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ABSTRACT

60% P2O5–30%V2O5–10%X where X is Li2O, Na2O, K2O, and BaO glass system were prepared by the melt-quenching technique. The produced glass were checked by x-ray to ensure the glassy state. Glass transition temperature, crystallization temperature, glass thermal stability, glass formability and electrical conductivity were measured and calculated. All the above mentioned properties decreases with increasing the ionic radius of the doped oxides. The results suggested the modifier position of the doped oxides.

INTRODUCTION

Considerable research has been done on vanadium phosphate glasses due to its interesting semiconducting properties and their applicability in electronic devices. The hopping mechanism between different states of transition metal ions were used to explain the electrical properties of vanadium phosphate glasses and the effect of heat treatment on crystallization also discussed(1). Magnetic susceptibility, x-ray diffraction, infrared, electrical conductivity and structural studies were done on vanadium phosphate glasses (2-9). The electrical conductivity were discussed according to hopping mechanism between two different ion states \(v^{4+}\) and \(v^{5+}\). Magnetic susceptibility were explained in relation to paramagnetic behavior of \(v^{4+}\) and diamagnetic behavior of \(v^{5+}\). Infrared studies confirms the presence of both \(v^{4+}\) and \(v^{5+}\). The main separated phase on crystallization process of vanadium glasses was \(V_2O_5\). Differential thermal analysis (DTA) is a technique for determining the temperatures of the phase transitions like melting point, solidification, re-crystallization and evaporation temperature. DTA curves can record the transformations where the heat is either absorbed or released (dehydration, decarbonation, burning of materials, ordering etc. (10). Glass transition temperature (TG) of silver phosphate glasses undoped and doped with transition metal halides were studied (11). TG of doped glasses are higher than those undoped glasses. The increasing of TG with increasing Cd/Zn halides concentration were attributed to the increasing of cross link density. TG of doped glasses with Cadmium halides are higher than those glasses doped with Zinc halides. TG values of silver phosphate glasses doped with Cd and/or Zn halides follow the decreasing order (\(Cl > Br > I\)). The decreasing order were explained on basis of ionic size, the increasing size of halide ions (\(I^− > Br^− > Cl^−\)) loosen the glass structure to greater extent and thereby the TG values are lowered as ne goes from Chloride to Iodide. DTA studies of PbO-PbF2-B2O3 glass system doped with V2O5 was studied (12). The good homogeneity of the prepared glasses were proved by the presence of one TG and one crystallization temperature. The change of TC, crystallization temperature (TC), glass forming ability \(K_{g1}\) and glass thermal stability (GTS) values were attributed to the variation of valance state of vanadium ions and its position in the glass network. The GTS of 20CaO-10ZnO-59.9P2O5-10Pb2O5-1x, (x= V2O5, Cr2O3, MnO and CuO) were studied (13). DSC curves shows endothermic and exothermic changes due to TG and TC. The calculation of GTS shows that glass containing vanadium oxide is most stable one. DTA of (MnO)x(P2O5)100−x(ZnO)x glass system were studied (14). The presence of one single peak attributed to the TG indicates the homogeneity of the prepared glasses and TG is not affected by ZnO addition. The GTS, \(K_{g1}\) decreases while the fragility index increases with increasing manganese oxide. Thermal

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properties of oxy-chloride bismuth-borate glasses doped with vanadium oxide were studied (15). The higher TG and GTS the higher density of the studied glasses. DTA of glasses with composition (30- x) Li₂O·xV₂O₅·20B₂O₃·50B₂O₃ (x=15, 10, 5) has been carried out in order to study the effect of replacing the Transition Metal Oxide with alkali oxide (16). The TG, the TC and K_{grl} decreases with replacing alkali oxide with transition metal oxide of the glasses which confirms that the glass become more fragile.

**Experimental**

Glass system with molar composition (60% P₂O₅– 30%V₂O₅– 10%X) where X is Li₂O, Na₂O, K₂O, and BaO was prepared from reagent grade chemicals (99% purity). Vanadium pentoxide (V₂O₅), ammonium dihydrogen orthophosphate (NH₄H₂PO₄), lithium carbonate (Li₂CO₃), sodium carbonate (Na₂CO₃), potassium carbonate (K₂CO₃), and barium carbonate (BaCO₃) were thoroughly mixed in a porcelain crucible and melted at 1200 °C for 3 h in a muffle furnace until a homogeneous melt was obtained. The melt was then quickly quenched to room temperature. Powder X-ray diffraction was performed on samples and the results showed that they were purely non-crystalline. The DC electrical conductivity measurements were carried out using Keithely 617 electrometer with range from 10 to 10⁻¹⁶ A. Discs about 2 mm thickness were used. The parallel surfaces were coated with silver paste to serve as electrodes. The thermal behavior of glass samples was carried out using a PerkinElmer TG/DTA 6300 thermal analyzer under Ar gas atmosphere. About 20mg of bulk glass was heated in Pt-holder with another Pt-holder containing α-alumina as a reference material. The DTA traces were recorded at heating rates 10 °C/min.

