ex}	Excitation Wavelength
LHPG	Laser Heated Pedestal Growth
LPS	Lutetium Pyrosilicate (Lu ₂ Si ₂ O ₇)
LSO	Lutetium Oxyorthosilicate (Lu ₂ SiO ₅)

LSO:Ce	Cerium-Doped Lutetium Oxyorthosilicate ($\text{Lu}_2\text{SiO}_5\text{:Ce}$)
LSO Std	Ball-milled Czochralski-grown $\text{Lu}_2\text{SiO}_5\text{:Ce}$ crystal
Lys	Lysine
Lys-GeO ₂	β -GeO ₂ Produced in the Presence of Lysine
MC	Mechanochemistry
MC-LSO:Ce	$\text{Lu}_2\text{SiO}_5\text{:Ce}$ Produced Through Mechanochemistry
MS	Mass Spectrometry
m/z	Mass-to-Charge Ratio
NRF	Nano Research Facility
PCL	Polymer Characterization Lab
PET	Positron Emission Tomography
PL	Photoluminescence
PMT	Photomultiplier Tube
PSA	Particle Size Analysis
PXRD	Powder X-Ray Diffraction
SC	Solution Combustion
SC-LSO:Ce	$\text{Lu}_2\text{SiO}_5\text{:Ce}$ Produced Through Solution Combustion
SEM	Scanning Electron Microscopy
S/N	Signal-to-Noise Ratio
Span 80	Sorbitane Monooleate
TCSPC	Time-Correlated Single Photon Counting
TEM	Transmission Electron Microscopy
TEOG	Germanium(IV) Ethoxide
TEOS	Tetraethoxysilane
TGA	Thermogravimetric Analysis
TGA-MS	Thermogravimetric Analysis with Mass Spectrometry
TX-114	Triton X-114

CHAPTER 1
INTRODUCTION

1.1. Nanoparticles

Nanoparticles (i.e. particles in the size range of 1-100 nm) have been studied for a wide range of fields and applications. This interest stems from their unique properties which differ from their macroscopic counterparts and can even vary based on the diameter of the nanoparticles themselves. Nanoparticle research is therefore commonly conducted based on specific applications or specific desired properties. Two particular areas of interest, which will be discussed in this dissertation, are scintillating materials and optically-active compounds.¹⁻²

1.2. Scintillators

1.2.1. Introduction to Scintillators

Scintillators are materials which luminesce upon interaction with radiation. This scintillation or emission of light was first observed in the early 1900's by Röntgen who used calcium tungstate (CaWO_4) in the discovery of X-rays and by William Crookes and Rutherford who used zinc sulfide (ZnS) for radiation detection and the study of alpha particle scattering, respectively. In the 1940's, the photomultiplier tube (PMT), which converts the emitted photons from scintillators into an amplified electrical signal, was developed, allowing better detection of radiation. Soon after, naphthalene and still widely-used NaI:TI scintillators were discovered and developed. This research led to the study and development of countless other scintillators over the last several decades, including noble gases, organic liquids and solids, and inorganic crystals.³⁻⁴

To maximize the efficiency of these scintillators for radiation detection and measurement, research has been primarily focused on the optimization of a set of idealized properties, which are listed below.

1. The material should be transparent to its own emission, so scintillations can escape the crystal and be measured outside of the material.
2. The emission wavelength should match a PMT or photodiode for amplification of the signal; however, a wavelength shifter may be used if the scintillator's emission does not match.
3. The total energy deposited into the crystal should be directly proportional to the light output. This property is known as the linearity of the scintillator and leads to

good energy resolution.

4. The light yield per energy unit deposited should be high to increase the scintillators efficiency.
5. The scintillations should have a short decay time, leading to better detection resolution.
6. The material should have a short radiation absorption length, which decreases the amount of material necessary for detection and measurement.
7. The index of refraction should be close to that of glass (about 1.5) to aid in the coupling of the scintillator to a PMT or photodiode.
8. Finally, the material should be chemically stable and capable of being produced in large quantities and sizes for industrial use.⁵

For practical use, the selection of scintillators requires compromising for the necessary properties as no one scintillator has all the above properties. For example, gaseous and organic scintillators usually have faster decay times than inorganic crystals. They are therefore more often used for fast timing studies. Conversely, inorganic crystals tend to have higher densities and effective atomic numbers, which lead to shorter attenuation lengths for photon detection.⁵⁻⁶

1.2.2. Inorganic Scintillators

For the detection and measurement of gamma-rays and X-rays, inorganic scintillators are typically used. These scintillators tend to have better energy resolution than organic scintillators. They also typically have higher densities and effective atomic numbers than gaseous and organic scintillators, which give them higher stopping powers for high-energy photons. This increased stopping power means they have shorter attenuation lengths and less material is required for the detection and measurement of this type of radiation.^{3, 5-7} All of these properties make them effective in applications in positron emission tomography (PET), oil well logging, monitoring in nuclear plants, high-energy physics, and some security purposes.^{4, 7-8}

The general mechanism for scintillation in inorganic scintillators (Figure 1.1) starts with the interaction of radiation with the scintillator. For gamma and X-ray detection, this interaction is through the photoelectric effect, Compton scattering, and/or pair

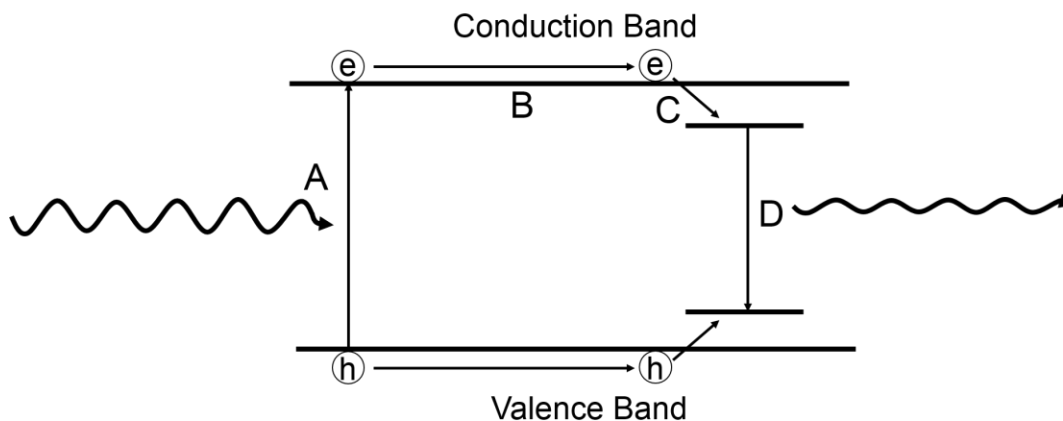


Figure 1.1. General mechanism for inorganic crystal scintillation. (A) A photon interacts with the crystal and excites an electron from the valence band to the conduction band, leaving a positively-charged hole in the valence band. (B) After partial relaxation through non-radiative processes, the electron and hole can move through the structure either together or separately. (C) The electron and the hole reach a dopant site, which has energy levels within the band gap. (D) Once both a hole and an electron are present at the dopant site, creating a dopant in its excited state, the two charge carriers recombine radiatively, emitting a photon with a longer wavelength than the initial photon.^{5-6, 8} Image adapted from references 5, 6, and 8.

production.⁸ When the incoming radiation has energy of approximately three times the band gap energy or more, the interactions can excite an electron from the valence band to the conduction band of the crystal. This excitation leaves a positively-charged hole in the valence band and creates an electron-hole pair.⁵ Partial relaxation then occurs through inelastic processes including electron-electron scattering and the production of secondary X-rays and Auger electrons.⁸ The electron and hole can then move through the crystal either together as an exciton or separately. When the hole travels separately from the electron, it reaches an activator site and ionizes the dopant because the dopant has a lower ionization energy than other sites in the crystal. Once an electron reaches this site, the dopant is returned to its original state but in an excited state. When the electron and hole travel together as an exciton, they reach the activator site simultaneously, creating a dopant in its excited state. The energy levels of the dopant fall within the band gap, which can lead to the emission a photon in the visible region when recombination of the electron and hole occurs.^{5-6, 8}

1.2.3. Synthesis of Inorganic Scintillators

Single Crystals

The main methods of producing single crystals of inorganic scintillators are Czochralski, Bridgman, floating zone, and micro-pulling down methods with the Czochralski and Bridgman methods being the prominent processes for large crystals.⁹⁻¹⁰ The Czochralski technique (Figure 1.2a) involves melting precursor materials and dipping a seed crystal into this melt. As this seed crystal is rotated and slowly drawn out of the melt, the melt crystallizes on its surface to form a single crystal boule.⁹ In the Bridgman technique (Figure 1.2b), starting materials are melted then slowly cooled from one end of the melt which contains a seed crystal to the opposite end, causing crystallization as it is cooled.⁹

These methods present several major issues. The first of which is high production costs. Expensive iridium crucibles are required to reach the temperatures needed to melt the precursors of many inorganic crystals.¹¹ The processes are also time-consuming with pull rates typically on the scale of a few millimeters per hour.¹² Furthermore, they can cause to inconsistent doping throughout the crystals, which changes the scintillation

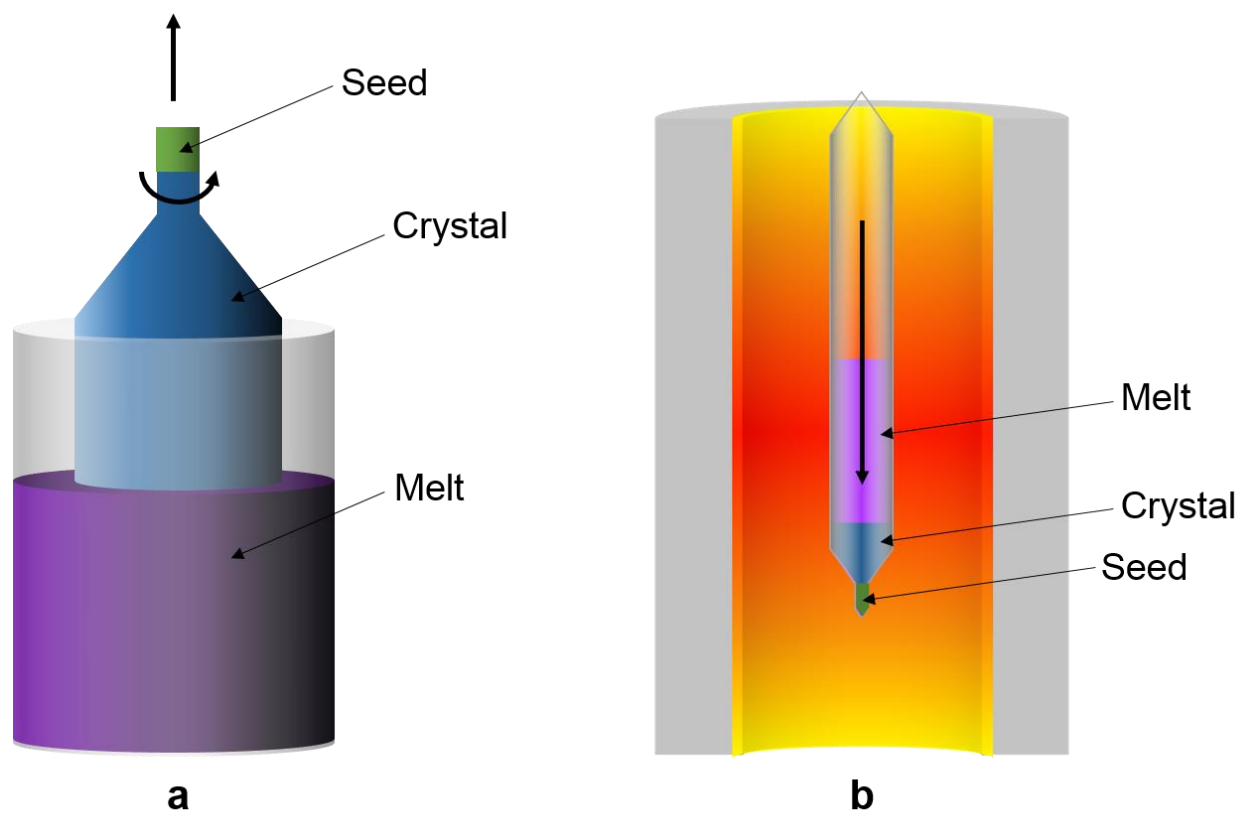


Figure 1.2. Illustrations of two common methods of producing large single crystals of inorganic scintillators. (a) Czochralski Growth and (b) Bridgman Growth. Images adapted from references by Lecoq, *et al.*,⁸ Dhanaraj, *et al.*,⁹ and Chen, *et al.*¹³

efficiency from the start of the crystal to the end.⁸

Ceramics

Due to the drawbacks that arise from the production of single crystals, there has been a shift from research of these large single crystals to transparent pellets made by pressing nanoparticles. These transparent pellets will be referred to as ceramics in this dissertation. Ceramics allow higher activator concentrations with better doping uniformity than their single crystal counterparts.¹⁴ They are also capable of reaching densities that are 99.9% of their single crystal counterparts.¹⁵ In contrast to single crystals, ceramic production has relatively low temperatures and short production times, which decrease the cost to generate these scintillators. The low temperatures further reduce overall costs by rendering the use of expensive iridium crucibles unnecessary.¹⁵⁻¹⁷

The scintillation properties of these ceramics can vary from the single crystals. The extent of these differences is dependent on the synthesis of the nanoparticles. This dependence may be due in part to better packing density and smaller pore sizes with the use of smaller nanoparticles with little to no aggregation or agglomeration.¹⁸ Research of various production methods for these types of nanoparticles is therefore paramount to the optimization of their scintillation properties in ceramics. Recent studies have therefore focused on the production of numerous scintillating nanoparticles through various methods, including sol-gel processes,¹⁹⁻²⁰ spray pyrolysis,^{14, 16, 21-23} hydrothermal methods,²⁴ solution/gel combustion,^{17, 22, 25} co-precipitation,²⁶⁻²⁷ molten salt methods,²⁸ mechanochemical processes,²⁵ and solid-state reactions.²⁹⁻³⁰ The nanoparticles are then pressed to form pellets followed by hot isostatic pressing (HIPing) at high temperatures and pressures to form ceramics.^{14-16, 27, 29, 31-32}

1.2.4. Cerium-Doped Lutetium Oxyorthosilicate (LSO:Ce)

Application and Properties of LSO:Ce

Cerium-doped lutetium oxyorthosilicate (LSO:Ce), usually with the $C 1 2/c 1$ space group, is most commonly used for gamma-ray detection, but it is also capable of detecting X-rays, cosmic rays, and 1-keV or higher energy photons.³³⁻³⁴ LSO:Ce is ideal for these applications due to several of its scintillation properties, which are listed in Table 1.1 along with the properties of NaI:Tl and Bi₄Ge₃O₁₂ (BGO) which have been used for similar

Table 1.1. LSO:Ce properties in comparison with other inorganic scintillators used for PET.

Detector	LSO:Ce (Lu ₂ SiO ₅ :Ce)	NaI:Tl	BGO (Bi ₄ Ge ₃ O ₁₂)
Effective Atomic Number (Z) ^a	66	51	75
Density (g/cm ³) ^a	7.4	3.67	7.13
Attenuation Length for 662-keV photon (cm) ^b	1.50	3.56	1.41
Attenuation Length for 511-keV photon (cm) ^b	1.15	2.92	1.04
Attenuation Length for 30-keV photon (μm) ^b	87	370	59
Relative Light Yield (%) ^a	75	100	15
Scintillation Decay Time (ns) ^a	40	230	300
Resolution (% FWHM at 662 keV) ^{c,d}	11	7	12
Refractive Index ^a	1.82	1.85	2.15
Maximum Emission Wavelength (nm) ^a	420	410	480
Rugged? ^a	Yes	No	Yes
Hygroscopic? ^a	No	Yes	No

^aElftmann, R.; Tammen, J.; Kulkarni, S. R.; Martin, C.; Böttcher, S.; Wimmer-Schweingruber, R., Characterization of an LSO scintillator for space applications. *Journal of Physics: Conference Series* **2015**, 632 (1), 012006.

^bThe attenuation length is the thickness of material through which a beam of light must travel before its intensity is decreased to 1/e of its initial intensity, which occurs when approximately 63% of photons have been absorbed. This value can be calculated using the equation $I(E)/I_0(E) = e^{-(\mu/\rho)\rho x}$, where $I(E)/I_0(E)$ is 1/e, μ/ρ is the total mass attenuation coefficient with coherent scattering for a given photon energy in cm²/g (found at the following reference³⁵), ρ is the density of the material in g/cm³, and x is the attenuation length in cm.⁵ Berger, M. J.; Hubbell, J. H.; Seltzer, S. M.; Chang, J.; Coursey, J. S.; Sukumar, R.; Zucker, D. S.; Olsen, K., XCOM: Photon Cross Sections Database. 2010 ed.; National Institute of Standards and Technology: Gaithersburg, MD, 2010; Vol. 1.5.

^cRusso, P.; Vo, D. *Gamma-ray detectors for nondestructive analysis*; LA-UR-05-3813; Los Alamos National Laboratory: 2005; p 42.

^dFWHM is full-width at half maximum.

applications. LSO:Ce has a high stopping power for gamma photons due to its high effective atomic number ($Z = 66$) and high density ($\rho = 7.4 \text{ g/cm}^3$).^{33, 36} These properties indicate a high detection efficiency and short attenuation length (1.14 cm for 511-keV gamma rays; 87 μm for 30-keV X-rays), which suggest that less material would be necessary to detect incoming photons.^{33, 35-36} The light yield of these crystals is approximately 26,000 ph/MeV or 75% that of NaI:Tl, which is commonly used as a standard due to its high light yield. LSO:Ce also has a short scintillation decay time of approximately 40 ns. This high light yield and short decay time result in higher counting rates and better resolution. The material's refractive index is about 1.82, and its maximum emission wavelength is about 420 nm. The index of refraction is close to that of glass, which aids in the transmission of photons from the scintillator into the PMT while the emission wavelength matches the PMT for efficient conversion of photons to electrons. LSO:Ce is rugged and non-hygroscopic, which is beneficial for production, storage, and use. This stability is a major advantage over materials like NaI:Tl, which is hygroscopic, and $\text{Gd}_2\text{SiO}_5\text{:Ce}$ (GSO:Ce), which cleaves easily.^{5, 33, 36-37}

Due to the properties listed above, Czochralski-grown crystals of LSO:Ce with the $C 1 2/c 1$ space group are currently widely-used in positron emission tomography (PET). In PET, a positron-emitter is injected into the patient. The emitted positrons will annihilate with an electron, and two 511 keV photons are emitted in opposite directions. The photons are absorbed by the LSO:Ce surrounding the patient.³⁸ A PET schematic of this portion of the process is depicted in Figure 1.3. The interaction between the LSO:Ce and the radiation leads to a Ce^{3+} atom in its excited state with an electron in the 5d orbital and a hole in the 4f orbital.^{17, 39-40} This electron non-radiatively relaxes to the lowest 5d level, and the subsequent $5d \rightarrow {}^2F_J$ ($J = 5/2$ or $7/2$) de-excitation of the electron results in the emission of visible light.^{17, 39-41} The visible light is converted into an electric signal and magnified by a PMT or photodiode.⁴²

Structure of LSO:Ce

Lanthanide oxyorthosilicates (Ln_2SiO_5) tend to have one of two structures. Smaller lanthanides (Y and Dy to Lu) typically have a monoclinic structure with the $C 1 2/c 1$ space group (Figure 1.4).⁴³ This structure has edge-sharing OLu_4 tetrahedra that form chains,

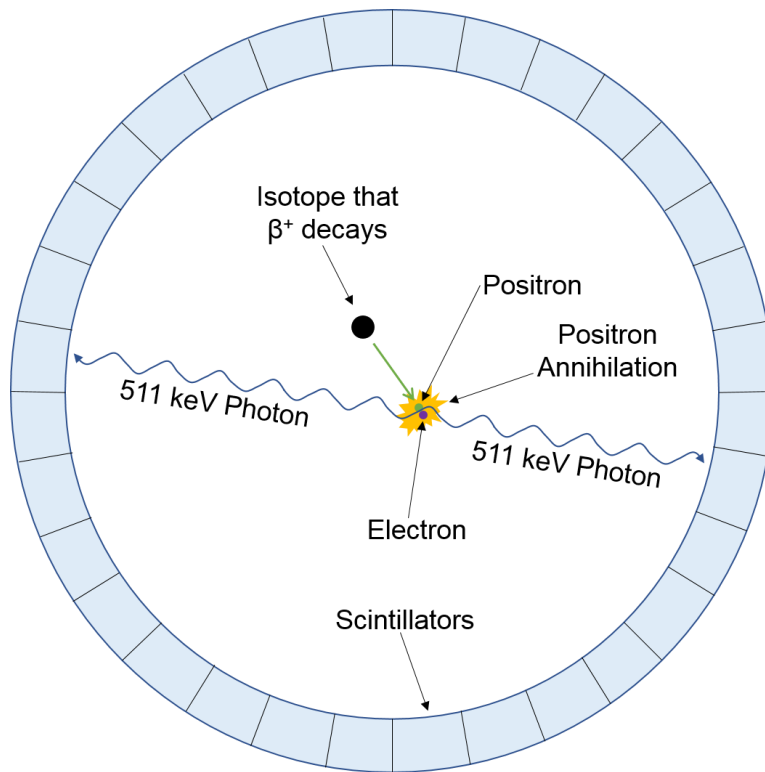


Figure 1.3. General schematic of a PET scanner. Image adapted from references by Tsoulfanidis, *et al.*⁶, Elftmann, *et al.*,³⁷ and van Eijk, *et al.*⁴⁵

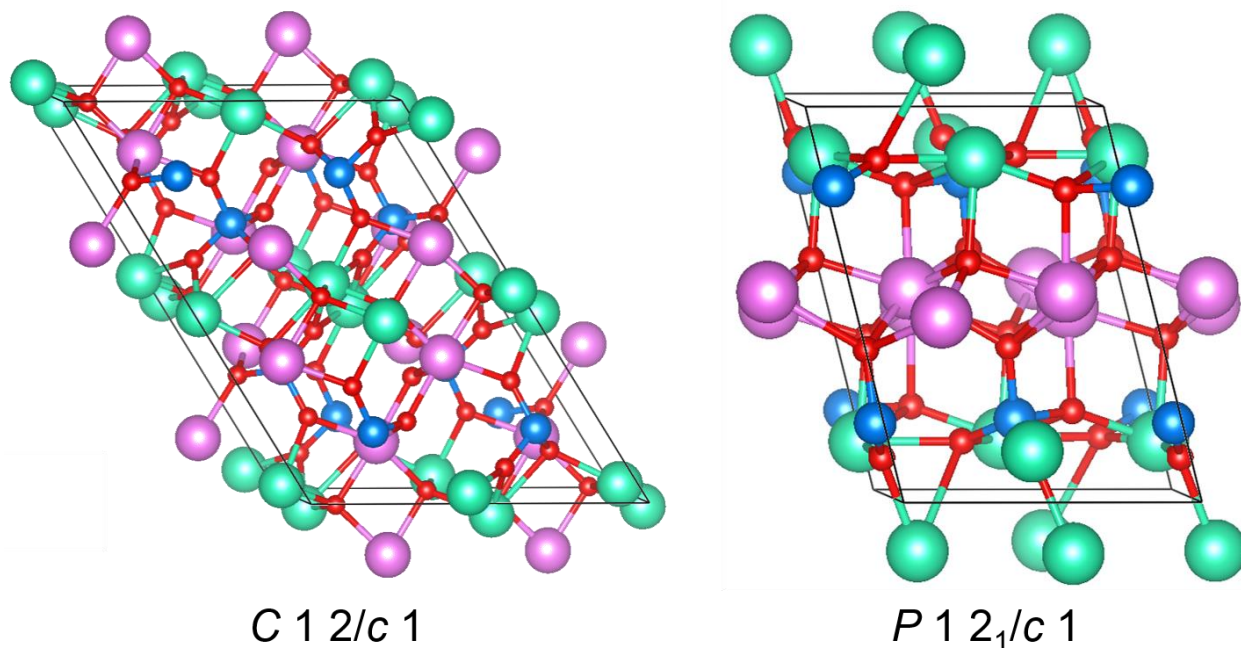


Figure 1.4. Crystal structures of Lu_2SiO_5 . The two crystallographically distinct lutetium sites are represented by pink and green spheres. Pink spheres represent the Lu1 site, which have oxygen coordinations of six and seven for the $C 1 2/c 1$ and $P 1 2_1/c 1$ structures, respectively. Green spheres represent the Lu2 site, which have oxygen coordinations of seven and nine for the $C 1 2/c 1$ and $P 1 2_1/c 1$ structures, respectively. The blue spheres are silicon, and the red spheres are oxygen. Image created using data from references by Gustafsson, *et al.*⁴⁶ and Müller-Bunz, *et al.*⁴⁷

which are connected by SiO_4 tetrahedra.⁴³⁻⁴⁴ It has two crystallographically distinct lanthanide sites with oxygen coordinations of six and seven.³⁹ Alternatively, larger lanthanides (La to Tb) tend to form a monoclinic structure with the $P 1 2_1/c 1$ space group (Figure 1.4).⁴³ In this structure, corner-linked OLu_4 tetrahedra form 2D networks that are connected by SiO_4 tetrahedra.⁴³⁻⁴⁴ This structure also has two crystallographically distinct lanthanide sites with oxygen coordinations of seven and nine.³⁹

Lutetium oxyorthosilicate (LSO) has been synthesized with both structures. The $C 1 2/c 1$ type typically forms with higher temperature syntheses like the Czochralski method while the $P 1 2_1/c 1$ type has been seen with lower temperature syntheses like nitrate-hexamethylenetetramine solution combustion.^{33, 43, 48-50}

Many of the properties listed for LSO:Ce are the same for both phases. The major differences are the maximum excitation and emission wavelengths. Where the maximum excitation and emission wavelengths for the $C 1 2/c 1$ space group are 357 nm and 420 nm, respectively, these values are red-shifted for the $P 1 2_1/c 1$ space group. With this structure, the LSO:Ce has maximum excitation and emission wavelengths of 369 nm and 435 nm, respectively.

Previous Syntheses of LSO:Ce

Single crystals and powders of LSO:Ce have been produced through a wide variety of methods. Large single crystals and fibers have been synthesized through the Czochralski technique,^{33, 42, 51} floating zone method,⁵² and laser heated pedestal growth (LHPG).⁵³ Powder syntheses have included sol-gel,⁵⁴⁻⁵⁵ solid-state,⁵⁶ hydrothermal,⁵⁷ spray pyrolysis,¹⁶ mechanochemical,⁵⁸ and solution combustion methods.^{17, 39}

The first reported synthesis of LSO:Ce by Melcher, *et al.*^{42, 51}, used the Czochralski method, which remains the most common process employed. In this first growth, Lu_2O_3 , SiO_2 , and CeO_2 or Ce_2O_3 were mixed before sintering for four hours at 1500 °C in an Ar, Ar+2% H_2 , or air atmosphere. This mixture was then melted, and the single crystal boule was pulled using the Czochralski method.^{42, 51} This technique requires an iridium crucible due to the high melting point of LSO:Ce (2150 °C).^{3, 53} At these high temperatures, the Ir crucibles will degrade during the synthesis which can render them unusable and

contaminate the crystals.⁵³ Both the initial purchase and the maintenance of these expensive crucibles drastically increases the overall cost of LSO:Ce production.^{16, 56, 59}

Researchers have therefore attempted to produce single crystals using methods that do not require the Ir crucible. Cooke, *et al.*⁵² used the floating zone method. Lu_2O_3 , SiO_2 , and rare-earth oxides were combined and mixed stoichiometrically. The mixed material was pressed into a rod, heated to 1000 °C for 20 h, and then heated to 1500 °C for 10 h. Single crystals were grown from this ceramic through the floating zone method, in which the rod was melted and crystallized as it was passed through a molten zone in a N_2 atmosphere with 3 ppm O_2 .⁵²

Raukas, *et al.*⁶⁰ generated fibers of LSO:Ce using the LHPG technique in 1997 using powdered LSO:Ce as a starting material. Following this initial study, Farhi, *et al.*⁵³ conducted LHPG to produce LSO:Ce fibers from oxide precursors. In this method, Lu_2O_3 , SiO_2 , and CeO_2 were mixed, pressed, and sintered at 1400 °C for 100 h in an Ar/H_2 atmosphere. This process formed ceramics that were then cut into rods. The end of the rod was melted with a CO_2 IR laser, and a seed crystal was used to pull fibers from the melt. These fibers were 20 mm in length and 0.6-1 mm in diameter. Although neither the floating zone nor the LHPG methods required the use of an Ir crucible, the processes still required long reaction times to form small crystals, which makes the processes impractical for production on a commercial scale.^{53, 60}

Since its first production, there has been a shift toward the production of ceramic LSO:Ce, which would lower reaction temperatures, shorten production times, and decrease the overall cost in comparison with current single crystal growth methods. This production would start with the synthesis of LSO:Ce nanoparticles. One such synthesis involved a sol-gel method conducted by Mansuy, *et al.*⁵⁴ In this process, potassium metal was reacted with 2-propanol. Stoichiometric amounts of LuCl_3 and CeCl_3 were added. This solution was refluxed for 2 h in an Ar atmosphere before tetraethoxysilane (TEOS) was added. This solution was stirred at room temperature for 4 h, and the KCl was removed. Subsequent hydrolysis of the resulting material led to an amorphous powder that was crystallized through heating at 1200 °C for 6 h.⁵⁴ This general process was later repeated with Eu^{3+} as the dopant.⁵⁵

In 2009, LSO:Ce powders were synthesized through several new methods. Wang, *et al.*⁵⁶ produced powders of LSO:Ce through a solid-state reaction in which stoichiometric amounts Lu_2O_3 , SiO_2 , and CeO_2 were combined with the flux Li_2SO_4 . These powders were then calcined in air or in a reducing atmosphere at 1300 °C for 5 h.⁵⁶ Yun, *et al.*⁵⁷ made powders through a hydrothermal method. In this process, a solution of Na_2SiO_3 with its pH adjusted to 7.5-8.0 using HCl was added to a mixture of $\text{Lu}(\text{NO}_3)_3$ solution, $\text{Ce}(\text{NO}_3)_3$ solution, and urea. This combined mixture was heated in a teflon cup in an acid digestion bomb at 200 °C for 10 h. Following washing, the powder was heated to 1000-1250 °C for 2 h.⁵⁷ In 2009, Wang, *et al.*¹⁶ researched LSO:Ce powder produced by spray pyrolysis by Nanocerox, Inc. (Ann Arbor, Michigan). This method of production was described by Kuntz, *et al.*¹⁴ The process involves the mixture of metal salts in an organic solvent, which is then atomized using O_2 before being passed through a methane/oxygen flame to produce nanoparticles.¹⁴

LSO:Ce powders with the $P 1 2_1/c 1$ space group have also been produced through combustion. In this general process, metal nitrates are combined with a fuel and then heated until they combust. Blair, *et al.*³⁹ first mentioned this method for LSO:Ce powder production in 2008, using glycine as the fuel. This research was followed in 2010 by Yukihiro, *et al.*¹⁷, using hexamethylenetetramine as the fuel. In this particular method, nitrate solutions of lutetium and cerium were combined with fumed silica and hexamethylenetetramine. The mixture was dried, combusted at 600 °C, and calcined at 1000 °C for 1 h.¹⁷

Tian, *et al.*⁵⁸ synthesized undoped LSO through mechanochemical methods followed by calcination. Lu_2O_3 and SiO_2 were combined stoichiometrically and milled with ethanol in a Si_3N_4 cup for 24 h. The resultant powder was dried and pressed into a pellet. The pellet was heated to 1000-1400 °C although no LSO was produced at 1100 °C and full conversion only occurred at 1400 °C.⁵⁸

Powders from several of these syntheses have been pressed into ceramics through HIPing.^{15-16, 58} These ceramics have exhibited relative densities (i.e. the percentage of the ceramic density compared to the single crystal density) of up to 99.8% with powders synthesized through mechanochemical processing or spray pyrolysis.^{16, 58}

As has been seen with other materials, the production of these LSO:Ce ceramics have lower temperatures, shorter production times, lower costs, and more uniform doping compared to their single crystal counterparts.^{16, 61}

Regardless of the past productions of LSO:Ce ceramics, new methods of particle production warrant further investigation as different syntheses and variations in syntheses have been shown to produce ceramics with different properties. These changes can affect the overall doping concentration, doping uniformity, and relative density of the ceramics.^{14-17, 58, 61} It is therefore important to synthesize LSO:Ce powder through various other methods to produce the most ideal ceramic at the lowest possible cost through processes which are scalable for industrial use.

1.3. Chiral Nanoparticles

1.3.1. Introduction to Chiral Nanoparticles

Optical activity was first observed in 1811 by F. Arago who saw that sunlight passing through quartz crystals formed colors. This observation was followed in 1812 by J.-B. Biot who discovered that the colors were caused by the rotation of light through the crystal which varied based on wavelength. He also discovered that the direction of this rotation was opposite for two forms, now known to be enantiomers, of quartz. Following these discoveries, Biot reported that this rotation of light also occurred when it was passed through turpentine and solutions of camphor, sugar, and tartaric acid. It was soon realized that this optical activity was caused by either molecular or crystal structures which are chiral with non-superimposable mirrored structures.⁶²⁻⁶³

Since the original discoveries of optical activity and enantiomers, countless materials have been found to be optically active, which has led to interest in chiral nanoparticles. Over the past two decades, chiral crystalline nanoparticles have grown in interest due to their prospective wide-scale applications in the fields of chemistry, biology, physics, and medicine. These materials have potential uses in heterogeneous enantioselective catalysis, enantiomeric separations, and enantioselective crystallizations, which are all possible due to the favorable stereoselective interactions between enantiomers. These interactions could be helpful in pharmaceutical development in the exploration and detection of enantiomerically-pure biological

compounds and the transportation of functionalized nanoparticles to these molecules. They could also accelerate enantioselective processes due to their larger surface areas.⁶⁴⁻⁷⁶

The preferential binding between enantiomers has been used in pharmaceutical development and biosensing because chiral biological compounds tend to solely form as one enantiomer in nature. For example, in the human body, amino acids typically take the L-form while sugars typically take the D-form. The two enantiomers of a chiral nanoparticle should therefore interact differently with these biological compounds.^{68, 77-79} These different interactions can be used for the exploration and detection of enantiomerically-pure biological compounds as well as for transportation of functionalized nanoparticles to these molecules.

The larger chiral surface area of these nanoparticles compared to their micron-scale or larger counterparts may also be used to accelerate enantioselective processes.^{64-65, 69, 73-75} The plausibility of using chiral nanoparticles for this type of surface application has been demonstrated by conducting these processes on larger structures with smaller chiral surface areas.⁷¹ For example, powdered L-quartz and powdered D-quartz (approximately 2.9-7.6 μm) have been used in the syntheses of various pyrimidyl alkanols with enantiomeric excess.⁷⁶

Although there is great potential for future applications of chiral nanoparticles, a better understanding of chiral materials and their optical activity must be achieved before these applications can be fully explored. Improvements must first be made in the synthesis of novel chiral nanoparticles, in control of their optical activity, and in the effect of nano-scale chirality on their overall properties. These improved properties and newly explored properties can then be applied in the research of chiral nanoparticles functionalities.

1.3.2. Types of Chirality in Nanoparticles

Although the importance of studying chiral nanoparticles for the above-listed applications has been noted in several reviews, very little work has been done on nanoparticles with chiral crystal structures.^{66, 68, 78, 80-82} These nanoparticles can be chiral in their overall shape, in their arrangement in relation to each other, or in the configuration

of their atoms. This work will focus on chirality in which the crystal structure (or configuration of atoms) is not superimposable with its mirror crystal structure.^{74, 83} These chiral nanomaterials are synthesized in the presence of a chiral capping agent, which acts as a protective coating to prevent aggregation and as a templating agent to initiate chirality. Based on previous investigations, two types of nanoparticle chirality can be templated: induced and intrinsic.^{78-80, 82, 84-86}

Induced Chirality

When a bulk crystal material is achiral, chirality can be induced in nanoparticles using chiral capping agents. These capping agents generate chirality or optical activity by several mechanisms. They may adsorb to the surface of the nanoparticle in a chiral pattern (Figure 1.5a). The optical activity may also be the result of electronic state hybridization between the chiral capping agent and the achiral nanoparticles. The chirality may also be induced by chiral distortions created by the capping agents in the surface atoms (Figure 1.5b). These distortions may then permeate into or through the nanoparticle. The induced chirality allows the nanoparticle to display optical activity which can be measured through optical rotation and circular dichroism. The chirality and resulting optical activity have thus far been lost when the chiral capping agent is replaced by an achiral capping agent or when the nanoparticles are heated because there are no chiral capping agents to create chiral distortions. The intensity of the optical activity is also decreased as the nanoparticle size increases to the point of being immeasurable with particles larger than approximately 5 nm.^{73, 84-92} At these sizes, the induced distortions have not yet been capable of pervading the majority of the structure. The achiral portion becomes large enough that any chiral dislocations still present are not concentrated enough to give a measurable signal.^{82, 93} Most previous studies of chiral nanoparticles, including the research of Au, Ag, CdS, CdSe, CdTe, ZnO, $\text{WO}_{3-x}\cdot\text{H}_2\text{O}$, Co_3O_4 , and TiO_2 , involve nanocrystals with this induced chirality.^{73, 84-92, 94}

Intrinsic Chirality

Materials in which the large crystals have a chiral crystal structure have also been shown to have nanoscale chirality.^{78-82, 84-86} This persistent chirality between the large crystals and the nanoparticles should be consistent for all other materials with chiral

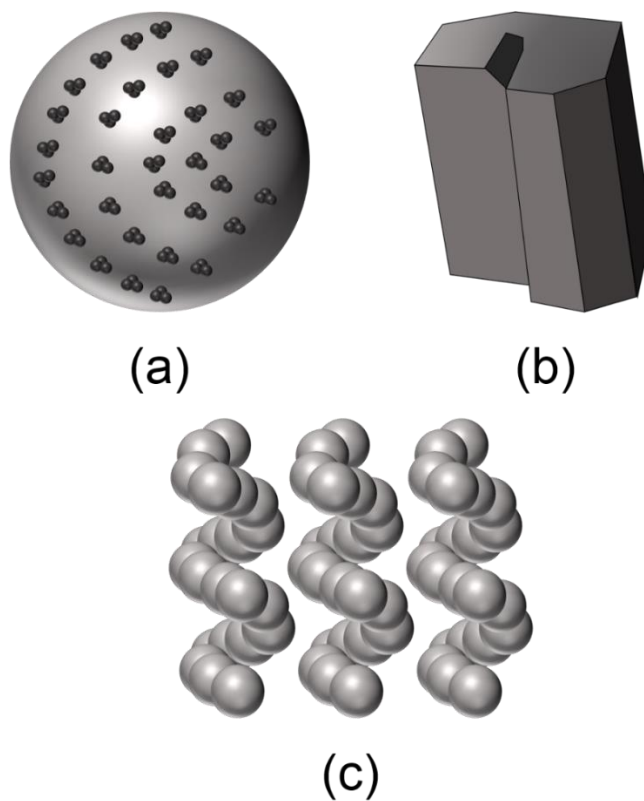


Figure 1.5. Examples of induced and intrinsic chirality. These illustrations represent induced chirality with (a) chiral capping agent adsorption and (b) chiral surface distortion and (c) intrinsic chirality through chiral crystal structure. Images adapted from references by Ma, *et al.*⁷⁴ and Ben-Moshe, *et al.*⁹⁵

crystal structures. This chirality, which is inherent to the material and its crystal structure, will be called intrinsic chirality for the purpose of this dissertation. For these chiral nanoparticles, both an enantiomerically-pure chiral capping agent and an achiral capping agent may create some slight distortions of the atoms on the nanoparticle surface, but the overall crystal structure is chiral and optically active (Figure 1.5c). An enantiomerically-pure capping agent could therefore be capable of initiating the crystal growth of one enantiomer, thereby preventing a racemic mixture from forming. These materials exhibit a retention of chirality, or chiral memory, when heated or when the chiral capping agent is replaced with an achiral capping agent. This chiral memory is important for enantioselective catalysis and separations.^{78-82, 84-86}

There are only three intrinsically chiral nanomaterials which have been previously investigated: Se, Te, and HgS. Synthesized Se and Te nanorods were optically active, but the authors attributed the majority of this optical activity to the chiral macrostructure of the twisted nanorods and chiral memory was not tested.⁷⁸ HgS nanoparticles exhibited optical activity at sizes larger than 5 nm while nanoparticles with induced chirality have thus far been 5 nm or smaller when exhibiting optical activity to the best of our knowledge.⁸² These HgS nanoparticles have also been shown to continue exhibiting optical activity when the chiral capping agent was replaced with an achiral capping agent and when heated to 100 °C with an achiral capping agent.⁸⁰ The chirality of the HgS nanoparticles was further tested through variations in the shape of the nanomaterials, including symmetrical particles with cubic, ellipsoidal, rod-like, and wire-like shapes and asymmetrical particles with a twisted bipyramidal shape. All of these shapes exhibited optical activity.⁸¹

Previous research of materials with intrinsic chirality (Se, Te, and HgS) involved the low-temperature (<100 °C) syntheses of chiral metal and metal sulfide nanoparticles. These low temperatures allowed the use of a wide variety of capping agents, as racemization was less likely to occur during the reaction than at higher temperatures. However, this field has not yet addressed intrinsically-chiral nanoparticles which require higher temperatures for production. At these high temperatures, many chiral capping

agents would quickly racemize or decompose, but the exploration of high-temperature syntheses might further our understanding of inorganic chirality in nanoparticles.⁹⁶⁻⁹⁸

1.4. Overview of Chapters

Chapter 2 details the characterization methods used in the projects that follow. These analytical techniques include powder X-ray diffraction (PXRD), transmission electron microscopy (TEM) with electron diffraction, scanning electron microscopy (SEM) with energy-dispersive X-ray spectroscopy (EDS) and elemental mapping, and dynamic light scattering (DLS) for all nanoparticles. For scintillator nanoparticles, Photoluminescent (PL) excitation and emission and time-correlated single photon counting (TCSPC) are described. For the work involving chiral nanoparticles, polarimetry, circular dichroism (CD) spectroscopy, thermogravimetric analysis (TGA), mass spectrometry (MS), and Fourier-Transform infrared spectroscopy (FTIR) are described.

Chapter 3 describes the experimental methods and analysis of cerium-doped lutetium oxyorthosilicate ($\text{Lu}_2\text{SiO}_5\text{:Ce}$) powder synthesized through mechanochemical methods. This chapter includes dry and wet milling and the optimization of the dry milling process.

Chapter 4 states the experimental procedure for $\text{Lu}_2\text{SiO}_5\text{:Ce}$ powder synthesis through solution or gel combustion using either a single fuel or mixed fuels. The characterization of these particles is also presented. A comparison is presented between $\text{Lu}_2\text{SiO}_5\text{:Ce}$ powders produced through mechanochemical syntheses to powders produced through solution combustion syntheses.

Chapter 5 involves the synthesis and characterization of chiral nanoparticles of $\beta\text{-GeO}_2$. The procedure for and characterization of the attempted templating of $\alpha\text{-quartz}$ using *rac*- $\beta\text{-GeO}_2$ is described.

Chapter 6 presents a summary of the previous chapters and suggests possible routes for future work on the above topics.

CHAPTER 2

INSTRUMENTATION AND CHARACTERIZATION

2.1. Introduction

The characterization of nano- and micron-sized powders typically begins with determining composition, size, and morphology as each of these factors can drastically change other properties of the material. Common techniques conducted after powder synthesis are therefore powder X-ray diffraction (PXRD), electron microscopy, and dynamic light scattering (DLS) for particle size analysis (PSA). These measurements help determine the particles' identity, crystallite size, particle size, degree of aggregation and agglomeration, crystallinity, and elemental composition. Following these general techniques, other characterization methods are selected based on the specific properties and applications of the powder.

2.1.1. Characterization of Scintillators

Following the successful production of a scintillator powder and prior to pressing it into a ceramic, the powder should exhibit several properties that match those of their single crystal counterparts. For example, the powder should have similar maximum excitation and emission wavelengths to the crystal and a decay time that indicates successful doping within the crystal structure. These properties can be verified through measurement of the powder's photoluminescence (PL) excitation and emission spectra and its decay time.

2.1.2. Characterization of Optically-Active Nanoparticles

Chiral materials are characterized by their optical activity. This measurement determines if a material consists of equal amounts of each enantiomer (called a racemic mixture) or an excess of one enantiomer. An enantiomeric excess can be verified using either polarimetry or circular dichroism (CD).

To synthesize chiral nanoparticles, a capping agent must be used initially. These capping agents can be quantified and their adsorption characterized using thermogravimetric analysis paired with mass spectrometry (TGA-MS) and infrared (IR) spectroscopy.

2.2. Powder X-Ray Diffraction

In PXRD, X-rays are diffracted off the periodic planes of a crystalline structure and interact constructively and destructively to form a diffraction pattern. This diffraction

pattern can aid in the determination of crystal phase or be compared to known patterns for identification purposes. PXRD instruments can detect transmitted or reflected X-rays based on the setup of their X-ray generator, sample holder, and detector (Figure 2.1).⁹⁹⁻¹⁰¹ In this dissertation, both configurations were used.

Transmission PXRD data were collected using an Olympus BTX II Bench-top instrument. This device utilized Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$; 10 W, 330 μA). The powder sample, which was sieved using a 45- μm mesh, was held between two windows in a convection-vibrated cell. The transmitted diffracted X-rays were detected using a 2-D Peltier-cooled charge coupled device (CCD) detector set to a temperature of $-45 \pm 1 \text{ }^\circ\text{C}$. Each pattern was produced by averaging between 250 and 1000 scans of $5\text{-}55^\circ 2\theta$ with a step size of 0.05° .

Reflection PXRD data were collected using PANalytical Empyrean Cabinet X-ray unit with the reflectance Bragg-Brentano geometry. This instrument also used Cu- K α radiation ($\lambda = 1.5406 \text{ \AA}$; 45 W, 40 mA). The photons were focused onto a spinning sample holder with the powder on a zero-background silicon crystal plate. A PIXcel3D detector was used to detect the diffracted radiation. Spectra were obtained using two programs. The first program measured patterns from $5\text{-}55^\circ$ with a 0.0131° step size and 20.4 s/step; the second program measured patterns from $5\text{-}75^\circ$ with a 0.0131° step size and 15.3 s/step.

