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Zone Refining of Raw Materials for Metal Halide Scintillator Crystal Growth

Thomas Williams McAlexander

University of Tennessee - Knoxville, tmcalexander08@yahoo.com

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I am submitting herewith a thesis written by Thomas Williams McAlexander entitled "Zone Refining of Raw Materials for Metal Halide Scintillator Crystal Growth." I have examined the final electronic copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Materials Science and Engineering.

Mariya Zhuravleva, Major Professor

We have read this thesis and recommend its acceptance:

Chuck Melcher, Claudia Rawn

Accepted for the Council:

Carolyn R. Hodges

Vice Provost and Dean of the Graduate School

(Original signatures are on file with official student records.)
Zone Refining of Raw Materials for Metal Halide Scintillator Crystal Growth

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Thomas Williams McAlexander
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ABSTRACT

In recent years, scintillators have been researched for homeland security applications where properties such as high light output and low energy resolution are required for efficient gamma ray spectroscopy. Several promising scintillators, including SrI₂ [Strontium Iodide], CsSrI₃ [Cesium Strontium Iodide], and KSr₂I₅ [Potassium Strontium Iodide] are activated with EuI₂ [Europium Iodide]. The quality of EuI₂ raw material is generally poor and inconsistent as-received from the manufacturer. Material purity is known to affect its scintillation performance, and so purification processes have been investigated to improve the performance of Eu-doped [Europium-doped] scintillators. In this work, zone refining is explored as a method to purify EuI₂ while ICP-MS [Inductively Coupled Plasma Mass Spectroscopy], DSC [Differential Scanning Calorimetry], and scintillation performance are used to determine the effectiveness of the treatment. It is seen that zone refining results in effective purification of the material at the center of the charge, as expected. Comparison of the light output and energy resolution of the as-received EuI₂ with that of EuI₂ from each of the refining batches indicates that refining EuI₂ greatly improves the performance of the material. Based on experience gained during this investigation, a miniature zone refining furnace was designed and constructed to enhance future refining efforts.
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CHAPTER I
INTRODUCTION TO SCINTILLATORS AND IMPURITIES

1.1 – Applications of Scintillators

1.1.1 – Requirements for Homeland Security

Since the discovery of NaI:Tl in the late 1940s, inorganic scintillators have been commonly used as radiation detectors [1]. Scintillators are materials which absorb high energy radiation such as gamma rays and x-rays, emitting photons of visible light in response that can then be converted into an electrical signal by a photodetector. This class of materials has applications in a variety of fields, including medical imaging, natural resource exploration, high energy physics, and homeland security. For homeland security applications, they are commonly used in radiation detectors found at border crossings, airports, shipyards, and other transportation hubs. Modern security concerns have necessitated the detection of high energy radiation on a large scale to identify nuclear threats while minimizing false alarms. These recent demands have sparked interest in the development of high performance scintillators capable of commercialized production [2].

To prevent illegal transport of radioactive material, it is necessary to detect the minute amounts of radiation which may escape from a shielded container. To increase the likelihood of producing a significant signal, the detector must emit a large number of photons after interaction with ionizing radiation. The resulting parameter, light output, is described in terms of the number of photons emitted per unit energy absorbed. In this context, scintillators with a high light output are more advantageous as they produce a scintillation pulse which is easily distinguished from the background.

Energy resolution is a derived parameter which quantifies the material's ability to discriminate between gamma rays with similar energies. The energy resolution is
defined as the full width of the full energy peak at half of its maximum divided by
the centroid position of the peak. In contrast to the light output, a smaller value of
energy resolution is desirable as it corresponds to a small variation in the energy
of emitted photons. This is important as it allows the detector to more effectively
distinguish between radionuclides likely to be used in a nuclear attack such as
$^{253}\text{U}$ and $^{240}\text{Pu}$ and those used in medical procedures.

It is not always easy to differentiate between the energies associated with these
two types of radioactive material. A common radioisotope used in medical
diagnostics is $^{99m}\text{Tc}$ [3] which has a half-life of ~6 hours and produces a gamma
ray with an energy of 140.511 keV [4]. This energy is within 45 keV of ~75% of
the gamma rays produced during the decay of $^{235}\text{U}$ [4], which is used in nuclear
weaponry. As seen in Figure 1, the spectroscopic capabilities of different
detectors vary widely and depending on the energy resolution of the detector,
possibly may lead to the gamma ray signature of these two isotopes being
confused. This comparison highlights the need for low energy resolution in
spectroscopic applications where the occurrence of false positives needs to be
minimized.

![Gamma-Ray Spectra of Natural Background](image)

Figure 1 - Comparison of Detector Resolution for Background Radiation [5]
1.1.2 – Current Detector Standards

The current benchmark scintillator is NaI:Tl, which has been heavily researched in the nearly 70 years since its discovery. This material is capable of being grown in boules over 500 mm in diameter without cracking. These large crystals can then be used in gamma cameras 500 x 600 x 10 mm in size [6]. This material is also very cheap, costing approximately $2/\text{cc}$, which allows for very cost effective, large scale detectors, especially when compared to other popular scintillators such as LSO:Ce (~$100/\text{cc}$) and LaBr$_3$:Ce (~$500/\text{cc}$) [7].

The highly desirable cost and crystal yield of NaI:Tl is not without any drawbacks, however. This material has a light yield of 37700 ± 5000 photons/MeV as reported by Holl, et al. [8]. This is much lower than what is reported for several more recent materials such as SrI$_2$:Eu and LaBr$_3$:Ce which have reported light yields as high as 110,000 ph/MeV and 60,000 ph/MeV, respectively [9], [10]. At 7% resolution for 662 keV gamma rays, NaI:Tl has an energy resolution that is inferior to these two materials as well [11]. SrI$_2$:Eu has a reported energy resolution for 662 keV gamma rays of 2.7%, while Sr$^{2+}$ codoped LaBr$_3$:Ce has been reported recently as having an energy resolution of 2.0% [9], [12].

For instances where the spectroscopic capability of the detector is the only concern, the material of choice is a semiconductor: high purity germanium (HPGe). This detector material provides an unparalleled 0.2% energy resolution at 662 keV [13]. This outperforms all current scintillators, but has a few detriments which keep it from being used in all situations. Because of the small size of its band gap, 0.7 eV, HPGe requires cryogenic temperatures to operate effectively [1]. When operated at room temperature, the thermal noise is sufficient to destroy the resolution of the detected signal. The other issues are related to material processing and availability.

Germanium detectors must be made from very pure raw materials to ensure that any electrons or holes which contribute to the current through the material are a
result of interaction with radiation. To this end, the material which is used in germanium detectors has an impurity concentration near $10^{-6}$ ppm, which is very difficult to achieve commercially [14]. This purity is the major source of the final problem: price. The amount of work necessary to produce the material with the requisite purity, and then grow it into a single crystal for use in a detector means the final product is expensive enough to prohibit large-scale implementation. The resulting price for HPGe instruments can be prohibitively expensive as a result, costing over $130,000 for one instrument [14].

More recently, scintillators such as LaBr$_3$:Ce and SrI$_2$:Eu have been a major focus of research efforts to replace NaI:Tl as the next generation of detectors used for low cost gamma ray spectroscopy [15]. As mentioned previously, both of these scintillators have high light outputs and excellent energy resolution compared to NaI:Tl, though they each have challenges to overcome. A major drawback of LaBr$_3$ is the presence of $^{138}$La. This isotope emits gamma radiation with energies 788.7 keV and 1435.8 keV which may interfere with certain measurements [4]. It also tends to crack during growth, making large single crystals difficult to obtain [16]. This limits the obtainable crystal yield and increases the cost of a detector. For SrI$_2$:Eu, the major problem is the relatively long decay time characteristic of Eu$^{2+}$-activated scintillators, in this case 670 ns [17]. Both materials are also hygroscopic. Packaging technology has advanced enough to allow encapsulation of both materials to protect them for an extended period of time. This does not, however, prevent the need for careful handling of the material during growth and processing which hinders these scintillators ability to be easily scaled to industrial production capacities.
1.2 – Impurities in Scintillators

1.2.1 – Intentional Impurities

In scintillators, intentional impurities are generally either activators or codopants. When an impurity is intentionally added to a scintillator, it is said to be doped with that element. Some materials are intrinsic scintillators and don’t require an activator. Other materials require the addition of an activator which creates energy levels in the host material’s band gap capable of producing a photon of visible light. Examples include Tl⁺, Eu²⁺, Ce³⁺, and Pr³⁺, though others exist.

The second class of intentional impurity, the codopant, is commonly used to tune the physical and scintillation properties of a material. By adding Ba²⁺ to CsSrI₃, it has been seen that the hygroscopicity of the scintillator decreases. Over a period of 2 hours, the amount of water absorbed by the sample is cut in half for high levels of Ba-doping [18]. A crystal’s scintillation properties are typically more sensitive to codoping. Recently it has been seen that adding 200 ppm of Sr²⁺ to LaBr₃:Ce greatly improves the energy resolution of the scintillator from 2.9% to 2.0% [19], [12].

1.2.2 – Unintentional Impurities

Just as impurities may be added to a scintillator to improve its properties, impurities may be present in the material as residue from the manufacturing process or as a result of contamination. There are two main classes of impurities in metal halide scintillators: adsorbed gases and metallic impurities.

Adsorbed Gas Impurities

Metal halide materials are characteristically hygroscopic, i.e. they absorb or adsorb moisture from their surroundings. Because of this, sorption of water vapor is a major concern in the preparation and handling of metal halide materials. Any contact with atmosphere results in the sample taking up moisture, resulting in
sample degradation as it dissolves in its absorbed water. Similarly, oxygen contamination is a major issue as it reacts with many metal halide compounds to form either oxides or oxyhalides such as perchlorates and iodates. In an effort to minimize atmospheric contamination, many metal halide materials are grown using the Bridgman technique which allows the material to be directionally solidified in a sealed container. By virtue of this sealed environment, any impurities or contaminants which are present when the ampoule is sealed are trapped. Since oxides and oxyhalides typically melt at a much higher temperature than the associated metal halide salts, atmospheric contamination make it difficult to produce a single crystal as the oxide and oxyhalide particles act as nucleation sites for competing grains.

In addition to atmospheric exposure, gaseous impurities are also found in metal halides due to incomplete reaction. Commonly, metal halides are manufactured by reaction of oxides or carbonates with acids, yielding the metal halide salt and some combination of oxygen, carbon dioxide, and water [20], [21]. An example reaction is shown as Equation 1, from which it may be seen that the reaction is in equilibrium. If there is an excess of hydriodic acid being passed over the solid, the equilibrium is shifted to the right side. This works against the system when water vapor is present in small amounts.

\[
\text{Equation 1 - Ion Exchange Synthesis for Divalent Iodide from Oxide}
\]

\[
+ 2 \quad + \quad ( )
\]

When water is present in large amounts, metal halides will dissolve due to their natural deliquescence. Smaller amounts of water can drive the formation of the oxide form of the metal as seen in Equation 1, or the formation of oxyhalides or hydrides when heat is applied. Several of the lanthanide halides have multiple
stable valences. It has been reported that lanthanide halides such as EuI$_2$ can be made to change valence depending upon the surrounding atmosphere. An oxidizing atmosphere will stabilize the trivalent halide state; a reducing atmosphere will stabilize the divalent halide state \[22\]. The stability of the Eu$^{2+}$ salt is of concern from a scintillation perspective.

