



Electrical response of bivalent modifier cations into a vanadium–tellurite glassy matrix



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ABSTRACT

In this work, we suggest an explanation of the electrical conductivity behavior of tellurite glassy systems modified with barium when transition metal oxides (V_2O_5 - MoO_3) present in the glassy matrix are replaced progressively by barium oxide. These glasses of formula $x BaO (1 - x) (0.5V_2O_5 \cdot 0.5MoO_3) 2 TeO_2$ are obtained by the standard quenching technique and analyzed by means of impedance spectroscopy. We also report some structural results that explain the effect of the bivalent cation (Ba^{+2}) on the electrical response in comparison to the effect of univalent cations on this kind of glassy matrix. The results confirm the existence of a transition from a typical hopping of small polarons response (when the content of BaO is low) to a weak ionic conductive response (when more than 50% of the transition metal oxides content has been replaced by BaO). The independent migration path is suggested by the observed electrical conductivity behavior. In this system, vanadium gives the active centers responsible for the polaron hopping mechanism while barium cations seem to be responsible for the ionic transport regimen.

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1. Introduction

During the last decades, many works have tried to explain the structural features of tellurite glasses. It has been shown that the main structural units in the glassy tellurite matrix are trigonal bipyramid TeO_4 and that the proportion of trigonal pyramids increases when the concentration of modifier oxides rises [1].

The study by Raman spectroscopy of binary tellurite glassy systems modified with oxide of Mg, Sr, Ba and Zn reveals that glasses with low BaO concentration have a continuous network constructed by shared corners of TeO_4 trigonal bipyramids and of $TeO_3 + 1$ polyhedron, having one non-bridging oxygen (NBO) atom. In these glasses, the TeO_3 trigonal pyramids with NBO atoms are also formed in the continuous network but, a high BaO concentration tellurite glass shows isolated structural fragments, such as TeO_3^{2-} and $Te_3O_8^{4-}$ ions, coexisting with but not bonded to the surrounding network [2].

Additionally, it is also well known that the incorporation of transition metal oxides like V_2O_5 in the tellurite glasses gives an electrical conduction response that can be described by the hopping of small polarons among different valence states V^{ox}/V^{red} . S. Sen and A. Ghosh have studied the temperature dependence of the electrical conductivity for the semi-conducting glasses of formula $(100 - x)BaO xV_2O_5$ and they have found that Mott's variable range hopping model is consistent with the data at lower temperatures. The values of the parameters obtained from

the fits of the model compared to the experimental data are in reasonable agreement and the polaron hopping model of Schnakenberg is also consistent with the temperature dependence of the conductivity [3]. After that, glasses of formula V_2O_5 - TeO_2 - BaO , with several BaO concentration (15–30%) and different ratios of V_2O_5/TeO_2 were studied. In every case, a polaron hopping in the conductivity behavior was found but, depending on the vanadium oxide concentration, the conduction was adiabatic or non-adiabatic [4]. On the other hand, it was observed a deep minimum in the conductivity isotherm of glass system of formula $Li_2O:WO_3:P_2O_5$ due to the strong coupling of the oppositely charged current carriers, an effect designated as ion-polaron-effect, which appears because the mobilities of ions and electrons are comparable in magnitude [5].

In this work, we have analyzed the system of formula $x BaO (1 - x) (0.5V_2O_5 \cdot 0.5MoO_3) 2 TeO_2$ and our main objective is to show that the MoO_3 can reduce the electronic conductivity given by the vanadium oxide. Additionally, its incorporation allows us to measure the ionic conductivity given by the BaO. The incorporation of this alkaline-earth oxide raises the transition temperatures (with the increase of barium oxide) and this allows having the glassy (solid) state in a larger temperature domain, a much appreciated improvement for technological applications.

Furthermore, the incorporation of barium oxide in tellurite glasses develops a larger activation enthalpy for structural relaxation which involves slower aging of the material.

