Improvement in the optical quality and energy resolution of CsSrBr₃: Eu scintillator crystals

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Abstract: The crystal growth of CsSrBr₃: Eu with improved energy resolution for use in gamma-ray detection applications is reported. CsSrBr₃ boules doped with 5% Eu were grown by the vertical Bridgman method in quartz ampoules of 17 mm and 22 mm diameter. It was observed that the addition of an excess of CsBr in the melt improved the optical transparency and energy resolution of the scintillator crystals. The energy resolution of the gamma-ray spectra recorded with crystals measuring $\varnothing$ 22 mm $\times$ 15 mm was 7.4% at 662 keV (for a crystal with non-optimized stoichiometry) and 6.2% at 662 keV (for a crystal with optimized stoichiometry i.e. excess CsBr in the melt), which is a significant improvement over previous reports. Temperature dependent powder XRD measurements were also carried out to study the solid-solid phase transition which occurs as the crystals are cooled after growth.

KEYWORDS – A2 Growth from melt, B1 Halides, B1 Rare earth compounds, B3 Scintillators.

I. Introduction

Scintillator materials are utilized for x-ray and gamma-ray detection in nuclear non-proliferation and domestic security applications. For a long time, the applications involving the detection and identification of radionuclides have depended on scintillation based detectors such as NaI: Tl, which has relatively low energy discrimination ability. Therefore, the advancement of the detector technology has relied on the discovery of new scintillator materials as well as on the improvements to the existing materials. In order to attain improved spectroscopic performance over the previous generation of detectors for the different radiation detection applications, there have been a number of scintillator materials that have been developed. Cerium (Ce³⁺) activated scintillators such as LaBr₃: Ce and Lu₂SiO₅: Ce show high light yield as well as fast scintillation decay [1], [2]. Similarly, europium (Eu²⁺) activated scintillator materials have shown significant potential. Several promising compounds including SrI₂: Eu, CsSrI₃: Eu, BaI₂: Eu, Ba₂CsI₅: Eu, KSr₂I₅: Eu, and BaBrI: Eu are currently being developed [3]-[7].

The effort towards developing scintillators with promising performance have yielded many new materials, which may offer lower cost of development in addition to improved performance over current scintillators like NaI: Tl [8],[9]. These new materials include ternary compound scintillators such as CsCaBr₃: Eu which possesses a light yield of ~29,000ph/MeV and an energy resolution of 9.3% at 662 keV [10], and CsSrBr₃: Eu which has been previously reported with a

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light yield of $\sim 31,300\text{ph/MeV}$ and an energy resolution of 8.8% at 662 keV [11]. This good performance exhibited by CsSrBr_3 makes it a suitable scintillator for applications in medical imaging and national security.

CsSrBr_3 belongs to the ABX_3 family of perovskite-type compounds ($A = \text{Cs, K}$; $B = \text{Ca, Sr, Ba}$; $X = \text{Cl, I, Br}$). CsSrBr_3 has a density of 3.76 gm/cm^3 and it crystallizes in the orthorhombic GdFeO_3 structure type with the space group Pnma (no.62) [12]. Due to the tilted position of the corner-sharing $[\text{SrBr}_6]^{4-}$ octahedra, Cs^+ ions are only (8+2)-fold coordinated by Br^- ions. The Sr^{2+} ions occupy the 4b sites with local C_i symmetry. The average Sr–Br distance is $2.98\text{\AA}$ [13].

Typically the crystal growth of CsSrBr_3 : Eu by the vertical Bridgman technique yields single crystal boules that are optically translucent. This overall poor optical quality may limit the performance of the crystals, particularly for crystals of large size. Therefore, improving the optical transparency of the crystals may in turn further improve their energy resolution. In consideration for gamma-ray spectroscopy applications, scintillator crystals with good energy resolution at detector volumes approaching 1 cubic inch represents a milestone for development. Therefore, the main objective of this work was to produce CsSrBr_3 : Eu crystals with improved energy resolution at large detector volumes.

