Ionic conductivity enhancement achieved by the incorporation of ZnO in a lithium tellurite glass

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ABSTRACT

The reinforcement of the ionic conductivity in a lithium-vanadium-molybdenum tellurite glass is possible by modified with zinc oxide {0.7 [x ZnO $(1 - x)$ Li$_2$O] 0.3 [0.5 V$_2$O$_5$. 0.5 MoO$_3$]. 2TeO$_2$}. Structural features induced by zinc cation on the glassy matrix have a positive effect on the electrical behavior of the modified glass. The electrical response of the Zn/Li tellurite glass studied in the present work gives evidence that its ionic conductivity is improved due to the incorporation of small quantities of ZnO suggesting a potential solid ionic electrolyte useful in solid electrochemical devices.

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1. Introduction

When a solid electrolyte can be used at high temperatures and high applied voltage, its performance in an electric device is safer and more durable. If, in addition, it has charge carriers with high mobility it becomes an attractive material to be applied also in electrochemical devices. What is more, when the solid electrolyte is a glassy material more advantages are included: it is possible to prepare the material with a great variety of compositions, glasses have isotropic properties in the standard dimensions, they do not present grain boundaries like happens in ceramic materials, and their synthesis' methods are frequently simple. Several tellurite based glasses modified with ZnO [1,2,3] have been reported in the literature. Other works have reported that the incorporation of ZnO promotes a structural improvement through the ions vibration and breakage of covalent bonds which allow the ions to move through the non-bridging oxygen under the influence of an external electric field with enhanced lithium mobility [4,5]. Zinc Tellurite (ZnO-TeO$_2$) glass is stable and easy to prepare due to the formation of ZnTeO$_3$ structural units [6,7].

In materials design, the prediction and understanding of the physical properties are essential to develop new kinds of functionalized materials, one way to address this target is using transition metal oxides to induce modifications on the physical properties of a glassy matrix which is of technological interest. It was observed that the incorporation of ZnO in a tellurite glass decreases the elastic module and induces depolymerization of the matrix. Additionally, a large fraction of nonbridging oxygen is created [8,9,10,11,12]. Some

common application of Tellurite glasses is in optoelectronic areas (as are lasers and fiber optics) due to their high density, chemical stability, high homogeneity [13,14,15,16]. Therefore, in addition to the facts of their low transformation temperatures and the absence of hygroscopic properties (which limits the application of phosphate, silicate and borate glasses), making them more advantageous materials for technological applications [17,18].

In this work, we report the success of the ion conductivity improvement in a Tellurite glass of formula: 0.7 [x ZnO $(1 - x)$ Li$_2$O] 0.3 [0.5 V$_2$O$_5$. 0.5 MoO$_3$]. 2TeO$_2$ (formula expressed in mol) only by the incorporation of ZnO, making these glasses good solid electrolytes [19,20].

2. Material and methods

The stoichiometric amount of components (analytical grade 99.99%, TeO$_2$, V$_2$O$_5$, MoO$_3$, ZnO and Li$_2$CO$_3$) in order to obtain 5 g of sample by batch were well mixed and placed in a platinum crucible. One of the most reliable method, the standard melt quenching technique [21,22, 23,24,25,26] was used to prepare our glasses. The decarboxylation of the process of the Li$_2$CO$_3$ was done at a lower temperature, 200 °C less than the mix melting point and, when the effervescence finished, the mix was heated for 1 h at 850 °C in an electric furnace. During the melting process, the crucible was shaken enough to ensure the homogenization and to avoid gas retention in the melt. Next, the molten material was poured forming drops on a preheated aluminum plate and held for annealing at 200 °C during 2 h, in order to relax the mechanical stress retained at the quenching, see Fig. 1. The amorphous character of the resulting solids was tested by X-ray diffraction analysis and their glass state were confirmed by the differential scanning calorimetry (DSC) through the characteristic slope change which is associated to the

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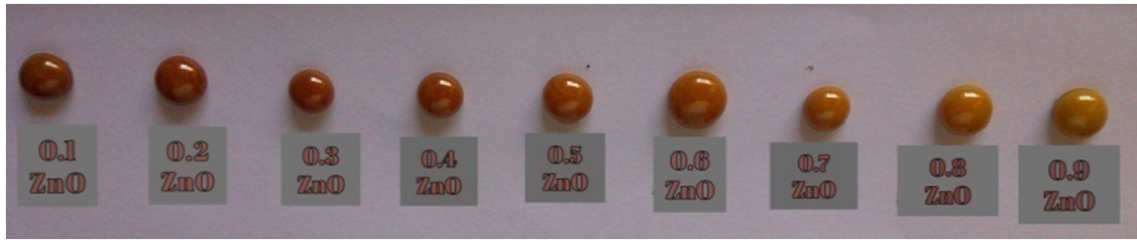E-mail address: frechero@uns.edu.ar (M.A. Frechero).

