

Graphite as Conduction Modifier for Copper Superionic Glasses

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Abstract: Cu⁺ conducting glasses were prepared in the Cu₂O-MoO₃-P₂O₅ system. These glasses, known for their high ionic conductivity, are promising in applications to solid state batteries and other energy storage devices. The amorphous state of the samples has been confirmed through X-ray diffraction. The electronic conductivity was measured by means of the Wagner polarization method. Colloidal graphite has been used in order to maintain a reducing medium, necessary to stabilize the copper at the lower state of valence. The variations of the conductivity, activation energy and transference number vs. the graphite amount has been investigated. The records show a constant rise until 1 % wt. graphite. Once this amount has been exceeded, the conductivity drops below that of the sample without graphite.

Keywords: glass, conductivity, activation energy

1. Introduction

Molten glasses usually exhibit good ionic conductivity but in the solid state they are rather poor conductors. Even so, it was found that by using the rapid cooling techniques a special fast ion-conducting glass (FIC) could be prepared. These materials have been studied for several years with the intention to use them as solid electrolytes for various electrochemical solid state devices such as rechargeable batteries and chemical sensors [1-3]. These glassy electrolytes have no grain boundaries that may cause problems for the transport of ions and their composition within a glass-forming region can be changed almost continuously.

Cu⁺ is mentioned to be a fast conducting ion in a number of glass systems [4, 5]. Although silver and lithium ion conducting glasses have been studied extensively during the last decade, copper ion conducting glasses, having comparable conductivities and lower costs, have not received much attention.

2. Experimental

The investigated glasses from the ternary system: 60Cu₂O-30MoO₃-10P₂O₅ containing x (% wt) graphite, (x = 0; 0,25; 0,50; 0,75; 1,00; 1,25; 1,50; 1,75 and 2,00) were prepared by the melt-quench method, using the following analytical grade reagents: Cu₂O, (NH₄)₆Mo₇O₂₄, (NH₄)₂HPO₄ and colloidal graphite as starting materials. The melting process (at a 10 grams scale) was carried out at 1073 K for 1 hour in an electrical furnace. Disk shaped samples for conductometric studies were prepared by quenching liquid drops between two cold stainless steel plates. In order to relieve the samples of any mechanical stress, they were annealed for 2 hours at 433 K. The amorphous state of the samples has been confirmed through X-ray diffraction (CuK_α).

The ionic transfer number was obtained by means of the Wagner polarization method. The electrical measurements were conducted in open air, at 293 K, using the electrochemical cell:



where Cu and Ag are the reversible and blocking electrodes, respectively, applied to the two parallel faces by vacuum deposition.

The cell was polarized by applying a dc potential in the range of 1-10 V across the evaporated Cu (negative) and evaporated Ag (positive) electrodes.

Alternating current conductivity, conductance G and the capacitance C, were measured in open air, using an impedance bridge in the frequency range of 10 to 100 kHz at temperatures between 298 - 323 K. The silver electrodes were applied by vacuum deposition. The sample temperature was measured with a Pt-Rh thermocouple placed above the glass sample. The measurements started after the sample temperature had equilibrated.

The dc conductivity of the glasses was determined using the complex impedance analysis [6]. The real (Z') and the imaginary (Z'') of the complex impedance (Z*) were calculated using the relations:

$$Z' = \frac{G}{G^2 + \omega^2 C^2}$$

$$Z'' = \frac{\omega C}{G^2 + \omega^2 C^2} \quad (1)$$

where $\omega = 2\pi f$ is the angular frequency of the electrical signal.

The bulk conductivity was obtained from the relation:

$$\sigma = \frac{d}{S R} \quad (2)$$

where R is the dc resistance, obtained from the complex impedance plots, d is the sample thickness and S is the effective electrode area.

The temperature dependence on the conductivity was studied using the Arrhenius equation:

$$\sigma = \sigma_0 e^{-\frac{W}{kT}} \tag{3}$$

where σ_0 is the pre-exponential factor, T is the thermodynamic temperature, and k is the Boltzmann constant and W is the activation energy.

