Optical and dosimeter properties of $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3$ based glasses

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In this study, we report on the optical and thermoluminescence (TL) properties of newly developed $(30-x)\text{Li}_2\text{O}-20\text{Al}_2\text{O}_3-50\text{B}_2\text{O}_3-2x\text{CeO}_2$ (values are in mol %) glass dosimeters prepared by a conventional melt quenching method. The optical absorption spectra showed broad absorption band in the 200–370 nm wavelength with Ce-doping. The photoluminescence (PL) band appeared near the wavelength of 365 nm under excitation at 240, 270, and 315 nm, which is due to the transition from 5d excited states to 4f ($^2\text{F}_{5/2}$, $^2\text{F}_{7/2}$) ground states of Ce^{3+} . In the TL glow curve measurements, the Ce-doped glasses exhibited a dominant glow peak in the 370–425 K temperature range. The 0.5 cat % Ce-doped glass ($x = 0.5$) showed the highest TL intensities in our prepared glasses. The 5d–4f ($^2\text{F}_{5/2}$, $^2\text{F}_{7/2}$) emission band of Ce^{3+} also appeared in the 365 nm wavelength range in the TL spectrum. TL response in the dynamic range was confirmed using the 0.5 cat % Ce-doped glass over 10^{-3} – 10^2 Gy X-ray dose.

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1. Introduction

There is a continuous growing interest in thermoluminescence (TL) materials for radiation dosimetry, especially in the fields of environmental,^{1),2)} personal²⁾ and medical^{2),3)} applications. TL phenomenon are attributed to the recombination of the electrons and holes at metastable levels in the irradiated material. When ionizing irradiation such as X-ray and gamma-ray irradiated the material, free charge carriers, electrons and holes are produced which are subsequently trapped by the structural defects within the material. During heating the electrons and holes are thermally released from the defects and recombine giving rise to the excitation of the emission centers resulting in TL. TL glow curve measurement is most known technique to study the TL material, which is based on the TL intensity as a function of heating temperature. The temperature, shape, and intensity of the glow peaks are related to the properties of the trapping states responsible for the TL material. The typical requirements for applying TL dosimeter is good linearity with dynamic range, chemical and thermal stability and low hygroscopicity. Additionally, it is ideal for the personal dosimetry to be tissue equivalent material because of the more accurate determination of absorbed dose in human tissue exposed to ionizing radiation. However, not all of these requirements can be satisfied in the commercially available TL dosimeters and there is a large demand for new TL materials with superior performance. Various TL materials such as silicate-,^{4),5)} phosphate-,^{6)–8)} borate-,^{9)–13)} sulfide-,^{14),15)} and fluoride-^{16)–18)} based ceramics and glasses have been studied for the personal dosimetry application. Among the materials reported recently, the borate-based materials activated with rare-earth-ions have a good

tissue equivalence property and excellent sensitivity to X-rays and gamma-rays.^{9),10)} We have also studied and reported new borate-based TL materials such as Ce^{3+} - and Dy^{3+} -doped $\text{CaO}-\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3$ based glasses and Ce^{3+} -doped CaB_2O_4 crystal, which has good sensitivity and linearity to X-ray.^{11)–13)}

The present study focuses on $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3$ based glass as host material since its effective atomic number is close to that of human tissue ($Z_{\text{eff}} = 7.42$) or bone ($Z_{\text{eff}} = 11.6$ to 13.8), which has demonstrated excellent TL properties owing to high concentration of electron and hole trapping centers in glass matrix and rare-earth ionic dopants. Additionally, glass compounds ideal materials because they can be easily and economically fabricated in the form of large structures and complex shapes for optically device applications. Previously Ayta et al. reported the TL properties of $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3$ glasses co-doped with $\text{CaF}_2-\text{Mn}^{19)}$ and $\text{LiF}-\text{TiO}_2^{20)}$ with different concentrations. From the study, these glasses are found to show good linear response to high dose gamma-ray. According our knowledge the TL properties of $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3$ based glass activated by Ce^{3+} have not been reported up to now.

Thus in this study, we newly developed $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3-\text{CeO}_2$ glasses where the effective atomic number calculated is about ~ 9.26 , using a conventional melt-quenching technique, and the optical and TL properties were evaluated in order to examine the potential for TL materials.

2. Experimental procedures

Glass samples of $(30-x)\text{Li}_2\text{O}-20\text{Al}_2\text{O}_3-50\text{B}_2\text{O}_3-2x\text{CeO}_2$ ($x = 0, 0.25, 0.50, 1.0$, and 2.0 mol %) were prepared by a conventional melt quenching method using an alumina combustion boat in nitrogen atmosphere. High purity powders of Li_2CO_3 (99.99%), Al_2O_3 (99.99%), H_3BO_3 (99.99%), and CeO_2 (99.99%) were used as starting materials. The mixed powder in the alumina combustion boat was loaded into an electric furnace and then

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melted at 950°C in nitrogen atmosphere for 30 min. Finally, the glass melt was quenched into a stainless mold at ~300°C, which is below the glass transition temperature. As prepared glasses were cut and polished with typical dimensions of $3 \times 3 \times 1 \text{ mm}^3$ for optical and radiation measurements.

