Journal of Non-Crystalline Solids 356 (2010) 2211–2217

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/locate/jnoncrysol

Vibrational spectral analysis of structural modifications of Cr_2O_3 containing oxyfluoroborate glasses

B.K. Sudhakar [a], N.R.K. Chand [a], H.N.L. Prasanna [a], G. Srinivasa Rao [a,*], K. Venkateswara Rao [b], Vivek Dhand [b]

[a] *Department of Physics, Andhra Loyola College, Vijayawada, AP, India*
[b] *Center for Nano Science and Technology, JNT University, Hyderabad, AP, India*

ARTICLE INFO

Article history:
Received 2 July 2010
Received in revised form 18 August 2010
Available online 20 September 2010

Keywords:
Borate glasses;
Density;
Oxygen packing density;
Infrared and Raman spectra

ABSTRACT

Infrared and Raman spectra of oxyfluoroborate glasses of the compositions $20CaF_2$–20 ZnO–(60-x) B_2O_3-x Cr_2O_3 with $0 \leq x \leq 0.10$ mol% (x = 0, 0.02, 0.04, 0.05, 0.06, 0.07, 0.08 and 0.1) have been analyzed in order to explain the role of Cr_2O_3 on the structure of these glasses. Density, molar volume, oxygen molar volume and oxygen packing density are determined to explain the packing of the atoms in the glasses. From these studies, the existence of different borate groups like di-, tri-, tetra-, penta-, ortho-, pyro- and metaborates in these glasses is established. With the increase in the concentration of Cr_2O_3 up to 0.06 mol%, conversion of BO_3 units into BO_4 units and above this mole fraction the reconversion of BO_4 units into BO_3 units is observed. The breaking and reforming of the boroxol ring is explained from the Raman spectral studies of these glasses.

1. Introduction

Glass due to its wide ranging properties has become a potential element in the recent scientific and technological applications [1–7]. Among various inorganic glasses, borate glasses are classical vitreous materials due to the appearance of various structural units over a wide range of compositions [8–10]. Zinc oxide glasses are of special interest owing to their applications in different fields like solar blind UV sensors and optical fibers [11]. Vitreous boron trioxide is a transparent hygroscopic glass with refractive index ~1.48 in the visible region [12]. The ability of boron to exist in both three and four coordinated environments and high strength of the covalent B-O bonds, imparts borates, the ability to form stable glasses. B_2O_3 is one of the most common glass formers. According to Krogh-Moe [13] the structure of vitreous B_2O_3 consists of a random network of boroxol rings and BO_3 triangles connected by B–O–B linkages. When a modifier oxide is added, it causes a transformation of some BO_3 triangles to BO_4 tetrahedral units and results in the formation of various cyclic units like diborate, triborate, tetraborate or pentaborate groups with the production of non bridging oxygens [14–18].

Zinc oxide also called as zincite, has the hexagonal wurtzite structure with all zinc and oxygen atoms in tetrahedral coordination. It is a semiconductor with a wide band gap of about 3.3 eV at room temperature. ZnO glasses are important due to their non-toxicity, non hygroscopic nature, lower cost and their useful optical, electrical and magnetic properties [19,20]. ZnO can act as both a six-coordinated network modifier and four-coordinated network former [21,22]. Zn^{2+} ions in oxide glasses enhance mechanical properties and chemical resistivity through the formation of tetrahedral co-ordination. ZnO is a key constituent for the preparation of multi-component oxide glasses with a high thermal resistance against crystallization [23,24]. It has been established that ZnO in oxide glasses and glass ceramics can lower the melting point and glass transition temperature and improve the thermal expansion coefficient [25,26]. Fining agents such as calcium fluoride are added to the glass mixture to remove bubbles from the melt [27].

Extensive investigations on the infrared, Raman, optical absorption, luminescence and electron spin resonance spectroscopy of different transition metal ions in a variety of inorganic glasses have been made in the recent years in view of their technological applications [28–32]. Transition metal ions are known to influence the optical, electrical and magnetic properties of glasses due to their high sensitive response to the changes in the surrounding actions. Further, these ions can be used as better candidates to probe the glass structure due to their broad radial distribution of outer *d*-orbital electron functions and their sensitive response to the surrounding actions [33]. Transition metals present in-depth knowledge about many detailed aspects like the geometry of structural units present in the glass, the character of chemical bonds as well as the coordination polyhedra [34]. Transition metal ions such as chromium dissolved in glasses make them colored and have strong influence over the insulating character and optical transmission of these glasses, since Cr_2O_3 also participates in the glass network forming with different structural units. Chromium may exist in both Cr^{3+} and Cr^{6+} states in the glass network. Cr^{3+} ion enters in the network as modifier where as Cr^{6+} ion enters as network former with CrO_4^{2-} structural units [35]. Chromium ion is widely used as a tool for studying the structure and the local symmetry of glass materials [36]. Zinc borate glasses have

---

* Corresponding author. Tel.: +91 866 2494499.
E-mail address: gsrinivasarao64@yahoo.com (G.S. Rao).