3. Results and Discussion

The starting composition: 60Cu₂O-30MoO₃-10P₂O₅ (molar %) corresponds to the maximum amount of Cu₂O that allow the synthesis of vitreous samples by rapid quenching in our experimental conditions. During melting in open air, a large quantity of Cu⁺ ions is oxidized to Cu²⁺ in the presence of O₂ at high temperatures. The usual method to avoid this undesirable process is the vacuum melting, but the present study had in view the stabilization of the copper ions at the lower state of valence through by

creating a reducing medium in the melt, using colloidal graphite;

The amounts of colloidal graphite added to the starting glass composition: 60Cu₂O - 30MoO₃ - 10P₂O₅ are presented in Table 1.

All the glass samples were black and transparent (disk shaped with thickness under 1 mm). Starting with the fifth sample (1,25 % wt graphite), graphite residuum remained on the crucible's walls.

TABLE 1. Amounts of graphite added to the 60Cu₂O-30MoO₃-10P₂O₅ glass matrix

Sample no	graphite (% wt)
1	0,25
2	0,50
3	0,75
4	1,00
5	1,25
6	1,50
7	1,75
8	2,00

AC conductivity measurements

Figure 1 shows complex impedance plots for the glass 60Cu₂O-30MoO₃-10P₂O₅ with different graphite amounts at 303 K.

