



Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/locate/jnoncrysol

A weak mixed mobile ion effect in vanadium–tellurite oxide glass modified by silver and lithium cations

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ARTICLE INFO

Article history:

Received 22 December 2009

Received in revised form 27 August 2010

Available online xxxxx

Keywords:

Tellurite glasses;

Ionic conductivity;

Impedance spectroscopy

ABSTRACT

The effect of the partial replacement of lithium oxide by silver oxide in a glassy vanadium–molybdenum–tellurite oxides matrix is analyzed by means of impedance spectroscopy. We find that a weak mixed mobile ion effect (MMIE) is due to the different kind of modifications silver and lithium oxides induce in the glass of formula $0.7[x \text{ Ag}_2\text{O} (1-x) \text{ Li}_2\text{O}] 0.3[0.5 \text{ V}_2\text{O}_5 0.5 \text{ MoO}_3] 2 \text{ TeO}_2$.

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1. Introduction

Solid electrolytes have several advantages over conventional liquid electrolytes. They often exhibit a higher chemical and electrochemical stability, resulting in reduced safety problems in batteries. Furthermore, miniaturized electrochemical cells, such as micro batteries, can be manufactured from multilayer stacks of thin electrode and electrolyte films.

Oxide glasses formed with TeO_2 as network former possess many interesting physical properties such as low melting point, high chemical durability, high refractive index and good infrared transmittivity, which make them attractive not only from the fundamental point of view, but also for practical applications [1]. On the other hand, when a modifier oxide is introduced into the tellurite network different structural units are formed at different oxide contents and, this is a very different behavior from the traditional glass formers such as P_2O_5 , SiO_2 , etc. [2].

From a microscopic point of view, at the atomic scale, the structure of an oxide glass is complex. Most of the authors continue using the continuous random network of Zachariasen in order to rationalizing well-defined short-range order, i.e. any kind of periodicity in it. But when we speak about ionic diffusion the truth is what is important is the intermediate range order because the mobile ions in the network interact and sometimes some cooperative phenomena plays out and in the short-range of these materials, there is a sort of invariant order which reflect the dominant chemical interactions [1].

A large number of studies of ionic conductivity in alkali oxide glasses have been reported. However, no clear consensus on the

conductivity process has emerged so far. Particularly, silver tellurite glasses have mobile silver ions which are monovalent ions like alkali ions but with higher mobility and conductivity and they, silver tellurite glasses, exhibit structural transition from TeO_4 trigonal bipyramids polyhedron to TeO_3 trigonal pyramids through TeO_{3+1} polyhedron with increasing silver content. But this effect depends not only on the oxide content: the nature of the modifier oxide is important too, e.g. for the same content of Li_2O as Ag_2O , the predominant tellurite polyhedrons are different [3]. Then the results of electrical conductivity both depends on the modifier oxide concentration and its nature as well [4–8].

Under the light of these facts, we are interested in revealing the influence on the electrical conductivity process when silver ions and lithium ions are simultaneously in tellurite matrix when the total ion concentration is constant. This work informs about the effects of gradual replacement of Li_2O by Ag_2O in the tellurite matrix in a system of formula $0.7[x \text{ Ag}_2\text{O} (1-x) \text{ Li}_2\text{O}] 0.3[0.5 \text{ V}_2\text{O}_5 0.5 \text{ MoO}_3] 2 \text{ TeO}_2$ and in which the conductivity is predominantly ionic both for silver or lithium cations, the electronic conductivity is already negligible and this concentration of modifier oxides is still stable for silver oxide concentration in these glasses [7,9]. Particularly, we discuss certain kind of mixed mobile ion effect.

