Growth of 2 Inch Eu-Doped SrI_2 Single Crystals for Scintillator Applications

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ABSTRACT

A vertical Bridgman (VB) crystal growth process was established using modified micro-pulling-down (μ -PD) crystal growth system with a removable chamber that was developed for the growth of deliquescent halide single crystals because conventional μ -PD method does not allow growth of large bulk single crystals. Eu: SrI_2 crystals were grown from the melt of $(\text{Sr}_{0.98}\text{Eu}_{0.02})\text{I}_2$ composition using carbon crucibles. Undoped μ -PD SrI_2 crystals were used as seeds that were affixed to the bottom of the crucible. All the preparations preceding the growths and the hot zone assembling were performed in a glove box with Ar gas. Then the removable chamber was taken out of the glove box, attached to the μ -PD system, connected with a Turbo Molecular pump, and evacuated down to 10^{-4} Pa at $\sim 300^\circ\text{C}$. After the baking procedure, high purity Ar gas (6N) was injected into the chamber. The crucible was heated by a high frequency induction coil up to the melting point of Eu: SrI_2 . After melting the starting materials, the crucible was displaced in downward direction for the crystal growth and then cooled down to room temperature. Thus, 2 inch and crack-free Eu: SrI_2 bulk crystals were produced. The crystals had high transparency and did not contain any visible inclusions. The crystals were cut and polished in the glove box and then sealed in an aluminum container with an optical window for characterization. The details of the crystal growth are discussed.

Keywords:

A2. Bridgman technique, A2. Growth from melt,

B1. Halides, B2. Scintillator materials

1 Introduction.

Strontium iodide (SrI_2) is a simple binary inorganic compound, which has orthorhombic structure. After the rediscovery of Cherepy et al.[1], Eu-doped SrI_2 ($\text{Eu}:\text{SrI}_2$) is recognized as a high performance scintillator with high light yield and high energy resolution [1-6]. However, it is water-soluble and highly hygroscopic. Therefore, it is not structurally and chemically stable at normal atmospheric conditions due to effect of humidity and moisture. According to [2], the SrI_2 crystals containing 2% Eu^{2+} demonstrate most favorable properties among the crystals containing various amounts of the Eu-dopant. Such crystals had the greatest photon yield of 90,000 photons/MeV for the 10-25 mm thick samples at room temperature. On the other hand, other sources [7] reported that maximum light yield corresponds to 5-6% Eu-concentration. Moreover, the light yield of 115,000 photons/MeV was detected in [8]. Notably, the segregation coefficient of Eu^{2+} in SrI_2 crystals produced by the μ -PD process was determined to be close to unity [9].

Single crystals of $\text{Eu}:\text{SrI}_2$ are normally produced by the vertical Bridgman (VB) method [1,6,7,10] using a silica/quartz ampoule as melt container. Recently, these crystals were also produced by the micro-pulling-down (μ -PD) crystal growth method [11,12] using an apparatus that was adapted for the growth of various halide crystals including chlorides, bromides, and iodides [3]. The uniqueness of this newly designed growth system is based on application of a removable growth chamber. The chamber is assembled together with hot zone unit in isolated water-less atmosphere of the glove box that can be positioned distantly from the growth apparatus. The chamber design allows construction of the hot zone containing crucible with starting raw materials and the seed inside the glove box. Thereafter, the growth chamber is sealed inside the box, and then it is transported from the box to the growth machine without direct contact of the starting materials with air.

Melting point of SrI_2 is 515°C [13], 526°C (5%Eu-doped) [10], or 540°C [7] depending on source. This temperature is relatively low, and is suitable for the crystal growth apparatus experimentation and its operation. Moreover, the growth systems applied in the μ -PD and VB methods and the shape of the crucibles are in some degree alike, as it is illustrated in Fig.1. Therefore, the idea was to apply existing μ -PD apparatus designed and produced for the halide fiber crystal growth for realization of the VB process without considerable modifications of the existing hardware. This way, the growth system representing simply a seeded Bridgman technique was developed. Following this idea, growth of 5.0% and 7.5% Eu-doped SrI_2 crystals of 1 inch in diameter was established recently [4]. However, the crystals reported in [4] were not crack-free and their dimensions were not sufficient for

number of practical applications. Therefore, the purpose of the current project was to develop a crystal growth process suitable for fabrication of relatively large (2 inch diameter) and macro-defect-free crystals that may be considered for their industrial applications in scintillation devices.