All spectra were analyzed using the X'Pert HighScore Plus program with the Inorganic Crystal Structure Database (ICSD) and Scherrer calculator. Using patterns within the ICSD, samples were compared with known compounds to determine their identity. The major peaks and their corresponding Miller indices and relative peak intensities are listed in Table 2.1 for two structures of LSO:Ce and in Table 2.2 for $\beta\text{-GeO}_2$ and $\alpha\text{-quartz}$. The Scherrer calculator within the program was also used to find peaks' full width half maxima (FWHM) and to calculate crystallite sizes, using the Scherrer equation (Equation 2.1):

$$D = \frac{K\lambda}{\beta \cos\theta} \quad (2.1)$$

In this equation, D is the average crystallite size in nm, K is a crystallite shape constant

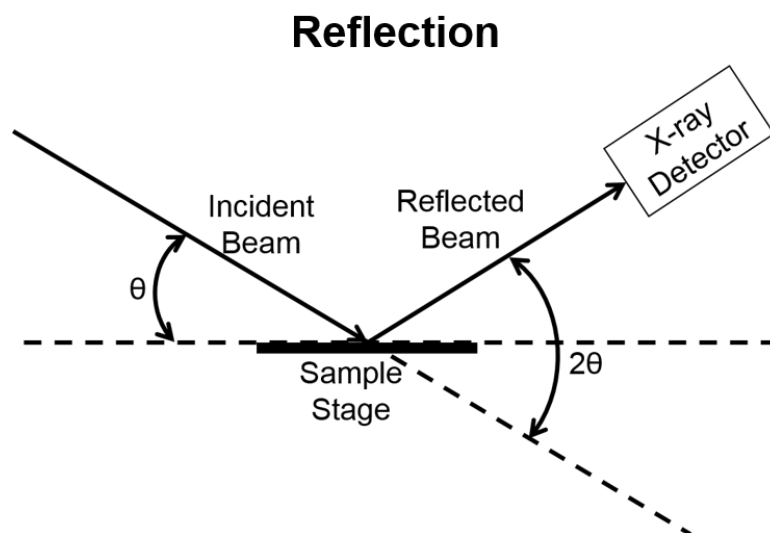
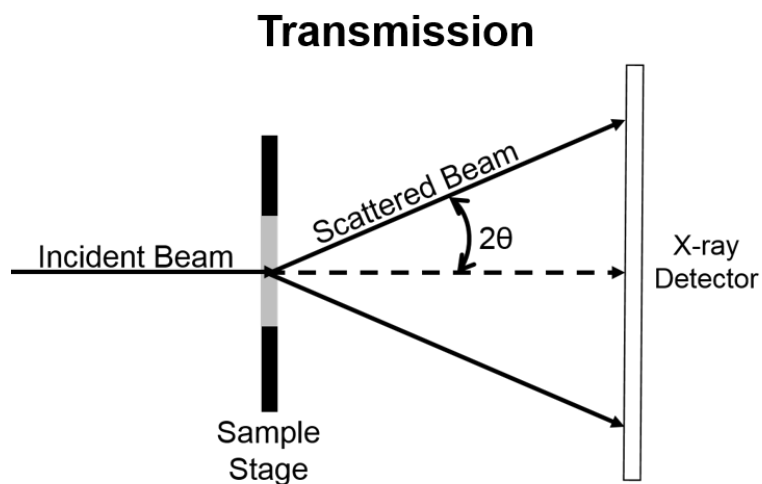


Figure 2.1. PXRD geometries for data collection through transmission and reflection modes. Images adapted from reference by Pecharsky.¹⁰²

Table 2.1. List of the main peaks for PXRD patterns of the two space groups ($C 1 2/c 1$ and $P 1 2_1/c 1$) of LSO:Ce with their Miller indices and relative intensities.⁴⁶⁻⁴⁷

$C 1 2/c 1$			$P 1 2_1/c 1$		
2 Θ (°)	(h k l)	Relative Intensities (%)	2 Θ (°)	(h k l)	Relative Intensities (%)
14.7	(2 0 0)	36.7	10.1	(1 0 0)	14.9
15.2	(1 1 0)	42.7	16.7	(1 1 0)	62.5
22.2	(1 1 -2)	23.2	19.2	(0 1 -1)	33.5
23.0	(3 1 -1)	100.0	20.4	(2 0 0)	21.6
25.4	(4 0 -2)	58.2	23.3	(1 1 1)	21.0
26.8	(0 2 0)	20.4	27.2	(1 0 -2)	33.8
28.8	(0 2 1)	61.5	30.1	(0 2 -1)	60.0
29.9	(3 1 -3)	89.3	30.3	(2 0 -2)	51.6
30.7	(2 2 0)	44.2	30.4	(1 1 -2)	34.7
30.8	(1 1 -3)	46.1	30.8	(3 0 0)	78.0
31.1	(2 0 2)	97.8	32.1	(1 0 2)	58.6
34.0	(0 2 2)	24.5	32.9	(1 2 1)	100.0
35.5	(5 1 -1)	51.5	33.2	(2 1 -2)	23.8
35.8	(2 0 -4)	19.0	33.4	(3 1 -1)	17.5
37.4	(4 2 -1)	20.2	33.6	(3 1 0)	17.6
37.8	(2 2 -3)	18.2	34.5	(2 2 -1)	70.0
40.2	(3 1 2)	16.4	44.2	(4 0 -2)	16.0
41.6	(2 2 2)	22.1	46.1	(3 2 1)	31.8
41.8	(1 3 -1)	31.1	49.5	(1 2 -3)	46.5
41.9	(6 0 -4)	30.9	59.4	(4 2 -3)	24.4
49.8	(2 2 3)	15.8	59.5	(2 2 3)	25.3
52.9	(7 1 -5)	20.7			
53.0	(4 2 2)	20.3			
53.6	(5 3 -3)	30.9			

Table 2.1. (continued)⁴⁶⁻⁴⁷

<i>C</i> 1 2/ <i>c</i> 1			<i>P</i> 1 2 ₁ / <i>c</i> 1		
2 Θ (°)	(h k l)	Relative Intensities (%)	2 Θ (°)	(h k l)	Relative Intensities (%)
53.7	(-4 0 6)	21.9			
59.6	(0 4 2)	15.9			
	(-8 2 4)	15.9			
61.9	(-3 3 5)	22.9			
	(-7 3 3)	22.9			
62.1	(-9 1 2)	14.7			
	(-2 4 3)	14.7			

Table 2.2. List of the main peaks for PXRD patterns of β -GeO₂ and α -quartz with their Miller indices and relative intensities.¹⁰³⁻¹⁰⁴

β -GeO ₂			α -Quartz		
2 Θ (°)	(h k l)	Relative Intensities (%)	2 Θ (°)	(h k l)	Relative Intensities (%)
20.5	(0 1 0)	18.8	20.9	(0 1 0)	20.9
25.9	(0 1 1)	100.0	26.6	(0 1 1)	100.0
36.0	(1 1 0)	9.7	36.5	(1 1 0)	7.5
38.0	(0 1 2)	19.5	39.5	(0 1 2)	7.4
39.5	(1 1 1)	12.2	40.3	(1 1 1)	3.5
41.8	(0 2 0)	15.8	42.4	(0 2 0)	5.6
44.9	(0 2 1)	1.9	45.8	(0 2 1)	3.0
48.3	(0 0 3)	4.2	50.1	(1 1 2)	13.1
48.7	(1 1 2)	10.3	54.9	(0 2 2)	4.1
53.0	(0 1 3)	2.2	55.3	(0 1 3)	1.8
53.4	(0 2 2)	5.7	59.9	(1 2 1)	9.2
56.3	(1 2 0)	1.8	64.0	(1 1 3)	1.9
58.8	(1 2 1)	13.8	67.7	(1 2 2)	6.3
61.7	(1 1 3)	3.9	68.1	(0 2 3)	6.9
65.7	(0 2 3)	8.3	68.3	(0 3 1)	4.6
66.0	(1 2 2)	10.0	73.4	(0 1 4)	2.3
67.0	(0 3 1)	7.5			
70.0	(0 1 4)	5.4			
73.8	(0 3 2)	4.1			

(0.89 for LSO:Ce; 0.9 for α -quartz and β -GeO₂), λ is the wavelength of the X-rays (0.15406 nm for Cu-K α emission line), β is the FWHM in radians, and θ is the Bragg angle in radians.¹⁰⁵⁻¹⁰⁷ For mechanochemically-produced LSO:Ce studies, the 23.0° 2 θ was used due to its high intensity and resolution from surrounding peaks. Solution-combustion studies required the use of the 14.6° and 15.2° 2 θ peaks for the *C* 1 2/*c* 1 phase and the 16.6° and 19.2° 2 θ peaks for the *P* 1 2₁/*c* 1 phase due to the overlap of other peaks. For β -GeO₂ powder in chiral nanoparticle studies, the 25.9° 2 θ was used as it has the highest intensity and best resolution.

2.3. Electron Microscopy

Particle size and morphology are commonly found using electron microscopy. It can also help determine surface structure, show the degree of hard and soft agglomeration, show coating thicknesses, verify crystallinity, and determine atomic composition.¹⁰⁸⁻¹¹⁰ Both scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used in this dissertation work.

2.3.1. Scanning Electron Microscopy

With SEM, images of samples' surface structures are created through the detection of secondary electrons resulting from the bombardment of the sample with an electron beam. This image can show morphology, surface characteristics, particle size, and degree of agglomeration.¹⁰⁸ These microscopes can also be used for energy-dispersive X-ray spectroscopy (EDS). This technique focuses on the interactions between the electron beam and inner shell electrons which result in ionization. The resultant X-ray from the de-excitation of an outer shell electron to fill the newly-formed hole is then detected. These X-rays have characteristic energies which can be used to determine the atomic composition of the sample. These X-rays can also be used in elemental mapping.¹⁰⁸⁻¹⁰⁹ The scanning electron microscope used in this dissertation was a Zeiss Auriga 40 Crossbeam focused-ion beam scanning electron microscope at the Joint Institute for Advanced Materials (JIAM) at the University of Tennessee with help from Dr. John Dunlap.

2.3.2. Transmission Electron Microscopy

Using a TEM instrument, an image is produced by detecting electrons transmitted through a sample. These images are useful in determining degree of agglomeration and can be used to study morphology (including coating thicknesses) and particle size. Electrons transmitted through the sample can also be used to form an electron diffraction, which can help determine crystallinity.¹¹⁰ The work in this dissertation used a Zeiss Libra 200 HT FE transmission electron microscope at JIAM with assistance from Dr. John Dunlap.

2.4. Dynamic Light Scattering

Particle size distributions can be measured using dynamic light scattering (DLS). In DLS, the elastically-scattered light from a beam directed at the sample is detected over time and statistically analyzed. Fluctuations in the intensity of the light detected can be used to determine particle speed. The Brownian motion of larger particles is slower than that of smaller particles, so the light intensity data can be used to determine particle size distributions.¹¹¹ These distributions are more representative of the sample than measurements from electron microscopy images.

In this work, samples suspended in water were measured using a Malvern Instruments Zetasizer Nano ZS by Washington State University Nano Research Facility (NRF). Each sample was measured in triplicate at 25 °C and averaged.

2.5. Photoluminescence Excitation and Emission Spectroscopy

Photoluminescence (PL) excitation and emission curves are measured using a fluorimeter. For scintillators like LSO:Ce, excitation peaks are indicative of the absorption of energy which excites the dopant (Ce^{3+}) electron from the 4f band to the 5f band. The following emitted light has a higher wavelength than the excitation wavelength as the excited electron has first lost energy through non-radiative processes. The maximum emission band results from the $5d \rightarrow {}^2F_J$ ($J=5/2$ or $7/2$) transition. Changes in the maximum excitation and emission wavelengths can be indicative of LSO:Ce structural shifts.^{17, 39-41,}

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This work used a Perkin-Elmer LS 55 fluorescence spectrometer for LSO:Ce measurements. The emission wavelengths and excitation wavelengths will be listed in

either the figure or the figure description for all PL spectra.

2.6. Photoluminescent Decay Time Measurements

Decay time for scintillators can be measured through excitation by gamma radiation (scintillation decay time) or by UV-Vis radiation (photoluminescent decay time). In the measurement of scintillation decay time, gamma excitation typically excites an electron from the valence band of the crystal to its conduction band while UV-Vis causes the direct excitation of the dopant during PL decay time measurements.^{5, 33-36, 112} Scintillation decay time could not be measured for the synthesized powders due to the long radiation length of gamma rays and the powders' opacity, therefore the PL lifetimes were measured for comparison with literature values.

PL lifetimes were measured using a time-correlated single photon counting (TCSPC) technique.¹¹³ With the assistance of Dr. Charles Melcher, these measurements were conducted using a Horiba Jobin Yvon Fluorolog-3 Spectrofluorometer with a 360-nm NanoLED as a light source and Hamamatsu R928 photomultiplier tube (PMT) as a detector. Samples were pressed into thin disks, and measurements were conducted using a 360-nm excitation wavelength, a 420-nm emission wavelength, and 4-nm slit widths.

2.7. Optical Activity

There are two main methods of measuring optical activity. It can be measured either through the rotation of linearly polarized light (polarimetry) or through the differential absorption of left- and right-circularly polarized light (CD).¹¹⁴

2.7.1. Polarimetry

In this work, a Perkin-Elmer Model 241 polarimeter with a Hg high pressure lamp was used to measure the rotation of linearly polarized light through solutions of both capped and uncapped β -GeO₂ nanoparticles. Measurements were taken at 436 nm and 546 nm using a pathlength of 1 dm. Rotation should occur if an enantiomeric excess is present in the sample.¹¹⁴ This instrument measures rotation with an accuracy of $\pm 0.002^\circ$ for rotations less than 1° . For all measurements, an integration time of 5 s was used to decrease noise, and measurements were conducted in triplicate and averaged to decrease error.¹¹⁵

2.7.2. Circular Dichroism Spectroscopy

The main optical activity measurement technique for chiral nanoparticles is CD spectroscopy, which measures the difference in the absorptions of right and left circularly polarized light. Optical activity can be more easily established for multiple chiral materials in a single sample using CD spectroscopy compared to polarimetry because absorption wavelengths are dependent on material.¹¹⁴ However, polarimetry can be used for transparent crystals.

The work presented in this dissertation used an AVIV 202 CD Spectrophotometer at the Bioanalytical Resource Facility at the University of Tennessee with help from Dr. Ed Wright. Samples were prepared immediately before characterization by adding 8-11 mg of powder to 10 mL of solvent. Samples were run in 200-210 nm increments from 190-800 nm at 0.5 s/step in 1 nm steps. In areas of interest, samples were run in 100 nm increments at 1 s/step in 1 nm steps. Background spectra were measured for solvents and subtracted from sample spectra.

2.8. Thermogravimetric Analysis

The mass percentage of capping agent within a nanoparticle powder can be determined using thermogravimetric analysis (TGA) by decomposing the capping agent and determining the weight change. For chiral nanoparticles, this percentage can assist in determining the optical activity caused by the nanoparticle versus that caused by the capping agent. When paired with a mass spectrometry (MS), the mass-to-charge ratio of the ionized decomposition products can be detected. This fragmentation can aid in verifying the presence of a capping agent.

The research presented in this dissertation used a TA Discovery TGA-MS at the Polymer Characterization Lab (PCL) at JIAM with assistance from Dr. Katrina Pangilinan. When first characterizing the capped samples, only TGA was run. The powders were heated in a N₂ atmosphere from room temperature to 900 °C at 100 °C/min and then held at 900 °C for 20 minutes to ensure complete decomposition of the capping agent. When paired with MS, the powders were heated in a N₂ atmosphere from room temperature to 600 °C at 10 °C/min.

2.9. Fourier Transform Infrared Spectroscopy

Infrared (IR) spectroscopy can be used to monitor the presence of capping agents on nanoparticle surfaces. In this method, a sample is irradiated with IR radiation, and absorption is measured. The energies which are absorbed correspond to vibrational modes of the compound being measured. Characteristic lines for the capping agent can be monitored for shifts in these absorption bands which would indicate adsorption.^{111, 116} For example, the adsorption of an amine group would appear as the $\delta(\text{N-H})$ band broadening and shifting to lower frequencies or disappearing.⁹² Fourier transform (FT) allows shorter acquisition times with better resolution.^{111, 116} In this work, a Thermo Scientific Nicolet iS50 FT-IR Spectrometer at PCL was used with assistance from Dr. Katrina Pangilinan. Samples were run as dried powders in the range of 525-4000 nm.

CHAPTER 3
THE MECHANOCHEMICAL SYNTHESIS OF
CERIUM-DOPED LUTETIUM OXYORTHOSILICATE POWDERS

A portion of the initial dry mechanochemical synthesis of LSO:Ce described in this chapter was published by Melissa N. Bailey and George K. Schweitzer:

Bailey, M. N.; Schweitzer, G. K., The mechanochemical and solution combustion syntheses of cerium-doped lutetium oxyorthosilicate powder. *J Alloy Compd* **2018**, 734, 258-265.

All work from this article presented in this chapter was conducted by Melissa Bailey with advisement from George K. Schweitzer.

A portion of the optimization of the dry mechanochemical synthesis of LSO:Ce described in this chapter was published by Kaitlyn A. McDonald, Matthew R. McDonald, Melissa N. Bailey, and George K. Schweitzer:

McDonald, K. A.; McDonald, M. R.; Bailey, M. N.; Schweitzer, G. K., Parametric study on the production of the GAGG:Ce and LSO:Ce multicomponent oxide scintillator materials through use of a planetary ball mill. *Dalton T* **2018**, 47, 13190-13203.

In this article, the theoretical calculations and analyses were conducted by Kaitlyn A. McDonald and Matthew R. McDonald. All work involving GAGG:Ce was conducted by Kaitlyn A. McDonald. All experimentation and characterization of LSO:Ce was conducted by Melissa N. Bailey. George K. Schweitzer acted as advisor for all the work presented in the article.

3.1. Abstract

Lu₂SiO₅:Ce powders were synthesized by solvent-free mechanochemical processing of the constituent oxides followed by either microwave or furnace sintering. Using the Burgio-Rojac model for the planetary ball mill, a parametric study of this synthesis was conducted, investigating the effect of varying the powder mass, the vial and ball density, the number of balls, the diameter of the balls, and the rotation rate of the mill on reaction time. The influence of additives was researched with Zn possibly leading to increased reduction of Ce⁴⁺ to Ce³⁺ and with various solvents hindering or preventing Lu₂SiO₅:Ce production. These powders were characterized using powder X-ray diffraction (PXRD), photoluminescence (PL) excitation and emission spectroscopy, time-correlated single photon counting (TCSPC), dynamic light scattering (DLS) for particle size analysis (PSA), and scanning electron microscopy (SEM).

3.2. Introduction

3.2.1. Mechanochemistry

Reactions in which mechanical energy is converted to chemical energy are called mechanochemical reactions. One of the first recorded instances of such a reaction occurred in approximately 315 B.C. when Theophrastus of Eresus wrote about grinding cinnabar (HgS) in a copper mortar and pestle to obtain mercury in his “On Stones” book.¹¹⁷⁻¹¹⁸ These types of reactions became established as a separate field of chemistry in the 1800s, and the term mechanochemistry was first used in 1919 by Wilhelm Ostwald.¹¹⁸ Since that time, countless reactions have been conducted in a similar manner, and the process has become more widely documented.¹¹⁷⁻¹¹⁹

The increasing popularity of mechanochemical syntheses has been motivated in part by a desire for fast, low-temperature, minimal-solvent processes. Mechanochemistry (MC) allows quick (typically less than 24 h), quantitative reactions to occur at or close to room temperature. It is a one-step process which allows homogenization of the reactants, nucleation of the product, and growth of product particles. These processes require little to no solvent, making them less wasteful and better for the environment than solvent-based reactions.¹¹⁸⁻¹¹⁹

As mechanochemistry has grown as a field, the development of new instrumentation has led to increased mechanical energy, resulting in faster reactions. A few of the instruments which are commonly used are mills. Several varieties of mills are shown in Figure 3.1, including a ball mill, a vibration mill, an attritor (stirring ball mill), a pin mill, a rolling mill, and a planetary ball mill. The type of mill used is selected based on application. When a specific use for the mill requires high imparted energy, planetary ball mills are commonly employed because of their simple set up and relatively short processing times. Ball mills including these planetary ball mills use the mechanical energy created by balls within a sample container colliding with the walls of the container and with themselves to induce chemical reactions.¹²⁰⁻¹²¹

3.2.2. Planetary Ball Mills

Of the above listed mill types, planetary ball mills are capable of the highest energy transfer. These mills consist of two or four vials which are situated on a disk evenly

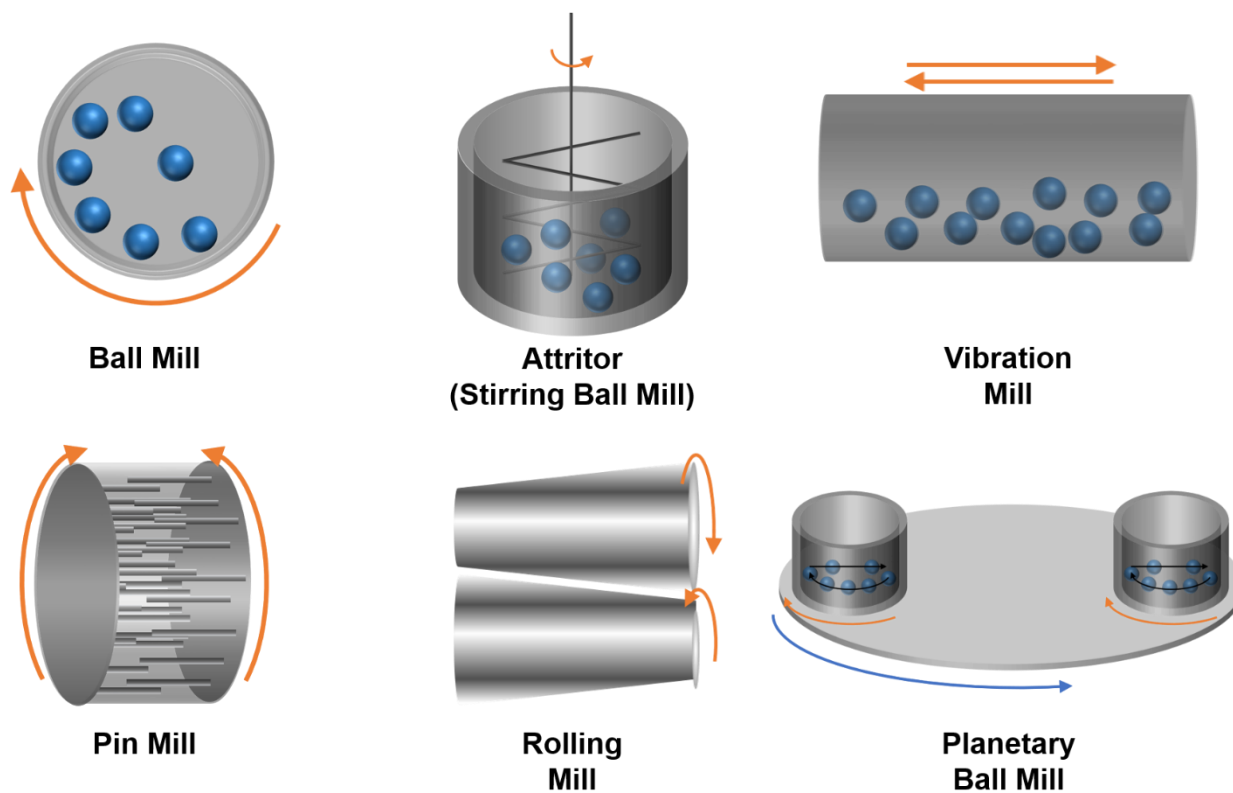


Figure 3.1. Depictions of several common-used types of mills for mechanochemistry. Image adapted from reference by Balaz, *et al.*¹²⁰

separated from each other. These vials rotate in the opposite direction of the main disk. The rotational speed of the disk and vials determines the motion of balls inside the vials, which can move by cascading, cataracting, or centrifuging (Figure 3.2). The impacts between the balls and the vial wall and between the balls themselves caused by the cataracting motion can release large amounts of energy. During the comminution of a powder in this mill, chemical reactions or transformations can be induced by the energy released during a collision.¹²¹

Mechanochemical production of LSO:Ce powder using a planetary ball mill may provide a room-temperature synthetic method with little or no solvent and much shorter reaction times. Currently, the synthesis of LSO:Ce single crystals involves high temperatures which require Ir crucibles, and the synthesis of LSO:Ce powder typically requires high temperatures, long reaction times, or the use of relatively large amounts of solvents.^{3, 16, 33, 42, 51-57, 59} Mechanochemistry is an advantageous alternative to these processes which eliminates these problems.

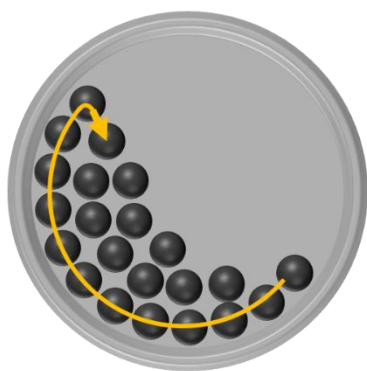
3.2.3. Planetary Ball Mill Mathematical Modeling

Several studies have been conducted attempting to mathematically model the energy transfer that occurs in planetary ball mills. One of the first models produced was by Burgio, *et al.*¹²² in 1990, who attempted to kinematically describe ball mills. Over the next several years, many other researchers worked to refine this model.¹²³⁻¹²⁶ One such researcher, Rojac, *et al.*¹²⁷ adjusted the Burgio model to relate the various parameters associated with the ball mill to the energy imparted by a single ball's impact and the total energy imparted during milling. This Burgio-Rojac model has been tested by Rojac, *et al.* as well as several other groups.¹²⁸⁻¹³⁴ The equations for the model are as follows (Equations 3.1-2):

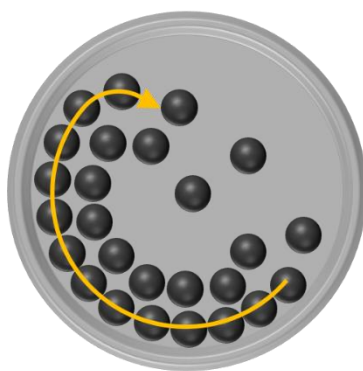
$$E_{tot} = \frac{1.5E_c N(S-s)t}{m} \quad (3.1)$$

$$E_c = \frac{\pi d^3 D S s (W-d)}{24} \left[\frac{s(W-d)}{2S} \left(1 - \frac{2s}{S} \right) - 2R - \frac{s(W-d)}{2S} \right] \quad (3.2)$$

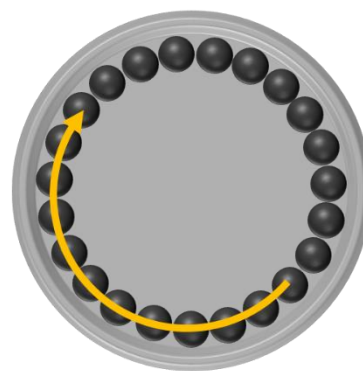
where E_{tot} is the accumulated energy per mass of powder in J/g, E_c is the energy transferred in a single collision in J/collision, N is the number of balls, S is the disk rotational speed in revolutions per second, s is the vial rotational speed in revolutions per



Cascading



Cataracting



Centrifuging

Figure 3.2. Illustration of ball movement within a planetary ball mill as rotational rate is increased. Image adapted from reference by Burmeister, *et al.*¹²¹

second, t is time in seconds, m is the mass of the powder in grams, d is the diameter of the balls in meters, D is the density of the vials and balls in g/m^3 , W is the diameter of the vial in meters, and R is the interaxial distance between the center of the vial and the center of the disk in meters.

Although the model attempts to mathematically describe energy transferred while running a planetary ball mill, it does not quantitatively describe energy transferred to a powder sample. The discrepancy between these two values is in part due to the energy lost to the environment. Among other variables, the equation also does not consider the hardness of the vial/ball material or of the powder or the degradation of the vials and balls as they are used.¹³⁵

The model has been shown, however, to be capable of qualitatively estimating the effect of each parameter on a reaction.¹²⁸ Theoretical analysis of Equation 3 shows that reaction time (t) should be proportional to the mass of the powder (m) and inversely proportional to the number of balls (N), the density of the vials and balls (D), and the rotation rate of both the vial and balls cubed (S^3 or s^3). This analysis also shows that the total energy transferred to the powder first increases with ball diameter (d) before decreasing as the size becomes too large and ball movement is restricted. The reaction time will change in the opposite fashion (i.e. first decreasing before increasing as ball diameter increases).¹³⁵

A parametric study of the above model has been conducted for the mechanochemical synthesis of LSO:Ce powder. This study allows the optimization of the reaction by systematically reducing reaction time while also exposing problems arising from vial/ball degradation, contamination, and side reactions.

3.2.4. Liquid-Assisted Grinding

Although many mechanochemical syntheses are conducted under solvent-free conditions, the presence of a small amount of liquid has been shown to accelerate some reactions and has even allowed some previously impossible mechanosyntheses to occur. These processes involving liquids are commonly referred to as liquid-assisted grinding (LAG), solvent-assisted grinding, or solvent-drop grinding. The liquid in these reactions may be directly added to the vessel, or it may be a liquid by-product of the solid-state

reaction, such as water from a hydrate, or material that has melted on the particle surface.^{119, 136-138}

LAG is believed to facilitate more intimate mixing between solids reactants. The added liquid may act as a solvent for one or more of the solid reactants, which would aid in transport through convection or diffusion. This theory is partially supported by experimental evidence which suggests that facilitation of mechanochemical reactions is dependent on solvent type.^{119, 136-137} This dependence means screening of solvents is especially important.

The presence of a small amount of liquid may lead to higher product yields during mechanochemical reactions. The addition of these solvents can lead to a favorable partial dissolution of the reactants. In solvent-based reactions, complete dissolution of the reactants leads to a decreased product yield. However, in LAG, the minimal amount of solvent results in only a small portion of the reactants dissolving, possibly leading to higher product yields.¹³⁶

LAG has also been shown to increase the crystallinity of the products. It is believed that in these cases, the product may partially dissolve in the solvent, forming a supersaturated solution at the grain surface. Repeated dissolution and recrystallization may lead to higher crystallinity overall.¹³⁶

The amelioration of the reaction or improved crystallinity of the product have been shown to be dependent on the solvent used, which suggests dissolution plays a role in the process. Screening of solvents with varying polarities is therefore important in determining the efficacy of LAG in each individual reaction. Some previously-used solvents in LAG are water, methanol, ethanol, 1-propanol, and DMF.^{119-120, 136, 138}

3.2.5. Instrumentation

All mechanochemical productions of LSO:Ce powder were conducted using a Fritsch Pulverisette 7 Premium Line planetary ball mill. This instrument has a set S:s ratio of 1:-2 and an R of 0.07 m. Syntheses were run in air using Si₃N₄ (D = 3.25 g/cm³), ZrO₂ (D = 5.7 g/cm³), or WC (D = 14.9 g/cm³) vials and balls. All vials had volumes of 45 mL and interior diameters of 0.045 m.

3.3. LSO:Ce Standards

As one method of identifying the successful synthesis of LSO:Ce, PXRD reference patterns were obtained for Lu_2O_3 , SiO_2 , CeO_2 , stoichiometrically-mixed starting materials, and crystalline LSO:Ce powder (Figure 3.3). The PXRD patterns of Lu_2O_3 , SiO_2 , and CeO_2 powders were obtained because they were the starting materials used for all ball mill syntheses. These powders were then mixed in stoichiometric ratios for the possible production of Lu_2SiO_5 with 0.05% Ce doping. To ensure thorough mixing without perceptible reaction, the materials were milled at 850 rpm in a Si_3N_4 vial with seven 10-mm balls for 30 min. As can be seen in the PXRD of these starting materials, the mixed starting materials' pattern consists of Lu_2O_3 and SiO_2 peaks. CeO_2 peaks are not visible in the mixture's pattern due to its low stoichiometric amount.

Crystalline LSO:Ce powder was produced by hand-grinding disks of Czochralski-grown crystals obtained from a commercial supplier. The resulting powder was then milled at 850 rpm for 45 min in a Si_3N_4 vial with seven 10-mm balls to further reduce particle size. This powder will hereafter be referred to as the LSO:Ce Std. Separate single crystals were milled for up to 48 h to obtain amorphous LSO:Ce powder. The LSO:Ce Std pattern consists of peaks exclusively for LSO:Ce with the space group $C 1 2/c 1$. As the LSO:Ce crystals were milled for longer durations of time, these LSO:Ce peaks became less intense and peaks corresponding to Si_3N_4 appeared, indicating both the amorphization of the LSO:Ce crystal and the degradation of the vial over time. This transition can be seen in the PXRD in Figure 3.4.

Photoluminescence measurements were conducted for hand-ground and milled Czochralski-grown LSO:Ce (Figure 3.5). The maximum excitation and emission wavelengths of 357 nm and 410 nm, respectively, of the LSO:Ce Std approximately match those seen in the literature for Czochralski-grown LSO:Ce. A drastic decrease in intensity occurs after two hours of milling, possibly indicating a quick loss of crystallinity during this initial milling. As the powder becomes more amorphous, the photoluminescence intensity decreases to nearly background intensity. This loss of photoluminescence is expected in the absence of the LSO:Ce crystalline structure.

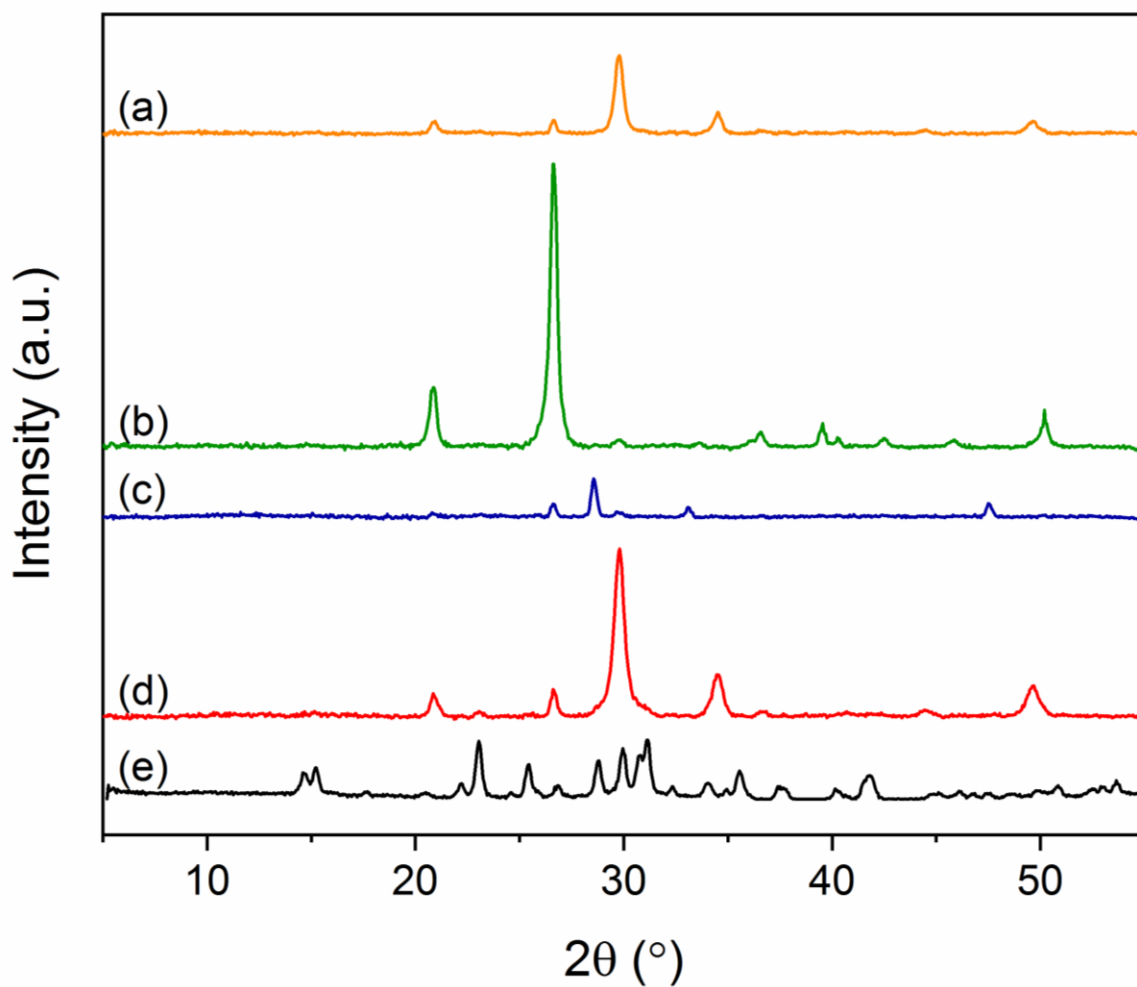


Figure 3.3. PXRD patterns of (a) Lu_2O_3 , (b) SiO_2 , (c) CeO_2 , (d) stoichiometrically-mixed starting materials to produce $\text{Lu}_{1.999}\text{Ce}_{0.001}\text{SiO}_5$ powder, and (e) Czochralski-grown LSO:Ce, which was hand ground and milled for 45 min to reduce particle size.

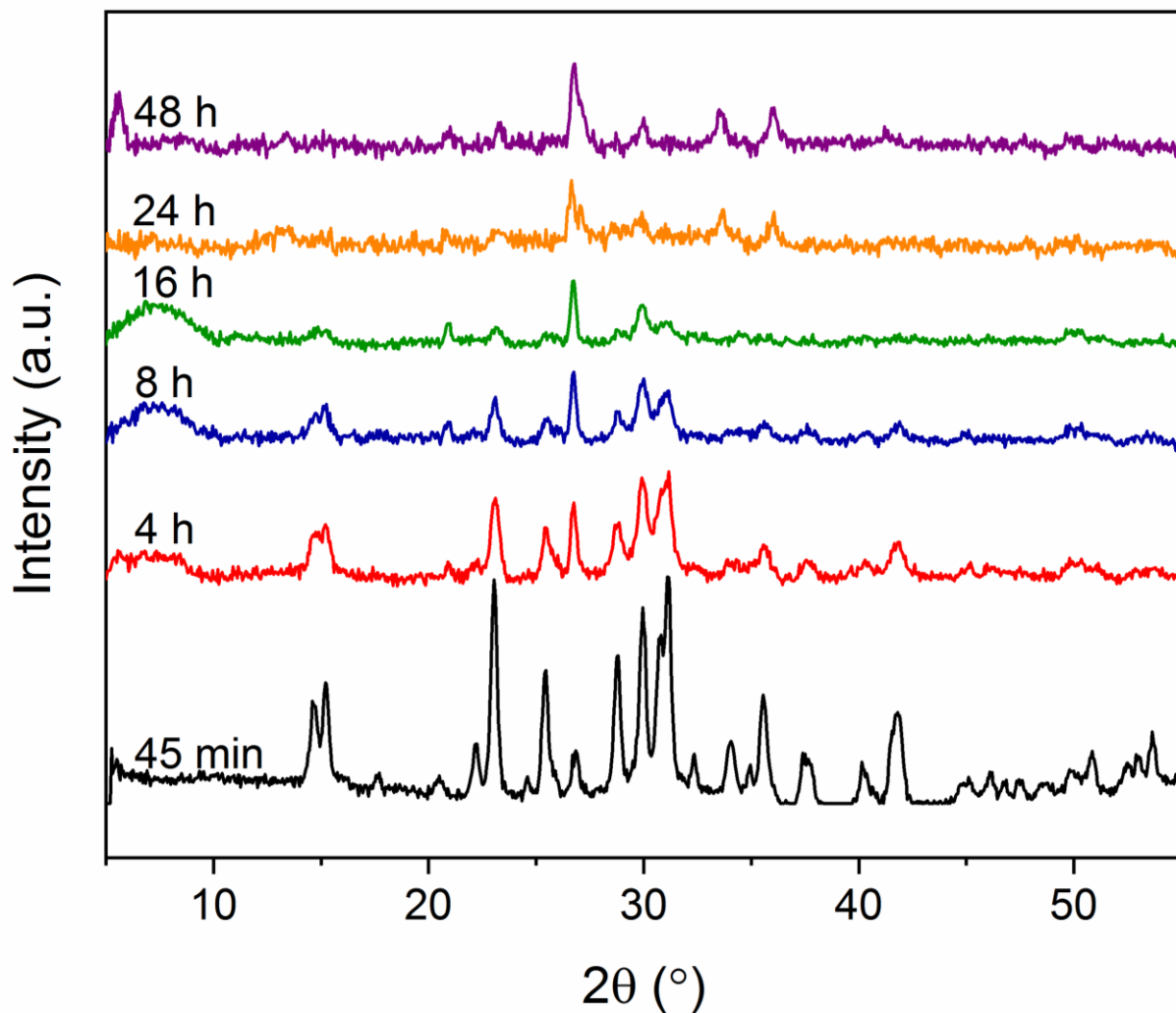


Figure 3.4. PXRD patterns of crystalline LSO:Ce milled for up to 48 h. PXRD patterns depict the transition that occurs during milling from crystalline LSO:Ce to amorphous LSO:Ce. Powders were produced from hand-ground crystals of LSO:Ce that were milled in a Si_3N_4 vial with seven 10-mm, Si_3N_4 balls at 850 rpm for up to 48 h.

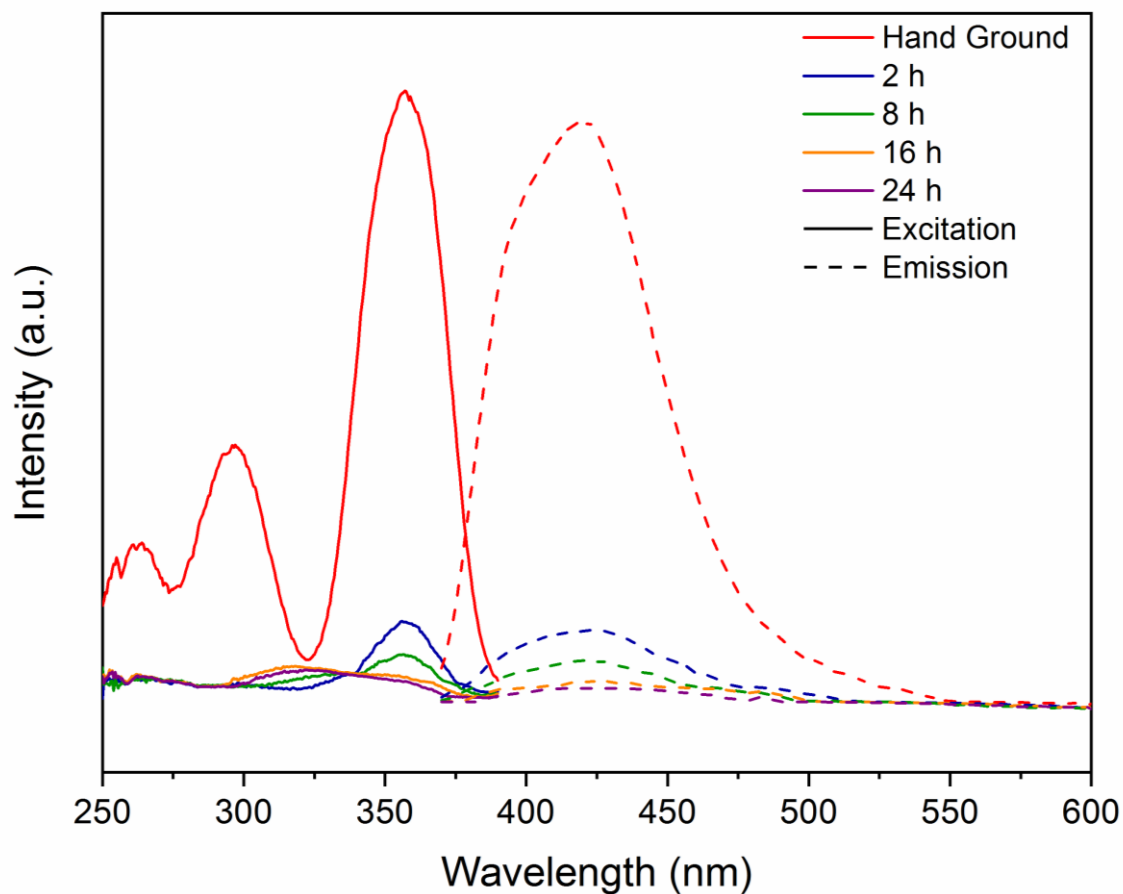


Figure 3.5. PL excitation ($\lambda_{\text{em}} = 410 \text{ nm}$) and emission ($\lambda_{\text{ex}} = 357 \text{ nm}$) spectra for Czochralski-grown LSO:Ce crystals which were hand ground and then milled for up to 24 h.

3.4. Initial Dry Mechanochemical Synthesis of LSO:Ce

The mechanosynthesis of LSO:Ce was first investigated using ball mill parameters suggested by the ball mill supplier. The results of this original synthesis led to a parametric study of this production method, the addition of reductants to test their effect on luminescence, and experimentation of LAG during the LSO:Ce mechanochemical synthesis.

3.4.1. Experimental Method

Lu_2O_3 , SiO_2 , and CeO_2 were obtained from commercial sources and had 99.99% or higher purity. The starting oxides were mixed stoichiometrically to form 4 g of $\text{Lu}_2\text{SiO}_5\text{:Ce}$ with 0.05% Ce doping. These oxides were milled at 850 rpm in a 45-mL Si_3N_4 ball mill vial with seven 10-mm Si_3N_4 balls. Samples were collected at 30 min and in one-hour increments up to 9 h. The LSO:Ce powder was then microwave sintered to approximately 1800 °C, followed by furnace sintering at 1100 °C for 8 h. Separate samples were solely furnace sintered to 1100 °C for 4 hours.

3.4.2. Results

The synthesis of LSO:Ce from starting material oxides was monitored through PXRD. Figure 3.6 shows the normalized PXRD patterns of LSO:Ce synthesized through the Czochralski method followed by grinding into a powder (LSO Std) and of a stoichiometric mixture of Lu_2O_3 , SiO_2 , and CeO_2 milled for up to 9 h. At 30 min and 1 hour of grinding, the mixture's pattern consists only of starting oxide peaks. By two hours, peaks for monoclinic LSO:Ce with $C 1 2/c 1$ symmetry appear. These peaks increase in intensity as milling time increases while the starting material peak intensities gradually decrease. At four hours of milling, no observable peaks of the starting materials are present. The pattern's peak positions and relative intensities match theoretical values for monoclinic LSO:Ce with the $C 1 2/c 1$ space group.⁴⁶ Milling for a longer duration of time (up to 9 h) does not appear to change the crystal structure.

LSO:Ce produced through ball milling for 4 h was then sintered. Comparison of the PXRD of the unsintered, microwave-sintered, and furnace-sintered LSO:Ce (Figure 3.7) shows refinement of the peak shapes after sintering by either method, which indicates crystallite growth in the LSO:Ce powder as is typical with sintering as the crystallites

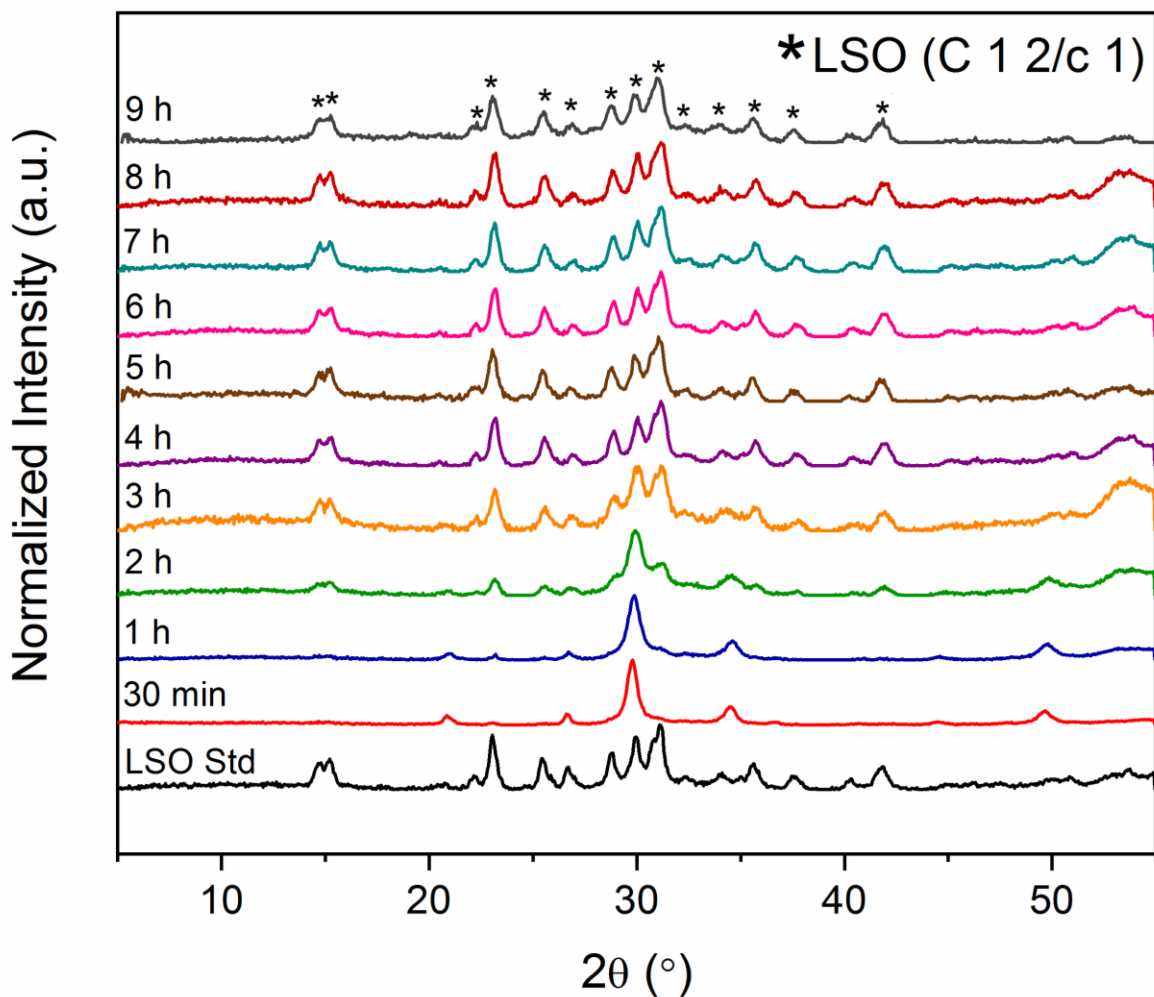


Figure 3.6. PXRD patterns of Lu_2O_3 , SiO_2 , and CeO_2 powders after mechanochemical treatment for up to 9 h. The LSO Std was synthesized through the Czochralski method, crushed, and then milled for 45 m to decrease particle size.

