Infrared spectra of zinc doped lead borate glasses

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Abstract. The infrared spectra of zinc-doped lead borate glasses (10–30 mol% ZnO) were measured over a continuous spectral range (400–4000 cm^{-1}) in an attempt to study their structure systematically. No boroxol ring formation was observed in the structure of these glasses. The formation of Zn in tetrahedral coordination was not observed. The conversion of three-fold to four-fold coordinated boron took place.

Keywords. Zn; lead borate glasses.

1. Introduction

Infrared spectroscopy has been extensively employed over the years to investigate the structure of glasses (Kamitsos *et al* 1987). Borate glasses, in particular, have been the subject of numerous infrared studies due to their structural peculiarities (Wang and Angell 1976; Kamitsos and Karakassides 1989). Recently, the study of oxide glasses has received considerable attention due to their structural peculiarities. In borate glasses, B_2O_3 is a basic glass former because of its higher bond strength, lower cation size, smaller heat of fusion and valence (= 3) of B. In borate glasses, B^{3+} ions triangularly coordinated by oxygen, form glasses easily. In B_2O_3 the units are triangles, which are corner bonded in a random configuration (Yawale *et al* 2000). The NMR investigation (Silver and Bray 1958; Bray *et al* 1963) as well as the vibrational spectroscopic work (Krogh Moe 1965; Konijnendijk and Stevels 1975) have been particularly helpful in identifying various boron–oxygen arrangements at different modification levels in alkali borate glasses. PbO and ZnO can enter the glass network both as a network former and also as a network modifier and due to this the structure of this glass is expected to be different from that of alkali borate glasses. The structure of borate glasses is different than other glasses such as phosphates and silicates. Soppe and Marel (1988) suggested that, the structure of borate glasses heavily depend upon the cooling rate of the melt through the range of glass transition temperature. Introducing ZnO at the expense of PbO may change the distribution of PbO in these glasses (Doweidar *et al* 1991).

In the present paper the structure of PbO–ZnO–B_2O_3 glasses is discussed with the help of infrared spectra. To elucidate the conduction mechanism in present glass system, one has to know the structure. Since infrared spectroscopy is the most advantageous tool for the study of amorphous materials, we have used it to determine the structure of borate glasses containing varying amounts of PbO_2 and ZnO.

2. Experimental

2.1 *Sample preparation*

Zinc doped lead–borate glasses were prepared from reagent grade powders of ZnO, PbO_2 and H_3BO_3, which were thoroughly mixed, in appropriate proportions. Melting was performed in porcelain crucibles placed in an electric furnace for about 2 h at temperatures ranging from 973–1073 K. The homogenized molten glass was cast in two metal blocks. Samples were quenched at 423 K so as to avoid cracking and shattering of the glass. After quenching the glass, all the samples were immediately transferred to annealing furnace. All the samples were annealed at 423 K. The general formula was $XPbO_2$–$(50 - X)ZnO$–$50B_2O_3$, here $X = 10, 15, 20, 25$ and 30 mol%.

2.2 *X-ray diffraction*

The X-ray powder diffraction data for all glasses was obtained from R.S.I.C. Nagpur, India. The Philips PW 1710 X-ray powder diffractometer was used. The results were recorded using a PM 8208A chart recorder and an A100 (Digital) printer with VT 125 terminal simultaneously. Details of the operating conditions were as mentioned: generator settings, 35 kV, 20 mA; radiation: $CuK\alpha$ (angle range: 5 to 100°, step size: 0·020, time per steps: 0·500 s and divergence slit: 10). X-ray diffraction technique was used to check for possible crystallinity

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of the sample after quenching and annealing. All samples were found to be completely amorphous in nature.

2.3 *Infrared spectra*

The vibration spectra of various glasses were obtained using KBr pellet technique in the range 400–4000 cm^{-1} on Perkin–Elmer 467 IR spectrometer. The resolution was 1 cm^{-1}.

3. **Results and discussion**

The broad composite bands extending from 3200–3600 cm^{-1} are attributed to hydroxyl or water groups (Adams and Douglas 1959; Scholzelt 1991). The peak at 2700–3000 cm^{-1} originates from hydrogen bonding. The absorption bond at 3450 cm^{-1} is attributed to O–H stretching vibration (Bray 1967). The OH^{-} groups form non bridging oxygen sites and should contribute to those formed upon introducing into the glasses. In figure 1, it can be seen that there is no effect of composition on the types of the structural groupings in the present case. This may be due to presence of symmetric $(BO_3)^{3-}$ triangles, BO^{4-} tetrahedral and asymmetric $(BO_3)^{3-}$ units (i.e. non-bridging oxygen) in each sample of PbO–ZnO–B$_2$O$_3$ glasses.

