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Physical vapor deposition and defect engineering of europium doped lutetium oxide

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Dissertation

PHYSICAL VAPOR DEPOSITION AND DEFECT ENGINEERING
OF EUROPIUM DOPED LUTETIUM OXIDE

by

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DEDICATION

To my parents, Karen and Michael,
my brother Kevin, my sister Janae, my nephew Owen,
and most of all, my fiancée Elizabeth,
for all the love and support I could have ever wanted.
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ABSTRACT

Lutetium oxide doped with europium (Lu$_2$O$_3$:Eu$^{3+}$) has been established as a promising scintillator material with properties that are advantageous when compared to other scintillators such as cesium iodide doped with thallium (CsI:Tl). Due to high X-ray attenuation characteristics, Lu$_2$O$_3$:Eu$^{3+}$ is an attractive material for use in high resolution digital X-ray imaging systems. However, challenges still remain especially in the area of light output for Lu$_2$O$_3$:Eu$^{3+}$. Processing by physical vapor deposition (PVD) and manipulation of oxygen defect structure was explored in order to better understand the effect on the scintillation phenomena.

PVD results were obtained using high temperature radio frequency sputtering (RF) and pulsed laser deposition (PLD) systems. Characterization of light output by radial noise power spectrum density measurements revealed that high temperature RF films were superior to those obtained using PLD. Optimization of sputtered films based on light output over a range of process parameters, namely temperature, power, pressure, and substrate orientation was investigated. Parameterization of deposition conditions revealed that: 75 watts, 10.00 mtorr, and 800°C were optimum conditions for Lu$_2$O$_3$:Eu$^{3+}$ films.
Manipulation of anionic defect structure in similar material systems has been shown to improve scintillation response. Similar methods for Lu₂O₃:Eu³⁺ were explored for hot pressed samples of Lu₂O₃:Eu³⁺; via controlled atmosphere annealing, and use of extrinsic co-doping with calcium. The controlled atmosphere experiments established the importance of oxygen defect structure within Lu₂O₃:Eu³⁺ and showed that fully oxidized samples were preferred for light output. The second method utilized co-doping by the addition of calcium which induced oxygen vacancies and by Frenkel equilibrium changed the oxygen interstitial population within the Lu₂O₃:Eu³⁺ structure. The addition of calcium was investigated and revealed that scintillation was improved with a maximum response occurring at 340ppm of calcium. PVD optimization and co-doping experimental results provided a template for the use of calcium co-doped Lu₂O₃:Eu³⁺ targets for deposition of films. Preliminary deposition results were promising and revealed that small additions (around 550 ppm) of calcium resulted in better activator efficiency. Calcium co-doped films have a predicted increase in the light yield greater than 14% when compared to analogous un-doped Lu₂O₃:Eu³⁺ films at 60keV.
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Chapter 1

1. Introduction

1.1. History of X-rays

X-rays were discovered in the fall of 1895 by Professor Wilhelm Roentgen. He was conducting a cathode-ray tube experiment when he noticed the faint green glow of a barium platinocyanide material some meters away in his lab. Exploring the new phenomena he moved the material closer to the enclosed tube and noticed that passing different materials between the paint and the tube caused a shadowing effect. Excited by the prospect of his discovery he had his trusting wife pose for a picture and her hand was immortalized as the first radiograph in human history (Figure 1-1) [1].

The next week, he repeated this feat at a public demonstration in which he X-rayed the hand of the hairmen of the anatomy department. Dr. Roentgen gave these previously unknown rays the name “X”, which is the popular symbol from algebra synonymous with the unknown. Soon after their discovery of X-rays, radiographs such as these would become an indispensable tool for scientists and medical clinicians everywhere.

Today the application of X-rays as diagnostic and sensing devices are seen all around us: from the ubiquitous medical techniques of CT and mammography, to the
exploration of biological and material structures using X-ray crystallography, and the exploration of the cosmos using X-ray telescopes. X-ray technology has truly been an indispensable tool for science in the last century, allowing us to deduce the interworking of our materials and biology as well as the expansive history of our own universe.

In order to properly utilize X-rays, it is necessary to produce a detector that efficiently captures the radiation and then changes these high energy photons into a more manageable signal which can easily be used for imaging. Scintillators are a class of useful radiation detection materials that fluoresce upon interaction with X-rays and other ionizing radiation and are the focus of this research.

1.2. X-ray Interactions

Fundamentally the reaction of light or electromagnetic radiation with matter occurs when light interacts with the electrons of the material. Such interaction can excite electrons and induce a host of phenomena, which are used in many different scientific pursuits. The excitation of a material by an X-ray can have different kinds of interaction within the matter. In general, the total attenuation of X-rays by a material is the sum of all interactions between a material and photons. The attenuation is governed exponentially by Beer-Lambert law [2]:

\[ I = I_0 e^{-\mu x} \]  

(1.1)

where I and I_0 are the intensity of photons transmitted and incident respectively, \( \mu \) is the linear attenuation coefficient of the material, and x is the depth or thickness of the material which the photon is interacting. An attenuation coefficient of a material is a composite number, which consists of the attenuation primarily associated with different
matter and photon interactions. The primary interaction in the X-ray energy regimes includes: coherent or Rayleigh scattering, Photoelectric Effect, Compton Scattering, and Pair Production.

Rayleigh scattering occurs when low energy X-ray photons interact with individual atoms displacing the atom and upon recoil, the atom releases an X-ray of equivalent energy and wavelength but with a different direction (scattering) [3]. Rayleigh scattering occurs mostly in the forward direction with no loss of incident X-ray energy it does not strongly effect attenuation.

At low and moderate energy levels (10–100 keV) the photoelectric interaction dominates X-ray interactions. At these energies, the incoming photon has enough energy to interact with an inner shell electron and eject the electron to the conduction band of the material. The energy of the photon is completely consumed and the emitted photoelectron has the energy of the impinging X-ray photon minus the binding energy of the electron. This high-energy electron may now interact with other electrons in the material leading to secondary ionization. The ejected electron leaves behind a hole that is filled by a higher energy electron in an outer shell of the affected atom. This recombination of the hole with a higher energy electron produces a photon emission of its own. The created photon has a very specific energy, which is due to the discrete nature of the electron energy levels within the atom. The characteristic nature of this emission allows for identification of individual atomic species by the electron transitions and gave rise to most modern spectroscopy. The probability of photoelectric interaction can be understood through a simplified power law relationship which scales with the effective atomic number of the
material shown by the following relation [4]:

$$\tau \propto \frac{Z_{\text{eff}}^n}{E^3}$$

(1.2)

where $\tau$ is the probability of photoelectric interaction and $Z_{\text{eff}}$ is the material's effective atomic number and $E = h\nu$ is the energy of the impinging photons. Generally, $n$ is assigned an empirical value between 3 and 4. It is apparent from this relationship that as the effective atomic number or $(Z_{\text{eff}})$ increases the probability of photoelectric interaction is greatly increased and will be an important relation to remember when thinking about scintillation detectors.

At intermediate excitation energies (100 keV–10 MeV) Compton scattering becomes more prevalent [5]. A Compton interaction occurs when a photon collides with an outer shell electron transferring some of its energy to the electron, which results in its path being altered or scattered. The prevalence of Compton scattering is correlated to the density of loosely bound electrons in the material, which are able to interact in this way. Due to this, Compton scattering does not vary much and only weakly decreases as photon energies increase. However, as the energy of incoming photons increase the relative ratio of Compton to photoelectric interactions increases. For detector systems, it is advantageous to avoid energies with high Compton scattering as this phenomenon is a source of spatial noise for X-ray and matter interactions due to the scattered nature of the interaction.

Finally, at high energies (>1.02 MeV) Pair production becomes significant [5]. In this phenomenon, the impinging X-ray interacts with the nucleus of the atom causing the
creation of an electron and a positron. The positron is an anti-particle and when it encounters an electron the two annihilate. The annihilation of the positron and electron create two photons with 511 keV of energy, which radiate in opposite directions. This interaction is important in medical imaging techniques such as PET scans or gamma ray detection (~tens of MeV), which utilize high energy ionizing radiation.

1.3. X-ray Detectors

The function of an X-ray detector is to utilize the physical reactions of matter with X-ray photons and to convert the X-rays into a usable signal. Generally, this usable signal takes the form of electrons in the case of photoconductors and noble gas detectors or lower energy photons in photostimulable phosphors and scintillators. These forms of energy can be easily measured and allow for the digitalization of information and subsequent image processing. In a sense, detectors modulate high-energy particles and photons to lower energy particles and photons which are more easily measured with modern electronics.

Photoconduction systems utilize a semiconductor material such as amorphous silicon or selenium in which the impinging X-rays excite electrons into the conduction band of the material and these electrons cause a variance in the conductivity, which is proportional to the absorbed X-ray energy.

Similar to photoconduction, noble gas detectors utilize incoming X-ray to ionize gases within the detector to form positive ions and electrons. The electrons are captured using a biased electrode and the measurement of ionized electrons in the detector element provide the imaging signal.
Photostimulable phosphors rely on impinging X-rays to excite core electrons to the conduction band (photoelectric interaction). These electrons are effectively ‘trapped’ in electron energy levels at special impurity complexes located below the conduction band of the material. After exposure to X-rays is complete these screens are developed using a laser, which liberates the trapped electrons. The liberated electrons go through a relaxation process at an activation center, which produces visible light. The light that is generated from the photostimulable phosphor is subsequently captured by a photosensitive element and used for imaging.

Similarly, scintillator based systems utilize a doped wide band gap material in which X-rays excite electrons from the valance band to the conduction band of the material (photoelectric interaction). These conduction band electrons are captured at impurity energy levels where they are rapidly de-excited to a lower energy ground state. This de-excitation emits a characteristic spectrum of photons, which is unique to each material system.

Scintillation detector architecture requires that the scintillator is optically coupled to a photodetector. The photodetector in this arrangement can be photomultiplier tubes (PMT), photodiodes, charged coupled devices (CCD), etc. The selection of the photodetector is multifaceted and depends on many design elements but it is important that the characteristic spectrum produced by the scintillator is well matched to the most sensitive absorption wavelengths of the photodetector.
1.3.1. High Resolution X-ray Detection

New high-resolution X-ray detection systems utilize thin scintillator sections coupled to light microscope objectives which focus the emitted light from the scintillator onto a photodetector (Figure 1-2). Similar to standard light microscopy techniques there is a finite depth of field that limits the ability of the system to bring all points of light into focus. This limitation can be especially difficult in modern scintillation devices, which have thicknesses into the hundreds of microns. These high-resolution systems require a scintillator with excellent X-ray attenuation in order to utilize as much of the incoming X-rays as possible. This is especially important because of reduced light yield inherent for scintillators with small thicknesses.

Based on the schematic Figure 1-2 from Martin and Koch [3], it has been suggested that as detector thickness increases the resolution of the system decreases and is given by the empirical function [3], [6].

\[
R = \left[ \left( \frac{p}{NA} \right)^2 + (qzNA)^2 \right]^{1/2}
\]  (1.3)

With fitting parameters p=0.18 and q=0.075 and z accounting for the detector thickness and NA the numerical aperture of the system. The equations two terms correspond to diffraction limited first term and the scintillator thickness dependent term. The resolutions of such a system are modeled in Figure 1-3 and it can be seen that detector thicknesses below 10 micrometers allow for high resolutions across all numerical apertures.
Figure 1.2 Cross sectional view of a simplified detector section highlighting how the thickness of the detector affects the ultimate resolution of the detector [6].

Figure 1.3 Calculated resolution of high resolution X-ray systems for different scintillation layer thicknesses [6].

1.4. Scintillation

The scintillation phenomenon has three basic steps which occur in order to produce a photonic event: the creation of electron-hole pairs, the transport of excited
electrons and holes to luminescent centers, and the recombination of electron-hole pairs to create photons. Each process has factors that affect the efficiency and these factors should be taken into account in order to produce efficient scintillators. Due to the immense amount of interactions and factors present for any one scintillation event, it is necessary to introduce a simplified equation for light yield which is expressed in an equation given by Lempicki and Wojtowicz [7]:

\[ Y = N_{eh}SQ \]  

where \( Y \) is the light yield, \( N_{eh} \) number of electron-hole pairs created, \( S \) is the transfer efficiency of electrons and holes to radiative centers, and \( Q \) the efficiency of the photonic relaxation (photon emission) at the luminescent centers.

In this process, the creation of electron-hole pairs (\( N_{eh} \)) may be estimated in an ideal system as a ratio of the impinging photon energy and the energy needed to create and electron-hole pair. Typically, the energy required to accomplish this type of interaction has been accepted as multiples of the band gap of the material \( (2E_g - 3E_g) \). Therefore, as the band gap increases so does the energy needed to create electron-hole pairs, which in principle would reduce the amount of available electron-hole pairs. The relation can be seen in the equation below:

\[ N_{eh} = \frac{E_{in}}{E_{eh}} = \frac{E_{in}}{2E_g} \]  

where \( N_{eh} \) is the number of electron hole pairs created and \( E_{in}, E_{eh}, \) and \( E_g \) are the energies of incident photons, the creation of electron hole pairs, and band gap respectively.
Transfer efficiency (S) is the ability of a charge carrier to migrate to a luminescent center. During transit to luminescent centers, electrons and holes interact with many other parts of the lattice such as other subatomic particles, lattice defects, trapping centers, etc. These interactions can both aid or compete with the luminescent centers and affect the probability that the electrons or holes are able to reach the luminescent center. This necessitates the careful production of scintillation elements, which are pure and without unintended defect species. However, with careful planning, the addition of a fractional amount of a defect can in fact aid the scintillation phenomenon and can be an important tool for use in crystal engineering of advanced scintillators.

Finally, the probability of radiative transition (Q) at the luminescent center is also in competition with non-radiative transition processes such as electron-phonon relaxation, charge transfer, concentration quenching, and reabsorption. It is apparent that despite the idealized example presented there are many areas in which the scintillation phenomena can become rather inefficient and understanding these regimes is important when engineering novel scintillation systems.

Ideally, a scintillator for most applications would have the appropriate combination of the high probability of photoelectric interaction and high attenuation coupled with high light yield and fast decay times with no afterglow. Striving to improve these areas of a scintillation detector is challenging and involves careful selection of materials and processing of the materials. These goals are not without challenges and altering one of the properties can often have deleterious effects on one another.
The current state of the art technology for general scintillation detectors utilize cesium iodide doped with thallium (CsI:Tl) films. The films are vapor deposited onto silicon photodiodes for signal transduction. These coatings have a specific columnar morphology, highlighted in Figure 1-4, that allows for the reduction of the amount of light spreading compared to single crystal scintillators. Normally light produced in a single crystal detector can radiate unimpeded but due to the needle like morphology of the deposition microstructure, each needle acts as a so called ‘light pipe’ by means of total internal reflection [8]. This process is analogous to how fiber optics work in that a difference in index of refraction allows for most of the light to be channeled along the length of a material without escaping from the edges. The increase in resolution coupled with the particularly high light output of CsI:Tl makes this system the current bench mark for digital imaging systems providing very good raw scintillation due to the high efficiency with a good spatial resolution for most imaging modalities.

