



# The influence of transition metal oxides type $M^+/M^{++}$ on the vanadium–tellurite glasses electrical behavior



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## ABSTRACT

In this work, the electrical behavior and structural features of the system  $x\text{Cu}_2\text{O} (1-x)$  ( $0.5\text{V}_2\text{O}_5 \cdot 0.5\text{MoO}_3$ )  $2\text{TeO}_2$  compared to  $x\text{Ag}_2\text{O} (1-x)$  ( $0.5\text{V}_2\text{O}_5 \cdot 0.5\text{MoO}_3$ )  $2\text{TeO}_2$  (which was already studied) are explored. The main goal is to determine whether the electronic configuration of  $\text{Cu}^+$  and  $\text{Ag}^+$  ions is the key to understand the interactions of these ions with vanadium ions in the glassy matrix studied and to establish the nature of the particular electrical conductivity response. It is shown that despite the fact that both ions ( $\text{Cu}^+$  and  $\text{Ag}^+$ ) have similar electronic configurations but different sizes they have similar electrical behaviors contrary to what is commonly accepted (*i.e.* silver modified glasses are completely ionic systems, while copper modified glasses are purely electronic –polaronic- semi-conductors). It is expected that both behave as mixed electrical conductors, neither pure polaronic nor pure ionic. It has been found that the minimum observed in the isotherm of conductivity can be explained by the structural features of this glassy matrix and not by a change in its mechanism of conduction.

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## 1. Introduction

The study of oxide glasses with transition-metal ions in their composition is of technological interest because of the many potential applications such as memory switching, micro-ionic devices based on ion conduction or ion exchange properties, electrical and optical devices, etc. [1,2].

Particularly, the electrical conductivity behavior of these glasses shows a semiconducting nature when the transition metal ions are present in different oxidizing states simultaneously [3]. In 1954, E.P. Denton, H. Rawson and J.E. Stanworth [4] explained that vanadium tellurite glasses are remarkable for their physical properties such as low annealing temperature, relatively low electrical resistivity and, in spite of the fact that their color is rather dark they have quite good infra-red transmission properties. In their work they showed that all the vanadium glasses prepared for their studies were semiconductors and their conduction was of an n-type. Later, in 1957, P.L. Baynton, H. Rawson and J.E. Stanworth studied the electrical properties of several other vanadium glasses [5] of formula  $\text{BaO}-\text{V}_2\text{O}_5-\text{P}_2\text{O}_5$  and  $\text{Na}_2\text{O}-\text{BaO}-\text{V}_2\text{O}_5-\text{P}_2\text{O}_5$  with  $\text{V}_2\text{O}_5$  contents

ranging between 50 and 87 mol% which behave as semiconductors; the highest  $\text{V}_2\text{O}_5$  contents having a specific conductivity of the order of  $10^{-5} \text{ S cm}^{-1}$  at room temperature. From those results, they have postulated that the introduction of other oxides like  $\text{Na}_2\text{O}$  or  $\text{BaO}$  into the glass disturbs the balance of the  $\text{V}^{5+} \rightleftharpoons \text{V}^{4+}$  equilibrium. When vanadium oxide is present in glassy matrices, it usually shows mixed valence states such as  $\text{V}^{\text{reduced}}$  and  $\text{V}^{\text{oxidized}}$  which then in turn build a path between those different valence states, *i.e.* a chain where the charge transfer extends depending on the percentage of  $\text{V}_2\text{O}_5$  present. This kind of chains seems to be disrupted by the presence of the alkali and alkali-earth oxides.

In our previous works [6–10], we have investigated other tellurite glassy systems of general formula:  $x\text{M}_2\text{O} \cdot (1-x)$  ( $0.5\text{V}_2\text{O}_5 \cdot 0.5\text{MoO}_3$ )  $\cdot 2\text{TeO}_2$ ;  $x \text{M}_2\text{O} \cdot (1-x)\text{V}_2\text{O}_5 \cdot 2\text{TeO}_2$  ( $M = \text{Li}, \text{Na}, \text{Ag}$ ) and  $x\text{NO} \cdot (1-x)$  ( $0.5\text{V}_2\text{O}_5 \cdot 0.5\text{MoO}_3$ )  $2\text{TeO}_2$  ( $N = \text{Mg}, \text{Ca}, \text{Sr}, \text{Ba}$ ). We have shown that all the  $M$  ions decrease their electrical conductivity response when their concentrations increase from 0.0 to around 0.5. Then, when  $x$  reaches a value between 0.5 and 1.0, the conductivity increases again but now due to the ionic conductivity of the mobile cations in those systems. An important difference is observed for  $N$  ions ( $\text{Mg}, \text{Ca}, \text{Sr}, \text{Ba}$ ), they involve a more intense conductivity decrease in the same range (from 0.0 to about 0.5). Nevertheless, for greater  $x$  values of alkali earth cations with larger radius, the conductivity either becomes constant or it increases (*e.g.*

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Ba<sup>2+</sup>). But, alkali earth cations with smaller radius decrease the conductivity even further (e.g. Mg<sup>2+</sup>). Although it is commonly accepted in the literature that silver cations behave as pure ionic conductors in many glasses, they behave quite differently from the aforementioned univalent cations.

An increase in the conductivity response in these matrices [(1 - x) (0.5V<sub>2</sub>O<sub>5</sub>-0.5MoO<sub>3</sub>) 2TeO<sub>2</sub>] (when x > 0.5, no matter if MoO<sub>3</sub> is present or not) has been observed in our previous works [9]. Silver cations increase the glass conductivity several orders of magnitude more than Li<sup>+</sup> or Na<sup>+</sup> modifier oxides. In addition, the activation energy of the conduction process of silver cations is almost half the one for Li<sup>+</sup> and Na<sup>+</sup> cations. Therefore, the nature of a silver cation -as a transition metal- has a different influence on the conductivity behavior. Its electronic configuration compared to the other monovalent cations leads to other possible interactions between the structure and the charge carrier in these Vanadium–Tellurite glassy matrices.