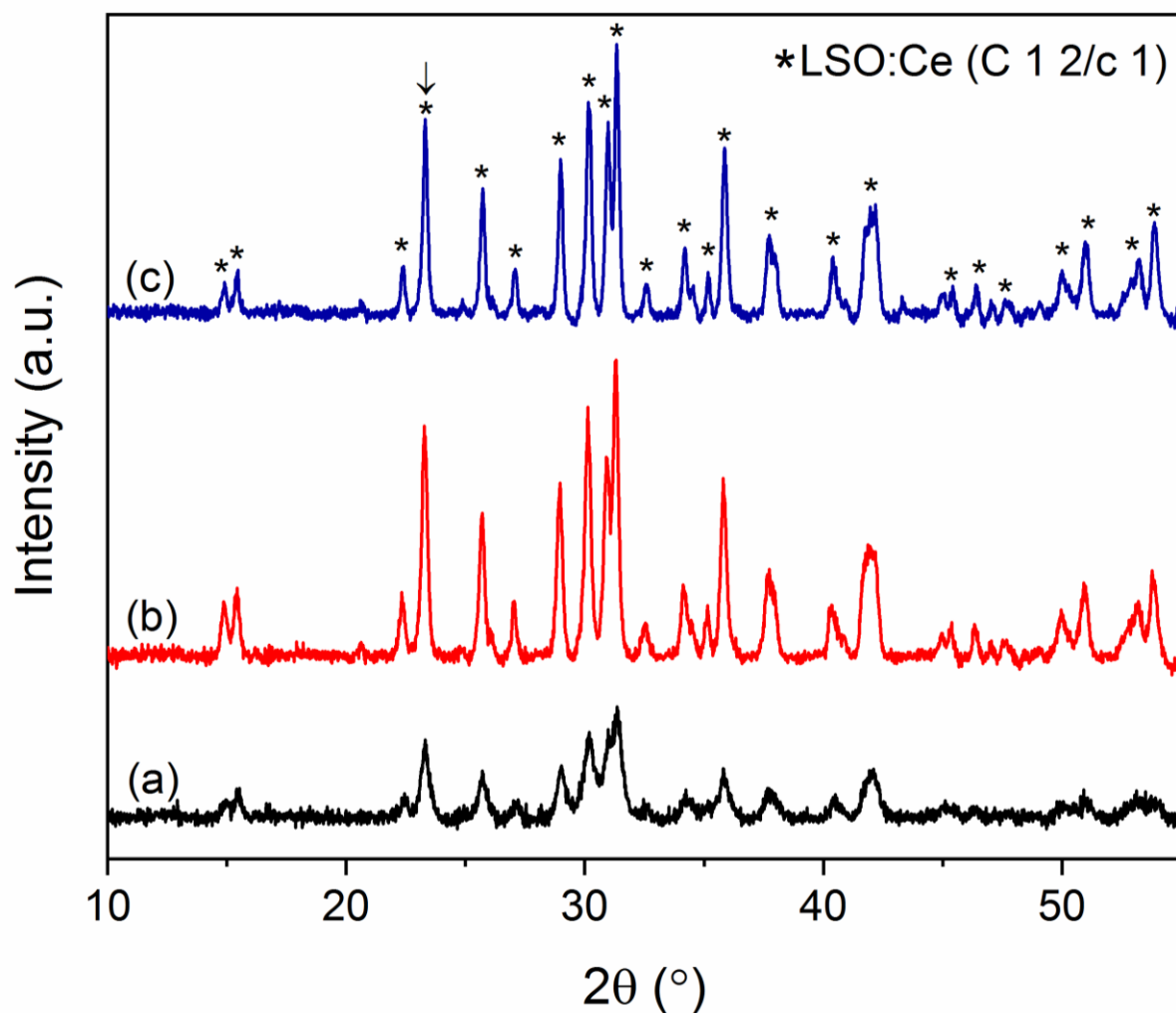


Figure 3.7. PXRd spectra of LSO:Ce (a) without sintering, (b) with microwave sintering, and (c) with furnace sintering. The peak used in the Scherrer equation calculations is marked with an arrow.

aggregate. This growth was confirmed using the Scherrer equation, which gave crystallite sizes of 26 nm, 31 nm, and 39 nm for the sample before sintering, after microwave sintering, and after furnace sintering, respectively.

All samples both before and after sintering appear to be nonporous at the magnifications used with a wide distribution of sizes and shapes as can be seen in the SEM micrographs in Figure 3.8. Prior to sintering, the 4-h milled sample showed a size range of 75 nm to 40 μm . An average particle size of 804 nm was determined using DLS, which supports with range found by SEM. Following microwave sintering and furnace sintering, the ranges were measured as 80 nm to 55 μm and 100 nm to 225 μm , respectively. Although these ranges significantly overlap, there may be a minor indication that particle size is increasing slightly with microwave sintering and more significantly with furnace sintering.

Photoluminescence excitation and emission spectra were measured as a second form of identification and to ensure that at least partial reduction of the Ce^{4+} to Ce^{3+} had occurred (Figure 3.9). In the spectra for samples milled for 4 h without sintering and with furnace sintering, the maximum excitation wavelength is 357 nm while the emission showed a broad band between 395 nm and 430 nm centered at 410 nm. These bands represent the 4f to 5d transitions and the $5d \rightarrow {}^2F_J$ ($J = 5/2$ or $7/2$) transitions, respectively.^{17, 39-41} These values correspond to those typically seen with Ce^{3+} in Ce^{3+} doped LSO:Ce.⁶¹ The microwave-sintered powder did not fluoresce, but PL decay time was measured. These conflicting data indicate that fluorescence decreases in intensity below the measurement capabilities of the fluorimeter but is still present. The quenching of LSO:Ce fluorescence typically occurs through three different routes: (1) the presence of hydroxide groups, (2) oxidation of Ce^{3+} to Ce^{4+} , and (3) the presence of oxygen vacancies. As there is no evidence that hydroxides groups occur as a result of microwave irradiation of oxides, this option was not likely the cause of the photoluminescence quenching.¹³⁹⁻¹⁴⁰ The microwave-sintered, mechanochemically-produced sample was therefore furnace heated in air, which would decrease the concentration of oxygen vacancies without reducing any Ce^{4+} within the sample. The characteristic peaks for Ce^{3+} doped LSO:Ce were present in the resulting PL excitation and emission spectra, which

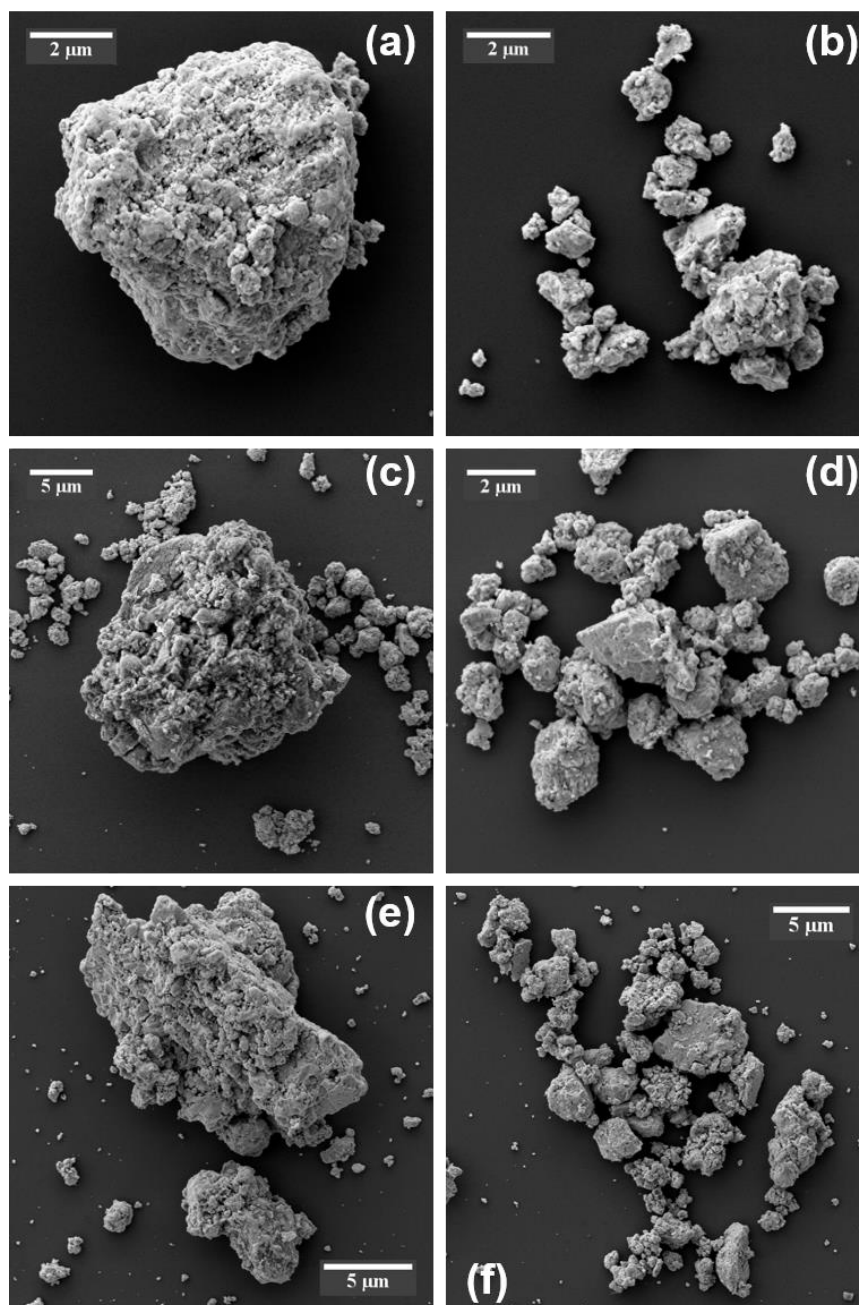


Figure 3.8. SEM images of powder subjected to 4 h of mechanochemical treatment (a-b) before sintering, (c-d) after microwave sintering, and (e-f) after furnace sintering.

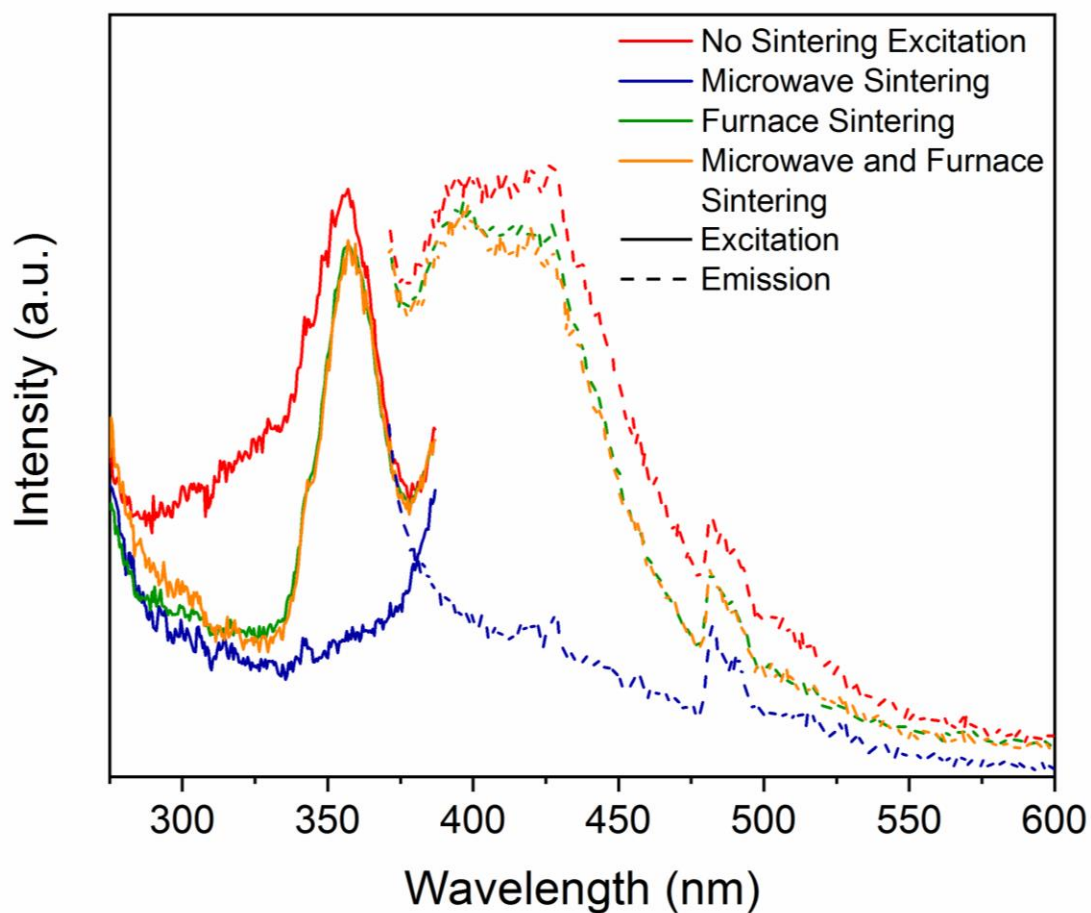


Figure 3.9. PL excitation ($\lambda_{em} = 410$ nm) and emission ($\lambda_{ex} = 357$ nm) spectra for LSO:Ce synthesized through mechanochemistry. Spectra were measured of powders before sintering, with microwave sintering, with furnace sintering, and with microwave sintering followed by furnace sintering.

suggests the most likely reason for the PL quenching was the presence of oxygen vacancies. All spectra showed a small peak between the wavelengths 475 nm and 500 nm, which has not yet been identified and is believed to be related to the instrumentation as it is seen with all samples.

PL lifetimes of the 4-h milled powder before and after sintering were calculated from the decay curves shown in Figure 3.10. Each of the curves was fitted with two decay time components: a longer component of 25-27 ns and a shorter component of 7-9 ns. The longer decay matches the literature values for the UV excitation of Ce^{3+} in $\text{LSO}:\text{Ce}$.^{40, 141} The source of the second component is undetermined although it has been seen in previous $\text{LSO}:\text{Ce}$ investigations.^{40, 142} It is believed that this shorter component may be due to instrumental factors.

3.5. Application of the Burgio-Rojac Model to the Mechanochemical Synthesis of $\text{LSO}:\text{Ce}$

The Burgio-Rojac equation was used to optimize the ball mill parameters for the dry mechanochemical synthesis of $\text{LSO}:\text{Ce}$. This study investigated the changes in reaction time caused by variations in the powder mass (m), the ball and vial density (D), the number of balls (N), the main disk rotation rate (S), and the ball diameter (d).

3.5.1. Experimental Method

$\text{Lu}_2\text{SiO}_5:\text{Ce}$ (with 0.05% Ce doping) powder was synthesized using stoichiometrically-mixed Lu_2O_3 , SiO_2 , and CeO_2 . These powders were then milled in air in 45-mL vials made of Si_3N_4 , ZrO_2 , or WC with balls made of the same material. A list of the experiments conducted with their reaction times can be seen in Table 3.1.

3.5.2. Results

The reaction times seen in Table 3.1 were determined by conducting PXRD measurements of the powders every hour during milling with occasional measurements taken below 1 h for powders reacted in WC vials. As evidenced by the reaction times, the samples follow the general predictions from the Burgio-Rojac model. In other words, the reaction time required for complete mechanochemical synthesis decreases as the mass of the powder decreases, the number of balls increases, the density of the vials and balls

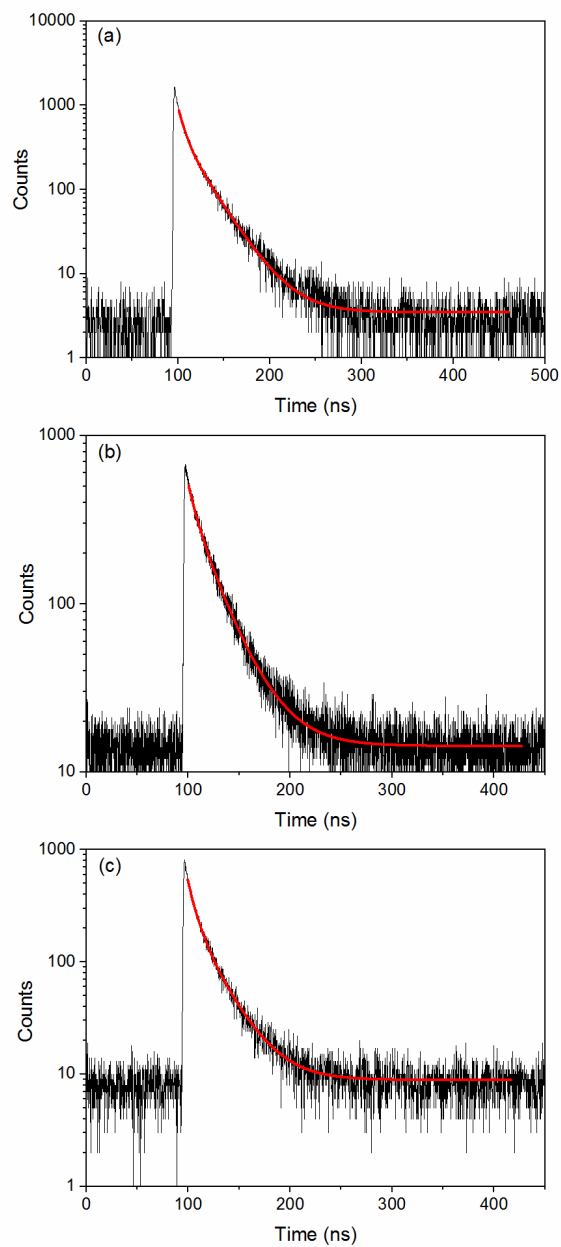


Figure 3.10. Decay time spectra for powder subjected to 4 h of mechanochemical treatment (a) before sintering, (b) after microwave sintering, and (c) after furnace sintering.

Table 3.1. Parameters and reactions times from Burgio-Rojac model experiments for the synthesis of LSO:Ce in a planetary ball mill

Vial and Ball Material	Density of Vial and Balls (g/cm ³)	Mass of Powder (g)	Number of Balls	Diameter of Balls (mm)	Rotational Rate (rpm)	Reaction Time	Crystallite Size (nm)
Si ₃ N ₄	3.25	4	3	10	850	NR	-
		4	7	10	850	4 h	26
		4	11	10	850	3 h	-
		4	7	10	400	NR	-
		4	7	10	650	9 h	-
		2	7	10	850	2 h	32
		8	7	10	850	10 h	23
		4	11	10	700	6 h	-
		4	3	15	700	10 h	-
ZrO ₂	5.7	4	3	10	850	NR	-
		4	7	10	850	4 h	31
		4	11	10	850	2 h	-
		4	7	10	400	NR	-
		4	7	10	650	6 h	-
		2	7	10	850	2 h	32
		8	7	10	850	10 h	20
		4	11	5	850	NR	-
		4	11	10	700	4 h	-

Table 3.1. (continued)

Vial and Ball Material	Density of Vial and Balls (g/cm³)	Mass of Powder (g)	Number of Balls	Diameter of Balls (mm)	Rotational Rate (rpm)	Reaction Time	Crystallite Size (nm)
ZrO ₂ , cont.	5.7	4	3	15	700	5 h	-
		4	3	15	650	7 h	20
WC	14.3	4	3	10	850	NR	-
		4	7	10	850	1 h	31
		4	11	10	850	30 min	-
		4	7	10	400	NR	-
		4	7	10	650	2 h	-
		2	7	10	850	45 min	-
		8	7	10	850	2 h	-
		4	7	10	650	1 h	-
		4	11	10	700	1 h	-

increases, the rotation rate increases, and the ball diameter increases (within the variations used).

Powder Mass

The Burgio-Rojac model predicts increased reaction times with increased powder mass. This correlation is clearly seen in the synthesis of 2 g, 4 g, and 8 g of LSO:Ce in Si₃N₄ vials with seven 10-mm Si₃N₄ balls and a disk rotation of 850 rpm. The proportionality can be seen in the PXRD patterns (Figure 3.11), which show reaction times of 2 h, 4 h, and 10 h for 2-g, 4-g, and 8-g samples, respectively.

Vial and Ball Density

The densities of Si₃N₄, ZrO₂, and WC are 3.25 g/cm³, 5.7 g/cm³, and 14.3 g/cm³. For all samples run in these vials, reactions times for Si₃N₄ and ZrO₂ samples were typically similar while reaction times for WC samples were consistently lower. The effect of density on reaction time was most evident with 4 g of powder using seven 10-mm balls and a main disk rotational rate of 650 rpm. As vial and ball density increased (3.25 g/cm³ to 5.7 g/cm³ to 14.3 g/cm³), the reaction time decreased (9 h to 6 h to 2 h).

Number of Balls

As the number of balls added to the vials during synthesis was increased, the reaction time decreased. This inverse proportionality was illustrated by syntheses using 4, 7, and 11 balls in all systems (Si₃N₄, ZrO₂, and WC) with all other parameters constant (4 g of powder, 10-mm balls, and a disk rotational rate of 850 rpm). In all syntheses involving three balls, no reaction occurred within 10 h of milling, indicating that the collisional and cumulative energy were not sufficiently high for a complete reaction. Syntheses using seven balls (Si₃N₄: 4 h; ZrO₂: 4 h; WC: 1 h) were always longer than syntheses using eleven balls (Si₃N₄: 3 h; ZrO₂: 2 h; WC: 30 min).

Rotational Rate

According to the Burgio-Rojac model, the reaction time should decrease with increasing rotational rate. For the production of LSO:Ce powder, disk rotational rates of 400 rpm, 650 rpm, and 850 rpm were used for all systems with 4 g of powder and seven 10-mm balls. These experiments followed the Burgio-Rojac model's estimated trend. In all systems run at 400 rpm, no reaction occurred within the 10 h milling period, suggesting

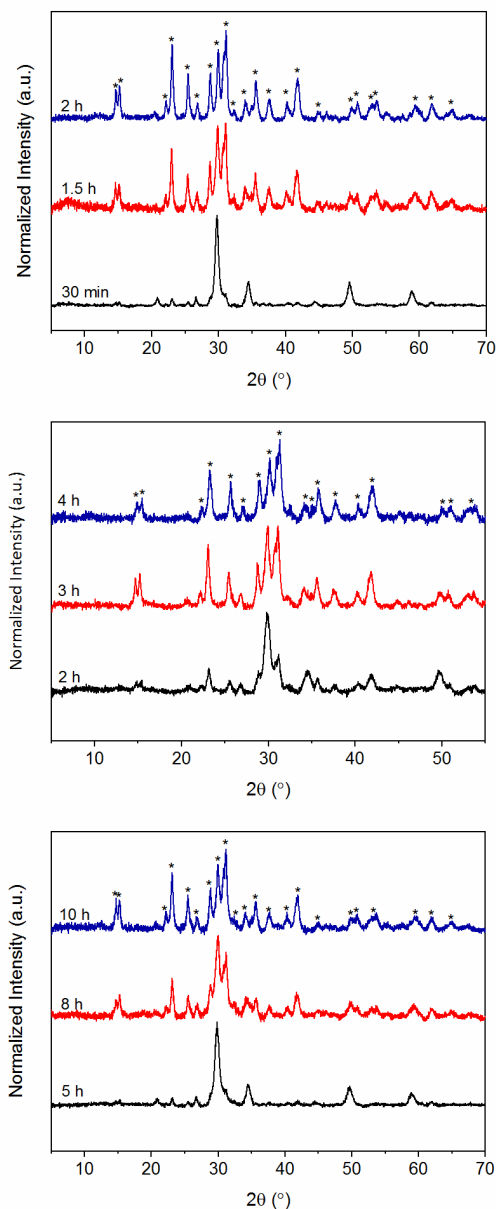


Figure 3.11. PXRD patterns depicting the effects of variations in powder mass (top: 2 g, middle: 4 g, bottom: 8 g) during mechanochemical synthesis of LSO:Ce in a planetary ball mill. All other parameters were held constant (Si_3N_4 vials and balls, seven 10-mm balls, 850 rpm rotation rate). The * marked peaks indicative of LSO:Ce at fully reacted timepoints.

greater collisional or cumulative energy is required for complete formation of LSO:Ce. Complete reaction did occur in all systems run at 650 rpm and 850 rpm with reactions in experiments run at 650 rpm (Si_3N_4 : 9 h; ZrO_2 : 6 h; WC: 2 h) requiring longer milling times than experiments run at 850 rpm (Si_3N_4 : 4 h; ZrO_2 : 4 h; WC: 1 h).

Diameter of Balls

Ball sizes were increased from 10 mm to 15 mm in Si_3N_4 and ZrO_2 systems, which appeared to increase the reaction time. Syntheses involving three 10-mm balls added to 4 g of powder and milled at 850 rpm did not react within 10 h. In comparison, milling runs with three 15-mm balls added to 4 g of powder and milled at 700 rpm resulted in complete synthesis of LSO:Ce within 10 h (Si_3N_4 : 10 h; ZrO_2 : 5 h).

The correlation between ball size and reaction time was also demonstrated by comparing the ZrO_2 system with 4 g of powder, eleven 5-mm balls, and a rotational speed of 850 rpm to the ZrO_2 system with 4 g of powder, eleven 10-mm balls, and a rotational speed of 700 rpm. With 5-mm balls at a faster rotation, LSO:Ce powder was not produced within 10 h whereas the reaction with 10-mm balls at a slower rotation occurred in 4 h.

In each of these comparisons, the milled powder was run at faster rotation rates for smaller ball sizes. The increased rotation should theoretically be decreasing the reaction time as discussed in the “Rotational Rate” section, but the decreased ball size decreases the energy imparted to the powder enough to prevent the reaction from occurring within the 10 h milling. In comparison, there is sufficient energy transfer by larger balls at slower rotational speeds.

3.5.3. Degradation, Contamination, and Particle Size

Throughout this parametric study of the mechanochemical synthesis of LSO:Ce powder, several issues with the milling process were observed. The most common issue which arose involved the degradation of the vials and balls, which contaminated all samples. This contamination was first evident in all systems as the powder color shifted from white to gray or black as milling time increased. This color change was most perceptible in LSO:Ce powders synthesized using WC vials and balls, which may indicate greater amounts of impurity.

The contamination by vial material was further verified through PXRD. In the 2-g

powder sample milled in a WC vial with seven 10-mm WC balls at 850 rpm for 2 h (Figure 3.12), WC peaks appeared in the pattern. Si_3N_4 contamination was not seen in PXRD except after 24-48 h of milling the Czochralski-grown crystal (Figure 3.4) although it must be significant due to the drastic color change of the powder.

Contamination of the LSO:Ce powder by ZrO_2 presented differently than either Si_3N_4 or WC impurities. As can be seen in PXRD patterns of LSO:Ce powder synthesized in a ZrO_2 vial with seven 10-mm balls and a rotational rate of 850 rpm (Figure 3.13a), ZrO_2 reacted with LSO:Ce powder to form $\text{Lu}_4\text{Zr}_3\text{O}_{12}$. This reaction between LSO:Ce and ZrO_2 was further demonstrated by milling Czochralski-grown LSO:Ce crystals in the ZrO_2 vial, which once again resulted in the formation of $\text{Lu}_4\text{Zr}_3\text{O}_{12}$ as indicated by the PXRD measurements (Figure 3.13b).

The effects of the degradation of the vials increased the longer they were used. This intensified influence was most apparent using the Si_3N_4 and ZrO_2 vials, which can be seen in the PXRD in Figure 3.14. With Si_3N_4 vials, the reaction time required to produce LSO:Ce increased. As can be seen in the PXRD, powders synthesized using a newly-purchased vial and a three-year-old vial with all other conditions held constant (4 g of powder, seven 10-mm balls, and a rotational rate of 850 rpm) had reaction times of 4 h and 6 h, respectively. This increase in reaction time is believed to be caused by increased padding within the vial as it is used and degraded.¹³⁵ With ZrO_2 vials, the increased effect of degradation can be seen in the decreased time in which $\text{Lu}_4\text{Zr}_3\text{O}_{12}$ formed. In a sample synthesized in 2014, complete formation of $\text{Lu}_2\text{Zr}_3\text{O}_{12}$ occurred in 10 h; in 2018, this same reaction occurred in 6 h when using the same vial.

3.6. Addition of Reductants to the Dry Mechanochemical Synthesis of LSO:Ce

As can be seen in the characterization of the initial dry mechanochemical reaction, the luminescence intensity is fairly low. Reductants, specifically Zn and Mg, were added in an attempt to reduce any remaining Ce^{4+} to Ce^{3+} . This reduction may increase the intensity of the photoluminescence excitation and emission intensities.

3.6.1. Experimental Method

For these reactions, Lu_2O_3 , SiO_2 , and CeO_2 were stoichiometrically combined to form LSO:Ce with 0.05% Ce doping. Zn or Mg powders were added with Zn/Mg:Ce molar

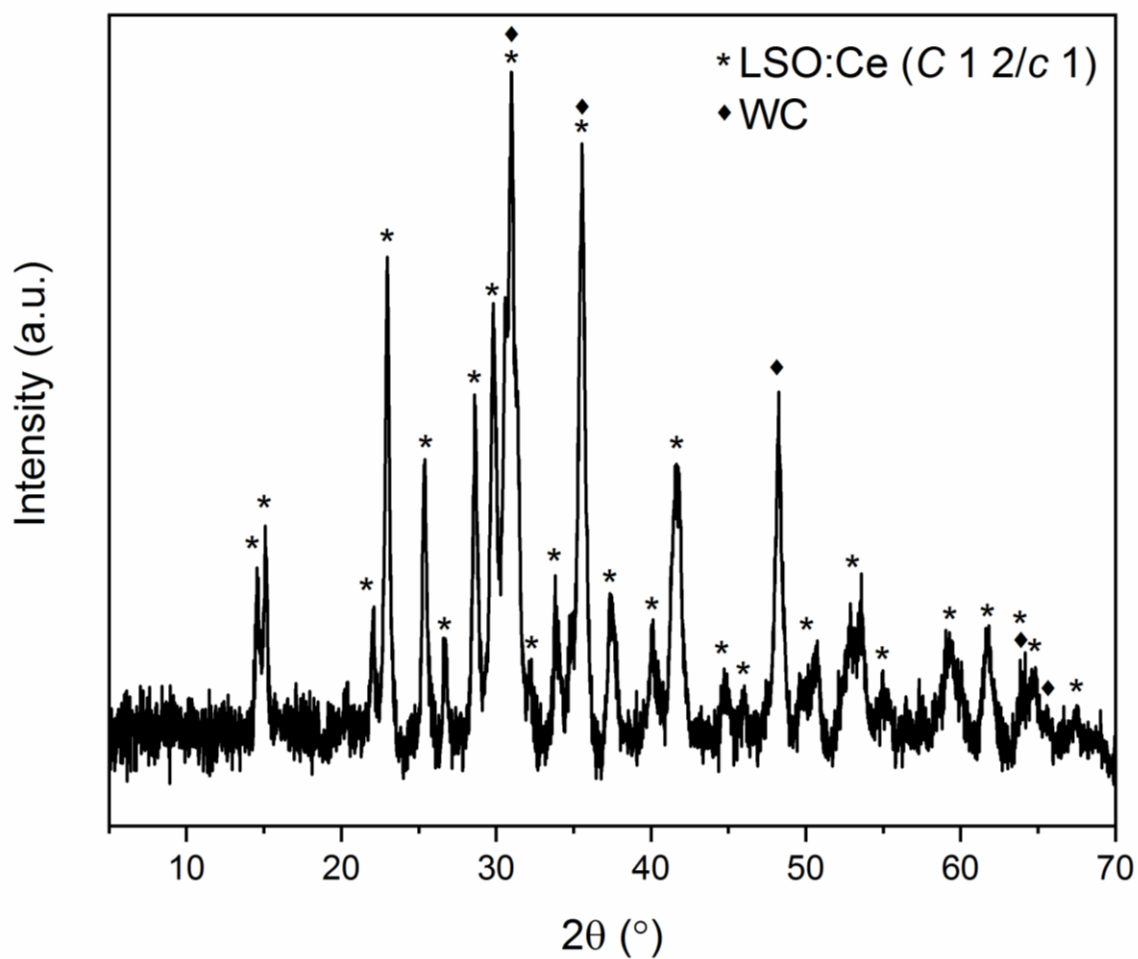


Figure 3.12. PXRD pattern revealing the degradation of WC vials during the mechanochemical synthesis of LSO:Ce. In this experiment, 2 g of LSO:Ce powder were milled in a WC vial with seven 10-mm WC balls using a rotational rate of 850 rpm for 2 h.

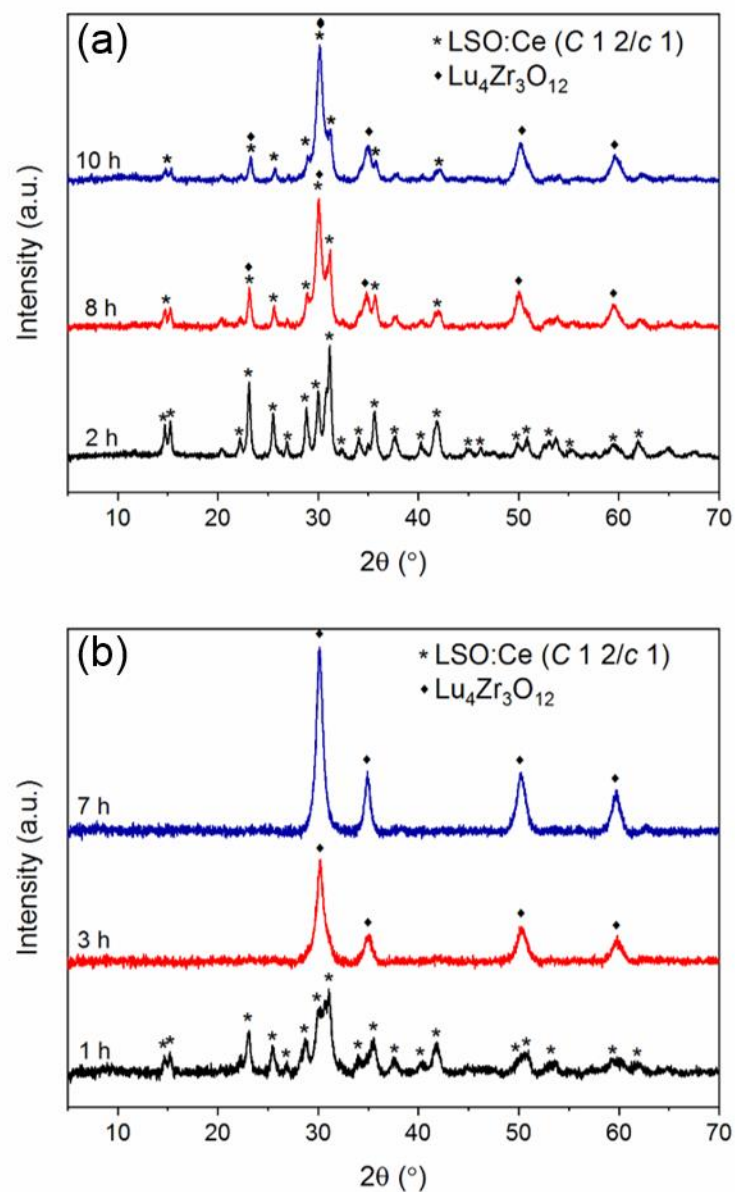


Figure 3.13. PXRD patterns depicting the reaction of LSO:Ce with ZrO_2 . (a) The mechanochemical synthesis and subsequent reaction of 2 g LSO:Ce in a ZrO_2 vial with seven 10-mm ZrO_2 balls and a rotation rate of 850 rpm. (b) The reaction of hand-ground, Czochralski-grown LSO:Ce in a ZrO_2 vial with seven 10-mm ZrO_2 balls and a rotation rate of 850 rpm.

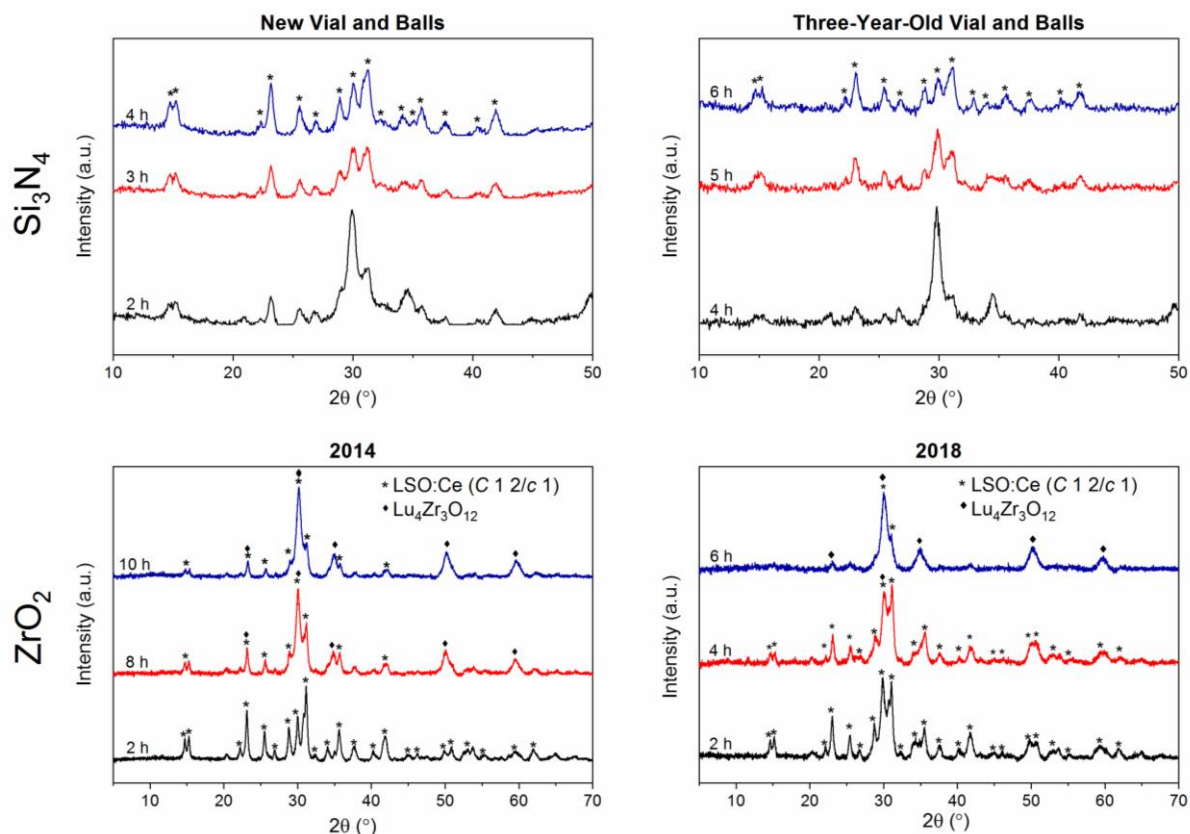


Figure 3.14. PXRD patterns depicting the effect of Si_3N_4 (top) or ZrO_2 (bottom) vial degradation over time. In the top sets of patterns, 4-g of LSO:Ce powder was synthesized in new (left) and three-year-old (right) Si_3N_4 vials with seven 10-mm Si_3N_4 balls rotated at 850 rpm. In the bottom sets of patterns, 2-g of LSO:Ce was synthesized in the same ZrO_2 vial in 2014 (left) and 2018 (right) with seven 10-mm balls rotated at 850 rpm.

ratios of 1:1. Each powder was milled at 850 rpm in a Si₃N₄ vial with seven 10-mm balls for up to 8 h with aliquots removed every 2 h.

3.6.2. Results

PXRD patterns were measured for each aliquot from each reaction to determine the optimum reaction time. All samples reacted in 4-6 h as with the initial dry synthesis of LSO:Ce. Any difference in reaction time is believed to be caused by degradation of the vial.

The fluorescence from powders collected at the optimum reaction times were measured and compared to the initial dry mill reaction. As can be seen in Figure 3.15, no significant difference was seen in the fluorescence with the addition of Mg, but there was a slight increase in the fluorescence intensity with the addition of Zn. This increase may be caused by reduction of a small portion of Ce⁴⁺ to Ce³⁺. It could also be caused in part by the solid-state sample preparation during fluorescence measurements. As mentioned in Section 3.3, the presence of amorphous LSO:Ce would drastically decrease the fluorescence intensity, which would explain the low intensity from all samples mechanochemically-synthesized powders. Further studies must be conducted to determine the degree to which Ce⁴⁺ has caused the low photoluminescence intensity and the degree to which it is caused by amorphous LSO:Ce.

3.7. Liquid-Assisted Mechanochemical Synthesis of LSO:Ce

Following the successful synthesis of LSO:Ce by the initial dry grinding method, liquid-assisted grinding (LAG) was attempted to decrease the reaction time.

3.7.1. Experimental Method

During these processes, the oxides were mixed in the same manner as during dry grinding with the addition of 900 μ L of various solvents. These solvents included water, methanol, ethanol, 0.05 M disodium ethylenediaminetetraacetate (EDTA) in water, dimethylsulfoxide (DMSO), dimethylformamide (DMF), 1-octanol, an aqueous solution of Lu³⁺, and an aqueous solution of SiO₃²⁻. The combined powders and solvents were milled at 850 rpm in Si₃N₄ vials with seven 10-mm balls, and samples were taken in 2-h increments up to 8 h.

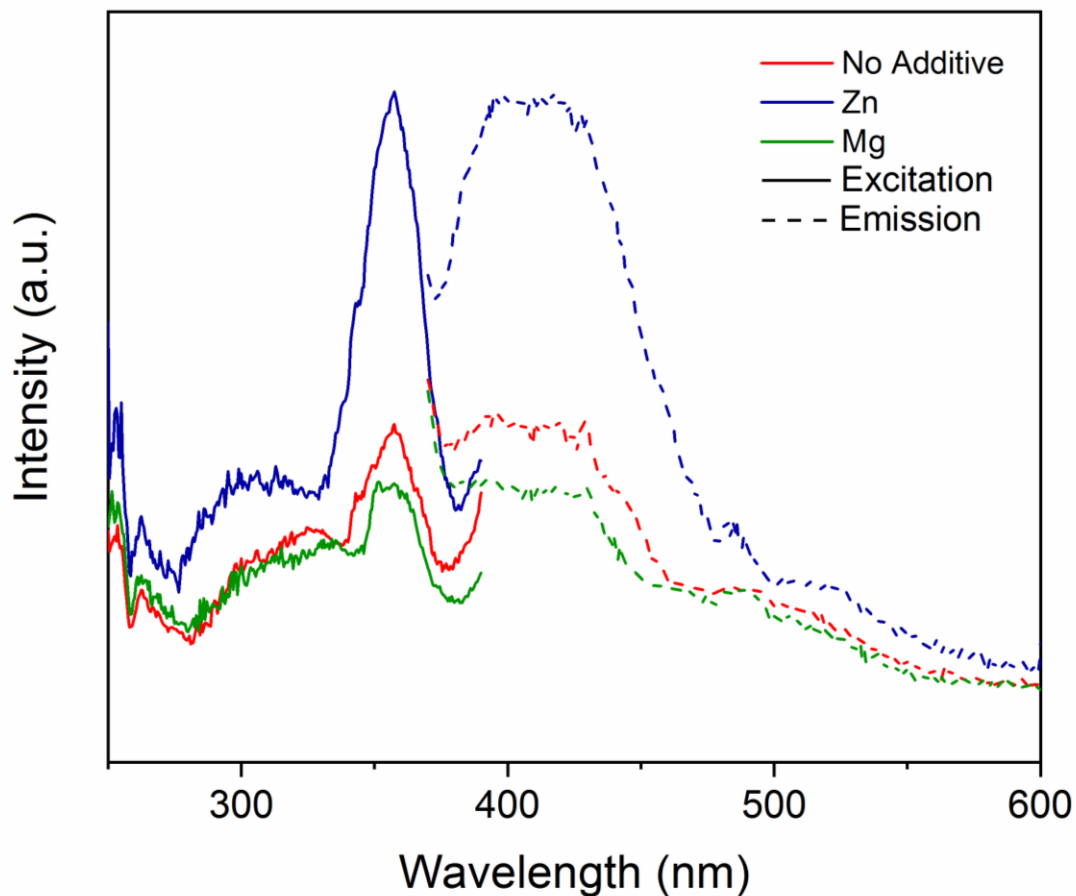


Figure 3.15. PL excitation ($\lambda_{\text{em}} = 410 \text{ nm}$) and emission ($\lambda_{\text{ex}} = 357 \text{ nm}$) spectra of LSO:Ce powder synthesized by mechanochemistry using Si_3N_4 vials with seven 10-mm, Si_3N_4 balls rotated at 850 rpm. The spectra correspond to LSO:Ce powder produced without any additives (black), with the addition of Zn (red), and with the addition of Mg (blue).

3.7.2. Results

Through PXRD patterns, the reaction time was determined for each LAG synthesis. All LAG experiments had longer reaction times than the initial dry synthesis. LAG with water and EDTA caused an increase in reaction time to 8 h while reactions using methanol and ethanol occurred in 6 h. DMF and 1-octanol LAG resulted in no formation of LSO:Ce within 8 h of milling. The longer reaction times suggest that oxides are not dissolving or forming a supersaturated solution prior to crystallizing into LSO:Ce in any of these systems. They may also indicate that the solvent must evaporate prior to the start of the reaction.

Aqueous solution of Lu^{3+} and Na_2SiO_3 were added separately for LAG to attempt to initiate ion exchange during milling. The reaction time during LAG using an aqueous solution of Lu^{3+} was 8 h. This matches the reaction time with the addition of water, which indicates that the increase in Lu^{3+} within the system does not aid or hinder the reaction. The addition of an aqueous solution of Na_2SiO_3 led to the formation of lutetium pyrosilicate ($\text{Lu}_2\text{Si}_2\text{O}_7$, LPS), which is expected with the addition of excess silicon.

3.8. Conclusion

Mechanochemistry using a planetary ball mill is a fast, room-temperature technique using little or no solvent. In the synthesis of LSO:Ce powders, it could negate the need for expensive Ir crucibles, high temperatures, long reaction times, and the use of large amounts of solvent. This solvent-free mechanochemical production of LSO:Ce powder has been successfully accomplished and proven to be faster than LAG. The solvent-free technique has been parametrically studied to demonstrate decreasing reaction times as mass of the powder decreased, number of balls increased, density of the vials and balls increased, rotation rate of the disk/vial increased, and ball diameter increased (within the variations used). These observations follow general trends predicted by the Burgio-Rojac model. Throughout this work, vial and ball degradation was monitored and shown to lead to decreased crystallinity, longer reaction times, and significant contamination, especially when using ZrO_2 which reacted with the powder to form $\text{Lu}_2\text{Zr}_3\text{O}_{12}$. Additionally, reductants (Zn and Mg) were added to the initial starting materials. These additives led to a minor increase in the reduction of Ce^{4+} to Ce^{3+} during

milling without altering the structure.