The exact nature of the process which may cause the cloudiness/translucent appearance of the CsSrBr_3 crystals is yet to be determined. However, it has been theorized that the volatilization of cesium bromide (CsBr) during crystal growth may lead to an imbalance in the stoichiometry, which may be responsible for the cloudiness of the crystals. The partial pressure of CsBr at and above the melting temperature of CsSrBr_3 is larger than that of SrBr_2 [14] and hence it may have a higher susceptibility to volatilize. Furthermore, in order to ensure that CsBr and SrBr_2 both react to form CsSrBr_3 the raw materials have to be heated to a temperature equal to or greater than the compound melting temperature. At this high temperature, CsBr may volatilize and cause a change in the stoichiometric composition of the melt. Thus the crystal transparency may be improved by either preventing or compensating for the volatilization of CsBr .

In this work, the effect of varying the ratio of the starting raw materials as a means to compensate for the volatilization of CsBr was therefore investigated. We report the results for single crystal growth of CsSrBr_3 : Eu 5% using the vertical Bridgman method. We also report a significant improvement in the optical transparency and energy resolution of the scintillator crystals, especially at large crystal volumes.

II. Experimental

A. Crystal Growth

Differential scanning calorimetry (DSC) measurements of CsSrBr_3 are shown in Figure 1. The DSC plot shows that CsSrBr_3 melts at around 760°C . The measurement was conducted at a heating and cooling rate of 5 K/min . From the DSC plot it can be seen that the melt of CsSrBr_3 exhibits a characteristic supercooling in the absence of any solidified portion. Therefore, this necessitates the use of an ampoule with a capillary tip in order to control the self-seeding of the crystal. The inset of the DSC plot shows small exothermic and endothermic peaks occurring at a

temperature of around 235 °C. These peaks may be evidence of a solid-solid phase transition that CsSrBr_3 undergoes at this temperature. Thus the orthorhombic phase observed at room temperature may not be what crystallizes from the melt. The investigation of this phase transition will be discussed in the following sections.

Figure 1. DSC heating and cooling curves for CsSrBr_3 .

CsSrBr_3 melts congruently making it relatively easy to grow large crystals via the vertical Bridgman method from a molten mixture of binary metal halides. In general, the CsBr , SrBr_2 , and EuBr_2 raw materials of 4N purity were loaded into a quartz ampoule that had previously been cleaned with 10% dilute hydrofluoric acid. Since the raw materials are sensitive to moisture, the mixing and loading was done in a nitrogen purged glove box. The ampoule loaded with the raw material was then dried at 250 °C under a vacuum of 10^{-6} Torr for 12 hours and then sealed. The raw materials were then melted and the compound was synthesized at a temperature of 790 °C for a period of 20 hours in a vertical furnace.

As has been discussed previously it is hypothesized that CsBr volatilizes during synthesis and crystal growth, which may have a deleterious effect on the crystal quality. Therefore, the crystal quality may be improved by compensating for the loss of CsBr . This can be achieved by growing crystals from melt compositions with an excess of CsBr . In order to investigate this hypothesis, crystals with different raw material compositions were grown. Table 1 shows the different compositions that were investigated. In order to dope the crystal with the divalent europium activator, 5% of the SrBr_2 was substituted with EuBr_2 . This activator concentration was previously determined to produce optimal results in CsSrBr_3 [11].

Table 1. CsSrBr_3 : Eu crystals grown with different ratios of CsBr and SrBr_2 in the melt

The crystal growth was carried out in a three zone vertical Bridgman furnace. A 5mm thick diaphragm was installed between the middle (hot) and bottom (cold) zones in order to have a better control over the thermal gradient and to control the position of the growth interface. Thermocouples placed about 1 mm above and below the diaphragm were used to monitor and set the appropriate zone temperatures in order to obtain a thermal gradient of 25 – 30 °C/cm across the diaphragm. The zone temperatures were also adjusted so that the solid-liquid interface would be positioned just above opening of the diaphragm. This insures a flat or convex interface, both of which are better suited for improved crystal growth. Previous crystal growth experiments carried out in a transparent furnace have suggested that the use of a diaphragm also minimizes the migration of the growth interface due to a heat sinking effect of the charge, which may cause the growth rate to fluctuate over time [15]. The crystal was then grown by translating the ampoule through the furnace at a pulling rate of 0.5 mm/hour. After growth the crystal was cooled to room temperature at a rate of 7 - 10 °C/hour.

