FULL PAPER

Dosimetric properties of Tb-doped LiF/CaF₂ eutectic composite

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We have developed a LiF/CaF₂:Tb eutectic composite as a novel thermoluminescence (TL) dosimetric material. The LiF/CaF₂:Tb eutectic composite was obtained using a melt-solidification method with a lower melting temperature than that of LiF and CaF₂. The results of the PL emission and excitation spectra, the X-ray induced radioluminescence decay curve, and the TL emission spectrum indicate that the emissions of LiF/CaF₂:Tb eutectic composite are due to 4f-4f transitions of the Tb³⁺ ion. The integrated TL intensity of the LiF/CaF₂:Tb eutectic composite was 3.6 times higher than that of the commercial CaSO₄:Tm dosimetric material that is known to show a relatively high TL intensity. The dose response curve of the LiF/CaF₂:Tb eutectic composite was measured and the lower detection limit was 0.01 mGy which is the lowest value among the LiF/CaF₂ based composites.

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1. Introduction

Although various single crystals, sintered ceramics, glasses, and powders have been studied as inorganic phosphor materials, there are few studies on eutectic composites for phosphor applications. Eutectic is a state in which a liquid phase becomes multiple solid phases when an inorganic matter solidifies. In eutectic phase, composite materials with a micrometer sized structure can be obtained.^{1),2)} In general, eutectic compositions have relatively lower melting points than their similar compositions; therefore, eutectics are expected to be manufactured at low cost. As one of the few examples, Al₂O₃/Y₃Al₅O₁₂:Ce eutectics have been studied for a yellow phosphor layer in white LEDs and LDs.³⁾ Since the Al₂O₃/Y₃Al₅O₁₂ eutectic is known as a sufficiently high strength and stable material,⁴⁾ the Al₂O₃/Y₃Al₅O₁₂:Ce eutectic can be regarded as a material having both an efficient luminescence property and a high mechanical property. We have also been interested in eutectic composites as neutron scintillators^{5)–7)} that have a function to convert neutrons to photons. A neutron scintillator is combined with a photodetector and used for a neutron detector.⁸⁾ We have studied LiF/CaF₂:Ce and LiF/CaF₂:Eu eutectics as neutron scintillators. In particular, the LiF/CaF₂:Eu eutectic shows a high light yield and neutron detection efficiency.^{9),10)} Its performance is comparable to those of other fluoride single crystals.¹¹⁾

These studies are the examples of eutectic composites for phosphor applications.

In recent years, we are focusing on eutectic composites for dosimeter applications. Dosimeters have a function to measure radiation dose during certain terms and phosphor-type dosimeters are mainly used. Such phosphors applied for dosimeters can be classified as the following three types: thermoluminescence (TL),¹²⁾ optically-stimulated luminescence,^{13)–15)} and radio-photoluminescence^{16)–18)} dosimetric materials. Since their luminescence intensities monotonically increase with increasing radiation doses, these phosphors can be applied for radiation dosimetry. Among them, TL dosimetric materials are the most traditional and widely studied material. As the TL dosimetric materials, for example, LiF:Mg,Ti, LiF:Mg,Cu,P, Mg₂SiO₄:Tb, and CaSO₄:Tm are known.¹⁹⁾ Such TL dosimetric materials are mainly sintered ceramics or inorganic powder composites with an organic matrix. On the other hand, we have reported TL dosimetric properties of LiF/CaF₂:Ce,²⁰⁾ LiF/CaF₂:Eu,²¹⁾ and non-doped LiF/CaF₂²²⁾ eutectic composites. These eutectics are the rare reported examples of inorganic–inorganic composites as TL dosimetric materials. We have shown that LiF/CaF₂:Ce, LiF/CaF₂:Eu, and non-doped LiF/CaF₂ can act as TL dosimetric materials and are potentially cost effective, however, their lower detection limits were 0.1–1 mGy that are not sufficient values compared with those of other efficient materials (e.g., 0.01 mGy by the LiCaAlF₆:Tb single crystal²³⁾) evaluated by the same measurement setups in our group.

