Electrical properties of some copper-containing phosphate glasses

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Ionically conductive glasses have come to the forefront of scientific interest because of their applications in electronic devices, batteries and electro-chemical sensors [1–3]. Primary and secondary electro-chemical cells based on glassy materials were also used successfully for production and storage of electricity. Glasses have many advantages over the crystalline electrolyte because of the possibility of selection of a wide range of composition, and thereby a wide range of property control and good workability [4, 5]. Because of the superior properties such as safety, long cell-life, ease of utilization and miniaturization, the solid state cells with glassy materials have the potential to obtain high power and energy density for room temperature applications [6, 7]. Glass electrolytes should meet some criteria, but the most important one is its high ionic conductivity at room temperature such as those attained in Ag^+-containing glasses [8, 9]. Due to silver shortage [6], it is necessary to find new glass compositions with a conductivity comparable to Ag^+-containing glasses. From a theoretical point of view, the similarity of electronic configuration and the small ionic radius of Cu^+ ion in comparison with that of Ag^+ ion gives a good chance to achieve conductivity comparable with the Ag^+ conductive glasses [4]. The glass formation and electrical properties of many systems containing Cu^+ conductive ions were investigated [10, 11]. Glass systems containing Cu^+ ions prepared using P_2O_5 or MoO_3 as "glass forming oxide," showed high conductivity, yet they still have low chemical durability for some applications [12]. In the present work, trials were made to obtain durable glasses with conductivity values in the range of semiconductors.

The glass samples (Table I) were prepared using chemical grade AR. P_2O_5 was introduced as ammonium dihydrogen phosphate, CuO was introduced as such, PbO as red Pb_3O_4 and sodium, potassium, lithium, magnesium, and calcium oxides as their corresponding anhydrous carbonates. Appropriate amounts of the various raw materials were mixed to obtain homogenized batches. Melting was carried out using silica crucibles at 1100 °C for 2 hr, and the crucibles containing the melt were taken out of the furnace at intervals and swirled about to promote mixing and to ensure homogeneity. After melting, the melts were poured onto a stainless plate and cast in the form of circular slabs, then transferred to a muffle furnace for the annealing process. Most of the copper-containing glasses prepared in this work were very deeply colored. X-ray diffraction was employed for all prepared samples to confirm non-crystallinity. Cu^+ and $Cu_{tot.}$ of these glass samples were determined using a wet chemical method, the details of this method are described elsewhere [13]. The glass samples were ground and polished to 400 μm thickness while the diameter was 1 cm. Silver electrodes were deposited onto both sides of the glass samples to ensure a better electrical contact between the electrodes and the sample surfaces. DC constant voltage of 250 V across the probe electrodes was maintained by stabilized DC power supply (0–300 V), and the current flow was detected by an electrometer (Keithly 614) at room temperature then the resistivity was calculated from the geometry of the electrodes and the thickness of the samples. Some conductivity measurements were carried out over a temperature range from 298 to 500 K. Since the melting temperature, time, and other environmental conditions influence the copper redox states, the results from the glass samples melted at the same conditions will only be compared to each other.

Table I lists the electrical conductivity values at room temperature and $Cu^+/Cu_{tot.}$ ratios for all studied glasses. For the binary glasses, the increase of the $Cu^+/Cu_{tot.}$ ratios with the decrease of CuO content from 50 to 40 mol% (Table I) is due to the decrease in the glass basicity on crossing from metaphosphate to ultraphosphate

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DOI: 10.1007/s10853-005-4227-2

TABLE I Glass compositions, $Cu^+/Cu_{tot.}$ ratios, and room temperature electrical conductivities of glass samples

Composition (mol%)				
P_2O_5	CuO	R_2O or RO	$Cu^+/Cu_{tot.}$	σ_{25}
50	50	–	0.03	7.07×10^{-13}
55	45	–	0.08	12.3×10^{-13}
60	40	–	0.15	44.6×10^{-13}
50	30	$20K_2O$	0.04	1.09×10^{-10}
50	30	$20Na_2O$	0.06	2.81×10^{-8}
50	30	$20Li_2O$	0.13	3.04×10^{-7}
50	30	20MgO	0.25	9.77×10^{-12}
50	30	20ZnO	0.21	1.25×10^{-12}
50	30	20CaO	0.15	0.31×10^{-12}
50	30	20PbO	0.63	2.51×10^{-10}
50	30	20PbO[a]	0.97	1.25×10^{-6}

[a] Melted under reducing conditions.

