FTIR and ultrasonic investigations on modified bismuth borate glasses

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ABSTRACT

Studies on xRO $\cdot$ 30Bi$_2$O$_3$ $\cdot$ (70−x)B$_2$O$_3$ glasses have been carried out ($0 \leqslant x \leqslant 30$ mol%, R = Zn, Ba). Elastic properties and Debye temperature have been investigated using sound velocity measurements at 4 MHz. The ultrasonic parameters along with the IR spectroscopic studies have been employed to explore the role of divalent cations in the structure of the studied glasses. Analysis of infrared spectra indicates that RO is preferentially incorporated into the borate network, forming BO$_4$ units. It is assumed that Bi$_2$O$_3$ enters the structure in the form of BiO$_6$ only. The change of density and molar volume with RO content reveals that BO$_4$ units linked to R^{2+} cations are denser than those linked to positive sites in the Bi$_2$O$_3$ network. Predicted values of four co-ordinated boron put forward questions about the reliability of assignment of structural units that Bi$_2$O$_3$ may form.

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1. Introduction

Boron atoms in borate crystals and glasses usually co-ordinate with either three or four oxygen atoms forming BO$_3$ or BO$_4$ structural units. These two fundamental units can arbitrarily be combined to form either 'super-structural' units or different B$_x$O$_y$ groups like boroxol rings, pentaborate, tetraborate and diborate groups, etc. The fraction of these structural units depends on the nature and concentration of the added modifiers [1–5].

In terms of the crystalline configuration, Bi$_2$O$_3$ is an oxide having a high valence cation of low field strength and high polarizability. So, its glassy phase cannot conventionally be compared with pure B$_2$O$_3$ glass. Bi$_2$O$_3$ like ZnO can occupy both network-forming and network modifying positions in the borate network glasses and, as a result, the physical properties of such glasses exhibit discontinuous changes when the structural role of the cation changes [6–12]. Recent IR, UV–Vis and thermal studies on bismuthate-based glasses revealed the presence of distorted BiO$_6$ polyhedra as the main structural units in such glasses [13–15].

On these bases, glasses containing Bi$_2$O$_3$ and ZnO have attracted a considerable attention due to their wide applications in the field of glass–ceramics, thermal and mechanical sensors, reflecting windows, or may be used as layers for optical and opto-electronic devices, etc. These glasses have a long infrared (IR) cut-off, and high third-order non-linear optical susceptibility which makes them ideal candidates for applications as infrared transmission components, ultra fast optical switches, and photonic devices [16–25].

The aim of the present work is to investigate the influence of divalent oxides such as ZnO, and BaO on the structure and properties of the thermally stable 0.3Bi$_2$O$_3$–0.7B$_2$O$_3$ [4] glasses by means of IR, density and ultrasonic techniques.

2. Experimental procedures

Glass samples of the formula xRO $\cdot$ 30Bi$_2$O$_3$ $\cdot$ (70−x)B$_2$O$_3$, $0 \leqslant x \leqslant 30$ mol%, (R = Zn or Ba), have been prepared by the melt quenching technique. Required quantities of Analar grade ZnO, BaO, Bi$_2$O$_3$, and H$_3$BO$_3$ were mixed together by grinding the mixture repeatedly to obtain a fine powder. The mixtures were melted in porcelain crucibles in an electrically heated furnace under ordinary atmospheric conditions at a temperature of about 1273 K for

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3 h to homogenize the melt. The glass formed by quenching the melt on a preheated stainless-steel mold was immediately transferred to another furnace where it was annealed at 623 K for 3 h. The obtained glasses were lapped and two opposite sides were polished to be suitable for the use in the ultrasonic velocity measurements. Non-parallelism of the two opposite side faces was less than 0.01 mm.

X-ray diffraction patterns were recorded to check the non-crystallinity of the glass samples using a Philips X-ray diffractometer PW/1710 with Ni-filtered, Cu Kα radiation (λ = 1.542 Å) powered at 40 kV and 30 mA. The patterns (not shown) revealed broad humps characteristic of the amorphous materials and did not reveal discrete or any sharp peaks.

KBr pellet technique was used to obtain the infrared spectra of the glasses, at room temperature. The spectra were recorded in the wavenumber range of 400–2000 cm^{-1} with a resolution of 4 cm^{-1} by an infrared spectrophotometer type JASCO, FT/IR – 430 (Japan). The infrared spectra were corrected for the dark current noises, and normalized to eliminate the concentration effect of the powder sample in the KBr disc. The obtained spectra were deconvoluted to enable shedding further light on the structural changes of BO$_3$ triangles and BO$_4$ tetrahedra, as they are the basic units in these glasses.

The density (D) of the glass samples was determined using Archimedes technique by using toluene as an immersion fluid. At least, three samples of each glass were used to determine the density. A random error in the density values was found as ±1%. The molar volume (V_m), and the mean atomic volume (V_a), have been determined as M/D, and V_m/n, respectively, where M is the molar weight of the glass and n is the number of atoms in the unit formula.

