Crystal Growth and Spectroscopic Performance of Large Crystalline Boules of CsCaI₃:Eu Scintillator

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Abstract

The crystal growth of CsCaI₃:Eu with improved quality over prior efforts for use in X-ray and gamma-ray detection applications is reported. Boules were grown using the vertical Bridgman technique in quartz ampoules at 15, 22, and 35mm diameters. CsCaI₃:Eu crystals show evidence of a heavily twinned microstructure likely caused by a solid-solid phase transformation of the crystal during the cooling process. Energy resolution (FWHM) in large and small samples taken from crystalline boules vary between 13% and 4.5% for 662 KeV gamma rays indicating volumetric non-uniformity. Scintillation decay time is shown to increase with volume. Proportionality of the light yield of CsCaI₃:Eu is reported for the first time.

Keywords

Bridgman technique, Halides, Calcium compounds, Scintillator materials, Scintillators

1. Introduction

Improvements to the capabilities and cost of radiation detection and radioactive isotope identification devices are an integral component to the increasing needs of national security operations and the medical imaging industry. The evolving geopolitical climate requires efforts to enforce nuclear non-proliferation agreements as well as enhance domestic security to prevent the movement and trade of illegal radiological contraband across and within borders. Despite the unsurpassed performance in radionuclide identification, the cost associated with production and operation of semiconductor based radiation detectors such as high purity germanium (HPGe) and cadmium telluride prohibits their widespread use and availability. As a result, research and development into detector technology based on new scintillator materials with improved spectroscopic performance, namely light yield and energy resolution, is required to advance this capability [1].

Single crystal metal halide scintillators offer superior light yield and detection efficiency over organics, liquids, and many oxide based scintillators. One drawback is the difficulty encountered when attempting to scale up the growth process to larger diameters for economical detector fabrication. Single crystal synthesis using melt growth techniques are more readily scalable over vapor deposition or solution growth methods to meet the demand for industry. Adapting growth processes developed at the laboratory scale to an industrial scale is a fundamental challenge to development of new metal halide scintillator materials. Over the last decade, a few binary metal

halide materials with energy resolution of ~3% (FWHM) at 662KeV have been commercialized such as $\text{SrI}_2\text{:Eu}$, $\text{LaBr}_3\text{:Ce}$ and CeBr_3 , [2, 3]. However, the cost of these new generation of materials remains prohibitively high due to the low yield of high quality crystals that is in part due to growth processes which remain difficult to scale up to larger diameters. Obstacles may include large anisotropy in thermal expansion which requires control over the orientation of the growing crystal. Additionally, coupled with the typically low mechanical strength of metal halides, large single crystals are prone to fracture during growth and cooling rendering them unusable. Consequently, these effects have caused the deployment of these next generation materials to be limited.

In recent years, the search for new ternary compositions with similar performance to the aforementioned binary compositions have yielded many new materials which may offer reduced cost of development with improved performance over current technology utilizing NaI:Tl [4, 5]. Each new ternary composition poses unique advantages and disadvantages to their development such as activator distribution, optical quality, and mechanical strength. Moreover, compositions possessing promising performance at the laboratory scale ($<1 \text{ cm}^3$) must be assessed in terms of their feasibility for scale up to larger diameter growth processes. This is largely assessed by volumetric uniformity in scintillation performance, and a resistance to fracture. Complicating this effort is the hygroscopic nature of nearly all of the metal halides requiring special care to be taken in the preparation, handling, and investigation of these materials.

Research into new ternary compositions with promising scintillation performance has accelerated in the last decade. For instance, melt grown crystals of $\text{CsCaBr}_3\text{:Eu}$ are reported possess a light yield of ~29,000 photons/MeV and 9.3% energy resolution at 662 KeV [6]. Recent reports on the scintillation properties of $\text{CsCaI}_3\text{:Eu}$ (CCI) crystals grown from the melt using the vertical Bridgman technique (VBT) have shown promising performance with ~40,000 photons/MeV yet cite poor crystalline quality and inhomogeneity as causes of decreased energy resolution [7, 8]. This has prompted an effort to produce higher quality crystals of CCI through growth experiments aimed at identifying and obviating commonly encountered bulk defects using VBT. In this manner we hope to assess the potential performance of CCI and evaluate the advantages and disadvantages to its further development.

