Directionally solidified Eu doped $\text{CaF}_2/\text{Li}_3\text{AlF}_6$ eutectic scintillator for neutron detection

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Abstract

Eu doped $\text{CaF}_2/\text{Li}_3\text{AlF}_6$ eutectics were grown by μ -PD method. The directionally solidified eutectic with well-aligned 600 nm diameter Eu: CaF_2 scintillator fibers surrounded with Li_3AlF_6 was prepared. The grown eutectics showed an emission peak at 422 nm ascribed to Eu^{2+} 4f-5d transition from Eu: CaF_2 scintillation fiber. Li concentration in the Eu: CaF_2 - Li_3AlF_6 eutectic is around 0.038mol/cm^3 , which is two times higher than that of LiCaAlF_6 single crystal (0.016mol/cm^3). The light yield of Eu: CaF_2 - Li_3AlF_6 eutectic was around 7000 ph/neutron. The decay time was about 550 ns (89%) and 1450ns(11%).

1. Introduction

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. In these applications, solid scintillators for thermal neutron detection have recently attracted increased attention due to diminishing resources of ^3He gas. 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 would replace the contemporary ^3He -based systems.

In this decade, some novel inorganic scintillators for neutron detection have been reported. Among them, LiCaAlF_6 and $\text{Cs}_2\text{LiYCl}_6$ based scintillator are promising candidates [3-5]. LiCaAlF_6 includes Li in the host lattice and enables the pulse shape discrimination between neutrons and gamma-rays [6]. Li content is limited by the chemical formula and cannot be increased in single crystals. Thus, if we need higher neutron detection efficiency, we have to find another 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 conventional neutron scintillators like Li-glass, $\text{Eu}:\text{LiI}$, LiF/ZnS [9]. The aim of this study is not only to increase Li content but also investigate the possible design of high resolution neutron imager using the directionally solidified eutectic (DSE) system coupled with high resolution photo detectors. Possibility of high resolution detection using DSE system for X-ray CT application has been proposed for $\text{GdAlO}_3/\text{Al}_2\text{O}_3$ [10], CsI/NaCl [11], $\text{SrHfO}_3/\text{Al}_2\text{O}_3$ [12] and other eutectics. Some eutectics containing Li are investigated for neutron detection system, for example $^6\text{LiF}-\text{SrF}_2$ [13] and $^6\text{LiF}-\text{CaF}_2$ [14], $\text{LiF}/\text{LiGdF}_4$ [15] and $\text{LiF}/\text{CaF}_2/\text{LiBaF}_3$ [16] eutectics.

In this study, DSE system on $\text{CaF}_2/\text{Li}_3\text{AlF}_6$ eutectic was investigated. Eu doped $\text{CaF}_2/\text{Li}_3\text{AlF}_6$ eutectics were grown by micro-pulling down ($\mu\text{-PD}$) method. Luminescence and scintillation properties excited by neutron were evaluated.

2. Experimental

2.1 Crystal Growth

Starting materials were prepared from high-purity fluoride powders of LiF , CaF_2 , AlF_3 and EuF_3 (4N, produced by Stera Chemifa Corporation). $(\text{Ca}_x\text{Eu}_{1-x})\text{F}_2-\text{Li}_3\text{AlF}_6$ ($x=0.01$) eutectics were grown at

the eutectic composition of (CaF₂:40 mol%, Li₃AlF₆:60 mol%)[17,18]. 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.[19,20]. In the unidirectional solidification processes such as μ -PD method, CaF₂ and Li₃AlF₆ phases deposit from the melt on their own formed solid phases. 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. The platinum wire was used as the seed and the growth speed was 1.00 mm/min. During the crystal growth, the solid-liquid interface was maintained at the position of die.

2.2 Structural evaluation of eutectic composites

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. The growth direction of the rod phase was investigated by electron diffraction pattern using Joel JSM-5400.

2.3 Luminescence and scintillation properties measurement procedure

The photoluminescence properties were investigated by a spectrometer (Edinburgh FLS920) using optical source (Edinburgh Xe 900). The radioluminescence spectra were investigated by a spectrofluorometer (Edinburgh FLS920) under α -ray excitation from a ²⁴¹Am radiation source. Pulse-height spectra and decay time under neutron excitation from a ²⁵²Cf radiation source were investigated 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/neutron [21] was used as a reference.

3 Result and discussion

3.1 Crystal growth and phase identification

Eutectic crystals were grown at the speed of 1.00 mm/min. Example photograph of the grown crystal was shown in Fig.1. White rod crystal with 2 mm diameter was obtained. BEI of grown crystals in vertical and transverse cross-section were observed and grown eutectic showed phase-separated structure of CaF_2 rods surrounded by Li_3AlF_6 matrix. Up to now, some groups investigated transformation between rod-like shape and lamellar shape in eutectic structure [22-25]. They conclude that the transformation of the eutectic depended on the volume ratio of the components and the relative interface energy [26]. Volume ratio of CaF_2 : Li_3AlF_6 in this component is about 0.222:0.778 and the rods were formed by the CaF_2 phase which was confirmed by the EDX result. It is in good agreement with previous reports [26]. The average rod size was about 600 nm in Fig. 2(b) for the growth speed of 1.00 mm/min. The length of the longest rod along the growth direction at the growth speed of 1.00 mm/min was about 100 μm in Fig. 2 (d). Result of powder XRD of the grown eutectic was shown in Fig.3. The grown eutectic showed two phases of cubic CaF_2 and orthorhombic Li_3AlF_6 . TEM image and electron diffraction patterns from CaF_2 rod phase are shown in Fig. 4. The electron diffraction pattern of the rod phase agreed well with a sample of non-doped CaF_2 crystal and the growth direction seemed to be [001] direction. Li concentration in the Eu: CaF_2 - Li_3AlF_6 eutectic is around $0.038\text{mol}/\text{cm}^3$, which is two times higher than that of LiCaAlF_6 single crystal ($0.016\text{mol}/\text{cm}^3$). The directionally solidified eutectics with Eu: CaF_2 scintillator fibers embedded in Li-rich matrix phase takes advantage both from the properties of an optical fiber like $\text{GdAlO}_3/\text{Al}_2\text{O}_3$ eutectics[10] and an ability of neutron-to-light conversion. However Li_3AlF_6 has first order phase transition from orthorhombic to cubic at 584°C below its eutectic point of 720°C [18]. Micro cracks of the Li_3AlF_6 matrix phase coming from the phase transition cannot be avoided. Eu: CaF_2 /LiF eutectic is not transparent even the eutectic showed well aligned scintillation fiber structure.