Besides CsI:Tl there are several important industrial scintillator materials which utilize impurity doping such rare earth elements such as trivalent Ce³⁺, Pr³⁺, or Eu³⁺ in rare earth oxides, halides, and aluminates. Properties of some these materials are highlighted in Table 1-1.
Table 1-1 Summary of selected scintillators and their properties [9]–[12]

<table>
<thead>
<tr>
<th>Material</th>
<th>Density (g/cc)</th>
<th>Light output (Photon/MeV $\times 10^3$)</th>
<th>Decay time (ns)</th>
<th>Emission Wavelength Maximum (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaF$_2$</td>
<td>4.88</td>
<td>1.5</td>
<td>0.6–0.8</td>
<td>550</td>
</tr>
<tr>
<td>Bi$_4$Ge$<em>3$O$</em>{12}$</td>
<td>7.1</td>
<td>8.6</td>
<td>300</td>
<td>480</td>
</tr>
<tr>
<td>CdWO$_4$</td>
<td>7.9</td>
<td>20</td>
<td>5000</td>
<td>495</td>
</tr>
<tr>
<td>CsI:Tl</td>
<td>4.51</td>
<td>66</td>
<td>800</td>
<td>550</td>
</tr>
<tr>
<td>Gd$_2$SiO$_5$:Ce</td>
<td>6.7</td>
<td>8</td>
<td>60</td>
<td>420</td>
</tr>
<tr>
<td>K$_2$LaI$_3$:Ce</td>
<td>4.4</td>
<td>55</td>
<td>24</td>
<td>420</td>
</tr>
<tr>
<td>LaBr$_3$:Ce</td>
<td>5.3</td>
<td>6.1</td>
<td>35</td>
<td>358</td>
</tr>
<tr>
<td>LuAlO$_3$:Ce</td>
<td>8.34</td>
<td>12</td>
<td>18</td>
<td>365</td>
</tr>
<tr>
<td>Lu$_3$Al$<em>5$O$</em>{12}$:Ce</td>
<td>6.67</td>
<td>12.5</td>
<td>55</td>
<td>530</td>
</tr>
<tr>
<td>Lu$_2$SiO$_5$:Ce</td>
<td>7.4</td>
<td>26</td>
<td>30</td>
<td>390</td>
</tr>
<tr>
<td>NaI:Tl</td>
<td>3.67</td>
<td>41</td>
<td>230</td>
<td>410</td>
</tr>
<tr>
<td>PbWO$_4$</td>
<td>8.28</td>
<td>0.3</td>
<td>2–3</td>
<td>410</td>
</tr>
<tr>
<td>YAlO$_3$:Ce</td>
<td>5.6</td>
<td>21</td>
<td>20–30</td>
<td>360</td>
</tr>
<tr>
<td>Y$_3$Al$<em>5$O$</em>{12}$:Ce</td>
<td>4.56</td>
<td>24</td>
<td>90–120</td>
<td>550</td>
</tr>
<tr>
<td>Lu$_2$O$_3$:Eu</td>
<td>9.42</td>
<td>30–90</td>
<td>$10^6$</td>
<td>611</td>
</tr>
</tbody>
</table>

1.5. Manufacture of Scintillators

The production of scintillators has traditionally employed single crystal methods such as the Czochralski or Bridgman-Stockbarger, which utilize a seed material slowly pulled from a melt to induce single crystal solidification. These techniques are especially useful for lower melting point materials such as CsI:Tl and NaI:Tl (621°C and 661°C) and produce transparent single crystal scintillators with high light yields [13]. Once these single crystal sensors are created they must be machined and pixelated in an effort to reduce possible light spreading which reduces the resolution of the detector. The pixilation requires a very precise and time consuming laser ablation process.

For higher melting temperature scintillators such as rare earth oxides, aluminates, and orthosilicates single crystal growth is impractical. Traditional processing for these
high temperature ceramics rely on a multi-step process which includes: production of nanopowders, densification of polycrystalline solid, machine the piece to size, polishing, and pixilation by laser ablation which is analogous to the single crystal processing. Each of the steps mentioned has their own technical challenges and elimination of any of the steps would be very advantageous in the production of scintillation devices.

Due to the restrictive multi-step processes highlighted above, researchers have been interested in using novel vapor deposition techniques to create new scintillation devices. Vapor deposition is an attractive option for use in scintillators due to the flexibility of microstructural control as well as detectors which can be made to thickness without any extra processing steps [14]. An example of the favorable microstructure is highlighted in Figure 1-4 in which CsI:TI is deposited in long columnar grains, which are beneficial for shuttling scintillation light toward the detector. These long columnar microstructures allow for the elimination of the pixilation processing steps, which are necessary for the production of traditional scintillators by single crystal or polycrystalline methods.

Properties in the order of importance for general scintillation detection for medical imaging as established by Nikl [9] and are:

a) Light yield
b) X-ray stopping power
c) Scintillation response – Decay Time
d) Spectral matching between scintillation and photodetector
e) Chemical stability
f) Radiation hardness

g) Linear light response with incident X-ray energy – energy resolution (especially important for higher energy X-ray imaging)

h) Cost of production

These properties were used as a guideline for the optimization efforts of our novel vapor deposited scintillator system of Lu$_2$O$_3$:Eu$^{3+}$. 
Chapter 2

2. Lutetium Oxide doped with Europium (Lu₂O₃:Eu³⁺)

The discovery of novel high density and high atomic number scintillation materials such as lutetium oxide doped with europium (Lu₂O₃:Eu³⁺) has implications for both medical imaging and high energy physics [15]. Due to its very high density, Lu₂O₃:Eu³⁺ (~9.4 g/cm³) has superior stopping power relative to commercially available scintillators and would in principle allow the construction of scintillation detectors capable of sub-micron imaging resolutions. Although challenges still exist, possible applications for Lu₂O₃:Eu³⁺ include: radiography, mammography, computed tomography (CT), and radiation detectors (X-ray and gamma ray). Additionally, Lu₂O₃:Eu³⁺ has also received interest as light emitting phosphor in areas such as cathode ray tubes, plasma display panels, field emission display, thermometry, and security printing features [16].

The objective of this research was to help advance the understanding and application of X-ray imaging technologies as it pertains to the use of Lu₂O₃:Eu³⁺ scintillators. X-ray energies of 8keV and 60keV were investigated.

2.1. Properties of Lu₂O₃

Lu₂O₃:Eu³⁺ has very promising physical properties for application in X-ray imaging systems. The greatest advantage that Lu₂O₃:Eu³⁺ possesses is very high density and effective atomic (Z_{eff}=68.8) number when compared to most scintillators. The effective attenuation of X-ray photons in principle allows for very thin detection layers. The increase in attenuation per thickness of the detector has direct implications for the resolution of the imaging system as highlighted in section 1.3.1. The increased resolution
can be understood as the reduction of light spreading within the detector element before reaching the photosensitive part of the system. Additionally, when compared to CsI:Tl, Lu₂O₃:Eu³⁺ does not degrade in air and as such its fabrication does not require any special enclosures or processing environments to reduce degradation by water in the atmosphere. Some other physical and optical properties of host species Lu₂O₃ are listed in Table 2-1, Table 2-2, and Table 2-3.

**Table 2-1 Material properties of Lu₂O₃ [10]**

<table>
<thead>
<tr>
<th>Material property</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>9.42</td>
<td>g/cc</td>
</tr>
<tr>
<td>Atomic Number</td>
<td>Zₘₐₜ=71, Zₒ=16, Zₑₐₓ=68.8</td>
<td></td>
</tr>
<tr>
<td>Unit Cell</td>
<td>Body Centered Cubic (BCC)</td>
<td></td>
</tr>
<tr>
<td>Lattice Parameter</td>
<td>10.390</td>
<td>Å</td>
</tr>
<tr>
<td>Melting Temp</td>
<td>2490</td>
<td>°C</td>
</tr>
</tbody>
</table>

**Table 2-2 Optical and scintillating properties of Lu₂O₃:Eu³⁺ [10], [11], [17], [18]**

<table>
<thead>
<tr>
<th>Optical property</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Index of Refraction</td>
<td>1.94 @ 510 nm</td>
<td></td>
</tr>
<tr>
<td>Color</td>
<td>C₁ = 6.6x10⁻³, C₂ = 0.3833</td>
<td></td>
</tr>
<tr>
<td>Total Emission</td>
<td>30,000–90,000</td>
<td>Ph/MeV</td>
</tr>
<tr>
<td>Lu₂O₃ Band Gap</td>
<td>5.5 [225.4]</td>
<td>eV [nm]</td>
</tr>
<tr>
<td>Eu₂O₃ Band Gap</td>
<td>4.4 [281.8]</td>
<td>eV [nm]</td>
</tr>
<tr>
<td>Peak Emission Wavelength</td>
<td>611</td>
<td>nm</td>
</tr>
<tr>
<td>Decay time</td>
<td>~1.0 @ 611 nm</td>
<td>ms</td>
</tr>
</tbody>
</table>
Table 2-3 Mechanical properties of Lu₂O₃ [10]

<table>
<thead>
<tr>
<th>Mechanical property</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elastic modulus</td>
<td>174</td>
<td>GPa</td>
</tr>
<tr>
<td>Hardness</td>
<td>4</td>
<td>GPa</td>
</tr>
<tr>
<td>CTE</td>
<td>5.9 @ 27°C, 8.2 @ 1300°C</td>
<td>µm/(m*K)</td>
</tr>
</tbody>
</table>

2.1.1. *Lu₂O₃ Structure*

Lutetium is a rare earth (RE) lanthanide material. The lanthanide period is characterized by inner shell 4f electron energy levels. When moving through the lanthanide period of the periodic table each subsequent species adds an electron into the 4f orbital. These shielded electrons have lower energy than 6s and 5d electrons, which make up the valence band of the material and because of this the valance states and chemical interactions are generally similar across the lanthanide period. Commonly REs have a valance oxidation state of 3+ forming RE₂O₃ structured oxides. Additionally, REs undergo a phenomenon called lanthanide contraction, in which the addition of protons to the nucleus and inadequate shielding from 4f elections causes RE ions to radially contract as they increase in atomic number (La (Z=57) ~103 pm and Lu (Z=71) ~ 86.1 pm). This contraction of atomic radius along with the increase in atomic mass allows for the density of Lu₂O₃ to be greater than that of its preceding lanthanide period elements. This contraction allows for the desirable high density of electronic states of Lu₂O₃, which makes Lu₂O₃ a very good X-ray attenuating material and thus a very good candidate as a host lattice for scintillators.
The structure of Lu$_2$O$_3$ forms a stable bixbyite BCC CaF$_2$ type structure, Figure 2-1, in which the cation (calcium) sites have lutetium atoms and the anion (fluorine) sites have oxygen atoms. However, to maintain charge neutrality of the lattice, oxygen only occupies a fraction of the anion sites. Thus, the unit cell of the Lu$_2$O$_3$ contains 48 oxygen anions and 32 lutetium cations leaving 16 anion vacancies from the original CaF$_2$ lattice. Two distinct cationic sites emerge from this configuration: C$_2$ sites comprise 24 cation sites which have non-centrosymmetric monoclinic symmetry and S$_6$ sites constitute 8 positions with centrosymmetric trigonal symmetry. These site differences can have some effects on the scintillation phenomena of the material and will be explored in the subsequent sections.
2.2. Scintillation properties of Lu$_2$O$_3$:Eu$^{3+}$

As mentioned previously, the origin of scintillation for insulating material requires the addition of impurities within the lattice. These cation impurities serve as so-called ‘acceptor’ ions where electrons and holes can radiatively recombine to release characteristic photons known as the emission spectrum of the material. In the case of Lu$_2$O$_3$, europium (Eu$^{3+}$) can be added as an isoivalent impurity dopant. Eu$^{3+}$ provides energy levels within the band gap of the Lu$_2$O$_3$, which produce a characteristic spectrum shown in Figure 2-2. This emission is primarily composed of a $^5$D$_0$-$^7$F$_2$ long wavelength red emission (611nm) with minor less favored $^5$D$_n$-$^7$F$_j$ transitions making up the rest of the spectrum. The high intensity of the peak is common for Eu activated materials and matches very well with the quantum efficiency curve of CCD detectors used in X-ray imaging systems shown in Figure 2-2. The achievable intensity of light yield is still under some scrutiny and differing processing conditions in the literature resulted in light yields ranging from 30,000 to 90,000 [11] photons per mega electron volt (Ph/MeV). These light yield results are promising and are between 45% and 136% the value of CsI:Tl (66,000 Ph/MeV).

Additionally, due to its relatively high density and attenuation coefficient Lu$_2$O$_3$:Eu$^{3+}$ has a very high absorption efficiency in the energy ranges utilized for important medical and lab techniques as shown in Figure 2-3. This high absorption efficiency is crucial for efficient scintillation in thin films, and as evident in the ranges 10–30 keV and greater than 63 keV Lu$_2$O$_3$:Eu$^{3+}$ is superior to other scintillation materials including CsI:Tl. Furthermore, the K shell edge for Lu containing compounds occur at 63
keV and allows a continuous absorption curve within the major medical diagnostic regime.

Despite these advantages, Lu$_2$O$_3$:Eu$^{3+}$ suffers from some undesirable scintillation characteristics such as its slow decay time (1 ms), which is attributed to the lower probability scintillation of Eu on S$_6$ sites which delay scintillation. This fact may preclude Lu$_2$O$_3$:Eu$^{3+}$ to be used as fast scintillator but should not limit its use in modalities which do not have strict temporal limitations.
Figure 2-2 Characteristic photonic emission of the Lu$_2$O$_3$:Eu$^{3+}$ scintillator. Notice the sharp emission at ~611 nm (red) which matches well with the quantum efficiency of CCD type photodetectors [15].

