JCS-Japan

February

vol.128

Journal of the Ceramic Society of Japan

2020

FULL PAPER

Scintillation and dosimetric properties of Dy-doped CaF_2 translucent ceramic and single crystal

Naoki KAWANO^{1,†}, Daisuke NAKAUCHI², Fumiya NAKAMURA² and Takayuki YANAGIDA²

¹Graduate School of Engineering Science, Akita University, Akita 010-8502, Japan

²Graduate School of Science and Technology, Nara Institute of Science and Technology (NAIST), Ikoma, Nara 630-0192, Japan

We synthesized a Dy-doped CaF_2 translucent ceramic by the spark plasma sintering method, and investigated its scintillation and dosimetric properties compared with those of the single crystal. Both the samples showed sharp peaks across 480–670 nm due to the 4f–4f transitions of Dy^{3+} , and a broad peak approximately at 300 nm due to the self-trapped excitons. The decay time constants of both the samples in scintillation were approximately 5 ms, which was close to those for the 4f–4f transitions of Dy^{3+} . Regarding thermally-stimulated luminescence, the translucent ceramic exhibited higher sensitivity than the single crystal, and the dynamic range was at least 0.01–100 mGy. In addition, both the samples showed optically stimulated luminescence due to the 4f–4f transitions of Dy^{3+} during 590 nm stimulation light, but the lowest detection limit of both the samples was approximately 10 mGy.

©2020 The Ceramic Society of Japan. All rights reserved.

Key-words : CaF_2 , Translucent ceramic, Dy, SPS

[Received July 18, 2019; Accepted December 2, 2019]

1. Introduction

Dosimeters based on solid-state phosphor materials have received much attention for investigation of accumulated radiation dose, energy and spatial distribution.^{1)–3)} The dosimeters are used in various application fields such as environmental dosimetry, individual radiation monitoring and retrospective accidental dosimetry.¹⁾ The phosphor materials for the dosimeters have a capability to store radiation energy as a form of trapping electrons and holes. The absorbed energy can be read out as photon emissions by external stimulation, which decapture the electrons and holes followed by recombination. When stimulated by heat or light, the resulting light is called thermally stimulated luminescence (TSL) or optically stimulated luminescence (OSL), respectively.^{3)–5)} Basic requirements for the phosphor materials include high sensitivity, dose linearity and low fading. To date, many kinds of the phosphor materials such as Mg and Ti doped LiF, C-doped Al_2O_3 are used for dosimetric applications.^{1),3)}

CaF_2 with an impurity is one of the well-known phosphor materials for radiation dosimetric method owing to high sensitivity and low effective atomic number. For example, Mn-doped CaF_2 is commercially known as TLD-400.⁶⁾ Its TSL sensitivity is much higher than that of TLD-100, and the dynamic range is 0.1 μGy –100 Gy. It is used for environmental radiation dosimetry and high dose measurement.^{6),7)} Furthermore, Tm-doped CaF_2 shows two TSL glow peaks approximately at 150 and 250°C, and are

of interest for dose measurements in mixed radiation field since the relative TSL intensity of the glow peaks depends on the linear energy transfer of incident radiation.^{6)–8)} In addition, Dy-doped CaF_2 is commercially available as TLD-200. It shows excellent TSL sensitivity, and a linear TSL response over the dose range of 0.1 μGy –10 Gy. Therefore, it has been used in the field of environmental radiation dosimetry.^{6),7)} From these examples, the phosphor materials based on CaF_2 with an impurity can be one of the promising materials for dosimeter materials. Up to now, there are many studies on CaF_2 with an impurity in various forms such as crystals and ceramics,⁶⁾ but a few studies in a form of translucent ceramics, although the translucent ceramics have some advantages such as high luminescence intensity, high uniformity and high mechanical strength.^{9)–11)}

In this study, we synthesized a Dy-doped CaF_2 translucent ceramic by the spark plasma sintering (SPS) method, and investigated scintillation and dosimetric properties compared with those of the single crystal. The translucent ceramic synthesized by the SPS could show better dosimetric properties than the single crystal because a large amount of anion vacancies involved in TSL and OSL could be generated in the translucent ceramic due to the synthesis in reducing atmosphere.^{10)–14)} After the synthesis of the translucent ceramic and single crystal, we evaluated their scintillation, TSL and OSL properties.

