High-Performance Doped Strontium Iodide Crystal Growth Using a Modified Bridgman Method

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High-Performance Doped Strontium Iodide Crystal Growth Using a Modified Bridgman Method

A dissertation submitted in partial satisfaction of the requirements for the degree of Doctor of Philosophy in Electrical Engineering at Virginia Commonwealth University.

by

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Abstract

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A research dissertation submitted in partial satisfaction of the requirements for the degree of Doctor of Philosophy in Electrical Engineering.

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The importance of gamma-ray spectroscopy – the science of determining the distribution of energy in a gamma field – can rarely be overstated. High performance scintillators for gamma-ray spectroscopy in Nuclear Nonproliferation applications and homeland security require excellent energy resolution to distinguish neighboring element and isotope lines while minimizing the time and exposure to do so. Semiconductor detectors operate by converting incident photons directly into electrical pulses, but often have problems of high costs due to constituent segregation and surface states as is the case for Cadmium Zinc Telluride. The ideal scintillator material for gamma spectrometer will therefore requires high light yield, excellent proportionality between light yield and gamma photon energy, and material uniformity. A scintillator should possess the following properties; it should convert the kinetic energy of the
generated charged particles (typically K-shell electrons) into detectable visible light. This conversion should be linear—the light yield should be proportional to deposited energy over as wide a range as possible. For good light collection, the medium should be transparent to the wavelength of its own emission. The decay time of the induced luminescence should be short so that fast signal pulses can be generated. The medium should be of good optical quality and subject to manufacture in sizes large enough to be of interest as a practical detector. Its index of refraction should be near that of glass (~1.5) to permit efficient coupling of scintillation light to a photomultiplier tube or other photo-sensor.

In the past decade, inorganic scintillator research has focused less on improving the characteristics of known scintillators, but rather on the search for new hosts capable of fast response and high energy resolution. Extensive searches have been made for hosts doped with lanthanide activators utilizing the allowed 5d-4f transition. These 5d-4f transitions are dipole-allowed and thus are about $10^6$ times stronger than the more frequently observed 4f-4f transition in the trivalent rare earth ions. Ce$^{3+}$, Nd$^{3+}$ and Pr$^{3+}$ have been investigated for fast response applications while Ce$^{3+}$, Eu$^{2+}$ and Yb$^{2+}$ stand out as the most promising activators offering high light yield, and high energy resolution. Using a modified Bridgman growth technique we have grown crystals with a low energy resolution of 2.6% at 662 keV, which is lower than the previous 2.8% reported for SrI$_2$:Eu$^{2+}$. The modified technique (called so for its vertical crystal growth orientation) is necessary due to the anisotropic thermal expansion coefficient of Strontium Iodide. The problem plaguing the growth of the crystal is spontaneous cracking, which usually appear during cooling in the bulk. With the use of a zone separating shield, one can achieve more control of the temperature gradient between the two zones without compromising the actual temperature of the two zones. Additionally the use of codopants, in
particular divalent magnesium improved the crystalline quality by acting as a gathering for iodine ions, which led to reduction of defect density.
Chapter 1: Introduction

Two large groups of solid-state radiation detectors dominate the area of ionizing radiation spectroscopy measurements, semiconductor diodes and scintillators (Figure 1). The difference is what happens with the charge carriers at the end of the energy tack. In semiconductor diodes the thermalized electrons and holes are rapidly swept out with the application of an electric field and recorded as an electronic pulse with the number of charge carriers being proportional to the energy of the incident photon. Scintillators detect high-energy radiation through the generation of light which is subsequently detected by a photo-detector (PMT or photodiode) that converts the light pulse into an electrical signal with the number of photons being proportional to the energy of the incident photon. Scintillator detectors are preferred over semiconductor detectors in applications where low cost and large detector volumes are needed for efficient radiation absorption. Another advantage of scintillator detectors is the room temperature operation compared for example with high purity germanium (HPGe)-detectors requiring cryogenic cooling [1].
Scintillators are classified according to their composition. The major groups are organic, and inorganic. Organic scintillators typically have shorter decay time, lower density, and are generally useful for direct detection of electrons and alpha particles, but yield less light. Inorganic scintillators tend to have the best light output and proportionality, but are typically slower in response time. The high Z-value of the constituents and high density of inorganic crystals makes them favorable for gamma-ray spectroscopy, whereas organics are often preferred for beta spectroscopy and fast neutron detection due to their hydrogen, lithium or boron content.

There are a variety of applications for scintillators as radiation detectors. Scintillators are used in high energy physics experiments to measure the energy of particles, in X-ray imaging, X-ray radiography, Computed Tomography (CT) scan, mammography, Positron Emission Tomography (PET) scan, and medical diagnostics for a high resolution measurement of the spatial distribution of radiation intensity in different organs, space and planetary exploration, as
radiation detector in industrial measuring systems that use X-rays, in exploration and mining processes and in nuclear non-proliferation, homeland security and national defense, to identify radioactive sources and their gamma ray signatures. By identifying the isotope giving rise to a particular radiation, information can be provided on the radiation type and its energy. This is the target application of our crystals in question

An important advantage of SrI₂ in comparison to other high resolution scintillators, for example LaCl₃:Ce³⁺, LaBr₃:Ce³⁺, Lu₂SiO₅: Ce³⁺, LuI₃: Ce³⁺, is the absence of self-activity due to their natural long-lived radioactive isotope constituent (as ¹³⁸La in lanthanum and ¹⁷⁶Lu in lutetium).

Scintillation detectors are used to detect gamma photons and almost all charged particles. A typical scintillation detector consists of a scintillator, and a photodetector that can be either a photomultiplier tube (PMT) or a photodiode. A photomultiplier tube (PMT), Figure 2, is the most widely used photoelectric conversion device with silicon photodiode as an alternative. When an ionizing particle enters the scintillator, atoms or molecules are excited. During the subsequent de-excitation, the scintillator emits a photon in the ultraviolet to visible range. To enhance the probability of visible photon emission during the de-excitation process, impurities are added. Deliberately added impurities, called activators or dopants, create special sites in the lattice, or interstitial bands within the bandgap, at which the normal energy band structure is modified from that of the pure crystal. For the case of strontium iodide the most efficient dopant is the divalent europium (Eu²⁺) ion. The light emitted from the scintillator is guided to a photomultiplier tube where it is captured by the PMT and generates photoelectrons via the photoelectric effect. The interaction of one photon striking the photocathode of the PMT ejects an electron which is guided, with the help of an electric field, towards the first dynode. A PMT
contains a chain of dynodes, these dynode are coated with secondary emissive material and are held at a potential relative to the next. The secondary electron from the first dynode is increased and moves toward the second dynode and so on until the final dynode. Secondary electron emission is the process by which an electron strikes a material, and ejects other electrons from the metal by transferring some of its kinetic energy to them. These secondary electrons are accelerated from dynode to dynode so more than a million electrons can be created for each electron starting at the photocathode. After the subsequent multiplication, these photoelectrons form an electric pulse whose charge is proportional to the energy deposition by the incident particle.

Figure 2: Schematic diagram of a scintillation detector comprising a scintillation material coupled to a photomultiplier tube.[2]

SrI₂ has a high conversion efficiency of X-ray radiation and gamma radiation into optical photons [3]. Unfortunately it is also hygroscopic and oxygen sensitive, making the crystal growth and field application rather challenging. SrI₂ is still a relatively young material in development terms and can be considered representative of a new class of high-performance scintillators involving alkaline-earth iodides, so the full potential in improving the energy resolution is yet to be explored.
The goal of this work is to decouple and address the factors responsible for the overall performance: nonproportionality (via effect of dopants), photon statistics (improvement of light collection, crystal geometry and nonuniformity of the photocathode), and PMT electronic contribution (photocathode uniformity). Separating the components will allow a more sensitive feedback on the crystal processing and scintillator fabrication factor contributing to the overall energy resolution of the scintillator. Therefore, the main objective of this work is to produce inorganic single scintillator crystals that will be used to detect the high energy X-ray radiation and gamma ray radiation.
Chapter 2: Technical Background

The charged particle passing through the scintillator will create a large number of electron-hole pairs from the elevation of electrons from the valence band to the conduction band. The holes will quickly drift to the location of an activator site and ionize it, as the ionization energy of the activator will be less than that of the lattice site. The electron is free to migrate through the crystal until it encounters an ionized activator. At this point the electron can drop into the activator site, creating a neutral configuration that has its own set of excited energy states. If the newly formed activator state is an excited configuration with an allowed transition to the ground state, its de-excitation will occur very quickly and with high probability of the emission of the corresponded photon. Typical lifetimes are of the order of 30-500 ns. The migration time of the electron is much less so all the excited activator sites are essentially formed at once and will then de-excite with the half-life characteristic of the excited state. Therefore it is the decay time of these states that determines the time characteristic of the emitted scintillation light. There is can also be a less desired competing process, whereas the electron upon arriving at the activator site creates an excited configuration whose transition to the ground state is forbidden. Such a state requires additional energy, in the form of a phonon, to raise them to a higher lying state where de-excitation to the ground stated is allowed. The phonon energy and the resulting slow component of light are referred to as phosphorescence and is a significant source of afterglow in scintillators. Another undesired loss mechanism is quenching, where the de-excitation of the electron results in non radiative relaxation to the ground state.
Figure 3: The concepts of absorption, fluorescence and phosphorescence are shown with respect to varied energy levels.

Inorganic Scintillation Mechanism

The scintillation mechanism differs between organic and inorganic scintillators. For the purpose of this dissertation only the mechanisms relevant to inorganic scintillators shall be considered, as all materials researched were such.

Figure 4: Principle of scintillation light production and scintillation mechanism
The scintillation mechanism is divided into three stages: energy cascade; thermalization and migration of charge carriers to the luminescence center; and the excitation and emission of the luminescence center.

The energy cascade starts with the absorption of a high energy photon, $h\nu$, by an atom $A$. The creation of a high energy primary electron $e^-$, and an inner shell hole as shown below

$$A + h\nu \rightarrow A^+ + e^-$$  \hspace{1cm} (2.1)

The primary electron and the inner shell hole relax differently, whereas the inner shell hole relaxes radioactively emitting a photon or nonradiatively producing an Auger electron. There is the probability that a phonon emitted during a radiative relaxation can leave the crystal or be absorbed by another atom yielding a new deep hole and a free electron. The probability of nonradiative decay is usually higher than that of radiative decay [4]. The Auger electron loses its energy through electron scattering. The primary electron relaxes by the inelastic scattering of atoms on electrons (electron-electron relaxation) as follows

$$A + e^- \rightarrow A^+ + 2e^-.$$  \hspace{1cm} (2.2)

After the ionization, the primary electron causing the ionization and the produced secondary electron are indistinguishable and may produce more ionization giving rise to an avalanche of electrons and holes [5]. This electron multiplication process continues until the energy of the electrons is less than the ionization threshold, $2E_g$. In the general case the electrons are produced in the conduction band and all the holes will occupy the valence band with no core band lying above the auger process threshold [6]. Figure 5 illustrates this in what can be called the first stage, $10^{-16} < t \leq 10^{-14}$, where the energy cascade takes place. Plasmons are created when primary electrons lose their energy through the interaction with valence electrons. When a
high energy photon is absorbed the number of electron-hole pairs, $N_{eh}$, created is given as a the following ratio

$$N_{eh} = \frac{E_p}{\beta E_g}$$

(2.3)

where $E_p$ is the photon energy, $E_g$ is the bandgap, and $\beta$ is a constant (1.5-2 for ionic crystal scintillators).

Figure 5: General scheme of relaxation of electronic excitations in an insulating material.[7]

The thermalization and migration of charge carriers to the luminescence center occur at the end of the energy cascade, where hot electrons and holes interact with the host lattice through
electron-phonon relaxation. This second stage takes place in a time scale of $10^{-14} \leq t \leq 10^{-10}$, as shown in Figure 5. The electrons thermalize to the bottom of the conduction band, while the holes move to the top of the valence band. The thermalization process is described as carrier migration with a characteristic length $L = 10^2 - 10^3 \text{nm}$ for ionic crystal scintillators [8]. During the migration, electrons and holes can be captured by traps where free and bound self-trapped exciton (STE) is created.