Sintering of the powder in a microwave led to PL quenching which was caused by the formation of oxygen vacancies. This issue did not occur with the use of a furnace for sintering, and furnace sintering was able to restore the PL of the microwave-sintered powder.

Through this work, it was determined that the dry mechanochemical production of LSO:Ce is an attractive synthetic approach due to its short reaction time, lack of solvent, scalability, and simplicity. The process warrants further studies to form smaller particles with a narrower size distribution and to optimize the process for industrial scale applications.

CHAPTER 4
THE COMBUSTION SYNTHESIS OF
CERIUM-DOPED LUTETIUM OXYORTHOSILICATE POWDERS

A portion of the work presented in this chapter was published by Melissa N. Bailey and George K. Schweitzer:

Bailey, M. N.; Schweitzer, G. K., The mechanochemical and solution combustion syntheses of cerium-doped lutetium oxyorthosilicate powder. *J Alloy Compd* **2018**, 734, 258-265.

All work presented in this chapter was conducted by Melissa Bailey with advisement from George K. Schweitzer.

4.1. Abstract

The synthesis of $\text{Lu}_2\text{SiO}_5\text{:Ce}$ (LSO:Ce) powders was attempted through solution and gel combustion using urea and hexamethylenetetramine both separately and as a mixture for fuel. Of these synthetic processes, the mixed-fuel solution combustion method was able to successfully produce LSO:Ce powders and was most easily replicable. This method produced LSO:Ce powders with a combination of the $P 1 2_1/c 1$ and $C 1 2/c 1$ space groups, which were compared to mechanochemically-produce LSO:Ce powders with $C 1 2/c 1$ symmetry. These powders were characterized before and after furnace and microwave sintering using powder X-ray diffraction (PXRD), photoluminescence (PL) excitation and emission spectroscopy, time-correlated single photon counting (TCSPC), dynamic light scattering (DLS) for particle size analysis (PSA), and scanning electron microscopy (SEM).

4.2. Introduction

4.2.1. Combustion Reactions

The first nanoparticle synthesis using solution combustion methods occurred in the 1980s with the thermal decomposition of metal hydrazinecarboxylates. These exothermic decompositions could be conducted at 125-250 °C and produced fine metal oxide powders and large amounts of gases. Following these reactions, α -alumina was produced using aluminum nitrate nonahydrate as the oxidizer and urea as the fuel. Both materials were dissolved in water and heated to 500 °C to initiate combustion.¹⁴³ Since these initial studies, countless metal oxides materials have been made through similar processes.¹⁴³⁻

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These syntheses involve a variation of one general process, which is depicted in

Figure 4.1. A fuel and oxidizer are dissolved in a solvent (usually water). In some syntheses, these solutions are partially dried below the boiling point of the solvent to form a gel. The undried solution or the gel can then be placed in a preheated furnace or on a preheated hot plate. The water evaporates, and foam forms. This foam then ignites as combustion occurs, allowing the foam material to reach higher temperatures than that of the initial heat source. One alternative method to ignition is inducing ignition in a small portion of the gel material and allowing the combustion reaction to self-propagate throughout the remainder of the gel. These combustion syntheses typically produce polycrystalline nanopowders.¹⁴³

These combustion reactions and their products are affected by several parameters, including fuel selection, fuel-to-oxidizer ratio, the temperature at which ignition occurs, the initial amount of water (or solvent), and the ratio of the mass of the mixture to the volume of the container.¹⁴⁶⁻¹⁴⁷ These factors can affect the product produced, the crystallite size, and the particle size.

The solution combustion (SC) and gel combustion (GC) processes are favored because they are quick, facile syntheses that require simple equipment and relatively low temperatures. Combustion synthesis allows homogeneous mixing of the metals at the molecular level because it starts with an aqueous solution. The large amounts of gases released during combustion expand the solid product, which leads to a fast decrease in the temperature once the reaction is over. This leads to the production of porous powders and to the possibility of forming multiple products.^{143, 145-146}

4.2.2. Oxidizers, Fuels, and Solvents

Combustion reactions can be categorized based on their oxidizer, fuel, and solvent. Some possible solvents are water, kerosene, benzene, ethanol, methanol, and formaldehyde. Of these, water is most commonly used. The solvents are used to dissolve the oxidizer and fuel, which leads to more homogenous mixing even down to the molecular level. This mixing allows the reaction to form a more uniform product.¹⁴³

The most common oxidizers in these reactions are nitrates because they decompose at low temperatures and are soluble in water. Nitrates can be in the form of metal nitrates, ammonium nitrate, or nitric acid. With metal nitrates, the nitrate acts as the oxidizer while

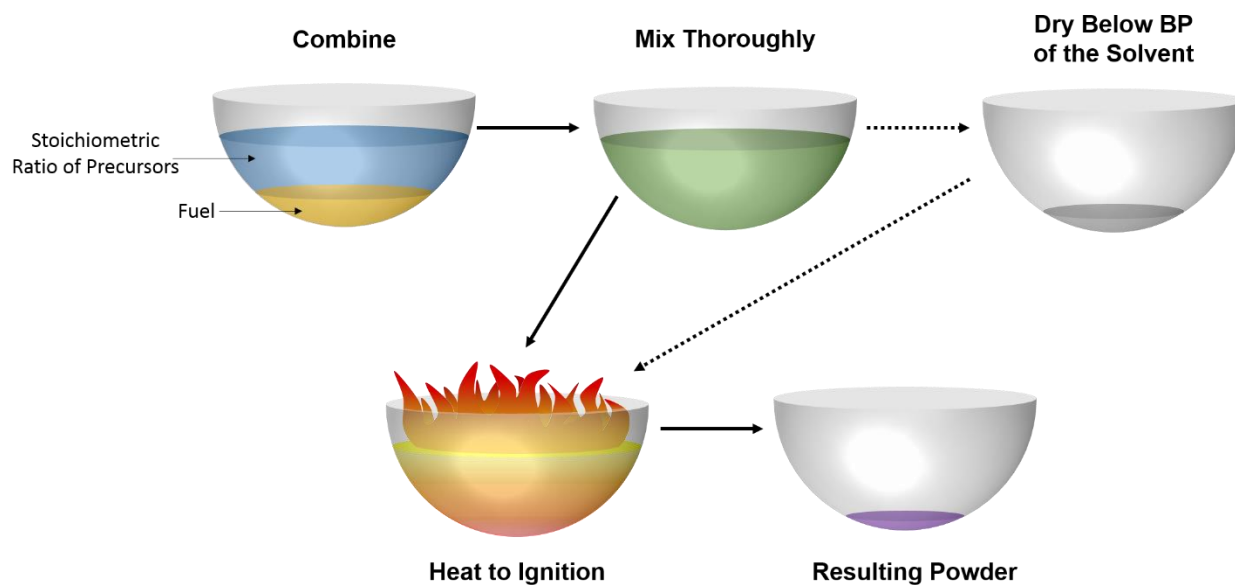


Figure 4.1. Illustration of the general process of combustion synthesis. Solid arrows represent the solution combustion method while dotted arrows represent the deviation from the process to conduct gel combustion synthesis. In this gel combustion method, a step is added in which the mixed materials are partially dried below the boiling point of the solvent. This drying results in the formation of a gel, which can then be heated to ignition.

the metal forms the solid metal oxide product.^{143, 146}

Urea, glycine, sucrose, glucose, citric acid, hydrazine, and derivatives of hydrazine like hexamethylenetetramine are a few examples of fuels used in combustion reactions.^{143, 145} These fuels are carbon and hydrogen sources which have highly exothermic decomposition reactions. Most are chosen because they are soluble in water, ignite at low temperatures, produce large quantities of gases upon decomposition with little to no residue, do not react explosively with metal nitrates, are commercially available, and are inexpensive.^{143, 145-146}

There are several important factors to consider in the selection of these materials. The combustion between the fuel and oxidizer should not be violent. The release of large amounts of these gases should allow the heat to dissipate quickly and reduce particle contact during the reaction.¹⁴⁶ Finally, the fuel should complex with the metal ion, which helps optimize homogeneity.^{143, 145-146}

Mixture of Fuels

Although many of the first combustion syntheses involved the use of only one fuel, a novel mixture-of-fuels approach has recently become increasingly popular. These combinations allow more control of the reaction by combining fuels with different negative heats of combustion or complexation proficiency. The method first started with Aruna and Rajam¹⁴⁸ who combined ammonium acetate, glycine, and urea. They saw that this mixture led to smaller particle sizes in the production of alumina and zirconia when compared to the single fuel syntheses.¹⁴⁸ Soon after Banerjee and Devi¹⁴⁹ synthesized ceria particles using a combination of citric acid and glycine. These particles exhibited better sinterability than those formed using a single fuel.¹⁴⁹ It is believed that combining fuels gives better control over the temperature of the flame during the combustion reaction because of the difference in the fuels' negative heats of combustion.¹⁵⁰⁻¹⁵¹ For example, the combination of glycine and citric acid was chosen because glycine is more reactive but citric acid exhibits less violent reactions.¹⁵¹ Urea and starch have also been used together. The urea can form stable polymeric intermediates and is less capable of dissipating heat, but starch has a less negative combustion enthalpy and higher adiabatic flame temperature. The combination results in a lower flame temperature than reactions

with urea alone. This lowered temperature reduces the average crystallite size of the powder because sintering is reduced.¹⁵²

4.3. Starting Material Production

In each of the following solution and gel combustion syntheses, solutions of $\text{Lu}(\text{NO}_3)_3$ and $\text{Ce}(\text{NO}_3)_3$ were used. These materials were first synthesized from the lanthanide (III) oxides, i.e. Lu_2O_3 and Ce_2O_3 . Powders of each of these oxides were added to concentrated HNO_3 . These mixtures were gently heated while stirring until the oxide dissolved to form lanthanide (III) nitrate solutions. The resulting $\text{Lu}(\text{NO}_3)_3$ solutions had concentrations ranging from 0.4 M to 0.6 M while the $\text{Ce}(\text{NO}_3)_3$ solutions had concentrations ranging between 2 M and 3M.

4.4. Single-Fuel Solution Combustion Synthesis of LSO:Ce Powder

Urea was used as the single fuel in initial studies of the solution combustion synthesis of LSO:Ce powder because it has commonly been used in previous solution combustion syntheses.¹⁴⁵⁻¹⁴⁶ Following these experiments, urea was replaced by hexamethylenetetramine because its combustion is more exothermic.¹⁵³

4.4.1. Experimental Method

This synthesis method was conducted based on previous processes by Blair, *et al.*³⁹ and Yukihiro, *et al.*¹⁷ Aqueous solutions of $\text{Lu}(\text{NO}_3)_3$ and $\text{Ce}(\text{NO}_3)_3$ were produced by dissolving Lu_2O_3 and Ce_2O_3 powders in HNO_3 . These solutions were mixed in an evaporation dish with either fumed silica or TEOS (tetraethoxysilane) (with the addition of approximately 0.5 mL of isopropyl alcohol to aid with miscibility) to form 2 g of LSO:Ce with 0.05% Ce doping. In syntheses with urea, a 1:16 molar ratio (Lu+Ce+Si:urea) was used. The mixtures were placed in a furnace pre-heated to 650 °C. The sample was removed from the furnace after complete combustion. A portion of the resulting powder was then sintered in a microwave for 7 min to approximately 1800 °C.

The combustion syntheses were then repeated with hexamethylenetetramine using molar ratios (Lu+Ce+Si:hexamethylenetetramine) of 2:9 and 2:1. The mixtures were combusted on a hot plate to allow the reaction process to be observed. The resulting products were not sintered following combustion.

4.4.2. Results

PXRD patterns were measured for all syntheses using urea. Representative examples of these PXRD patterns are in Figure 4.2. As can be seen in the patterns shown, the solution combustions involving urea showed only peaks for Lu_2O_3 . Following sintering, LSO:Ce peaks and low-intensity lutetium pyrosilicate peaks became evident in the PXRD pattern. The formation of the LSO:Ce following sintering may indicate that although the combustion was capable of decomposing $\text{Lu}(\text{NO}_3)_3$ into Lu_2O_3 , it was not exothermic enough to react that Lu_2O_3 with the fumed SiO_2 to form LSO:Ce. PXRD patterns measured for syntheses with urea and TEOS showed only Lu_2O_3 peaks both before and after sintering.

Hexamethylenetetramine was therefore used as a fuel as it has a more exothermic combustion reaction. A synthesis using a molar ratio of 2:9 was attempted first. This combustion was more violent than reactions with urea. Most of the water evaporated, the solid remaining turned brown before forming a foam. The foam combusted with a sudden, large flame which resulted in the loss of a significant portion the sample.

To reduce the explosiveness of the reaction involving hexamethylenetetramine, a molar ratio of 2:1 was attempted. In this reaction, the water evaporated, and then a yellow-brown gas was emitted until the sample was completely dry. A white film formed at the bottom of the beaker, but there was not enough recoverable product in either method using hexamethylenetetramine to measure PXRD patterns.

4.5. Mixed-Fuel Solution Combustion Synthesis of LSO:Ce

Due to the limited success of single-fuel solution combustion synthesis, LSO:Ce powder synthesis was attempted using a combination of urea and hexamethylenetetramine as the fuel. This combination may allow a less violent reaction to occur while also increasing the exothermicity of the reaction to produce LSO:Ce without further sintering.

4.5.1. Experimental Method

A 0.42-M solution of $\text{Lu}(\text{NO}_3)_3$ and a 2.21-M solution of $\text{Ce}(\text{NO}_3)_3$ were combined to form a mixed solution with a Lu-to-Ce molar ratio of 1.999:0.001 for 0.05% Ce doping. Fumed SiO_2 was added to this solution (Lu-to-Si molar ratio of 2:1). This suspension was

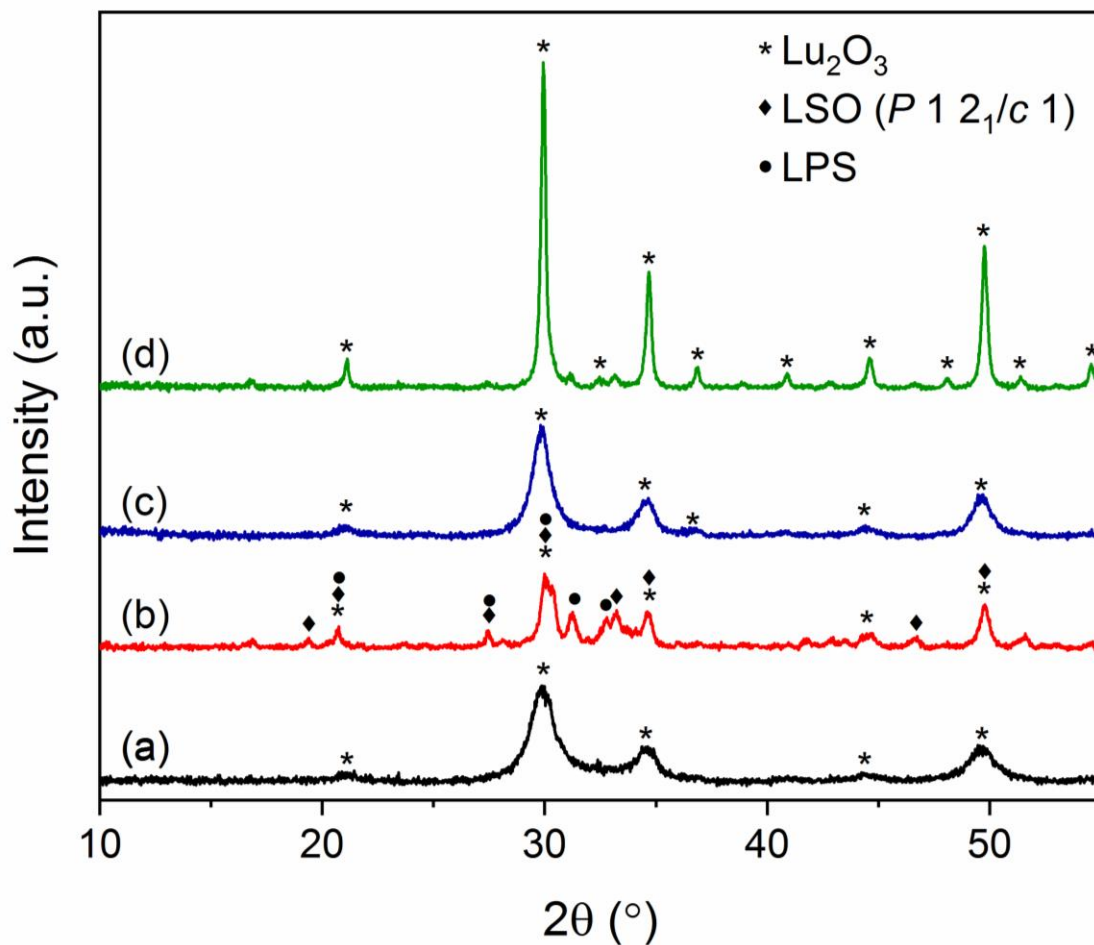


Figure 4.2. PXRD patterns from single fuel urea-based solution combustion syntheses of LSO:Ce. Syntheses used either fumed silica (a-b) or TEOS (c-d) as the silicon source, and PXRD patterns were measured before (a, c) and after (b, d) sintering the powders.

added to a mixture containing 3.23 g of urea and 0.44 g of hexamethylenetetramine (a 17:1 molar ratio). This mixture was heated to 650 °C in a MTI Corporation KSL 1100X furnace for approximately 30 min. During this time, vigorous boiling was observed followed by combustion of the mixture. The products were removed when the temperature of the furnace returned to approximately 650 °C. These solution combustion materials were microwave sintered for 7 min to approximately 1800 °C. Separate samples were heated in the furnace to 1100 °C for 4 hours.

The combustion reaction portion of this synthesis was then repeated with constant molar ratios of LSO:Ce starting materials and fuels but with various nitrate solution volumes between 10 mL and 35 mL. These mixtures were heated in beakers on a hot plate heated to approximately 430 °C until combustion completed.

4.5.2. Results

The normalized PXRD patterns of LSO:Ce powders synthesized through the initial solution combustion method before and after sintering are displayed in Figure 4.3. The peaks observed before sintering in the SC synthesized powders are indicative of the presence of monoclinic LSO:Ce with a mixture of the $P 1 2_1/c 1$ space group and the $C 1 2/c 1$ space group.^{17, 39, 46} A weak signal of $\text{Lu}_2\text{Si}_2\text{O}_7$ (LPS) can also be observed in the pattern. As with the LSO:Ce crystal and the LSO:Ce nanophosphors synthesized using the ball mill, the $C 1 2/c 1$ space group has the two crystallographically unique Lu ion sites having oxygen coordinations of six and seven. The LSO:Ce with $P 1 2_1/c 1$ symmetry also has two crystallographically unique Lu ion sites but with oxygen coordination numbers of seven and nine. The main 2θ values corresponding to the $C 1 2/c 1$ space group and the $P 1 2_1/c 1$ space group are listed in Table 2.1 with their Miller indices and relative intensities.⁴⁶⁻⁴⁷ For each space group, the peak positions of the patterns quantitatively match the theoretical values while their intensities semi-quantitatively match the theoretical values of the overlapping patterns. The $C 1 2/c 1$ space group is typically seen in high temperature reactions with the oxyorthosilicates of the smaller rare earth ions while the $P 1 2_1/c 1$ space group is typically seen in lower temperature reactions involving the oxyorthosilicates of the smaller rare earth ions.^{43, 48-50, 154} These results would therefore indicate the reaction occurred with varied temperature throughout the sample

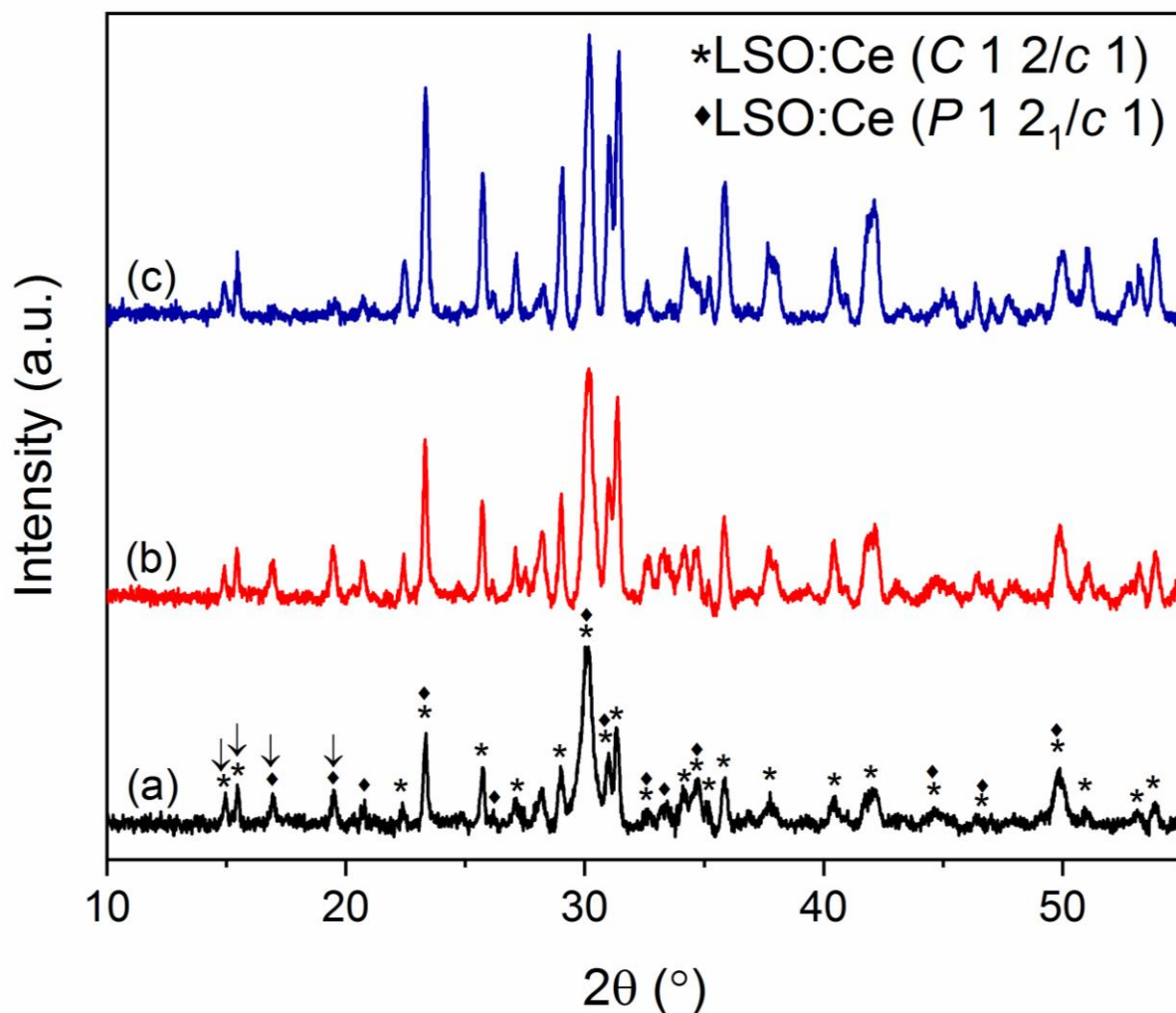


Figure 4.3. PXRD patterns of LSO:Ce synthesized through mixed-fuel solution combustion method (a) without sintering, (b) with microwave sintering, and (c) with furnace sintering. The peaks used in the Scherrer equation calculations are marked with arrows.

or near the transition temperature between the two phases.

After microwave sintering, the peaks for the $C 1 2/c 1$ space group become more prominent while the $P 1 2_1/c 1$ peaks have similar intensities to those before sintering. With the furnace-sintered material, the $C 1 2/c 1$ peaks are more intense than the peaks in the microwave-sintered material's spectrum, and the $P 1 2_1/c 1$ peaks have almost disappeared. This behavior is similar to that of $Y_2SiO_5:Ce$. For this compound, the $P 1 2_1/c 1$ material is stable up to 1100 °C and will convert to the $C 1 2/c 1$ space group at higher temperatures.⁴⁸⁻⁵⁰ This conversion from one phase to the other shows the greater stability of the $C 1 2/c 1$ phase at higher temperatures for lanthanide oxyorthosilicates.

From the PXRD spectra in Figure 4.3, crystallite sizes were calculated through use of the Scherrer equation. Peaks were selected for analysis due to their lack of overlap with other peaks rather than their intensity. Because the spectra have significant overlap within the majority of the peaks and because the chosen peaks have low intensity, multiple fitting methods within the X'Pert HighScore program were utilized, leading to a range of particle sizes for each material and phase. The peaks chosen for crystallite size analysis of the $C 1 2/c 1$ space group material were 14.7° and 15.2°, which correspond to the Miller indices (2 0 0) and (1 0 0). For analysis of the $P 1 2_1/c 1$ material, peaks at 16.6° and 19.2° with the Miller indices (1 0 0) and (0 0 -1), respectively, were chosen. The crystallite sizes calculated for $C 1 2/c 1$ phase were 39-52 nm for the unsintered powder, 39-53 nm for the microwave sintered powder, and 31-62 nm for the furnace sintered powder. For the $P 1 2_1/c 1$ phase, the crystallite sizes calculated were 30-62 nm for the unsintered material and 26-35 nm for the microwave sintered material. Considering the significant error associated with the peak fitting process and with the Scherrer equation's β and K variables, no judgement can be made about trends in these data, given the ranges of the crystallite sizes.¹⁵⁵

SEM was used to determine the morphology and particle size distribution of this SC synthetic material before and after sintering (Figure 4.4). Although the sizes and shapes of the samples vary significantly within each sample, all samples showed evidence of significant porosity within the particles.

The particle size distributions of the unsintered and microwave-sintered samples

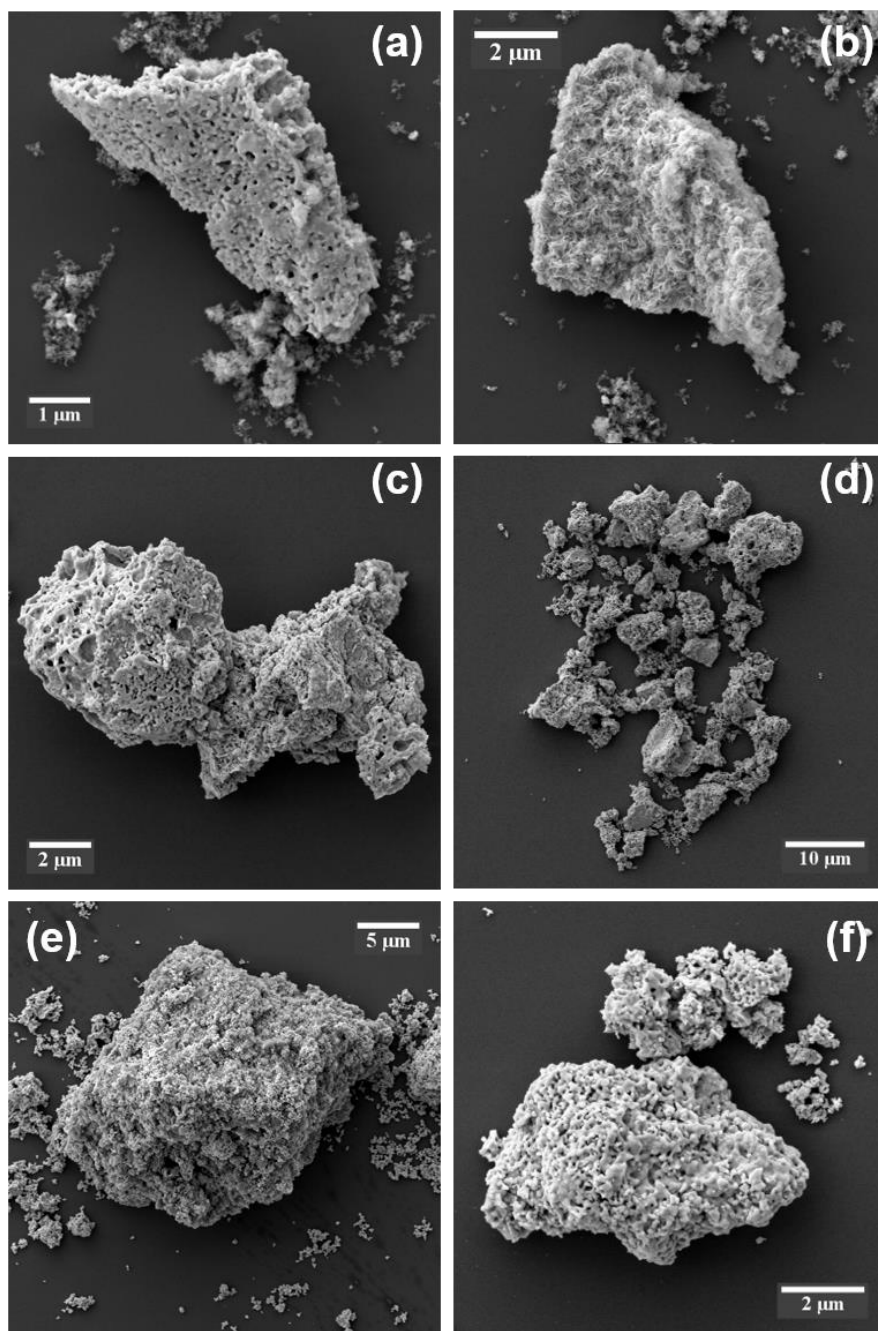


Figure 4.4. SEM images of LSO:Ce powder synthesized through solution combustion method (a-b) before sintering, (c-d) after microwave sintering, and (e-f) after furnace sintering at different magnifications.

were also determined using SEM with PSA measurements to verify the results. The DLS measurements were conducted at approximately 25 °C in quadruplicate for the SCS material before sintering and triplicate after microwave sintering. From the SEM, the ranges for the unsintered, microwave-sintered, and furnace-sintered materials were 65 nm to 43 µm, 100 nm to 59 µm, and 80 nm to 60 µm, respectively. The average particle sizes from the PSA were 576 nm before sintering and 837 nm after microwave sintering. Each of the averages falls within the range given by SEM. As with the mechanochemically-synthesized LSO:Ce, particle size seems to increase with sintering.

Figure 4.5 presents the photoluminescence excitation and emission spectra of LSO:Ce nanophosphors synthesized through initial mixed-fuel solution combustion method. For the material before sintering, the excitation spectrum used an emission wavelength of 435 nm, and the emission spectrum used an excitation wavelength of 369 nm. The excitation and emission spectra display a red shift in the peaks when compared to powdered Czochralski-grown LSO:Ce with peaks at about 369 nm and about 435 nm, respectively. This shift corresponds to LSO:Ce nanophosphors with the space group $P 1 2_1/c 1$, but are attributed to the same transitions as with the $C 1 2/c 1$ space group.^{17, 39} The larger Stokes shift of the $P 1 2_1/c 1$ -type crystal indicates greater dopant-lattice coupling than the $C 1 2/c 1$ -type crystal.¹⁵⁶ Both the PL excitation and emission spectra of the microwave-sintered and furnace-sintered materials show a shift toward lower wavelengths and a broadening of the emission band. The shift is consistent with the increased crystallinity of the LSO:Ce with the $C 1 2/c 1$ space group within the sample, and the broadening may indicate greater splitting of the 4f levels in LSO:Ce with the $C 1 2/c 1$ space group. Microwave-sintered powders had slightly decreased intensities for their excitation and emission spectra, which was most likely due to the presence of oxygen vacancies in the crystal structure as was similarly concluded in Chapter 3.

Decay time measurements were plotted in Figure 4.6 for this solution combustion synthesized LSO:Ce before sintering and after microwave and furnace sintering. Each curve was best fitted using two components representing two lifetimes. The shorter lifetimes for the unsintered, microwave-sintered, and furnace-sintered materials were 8 ns, 15 ns, and 18 ns, respectively. The longer lifetimes for the three samples were 34-39

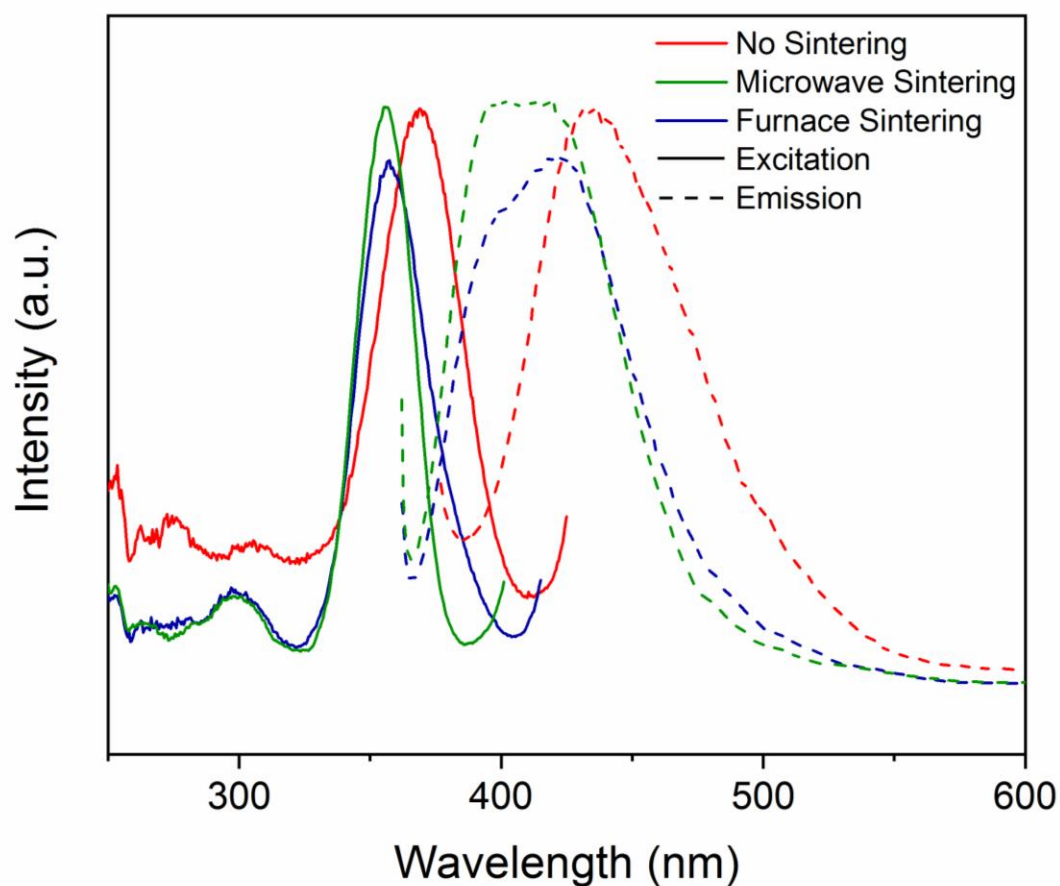


Figure 4.5. PL excitation and emission spectra for LSO:Ce synthesized through solution combustion. Spectra were measured of powders before sintering ($\lambda_{em} = 435$ nm; $\lambda_{ex} = 369$ nm), with microwave sintering ($\lambda_{em} = 423$ nm; $\lambda_{ex} = 357$ nm), and with furnace sintering ($\lambda_{em} = 410$ nm; $\lambda_{ex} = 357$ nm).

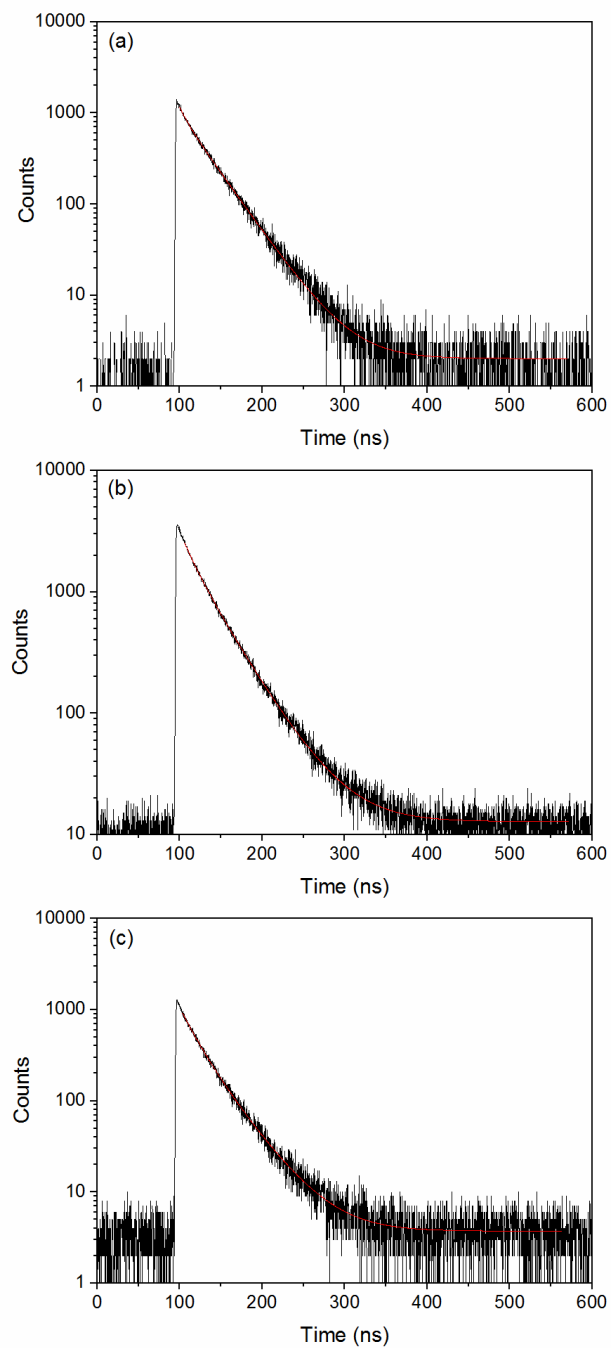


Figure 4.6. Decay time spectra for LSO:Ce powder synthesized through solution combustion method (a) before sintering, (b) after microwave sintering, and (c) after furnace sintering.

ns. The longer components match the literature value for the excitation of Ce^{3+} in LSO:Ce while the source of the shorter component is not known.^{40, 141-142}

The use of beakers and a hot plate when varying mixture volumes allowed the synthesis to be monitored during combustion. Once the beaker was placed on the hot plate, the solution boiled until most of the solvent had evaporated. A white and brown foam then formed, typically to four times the volume of the original solvent at the concentrations used. Gas was then released from the foam until only a small amount of foam remained. Flame ignition then occurred, leaving a white and brown powder. PXRD patterns for these solution combustion syntheses were measured to test replicability and scalability. All patterns matched those of the initial solution combustion synthesis, which indicates the process is highly replicable and scalable, which is crucial for its use in industry.

4.5.3. Comparison of the Mechanochemical Synthesis and Solution Combustion Synthesis of LSO:Ce

This initial mixed-fuel solution combustion method of producing LSO:Ce (SC-LSO:Ce) allows comparisons to be made with mechanochemically-synthesized LSO:Ce (MC-LSO:Ce) in which stoichiometrically-mixed oxides were milled for 4 h in a Si_3N_4 vial with seven 10-mm Si_3N_4 balls at 850 rpm (described in Section 3.4). The most significant difference between the LSO:Ce powders is their symmetry. As can be seen through both PXRD (Figure 4.7) and photoluminescence (Figure 4.8) measurements, MC-LSO:Ce has $C 1 2/c 1$ symmetry while SC-LSO:Ce has a mixture of $P 1 2_1/c 1$ and $C 1 2/c 1$ symmetry. This mixture of phases in the SC-LSO:Ce red-shifts the photoluminescence spectra which may result in a smaller degree of self-absorption during radiation measurements.^{17, 39} Ceramics of the material would have $C 1 2/c 1$ symmetry regardless of the method due to the shift in phase with heating, and mechanochemistry is a more direct route to this symmetry.

Comparison of the photoluminescence measurements of microwave-sintered SC-LSO:Ce and MC-LSO:Ce shows a decrease in intensity in both excitation and emission spectra when compared to unsintered SC-LSO:Ce and MC-LSO-Ce. This intensity decrease suggests that the cause must be related to the LSO:Ce itself rather than a

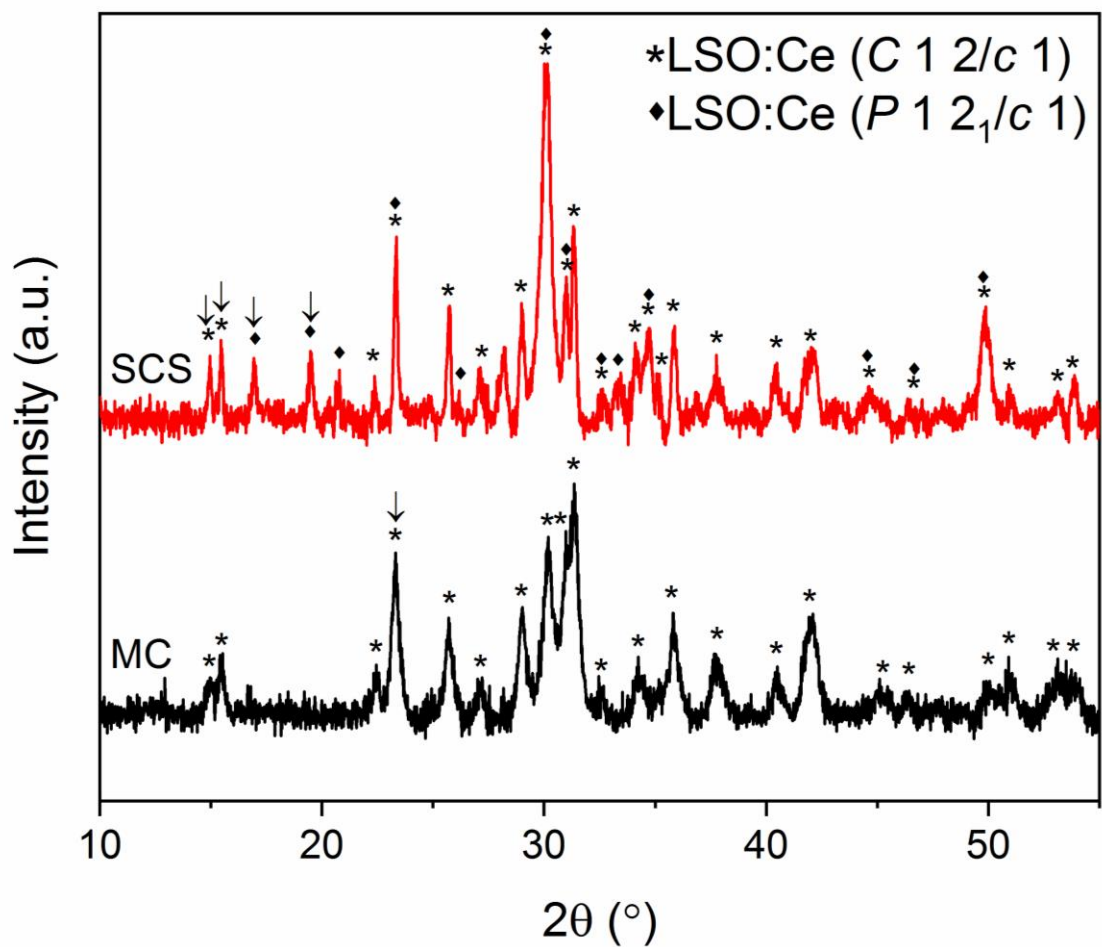


Figure 4.7. PXRD comparison of mechanochemically-synthesized LSO:Ce (MC) and solution combustion-synthesized LSO:Ce (SC). Peaks used for Scherrer equation calculations of crystallite size are marked with arrows.

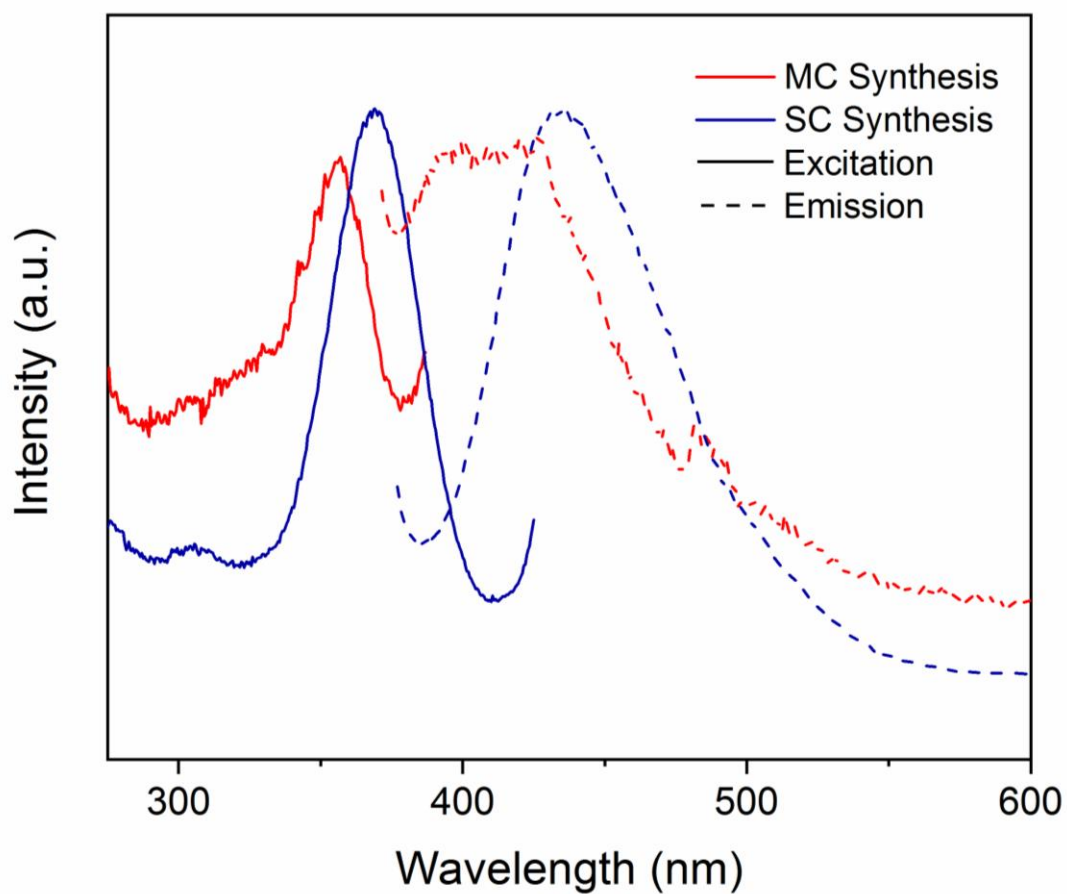


Figure 4.8. PL excitation and emission spectra for LSO:Ce synthesized through mechanochemical ($\lambda_{em} = 410$ nm; $\lambda_{ex} = 357$ nm) and solution combustion ($\lambda_{em} = 435$ nm; $\lambda_{ex} = 369$ nm) methods.

product of the synthetic method. It was determined that the loss in intensity for the MC-LSO:Ce was caused by an increase in oxygen vacancies (as described in Section 3.4.2); it can therefore be assumed that oxygen vacancies would also decrease the intensity for SC-LSO:Ce.

The signal-to-noise ratio (S/N) is much higher for the SC-LSO:Ce photoluminescence measurements. This high S/N may be indicative of greater Ce³⁺ concentrations, greater crystallinity, fewer oxygen vacancies, or greater dopant dispersion.³⁹ All of which would make solution combustion a more favorable method of producing LSO:Ce powders and ceramics.