Other common statement accepted in the literature is that the presence of copper (I) oxide in a glass tends to increase the electrical conductivity. This conduction process is governed by electronic hopping between Cu<sup>+</sup> and Cu<sup>2+</sup> ions. Notwithstanding that, the Cu<sup>+</sup>/Cu<sup>2+</sup> total ratio controls the mechanism [11].

Cuprate glasses based on conventional network formers such as P<sub>2</sub>O<sub>5</sub> and B<sub>2</sub>O<sub>3</sub> have been studied extensively [12–16]. In many of these works, the high activation energy (around of 1 eV) has been observed and explained assuming a hopping of electrons between non-identical copper sites [13]. Additionally, T. Tsuchiya and T. Moriya [12] have observed mixed electronic and ionic conduction in copper phosphate glasses and they have interpreted their results assuming that the copper ions exist in sites with different bending forces. The structural studies [3] of these systems have shown that copper ions occupy the network forming position and thus, they are unable to diffuse through the host matrix assuming the absence of ionic conduction in these cuprate glasses. Hazra and Gosh [3] have shown that when the glassy system is formed by PbO and CuO and it is coupled with a magnetic field, the copper ions exist in two oxidation states (Cu<sup>+</sup> and Cu<sup>2+</sup>) in every glass composition. They have shown that the concentration of the reduced copper ions [Cu<sup>+</sup>] rises with the increase of total copper ion concentration in glass compositions and, this ratio is approximately constant for every glass.

In the light of these facts and taking into account that many researchers (including ourselves) consider glasses modified with silver oxide as pure ionic conductors, we aim to explore the electrical behavior and structural features of the system xCu<sub>2</sub>O (1 - x) (0.5V<sub>2</sub>O<sub>5</sub>-0.5MoO<sub>3</sub>) 2TeO<sub>2</sub> and compare it to xAg<sub>2</sub>O (1 - x) (0.5V<sub>2</sub>O<sub>5</sub>-0.5MoO<sub>3</sub>) 2TeO<sub>2</sub> (which we studied in the past). Our main goal is to clarify if their electronic configuration is the key to understand their possible interaction with vanadium ions in these glassy systems. We aim to determine the nature of their electrical conductivity behavior considering that both modifier ions (Cu<sup>+</sup> and Ag<sup>+</sup>) have similar electronic configuration but different sizes (because they belong to the third and fourth period of the periodic table). Furthermore, we wanted to explore if these silver glasses are truly completely ionic systems while, copper modified glasses are purely electronic (polaronic) semiconductors.

## 2. Experimental

Glasses of formula: xCu<sub>2</sub>O (1 - x) (0.5V<sub>2</sub>O<sub>5</sub>-0.5MoO<sub>3</sub>) 2TeO<sub>2</sub> with x = 0.0–0.9 were prepared by the standard melt quenching technique. Analytical reagent grade chemicals of TeO<sub>2</sub>, Cu<sub>2</sub>O, MoO<sub>3</sub> and V<sub>2</sub>O<sub>5</sub> were used to prepare the glass samples. The stoichiometric compositions for batches of 5 g were mixed thoroughly and placed in a porcelain crucible. Then, the crucible was put in an

electric furnace which was heated at 850 °C for 40 min. It was stirred twice to ensure homogenization. The molten mix was poured in drops on a preheated aluminum plate. Then, these drops were kept for annealing at 200 °C during 2 h.

Differential Scanning Calorimetry (DSC) and X-Ray diffraction (XRD) analysis were done on each composition to confirm the amorphous nature of the samples. Every DSC thermograms (with a heating rate of 10 °C/min) have shown the characteristic endothermic peak which is associated to the glass transition temperature (T<sub>g</sub>). The X-Ray diffraction was performed with PW1710 BASED in continuous scan mode with a copper anode and 45 kV–30 mA for the tension and electrical current generator respectively. The samples were exposed to the Cu K<sub>α</sub> radiation (λ = 1.54 Å) at room temperature in the 2θ range: 3°–60°.

The samples were polished with very fine sand papers in order to obtain glass disks with two parallel faces of thickness ranging between 0.4 and 0.8 mm. Each sample was coated uniformly with a thin layer of silver paint with the purpose of having proper electrical contact. Impedance measurements were carried out with an Agilent 4284A LCR meter in frequency range from 20 Hz to 1 MHz in the temperature range: 25 °C to [T<sub>g</sub> - 15]°C.

Density measurements of each glass sample were obtained using isopropyl alcohol as the secondary displacement medium in the Archimedean method and, the values reported here are the averages of three independent density measurements with their respective deviation. The OPD (oxygen packing density) for each composition was calculated from the average density values according to OPD = mol oxygen number/molar volume.

## 3. Structural results

Fig. 1 shows the X-ray diffraction results. The absence of sharp peaks in every pattern confirms that each prepared sample is a glass.

Fig. 2 shows the corresponding T<sub>g</sub> as a function of x (Cu<sub>2</sub>O or Ag<sub>2</sub>O content) for every composition. We learn from these data that for copper oxide modified glasses, their T<sub>g</sub> values increase to reach a maximum at x = 0.5, around 18% higher than the pure glassy matrix (i.e. x = 0.0) and then they decrease again to a T<sub>g</sub> similar to its symmetrical composition on the left of the figure (i.e. x = 0.2 is almost equal to x = 0.8). While for silver oxide modified glasses, their T<sub>g</sub> values decrease continuously and the T<sub>g</sub> of the highest silver oxide content (x = 0.8) is about 30% lower than the pure glassy matrix.

