Journal of Optoelectronics and Advanced Materials Vol. 5, No. 1, March 2003, p. 185 - 190

FAST ION CONDUCTION IN SILVER MOLYBDENUM PHOSPHATE GLASSES

A. Latia*, C. Vancea

"Politehnica" University of Timisoara, Faculty of Industrial Chemistry,
Department of Science and Engineering of Oxidic Materials, Timisoara, Romania

Investigation of the transport phenomena in silver molybdenum phosphate glasses has revealed that the observed fast ionic transport is due to silver ions. The structure of these glasses, investigated using infrared spectra, shows that MoO_3 and P_2O_5 are the glass formers, the role of the last one being more important as the MoO_3 content decreases. The densities of the glasses, measured using the displacement method show that the addition of Ag_2O to the binary MoO_3-P_2O_5 system causes a constant increase in the density of the glasses. AC conductivity measurements of the glasses were conducted in open atmosphere from 5 Hz to 100 kHz by use of a HP 4142 impedance-meter in the temperature range of 303 - 423 K. The glasses exhibited high ion conductivities in the range of 10^{-4} to 10^{-1} Sm^{-1} at room temperature. The conductivities of the glasses increase and the activation energies of the conduction process decrease with the Ag_2O content. The total conductivity of the glasses was recorded using the two electrodes method. The investigated glasses have a very similar behavior in direct and alternative current, respectively, the activation energies being close. The obtained values for the transport number, very close to unity, shows that the Ag^+ ions are the charge carriers in these glasses, the contribution of the electronic conductivity being negligible.

(Received August 2, 2002; accepted March 12, 2003)

Keywords: Superionic glass, Solid state ionics, Glass structure

1. Introduction

The electric conduction is divided into two categories: electronic and ionic conduction. The electronic conduction, basis of the "electronics" in the modern age, consists in the movement of electrons or positive holes in a semiconducting material. The term was born with the invention of transistor, which resulted in the change in the field of electron movement from gas (in the vacuum tube) to solid (in the transistor).

The ionic conduction is characteristic to the liquid electrolytes, since ions are very heavy and large in volume compared with the electrons and thus the movement of ions is usually very difficult in solids. The structural requirements are essential for ion movement in solid materials. Three types of such requirements are well known:

- the introduction of lattice defects, observed in stabilized zirconia,
- the special structure like layered structure in β-Al_2O_3,
- the averaged structure in α-AgI.

These conditions are identified in crystalline solids. We can expect that glasses, having random structure and thus much open space, show higher ion conductivities than crystals. The fast ion conduction in solid materials, crystalline or glass, is the basis for solid state "ionics" [1].

In this paper we are concerned with glasses in the ternary system xAg_2O-$(80-x)MoO_3$-$20P_2O_5$ (x = 10, 20, 30 and 40 mol%). Infrared spectra, conductivities and transport number of charge carriers are studied.

* Corresponding author: latia@banat.ro

2. Experimental

The investigated glasses having the compositions presented in table 1 were synthesized from raw materials: $AgNO_3$, H_2MoO_4 and $NH_4H_2PO_4$ using the standard procedure, in the dark.

Table 1. Composition of the investigated glasses and their densities.

Sample no.		P_0	P_1	P_2	P_3	P_4
Composition (mol %)	Ag_2O	0	10	20	30	40
	P_2O_5	20	20	20	20	20
	MoO_3	80	70	60	50	40
Densities (g/cm^3)		3,678	3,854	3,944	4,251	4,692

The raw materials weighed to the desired compositions were mixed and ground in a mortar. The mixture was melted at 950° C for 40 minutes in closed porcelain crucibles using an electric furnace and then rapidly quenched between two stainless steel plates. Infrared spectra were recorded on P_0, P_2 and P_4 samples with 0,5 wt% pulverized sample in 99,5 wt% KBr, using a Perkin-Elmer IR spectro-photometer. The ionic conductivity was measured using silver sputtered electrodes with an HP 4142 impedance-meter in a frequency range form 5 Hz to 100 kHz. The total conductivity of the glasses was recorded using the two electrodes method with graphite as electrodes. The densities of the glasses were measured using the displacement method with isopropanol as working liquid.

3. Results and discussion

3.1 Infrared absorption studies

Vibrational infrared spectroscopy is used as an analytical probe to elucidate the structural elements of the glass formers, which are assumed to be responsible for the variation in ionic conductivity with composition. Even though, there is no way of implicating the structure directly from the recorded spectra, it just provides some clues to the structural aspects of the solid electrolytes. Fig. 1 shows the IR spectra for the xAg_2O-(80-x)MoO_3-$20P_2O_5$ (x = 0, 20 and 40 mol%). The vibrational frequencies are grouped together on the basis of visual judgment of their position implying a common origin. Significant changes occur in both intensities and band shapes as a function of composition.

