

Infrared Absorption Study of Potassium-Boro-Vanadate-Iron Glasses

Dinesh K. KANCHAN, Harshvadan R. PANCHAL

Department of Physics
Faculty of Science
M.S. University of Baroda
Baroda-390 002, INDIA

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Abstract

The IR studies have been made in the $K_2O-B_2O_3-V_2O_5-Fe_2O_3$ glass system. The increase in intensity and shifting of vibrational bands towards lower wave number at $1400-1350\text{ cm}^{-1}$, 1200 cm^{-1} and $100-940\text{ cm}^{-1}$ in IR spectra have been ascribed to the formation of BO_3 to BO_4 and VO_5 to VO_4 tetrahedra along with the formation of non-bridging oxygens attached to boron and vanadium. In heat-treated glass samples, many new vibrational bands have been observed which were however, absent in the untreated samples. The preservation of the 1020 cm^{-1} band assigned to $V=O$ bond suggests that K_2O shows the preference for borate network upto 20 mole % and is responsible for bringing the changes in borate and vanadate networks. At higher amount of K_2O , the presence of both BO_4 and VO_4 groups facilitates the formation of homogeneous solid solution of the present glass system.

1. Introduction

Most of the borate glasses are insulating in nature. The addition of any transition metal oxide makes these glasses semiconducting in nature and the electrical conduction is observed due to the hopping of electrons [1-3]. V_2O_5 based glasses exhibit switching and semiconducting properties [4, 5] and may be used for making stable switching devices [6, 7], whereas, $B_2O_3-V_2O_5$ based glass system are likely to find applications as soldering and moulding materials [8].

Infrared spectroscopy is one of the important techniques used to study the molecular structure of inorganic oxide glasses. The various bonding energies of a solid may be found out by infrared absorption. When the separation of vibrational energy levels is larger and the transition occurs at high frequencies, then pure vibrational spectra are usually

observed in the range between 1 and 100 μm . Different ions surrounding vanadium oxygen polyhedra may lead to changes in the hopping of electrons. The IR studies of pure B_2O_3 - V_2O_5 have been extensively investigated. In boro-vanadate glasses, structure as well as distribution and the interaction between V-O-V and B-O-B polyhedra play a significant role in electron transport. In the present work, IR studies of potassium-boro-vanadate glass system with iron oxide have been made to understand the effect of addition of network modifier K_2O on the structure.

2. Experimental

Analytical grade K_2CO_3 , V_2O_5 , H_3BO_3 and Fe_2O_3 were used as the raw materials. These were weighed in appropriate amounts to prepare glass samples: $x\text{K}_2\text{O}:(95-x)(\text{B}_2\text{O}_3:2\text{V}_2\text{O}_5):5\text{Fe}_2\text{O}_3$, where $x=10$ to 35 in steps of 5. The weighed materials were thoroughly mixed and pulverized in an agate mortar. The finely mixed powdered materials were melted in glazed porcelain crucibles at 850-950°C in a muffle furnace for four hours. The melt was then poured onto a cleaned copper plate and subsequently pressed by another copper plate to provide a better quenching rate. Black shiny sheets of glass were produced. The glass were characterized by powder X-ray diffraction to confirm their amorphous nature. The glass samples were crushed to fine powder. A small amount of the glass powder was mixed and ground with a relatively large quantity of KBr which is transparent to IR radiation. Discs for measurement of IR absorption spectra were formed by pressing the mixture at a pressure of 10-15 tons for few minutes under vacuum. The infrared absorption spectra of the heat treated and as quenched samples were determined by using Perkin Elmer 577 Infrared Spectrometer in the range of 400 to 4000 cm^{-1} .

3. Discussion

Anderson et.al. [9] stated that pure borate glasses consisted of BO_3 triangles randomly oriented, sharing corners with each oxygen shared by two borons. When Na_2O is incorporated in the glass, some of the boron becomes tetrahedrally coordinated. The spectrum of fused B_2O_3 not only consisted of a completely continuous triangle-like coordinated network but contains some BO_4 tetrahedra as well. The absorption peaks at 1460, 1200 and 780 cm^{-1} are related to BO_3 triangles. The weaker peaks at 1115, 1030, 930 and 740 cm^{-1} correspond closely with four peaks in diborate and pentaborate which are assigned to BO_4 tetrahedra. The bands at 1220 to 1400 cm^{-1} [9, 10] are characteristic of $=\text{B}-\text{O}-\text{B}\equiv$ linkage in which one of the boron is tetrahedrally coordinated and those at 1333 to 1428 cm^{-1} show the presence of tetrahedrally coordinated boron in the structure.