At the end of the thermalization process, $t > 10^{-9}$, the charge carriers recombine to produce either intrinsic or extrinsic luminescence. The two types of intrinsic luminescence are excitonic and cross luminescence. Excitonic luminescence has been observed in many inorganic scintillators and is known to originate from the radiative annihilation of STEs [4]. The formation of STEs in inorganic scintillators is discussed with the SrI$_2$ scintillator as example under thermalization and migration of charge carriers to the luminescence center. Excitonic luminescence is efficient only at low temperatures; nonradiative processes dominate at high temperatures. Cross luminescence or core-to-valence luminescence is another type of intrinsic luminescence that involves valence band electrons and outermost core band. Extrinsic luminescence usually involves rare earth ions in the band gap of the host matrix. The rare earth ions are excited through impact excitation by subsequent electron-hole capture. Shown below, in Figure 6, is the potential energy diagram of a luminescence center. The energy is plotted against the configuration coordinate, or the distance between a luminescence center and the surrounding ions. Points A and B are the ground and excited states of the center respectively. During excitation, a transition occurs from A to C, a non-equilibrium energy state is created, and so the system will relax from C to B releasing a phonon. The emission corresponds to a transition from B to D followed the release of another phonon for the transition D to A. Depending on the
electron density at B, excited electrons can thermally be activated to reach F, where a transition from the excited state to the ground state would take place through lattice vibrations (quenching). A stokes shift is also possible, whereby a shift between the absorption band A and emission band B along the x-axis occur.

Figure 6: Potential energy diagram of a luminescence center [9]

Dopants

Dopants, also referred to as activators, enhance the probability of photon emission from the de-excitation in the luminescence centers. Some commonly used activators are Thallium (Tl\(^{1+}\)), Sodium (Na\(^{1+}\)), Cerium (Ce\(^{3+}\)) and Europium (Eu\(^{2+}\)). Scintillators which have been doped have the following abbreviated names: CsI:Tl\(^{1+}\) (Thallium doped Cesium Iodide), Na:Tl\(^{1+}\), SrI\(_2\):Eu\(^{2+}\). The addition of the doping creates interstitial bands in the bandgap of the material.
Through careful selection of the doping element it is possible to produce scintillation at visible wavelengths.

**Desired Properties of Scintillators**

With varying application of scintillators some properties are optimized. The typical metrics of a good scintillator are high light output, good energy resolution, fast scintillation decay time, resistance to radiation damage, high density, and emission in the photodetector spectral response. The relation between the above mentioned scintillator parameters and application is given in Table 1.

<table>
<thead>
<tr>
<th>Table 1: Relationship of scintillator parameters and application showing which parameters are required (*) and not (-).</th>
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</thead>
<tbody>
<tr>
<td><strong>Tomography</strong></td>
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<tr>
<td>Good Energy Resolution</td>
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<tr>
<td>High Light Yield</td>
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<tr>
<td>Fast Time Response</td>
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<tr>
<td>Nonproportional</td>
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<tr>
<td>High Density and Atomic (Z) # Radiation Stability</td>
</tr>
<tr>
<td>Large Crystal Size (&gt;1 cm³)</td>
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<td>Low Cost</td>
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</tbody>
</table>
High light output refers to a high conversion of ionizing radiation into optical photons. A light output, or light yield greater than 25,000 photons/MeV is considered high. The unit is the number of photons emitted per unit energy absorbed, typically 1 MeV, and is given as

\[ L = \frac{E}{\beta E_{\text{bandgap}}} \times S \times Q \]  

(2.5)

If the efficiency of transfer of charge carriers to the luminescence center, \( S \), and the quantum efficiency of the luminescence center, \( Q \), are assumed to be hundred percent, \( S = Q = 1 \), and the energy necessary to create an electron-hole pair is assumed to be equal to \( 2E_{\text{bandgap}} \), the theoretical light yield of inorganic scintillators can be calculated as follows

\[ L = \frac{0.5}{E_{\text{bandgap}}} \times 10^6 \left[ \frac{\text{photons}}{\text{MeV}} \right] \]  

(2.6)

This means that the light yield of inorganic scintillator is strongly dependent on the bandgap.

The energy resolution of a scintillator is its ability to separate two closely lying photopeaks. Typically measured as a function of the full width at half maximum (FWHM) the 662 keV photopeak of a \(^{137}\text{Cs}\) source a good resolution is one that is less than 3%. Resolution is defined as

\[ R = \frac{\Delta E}{E} \times 100[\%] \]  

(2.7)

where \( \Delta E \) is the FWHM of the photopeak located at energy \( E \).

The scintillation decay time, is the required time for the emission intensity to decrease to \( e^{-1} \). The rise time of emission intensity in scintillators is usually shorter than the decay time and is assumed to be at \( t = 0 \). The decay time of most scintillators is described by a simple exponential decay function
\[ I_t = I_0 \exp \left( \frac{t}{\tau} \right) \text{[s]} \] (2.8)

where \( I_t \) is the number of emitted photon at time \( t \), \( I_0 \) is the total number of emitted photons at \( t = 0 \), and \( \tau \) is the decay constant. Some scintillators exhibit multiple decay processes that are best described by a more complex component exponential decay function

\[ I_t = \sum_{n=1}^{n} I_n \exp \left( \frac{t}{\tau_n} \right) \] (2.9)

During these multiple decay processes, one commonly encounters a fast, \( \tau_f \), and a slow \( \tau_s \), component. Depending on the count rate required in applications, a fast (10ns - 5\( \mu \)s) scintillation decay time is necessary for fluorescence to avoid instrumental signal pile up. Fluorescence is the emission of light by a substance that has absorbed light or other electromagnetic radiation. This light is produced during radiative transitions from the lowest excited singlet states to the ground state with a typical nanosecond lifetime. Afterglow comes into play when the decay time is too slow and exhibits phosphorescence. Phosphorescence is caused by metastable triplet state with non-radiative initial conversion from the excited state. The metastable state is located below the lowest excited singlet states. The electron in the metastable state may acquire enough thermal activation energy over time to return to the lowest excited state leading to delayed fluorescence. Afterglow is the residual light measured after the primary decay time of the main emission, the decay time of the afterglow, \( \tau_s \), is given by

\[ I_t = kN_s \frac{t}{\tau_s} \exp \left( \frac{t}{\tau_s} \right) \] (2.10)

where \( k \) is the probability that a luminescent center captures the carrier and \( N_s \) is the number of carriers captured by traps.
A good scintillator must be resistant to radiation damage. The detector should be able to resist radiation damage that may create dislocations and shallow traps. Dislocation within the matrix lead to the formation of optical centers that can absorb emitted photons leading to decreased optical transmission. Radiation induced shallow traps tend to increase the level of afterglow, thereby increasing the decay time.

A good scintillator must have a high density. High density scintillators are desirable particularly for gamma-ray and high energy particle detection. A high atomic number, Z, maximizes the gamma quanta absorption through a photoelectric effect. The gamma-ray absorption by photoelectric effect per cubic centimeter is proportional to the product of the materials density, \( \rho \), the effective atomic number cubed [10].

The use of a scintillator requires a secondary detection media such as a PMT, photodiode, or other photodetector. Therefore, emission in the photodetector spectral response is paramount. The emission wavelength of a scintillator should lie near the maximum quantum efficiency of the photodetector. The PMT used in this study is a super bialkali Hamamatsu R6231-100, whose spectral response characteristic (blue) is shown in Figure 7.
Figure 7: Typical spectral response characteristics of Hamamatsu PMT [11].

Not only should the scintillators light output fall within the range of the spectral response of the PMT, it must also have a refractive index close to that of the PMT window. If the refractive index, \( n \), of a scintillator, a fraction of the light intensity incident normally on a scintillator-air interface, is internally reflected beyond the critical angle \( \theta_{\text{crit}} \) the light is totally internally reflected.

\[
\theta_{\text{crit}} = \sin^{-1}\left(\frac{1}{\mu}\right)
\]  

(2.11)

Because the refractive index of solid scintillators is greater than \( \sqrt{2} \), their critical angle is less than 45°.
\[
\left( \frac{\mu -1}{\mu + 1} \right)^2 = [\%] \]

(2.12)

The main objective in many applications of radiation detectors is to measure the energy
distribution of the incident radiation. This can be examined by noting its response to a
monoenergetic source of that radiation. A common monoenergetic gamma ray source is a
radioisotope of cesium, \(^{137}\)Cs, whose photon energy is 662 keV. The energy response of the
detector when subjected to a radioisotope source is called the response function and is measured
by the FWHM of peak at the pulse height.

Time response is a basic property of scintillators as mentioned above it represents the
decay time of prompt fluorescence. An approach to describing these phenomena assumes that
the population of the optical levels is also exponential so the overall shape of light pulse is given
by

\[
I = I_0(e^{-t/\tau} - e^{-t/\tau_1})
\]

(2.13)

where \(\tau_1\) is the time constant describing the population of the optical levels and \(\tau\) is the time
constant describing their decay. The population step is often better represented by a Gaussian
function \(f(t)\) characterized by a standard deviation \(\sigma_{ET}\). The overall light versus time profile is
then described by

\[
\frac{I}{I_0} = f(t)e^{-t/\tau}.
\]

(2.14)

Experimentally, the rise and fall of the light output can be characterized by the full width at half
maximum (FWHM) of the resulting light versus time profile.

Light output is another important parameter of a scintillator. In a scintillator, only a
small fraction of the energy loss of a charged particle in the scintillator is converted into visible
light. This fraction (scintillation efficiency) of particle energy depends on both particle type and its energy.

A good resolution is one where the FWHM is less than 4%. The energy resolution, $R$, is described as the squared sum of three contributions

$$R^2 = R_{\text{stat}}^2 + R_{\text{inhom}}^2 + R_{\text{nonprop}}^2$$

(2.15)

where $R_{\text{stat}}$ decreases with higher number of detected photon, $R_{\text{inhom}}$ is the inhomogeneous properties of the crystal, reflector, photocathode etc., and $R_{\text{nonprop}}$ is the contribution due to non-proportional response. The statistical contribution, $R_{\text{stat}}$, is due to the variance in the number of detected photons, $N_{dp}$, plus the variance, $\nu (=0.1-0.2)$, due to the electron multiplication in the PMT. This contribution is described by Poisson statistics [12]

$$R_{\text{stat}} = \sqrt{\frac{1+\nu}{N_{dp}}}$$

(2.16)

SrI$_2$:Eu$^{2+}$ is a relatively young material in development terms and can be considered representative of a new class of high-performance scintillators involving alkaline-earth iodide, so it is not known yet how much the resolution can be improved or how to do it. The theoretical maximum light yield of a scintillator is determined by its bandgap and the $\beta (=2.5)$ factor [13] using the following equation

$$N_{eh} = \frac{1000}{\beta E_{\text{bandgap}}}$$

(2.17)

Therefore an accurate bandgap is needed to estimate the maximum light yield possible in strontium iodide. Using Density Functional Theory (DFT) Sigh et. al. calculated a bandgap of 3.7 eV in the Local-Density Approximation (LDA) and 4.5 eV using the Engel-Vosko
Generalized Gradient Approximation (GGA) [14]. He comments that the 4.5 eV value should be the more accurate of the two, but uncertainties of at least 20% are generally associated with DFT which implies a similar bandgap for both approximations. Dorenbos estimated a 5 eV gap in considering ultimate light yield possible in strontium iodide [12] and Bourret-Courchesne stated a 5.6 eV bandgap in a recent oral report [15].

Scintillator based detectors are typically characterized using the Cesium 137 isotope (\(^{137}\text{Cs}\)). \(^{137}\text{Cs}\) decays by beta particle emission to the Barium 137 isotope (\(^{137}\text{Ba}\)). The \(^{137}\text{Ba}\) isotope is unstable and would attain a ground state by the emission of 662 keV gamma ray in 94% of the time, in the remaining 6%, a conversion electron is emitted followed by ~ 32 keV K-shell characteristic X-ray, as shown in Figure 11.

**Gamma-Ray Interaction with Matter**

Energetic particles interact with matter in three different ways: photoelectric absorption, Compton Scattering, and pair production [1]. The type of interaction depends on the energy of the electromagnetic radiation and also on the nature of the absorber. During these processes, the radiation energy is transferred to the atomic electron completely through total absorption or partially through scattering at a significant angle. Photoelectric absorption is dominant for low energy gamma rays \((h\nu < 0.256\text{MeV})\), pair production is dominant for high energy gamma rays \((h\nu > 1\text{MeV})\), and Compton scattering is the most probable process within the two energy ranges.

