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Growth of Eu:SrI_2 bulk crystals and their scintillation properties

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ABSTRACT

Eu doped SrI_2 [Eu:SrI_2] bulk single crystals with 1 in. diameter were grown using a special-shaped carbon crucible and a modified micro-pulling-down furnace and their scintillation properties were investigated. As-grown Eu:SrI_2 bulk crystals indicated high transparency while they included several cracks in the crystals. Grown crystals indicated a single phase of SrI_2 structure in the powder X-ray diffraction measurement. In the X-ray radioluminescence spectrum, there was a sharp emission peak around 435 nm which originated from 5d–4f transition of Eu^{2+} ion. Light yields of Eu5% and 7.5%:SrI_2 crystals under γ-ray irradiation from ^{137}Cs radiation source were 83,000 and 85,000 ph/MeV, respectively. Their decay times under γ-ray irradiation were approximately 2 μs.

1. Introduction

A micro-pulling-down (μ-PD) method has been used for some material researches of functional single crystals as represented by piezoelectric, scintillator and laser crystals [1–5]. There are some advantages of the μ-PD method compared to the conventional melt-growth methods such as Czochralski (Cz) and Bridgeman–Stock-barger (BS) . One of the advantages is that the μ-PD method can grow one crystal at approximately ten times higher growth rate than the conventional methods and perform material researches of novel functional single crystals in a short period. In addition, the amounts of starting materials required for crystal growth by μ-PD method are much less than those of Cz and BS methods and it is an efficient method especially in the case of crystal growth of materials composed of high-cost elements. The μ-PD method can control the shape of crystal and crystal samples with the suitable shape for measurements can be obtained. Therefore, many novel functional single crystals have been developed by the μ-PD method.

Recently, halide scintillator crystals have been focused due to the high light yield and energy resolution originated from the small band-gap. The relationship between light yield and band-gap of host material has been investigated for various scintillator materials and previous reports indicated that light yield was inversely proportional to the band-gap [6,7]. In addition, energy resolution is inversely proportional to the one-half power of number of detected photons. In other words, the scintillator with the small band-gap of host material indicates high light yield and the high light yield results in high energy resolution. Especially, Eu doped SrI_2 [Eu:SrI_2] and Ce doped $LaBr_3$ [Ce:$LaBr_3$] crystals have been gathering worldwide attention due to the great high light yield and approximately 3% energy resolution [8–10]. However, most halide materials have relatively high hygroscopicity and it is difficult to obtain their single crystals with high crystal quality.

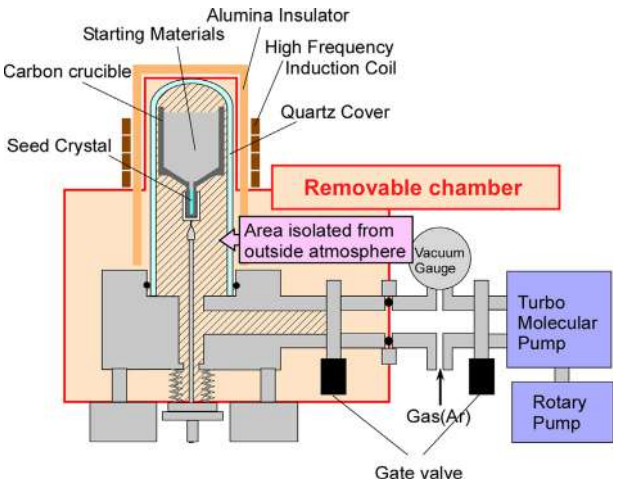

Fig. 1. Schematic of modified μ-PD method for growth of bulk halide crystal.

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Therefore, their single crystals have mainly grown just by the BS method using a sealed quartz ampoule.