The IR spectra of crystalline B_2O_3 and V_2O_5 is given in Figure 1 for the sake of comparison with that of the glasses. According to Bachman et.al. [11], the V_2O_5 structure is built up by deformed VO_5 trigonals bonded in zigzag chains. Each VO_5 group contains a short $\text{V}=\text{O}$ bond (vanadyl group). The band at 1020 cm^{-1} is assigned to its vibrations, while at 830 cm^{-1} is related to a symmetric stretching vibrations along V-O-V chains involved in corner sharing of VO_5 polyhedra [12]. The broadening of peak at 830 cm^{-1} suggests that it is the sum of a number of absorption bands corresponding to V-O-V

bonds of slightly varying bond lengths and angles. The peaks at 720 and 480 cm^{-1} are due to symmetrical and bending modes of V-O-V bonds [13], respectively.

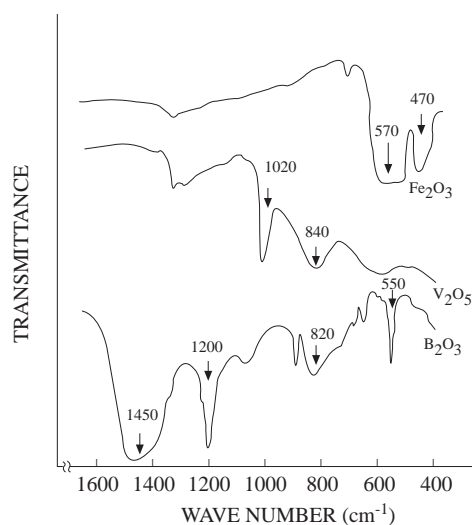


Figure 1. IR spectra of crystalline V_2O_5 , B_2O_3 and Fe_2O_3 .

The IR spectra of all glass samples for K_2O =10 to 35 mole % are given in Figure 2. The main features of IR spectra are being the appearance of resonance peaks at 1400-1350 cm^{-1} , 1250 cm^{-1} , 1000-940 cm^{-1} and a very weak broad band between 800-650 cm^{-1} . Close examination of IR spectra reveals that the vibration band shifts from 1400 cm^{-1} to 1350 cm^{-1} and intensity increases gradually as K_2O increases. In pure borate glasses, the main structural element is the boroxol ring of plane triangular configuration with a B-O bond length $1.36 \pm 0.005 \text{ \AA}$, whereas, the B-O bond length for BO_4 tetrahedra was observed to be $1.47 \pm 0.01 \text{ \AA}$. In IR spectra, the increase in bond length is seen as a shifting of an absorption band towards lower wave number. In binary borate glass, up to 14 %, K_2O does not break bridging in the BO_3 groups to form BO_4 tetrahedra. One K_2O causes the formation of two BO_4 tetrahedra, which participate in a three dimensional network, thus, strengthening the structure [14]. Dimitriev et.al. [15] have pointed out that B_2O_3 and V_2O_5 do not have any chemical affinity for each other because of the presence of the main structural polyhedra VO_5 and BO_3 in amorphous V_2O_5 and B_2O_3 [16, 17]. Due to these structural differences, the pure B_2O_3 and V_2O_5 do not form a single solid solution. It is also well established that the tendency of iron to dissolve into B_2O_3 in the absence of any modifier is negligibly small [18, 19], whereas, iron makes glass of a wide range, 0-50 mole %, with V_2O_5 [20]. Hence it is the modifier, K_2O , which may be responsible in bringing changes to vibrational bands related to borate groups in the present glass system. For $x=10$ and 15 mole %, a shift in vibrational band from 1400 cm^{-1} to 1390 cm^{-1} is observed but the increase in intensity is found to be very small.

