Neutron-induced thermoluminescence properties of Tb3+-doped CaO–Al2O3–B2O3 glasses

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We fabricated neutron detection glasses, Tb3+-doped CaO–Al2O3–B2O3 glasses, including 10B-enriched (10B glass) and 11B-enriched (11B glass) glasses. The glasses were irradiated with X-rays, heavy particles, or neutrons and their thermoluminescence (TL) properties were investigated. The TL properties after X-ray or heavy particle irradiation were the same for the 10B and 11B glasses. Meanwhile, after neutron irradiation, the TL properties of the 10B and 11B glasses were significantly different. The TL intensity of the 10B glasses was higher than that of the 11B glasses, and the TL peak intensity of 10B (n, α) reaction had good linearity in the irradiation range of 109–1013 neutrons/cm2.

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1. Introduction

Neutrons are used in various fields including industry (manufacture of radioisotopes), science (elemental analysis and radiography), and medicine (boron neutron capture therapy). The detection and measurement techniques are indispensable to use neutrons properly. However, neutrons have no charge, unlike other radiation such as γ-ray, and γ-ray. Therefore, to detect neutrons, it is necessary to generate charged particles by a nuclear reaction and measure the reaction between the charged particles and the detector. Hence, it is necessary to use nuclides that cause a nuclear reaction to convert neutrons to charged particles. 3He or BF3 proportional counters,1,2 LiF/ZnS sheets,3 Ce3+-doped LiCaAlF6 single crystals,4 LiCaAlF6:Eu2+ single crystals,5 ZnS:Ag/LiF, Li-glass,6 Gd-imaging plates (BaFBr:Eu and Gd2O3),7 and LiF are used for neutron detection in which 3He, 6Li, 10B, and Gd function as converters. Among them, 10B has a large reaction cross-section for neutrons. For the nuclear reaction of 10B and a neutron, 94% of the reactions produce 1.47 MeV α-rays and 0.84 MeV 7Li* (7Li* nuclide in its excited state), and 6% of the reactions produce 1.78 MeV α-rays and 1.01 MeV 7Li. For the latter case, 7Li* relaxes to 7Li with 0.48 MeV γ-rays emission. Therefore, γ-rays are finally emitted from 10B (n, α) reaction.8 In addition, 10B has low reactivity with γ-rays because the atomic number of boron is small; boron is also excellent in availability and safety. Hence, it is expected to be applied to detection elements that replace existing detection elements, as reported by many studies, e.g. Multi-Blade detectors,9 10B-doped liquid scintillators,10 and 10B-based semiconductors.11 In this study, we report a new neutron dosimeter with 10B.

Dosimeter materials are used to monitor the cumulated dose, and the thermoluminescence (TL), optically stimulated luminescence, and radiophotoluminescence are commonly used for passive dosimetry.12 In particular, TL materials are used in diverse applications in radiation therapy,13 personal radiation exposure dosimeters,14 or medical imaging.15 TL phenomena are induced by the recombination of metastable electron–hole pairs trapped in different sites of the irradiated material. Upon exposure to ionizing radiation, electron–hole pairs are generated, and separately captured in trapping sites, such as impurities, defects, or imperfections in the lattice. When these materials are subjected to thermal stimulations, trapped electrons are released and the eventual electron–hole recombination induces the observed luminescence. The concen-
trations of trapped electrons and holes are directly related to the absorbed dose of ionizing radiation. TL dosimeters can be processed with an arbitrary shape using various elements; these dosimeters have high sensitivity and wide measurement dose range.\(^{(1-9)}\) Due to these advantages, TL dosimeters are widely used. Many materials have been developed as TL materials for neutron detection, such as Li$_2$BO$_3$:Cu (linear response in $10^2$–$10^6$ neutrons/cm$^2$),\(^{(1,7)}\) Mg$_2$SiO$_4$:Tb/LiF or Gd$_2$O$_3$ (linear response in $10^2$–$10^{12}$ neutrons/cm$^2$),\(^{(1,8)}\) and BaF$_2$:Eu$^{3+}$/Gd$_2$O$_3$ ($X$ = Br, I) (linear response in $10^3$–$10^6$ neutrons/cm$^2$).\(^{(3)}\)

