

Variation of electrical conductivity and activation energy in semiconducting glasses with combination of P₂O₅- CaO- MoO₃- Li₂O

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In the present investigation, 40P₂O₅-xCaO (40-x)MoO₃-20Li₂O glasses with x=5, 10, 15, 20, 25 mol% were prepared by conventional melt quenching method. X-ray diffraction analysis was carried out to demonstrate the amorphous nature of prepared samples. Then, their dc conductivity (σ) was determined in the temperature range of 300-385 K by two-probe method. According to Mott theory, analysis of electrical properties has been made in the light of small polaron hopping (SPH) model and it was observed that the electrical conductivity increases with increase in temperature. The composition dependence of electrical conductivity and activation energy were also evaluated. It revealed that increasing the CaO content results in increase and decrease of activation energy and electrical conductivity, respectively. Moreover, conduction is ascribed to non-adiabatic hopping of small polaron.

Keywords: Electrical conductivity, Mixed electronic-ionic conductivity, Activation energy, Small polaron hopping (SPH), Non-adiabatic hopping

1 Introduction

Oxide glasses containing transition metal ions were first reported to have semiconducting properties in 1954¹. In fact, glasses containing transition metal oxides (TMOs), such as Mo, Fe, Cu, V are known as semiconducting materials^{2,3}. The conductivity of these glasses has been illustrated by thermally activated hopping of electron (phonon-assisted) between two valance states of transition metal ions (TMIs) in terms of small polaron hopping (SPH). Formation of these different valance states is due to redox processes taking place at high temperatures during melting preparation. According to amorphous nature of these materials, Schottky and Frenkel defects are more than crystalline materials. So, unpaired electrons of the network can displace ambient ions and induced polarization around itself that leads to polaron formation. Finally, localized electron, hops between polaronic sites and contribute in conductivity⁴⁻⁶. Additionally, conduction by jumps across the localized states requires the aid of phonons. It may be noticed that in vitrify process, only some of oxides have glass forming nature, such as P₂O₅, Si₂O, B₂O₃. Among many sort of glasses, P₂O₅ based ones achieve extensive applications in optical data transmission, detection and laser technologies^{7,8}. In spite of this,

pure phosphate glasses have extreme moisture and unstable nature. So, it is advisable that with introduction of transition metals or alkaline ions to glass network, these characterizations of phosphate glasses improved, whereby more stable and durable structures are accessible^{9,10}. Presence of alkaline or earth alkaline ions in glass network, dependent on glass structure, can lead to ionic conductivity, giving rise to non-bridging oxygen and ultimately have profound effect on some chemical and physical properties of glasses^{11,12}. In the present investigation, phosphates act as glass former; existence of molybdenum and lithium oxides as glass modifiers results in polaronic and ionic conductivity, respectively. Calcium oxide can influence ionic conductivity and also can improve the glass structure. It has been proved that in such materials, activation energy in electrical conductivity is dependent on temperature¹³. It demonstrates that conductivity has two mechanisms at different temperature regimes: thermally activated process in higher temperatures; and variable range hopping in lower ones. In recent decades, various studies were carried out on electrical properties of mentioned materials. In 1998, Ungureanu *et al.*¹⁴ reported that the alkaline oxide is the agent of ionic conductivity and they observed mixed electronic-ionic conduction. This dual mechanism has been reported in several other

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works^{12,15,16}. Specially, Sinha *et al.*¹⁷ studied the ionic and electronic transport properties of their calcium doped samples. Mercier *et al.*¹⁸ also surveyed the role of TMOs in more general way.

The present paper aims to report the electrical properties, discussion about temperature and composition dependence of dc conductivity, high temperature activation energy and dominant hopping regime. The electrical properties of this glassy system have not been reported so far as per our knowledge.