In consideration for spectroscopic applications, reproducible detector volumes approaching 1 cubic inch represents a milestone for development. In this present work, we report the results of growth experiments using VBT in producing boules of CCI at 15, 22, and 35 mm diameters as well as their handling. The scintillation performance including light yield, energy resolution, and decay time for various volumes of CCI is shown. The proportionality of CCI is also reported for the first time.

2. Experimental Method and Equipment

2.1 Crystal Growth

Due to the hygroscopic nature of the precursor starting materials, all handling took place in a nitrogen flushed MBraun glove box maintaining <0.1 ppm moisture and oxygen to prevent deliquescence and or contamination prior to synthesis. Precursor materials consisting of anhydrous CsI, CaI_2 , and EuI_2 with 99.99% or better purity in beaded form were used for the synthesis of CsCaI_3 . A europium concentration of 3 mol % was attained through substituting EuI_2 for CaI_2 in an otherwise 1:1 mixture of $\text{CsI}:\text{CaI}_2$. This activator concentration was previously determined to produce optimal results in the CCI matrix [8]. Quartz growth ampoules were loaded with the precursor components within the controlled atmosphere and then transported to a high vacuum furnace and dried at 250°C and 10^{-7} torr for several hours prior to sealing with an $\text{H}_2\text{-O}_2$ torch. The vacuum sealed ampoules containing the unreacted charges were suspended into the growth furnace by a quartz hook attached at the top of the ampoule and connected to the translation mechanism. The charges were then heated to $\sim 800^\circ\text{C}$ for 24 hours in order to allow all the material to melt and mix thoroughly prior to beginning growth.

Growth experiments were performed in a custom built two zone transparent vertical Bridgman furnace and recorded with continuous observation of the growth process using time lapse photography. A more detailed description of the equipment can be found in [9]. Using this experimental setup, the crystal appearance along with the shape of the growth interface could be observed at all times. This is especially useful for growth of materials which exhibit a large supercooling behavior that naturally make the self-seeding process more challenging to control.

Differential scanning calorimetry (DSC) measurements of CCI are shown in Figure 1. The melt of CCI exhibits a characteristic supercooling of $\Delta T \approx 35^\circ\text{C}$ in the absence of any solidified portion. As a result of this, ampoules with a capillary section at the bottom were used to control the initial formation of a randomly oriented seed crystal. A melting point of 686°C is used to prevent remelting of the self-seed. Evidence of a suspected phase transition occurring at $\approx 255^\circ\text{C}$ can also be detected in the DSC heating and cooling curves (Inset of Figure 1).

Figure 1: The DSC heating and cooling curves for CCl.

During growth in the transparent furnace, the melting point isotherm is typically observed to migrate lower into the cool zone as the ampoule is translated downward due to a heat-sinking effect of the charge which may cause the growth rate to fluctuate over time. In our experience, this effect is minimized by the use of a diaphragm placed between the hot zone and cool zone but is not eliminated, thus some migration of the crystal-melt interface is unavoidable. This results in small variations of the growth rate and interface shape during crystallization.

For CCl grown in quartz ampoules with a wall thickness of 1.5 mm, the interface shape remains approximately flat or slightly convex towards the melt if it can be maintained approximately 1-2 mm on the hot zone side of a closely fitting diaphragm opening. If the interface is located too far below the diaphragm, (projecting into the cool zone) a slightly concave interface is produced resulting in wall nucleated grains in the boule. This trend is consistent with the theory established by numerical modeling performed by Fu, Chang and Wilcox [10, 11].

For each growth experiment, zone settings were tuned to locate the melt/crystal interface at full diameter just above the diaphragm. Prior to beginning translation, all material is remelted leaving a small self-seed a few mm in height within the bottom of the capillary.

