

IR absorption spectra of lithium and silver vanadium–tellurite based glasses

M.A. Frechero^a, O.V. Quinzani^a, R.S. Pettigrosso^a,
M. Villar^b, R.A. Montani^{a,*}

^a Universidad Nacional del Sur, Depto. de Química, Av. Alem 1250, 8000 Bahía Blanca, Argentina

^b Universidad Nacional del Sur, Depto. de Ingeniería Química, Av. Alem 1250, 8000 Bahía Blanca, Argentina

Received 28 March 2007

Abstract

The aim of the present paper is to give structural information in order to set a correlation between the electrical conductivity behavior and structures of lithium and silver vanadium–tellurite based glasses. We report our structural studies and compare the effect of the nature of the metallic cation on glasses of the form $XM_2O \cdot (1 - X)V_2O_5 \cdot 2TeO_2$ (where $0 \leq X < 1$ and $M = Li$ or Ag). Fourier transform infra-red (FTIR) spectra were recorded for all compositions and complementary differential scanning calorimetry (DSC) measurements and X-ray diffraction (XRD) measurements were also carried out. This paper should be considered as complementary to a previous article reporting the conductive behavior of these glasses. In the latter we reported the obtained results on electrical conductivity studies. The results confirm the existence of a transition from a typically electronic (polaronic) conductive regimen when the molar fraction (X) of M_2O is equal to 0, to an ionic conductive regimen when X tends to 1. The evidence for the independent migration path for both electrons and ions was put into evidence by studying the electrical conductivity behavior in a complementary system of the form $X M_2O \cdot (1 - X)[0.5V_2O_5 - 0.5MoO_3] \cdot 2TeO_2$. In this system vanadium was partially replaced by molybdenum which acts as a ‘diluting’ agent of the active centers involved in the electronic transport.

© 2007 Elsevier B.V. All rights reserved.

PACS: 72.80.N; 61.43.F

Keywords: X-ray diffraction; Conductivity; FTIR measurements; Tellurites; Calorimetry

1. Introduction

In recent papers we reported our studies on the effect of metallic oxides on the electronic (polaronic) conductivity on vanadium tellurite glasses of the form $XM_2O \cdot (1 - X)V_2O_5 \cdot 2TeO_2$ (X being either Li or Ag) [1,2]. For these glasses the existence of a deep minimum in the isotherms of conductivity was verified. The explanation for this minimum was given assuming the existence of two kinds of

independent migrating paths: one kind of path consisting of an electronic transfer in the chain V(IV)–V(V) and the other kind of path made by the regular position of non-bridging oxygens along the network-former chains allowing ion displacement. In a complementary paper, extra data supporting the first explanation were presented [3,4]. In that paper we studied the effect of changing the magnitude of only one type of conductivity (electronic) on the whole conductive behavior of the system, based on previous results on vanadium tellurite glasses given by Lebrun et al. [5]. Then, the electrical studies on the system of the form $XAg_2O \cdot (1 - X)[0.5V_2O_5 - 0.5MoO_3] \cdot 2TeO_2$ allowed us to conclude that the deliberate ‘dilution’ of *only* the electronic conducting centers, by the replacement of vanadium

* Corresponding author. Tel.: +54 (291) 4595101; fax: +54 (291) 4551447.

E-mail address: rmontani@criba.edu.ar (R.A. Montani).

by molybdenum ions, directly causes the diminution of *only* the electronic conductivity with a concomitant constancy on the ionic conductivity. This experimental result confirms the idea of the existence of two kinds of independent migrating paths: when adding the network modifier to the electronic $V_2O_5-2TeO_2$ glasses the electronic paths are progressively blocked causing the electronic conductivity to diminish. Consequently, the whole shape of the curves for isothermal conductivity can be seen as the intersection of two curves corresponding to electronic and ionic conductivities and the relative minimum corresponding to a change in the mechanism of the electrical transport process.