2 Experimental Procedure

Quaternary glass samples, with combination of 40P₂O₅-(40-x)MoO₃-xCaO-20Li₂O for x=5-10-15-20-25, were prepared by conventional melt quenching technique. Exact amounts of raw materials (Table 1) were weighed and thoroughly mixed in an alumina crucible. The mixture was preheated at 473 K, to get rid of the volatile yields. After that, the blend was heated up to melting temperature (about 980 K). While the mixture has been remained in this temperature for one hour, it swirled to ensure homogeneity. Acquired melt was immediately poured onto a steel plate preheated in the lower temperature for the sake of vitrify. In the next pace, the anneal furnace cooled down to the room temperature gradually. To confirm the amorphous character of the samples, the X-ray diffraction analysis (XRD) was achieved. Then, both sides of samples with suitable dimension were well polished by fine grade emery paper and vapour deposited by silver as electrode, in which the guard ring method was used to avoid the influence of surface currents in the measurements. Resistance and hence, dc conductivity was measured for samples by subsequent two probe method. An invariable dc voltage was utilized across the prepared sample and current passing through the sample was measured. It is noteworthy here that the transparency of prepared samples enhanced as CaO concentration increased.

3 Results and Discussion

The amorphous features of samples were exposed by XRD pattern, using Bruker-D8 Advance with Cu

radiation. As seen in Fig. 1, no sharp peak has been detected, which demonstrated the structure-less formation of present samples. The conductivity process has been expressed in terms of electron hopping between localized states (LSs) and the equation for such materials¹⁹ has been suggested as following (these LSs existed over a range of barriers owing to erratically oscillating field of disordered structures²⁰):

$$\sigma = \frac{V_0 e^2 c(1-c)}{k_B T R} \exp(-2\alpha R) \exp\left(-\frac{W}{k_B T}\right) \quad \dots (1)$$

$$\sigma = \frac{V_0 e^2 c(1-c)}{k_B T R} \exp(-2\alpha R) \quad \dots (2)$$

where, v_0 , is phonon frequency character; R , average distance of hopping; c , the fraction of reduced transition metal ions ($C = \frac{Mo^{5+}}{Mo_{tot}}$); α , the decay rate of electron wave function; W , the activation energy; e ,

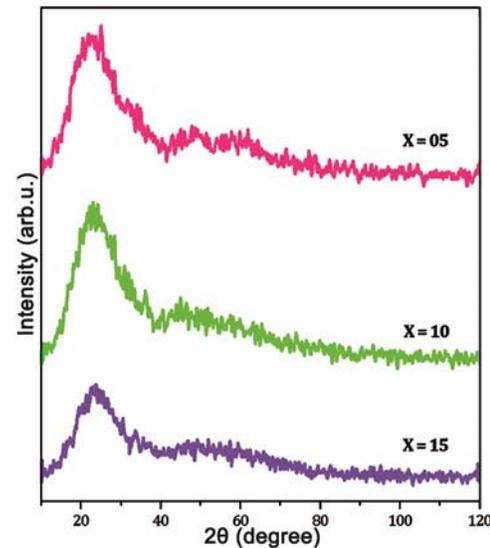


Fig. 1 — XRD pattern of 40P₂O₅-xCaO-(40-x)MoO₃-20Li₂O for x=5,10,15

Table 1 — Raw materials used in glass preparation

Reagent grade	Symbol	Purity [%]	Mole fraction used [%]
Ammonium di hydrogen orthophosphate - Scharlau	(NH ₄)-H ₂ PO ₄	99	40
Lithium carbonate - Merck	Li ₂ CO ₃	99.5	20
Calcium oxide - Riedel-de Haen	CaO	99	x
Molybdenum oxide - Merck	MoO ₃	99.5	40-x

the electrical charge; k_B , the Boltzmann constant; and T , the absolute temperature. At first, the electrical conductivity of each glass is computed using electrical resistance and dimensions of prepared samples. Variations of $\text{Ln}\sigma$ with $1/k_B T$ through the temperature range 302-385 K (Fig. 2) shows that the electrical conductivity increases linearly with increase of temperature. This behaviour is attributed to semiconducting nature of glassy samples and is consistent with previous observations on TMO glasses²¹⁻²⁶. The results of electrical conductivity in present investigation are lower than the previous work due to the absence of second TMO (Vanadium oxide) and higher concentration of calcium oxide²⁴. Actually, the first one has a major effect because of exceeding of polaronic conduction.

