Dosimeter properties of Ce and Eu doped LiCaAlF₆

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Abstract

Optical, scintillation, optical stimulated luminescence, and thermally stimulated luminescence of Ce 1, 3, and 5% doped and Eu 1, 1.5, and 2% doped LiCaAlF₆ crystals fabricated by Tokuyama Corp. were investigated. In transmittance, absorption was proportional to dopant concentrations and typical optical quantum yield of Ce and Eu-doped LiCaAlF₆ were 40 and 100%, respectively. Scintillation wavelength and decay time profiles were investigated under X-ray irradiation. Ce³⁺ and Eu²⁺ 5d-4f luminescence appeared around 300 nm and 370 nm with typical decay time of 40 ns and 1.5 μs, respectively. Optically stimulated luminescence of Ce-doped ones appeared under 405 nm stimulation with detectable intensity while those of Eu doped ones were quite weak. Thermally stimulated luminescence of Ce- and Eu-doped LiCaAlF₆ were enough strong and they exhibited good response function from 1 to 1000 mGy exposure.

Keywords: Scintillation; Scintillator; OSL; Ce³⁺; Eu²⁺; TSL; LiCaAlF₆

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1. Introduction

Scintillators for thermal neutron detectors have attracted much attentions recently due to a diminishing of ^3He gas for thermal neutron detection (Kouzes 2011). For this purpose, we developed rare-earth or transitional metal doped LiCaAlF_6 scintillators (Yanagida et al., 2009; Yanagida et al., 2011a; Yanagida et al., 2011b; Fujiwara et al., 2012; Koshimizu et al., 2013; Kawaguchi et al., 2013; Yanagida 2013a) by using enriched ^6Li raw materials and especially Ce^{3+} or Eu^{2+} -doped LiCaAlF_6 exhibited good scintillation properties. On the other hand, LiCaAlF_6 has low density (2.97 g/cm^3) and low effective atomic number ($Z_{\text{eff}} = 14$) and these properties are preferable for dosimeter applications which requires tissue-equivalent materials. Although Z_{eff} of LiCaAlF_6 was higher than that of Al_2O_3 ($Z_{\text{eff}} = 11.3$) or LiF ($Z_{\text{eff}} = 8.3$), LiCaAlF_6 was one of the lightest phosphor materials and was potentially a candidate for dosimeter applications.

Previously, LiCaAlF_6 crystals were investigated in thermally stimulated luminescence (TSL, McKeever 1985) for dosimeter applications (Martino et al., 2007; Shiran et al., 2004) as well as scintillation detectors. In these studies about TSL properties, LiCaAlF_6 activated with Eu 0.5%, and Ce 0.5 % co-doped with Na (not Ce singly doped LiCaAlF_6) were investigated (Martino et al., 2007; Shiran et al., 2004). However, recent studies revealed that Ce or Eu 1-2% doped LiCaAlF_6 showed more effective luminescence properties in scintillation or photoluminescence (PL). Therefore in this time, we investigated TSL and optical stimulated luminescence (OSL) of highly Eu or Ce doped LiCaAlF_6 crystals as well as basic optical and scintillation properties.

2. Experimental procedures

Eu 1, 1.5, and 2, Ce 1, 3, and 5% doped LiCaAlF_6 crystals used in this work were prepared by Tokuyama Corp. using the conventional Czochralski method. Dopant concentrations were nominal values since it was difficult to determine actual concentrations. They had a same size of $5 \times 5 \times 2 \text{ mm}^3$. Wide surfaces were polished for optical characterizations.

To evaluate a basic optical property, optical in-line transmittance was evaluated by using JASCO V670 spectrometer. Then, PL absolute quantum yield (QY) was studied by Hamamatsu Quantaurus-QY. The absolute QY was calculated by the following equation, $QY = N_{\text{emit}}/N_{\text{absorb}}$ where N_{emit} and N_{absorb} were number of emission and absorption photons, respectively (e.g., Yanagida et al., 2013b). As basic scintillation properties, X-ray induced radioluminescence spectra (Yanagida et al., 2013c; Yanagida et al., 2013d) and decay time profiles (Yanagida 2010b; Yanagida 2013e) were investigated to confirm that present samples were not specific ones. Based on radioluminescence results, monitoring wavelengths in Ce- and Eu-doped LiCaAlF_6 were 290 ± 15 nm and 370 ± 15 nm, respectively.