Divalent Europium is favored for metal halide scintillators due to the bright interconfigurational luminescence of the allowed 5d-4f transition as well as the alignment of its peak emission wavelength of $\sim$440nm to the peak detection wavelengths of standard photomultipliers \[23\]. The divalent and trivalent forms of Europium differ fundamentally in their scintillation characteristics. The scintillation decay of Eu$^{3+}$ is approximately 1000 times slower than the $\sim$1 $\mu$s decay intrinsic to the de-excitation of Eu$^{2+}$, a speed already much slower than other common activators such as Ce$^{3+}$. Additionally, the peak emission wavelength of Eu$^{3+}$ activated materials of $\sim$610 nm is too long for effective detection by common bialkali-type photomultiplier tubes \[24\].

**Metallic Impurities**

Though metallic impurities may be beneficial in controlled quantities, unregulated they may have a negative impact on the properties of scintillators. Much like adsorbed gas impurities, these impurities are the result of their handling errors or manufacturing deficiencies. These impurities may be the result of residual components of the parent ore from which the material was originally derived. Rare earth halides are derived from ores in which many of lanthanide elements are present \[25\].

The effects of metallic impurities can be similar to those caused by the presence of oxides and oxyhalides. In general, metallic impurities are much more likely to dissolve into the molten salt but there are cases where the impurity may remain solid in the melt, creating a nucleation site for secondary grain growth. These situations are more common when the halide component is different, as is the
case when a chloride is present in an iodide-based melt. When the metallic contaminant is incorporated into the melt, the matrix will be stressed as a result of the lattice mismatch caused by its integration into the solid. Depending on the severity of the mismatch, this strain may be forcibly released as a crack upon cooling, especially if the strain field interacts with similar defects. It is also possible that a crack which forms elsewhere is enlarged by the impurity in an effort to lower the total system energy [26]. Even in cases where the cracking behavior is not exacerbated by the impurity content, cracking behavior is still heavily influenced by it. For example, Kermode, et al. has reported that cracks can also be deflected by individual impurity atoms if the bond strength is sufficient [27].

The scintillation mechanism is heavily dependent upon the impurity content of the material. Depending upon the material system and impurity, scintillation may be adversely affected by luminescence quenching and charge defect formation. A literature search will provide insight into results for a specific system, as many groups have published studies on the effects of codoping in different matrices. A variety of lanthanide, alkali and transition metal elements have reported optical transitions which offer radiative de-excitation pathways for excitons. Such elements include not only common activators such as Ce$^{3+}$ and Eu$^{2+}$, but also elements such as Na$^+$, In$^+$, Pb$^{2+}$, and Yb$^{3+}$ [28].

When radiation interacts with a crystal, it produces electrons and hole which recombine to produce a scintillation photon. By having multiple activators in the same material, each luminescence center must compete for these electrons and holes. This competition results in neither site yielding a large number of photons per MeV absorbed by the crystal, effectively quenching the light output. In some instances, activators may cause mutual quenching by capturing different charged particles, preventing their recombination as is the case when Ce$^{3+}$ and Yb$^{3+}$ are present in the same matrix. Additionally, it is possible for luminescence to be
quenched through metal-metal charge transfer as seen in tungstates and vanadates doped with Ce$^{3+}$ [23]. The formation of charge defects can affect the scintillation properties in a very similar manner. By introducing aliovalent impurities, the charge balance of the crystal is perturbed, resulting in the addition of charge defects such as F centers and V centers that trap electrons and holes, respectively [29].

**Impurities in EuI$_2$**

The impurity content of EuI$_2$ is known to vary widely from batch to batch. Table 1 shows several common impurities in EuI$_2$ as detected in 4 different batches of material by the manufacturer, Sigma Aldrich. Elements with a range were reported in at least 2 material batches. Elements with a single value were either detected in only one batch, or were found in multiple batches in the same concentration. Determination of H$_2$O/OH$^-$ and O impurities is not performed on every batch and so the values listed are for a single batch, but are expected to be similar in other batches.

<table>
<thead>
<tr>
<th>Impurity</th>
<th>Concentration (ppm)</th>
<th>Impurity</th>
<th>Concentration (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>1.7-7.3</td>
<td>La</td>
<td>0.3</td>
</tr>
<tr>
<td>Ag</td>
<td>0.3</td>
<td>Na</td>
<td>0.5-0.8</td>
</tr>
<tr>
<td>Ba</td>
<td>0.3-1.1</td>
<td>Pb</td>
<td>0.2</td>
</tr>
<tr>
<td>Bi</td>
<td>0.2-1.8</td>
<td>Se</td>
<td>0.7-2.2</td>
</tr>
<tr>
<td>Cs</td>
<td>0.1</td>
<td>Sn</td>
<td>0.4</td>
</tr>
<tr>
<td>Cu</td>
<td>0.4-1.2</td>
<td>Sr</td>
<td>0.6-0.8</td>
</tr>
<tr>
<td>Fe</td>
<td>1.1-4.6</td>
<td>Th</td>
<td>0.2</td>
</tr>
<tr>
<td>Hg</td>
<td>0.2</td>
<td>Tl</td>
<td>0.5</td>
</tr>
<tr>
<td>K</td>
<td>3.1</td>
<td>W</td>
<td>0.5</td>
</tr>
<tr>
<td>H$_2$O/OH$^-$</td>
<td>16</td>
<td>O</td>
<td>82</td>
</tr>
</tbody>
</table>
As mentioned in the previous section, the presence of multiple impurities with optical transitions can quench luminescence through activator competition. Impurities such as Ag and Bi are known to facilitate scintillation in appropriate matrices [23], but Ti$^+$ and Pb$^{2+}$ have been reported by Novosad, et al. alongside Eu$^{2+}$ as being capable of effectively activating CaI$_2$. The authors do note that there is overlap between the thermoluminescence spectra which indicates that not all of the traps are directly related to the dopants. They posit that the cation impurities and intrinsic defects form complexes which act as hole traps, producing the measured spectra [30]. For effective activation of an iodide scintillator with Eu$^{2+}$, it is necessary that the concentration of these competitive impurities be minimized.

Lead impurities are seen to degrade the energy resolution, as reported by Shulz and Breiter. They report that lead impurities in the crystal create an absorption band at ~359 nm, near the maximum emission wavelength for NaI:Tl. The result of this is that the intensity of the scintillation light varies depending upon where in the crystal the scintillation photon is produced and how far it must travel before reaching the photodetector. For an 8 inch diameter by 8 inch tall NaI:Tl crystal, they measure an energy resolution of ~8% at 1.84 MeV versus the 4.5% typically measured for smaller crystals, which they attribute solely to lead impurity effects [31].

Impurities not associated with an optical transition must still be removed. As part of the effort to improve the scintillation properties of SrI$_2$:Eu, Nishimoto, et al. has recently published a study on the effects of codoping SrI$_2$:Eu with three different trivalent lanthanide elements, including one of the impurities reported in Table 1, lanthanum. Samples of SrI$_2$ were prepared with 7.5% Eu$^{2+}$ doping and 1% RE doping. The results of their study indicate that codoping with lanthanum decreases the light output by between 7% and 28%, depending on the actual incorporation of La. The energy resolution was likewise seen to suffer, more than doubling the 2.7% resolution of SrI$_2$:Eu for most samples [32].
In addition to the examples above, many of the impurities found in EuI₂ have stable oxidation states other than the divalent state of the matrix. This indicates that though they would likely conform to the divalent configuration, the possibility exists that they would be incorporated as an aliovalent impurity. A model has been proposed by Li, et al., in which the nonproportionality, and by extension the energy resolution, of a scintillator is directly affected by the free carrier mobility. Through the introduction of aliovalent impurities, charge traps such as F and V centers are incorporated into the crystal. These traps affect charge carrier mobility by either brief detention or complete entrapment of the carrier, and by limiting carrier movement they preferentially segregate charges, leading to nonlinearity of the light yield by preventing recombination [33].

1.3 – Techniques for Impurity Detection

1.3.1 – Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) is a thermal analysis technique which measures heat flow into a sample with respect to a reference. This technique is widely used to determine phase purity and to evaluate temperature-dependent transformations [34]. The measurement is performed by loading material into a crucible and then increasing its temperature. The heat flow required to increase the sample's temperature relative to a reference crucible is then recorded as a function of temperature. For every experiment, a baseline measurement is first performed with an empty crucible. This baseline is later subtracted to negate any effects from the crucible. Thermodynamics predicts that phase transitions and chemical reactions occur because of a change in the free energy of the system. This energy change is measured in the system as heat flow, providing quantitative information about the heat of transformation as well as the associated temperatures.
By convention, heat flow values are positive if heat is being released by the sample, i.e. the process is exothermic. Similarly, endothermic processes require heat to be absorbed by the sample and are presented as negative values. Phase transitions are typically reversible processes, and so occur in pairs as seen in Figure 2. Since the enthalpy of the transformation is constant, paired peaks should have similar heats of reaction, represented by the area under the curve.

Figure 3 shows the method used here to determine peak onsets, which is taken as the transformation temperature. A baseline is constructed across the peak base and the leading edge of the peak is extrapolated and the intersection of the extrapolation and the baseline is recorded as the onset temperature [35].
During crystal growth, scintillation materials are subjected to a range of temperatures as the charge is melted and then slowly solidified. The thermal environment produced during DSC emulates the growth process and provides a look at the thermodynamics affecting the material during solidification. DSC is also extremely sensitive to minor changes in the composition or temperature profile, able to detect heat flow with microwatt precision and temperature differences as small as 0.01°C [36]. For this level of resolution, it is necessary to scan at very slow rate, ~1-5 K/min. Depending on the melting point of the material and the thermal profile desired, this may cause the total measurement time to be 24 hours or more for one complete measurement.

Though DSC is a powerful tool, it has its limitations. The high sensitivity that allows the DSC to detect minute changes in heat flow also renders it sensitive to outside disturbances such as cell phone interference, RF generators, and vibrations. It is also not possible to interpret DSC scans without some outside knowledge of how the material behaves, even if this is purely anecdotal. Due to sample volatility, it is necessary to at least have an estimate of the melting temperature before measurement of metal halides is feasible [37].
1.3.2 – *Inductively Coupled Plasma Spectroscopy*

Inductively coupled plasma (ICP) spectroscopy is a set of techniques used to determine trace impurities in solid and liquid samples. Variations in the technique are based upon the detection modality, either by mass (MS) or emission energy (OES). Both processes begin by aspirating a solution in which the sample has been dissolved through plasma, usually composed of argon. This plasma treatment forcibly ionizes even the most stable molecules and atoms. Figure 4 displays a schematic of the aspiration and ionization process. After ionization, the differences between the methods become important.

For ICP-OES, the energy emitted by the ions as they de-excite is detected by a photodetector. As energy levels of each element are unique, the light emitted as ions de-excite is characteristic of the elemental species present. By examining the wavelengths of light produced after ionization and their ratios, it is possible to determine what elements are present and quantify their concentration when compared to known standards. ICP-MS instead looks at the mass-charge ratio of ions. ICP-OES is the preferred technique in situations where the mass-charge ratio of the analyte coincides with a background species, such as argon or oxygen. Conversely, ICP-MS is preferred when background interference prevents a clear signal in ICP-OES. Since the two measurements operate on similar principles, the choice between the two depends on what is being measured.