B. Crystal Characterization

In order to characterize the scintillation performance of the crystals, different sized samples were cut from the grown crystal boules. The crystal samples were polished using silicon carbide polishing pads with Buehler AutoMet™ low viscosity lapping oil. The energy resolution was determined from the full width at half maximum (FWHM) of a Gaussian fit of the 662 keV photopeak measured by coupling the crystal sample to a high quantum efficiency Hamamatsu R6231-100 PMT operated at a bias of -1000 V.

Absolute light yield of polished samples was measured by directly coupling the samples to the window of the Hamamatsu R2059 photomultiplier tube operated at a bias of -1500 V. The PMT was connected to a chain of electronics consisting of a Canberra model 2005 pre-amplifier, an Ortec 672 amplifier, and a Tukan 8k multichannel analyzer. The samples coupled to the PMT window were covered with mineral oil to inhibit degradation and a reflector dome made of Spectralon. The samples were then irradiated with 662 keV gamma-rays from a ¹³⁷Cs radiation source and the spectra were recorded. The quantum efficiency curve of the PMT was convolved with the radioluminescence emission spectrum of the sample to determine the integral quantum efficiency. The photoelectron yield i.e. the number of photoelectrons per MeV for the gamma-ray peaks was then measured and the light yield was calculated based on the position of the single photoelectron peak response from the PMT [16] - [17].

Steady state photoluminescence (PL) spectra were measured at room temperature with a Horiba Jobin Yvon Fluorolog-3 Spectrofluorometer equipped with a Xe lamp and dual scanning monochromators. Both the emission and excitation slits were kept at 1 nm. The scanning rate was 240nm/min and the step size was 1 nm.

Radioluminescence emission spectra were measured under continuous X-ray irradiation from a CMX-003 generator. The X-ray tube with a tungsten filament and copper target operated at 35 kV and 0.1 mA. The emission spectra were recorded with a 150 mm focal length monochromator (PI ACTON SpectraPro SP-2155 m) over a wavelength range of 200–800 nm.

Scintillation lifetime was determined under excitation from a Cs-137 source with a 20μs shaping time using the time-correlated single photon counting technique [18]. Optical transmission was measured with a Varian Cary 5000 UV-VIS-NIR Spectrophotometer operating in the range of 200-800nm.

In order to measure the optical transmission, 2 mm thick slabs were cut from the crystal boules. The flat surfaces of the slabs were polished with silicon carbide polishing pads in order to obtain smooth defect free surfaces. A Varian Cary 5000 UV-VIS-NIR Spectrophotometer operating in the range of 200-800nm was used for the measurement.

In order to confirm the phase and compositional homogeneity of the crystals X-ray powder diffraction (XRD) spectra were measured with a Bruker D2 Phaser diffractometer. The samples were ground in a nitrogen-purged glove box and loaded into an airtight Kapton sample holder. The X-ray tube voltage was 30kV and the current was 10 mA. The two-theta angle was scanned from 10 to 70° in 0.02° steps.

The phase transition occurring around 235 °C that was identified in DSC measurements was investigated using temperature dependent structure analysis on powder X-ray diffraction (PXRD) data. A Panalytical Empyrean 2 diffractometer combined with an Anton-Parr HTK1200 non-ambient stage was used to acquire diffraction data in the Bragg-Brentano geometry while the hygroscopic powder sample was heated between 25° and 400°C under a vacuum of 10^{-5} torr. The sample pan containing the powdered CsSrBr₃: Eu 5% was heated at 5 K/min and allowed to thermally stabilize for several minutes prior to acquiring each diffraction pattern. The GSAS-II software was used in the analysis of the data [19].

