

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



P.E. di Prátula, S. Terny, M.E. Sola, M.A. Frechero \*

INQUISUR-CONICET-Departamento de Química, Universidad Nacional del Sur (UNS), Av. Alem 1253, CP 8000 Bahía Blanca, Argentina

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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  $\{0.7 [x \text{ ZnO} (1 - x) \text{ Li}_2\text{O}] 0.3 [0.5 \text{ V}_2\text{O}_5, 0.5 \text{ MoO}_3], 2\text{TeO}_2\}$ . 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 ( $\text{ZnO}-\text{TeO}_2$ ) glass is stable and easy to prepare due to the formation of  $\text{ZnTeO}_3$  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:  $0.7 [x \text{ ZnO} (1 - x) \text{ Li}_2\text{O}] 0.3 [0.5 \text{ V}_2\text{O}_5, 0.5 \text{ MoO}_3], 2\text{TeO}_2$  (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%,  $\text{TeO}_2$ ,  $\text{V}_2\text{O}_5$ ,  $\text{MoO}_3$ , ZnO and  $\text{Li}_2\text{CO}_3$ ) 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  $\text{Li}_2\text{CO}_3$  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

\* Corresponding author.

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

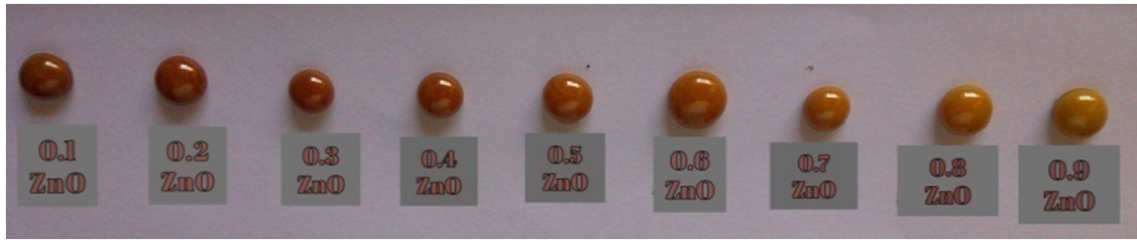


Fig. 1. Drop of samples of every ZnO content according to the general formula:  $0.7 [x \text{ ZnO} (1 - x) \text{ Li}_2\text{O}] 0.3 [0.5 \text{ V}_2\text{O}_5 \cdot 0.5 \text{ MoO}_3] \cdot 2 \text{ TeO}_2$ .

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  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.54 \text{ \AA}$ ) at room temperature in the  $2\theta$  range:  $3^\circ$ – $60^\circ$ . DSC curves were recorded during the heating process at a rate of  $10 \text{ K} \cdot \text{min}^{-1}$  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  $500^\circ \text{C}$  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  $15^\circ$  of the  $T_g$  by standard a.c impedance method. The measurements were carried out at  $V_{AC} = 0.80 \text{ V}$  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  $20^\circ$  to  $30^\circ$   $2\theta$  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  $0.7 [0.1 \text{ ZnO} 0.9 \text{ Li}_2\text{O}] 0.3 [0.5 \text{ V}_2\text{O}_5 \cdot 0.5 \text{ MoO}_3] \cdot 2 \text{ TeO}_2$  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:  $0.7 [x \text{ ZnO} (1 - x) \text{ Li}_2\text{O}] 0.3 [0.5 \text{ V}_2\text{O}_5 \cdot 0.5 \text{ MoO}_3] \cdot 2 \text{ TeO}_2$ ). From this figure, we learn that  $T_g$  values increase slightly, close to 5% in the total replacement of  $\text{Li}_2\text{O}$  by ZnO. It is interesting to mention here that this behavior is the expected one when the modifier oxide is an alkali-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  $\text{Te-O}$  coordination due to the conversion of  $\text{TeO}_4$  into  $\text{TeO}_3$  structural units [27].

The average of five density determinations of every sample is plotted in the Fig. 4 as function of  $x_{\text{ZnO}}$  (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 ( $\text{Li}_2\text{O} = 29.88 \text{ g/mol}$  and  $\text{ZnO} = 81.37 \text{ g/mol}$ ), we have analyzed the magnitude of the oxygen packing density (OPD = the number of mol of oxygen atoms per  $\text{dm}^3$  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

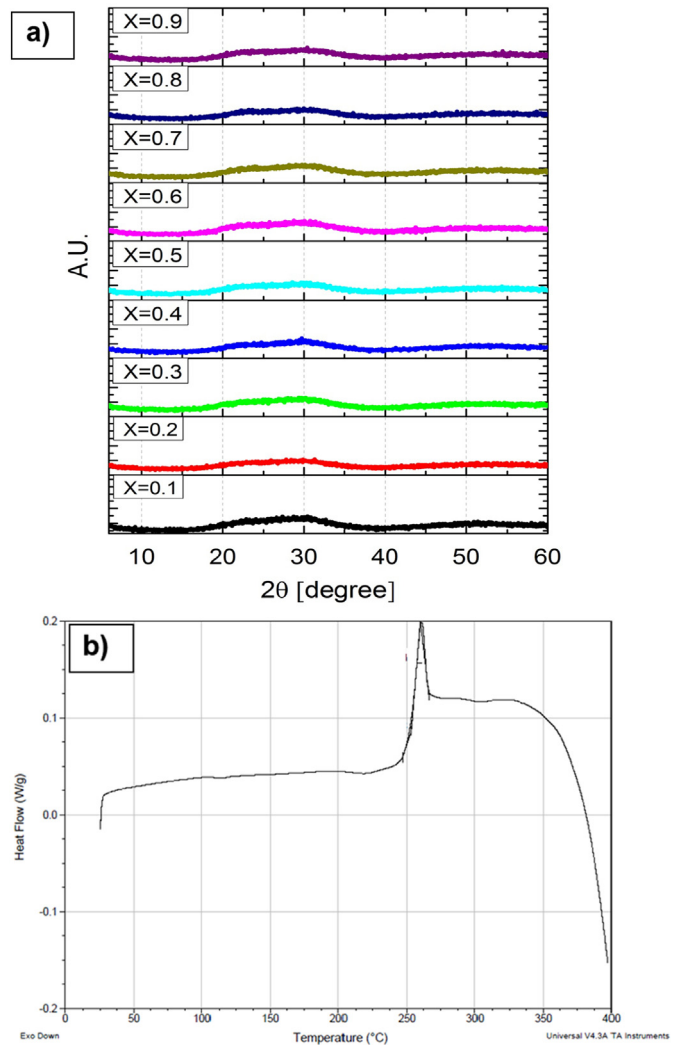


Fig. 2. a) X-ray diffraction patterns of studied systems:  $0.7 [x \text{ ZnO} (1 - x) \text{ Li}_2\text{O}] 0.3 [0.5 \text{ V}_2\text{O}_5 \cdot 0.5 \text{ MoO}_3] \cdot 2 \text{ TeO}_2$ ; b) DSC curve of  $0.7 [0.1 \text{ ZnO} 0.9 \text{ Li}_2\text{O}] 0.3 [0.5 \text{ V}_2\text{O}_5 \cdot 0.5 \text{ MoO}_3] \cdot 2 \text{ TeO}_2$  as example of the  $T_g$  determination.

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