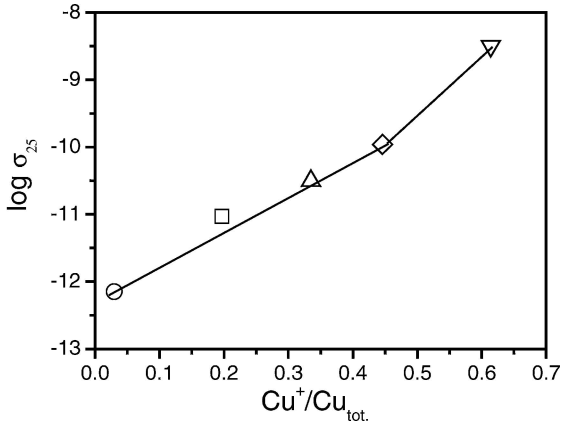

Figure 1 The electrical conductivity at room temperature (σ_{25}) as function of $Cu^+/Cu_{tot.}$ ratio of glass 50CuO–50P_2O_5 (mol%) melted under reducing condition for different periods of times; □: 5 min, Δ: 10 min, ◇: 20 min, ▽: 60 min, ○: melted under atmospheric condition.

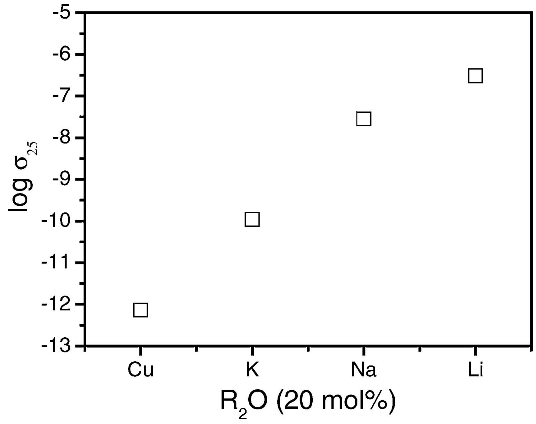

Figure 2 The effect of the type of alkali metal oxides on the room temperature electrical conductivity (σ_{25}) of $20R_2O$–30CuO–$50P_2O_5$ glasses (where R_2 = Li, Na or K).

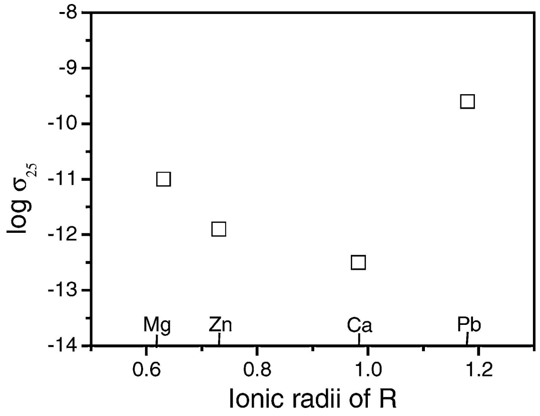

Figure 3 The effect of ionic radii of divalent cations on the conductivity at room temperature (σ_{25}) of ternary 20RO–30CuO–$50P_2O_5$ glasses (where R = Mg, Zn, Ca, and Pb).

compositions [14, 15]. The room temperature conductivities (σ_{25}) of the binary copper phosphate glasses (Table I) increase from 7.07 to 44.6 ($\times$ 10^{-13} Ω^{-1} cm^{-1}) with increase $Cu^+/Cu_{tot.}$ ratio from 0.03 to 0.15, respectively. To determine the role of Cu^+ ions on the electrical conductivity (σ_{25}) of different glass samples, the glass composition (50 CuO–50 P_2O_5) were re-melted under NH_3-gas passed over the melt for different periods of time, viz., 5, 10, 20, and 60 min. The room temperature DC conductivities measured for the glass samples, are shown in Fig. 1. The σ_{25} values gradually increase from 7.07×10^{-13} to 1.1×10^{-10} Ω^{-1} cm^{-1} with increasing $Cu^+/Cu_{tot.}$ ratios from 0.03 to 0.45, respectively. A significant increase of the σ_{25} (3.1×10^{-9} Ω^{-1} cm^{-1}) was observed when $Cu^+/Cu_{tot.}$ ratio exceeds ~0.5 (Fig. 1). From the results of Table I and Fig. 1, the main factor affecting σ_{25} values is the Cu^+ content.

