

Dosimetric properties of non-doped LiF/CaF₂ eutectic

Noriaki Kawaguchi^{*}, Hiromi Kimura, Yuma Takebuchi, Daisuke Nakauchi, Takumi Kato, Takayuki Yanagida

Nara Institute of Science and Technology, 8916-5 Takayama, Ikoma, Nara, 630-0192, Japan

ARTICLE INFO

Keywords:

Dosimeter
Fluoride
Eutectic

ABSTRACT

We have developed a non-doped LiF/CaF₂ eutectic for thermoluminescence (TL) dosimetry. The LiF/CaF₂ eutectic were obtained using a simple melt-solidification method with a lower melting temperature than that of CaF₂. The LiF/CaF₂ eutectic showed the lower scintillation intensity than that of a CaF₂ single crystal. In contrast, the TL intensity of the LiF/CaF₂ eutectic was significantly higher than that of the CaF₂ 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/CaF₂ 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/CaF₂ 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/CaF₂ eutectics ([Kawano et al., 2018a, 2018b](#)). The Eu-doped LiF/CaF₂ 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/CaF₂ eutectic obtained by the simple melt-solidification method. We have expected to obtain the intrinsic luminescence from CaF₂ 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 CaF₂ can show luminescence at room temperature.

2. Experimental

The non-doped LiF/CaF₂ eutectic was obtained using a simple melt-solidification method. The high-purity LiF (99.99%) and CaF₂ (99.99%) powders were mixed with a mole ratio at the eutectic point (LiF:CaF₂ = 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 H₂O. After removing H₂O, 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 crucible 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 CaF₂ single crystal as the reference sample, which was prepared by Tokuyama Corporation using the Czochralski method.

^{*} Corresponding author.

E-mail address: n-kawaguchi@ms.naist.jp (N. Kawaguchi).

<https://doi.org/10.1016/j.radmeas.2020.106254>

Received 31 October 2019; Received in revised form 17 January 2020; Accepted 29 January 2020

Available online 31 January 2020

1350-4487/© 2020 Elsevier Ltd. All rights reserved.

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_2 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/CaF₂ eutectic and the CaF₂ single crystal from Tokuyama Corporation. The sample sizes of the LiF/CaF₂ eutectic and the CaF₂ single crystal are approximately 9 mm diameter and 10 mm square, respectively. Thicknesses of both samples were approximately 1 mm. While the CaF₂ single crystal looks transparent, the LiF/CaF₂ eutectic looks opaque or semitransparent due to light scatterings at boundaries of LiF and CaF₂.

Fig. 2 shows the SEM image of the LiF/CaF₂ 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/CaF₂ eutectics. If the established melt-growth methods such as the

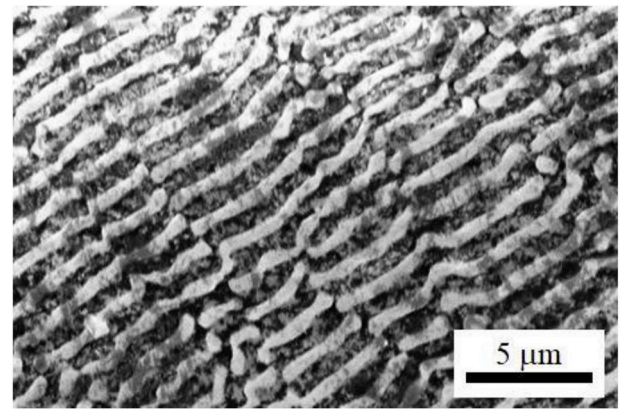


Fig. 2. The SEM image of the LiF/CaF₂ eutectic.

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. 3 shows X-ray induced scintillation spectra of the LiF/CaF₂ eutectic and the CaF₂ 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 CaF₂ (Williams et al., 1976). Fig. 4 shows X-ray induced scintillation decay curves of the LiF/CaF₂ eutectic and the CaF₂ single crystal. Obtained decay times of the LiF/CaF₂ eutectic and the CaF₂ single crystal were similar. They are typical decay times for the STE emission of CaF₂. The results of measurements on scintillation decay times are consistent with the results of those on the scintillation spectra. Although the LiF/CaF₂ 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/CaF₂ eutectic are originated from only CaF₂ layers.