Figure 2-3 Various scintillator absorption efficiency [20], notice that Lu$_2$O$_3$:Eu$^{3+}$ has higher absorption efficiency between 10 and 35 keV when compared to CsI:Tl.
2.2.1. \textit{Lu}_2\text{O}_3 \textit{Cation site effects}

As mentioned previously there is a distinct configurational difference between the two cationic sites intrinsic to the \( \text{Lu}_2\text{O}_3 \) lattice. The \( \text{C}_2 \) site is non-centrosymmetric while the \( \text{S}_6 \) site is centrosymmetric with respect to the anionic lattice. \( \text{C}_2 \) sites have six surrounding oxygen atoms at different distances from the central cation, and this allows for partial electric dipole-induced and magnetic dipole-induced transitions, while \( \text{S}_6 \) sites are restricted to magnetic dipole-induced transitions. Spectroscopically these sites have distinct features and Zych et al. [21] have shown that \( ^5\text{D}_0-^7\text{F}_1 \) emission for the respective sites varied and can be explored using spectroscopic response. \( \text{C}_2 \) sites show a characteristic peak at 579.5 nm while \( \text{S}_6 \) sites show a peak near 581.5 nm corresponding to the \( ^5\text{D}_0-^7\text{F}_0 \) and \( ^5\text{D}_0-^7\text{F}_1 \) emission respectively. These differences in site emissions can be used to understand the relative populations and charge transfer interactions between the two sites on the \( \text{Lu}_2\text{O}_3 \) host lattice.

2.2.2. \textit{Literature Survey of Lu}_2\text{O}_3:Eu\textsuperscript{3+} \textit{Scintillation}

An extensive literature survey was performed, focusing specifically on scintillation of \( \text{Lu}_2\text{O}_3:\text{Eu}^{3+} \) as well as disposition characteristics of \( \text{Lu}_2\text{O}_3 \) and related species. Studies that directly compare \( \text{Lu}_2\text{O}_3:\text{Eu}^{3+} \) with \( \text{CsI}:\text{Tl} \) are of particular interest as \( \text{CsI}:\text{Tl} \) is the current benchmark for imaging technologies. A survey of the most important results as it pertains to further optimization of \( \text{Lu}_2\text{O}_3:\text{Eu}^{3+} \) films are highlighted below.

Lempicki et al. [15] were the first group to realize the potential of \( \text{Lu}_2\text{O}_3:\text{Eu}^{3+} \) as an X-ray scintillation material. They fabricated a transparent optical ceramic (TOC) using a co-precipitation powder process along with a uniaxial hot press to densify \( \text{Lu}_2\text{O}_3:\text{Eu}^{3+} \)
ceramic disks. It was found that when coupled with a CCD detector \( \text{Lu}_2\text{O}_3:\text{Eu}^{3+} \) was close to 60% of the luminescent intensity CsI:Tl single crystal detectors. \( \text{Lu}_2\text{O}_3:\text{Eu}^{3+} \) showed indications that the ultimate resolution could approach and possibly exceed 1 \( \mu \text{m} \) resolution which was previously unobtainable by CsI:Tl systems.

Farman et al. [22], [23] directly compared \( \text{Lu}_2\text{O}_3:\text{Eu}^{3+} \) transparent oxide ceramic (TOC), vapor deposited CsI:Tl and Gd\(_2\)O\(_2\)S:Tb (GOS) on the basis of detector quantum efficiency (DQE) and modulation transfer function (MTF) at dental X-ray imaging powers of 70kVp and 8 mA. MTF is a measure of resolution that evaluates the imaging systems ability to resolve alternating black and white areas at different spatial frequency and DQE is the ratio of the output signal to noise ratio (SNR) and input SNR. All trials were done under identical testing parameters and coupled with a CCD detector specifically manufactured to couple with the CsI:Tl detector. Despite this fact, the TOC showed the highest DQE of all of the scintillators tested reaching 62% at a spatial frequency of 5 cycles/mm much higher than that of CsI:Tl which reached 22% at a spatial frequency of 2 cycles/mm. Additionally, testing of MTF at different spatial frequencies revealed that TOC out performed CsI:Tl and GOS with a maximum spatial frequency of 19.5 cycles/mm with a 5% MTF.

Zych et al. [24] successfully produced \( \text{Lu}_2\text{O}_3:\text{Eu}^{3+} \) of differing compositions and Ca co-doping by way of combustion synthesis. It was found that \( \text{Lu}_2\text{O}_3:\text{Eu}^{3+} \) with a 5% concentration of Eu preformed the best amongst the concentrations of Eu ranging from 3%–10%. Furthermore, the inclusion of 1% Ca stabilized the quantum efficiency of the sintered ceramics between 95%–80% for Eu concentrations between 3% and 10%
attributed to the decrease of extrinsic atomic oxygen in the lattice by addition of Ca which has been shown to increase scintillation characteristics noted by Lempicki et al. [15].

Seeley et al. [25] investigated the use of gadolinium (Gd) substitution in the Lu$_2$O$_3$:Eu$^{3+}$ host lattice. This by way of lattice relaxation allowed for a better solid solution of Eu eliminating the Eu-rich secondary phase. The secondary phase that develops in pure Lu$_2$O$_3$:Eu$^{3+}$ has adverse scattering effects on scintillation efficiency. The use of Gd as a substitutional host species had no observable adverse effects on scintillation and it is theorized that Gd will help improve the efficiency of scintillation by eliminating the Eu-rich light scattering phase.

Shi et al. [11] prepared transparent optical ceramic discs using co-precipitated nanopowders of Lu$_2$O$_3$:Eu$^{3+}$. Sintering at 1850°C for 6 hours under a hydrogen atmosphere yielded high optical linear transmittance (80% at 611 nm) and high light yield approaching 90,000 Ph/MeV. This value was the highest noted by any of the studies and if repeatable would surpass that of CsI:Tl, which has a value near 66,000 Ph/MeV.

Topping et al. [10] provided extensive research on the scintillation of physical vapor deposition (PVD) films of Lu$_2$O$_3$:Eu$^{3+}$ on both room temperature and elevated temperature depositions. Ultimately producing 10 µm films that produced resolutions less than one micrometer, very close to the diffraction limit of a 611 nm emission.

These studies suggest that despite some current challenges the PVD of Lu$_2$O$_3$:Eu$^{3+}$ is comparable to and, in some cases, better than commercially available and optimized CsI:Tl. Revisiting the list of important scintillator characteristics laid out by
Nikl in Chapter 1 an exhaustive literature search reveals that Lu₂O₃:Eu³⁺, when compared with CsI:Tl, has superior X-ray stopping power, chemical stability, and spectral matching to CCD; while being on par in terms of light yield and cost of production, and lagging in the area of temporal response.

Further, based on the strengths of Lu₂O₃:Eu³⁺, such as superior X-ray attenuation, it will be possible to produce films that provide previously unrealized resolution in digital imaging systems. If successful there may be other attractive applications in the related fields that do not require an incredibly quick response such as general radiography, dentistry, and hard X-ray application. For these reasons the following investigation focuses on the development of a scintillator based on the Lu₂O₃:Eu³⁺ system, using PVD processing as an inexpensive and flexible way to produce scintillation films for use in digital imaging systems.
Chapter 3

3. Physical Vapor Deposition

As mentioned in the previous sections the deposition of \( \text{Lu}_2\text{O}_3:\text{Eu}^{3+} \) by PVD provides an aspect of microstructure control that is impossible with current transparent optical ceramic manufacturing methods. The benefit of controlling microstructure has already been shown in the form of needle-like structures of CsI:Tl [8] which are the current standard for scintillator imaging modalities for medical devices. The goal of this study was to develop \( \text{Lu}_2\text{O}_3:\text{Eu}^{3+} \) films with dense tailored microstructures that will allow for the production of cost effective high-resolution large area scintillation screens.

PVD systems work on the rather simple principles of energy transfer by means of heat (evaporation) or momentum (sputtering). In the first mode heat is applied to a charge of material with sufficiently high temperatures that the target material obtains enough energy to vaporize atoms from the target and coat the surrounding surfaces. The process of evaporation is often done by resistive heating of a boat made of a refractive material, this fact limits the efficient evaporation of materials with relatively high melting temperature and is not preferred for oxides such as \( \text{Lu}_2\text{O}_3 \) (\( T_m = 2490^\circ \text{C} \)). However, such high melting temperature materials may be deposited by pulsed laser deposition (PLD), which is a form of evaporation in which a target material is locally heated to very high temperatures by a laser vaporizing the target material. The potential for very high heating rates using a laser ablation technique allows for the efficient deposition of high melting temperature materials such as \( \text{Lu}_2\text{O}_3:\text{Eu}^{3+} \).
The second mode of PVD is sputtering and it utilizes momentum transfer of inert gas species such as argon (Ar). In this configuration, the inert species is injected into an evacuated system and ionized by an electric field causing the Ar to become positively charged ion (Ar\(^+\)). The ionization allows for a negatively biased target to accelerate Ar\(^+\) ions toward the material slamming into the target with sufficient energies to cause the target species to be ejected from the surface. However, when using insulating targets such as Lu\(_2\)O\(_3\):Eu\(^{3+}\) it is important to recognize that charged species will not be conducted away from the surface of the material which is detrimental to the sputtering process. As such, many systems utilize radio frequency (RF) sputtering, which couples the target to a RF source. The alternating bias of the RF source allows for the surface to be positively biased for half of the cycle, allowing for electrons to sweep away any positive Ar\(^+\) ions. RF sputtering allows for the deposition of almost any kind of insulating material and is a good candidate for deposition of Lu\(_2\)O\(_3\):Eu\(^{3+}\).

After the target atoms are ejected from the target under normal deposition circumstances they encounter many gas phase collisions en route to the substrate. The number of collisions scales very closely with the energy of the ejected species and the gas pressure in the chamber. Upon reaching the substrate the species ideally condense and coalesce with other atoms forming nuclei and ultimately growing a film.

The effect that process parameters have on the microstructure of PVD coatings was first described by Movchan and Demchishin and extended by Thornton [26]. This so called ‘extended zone structural scheme’ provides valuable information about the expected microstructure as it pertains to the temperature of the substrate and the pressure
of the sputtering gas. As shown in Figure 3-1 the qualitative effect of inert gas pressure and temperature are separated into different zones which have distinct characteristic microstructures governed by diffusion, energy, and angle of impinging atoms being sputtered. Additionally, due to the dynamic nature of sputtering plasmas in RF applications, there is often gas species interaction that can further complicate the expected microstructure. The general zones and their properties are explained below and serve as a very important guide to when engineering favorable microstructures for scintillation.

Figure 3-1 Thornton’s modified standard zone scheme first proposed by Movchan and Demchishin. T/T_m indicates the relative temperature compared to the melting temperature of the coating species [22].

Zone 1 (T/T_m<0.1) is characterized by smaller needle like grains with boundaries, which are not dense. These structures form due to the low energy of the adatoms on the surface of the substrate. Low temperatures cause the atoms to stick very close to where they strike the substrate and as such nucleation is very small and homogenous across the
substrate and the effect of shadowing dominates the growth mechanism. Shadowing is simply a phenomenon that occurs in a deposition where the surfaces that are higher receive more atoms and the grains grow in needle-like columns without much intimate contact with neighboring grains. Mattox et al. [27] have attributed the suppression of Zone 1 in low pressure environments by increased ion bombardment which increases adatom mobility effectively smoothing out the hills and valleys typically seen during shadowing. This bombardment allows for microstructures that are denser and have atomically close contact with neighboring grains. However, bombardment is not without some drawback, often due to energetic gas phase and ion bombardment, there is a high occurrence of entrapped gas species within coatings causing films to have tensile stress [28].

In zone T (0.1<T/T_m<0.3), or transition zone, surface diffusion becomes more prevalent which allows for adatoms to diffuse more freely and overcome some of the shadowing effect seen in Zone 1. In this regime, the microstructures are fibrous and dense with increasing grain size proportional to reduced temperature (T/T_m). The topology of Zone T deposits is very smooth and grain sizes are often small.

Zone 2 (0.3<T/T_m<0.5) is characterized by fast surface mobility, which can form very dense microstructures with columnar multi-grain structures extending through the entire thickness of the coating. Once nucleated the grains tend to grow from the nucleation site and develop a strong preferential orientation.

Finally, in zone 3 (T/T_m>0.5) bulk diffusion becomes more important during the deposition and grain growth occurs. In grain growth, larger grains consume smaller
grains, which result in a more equiaxed microstructure in the film.

3.1. Literature Survey of Lu$_2$O$_3$:Eu$^{3+}$ for PVD coating

An extensive literature survey was undertaken on the subject of vapor deposition of Lu$_2$O$_3$:Eu$^{3+}$ and related compounds. Special attention paid to the microstructure and scintillation quality of films deposited under different conditions.

Nagakar and Topping [10], [20] explored the deposition of Lu$_2$O$_3$:Eu$^{3+}$ using PVD and chemical vapor deposition (CVD) methods. Both methods produced varying degrees of columnar microstructure, which was characterized using radioluminescence (RL) and MTF. It was shown that post deposition annealing greatly increased luminescence and that the deposited transparent oxide ceramic had superior MTF to that of conventionally made pixelated ceramics presumably due to the columnar morphology much like that seen in columnar deposits of CsI:Tl mentioned previously, as well as increased stopping power which can increase resolution.

Additionally, Topping [10] did many of the foundational studies for RF magnetron PVD of Lu$_2$O$_3$:Eu$^{3+}$ setting bench marks for room temperature deposition parameters and process rates. Depositions on quartz substrates at room temperature had coating rates near 1 µm/hr at 75 watts (W) RF power and 10 millitorr (mtorr) of Ar gas pressure produced dense coatings of Lu$_2$O$_3$:Eu$^{3+}$. These coatings were subsequently annealed at 400°C for 2 hours to replace oxygen deficiencies in the lattice due to the reducing environment within the vacuum chamber. The annealing step also reduced the intrinsic film stress and resulted in a sharper XRD pattern, indicating that nano-sized grains were coarsened by the annealing step. Finally, heated substrate depositions from
room temperature to 1000 °C showed the propensity for improved crystallinity and transparency leading to superior scintillation at elevated temperatures.

Roy et al. [29] successfully grew Lu$_2$O$_3$:Eu$^{3+}$ by means of RF magnetron sputtering and showed that 10 µm thick Lu$_2$O$_3$:Eu$^{3+}$ grown at temperatures between 800 °C and 1000 °C demonstrated higher RL than lower temperature deposits. Additionally, Lu$_2$O$_3$:Eu$^{3+}$ grown on single crystal yttrium (8%) stabilized zirconia (YSZ) substrates demonstrated preferred orientation based on the native substrate orientation. The study concluded that RL increased at higher temperature depositions and for coatings on YSZ (111) oriented substrates. These increases were attributed to improved crystallinity and defect concentration at elevated temperatures and increased stopping power due to increased atomic plane density in the (111) direction.


High temperature process optimization studies investigated processing parameters such as substrate temperature and orientation, pressure, and power based on morphology, structure, and fluorescence spectroscopy (FS) of the coatings.

By leveraging previous researchers work [10], [29] the baseline deposition conditions for all films were as follows: 50mm substrate to target separation, 200 sccm flow rate of sputtering gas, 10 mtorr gas pressure, 75 W forward power setting, and 800°C substrate temperature.

