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Enthalpy relaxation of the glassy matrix in vanadium–molybdenum–tellurite oxide glasses

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ABSTRACT

In this paper, we analyze using differential scanning calorimetry (DSC) how a disordered structure, obtained by the quenching of oxides melted into glass, is related to the nature of the modifier cation. We estimated the enthalpy relaxation in based tellurite oxide glasses of formula xM_2O $(1-x)(0.5V_2O_5{\cdot}0.5MoO_3)$ $2TeO_2$ when they are modified with univalent metal oxides as Na^+, Li^+ and Ag^+. As ionic conductors in tellurite oxide glasses, these cations have the same charge but different size, electronic configuration and, in addition, their electric behavior is quite different. We show that the jump in the C_p at T_g is also related to the nature of the modifier cation. We study the conventional view of the configurational entropy of liquid that is frozen below the glass transition temperature (T_g) with what is called entropy loss. We explore whether or not there is a relationship between the nature of the modifier oxide and its magnitude.

1. Introduction

It is well known that the simplest way to obtain a glass is to quench a suitable liquid from which a disordered solid is obtained, *i.e.* a glass. However, this particular state of the matter is still a challenge for scientists, both for its fundamental views and also for its potential uses in a huge variety of technological applications. This is why, many researchers today are still trying to describe the disordered structure of glasses and to design new ones to improve their technological applications. Controlling the preparation of glassy materials to obtain specific properties is an unquestionable challenge for scientists.

Therefore, and since glasses are in a non-equilibrium state, it is important to know the variation time dependence in physical properties after their formation (*e.g.* structural relaxation).

When we describe the glass transition process, we say that it is associated to the liquid structure which was frozen when it passed through the glass transition temperature but, after that, a very slow process determined by the thermodynamic temperature and called structural relaxation takes place. The frozen structure is directly related to the quenching process and also to its chemical composition.

As we know, the glass transition temperature is not a constant in a glass material because it also depends on many other parameters such as the heating rate during its measurements, its physical aging, *etc.* Moreover, the T_g will be different if we measure it while cooling a liquid instead of heating the glass. A complete explanation of the complexity of this phenomenon is yet to be developed; but we can take advantage of these particularities [1]. As many other authors have previously explained in great detail, there are several expressions to show the dependence of the T_g (more generally called T_f or fictive temperature, in order to avoid confusion with T_g that is commonly related to a particular rate of heating) on the heating/cooling rate during its measurement, $q^{\pm}$ [2–4]. In this work, our main objective is to evidence the way in which a particular liquid structure frozen in glass is related to its chemical composition and how this is reflected in its physical properties. Our goal is to determine whether or not the charge or the size of the modifier oxide cations acts more strongly than the electronic configuration on the glassy matrix. This is a profitable knowledge in the design of materials for specific technological applications.

The modifier oxides used in this work, lithium oxide, sodium oxide and silver oxide, have the same charge (+1) but their cation sizes are different and there are two very distinctive electronic configurations among them. We obtained the DSC thermograms with different heating rates (q^+) and, from these data, we have found the T_f and the magnitude of the jump in the C_p at each T_f for each composition. Then, from the relationship between T_f and q^+ we calculated the enthalpy relaxation as it is described later in this work. It is important to note here that these data have also been used to determine the liquid fragility index in order to attempt to correlate the kinetic fragility index with the thermodynamic property change at T_g. As explained in Ref. [5], an increase of this index leads to a corresponding increase of ΔC_p.

