Conductivity studies in some CaO and ZnO doped vanadophosphate glasses

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Abstract

Two different series of CaO and ZnO doped vanadophosphate glasses have been prepared by melt quench method. The dc electrical conductivity has been measured in the temperature range from 300K to 650K. High temperature activation energies were determined using Mott's SPH. The variation of conductivity and high temperature activation energy with composition revealed the possibility of ionic contribution to the conductivity and a transition from predominantly polaronic conductive regime to ionic conductive regime around 12-mol % of ZnO in ZnO doped glasses and around 14-mol % of CaO in CaO doped glasses. The low temperature data has been subjected to Mott's VRH theory and the density of states at Fermi level, N(E_F) was estimated in both the series of glasses.

Key words: glasses, alkaline earth element, conductivity, small polaron hopping, variable range hopping.

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I. Introduction

The glasses containing transition metal ions (TMI), such as Fe, Co, V, Mo, W, etc., are known to be electronically semiconducting [1-4]. Electron hopping (small polaron hopping) between the low and high valence states of TMI is believed to be the principal conduction mechanism for example, between V^{4+} and V^{5+}states in vanadium glasses and Fe^{2+} and Fe^{3+} in iron based glasses [5]. Electron hopping in vanadophophate glasses depends on the distance between the V^{4+} ions and V^{5+} ions and their concentration. Phosphate glasses have been well received because of their special properties and applications compared with other types of glasses; they have low melting and glass transition temperatures and are easy to prepare [6,7]. Phosphate glasses are being used as host materials for lasers, optical filters, and reference electrodes and also to store nuclear wastes. Pure phosphate glasses are highly hygroscopic and therefore one finds limited studies on them in the literature. However, alkali oxide modified phosphate glasses are quite stable and durable. In phosphomolbdate and phosphotungstate glasses [8] activation energies for dc conduction were found to be dependent on temperature and it has lead to a conclusion that variable-range hopping mechanisms were operated in different temperature regimes. Electrical conductivity was found to be increasing with iron content in iron phosphate glasses [2]. Ionic conduction was measured to be immeasurably small in caesium, sodium and potassium iron phosphate glasses up to a total of 20% alkali content [9,10]. Through dielectric studies in ternary vanadium phosphate glasses of the type, $(V_2O_5)_{0.3}$-$(P_2O_5)_{0.6}$-$(MO)_{0.1}$, where MO=TeO_2, GeO_2 and B_2O_3 [11], it was noted that at low temperatures the conductivity follows variable range hopping mechanism and at high temperature Mott's model of polaronic hopping theory is obeyed. The conductivity of glasses in the composition, $(V_2O_5)_{0.5}$-$(P_2O_5)_{0.5-x}$-$(A_2O)_{x,}$ where A=Li, Na, K, Rb have been investigated [12] as a function of frequency at a fixed temperature, over the range x=0.1 to 0.4. In zinc vanadophosphate glasses [13], electrical conductivity was observed to be remarkably dependent on the concentration of zinc concentration. Structural investigations on binary alkaline earth vanadate glasses [14] revealed that the increase in alkaline earth content reduces the total V-O coordination number and V-V distance significantly. The dc electrical conductivity studies in $(V_2O_5)_x(CaO)_{0.4}(P_2O_5)_{0.6-x}$ (0.1<x<0.3) have indicated a cross over of conduction mechanism from small polaron hopping (SPH) to variable range hopping (VRH) [15].

In general, in single alkali transition metal phosphate glasses both alkali ions and electrons (polarons) contribute to the electrical conduction at different temperatures. The electrical conductivity is expected to increase proportional to the concentration of alkali ions. The mixed alkali effect (MAE) has been observed in different physical properties including electrical conduction in silicate, borate, germanate and telluride glasses [16]. In this communication, we report density and dc conductivity studies on

Series (i): $(V_2O_5)_{0.4-x}(P_2O_5)_{0.6}(CaO)_x$; x=0.10, 0.14, 0.16, 0.18, 0.20 labeled as SC1, SC3, SC4, SC5 and SC6.

Series (ii): $(V_2O_5)_{0.4-x}(P_2O_5)_{0.6}(ZnO)_x$; x=0.10, 0.12, 0.14, 0.16, 0.20 labeled as SZ1, SZ2, SZ3, SZ4 and SZ6.

The vanadophosphate glasses in the above-mentioned composition have not been investigated previously for the properties reported here.