Additionally, a small amount of oxygen was injected into the argon gas stream at low atomic levels between 0.05%–0.075% of mass flow rate, it was found that this
addition of oxygen reduced the amount of film discoloration and produced better quality films. The addition of oxygen also produced coatings which scintillated under ultra violet (UV) excitation in the as deposited state, a sign that crystallinity was higher and the defect concentration was reduced compared to depositions without oxygen.

Substrates were purchased from MTI Corporation in three orientations of single crystal YSZ (8% yttrium) (100), (110), and (111). The addition of yttrium to YSZ allows for normally tetragonal zirconia to be ‘stabilized’ into a cubic structure very similar to that of Lu₂O₃ (~1% lattice mismatch) which is important for adherence and minimizing internal stress in the as deposited film. Samples were cleaned using oxygen and argon sputtering plasma followed by a 30 min acetone ultrasonic cleaning.

Targets for deposition were manufactured by co-precipitation of powders of Lu₂O₃ and of Eu₂O₃ with nominal purities of 99.995%. These powders were pressed into 50mm discs using a uniaxial hot press at 1600°C and 50 MPa. Pressed targets were annealed in air at 1300°C for 16 hours. Targets were then fixed to copper backing plates with indium metal to insure proper thermal and electrical contact to aid deposition uniformity as well as cooling the target material during deposition.

Films produced were characterized using a weight gain to determine thickness, X-ray diffraction (XRD), scanning electron microscopy (SEM), and Fluorescence spectroscopy (FS). XRD was utilized to determine crystal structure, SEM for topology and cross sectional microstructure of coatings, and FS, which can be correlated to activator efficiency.
Finally, selected substrates were then annealed to try to induce grain coarsening and replace any remaining oxygen deficiency in the coatings. These samples were characterized again in order to investigate the effect of a potential annealing step and grain size.

### 3.2.1. Deposition Results

Each deposition was performed on three different single crystal substrate orientation of YSZ. Results are summarized in a photographic matrix in Figure 3-2 and Table 3-1. Each orientation of YSZ was fixed against a resistive substrate heater and remained stationary during the deposition process.

<table>
<thead>
<tr>
<th></th>
<th>(100)</th>
<th></th>
<th>(110)</th>
<th></th>
<th>(111)</th>
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<td></td>
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</tr>
<tr>
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<td></td>
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<tr>
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<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>20.00 mtorr</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Figure 3-2 Photographic array of parameterization of RF magnetron sputtering depositions.**
Table 3-1 RF magnetron sputtering deposition results for thickness, coating rate, and UV scintillation.

<table>
<thead>
<tr>
<th>Power (W)</th>
<th>Substrate Temperature (°C)</th>
<th>Pressure (mtrrr)</th>
<th>Substrate Orientation</th>
<th>Thickness (µm)</th>
<th>Coating Rate (µm/hr)</th>
<th>UV Luminescence</th>
</tr>
</thead>
<tbody>
<tr>
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<td>10.00</td>
<td>(100)</td>
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<td>0.57</td>
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<tr>
<td></td>
<td></td>
<td></td>
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<td>0.57</td>
<td>✓</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(111)</td>
<td>4.99</td>
<td>0.62</td>
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</tr>
<tr>
<td>75</td>
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<td>10.00</td>
<td>(100)</td>
<td>3.48</td>
<td>0.57</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(110)</td>
<td>3.93</td>
<td>0.57</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(111)</td>
<td>3.93</td>
<td>0.62</td>
<td></td>
</tr>
<tr>
<td>75</td>
<td>600</td>
<td>10.00</td>
<td>(100)</td>
<td>2.87</td>
<td>0.64</td>
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<td></td>
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</tr>
<tr>
<td>75</td>
<td>800</td>
<td>5.00</td>
<td>(100)</td>
<td>3.66</td>
<td>0.52</td>
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</tr>
<tr>
<td></td>
<td></td>
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<td>0.60</td>
<td>✓</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(111)</td>
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<td>✓</td>
</tr>
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<td>(110)</td>
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<td></td>
<td></td>
<td>(111)</td>
<td>NA</td>
<td>NA</td>
<td>✓</td>
</tr>
</tbody>
</table>

As stated above the baseline deposition was performed at 800°C, 75W, and 10 mtorr for 8 hours. These parameters yielded clear and defect free films which served as the bench mark which all of the depositions were compared.

Low temperature deposition of 600°C was done for 4.5 hours and resulted in coatings which were brown and showed no luminescence when excited by UV source. Depositions at 700°C were performed for 8 hours and resulted in coating thicknesses between 3.5–4.0 µm. Although these coatings were less brown, they also showed no
apparent luminescence under UV excitation.

Pressure variation from the baseline (10 mtorr) of 5 mtorr and 20 mtorr were also investigated. The low pressure 5 mtorr samples were processed with a lower gas flow (121 sccm compared to the normal 200 sccm) in order accommodate our vacuum systems capabilities. The 5 mtorr samples were deposited at 800°C and 75W and yielded coatings with larger thickness variations (2.5–4.2 µm). It is probable that these variations were due to reduced gas phase collisions in the plasma environment resulting in more directed and less randomized coating flux on the substrates. Coatings were found to be clear and emitted light under UV excitation. Higher pressure 20 mtorr samples were processed for 7 hours at 800°C and 75W, yielding clear coatings which showed emission to UV excitation. The increase in pressure decreased the coating growth rate to 0.29 and 0.39 µm/hr. This effect was due to increased gas phase collisions, which reduced the amount of atoms reaching the substrates.

Increased power condition of 100 W depositions was done for 7 hours and yielded clear coatings, which emitted under UV excitation. The (110) and (111) YSZ substrates cracked and shattered respectively during deposition, and as such the shattered remains of the (111) substrate could not be characterized. The increased damage to substrates at higher pressure may be due to an increase internal film stress induced by the enhanced coating rate. Additionally, the internal stress of the films may have been increased by the repeated high energy atomic peening by energetic gas neutrals as well as sputtered species known to happen in PVD systems at higher energies [10].
3.2.2. **X-ray Diffraction (XRD)**

XRD was performed using a Bruker D8 Discover operated in Bragg-Brentano geometry utilizing a 40 kV 40 mA copper anode x-ray source (primary emission wavelength of 0.154 nm). Primary side optics included a Goebel mirror and 1.2 mm slit configuration and secondary side optics included a scintillation detector with a 0.2 mm anti-scatter slit and a variable absorption slit. XRD results for a characteristic co-precipitated powder of Lu$_2$O$_3$:Eu$^{3+}$ is shown in Figure 3-3 with major peaks labeled. Evaluation of XRD results showed that all samples showed a strong preference to orient along the direction of the YSZ substrate Figure 3-4. This finding was in line with other investigations. However, unlike results found by Roy et al. [29], no transition between preferred orientations below 600°C was observed.

![XRD results for co-precipitated Lu$_2$O$_3$:Eu$^{3+}$ powder calcined at 900°C for two hours.](image)

Figure 3-3 XRD results for co-precipitated Lu$_2$O$_3$:Eu$^{3+}$ powder calcined at 900°C for two hours.
Figure 3-4 Characteristic XRD results for all depositions showed a strong orientation preference toward the substrate onto which it is coated.

3.2.3. Fluorescence Spectroscopy (FS)

Emission FS was performed using a Horiba Jobin Yvon FluoroMax 3 Fluorimeter with 2 nm band pass filters and a Xeon lamp monochromator. It was found that the best emission spectrum was obtained at an excitation wavelength near 250 nm which is correlated with charge transfer region for Lu$_2$O$_3$:Eu$^{3+}$ [11], [24], [30]. At this energy the Lu$_2$O$_3$:Eu$^{3+}$ lattice is very efficient at absorbing the UV wavelengths, which corresponds to a charge transfer from excited O$^{2-}$ to Eu activator sites. Single spectrums were collected for all specimens and maximum intensity of the main (611 nm) peak was used to correlate to scintillation efficiency. To account for thickness variation in the samples the intensity is presented as a normalized intensity (Counts/µm) as shown in Figure 3-5.
The variation of fluorescence intensity with deposition temperature is evident and positively correlated with normalized intensity. The normalized intensity of the 800°C depositions was markedly higher than that of the 600°C or 700°C depositions. Therefore, it is apparent that at high temperatures Eu activator efficiency is greatly enhanced.

The effect of pressure was much less clear but samples generally showed a slight increase in fluorescence for the 10 mtorr depositions. This was only contradicted by the (111) substrate deposited at 5 mtorr, which showed the highest fluorescence efficiency among the (111) substrate samples.

Comparison of different power settings (75 and 100 W) was done on only (100) and (110) substrates. As expected the 100 W deposition delivered films with higher coating rate and yielded clear specimens with UV scintillation characteristics. However, upon inspection, it was found that the fluorescence intensity was less than that of the 75 W specimens in both orientations.
Figure 3-5 Fluorescence intensity normalized to the thickness of RF magnetron depositions versus substrate temperature (A), pressure (B) and power (C).

3.2.4. **Scanning Electron Microscopy (SEM)**

A Zeiss Supra 55 in secondary electron imaging mode with a voltage of 4 kV, a working distance of 7–9 mm, and a magnification of 1000X was utilized for SEM analysis. Figure 3-6, Figure 3-7, and Figure 3-8 show the topology of the temperature studies for respective substrate orientations (100), (110), and (111). Figure 3-9, Figure 3-10, and Figure 3-11 show the topology of the pressure study for substrate orientations (100), (110), and (111). Finally, Figure 3-12 and Figure 3-13 show the topology for of the power study for respective substrate orientations (100) and (110). All samples were heat
treated at 1000°C for 4 hours following deposition and then a 30 min thermal etch at 1400°C to better differentiate the grain structure.

The baseline deposition of 800°C, 75W, and 10.00 mtorr appeared to have the most equiaxed grains and showed grain sizes between 1 µm to 10 nm. The (100) and (111) substrates appeared similar with the (111) having slightly larger grain size. The (110) substrate showed a relatively flat surface with rather large grain clusters. The formation seen on the (110) seems to be consistent with a mixed growth such as Stranski–Krastanov (SK) growth in which layer growth is preceded by the formation of 2D or 3D structures on the surface. As the temperature is reduced there is an apparent increase in the amount of SK growth. The 600°C samples showed very fine (~100–200 nm) 3D islands on the (110) and the (111) substrates Figure 3-7 and Figure 3-8. A more extreme example is shown in the (100) substrate in which the island growths are very large (5–10 µm) Figure 3-6.

Variation of the pressure produced topologies very different than that of the 10 mtorr baseline deposition with both 5 and 20 mtorr deposition samples producing flatter surface morphologies. At low pressure, the reduction of gas phase collisions results in adatoms that had sufficient energy to form a flat interface through high adatom mobility. The flatness of the higher pressure sample could be due to the reduction in the coating growth rate which would allow for enough time for the adatoms to diffuse to more favorable locations which prevent the formation of islands.

Similar to the pressure studies it appeared that increasing the power of the deposition resulted in flat topographical features, which could have been due to the
occurrence of excessive ‘atomic peening’ at elevated energies. This peening phenomenon effectively increases the adatom energy by collision on the surface of the film resulting in energetically unfavorable atoms to be moved to more favorable positions.

Figure 3-6 Topology of RF deposition on substrate orientation (100) 800°C (top left), 700°C (top right), 600°C (bottom).
Figure 3-7 Topology of RF deposition on substrate orientation (110) 800°C (top left), 700°C (top right), 600°C (bottom).

Figure 3-8 Topology of RF deposition on substrate orientation (111) 800°C (top left), 700°C (top right), 600°C (bottom).
Figure 3-9 Topology of RF deposition on substrate orientation (100) pressure 5 mtorr (top left), 10 mtorr (top right), 20 mtorr (bottom).

Figure 3-10 Topology of RF deposition on substrate orientation (110) pressure 5 mtorr (top left), 10 mtorr (top right), 20 mtorr (bottom).
Figure 3-11 Topology of RF deposition on substrate orientation (111) pressure 5 mtorr (top left), 10 mtorr (top right), 20 mtorr (bottom).

Figure 3-12 Topology of RF deposition on substrate orientation (100) Power 75W (left) and 100W (right).
3.2.5. **Annealing study**

Due to the potential for grain size effects on the scintillation output of the coatings an annealing study was performed in which the 100W deposition samples were annealed in air for 12hr at 1250°C and 10 hr at 1500°C. After annealing steps XRD, FS, and SEM were done in order to observe changes that happened during the annealing cycles.

Figure 3-14 and Figure 3-15 show the evolution of the structure of the coatings before and after different annealing steps. As previously mentioned, the as deposited samples were observed to have small equiaxed grains that averaged less than 200 nm in size. The first annealing cycle the resulted in a slightly less rounded structure without much apparent grain growth. However, the second annealing cycle resulted in a discernible change within the film resulting in faceted gains that were greater than 200 nm in size. These observations were confirmed by cross sectional images (Figure 3-15) which showed similar structural changes following the grain growth.
Despite the apparent morphological change no discernible pattern emerged in the FS measurements. Initially, the FS measurement of the (100) substrate remained relatively constant and increased modestly after the second anneal. The highest value for FS in the (110) substrate occurred after the first anneal. It is possible that these long annealing cycles could have introduced excess oxygen interties [31] which may act as non-radiative traps that compete with scintillation activators. If this is the case, then the effect of increasing grain size could have been canceled out due to increased oxygen defects induced by long annealing in air.

Figure 3-14 Deposition on (100) at 100W. As deposited (top left), post 1250°C anneal for 12 hr (top right) and post 1500°C anneal for 10 hr (bottom).
3.3. Radio Frequency Magnetron Sputtering and Pulsed Laser Deposition

In order to evaluate the effect of different PVD modalities, a comparison between RF and PLD was undertaken. Samples were compared using film stress, RL, and X-ray imaging performance.

Targets and substrates for deposition were similar to section 3.2. RF sputter depositions were produced by using 50mm substrate to target separation, 50 sccm flow rate of argon sputtering gas, 10 mtorr gas pressure, 75 W forward power setting, and 800°C substrate temperature as measured by a pyrometer.

PLD depositions were executed in a chamber with base pressure near 2 e-8 torr and backfilled with 25 sccm of oxygen at 30 mtorr of pressure. The samples were placed
at 65 mm from the target and heated to 775°C. Ablation of the target was done using a Nd:YAG laser with a 248 nm wavelength and 20ns (FWHM) pulse duration. The measured power of the laser was 3.96 W with a spot size of 0.1 x 0.4 cm resulting in a laser fluency value of 1.98 J/cm^2.