![Figure 4 - Schematic of Sample Aspiration in ICP Spectroscopy](image_url)
The exact manner of mass detection used in ICP-MS varies according to the type and design of the mass separator. After mass separation, the ions are converted to an electrical signal through interaction with an element called a discrete dynode detector. This instrument functions in much the same way that a photomultiplier tube does. The charge of the ion is converted to electrons at the first dynode which are attracted to the next dynode, increasing in number at each subsequent dynode. In this way, ICP-MS is generally capable of detecting elemental concentrations across ~8 orders of magnitude, from ppt levels up to hundreds of ppm levels [38]. Detection limits of each element are displayed in Figure 5.

![Figure 5 - Periodic Table Showing Detection Limits of the Elements by ICP-MS [38]](image)

Data obtained from ICP spectroscopy is meaningful only when calibrated against known reference samples. Without this comparison, it is impossible to quantify the
concentrations of trace elements as each ion response is unique. In the case of ICP-MS, data analysis is often tricky as the mass-charge ratios for multiple species may overlap. In this case it is necessary to use a multi-peak analysis to determine elemental concentrations. As each element has a natural distribution of isotopes, Figure 5, it is possible to use the known distribution of isotopes to deconvolve any overlapping peaks by comparison with isolated peaks from other isotopes of the same element. It should be noted, however, that this is only possible in samples which have not been specifically enriched with a specific isotope [39].

The primary advantage of ICP spectroscopy is the fast acquisition of quantitative impurity concentrations. Even so, signal masking introduces uncertainty into the measurement. Some species, e.g. $^{40}\text{Ar}^+$, are introduced during the measurement and have the potential to mask other ions of interest, such as $^{40}\text{K}^+$. Workarounds exist, such as the above described isotope ratio comparison, though this is limited by the relative amounts of each isotope. In cases where the trace element's concentration is near the detection limit, it is probable that the secondary isotope is below the detection limit. Similarly, it is possible that multiple ions overlap in the same peak, complicating deconvolution efforts. Without an idea of what is expected, some peak overlaps may go unnoticed, leading to an incorrect quantitative analysis.

1.4 – Techniques for Impurity Mitigation

As described in Section 1.2, impurities have a variety of sources and properties. Techniques for impurity mitigation are similarly diverse. Depending upon the impurity, different aspects such as melt behavior, thermal stability, and chemical reactivity may be exploited to segregate the impurities so that they might be removed from the system.
1.4.1 – Zone Refining

Zone refining is a technique which utilizes the melt behavior of different impurity species to segregate them in a solid charge. Impurities which raise the melting point of the matrix move to the solidification front, while those which lower the melting point remain in the melt. This behavior is exploited by moving a heater repeatedly along a solid charge, melting the material in a discrete section which moves through the charge as the heater is moved with respect to the solid. At the end of the pass, the melt zone is reset without melting the charge on the return. In the end, the middle of the center has a lower net impurity content. This is due to impurities segregating at either ends of the charge, according to their stability in either the solid or the liquid phase [40]. As this purification method targets soluble impurities, it is typically applied to metallic impurities. The parameters affecting the effectiveness of the zone refining process are discussed in Section 2.3.

This technique exploits a fundamental aspect of material thermodynamics, and so may be applied to a variety of material systems. The only restrictions on zone refining are practical. The material must be thermally stable and not decompose before melting and it must experience a solid-liquid phase transition at a reasonable temperature which is to say that zone refining of elements such as iridium and helium are not realistic. Even with these requirements, many material systems lend themselves to zone refining.

Though the widespread applicability and high achievable purity are enticing, zone refining is by no means a perfect technique. Depending upon the matrix, some elements will not readily segregate due to negligible differences in melt and solid free energies. The refining speed also is slow, with pass speeds on the order of 1 cm/hr being typical for metal halide compositions [41]. In an effort to create a sharp melt zone, the thermal gradient at the melt edge is usually sharp. By moving this sharp gradient across the crucible many times, it is possible for
thermal stresses to build, ultimately resulting in cracking of the container. Improper selection of the crucible material can cause leaching of container elements into the purified material, negating any positive effects from refining.

1.4.2 – Chemical Reactions

Chemical equilibrium can be used to purify material as well. By reacting hydrated or oxidized material with a chemical more reactive with either oxygen or water the raw material may be stripped of these impurities. The reaction seen in Equation 1 provides an example of this process. By passing an acid over oxidized molecules, the anions exchange, producing the desire product and water. It is also possible to use a solid reactant for this process. Ammonium halides have been used for more than forty years to prepare oxygen-free halide materials [42]. These materials split into ammonia and acid when heated, providing a source of acid to react with any oxygen or hydroxyls. Byproducts are removed by vacuum, as this process is achievable at lower temperatures under evacuation.

This technique prevents the formation of halide vacancies by replacing any removed anions with the appropriate halide component [43]. Since the reaction is performed in vacuum, the reaction products are easily removed before they have a chance to be reintroduced. Any acid vapors should be contained or neutralized to prevent inhalation or corrosion of equipment. The most efficient way of accomplishing this is through the use of cold traps. Depending on the size of the operation, cost may be an issue as well since effective use of the ammonium halides requires a molar excess of the ammonium compound of ~4:1 for the target material [42].
1.4.3 – Vacuum Dehydration

In the process of handling metal halides, it is difficult to guarantee that the material is free of all trace amounts of moisture. In small amounts, moisture is generally considered to be lightly bound to the salt’s surface until high temperature reactions can occur. Several groups have reported the use of low temperature vacuum dehydration to remove this surface moisture before it reacts and forms oxyhalide compounds [44], [45], [46]. The moisture is then removed by vacuum.

This technique is easily implemented, requiring only a vacuum system with a wrap-around heater, of which several types exist. As it uses no consumables other than the treated material, this is also a very cost-effective and scalable process. The major variation between different reported methods is the drying temperature. There has been no published report to show the effects of time or temperature on the effectiveness of vacuum dehydration, possibly because of difficulty in producing reproducible results. Due to this disagreement, it is possible that temperatures are used which are sufficient to react the surface moisture rather than remove it.

1.4.4 – Melt Filtering

Melt filtering may be used to mitigate the impact of oxyhalides by physically removing them. As oxyhalide compounds are characteristically insoluble in the molten salt, by using a high temperature filter, they may be physically separated. By inserting a porous quartz frit below a previously synthesized charge, any oxyhalide materials will be separated once the charge is heated to melting prior to crystal growth, Figure 6 [47].

Since the frit is inserted into the growth assembly, there is no possibility of recontamination between purification and growth which minimizes the possibility
of user error. This does, however, present its own set of unique problems, notably a large addition to the ampoule. For ampoules without a frit, the area above the frit in Figure 6 can be omitted, nearly two thirds. Depending on the size of the furnace used for growth, the addition of the fritted assembly may require augmentation of the furnace to accommodate the increased size. When the material melts, it will bring the vacuum in the ampoule into equilibrium with its vapor pressure [48]. A larger volume above the melt requires more material to volatilize, disturbing the charge's stoichiometry.

![Figure 6 - Ampoule Geometry with Quartz Frit](image-url)
CHAPTER II
OVERVIEW OF ZONE REFINING

2.1 – Introduction

2.1.1 – Motivation

For the effective detection of nuclear threats, it is necessary to produce large radiation detectors with spectroscopic capabilities. As has been established in the last chapter, the unrestricted presence of impurities in a scintillator impairs both of these goals. EuI₂ has many impurity species present from the manufacturer, Table 1, including many metallic impurities which should respond well to zone refining. The effect of these impurities on the quality of as-received EuI₂ is highlighted in Figure 7, where the charge has been melted and allowed to solidify. Most notably, the two ends have a significant difference in clarity. The left side is a completely opaque, whereas the right side is mostly transparent though obscured in places by cracking. The as-received material is known to regularly vary between yellow, green, and tan colors, depending on impurity content. Variation in the color and transparency of materials are indicative of variations in the chemical content. As the material is nominally 99.99% EuI₂, this disparity is most likely due to impurities. By purifying this material, the crystal quality and scintillation performance of scintillators activated with Eu²⁺ being explored for nuclear nonproliferation efforts, including SrI₂, CsSrI₃, and CsCaI₃, are expected to improve. For these reasons, EuI₂ has been evaluated as a candidate for purification by zone refining.

Figure 7 - Visual Difference Between Opposite Ends of As-Received EuI₂ after Melting
2.1.2 – Hypothesis

EuI$_2$ is common activator used in scintillators being developed for implementation in next generation radiation detectors. It currently is known to contain impurities which are detrimental to its scintillation performance and crystal quality, including K, La, and Tl. By zone refining EuI$_2$, I believe that the concentration of these impurities can be reduced, improving the quality of scintillators made with this material.

2.1.3 – Approach

A literature survey has been conducted to examine the techniques and parameters used in zone refining of various materials. From this, it was concluded that a pass speed of ~2 cm/hr was reasonable for EuI$_2$. Material received from Sigma Aldrich was loaded into an ampoule and was melted in a horizontal position to consolidate the charge before refining. After several passes of the melt zone, the charge was extracted and sectioned to enable analysis of impurity content along the charge length. Thermal analysis was done using DSC to examine the differences in the thermal behavior of EuI$_2$ before and after refining. ICP-MS was used to provide quantitative impurity concentrations. A second sample was prepared and refined at a faster speed. The goal of this was to determine if comparable results are achievable after a shorter time. In order to facilitate future refining efforts, a miniature zone refining furnace was designed and implemented based upon lessons learned by working with the full-sized furnace. This miniature furnace provides a test bed for smaller batches of material, allowing more economical trial runs as well as refinement of less plentiful material.
2.2 – Literature Review

2.2.1 – Semiconductors

Germanium

Germanium is often used as in gamma ray spectroscopy due to its exceptional energy resolution. For this application, high purity germanium is needed since germanium’s electronic structure is extremely sensitive to impurities. Semiconductor-based radiation detectors function by separating the charge carriers that form as a result of interaction with ionizing radiation. The segregation of these carriers is only viable in the depletion region, the size of which is governed by Equation 2. In this equation, the depletion layer thickness, d, is shown to vary based on the reverse bias voltage, V, the impurity concentration, N, the material’s dielectric constant, \( \varepsilon \), and the elementary charge, e [1]. For a given material, the dielectric constant and elementary charge are constants. Thus, the size of the usable detection layer in germanium is determined by the impurity content and the applied voltage. The voltage does have an upper limit termed the breakdown voltage, \(~350 \text{ V in germanium at 77 K [49]. From this, the depletion layer size is heavily dependent upon impurity concentration.\)

\[
\frac{d}{V} = \frac{\varepsilon e}{4 N}
\]

Equation 2 - Dependence of the Depletion Layer Thickness on Impurity Concentration [1]

Yang, et al. reported an investigation into factors affecting the quality of zone refined Ge ingots. In this work, it is reported that the three major impurities present in HPGe are boron, phosphorous, and aluminum. Each of these is present in the raw materials, though the concentration of boron and phosphorous
is higher in ingots melted in carbon crucibles. Fortunately, it has been reported that for many impurities in germanium, the segregation coefficient is much less than one, allowing for efficient removal by zone refining. Also presented in this report is a discussion of the effects of pass speed and the ratio of ingot length to melt zone length. From a theoretical standpoint, pass speeds on a similar timescale to melt diffusion rates are preferred to allow time for the impurities to diffuse without getting trapped in the solid as the melt moves. From a practical point of view, however, refining at these speeds is not feasible. The ratio of charge length to melt zone length has a similar compromise to consider since it determines the achievable ultimate concentration and how fast it is approached. From their study, Yang, et al. found that a balance between performance and practicality was achieved for a pass speed of 7-8 cm/hr and a charge length to melt length ratio of 15:1 – 20:1 [50].