**RESULTS AND DISCUSSIONS**

In previous work (17) the density, the molar volume, the IR spectra, temperature dependence on electrical conductivity and magnetic susceptibility of the same glass system were carried out. The electrical conductivity results shoes semiconducting behavior and were explained according to non-adiabatic hopping mechanism of small polaron hopping conduction. The density and magnetic susceptibility decreases while the molar volume increases with increasing ionic radius of doped oxides. The hopping distance is given by (18)

\[ R = (4\pi N/3)^{-1/3} \]  

Where N is the number of transition metal ion per unit volume. The hopping distance and electrical conductivity at room temperature are shown in figs (1, 2).

The conductivity decreases while the hopping distance increases with increasing ionic radius of doped oxides, which confirms the modifier position of doped oxides, and the expansion of the glass network depends on the ionic radius of the doped oxides. These results are in agree with molar volume results (17). DTA and TGA results are shown in fig (3) and summarized in table 1. DTA curve exhibits three peaks (two endothermic peaks according to GT, melting temperature (TM) and exothermic peak according to TC). Presence of one peak of each temperature confirms the homogeneity and one phase of the prepared glasses (12, 14). The weight loss at the first stage can be attributed to the evaporation and dehydration of water on the sample surface, while the weight loss at the second stage may be attributed to combustion of residual organics probably predisposes to crystallization process and to the decomposition of the samples during crystallization process (14, 19). The glass transition temperature is given by (13)

\[ GTS = TC - TG \]  

Dependence of GT, TC and GTS on doping oxides are shown in figs (4, 5, 6). Thermal stability of glasses is an important property both fundamentally and technologically. It is a measure of degree of disorder of glassy state. In all curves one can see the decreasing of all measured and calculated parameters. This decreasing may be attributed to decreasing of oxygen packing density in the glass network, compactness of the samples, decreasing of cross link density, decreasing the number and strength of the cross-link between the cation and...
the oxygen atom and creating voids in the structure (15, 17, 20, 21). The decrease in the above mentioned parameters are confirmed by the decreasing of the density and increasing of the molar volume in previous study (17). Fig (7) shows the dependence of doping oxide on $K_{gl}$, which given by

$$K_{gl} = \frac{TC - TG}{TM - TC}$$

Figure 4 Dependence of glass transition temperature on doping oxides.

Figure 5 Dependence of crystallization temperature on doping oxides.

The higher value of $(T_c - T_g)$ delay the nucleation process and devitrification of the glass while the higher value of $(T_m - T_c)$ increases the nucleation and enhance the crystallization of glasses (22, 23). Glass-forming ability can be determining in order to compare devitrification tendency of the glass. The decreases of the thermal stability and the glass-forming ability with increasing ionic radius of doping oxide suggests high tendency of crystallization and the glasses become more fragile with increasing ionic radius (16, 20). Our results (the decreasing of all measured and calculated parameters except the hoping distance which increased) are in good agreement with the results carried out by Yang Li.et.al and H. Desirena.et.al (24, 25). They concluded that the decreasing of thermal parameters are related to the field strength of cation ions. The cation field strength increase with decreasing the ionic radius, which in turn increase the cross link density, and the glass network became stronger. This mechanism of compactness the glass network decrease all measured and calculated thermal parameter.

CONCLUSIONS

The decreasing of all measured and calculated properties except the hoping distance, which increases, with increasing ionic radii confirms the modifier position of the different oxides in the glass network. This behavior is attributed to the decreasing of cation field strength, density and increasing of molar volume.

<table>
<thead>
<tr>
<th>Element</th>
<th>TG</th>
<th>TC</th>
<th>$T_m$</th>
<th>$T_c$-TG</th>
<th>$K_{gl}$</th>
<th>Weight loss %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>122</td>
<td>590</td>
<td>950</td>
<td>360</td>
<td>1.3</td>
<td>-2.4</td>
</tr>
<tr>
<td>Na</td>
<td>110</td>
<td>580</td>
<td>940</td>
<td>360</td>
<td>1.29</td>
<td>-3.1</td>
</tr>
<tr>
<td>K</td>
<td>85</td>
<td>555</td>
<td>930</td>
<td>375</td>
<td>1.23</td>
<td>-5.2</td>
</tr>
<tr>
<td>Ba</td>
<td>79</td>
<td>550</td>
<td>925</td>
<td>375</td>
<td>1.22</td>
<td>-6.1</td>
</tr>
</tbody>
</table>

The higher value of $(T_c - T_g)$ delay the nucleation process and devitrification of the glass while the higher value of $(T_m - T_c)$ increases the nucleation and enhance the crystallization of glasses (22, 23). Glass-forming ability can be determining in order to compare devitrification tendency of the glass. The decreases of the thermal stability and the glass-forming ability with increasing ionic radius of doping oxide suggests high tendency of crystallization and the glasses become more fragile with increasing ionic radius (16, 20). Our results (the decreasing of all measured and calculated parameters except the hoping distance which increased) are in good agreement with the results carried out by Yang Li.et.al and H. Desirena.et.al (24, 25). They concluded that the decreasing of thermal parameters are related to the field strength of cation ions. The cation field strength increase with decreasing the ionic radius, which in turn increase the cross link density, and the glass network became stronger. This mechanism of compactness the glass network decrease all measured and calculated thermal parameter.

References

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