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Structural and Spectral Analysis Host Bi_2O_3-B_2O_3-LiF and RE^{3+}(Ho^{3+} or Pr^{3+}): Bi_2O_3-B_2O_3-LiF Glasses

Karuturi Srinivasa Rao*, Chandragiri Parthasarathi Reddy and Srinivasa Buddhudu

*Department of Physics, Vundavilli Satynarayana Murthy College, Ramachandrapuram-533255, A.P

Department of Physics, Sri Venkateswara University, Tirupati-517502, A.P

Abstract

Bismuth borate glasses in the composition of $20Bi_2O_3$-$50B_2O_3$-30LiF (BiBLF) have been prepared by using conventional melt quenching method. Thermal analysis (Tg-DTA) structural (XRD, FTIR and Raman), SEM micro graph and elemental (EDAX) analysis have been carried to the host glass matrix. TG-DTA profiles exhibit weight loss and glass transition temperature (Tg) at 125°C and also the glass melting temperature (Tm) at 570°C. XRD profile confirms the amorphous nature while the bands in FTIR and Raman spectra are assigned appropriately to their corresponding vibrations. Elemental analysis confirms presence of the host elements with regard to SEM micrograph shows no grains confirming amorphous nature. Absorption spectrum of Pr^{3+}or Ho^{3+}: BiBLF glasses have revealed a group of absorption bands assigned to their related transitions originating from $^3H_4$ and $^5I_8$ground state. The emission spectrum of Pr^{3+}: BiBLF glass has revealed three emission bands at 532 nm ($^3P_1 \rightarrow {}^3H_5$), 617 nm ($^1D_2 \rightarrow {}^3H_4$) and 647 nm ($^3P_0 \rightarrow {}^3F_2$) upon excitation at 470 nm. The florescence spectrum of Ho^{3+}: BiBLF glass excited at 454 nm has displayed two emission bands at 547 nm ($^5S_2$, $^5F_4 \rightarrow {}^5I_8$) and 660 nm ($^5F_5 \rightarrow {}^5I_8$) .

Keywords: Pr^{3+}doped glasses, melt quenching technique and spectral properties

Introduction

Bismuth borate based glasses have potential applications in optoelectronic circuits as ultra fast switches, IR windows, optical isolators. The non conventional glass forming Bi_2O_3, participates in the glass structure with two possible coordinates (BiO_3) pyramidal and (BiO_6) octahedral units. Further bismuth ion, has been found to be an efficient luminescent activator in applications in lasers as sensitizer for some rare earth ions [1-3]. Glasses with low phonon energies than that of silica offer the possibility of developing more efficient lasers and fiber optic amplifiers at wavelength not accessible with Silica. The reduced phonon energy increases the quantum efficiency of the luminescence from excited states of rare-earth (RE) ions and the up conversion efficiency. Trivalent Praseodymium is an attractive optical activator which offers the possibility of simultaneous blue, green and red emission for laser action as well as infrared emission. The Pr^{3+} systems are also interesting as short-wavelength up conversion laser materials [4-6]. Apart from Praseodymium, the Holmium ion has also been chosen to dope in the host glass as it has several high lying metastable levels which can give rise to short wave length transitions and also exhibits green emission at 550 nm can be excited using the frequency up conversion processes [7-10]. The present paper reports our results regarding the thermal behavior, structure and elemental analysis of the undoped BiBLF glass obtained by TG-DTA measurement, XRD, FTIR, Raman, SEM and EDAX profiles. This paper also reports on the optical, spectral analysis and dielectric properties of Pr^{3+} and Ho^{3+} ions separately doped BiBLF glasses by obtaining their absorption and emission spectra.