Variation of electrical conductivity with calcium oxide percentage in constant temperature has been plotted in Fig. 3. As seen, $\text{Ln}\sigma$ decreases with increase of CaO concentration. Such behaviour has been reported by Hager²⁷ and Sujatha *et al.*²¹ which is attributed to increase of mean distance between TMIs. Lahcen Bih *et al.*²⁸, in their electrical and structural investigations, have reached to higher values of conductivity in $\text{P}_2\text{O}_5\text{-MoO}_3\text{-Li}_2\text{O}$ glasses (compared to the present results). It can be ascribed to blocking the movement paths of more mobile Li^+ ions by the Ca^{2+} ions, which are heavier than earlier. It seems that Ca^{2+} ions placed in empty spaces of glass network (owing to Schottky and Frenkel defects in solid state

materials) influence the mobility of Li^+ ions²⁹. Davidas *et al.*¹⁶ reported that the presence of second alkaline (earth) oxide may lead to considerable decrease of conductivity. According to Eq. (1), slope determination of curves exhibited in Fig. 2, leads to calculation of the activation energy of samples. Simultaneous variations of W and $\text{Ln}\sigma$ (at 326 K) against CaO concentration are depicted in Fig. 4. Enhancement of calcium oxide leads to increase in required energy for hopping between LS, while $\text{Ln}\sigma$ has reverse tendency and move to lower amounts. This behaviour of glasses that conductivity has largest values while activation energy get the lower values, is the features of SPH^{7,30}. Moreover, in the present system, conduction is mixed electronic-ionic conductivity due to presence of MoO_3 and Li_2O , where Li^+ concentration is constant. So, increase in CaO content leads to (i) detraction of MoO_3 density and (ii) decrease in ionic conduction by obstructing

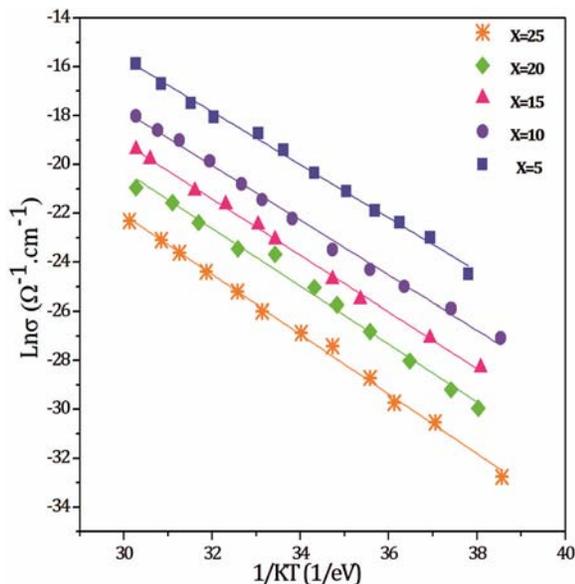


Fig. 2 — Variation of $\text{Ln}\sigma$ with $1/k_B T$ in $40\text{P}_2\text{O}_5\text{-xCaO-(40-x)MoO}_3\text{-20Li}_2\text{O}$ glasses

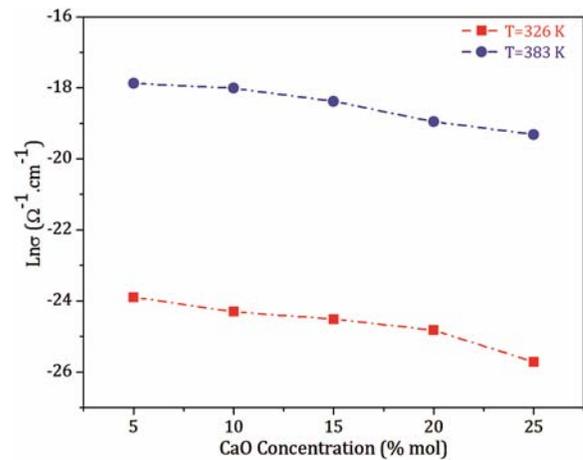


Fig. 3 — Effect of CaO concentration on $\text{Ln}\sigma$ (at two constant temperatures)

