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Procedia Engineering 32 (2012) 855 – 861

**Procedia
Engineering**www.elsevier.com/locate/procedia

I-SEEC2011

Luminescence Property of Rare-Earth Doped Bismuth-Borate Glasses

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Abstract

We fabricated rare-earth doped bismuth borate glasses by using melt-quench technique. Two different types glass samples of $x\text{Bi}_2\text{O}_3 : (100-x)\text{B}_2\text{O}_3$ ($x=30$ and 50) were made to compare the luminescence properties. We measured x-ray luminescence of Bi-glass by using a x-ray tube. Several dopants were doped into the Bi-glass to measure the x-ray luminescence such as CeO_2 , Nd_2O_3 , Er_2O_3 , Dy_2O_3 , Pr_2O_3 , Sm_2O_3 , Ho_2O_3 , Gd_2O_3 and CeF_3 . Among them, Dy_2O_3 , Nd_2O_3 and Sm_2O_3 doped Bi-glass emitted luminescence. We measured emission spectrum of each samples. Dy_2O_3 doped bi-glass has emission band at 482 nm, 575 nm, 662 nm and 765 nm. Nd_2O_3 doped bi-glass have emission band at 895 nm and Sm_2O_3 doped Bi-glass has emission band at 569 nm, 598 nm, 641 nm and 705 nm. Moreover, Bi-glass scintillators with high light yield with good radiation hardness and low cost can be applied in high energy and nuclear physics, medical imaging, homeland security and radiation detection.

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Open access under [CC BY-NC-ND license](http://creativecommons.org/licenses/by-nc-nd/3.0/).**Keywords:** Rare earth ions; Dy; Nd; Sm; X-ray luminescence; Glass

1. Introduction

Glasses doped with rare earth ions emit luminescence in the visible range. These materials have luminescence due to 4f-4f and 4f-5d electronic transitions in the rare earth ions. The 4f-4f transition emits

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sharp emission bands from UV to infrared region. Nowadays, Glass materials doped with rare earth ions are drawing attention as phosphors, three-dimensional displays and fiber laser materials [1-3].

Trivalent bismuth cation the inorganic compounds or hosts shows luminescence originality from the $6S6P \rightarrow 6S^2$ transition. Due to the high density and high effective atomic number Z_{eff} , bismuth compounds ensure high effective recording of ionization radiation. Specially it has high detection efficiency on x-ray and gamma-ray. Thus, an investigation of compounds containing bismuth has great potential for the discovery of new luminescent material. However most of bismuth compounds quench the luminescence at room temperature [4]. Pure Bi_2O_3 has several crystallographic polymorphs and melts points is known to be 817°C and density is 8.9g/cm^3 . Since Bi_2O_3 itself is not luminescent and it can't form a glass, Bi_2O_3 - B_2O_3 system were studied. They are formed in the system over wide compositional range and with high indices of refraction. Since bismuth borate glass is not luminescent at room temperature, we produced rare-earth doped glasses for luminescence study.

Bi^{3+} ion has high density and transparency, but is strong in small field. So it cannot form a glass. But boric oxide (B_2O_3) is able to form glass structure. So we produce a rare-earth doped bismuth borate glass. Rare-earth doped bismuth-borate glass has high density and radiation hard property. Also it is easy to made, can be produced with low cost and wide range of emission band. Therefore, it is a good candidate for radiation detector and possible to apply high energy and nuclear physics, medical imaging, homeland security and radiation detection. We studied luminescence property of rare-earth ions (Ce, Nd, Er, Dy, Pr, Sm, Ho and Gd) doped bismuth-borate glasses with different rare earth oxide concentration for applying many fields [3]. By using x-ray tube (DRGEM Co.), we measured x-ray luminescence of rare-earth doped bismuth-borate glass. As a result, we were able to show emission spectra of each Dy_2O_3 , Nd_2O_3 and Sm_2O_3 doped bismuth-borate glass.