2. Material and methods

Tellurite glasses of the formula: $x BaO (1 - x) (0.5V_2O_5 \cdot 0.5MoO_3) 2 TeO_2$ with $x = 0.0$ to 0.9 were prepared by the standard melted

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quenching technique. Analytical reagent grade chemicals of TeO_2 , BaCO_3 , MoO_3 and V_2O_5 were used to prepare the glass samples. The stoichiometric compositions for batches of 10 g were mixed thoroughly and placed in a platinum crucible. First, a decarboxylation process of the BaCO_3 took place under moderate heat. Secondly, when the effervescence was finished, the platinum crucible was put in an electric furnace which was heated at 850°C for 20 min. It was necessary to stir it several times 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. $x = 0.9$ was melted several times in order to obtain a glassy sample but all efforts were useless since the samples obtained partially crystallized.

X-ray diffraction analysis (XRD) and differential scanning calorimetry (DSC) studies were done at every stage to confirm the amorphous nature of the samples. All the DSC thermograms (with a heating rate of $10^\circ\text{C}/\text{min}$) showed the characteristic endothermic peak which is associated to the glass transition temperature (T_g). 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 $K\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$) 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 1.2 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 the frequency range from 20 Hz to 1 MHz in the temperature domain from 25°C to $[T_g - 15]^\circ\text{C}$.

The density of the glass samples was measured using isopropyl alcohol as the secondary displacement medium in the Archimedeian method and, the values shown in Fig. 3 are the average of three density independent measurements. From these density values were calculated the OPD (oxygen density packing) for each composition according to $\text{OPD} = \text{mol oxygen number}/\text{molar volume}$.

3. Results

The amorphous state of the samples was analyzed with DSC and XRD. The XRD patterns shown in Fig. 1 (none of them exhibiting a sharp peak) confirm the glassy nature of the samples, except for the BVMT09 which is not completely amorphous—as we said before.

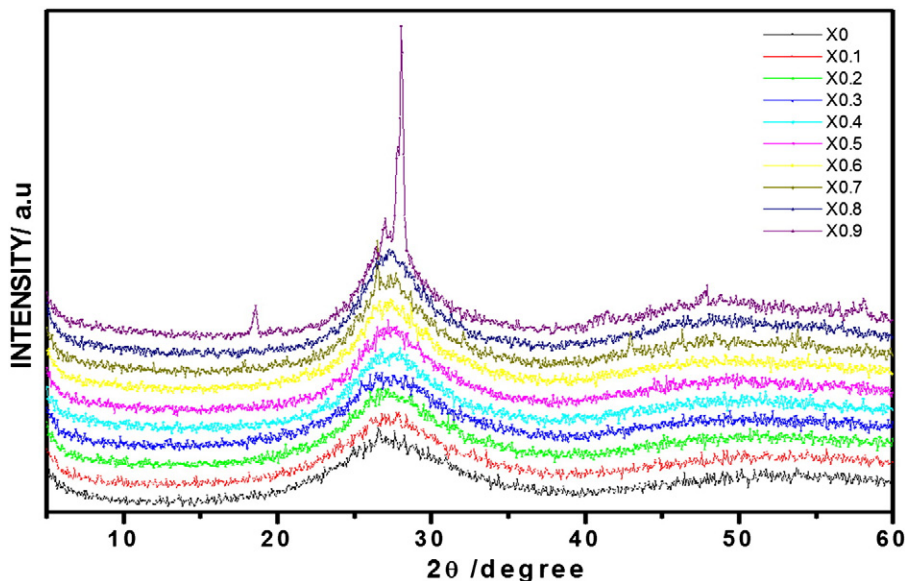


Fig. 1. X-ray diffraction patterns for each composition. The inset corresponds to the content of BaO according to the formula $x \text{ BaO} (1 - x) (0.5\text{V}_2\text{O}_5 \cdot 0.5\text{MoO}_3)_2 \text{TeO}_2$.

In Fig. 2, the glass transition temperatures (T_g) are plotted as a function of x (the BaO content). Each value is obtained from the temperature at the middle point of the jump in the C_p on the thermogram that is characteristic of a glass transition. This plot shows a total increment of 18.9% in the T_g value for the maximum BaO content.