III. Results and Discussion

A. Crystal Growth

Large single crystals of CsSrBr₃: Eu were grown successfully using the methods described in the previous sections. The crystals were of diameter of 22 mm and 17 mm, where typically the $\varnothing$ 22 mm crystals were 40 mm long and the $\varnothing$ 17 mm crystals were 30 mm in length. All crystals were grown using the same optimized growth parameters resulting in large uncracked crystals. Towards the end of the of the crystal boules, a last to freeze region comprising the last 1–3% of the total volume was observed to develop at the top of the charge. This last to freeze region was typically observed to be polycrystalline. It may be assumed that this region forms due to segregation of impurities during crystal growth. Some black impurities thought to be trace carbonates from the precursor materials also tend to segregate in this region. Melt filtering of the charge prior to growth may be effective in removing these impurities.

Figure 2. CsSrBr₃: Eu 5% single crystal boules grown by the vertical Bridgman technique, A) Crystal 1 (crystal with 1:1 ratio of starting raw materials), B) Crystal 4 (crystal with excess CsBr added to starting raw materials).

Figure 2A and 2B show CsSrBr₃: Eu crystals grown from melt compositions with different ratio of CsBr and SrBr₂. Neither of the crystals showed any cracking, however the difference between the optical transparencies of the two boules was significant. Crystal 1 had a cloudy appearance, while Crystal 4 was highly transparent. Typically it was observed that all the crystals grown with an excess of CsBr were transparent, while crystals grown with an excess of SrBr₂ or from a melt with CsBr and SrBr₂ in the ratio of 1:1 were cloudy. It may therefore be hypothesized that in crystals with a deficiency of CsBr, the excess Sr forms some light scattering defects which make the crystals appear cloudy and adversely affect the optical transmission. The exact nature of these light scattering defects has not yet been determined. The effect of stoichiometric imbalance on the optical transmission characteristics of the crystals has also been reported for scintillators such as CdWO₄ [20].

Figure 3. Polished CsSrBr₃: Eu single crystal slabs for A) Crystal 1 ($\varnothing$ 22 × 15 mm³), B) Crystal 2 ($\varnothing$ 17 × 7 mm³), C) Crystal 3 ($\varnothing$ 17 × 7 mm³), D) Crystal 4 ($\varnothing$ 17 × 7 mm³), and E) Crystal 5 ($\varnothing$ 22 × 15 mm³).

To further observe the difference in the optical transparency, the crystals were cut into cylindrical slabs and their flat surfaces were polished. The pictures of the polished slabs are

shown in Figure 3A – 3E. The dimensions of the crystal slabs shown in Figure 3A and 3E were $\varnothing 22 \times 15 \text{ mm}^3$, while the slabs shown in Figure 3B, 3C, and 3D were all $\varnothing 17 \times 7 \text{ mm}^3$. The surfaces of all the crystal slabs were prepared using the same procedure. The only other difference between the crystal slabs apart from their dimensions was the composition of the melt from which they were grown. Thus, the difference in the optical transparency of the crystals supports the hypothesis that the cloudy appearance of the crystals is due to a deficiency of CsBr. In case of Crystal 1, the deficiency of CsBr may be caused by its volatilization from the melt. In case of Crystal 2 the deficiency of CsBr was deliberately caused by adding an excess of SrBr_2 to the melt. The exact nature of the process which causes the cloudiness in crystals deficient in CsBr is yet unknown and will be the subject of future investigations.

Of the different crystals grown, the samples prepared from Crystal 1 and Crystal 5 had the largest detector volumes ($\varnothing 22 \times 15 \text{ mm}^3$). As the main objective of the study was to compare the improvement in energy resolution at large crystal volumes the following results will primarily focus on these two crystals. Crystal slabs of identical thickness (5 mm) were prepared from Crystal 1 and Crystal 5 for a more direct comparison of the optical transparency. And as can be seen in Figure 4A and 4B, the sample cut from Crystal 5 was clear enough so that the lettering can be easily read through its thickness, whereas for Crystal 1 the letters appear blurred.