An interesting aspect related to the changes observed in the

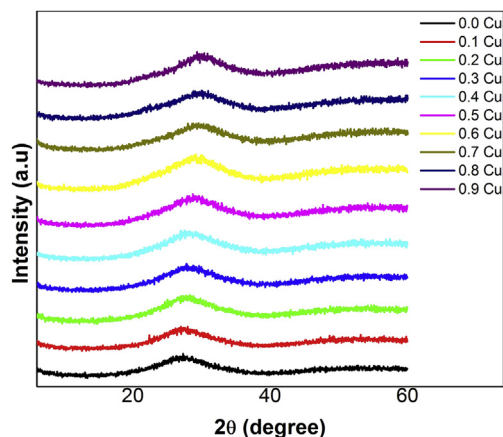
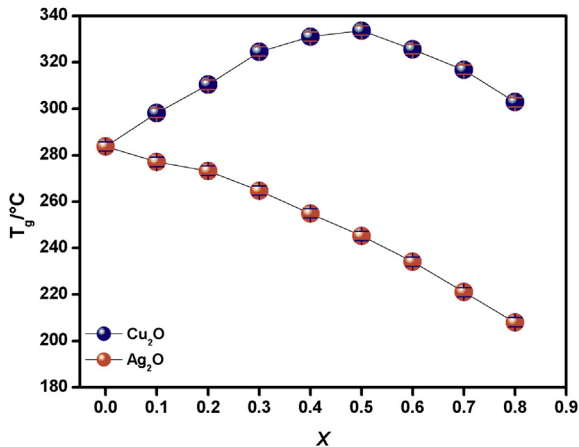


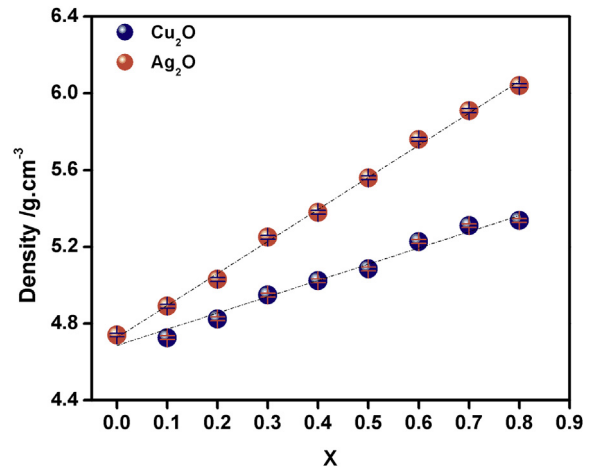
Fig. 1. X-Ray Diffraction patterns of the systems: xCu<sub>2</sub>O · (1 - x) (0.5V<sub>2</sub>O<sub>5</sub> · 0.5MoO<sub>3</sub>) · 2TeO<sub>2</sub> at room temperature.



**Fig. 2.** Glass transition temperature ( $T_g$ ) as a function of the modifier content ( $x$ ) of systems:  $x\text{Cu}_2\text{O}\cdot(1-x)(0.5\text{V}_2\text{O}_5\cdot0.5\text{MoO}_3)\cdot2\text{TeO}_2$  and  $x\text{Ag}_2\text{O}\cdot(1-x)(0.5\text{V}_2\text{O}_5\cdot0.5\text{MoO}_3)\cdot2\text{TeO}_2$ .

local order structure of oxide glasses appears when transition metal oxides are incorporated in the composition. This has been deeply studied in silicate glasses and an unusual coordination environment of those transition metal oxides has been observed [17–19]. These oxides do not form glasses by themselves and are not true modifiers as alkalis and alkaline earth oxides. Because of this, they are commonly named “intermediates”. EXAFS experiments give lower coordination numbers compared to crystalline states and this has been interpreted as a position exchange, assuming that they occupy network-former sites rather than modifier sites [20]. Other works have shown that many transition metal cations are surrounded by modifying cations when they are in the glassy matrix because of the network former polyhedra cannot balance their charge. The intermediate cations can be seen as occupying sites at the interface between the network and the modifiers in a glass structure, influencing the solubility of other ions in the melt, the chemical strength and color of the glass [18,19,21]. The literature mentions that the transition temperature of an oxide glass increases with the cross-link density of the network caused by the strength of the bonds it is composed of and the tightness of its packing in the network. In general, the cross-linking has a greater effect than the bond strength [22]. Therefore, the effect of replacement of  $\{\text{V}_2\text{O}_5\text{--MoO}_3\}$  by copper or silver oxide on the  $T_g$  in these glasses indicates that it is easier for  $\text{Cu}_2\text{O}$  to form part of this tellurite glassy matrix than it is for  $\text{Ag}_2\text{O}$ . The slight modification of the copper glass  $T_g$  is because copper ions fit the matrix as vanadium ions do (they have a similar size, contrary to what happens with silver cations) [23]. The radii of vanadium, copper and molybdenum ions are quite similar, while the radius of a silver ion is almost twice as big as the others. This mismatch in size explains the decrease in the  $T_g$  value of silver glasses when the  $\text{Ag}_2\text{O}$  content increases. Then, the increase in the  $T_g$  value of copper glasses suggests a more favorable interaction (a less interrupted matrix) between copper ions and tellurite polyhedra in the network former positions; different from what is observed in the ones resulting from  $\{\text{V}_2\text{O}_5\text{--MoO}_3\}$  and tellurite polyhedra due to a variety of coordination environments of such oxide mix.