Both before and after sintering, the photoluminescence decay times of the SC-LSO:Ce at 34-39 ns was slightly longer than that of the MC-LSO:Ce at 25-27 ns. These analyses directly measure the decay time of the Ce³⁺, so they will vary as the crystal structure around the dopant shifts. The symmetry differences between the two powders may cause the variation in decay times, but they are still within the error of what is commonly measured for Ce³⁺ in LSO:Ce.

Crystallite sizes cannot currently be compared due to the significant error involved in the use of the Scherrer equation for SC-LSO:Ce because of the mixed phases and the need to use lower intensity peaks. Based on SEM, their particle size ranges (Table 4.1) were similar with a slight increase with sintering. This increase is minimal and may be due to the error of the measurements and the small sample size.

As seen in the SEM image (Figure 4.9) Both samples were a wide range of sizes and shapes. However, the SC-LSO:Ce was considerably more porous than the MC-LSO:Ce due to gas evolution during combustion. More experimentation is necessary to determine how this porosity would affect the formation of ceramics.

Both the SC and MC methods involve simple, scalable reactions with short reaction times. In selecting mechanochemistry or solution combustion as a synthesis method for LSO:Ce, the final application and most beneficial properties must be taken into account. Mechanochemistry allows the more direct route to producing C₁/2C₁-type LSO:Ce although the vials and balls themselves do contaminate the powder. MC synthesis also involves a room temperature reaction with no solvents. Conversely, SC-LSO:Ce has

Table 4.1. Particle size ranges for LSO:Ce synthesized through solution combustion and mechanochemistry.

Synthesis Method	Processing	Particle Size Range
Solution Combustion	No Sintering	65 nm - 43 μ m
	Microwave Sintering	100 nm - 59 μ m
	Furnace Sintering	80 nm - 60 μ m
Mechanochemistry	No Sintering	75 nm - 40 μ m
	Microwave Sintering	80 nm - 55 μ m
	Furnace Sintering	100 nm - 225 μ m

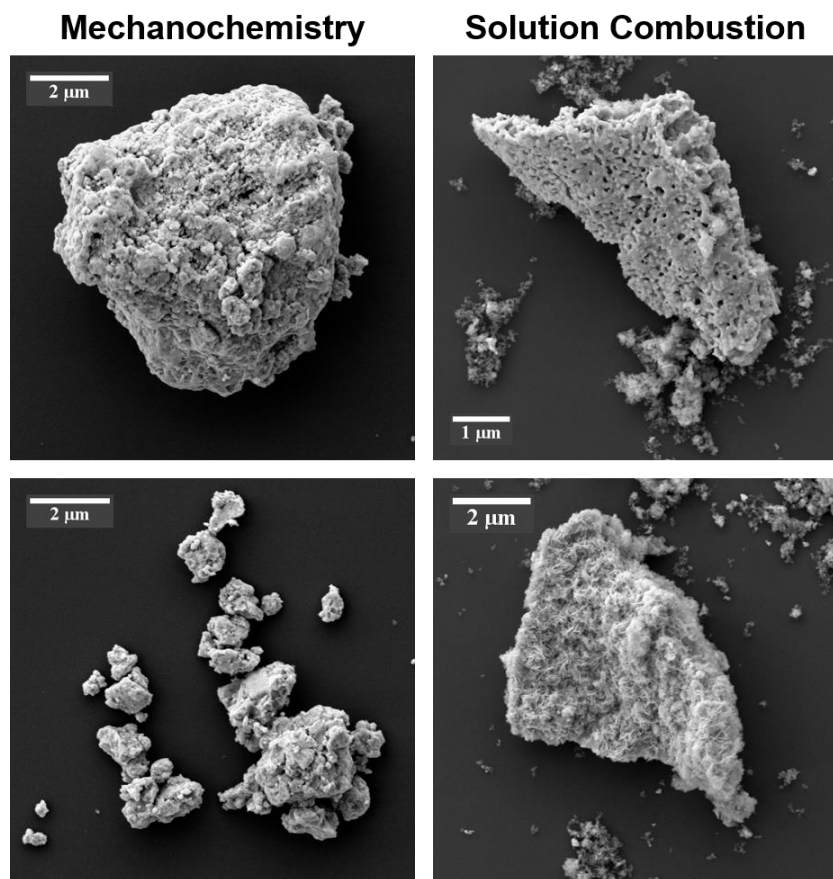


Figure 4.9. SEM comparison of particle morphology following the mechanochemical (left) and solution combustion (right) syntheses of LSO:Ce powders.

better S/N with photoluminescence measurements which may indicate greater dopant dispersion, greater dopant concentrations, greater crystallinity, or fewer oxygen vacancies. It has shorter reaction times and is more easily scalable. However, it does produce porous powders which may affect future pressing of ceramics. With either method, more study is necessary before use in industry, but both show promise for future applications.

4.6. Gel Combustion of LSO:Ce Powder

In several previously-conducted gel combustion syntheses, the prepared solutions were first dried at temperatures below the boiling point of the solvent to form a gel. This gel was then combusted.^{19, 157-160} Studies were conducted to determine if the LSO:Ce synthesis and structure would vary between solution combustion and gel combustion, using both single and mixed fuel methods.

4.6.1. Experimental Method

Single Fuel Method

In these syntheses, the lutetium(III) nitrate and cerium(III) nitrate solutions were combined with fumed silica with Lu:Ce:Si molar ratios of 1.99:0.01:1. The molar ratio of these elements-to-urea was 3:5. These precursors were combined to produce between 0.4 g and 2.0 g of LSO:Ce. After mixing the precursors in a 50-mL beaker, they were partially dried in an oven at 70 °C overnight. The gels were then placed on a hot plate preheated to approximately 430 °C until combustion completed.

Mixed Fuel Method

Stoichiometric ratios of aqueous solutions of lutetium(III) nitrate and cerium(III) nitrate were combined with fumed silica to form 0.25-2.50 g of $\text{Lu}_{1.99}\text{Ce}_{0.01}\text{SiO}_5$. Urea and hexamethylenetetramine were added with a molar ratio of 4:17:1 (Lu+Ce+Si:urea:hexamethylenetetramine). The precursors were either partially or thoroughly dried overnight at 70 °C and then placed on a hot plate preheated to approximately 430 °C until combustion was completed.

4.6.2. Results

Single Fuel Method

Partially drying the mixtures of urea and the starting materials of LSO:Ce resulted in a tacky (i.e. sticky) film at the bottom and on the sides of the beaker which became stickier as initial solution volume increased. Combustion of these films results in powder which ranged in color from white to yellow as the initial volume increased. As can be seen the representative pattern in Figure 4.10, PXRD measurements showed primarily amorphous material with low intensity peaks which could not be identified.

Mixed Fuel Method

The drying time of the mixed fuel samples was varied between experiments. Samples were dried to form a gel (usually containing some white solid), solely white solid flakes, or yellow solid flakes. With the combustion of the white crystals and gels, yellow-brown gas evolved, but ignition did not occur. PXRD patterns (Figure 4.11) showed Lu_2O_3 and an unidentifiable contaminant. During the combustion of dried samples which were yellow crystals, a yellow-brown foam formed from the solid and deflated before flame ignition occurred. PXRD pattern (Figure 4.11) showed that these combustions resulted in the formation of LSO:Ce with both $P 1 2_1/c 1$ and $C 1 2/c 1$ symmetry. The differences between these reactions were most likely caused by variations in drying. More experimentation is required to determine why and how the yellow solid formed and why it was able to ignite while the gel/white solid did not.

4.7. Conclusion

Through urea/hexamethylenetetramine-nitrate-based solution combustion, LSO:Ce powders were successfully produced with a mixture of $P 1 2_1/c 1$ and $C 1 2/c 1$ symmetries, which shifted to solely $C 1 2/c 1$ symmetry upon subsequent heating. These powders had a better signal-to-noise ratio for its photoluminescence spectra than those of mechanochemically-produced LSO:Ce powders, which may indicate greater dispersion of Ce^{3+} , higher concentrations of Ce^{3+} , or fewer oxygen vacancies. A similar method using urea/hexamethylenetetramine-nitrate-based gel combustion, which adds a slow drying step prior to ignition, was also effective, but it required an extra drying step and was not reliably replicable.

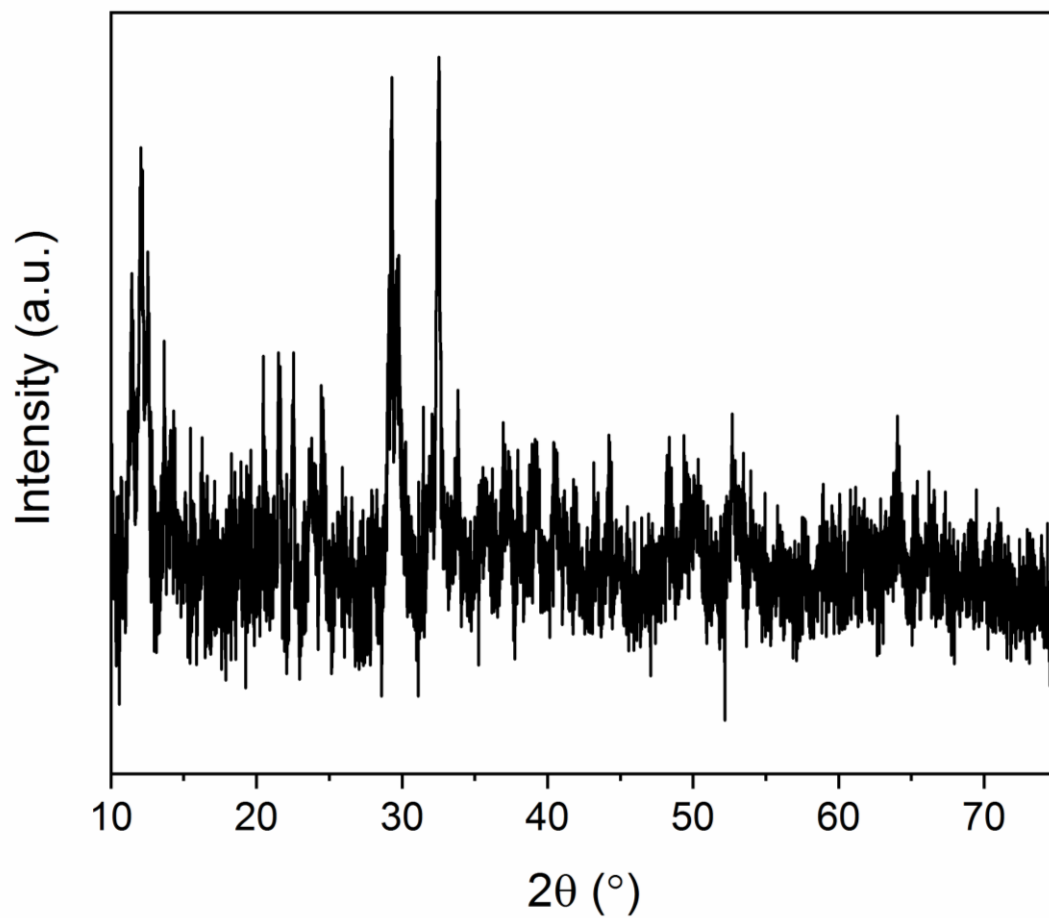


Figure 4.10. Representative PXRD pattern from an attempt to form LSO:Ce by gel combustion using urea as the fuel.

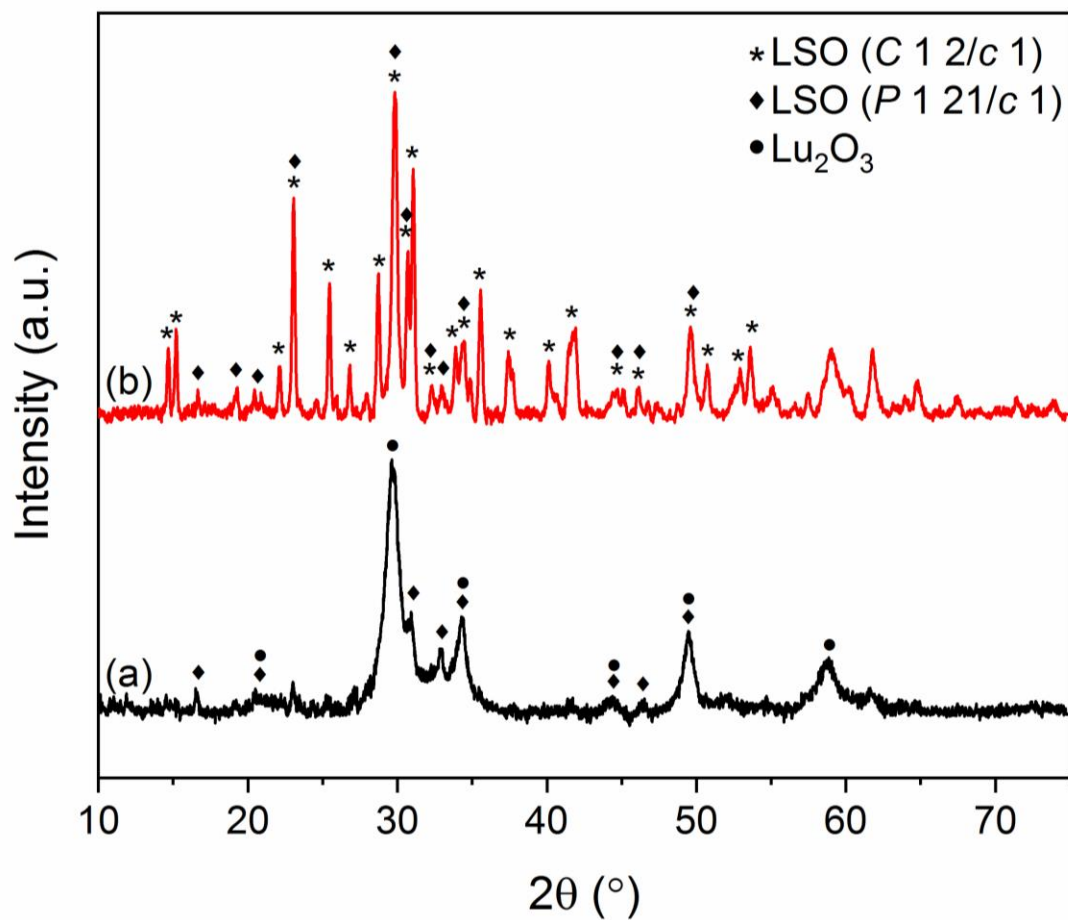


Figure 4.11. Representative PXRD patterns following the mixed-fuel gel combustion syntheses of LSO:Ce. The dried material before combustion consisted of (a) gels and/or white flakes of solid or (b) yellow solid flakes.

The mixed-fuel solution combustion production of LSO:Ce provides an appealing synthetic approach owing to its short reaction time, scalability, simplicity, and replicability. Due to these advantages, further studies into the effect of other fuels and optimizing the process for industrial use is merited.

CHAPTER 5
EXPLORATORY STUDIES INTO THE SYNTHESIS OF OPTICALLY-ACTIVE β -GeO₂
AND α -QUARTZ NANOPARTICLES USING CHIRAL TEMPLATING AGENTS

5.1. Abstract

Initial studies were conducted to synthesize optically-active α -quartz nanoparticles using enantiomeric optically-active β -GeO₂ as a template. First, an attempt was made to template chirality in β -GeO₂ nanoparticles with an enantiomeric excess using L-lysine and (R)-(+)-1,2-diaminopropane as capping/templating agents. No measurable optical activity through polarimeter or CD measurements was observed for the synthesized nanoparticles with either capping agent. The formation of a racemic mixture is most likely due to insufficient adsorption of the templating agent as confirmed by FTIR and TGA-MS. Separately, tetraethoxysilane and germanium (IV) ethoxide were hydrolyzed in one solution in an effort to produce α -quartz with β -GeO₂ as a template. This powder was subsequently heated in various basic solvents to crystallize α -quartz. Heating with solutions containing NaOH, NH₄OH, and Ba(OH)₂ resulted in partial or complete reaction of the powders. Powders heated in CsOH solutions did not show measurable contamination through PXRD, but α -quartz did not crystallize, which was verified by PXRD and electron diffraction measurements.

5.2. Introduction

5.2.1. Previously-Synthesized Optically-Active Nanoparticles

Before the potential applications of optically-active nanomaterials can be fully explored, a better understanding of chiral materials and their optical activity must be achieved. Improvements must first be made in the synthesis of novel chiral nanoparticles and in the control of their chiral structure and optical activity. These improved and/or newly explored properties can then be applied in the research of chiral nanoparticles' functionalities.

The majority of studies on chiral nanoparticles has occurred within the last five years with focus primarily on induced-chirality with materials like Au, Ag, CdS, CdSe, CdTe, ZnO, WO_{3-x}·H₂O, and TiO₂.^{73, 84-92} Recently, attention has shifted slightly toward intrinsically-chiral optically-active metal (e.g. Se and Te) and metal sulfide (e.g. HgS) nanoparticles. The syntheses of these chiral nanoparticles have thus far involved low-temperature (<100 °C) reactions. These low temperatures allow the use of a wide variety of capping agents because racemization is less likely to occur than in a high-temperature

synthesis. Research of chiral nanoparticles has not yet addressed intrinsically-chiral nanoparticles which require higher temperatures for production. At these high temperatures, many chiral capping agents would quickly racemize or decompose, but the exploration of high-temperature syntheses might further our understanding of inorganic chirality in nanoparticles.⁹⁶⁻⁹⁸

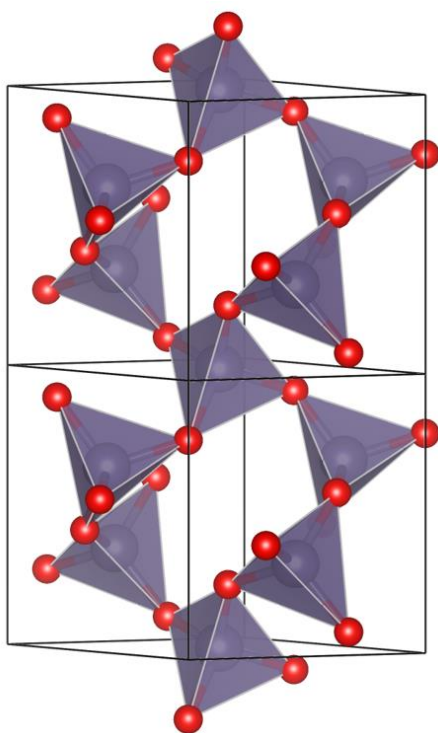
5.2.2. β -GeO₂ and α -Quartz

Two materials which exhibit intrinsic chirality in their macroscopic structures are β -GeO₂ and α -quartz (α -SiO₂). Both materials have monoclinic crystal structures composed of corner-linked SiO₄ tetrahedra (Figure 5.1). These linked-tetrahedra form either a right-handed ($P 3_2 2 1$ space group) or a left-handed ($P 3_1 2 1$ space group) spiral. The structures are mirror-images of each other and rotate light in opposite directions.¹⁶¹⁻¹⁶³

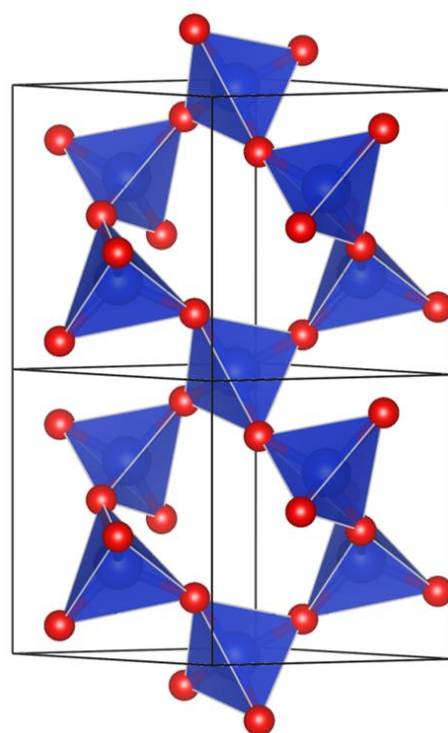
Large optically-active crystals of each material are relatively simple to produce. Chiral quartz crystals are found in nature and can be separated into their enantiomers through mechanical methods. Optically-active crystals can also be grown by a hydrothermal method in which silica is dissolved in water in an autoclave above 350 °C. A seed crystal of a single enantiomer of quartz is added to grow crystals with a matching enantiomeric structure.¹⁶⁴ Although β -GeO₂ crystals are not found in nature, they can be grown through similar hydrothermal methods as α -SiO₂, using temperatures below 185°C and quartz seed crystals to promote the formation of one enantiomer over the other.¹⁶⁵

Optically-active nanoparticles of β -GeO₂ and α -quartz have not previously been produced although there have been several nanoparticle syntheses for racemates of each. Rac- β -GeO₂ nanostructures in particular have been synthesized through a wide variety of techniques including co-precipitation, laser ablation, thermal oxidation, sol-gel, chemical vapor deposition, hydrothermal methods, electrospinning, reverse micelle, and germanate decomposition.¹⁶⁶⁻¹⁷³

Davis, *et al.*¹⁷⁴ first synthesized β -GeO₂ nanoparticles in 2007 to compare the hydrolysis of tetraethoxysilane (TEOS, Si(OEt)₄) to the hydrolysis of germanium (IV) ethoxide (TEOG, Ge(OEt)₄). In this reaction, Ge(OEt)₄ was combined with water, ethanol, and in some cases lysine while vigorously stirring the solution at room temperature. The hydrolysis resulted in approximately 100 nm or larger particles.



β -GeO₂
 $P 3_1 2 1$



α -Quartz
 $P 3_2 2 1$

Figure 5.1. Mirror-image crystal structures of β -GeO₂ ($P 3_1 2 1$) and α -quartz ($P 3_2 2 1$). Although each material can form either space group, there are minor differences in the lattice parameters. Images created from data in reference by Lignie, *et al.*¹⁶¹

In 2010, Ramana, *et al.*¹⁶⁹ started their β -GeO₂ powder synthesis by heating GeO₂ in water. NH₄OH was added, which led to the formation of soluble germanate ions. When nitric acid (HNO₃) was added, a white precipitate formed. These GeO₂ particles were about 500 nm in diameter.

In an attempt to decrease the size of the GeO₂ nanoparticles, Javadi, *et al.*¹⁷⁰ also synthesized crystalline β -GeO₂ nanoparticles at room temperature through germanium (IV) ethoxide hydrolysis. In this process, size was controlled by varying the water content (10 (v/v)% to >70 (v/v)%) of the solvent with sizes ranging from approximately 13 nm to 0.5 μ m. The smallest nanoparticles were produced using a 10 (v/v)% water solution.¹⁷⁰

In 2015, Nejaty-Moghadam, *et al.*¹⁷² and Esmaeili-Bafghi-Karimabad, *et al.*¹⁷¹ attempted syntheses using GeCl₄. Nejaty-Moghadam, *et al.*¹⁷² added GeCl₄ to a solution of acetylacetone (acac) and ethylene glycol (EG), varying the acac:GeCl₄ molar ratio. Water was then added to the solution dropwise while heating to various temperatures, and the mixture was stirred until a precipitate formed. The smallest nanoparticles at approximately 70 nm were formed using an acac:GeCl₄ molar ratio of 2:1 and a temperature of 110 °C while adding water. Esmaeili-Bafghi-Karimabad, *et al.*¹⁷¹ added GeCl₄ to solutions of EG and one of three acids (citric acid, maleic acid, and succinic acid) with various ratios of acid:EG. The mixture was stirred for approximately 1 h until a gel formed. After the gel formed, water was added dropwise while heating, and the mixture was stirred until a white precipitate formed. Using citric acid, an acid:EG molar ratio of 1:3, and 90 °C while adding water, 10-20 nm nanoparticles were formed.

The synthesis of α -quartz requires higher temperature (>200 °C) and pressure reactions, longer reaction times, or complicated additives compared to the synthesis of β -GeO₂ nanoparticles. The first evidence of nanocrystalline α -quartz formation was observed by Mackenzie, *et al.*¹⁷⁵ in 1971 when a mixture of sea water and powdered α -quartz was agitated on a shaker for three years. Over this period of time, the silica concentration in the water increased before small α -quartz crystals began to appear on the surface of the powder.¹⁷⁵

This observation was followed in 2003 with the growth of sub-micron and nanoparticle α -quartz. Huang, *et al.*¹⁷⁶ heated opal (amorphous silica) in sea water,

distilled water, or an aqueous 0.5-M KOH solution to 50-450 °C with pressures between 50 MPa and 3 GPa. Their results show that increasing the pressure increases the nucleation and growth rates of sub-micron α -quartz powder.¹⁷⁶ In the same year, Bertone, *et al.*¹⁷⁷ formed particles of α -quartz by heating amorphous silica in a 0.1-M NaOH solution from room temperature to 200-300 °C at a ramp rate of 6 °C/min. At temperatures above 250 °C, α -quartz precipitated in less than 5 h. Although this precipitate contained powders with sizes up to 440 nm, the particles could be partially separated by size with the smallest samples at 18 ± 5 nm.¹⁷⁷ A third publication in this area by Li, *et al.*¹⁷⁸ combined 0.25-M NaOH and amorphous silica, produced by adding HCl to an aqueous sodium silicate solution. This mixture was heated to 210 °C under vapor pressure for 26 h to produce sub-micron particles of α -quartz with sizes ranging from 50 nm to 300 nm and an average size of 182 nm.¹⁷⁸

A few years later, Bansal *et al.*¹⁷⁹ used the fungus *Fusarium oxysporum* shaken at 200 rpm for 24 h with rice husks, which contain silica, to form protein-capped α -quartz at room temperature. These nanocrystals were approximately 2-6 nm within a biomolecular matrix.¹⁷⁹

In 2011, Jiang, *et al.*¹⁸⁰ first formed silica nanoparticles by the Stöber method in which water, ethanol, and ammonium hydroxide are combined and TEOS is added dropwise while stirring. Sodium chloride and either sodium hydroxide or potassium hydroxide were added, and the solution was heated to approximately 200 °C with 1.5 MPa of pressure for 3 days. The reaction led to the formation of 45-nm α -quartz nanoparticles.¹⁸⁰

This study was followed in 2015 by Sochalski-Kolbus, *et al.*¹⁸¹ In this study, TEOS, toluene, oleic acid, and ethanol were combined with 0-0.45 g of NaF and heated to 300 °C under pressures of 79-91 bar for 14-18 h. Without NaF, nanorods with lengths of 100 nm to a few micrometers and diameters of 10-100 nm formed. With the addition of NaF, these rods shortened and became more spherical.¹⁸¹

Most recently, Hargreaves, *et al.*¹⁸² used microemulsions to form α -quartz nanoparticles. Two microemulsion systems were used: Triton X-114 (TX-114)/cyclohexane, and sorbitane monooleate (Span 80)/polyoxyethylene (23) lauryl ether

(Bij 30)/heptane. At low concentrations of sodium metasilicate (<6 wt% in the TX-114/cyclohexane system and <7.5 wt% in the Span 80: Brij30/heptane system) and low pH, α -quartz nanoparticles formed at room temperature. Above these concentrations, cristobalite and amorphous silica were seen.¹⁸²

The major differences between the syntheses of α -quartz and the syntheses of β -GeO₂ are their required temperatures and pressures, which makes them ideal for studying chiral templating. The low temperatures involved in the production of β -GeO₂ nanoparticles could allow optically-active capping agents to be used to template chirality in the nanoparticles without significant racemization or decomposition of the organic compound. The same capping agents are not viable templating agents for α -quartz due to its higher reaction temperature. The optically-active β -GeO₂ nanoparticles must therefore be used as templating agents by coating optically-active α -quartz on the surface of the nanoparticles.

5.2.3. Capping Agents

Current methods of inducing optical activity in nanoparticles involve chiral capping agents. These capping agents allow favorable interactions between enantiomers, thus initiating the formation of one nanoparticle enantiomer in excess during crystal growth. Chiral capping agents are typically selected based on their commercial availability and the presence of multiple functional groups, which have been shown to affect the success of templating chirality in nanoparticles.¹⁸³⁻¹⁸⁴ Two common examples of these capping agents are cysteine and penicillamine. The presence of a thiol group leads to greater adsorption strengths with HgS, Se, and Te.^{78, 80, 82}

Of the amino acids, lysine, arginine, and tyrosine (Figure 5.2) have been shown through DFT calculations or experimental studies to adsorb strongly to either silica or quartz surfaces, which have similar properties to β -GeO₂ surfaces.¹⁸⁵⁻¹⁸⁹ Alanine enantiomers have also been shown to interact differently with an optically-active quartz surface, which has been shown through enantiomeric separations of the amino acid.^{70, 75} Following the pattern that these amino acids present, structures which involve multiple amine groups with various carbon chain lengths between them may aid in templating an enantiomeric excess of β -GeO₂ during nanoparticle production. 1,2-Diaminopropane

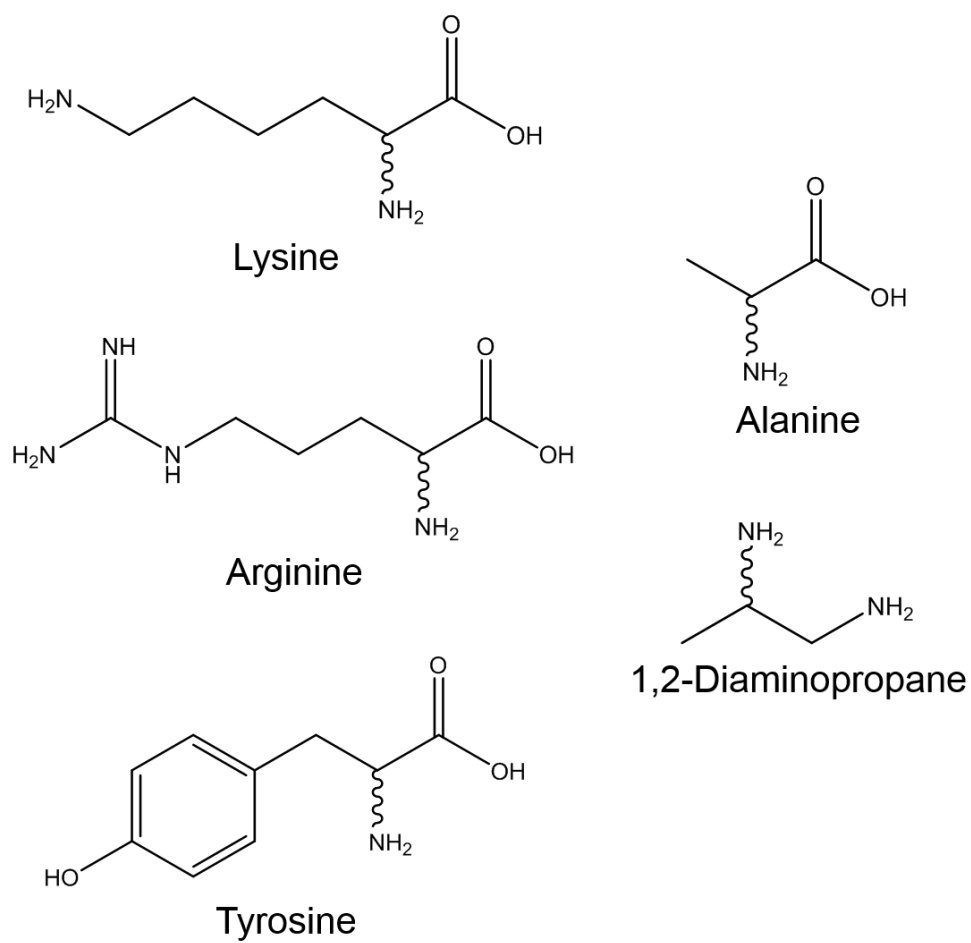


Figure 5.2. Potential capping agents for templating optical-activity in $\beta\text{-GeO}_2$ nanoparticle synthesis.

(Figure 5.2) would be one option for comparison with the above-listed amino acids as it has a shorter hydrocarbon chain, no carboxyl group, and amine groups on neighboring carbons.

5.3. Materials

Hydrolysis solvents were produced using MilliporeSigma ACS grade ethanol absolute ($\geq 99.5\%$), Fisher Scientific molecular biology grade water, and Alfa Aesar aqueous ammonium hydroxide (28-30%) (NH_4OH). Alfa Aesar TEOG ($\geq 99.995\%$) and TEOS (99+%) were used as precursors for GeO_2 and SiO_2 , respectively. VWR L(+)-Lysine monohydrochloride (98.5-101.5% purity, Lys) powder and Sigma Aldrich (R)-(+)-1,2-diaminopropane dihydrochloride (99% purity, DAP) were used as chiral capping agents.

For heating $\text{SiO}_2/\text{GeO}_2$ powders, solvent reagents included MilliporeSigma ACS grade ethanol absolute ($\geq 99.5\%$), Fisher Scientific molecular biology grade water, Fisher Chemical acetone (ACS grade), Fisher Chemical methanol (ACS grade), Alfa Aesar aqueous ammonium hydroxide (28-30%) (NH_4OH), Mallinckrodt Chemical Works NaOH pellets, Alfa Aesar CsOH (50% (w/w) in aqueous solution), and Mallinckrodt Chemical Works anhydrous $\text{Ba}(\text{OH})_2$.

5.4. β - GeO_2 Nanoparticle Synthesis Replication

The β - GeO_2 synthesis utilized by Javadi, *et al.*,¹⁷⁰ produced racemic nanocrystals with diameters smaller than 20 nm. In this procedure, TEOG was added to a solution of NH_4OH in water/ethanol (10 (v/v)% H_2O). The precipitate was collected by centrifugation, washed with ethanol, and dried. This process produced pseudospherical β - GeO_2 nanoparticles with diameters of approximately 13 ± 3 nm. This particular method was selected for replication due to the small size of the nanocrystals produced at room temperature and no need of a capping agent.¹⁷⁰

5.4.1. Experimental Method

Solvents consisted of 90 (v/v)% ethanol, 10 (v/v)% H_2O , and $0\text{-}10^{-1}$ M NH_4OH . While stirring vigorously, TEOG ($\geq 99.995\%$) was added dropwise (100 μL TEOG per 1.00 mL solvent). A clear/white gel formed immediately and was dispersed by the stirring. The mixture continued to be stirred for 24 h, producing a white suspension. The white solid

was collected and washed twice with ethanol through centrifugation. The collected powder was then dried overnight at approximately 60-65 °C.

5.4.2. Results

PXRD patterns of the dried powders showed the successful production of β -GeO₂ through this method for all NH₄OH concentrations as can be seen in Figure 5.3. Crystallite sizes were calculated from these patterns based on the 26.0° 2 θ peak, which has the highest intensity and best resolution. An increase in crystallite size was seen with increasing NH₄OH concentration with approximately 10-20 nm crystallites for 0-10⁻³ M to approximately 45 nm for 10⁻¹ M.

5.5. L-Lysine-Capped β -GeO₂ Nanoparticles

Lysine is insoluble in the ethanol/water (10 (v/v)% H₂O) solvent used in the Javadi, *et al.*, synthesis of β -GeO₂; therefore, the method of synthesizing β -GeO₂ was changed to the process used by Davis, *et al.*¹⁷⁴ This method produced Lys-germanate sols, which crystallized into β -GeO₂ particles. In this synthesis, TEOG was added dropwise to a solution of lysine (Lys) in water and ethanol with molar ratios of x Lys: g GeO₂: 9500 H₂O: 4g ethanol (x=0, 5.8 and 0≤g≤60). This process resulted in 100 nm particles of GeO₂. This work was first replicated with higher Lys:GeO₂ molar ratios in an attempt to template an enantiomeric excess of β -GeO₂.

Following these syntheses, the Lys concentration was increased further to determine its effect on templating an enantiomeric excess. These increased concentrations may either increase the rate of capping agent exchange on the surface of the nanoparticle or aid in the adsorption of higher concentrations of the capping agent.

5.5.1. Experimental Method

VWR L(+)-Lys monohydrochloride (98.5-101.5% purity) powder was added to a solution of water and ethanol. The solution was rapidly stirred until Lys fully dissolved before TEOG was added dropwise. Lys:GeO₂:H₂O:ethanol molar ratios of x:6:950:24 (x=0.6-8.0) were used. The solutions were stirred for 24 h, which produced a clear/white gel that slowly changed to a white solid. This solid was collected and washed twice with water using centrifugation before drying overnight at 60-65 °C.

Higher concentrations were then used to shift the capping agent equilibrium toward

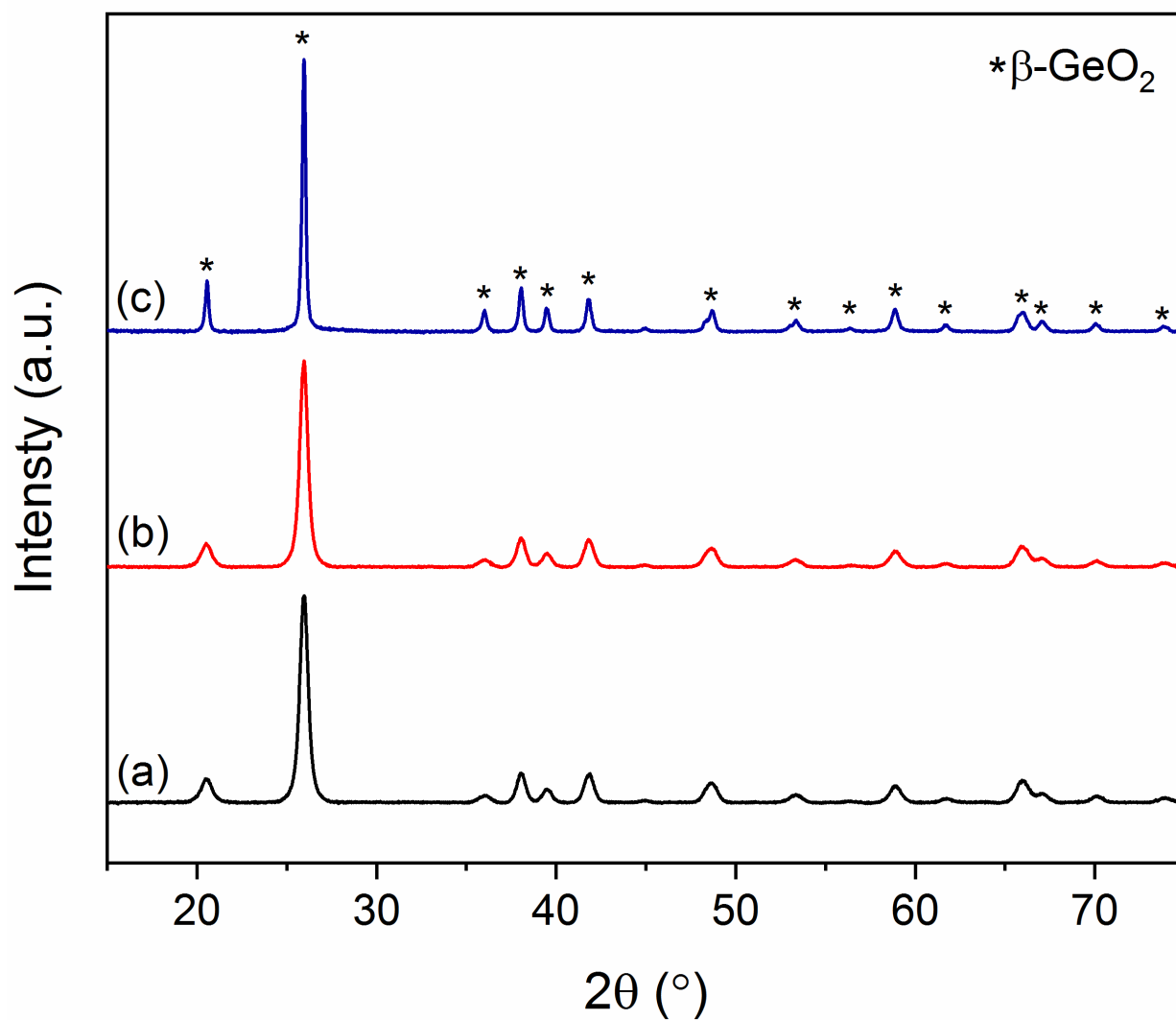


Figure 5.3. PXRD patterns for β - GeO_2 nanoparticles synthesized through the Javadi, *et al.*¹⁷⁰ method (a) without NH_4OH and using (b) 10^{-3} M or (c) 10^{-1} M NH_4OH .

greater adsorption concentrations. The first higher-concentration reaction used 5.00 g Lys in 10 mL H₂O in which all the Lys dissolved for an approximately 2.7 M Lys solution. The second higher-concentration reaction used 5.00 g Lys in 5 mL H₂O in which the Lys did not fully dissolve. To both solutions, 750 μ L TEOG was added dropwise while vigorously stirring. As with the previous syntheses, the solid was collected and washed twice with water using centrifugation. The washed powder was dried overnight at 60-65 °C.

5.5.2. Results

The successful production of β -GeO₂ was verified through PXRD. Through the Scherrer equation using the 26.0° 2 θ peak, the crystallite size was calculated to be approximately 65 nm for all samples regardless of the ratio of Lys:GeO₂ used.

The mass percentages of adsorbed compounds on the surface of nanoparticles synthesized with $x=1$ and $x=2$ were determined using TGA. Samples were first heated from room temperature to 900 °C at 100 °C/min and then kept at 900 °C for 20 min to ensure complete desorption and decomposition of the capping agents. A representative spectrum of these measurements is shown in Figure 5.4 from the TGA of GeO₂ powder produced in the presence of Lys (Lys-GeO₂), where $x=2$. As GeO₂ does not decompose at these temperatures, the mass difference is attributed solely to the adsorbed compounds. Using this assumption, the $x=1$ powder is 1.5% capping agent by mass and the $x=2$ powder is 1.7% capping agent by mass. To determine the maximum possible rotation caused by Lys, it is assumed that the adsorbed molecules consist solely of Lys. Even with this maximum concentration of the chiral capping agent, the lysine should not have measurably contributed to optical rotation or circular dichroism caused by the powders due to its low concentration.

FTIR spectroscopy was used to characterize β -GeO₂ nanoparticles with ($x=2$) and without the addition of lysine, which can be seen in Figure 5.5. The absorption peak at ~ 840 cm⁻¹ is attributed to a vibrational mode of the β -GeO₂ tetrahedra (Ge–O–Ge stretch). The peak at ~ 525 cm⁻¹ is characteristic of the hexagonal GeO₂ structure as well and is caused by Ge–OH stretching. The triplet peaks around 1320-1550 cm⁻¹ may indicate the adsorption of water on the nanoparticle structure although these peaks are typically around 1620-1650 cm⁻¹. There is also a broad, low-intensity peak at ~ 3000 -3600 cm⁻¹,

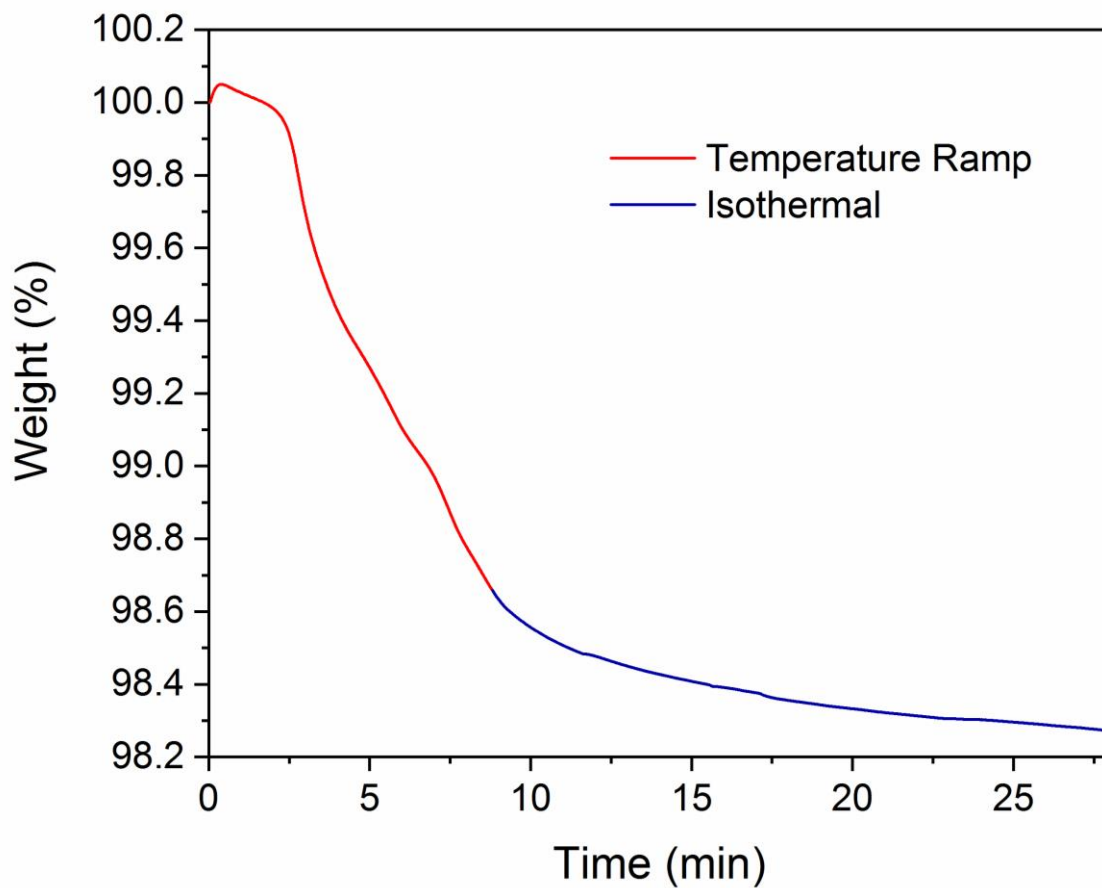


Figure 5.4. TGA spectrum of Lys-GeO₂ (x=2). The temperature was ramped from room temperature to 900 °C at 100 °C/min and then held at 900 °C for 20 min.

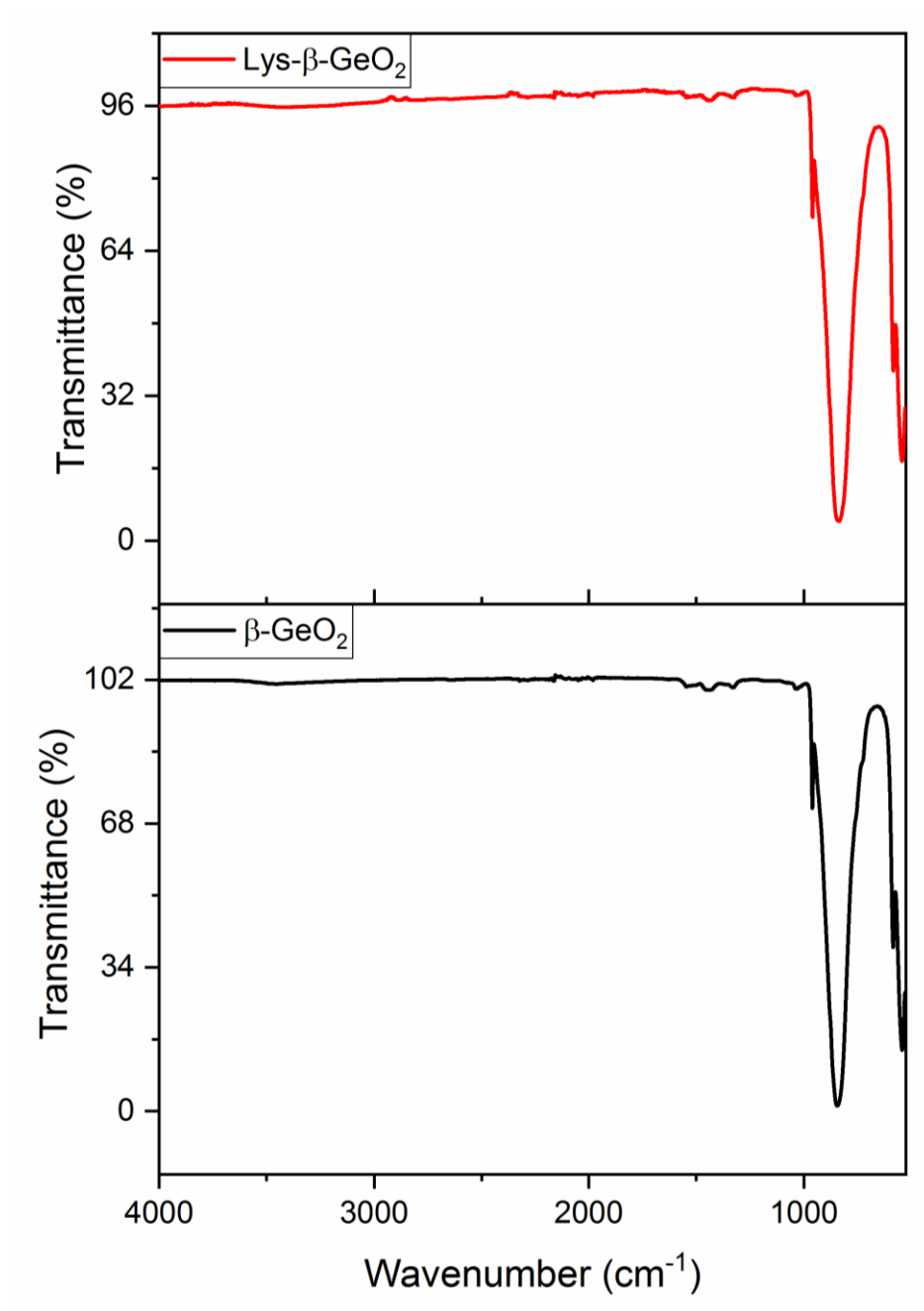


Figure 5.5. FTIR spectra of β -GeO₂ nanoparticles synthesized (top) in the presence of Lys ($x=2$) and (bottom) without Lys.

which is usually seen with this adsorption.¹⁷¹⁻¹⁷³ With the low intensity of the adsorbed molecules' peaks, these spectra suggest greater adsorption of water than lysine but do not discount the presence of a small concentration of lysine on the surface.

