LUMINESCENCE ANALYSIS OF SAMARIUM (III) IONS DOPED IN Bi_2O_3-BaO-B_2O_3 GLASSES

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ABSTRACT

A novel glass system, obtained from conventional melt-quenching technique, was synthesized using (40-x)B_2O_3 : 40Bi_2O_3 : 20BaO : xSm_2O_3, over the concentration region of 0–2.5 mol%. All of glasses from the new system were characterized using X-Ray Diffractometer (XRD) and Fourier Transform Infrared (FTIR). The spectroscopic properties of Sm^{3+} ions were modeled within modified Judd-Ofelt(J-O) theory, yielding absorption oscillator strength. Under the J-O theory, the set of modeling parameters are Ω_2 = 28.62, Ω_4 = 14.31 and Ω_6 = 2.91 in unit of 10^{-20} cm^2. The emission spectrum of Sm^{3+}:BiBaBO glass has revealed four transitions ($^4G_{7/2}\rightarrow{}^6H_{5/2}$, $^6H_{7/2}$, $^6H_{9/2}$ and $^6H_{11/2}$) located at 564, 600, 645 and 709 nm respectively with λ_{exc} = 408 nm ($^6H_{5/2}\rightarrow{}^4G_{7/2}$). The X-ray luminescence is dominated by the emission from Sm^{3+} ions, similar to photoluminescence spectra. CIE color coordinates are an evidence supporting the potentiality analysis of the glasses for orange emission. One significant advantage of the new glass system is that it can emit light with high intensity. In this work, the development of Sm^{3+}- doped in BiBaBO glasses was discussed and can be used as a solid state lighting materials application.

KEYWORDS: *BiBaBO:Sm_2O_3, Judd-Ofelt theory, X-ray Luminescence*

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INTRODUCTION

In recent years, a special attention is on the rare earth (RE) ions doped glasses on the fabrication of new generation solid state devices like white LEDs, solid state lasers, flat panel displays, planar waveguide, optoelectronic devices and broadband amplifiers etc., due to their inhomogeneous line widths, flexibility in the selection of wide range of chemical composition and mass production [1-2]. Among the various glass, borate glasses are excellent host matrices because boron troxide (B_2O_3) acts as a good glass former and flux material [3]. Borate glasses are structurally more intricate as compared to phosphate or silicate glasses due to two types of coordination of boron atoms with 3 and 4 oxygens and the structure of vitreous B_2O_3 consists of a random network of boroxyl rings and BO_3 triangles connected by B-O-B linkages. Moreover, the addition of a modifier oxide causes a progressive change of some BO_3 triangles to BO_4 tetrahedra and results in the formation of various cyclic units like diborate, triborate, tetraborate or pentaborate groups [4].

The heavy metal ions like Bi_2O_3, PbO, PbF_3, etc., containing in borate glasses, decreases the host phonon energy and thereby improves the effective fluorescence [5]. Moreover, bismuth oxide contained host glass matrix improves chemical durability of the glass [6]. Despite the Bi_2O_3 is not a classical network former, it exhibits some superior physical properties like high density, high refractive index, high optical basicity, large polarizability and large nonlinear optical susceptibility [7]. The presence of two network forming oxides such as classical B_2O_3 and the conditional Bi_2O_3 glass former, the possible participation in the glass structure of both boron and bismuth ions with more than one stable coordination, the capability of the bismuth polyhedral and of the borate structural groups to form independent interconnected networks [8]. Over the last several years, bismuth barium borate glasses are also useful for variety of optical applications such as radiation shielding window, gamma-rays shielding materials and scintillation counters [9-10]. Moreover, Sm^{3+} doped glasses give high power lasers in the red-orange visible region, having applications inpreclinical radiation treatment for cancer known as micro beam radiation therapy (MRT) [11]. In this study, the bismuth barium borate (BiBaBO) glasses doped with Sm^{3+} ions were prepared by the conventional melt quenching technique and investigate their structural, optical, luminescence and CIE color coordinates properties for photonics and solid state lighting materials development.