0022-3093/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.jnoncrysol.2010.08.034

been extensively studied over the years to elucidate the nature and the relative concentration of the various borate units constituting the glass network [37–40]. However, the studies on CaF_2–ZnO–B_2O_3 glasses doped with Cr_2O_3 are not available in the literature. The objective of the present work is to study the influence of Cr_2O_3 addition on the structure of CaF_2–ZnO–B_2O_3 glass and the mechanism of the conversion of $BO_3 \leftrightarrow BO_4$ units in this glass with special reference to different borate structural groups like di-, tri-, penta-, ortho-, meta-, and pyroborates using density, molar volume, infrared and Raman spectral studies. The importance of the present study is that it establishes the foundation for the structure of borate-based glasses useful for industrial and technological applications.

2. Experimental methods

A number of glass samples with the chemical formula 20 CaF_2–20 ZnO–(60-x) B_2O_3-x Cr_2O_3 with $0 \leq x \leq 0.10$ mol% (x = 0, 0.02, 0.04, 0.05, 0.06, 0.07, 0.08 and 0.1) are prepared by the melt quenching method; among various compositions, these samples seem to have formed a relatively clear and transparent glass. Appropriate amounts (all by mol%) of reagent grades of boric acid, zinc oxide, calcium fluoride and chromium trioxide powders are thoroughly mixed in an agate mortar and melted in a thick walled platinum crucible at 950 °C in microcontroller regulated pit furnace (Krishna Enterprises, Hyderabad, India) for about 1 h until a bubble free liquid is formed. The resultant melt is then poured in a brass mould and subsequently annealed at 330 °C. The density of the glass samples is determined to an accuracy of ± 4 kg m^{-3} by the standard Archimedes principle. The measurements are done with a digital balance (Shimadzu AUY 220 accuracy 0.0001 gm) and *o-xylene* as an inert immersion liquid. The amorphous state of the glasses is checked by X-ray diffraction spectra (Fig. 1) recorded using Bruker D8 diffractometer in the step scan mode, with Cu K_α radiation of wavelength 1.542 Å at a voltage of 30 kV and 20 mA anode current with a step value of 0.02^0 per 3 s from 0^0 to 90^0. The infrared spectra of the glass samples are recorded at room temperature in the wave number range of 1800–400 cm^{-1} with a resolution of 4 cm^{-1} by an IR spectrophotometer of type alpha by Bruker powered by a 240 V and 10 A ac supply using the KBr pellet technique. The resulting spectra are deconvoluted and peak fitted for a comprehensive study of the glass structure. DeltaNu Advantage NIR Raman Spectrometer is used to record the Raman spectra of the glass samples.

3. Results

The absence of peaks in x-ray diffraction spectra and the broad nature of IR spectral bands indicate the amorphous nature of the glasses under study.

The density and molar volume of CaF_2–ZnO–B_2O_3 glass doped with Cr_2O_3 are presented in Fig. 2. The density of the pure glass CaF_2–ZnO–B_2O_3 is 2774 kg m^{-3}. With the introduction of 0.02 mol% of Cr_2O_3 into the glass matrix, the density changes to 2810 kg m^{-3} (Table 1) and with the further increase in the concentration of Cr_2O_3 the density of the glass increases up to 0.06 mol% of Cr_2O_3 and then decreases above this mol%, as shown in Fig. 2. Such a decrease in the density above 0.06 mol% of Cr_2O_3 is unexpected as Cr_2O_3 has a higher density than B_2O_3. On the other hand, the values of molar volume decreased from 26.55×10^{-6} to 25.89×10^{-6} m^3 mol^{-1} with an increase of Cr_2O_3 content up to 0.06 mol%. Fig. 3 represents the variation of oxygen molar volume and oxygen packing density with mol% of Cr_2O_3 of the glasses under study.