Based on these backgrounds, we have developed a modified μ-PD method for growth of halide scintillator crystals with hygroscopicity [11]. Eu:SrI_2 and Ce:$LaBr_3$ crystals have been grown by the modified μ-PD method and their scintillation properties were investigated in our previous reports [12,13]. The modified μ-PD method can grow a halide crystal at approximately ten times faster growth rate as compared to the conventional methods and it is suitable for material research of halide single crystal. However, the modified μ-PD method can grow only fiber crystal with a diameter of 2–5 mm and therefore bulk crystal with a diameter of several inches cannot be obtained for practical use. For some applications of radiation detector, the bulk crystal with more than 1 in. diameter is required.

Therefore, we grew Eu:SrI_2 bulk crystals with a diameter of 1 in. using the modified μ-PD furnace and their scintillation properties were investigated.

2. Experimental

Eu:SrI_2 bulk single crystals were grown by the modified μ-PD furnace using the special-shaped carbon crucible. The schematic of

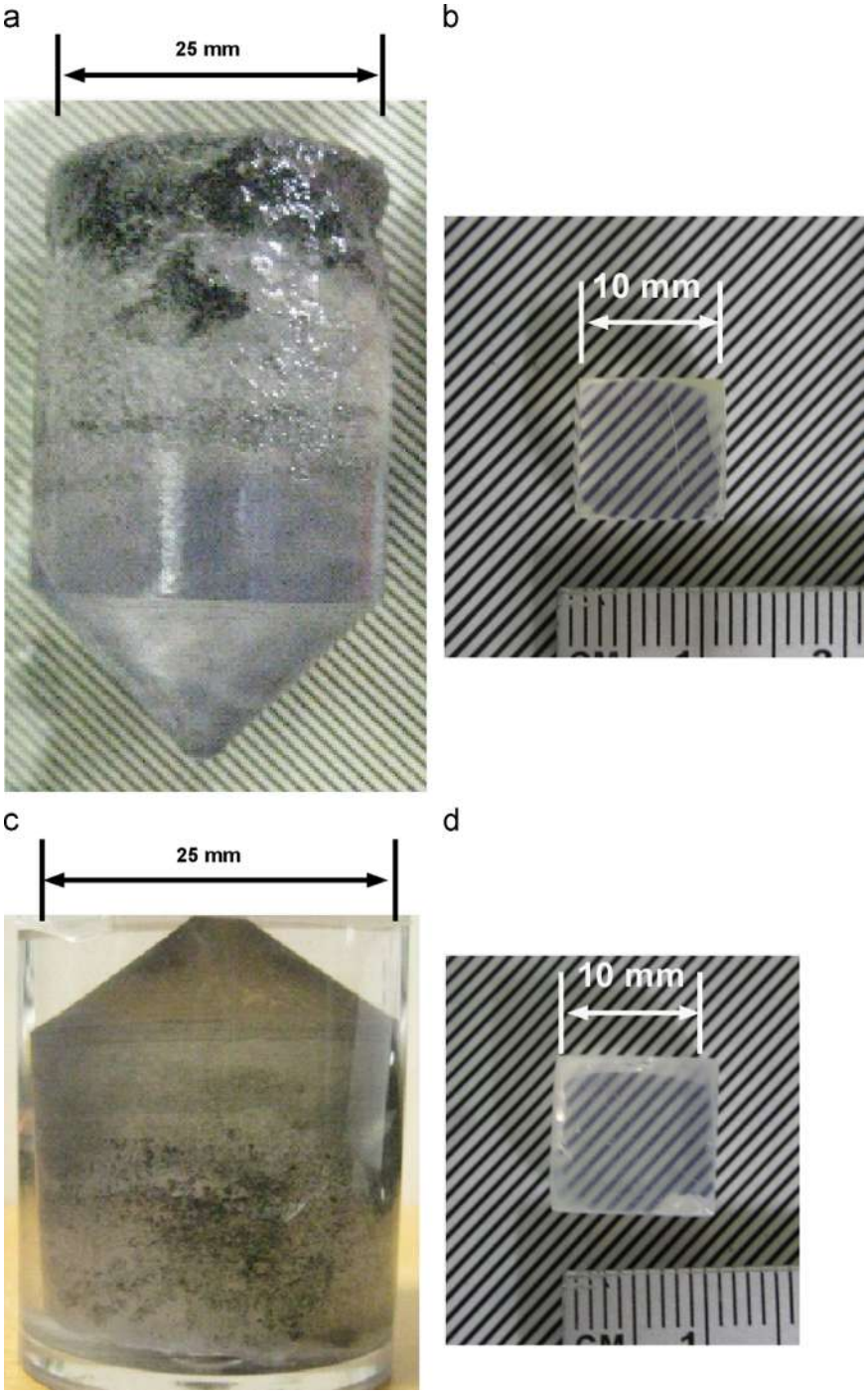

Fig. 2. Grown Eu:SrI_2 bulk single crystals. (a) Eu5%:SrI_2 as-grown, (b) Eu5%:SrI_2 polished, (c) Eu7%:SrI_2 as-grown and (d) Eu7%:SrI_2 polished crystals.

bulk crystal growth using the modified μ-PD furnace is described in Fig. 1. Mixed powders were prepared from starting materials, SrI_2 (4N, Alfa Aesar) and EuI_2 (3N, Aldrich) as nominal compositions of $(Sr_{1-x}Eu_x)I_2$ with $x=0.05$ and 0.75 in a glove box which was filled with Ar gas. Mixed powders were set in the carbon crucible with 1 in. internal diameter and the crucible was set in a removable chamber. After a quartz cover was set in the chamber and a gate valve of the chamber was closed, the chamber was taken out from the glove box through a pass box. The chamber was connected with a turbo molecular pump and inside of the chamber was evacuated up to 10^{-4} Pa at 300 °C to remove the moisture on the surface of starting materials, crucible and insulators. After