Growth and optical properties of LiF/LaF₃ eutectic crystals

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Abstract

Neutron imaging devices employing a scintillator can be used in various fields, and eutectic crystals can be suitable for the imaging with a fine position resolution of a few hundred μm . Since LiF and LaF₃ have different refractive indexes of 1.41 and 1.64 at 300 nm, respectively, the eutectic crystal is expected to behave as a scintillator with light guiding properties. Thus, the optical properties of Ce-doped LiF/LaF₃ eutectic crystal grown by micro-pulling down method were investigated. The light output of LiF/Ce:LaF₃ eutectic crystal was relatively small. The emission peaks at 300 nm originating from Ce³⁺ of 5d-4f transition were observed under excitation by UV photons and 5.5 MeV alpha rays. Moreover, the photo-luminescence decay time of Ce-doped LiF/LaF₃ eutectic crystal was estimated to be 17 ± 1 ns.

Keywords: Eutectic crystal; Neutron Scintillator; LaF₃; LiF

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1. Introduction

Neutron detection and imaging devices are (expected to be) used in various fields such as crystallography, homeland security, etc. [1, 2]. Since ^3He has an unusually large cross-section for neutron capture (approximately 5300 barns for thermal neutrons [3]), a ^3He -gaseous detector has been used for neutron detection [3, 4]. However, the ^3He sources are being depleted, and an alternative suitable nuclei are searched for. Then several scintillator crystals containing elements with high-cross-section nuclei, like ^{10}B (~3,800 barns [3]), ^6Li (~940 barns [3]), have been investigated for detection of thermal neutrons [5-8]. In addition, some groups have studied neutron imaging with a scintillator [9-11].

When ^6Li undergoes a nuclear reaction after absorption of a thermal neutron, it disintegrates into an alpha particle and a triton ($^3\text{H}_1$) as follows:

the 4.78-MeV energy, called Q-value, is distributed between the triton (2,728 keV) and the alpha particle (2,055 keV). Due to these particles, scintillation light is emitted. On the other hand, ^{10}B undergoes the following reactions:

and

where the branching ratios of (2) and (3) are 94 and 6%, respectively. Although ^{10}B has a larger cross section for a thermal neutron than ^6Li , the Q-value and the alpha-ray energies produced by reactions (2) or (3) are twice as small as that of the reaction (1). Moreover, gamma rays can be generated from the (2) as a noise. Thus, signal-noise-ratio for ^6Li -containing scintillator is expected to be better than that of ^{10}B -containing scintillator. We have investigated neutron scintillators containing ^6Li , such as Ce-doped LiCaAlF_6 [8], which had good signal-noise-ratios (alpha-gamma ratio). Since fluoride crystals have generally low melting points with respect to the other crystals such as oxide crystals, they can be produced with a lower cost.

In order to readout position-sensitive signals (electrons) in the gaseous neutron detector, micro pattern gaseous detectors with an anode pitch of a few hundred μm are used [4]. As a result, the gaseous type has a position resolution of a few hundred μm . Meanwhile, the scintillation type has worse position resolution, because a scintillation array camera has a pixel pitch of more than ~1 mm. Even if a monolithic crystal is coupled to a fine structure photo detector, like a Charge Coupled Device (CCD) camera, the scintillation light would be spread in the crystal.

Recently, a light-guide scintillator based on eutectic crystals consisting of components with different refractive indexes has been reported for X-ray imaging [12]. This needle-like shape crystal scintillator was grown by micro-pulling (μ -PD) down method. Thus, we decided to study ^6Li -containing eutectic crystals for neutron detector in this paper.

Figure 1 shows a schematic view of position-sensitive eutectic crystals for neutron scintillator: (i) normal type (Lamellar structure) and (ii) cylinder type consisting of two components with different refractive indexes, respectively. The latter type has a cylinder (tube)-shape component. When this cylinder part has a higher refractive index than the other component, the scintillation light can be guided through the cylinder like in an optical fiber cable (Fig. 1 (ii-1)). Both types consist of LiF as a neutron-alpha ray converter and an emitter excited by the resulting alpha rays. Using Monte Carlo method including Bethe-Bloch formula, the stopping range of 2055-keV alpha ray (distance of passing through matter until their energy become to zero) is $5.5\ \mu\text{m}$ in the LiF crystal, therefore the Lamellar pitch or phase width should be less than $5.5\ \mu\text{m}$ so that the alpha ray can reach the emitter zone.