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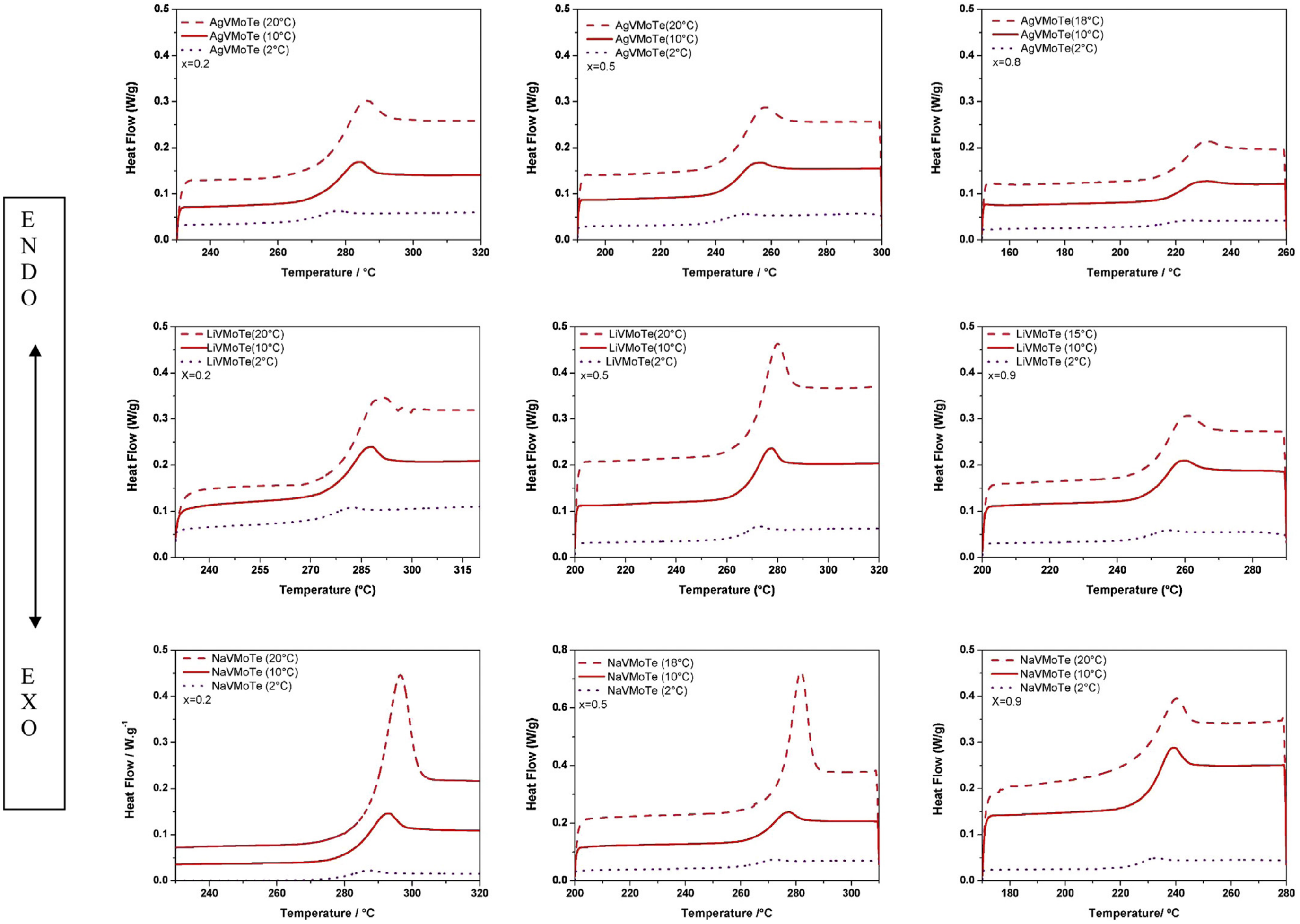

Fig. 1. Thermograms of the systems, which we studied, at different heating rates.

As we reported in our previous work, the nature of the cation is what defines the properties of the glass and not just the fact that they have the same charge and different size [6]. Other authors have reported the effect of the charge of the modifier cations and also the effect of mix modifier cations of different charges on other kind of glassy matrices [7].

On the other hand, Grupta and Mauro [8] contrast the conventional view of the configurational entropy of liquid that is frozen below the glass transition temperature (T_g) with what they call "entropy loss" associated with the liquid going toward its glass transition. In this work, we explore this and the relationship between the nature of the modified oxide and its magnitude, if any.

