High Speed Growth of SrI₂ Scintillator Crystals by the EFG Process

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ABSTRACT

Strontium iodide (SrI₂), an important new scintillator crystal having a high light yield and excellent energy resolution, was grown for the first time by the edge-defined film-fed (EFG) growth method. Using high purity starting materials and floating dies made of graphite, fused quartz or AlN, large cylindrical, planar or square cross-section single crystals (12-15 mm across and > 7 cm long) were produced at growth rates up to 15 mm/h, significantly faster than the current Bridgman growth technology. Details on the equipment used to grow this deliquescent material and on its growth behavior are given along with some discussion of crystalline quality.

Keywords: A1. Purification; A2. Edge defined film fed growth; B2. Scintillator materials; B1. Halides

1. Introduction

While europium-doped strontium iodide (Eu²⁺:SrI₂), was first discovered by Hofstadter in the 1960's [1], its outstanding scintillator properties were only recently revealed through improvements in material purity and the preparation of high quality single crystals [2,3]. It has now been shown to hold great promise for use in certain radiation detector applications. It provides a dramatically improved light yield and energy resolution over currently available materials, making it an attractive candidate for use in the field to selectively detect and identify illicit fissionable material being transported across international borders.

SrI₂ has an orthorhombic crystal structure, with lattice constants $a = 15.268 \text{ \AA}$, $b = 8.2351 \text{ \AA}$ and $c = 7.896 \text{ \AA}$. As a result, it has anisotropic properties that can affect both crystal preparation and device properties. In addition, the compound is deliquescent, and the preparation of high-efficiency detectors requires exceptional care in its handling during all stages of processing and characterization. Currently high quality crystals are being produced in sealed quartz ampoules by the Bridgman method [2]. The variable quality of the commercial starting material has been a problem and so usually the melts have to be filtered, and sometimes zone-refined prior to growth to eliminate any insoluble by-products (hydrates and/or oxy-iodates) resulting from the synthesis process. Often zone refining is used to enhance material purity, particularly for the EuI₂ dopant, which cannot be obtained commercially in ultra-high purity form. Some relevant properties of SrI₂ are given in Table 1.

Currently the cost of SrI₂ single crystals prohibits its wide scale deployment in radiation detection devices. To begin with the starting material is very expensive. Pre- and post-growth processing add to the cost. To achieve high quality crystals using the Bridgman method the growth rates have to be rather slow, on the order of 0.4-0.8 mm/h [2], and therefore crystal throughput is a rate limiting step. One way to reduce some of the cost is to dramatically improve the crystal growth rates and reduce the amount of post growth fabrication necessary to produce a device size element.

The edge-defined film-fed (EFG) process used in this study [4] is meant to address this problem. EFG is a meniscus controlled, shaped crystal growth method similar to the Czochralski method. Unlike Czochralski growth, however, the crystal does not sit directly on the melt surface but on the top of a shaped die that is wetted by the melt, and while it is pulled upward, as in Czochralski growth, it is done so without rotation. The EFG process thus involves a melt that wets the die material to a relatively high degree. The die maintains the thin liquid film on its top surface via a capillary that draws melt upward to feed the growing crystal. The crystal takes the cross-sectional shape of the die perimeter.

Growth takes place from this thin film and the growth interface thus sees a higher axial thermal gradient than if it were directly touching the melt surface (as it does in classical Czochralski growth), and the high gradients permits higher growth rates. Excellent descriptions of EFG fundamentals are given in [5,6]. Another advantage of the EFG process is that multiple crystals can be grown simultaneously. The method has been used successfully for the commercial production of silicon and the simultaneous growth of sapphire ($\alpha\text{-Al}_2\text{O}_3$) crystal plates[7], the latter material also in rod and tube form. Two basic types of EFG dies have been used: one which floats on the melt surface and the other which is non-floating (fixed in place). In this feasibility study we used the floating die technique.