To confirm the amorphous nature of the prepared glasses, powder X-ray diffraction (XRD) analysis was performed in a 2θ range from 5 to 80° using an Ultima IV diffractometer (RIGAKU). The X-ray source was Cu K α with an accelerating voltage of 40 kV and a tube current of 40 mA.

Optical absorption spectra were recorded in a wavelength region from 200 to 600 nm with a Hitachi U-3500 spectrometer. In comparison to the Ce-doped glasses, undoped glass was also measured using similar spectrometer.

Excitation and emission spectra were measured using a Hitachi high-tech F-7000 fluorescence spectrophotometer and a xenon-lamp as the excitation source.

TL glow curves of the undoped and Ce-doped glasses were recorded from room temperature up to 650 K at a heating rate of $0.5 \text{ K} \cdot \text{s}^{-1}$ in air atmosphere with our original setup.^{13),21),22)} The temperature was controlled with a programmable thermoregulator (SCR-SHQ-A, Sakaguchi). A photon-counting head (H11890-210, Hamamatsu) was used as a detector, which had a spectral sensitivity region of 230–700 nm. The data were acquired as 3 s intervals with a sampling time of 12 min. A thermal cut filter was used to avoid direct irradiation of the detector by the thermal radiation from the sample. An X-ray generator (RINT2200, Rigaku) equipped with a copper target was used as the X-ray irradiation source. High voltages of 20–40 kV and currents of 2–40 mA supplied the generator. X-ray irradiation doses of 1, 10, 100 mGy, 1, 10, and 100 Gy were chosen for the dose response measurements. The dose response of a CaSO $_4$:Tm reference dosimeter, which was produced by Matsushita and had a size of 5 mm diameter and 200 mm thickness, was also measured to compare with our developed glasses. The TL spectrum was measured using a fluorescence spectrometer (DeltaFlex, HORIBA).

3. Results and discussions

Figure 1 illustrates as-prepared undoped and Ce-doped glasses. Visual observation indicates that the glasses are clear, transparency, and non-hygroscopic. In addition, the color of as-prepared glasses becomes yellowish gradually with the increasing concentration of Ce-dopant, which may be caused by Ce $^{4+}$ ions.²³⁾

Fig. 1. As prepared $(30 - x)\text{Li}_2\text{O}-20\text{Al}_2\text{O}_3-50\text{B}_2\text{O}_3-2x\text{CeO}_2$ ($x = 0, 0.25, 0.5, 1.0, \text{ and } 2.0 \text{ mol\%}$) glasses by a conventional quenching method.

The XRD patterns of the as-prepared glasses are shown in **Fig. 2**. All prepared glasses exhibit a dominant broad band centered at about 24°, which is characteristic of the amorphous glass phase. Additionally the broad band seems to include some weak diffraction peaks. The origin of the weak peaks is beyond the scope of our present study, however we speculate that they are due to precipitation of nano-crystallites.

Figure 3 illustrates optical absorption spectra of the undoped and Ce-doped glasses in the 200–600 nm wavelength region. While the undoped glass has no absorption band in this region, the Ce-doped glasses show a broad absorption band at 200–370 nm, which is owing to inclusions of Ce $^{3+}$ and Ce $^{4+}$ ions within the glasses. Furthermore, the Ce-doped glasses exhibit red-shift of the UV absorption band edge associated with the increasing of the Ce concentration. This is consistent with the coloring of the heavily Ce-doped glasses.

The excitation and emission spectra of the Ce-doped glasses are shown in **Fig. 4**. The excitation spectra [Fig. 4(a)] monitored at the emission wavelength of 365 nm show band peaking at 240, 270, and 315 nm. The excitation bands are owing to the allowed transition from the 4f ground states to the 5d excited states (t_{2g}, e_g) of Ce $^{3+}$. The 0.5 cat% Ce-doped glass shows the highest peak intensities in our prepared glasses. Meanwhile, the peak intensities for 1.0 and 2.0 cat% Ce-doped ones drastically decrease that is caused by concentration quenching of the Ce $^{3+}$ emission. In the emission spectrum [Fig. 4(b)] under excitation at 315 nm, a broad emission band peaking at 365 nm can be observed. The observed UV emission band can be ascribed to the allowed transition from the 5d (t_{2g}) state to the 4f ground-state levels ($^2F_{5/2}$ and $^2F_{7/2}$) of Ce $^{3+}$ ions. The Stokes shift of the Ce $^{3+}$ emission was calculated to be about $4,350 \text{ cm}^{-1}$ ($\sim 0.54 \text{ eV}$). The value of the Stokes shift is relatively larger than that of other Ce-doped glasses such as phosphate ($\sim 2,570 \text{ cm}^{-1}$),²⁴⁾ silicate ($\sim 2,820 \text{ cm}^{-1}$),²⁵⁾ and borosilicate ($3,500\text{--}5,000 \text{ cm}^{-1}$)²⁶⁾ glasses. This difference may be owing to both bandgap energy and coordination environment of Ce $^{3+}$ in glass matrix that change the

Fig. 2. XRD patterns of the undoped and Ce-doped glasses at room temperature.