2. Experimental

The samples were prepared by a standard melt quenching technique from initial mixtures with the proper quantity of components (TeO_2:Sigma–Aldrich99+, V_2O_5:Cerac 99.9%, MoO_3:Cerac 99.9%, Ag_2O:Alfa-Aesar 99+, Na_2CO_3:Anedra 99.0% and Li_2CO_3:Anedra 99.0%) as starting materials. These powders were mixed in an agate mortar; then, transferred to a platinum crucible, and put in a furnace at 850 °C during 40 min. During this time, they were mixed mechanically twice to maintain a homogeneous liquid. The molten liquid was quickly poured into a preheated (200 °C) aluminum mold and kept at this temperature during 2 h for annealing treatment. The glassy nature of the resulting solids was tested using X-ray diffraction (XRD) analysis and differential scanning calorimetry (DSC). The X-Ray powder diffraction was carried on a PW1710 BASED diffractometer in a continuous scan mode with a copper anode and 45 kV–30 mA (tension and current respectively), on portions of the solid obtained earlier which had been previously minced in agate mortar.

DSC curves were recorded during heating rates using a Q20-0836. First, we looked at the T_g of each sample with a heating rate of 10 K min^{-1} in an alumina pan, starting from room temperature up to 400 °C, using 20–30 mg of glass samples previously crashed in an agate mortar. It is important to note there is a calorimeter software error of less than a degree in the T_g determination and, among the different samples – obtained from different batches – of less than 5°. Secondly, starting from 20 to 30 mg of fresh sample (*i.e.* the solid as was obtained from the quenching of the melt and its subsequent annealing as described before) using again alumina pans and 20–30 mg of glass samples previously crashed in an agate mortar, we made the different cycles of heating–cooling, on the same sample, avoiding reaching the crystallization temperature for each of them in order to prevent the growing of crystalline forms. The set of the heating–cooling cycles around each T_f were: *i* – q_h 20 K min^{-1}–q_c 20 K min^{-1}; *ii* – q_h 10 K min^{-1}–q_c 10 K min^{-1}; *iii* – q_h 5 K min^{-1}–q_c 5 K min^{-1} and just in the case of $x_{Na} = 0.2$ we explored q_c 10 K min^{-1}–q_h 2 K min^{-1} in order to see if another ratio cooling-heating changed the behavior or not. To analyze the DSC scans, we used the TA Q 4.6 software, and the corresponding temperature to each ΔC_p jump was the T of the middle point of the jump during the heating.

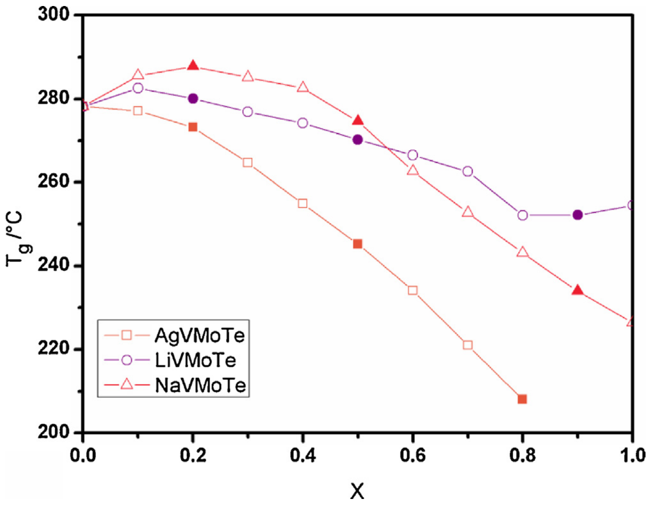

Fig. 2. Glass transition temperatures (T_g) for each composition as function of the modifier oxide content x.

3. Results and discussion

The amorphous nature of the prepared samples was analyzed by DSC and XRD. The XRD patterns (no displayed here) do not show any kind of sharp peaks on them, confirming the absence of crystalline faces in the samples. On the other hand, Fig. 1 shows all the DSC curves registered during the heating cycles (we just show three rates to make the plot simpler). In these, we can observe the typical slope change, which indicates the transition from glassy state to super cooled liquid. In Fig. 2, we show the results of the glass transition temperature (T_g) measured at 10 K min^{-1} for each composition of the system.