The difficulties associated with the deliquescent nature of SrI_2 led us initially to test the EFG method on a similar material, cesium iodide (CsI), a commercially available halide scintillator compound [8]. Using a controlled-atmosphere NRC bulk silicon crystal growth system, CsI boules 12-15 mm diameter and 8 cm in length were easily grown at rates up to 45 mm/h using floating graphite dies. The use of graphite dies was not problem-free, however, and often led to the formation of bubble tracks propagating along the growth axis near the boule surface. This problem was eliminated when fused quartz dies were introduced [8].

While the NRC growth system worked well with CsI, it did not prove sufficiently airtight for use with SrI_2 . In addition, it contained internal metal parts that were found to react with vapors from the slow evaporation of the SrI_2 melts. Therefore, as described below, we designed and built an entirely new growth apparatus containing no metal components. This new growth system, after a series of modifications, was capable of growing scintillator- grade SrI_2 crystals in a variety of sizes and shapes.

Table 1 here

2. Experimental Procedure

2.1 Growth

The starting materials, SrI_2 (99.99%) and EuI_2 (99.9%), were obtained from Sigma Aldrich in the form of small pellets. The Eu^{2+} dopant concentration used was 3 mole %. All pre- and post-processing was done either in a N_2 filled glove box or in the dual-use growth capsule, which could be sealed during transfer from the glove box to the growth station and back again. The growth capsule and associated gas-handling set-up is shown schematically in Fig. 1. The growth capsule (Fig. 2a) was made from fused quartz as was the upper flange, the input and output gas ports and the crucible. The capsule allows the crucible, charge and seed to be transported in an inert atmosphere to and from the dry box and furnace. Once the capsule was installed into the furnace, the gas lines were attached and a pulling system attached to the seed rod.

Before growth the charge was purified by filtering. The two iodides were weighed, mixed and then placed in a Buchner-like fused quartz funnel (Fig. 2b) containing a fused quartz frit. The schematic in Fig. 2b shows the growth crucible at the bottom, the fused quartz filter funnel containing the fused-in-place quartz frit at the bottom and an inverted crucible that can be placed on top of the filter funnel so that previous charges could be re-filtered and reused. Three different pore size frits were evaluated, 40-90 μm , 15-40 μm and 4-15 μm . In the filtering process the funnel was placed on top of the growth crucible and the assembly loaded into the reusable quartz growth chamber (Fig. 2c). When the clarity of the crystals grown from melts filtered through the different frits was compared to those grown without filtering, the finest filter was found to produce both the clearest melts and the clearest crystals, and was used in most of the later experiments.

The growth crucibles and frit filters used were heavy-walled with a rounded bottom to prevent cracking upon cooling. In our experiments the crucibles were 50 mm OD, 42 mm ID

and 40 mm high. The typical charge was approximately 85 grams and the corresponding melt height was 30 mm.

Fig. 1 here

Fig. 2. Here

The growth procedure was as follows: First the growth capsule was loaded in the drybox (0.5 ppm H₂O) with a crucible containing a melt-filtered, Eu-doped charge. The floating die (discussed later) was placed on top of the charge and the seed rod inserted into the flange along with an auxiliary rod for various adjustments. The gas valves were shut, trapping nitrogen in the growth capsule, and the capsule then transferred from the glove box to the growth furnace. After transferring the capsule to the furnace, all the gas and vacuum lines were attached and the seed rod connected to a portable pulling system and aligned with the center of the die. The capsule was first vacuum purged (mechanical pump) and then filled with purified argon. This process was repeated several times. A by-pass flow rate of

200 cc/min was monitored with a series of mineral oil bubblers at the gas outlet. The Ar pressure within the capsule was held at a constant 1 psi. After this, the charge was melted (to ~700 °C) in Argon and then degassed under vacuum, allowing the die to float on the melt surface. Vigorous bubbling in the melt was observed during the initial stage of evacuation but diminished over 5-10 minutes. If left for extended periods in argon, bubbling in the melt would reappear when re-evacuated.

When molten, the melt flows upward through a hole in the die toward to the die surface by capillary action. It was essential that the melt wet the top of the die surface as well as the interior surface of the capillary hole, and lacking a surfactant in the melt, it was sometimes necessary to push the die below the melt surface to facilitate complete wetting of its surface (especially with graphite dies).