The ultrasonic velocities, longitudinal (v_L) and shear (v_T), at room temperature ($\sim$300 K) were obtained using the pulse-echo method. In this method, x-cut and y-cut transducers (KARL DEUTSCH), operated at a fundamental frequency 4 MHz, and a digital ultrasonic flaw detector (KARL DEUTSCH Echograph model 1085) were used. The uncertainty in the measurement of the ultrasonic velocity is ±10 m/s. The two velocities besides the density were utilized in determining two independent second-order elastic constants (SOECs), namely, the longitudinal (C_{11}) and shear (C_{44}) moduli. C_{11} and C_{44} describe the elastic strain produced by a small stress in isotropic amorphous solids like glasses. For pure longitudinal waves $C_{11} = D\, v_L^2$, and for pure transverse waves $C_{44} = D\, v_T^2$. The elastic bulk modulus (K_e), Young's modulus (Y), Debye temperature (θ_D) and the micro-hardness (H) can be determined from C_{11} and C_{44} [2]. The uncertainty in the elastic moduli is ±0.15 GPa.

3. Results

Figs. 1 and 2 show the effect of composition on the infrared spectra of the studied glasses. In general, there are three principle bands at around 700, 1000 and 1350 cm^{-1} with a shoulder at 1240 cm^{-1} for all glasses. Shoulders or weak bands appear around 445, 485, 520 and 565 cm^{-1}. In the spectra of xZnO $\cdot$ 30Bi$_2$O$_3$ $\cdot$ (70−x)B$_2$O$_3$ glasses (Fig. 2), the broad band around 1000 cm^{-1} seems to be convoluted of two bands around 900 and 1050 cm^{-1}. The spectra in Figs. 1 and 2 show mostly no change with composition in the center of the band around 1350 cm^{-1}. In the case of xBaO $\cdot$ 30Bi$_2$O$_3$ $\cdot$ (70−x)B$_2$O$_3$ glasses (Fig. 1), the center of the bands around 1000 cm^{-1} shifts to lower wavenumbers, as the BaO content increases. In addition to the above features a small absorption band appears in the spectra of all glasses around 3465 cm^{-1} (not shown in the figures). Such a band is attributed to stretching vibration of –OH ion [25]. The spectra do not show any appreciable change in the peak position and the intensity with the modifier oxide content or its type.
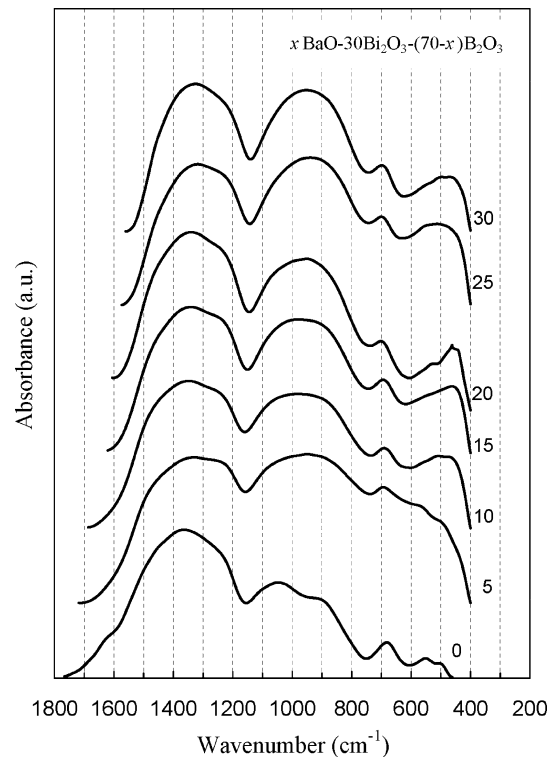

Fig. 1. Infrared spectra of the investigated xBaO $\cdot$ 30Bi$_2$O$_3$ $\cdot$ (70−x)B$_2$O$_3$ glasses. Numbers at the plots represent BaO content in mol%.
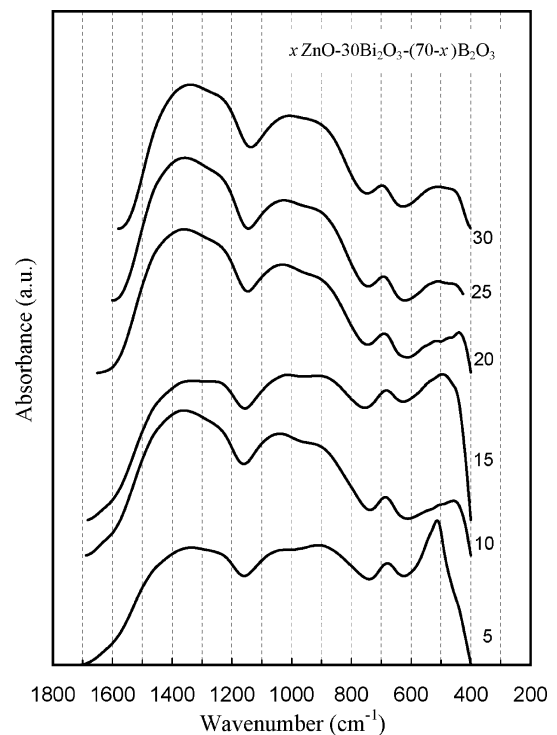
Fig. 2. Infrared spectra of the investigated xZnO $\cdot$ 30Bi$_2$O$_3$ $\cdot$ (70−x)B$_2$O$_3$ glasses. Numbers at the plots represent ZnO content in mol%.

Table 1 summarizes determined and derived data for the studied glasses. The data reveal a linear increase in D for both glass series. It is noticed that the density of BaO-containing glasses is higher than the corresponding glasses containing ZnO. Similarly, the