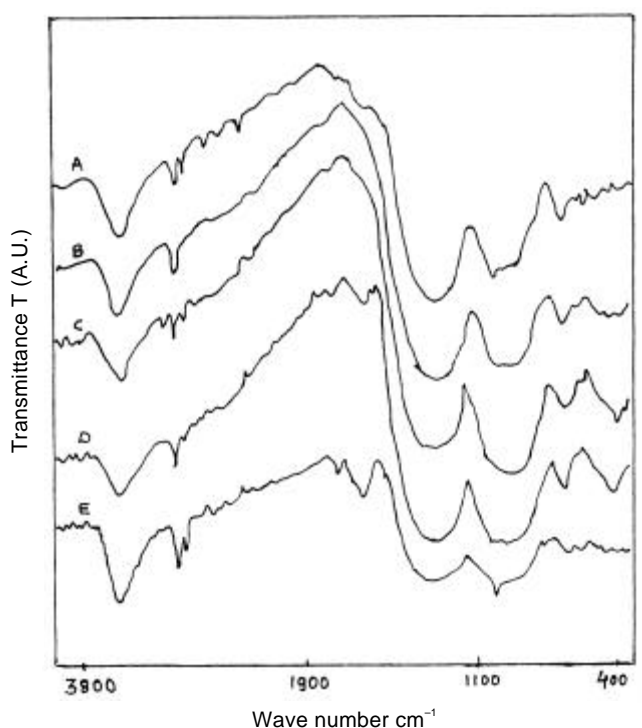**Figure 1.** IR spectra of glass series X PbO$_2$–(50–X) ZnO–50B$_2$O$_3$ (A. 20PbO$_2$–30ZnO–50B$_2$O$_3$; B. 25PbO$_2$–25ZnO–50B$_2$O$_3$; C. 30PbO$_2$–20ZnO–50B$_2$O$_3$; D. 35PbO$_2$–15ZnO–50B$_2$O$_3$ and E. 40PbO$_2$–10ZnO–50B$_2$O$_3$).

Furthermore, it seems that the spectra containing different concentrations of ZnO do not change the structure. Similarly in Na$_2$O–B$_2$O$_3$–SiO$_2$, PbO–B$_2$O$_3$, PbO–V$_2$O$_5$–B$_2$O$_3$, CdO–PbO–B$_2$O$_3$ glasses, it is seen that the absorption bands are related to the types of B-bands rather than to the cations associated with the structural groups.

According to the Krogh Moe's (1965) model, the structure of boron oxide glass consists of a random network of planar BO$_3$ triangles with a certain fraction of six membered (boroxol) rings. X-ray and neutron diffraction data suggest that glass structure consists of a random network of BO$_3$ triangles without boroxol rings. Similar findings have also been reported from the molecular dynamic studies (Soules 1980).

The vibrational modes of the borate network are seen to be mainly active in three infrared spectral regions, which are similar to those reported by several workers (Kamitsos *et al* 1987; Ezz Eldin *et al* 1995; Ghoneun *et al* 1996): (i) the first group of bands which occur at 1200–1600 cm^{-1} is due to the asymmetric stretching relaxation of the B–O band of trigonal BO$_3$ units, (ii) the second group lies between 800 and 1200 cm^{-1} and is due to the B–O bond stretching of the tetrahedral BO$_4$ units and (iii) the third group is observed around 700 cm^{-1} and is due to bending of B–O–B linkages in the borate networks.

The infrared spectra of these glasses show eight to nine absorption peaks. The peaks are sharp, medium and broad. The broad bands are exhibited in the oxide spectra, most probably due to the combination of high degeneracy of vibrational states, thermal broadening of the lattice dispersion band and mechanical scattering from powder samples. In the present glass system the absence of absorption peak of 806 cm^{-1} indicates the absence of boroxol ring formation. The progressive substitution of boroxol rings by triborate and tetraborate groups is observed. In pure B$_2$O$_3$ glass, the 806 cm^{-1} frequency is a characteristic of boroxol ring. The vanishing of 806 cm^{-1} means no boroxol ring in the glass structure; ultimately it consists of BO$_3$ and BO$_4$ groups. These groups may be attached in the form of random network. This corresponds to the progressive substitution of boroxol ring by BO$_3$ and BO$_4$ groups. This type of behaviour is observed in B$_2$O$_3$–Li$_2$O glasses by Kulkarni *et al* (1984), Galeener *et al* (1980) and Kanehisa and Elliot (1989). The absorption band at 1307 cm^{-1} and for 35 PbO mol% is associated with B(III)–O–B(IV) stretching vibrations. The band around 1357 cm^{-1} in 40 mol% glass is assigned to B–O stretching vibrations of trigonal $(BO_3)^{3-}$ units in metaborates, pyroborates and orthoborates (Chekhovskii *et al* 1985). On passing from boron trioxide to borate glasses, a change in the coordination number of boron takes place. In these glasses, the boron is tetrahedrally surrounded by four oxygen atoms (Biscoe and Warren 1938). The band around 1292 cm^{-1} is due to B–O asymmetric stretching of BO$_3$ unit (Heaton and Moore 1987). The shoulder at 1234 cm^{-1} may arise from B–O stretching vibrations of

Table 1. Peak frequencies from IR spectra for X PbO$_2$–(50–X)ZnO–50B$_2$O$_3$.