### 3.3.1. Deposition Results

To evaluate the effectiveness of different sputtering modalities samples were prepared using two different sputtering modes. Deposition results are summarized below in Table 3-2. Both RF magnetron and PLD sputtered depositions had coating rates around 0.8 um/hr. The films were optically clear, defect free, and scintillated under UV excitation.

#### Table 3-2 Deposition results of RF sputtering and PLD.

<table>
<thead>
<tr>
<th>Name</th>
<th>Method</th>
<th>Substrate Orientation</th>
<th>Thickness (µm)</th>
<th>Coating Rate (µm/hr)</th>
<th>UV Luminescence</th>
<th>Film Stress (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVD 37</td>
<td>Sputter</td>
<td>A-(100)</td>
<td>10</td>
<td>0.80</td>
<td>✓</td>
<td>0.46</td>
</tr>
<tr>
<td></td>
<td></td>
<td>B-(110)</td>
<td>10</td>
<td>0.80</td>
<td>✓</td>
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<tr>
<td></td>
<td></td>
<td>C-(111)</td>
<td>10</td>
<td>0.80</td>
<td>✓</td>
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<tr>
<td>PVD 40</td>
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<td>0.76</td>
<td>✓</td>
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<tr>
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<td></td>
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</tr>
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<td>C-(111)</td>
<td>7</td>
<td>0.76</td>
<td>✓</td>
<td>2.81</td>
</tr>
</tbody>
</table>

Film stress was inferred using a profilometer to evaluate the radius of curvature from scans calculated using Stoney’s formula:

\[
\sigma_f = \frac{E_s t_s^2}{6(1 - \nu_s)t_f} \left(\frac{1}{R}\right) \quad (3.1)
\]
where $E_s$, $t_s$, and $\nu_s$ are the elastic modulus of the substrate, substrate thickness, and Poisson’s ratio of the substrate; and $t_f$ and $R$ are film thickness and radius. All samples were in a compressive stress mode which is similar to earlier works where compressive stress was attributed to atomic ‘peening’ [32]. This phenomenon occurs when high energy particles collide with the growing film inducing compressive surface stresses throughout the coating process. It appears that sputtered (100) sample showed the lowest inherent film stress when compared to all other samples. Interestingly, this did not seem to have a beneficial effect on the scintillation characteristics since the (100) sample was far below the best sample.

Figure 3-16 Cross section profile of PLD film on (100) YSZ substrate.

Films were evaluated and characterized based on their feasibility for use in hard X-ray CT machines. The first characterization was light output by means of radial noise power spectrum density measurements (RNPSD). RNPSD measurements are an effective way to quantify the number of photons produced per X-ray interaction. The measurement is done by comparing raw noise X-ray images with images taken with a scintillation
detector and ratio between photon emission and photon starvation plateaus is correlated to emission.

It is important to note that specimens coated using RF magnetron sputtering mode achieved the highest RNPSD and normalized counts per micron on (110) and (111) oriented substrates. Results are summarized in and although RF sputtered were the best amongst the specimens tested there is still much room for improvement as the samples were well below results by other processing methods (90,000 Ph/MeV [11]).

![Bar chart showing photons vs. MeV for different samples.](image)

**Figure 3-17 Raw light yield for RF and PLD produced films.**

Upon inspection of X-ray exposures, a certain level of defects were present in all the samples Figure 3-18 and Figure 3-19. These defects manifest as white spots in the X-ray image and can impede the accuracy of scintillation measurements as well as the quality of the X-ray image taken. Despite this, increased defects in the X-ray image did not correlate with decreased scintillation response. The origin of the defects is unclear at this time and may have emerged from different sources such as environmental, handling, target, substrate, or system sources.
In the PLD deposited samples, the defects appear to be more prevalent and may be inherent in the process itself. The physical act of high energy laser ablation can release large particles from the surface of the target and land on the substrate. This effect can be exacerbated by the use of brittle ceramic target materials. Attempts to reduce power and spot size were done but these measures did not affect the defect density of the PLD process on Lu$_2$O$_3$:Eu$^{3+}$.

Figure 3-18 PVD 37 X-ray imaging of RF sputtered samples. Left (100), Center (110), and Right (111).

Figure 3-19 PVD 40 X-ray imaging of PLD samples. Left (100), Center (110), and Right (111).
3.4. Conclusions

Parameterization of RF magnetron sputtering of Lu$_2$O$_3$:Eu$^{3+}$ was performed across high temperature, pressure, and power regimes. Results showed that all high temperature depositions (600°C – 800°C) were influenced by the underlying substrate and showed strong X-ray diffraction response with the same orientation as the underlying substrate. UV scintillation tests revealed that only the depositions performed at 800°C scintillated. Visual inspection showed that typically the lower temperature depositions had a brownish tint. FS confirmed the above scintillation test results and showed a clear increase in fluorescence for the 800°C depositions. Morphological differences between the various depositions were apparent and the SEM images indicate a change in growth condition between 600°C to 800°C. 800°C depositions on (100) and (111) showed an equiaxed topology and all 600°C depositions showed SK growth with small island formations on the surface.

Pressure and substrate variations did not show a significant effect on fluorescence despite having rather pronounced morphological effects. Lower (5 mtorr) and higher (20 mtorr) deposition pressures resulted in flat topology without much grain definition.

Increases in power from 75W to 100W conferred an increase in the overall coating rate but resulted in a decrease in fluorescence. As in the pressure study, the high power deposition resulted in a flat surface morphology without grain definition.

Annealing of the high power deposition at 1250°C for 12 hours and 1500°C for 10 hours resulted in a larger grain structure. These changes in morphology did not have an affect on FS and in the case of (110) deposition the FS was reduced.
Profilometry experiments confirmed that both RF sputtered and PLD samples showed a compressive film stress. Sputtered samples on (100) showed a significant decrease in film stress, however, this did not translate into any advantage in the FS effects. RNPSD measurements of RF and PLD samples revealed that RF samples had superior light output with a maximum scintillation value of 22,915 photons/MeV. This value still falls short of the maximum measured limit for Lu$_2$O$_3$:Eu$^{3+}$ of 90,000 photons/MeV. Imaging defects were qualitatively characterized showing that RF samples had a lower density of defects than the PLD samples. For these two reasons, it appears that RF magnetron sputtering of Lu$_2$O$_3$:Eu$^{3+}$ may be better suited for X-ray imaging applications.
Chapter 4

4. Oxygen Defect Structure Manipulation

4.1. Defect Identification and Engineering

Preliminary PVD studies focused on the parameterization and processing of Lu$_2$O$_3$:Eu$^{3+}$ films for high resolution detectors. Process parameters were varied in order to beneficially affect the scintillation phenomena of the films. However, the results did not show a large enough scintillation increase when compared to transparent optical ceramics. A new approach focused on oxygen defect structure has been undertaken in the subsequent sections. In order to truly realize the potential of Lu$_2$O$_3$:Eu$^{3+}$ as a state of the art scintillation material, it is necessary to understand how the host lattice and the defect chemistry of the films as it relates to the scintillation characteristics. There is ample literature which indicates that appropriate modification of defect structures can result in better scintillation characteristics ranging from increased efficiency and light output [33] to reduction in afterglow and decreased decay time of luminescence [21], [34], [35].

In rare earth oxides such as Lu$_2$O$_3$, there is an ordered set of anion vacancies which provide many accessible sites for defects, in particular oxygen interstitials, which have been theorized to compete with Eu$^{3+}$ activation sites and reduce scintillation [15][31]. The structure of Lu$_2$O$_3$ is reprinted from Chapter 2 (Figure 4-1) and has a CaF$_2$ type fluorite structure.
Due to charge neutrality constraints, the configuration of oxygen vacancies gives rise to two cationic sites with different coordination. These intrinsic oxygen vacancies within the lattice make it very easy for oxygen atoms to occupy interstitial sites by way of anionic Frenkel defects. For these defects the intrinsic oxygen deficiency of the lattice serves as favorable spots for oxygen interstitial occupation in a normal Frenkel defect incorporation. Empirical and theoretical studies confirm that anion Frenkel defects is the most energetically favorable defect across all bixbyite rare earth oxide compounds [36–39]. Kröger-Vink notation is used to show the Frenkel equilibrium equation below:

\[
\frac{[V'_o][O''_i]}{[V'_i][O'_o]} = K_{AF}(T) = e^{(\Delta S_{AF}/k)} e^{(-\Delta H_{AF}/kT)}
\]  

(4.1)
where bracketed terms denote the concentration of species, $K_{AF}$ is the equilibrium constant for anion Frenkel pairs, $\Delta S_{AF}$ and $\Delta H_{AF}$ are entropy and enthalpy of defect pair formation respectively, and $k$ and $T$ are Boltzmann’s constant and temperature respectively. At a given temperature and pressure $K_{AF}$ remains constant and as such anything that can increase the number of oxygen vacancies in the lattice will act to reduce the concentration of oxygen interstitials and vice versa.

Two approaches for reducing oxygen interstitials in similar compounds to Lu$_2$O$_3$ have included the treatment of materials in a controlled environment ranging from reducing to oxidizing, and the introduction of extrinsic aliovalent dopants that induce oxygen defects through compensation of electric charge. The results of these studies are categorized below.

Bratton [40] explored the effects of aliovalent metal oxides on the defect structure of Y$_2$O$_3$ and concluded that incorporating effectively negative cation impurity species such as divalent Ca$^{2+}$ on a Y$^{3+}$ lattice site will reduce oxygen interstitial concentration which is consistent with Frenkel defects. An investigation by van Schaik [31] revealed that co-doping of Y$_2$O$_3$:Eu$^{3+}$ with 1% Ca$^{2+}$ and 1% Zr$^{4+}$ increased quantum efficiency in the case of Ca and decreased in the case of Zr. This indicates that the manipulation of oxygen interstitials has an effect on scintillation of Y$_2$O$_3$:Eu$^{3+}$. Due to common electronic states and structure of the Y$_2$O$_3$ host lattice, it is reasonable to assume that similar effects would also take place in a Lu$_2$O$_3$ host lattice. Using the Kröger-Vink notation for the defect incorporation both divalent and tetravalent reactions are listed.
It is apparent that due to Frenkel equilibrium that extrinsic doping using a divalent metal oxide such as CaO will increase the concentration of oxygen vacancies in the crystal and in turn reduce the amount of oxygen interstitial due to the Frenkel equilibrium explained above. Additionally van Schaik et al. [31] also showed that the reduction of oxygen partial pressure was correlated with increase scintillation efficiency in Y$_2$O$_3$:Eu$^{3+}$ systems and from this it was inferred that the number of oxygen interstitials was reduced with an increase in oxygen vacancy concentration. These results show that it is very likely that similar manipulations of the Lu$_2$O$_3$:Eu$^{3+}$ structure may be used to increase scintillation.

4.2. Effects of oxygen and defect structure

In order to better understand the role that oxygen plays in the scintillation phenomena of Lu$_2$O$_3$:Eu$^{3+}$ several experiments were performed on hot pressed samples of Lu$_2$O$_3$:Eu$^{3+}$. The first set of experiments explored the effect of oxygen partial pressure by controlled atmosphere annealing. The second experiments explored the use of co-doped samples with different aliovalent doping species in order to manipulate the oxygen defect structure of the material. The co-dopant species tested were calcium (Ca) and magnesium (Mg). The co-dopants were chosen due to the reduced valence states when compared to the host lattice Lu$^{3+}$ cation. The act of manipulation of oxygen defect structures has been

\[
2CaO \xrightleftharpoons{Lu_2O_3} 2Ca'_{Lu} + 2O'_o + V'_o \tag{4.2}
\]

\[
2ZrO_2 \xrightleftharpoons{Lu_2O_3} 2Zr'_{Lu} + 3O'_o + O''_i \tag{4.3}
\]
shown by other researchers to improve the scintillation of related scintillating materials [15], [24], [36].

4.3. Sample Preparation

Powders were co-precipitated using 4N5 starting powders: lutetium, europium, and co-dopants were mixed stoichiometrically and dissolved in a nitric acid solution. Once fully dissolved the solution was precipitated using oxalic acid and ammonium hydroxide. The precipitate was filtered from the solution and rinsed with DI water and ethanol three times. Powders underwent a drying and calcination step at 900°C for 2 hours. Particle size distribution (PSD) results were obtained and showed that powders were in a single distribution ranging between 500 nm and 6 µm for all powder precipitates. XRD results of each powder indicated a single phase well matched to database values of Lu₂O₃.

Powders were loaded into a carbon die lined with graphite paper and then cold pressed at 50 MPa for 30 minutes. Conditions for hot pressing were suggested by Podowitz [41]; die and powder charge were loaded into a graphite element furnace and hot pressed at 1580°C for 6 hours at a pressure of 40 MPa. Due to the inherent reducing environment within the hot pressed chamber all samples were very dark but translucent and luminescenced under UV excitation. Samples required a 12 hour 1200°C anneal in order to bring the samples to a state of full oxidation. Upon oxidation, samples were found to be white and translucent and all samples scintillated under UV excitation.
4.4. Controlled atmosphere

Hot pressed and oxidized samples underwent a battery of annealing experiments that varied the oxygen partial pressure. The hot pressed Lu$_2$O$_3$:Eu$^{3+}$ sample was annealed for 12 hours at 1200°C in different atmospheres. Oxygen partial pressures of $10^{-15}$ and $10^{-12}$ atm were established in a tube furnace using a hydrogen and water bubbler setup to control the oxygen partial pressure. The partial pressure of $10^{-4}$ atm was reached using a specialty high purity mixture of oxygen and argon, and the $10^{-1}$ atm sample was annealed in air. Samples were evaluated using density measurements, XRD, RL, and FS. Density was obtained by use of Archimedes’ method in which samples are submerged in water and the buoyancy of the sample is used to infer the density.

XRD was performed using a Bruker D8 Focus operated in Bragg-Brentano geometry utilizing a 40 kV 40 mA copper anode x-ray source (primary emission wavelength of 0.154 nm). Full scans were taken in order to validate the crystallinity of the samples as well as the dominate phase present. Lu$_2$O$_3$ has a cubic structure and the lattice parameter was measured using the (222) peak position. Scans were taken and adjusted using potassium chloride (KCl) standard and database values for KCl. Once adjusted the (222) Lu$_2$O$_3$ lattice plane spacing was evaluated using Bragg’s Law and subsequent d-spacing can be related to a cubic lattice by the following equation as given by Cullity [42]:

$$d = \frac{n\lambda}{2\sin\theta} \quad (4.4)$$
\[ a = \frac{d}{\sqrt{h^2 + k^2 + l^2}} \]  

(4.5)

where \( d \) is the parallel plane spacing, \( \lambda \) is the primary X-ray energy of the source, \( \theta \) is the angle of incidence, \( a \) is the lattice spacing of a cubic system, and \((hkl)\) are the Miller indices of the particular plane being evaluated.