Furhter addition of K_2O causes a shift in the vibrational band from 1380 cm^{-1} to 1350 cm^{-1} with a noticeable increase in intensity of these peaks. The shift of the vibrational band towards the lower wave number is ascribed to the increase in bond length of B-O groups and the formation of BO_4 units. From 20 to 35 mole % of K_2O , the increase in intensity of the vibrational bands suggests that the non-bridging oxygens start appearing in the structure in larger number and may form other borate groups. The appearance of another vibrational band near to 1260 cm^{-1} for $K_2O=10$ to 35 mole %, is assigned to $=B-O-B\equiv$ group [21] in which one of the borons is tetrahedrally coordinated. Hence, the increase in intensity of this band possibly indicates that at least some of the B^{3+} ions are occupying a tetrahedral environment with the addition of K_2O .

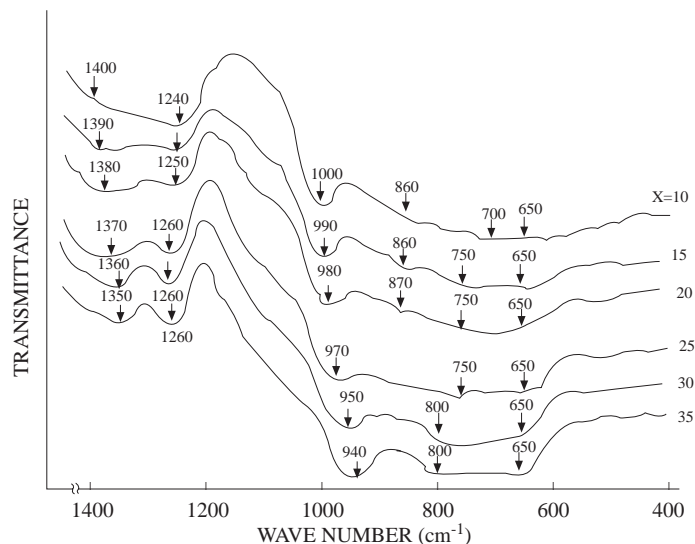


Figure 2. IR spectra of glass samples from X=10 to 35 mole %.

Another distinguished feature of all glass samples is the shift of the broad and intense band from 1000 cm^{-1} , indicating that V^{5+} exist in octahedral coordination. With the addition of K_2O , the shift of this vibrational band towards lower wave number suggests the increase in bond length of isolated $V=O$ bond. It is due to the fact that added K_2O goes into the structure at the interstitial positions leaving its oxygens. K^+ ions now directly interact with the oxygen of the $V=O$ bond, which are thereby weakened and the frequency of vibration shifts towards the lower wave number. The added K_2O also gives rise to the formation of non-bridging oxygens, thereby creating VO^- units. It is obvious that the oxygen, which becomes non-bridging and acquires a negative charge, will move closer to the connected vanadium, consequently reducing the positive charge on the vanadium ion and thereby resulting in a decrease in the binding of other oxygens attached to this particular ion; the length of the $V=O$ bond therefore increases. Also, due to the irregular and random distribution of atoms in the glass structure, the K^+ ions take positions

interstitially that are more symmetrical among other units. Therefore, V=O bonds are affected to different degrees depending upon the exact position that the potassium ion occupies. This fact is supported by the IR spectra of the heat-treated samples discussed below. Therefore, the appearance of a broad absorption band and shifting towards lower wave number is thus expected. The IR studies of $K_2O-V_2O_5$ [15], $Fe_2O_3-V_2O_5$ [20] and $Na_2O-V_2O_5-Fe_2O_3$ [22] glasses revealed the formation of non-bridging oxygens, breaking of the V-O-V chains, increase in the symmetry of V-O polyhedra, equalization of the lengths of V-O bonds and decrease in the coordination number of vanadium. The DTA studies of the present glasses showed that the glass transition temperature T_g decreases gradually as the amount of K_2O increases. The decrease in T_g is generally ascribed to the decrease in coordination number of the network forming atoms [23]. Therefore, according to the observed changes in the IR spectra and DTA studies of the present glass system, the change in coordination from VO_5 polyhedra to VO_4 is thus expected. Generally, a vibration band due to tetrahedrally coordinated boron is also expected near about 950 cm^{-1} . The observed high intensity of the peak between 1000 to 940 cm^{-1} suggests that this absorption is not due merely to the presence of non-bridging $V-O^-$ units as well as elongation of V=O bond but due to the presence of BO_4 polyhedra also. The strong absorption band between 1000 cm^{-1} to 940 cm^{-1} is thus probably due to $V-O^-$ units as well as elongation of V=O bond but due to the presence of BO_4 polyhedra also. The high absorption band between 1000 cm^{-1} to 940 cm^{-1} is thus the cumulative effect of BO_4 and VO_4 units. The presence of very weak and wide absorption band between $800-650\text{ cm}^{-1}$ cannot be assigned to any vibrational group because of their positions cannot be accurately located.

