STRUCTURAL AND PHOTOLUMINESCENCE PROPERTIES OF Dy^{3+} ION IN ZINC BISMUTH BORATE GLASSES

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Abstract

The zinc bismuth borate (ZBB) glasses doped with Dy^{3+} were prepared by the melt quenching technique and their structural and spectroscopic behavior were studied through XRD, FTIR and photoluminescence measurements. Glasses of chemical composition (in mol%) were $59B_2O_3$: $30Bi_2O_3$: 10ZnO: $1Dy_2O_3$. X-ray diffraction studies were performed in order to confirm the amorphous nature of the sample. The analysis of FTIR spectrum of the sample depicts that the glass network is built up of mainly BiO_3, BO_3 and BO_4 units. Its detailed analysis also revealed that the glass structure depends upon the amount of ZBB in the glass matrix and hence it acts as a modifier in the glass network. The excitation spectrum registered four bands are related to transitions from the $^6H_{15/2}$ ground state to the $^4M_{7/2} + {}^6P_{7/2}$, $^4I_{11/2}$, $^4I_{13/2} + {}^4F_{7/2}$ and $^4G_{11/2}$ excited states.The emission spectrum exhibited three emission bands corresponding to the $^4F_{9/2} \rightarrow {}^6H_{15/2}$ (483 nm; blue), $^4F_{9/2} \rightarrow {}^6H_{13/2}$ (575 nm; yellow) and $^4F_{9/2} \rightarrow {}^6H_{11/2}$ (664 nm; red) transitions.

Keywords: Structural, photoluminescence, dysprosium, glass

Introduction

Over the last several years, considerable attention has been paid to rare earth doped solid state materials due to their potential applications such as color displays, illumination and optoelectronic devices (Yang, 2013 and Nishiura, 2011). The electronic energy levels of rare earth ions determine the lasing characteristics of rare earth doped materials and are influenced by the host matrix (Murugesn, 2007). Among all the classical

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network formers, boric oxide (B_2O_3) is one of the significant glass former and flux material (Becker, 1998). Recently, glasses based on heavy metal oxides such as Bi_2O_3, PbO and Ga_2O_3 have wide applications in the field of glass ceramics, layers for optical and electronic devices (Hall, 1989 and Stehle, 1998). It is well known that the Bi_2O_3 is not a classical glass network former. However, glasses based on Bi_2O_3 show interesting physical properties such as high density, high linear and non-linear refractive index enabling their extensive applications in optical and optoelectronics (Culca, 2009 and Agarwal, 2003). In addition, Bi_2O_3 borate improves the chemical durability, thermal stability and reduces the phonon energy of the glasses. Among trivalent lanthanides, Dy^{3+} ion have been successfully incorporated into several glasses and crystals in order to obtain two primary colors yellow and blue luminescence materials (Ryba-Romanowski, 2009 and Murthy, 2010). The luminescence spectrum of Dy^{3+} doped glasses consists of two intense bands, corresponding to the blue ($^4F_{9/2}\rightarrow{}^6H_{15/2}$) and yellow ($^4F_{9/2}\rightarrow{}^6H_{13/2}$) regions. Intensity ratio (yellow/blue) can be modulated by varying the glass host, its chemical composition and activator (Dy^{3+}) concentration. Dysprosium doped glasses and crystals emit intense discrete radiation in the yellow (570–600 nm) and NIR (1.35 and 3.0 μm) regions that have potential applications in commercial displays and tele-communications (Karunakaran, 2010 and Suresh Kumar, 2010). In this investigation, we present the study of the structural properties, excitation spectrum and emission spectrum of Dy^{3+} ion doped zinc bismuth borate glass (ZBB).