MATERIALS AND METHODS

Glass compositions (in mol%) (40-x)B_2O_3:40Bi_2O_3:20BaO:xSm_2O_3 (where $0 \leq x \leq 2.50$) have been melted in alumina crucible at 1,100 °C for 3 hours by melt-quench technique. The melts were air quenched by pouring it onto a preheated stainless steel mould and annealed at 500 °C for 3 hours to decrease thermal strains. The polished glass samples were cut into 1.0×1.5×0.3 cm^3 size for structural, optical, luminescence and CIE color coordinates measurements. The amorphous nature of the prepared glass was confirmed through X-ray diffraction studies using a Shimadzu XRD-6100 diffractometer with X-ray tube Cu target operated at 40 kV and 30 mA. The scanning region of 2° was set from 10° to 80° with a step rate of 5 °/min. Infrared spectra of the present glasses were recorded at room temperature in the range 650–3,000 cm^{-1} using an Agilent-Cary 630 FT-IR spectrometer. The luminescence spectra were recorded by exciting at 408 nm using Cary Eclipse Fluorescence Spectrophotometer of xenon flash lamp as a source. The glass samples were further investigated for X-ray induced optical luminescence. The X-ray induced optical luminescence spectra were measured with a Cu target X-ray generator (Inel, XRG3D-E), whose X-ray source was operated at 50 kV and 20 mA, and the spectrometer (QE65 Pro, Ocean Optics) with an optical fibre to detect the emission spectra.

RESULTS AND DISCUSSION

Structural Properties

X-ray Analysis

The X-ray diffraction (XRD) pattern has been recorded in the range 10° to 80°. The XRD pattern of the Sm^{3+}-doped in BiBaBO glasses is shown in Fig. 1 as a representative case exhibit broad scattering at lower angles, which is the characteristic long range structural disorder confirms the amorphous nature of the prepared glass.

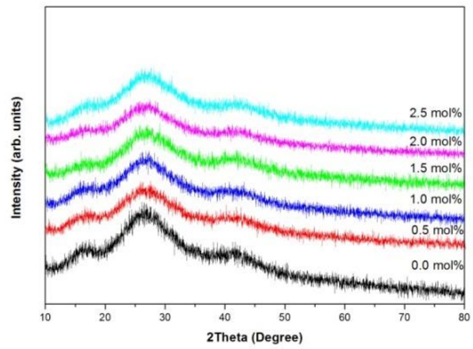

Fig. 1 XRD pattern of Sm^{3+}-doped in BiBaBO glasses.

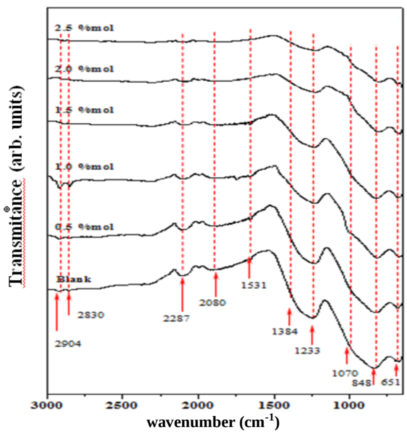

Fig. 2 Infrared spectra of Sm^{3+}-doped in BiBaBO glasses.

The Fourier Transform Infrared Spectrum

The FTIR spectra of Sm^{3+}-doped in BiBaBO glasses recorded at room temperature in the spectrum range 650–3000 cm^{-1} is shown in Fig. 2. The peaks of the IR spectra of the glasses under study are listed in Table 1. The bands observed in the region 2080–2940 in all the glass samples are attributed to the hydroxyl or water group [12]. The present set of glasses show transmission bands in regions 2904, 2830, 2287, 2080, 1531, 1384, 1233, 1070, 848 and 651 cm^{-1}. It has been reported that the bands observed in the region 1233 cm^{-1} are due to the asymmetrical stretching relaxation of the B-O bond of trigonal BO_3 units [13]. The band around 1070 cm^{-1} originates from B-O bond stretching of the tetrahedral BO_4 units and is due to the vibration of some boron atoms attached to the non-bridging oxygen in the form of BO_4 vibrations [14]. The shoulder around 848 cm^{-1} is related to the symmetrical stretching vibration of Bi-O in [BiO_3] group [15]. The band observed around 651 cm^{-1} is the bond bending mode of B-O-B vibrations [16].

