

Ce and Eu-doped LiSrAlF₆ scintillators for neutron detectors

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ABSTRACT

Ce 1%, Eu 1%, and Eu 2%-doped LiSrAlF₆ (LiSAF) single crystals were grown by the micro-pulling-down method for thermal neutron applications. The crystals were transparent, 2.0 mm in diameter and 20–40 mm in length. Neither visible inclusions nor cracks were observed. Their transmittance spectra were measured. The strong absorption lines were observed at 200, 240, and 300 nm for Ce:LiSAF due to Ce³⁺ 4f–5d transition. In Eu:LiSAF, 200 (4f–5d) and 300 (4f–4f) nm absorption lines were detected. The samples demonstrated strong emission peaks at 300 nm (Ce:LiSAF) and 370 nm (Eu:LiSAFs) when they were irradiated with ²⁴¹Am α -rays simulating the α -particles from the ⁶Li(n, α) reaction. Thermal neutron responses were examined under ²⁵²Cf irradiation. The absolute light yield of Ce, Eu 1%, and Eu 2% crystals were 3400, 18000, and 30000 ph/n, respectively. Main components of the scintillation decay time of Ce, Eu 1%, and Eu 2%-doped LiSAFs were 63, 1293, and 1205 ns.

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1. Introduction

After the terrorism attacks of 9.11, neutron sensing techniques attract a great deal of interest because neutrons can penetrate even in a heavy metal boxes that cannot be inspected by the conventional X-ray scanners. Historically, ³He gas counters have been used as basic sensors for thermal neutron detection. However, increased consumption of ³He gas counters resulted ³He supply crisis. The only practical source of ³He in the world is the radioactive decay of tritium (³H). Tritium decays to ³He at a rate of 5.5% per year. It was produced over the time frame from 1955 to 1988 for use as a critical ingredient of nuclear weapons. The current worldwide supply of ³He is estimated at 20 kL/y, while the current estimation of ³He demands is about 100 kL/y. Thus, replacement of ³He is an urgent issue.

As the alternative for ³He gas, we propose application of ⁶Li based inorganic thermal neutron scintillator, because ⁶Li has high stopping power for thermal neutrons and high Q-value (4.8 MeV) for the reaction of ⁶Li + n → T + α . Up to now, number of rare earth doped LiCaAlF₆ scintillators were intensively studied (Gektin et al., 2002; Yanagida et al., 2009, in press; Shimizu et al., 2009; Yoshikawa et al., 2010; Kawaguchi et al., in press). Among them,

Ce³⁺ and Eu²⁺ doped ones exhibited good scintillation properties under neutron excitation.

In the present work, we examine scintillation properties of Ce and Eu-doped LiSrAlF₆ crystals. Substitution of Ca of LiCaAlF₆ with Sr simplifies doping of these crystals with large rare earth cations, because the ion radius of Sr²⁺ host cation is much larger than that of Ca²⁺. Optical properties of these materials such as absorption and emission spectra were well studied by other groups (Kirm et al., 2005; Shiran et al., 2004, 2005), but α -ray and neutron irradiated scintillation properties were not reported. Ce 1%, Eu 1%, and Eu 2%-doped LiSAF crystals were produced by the micro-pulling-down (μ -PD) technique (Yoshikawa et al., 2004). The crystals were cut and polished, and their transmittance and radio luminescence spectra were then recorded. Finally, ²⁵²Cf excited pulse height and decay time were evaluated.

2. Experimental procedures

The crystals of nominal compositions of Li(Sr_{1-x}RE_x)AlF₆ (x = 0.01 or 0.02, RE = Ce or Eu) were grown using mixtures of 4N LiF (natural, 7.5% ⁶Li), SrF₂, AlF₃, and CeF₃ powders (Stella Chemifa Co. Ltd.) as starting materials. In LiSAF, the number density of Li is $9.1 \times 10^{21} \text{ cm}^{-3}$, which is a comparable to that of Li-glass ($1.5 \times 10^{22} \text{ cm}^{-3}$). Crystal growth was performed by the μ -PD method from graphite crucible under Ar + CF₄ atmosphere. The starting materials were baked together with the crucible, the

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heater, and the insulators in high vacuum ($<10^{-4}$ Pa) to prevent contamination with oxygen. Tungsten–Rhenium wire was used instead of the seed for the growth initiation, and the growth rate was approximately 0.1 mm/min. The typical thermal setup and the details of the baking procedure for the fluoride crystal growth were reported previously (Yoshikawa et al., 2004).