the baking process of several hours, high-purity Ar gas (99.9999%) was introduced in the chamber and the crucible was heated up to the melting point of Eu:SrI_2 by a high-frequency induction coil. Then the bulk crystal was grown by pulling-down the crucible at 0.6 mm/h. Undoped SrI_2 crystal was used as a seed crystal and it was set below the mixed powder in the crucible. After the crystal growth, the crucible was cooled to room temperature and the chamber was entered in the glove box again. Finally, the grown bulk crystal was obtained from the inside of crucible.

The grown bulk crystal was cut and polished in the glove box using synthesis oil. Phase of grown Eu:SrI_2 crystal was identified by the powder X-ray diffraction (XRD) measurement using a tight chamber with a Beryllium window which was filled with Ar gas. Lattice parameters, *a*-, *b*- and *c*-axis lengths, were calculated from the XRD pattern using Si powder as an internal standard. Radioluminescence spectrum of grown crystal under X-ray irradiation (30 kV, 10 mA) was measured by the spectroscope and Charge Coupled Device (CCD) using the optical cable and a sealed sample container with a Beryllium window which was filled with Ar gas. γ-ray response measurements, pulse-height spectrum and decay curve were performed by investigating the responses of crystals exposed to ^{137}Cs radiation source emitting γ-ray with PMT (HAMAMATSU R7600U) in the glove box filled with Ar gas. Polished crystals were covered by Teflon tape except for one side which was attached to the light entrance window of PMT with optical grease. Signals from the PMT were converted into digital signals by a multi channel analyzer (AMPTEK Co. Pocket MCA 8000A) with 2 μs shaping time and decay time was investigated by an oscilloscope (TEKTRONIX TDS3034B). $Bi_4Ge_3O_{12}$ (BGO) crystal with almost the same dimension as Eu:SrI_2 crystal samples was used as a reference and the light yields of Eu:SrI_2 crystal samples were estimated using BGO (8000 ph/MeV) and quantum efficiency of PMT at each emission wavelength.

