Asian Journal of Chemistry Vol. 15, No. 2 (2003), 1173–1177

NOTE

Infrared Spectra of Fe_2O_3-Li_2O-B_2O_3-MoO_3 Glasses

L.S. BHAGAT
Department of Physics, Dr. Ambedkar College, Nagpur-440 010, India

Changes in network structures of lithium-molybdenum-iron-borate glasses were investigated by means of infrared spectroscopy and X-ray analysis. Analysis of the network structures were carried out based on a (1) networks unmodified by MoO_3 and (2) Fe_2O_3-modified network. The unmodified networks are made by three dimensional array of clusters with unmodified BO_3 and BO_4 groups. MoO_3 reduction and Fe_2O_3 addition both gives contribution to four coordinated boron which governs the glass structure.

Key Words: Fe_2O_3, MoO_3, Lithium borate, IR spectra.

A number of spectroscopic studies such as IR, NMR, Raman etc. have been carried out on the glasses so as to know the geometry and distribution conduction sites responsible for ionic migration[1–3]. Boron atoms have coordination number three or four in borates and forms the fundamental triangular BO_3 and tetrahedral BO_4 groups. The network structure of pure boron oxide is thought to consist predominantly of connected boroxol rings built up of only BO_3 groups[4], while borate structures containing network modifiers involve BO_3 and BO_4 groups in clusters[5]. In this study, infrared spectra of the glasses made at room temperature were investigated to understand the changes in the borate network structure.

The compositions prepared have been tabulated in Table-1. Glasses were synthesized using reagent grade of starting materials of H_3BO_3, Li_2CO_3, Fe_2O_3, MoO_3. The corresponding four oxides in appropriate amounts of well dried and desiccated ingredients were throughly wet-mixed in an agate mortar for about 2 h in acetone. The well-mixed and dried oxides were melted in a silica crucible for 2 h at around 1100°C. The melt was then finally vitrified onto aluminium plate.

These glasses were examined by X-ray powder diffractometry to determine if they contain any crystallites. The IR absorption spectra of glasses were obtained in KBr pellet, using Specord-75 spectrophotometer to understand the changes in the borate network structure.

The X-ray diffraction spectra of all the glasses are depicted in Fig. 1. It is clear from the graph that, the glasses containing 20 and 15 mol % MoO_3 are found to be partially crystalline and all other glasses are amorphous in nature. It is also clear from the diffractograms that the amorphousness increases with decreasing molybdenum oxide content and with increasing iron oxide content.

TABLE-1

Glass No.	Composition mol (%)				Specification
	Fe_2O_3	B_2O_3	Li_2O	MoO_3	
I	0	-40	-40	-20	* mol % of B_2O_3 and Li_2O
II	5	-40	-40	-15	is constant
III	10	-40	-40	-10	*Fe_2O_3 is increased at the
IV	15	-40	-40	-5	cost of MoO_3 between 0–20
V	20	-40	-40	-0	mol %