Figure 4. Comparison of the transparency of the $\text{CsSrBr}_3\text{:Eu}$ crystals, A) Crystal 1, B) Crystal 5, and C) Optical transmittance for 2 mm thick slabs of the Crystal 1 and Crystal 5.

The optical transmission measurement confirmed the difference in the transparency between the two crystals. The absorption edge at 440 nm corresponds to the optical absorption band of the Eu^{2+} activator in the CsSrBr_3 matrix. The crystal with the excess CsBr had an excellent transparency ($> 80\%$) for photons with wavelengths longer than 440 nm, whereas the crystal grown from raw materials with 1:1 ratio of Cs and Sr had an overall poor transparency for these wavelengths (between 40% - 60%).

Figure 5. Typical powder XRD spectra of $\text{CsSrBr}_3\text{:Eu}$ samples harvested from Crystal 1 ($\text{CsBr}:\text{SrBr}_2 = 1$) and Crystal 5 ($\text{CsBr}:\text{SrBr}_2 = 1.07:0.93$). The spectra for both samples show identical diffraction peaks.

Powder XRD measurements were used to confirm the homogeneity of the crystal boules. A number of samples were harvested from different parts of the crystal boules for the measurement. Typically it was observed that all the samples from all the crystals exhibited the same patterns, the diffraction patterns for two such samples are shown in Figure 5. The samples were taken from the Crystal 1 and Crystal 5 and as can be seen from the figure, both the samples have identical peaks in the powder XRD scans. It can be inferred from the scans that there is no significant compositional or phase inhomogeneity between the two crystals. Thus the transparent crystals grown from melts with an excess of CsBr have the same phase composition as the cloudy crystals grown from melts with 1:1 ratio of CsBr and SrBr_2 .

Figure 6. Polarized light microscope images of A) Crystal 1 and B) Crystal 5. The samples were prepared by cutting 2 mm thick slabs from the crystal boules.

Polarized light microscope images reveal the details of the microstructure of the crystals (Figure 6). In all samples of CsSrBr_3 , lamellar twinning can be observed. It is important to note that the twinning appears to be more prominent in crystals grown with an excess of CsBr in the melt. And while the twinning does not appear to affect the optical transparency of the crystals it may have some effect on the scintillation performance.

Similar twinning can be observed in other metal halide scintillator crystals like europium doped cesium calcium iodide (CsCaI_3 : Eu) [15]. The twinning in CsSrBr_3 is thought to arise due to a solid-solid phase transition. Evidence of this phase transition was originally observed in the DSC measurement as was discussed in the previous section. Similar phase transitions have been studied for other iso-structural perovskite [21]. The solid-solid phase transition was investigated by acquiring temperature dependent powder x-ray diffraction data in order to identify the high temperature phase. Figure 7 includes a section of the pattern where diffraction peaks disappear (increase in symmetry) upon heating above the phase transition temperature.

The structural evolution of the CsSrBr_3 lattice is shown in Figure 7. With increasing temperature, the low intensity superlattice reflections due to the tilted SrBr_6 polyhedra continually diminish in intensity. The diffraction pattern taken at 300°C contains only intense reflections belonging to the ideal perovskite phase belonging to the P23 space group consisting of a cubic unit cell with a central Sr atom surrounded by Cs atoms at the cube corners and Br atoms at the face centers.

Figure 7. Temperature dependent PXRD patterns of CsSrBr_3 showing the lattice expansion and transition to the cubic phase (left) and detail of the diffraction pattern with the indexed peaks of the low (Pnma) and high temperature (P23) phases (right).

While the structure data is not available closer to the melting point of CsSrBr_3 (760°C), it is assumed the compound crystallizes with the cubic symmetry present at 300°C and undergoes at least one phase transition to the orthorhombic phase observed at room temperature. From the DSC and high temperature PXRD data, we suspect the critical temperature of this transition is $\approx 235^\circ\text{C}$. This finding is in accordance with the general ease with which CsSrBr_3 can be grown into single crystals, as well as the highly strained and usually twinned morphology observed.

