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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of BaO is low) to a weak ionic conductive response (when more than 50% of the transition metal oxides content has been replaced by BaO).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.

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 semiconducting 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 $(1-x)$ $(0.5V_2O_5.0.5MoO_3)$ 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 $(1-x)$ $(0.5V_2O_5.0.5MoO_3)$ 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 °C/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 Kα radiation ($\lambda = 1.54$ Å) 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 $[T_g - 15]$ °C.

The density of the glass samples was measured using isopropyl alcohol as the secondary displacement medium in the Archimedean 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 OPD = mol oxygen number/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.

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 contain 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:

$$\sigma_{dc} = \frac{\sigma_0}{T} e^{-\left(\frac{E_a}{k.T}\right)} \tag{1}$$

where E_a is the activation energy of the conductivity process, σ_0 is the preexponential factor and $k.T$ 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 ($T = 500$ 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.

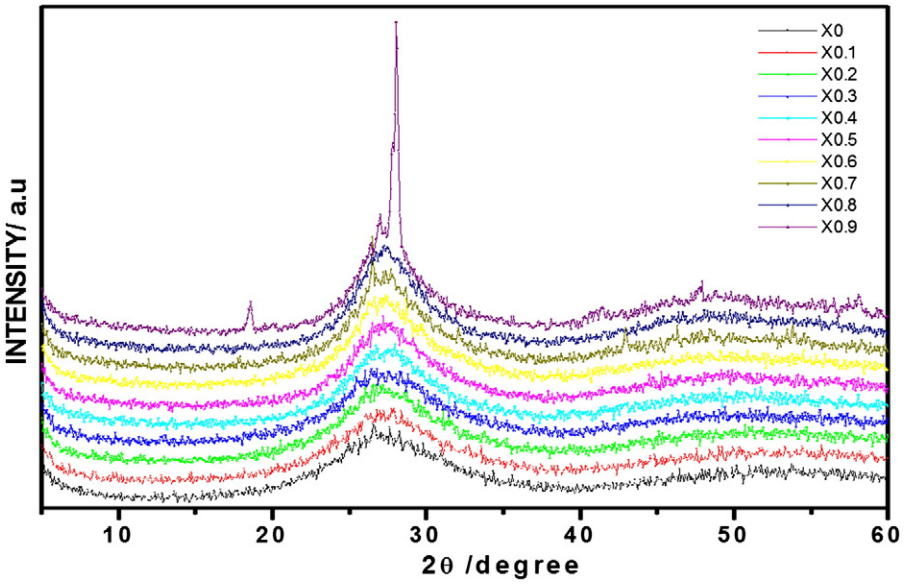

Fig. 1. X-ray diffraction patterns for each composition. The inset corresponds to the content of BaO according to the formula x BaO $(1 - x)$ $(0.5V_2O_5 \cdot 0.5MoO_3)$ 2 TeO_2.