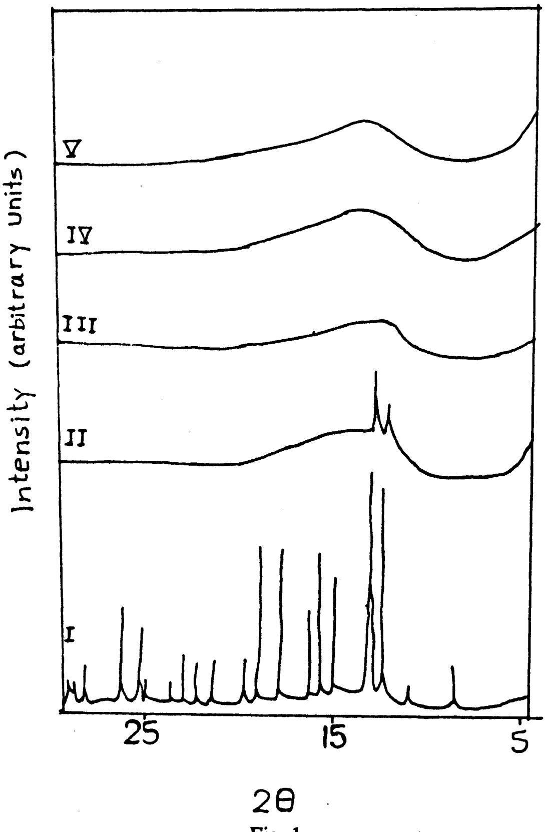

Fig. 1

Figure 2 exhibits the IR absorption spectra for all the glasses and their constituent oxides, *viz.*, Fe_2O_3, MoO_3. To assign the various peaks observed in the above spectra, the IR spectrum of 50 Li_2O : 50 B_2O_3 (here after referred as 50 L-B) glass which is prepared by similar method as used in the present work and is shown for comparison. The IR spectra of 50 L-B glass exhibits three absorption bands at 1350, 1100 and 700 cm^{-1}.

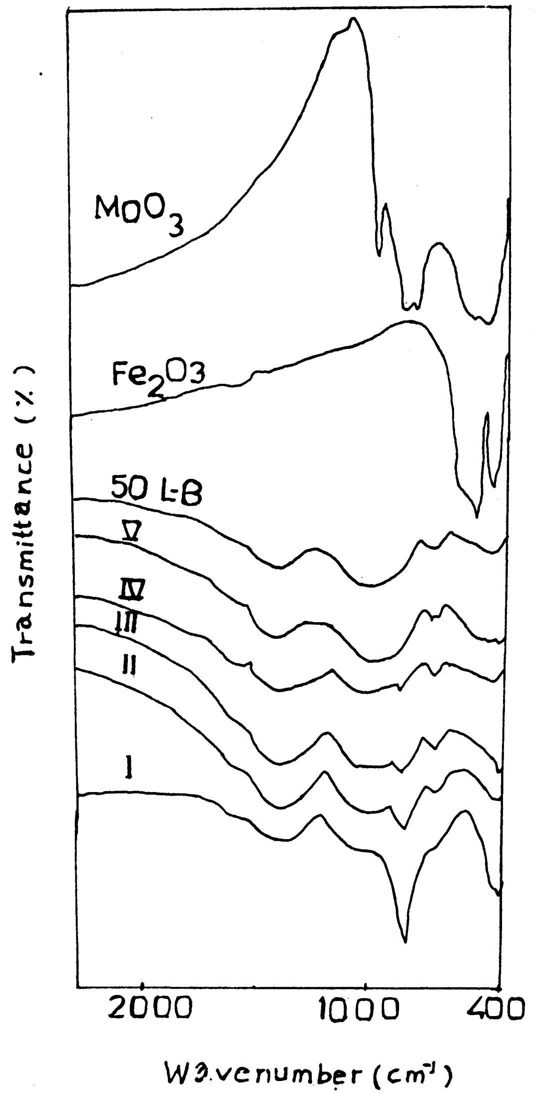

Fig. 2

First of all the band in the region 1400–1300 cm^{-1} is detected in all the glasses in Fig. 2. As the network of vitreous B_2O_3 is formed with connected boroxol rings, the infrared spectrum of vitreous B_2O_3 consists predominantly of the vibrations of BO_3 groups, the boroxol rings and B—O—B bridging oxygens. This bond is due to the vibration of the BO_3 group, built up in the molten state.[4, 6, 8 11].

The shoulder (in glass I and II) and band (in glass III, IV and V) at 1100 cm^{-1} is considered to be due to vibration of BO_4 groups. Band at 825 cm^{-1} is the characteristic of Mo—O bond in Mo—O_6 groups, which is maintained in glasses I and II, but not found in other glasses.

The decrease in intensity of absorption peak at 825 cm^{-1}, appeas a weak band at 700 cm^{-1}, intensity of which again increases with the increase of iron oxide content. A weak shoulder is also appeared in glass I at 700 cm^{-1}. This shoulder and band at 700 cm^{-1} is due to the vibration of non-bridging oxygen. This band is slightly shifted to 720 cm^{-1} in glass V appearing a weak shoulder at 700 cm^{-1}. This shift in the band is considered to be due to the formation of B—O—B bridging oxygens at 720 cm^{-1} while reducing the non-bridging oxygens.