Fig. 1. Drop of samples of every ZnO content according to the general formula: 0.7 [x ZnO (1 − x) Li$_2$O] 0.3 [0.5 V$_2$O$_5$·0.5 MoO$_3$]·2TeO$_2$.

temperature of vitreous transition T$_g$, a signature of the glassy state. The XRD patterns of powdered samples, after annealing, were 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. Samples were exposed to the Cu K$_\alpha$ radiation (λ = 1.54 Å) at room temperature in the 2θ range: 3°–60°. DSC curves were recorded during the heating process at a rate of 10 K·min^{-1} using a SDT–Q600 TA Instruments in order to find the glass transition temperature (T$_g$) of each sample, starting from room temperature up to 500 °C using 15–20 mg of sample milled in an agate mortar. Each value of T$_g$ was obtained from the middle point of the C$_p$ (heat capacity) jump. The associated upper limit error of the temperature measurements is one degree, taking into account the middle point procedure using the TQA software.

Disks of each sample of a thickness ranging between 0.5 and 1.0 mm were obtained by polishing the drop with very fine quality lapping papers. The electrical contacts were formed by silver paint. The conductivities of the samples were determined in a temperature domain below 15° of the T$_g$ by standard a.c impedance method. The measurements were carried out at V$_{AC}$ = 0.80 V with an Agilent 4284A LCR meter in a frequency range from 20 Hz to 1 MHz. Room-temperature densities were determined by the Archimedes's principle using 2-propil alcohol as the immersion liquid, being the informed values the average of five independent determinations.

3. Results

As was mentioned above, the amorphous character of the resulting solids was tested by X-ray diffraction analysis. Fig. 2a shows the X-Ray Diffraction patterns. The base line deviation intensity in the pattern (in a range from 20° to 30° 2θ degrees) is smooth and does not present sharp peaks. Therefore, we confirmed that every sample was a glass material.

Complementary to the X-ray results, the glassy state of the samples was also confirmed by DSC through the slope changes which indicate the temperature of the glass transition (T$_g$). Fig. 2b shows the DSC curve of 0.7 [0.1 ZnO 0.9 Li$_2$O] 0.3 [0.5 V$_2$O$_5$·0.5 MoO$_3$]·2 TeO$_2$ as example of the T$_g$ determination as is explained above. Next, Fig. 3 shows the corresponding T$_g$ as a function of x (ZnO content according to the glass formula: 0.7 [x ZnO (1 − x) Li$_2$O] 0.3 [0.5 V$_2$O$_5$·0.5 MoO$_3$]·2 TeO$_2$). From this figure, we learn that T$_g$ values increase slightly, close to 5% in the total replacement of Li$_2$O by ZnO. It is interesting to mention here that this behavior is the expected one when the modifier oxide is an alkaline-earth oxide which causes the fixing (rigidity) of the glassy matrix due to the interaction of bivalent cations with the oxygen framework [6,7,8]. This stiffness causes an effect on the glass transition temperature which rises. In the case of our glass it is observed the same behavior with the augmentation of ZnO content indicating that the network connectivity has also increased. However, there are some works where through the X-ray and neutron scattering measurements have shown that in zinc Tellurite glasses when the ZnO content is increased, there is a decrease in Te–O coordination due to the conversion of TeO$_4$ into TeO$_3$ structural units [27].

The average of five density determinations of every sample is plotted in the Fig. 4 as function of x_{ZnO} (error bars are the experimental

dispersion). In this figure we observe a non-linear variation of the density as the ZnO content increases. Instead, a subtle maximum appears at x = 0.5, barely 1.14% higher than the extreme compositions.