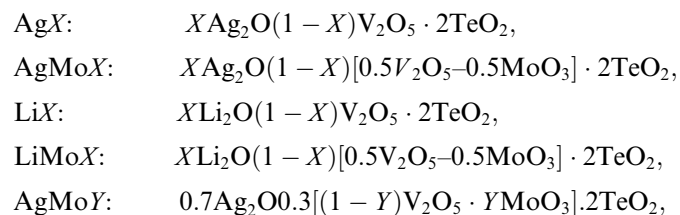
The present paper can then be considered as complementary of these previous articles, its main purpose being to report our new results on the structural aspects of the systems and to correlate these data with the reported electrical behavior. The experimental data mainly includes our results on FTIR spectroscopy and also complementary results on DSC and X-ray diffraction analysis.

2. Experimental

The samples were prepared following the experimental procedure given in a previous work [1]. The amorphous character of the resulting solids was tested by X-ray diffraction analysis and confirmed by the differential scanning calorimetry (DSC). In fact, the DSC thermograms showed the characteristic endothermic peak, which is associated to the temperature of transition (T_g).

The IR spectra of tellurite glasses and pure oxides, previously grounded to fine powders were registered as Nujol mulls on a Nicolet Nexus FTIR instrument, in the $2000-400\text{ cm}^{-1}$ range using KBr windows at room temperature. Differential Scanning calorimetry studies were performed using a Perking Elmer Pyris 1 instrument at a heating rate of $10^\circ/\text{min}$ in the interval ranging from 100 to 400°C , and the data were analyzed using the software included in the instrument. The X-ray powder diffraction was performed with the help of a Rigaku instrument using the $\text{Cu K}\alpha$ radiation at room temperature.

For the sake of simplicity, in the future we will identify the different systems in a compact manner as follows:



where Ag or Li indicates the presence of Ag_2O or Li_2O as a modifier oxide, respectively. When molybdenum is present 'Mo' is added to the denomination. The 'X' indicates that the *varying* amounts are those corresponding to the modifier metallic oxide. The 'Y' indicates that the *varying* amount corresponds to molybdenum oxide.

3. Results

3.1. IR spectra

For several decades the structures and properties of crystalline forms of TeO_2 and binary and ternary tellurite glasses have been investigated using the IR and Raman spectroscopic techniques as central or complementary tools (see [6,7]-and references cited therein). For these glasses, the complex spectra are dominated by the strong bands produced by vibrations of the TeO_4 or TeO_3 basic structural units and by the polyhedra of several modifiers like MoO_3 and V_2O_5 [6,8,9]. In Figs. 1–4, we present a selected portion of our FTIR spectra for the complete series of

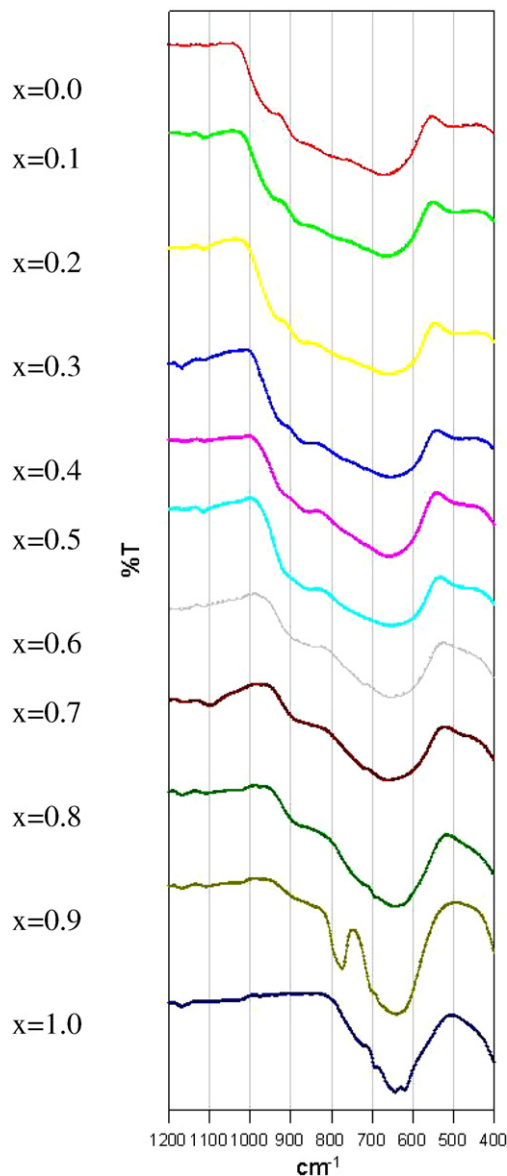


Fig. 1. IR spectra for $X\text{Ag}_2\text{O} \cdot (1-X)[0.5\text{V}_2\text{O}_5-0.5\text{MoO}_3] \cdot 2\text{TeO}_2$ systems.