**Photoelectric Absorption**

This is the dominant process whereby an inner shell electron is able to completely absorb the incident photon energy. This means that the electron has enough energy to break from its
bound (shell) and is ejected from the atom, leaving behind a vacancy (hole). The energy of the photoelectron produced by the photoelectric process is given as

\[ E_e = h\nu - E_B \]  \hspace{1cm} (2.18)

where \( E_e \) is the photoelectron energy, \( h\nu \) is the incident photon energy and \( E_B \) is the electron binding energy. The atom becomes ionized and the hole is filled by an electron from a higher energy level. The byproduct of radiative transitions is the emission of characteristic X-rays, while Auger electrons are produced during non-radiative transitions. The Auger electrons have extremely short range because of their low energy. The characteristic X-Ray have a higher mean free path before either being reabsorbed through photoelectric interaction with less tightly bound electron shells or escape the matrix. The probability of a photoelectric effect increases with the binding energy and decreases with the photon energy. The cross section for the photoelectric effect \( \sigma_{ph} \) depends strongly on the atomic number \( Z \) and the photon energy \( E_\gamma \) as follows

\[ \sigma_{ph} \propto \frac{Z^5}{E_\gamma^{3.5}} \]  \hspace{1cm} (2.19)

**Compton Scattering**

Compton scattering, Figure 8, is an elastic collision between a photon and an electron which yields a recoil electron and scattered gamma ray with the division of energy between the two dependent on the scattering angle \( \phi \).

\[ h\nu' = \frac{h\nu}{1 + \left(\frac{h\nu}{mc^2}\right)(1 - \cos \phi)} \]  \hspace{1cm} (2.20)

\[ E_e = h\nu - h\nu' \]
From Figure 9 we see that Compton scattering is the dominant mechanism for strontium iodide at 662 keV since the effective $Z$ is 49. Ideally we would like to operate where the photoelectric effect is dominant for a more effective conversion for gamma photon to optical photons.
Pair Production

Pair production, Figure 10, starts at incidence photon energy of 1MeV $E_\gamma = 2mc^2$ or twice the electron rest mass. Pair production takes place in the coulomb field of a nucleus and not with the atomic electrons [5]. During a pair production interaction, the incident photon energy

$$h\nu \geq 1.02MeV$$

$$E^- + E^+ = h\nu - 2mc^2$$

(2.21)

![Figure 10: Schematic representation of pair production.](image)

Energy Resolution and Light Yield

Scintillator based detectors are normally characterized using the Cesium-137 isotope. Cesium is a shiny, gold colored metal that reacts violently with oxygen or water, and has a melting point of 28.4 °C. Of the forty known radioactive isotopes, Cesium-133 is the only stable, naturally occurring isotope that is non-radioactive. The atomic masses of these isotopes range from 112 to 151. All other isotopes, including the more common cesium-137 ($^{137}\text{Cs}$), are produced by human activity, and are produced by reactors as a fission byproduct. $^{137}\text{Cs}$ has a half-life of 30.17 years. $^{137}\text{Cs}$ decays by emitting beta particles and gamma rays when it decays to barium-137, which then decays to non-radioactive barium. The $^{137}\text{Ba}$ is unstable and would attain a ground state by the emission of 662 keV gamma ray 94% of the time, in the remaining
6%, a conversion electron is emitted followed by ~ 32 keV K-shell characteristic X-ray, as shown in Figure 11.

\[
\text{55Cs137} \quad 30.17 \text{ a}
\]

\[
\begin{align*}
\text{max 0.5120 MeV } \beta^- & \quad \text{max 1.174 MeV } \beta^- \\
56\text{Ba137m} & \quad 0.6617 \text{ 11/2-} \\
0.6617 \text{ MeV } \gamma & \\
56\text{Ba137} & \quad 0 \quad 3/2^+
\end{align*}
\]

Figure 11: Nuclear level diagram of the Cesium 137 isotope.

A typical pulse height spectrum of \(^{137}\)Cs is illustrated in Figure 12 adapted from [17]. The spectrum is composed of the photopeak (A) corresponding to the complete absorption of 662 keV photon energy and normally Gaussian in shape; the Compton continuum (B) corresponds to Compton events with the scattered Compton photon escaping the crystal; the Compton edge (C) marks the upper limit of the Compton continuum; the backscatter peak (D) arises from photons that scatter from the reflector into the detector; barium X-ray photopeak (E) corresponds to the absorption of barium K-shell X-rays (31 – 37 keV) and the lead K-shell X-rays photopeak (F) from the shields.
The photopeak is quantified through the energy resolution is measured at half the maximal height of the photopeak. The photopeak width arises from the fluctuations in the number of ionizations and excitations produced [18].

Light yield is a measure of the scintillator response to a particular radiation. The detectable scintillator light yield is strongly dependent on the type of reflector, optical coupling to the PMT, the crystals geometry, and on the efficiency of photon transfer to the PMT’s photocathode. There exist two types of light yields; absolute and relative. Absolute light yield \( \eta \) is the ratio of total photon energy \( E_{ph} \) to the energy deposited in a scintillator \( E_{\gamma} \):

\[
\eta = \frac{E_{ph}}{E_{\gamma}}.
\]  

(2.22)
Absolute light yield is difficult to determine due to the difficulties and errors associated with the measurement of the scintillator light collection efficiency. Relative light yield is the ratio of total energy of scintillation photons $T_{ph}$ detected at the photocathode to the energy $E_\gamma$ deposited in the scintillator by ionizing radiation:

$$L = \frac{T_{ph}}{E_\gamma}.$$  

(2.23)

The light yield reported in this work as well as other reports is the relative light yield which is calculated using one of four methods: pulse, single electron, intrinsic resolution and comparison. In the pulse method technique the signal amplitude of PMT after the preamp is measured in order to calculate the scintillation photons:

$$T_{ph} = \frac{V_\epsilon C}{\Sigma_a \mu E e}$$  

(2.24)

where $V$ is the signal amplitude measured at the preamp, $\epsilon$ is the energy of photon, $C$ is the output capacity of the PMT, $\Sigma_a$ is the anode sensitivity of the PMT, $E$ is the energy of the incident gamma radiation (662 keV for a $^{137}$Cs source), and $e$ is the electron charge. The single electron method compares the measured single amplitude to that of the single electron distribution of the PMT. The PMT intrinsic resolution method measures the number of photoelectrons $N_{pe}$ produced at the photocathode and then calculating the number of photons $N_p$ as:

$$N_p = \frac{N_{pe}}{Q_{PMT}}$$  

(2.25)
where $Q_{\text{mtr}}$ is the quantum efficiency of the PMT. The comparison is the most widely used of the above listed methods. The quantum efficiency corrected signal amplitude is compared to that of a known scintillator, typically sodium iodide or bismuth germanate (BGO).

**Decay Time**

The fast component arises mostly from excitonic emission and the slow component from sequential electron-hole capture or hole-electron capture and the excitation of certain metastable states that lead to emission. Decay time constants are calculated from single or multiple exponential decay functions fitted to the experimental data.
Chapter 3: Modified Bridgman Growth

The vertical or modified Bridgman growth configuration, where the hot zone separated by an insulating layer from the cold zone, has been widely used for the growth of semiconductors, such as InSb, CdTe, In$_x$Ga$_{1-x}$As, and GaAs [19][20][21][22][23][24]. The growth of SrI$_2$ in this work was carried out by a modified Bridgman method, using a transparent resistively heated two-zone custom built Mellon furnace. The temperatures of the two zones were controlled with a Mellon controller. In order to obtain a high temperature gradient for the crystal growth an insulating baffle made of Zirconia was placed between the top and bottom zones. The temperature profile was established such that the solid liquid interface was 4 cm above the insulating baffle. The furnace is setup with a Mellon linear translation system with a motion range of 60 cm. The insulation ring is placed between the top and bottom coil and is suspended using a 50mm process tube. The insulation ring was 14 mm thick with 85 mm outside diameter and roughly 50 mm inside diameter.

Crystal Growth

During crystal growth, a heat balance is set up by the conservation of heat flux at the interface which can be written as [25]

$$\rho_s LR = K_s G_s - K_L G_L$$  \hspace{1cm} (3.1)

where $K_s$ and $K_L$ are the thermal conductivity of solid and liquid respectively, $G_s$ and $G_L$ are the temperature gradient in solid and liquid at the solid-liquid interface respectively, $\rho_s$ is the density of the solid, $L$ is the latent heat of the melt, and $R$ is the growth rate. The left side of the equation indicates the heat generated at the interface due to solidification. The first term on the
right hand side of the equation is the heat flux going out of the solid-liquid interface, and the
second term refers to the heat flux coming into the interface. This equation shows that the
growth rate can be controlled by independently adjusting the temperature gradient in solid and
liquid at the solid-liquid interface. In a cylindrical system [26], as is the case for a quartz
ampoule, the heat conduction in a solid can be described as

\[
\frac{\partial}{\partial z} \left[ K_s \frac{\partial T}{\partial z} \right] = \rho_s C_s \left[ \frac{\partial T}{\partial t} + R \frac{\partial T}{\partial z} \right] \tag{3.2}
\]

where \( C_s \) is the specific heat of the solid, and \( z \) is the coordinate parallel to the growth direction.
The term on the left represents the net rate of heat conduction away from the solid per unit volume.
The first term on the right side represents the decrease rate of internal energy per unit volume,
and the second term is the rate of energy released per unit volume due to the moving interface.
The growth rate and ampoule size must be considered as they are related and especially
important. The best crack free crystals are obtained when the growth rate is several orders of
magnitude slower than the permitted heat flow through the ampoule. The amount of heat being
conducted through the solidifying mass is three to five orders of magnitude greater than the
amount of heat given off by the solid is formed due to latent heat of fusion.

Thermodynamics of Crystal Growth

The driving force in all crystallization processes is the free energy released. Nucleation
occurs in all phases and is the localized formation of a distinct thermodynamic phase. At the
beginning of crystallization, millions of seed-embryos are formed, those that reach the critical
radius become stable seed-crystals, but at the end only one seed-crystal is thermodynamically
favored to grow into a bulk single crystal. The ability of one seed-crystal outgrowing the rest
does not depend only on the prevailing thermodynamic conditions, but also on the use of grain selectors to suppress multiple grain growth.

**Gibbs Free Energy**

Gibbs free energy is a state function that relates enthalpy and entropy

\[
[\Delta G] = \Delta H - T\Delta S
\]  

(3.3)

The \( \Delta \) imply difference so that \( \Delta H \) and \( \Delta S \) are the changes in enthalpy and entropy occurring when crystallization takes place at temperature \( T \).

**Nucleation**

Fluctuations within the supersaturated solution give rise to small clusters of molecules, known as "embryos." The probability that an embryo will grow to form a stable nucleus depends on the change in free energy associated with its growth or decay. Two types of nucleation will be described; Homogeneous and Heterogeneous. The change in Gibbs free energy associated with the formation of a spherical embryo of radius, \( r^* \), that will be derived below.

**Homogeneous Nucleation**

Homogeneous nucleation occurs spontaneously and randomly, but it requires superheating or supercooling, and results in polycrystalline materials. Assume a spherical cluster with radius, \( r \), then the Gibbs free energy is defined as

\[
\Delta G_{\text{Homo}} = \frac{4}{3} \pi r^3 \Delta G_v + 4\pi r^2 \sigma + \Delta G_E + \Delta G_C
\]  

(3.4)

where \( \sigma \) is the interfacial surface energy of the solid phase and \( \Delta G_v \) is the difference in the Gibbs free energy per unit volume between the solid and liquid phases. The last two terms, \( \Delta G_E \) and \( \Delta G_C \), represent the Gibbs free energy due to the strain energy and to the entropy change.
associated with the replacement of internal degrees of freedom of bulk crystal by rotational and translational degrees of freedom of isolated embryos, respectively [27]. The terms are typically neglected as a first approximation. As \( r \) increases from zero, the Gibbs free energy increases up to a critical value \( r^* \) and then decreases during the formation of a nucleus, therefore \( r^* \) represents the minimum radius of a stable nucleus. Solving for the critical size of the cluster we get

\[
\frac{d\Delta G_{\text{Homo}}(r)}{dr} = 4\pi r^2 \Delta G_v + 8\pi r \sigma = 0
\]

\( r^* = \frac{2\sigma}{\Delta G_v}. \)  

The available energy for nucleation is then

\[
\Delta G_{\text{Homo}}^* = \frac{4}{3} \pi r^3 \Delta G_v + 4\pi r^* \sigma^2 \sigma = \frac{16\pi\sigma^2}{3\Delta G_v^2} \]

\( (3.7) \)

**Heterogeneous Nucleation**

Heterogeneous nucleation occurs on a foreign material such as a particle or a surface and requires less energy. Wetting angle, as shown in Figure 13, is determined by the balance of the three surface energy between the solid, liquid, and foreign surface. The Gibb’s free energy for a cluster is given by

\[
\Delta G_{\text{Hetero}} = -V \Delta G_v + \Phi
\]

\[
V = \frac{4}{3} \pi r^3 \left( 1 - \cos \theta \right)^2 \left( 2 + \cos \theta \right)
\]

\[
\Phi = 2\pi r^2 (1 - \cos \theta) \sigma_{sl} + \pi r^2 \sin^2 \theta \left( \sigma_{fs} - \sigma_{fl} \right)
\]

Equilibrium condition can be expressed by the Laplace-Young equation:

\[
\sigma_{fl} = \sigma_{fs} + \sigma_{sl} \cos \theta
\]

\( (3.9) \)
\[
\Delta G_{\text{Hetero}} = \left( -\frac{4}{3} \pi r^3 \Delta G_v + \pi r^3 \sigma_{sl} \right) \left( \frac{1 - \cos \theta}{2 + \cos \theta} \right) = \Delta G_{\text{Homo}} f(\theta)
\] (3.10)

Figure 13: Diagram of wetting angles of heterogeneous nucleation.

