

Infrared spectroscopic study of zinc doped iron borate glasses

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The infrared absorption spectra of $x\text{ZnO}(40-x)\text{Fe}_2\text{O}_3.60\text{B}_2\text{O}_3$ glasses ($x = 0, 10, 15, 20$ and 30 mol% of ZnO) have been investigated to find out the role played by zinc on the structure of these glasses. ZnO was gradually introduced to replace Fe_2O_3 in the series of zinc doped iron borate glasses containing 60% B_2O_3 . The structural changes were inferred by monitoring the infrared spectra of these glasses in the range $200\text{--}4000\text{ cm}^{-1}$ by KBr technique. Very small change in absorption bands may occur on addition of ZnO impurity in the series of zinc doped iron borate glasses. No boroxyl ring formation is observed in the structure of these glasses. Similarly, tetrahedral formation of zinc is not observed. The absence of absorption band corresponding to a frequency of 806 cm^{-1} is attributed to the progressive substitution of boroxol ring by triborate (BO_3) and tetraborate (BO_4) groups.

Keywords: Infrared spectroscopy, Iron borate glasses, Glasses

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1 Introduction

Study of zinc doped iron borate glasses received attention due to the unique properties of zinc oxide. As zinc oxide is an important multifunctional material and due to its specific chemical, surface and micro structural properties, it is used in various applications¹ such as varistors, gas sensors, SAW devices, transparent electrodes, catalysts etc. Generally, glasses are disordered amorphous materials, having non-periodic arrangement of atoms. However even though they are non-crystalline, these solids exhibit some local order, either in the form of regular co-ordination of long chain molecules. Several metal oxides such as ZnO mixed together with P_2O_5 , SiO_2 , GeO_2 , B_2O_3 etc. form glasses. According to Zachariasen rules² if the coordination number of oxide is small (either 3 or 4) then glass formation occurs. In borate glasses, B_2O_3 is basic glass former because of its higher bond-strength, lower cation size, smaller heat of fusion and trivalency of boron. In borate glasses B^{3+} ions are triangularly coordinated by oxygen to form glasses easily. An inorganic compound tends to be amorphous (non-crystalline) if (I) each anion is bounded to only two cations, (II) no more than four anions are bounded to a cation, (III) the anion polyhedra share corners but not edges or faces and (IV) the compound has a large number of constituents distributed irregularly through

its network. In B_2O_3 the units are triangles, which are corner bonded in a random configuration³. The main structural units of borate glasses are BO_3 groups either as a random network of boroxol rings beside some fraction of BO_3 triangles connected by B-O-B linkage⁴ (bridging atoms). The boroxol group is composed of three corner sharing BO_3 triangles, which form a very high planar ring called 'boroxol ring'. Recent studies⁵ concluded that any model which attempts to give a full description of the structure of B_2O_3 must include a high concentration of boroxol group. The addition of metal oxides modifies the boroxol ring in to complex borate groups⁶ with one, two or four coordinated boron atoms. ZnO/FeO can enter the glass network both as network former and also as a network modifier and due to this the structure of borate glasses is different than that of other glasses such as phosphate, silicate, etc. The structure of borate glasses heavily depends upon the cooling rate of melt through the range of the glass transition temperature⁷. The studies on borate glasses containing a specified amount of network modifier exhibit certain unique features⁸ at certain value of $x\text{MeO}(1-x)\text{B}_2\text{O}_3$, where Me is the network modifying cation. This effect is known as boron anomaly. Phosphate and silicate glasses do not show such properties.

In the present work, the structure of zinc doped iron borate glasses is discussed with the help of infrared spectra. Since infrared spectroscopy is the most

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advantageous tool and has been extensively employed over the years to investigate the structure of glasses. We have used it to determine the structure of borate glasses containing various amounts of ZnO and Fe₂O₃. Here we have varied iron oxide by zinc oxide composition in the series of $x\text{ZnO}(40-x)\text{Fe}_2\text{O}_3 \cdot 60\text{B}_2\text{O}_3$ glass system.

