Growth and scintillation properties of Eu doped BaCl₂/LiF eutectic scintillator

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Abstract

Eu doped BaCl₂/LiF eutectics were grown by the micro-pulling down method and their directionally solidified eutectic (DSE) system has been investigated. The grown eutectic showed main phases of cubic LiF and orthorhombic BaCl₂. In these eutectics, the 399 nm emission of Eu²⁺ 4f5d was obtained. It shows the intrinsic decay time of about 410 ns. The light yield of the 1-mm-thick eutectic showed 7000 ph/5.5MeV alpha-ray.

1. Introduction

Inorganic scintillators have been playing a major role in many fields of radiation detection, including medical imaging, security system, astrophysics, and well logging. In these applications, scintillators for thermal neutron detection have recently attracted increased attention due to diminishing resources of ^3He gas. Up to now, most of the thermal neutron detectors are the ^3He gas counters with high thermal neutron cross section and low background gamma-ray sensitivity. However, the recent demand for ^3He gas highly exceeds its supply because of increasing demand of neutron detectors for national security and oil logging applications. The research-and-development efforts in alternative neutron detection technology have been performed recently [1,2]. This huge discrepancy between the demand and supply of ^3He gas motivates us to develop novel thermal neutron scintillators which could replace the contemporary ^3He based systems.

In this decade, some novel inorganic scintillators such as Li-glass, Eu:LiI [3], $^6\text{LiF}/\text{ZnS}$ [3] for neutron detection have been reported. Among them, LiCaAlF_6 based scintillator is one of the most promising candidates [4,5]. LiCaAlF_6 includes Li in the host lattice and enables the pulse shape discrimination between neutrons and gamma-rays [6]. As it is single crystal, Li content is limited by the chemical formula and can't be increased. Thus, if we need higher neutron detection efficiency, we have to find other way. As a candidate for novel neutron detectors, Eu activated LiF/CaF_2 eutectic scintillators were developed and their scintillation properties under ^{252}Cf neutron exposure were examined [7,8].

The most important advantage of eutectic scintillators is higher Li content than that of LiCaAlF_6 . The aim of this study is not only to increase Li content but also to investigate the possible design of high resolution neutron imager using the directionally solidified eutectic (DSE) system coupled with high resolution photo detectors. The schematic view of that is shown in Fig.1. Possibility of high resolution detection using DSE system for X-ray CT application has been proposed for $\text{GdAlO}_3/\text{Al}_2\text{O}_3$ [9] and CsI/NaCl [10]. Some eutectics containing Li have been investigated for neutron detection system, for example LiF/SrF_2 [11], LiF/CaF_2 [12], $\text{LiF}/\text{LiGdF}_4$ [13] and $\text{LiF}/\text{CaF}_2/\text{LiBaF}_3$ [14].

In this study, LiF/BaCl_2 eutectic was investigated as a scintillator material for neutron detection application. Favorable scintillation properties of the Eu doped BaCl_2 single crystal scintillator such as 52,000 ph/MeV and 3.5% of energy resolution under ^{137}Cs gamma-ray excitation were reported [15]. Here, we designed DSE with LiF fibers embedded in the matrix scintillation phase of Eu doped BaCl_2 at the composition corresponding to the eutectic point of LiF/BaCl_2 [16] (See Fig. 1). Irradiated neutrons are absorbed in ^6Li in the LiF microrod phase and LiF generate alpha-ray. Luminescent BaCl_2 matrix absorb the alpha-ray and generate visible light. Crystal growth was performed by the micro-pulling down (μ -PD) method. Luminescence and scintillation properties excited by neutron were evaluated.