Overview of Growth Technique

In this work, the crystal growth ampoule was carried out in a quartz ampoule. Quartz was selected due to its ability not to react with the charge, and thermal diffusion. The ampoule inner diameter was 25 mm tapered to either a V shape or a bubble tip. The quartz ampoule as well as the sealing plug (24 mm outside diameter) was cleaned with diluted hydrofluoric acid for a period of about thirty minutes, then rinsed thoroughly with DI water. The ampoule and sealing plug was then further rinsed in methanol to remove any organic contaminant. The ampoule was simultaneously evacuated down to a vacuum in the order of \(10^{-5}\) Torr, using the vacuum preparation system shown in Figure 14, and annealed at 900 °C in a muffle furnace. Heating the ampoule serves a dual purpose of outgasing any residual contaminants that was not removed during the clean and alleviate and residual thermal stress in the ampoule. Of major concern is the thermal stress as it is believed to lead to crystal cracks during growth. The ampoule was annealed for thirty minutes then allowed to cool to room temperature while still under vacuum.
Preparation of Charge

In most of the growth runs carried out in this study, a stoichiometric charge of the elements was used for the growth. The highest purity, anhydrous raw materials were used as the starting material. Primarily obtained from Sigma Aldrich, the starting material had a nominal purity of 99.99% (typical beads about 1mm, -10 mesh) for strontium iodide and 99.99% chunks of zone refined europium iodide. The raw materials were calculated to the desired fractional weight of components based on the stoichiometry of the material in a glovebox. The argon filled glovebox used, pictured below, is an MBraun model UNILAB which maintains a moisture and oxygen levels less than 0.1 ppm. The argon gas in the glovebox is dried by continuously circulating it through an absorber canister containing molecular sieve and copper metal. The molecular sieve absorbs moisture while copper metal reacts with oxygen to copper oxide as followed:

\[ Cu + 0.5O_2 \rightarrow CuO. \]  \hspace{1cm} (3.11)
The absorber canister is regenerated bimonthly by purging with Ar/H\textsubscript{2}.

The aforementioned cleaned and evacuated ampoule is connected to the vacuum stage via a quick flange vacuum valve and a quick flange to quick-connect glass coupling. After closing the ampoule valve and the upstream isolation valve, the empty annealed ampoule is transferred to the large antechamber of the glovebox. The glovebox antechamber was pump-purged three times prior to introducing its contents into the glovebox. The glass coupling was removed from the quartz ampoule in order to load the charge. Figure 16 shows the as received strontium iodide on the left and charge loaded in a 25 mm ampoule tapered to a point.
Figure 16: (left) As received starting Material and (right) charge loaded in an ampoule tapered to a point.

After the charge was loaded in the ampoule some cleaning was done with a rolled Kimwipes® rod to remove any residual powders to the inner wall. The plug was placed in the ampoule and the coupling was reattached to the vacuum valve. Care was taken at this point to ensure the valve and coupling were air tight while in the glovebox as well as maintaining the plug a distance of 5 cm from the top of the charge in a horizontal position. The closed valve ampoule is taking out of the glovebox and reattached to the vacuum stage. Prior to evacuating the charge the vacuum line up to the ampoule valve is evacuated and left under vacuum for 30 minutes with a liquid nitrogen cooled cryo-trap. The ampoule valve is slowly opened so as to not disturb the location of the plug and charge. The ampoule is evacuated down to a vacuum in the order of $10^{-5}$ Torr it is heated sequentially at 75 °C for 16 hour then 150 °C for 4 hours. This sequential heating process is done to further drive out any residual moisture in the charge. After the dehydration process, using a hydrogen-oxygen flame, the ampoule was then sealed using the plug about 5 cm from the top of the charge. As a precaution, the charge was kept cool with a water soaked insulation cloth during the sealing. Using the flame, ampoule wall was gently melted until it collapsed under the influence of vacuum forming a sealed neck. Once the
ampoule is sealed it is taken off of the vacuum stage, placed vertically where a quartz handle is welded on the top ring for hanging.

Figure 17: Gold coated semi-transparent furnace with two independently controlled heating coils (zones).

Material Purification by Zone Refining

Zone refining was developed in the early 1950s at Bell Telephone Laboratories in response to the need for extremely pure germanium [28]. It was an essential step for the development of the transistor and thus for the entire electronics revolution. Prior to zone refining, progressive freezing was the purification workhorse. A melt was slowly frozen, causing more impurities to be concentrated in the last melt to freeze portion. However, a single solidification
did not give sufficient purification and remelting would redistribute the impurities in the last to freeze portion.

The possibility of removing extrinsic impurities from a congruently melting material is based on the segregation phenomenon: the different solubility of impurities (solutes) in the solid or molten material. The removal of an impurity element depends on its distribution coefficient $k_0$ defined as

$$k_0 = \frac{c_s}{c_l} \quad (3.12)$$

the ratio of the initial impurity concentration in the solid phase, $c_s$, and liquid phase, $c_l$. The impurity concentration of the solid and the liquid are typically not at equilibrium so the distribution coefficient $k_0$ is replaced with the effective distribution coefficient, $k_{\text{eff}}$ [29]. If the solute’s segregation coefficient $k_i$ is 0.1, then, at each point along the crystal-melt interface, the local solute concentration is one-tenth that in the melt. Unfortunately, a crystal can solidify with severe segregation due to a segregation coefficient that is not equal to unity and due to convective species transport in the melt.

Zone refinement is only possible for elements in which the impurity is enriched in the liquid phase, or $k_{\text{eff}} < 1$. 

48
The illustration in Figure 18, from [28], shows an impure ingot of total length $L$ being passed horizontally through a furnace that creates a small molten zone of length $l$ (typically $l \leq \frac{L}{10}$). Multiple passes are done to reduce the impurity distribution. The calculation of the resulting impurity distributions for a finite number of passes is complicated, since the starting composition of the ingot is no longer uniform. Nevertheless, a variety of numerical and analytical results has been obtained for infinite and for finite rods lengths and passes [30][31][32][33]. Assuming an infinite number of passes, the impurity distribution in a finite length ingot can be approximated by the exponential function

$$c_i(x) = Ae^{Bx}$$  \hspace{1cm} (3.13)

where $x$ is the crystallized ingot fraction of the total length $L$, the coefficients $A$ and $B$ are obtainable from

$$k_{\text{eff}} = \frac{B_1}{c^B} - 1$$  \hspace{1cm} (3.14)
In the context of this work, the approximation of equations (3.13), (3.14), and (3.15) is satisfactory, as the end part of the ingot was always excluded for crystal growth.

**Strontium Iodide Growth**

Prior to growth strontium iodide the procedures are as followed: The entire charge is melted in the upper zone for two days to allow for mixing and ensure a homogeneous melting. A portion of the ampoule is lowered to the cold zone to obtain a solid phase by abrupt freezing. This process initiates the seeding process and the transparent furnace allows to visually locate the solid liquid interface. The ampoule is raised slowly to minimize the solidified material to a tiny fraction of in the tip, see Figure 20. Once the seed is approximately 1 cm, the ampoule is raised to the upper zone then quickly lowered to create some separation between to the seed and the wall of the ampoule. The growth is initiated by starting the lowering motion of the ampoule along the temperature gradient at a rate of 0.67cm/day.

![Figure 19: Illustration of the crystal in a tapered ampoule.](image-url)
The ampoule, with the charge inside was placed in a vertical position in the Bridgman furnace. This was done by attaching 18 gauge Ni-Cr wire from the quartz hanger to the mechanical lowering mechanism of the motion assembly. With the furnace on standby, set to 30 °C, the ampoule was positioned in the center of the top zone of the furnace. The seal in the ampoule was such that it remained in the heating zone of the furnace. The furnace temperature is raised slowly from room temperature to about 600 °C at a rate of about 1 °C/min, in order to avoid iodine dissociation in the top zone. Iodine dissociation can be seen, in Figure 21 as a purple plume above the melt, and can also occur around the seal if it is located outside the heating and/or insulation of the furnace. The iodine gas will be sublimated out of the matrix and will form crystals around the seal. To ensure homogenization of the melt, the ampoule was maintained at 600 °C for 24 hours and given manual agitation by physically shaking the ampoule.
in an up and down manner during the soaking period. In the event of the seal being made in such a manner that the charge will not melt then the bottom zone temperature will be increased to the top zone temperature to aid in melting and homogenization.

Figure 21: Strontium iodide growth showing a violet plume from iodine disassociation from the matrix.

After the soaking and subsequent homogenization of the charge the bottom zone temperature is set to 400 °C and allowed to stabilize. This resulted in a temperature gradient of about 20 °C/cm between the top and the bottom zone. The ampoule, in the top zone, was slowly translated downward towards the bottom. The charge was lowered to the temperature gradient area and allowed to supercool in order to initiate the growth. Growth parameters are manually recorded and monitored.

The hot zone is set above the cold zone, and the growth ampoule is translated down in the furnace. The melt in the growth ampoule solidifies first at the bottom of the ampoule and grows upward as the ampoule is lowered to the cold zone. This setup allows one to control the interface shape and the temperature gradient in the furnace independently. It is believed that in this
thermally stable crystal growth configuration, free convection effects in the melt can be minimized.

![Temperature profile](image)

**Figure 22:** a) Sealed ampoule in growth furnace, (top) yellow liquid - hot zone (bottom) clear solid - cold zone. b) Corresponding temperature profile showing both zones and the temperature of the solid liquid interface.

![Ingot images](image)

**Figure 23:** Resulting ingot in (left) growth quartz ampoule and (right) extracted ingot from growth ampoule.

The growth was continued for about 30 days until the ingot was completely solidified, fully into the bottom zone. After solidification, the temperature of the top zone was reduced to that of the bottom zone and the entire furnace was cooled to room temperature 6 °C/hr. The resulting ingot
is shown in Figure 23 inside of the growth ampoule (left) and extracted from the ampoule (right). The ingot contained some cracks, which will be discussed at a later time. The grown ingot was removed from the ampoule and observed under an ultraviolet light source which confirmed the incorporation of the dopant from the fluorescence.

The scintillation performance of one of the crystals is shown below where a gamma-ray spectrum of $^{137}$Cs is shown in with an energy resolution of $3.27\%$ at 662 keV.

![SrI$_2$ Eu 2.5\% Spectrum](image)

*Figure 24: (left) Strontium iodide crystal grown at Fisk University (right) $^{137}$Cs Spectrum of the crystal using a Hamamatsu 6231-100 PMT biased at 900V with a preamp shaping time of 6 µs.*

It should be noted that the methods described here have also been applied to the growth of double salt halide (described in recommendations), iodide scintillators, and a wide range of halide scintillators. Also of note is that the mechanical stress induced by gravity could be alleviated by tilting the ampoule for crystal growth. The cross sectional area will be increased by the tilting thus decreasing the stress applied on it. Alternatively, partial of the gravitational force will be taken by the ampoule therefore the actual gravitational force applied on the crystal will be greatly decreased. The angle of tilt needs to be calculated for the crystal growth.
Chapter 4: Europium doped Strontium Iodide

The ground state electronic configuration of Eu$^{2+}$ is the half-filled 4f-shell ($4f^76s^2$) corresponding to the $4f^7(^8S_{7/2})$ ground state. Absorption spectra of Eu$^{2+}$ activated scintillators show the transition from the ground state to the excited state as given by the following equation:

$$4f^{n-1}5d \rightarrow 4f^n$$  \hspace{1cm} (4.1)

This corresponds to the electronic transition in Eu$^{2+}$

$$4f^7 \rightarrow 4f^65d$$  \hspace{1cm} (4.2)

In a scintillators, the energy of the photon released when an electron recombines with a hole is similar to the energy required to form an electron-hole pair. When scintillators are doped, luminescence centers with emission wavelength much less than the electron-hole pair energy are produced. The host matrix becomes transparent to its scintillation light due to less self absorption.