I. Experimental

Appropriate amounts of analytical grade vanadium pentoxide (V_2O_5), ammonium dihydrogen orthophosphate ($NH_4H_2PO_4$), calcium carbonate ($CaCO_3$) and zinc oxide (ZnO) were thoroughly mixed in a porcelain crucible and heated up to 1000 ^{0}C in a muffle furnace (make:INDFUR) and stayed there for half an hour for homogenization of melt. The melt was quickly quenched to room temperature and the random pieces of glasses thus formed were collected. It is possible that porcelain crucible can get attacked by corrosive melts at high temperatures. However, there are many reports wherein the glasses were prepared at the temperatures operated here [17-19] and no chemical analysis on the samples was carried out and the set compositions were assumed. Due to unavailability of the facilities and expertise no chemical analysis has been performed on the present glasses and the set compositions are taken for granted. Moreover, the integrity of our crucibles after quenching the melt was observed to be intact. This observed unaffected integrity of the crucible after the melt quenching ensures that the melt has not been contaminated by the impurities that might be expected from crucible. To remove mechanical strains present, if any, the samples were annealed for an hour at 300^{0}C. Powder X-ray diffraction studies were performed and the spectra did not show any sharp peaks indicating that the samples were non-crystalline in nature.

Samples of suitable dimensions were selected and silver electrodes were painted on to the two major surfaces of the samples and their electrical resistance was measured by following two-probe method. A constant dc voltage was applied across the sample and the current through the sample was measured with the help of a Keithley make DMM [20]. To avoid electrode like polarizations the actual current measurements were started after half an hour of applying constant voltage across the sample. These measurements were performed in the temperature range 300K to 650K for both series (i) and (ii) glasses. The voltage was measured using a voltmeter to the accuracy of ±10mV. The current was measured to the accuracy of ±10nA and ±50nA at temperatures above and below ~100^{0}C respectively. Temperature was measured using a chromel-alumel thermocouple and a micro-voltmeter to an accuracy of ±1^{0}C. Dimensions of the samples were determined using a traveling microscope with a least count of 0.001cm. Experiments were repeated to confirm the reproducibility of the data.

Using the measured electrical resistance, r, and dimensions of the sample the conductivities, σ, were determined [20] as per, $\sigma = (1/\rho)$, where resistivity, $\rho = (rA/t)$, A is cross sectional area and t is thickness of the sample. The error on conductivity, Δσ, was estimated taking into account of errors on the measured voltages, ΔV, and currents, ΔI, according to the relation, $\Delta\sigma = (\Delta\rho/\rho^2)$, where error on resistivity, $\Delta\rho = \Delta r(A/l)$, $(\Delta r/r) = (\Delta V/V)-(\Delta I/I)$. The estimated errors on conductivity were found to lie in the range of 2 to 3% and 3 to 4% at temperatures above and below ~100^{0}C respectively.

II. Theoretical

Based on diffusion model, Mott [21,22] et al have discussed the conduction process in terms of hopping of electrons between localized states and has proposed an expression for the electrical conductivity in semiconducting glasses:

$$\sigma = \frac{\nu_{el} e^2 C(1-C)}{k_B T R} \exp(-2\alpha R) \exp(-W/k_B T) \quad (1)$$

Where α is the rate of wave function decay, C the ratio of ion concentration in low valence state to total concentration of transition metal ions, R the average hopping distance, W the activation energy, e the electronic charge, k_B the Boltzman constant and T the absolute temperature. Equation (1) describes a nonadiabatic regime of small polaron hopping and is usually used to analyse the dc conductivity of glasses containing transition metal oxides. The nonadiabatic term $\nu_{el}\exp(-2\alpha R)$ describes the probability of an electron tunneling from the potential well. Equation (1) is comparable with Arrhenius equation

$$\sigma = \sigma_0 \exp(-E_{dc}/k_B T) \quad (2)$$

where σ_0 is equal to the pre-exponential factor in equation (1), E_{dc} is activation energy for dc conductivity.

Mott's model is applicable in the temperature range where the activation energy is constant. The activation energy, W, due to electron lattice interaction and static disorder can be expressed as

$$W = W_H + \frac{1}{2} W_D \qquad \text{for } T > (1/2)\,\theta_D \quad (3)$$

$$W = W_D \qquad \text{for } T < (1/4)\theta_D \quad (4)$$

Where W_H the hopping energy, W_D the average disorder energy, θ_D the Debye's temperature is defined by $\hbar\omega = k_B\theta_D$ is the temperature characteristic of the average optical-phonon frequency, ω.

Austin and Mott have opinioned that at low temperature the disorder energy plays a dominant role and the polaron hops occur beyond nearest neighbours and, it may be treated as variable range hopping (VRH). Based on single optical phonon approach the expression for conductivity at temperature has been derived [23-25] to be

$$\sigma = A\exp(B/T^{-1/4}) \qquad (5)$$

Where,

$$A = 4\left[2\alpha^3/9\pi kN(E_F)\right]^{1/4} \qquad (6)$$

$$B = \left[e^2/2(8\pi)^{1/2}\right]\upsilon_0\left[N(E_F)/\alpha kT\right]^{1/2} \qquad (7)$$

The VRH is said to be valid only at much lower temperatures i.e., below $\theta_D/4$, but it has been pointed out that depending on the strength of the Columb interaction the density of states at the Fermi level changes and the VRH may then become applicable even at temperatures 300 K and above [23-25].