**Silicon**

Silicon is primarily used in the electronics and photovoltaic industries, each with their own purity requirements. As with germanium, very pure material is needed for effective application, less than 1 ppm of impurities for electronics applications. Cheaply produced metallurgical grade silicon (maximum 10,000 ppm impurities) is widely used as starting material for either application, though purification is necessary before it is useful [51]. In the photovoltaic industry, silicon is used as the primary material in the photocell. The incident sunlight creates electron-hole pairs which may be separated to produce a current flow. In the electronics industry, silicon is used as a substrate for integrated electronics and as a component in computer chips. Though this accounts for a relatively small fraction of the total silicon volume used each year, the increase in purity from metallurgical grade to electronics grade is accompanied by a 30-50 fold increase in the price [52].
Due to its relatively high melting point, silicon zone refining is done using an electron beam furnace to produce the melt zone as is reported by Mei, et al. To begin, metallurgical grade silicon is placed in a water-cooled copper crucible and placed under a vacuum to prevent oxidation. Using the electron beam, the material was melted twice to ensure homogeneity. The ingot refined by Mei et al. was 150 mm long, with a melt zone width of 10 mm, giving a ratio of 10. The pass speed for their experiment varied between 1 mm/min and 10 mm/min (6 cm/hr and 60 cm/hr, respectively). In a related publication, Mei, et al. determined that all of the impurities investigated in their silicon zone refining studies had an equilibrium segregation coefficient less than 1, i.e. they all moved with the melt to the end of pass region. These values ranged from 0.8 for B, to 1.6·10⁻⁸ for Zr [53].

2.2.2 – Metals

Aluminum

Aluminum alloys are used in many modern applications where a balance of strength and weight is needed and the demand for these alloys has resulted in increased production. To keep up, aluminum recycling has become popular, and so it is necessary to remove previous alloying agents and other impurities introduced during manufacture or usage. The properties of metal alloys are based, in part, on the impurities present in the material and any impurities with detrimental effects on the alloy properties, such as Fe, need to be removed.

Zone refining, one of the most effective methods of purifying Al, has been used to produce aluminum with 7N purity. Optimal zone refining of Al was reported to consist of a 30 mm zone being passed through a charge 10 times at speeds between 24 and 55 mm/hr [54]. Kino, et al. presented a study on the zone refining of aluminum where they varied several parameters to determine the most effective parameters for purifying aluminum. Using an inductive heating coil, they
produced a melt zone varying between ~20 and 50 mm in an ingot 900 mm long. The number of passes varied between 1 and 20, using speeds between 236 and 11 mm/hr. The effectiveness of step-refining was tested by passing a 30 mm wide molten region through the charge at a rate of 236 mm/hr for 5 passes, and then following that with 3 passes at 11 mm/hr. The purity of an ingot which was refined for 5 passes at 11 mm/hr with a melt zone length of 20-25 mm was determined by correlating electrical conductivity to impurity concentration. By this method, the purity of the ingot was 1ppm at the beginning of pass region and 100 ppm at the end of pass region [55].

**Cadmium and Tellurium**

Cadmium and tellurium are primarily used to produce semiconductors such as CdTe and Cd$_{1-x}$Zn$_x$Te (CZT), both of which are used in radiation detection. As with Ge and Si, the performance of these detectors is dependent upon the purity of the material. Impurity concentrations below 1 ppm have been seen to affect the mechanical properties of these materials, inhibiting large scale crystal growth. To improve the detection and physical properties of these compounds, Zaiour, et al. have produced 7N pure Te. After using vacuum distillation to purify Te to 5N, they used zone refining to purify the material to the desired level. It was found that some impurities, including Ag, Ni, Pb, Zn, and Fe, were effectively removed from the bulk of the material and deposited at the end after 9 refining passes. To achieve this, a melt zone 1.5 cm wide was passed through a 20 cm long charge at ~6 cm/hr. They note that due to size considerations, large impurities such as Xe were found to have a segregation coefficient close to unity due to their sluggish diffusion rates. Impurities which tend to form the same crystal structure in the bulk, such as Se and As, were also found to segregate poorly [56].

Similar work has been done to purify Cd by Munirathnam, et al. The refining of Cd is complicated due to its high thermal conductivity. Because of this, forming a stable melt zone is problematic. For this report, a melt zone size of 65 mm was
estimated in an ingot 560 mm long. A zone speed of 30 mm/hr was used to draw the melt zone through the ingot for a total of 4 cycles, each 15 passes long and culminating in the removal of one zone length at either end. The remaining material is used as feed stock for subsequent cycles. This process resulted in 6N pure Cd, with less than 0.1ppm for 14 of the 15 tested impurities [57].

2.2.3 – Halides

Thallium Bromide

Several popular room-temperature semiconductor radiation detectors, including HPGe, CdTe, and CZT, have disadvantages which hamper their large-scale implementation. Thallium bromide is becoming a competitive alternative to these detector materials due to its high density (7.5 g/cm3), its easily grown cubic crystal structure, low temperature congruent melting point (480°C), and its band gap (2.7 eV), which is wide enough to allow room temperature operation [58]. This material was widely ignored for many years due to its poor carrier mobility, but zone refining has been shown to improve the carrier mobility-lifetime product [59].

The effectiveness of zone refining TlBr has been reported by Hitomi, et al. over the course of their development of the material [59]. They have reported the results of high pass numbers on the concentration of impurities in initially 4N pure TlBr. The details of the refining were not shared other than the pass speed, 5 cm/hr. The characterization results for TlBr as a function of zone refining pass number, however, show an impressive improvement. A detector made from material refined for 1 pass shows an energy resolution of >30% at 59.5 keV. Material refined for 300 passes, by comparison, produced a peak with an energy resolution of only 11% at the same energy [60]. This performance is expected to improve with further development as is reported by Dmitriev, et al several years later where a value of 6.5% is reported at 60 keV [58].
A more detailed account of TlBr zone refining is provided by Oliveira, et al. who reports that they used 40 cm long ingots, which had a 3 cm long molten zone passed through it at 2 cm/hr. The material was refined for 1, 20, and 30 passes. The concentration of impurities was reported to fall by 1-2 orders of magnitude after one pass for each of 7 reported impurities. After 30 passes, two thirds of the reported impurities were reported in concentrations less than 1 ppm, including Ba, which initially was determined to be 324.72 ppm [61]. Additional details can be found in a publication by Churilov, et al. where the refinement is said to have taken place at 5 cm/hr for 50-100 passes. The ingot length is estimated to be ~26 cm based upon images in the paper. The melt zone is said to have been maintained at a width of 2-2.5 cm. Though no trace metal analysis was reported, the mobility-lifetime product was determined to increase by three orders of magnitude after zone refining, improving the charge carrier collection efficiency [59].

2.3 – The Zone Refining Process

Zone refining is accomplished by moving a molten zone through a solid charge. As seen in Figure 8, the process requires that a heater move around a solid charge, heating a small section of the material enough to melt it. The heater is moved slowly along the charge until the opposite end is reached, at which point the heater quickly resets its position. The material does not melt on the return pass. This is repeated until the material is adequately purified. The number of passes required to reach this point varies based on the refining parameters used and is generally experimentally determined. Impurity migration is displayed Figure 9. As more passes are completed, impurities segregate toward either end, resulting in a net purified material in the center. The greatest achievable segregation, called the ultimate distribution, is dependent upon the size of the
melt zone. By decreasing the size of this zone relative to the charge length, the width of the purified zone may be increased.

Figure 8 - Schematic of Zone Refining Process
Figure 9 - Segregation of Impurities as a Result of Zone Refining
2.4 – Important Parameters for Zone Refining

2.4.1 – Segregation Coefficient

The thermal behavior of a material varies significantly with composition. This is especially true for the melting temperature, which may either be raised or lowered by the addition of solute. One of the parameters central to zone refining is the segregation coefficient (also called the partition or distribution coefficient), a value quantifying the effect that an impurity has on melting point of the matrix in which it is dissolved. For impurities which result in the lowering of the melting point, the segregation coefficient is less than unity. The reverse is also true, as is seen in Figure 10. At its most basic, the segregation coefficient of an impurity in a solvent is the ratio of the impurity’s concentration in the solid versus the liquid, Equation 3, corresponding to what is schematically displayed in Figure 10.

![Figure 10 - Correlation of Melt Behavior with Segregation Coefficient](image)

Equation 3 - Equilibrium Segregation Coefficient, [63]
Since the segregation coefficient describes the preference of an impurity to exist in the melt or solid, it may be used as an indicator of zone refining effectiveness. The distribution of impurities in a zone refined charge after a finite number of passes is seen in Figure 11 for various segregation coefficients. In general, the further from unity the segregation coefficient, the faster the impurity may move. Impurities with \( k < 1 \) typically segregate faster as they are able to "ride" the liquid zone further before getting trapped in the solid. Those impurities with \( k > 1 \) move opposite the pass direction, and so must diffuse through the melt to the advancing solidification front. This movement is much less efficient as the diffusion rates in the liquid are much higher than those of the solid and so the impurity at best can move \(~1\) zone length each pass. Impurities with a \( k \approx 0 \) are considered unresponsive to zone refining and will not move except through mechanical means, such as melt convection. This efficiency is displayed in Figure 12 as a function of pass number.

Figure 11 - Effect of Segregation Coefficient on Impurity Concentration after Zone Refining, [40]
2.4.2 – Length Ratio

Zone refining requires the movement of a melt zone through a solid charge. As the size of the melt increases, the refining process becomes less effective. The length ratio is an operational parameter derived from the charge length, \( L \), and the melt zone length, \( l \), as shown in Equation 4. In his work on zone refining, Pfann shows the effect that the length ratio can have on the purity of a material.

\[ \frac{L}{l} = \]  

Equation 4 - Length Ratio

By comparing Figure 13 and Figure 14, it is evident that a larger length ratio is desirable. The x-axis values of \( x/L \) are used to indicate that the charge length
required for effective refining is based on the size of the melt zone. In these figures not only is the relative concentration of impurities six times smaller at the beginning of the charge after 20 passes for the larger ratio, the length of material which has been purified is also larger. This is a result of the impurities moving further with each pass. When the melt zone is small, the distance an impurity must diffuse through to reach either the bulk of the liquid (k<1) or the solidification interface (k>1) is decreased. If it is not able to diffuse fast enough, the solidifying edge of the melt zone will freeze the impurity in place as the heater moves down the charge [62]. Impurities which do not move much each cycle require more refining passes to appreciably segregate. Charges with a small length ratio have a poor achievable ultimate distribution and reach their maximum purification rather quickly [64].

**Figure 13 - Impurity Distribution After Completing Various Refining Passes, n, for a Length Ratio of 10, [62]**
2.4.3 – Pass Speed

The effects of pass speed can be intuited by considering the diffusion processes taking place during zone refining. If the speed is too fast, impurities do not have sufficient time to diffuse before they are ensnared by the solid again. Very fast pass speeds destabilize the melt zone, causing dendritic growth that trapping pockets of liquid in an advancing solid as seen in Figure 15. This growth instability retards effective impurity segregation by locking in the impurities instead of allowing them to move as dictated by the segregation coefficient. Excessively slow pass speed, however, prevents diffusion in the solid from being a negligible process. In this case, diffusion between the solid and liquid negates the effects of zone refining [40]. This need for a slow pass speed is tempered by practical considerations. The purpose of zone refining is to efficiently purify an
impure feedstock for some future application. If zone refining does not proceed at a reasonable rate, it is impractical and irrelevant. It is for this reason that refining speeds are typically in the region of 1-10 cm/hr as described in Section 2.2 though the most effective speed is likely lower.