Fig. 3a shows the average density and the oxygen density packing (OPD) for each composition of the system. Therefore, we noticed an increase of 11.93% in their density values for the sample with the maximum content of barium oxide. This variation on the density causes the oxygen density packing (OPD = oxygen mol number/molar volume) to diminish near 30% on high concentration of BaO in the system. On the other hand, in Fig. 3b we see that the molar volume and oxygen mol number for each composition of the system decrease continuously as the barium content increases.

To investigate the characteristics of the electrical conduction, the impedance (Z) and the phase angle (ϕ) of each sample have been measured as a function of frequency at each temperature in the corresponding range as was pointed out before.

The electrical conductivity measured rises with increasing temperature and we can represent this behavior through the Arrhenius-type equation as:

$$\sigma_{\text{dc}} = \frac{\sigma_0}{T} e^{-\left(\frac{E_a}{kT}\right)} \quad (1)$$

where E_a is the activation energy of the conductivity process, σ_0 is the preexponential factor and kT have their usual meaning.

Fig. 4 shows the electrical conductivity in an Arrhenius plot according to Eq. (1). We noticed that there is only one slope for each composition curve and this can be interpreted as them having single activation energy.

Fig. 5 shows the electrical conductivity isotherms at two temperatures ($T = 500 \text{ K}$ and 550 K). We see here that a not very pronounced minimum appears near the $x = 0.6$ but, the increase in the conductivity in systems with high BaO content is very modest or almost imperceptible depending on the temperature.

Fig. 6 shows E_a as a function of x . From this, we learn that the maximum in the curve is at the same x where the isotherms have their minimum and, the energy values diminish for compositions with x greater than 0.6 despite the fact that this behavior is not reflected in the electrical conductivity.

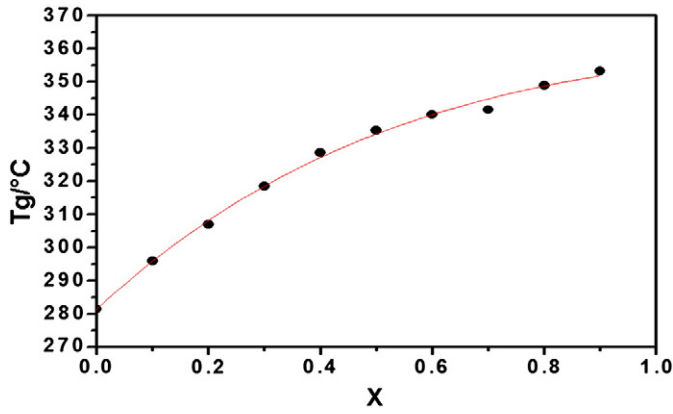


Fig. 2. Glass transition temperatures (T_g) plotted as a function of x (BaO concentration).

Fig. 7 shows the real part of the complex relative dielectric permittivity $\epsilon'(\omega)$. We note a sharp increase in the region of low frequency which is undoubtedly due to blocking electrode phenomena.

4. Discussion

From now on we will refer to transition metal oxides as TMO and alkaline metal oxides as AMO.

Systems with tellurite oxide as glassy former which contain TMO and AMO are expressed by the general formula $x\text{AMO} \cdot (1 - x)\text{TMO}$.