III. Results

The conductivity was found to lie in the range 10^{-6}-10^{-7} ohm^{-1}m^{-1} and 10^{-5}-10^{-6} ohm^{-1}m^{-1} for series (i) and (ii) glasses respectively. The conductivity was found to be increasing with temperature in both the series of glasses indicating the semiconducting behavior, which is in accordance with the literature on variety of transition metal ion, doped glasses.

A close look at the variation of conductivity with CaO content in series (i) glasses revealed that the conductivity of a glass with 14-mol % of CaO has exhibited less conductivity by an order of magnitude compared to other glasses in the same series. For concentration above 14-mol % of CaO the conductivity has increased with the increase of Cao. The glass with 10-mol % CaO has more conductivity than the one with 14-mol % of CaO.

The variation of conductivity with ZnO content in series (ii) glasses revealed that the conductivity of a glass with 12-mol % of ZnO has exhibited less conductivity by an order of magnitude compared to other glasses in the same series. For concentrations above 12-mol % of ZnO the conductivity has increased with the increase of ZnO. The glass with 10-mol % ZnO has more conductivity than the one with 12-mol % of ZnO. The variation of conductivity at 500K with mol % of CaO and ZnO is plotted in Fig.1 for both series (i) and series (ii) glasses.

IV. Discussion

(a) Conductivity in the high temperature region

Series (i)

The increase in conductivity with CaO for above 14-mol % in ZnO doped glasses is in agreement with literature on other alkali/alkaline earth doped vanadophosphate glasses [13, 26] and iron phosphate glasses [10] but contrary to the observation made in [12], where conductivity was found to decrease with increase in alkali content. However, it may be noted that composition of systems studied in [12] were very much different from our systems where vanadium content was fixed at mol % 50 and alkali content was varied over a wide range. There is a general notion that only an alternating current technique can detect ionic conductivity, but several researchers have reported ionic conductivity results through dc conductivity studies [20, 27-30].

The dc conductivity is a thermally activated process and the activation energy, E_{dc}, can be determined from the slope of ln(σ) vs (1/T) curves as shown in Fig.2 for series (i) glasses. Above the temperature 500K the ln(σ) vs (1/T) curves of all the glasses were appeared to be linear obeying Arrhenius expression mentioned in Eqn. 2 and nonlinear at low temperature. The least square linear lines were fit to the data corresponding to the temperature range 500K to 650K. The slopes of the fit lines gave E_{dc} values for series (i) glasses in the range 0.105eV to 0.470eV. Activation energy as a function of CaO for series (i) is shown in Fig.3. It can be seen from the figure that the activation energy increases with increase of CaO up to 14-mol% and decreases for further increase of CaO in series (i) system. The observed trend of decrease of conductivity and increase of activation energy with CaO content up to 14-mol% and their opposite behavior for higher concentrations of CaO agree with the observations reported in [13,17,25,31,32]. Based on this result, it can be argued that a transition in the conduction mechanism is taking place in the series (i) glasses around 14-mol% of CaO. For example, electronic conductivity was predominant up to 14-mol% of CaO and ionic conductivity was predominant thereafter.