2.2 Growth Furnace and thermal gradient issues

The furnace set-up, as shown in Fig. 3a, employed a cylindrical Kanthal wire-wound heater. The still-sealed growth capsule was positioned about 6 cm below the top of the furnace (Fig. 3b) such that the melt and die were in a position to maximize the thermal gradient and facilitate a high growth rate. Beneath the furnace is a platform which allows the furnace to move in the x-y plane to aid in aligning the seed and capillary.

Fig. 3 here

A computational model of the edge-defined film-fed crystal growth method (EFG) was previously used to study the growth of cesium iodide (CsI), a similar scintillator crystal [8-9]. The model, which includes fluid flow, heat transfer, and gravitational effects, was solved numerically by the finite element method to predict crystal diameter as a function of growth rate and die geometry. The model computed the location and shape of the crystal-melt interface and the meniscus to satisfy a self-consistent formulation of phase change and

capillary dynamics.

Modeling the growth of CsI in a similar EFG system provided many insights to growth behavior, notably the importance of die design on growth stability and the influence of axial thermal gradients through the system. The melting point of SrI_2 is approximately 100 K lower than that of CsI, so we expect radiation heat transfer to be comparatively reduced in this lower temperature range.

The axial thermal profiles were also measured experimentally with a thermocouple inserted through the quartz vacuum flange and into the melt within the capsule. The measurements were made from below the bottom side of the die (within the melt), up through the capillary, and from above the die surface into the gas space directly above. The measurements were done in argon, vacuum and helium. The radial thermal profiles across the die surface were measured from the middle of the capillary outward to the die edge. These profiles are shown in Figs. 4 and 5. The axial gradients under argon (Fig 4) were significantly different than those under vacuum and helium. Under argon there was a very steep drop in temperature just above the die surface. (This was viewed as helpful for maximizing the growth rates). In Fig. 5, the radial profiles show a similar trend with the behavior under Ar significantly different from those under vacuum and He atmospheres. In the plot, the center of the capillary is at “0” while the die edge is at 6 mm (for a 12 mm diameter die). Under argon, the radial temperature gradients across the die surface, (from the center to the die edge), decreased much more rapidly over the fused quartz die than over the graphite or aluminum nitride dies. This was due to the much higher thermal conductivities of graphite and AlN (Table 2). This made widening the crystal out to the die edge on the fused quartz dies more difficult to control.

Fig. 4. Here

Fig. 5. Here

As mentioned before, crystal pulling was used without rotation. The temperature was maintained and programmed using a Eurotherm PID controller. All the parts (ampoule, die, crucible and seed) were initially baked out in vacuum in the furnace prior to loading the charge. In particular, it was found that the clarity of EFG grown SrI_2 crystals grown using graphite dies (which contained some open porosity) could be significantly improved by first baking the dies out in vacuum at $\sim 700^\circ\text{C}$ [10]. The seeds were obtained from Bridgman boules grown elsewhere [11]. They were oriented along the Bridgman boule growth axis. Growth rates in the range of 5-25 mm/h were studied. During the course of a growth run the temperature was lowered to compensate for the drop in melt level into the hotter region of the furnace.

The low melting temperature and high boiling point of SrI_2 leads to a negligible vapor pressure over the melt, and hence the upper regions of the ampoule do not get coated with condensate unless a leak in the furnace caused melt dissociation.

2.3 Die Designs

Three different floating die materials were used in this study: 1) Poco graphite (EDM-3 grade), 2) fused quartz, and 3) high density aluminum nitride ceramic. The dies themselves were embedded in a flat disc (float) which covered most of the melt surface. The float contained several holes to facilitate gas removal during and after melting. Some examples of the dies are shown in Fig. 6. Note: the number and size of the capillaries can be varied along with their shape. Except for the quartz die, which had five uniformly spaced, 1 mm diameter capillaries, the other floats made from different materials typically had a single 2 mm capillary hole on center.