As the FTIR results are inconclusive, TGA-MS was run on the $x=1$ Lys-GeO₂ powder. The powder was heated in a N₂ atmosphere from room temperature to 600 °C at 10 °C/min in an attempt to increase the resolution of the MS; however, the material did not fully degrade. This lack of total decomposition of the capping agent is seen by the constant decrease in mass up to 600 °C and led to a slowly increasing ion current amperage rather than peaks in the MS. Representative examples of the combined TGA and MS data can be seen in Figure 5.6. These data verified fragments with m/z of 17, 18, 29, and 40. While fragments with m/z of 17 and 29 may result from several possible adsorbed compounds, the data confirm the presence of H₂O on the surface ($m/z = 18$) and may also confirm the presence of Lys. The most likely fragments with a m/z of 40 are C₃H₄ and CH₂CN, which could only result from Lys in this powder. Between the FTIR and MS spectra, it can be assumed that if Lys is adsorbed on the surface of β -GeO₂, it is in exceedingly small concentrations.

Optical Activity

To determine optical rotation of Lys-GeO₂ powders, the rotations of aqueous solutions with various concentrations of Lys were first measured. Aqueous solutions were made with Lys concentrations ranging from 0 M to 10 M. Rotations were measured at 365 nm, 436 nm, and 546 nm and used to form Lys optical rotation versus concentration curves (Figure 5.7) with the best linear fit crossing the y-axis at (0,0) for each wavelength. These curves were used to determine the degree of rotation in a Lys-GeO₂ sample caused by the Lys. Using these curves in conjunction with TGA, it was verified that Lys should not contribute any measurable rotation to Lys-GeO₂ powders with $x=1, 2$.

The optical rotation measurements of these nanoparticle samples required the use of water as a solvent because the samples quickly dropped out of solution with most other solvents, including methanol, ethanol, acetone, and acetonitrile. Both lysine and β -GeO₂ are soluble in water. To ensure minimal dissolution, polarimeter measurements were made immediately following the production of suspensions of the nanoparticles. These

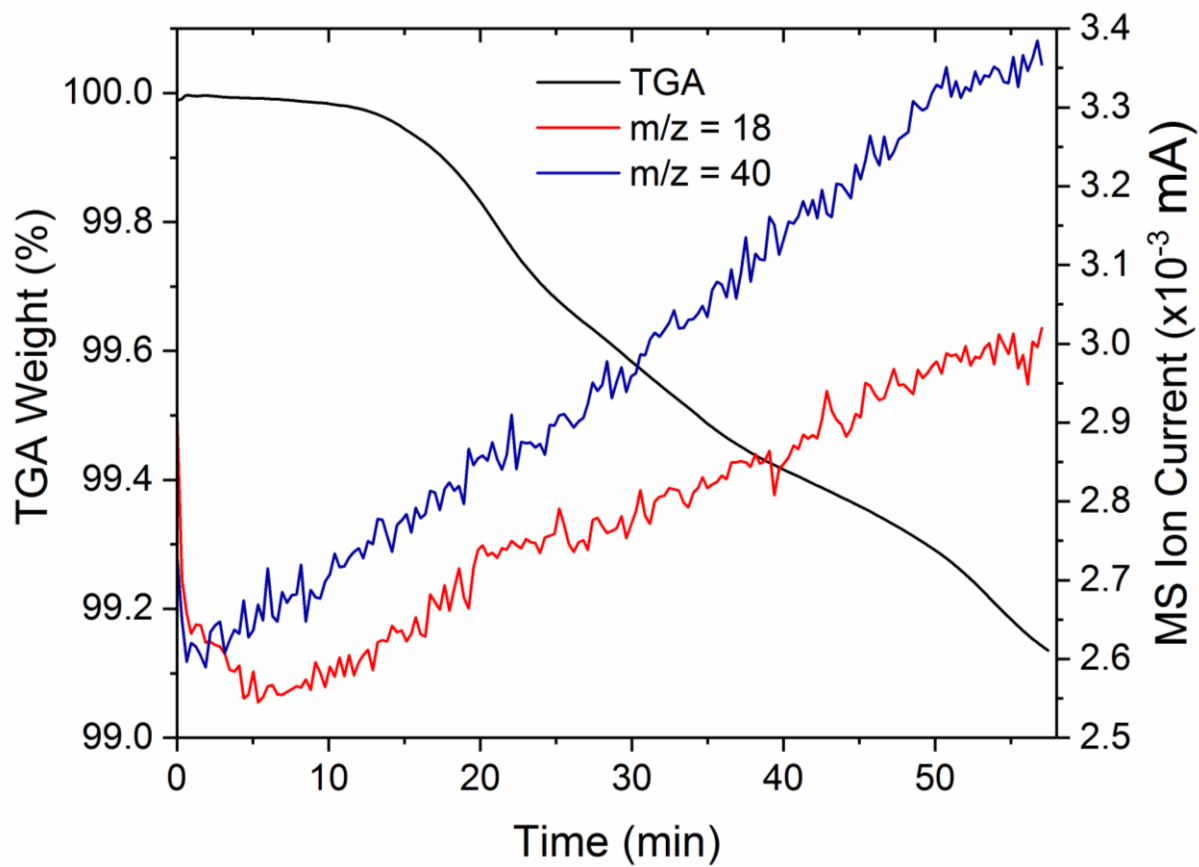


Figure 5.6. TGA spectrum for Lys-GeO₂ (x=1) powder with overlaid MS data for m/z of 18 and 40.

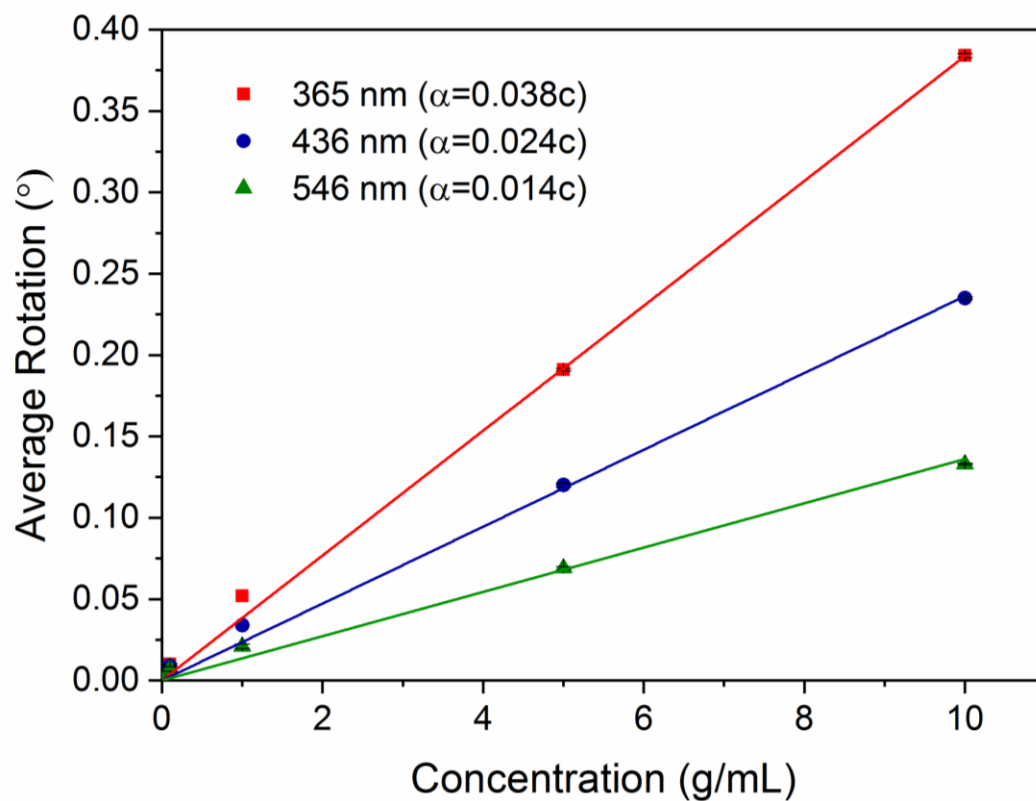


Figure 5.7. Plots of optical rotation versus Lys concentration at 365 nm, 436 nm, and 546 nm. Data were fitted using a linear fit with the y-intercept set as (0,0). All R^2 values were >0.99 .

suspensions were made with low powder concentrations of <0.2 mg/mL because the particles are opaque. Higher amounts of powder could not be measured with the polarimeter as the polarized light could not penetrate the entire pathlength through the sample. Wavelengths of 365 nm, 436 nm, and 546 nm were used as they gave the most consistent results. Most results are within what is believed to be the error of the instrument and showed no significant rotation. However, the $x=1$ and $x=2$ powder suspensions measured slightly outside of this error at 365 nm with rotations up to approximately $+0.008^\circ$ and $+0.011^\circ$, respectively, possibly indicating a minor enantiomeric excess. These optical rotation measurements were not replicable.

CD analysis was also used to measure optical activity. The $x=1$ powder was measured as it had a higher degree of rotation for linearly polarized light. Concentrations of 0.9-1.5 mg/mL were used because the shorter pathlength of the CD sample holder (1 mm for CD versus 1 dm for the polarimetry) allowed a higher concentration to be used. To reduce dissolution during the run, samples were run in 200-210 nm increments. As can be seen in Figure 5.8, there is one minor peak that appears at approximately 310 nm. This peak may indicate optical activity of the nanoparticles, but it was not able to be replicated in following measurements. If the nanoparticles are optically active, this peak would be caused by defects or distortions in the structure and not come from the structure itself because β -GeO₂ is transparent. The defects/distortions would cause absorption of the circularly polarized light.

Although β -GeO₂ was successfully produced by the Davis, *et al.*¹⁷⁴ method using Lys, there is no decisive or replicable evidence that the nanoparticles are capped with Lys or that they are optically active. If the material is optically active, the enantiomeric excess is minimal and cannot be successfully measured by currently available instrumentation. There seems to be a small concentration of Lys within the powder, but this minute amount indicates that the adsorption strength for the capping agent is not high enough to cause templating of one enantiomer of β -GeO₂. It may also suggest that the distance between the two amine groups is too large to aid in templating or that the solubility of the Lys was not high enough to successfully cap the particles as the ethanol concentration increased during hydrolysis.

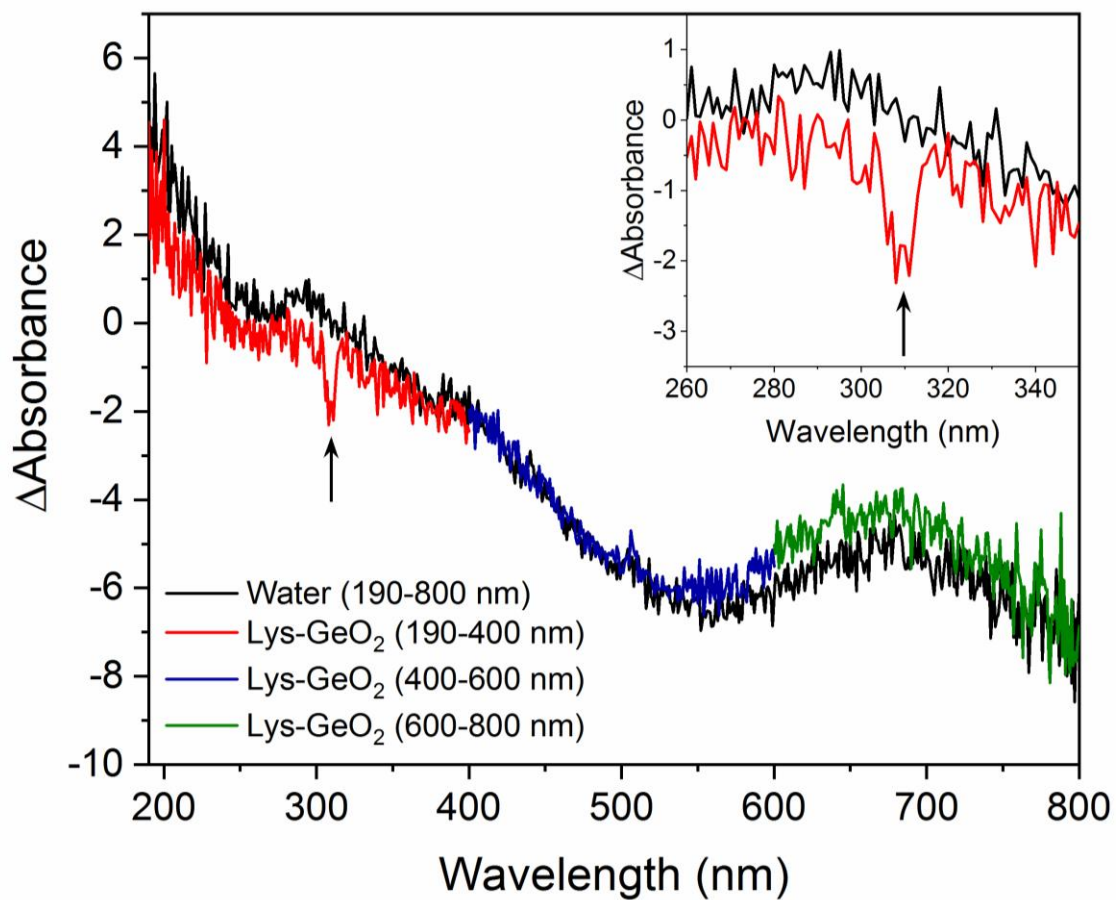


Figure 5.8. CD spectra of water (solvent) and Lys-GeO₂ powder suspended in water. The inset shows more detail of the 260-350 nm range in which the peak appeared.

5.6. (R)-(+)-1,2-Diaminopropane-Capped β -GeO₂ Nanoparticles

Lys was then replaced by DAP as a capping agent in the synthesis of β -GeO₂ nanoparticles. DAP has greater solubility in ethanol/water mixtures than Lys and a shorter carbon chain between amine groups. This capping agent also enabled the use of a Javadi, *et al.*¹⁷⁰ β -GeO₂ synthesis variation, which would produce smaller particles with a greater surface area for capping agent adsorption.

5.6.1. Experimental Method

Powders were prepared using DAP:GeO₂ molar ratios of x:6, where x=1, 2. DAP (70 mg for x=1 and 140 mg for x=2) was added to 8.00 mL of a solution of 90 (v/v)% ethanol, 10 (v/v)% H₂O, and 10⁻³ M NH₄OH. The solution was stirred until the DAP fully dissolved. 780 μ L TEOG was then added dropwise while stirring vigorously. The solutions were stirred for 24 h, which produced a clear/white gel that slowly changed to a white solid. This solid was collected and washed twice with ethanol through centrifugation before drying overnight at 60-65 °C. The resulting powders will be referenced as DAP-GeO₂.

5.6.2. Results

The successful production of β -GeO₂ was confirmed by PXRD for both the x=1 and x=2 syntheses. The crystallite sizes calculated using these patterns were 25-30 nm for both powders. These smaller crystallite sizes compared to the Lys-GeO₂ particles' crystallite sizes are consistent with previous literature, which shows that decreasing the volume percentage of water decreases β -GeO₂ particle size.¹⁷⁰

The mass percentage of capping agent present in the x=1 DAP-GeO₂ powders was determined using TGA. As with Lys-GeO₂, portions of the powder were first heated from room temperature to 900 °C at 100 °C/min and then held at 900 °C for 20 minutes to ensure complete decomposition of the capping agents. This method showed a mass percentage of 1.3% capping agent. Under the assumption that the only adsorbed compound is DAP, this small concentration should have no measurable rotation with the instrumentation used similar to Lys-GeO₂ powders.

Following the TGA measurement, TGA-MS was used to determine if the material decomposing was DAP in the x=1 DAP-GeO₂ powder. The MS data showed the presence

of fragments with m/z of 18, 29, and 40. The fragment with m/z of 18 is most likely the result of H_2O . The fragment with m/z of 29 could result from DAP or ethanol. As with Lys, the fragment at m/z of 40 is most likely C_3H_4 and CH_2CN , which suggests at least a small concentration of DAP within the powder.

Optical Activity

The specific rotation of DAP was assumed to be insignificant during polarimetry measurements due to its low concentration. This assumption is supported by the results involving the capping agent Lys, which has a higher specific rotation than DAP.

DAP- GeO_2 powders were dispersed in acetone with concentrations of less than 2 mg/mL for polarimetry measurements. At these low concentrations, the solutions were opaque when using a 1 dm pathlength. The polarimeter was unable to make an accurate or reproducible measurement for either $x=1$ or $x=2$ DAP- GeO_2 powders.

DAP- GeO_2 ($x=2$) powders were then dispersed in acetone with starting concentrations of approximately 0.9-2.0 mg/mL for CD measurements. These spectra showed no peaks, indicating that there were no chiral defects which may have formed due to DAP adsorption.

Through this method, β - GeO_2 was successfully produced in the presence of DAP with smaller crystallite sizes than in the previous Lys- GeO_2 process. Although there is some evidence that DAP is present in the powder, its concentration is excessively low. With no measurable optical activity, this low concentration most likely means the compound does not adsorb well to the β - GeO_2 surface and cannot template an excess of one enantiomer of β - GeO_2 .

5.7. Templating α -Quartz Using Racemic β - GeO_2 Nanoparticles

The final goal of this work was to template optically-active α -quartz (α - SiO_2) using optically-active β - GeO_2 nanoparticles. Templating of α - SiO_2 using racemic β - GeO_2 nanoparticles was thus attempted to ensure the materials were compatible for this process.

5.7.1. Crystallizing α -Quartz

Prior to templating α -quartz on β - GeO_2 , a previous synthesis of α -quartz nanoparticles was replicated. The Jiang, *et al.*¹⁸⁰ process was chosen because it

produced small particles at relatively low temperatures. In this method, amorphous Stöber silica was produced by hydrolyzing TEOS in an NH_4OH , H_2O , and ethanol solution. α -Quartz nanoparticles were synthesized by heating the Stöber silica in NaOH or KOH solution to $200\text{ }^\circ\text{C}$ at 1.5 MPa for 3 days. This method formed 45-nm α -quartz nanoparticles.¹⁸⁰

To replicate this synthesis prior to templating studies, Stöber silica was first produced by dripping TEOS into vigorously stirred solvent consisting of 50.00 mL methanol, 3.00 mL NH_4OH (28-30%), and 1.00 mL H_2O . This solution was stirred for 2 days and collected through centrifugation. Approximately 80 mg of the resulting amorphous SiO_2 powder was then combined with 1 mL aqueous 0.1 M NaOH solution and 1 mL ethanol. The solution was added to a makeshift steel autoclave made using a $\frac{1}{4}$ -inch hex nipple and two $\frac{1}{4}$ -inch pipe caps, which could hold 2-3 mL of solution. This autoclave was then heated to $250\text{ }^\circ\text{C}$ for 3 days. The PXRD patterns in Figure 5.9 show an amorphous powder before heating and α -quartz peaks with no contaminant after heating. The Scherrer equation gives a crystallite size of 53 nm for the α -quartz powder.

5.7.2. Heating β - GeO_2 Nanoparticles in NaOH Solution

Following the successful production of α -quartz powder, β - GeO_2 powder produced through the Javadi, *et al.*¹⁷⁰ method was heated to determine the maximum temperature before structural changes made the nanoparticles achiral. 50 mg of powder was combined with 1 mL ethanol and 1 mL of 0.1 M aqueous NaOH in a steel autoclave. The mixture was heated to either $180\text{ }^\circ\text{C}$ or $250\text{ }^\circ\text{C}$ for 3 days. As can be seen in the PXRD patterns in Figure 5.10, the GeO_2 was contaminated with $\text{Ge}_9\text{Na}_4\text{O}_{20}$ at both temperatures due to the presence of NaOH . At $180\text{ }^\circ\text{C}$, the primary crystal structure remained β - GeO_2 while at $250\text{ }^\circ\text{C}$, the crystal structure shifted to α - GeO_2 , which is achiral.

5.7.3. SiO_2/β - GeO_2 Powder

After working with each material separately, SiO_2 and β - GeO_2 powders were synthesized together in an attempt to template the α - SiO_2 at room temperature or to produce powder which could be heated to induce templating.

Solvents for these reactions were 10^{-3} - 10^{-1} M NH_4OH in ethanol/water (10 (v/v)% H_2O). TEOG and TEOS were added dropwise to these solvents while rapidly stirring with

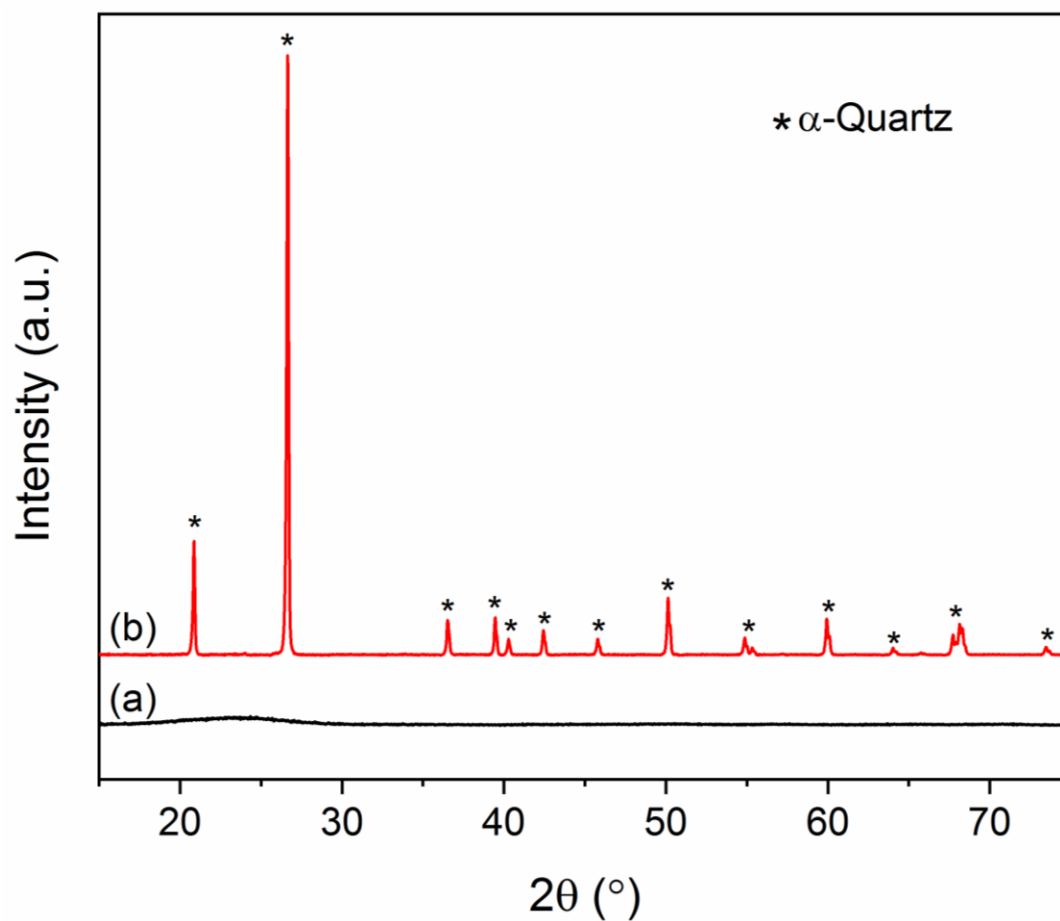


Figure 5.9. PXRD patterns of (a) Stöber silica and (b) α -quartz powder.

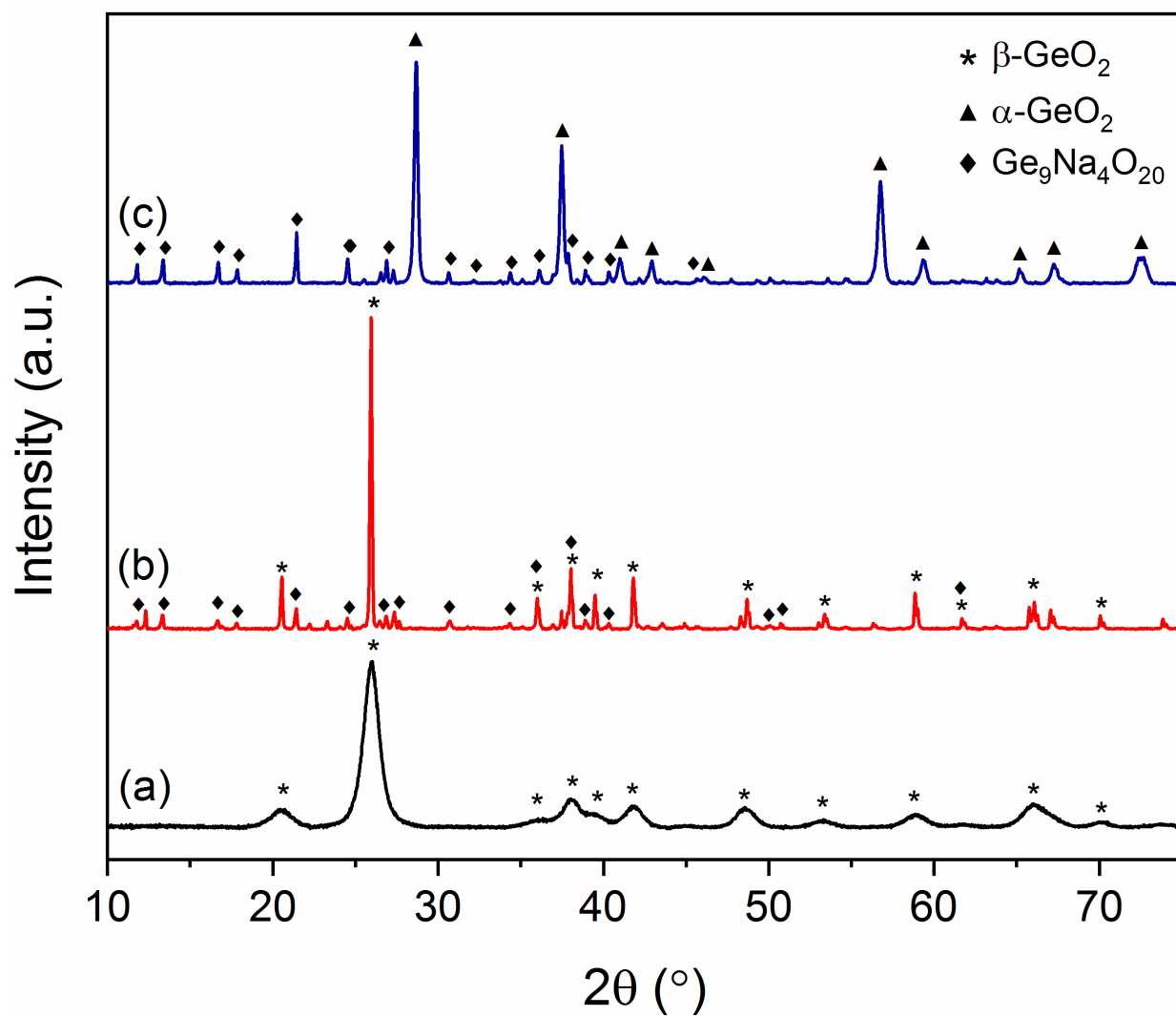


Figure 5.10. PXRD patterns of heated β - GeO_2 . Patterns were measured (a) prior to heating, (b) after heating in a NaOH solution to 180 $^{\circ}\text{C}$ for 3 days, and (c) after heating in a NaOH solution to 250 $^{\circ}\text{C}$ for 3 days.

a volume ratio of 10:1:1 (solvent:TEOG:TEOS). The two reagents were added in one of the following four ways:

1. TEOG and TEOS were mixed and added to the solvent together. This mixing would possibly lead to Si within the crystallized structure of β -GeO₂. This method will be referred to as the mixed synthesis.
2. TEOS was added to the solvent immediately following the addition of TEOG. The TEOG would partially form a gel before the addition of TEOS. This method will be referred to as the 0 h synthesis.
3. TEOS was added 2 h after TEOG which may have allowed a portion of the β -GeO₂ to crystallize without TEOS present. This method will be referred to as the 2 h synthesis.
4. TEOS was added 24 h after TEOG which allowed crystallization of β -GeO₂ before TEOS hydrolyzed. This method will be referred to as the 24 h synthesis.

The mixtures were then stirred for 24 h, after the TEOS was dripped into the solvent. The resultant powder was collected and washed twice with ethanol by centrifugation before drying 0.5-3 days at 60 °C.

Results

PXRD patterns (Figure 5.11) reveal the crystallization of β -GeO₂ in mixed, 0 h, and 24 h syntheses with vigorous stirring. In mixed, 0 h, and 24 h syntheses in which the gel decreased the rate of stirring significantly due to a smaller-diameter reaction vessel, the patterns show the powders are completely or primarily amorphous, indicating that stirring is crucial to β -GeO₂ crystallization. There were no observable α -SiO₂ peaks in any pattern.

PXRD results are representative of the entire powder. There are also patterns within the database which indicate only minor differences may exist between β -GeO₂ and α -SiO₂ patterns. If α -SiO₂ templated within or onto the β -GeO₂ nanoparticles, it may not have been observable with PXRD. TEM images with electron diffractions (Figure 5.12) were obtained to determine the crystallinity of smaller areas of the 0 h-synthesis powder. The powder consisted of aggregated particles, which appeared to be predominantly amorphous with only a few diffraction spots visible. This evidence of crystallinity was

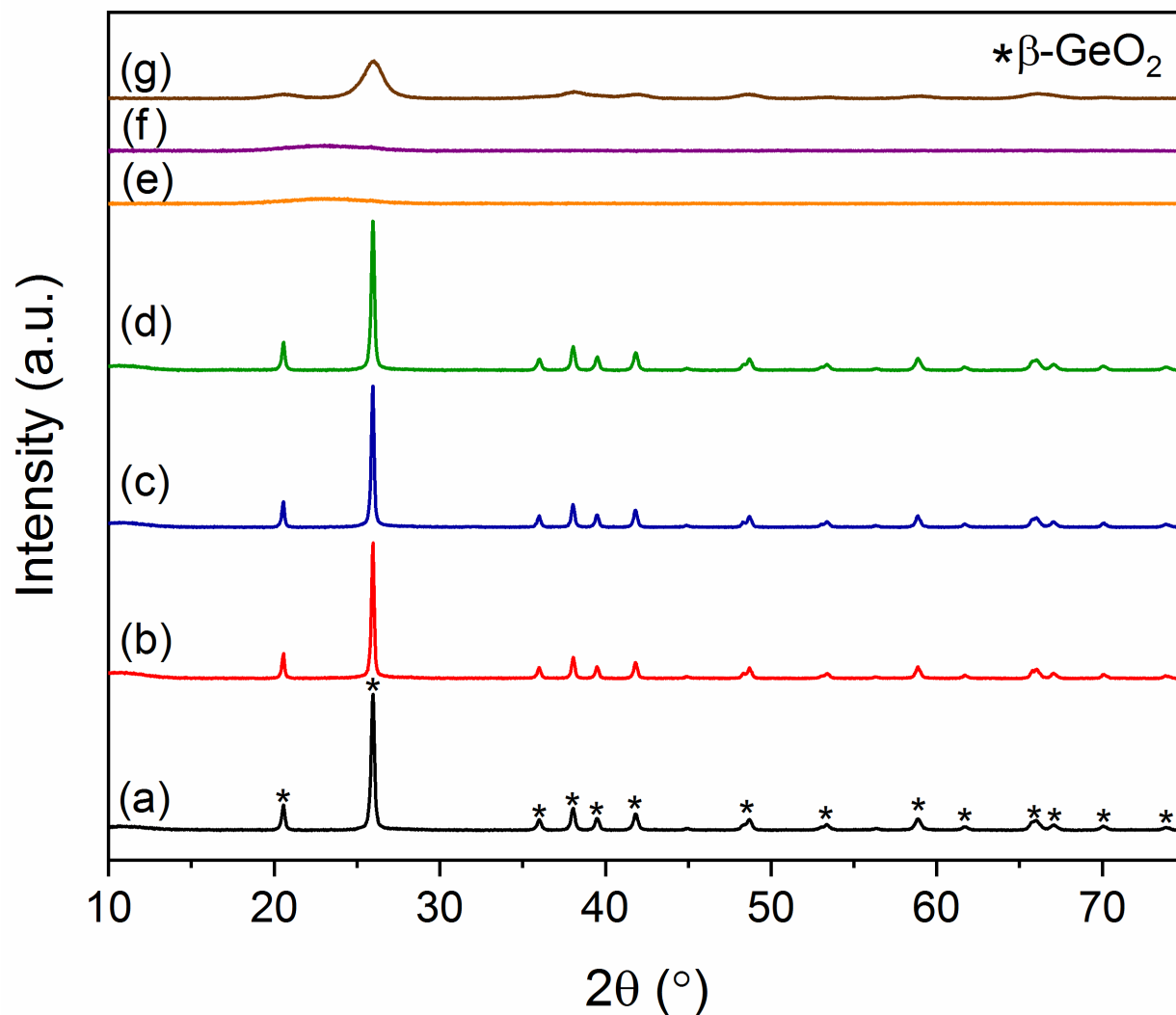


Figure 5.11. PXRD patterns following the hydrolysis of TEOG and TEOS mixtures. (a) TEOG, (b,e) TEOG and TEOS combined before adding to solvent (mixed synthesis), (c, f) TEOS added to solvent immediately after the addition of TEOG (0 h synthesis), (d, g) TEOS added 24 h after adding TEOG (24 h synthesis); (a-d) vigorously stirred, (e-g) gel formed and reduced stirring rate and time.

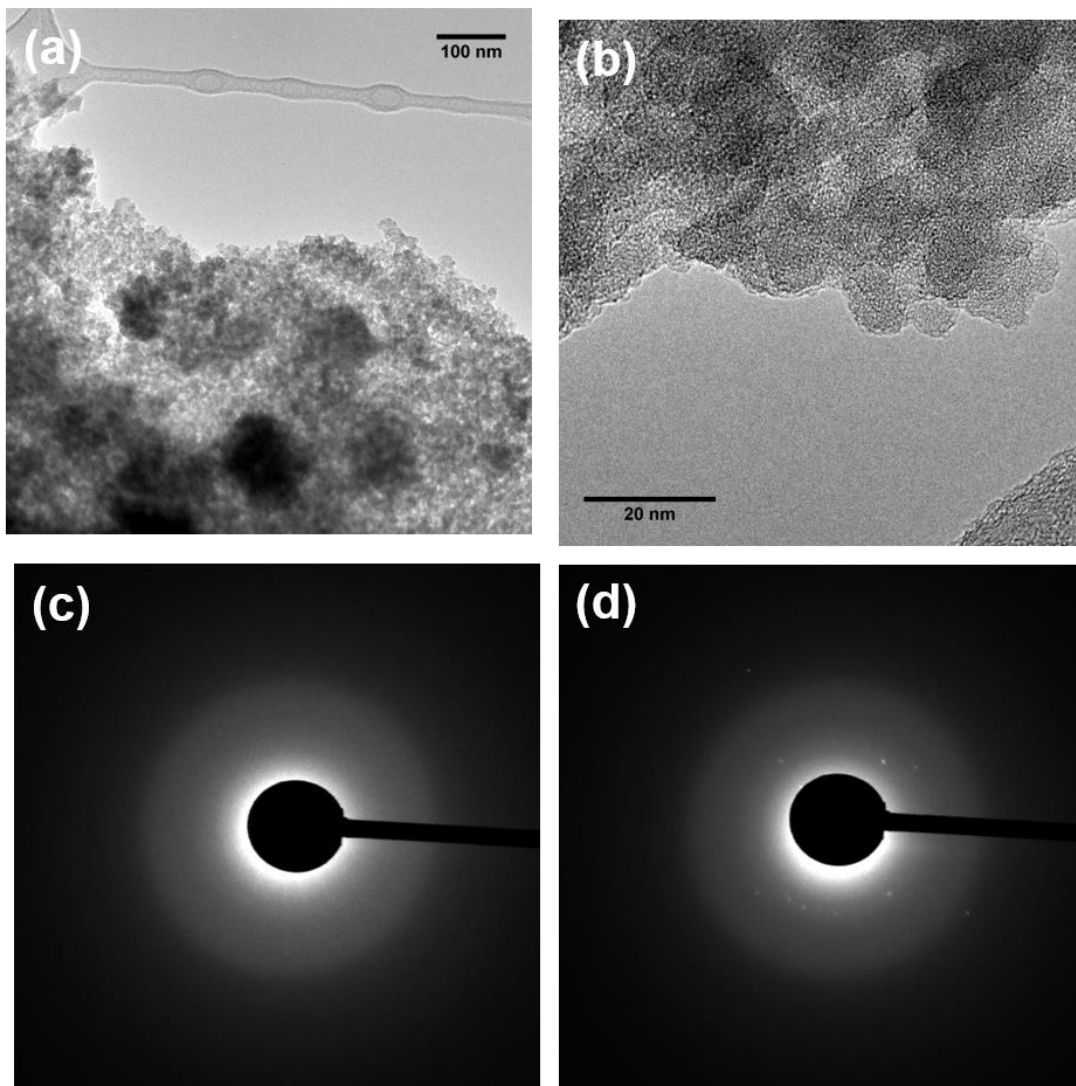


Figure 5.12. TEM images and electron diffraction patterns of $\text{SiO}_2/\beta\text{-GeO}_2$ powder synthesized through hydrolysis.

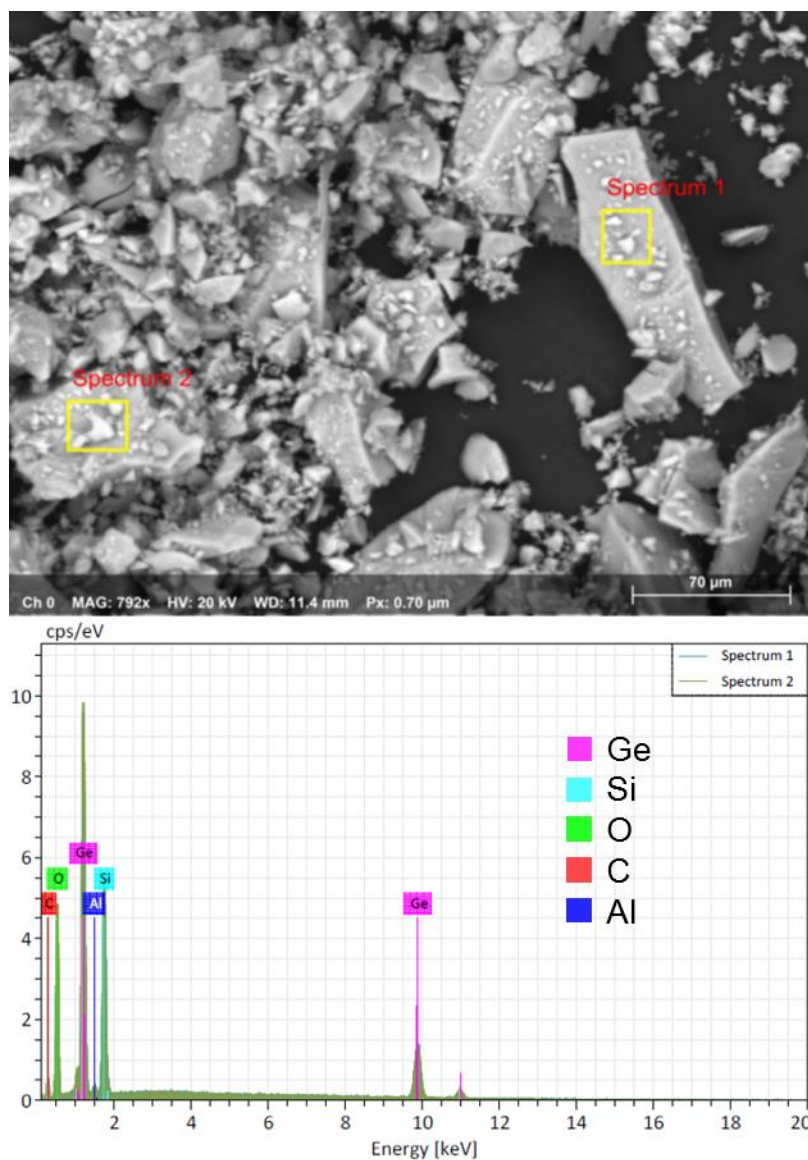
made more difficult to obtain by the electron beam sensitivity of the material, which led crystalline portions of the powder to become amorphous. From the images and diffractions, it was concluded that the most likely source of any diffraction spots was β -GeO₂ and that the crystallization of α -SiO₂ is insignificant or non-existent at room temperature.

To verify the presence of SiO₂ and GeO₂ within the powder, SEM images with EDS spectra (Figures 5.13-14) were obtained for mixed-synthesis and 0 h-synthesis powders. Both EDS spectra confirm the presence of Ge, Si, and O with minimal Al and C contamination. These results show that the SiO₂ is not completely removed during the washing stage of the procedure. Elemental mapping (Figure 5.15) was then employed for 0 h-synthesis powder to determine if there was separation between the Ge and Si. These images showed some overlap of the two elements as well as partial separation. This separation would most likely prevent α -SiO₂ from templating.

5.7.4. Heating in Basic Solutions

As templating was not successful at room temperature during the crystallization of β -GeO₂, synthesized SiO₂/ β -GeO₂ powder was heated in various bases to help induce templating and production of α -SiO₂. In these studies, SiO₂/ β -GeO₂ powder, a solvent, and basic solution were added to a steel autoclave. More details for these reagents are listed in Table 5.1. The autoclave was then heated to 175 °C for 3 days. The subsequent powder was collected and washed twice with ethanol through centrifugation before it was dried at 60 °C for up to 3 days.

The powders were first characterized by PXRD, which can be seen in Figure 5.16. The first base used was NaOH, which resulted in significant contamination of the powder with Ge₉Na₄O₂₀ as the base reacted with the β -GeO₂ similar to what was seen in Section 5.7.2. Using NH₄OH as the base resulted in a complete conversion from β -GeO₂ to H_xGe_yO_z, which could be hydrated forms of GeO₂. The dry powder was therefore heated to try to dehydrate it. After the initial drying at 65 °C overnight, the dry powder was again heated to 65 °C for an additional 18 h, followed by heating at 120 °C for 15 h, and 160 °C for 24 h. After each heating, PXRD patterns (Figure 5.17) were obtained. The crystal structure of the powder remained H_xGe_yO_z up to 120 °C but became amorphous after



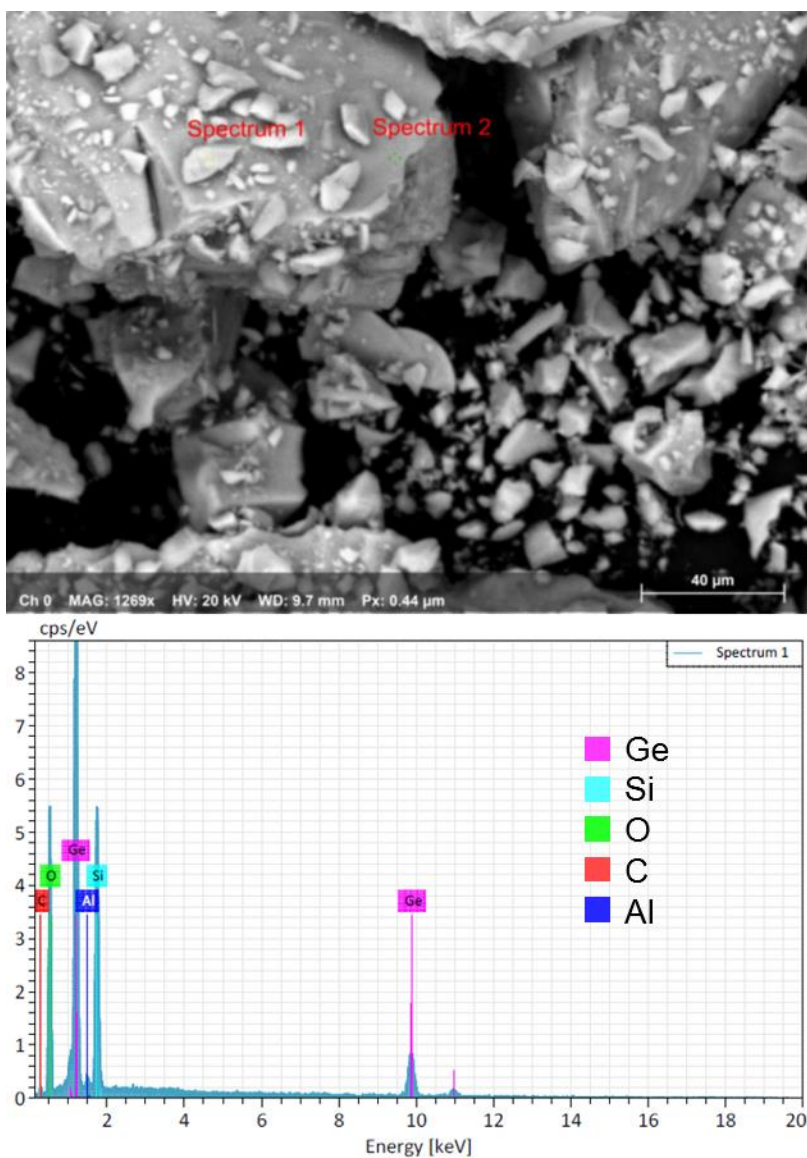


Figure 5.14. SEM image (top) and EDS spectra (bottom) for $\text{SiO}_2/\beta\text{-GeO}_2$ powder synthesized through hydrolysis by 0 h synthesis. EDS spectra were obtained for the areas in the yellow squares on the SEM image.