Meterial and Methods

ZBB glasses of chemical composition (in mol%) $59B_2O_3$:$30Bi_2O_3$:10ZnO: $1Dy_2O_3$ were prepared by normal melt quenching method. All glass samples with the weight of 20 g batch compositions of homogeneous powders were melted at 1100 °C in alumina crucibles for about 3 h in an electrical furnace. The melts were air quenched by pouring it onto a preheated stainless steel mould and annealed at 500°C for 3 h to remove thermal strains associated with the quenching process and to increase the mechanical strength of the prepared glass. The polished glass samples were cut into $1.0\times1.5\times0.3$ cm^3 shape for structural and photoluminescence 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 angles was set from 10° to 80° with a step rate of 5°/min. Infrared spectra of the glass samples were recorded at room temperature in the range 650-2500 cm^{-1} using anAgilent-Cary-630 FT-IR spectrometer. The excitation spectrum and emission spectrum measurements were carried out using Cary Eclipse Fluorescence Spectrophotometer with 388 nm excitation wavelength of xenon flash lamp.

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 ZBB glass is shown in Figure 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.

The Fourier Transform Infrared Spectrum

The Fourier transform infrared spectrum of $59B_2O_3$: $30Bi_2O_3$: 10ZnO: $1Dy_2O_3$ glass compositions recorded at room temperature in the spectrum range 650–2500 cm^{-1} is shown in Figure 2. The peak observed in the band around 691 cm^{-1} in all the glass samples may be assigned to the bending vibrations of B-O-B linkage in borate network (Doweidar, 2009 and Pascuta, 2009). The transmission band around 708 cm^{-1} attributed to the symmetric stretching vibrations of Bi-O bonds in BiO_3 pyramidal units which can be assumed

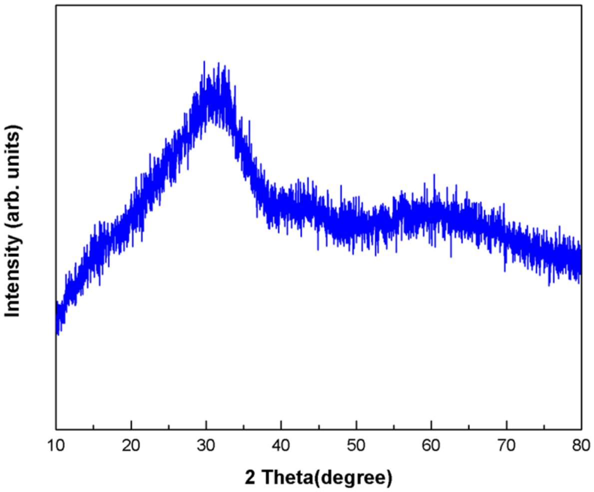

Figure 1. XRD pattern of59B_2O_3:30Bi_2O_3:10ZnO: 1Dy_2O_3: ZBB glass

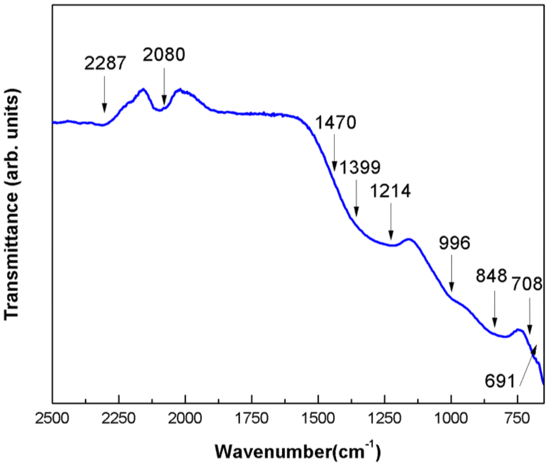

Figure 2. FTIR transmission spectrum of 59B_2O_3:30Bi_2O_3:10ZnO: 1Dy_2O_3:ZBB glass

to be superposed with the O_3B-O-BO_3 bending vibrations (Ardelean, 2008 and Kaur, 2013). The shoulder around 848 cm^{-1} is related to the symmetrical stretching vibration of Bi-O in [BiO_3] group (Saritha, 2008). The band around 996 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 (Ito, 1983). In this broad region the component peaks observed in the band 1214cm^{-1} may be attributed to the B-O stretching vibrations of trigonal BO_3 units in boroxol rings (Mansour, 2012 and Pascuta, 2008) while the peaks in the band 1399 cm^{-1} may be assigned to the B-O stretching vibrations of trigonal BO_3 units in metaborate, pyroborate and orthoborate groups (Shaaban, 2008 and Kundu, 2014). The peaks found in the band 1470cm^{-1} have been ascribed to the