A suitable die/float material has to be non-reactive with and be wet by the melt. Wettability depends on a number of factors including the die material, the surface finish and the growth atmosphere. The material also has to have a low enough density so that it will float on the melt surface. Some relevant properties of the die/float materials are given in Table 2.

Fig. 6 here

Table 2 here

The exact die and float designs were dictated by the machinability of the different materials. Graphite was the easiest to work with and the dies were made in two parts, a circular disc as the float into which the die could be screwed in. This made it convenient to interchange different die shapes and sizes within the same float (Fig. 6). The quartz and AlN dies and floats had to be made in one piece. The size of the die (hence crystal) was limited by the aspect ratio of the system. The dies used most frequently were either 12 mm diameter or 15 mm x 15mm square. While various capillary and die configurations were studied, a single 2mm diameter hole in the die center was found suitable for most die shapes. However, with fused quartz it was found helpful to have multiple capillaries distributed around the die surface due its much lower thermal conductivity which led to a very steep decrease in temperature toward the die edge as discussed below.

The shape of the die top can strongly influence the interface shape [12]. Much better results are predicted, and have been found in practice, for a die top featuring a concave shape and thereby producing a convex melt-crystal interface. The upward-sloping die edges lead to a

larger apparent contact angle of the meniscus with the die, which makes wetting instabilities far less likely for this geometry [13,14]. In practice, dies with recessed (inclined or conical) surfaces, such as the bottom geometry, were found to result in easier growth. As a result, the dies used in this study were fabricated with an inclined surface from the edge toward the capillary. For all the dies studied the edge was 1 mm higher than the center of the die with a corresponding angle of 9° for the 12 mm diameter circular die and 7.5° for the 15 mm x 15 mm square die.

2.4 Characterization

Crystal characterization is quite challenging for materials like SrI_2 which are super hygroscopic. Even small exposures to the atmosphere are detrimental, limiting the types of measurements that can be made. For Laue x-ray orientation experiments the samples were covered in polyethylene stretch wrap, which was held in place on an aluminum bar with tape. Mounting of the sample was done in the dry box. The sample was then sealed in a jar with a N_2 atmosphere for transport to the x-ray apparatus and then immediately removed from the jar and placed into the Laue system.

The photographic and microscope imaging of macroscopic defects in polished SrI_2 samples were all done while under paraffin oil using natural and polarized light microscopy. Samples were typically polished in ambient air while immersed in paraffin oil, first with 400 grit coarse sandpaper, then with 1200 grit paper. This was followed by a chemical-mechanical polish in an acetone/oil mixture on a paper towel. Finally, the surface was further buffed in oil on paper to remove any reacted surface layer.

Measurements of scintillator properties were made on EFG samples cut to shape with a diamond impregnated wire under a continuous flow of mineral oil. The pre-shaped crystals were then polished to final shape using abrasives of gradually finer grits and rinsed well after

each abrasive grade. Rinsing and storage was also done under ultra-dry mineral oil. The scintillator properties of freshly polished SrI_2 crystals were also measured while immersed in ultra-dry mineral oil in a fused quartz container of an appropriate size for the dimensions of both the crystal and PMT (Hamamatsu R6231-100). The container was covered with a Spectralon reflector to direct photons generated in the crystal toward the PMT. The entire assembly was covered with a light blocking cover upon which the radiation source was placed.

3. Results and Discussion

The floating-die EFG growth method was found to be a very straightforward way to grow SrI_2 crystals in various shapes and sizes (up to 15 x 15 mm). Fig. 7 shows some examples of crystals grown using different shaped dies. In this study growth rates up to 20 mm/h were achieved, but crystal quality as a function of growth rate strongly depended on crystal size, thermal gradients and material purity. While nominally high purity commercial starting materials were used in this study (Sigma Aldrich SrI_2 and EuI_2), the difficult synthesis processes used in their preparation leave some residual contaminants, in particular a black carbonaceous-like material observed after melting. Therefore, most SrI_2 crystal growers further purify their materials by filtration and/or zone refining. In this study the filtering procedure, as discussed above, removed the black component of our starting materials. As mentioned before the finest frit filter, (5-14 μm), produced not only the clearest melts but also the clearest crystals with the highest optical quality.