Crystal Structure

The use of a seed crystal is restricted due to the properties of the melt. The resulting crystal is not oriented and therefore does not have a cleavage plane or preferential orientation. As a result X-Ray Diffraction is used only for the sake of verification of material and not to identify epitaxial planes. SrI$_2$ crystallizes in the orthorhombic crystal system (space group: $Pbca$) and the lattice constants are: $a=15.22$ Å, $b=8.22$ Å, and $c=7.90$ Å. A SrI$_2$ unit cell contains a sum of 8 formula units [34], one central strontium-ion with seven neighboring iodine ions, Figure 25. The coefficients of thermal expansion along the crystallographic axes are [35]:

55
\[ a = 1.552 \times 10^{-5} \, ^\circ\text{C} \]
\[ b = 2.164 \times 10^{-5} \, ^\circ\text{C} \]
\[ c = 0.924 \times 10^{-5} \, ^\circ\text{C} \]  

(4.3)

Figure 25: The 24 atom orthorhombic cell of Strontium Iodide with two inequivalent iodine sites.

Properties of SrI\(_2\)

In general, hygroscopic behavior is a physical process and defined as the property of a concentrated aqueous solution of a salt to attract H\(_2\)O for example from air moisture. This occurs if the moisture vapor pressure of the solution is lower than the partial pressure of the moisture vapor contained in the surrounding air. The solid salt would thus be dissolving in the air moisture until saturation is reached. The limit solubility of SrI\(_2\) in water is 17.8 g/l at 20\(^\circ\text{C}\) [NIST], compared to 3.6 g/l for common table salt.

The solubilities of SrI\(_2\) in water and alcohol are 177.8 g/100 ml (20 \(\circ\text{C}\)) and 3.1 g/100 ml (4 \(\circ\text{C}\)) respectively [36]. When heated in the presence of oxygen, SrI\(_2\) decomposes to strontium-oxide according to the equation below

\[
2\text{SrI}_2(s) + O_2(g) \overset{\text{heat}}{\rightarrow} 2\text{SrO}(s) + 2I_2(g) 
\]

(4.4)

A high density combined with a high effective atomic number \(Z_{eff}\) is necessary for strong interactions through photoelectric effect. The \(Z_{eff}\) for SrI\(_2\) is 49.4 and is calculated as such

\[
Z_{eff} = 2.94\sqrt{f_1x(Z_1)^2 + f_2x(Z_2)^2} 
\]

(4.5)

where \(f_1\) is the fraction of strontium in strontium iodide (0.33), \(f_2\) is the fraction of iodine (0.67), \(Z_1\) is the atomic number of strontium (38) and \(Z_2\) is the atomic number of iodine (53).
### Table 2: Solubility Table

<table>
<thead>
<tr>
<th>Substance</th>
<th>0 °C</th>
<th>20 °C</th>
<th>40 °C</th>
<th>60 °C</th>
<th>80 °C</th>
<th>100 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>SrI₂</td>
<td>165</td>
<td>178</td>
<td>192</td>
<td>218</td>
<td>270</td>
<td>383</td>
</tr>
<tr>
<td>Sr(OH)₂·H₂O</td>
<td>0.91</td>
<td>1.77</td>
<td>3.95</td>
<td>8.42</td>
<td>20.2</td>
<td>91.2</td>
</tr>
<tr>
<td>NaI</td>
<td>159</td>
<td>178</td>
<td>205</td>
<td>257</td>
<td>295</td>
<td>302</td>
</tr>
</tbody>
</table>

### Table 3: Properties of SrI₂:Eu²⁺

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/cm³)</td>
<td>4.59</td>
<td>[37]</td>
</tr>
<tr>
<td>Melting Point (°C)</td>
<td>538</td>
<td>[37]</td>
</tr>
<tr>
<td>Structural Type</td>
<td>Orthorhombic</td>
<td>[37]</td>
</tr>
<tr>
<td>Index of Refraction</td>
<td>1.85</td>
<td></td>
</tr>
<tr>
<td>Wavelength of emission (nm)</td>
<td>435</td>
<td>[37]</td>
</tr>
<tr>
<td>Light Yield (photons/MeV)</td>
<td>80,000</td>
<td>[38]</td>
</tr>
</tbody>
</table>
Bandgap

The ground state electronic configuration of Eu$^{2+}$ is the half-filled 4f-shell ($4f^76s^2$) corresponding to the $4f^7(^8S_{7/2})$ ground state. Absorption spectra of Eu$^{2+}$ activated scintillators show the electronic transition from the ground state to the excited state as given by $4f^7 \rightarrow 4f^65d$. Given the bandgap of SrI$_2$ is 5.6eV [15], the band diagram can best be represented below where the blue arrow is the electronic transition.
Crystal Characterization

The measurements performed are for light output, time response, and pulse shape discrimination. The scintillation light produced by the samples was detected by a Hamamatsu R6231-100 PMT. The signals were shaped with a Tennelec TC 244 spectroscopy amplifier and recorded with an Amptek MCA8000-A multi-channel analyzer for offline analysis. The scintillation light yields of the samples were measured using a 20 μCi $^{137}$Cs gamma ray source. The setup for the gamma ray testing consisted of the aforementioned PMT biased at 900V, connected to an Ortec 113 preamplifier, an Ortec 671 spectroscopic amplifier, and a Canberra MP2 multichannel amplifier. Polished samples are immersed in a mineral oil filled quartz cuvette optically coupled to the PMT window using Saint Gobain optical grease.
Differential Scanning Calorimetry (DSC)

enthalpy determinations were carried out using a TA Instrument TDA-DSC 2960. The instrument was calibrated by means of the heat of fusion of zinc. Both the heating and cooling rate were 20 °C/min with a transition stabilization of five minutes.

DSC measures the energy required to keep a sample and an inert reference material at the same temperature while subjecting them both to identical heating or cooling programs.

Figure 28: DSC measurement setup

Scintillation Detection Measurements

Figure 29: Scintillation detection diagram
Using the figure above as a guide we will describe in detail the scintillation measurement process. As mentioned before the most common optical detection module for reading scintillation light output is a photomultiplier tube. Vacuum conditions are maintained within the PMT glass casing so that low-energy electrons can be accelerated by an electric fields, provided by a high voltage power supply, Figure 30a. One of the two main components of a PMT is the photocathode which converts optical photons into photoelectrons. The more vital component to the PM tube's structure is the dynodes which create the electron multiplication. The dynodes are held at a large positive potential, from the high voltage power supply, so electrons are accelerated towards them and by doing so their energy increases. A common potential difference between each dynode is about 100 V; therefore electrons strike the dynode with 100 eV of energy. Dynodes make use of the secondary electron emission phenomenon; therefore the output of a PMT is amplified current.
Figure 30: Scintillator detector measurement setup; a) High power supply, b) Pulser, c) Multichannel Analyzer, d) Shaping amplifier, and d) Power supply.

The output of the PMT, current, is then sent to a preamplifier which is essentially a current to voltage amplifier. The output of the preamp is a 0-5 V pulse signal that is sent to the shaping amplifier, Figure 30d. The shaping amplifier only amplifies the signals within a user defined shaping time. This shaping time should be 20% longer than the decay time to allow for a full event. Unlike the continuous current source of an LED, a scintillators gamma source is sporadic in nature. The 0-10 V output of the shaping amplifier is sent to a multichannel analyzer (MCA), Figure 30c. The MCA displays the pulse amplitude from the shaping amplifier as a function of channel number or energy, Figure 30.
There exist three types of reflection: specular, diffused and spread. Specular reflection typically consists of a smooth surface and is defined as when the incident angle of the light equals the reflected angle. An example of such a reflection is the reflection of light off of a mirror. Diffused reflection is typically a rough surface that scatters light in all directions.
Spread reflection consists of a surface that has a combination texture and smooth surface. We are concerned with diffuse and specular reflections so a GORE reflector is used, Figure 33.

![GORE reflector](image)

**Figure 33: GORE reflector**

**Effects of Europium Concentration**

In order to evaluate the concentration of europium incorporation in the crystal a SrI$_2$:Eu$^{2+}$ (5 at%) was grown using standard growth conditions. Using a scanning electron microscope (SEM) was able to determine the europium spatial concentration along the length of the ingot using Energy Dispersive X-Ray Spectroscopy and Atomic Backscatter Spectroscopy, Figure 34. From the graph below we see that the average of the EDX and the ABS has a low variance about 5 at%. This shows that there is little to no europium segregation along the length of the boule.
Proving that europium does not segregate in the bulk, the task of obtaining the optimal concentration is at hand. From Figure 35 we see the gamma radiation response of strontium iodide with 0.2, 0.7, 1, 1.5, 2.5, 5, and 10 atomic percentage of europium iodide dopant. All crystals were taken from the same batch and grown using the same procedure. The measured crystals were of similar size and shape and all measured the same day. The source used was $^{137}\text{Cs}$ and the different channel numbers of the photopeak indicate a change in the light output. Figure 36 shows the decay times for the associated gamma response and Figure 37 compiles the both the energy resolution and decay time as a function of the europium concentration.
Figure 35: Gamma radiation response of SrI2 with 0.2% (black), 0.7% (red), 1% (blue), 2.5% (green), 5% (magenta), 10% (olive) europium concentration.

Figure 36: Decay time for strontium iodide with 1, 2.5, 5, 10 atomic percentage of europium iodide.
The purpose of this work and isotope identification, so energy resolution is the most important metric. As you can see from the above graph that the ideal europium concentration for is 2.5 at%. Had the application been medical imaging a smaller concentration would have been selected as it boasts fast decay time.

**Optical Absorption**

The temperature dependent absorption was taken with a Cary UV-Vis Spectrometer. Figure 38 shows the hermetically sealed sample using a quartz plate, gel, and optical cement. The absorption of the aforementioned materials was independently observed, results shown in Figure 39.
The temperature dependent absorption is shown below in Figure 40.
Scintillation Non Proportionality

In 1994 Valentine et al. developed a Compton Coincidence Technique to measure electron response for crystals, study of electron response, simulation of intrinsic resolution due to $\gamma$-rays [39]. The upgraded facility based on Valentine’s setup was named Scintillation Light Yield Non-proportionality Characterization Instrument (SLYNCI) which was built at Lawrence Livermore National Laboratory and was used to understand nonproportionality in many classes of scintillator materials.
Modeling of transport and quenching in electron tracks conducted by our collaborators has suggested that nonproportionality will be improved if the stopping of energetic radiation and the emission of luminescence take place in dedicated, spatial regions. The electron hole density at a point along and electron track approximated as cylindrical scales as the inverse square of the track radius at that radius. Even small radial diffusion can have important effects on quenching, and the huge radial concentration gradient in a track promotes diffusion that can be dramatic [40][41]. Although nonlinear 2nd and 3rd order quenching is widely acknowledged to be at the
heart of nonproportionality response, the 2nd order dipole-dipole quenching rate constant has been measured so far in CdWO₄[42] and recently in CsI, CsI:Tl, and NaI:Tl [43][40]. The 3rd order valence-conduction Auger rate constant has not been experimentally measured for any of the conventional, non-semiconductor scintillators. There is a great deal of activity on Auger rates in wide bandgap semiconductors like InGaN now due to LED Efficiency Droop problems [44], but the activity has not yet been explored in wider gap materials used as scintillators. The Auger rate constant generally decreases with increasing bandgaps [45], so it becomes harder to measure in wider gap materials, but it still needs to be confirmed experimentally to access if it a significant factor at the e-h densities of electron tracks.

Discussion and Summary

The methods applied here have been successfully applied to the growth of single crystal of high performance doped strontium iodide with crystal diameters of 2.5cm. Light yield of 90,000 photons/MeV and high energy resolution of 2.6% for 662 keV gamma rays from $^{137}$Cs was obtained, Figure 43 and Figure 44. This approaches the empirical limiting value of 2.2% for a room temperature energy resolution of a scintillator. Achieving further decrease in this value for energy resolution remains an important and ongoing goal of scintillator research and development. However, energy resolution values of mid to upper 4% are, in fact routinely obtained.
Figure 43: Best reported Strontium Iodide resolution of 2.62 %

Figure 44: Decay time of best crystal

SrI$_2$:Eu(2.5%)-Ba(0.9%)

Energy Resolution
662 keV FWHM = 2.62%

Td = 1.1 μs
The ability to grow high quality, uncracked crystals of strontium iodide is strongly dependent on the quality of the starting component. As this is a binary incorporating both strontium iodide and europium iodide, both of these components need to be of high quality. The former is more complicated as it is synthesized from naturally occurring strontium carbonate and hydroiodic acid while the former can be further purified with the use of zone refining.
Chapter 5: Other Rare Earth Dopants

In the past decade, inorganic scintillator research has focused less on improving the characteristics of known scintillators, but rather on the search for new hosts capable of fast response and high energy resolution. Extensive searches have been made for hosts doped with lanthanide activators utilizing the allowed $5d$-$4f$ transition \[46][47]. These $5d$-$4f$ transitions are dipole-allowed and thus are about $10^6$ times stronger than the more frequently observed $4f$-$4f$ transition in the trivalent rare earth ions.