For the 15 mm diameter growth experiments, the aforementioned process was rather straightforward. Considerable difficulty was encountered in controlling the interface shape

during the 35 mm diameter experiment due to the larger cross-sectional area of the interface. A translation rate of 1 mm/h was used in all experiments. After all melt had solidified, the crystalline boules were cooled from $\approx 500^\circ\text{C}$ to room temperature at constant rates varying from $4^\circ/\text{h}$ to $20^\circ/\text{h}$. Slower rates were used for larger diameters to minimize thermo-elastic stress. After growth and cooling, the ampoules were opened with subsequent cutting and polishing taking place within a nitrogen flushed glove box to prevent decomposition from contact with moisture in the atmosphere. For the purposes of characterization, circular slabs as well as rectangular pixels from each diameter boule were cut using a low speed wire saw with mineral oil as a lubricant.

2.2 Optical and Scintillation Characterization

A polariscope coupled with an optical microscope was used to inspect macroscopically observable bulk defects in the grown boules. Contrast was produced through either the Senarmont method or the sensitive color method. Photoluminescence emission and excitation spectra were acquired using a Horiba Fluorolog with a 450W Xenon lamp and a Hamamatsu R928 PMT.

A Hamamatsu 2059 PMT was used for absolute light output measurements under excitation from a ^{137}Cs source on polished samples directly coupled to the PMT window and covered with mineral oil and a diffuse reflector dome made of Spectralon. The manufacturer supplied quantum efficiency for this PMT was convolved with the radioluminescence spectrum of CCI to determine the light yield assuming the light collection efficiency is ideal. Scintillation light yield proportionality was determined as a function of excitation energy using a set of sealed radiation sources with gamma energies ranging from 14 keV to 662 keV (^{241}Am , ^{57}Co , ^{22}Na , ^{137}Cs). A higher quantum efficiency Hamamatsu R6231-100 PMT was used to acquire pulse height spectra for several volumes of CCI excited by a ^{137}Cs source. Energy resolution was determined from the full width at half maximum (FWHM) of a Gaussian fit of the 662 keV photopeak. Scintillation lifetime was determined under excitation from a Cs-137 source with a $20\mu\text{s}$ shaping time using the time-correlated single photon counting technique [12].

3. Results and Discussion

3.1 Crystal Growth

The grown boules varied in size with 65 mm L at $\varnothing$ 15 mm, 55 mm L at $\varnothing$ 22 mm, and 55 mm L at $\varnothing$ 35 mm. Thermal gradients over $40^\circ\text{C}/\text{cm}$ at the diaphragm were prone to cause the crystal to readily crack during growth at 22 mm and 35 mm diameters. A reduced thermal gradient of ≈ 20 - $25^\circ\text{C}/\text{cm}$ at the diaphragm resulted in preventing severe cracks extending through the entire boule. The formation of transverse cracks occurred more readily for boules with large aspect ratios (length to diameter) at cooling rates above $20^\circ\text{C}/\text{h}$. Conversely, boules with aspect ratios closer to 1 did not exhibit any transverse cracking. Boules vary from transparent to slightly cloudy or translucent with a slight yellowish tint under LED light and the bluish emission of the Eu^{2+} activator in the CCI matrix ($\sim 455\text{ nm}$) can be observed under fluorescent light. Boules shine a bright blue under ultra-violet light and appear uniform (Figure 2).

Figure 2: Grown boules of CCI after removal from the ampoule along with polished slabs under fluorescent room light and UV light for Ø 15 mm (a), Ø 22 mm (b), and Ø 35 mm (c).

Polished slabs cut from 15 mm 22 mm and 35 mm boules are clear enough so that fine type can be read through 20 mm of thickness. Cloudiness in the bulk crystal is more evident in the 22 mm and 35 mm diameter boules. Samples of CCI cut easily using a low speed wire saw and can be shaped into rectangular pixels or circular slabs and manually polished using a combination of grinding papers and anhydrous lapping oil.

Towards the end of the crystallization process, a last to freeze region comprising a small fraction of the total volume ($\approx 1-3\%$) develops at the top of the charge having a reduced freezing point. It is assumed from experience this forms through segregation of some europium as well as unintentionally added impurities concentrated in this region. Some black impurities thought to be trace carbon also collect here. This impurity laden last to freeze region is typically polycrystalline and is discarded afterwards.

