

Luminescence Property of Rare-earth-doped Bismuth-borate Glasses with Different Concentrations of Bismuth and Rare-earth Material

J. M. PARK and H. J. KIM*

Department of Physics, Kyungpook National University, Deagu 702-701, Korea

P. LIMSUWAN

*Department of Physics, Faculty of Science and Technology,
King Mongkut's University of Technology Thonburi (KMUTT), Bangkok 10140, Thailand and
Thailand Center of Excellence in Physics, CHE,
Ministry of Education, CHE, Bangkok 10400, Thailand*

J. KAEWKHAO

*Thailand Center of Excellence in Physics, CHE,
Ministry of Education, Bangkok 10400, Thailand and
Center of Excellence in Glass Technology and Materials Science (CEGM),
Nakhon Pathom Rajabhat University, Nakhon Pathom 73000, Thailand*

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Bismuth-borate glass scintillators have high density and good radiation hardness. Thus, if they are highly luminescent, they can be applied in astrophysics, high-energy and nuclear physics, homeland security, radiation detection and medical imaging. Bismuth-borate glasses with the formula $x\text{Bi}_2\text{O}_3:(100-x)\text{B}_2\text{O}_3$ ($x = 30, 50, \text{ and } 66.7$ mol%) were fabricated and doped with Nd, Er, Dy, Pr, Sm, Ho, Gd, and Ce in different dopant concentrations by using the melt-quenching technique. The X-ray emission spectra for the bismuth-borate glasses were measured and showed that only Sm-, Dy-, and Nd-doped glass scintillators had noticeable luminescence. Also, we measured the photo-luminescence and the proton-induced emission spectra. We obtained the result that Sm- and Dy- doped glass scintillators emitted luminescence. The emission peaks of the Sm- doped glass were 569, 598, 641, and 708 nm and were due to (${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_J$) ($J = 5/2, 7/2, 9/2, 11/2$) transitions, respectively. The emission peaks of the Dy- doped glass were at 485 nm (${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{15/2}$), 575 nm (${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{13/2}$), 660 nm (${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{11/2}$), and 755 nm (${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{9/2} + {}^6\text{H}_{11/2}$), and that of the Nd-doped glass was at 895 nm due to the (${}^4\text{F}_{3/2} \rightarrow {}^4\text{I}_{9/2}$) transition. The luminescence intensities were compared in terms of different Bi concentrations and dopant concentrations.

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I. INTRODUCTION

Glass scintillators are easy to fabricate in large sizes and various shapes. Production cost of the melt-quenching method is lower than those of other methods [1].

As boric oxide (B_2O_3) has a long bond length, a smaller heat of fusion and a smaller cation, it is a candidate for a glass former and a flux material. The B^{3+} combined with oxygen is easily able to form a glass structure. The Bi^{3+} has a high density and is transparent, but it can not form glass structure of itself because it has

a small bond length. Thus, we produce glass scintillator with B_2O_3 in combination with Bi_2O_3 .

Rare-earth-doped bismuth-borate glass has a high density and a great radiation tolerance. Thus, rare-earth-doped bismuth-borate glass can be applied to medical imaging, homeland security, radiation detection, nuclear physics, and high-energy physics. Also, it can be used for astrophysics applications for high-energy cosmic-ray detection. Rare-earth-doped bismuth-borate glass can also have high emission efficiencies. It can emit luminescence in the range from 400 nm to 700 nm. The rare-earth elements have inner $4f^n$ shell and outer $5s^2$ and $5p^6$ shells. Thus, rare-earth-doped bismuth-borate glass has transitions in the range from the ultraviolet to the infrared

*E-mail: hongjooknu@gmail.com; Fax: +82-53-950-5325

region. The transitions of rare-earth 4f states determine the emission peaks of rare-earth-doped bismuth-borate glass [2-5].

We studied luminescence properties of different concentration rare-earth (Nd, Er, Dy, Pr, Sm, Ho, Gd, and Ce)-doped bismuth-borate glasses with different concentrations of Bi^{3+} . By using X-rays, a Xe source and a 45-MeV proton beam, we measured X-ray, photo-, and proton-induced luminescence spectra of rare-earth-doped bismuth-borate glasses. Among the rare-earth-doped bismuth-borate glasses, only Sm-, Dy-, and Nd-doped bismuth-borate glasses emit a sizable luminescence.