LiF and LaF_3 have refractive indexes of 1.41 and 1.64 at 300 nm [13, 14] therefore LaF_3 is expected to guide or separate the scintillation light into position-sensitive photo detectors. In addition, Moses et al reported that 1-mol% Ce doped LaF_3 has a scintillation light output of 440 photons/MeV excited by gamma rays [15], thus, $\text{Ce}:\text{LaF}_3$ can be also used as emitter. Although the light output of $\text{Ce}:\text{LaF}_3$ is smaller when compared to well-known fluoride scintillators such as CaF_2 , BaF_2 , this material has a larger refractive index (n) than CaF_2 ($n=1.46$ at 300 nm), BaF_2 ($n=1.51$ at 300 nm). In this paper, first we report the structure of LiF/ LaF_3 eutectic crystals grown by the μ -PD method, and then we show the optical properties of Ce-doped LiF/ LaF_3 eutectic crystals in order to study its feasibility for the neutron scintillator.

2. Materials and Experimental Methods

Pure and Ce-doped LiF/ LaF_3 eutectic crystals were grown by the μ -PD method (details of the μ -PD method are described in Ref. [16,17]). Here the eutectic point of LiF/ LaF_3 system is LiF : $\text{LaF}_3 = 83.8 : 16.2$ at approximately 770°C [18], so the initial composition was $(\text{LiF})_{83.8}\{(\text{La}_{1-x}, \text{Ce}_x)\text{F}_3\}_{16.2}$ ($x = 0$ or 0.01). The powders of the crystal materials (LiF, LaF_3 and CeF_3) were of 99.99% purity, and the atmosphere was a gas mixture of $\text{Ar}:\text{CF}_4$ in a pressure ratio of 97:3 at 1 atm (sealed). A Pt wire was used as the seed, and the pulling rates were 0.1, 0.5, 1.0, 2.0 mm / min for pure LiF/ LaF_3 eutectic crystals. In order to confirm that a phase width (Lamellar pitch) is of less than approximately $5.5\ \mu\text{m}$, field emission scanning Electron Microscope / Electron Probe Micro Analyzer (FE-SEM/EPMA, JEOL, JXA-8530F, 10kV, 20nA) was used. After checking, 1-mol% Ce-doped LiF/ LaF_3 eutectic crystals were grown by the μ -PD method with an optimized pulling rate (we decided the rate of 0.5 mm / min). In order to check the phase of the obtained crystals, powder X-ray diffraction analysis was performed from 20° to 80° using a diffractometer (RIGAKU, RINT2000). The X-ray source was using $\text{CuK}\alpha$ line with an accelerating voltage of 40 kV, and tube current of 40 mA.

We investigated some optical properties of the samples after cutting and polishing; (i) Transmittance

was measured with a spectrophotometer (JASCO, V-530), (ii) Photo-luminescence spectra (emission and excitation) were measured with a spectrofluorometer (Edinburgh Instruments, FLS920), (iii) Photo-luminescence decay curves were obtained with the spectrofluorometer and a Flash lamp (Edinburgh Instruments, nF900) (iv) the radio-luminescence spectra at room temperature were measured using the same spectrofluorometer and 5.5-MeV alpha rays (^{241}Am) as the excitation source.

3. Results and discussion

The pure LiF/LaF₃ (LiF : LaF₃ = 83.8 : 16.2) eutectic crystal was successfully grown by the μ -PD method (Fig. 2). Powder X-ray diffraction patterns for the LiF/LaF₃ eutectic crystal showed peaks consistent with the expected LiF and LaF₃ phase, which possesses cubic and trigonal crystal systems with space groups *Fm3m* and *P3c1*, respectively, as shown in Fig. 3.

Back Scattering Electron (BSE) images for several pure LiF/LaF₃ eutectic crystals grown with pulling rates of 0.1, 0.2, 0.5, 1.0 and 2.0 mm / min are shown in Fig.4. As the pulling rate increased, the phase thickness of LiF and LaF₃ became smaller: roughly 5, 3, 1.6, 1.2 and 0.8 μm at 0.1, 0.2, 0.5, 1.0 and 2.0 mm / min, respectively. Although the phase thickness for all the samples was less than the stopping range of 2,055-keV alpha particle (5.5 μm), the thickness smaller than 2.75 (= 5.5 / 2) μm is more acceptable. Therefore, pulling rate should be faster than 0.5 mm / min. On the other hand, it was difficult to grow a eutectic crystal with a pulling rate of over 2.0 mm / min.

Normal structures were obtained at 0.1, 0.2 1.0 and 2.0 mm/min whereas a cylinder structure was formed at 0.5 mm/min; even over 90% of the area was normal one (Fig. 4). Therefore, a 1-mol% Ce-doped LiF/LaF₃ eutectic crystal was grown with a pulling rate of 0.5 mm / min.

