Growth and characterization of SrI_2:Eu crystals fabricated by the Czochralski method

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Abstract— This work presents the Czochralski growth of SrI2:Eu scintillation crystals. SrI2:Eu is among the brightest recently discovered scintillators with an excellent energy resolution for spectroscopic identification of radioactive isotopes. The Czochralski crystal growth method is optimal from the point of scaling up of crystal production with minimal investment into upgrade of crystal growth equipment. In this study SrI_2:Eu crystals with the diameter of up to 50 mm were produced by the developed process based on the Czochralski method. The crystals are prone to cracking, and thermal fields in the crystallizer still should be optimized. Nevertheless the scintillation parameters of detectors cut from the grown crystals are similar to that in detectors fabricated by the conventional Bridgman-Stockbarger technology. The Eu2+ activator concentration across the crystals is uniform within 5%, as well as the energy resolution, which ranges within 3.6±0.1% at 662 keV. Also, the decay times under X-rays, and non-proportionality of scintillation light yield on excitation energy in the range of 31 – 1274 keV have been determined.

Index Terms— Crystals, Energy resolution, Fabrication, Scintillators, Solid scintillation detectors.

INTRODUCTION

There is an increasing demand in low cost detectors enabling a prompt and trustworthy detection of radioactive isotopes. For radio isotope identification, the energy resolution of detector is a key parameter determining their spectroscopic performance. Despite extremely high energy resolution of semiconductor

radiation detectors, their cost is still too high for a wide practical application. Scintillators, despite they are behind in energy resolution, comprise a potentially lower cost alternative to semiconductor detectors for such application. Nowadays the commercially available halide scintillators comprise NaI:Tl, CsI:Tl, and $LaBr_3$:Ce. An advanced technology of large NaI:Tl, CsI:Tl crystals production by the modified Czochralski-Kyropoulos technology [1] provides the low cost and high production yield of scintillation detectors. However, the energy resolution of a "standard" NaI:Tl is ~6.5 % at 662 keV [2]. Despite recent reports on improvement of energy resolution in NaI:Tl to ~5 % by the codoping approach [3], there seems no room to further significant progress. Meanwhile, the high cost of LaBr3:Ce detectors with the excellent energy resolution of 2% limits the practical applications.

Eu2+ activated halides since the discovery in 1960s (i.e., the patent by Hofstadter [4]) had not attracted much attention because of relatively low performance (6% energy resolution) reflecting both low quality raw material, and non-optimized growth technology. Recently, mainly due to the progress in the raw material purification, a significant number of bright Eu2+-doped alkali earth halide scintillation materials were introduced with the energy resolution within 2.5 - 4 % at 662 keV (see, for ex., [5]).

Despite many reports on alkali earth halide growth by the Bridgman method and its modifications, no significant progress has been achieved in development of large size crystal growth technologies capable to reduce the production cost. Most efforts were related to SrI_2:Eu, however still just up to 2"-diameter detectors are commercially available [6]. A few efforts have been made to adapt other conventional growth methods to the halides owing to their high hygroscopicity and related difficulty to maintain the necessary content of water and other oxygen-containing impurities in the growth chamber. To our knowledge, just the example of Ba-mixed halides is known [7, 8] to adapt the Czochralski growth process to this type of materials, as well as efforts to use EFG [9] and modified μ-PD [10] methods for growth of SrI_2:Eu and other halides.

Therefore, industrial scale production still does not exist for SrI_2:Eu despite of about 50 year history of its development. With this study we present an alternative approach to crystal growth of this material. This

work is focused on Czochralski growth and characterization of SrI_2:Eu crystals with diameters of up to 50 mm.

Experimental

SrI2 raw material of 4N purity (metal base) was synthesized by the procedure described in [11]. Herein, pH of water solution was controlled to be < 6. EuI2 raw material of 4N purity (metal base) was synthesized by the reaction of Eu2O3 with NH4I. The Eu2+ concentration in the raw material was around 0.5 at.%. Concentration of Eu2+ in crystals was determined by titrimetric analysis.