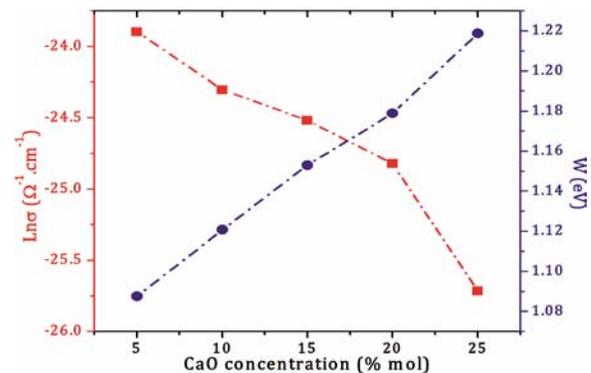


Fig.4 — Variation of $\text{Ln}\sigma$ (at 326 K) and W against CaO concentration in $\text{P}_2\text{O}_5\text{-CaO-MoO}_3\text{-Li}_2\text{O}$ glasses

the Li⁺ ions movement. Covalent character of Ca²⁺ is also prominent factor for binding metal ions more stronger than before to oxygen ions, which lead to blockading mobility of these ions and hence, decrease the electrical conduction in glass structure³¹ (higher Ionic-Polaronic interaction³²).

Other justifications suggest that increase of alkali oxide contents should increase the average distance (R) between TMIs in different valence states (LS) and subsequently hopping probability of electron decreases^{8,14,27}. Moreover, increase of Ca concentration may cause a stronger columbic attraction force between ions and polarons, which results in decrease of electronic and ionic movement^{30,33}. This change is observed in higher density of Ca at which the electrical conduction takes more reduction. A good correlation is found to exist between these phenomena. Figure 4 displays a good consistency between W and $\text{Ln}\sigma$ values. It is worthwhile to note that in this optical measurement of present samples, which has not published yet, a good correspondence is found between optical and electrical band gap.

Measured values of activation energy in this study are consistently lower than optical band gap of these samples due to the Franck- Condon effect. In the last part of Eq. (1), activation energy (W) can be considered with following conditions:

$$W = W_H + \frac{W_D}{2} \quad T > \frac{\theta_D}{2} \quad \dots (3)$$

$$W = W_D \quad T < \frac{\theta_D}{4} \quad \dots (4)$$

where, W_H , is hopping energy; W_D , disordered energy due to different energy of polaronic sites; and θ_D , Debye's temperature in the relation, $\hbar\omega = k_B\theta_D$ (the temperature trait of the optical phonon frequency, ω) (Ref. 6). The value of exponential factor (αR), in the adiabatic regime, in Eq. (1), is trivial so it can be regardless. Therefore, the main factor of conduction in adiabatic regime is activation energy^{4,6}. In adiabatic regime, σ_0 is independent of MoO₃ content and changes hardly^{30,34}. Figure 5 represents the variation of $\text{Ln}\sigma_0$ (at 326 K) as a function of MoO₃ concentration. Existence of appreciable changes in $\text{Ln}\sigma_0$, means that polaronic conductivity in present glasses occurred in non-adiabatic regime³⁵.

According to Mott's model, the nature of hopping mechanism can be recognized by plotting $\text{Ln}\sigma$ as a function of W in tentative temperatures (Fig. 6) (Ref. 6). It is suggested that hopping occurs in adiabatic regime if temperature obtained from this curve is similar to arbitrary experimental temperature. Otherwise, hopping would be in non-adiabatic regime^{6,36}. The temperature yielded from this curve is $T_M = 886.5$ K but temperature used for determination of $\text{Ln}\sigma$ is $T = 326$ K and according to previous explanations, it is another reason to non-adiabatic regime in polaronic hopping process. Similar behaviour is observed in several reports^{37,38}.

