

Crystal growth of Eu:SrI₂ single crystals by micro-pulling-down method and the scintillation properties



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ABSTRACT

Undoped and Eu doped SrI₂ (Eu:SrI₂) single crystals were grown by the modified micro-pulling-down (μ -PD) method and their scintillation properties were investigated. Undoped and Eu:SrI₂ single crystals with Eu 1%, 2%, 3% and 5% concentrations were obtained by the modified μ -PD method with the removable chamber system and their crystals with approximately 2 mm diameter and 2–3 cm length indicated high transparency. Powder X-ray diffraction patterns of grown Eu:SrI₂ crystals revealed that the Eu:SrI₂ crystals had a single phase of SrI₂ structure and similar lattice parameters regardless of Eu concentrations. In the X-ray radioluminescence spectrum of Eu:SrI₂ crystal, the emission peak around 430 nm which was due to the 5d–4f transition of Eu²⁺ ion was observed. Light yields, energy resolutions and decay times of grown Eu:SrI₂ crystals irradiated under γ -ray were evaluated.

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1. Introduction

Chloride, bromide and iodide materials are well-known to have large potential as a scintillator crystal with the high light yield and high energy resolution originated from the small band-gap [1]. High light yield and energy resolution for scintillator crystal can improve the resolution of radiation imaging system and increase the sensitivity of radiation detectors. However, most halide materials have a strong hygroscopic nature and it is difficult to make their single crystals with high crystallinity and transparency. Therefore, these halide scintillator crystals have been grown by just the Vertical Bridgeman (VB) method with a sealed quartz ampoule or Czochralski (Cz) method in dry room [2–4].

We have developed various novel oxide and fluoride scintillator crystals by the micro-pulling-down (μ -PD) method which can grow single crystals using the metal or carbon crucible with a hole at the bottom [5–7]. Compared to the conventional methods such as VB and Cz methods, the μ -PD method can grow a single crystal at about 10 times faster growth speed. Therefore, the μ -PD method has been mainly used for the research of novel functional single crystals and we have already developed various scintillators represented by Pr doped LuAG [8] and Ce doped LiCAF [9]. On the

basis of the μ -PD method for oxide and fluoride crystals, we have developed the modified μ -PD method for the growth of halide crystals with a hygroscopic nature. The modified μ -PD furnace is composed of a removable chamber, turbo molecular pump, high-frequency (HF) induction coil for heating and CCD camera for observation of liquid–solid interface. The removable chamber can be entered into a glove box through a pass box without exposing the inside of chamber to outside atmosphere. By the modified μ -PD method, we have successfully achieved the growth of chloride and bromide scintillator crystals with high quality [10,11].

Eu doped SrI₂ (Eu:SrI₂) has been investigated as a scintillator for gamma-ray with high light yield and energy resolution and the single crystals have been grown by the Vertical Bridgeman (VB) method with the quartz ampoule [12–16]. Therefore, the Eu:SrI₂ crystal with relatively large density and atomic number is one of the candidate for the scintillator of gamma-ray detectors. However, the Eu:SrI₂ crystals have a strong hygroscopic nature and there is no report about the growth of Eu:SrI₂ single crystal by other growth method. In this paper, we grew the Eu:SrI₂ single crystals with various Eu concentrations by the modified μ -PD method and the scintillation properties were investigated.

2. Experimental

Eu:SrI₂ single crystals with various Eu concentrations were grown by the modified micro-pulling-down (μ -PD) method for the

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growth of halide single crystals. The details of the modified μ -PD method was described in Refs. [10,11]. Starting materials, SrI_2 (Alfa Aesar, anhydrous, metal basis, > 4 N purity) and EuI_2 (Alfa Aesar, anhydrous, metal basis, > 3 N purity), were mixed as nominal compositions, $(\text{Sr}_{1-x}\text{Eu}_x)_2\text{I}_2$, where $x=0, 0.01, 0.02, 0.03$, and 0.05 , in the glove box which was filled with high-purity Ar gas (99.99999%). In the glove box, concentrations of oxygen and moisture are controlled less than 1 ppm. The mixed powders were put into a carbon crucible with a $\varnothing 2$ mm hole at the bottom. The density of carbon was 1.77 g/cm^3 and the carbon crucible can be heated by the high-frequency induction. The crucible, aluminum insulator and quartz tube were set in the chamber and the gate valve was closed in order not to let in the outside atmosphere. Then the chamber was taken out from the glove box to outside through the pass box after the gate valve was closed. The gate valve of the chamber was attached to the turbo molecular pump and the gate valve was opened after the junction between the chamber and pump was filled in Ar gas. The inside of chamber was vacuumed up to $\sim 10^{-4}$ Pa. During the vacuuming process, the crucible was heated at about 300°C by the high-frequency induction coil in order to remove the moisture on the surface of starting materials, crucible, insulator and quartz tubes. After the vacuuming process, the high-purity Ar gas (99.99999%) was put in the chamber up to atmosphere pressure and the crucible was heated up to the melting point of SrI_2 . Melt of Eu:SrI_2 came out from the inside of crucible through the hole in the crucible and crystal growth was performed by pulling-down the melt at 0.05 – 0.1 mm/min growth rate using tungsten wire as a seed. After crystal growth, the grown crystal was cooled to room temperature for 2 h. Then, the chamber was separated from the pumps and it was put in the glove box again. Finally, the grown crystal was taken out from the chamber. Grown crystals were polished in mineral oil for measurements of scintillation properties.