2. Experimental

The samples were prepared by a standard melt quenching technique from initial mixtures of properly quantity of components (quality 99.99%, TeO_2 , V_2O_5 , MoO_3 , Ag_2O and Li_2CO_3) as we detailed in our previous papers [1–5]. The amorphous character of the resulting solids was tested by X-ray diffraction analysis and confirmed by the Differential Scanning Calorimetry (DSC). The DSC thermograms showed the characteristic slope change which is associated to the

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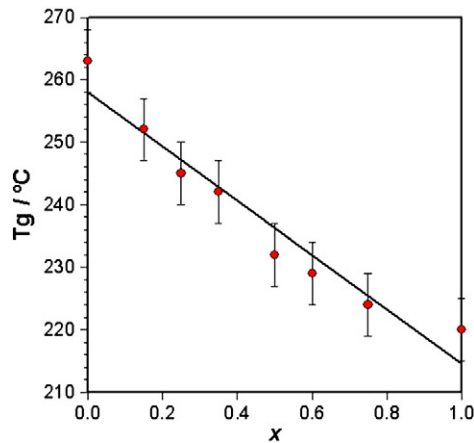


Fig. 1. Glass transition temperature as function of x .

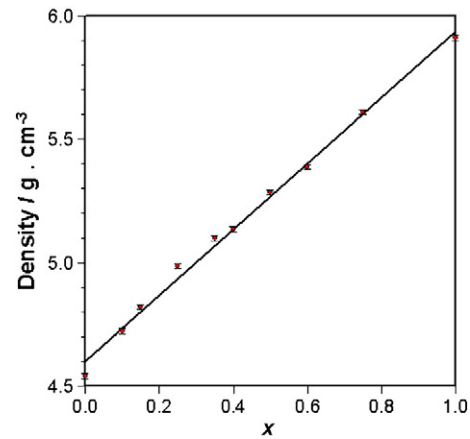


Fig. 3. Density as function of x .

temperature of vitreous transition T_g (a true signature of the glassy state). Glass disks of thickness ranging between 0.5 and 1.0 mm, were cut from the obtained cylinder and polished with very fine quality lapping papers. The electrodes for electrical measurements were made using silver conducting paint to which metallic leads were attached. The conductivities of the samples were determined in a temperature domain below 15° of the T_g by standard a.c impedance methods in a frequency range from 20 Hz to 1 MHz, using an Agilent 4284A impedance meter. The data has being processed by means of appropriate software, Boukamp. For each resistance obtained through this method we focus on those once which the CNRLS (Complex Non-linear Regression Least-Squares) that have an error lower than 5%.

The X-Ray powder diffraction was performed with a PW1710 BASED in a continuous scan mode with a copper anode and 45 KV–30 mA for the tension and current generator respectively. The density of the samples was determined by the Archimedeian method using isopropyl alcohol, and the values informed are the average of three independent density measures which do not differ more than 0.1% among them.

3. Results

In order to ensure the amorphous nature of the prepared samples we analyzed them by DSC and XRD. In Fig. 1, the glass transition temperatures (T_g) are plotted as function of x for the system and each

value is the temperature of the characteristic change in the slope of their thermograms. The XRD patterns showed in Fig. 2; do not show any kind of sharp peaks on them. Then, both results confirm that all of them are glassy.

Fig. 3 shows the density for each composition of the system. Both Figs. 1 and 3 show a linear variation as the cation ratio changes. As we expected the density increases as the system is richer in silver oxide, whereas the T_g values strongly go down.

To investigate the conduction characteristics, the impedance (Z) and phase angle (θ) of each sample of different compositions have been measured as a function of frequency. These values were used to obtain the real (Z') and imaginary (Z'') parts of the complex impedance and they were plotted on a complex plane like in Fig. 4. These data were analyzed using specific software “EQUIVCRT” non-linear least squares fitting program [10] to obtain the bulk resistance and to calculate the conductivity at each temperature. Fig. 5 shows the variation of $\log(\sigma \cdot T)$ vs. T^{-1} for each composition and all of them has been fitted linearly in a good agreement with the Eq. (1):

$$\sigma \cdot T = \sigma_0 \exp(-E_a / kT) \quad (1)$$

The evaluated conduction parameters from Eq. (1), activation energy (E_a) and pre-exponential factor (σ_0) vs. silver oxide concentration (x) are plotted in Fig. 6a and b.