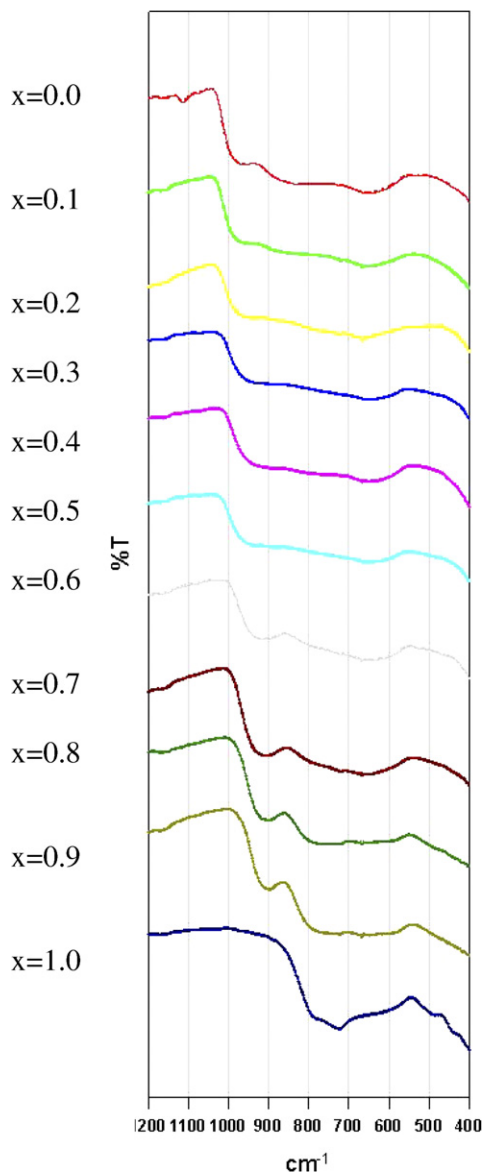


Fig. 2. IR spectra for $x\text{Li}_2\text{O} \cdot (1 - x)\text{V}_2\text{O}_5 \cdot 2\text{TeO}_2$ systems.

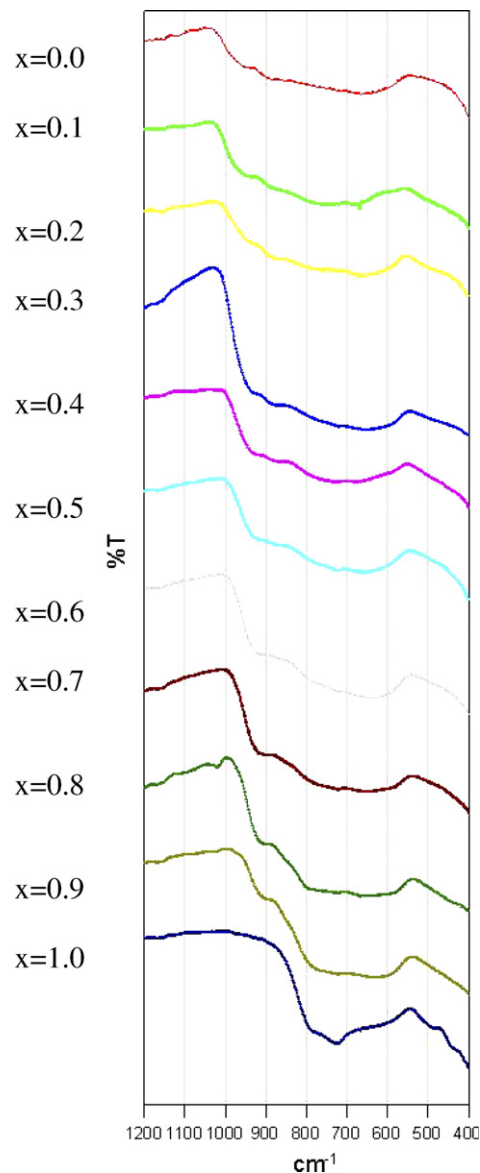


Fig. 3. IR spectra for $x\text{Li}_2\text{O} \cdot (1 - x)[0.5\text{V}_2\text{O}_5 - 0.5\text{MoO}_3] \cdot 2\text{TeO}_2$ systems.

compounds and, in Table 1 the positions and assignments of the principal features.