B. Scintillation Performance Characterization

The photoluminescence excitation and emission spectra of Crystal 1 and Crystal 5 can be seen in Figure 8. The samples were excited at 370 nm and an emission band peaking at 430 nm was observed. This band along with the broad excitation bands from 250 to 420 nm can be assigned to the $5d \rightarrow 4f$ transitions due to the Eu^{2+} ions which are common for Eu^{2+} doped scintillators [22]. The overlapping of the excitation and emission bands indicates that self-absorption may be likely. These results are similar to ones obtained previously [23].

Figure 8. Photoluminescence excitation ($\lambda_{em} = 430$ nm) and emission ($\lambda_{ex} = 370$ nm) spectra

The x-ray excited radioluminescence spectra of Crystal 1 and Crystal 5 can be seen in Figure 9A. Both spectra present an emission peak centered at 440 nm related to the $5d \rightarrow 4f$ de-excitation of Eu^{2+} . Since the emission peaks are the same amplitude for both crystals, it may indicate that the concentration of Eu^{2+} is the same for both crystals. The overall symmetry of the emission peaks may be ascribed to the absence of any impurity or defect emissions.

Figure 9. A) X-ray excited radioluminescence spectra of Crystal 1 and Crystal 5, measured using transmission mode, B) Scintillation decay time profiles of Crystal 1 and Crystal 5 under irradiation with 662 keV gamma-rays.

The scintillation decay time profiles of samples prepared from Crystal 1 and Crystal 5 are plotted in Figure 9B. Both the decay curves could be fitted by a single exponential function. The decay constant for the sample with the excess CsBr is larger, this difference may be due lower efficiency of the scintillation process prior to free charge carrier capture by Eu^{2+} ions. The lengthening of the scintillation lifetime may be ascribed to a greater concentration of bulk defects or traps.

The ^{137}Cs gamma-ray spectra recorded using samples prepared from Crystal 1 can be seen in Figure 10. The best performance was obtained for samples of small crystal volume, where the energy resolution measured for a $5 \times 5 \times 5 \text{ mm}^3$ polished cube was approximately 5.2%, while in the case of the $\varnothing 22 \text{ mm} \times 15 \text{ mm}^3$ thick slab it was approximately 7.4%. As the size of the crystals was increased, the pulse height position of the 662 keV gamma-ray peak measured using the crystals was also reduced due to less light being collected from the sample. This volumetric dependence of the energy resolution and the light collection efficiency of Crystal 1 may be attributed to a combination of self-absorption effects and the overall poor optical quality of the crystal.

Figure 10. Pulse height spectra under ^{137}Cs irradiation of samples of Crystal 1, Sample A: measuring $5 \times 5 \times 5 \text{ mm}^3$, Sample B: measuring $10 \times 10 \times 5 \text{ mm}^3$, and Sample C: measuring $\varnothing 22 \text{ mm} \times 15 \text{ mm}^3$.

The crystal growth with excess CsBr resulted in an improvement in not only the optical quality but also the energy resolution of the CsSrBr_3 : Eu 5% scintillator crystals. This improvement was most clearly observed for Crystal 5. The gamma-ray spectra recorded using samples prepared from Crystal 5 can be seen in Figure 11. The spectra measured using the different samples prepared from Crystal 5 show an improvement in energy resolution for all the crystal volumes compared. The best performance was once again obtained for samples of small crystal volume, where the energy resolution measured for a $5 \times 5 \times 5 \text{ mm}^3$ polished cube was approximately 4.9%. In the case of the $\varnothing 22 \text{ mm} \times 15 \text{ mm}^3$ thick sample however, it was approximately 6.2% which is a significant improvement compared to the similar sized sample prepared from Crystal 1.

Similar to Crystal 1 there was a reduction in the light collection efficiency as the volume of the samples was increased. The magnitude of this change in Crystal 5 was reduced compared to that observed for Crystal 1. Since the photoluminescence spectra indicate that both Crystal 1 and

Crystal 5 have similar self-absorption effects, the reduction in the volumetric dependence of the crystal may therefore be ascribed to the improvement in its optical quality.