**2.5 – General Considerations for Zone Refining Equipment**

The practical considerations for zone refining manifest themselves in the design of the furnace. Figure 16 shows the most general components of a zone refining furnace: the chamber (optional), the heater, ampoule, and the translation mechanism. The most general considerations made during the design of a zone refining furnace concern the heater and the ampoule as these items relate to how the melt zone is formed and how it is contained.

All other aspects of the design are fixed, in their presence if not their specific manifestation. This includes the translation mechanism of the furnace as it specific design or implementation of the motor is irrelevant as long as it can move the molten zone. The design of this component doesn't matter so long as it is capable of moving at an appropriate speed. Other parts such as the inclusion
of a chamber heater, on the other hand, can have a large impact on the refining process.

![Figure 16 - Schematic Showing the Basic Components of a Zone Refining Furnace](image)

2.5.1 – Consequences of Using a Chamber Heater

The thermal expansion of some materials is quite aggressive, resulting in the fracture of the brittle containers if the material adheres to the walls of the vessel. To minimize this occurrence, it is possible to maintain the entire charge at an elevated temperature, below the melting temperature, thereby limiting the amount of thermal expansion. The trade-off with this addition is the lower achievable thermal gradient at the melt interface. As the entire charge is hot, the rate of heat dissipation is lowered impeding the formation of a stable, narrow melt zone.

With a conventional furnace, it is necessary to heat a large area around the charge to keep it at an elevated temperature. This requires a large amount of
insulation to minimize heat losses for practical application. The addition of this insulation comes at the cost of material visibility. It is advantageous to be able to watch for the first signs of container failure as it allows the impact of this event to be minimized. A second benefit is the ability to monitor refining progress in situ. When purifying a contaminated material, a change in the melting temperature is expected. Depending on the magnitude of this change, the material may cease to melt at the original temperature. The converse of this is the material’s melting temperature is lowered and the melt zone elongates during refining. By monitoring the refining process, adjustments may be made as necessary.

2.5.2 – Heater Design Requirements

Regardless of whether a chamber heater is included, the heater is a core component of a zone refining furnace. A narrow melt zone is required for efficient refining, as previously established. To achieve this, the heater must be narrow, relative to the average charge size. Smaller heaters are more delicate, susceptible to both mechanical fracture and oxidation corrosion, especially at high temperature. The heater must also closely fit the typical vessel size used with it. A large mismatch wastes heat and produces a wider melt zone as the radiant heat warms the nearby charge.

The melt zone may be divided or minimized by using a cooling system. This is especially popular in lower temperature zone refining apparatuses, mostly due to the types of coolants available at lower temperatures. Water is an obvious choice as a coolant, but above 100°C, this isn’t a possibility. Oil is another possibility and is capable of reaching higher temperatures, though is not encouraged for use in a furnace. The coolant must be cool enough to absorb heat from the system effectively without inducing thermal shock in the container material. To improve the coolants thermal contact, copper tubing is used to contain the coolant, improving the efficiency of the heat exchange. At higher temperatures, it
is much more efficient to simply manipulate the size of the heater itself or use air circulation to promote cooling.

2.5.3 – Material Containment Considerations

For materials which are not hygroscopic, it may still be advantageous as steps may be taken to reduce melt convection. Even in moderately deep melts, convection can cause an irregularly shaped molten zone where the top of the melt is wider than the bottom. This problem, detailed by Pfann, is easily prevented by rotating the ampoule about its long axis during refining. By rotating the ampoule, there is no static for the melt to rise towards, and so the solid-liquid interfaces are stabilized.

Ampoule rotation requires that the entire ampoule cross-section be filled with material. Should it be only half full, the material will coat the ampoule walls during solidification. This full-ampoule geometry is not always feasible due to thermal expansion and outgassing. If the material expands upon heating, the material may burst the ampoule during melting. If the material releases gases during heating, such as through decomposition or outgassing, these gases will accumulate in the ampoule and can cause fracture through pressurization. To counteract these concerns, a half-filled ampoule geometry may be adopted to provide headroom into which the material may expand or give off gases without fracturing.

2.5.4 – Container Material

The choice of container material is based mostly on what is being refined. Quartz is a common container material for zone refining due to its high melting point, chemical stability, transparency, low thermal expansion coefficient, and low cost. The major drawback of quartz is that it is very brittle. Because of this low fracture strength, it is very susceptible to fracture due to thermal expansion or in cases...
where the material adheres to the container wall. A second common material is vitreous carbon (also known as glassy carbon). This material is more nonreactive than quartz, lowering the chances that material will adhere to it. Vitreous carbon is also very brittle, however, and is comparatively expensive in addition to being opaque. The only major alternative to these materials is a metal foil to coat one of the previous materials. Boats made only from metal are not common as metal is not as chemically inert and may leech impurities into the zone refined charge.

2.5.5 – Process Orientation

Zone refining may be done in either a vertical or horizontal orientation, with an appropriate boat geometry. The primary difference between the two methodologies is the influence of gravity and convective processes on the chemically-based segregation governed by $k$ in the vertical configuration. The influences of gravity may either enhance or retard the segregation of impurities depending on whether they increase or decrease the density, much as the melting differential determines zone refining behavior in general. Depending on the impurities which are being removed, the vertical arrangement may be used to complement segregation. If the melt viscosity is high enough to neglect melt convection, or the process is done in a low gravity environment, the difference between orientations should be negligible.
CHAPTER III
EXPERIMENTAL METHODS

3.1 – Zone Refining

3.1.1 – Description of Equipment

The zone refining furnace used for the majority of this work is seen below in Figure 17. The furnace consists of a main chamber which is capable of reaching ~800°C and a heater able to reach ~1000°C. The heater has an inner diameter of 3.5 inches, surrounding a secondary containment tube which is 2.75 inches in diameter. The heater is 3 inches wide, and based upon thermal profiles of the furnace, typically produces a melt zone of a similar size. This setup is seen in more detail in Figure 18. Since failure of the ampoule during refining would result in the release of molten salt, as well as halide or acid vapors, the containment tube limits the spread of these hazardous materials while the furnace cools.
The heater is capable of travelling up to 80 cm at speeds as low as half a centimeter per hour. The translation of the heater may be managed without a computer by making use of a set of switches which act as a hard-coded binary decision tree. As the translation speed is set in nonvolatile memory prior to refining, the adaptability of this method is limited. When connected to a computer, PuTTY, an open-source serial console program, is used to monitor and control the translation of the heater with greater adaptability than the switches alone.

The greatest disadvantage of the zone refining furnace is a size mismatch between its operating capacity and the volume needed for research. The refinement of large batches of material is both expensive and unnecessary for our purposes. It is impractical for us to prepare large ampoules of material due to size limitations imposed by the antechambers of our glove box. Ampoules must be ~20 inches or less in length so that they may be loaded into the glove box. Because of the ampoule design and the length lost when the ampoule is sealed,
this allows a maximum charge length of 12 inches. Combined with the melt zone width of 3 inches achievable with the aforementioned heater design, this produces a relatively low length ratio of 4.

### 3.1.2 – Material Handling Procedures

The feedstock EuI$_2$ was received sealed under argon in a quartz ampoule from the manufacturer, Sigma Aldrich. It was nominally 99.99% pure EuI$_2$. The ampoule was opened in a dry nitrogen glove box with oxygen and moisture levels less than 1 ppm. One hundred grams of EuI$_2$ was loaded into two boat-style refining ampoules, seen schematically in Figure 19. This ampoule was then transferred to an evacuation station where each was evacuated while being heated. The heating program used consisted of heating the ampoule to 125°C for 18 hours and then holding the ampoule at 200°C for 6 hours. The material is visibly different after drying, as seen in Figure 20 where the material goes from a light green to a tan color. After the ampoule cooled, the pressure in each ampoule was approximately $1 \times 10^{-6}$ torr. At this point, the ampoule was sealed under vacuum using a hydrogen-oxygen torch.

![Figure 19 - Boat-Style Zone Refining Ampoule](image1)

![Figure 20 - Comparison of EuI$_2$ Raw Material Before and After Drying](image2)
After sealing, the material was transferred to the zone refining furnace. Prior to refining, the furnace was used to melt raw material beads. This was done to provide a better point of comparison for the refined material. After solidification, the material was photographed for later visual assessment of zone refining. In order to measure the impurity concentration as a function of charge position, each twelve inch charge was subdivided into 7 sections after refining. These sections, designated A through G, were kept separate for testing purposes. As a matter of convention, Section A is taken as the first inch at the beginning of the pass. Sections B through F are each two inches long, with Section G being the final inch at the end of the pass. This is seen in Figure 21 where the zone refined charge is marked in the ampoule with the pass direction labeled. Each pair of lines indicates a 1 inch segment.

![Figure 21 - Subdivision of the Zone Refined EuI$_2$](image)

### 3.1.3 – Parameters Used for Zone Refining EuI$_2$

The ampoule design and volume refined was held constant between refining runs. As a result of this, the length ratio of the samples was also constant, 4. The other refining parameters were similar, as seen in Table 2. The temperatures were reduced slightly for the second experiment in an attempt to reduce the melt zone size. The purpose of the second refining experiment was to determine whether a similar level of purification was achievable with a faster pass speed. At the end of each pass, the heater was reset by quickly passing it back over the charge. This was done at a much faster speed to prevent melting of the charge.
during the resetting process. As the speed was increased, a higher number of passes were performed with the intent to offset any negative effects of increased refining.

Table 2 - Summary of EuI₂ Refining Parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Sample 1</th>
<th>Sample 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Length Ratio</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Chamber Temperature</td>
<td>420°C</td>
<td>410°C</td>
</tr>
<tr>
<td>Heater Temperature</td>
<td>630°C</td>
<td>600°C</td>
</tr>
<tr>
<td>Pass Speed</td>
<td>~2 cm/hr</td>
<td>~8 cm/hr</td>
</tr>
<tr>
<td>Passes Completed</td>
<td>23</td>
<td>33</td>
</tr>
</tbody>
</table>

3.2 – Inductively Coupled Plasma Mass Spectroscopy

3.2.1 – Sample Preparation

Representative samples were chosen from each charge section. When possible, these samples were taken from near the center of the section so that impurity concentration could be better correlated to charge location. In some cases, this is not possible as fracturing of the charge upon extraction from the ampoule prevented this from being accurately tracked. From these samples, 3 ± 1.5 mg of each was dissolved in 50 mL of a 2% nitric acid solution. After initial dissolution, each sample was diluted to a uniform 64 ppm. All non-consumable instruments were cleaned prior to use by soaking in a nitric acid bath for 6 hours before being rinsed thoroughly with ultra-pure water.

3.2.2 – Measurements Methods and Parameters

To provide a standard for comparison, the response of the instrument was calibrated using the standard addition method. This method is used to neglect the effects of the matrix on the measurement. To do this, 4 samples were
prepared using a solution containing 64 ppm of the raw material as a basis for addition. To this, 0, 10, 50, and 100 ppt of the impurities were added from a commercially available reference standard. The measured response is correlated to the known, added concentration of impurities, and a calibration curve is produced as a result. These curves are used to interpret the raw counts as a concentration of impurities.