Experimetal method and techniques

The transparent and stable host glass in the composition of $20Bi_2O_3$-$50B_2O_3$-30LiF (BiBLF) and rare earth ion doped glasses in the compositions of $20Bi_2O_3$-$49B_2O_3$-30LiF:1mol% Pr_6O_{11} and $20Bi_2O_3$-$49B_2O_3$-30LiF:1mol% Ho_2O_3 were prepared using melt quenching method. Spectral pure chemicals of Bi_2O_3, H_3BO_3, LiF, Pr_6O_{11} and Ho_2O_3 were weighed appropriately based on their chemical compositions and transformed into agate mortar for thoroughly

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mixing them with a pestle, and each of these mixed chemicals was transformed into a porcelain crucible and was melt them in an electrical furnace at a 970° C for 1 hr for each batch. The chemicals melts were quenched in between two smooth surfaced brass plates for obtaining transparent and air bubble free clear glasses. The TG-DTA simultaneous measure was carried out for the as-prepared sample on a Net. Zsch STA 409 for understanding the thermal properties with N2 gas atmosphere at heating rate of 10°/min. The prepared host glass BiBLF glass was characterized by XRD system namely 3003 TT SEIFERT X-ray diffraction with CuK_α line (λ=1.5406 Å) to understand their structures. The FTIR spectrum of the host BiBLF in the 300 – 4000 cm^{-1} spectral range was obtained with a Thermo Nicolate 5700 Spectrometer using KBr pellet technique. The Raman spectrum for the host BiBLF glass was measured on a high resolution Horiba Jobin Yvon model HR 800 Labran system that was attached with a He-Ne (633 nm) laser as excitation source, with an output power of 15 mW having a laser beam spot size in 100 µm from an appropriate lense system. The elemental analysis of the host glass was carried out by an Energy Dispersive X-ray Analysis (EDAX) using an X-ray detector attached to the SEM instrument. The absorption spectra of host BiBLF and Pr^{3+} doped BiBLF glasses are measured on Varian-Cary-Win Spectrometer (JASCO V – 570). The emission spectrum of Pr^{3+} doped BiBLF glasses are were recorded on a JOBIN YVON Fl3-21 Spectrofluorometer equipped with a 450W Xenon arc lamp at room temperature.

Results and discussion

The thermal behavior of the host BiBLF glass is shown in Fig. 1. As shown in TG graph, the weight loss of 10% up to 125°C temperature is due to the loss of OH and compositions of hydroxide. The weight loss up to the temperature 175 °C is due to the loss of water and evaporation of organic species in the reaction mixture and next weight loss is observed around 550°C and beyond this no appreciable weight loss in the precursor chemical mix is noticed. The endothermic peak in DTA curve located at temperature 125°C indicates the glass transition temperature while exothermic peaks appearing at 150 °C and 175 °C are due to the evaporation of water and also the residual solvents that correspond to the weight loss TG curve. The peak at 575°C in DTA curve is attributed to the crystallization temperature (Tc).

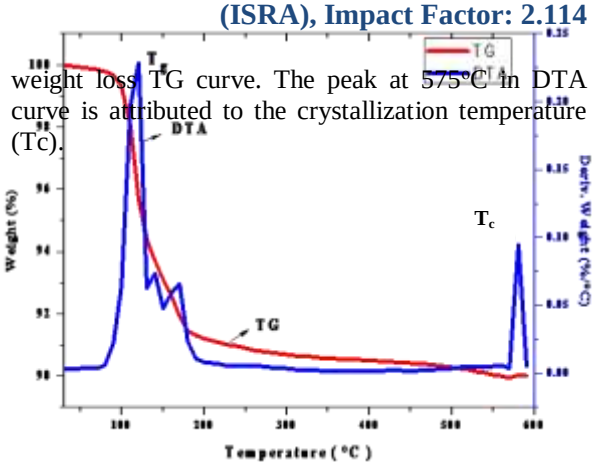

Figure. 1 : *TG-DTA profiles of host Bi_2O_3-B_2O_3-LiF precursor chemical mix*

Fig. 2 presents the XRD profile shows a broad band confirming the amorphous nature of host BiBLF glass.