RL measurements were taken using a copper anode X-ray source that emits a characteristic wavelength of 0.154 nm (8 keV). The emission spectrum was captured using a portable spectrometer equip with CCD detector 600g/mm diffraction grating, 6 nm resolution, and a fiber optic cable. Samples were polished and then placed in a holder such that the surface of the \( \text{Lu}_2\text{O}_3:\text{Eu}^{3+} \) normal to the detector fiber optic at a distance of \( \sim 3 \) cm. Incident X-rays were at an angle of 30° relative to the surface of the sample being evaluated. Emission spectrums were normalized by the integration time of each measurement in order to compare across different samples.

Emission FS was performed using a Horiba Jobin Yvon FluoroMax 3 Fluorimeter with 2 nm primary and secondary side slits and a xenon lamp with a monochromator. The most intense emission spectrums were obtained at excitation wavelengths between 239 nm and 242 nm, which is correlated with charge transfer regime of the Eu activator ion absorption. Single spectrums were collected for all specimens and maximum intensity of the main (611 nm) peak was used to correlate Eu activator efficiency and localized charge transfer.

Site-specific spectroscopy was performed on the fluorimeter at excitation wavelengths of 465 nm and 526 nm using 0.5 nm slits and averaging over three separate
scans. These wavelengths excite the two distinct cationic sites differently and can be used to understand the population and charge transfer mechanisms between the C\(_2\) and S\(_6\) sites, which were discussed in the introduction to this chapter. Zych et al. [21] showed that the wavelengths mentioned above preferentially excite the cationic sites; the 465 nm excitation correspond to the \(7F_0-^5D_2\) transition while the 526 nm transition corresponds to the \(7F_0-^5D_1\) transition.

The 465 nm excitation is partially allowed for the C\(_2\) site but is a forbidden transition for the S\(_6\) site. Due to the constrained centrosymmetric anionic structure, the S\(_6\) sites inversion symmetry does not allow for electric dipole induced transitions, which are partially allowed for the C\(_2\) site. S\(_6\) sites only allow for magnetic dipole-induced transitions where changes in the total angular momentum quantum number (\(j\)) does not exceed 1 (\(\Delta j = 0\) or 1 where \(j = 1 + m_s\); the orbital quantum number and the spin quantum number respectively) so the \(7F_0-^5D_2\) transition is forbidden.

The 526 nm excitation corresponds to the \(7F_0-^5D_1\) which have a \(\Delta j=1\) and is an allowed transition for both the C\(_2\) and S\(_6\) sites. Emission spectra were taken between 579 nm and 605 nm, this area corresponds to \(^5D_0-^7F_0\) and \(^5D_0-^7F_1\) transitions for the Eu activator ions [21], [43], [44]. Due to the nature of the surrounding anionic lattice, the C\(_2\) and S\(_6\) site show characteristic emissions near 579.5 nm and 581.5 nm respectively shown in Figure 4-2.
Figure 4-2 Enlarged view of the $^5\text{D}_0-^7\text{F}_1$ and $^5\text{D}_0-^7\text{F}_0$ transition emphasizing the different site emissions: $S_6$ at 581.5 nm and $C_2$ at 579.5 nm respectively.

It is important to note that there is a distinction between fluorescence excitation and the RL excitation. Fluorescence excitations occur near 240 nm which corresponds to the Eu activator charge transfer energy [11], [15], [44], [45]; in which Eu activator ions receive charge transferred electrons from localized $\text{O}^2-$ excited states. In the case of ionizing radiation, the mechanism of scintillation is quite different. High energy ionizing X-rays excite electrons well above the conduction band [5]. In this manner one can think of the fluorescence measurement as a measure of the relative efficiency of the localized charge transfer and quantum emission efficiency of the Eu activator ion, while the RL measurement examines a complete scintillation phenomenon which includes absorption of high energy quanta, charge migration to luminescent sites, and quantum yield from these luminescent sites.

4.4.1. Results

A summary of the results of the controlled atmosphere study is shown in Table 4-1. At a $P_{O2} = 0.21$ atm, the density of the sample was lowest at 9.28 g/cc and for all the
remaining samples it was found to be 9.32 g/cc. Using the rule of mixtures for a 5% doped Lu$_2$O$_3$:Eu$^{3+}$ the theoretical density would be 9.35 g/cm$^3$ and shows that samples were very close to full density after hot pressing. The annealing experiments at high temperature and varying oxygen partial pressure were performed sequentially, and this repeated high temperature exposure explains the increased density after the first annealing steps. These additional oxygen partial pressure runs probably reduced the void population, which accounts for the increased density.

Results from XRD lattice parameter measurements were very similar and all samples were within 0.1%. Figure 4-3 shows a characteristic full scan, every sample was shown to have nearly identical diffraction patterns regardless of the oxygen atmosphere tested, indicating that the reducing atmosphere did little to affect lattice strain or crystallinity.

**Table 4-1 Summary of results of the controlled atmosphere experiment.**

<table>
<thead>
<tr>
<th>Log(Po$_2$)</th>
<th>Lattice Spacing (nm)</th>
<th>Density (g/cm$^3$)</th>
<th>Radio-luminescence</th>
<th>Fluorescence (x10$^{10}$)</th>
<th>C2/S6 Intensity ratio (465 nm Ex)</th>
<th>C2/S6 Intensity ratio (526 nm Ex)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1</td>
<td>1.0392</td>
<td>9.28</td>
<td>149</td>
<td>1.31</td>
<td>2.11</td>
<td>0.54</td>
</tr>
<tr>
<td>-4</td>
<td>1.0378</td>
<td>9.32</td>
<td>116</td>
<td>1.09</td>
<td>2.33</td>
<td>0.52</td>
</tr>
<tr>
<td>-12</td>
<td>1.0382</td>
<td>9.32</td>
<td>84</td>
<td>0.81</td>
<td>2.66</td>
<td>0.62</td>
</tr>
<tr>
<td>-15</td>
<td>1.0396</td>
<td>9.32</td>
<td>39</td>
<td>0.78</td>
<td>2.66</td>
<td>0.61</td>
</tr>
</tbody>
</table>
Figure 4-3 X-ray diffraction pattern of Lu₂O₃:Eu³⁺ hot pressed and annealed with major peaks labeled with Miller indices.

Figure 4-4 shows the visual evolution of the sample at different oxygen partial pressures. Moving from the left (higher oxygen partial pressure) to right (lower oxygen partial pressure) the figure reveals that low oxygen partial pressure samples were dark especially around the edges. These samples are reduced and are beginning to resemble the as pressed condition pictured on the left which is expected due to the reducing atmosphere of the hot pressing environment. High partial pressure samples PO₂ = 10⁻¹ and 10⁻⁴ looked very similar and are both white and translucent.
Figure 4-4 Photographic array of Lu$_2$O$_3$:Eu$^{3+}$ annealed at 1200C for 12 hours in different oxygen partial pressure environments. (A) As pressed. (B) PO$_2 = 10^{-1}$. (C) PO$_2 = 10^{-4}$. (D) PO$_2 = 10^{-12}$. (E) PO$_2 = 10^{-15}$. Each sample is shown in front illumination (top pictures) and back illumination (bottom pictures).

RL and FS results are shown in Figure 4-5 -Figure 4-7 and it is clear that oxygen atmosphere has an effect on the scintillation phenomena in Lu$_2$O$_3$:Eu$^{3+}$. RL and FS show an increasing response when the atmosphere becomes more oxygen rich. In terms of defects in the structure, it is very probable that the more reducing the atmosphere the greater the oxygen vacancy population. This initial result indicates that oxygen plays a significant role in the scintillation of Lu$_2$O$_3$:Eu$^{3+}$. As the sample underwent deep reduction indicated by the color change and scintillation values. At the levels of reduction tested in this section, the introduction of oxygen vacancies was detrimental to scintillation. Positively charged oxygen vacancies are known as electron traps [46] and it is possible that the magnitude of vacancies introduced was large enough to out compete the Eu activator ions for charge carriers.
The intended effect of increased scintillation was based on the evidence that the reduction of negatively charged oxygen interstitials adversely affects scintillation through strong hole trapping [33], [47]. However, it appears that the oxygen partial pressure experiments at the current level of oxygen vacancy population the desired effect is superseded and the current experiment does not have the appropriate resolution to realize the benefits from oxygen interstitial reduction.

Site-specific spectroscopy also showed a trend for decreasing emission from the C₂ site compared to the S₆ for both 526.2 nm and the 465.2 nm excitations and is shown in Figure 4-8. For both excitation wavelengths, the C₂/S₆ intensity ratio was negatively correlated with the oxygen partial pressure with the minimum ratio occurring for PO₂ (10⁻¹) = 2.11 for the 465nm excitation. The reduction of the C₂/S₆ ratio is coupled with the increase in the overall scintillation intensity. The oxidative annealing steps affect the C₂/S₆ site fraction population of activator ions (Eu) or the efficiency of charge transfer between activator ions are being affected, or a combination of the two. Eu activator ion distribution the Lu₂O₃ lattice for high temperature long duration processes such as annealing have a site preference toward C₂ sites [48] and the long high temperature process of annealing is unlikely to appreciably change the Eu site fraction as the process should be near equilibrium for all steps and therefore should not change. It is probable that the decreased site ratio intensity response C₂/S₆ is from improving charge transfer between Eu activator ion sites which is in line with the conclusion of increased vacancy trapping in more reduced samples presented above.
Figure 4-5 Radioluminescence emission spectra of hot pressed Lu$_2$O$_3$:Eu$^{3+}$ annealed at 1200°C for 12 hours at different oxygen partial pressures.

Figure 4-6 Fluorescence emission spectra of hot pressed Lu$_2$O$_3$:Eu$^{3+}$ annealed at 1200°C for 12 hours at different oxygen partial pressures.
Figure 4-7 Radioluminescence (●) and fluorescence (Δ) maximum emission (611 nm) of Lu₂O₃:Eu³⁺ vs. oxygen partial pressures.

Figure 4-8 C₂/S₆ intensity ratio vs. Log (P₀₂). Site-specific spectroscopy of Lu₂O₃:Eu³⁺ at two different excitation wavelengths: 465 nm (■) and 526 nm (●).
4.5. Co-Doping

After establishing the important role that oxygen plays in the scintillation phenomena of Lu$_2$O$_3$:Eu$^{3+}$ studies were performed on the effect different co-dopants may have. Several publications [16], [33], [36], [49], [50] indicated the addition of aliovalent species to scintillators similar to Lu$_2$O$_3$:Eu$^{3+}$ can have a positive effect on light output and quantum efficiency. The following section is dedicated to the investigation of such doping strategies for Lu$_2$O$_3$:Eu$^{3+}$ and hot pressed samples were prepared to explore the effect of different co-dopants within the Lu$_2$O$_3$:Eu$^{3+}$ structure.

Two different co-dopants were explored in the current study, calcium (Ca$^{2+}$) and magnesium (Mg$^{2+}$). These species were chosen based the reduced valence relative to Lu$^{3+}$ as well as the size differences. Theoretical calculations done by Levy et al. [36] indicate that the implementation of aliovalent dopants in bixbyite rare earth compounds should directly affect the oxygen Frenkel equilibrium. Additionally, there are some simple size concerns that may be considered. Returning to the structure of Lu$_2$O$_3$ it is clear that there are different sites in which the cationic species may occupy on the lattice. The C$_2$ and S$_6$ sites have different surrounding environments and due to the symmetry, the bond length between oxygen and the cation are different. This would presumably affect the preferred site occupation by dopant ions. S$_6$ sites have a larger volume for dopants to occupy and as such it is expected that dopants will preferentially occupy S$_6$ if they are significantly larger than the Lu ion and the C$_2$ site if the dopant is smaller than Lu. Due to this, it is expected that Ca$^{2+}$ would occupy this S$_6$ site while Mg$^{2+}$ prefer the C$_2$ site.
A summary of pertinent values for the different species as it pertains to size and
defect compensation is shown in Table 4-2. The compensating defects of the divalent
ions are well supported by analytical defect models for bixbyite sesquioxides like Lu$_2$O$_3$
[35], [36], [38], [51]. This mechanism seems likely due to the intrinsic structure of the
Lu$_2$O$_3$ lattice, which has a relatively open anionic lattice, and as such it is energetically
easy to form Frenkel type defects.

**Table 4-2 Summary of size, charge, and compensating defect within the Lu$_2$O$_3$
lattice.**

<table>
<thead>
<tr>
<th>Atomic Species</th>
<th>Ionic Radius (pm)</th>
<th>Percent Diff from host Lu2O3</th>
<th>Valence compared to host Lu2O3</th>
<th>Compensating defect</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lutetium (Lu)</td>
<td>100.1</td>
<td>0%</td>
<td>0</td>
<td>NA</td>
</tr>
<tr>
<td>Europium (Eu)</td>
<td>108.7</td>
<td>8.7%</td>
<td>0</td>
<td>NA</td>
</tr>
<tr>
<td>Calcium (Ca)</td>
<td>114</td>
<td>14%</td>
<td>-1</td>
<td>$1/2V^+_O$</td>
</tr>
<tr>
<td>Magnesium (Mg)</td>
<td>86</td>
<td>-14%</td>
<td>-1</td>
<td>$1/2V^+_O$</td>
</tr>
</tbody>
</table>

Samples were prepared by co-precipitation of 4N5 pure oxide and nitrate powders
mixed stoichiometrically and calcined for 2 hours at 900°C. Calcined powders were then
hot pressed using the same parameters laid out in the oxidation study (section 4.4).
Samples were ground and polished to less than 7 microns and underwent an oxidative
annealing step at 1200°C for 12 hours. As before samples changed from dark in the as
pressed condition to white with varying levels of translucency after oxidation.

A similar testing regime was undertaken in order to characterize the samples
using XRD, density, FS, and RL. Fracture surfaces were created in order to analyze the
microstructure for comparison across different dopant levels. Grain size was obtained by
grain intercept method, where lines of a known length are transposed on the micrograph
and the grain intersections on the line are tabulated and the length of the line is divided by these intersections to find the average grain diameter. The different micrographs were examined and 4 lines in different orientations were utilized in order to get an average grain size.

4.5.1. Results

Summarized results of the co-dopant study can be found in Table 4-3. Lattice spacing revealed little change among different co-doped samples. Density was highest for the Mg doped sample at 9.26 g/cc with the pure Lu2O3:Eu3+ and Ca doped, measuring 9.23 g/cc. A visual photographic array of the samples is shown in Figure 4-9. The pure Lu2O3:Eu3+ sample was white but showed the least amount of translucency. It is evident that Mg doped samples were much more translucent, while the Ca doped sample was slightly green/yellowish color. The translucency of the doped samples indicates that the dopant elements seemed to improve the sintering characteristics when compared to the undoped sample.