OSL properties were examined by X-ray generator and JASCO FP8600 spectrofluorometer. Supplied bias voltage of the generator and tube current were 40 kV and 5 mA, respectively. In our geometry, the irradiated dose was 1 Gy/min under this condition and the dose was calibrated by using X-ray ionization chamber. OSL intensity was compared with $\text{C:Al}_2\text{O}_3$ which was a product of Nagase Landauer and had a size of $5 \times 5 \times 0.17$ mm³. TSL properties were evaluated by using Nano-gray TL2000. The detailed explanation about TSL evaluations can be seen our recent work (Yanagida et al., 2013f). The irradiated dose was from 1 to 1000 mGy. TSL intensity was compared Tm-doped CaSO_4 ($Z_{\text{eff}} = 15.7$) which was once a product of Matsushita and had a size of 5 mm diameter and 200 μm thickness. In TSL characterization, TSL spectra were also investigated by using a heater and CCD based spectrometer (Andor DU420A-BU2). In OSL and TSL evaluations, all samples were heated at 450 °C in 10 minutes to release all storage energies before each irradiation step.

3. Results and discussion

In-line transmittance spectra of Ce and Eu-doped LiCaAlF_6 crystals are shown in figure 1. Ce^{3+} 4f-5d absorption bands appeared at 200 and 270 nm and absorption depths were

proportional to nominal Ce concentrations. On the other hand, Eu^{2+} 4f-5d and Eu^{3+} 4f-4f absorption bands were observed at 200 and 300 nm, respectively. In Eu-doped LiCaAlF_6 , higher Eu concentration samples showed high absorption. Though doping levels were quantitatively unclear, actual doping concentrations were in proportional to nominal chemical compositions.

PL *QY* of Ce- and Eu-doped LiCaAlF_6 is represented in figure 2. Spectra are not shown in this figure since they are similar with those of scintillation described later. Eu-doped LiCaAlF_6 showed $\sim 100\%$ *QY* in all samples while those of Ce-doped ones 30-40%. PL *QY* of the most famous phosphor material, Ce-doped YAG utilized in white LED, is around 90% so that Eu-doped LiCaAlF_6 has quite high energy transfer efficiency inside the band gap. On the other hand, *QY* of Ce-doped ones were not so high and decreased when the doping concentration increased. In previous report, scintillation light yield was improved when the Ce concentration increased. It suggests that energy transfer efficiency from the host to emission centers would be improved in higher Ce concentration.

Figure 3 demonstrates X-ray excited scintillation spectra of samples. Ce^{3+} 5d-4f transition luminescence appeared at 270 and 320 nm that was similar with previous result (Gektin et al., 2002). In Eu-doped LiCaAlF_6 , Eu^{2+} 5d-4f emission was observed at 370 nm that was also consistent with previous results (Yanagida 2011a). In figure 4, X-ray excited scintillation decay time profiles of all samples are depicted. Scintillation decay time became faster when doping concentration increased in both material systems. Typical scintillation decay times of Ce and Eu-doped LiCaAlF_6 resulted 40 ns and 1.5 μs , respectively.

OSL of Ce-doped LiCaAlF_6 after 10 Gy X-ray exposure is shown in figure 5. In Ce-doped LiCaAlF_6 , stimulation wavelength was 405 nm and highly Ce doped sample exhibited higher OSL intensity since higher Ce concentration increased defects due to a charge imbalance of Ce^{3+} and Ca^{2+} . On the other hand, OSL of Eu-doped LiCaAlF_6 was not observed. **Reference**
OSL spectrum of $\text{C:Al}_2\text{O}_3$ was observed after 10 Gy exposure, as shown in Fig. 5 inset.

Although this is a rough estimation, taking into account the difference of the volume (1 digit) and similar effective atomic number of LiCaAlF_6 (14) and Al_2O_3 (11.3), Ce 3 and 5% doped would show comparable OSL intensity with $\text{C}:\text{Al}_2\text{O}_3$.

