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# Effects of Eu concentration control on crystal growth and scintillation properties for Eu:LiSrAlF$_6$ crystals

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ABSTRACT

Eu doped LiSrAlF$_6$ (Eu:LiSAF) crystals with various Eu concentrations were grown by a micro-pulling-down (μ-PD) method and the effects of Eu concentration control on crystal growth and scintillation properties for Eu:LiSAF crystals were investigated as a neutron scintillator. As-grown Eu0.3%:LiSAF crystal had no visible inclusion while milky parts were observed in the crystals with higher Eu contents. The secondary phases with the chemical composition of $EuF_2$ or $EuF_3$ in the Eu:LiSAF matrix were observed for the crystals with high Eu contents while the secondary phase couldn't be observed in the powder XRD patterns. In the radioluminescence spectra of Eu:LiSAF crystals under α-ray irradiation, emission peaks around 375 nm originated from 5d–4f transition of $Eu^{2+}$ ion were observed. The light yields systematically increased with an increase of actual Eu contents in the crystals and the decay times were 1490–1620 ns.



## 1. Introduction

Scintillating materials which can detect thermal neutron have been widely used for neutron detectors of security devices at airport and harbor. Host material of the neutron scintillator crystal is required to contain elements with high cross-section for thermal neutron as represented by $^{10}B$, $^{6}Li$, $^{155}Gd$ and $^{157}Gd$. Luminescent centers such as rare-earth ions and transition metals which are added in the host material of neutron scintillator crystal can emit luminescence under the excitation by α-ray which is generated by reaction between neutron and the elements with high cross-section for thermal neutron. At the same time, the host material has to be composed of the elements with low effective atomic number in order to decrease the effects by γ-ray. If the host material has high sensitivity to γ-ray, it is difficult to separate the effects by neutron and γ-ray.

The $^{3}He$ gas with high cross-section to thermal neutron and low sensitivity to background γ-ray has been widely used in some neutron detectors. However, by increasing worldwide demand of the neutron detection for some security applications, $^{3}He$ supply crisis was caused and alternatives for neutron detection have been required [1]. Therefore, novel neutron scintillators have been energetically investigated in the world [2].

In these researches, we have developed Eu doped LiCaAlF$_6$ (Eu:LiCAF) and LiSrAlF$_6$ (Eu:LiSAF) scintillator crystals. The crystals indicated some attractive properties as represented by high stopping power for thermal neutrons, low sensitivity to γ-ray, high light yield and no hygroscopicity [3–6]. However, the segregation coefficients of $Eu^{2+}$ ion in LiCAF and LiSAF crystals are extremely small and milky parts including $EuF_2$ impurity are easily generated in the crystals with high Eu concentrations [7]. The milky parts in the crystals cause a decrease in transmittance and the light yield of the scintillator crystals generally is decreased by a decrease of emission light. The generation of milky parts in the crystals was also observed in the case of the large bulk single crystal grown by the Czochralski method and inhomogeneity of light yield in the bulk crystal is considered as a commercial problem.

In this paper, Eu doped LiSr$_{1-x}$Eu$_x$AlF$_6$, $x$ = 0, 0.003, 0.006, 0.008 and 0.01 (undoped LiSAF and Eu0.3, 0.6, 0.8 and 1 mol% doped LiSAF) single crystals were grown by a micro-pulling-down (μ-PD) method and their structures, chemical compositions and scintillation properties were investigated. These results can reveal the effects of Eu concentration and the milky part on crystal growth and scintillation properties of Eu:LiSAF crystals.

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## 2. Experimental

### 2.1. Crystal growth

$^{6}$Li-enriched LiF (95% $^{6}$Li), $SrF_2$, $AlF_3$, $EuF_3$ powders with 4 N purity were used as starting materials to prepare mixed powders with nominal compositions of $LiSr_{1-x}Eu_xAlF_6$, $x = 0$, 0.003, 0.006, 0.008 and 0.01. Mixed powders were set in a graphite crucible and the crucible was placed in the center of a High-frequency induction coil in a vacuum-tight chamber. Inside of the chamber was evacuated up to $10^{-4}$ Pa and the crucible was heated at approximately 300 °C during the baking process in order to remove oxygen traces caused by the moisture of raw materials, crucible, insulator and adsorbates on the chamber surface. Then, inside of the chamber was filled with mixed gas of 90% Ar (99.9999%) and 10% $CF_4$ (99.999%) up to ambient pressure. Platinum wire was used as the seed for crystal growth and growth rate was 0.1 mm/min during crystal growth. As-grown crystals were cut and polished for measurements of optical and scintillation properties. Thicknesses of specimens for the measurements are 1 mm.