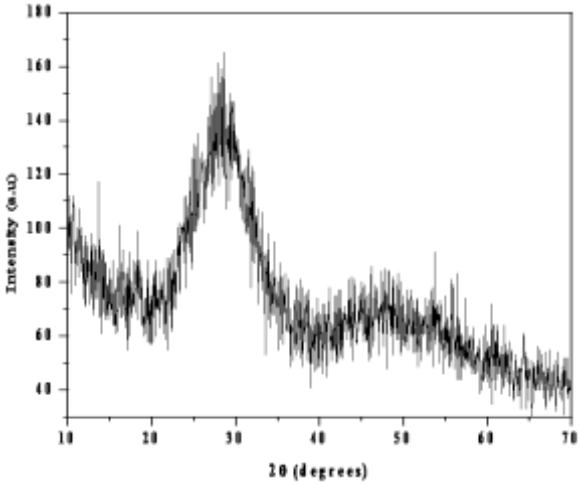

Figure. 2 : *XRD profile of host Bi_2O_3-B_2O_3-LiF glass*

FTIR spectrum of the host BiBLF glass is shown in Fig.3 revealing eight bands which are assigned to the corresponding stretching modes following the available reports from the literature on the FTIR spectra [11-16]. The bands located at 352 $cm^{-1}$and 460 cm^{-1} are assigned to Bi-O vibrations. The band at 702 cm^{-1} is attributed to the bending vibrations of B-O-B linkages of BO_3 units where as the band at 1014 cm^{-1} is assigned to V_1 mode of BO_4 tetrahedral units.

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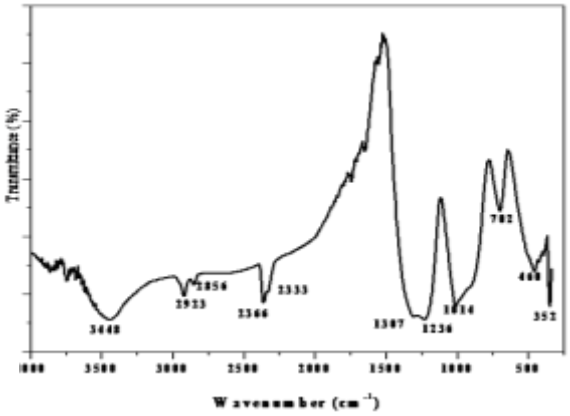

Figure. 3 : ***FTIR spectrum of host Bi_2O_3-B_2O_3-LiF glass***

The band at 1236 cm^{-1} is assigned to B-O stretching vibrations, the band at 1307 cm^{-1} is assigned to V_3 mode of planar BO_3 group, the band at 2366 cm^{-1}, 2856 cm^{-1}, 2923 cm^{-1} are assigned to Hydrogen bonding and the band at 3448 cm^{-1} is attributed to O-H stretching vibration.