II. EXPERIMENTS

1. Process of Glass Melting

The preparations of the bismuth-borate glasses doped with rare-earth elements are divided into 3 groups as follows:

1. $30\text{Bi}_2\text{O}_3:(70-x)\text{B}_2\text{O}_3:x\text{RE}_x\text{O}_y$, where $\text{RE}_x\text{O}_y = \text{CeO}_2, \text{Nd}_2\text{O}_3, \text{Er}_2\text{O}_3, \text{Dy}_2\text{O}_3,$ and Pr_2O_3 with $0 \leq x \leq 2.5$ (mol%),
2. $50\text{Bi}_2\text{O}_3:(50-x)\text{B}_2\text{O}_3:x\text{RE}_x\text{O}_y$, where $\text{RE}_x\text{O}_y = \text{Nd}_2\text{O}_3, \text{Er}_2\text{O}_3, \text{Dy}_2\text{O}_3, \text{Pr}_2\text{O}_3, \text{Sm}_2\text{O}_3, \text{Ho}_2\text{O}_3, \text{Gd}_2\text{O}_3,$ and CeF_3 with $0 \leq x \leq 2.5$ (mol%),
3. $66.7\text{Bi}_2\text{O}_3:(33.3-x)\text{B}_2\text{O}_3:x\text{RE}_x\text{O}_y$, where $\text{RE}_x\text{O}_y = \text{Nd}_2\text{O}_3, \text{Er}_2\text{O}_3, \text{Dy}_2\text{O}_3, \text{Pr}_2\text{O}_3, \text{Sm}_2\text{O}_3, \text{Ho}_2\text{O}_3, \text{Gd}_2\text{O}_3,$ and CeF_3 with $0 \leq x \leq 2.5$ (mol%).

All component powders, chemical weights of 30 g, were mixed finely by hand milling for each batch. Glass samples were melted in alumina crucibles in an electrical furnace for 3 hours, at 1,100 °C by using the melt-quenching technique. These melted components were quenched between two stainless-steel plates. These glasses were all annealed at 500 °C for 3 hours before being cooled to room temperature to remove the thermal strains in the glasses. As shown in Fig. 1, glass samples were cut and then finely polished to dimensions of 1.0 cm × 2.0 cm × 0.3 cm.

2. Experimental setup

In order to compare the luminescence intensities of the three types of bismuth-borate glasses in terms of different Bi_2O_3 and dopant concentration, we measured the X-ray-induced luminescence. We used an X-ray tube (DRGEM Co.), a QE65000 spectrometer (Ocean Optics Co.) and an optical fiber for measuring the X-ray-induced luminescence. The rare-earth-doped bismuth-borate glass was attached to an optical fiber by using a