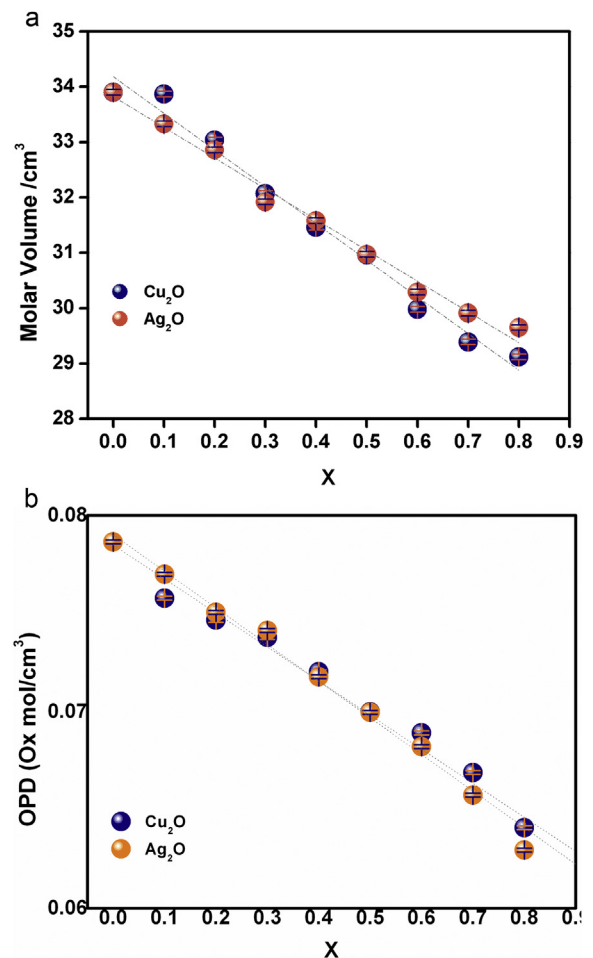
In Fig. 3, we show the density values of every composition. Those results could be predicted in the case of the silver glassy system because of the influence of its silver atomic masse. However, considering that the replacement  $\{\text{V}_2\text{O}_5\text{--MoO}_3\}$  by  $\text{Cu}_2\text{O}$  is between similar masses, the increase in the copper glass density already suggests a stronger interaction in the matrix. A different



**Fig. 3.** Density as a function of modifier content ( $x$ ) of systems:  $x\text{Cu}_2\text{O}\cdot(1-x)(0.5\text{V}_2\text{O}_5\cdot0.5\text{MoO}_3)\cdot2\text{TeO}_2$  and  $x\text{Ag}_2\text{O}\cdot(1-x)(0.5\text{V}_2\text{O}_5\cdot0.5\text{MoO}_3)\cdot2\text{TeO}_2$ .

perspective is needed being the changes induced in the matrix network. To do that, the oxygen packing density (OPD: the number of mol of oxygen per  $\text{cm}^3$  of glass) is an appropriate magnitude to analyze the compactness of that structure.

Fig. 4a and b, show the molar volume ( $V_M$ ) and OPD of both



**Fig. 4.** a) Molar Volume and b) OPD, as a function of modifier content ( $x$ ) of systems:  $x\text{Cu}_2\text{O}\cdot(1-x)(0.5\text{V}_2\text{O}_5\cdot0.5\text{MoO}_3)\cdot2\text{TeO}_2$  and  $x\text{Ag}_2\text{O}\cdot(1-x)(0.5\text{V}_2\text{O}_5\cdot0.5\text{MoO}_3)\cdot2\text{TeO}_2$ .

systems. The  $V_M$  and the OPD diminish approximately 17% and 18% respectively, for both oxides in the whole replacement of ( $V_2O_5 + MoO_3$ ).

If we assume that the mean spacing between two vanadium ions in the glassy matrix can be estimated from the composition of the samples as proposed by Hirashima et al. [24] in the same way as it was applied by N. Lebrun et al. in other tellurite glassy systems [25]:

$$a = \left( \frac{M_m}{1.2\rho N} \right)^{1/3} \quad (1)$$

where  $M_m$  is the molar mass sample,  $\rho$  is the density determined by the liquid displacement method and  $N$  is the Avogadro's number. Fig. 5 shows the results as a function of the  $Cu_2O$  and  $Ag_2O$  content.

From the results obtained applying Eq. (1), Fig. 5 shows that the inter-ionic distances do not show a strong influence of the type of modifier oxide ( $Cu_2O$  or  $Ag_2O$ ). Clearly, we have arrived to a similar result as the one showed in previous Figs. Where the  $V_M$  of the equivalent compositions are similar as are, in average, their ionic distances.

Therefore, the structural changes are not caused by the replacement of the  $\{V_2O_5 - MoO_3\}$  by  $Cu_2O$  or  $Ag_2O$ . The reason of such a different behavior of their  $T_g$ s and its explanation has to be found in the strength of the bonds. We analyze the electrical response in order to obtain additional evidence for this hypothesis.

#### 4. Electrical results

Tellurite glasses have shown two possible types of electric carriers: electrons (polarons) and/or ions according to the type of the modifier oxide incorporated.

When vanadium oxide is present in a glassy matrix, vanadium cations usually appear in different (mixed) oxidation states,  $V^{reduced}$  and  $V^{oxidized}$ . In such cases, the conduction process takes place through an electron transfer between those available centers [14,26–30]. While the electron moves through the matrix, a distortion emerges and both, the electron and the distortion, move together as a whole. This electron-distortion set is considered as a quasi-particle and is called *polaron* (analyzed in terms of a phonon assisted tunneling effect). When this distortion extends itself over the lattice constant, it is called *small polaron* [30,31]. When the electron hops between the two thermally equilibrium sites, it is

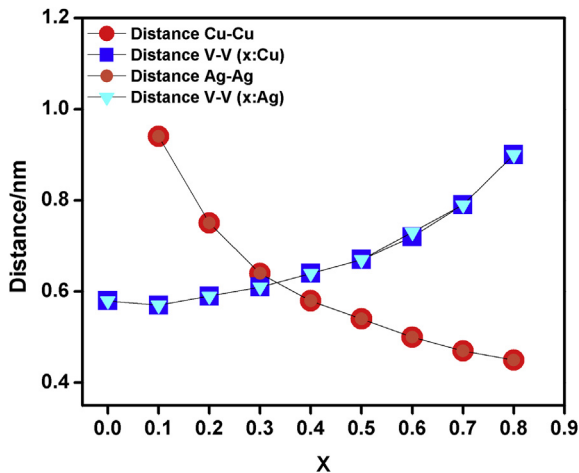


Fig. 5. Inter-ionic distance as a function of modifier oxide content ( $x$ ) of systems:  $xCu_2O (1-x)(0.5V_2O_5-0.5MoO_3)2TeO_2$  and  $xAg_2O (1-x)(0.5V_2O_5-0.5MoO_3)2TeO_2$ .

