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Dosimetric properties of non-doped LiF/CaF_2 eutectic

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ABSTRACT

We have developed a non-doped LiF/CaF_2 eutectic for thermoluminescence (TL) dosimetry. The LiF/CaF_2 eutectic were obtained using a simple melt-solidification method with a lower melting temperature than that of CaF_2. The LiF/CaF_2 eutectic showed the lower scintillation intensity than that of a CaF_2 single crystal. In contrast, the TL intensity of the LiF/CaF_2 eutectic was significantly higher than that of the CaF_2 single crystal. Furthermore, it monotonically increased as a function of X-ray dose from 0.1 to 3000 mGy.

1. Introduction

Over the past few decades, dosimetric materials showing thermoluminescence (TL; McKeever, 1985), optically-stimulated luminescence (OSL; McKeever, 2011), and radio-photoluminescence (RPL; Nanto et al., 2018) have been intensively studied. Although many types of materials including crystalline powders, single crystals, ceramics, and glasses have been reported as the dosimetric materials, there were few studies on dosimetric properties of eutectic materials.

The LiF/CaF_2 eutectic materials can be obtained using the cost-effective simple melt-solidification method with the lower eutectic temperature than the melting points of raw materials, and the Eu-doped LiF/CaF_2 eutectic has been studied as a novel neutron scintillator (Kawaguchi et al., 2011; Masai et al., 2015) after the ^3He supply crisis (Kouzes, 2011; Kouzes et al., 2011). Our group have been interested in eutectic materials also for the dosimetry due to their simple production process; therefore, we studied the TL and OSL dosimetric properties of Eu-doped and Ce-doped LiF/CaF_2 eutectics (Kawano et al., 2018a, 2018b). The Eu-doped LiF/CaF_2 eutectic showed promising dosimetric properties; however, the segregation of Eu or Ce ions can be a problem for its production using the simple melt-solidification method. Therefore, the Eu-doped eutectic samples as the neutron scintillator in the previous study (Kawaguchi et al., 2011) had been prepared by using the established melt-growth method such as the Bridgman–Stockbarger method. However, such methods are not cost effective due to their production time and the furnace with the moving parts. In general, homogeneous non-doped materials can be easily prepared because they do not require dopants such as rare-earth ions, then production costs can be reduced. In this study, we have investigated dosimetric properties of the non-doped LiF/CaF_2 eutectic obtained by the simple melt-solidification method. We have expected to obtain the intrinsic luminescence from CaF_2 due to the self–trapped exciton (STE; Williams et al., 1976). When electrons or holes strongly coupled to the crystal lattice, they are self-trapped. Excitons are localized in its own lattice distortion field. The STE can show wide emission bands even in the case of perfect lattice (Kabler, 1964). The well-known STE of CaF_2 can show luminescence at room temperature.

2. Experimental

The non-doped LiF/CaF_2 eutectic was obtained using a simple melt-solidification method. The high-purity LiF (99.99%) and CaF_2 (99.99%) powders were mixed with a mole ratio at the eutectic point ($LiF:CaF_2 = 80:20$) and poured into a carbon crucible. The mixed powders were heated under vacuum (8×10^{-4} Pa) at 500 °C for 5 h using a vacuum chamber equipped with a carbon heater and carbon heat insulators in order to remove H_2O. After removing H_2O, the crucible was heated from 500 °C to 850 °C at a heating rate of 10 °C/min under Ar atmosphere and the mixed powders were melted. The crusible was kept at 850 °C for 30 min, then it was cooled to 20 °C at a cooling rate of 4 °C/min. The obtained eutectic boule is polished to a thickness of 1 mm. A scanning electron microscope (SEM) image was obtained using a desktop SEM (JCM-6000Plus; JEOL) in order to observe a microstructure of the eutectic sample. We have also used the non-doped CaF_2 single crystal as the reference sample, which was prepared by Tokuyama Corporation using the Czochralski method.