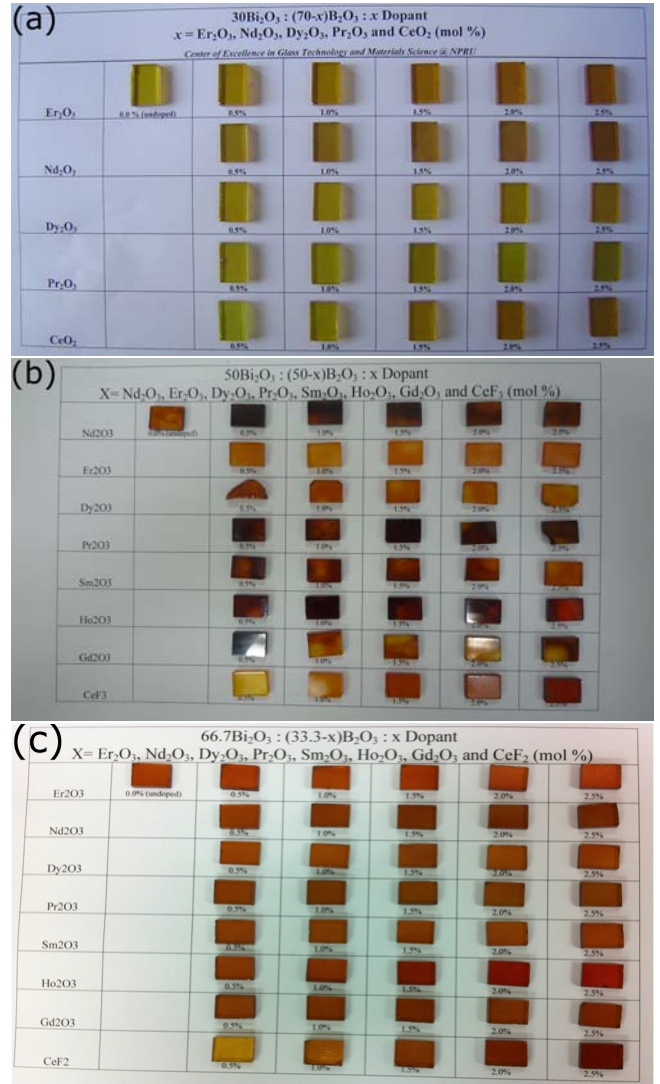


Fig. 1. (Color online) (a) $30\text{Bi}_2\text{O}_3:(70-x)\text{B}_2\text{O}_3:x$ dopant (dopant = $\text{CeO}_2, \text{Nd}_2\text{O}_3, \text{Er}_2\text{O}_3, \text{Dy}_2\text{O}_3,$ and Pr_2O_3), (b) $50\text{Bi}_2\text{O}_3:(50-x)\text{B}_2\text{O}_3:x$ dopant (dopant = $\text{Nd}_2\text{O}_3, \text{Er}_2\text{O}_3, \text{Dy}_2\text{O}_3, \text{Pr}_2\text{O}_3, \text{Sm}_2\text{O}_3, \text{Ho}_2\text{O}_3, \text{Gd}_2\text{O}_3,$ and CeF_3), and (c) $66.7\text{Bi}_2\text{O}_3:(33.3-x)\text{B}_2\text{O}_3:x$ dopant (dopant = $\text{Nd}_2\text{O}_3, \text{Er}_2\text{O}_3, \text{Dy}_2\text{O}_3, \text{Pr}_2\text{O}_3, \text{Sm}_2\text{O}_3, \text{Ho}_2\text{O}_3, \text{Gd}_2\text{O}_3,$ and CeF_3).

Teflon holder. In order to reduce the thermal noise in the charge-coupled device (CCD), we cooled the QE65000 spectrometer to -15 °C. Scintillation light produced by the sample irradiated with X-rays was transmitted through the optical fiber to the QE65000 spectrometer (Ocean Optics Co.). Windows-based software provided by the manufacture was used for acquiring data and for plotting the emission spectra of the rare-earth-doped bismuth-borate glass samples [6,7].

By using a Xenon lamp (HORIBA Jobin Yvon Inc.), we measured the photoluminescence spectra of the rare-earth-doped bismuth-borate glass samples. All glass samples were measured at room temperature. The excitation and the emission signals were detected by using a pho-

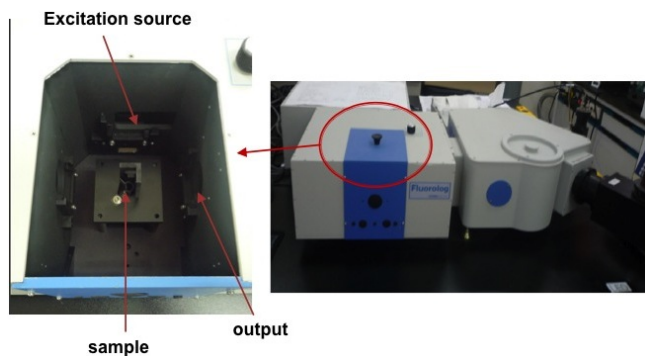


Fig. 2. (Color online) Photographic view of the experimental setup for measuring the photoluminescence at Kyungpook National University.

tomultiplier tube (PMT, R928P, Jobin Yvon Inc.). This detector was sensitive in the UV region through the visible region. The Xe source was placed at a right angle to the detector, so the sample was located at 45° from the excitation Xe source. The experimental setup for the measurement of the photoluminescence is shown in Fig. 2. The excitation and the emission spectra of the rare-earth-doped bismuth-borate glass samples were drawn by using the FlourEssence software package for Windows.

The 50-MeV proton beam test facility at the MC-50 cyclotron of KIRAMS (Korea Institute of Radiological & Medical Science) was established by the PEFPP (Proton Beam Engineering Frontier Project) of the Korea Atomic Energy Research Institute (KAERI). For studies, the facility uses low-flux proton beams, $10^4 \sim 10^{10}$ /cm²-sec. We used 45-MeV proton beams to measure the luminescence. The 45-MeV incoming proton beam passed through the 0.2-cm-thick aluminum window capping the beam pipe and lost energy down to 38 MeV [8]. The bismuth-borate samples were irradiated with a 10-nA proton beam for 10 sec.