said that a non-adiabatic small polaron hopping (nASPH) motion appears. In this case,  $dc$  conductivity is expressed as [30,32]:

$$\sigma = c.(1-c).N.\frac{e^2 a^2 v_0}{6k_B T}.\exp[-2\alpha a].\exp\left[-\frac{E_\sigma}{k_B T}\right] \quad (2)$$

where  $c$  and  $(1-c)$  are the occupied and available sites ( $V^{reduced}$  and  $V^{oxidized}$ ) of the total concentration  $N$ ;  $a$  is the average distance between two adjacent V with different oxidation state;  $v_0$  is the phonon frequency;  $\alpha$  is the tunneling factor;  $E_\sigma$  is the activation energy;  $k_B$  and  $T$  have the usual meaning.

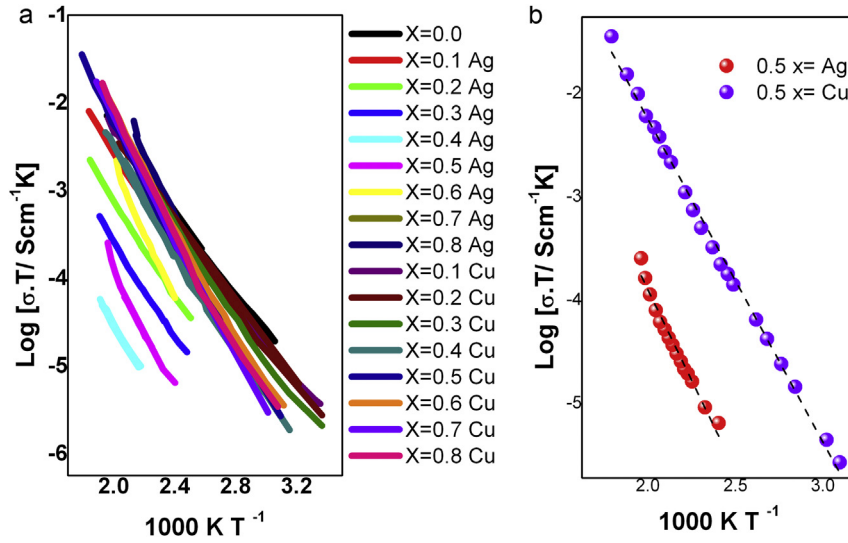
The temperature dependence of the conductivity is expressed as:

$$\sigma.T = \sigma_0.\exp\left[-\frac{E_a}{k_B T}\right] \quad (3)$$

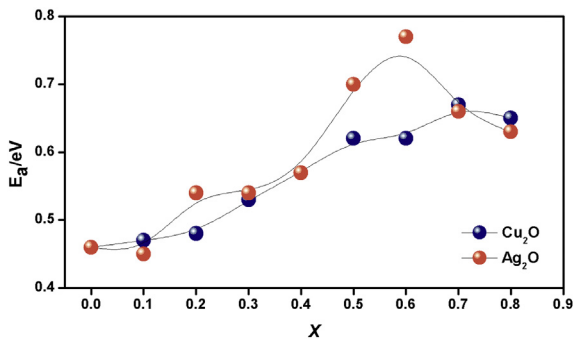
In Fig. 6a the variation of  $\log(\sigma.T)$  vs.  $T^{-1}$  is shown for both systems ( $Cu_2O$  and  $Ag_2O$  glass modified). It is very important to note that a slight linearity deviation to the corresponding linear fitting according to Eq. (3) is observed in these plots as Fig. 6b shows in more detail for two compositions, as an example. In spite of this fact, in Fig. 7 we present the  $E_a$  parameter plotted vs.  $x$  ( $Cu_2O$  and  $Ag_2O$  content). The  $E_a$  in Eq. (3) can be considered as the potential barrier that the electron has to overcome due to the phonon vibrations in the direction of the  $V^{red}-V^{oxid}$  pair [33,34] and at intermediate  $Ag_2O$  content Fig. 7 shows that there is an important augmentation of such barrier that involves an extra difficulty for the charge carrier that comes from changes in the structure.

The electrical conductivity of the ternary system  $0.4TeO_2-0.6(yV_2O_5-(1-y)MoO_3)$  has been studied previously [25]. It has been shown that the conductivity continuously increases and the activation energy diminishes with the increase of  $y$  (higher  $V_2O_5$  content). This is due to the electronic (polaronic) conduction between transition metal ions with different oxidation states (the "small polaron" model). Vanadium ions are the only atoms involved in the process  $V^{red} \rightarrow V^{oxid}$ . Molybdenum ions are not involved in the process conduction due to they need high energy to be thermally activated. Frechero et al. have shown through FTIR results, that while molybdenum is homogeneously mixed in the Tellurite glassy matrix, vanadium oxide is clearly distinguished from the spectra through its own bands [35]. As the  $V_2O_5$  concentration grows, the average distance between two vanadium atoms diminishes and therefore the electrical conductivity augments. Another important point to take into account is the ratio  $V^{red}/V^{oxid}$ . This is something that is conditioned by its composition because it depends strongly on its redox environment [36–38].