### 2.2. Crystal structure and chemical composition

To identify the phases of grown crystals, powder X-ray Diffraction (XRD) measurement using RINT-2000 (RIGAKU) was carried out in the $2\theta$ range from 15° to 70°. The X-ray source was Cu Ka (accelerating voltage: 40 kV, beam current: 40 mA) and the scan step and speed were 0.02° and 2°/min, respectively. The chemical compositions of grown crystals were investigated by Scanning Electron Microscope (SEM) (Hitachi, S-3400 N) with Energy Dispersive X-ray Spectroscopy (EDS) (Horiba, EMAX X-act) and Field Emission Scanning Electron Microscopy (FE-SEM) with Electron Probe Micro-Analyzer (EPMA) (JEOL, JXA 8530F).

### 2.3. Optical and scintillation properties

The transmittance spectra were measured by the JASCO V550 spectrofluorometer in the wavelength range of 190–900 nm. The radioluminescence spectra were investigated by the Edingburgh FLS920 under α-ray irradiation from $^{241}$Am radiation source.

In the evaluations of neutron responses, pulse height spectra under neutron excitation from a $^{252}$Cf radiation source were performed. $^{6}$Li-loaded glass scintillator with the size of $2 \times 6 \times 1^{t}$ mm$^3$ (GS20; Saint Gobain) which had the light yield of 6,000 ph/n [8] was used as a standard sample. The crystals were optically coupled to a window of photomultiplier tube (PMT, Hamamatsu R7600U) with optical grease (OKEN 6262A). Electrical pulse signals detected by the PMT were fed into a preamplifier (ORTEC 113), the shaping amplifier (CLEAR-PULSE 4479), the multichannel analyzer (Amptec 8000A) and the personal computer for data analysis. Decay curves were measured by a oscilloscope under same condition.

## 3. Results and discussions

### 3.1. Crystal growth

Undoped and Eu doped $LiSrAlF_6$ crystals grown by the μ-PD method are showed in Fig. 1. All grown crystals with 2 mm diameter had no visible crack in the crystals. Undoped and Eu0.3%: $LiSrAlF_6$ crystals indicated high transparency and there were no visible crack and inclusions in these crystals. In contrast, milky parts were observed in the Eu0.6, 0.8 and 1%:$LiSrAlF_6$ crystals and amount of the milky parts increased with increase of Eu contents.

### 3.2. Crystal structure and chemical composition

Parts of the grown crystals were perfectly ground by an agate mortar to identify their phases of grown crystals by the powder XRD measurement. Powder XRD patterns of the specimens are shown in Fig. 2. All diffraction peaks of as-grown crystals were identified by the LiSAF structure and no secondary phase was observed. Amounts of the milky parts in the crystals with high Eu concentration are considered to be smaller than the detection limit of the apparatus. The relative intensities of some diffraction peaks in the XRD patterns varied in the crystals and the result are considered to be due to the appearance of one particular plane by cleavage during grounding the crystals. Polished surfaces perpendicular to the growth direction were observed by the SEM with back scattering electron (BSE) and the BSE images are shown in Fig. 3. In the images, secondary phases were observed in the Eu:LiSAF matrix and the milky parts are considered to be composed of $EuF_2$ or $EuF_3$ phases according to the analysis of chemical composition by EDX. Actual Eu concentrations in the Eu0.3, 0.6, 0.8 and 1 mol%:

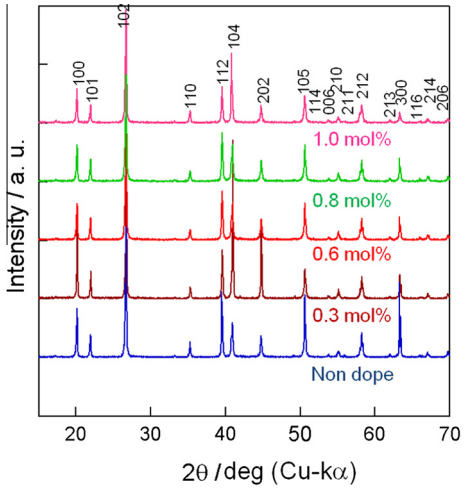


**Fig. 2.** Powder XRD patterns of Eu:LiSAF crystals.

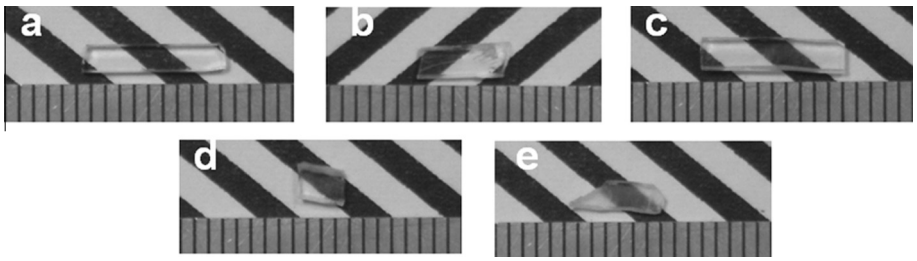


**Fig. 1.** Polished Eu:LiSAF crystals. (a) undope, (b) Eu0.3%, (c) 0.6%, (d) 0.8% and (e) 1%.

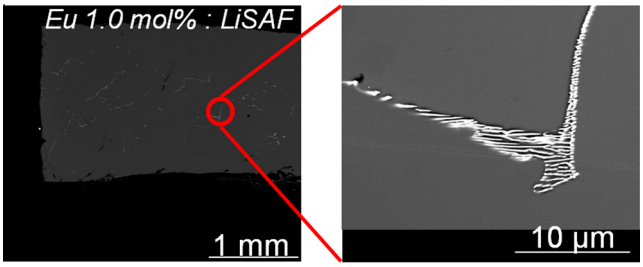


**Fig. 3.** BSE images of Eu1%:LiSAF crystal.

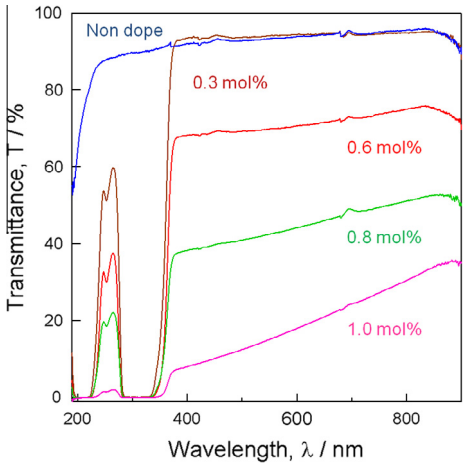


**Fig. 4.** Transmittance spectra of Eu:LiSAF crystals.

LiSAF specimens were approximately 0.22, 0.27, 0.30 and 0.49 mol%.

### 3.3. Optical and emission properties

Fig. 4. indicates the transmittance spectra of Eu:LiSAF crystals. Eu doped specimens showed absorption peaks around 300 and 200 nm which originated from the transition from the 4f ground level to the excited 5d levels of $Eu^{2+}$ ion. Transmittance of Eu0.3%: LiSAF crystal above 300 nm was almost same as that of undoped LiSAF crystal. In contrast, the transmittance of Eu:LiSAF crystals with high Eu contents systematically decreased with an increase of Eu contents. Radioluminescence spectra of Eu:LiSAF crystals under α-ray excitation from $^{241}Am$ radiation source are shown in Fig. 5. All Eu:LiSAF crystals indicated emission peaks around 380 nm which originated from the 5d–4f transition of $Eu^{2+}$ ion. Wavelength of the emission peaks were systematically increased