The proton-induced emission spectrum of rare-earth-doped bismuth-borate glass was recorded by using an optical fiber and the USB4000 spectrometer (Ocean Optics Co.). A figure and a schematic diagram of the experimental setup for the measurements of the proton-induced emission spectrum are shown in Fig. 3. The glass sample was attached to an optical fiber by using a Teflon holder. Scintillation light was transmitted through the optical fiber to the USB4000 spectrometer (Ocean Optics Co.).

III. RESULT

1. X-ray induced luminescence

We measured the X-ray-induced luminescence spectra of bismuth borate doped with rare-earth elements such as Nd, Er, Dy, Pr, Sm, Ho, Gd and Ce. We made three

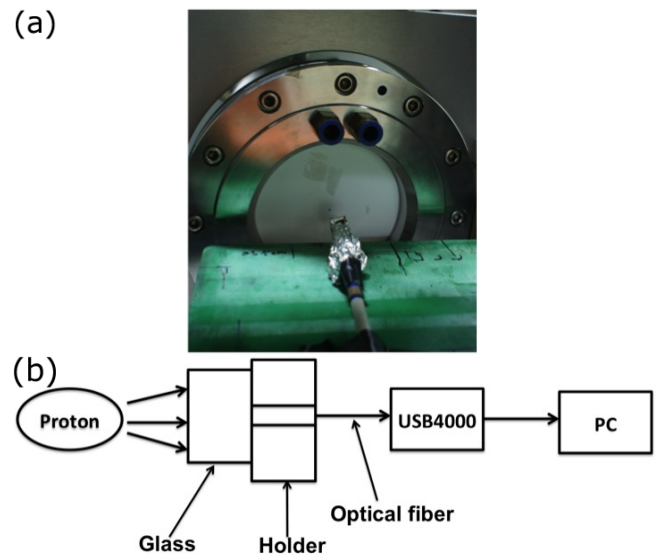


Fig. 3. (Color online) (a) Photograph of an exit window in the proton beam line with a glass sample attached to the optical fiber. (b) Schematic diagram of the experimental setup for measuring the proton-induced luminescence.

types of samples with different Bi³⁺ concentration. The first sample's concentration was $30\text{Bi}_2\text{O}_3$, $(70-x)\text{B}_2\text{O}_3$, and $x\text{RE}_x\text{O}_y$. This sample was named sample A. The second sample's concentration was $50\text{Bi}_2\text{O}_3$, $(50-x)\text{B}_2\text{O}_3$, and $x\text{RE}_x\text{O}_y$. This sample was named sample B. The third sample's concentration was $66.7\text{Bi}_2\text{O}_3$, $(33.3-x)\text{B}_2\text{O}_3$, and $x\text{RE}_x\text{O}_y$. This sample was named sample C.

An X-ray source with a high voltage of 100 kV and current of 0.5 mA irradiated all prepared samples. Among the prepared samples, Sm-, Dy- and Nd-doped bismuth-borate glasses emitted noticeable luminescence. As shown in Fig. 4(a), the emission peaks of Sm-doped sample C were located at 569 nm, 600 nm, 641 nm, and 710 nm. The luminescence intensity of 2.5-mol% Sm-doped sample C was the strongest for Sm-doped samples C, and as shown in Fig. 4(b), the luminescence intensity of 2.5-mol% Sm-doped sample C was two times stronger than 0.5-mol% Sm-doped sample C. The luminescence intensities of the 2.5-mol% doped samples A and B were the strongest in each type of samples, and the 2.5-mol% Sm-doped sample B showed the strongest luminescence of Sm-doped samples [1,9]. Thus, we obtained the result that the luminescence intensity increased as the rare-earth doping concentration increased.