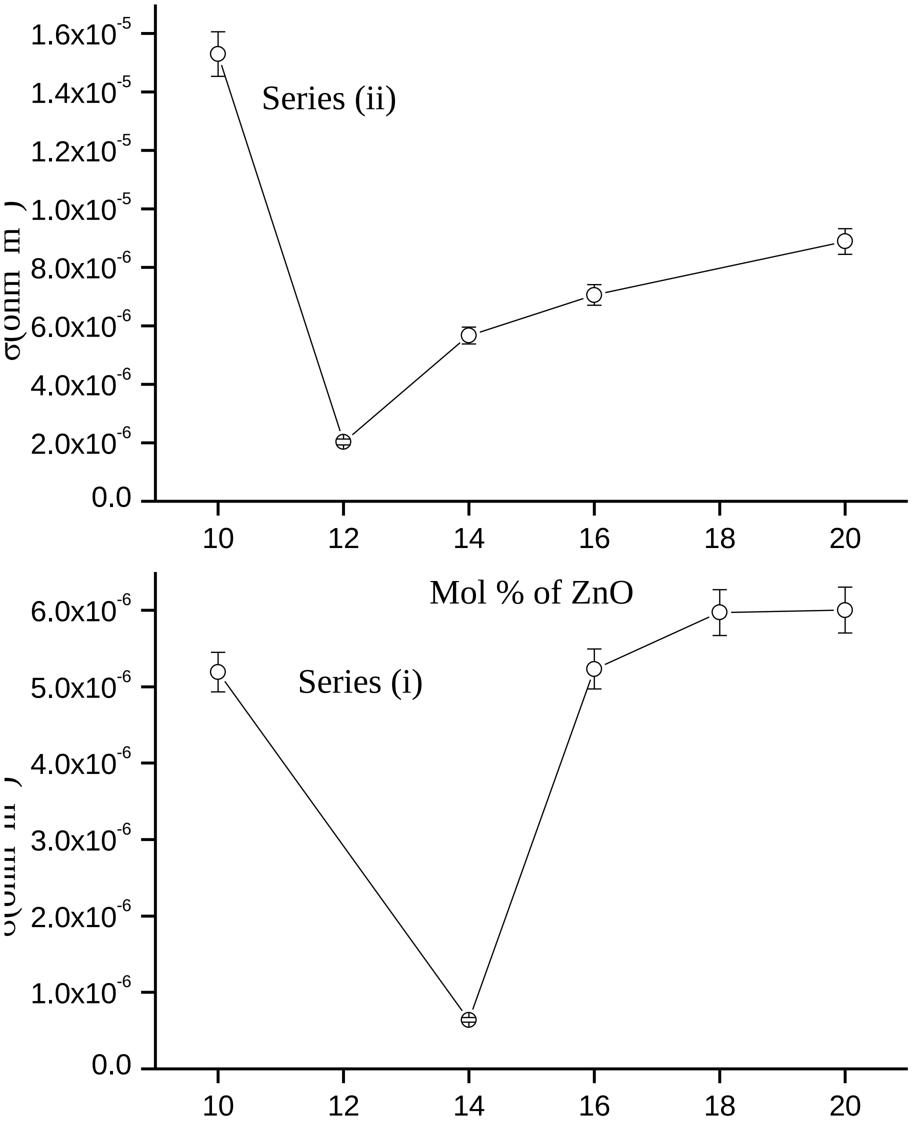

Fig.1. Conductivity, σ, at 500K versus mol % of CaO for series (i) glasses and mol % of ZnO for series (ii) glasses.

Series (ii)

By following the procedure adopted for series (i) glasses, activation energies for series (ii) glasses were determined from the plots shown in Fig.2. These activation energies were found to be in the range 0.125eV to 0.423eV and they are in the range of values reported for zinc vanadophosphate glasses [13]. Variation of activation energy with ZnO mol% for series (ii) glasses is shown in Fig.3. From this figure, one can notice that the activation energy increases with increase of ZnO up to 12-mol % and decreases for further increase of ZnO. This may be due to the fact that around 12-mol % ZnO there is a transition in the conduction mechanism taking place in the present glasses similar to what has been observed in series (i) glasses. This is supported by our observation that for glass containing 12-mol % ZnO, the conductivity was measured to be minimum compared to other glasses in series (ii).