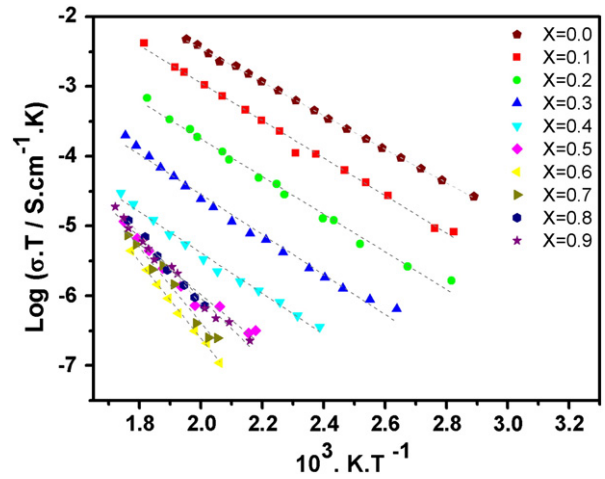


Fig. 4. Arrhenius plot for the measured conductivity. The inset corresponds to the content of BaO according to the formula: $x\text{BaO} (1 - x) (0.5\text{V}_2\text{O}_5 \cdot 0.5\text{MoO}_3) 2\text{TeO}_2$.

TeO_2 usually presents electronic conduction by diffusion like motion called hopping mechanism—when the ratio of TMO/AMO is greater than 1. The hopping mechanism seems to apply to the low mobility oxide semiconductors and the charge carrier in this case is called a small-polaron. Also, this kind of glasses frequently behaves as ionic conductors when this ratio is lower than 1 [3]. Habitually at intermediate concentrations (when the ratio is close to 0.5) we find that the conductivity is mixed, i.e. both types of charge carriers move, polaronic plus ionic conductivity.

Results from other works suggest that each charge carrier goes through independent pathways and if the concentration of TMO decreases, the electronic (polaronic) conductivity goes down and, at the same time, if the concentration of AMO increases then, the ionic conductivity goes up [6–9]. In different glassy systems with different TMOs and AMOs the isotherms of the electrical conductivity show a deep minimum near the $x = 0.5$ (when the ratio TMO/AMO is almost one); apparently, they are disrupting each other [5].

On the other hand, as commonly shown in the literature it can be considered that both alkaline modifier oxides and alkaline-earth modifier oxides (AEMO) behave in exactly the same way, i.e. as ionic conductors [10]. Nevertheless, we learnt from our results (see Fig. 5) that in our system $\{x\text{BaO}(1 - x) (0.5\text{V}_2\text{O}_5 \cdot 0.5\text{MoO}_3) 2\text{TeO}_2\}$ the replacement of TMOs ($0.5\text{V}_2\text{O}_5 \cdot 0.5\text{MoO}_3$) by an AEMO (BaO) causes a similar behavior than AMOs when x is less than or equal to 0.5 but, for greater values of x we have a different behavior. It is important to note that while the