2. Experimental methods

A Dy-doped CaF_2 translucent ceramic was synthesized by the SPS method using Sinter Land LabX-100. CaF_2 (99.99%) and DyF_3 (99.9%) were mixed in a weight ratio

[†] Corresponding author: N. Kawano; E-mail: n-kawano@gipc.akita-u.ac.jp

of 99.9:0.1. Subsequently, the mixture was loaded in a graphite die and held between graphite punches. In the sintering process, the temperature was increased from 25 to 1070°C at a rate of 23 °C/min and held for 15 min under pressure of 70 MPa. After that, the surfaces of the ceramic were polished mechanically. Furthermore, a Dy-doped single crystal was synthesized as follows. The mixture of CaF_2 and DyF_3 in a weight ratio of 99.9:0.1 were put into a carbon crucible, which was set in the SUS chamber of the original furnace (Toei Scientific Industrial). After setting of crucibles and hot zone made of high purity carbon, the chamber was evacuated up to 10^{-4} Pa. Then, the crucible was heated at 400°C for 20 min for baking, and the chamber was filled with Ar gas up to ambient pressure. Then, the crucible was heated at the temperature no less than the melting point of CaF_2 for 30 min and cooled naturally. After the mechanical polish, the Dy-doped single crystal was obtained.

Scintillation spectrum under X-ray irradiation was measured using our original setup.¹⁰⁾ The X-ray generator with a tungsten anode target (XRB80P&N200×4550, Spellman) was operated by applying a voltage of 80 kV and a tube current of 1.2 mA for X-ray irradiation. The scintillation light from the samples was guided to a spectrometer (DU-420-BU2 CCD and 163 monochromator, Andor) using an optical fiber. Further, scintillation decay time profile was measured using an afterglow characterization system with a pulse X-ray tube.¹⁵⁾ The time resolution was a few ns, and the detection wavelength range of the photomultiplier tube (R7400P-06, Hamamatsu photonics) was across 160–650 nm. As a dosimetric property, TSL glow curve was measured using a spectrometer (TL-2000, Nanogray).¹⁶⁾ The temperature range was from 50 to 350°C, and the heating rate was 1 °C/s. In addition, OSL spectra and OSL decay time profile were measured using a spectrometer (FP-8600, JASCO). The stimulation wavelength was 630 nm, and the monitoring wavelength for the OSL profile was 480 nm.

3. Results and discussion

Figure 1 represents the photograph of the Dy-doped translucent ceramic and single crystal. The thickness of both the samples was about 1.0 mm. The single crystal

Fig. 1. Photograph of the Dy-doped translucent ceramic and single crystal.

seemed to be highly transparent, and have no cracks and defects such as grain boundaries. However, the transparency of the translucent ceramic was not so high that the check pattern on the back of the translucent ceramic was not clearly observed, whereas the pattern beneath the single crystal could be seen through.

Figure 2 shows the in-line transmittance spectra of the Dy-doped translucent ceramic and the single crystal. The single crystal showed high transmittance over 40% in the spectral range of 350–2700 nm, whereas the translucent ceramic exhibited low transmittance. In addition, no clear absorption peak due to the transitions of Dy ions was observed in both the samples.

Figure 3 exhibits the scintillation spectra of the Dy-doped translucent ceramic and single crystal under X-ray irradiation. Sharp emission peaks approximately at 480–490, 570–590, 650–670 nm were observed while a broad peak approximately at 300 nm was observed in both the samples.^{17)–20)} The spectral features of the sharp emission peaks were similar to those for other Dy^{3+} -doped materials, thus the sharp emission peaks should be ascribed to the 4f–4f transitions of Dy^{3+} .^{17)–20)} Furthermore, the spectral feature of the broad peak was typical for the self-trapped excitons (STE) in CaF_2 host, thus the broad peak was attributed to the STE.^{12),21),22)} The scintillation intensity of 480–670 nm emissions for the translucent ceramic was slightly higher than those for the single crystal. This might be because Dy^{3+} ions were more uniformly dis-

Fig. 2. In-line transmittance spectra of the Dy-doped translucent ceramic and single crystal.

Fig. 3. X-ray induced spectra of the Dy-doped translucent ceramic and single crystal.