We compared 2.5-mol% rare-earth-doped bismuth-borate glasses with different Bi₂O₃ concentrations, named as A, B, and C. The emission spectra are presented in Fig. 5. As shown in Fig. 5(a), the emission peaks of both 2.5-mol% Sm-doped glass samples were located at 569 nm, 598 nm, 641 nm, and 705 nm. The intensity of the luminescence from the 2.5-mol% Sm-doped sample B was stronger than that from sample C. As shown in

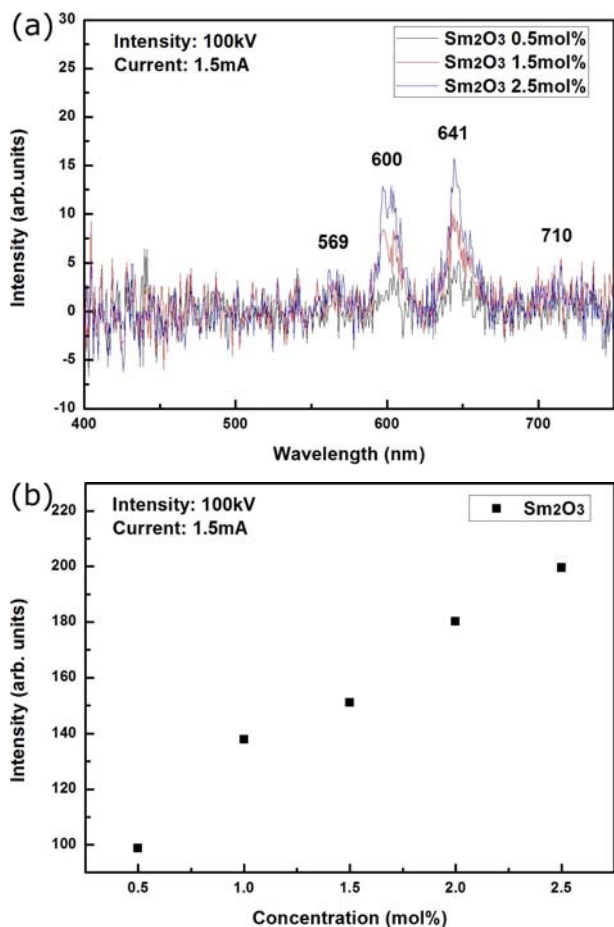


Fig. 4. (Color online) (a) The X-ray emission spectra of Sm-doped sample C with different Sm doping concentrations. (b) Luminescence intensity of Sm-doped sample C with different Sm doping concentrations.

Fig. 5.(b), all 2.5-mol% Dy-doped glass samples emitted luminescence with emission peaks at 482 nm, 575 nm, 660 nm, and 750 nm. The emission spectra showed that the luminescence intensity of 2.5-mol% Dy-doped sample A was stronger than those of sample B or sample C and that the luminescence intensity of the 2.5-mol% Dy-doped sample B was similar to that of sample C. As shown in Fig. 5(c), all three types of 2.5-mol% Nd-doped glass samples showed weak enhancement around the 895 nm region. The emission peak was due to the $^4F_{3/2} \rightarrow ^4I_{9/2}$ transition [10] and all samples showed similar luminescence intensities.

2. Photoluminescence

When we measured the X-ray luminescence from the glass samples, the highest doping concentration sample showed the strongest luminescence. Thus, we measured the photoluminescence from the 2.5-mol% Sm-doped sample B and from the 2.5-mol% Dy-doped sam-