Fig. 7 shows the isothermal variation of electrical conductivity as a function of x at 400 K, we can observe in this plot a slight minimum of

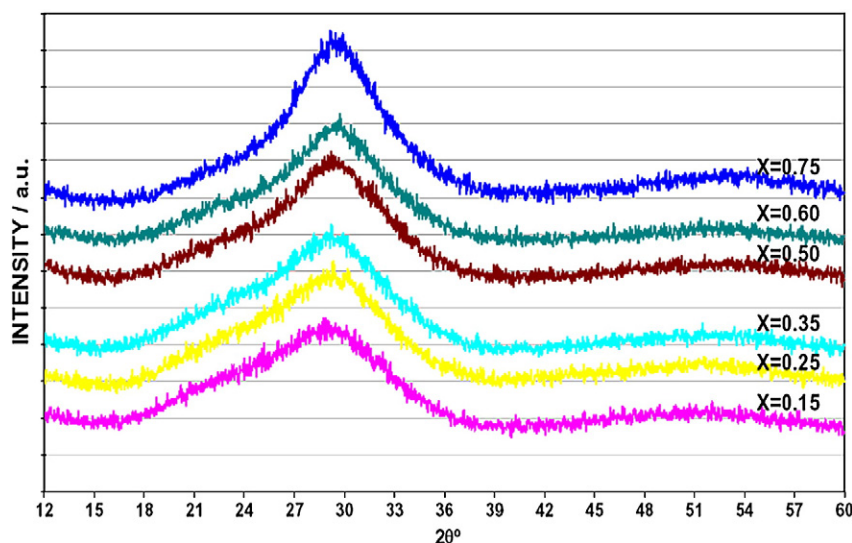


Fig. 2. XRD patterns for the samples under study.

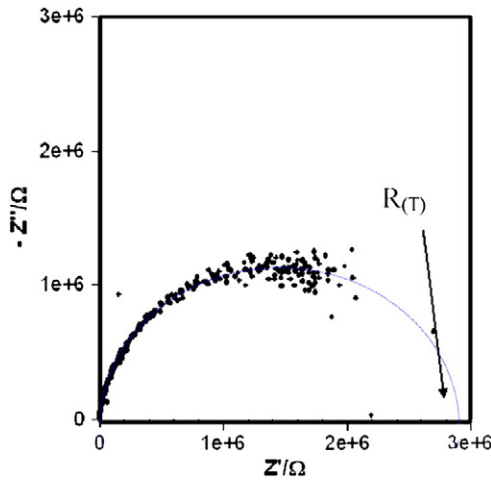


Fig. 4. Nyquist plot: the real (Z') and imaginary (Z'') parts of the impedance (472 K).

about one order of magnitude in electrical conductivity near of $x = 0.35-0.4$ and it looks like a behavior similar to the so called Mixed Mobile Ion Effect (MMIE) that we discuss further in the following section.

4. Discussion

From Fig. 1 we can realize that silver oxide acts as a stronger modifier oxide than lithium oxide because when the silver oxide concentration is increased, the T_g (vitreous transition temperature) strongly goes down in a similar way than as when the only modifier is silver oxide [7,8] because this oxide acts drastically cutting the glassy matrix.

On the other hand, from the XRD pattern in Fig. 2, we can observe that its shape gradually changes according to the replacement of one cation for the other (Li^+-Ag^+). Thus, we can learn from this figure that each cation promotes a different kind of modification in the glassy matrix.

