Eu concentration dependence on scintillation properties of Eu doped SrI₂ single crystals grown by modified micro-pulling-down method

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1. Introduction

Scintillator materials have been widely applied as medical cancer detector, homeland security, survey meter and others. Among them, performance of devices using the gamma-ray detector is dependent on not only the acceptance unit but also the scintillator crystal. Especially, high light-yield and energy resolution are required for the gamma-ray scintillator crystals [1–6] and halide crystals with relatively small band-gap have been expected. In the results of vigorous investigations about halide scintillator materials, many halide scintillator crystals with high light yield and energy resolution as represented by Ce doped LaBr₃ [7] and Eu doped BaBr₂ [8] have been developed. In addition, Eu doped SrI₂ (Eu:SrI₂) crystals which was discovered by Hofstadter in 1968 [9] have attracted worldwide attentions due to the extremely high scintillation properties.

However, there is no systematic study about effects of actual Eu concentration in the Eu:SrI₂ crystals on scintillation properties as represented by the light yield and energy resolution while various studies about their scintillation properties have been already reported [10–13]. In the previous reports, the Eu:SrI₂ single crystals were grown by Bridgeman technique using a quartz ampoule and the nominal Eu concentrations in the crystals were 0.5%, 1%, 3%, and 5 mol%. However, in the range of Eu concentration, the concentration quenching has not been observed due to the low Eu concentration. In addition, there was no information about the actual Eu concentration in the Eu:SrI₂ crystals in the previous reports. Therefore, in this paper, Eu:SrI₂ crystals with wide range of Eu concentration, 1%, 5%, 7.5%, 10%, and 15%, were grown by a modify micro-pulling-down (μ-PD) method which could grow a single crystal at approximately ten times faster than the conventional methods [14]. In addition, their chemical compositions were evaluated to identify the actual Eu concentrations in the grown crystals and their scintillation properties were investigated and effects of Eu contents on scintillation properties were revealed.

2. Experiment

2.1. Crystal growth

Mixed powders with nominal compositions of \((\text{Sr}_{1-x}\text{Eu}_x)\text{I}_2\) [\(x = 0.01, 0.05, 0.075, 0.1\) and 0.15] were prepared with starting materials, SrI₂ (Alfa Aesar, 4 N) and EuI₂ (Aldrich, 3 N), in a glove box which was filled with high-purity Ar gas. The mixed powders were set in a carbon crucible with a ø2 mm diameter hole at the bottom. The crucible, aluminum insulator and quartz cover were placed at the top of the chamber and it was taken out from inside of the glove box without exposing the inside of chamber to outside atmosphere. The chamber was connected with a turbo molecular pump and inside of the chamber was evacuated up to \(10^{-4}\) Pa for several hours. During the vacuuming process, the crucible
was heated at approximately 300 °C by the high-frequency induction coil in order to remove the moisture on the surfaces of starting materials, crucible, insulator, and quartz tubes. After the baking process, high-purity Ar gas (99.9999%) was introduced in the chamber and the crucible was heated up to the melting point of Eu: SrI₂, 528 °C. Crystal growth was performed by pulling-down the melt in the crucible using a Pt wire as a seed. During crystal growth, growth rate was 0.05–0.1 mm/min. The grown crystals were cut and polished using mineral oil for the measurements of scintillation properties.

2.2. Crystal structure and chemical composition

Phases of grown crystals were identified by the powder X-ray Diffraction (XRD) measurement (RIGAKU, RINT2000) using a tight chamber with a beryllium window. Actual cation ratios in the grown crystals were evaluated by the inductively Coupled Plasma (ICP) analysis (Thermo Fisher Scientific, IRIS Advantage DUO).

2.3. Scintillation properties

Radioluminescence spectra of the polished specimens were measured with the spectrometer and CCD camera (ORIEL, Thermo) using X-ray as the excitation source and a tight chamber which has a beryllium window. Pulse-height spectra of the polished specimens under γ-ray irradiation from 137Cs radiation source were evaluated to estimate their light yields and energy resolutions. Specimens were optically coupled with a Photomultiplier Tube (PMT) (HAMAMASTU, R7600U) by optical grease in the glove box which was filled with Ar gas. Signals from the PMT were converted to digital signals by a multi-channel analyzer (AMPTEK CO. Pocket MCA 8000A). At the same time, their decay curves were also measured using an oscilloscope (TEKTRONIX, TBS1102).