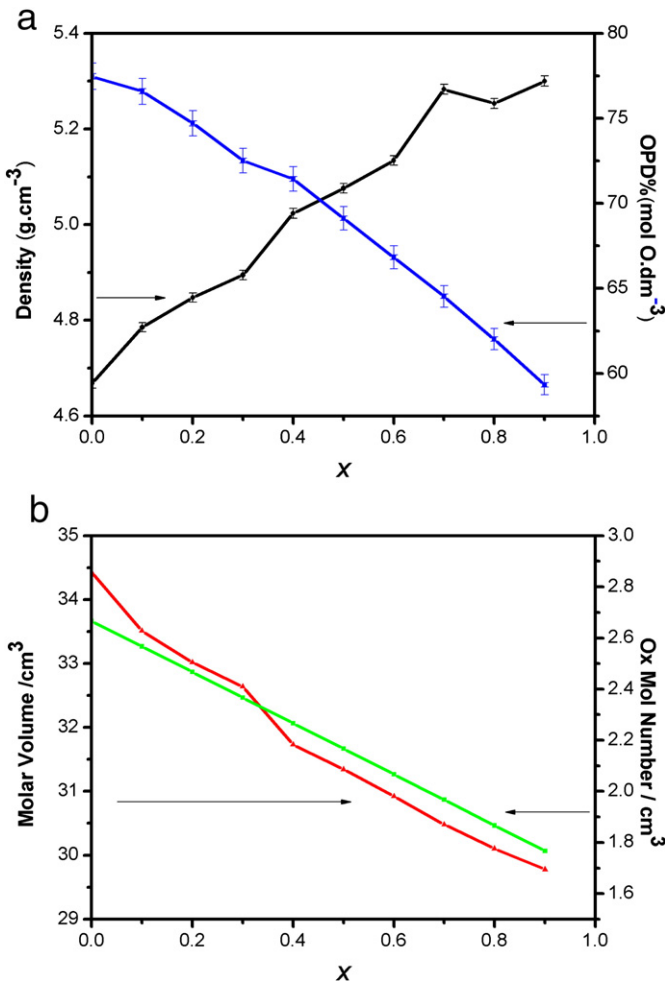


Fig. 3. a) Density and OPD; b) molar volume and oxygen mol number for each composition of the system.

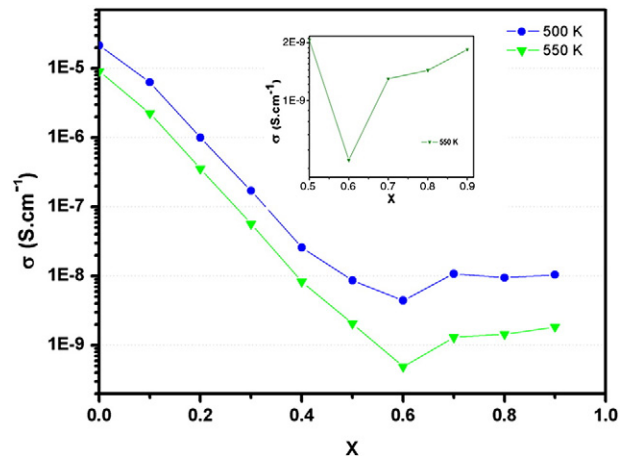


Fig. 5. Variation of the electrical conductivity as a function of x for two temperatures (500 K and 550 K). Inset: electrical conductivity for $x = 0.6$ to $x = 0.9$ at 550 K.

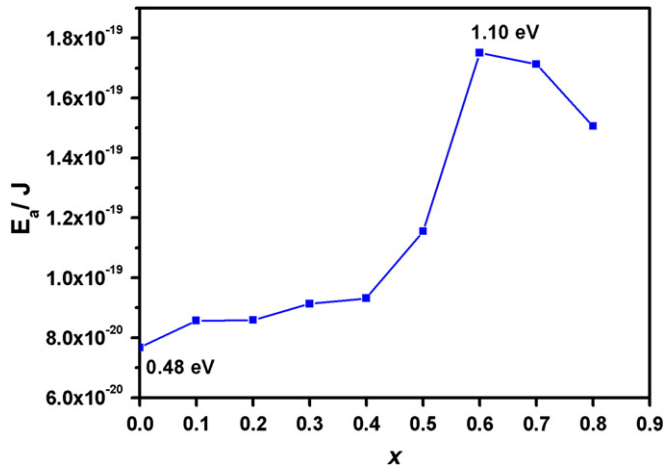


Fig. 6. Activation energy as a function of x (BaO content).

ratio of TMOs/AEMO is greater than 1, the conductivity of the system varies in a linear fashion with x . This behavior makes it clear that the electrical conductivity is governed by the existence of TMOs pathways through which the charge carriers move. The charge carrier hopping between reduced/oxidized centers among the glassy matrix has the typical activation energy value around 0.4 eV ($6.40 \cdot 10^{-20}$ J). This kind of conduction is regarded as a small polaron hopping mechanism [11].

But, when the ratio of TMOs/AEMO is lower than 1, it seems that the electrical conductivity has a non-linear response as a function of the BaO concentration. Then, the electrical conductivity remains almost constant despite the increase of the modifier oxide concentration (x augmentation) while the activation energy decreases lightly. Such a behavior is very different from that observed in the $[V_2O_5-MoO_3-TeO_2]$ glasses when they are modified by alkaline oxides like Li_2O , Na_2O or K_2O whose electrical conductivity typically increases as the alkaline oxide content is larger [7,8,12].

