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Dosimetric and scintillation properties of Ce-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 (0, 0.1, 0.2, 0.5, and 1.0%) of Ce and studied the optical, dosimetric and scintillation properties. The Ce-doped samples showed scintillation and photoluminescence (PL) due to the 5d–4f transitions of Ce^{3+} with a broad spectral feature peaking around 350 nm. The scintillation and PL decay times were 55–62 ± 0.03 ns and 29–31 ± 0.03 ns, respectively. The PL quantum yield (*QY*) was about 15.3 ± 2% for the 0.1%-doped sample, and it decreased with increasing the concentration of Ce. The thermally-stimulated luminescence (TSL) was observed in all the samples after irradiating with X-rays, and the 0.1% Ce-doped sample showed the highest sensitivity with the dynamic range confirmed from 0.1 mGy to 10 Gy, which was equivalent to commercial detectors. Moreover, optically-stimulated luminescence (OSL) was observed in the 0.1%Ce-doped sample after X-ray irradiation. Overall, doping with Ce enhanced the PL, scintillation, TSL and OSL properties. The optimal concentration of Ce was 0.1% to be used for radiation detector applications.

1. Introduction

Ionizing radiations such as X-rays, γ-rays and neutrons are widely used in many application fields; for example, medicine [1], security [2] and astrophysics [3]. Since these radiations are invisible to our eyes, the measurement techniques of the radiations have been always required since the discoveries by H. Becquerel and W. Roentgen in the late 19th century. Regarding the measurements of ionizing radiations, inorganic luminescent materials are often used in addition to semiconductor detectors. There are mainly two types of luminescent materials used for ionizing radiation detectors which are called scintillators and storage phosphors [4,5]. The former absorbs high energy quanta and promptly converts them into a large amount of low energy photons such as ultraviolet and visible light [6]. Such scintillators are utilized in many fields as radiation detectors combined with photo-detectors (e.g., photomultiplier tube and Si-photodiode). In contrast, the latter has a function that temporarily stores the incident radiation energy as a form of carriers trapped at localized centers and releases the storage energy by a thermal or optical stimulation. When the stimulation is done thermally, the resultant luminescence is called the thermally-stimulated luminescence (TSL) while it is called optically-stimulated luminescence (OSL) [7] as the stimulation is light. While the OSL and TSL dosimeters lose the stored carriers (dose information) once read out, another type of dosimeter using radio-photoluminescence (RPL) phenomenon permanently stores the memory of radiation dose, so the signal can be read out multiple times without fading [8]. These dosimetric properties are mainly applied for individual personal dose monitoring and environmental monitoring [9,10].

Today, most dosimeter materials used in personal dose monitoring applications are single crystals and ceramics. For example, C-doped Al_2O_3 single crystal [11], Mg and Ti co-doped LiF ceramics [12], BeO ceramics [13], Tm- and Dy-doped CaF_2 single crystals [14,15], Cu-doped $Li_2B_4O_7$ single crystal [16] and Dy-doped $CaSO_4$ ceramics [17] are typical dosimeter materials [18]. However, among inorganic phosphor materials, glasses are known to show good luminescence properties in addition to ceramics and crystals. Glass materials have some preferable properties for radiation measurement applications such as inexpensive productivity on a large scale, flexible chemical composition and design and high chemical stability. In spite of these attractive properties for detector materials, there are much less reports on radiation detector properties of glasses. Today, only a couple of glass materials are used in practice for radiation measurements: $NaPO_3$-$Al(PO_3)_3$ glass as a dosimeter [19] and Li-glass [20] as a scintillator. Therefore, there is much room for studying glass materials in radiation measurements.

The aim of this study is to investigate a new borate glass for radiation measurement applications. Previous study clarified that Li_3PO_4-$Al(PO_3)_3$ glasses (effective atomic number: Z_{eff} = 11.9), which have a

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lower Z_{eff} than the commercial Ag-doped $NaPO_3$-$Al(PO_3)_3$ glass dosimeters (Z_{eff} = 12.4), show effective X-ray induced luminescence when doped with Ce^{3+} ion [21]. In the present work, we have improved the tissue equivalency by modifying the glass composition to Li_3PO_4-B_2O_3 (Z_{eff} = 9.95) in order to reduce Z_{eff} and make it closer to human body tissue (Z_{eff} = 7.29) [22]. Today, common luminescent materials consist of a host matrix and emission center. For the dosimeter and scintillator uses, the host has a function to absorb incoming radiation, and the emission center has a role to emit photons such as scintillation, OSL, TSL and RPL. Among borate glasses reported so far, especially borate glasses doped with Ce^{3+} ion as an emission center indicate notable luminescent properties in photoluminescence (PL) [23], scintillation [24] and storage luminescence for dosimeter applications [25] since Ce-doped materials tend to show two key characteristics including an intense emission and fast fluorescence decay time due to the parity- and spin-allowed 5d–4f transitions. Therefore, in this research, we have investigated the optical, PL, scintillation and storage luminescence properties of Ce-doped Li_3PO_4-B_2O_3 glasses.

2. Experimental

Ce-doped $50Li_3PO_4$-$50B_2O_3$ glass samples were prepared by the conventional melt quenching technique. The concentration of Ce varied as 0, 0.1, 0.2, 0.5 and 1.0 mol%. The doping concentration was defined as a fraction of Ce^{3+} ions to the whole host; for example, 1.0 mol% doped sample indicates the ratio of chemical composition as CeO_2:Li_3PO_4:B_2O_3 = 1:50:50. After that 1.0 mol% doped sample is written as 1.0%. As the starting materials, Li_3PO_4 (3N), B_2O_3 (5N) and CeO_2 (4N) powders were stoichiometrically mixed. After the mixing process, using an electric furnace warmed to 1300 °C in prior to the melting process, the mixture was melted in an alumina crucible for 30 min in air. Then, the melt was quenched on a preheated stainless plate at 300 °C, and then the glass samples were kept for 20 min. The obtained glass samples were characterized by the following experiments after cutting and polishing the samples with the thickness of 1.30 ± 0.1 mm.

