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X-ray and Proton Luminescences of Bismuth-borate Glasses

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Heavy scintillators with good radiation hardness and low cost can be applied in high -energy physics, astrophysics, homeland security and radiation detection. It is possible to make heavy-ion-doped glass scintillators that can meet these requirements. We fabricated bismuth-borate glasses, $Bi_2O_3(30)$: $B_2O_3(70)$, doped with CeO_2, Nd_2O_3, Er_2O_3, Dy_2O_3, and Pr_2O_3 in difference concentrations by using the melt-quench technique. An X-ray luminescence study showed that only Dy_2O_3-doped glass emitted luminescence with a peak at 575 nm. Absorption spectra of the Dy_2O_3-doped glass were studied to understand the optical property. Proton luminescence of Dy_2O_3-doped glass was studied by using the 45-MeV proton beam from the MC-50 cyclotron at the Korea Institute of Radiological and Medical Sciences (KIRAMS). The results for the proton and the X-ray luminescences were compared.

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I. INTRODUCTION

Glasses doped with rare-earth ions (RE^{n+}) are proving to be luminescent materials as they have high emission efficiencies. These emissions correspond to 4f-4f and 4f-5d electronic transitions in the RE^{n+} ion. The 4f-4f transition gives an especially sharp fluorescence pattern from the ultraviolet (UV) to the infrared region. This is due to shielding effects of the outer 5s and 5p orbitals on the 4f electrons. In recent years, glasses doped with rare-earth ions have drawn much attention due to their potential applications in solid-state lasers, optical amplifiers and three-dimensional displays [1-4].

The good properties of Bi^{3+} in oxide glasses make them suitable for optical devices, such as ultra-fast all optical switches and optical isolators. Due to the high density and transparency, these are also useful for variety of optical applications, such as radiation shielding windows and scintillation counters [5]. The Bi^{3+} ion has a small field strength, so Bi_2O_3 cannot form a glass by itself. However, in the presence of a borate glass structure (B_2O_3), formation is possible. On the other hand, when higher-valence oxides, such as Bi_2O_3, the used as modifiers, the cation produces important structural effects due to its highest valence.

If it emits scintillation light, rare-earth doped bismuth-borate glass can be used for radiation detector in ap-

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Table 1. Densities of bismuth-borate glass doped with RE_xO_y (RE = CeO_2, Nd_2O_3, Er_2O_3, Dy_2O_3, and Pr_2O_3).

Concentration	Type of rare earth				
	CeO_2	Nd_2O_3	Er_2O_3	Dy_2O_3	Pr_2O_3
0.00	4.2065	4.2065	4.2065	4.2065	4.2065
0.5	4.1306	4.1660	4.1693	4.1473	4.2115
1.00	4.1323	4.1841	4.1441	4.1526	4.1866
1.50	4.1649	4.1765	4.1560	4.1745	4.1878
2.00	4.0993	4.2025	4.2069	4.1708	4.1879
2.50	4.0808	4.1934	4.2195	4.1803	4.2143

plications of high-energy physics, homeland security and radiation detection because it has high density, and hard property radiation, because it can be produced with low cost, and because mass production is feasible. Therefore, the aims of the present study are to dope rare earth ions (Ce, Nd, Dy, Er, and Pr) into bismuth-borate glass with different rare-earth oxide concentrations and investigate the effect of rare-earth ion content on the optical and the luminescence properties to demonstrate the possibility of using then for scintillator applications.

II. EXPERIMENTS

1. Bismuth-borate Sample Preparation

The following rare-earth-doped bismuth-borate glass samples $Bi_2O_3(30):B_2O_3(70\text{-}x):RE_xO_y(x)$ (RE = CeO_2, Nd_2O_3, Er_2O_3, Dy_2O_3, and Pr_2O_3) with $0 \leq x \leq 2.5$ (mol%) were prepared by using the normal melt-quenching technique. The analytical reagent grade chemicals used in the present study consisted of Bi_2O_3, H_3BO_3, CeO_2, Nd_2O_3, Er_2O_3, Dy_2O_3, and Pr_2O_3. They were thoroughly mixed by hand milling in a high purity alumina crucible for 30 min and were then melted at 1100 °C in an electrical furnace for 3 h. The temperature was sufficient to produce a clear, bubble-free melt. After complete melting, the melts were then quickly poured into a preheated stainless-steel and were annealed at 500 °C for 3 h before being cooled to room temperature. Finally, the as-prepared glass samples were cut and then finely polished to dimensions of 1.0 cm × 2.0 cm × 0.3 cm.