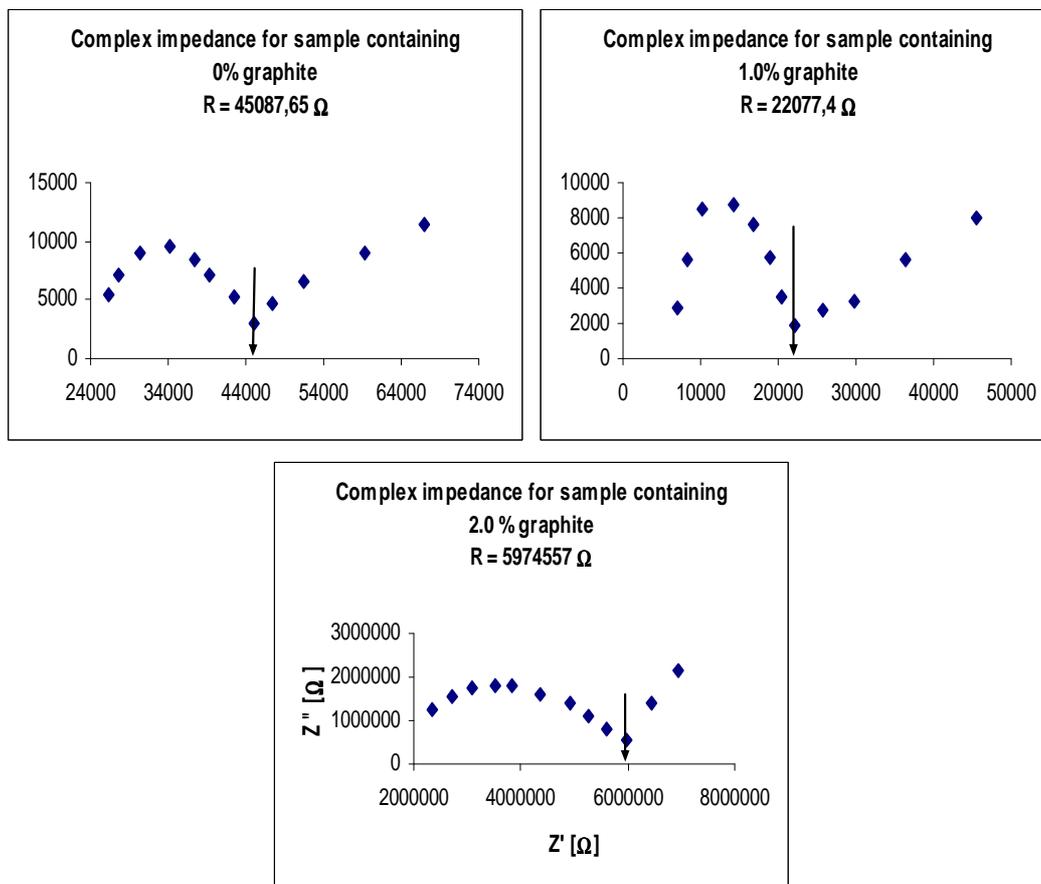


Figure 1. Complex impedance plots for various amounts of graphite at 303K

Figure 1 shows the real (Z') versus imaginary (Z'') parts of the complex impedance data for the $60\text{Cu}_2\text{O}-30\text{MoO}_3-10\text{P}_2\text{O}_5$ glass. The bulk impedance is attributed to the semicircle observed at each temperature, and thus the bulk resistance is identified as the intersection point of the semicircle with the real axis. The bulk conductivity was calculated using the bulk resistance and the sample dimensions. Similar results were obtained for the other glasses. The inclined straight line at the low frequency region could be the effect of mixed electrode and electrolyte interface.

The variation of the dc conductivity vs. reciprocal temperature for the same samples is showed in figure 2. The plots indicate an Arrhenius behavior for all the samples.

The variations of the conductivity and the activation energy vs. the graphite amount at room temperature are presented in Figure 3 (a, b).

A constant rise of the conductivity up to 1 % wt. graphite can be observed. Once this amount has been exceeded, the conductivity drops below to that of the sample without graphite. A correlated variation of the activation energy (E_{dc}) upon the graphite amount, calculated using the Arrhenius equation (3) is presented in fig. 3b.

DC conductivity measurements

The global conductivity of the investigated glasses was measured in DC current using a standard two electrodes method by constructing the following type of cell: (-)Ag/Glassy Electrolyte/C(+), where C is graphite used as a blocking electrode, and Ag is silver used as a non-blocking electrode. The schematic diagram for measuring the electronic conductivity is shown in fig. 4.

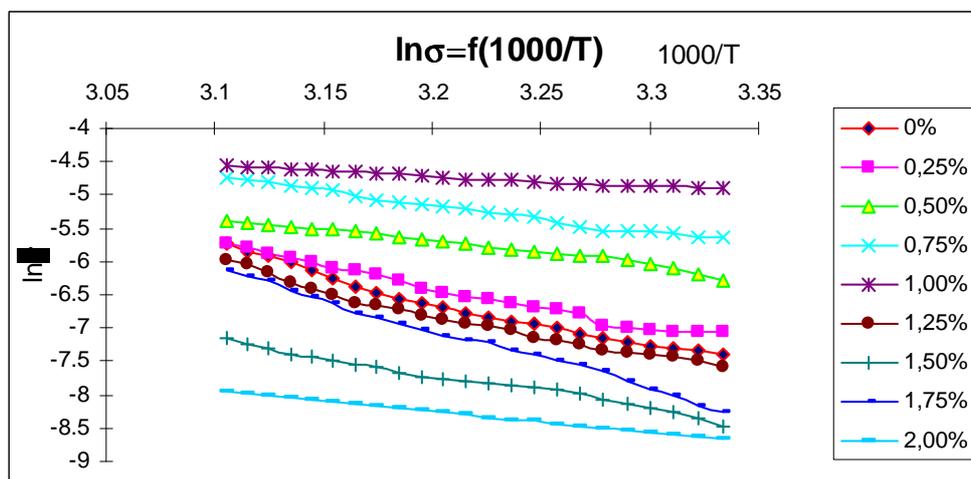


Figure 2. The variation of the dc conductivity vs. reciprocal temperature for the $60\text{Cu}_2\text{O}-30\text{MoO}_3-10\text{P}_2\text{O}_5$ glass matrix for various amounts of graphite