It is well known that, when the heating rate is slow, the T_g decreases and this is what we observed, as Moyniham et al. describe in detail in Ref. [9]. Now, if we take into account that when the melt is cooled through the glass transition region, there is an enormous increase in the relaxation time for a given cooling rate (q^-), a structure is actually fixed or "frozen" in a solid system. Then, when we reheat the system, as we can see in the thermograms in the Fig. 1, the flux of the heat is proportional to the heat capacity (C_p) and the characteristic temperature T_g (or T_f) reflects – in some way – the features of the frozen structure. This dependence is related to the relaxation time τ according to the so-called Tool–Narayanaswamy (Eq. (4) of Ref. [9]). Considering this simple idea, one gets a relationship between the temperature dependence of the structural relaxation time and the rate of cooling or reheating, and from this, we found out the activation enthalpy for the structural relaxation (ΔH^*) through the following equation:

$$\frac{d\ \ln\tau}{dT^{-1}} = -\frac{d\ln q_h}{dT_g{}^{-1}} = \frac{\Delta H*}{R} \qquad (1)$$

This quantity ΔH^* is a magnitude that reflects the relative stability of the glassy matrix, in our case: *VMoTe*. But, what happens with this enthalpy if the glass is modified with different oxides (whose cations have a charge of +1 but different sizes – diameters – and different electronic configurations when they are present in different concentrations)?

According to Moynihan [9] and Hodge [10], if we limit the heating–cooling cycles to a narrow range area around the T_g, we can obtain the dependence of the temperature where the jump in the C_p is observed (T_f: fictive temperatures) with the heating rates in an Arrhenius form. From their slopes, we can estimate the activation enthalpy relaxation-assuming that it behaves, in this very small range, in a linear way, even when we know that this is not strictly so, according to the Adam-Gibbs and Tool–Narayanaswamy–Moynihan equations [9,11–14].

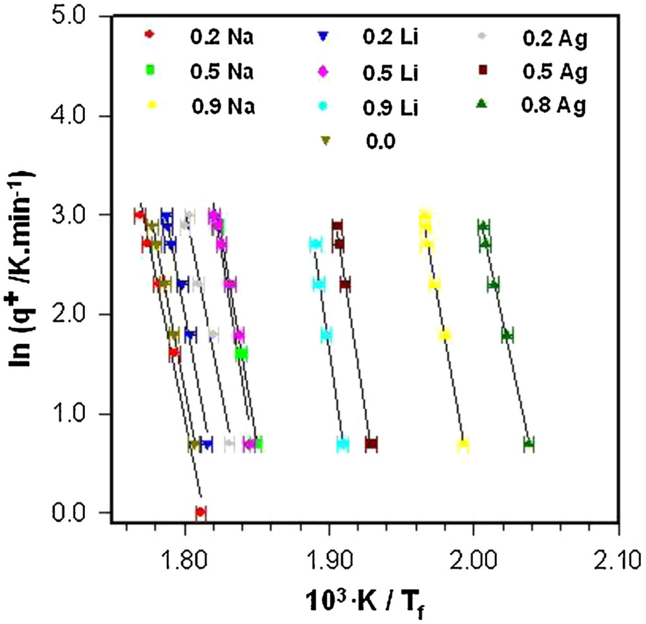

Fig. 3. Logarithm of the heating rate as function of $(T_f)^{-1}$ (linear regression fit of each curve: $R^2{}_{x(\mathrm{Na})0.2} = 0.9845$; $R^2{}_{x(\mathrm{Na})0.5} = 0.9956$; $R^2{}_{x(\mathrm{Na})0.9} = 0.9934$; $R^2{}_{x(\mathrm{Li})0.2} = 0.9859$; $R^2{}_{x(\mathrm{Li})0.5} = 0.9610$; $R^2{}_{x(\mathrm{Li})0.9} = 0.9919$; $R^2{}_{x(\mathrm{Ag})0.2} = 0.9699$; $R^2{}_{x(\mathrm{Ag})0.5} = 0.9978$; $R^2{}_{x(\mathrm{Ag})0.8} = 0.9959$; $R^2{}_{x(-)0.0} = 0.9982$).