2 Experimental Details

2.1 Sample preparation

Zinc doped iron borate glasses were prepared from reagent grade powders of ZnO, Fe₂O₃ and H₃BO₃, which were thoroughly mixed, in appropriate proportions. Zinc oxide was introduced as ZnO, B₂O₃ was introduced as orthoboric acid while hematite was in the form of Fe₂O₃. The batch materials were dry mixed and melted in platinum crucibles placed in an electrically heated muffle furnace at $1300 \pm 20^\circ\text{C}$ for about 2 h, until a bubble free liquid was formed. The molten glass was equilibrated at the melting temperature until a clear and homogeneous melt was obtained. The melt was cast on to a stainless steel plate and annealed at about 450°C in a muffle furnace which was left to cool down to room temperature at a rate of $30^\circ\text{C}/\text{hr}$. The glasses obtained were subsequently annealed to release strain. The general formula was $x\text{ZnO}(40-x)\text{Fe}_2\text{O}_3 \cdot 60\text{B}_2\text{O}_3$, with $x = 0, 10, 15, 20$ and 30 in mol %.

2.2 X-ray diffraction measurements

The X-ray powder diffraction experiment was carried out on Philips PW 1140/09 X-ray powder diffractometer. The details of operating conditions were as follows: generator rating, 35 kV, 20 mA; radiation Cu-K α (angle range 5 to 90°) and step size 1 cm/min. X-ray diffraction data was used to check for possible crystallinity of the sample after quenching and annealing. All samples were found to be completely amorphous in nature.

2.3 Infrared measurements

The vibration spectra of the various glasses were obtained at room temperature using KBr pellet technique in the range 200 - 4000 cm^{-1} on Jasco FT/IR-300E spectrophotometer. The investigated samples were ground to fine particles and then mixed with KBr in the ratio $2:200$. The mixture was then subjected to a pressure of 5 ton/cm². The spectra were measured immediately after preparing the desired disks.

3 Results and Discussion

The vibrational modes of the borate network are seen to be mainly active in three infrared regions, which are similar to those reported earlier⁹⁻¹². The first group of bands that occur at 1200 - 1600 cm^{-1} is due to the asymmetric stretching relaxation of B-O bond of the trigonal BO₃ units. The second group lies between 800 - 1200 cm^{-1} and is due to B-O bond stretching of the tetrahedral BO₄ units. The third group of band is observed at around 700 cm^{-1} and is due to bending of B-O-B linkages in the borate network. The infrared spectra of the present glass systems show nine to ten absorption peaks as shown in Fig. 1. The peaks are sharp, medium and broad. The broad bands are generally due to combination of factors such as high degeneracy of vibrational state, thermal broadening of lattice dispersion band and mechanical scattering from the powdered samples. In borate glasses, the absorption bands at 806 cm^{-1} in IR spectra and 805 cm^{-1} in Raman spectra are the characteristics of boroxol ring (boron in III coordination) reported by many researchers^{13,14}. The absence of the band at 806 cm^{-1} signifies that no boroxol ring is present in the glasses under study. This corresponds to the progressive substitution of boroxol ring by BO₃ and BO₄ groups. These groups may be attached in the form of random network. This type of behaviour has also been observed by other researchers^{9,15-17} in borate glasses doped with metal ions such as Mn and Zn.

In the present glass system $x\text{ZnO}(40-x)\text{Fe}_2\text{O}_3 \cdot 60\text{B}_2\text{O}_3$, when ZnO is absent i.e. $x = 0$, nine peaks are observed as shown in Fig. 1. The first group of band is located in the region 1195 - 1472 cm^{-1} and associated with the fundamental asymmetrical stretching vibration of the B-O bond of the trigonal BO₃ units (Table 1). The other group of band is located in the region 922 - 1020 cm^{-1} and originates from B-O bond stretching of the tetrahedral BO₄ units and is due to the vibration of some boron atoms attached to the non-bridging oxygen in the form of BO₄ vibrations¹⁸. The shoulder at around 1020 cm^{-1} indicates the formation of diborate group in the present glass system. In the infrared spectra of PbO₂B₂O₃.ZnO glasses, the absorption band at about 993 cm^{-1} is attributed to a B-O stretching vibration of B-O-Pb linkage¹⁷. In the present glasses, a lower frequency band observed at 922 cm^{-1} is most probably due to the greater M-O interaction in B-O-M linkage resulting in weakening of B-O bond and hence lowers its frequency. This can be attributed to B-O stretching vibration of B-O-M linkage

