Scintillation and Dosimetric Properties of Monocrystalline and Polycrystalline Li$_2$B$_4$O$_7$

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We have performed a comparative study on the scintillation and dosimetric properties of monocrystalline and polycrystalline Li$_2$B$_4$O$_7$ samples. The scintillation light yield of the monocrystalline Li$_2$B$_4$O$_7$ sample was higher than that of the polycrystalline Li$_2$B$_4$O$_7$ sample. In contrast, the thermoluminescence (TL) intensity of the polycrystalline Li$_2$B$_4$O$_7$ sample was higher than that of the monocrystalline Li$_2$B$_4$O$_7$ sample. These results can be explained by the difference in trap concentration between the monocrystalline and polycrystalline Li$_2$B$_4$O$_7$ samples. It has been assumed that the monocrystalline Li$_2$B$_4$O$_7$ sample shows a higher scintillation light yield owing to its lower trap concentration, and the polycrystalline Li$_2$B$_4$O$_7$ sample shows a higher TL intensity owing to its higher trap concentration.

1. Introduction

Industrial, medical, and scientific applications of ionizing radiation require both radiation detection and dosimetry techniques. The radiation detection technique allows us to measure energies and amounts of ionizing radiation immediately, and the radiation dosimetry technique allows us to measure radiation doses for a certain period of time.

In the radiation detection technique, scintillation counters are widely used because their detection efficiency is higher than those of gas proportional counters and semiconductor-type detectors. This higher detection efficiency is achieved by scintillators that are one of the elementary components of scintillation counters. Typical scintillators are solid-state phosphors with higher densities than gases and larger thicknesses than semiconductor film devices. Scintillators can more efficiently convert ionizing radiation to visible light than many other phosphors and are combined with photodetectors; thus, scintillation counters can indirectly detect ionizing radiation. Since there are various types of scintillator, scintillation counters can detect different types of ionizing radiation, such as X-rays, γ-rays, charged particles, and

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neutrons. These scintillators are used for medical imaging, nondestructive inspection, and well logging. Although many types of scintillator have been reported, it is still attractive to develop novel scintillators with higher light yields and shorter decay times.

In the radiation dosimetry technique, personal dosimeters are made of dosimetric materials that are mainly solid-state storage phosphors. Storage phosphors can store excited electrons and holes in their trapping centers after irradiation. Captured electrons and holes can be released by thermal or optical stimulation and recombine at luminescent centers. Storage phosphors that emit light by thermal and optical stimulations are called thermoluminescence (TL) and optically stimulated luminescence (OSL) dosimetric materials, respectively. Radio-photoluminescence (RPL) dosimetric materials are another choice for the radiation dosimetry technique. In RPL materials, new luminescent centers are generated by irradiation typically owing to valence changes of dopant ions. As well as research for scintillators, it is still attractive to develop novel TL, OSL, and RPL materials.

In addition to the novel material research for scintillators and dosimetric materials, we are interested in comparisons between scintillation and dosimetric properties. In general, scintillators and dosimetric materials are individually studied; however, some materials can show both scintillation and storage luminescence (TL and OSL) and their correlation is also attractive. We have actually reported an inverse correlation between OSL intensities and scintillation light yields of Ce-doped CaF₂ single crystals with similar compositions. This correlation is assumed to be due to a difference in trap concentration; that is, an increase in the trapping center density of phosphor materials tends to reduce their scintillation light yield and increase their storage luminescence intensity. In this manner, the comparative study between scintillation and dosimetric properties can be useful for a better understanding of the luminescence phenomena of phosphors after exposure to ionizing radiation. We are expecting that this study will contribute to the novel material research.

