

EPR INVESTIGATION AND THERMAL STUDY OF $\gamma\text{A}_2\text{O}-(1-\gamma)[0.25(\text{WO}_3)_2-0.75(\text{P}_2\text{O}_5)]$ ($A=\text{Li}, \text{Na}$) GLASSES

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Glasses belonging to the series $\gamma\text{A}_2\text{O}-(1-\gamma)[0.25(\text{WO}_3)_2-0.75\text{P}_2\text{O}_5]$ ($\gamma=0.10-0.60$) are elaborated. DTA experiments reveal that the glass-network of the glasses are broken with increasing of modifier content. EPR spectra show the presence of two signals due to W^{5+} and Mo^{5+} , as impurities. The intensity of these EPR centres decreases when the concentration of A_2O increases. The variation of T_g upon the modifier content is ascribed to structural changes occurring in the matrix of these glasses.

Keywords: EPR spectra, glass transition temperature, phosphotungstate glasses

Introduction

The study of physical-chemical properties of tungsten oxide based glasses and ceramics is important due to the electro chromic effects observed in these materials [1], their application in microwave devices [2], and their semiconducting [3] and non-linear optical properties [4]. These features are based on the relative ease of tungsten to change valence states so that W^{6+} and W^{5+} ions are present in these materials.

Many transition-metal containing glasses have attracted attention because of the electronic properties and high ionic conductivities exhibited by their alkali doped glasses. WO_3 and MoO_3 are two transition metal oxides which form binary glasses with conventional glass forming oxides like P_2O_5 over a wide range of composition. In these glasses, hopping between W^{6+} and W^{5+} appears to be responsible for conduction. Addition of modifier oxide to a glass former involves the incorporation of oxygen atoms with the covalent network, thus becoming a macro anion. The mechanism of this incorporation chiefly depends upon the valency and the characteristic coordination chemistry of the glass former element.

The structure and the properties of the $\text{A}_2\text{O}-\text{A}_2\text{WO}_4-\text{P}_2\text{O}_5$ ($A=\text{Li}, \text{Na}$) [5] are depending strongly on the nature and the concentration of the constituent oxides. In these glasses, the modifier atoms cause the network to break and the phosphorus atoms retains its four coordination. In order to understand more about the effect of A_2O on the thermal properties of glasses insight the $\text{A}_2\text{O}-(\text{WO}_3)_2-\text{P}_2\text{O}_5$ systems, we have carried out the studies on $\gamma\text{A}_2\text{O}-(1-\gamma)[0.25(\text{WO}_3)_2-0.75\text{P}_2\text{O}_5]$ glasses.

Experiments

Alkali tungstophosphate $\gamma\text{A}_2\text{O}-(1-\gamma)[0.25(\text{WO}_3)_2-0.75\text{P}_2\text{O}_5]$ glasses of several compositions have been prepared starting from A_2CO_3 ($A=\text{Li}, \text{Na}$) (Merck 99.5%), $\text{NH}_4\text{H}_2\text{PO}_4$ (Merck, 99.5% and WO_3 (Merck 99.9%). Required quantities of the above materials were thoroughly mixed and heated in a platinum crucible to 650 K in an electrically heated muffle furnace for several hours in order to remove the volatile products. The samples were then melted and held at 1100–1200 K for a few hours with frequent stirring to ensure homogeneity. The melt was then poured on a stainless steel plate preheated at 450 K to avoid shattering of the quenched samples due to thermal stress. Finally the vitreous samples were annealed for 6 h at 550 K to relieve residual internal stress and slowly cooled to room temperature.

Selected samples were characterized by means of X-ray diffraction ($\lambda_{\text{CuK}\alpha}=1.54051 \text{ \AA}$) analysis, using a Seifert XRD 3000 diffractometer, differential thermal analysis (DTA), using a Seiko DTA thermal analysis with a heating rate of 10°C mn^{-1} and is accurate to $\pm 5^\circ\text{C}$. XRD analysis have shown that the samples under study consisted of amorphous phase. A structureless spectrum should be obtained for an amorphous sample. DTA scans permitted to find particularly the temperature of glass transition (T_g).

