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Electrical conductivity of copper lithium phosphate glasses

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ABSTRACT

Copper based oxide glasses are especially interesting for the possibility of ionic-electronic mixed conduction, which has potential applications in energy and switching devices. Accordingly, lithium metaphosphate glasses are investigated within the (100-x) Li_2O - xCu_2O - 50P_2O_5 series, where Li^+ ions are gradually replaced by copper ions. Based on the changes in glass transition temperature and thermal stability via structural modification, the glasses are shown to be predominantly ionic conductors. In fact, they exhibit signs of classic mixed mobile ion effect (MMIE), a hallmark of ion conduction in glass, which would be due to Li^+ and Cu^+ ions in the present case.

1. Introduction

Phosphate glasses are of much current interest due to their easy preparation at low temperatures, strong glass forming character, high ionic conductivities and potential for different applications [1–6]. The properties of phosphate glasses can be modified by the addition of halides or oxides of alkali, alkaline earth and transition metals into the glassy network [7–10]. Among them glasses containing transition metal (TM) ions are especially attractive because of their applications as cathode materials in batteries, memory switching, electrical threshold and optical switching devices [11–13].

Glasses containing high concentration of transition metal oxide (TMO) are usually amorphous semiconductors that are employed as electronic conductors with conductivity value in the range of 10^{-4} to 10^{-11} Ω^{-1} cm^{-1} at 300 K and negative temperature coefficient of resistivity [14,15]. The general condition for electronic conduction is that the TM ion should be capable of existing in more than one valence state so that conduction can take place by the electron transfer from ions in a lower valence state to those in a higher valence state [11,16–21]. The unpaired electron induces a polarization of the TM ion around it and forms a polaron [22]. When significant amount of alkali oxide is added into the glass network, mixed electronic-ionic conduction can be observed. The glasses exhibiting mixed electronic–ionic conduction can be employed as cathode materials whereas purely ionic conducting glasses can be used as solid electrolytes in electrochemical cells [23]. Interesting results have been reported in literature on copper containing glasses as the mixed electronic-ionic conductors as well as fast ion conductors (FIC) [24–29]. In such glasses, where copper ions exist in two valence states, Cu^+ and Cu^{2+}, the electronic conduction occurs by polaron hopping between these two ions, while the ionic conduction arises from Cu^+ ion diffusion [30–33]. A potential transition of nature of the conduction from mixed conductor to FIC is promising for their application in integrated batteries either as electrodes or as electrolytes. To fully exploit the useful characteristics of copper based glasses in applications, it is important to understand the transport mechanism in relation to their structure. Therefore, compositions belonging to lithium copper phosphate system (Li_2O - Cu_2O -P_2O_5) were synthesized and characterized to provide a mechanistic insight into the ion-polaron correlation effect and the electron/ion hopping phenomenon, as well as their correlation with the ultimate electrical properties. Copper oxide has been introduced as Cu_2O since most of the past works focused on the electrical properties of copper phosphate glasses obtained by introducing copper as CuO.

2. Experimental procedure

2.1. Glass preparation

To prepare glasses of (100-x) Li_2O - xCu_2O - 50P_2O_5 (x = 0, 5, 10, 15, 20 mol%) compositions as identified in Table 1, appropriate amounts of Cu_2O (Carlo Erba, 98%), ammonium dihydrogen orthophosphate ($NH_4H_2PO_4$, Carlo Erba, 98%) and lithium carbonate (Li_2CO_3, Carlo Erba, 98%) were mixed for 15 minutes and heated in a muffle furnace from room temperature to 400°C and maintained there for 3 hours to decompose $NH_4H_2PO_4$. Next, the mixture was heated to and kept at 900°C for 1 h to ensure good homogeneity of the melt. The melt was then quickly cast in a graphite mold at room temperature and annealed for 2 hours at approximately 10°C below the glass transition temperature (T_g) in order to relieve stresses.

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Table 1
Label of the obtained glasses.

Composition (mol%)	Label
$50Li_2O–50P_2O_5$	CG0
$45Li_2O–5Cu_2O–50P_2O_5$	CG5
$40Li_2O–10Cu_2O–50P_2O_5$	CG10
$35Li_2O–15Cu_2O–50P_2O_5$	CG15
$30Li_2O–20Cu_2O–50P_2O_5$	CG20

2.2. Glass characterization

For X-ray diffraction (XRD) and differential thermal analysis (DTA) the samples were crushed to a fine powder (<20 μm) with pestle and mortar. XRD analysis was performed using a PANAlytical X'Pert PRO diffractometer (Cu-α radiation λ = 1.5405 Å). Diffraction patterns were acquired on finely ground samples for 2θ values ranging from 5 to 80 degrees. The density (ρ) of all the glass samples was obtained employing Archimedes principle. The molar volume (V_m) of each glass was evaluated from the density (ρ) and the molecular weight (M) according to $V_m = M/\rho$.

The thermal properties of all glasses were determined using differential scanning calorimetry (Thermal Analysis Instruments, Model DSC 2920) from 25 to 600°C at 10°C/min to determine the glass transition temperature (T_g), the onset of crystallization (T_x), the peak crystallization temperature (T_c) and the thermal stability that is defined as: $\Delta T = T_x - T_g$. When more than one T_c (and then T_x) is observed, its lowest value is considered in calculating ΔT.