TSL glow curves of Ce 5% and Eu 2% doped LiCaAlF_6 are demonstrated in figure 6. TSL intensities were in proportional to doses. Although peak temperatures of Eu-doped LiCaAlF_6 were same with the previous result (Martino et al., 2007), those of Ce-doped LiCaAlF_6 was slightly different with the previous one (Martino et al., 2007) possibly due to the existence of Na co-dopant in that study. Dose response functions of Ce- and Eu-doped LiCaAlF_6 are represented in figure 7. Accumulation ranges of Ce- and Eu-doped ones were 200-450 °C and 130-400 °C, respectively. Both material series exhibited linear response against the dose and especially Eu-doped ones showed better linearity. We compared TSL intensities with one of the standard TSL materials, Tm-doped CaSO_4 (5 mm in diameter $\times$ 200 μm thickness). Unlike LiCaAlF_6 series, it exhibited one intense glow peak and easy to analyze in TSL. Taking into account raw signal intensities and difference of the sample volume, TSL sensitivity of LiCaAlF_6 crystals were slightly worse than Tm-doped CaSO_4 . In TSL glow curves and dose response functions, no significant differences were observed in different doping levels.

Finally, to confirm the origin of TSL emission, we investigated TSL spectra of Ce 5% and Eu 2% doped samples. Figure 8 depicts TSL spectra of them. Due to a limitation of photon statistics, two emission peaks of Ce^{3+} 5d-4f transition seemed one peak. In Eu-doped LiCaAlF_6 , Eu^{2+} 5d-4f luminescence at 370 nm was clearly observed and very weak peak at 590 nm was Eu^{3+} 4f-4f emission peak. Intrinsic luminescence of LiCaAlF_6 host (Gektin et al., 2002) was not observed in this experiment and it was concluded that TSL in Ce- and Eu-doped LiCaAlF_6 were originated from doping emission centers.

4 Conclusion

Ce 1%, 3%, and 5% and Eu 1%, 1.5%, and 2% doped LiCaAlF₆ crystals were prepared by Tokuyama Corp. and their optical, scintillation, and dosimeter properties were investigated. PL QY of Ce- and Eu-doped series resulted 30-40% and 100%, respectively. Scintillation emission wavelengths of Ce- and Eu-doped crystals were 270-320 nm and 370 nm due to allowed 5d-4f transition with typical decay times of 40 ns and 1.5 μs, respectively. OSL sensitivity of Ce 3% and 5% doped LiCaAlF₆ was roughly similar level with that of C:Al₂O₃ while Eu-doped samples did not show detectable OSL signal. TSL intensities of Ce- and Eu-doped LiCaAlF₆ Dose response functions from 1 to 1000 mGy exhibited linear response and especially Eu-doped ones had better linearity.

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Figure Captions

Figure 1 Transmittance spectra of Ce-doped (a) and Eu-doped (b) LiCaAlF_6 .

Figure 2 PL QY of Ce-doped and Eu-doped LiCaAlF_6 plotted against doping concentrations.

Figure 3 X-ray induced radioluminescence spectra of Ce- (a) and Eu-doped (b) LiCaAlF_6 .

Figure 4 X-ray induced scintillation decay time profiles of Ce- (left) and Eu-doped (right) LiCaAlF_6 .

Figure 5 OSL of Ce-doped LiCaAlF_6 under 405 nm stimulation after 10 Gy X-ray exposure.

Inset shows OSL of $\text{C:Al}_2\text{O}_3$ after 10 Gy exposure.

Figure 6 TSL glow curves of Ce 5% (a) and Eu 2% (b) doped LiCaAlF_6 . In both panels, TSL glow curve of Tm-doped CaSO_4 after 1 Gy exposure was plotted.

Figure 7 Dose response functions from 1 to 1000 mGy in Ce- (a) and Eu-doped (b) LiCaAlF_6 .

Figure 8 TSL spectra of Ce 5% and Eu 2% doped LiCaAlF_6 .

Figure1

Figure2

Figure3

Figure4

Figure5

Figure6

Figure7

Figure8