dc Electrical conductivity of V$_2$O$_5$-P$_2$O$_5$ binary glassy systems

R. V. Barde$^a$ and S.A. Waghuley$^b$
$^a$Dept. of Engg. Physics, H.V.P.M. College of Engg. & Technology, Amravati 444 601, India.
$^b$Department of Physics, Sant Gadge Baba Amravati University, Amravati 444 602, India.

Corresponding author(s) e- mail: rajesh_barde@indiatimes.com, sawaghuley@indiatimes.com

Abstract. Electrical conductivity of V$_2$O$_5$-P$_2$O$_5$ binary glassy systems prepared by melt quenching technique was studied in temperature range 303-470 K. The mole of P$_2$O$_5$ was varied from 0.2-1 M with constant 1 M V$_2$O$_5$ in the preparation of glass samples. The dc electrical conductivity of samples was measured and found to be higher for sample 1:0.2 M V$_2$O$_5$-P$_2$O$_5$. Using the Arrhenius equation of conductivity, the activation energy of conduction is evaluated. The conduction in these glasses takes place by the transfer of electron from V$^{4+}$ to V$^{5+}$ ions.

1. Introduction

Glassy electrolytes are of particular importance because of their inherent advantages such as isotropic conductivity, ease of preparation, better thermal stability, the large available composition ranges which make them potential candidates for technological applications (new solid-state batteries, fuel cells, chemical sensors, “smart windows”), and also the search for a general theory of ion-transport in glassy materials [1]. Transition metal oxides such as V$_2$O$_5$, P$_2$O$_5$ etc can form glasses when mixed with glass forming oxides. Electrical conduction of glasses containing transition metal oxides (TMO) is known to be semi-conducting. The dc conduction in TMO glasses is the reason of transfer of electron from lower valance to higher valance state of transition metal ions. Small polarons are charge carriers trapped by self-induced lattice distortions that extend over the near surrounding. Generally small polarons hopping model can explain the dc conduction and transport properties of vanadate glasses. The strong interaction of electrons with ions produces the localization and the formation of polarons in the vanadium glasses [2-5]. The small polarons theory has been extensively used to describe the electrical properties of a wide range of TMO glasses, the best agreement between experiment and theory has been found for vanadate glasses such as V$_2$O$_5$-P$_2$O$_5$. It appears probable that the electrical properties of all the 3d transition-metal oxide phosphate glasses will not succumb to a single theory. The experimental determination of activation energies from the electrical conductivity ($\sigma$), as a function of temperature (T), is sometimes different; the Arrhenius plot (ln $\sigma$ versus 1000/T) may not be linear. This may be due to process involving several similar activation energies, conduction by polarons or variable range hopping of carriers [6].

In the present work, the electrical conductivity of V$_2$O$_5$-P$_2$O$_5$ binary glassy systems prepared by melt quenching technique was studied in temperature range 303-470 K by varying the mol% P2O5. The glass sample was characterized by XRD.
2. Experimental
The glass sample of V$_2$O$_5$-P$_2$O$_5$ in which mole of P$_2$O$_5$ was varies from 0.2-1 M with constant 1 M V$_2$O$_5$ was prepared by the melt quenching technique. The required quantities of V$_2$O$_5$ and P$_2$O$_5$ were mixed together by grinding the mixture repeatedly to obtain a fine powder. The mixture was dried at 373 K for 30 min. Then 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. The melted mixture was poured on mercury leveled 2×1 cm$^2$ silica substrate to form bulk glass. For electrical contact, the two opposite faces of the sample were coated with silver paste. The sample was kept at 400 K for drying the electrical contacts. For dc characteristics measurement, the sample was mounted on a sample holder, the temperature of which can be varied over the range 303-473 K. The X-ray diffraction pattern of sample 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°–90°.

3. Results and Discussion
3.1. X-Ray diffraction (XRD) analysis
Fig. 1 shows the X-ray patterns of V$_2$O$_5$-P$_2$O$_5$ glass ceramic. The XRD spectra of sample was recorded between 2θ= 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.

![Figure 1](image1.png)  
**Figure 1.** XRD spectra of 0.2 mol% P$_2$O$_5$ glass ceramic.