Figure 45: Timeline of scintillator activator. From Dorenbos

Ce$^{3+}$, Nd$^{3+}$ and Pr$^{3+}$ have been investigated for fast response applications and Ce$^{3+}$ and Eu$^{2+}$ stand out as the most promising activators offering high light yield, and high energy
resolution, as low as 2.6% at 662 keV for the best performing crystals, such as LaBr$_3$:Ce$^{3+}$ and SrI$_2$:Eu$^{2+}$ [48][49][35]. Meanwhile, Ce$^{3+}$, Tb$^{3+}$, Eu$^{3+}$ and Yb$^{3+}$ dopants have been investigated extensively as luminescent ions for green and red phosphor applications. In the strontium iodide lattice a divalent activator is needed in order to maintain charge neutrally and avoid any vacancies. Most of the rare earth activator occur naturally trivalent but they can be reduced to form stable divalent ions.

![Figure 46: Reduction potentials of rare earth lanthanides](image)

Illustrated above is the reduction potential of the rare earth lanthanides [50]. The reduction potential is given by:

$$Ln^{3+} + e^- \rightarrow Ln^{2+}$$ (5.1)

and is a measure of the tendency of a chemical species to acquire electrons and thereby be reduced. The more positive the potential, the greater the species' affinity for electrons and tendency to be reduced. The most stable divalent lanthanide is europium with a reduction potential of -0.35V and a half filled 4f electron shell, ytterbium with a reduction potential of -1.05V and a full 4f electron shell, and to a lesser extent samarium with a reduction potential of -1.5V. Show below is the electronic configuration of the lanthanides. In this study we strive to evaluate both ytterbium and samarium as a viable alternative dopant to europium.
Rare-earth Elements

The elements of the periodic table constituting the lanthanide series, ranging from cerium (atomic number 58) to lutetium (atomic number 71), are often known as the rare earth (RE) elements, Figure 47.

![Lanthanides Table]

<table>
<thead>
<tr>
<th>Atomic #</th>
<th>Element</th>
<th>Electronic Configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>57</td>
<td>Lanthanum (La)</td>
<td>[Xe] 4f° 5d¹ 6s²</td>
</tr>
<tr>
<td>58</td>
<td>Cerium (Ce)</td>
<td>[Xe] 4f¹ 5d¹ 6s²</td>
</tr>
<tr>
<td>59</td>
<td>Praseodymium (Pr)</td>
<td>[Xe] 4f³ 5d⁰ 6s²</td>
</tr>
<tr>
<td>60</td>
<td>Neodymium (Nd)</td>
<td>[Xe] 4f⁴ 5d⁰ 6s²</td>
</tr>
<tr>
<td>61</td>
<td>Promethium (Pm)</td>
<td>[Xe] 4f⁵ 5d⁰ 6s²</td>
</tr>
<tr>
<td>62</td>
<td>Samarium (Sm)</td>
<td>[Xe] 4f⁶ 5d⁰ 6s²</td>
</tr>
<tr>
<td>63</td>
<td>Europium (Eu)</td>
<td>[Xe] 4f⁷ 5d⁰ 6s²</td>
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<td>Gadolinium (Gd)</td>
<td>[Xe] 4f⁸ 5d⁰ 6s²</td>
</tr>
<tr>
<td>65</td>
<td>Terbium (Tb)</td>
<td>[Xe] 4f⁹ 5d⁰ 6s²</td>
</tr>
<tr>
<td>66</td>
<td>Dysprosium (Dy)</td>
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<td>Holmium (Ho)</td>
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<td>Erbium (Er)</td>
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<td>Thulium (Tm)</td>
<td>[Xe] 4f¹³ 5d⁰ 6s²</td>
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<tr>
<td>70</td>
<td>Ytterbium (Yb)</td>
<td>[Xe] 4f¹⁴ 5d⁰ 6s²</td>
</tr>
<tr>
<td>71</td>
<td>Lutetium (Lu)</td>
<td>[Xe] 4f¹⁵ 5d⁰ 6s¹⁰</td>
</tr>
</tbody>
</table>

Figure 47: The rare earth elements with associated atomic number and electronic configuration

The term rare earth was proposed due to the fact that when the first rare earths were discovered they were thought to exist only in the earth crust in small quantities and because they had to be extracted from materials like lime and alumina then known as "earths." Today most of them are more common than platinum, gold or silver. They are all chemically very similar, a fact that makes their complete isolation and high purity is very difficult.
Properties of Rare-earths

The rare earth elements are metals with high luster and electrical conductivity. Their bulk color is often silver, silvery-white or grey. Rare-earth rapidly react with oxygen in air, forming oxides. They all have elevated melting points and tend to form ionic compounds. Most RE-ions are trivalent, with samarium, europium, thulium and ytterbium also having valence +2 and cerium, praseodymium and terbium +4. Their electronic configuration is \([\text{Xe}]\ 4f^n5d^06s^2\) with \(n\) varying from 1 (Ce) to 15 (Lu) see Figure 47. Given that the bandgap of SrI\(_2\) is 5.3eV, the band diagram showing the free divalent lanthanide energy level can best be represented below where the red arrow is the electronic transition.

![Idealized free divalent lanthanide energy level in strontium iodide. Adapted from[47]](image)

Ytterbium Characterization

Enthalpy determinations were carried out using a TA Instrument TDA-DSC 2960 differential scanning calorimeter (DSC). The instrument was calibrated by means of the heat of
fusion of zinc. Both the heating and cooling rate were 2 °C/min with a transition stabilization of five minutes. The samples were studied under a dry nitrogen atmosphere at a flow rate of 140 L/min in an alumina crucible. Sample sizes ranged from 20 to 30 mg.

Beta radioluminescence utilizing $^{90}$Sr/$^{90}$Y source (~1 MeV average beta energy) spectra were collected with a Princeton instrument/Aceton Spec 10 spectrograph coupled to a thermoelectrically cooled CCD camera at Lawrence Livermore National Labs. The scintillation light produced by the samples was detected by a Hamamatsu R6231-100 photomultiplier tube (PMT). The signals were shaped with a Tennelec TC 244 spectroscopy amplifier and recorded with an Amptek MCA8000-A multi-channel analyzer for offline analysis.

The scintillation light yields of the samples were measured using a $^{137}$Cs $\gamma$ source. The setup for the $\gamma$-ray testing consisted of a Hamamatsu R6231-100 PMT biased at 900V, connected to an Ortec 113 preamplifier, an Ortec 671 spectroscopic amplifier, and a Canberra MP2 multichannel amplifier. Polished samples of 100 - 200 mm$^3$ were immersed in a mineral oil filled quartz cuvette optically coupled to the PMT window using Saint Gobain optical grease. Figure 49(a) shows samples prior to characterization. A Labsphere’s Spectralon® plastic dome was used as a reflector to increase light collection of diffuse reflections.
Figure 49: (a) Photo of strontium iodide scintillators doped with europium and with ytterbium. (b) Photo of same crystals under UV illumination. In the top row (left to right), 0.5% Yb-doped, 0.7% Eu-doped and 1% Eu-doped SrI$_2$ crystals are shown. In the bottom row (left to right) are pure SrI$_2$ and 0.2% Eu doped SrI$_2$.

Thermal Analysis

Differential Scanning Calorimetry (DSC) measurements were used to detect phase transitions in the feedstock material. The melting peak of strontium iodide, which has an orthorhombic crystal structure, can be seen in Figure 50 as an endothermic reaction in the heating cycle at 535 °C. The supercooling, temperature difference between melting and crystallization, for strontium iodide is $\Delta T = 55^\circC$. 
Figure 50: DSC curve of strontium iodide source material at heating and cooling rate of 2 °C/min: black line - heating endothermic; blue line - cooling exothermic.

ΔT = 55°C

Figure 51: DSC curve of cesium dibarium iodide source material at heating and cooling rate of 2 °C/min: black line - heating endothermic; red line - cooling exothermic.

ΔT = 80°C
Cesium dibarium iodide is a double salt consisting of CsI and 2BaI$_2$ with a monoclinic crystal structure. DSC scan of the source material shows a melting point around 622 °C, with a supercooling of $\Delta T = 80^\circ C$ (Figure 51). Another peak was observed around 460 °C during cooling the material cycle which we attribute to phase separation due to the melting point difference (about 100˚C) of its constituent materials that affects the transparency of the crystal.

**Scintillation Properties**

Beta-exited Radioluminescence spectra for SrI$_2$ and CsBa$_2$I$_5$ are presented in Figure 52. The undoped SrI$_2$ exhibits weak band-edge emission starting at ~380 nm, and is dominated by the defect-mediated exciton band, centered at about 550 nm. We also see that both SrI$_2$(Eu$^{2+}$) and SrI$_2$(Yb$^{2+}$) exhibit blue rare-earth luminescence as well as the defect-mediated STE band of strontium iodide. Results published elsewhere show that higher Eu$^{2+}$ doping increases the light yield into the Eu$^{2+}$ band and reduces the intensity of the exciton band [51].

A STE would be created in the SrI$_2$ lattice for example, if a hole localizes to one iodine ion on reaching the top of the valence band resulting in the creation of an unstable iodine atom as shown below

$$I^- \rightarrow I^0$$ \hspace{1cm} (5.2)

The iodine atom would then polarize its environment resulting in the sharing of the hole with another iodine ion as follows

$$I^0 + I^- \rightarrow I_2$$ \hspace{1cm} (5.3)
This state of the iodine molecule is called cation vacancy (Vk) or self trapped hole (STH). The self trapped hole tends to capture an electron forming a STE as

\[ I_2^- + e^- \rightarrow \left( I_2^{-} \right)^* \]  

(5.4)

The STE can emit a photon (excitonic emission) which has been reported in SrI\(_2\) scintillators by [52]. Excitons have lifetimes on the order of nanoseconds, after which time the ground electronic state are restored with the emission of photons or phonons[53].

Also we note from Figure 49(b) that under UV illumination both the ytterbium and europium activated crystals fluoresce with 254 nm excitation, while the undoped crystal does not. The radioluminescence spectrum of CsBa\(_2\)I\(_5\):Yb\(^{2+}\) on the other hand shows strong Yb\(^{2+}\) luminescence centered at 414 nm, and a very weak exciton band.
Figure 52: Radioluminescence spectra of SrI\(_2\) (top); undoped, doped with 0.5% Eu\(^{2+}\) and doped with 0.5% Yb\(^{2+}\). Bottom Radioluminescence spectra of CsBaI\(_5\) doped with 0.5% Yb\(^{2+}\) and 1% Yb\(^{2+}\).

Figure 53: UV excited spectra of 0.5% doped: SrI\(_2\):Eu\(^{2+}\) (blue), SrI\(_2\):Yb\(^{2+}\) (red), and CsBaI\(_5\):Yb\(^{2+}\) (black).

UV-excited spectra of the two ytterbium activated samples (Figure 53) exhibit a nearly identical Yb\(^{2+}\) band at 414 nm, while the europium activated sample exhibits the Eu\(^{2+}\) band at
432 nm. The 432 nm band also appears in SrI₂ (Yb²⁺) as a weak shoulder, likely due to a small concentration of Eu²⁺ derived in the crystal as a feedstock impurity.

The energy resolution, defined as the full width at half maximum of the 662 keV absorption peak, for the Yb-activated SrI₂ is 4.5-4.65 %; considered good compared to other scintillators. Sub-microsecond decay times are measured for Yb-doped SrI₂ and CsBa₂I₅; faster than for Eu-doped samples. Energy resolution of Yb-doped CsBa₂I₅ is not as good, with 5.7% measured for a 1 % Yb-doped CsBa₂I₅ crystal. More work needs to be done to optimize the Yb-doping concentration, but the fast decay time make divalent ytterbium a promising alternative to europium. The energy resolution as well as the time decay of the ytterbium activated samples are shown below in Figure 54, Figure 55, Figure 56, and Figure 57.
Figure 54: Scintillation characteristics of 0.5% ytterbium activated strontium iodide; (top) energy resolution, (bottom) time decay.
Figure 55: Scintillation characteristics of 1% ytterbium activated strontium iodide; (top) energy resolution, (bottom) time decay.
Figure 56: Scintillation characteristics of 0.5% ytterbium activated cesium dibarium iodide; (top) energy resolution, (bottom) time decay.
Figure 57: Scintillation characteristics of 1% ytterbium activated strontium iodide; (top) energy resolution, (bottom) time decay.

- CsBa$_{2.5}$I$_5$ · Yb (1%)
- Energy Resolution
- $662$ keV FWHM = 5.7%
- $^{137}$Cs
- CsBa$_{2.6}$I$_5$ · Yb (1%)
- Scintillator Time Delay
- $T_c = 0.84 \, \mu$s

Decay times:
- $\tau_{\text{slow}} = 2.77 \pm 0.1 \, \mu$s (30.9%)
- $\tau_{\text{fast}} = 0.87 \pm 0.01 \, \mu$s (67.7%)
- $\tau_{\text{fast}} = 74 \pm 2 \, \text{ns} (1.4\%)$
Table 4: Ytterbium doped scintillator properties.