In Fig. 3, we plot the results for the same glassy matrix with the three different modifier oxides: Ag_2O, Li_2O and Na_2O, at three different concentrations. For comparison, we include the results of the pure glassy matrix in the same graph, *i.e.* without any modifier oxide. Also, the results are summarized in Table 1 in order to have a clearer idea of their magnitudes.

From Fig. 3, we learn that, when the amount of modifier oxide is low (here $x < 0.5$), there is not a significant difference in the ΔH^* among the studied systems (near 10% referring to $x = 0.0$); but, when the concentration of the modifier oxide is higher, *i.e.* near $x = 1.0$, small cations (Li^+) increase the ΔH^* value (near 24% in reference to $x = 0.0$), Na^+ does not seem to undergo any noticeable changes in ΔH^* value, while Ag^+ decreases the ΔH^* near 19%.

From these results, we observe that the stability of the glassy matrix in this work depends on the size and nature of the cation modifier oxide even when the corresponding T_gs are affected in different way: $T_{gLi} > T_{gNa} > T_{gAg}$ for the highest concentration of modifier oxide analyzed in this work ($x \to 1.0$). Although, silver cations have quite different behaviors compared to sodium cations, the T_{gAg} is near 30 °C lower that the T_{gNa}, despite the fact that the both have quite similar radii.

Moreover, it is evident that lower T_gs do not always involve lower ΔH^* (at least in the tellurite glasses studied here). From our

Table 1
Enthalpy relaxation for the same glassy matrix.

$X = 0.0$	$\Delta H^* = 694$ kJ mol^{-1}	
Li^+	Na^+	Ag^+
$X = 0.2$ $\Delta H^* = 646$ kJ mol^{-1}	$X = 0.2$ $\Delta H^* = 592$ kJ mol^{-1}	$X = 0.2$ $\Delta H^* = 618$ kJ mol^{-1}
$X = 0.5$ $\Delta H^* = 757$ kJ.mol^{-1}	$X = 0.5$ $\Delta H^* = 702$ kJ.mol^{-1}	$X = 0.5$ $\Delta H^* = 767$ kJ mol^{-1}
$X = 0.9$ $\Delta H^* = 863$ kJ mol^{-1}	$X = 0.9$ $\Delta H^* = 686$ kJ mol^{-1}	$X = 0.8$ $\Delta H^* = 564$ kJ mol^{-1}