CCI is observed to wet the ampoule forming a concave meniscus with the melt. Separation of the crystal from the ampoule wall upon cooling is indicated by an optical decoupling of the crystal which occurs at temperatures below 400°C . Following separation from the ampoule wall, vapor species present above the melt charge during and after crystallization first condense and then crystallize on the boule surface as the temperature is decreased. This produces a thin layer of an unidentified secondary phase over most of the exterior which is marked by a significant reduction in transparency looking through the diameter of the ampoule. A time-lapse video documenting the growth and cooling to room temperature of a Ø 22 mm crystal of CCI using the above equipment is provided along with the electronic version of this text ([Link to Video Here](#)).

Rapid decomposition of CCI occurs in normal ambient conditions. Brief exposure to ambient air causes a yellowing of the exterior surface of polished specimens, eventually turning into a white opaque substance from subsequent moisture uptake into the bulk. The yellowing of the surface is believed to be a layer of disassociated iodine caused by decomposition with air. This layer

greatly impedes light emission from the crystal but can be restored to a pristine condition by removal of the damaged layer by re-polishing. Alternatively, the extreme hygroscopicity of CCI prevents the restoration of scintillation properties if the crystal has adsorbed moisture through deliquescence.

While crystal specimens appear to be single crystals at first approximation, under the polarized light microscope details of the grain macrostructure can be more easily observed (Figure 3). For example, grain boundaries in CCI which appear invisible to the unaided eye can be resolved by the contrast produced by changes in the polarization of the transmitted light. The apparent optical isotropy observed in CCI is in agreement with theoretical calculations predicting a negligible optical anisotropy despite the anisotropic structure [13].

Wall nucleated grains can be observed in the $\varnothing$ 22 mm and $\varnothing$ 35 mm boules where a concave crystal-melt interface was produced during growth. The polycrystalline grain structure is coarse with grains of a few mm in diameter. When a flat or convex interface could be achieved, some secondary grains are formed but in general, single grains approaching 10 mm in diameter are present which is more easily achieved in the $\varnothing$ 15 mm boules.

In all samples of CCI investigated, lamellar twinning is observed. One proposed mode of twinning is possible through a solid-solid phase transition from a tetragonal phase at high temperature to the orthorhombic phase observed at room temperature. Evidence of the transition was originally observed through changes to the twin domains when the crystal was heated above $\approx 250^{\circ}\text{C}$ and subsequently cooled after which the original twin domain structures can no longer be observed. A loss in symmetry upon cooling below the suspected transition temperature has been confirmed through high temperature X-ray diffraction studies and will be discussed in detail in a separate manuscript. Similar transitions have been studied for other isostructural perovskite [14] but not specifically for CCI.

Figure 3: Polarized light microscopy images of CCI grown at $\varnothing$ 15 mm exhibiting lamellar twinning of an uncracked singular grain (left) and at $\varnothing$ 22 mm the macrostructure is comprised of wall nucleated grains and twinning (right). Arrows are shown depicting the growth of these grains into the bulk. The $\varnothing$ 35 mm boule is comprised of heavily strained and twinned grains.

3.2 Optical and Scintillation Characterization

The photoluminescence emission and excitation spectra for CCI at 300K is shown in Figure 4. The broad excitation band is seen to overlap the 455 nm emission of the Eu 5d-4f transition which indicates radiation trapping or self-absorption is likely. These observations are in good agreement with previous reported results from reference [8]. The gamma spectra under excitation from a Cs-137 source of various size samples ranging from 0.1 cm³ to 20 cm³ are shown in Figure 5. It is clear that the asymmetry in the photopeak for larger volume samples indicates inhomogeneity and requires further investigation to determine its nature. It is believed to stem from activator segregation during directional solidification. The difference in the 6 coordinated ionic radius of Eu²⁺ compared with Ca²⁺ is large (1.17Å vs 1.00Å respectively) [15]. Based upon the ionic radii mismatch, the effective segregation coefficient of Eu on Ca sites in CCI is expected to be << 1.