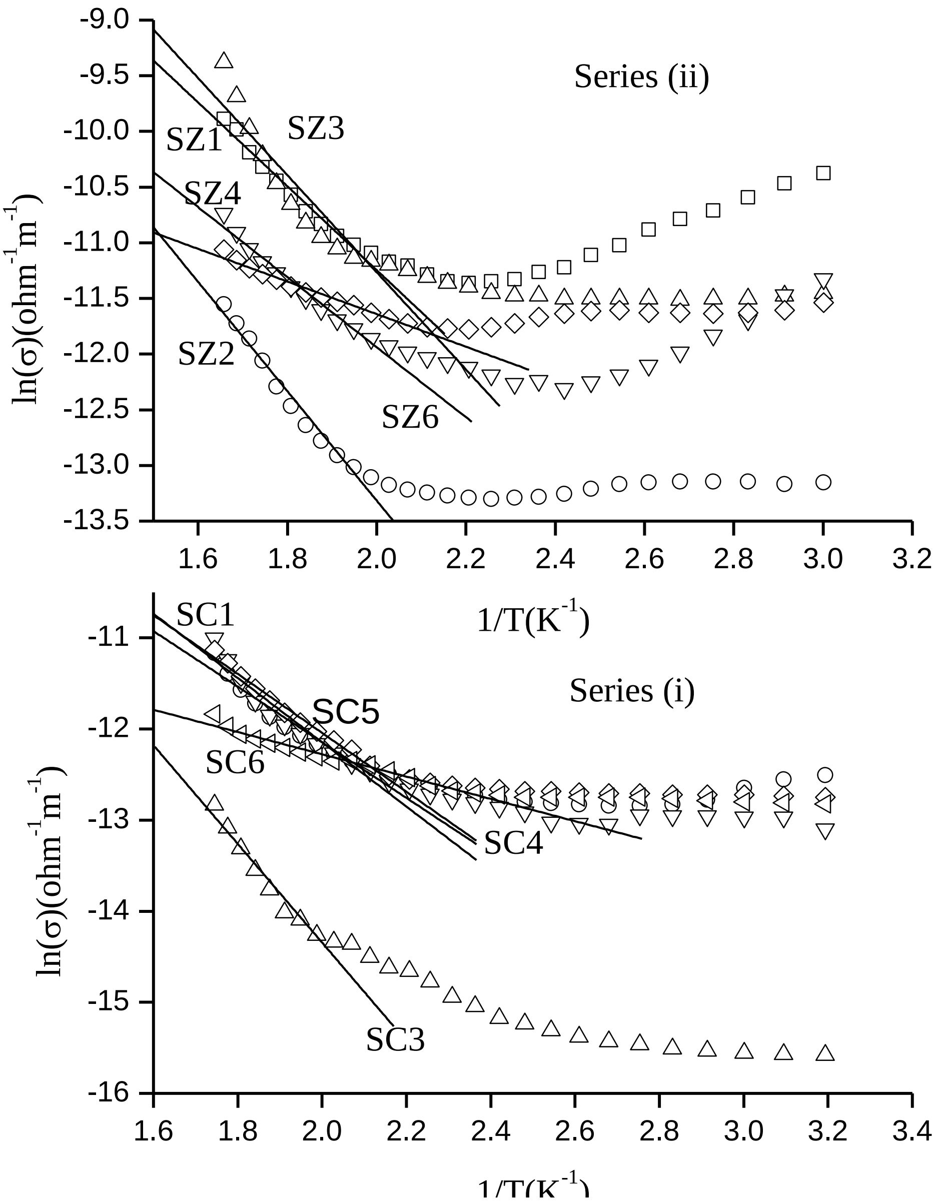

Fig.2. The ln(σ) versus (1/T) for series (i) and series (ii) glasses. The solid lines are the Mott's SPH model fits to the data in the high temperature region.

It can always be argued that Ca^{++} and Zn^{++} are being doubly charged, less mobile and heavier compared to alkali ions such as Na^{+}, K^{+} and Li^{+} and therefore there cannot be any conductivity due to them. In the present two series of glasses, it has been clearly observed that there is a decrease in total conductivity with increase in CaO and ZnO contents up to 14-mol % and 12-mol % in series (i) and series (ii) respectively and conductivity increases for further increase of CaO and ZnO concentrations in them.