2 Experimental

Originally, the μ -PD apparatus with removable chamber was developed in order to grow fiber-shaped halide single crystals at growth rates exceeding those practiced in VB method. This apparatus was used to perform VB process without considerable modifications of the existing hardware. View of the functional growth section of the μ -PD apparatus is illustrated in Fig.2.

The Eu:SrI₂ single crystals were grown from the melt of (Sr_{0.98}Eu_{0.02})I₂ (Eu2%:SrI₂) composition using carbon crucibles. The crucibles were fabricated according to the diagram shown in Fig.2 without opening in the bottom. Nevertheless, the crucibles were equipped with elongated hollow section (seed holder) of 3 mm in inner diameter at the tip of the conical base for accommodation of the seed crystal inside it (Figs. 1 and 2). The starting material had purity exceeding 99.99% and it was produced in the shape of dense spherical granules (or beads) with diameter ranging from 0.5 to 1.0 mm. The granules were charged into the crucible of about 51-52 mm (2 inches) in inner diameter.

For the first growth, the undoped SrI₂ fiber crystal produced by the conventional μ -PD method (Fig.1 top) was used as a seed, and it was placed inside the seed holder. In the following growths, the seeds cut from the previous crystals grown by the VB method were used. The seeds had cross-sections of $2 \times 2 \text{ mm}^2$ and lengths of several millimeters. The seed was placed into the seed holder, and part of the seed (about 3 mm in length) penetrated the starting solid-state materials. It is noted that typically [10,13] the Eu:SrI₂ crystals are produced by the VB method without application of any seed. In such scenarios, the Bridgman crucible is designed with small diameter nucleation section that plays the role of the grain selector used to limit the number of grains that propagate into the main section of large diameter of the crucible. This process is similar to the necking procedure practiced in the Czochralski growth process when a seed crystal is not available.

All the preliminary manipulations were performed in a glove box containing high purity Ar gas. The hot zone unit was assembled in the removable chamber (Fig.2). After complete isolation of the growth chamber from the atmosphere of the glove box, the chamber was taken out of the glove box and transferred to the μ -PD apparatus. Thereafter, the chamber was

fastened to the growth apparatus and sealed again for its complete isolation from external atmosphere. Then, the chamber was connected with a Turbo Molecular pump and it was evacuated down to 10^{-4} Pa at $\sim 300^{\circ}\text{C}$. After the baking process, high purity Ar gas (6N) was injected into the chamber to establish water-less atmosphere inside it and to eliminate any direct contact between the starting materials and any source of moisture.

The crucible was heated by a high frequency induction coil (Fig.2, left) up to the melting point of Eu:SrI_2 . This way, the starting solid granules were co-melted and then the crucible was translated in downward direction for the crystal growth as in conventional VB process. After the growth procedure was completed, the crucible was cooled down to room temperature for 24 hours. Thereafter, the chamber with the crucible and the as-grown crystal was isolated from the growth system again and transferred to the glove box.

After unsealing the chamber in the glove box, the crucible was taken out of the chamber, and the crystal was removed from the crucible for further treatment. To remove the as-grown crystals, the wall of the crucible was cut for about 50% of its thickness on one side. Thereafter, the crucible became easily breakable to two approximately equal fragments. These fragments were separated from the crystal without problems because of low adhesion between the crucible material (carbon) and the Eu:SrI_2 crystal. After that, the as-separated crystal was cut to the desired shape and polished (also in the glove box). To produce a sample suitable for the characterization, the crystal was wrapped with Teflon tape, fixed inside the aluminum cup of approximately same diameter, covered with quartz window, and sealed. The as-produced specimen is illustrated in Fig.9 (right).

Because of low adhesion between the crystal and the crucible walls, it was sometimes possible to remove the crystal without cutting the crucible. In such cases, the same crucible could be used for the following growths. Nevertheless, each crucible was used for a unique growth only because the interior surface of the crucible was somehow damaged after one growth cycle. Therefore, it was decided to avoid multiple uses of the same crucible to stay away from the problems associated with after-growth crystal removal from the crucible. Following the above process, number of 2 inch crack-free Eu:SrI_2 bulk crystals were produced. The crystals were highly transparent and they did not demonstrate any visible inclusions (Fig.3).