Energy resolution under irradiation with 662 keV γ-quanta, 137Cs isotope was determined from amplitude spectra measured using a setup described in [12] based on a R1307 PMT, U=690V, shaping time 12 μs. Scintillation decay times were determined at X-ray excitation (10kHz excitation repetition rate, filter λ> 400nm) Pulsed X-ray decay measurements were performed with the same light collection system and a Hamamatsu N5084 light-excited X-ray tube set at 30 kV as irradiation source. The optical excitation of the tube was performed with a Hamamatsu PLP-10 picosecond light pulser. Nonproportionality of SrI2:Eu has been evaluated by the measurement of the scintillation yield, with a shaping time of 10 □s using several radioactive sources with energies ranging from 31 to 1274 keV. The details are described in [13].

Crystal growth

The development of Czochralski process for highly hygroscopic substances must include the optimized conditions of raw materials preparation and their loading into the growth chamber, as well as precise control over admixture content in the raw materials and growth atmosphere. For instance, pH of the raw material water solution was shown to be a key criterion of the raw material quality [14]. A procedure of loading of up to 1 kg of SrI2:Eu raw material in the form of powder or crystalline chunks to a conventional

Czochralski growth setup was developed, as well as a procedure of atmosphere purification from residual moisture and oxygen in the growth chamber. The raw materials were loaded into an ampoule and sealed inside a glovebox with controlled atmosphere. Then the ampoule was connected to the growth chamber via the transport tube 4 (Fig. 1). The growth chamber was filled with inert gas. Therefore, raw materials while loaded were exposed just to the carefully purified atmosphere, thus avoiding interactions with residual oxygen and moisture.

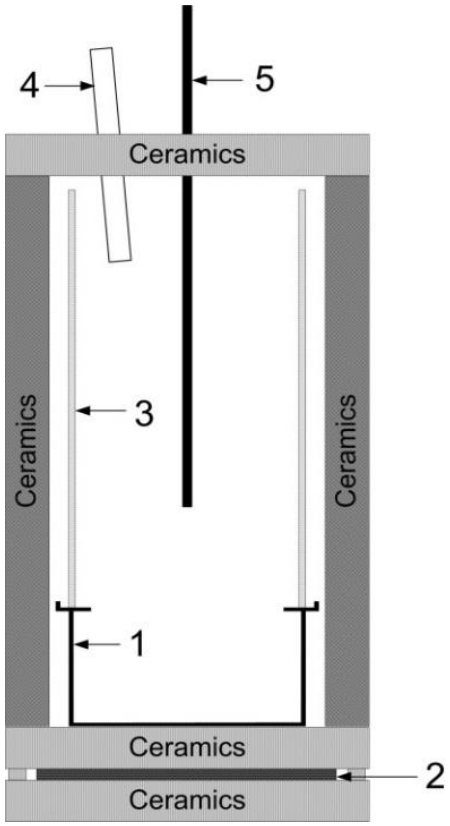

Fig. 1. Scheme of the crystallizer: 1 – crucible, 2 – bottom heater, 3 – upper heater, 4 – tube for raw material loading, 5 – seed holder.

The growth process was performed in a conventional Czochralski R&D scale growth furnace with crystal diameter control by weight sensor. For all growth experiments we used the seeds cut along the same direction from the crystal grown by Stockbarger method along a random growth orientation. However, the

crystallographic orientation of the seeds was not determined, because it was impossible to provide X-ray diffraction analysis in oxygen- and water-free atmosphere.