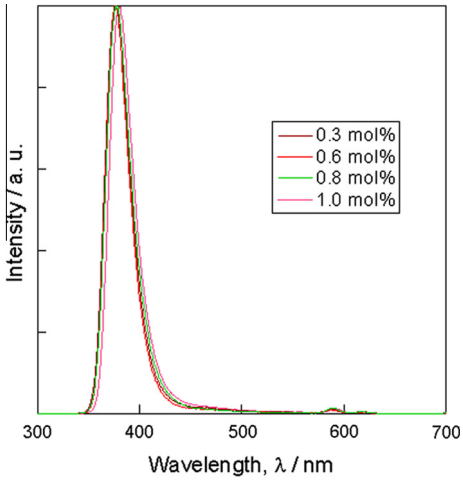


**Fig. 5.** Radioluminescence spectra of Eu:LiSAF crystals under α-ray excitation.

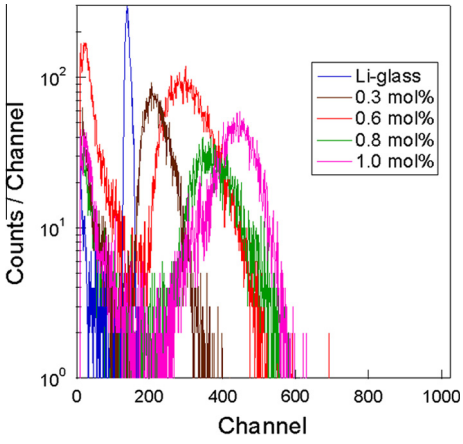


**Fig. 6.** Pulse-height spectra of Eu:LiSAF crystals under neutron irradiation.

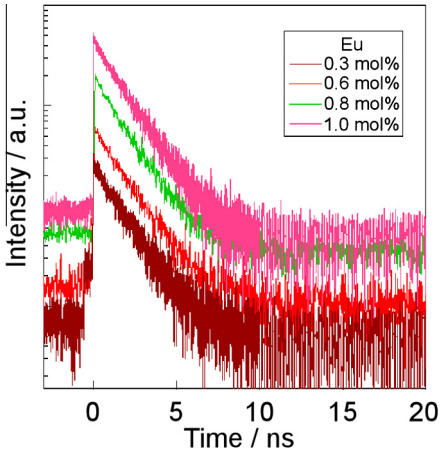


**Fig. 7.** Decay curves of Eu:LiSAF crystals under neutron irradiation.

with an increase of Eu contents. The results are considered to be due to the increase of self-absorption from Eu ion.

### 3.4. Scintillation properties

The pulse-height spectra of the specimens under neutron excitation are shown in Fig. 6. Peaks which originated from emission from Eu ion were observed for all Eu:LiSAF crystals and channels of the peaks were systematically increased with an increase of Eu content. The result means that the light yield of Eu:LiSAF crystals increased with an increase of actual Eu content in the crystals and the increases were more than the decrease of light yield by the generation of milky parts. The light yields of Eu0.3%, 0.6%, 0.8% and 1%:LiSAF crystals were 9200, 13,000, 15,000, and 20,000 photons/neutron, respectively. In the same condition, decay curves of the crystals under neutron irradiation were measured and the results are shown in Fig. 7. The decay curves could be fitted by the single exponential decay expression. Estimated decay times of the crystals with Eu0.3%, 0.6%, 0.8% and 1% concentrations were 1540, 1620, 1490 and 1550 ns, respectively. Especially, Eu0.6%:LiSAF crystal indicated minimum decay time and Eu0.8%:LiSAF crystal was maximum.

## 4. Conclusion

Eu doped LiSAF crystals (Undope, Eu0.3, 0.6, 0.8 and 1 mol%) were grown by the μ-PD method and fiber crystals 2 mm in diameter were obtained. There was no visible inclusion in undoped and Eu0.3%:LiSAF crystal while milky parts were observed in the Eu0.6, 0.8 and 1%:LiSAF crystals and the milky parts which were composed of $EuF_2$ or $EuF_3$ phases increased with an increase of Eu contents. Transmittance of Eu0.3%:LiSAF crystal above 300 nm was almost same as that of undoped LiSAF crystal while the transmittance of Eu:LiSAF crystals with high Eu contents systematically decreased with an increase of Eu contents. The emission peaks around 380 nm were observed in the Eu:LiSAF crystals under α-ray irradiation and the emission was due to the 5d–4f transition of $Eu^{2+}$ ion. The light yields systematically increased with an increase of Eu contents despite the generation of milky parts. The results suggest that more increase of the light yield is expected by the decrease of milky parts, in other words, maintenance of high transmittance for Eu:LiSAF crystal with high Eu concentration.

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