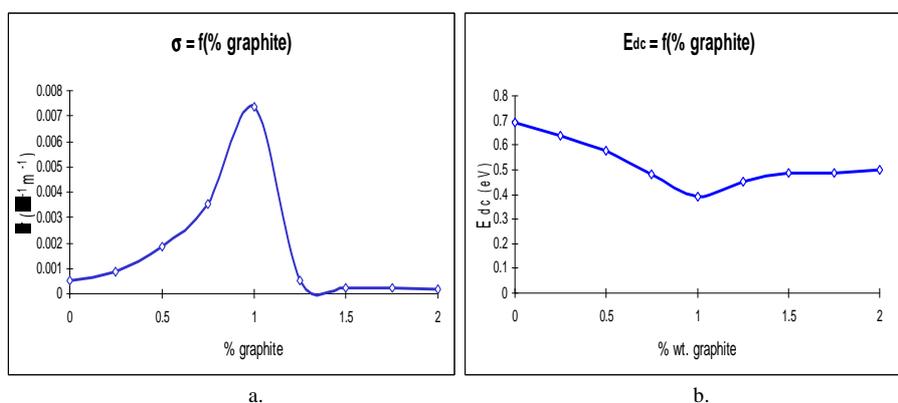


Figure 3. Variation of conductivity (a) and activation energy (b) vs. graphite amount at the room temperature for the $60\text{Cu}_2\text{O}-30\text{MoO}_3-10\text{P}_2\text{O}_5$ glass matrix.

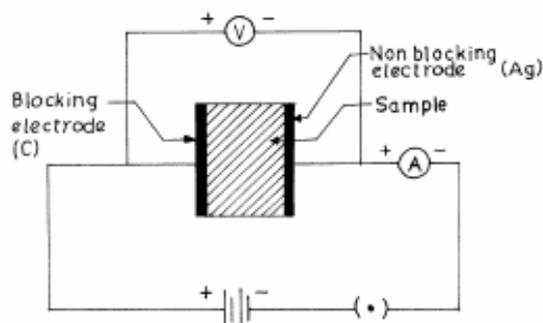
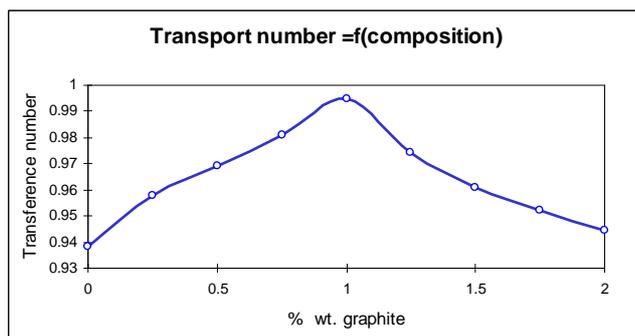


Figure 4. Schematic diagram for measuring the DC conductivity

The DC conductivities reflect both the electronic and ionic conduction in the glass. The importance of the ionic conduction upon the total conduction is expressed by the transport number (4) [2]:

$$t = \frac{\sigma_{AC}}{\sigma_{global}} = \frac{\sigma_{AC}}{\sigma_{DC}} \quad (4)$$

The dependence of the transport number upon the graphite amount is reflected in figure 5.

Figure 5. Variation of the transport number upon graphite amount for the 60Cu₂O-30MoO₃-10P₂O₅ glass matrix

The values of the transport number, very close to unity shows the major contribution of the ionic conductivity in these glasses. The electronic contribution is negligible; Cu⁺ ions moving through the conduction pathways are the charge carriers for the conduction process. The effect of the reducing environment created by graphite is favorable up to 1%, where the higher transport number was reached. Over that value, the transport number drops, but not under 0.90, confirming the ionic mechanism of charge transport for these glasses.

4. Conclusions

The investigated glasses from the ternary 60Cu₂O-30MoO₃-10P₂O₅ system are fast ion conducting, the charge transport is carried out by Cu⁺ ions moving through the conduction pathways.

Using graphite as reduction medium in order to shift the redox equilibrium: Cu⁺ ⇌ Cu²⁺ to the lower state of valence, enhancing the ionic conductivity was favorable for up to 1 wt %. The corresponding transport number, 0.993, very close to unity reflect the higher proportion of Cu⁺ in these glass compared to the glass without graphite, having the transport number 0.94.

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