3.2 Luminescence and scintillation properties

Radio-luminescence and photo-luminescence spectra of the mirror-polished 0.3-mm-thick eutectic sample are shown in Fig.5 and Fig.6. They showed an emission peak at 422 nm ascribed to Eu^{2+} 4f-5d transition from Eu: CaF_2 scintillation fiber which was in good agreement with the previous report [14]. Fig. 7 shows pulse height spectra of the grown Eu: CaF_2 / Li_3AlF_6 eutectic scintillator under ^{252}Cf neutron irradiation compared with the Li-glass scintillator standard. As clearly seen, neutron peaks were detected in both samples. The quantum efficiencies of the PMT at 380nm (emission of Li-glass) and 422 nm (Eu: CaF_2) are approximately 40% and we can directly compare their light yield from ^{252}Cf neutron peak

channels. The light yield of Eu:CaF₂-Li₃AlF₆ eutectic was around 7000 ph/neutron. This value is lower than that of Eu:CaF₂/LiF eutectic in our previous report (8000 ph/neutron)[15]. Scintillation decay under neutron excitation of Eu:CaF₂/Li₃AlF₆ is shown in Fig. 8. Scintillation decay is approximated by the sum of two exponentials according to the equation (1).

$$I(t) = \sum A_i \exp[-t/\tau_i], i= 1,2. \quad \text{--- (1)}$$

Ratio (%) is calculated by $A_1\tau_1/(A_1\tau_1 + A_2\tau_2) \times 100\%$. The decay time was about 550 ns (89%) and 1450ns(11%) which is slightly longer than the value from the previous report on Eu:CaF₂/LiF eutectic [15].

4 Conclusion

The directionally solidified eutectic with well-aligned 600 nm diameter Eu:CaF₂ scintillator fibers surrounded with Li₃AlF₆ was prepared by μ -PD method. The grown eutectics showed an emission peak at 422 nm ascribed to Eu²⁺ 4f-5d transition from Eu:CaF₂ scintillation fiber. Li concentration in the Eu:CaF₂-Li₃AlF₆ eutectic is around 0.038mol/cm³, which is two times higher than that of LiCaAlF₆ single crystal (0.016mol/cm³). The light yield of Eu:CaF₂-Li₃AlF₆ eutectic was around 7000 ph/neutron. The decay time was about 550 ns (89%) and 1450ns(11%). The directionally solidified eutectics with Eu:CaF₂ scintillator fibers embedded in Li-rich matrix phase takes advantage from an ability of neutron-to-light conversion.

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Figure captions

Figure 1. Photograph of the Eu doped $\text{CaF}_2/\text{Li}_3\text{AlF}_6$ eutectic crystal grown by μ -PD method at the composition of CaF_2 :49.5 mol% and Li_3AlF_6 :50 mol% and EuF_3 :0.5 mol%.

Figure 2. BEI of polished Eu doped $\text{CaF}_2\text{-Li}_3\text{AlF}_6$ eutectic crystal shown in Fig. 1 grown at the speed of 1.00 mm/min. a), b) transverse cross-section and c), d) vertical cross-section along growth direction.

Figure 3. a) Powder X-ray diffraction pattern for the 0.5 mol% Eu doped 49.5 mol% CaF_2 -50 mol% Li_3AlF_6 eutectic.

Figure 4. Transmission electron microscope analysis a) TEM image of the transverse cross-section of 0.5 mol% Eu doped 49.5 mol% CaF_2 /50.0 mol% Li_3AlF_6 eutectic crystal at the growth speed of 1.00 mm/min, electron diffraction pattern from [001] incidence direction of b) CaF_2 rod phase and c) a sample of non-doped CaF_2 crystal as reference.

Figure 5. Radioluminescence spectra of Eu: $\text{CaF}_2/\text{Li}_3\text{AlF}_6$ eutectic under α -ray excitation.

Figure 6. Photoluminescence spectra of grown Eu: $\text{CaF}_2/\text{Li}_3\text{AlF}_6$ eutectic excited at 340 nm.

Figure 7. Pulse-height spectra of Eu: $\text{CaF}_2/\text{Li}_3\text{AlF}_6$ eutectic under ^{252}Cf neutron excitation. Red line is Eu: $\text{CaF}_2/\text{Li}_3\text{AlF}_6$ and blue line is Li-glass.

Figure 8. Decay curve of Eu: $\text{CaF}_2/\text{Li}_3\text{AlF}_6$ eutectic under neutron excitation.

Kamada, et al, Figure 1

Kamada, et al, Figure 2

Kamada, et al, Figure 7