The IR spectra of the tellurite glass without Ag_2O ($X=0$) are similar to those of the $\text{MoO}_3 \cdot \text{TeO}_2$ mixtures with approximately 70 mol% of TeO_2 obtained by Dimitriev et al. [7]. This result suggests that the glassy structure depends greatly on the MoO_3 and TeO_2 components. Thus, the presence of a broad and intense band centered at 670 cm^{-1} (with a shoulder at 630 cm^{-1}) and the 793 cm^{-1} weak band indicates a structure built basically from slightly distorted TeO_3 groups, with minor proportion of TeO_4 groups [7,8].

As far as we know, the network-modifier MoO_3 , at the low concentrations used here, must be present as MoO_4 polyhedra and produce IR absorptions around $850\text{--}790\text{ cm}^{-1}$ [10]. We cannot assign these motions in the spec-

tra because the expected bands have been masked by stronger absorptions of the TeO_x and VO_4 .

According to the results obtained by Dimitriev et al. [7,11] and Krasowski et al. [12], the mid it bands appearing at 943 and 870 cm^{-1} must be assigned to symmetric and antisymmetric vibrations of two non-bridging V–O bonds of distorted VO_4 polyhedra. Moreover, in the upper tail of the 793 cm^{-1} band there appears a weak and broad shoulder, centered at *ca.* 820 cm^{-1} , assigned to the asymmetric stretching of V–O–V bridges formed of two corner-connected VO_4 groups. This observation suggests that vanadium does not mix homogeneously into the TeO_2 structure in the same way as MoO_3 does.

The paulatine continuous incorporation of Ag_2O or Li_2O into the tellurite glass produces progressive transformations in the IR spectra.

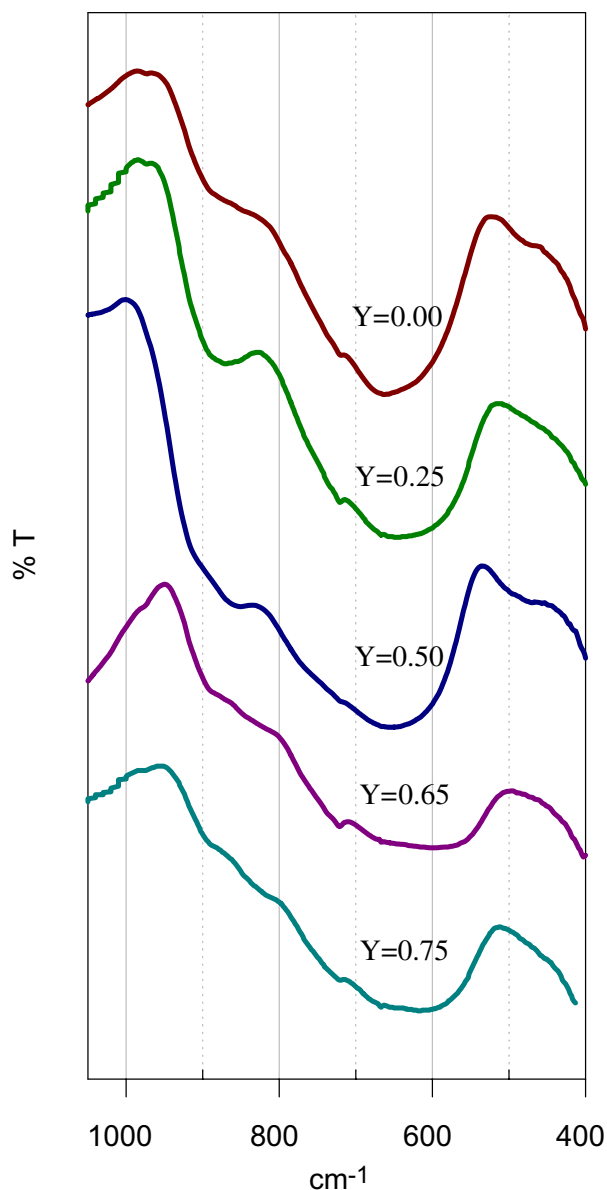


Fig. 4. IR spectra for $0.7\text{Ag}_2\text{O} \cdot 0.3[(1 - Y)0.5\text{V}_2\text{O}_5 - Y0.5\text{MoO}_3] \cdot 2\text{TeO}_2$ systems.