The measurement itself is performed by aspirating the previously prepared solution into ultra high purity argon gas plasma at a rate of 0.975 L/min inside an Optimass 9500 ICP-MS. A skimmer voltage of 1300 V was used in conjunction with a reflectron voltage of 550 V and a signal multiplier gain of 2450 V. The 4 calibration samples prepared using the raw material was run first, with each of the 7 sections from either refining experiment being run afterwards. Between the sample sets, 2 blank scans were performed to ensure that there was no interference from previous measurements. The concentration of each impurity was determined as the average of three repeated samplings.

3.2.3 – Data Treatment and Analysis

The majority of the data treatment was performed using the instrumental software suite which is packaged with the Optimass 9500. This software keeps track of all data acquired during each measurement, plotting the average counts from each replicate as a function of atomic mass. From this, each peak is labeled based on what species would have produced it. This is generally done by inputting expected species and letting the software determine the contribution of each to the measured spectrum. For the remaining unassigned peaks, suggested species are presented based on position. To improve the resolution of the trace elements, certain ranges are ignored during the scanning process. In this case, these ranges include the main Eu peaks as well as the range between 10-40 amu where large contributions from oxygen, carbon, and argon obscure much of
the detectable signal. The standard addition calibration curve is constructed using Origin 9.0. From this curve, the data measured by the Optimass 9500 was converted to bulk impurity concentrations in units of ppm.

3.3 – Differential Scanning Calorimetry

3.3.1 – Sample Preparation

In order to prevent interference from thermal contact variations, all DSC samples were composed of single pieces of EuI₂. Sample sizes were between 30 mg and 50 mg and were generally taken from the center of the charge, across the short axis of the section. All samples were held in desiccant inside of a dry nitrogen glove box prior to measurement to prevent any moisture or oxygen contamination. Samples were loaded into the measurement crucible inside of the glove box and transferred to the Labsys Evo DSC inside of a sealed jar to prevent as much atmospheric contamination as possible.

3.3.2 – Measurement Methods and Parameters

After transferring the sample to the DSC, the furnace was flushed with ultra-high purity argon. Instrument calibrations and measurements were done under a flow of high purity argon. All calibration constants may be found in the appendix. This is done to prevent sample degradation during measurement. The each measurement consists of two segments, a baseline and an experiment, each consisting of two melts. After completing both runs, the experiment has the baseline subtracted so that any effects of the crucible or other consistent error sources may be excluded. Because of this, the same crucible and thermal profile is used for both scans. A 100 μL alumina crucible with a perforated lid is used for all measurements.
The thermal profile used for all measurements may be seen in Figure 22. It consists of a stabilization step above room temperature (40°C), after which the temperature is increased at a rate of 3°C/minute up to the maximum temperature of 580°C. After reaching the maximum temperature, the sample temperature is allowed to stabilize for 5 minutes before ramping down to 40°C at the same rate. This process is then repeated, as mentioned previously.

![Figure 22 - Standard Measurement Profile for DSC Analysis](image)

### 3.3.3 – Data Treatment and Analysis

Using the Calisto software suite provided by the DSC manufacturer, Setaram Instrumentation, all experimental measurements were subjected to a baseline subtraction. After this is completed, a baseline is constructed across all noticeable peaks. The only peaks present for pure EuI₂ are the melting and crystallization peaks; any extraneous peaks are due to either measurement artifacts or impurities. The onset and offset of each peak were determined using the method outlined in Section 1.3.1 where the linear portions of the peak are extrapolated to the point where they intersect with the artificially constructed baseline as seen in Figure 3 for the onset determination. The peak area is determined with respect to the same baseline by the Calisto software. This is equivalent to the enthalpy of the transformation, following the same heat flow conventions previously discussed.
CHAPTER IV
RESULTS AND DISCUSSION

4.1 – Visual Observations

The number of passes needed to purify EuI$_2$ is unclear and as a result visual observation was used to determine what progress had been made during refining. Prior to refining, both charges were green as seen in Figure 7. This is contrasted by the yellow color seen in the refined EuI$_2$ of Z-2, Figure 23. There are a few black specks present even after refining, though these were found to only be present on the surface of the material and easily removed. Segregation of impurities is seen to present differently depending upon the segregation coefficient. Concentrating impurities with k>1 produced a yellow streak on the bottom of the ampoule, Figure 24. This was not, however, accompanied by any visible difference in the emission under UV irradiation. Impurities with k<1 caused a red-shift in the emission, visible under UV irradiation, Figure 25. Under white light, this region has become brown. A similar effect is seen in Z-3, Figure 26. Unfortunately, due to ampoule failure at the end of refining, the appearance of the material at that point was not documented.

Figure 23 - Z-2 Middle of Charge after 23 Passes
Figure 24 - Z-2 Beginning of Pass after 23 Passes

Figure 25 - Z-2 End of Pass Region after 23 Passes
4.2 – ICP-MS Results

While visual analysis can be used to gauge the progression of zone refining, ICP-MS measurements provide a deeper understanding of what is happening in the charge. The quantitative analysis of impurities in Z-2 is seen in Table 3. From this, it is seen that a majority of the impurities present in the charge tend to segregate towards one end of the charge. Since it is easier for impurities to move with the refining pass, impurities with $k<1$ should show greater segregation compared with impurities with $k>1$. By comparing the difference in concentration at either end of the charge, it can be seen that the end of pass region is generally more contaminated than the beginning of pass region.

Impurities having $k<1$ are also appear more commonly as the changes in their concentration can be more easily tracked, a fact seen by comparing Figure 27 and Figure 28. Some impurities are not expected to more appreciably. Figure 29 shows the variation across the charge for 3 impurities which display no discernable trend. The curves shown in these figures are normalized according the maximum and minimum concentration detected for the impurity in Z-2. A
The majority of impurities are seen to segregate towards the end of pass region as expected. Some impurities, notably Ba and Cs were detected in high concentrations relative to the raw material. While it is expected that the concentration of impurities in the charge may be either higher or lower than what is seen in the raw material, the values measured for these impurities do not seem reasonable. For this reason, it is believed that the measurement was contaminated or somehow skewed to artificially produce these values.

Table 3 - Z-2 Impurity Concentrations (ppm) from ICP-MS

<table>
<thead>
<tr>
<th>Impurity</th>
<th>Sect A</th>
<th>Sect B</th>
<th>Sect C</th>
<th>Sect D</th>
<th>Sect E</th>
<th>Sect F</th>
<th>Sect G</th>
<th>Raw Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>1.474</td>
<td>1.219</td>
<td>1.202</td>
<td>1.113</td>
<td>1.124</td>
<td>1.095</td>
<td>1.060</td>
<td>1.154</td>
</tr>
<tr>
<td>Ag</td>
<td>0.046</td>
<td>0.085</td>
<td>0.061</td>
<td>0.054</td>
<td>0.133</td>
<td>0.237</td>
<td>1.768</td>
<td>0.863</td>
</tr>
<tr>
<td>Bi</td>
<td>0.029</td>
<td>0.024</td>
<td>0.0178</td>
<td>0.015</td>
<td>0.020</td>
<td>0.017</td>
<td>0.17</td>
<td>0.023</td>
</tr>
<tr>
<td>Ca</td>
<td>1.238</td>
<td>1.539</td>
<td>1.411</td>
<td>1.431</td>
<td>1.979</td>
<td>2.187</td>
<td>1.841</td>
<td>1.625</td>
</tr>
<tr>
<td>Cs</td>
<td>23.059</td>
<td>0.729</td>
<td>0.622</td>
<td>0.654</td>
<td>15.434</td>
<td>2.131</td>
<td>2.614</td>
<td>0.807</td>
</tr>
<tr>
<td>La</td>
<td>0.179</td>
<td>0.177</td>
<td>0.185</td>
<td>0.225</td>
<td>1.944</td>
<td>3.342</td>
<td>3.594</td>
<td>0.567</td>
</tr>
<tr>
<td>Pb</td>
<td>0.575</td>
<td>0.563</td>
<td>0.520</td>
<td>0.486</td>
<td>0.737</td>
<td>0.744</td>
<td>1.18</td>
<td>0.587</td>
</tr>
<tr>
<td>Th</td>
<td>0.035</td>
<td>0.058</td>
<td>0.040</td>
<td>0.038</td>
<td>0.065</td>
<td>0.053</td>
<td>0.043</td>
<td>0.005</td>
</tr>
<tr>
<td>Tl</td>
<td>0.017</td>
<td>0.016</td>
<td>0.014</td>
<td>0.012</td>
<td>0.011</td>
<td>0.014</td>
<td>0.064</td>
<td>0.004</td>
</tr>
<tr>
<td>U</td>
<td>0.016</td>
<td>0.0182</td>
<td>0.018</td>
<td>0.018</td>
<td>0.021</td>
<td>0.023</td>
<td>0.022</td>
<td>0.010</td>
</tr>
<tr>
<td>Lu</td>
<td>0.322</td>
<td>0.459</td>
<td>0.390</td>
<td>0.382</td>
<td>0.415</td>
<td>0.412</td>
<td>0.426</td>
<td>0.425</td>
</tr>
<tr>
<td>Ce</td>
<td>0.704</td>
<td>0.262</td>
<td>0.310</td>
<td>0.313</td>
<td>0.353</td>
<td>0.357</td>
<td>0.341</td>
<td>0.128</td>
</tr>
<tr>
<td>Total</td>
<td>34.555</td>
<td>11.723</td>
<td>11.677</td>
<td>10.342</td>
<td>29.359</td>
<td>17.775</td>
<td>21.860</td>
<td>9.663</td>
</tr>
</tbody>
</table>
Figure 27 - Normalized Concentration of Impurities in Z-2 with Experimental $k<1$

Figure 28 - Normalized Concentration of Impurities in Z-2 with Experimental $k>1$
Just as Table 3 shows the impurity concentrations detected in Z-2, Table 4 holds the detected impurity concentrations for Z-3. For the most part, the same trends observed in Z-2 hold for Z-3. With the exception of the Ba values, none of the measured data is problematic. Certain data points, such as the concentrations of Lu and Tl in Section A are unexpectedly low, though further measurement is necessary to shed light on the accuracy of these values. The tendency of impurities to segregate with the refining pass is seen in Z-3 as well, Figure 30. In contrast to what is seen in Figure 27, the impurities in Figure 30 are not pushed towards the end of pass region as completely. This is likely a result of the increased pass speed. As mentioned previously, when the pass speed is too high impurities which prefer to move with the pass will attempt to do so, but are trapped by the advancing solidification front before they have time to diffuse into the bulk of the melt zone. This effect is mitigated by the greater number of passes used for Z-3, though evidence such as this remains. Figure 31 shows a similar result, where the size of the purified region is smaller compared to what is shown for Z-2.
The behavior of some impurities changed between the two runs. Calcium, which was seen to segregate with the pass in Z-2, is seen to exhibit more of a random behavior in Z-3. This is likely due to the pass speed being too high, preventing effective segregation of Ca. Interestingly, Th shows a trend opposite that of Ca; it is seen to segregate more efficiently in Z-3. The cause of this requires more investigation to pinpoint, as it could be due to either the increased pass speed or the increased number of passes. If the diffusion rate of Th in the solid is similar to the slower translation rate, it is possible diffusion and the refining process would negate one another. The segregation of Ce is also adversely affected by the increased pass speed. While it strongly segregates against the pass direction in Z-2, it behaves more like an impurity with a neutral segregation coefficient in Z-3. Unlike Ca, however, this issue may be solved by simply performing more passes. It appears as though there is a buildup of Ce near the center of the charge, possibly due to the trapping mechanism previously described.
Figure 30 - Normalized Concentration of Impurities in Z-3 with Experimental $k<1$

Figure 31 - Normalized Concentration of Impurities in Z-3 with Experimental $k>1$
Due to the nature of the measurement, ICP-MS is susceptible to error from many sources including cross-contamination and artifacts due to sample size. Cross contamination is a constant source of concern due to the sensitivity of the measurement. The elements which appear in unexpectedly high concentrations, such as Cs in Section A and Section E of Z-2, are probably due to sample contamination, either due to residue on a reusable component of the system or contact with Cs-containing material during sample preparation. Repeating the measurement with a fresh sample should resolve this inconsistency. Should the problem persist, it is likely due to the second primary issue: the small sample size.