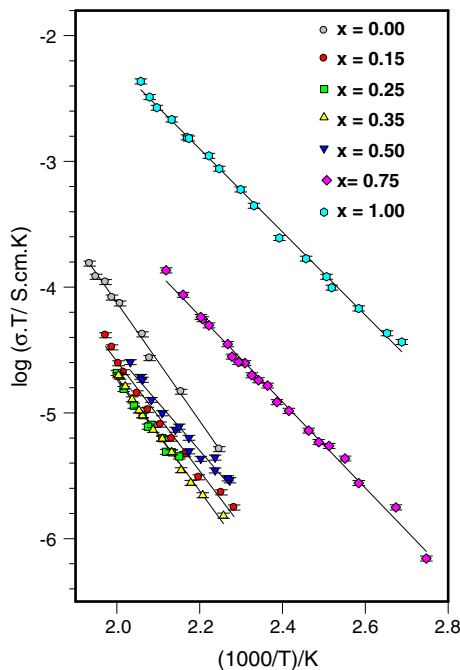


Fig. 5. Arrhenius plot for the electrical conductivity.

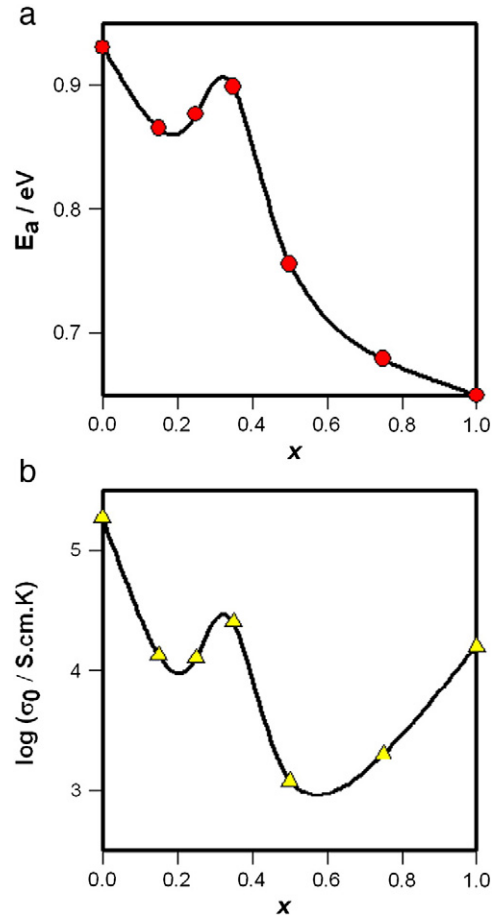


Fig. 6. a) Activation energy and b) pre-exponential factor, obtained of the Arrhenius plot as a function of x for both cases.

In the same way than Sidebottom et al. [11] did, we can also conclude that silver cation promotes a kind of order within the medium range of the system, although within the long range we can still consider the system as an amorphous one. But, when the lithium cation is in higher proportion as modifier oxide, it promotes a re-polymerization of the glassy matrix. Then, the size of the modifier cation plays a specific role in this sense.

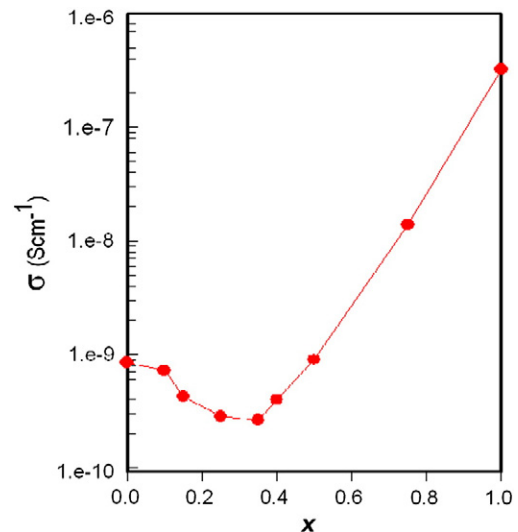


Fig. 7. Composition-dependent isotherms of electrical conductivity at 400 K.