Table 4-3 Summary of results for different co-dopant species.

<table>
<thead>
<tr>
<th>Co-dopant (%)</th>
<th>Lattice Spacing (nm)</th>
<th>Density (g/cm³)</th>
<th>Radioluminescence (AU)</th>
<th>Fluorescence (x10¹⁰)</th>
<th>C2/S6 Intensity ratio (465 nm Ex)</th>
<th>C2/S6 Intensity ratio (526 nm Ex)</th>
<th>Grain Size (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>1.0392</td>
<td>9.23</td>
<td>139</td>
<td>1.02</td>
<td>2.11</td>
<td>0.54</td>
<td>NA</td>
</tr>
<tr>
<td>Ca 1%</td>
<td>1.0385</td>
<td>9.23</td>
<td>88</td>
<td>0.70</td>
<td>2.42</td>
<td>0.77</td>
<td>4.03</td>
</tr>
<tr>
<td>Mg 1%</td>
<td>1.0392</td>
<td>9.26</td>
<td>112</td>
<td>1.01</td>
<td>2.42</td>
<td>0.74</td>
<td>0.71</td>
</tr>
</tbody>
</table>
Figure 4-9 Photographic array of hot pressed samples with different co-dopant. (A) Undoped, (B) 1% Calcium, and (C) 1% Mg.

RL (Figure 4-10) of the samples revealed that the most intense scintillation occurred for the undoped Lu$_2$O$_3$:Eu$^{3+}$ sample followed in succession by Mg and Ca doped samples respectively. FS results showed a similar trend, however, in the case of FS the Mg sample was nearly identical to the pure Lu$_2$O$_3$:Eu$^{3+}$. This indicates that the localized charge transfer band and quantum yield of the Eu ion for the un-doped and Mg co-doped samples are similar. The reduction in overall scintillation is likely due to increased charge trapping during carrier migration by increased oxygen vacancies.
Figure 4-10 Radioluminescence emission spectra of Lu₂O₃:Eu³⁺ with magnesium and calcium co-dopants.

Figure 4-11 Fluorescence emission spectra of Lu₂O₃:Eu³⁺ with different magnesium and calcium co-dopants.
Site-specific spectroscopy revealed that all co-doped specimens showed an increase in the ratio of $C_2/S_6$ emission this indicates that the dopants are in fact having some effect on the electronic structure of the area surrounding the Eu activator ion. As discussed previously there at two different possibilities to consider which are: the population of Eu ion site occupancy is changing or that the charge transfer between activator ions is being affected. However, due to the small amount of dopant (1%) when compared to the sites available it is unlikely that co-dopants are appreciably affecting the site occupancy of the Eu ions. It appears that the increase in site intensity ratio, which was revealed by site-specific spectroscopy, was due to charge transfer effects induced by oxygen vacancy population increase. The effect seems relatively invariant to the co-dopant ions with both co-dopants showing very similar $C_2/S_6$ ratios indicating that oxygen vacancy populations are the probable cause of the effect rather than the co-dopant species site occupation.

Figure 4-12 Site specific spectroscopy of Lu$_2$O$_3$:Eu$^{3+}$ with magnesium and calcium co-dopants.
SEM micrographs of the fracture surfaces reveal some interesting differences between the co-doped specimens. There is a large difference in the grain size when comparing Ca to the Mg co-dopant. Ca doped sample has a grain size of 4.03 µm while Mg has a much smaller grain size at 0.71 µm. Conspicuously this grain size correlates closely with scintillation values of the co-doped samples. The Mg sample shows a microstructure that is more rounded indicating that the Mg co-dopant may have been a better sintering aid when compared to the other dopants. From the findings in the previous section, it is still unclear if the scintillation phenomena in co-doped materials are more affected by the defect engineering or the microstructural changes. The next section should help to make the relation more clear as the focus will turn to the evaluation of a single co-dopant at varied compositions.

**Figure 4-13** SEM fracture surface of different co-doped samples of Lu with (A) Ca 1 atomic% at 2000x magnification and (B) Mg 1 atomic% at 6000x magnification.

### 4.6. Calcium Co-doping

Exploration of different levels of co-dopants was performed only on the Ca co-dopant. The decision to use Ca was due to other researchers relative success using this co-dopant as well as fairly simple size arguments presented in the previous section. It is
theorized that using a larger dopant species should preferentially occupy the S₆ site increasing the probability that the Eu activator ion would occupy the favored C₂ site and due to its superior spectroscopic properties should help to enhance the light yield of the scintillator.

As done in previous sections samples were co-precipitated, hot pressed, polished and oxidized prior to characterization. Ca co-dopant was added to the co-precipitate mixture in atomic ratios of 0.5%, 2%, 5%, 10% and 15% at the expense of the Lu host cation. Similar characterizations to previous experiments were done which included XRD, FS, RL, density, and SEM analysis. Additional testing of the microstructure was done using the energy dispersive spectroscopy (EDS) and wavelength dispersive spectroscopy (WDS) to evaluate co-dopant concentration along with any secondary phases for higher co-doped specimens. Finally to evaluate the effect of grain size independent of Ca dopant the Ca0.5 sample underwent a grain growth experiment. The sample was annealed in air for 96 hours at 1500°C and evaluated for RL and grain size in the same manner as the above samples.

For clarity the samples will be referred to by the nominal concentration of added Ca in the powder precipitate, for example, 0.5%, 2%, 5%, 10% and 15% Ca samples will be Ca0.5, Ca2, Ca5, Ca10, and Ca15 respectively.

4.6.1. Structural Results

Major results are summarized in Table 4-4. Figure 4-14 shows a photographic array of hot pressed and oxidized samples. Lower dopant level samples Ca0.5 and Ca2 samples were more translucent and yellowish colored than the higher dopant level
samples. Ca5, Ca10, and Ca15 samples were visually similar with a white appearance and translucent under back illumination. The change in translucency as Ca content increased would indicate that light scattering is more prevalent at higher concentrations. The two most likely scenarios include scattering from secondary phase precipitates found in the material or excessive porosity.

Table 4-4 Summary of results for different concentrations of calcium co-dopant species

<table>
<thead>
<tr>
<th>Nominal Ca (%)</th>
<th>Lattice Spacing (nm)</th>
<th>Density (g/cm³)</th>
<th>Radio-luminescence</th>
<th>Fluorescence (x10¹⁰)</th>
<th>C2/S6 Intensity Ratio (465 nm Ex)</th>
<th>C2/S6 Intensity Ratio (526 nm Ex)</th>
<th>Grain Size (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>1.0396</td>
<td>9.25</td>
<td>64</td>
<td>0.67</td>
<td>2.42</td>
<td>0.86</td>
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<td>1.0385</td>
<td>9.26</td>
<td>112</td>
<td>1.08</td>
<td>2.40</td>
<td>0.77</td>
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<td>5</td>
<td>1.0403</td>
<td>9.07</td>
<td>150</td>
<td>1.17</td>
<td>2.24</td>
<td>0.87</td>
<td>1.89</td>
</tr>
<tr>
<td>10</td>
<td>1.0392</td>
<td>8.95</td>
<td>202</td>
<td>1.43</td>
<td>2.51</td>
<td>0.79</td>
<td>6.52</td>
</tr>
<tr>
<td>15</td>
<td>1.0396</td>
<td>8.89</td>
<td>184</td>
<td>2.15</td>
<td>2.55</td>
<td>0.93</td>
<td>6.51</td>
</tr>
</tbody>
</table>

Figure 4-14 Photographic array of hot pressed samples with different nominal concentrations of calcium co-dopant. (A) Ca0.5, (B) Ca2, (C) Ca5, (D) Ca10, and (E) Ca15

Examination of select samples with WDS and EDS reveals that, despite the nominal doping levels, the detection of Ca within the bulk of the sample was lower than 77
expected based on the nominal addition of Ca. WDS analysis revealed that nominal powder preparation and subsequent hot pressing for Ca0.5 was less than the detection limit (~150 ppm) and for the Ca10 sample was 340 ppm Ca. Examination of the nominal Ca10 powder sample reveals that the powder had a higher Ca content near 4,000 ppm. It is apparent that both powder processing and hot pressing steps decrease the amount of Ca compared to the nominal concentrations.

As previous studies indicated, there is very little change between specimens when being characterized by XRD. All samples appeared to be single phased Lu$_2$O$_3$:Eu$^{3+}$ structure and lattice parameter measurements revealed that all samples were within 1% of the other samples with the Ca5 sample having the largest and Ca2 sample having the smallest lattice parameter at 1.0385 nm and 1.0403 nm respectively. This similarity in the lattice parameter seems to confirm that the level of co-dopant actually present within the sample is quite low and confirms the results from WDS, which indicate that the amount of Ca within the bulk is on the order of hundreds of ppm.

Density results consistently decreased with increasing Ca content. The decrease in density compared to theoretical can be attributed to an increase of porosity for the samples. This is supported by the macroscopic photographic array (Figure 4-14) in which the opacity of individual samples increased as Ca dopant was increased and the presence of voids in the SEM images. The porosity of samples has a very strong effect on light scattering within a material and samples of Ca5 and greater had between 2.6% and 4.6% 95.4% and 97.4% dense. While lower dopant levels less than or equal to Ca2 showed density greater that 99.25% making them more translucent.
The origin of the porosity in the samples was traced to the powder preparation. Higher concentration of co-dopant in the powder mixture agglomerated much easier and did not flow as easily as lower concentration Ca powders. Investigation of the co-precipitated powders was characterized using SEM (Figure 4-15). The micrographs of the powders reveal that powder particle size and agglomeration were larger at higher dopant levels of Ca. Lower dopant level particles (Ca0.5 and Ca2) were irregular while higher Ca dopants (Ca5, Ca10, Ca15) produced larger particles with high aspect ratio rods present. These large particles sizes and high aspect ratio elements pack very inefficiently and are likely the reason why the porosity is much higher in higher dopant samples.

![A B](image)

**Figure 4-15 Powder morphology of co precipitation process with (A) Ca0.5 and (B) Ca5 at 1000x magnification.**

SEM results are shown in Figure 4-16 and Figure 4-17 respectively. The character of each fracture surface seems to have similar morphologies. However, grain size is quite different across the Ca concentrations tested. At lower concentrations of Ca0.5, Ca2, and Ca5 the grain sizes were between 1.5 and 2.2 µm. Higher concentrations of Ca10 and Ca15 showed an elevated grain size near 6.5 µm. The increase in grain size can be attributed to the increase in powder particle size which was highlighted in the last section.
Additionally, at higher concentration Ca doped samples there is evidence of void formation in intergranular sites. These pores confirm earlier evidence of density measurements and indicate that increased Ca content promotes the formation of pores in the co-doped samples.

EDS line scans revealed that there is no discernible Ca concentration gradient within grains or in the grain boundary areas where there is not secondary phase present. However, in samples with Ca5 and above there are discernable secondary phases present in the grain boundaries. The secondary phase composition is confirmed by the use of EDS mapping in Figure 4-17. Ca EDS map are shown in green and it appears that dark areas on the secondary electron images are Ca rich. The Ca in this secondary phase seems to be replacing the Lu (yellow map) and should be expected to adversely affect scintillation due to scattering of light and charge trapping. These results of secondary phase identification confirm earlier suspicions, which concluded that translucency and color change at Ca5 and greater concentrations were microstructurally driven.
Figure 4-16 SEM fracture surface of different concentrations of calcium co-doped samples of Lu$_2$O$_3$:Eu$^{3+}$ with (A) 0.5% (B) 2% (C) 5% at 2000x magnification and (D) 10% (E) 15% at 1000x magnification.
4.6.2. Spectroscopic Results

RL and FS are summarized in Figure 4-18. It is apparent that the increase of Ca content in the samples is beneficial to the maximum intensity of RL at 611 nm. The best sample in terms of intensity and peak integration was the Ca10, which had a peak RL value 202 normalized counts. The addition of more Ca dopant to Ca15 sample decreased the RL and it can be assumed that the effect that Ca is having on the RL has reached a concentration threshold in which additional Ca becomes detrimental to the scintillation response.

FS revealed a similar trend to the RL, however, there was no maximum reached across the Ca concentration tested. The Ca15 sample was very efficient at producing scintillation when exposed to lower energy UV excitation. The two trends indicate that
although the increased Ca content may be advantageous for Eu activator efficiency it is not helpful for overall scintillation at a certain point. These findings would be consistent with decreased charge carrier migration efficiency to the luminescent centers under ionizing radiation. It appears that the addition of excess Ca and its compensating defects, as well as increasing amount of secondary phase, is inhibiting charge transfer and serving as trapping centers for charge carriers.

![Figure 4-18 Radioluminescence and fluorescence maximum emission of Lu2O3:Eu³⁺ vs. nominal concentration of calcium co-dopant.](image)

Site specific spectroscopy was also performed for the Ca samples and is shown in Figure 4-19 as a ratio of C₂/S₆ sites. 465 nm excitation results showed a significant C₂/S₆ increase when compared to the undoped specimens (C₂/S₆ (465) = 2.11) and a smaller positive correlation to Ca dopant percentage. The maximum C₂/S₆ ratio occurs for the Ca15 doped sample (C₂/S₆ (465) = 2.55), however, most of the change in ratio seems to occur for even small amounts of co-dopant. Remembering that the S₆ make up a fourth of
the cationic sites, the large jump in C₂/S₆ site ratios does not seem to be a simple argument of the population of S₆ sites being taken up by Ca co-dopant ions. Rather the evidence suggests that the addition of the co-dopant again seems to be inhibiting charge transfer between Eu activator ions. 526nm excitation spectroscopy results showed that as Ca content was increased there is a trend toward increasing C₂/S₆ ratio especially when you compare the co-doped results with an undoped Lu₂O₃:Eu³⁺ sample. These results seem to lend credence to the earlier observation that the increase in the C₂/S₆ ratio may be due to decreased charge transfer between Eu sites by the addition of Ca co-dopants inducing oxygen vacancies.

Figure 4-19 Site specific spectroscopy of Lu₂O₃:Eu³⁺ with different nominal concentration of calcium co-dopant. Pure Lu₂O₃:Eu³⁺ is included for comparison.

4.6.3. Grain Growth Results

As mentioned in section 4.6 a grain growth experiment was undertaken in order to try to isolate the relation of grain size and scintillation. It is known that within transparent ceramic samples grain size plays and important role in the propagation of light within a
ceramic solid. In short grain sizes very close to the wavelength of light being propagated are scattered very strongly and as the grain size becomes significantly larger or smaller than the propagating light the scattering is expected to be reduced. The Ca0.5 sample was chosen as a candidate because of its low overall scintillation value and it had a grain size that was closest to the characteristic wavelength of light (611 nm). The sample was annealed for 96 hours at 1500°C and SEM micrographs are shown in Figure 4-20. Examination of average grain size the sample was 1.54 µm prior to annealing and 6.11 µm after.