The typical temperature profile established in the hot zone of the growth system is illustrated in Fig.4 (top) with the arrows indicating starting and finishing points of the growth run. The measurement of the profile was performed with a thermocouple attached to the outer surface of the bottom (conical part) of the crucible, and the measured data were read out

during actual growth process with crucible pulling rate of 0.54 mm/h. It is noted that the temperature profile data were slightly different from process to process, but comparable.

3 Results and Discussion

At the stage of preliminary growths, the length of cylindrical parts of the crystals was set to be about 10 mm, and this length was controlled with the amount of starting material charged into the crucible. These crystals were produced from the crucibles with angle of conical part of 90°. The results are demonstrated in Fig.3. Some of the crystals produced in such conditions contained cracks leading to crystal fragmentation. Also, formation of bubbles was noticed in the crystals. Therefore, additional efforts were applied to the growth procedure to improve structural perfection of the crystals as follows.

3.1. Bubble capture

Regarding the bubbles' formation, it was assumed that the step of co-melting of non-reacted starting SrI_2 and EuI_2 powders is most responsible for the gas generation and following bubble nucleation similar to that noticed in [14]. One of the reasons for integration of the bubbles into the grown crystals is associated with low solubility of the gases in the solid state as compared with their solubility in liquids [15]. Therefore, at the same level of gas concentrations in condensed substances of a melt and a crystal, the system can be a homogeneous single-phase material in liquid phase and it is not when it solidifies, separating to two phases of solid (crystal) and gas (bubbles). Also, in the process discussed here the crucible pulling rate was relatively high (0.36-0.60 mm/h). In such conditions, the melt in the vicinity of the solid-liquid interface became excessively saturated with dissolved gases. As a result, bubble nucleation was initiated at the growth interface with their following capture by the growing crystal [16].

To decrease probability of the bubble formation, special treatment of the melt before the growth was performed according to the thermal schedule illustrated in Fig.4 (bottom). At first, the starting materials were heated in the normal way until their complete melting. Thereafter, the melt was kept at a constant temperature for 1-2 hours to allow sufficient reaction of the initial solids and homogenization of the melt. As a next step, the melt was cooled down to complete solidification. It was assumed that a considerable amount of dissolved gases was removed from the starting material as a result of first solidification. Finally, the as-solidified material was heated for a second time to produce melt again, and this secondary melt was used for the crystal growth. Such treatment of the melt resulted in

significant improvement of the crystal quality regarding the number of the bubbles detected. However, such crystals were not bubble-free. The as-grown crystal produced according to the process presented in Fig.4 (bottom) and having reduced concentration of the bubbles is shown in Fig.5.

The possible mechanism of the bubble removal may be associated with the first round solidification of the melt as follows. According to [17], only relatively small bubbles formed on the solidification front are captured by the grown crystal, while bigger ones are rejected from the growth interface back to the melt remaining in the crucible. Size of the captured bubbles depends on the solidification rate, and greater growth rate corresponds to larger bubbles that can be captured by the growing crystal. Following these reasons, a considerable amount of the dissolved gases is removed from the melt-crystal system after first round solidification of the melt. Thus, this process in some degree corresponds to the zone refining regarding removal of the gases dissolved. Therefore, the melt produced after secondary heating did not contain as much gas as that produced after first heating.

It is also noted that first round solidification of the melt in the process illustrated in Fig. 4 (bottom) in high degree corresponds to the Vertical Gradient Freeze (VGF) method [18,19] that can be also easily established in the system configuration that is demonstrated in Figs.1(bottom) and 2. In the VGF technique, the position of the crucible is fixed during the whole process, and the solidification is performed following continued cooling of the crucible in temperature gradient conditions. Alternatively, in the VB method, the power supplied to the crucible is fixed, and the solidification is performed following continued displacement of the crucible from the high temperature zone to the low temperature zone.