3. Results and discussions

Eu5% and 7.5%:SrI_2 bulk crystals with the diameter of 1 in. were grown by the modified μ-PD furnace as shown in Fig. 2(a) and (c). As-grown Eu:SrI_2 bulk crystals indicated high transparency while they had several cracks in the crystals. Black deposits were observed just on the surface of as-grown crystals and there was no deposit in the crystals. Polished crystals are shown in Fig. 2(b) and (d). There was no visible crack and inclusion in the polished crystals. Thickness of the polished crystals was approximately 5 mm and they were used for measurements of optical and scintillation properties. In the growth method of bulk crystal by the modified μ-PD furnace, the crystal is grown in the carbon crucible and therefore the growth method is almost same as the BS method rather than the μ-PD method. However, this method has several advantages compared to the previous BS method for halide crystal growth. In this method, the carbon crucible is used instead of quarts ampoule and the carbon crucible can be used many times while the quarts ampoule can be used just one time. In addition, by the direct heating of the crucible using high-frequency induction coil, steep temperature gradient can be achieved easily and there is no possibility that whole seed crystal is melted before crystal growth in comparison with the resistance heating.

Powder XRD of Eu5%:SrI_2 bulk crystal was measured to identify the phase and lattice parameters. Obtained powder XRD pattern is shown in Fig. 3. All diffraction peaks in the XRD pattern were indexed by the SrI_2 structure (*Pbca*, orthorombic) [14]. Lattice parameters, *a*-, *b*- and *c*-axis lengths, were calculated from the powder XRD pattern using Si powder as an internal standard. Obtained *a*-, *b*- and *c*-axis lengths were 15.28, 8.244 and 7.879 Å, respectively. They were almost consistent with that of SrI_2 in the previous report [14]. Ionic radius of Eu^{2+} ion is almost same as

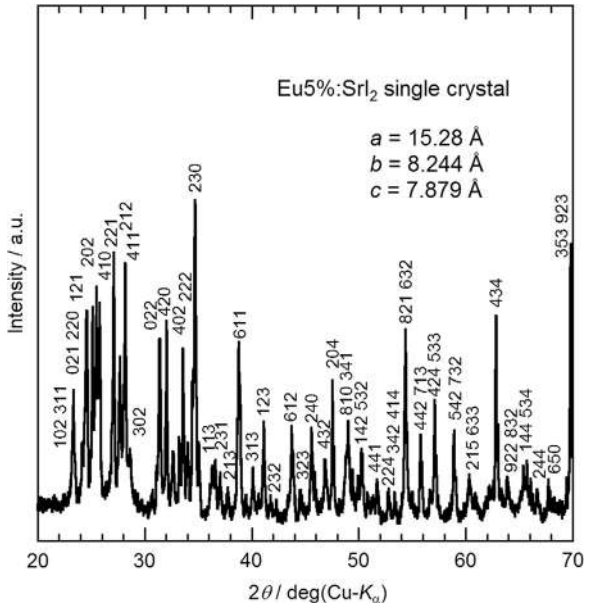

Fig. 3. Powder XRD pattern and lattice parameters of Eu5%:SrI_2 single crystal.

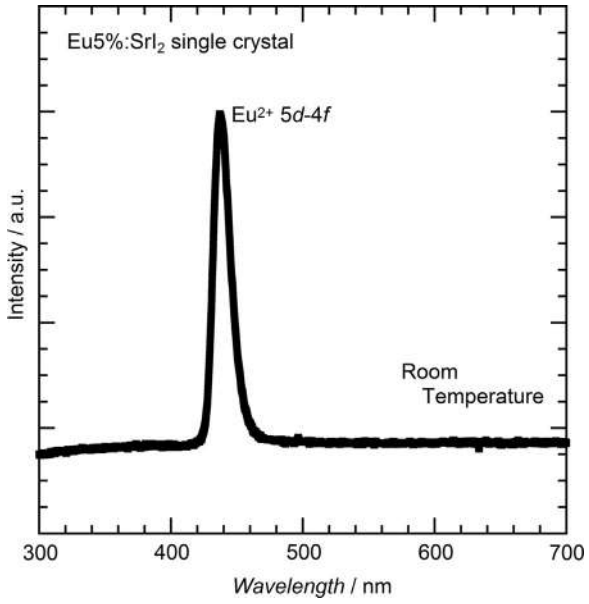

Fig. 4. Radioluminescence spectrum of Eu5%:SrI_2 single crystal under X-ray irradiation.