We have previously reported the high TL intensity of rare-earth-doped CaO–Al$_2$O$_3$–B$_2$O$_3$ glasses.\(^{(19-21)}\) Among them, Tb$^{3+}$-doped CaO–Al$_2$O$_3$–B$_2$O$_3$ glasses proved to be sensitive to X-ray and linearity with a wide dynamic range from 1.0 mGy to 10 Gy.\(^{(19)}\) In this study, Tb$^{3+}$-doped CaO–Al$_2$O$_3$–B$_2$O$_3$ glasses were prepared with $^{10}$B ($^{10}$B glass) to detect neutrons and $^{11}$B ($^{11}$B glass) to measure the background. Then, they were irradiated with X-ray, heavy-particles, or neutrons, and their TL properties were investigated. The X-ray-induced TL was measured to evaluate the basic TL properties and to grasp the effect of prompt $\gamma$-rays, while the heavy-particle-induced TL was measured to evaluate the TL properties after irradiation with the charge particles from the $^{10}$B ($n$, $\alpha$) reaction.

### 2. Experimental

Glass samples of 35CaO–15Al$_2$O$_3$–50B$_2$O$_3$+$x$Tb ($x = 0, 1, 3, and 5$ mol % against Ca) were prepared according to a conventional melt-quenching method using an alumina crucible under atmospheric pressure and air. High purity CaCO$_3$ (99.99%, Rare Metallic Co., LTD), Al$_2$O$_3$ (99.99%, High Purity Chemicals), H$_2$^{10}BO$_3$ ($^{10}$B > 96%, Stella-Chemifa Co.), and Tb$_2$O$_3$ (99.9%, Rare Metallic Co., LTD) powders were used as the starting materials. The mixture in the alumina crucible was melted at 1100°C for 20 min, the melt was placed onto a stainless-steel plate at 500°C, and the glass was formed by pressurization, and then quenched at room temperature. Using H$_3^{11}$BO$_3$ ($^{11}$B > 99.0%, Yamanaka Ceradyne, INC.) instead of H$_3^{10}$BO$_3$, the $^{11}$B glasses were prepared in the same manner. Figure 1 shows the samples. All glasses are transparent and non-hygrosopic, and the thickness was 3.1–3.3 mm.

The excitation and emission spectra were measured with an F-7000 spectrometer (Hitachi High-Technologies), the light source of 150 W xenon lamp.

For the X-ray-induced TL measurement, the glasses were exposed to X-rays at a dose rate of 1 Gy/min. Cu K$_\alpha$ radiation from an X-ray generator (Rigaku Co., Japan) operated at 40 kV and 40 mA was used for irradiation. The TL glow curves of the glass samples were recorded from 307 to 673 K at a heating rate of 0.5 K/s in an air atmosphere. The temperature was controlled with a programmed heater (SCR-SHQ-A, Sakaguchi). The TL photons from the sample were detected with a photomultiplier tube (PMT; H11890-210, Hamamatsu) with a wide range of spectral sensitivity (230–700 nm). A radiation cut filter was used to avoid the thermal radiation from the samples.

### 3. Results and discussion

Figure 2 shows the excitation and emission spectra of 1 mol % Tb$^{3+}$-doped glasses. The excitation spectra were recorded at an emission wavelength of 548 nm. The emission spectrum monitored at an excitation wavelength of 233 nm showed emission bands at 491, 547, 589, and 625 nm, which are attributed to the $^5$D$_{4}$→$^7$F$_{6}$, $^5$D$_{4}$→$^7$F$_{5}$, $^5$D$_{4}$→$^7$F$_{4}$, and $^5$D$_{4}$→$^7$F$_{3}$ electronic transitions of Tb$^{3+}$, respectively.\(^{(22)}\)
Figure 3 shows the TL glow curves of Tb$^{3+}$-doped glasses after X-ray irradiation of 0.1 Gy. We measured the TL glow curves of three samples of the same composition after X-ray irradiation, and the averaged curves are shown in Fig. 3. TL peaks were observed at 380 and 550 K for all Tb$^{3+}$-doped samples. Figure 4 shows the TL intensities at 380 K of 1, 3, and 5 mol % Tb$^{3+}$-doped glasses after X-ray irradiation of 0.1 Gy. The error bars are shown as the maximum and minimum values among the three measurements. This result suggests that the TL properties do not significantly depend on the concentration in the range of 1–5 mol %.