For electrical measurements, a gold film was deposited on the samples by vacuum evaporation. The deposited electrodes were sufficiently thick and adhered to the glass substrate in order to provide electrical continuity at all temperatures. The AC conductivity (σ_{AC}) of glasses was measured with a precision automated capacitance bridge (Carl Andeen Model CGA-83) in the frequency range of 10 Hz to 100 kHz at different temperatures. Additional AC response was recorded using a Potentiostat/galvanostat VersaStat3-400 equipped with an FRA module (Frequency Response Analyzer). The temperature was varied from ambient to 200°C depending on the glass composition. The complex impedance data, $Z^*(\omega)$, were plotted on the complex plane with real part $Z'(\omega)$ on the *x*-axis vs. imaginary part $Z''(\omega)$ on the *y*-axis. Each point on this plot represents a measurement of $Z'(\omega)$ and $Z''(\omega)$ at a specific angular frequency ($\omega = 2\pi f$). DC conductivity was determined as the intersection of the high frequency arc with the real axis.

3. Results

The prepared binary and ternary glasses were homogeneous and free of bubbles. The X-ray powder diffraction confirmed the vitreous nature of all the samples. Indeed, the X-ray patterns comprised only broad humps, typical of vitreous solids as shown in Fig. 1 for the CG5 sample as a representative example. $Li_2O–P_2O_5$ glass was transparent and colorless, while glasses doped with Cu_2O appeared from light to dark green as the Cu_2O content increased, due to the presence of Cu^{2+} ions.

3.1. Density and Molar Volume

Table 2 shows the density (ρ) and molar volume (V_m) as a function of glass composition. The molar volume of a glass depends on the density and its structure. Thus its measure, as a function of the chemical composition, can be useful to provide the first order structural information. With increasing copper oxide content V_m shows an increment from 0 to 10 mol% followed by a slight decrease on further increase to 20 mol%.

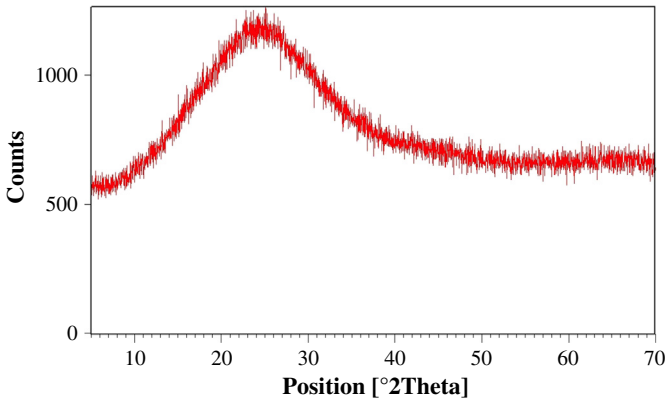

Fig. 1. X-Ray Diffraction pattern of the CG5 glasses.

3.2. Differential scanning calorimetry (DSC)

The DSC curve usually consists of endothermic peaks, which indicate the occurrence of glass transition and melting, and exothermic peak as a result of crystallization. These peaks establish thermal stability ΔT as defined above from the DSC analysis. A large value of ΔT is essential for most commercial applications of such glasses. Increasing the Cu_2O content raises the T_g gradually (Table 2), reaching 350 °C at 20 mol% of Cu_2O (CG20). As concerns the T_c, we have observed that CG5 and CG20 glasses show two crystallization peaks, whereas CG10 and CG15 glasses exhibit just one such peak (see Fig. 2 for CG5 and CG15 as examples). The presence of two crystallization peaks may be due to the presence of distinct phase transformations, different crystallization mechanisms (such as surface and bulk crystallization), or different crystallization products (such as the formation of $Li_4P_2O_7$) [34]. We do not evaluate these possibilities as they do not pertain to the object of this work. A progressive increase of ΔT (Table 2) is observed from 0 to 15mol% of Cu_2O, then a decrease is detected for 20 mol%, indicating a lower thermal stability of the CG20 with respect to the other glasses of the present series.

3.3. Electrical properties

The electrical measurements of the CG glasses were performed in order to explore the conduction mechanism of the vitreous samples. The AC electrical conductivity (σ_{AC}) of various glasses was measured as a function of frequency and temperature as shown in Figs. 3 and 4 for CG0 and CG5 compositions, as representative examples. The other glasses exhibited similar behavior. To better understand the role of copper and lithium on the transport properties, the DC conductivity, σ_{DC}, as obtained from complex impedance plots or from the plateau of the σ_{AC} plots was fitted to the Arrhenius equation (Eq. (1)):

$$\sigma_{DC} = (\sigma_0/T)\exp(-E_a/kT) \quad (1)$$

where σ_0 is the pre-exponential factor, k is the Boltzmann constant, T is the absolute temperature and E_a is the activation energy for conduction. All the glasses show the same general behavior i.e. with increasing temperature the conductivity rises exponentially (Fig. 5). The values of the

Table 2
Density (ρ), molar volume (Vm), glass transition temperature (Tg), thermal stability (ΔT), activation energy (E_a) and pre-exponential factor (σ_0) variations with composition.

Glass	ρ (g/cm^3)	Vm (cm^3/mol)	Tg (°C)	ΔT (°C)	E_a (eV)	σ_0 (Ω cm^{-1})
CG0	2.40 ± 0.01	35.80 ± 0.01	320 ± 5	100 ± 5	0.77	3.56×10^6
CG5	2.49 ± 0.01	36.78 ± 0.01	325 ± 5	100 ± 5	0.92	4.91×10^7
CG10	2.51 ± 0.01	38.74 ± 0.01	330 ± 5	110 ± 5	1.04	2.04×10^8
CG15	2.69 ± 0.01	38.25 ± 0.01	345 ± 5	120 ± 5	1.08	5.66×10^6
CG20	2.88 ± 0.01	37.69 ± 0.01	350 ± 5	85 ± 5	1.07	2.78×10^6

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