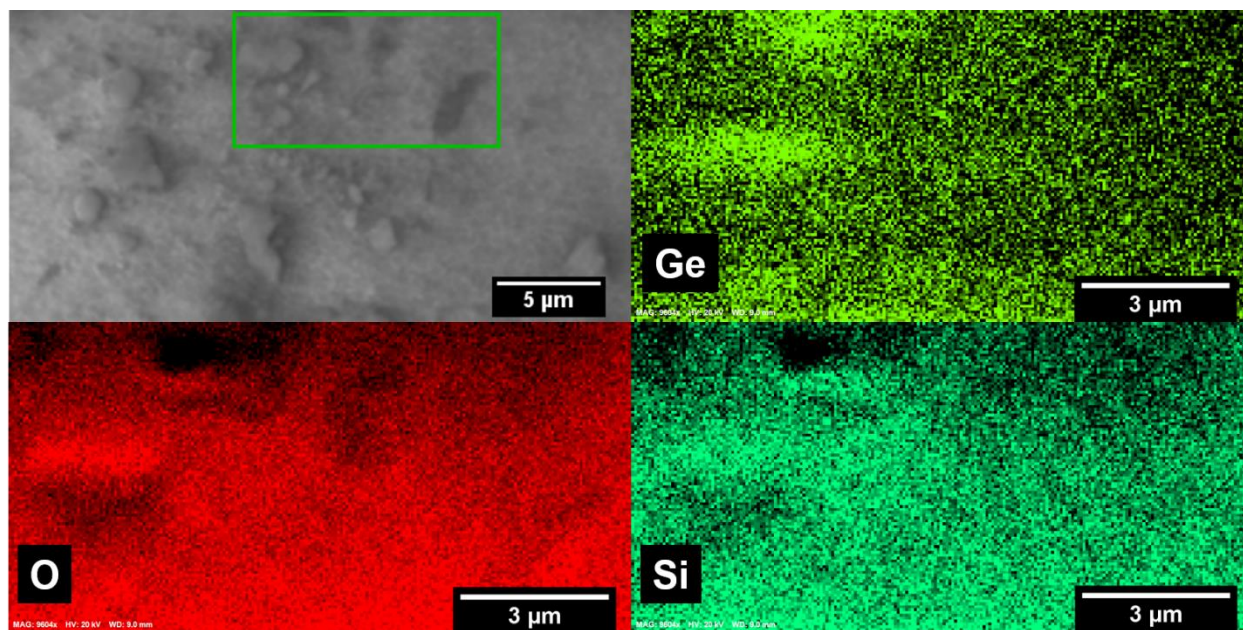


Figure 5.15. Elemental mapping of $\text{SiO}_2/\beta\text{-GeO}_2$ powder synthesized through hydrolysis. TEOS was added to the solvent immediately after TEOG (0 h synthesis). The elemental mapping area is marked by a green square on the SEM image.

Table 5.1. Experimental conditions for heating SiO₂/β-GeO₂ powder to template α-SiO₂.

SiO ₂ /β-GeO ₂ Powder Mass (mg)	Solvent	Solvent Volume (mL)	Base	Basic Solution Volume (μL)	Product*
45	Ethanol	1.8	0.1 M aqueous NaOH	200	β-GeO ₂ , Ge ₉ Na ₄ O ₂₀
20	Ethanol	1.5	28-30% aqueous NH ₄ OH	500	H _x Ge _y O _z
54	Ethanol	1.8	Saturated aqueous Ba(OH) ₂ (pH=12)	200	β-GeO ₂ , BaGe ₄ O ₉
53	Ethanol	1.8	0.1 M aqueous CsOH	200	β-GeO ₂ , H ₁₂ Ge ₇ O ₂₀ •3H ₂ O
45	Ethanol	~2.1	0.1 M aqueous CsOH	200	β-GeO ₂ , H ₁₂ Ge ₇ O ₂₀ •3H ₂ O
52	Methanol	~2.1	0.1 M aqueous CsOH	200	β-GeO ₂
50	Acetone	~2.1	0.1 M aqueous CsOH	200	β-GeO ₂

*Products were determined using PXRD by matching peaks to patterns in the ICSD.

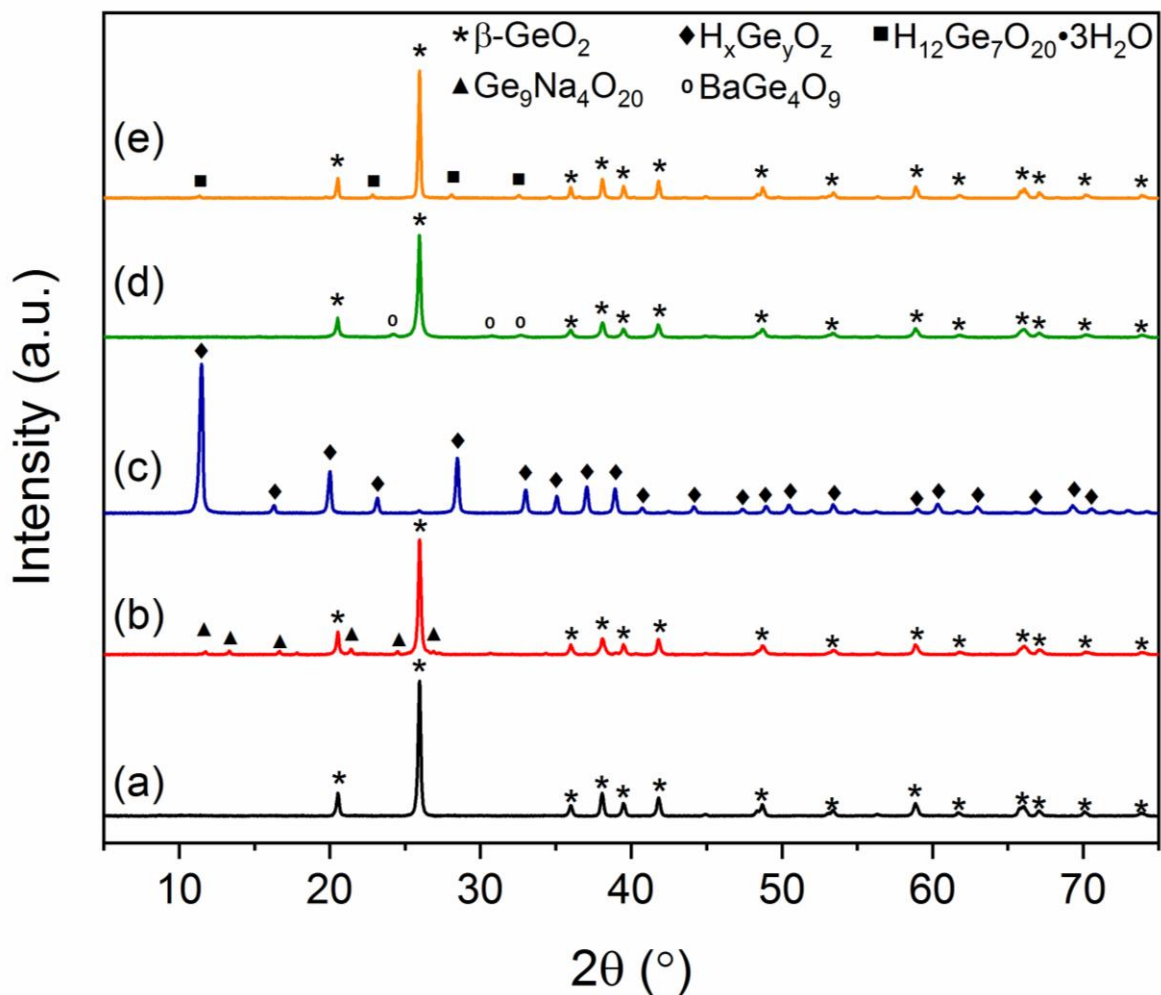


Figure 5.16. PXRD patterns of $\beta\text{-GeO}_2$ and silica powder (a) before heating and (b-e) after heating to 175 $^{\circ}\text{C}$ for 3 days in basic solutions. Bases: (b) NaOH, (c) NH_4OH , (d) $\text{Ba}(\text{OH})_2$, and (e) CsOH.

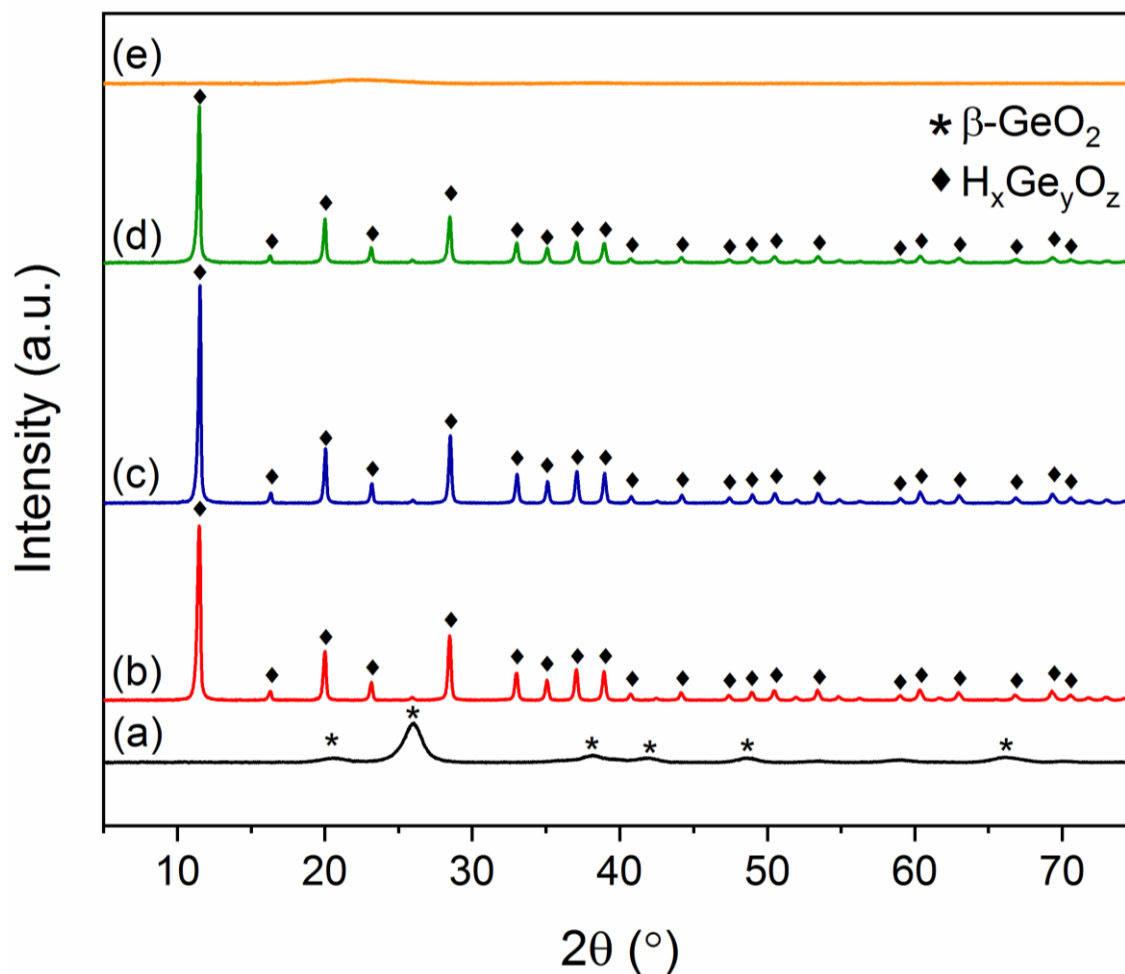


Figure 5.17. PXRD patterns of $\beta\text{-GeO}_2/\text{SiO}_2$ powder after heating in a NH_4OH solution. (a) $\beta\text{-GeO}_2/\text{SiO}_2$ powder was (b) heated in a NH_4OH solutions to 175 °C for 3 days before washing and drying at 60-65 °C overnight. The resulting powder was then (c) heated to 65 °C for an additional 18 h followed by (d) heating to 120 °C for 15 h and then (e) to 160 °C for 24 h.

heating at 160 °C. The use of $\text{Ba}(\text{OH})_2$ resulted in the production of BaGe_4O_9 as a minor contaminant while the use of CsOH lead to a minor $\text{H}_{12}\text{Ge}_7\text{O}_{20}\cdot 3\text{H}_2\text{O}$ impurity. The PXRD pattern shows no observable evidence of Cs^+ reacting with the powder. No α -quartz peaks were observed in any PXRD patterns.

α -Quartz may not have crystallized for two main reasons: the temperature is too low or the pressure is too low. The temperature could not be increased because the β - GeO_2 will shift structurally and lose its chirality. An increased pressure was tried by changing the solvent and increasing the volume of the solvent. SiO_2/β - GeO_2 powder was heated with aqueous CsOH solution combined with either methanol or acetone, which have higher vapor pressures than ethanol.¹⁹⁰ PXRD patterns (Figure 5.18) revealed that the use of these solvents appears to have eliminated the formation of the $\text{H}_{12}\text{Ge}_7\text{O}_{20}\cdot 3\text{H}_2\text{O}$ impurity, but no α -quartz formed.

Although no identified crystal structures contained Cs in the PXRD patterns of SiO_2/β - GeO_2 powder heated in CsOH solution, EDS spectra (Figures 5.19-21) were obtained to determine their atomic composition. The spectra show the presence of Ge, Si, and Cs in all powders. These data signify that SiO_2 was not removed at any point during the synthesis but that Cs also remained within the powder.

Elemental mapping of the SiO_2/β - GeO_2 powder heated in a CsOH water/methanol solution (Figure 5.22) was then used to determine how these elements were separated within the powder. These images show greater separation between the Si and Ge than prior to heating, which may be caused by dissolution of SiO_2 in the basic solution at the high temperature. Cs was shown be present in higher concentrations within the SiO_2 powder, which may also be caused by SiO_2 dissolution.

TEM images with electron diffractions (Figure 5.23) were obtained to determine the crystallinity of smaller areas of this powder as was done prior to heating. These diffractions showed the powder to have both amorphous and polycrystalline portions. Although the material was still sensitive to the electron beam, which can be seen by multiple diffraction patterns of the same sample area (Figure 5.24), the patterns from heated powders were initially more intense than those before heating. This greater

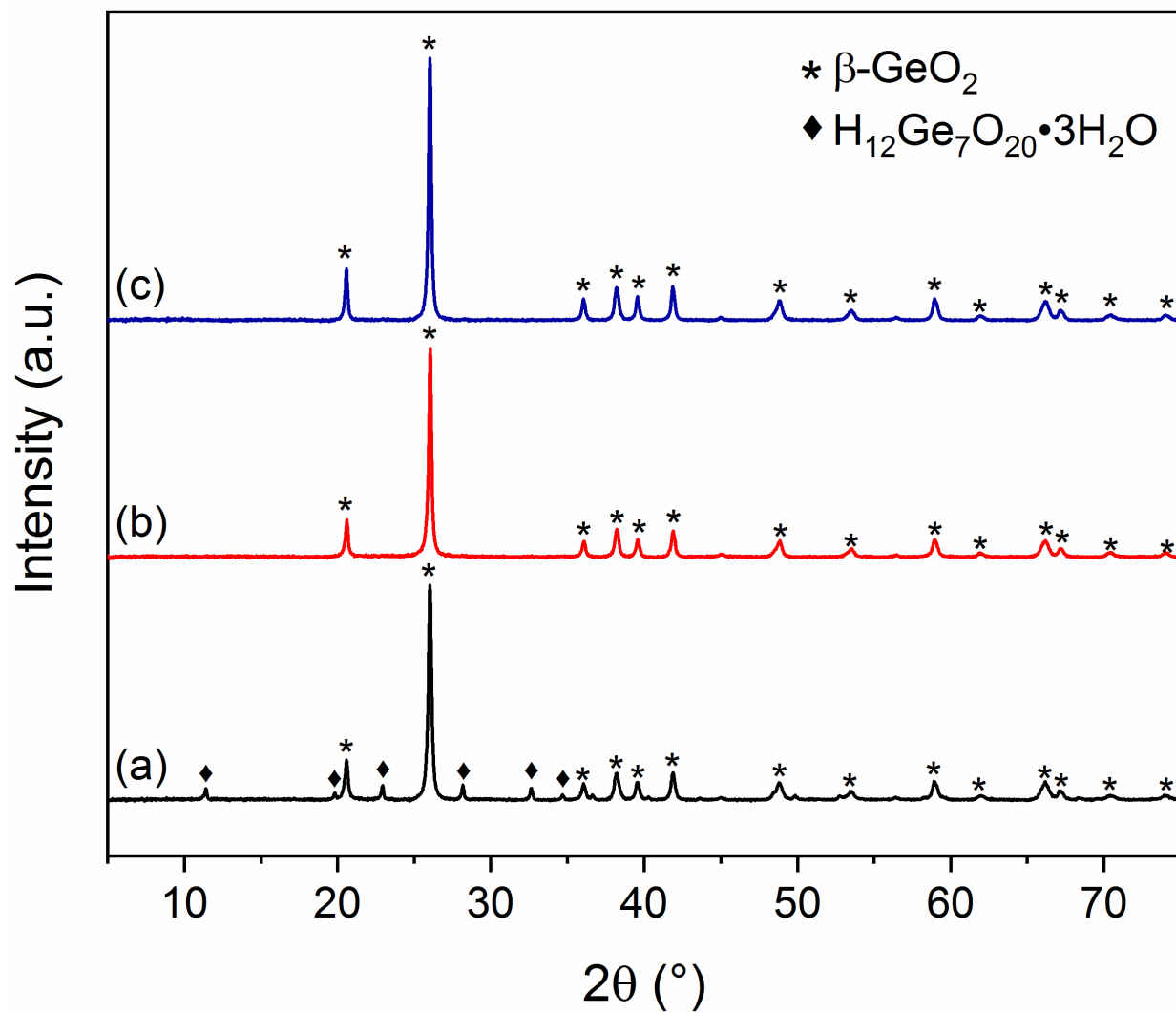


Figure 5.18. PXRD patterns of $\beta\text{-GeO}_2/\text{SiO}_2$ heated to 175 °C for 3 days in CsOH solutions using (a) ethanol, (b) methanol, and (c) acetone as the solvent.

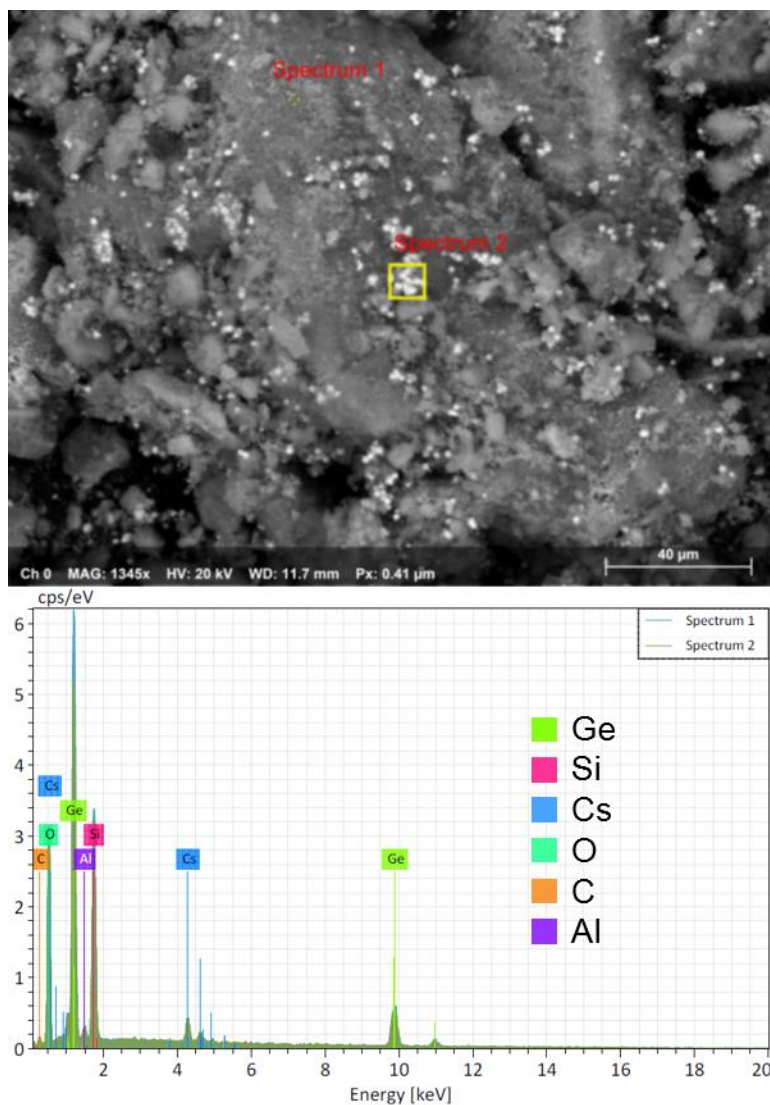


Figure 5.19. SEM image (top) and EDS spectra (bottom) for $\text{SiO}_2/\beta\text{-GeO}_2$ powder heated in CsOH ethanol/water solution. EDS spectra were obtained for the areas in the yellow squares on the SEM image.

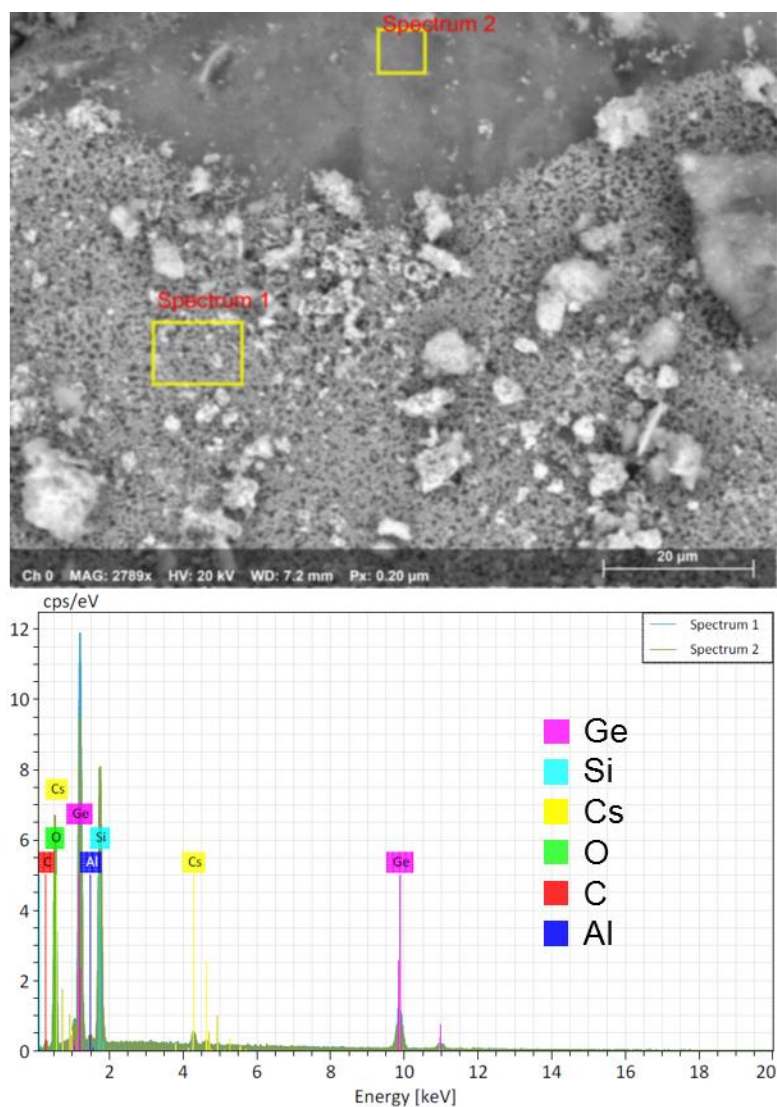


Figure 5.20. SEM image (top) and EDS spectra (bottom) for $\text{SiO}_2/\beta\text{-GeO}_2$ powder heated in CsOH methanol/water solution. EDS spectra were obtained for the areas in the yellow squares on the SEM image.

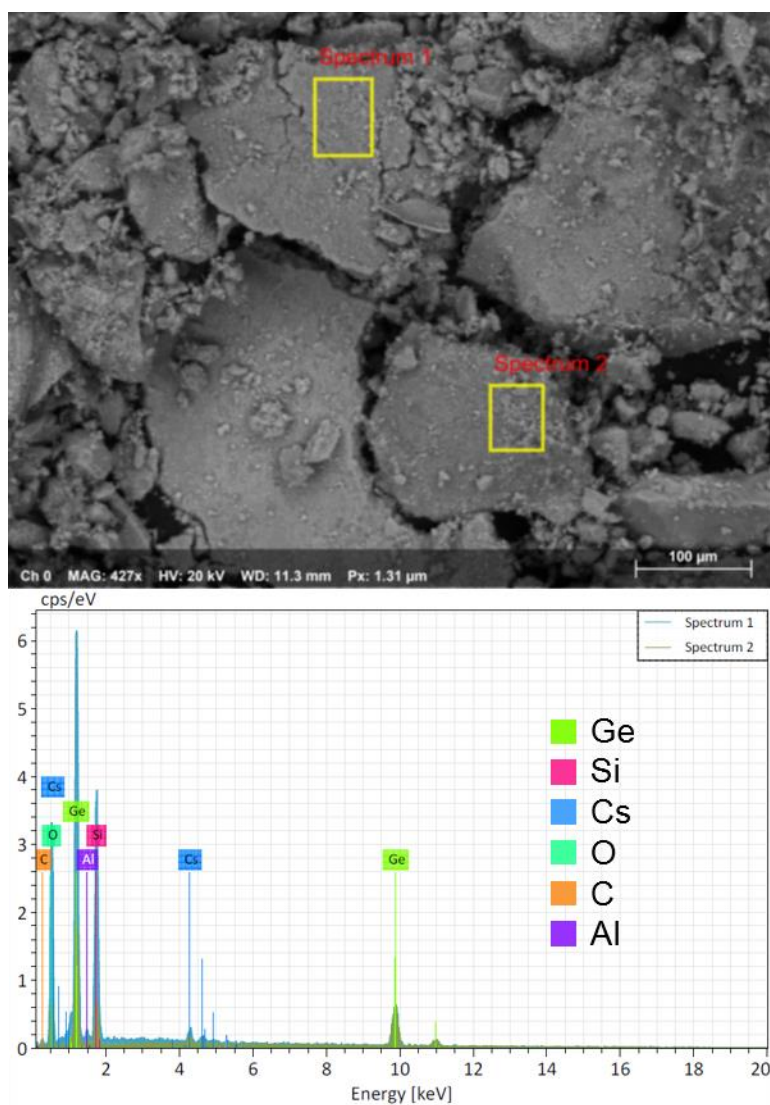


Figure 5.21. SEM image (top) and EDS spectra (bottom) for $\text{SiO}_2/\beta\text{-GeO}_2$ powder heated in CsOH acetone/water solution. EDS spectra were obtained for the areas in the yellow squares on the SEM image.

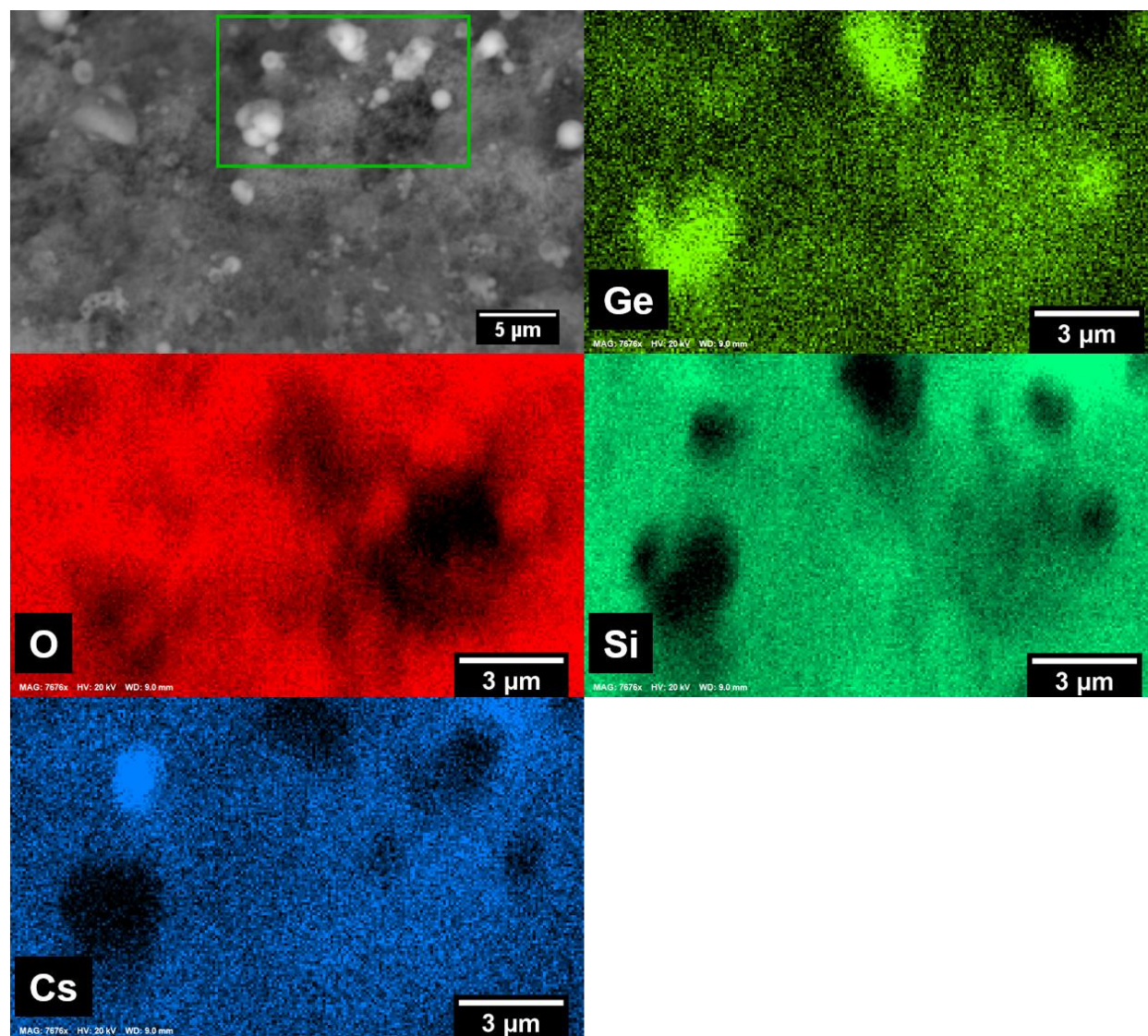


Figure 5.22. Elemental mapping of $\text{SiO}_2/\beta\text{-GeO}_2$ powder heated in a CsOH water/methanol solution. The elemental mapping area is marked by a green square on the SEM image.

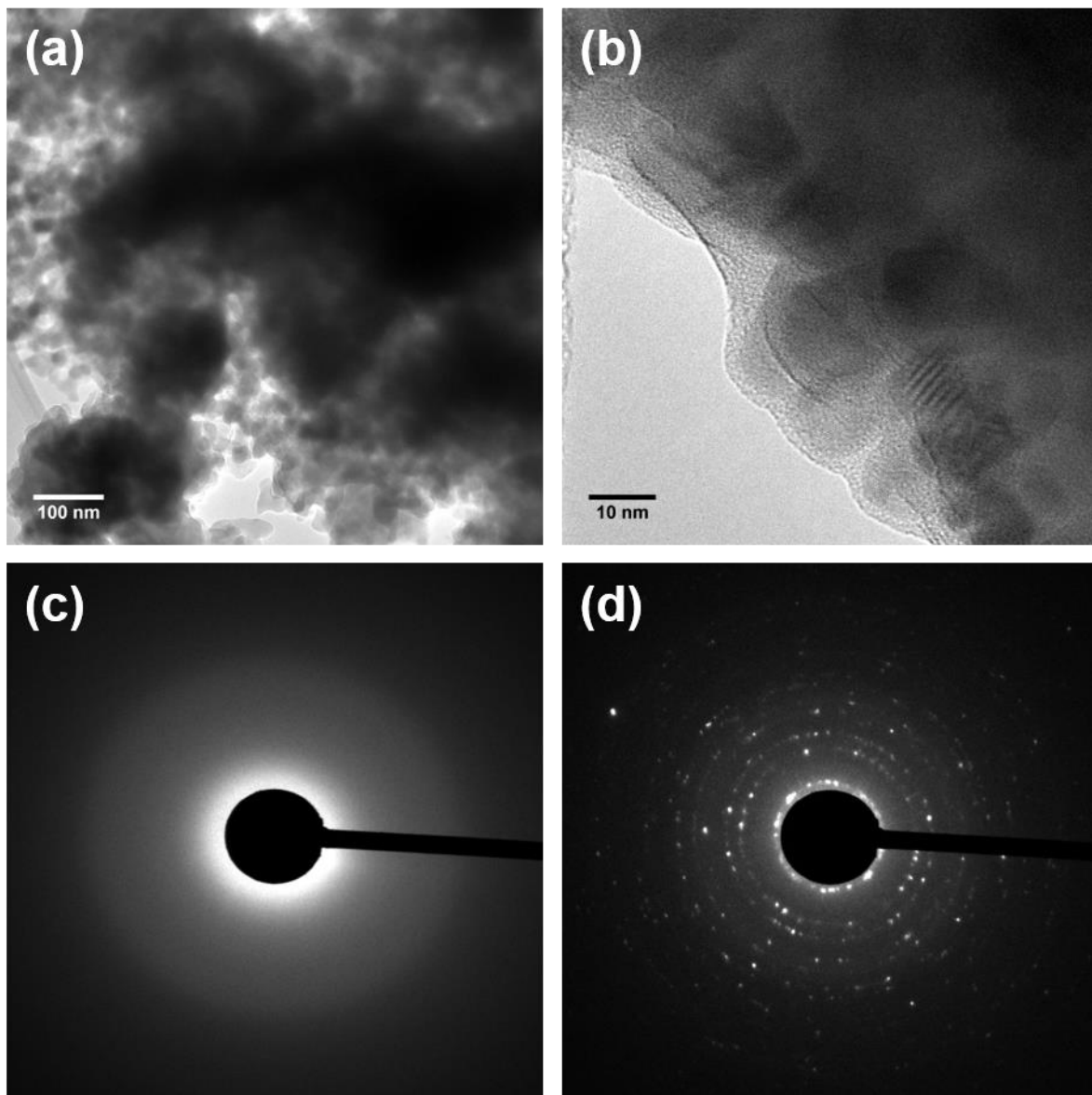


Figure 5.23. TEM images (a-b) and electron diffraction patterns (c-d) of $\text{SiO}_2/\beta\text{-GeO}_2$ powder heated in a CsOH water/methanol solution.

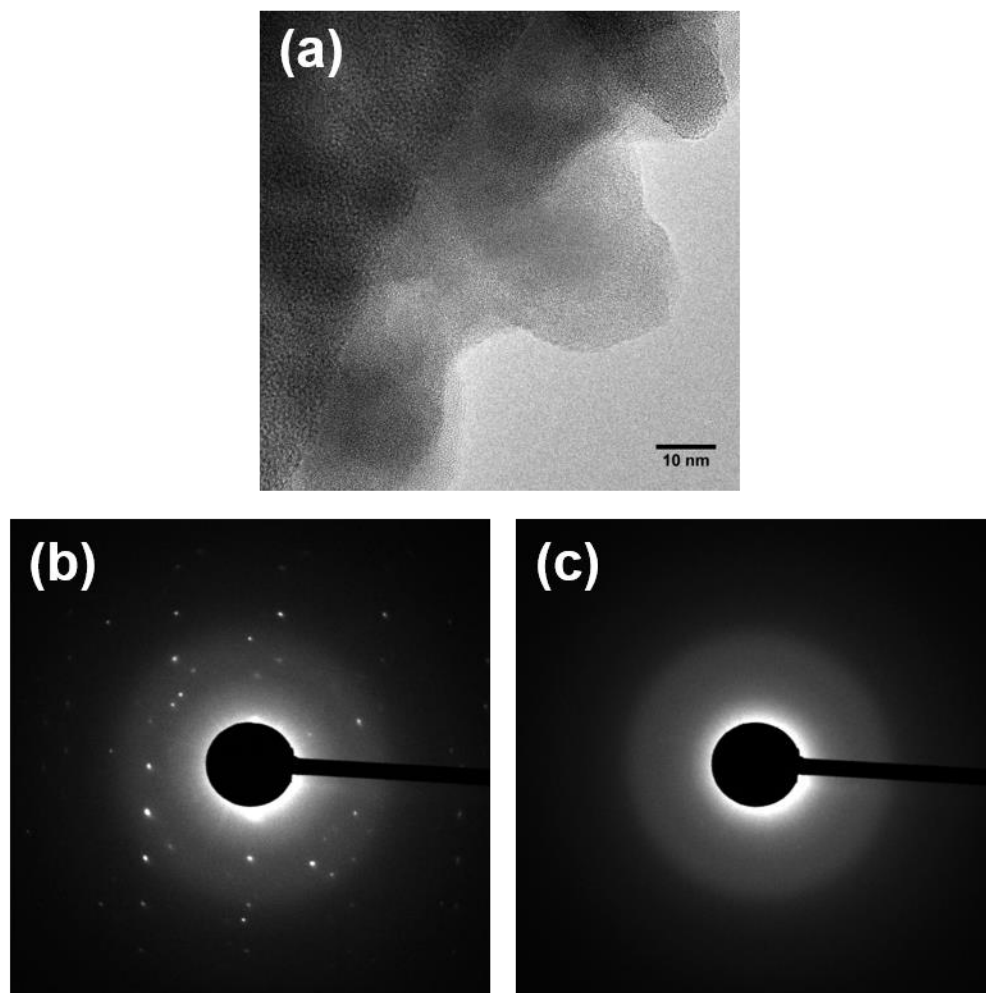


Figure 5.24. Electron beam sensitivity of $\text{SiO}_2/\beta\text{-GeO}_2$ powder heated in a CsOH water/methanol solution shown by (a) a TEM image and (b-c) its corresponding electron diffraction patterns. The electron diffraction patterns were measured in the same area of the TEM image.

intensity of the polycrystalline portion of the powder may result from greater separation of the amorphous SiO₂ and crystalline β -GeO₂ or from sintering of the β -GeO₂ particles.

5.8. Conclusion

Initial studies into a novel production method for optically-active α -quartz nanoparticles using β -GeO₂ nanoparticles were conducted. The first step to this process would be the synthesis of optically-active β -GeO₂ nanoparticles. The templating of an enantiomeric excess of β -GeO₂ nanoparticles was attempted using Lys or DAP as a capping agent during the hydrolysis of TEOG. Although PXRD patterns indicated the successful production of β -GeO₂, TGA-MS indicated the presence of only a small concentration of each capping agent. This negligible adsorption was insufficient to induce templating; therefore, there was no measurable optical activity in most trials. Although Lys-GeO₂ ($x=1, 2$) powders exhibited a small optical rotation in polarimetry measurements and one minor peak was measured in a CD spectrum of Lys-GeO₂ ($x=1$), no measurements were replicable.

As the final goal of this work would involve using optically-active β -GeO₂ to template optically-active α -quartz nanoparticles, templating of *rac*- α -quartz with *rac*- β -GeO₂ was first attempted. In this study, TEOG and TEOS were hydrolyzed to form one powder containing both SiO₂ and β -GeO₂. PXRD and electron diffraction patterns indicated that α -quartz does not crystallize at room temperature, which was expected as higher temperatures and pressures are usually required. The powder was then heated in various basic solutions. Powder heated in water/ethanol solutions with NaOH, NH₄OH, or Ba(OH)₂ as the base resulted in the complete or partial reaction of the β -GeO₂ powder as determined by PXRD. Powder was also heated in CsOH solutions using water combined with ethanol, methanol, or acetone as the solvent. These powders showed little or no contamination on PXRD, but EDS and elemental mapping showed Cs throughout the powder. α -Quartz did not form in any powders.

CHAPTER 6

CONCLUSIONS AND FUTURE *W*ORK

6.1. LSO:Ce Powder Synthesis

6.1.1. MC Synthesis of LSO:Ce Powder

LSO:Ce powder was produced through mechanochemical (MC) techniques using a planetary ball mill. This process presents a fast, room-temperature, solvent-free alternative to previously-conducted syntheses. To better understand this synthesis, a parametric study was conducted using the Burgio-Rojac model. This study showed a decrease in reaction time as ball diameter increased (within the sizes used), rotation rate of the vial/disk increased, mass of the powder decreased, density of the balls/vial increased, and number of balls increased. This research also demonstrated the effect of vial degradation during the syntheses as crystallinity decreased and reaction time increased as the vials were used over several months. Contamination was seen when using all three vial/ball materials (Si_3N_4 , WC, and ZrO_2). While Si_3N_4 and WC mixed with the powder, ZrO_2 reacted with the LSO:Ce during the milling process to form $\text{Lu}_3\text{Zr}_3\text{O}_{12}$, making it unsuitable for the synthesis of this scintillator.

6.1.2. Future Work on MC Synthesis of LSO:Ce

The most prominent problem in the MC synthesis of LSO:Ce was contamination. A more extensive study to address this issue is essential. First, the amount of material from each type of vial/ball should be determined both throughout a single run and over multiple runs. It is possible the degree of contamination could be related to the brittleness or hardness of the vial. This relationship should be studied to find the extent of the correlation. Another interesting project would be to optimize the reaction in terms of contamination versus reaction time. For instance, the WC is a harder material, which may lead to greater contamination than Si_3N_4 over a constant milling time, but it has a shorter reaction time, which may result in less contamination. The degree of contamination over several runs would also be crucial to understand for long-term, industrial use.

The PL spectra's signal-to-noise ratio (S/N) for MC-LSO:Ce was significantly lower than that of SC-LSO:Ce. It was theorized that this may be due to fewer oxygen vacancies, higher Ce^{3+} concentrations, or greater dispersion of the Ce^{3+} . Furnace sintering increased S/N, but it still did not compare to SC-LSO:Ce's ratio. This suggests that either oxygen

vacancies are not the primary cause of the low S/N or longer or higher temperature sintering is required. The addition of reductants seemed to increase the PL intensity, signifying that the Ce^{4+} is not fully reduced during milling despite the high temperatures at collision points. Using Ce_2O_3 during the MC synthesis would increase the concentration of Ce^{3+} , which would appear as increased S/N in the PL spectra.

6.1.3. Combustion Synthesis of LSO:Ce Powder

LSO:Ce powder was synthesized through combustion methods. The most successful synthesis involved a solution combustion (SC) process using a mixture of urea and hexamethylenetetramine as the fuel. Although this method produced LSO:Ce with both the $P 1 2_1/c 1$ and $C 1 2/c 1$ symmetries, heating the powder in the furnace shifted the structure to solely the $C 1 2/c 1$ space group. LSO:Ce powder synthesized through the SC synthesis exhibited a greater signal-to-noise ratio in its photoluminescence spectra than powder synthesized through MC, which suggests fewer oxygen vacancies, higher Ce^{3+} concentrations, or greater dispersion of the Ce^{3+} .

6.1.4. Future Work on Combustion Synthesis of LSO:Ce

The work presented in Chapter 4 concluded that solution combustion was more facile and more replicable than gel combustion for LSO:Ce powders. This SC method should therefore be the focus of future work. In this work, the SC synthesis of LSO:Ce powders resulted in a mixture of two space groups of the material, and past research has synthesized exclusively $P 1 2_1/c 1$ LSO:Ce.^{17, 39, 49} There has been no successful SC production of LSO:Ce that results in only the $C 1 2/c 1$ symmetry. This research could either use various molar ratios of hexamethylenetetramine:urea, greater concentrations of fuel, or attempt the synthesis with other mixtures of fuels which are more exothermic. During these studies, the effect of each of the parameters on crystallite and particle sizes might be of interest. Smaller sizes would allow better pressing of ceramics through hot isostatic pressing.

6.2. Optically-Active β -GeO₂ and α -Quartz Nanoparticles

6.2.1. Optically-Active β -GeO₂ Nanoparticle Synthesis

Attempts to produce optically-active β -GeO₂ nanoparticles using lysine (Lys) and 1,2-diaminopropane (DAP) as capping agents were unsuccessful. The adsorption strength of each chiral organic compound was too weak to induce the production of an enantiomeric excess of β -GeO₂. Any optical activity measured through polarimetry or circular dichroism was not reproducible.

6.2.2. Future Work on Optically-Active β -GeO₂ Nanoparticle Synthesis

As templating an enantiomeric excess of β -GeO₂ nanoparticles was unsuccessful, subsequent work can take a couple different directions. One option would be to use different capping agents. If the surface is negatively charged as is expected for this material, research should be continued with other positively-charged capping agents, like arginine. These reactions may require the use of more acidic reactions. Cysteine and penicillamine derivatives should also be used as they have been successful in other chiral nanoparticle syntheses although the negatively-charged surface of the β -GeO₂ makes their adsorption unlikely.^{80, 82, 191} Phosphates and silanes have previously been used to functionalize the surface of oxide nanoparticles, so it may be beneficial to try chiral capping agents containing these groups.¹⁹² The listed capping agents may have greater adsorption strengths for β -GeO₂, which would help in templating optical activity.

Another option would be to use a different chiral inorganic nanoparticle. Halasyamani and Poeppelmeier list a wide variety of possible chiral oxide compounds although most have not yet been synthesized as nanoparticles and others require high temperatures.¹⁹³ Other options, which have been mentioned by Ben-Moshe, *et al.*,⁷⁸ include HgO, AlPO₄, CrSi₂, TeO₂, and Ag₂Se. The available capping agents may adsorb more strongly and in higher concentrations to these materials, leading to the production of optically-active nanoparticles.

6.2.3. Templating α -Quartz Using β -GeO₂

α -Quartz did not form under the conditions described in this dissertation. Although amorphous silica remained in the powder, it did not crystallize when heated. When heated

with NaOH, NH₄OH, Ba(OH)₂, or CsOH in water/ethanol, the β -GeO₂ partially or fully reacted with the base. Based on PXRD patterns, powder heated with CsOH as the base combined with water and methanol or acetone had no observable contamination, but EDS revealed Cs within the powder. Elemental mapping showed greater separation of the Ge and Si after heating as well as greater overlap between Si and Cs. These two observations suggest that silica dissolves during heating, but nucleation of α -quartz does not occur.

6.2.4. Future Work on Templating α -Quartz Using β -GeO₂

α -Quartz did not crystallize in any of the studies described in Chapter 5. In these experiments, the temperature and pressure were lower than what is typically used in α -SiO₂ nanoparticle syntheses. The temperature cannot be increased because β -GeO₂ will shift structurally to achiral α -GeO₂. Pressure, however, could be increased by using an autoclave with an adjustable pressurization system. Increasing the pressure in α -quartz nanoparticle syntheses has been shown to lead to increased nucleation rates in sub-micron α -quartz powders.¹⁷⁶ An increased nucleation rate may lead to the successful formation of α -quartz from the dissolved silica.

6.3. General Conclusion

This dissertation focuses on two different areas of nanoparticles: scintillators and optically-active inorganic compounds. Scintillator syntheses concentrated on producing the well-known LSO:Ce material through novel methods for use in ceramics. Both MC and SC syntheses were successful in producing LSO:Ce, but future work into better understanding and optimizing the processes is essential for industrial use. Chiral nanoparticle studies centered around the use of one optically-active nanoparticle (β -GeO₂) to induce optical activity in another (α -quartz). This process would be the first production of an optically-active inorganic nanoparticle synthesized at high temperatures (>150 °C). Although all attempts at producing optically-active β -GeO₂ nanoparticles or templating α -quartz using *rac*- β -GeO₂ were unsuccessful, this research can lead to future work involving new capping agents, new low-temperature optically-active nanoparticle

syntheses, and possibly a new method for forming optically-active nanoparticles using inorganic templates at higher temperatures.