To make progress in this comparative study, we have focused on another material, Li₂B₄O₇, which has been reported as both a neutron scintillator and a dosimeter material. There are few host crystals that can be used for both applications. For example, CaF₂ is applied as the host crystal of both materials. It is known that Eu-doped CaF₂ is used for the scintillator and Mn-doped CaF₂ is used for the dosimetric material. In the case of Li₂B₄O₇, both Cu-doped Li₂B₄O₇ and nondoped Li₂B₄O₇ were reported as the scintillator and dosimetric material. Only as the dosimetric material, Mn-doped Li₂B₄O₇ was studied. Since it is easier to obtain polycrystalline and monocrystalline samples using nondoped Li₂B₄O₇, we have performed a comparative study on the scintillation and dosimetric properties of nondoped Li₂B₄O₇.

2. Materials and Methods

We prepared a polycrystalline Li₂B₄O₇ sample by atmospheric sintering in air. As raw materials, high-purity Li₂CO₃ and B₂O₃ powders were used. The raw powders were mixed in the mole ratio of Li₂B₄O₇ (Li₂CO₃:B₂O₃ = 1:2) and poured into an aluminum crucible. The mixed powders were calcined at 800 °C for 3 h in order to remove CO₂ and react into Li₂B₄O₇.
The obtained powder was pressed into a pellet; then, it was sintered at 800 °C for 3 h. As a monocrystalline Li$_2$B$_4$O$_7$ sample, we used a commercial Li$_2$B$_4$O$_7$ single crystal (OXIDE, Hokuto, Japan) that was cut and polished from a Li$_2$B$_4$O$_7$ single crystal ingot grown by the vertical Bridgman method.

To investigate the optical property of the monocrystalline Li$_2$B$_4$O$_7$ sample, the in-line transmittance spectrum was measured using a spectrophotometer (V-670; JASCO, Hachioji, Japan) across a spectral range from 190 to 2700 nm in 1 nm steps. To compare porosities of the samples, their densities were measured by Archimedes’ principle using water as the immersion fluid. Furthermore, X-ray diffraction (XRD) patterns were measured using a diffractometer equipped with a Cu-Kα X-ray source (MiniFlex600; Rigaku, Akishima, Japan). Their crystal phases were identified using the Crystallography Open Database (COD).

X-ray-induced scintillation spectra of the samples were measured using our customized setup including an X-ray generator, an optical fiber, and a spectrometer, the details of which are found elsewhere. The samples were irradiated with X-rays from an X-ray generator (XRB80P&N200X4550; Spellman High Voltage Electronics, Hauppauge, New York, United States), and their luminescence was guided to the monochromator (Shamrock 163; Andor Technology, Belfast, Northern Ireland) on a CCD-based spectrometer (DU920-BU2NC; Andor Technology). In this experiment, the applied tube voltage and current were set to 40 kV and 1.2 mA, respectively. To evaluate their scintillation light yields, pulse height spectra were measured using a $^{252}$Cf sealed source with a polyethylene modulator as a thermal neutron source and a photomultiplier tube (PMT; R7600U-200; Hamamatsu Photonics, Hamamatsu, Japan) as a photodetector. The detailed setup including analog modules for signal analysis is shown in our previous report.

To investigate the dosimetric properties of the samples, TL glow curves were measured using a TL reader (TL-2000; Nanogray, Minoh, Japan). The samples were heated at a rate of 1 °C/s by elevating the temperature from 50 to 250 °C. Before the measurements, the samples were irradiated with X-rays at certain doses using an X-ray generator (XRB80N100/CB; Spellman High Voltage Electronics). The absorbed doses (air kerma) were determined using an ionization chamber (Model 30013; PTW, Freiburg, Germany). The measurements were repeated with several different irradiation doses from 1 mGy to 10 Gy to obtain the dose–response curves of the samples, which show a correlation between the TL emission intensities and the irradiation doses.