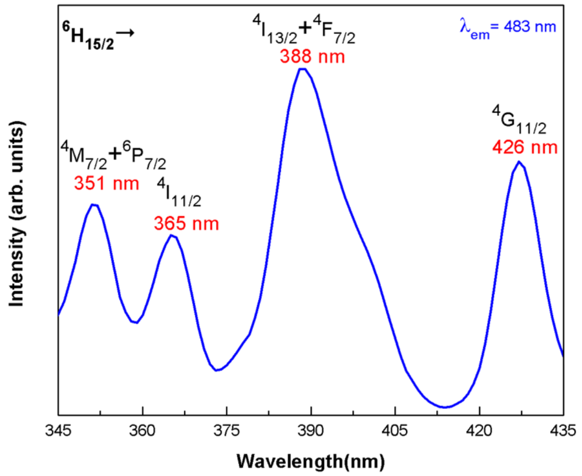

Figure 3. Excitation spectrum of $59B_2O_3$:$30Bi_2O_3$:10ZnO: $1Dy_2O_3$:ZBB glass

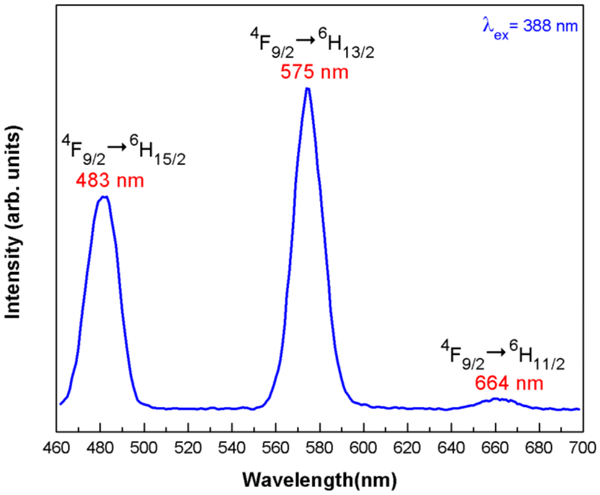

Figure 4. Emission spectrum of $59B_2O_3$:$30Bi_2O_3$:10ZnO: $1Dy_2O_3$:ZBB glass

asymmetric stretching vibrations with three non-bridging oxygens (NBO's) of B-O-B groups (Shaaban, 2008 and Kundu, 2014).The bands observed in the region 2080-2287 cm^{-1} in all the glass samples are attributed to the hydroxyl or OH group (Scholzelt, 1991). In the IR spectra of the present glass system, it was found that the incorporation of ZnO did not show much effect on the structure of the glasses under study. The addition of ZnO into the present glass system produces a very small change in the IR bands that does not account for the major structural changes. However, in many glass systems in which ZnO is a major constituent the possibility of ZnO_4 formation may be higher (Motke, 2012). S. Bale et al. (Bale, 2008) had reported the formation of ZnO_4 units with the increase of zinc oxide content.