2. Experimental

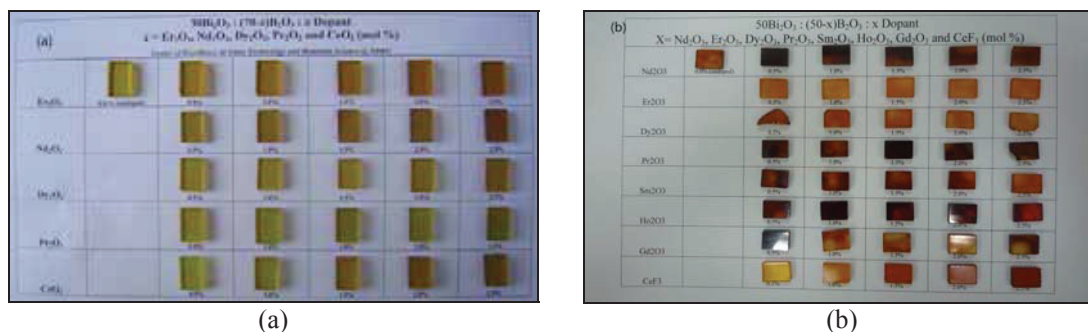


Fig. 1. (a) $30\text{Bi}_2\text{O}_3 : (70-x)\text{B}_2\text{O}_3 : x$ Dopant (Dopant = CeO_2 , Nd_2O_3 , Er_2O_3 , Dy_2O_3 and Pr_2O_3) (b) $50\text{Bi}_2\text{O}_3 : (50-x)\text{B}_2\text{O}_3 : x$ Dopant (Dopant = Nd_2O_3 , Er_2O_3 , Dy_2O_3 , Pr_2O_3 , Sm_2O_3 , Ho_2O_3 , Gd_2O_3 and CeF_3)

2.1. Process of glass melting

The preparation of bismuth borate glasses are as follows.

(1) $30\text{Bi}_2\text{O}_3 : (70-x)\text{B}_2\text{O}_3 : x(\text{Rare earth})$ where $x=0.0, 0.5, 1.0, 1.5, 2.0$ and 2.5 mol %. (Sample A)

(2) $50\text{Bi}_2\text{O}_3 : (50-x)\text{B}_2\text{O}_3 : x(\text{Rare earth})$ where $x=0.0, 0.5, 1.0, 1.5, 2.0$ and 2.5 mol %. (Sample B)

where $x = \text{CeO}_2$, Nd_2O_3 , Er_2O_3 , Dy_2O_3 , Pr_2O_3 , Sm_2O_3 , Ho_2O_3 and Gd_2O_3 . All component powder of chemical weight 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 $1,100^\circ\text{C}$ by the use of normal quenching technique. These melting components were quenched between two stainless steel plates. These glasses

thus obtained were all annealed at 500 °C for 3 hours before cooled down to room temperature to remove thermal strains in the glasses. As shown Fig. 1, we cut and polished glass samples to dimensions of 1.0 cm x 2.0 cm x 0.3 cm. Since the glass samples were doped Bi₂O₃, all samples show light yellow color.

2.2. Experimental setup

In order to measure the x-ray luminescence of the rare-earth doped bismuth borate glass samples at room temperature, x-ray tube (DRGEM Co.) was used and faces of the glass sample were wrapped with several layers of Teflon tape excepting the one for attaching to the optical fiber. Signals from the glass sample by the induced x-ray were measured using a QE65000 spectrometer (Ocean Optics Co.) The QE65000 was cooled to -15°C to reduce thermal noise in the CCD. It was used to plot the x-ray emission spectrum of the glass sample by window based-software [5, 6].

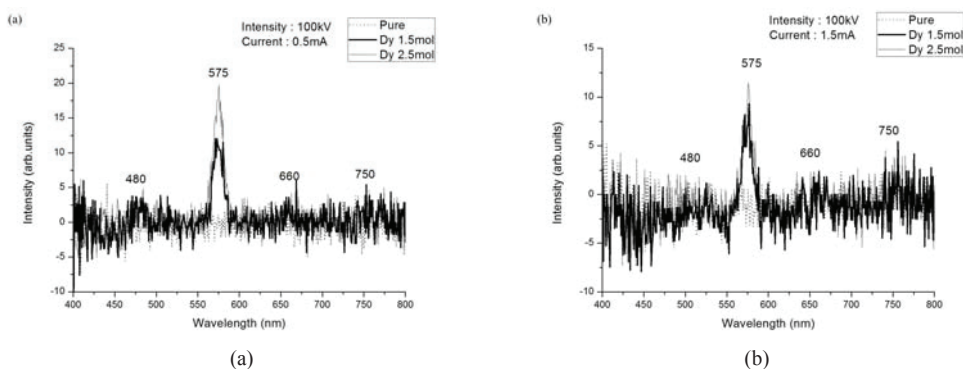
3. Results and discussions

Sample A were measured by using x-rays of intensity 100kV and current 0.5mA and sample B were measured by using x-rays of intensity 100kV and current 1.5mA. Among them, only Dy₂O₃, Nd₂O₃ and Sm₂O₃ doped Bi-glass emitted luminescence.