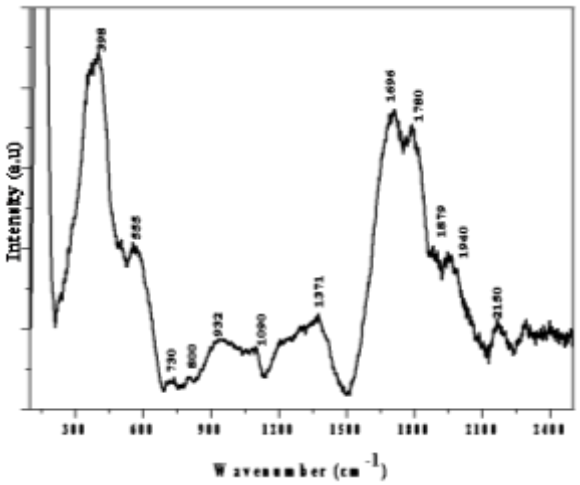

Figure. 4 : ***Raman spectrum of host Bi_2O_3-B_2O_3-LiF glass***

The Raman spectrum of the host BiBLF glass is presented in Fig. 4 which reveals bands at 398 cm^{-1}, 555 cm^{-1}, 730 cm^{-1}, 800 cm^{-1}, 932 cm^{-1}, 1090 cm^{-1},1371 cm^{-1}, 1696 cm^{-1}, 1780 cm^{-1}, 1879 cm^{-1}, 1940 cm^{-1} and 2150 cm^{-1}. The band at 398 cm^{-1} is assigned to Bi-O-Bi stretching vibration in the distorted BiO_6 octahedral units [18]. The band at 555 cm^{-1} is attributed to both vibration of Bi-O-Bi in distorted BiO_6 polyhedra and vibrations of ring type metaborate groups [17-21]. The band at 730 cm^{-1} is characteristic to the vibrations of chain type meta-borate groups [19-23]. The band centered at 800 cm^{-1} is assigned to the vibrations of pyro-borate groups [17-21]. The band centered at 932 cm^{-1} is assigned to vibrations of ortho-borate groups [18-21]. The bands centered at 1370 cm^{-1} and 1696 cm^{-1} are assigned to B-O stretching vibrations in various borate groups [17, 24, 25].

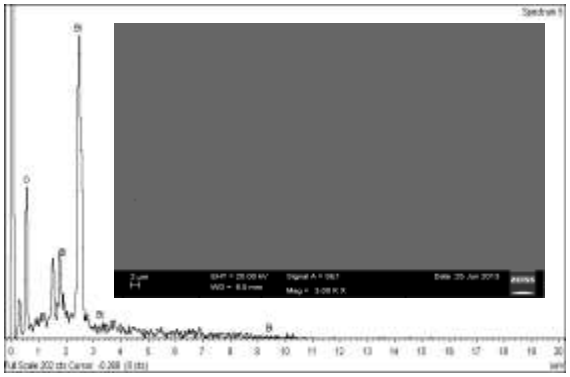

Figure. 5 : ***EDAX profile of host Bi_2O_3-B_2O_3-LiF glass (inset fig : SEM micrograph)***

Fig. 5 presents the EDAX profile which confirms the presence of elements in the prepared host glass and smooth surface of SEM micrograph inserted in Fig. 5 exhibits no structural changes like presence of gains supporting the amorphous nature of host BiBLF glass.

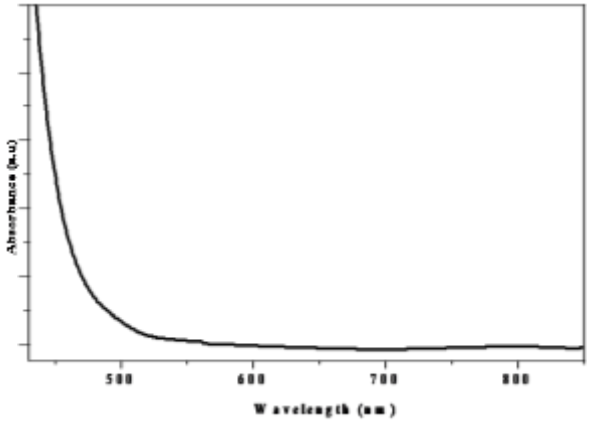

Figure. 6 : Absorption spectrum of host Bi_2O_3-B_2O_3-LiF glass

In Fig. 6, room temperature absorption spectrum of the host BiBLF glass was obtained in the wavelength range 400 nm – 800 nm and it shows the babnd edge lies at 425 nm due to the presence of non-bridging oxygens with addition of Bi_2O_3.

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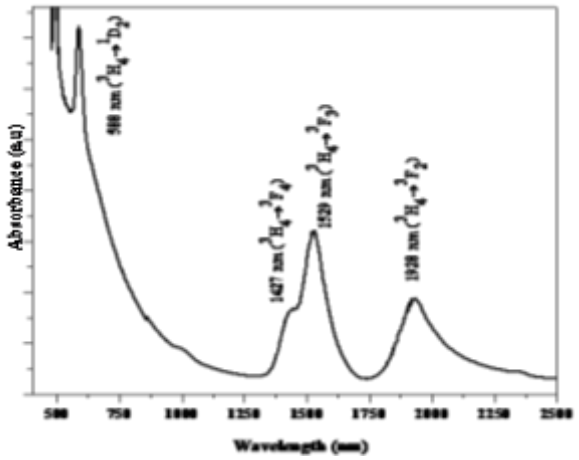