LIST OF REFERENCES

1. Horikoshi, S.; Serpone, N., Introduction to Nanoparticles. In *Microwaves in Nanoparticle Synthesis: Fundamentals and Applications*, Horikoshi, S.; Serpone, N., Eds. Wiley-VCH: Weinheim, Germany, 2013; Vol. 1, pp 1-24.
2. de Mello Donegá, C., The Nanoscience Paradigm: “Size Matters!”. In *Nanoparticles: Workhorses of Nanoscience*, de Mello Donegá, C., Ed. Springer Berlin Heidelberg: Berlin, Heidelberg, 2014; pp 1-12.
3. Derenzo, S. E.; Weber, M. J.; Bourret-Courchesne, W. E.; Klintenberg, M. K., The quest for the ideal inorganic scintillator. *Nucl Instrum Meth A* **2003**, 505 (1-2), 111-117.
4. Weber, M. J., Inorganic scintillators: today and tomorrow. *J Lumin* **2002**, 100 (1), 35-45.
5. Knoll, G. F., Scintillation Detector Principles. In *Radiation Detection and Measurement*, 4th ed.; John Wiley & Sons, Inc.: Hoboken, NJ, 2010; pp 223-274.
6. Tsoulfanidis, N.; Landsberger, S., Scintillation Detectors. In *Measurement and Detection of Radiation*, 4th ed.; CRC Press: Boca Raton, 2015; pp 195-216.
7. van Eijk, C. W. E., Inorganic-scintillator development. *Nucl Instr Meth Phys Res A* **2001**, 460 (1), 1-14.
8. Lecoq, P.; Annenkov, A.; Gektin, A.; Korzhik, M.; Pedrini, C., Inorganic Scintillators for Detector Systems: Physical Principles and Crystal Engineering. Springer: Netherlands, 2006.
9. Dhanaraj, G.; Byrappa, K.; Prasad, V.; Dudley, M., Crystal Growth Techniques and Characterization: An Overview. In *Springer Handbook of Crystal Growth*, Dhanaraj, G.; Byrappa, K.; Prasad, V.; Dudley, M., Eds. Springer Berlin Heidelberg: Berlin, Heidelberg, 2010; pp 3-16.
10. *Fiber Crystal Growth from the Melt*. Springer-Verlag: Berlin, 2003; Vol. 6.
11. Xu, J.; Fan, L.; Shi, Y.; Li, J.; Xie, J.; Lei, F., Effects of Ce³⁺ doping concentrations on microstructure and luminescent properties of Ce³⁺:Lu₃Al₅O₁₂ (Ce:LuAG) transparent ceramics. *Opt Mater* **2014**, 36 (12), 1954-1958.
12. Yoshikawa, A.; Chani, V.; Nikl, M., Czochralski Growth and Properties of Scintillating Crystals. *Acta Phys Pol A* **2013**, 124 (2), 250-264.

13. Chen, D.; Lin, C.; Maljuk, A.; Zhou, F., Crystal Growth and Characterization of Iron-Based Superconductor. In *Growth and Characterization of Bulk Superconductor Material*, Springer International Publishing: Cham, 2016; pp 143-191.
14. Kuntz, J. D.; Roberts, J. J.; Hough, M.; Cherepy, N. J., Multiple synthesis routes to transparent ceramic lutetium aluminum garnet. *Scripta Mater* **2007**, 57 (10), 960-963.
15. Lempicki, A.; Brecher, C.; Lingertat, H.; Miller, S. R.; Glodo, J.; Sarin, V. K., A ceramic version of the LSO scintillator. *IEEE T Nucl Sci* **2008**, 55 (3), 1148-1151.
16. Wang, Y. M.; van Loef, E.; Rhodes, W. H.; Glodo, J.; Brecher, C.; Nguyen, L.; Lempicki, A.; Baldoni, G.; Higgins, W. M.; Shah, K. S., Lu_2SiO_5 : Ce Optical Ceramic Scintillator for PET. *IEEE T Nucl Sci* **2009**, 56 (3), 887-891.
17. Yukihiro, E. G.; Jacobsohn, L. G.; Blair, M. W.; Bennett, B. L.; Tornga, S. C.; Muenchausen, R. E., Luminescence properties of Ce-doped oxyorthosilicate nanophosphors and single crystals. *J Lumin* **2010**, 130 (12), 2309-2316.
18. Salamon, D., Advanced Ceramics. In *Advanced Ceramics for Dentistry*, Shen, J. Z.; Kosmač, T., Eds. Elsevier Science & Technology: Amsterdam, 2013; pp 103-122.
19. Li, H.-L.; Liu, X.-J.; Huang, L.-P., Luminescent properties of $\text{LuAG}:\text{Ce}$ phosphors with different Ce contents prepared by a sol–gel combustion method. *Opt Mater* **2007**, 29 (9), 1138-1142.
20. Hassanzadeh-Tabrizi, S. A.; Taheri-Nassaj, E.; Sarpoolaky, H., Synthesis of an alumina–YAG nanopowder via sol–gel method. *J Alloy Compd* **2008**, 456 (1), 282-285.
21. Kim, H. T.; Kim, J. H.; Lee, J.-K.; Kang, Y. C., Green light-emitting $\text{Lu}_3\text{Al}_5\text{O}_{12}:\text{Ce}$ phosphor powders prepared by spray pyrolysis. *Mater Res Bull* **2012**, 47 (6), 1428-1431.
22. Cutler, P. A. Synthesis and Scintillation of Single Crystal and Polycrystalline Rare Earth-Activated Lutetium Aluminum Garnet. Master's Thesis, University of Tennessee, 2010.
23. Kang, Y. C.; Lenggoro, I. W.; Park, S. B.; Okuyama, K., YAG:Ce phosphor particles prepared by ultrasonic spray pyrolysis. *Mater Res Bull* **2000**, 35 (5), 789-798.

24. Moore, C. A.; McMillen, C. D.; Kolis, J. W., Hydrothermal Growth of Single Crystals of $\text{Lu}_3\text{Al}_5\text{O}_{12}$ (LuAG) and Its Doped Analogues. *Cryst Growth Des* **2013**, 13 (6), 2298-2306.
25. McDonald, K. A.; Schweitzer, G. K., Synthesis of GAGG:Ce³⁺ powder for ceramics using mechanochemical and solution combustion methods. *J Am Ceram Soc* **2018**, 101 (9), 3837-3749.
26. Xu, J.; Fan, L.; Shi, Y.; Li, J.; Xie, J.; Lei, F., Scintillation and Luminescent Properties of Cerium Doped Lutetium Aluminum Garnet (Ce:LuAG) Powders and Transparent Ceramics. *IEEE T Nucl Sci* **2014**, 61 (1), 373-379.
27. Jing, W.; Li, F.; Yu, S.; Ji, X.; Xu, T.; Zhang, J.; Pan, Z.; Yuan, Z.; Kang, B.; Deng, J.; Yin, W.; Huang, H., High efficiency synthesis of Nd:YAG powder by a spray co-precipitation method for transparent ceramics. *J Eur Ceram Soc* **2018**, 38 (5), 2454-2461.
28. Seferis, I. E.; Zych, E., On the synthesis of LuAG:Ce fine powders by molten salts methods and spectroscopic properties of the products. *J Lumin* **2016**, 169, 838-843.
29. Liu, S.; Feng, X.; Shi, Y.; Wu, L.; Luo, J.; Wang, W.; Pan, Y., Fabrication, microstructure and properties of highly transparent Ce³⁺:Lu₃Al₅O₁₂ scintillator ceramics. *Opt Mater* **2014**, 36 (12), 1973-1977.
30. Li, H.-L.; Liu, X.-J.; Huang, L.-P., Fabrication of Transparent Cerium-Doped Lutetium Aluminum Garnet (LuAG:Ce) Ceramics by a Solid-State Reaction Method. *J Am Ceram Soc* **2005**, 88 (11), 3226-3228.
31. Cherepy, N. J.; Kuntz, J. D.; Seeley, Z. M.; Fisher, S. E.; Drury, O. B.; Sturm, B. W.; Hurst, T. A.; Sanner, R. D.; Roberts, J. J.; Payne, S. A., Transparent Ceramic Scintillators for Gamma Spectroscopy and Radiography. *P Soc Photo-Opt Ins* **2010**, 7805.
32. Rabinovitch, Y.; Bogicevic, C.; Karolak, F.; Tétard, D.; Dammak, H., Freeze-dried nanometric neodymium-doped YAG powders for transparent ceramics. *J Mater Process Tech* **2008**, 199 (1–3), 314-320.

33. Melcher, C. L.; Schweitzer, J. S., Cerium-Doped Lutetium Oxyorthosilicate - a Fast, Efficient New Scintillator. *Conference Record of the 1991 IEEE Nuclear Science Symposium and Medical Imaging Conference, Vols 1-3* **1991**, 228-231.
34. Melcher, C. L.; Schweitzer, J. S., A Promising New Scintillator - Cerium-Doped Lutetium Oxyorthosilicate. *Nucl Instrum Meth A* **1992**, 314 (1), 212-214.
35. Berger, M. J.; Hubbell, J. H.; Seltzer, S. M.; Chang, J.; Coursey, J. S.; Sukumar, R.; Zucker, D. S.; Olsen, K., XCOM: Photon Cross Sections Database. 2010 ed.; National Institute of Standards and Technology: Gaithersburg, MD, 2010; Vol. 1.5.
36. Michail, C. M.; Fountos, G. P.; David, S. L.; Valais, I. G.; Toutountzis, A. E.; Kalyvas, N. E.; Kandarakis, I. S.; Panayiotakis, G. S., A comparative investigation of $\text{Lu}_2\text{SiO}_5\text{:Ce}$ and $\text{Gd}_2\text{O}_2\text{S:Eu}$ powder scintillators for use in x-ray mammography detectors. *Meas Sci Technol* **2009**, 20 (10), 1-9.
37. Elftmann, R.; Tammen, J.; Kulkarni, S. R.; Martin, C.; Böttcher, S.; Wimmer-Schweingruber, R., Characterization of an LSO scintillator for space applications. *J Phys Conf Ser* **2015**, 632 (1), 012006.
38. The Physical Basis of Positron Emission Tomography. In *Positron Emission Tomography*, Granov, A.; Tiutin, L.; Schwarz, T., Eds. Springer-Verlag: Berlin, 2013; pp 3-24.
39. Blair, M. W.; Jacobsohn, L. G.; Bennett, B. L.; Muenchausen, R. E.; Sitarz, S. C.; Smith, J. F.; Cooke, D. W.; Crozier, P. A.; Wang, R., Structure and Luminescence of Ce-doped Lu_2SiO_5 Nanophosphor. *MRS Proceedings* **2007**, 1056.
40. Ren, G. H.; Qin, L. S.; Lu, S.; Li, H. Y., Scintillation characteristics of lutetium oxyorthosilicate ($\text{Lu}_2\text{SiO}_5\text{:Ce}$) crystals doped with cerium ions. *Nucl Instrum Meth A* **2004**, 531 (3), 560-565.
41. Singh, S.; Lakshminarayana, G.; Sharma, M.; Dao, T. D.; Chen, K.; Wada, Y.; Takeda, T.; Nagao, T., Excitation Induced Tunable Emission in $\text{Ce}^{3+}/\text{Eu}^{3+}$ Codoped BiPO_4 Nanophosphors. *J Spectrosc* **2015**, 1-10.
42. Melcher, C. L. Lutetium orthosilicate single crystal scintillator detector. US 4,958,080 A, 1990.

43. Felsche, J., The crystal chemistry of the rare-earth silicates. In *Rare Earths*, Springer: Berlin, Heidelberg, 1973; pp 99-197.
44. Brandle, C. D.; Valentino, A. J.; Berkstresser, G. W., Czochralski Growth of Rare-Earth Orthosilicates (Ln_2SiO_5). *J Cryst Growth* **1986**, 79 (1-3), 308-315.
45. van Eijk, C. W. E., Radiation detector developments in medical applications: Inorganic scintillators in positron emission tomography. *Radiat Prot Dosim* **2008**, 129 (1-3), 13-21.
46. Gustafsson, T.; Klintenberg, M.; Derenzo, S. E.; Weber, M. J.; Thomas, J. O., Lu_2SiO_5 by single-crystal X-ray and neutron diffraction. *Acta Crystallogra C* **2001**, 57 (6), 668-669.
47. Müller-Bunz, H.; Schleid, T., Über die Oxidsilicate $\text{M}_2\text{O}[\text{SiO}_4]$ der schweren Lanthanoide ($\text{M}=\text{Dy}-\text{Lu}$) im A-Typ. *Z Anorg Allg Chem* **1999**, 625 (4), 613-618.
48. Cooke, D. W.; Lee, J. K.; Bennett, B. L.; Groves, J. R.; Jacobsohn, L. G.; McKigney, E. A.; Muenchausen, R. E.; Nastasi, M.; Sickafus, K. E.; Tang, M.; Valdez, J. A.; Kim, J. Y.; Hong, K. S., Luminescent properties and reduced dimensional behavior of hydrothermally prepared Y_2SiO_5 : Ce nanophosphors. *Appl Phys Lett* **2006**, 88 (10).
49. Muenchausen, R. E.; McKigney, E. A.; Jacobsohn, L. G.; Blair, M. W.; Bennett, B. L.; Cooke, D. W., Science and application of oxyorthosilicate nanophosphors. *IEEE T Nucl Sci* **2008**, 55 (3), 1532-1535.
50. Cannas, C.; Mainas, M.; Musinu, A.; Piccaluga, G.; Speghini, A.; Bettinelli, M., Nanocrystalline luminescent Eu^{3+} -doped Y_2SiO_5 prepared by sol-gel technique. *Opt Mater* **2005**, 27 (9), 1506-1510.
51. Melcher, C. L. Lutetium orthosilicate single crystal scintillator detector. 0373976 A1, 1989.
52. Cooke, D. W.; Muenchausen, R. E.; McClellan, K. J.; Bennett, B. L., Spectral emission of rare-earth doped Lu_2SiO_5 single crystals. *Opt Mater* **2005**, 27 (12), 1781-1786.

53. Farhi, H.; Lebbou, K.; Belkahla, S.; Grosvalet, L.; Hautefeuille, B.; Caramanian, A.; Dujardin, C.; Tillement, O.; Pedrini, C., Fiber single crystal growth by LHPG technique and optical characterization of Ce³⁺-doped Lu₂SiO₅. *Opt Mater* **2008**, 30 (9), 1461-1467.
54. Mansuy, C.; Mahiou, R.; Nedelec, J. M., A new sol-gel route to Lu₂SiO₅ (LSO) scintillator: Powders and thin films. *Chem Mater* **2003**, 15 (17), 3242-3244.
55. Mansuy, C.; Leroux, F.; Mahiou, R.; Nedelec, J. M., Preferential site substitution in sol-gel derived Eu³⁺ doped Lu₂SiO₅: a combined study by X-ray absorption and luminescence spectroscopies. *J Mater Chem* **2005**, 15 (38), 4129-4135.
56. Wang, Y. Z.; He, Q. Y.; Chu, B. L., Synthesis and characterization of Ce-doped Lu₂SiO₅ powders by the solid-state reaction with Li₂SO₄ flux. *J Alloy Compd* **2009**, 479 (1-2), 704-706.
57. Yun, P.; Shi, Y.; Zhou, D.; Xie, J., Hydrothermal synthesis of Ce: Lu₂SiO₅ scintillator powders. *J Rare Earth* **2009**, 27 (5), 801-805.
58. Tian, Z.; Sun, L.; Zheng, L.; Wang, J.; Li, J.; Hu, Z., In situ hot pressing/reaction synthesis, mechanical and thermal properties of Lu₂SiO₅. *J Eur Ceram Soc* **2014**, 34 (16), 4403-4409.
59. Fan, L.; Shi, Y.; Xu, J.; Xie, J.; Lei, F., Consolidation of translucent Ce³⁺-doped Lu₂SiO₅ scintillation ceramics by pressureless sintering. *J Mater Res* **2014**, 29 (19), 2252-2259.
60. Raukas, M.; Basun, S. A.; VanSchaik, W.; Happek, U.; Yen, W. M., Cerium luminescence efficiency in lutetium-based crystals. *Mater Sci Forum* **1997**, 239-, 249-252.
61. Fan, L. C.; Zhang, X. X.; Lin, D. B.; Shi, Y.; Zhang, J. Y.; Xie, J. J.; Lei, F.; Zhang, L.; Chen, L.; Yuan, H., Luminescence characteristics of Lu₂SiO₅:Ce³⁺ (LSO:Ce) ceramic scintillators under VUV-UV excitation. *Nucl Instrum Meth A* **2016**, 806, 325-329.
62. Barron, L. D., A historical review of optical activity phenomena. In *Molecular Light Scattering and Optical Activity*, 2 ed.; Cambridge University Press: Cambridge, 2004; pp 1-52.

63. Mason, S. F., Pasteur on Molecular Handedness-and the Sequel. In *Chirality in Natural and Applied Science*, Lough, W. J.; Wainer, I. W., Eds. Blackwell Science Ltd: Oxford, 2002; pp 1-21.
64. Govan, J.; Gun'ko, Y. K., Recent progress in chiral inorganic nanostructures. In *Nanoscience*, O'Brien, P.; Thomas, P. J., Eds. Royal Society of Chemistry: Cambridge, 2016; Vol. 3.
65. Moloney, M. P.; Govan, J.; Loudon, A.; Mukhina, M.; Gun'ko, Y. K., Preparation of chiral quantum dots. *Nat. Protocols* **2015**, *10* (4), 558-573.
66. Xia, Y.; Zhou, Y.; Tang, Z., Chiral inorganic nanoparticles: origin, optical properties and bioapplications. *Nanoscale* **2011**, *3* (4), 1374-1382.
67. Govorov, A. O.; Gun'ko, Y. K.; Slocik, J. M.; Gerard, V. A.; Fan, Z.; Naik, R. R., Chiral nanoparticle assemblies: circular dichroism, plasmonic interactions, and exciton effects. *J Mater Chem* **2011**, *21* (42), 16806-16818.
68. Wang, Y.; Xu, J.; Wang, Y.; Chen, H., Emerging chirality in nanoscience. *Chem Soc Rev* **2013**, *42* (7), 2930-2962.
69. Lidor-Shalev, O.; Pliatsikas, N.; Carmiel, Y.; Patsalas, P.; Mastai, Y., Chiral Metal-Oxide Nanofilms by Cellulose Template Using Atomic Layer Deposition Process. *ACS Nano* **2017**, *11* (5), 4753-4759.
70. Bonner, W. A.; Kavasmaneck, P. R.; Martin, F. S.; Flores, J. J., Asymmetric adsorption by quartz: A model for the prebiotic origin of optical activity. *Origins Life Evol B* **1975**, *6* (3), 367-376.
71. Mallat, T.; Orglmeister, E.; Baiker, A., Asymmetric catalysis at chiral metal surfaces. *Chem Rev* **2007**, *107* (11), 4863-4890.
72. Berthod, A., Chiral Recognition Mechanisms. *Anal Chem* **2006**, *78* (7), 2093-2099.
73. Gautier, C.; Burgi, T., Chiral inversion of gold nanoparticles. *J Am Chem Soc* **2008**, *130* (22), 7077-7084.
74. Ma, W.; Xu, L.; de Moura, A. F.; Wu, X.; Kuang, H.; Xu, C.; Kotov, N. A., Chiral Inorganic Nanostructures. *Chem Rev* **2017**, *117* (12), 8041-8093.

75. Bonner, W. A.; Kavasmaneck, P. R.; Martin, F. S.; Flores, J. J., Asymmetric Adsorption of Alanine by Quartz. *Science* **1974**, *186* (4159), 143-144.
76. Soai, K.; Osanai, S.; Kadowaki, K.; Yonekubo, S.; Shibata, T.; Sato, I., D-and L-quartz-promoted highly enantioselective synthesis of a chiral organic compound. *J Am Chem Soc* **1999**, *121* (48), 11235-11236.
77. Nguyen, L. A.; He, H.; Pham-Huy, C., Chiral Drugs: An Overview. *Int J Biomed Sci* **2006**, *2* (2), 85-100.
78. Ben-Moshe, A.; Wolf, S. G.; Sadan, M. B.; Houben, L.; Fan, Z.; Govorov, A. O.; Markovich, G., Enantioselective control of lattice and shape chirality in inorganic nanostructures using chiral biomolecules. *Nat Commun* **2014**, *5*, 4302.
79. Mukhina, M. V.; Maslov, V. G.; Baranov, A. V.; Fedorov, A. V.; Orlova, A. O.; Purcell-Milton, F.; Govan, J.; Gun'ko, Y. K., Intrinsic Chirality of CdSe/ZnS Quantum Dots and Quantum Rods. *Nano Letters* **2015**, *15* (5), 2844-2851.
80. Kuno, J.; Kawai, T.; Nakashima, T., The effect of surface ligands on the optical activity of mercury sulfide nanoparticles. *Nanoscale* **2017**, *9*, 11590-11595.
81. Wang, P.-P.; Yu, S.-J.; Govorov, A. O.; Ouyang, M., Cooperative expression of atomic chirality in inorganic nanostructures. *Nat Commun* **2017**, *8*, 14312.
82. Ben-Moshe, A.; Govorov, A. O.; Markovich, G., Enantioselective Synthesis of Intrinsically Chiral Mercury Sulfide Nanocrystals. *Angew Chem Int Edit* **2013**, *52* (4), 1275-1279.
83. Milton, F. P.; Govan, J.; Mukhina, M. V.; Gun'ko, Y. K., The chiral nano-world: chiroptically active quantum nanostructures. *Nanoscale Horizons* **2016**, *1* (1), 14-26.
84. Nakashima, T.; Kobayashi, Y.; Kawai, T., Optical Activity and Chiral Memory of Thiol-Capped CdTe Nanocrystals. *J Am Chem Soc* **2009**, *131* (30), 10342-10343.
85. Gallagher, S. A.; Moloney, M. P.; Wojdyla, M.; Quinn, S. J.; Kelly, J. M.; Gun'ko, Y. K., Synthesis and spectroscopic studies of chiral CdSe quantum dots. *J Mater Chem* **2010**, *20* (38), 8350-8355.
86. Zhou, Y.; Yang, M.; Sun, K.; Tang, Z.; Kotov, N. A., Similar Topological Origin of Chiral Centers in Organic and Nanoscale Inorganic Structures: Effect of Stabilizer

Chirality on Optical Isomerism and Growth of CdTe Nanocrystals. *J Am Chem Soc* **2010**, *132* (17), 6006-6013.

87. Fanelli, R.; Milli, L.; Cornia, A.; Moretto, A.; Castellucci, N.; Zanna, N.; Malachin, G.; Tavano, R.; Tomasini, C., Chiral Gold Nanoparticles Decorated with Pseudopeptides. *Eur J Org Chem* **2015**, *2015* (28), 6243-6248.

88. Qi, H.; Hegmann, T., Postsynthesis Racemization and Place Exchange Reactions. Another Step To Unravel the Origin of Chirality for Chiral Ligand-Capped Gold Nanoparticles. *J Am Chem Soc* **2008**, *130* (43), 14201-14206.

89. Nishida, N.; Yao, H.; Kimura, K., Chiral functionalization of optically inactive monolayer-protected silver nanoclusters by chiral ligand-exchange reactions. *Langmuir* **2008**, *24* (6), 2759-2766.

90. Chwojnowska, E.; Wolska-Pietkiewicz, M.; Grzonka, J.; Lewinski, J., An organometallic route to chiroptically active ZnO nanocrystals. *Nanoscale* **2017**, *9* (39), 14782-14786.

91. Cleary, O.; Purcell-Milton, F.; Vandekerckhove, A.; Gun'ko, Y. K., Chiral and Luminescent TiO₂ Nanoparticles. *Adv Opt Mater* **2017**, *5* (16), 1601000.

92. Jiang, S.; Chekini, M.; Qu, Z.-B.; Wang, Y.; Yeltik, A.; Liu, Y.; Kotlyar, A.; Zhang, T.; Li, B.; Demir, H. V.; Kotov, N. A., Chiral Ceramic Nanoparticles and Peptide Catalysis. *J Am Chem Soc* **2017**, *139* (39), 13701-13712.

93. Ben-Moshe, A.; Szwarcman, D.; Markovich, G., Size Dependence of Chiroptical Activity in Colloidal Quantum Dots. *ACS Nano* **2011**, *5* (11), 9034-9043.

94. Yeom, J.; Santos, U. S.; Chekini, M.; Cha, M.; de Moura, A. F.; Kotov, N. A., Chiro-magnetic nanoparticles and gels. *Science* **2018**, *359*, 309-314.

95. Ben-Moshe, A.; Maoz, B. M.; Govorov, A. O.; Markovich, G., Chirality and chiroptical effects in inorganic nanocrystal systems with plasmon and exciton resonances. *Chem Soc Rev* **2013**, *42* (16), 7028-7041.

96. Neuberger, A., Stereochemistry of Amino Acids. In *Advances in Protein Chemistry*, Anson, M. L.; Edsall, J. T., Eds. Academic Press Inc.: New York, 1948; Vol. 4th, pp 298-383.

97. Chen, S.-T.; Wu, S.-H.; Wang, K.-T., Rapid racemization of optically active amino acids by microwave oven-based heating treatment. *Int J Pept Prot Res* **1989**, 33 (1), 73-75.
98. Yamada, S.; Hongo, C.; Yoshioka, R.; Chibata, I., Method for the Racemization of Optically-Active Amino-Acids. *J Org Chem* **1983**, 48 (6), 843-846.
99. Rankin, D. W. H.; Mitzel, N. W.; Morrison, C. A., *Structural Methods in Molecular Inorganic Chemistry*. 1st ed.; John Wiley & Sons, Ltd: Sussex, United Kingdom, 2013.
100. Suryanarayana, C.; Norton, M. G., *X-Ray Diffraction: A Practical Approach*. Springer: Boston, 1998.
101. Hammond, C., *The Basics of Crystallography and Diffraction*. 4th ed.; Oxford University Press: Oxford, 2015.
102. Pecharsky, V. K.; Zavalij, P. Y., *Fundamentals of Powder Diffraction and Structural Characterization of Materials*. Springer Science+Business Media, Inc.: New York, 2003.
103. Glinnemann, J.; King, H. E., Jr.; Schulz, H.; Hahn, T.; la Placa, S. J.; Dacol, F., Crystal structures of the low-temperature quartz-type phases of SiO₂ and GeO₂ at elevated pressure. In *Zeitschrift für Kristallographie*, 1992; Vol. 198, p 177.
104. Le Page, Y.; Donnay, G., Refinement of the crystal structure of low-quartz. *Acta Crystallogr B* **1976**, 32 (8), 2456-2459.
105. Li, Y.; You, B. G.; Zhang, W. P.; Yin, M., Luminescent properties of β -Lu₂Si₂O₇:RE³⁺ (RE=Ce, Tb) nanoparticles by sol-gel method. *J Rare Earth* **2008**, 26 (3), 455-458.
106. Liu, X. L.; Fan, Y. Y.; Chen, S. W.; Gu, M.; Ni, C.; Liu, B.; Huang, S. M., Luminescence properties of Li-codoped Lu₂SiO₅:Ce thin-film phosphors prepared by sol-gel processing. *Mater Res Bull* **2013**, 48 (6), 2370-2374.
107. Boix, E.; Puddu, V.; Perry, C. C., Preparation of hexagonal GeO₂ particles with particle size and crystallinity controlled by peptides, silk and silk-peptide chimeras. *Dalton Trans* **2014**, 43 (44), 16902-16910.
108. Carlton, R. A., *Pharmaceutical Microscopy*. Springer Science+Business Media, LLC: New York, 2011.

109. Loveland, W. D.; Morrissey, D. J.; Seaborg, G. T., *Modern Nuclear Chemistry*. John Wiley & Sons, Inc.: Hoboken, NJ, 2006.
110. Williams, D. B.; Carter, C. B., *Transmission Electron Microscopy: A Textbook for Materials Science*. Springer Science+Business Media, LLC: New York, 2009.
111. Kalantar-zadeh, K.; Fry, B., *Characterization Techniques for Nanomaterials*. In *Nanotechnology-Enabled Sensors*, Springer Science+Business Media, LLC: New York, 2008.
112. Birks, J. B., *The Theory and Practice of Scintillation Counting*. Pergamon Press: Oxford, 1964; Vol. 27.
113. Bollinger, L.; Thomas, G. E., Measurement of Time Dependence of Scintillation Intensity by a Delayed-Coincidence Method. *Rev Sci Instrum* **1961**, 32 (9), 1044-+.
114. Hammes, G. G., Circular Dichroism, Optical Rotary Dispersion, and Fluorescence Polarization. In *Spectroscopy for the Biological Sciences*, John Wiley & Sons, Inc: New Jersey, 2005.
115. *Models 241 & 241 MC Polarimeters: Operator's Manual*. Perkin-Elmer: Norwalk, CT.
116. Stuart, B. H., Experimental Methods. In *Infrared Spectroscopy: Fundamentals and Applications*, John Wiley & Sons, Ltd: West Sussex, England, 2004.
117. Takacs, L., The historical development of mechanochemistry. *Chem Soc Rev* **2013**, 42 (18), 7649-7659.
118. Šepelák, V.; Duvel, A.; Wilkening, M.; Becker, K.-D.; Heitjans, P., Mechanochemical reactions and syntheses of oxides. *Chem Soc Rev* **2013**, 42 (18), 7507-7520.
119. James, S. L.; Adams, C. J.; Bolm, C.; Braga, D.; Collier, P.; Friscic, T.; Grepioni, F.; Harris, K. D. M.; Hyett, G.; Jones, W.; Krebs, A.; Mack, J.; Maini, L.; Orpen, A. G.; Parkin, I. P.; Shearouse, W. C.; Steed, J. W.; Waddell, D. C., Mechanochemistry: opportunities for new and cleaner synthesis. *Chem Soc Rev* **2012**, 41 (1), 413-447.
120. Balaz, P.; Achimovicova, M.; Balaz, M.; Billik, P.; Cherkezova-Zheleva, Z.; Criado, J. M.; Delogu, F.; Dutkova, E.; Gaffet, E.; Gotor, F. J.; Kumar, R.; Mitov, I.; Rojac, T.;

Senna, M.; Streletskii, A.; Wieczorek-Ciurowa, K., Hallmarks of mechanochemistry: from nanoparticles to technology. *Chem Soc Rev* **2013**, 42 (18), 7571-7637.

121. Burmeister, C. F.; Kwade, A., Process engineering with planetary ball mills. *Chem Soc Rev* **2013**, 42 (18), 7660-7667.

122. Burgio, N.; Iasonna, A.; Magini, M.; Padella, F., Mechanical alloying of the Fe-Zr system in different milling conditions. *J Phys Colloques* **1990**, 51 (C4), 265-271.

123. Burgio, N.; Iasonna, A.; Magini, M.; Martelli, S.; Padella, F., Mechanical Alloying of the Fe-Zr System - Correlation between Input Energy and End-Products. *Nuovo Cimento D* **1991**, 13 (4), 459-476.

124. Chattopadhyay, P. P.; Manna, I.; Talapatra, S.; Pabi, S. K., A mathematical analysis of milling mechanics in a planetary ball mill. *Mater Chem Phys* **2001**, 68 (1), 85-94.

125. Padella, F.; Paradiso, E.; Burgio, N.; Magini, M.; Martelli, S.; Guo, W.; Iasonna, A., Mechanical Alloying of the Pd-Si System in Controlled Conditions of Energy-Transfer. *J Less-Common Met* **1991**, 175 (1), 79-90.

126. Iasonna, A.; Magini, M., Power measurements during mechanical milling. An experimental way to investigate the energy transfer phenomena. *Acta Mater* **1996**, 44 (3), 1109-1117.

127. Rojac, T.; Kosec, A.; Malic, B.; Holc, J., The application of a milling map in the mechanochemical synthesis of ceramic oxides. *J Eur Ceram Soc* **2006**, 26 (16), 3711-3716.

128. Kozma, G.; Puskas, R.; Papp, I. Z.; Belteky, P.; Konya, Z.; Kukovecz, A., Experimental validation of the Burgio-Rojac model of planetary ball milling by the length control of multiwall carbon nanotubes. *Carbon* **2016**, 105, 615-621.

129. Rojac, T.; Kosec, M.; Malic, B.; Holc, J., Mechanochemical synthesis of NaNbO₃. *Mater Res Bull* **2005**, 40 (2), 341-345.

130. Rojac, T.; Masson, O.; Guinebretiere, R.; Kosec, M.; Malic, B.; Holc, J., A study of the mechanochemical synthesis of NaNbO₃. *J Eur Ceram Soc* **2007**, 27 (5), 2265-2271.

131. Singh, S.; Godkhindi, M. M.; Krishnarao, R. V.; Murty, B. S., Effect of milling energy on mechanical activation of (Mo+Si₃N₄) powders during the synthesis of Si₃N₄–MoSi₂ in situ composites. *J Eur Ceram Soc* **2009**, 29 (10), 2069-2077.
132. Wu, C. X.; Zhu, S. G.; Ma, J.; Zhang, M. L., Synthesis and formation mechanisms of nanocomposite WC–MgO powders by high-energy reactive milling. *J Alloy Compd* **2009**, 478 (1), 615-619.
133. Rojac, T.; Kosec, M.; Połomska, M.; Hilczer, B.; Šegedin, P.; Bencan, A., Mechanochemical reaction in the K₂CO₃–Nb₂O₅ system. *J Eur Ceram Soc* **2009**, 29 (14), 2999-3006.
134. Rojac, T.; Kosec, M.; Malič, B.; Holc, J., The Mechanochemical Synthesis of NaNbO₃ Using Different Ball-Impact Energies. *J Am Ceram Soc* **2008**, 91 (5), 1559-1565.
135. McDonald, K. A.; McDonald, M. R.; Bailey, M. N.; Schweitzer, G. K., Parametric study on the production of the GAGG:Ce and LSO:Ce multicomponent oxide scintillator materials through use of a planetary ball mill. *Dalton Trans* **2018**, 47, 13190-13203.
136. Bowmaker, G. A., Solvent-assisted mechanochemistry. *Chem Commun* **2013**, 49 (4), 334-348.
137. Braga, D.; Maini, L.; Grepioni, F., Mechanochemical preparation of co-crystals. *Chem Soc Rev* **2013**, 42 (18), 7638-7648.
138. Hernández, J. G.; Bolm, C., Altering Product Selectivity by Mechanochemistry. *J Org Chem* **2017**, 82 (8), 4007-4019.
139. Karayannis, V. G., Microwave sintering of ceramic materials. *IOP Conf Ser-Mat Sci* **2016**, 161 (1), 012068.
140. Das, S.; Mukhopadhyay, A. K.; Datta, S.; Basu, D., Prospects of microwave processing: An overview. *B Mater Sci* **2009**, 32 (1), 1-13.
141. Kamenskikh, I. A.; Mikhailin, V. V.; Munro, I. H.; Petrovykh, D. Y.; Shaw, D. A.; Studenikin, P. A.; Vasilev, A. N.; Zagumennyi, I. A.; Zavartsev, Y. D., LSO-Ce fluorescence spectra and kinetics for UV, VUV and X-ray excitation. *Radiat Eff Defect S* **1995**, 135 (1-4), 889-894.

142. Suzuki, H.; Tombrello, T. A.; Melcher, C. L.; Schweitzer, J. S., UV and gamma-ray excited luminescence of cerium-doped rare-earth oxyorthosilicates. *Nucl Instr Meth Phys Res A* **1992**, 320 (1), 263-272.
143. Varma, A.; Mukasyan, A. S.; Rogachev, A. S.; Manukyan, K. V., Solution Combustion Synthesis of Nanoscale Materials. *Chem Rev* **2016**, 116 (23), 14493-14586.
144. Aruna, S. T., *Solution combustion synthesis-an overview*. 2010; p 206-221.
145. Patil, K. C.; Aruna, S. T.; Mimani, T., Combustion synthesis: an update. *Current Opinion in Solid State and Materials Science* **2002**, 6 (6), 507-512.
146. Alves, A.; Bergmann, C.; Amorim Berutti, F., *Combustion Synthesis*. 2013; p 11-22.
147. Kingsley, J. J.; Patil, K. C., A Novel Combustion Process for the Synthesis of Fine Particle Alpha-Alumina and Related Oxide Materials. *Mater Lett* **1988**, 6 (11-12), 427-432.
148. Aruna, S. T.; Rajam, K. S., Mixture of fuels approach for the solution combustion synthesis of Al₂O₃–ZrO₂ nanocomposite. *Mater Res Bull* **2004**, 39 (2), 157-167.
149. Banerjee, S.; Devi, P. S., Sinter-active nanocrystalline CeO₂ powder prepared by a mixed fuel process: Effect of fuel on particle agglomeration. *J Nanopart Res* **2007**, 9 (6), 1097-1107.
150. Aruna, S. T.; Kini, N.; Rajam, K. S., *Solution Combustion Synthesis of CeO₂–CeAlO₃ Nano-Composites by Mixture-of-Fuels Approach*. 2009; Vol. 44, p 728-733.
151. Palneedi, H.; Mangam, V.; Das, S.; Das, K., Effect of fuel-to-nitrate ratio on the powder characteristics of nanosized CeO₂ synthesized by mixed fuel combustion method. *J Alloy Compd* **2011**, 509 (41), 9912-9918.
152. Tahmasebi, K.; Paydar, M. H., The effect of starch addition on solution combustion synthesis of Al₂O₃–ZrO₂ nanocomposite powder using urea as fuel. *Mater Chem Phys* **2008**, 109 (1), 156-163.
153. Erri, P.; Pranda, P.; Varma, A., Oxidizer–Fuel Interactions in Aqueous Combustion Synthesis. 1. Iron(III) Nitrate–Model Fuels. *Industrial & Engineering Chemistry Research* **2004**, 43 (12), 3092-3096.

154. Melcher, C. L.; Schweitzer, J. S., Cerium-Doped Lutetium Oxyorthosilicate - a Fast, Efficient New Scintillator. *IEEE T Nucl Sci* **1992**, 39 (4), 502-505.
155. Alexander, L.; Klug, H. P., Determination of Crystallite Size with the X-Ray Spectrometer. *J Appl Phys* **1950**, 21 (2), 137-142.
156. Blasse, G., Luminescence of inorganic solids: From isolated centres to concentrated systems. *Prog Solid State Ch* **1988**, 18 (2), 79-171.
157. Li, J.; Pan, Y.; Qiu, F.; Wu, Y.; Guo, J., Nanostructured Nd:YAG powders via gel combustion: The influence of citrate-to-nitrate ratio. *Ceram Int* **2008**, 34 (1), 141-149.
158. Roy, S.; Sigmund, W.; Aldinger, F., Nanostructured Yttria Powders Via Gel Combustion. *J Mater Res* **2011**, 14 (4), 1524-1531.
159. Li, J.; Wu, Y.; Pan, Y.; Liu, W.; Zhu, Y.; Guo, J., Agglomeration of α -Al₂O₃ powders prepared by gel combustion. *Ceram Int* **2008**, 34 (6), 1539-1542.
160. Xia, G.; Zhou, S.; Zhang, J.; Xu, J., Structural and optical properties of YAG:Ce³⁺ phosphors by sol–gel combustion method. *J Cryst Growth* **2005**, 279 (3), 357-362.
161. Lignie, A.; Granier, D.; Armand, P.; Haines, J.; Papet, P., Modulation of quartz-like GeO₂ structure by Si substitution: an X-ray diffraction study of Ge_{1-x}Si_xO₂ (0 ≤ x < 0.2) flux-grown single crystals. *J Appl Crystallogr* **2012**, 45, 272-278.
162. Jorgensen, J. D., Compression mechanisms in α -quartz structures – SiO₂ and GeO₂. *J Appl Phys* **1978**, 49 (11), 5473-5478.
163. Yamanaka, T.; Ogata, K., Structure Refinement of GeO₂ Polymorphs at High Pressures and Temperatures by Energy-Dispersive Spectra of Powder Diffraction *J Appl Crystallogr* **1991**, 24, 111-118.
164. Byrappa, K.; Yoshimura, M., *Handbook of Hydrothermal Technology*. 2nd ed.; Elsevier Science: Oxford, UK, 2013.
165. Glushkova, T. M.; Kiselev, D. F.; Firsova, M. M.; Styrkova, A. P., Optical rotatory power of trigonal quartz and germanium dioxide single crystals. *Proc SPIE* **1997**, 3094, 175-177.
166. Kawai, T.; Usui, Y.; Kon-No, K., Synthesis and growth mechanism of GeO₂ particles in AOT reversed micelles. *Colloid Surface A* **1999**, 149 (1), 39-47.

167. Wu, H. P.; Liu, J. F.; Ge, M. Y.; Niu, L.; Zeng, Y. W.; Wang, Y. W.; Lv, G. L.; Wang, L. N.; Zhang, G. Q.; Jiang, J. Z., Preparation of Monodisperse GeO₂ Nanocubes in a Reverse Micelle System. *Chem Mater* **2006**, *18* (7), 1817-1820.
168. Chen, X.; Cai, Q.; Zhang, J.; Chen, Z.; Wang, W.; Wu, Z.; Wu, Z., Synthesis and growth of germanium oxide nanoparticles in AOT reversed micelle. *Mater Lett* **2007**, *61* (2), 535-537.
169. Ramana, C. V.; Carbajal-Franco, G.; Vemuri, R. S.; Troitskaia, I. B.; Gromilov, S. A.; Atuchin, V. V., Optical properties and thermal stability of germanium oxide (GeO₂) nanocrystals with α -quartz structure. *Mater Sci Eng B-Adv* **2010**, *174* (1), 279-284.
170. Javadi, M.; Yang, Z.; Veinot, J. G. C., Surfactant-free synthesis of GeO₂ nanocrystals with controlled morphologies. *Chem Commun* **2014**, *50* (46), 6101-6104.
171. Esmaeili-Bafghi-Karimabad, A.; Nejati-Moghadam, L.; Gholamrezaei, S.; Salavati-Niasari, M., Photoluminescence, photocatalytic and solar cell behaviors of as-prepared germania nanoparticles from a sol-gel route. *J Mater Sci- Mater Electron* **2015**, *26* (8), 5822-5832.
172. Nejaty-Moghadam, L.; Esmaeili-Bafghi-Karimabad, A.; Gholamrezaei, S.; Hamadanian, M.; Salavati-Niasari, M., Facile synthesis of GeO₂ nanostructures and measurement of photocatalytic, photovoltaic and photoluminescence properties. *J Mater Sci- Mater Electron* **2015**, *26*, 6386-6394.
173. Atuchin, V. V.; Gavrilova, T. A.; Gromilov, S. A.; Kostrovsky, V. G.; Pokrovsky, L. D.; Troitskaia, I. B.; Vemuri, R. S.; Carbajal-Franco, G.; Ramana, C. V., Low-Temperature Chemical Synthesis and Microstructure Analysis of GeO₂ Crystals with α -Quartz Structure. *Cryst Growth Des* **2009**, *9* (4), 1829-1832.
174. Davis, T. M.; Snyder, M. A.; Tsapatsis, M., Germania Nanoparticles and Nanocrystals at Room Temperature in Water and Aqueous Lysine Sols. *Langmuir* **2007**, *23* (25), 12469-12472.
175. Mackenzie, F. T.; Gees, R., Quartz: Synthesis at Earth-Surface Conditions. *Science* **1971**, *173* (3996), 533-535.

176. Huang, W.-L., The nucleation and growth of polycrystalline quartz : Pressure effect from 0.05 to 3 GPa. *Eur J Mineral* **2003**, 15 (5), 843-853.
177. Bertone, J. F.; Cizeron, J.; Wahi, R. K.; Bosworth, J. K.; Colvin, V. L., Hydrothermal Synthesis of Quartz Nanocrystals. *Nano Letters* **2003**, 3 (5), 655-659.
178. Li, L.-J.; Fang, J.-N.; Lo, H.-J.; Song, S.-R.; Chen, Y.-L.; Chen, H.-F.; Lin, I.-C., A Preliminary Study on the Synthesis of Nano-Sized Quartz. *J Chin Chem Soc* **2003**, 50 (3A), 395-398.
179. Bansal, V.; Ahmad, A.; Sastry, M., Fungus-Mediated Biotransformation of Amorphous Silica in Rice Husk to Nanocrystalline Silica. *J Am Chem Soc* **2006**, 128 (43), 14059-14066.
180. Jiang, X.; Jiang, Y.-B.; Brinker, C. J., Hydrothermal synthesis of monodisperse single-crystalline alpha-quartz nanospheres. *Chem Commun* **2011**, 47 (26), 7524-7526.
181. Sochalski-Kolbus, L. M.; Wang, H.-W.; Rondinone, A. J.; Anovitz, L. M.; Wesolowski, D. J.; Whitfield, P. S., Solvothermal Synthesis and Surface Chemistry To Control the Size and Morphology of Nanoquartz. *Cryst Growth Des* **2015**, 15 (11), 5327-5331.
182. Hargreaves, N. J. Crystallisation of nano-quartz and nano-graphite from microemulsions under ambient conditions. Ph.D. Dissertation, Durham University, Durham, UK, 2016.
183. Amabilino, D. B., *Chirality at the Nanoscale: Nanoparticles, Surfaces, Materials and More*. Wiley: Germany, 2009.
184. Varga, K.; Tannir, S.; Haynie, B. E.; Leonard, B. M.; Dzyuba, S. V.; Kubelka, J.; Balaz, M., CdSe Quantum Dots Functionalized with Chiral, Thiol-Free Carboxylic Acids: Unraveling Structural Requirements for Ligand-Induced Chirality. *ACS Nano* **2017**, 11 (10), 9846-9853.
185. Rimola, A.; Costa, D.; Sodupe, M.; Lambert, J.-F.; Ugliengo, P., Silica Surface Features and Their Role in the Adsorption of Biomolecules: Computational Modeling and Experiments. *Chem Rev* **2013**, 113 (6), 4216-4313.

186. Rimola, A.; Sodupe, M.; Ugliengo, P., Affinity Scale for the Interaction of Amino Acids with Silica Surfaces. *J Phys Chem C* **2009**, *113* (14), 5741-5750.
187. Churchill, H.; Teng, H.; Hazen, R. M., Correlation of pH-dependent surface interaction forces to amino acid adsorption: Implications for the origin of life. *Am Mineral* **2004**, *89* (7), 1048-1055.
188. Vlasova, N. N.; Golovkova, L. P., The adsorption of amino acids on the surface of highly dispersed silica. *Colloid J+* **2004**, *66* (6), 657-662.
189. Deringer, V. L.; Dronskowski, R., Pauling's third rule beyond the bulk: chemical bonding at quartz-type GeO₂ surfaces. *Chem Sci* **2014**, *5*, 894-903.
190. Smallwood, I. M., *Handbook of Organic Solvent Properties*. Arnold: London, 1996.
191. Kuno, J.; Imamura, Y.; Katouda, M.; Tashiro, M.; Kawai, T.; Nakashima, T., Inversion of Optical Activity in the Synthesis of Mercury Sulfide Nanoparticles: Role of Ligand Coordination. *Angew Chem Int Edit* **2018**, *57* (37), 12022-12026.
192. Neouze, M.-A.; Schubert, U., Surface Modification and Functionalization of Metal and Metal Oxide Nanoparticles by Organic Ligands. *Monatshe Chem* **2008**, *139* (3), 183-195.
193. Halasyamani, P. S.; Poeppelmeier, K. R., Noncentrosymmetric Oxides. *Chem Mater* **1998**, *10* (10), 2753-2769.

Vita

Melissa (Lassig) Bailey was born in Snellville, Georgia and raised in Lawrenceville, Georgia. She graduated from North Forsyth High School in May 2008. After graduating, she attended the University of Georgia. In May 2012, she graduated cum laude with a Bachelor of Science degree in chemistry with ACS certification. While at the University of Georgia, Melissa worked as an undergraduate research assistant with Dr. Tina Salguero, studying the production and characterization of suspended nanosheets. She continued this research until December 2012. From January to July 2013, Melissa worked as a quality control analyst for Alkermes PLC.

In August 2013, Melissa enrolled at the University of Tennessee-Knoxville to earn her doctoral degree in inorganic chemistry, where she began research with Dr. George K. Schweitzer. Her work involved the synthesis of cerium-doped lutetium oxyorthosilicate powders through mechanochemical and combustion methods as well as the synthesis of α -quartz nanoparticles and optically-active β -GeO₂ nanoparticles through hydrolysis in the presence of chiral templating agents. Melissa received her Doctor of Philosophy in chemistry in August 2019.