In order to avoid a mistaken interpretation of the 3D atomic arrangement of the glasses under study, and taking into account the differences in the masses of the components that are changing (Li$_2$O = 29.88 g/mol and ZnO = 81.37 g/mol), we have analyzed the magnitude of the oxygen packing density (OPD = the number of mol of oxygen atoms per dm^3 of glass) of the matrix of oxygen atoms that hosts the atoms who are responsible for the density variation observed (Fig. 5). Thinking of a glass as one three dimensional skeleton of connected oxygen-tellurite polyhedra, the OPD of glass becomes an appropriate magnitude to
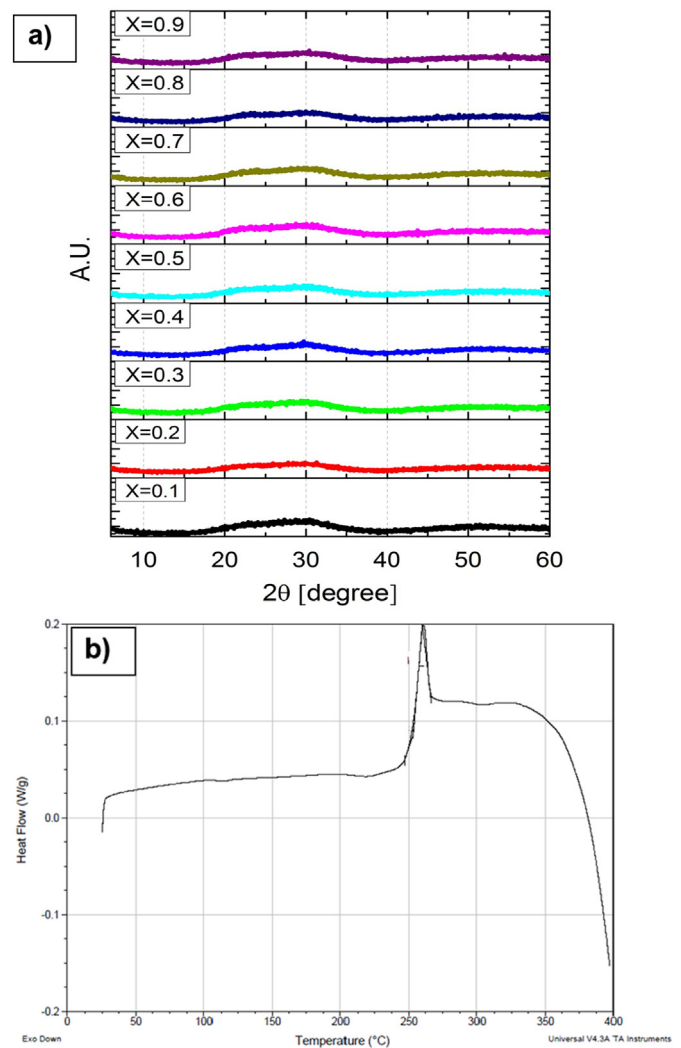

Fig. 2. a) X-ray diffraction patterns of studied systems: 0.7 [x ZnO (1 − x) Li$_2$O] 0.3 [0.5 V$_2$O$_5$·0.5 MoO$_3$]·2 TeO$_2$; b) DSC curve of 0.7 [0.1 ZnO 0.9 Li$_2$O] 0.3 [0.5 V$_2$O$_5$·0.5 MoO$_3$]·2 TeO$_2$ as example of the T$_g$ determination.
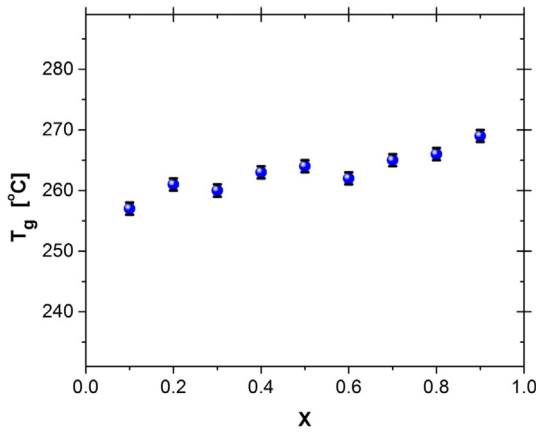
Fig. 3. T_g as a function of x (ZnO content according to the glass formula: 0.7 [x_{ZnO} (1 − x) Li$_2$O] 0.3 [0.5V$_2$O$_5$·0.5MoO$_3$]·2TeO$_2$).

expose the compactness of the oxygen skeleton and its variations caused by the incorporation of a modifier oxide.