3.1. Dy₂O₃ doped in bismuth borate glasses

Fig. 2(a) showed the x-ray induced emission spectra of Dy₂O₃ doped in sample A. Emission peaks were observed at 480nm, 575nm, 660nm and 750nm [3, 7]. Emission spectra of Dy₂O₃ doped in sample B were presented in Fig. 2(b), emission peaks were observed similar with sample A. The light yields of both samples of Bi glass at 575 nm are shown in Fig. 3. The emission intensities of both samples were increased with increasing of Dy₂O₃ concentration and can observe the intensity of Dy₂O₃ doped sample A was stronger than sample B at all Dy₂O₃ concentration. Fig. 4 compare the x-ray induced emission spectra of 2.5% mol of Dy₂O₃ between both samples. Light yield at 2.5 mol% of Dy₂O₃ doped in sample A is approximately three times higher than doped in sample B.

Both samples emitted a luminescence with the emission peaks at 482nm, 573nm, 662nm and 756nm [3]. The emission spectra were the strongest due to the ⁴F_{9/2}→⁶H_{15/2} (480nm), ⁴F_{9/2}→⁶H_{13/2} (575nm), ⁴F_{9/2}→⁶H_{11/2} (660nm) and ⁴F_{9/2}→⁶H_{9/2}+⁶F_{11/2} (750nm) [8] respectively. These emission bands were showed other glass materials as P₂O₅-Al₂O₃-Na₂O:Dy₂O₃ [9]. The energy level scheme for all the observed absorption of Dy³⁺ doped Bi-glass is shown in Fig. 2(c).



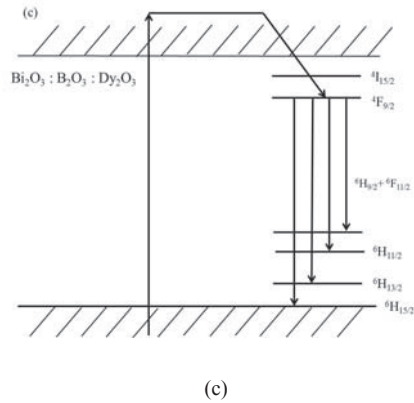


Fig. 2. The x-ray induced emission spectra of difference concentration Dy₂O₃ doped glass scintillator (a) 30Bi₂O₃ : (70-x)B₂O₃ : xDy₂O₃ (b) 50Bi₂O₃ : (50-x)B₂O₃ : xDy₂O₃ and (c) transition schematic

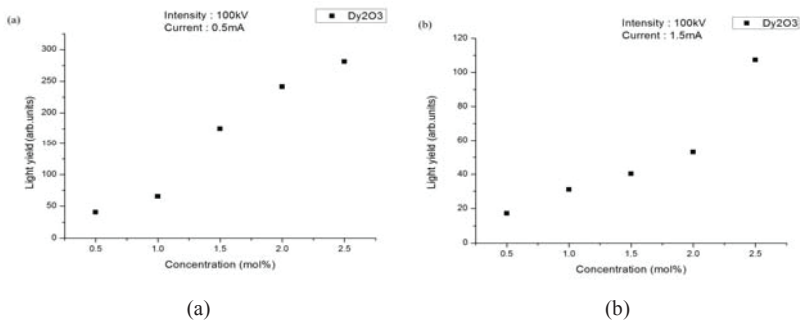


Fig. 3. The light yield of Dy₂O₃ doped glass scintillator around 575nm (a) 30Bi₂O₃ : (70-x)B₂O₃ : xDy₂O₃ , (b) 50Bi₂O₃ : (50-x)B₂O₃ : xDy₂O₃

