The Effects of Bi$_2$O$_3$ on Optical, FTIR and Thermal Properties of SrO-B$_2$O$_3$ Glasses

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Abstract Combined optical and FTIR were measured for binary bismuth borate glass together with samples containing 2.5 – 15 mol % Bi$_2$O$_3$ glasses to justify the role of bismuth (Bi$^{3+}$) ions on the spectral properties. The density and molar volume values were calculated to obtain some insight on the compactness and structural arrangement in the network. DTA measurements were carried out to calculate the thermal transition parameters of the studied glasses and to justify their stability. Optical spectra reveal three strong UV-near visible absorption bands at 250, 275 and 310 nm due to collective absorption of trace iron (Fe$^{3+}$) impurities together with absorption from Bi$^{3+}$ ions at 360 nm. The absorption edges reveal an obvious increase with the Bi$_2$O$_3$ content. FTIR spectra reveal vibrational bands characteristic for triangular borate groups at 1200-1600 cm$^{-1}$, tetrahedral borate groups at 800 – 1200 cm$^{-1}$ together with interference of Bi-O vibrations upon the introduction of Bi$_2$O$_3$. The observed bands at about 429, 465, and 595 cm$^{-1}$ are related to BiO$_6$ and the band at 879 cm$^{-1}$ is related to Bi$_3$O$_3$ in the host sample 15 % Bi$_2$O$_3$. Thermal properties are found to depend on the Bi$_2$O$_3$ content depending on the specific role of the formed groups (BiO$_6$, BO$_3$) and their function as modifier or former together with the formation of nonbridging oxygens.

Keywords Strontium borate glass · Bi$_2$O$_3$ Optical and FTIR spectra · Differential thermal analysis

1 Introduction

Borate glasses are promising vitreous materials due to their numerous technological applications. B$_2$O$_3$ is one of the commonest glass network formers. The structure of vitreous boric oxide is assumed to consist of major boroxol rings and few BO$_3$ triangles connected by B-O-B linkages [1]. SrO is known as a modifier oxide which like alkali oxides transforms some of the trigonal borons to tetrahedral coordination and the strontium cations occupy interstitial positions in the glass network [2]. After a certain limit, the formation of BO$_4$ groups ceases and SrO begins to form non-bridging oxygens.

Bismuth – containing glasses have a variety of applications in the field of glass ceramics, layers for optical and electronic devices, thermal and mechanical sensors, reflecting windows [3], and are ideal candidates for optical transmission due to their long infrared cutoff [4]. Furthermore, bismuth glasses have been considered as a promising candidate for protection from gamma rays irradiation [5, 6].

Bismuth oxide cannot be classified as a classical glass network former as a result of its small field strength and the high polarizability of Bi$^{3+}$ ions. However, if Bi$_2$O$_3$ is combined with a high content (40 mol% or more) of any conventional glass network former such as B$_2$O$_3$, SiO$_2$, P$_2$O$_5$, it forms stable glasses which can build a glass network of [BiO$_3$] pyramidal units and/or [BiO$_6$] octahedral units [7–11].

Moreover, it has been reported that the addition of a heavy metal oxide [such as Bi$_2$O$_3$ or PbO] to B$_2$O$_3$, shares in the progressive change of some of the boron atoms coordination from 3 to 4, and the in formation of various borate units like diborate, triborate, or tetraborate groups [12]. After a certain limit of BO$_4$ formation, nonbridging oxygens begin to be formed.
The present work aims to investigate and characterize some optical, FTIR and thermal properties of binary SrO-B₂O₃ glass together with samples of the same base composition containing different percents of Bi₂O₃ in order to understand and justify the role of Bi³⁺ ions in such host strontium borate glasses for their possible use in optical applications.