In the literature, the electrical conductivity (σ_{dc}) in glasses is represented by the following equation:

$$\sigma = N \cdot q \cdot \mu \quad (2)$$

where N is the number of charge carriers and q is its charge and μ is its mobility. There are also several interpretations related to N (to consider that all the ions will be able to move in the system or to assume a kind of

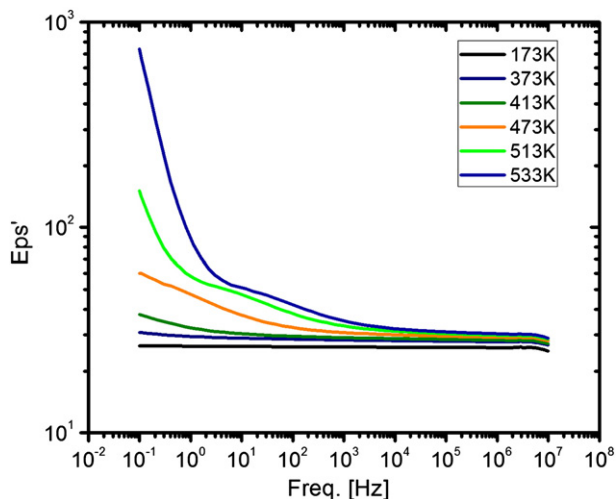


Fig. 7. Real part of the complex relative dielectric permittivity $\epsilon'_{(\omega)}$ as a function of frequency for a set of temperatures (inset).

weak electrolyte behavior) [9,13–15] but, we expect a rise in the electrical conductivity when the concentration of the modifier oxide increases. However, the system in this work does not seem to react in exactly the same way. Nevertheless, it is important to note that the value of the electrical conductivity varies slightly when the modifier oxide increases its concentration, i.e. not several magnitude orders, but as we see in the inset of Fig. 6, the conductivity increases continuously with the increase of the barium oxide concentration. However, there is an important variation in the activation energy values.

M. Ingram and B. Rolling [10] have studied the effect of the introduction of divalent ions in glasses. They found that in mixed alkaline and alkaline-earth silicate glasses, univalent cations are more mobile than divalent cation even with equivalent ionic radii, e.g. $r(Ca^{2+}) = 106$ pm and $r(Na^+) = 99$ pm [16]. When divalent and univalent cations with similar size are mixed, the divalent cation becomes more mobile compared to the other divalent cations because it requires a smaller amount of network distortion for the hopping.

Considering the following equation is an accepted expression for the cationic conductivity (just as Eq. (2) [17]):

$$\sigma_+ = N_+ \cdot q_+ \cdot \mu_+ \quad (3)$$

We may assume—in this work—that $\sigma_{x=0.7}/\sigma_{x=0.8}$ is near to 1 (for example at temperatures close to 500 K as we can see from Fig. 5). On the other hand, if we estimate the ion charge carrier concentration from the dielectric relaxation strength of the space charge polarization and we combine this result with dc conductivity, we obtain an approximation to the ionic mobility [18]. From the real part of the complex relative dielectric permittivity $\epsilon'_{(\omega)}$ frequency spectra, we found according to ref. [18] the following: $\Delta\epsilon_{0.8} > \Delta\epsilon_{0.7}$ then $n_{0.8} > n_{0.7}$, i.e. the ion charge carrier concentration for $x = 0.8$ is greater than $x = 0.7$. Then, it follows from Eq. (3) that the mobility is $\mu_{x=0.8} < \mu_{x=0.7}$ in diffusivity times.

On the other hand, considering the results of M. Garza-García et al. [19], in silicate glasses, a kind of “stuffing effect” appears in samples with high BaO concentration caused by the big size of the Ba^{2+} in the glass network. They also believed that a formation of NBO–Ba–NBO bridges is responsible for the increase in the T_g values when the BaO concentration rises—as it has been proposed earlier by Y. Hu, H-T. Tsai [20]. Then, M. Garza-García et al. assumed that BaO acts like a stabilizer for the glassy matrix [19].