Figure. 7 : Absorption spectrum of Pr^{3+}: Bi_2O_3-B_2O_3-LiF glass

The absorption spectrum of Pr^{3+}: BiBLF glass was recorded in the range 1200 nm – 2500 nm and is shown

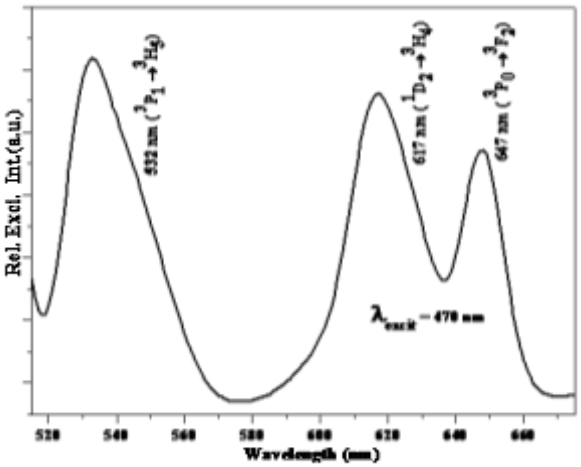

Figure. 8 : Excitation spectrum of Pr^{3+}: Bi_2O_3-B_2O_3-LiF glass

Fig. 7. It consists of several bands corresponding to the transmission between $^3H_4$ ground state and the excited multiplets belonging to the $4f^2$ configurations of Pr^{3+} ions. The bands in the absorption spectrum located at 588 nm, 1427 nm, 1529 nm and 1929 nm correspond to transitions of ($^3H_4 \rightarrow {}^1D_2$), ($^3H_4 \rightarrow {}^3F_4$), ($^3H_4 \rightarrow {}^3F_3$), and ($^3H_4 \rightarrow {}^3F_2$) respectively [26-29]. The excitation spectrum of Pr^{3+}: BiBLF with the emission at 617 nm wavelength is shown in Fig. 8. The bands in the excitation spectrum Pr^{3+}: BiBLF are located at 448 nm, 470 nm and 485 nm which correspond to transitions ($^3H_4 \rightarrow {}^3P_2$), ($^3H_4 \rightarrow {}^3P_1$) and ($^3H_4 \rightarrow {}^3P_0$) respectively [30]. After excitation at $^3P_1$ level (470 nm) there is emission from $^3P_0$, $^1D_2$ and $^3P_1$ levels at room temperature.

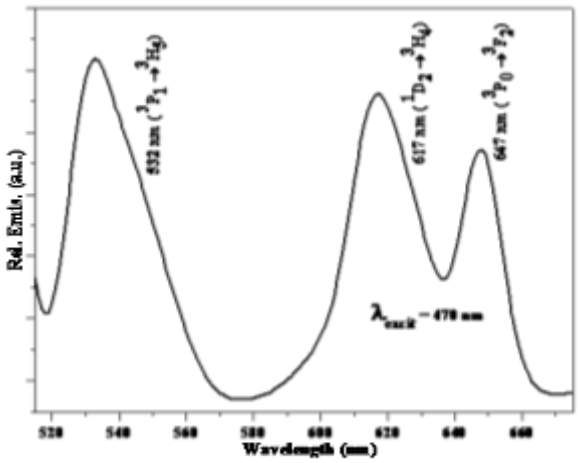

Figure. 9 : Emission spectrum of Pr^{3+}: Bi_2O_3-B_2O_3-LiF glass

Fig. 9 represents the emission spectrum of Pr^{3+}: BiBLF has revealed 3 bands at 532 nm ($^3P_1 \rightarrow {}^3H_5$), 617 nm ($^1D_2 \rightarrow {}^3H_4$) and 647 nm ($^3P_0 \rightarrow {}^3F_2$) [31-35].

