INVESTIGATION OF ELECTRICAL CONDUCTION IN VANADATE BASED GLASSES

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The binary glassy systems $60\text{V}_2\text{O}_5-(40-x)\text{P}_2\text{O}_5-x\text{B}_2\text{O}_3$ were prepared by melt quenching technique. The mole of B_2O_3 was varies from 5 to 20 mol % with constant mol % of V_2O_5 during preparation of glass samples. The dc electrical conductivity of samples was measured in temperature range 303-473 K and found to be higher for sample 60 V_2O_5 -20 P_2O_5 -20 B_2O_3 . Using the Arrhenius equation of conductivity, the activation energy of conduction is estimated. The conduction in these glasses is takes place by phonon-assisted hopping between the localized states.

Keywords: Glass; Ceramics; Electrical conduction

1. Introduction

Fast ion-conducting glasses have been paid considerable attention for the recent past for their potential applications in solid state electrochemical devices, such as batteries, sensors, etc. There are many experimental and theoretical reports on ion conduction of these fast ion-conducting glasses. However, the conduction mechanism of these glasses is not properly understood yet because of the difficulty in separating the contribution of the ion concentration and mobility from the measured conductivity¹⁻³. Glasses containing large amounts of transition metal oxides exhibit electronic conductivity. Their electrical properties are determined by the presence of the transition metal ions in two different valence states and the conductivity is described by the mechanism of small polaron hopping between such ions⁴.

The structure of V_2O_5 is built of octahedrons, where the pentavalent vanadium has 5-coordination with oxygen atoms, the V_2O_5 -rich glasses in which V_2O_5 acts as the network former have the network structure mainly consisting of corner-sharing branched VO_4 tetrahedral of the same structural units as found in phosphate glasses. The network structure was reported to be made-up unaffected VO_5 groups as in vitreous V_2O_5 and affected VO_5 groups with alkaline earth ions in contrast to the vanadate glasses formed by conventional network formers in which only unaffected VO_5 groups are present. These glasses are known to contain V^{4+} and V^{5+} ions where the electrical conduction was

attributed to the hopping of 3d1 unpaired electron from V^{4+} to V^{5+} site, which induces a polarization of the vanadium ion around it and forms a polarons. Vanadate has received greater attention as a new branch in semi-conducting glasses because of its wider glass-forming region in the phase diagram and its possible technological applications in threshold switching, memory switching, electrical threshold, electrochemical batteries and optical switching devices ⁵⁻⁶.

B_2O_3 glasses are found to be very interesting amorphous materials whenever the specific structure and physical properties of which taken into consideration. In these glasses, two groups of bands are obtained: (i) due to trigonal BO_3 and (ii) due to the tetrahedral BO_4 units. By the addition of transition metal ions to the borate glasses, they would exhibit specific physical properties ⁷⁻⁹.

In the present work, glass samples of $60 V_2O_5-(40-x) P_2O_5 -x B_2O_3$ are prepared by melt-quenching method. The dc conductivity is investigated for synthesized glass system. The optical properties studied form FTIR analysis. The glass sample was characterized by XRD.

2. Experimental

The glass sample of $60 V_2O_5-(40-x)P_2O_5 -x B_2O_3$ with $x = 5, 10$ and 20 mol % were prepared by the melt quenching technique. Required quantities of V_2O_5 , P_2O_5 and H_3BO_3 were mixed together by grinding the mixture repeatedly to obtain a fine powder. The mixture was dried at 373 K for 30 min. Then the mixture was melted in a silica crucible in an electrically heated furnace under ordinary atmospheric conditions at a temperature of about 1100 K for 3 h to homogenize the melt and the melts was stirred to remove CO_2 . The melted mixture was poured on mercury leveled 2×1 cm² silica substrate to form bulk glass. For electrical contact, the silver electrodes were deposited on adjacent sides. The samples were kept at 400 K for drying the silver contacts. The X-ray diffraction pattern was recorded on Rigaku X-ray diffractometer using Cu $K\alpha$ radiation ($\lambda = 1.54$ Å). The diffractogram was in terms of 2θ in the range 10° – 70° . The FTIR transmission spectra of the glasses in the 400 – 4000 cm⁻¹ spectral range were obtained with a Shimadzu FT-IR spectrometer, using the KBr pellet technique. The temperature dependence of the electrical conductivity was measured by using two probe methods.

