GROWTH AND SCINTILLATION PROPERTIES OF Tb DOPED LiGdF₄/LiF EUTECTIC SCINTILLATOR

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Abstract:

Tb-doped LiGdF₄-LiF eutectics were grown at various growth rate and their directionally solidified eutectic (DSE) system has been investigated. Well aligned fiber like eutectic structure with around 1.7 μm in diameter and 1200 μm in maximum length was obtained the growth speed of 0.15 mm/min. The sample showed optical transparency like bundle optical fibers and around 40% of transmittance at 1.5mm thick was achieved in 380-630 nm range. The expected 380-630 nm emission excited by UV and α -ray, and 270-330nm excitation of Tb³⁺ ⁸S -⁶P transition have been observed. The weak emission of Gd³⁺ 4f-4f transition at 310 nm was also observed under alpha-ray excitation. The Observed excitation bands peaking at around 275 nm and 310 nm correspond respectively to the ⁸S^{7/2}-⁶I_{7/2} and ⁸S_{7/2}-⁶P_J absorption bands of Gd³⁺.

Keywords: eutectic, scintillator, terbium, fluoride, radiation detection.

1. Introduction

Inorganic scintillators have been playing a major role in many fields of radiation detection, including medical imaging, security systems, astrophysics, and oil 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 would replace the contemporary ^3He -based systems.

In this decade, some novel inorganic scintillators for neutron detection have been reported. Among them, LiCaAlF_6 based scintillator is one of the most promising candidates [3,4]. LiCaAlF_6 includes Li in the host lattice and enables the pulse shape discrimination between neutrons and gamma-rays [5]. As it is single crystal, Li content is limited by the chemical formula and cannot be increased. 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 [6,7].

The most important advantage of eutectic scintillators is higher Li content than that of conventional neutron scintillators like Li-glass, Eu:LiI , LiF/ZnS [8]. 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 $\text{GAP-Al}_2\text{O}_3$ [9] and CsI-NaCl [10]. Some eutectics containing Li are investigated for neutron detection system, for example $^6\text{LiF-SrF}_2$ [11] and $^6\text{LiF-CaF}_2$ [12]. Recently our group reported Ca,Ce co-doped $\text{LiGdF}_4\text{-LiF}$ eutectics and Ce^{3+} -perturbed emission within 340-380 nm was found also in this material system [13]. However, any scintillation light could not be detected under radiation excitation.

In this study, Tb doped $\text{LiGdF}_4\text{-LiF}$ eutectics were fabricated by the micro-pulling down ($\mu\text{-PD}$) method. Tb was selected as emission center to obtain enough scintillation light. Growth condition was optimized to get well aligned eutectic structure and optical transparency. Crystal structure analysis and evaluation of scintillation properties were performed.

2. Experimental procedure

a) Crystal growth

The starting material was prepared from

We designed the eutectic material system comprising matrix scintillation phase and LiF fiber (See Fig. 1). Neutrons are converted to α -rays by (n, α) reaction of ^6Li in LiF and LiGdF phases. The α -rays absorbed in Tb:LiGdF phases are converted to scintillation light. Refractive index of LiF and LiGdF₄ are 1.38 and 1.45@1064nm, respectively. Scintillation light from LiGdF₄-phase shows 72° of total reflection at the interface. Starting materials were prepared from high-purity fluoride powders of LiF, GdF₃ and TbF₃ (4N, produced by Stela Chemifa Corporation) according to the chemical formula of $\text{Li}_{0.75}(\text{Gd}_{0.99}\text{Tb}_{0.01})_{0.25}\text{F}_3$ at the eutectic point of LiF/LiGdF₄ (See Fig. 2). [14]. $\text{Li}_{0.75}(\text{Gd}_{0.99}\text{Tb}_{0.01})_{0.25}\text{F}_3$ eutectics were grown at the composition of eutectic point of LiF:75 mol%, GdF₃:25 mol%. Crystal growth was performed by the μ -PD method with the tight-vacuum chamber. The detail of crystal growth by the μ -PD method was described in Ref.[13]. In the unidirectional solidification processes such as μ -PD method, LiF and LiGdF₄ 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 0.1-2.0 mm/min. During the crystal growth, the solid-liquid interface was maintained at the position of die.

Fig.1. Schematic drawing of the phase-separated Tb:LiGdF₄-LiF eutectic scintillator.

Fig.2 Phase diagram of GdF₃/LiF

b) Structural evaluation of eutectic composites

Circular and rectangular samples and with 1 mm thickness 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 X-ray radiation (XRD) using RIGAKU RINT-2000.

c) Measurements of luminescence properties

Absorption spectra were measured by the Shimadzu 3101PC spectrometer in the 240-800 nm range. Photoluminescence properties were investigated by a spectrometer (Edinburgh FLS920) using optical source (Edinburgh Xe 900). At the SR-163 spectrometer (ANDOR TECHNOLOGY) equipped with the CCD detector DU920P (ANDOR TECHNOLOGY) the radioluminescence spectra were measured under an α -ray from a ²⁴¹Am source.