Results and discussion

In general, the properties of a glass depend upon its composition and to a considerable extent upon its struc-

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ture. Vitreous alkaline tungsten phosphates $A_2O-(WO_3)-P_2O_5$ ($A=Li, Na$) have a complex composition and are an admixture of network formers, intermediates and modifiers. P_2O_5 is a well-known network former with PO_4 structural units with one of the four oxygen atoms in PO_4 tetrahedron is doubly bonded to the phosphorus with a substantial π - bond character to account for the pentavalency of phosphorus. The PO_4 tetrahedrons are linked together with covalent bonding in chains or rings by bridging oxygens. Tungsten oxide belongs to the intermediate class forming oxides. It is an incipient glass network former and as such does not readily form the glass but does so in the presence of the modifier oxides. When the network modifier A_2O ($A=Li, Na$) is added, a change in the phosphate and/or tungstate units takes place. The modifier creates a negative charge on one of the bridging oxygens.

X-ray analysis of samples obtained by quenching revealed the presence of wide glassy range in the systems $A_2O-(WO_3)-P_2O_5$ ($A=Li, Na$) in agreement with previous works [5–7]. This range is divided into two parts, the first includes transparent glasses with a high A_2O contents, the second is wider, where the glasses are coloured and have a low A_2O content. In the glasses of the first region, the tungsten ions are mainly in the high valence state W^{6+} , the glasses of the second region, whose colour is due to the presence of W^{5+} ions, contain tungsten at different valence states (W^{5+} and W^{6+}). Therefore, these glasses could be mixed ionic-electronic conductors. On the contrary, those of the first region could be ionic conductors via Li^+ or Na^+ ions.

The analysis of the valency states of tungsten ions in glasses $yA_2O-(1-y)[0.25(WO_3)_2-0.75P_2O_5]$ was carried out by electron parametric resonance (EPR) spectroscopy. Whereas no EPR signals were observed in the colourless glasses (high y -values), EPR spectra have been obtained for the coloured glasses (low y -values).

The unreduced ion core W^{6+} is diamagnetic and hence cannot be detected directly by EPR, while the reduced ion W^{5+} has spin $S=1/2$ leading to single resonance line influenced by nuclear hyperfine interactions. The combined effect of this interaction and the interaction of adjacent paramagnetic species in an amorphous material result in a line shape which should be characteristic of each glass. Figures 1a and 1b show the EPR signals observed in lithium- and sodium-phosphotungstate glasses. These spectra are similar to those observed in $yLi_2O-0.1Li_2WO_4-(0.9-y)P_2O_5$ ($0.1 \leq y \leq 0.4$) glasses [5–9]. The corresponding paramagnetic centres are Mo^{5+} , as impurity and W^{5+} . One can observe that a weak intensity molybdenum signal shows a strong line resulting from the even-mass Mo isotopes ($I=0$) with an abundance ratio 74.32%, and less intense satellite lines, centred on the main line, corresponding to the odd-mass ^{95}Mo

and ^{97}Mo isotopes with $I=5/2$ and a total abundance 25.68%. Tungsten EPR signal exhibits a strong line associated with W ($I=0$), and weak shoulders attributed to hyperfine interaction with a single nucleus of the 14.28% abundant ^{183}W isotope ($I=1/2$). The spectra differ depending on whether the A_2O rate is low or high. In the former, W^{5+} signal is more intense compared to that of Mo^{5+} , while in the latter case the Mo^{5+} signal dominates spectrum.