Judd-Ofelt modeling

From the absorption oscillator strengths for observed absorption bands of Sm^{3+} in the studies glass were calculated by using Judd-Ofelt(J-O) theory[17-18], yielding absorption oscillator strength. Under the J-O theory, the set of modeling parameters are Ω_2 = 28.62, Ω_4 = 14.31 and Ω_6 = 2.91 [10^{-20} cm^2].

Luminescence Properties

Photoluminescence properties

The luminescence spectra were recorded by exciting at 408 nm wavelengths using the xenon flash lamp shown in Fig. 3.The spectra consist of four emission peaks corresponding to the $^4G_{7/2} \rightarrow {}^6H_{5/2}$ (564 nm yellow, weak), $^4G_{7/2} \rightarrow {}^6H_{7/2}$ (600 nm orange, strong), $^4G_{7/2} \rightarrow {}^6H_{9/2}$ (645 nm red, strong) and $^4G_{7/2} \rightarrow {}^6H_{11/2}$ (709 nm red, weak) transitions and highest intensity was obtained at 1.00 % mol of Sm_2O_3. Higher than 1.00 % mol, the emission intensity was decreased due to concentration quenching. Fig. 5 shows the partial energy level diagram of Sm^{3+} ions in the BiBaBO glasses along with emission and non-radiative (NR) process. When the Sm^{3+} ions are excited to any level above the $^4F_{7/2}$, there were decreased the energy by using non-radiative process to $^4G_{7/2}$ level and given the emission energy takes place from the state of $^4G_{7/2}$ to lower energy levels state in VIS- NIR region [19–21].

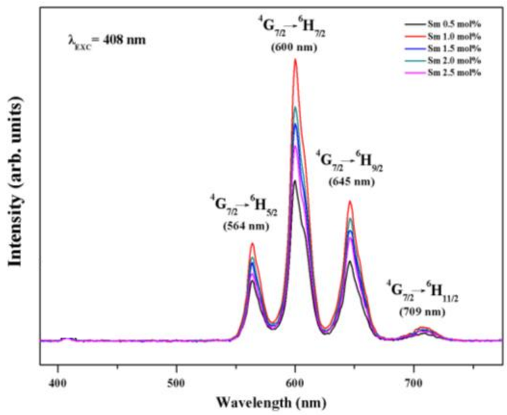

Fig. 3 The emission spectra (λ_{exc} = 408 nm) of BiBaBO glasses doped with Sm^{3+} ions.

X-ray induced luminescence

Fig. 4 shows the X-ray induced emission spectra of the Sm^{3+}-doped in BiBaBO glasses, which were irradiated with X-ray at 50 kV and 20 mA. Although the excitation source was different, the spectral results were nearly identical to those from the photoluminescence. Also, two luminescence bands were obtained at 600 and 645 nm. $^4G_{5/2} \rightarrow {}^6H_J$ (J: 7/2 and 9/2) transitions of Sm^{3+} [22].

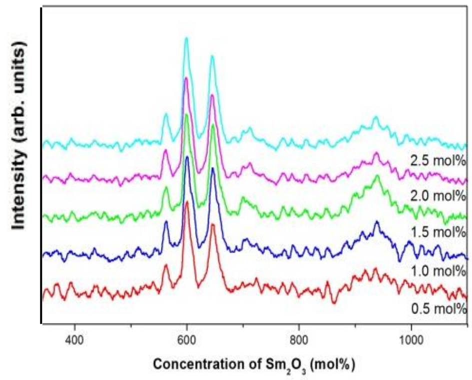

Fig. 4 X-rays induced optical luminescence spectra of the Sm^{3+}-doped in BiBaBO glasses.