Figure 11. Pulse height spectra under ^{137}Cs irradiation of samples of Crystal 5, Sample A: measuring $5\times5\times5\text{ mm}^3$, Sample B: measuring $10\times10\times5\text{ mm}^3$, and Sample C: measuring $\varnothing 22\text{ mm} \times 15\text{ mm}^3$.

The light yield for the scintillator crystals was estimated by using the wavelength-weighted quantum efficiency of the R2059 PMT, which for $\text{CsSrBr}_3:\text{Eu}5\%$ is about 24.8%. Multiple samples measuring $5\times5\times5\text{ mm}^3$ were prepared, and in case of Crystal 1 the light yield of the samples was estimated to be $55,600\pm1000\text{ ph/MeV}$, while that for Crystal 5 it was $40,200\pm1000\text{ ph/MeV}$. A similar trend was observed for the other $\text{CsSrBr}_3:\text{Eu}$ crystals grown during this investigation. The crystals grown with an excess of CsBr in the melt all had similar light yields. On the other hand, the crystal grown with an excess of SrBr_2 in the melt had similar light yield as Crystal 1. Table 2 summarizes the light yield of similar sized samples prepared from the different crystals.

Table 2. Light yield of samples measuring $5 \times 5 \times 5\text{ mm}^3$

As discussed in the previous sections, it was observed that while all CsSrBr_3 crystals exhibited twinning, the twinning was more prominent in the crystals with excess CsBr . It is therefore hypothesized that the twins may act as areas of disorder at the atomic scale, which are likely locations for defects to be generated. The defects may influence the charge migration negatively, which in turn may influence the charge recombination leading to fewer scintillation photons being emitted. The light scattering caused by the twins may also reduce the light collection efficiency of the crystals and may be the reason for the lower light output of the crystals with excess CsBr . Further investigation is needed to determine the exact cause of the lower light output.

IV. Summary

We have demonstrated the growth of $\text{CsSrBr}_3:\text{Eu}$ using the vertical Bridgman technique with improved energy resolution and optical quality over previously reported results. It was hypothesized that the poor optical quality of the crystals grown and reported in the past may be caused due to the volatilization of CsBr during synthesis and crystal growth. The results reported in this work support this hypothesis. Significant improvement in the optical quality was observed for CsSrBr_3 crystals grown with excess CsBr added to the melt. The CsSrBr_3 crystals grown from melts with excess CsBr showed an improvement in energy resolution, particularly at large crystal volumes.

It was observed that CsSrBr_3 undergoes a solid-solid phase transition from cubic at high temperatures to the orthorhombic phase at room temperature, which was confirmed by high temperature XRD. From the DSC and high temperature PXRD data, the critical temperature of this transition was found to be $\approx 235^\circ\text{C}$. This finding is in accordance with the general ease with

which CsSrBr₃ can be grown into single crystals, as well as the highly strained and usually twinned morphology observed.

While all CsSrBr₃ crystals exhibited twinning, the twinning was more prominent in the crystals with excess CsBr. It is therefore hypothesized that the twins may act as areas of disorder at the atomic scale, which are likely locations for defects to be generated. The defects along with the areas of disorder may have a deleterious effect on the charge migration in the crystal, which in turn may affect the scintillation process and cause a decrease in the number of scintillation photons being emitted. In addition, the twins may also act as light scattering sites and affect the light collection efficiency of the crystals and may be the reason for the lower light output of the crystals with excess CsBr. Further investigation is needed to determine the exact cause of the lower light output. Therefore, the primary focus of the future development of CsSrBr₃ will be the prevention of the formation of twinning in order to further improve the scintillation performance.

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Figure 1. DSC heating and cooling curves for CsSrBr₃.

Figure 2. CsSrBr₃: Eu 5% single crystal boules grown by the vertical Bridgman technique, A) Crystal 1 (crystal with 1:1 ratio of starting raw materials), B) Crystal 4 (crystal with excess CsBr added to starting raw materials).