Fig. 5 shows the TL emission spectrum of the LiF/CaF₂ eutectic after exposure to 40 Gy of X-rays. Because we could not obtain any TL emission peaks from the CaF₂ single crystal, only the result by the LiF/CaF₂ eutectic is shown. Fig. 6 shows TL glow curves of the LiF/CaF₂ eutectic and the CaF₂ 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

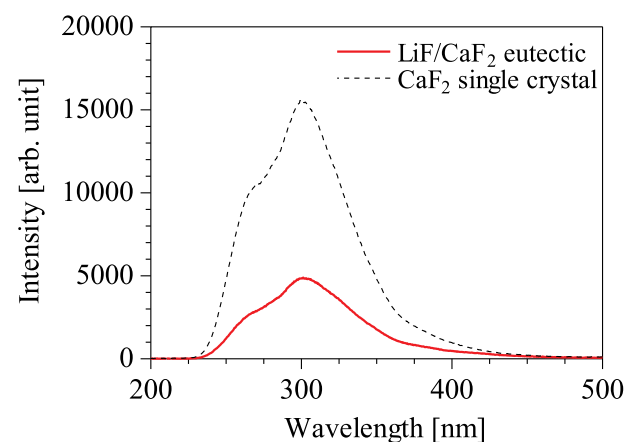


Fig. 3. X-ray induced scintillation spectra of the LiF/CaF₂ eutectic and the CaF₂ single crystal.

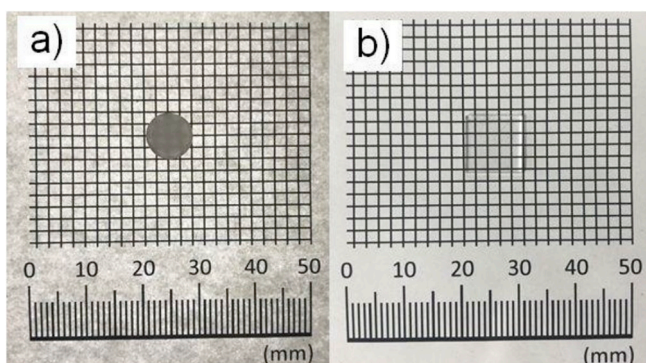


Fig. 1. The samples of a) LiF/CaF₂ eutectic and b) CaF₂ single crystal.

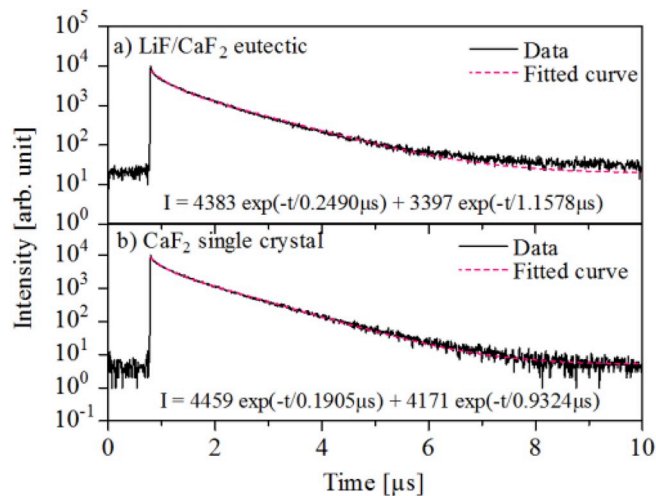


Fig. 4. X-ray induced scintillation decay curves of the LiF/CaF₂ eutectic and the CaF₂ single crystal.

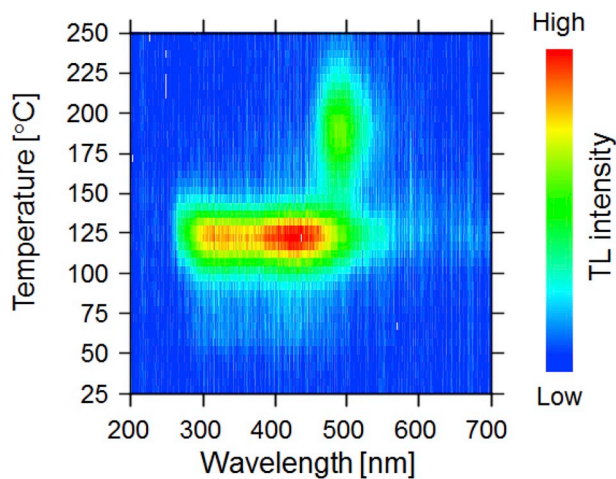


Fig. 5. The TL emission spectrum of the LiF/CaF₂ eutectic after exposure to 40 Gy of X-rays.

sensitivity comparing with that of TL emission spectra. The TL glow curves of the LiF/CaF₂ eutectic and the CaF₂ 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 CaF₂. 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 CaF₂ 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 F³⁺ 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/CaF₂ 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 CaF₂ 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 CaF₂.