X-ray diffraction (XRD) patterns were measured to confirm that all the samples were amorphous with MiniFlex 600 (RIGAKU). The optical in-line transmittance spectra were measured by using a spectrophotometer (V670, JASCO) in the spectral range of 190–2700 nm with 1 nm interval. Further, the PL excitation-emission contour graph and quantum yield (*QY*) were evaluated by Quantaurus-QY (C11347-01, Hamamatsu). The spectral ranges for the excitation and emission were 250–400 and 200–900 nm, respectively. In addition, PL decay curves were measured by using Quantaurus-τ (C11367, Hamamatsu). The monitoring wavelength was 360 nm, and the excitation wavelength was 280 nm.

The X-ray induced scintillation spectra were observed by using our lab-constructed set-up, which was previously described in detail [26]. The X-ray source used here was a conventional X-ray tube equipped with a tungsten anode target and beryllium window. The applied bias voltage and tube current of 80 kV and 1.2 mA, respectively. The scintillation photons were fed into an optical fiber and guided to a monochromator equipped with a CCD spectrometer (DUS420, Andor) to obtain a spectrum. The scintillation decay curves were measured by using our lab-constructed set-up [27,28]. The system was equipped with a pulse X-ray tube, in which the applied tube voltage was 30 kV and the system offers the time resolution of ~1 ns.

Recently, we have pointed out that the scintillation and storage luminescence properties show a complementary relationship [5,29]; thus, it is important to measure both of the properties in the material of interest in order to understand radiation induced luminescence phenomenon comprehensively. As a dosimeter property, TSL and OSL were characterized. The TSL glow curves were measured by using TL-2000 (Nanogray Inc.) after an irradiation with X-rays of several different doses. The measurement temperature range was from 50 to 490 °C at a heating rate of 1 °C/s. The OSL spectra were measured by spectrofluorometer (FP-8600, JASCO). In these measurements, the stimulation wavelength was 420 nm, and the measured emission range was from 200 to 390 nm.

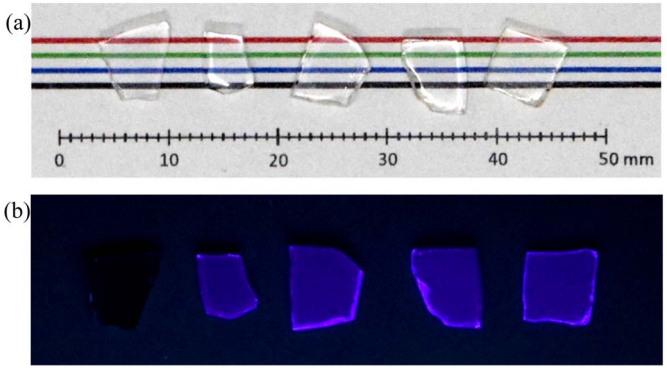

Fig. 1. Photograph of Li_3PO_4-B_2O_3 glasses (a) under room light and (b) under UV light (302 nm). From left to right, the Ce concentrations are 0, 0.1, 0.2, 0.5 and 1.0%, respectively. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

All the measurements mentioned above were carried out at room temperature unless stated. The systematic error was deduced by the multiple time measurements of the samples.

3. Results & discussion

Fig. 1(a) indicates a photograph of Ce-doped Li_3PO_4-B_2O_3 glass samples under room light. The samples are placed in an ascending order (0, 0.1, 0.2, 0.5 and 1.0%) from left to right. The prepared samples were visually transparent and colorless. As the concentration of Ce increased, the color became yellow slightly. The photograph of Ce-doped samples under UV lamp (302 nm) is shown in Fig. 1(b). The Ce-doped samples showed the luminescence in purple color while we could not observe luminescence from the non-doped sample. At least by naked eye, the luminescence intensity looked consistent in all the samples regardless of the difference of Ce concentration.

The XRD patterns of non-doped and Ce 1 mol% doped glass samples are showed in Fig. 2. From the XRD patterns, the non-doped and Ce-doped glass samples showed only the halo structure, and they did not have any crystalline phases. Therefore, the synthesized samples had the amorphous state.

The in-line transmittance spectra of the Ce- and non-doped glass samples are shown in Fig. 3. All the samples showed high transmittance, and Ce^{3+} absorption bands were confirmed from 300 to 360 nm

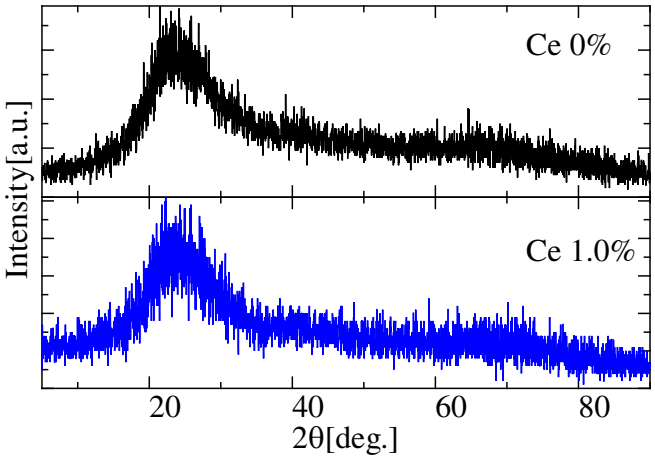

Fig. 2. The XRD patterns of non-doped and Ce 1 mol% doped glass samples.