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To investigate basic luminescence properties, X-ray induced scintillation spectra and X-ray induced decay curves were measured. The X-ray induced scintillation spectra were obtained using our customized setup equipped with an X-ray generator (XRB80N100/CB; Spellman), an optical fiber, a monochromator (Shamrock 163; Andor), and a CCD-based spectrometer (DU920-BU2NC; Andor). Its details are found elsewhere (Yanagida et al., 2013a). The samples were irradiated with X-rays from the generator (tube voltage: 40 kV; tube current: 1.2 mA), and the scintillation spectra were recorded using a CCD-spectrometer. The X-ray induced scintillation decay curves were measured by a time-correlated single photon counting system equipped with a pulse X-ray source and a photomultiplier tube (R7400P-06; Hamamatsu). Its details are described elsewhere (Yanagida et al., 2014a). This system has a time resolution of a few ns. In the measurements, the X-ray tube voltage was set 30 kV. The obtained decay curves were fitted by

$$I(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) + C \quad (1)$$

where I(t) is the luminescence intensity as a function of time t, τ_1 and τ_{12} are scintillation decay times, and A_1, A_2, and C are constants.

To investigate dosimetric properties, TL emission spectra and TL glow curves were measured. The TL emission spectra were obtained using an electric heat equipment (SCR-SHQ-A; Sakaguchi E.H Voc) and a CCD-based spectrometer (QE Pro; Ocean Optics) in the temperature range from 50 to 250 °C. Before measurements, the samples were irradiated with 40 Gy of X-rays. Its details are shown elsewhere (Okada et al., 2016). The TL glow curves were measured using a TL reader (TL-2000; Nanogray) by heating samples with a rate of 1 °C/s in the temperature range from 50 to 250 °C. The measurements were repeated with different irradiation doses to obtain the dose response curves. Before each measurements, the samples were irradiated with 0.1 mGy–10 Gy of X-rays. The details of this measurement method are reported elsewhere (Yanagida et al., 2013b). In all the measurements of TL emission spectra and TL glow curves, X-rays are irradiated using a generator (XRB80P&N200X4550; Spellman) and these doses (air kerma) were determined using an ionization chamber (Model 30013; PTW).

3. Results and discussion

Fig. 1 shows the obtained LiF/CaF_2 eutectic and the CaF_2 single crystal from Tokuyama Corporation. The sample sizes of the LiF/CaF_2 eutectic and the CaF_2 single crystal are approximately 9 mm diameter and 10 mm square, respectively. Thicknesses of both samples were approximately 1 mm. While the CaF_2 single crystal looks transparent, the LiF/CaF_2 eutectic looks opaque or semitransparent due to light scatterings at boundaries of LiF and CaF_2.

Fig. 2 shows the SEM image of the LiF/CaF_2 eutectic. Its micro-sized lamellar structure is observed and the widths of each layers are approximately 1 μm. In general, similar lamellar structures are observed in LiF/CaF_2 eutectics. If the established melt-growth methods such as the Bridgman–Stockbarger method are used, longer-length lamellar structures will be obtained as well as the previous our work (Kawaguchi et al., 2011). However, such methods are not cost-effective and such structures may not be important for the dosimetric properties. It has been confirmed that at least the shorter-length lamellar structure can be easily obtained by the cost-effective simple melt-solidification method shown in this study.

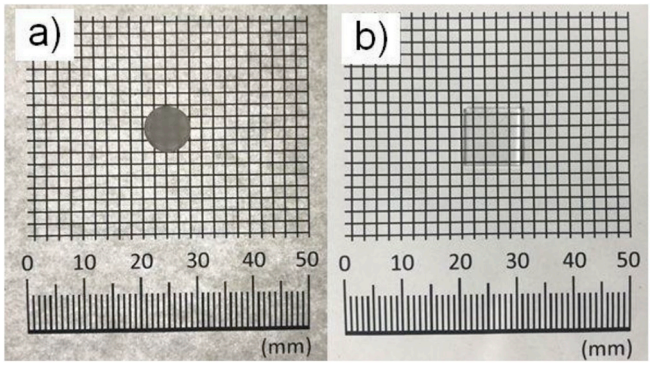

Fig. 1. The samples of a) LiF/CaF_2 eutectic and b) CaF_2 single crystal.