In this study, we have developed LiF/CaF₂:Tb as a novel eutectic TL dosimetric material. Because the Tb³⁺ ions can be used for a luminescent center of TL dosimetric

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materials (e.g., $\text{Mg}_2\text{SiO}_4\text{:Tb}$), we had expected to obtain the more efficient eutectic TL dosimetric material. In order to demonstrate the potential of the eutectic composite as the TL dosimetric material, we have investigated its dosimetric properties comparing with the non-doped LiF/CaF_2 eutectic composite and the commercial material.

2. Experimental procedure

The $\text{LiF/CaF}_2\text{:Tb}$ eutectic composite was prepared using a melt-solidification method. The high-purity LiF , CaF_2 , and TbF_3 powders (99.99 %, Stella chemifa) were mixed with a mole ratio at the eutectic point of LiF and CaF_2 ($\text{LiF:CaF}_2 = 79.2:20.8$) together with 0.1 mol % of TbF_3 for CaF_2 . The mixed powders were poured into a carbon crucible and heated to remove water under vacuum (8×10^{-4} Pa) at 500 °C for 5 h in a vacuum chamber with a carbon heater and carbon heat insulators. After removing water from the mixed powders, the temperature of the crucible was changed from 500 to 850 °C at a heating rate of 10 °C/min under Ar atmosphere. The temperature was kept at 850 °C for 30 min for melting the mixed powders, then it was decreased to 20 °C at a cooling rate of 4 °C/min. This temperature profile is the same as that for the non-doped LiF/CaF_2 eutectic composite in the previous report.²²⁾ The obtained eutectic is polished to a thickness of approximately 2 mm and it is used as the sample for investigation on the luminescence and dosimetric properties.

In order to investigate luminescence properties, the photoluminescence (PL) spectra and the X-ray induced radioluminescence decay curve were measured. The PL emission and excitation spectra were measured using a PL spectrometer (FP-8600; JASCO). The PL emission spectrum was measured with 230 nm excitation wavelength. The PL excitation spectrum was measured with 543 nm emission wavelength. The X-ray induced radioluminescence decay curve was measured by a time-correlated single photon counting system using a pulse X-ray source and a photomultiplier tube (R7400P-06; Hamamatsu). The detail is described elsewhere.²⁴⁾ In this experiment, the X-ray tube voltage was set 30 kV. The decay time was estimated by fitting the obtained decay curve to a single exponential function.

In order to investigate TL dosimetric properties, the TL emission spectrum and TL glow curves were measured. Before both measurements, the samples were irradiated with certain doses of X-rays using an X-ray generator (XRB80P&N200X4550; Spellman). The X-ray doses (air kerma) were estimated using an ionization chamber (Model 30013; PTW). The TL emission spectrum was measured in the temperature range from 50 to 300 °C by a CCD-based spectrometer (QE Pro; Ocean Optics) with heating the sample by a ceramic heater (SCR-SHQ-A; Sakaguchi E.H Voc). The detail of the measurement is shown elsewhere.²⁵⁾ The TL glow curves were obtained using a TL reader (TL-2000; Nanogray) with a heating rate of 1 °C/s from 50 to 400 °C. To obtain the dose response curves, this measurement is repeated under different X-ray

doses from 0.1 to 10 mGy. The details of this measurement is shown elsewhere.²⁶⁾ In the TL glow curve measurements, the commercial $\text{CaSO}_4\text{:Tm}$ dosimetric material (Panasonic) was used as the reference sample. The reason why $\text{CaSO}_4\text{:Tm}$ was selected was that it has relatively high TL intensity among well-known TL dosimetric materials.¹⁹⁾ The non-doped LiF/CaF_2 eutectic composite, that had been obtained in the previous study,²²⁾ was also used for the reference sample.

3. Results and discussion

The $\text{LiF/CaF}_2\text{:Tb}$ eutectic composite was obtained after the melt-solidification process. The $\text{LiF/CaF}_2\text{:Tb}$ eutectic composite was able to be easily taken from the carbon crucible. This carbon crucible can be reused due to its low wettability with fluorides. In addition, it was easy to polish the $\text{LiF/CaF}_2\text{:Tb}$ eutectic composite due to its excellent machinability.