The temperature schedule illustrated in Fig.4 (bottom) was not sufficient to eliminate the bubbles' generation. Therefore, the standard vacuum degassing procedure was additionally applied to the starting melt. To establish this step, the growth zone was evacuated during heating of the crucible and melting of the starting materials. As a result, the amount of the gases dissolved in the melt was reduced proportionally to their partial pressure in the atmosphere of the growth chamber according to Henry's law. Normally, excessive heating of the melt may also increase expelling of the gases from the liquid phase. However, this approach was not completely acceptable for the SrI_2 melt and the process discussed here because excessive overheating of the melt before the growth process could result in increased probability of unwanted seed dissolution. Our results demonstrated that the treatment of the melt under vacuum was successful and resulted in considerable reduction of the bubble formation. Optimal overheating of the melt was approximately 100°C.

3.2. Crack Formation

As for the crack-formation, the main reason for such imperfection reported elsewhere [11] was associated with assumption that quality of the crystals strongly depends on the quality of the starting materials. Another conclusion [13] was based on the hypothesis that crack nucleation mostly occurred well below the solidification point when the crystal itself is already formed. Most probably this is correct. However, in this report, the efforts were firstly concentrated on the experience obtained for the Czochralski (CZ) growth process. One of the ways to avoid crack formation in CZ growth is to reduce the cone angle on the seed side of the crystal. This approach was discussed in [20,21]. In the case of CZ, the cone angle is managed by appropriate combination of power supplied to the crucible (and the melt) and pulling rate. These two parameters control the amount of solidified material per unit of time and the speed of removal of the solidified material from the melt, respectively. However, in the VB process, the only way to vary the crystal shape (its cone part) is to modify the crucible shape, which was actually performed in our experiments. The shapes of the two types of crucibles with the cone angles of 90° and 70° used in this project are illustrated in Fig.6, top. Opposite to expectations, the crystals produced from the crucibles having reduced cone angle of 70° did not demonstrate considerable reduction in number of cracks observed in the crystals (Fig.6, bottom). Notably, the cone angle of the quartz ampoule used as a crucible in [10] was approximately 45° for the 1.5 inch crystal growth with pulling rate of 19 mm/day. However, crack-formation was not discussed there. In the case of the optimized growth conditions reported here, the pulling rate was 0.54 mm/h (about 13 mm/day), which was comparable to that of the prototype process [10] regarding the amount of the material solidified per unit of time (notice the different crystal diameters). It is noted that actual growth rate could be somehow different from the pulling rate, but it was difficult to evaluate this difference in the VB process presented here.

The best way to reduce probability of crack formation was to avoid excessive overheating of the melt before starting the growth. A number of growth experiments was performed to optimize the melt temperature and it was found that the crystals were mostly crack-free when excessive melting of the seed crystal was avoided. In the case of extreme overheating, when the seed crystal was excessively melted with remaining length shorter than the length of the seed holder as illustrated in Fig 7 (top, route 1), the crystals had a tendency to crack. Oppositely, at moderate heating, when a smaller portion of the top part of the seed

was melted (Fig.7, bottom, route 2) and the top of the seed slightly protruded above the bottom of the crucible, the crystals were normally crack-free.

It was impossible to control melting of the seed during the growth process. Therefore, the degree of melt overheating that is safe regarding excessive melting of the seed was optimized by optimization of the growth parameters. The parameters modified included positions of the RF coil and the seed and power of the RF coil. Finally, it was found that the overheating of approximately 100°C was acceptable and resulted in desirable moderate melting of the seed. In some fortunate cases, the as-grown crystals could be removed from the crucible together with the seed as illustrated in Fig.9, middle.

3.3. Crack-Free Crystal Growth

Modification and improvement of the hot zone design were also carefully performed together with slow cooling of the as-grown crystal to room temperature. As a result, the crack-free Eu:SrI₂ single crystals were produced using crucibles with cone angle of 90° at crucible pulling rate of 0.36 mm/h. The views of the crystals produced in such conditions are presented in Fig.8.