These ICP-MS data are intended to provide a representative view of the impurity content across the refined charge. For each of the samples prepared, less than a tenth of a gram of material is used to characterize a section of material 1-2 inches in length. The impurity content does not vary according to this step size, but is shifting down the entire length of the charge. A more accurate quantification of the impurity concentration versus charge position would require
more samples to decrease the length of charge each sample represents. This same idea applies to the accuracy of the information reported by the manufacturer. All impurity analysis provided is for a small subset of the total batch and is expected to be representative of the whole. This is not to say that the difference between multiple measurements will be large, but it does explain why there is a difference between the reported Certificate of Analysis and the measured impurity concentrations in the raw materials.

The impurity content measured by ICP-MS is inconsistent with what was reported by the manufacturer for the material. Comparison of these values, Table 5, shows that the concentration of some impurities – Ca, La, and Pb – were found to be similar to the reported values. Other impurities, notably Ba, were measured in concentrations an order of magnitude different from the manufacturer’s determination. This variation could be the result of measurement error or sample contamination. Further investigation is needed to determine how reproducible these measurements are across independently prepared samples. Several impurities are listed as not reported in Table 5. Several of the impurities which are missing from the measured impurity list are missing due to either signal interference or lack of a standard. These impurities include Au, Cu, Fe, Hg, Ni, Pd, Se, Sn and W. Additional measurements with appropriate standards are expected to increase the number of quantified impurities.
Table 5 - Reported vs. Measured Impurity Content in As-received Material

<table>
<thead>
<tr>
<th>Element</th>
<th>Reported Impurity Content</th>
<th>Measured Impurity Content</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>2.4</td>
<td>1.154942</td>
</tr>
<tr>
<td>Ag</td>
<td>0.3</td>
<td>0.863968</td>
</tr>
<tr>
<td>Au</td>
<td>0.2</td>
<td>Not Reported</td>
</tr>
<tr>
<td>Ba</td>
<td>0.7</td>
<td>3.459344</td>
</tr>
<tr>
<td>Bi</td>
<td>1.8</td>
<td>0.023303</td>
</tr>
<tr>
<td>Ca</td>
<td>1.2</td>
<td>1.625207</td>
</tr>
<tr>
<td>Ce</td>
<td>Not Reported</td>
<td>0.128863</td>
</tr>
<tr>
<td>Cs</td>
<td>0.1</td>
<td>0.807438</td>
</tr>
<tr>
<td>Cu</td>
<td>0.4</td>
<td>Not Reported</td>
</tr>
<tr>
<td>Fe</td>
<td>1.6</td>
<td>Not Reported</td>
</tr>
<tr>
<td>Hg</td>
<td>0.2</td>
<td>Not Reported</td>
</tr>
<tr>
<td>La</td>
<td>0.3</td>
<td>0.56759</td>
</tr>
<tr>
<td>Lu</td>
<td>Not Reported</td>
<td>0.425211</td>
</tr>
<tr>
<td>Na</td>
<td>0.5</td>
<td>Not Reported</td>
</tr>
<tr>
<td>Ni</td>
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</tr>
<tr>
<td>Pb</td>
<td>0.2</td>
<td>0.5875</td>
</tr>
<tr>
<td>Pd</td>
<td>0.4</td>
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</tr>
<tr>
<td>Se</td>
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</tr>
<tr>
<td>Sm</td>
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<td>Not Reported</td>
</tr>
<tr>
<td>Sn</td>
<td>0.3</td>
<td>Not Reported</td>
</tr>
<tr>
<td>Th</td>
<td>0.2</td>
<td>0.005322</td>
</tr>
<tr>
<td>Ti</td>
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<td>0.004707</td>
</tr>
<tr>
<td>W</td>
<td>0.5</td>
<td>Not Reported</td>
</tr>
<tr>
<td>U</td>
<td>Not Reported</td>
<td>0.010584</td>
</tr>
<tr>
<td>Total</td>
<td>14.2</td>
<td>9.663979</td>
</tr>
</tbody>
</table>
4.3 – DSC Results

Analysis of the DSC endotherms measured for different sections of each zone refined charge has shown that the either end of the charge becomes more impure while the concentration of impurities in the center the charge lowers. For clarity only the endotherms measured for Section A, Section D, Section G, and the raw material are presented. In Figure 33, the endotherms for Z-2 may be seen, normalized for greater clarity. The peak for Section G is noticeably different from the other peaks, not only due its lower temperature peak position, but also because of its more gradual slope leading up to its peak. This wider leading edge indicates that melting occurs over a large temperature range. The other curves all begin sloping downward at approximately the same temperature, showing that there is no melting point depression present in these samples.
On the other side of these peaks, it is seen that Section D is the narrowest peak. Since peak width is an indication of sample purity [65], this indicates that the middle of the charge is the purest section of the charge. While they both begin melting at approximately the same time, Section A is much wider, trailing Section D on the high temperature side of the peak. This is due to the presence of impurities which raise the melting temperature of the solid. This behavior is expected as the impurities which lower melting temperature of the solid have a segregation coefficient less than one, migrating towards Section G. Likewise, impurities having a segregation coefficient greater than one raise the melting temperature and will move towards Section A.

The endotherms measured for Z-3 are seen in Figure 34. Where the endotherm for Section G was seen to begin at a much lower temperature for Z-2, the endotherm for the same region in Z-3 begins only marginally sooner than the endotherm of Section D. The curve for Section G is still the widest, indicating that it still has the highest concentration of impurities, but these impurities are not lowering the melting temperature of the region. This is possibly due to the presence of impurities which raise the temperature, \( k>1 \), but haven’t been removed effectively from the region. This is echoed by the endotherm for Section A which, while wider than Section D’s endotherm, is still narrower than the raw material peak. This is likely the result of impurities with \( k<1 \) moving being removed from the section but impurities with \( k>1 \) not segregating to the region. Since the pass speed of Z-3 is ~4 times that of Z-2, it is understandable that impurities with \( k<1 \), which segregate more easily, have moved more than those with \( k>1 \).
As seen in Table 6, the enthalpies of fusion are highest in the most pure area, Section D. The enthalpy of fusion for Section A and Section G for Z-2 are much lower, indicating that they are less stable. The data for Z-3 shows that Section A and Section D have similar enthalpies of fusion. This is likely the result of incomplete segregation of impurities due to the increased pass speed. With additional passes, this is expected to show the same trend seen for Z-2. It can be seen that the enthalpy for Section D is higher in Z-3 than it is in Z-2, which is probably a result of the increased number of passes. The enthalpy of Section G for Z-2 is much lower than it is for the same part of Z-3. This points to the segregation of impurities to the end of pass region in Z-2 being more complete than the segregation in Z-3. Since impurities with k>1 are not able to segregate as efficiently, especially given the increased pass speed of Z-3, it is not surprising that the enthalpy of Section A shows it to be more pure in Z-3 than in
Z-2. In this section, impurities with k<1 move out of the region faster than impurities with k>1 are moved into the region.

<table>
<thead>
<tr>
<th>Section</th>
<th>Z-2 (J/g)</th>
<th>Z-3 (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.06</td>
<td>0.065</td>
</tr>
<tr>
<td>D</td>
<td>0.063</td>
<td>0.065</td>
</tr>
<tr>
<td>G</td>
<td>0.056</td>
<td>0.06</td>
</tr>
</tbody>
</table>

4.4 – Impact on Scintillation Performance

The luminescent properties of a scintillator are very sensitive to impurity content. By zone refining the EuI₂ raw material, it is believed that impurities are segregated are removed from the bulk of the charge, improving the scintillation properties of any crystal containing this material. To investigate this effect, the scintillation properties of the refined EuI₂ are compared to those of the raw material. The samples used in these measurements were irregular, unpolished pieces measuring ~4x4x2 mm extracted from melt samples 1-2 grams in size and treated identically. In Figure 35, the x-ray excited luminescence emission is shown for the unrefined EuI₂ as well as both refined charges. From this, it can be seen that the emission wavelengths are very consistent in spite of changing impurity content due to zone refining, though the emission of Z-2 is narrower that the other two.
Though the emission wavelength is not affected, the light output and energy resolution of the samples vary considerably with material processing. The pulse height spectrum of the raw material for $^{137}$Cs is shown in Figure 36. From this it can be seen that the photopeak is ill defined, almost merging completely with the Compton edge in the spectrum. Though completely undesirable, this provides a good point of comparison for the zone refined samples. In Figure 37, the spectrum measured for Z-2 shows a distinct photopeak with good energy resolution compared to the raw material. These values are further improved in Z-3, shown in Figure 38. The light output of Z-2 is $\sim 4,000$ ph/MeV brighter than the unrefined material, and is accompanied by a drop in energy resolution of 10%. Z-3 is even brighter at $\sim 30,000$ ph/MeV with an energy resolution nearly a third that of the unrefined material, Table 7.

![Figure 35 - X-ray Excited Luminescence Spectrum of Three EuI₂ Samples](image)
Figure 36 - $^{137}\text{Cs}$ Pulse Height Spectrum of Unrefined Eu$_2$O$_3$

Figure 37 - $^{137}\text{Cs}$ Pulse Height Spectrum of Refined Eu$_2$O$_3$, Z-2
Table 7 - Summary of the Scintillation Properties of Refined and Unrefined EuI$_2$

<table>
<thead>
<tr>
<th>Sample</th>
<th>Light Output (ph/MeV)</th>
<th>Energy Resolution (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unrefined</td>
<td>23,000</td>
<td>28.59 ± 4.46</td>
</tr>
<tr>
<td>Z-2</td>
<td>27,000</td>
<td>18.25 ± 1.30</td>
</tr>
<tr>
<td>Z-3</td>
<td>30,000</td>
<td>11.79 ± 0.67</td>
</tr>
</tbody>
</table>

4.5 – Effectiveness of Zone Refining EuI$_2$

By considering the data presented in previous sections, it is seen that zone refining was successful in purifying EuI$_2$. The material which was visibly inhomogeneous after melting showed segregation of impurities at either end after refining. Likewise, the ICP data shows that the centers of the refined charges
contain fewer impurities than the raw material. Though there are inconsistencies between the impurity content of Z-2, Z-3 and the raw materials, these are believed to be due to the ICP-MS methods rather than the refining process. DSC measurements confirm the segregation of impurities, showing that the slower pass speed of Z-2 results in better segregation of impurities compared with Z-3 which has a faster pass speed and more passes. Though impurities are not seen to segregate as completely in Z-3, scintillation characterization shows that Z-3 has the highest light output and the lowest energy resolution. Both of these characteristics are expected to remain when the EuI₂ is used as a dopant. Given the performance of the as-received material versus the refined material, I believe that refining of EuI₂ is very beneficial and should be done before using EuI₂ for crystal growth.
5.1 – Merits of Having a Miniature Zone Refining Furnace

In order to better fit research-scale refining efforts, a second zone refining furnace was built. This furnace, dubbed the ZRmini, improves upon the design of the larger furnace in that it allows for a smaller charge size, incorporates a smaller heater, and has a modular design allowing for easy upgrades as necessary. All of this is achieved while also increasing the total number of furnaces available for material purification.