The Ce and Eu-doped LiSAF samples were cut to the plates with the dimensions of $1 \times 2 \times 5\text{--}10\text{ mm}^3$ and then polished. Transmittance was measured using a JASCO V550 spectrometer in the 190–900 nm range. The radio luminescence spectra were recorded by using Edingburgh FLS920 under ^{241}Am α -ray excitation the α -particles from the $^6\text{Li}(n, \alpha)$ reaction. The main purpose of the radio luminescence measurements was to characterize emission wavelength under α -ray excitation, because the emission intensity of this kind of integrated type measurement is not a quantitative value. The step in the spectra acquisition was set to be 1 nm at each measurement, and all the measurements were carried out at room temperature.

In neutron response evaluations, we mounted the wide surface of each crystal on the PMT (R7600, Hamamatsu) with silicon grease (OKEN 6262A). Thus, self absorption of scintillation photons was negligible because all the samples had 1 mm thickness with several tenth % of transmittance. When neutron from ^{252}Cf was detected, the signals were fed into a preamplifier (ORTEC 113), a shaping-amplifier (ORTEC 572) with 2 μs shaping time, a multichannel analyzer (hereafter MCA, AmpTec 8000 A), and finally to a personal computer. At the same time, decay time profiles were recorded by WE7311 digital oscilloscope (Yokogawa). In the pulse height measurements, the moderator of 5 cm thick polyethylene blocks surrounding the detector was used to decrease the velocity and kinetic energy of fast neutrons from ^{252}Cf . Furthermore, 5 cm thick Pb slabs were placed between the detector and the polyethylene blocks in order to cut background gamma-rays. Since our samples were not enriched by ^6Li , we did not evaluate the detection efficiency.

3. Experimental results

The as cut and polished crystals are illustrated in Fig. 1. It is well seen that Ce 1% and Eu 1%-doped LiSAFs were clearly transparent. On the other hand, Eu 2%-doped specimen was translucent possibly due to the segregation of Eu^{2+} ion. These materials were not hydroscopic. The physical dimensions of Ce 1%, Eu 1%, and Eu 2%-doped LiSAF samples were $2 \times 8 \times 1\text{ mm}^3$, $2 \times 5 \times 1\text{ mm}^3$, and $2 \times 10 \times 1\text{ mm}^3$, respectively.

Fig. 2(a) and (b) demonstrate transmittance spectra of Ce and Eu-doped LiSAFs. Strong absorption lines due to Ce $4f\text{--}5d$ transitions were detected at 200, 240, and 300 nm in Ce:LiSAF, and $\sim 80\%$ transmittance in the wavelength range >310 nm was also observed. Eu:LiSAFs had strong absorption due to Eu^{2+} $4f\text{--}5d$ transitions at 200 and Eu^{2+} $4f\text{--}4f$ transitions at 300 nm. Eu 1% doped crystal was transparent at wavelength range >400 nm, while Eu 2% doped one was translucent (30–40%). Thus, these

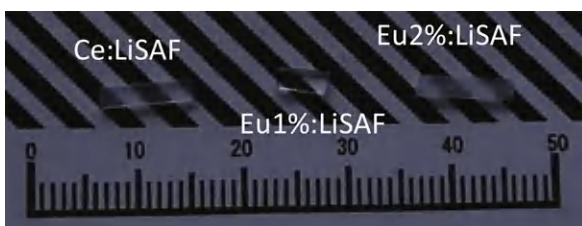


Fig. 1. View of Ce 1% (left), Eu 1% (center), and Eu 2% (right) – doped LiSAF single crystalline samples.