By applying Archimedes principle, we measured the weight of the prepared glass samples in air and in xylene by using a 4-digit sensitive microbalance (Denver, Pb214). Then, the density, ρ, was determined from the relation

$$\rho = \frac{W_a}{W_a - W_b} \times \rho_b, \quad (1)$$

where W_a is the weight in air, W_b is the weight in xylene, and ρ_b is the density of xylene ($\rho_b = 0.863$ g/cm^3). As can be seen in Table 1, the density values of all glasses are in the range 4.0808 – 4.2195 g/cm^3. The density values were found not to be related to the rare-earth oxide concentration for all the glasses.

2. X-ray-induced Emission and Optical Absorption Spectroscopy

We measured the luminescence excited by X-rays in the rare-earth-doped bismuth-borate glasses by using an X-ray tube (DRGEM Co.). The glasses, except for the one to be attached to an optical fiber, were wrapped with several layers of teflon tape. To avoid light loss when the glasses were attached to the optical fiber, we made a holder with a hole at its center from the teflon material. Scintillation light from the glass due to X-ray irradiation was transmitted through the optical fiber to a QE65000 spectrometer (Ocean Optics Co.). The spectrometer was cooled to -15 °C to reduce thermal noise in the Charge-Coupled Device (CCD). Windows-based software provided by the manufacturer of the spectrometer was used to plot the X-ray emission spectrum of the sample. The optical absorption spectra were recorded at room temperature by using a UV-visible-NIR spectrophotometer (Shimadzu, UV-3100) in the range in 190 nm – 2100 nm.

3. Proton Luminescence

The 50-MeV proton beam test facility at the MC-50 Cyclotron of KIRAMS (Korea Institute of Radiological & Medical Sciences) was established by the PEFP (Proton beam Engineering Frontier Project) of the Korea Atomic Energy Research Institute (KAERI). This facility will be used for pilot studies of the PEFP, especially, for studies using a very low proton beam flux, $10^4 - 10^{10}$ /cm^2-sec [6]. The beam line is composed of a collimator, a Faraday cup, a vacuum tube for the beam drift, bellows for easy alignment, a BPM (beam profile monitor), an exit window for an external beam, a phosphor screen, a scattering foil, an energy degrader, a target stage, an irradiation uniformity measurement system, a dose measurement system, an energy measurement system, *etc.* [6]. The 45-MeV incoming proton beam passes through a 0.2-cm-thick aluminum window capping the beam pipe with 10 cm of air and loses energy down to 38 MeV. A proton beam current of 10 nA was used for 10 s for this study.

The signal from the rare-earth-doped glass sample due to 38-MeV proton beam irradiation was transmitted through an optical fiber to the USB4000 spectrometer (Ocean Optics Co.) Figure 1 shows a schematic diagram of the setup. Windows- based software provided by the manufacturer of the spectrometer was used to plot the proton-beam-induced emission spectrum of the sample.

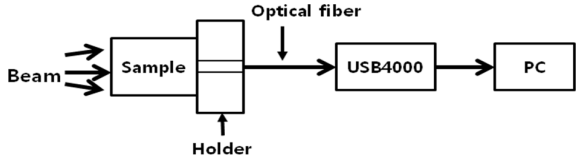

Fig. 1. Schematic diagram of the experimental setup for the measurements of the 38-MeV proton-beam-induced emission spectrum.

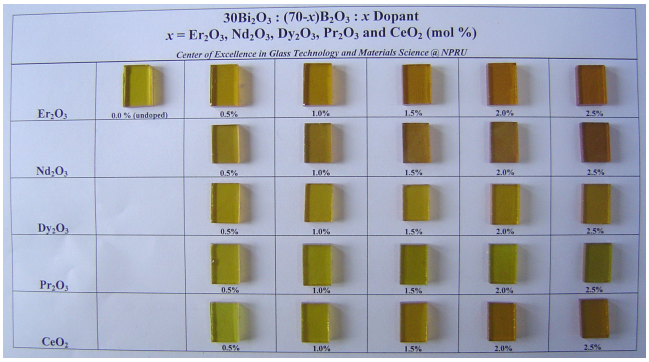

Fig. 2. (Color online) Bismuth borate glass doped with RE_xO_y (RE = CeO_2, Nd_2O_3, Er_2O_3, Dy_2O_3, and Pr_2O_3).