The infrared spectra of heat-treated glass samples shown in Figure 3 reveal some new bands at 1110 , 1020 , 1000 , 990 , 960 , 930 , 875 , 850 , 820 , 725 , 540 and 470 cm^{-1} , which were absent in untreated samples. The presence of a band at 1110 cm^{-1} is assigned to the presence of BO_4 groups which was absent in the glass samples. For $K_2O = 10$, 15 and 20 mole % the presence of a band at 1020 cm^{-1} assigned to V=O bond indicates that the added K_2O probably has a greater preference for borate network and larger amount of the added K_2O is utilised for the conversion of the boron coordination and hence the effect of K^+ ions on the V=O bond is very small and the position of $\nu_{V=O}$ at 1020 cm^{-1} up to 20 mole of K_2O , is thus observed in the IR spectrum of the heat-treated samples. At higher amounts of K_2O , the disappearance of the 1020 cm^{-1} peak and the emergence of peaks at 1000 , 990 , 960 , 955 , 930 cm^{-1} clearly indicate the elongation of the V=O bond by different degrees, depending upon the position of K^+ ion with respect to V=O bond in the structure and the formation of non-bridging oxygens. The peaks assigned to BO_4 tetrahedra in danburite and pentaborate are close to the 930 cm^{-1} bond [9]. Therefore, the presence of IR bands between $1000-930\text{ cm}^{-1}$ can be ascribed due to the net effect of VO_4 and BO_4 units. The appearance of a band at $820-875\text{ cm}^{-1}$ is assigned to V-O-V stretching vibrations. The band at 725 cm^{-1} is probably due to B-O-V-O-B or possibly to BO_4 units [21], which suggests the interaction of borate and vanadate network, whereas, bands at 530 and 470 cm^{-1} indicate the presence of Fe_2O_3 in the chains. These peaks are, however, absent in as-quenched glasses. Mossbauer studies of these glasses [24] suggest

that for a small amount of K_2O , a small amount of Fe is observed as a glass former in the chains as FeO_4 , with the remainder of the iron as glass modifier ions at interstitial positions in the local tetrahedral and/or octahedral environment. As the amount of K_2O increases, the amount of iron at interstitial sites in the role of glass modifier increases, whereas the fraction of iron as FeO_4 at substitutional sites decreases. The IR spectra of heat treated samples (Figure 3) also show reduction in intensity at bands at 530 and 470 cm^{-1} , and is due to the fact that with increase of glass modifier in the system, most of the Fe_2O_3 gradually converts from FeO_4 to Fe^{3+} ions at interstitial positions. Hence, reduction in intensity at 530 and 470 cm^{-1} due to decrease in the number of FeO_4 polyhedra with increase of K_2O is expected.

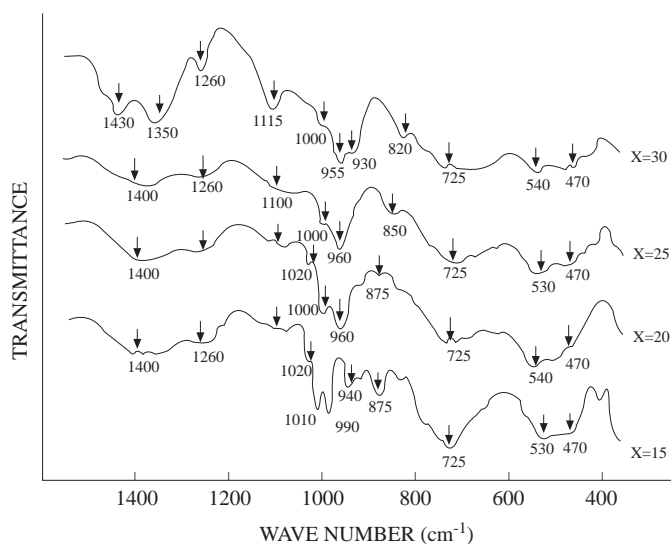


Figure 3. IR spectra of heat-treated glass samples from X=15 to 30 mole %.