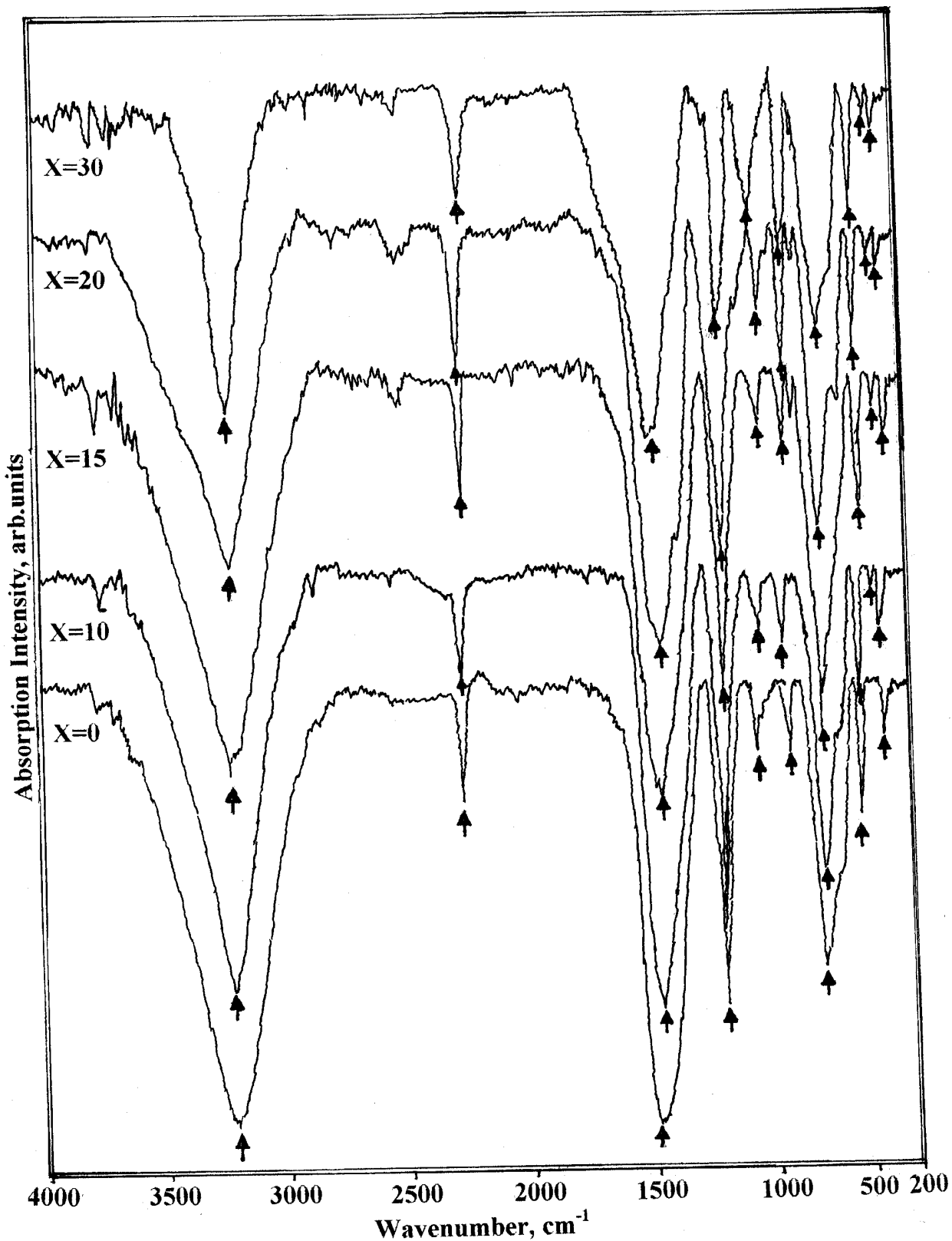


Fig. 1—IR absorption spectra for $x\text{ZnO}(40-x)\text{Fe}_2\text{O}_3.60\text{B}_2\text{O}_3$ glass system, for $x=0, 10, 15, 20, 30$ mol %, Peak positions of each ten bands as listed in Table 1 are indicated by an arrow in the same order as assigned in Table 1.