Structural phases and lattice parameters of grown crystals were investigated by X-ray diffraction (XRD) measurements using a sealed sample container filled with Ar gas with Beryllium windows. The crystals were ground by the mortar in the glove box for powder XRD measurements. The lattice parameters were calculated from the XRD patterns using Ti powder as an internal standard. Actual concentration of Eu in the crystal was measured by the Inductively Coupled Plasma (ICP) analysis. The cation ratio in the $\text{Eu } 1\%:\text{SrI}_2$ and $\text{Eu } 5\%:\text{SrI}_2$ crystals was $\text{Sr}:\text{Eu}=99.1:0.9$ and $95.8:4.2$, respectively. Radioluminescence spectrum was obtained from the grown Eu:SrI_2 crystal which was put into a sealed sample container filled with Ar gas with a Beryllium window and irradiated by X-ray with 40 kV and 40 mA. Emission light from the crystals excited by X-ray was led to the spectroscopy and CCD by the optical cable. γ -ray measurements were performed by investigating the response of crystals exposed to a ^{137}Cs radiation source emitting γ -ray with PMT (HAMAMATSU R7600U) in the glove box filled with Ar gas. 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 to digital signals by a multi-channel analyzer (AMPTTEK CO. Pocket MCA 8000A) and decay time was investigated by an oscilloscope (TEKTRONIX TDS3034B).

3. Results and discussions

The carbon crucible with a $\varnothing 2$ mm die which had a $\varnothing 0.5$ mm hole in the center was used for crystal growth on the first try. However, the melt of SrI_2 did not spread in the bottom of die due to the bad wetting between the melt and carbon. Therefore, the design of crucible was changed to that with a $\varnothing 2$ mm hole which was identical to that for the growth of fluoride crystals by the μ -PD

method [9]. Fig. 1(a) is the liquid–solid interface during crystal growth of Eu:SrI_2 single crystal observed by the CCD camera. After the melting of starting materials in the crucible, the melt was touched by Pt wire seed through the hole of crucible. During the crystal growth, the liquid–solid interface is flat and the thickness was approximately 100 – 200 μm . The diameter of the grown crystals was controlled by the hole of crucible. The temperature gradient around the liquid–solid interface was measured by the thermocouple and it was approximately 20°C/mm which is more than 10 times higher than that of the VB method [2]. When the pulling rate during crystal growth was below 0.1 mm/min, the liquid–solid interface was stable.

Then, undoped SrI_2 and Eu:SrI_2 crystals with Eu 1%, 2% and 5% concentrations were obtained (Fig. 1(b)). All crystals had approximately 2 mm diameter and 2–3 cm length. There was no visible cracks and inclusions in the crystals and Eu:SrI_2 single crystals indicated high transparency while undoped SrI_2 crystal had lower transparency compared to Eu:SrI_2 crystals. Polished Eu:SrI_2 crystals with Eu 1%, 5% and 10% are shown in Fig. 1(c). All polished transparent crystals without cracks and visible inclusions were used for the measurements of optical and scintillation properties. The yellow regions of the polished crystals appeared after cutting and polishing. It would be generated after the surface of halide crystals reacted to the moisture in surrounding atmosphere or oil.