Fig. 4. X-ray induced scintillation decay time profiles of the Dy-doped translucent ceramic and single crystal.

persed in the translucent ceramic compared with the single crystal due to solid state reaction by the SPS method.¹⁰⁾

Figure 4 represents the scintillation decay time profiles of the Dy-doped translucent ceramic and single crystal under X-ray irradiation. Each decay time profile was approximated by an exponential decay function. The derived decay time constants were 5.3 ms for the translucent ceramic and 5.5 ms for the single crystal. They were close to the typical decay time constants (0.1–3.5 ms) for Dy³⁺-doped CaF₂ at 77K and the Dy³⁺-doped materials in photoluminescence (PL).^{23)–25)} Therefore, the emissions should be ascribed to the 4f–4f transitions of Dy³⁺ since scintillation decay time tends to be longer than PL one due to the additional energy migration processes in scintillation.²⁶⁾ Such phenomenon is often observed in various materials.^{27),28)} In addition, the decay time constants of both the samples in scintillation were almost identical.

Figure 5 shows the TSL glow curves of the Dy-doped translucent ceramic and single crystal. Both the samples were irradiated by X-ray (100 mGy) prior to the measurement. The translucent ceramic exhibited two main glow peaks approximately at 95 and 165°C while the single crystal showed several glow peaks over the temperature range of 90–210°C. Furthermore, the translucent ceramic showed much higher TSL sensitivity than the single crystal. This should be because many defects responsible for TSL were generated in the translucent ceramic during the synthesis of reducing atmosphere. In addition, glow peak temperature, activation energy and frequency factors were calculated by numerical approximation assuming first-order kinetics as follows.²⁹⁾

$$I(T) = I_M \exp \left[1 + \frac{E}{kT} \frac{T - T_M}{T_M} - \frac{T^2}{T_M^2} \left(1 - \frac{2kT}{E} \right) \right] \times \exp \left(\frac{E}{kT} \frac{T - T_M}{T_M} - \frac{2kT}{E} \right)$$

Fig. 5. TSL glow curves of the Dy-doped translucent ceramic and single crystal.

Table 1. Glow peak temperature, activation energy and frequency factors

		Glow Peak Temperature (T_M) [°C]	Activation Energy (E) [eV]	Frequency Factors (s) [s^{-1}]
Translucent Ceramic	Peak1	90	0.8	9.7×10^9
	Peak2	110	0.9	5.0×10^{10}
	Peak3	160	0.9	1.6×10^9
	Peak4	195	1.0	9.0×10^8
	Peak5	250	1.1	1.9×10^9
Single Crystal	Peak1	90	0.8	9.7×10^9
	Peak2	110	0.9	5.0×10^{10}
	Peak3	140	0.9	6.7×10^9
	Peak4	170	0.9	9.8×10^8
	Peak5	210	1.0	3.5×10^8

Here, $I(T)$ is the glow peak intensity, I_M is the glow peak top intensity, T is the absolute temperature, T_M is the glow peak temperature, E is the activation energy and k is Boltzmann constant. In addition, the frequency factor can be expressed as $s = \beta E / [k(T_M)^2] \times \exp[E/(kT_M)]$, and the heating rate β is 1 °C/s.²⁹⁾ The calculation results are summarized in **Table 1**. Compared with the above two samples and TLD-200 (Dy-doped CaF₂) in the past study,³⁰⁾ the glow peak temperature and the activation energy were found to be different for each of the three samples. It is suggested that different defects involved in TSL might be generated in each of the three samples. Moreover, the high values of the frequency factors in Table 1 suggested that the thermal ionization should be main detrapping processes for TSL in the translucent ceramic and the single crystal.

Figure 6 shows the TSL dose response curves of the Dy-doped translucent ceramic and single crystal. Here, the integrated intensity of the TSL glow peaks in the temperature range of 50–300°C was used as a TSL intensity. Both

Fig. 6. TSL dose response curves of the Dy-doped translucent ceramic and single crystal.