On the other hand, the effects of the new modifier become more intense for mixtures with greater than 25 mol% ($X = 0.5$). The IR spectra can then be grouped and analyzed into two composition zones, depending on Ag_2O or Li_2O concentrations: zone I and zone II. As was settled previously [1,2], the nature of electrical conductivity is electronic in zone I and ionic in zone II.

Due to the fact that the effect on the IR spectra is more pronounced with the addition of silver oxide, we shall start by analyzing the case of silver oxide and introducing the appropriate comments with reference to lithium oxide.

3.2.1. Zone I

The progressive addition of Ag_2O at amounts ranging from $X = 0.1$ to 0.4 gradually modifies the IR spectra, as can be seen from: (a) the strong intensity reductions of the 943 cm^{-1} and the loss of 820 cm^{-1} bands (the former also red shifted); (b) the small reduction of the intensity of the 878 cm^{-1} absorption; (c) the small displacement to lower frequencies of the bands centered at 670 and 793 cm^{-1} .

As can be expected, the intensity of the band at 943 cm^{-1} reflects principally the reduction in the proportion of V_2O_5 as the amount of Ag_2O in the glasses increases. Moreover, the band moves to lower frequencies and at the same time a very rapid disappearance of the band at 820 cm^{-1} is observed, suggesting a selective break of V–O–V bridges. The whole picture implies that silver cations interact principally with the VO_4 groups in the structure. The band at 870 cm^{-1} principally due to vibrations of the VO_4 groups remains almost unaltered in the spectra for the first steps of the series because, while the amount of modifier comes down, another band centered at 850 cm^{-1} grows in, owing to non-bridging Te–O bond stretching [7].

The small displacements of the 670 and 793 cm^{-1} bands to lower frequencies without change in their intensity, can be explained by considering that the glass structure becomes richer in the TeO_4 polyhedra, along with the reduction of the amount of V_2O_5 and MoO_3 network

Table 1
Band positions (cm^{-1}) in the FTIR spectra of studied glasses

Assignments	$\nu_s(\text{V-O}_2)\text{nb}$ (a)	$\nu_s(\text{Te-O})\text{nb}$ (b)	$\nu_{\text{as}}(\text{V-O}_2)\text{b}$ (a)	$\nu_{\text{as}}(\text{Te-O})\text{nb}$ (b) + $\nu(\text{Mo-O})$ (c)	$\nu_{\text{as}}(\text{V-O-V})$	$\nu(\text{Te-O})$ (d) + $\nu(\text{Mo-O})$ (c)	$\nu(\text{Te-O})$ (d)	$\nu(\text{Te-O-Mo})$
X								
0.0	943	–	870	–	(820)br	793	670	505
0.1	932	–	871	–	(820)br	795	661	503
0.2	929	–	865	–	–	780	661	497
0.3	919	–	863	–	–	775	662	493
0.4	920	–	854	–	–	767	660	489
0.5	–	907	–	850	–	762	653	481
0.6	–	891	–	851	–	763	653	–
0.7	–	878	–	845	–	740	620	–
0.8	–	875	–	846	–	727	622	–
0.9	–	(886)	–	847	–	701	621	–
1.0	–	–	–	–	–	772	619	–

nb: Non-bridging, (a) in VO_4 groups, (b) in TeO_4 groups, (c) in MoO_4 groups, (d) in TeO_3 or TeO_4 groups.

modifiers. The inverse effect was observed by Dimitriev et al. when pure TeO_2 samples were mixed with increasing amounts of the former oxides [6].

3.2.2. Zone II

The IR spectra of the mixtures with Ag_2O compositions ranging from $X = 0.5$ to 1.0 greatly change, specially for the Ag_2O richer mixtures.