Taking into account the two possible different regions in the studied range of temperature (two distinguishable slopes), we plot in Fig. 8 the isothermal variation of the electrical conductivity as a function of  $x$  ( $Cu_2O$  and  $Ag_2O$  glasses). Fig. 8 shows a significant reduction in the conductivity when  $xAg_2O$  is in between of 0.4 and 0.5; but, this behavior is almost imperceptible on  $Cu_2O$  glass in every isotherm presented here. It was assumed in Ref. [7,9] by comparison with the alkali cations behavior that the deep minimum observed in the isotherm in the silver cations concentration near  $x = 0.5$  was crossover from pure polaronic conductivity to ionic conductivity due to  $Ag^+$ . But, in the present work, when the system increases the  $Cu_2O$  or  $Ag_2O$  concentration, the  $V_2O_5$  content is reduced and, as a consequence, the  $V^{red}-V^{oxid}$  average distance becomes larger (according to Eq. (1)) and, in addition,  $V^{red}/V^{oxid}$  ratio changes. Both changes should decrease the electronic (polaronic) conduction. Nevertheless, while  $Cu_2O$  replaces  $V_2O_5$ , the conductivity value does not change (the



**Fig. 6.** a) Temperature dependence of dc conductivity of systems:  $x\text{Cu}_2\text{O} (1 - x) (0.5\text{V}_2\text{O}_5 \cdot 0.5\text{MoO}_3) \cdot 2\text{TeO}_2$  and  $x\text{Ag}_2\text{O} (1 - x) (0.5\text{V}_2\text{O}_5 \cdot 0.5\text{MoO}_3) \cdot 2\text{TeO}_2$ ; b) Temperature dependence of dc conductivity of systems:  $0.5\text{Cu}_2\text{O} \cdot (0.5) (0.5\text{V}_2\text{O}_5 \cdot 0.5\text{MoO}_3) \cdot 2\text{TeO}_2$  and  $0.5\text{Ag}_2\text{O} \cdot (0.5) (0.5\text{V}_2\text{O}_5 \cdot 0.5\text{MoO}_3) \cdot 2\text{TeO}_2$ .

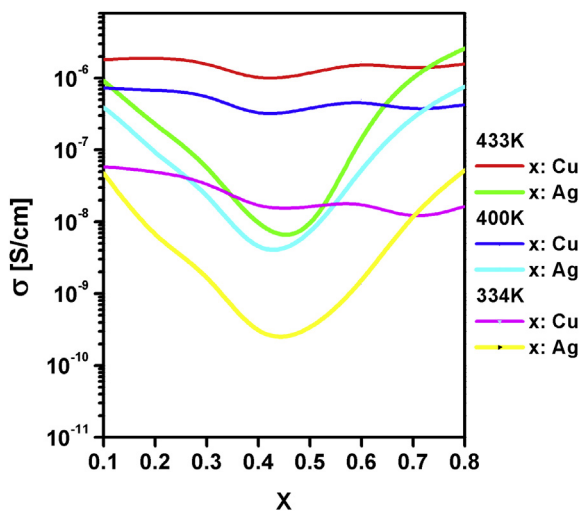


**Fig. 7.**  $E_a$  as a function of modifier oxide content ( $x$ ) of systems:  $x\text{Cu}_2\text{O} (1 - x) (0.5\text{V}_2\text{O}_5 \cdot 0.5\text{MoO}_3) \cdot 2\text{TeO}_2$  and  $x\text{Ag}_2\text{O} \cdot (1 - x) (0.5\text{V}_2\text{O}_5 \cdot 0.5\text{MoO}_3) \cdot 2\text{TeO}_2$ .

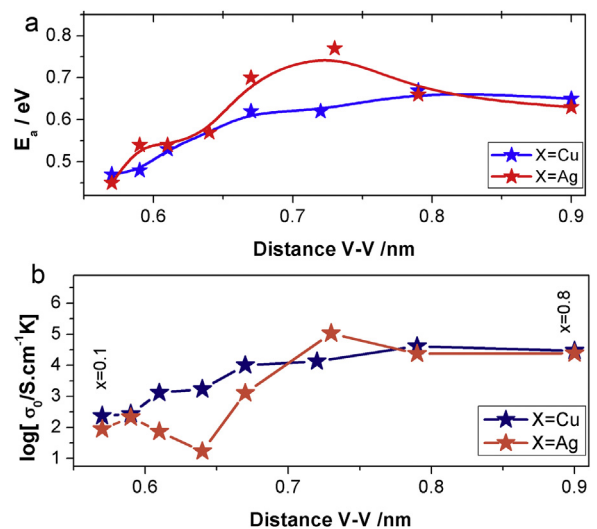
conductivity remains almost constant) as if the hopping sites were not different for the polaron in presence of the mix  $\text{V}_2\text{O}_5 + \text{Cu}_2\text{O}$ . When,  $\text{Ag}_2\text{O}$  replaces  $\text{V}_2\text{O}_5$ , the conductivity value diminishes due to the polaron feels very different environments in presence of the mix  $\text{V}_2\text{O}_5 + \text{Ag}_2\text{O}$ .

When the  $\text{Ag}_2\text{O}$  concentration is high enough ( $x = 0.6$  or above) the  $V^{\text{red}} - V^{\text{oxid}}$  path is harshly interrupted; but, a new path among silver sites emerges adding the ionic conductivity, *i.e.* a better interpretation of the conductivity is that a mixed conduction appears. Then, the mixed conductivity explains the low  $E_a$  values (not common for pure ionic conductivity) and the conductivity values (almost the same for  $\text{Cu}_2\text{O}$  and  $\text{Ag}_2\text{O}$  glasses) observed. This interpretation of the electrical conduction phenomenon is supported by the data in Fig. 9a and b which represent both the  $E_a$  and the pre-exponential factor (Eq. (3)) as a function of the main distance between vanadium ions.

The Eq. (2) expresses the displacement of one electron from one



**Fig. 8.** Isotherm of conductivity at three temperatures (433 K, 400 K and 334 K) as a function of modifier oxide content ( $x$ ) of systems:  $x\text{Cu}_2\text{O} (1 - x) (0.5\text{V}_2\text{O}_5 \cdot 0.5\text{MoO}_3) \cdot 2\text{TeO}_2$  and  $x\text{Ag}_2\text{O} \cdot (1 - x) (0.5\text{V}_2\text{O}_5 \cdot 0.5\text{MoO}_3) \cdot 2\text{TeO}_2$ .