SrI2:Eu crystals with the diameters of up to 50 mm (Fig. 2) were grown from Pt crucibles. The crystal pulling rate was 0.5–5 mm/hour, and rotation rate was 2–10 min-1. The crystals grown by the optimized procedure were transparent. Meanwhile, we succeeded in growth of crack-free crystals just with the diameters of up to 30 mm. SrI2:Eu and similar crystals of alkali earth halide family are much more prone to cracking compared to NaI and CsI classic scintillators, as was pointed before in [15]. We also faced the difficulties to control the crystal diameter and to maintain the stable cylindrical shape of crystals. Therefore, a special attention was paid to thermal field control inside the crystallizer. Thermal fields were adjusted by upper and lower heaters besides the RF-heated crucible. The measurements indicate that the axial gradient above the melt of about 10 K/cm is enough to sustain the stable crystallization process. This provided us with transparent crystals with few inclusions, though the problem of cracking has not been eliminated for 50 mm dia. crystals. Crystal cracking nature is still unknown. It may be of complex nature, but clearly relates just to optimization of technology (choice of seed orientation, minimization of impurities in the raw material, thermal field optimization).

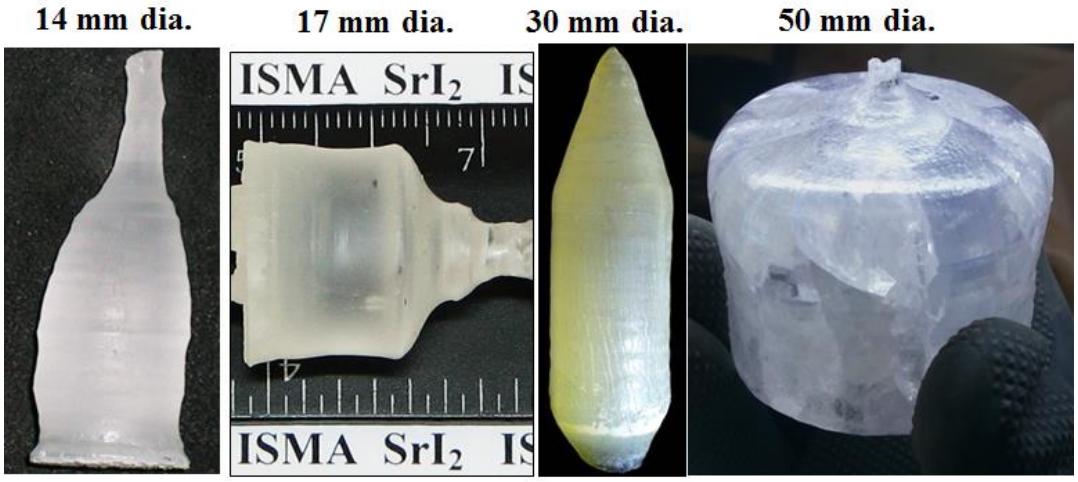

Fig. 2. Stages of SrI2 and SrI2:Eu Czochralski growth process elaboration at Institute for Scintillation Materials (ISMA).The 50 mm dia. SrI2:Eu crystal taken for measurements of scintillation parameters is shown at the right photo.

TABLE I

CONCENTRATION OF EU2+ ACTIVATOR IN DIFFERENT PARTS OF 50 MM DIA. AND 50 MM LENGTH SrI_2:EU CRYSTAL GROWN BY THE CZOCHRALSKI METHOD.

Part of the crystal	Eu^{2+} concentration, at.%
head	0.52
middle	0.53
bottom	0.55

A good uniformity of Eu2+ concentration along the crystals within +/- 5 % was detected in the produced crystals (Table I). This indicates a very high activator segregation coefficient of around 1 due to the similar ionic radii of Sr2+ and Eu2+ and supports the results [16] obtained for the Bridgman-Stockbarger method.

Scintillation parameters

The comparative measurements of optical and scintillation properties of SrI2:Eu crystals grown by the Bridgman and Czochralski methods were carried out. For this purpose the detectors with the size of 10 mm dia. and 10 mm length were fabricated from different parts of Czochralski grown crystal with Eu concentrations within the 0.52 – 0.55 at.% range (Fig. 3). Crystals grown by the Bridgman method contained 5 at.% of Eu accordingly to the optimal concentrations reported in literature.