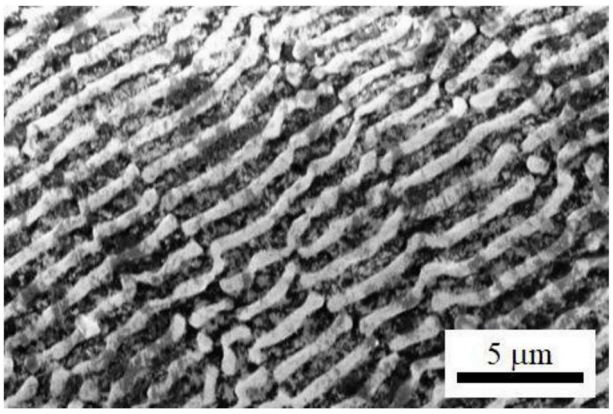

Fig. 2. The SEM image of the LiF/CaF_2 eutectic.

Fig. 3 shows X-ray induced scintillation spectra of the LiF/CaF_2 eutectic and the CaF_2 single crystal. Both samples showed a similar broad emission band in the wavelength range from 230 to 500 nm having a peak at around 300 nm. These emissions can be explained by luminescence from the STE of CaF_2 (Williams et al., 1976). Fig. 4 shows X-ray induced scintillation decay curves of the LiF/CaF_2 eutectic and the CaF_2 single crystal. Obtained decay times of the LiF/CaF_2 eutectic and the CaF_2 single crystal were similar. They are typical decay times for the STE emission of CaF_2. The results of measurements on scintillation decay times are consistent with the results of those on the scintillation spectra. Although the LiF/CaF_2 eutectic has LiF layers, we could not observe any emission peaks and decay components originated from LiF. At least, we consider that high-efficient luminescence centers in the LiF/CaF_2 eutectic are originated from only CaF_2 layers.

Fig. 5 shows the TL emission spectrum of the LiF/CaF_2 eutectic after exposure to 40 Gy of X-rays. Because we could not obtain any TL emission peaks from the CaF_2 single crystal, only the result by the LiF/CaF_2 eutectic is shown. Fig. 6 shows TL glow curves of the LiF/CaF_2 eutectic and the CaF_2 single crystal after exposure to 1 Gy of X-rays with the fitting analysis by glow-curve decomposition (GCD) functions (Kitis et al., 1998). In the measurements of TL glow curves, we could obtain the glow peaks from both samples because this measurement has higher

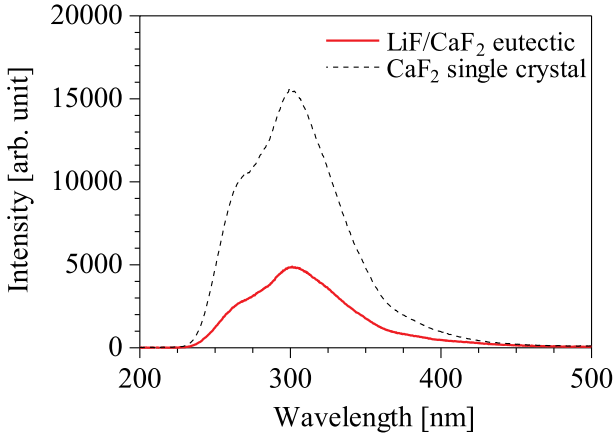

Fig. 3. X-ray induced scintillation spectra of the LiF/CaF_2 eutectic and the CaF_2 single crystal.