Normalized FTIR absorption spectra of CaF_2–ZnO–B_2O_3:Cr_2O_3 glasses along with vitreous B_2O_3 recorded in the wave number region 1800–400 cm^{-1} at room temperature are shown in Fig. 4. The infrared absorption spectrum of vitreous B_2O_3 contains (i) a band at ca 690 cm^{-1} which is assigned to the bending vibrations of B—O—B linkage in the borate network and (ii) a sharp peak in the region 1600–1200 cm^{-1} which is attributed to the B—O stretching vibrations of trigonal BO_3 units [41,42]. Addition of ZnO to B_2O_3 causes spectral changes that reflect structural vibrations in the glass matrix. Experimental IR spectrum of undoped CaF_2–ZnO–B_2O_3 glass (G_0) has exhibited two bands at 466 (P_1) and 690 cm^{-1} (P_2) which are assigned to ZnO_4 tetrahedral units [43,44] and bending vibrations of B—O—B linkages of pentaborate units [41,42] in the borate network respectively. In addition, two prominent bands in the regions 1600–1200 cm^{-1} and 1200–800 cm^{-1} are observed in the undoped reference glass; the band in the first region is due to asymmetric stretching relaxation of the B—O bond of trigonal BO_3 units and the band in the second region is due to B—O bond stretching of tetrahedral BO_4 units [45–47]. Assignments of various prominent infrared bands for the pure glass (G_0) are presented in Table 2.

Addition of Cr_2O_3 into the glass matrix does not produce additional bands. With the increase in the concentration of Cr_2O_3 from 0 to 0.06 mol%, the following changes are observed in the vibrational bands: (i) the band at 466 cm^{-1} due to ZnO_4 structural units shifts towards lower wave number side with slight increase in intensity, (ii) the wave number of vibrational band due to B—O—B bending vibrations at 690 cm^{-1} is found to be constant with slight decrease in intensity, (iii) the intensity of the band in the region 1600–1200 cm^{-1} is observed to decrease with a blue shift of the center of the band and (iv) the intensity of the vibrational band in the region 1200–800 cm^{-1} is found to increase with decreasing wave number of the meta center.

From the normalized infrared spectra one can obtain only qualitative information. This explanation gives no account for the specific borate groups containing BO_3 and BO_4 units. A comprehensive

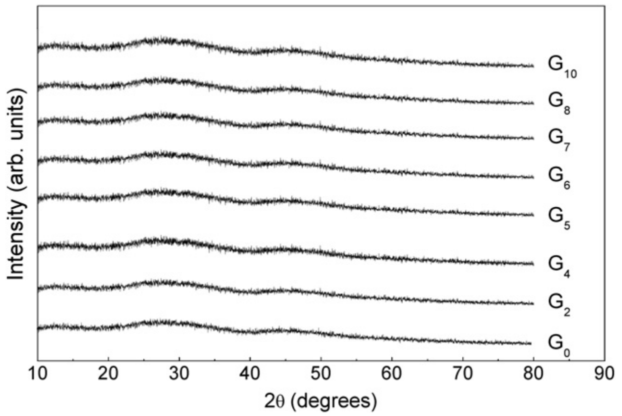

Fig. 1. X-ray diffraction patterns of CaF_2–ZnO–B_2O_3:Cr_2O_3 glasses.

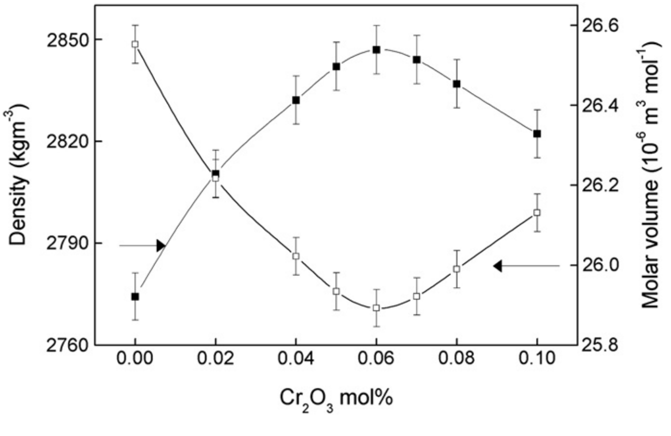

Fig. 2. Variation of density and molar volume of CaF_2–ZnO–B_2O_3 glasses with Cr_2O_3 concentration.