Figure 5 shows the TL glow curves of 1 mol % Tb$^{3+}$-doped glasses as a function of the X-ray dose from 0 Gy to 1.0 Gy, and Fig. 6 shows the TL intensity at the largest glow peak of those glasses after X-ray irradiation (0–1.0 Gy). A peak was observed at 380 K for all doses, whose intensity increased with the irradiation dose. Additionally, a broad TL peak was observed at 500–600 K. Figure 7 shows the afterglow spectra of 1 mol % Tb$^{3+}$-doped glasses after X-ray irradiation of 10 Gy. These spectra show TL emission bands at 491, 547, 589, and
625 nm, which are attributed to the $^5D_4 \rightarrow ^7F_6$, $^5D_4 \rightarrow ^7F_5$, $^5D_4 \rightarrow ^7F_4$, and $^5D_4 \rightarrow ^7F_3$ electronic transitions of Tb$^{3+}$. These results suggest that these glasses have high sensitivity to X-rays and are expected to have sensitivity to $\gamma$-rays.

Figure 8 shows the TL glow curves of 1 mol % Tb$^{3+}$-doped glasses after X-ray irradiation of 1 Gy. These TL glow curves were measured 0, 2, and 5 days after X-ray irradiation. The largest TL peak intensity was 57% after 2 days and 39% after 5 days in the $^{10}$B glass, and 68% after 2 days and 49% after 5 days in the $^{11}$B glass. The largest TL peak was observed at 369, 428, and 416 K in $^{10}$B glass measured 0, 2, and 5 days after, and that was observed at 403, 425, and 419 K in $^{11}$B glass measured 0, 2, and 5 days after. This result suggests that the electrons trapped at shallow depths are preferentially released at room temperature.

Figure 9 shows the X-band ESR spectra at room temperature of 1 mol % Tb$^{3+}$-doped glasses after X-ray irradiation of 1 Gy. The observed spectrum is a superposition of at least two defect centers, and the ESR signals of the $^{10}$B glass and $^{11}$B glass were similar. The peaks at 314, 322, 331, 340, 349, and 358 mT considered to originate from the holes captured at an oxygen, because the nuclear spin quantum number of $^{16}$O is 5/2. The peak at 334 mT is considered to originate from the electron captured at an anion vacancy. If electrons or holes were captured at sites around boron, the number of peak splits would be different because the nuclear spin quantum number of $^{10}$B is 3/2 and that of $^{11}$B is 3. The spectra show that the trapping site of electrons and holes is not around boron.

Figure 10 shows the TL glow curves of 1 mol % Tb$^{3+}$-doped $^{10}$B glass after irradiation of 150 MeV/nucleon He or 135 MeV/nucleon C ions. A TL peak was observed at 380 K. Figure 11 shows the TL spectra of this glass at 380 K. TL emission bands were observed at 491, 547, 589, and 625 nm. These results suggest that this glass is sensi-
Effective to the α-rays from 10B (n, α) reaction. These results were very similar to those after X-ray irradiation.

Figure 12 shows the TL glow curves of 1 mol % Tb³⁺-doped 10B glasses measured 2 days after neutron irradiation of 10¹¹ neutrons/cm². The TL intensity of the 10B glass is much higher than that of the 11B glass (6 times at 420 K and 22 times at 530 K). This result suggests that the α-ray and γ-ray from 10B (n, α) reaction efficiently induced TL. In the 11B glass, TL peak was observed at 420 K. This result suggests that the γ-rays from the neutron source also induced TL. In addition, the TL peak at 530 K after neutron irradiation in 10B glass was much clearer than that after X-ray irradiation shown in Fig. 8. This was measured 2 days after neutron irradiation. Therefore, this result suggests that the peak at low temperature faded preferentially and the peak at high temperature became remarkable.

Figure 13 shows the TL glow curves of 1 mol % Tb³⁺-doped 10B glasses induced by 10B (n, α) reaction (10⁸–10¹³ neutrons/cm²). These were measured 8, 18, 2, 3, and 6 days after neutron irradiation. The neutron sources used in this experiment generates neutrons and gamma rays. Therefore, we fabricated 11B glass to estimate the contribution of the gamma rays and subtracted the TL intensity of 11B glass from that of 10B glass to extract the contribution of 10B (n, α) reaction. As the neutron irradiation dose increased, TL intensity increased. We observed that the TL intensity of 10B glass is significantly higher than that of 11B glass in TL after irradiation of 10⁸ neutrons/cm². In addition, these glasses had good linearity in the neutron fluence range of 10⁸–10¹³ neutrons/cm² at 530 K. This indicates that these glasses can be applied as a neutron dosimeter material.