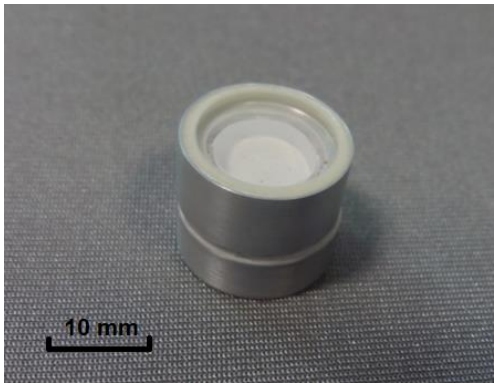

Fig. 3. A SrI2:Eu detector with Eu concentration of 0.5 at% fabricated from a Czochralski grown crystal.

A good uniformity of light yield and energy resolution across the produced Czochralski crystals was detected. The detectors fabricated from different places of Czochralski- grown crystal showed the high energy resolution of 3.6±0.1% at the 662 keV γ-quanta excitation (Fig. 4). Note such a high energy resolution was obtained with the weak Eu-doping, though in Bridgman-grown crystals the similar energy resolution was achieved at Eu concentration around 5 at.%. This result shows a potential to sustain a very high energy resolution in SrI2:Eu even at decrease by the order of magnitude the concentration of an extremely expensive EuI2 activator. The lower Eu2+ concentration also potentially prevents from a strong self-absorption for large-size crystals. Such a high energy resolution in Czochralski-grown crystals can be related to improvement of raw materials quality. As EuI2 is both activator and a good scavenger of oxygen-containing impurities [17, 18], it is needed in high concentration to inactivate them in contaminated raw materials. Here, with optimized raw material synthesis procedure, the ~0.5% Eu concentration seems to be enough to provide a high energy resolution. Meanwhile, better uniformity of Eu distribution over the crystal due to good melt mixing and easier crystallization interface control in the Czochralski method should also favor a high energy resolution.

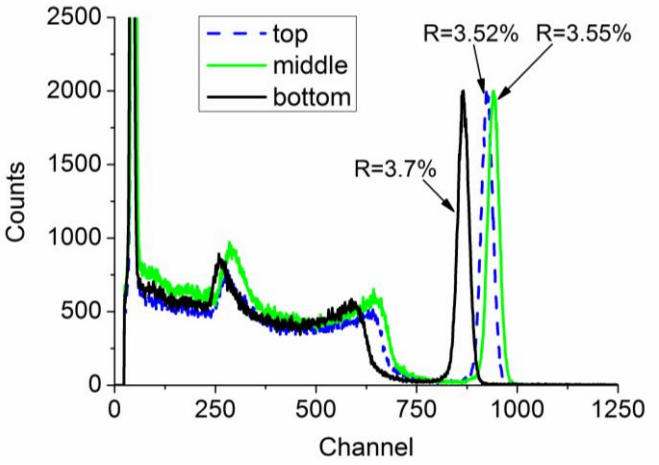

Fig. 4. Amplitude spectra of scintillation detectors fabricated from different parts of a Czochralski-grown SrI2:Eu crystal.

The faster scintillation decay time at smaller Eu concentrations in SrI2:Eu is an additional reason to reduce the activator concentration (Fig. 5). Besides the observed quenching in the first several hundreds of ns, the exponential fit of experimental points gives the main decay constants of 1.975 μs and 0.974 μs for samples fabricated from the Bridgman and Czochralski-grown crystals, respectively. These values are in the qualitative agreement with the data on decay times in dependence on Eu concentration in SrI2:Eu reported in [19] and confirm the reduction of the self-absorption phenomena in our weakly doped crystal.