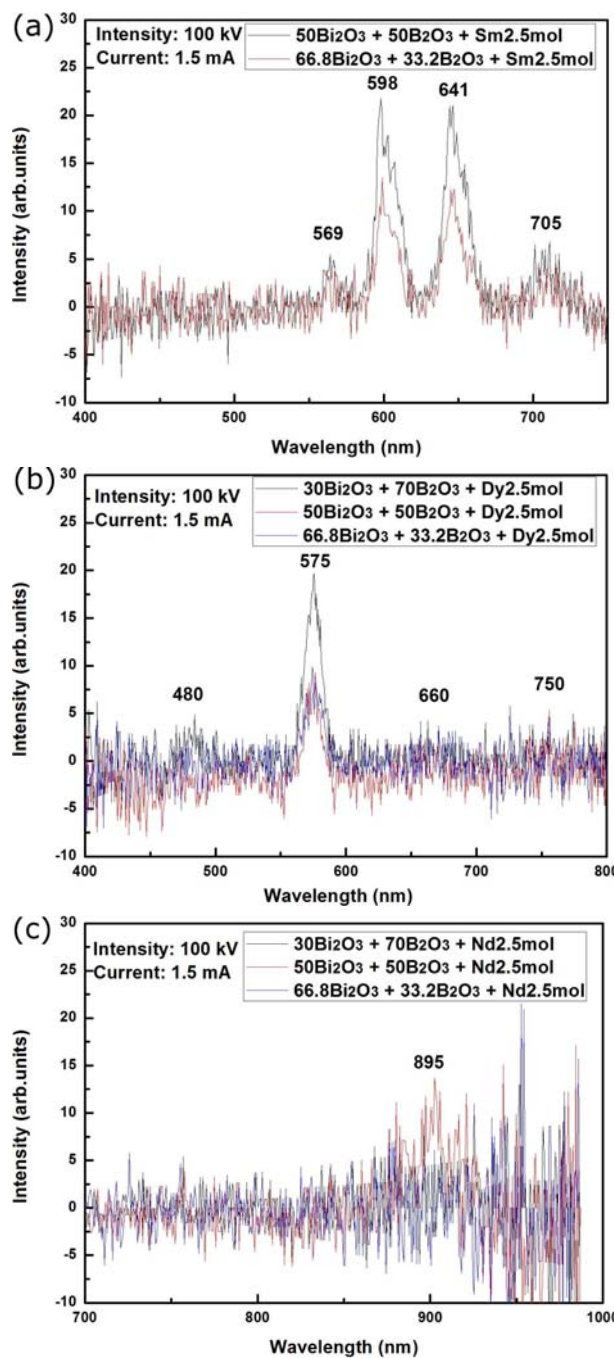


Fig. 5. (Color online) Luminescence intensity comparison of 2.5 mol% (a) Sm-, (b) Dy-, and (c) Nd-doped bismuth-borate glasses with different concentrations of Bi_2O_3 .

ples A and B.

The emission spectrum of the Sm-doped sample B excited at 404 nm is presented in Fig. 6(a). As shown in Fig. 6(a), the Sm-doped sample B had emission bands at 560 nm ($^4G_{5/2} \rightarrow ^6H_{5/2}$), 600 nm ($^4G_{5/2} \rightarrow ^6H_{7/2}$), 645 nm ($^4G_{5/2} \rightarrow ^6H_{9/2}$), and 710 nm ($^4G_{5/2} \rightarrow ^6H_{11/2}$) [11]. The excitation spectrum of the 2.5-mol% Sm_2O_3 -doped sample B was measured for an emission peak of

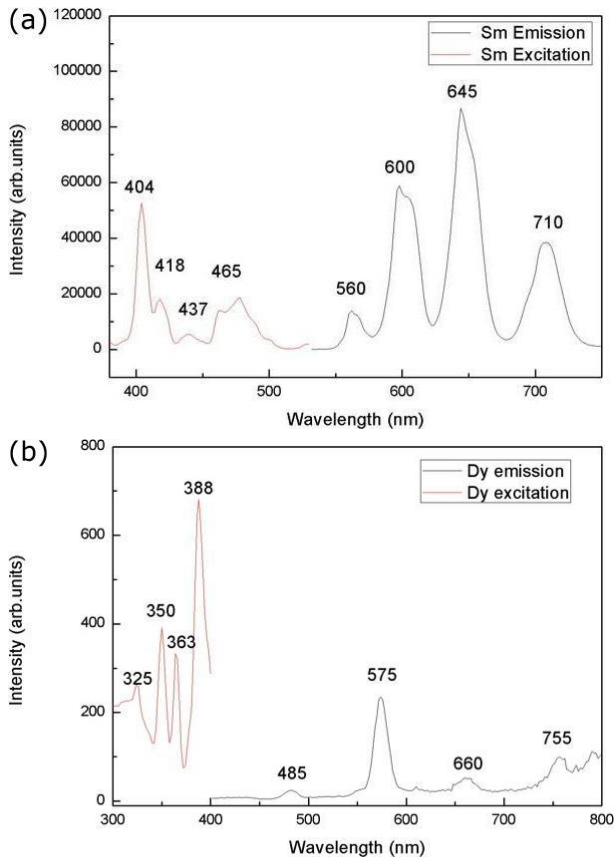


Fig. 6. Photoluminescence of (a) 2.5-mol% Sm-doped sample B and (b) 2.5-mol% Dy-doped sample A.

649 nm. The excitation peaks of the Sm-doped sample B were located at 404 nm, 418 nm, 437 nm, and 465 nm.