Therefore, we conclude that the behavior observed on the density values is mostly due to the masses of the modifier oxides interchanging instead of the rearrangement of the glass skeleton. Moreover, the OPD behavior is in well agreement with the T_g increase as the ZnO content is larger. The modification induced by the incorporation of ZnO makes the tellurite glassy matrix more stable against structural changes when the temperature is increased. Higher temperature is needed to softening the skeleton when the content of ZnO in the glassy matrix is augmented. On the other hand, the expansion observed in the net of oxygen atoms (OPD) has a direct relationship with the bivalent cation (Zn^{2+}) and the lithium ions have more free space to fit and to move in the matrix without additional network expansion due to coulombic interactions considering the simplest model of charge transport proposed by Stuart and Anderson in [1,28] other similar Tellurite glasses without ZnO does not change their T_g values when the Li$_2$O content is increased [29,30] but its OPD change close to.

To study the electrical conductivity behavior of our glasses we apply the impedance spectroscopy and the impedance (|Z|) and the phase angle (ϕ) of every sample have been measured as a function of frequency and temperature. These data were analyzed through Nyquist plots using specific software: EIS Spectrum Analyser [31] in order to obtain the bulk resistance and to calculate the bulk conductivity at each temperature. Supplementary material shows in Fig. S1 that as the ZnO content increases the blocking effect at the electrodes is less evident as a
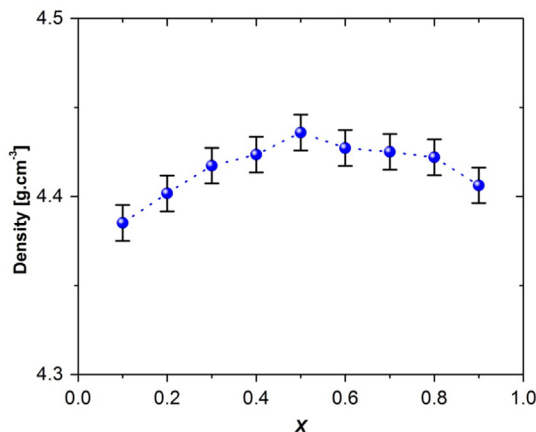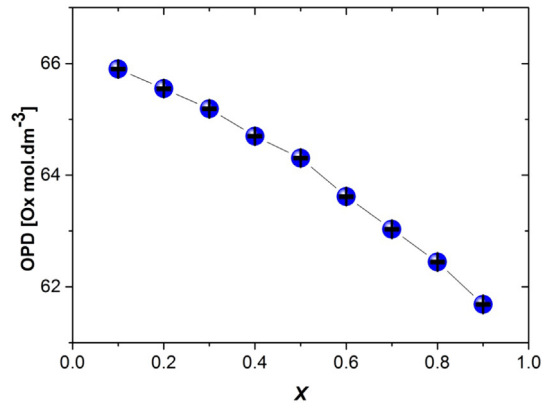

Fig. 5. Oxygen packing density as a function of x_{ZnO} content.

consequence of the lower number of most mobile lithium ions. Fig. 6 shows the variation of log[σ·T] *vs* T$^{−1}$ for each composition. Every composition's data were fitted with the Eq. (1):

$$\sigma \cdot T = \sigma_0 \, \exp\left(-\frac{E_a}{k \cdot T}\right) \qquad (1)$$

where E_a is the activation energy of the conductivity, σ_0 is the pre-exponential factor, k is the Boltzmann's constant and T the absolute temperature. Linear behavior is in good agreement with Eq. (1) (see Supplementary material). Therefore, as we see one slope for each system - in the range of temperatures plotted (90 °C to 230 °C) - only one activation energy can be considered and, as a consequence, the charge transport process is dominated by only one charge transport mechanism.

Fig. 7 shows the conduction parameters obtained from Eq. 1; *i.e.* activation energy (E_a) and pre-exponential factor (σ_0) as a function of the zinc oxide content (x).