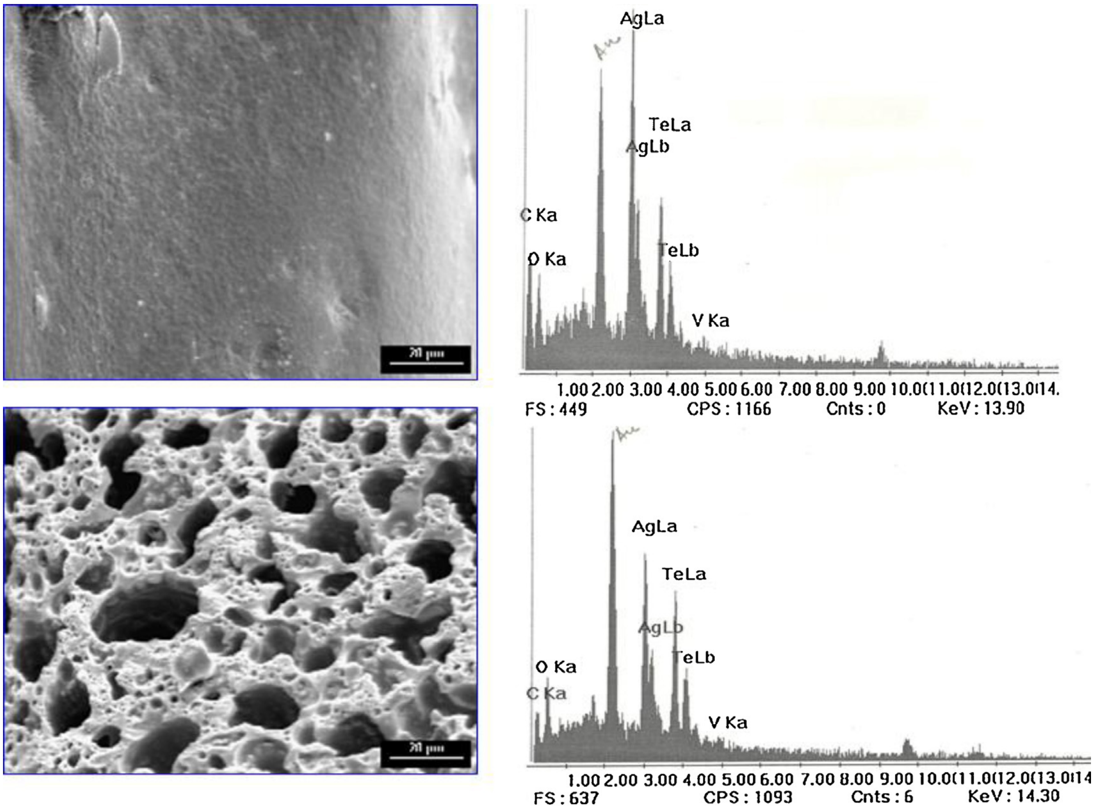

Fig. 4. SEM images of the $0.9Ag_2O$ $0.1(0.5\,V_2O_5{\cdot}0.5MoO_3)$ $2TeO_2$. Surface and bulk with their corresponding EDS analysis (on the right).

results, it is clear that those changes are caused by high concentrations of Ag^+. Therefore, we could say that this cation changes the glassy matrix in a dramatic way. Silver modifier oxide involves a decrease of the ΔH^* and a sharp drop on the T_g values when its concentration is increased in this glassy matrix.

The aforementioned results are the main reason why we have decided not to inform the results of the sample $0.9Ag_2O$ $0.1(0.5V_2O_5{\cdot}0.5MoO_3)$ $2TeO_2$. We observed that this system (after the thermal treatment suffered during the measuring of its electrical conductivity behavior-as function of the temperature carefully heated up to 15 °C below its T_g shows an enriched concentration of silver on the surface compared to the bulk. This was evidenced through the images and the analysis of the SEM/EDS (Scanning Electron Microscopy and Energy Dispersive Spectroscopy). Fig. 4 shows the images of its surface and inside bulk with their corresponding EDS analysis.

On the other hand, the images show a spectacular morphological change inside the bulk. “Channels” appear, probably as a result of the migration of the silver cations from the bulk to the surface. There is no doubt that it would be interesting to speculate whether these are the so-called “migrating channels” (the ones often mentioned in the specific literature as the paths of the ions in the ionic conductivity) [15–18].

Lately, there have been several interpretations related to the thermodynamic view of the “entropy variation” around the glass transition. As we mentioned before, J. Zarzycki relates it with the magnitude of the $\Delta C_{p(Tg)}$, Gupta and Mauro postulate an “entropy loss” at the glass transition [8] while, Goldstein proposes a different interpretation while he says that the calorimetrically measured configurational entropy has a real physical meaning and it does not vanish on kinetic freezing [19]. Other works present alternative views [20–22]. Then, before calculating an entropy quantity in our glasses, we looked for a relationship between the ΔC_p around a very narrow interval of T_g for each composition, with the modifier oxide concentration which could be related to that. Then, we measured the ΔC_p at the T_g ($q^+ = 10\,K\,min^{-1}$). Fig. 5 shows these results as function of the modifier oxide concentration.

J. Zarzycki (in his book of *Glasses and Vitreous State* [23]) considers that a liquid system that is cooled at a given rate can either crystallize at a certain temperature T_m or pass to a vitreous state at a lower temperature T_g depending on the rate of cooling. The specific heat of the system at a constant pressure, $C_p = (\partial H/\partial T)_p$, registered during a DSC scan shows that as the system vitrifies, the passage through T_m does not show a discontinuity (*i.e.* does not crystallize) and then diminishes rapidly in the neighborhood of T_g. The specific heat of the glass tends toward that of the crystal. Then, the variation of entropy is:

$$dS = \frac{C_p dT}{T} = C_p d\ \ln T \tag{2}$$

Representing C_p as a function of ln(T), the variations in the entropy could be deduced from the areas under the curves.