Structural phases of the grown Eu:SrI_2 crystals were identified by the powder XRD measurement and their powder XRD patterns are shown in Fig. 2. The XRD patterns indicated that the grown Eu:SrI_2 crystals were a single phase of SrI_2 structure, orthorhombic and space group: $Pbca$. Their lattice parameters, a - and c -axes length, were calculated from the powder XRD patterns with the

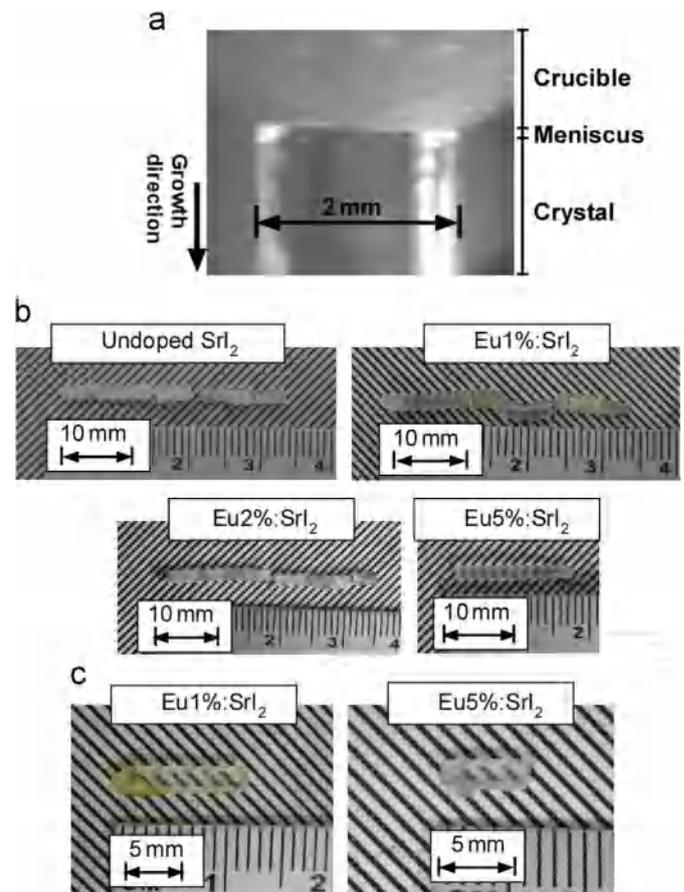


Fig. 1. (a) Liquid–solid interface during crystal growth. (b) Eu:SrI_2 single crystals grown by the modified μ -PD method. (c) Polished Eu:SrI_2 single crystals.

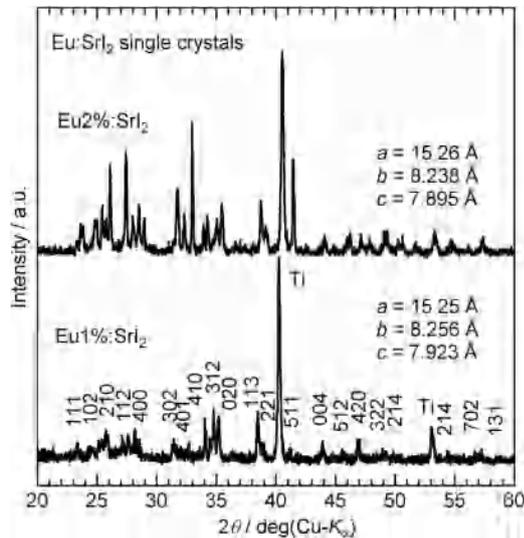


Fig. 2. Powder XRD patterns and lattice parameters of Eu:SrI₂ single crystals.

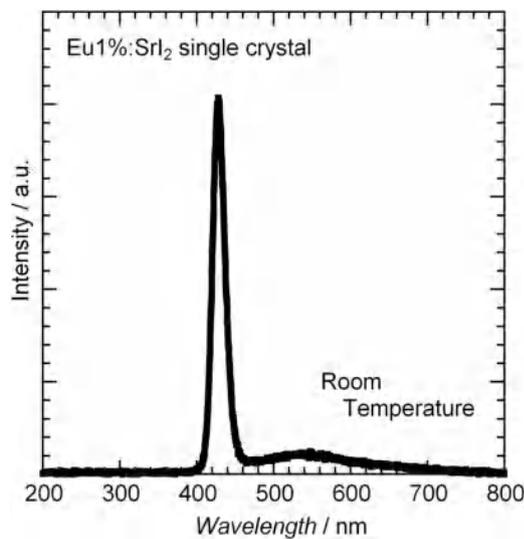


Fig. 3. X-ray radioluminescence spectrum of Eu:SrI₂ single crystal.

Ti powder as the internal standard. Calculated lattice parameters were almost constant regardless of Eu concentrations and the constant lattice parameters between Eu:SrI₂ crystals with different Eu concentrations are due to the ionic radius of Eu²⁺ ion which is similar to that of Sr²⁺ ion.

Radioluminescence spectra of the polished Eu:SrI₂ crystals were investigated under X-ray irradiation as shown in Fig. 3. An emission peak which originated from the 5d–4f transition of Eu²⁺ ions was observed around 430 nm. The wavelength of emission peak for Eu:SrI₂ crystal was almost consistent with that of crystal grown by the VB method in the previous report [12]. Additionally, there was a broad peak around 550 nm which was considered to be due to the emission from the SrI₂ host material. The similar emission was observed in the undoped SrI₂ crystal grown by the VB method [14].