4. Discussion

The activation energy values, E_a, and the conductivity pre-exponential factor plotted in Fig. 7 show a maximum at the same x value (0.5). However, in the electrical conductivity isotherm - the red (continuous) curve
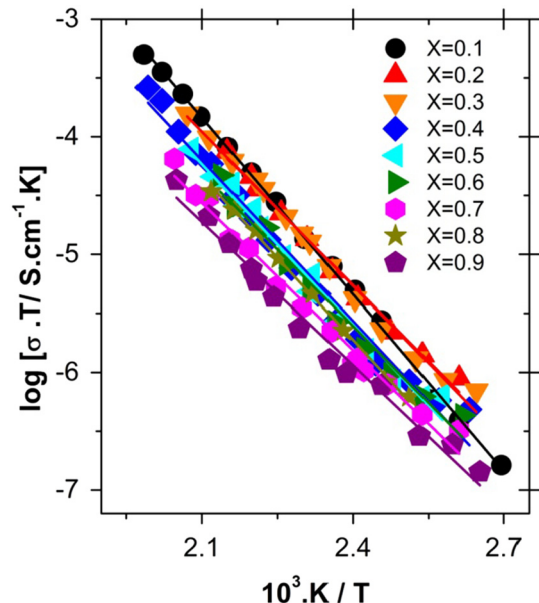

Fig. 4. Density values as a function of x_{ZnO} content.

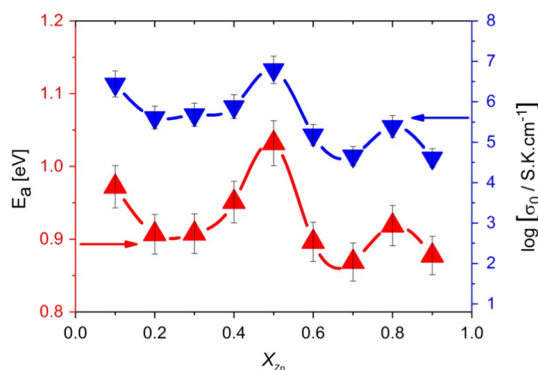**Fig. 6.** Arrhenius plots of measured conductivity of every composition.

Fig. 7. Activation energy (E_a; error bars of the fit = 3%) and pre-exponential factor (σ_0; error bars of the fit = 5%) as function of zinc oxide content (x). Errors are estimated by the linear regression of data.

Fig. 9. Conductivity values at 454 K as a function of the variation of the oxygen packing density – due to the ZnO incorporation.

plotted in Fig. 8 - does not evidence the minimum expected if the mixed mobile ion effect would have been present. Although, if we compare the conductivity values of the system where only 10% of the lithium ions have been replaced by Zn ions to the system with the 100% of lithium ions, i.e. $\sigma\{x = 0.1\}$ vs $\sigma\{x = 0.0\}$ (blue point in Fig. 8, studied previously [32,33], we have to accept that the Zn^{2+} is able to transport charge in this matrix, due to the fact that when Li_2O is almost completely replaced ($x \to 1$), the glass conductivity is almost equal to the one obtained when only lithium is present ($x \to 0$).

Swenson and Adams [34] found by means of bond-valence analysis of reverse Monte Carlo study of the $Li_xRb_{1-x}PO_3$ glass system, that mixed alkaline effect (MAE) is very pronounced, the isotherm of conductivity decreases by 6–8 orders of magnitude at the intermediate composition ($x = 0.5$) and the results obtained by Hall et al. [35] for the $Ag_xNa_{1-x}PO_3$ 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. Additionally, in a previous work, we analyzed the electrical response of a glass of formula 0.7 $[xAg_2O (1-x)Li_2O]$ 0.3 $[0.5V_2O_5 \cdot 0.5MoO_3] \cdot 2TeO_2$ and we found a minimum on the conductivity isotherm in $x = 0.4$ because the mixed mobile ion effect was present [21]. The electrical conductivity when mobile ions are mixed shows a strong dependence on the nature of modifier cations and on the structure of the glassy matrix. This dependence is mostly related to the charge and size of the modifier oxides incorporated in the glassy matrix (see R. Shannon Table [36] for ionic radius according coordination number). In the Li-Zn tellurite glass of the present work, there seems to be no evidence that the presence of zinc
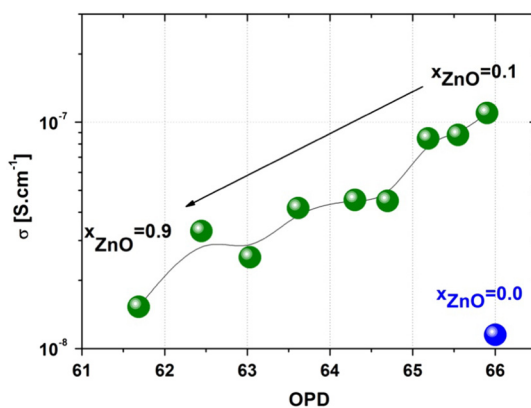
cations disturbs the conductivity pathway in the lithium cation migration. On the contrary, what is observed is that the total electrical conductivity is reinforced when ZnO is present. In this scenario, an improved connected pathway in the lithium rich domain is due to the presence of a small number of zinc cations which allows for freer ion diffusion in spite of the fact that there is no evidence of a strong modification in the glassy matrix since the OPD only varies a 14% and the T_g only varies a 6%.