2. Experimental

2.1 *Crystal Growth and phase identification*

Starting materials were prepared from high-purity powders of LiF, BaCl₂ and EuF₃ (4N). Eutectics were grown with the eutectic composition (BaCl₂:64.30 mol%, LiF:35.70 mol%) and 1 % of BaCl₂ were replaced with EuF₃ at the composition. Crystal growth was performed by the micro-pulling-down (μ -PD) method with the tight-vacuum chamber. The detail of crystal growth by the μ -PD method was described in Ref. [17,18]. Mixed powders were set in a graphite crucible with a 3 mm die which has a 2 mm hole in the center and the crucible was heated by the high-frequency induction coil in Ar/CF₄ mixed gas after baking process under high vacuum ($\sim 10^{-4}$ Pa) to eliminate water and oxygen. A platinum wire was used as the seed and the growth speed was 0.30 - 0.50 mm/min. During the crystal growth, the solid-liquid interface was maintained at the position of the hole and the growth speed was changed.

Circular and rectangular samples were obtained from the grown crystal. The cut surface was optically polished and the eutectic phase structure was observed by back scattered electron image (BEI) using Hitachi S3400N. The eutectic structures on transverse and vertical cross-section were observed. The obtained phases in the eutectics were investigated by powder X-ray diffraction (XRD) using RIGAKU RINT-2000.

2.2 *Luminescence and radiation response measurement procedure*

The photo-luminescence properties were investigated by a spectrometer (Edinburgh FLS920) using optical source (Edinburgh Xe 900). The radio-luminescence spectra were investigated under X-ray and the pulse-height was investigated under α -ray excitation from an ²⁴¹Am radiation source by photomultiplier tube (PMT, Hamamatsu R7600U-200). The signal was fed into a shaping amplifier (ORTEC 572A), a multichannel analyzer (MCA) (ORTEC 926), and finally to a personal computer. The shaping time was set as 10 μ s. The bias for the PMT was supplied by an ORTEC 556. For the decay time measurement the same setup with the PMT and digital oscilloscope TD5032B were used. In the measurements, ⁶Li-loaded glass scintillator (GS20; Saint Gobain) with the size of 1 $\times$ 2 $\times$ 6 mm³ which had the light yield of 6,000 ph/n [13,14] was used as a reference. The polished crystal was optically coupled to the window of the PMT with an optical grease (OKEN 6262A).

3. Result and discussion

3.1 Crystal growth and phase identification

Eutectic crystals were grown at various growth speeds in an attempt to generate fiber-like microstructure. A photograph of the grown crystal is shown in Fig. 2. White rod with 2 mm diameter and 60 mm length was obtained. Pulling rates were 0.3 and 0.5 mm/min at the beginning and end part of the grown eutectic, respectively. BEI of grown crystals in vertical and transverse cross-section are shown in Fig. 3. microrod phases were observed on each transverse cross-section as shown in Fig. 3 (a) – (d). The average microrod size was about 2-3 μm in Fig. 3(b) for the growth speed of 0.30 mm/min and 4-5 μm in Fig. 3(d) for the growth speed of 0.50 mm/min. The result of powder XRD of the grown eutectic was shown in Fig. 4. The grown eutectic showed main phases of cubic LiF and orthorhombic BaCl₂ with a trace of barium chlorate hydrate phase. This hydrate phase was arised during drushing the eutectic. According to obtained results, white matrix phase is LiF and black microrod phase is BaCl₂ in the BEI.

Up to now, some groups investigated transformation between rod-like shape and lamellar shape in eutectic structure [19-21]. They concluded that transformation of the eutectic depended on the volume ratio of components and the relative interface energy [22]. If the volume ratio is below 3/7, microrod and matrix phase were formed in eutectics. In our case, if the eutectics were composed of BaCl₂/LiF, the volume ratio of BaCl₂/LiF in this system at the starting composition is BaCl₂: LiF = 82.3: 17.7 and LiF could form the microrod phases. LiF microrod phase and BaCl₂ matrix was directionally solidified along the growth direction.