3. Results and Discussion

Figure 1 shows the monocrystalline and polycrystalline Li$_2$B$_4$O$_7$ samples. Both samples have no visible cracks and they seem colorless. The monocrystalline Li$_2$B$_4$O$_7$ sample looks highly transparent. Figure 2 shows the in-line transmittance spectrum of the monocrystalline Li$_2$B$_4$O$_7$ sample. The in-line transmittances of the monocrystalline Li$_2$B$_4$O$_7$ sample in the wavelength range from 400 to 2700 nm are from approximately 80 to 90%. Its spectral feature is consistent with that of the Li$_2$B$_4$O$_7$ single crystal for nonlinear optical applications in the previous report. Our monocrystalline Li$_2$B$_4$O$_7$ sample for this study also seems to have an
excellent optical property. The measured densities of the monocrystalline and polycrystalline Li$_2$B$_4$O$_7$ samples are 2.42 and 2.16 g/cm$^3$, respectively. The polycrystalline Li$_2$B$_4$O$_7$ sample is more porous than the monocrystalline Li$_2$B$_4$O$_7$ sample. Figure 3 shows XRD patterns of monocrystalline and polycrystalline Li$_2$B$_4$O$_7$ samples. The small parts of the samples were used for the measurements. Both samples show XRD peaks that are ascribed to those of the Li$_2$B$_4$O$_7$ phase found in the database (COD 1511473).

Figure 4 shows X-ray-induced scintillation spectra of the monocrystalline and polycrystalline Li$_2$B$_4$O$_7$ samples. Both samples show the broad emission band peaking at the wavelength of 340 nm. These spectral features are similar to those in the previous report.$^{(50)}$ It is considered that these are related to the defect-related luminescence of nondoped Li$_2$B$_4$O$_7$. Figure 5 shows a pulse height spectrum related to the monocrystalline Li$_2$B$_4$O$_7$ sample under neutron irradiation using the $^{252}$Cf sealed source. In this measurement, the polycrystalline Li$_2$B$_4$O$_7$ sample showed no significant signals probably owing to its significantly lower light yield. Therefore, we show only the pulse height spectrum of the monocrystalline Li$_2$B$_4$O$_7$ sample. From the result, we confirmed two detection peaks that are ascribed to nuclear reactions of $^6$Li and $^{10}$B with neutrons. These nuclear reactions are shown below.$^{(7)}$

$$^6\text{Li} + n \rightarrow ^3\text{H} (2.73 \text{ MeV}) + ^4\text{He} (2.05 \text{ MeV})$$  \hspace{1cm} (1)
$^{10}\text{B} + n \rightarrow ^7\text{Li} (0.84 \text{ MeV}) + ^4\text{He} (1.47 \text{ MeV}) + \gamma\text{-ray} (0.48 \text{ MeV}) [93\%] \quad (2)$

$\rightarrow ^7\text{Li} (1.01 \text{ MeV}) + ^4\text{He} (1.78 \text{ MeV}) [7\%] \quad (3)$

The peak channels formed by $^{10}\text{B}$ and $^6\text{Li}$ are 60 and 200, respectively. In the same measurement, a standard neutron scintillator GS20 (Ce-doped lithium silicate glass) shows a peak at 7400 channels. If the light yield of GS20 is 6000 photons/MeV,$^7$ the peaks generated by the monocrystalline Li$_2$B$_4$O$_7$ sample are equivalent to the peaks for 50 and 160 photons/neutron. It is assumed that the polycrystalline Li$_2$B$_4$O$_7$ sample has a lower light yield than the monocrystalline Li$_2$B$_4$O$_7$ sample because the pulse height spectrum of the polycrystalline Li$_2$B$_4$O$_7$ sample did not show any signals exceeding the thermal noise level of the PMT located at the channel lower than the two peaks generated by the monocrystalline sample. Only the monocrystalline Li$_2$B$_4$O$_7$ sample acted as the neutron scintillator.