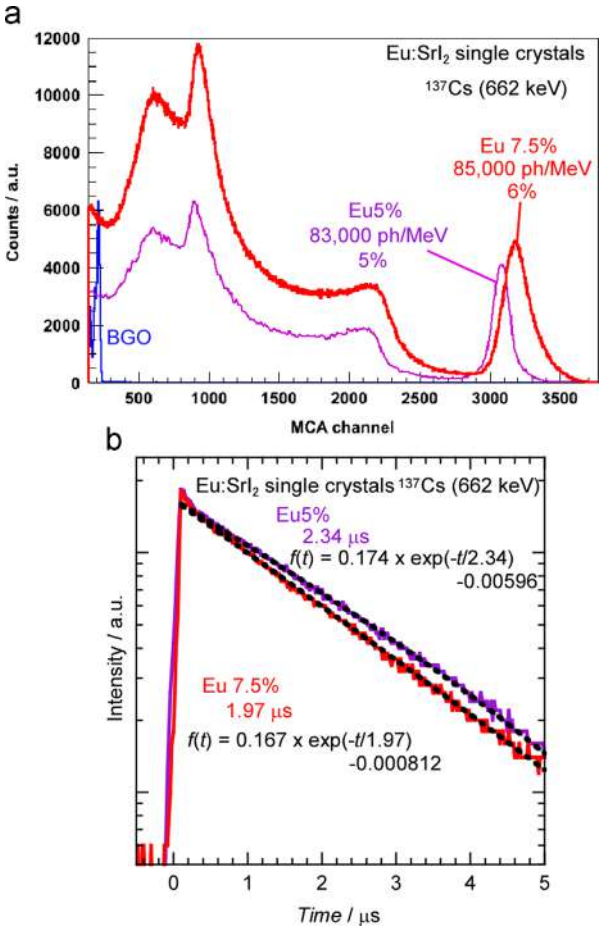

Fig. 5. (a) Pulse-height spectra and (b) decay curves of Eu:SrI_2 single crystals under γ-ray irradiation from ^{137}Cs radiation source.

that of Sr^{2+} ion and therefore lattice parameters of Eu:SrI_2 crystal were accorded with that of SrI_2 crystal without Eu ion.

Radioluminescence spectrum of Eu5%:SrI_2 crystal under X-ray excitation was evaluated as shown in Fig. 4. A sharp emission peak around 435 nm was observed and the emission originated from 5d–4f transition of Eu^{2+} ion.

Pulse-height spectra of Eu:SrI_2 crystals under γ-ray irradiation from ^{137}Cs radiation source was measured in the glove box. Fig. 5 is the pulse-height spectra of Eu:SrI_2 crystals with a thickness of 5 mm and BGO crystal as a reference. The light yields of Eu:SrI_2 crystals were estimated by comparing their positions of photo-peaks to that of BGO using quantum efficiency of PMT at each emission peak. The light yield and energy resolution of Eu5%:SrI_2 crystal were 83,000 ph/MeV and 5%, respectively. On the other hand, the result of Eu7.5%:SrI_2 crystal indicated 85,000 ph/MeV light yield and 6% energy resolution. These light yields and energy resolutions were comparable to previous reports [8,9].

Decay curves of Eu:SrI_2 crystals under γ-ray irradiation from ^{137}Cs radiation source were also measured in the glove box. Their decay curves could be fitted by a single exponential decay equation and decay times of Eu5% and 7.5% were 2.3 and 1.9 ns, respectively. Reason of the decrease of decay time with an increase of Eu concentration is not clear now. However, there is a possibility that the decrease of decay time is relevant to the concentration quenching or inhomogeneity in the crystal. These decay times were slightly slower than those of previous reports [8] and it was considered to be attributable to the size of measured crystal [15]. Re-absorption in the Eu:SrI_2 crystal means that a photon emitted from Eu ion is re-absorbed by another Eu ion and the re-absorption probability increases with the size of the sample. The increase of re-absorption probability results in the increase of decay time.