Fig. 7. OSL decay time profiles of the Dy-doped translucent ceramic and single crystal.

the samples showed a linear TSL response against the X-ray dose, and the dynamic range of each sample was confirmed to be 0.01–100 mGy for the translucent ceramic and 0.1–100 mGy for the single crystal. The lower detection limit (0.01 mGy) of the translucent ceramic was found to be comparable to that of commercialized TSL dosimeter (TLD-100).⁶⁾ It should be noted that our measurement setup did not allow dose delivery lower than 0.01 mGy, and the TSL signals from the translucent ceramic and single crystal were saturated in the TSL reader under X-ray irradiation over 100 mGy.

In addition to the TSL properties, we also investigated the OSL properties. **Figure 7** represents the OSL decay time profiles of the Dy-doped translucent ceramic and the single crystal after X-ray irradiation of 1 Gy. The stimulation and monitoring wavelengths were 630 and 480 nm, respectively. The signal intensity decreased gradually over time, suggesting that the signals were derived from OSL. In addition, the decay time profiles were approximated by two exponential decay functions. The obtained decay time constants were approximately 144 and 2400 s for the translucent ceramic, and 129 and 2000 s for the single crystal. These results suggested that there were at least two detrapping processes involved in OSL in both the samples. **Figure 8** shows the OSL spectra of the Dy-doped translucent ceramic and single crystal. Both the samples were irradiated by X-rays (1 Gy) before the measurement.

Fig. 8. OSL spectra of the Dy-doped translucent ceramic and single crystal.

Fig. 9. OSL dose response curves of the Dy-doped translucent ceramic and single crystal.

Emission peaks approximately at 480 and 580 nm were observed in both the samples during the optical stimulation (630 nm). The spectral features were similar to those for the Dy³⁺ doped materials in PL,^{17)–20)} thus the OSL was attributed to the 4f–4f transitions of Dy³⁺. In addition, the OSL intensity of the translucent ceramic was much higher than that of the single crystal as well as the TSL results shown in Fig. 5. **Figure 9** shows the OSL dose response curves of the Dy-doped translucent ceramic and the single crystal. The peak top intensity was defined as the OSL intensity. A linear correlation between X-ray dose and the OSL intensity was observed in both the samples. However, the lowest detection limit of both the samples was about 10 mGy, which was much higher than that of conventional OSL materials such as C-doped Al₂O₃.¹⁾ Throughout this study, we evaluated scintillation and dosimetric properties of the Dy-doped translucent ceramic and single crystal, and the dosimetric properties of the translucent ceramic were superior to those of the single crystal. Furthermore, the translucent ceramic showed excellent TSL sensitivity comparable to commercial TSL dosimeter (TLD-100), thus the Dy-doped CaF₂ translucent ceramic should be promising candidate for TSL materials.

4. Conclusion

We characterized scintillation, TSL and OSL properties of the Dy-doped CaF₂ translucent ceramic and single crystal. The Dy-doped samples exhibited scintillation due to the STE and the 4f-4f transitions of Dy³⁺. Further, the Dy-doped translucent ceramic showed higher TSL sensitivity than the single crystal, and its TSL dose range was confirmed to be 0.01–100 mGy. In addition, OSL due the 4f-4f transitions of Dy³⁺ was observed in both the samples, but the OSL sensitivity was much lower than that of common OSL materials.

Acknowledgements This work was supported by Grant-in-Aid for Scientific Research (A) (17H01375) and Grant-in-Aid for Research Activity Start-up (17H06867) from the Ministry of Education, Culture, Sports, Science and Technology of the Japanese government (MEXT).