Additionally, in Fig. 6 we see that the E_a decreases. Considering that this is a microscopic quantity (the sum of the energy that the cation needs for the migrating process plus the energy to remove it from its site), in this work, we expected higher conductivity values according to the general electrical response. Nevertheless, taking into account the results in Fig. 3, the higher the BaO concentration, the lower the oxygen packing in the glassy matrices. However, at the same time, their molar volume decreases as much as their oxygen mol number. Then, even though we might expect the charge carriers to move more freely in the glassy matrix, they have less opportunity to migrate because the matrix gives them less available sites to do it. Then, the system conductivity cannot rise. Taking into account the work of G. Magnus et al. who has found a kind of tellurites tubes forming in $BaTe_3O_7$ and $BaTe_4O_9$, for high BaO content in our glasses we suspect that a similar three-dimensional network could emerge making the conductivity energy activation lower and increasing slightly the conductivity magnitude [21].

At this point, we can compare the electrical conductivity values among similar systems, i.e. with the same glassy matrix composition but with different modifier oxides:

$$0.8 Li_2O \cdot 0.2 (0.5 V_2O_5 \cdot 0.5 MoO_3) \cdot 2 TeO_2; \sigma_T = 400K \\ = 2.9 \cdot 10^{-9} S cm^{-1}$$

$$0.8 \text{ Na}_2\text{O} \cdot 0.2 (0.5 \text{ V}_2\text{O}_5 \cdot 0.5 \text{ MoO}_3) \cdot 2 \text{ TeO}_2: \sigma_T = 400\text{K} \\ = 1.3 \cdot 10^{-10} \text{ S cm}^{-1}$$

$$0.8 \text{ BaO} \cdot 0.2 (0.5 \text{ V}_2\text{O}_5 \cdot 0.5 \text{ MoO}_3) \cdot 2 \text{ TeO}_2: \sigma_T = 400\text{K} \\ = 8.1 \cdot 10^{-12} \text{ S cm}^{-1}$$

$$0.8 \text{ Ag}_2\text{O} \cdot 0.2 (0.5 \text{ V}_2\text{O}_5 \cdot 0.5 \text{ MoO}_3) \cdot 2 \text{ TeO}_2: \sigma_T = 400\text{K} \\ = 1.0 \cdot 10^{-6} \text{ S cm}^{-1}$$

If $(q \cdot N)$ in Eq. (3) was quite similar for these systems, we would expect a similar behavior among them as Jean-Louis Souquet et al. found in silicate glasses [17]. However, from our results in the present work, it is clear that the conductivity value obtained from these ionic conducting glasses is a result of a kind of agreement between the glassy matrix structure and the nature of cation carrier concentration (charge and radii even when they have similar electronic configuration) [22]. However, when the charge carrier has also different kinds of electronic configuration, as it happens with transition metal cations, they have a different behavior on the electrical transport process; as we have shown in our previous paper with silver oxide as modifier in the same glassy matrix of this work [6,23].

5. Conclusion

We showed that the glass of the formula $x \text{ BaO} (1 - x) \cdot [0.5\text{V}_2\text{O}_5 \cdot 0.5\text{MoO}_3] \cdot 2 \text{ TeO}_2$ has an electrical conductivity behavior that depends on the nature of the modifier oxide which is present in the system in major proportion. When the transition metal oxides are the main proportion, the system has an electronic conductive behavior which varies in a linear fashion with its relative concentration. However, when the BaO exceeds the transition metal oxide concentration, this system behaves as an ionic conductor. Nevertheless, an increase in the BaO content does not involve a notorious rise in the conductivity response. The structure that the glassy matrix achieves seems to disturb the cation mobility. The sites in the conductivity pathway for the barium cation migration are overcrowded because of the effect of the cation itself on the glassy matrix. In this scenario, the mechanism for the present system is a less connected independent pathway in the barium domain. The migra-

tion is impeded by a less free diffusion of cations due to the changes experienced by the glassy matrix under the circumstances described in this work and similar results from other kind of glasses [24].

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