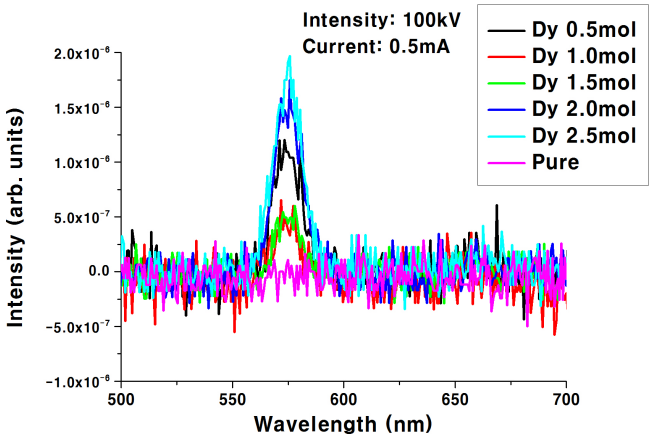

Fig. 3. (Color online) X-ray induced emission spectrum of Dy_2O_3 doped glass scintillators with different concentrations of Dy_2O_3 at room temperature.

III. RESULTS

Transparent rare earth doped bismuth borate glasses were obtained with rare-earth oxide doping, as shown in Fig. 2. All samples show light yellow color, which could be caused by Bi_2O_3.

We measured the emission spectrum of the bismuth-borate glass scintillators doped with CeO_2, Nd_2O_3, Er_2O_3, Dy_2O_3, and Pr_2O_3 (0 – 2.5 mole%) by using the X-rays at room temperature. X-rays with an intensity of 100 kV and a current of 0.5 mA irradiated each rare-earth doped glasses. Only the Dy_2O_3-doped glass was found to show a strong luminescence. Figure 3 shows the emission

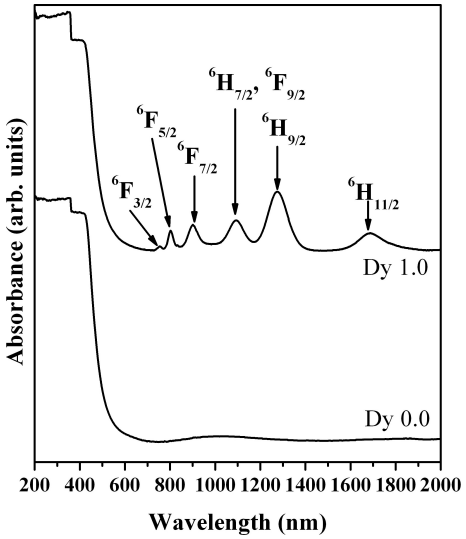

Fig. 4. Typical absorption spectra of bismuth-borate glass with 1.0 mole% Dy_2O_3 doping and without Dy_2O_3 doping.

spectra of different concentration, of Dy_2O_3 for Dy_2O_3-doped glass at room temperature. The Dy_2O_3 doped glasses exhibit a narrow emission band located between 560 and 590 nm and peaking at 575 nm. The intensity of luminescence increases as the doping concentration increases, as shown in Fig. 3. The luminescence study revealled that Dy_2O_3-doped glass predominantly exhibited a greenish-yellow emission due to a strong $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition at 575 nm [7].

The optical absorption spectra of bismuth borate glass doped with Dy_2O_3 are similar for each Dy_2O_3 concentration. Figure 4 shows the typical absorption spectra of undoped bismuth-borate glass, and of bismuth-borate glass doped with Dy^{3+} at 1.0 mol%. The bands are assigned from the ground state, $^6H_{15/2}$. The transitions from the next excited state $^6H_{13/2}$ may be ruled out due to thermalization because the energy gap between $^6H_{15/2}$ and $^6H_{13/2}$ is approximately 3000 cm^{-1}. In therer this spectra, the levels of $^4I_{13/2}$, $^4F_{7/2}$, $^4G_{11/2}$, and $^4I_{15/2}$ are not observed. The absorption peaks at $^6F_{3/2}$ (762 nm), $^6F_{5/2}$ (805 nm), $^6F_{7/2}$ (905 nm), ($^6H_{7/2}$, $^6F_{9/2}$) (1100 nm), ($^6F_{11/2}$, $^6H_{9/2}$) (1280 nm), and $^6H_{11/2}$ (1695 nm) are observed and well resolved. The positions and the intensities of certain transitions of rare-earth ions are found to be very sensitive to the environment around the ion. Such transitions are termed as hypersensitive transitions [8]. All known hypersensitive transitions obey the selection rules $|\Delta S| = 0$, $|\Delta L| \leq 2$, $|\Delta J| \leq 2$ [8]. In the case of the Dy^{3+} ($^4f_9$) ion, the hypersensitive transition ($^6F_{11/2} \rightarrow {}^6H_{9/2}$) is found to be more intense than the other transitions.