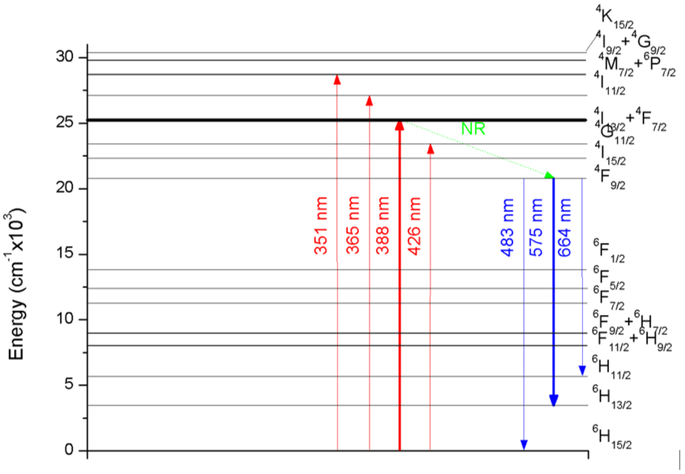

Figure 5. The diagram of partial energy levels of Dy^{3+}: ZBB glass

Luminescence Properties

Excitation Spectra

Photoluminescence excitation spectrum for 1 mol% Dy^{3+} doped ZBB glass in the range 345–435 nm (by monitoring the yellow transition, $^4F_{9/2} \rightarrow {}^6H_{13/2}$) is shown in Figure 4. The registered four bands are related to transitions from the $^6H_{15/2}$ ground state to the $^4M_{7/2}$ + $^6P_{7/2,}$ $^4I_{11/2}$, $^4I_{13/2}$ + $^4F_{7/2}$ and $^4G_{11/2}$ excited states. The spectrum consists of several excitation bands which are ascribed to different transitions from ground state ($^6H_{15/2}$) to various excited states of Dy^{3+} ion. The excitation maximum located at 388 nm corresponds to the transition from the ground $^6H_{15/2}$ to $^4I_{13/2}$ + $^4F_{7/2}$ level.

Emission Spectra

Photoluminescence emission spectrum of Dy^{3+} ion ZBB glass was registered under excitation by 388 nm line. Three characteristic emission bands corresponding to $^4F_{9/2} \rightarrow ^6 H_{J/2}$ (where J=15, 13, 11) transition of Dy^{3+} are observed (Figure 4). The main luminescence bands are located at 483 nm (blue) and 575 nm (yellow). Among these two transitions, the $^4F_{9/2} \rightarrow {}^6H_{15/2}$ is magnetic dipole transition, while $^4F_{9/2} \rightarrow ^6 H_{13/2}$ is electric dipole transition and is strongly influenced by the environment of dysprosium ion. The ratio of integrated emission intensity of the $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition to the $^4F_{9/2} \rightarrow {}^6H1_{15/2}$ transition, defined as yellow-to-blue luminescence intensity ratio Y/B, was determined. The value of Y/B is equal to 1.51 and indicates high degree of covalence between Dy^{3+} and O^{2-}.

Figure 5 shows the partial energy level diagram of Dy^{3+} ions in the ZBB glass along with emission and non-radiative (NR) channels. When the Dy^{3+} ions are excited to any level above the $^4F_{9/2}$, there is a fast non-radiative relaxation to $^4F_{9/2}$ level and the emission takes place from $^4F_{9/2}$ level to lower levels, ^6H_J.

Conclusions

The Dy^{3+} doped zinc bismuth borate glasses have been prepared and their structural and photoluminescence properties were studied for the development of white LEDs and laser applications.The amorphous nature studied zinc bismuth borate glass system was confirmed by X-ray diffraction data. The presence of various structural units such as BiO_3, BO_3 and BO_4 was identified through FTIR spectrum analysis. The excitation spectrum registered four bands are related to transitions from the $^6H_{15/2}$ ground state to the

Table 1. FTIR analysis of $59B_2O_3$:$30Bi_2O_3$:10ZnO: $1Dy_2O_3$:ZBB glass

Wavenumber (cm^{-1})	Assignment
691	The bending vibrations of B-O-B linkage in borate network
708-848	Symmetric stretching vibrations of Bi-O bonds in BiO_3 pyramidal units B-O B-
996	O bond stretching of the tetrahedral BO_4 units
1214	The B-O stretching vibrations of trigonal BO_3 units in boroxol rings
1399	The B-O stretching vibrations of trigonal BO_3 units in metaborate, pyroborate and orthoborate groups
1470	Asymmetric stretching vibrations with three non-bridging oxygens (NBO's) of B-O-B groups
2080-2287	OH group

$^4M_{7/2}$ + $^6P_{7/2}$, $^4I_{11/2}$, $^4I_{13/2}$ + $^4F_{7/2}$ and $^4G_{11/2}$ excited states. The emission spectrum exhibited three emission bands corresponding to the $^4F_{9/2} \rightarrow {}^6H_{15/2}$ (483 nm; blue), $^4F_{9/2} \rightarrow {}^6H_{13/2}$ (575 nm; yellow) and $^4F_{9/2} \rightarrow {}^6H_{11/2}$ (664 nm; red) transitions.

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