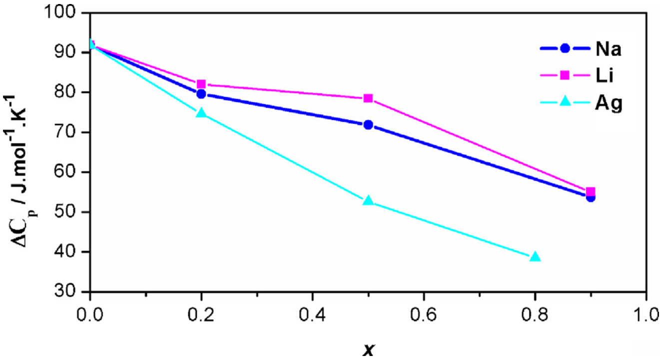

Fig. 5. $\Delta C_{p(Tg)}$ measured at $q^+ = 10\,K\,min^{-1}$ and plotted as function of the modifier oxide concentration x.

If we assume that the jump in the $\Delta C_{p(Tg)}$ is a kind of "measure of an entropy retained" during the quenching as other authors have assumed before [24], considering that in the course of the transition the systems seek unsuccessfully to reduce the entropy and some entropy is retained at the temperature that the system is trapped in a solid state, this can be thought of as a configurational disorder of the liquid which is retained at the moment of glass formation.

Fig. 5 shows the $\Delta C_{p(Tg)}$ as a function of the modifier oxide concentration. In those compositions where the modifier oxide concentration is *low* ($x = 0.2$), the $\Delta C_{p(Tg)}$ is very similar to the *pure* glassy matrix, *i.e.* when no modifier oxide is present, considering that the inaccuracy in its determination is near 5%. Also, they are very similar among the different modifier oxides that we have explored. In this sense, a small concentration of modifier oxide seems not to induce a strong influence (structural changes) on the glassy matrix. But, when the modifier oxide concentration is *high* ($x \to 1$), there is a notorious difference in this $\Delta C_{p(Tg)}$ between the alkaline oxides and the transition metal oxide as a modifier. It is possible to think that transition metal cations (here Ag^+) could induce some kind of interactions on the system even when the system is still a supercooled liquid that do not change too much at the moment to become a solid. This behavior is quite different to the alkaline metal cations on the glassy matrix that we have studied in this work and probably we could look for an explanation in their very different electronic configurations. At present, we are testing this behavior on different glassy matrices. This idea has not been deeply explored up to now and major investigation of it is needed. It is interesting to note here that Y. Yue has related the $\Delta C_{p(Tg)}$ with the kinetic fragility. He found at least for inorganic glasses that usually a high $\Delta C_{p(Tg)}$ value is correlated with a high kinetic fragility index from the relationship between viscosity and calorimetric data on the 24 different glasses [25]. Then, it is necessary to understand all the information that could be obtain from the $\Delta C_{p(Tg)}$ and $\Delta C_{p(Tf)}$.

4. Conclusion

We have studied the relaxation of glassy tellurite matrices modified with several modifier oxides and we have observed that the stability of the glassy matrix depends on the size and the electronic configuration of the modifier oxide cation. Silver cations have quite a different behavior compared to sodium cations despite the fact that they both have quite similar cation radii and the same cation charge (+1). It is necessary to consider that the influence of the electronic configuration of the cation could be more important and that this has to be more carefully investigated. Additionally, it is important to take into account that the value of the T_g of a glassy system is not enough to be considered, as a consequence, a less stable glass or, from its technological point of view, with more tendencies to aging and less durable. It is necessary to evaluate other properties in order to understand the glassy matrix behavior as a function of the temperature, type and concentration of modifier oxide and also the behavior as a function of the pressure, a field that is commonly less explored.

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