Since the 2.0-mol% Dy_2O_3-doped glass scintillator showed a strong X-ray luminescence. as shown in Fig. 3, it was selected for the proton luminescence. The sample, except for one side where it was attached to the sample

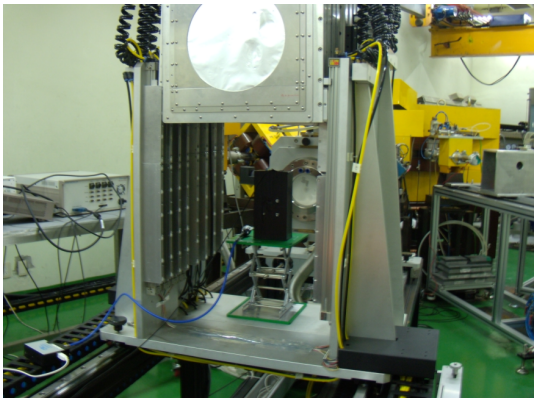

Fig. 5. (Color online) Photograph of an exit window in the proton beam line with a sample glass scintillator attached to the sample holder.

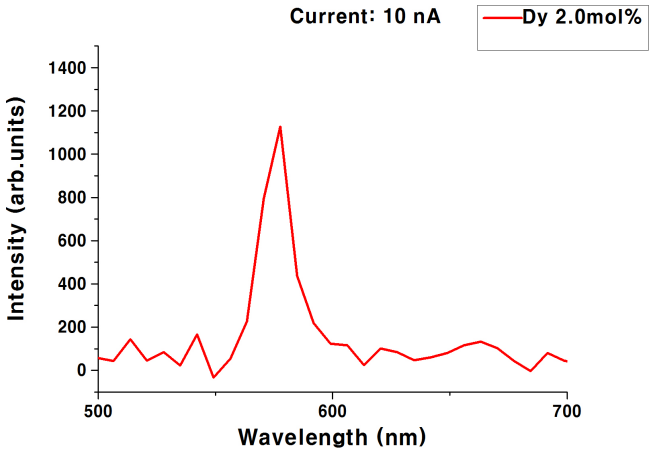

Fig. 6. (Color online) Induced emission spectrem of the Dy_2O_3 doped glass scintillator under the 38-MeV proton for 10 sec with a 10 nA beam current.

holder, was wrapped with 0.1-mm of Teflon tape for light shielding. Figure 5 shows a glass scintillator attached to a sample holder in the proton beam line. A 38-MeV proton beam of 10 nA for 10 s irradiated the 2.0-mol% Dy_2O_3-doped glass scintillator, and data were taken during proton irradiation. The emission spectrum of Fig. 6 shows that the 2.0-mol%- doped glass scintillator emits a luminescence with an emission peak at 575 nm.

IV. CONCLUSION

The rare-earth-doped bismuth-borate glass samples $Bi_2O_3(30):B_2O_3(70\text{-}x):RE_xO_y$ (x) (RE = CeO_2, Nd_2O_3, Er_2O_3, Dy_2O_3, and Pr_2O_3) with $0 \leq x \leq 2.5$ (mol%) were prepared by using the normal melt-quenching technique. Among those samples, only the Dy_2O_3-doped glass samples showed noticeable X-ray luminescence, with a peak at 575 nm, due to the strong $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition by the Dy^{3+} ion. The result of X-ray luminescence showed that the intensity of the luminescence increased as the doping concentration were increased up to 2.5%. Absorption spectra of Dy_2O_3-doped glass samples showed several absorption peaks' $^6F_{3/2}$ (762 nm), $^6F_{5/2}$ (805 nm), $^6F_{7/2}$ (905 nm), ($^6H_{7/2}$, $^6F_{9/2}$) (1100 nm), ($^6F_{11/2}$, $^6H_{9/2}$)(1280 nm), and $^6H_{11/2}$ (1695 nm).

To confirm the scintillation property of the Dy_2O_3 doped bismuth-borate glass sample, we irradiated a 2.0-mol% Dy_2O_3-doped glass sample with the 38-MeV proton beam from the MC-50 cyclotron at the KIRAMS. The emission peaks of the proton and the X-ray luminescence were consistent, which showed that Dy_2O_3-doped Bismuth-Borate glass is a candidate for a glass scintillator.

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