![Figure 2](image2.png)  
**Figure 2.** Temperature dependence of dc conductivity (σ) for different mole % of P$_2$O$_5$.
3.2. DC conductivity

The DC electrical conductivity of the sample was measured in temperature range of 303–345K and the conductivity curve is shown in Fig. 2. The conductivity data may be fitted to straight lines, where conductivity can be analyzed by an Arrhenius equation of the form

$$\sigma = \sigma_0 \exp\left(-\frac{\Delta E}{kT}\right)$$

(1)

where, $\sigma_0$ is the pre-exponential factor and $\Delta E$ is the activation energy for conduction. The activation energy and the pre-exponential factor were determined for each conduction region as shown.

In many cases, the electrical conduction in glasses has been proved to be electronic in nature. The conduction process is believed to occur by electron hopping between the ions existing in different valence states in the glass. Fig. 2 clearly gives the linear relationship between $\ln(\sigma)$ and $1000/T$. The slope of the curves, which gives the activation energy for conduction, however, has two different values, and increases towards higher temperatures. According to Austin and Mott [7], the electrical conductivity and temperature for the glass is related by Arrhenius equation. In Fig. 2, the dc conductivity varied linearly against 1000/T at the two temperature regions, indicating that the conduction of the present system is mainly electronic [8]. The higher value of conductivity at room temperature (303 K) was found to be $2.53 \times 10^{-5}$ S cm$^{-1}$ for 0.2 mole % P$_2$O$_5$ glass. This is the lower value of activation energy as compared to others. This shows the agreement with theoretical aspects. The conductivity of all the samples increases with the temperature. The values of activation energies are calculated at two temperature regions. The region I and region II are assigned for the low and high temperature. The activation energy for 0.2 mole % P$_2$O$_5$ for region I was found to be 0.38 eV and that for region II, 0.19 eV.

These two activation energies are associated with the intramolecular and the intermolecular conductivity process. Particularly, the lower values of $\Delta E$ are associated with the intermolecular conduction process, while the higher values are related to the intramolecular conduction process. In this sample, there are two stages in the movement of carrier motion within the sample, which are the intramolecular and intermolecular transfer of the current carrier. In the intramolecular transfer of electrons, electrons can hop from one atomic site to another if orbitals exist at these sites with the same energy levels. In the case of intermolecular orbital overlap, electrons or holes can travel from one kind of macromolecule to another [9]. The electrical conduction is controlled by strong electron phonon interaction and result in the formation of small polarons between V$^{4+}$ to V$^{5+}$ ions.

4. Conclusions

In binary glassy system V$_2$O$_5$-P$_2$O$_5$, the value of conductivity at room temperature was found to be higher for 0.2 mole % P$_2$O$_5$. The activation energy value was observed to be lower as compared to others. The XRD study reveals that the amorphous nature of 0.2 mole % P$_2$O$_5$ glass. The region I and region II are assigned for the low and high temperature. The activation energy for 0.2 mole % P$_2$O$_5$ for region I was found to be 0.38 eV and that for region II, 0.19 eV.

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References

[1] Nascimento M L F, Nascimento E, Pontuschka W M, Matsuoka M and Watanabe S 2006 Ceramica 52 22
[2] Sreenivasu D and Chandramouli V 2000 Bull. Mater. Sci. 23 281
[3] Shukla D K and Mollah S 2007 Indian journal of pure and applied physics 45 52
[4] Al-Hajry A, Soliman A A and El-Desoky M M 2005 Thermochimica Acta 427 181
[5] Simockov J, Miklos P and Saly V 2000 Acta physica slovaca 50 685
[6] Al-Shukri A M, Khattak G D and Salim M A 2000 J. Of Materials Science 35 123
[7] Al-Hajry A, Soliman A A and El-Desoky1 M M 2005 Thermochimica Acta 427 181
[8] El-Desoky M M and Kashif I 2002 Phys. Stat. Sol. A 194 89
[9] Yakuphanoglua F, Aydogdua Y, Schatzschneiderb U and Rentschlerb E 2003 Physica B 334 443