The disappearance of the W^{5+} signal with increasing y -value can explain the change of the glass colour from deep-blue to light as A_2O oxide was increased in glasses. The persistence of the Mo^{5+} EPR signal at high modifier content is probably due to higher reducibility of Mo^{6+} than that of W^{6+} . For $y \geq 0.4$ in sodium glasses, the W^{5+} EPR signal has disappeared completely, and that of Mo^{5+} is greatly re-

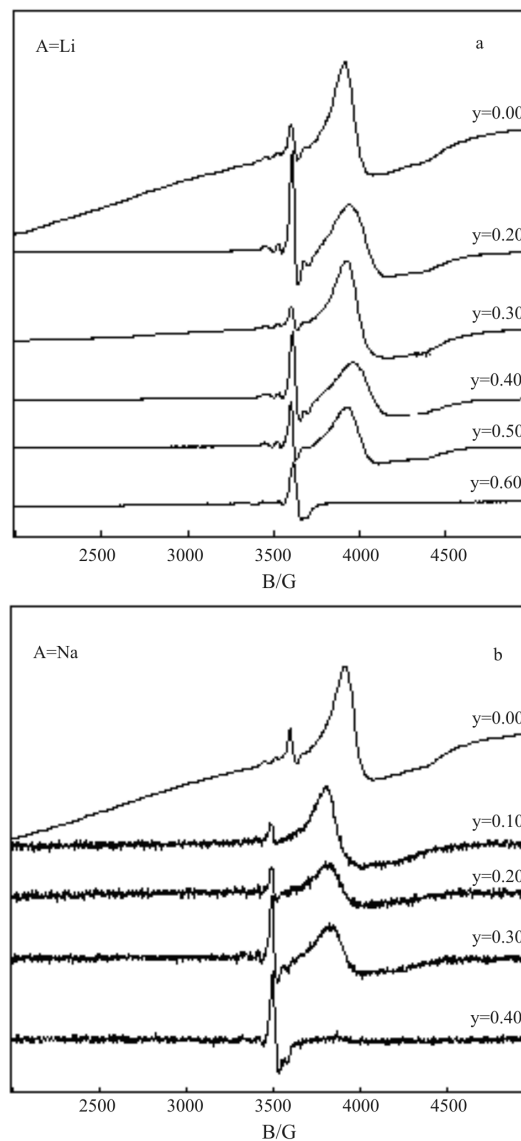
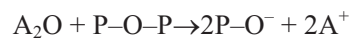


Fig. 1 EPR spectra of glasses $yA_2O-(1-y)[0.25(WO_3)_2-0.75P_2O_5]$: a – $A=Li$ and b – $A=Na$

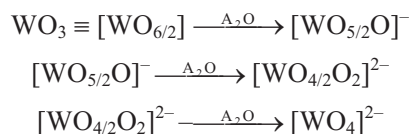
duced in intensity, but is still distinguishable. For the homologous lithium glass ($y=0.40$), both W^{5+} and Mo^{5+} signals are still observed, resulting in a smaller paramagnetic species for the sodium glass, in agreement with its less deep coloration. That larger aptitude of Na^+ ions to stabilize the valence +6 of tungsten justifies the disappearance of EPR signal in the sodium glasses with a high Na_2O content. A similar result has been already suggested for phosphomolybdate glasses [10]. Since W^{5+} and Mo^{5+} ions in the glass matrix increase the cross-link density [10], the presence of a larger number of paramagnetic species in lithium based glasses compared to that of sodium could have an effect on the composition dependence of the glass transition temperature. Particularly, we expect that T_g for the lithium glasses will be higher than that for corresponding sodium glasses.