4. Conclusions

We fabricated Tb³⁺-doped CaO–Al₂O₃–B₂O₃ glasses, including 10B and 11B, which were irradiated with X-rays, heavy particles, or neutrons; the TL properties of these
glasses were investigated. TL peaks in the glow curves were observed at 380 K after X-ray or heavy-particle irradiation. Therefore, these glasses are sensitive to $\gamma$-rays and $\alpha$-rays. Meanwhile, TL peaks in the glow curves were observed at 420 and 530 K after neutron irradiation, and the TL intensity of the $^{10}$B glasses was found to be higher than that of the $^{11}$B glasses. The minimum detectable fluence was $10^8$ neutrons/cm$^2$ and these glasses exhibited linearity over the range of $10^9$–$10^{13}$ neutrons/cm$^2$.

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References

1) A. Ravazzani, A. F. Para, R. Jaime, M. Looman, M. M. Ferrer, P. Peerrani and P. Schillebeeckx, Radiat. Meas., 41, 582–593 (2006).
2) S. Sakamoto and A. Morioka, Nucl. Instrum. Meth. A, 353, 160–163 (1994).
3) S. Stave, M. Bliss, R. Kouzes, A. Lintereur, S. Robinson, E. Siciliano and L. Wood, Nucl. Instrum. Meth. A, 784, 208–212 (2015).
4) Saint-Gobain, https://www.crystals.saint-gobain.com/.
5) T. Yanagida, N. Kawaguchi, Y. Fujimoto, K. Fukuda, Y. Yokota, A. Yamazaki, K. Watanabe, J. Pejchal, A. Uritani, T. Iguchi and A. Yoshikawa, Opt. Mater., 33, 1243–1247 (2011).
6) J. Iwanowska, L. Swiderski, M. Moszynski, T. Yanagida, Y. Yokota, A. Yoshikawa, K. Fukuda, N. Kawaguchi and S. Ishizu, Nucl. Instrum. Meth. A, 652, 319–322 (2011).
7) S. Tazaki, K. Neriishi, K. Takahashi, M. Etoh, Y. Karasawa, S. Kumazawa and N. Niimura, Nucl. Instrum. Meth. A, 424, 20–25 (1999).
8) http://accww2.kek.jp/oh/OHOtxt/OHO-2016/06-Sakasai.Kaoru.pdf.
9) F. Piscitelli, F. Messi, M. Anastasopoulos, T. Bryš, F. Chicken, E. Dian, J. Fuzi, C. Höglund, G. Kiss, J. Orban, P. Pazmandi, L. Robinson, L. Rosta, S. Schmidt, D. Varga, T. Zsiros and R. Hall-Wilton, J. Instrum., 12, P03013 (2017).
10) S. Hunt, C. Iliadis and R. Longland, Nucl. Instrum. Meth. A, 811, 108–114 (2016).
11) H. Zheng, B. Ramalingam, S. Mukherjee, Y. Zhou, K. Gangopadhyay, J. D. Brockman, M. W. Lee and S. Gangopadhyay, Sens. Biosens. Res., 9, 1–6 (2016).
12) P. Aramrun, N. A. Beresford and M. D. Wood, J. Environ. Radioactiv., 182, 128–137 (2018).
13) B. C. Bhatt, Radiat. Prot. Environ., 34, 6–16 (2011).
14) J. R. Cassata, M. Moscovitch, J. E. Rotunda, K. J. Velbeck, Y. S. Horowitz and L. Oster, Radiat. Prot. Dosim., 101, 27–42 (2002).
15) T. Kron, Radiat. Prot. Dosim., 85, 333–340 (1999).
16) https://www.jstage.jst.go.jp/article/radioisotopes1952/19/4/19.4.201.pdf.
17) E. N. D. Santos and R. Muccillo, Nucl. Instrum. Methods, 165, 561–564 (1979).
18) T. Matsumoto, Nucl. Instrum. Meth. A, 301, 552–557 (1991).
19) H. Ono, Y. Fujimoto, T. Yanagida, M. Koshimizu and K. Asai, Opt. Mater., 87, 24–28 (2019).
20) Y. Fujimoto, T. Yanagida, Y. Futami and H. Masai, Jpn. J. Appl. Phys., 53, 05FK05 (2014).
21) T. Yahaba, Y. Fujimoto, T. Yanagida, M. Koshimizu, H. Tanaka, K. Saeki and K. Asai, Nucl. Instrum. Meth. B, 392, 36–40 (2017).
22) J. C. Mittania, M. Prokic and E. G. Yukihiara, Radiat. Meas., 43, 323–326 (2008).