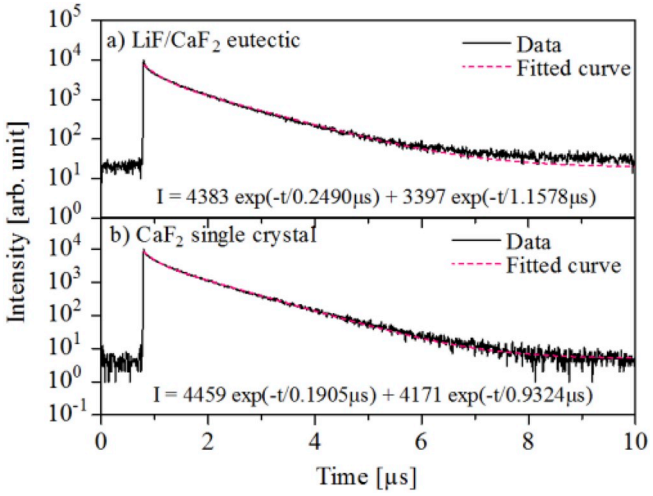

Fig. 4. X-ray induced scintillation decay curves of the LiF/CaF_2 eutectic and the CaF_2 single crystal.

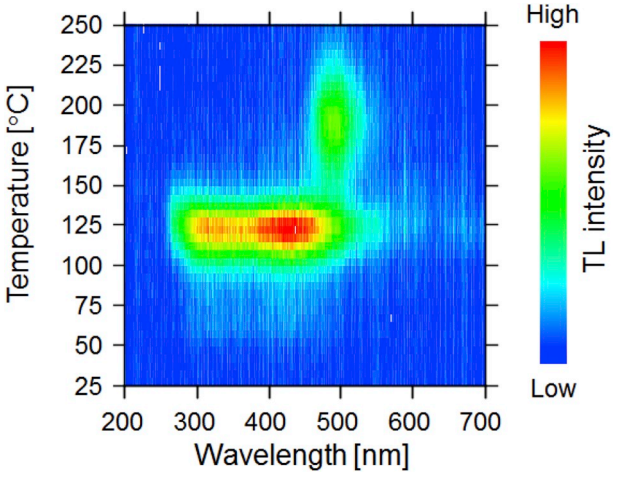

Fig. 5. The TL emission spectrum of the LiF/CaF_2 eutectic after exposure to 40 Gy of X-rays.

sensitivity comparing with that of TL emission spectra. The TL glow curves of the LiF/CaF_2 eutectic and the CaF_2 single crystal could be fitted to the curves having three and two peaks, respectively.

From Fig. 5, we observed two TL emission bands with different stimulation temperatures. The TL emission band at the stimulation temperature of 120 °C may be ascribed to the STE emission of CaF_2. The TL spectrum at 120 °C shows longer emission wavelength than that of the scintillation spectrum, but we consider that this is because our measurement set-up for the TL emission spectra has lower sensitivity at the shorter wavelength range. The TL emission band peaking at the stimulation temperature of 200 °C can be explained by the TL from LiF layers, because the glow curve of the CaF_2 single crystal in Fig. 6 has no peaks at around 200 °C. We consider that the TL emission band at around 500 nm from LiF layer is originated from F^{3+} centers of LiF (Shiran et al., 2013) because its wavelengths and temperature stabilities are consistent. From Fig. 6, the TL intensity of the peak at around 200 °C is relatively lower than those of other peaks at around 80–90 °C and 140 °C. Therefore, the peak at around 200 °C is not suitable for dose measurements compared to other peaks. Incidentally, the peak temperatures from the TL spectrum and the TL glow curve of LiF/CaF_2 eutectic are not equal due to the difference in the heating condition by the different measurement set-ups. In Fig. 6, the glow peaks at around 80–90 °C and 140 °C are consistent with glow peaks by pure CaF_2 single crystal in the previous study (Podgoršak et al., 1974). We consider that these trapping levels may be originated from some types of defect levels of pure CaF_2.

The significant difference between TL glow curves of the LiF/CaF_2 eutectic and the CaF_2 single crystal was found in the peak around 140 °C. In the case of the LiF/CaF_2 eutectic, this peak is clearly enhanced. As the result, the TL intensity of the LiF/CaF_2 eutectic was significantly higher than that of the CaF_2 single crystal. Its mechanism is still not clear, but we consider that the amount of some types of the defects in CaF_2 increased due to its melt-solidification process with LiF. Defects can act as the trapping centers, and furthermore, scintillation intensities and TL or OSL intensities can show the inverse proportional relationship due to the difference in the amount of the trapping-centers (Yanagida et al., 2014b, 2019; Yanagida, 2018).