References

- 1) B. C. Bhatt, *Radiat. Prot. Environ.*, **34**, 6–16 (2011).
- 2) M. R. Mayhugh, R. W. Christy and N. M. Johnson, *J. Appl. Phys.*, **41**, 2968–2976 (1970).
- 3) S. W. S. McKeever, *Radiat. Meas.*, **46**, 1336–1341 (2011).
- 4) A. J. J. Bos, *Nucl. Instrum. Meth. B*, **184**, 3–28 (2001).
- 5) T. Yanagida, *J. Lumin.*, **169**, 544–548 (2016).
- 6) Data sheet of TLD materials from thermoscientific, <https://assets.thermofisher.com/TFS-Assets/LSG/Catalogs/Dosimetry-Materials-Brochure.pdf>.
- 7) V. E. Kafadar, A. N. Yazaci and R. G. Yildirim, *Nucl. Instrum. Meth. B*, **267**, 3337–3346 (2009).
- 8) G. Massillon-JL, I. Gamboa-deBuen, A. E. Buenfil, M. A. Monroy-Rodriguez and M. E. Brandan, *Nucl. Instrum. Meth. B*, **266**, 772–780 (2008).
- 9) S. F. Wang, J. Zhang, D. W. Luo, F. Gu, D. Y. Tang, Z. L. Dong, G. E. B. Tan, W. X. Que, T. S. Zhang, S. Li and L. B. Kong, *Prog. Solid State Ch.*, **41**, 20–54 (2013).
- 10) T. Yanagida, K. Kamada, Y. Fujimoto, H. Yagi and T. Yanagitani, *Opt. Mater.*, **35**, 2480–2485 (2013).
- 11) N. Kawano, T. Kato, G. Okada, N. Kawaguchi and T. Yanagida, *Opt. Mater.*, **73**, 364–370 (2017).
- 12) N. Kawano, D. Nakauchi, F. Fukuda, G. Okada, N. Kawaguchi and T. Yanagida, *Jpn. J. Appl. Phys.*, **57**, 102401 (2018).
- 13) T. Kato, N. Kawano, G. Okada, N. Kawaguchi, K. Fukuda and T. Yanagida, *Optik*, **168**, 956–962 (2018).
- 14) N. Kawano, T. Kato, G. Okada, N. Kawaguchi and T. Yanagida, *Opt. Mater.*, **88**, 67–73 (2019).
- 15) T. Yanagida, Y. Fujimoto, T. Ito, K. Uchiyama and K. Mori, *Appl. Phys. Express*, **7**, 062401 (2014).
- 16) T. Yanagida, Y. Fujimoto, N. Kawaguchi and S. Yanagida, *J. Ceram. Soc. Jpn.*, **121**, 988–991 (2013).
- 17) R. Sharma and A. S. Rao, *J. Non-Cryst. Solids*, **495**, 85–94 (2018).
- 18) S. S. Babu, P. Babu, C. K. Jayasankar, Th. Troster, W. Sievers and G. Wortmann, *Opt. Mater.*, **31**, 624–631 (2009).
- 19) M. Ayvacikli, A. Ege and N. Can, *Opt. Mater.*, **34**, 138–142 (2011).
- 20) A. A. El-Maaref, K. H. S. Shaaban, M. Abdelawwad and Y. B. Saddeek, *Opt. Mater.*, **72**, 169–176 (2017).
- 21) F. Nakamura, T. Kato, G. Okada, N. Kawaguchi, K. Fukuda and T. Yanagida, *Ceram. Int.*, **43**, 604–609 (2017).
- 22) F. Nakamura, T. Kato, G. Okada, N. Kawaguchi, K. Fukuda and T. Yanagida, *J. Eur. Ceram. Soc.*, **37**, 1707–1711 (2017).
- 23) C. T. Kwan, *Electronic Theses and Dissertations*. 6102 (1971).
- 24) P. Babu, K. H. Jang, E. S. Kim, L. Shi, R. Vijaya, V. Lavin, C. K. Jayasankar and H. J. Seo, *J. Non-Cryst. Solids*, **356**, 236–243 (2010).
- 25) G. Lakshminarayana, H. Yang, Y. Teng and J. Qiu, *J. Lumin.*, **129**, 59–68 (2009).
- 26) A. Lempicki, A. J. Wojtowicz and E. Berman, *Nucl. Instrum. Meth. A*, **333**, 304–311 (1993).
- 27) N. Kawano, M. Koshimizu, G. Okada, Y. Fujimoto, N. Kawaguchi, T. Yanagida and K. Asai, *Sci. Rep.*, **7**, 14754 (2017).
- 28) N. Kawano, N. Kawaguchi, K. Fukuda, G. Okada and T. Yanagida, *Opt. Mater.*, **82**, 60–64 (2018).
- 29) G. Kitis, J. M. Gomez-Ros and J. W. N. Tuyn, *J. Phys. D Appl. Phys.*, **31**, 2636–2641 (1998).
- 30) A. N. Yazici, R. Chen, S. Solak and Z. Yegingil, *J. Phys. D Appl. Phys.*, **35**, 2526–2535 (2002).