3.2 Luminescence properties

Radio-luminescence spectra were measured by X-ray excitation. That is shown in Fig.5. The emission peak was observed at 399 nm. Photo-luminescence spectra were also measured around 399 nm as shown in Fig.6. The emission peak was observed at 399 nm, with excitation maximum at 290 nm. The photoluminescence decay curve (ex.=290nm,em.399nm) was shown in Fig.7. The decay time of the emission at 399 nm was about 410 ns. The broad emission band around 399 nm may be $4f^65d-4f^7$ transition of Eu²⁺ ions. These results are good agreement with previous report on Eu doped BaCl₂ single crystal [15].

3.3 Scintillation properties

Pulse-height spectra was investigated with 0.4 mm thick crystal under α -ray excitation from an ²⁴¹Am radiation source. In the measurements, ⁶Li-loaded glass scintillator (GS20; Saint Gobain) with the size of 1 × 2 × 6 mm³ which had the light yield of 6,000 ph/5.5MeV alpha-ray was used as a reference.

Pulse-height spectra of the Eu doped BaCl₂/LiF and GS20 were shown in Fig.8. The quantum efficiencies of the PMT at 380 nm (emission of Li-glass) and 399 nm (Eu:BaCl₂) are almost the same and we can directly compare their light yield from alpha-ray peak channels. The light yield of the 1-mm-thick eutectic showed the light yield of 7000 ph/5.5MeV alpha-ray. The Eu doped BaCl₂/LiF eutectic have lower theoretical density of 2.74 g/cm³ and faster decay time of 410ns comparing to LiCAF (2.98 g/cm³ and 1400 ns). At the point of view of sensitivity for gamma-ray and timing properties, the Eu doped BaCl₂/LiF eutectic is superior to LiCAF. Though light yield of Eu doped BaCl₂/LiF eutectic was lower than that of LiCAF, light yield can be improved by increasing transparency after optimizing of growth conditions such growth speed, melt composition and temperature gradient along the growth direction and polishing process for hygroscopic materials.

4 Conclusion

The 1%Eu:BaCl₂/LiF eutectic scintillator was fabricated. The directionally solidified eutectic with well-aligned 3-5 μm diameter LiF fibers surrounded with BaCl₂ matrix was prepared by μ-PD method. Emission peak of Eu²⁺ in BaCl₂ was observed at 399 nm by 290nm and x-ray excitation. The photo luminescence decay time of the emission at 399 nm was about 410 ns. The light yield of the 1-mm-thick eutectic showed 7000 ph/5.5MeV alpha-ray. The directionally solidified eutectics with Eu:BaCl₂ scintillator matrix embedded in LiF microrod phase takes advantage from an ability of neutron-to-light conversion.

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Figure captions

Figure 1. Schematic drawing of the phase-separated BaCl₂/LiF eutectic scintillator.

Figure 2. Photograph of the 1%Eu:BaCl₂/LiF eutectic crystal grown by μ -PD method.

Figure 3. BEI of polished 1%Eu:BaCl₂/LiF eutectic crystal, a) transverse cross-section of the eutectic grown at the speed of 0.30 mm/min, b) microrod phase of the eutectic grown at the speed of 0.30 mm/min. c) transverse cross-section of the eutectic grown at the speed of 0.50 mm/min, d) microrod phase of the eutectic grown at the speed of 0.50 mm/min.

Figure 4. Powder X-ray diffraction pattern for the 1%Eu:BaCl₂/LiF eutectic.

Figure 5. Radio-luminescence spectra of 1%Eu:BaCl₂/LiF eutectic excited by X-ray.

Figure 6. Photo-luminescence spectra of 1%Eu:BaCl₂/LiF eutectic. (Excitation:290nm, Emission:399nm).

Figure 7. Photo-luminescence decay time of emission at 399nm .

Figure 8. Pulse-height spectra of the 1-mm-thick Eu:BaCl₂/LiF eutectic under ²⁴¹Am excitation. Red line is Eu:BaCl₂/LiF and blue line is Li glass.

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