As expected, there is a rapid reduction in the intensity of the 907 and 850 cm^{-1} bands, the VO_4 groups practically disappearing in the glassy structures from $X = 0.5$ to 0.8. Simultaneously, the band centered at 653 cm^{-1} moves to 622 cm^{-1} and becomes sharper, indicating the continuous increase in the proportion of TeO_4 groups present in the structure of the glasses [6,7].

The spectrum of the $X = 0.9$ mixture, with a sharp and intense band centered at 774 cm^{-1} is very similar to those obtained with crystalline TeO_2 and other crystalline tellurites [7]. This means that the V–Mo concentration may probably be insufficient to sustain the glassy structure and, consequently, the mixture partially crystallises.

When the metallic oxide is lithium oxide, the effect on the IR spectra is not as pronounced and the separation into two zones is not as evident as in the case of silver oxide either. By comparing the spectra and the intensity of the bands assigned to TeO_3 and TeO_4 groups, it appears that for the lithium based glasses the greater proportion corresponds to TeO_3 groups. In the case of the AgMoY system, we can affirm that the bands in the region from 950 to 800 cm^{-1} are due to vanadium groups. This is supported by the consequent diminution of the intensity with the augmentation of Y (the Mo fraction). Besides, due to the fact that the difference of the rest of the spectra is negligible – if it ever exists – we can conclude that the matrix structure strongly depends on the MoO_3 concentration.

3.2. DSC

In this section we compare the results obtained on Tg measurements [1–4]. In AgMoX and AgX systems we found a diminution of about 30 and 20% in Tg values, respectively. For lithium based glasses we found a diminution of about 10% in LiMoX systems and it remains almost constant in LiX systems. In the case of AgMoX where modifier oxide concentration remains fixed, Tg augments in about 10%.

We also found that silver oxide has the stronger effect on those changes on the network related to Tg. In fact, at any value of X , silver modified glasses have the lowest value on Tg when we compare them with lithium based oxides and this difference in Tg values augments as the value of X augments; then it can be said that silver oxide produces a higher bond-breaking depolymerization process. Addition of MoO_3 increases the cross-linking of the matrix with the concomitant augmentation of Tg. The effect is more pronounced for $X \leq 0.3$.

This effect is more evident in systems AgMoY where Tg augments with the incorporation of MoO_3 , even when the predominant effect is bond-breaking depolymerization process. Then it can be concluded that the addition of MoO_3 to TeO_2 causes a better vitrification process than V_2O_5 does.

3.3. X-ray diffraction analysis

The X-ray diffraction pattern for the systems under study confirms the amorphous nature of the samples except for $X = 0.9$ and $X = 1.0$ on AgX and AgMoX systems. As was pointed out in the previous paper [1] we have been unable to obtain the glass corresponding to $X = 0.9$ for AgX systems because of its tendency to form a second crystalline phase. However, we finally obtain an amorphous solid phase for this composition by remelting and further quenching the previously prepared ('crystalline') sample. During this procedure the original composition is maintained. This same procedure allows us to obtain $X = 0.9$ for AgMoX systems. Conductivity measurements [1,2] for both these samples, showed electrical conductivity values greater than those expected considering the isotherms of conductivity at any given temperature. After the thermal treatment produced during the conductivity measurements for AgX systems, the $X = 0.9$ sample showed a structural transformation, consisting of the silvering of the surface. SEM images reveal that the macroscopic aspect is accompanied by a spongiform aspect of the bulk. The corresponding diffractogram for this composition shows several incipient weak peaks indicating the existence of small crystalline phases. On the other hand, for AgMoX systems, this partial crystallization is absent in the diffractograms but, surprisingly, the corresponding IR spectrum indicates the existence of sharp lines which are compatible with the existence of zones with long range order or crystalline arrangement.

3.4. Density and molar volume

Fig. 5, shows the measurements of density. For the AgMoX systems, a 30% increment of density is verified when X increases, whereas this increment reaches 40% for the AgX systems. On the other hand, when the modifier is lithium oxide, density diminishes about 5% in systems of the form LiMoX , whereas for LiX systems it remains almost constant. These are the reasonable results taking into account the difference between molar masses of Ag_2O and Li_2O : silver oxide promotes a high increment in density due to the fact that its molar mass is greater than those corresponding to vanadium and molybdenum oxides. On the other hand the molar volume calculated as the ratio between molar mass and density allows the study of packing effect in an independent way of the mass effect of ions. These results are showed in Fig. 6. This figure shows that when the modifier oxide concentration augments at the expense of the former oxides V_2O_5 and $\text{V}_2\text{O}_5/\text{MoO}_3$ the