Fig. 7. Here

Initially, graphite dies were used to demonstrate the viability of the EFG method for growing SrI_2 crystals at high growth rates. While graphite dies were found to work very well with respect to initiating growth on the seed crystal and expanding the crystal out to

the die edge, the optical quality of the early boules produced was initially found to be generally poor. Boule-to-boule variations were notable. The poor optical quality using graphite was attributed to its significant porosity and the potential for detrimental reactions with residual oxygen or moisture in the growth atmosphere. Neither of these factors was found to be relevant with the other die materials studied. When we switched to the nonporous, non-reactive fused quartz and AlN dies, the optical quality was greatly improved (see Fig. 8). Unfortunately, it was more difficult to grow from these alternate die materials. In the case of quartz this was partly due to its lower thermal conductivity and in the case of AlN its poorer wettability by SrI_2 melts. Also with AlN dies, some small, randomly spaced bubbles were encountered along the length of the boule. They were more concentrated in the center of the boule.

Fig. 8.

It was subsequently determined that graphite dies could be used to grow clear crystals if, in addition to purifying the charge, we prebaked the graphite dies in vacuum at elevated temperatures to drive out any gaseous or adsorbed impurities within the open pore network. A comparison between a boule produced from an unfiltered and unbaked graphite die with one grown from an optimized growth process is shown in Fig. 9.

Fig. 9. Here

The formation of cracks in a number of the SrI_2 crystals grown were due to a variety of factors. Anisotropic thermal expansion of the lattice, (Table 1) leads misoriented grains in polycrystalline boules to shrink differentially on cooling, generating large strains at the grain boundaries. The high axial thermal gradients used to promote high growth rates also lead to strain and cracking. Abruptly disconnecting a boule from the melt on the die surface is known to cause cracking. (Single crystal boules that are slow cooled to room temperature did not typically contain cracks.) Finally, mechanical stresses induced during sample handling can be another source of cracking.

The anisotropic nature of the SrI_2 structure manifested itself in the form of growth rate anisotropy. The seeds, oriented along the Bridgman boule axis, appeared to be close to a major crystallographic direction in the structure (i.e. the $[100]$, $[010]$ or $[001]$). Facets often formed on one set of opposing surfaces parallel to the growth axis until the boule reached the die edge all the way around (Fig. 10a). This indicates a slow growing direction normal to the growth axis and a correspondingly faster growth direction normal to the facet and the boule axis. A Laue pattern of the slow growth facet is shown in Figure 10b. This pattern was achieved directly off an unpolished facet plane. To date grinding and polishing SrI_2 has not yielded clean x-ray patterns due to either atmospheric surface damage and/or mechanical damage to the surface during sample preparation.

Fig. 10. Here

In this study diameter control was generally managed by the die configuration and the temperature adjustments made during growth. Typically, the furnace was cooled somewhat during growth, the extent of which depended on the die material used. While the dimensions were nominally the same as the die cross-section, there were surface fluctuations of two types. The first, long range sinusoidal variations and the second, fine surface striations (see Figs. 7-10). The long range surface perturbations may have been due to less than optimized temperature control (and hence control of meniscus height and angle) and also movement of the free floating die on the melt surface. There is a small clearance between the float edge and the crucible wall (0.5 mm) thereby allowing some lateral movement. Also, as the growth proceeds, the die moves downward in the crucible (ex. for each 10 mm length of a 12 mm diameter crystal grown, the melt level drops by 0.92 mm). Since the crucible was fixed in the furnace, the die and growth interface moved into the hotter part of the heater and therefore the need for some furnace cooling was required during growth. This downward movement may also have been irregular due to meniscus drag at the crucible wall (i.e. the meniscus is first stretched during pulling and then relaxes when stretched too far). The fine surface striations, often seen in meniscus controlled processes like Czochralski growth, are often attributed to meniscus drag. A more robust growth furnace system and automated control of the meniscus shape and thickness would be expected to reduce or eliminate these diameter variations.