Now, from every Nyquist plot like Fig. 4, for each composition at each temperature, we have obtained just an only one arc on them: the bulk response (we show an only representative plot to avoid confusion).

In Fig. 7 we show the isotherm for electrical conductivity values for all the compositions in this system at 400 K; we can see in that figure a non very deep minimum in the isotherm near the $x=0.3$, i.e. when 30% of the lithium oxide have been replaced by silver oxide. Now, if we consider the conductivity values in both extremes of the system, for compositions with 100% of silver oxide or 100% of lithium oxide as a modified oxide, we observe an enormous difference between their conductivity values: around 2.5 magnitude orders. Then, the minimum observed, around 0.8 of a magnitude order at 400 K, is significant because we can think that the simultaneous presence of two mobile cations (i.e. Li^+ and Ag^+) promotes a modification in their long-range transport properties. This effect is clearly more pronounced when the lithium cation starts to replace the silver cation: the conductivity decreases one order of magnitude when x vary from 1.0 to 0.9 and almost the same when x goes from 0.9 to 0.8. Under the light of these facts we can consider that lithium cations tend to make a stronger blocking effect at the sites for the silver conductivity because their sites are quite different. This effect is very different on the other extreme of the system because the silver oxide makes another kind of modification on the glassy matrix [3] and lithium cations seem to be able to migrate through the sites created by silver oxide.

Both, vitreous transition temperature and density vary linearly when we replace one of the modifier oxides by the other. Both, activation energy, E_a , and pre-exponential factor of the Eq. (1), σ_0 , vs. silver oxide concentration show a maximum at the same x where the isothermal variation of electrical conductivity shows a minimum, and when the temperature is lower the minimum in the isotherm is deeper (not showed in the plot). As we know, these are the experimental evidences of the mixed alkaline effect, in this case, mixed mobile ion effect because the cations are lithium and silver.

Swenson and Adams [12] found by means of bond-valence analysis of reverse Monte Carlo study of the $\text{Li}_x\text{Rb}_{1-x}\text{PO}_3$ glass system, that mixed alkaline effect (MAE) is very pronounced, the isotherm conductivity decreases by 6–8 orders of magnitude at the intermediate composition ($x=0.5$) and the results obtained by Hall et al. [13] for the $\text{Ag}_x\text{Na}_{1-x}\text{PO}_3$ glass system show that this effect (mixed mobile ion effect, in this case, MMIE) is less pronounced and they conclude that this is because both cations are very similar in their sizes. The present work actually shows that it is more important the nature of the cations of the modifier oxide – nature in the sense of the kind of modification these induce in the glassy matrix – than the ratio of their

sizes. These results show that the behaviour of silver cation is more than just a monovalent carrier charge, and then it is necessary to make more progress in our knowledge about the modifications which are induced by silver cation in the glassy matrix and about their relevance in the conductivity processes in glassy materials.

5. Conclusions

We can say that the glass system of formula $0.7 [x\text{Ag}_2\text{O} (1-x)\text{Li}_2\text{O} \cdot 0.3 [0.5\text{V}_2\text{O}_5 \cdot 0.5\text{MoO}_3] \cdot 2\text{TeO}_2$ shows a MMIE. Its electrical conductivity is strongly influenced by the nature of modifier cation and the structure of the glassy matrix is modified in different ways depending on the ratio of modified oxides. The sites in the conductivity pathway for the silver cation migration are more disturbed for the presence of the lithium cations than vice versa. In this scenario, the mechanism for mixed electrical conductivity due to silver and lithium cations can be assumed, for the present system, and the less connected pathways in the lithium rich domain are liberated because the presence of the silver cations and the more free diffusion for cations because of the modification in the glassy matrix is suggested.

Acknowledgements

Financial support by CONICET, CIC, Universidad Nacional del Sur, and FONCYT of Argentina is gratefully acknowledged. R.A.M is a Research Fellow of the C.I.C of Argentina. M.A.F is a Research Fellow of the CONICET of Argentina.

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