In order to analyze in much more detail the phenomena observed, in Fig. 8 is plotted together the isothermal (T = 454 K) variation of electrical conductivity as a function of x_{ZnO} (red curve) and x_{Ag2O} (grey curve, studied previously [37]) and the conductivity value of the system modified with the same molar proportion of Li_2O ($x = 0.7$) (blue point [33]). From the data in this figure we learn that the initial replacement of 10% of Li_2O by ZnO causes an amazing increase of the electrical conductivity and subsequent replacement of Li_2O by ZnO provokes that the electrical conductivity decreases continuously. However, such as unpredictably as it might be, when almost all the Li_2O is completely replaced by ZnO, the material recovers approximately the same conductivity value as when only the Li_2O modifier oxide is present, what is see is that the conductivity value when $x \to 1$ on the red curve is almost equal to the blue point on the plot (the single modified system where neither ZnO nor Ag_2O are present). Therefore, we have learn that small quantities of ZnO incorporated in the glassy matrix (e.g. $x = 0.1$) allow the lithium conductivity to increase close to an order of magnitude, in this case from 10^{-8} to 10^{-7} S·cm^{-1} at 454 K. Nevertheless, the lithium-silver tellurite glass shows a quite different electrical behavior. When the silver oxide
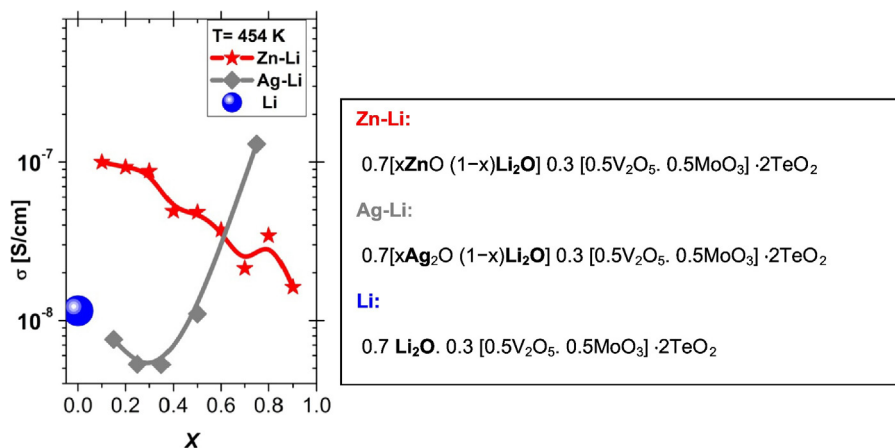
Fig. 8. Isothermal (T = 454 K) variation of electrical conductivity as a function of x_{ZnO} (red curve) and x_{Ag2O} (grey curve). The conductivity value of the same matrix modified with the same proportion ($x = 0.7$) of Li_2O only has been incorporated as a reference (blue point). See glass formulas on the right side of the plot. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