The grain size achieved in this experiment was very similar to higher Ca doped samples of Ca10 and Ca15. Scintillation and XRD of annealed specimen revealed that there was not a significant change in the phase or scintillation intensity. The effect mentioned above appears to be unimportant for the sample tested. The lack of initial transparency of the sample indicates that there are other more important light scattering factors that have a stronger effect, such as porosity and secondary phases, which are mentioned in the previous section.

![SEM images comparing the grain size of Ca0.5 (A) before 96 hour anneal and (B) after 96 hour anneal at 1500°C](image)

**Figure 4-20** SEM images comparing the grain size of Ca0.5 (A) before 96 hour anneal and (B) after 96 hour anneal at 1500°C
4.7. Conclusions

Investigation of the defect structure of Lu₂O₃:Eu³⁺ showed that oxygen defects had a significant effect on the scintillation of Lu₂O₃:Eu³⁺. Oxygen partial pressure studies revealed that increased scintillation occurred for samples subjected to increased oxygen partial pressures. This result did not show an optimum oxygen partial pressure for Lu₂O₃:Eu³⁺ as was hypothesized. The assumption that a reducing atmosphere would aid in the scintillation of Lu₂O₃:Eu³⁺ was based on results that indicated that oxygen interstitials are especially detrimental to scintillation by acting as hole traps. It was thought that by increasing the oxygen vacancy concentration to decrease the oxygen interstitial concentrations one could aid the scintillation response. However, in the large range of oxygen partial pressures tested (15 orders of magnitude) there was no maximum outside of the fully oxidized sample. This seems to indicate that the testing resolution was not high enough and additional oxygen partial pressure experiments using more oxygen partial pressures should reveal an optimum atmosphere for scintillation.

Site-specific spectroscopy for different oxygen partial pressures revealed that decreasing oxygen partial pressure was associated with increased C₂/S₆ intensity ratio. This increase C₂/S₆ intensity ratio is thought to occur because of oxygen vacancies interrupting charge transfer between activator sites.

Aliovalent co-doping strategies were explored and revealed that 1% co-doping of Ca²⁺ and Mg²⁺ produced similar site effects to the reducing atmosphere from oxygen partial pressure experiments. Due to low dopant levels compared to S₆ sites, it is assumed that site fraction of Eu activator ions remains relatively unchanged when compared to
undoped samples and it appears that oxygen vacancies decrease the charge transfer between Eu activator ions. Despite the increase in C$_2$ site ratio, the scintillation results did not increase when compared to pure Lu$_2$O$_3$:Eu$^{3+}$.

Further investigation of varying levels of Lu$_2$O$_3$:Eu$^{3+}$ co-doped with Ca ions revealed that despite high doping levels only a fraction of the Ca actually was present within the hot pressed sample bulk, near 350 ppm for Ca10 samples. Despite this low dopant level, there was a strong trend toward increasing scintillation across the range of nominal Ca concentration, which reached a threshold for Ca10, after which the scintillation decreased in the Ca15 sample. SEM results revealed that samples above Ca5 were more porous and showed evidence of secondary Ca-rich phase as well as grain sizes, which increased with Ca co-dopant concentration. Grain growth experiments reveal that the scintillation is independent of grain size for Ca0.5 sample.

From the results above it appears the Ca doping to increases scintillation in hot pressed samples was successful. These effects reach a maximum at Ca10 due to reduced oxygen interstitial populations, however, dopant level tested above Ca10 showed a reduced response due to unfavorable microstructure elements such as secondary phases and porosity. It appears that maximum scintillation in the Ca10 samples is due to better scintillation characteristics while maintaining an acceptable level of porosity and secondary phases. This is promising and provides an interesting starting point for the addition of co-dopant in a thin film for high-resolution scintillation.
Chapter 5

5. PVD of Lu$_2$O$_3$:Eu$^{3+}$ Co-doped with Calcium

Lu$_2$O$_3$:Eu$^{3+}$ thin films were fabricated using high temperature PVD coating parameters (Chapter 3) and aliovalent doping strategies (Chapter 4). Co-precipitated powder with cationic ratios of Lu (85%), Eu (5%), and Ca (10%) were prepared using the same process laid out in Chapter 4. After powder production, target and substrate preparations for deposition were similar to section 3.2.

Films were deposited using parameters from previous depositions runs. Substrates were coated for 10 hours with 75 W of power, 775°C substrate temperature, 10 mtorr of pressure, and a flow rate of 200 sccm of argon with trace amounts of oxygen (375 ppm).

Deposited films were evaluated using a weight loss thickness measurement, profilometry, XRD, SEM, EDS, WDS, FS, and RL measurements. Profilometry measurements for thickness and surface roughness, XRD were utilized to deduce crystal structure, SEM for the topology of coatings, WDS and EDS for the composition and FS and RL for spectroscopic characterizations.

5.1. Deposition Results

Results are summarized in Table 5-1. The deposition produced films that were clear and scintillated under UV excitation. Deposition rates were slightly decreased when compared to deposition without Ca in the target and due to this, the thicknesses were slightly less than films previously tested. The thickness of the films were between 6.6 and 6.2 µm. Surface roughness measurements reveal that the (100) sample had a
rough surface which was over 3 times as rough as the other films on the (110) and (111) samples.

Table 5-1 PVD 52 deposition of Lu₂O₃:Eu³⁺ co-doped with Ca

<table>
<thead>
<tr>
<th>Substrate Orientation</th>
<th>Thickness (µm)</th>
<th>Coating Rate (µm/hr)</th>
<th>UV Luminescence</th>
<th>Surface Roughness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(100)</td>
<td>6.6</td>
<td>0.66</td>
<td>✓</td>
<td>23.6</td>
</tr>
<tr>
<td>(110)</td>
<td>6.6</td>
<td>0.66</td>
<td>✓</td>
<td>7.4</td>
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<tr>
<td>(111)</td>
<td>6.2</td>
<td>0.62</td>
<td>✓</td>
<td>6.8</td>
</tr>
</tbody>
</table>

XRD of films revealed a strong texture within each of the samples as was noted in Section 3.2.2. The films were observed to be oriented along the same lattice plane as the underlying substrate material. The topography of PVD films shown in Figure 5-1 reveals that the surface of the growing film looks to be similar to Lu₂O₃:Eu³⁺ undoped films. The films were observed to have very fine grain structure less than 1 µm with no evidence of void formation. Similar to earlier depositions these films also displayed island-like growth modes that were attributed to an SK growth mechanism. The (110) substrate had rather large nodules growths on the surface. EDX analysis revealed that these nodules were significantly richer in Ca than the bulk of the material. Although this only occurred on the (110) sample it is not surprising due to the presence of such phases within the hot pressed samples with elevated nominal Ca co-dopants. WDS of the (111) substrate revealed that the coating had a Ca content around 550 ppm, which was considerably more than the Ca10 hot pressed sample despite similar powder preparations.
Table 5-2 Spectroscopic summary for calcium co-doped Lu$_2$O$_3$:Eu$^{3+}$ films prepared by PVD RF magnetron sputtering.

<table>
<thead>
<tr>
<th>Deposition</th>
<th>Dopant</th>
<th>Fluorescence (x10$^9$)</th>
<th>C2/S6 (241 nm Ex)</th>
<th>Radioluminescence (8keV) (A.U.)</th>
<th>Radioluminescence (60keV) (A.U.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(100)</td>
<td>Ca</td>
<td>4.11</td>
<td>1.63</td>
<td>0.62</td>
<td>0.56</td>
</tr>
<tr>
<td>(110)</td>
<td>Ca</td>
<td>3.70</td>
<td>2.68</td>
<td>0.87</td>
<td>0.75</td>
</tr>
<tr>
<td>(111)</td>
<td>Ca</td>
<td>3.72</td>
<td>2.17</td>
<td>0.96</td>
<td>1.00</td>
</tr>
</tbody>
</table>

Results of RL and FS for the three substrate orientations are summarized in Table 5-2. Comparison of Ca co-doped Lu$_2$O$_3$:Eu$^{3+}$ films with un-doped Lu$_2$O$_3$:Eu$^{3+}$ are summarized in Figure 5-2. RL measurements were done using the 8 keV source and the raw results were normalized for thickness of the coating in order to compare scintillation...
efficiency across films of different thicknesses. The Ca co-doped films showed a slightly depressed scintillation value when compared to un-doped samples for (110) and (111) substrates and an increased response of the (100) sample. However, the increased value of the (100) still fell well below the best co-doped sample. Characterization of RL for higher energies was tested for un-doped samples using of RNPSD and these measurements were used to extrapolate the raw scintillation of co-doped samples. The extrapolation of raw scintillation is then normalized to the thickness of the sample using the attenuation of Lu$_2$O$_3$ at 60 keV. These calculations predicted that at higher energies the normalized scintillation for Ca doped samples should have better light yield than un-doped films.

Site-specific spectroscopy reveals that the intensity ratio of C$_2$/S$_6$ was increased across all of the Ca co-doped samples. This trend followed previous observations (Chapter 4) implying that Ca increases the amount of oxygen vacancies within the host lattice which leads to decreased charge carrier transfer between activator ions. FS of the 610nm peak was increased by the addition of Ca, which can be correlated to increased activator efficiency. These results are promising and show that Ca co-dopant can be effective at changing the defect structure of the Lu$_2$O$_3$:Eu$^{3+}$ resulting in a predicted enhancement of scintillation light yield.
Figure 5-2 Comparison of Lu₂O₃:Eu³⁺ with and without Calcium co-dopant. (A) is the Radioluminescence for 8 keV excitation, (B) Radioluminescence for 60 keV excitation, (C) C₂/S₆ site ratio, and (D) fluorescence.
Chapter 6

6. Conclusions

Lu$_2$O$_3$:Eu$^{3+}$ has been established as a promising scintillator material with properties that are advantageous when compared to other scintillators such as CsI:Tl. Lu$_2$O$_3$:Eu$^{3+}$ has been shown to have excellent stopping power, with good light yield, and good spectral matching to modern photodetectors. These characteristics make Lu$_2$O$_3$:Eu$^{3+}$ an attractive new material for use in medical imaging such as mammography as well as for use in high-resolution, digital X-ray imaging systems. However, improvements are still needed for Lu$_2$O$_3$:Eu$^{3+}$ to become competitive with current state of the art scintillators and in the preceding studies the enhancement of light yield for Lu$_2$O$_3$:Eu$^{3+}$ was undertaken. Promising results were achieved by utilizing a combination of PVD processing and manipulation of oxygen defect structure in Lu$_2$O$_3$:Eu$^{3+}$.

6.1. Physical Vapor Deposition of Lu$_2$O$_3$:Eu$^{3+}$ Films

High temperature deposition parameterization of Lu$_2$O$_3$:Eu$^{3+}$ was undertaken using RF magnetron sputtering. Results characterized by FS indicated that depositions at 75 W, 10 mtorr, and 800°C substrate temperature were superior to other deposition parameters. SEM micrographs revealed a change in growth mode when moving for low to high temperature dispositions, and all depositions were highly textured and matched the orientation of the underlying YSZ substrate material. Grain growth of the film was successful at 1500°C for 10 hours but did not yield significant differences in light yield for the samples tested.
Utilizing the optimized results from RF magnetron sputtering studies a comparison of RF and PLD modalities was undertaken. Characterization of light output by RNPSD measurements revealed that high temperature RF films were superior to those obtained using PLD. RF films had a maximum light output of 23,000 photons/MeV. X-ray imaging defects were present in all samples, however, RF samples had a lower density of defects than the PLD samples. For these two reasons, it appears that RF magnetron sputtering of Lu₂O₃:Eu³⁺ is better suited for X-ray imaging applications.

6.2. Oxygen Defect Structure Manipulation of Lu₂O₃:Eu³⁺

Manipulation of anionic defect structure in similar systems to Lu₂O₃:Eu³⁺ has been shown to improve scintillation response. Confirmation of these studies was explored for hot pressed samples of Lu₂O₃:Eu³⁺ via controlled atmosphere annealing and use of extrinsic co-doping with Ca and Mg.

The controlled atmosphere experiment established the importance of oxygen defect structure within Lu₂O₃:Eu³⁺ and showed that fully oxidized samples were preferred for light output. RL and FS revealed that light output was positively correlated with oxygen partial pressure of individual annealing experiments. Site-specific spectroscopy revealed that oxygen vacancy formation was responsible for decreased charge transfer between Eu activator sites.

Initial co-doping of Lu₂O₃:Eu³⁺ was done using 1% Ca and Mg. Hot pressed samples showed that Mg doped samples had high translucency which was due to the small uniform grain size of the samples. By comparison, Ca samples were less translucent and had large grain sizes. RL results revealed that undoped Lu₂O₃:Eu³⁺
showed better light yield followed by Mg and then Ca samples. Site-specific spectroscopy revealed that both co-dopants had a similar effect of reducing the charge transfer between Eu sites due to oxygen vacancy formation.

Further investigation of Ca doped Lu$_2$O$_3$:Eu$^{3+}$ showed that increasing concentration of Ca within the hot pressed samples reduced the translucency of the compacts. The reduction in translucency was correlated to decreased density in high concentration samples. Higher concentration samples had elevated grain size near 6 micrometers, which were attributed to larger powder particle sizes. Spectroscopic results revealed that a maximum of RL was reached for the 10% nominally co-doped Ca sample, which had 340 ppm of Ca was in the bulk of the sample. This was well below the intended doping level and it is apparent that the co-precipitation and subsequent hot pressing steps did not fully incorporate Ca in to the structure. As in the previous experiments site specific spectroscopy revealed that for increasing Ca there was a decrease in the overall charge transfer between Eu activator sites which was due to oxygen vacancy formation.

6.3. Calcium Co-doped Lu$_2$O$_3$:Eu$^{3+}$ Films

PVD optimization and defect structure manipulation results were used to create a Ca co-doped Lu$_2$O$_3$:Eu$^{3+}$ film. Preliminary deposition results were promising and revealed that small additions (around 550 ppm) of Ca resulted in higher FS measurements and reduced charge transfer between Eu activator sites as with previous experiments. From these results, it is very likely that we have successfully incorporated additional oxygen vacancies within the structure. RL for 8keV excitation revealed similar light yield
between Ca co-doped and un-doped samples. However, extrapolation to higher energy regimes at 60keV predict that Ca co-doped depositions should outperform undoped films, with a predicted light yield increase of greater than 14% when compared to analogous undoped Lu₂O₃:Eu³⁺ films.
Bibliography