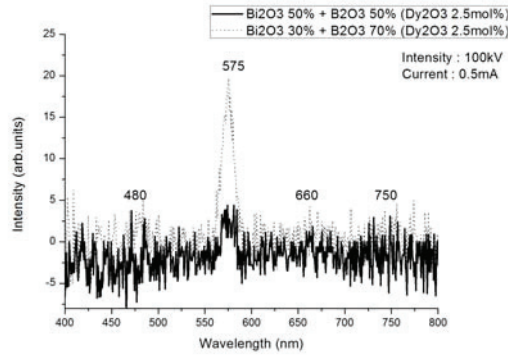


Fig. 4. X-ray luminescence spectra of 2.5mol % Dy₂O₃ doped sample A and sample B

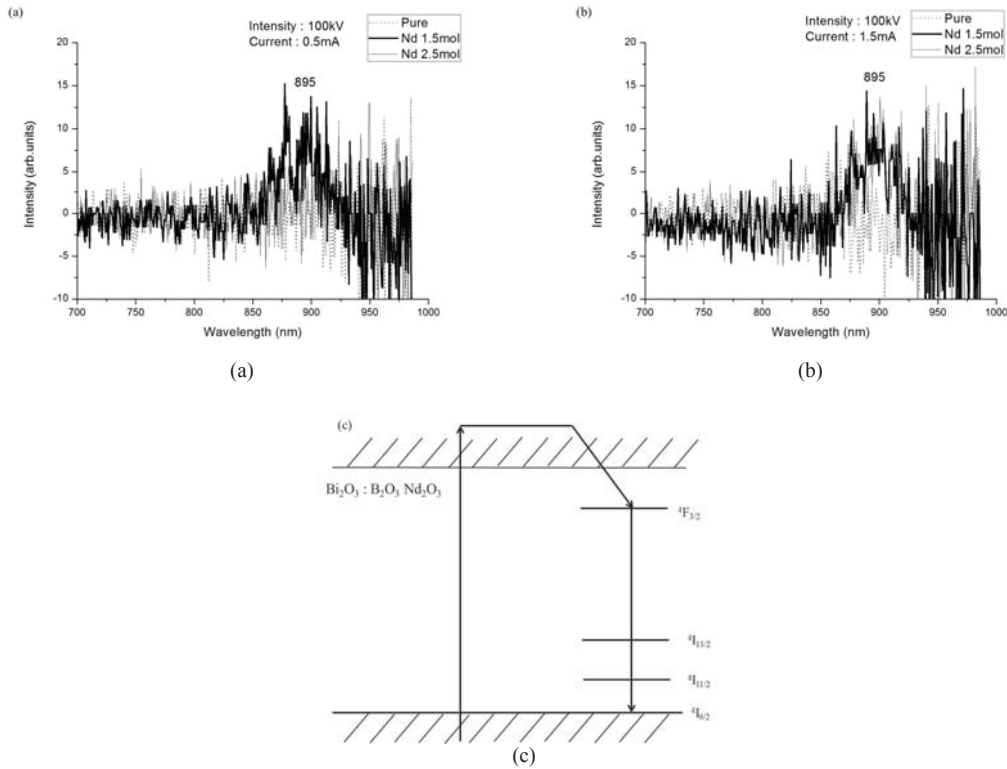


Fig. 5. The x-ray induced emission spectra of difference concentration Nd₂O₃ doped glass scintillator (a) 30Bi₂O₃ : (70-x)B₂O₃ : xNd₂O₃ (b) 50Bi₂O₃ : (50-x)B₂O₃ : Nd₂O₃ and (c) transition schematic

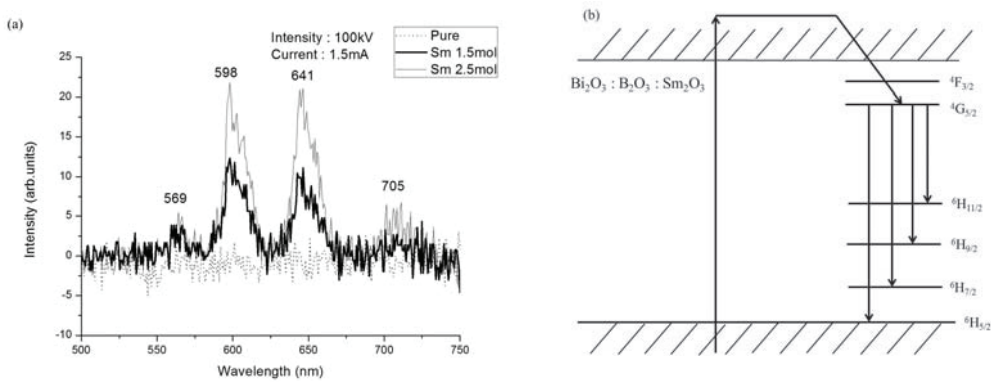


Fig. 6. (a) The x-ray induced emission spectrum of difference concentration Sm₂O₃ doped glass scintillator (30Bi₂O₃ : (70-x)B₂O₃ : xSm₂O₃) and (b) transition schematic