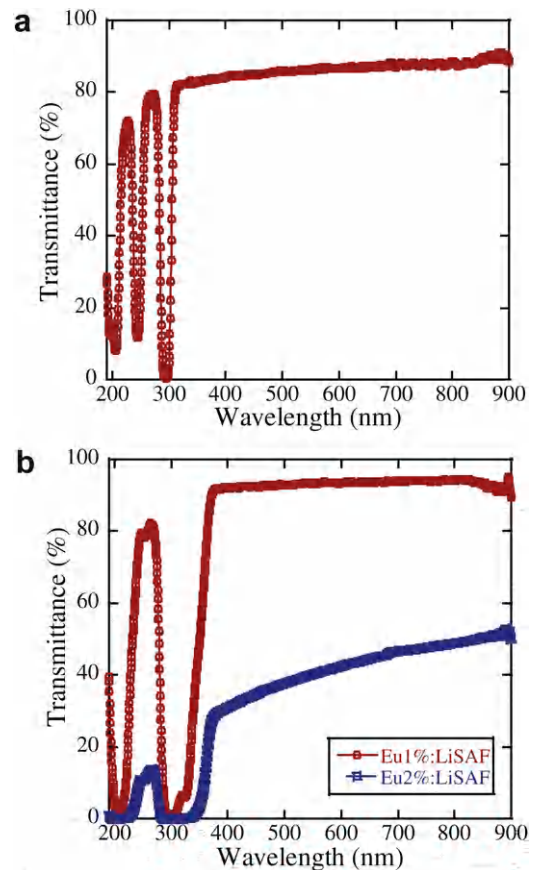


Fig. 2. Optical transmittance spectra of Ce (a) and Eu (b) doped LiSAF crystals.

results confirmed that rare earth cations substituted host cations in the LiSAF lattice.

Radio luminescence spectra under ^{241}Am α -ray excitation are shown in Fig. 3. Fig. 3(a) demonstrates the emission spectrum of Ce:LiSAF where intense emission was detected at 280 and 320 nm. This emission property is same as that of Ce-doped LiCaAlF_6 (Yanagida et al., 2009). Eu:LiSAF had one intense emission peak at 370 nm, as shown in Fig. 3(b). This intense emission was attributed to $4f^7 \rightarrow 4f^65d$ transition of Eu^{2+} ion that is consistent with the previous report of photoluminescence one at 9 K (Kirm et al., 2005). These results illustrate that Ce and Eu:LiSAFs act as actual scintillation devices at least in integrated type measurement.

Thereafter, pulse height analysis was performed. Fig. 4 represents pulse height spectra of LiSAFs compared with $2 \times 8 \times 1\text{ mm}^3$ Li-glass GS20 scintillator that has light yield of 6000 ph/n (van Eijk, 2004). The emission wavelengths of GS20 and Eu-doped LiSAF are close. Therefore, it was possible we can directly evaluate the absolute light yield of Eu:LiSAF scintillators. The peak channel of GS20, Eu 1%, and Eu 2% doped LiSAF were 300, 900, and 1500 ch, respectively. Thus, the absolute light yield of Eu 1% and Eu 2% doped LiSAF samples were evaluated as 18000 ± 2000 and 30000 ± 3000 ph/n, respectively. The peak channel of Ce:LiSAF was 150 ch. Therefore, taking into consideration the quantum efficiency of the PMT at 300 nm, the absolute light yield was calculated to be 3800 ± 400 ph/n. It is noted that the present value for Eu 2% doped crystal was achieved in the translucent sample (30–40% transparency). Thus, there is a chance to increase the light yield by improving the growth conditions and the crystal quality. Additionally, this translucence may affect the energy resolution.

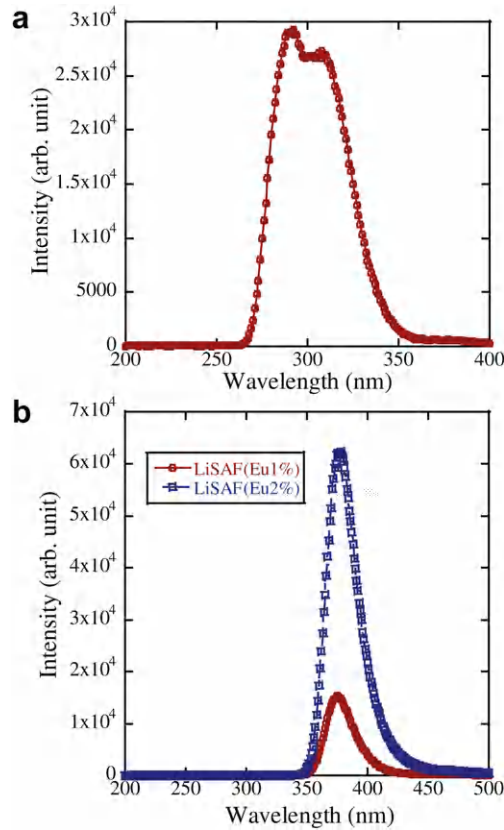


Fig. 3. ^{241}Am α -ray excited radio luminescence spectra of Ce-doped (a) and Eu-doped (b) LiSAF crystals.