**Fig. 9.** a) Activation Energy and b) pre-exponential factor of conductivity process (Eq. (3)) as a function of modifier oxide content ( $x$ ) of systems:  $x\text{Cu}_2\text{O} \cdot (1 - x) (0.5\text{V}_2\text{O}_5 \cdot 0.5\text{MoO}_3) \cdot 2\text{TeO}_2$  and  $x\text{Ag}_2\text{O} \cdot (1 - x) (0.5\text{V}_2\text{O}_5 \cdot 0.5\text{MoO}_3) \cdot 2\text{TeO}_2$ .

site to an adjacent one when the electron is between two sites with similar energy level; the temporary equalization of two adjacent positions being provided by phonon scattering. On that equation, the overlapping of the wave function is described by the  $\exp(-2\alpha a)$  term. This expression can be seen as formed by three factors [25]:

- the probability of having a donor and an acceptor sites in adjacent position:  $c \cdot (1-c)$
- the probability that two adjacent sites have the equivalent energy:  $v_0 \exp [W_e + W_D/2k_B T]$
- the tunneling factor, i.e. the probability for an electron to hop from site to site:  $\exp(-2\alpha a)$

Assuming that:

$$\sigma_0 = c \cdot (1-c) \cdot N \cdot \frac{e^2 a^2 v_0}{6k_B T} \cdot \exp[-2\alpha a] \quad (4)$$

from the data presented in Fig. 5, we can estimate for  $x_{Cu} = x_{Ag}$

$$\frac{\sigma_{0,Cu}}{\sigma_{0,Ag}} \cong \exp(\alpha_{Ag} - \alpha_{Cu}) \quad (5)$$

$$\text{If } \frac{\sigma_{0,Cu}}{\sigma_{0,Ag}} \cong 1 \rightarrow \alpha_{Ag} \cong \alpha_{Cu}; \quad \frac{\sigma_{0,Cu}}{\sigma_{0,Ag}} < 1 \rightarrow \alpha_{Ag} < \alpha_{Cu}; \quad \frac{\sigma_{0,Cu}}{\sigma_{0,Ag}} > 1 \rightarrow \alpha_{Ag} > \alpha_{Cu}.$$

from our results we obtain:

- $x = 0.1; 0.2; 0.6; 0.7$  and  $0.8$ :  $\alpha_{Ag} \cong \alpha_{Cu}$
- $x = 0.3; 0.4; 0.5$ :  $\alpha_{Ag} > \alpha_{Cu}$

According to Mott and Davis [39], when  $(\alpha a) \gg 1$ , the hopping of charge carriers is described by the nearest-neighbor hopping. On the other hand, if  $(\alpha a)$  is comparable or less than one, or at sufficiently low temperatures, hopping may preferably occur beyond the nearest neighbors by variable range hopping (VRH) process [40]. This explains the loss of effectiveness in the charge transport observed when  $Ag_2O$  is at intermediate concentration (close to  $x = 0.5$ ).

Finally, in order to clarify the non linearity showed in Fig. 6a, we explore the two regions with different slopes in Fig. 6b, one at high temperature and the other at relatively low temperature.

In the plot of  $\log \sigma_{dc}$  as a function of  $T^{-1}$ , considering that there are two linear regions, the intersection of the two straight lines determines a particular temperature which is different for every sample. This temperature equals half of Debye temperature ( $\theta_D$ ) [41], defined by the relation:  $h \cdot \nu_{ph} = k_B \cdot \theta_D$ , where  $\nu_{ph}$  is the optical phonon frequency,  $h$  is the Planck's constant and  $k_B$  is Boltzmann's constant. The Debye temperature of the glass samples is plotted in Fig. 10.

Fig. 10 shows that in silver containing glasses the Debye temperature reaches a maximum close to  $x = 0.5$  because of the influence of the larger ionic mass of the silver cation and not due to the different relative distances, as we have seen before. Thus, the effect of the silver ionic mass on the charge transport, evidenced through the Debye temperature, has a direct effect on the phonon propagation.

## 5. Conclusions

Our main goal was to clarify that the electronic configuration of  $Cu^+(3d$  orbital) and  $Ag^+(4d$  orbital) explains the different interactions of these ions with vanadium ions ( $3d$  orbital) in glassy systems which allow polaron hopping between the ions ( $V-Ag$  and

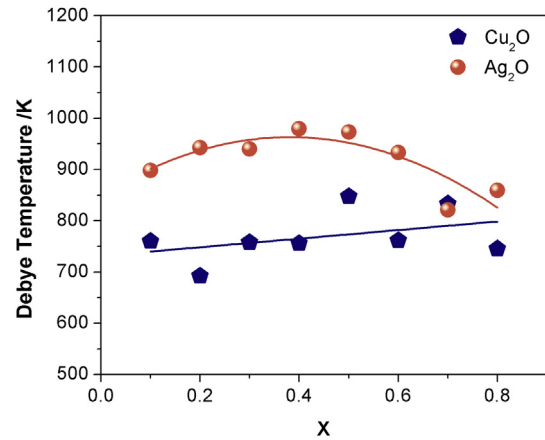


Fig. 10. Debye temperature as a function of modifier oxide content ( $x$ ) of systems:  $xCu_2O \cdot (1-x) \cdot (0.5V_2O_5 \cdot 0.5MoO_3) \cdot 2TeO_2$  and  $xAg_2O \cdot (1-x) \cdot (0.5V_2O_5 \cdot 0.5MoO_3) \cdot 2TeO_2$ .