Nevertheless, it should be mentioned that SPH process deduced to be in adiabatic regime for some TMO glasses with traditional glass formers^{27,30,34}. Though, the degree of agreement between T and T_M is not always satisfactory to be able to categorize the

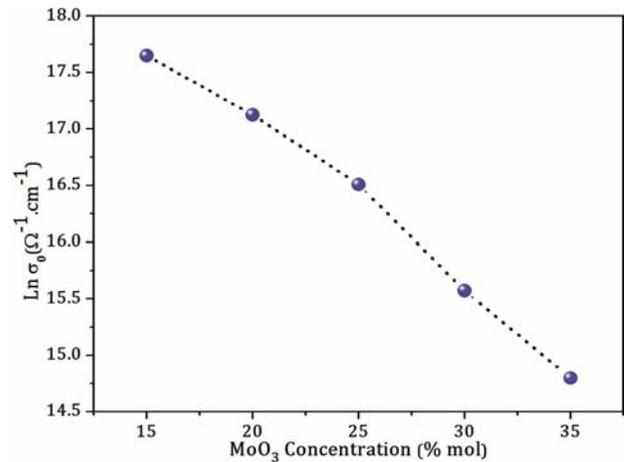


Fig. 5 — Dependence of $\text{Ln}\sigma_0$ on MoO₃ concentration (at 326 K) in 40P₂O₅-xCaO-(40-x)MoO₃-20Li₂O glasses

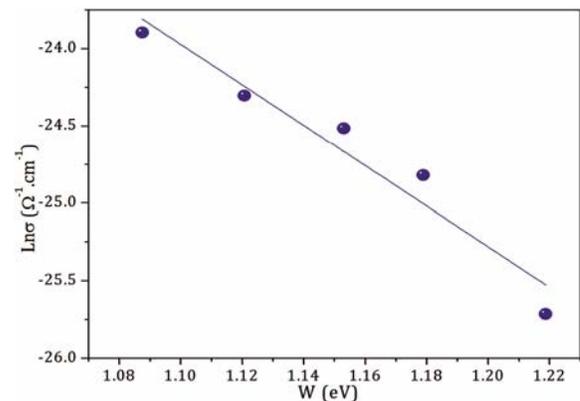


Fig. 6 — Variation of $\text{Ln}\sigma$ with W (at 326 K) in 40P₂O₅-xCaO-(40-x)MoO₃-20Li₂O glasses

Table 2 — Features and obtained data of prepared samples

P ₂ O ₅ - CaO - MoO ₃ - Li ₂ O [mol%]	Lnσ at 326 K [Ω ⁻¹ . cm ⁻¹]	Lnσ at 383 K [Ω ⁻¹ . cm ⁻¹]	Lnσ ₀ at 326 K [Ω ⁻¹ . cm ⁻¹]	W [eV]
40-5-35-20	-23.8967	-17.8742	14.79655	1.0875
40-10-30-20	-24.3035	-18.0104	15.571	1.1207
40-15-25-20	-24.5181	-18.3794	16.50568	1.153
40-20-20-20	-24.8216	-18.9517	17.12364	1.1789
40-25-15-20	-25.7151	-19.3114	17.64625	1.2187

systems into adiabatic or non-adiabatic; it can, however, supply an indication. Measurement data is shown in Table 2.

4 Conclusions

Glassy samples with combination of 40P₂O₅-xCaO-(40-x)MoO₃-20Li₂O, which x=5,10,15,20,25, were prepared using melt quenching technique. After the preparation of them, *I-V* measurements were accomplished and it was observed that:

- (i) The non-crystallinity of samples was confirmed using XRD analysis.
- (ii) Semiconducting behaviour of present glasses was demonstrated due to increase of conductivity with temperature.
- (iii) With increase of CaO content, electrical conductivity decreases. It can be attributed to increase of separation distance between MoO₃ ions, increase of columbic attraction between charge carriers and blocking movement paths of Li⁺ ions by the more covalent Ca²⁺ ions.
- (iv) In present glassy system, the conductivity mostly occurred in terms of SPH. Using the Mott's model, the main regime in SPH process of this system was indicated as non-adiabatic regime.

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