CIE chromaticity analysis

The *x*, *y* color chromaticity coordinates of the Sm^{3+}-doped in BiBaBO glasses have been presented in Fig. 6 along with the *x*, *y* color chromaticity coordinates of the reported Sm^{3+}doped systems. The chromaticity coordinates are an evidence supporting the potentiality analysis of the glasses for orange emission corresponding to the Sm^{3+}-doped in BiBaBO glasses.

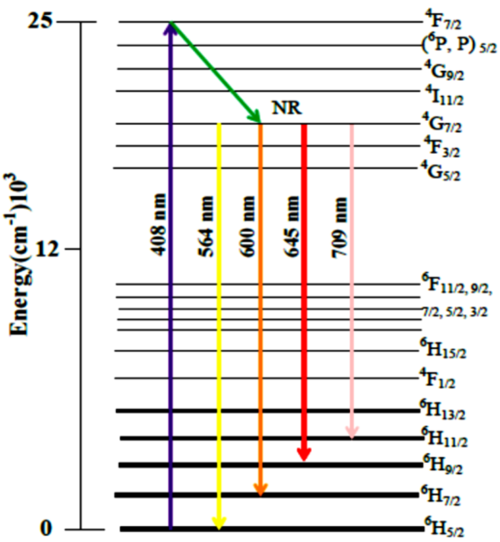

Fig. 5 Partial energy level diagram showing the possible emission transitions of Sm^{3+}-doped in BiBaBO glasses.

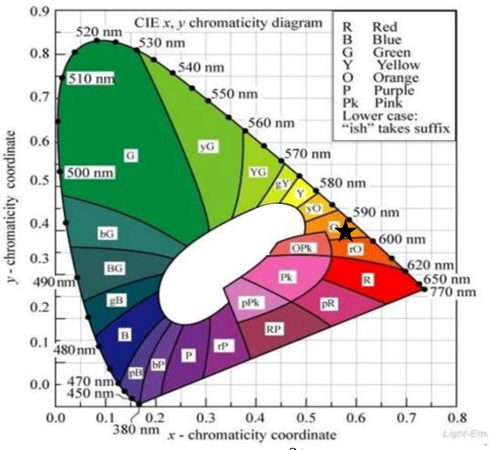

Fig. 6 The CIE diagram of Sm^{3+}-doped in BiBaBO glasses.

CONCLUSION

The Sm^{3+}-doped bismuth barium borate glasses was prepared from conventional melt-quenching technique, were synthesized using (40-x)B_2O_3 : 40Bi_2O_3 : 20BaO : xSm_2O_3, over the concentration region of 0-2.5 mol%. All of glasses from the new system were characterized using X-Ray Diffractometer (XRD) and Fourier Transform Infrared (FTIR). The spectroscopic properties of Sm^{3+} ions were modeled within modified Judd-Ofelt (J-O) theory, yielding absorption oscillator strength. Under the J-O theory, the set of modeling parameters are Ω_2 = 28.62, Ω_4 = 14.31 and Ω_6 = 2.91 in unit of 10^{-20} cm^2. The emission spectrum of Sm^{3+} : BiBaBO glass has revealed four transitions ($^4G7/2 \rightarrow {}^6H_{5/2}$, $^6H_{7/2}$, $^6H_{9/2}$ and $^6H_{11/2}$) located at 564, 600, 645 and 709 nm respectively with λ_{exc} = 408 nm. ($^6H_{5/2} \rightarrow {}^4G_{7/2}$). The X-ray luminescence is dominated by the emission from Sm^{3+} ions, like photoluminescence spectra. CIE color coordinates are an evidence supporting the potentiality analysis of the glasses for orange emission. The new glass system possess an advantage of the emission of light with high intensity. In this work, the development of Sm^{3+}-doped in BiBaBO glasses was discussed and can be used as a solid state lighting materials application.

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