



# Structure and electrical behavior relationship of a magnesium–tellurite glass using Raman and impedance spectroscopy



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## ABSTRACT

In this paper we present the study of the glassy systems of formula:  $x\text{MgO}(1-x)(0.5\text{V}_2\text{O}_5 \cdot 0.5\text{MoO}_3)_2\text{TeO}_2$ , with  $(0 < x < 1)$ . The aim of the work is to understand the relationship between in the induced changes in the glassy matrix by the incorporation of MgO in a vanadium–tellurite glass and the electrical response of the material. It has been found that the incorporation of MgO in the glassy matrix raises the glass transition temperature. The whole system's electrical behavior is explained by the small polaron hopping, in good agreement with the variable range polaron hopping model. In this matrix, an ionic transport by  $\text{Mg}^{2+}$  is not allowed. The study gives an opportunity to understand how to tune in the middle-range glassy structural order and, as a direct implication, how to control the electrical conduction process.

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## 1. Introduction

Structure and properties of oxides glasses depend strongly on the nature and concentration of network formers, and even more of modifiers. Tellurite glasses are of technical interest because of their low melting points and their absence of hygroscopic properties, which limit the uses of other glasses. These glasses have multiple applications due to their thermal, optical and electric properties being stable at room temperature [1,2]. They have low photon energy, high linear and non-linear refractive index and they are used for the design of photorefractive materials, non-linear devices, up-conversion lasers and optical amplifiers [3].

Many glasses containing transition metal ions, such as vanadium or iron, are semiconductors. It is generally recognized that the conductivity in those glasses is due to the presence of ions with more than one valence state, for instance  $\text{V}^{4+}$  and  $\text{V}^{5+}$  or  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ . In those systems, an electron can pass from one ion to another and, as a consequence, the electrical conductivity mechanism will be similar to that produced by impurities in ionic crystals, such as NiO [4].

In every kind of vanadium glasses there is evidence that the energies of an electron are spread over a small range of  $(k_B T)$  at room temperature on every vanadium site; being the ligand fields surrounding a  $\text{V}^{4+}$  and a  $\text{V}^{5+}$ , identical. Schmid [5] has suggested that at the temperature at which the glass solidifies, the electron moves rapidly from ion to ion in such a way that the average field acting on the surrounding

atoms during solidification is the same for every vanadium site. This is not necessarily so for all glasses: some glasses containing  $\text{Cu}^+$  and  $\text{Cu}^{2+}$ —investigated by Drake et al. [6] show a larger activation energy ( $\sim 1$  eV) in their conductivity, suggesting that the sites are not identical; therefore, more energy is needed to move an electron from  $\text{Cu}^+$  on to a  $\text{Cu}^{2+}$  site. Glasses containing iron may be intermediate [4].

We have studied previously glassy systems of formula  $x(\text{M}_2\text{O})(1-x)(0.5\text{V}_2\text{O}_5 \cdot 0.5\text{MoO}_3)_2\text{TeO}_2$  (with  $\text{M}=\text{Li}$ ,  $\text{Ag}$  or  $\text{Na}$ ) [7–11]. The electrical conductivity of these systems modified with alkaline oxides showed a deep minimum near  $x = 0.5$ . The conductivity isotherm of those systems evidences that the polaron conductivity decreases while the ionic conductivity rises. This behavior has not been explored on this matrix for earth alkaline modifiers, thus opening a promissory window to the exploration for new ionic conductor glasses. There are many studies on binary and ternary tellurite glasses modified with alkaline–earth elements [12–23] but there are only a few on quaternary tellurite glasses modified with divalent cations. The aim of this work is to present a structural and an electric study of the glass of formula  $x\text{MgO}(1-x)(0.5\text{V}_2\text{O}_5 \cdot 0.5\text{MoO}_3)_2\text{TeO}_2$  ( $x$ : mol number of magnesium oxide in the system) which behaves as a semiconducting glass for all compositions range in order to understand the role of the valence of the modifier ions and the nature of the modifications induced by the presence of transition metal oxides in the structure.