Figure 3. Polished CsSrBr₃: Eu single crystal slabs for A) Crystal 1 ($\phi 22 \times 15 \text{ mm}^3$), B) Crystal 2 ($\phi 17 \times 7 \text{ mm}^3$), C) Crystal 3 ($\phi 17 \times 7 \text{ mm}^3$), D) Crystal 4 ($\phi 17 \times 7 \text{ mm}^3$), and E) Crystal 5 ($\phi 22 \times 15 \text{ mm}^3$).

Figure 4. Comparison of the transparency of the CsSrBr₃: Eu crystals, A) Crystal 1, B) Crystal 5, and C) Optical transmittance for 2 mm thick slabs of the Crystal 1 and Crystal 5.

Figure 5. Typical powder XRD spectra of CsSrBr₃: Eu samples harvested from Crystal 1 (CsBr: SrBr₂ = 1) and Crystal 5 (CsBr: SrBr₂ = 1.07:0.93). The spectra for both samples show identical diffraction peaks.

Figure 6. Polarized light microscope images of A) Crystal 1 and B) Crystal 5. The samples were prepared by cutting 2 mm thick slabs from the crystal boules.

Figure 7. Temperature dependent PXRD patterns of CsSrBr₃ showing the lattice expansion and transition to the cubic phase (left) and detail of the diffraction pattern with the indexed peaks of the low (Pnma) and high temperature (P23) phases (right).

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Figure 8. Photoluminescence excitation ($\lambda_{\text{em}} = 430 \text{ nm}$) and emission ($\lambda_{\text{ex}} = 370 \text{ nm}$) spectra

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Figure 9. A) X-ray excited radioluminescence spectra of Crystal 1 and Crystal 5, measured using transmission mode, B) Scintillation decay time profiles of Crystal 1 and Crystal 5 under irradiation with 662 keV gamma-rays.

Sample A

Sample B

Sample C

Figure 10. Pulse height spectra under ^{137}Cs irradiation of samples of Crystal 1, Sample A: measuring $5\times5\times5\text{ mm}^3$, Sample B: measuring $10\times10\times5\text{ mm}^3$, and Sample C: measuring $\phi 22\text{ mm}\times 15\text{ mm}^3$.

Sample A

Sample B

Sample C

Figure 11. Pulse height spectra under ^{137}Cs irradiation of samples of Crystal 5, Sample A: measuring $5 \times 5 \times 5 \text{ mm}^3$, Sample B: measuring $10 \times 10 \times 5 \text{ mm}^3$, and Sample C: measuring $\phi 22 \text{ mm} \times 15 \text{ mm}^3$.

Table 1. CsSrBr_3 : Eu crystals grown with different ratios of CsBr and SrBr_2 in the melt

<i>Crystal I.D.</i>	<i>Ratio of CsBr and SrBr_2 in the melt (CsBr: SrBr_2)</i>
<i>Crystal 1</i>	<i>1:1</i>
<i>Crystal 2</i>	<i>0.99:1.01</i>
<i>Crystal 3</i>	<i>1.01:0.99</i>
<i>Crystal 4</i>	<i>1.03:0.97</i>
<i>Crystal 5</i>	<i>1.07:0.93</i>

Table 2. Light yield of samples measuring $5 \times 5 \times 5 \text{ mm}^3$

<i>Crystal I.D.</i>	<i>Ratio of CsBr and SrBr_2 in the melt (CsBr: SrBr_2)</i>	<i>Light yield (ph/MeV) of samples measuring $5 \times 5 \times 5 \text{ mm}^3$</i>
<i>Crystal 1</i>	<i>1:1</i>	<i>~55,600</i>
<i>Crystal 2</i>	<i>0.99:1.01</i>	<i>~53,400</i>
<i>Crystal 3</i>	<i>1.01:0.99</i>	<i>~36,200</i>
<i>Crystal 4</i>	<i>1.03:0.97</i>	<i>~37,000</i>
<i>Crystal 5</i>	<i>1.07:0.93</i>	<i>~40,200</i>