4. Conclusions

We grew Eu:SrI_2 bulk single crystals with 1 in. diameter using the modified μ-PD furnace and the special-shaped crucible. Eu5% and 7.5%:SrI_2 bulk crystals with several cracks in the crystals were obtained and polished crystals which were cut from the bulk crystals indicated high transparency. Powder XRD pattern of grown crystal demonstrated that the crystal was a single phase of SrI_2 structure. In the radioluminescence spectrum of the crystal under X-ray irradiation, a sharp emission peak around 435 nm was observed. Their light yields, energy resolutions and decay times were comparable to the previous reports. These results mean that this is the useful growth method for mass production of Eu:SrI_2 crystal.

References

[1] D. Yoon, I. Yonenaga, T. Fukuda, N. Ohnishi, J. Cryst. Growth 142 (1994) 339.
[2] A. Yoshikawa, T. Satonaga, K. Kamada, H. Sato, M. Nikl, N. Solovieva, T. Fukuda, J. Cryst. Growth 270 (2004) 427.
[3] Y. Yokota, T. Yanagida, N. Abe, N. Kawaguchi, K. Fukuda, M. Nikl, A. Yoshikawa, IEEE Trans. Nucl. Sci. 57 (2010) 1241.
[4] N. Abe, Y. Yokota, T. Yanagida, N. Kawaguti, K. Fukuda, M. Nikl, A. Yoshikawa, J. Pejchal, M. Nikl, IEEE Trans. Nucl. Sci. 57 (2009) 1320.
[5] Y. Yokota, Y. Fujimoto, T. Yanagida, H. Takahashi, M. Yonetani, K. Hayashi, I. Park, N. Kawaguchi, K. Fukuda, A. Yamaji, Y. Fukazawa, M. Nikl, A. Yoshikawa, Cryst. Growth Des. 11 (2011) 4775.
[6] A. Lempicki, A.T. Wojtowicz, E. Berman, Nucl. Instrum. Methods Phys. Res. A 333 (1993) 304.
[7] P. Dorenbos, Nucl. Instrum. Methods Phys. Res. A 486 (2002) 208.
[8] N.J. Cherepy, G. Hull, A.D. Drobshoff, S.A. Payne, E.v. Loef, C.M. Wilson, K.S. Shah, U.N. Roy, A. Burger, L.A. Boatner, W.S. Choong, W.W. Moses, Appl. Phys. Lett. 92 (2008) 083508.
[9] P. Belli, R. Bernabei, R. Cerulli, F.A. Danevich, E. Galenin, A. Gektin, A. Incicchitti, V. Isaienko, V.V. Kobychev, M. Laubenstein, S.S. Nagorny, R.B. Podviyanuk, S. Tkachenko, V.I. Tretyak, Nucl. Instrum. Methods Phys. Res. A 670 (2012) 10.
[10] W.M. Higgins, J. Glodo, E. Van Loef, M. Klugerman, T. Gupta, L. Cirignano, P. Wong, K.S. Shah, J. Cryst. Growth 287 (2006) 239.
[11] Y. Yokota, T. Yanagida, Y. Fujimoto, M. Nikl, A. Yoshikawa, Radat. Meas. 45 (2010) 472.
[12] Y. Yokota, N. Kawaguchia, K. Fukuda, T. Yanagida, A. Yoshikawa, M. Nikl, J. Cryst. Growth 318 (2011) 908.
[13] Y. Yokota, K. Nishimoto, S. Kurosawa, D. Totsuka, A. Yoshikawa, J. Cryst. Growth 375 (2013) 49.
[14] H. Barnighausen, N. Schulz, Acta Cryst. B 25 (1969) 1104.
[15] M.S. Alekhin, J.T.M. de Haas, K.W. Krämer, I.V. Khodyuk, L. de Vries, P. Dorenbos, Proceedings of the IEEE Nuclear Science Symposium Conference Record (2010) 1589.