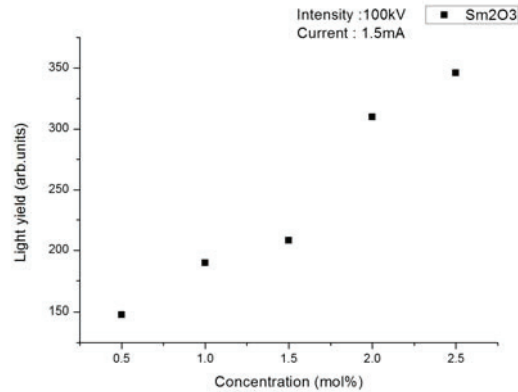


Fig. 7. The light yield of Sm_2O_3 doped glass scintillator around 598nm

3.2. Nd_2O_3 doped in bismuth borate glasses

Fig. 5(a) and Fig. 5(b) showed the emission spectra of Nd_2O_3 doped in sample A and sample B. As shown both figures, Nd_2O_3 doped glass peak emission of Nd_2O_3 doped glass is 895nm, but it showed weak luminescence. Therefore, intensity of Nd_2O_3 doped bismuth borate glass is not increased with increasing of Nd_2O_3 concentration. We compared intensity of Nd_2O_3 doped sample A with sample B. The result was that intensity of both samples was very similar. The luminescence spectra peak 895nm was due to the ${}^4\text{F}_{3/2} \rightarrow {}^4\text{I}_{9/2}$ [10]. The energy level scheme for all the observed absorption of Nd^{3+} doped Bi-glass is shown in Fig. 5(c).

3.3. Sm_2O_3 doped in bismuth borate glasses

Fig. 6(a) showed scintillation spectra of Sm_2O_3 doped Sample B. The emission wavelength observed at 569nm, 598nm, 641nm and 705nm and show energy level scheme in Fig. 6(b). As shown Fig. 7, the intensity of luminescence was increase with increasing doing concentration. Light yield of 2.5 mol % of Sm_2O_3 doped sample A is approximately 2.3 times higher than 0.5 mol % of Sm_2O_3 doped sample A. The luminescence spectra of the Sm_2O_3 doped Bi-glass were identified as ${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{5/2}$ (569nm), ${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{7/2}$ (598nm), ${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{9/2}$ (641nm) and ${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{11/2}$ (705nm) [11]. These emission bands also were showed other glass materials [9].

4. Conclusions

The rare earth doped bismuth borate glass samples ($30\text{Bi}_2\text{O}_3 : (70-x)\text{B}_2\text{O}_3 : x\text{RE}_x\text{O}_y$ and $50\text{Bi}_2\text{O}_3 : (50-x)\text{B}_2\text{O}_3 : x\text{RE}_x\text{O}_y$, RE= CeO_2 , Nd_2O_3 , Er_2O_3 , Dy_2O_3 , Pr_2O_3 , Sm_2O_3 , Ho_2O_3 , Gd_2O_3 and CeF_3) were made by the normal quenching technique. Among them, Only Dy, Nd and Sm doped samples emitted luminescence. The x-ray luminescence was as shown that emission peaks of Dy doped glass were 482nm, 575nm, 662nm and 765nm due to ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{15/2}$, ${}^4\text{F}_{9/2} \rightarrow {}^4\text{H}_{13/2}$, ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{11/2}$ and ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{9/2} + {}^6\text{F}_{11/2}$ transitions, Nd doped was 895nm due to ${}^4\text{F}_{3/2} \rightarrow {}^4\text{I}_{9/2}$ transition and Sm doped were 569, 598, 641 and 708nm due to ${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_J$ ($J = 5/2, 7/2, 9/2, 11/2$) transitions, respectively.

Acknowledgements

This work was supported by the National Research Foundation of Korea Grant funded by the Korean Government (NRF-2010-013-C00018). J. Kaewkhao and special thanks to National Research Council of Thailand (NRCT) and Commission of Higher Education under SP2 project for partially funding this research. P. Limsuwan would like to thanks Thailand Center of Excellence in Physics (ThEP) and King Mongkut's University of Technology Thonburi for partially funding under National Research University project.

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