2 Experimental Techniques

\( x \text{Bi}_2\text{O}_3 - (45-x) \text{SrO} - 55\text{B}_2\text{O}_3 \) glasses with \( x = 0, 2.5, 5, 7.5, 10, \) and 15 mol\% (labeled as base, BiB1, BiB2, BiB3, BiB4 and BiB5, respectively) were prepared by a conventional melt annealing method. All chemicals were obtained from Laboratory Rasayan (LR, India). Appropriate amounts of boric acid powder 99\%, strontium carbonate 99\%, and bismuth oxide 99\% were mixed in an agate mortar before transferring to platinum crucibles. The mixtures were melted in an electrical furnace at 1200 °C for 90 minutes. The platinum crucibles were occasionally rotated several times to achieve acceptable homogeneity. The molten material was cast into preheated stainless steel molds and the glassy samples were transferred immediately to a muffle furnace regulated at 400 °C for 1 hour. Then the muffle was switched off with the glasses inside to cool gradually to room temperature at a rate of 30 °C/hour.

The X-ray diffraction patterns of powdered glass samples were obtained by using a diffractometer type Philips, PW1390 with Cu–Kα radiation operating at 30 kV and 10 mA. The diffraction data were recorded for 2\( \theta \) values between 4° and 70° and the scanning rate was 2°/min. All the samples were found to be amorphous.

The Fourier transform infrared (FTIR) absorption spectra of the studied glasses were measured at room temperature in the wavenumber range 4000-400 cm\(^{-1}\) by a Fourier transform computerized infrared spectrometer type Nicolet iS10, USA using the KBr disc technique. The prepared glasses were examined as pulverized powders which were mixed with KBr with the ratio 1:100 mg glass powder to KBr, respectively. The weighed mixtures were then subjected to a pressure of 5 tons/cm\(^2\) to produce clear homogeneous discs. The IR measurements were immediately carried out after preparing the discs.

All spectra were fitted and carefully deconvoluted using a computer based program [Peak Fit Program (Jandel Scientific Peak Fit, copyright© 1990 AISN Software)] which defines a hidden peak as one which is not responsible for a local maximum in the data stream.

IR spectra were corrected for the dark current noises and background using two point base line corrections. Many successive trials were carried out using different band shapes until the best fitted data were obtained using spectral Gaussian peaks. The position, full width at half maximum (FWHM), area and intensity of each band were adjusted automatically by the program. In disordered systems, a distribution of individual geometries exists, which results in a distribution of vibrational wavenumbers. Also, a vibrational coupling with some degree of coherence between vibrating units is expected, which affects the observed band shape [13, 14].

A conventional Archimedes method was used to determine the glass densities by weighing the bulk samples in both air and liquid xylene of high purity (\( \rho = 0.863 \text{g/cm}^3 \)). The density was obtained from the relation:

\[
\rho = \frac{a}{(a - b)} \times 0.863
\]

where \( a \) is the weight of the glass sample in air, and \( b \) is the weight of the glass sample when immersed in liquid xylene. Three samples for each composition were measured and the density values were found to vary by \( \pm 0.01 \text{gm} / \text{cm}^3 \).

Differential thermal analysis (DTA) analysis measurement was carried out using a micro differential thermal analyzer DTA, Shimadzu DTG-60H (Japan) with a heating rate of 10 °C/min from room temperature up to 1000 °C. 20 mg of powdered specimens were tested in a platinum crucible with Al₂O₃ as a reference material. The accuracy of the results is ±5°C.

UV-visible absorption spectra of studied glasses were measured for polished samples of equal thickness (2 ± 0.1 mm) by a double beam spectrophotometer, type JASCO, Corp., V-570, Rel-00, Japan, in the range from 200–800 nm with air as a reference. The samples were measured twice to check the accuracy of the absorption peaks. The optical band gap and the Urbach energy were calculated from the experimental absorbance data.

3 Results and Discussion

3.1 Optical Properties

Figure 1 shows the optical absorption spectra of the studied glasses. The optical spectrum of the base strontium borate glass reveals strong UV absorption with three peaks at 250, 275 and 310 nm. On introducing 2.5 to 15 mol\% Bi₂O₃ replacing SrO within the glass, a further additional UV band is observed at 360 nm.

Several glass scientists [15–17] have agreed that trace impurities (e.g. Fe³⁺, Cr⁶⁺ ions) exhibit charge transfer ultraviolet absorption in various glasses due to an electron transfer mechanism. Also, they note that this strong UV absorption is observed even if the trace impurities are within the ppm level.