Fig. 3. Optical absorption spectra of the undoped and Ce-doped glasses.

Fig. 4. Excitation (a) and emission (b) spectra of the Ce-doped glasses with different concentration.

Fig. 5. TL glow curves of the Ce-doped glasses compared with undoped glass.

Ce^{3+} 5d crystal field splitting.^{27),28)} The emission peak intensity for the 0.5 cat% Ce-doped glass is the highest in the glasses that is consistent with the result of the excitation spectra. The concentration quenching of the Ce^{3+} emission is also observed in a similar Ce concentration range to that of excitation spectra.

Figure 5 illustrates the TL glow curves of the undoped and Ce-doped glasses irradiated by X-ray with a dose of 10 Gy. While the undoped glass has no TL glow peak, the Ce-doped glasses exhibit an intense glow peak at 390 K. In addition, broad glow peaks at 450–570 K temperature range can be observed for the Ce-doped glasses. This observation suggests that the Ce^{3+} ions within the glasses act as at least emission center or hole trapping center for TL. The trap depth for the dominant glow peak at 390 K of the 0.5 cat% Ce-doped glass was calculated using the initial rise method.²⁹⁾ From the calculation, the trap depth was found to be about 0.17 eV. Other Ce-doped glasses also showed similar value to that of 0.5 cat% one.

The TL intensities of the Ce-doped glasses irradiated with X-ray at 10 Gy dose are plotted with different Ce concentration, as shown in **Fig. 6**. In the case of the 0.5 cat% Ce concentration, the glass shows the highest TL intensity as emission spectra, which demonstrates that fluorescence efficiency of the emission center plays important role in the TL intensity.

Figure 7 illustrates the TL spectra of the Ce-doped glasses with different concentration. The spectra exhibit an emission band peaking at 365 nm, which is owing to Ce^{3+} ions. This can be explained that the trapped electrons at anion centers due to X-ray irradiation are released by thermal stimulation, and then

Fig. 6. TL intensities of the Ce-doped glasses with different concentration.

Fig. 7. TL spectra of the Ce-doped glasses with different concentration.

Fig. 8. TL intensities of the Ce-doped glasses (a) and $\text{CaSO}_4:\text{Tm}$ reference dosimeter (b) as functions of X-ray doses ranging from 1 mGy to 100 Gy.

they recombine with the trapped holes at Ce^{3+} ions. Finally, the recombination gives rise to the excitation of the Ce^{3+} emission centers resulting in the allowed transition from the 5d (t_{2g}) state to the 4f ground-state levels ($^2F_{5/2}$ and $^2F_{7/2}$) as TL.

The dose response of the TL intensity for the 0.5 cat% Ce-doped glass is shown in **Fig. 8(a)**. The glass exhibits the increasing of the TL intensity with irradiation dose addition in the dynamic range over 10^{-3} – 10^2 Gy. Meanwhile the linearity appears to be more poor than the $\text{CaSO}_4:\text{Tm}$ dosimeter [Fig. 8(b)] particularly in low irradiation dose region. Determining the cause of poor linearity is beyond the scope of our present study; however, we speculate that it is due to either low fluorescence efficiency of the Ce^{3+} emission, low concentration of the electron and hole trapping centers, and depth of the trapping centers. Future efforts toward understanding the cause of the poor linearity are expected to further more improve the TL properties.

4. Summary

In conclusion, we studied the optical and the TL properties of a newly developed $(30-x)\text{Li}_2\text{O}-20\text{Al}_2\text{O}_3-50\text{B}_2\text{O}_3-2x\text{CeO}_2$ glasses, whose Z_{eff} (~ 9.26) is close to that of human tissue and bone, for application in TL personal dosimeter for X-ray and gamma-ray. Our prepared glasses using a conventional melt quenching method, appeared clear, transparency, and non-

hygroscopic. We demonstrated interesting TL properties in the glasses such as TL spectra owing to the allowed transition from the 5d (t_2) state to the 4f ground-state levels ($^2F_{5/2}$ and $^2F_{7/2}$) of Ce^{3+} ions, and TL response to X-ray irradiation in the dynamic range over 10^{-3} – 10^2 Gy. We speculate that poor linearity in low dose range is related to either low fluorescence efficiency of the Ce^{3+} emission, low concentration of the electron and hole trapping centers, and depth of the trapping centers. Further studies are needed in order to understand the origin of the poor linearity and improve the performance. Our studies suggested that the $(30 - x)Li_2O$ – $20Al_2O_3$ – $50B_2O_3$ – $2xCeO_2$ glass based TL materials could be a promising candidate for personal dosimeter for X-ray and gamma-ray.

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