While industrial efforts generally require large throughput of material, research generally utilizes smaller batches to improve the process before scaling to such volume. Reducing the minimum batch size makes zone refining more reasonable on a small scale as it cuts down on unneeded excess, lowers the cost of refining, and allows less plentiful compounds to be investigated. These points are viable not only because of the smaller size of the ZRmini, but also because of the more optimized construction of the furnace. The main disadvantage of the larger furnace is its large heater and accompanying melt zone. The melt zone of the ZRmini is only ~1 cm in length, nearly a tenth of its predecessor. Everything else constant, this greatly improves the efficiency of refining.

5.2 – Construction of the Furnace

The ZRmini was built to improve upon the main disadvantages of the large zone refining furnace. These weaknesses were primarily a function of its size: the heater is too large to support a narrow melt zone and it is difficult to evaluate the progress of refining in situ. By making the heater closer in size to the expected
refining ampoule, it is possible to eliminate the need for a chamber heater or any insulation except in the region immediately surrounding the heater. Figure 39 shows the design of the ZRmini heater. This heater fits tightly around a 1 inch diameter containment tube, a feature which carried over for safety reasons.

![Figure 39 - ZRmini Heater Design](image)

The objective was for the heater to produce a melt zone 1 cm wide. To achieve this, the heater itself was designed to operate independently of a chamber heater, creating a very sharp drop in the charge temperature outside of the insulation. A 2 inch thick block of insulation was used to smooth out the gradient near the heater to prevent thermal stresses from inducing failure. Heat losses near the melt zone were also minimized using this design, allowing the heater temperature to be maintained with less stress on the heating coil. This coil, made of 24 gage nichrome wire, is imbedded in high temperature cement as seen in Figure 40. The positioning of the heating coil is visible in Figure 41 during construction. In order to seal the coil inside the heater and to reduce heat losses, high temperature cement was applied to the joint where the two halves of insulation met.
Power calculations were performed to determine the necessary length and wire gage for the heater based on current and voltage restrictions [66]. It was determined that a 70 inch length of 24 gage nichrome wire was sufficient to produce a temperature of ~950°C with a maximum current draw of 8 A. Thermal programming is controlled using an RKC Instruments REX-P300 controller along with a 120 V-20 A rated Triac power controller to modulate the current output to the heating element. The heater is situated on a translation stage visible in
Figure 39. Movement of this stage is achieved by interfacing with a computer using the COSMOS software package by Velmex Inc.

5.3 – Testing of the Miniature Furnace

5.3.1 – Thermal Profiling of the Furnace

To confirm the width of the melt zone, thermal profiling of the heater was performed using external thermocouples and beads of material as-received from the manufacturer. Thermocouples were arranged such that their ends were staggered half an inch (~1.25 cm) apart as seen in Figure 42. The heater was originally positioned with 2.5 inches from the center of the heater. After the heater reached the set point, 700°C, it was translated at an arbitrary rate of 31.5 cm/hr to investigate the size of the melt zone associated with a relatively fast translation rate. A speed of 2.7 cm/hr was used to determine the melt zone size at rates comparable to a real refining run. Data was recorded at 5 second intervals, allowing the width of the melt zone to be calculated using the known pass speed.

Figure 42 - Thermocouple Setup for Thermal Profiling
The melt zone produced was stable even when translating at 31.5 cm/hr. The process variable measured by the temperature controller was observed to vary less than 0.5°C from the set point during a pass. During a pass reset, the temperature dropped by ~30°C. The temperature stabilized again less than 3 minutes later. The external thermocouples experienced temperatures 30-40°C greater than the set point during translation. This discrepancy is believed to have two causes. The first is the distance between the control thermocouple and the heating element. The heating element is offset by ~3 mm from the heating element and is recessed slightly to prevent it from rubbing up against the containment tube. The external thermocouples also experience heating from all sides while the control thermocouple is partially shielded by the containment tube and refining charge. Though undesirable, by knowing that this radial gradient exists, it may be compensated for.

The thermal profile measured at 31.5 cm/hr is seen in Figure 43. This profile was used to calculate the melt zone width at 3 potential melting temperatures: 675°C, 700°C, and 725°C. These temperatures are represented in Figure 43 as the blue, black, and red dashed lines, respectively. The profile measured for a translation rate of 2.7 cm/hr is presented in Figure 44 with similar lines indicating the melting temperatures. The average melt zone widths and standard deviations are seen in Table 8. There is little difference between the sizes of the melt zone for the two pass speeds, likely due to the sharp drop caused minimal insulation. Since the reported values are averaged for the three thermocouple readings, the low standard deviation seen for all temperatures indicates that the melt zone is stable at zone refining speeds.
Table 8 - Melt Zone Widths Determined by Thermal Profiling

<table>
<thead>
<tr>
<th>Pass Speed (cm/hr)</th>
<th>Hypothetical Melting Temperature (°C)</th>
<th>Melt Zone Width (cm)</th>
<th>Standard Deviation (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>31.5</td>
<td>675</td>
<td>1.43</td>
<td>0.051</td>
</tr>
<tr>
<td></td>
<td>700</td>
<td>1.04</td>
<td>0.025</td>
</tr>
<tr>
<td></td>
<td>725</td>
<td>0.42</td>
<td>0.091</td>
</tr>
<tr>
<td>2.7</td>
<td>675</td>
<td>2.12</td>
<td>0.047</td>
</tr>
<tr>
<td></td>
<td>700</td>
<td>1.64</td>
<td>0.046</td>
</tr>
<tr>
<td></td>
<td>725</td>
<td>1.00</td>
<td>0.041</td>
</tr>
</tbody>
</table>

Figure 43 - Thermal Profile of the ZRmini at 31.5 cm/hr for a Fast Speed
After determining that the melt zone was stable, testing was performed to evaluate the width of the melt zone in a real material. For this test, SrI$_2$ was chosen as a representative material. SrI$_2$’s melting point is ~538°C; the target temperature was set to 535°C to compensate for the center being hotter than the set point [67]. To better observe the width of the melt, beaded raw material was used. After ramping, the heater was moved around the material and allowed to melt the material. The width of the melt zone was then evaluated and found to be ~1 cm, Figure 45.
5.3.2 – Adjustments Made after Initial Construction

The initial design of the ZRmini used a narrow, tightly wound heating coil ~5 mm in diameter. The winding of this coil proved too close, making it prone to short circuiting. Figure 46 shows a segment of a failed heating element. From this it is seen that the element melts and breaks apart in areas where adjacent loops are touching. This element was also only partially imbedded in cement, leading to embrittlement caused by oxidation. Later iterations of the heater saw the element almost fully buried in cement. At present, approximately 10% of the height of the element was left exposed to allow radiative heat transfer. Cement was used to electrically isolate the element, preventing the short circuiting seen in Figure 46 as well as to physically lock the element into place. By minimizing the movement of the element, thermal fatigue is prevented, increasing the durability of the element.
After implementation, the two halves of the heater were clamped together to allow recycling of the insulation if the element failed in contrast to previous designs where the sides were cemented together. Figure 47 shows the current design of the heater. By relying on clamps to affix the heater, modification and maintenance of the heater may be performed more easily. Vibrations caused by the translation mechanism when moving at high speeds (such as during pass reset) have been seen to cause the containment tube to fall off the ampoule supports. This has been remedied by using a strap to secure the tube on both ends. In this case, a heat resistant tape was sufficient to prevent movement of the ampoule.
Figure 47 - Current Heater Design
CHAPTER VI
CONCLUSIONS AND RECOMMENDATIONS

6.1 – Summary

Impurities play a large role in the luminescent properties of scintillators. Homeland security applications require large detectors with good energy discrimination capabilities and high light output. Several scintillators being researched for these applications are activated with EuI₂, including SrI₂, CsSrI₃, and KSrI₅. As it is received from the manufacturer, the quality EuI₂ is poor and inconsistent. Zone refining has been explored as a method to improve the quality of EuI₂ as a way to improve the performance of Eu-doped scintillators. Analytical techniques including ICP-MS and DSC have been used to determine the impurity distribution in zone refined charges of EuI₂ and have found that zone refining produces a purified section at the center of the charge. ICP-MS quantitatively determined that the middle of the charge was net-purified as compared to the as-received material. This was qualitatively confirmed by DSC measurements. Segregation trends have been observed for several impurities, providing an experimental determination of segregation coefficient for these impurities. Arsenic and bismuth have been found to strongly segregate to the beginning of pass region, while silver, thallium, and lanthanum were seen to easily segregate to the end of pass region. Other impurities, such as Ba and Pb, were seen to consistently segregate, though more slowly.

Comparison of the light output and energy resolution of the as-received EuI₂ with that of EuI₂ from each of the refining batches indicates that refining EuI₂ greatly improves the performance of the material. After zone refining, the light output was increased by up to 30%, while the energy resolution was seen to improve by up to 58%. Fine-tuning of the refining procedure is expected to further improve the results achieved with zone refining. To aid in this effort, a miniature zone refining furnace, the ZRmini, was designed and constructed. Thermal profiling of
the furnace has shown that it is capable of maintaining a stable melt zone in a charge approximately one tenth the width of the melt zone achievable with the larger furnace used in this work.

6.2 – Suggestions for Future Work

Future zone refining efforts should be preceded by modifications to the larger zone refining furnace to decrease the width of the melt zone. Doing so will improve the efficiency of zone refining in this furnace. While the refining speed used for Z-3 was too fast to effectively segregate the impurities to the extent that they were in Z-2, the material from Z-3 was found to produce the greater increase in light output and energy resolution. By experimenting with pass speeds 2 cm/hr and 8 cm/hr, it is expected that an optimum pass speed can be determined for EuI₂. Future research would also benefit from an improved impurity quantification procedure. At present, the ICP-MS results show unexpected variations which are attributed to measurement error and incomplete calibration. By exploring other material handling and treatment procedures, as well as different techniques, the process most appropriate for metal halides should be ascertained. The methods developed here for EuI₂ can easily be adapted for other materials. Anecdotally, there are several raw materials which would likely benefit from purification prior to growth. These materials, which would be excellent candidates for further research, include SrI₂, SrBr₂, BaI₂, and EuBr₂.
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VITA

Thomas Williams McAlexander, known to his friends as Will, was born and raised in West Tennessee. He earned his Bachelor of Science degree in Materials Science and Engineering at the University of Tennessee, Knoxville in 2008. Will’s natural curiosity was fostered early on by his mother who got him addicted to reading. Though many things have changed over the years, his love of reading has remained. In high school, he was inspired by two particularly passionate teachers: Mr. Bill Weedon and Mr. Brian Lane, whose commitment to personal integrity has left a lasting impression. Over the years, his interests have diversified to include video games, photography and traveling, as well as a passion for cooking. For Will, variety is the spice of life, especially true, lest life get too predictable.