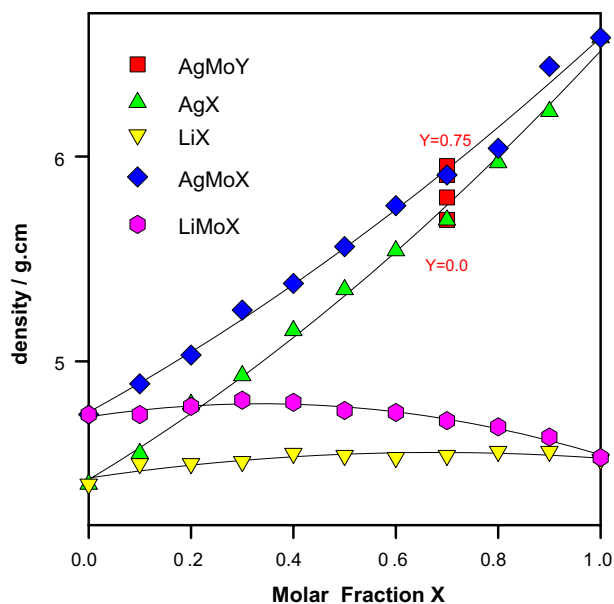


Fig. 5. Density as a function of X . At $X=0.7$, squares corresponds to AgMoY systems with $Y=0.75$ to $Y=0.00$ from top to below.

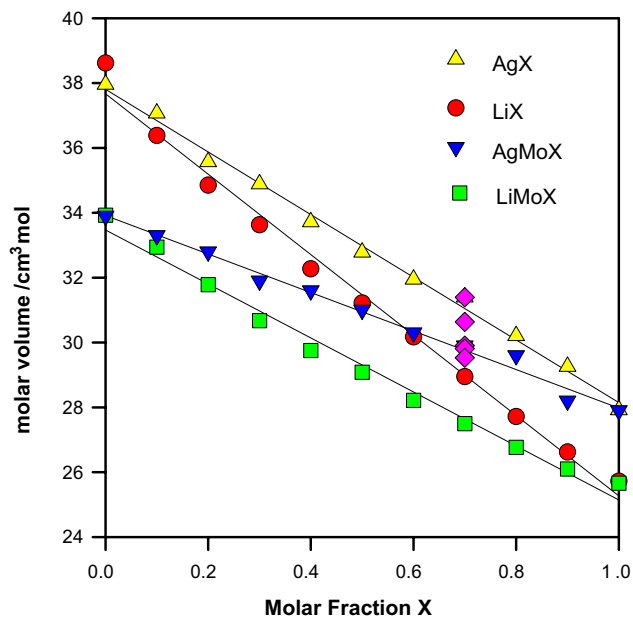


Fig. 6. Molar volume as a function of X . At $X=0.7$, diamonds corresponds to AgMoY systems with $Y=0.75$ to $Y=0.00$ from top to below.

V_m diminishes. This diminution is of about 10% for the AgMoX systems, 20% in the case of LiMoX and 30% for the case of LiX systems. Then the influence of the nature of the modifier as well as the presence of MoO_3 becomes evident. If we assume as suggested by Chowdari et al. [8] that this diminution in the molar volume suggests a diminution of free space in the structure, we can clearly conclude that lithium oxide promotes a more compact glassy matrix. This conclusion can also be achieved studying the

