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Radiation-induced luminescence properties of Tb-doped Li_3PO_4-B_2O_3 glasses

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ABSTRACT

In this study, we developed Li_3PO_4-B_2O_3 glasses doped with different concentrations of Tb (0.1, 0.3, 1.0, 3.0, and 10.0%) as well as undoped glass, and then the prepared glasses were studied for the optical, dosimeter and scintillator properties. The Tb-doped samples indicated radioluminescence and photoluminescence (PL) due to the 4f-4f transitions of Tb^{3+} with sharp spectral features peaking around 375, 410, 435, 480, 540, 590 and 620 nm. The luminescence decay times of radioluminescence and PL were 2.3−2.7 ms and 2.7−2.9 ms, respectively. The shorter radioluminescence decay time than that of PL indicated quenching effect of excited states in radioluminescence. As the concentration of Tb increased, both the radioluminescence intensity and PL quantum yield (*QY*) increased, and the 10.0% Tb-doped sample showed the highest radioluminescence intensity and *QY* (54.3%). In addition, thermally-stimulated luminescence (TSL) was observed after irradiating with X-rays. The sensitivity was the highest for the 3.0% Tb-doped sample having a dynamic range from 0.1 mGy to 10 Gy, which was equivalent to commercial dosimeters. The comprehensive studies suggested that X-ray generated charges are captured at TSL-active centers more effectively at lower concentrations of Tb whereas the recombination probability at Tb center during irradiation increases with the concentration of Tb. Consequently, the optimal Tb concentration was 10% as scintillator and 3.0% for TSL dosimeter, among the present samples.

1. Introduction

Ionizing radiations such as X-rays, γ-rays and neutrons are utilized for many application fields; for example, medicine [1], security [2] and resource exploration [3]. For detecting ionizing radiations, inorganic luminescent materials and semiconductors are typical choice. The luminescent materials are used to convert radiation to light, which can be detected by conventional photodetectors. Such luminescent materials can be classified into mainly two types, scintillators and storage phosphors [4,5]. The former absorbs high energy quanta and promptly converts into a large number of low energy photons such as ultraviolet and visible light [6]. In contrast, the latter has a function to temporarily store the incident radiation energy as a form of carriers trapped at localized centers and release the stored energy by thermal or optical stimulation. The luminescence by thermal and optical stimulation is called thermally-stimulated luminescence (TSL) and optically-stimulated luminescence (OSL) [7], respectively. Since the luminescence intensity is proportional to the incident radiation dose, TSL and OSL are used in dosimetry. Furthermore, another radiation-induced luminescence phenomenon called radio-photoluminescence (RPL) is used for radiation detections. While the OSL and TSL dosimeters lose recorded information once read out, measurement of RPL signal do not involve such information loss and can be read out multiple times without fading [8]. These dosimetric properties are mainly utilized for individual personal and environmental dose monitoring applications [9,10].

The forms of luminescent materials for radiation detection applications are typically bulk single crystals, ceramics and glasses. Among these materials, glass has preferable properties such as inexpensive productivity on a large scale and flexible chemical composition and design. However, there are much less reports on radiation detector properties of glasses compared with those of single crystals and ceramics. Today, in personal dose monitoring applications, most researches deal with single crystals and ceramics. For instance, C-doped Al_2O_3 single crystal [11], Mg and Ti

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co-doped LiF ceramic [12], BeO ceramic [13], Tm- and Dy-doped CaF_2 single crystals [14,15], Cu-doped $Li_2B_4O_7$ single crystal [16] and Dy-doped $CaSO_4$ ceramic [17] are typical dosimeter materials. Glass materials used for radiation measurements in practice are only Ag-doped phosphate glass [18] as a dosimeter and Ce-doped lithium silicate glass [19] as a scintillator. Therefore, there is much room for studying new compositions of glass materials in radiation measurements.

The purpose of this study is to develop tissue-equivalent glasses for radiation measurement applications. Previously, we have shown that Li_3PO_4-$Al(PO_3)_3$ glasses have notable TSL properties. However, the effective atomic number (Z_{eff}) is relatively high so the tissue-equivalency is considered to be low (the Z_{eff} of soft tissue is 7.29 [20]), so the material may not be suitable for dosimetric applications. Therefore, in this study, we considered a new glass composition, Li_3PO_4-B_2O_3, in which the $Al(PO_3)_3$ of previous glass has been replaced by B_2O_3 in order to reduce the effective atomic number to 9.95 and to be lower than those of Ag-doped phosphate glass ($Z_{eff} = 12.4$) [18] and Li_3PO_4-$Al(PO_3)_3$ glass ($Z_{eff} = 11.9$) [21].

For radiation measurements, Tb-doped materials such as Mg_2SiO_4:Tb [22] and Gd_2O_2S:Tb [23] have been actively studied. In addition, the host of Tb is not limited to crystals but glasses for the radiation measurement researches [24]. Tb-doped materials generally show intense luminescence with green color which is suitable for detection by, for example, PMT and Si-APD. In addition, a number of Tb-doped glasses were reported to show notable luminescence properties such as photoluminescence (PL) [25], radioluminescence [26] and storage luminescence for dosimeter applications [27].

For the reasons above, we have synthesized Tb-doped Li_3PO_4-B_2O_3 glasses and comprehensively characterized the luminescence properties such as PL, radioluminescence and TSL. It should be noted that radioluminescence and storage luminescence properties are inversely related in some materials; therefore, it is important to study both the properties in order to understand the radiation-induced luminescence phenomena comprehensively.