3. Results and Discussion

3.1. X-Ray diffraction (XRD) analysis

Fig. 1 shows the X-ray patterns of $60 V_2O_5-(40-x)P_2O_5 -x B_2O_3$ with $x=5, 10$ and 20 mol % glass ceramic. The XRD spectra of sample was recorded between $2\theta= 10$ – 90° . The X-ray pattern of sample shows noisy spectra and the peak was observed at the position 25° which is attributed to the amorphous halos nature of glass ceramics.

Fig. 1. XRD of 60 V_2O_5 -(40-x) P_2O_5 -x B_2O_3 (a)x=5, (b)x=10 and (c)x=20

3.2. FTIR analysis

FTIR have been carried out on powdered samples dispersed in KBr pellets and shown in Fig. 2 for the range 400–4000 cm^{-1} . For all glasses, water band around 3400 cm^{-1} and –OH stretching peaks around 2400 cm^{-1} were observed. A peak was observed at 1646 cm^{-1} for all glasses and is independent of the concentration of the constituents of the glasses. The origin of these peaks is not obvious, but the –OH bending mode gives rise to absorption in this region and the possibility of some adsorbed water giving rise to these peaks cannot be ruled out. Hence, the bands observed in the range 1600–3400 cm^{-1} are possibly due to the hygroscopic nature of powdered samples. The first group of bands that occurs from 1200 to 1600 cm^{-1} is due to the asymmetric stretching–relaxation of the B–O bond of triangle BO_3 units. The second group lies between 900 and 1200 cm^{-1} and is

Fig. 2. FTIR spectra of 60 V_2O_5 -(40-x) P_2O_5 -x B_2O_3 (a) x=5, (b) x=10 and (c) x=20

due to B–O bond stretching of the tetrahedral BO_4 units. The third group is around 800 and 900 cm^{-1} and is due to the bending of B–O–B linkages in borate networks. The strong band observed for V_2O_5 at 1019 cm^{-1} , which was reported at 1020 cm^{-1} by previous studies, has been assigned to the vibration of the isolated $\text{V}=\text{O}$ non-bridge bonds in the VO_5 trigonal bipyramids¹⁰. The absorption peaks at 1192, 1445, 1537, and 1549 cm^{-1} are related with the fundamental asymmetrical stretching vibration of the B–O bond of the trigonal BO_3 units^{11,12}.

3.3. Temperature dependence of dc conductivity

In general for a semiconducting materials, dc conductivity increases exponentially with temperature indicating that the conductivity is a thermally activated process. Mathematically, it can be expressed by the well-known Arrhenius relation as

$$\sigma_{\text{dc}} = \sigma_0 \exp(-E_{\text{dc}}/KT) \quad (1)$$

where σ_0 is called pre-exponential factor, E_{dc} is called the activation energy, T is the absolute temperature and k is Boltzmann constant. These parameters are of significance to differentiate the nature of various conduction mechanisms. Fig. 3 shows temperature dependence of dc Conductivity (σ_{dc}), for 60 V_2O_5 -(40- x) P_2O_5 - x B_2O_3 with $x=5, 10$ and 20 mol % respectively. From the figure, it is clear that the dc conductivity (σ_{dc}) varies exponentially with temperature, as $\ln\sigma_{\text{dc}}$ vs. $1000/T$ curves are straight lines. Such behavior is consistent with equation (1). It is observed that the dc conductivity for all the glass compositions increases with the increase in temperature, indicating typical semi conducting behavior. The values of electrical parameters σ_{dc} , E_{dc} and σ_0 are listed in Table 1. From this we can say that the conduction occurs by phonon-assisted hopping between the localized states. The electrical conduction of the samples follows a mechanism in which the electron or hole hops from one localized site to the next.