The significant difference between TL glow curves of the LiF/CaF₂ eutectic and the CaF₂ single crystal was found in the peak around 140 °C. In the case of the LiF/CaF₂ eutectic, this peak is clearly enhanced. As the result, the TL intensity of the LiF/CaF₂ eutectic was significantly higher than that of the CaF₂ single crystal. Its mechanism is still not clear, but we consider that the amount of some types of the defects in CaF₂ 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/CaF₂ eutectic and the CaF₂ 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/CaF₂ eutectic monotonically increases as a function of X-ray dose from 0.1 to 3000 mGy while the TL intensity of the CaF₂ 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/CaF₂ eutectic is clearly wider than that with the CaF₂ single crystal. This is due to its significantly higher TL intensity. The measurable dose range of the LiF/CaF₂ 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/CaF₂ eutectic will be improved if the read-out process is optimized. In this study, we investigate the dosimetric properties of the non-doped LiF/CaF₂ 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.

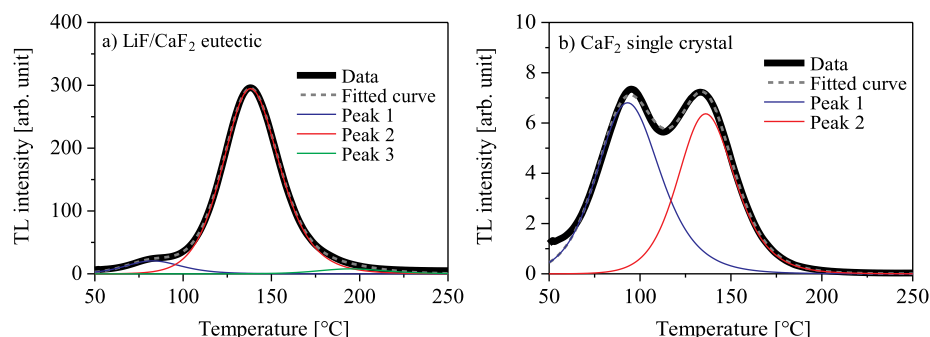


Fig. 6. TL glow curves of the LiF/CaF₂ eutectic and the CaF₂ single crystal after exposure to 1 Gy of X-rays.

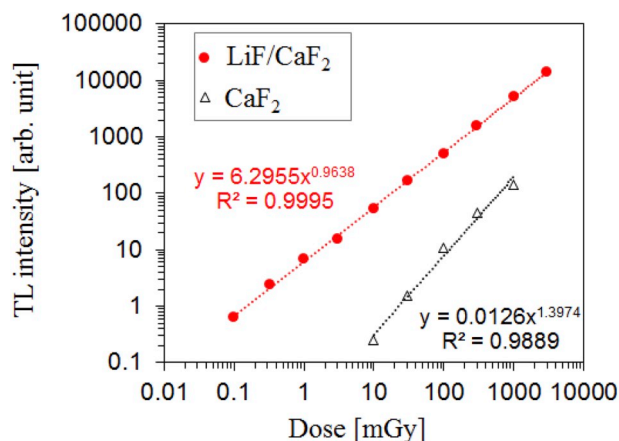


Fig. 7. TL dose response curves of the LiF/CaF₂ eutectic and the CaF₂ single crystal.

4. Conclusion

The non-doped LiF/CaF₂ eutectic is obtained by the simple melt-solidification method. It shows the significantly higher TL intensity than that of the non-doped CaF₂ single crystal. In addition, the TL intensity of the non-doped LiF/CaF₂ eutectic monotonically increases as a function of X-ray dose from 0.1 to 3000 mGy.

Acknowledgements

This work was supported by Grant-in-Aid for Scientific Research A (17H01375) and B (18H03468 and 19H03533), Young Scientists B (17K14911) and Early-Career Scientists (18K14158) from JSPS. The Cooperative Research Project of Research Institute of Electronics, Shizuoka University, Murata Foundation and Nippon Sheet Glass Foundation are also acknowledged.

References

Kabler, M.N., 1964. Low-temperature recombination luminescence in alkali halide crystals. *Phys. Rev.* 136, A1296–A1302.