$V-Cu$ ). Considerably different interactions appear when alkali cations as  $Li^+$  or  $Na^+$  are incorporated in a glassy system. Considering that both modifier ions ( $Cu^+$  and  $Ag^+$ ) have a similar electronic configuration but different sizes and masses, the results in the present work demonstrate that both modifier oxides ( $Cu_2O$  and  $Ag_2O$ ) behave as mixed electrical conductors, neither pure polaronic nor pure ionic. Therefore, we have found an explanation for the minimum observed in the isotherm of conductivity of the silver containing glass on the structural bases of the glassy matrix studied in this work.

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## References

- J. Livage, J.P. Jolivet, E. Tronc, J. Non Cryst. Solids 121 (1990) 35–39.
- A. Ghosh, J. Appl. Phys. 64 (1988) 2652–2655.
- S. Hazra, A. Ghosh, J. Phys. Condens. Matter 9 (1997) 3981–3986.
- E.P. Denton, H. Rawson, J.E. Stanworth, Nature 29 (173) (1954) 1030–1032.
- P.L. Baynton, H. Rawson, J.E. Stanworth, J. Electrochem. Soc. 104 (4) (1957) 237–240.
- C.S. Terny, E.C. Cardillo, P.E. di Prátula, M.A. Villar, M.A. Frechero, J. Non Cryst. Solids 387 (1) (2014) 107–111.
- E.C. Cardillo, R.A. Montani, M.A. Frechero, J. Non Cryst. Solids 356 (50–51) (2010) 2760–2763.
- M.A. Frechero, C.S. Terny, E.C. Cardillo, Lithium Glasses: Improvements as Solid Electrolyte, in: Lithium: Technology, Performance and Safety, Nova Science Publishers, Inc., 2013, ISBN 978-162417634-0.
- R.A. Montani, M.A. Frechero, Solid State Ionics 177 (2006) 2911–2915.
- S. Terny, M.A. De la Rubia, S. Barolin, R.E. Alonso, J. De Frutos, M.A. Frechero, Bol. Soc. Española Cerámica Vidr. 53 (1) (2014) 15–20.
- M. Malik, C. Hogarth, K.A. Lott, J. Mater. Sci. Lett. 8 (1989) 1344–1347.
- T. Tsuchiya, T. Moriya, Cent. Glass Ceram. Res. Inst. Bull. 22 (1975) 55–65.
- C.F. Drake, I.F. Scanlan, J. Non Cryst. Solids 4 (1970) 234–247.
- I.G. Austin, N.F. Mott, Adv. Phys. 18 (1969) 41–102.
- M. Sayer, A. Mansingh, Phys. Rev. B 6 (1972) 4629–4633.
- I.G. Austin, M. Sayer, J. Phys. C. Solid State Phys. 7 (1974) 905–924.
- G.N. Greaves, S. Sen, Adv. Phys. 56 (1) (2007) 1–166.
- L. Galois, G. Calas, Geochim. Cosmochim. 57 (1993) 3613–3627.
- N.E. Brese, M. O'Keefe, Acta Cryst. B 47 (1991) 192–197.
- G.N. Greaves, in: D.H. Uhlmann, N. Kreidl (Eds.), Glass Science and Technology, Academic Press, New York, 1990, pp. 1–76.
- G. Lusvardi, G. Malavasi, L. Menabue, M.C. Menziani, J. Phys. Chem. B 106 (2002) 9753–9769.
- N.H. Ray, J. Non Cryst. Solids 15 (3) (1974) 423–434.

- [23] R.D. Shannon, *Acta Cryst. A* 32 (1976) 751–767.
- [24] H. Hirashima, D. Arai, T. Yoshida, *J. Am. Ceram. Soc.* 68 (1985) 486–489.
- [25] N. Lebrun, M. Lévy, J.L. Souquet, *Solid State Ionics* 40/41 (1990) 718–722.
- [26] G. Vijaya Prakash, D. Narayana Rao, A.K. Bhatnagar, *Solid State Commun.* 119 (2001) 39–44.
- [27] N.B. Mohamed, A.K. Yahya, M.S.M. Deni, S.N. Mohamed, M.K. Halimah, H.A.A. Sidek, *J. Non Cryst. Solids* 356 (2010) 1626–1630.
- [28] J. Ozdanova, H. Ticha, L. Tichy, *J. Non Cryst. Solids* 355 (2009) 2318–2322.
- [29] H. Hirashima, T. Yoshida, *J. Non Cryst. Solids* 95–96 (1987) 817–824.
- [30] S. Szu, Shing Gwo Lu, *Phys. B* 391 (2007) 231–237.
- [31] T. Sekiya, N. Mochida, A. Ohtsuka, *J. Non Cryst. Solids* 168 (1994) 106–114.
- [32] A. Ghosh, *J. Appl. Phys.* 74 (1993) 3961–3965.
- [33] L. Murawski, C. Chung, J. Mackenzie, *J. Non Cryst. Solids* 32 (1979) 91–96.
- [34] N.F. Mott, *J. Non Cryst. Solids* 1 (1968) 1–17.
- [35] M.A. Frechero, O. Quinzani, R. Pettigrosso, M. Villar, R. Montani, *J. Non Cryst. Solids* 353 (2007) 2919–2925.
- [36] B.B. Das, D. Mohanty, *Indian J. Chem.* 45 (2006) 2400–2405.
- [37] S. Sen, A. Ghosh, *J. Appl. Phys.* 86 (4) (1999) 2078–2082.
- [38] S. Sen, A. Ghosh, *J. Appl. Phys.* 87 (7) (2000) 3355–3359.
- [39] N.F. Mott, E.A. Davis, *Electronic Processes in Non-crystalline Materials*, Oxford University Press, Oxford, 1979.
- [40] R. Punia, R. Kundu, S. Murugavel, N. Kishore, *J. Appl. Phys.* 112 (2012) 113716–113717.
- [41] F. Abdel-Wahab, M. Aziz, A. Mostafa, E. Ahmed, *Mater. Sci. Eng. B* 134 (2006) 1–8.