The decay curves are shown in Fig. 5. As it is well seen in the figure, decay time profiles of Ce:LiSAF and Eu:LiSAF can be well reproduced by double or single exponential function. The decay time components of Ce:LiSAF were 63 ± 11 and 958 ± 32 ns. The faster one is $\text{Ce}^{3+} 5d-4f$ transition related emission, while the origin of the slower one is unclear. The existence of such a slow component in Ce:LiSAF was also pointed out in previous report (Shiran et al., 2005). The decay time constants of Eu 1% and 2% LiSAF were 1293 ± 9 and 1205 ± 7 ns, respectively. They are typical for $\text{Eu}^{2+} 5d-4f$ emission. As the concentration of Eu^{2+} increased, the decay became faster. This tendency is generally observed in rare earth doped scintillators.

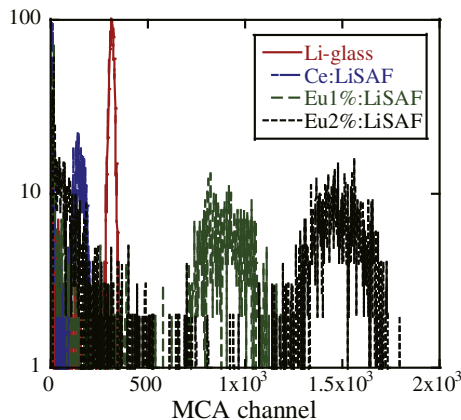


Fig. 4. ^{252}Cf pulse height spectra of Ce and Eu-doped LiSAF scintillators compared with Li-glass GS20 scintillator.

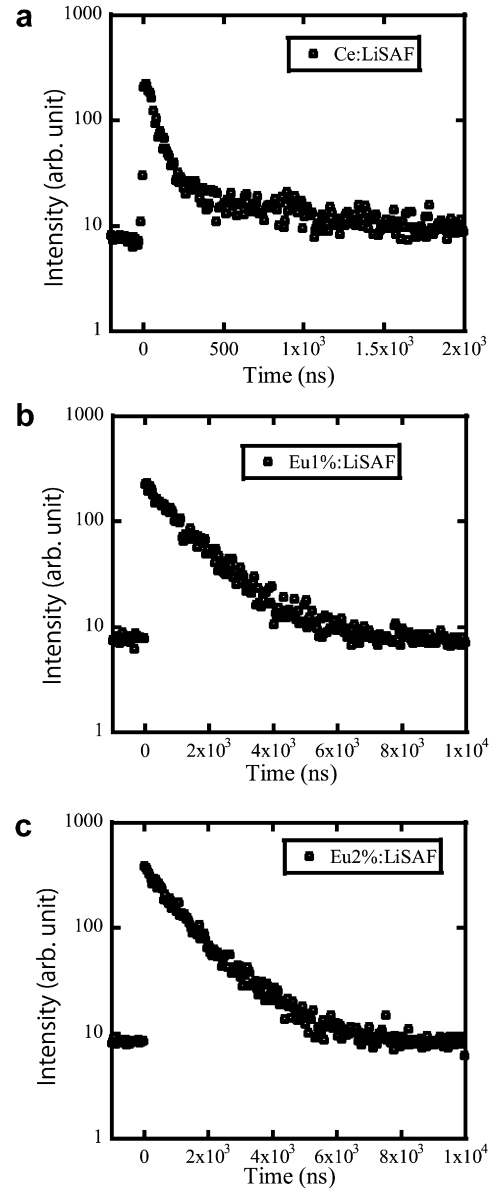


Fig. 5. From top to bottom, ^{252}Cf excited decay time profiles of Ce (a), Eu 1% (b), and Eu 2% (c) doped LiSAF scintillators.

4. Conclusion

Ce 1%, Eu 1%, and Eu 2% doped LiSAF crystalline scintillators were grown by the μ -PD method. Their α -ray induced emission spectra, neutron excited pulse height spectra and decay time profiles were reported for the first time. The absolute light yield of Ce 1%, Eu 1%, and Eu 2% doped LiSAF were 3800 ± 400 , 18000 ± 2000 and 30000 ± 3000 ph/n, respectively. By improvement of the transmittance of Eu 2% doped crystal through optimization of the growth conditions, higher absolute light yield is expected.

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