3. Result and discussion

3.1. Crystal growth

Melt in the crucible was touched by the Pt wire and single crystal was grown by pulling-down the melt using the Pt wire after the mixed powder in the crucible was completely melted. During the crystal growth, pulling rate was approximately 0.1 mm/min and the liquid–solid interface below the bottom of crucible was stable. In the result, Eu 1%, 5%, 7.5%, 10% and 15% doped SrI₂ single crystals were obtained as it is shown in Fig. 1. All as-grown crystals had approximately 0.2 mm diameter and several centimeters length. There were no visible crack and inclusion in the all as-grown Eu: SrI₂ crystals. The polished crystals with a thickness of 0.7 mm indicated high transparency.

3.2. Chemical composition and crystal structure

Chemical compositions of the Eu: SrI₂ crystals were analyzed by the ICP measurement. In the result, the cation ratios of the Eu 1%, 5%, 7.5%, 10% and 15%: SrI₂ crystals were Sr: Eu = 98.9:1.11, 94.81:5.19, 92.61:7.39, 90.42:9.58 and 83.20:16.80, respectively and actual Eu concentrations in all crystals were almost same as the nominal compositions. The result is due to the almost same ionic radius of Eu²⁺ ion as Sr²⁺ ion.

The powder XRD of Eu 1% and 10%: SrI₂ crystals were measured to identify their phases. Obtained powder XRD patterns were illustrated in Fig. 2. All diffraction peaks of these XRD patterns were identified by the SrI₂ structure and there was no secondary phase.

3.3. Scintillation properties

Radioluminescence spectra of the polished specimens under X-ray irradiation were investigated as it is shown in Fig. 3. Emission peaks originated from 5d to 4f transition of Eu²⁺ ion were observed around 435 nm for all crystals and the wavelength was almost same as previous report [15]. Additionally, in the spectra of Eu 1%: SrI₂ crystal, a broad peak in the range of wavelength from 400 to 700 nm. The broad peak was considered to be due to the luminescence from SrI₂ host material and the similar emission has already reported in the previous report [16]. In Fig. 3, the intensities of emission peaks at 435 nm are normalized. However, the intensities of emission peaks at 435 nm are considered to increase with an increase of Eu concentration. Therefore, the additional broad peak from 400 to 700 nm was not observed in the crystals except for Eu 1%: SrI₂ due to the relatively strong emission from Eu²⁺ ion in the crystals.

Light yields of Eu: SrI₂ crystals under γ-ray irradiation from 137Cs radiation source were evaluated by the pulse-height spectra using PMT in the glove box. Fig. 4(a) shows the pulse-height spectra and the photo-peaks were observed for all Eu: SrI₂ crystals. The photo-peaks were fitted by the Gaussian function to obtain their photo-peak positions and calculate their energy resolutions. In addition, the light yields were estimated by comparing the photo-peak positions between Eu: SrI₂ crystals and Bi₄Ge₃O₁₂ (BGO) standard crystal (8000 ph/MeV). The light yields and energy...
resolutions are shown in Fig. 4(b). The light yield increased with an increase of Eu content and Eu7.5%:SrI₂ crystals indicated maximum light yield, 78,000 ph/MeV. In contrast, the light yields decreased with an increase of Eu content for Eu10% and 15%:SrI₂ crystals. The decrease of light yield is considered to be due to the concentration quenching \[17\]. Additionally, energy resolution of Eu7.5%:SrI₂ crystal was smallest, 3.7%, among these crystals.

The decay curves of Eu: SrI₂ crystals under γ-ray irradiation are shown in Fig. 5(a). All decay curves could be fitted by a single exponential decay equation. Obtained decay times are indicated in Fig. 5(b). The decay times systematically increased with an increase of Eu content. The result suggests that possibility of the charge transfer between Eu²⁺ ions was increased by the increase of Eu content in the crystal.

4. Conclusion

We grew Eu:SrI₂ single crystals with various Eu concentrations by the modified μ-PD method and investigated their chemical compositions and scintillation properties. By the powder XRD measurement, all grown crystals were identified a single phase of SrI₂ structure. The light yield increased and energy resolution decreased with an increase of Eu content and Eu7.5%:SrI₂ crystals indicated maximum light yield, 78,000 ph/MeV and minimum energy resolution, 3.7%. Then, the light yield decreased and energy resolution increased with an increase of Eu content. The Eu:SrI₂ crystals with high light yield and energy resolution have
a potential to some applications for survey meter, spectrometer, food radiation detector, whole-body counter and others.

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References


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