Figure 4. Photoluminescence spectra of CCI. $\lambda_{em}=465$ nm $\lambda_{ex}=371$ nm.

Due to the peak asymmetry, a fitting of the photopeak using multiple peaks was often required with greater resolution and photopeak symmetry achieved in smaller volume specimens. The energy resolution measured for the Ø 35 mm x 20 mm thick slab is approximately 13% (FWHM/centroid) while an energy resolution for a 2 x 2 x 2 mm³ polished cube is approximately 4 - 4.5%. The improvement in spectroscopic performance is largely attributed to improved volumetric uniformity in the smaller sample as well as the absence of multiple grains of mm dimension. A slight increase in the measured light yield with decreasing volume can be attributed to improved light collection efficiency as well as fewer scattering sites stemming from twins and grain boundaries. In addition to acting as light scattering sites, grain boundaries are likely locations for impurities to concentrate and are areas of disorder at the atomic scale which would affect charge migration in the crystal.

Figure 5: CCI pulse height spectra under excitation by ^{137}Cs gamma source for different sample volumes.

The proportionality of light yield (photons/MeV) with photon energy for CCI is shown normalized to the 662 keV response in Figure 6. The sample measured was a $2 \times 2 \times 2 \text{ mm}^3$ cleaved specimen containing no visible defects immersed in oil within a quartz cell. Results show very good non-proportionality of less than 5% at energies as low as 14 keV. Error bars provided show variation in repeated measurements.

Figure 6: Non-proportionality measurement for CCI.

Scintillation life-time is shown to increase with volume from $\sim 2 \mu\text{s}$ (principle component) in a sample measuring $2.5 \times 4 \times 6 \text{ mm}^3$ to $\sim 3.8 \mu\text{s}$ in a sample measuring $20 \text{ mm L} \times \text{Ø } 35 \text{ mm}$ as presented in Figure 7. The lengthening of the scintillation lifetime may be ascribed to the greater bulk defect concentration in the larger crystals but the exact mechanism is unknown at this time. Similar decay time lengthening ascribed to radiation trapping (self-absorption) effects has been observed in other Eu^{2+} activated compounds as reported in [16]. With regard to pulse height measurements, the longest shaping time used in our investigation was $10 \mu\text{s}$ which may limit collection of all scintillation photons for large volume samples with longer decay times and may influence the measured light yield. A summary of scintillation characterization for samples of various volumes of CCI is shown in Table I.

Figure 7: Scintillation decay of CCI for various sample volumes.

Table I. Scintillation Properties of CCI at Various Volumes

Sample Size	Estimated Light Yield (ph/MeV)	Energy Resolution at 662 keV (FWHM %)	Scintillation Lifetime (μ s)
2 x 2 x 2 mm ³	30,000	~4.5	NA
2.5 x 4 x 6 mm ³	NA	NA	2.1
5 x 5 x 5 mm ³	27,000	~9.5	NA
Ø 22 mm x 12 mm	24,000	~11	NA
Ø 22 mm x 20 mm	NA	NA	3.3
Ø 35 mm x 20 mm	22,000	~13	3.9

4. Conclusion

We have demonstrated the growth of crystals of CCI using the vertical Bridgman technique with improved energy resolution and optical quality over previously reported results. The measured energy resolution for a single crystal approaches 4% (FWHM) at 662 keV which is a large improvement over early estimates of 8% [8] and 16% as reported in [7]. Single crystals isolated from polycrystalline boules present promising performance with both energy resolution and proportionality that surpasses that of NaI:Tl. With further optimization of the growth process, similar performance may be reproducible in detector sized single crystals approaching 1in³. One drawback encountered in CCI is the demonstrated non-uniformity which may be due to inhomogeneous activator distribution as other investigators have pointed out. To confirm the segregation behavior of the activator, an analysis of the Eu concentration changes across the volume of the crystal is required. Moreover, the primary challenges to the further development of CCI lay in improving uniformity in larger volume crystals and prevention of secondary grain growth as well as twinning.

5. References

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