Fig. 3. Temperature dependent conductivity of 60 V_2O_5 -(40- x) P_2O_5 - x B_2O_3

Table 1. dc conductivity (σ), activation energy(E_{dc}), pre-exponential factor (σ_0)

Sample	$\sigma_{dc}(S.Cm^{-1})$ at R.T.	$\sigma_{dc}(S.Cm^{-1})$ at 473 K	$E_{dc}(eV)$	σ_0
60V ₂ O ₅ -35P ₂ O ₅ -5 B ₂ O ₃	2.2469x10 ⁻⁷	7.83388x10 ⁻⁵	0.491	2.017784
60 V ₂ O ₅ -30P ₂ O ₅ -10 B ₂ O ₃	2.3877x10 ⁻⁷	1.19982x10 ⁻⁴	0.459	6.820958
60 V ₂ O ₅ -20P ₂ O ₅ -20 B ₂ O ₃	3.763868x10 ⁻⁷	3.17927x10 ⁻⁴	0.378	56.20468

Whenever it is transferred to another site, the surrounding molecules respond to this perturbation with structural changes and the electron or hole is temporarily trapped in the potential well leading to atomic polarization. The electron resides at this site until it is thermally activated to migrate to another site.

4. Conclusions

The binary glassy systems 60 V₂O₅-(40-x)P₂O₅ -xB₂O₃ were prepared by melt quenching technique. The value of conductivity at room temperature was found to be higher for 20 mol % B₂O₃. The activation energy value was observed to be lower as compare to others. This represents the theoretical agreement. The XRD study reveals that glassy systems shows the amorphous nature. The chemical composition in the system was confirmed through FTIR analysis.

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References

1. St. Adams and J. Swenson, "Relaxation dynamics in AgI-doped silver vanadate superionic glasses", *Phys. Rev. Lett.* **84**, 4144 (2000).
2. St. Adams and J. Swenson, *Phys. Rev.*, **B 63**, 54201 (2000).
3. S. Bhattacharya and A. Ghosh, "Conductivity relaxation in some fast ion-conducting AgI-Ag₂O-V₂O₅ glasses", *Solid State Ionics* **161**, 61–65 (2003).
4. R.J. Barczyński, P. Król and L. Murawski, "Ac and dc conductivities in V₂O₅-P₂O₅ glasses containing alkaline ions", *Journal of Non-Crystalline Solids* **356**, 1965–1967 (2010).
5. R.V. Barde and S.A. Waghuley, "dc Electrical conductivity of V₂O₅-P₂O₅ binary glassy systems", *J. Phys.:Conference Series*, **365**, 012019 (2012).
6. R.V. Barde and S.A. Waghuley, "V₂O₅-P₂O₅ Glass Ceramic as a Resistive Solid-State CO₂ Gas Sensor", *Asian Journal of Chemistry*; Vol. 24, No. **12**, 5622-5624 (2012).
7. A. Terczynska-Madej, K. Cholewa-Kowalska and M. Laczka, "The effect of silicate network modifiers on colour and electron spectra of transition metal ions", *Opt. Mater.* **32**, (11) 1456 (2010).

8. P. V. Reddy, C. Laxmikanth, V. Prasanth Kumar, N. Veeraiah and P. Kistaiah, "Optical and thermoluminescence properties of R_2O - RF - B_2O_3 glass systems doped with MnO ", *J. Non-Cryst. Solids* **351**, 3752 (2005).
9. A. Ramesh Babu, Ch. RajyaSree, P.M. Vinaya Teja, S. Yusub and D. Krishna Rao, "Influence of manganese ions on spectroscopic and dielectric properties of LiF - SrO - B_2O_3 glasses", *Journal of Non-Crystalline Solids* **358**, 1391–1398 (2012).
10. G.D. Khattak and A. Mekki, "Structure and electrical properties of SrO -borovanadate
11. $(V_2O_5)_{0.5}(SrO)_{0.5}(B_2O_3)_y$ glasses", *J. of Phys. and Chem. of Solids* **70**, 1330–1336 (2009).
12. Y. D. Yiannopoulos, G. D. Chryssikos and E. I. Kamitsos, "Structure and properties of alkaline earth borate glasses", *Physics and Chemistry of Glasses*, **42** (3), 164–172(2001).
13. E. E. Horopanitis and G. Perentzis, A. Beck, L. Guzzi, G. Peto, and L. Papadimitriou, "Structural and Physical Properties of Fe_2O_3 - B_2O_3 - V_2O_5 Glasses", *J. of Non-Crystalline Solids*, **354**, 374–379 (2008).