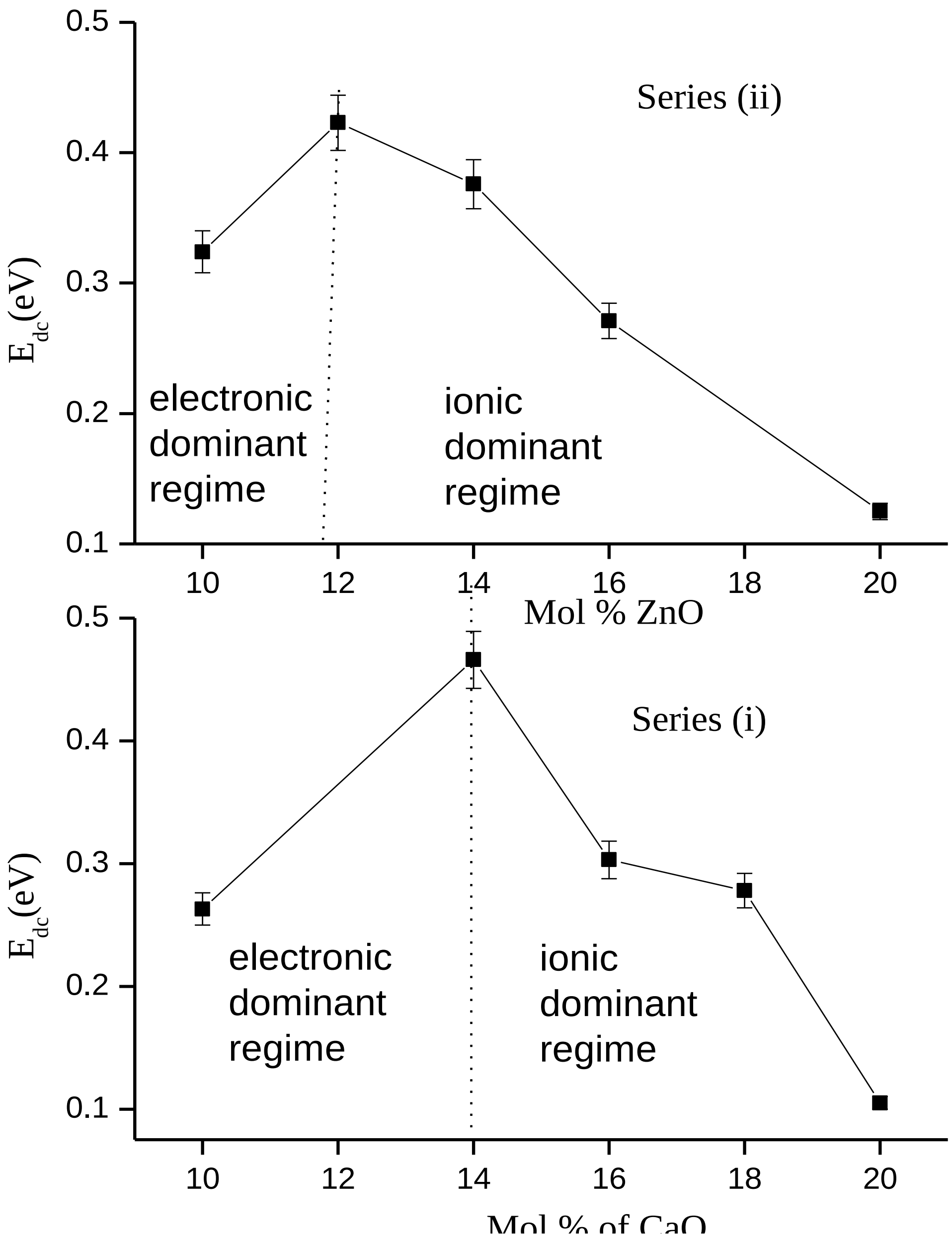

Fig.3. Activation energy, E_{dc} versus mol % of CaO for series (i) and mol % of ZnO for series (ii) glasses.

The variation in activation energy with CaO and ZnO contents in series (i) and (ii) glasses respectively shown opposite behavior with that of conductivity. If Ca and Zn ions were not contributing to conductivity and impurities present, if any, in the glasses were actually the contributories to the conductivity then the observed trends of systematic variations in conductivity and activation energy with CaO and ZnO contents would not have been detected in the present glasses. Further, the observed variations of conductivity and activation energy of these glasses are similar to that reported in [13,17,25,31,32] and therefore, it can be thought that there is a ionic contribution to the conductivity and the transition of conduction mechanism is taking place in both the studied glass series.

There exist two kinds of explanations for transition from electronic regime to ionic regime. One is due to

Bazan et al [33] and other is due to Jayasinghe et al [34]. According to Bazan et al moving electrons (polarons) are attracted to positively charged cations. These cation-polaron pairs tend to move together as a neutral entity leading to no net transfer of charge. This process does not contribute to electrical conductivity. As per Jayasinghe et al, there exist two independent paths; one for electrons that is V^{4+}-V^{5+} chain and the other for ions made by the regular position of non-bridging oxygen along the network-former chains. When Cao or ZnO are increasingly added, electronic paths are progressively blocked thereby electronic current is lowered. At the same time there is an equivalent increase in the ionic mobility. In our case, Jayasinge et al proposal explains the observed results. That is, electronic paths were increasingly blocked up to 14-mol % CaO in series (i) glasses and up to 12-mol % ZnO in series (ii) glasses, after these concentrations ionic motions dominated conduction. The existence of ion-polaron conduction in glasses is of great interest in electrochromic and other electrochemical devices.

(b) Conductivity in the low temperature region

The low temperature behavior of ln(σ) with (1/T) indicates a temperature dependent activation energy, which decreases with decrease in temperature. As per Eqn. 5, ln(σ) vs ($T^{-1/4}$) plots were made for both the series of glasses for the data corresponding to temperature range 400K to 500K as shown in Fig.4. The least square linear lines were fit and the coefficients A and B were derived. The correlation coefficients of these