The as grown 1mol% Ce-doped LiF/LaF₃ crystal was cut and polished to 1-mm thick samples. EPMA elemental analysis (Fig. 5) shows that Ce and La are distributed in the same phase suggesting a substitution at the La³⁺ sites by Ce³⁺. This is a confirmation of successful growth of LiF/Ce:LaF₃ eutectic crystal. However, only normal type structure (Lamellar structure) was observed. Moreover, phase width was roughly 1.2-1.4 μm which is smaller than that in pure LiF/LaF₃ with the same pulling rate. For this material, the cylinder structure was found to be unstable.

Photo-luminescence emission and excitation spectra are shown in Fig. 6, where excitation and emission wavelength were 266 and 297 nm for emission and excitation spectra, respectively. 297-nm emission was ascribed to Ce³⁺ 5d-4f emission. In addition, broad peak was found over 350 nm, and this broad component can be due to defect emission or color center. Moreover, a photo-luminescence decay time was measured and fitted using a following equation:

$$f(t) = a \cdot \exp(-t/b) + c, \quad (4)$$

where *a* and *b* are free parameters, and *c* is the constant. Using *b*, a decay time of Ce-doped LiF/LaF₃ eutectic crystal was estimated to be 17 $\pm$ 1 ns (Fig. 7). This decay time is similar to that of other scintillators

doped with Ce^{3+} [19, 20]; 1 mol% Ce-doped LaF_3 has the photo-luminescence decay time is 17 ± 1 ns. Figure 8 shows the intensity of 5.5-MeV alpha-ray (^{241}Am) excited radio-luminescence as a function of wavelength. The emission peak at 300 nm originating from Ce^{3+} of 5d-4f emission resembled to that in the photoluminescence spectrum.

We also measured the light output and scintillation decay time excited by 5.5-MeV alpha-ray (^{241}Am) or neutrons (^{251}Cf) using a photo multiplier. It was difficult to determine the light output and decay time using photon-counting method because of the small signal. However, the scintillation emission peak originating from 5d-4f transition of Ce^{3+} was observed in the radio-luminescence.

4. Conclusions

LiF/LaF_3 eutectic crystal, $(\text{LiF})_{83.8}\{(\text{La}_{1-x}, \text{Ce}_x)\text{F}_3\}_{16.2}$ ($x = 0$ or 0.01) was successfully grown by the μ -PD method for the neutron-imaging application for the first time. Although some area (less than 10%) of pure LiF/LaF_3 eutectic crystal grown at a pulling rate of the μ -PD was 0.5 mm / min, had a cylinder type structure, most crystal samples were found to be the normal type ones (with lamellar structure). Ce-doped LiF/LaF_3 eutectic crystal, grown by the μ -PD method with the rate of 0.5 mm / min, had only normal type structure (Lamellar structure). From the above results, we found the cylinder structure was not created.

All the samples had low transmittance of less than 1% due to the light scattering. Although the light output of LiF/Ce:LaF_3 eutectic crystal was small, this crystal had an emission peak at 300 nm originating from Ce^{3+} of 5d-4f transition excited by 5.5 MeV alpha rays. Even this material was formed as the normal type (Lamellar structure), we succeeded in detection of the scintillation light. As a next step, we test other materials such as LiF/Ce:BaF_3 , or Li-containing oxide eutectic crystal to realize the cylinder structure..

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Figure captions

Figure1. Schematic view of eutectic scintillation crystals. n_i ($i=1,2$) denote the refractive indexes. (i) normal type ($n_1 \approx n_2$), (ii) light-guide type, $n_1 < n_2$ and $n_1 > n_2$ for (ii-1) and (ii-2), respectively. Dotted arrows denote scintillation light.

Figure2. Photograph of the as-grown LiF/LaF₃ eutectic crystal.

Figure3. Powder X-ray diffraction patterns of pure LiF/LaF₃ eutectic crystal. Closed triangles and open circles denote the LiF and LaF₃ phase, respectively (X-ray diffraction powder catalogue card 45-1460 and 32-0483 for LiF and LaF₃ phase, respectively).

Figure4. Back Scattering Electron (BSE) images for several pure LiF/LaF₃ eutectic crystals grown with pulling rates of 0.1 (a), 0.2 (b), 0.5 (c), 1.0 (d) and 2.0 (e) mm / min.

Figure5. Element Mapping for Ce-doped LiF/LaF₃ eutectic crystal. (a)-(c) denote the La, F and Ce mapping, respectively.

Figure6. Excitation (a) and emission (b) spectra of Ce-doped LiF/LaF₃ eutectic crystal.

Figure7. photo-luminescence decay curve (a), and the instrumental response (b). Red line denotes the best-fitting line.

Figure8. Emission spectrum of Ce-doped LiF/LaF₃ eutectic crystal excited by 5.5 MeV alpha rays.

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Fig 10