2. Experimental

Undoped and Tb-doped $50Li_3PO_4$-$50B_2O_3$ glasses were synthesized by the conventional melt-quenching method. The concentration of Tb varied as 0.1, 0.3, 1.0, 3.0 and 10.0%. At first, Li_3PO_4 (3N), B_2O_3 (5N) and Tb_4O_7 (4N) powders were homogeneously mixed in a stoichiometric composition. The doping concentration was defined as a fraction of Tb^{3+} ions to the whole host; for example, 10%-doped sample indicates the ratio of chemical composition as Tb_4O_7: Li_3PO_4: B_2O_3 = 2.5:50:50. Next, the mixture was melted in an alumina crucible using an electric furnace at 1300 °C for 30 min in air, and then the melt was quenched on a stainless plate preheated at 300 °C. The obtained glass samples were cut and polished to the thickness of 1.30 ± 0.1 mm for characterizations below.

Using a spectrophotometer (V670, JASCO), the optical in-line transmittance spectra were measured in the spectral range of 190–2700 nm with 1 nm interval. The PL excitation-emission contour graphs and quantum yields (*QY*) were obtained by Quantaurus-QY (C11347-01, Hamamatsu). The spectral ranges for the excitation and emission were 250–500 and 200–900 nm, respectively. In order to calculate *QY*, the numbers of absorbed photons (380 nm) and emitted photons (from 400 to 700 nm) were determined by the instrument. The PL decay curves were measured by using Quantaurus-τ (C11367, Hamamatsu). Here, the monitoring wavelength and excitation wavelength were 540 nm and 340 nm, respectively.

The X-ray induced radioluminescence spectra were evaluated by using our lab-constructed set-up, which was previously described in detail [28]. The irradiation source (XRB80, Spellman) was a conventional X-ray tube which was equipped with a tungsten anode target and beryllium window. The applied tube voltage and current were 40 kV and 1.2 mA, respectively. The radioluminescence photons were provided to a spectrometer equipped with a CCD detector module (iDUS420, Andor) and monochromator (SR163, Andor) through an optical fiber to obtain a spectrum. The radioluminescence decay curves were measured by using an X-ray induced afterglow characterization system [29,30]. The system was equipped with a pulse X-ray tube, in which the applied tube voltage was 30 kV.

The TSL glow curves were measured by using TL-2000 (Nanogray Inc.) after an irradiation with X-rays of several different doses. The irradiated dose was calibrated by an air-filled ionization chamber (TN30013, PTW), and the X-ray tube was operated at a constant voltage (40 kV) but varying tube current between 0.052 and 5.2 mA in order to change the dose rate. In addition, lower doses were irradiated at a longer distance from the source to decrease further the dose rate. The TSL glow curves were measured over a temperature range from 50 °C to 490 °C at a heating rate of 1 °C/s.

To discuss the observed TSL glow curves in detail, Raman spectra were obtained with Versatile Laser Raman Spectrometer (RMP-510, JASCO). The spectral range of measurement was from 47 to 1357 cm^{-1}, and the wavelength of laser probe was 532 nm.

3. Results & discussion

Fig. 1(a) indicates a photograph of Tb-doped Li_3PO_4-B_2O_3 glass samples under room light. The samples are placed in an ascending order of Tb-concentration (0, 0.1, 0.3, 1.0, 3.0 and 10.0%) from left to right. The prepared samples were visually transparent and colorless. A photograph of Tb-doped samples under UV lamp (365 nm) is shown in Fig. 1(b). The Tb-doped samples showed luminescence in yellow/green color while any emission was not observed from the undoped sample. The emission intensity strongly depended on the concentration of Tb.

The in-line transmittance spectra of the Tb- and undoped glass samples are shown in Fig. 2. All the samples showed high transmittance in the wavelengths longer than approximately 250 nm. As the Tb concentration increased, the absorption bands around 1600–2500 nm tended to gradually increase. The origin of the latter absorption bands was ascribed to Tb^{3+} for its typical feature [31]. In addition to the Tb^{3+} absorption, another absorption band was observed in the wavelengths longer than 2500 nm due to O-H stretching [32], indicating an inclusion of water in glass. The band gap energy of Li_3PO_4-B_2O_3 glasses were estimated to be approximately 5 eV judging from the absorption edge of undoped sample (~250 nm). The optical absorption edge at short wavelength of Tb-

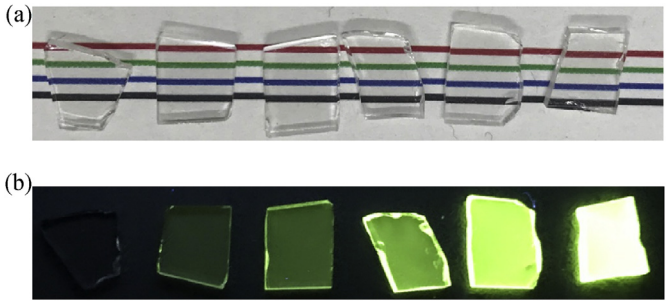

Fig. 1. Photographs of Li_3PO_4-B_2O_3 glasses (a) under room light and (b) under UV light (365 nm). From left to right, the Tb concentrations are 0, 0.1, 0.3, 1.0, 3.0 and 10.0%.