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

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Abstract
The IR studies have been made in the K$_2$O-B$_2$O$_3$-V$_2$O$_5$-Fe$_2$O$_3$ glass system. The increase in intensity and shifting of vibrational bands towards lower wave number at 1400-1350 cm$^{-1}$, 1200 cm$^{-1}$ and 100-940 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$_2$O shows the preference for borate network up to 20 mole % and is responsible for bringing the changes in borate and vanadate networks. At higher amount of K$_2$O, 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$_2$O$_5$ based glasses exhibit switching and semiconducting properties [4, 5] and may be used for making stable switching devices [6, 7], whereas, B$_2$O$_3$-V$_2$O$_5$ 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 B₂O₃-V₂O₅ 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 K₂O on the structure.

2. Experimental

Analytical grade K₂CO₃, V₂O₅, H₃BO₃ and Fe₂O₃ were used as the raw materials. These were weighed in appropriate amounts to prepare glass samples: xK₂O: (95-x)(B₂O₃:2V₂O₅):5Fe₂O₃, 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 BO₃ triangles randomly oriented, sharing corners with each oxygen shared by two borons. When Na₂O is incorporated in the glass, some of the boron becomes tetrahedrally coordinated. The spectrum of fused B₂O₃ not only consisted of a completely continuous triangle-like coordinated network but contains some BO₄ tetrahedra as well. The absorption peaks at 1460, 1200 and 780 cm⁻¹ are related to BO₃ 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 BO₄ tetrahedra. The bands at 1220 to 1400 cm⁻¹ [9, 10] are characteristic of =B-O-B= 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 B₂O₃ and V₂O₅ is given in Figure 1 for the sake of comparison with that of the glasses. According to Bachman et.al. [11], the V₂O₅ structure is built up by deformed VO₅ trigonals bonded in zigzag chains. Each VO₅ group contains a short V=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 VO₅ 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$_2$O$_5$, B$_2$O$_3$ and Fe$_2$O$_3$.](image)

The IR spectra of all glass samples for K$_2$O=10 to 35 mole % are given in Figure 2. The main features of IR spectra are 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$_2$O increases. In pure borate glasses, the main structural element is the boroxol ring of plane triagonal configuration with a B-O bond length 1.36 ± 0.005 Å, whereas, the B-O bond length for BO$_4$ tetrahedra was observed to be 1.47 ± 0.01 Å. 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$_2$O does not break bridging in the BO$_3$ groups to form BO$_4$ tetrahedra. One K$_2$O 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$_2$O$_3$ and V$_2$O$_5$ 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$_2$O$_5$ and B$_2$O$_3$ [16, 17]. Due to these structural differences, the pure B$_2$O$_3$ and V$_2$O$_5$ do not form a single solid solution. It is also well established that the tendency of iron to dissolve into B$_2$O$_3$ in the absence of any modifier is negligibly small [18, 19], whereas, iron makes glass of a wide range, 0-50 mole %, with V$_2$O$_5$ [20]. Hence it is the modifier, K$_2$O, 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.
Further 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 $=B-O-B$ 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 %.](image)

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$_2$O-V$_2$O$_5$ [15], Fe$_2$O$_3$-V$_2$O$_5$ [20] and Na$_2$O-V$_2$O$_5$-Fe$_2$O$_3$ [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$_2$O 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 due 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 expected 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 eect of BO$_4$ and VO$_4$ units. The presence of very weak and wide absorption band between 800-650 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$_2$O = 10, 15 and 20 mole % the presence of a band at 1020 cm$^{-1}$ assigned to V=O bond indicates that the added K$_2$O probably has a greater preference for borate network and larger amount of the added K$_2$O 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$_2$O, is thus observed in the IR spectrum of the heat-treated samples. At higher amounts of K$_2$O, 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 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 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$_2$O$_3$ 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 %](image)

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$_2$O 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$_2$O 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

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