Table 1—Peak frequencies from IR spectra for $x\text{ZnO} \cdot (40-x)\text{Fe}_2\text{O}_3 \cdot 60\text{B}_2\text{O}_3$ glass system

| Glass No. | Composition (mol%) | | | Peak positions (cm^{-1}) | | | | | | | | |
|-----------|--------------------|-------------------------|------------------------|-------------------------------------|-------|-------|-------|-------|---------------|---------------|------------------------|-------------|
| | ZnO | Fe_2O_3 | B_2O_3 | Zn-O | Fe-O | O-B-O | B-O-B | B-O-M | BO_4 | BO_3 | OH^{-1} group | |
| A | 0 | 40 | 60 | — | 353.2 | 642.7 | 724.2 | 921.5 | 1020.5 | 1194.8 | 1472.6 | 2260 3215.8 |
| B | 10 | 30 | 60 | 414 | 352.7 | 644.2 | 727.1 | 923.8 | 1020.2 | 1193.9 | 1460.9 | 2263 3209.6 |
| C | 15 | 25 | 60 | 418 | 355.0 | 643.8 | 726.0 | 924.2 | 1027.7 | 1189.2 | 1460.6 | 2261 3221.6 |
| D | 20 | 20 | 60 | 420 | 355.4 | 642.9 | 723.9 | 927.0 | 1026.4 | 1195.3 | 1461.2 | 2263 3209.6 |
| E | 30 | 10 | 60 | 419 | 354.0 | 645.9 | 722.8 | 936.3 | 1024.9 | 1194.8 | 1490.7 | 2280 3215.8 |

where M represents a metal ion ($\text{Zn}^{2+}/\text{Fe}^{3+}$). However, the frequency of B-O-M linkage increases on addition of ZnO. This is due to the fact that iron oxide is replaced by zinc oxide i.e. stronger B-O-M (Fe^{3+}) bond is replaced by weaker B-O-M (Zn^{2+}) bond. Therefore, the frequency of the B-O-M linkage increases on ZnO doping. The third group of band is observed at around 724 cm^{-1} and is due to bending of B-O-B linkage in the borate network. The absorption band observed at 643 cm^{-1} is due to bending of O-B-O linkage¹⁷. This possibility is more in borate glasses where the boroxol ring is absent. In borate glasses, boron is network-forming cation, it may occupy the centers of oxygen triangles or tetrahedral sites. The low frequency band observed at 353.2 cm^{-1} is assigned to Fe-O stretching vibration¹⁹. In our previous study¹⁵, the frequency band observed at around 925 cm^{-1} in IR spectra attributed to B-O-M linkage. On replacing iron oxide by manganese oxide, the frequency of B-O-M linkage remains almost the same. This is due to the fact that the similar Fe^{3+} ions are replaced by Mn^{3+} ions. However, in the present glass system the frequency band observed at 922 cm^{-1} attributed to B-O-M linkage goes on increasing with zinc oxide concentration. Iron oxide (Fe^{3+}) is replaced by zinc oxide (Zn^{2+}) i.e. stronger B-O-M (Fe^{3+}) bond is replaced by B-O-M (Zn^{2+}) weaker bond, therefore the frequency of the observed band increases on increasing the zinc oxide concentration. Besides the vibrational bands due to borate network, the spectra also reveal, a group of prominent absorption bands in the infrared range $2200\text{-}3200 \text{ cm}^{-1}$ due to hydroxyl or water groups and these are persistent in all the compositions. The fundamental frequency¹⁷ at 960 cm^{-1} due to BO_3^{3-} groups is not observed in the present glasses as the structure of borate glasses heavily depends on their thermal history. The different rates of cooling of the melt and quenching temperature also affect the structure of the borate glasses.

On addition of ZnO, i.e. at $x=10$, the appearance of an additional band around 414 cm^{-1} is assigned to Zn-O bond formation. The absorption band lying in the region $922\text{-}1196 \text{ cm}^{-1}$ gets slightly intensified. On further addition of ZnO, there is very small change in absorption bands, which show that the structure of the present glass system is independent of composition. In the present glasses, it is found that there is no frequency band observed at around 840 cm^{-1} which is the characteristic of the formation of tetrahedral MO_4 units¹⁷. The absence of this band in the present IR spectra clearly indicates that the tetrahedral formation of $\text{Zn}(\text{ZnO}_4)$ do not occur in the present glass system. Also, no boroxol rings formation is observed. From the above results, it is concluded that the structure of zinc doped iron borate glasses consists of randomly connected BO_3 and BO_4 units.

3 Conclusion

It is concluded that the structure of zinc doped iron borate glasses 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 these glasses, no tetrahedral formation of ZnO occurs. Similarly the boroxol ring formation is not observed.

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