As already discussed, in the absence of K_2O at low concentration, BO_3 and VO_5 are the main structural groups present in the glasses. If these two structural groups, BO_3 & VO_5 , certainly have a different demand for spatial arrangement in the glass structure, then the miscibility of B_2O_3 and V_2O_5 at low modifier concentration is limited and may tend to phase separate; but more detailed and proper studies are needed to confirm this. At high concentration of potassium oxide, the formation of VO_4 and BO_4 tetrahedra, as well as non-bridging oxygens attached to boron and vanadium, can contribute to the formation of a homogenous solid solution in the boro-vanadate-iron glass system. As the amount of iron oxide has been kept fixed, any change in the IR spectra due to iron oxide is not observed.

4. Conclusion

From the IR studies of potassium boro-vanadate-iron glass system, it is concluded that K_2O is found to have more preference for borate network when less than 20 mole % and is responsible for bringing about any changes initially in borate network and converts BO_3 units to four-fold coordination. Further addition of K_2O produces non-bridging oxygens in the borate as well as in the vanadate network along with the formation of VO_4 groups. The presence of tetrahedra of both boron and vanadium, thus formed, facilitates the formation of homogeneous and solid solution of the present glass system.

References

- [1] J.D. Mackenzie, *J. of American Ceram. Soc.*, **47** (1964) 211.
- [2] I.G. Austin & N.F. Mott, *Adv. Phys.* **18** (1969) 41.
- [3] T. Nishida, T. Hirai & Y. Takashiman, *Phys. Chem. Glasses*, **24** (5) (1983) 113.
- [4] H.R. Panchal & D.K. Kanchan, *Solid State Physics Symposium (Mumbai, India)* **39C** (1996) 218.
- [5] H.R. Panchal, D.K. Kanchan & D.R.S. Somayajulu, *J. of Material Science Forum*, **223-224** (1996) 301-306.
- [6] M. Regan & C.F. Drake, *Mat. Res. Bull.*, **6** (1971) 487.
- [7] M. Nagaswa & H. Watanabe, U.K. Patent, 1358930 (1971).
- [8] I. Wozniak & P.F. James, *Glass Technol.* **25**(2) (1984) 98.
- [9] S. Anderson, R.L. Bohon & D.D. Kimpton, *J. Amer. Ceram. Soc.* **38** (1955) 370.
- [10] P.E. Jellyman & J.P. Proctor, *Trans. Soc. Glass Technol.* **39** (1955) T173.
- [11] H.G. Bachman, F.R. Ahmed & W.H. Barnes, *Z. Kristallogr.* **115** (1961) 110.
- [12] L.D. Fredrickson & D.M. Hausen, *Analyt. Chem.* **35** (1963) 825.
- [13] L. Rivoalen, A. Revcolevschi, J. Livage & R. Collongues, *J. Non. Cryst. Solids*, **21** (1976) 171.
- [14] W. Vogel and N. Kriedle, *Chemistry of Glass*, Published by the American Ceramic Society Inc., Columbus, Ohio (1985).
- [15] Y. Dimitriev, V. Dimitrov, M. Arnaudov & D. Topalov, *J. Non. Cryst. Solids*, **57** (1983) 147.
- [16] A. Mossit, P. Lecante, J. Galy & J. Livage, *Phil. Marg.*, **B46** (1982) 137.
- [17] P.H. Bray, *J. Chem. Phys.*, **29** (1958) 984.

- [18] N. Kishore, T.K. Bansal, R. Kamal, R.G. Mendiratta, *J. Non. Cryst. Solids*, **69** (1985) 213.
- [19] R. Kamal, S.S. Shekhon, N. Kishore, R.G. Mendiratta, *J. Non Cryst. Solids*, **53** (1982) 227.
- [20] V. Dimitrov, Y. Dimitriev & V. Mihailova, *Monatshefte Fur Chemie*, **114** (1983) 669.
- [21] C.A. Hogarth & M.M. Ahmed, *J. Mat. Sci. Lett.*, **2** (1983) 649.
- [22] D.K. Kanchan, R.G. Mendiratta & R.K. Puri, *J. Mat. Sci.* **21** (1986) 2418.
- [23] T. Nishida and Y. Takashima, *J. Non. Cryst. Solids*, **94** (1987) 229.
- [24] D.K. Kanchan, H.R. Panchal & A.K. Gupta, *DAE Solid State Physics Symposium, Kochi, Kerala, India, 40C* (1997) 241.