- Kawaguchi, N., Fukuda, K., Yanagida, T., Fujimoto, Y., Yokota, Y., Suyama, T., Watanabe, K., Yamazaki, A., Yoshikawa, A., 2011. Fabrication and characterization of large size ⁶LiF/CaF₂:Eu eutectic composites with the ordered lamellar structure. *Nucl. Instrum. Methods* 652, 209–211.
- Kawano, N., Kawaguchi, N., Fukuda, K., Okada, G., Yanagida, T., 2018a. Scintillation and dosimetric properties of ⁶LiF-CaF₂:Eu eutectic composites. *J. Mater. Sci. Mater. Electron.* 29, 8964–8969.
- Kawano, N., Kawaguchi, N., Fukuda, K., Okada, G., Yanagida, T., 2018b. Scintillation and dosimetric properties of Ce-doped ⁶LiF-CaF₂ eutectic composites. *Opt. Mater.* 82, 60–64.
- Kitis, G., Gomez-Ros, J.M., Tuyn, J.W.N., 1998. Thermoluminescence glow-curve deconvolution functions for first, second and general orders of kinetics. *J. Phys. D Appl. Phys.* 31, 2636–2641.
- Kouzes, R.T., 2011. Overview of ³He Supply Issues. *IEEE NSS MIC*, 2011.
- Kouzes, R.T., Ely, J.H., Lintreuer, A., Mace, E.K., Stephens, D.L., Woodring, M.L., 2011. Neutron detection gamma ray sensitivity criteria. *Nucl. Instrum. Methods A* 654, 412–416.
- Masai, H., Yanagida, T., Mizoguchi, T., Ina, T., Miyazaki, T., Kawaguchi, N., Fukuda, K., 2015. Local coordination state of rare earth in eutectic scintillators for neutron detector applications. *Sci. Rep.* 5, 13332.
- McKeever, S.W.S., 1985. *Thermoluminescence of Solids*. Cambridge University Press.
- McKeever, S.W.S., 2011. Optically stimulated luminescence: a brief overview. *Radiat. Meas.* 46, 1336–1341.
- Nanto, H., Hirasawa, K., Takei, Y., Yanagida, Y., Koguchi, Y., Yamamoto, Y., 2018. Photostimulable phosphor Glass for ionizing radiation monitoring. *MDPI Proc.* 2, 706.
- Obryk, B., Bilski, P., Olko, P., 2011. Method of thermoluminescent measurement of radiation doses from micrograys up to a megagray with a single LiF:Mg,Cu,P detector. *Radiat. Protect. Dosim.* 144, 543–547.
- Okada, G., Kato, T., Nakauchi, D., Fukuda, K., Yanagida, T., 2016. Photochromism and Thermally and Optically Stimulated luminescences of AlN ceramic plate for UV sensing. *Sensor. Mater.* 8, 897–904.
- Podgoršak, E.B., Fuller, G.E., Moran, P.R., Podgorsak, E.B., 1974. Thermoluminescent supralinear response as an optical emission effect for CaF₂ V_k-Centers. *Radiat. Res.* 59, 446–452.
- Shiran, N., Belsky, A., Gektin, A., Gridin, S., Boiaryntseva, I., 2013. Radioluminescence of color centers in LiF crystals. *Radiat. Meas.* 56, 23–26.
- Williams, R.T., Kabler, M.N., Hayes, W., Stott, J.P., 1976. Time-resolved spectroscopy of self-trapped excitons in fluorite crystals. *Phys. Rev. B* 14, 725–740.
- Yanagida, T., 2018. Inorganic scintillating materials and scintillation detectors. *Proc. Jpn. Acad. B* 94, 75–97.
- Yanagida, T., Kamada, K., Fujimoto, Y., Yagi, H., Yanagitani, T., 2013a. Comparative study of ceramic and single crystal Ce:GAGG scintillator. *Opt. Mater.* 35, 2480–2485.
- Yanagida, T., Fujimoto, Y., Kawaguchi, N., Yanagida, S., 2013b. Dosimeter properties of AlN. *J. Ceram. Soc. Jpn.* 121, 989–991.
- Yanagida, T., Fujimoto, Y., Ito, T., Uchiyama, K., Mori, K., 2014a. Development of X-ray induced afterglow characterization system. *Appl. Phys. Exp.* 7, 062401.
- Yanagida, T., Fujimoto, Y., Watanabe, K., Fukuda, K., Kawaguchi, N., Miyamoto, Y., Nanto, H., 2014b. Scintillation and optical stimulated luminescence of Ce doped CaF₂. *Radiat. Meas.* 71, 162–165.
- Yanagida, T., Okada, G., Kawaguchi, N., 2019. Ionizing-radiation-induced storage-luminescence for dosimetric applications. *J. Lumin.* 207, 14–21.