Replacing alkali metal oxide for 20 mol.% CuO in copper metaphosphate glass results in an increase in the electrical conductivity (Fig. 2). As the ionic radii of alkali ions decrease, the σ_{25} values (Table I) increase from 1.09×10^{-10} to 2.81×10^{-8} to 3.04×10^{-7} Ω^{-1} cm^{-1} for K, Na and Li containing glasses, respectively. The results can be explained based on the contribution of mobile alkali ions in an ionic conduction process [16]. Since the glass is known to possess a structure lacking long-range order, therefore the conduction is best viewed from a defect type mechanism [1]. Because of the disorder of the structure, the mobile ions can move from one interstice to another in the glassy network [17]. The factors that are believed to control the magnitude of conductivity in glass are associated with the binding energies holding the mobile ions in their equilibrium (metastable) sites and the migration barriers that the ions face due to the ionic size requirements for their movement [18]. Therefore, K^+ ion is bound more weakly in the glass network, but it provides a stronger resistance to diffusion compared with Na^+ and Li^+ ions because of its larger radius. The same behavior is observed [19] in some of the non-phosphate glasses, where, σ_{25} was found to increase in the order K < Na < Li. The conductivities of the ternary glasses MgO-, CaO-, ZnO- and PbO-containing copper phosphate glasses showed that; as the divalent ionic radius increases the room temperature conductivities decrease in the order MgO > ZnO > CaO (Fig. 3). It worth mentioning that

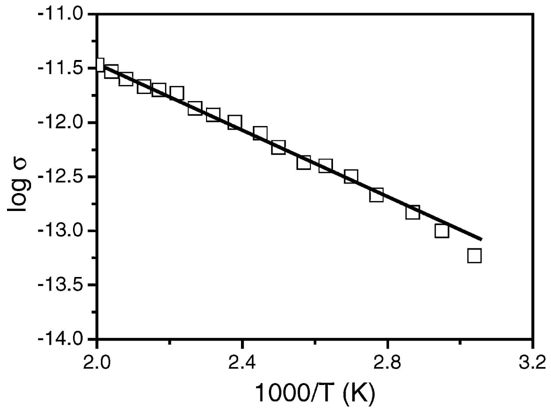

Figure 4 Temperature dependencies of the conductivity of ternary 30CuO–20PbO–50P_2O_5 glass melted under reducing conditions.

in all glass systems, the Cu^+ content decrease with the increase in the glass basicity.

According to the conduction theory by hopping mechanism in glasses containing transition metal ions, it is generally considered that "hopping" of charge carriers takes place from one strongly localized state to another [20]. These two states are the possible two valence states or coordination states of the transition metal ion. According to Mott equation [21], the maximum conductivity values via electron hopping mechanism should appear when the ratio of the reduced state to the total metal-ion concentration is equal to 0.5 ($Cu^+/Cu_{tot.} = 0.5$). On the contrary, the room temperature DC conductivity significantly increases when the ratio $Cu^+/Cu_{tot.}$ exceeds 0.5 (Fig. 1). Also, the conductivity of the ternary PbO-containing glass ($Cu^+/Cu_{tot.} = 0.63$) has a higher conductivity compared with the alkaline copper phosphate glasses (Fig. 3). According to Tsuchiya and Moriya [22], these observations can be explained due to the existence of two different sites for Cu^+ ions: one forming Cu^{2+}–O–Cu^+ bonds, responsible for the hopping conduction (by electron transfer between different localized sites) and the other in the clusters, within which Cu^+ ions should have a higher mobility and being able to act as charge carriers in an ionic conduction mechanism. Therefore, the conduction mechanism in the present study can be attributed to the electron transfer between different localized sites (Cu^+—O—Cu^{2+} ↔ Cu^{2+}—O—Cu^+), which is enhanced by an ionic conduction mechanism through the mobility of Cu^+ ions in the glass samples having high concentrations of Cu^+ content.

To further prove these results, it is expected that if the $Cu^+/Cu_{tot.}$ ratio of Pb-containing glass is increased, its σ_{25} value would further increase. Batch composition 30CuO–20PbO–50P_2O_5 has been re-melted under a reducing atmosphere (NH_3-gas) to obtain a higher proportion of Cu^+ ions. The ratio $Cu^+/Cu_{tot.}$ is found to be equal to 0.97 with corresponding σ_{25} values equal to 1.25×10^{-6} (Table I). For this glass sample, the conductivity over a high temperature range (Fig. 4) was measured, the data fit the Arrhenius equation $\sigma = \sigma_0 \exp^{(-Ea/kT)}$. The activation energy (E_a) is found to be 0.15 eV, which confirms the similarity with the semiconducting materials.

It can be concluded that in glasses with $Cu^+/Cu_{tot.} < 0.5$, Cu^+ ions are likely to be in localized sites and conduction would be produced by electron transfer between the different localized sites, which is in agreement with the small polaron model. As the Cu^+ ion content increases ($Cu^+/Cu_{tot.} > 0.5$), clusters are tended to be formed and the ionic conduction of Cu^+ ions may be responsible for further increase of the conductivity.

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Received 8 March
and accepted 15 July 2006