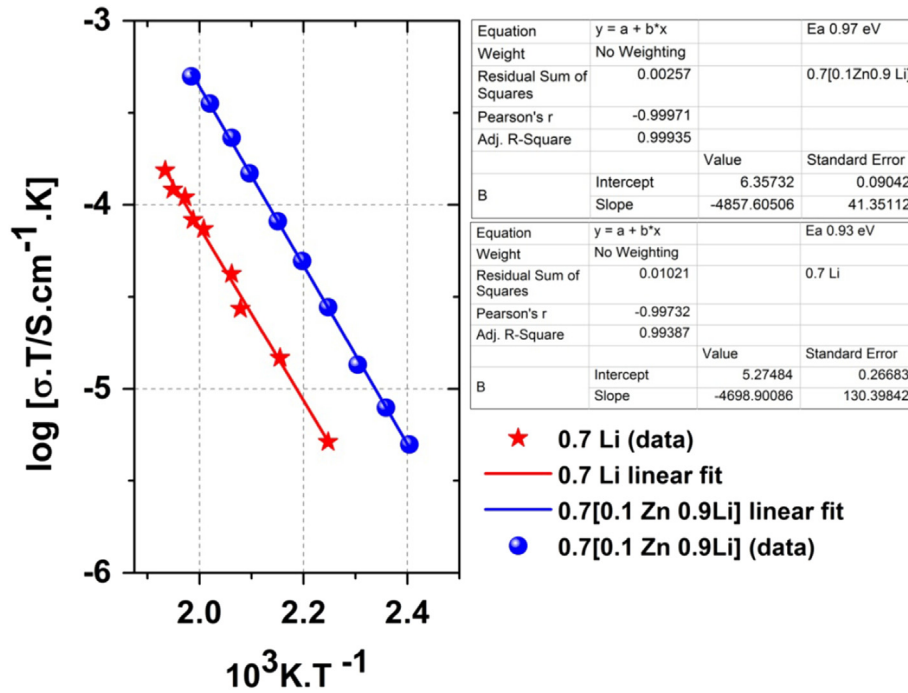| Equation	y = a + b*x		Ea 0.97 eV
Weight	No Weighting		
Residual Sum of Squares	0.00257		0.7[0.1Zn0.9 Li]
Pearson's r	-0.99971		
Adj. R-Square	0.99935		
		Value	Standard Error
B	Intercept	6.35732	0.09042
	Slope	-4857.60506	41.35112
Equation	y = a + b*x		Ea 0.93 eV
Weight	No Weighting		
Residual Sum of Squares	0.01021		0.7 Li
Pearson's r	-0.99732		
Adj. R-Square	0.99387		
		Value	Standard Error
B	Intercept	5.27484	0.26683
	Slope	-4698.90086	130.39842

★ 0.7 Li (data)
— 0.7 Li linear fit
— 0.7[0.1 Zn 0.9Li] linear fit
● 0.7[0.1 Zn 0.9Li] (data)

Fig. 10. Arrhenius plots of conductivity data of compositions: $0.7[0.1ZnO\ 0.9Li_2O]\ 0.3\ [0.5V_2O_5 \cdot 0.5MoO_3] \cdot 2TeO_2$ and $0.7Li_2O \cdot 0.3\ [0.5V_2O_5 \cdot 0.5MoO_3] \cdot 2TeO_2$.

content has replaced >40% of the lithium oxide, the conductivity value of the system continuously increases as the replacement of the lithium is higher, for x > 0.4. Such behavior has been explained by P. E. di Prátula et al. [25] assuming that the conductivity is mixed conductivity (polaronic plus ionic) instead of pure ionic conductivity. Therefore, if we focus only on the conductivity values in the range of x from 0.1 to 0.4 that Fig. 8 shows, we understand that the effect of the replacement of lithium oxide by silver oxide provokes a different behavior than the ZnO does. The replacement of Li_2O by small quantities of Ag_2O diminishes the glass conductivity value, while ZnO increases. However, in the ranges x = 0.1 to x = 0.4, the replacement of Li_2O by both Ag_2O and ZnO decreases the electrical conductivity. Such a comparison reinforces the conclusion about the positive effect given by the ZnO incorporation on the lithium conductivity in the tellurite matrix studied. Even more, in Fig. 9 now we plot the variation of the conductivity values as a function of the variation of the oxygen packing density -due to the ZnO incorporation. At a first glance, one can suppose that the result of the increment of the value conductivity obtained by the incorporation of ZnO is due to the fact of an increment of the lithium ion mobility in this tellurite glasses. Nonetheless, from the analysis of the correlation between OPD and conductivity presented in Fig. 9, it is possible to assume that both modifier oxides (Li_2O and ZnO) follows a mechanism of independent pathways, the total conductivity measured is the result

of the summation of both ion conductivities, the effect known as Mixed Mobile Ion Effect (MMIE) is not evident here.

