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Dielectric relaxation of vanadium–molybdenum tellurite glasses modified by alkaline-earth oxides

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ABSTRACT

Electrical response changes due to the incorporation of alkaline-earth oxides in the vanadium–molybdenum tellurite glassy matrix have been studied. The results are explained by analyzing the electric formalisms representations. A non-straightforward relationship to the modifier oxide ionic radius was found and the results suggest poor charge carrier interactions even at high alkaline-earth concentrations. The electrical behavior of the studied materials gives strong evidence that alkaline-earth modified tellurite glasses are poor candidates to become good ionic glassy conductors.

1. Introduction

In 1998, C.T. Moynihan had showed that the use of the electric modulus M* in analysis of electrical responses in ionically-conducting glasses is useful because it allows a comparison between electrical relaxation results and structural relaxations results [1]. When one discusses the electrical response of ionic conductors, it is necessary to make a distinction between relaxation and dispersion as J.R. Macdonald highlighted in his review in 2010, he distinguishes between a dispersion of dielectric relaxation times (Debye's response contains a single time constant) and resistive relaxation times (which consist of a discrete or continuous distribution of relaxation times) that involve mobile charges [2].

Electrical measurements in ionic glasses are very useful to carry out in a frequency domain. In general, what is measured is the parallel conductance (G) and the capacitance (C) of the sample using an admittance bridge or the magnitude of the sample impedance |Z| and the phase angle ϕ, using an impedance meter. Usually, those results are expressed in terms of complex permittivity (ε^*) or the complex conductivity (σ^*) which are related by the following expression:

$$\sigma^* = i\omega\varepsilon_0\varepsilon^* \tag{1}$$

where ε_0 is the permittivity of vacuum, ω is the angular frequency and *i* is the imaginary unity.

Two characteristic properties of a material, definable in terms of the quantities presented in Eq. (1) are: the dc electrical conductivity which involve the long range displacement of mobile ions, σ_{dc} (when $\omega \to 0$); and the high frequency dielectric constant, ε_∞ (when $\omega \to \infty$).

However, nowadays, analysis of such data tends to focus on the frequency dependence of either the real part of the conductivity or of the complex modulus. The electric modulus formalism, M*, was firstly developed by Macedo et al. [3,4] to consider the electrical response as a function of frequency, in an analogous manner to the mechanical shear stress relaxation in liquids, where a system initially in equilibrium is perturbed. The kinetics of its approach to a new equilibrium state is described in terms of a relaxation function in the time domain $\phi_{(t)}$. In the time domain, the relaxation (to zero at long times) of the electric field $\mathbf{E}_{(t)}$ in an ionic conductor under the constrain of the constant displacement vector **D** imposed at time zero is given by:

$$\mathbf{E}_{(t)} = E(0)\int_0^\infty g_{(\tau)} \cdot \exp\left(-\frac{t}{\tau}\right)d\tau \tag{2}$$

where $\phi_{(t)}$ is the electric field relaxation function, τ an electric field relaxation time and $g_{(\tau)}$ is the normalized probability density function for τ.

In the frequency domain, the corresponding electric field relaxation is described in terms of the electric modulus M*:

$$M^* = M' + iM'' = M_\infty\int_0^\infty g_{(\tau)}\left[\frac{i\omega\tau}{(1+i\omega\tau)}\right]d\tau. \tag{3}$$

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The time scale for the electric field relaxation is parameterized by mean relaxation time $\langle\tau\rangle$, whose value is in turn given by:

$$\tau = \int_0^\infty g_{(\tau)}\tau d\tau = \varepsilon_0\varepsilon_\infty/\sigma = \frac{\varepsilon_0}{M_\infty}. \quad (4)$$

Most of the relaxation of the electric field is expected to occur at frequencies in the vicinity of the frequency where $\omega \cdot \langle\tau\rangle = 1$. This characteristic frequency corresponds closely to the frequency of the maximum in M'' and to the frequency range where M' changes more rapidly.

The most important feature of electrical relaxation data analysis for conducting glasses, which focuses on frequency dependence of σ', is often given a very literal interpretation: a measure of the flux of electrical charge due to the motion of mobile charge carriers (ions, polarons or both) [5]. However, if a whole analysis of the electrical relaxation behavior of the system is done from the electric formalisms for description of electrical relaxation data it is possible to understand, more deeply, the way that the system responds to an applied external electrical field. More than that, the change on the electrical response induced by the presence of different modifier oxides in the glassy matrix is done more obvious. Because of this, we present here our results in such a comparative way in order to show the differences provoked by four alkaline-earth oxides on the same tellurite glassy matrix. A priori, the only property that is changed is the alkaline-earth cation radius (Mg: 0.60 Å; Ca: 1.00 Å; Sr: 1.20 Å; Ba: 1.40 Å) [6]. The general formula of the glassy system studied in this work is: xMO$(1 - x)$[$0.5V_2O_5 0.5MoO_3$]$2TeO_2$ with M = Mg, Ca, Sr or Ba which allow us to focus only on the modifier oxide cation. For the sake of clarity we have emphasized on some figures the results of samples with the lowest and highest modifier oxide content. The obtained results show that other properties of the modifier oxide than their cation radius is involved in the electric response of these glasses and we argue about those.