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Light Yield (x10^3) (ph/MeV)</th>
<th>Peak Emission Wavelength (nm)</th>
<th>Energy Resolution 662 keV FWHM (%)</th>
<th>Principal Decay Time (μs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CsBa(_2)I(_5):Eu(^{2+}) 7% [51]</td>
<td>97</td>
<td>432</td>
<td>3.8</td>
<td>1.5</td>
</tr>
<tr>
<td>CsBa(_2)I(_5):Yb(^{2+}) 0.5%</td>
<td>51</td>
<td>414</td>
<td>6.78</td>
<td>0.86</td>
</tr>
<tr>
<td>CsBa(_2)I(_5):Yb(^{2+}) 1%</td>
<td>54</td>
<td>414</td>
<td>5.7</td>
<td>0.87</td>
</tr>
<tr>
<td>SrI(_2):Eu(^{2+}) 0.5%</td>
<td>45</td>
<td>432</td>
<td>4.65</td>
<td>0.92</td>
</tr>
<tr>
<td>SrI(_2):Eu(^{2+}) 2.5%</td>
<td>104</td>
<td>432</td>
<td>2.62</td>
<td>1.1</td>
</tr>
<tr>
<td>SrI(_2):Yb(^{2+}) 0.5%</td>
<td>56</td>
<td>414</td>
<td>4.35</td>
<td>0.61</td>
</tr>
<tr>
<td>SrI(_2):Yb(^{2+}) 1%</td>
<td>39</td>
<td>414</td>
<td>4.5</td>
<td>0.74</td>
</tr>
</tbody>
</table>

The time decay of all the Yb\(^{2+}\) samples exhibit a fast component that contributes less than 2% of the time, a slow component that contributes about 30% of the time and a main component that has the remaining contribution. The scintillation properties of the materials studied are presented below in Table 4.

**Samarium**

Samarium was also evaluated as an alternative dopant to europium. The first attempt was done with a molar concentration of 0.5 m%. We found that the 0.5m% of samarium did not dissolve in the melt Figure 58a and would require further reduction. Figure 58b is the reduced concentration of 0.1m% which appeared to have similar dissolving issues.
These crystals including a lesser 0.05 m% Sm$^{2+}$ scintillated outside the detection range of the PMT.
Figure 59 above shows the samarium doped strontium iodide under a) UV light and b) IR light. We can see from the figure that as you reduce the Sm$^{2+}$ concentration the florescence is blue shifted.

**Summary**

This was the first report on the use of Yb$^{2+}$ and Sm$^{2+}$ as an activator for a gamma spectroscopy scintillator [54]. Samarium as a dopant was not successful as the raw material had problems dissolving, and the emission falls outside the detection range of the PMT. These shortcoming led to the suspension of further exploration. Using our previous expertise in the growth of halide scintillators, we have grown crystals of SrI$_2$ and CsBa$_2$I$_5$ doped with 0.5-1% Yb$^{2+}$. Both materials exhibit an Yb$^{2+}$ radioluminescence peak at 414 nm, decay times of $<1$ μs and light yields exceeding 50,000 Photons/MeV with energy resolution ~5% at 662 keV. The quality of the activated crystals will improve as the doping level is optimized and optical quality of the crystals is developed.
Chapter 6: Co-Doping and Annealing of Strontium Iodide

Co-doping

The importance of gamma ray spectroscopy in the age of nonproliferation can hardly be overstated. While the industrial use of gamma ray spectroscopy is constantly changing, what remains is the need for crystals with high energy resolution and non proportional. Devoid of native radioactive isotopes, europium doped strontium iodide is a prime for commercialization. In this section we report co-doping as a fine tuning for lattice hardening and scintillation properties. It has been shown with LaBr$_3$:Ce$^{3+}$ that co-doping with divalent strontium or calcium that the scintillator was a factor of three more tolerant towards high ionization density recombination [55].

The starting materials for the strontium iodide doped with 2.5 m% europium iodide were 99.999% pure anhydrous SrI$_2$ beads and 99.999% EuI$_2$ beads. This material was synthesized using quick Bridgman then partitioned for the use of the co-dopants. The codopants used in this experiment were NaI, KI, MgI$_2$, and CaI$_2$ with a selected molar percentage of 0.1%. Using a slotted steel cartridge, five samples were grown simultaneously in one Bridgman run. Illustrated in Figure 60 is the five samples under UV light where a) is the SrI$_2$:Eu$^{2+}$ (2.5 mol %) control; b) SrI$_2$:Eu$^{2+}$/Ca$^{2+}$ (2.5/0.1 at %); c) SrI$_2$:Eu$^{2+}$/K$^{1+}$ (2.5/0.1 at %); d) SrI$_2$:Eu$^{2+}$/Na$^{1+}$ (2.5/0.1 at %); and e) SrI$_2$:Eu$^{2+}$/Mg$^{2+}$ (2.5/0.1 at %).
Figure 60: The five samples under UV light where a) is the SrI$_2$:Eu$^{2+}$ (2.5 mol %) control; b) SrI$_2$:Eu$^{2+}$/Ca$^{2+}$ (2.5/0.1 at %); c) SrI$_2$:Eu$^{2+}$/K$^{1+}$ (2.5/0.1 at %); d) SrI$_2$:Eu$^{2+}$/Na$^{1+}$ (2.5/0.1 at %); and e) SrI$_2$:Eu$^{2+}$/Mg$^{2+}$ (2.5/0.1 at %)

Table 5: Co-doped sample properties

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Resolution at 662 keV (%)</th>
<th>Decay Time (ns)</th>
<th>Light Yield (x NaI)</th>
<th>Ionic radius Normalized to Strontium</th>
</tr>
</thead>
<tbody>
<tr>
<td>SrI$_2$:Eu$^{2+}$(2.5 at %)</td>
<td>3.4</td>
<td>1000</td>
<td>2.5</td>
<td>1</td>
</tr>
<tr>
<td>SrI$_2$:Eu$^{2+}$/Ca$^{2+}$ (2.5/0.1 at %)</td>
<td>4.2</td>
<td>854</td>
<td>2.4</td>
<td>0.9</td>
</tr>
<tr>
<td>SrI$_2$:Eu$^{2+}$/K$^{1+}$ (2.5/0.1 at %)</td>
<td>4.1</td>
<td>708</td>
<td>1.7</td>
<td>1.2</td>
</tr>
<tr>
<td>SrI$_2$:Eu$^{2+}$/Na$^{1+}$ (2.5/0.1 at %)</td>
<td>3.1</td>
<td>845</td>
<td>2.2</td>
<td>0.9</td>
</tr>
<tr>
<td>SrI$_2$:Eu$^{2+}$/Mg$^{2+}$ (2.5/0.1 at %)</td>
<td>2.9</td>
<td>1020</td>
<td>2.5</td>
<td>0.7</td>
</tr>
</tbody>
</table>

Annealing

Samples were produced from a boule of SrI$_2$:Eu$^{2+}$ (2.5 m%). The as grown pristine sample had the dimension $8.4 \times 7.8 \times 3.3 \text{mm}^3$ the short annealed is $8.6 \times 7.6 \times 3.5 \text{mm}^3$ and the long anneal is $8.6 \times 5.7 \times 3.6 \text{mm}^3$. The two annealing conditions that were performed are: Short anneal at 300 °C for 14hrs, and a long anneal at 350 °C for 72 hrs. The annealing showed improvements in the energy resolution, Figure 61. The samples exhibiting the most improvement in energy resolution were measured at VCU for PL measurements. The long
annealed sample displayed a 35% higher PL intensity, Figure 62, and varied linearly with the excitation density within the excitation range of 12-120 Wcm$^{-2}$.

Figure 61: Energy resolution of annealed samples.

Figure 62: Room temperature PL spectra of SrI$_2$:Eu$^{2+}$ (2.5m%)
The peaks near 840 nm are due to second order diffraction that is eliminated in Figure 63 using a
long pass filter. Figure 63 illustrates the temperature dependent PL of the as grown sample. The
temperatures indicated are the cold finger temperatures. Sample temperature is higher as it is not
directly in contact with the cold finger. As you can see the PL intensity decreases with
increasing temperature. (Most of the change is from 15 K to 50 K). The variation in PL intensity
across the sample is small (~ 10%).
Chapter 7: Conclusions and Recommendations

The increasing demand for room temperature gamma-ray detectors, due to nonproliferation have encourages the discovery and development of high quality scintillating materials. The required material properties include high density and atomic numbers for high gamma-ray detection efficiency; high efficiency for converting the kinetic energy of charged particles into detectable light with a high scintillation; and the absence of natural long-lived radioactive isotopes (as $^{138}$La in lanthanum and $^{176}$Lu in lutetium). Strontium Iodide meets all these criteria thus has the potential to be a successful material for room temperature gamma-ray detection applications. The aim of this work was to grow and establish an understanding of the scintillator Strontium Iodide highlighting its superior energy resolution for the use of security applications.

Crystal growth is often the most challenging and time consuming stage of developing any new material. This work presented the efforts of growing single crystals of rare earth doped Strontium iodide using the vertical Bridgman method. The entire growth process is composed of multiple stages including heat ramp from room temperature to a thermal homogenization temperature, soaking for a period of time, cooling down to growth temperature, crystal growth, and post-growth cooling to room temperature. Each stage has been carefully designed and tested to ensure a successful growth run. The crystal growth was conducted and dopants were selected based on the ionic radius of Strontium. A new strontium iodide energy resolution benchmark of 2.6% was achieved with divalent europium doping. The improvement in energy resolution is
attributed to improve growth procedures to decrease moisture, and other hydroxyl content in the starting material and post growth material handling processes to improve the collection optical photons. There were some variations in the resolution of repeated growths with some resolutions as high as 3.4%.

This work reports the first use of Yb$^{2+}$ and Sm$^{2+}$ as an activator for a gamma spectroscopy scintillator. Samarium as a dopant did not scintillate within the detection range of the PMT so it was no longer explored. Using previous expertise in the growth of halide scintillators, crystals of SrI$_2$ and CsBa$_2$I$_5$ (discussed below) doped with 0.5-1% Yb$^{2+}$ were grown. Both materials exhibit an Yb$^{2+}$ radioluminescence peak at 414 nm, decay times of <1 μs and light yields exceeding 50,000 Photons/MeV with energy resolution ~5% at 662 keV. Ytterbium as a dopant is promising as an alternative to europium and should be a candidate for further refinement as the material used in this study was 3N purity.

Through the scintillation characterizations of the europium doped strontium iodide single crystals grown in this work, it was found that the crystals have defect mediated self trapped exciton (STE) peak obtained from Beta excited Radioluminescence. The STE is created in the SrI$_2$ lattice when a hole localizes to one iodine ion on reaching the top of the valence band resulting in the creation of an unstable iodine atom. The iodine atom then polarizes its environment resulting in the sharing of the hole with another iodine ion. This state of the iodine molecule is called cation vacancy (Vk) or self trapped hole (STH). The self trapped hole tends to capture an electron forming a STE. The STE can emit a photon (excitonic emission). Other results published elsewhere show that higher Eu$^{2+}$ doping increases the light yield into the Eu$^{2+}$ band and reduces the intensity of the exciton band. Using X-Ray Excited Optical Luminescence, it was verified using the crystals that were grown. Excitons have lifetimes on the order of
nanoseconds, after which time the ground electronic state are restored with the emission of photons or phonons. Annealing the crystal improved the resolution but reduction in the excitonic peak was not observed.

The crystal quality of orthorhombic strontium iodide is prone to defect due to its complicated lattice structure as compared to commercially available sodium iodide crystals with its cubic structure. These defects lead to cracking and nonradiative centers which are prohibitive to the growth of large boules and improvements in scintillation properties, despite its inherent superior resolution and light yield to sodium iodide. The use of codopants was explored for the purpose of reducing optical defects that leads to crystal cracking. Of the five codopants investigated, (Ca$^{2+}$, Mg$^{2+}$, K$^{+}$, and Na$^{+}$) divalent magnesium with a maximum molar percentage of 0.1% have proven to improve crystal structure without sacrificing the scintillation property. Segregation was a problem with increased concentration, as evident from a red ring on the last to freeze portion. More work should be done to optimize the concentration and explore other codopants that may fine tune the resolution as the reported value is close to the theoretical limit of 2.2%.

Other recommendation is the exploration of double salt halides in particular cesium barium iodide (CBI), cesium calcium iodide (CCI), and barium bromine iodide (BBI). Double salt halides inherently have high density and atomic number which translates to good stopping power for energetic particles, in particular gamma rays.