## 2. Experimental

All the glassy compositions have been prepared through the standard melt quenching technique using reagent grade chemicals of

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TeO<sub>2</sub>, MgCO<sub>3</sub>, MoO<sub>3</sub> and V<sub>2</sub>O<sub>5</sub>. Appropriate amounts of the components were weighed properly with a laboratory scale sensitive to 0.1 mg, well mixed and placed in a platinum crucible. Next, the decarboxylation process was made at a lower temperature than the mix melting point. When the effervescence finished, the mix was heated to reach 1173 K. All of this process was done in an electric furnace for about 1 h. During the process, the crucible was shaken frequently to ensure homogenization. Then, the molten material was poured on a preheated aluminum plate in form of drops and held at 200 °C during 2 h for annealing.

The amorphous character of the samples was tested by X-ray diffraction analysis (XRD) and by differential scanning calorimetry (DSC). X-ray diffraction (XRD) patterns of powdered samples after the annealing were collected with a standard Phillips PW-1710 diffractometer provided with a scintillation counter and an exit beam graphite monochromator at room temperature. The samples were exposed to Cu K<sub>α</sub> radiation ( $\lambda_{\text{average}} = 1.5418 \text{ \AA}$ ) in a  $2\theta$  range of 3° to 60°.

The glass transition temperatures ( $T_g$ ) of each compositions were determined by differential scanning calorimetry (DSC). DSC curves were recorded using a Q20-0836 at a heating rate of 10 °C/min in the temperature range of (25–400) °C. The associated upper limit error of the temperature measurements is one degree according to the middle point procedure with the TQA software. The characteristic endothermic peak was associated to  $T_g$ .

Raman spectra were recorded at room temperature in the 0–4000 cm<sup>-1</sup> range using a Raman spectrometer with  $\lambda = 532 \text{ nm}$ . The sample focalization was done using a microscope with an  $\times 20$  objective. The measurements were performed using a laser power of 42 mW in order to avoid damage or localized heating of the glasses.

For the electric conductivity measurements the samples were polished with finely grained sandpaper in order to obtain glass disks with parallel faces and thickness between 0.5 and 0.8 mm. Then, both faces of the samples were uniformly coated with a thin layer of silver conducting paint to have proper electrical contact. For the impedance determinations, a Solatron Impedance Analyzer 1260 was used in the frequency range  $1.10^{-2} \text{ Hz} - 1.10^7 \text{ Hz}$  with AC voltage amplitude of 800 mV. The impedance  $Z$  and phase angle  $\phi$  of each composition have been measured as a function of frequency and temperature. The data was analyzed using the specific software “ZVIEW” in order to obtain the bulk resistance and to calculate the conductivity at each temperature. For each composition the spectra were carried out in a temperature range starting at 25 °C up to a temperature 15 °C below  $T_g$  in order to avoid changes in the sample.

Finally, density measurements were done following the Archimedeian's method using distilled water as secondary displacement medium. In order to obtain the average density values, three independent measurements were carried out per composition.

### 3. Results and discussion

#### 3.1. XRD, DSC and density

Fig. 1 shows the X-ray diffraction patterns. The base line deviation intensity in the pattern (in the range from 20° to 30°  $2\theta$  degrees) is smooth and do not present sharp peaks. From these results we assume that the samples are glasses. But, the composition  $x = 1.0$  could not be obtained. After several attempts varying different quenching rates, all of them presented significant peaks in their XRD pattern (not shown) indicating the presence of crystalline phases.

Fig. 2 shows the corresponding  $T_g$  as a function of  $x$  (MgO content) for the whole system. From this Fig., we learn that  $T_g$  values increase to around 34% with the augmentation of the MgO content (from  $x = 0.0$  to  $x = 0.9$ ). According to N. H. Ray [24], 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. Also, they mention that, in general, the cross-linking has a greater effect than the bond strength.