The luminescence spectrum of the Dy-doped sample A under excitation at 315 nm is shown in Fig. 6(b). The Dy-doped sample A showed emission bands at 485 nm ($^4F_{9/2} \rightarrow ^6H_{15/2}$), 575 nm ($^4F_{9/2} \rightarrow ^6H_{13/2}$), 660 nm ($^4F_{9/2} \rightarrow ^6H_{11/2}$), and 755 nm ($^4F_{9/2} \rightarrow ^6H_{9/2} + ^6H_{11/2}$) [11]. The excitation peaks for sample A were located at 325 nm, 350 nm, 363 nm, and 388 nm, respectively. We used four different excitation peaks to check the emission spectra, and they all showed emission spectra with the same shape. We also measured the photoluminescence from the 2.5-mol% Dy-doped sample B. While the excitation spectrum of the Dy-doped sample B was similar to those of sample A, the intensity of the emission peak was 2 times lower than that of sample A.

3. Proton-induced luminescence

We measured the proton-induced luminescences from 2.5-mol% Sm-doped sample B and from Dy- and Nd-doped samples A. All samples were irradiated with a 38-MeV proton beam of 10 nA for 10 sec. Among the three samples, only the Sm- and Dy-doped samples emitted

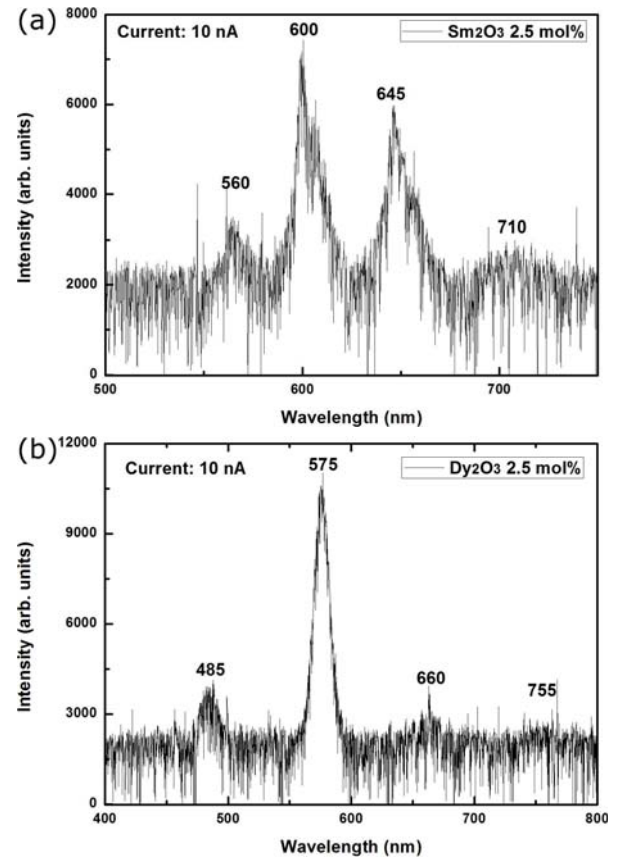


Fig. 7. Protonluminescence of (a) 2.5-mol% Sm-doped sample B and (b) 2.5-mol% Dy-doped sample A.

luminescence. As shown in Fig. 7, the peaks of proton-induced luminescence were similar to those of the X-ray-induced luminescence [1].

IV. CONCLUSION

Rare-earth-doped bismuth-borate glass samples, $x\text{Bi}_2\text{O}_3:(100-x)\text{B}_2\text{O}_3:y\text{RE}$ ($x = 30, 50, \text{ and } 66.7\%$) (RE = Nd, Er, Dy, Pr, Sm, Ho, Gd, and Ce $0 \leq y \leq 2.5$ (mol%)), with different rare-earth concentrations were measured with X-ray, photo- and proton-induced luminescence. We obtained the result that only Sm-, Dy-, and Nd-doped bismuth-borate glass samples showed sizable luminescence. When the emission spectra induced by X-rays, a Xe source and protons were measured, we observed similar results, the emission peaks of the Sm-doped bismuth-borate glass sample were at 560 nm, 600 nm, 645 nm, and 710 nm. For the Dy-doped glass sample, the emission peaks were at 485 nm, 575 nm, 660 nm, and 755 nm. The Nd-doped bismuth-borate glass sample showed weak X-ray-induced luminescence. The emission peak of Nd was around 895 nm.

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