FULL PAPER

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 α -ray, β -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-

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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.¹⁶⁾ Due to these advantages, TL dosimeters are widely used. Many materials have been developed as TL materials for neutron detection, such as Li₂B₄O₇:Cu (linear response in 10⁵–10⁶ neutrons/cm²),¹⁷⁾ Mg₂SiO₄:Tb/LiF or Gd₂O₃ (linear response in 10⁹–10¹² neutrons/cm²),¹⁸⁾ and BaFX:Eu²⁺/Gd₂O₃ (*X* = Br, I) (linear response in 10³–10⁶ neutrons/cm²).⁷⁾

We have previously reported the high TL intensity of rare-earth-doped CaO–Al₂O₃–B₂O₃ glasses.^{19)–21)} Among them, Tb³⁺-doped CaO–Al₂O₃–B₂O₃ 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, Tb³⁺-doped CaO–Al₂O₃–B₂O₃ glasses were prepared with ¹⁰B (¹⁰B glass) to detect neutrons and ¹¹B (¹¹B 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 γ-rays, while the heavy-particle-induced TL was measured to evaluate the TL properties after irradiation with the charge particles from the ¹⁰B (*n*, α) reaction.

2. Experimental

Glass samples of 35CaO–15Al₂O₃–50B₂O₃:*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 CaCO₃ (99.99%, Rare Metallic Co., LTD), Al₂O₃ (99.99%, High Purity Chemicals), H₃¹⁰BO₃ (¹⁰B > 96%, Stella-Chemifa Co.), and Tb₄O₇ (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 H₃¹¹BO₃ (¹¹B > 99.0%, Yamanaka Ceradyne, INC.) instead of H₃¹⁰BO₃, the ¹¹B glasses were prepared in the same manner. **Figure 1** shows the samples. All glasses are transparent and non-hygroscopic, 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 Kα 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.

Fig. 1. Glass samples of 35CaO–15Al₂O₃–50B₂O₃:*x*Tb (*x* = 0, 1, 3, and 5 mol % against Ca) prepared using a conventional melt-quenching method.

The TL spectra were measured using a fluorescence spectrometer (DeltaFlex, HORIBA).

X-band Electron Spin Resonance (ESR) measurements were performed at room temperature using a JES-X330 (JEOL) spectrometer.

For the heavy-particle-induced TL measurement, the glasses were exposed to He of 150 MeV/nucleon or C ion beams of 135 MeV/nucleon at HIMAC at the National Institute of Radiological Sciences. The TL glow curves were recorded from 307 to 673 K at a heating rate of 1 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 PMT (H11890-210, Hamamatsu) with a wide range of spectral sensitivity (230–700 nm) and charge-coupled device (Ocean Photonics, QE pro).

For the neutron-induced TL measurement, the glasses were exposed to thermal neutrons (10⁸, 10⁹, 10¹⁰, 10¹¹, 10¹², and 10¹³ neutrons/cm²) at NASBEE at the National Institute of Radiological Sciences. The TL glow curves were obtained 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 PMT (H11890-210, Hamamatsu) with a wide range of spectral sensitivity (230–700 nm).

3. Results and discussion

Figure 2 shows the excitation and emission spectra of 1 mol % Tb³⁺-doped glasses. The excitation spectra were recorded at an emission wavelength of 548 nm. The emission spectra monitored at an excitation wavelength of 233 nm showed emission bands at 491, 547, 589, and 625 nm, which are attributed to the ⁵D₄→⁷F₆, ⁵D₄→⁷F₅, ⁵D₄→⁷F₄, and ⁵D₄→⁷F₃ electronic transitions of Tb³⁺, respectively.²²⁾

Fig. 2. Excitation spectra monitored at an emission wavelength of 548 nm and emission spectra monitored at an excitation wavelength of 233 nm of 1 mol % Tb^{3+} -doped glasses.

Fig. 3. TL glow curves of Tb^{3+} -doped glasses after X-ray irradiation of 0.1 Gy.

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

Fig. 4. TL intensities at 380 K of 1, 3, and 5 mol % Tb^{3+} -doped glasses after X-ray irradiation of 0.1 Gy.

Fig. 5. TL glow curves of 1 mol % Tb^{3+} -doped glasses after X-ray irradiation of 0–1.0 Gy.