3. Results and discussion

a) DSE system of LiGdF₄-LiF eutectic

White rod with 2 mm diameter and 60 mm length was obtained by the μ -PD method (See Fig. 3). A 2 mm diameter and 1.5 mm height sample was cut and polished. The result of powder XRD of the grown eutectic was shown in Fig. 4. The grown eutectic showed two phases of LiF and LiGdF₄. The BEI of the grown crystals in vertical and transverse cross-section are shown in Fig. 5. The grown eutectic structure showed rod-like shape. Up to now, some groups investigated transformation

between rod-like shape and lamellar shape in eutectic structure [16-19]. They conclude that transformation of the eutectic depended on the volume ratio of components and the relative interface energy [20]. Volume ratio of LiF:LiGdF₄ in this system is about 3:7 and LiF formed the rods as proved by the EDX results on the obtained eutectics. It is in good agreement with the previous reports. The average rod size was about 1.7 μm in Fig. 5-b and the fiber density was about 6600 fibers/mm² at the growth speed of 0.15 mm/min. At the growth speed of 1.00 mm/min, the average rod size was about 1.3 μm in Fig.5-e and the fiber density was about 12600 fibers/mm². The average rod diameter of LiF phase in the LiGdF₄/LiF eutectic was found to be quite consistent. The average rod diameter of LiF phase as a function of pulling rate is plotted in Fig. 6. The generally accepted relation $\lambda \sim v^{-1/2}$, where λ is the average rod diameter and v is the solidification rate[21], appears to apply well to the LiGdF₄/LiF system. Well aligned fiber like eutectic structure was obtained the growth speed of 0.15 mm/min. The longest rod at the growth speed of 0.15 mm/min was about 1200 μm in Fig. 5-f. Fig. 7 showed a polished sample cut from the grown eutectic at the growth speed of 0.15 and 0.20 mm/min. The sample grown at speed of 0.15mm showed optical transparency like bundle optical fibers and the background line is visible on the surface through the transparent rods grown in the material.

Fig. 3. Photograph of the LiGdF₄/LiF eutectic crystal grown by μ -PD method.

Fig. 4. Powder X-ray diffraction pattern for the LiGdF₄-LiF eutectic.

Fig. 5. BEI of the polished LiGdF₄/LiF eutectic crystal, a) transverse cross-section of the eutectic grown at the speed of 0.1 mm/min, b) 0.15 mm/min, c) 0.2 mm/min, d) 0.5 mm/min and e) 1.0 mm/min. f) vertical cross-section of the eutectic along growth direction at the speed of 0.15 mm/min.

Fig. 6. Average LiF rod size versus pulling rate for the LiGdF₄-LiF eutectic

Fig. 7. Photograph of the polished samples cut from the grown eutectic at the growth speed of 0.15 and 0.20 mm/min.

b) Luminescence and scintillation properties.

Transmittance spectra of the grown eutectics at the growth speed of 0.15 and 0.20 mm/min were shown in Fig. 8. Around 40% of transmittance at 1.5mm thick was observed in 380-630 nm range at the growth speed of 0.15 and 0.20 mm/min sample. Emission and excitation spectra of the grown Tb doped LiGdF₄-LiF eutectic were measured at 274 nm excitation and 450-650 nm emission, respectively (fig. 9). Radioluminescence spectra of the grown Tb doped LiGdF₄-LiF eutectics at the growth speed of 0.15 and 0.20 mm/min measured under α -ray excitation from a ²⁴¹Am source was shown in Fig. 10. The expected 380-630 nm emission of Tb³⁺ ⁸S-⁶P transition have been observed. The weak emission of Gd³⁺ 4f-4f transition at 310 nm was observed under alpha-ray excitation. The Observed excitation bands peaking at around 275 nm and 310 nm on Fig.9 correspond respectively to the ⁸S^{7/2}-⁶I_{7/2} and ⁸S_{7/2}-⁶P_J absorption bands of Gd³⁺. Emission intensity of the 0.15 mm/min sample was higher emission intensity comparing to the 0.20 mm/min sample and around 9% of a commercially available Td:Gd₂O₂S (GOS) scintillator plate. Well aligned eutectic structure was realized by optimization of growth speed and, transparency was improved. Higher transparency affected to increase of emission intensity.

Fig. 8 Transmittance spectrum of the grown eutectic at the growth speed of 0.15 mm/min.

Fig. 9. Emission and excitation spectra of the grown Tb doped LiGdF₄-LiF eutectic

Fig. 10. Radioluminescence spectra of the grown Tb doped LiGdF₄-LiF eutectic grown at 0.15 and 0.2 mm/min measured under an α -ray from a ²⁴¹Am source.

4. Conclusion

Tb-doped LiGdF₄-LiF eutectics were grown at various growth rates and their directionally solidified eutectic (DSE) system has been investigated. Well aligned fiber like eutectic structure with around 1.7 μ m in diameter and 1200 μ m in maximum length was obtained for the growth speed of 0.15 mm/min. The sample showed optical transparency like bundle optical fibers and around 40% of transmittance at 1.5mm thick was achieved in 380-630 nm range. The expected 380-630 nm emission excited by UV and α -ray, and 270-330nm excitation of Tb³⁺ ⁸S-⁶P transition have been observed. The weak emission of Gd³⁺ 4f-4f transition at 310 nm was also observed under alpha-ray excitation. The Observed excitation bands peaking at around 275 nm and 310 nm correspond respectively to the ⁸S^{7/2}-⁶I_{7/2} and ⁸S_{7/2}-⁶P_J absorption bands of Gd³⁺. We are planning to grow Tb-doped LiGdF₄-LiF eutectics using ⁶LiF as the starting material and evaluate neutron response.

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