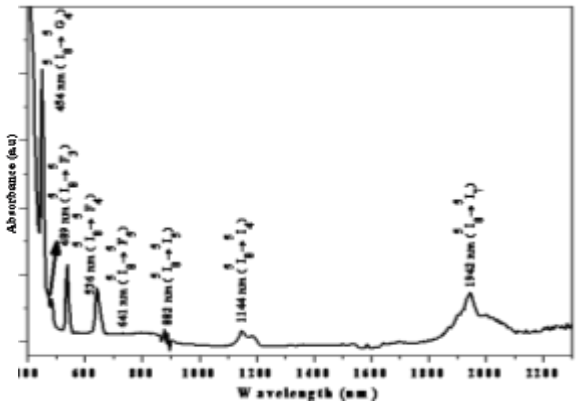

Figure. 10 : Absorption spectrum of Ho^{3+}: Bi_2O_3-B_2O_3-LiF glass

Fig. 10 shows the absorption spectrum of Ho^{3+}: BiBLF glass has revealing seven absorption bands at 454 nm, 489 nm, 536 nm, 641 nm, 882 nm, 1144 nm and 1942 nm and that are labeled to the transitions of ($^5I_8 \rightarrow {}^5G_6$), ($^5I_8 \rightarrow {}^5F_3$), ($^5I_8 \rightarrow {}^5F_4$), ($^5I_8 \rightarrow {}^5F_5$), ($^5I_8 \rightarrow {}^5I_5$), ($^5I_8 \rightarrow {}^5I_4$) and ($^5I_8 \rightarrow {}^5I_7$) respectively [36].

The florescence spectrum of the glass containing 1 mol % Ho^{3+} (Ho^{3+}: BiBLF) at room temperature excited at 454 nm has displayed two

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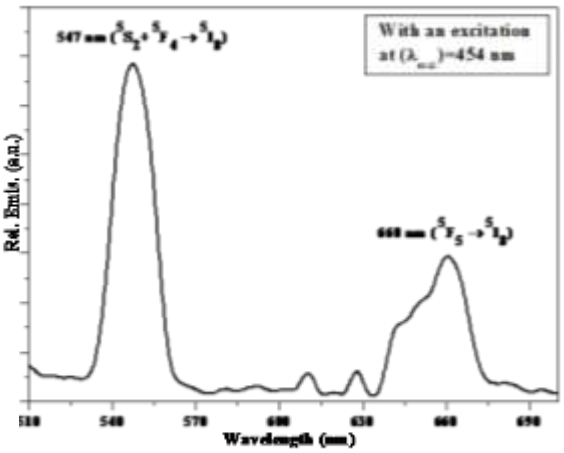

Figure. 11 : Emission spectrum of Ho^{3+}: Bi_2O_3-B_2O_3-LiF glass

emission bands at 547 nm ($^5S_2$, $^5F_4 \rightarrow {}^5I_8$) in the green-yellow region and 660 nm ($^5F_5 \rightarrow {}^5I_8$) in the red region, among which the 547 nm ($^5S_2$, $^5F_4 \rightarrow {}^5I_8$) is the intense peak in green-yellow region as it is shown in Fig. 11 [37-40].

Conclusion

It is summarized that the thermal and structural properties for the host Bi_2O_3-B_2O_3-LiF glass have been studied based on the results obtained from TG-DTA, XRD, FTIR, Raman, SEM and elemental analysis. Absorption spectra of host Bi_2O_3-B_2O_3-LiF, Pr^{3+}:Bi_2O_3-B_2O_3-LiF and Ho^{3+}:Bi_2O_3-B_2O_3-LiF glasses have also been carried out. The emission spectra of these Pr^{3+} or Ho^{3+} glass has been measured and their spectra have appropriately been assigned to the electronic transitions. Based on the results, such optical glasses could be suggested as potential novel materials of scientific and technological importance.

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