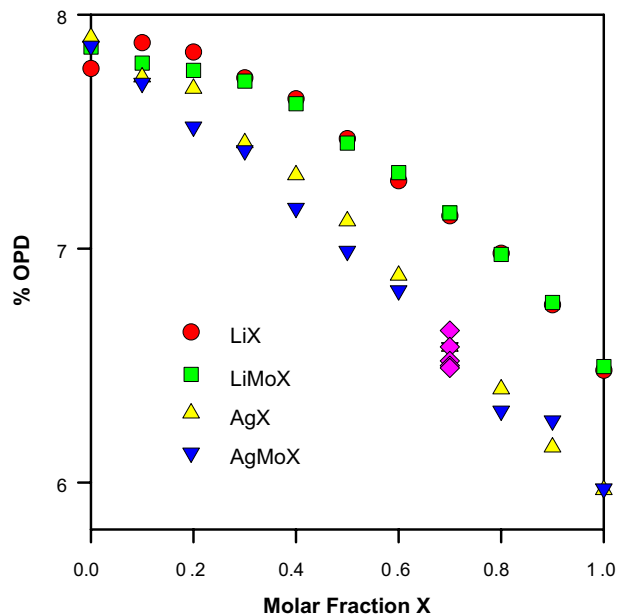


Fig. 7. The oxygen packing distribution (OPD) as a function of X . At $X=0.7$, diamonds corresponds to AgMoY systems with $Y=0.75$ to $Y=0.00$ from top to below.

OPD (the oxygen packing density) defined as the number of mole of oxygen atoms contained in 1 dm^3 of the system. The calculated OPD values as a function of X (shown in Fig. 7) indicates that lithium oxide modified the glassy matrix in a more strongly than silver oxide does. This experimental fact can be explained considering the cation size of the metallic oxide. In the present case we conclude that lithium cation promotes a more important cross-linking of the glassy matrix. This conclusion goes in the same direction as the one obtained by Sidebottan [13], who established that in the case of phosphate glasses the smaller cation radii promotes a re-polymerization of the glassy matrix. On AgMoY systems where the ratio $\text{V}_2\text{O}_5/\text{MoO}_3$ varies (*i.e.* the Ag_2O content remains constant) we observe an increment on V_m , and a diminution of the OPD. This diminution does not agree with the results obtained by Choudary.

4. Conclusions

The incorporation of metallic cations as Ag_2O and Li_2O , and of MoO_3 in a semiconducting glassy matrix of the form $\text{V}_2\text{O}_5 \cdot 2\text{TeO}_2$ leads to modifications on the structure, electrical and thermal properties. We show that the most important changes on the matrix are those promoted by the nature of the metallic oxides.

We find that lithium having a smaller radii than silver, increases the cross-linking of the network and acts as re-polymerization process.

The variation of the ratio V/Mo promotes better thermic properties (mainly those related to the T_g) with negligible changes – if any – on the ionic electrical conductivity.

Acknowledgements

Financial support by CONICET, CIC, Universidad Nacional del Sur, and FONCYT of Argentina is gratefully acknowledged. R.A.M. is a Research Fellow of the C.I.C. of Argentina. Thanks to Drs G. Mas and O. Pieroni for fruitful discussions leading to the completion of the X-ray and IR sections, respectively.

References

- [1] R.A. Montani, A. Lorente, M.A. Vincenzo, *Solid State Ionics* 130 (2000) 91.
- [2] R.A. Montani, S.E. Giusia, *Phys. Chem. Glasses* 42 (2001) 12.
- [3] R.A. Montani, M.A. Frechero, *Solid State Ionics* 158 (2003) 327.
- [4] R.A. Montani, M.A. Frechero, *Solid State Ionics* 177 (2006) 2911.
- [5] N. Lebrum, M. Levy, J.L. Souquet, *Solid State Ionics* 40 & 41 (1990) 718.
- [6] Y. Dimitriev, Y. Ianova, M. Dimitrova, E.D. Lefterova, P.V. Angelov, *J. Mater. Sci. Lett.* 19 (2000) 1513.
- [7] Y. Dimitriev, V.D. Dimitrov, M. Arnaudov, *J. Mater. Sci.* 18 (1983) 1353.
- [8] B.V.R. Chowdari, P.P. Kumari, *Solid State Ionics* 113–115 (1998) 665.
- [9] J. Zarzycki, *Glasses and the Vitreous State*, Cambridge University, 1991.
- [10] T. Minami, T. Katsuda, M. Tanaka, *J. Non-Cryst. Solids* 29 (1978) 389.
- [11] Y. Dimitriev, V.D. Dimitrov, M. Arnaudov, *J. Mater. Sci.* 14 (1979) 723.
- [12] Krasowski, J.E. Garbacz, M. Wasiucioneck, *Phys. Stat. Sol. A* 181 (2000) 157.
- [13] D.L. Sidebottom, *J. Phys.:Condens. Mat.* 15 (2003) S1585.