Finally, it is important to note that the activation energy of the system single modified (only content lithium ions) is 0.93 eV [33] while is 0.96 eV when only 10% of lithium oxide has been replaced by zinc oxide (x = 0.1) but, the pre-exponential factor (Eq. (1)) of that zinc modified system is $2.7\ 10^6\ S \cdot K \cdot cm^{-1}$, around 10 times larger than the system without ZnO ($1.9\ 10^5\ S \cdot K \cdot cm^{-1}$). These results are obtained from the linear fit of the corresponding data plotted in Fig. 10. Consequently, this difference in the pre-exponential factor justify the increase of the electrical response observed when 10% of Li_2O is replaced by ZnO in the glass and can be explained by the proposed equation for ionic conductivity by Almond y West [38]:

$$\sigma_0 = Ne^2a^2c(1-c)\gamma k^{-1}\omega_0 \exp\left(\frac{S_a}{k}\right) \qquad (2)$$

where c: concentration of mobile ions, N: equivalent sites per unit volume, a: distance of hopping, e: the electronic charge, γ: is a correlation factor, ω_0: ion vibrational frequency, S_a: entropy of activation. From this equation we can assume that the incorporation of ZnO plays an important role both on the N as in the S_a, considering that the other factors in the equation do not vary significantly.

In Table 1 we resume all the results presented in the figures of the present work in order to facilitate a whole comparison of the system's properties studied.

5. Conclusions

The glass system of formula $0.7\ [x\ ZnO\ (1 - x)\ Li_2O]\ 0.3\ [0.5V_2O_5 \cdot 0.5MoO_3] \cdot 2TeO_2$ has an electrical conductivity strongly influenced by the content of total modifier cation while the structure of the glassy matrix is slightly modified as the modifier oxide (Li_2O) is systematically replaced by ZnO. The mentioned combination of modifier oxides does not show the mixed mobile ion effect as it is known. A minimum in an isotherm of conductivity is not evident neither a maximum. The sites of the conductivity pathway for the lithium cation migration are not disturbed for the presence of the zinc cations;

Table 1
X_{ZnO} according to the given formula; conductivity at 454 K; activation energy; logarithm of the pre-exponential factor in Eq. (1); density and glass transition temperature.

$0.7[x_{ZnO}\ (1 - x)Li_2O]\ 0.3\ (0.5V_2O_5\ 0.5MoO_3) \cdot 2TeO_2$					
X	$\sigma_{(454K)}$ [S·cm⁻¹]	E_a [eV]	$\log[\sigma_0/S \cdot K \cdot cm^{-1}]$	δ [g·cm⁻³]	T_g [°C]
0.1	$1.04E^{-7}$	0.96 ± 0.01	6.35 ± 0.09	4.39 ± 0.01	257 ± 5
0.2	$8.77E^{-8}$	0.91 ± 0.03	5.61 ± 0.24	4.40 ± 0.01	261 ± 5
0.3	$8.47E^{-8}$	0.91 ± 0.03	5.68 ± 0.18	4.42 ± 0.01	260 ± 5
0.4	$4.49E^{-8}$	0.95 ± 0.03	5.88 ± 0.29	4.42 ± 0.01	263 ± 5
0.5	$4.53E^{-8}$	1.03 ± 0.03	6.79 ± 0.34	4.44 ± 0.01	264 ± 5
0.6	$4.17E^{-8}$	0.90 ± 0.03	5.18 ± 0.26	4.43 ± 0.01	262 ± 5
0.7	$2.53E^{-8}$	0.87 ± 0.03	4.66 ± 0.23	4.43 ± 0.01	265 ± 5
0.8	$3.30E^{-8}$	0.92 ± 0.03	5.39 ± 0.27	4.42 ± 0.01	266 ± 5
0.9	$1.53E^{-8}$	0.88 ± 0.03	4.61 ± 0.23	4.41 ± 0.01	269 ± 5

instead, an improved connectivity seems to appear. More interesting to note is the conductivity obtained with a very little content of Li_2O, only the 10% of that and 90% of ZnO, where the electrical response is almost equal to the 100% of Li_2O in the same glassy matrix in absence of ZnO. In this scenario, the mechanism for mixed conductivity due to zinc and lithium cations is evident and the better connected pathway in the lithium rich domain is because of the presence of the zinc cations which provide freer ion diffusion.

Acknowledgements

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx. doi.org/10.1016/j.jnoncrysol.2017.01.039.

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