Figure 1 shows the prepared $\text{LiF/CaF}_2\text{:Tb}$ eutectic composite illuminated by white LED and 254 nm UV light source. The size of the prepared sample is approximately 10 mm diameter and thickness of approximately 2 mm. There are no visible large cracks in the sample. Under UV irradiation, green luminescence was observed from the sample as the PL phenomenon. Because it was not observed in the non-doped LiF/CaF_2 eutectic composite, it is considered to be due to doped Tb^{3+} ions.

Figure 2 shows the PL emission and excitation spectra of the $\text{LiF/CaF}_2\text{:Tb}$ eutectic composite. The excitation spectrum of the PL emission at 543 nm shows the excitation band peaking at around 230 nm. In the PL emission spectrum excited at 230 nm, several PL emission peaks are observed in the wavelength range from 380 to 630 nm that can be the origin of green luminescence under UV irradiation in the visual observation. These peaks can be attributed to 4f-4f transitions of the Tb^{3+} ion ($^5\text{D}_3 \rightarrow ^7\text{F}_6$, $^5\text{D}_3 \rightarrow ^7\text{F}_5$, $^5\text{D}_3 \rightarrow ^7\text{F}_4$, $^5\text{D}_3 \rightarrow ^7\text{F}_3$, $^5\text{D}_3 \rightarrow ^7\text{F}_2$, $^5\text{D}_4 \rightarrow ^7\text{F}_6$, $^5\text{D}_4 \rightarrow ^7\text{F}_5$, $^5\text{D}_4 \rightarrow ^7\text{F}_4$, and $^5\text{D}_4 \rightarrow ^7\text{F}_3$ transitions).

Figure 3 shows the X-ray induced radioluminescence decay curve of the $\text{LiF/CaF}_2\text{:Tb}$ eutectic composite. The obtained decay curve was fitted to a single exponential function and the estimated decay time was 3.69 ms. This value is consistent with the emission from 4f-4f transitions of the Tb^{3+} ion. At least, the dominant radioluminescence of the $\text{LiF/CaF}_2\text{:Tb}$ eutectic composite is considered to be due to 4f-4f transitions of the Tb^{3+} ion.

The results of the PL emission spectrum and the X-ray induced radioluminescence decay curve indicate that the

Fig. 1. The $\text{LiF/CaF}_2\text{:Tb}$ eutectic composite illuminated by a) white LED and b) 254 nm UV light source.

Fig. 2. The PL a) emission spectrum at 230 nm excitation and b) excitation spectrum at 543 nm emission of the LiF/CaF₂:Tb eutectic composite.

Fig. 3. The X-ray induced radioluminescence decay curve of the LiF/CaF₂:Tb eutectic composite.

LiF/CaF₂:Tb eutectic composite shows the emission due to 4f-4f transitions of the Tb³⁺ ion. In the contrast, the non-doped LiF/CaF₂ eutectic composite have shown the emission with self-trapped exciton (STE) in CaF₂.²²⁾ It is considered that Tb³⁺ ions substitute Ca²⁺ sites and the STE emission is quenched.

The TL emission spectra of the LiF/CaF₂:Tb eutectic composite were measured in the temperature range from 50 to 300 °C after exposure to 1 Gy of X-rays. We observed emission bands due to 4f-4f transitions of the Tb³⁺ ion in the temperature range from 50 to 300 °C. **Figure 4** shows the selected TL emission spectra at 50, 150, and 250 °C. The TL emission peaks can be attributed to 4f-4f transitions of the Tb³⁺ ion ($^5D_3 \rightarrow ^7F_6$, $^5D_3 \rightarrow ^7F_5$, $^5D_3 \rightarrow ^7F_4$, $^5D_3 \rightarrow ^7F_3$, $^5D_3 \rightarrow ^7F_2$, $^5D_4 \rightarrow ^7F_6$, $^5D_4 \rightarrow ^7F_5$, $^5D_4 \rightarrow ^7F_4$, and $^5D_4 \rightarrow ^7F_3$ transitions), as is the case for the PL emission spectrum. Emission peaks had no change depending on the stimulation temperature.