The clearest crystals were produced at growth rates in the range of 5-10 mm/h. Faster rates yielded light-scattering defects. It should be stated that the scattering centers observed in cloudy boules have not been identified analytically, but can probably be attributed to the presence of oxyiodides or hydrates since the presence of oxygen or H₂O in the starting material or growth atmosphere leads to cloudier crystals. The presence of such contaminants in high enough concentrations can affect crystal transparency even at slower growth rates.

As mentioned previously, small bubbles (as seen in Fig. 8) were observed more often in the boules grown using AlN dies. These were randomly distributed and could be from residual Ar dissolved in the melt. Occasionally skin-deep surface grooves or smaller linear ridges running along the length of some crystals were likely due to imperfect wetting near the die edge due to surface contamination on the die.

The scintillator properties of some crystals produced in this study were evaluated. The first samples were from an early square cross section boule grown from an unbaked graphite die and a 3% Eu-doped charge filtered through a 40-90 μm frit. The growth rate was 5 mm/h and the crystal was cloudy. The light scattering defects, as shown in Fig. 11, consisted of parallel bands along the growth axis with a spacing of 0.1 mm and individual particles uniformly of ~ 0.01 mm diameter. A few small bubbles were also observed. The core region above the capillary was clearer than the rest of the boule.

Fig. 11 here

Three different size samples from different parts of the boule were measured. The light yields (LY) varied from 90,000-107,000 ph/MeV and the energy resolution (ER) from 5.96 to 3.69%. The poorest ER sample had both a lower LY and some entrained bubbles or particles, while the best performing sample had the highest LY and was bubble-free. The pulse height and scintillation timing curves for the best sample are shown in Fig. 12. Even though the process was not optimized, the properties of our best sample were similar to Bridgman-grown crystals

Fig. 12 Here

The later EFG growths of SrI_2 using of vacuum baked graphite dies together with a charge filtered through the finest frit gave very clear crystals without the defects shown in Fig. 9b. This suggests that the particles filtered out and/or the porosity in the graphite pores gave rise to the defects that led to reduced transparency.

In Fig. 13 the timing curve and pulse height spectra are shown for a section of an early crystal of 3% Eu:SrI_2 grown from a 2 cm diameter, new graphite die at 5 mm/h. The melt was filtered through a 4-15 μm frit but the die was not pre-baked in vacuum. This boule, shown in Fig. 14a-b, had facets similar to the one shown in Fig. 12. The boule was very clear in the core region but had bubbles and bubble tracks in the outer edges away from the facet faces (Fig. 14c). This was also observed for EFG grown CsI using graphite dies (Gugushev et al [8]).

There were some cracks in the shoulder region and near the bottom due to thermal shock on cooling. The current furnace system does not have an after-heater to adjust (reduce) the axial thermal gradients during cooling and so this rather large boule had some internal strain. The sample measured was cut from the clear core and within the shoulder region. It contained a crack but was very transparent and without bubbles. The data shown in Fig. 13 were from a crack-free fragment of this sample (Fig. 14d). The light yield was very high and the energy resolution lower than in previous samples.

Fig. 13 Here

Fig. 14 Here

4. Conclusions

High quality, shaped crystals of SrI_2 can easily be grown by the EFG method using floating dies made from graphite, fused quartz or aluminum nitride. A removable, fused quartz growth chamber containing a purified argon atmosphere provided a contamination-free environment. Growth rates up to 10 mm/h produced the most transparent crystals. Growth from graphite dies and floats that had been vacuum pre-baked at 700°C significantly improved the crystal clarity. In all the experiments crystal transparency was greatly improved using charges filtered through the finest fused quartz frit filters (4-15 μm). The scintillator properties of the crystals produced were similar to those grown by the Bridgman method.

Acknowledgments

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Figure captions

Fig. 1. Schematic of the SrI_2 gas handling system

Fig. 2. (a) Demountable dual-use quartz growth and/or filtering capsule being placed into the dry box. (b) A schematic of the fused quartz filtering system. (c) A photograph of the system after a filtering run.