2. Experimental

The samples of this work of general formula: x**M**O$(1 - x)$[$0.5V_2O_5 0.5MoO_3$]$2TeO_2$ (**M** = Mg, Ca, Sr, Ba) were prepared by a standard melt quenching technique starting from reagent grade chemicals of TeO_2, MoO_3, V_2O_5, $MgCO_3$, $CaCO_3$, $SrCO_3$ and $BaCO_3$. Appropriate amounts of the components were well mixed and placed in an alumina crucible. Next, the carbonate decarboxylation process was made at a lower temperature than the mix melting point. When the effervescence finished, the mix was heated to reach a temperature of 1373 K in an electric furnace for 1 h. During the process, the crucible was shaken frequently to ensure homogenization. After this procedure the molten material was poured onto a preheated aluminum plate in form of drops and held at 250 °C during 2 h for annealing.

The amorphous character of the samples was tested by X-ray diffraction (XRD) analysis. The X-ray diffraction patterns of powdered samples after the annealing were collected with a Bruker D8 Advance diffractometer 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 K_α radiation ($\lambda = 1.54$ Å) at room temperature in the 2θ range: 10°–60°.

Differential Scanning Calorimetry (DSC) curves were recorded during heating rate a 10 K min^{-1} using a SDT-Q600 in order to find the glass transition temperature (T_g) of each sample starting from room temperature up to 600 °C and using 15–20 mg of glass samples previously milled in an agate mortar. Each value of T_g is obtained from the middle point of the C_p jump during the heating. The associated upper limit error of the temperature measurements is one degree according to the middle point procedure with the TQA software.

In order to obtain the electrical characterization of our materials, the samples were polished with very fine sand papers to obtain glass disks with two parallel faces of thickness ranging between 0.5 and 0.7 mm. Each sample was coated uniformly with a thin layer of silver paint with the purpose of having proper electrical contact. For the impedance determinations, Impedance/Gain-phase Solartron analyzer with 1296 a dielectric measuring module, which allows analysis within the range of frequencies from 10 μHz to 10 MHz, of 10^2 to 10^7 Ω impedances. To do the analysis of the results has been used the Solartron ZPlot software package. The measured were carried out at $V_{AC} = 0.80$ V, in a frequency range of [10^{-2}–10^6] (only for barium oxide modified system the impedance measurements were carried out with an Agilent 4284A LCR meter in frequency range from 20 Hz to 1 MHz). For each composition the spectra were carried out in a temperature range starting at 100 °C up to a temperature 15 °C below its T_g to avoid sample structural changes.

Density measurements were done following the Archimedean'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

Fig. 1 shows the X-ray diffraction patterns. The base line deviation intensity in the pattern (in the range from 20° to 30° 2θ degrees) is smooth and do not present sharp peaks. From these results we assume that every sample is a glass material.

Fig. 2a shows the corresponding T_g as a function of x (alkaline-earth content) for every studied glass system. From this figure, we learn that T_g values increases between 20% and 50% depending on the alkaline-earth oxide. This behavior is the opposite of that observe when the modifier oxide is an alkaline oxide (T_g decreases when the alkaline oxide content increases in this type of glassy matrix) [7].

Fig. 2b shows the corresponding T_g as a function of radius modifier cation. There is not a direct correlation between the cation modifier radius with the of the T_g value. According to N.H. Ray [8], 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. Considering this explanation from this Fig. 2b we learn that Sr^{2+} has the better size to this type of glassy matrix while to reach a similar effect with Mg^{2+} is needed larger quantity of MgO. Ca^{2+} and Ba^{2+} do not fit very well and do not reach the same behavior even they induce the necessary cross-linking to increases the T_g. Fig. 2c gives the tree properties simultaneously: cation radius vs. cation modifier content vs. T_g and it shows clearly that there is not a direct and unique relationship among them.

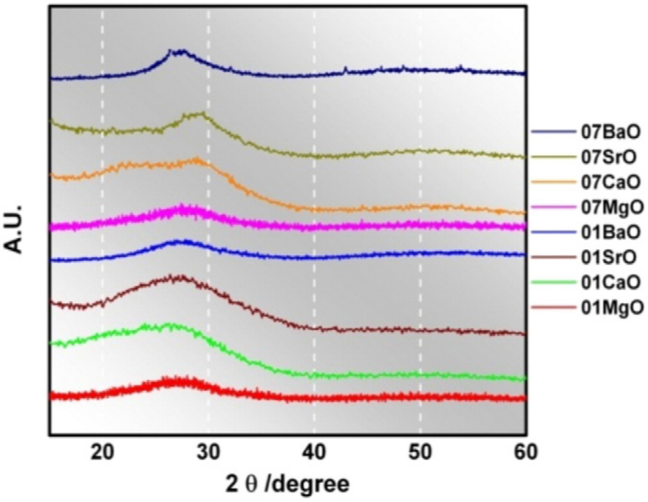

Fig. 1. X-ray diffraction patterns of the studied systems.