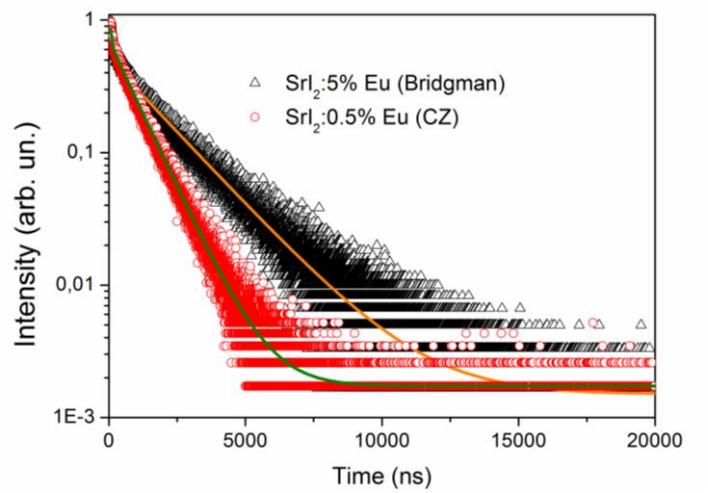

Fig. 5. Decay curves of the samples fabricated from Bridgman- and Czochralski grown crystals under X-ray excitation.

Another advantage of SrI2:Eu crystals is their excellent light yield proportionality on the excitation energy. The non-proportionality of Czochralski-grown SrI2:Eu crystal is presented in Fig. 6 in comparison with Bridgman-grown crystal produced in the work [13]. One can see the similar trends of light yield on energy with variation just within +/- 5% relatively to the light yield at 662 keV excitation. The Czochralski-grown crystal preserves this excellent non-proportionality behavior.

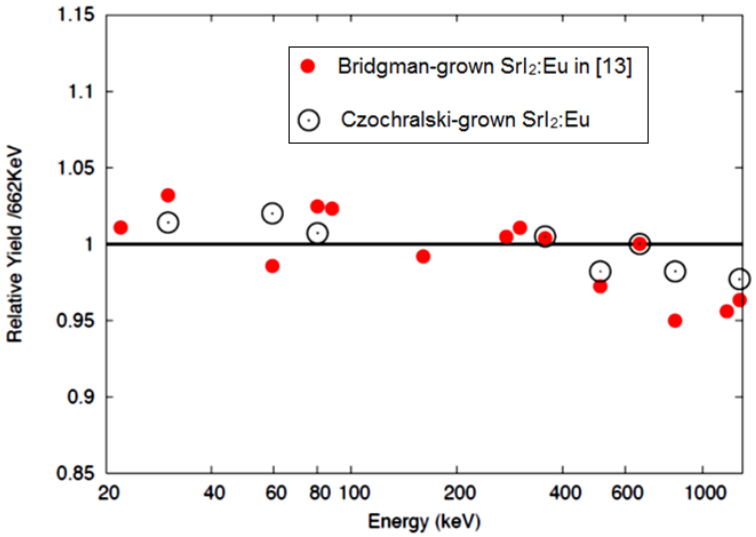

Fig. 6. Non-proportionality of Czochralski-grown SrI2:Eu using various typical radioactive sources vs. Bridgman-grown SrI2:Eu in [13]. The values are normalized by the light yield at 662 keV.

Summary

The growth of 50 mm dia. SrI2:Eu crystals in R&D scale furnaces is the first step in adaptation to the growth of large size crystals of alkali earth halide family at industrial setups. Good scintillation properties of obtained crystals (energy resolution, scintillation decay time, non-proportionality on the excitation energy) indicate that the developed growth process by the Czochralski method is ready for scaling up to produce larger crystals after optimization of thermal conditions of the process. Further advance will be

based on the well-developed industrial growth technology of large CsI, CsI(Na) and NaI(Tl) alkali halide crystals with the diameter of up to 500 mm by the Modified Czochralski-Kyropoulos method [1].

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