Light yield and decay time of grown Eu:SrI₂ single crystals under γ -ray irradiation from ¹³⁷Cs radiation source were evaluated using PMT in the glove box. Fig. 4 is the pulse-height spectra of grown Eu:SrI₂ crystals. Photo-peaks in the pulse-height spectra were observed for all Eu:SrI₂ crystals. The photo-peak positions and full width of half maximums (FWHMs) on the photo-peaks were obtained by fitting the photo-peaks to a Gaussian. The light yields were estimated by comparing the photo-peak positions to

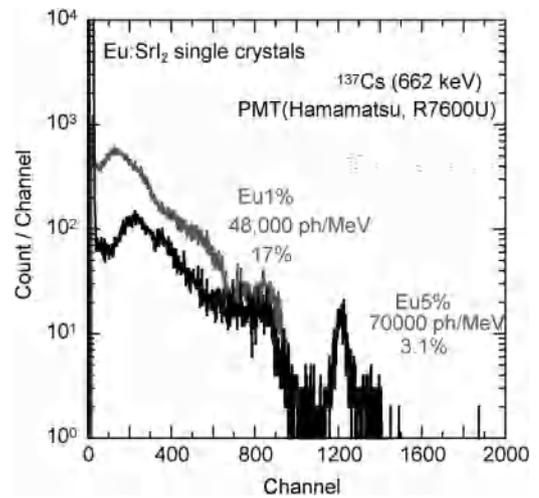


Fig. 4. Pulse-height spectra of Eu:SrI₂ single crystals under γ -ray irradiation.

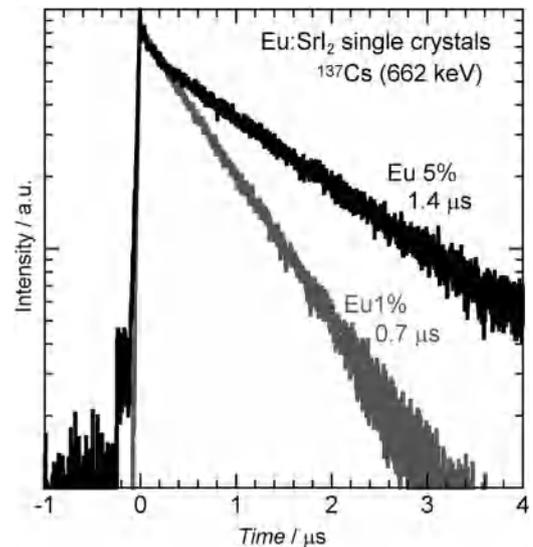


Fig. 5. Decay curves of Eu:SrI₂ single crystals under γ -ray irradiation.

the standard sample; BGO crystal and energy resolutions were obtained from the FWHM on the photo-peaks. The estimated light yield of grown Eu:SrI₂ crystals were 48,000 and 70,000 ph/MeV for Eu:SrI₂ crystals with Eu 1% and 5% concentrations, respectively. In addition, their energy resolutions were from 17% and 3.1% for Eu 1% and 5% concentrations, respectively. The light yields were slightly smaller than that of the crystals grown by the VB method [12]. The results are considered to be due to the difference of Eu concentration in the crystal and the improvement of light yield can be expected by the optimization of Eu concentration. In contrast, the energy resolution of Eu 5%:SrI₂ crystal was comparable to that of the crystal grown by the VB method.

The decay curves of Eu:SrI₂ crystals are shown in Fig. 5 and the decay curves could be fitted by the single exponential decay equation. The decay times increased from 0.70 to 1.40 μ s with an increase of Eu concentrations from 1% to 5%. The increase of decay times was almost consistent with that of the crystals grown by the VB method [15,16].

4. Conclusions

Eu doped SrI₂ single crystals with various Eu concentrations were grown by the modified μ -PD method with the removable

chamber and the structural phases and scintillation properties were investigated. Eu:SrI₂ single crystals with high transparency were obtained and their structural phases were identified to be a single phase of SrI₂ structure by the XRD measurement. In the X-ray radioluminescence spectrum, an emission peak that originated from the 5d–4f transition of Eu²⁺ ion was observed around 430 nm. Under γ -ray irradiation, Eu:SrI₂ single crystals indicated comparable light yield, energy resolution and decay time compared to the previous reports. These results reveal that the modified μ -PD method for halide materials has a sufficient performance for material research of halide scintillators and this study is the first step for crystal growth of iodide scintillator crystals by the μ -PD method.

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