Fig. 4. TL emission spectra of the LiF/CaF₂:Tb eutectic composite at 50, 150, and 250 °C after exposure to 1 Gy of X-rays.

Fig. 5. TL glow curves of LiF/CaF₂:Tb, CaSO₄:Tm, and non-doped LiF/CaF₂ after exposure to 10 mGy of X-ray. The inset graph has a logarithmic scale on the vertical axis.

Figure 5 shows the TL glow curves of LiF/CaF₂:Tb, CaSO₄:Tm, and non-doped LiF/CaF₂ after exposure to 10 mGy of X-ray. Between each measurement, TL glow curves using no samples were measured for background subtraction. Furthermore, the TL intensity on the vertical axis was corrected by the sample weight. While the TL intensities of LiF/CaF₂:Tb and CaSO₄:Tm are comparable, that of non-doped LiF/CaF₂ is significantly lower. Broad TL glow peaks of LiF/CaF₂:Tb are observed at around 100, 250, and 300 °C. In non-doped LiF/CaF₂, TL glow peaks at 250 and 300 °C are not observed. In general, a glow peak temperature is related to a trap depth. It is possible that trapping centers corresponding to these peaks are induced by Tb-doping.

Table 1 shows integrated TL intensities of LiF/CaF₂:Tb, non-doped LiF/CaF₂, and CaSO₄:Tm in the temperature range from 100 to 300 °C after exposure to 10 mGy of X-ray. The integrated TL intensity of the LiF/CaF₂:Tb eutectic composite is 3.6 times higher than that of the commercial CaSO₄:Tm dosimetric material. In addition, comparing with non-doped LiF/CaF₂, it is confirmed that Tb-doping drastically increase the TL intensity.

Figure 6 shows the dose response curve of the LiF/CaF₂:Tb eutectic composite. The value for vertical axis is the integrated TL intensity (I_{TL}) in the temperature range from 100 to 300 °C. The I_{TL} of the LiF/CaF₂:Tb eutectic composite monotonically increases increasing with X-ray dose (D) from 0.01 to 10 mGy. The lower detection limit is 0.01 mGy. **Table 2** summarize the lower detection limits of LiF/CaF₂:Ce, LiF/CaF₂:Eu, non-doped LiF/CaF₂, and LiF/CaF₂:Tb. In the table, the LiF/CaF₂:Tb eutectic composite shows the lowest value among the LiF/CaF₂ based composites. It is due to its high TL intensity which is 3.6

Table 1. Integrated TL intensities of LiF/CaF₂:Tb, non-doped LiF/CaF₂, and CaSO₄:Tm after exposure to 10 mGy of X-ray

	TL intensities (nC/mg)	Relative TL intensities
LiF/CaF ₂ :Tb	158	3.6
non-doped LiF/CaF ₂	0.57	0.013
CaSO ₄ :Tm	44	1

Fig. 6. The dose response curve of the LiF/CaF₂:Tb eutectic composite.**Table 2.** Lower detection limits of LiF/CaF₂:Ce, LiF/CaF₂:Eu, non-doped LiF/CaF₂, and LiF/CaF₂:Tb

	Lower detection limits (mGy)	References
LiF/CaF ₂ :Ce	0.1–1	20)
LiF/CaF ₂ :Eu	1	21)
non-doped LiF/CaF ₂	0.1	22)
LiF/CaF ₂ :Tb	0.01	This work

times higher than that of the commercial CaSO₄:Tm dosimetric material after exposure to 10 mGy of X-ray.

4. Conclusions

The LiF/CaF₂:Tb eutectic composite was obtained by the melt-solidification method. In the PL emission and excitation spectra, the X-ray induced radioluminescence decay curve, and the TL emission spectrum, we confirmed luminescence properties that are considered to be due to 4f-4f transitions of the Tb³⁺ ion. The integrated TL intensity of the LiF/CaF₂:Tb eutectic composite was 3.6 times higher than that of the commercial CaSO₄:Tm dosimetric material. From the dose response curve, it was confirmed that the lower detection limit is 0.01 mGy. The LiF/CaF₂:Tb eutectic composite showed the lowest detection limit among the LiF/CaF₂ based composites.

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