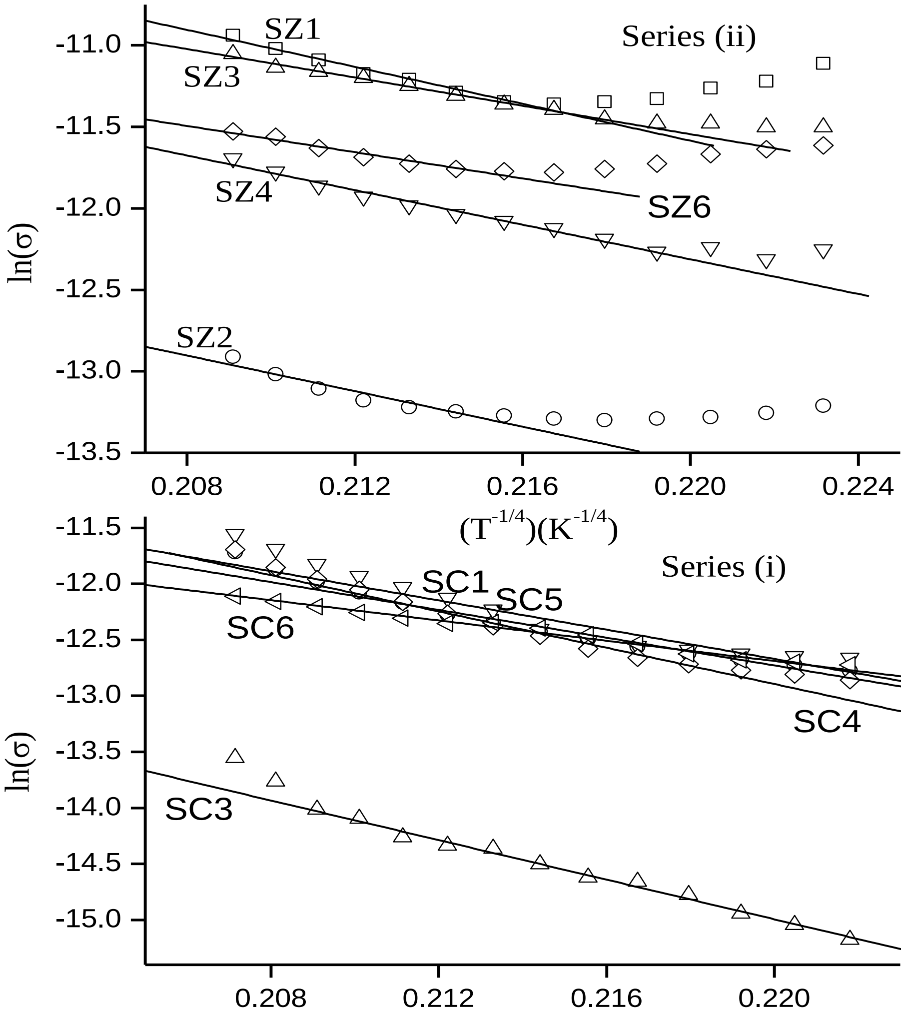

Fig.4. The plots of ln(σ) versus $T^{-1/4}$ for series (i) and series (ii) glasses. The solid lines are the Mott's VRH model fits at low temperatures.

least square linear fits were between 0.93 and 0.99. The range of data has been selected in both the series for applying Mott's VRH model in such a way that the high temperature data obeying Mott's SPH model and the data at low temperature below 400K has been avoided as, the data below 400K has more experimental errors. Using Eqn.(6) and assuming α=20nm^{-1} [35] the density of states at Fermi level, N(E$_F$) were estimated. Here we have assumed α value given for pure TMI doped glasses as α value for alkaline doped vanadophophate glasses could not be found from the literature for TMI and. The N(E$_F$) values obtained are tabulated in Table 1.

Table: Density of states at Fermi level, N(E$_F$) values derived from Mott's VRH model

Glass Series (i)	N(E$_F$) (eV^{-1}m^{-3})	Glass Series (ii)	N(E$_F$) (eV^{-1}m^{-3})
SC1	1.79x10^{28}±0.03x10^{28}	SZ1	2.77x10^{26}±0.07x10^{26}
SC3	6.81x10^{25}±0.20x10^{25}	SZ2	2.05x10^{28}±0.05x10^{28}
SC4	4.51x10^{25}±0.08x10^{25}	SZ3	1.74x10^{27}±0.06x10^{27}
SC5	3.29x10^{27}±0.08x10^{27}	SZ4	3.15x10^{26}±0.08x10^{26}
SC6	4.67x10^{26}±0.14x10^{26}	SZ6	4.38x10^{28}±0.12x10^{28}

The N(E$_F$) values for both the glass systems are in the range between 10^{25} eV^{-1}m^{-3} and 10^{28} eV^{-1}m^{-3}. These density of state values are in close agreement with CaO doped vanadophosphate glasses [15]. The precise nature of variation of N(E$_F$) with composition could not be determined as the size of uncertainties on low temperature data are larger than that of high temperature data.

6. Conclusions

Two different series of CaO and ZnO doped vanadium phosphate glasses were prepared by melt quench technique and their non-crystallinity was confirmed by XRD studies.

DC conductivity was measured in the temperature range 300K to 650K. The conductivity decreased with CaO content up to 14-mol % in series (i) and up to 12-mol % of ZnO in series (ii) glasses and, increased for higher concentrations of CaO and ZnO in their respective glasses. The high temperature conductivity was analysed in the light of small polaron hopping theory and using Arrhenius equation. Activation energy was found to increase up to 14-mol% of CaO in series (i) and up to 12-mol % of ZnO in series (ii) and, then decreased for further increase of CaO and ZnO in their respective glasses. These trends of variations in conductivity and activation energy with CaO and ZnO in series (i) and series (ii) glasses reveal the possibility of ionic contribution to the electrical conductivity and the transition of conduction mechanism from predominantly electronic to ionic regimes in both the series of glasses. The theory due to Jayasinghe et al is found to be adequate in explaining the observed transition from electronic to ionic conduction in the glasses studied here.

