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A new transition metal-tellurite glass family: Electrical and structural properties

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ABSTRACT

Glasses of composition 0.8 [xBaO.(1 − x)MgO]. 0.2*TM*.2TeO_2 with *TM*: MoO_3, WO_3, V_2O_5 or Nb_2O_5 (x = mol content) were obtained by the melt quenching technique. Raman Spectroscopy, Density and Differential Scanning Calorimetry were used to infer their microscopic structure and electrical properties were studied using Impedance Spectroscopy. Some singularities in their electrical and structural properties appeared. Deviations from linearity as a function of alkaline-earth oxide modifier content were observed both on the electrical and structural properties. They were analyzed considering the intensity of the electrical field of the mix of alkaline earth cations which induced changes on the glassy matrix and the mixed alkaline-earth effect was considered. The observed relationships between their electrical and structural properties and the mix of alkaline earth cations were different according to the transition metal oxide present.

1. Introduction

Tellurite-based glasses are the subject of extensive research because of their electrical and optical properties. Some of their main features include extended infrared transmittance, high non-linear optical indices and low fusion temperature. Also, they constitute an excellent matrix for active element doping [1].

Many oxide glasses modified with a mix of alkali oxides exhibit a non-additive variation of certain properties. This is known as the "mixed alkali effect (MAE)" and it is still an unsolved phenomenon in glass science. The MAE especially manifests itself in non-additive discrepancies in transport properties, such as diffusion, conductivity and viscosity. These dynamical properties contrast with static properties such as density, refractive index and molar volume; all of which usually exhibit relatively small deviations from linearity [2–3].

However, there is still much to understand about the "mixed alkaline-earth effect (MAEE)". MAEE seems to be phenomenologically analogous to MAE considering that one alkaline-earth ion is partially replaced by another alkaline-earth ion. Deviations from linearity on their property behavior as a function of the alkaline-earth ratio are observed although certain dynamical properties behave differently depending on the *nature* of the glassy matrix composition and the peer of alkaline-earth cations mixed [4–16]. Since alkaline-earth cations affect the glass properties in a non-predictive manner, it is important to study this effect from both the scientific and the technological points of view.

Despite the technological and scientific relevance of tellurite glasses, so far, there is no available data of this effect in the literature. Then, the aim of this work is to study systematically the structural and electrical properties of a family of glasses of general formula: 0.8[xBaO (1 − x)MgO] 0.2*TM*. 2TeO_2 with *TM* = Nb_2O_5, V_2O_5, MoO_3 or WO_3. We carefully study how the materials' properties are affected by the partial replacement of MgO by BaO (i.e. when x mol content ➔ 0.0 the system composition is: 0.8 MgO 0.2*TM*. 2TeO_2 and when x mol content ➔ 1.0 the system composition is: 0.8 BaO 0.2*TM*. 2TeO_2) and how the structure of the glassy framework varies by changing the transition metal oxide which acts as a former-modifying oxide, considering that TeO_2 is a glass former oxide while BaO and MgO are modifier oxides. These transition metal oxides have been carefully chosen in order to change the ion size and its electronic configuration, i.e. the kind of polyhedron that each transition metal cation forms with the oxygen atoms.

2. Materials and methods

2.1. Sample preparation

The samples were prepared by a standard melt quenching technique using reagent grade chemicals of TeO_2, $MgCO_3$, $BaCO_3$, MoO_3, WO_3, Nb_2O_5 and V_2O_5. Starting from the nominal composition expressed through the general formula, every component (all of chemical grade; 99.9%) was properly weighted with a laboratory scale sensitive to 0.1 mg in order to obtain (10.00 ± 0.01) g of each sample. Next, the components were well mixed and placed in an alumina crucible and the carbonate decarboxylation process (when carbonates were used)

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was made at a lower temperature than the mix melting point. When the effervescence finished, the mix was heated to reach 1323 K and after that, it was held for an hour in an electric furnace. 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 for annealing at 523 K during 2 h.

2.2. X-ray diffraction analysis (XRD)

The amorphous character of the samples was tested by X-Ray Diffraction. The XRD patterns of powdered samples after the annealing were collected with a Bruker D8 Advance Diffractometer at 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°.

2.3. Glass transition temperature and isobaric heat capacity

DSC curves were recorded during heating rates using a SDT-Q600 calorimeter. We search the glass transition temperature (T_g) of each sample with a heating rate of 10 $K \cdot min^{-1}$, starting from room temperature up to 600 °C, using 15–20 mg of glass samples previously crashed in an agate mortar. The T_g values were obtained from the middle point of the C_p jump during the heating. The associated upper-limit error of the temperature measurements is an interval of one degree according to the middle point procedure with the TQA software. The heat capacity change at glass transition ($\Delta C_{p(Tg)}$) was measured from the DSC thermogram for each composition.