It was observed from the IR spectra, that the intensity of shoulder at 1100 cm^{-1}, increases with the addition of 5 mol % Fe_2O_3 and for further increase of iron oxide content, the band at 825 cm^{-1} merges in this shoulder which results in enhancing the four coordinated boron, *i.e.*, BO_4 groups which strengthens the glass structure.

It was also observed from the graph that increase in energy of the spectrum at 1100 cm^{-1} and decrease in energy of the spectrum at 1400 cm^{-1} in glass V, increases the size of the BO_4 groups[12].

The band broadening of fig. 2 may be explained as follows. The vibrations of chemical bonds are affected by their surroundings and since no long range order exists in glasses and the surroundings of each chemical bond is somewhat different, the spectral peaks of amorphous materials are broader than those of crystalline substances[10].

Conclusion

From X-ray analysis and from IR spectroscopy the iron rich glasses are thought to have the modified network structure of simple BO_3, BO_4 groups and non-bridging oxygens in which Fe_2O_3 functions as a network modifier which strengthens the glass structure by increasing more BO_4 groups and hence controls the process of precipitation. Whereas, the molybdenum rich glasses to have the unmodified network structure made by three-dimensional array of clusters with unmodified BO_3 and BO_4 groups which co-exist with MoO_3 particles, thereby ceases BO_4 tetrahedra, causing precipitation.

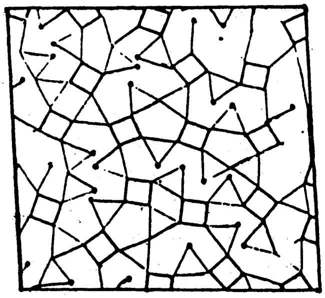

Fig. 3. Two-dimensional models of the structure of alkali-borate glass
□ BO_4 group; Δ BO_3 group; — Non-bridging oxygen

REFERENCES

1. W.N. Konijnedijk and J.M. Stevels, *J. Non-Cryst. Solids*, **18**, 307 (1975).
2. E.I. Kamitsos, M.A. Kavakassites and G.D. Chryssikos, *J. Phys. Chem.*, **91**, 5807 (1987).
3. W. Soppe, C.V.D. Marcel and H.W.D. Hartog, *J. Non-Cryst Solids*, **101**, 101 (1988).
4. I.N. Chakravorty and R.A. Condrate, *J. Non-Cryst Solids*, **81**, 271 (1986).
5. P.J. Bray and J.G.O. Keefe, *Phys. Chem. Glasses*, **4**, 37 (1963).
6. Z. Wang, B. Sui and S. Wang, *J. Non-Crystalline Solids*, **80**, 160 (1986).
7. N. Kishore, K. Aggarwal, R. Kamal and R.G. Medirata, *Phys. Chem. Glasses*, **23**, 202 (1982).
8. N.N. Greenwood and A. Earnshow, Chemistry of the Elements Pergamon Press, Oxford, pp. 228 (1984).
9. G.D. Cryssikos, D.E. Turcote, R.V. Mulkern P.Y. Bray and W.M. Risen, *J. Non-Crystalline Solids*, **85**, 54 (1986).
10. F. Gan, G. Haung and S. Chen, *J. Non-Cryst. Solids*, **52**, 203 (1982).
11. I.N. Chakraborty, H.L. Rutz and D.E. Day, *J. Non-Crystalline Solids*, **84**, 86 (1986).
12. Yoo Young Kim, Keu Hong Kim and Jai Shi Choi, *J. Phys., Chem. Solids*, **50**, 903 (1989).

(*Received*: 11 October 2002; *Accepted*: 22 January 2003) AJC-3005

FARADAY DISCUSSION 124:
QUANTUM INORGANIC CHEMISTRY

YORK, UK

APRIL 14–16

Contact:
Christine Hall
Royal Society of Chemistry
Burlington House, Piccadilly, London W1J 0BA, UK
Tel: +44 (0) 20 7440 3336 Fax: +44 (0) 20 7734 1227
E-mail: hallc@rsc.org
http://www.rsc.org/lap/confs/fara 124.htm