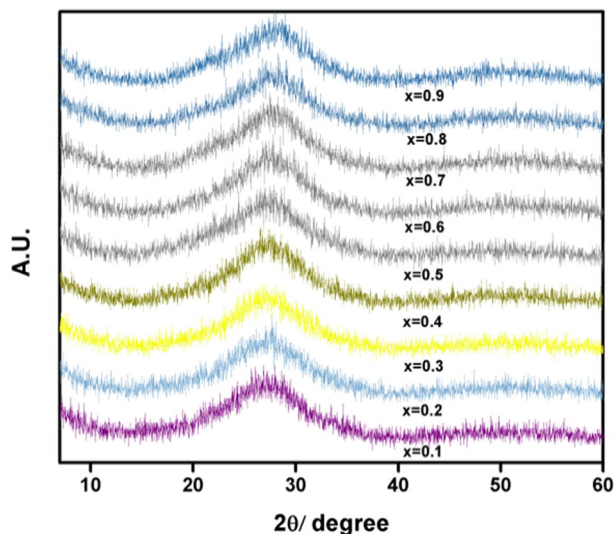


Fig. 1. X-ray diffraction patterns of the systems:  $x\text{MgO}(1-x)(0.5\text{V}_2\text{O}_5 \cdot 0.5\text{MoO}_3)_2\text{TeO}_2$  at room temperature.

Fig. 3 shows the density averages as a function of  $x$  MgO content. There is a tendency to increase its value the replacement of the mix of ( $\text{V}_2\text{O}_5 + \text{MoO}_3$ ) by MgO; a different behavior is observed for compositions  $x = 0.3$  and  $x = 0.4$  where the density diminishes. Given that MgO is lighter than ( $\text{V}_2\text{O}_5 + \text{MoO}_3$ ) the average increment in the density must be directly related with anomalous peculiar structure ordering.

Fig. 4 shows the molar volume ( $V_M$ ) and the oxygen packing density. The  $V_M$  diminishes approximately 30% in the whole replacement of ( $\text{V}_2\text{O}_5 + \text{MoO}_3$ ) by MgO. Considering a glass as a kind of oxygen polymer – connected by mainly covalent bonds through much smaller linking atoms – the oxygen packing density (OPD: the number of mol of oxygen per dm<sup>3</sup> of glass) becomes a relevant magnitude to analyze the compactness of the structure. In this Fig., we observe that the OPD is almost constant when  $x$  goes from  $x = 0$  to  $x = 0.3$ . Then, the packing diminishes from  $x = 0.3$  to  $x = 0.5$ , remaining almost constant up to  $x = 0.7$  and, finally, diminishes again. Taking into account that density is a ratio between two quantities which decreasing with the augmentation of the MgO content (the molar mass of the samples and the molar volume) the resulting density behavior is related to this ratio. As the molar mass can be represented by a linear decreasing function, the

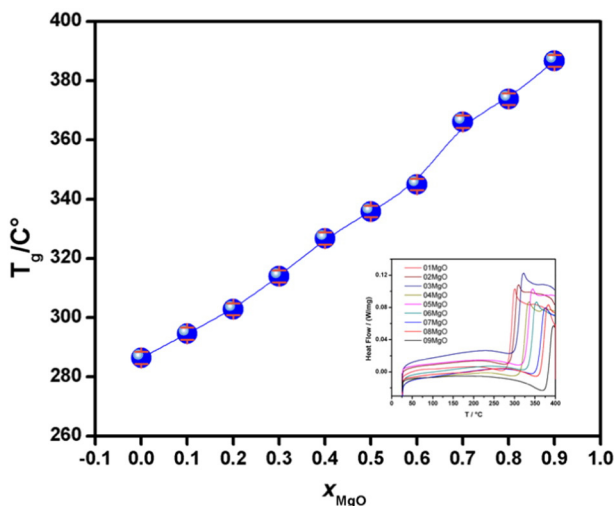


Fig. 2. Glass transition temperature ( $T_g$ ) as a function of MgO content ( $x$ ) of the systems:  $x\text{MgO}(1-x)(0.5\text{V}_2\text{O}_5 \cdot 0.5\text{MoO}_3)_2\text{TeO}_2$ . Inset: DSC scans.

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