2.4. Vickers micro-hardness

Every glass sample was mirror like polished and Vickers microhardness (H_V) was measured using a Duramin 5 indenter (Struers A/S). A total of 34 indents were conducted on each sample using an indentation time of 0.05 s and an indentation load of 500 mN. The measurements were performed in a regular atmosphere, i.e. air (no gas composition controlled) at room temperature.

2.5. Structural aspects

Raman spectra were collected at room temperature on glass samples in the 0–4000 cm^{-1} range using a Raman spectrometer with a 532 nm green laser as the probing light source. The sample focalization was done using a microscope with a ×20 objective. The measurements were performed using a laser power of 42 mW in order to avoid damage or localized heating of the glasses. The obtained spectra were deconvoluted using Gaussian fitting to determine the Raman peak positions.

2.6. Electrical characterization

The samples were polished with very fine sand papers in order to obtain glass disks with two parallel faces with thickness ranging

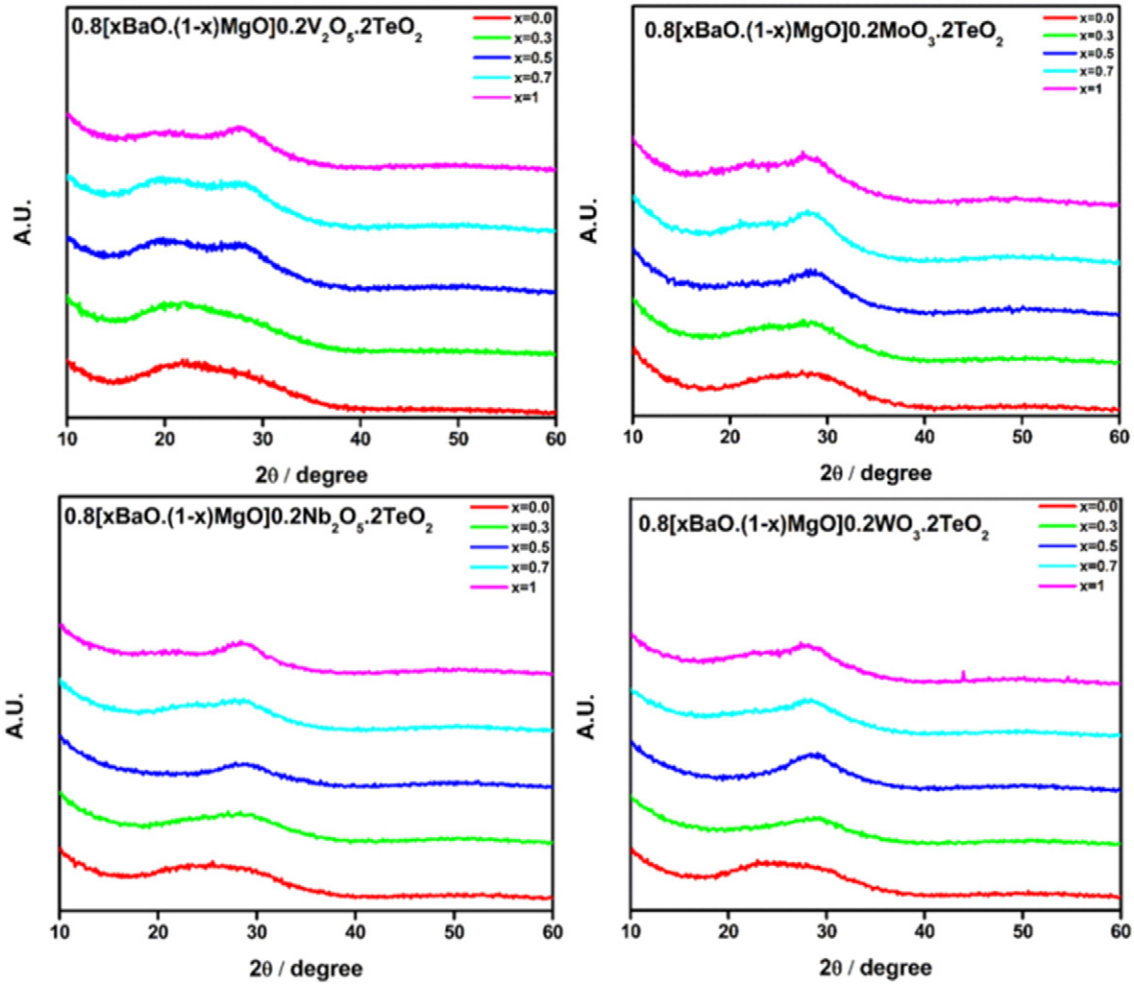

Fig. 1. XRD patterns for each composition of every studied system.