The low temperature data has been analysed using Mott's VRH model and the density of states at Fermi level has been estimated.

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References

[1] M.M.El-Deskoky and M.Y. Hassaan, Phys. Chem.Glasses. 43 1 (2002) 1.
[2] A.Mogus-Milankovic, D.E.Day and B.Santic, Phys. Chem. Glasses. 40 2 (1999) 69.
[3] I.A.Gohar, Y.M.Moustafa, A.A.Megahed and E.Mansour, Phys.Chem. Glasses, 39 1 (1998) 56.
[4] R.V.Anavekar, N. Devaraj and J.Ramakrishna, Phys. Chem. Glasses. 32 3 (1991) 103.
[5] N.F. Mott, Adv. Phys. 16 (1967) 49.
[6] Wancheng Zhou, Hongsheng Zhao and Dongmei Zhu, J. Non Cryst. Solids. 263 & 264 (2000) 277.
[7] A.E. Marino, S.R. Arrasmith, L.L. Gregg, S.D. Jacobs, Guorong Chen and Yonguan Duc. J. Non Cryst. Solids. 289, (2001) 37.
[8] U.Selvaraj and K.J. Rao, Phil. Mag. B 58 2 (1988) 203.
[9] A.Mogus-Milankovic, B.Santic, K.Furic and D.E.Day, Phys. Chem. Glasses. 40 6 (1999) 305.

[10] A.Mogus-Milankovic, B.Santi, D.E.Day, and C.S.Ray, J. Non cryst. Solids, 283 (2001) 119.

[11] M.G.El-Shaarawy, J. Phy. Soc. Japan, 71 4 (2002) 1118.
[12] R.J. Barczynski and L.Murawski, Materials science-Poland, 24 1(2006) 221.
[13] B.Eraiah and R.V.Anavekar, Phys. Chem. Glasses. 42 1 (2001) 121.
[14] U. Hoppe, R.Kranold, J.M.Lewis, C.P.O'Brien, H.Feller, S.Feller, M.affatgato,J.Neuefeind and A.C.Hannon, Phys. Chem. Glasses. 44 4 (2003).
[15] B.Sharma and A.Srinivasan, J. Mat. Sci. 40, 19, (2005) 5125.
[16] P.Roychoudhury, S.K.Batabyal, A.Paul and C.Basu, J. Appl. Phys. 92 7 (2002) 3530.
[17] G.B.Devidas, T.Sankarappa, B.K.Chougule and G.Prasad, J.Non-Cryst. Solids, 353, (2007) 426.
[18]. N.Nagaraja, T.Sankarappa and M.Prashant Kumar, J.Non-Cryst. Solids, 354, (2008) 1503.
[19]. M.I.Mohammed, Kh. Ab-Allah, M.Y.Hassaan, Egypt, J.Solids 27 (2) (2004) 299.
[20] M.Harish Bhat, M.Kandavel, M.Ganguli, K.J.Rao, Bul. Mat. Res. 27 (2004) 2.
[21] N.F.Mott, J. Non-Cryst. Solids, 1, 1 (1968).
[22] M.Sayer and A. Mansingh, Phys. Rev. B 6 12 (1972) 4629.
[23] I.G.Austin and N.F.Mott, Adv. Phys. 18, 41 (1969).
[24] A.Ghosh, J.Phys: Cond. Matt., 1, (1989) 7819.
[25]. M.Prashant Kumar and T.Sankarappa, Solid State Ion., 178, (2008) 1719.
[26] Satish Kumar, M.Phil. thesis (2005), Gulbarga University, Gulbarga, India.
[27] M.El-Hofy and I.Z.Hager, Phys.Stat.Sol.(a) 199(3), (2003) 448.
[28] A.Al-Shahrani, A.Al-Hajry and M.M.El-Desoky, Phys.Stat.Sol.(a) 200(2) (2003) 378.
[29] F.H.Batal and A.H.Ashour, Mat.Chem.Phys. 77 (2002) 677.
[30] I.A.Gohar, Y.M.Moustafa, A.A.Megahed and E.Mansour, Phys.Chem. Glasses, 39, 01 (1998) 56.
[31] R.A.Montani and S.E.Giusia, Phys. Chem. Glasses, 42 1 (2001) 12.
[32] R.A.Montani, A. Lorente and M.A. Vincenzo, Solid state ion. 130 (2000) 91.
[33] J.C.Bazan, J.A. Duffy, M.D Ingram, M.R.Mallace, Solid state ions 86-88(1996) 497.
[34] G.D.L.K. Jayasinghe, M.A.K.L. Dissanayake, M.A.Careem, J.L.Souquet, Solidstate ion. 93 (1997) 291.
[35] H.Sakata, K.Sega and B.K.Chaudhari, Phys. Rev.B, 60, 5, (1999) 3230.