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

Fig. 6. TL intensities at the largest peak in the glow curves (Fig. 5) of 1 mol % Tb³⁺-doped glasses after X-ray irradiation (0–1.0 Gy).

Fig. 7. Afterglow spectra of 1 mol % Tb³⁺-doped glasses after X-ray irradiation of 10 Gy.

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 Tb³⁺. These results suggest that these glasses have high sensitivity to X-rays and are expected to have sensitivity to γ -rays.

Figure 8 shows the TL glow curves of 1 mol % Tb³⁺-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 ¹⁰B glass, and 68% after 2 days and 49% after 5 days in the ¹¹B glass. The largest TL peak was observed at 369, 428, and 416 K in ¹⁰B glass measured 0, 2, and 5 days after, and that was observed at 403, 425, and 419 K in ¹¹B 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 % Tb³⁺-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 ¹⁰B glass and ¹¹B 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 ¹⁶O is 5/2. The peak at 334 mT is considered to originate from the electron captured at an

Fig. 8. TL glow curves of 1 mol % Tb³⁺-doped glasses after X-ray irradiation of 1 Gy.

Fig. 9. X-band Electron Spin Resonance spectra at room temperature of 1 mol % Tb³⁺-doped glasses after X-ray irradiation of 1 Gy.

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 ¹⁰B is 3/2 and that of ¹¹B 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 % Tb³⁺-doped ¹⁰B 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-

Fig. 10. TL glow curves of 1 mol % Tb^{3+} -doped ^{10}B glass after irradiation of 150 MeV/nucleon He or 135 MeV/nucleon C.

Fig. 11. TL spectra at 380 K of 1 mol % Tb^{3+} -doped ^{10}B glasses after irradiation of 150 MeV/nucleon He or 135 MeV/nucleon C.

Fig. 12. TL glow curves of 1 mol % Tb^{3+} -doped glasses 2 days after neutron irradiation (10^{11} neutrons/cm²).

tive to the α -rays from ^{10}B (n, α) reaction. These results were very similar to those after X-ray irradiation.

Figure 12 shows the TL glow curves of 1 mol % Tb^{3+} -doped glasses measured 2 days after neutron irradiation of 10^{11} neutrons/cm². The TL intensity of the ^{10}B glass is much higher than that of the ^{11}B glass (6 times at 420 K and 22 times at 530 K). This result suggests that the α -ray and γ -ray from ^{10}B (n, α) reaction efficiently induced TL. In the ^{11}B 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 ^{10}B glass was much clearer than that

Fig. 13. TL glow curves of 1 mol % Tb^{3+} -doped ^{10}B glasses induced by ^{10}B (n, α) reaction (10^8 – 10^{13} neutrons/cm²).

Fig. 14. TL intensities at 420 and 530 K in the glow curves (shown in Fig. 13) of 1 mol % Tb^{3+} -doped ^{10}B glasses after neutron irradiation (10^8 – 10^{13} neutrons/cm²).

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 % Tb^{3+} -doped ^{10}B glasses induced by the ^{10}B (n, α) reaction, and Fig. 14 shows the TL intensities of those glasses at the 420 and 530 K peaks in the glow curves after neutron irradiation (10^8 – 10^{13} neutrons/cm²). These were measured 8, 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 ^{11}B glass to estimate the contribution of the gamma rays and subtracted the TL intensity of ^{11}B glass from that of ^{10}B glass to extract the contribution of ^{10}B (n, α) reaction. As the neutron irradiation dose increased, TL intensity increased. We observed that the TL intensity of ^{10}B glass is significantly higher than that of ^{11}B glass in TL after irradiation of 10^8 neutrons/cm². In addition, these glasses had good linearity in the neutron fluence range of 10^9 – 10^{13} neutrons/cm² at 530 K. This indicates that these glasses can be applied as a neutron dosimeter material.

4. Conclusions

We fabricated Tb^{3+} -doped $\text{CaO-Al}_2\text{O}_3\text{-B}_2\text{O}_3$ glasses, including ^{10}B and ^{11}B , 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 γ -rays and α -rays. Meanwhile, TL peaks in the glow curves were observed at 420 and 530 K after neutron irradiation, and the TL intensity of the ¹⁰B glasses was found to be higher than that of the ¹¹B glasses. The minimum detectable fluence was 10⁸ neutrons/cm² and these glasses exhibited linearity over the range of 10⁹–10¹³ neutrons/cm².

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