Glass No.	Composition (mol%) PbO$_2$–ZnO–B$_2$O$_3$			Peak positions (cm^{-1})																					
A	20	30	52	412	444	453	–	695	1004	1292	1696	–	2187	2268	2234	2364	–	2565	–	2620	2676	2854	2919	3470
B	25	25	50	418	467	–	–	694	917	1234	1716	1739	–	–	2333	2357	2423	2457	–	2603	–	2855	2929	3447
C	30	20	50	–	457	–	–	698	993	1292	–	1740	–	2270	2333	2357	–	–	–	–	2690	2854	2928	3420
D	35	15	50	419	456	486	–	966	1021	1307	1599	1747	1825	2298	2334	–	–	2509	2568	2625	2605	–	2925	3440
E	40	10	50	–	–	–	616	682	1014	1357	1622	1743	–	2297	2333	2345	2467	2509	–	2608	2665	2853	2922	3443

(BO^3)$^{3-}$ unit in metaborate chains and orthoborates (Kamitsos *et al* 1990). Similarly the band at 1004 cm^{-1} is due to vibration of some boron atoms attached to non-bridging oxygen in the form of BO$_4$ vibration (Ito *et al* 1983). The absorption around 1000 cm^{-1} indicated formation of diborate group in present glasses. The shoulder at 1021 cm^{-1} can be referred to stretching vibrations of BO$_4$ tetrahedra. In IR spectra of Na$_2$O–B$_2$O$_3$–SiO$_2$ glasses the band at about 995 cm^{-1} is attributed to a stretching vibration of B–O–Si linkage (Tenny and Wong 1972). Similarly the presence of the band at 993 cm^{-1} in the spectra may be assigned to a stretching vibration of B–O–M (B–O–Pb) linkage where M represents a metal ion.

The absorption band at 694 cm^{-1} is assumed to be due to combined vibration of BO$_4$ and PbO$_4$ groups (Heaton and Moore 1957). The band around 699 cm^{-1} indicates that oxygen bridges two trigonal boron atoms. These PbO–ZnO–B$_2$O$_3$ glasses show absence of bands around 960 cm^{-1} suggesting fundamental frequency of (BO$_3$)$^{3-}$ groups. This may be due to the fact that the structure of borate glasses heavily depends on the thermal history of the glass. The different rates of cooling of the melt and quenching temperature, affect the structure of the borate glasses (Soppe and Marel 1988).

In 40 mol% PbO content glass the absorption at 616 cm^{-1} are due to bending of O–B–O. This possibility is more in borate glasses in which boroxol rings are absent. Boron ion is a network forming cation. It may occupy the centres of oxygen triangles or tetrahedral. Similarly PbO has the ability to form stable glasses. This tendency of lead is due to dual role of Pb^{2+} cations in glass structure. In glass structure Pb^{2+} cations play the role of network modifier when these cations are ionically bonded. On the other hand, if Pb–O bond is covalent Pb^{2+} cation will act as glass former (Azhra and Zahra 1993). Because of dual role, lead ions may disrupt the glass network and form BO$_4$ tetrahedral. The low frequency band 453 cm^{-1} in the spectra of investigated glasses can be attributed to vibration of metal cations such as Pb^{2+} or Zn^{2+}. The same band is also present in PbO–B$_2$O$_3$ glasses that is attributed to the vibrations of Pb^{2+} cations (Bray and O Keefe 1963).

In 50 PbO–50 B$_2$O$_3$ glass system the absorption band at 828, 946, 1130 cm^{-1} was reported by Doweidar *et al* (1991). In present PbO–ZnO–B$_2$O$_3$ glasses, it is found that the bands reported by Doweidar *et al* (1991) are absent. Probably this may be due to substitution of ZnO for fraction of PbO contents. The absorption at 840 cm^{-1} is not observed in these glasses, which suggest that the formation of tetrahedral coordination of Zn (i.e. ZnO$_4$) is absent (Yawale *et al* 1995).

The absorption peak around 420 cm^{-1} suggests the ZnO bond formation. The peak at 412 cm^{-1} corresponds to bending of Zn–O bond in 30 mol% ZnO content glass.

4. Conclusions

It is concluded that the structure of Zn-doped borate glass consists of randomly connected BO$_3$ and BO$_4$ groups. The structure of present glass system is independent of composition. Very small change in the absorption bands may occur that do not account for major structural changes. In many systems in which ZnO is a major constituent, the possibility of formation of ZnO$_4$ may be more. But in these glasses no tetrahedral formation of ZnO occurs. Similarly the boroxol ring formation is not observed.

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