The correlation between T_g and glass structure has been studied extensively. Generally, T_g of an oxide glass depends on bond strength, cross-link density and closeness of packing of the glass [11]. It seems reasonable to assume that the viscosity at a given temperature, and therefore T_g , will decrease when the fraction of ruptured bonds increases, so that T_g should increase with bond strength. For chains and two-dimensional network melts the only obvious impediment to relative motion of successive chains or network layers is the Van der Waals forces between the layers. In comparison, for three-dimensional networks, it seems entirely reasonable to assume that T_g will increase with mean cross-link density. In addition, it seems reasonable to assume that the ease with which flow can take place in a network depends upon the available free volume into which mobile ions or network segments can diffuse. So it has been proposed [11] that T_g will increase with the closeness of packing of the network. The cross-link density may be defined as the average number of bridging oxygen atoms excess of two per network forming atom [11]. The oxygen packing density, expressed as the number of gram atoms of oxygen per litre of glass, can be calculated from the density and the chemical composition [11]. The more open the macromolecular structure, the smaller the interval energy required to attain the mobility which is needed for the glass transition. Thus T_g decreases when the network becomes less tightly packed. Furthermore, binary $\text{WO}_3\text{-P}_2\text{O}_5$ glasses are built up of corner shared octahedral $[\text{WO}_6]$ and tetrahedral $[\text{POO}_{3/2}]$ units [12]. The three-dimensional network structure of such glasses is gradually broken down by the incorporation of alkali oxides in the ternary glasses. Modification requires the oxide ion of the modifier to reach the site where bond breaking takes place. Since O^{2-} ions carry a negative charge of two units, they drift towards a linkage where the

coulombic interaction is energetically favorable; coulombic interactions with the partial charges on the atoms in the linkage direct the position of the oxide ion corresponding to a minimum energy (maximum coulombic attraction and minimum coulombic repulsion). This is followed by bond breaking which results in the formation of non-bridging oxygens. Some of the strong covalent P-O and W-O bonds in the glass network would be expected to be replaced by weak ionic $\text{A}^+\dots\text{O}^-$ bonds as follows:



According to the above information, what do we anticipate will happen to T_g as A_2O is added to the $[0.25(\text{WO}_3)_2-0.75\text{P}_2\text{O}_5]$ glass and a covalent network (W-O-W and/or P-O-M, $M=\text{P}, \text{W}$) is likely replaced by ionically $\text{A}^+\dots\text{O}^-$ bonds? We anticipate both for sodium and lithium-glasses that T_g will decrease with A_2O content across the entire composition range studied. Effectively, the results plotted in Fig. 2 for the glasses $y\text{A}_2\text{O}-(1-y)[0.25(\text{WO}_3)_2-0.75\text{P}_2\text{O}_5]$ show that T_g decreases with increasing A_2O ($A=\text{Li}, \text{Na}$) content. This variation of T_g is in agreement with the results obtained by EPR spectroscopy. These trends in the glass transition temperature naturally indicate that T_g is in some way influenced by the three parameters discussed above. Firstly, a ternary $\text{A}_2\text{O}-(\text{WO}_3)_2\text{-P}_2\text{O}_5$ ($A=\text{Li}, \text{Na}$) glass would have lower mean bond strength than a binary $(\text{WO}_3)_2\text{-P}_2\text{O}_5$ glass with the same P_2O_5 to (WO_3) ratio, since same strong covalent P-O and W-O bonds would be replaced by weak ionic $\text{A}^+\dots\text{O}^-$ bonds. Secondly, it is evident from the Fig. 3 that the oxygen packing and T_g decrease with the increase in A_2O content implying that they may be related to each other. This variation of T_g with A_2O content is expected. If the vitreous matrix contains enough voids, only a small internal energy for the chain mobility is needed for the glass transition. Hence the T_g decreases when the network becomes less tightly packed (Fig. 3). Lastly, in an alkali phosphate glass the classic concept of the function of alkaline oxide is to provide oxygen that enters the phosphorus-oxygen network to form singly bonded oxygen [11]. It was concluded that in phosphotungstate glasses [5], P-O-P units were preferentially modified to produce P-O $^-$ units; on the other hand, WO_3 in modified phosphotungstates could exhibit the following tendency [13]:



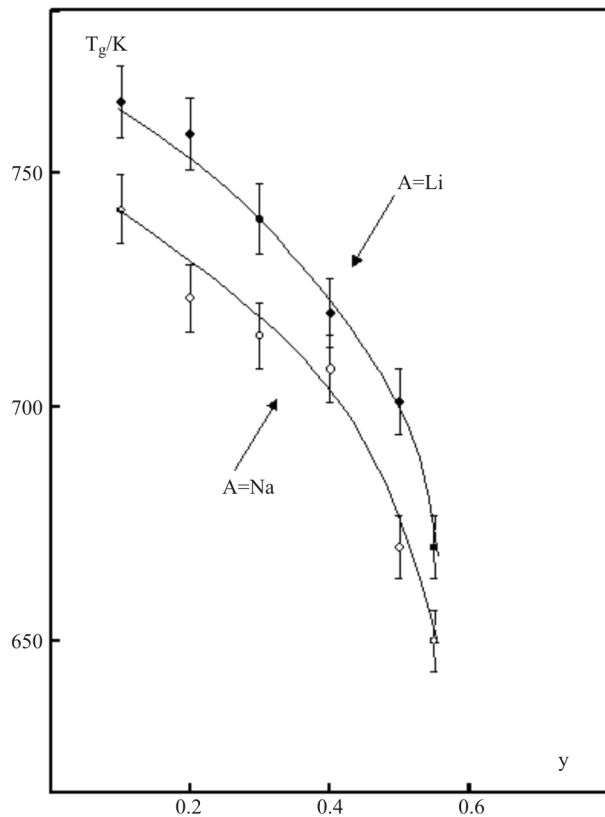


Fig. 2 Transition temperature (T_g) as a function of the A_2O content

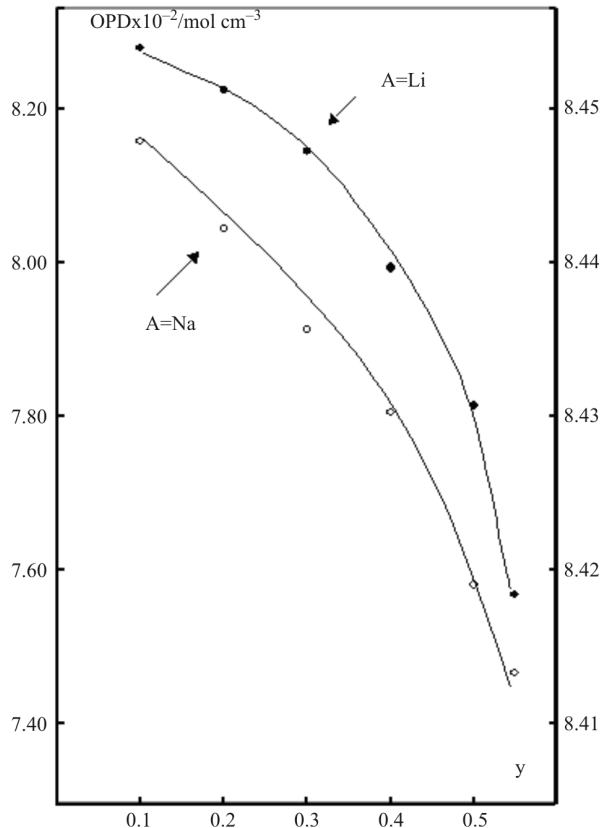


Fig. 3 Oxygen packing density (OPD) as a function of the A_2O content

Both these structural changes, occurring on phosphate and tungstate units, indicate that the mean values of cross-link density could decrease with increasing modifier content. It appears consequently that the decreasing of T_g with increasing A_2O content, in the glasses under study, results from the concomitant decreasing of the mean bond strength, oxygen packing density and cross-link density.

Conclusions

Alkali phosphotungstate glasses inside the ternary $A_2O-(WO_3)_2-P_2O_5$ ($A=Li, Na$) systems have been studied with EPR and DTA analysis. The composition dependence of the glass transition temperature T_g has been investigated along the series of glasses $yA_2O-(1-y)[0.25(WO_3)_2-0.75P_2O_5]$ ($A=Li, Na$). Results show that T_g data can be understood in terms of the structural units, cross-link density, mean bond strength and the oxygen packing density of the glass network. The composition dependence of T_g is confirmed by EPR investigation.

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