Figure 6 shows TL glow curves of the monocrystalline and polycrystalline Li$_2$B$_4$O$_7$ samples after 3 Gy of X-ray irradiation. The monocrystalline Li$_2$B$_4$O$_7$ sample shows broad glow peaks at approximately 60, 120, and 150 °C, and the polycrystalline Li$_2$B$_4$O$_7$ sample shows a high-intensity peak at approximately 120 °C and a broad peak at approximately 220 °C. This difference in the glow curves is due to the difference in trapping center density between the samples. In general, the glow peak temperature depends on the energy depth of trapping centers. Because both samples show a continuous distribution in the glow curves, it is considered that both samples have various energy levels of trapping centers. Both samples show TL emissions in similar temperature ranges, but the intensity ratios of their glow peaks seem to be different. In the polycrystalline Li$_2$B$_4$O$_7$ sample, the peak intensity at 120 °C is higher than those at other temperatures. This is possibly due to an increase in the density of some trapping centers with similar energy depths equivalent to the glow peak at 120 °C, but the details are unclear. In addition, although the monocrystalline Li$_2$B$_4$O$_7$ sample has an advantage in the light extraction efficiency from its inner parts owing to its highly transparent body, the TL intensity
of the polycrystalline Li$_2$B$_4$O$_7$ sample is higher than that of the monocrystalline Li$_2$B$_4$O$_7$ sample. Figure 7 shows TL dose–response curves of the monocrystalline and polycrystalline Li$_2$B$_4$O$_7$ samples. In the case of the Li$_2$B$_4$O$_7$ monocrystalline sample, a monotonic increase in its TL intensity is observed in the range of 100 mGy to 3 Gy. In contrast, in the case of the polycrystalline Li$_2$B$_4$O$_7$ sample, a monotonic increase in its TL intensity is observed in a wide range from 10 mGy to 10 Gy owing to its high TL intensity. The polycrystalline Li$_2$B$_4$O$_7$ sample clearly shows better dosimetric properties than the Li$_2$B$_4$O$_7$ monocrystalline sample. The TL intensity of the monocrystalline Li$_2$B$_4$O$_7$ sample saturates at 10 Gy owing to its lower trap concentration.

In summary, the monocrystalline Li$_2$B$_4$O$_7$ sample showed a higher light yield than the polycrystalline sample and, conversely, the polycrystalline sample showed a higher TL intensity than the monocrystalline Li$_2$B$_4$O$_7$ sample. This result can be explained by the trap concentration of the polycrystalline Li$_2$B$_4$O$_7$ sample being higher than that of the monocrystalline Li$_2$B$_4$O$_7$ sample. In general, trapping centers are related to crystal defects and a lower defect concentration is expected in the monocrystalline Li$_2$B$_4$O$_7$ sample obtained by the well-established growth technique. In addition, the polycrystalline Li$_2$B$_4$O$_7$ sample can have a larger number of dangling bonds on the surfaces of its grains than the monocrystalline Li$_2$B$_4$O$_7$ samples without grains.

4. Conclusions

Scintillation and dosimetric properties of monocrystalline and polycrystalline Li$_2$B$_4$O$_7$ samples were studied. In the pulse height spectrum under neutron irradiation, the monocrystalline Li$_2$B$_4$O$_7$ sample showed two detection peaks owing to nuclear reactions of $^6$Li and $^{10}$B with neutrons. It is concluded that the light yield of the monocrystalline Li$_2$B$_4$O$_7$ sample is higher than that of the polycrystalline Li$_2$B$_4$O$_7$ sample that showed no peaks
exceeding the thermal noise level of the PMT. In contrast, the polycrystalline Li$_2$B$_4$O$_7$ sample showed a higher TL intensity than the monocrystalline Li$_2$B$_4$O$_7$ sample. The TL intensity of the polycrystalline Li$_2$B$_4$O$_7$ sample monotonically increased with the X-ray dose in a wider range from 10 mGy to 10 Gy than that of the monocrystalline Li$_2$B$_4$O$_7$ sample. From these results, it is assumed that the monocrystalline Li$_2$B$_4$O$_7$ sample has a lower trap concentration than the polycrystalline Li$_2$B$_4$O$_7$ sample. This lower trap concentration can be achieved using a high-quality single crystal with a lower crystal defect density.

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