Fig. 7 shows the TL dose response curves of the LiF/CaF_2 eutectic and the CaF_2 single crystal. As the values for vertical axes, integrated TL intensities in the temperature range from 120 to 140 °C were used. The TL intensity of the LiF/CaF_2 eutectic monotonically increases as a function of X-ray dose from 0.1 to 3000 mGy while the TL intensity of the CaF_2 single crystal monotonically increases as a function of X-ray dose from 10 to 1000 mGy. The X-ray dose measurable range with the LiF/CaF_2 eutectic is clearly wider than that with the CaF_2 single crystal. This is due to its significantly higher TL intensity. The measurable dose range of the LiF/CaF_2 eutectic is not sufficient compared to commercial materials, for example, LiF:Mg,Cu,P can show the wider range from about 1 μGy to 1 MGy (Obryk et al., 2011). However, our experiment was performed using the general TL reader and we believe that the measurable dose range of the LiF/CaF_2 eutectic will be improved if the read-out process is optimized. In this study, we investigates the dosimetric properties of the non-doped LiF/CaF_2 obtained by using the cost-effective simple melt-solidification methods, and we have observed the unexpected enhancement of the TL intensity. If this enhancement of the TL intensity is observed also in other eutectic materials, the non-doped eutectic materials can be candidates for novel TL dosimetric materials.

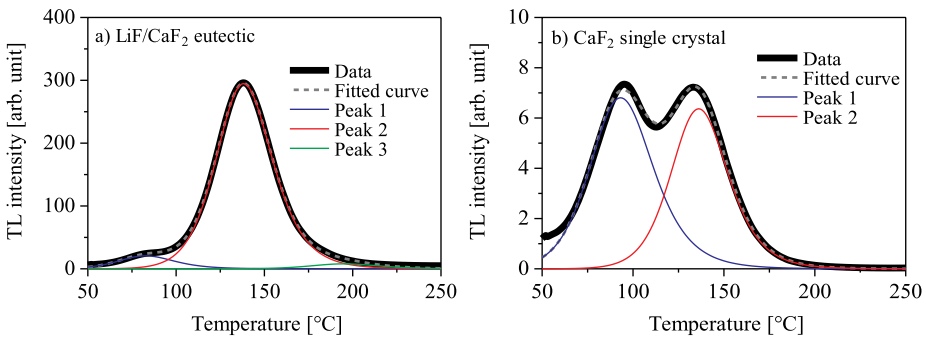

Fig. 6. TL glow curves of the LiF/CaF_2 eutectic and the CaF_2 single crystal after exposure to 1 Gy of X-rays.

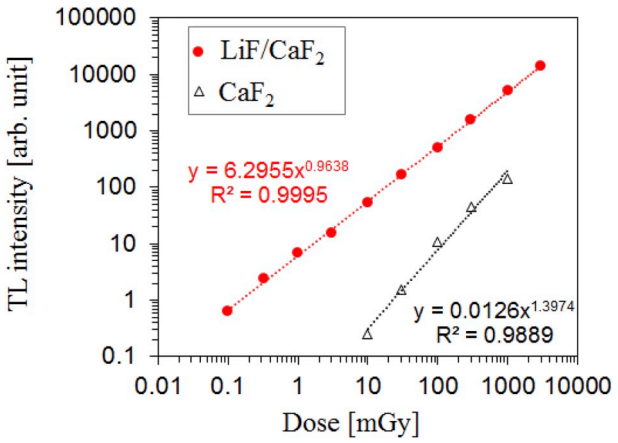

Fig. 7. TL dose response curves of the LiF/CaF_2 eutectic and the CaF_2 single crystal.

4. Conclusion

The non-doped LiF/CaF_2 eutectic is obtained by the simple melt-solidification method. It shows the significantly higher TL intensity than that of the non-doped CaF_2 single crystal. In addition, the TL intensity of the non-doped LiF/CaF_2 eutectic monotonically increases as a function of X-ray dose from 0.1 to 3000 mGy.

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