Fig. 3. (a) Growth system setup prior to attaching the vacuum/purge lines. (b) An illustration of the capsule mounted in the resistance-heated furnace showing (1) the growing crystal, (2) the floating die and (3) the melt.

Fig. 4. Axial thermal profiles normal to the die surface for aluminum nitride, fused quartz and graphite dies in Ar, vacuum and He atmospheres respectively. The lower curves are for an Ar atmosphere while the upper curves are for vacuum and He. The die surface is at position 0.

Fig. 5. Radial thermal profiles for aluminum nitride, graphite and fused quartz die materials under argon, vacuum and helium. The die surface is at the 6 cm position.

Fig. 6 Typical dies and floats design made from graphite, quartz and aluminum nitride.

Fig. 7. Three different shaped SrI_2 crystals; (a) a 12 mm diameter crystal grown from a 12 mm dia. circular graphite die, (b) a crystal grown from a 15x15 mm square graphite die (inset shows the cross-sectional shape) and (c) a sheet crystal grown from a 3 mm thick and 2.5 cm wide quartz die.

Fig. 8. An example of a crystal grown using an AlN die. Notice the excellent optical transparency. The cracks at the bottom were formed during grinding and polishing. Notice also that the seed region is tilted with regard to the boule axis suggesting that the fast growth direction in the seed was not perfectly aligned with the Bridgman boule axis.

Fig. 9. Comparison between two single crystal boules of SrI_2 . In (a), the crystal was grown from an unfiltered melt using a graphite die which had not been subjected to a prior

vacuum bake-out. It shows poor optical transparency with periodic light scattering bands of variable intensity. In (b) a very transparent (water-clear) boule grown from a melt filtered through a 4-15 μm frit and a baked-out graphite die.

Fig. 10. (a) Boule being grown from a circular 12 mm diameter die as it was filling out to the full cross-section. Note that at this point it has only reached the die edge in one of the orthogonal growth directions. The facet is facing forward and the Laue pattern in (b) was taken from the unpolished facet surface showing that it is one of the major planes in the orthorhombic system, preliminary analysis suggesting it is the (001).

Fig. 11. (a) Scattering defects from two sections along the length of an early boule grown at 5 mm/h from a filtered (40-90 μm frit) 3% Eu-doped charge. The linear features are along the growth axis. (b) Similar, but more pronounced, linear defects from the unfiltered and un-doped crystal shown in Fig. 9a.

Fig. 12 (a) The scintillation timing curve for the best section of an early 3% Eu doped SrI_2 boule and (b) the pulse height spectra from the same sample.

Fig. 13 Timing curve and pulse height spectra for a portion of a very clear 3% Eu-doped crystal of SrI_2 grown from a charge filtered through the finest frit and a 2 cm graphite die.

Fig. 14 (a) Large boule grown from 20 mm diameter graphite die showing faceting, (b) a 6mm thick polished section showing a clear center section, some cracks, and faint banding (broad striations). (c) bubbles and bubble tracks near the outer surface of the boule and (d) a cut and polished section the upper left quadrant used for scintillator property measurements shown in Fig. 13.

Table 1

Some relevant properties of SrI_2 .

Solid Density	4.59 g/cm ³
Melt Density	~4.08 g/cm ³ (estimated)
Melting Temperature	538 °C
Boiling Point	1,773 °C
Solubility	164-177 g/100ml H ₂ O
Thermal Expansion Coefficient	a=15.5x10 ⁻⁶ , b=21.6x10 ⁻⁶ , c=9.2x10 ⁻⁶ /°C
Surface tension	8.5 x 10 ⁻² N/m

Table 2

Average properties of the die materials studied.

Material	Graphite POCO EDM3	Fused Quartz GE Quartz 124	Aluminum Nitride
Density, g/cm ³	1.81	2.2	3.26
Porosity	open pores	none	negligible
Thermal Conductivity, W/(mK)	115 @RT 75 @500°C	1.38 @ RT ~2 @ 500°C	150-210

Figure 1.

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

(a)

(b)

Figure 10.

(a)

(b)

Figure 11

(a)

(b)

Figure 12

Figure 13

Figure 14.

(a)

(b)

(c)

(d)