*Cesium Barium Iodide.* Europium-doped cesium barium iodide (CBI) was reported by Bourret-Courchesne et. al. with 9% (± 2%) Eu$^{2+}$ [51] and by Gahane, et al. [56]. CBI is a double salt consisting of CsI (cubic) and 2BaI$_2$ (orthorhombic) with a monoclinic P21/c crystal structure
Using the Tran-Blaha Modified Becke Johnson (TB-mBJ) Singh calculated the bandgap to be 4.49 eV [58]. The reported scintillation properties are shown below in Table 6.

Table 6: Double salt halide crystal scintillation properties.

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Light Yield (ph/MeV)</th>
<th>Principal Decay Time (ns)</th>
<th>Peak Emission Wavelength (nm)</th>
<th>Energy Resolution 662 keV FWHM (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SrI₂:Eu 3%</td>
<td>115,000</td>
<td>1,200</td>
<td>435</td>
<td>2.8</td>
</tr>
<tr>
<td>CsBa₂I₅:Yb 0.5%</td>
<td>51,000</td>
<td>860</td>
<td>414</td>
<td>6.8</td>
</tr>
<tr>
<td>SrI₂:Yb 0.5%</td>
<td>56,000</td>
<td>610</td>
<td>414</td>
<td>4.4</td>
</tr>
<tr>
<td>CsBa₂I₅:Yb 1%</td>
<td>54,000</td>
<td>840</td>
<td>420</td>
<td>5.7</td>
</tr>
<tr>
<td>SrI₂:Yb 1%</td>
<td>39,000</td>
<td>740</td>
<td>414</td>
<td>4.5</td>
</tr>
<tr>
<td>CsCaI₃:Eu 3%</td>
<td>50,675</td>
<td>9 (Fast)</td>
<td>468</td>
<td>16.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.920 (Slow)</td>
<td></td>
</tr>
<tr>
<td>BaBrI:Eu 8%</td>
<td>46,000</td>
<td>462</td>
<td>421</td>
<td>3.56</td>
</tr>
<tr>
<td>BGO</td>
<td>8,200</td>
<td>-</td>
<td>540</td>
<td>-</td>
</tr>
</tbody>
</table>

The CBI crystal, shown in Figure 64, was doped only with ytterbium. A comparison is made with SrI₂ doped with the same molar percentage of Ytterbium and the standard 3 mol% SrI₂. The stability of divalent europium and divalent ytterbium (II) halides is explained by the presence of [Xe]4f⁷ and [Xe]4f¹⁴ configurations [59]. DSC scan of the source material shows a melting point around 622 °C, with a supercooling of ΔT = 80 °C (Figure 65). Another peak was observed around 460 °C during the cooling cycle which we attribute to phase separation due to the melting point difference (about 100 °C) of its constituent materials that affects the transparency of the crystal. More work should be done to investigate further.
Cesium Calcium Iodide. Cesium calcium iodide has been utilized as a host material for Tm$^{2+}$ laser applications, but Zhuravleva et al [60] first reported CsCaI$_3$ and CsCaCl$_3$, as a scintillating crystal [61][62]. They reported an optimized europium concentration for maximum scintillation light yield in the CsCaI$_3$ and CsCaCl$_3$ systems to be 3% Eu and 10% Eu respectively. The CsCaI$_3$ system is reported to melt congruently at 686 °C and has an orthorhombic structure. This host
material is more dense and has higher effective atomic number than the traditional NaI:Tl scintillator giving it a higher stopping power, and smaller photon mean free path. A bandgap of 4.02 eV is calculated using the full potential linearized augmented plane wave (FPLAPW) method within the framework of Density Functional Theory [60]. Due to the difference in ionic radii of Ca$^{2+}$ (1.06 Å) and Eu$^{2+}$ (1.20 Å) (for coordination number 7), some europium segregation is expected [63].

The boule obtained from the growth is shown in Figure 66 under UV light. A europium iodide molar concentration of 2.5% was used, based on previous scintillator experience. Albeit the crystal was crack free, under UV illumination one can see variation in brightness that may be attributed to segregation during growth. The Beta-Excited Radioluminescence spectrum for CCI is presented in Figure 67. The emission peak is at 468 nm which is similar to what has been reported [61]. The measured energy resolution 16.3%, which was extracted from the spectra illustrated in Figure 68. This result is lower compared to reported CCI resolution and some other scintillators. The light yield of 50,675 Ph/MeV is slightly better than the reported 35,500 Ph/MeV. Two individual events were observed for the CCI time component (Figure 69); a very fast 9 ns event and a slower 1900 ns event. This may suggest photoelectric absorption in CsI micro segregations.
Figure 67: Radioluminescence spectra of BaBrI doped with 8% Eu$^{2+}$ (red), CsCaI3 doped with 2.5 % Eu$^{2+}$ (black) and reference BGO (blue).

Figure 68: Pulse-height spectra for CCl doped with 2.5 w% EuI2 irradiated by 137Cs gamma rays.
**Barium Bromine Iodide.** Barium halides activated by divalent europium have been previously studied as X-ray phosphors, and they have now garnered some attention for use as scintillators [64][65][66][67][68]. The starting materials used in this study were BaBr$_2$ and BaI$_2$ with a nominal divalent europium percentage of 8% consisting of equal parts EuBr$_2$ and EuI$_2$. Barium bromine iodide, with an orthorhombic *Pnma* crystal structure, is a double salt consisting of barium iodide and barium bromide. The TB-mBJ functional estimates a bandgap of 4.45 eV [58].
The crystal used in this study was activated with 8 m% europium iodide. As can be seen in Figure 70, the crystal had a slight reaction with the quartz ampoule, as we have not encountered this with the growth of its individual constituents. We attribute this to heat cycling and undissolved material. We plan to mitigate this issue with an external synthesis step to promote homogeneity prior to growth. Figure 71 shows the 70 mm$^3$ sample used for characterization. Based on DSC (Figure 72) the melting and freezing point of BBI are 780 °C
and 763 °C, respectively. With such a low supercooling the material was self-seeding, therefore the formation of a tip was not necessary to initiate growth. The beta-excited Radioluminescence spectra for BBI is also presented in Figure 67. The emission peak is at 421 nm, the energy resolution, is 3.56%; and the decay time is 462 ns all similar to what has been reported [68]. The light yield of 46,000 Ph/MeV is less than what is reported. This may be due to defects in the crystal.

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[94] Chemicalc v4 software.
Appendices

Classic ‘Dieke Diagram’ for Rare Earth Ions

G. H. Dieke. Spectra and energy levels of rare earth ions in crystals (Interscience Publishers, New York, 1958)
Vita

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  Virginia Commonwealth University, Richmond, VA
  Jan 2011-May 2011
  Teaching the laboratory portion for Introduction to Microelectronic Fabrication. Present lectures on clean room equipment and processes based on silicon such as mask making,
photolithography, oxidation, diffusion, and metallization. The aim is to complete a metal gate PMOS.

Research Assistant
Department of Electrical Engineering
Virginia Commonwealth University, Richmond, VA  
Aug 2007 - Nov 2010
The research is focused on RF Sputtering and Liquid Phase Epitaxy (LPE) growth, microwave, electrical, and structural characterization of Barium Strontium Titanate (BST) and Barium Hexaferrite (BaM) based devices. Research includes growth of BaM by LPE for dual tunable high frequency phase shifters. Experience includes: Growth of epitaxial films by MBE, LPE, and RF Sputtering and use of various metrology tools such as Reflection High-Energy Electron Diffraction (RHEED), Capacitance Voltage (CV), X-ray Diffraction (XRD), and Atomic Force Microscope (AFM).

Additional clean room experience (Class 100) including fabrication and processing experience using: Karl Suss mask aligner, metal deposition equipment (E-beam, resistive, and sputtering), wet and dry etching, and wire bonders. Instrumental in the acquisition of major lab tools as well as power requirements.

Undergraduate Researcher
Electrical Material Research Group,  
Department of Electrical Engineering  
NC A&T, Greensboro, NC  
Summer 2003
Conducted research on Pulsed Laser Deposition growth procedure, and characterization of YBCO on STO buffered silicon thin films. Performed low temperature electrical measurements in order to prove the superconducting properties of the YBCO thin films. Published and presented research for North Carolina Louis Stokes Alliance for Minority Participation Conferences.

INDUSTRY EXPERIENCE:
Electrical Engineer
HC YU and Associates, Richmond, VA  
July 2006 - July 2007
Provided electrical engineer support for commercial and industrial power distribution based on the National Electrical Code. Developed and lead electrical strategies, improvements and procedures. Developed power riser diagrams based on building load calculations. Specified lighting and power equipment used for expansions and new constructions. Collaborated with multi-discipline engineering and architect team to support and design lighting, power, and lightning plans.

Process Engineer
Cree Research, Inc., RTP, NC  
Designed and planned layouts for MOCVD epitaxial growth process of opto-electronic devices. Resolved parameter issues using SPC charts to improve production yields. Collaborated with team of engineers and scientists to produce new Gallium Nitride epitaxial structures. Supervised team of technicians and operators for proper execution of growth plans. Performed routine equipment maintenance such as chamber clean and Alkyl cylinder changes. Created and assisted in the production of controlled process documents, operating manuals, and equipment procedures to be followed by new engineers, technicians, and operators. Analyzed metrology data in order to improve production yields and throughput.
Electrical Designer
O’Neal, Inc., Atlanta, GA


Designed power distribution systems based on codes from the NEC, for lighting, main and backup power. Provided electrical design support for on-going expansion and remodeling efforts for manufacturing, office and laboratory environments. Developed site, electrical, power, and systems drawings using AutoCAD. Performed lighting calculations Lithonia software for specific environments. Collaborated with team of architects and mechanical engineers for client design requirements. Designed and drafted the lighting and the power for Emory University’s Yerkes National Primate Research Center.

INSTRUMENTATIONAL SKILLS:
- Growth: PLD, Emcore MOCVD, Riber 32 MBE, KJL RF Sputtering, LPE, Cambridge NanoTech ALD, E-Beam Evaporation, ACRT, Bridgman
- Metrology: XRD, SEM, AFM, Hall measurement, RHEED, Ellipsometer, Scintillator pulse height spectra, Scintillator decay time, Differential Scanning Calorimetry

PUBLICATIONS


PRESENTATIONS:

• E. Rowe, E. Tupitsyn, P. Bhattacharya, Y. Cui, M. Groza, V. Buliga, A. Burger, S. Payne, N. Cherepy R. Williams "New Scintillator Activator Candidate" Scintillator Nonproportionality Workshop, Oakland, CA, May 18, 2012 (oral presentation)


• E. Rowe, B. Xiao, Ü. Özgür, V. Avrutin, and H. Morkoç, Magnetoelectric Effect in LSMO on Stripe Patterned PZT Grown by RF Sputtering, VCU-LSAMP I-GEEAR Research Symposium, March 27, 2010 (Oral Presentation)

• E. Rowe, B. Xiao, Ü. Özgür, V. Avrutin, and H. Morkoç, Magnetoelectric effect in patterned PZT/LSMO bilayers grown by RF sputtering, MRS Fall Meeting 2008, Symposium C: Theory and Applications of Ferroelectric and Multiferroic Materials. Boston, November 30 - December 1, 2008 (Poster Presentation)


• H. Morkoç and colleagues, "Preparation of complex FE and FM oxides and investigation of their structural and magnetoelectrical properties for device applications", Office Of Naval Research Progress Report Symposium, Nov. 5, 2008
• R. Williams, B. Ucer, J. Grim, Q. Li, A. Burger, P. Bhattacharya, E. Tupitsyn, E. Rowe, V. Buliga, G. Bizarri, B. Moses, S. Payne, B. Sadigh, D. Aberg, F. Gao, "Z-Scan and τ Measurement of K₂, K₃, C₂, Deh/C₂ Dext; Track Radius From Experiment; e- Yield (Eᵢ) ; Synchrotron excitation of SrI₂:Eu nad BaIₑ; 'Halide Rule'; K₁, (dE/dx)Birks, ηₑ" NA-22 Workshop, PNNL, March 9, 2012.
• E. Rowe, Crystal Plasticity: Life Estimation of metals, General Electric Research Summit, Morehouse College, July 2001 (Oral Presentation)

MEMBERSHIPS:

NC-VA LSAMP – Assistant Director – 2009 – 2012
VCU Toastmasters – President – FY 2011
VCU Toastmasters – VP Education – FY 2010
Bread of Life WCC – Youth Leader - 2004
LSAMP – Member – 2003 – 2004
Institute of Electronics and Electrical Engineer – Student Member – 2003 - Present
National Society of Black Engineers - Member – 2000 – Present
Phi Beta Sigma Fraternity, Inc – 1999- Present
Morehouse Football Alumni Association, LLC – Founder – 2008 - Present