4 Characterization

The cut and polished Eu:SrI₂ single crystals of 2 inch in diameter and 2 inch in length were sealed into the aluminum container with one quartz window (Fig.9, right). The as-produced Eu:SrI₂ single crystal specimen was irradiated with 662-keV gamma rays emitted by a ¹³⁷Cs source. The scintillation photons were detected by a photomultiplier (PMT, R7600U, Hamamatsu), and then the signals from the PMT were amplified (model 113, ORTEC), shaped (572A, ORTEC), and read out with a multi-channel analyzer (8000A, AMPTEK). The pulse height spectrum of the 2 inch Eu:SrI₂ crystal was comparable to corresponding spectrum of the 1.5 inch Eu:SrI₂ shown in Fig.10. The pulse height of the NaI(Tl) crystal was also measured for the reference purposes.

It is noted that the dimensions of the reference NaI(Tl) cylindrical specimen were Ø 0.5 inch × 0.5 inch (length). Therefore, the effect of its self-absorption was relatively low. Even in such circumstances, the light yield of the Eu:SrI₂ was estimated to be 87,000 ph./MeV, and its energy resolution was 3.5 % (662 keV, FWHM) at room temperature. This value was obtained following the fitting and assumption that light yield of NaI(Tl) is 45,000 ph./MeV.

5 Summary

2-inch diameter macro-defect-free SrI_2 crystals were grown by the vertical Bridgman method using a crystal growth apparatus that was originally designed for the micro-pulling-down crystal growth process. The growth system was equipped with removable and well-isolated growth chamber made of quartz glass ampoule suitable for the crystal growth of highly hygroscopic materials. Bubble- and crack-formation were detected in the crystals produced at the initial stage of the experiments as typical defects. The amount of bubbles captured by the crystals was reduced considerably after preliminary vacuum degassing. The number of cracks in the as-grown crystals was not reduced significantly after modification of the crucible shape and reducing the cone angle of the bottom of the crucible from 90° to 70° . However, decrease of the temperature of the melt at initial stage of the growths with corresponding elimination of the seed over-melting, and slow cooling of the as-grown crystals resulted in formation of macro-defect free $\text{Eu}:\text{SrI}_2$ crystals.

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Fig.1. Comparison of μ -PD (top) and vertical Bridgman (bottom) growth methods regarding growth interface and displacement of the parts of the growth system (seed or crucible, respectively) resulting in progressing solidification and replication of the structure of the seed.

Fig.2. View of the μ -PD system with removable growth chamber adapted for the VB crystal growth of halide crystals.

Fig.3. Results of preliminary growth of SrI_2 crystals produced at 0.54 mm/h pulling rate with shoulder cone angle of 90 degrees. The crystal dimensions were approximately $\text{Ø}51 \times 10$ (length of cylindrical part) mm. Some of the crystals were macroscopic-defect-free (A and B). However, other ones contained some cracks (C) and/or bubbles (D).

Fig.4. Typical temperature profile established in the growth system (top) and temperature schedule applied to the crucible to decrease bubble formation in the SrI_2 crystals (bottom)

Fig.5. View of the as-grown SrI₂ crystal having reduced concentration of bubbles produced according to the temperature schedule illustrated in Fig.4, bottom. The crucible is 2 inch (51-52 mm) in inner diameter.

Fig.6. Shape of the carbon crucibles produced with different cone angles of 90° and 70° (top) and views of corresponding $(\text{Sr}_{0.98}\text{Eu}_{0.02})\text{I}_2$ crystals grown at 0.54 mm/h pulling rate with the same shoulder cone angles. The crystals had some cracks.

Fig.7. Two scenarios (routes) of the crystal formation with excessive (1) and optimized (2) melt overheating. Note over-melting of the seed and resulting crack formation on the diagram corresponding to route 1.

Fig.8. View of 2-inch crack-free Eu:SrI₂ single crystals produced at crucible pulling rate of 0.36 mm/h with shoulder cone angle of 90° under normal (top) and ultra-violet (bottom) lighting.

Fig.9. View of 2-inch crack-free Eu:SrI₂ single crystals produced at pulling rate of 0.54 mm/h with shoulder cone angle of 90° (left and middle) and the crystal sealed into the aluminum container with one quartz window (right). Note that in some cases, it was possible to remove the crystal from the crucible together with the seed attached (middle).

Fig.10. The pulse height spectra of the sealed 1.5 inch (38 mm) $\text{Eu}:\text{SrI}_2$ single crystal together with that of Tl-doped NaI as a reference. Dimensions of the specimens are shown in the figure.