For the binary $MoO_3 – P_2O_5$ glass spectra shows a peak at 1034 cm^{-1}, assigned to the $\nu_s(PO_3)$ terminal groups [2]. The bands at 985 cm^{-1} and 783 cm^{-1} are assigned to the υ_1 and υ_3 stretching vibrations of the MoO_4^{2-} anions [3]. The peak at 664 cm^{-1} is assigned to the infrared active υ_3 mode of MoO_6^{6-} molybdate octahedral that can result from a disproportionation of MoO_4^{2-} tetrahedral such as [3]:

$$5MoO_4^{2-} \Leftrightarrow MoO_6^{6-} + 2Mo_2O_7^{2-} \quad (1)$$

The introduction of Ag_2O in the glass by lowering the MoO_3 content influences the glass structure. The glass network is formed not only by Mo-O-Mo bridges, but also by P-O-P bridges, as it is shown by the presence of the peaks at 932 cm^{-1} (P_2) and 907 cm^{-1} (P_4) for $\boldsymbol{\nu}_{as}$(P-O-P) and 708 cm^{-1} (P_2) and 705 cm^{-1} (P_4) for ν_s(P-O-P) vibrations. The intensity of both symmetrical and asymmetrical peaks increases at higher Ag_2O contents. The υ_{as}(Mo-O-Mo) is shifted to lower wavenumbers compared to the binary glass sample (633 cm^{-1} for P_2 and 611 cm^{-1} for P_4). The strong peak at 534 cm^{-1} for the P_4 glass sample can be assigned to the $\nu_4(PO_4^{3-})$ vibration mode for the [PO_4] tetrahedral units.

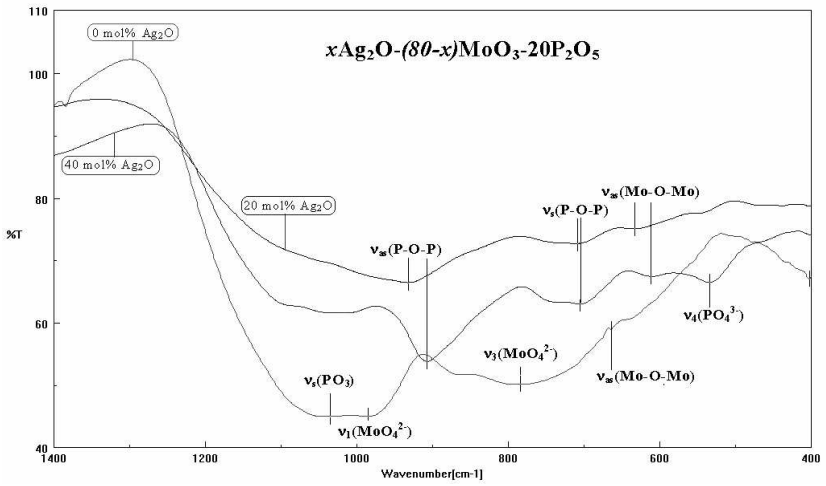

Fig. 1. Infrared spectra in KBr pellets of the glasses containing x = 0, 20 and 40 mol % Ag_2O.

The above results lead to the conclusion that the decrease of MoO_3 content increases the importance of phosphor as glass former. The IR spectra show the presence of Mo-O-Mo and P-O-P structural bridges, but no mixed Mo-O-P bonds can be identified.

3.2 Density measurements

The densities of the glasses were measured using the displacement method with isopropanol as working liquid.

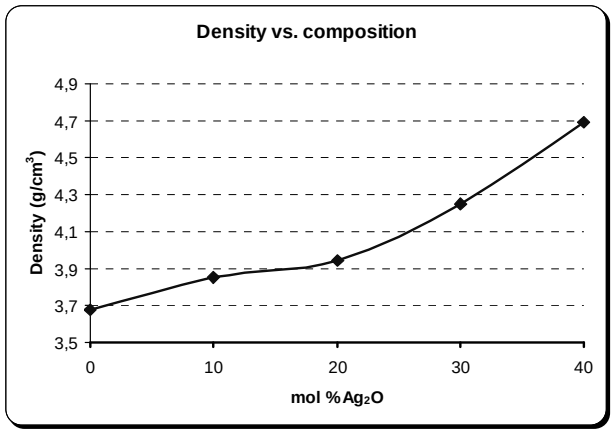

Fig. 2. The influence of the composition upon the density of the glass samples.

As it is shown in Fig. 2, the addition of Ag_2O to the binary MoO_3-P_2O_5 system causes a constant increase in the density of the glasses.

3.3 Ionic conductivity measurements

Fig. 3 shows the complex impedance plots for the glass $20Ag_2O$-$60MoO_3$-$20P_2O_5$ as an example at various temperatures.

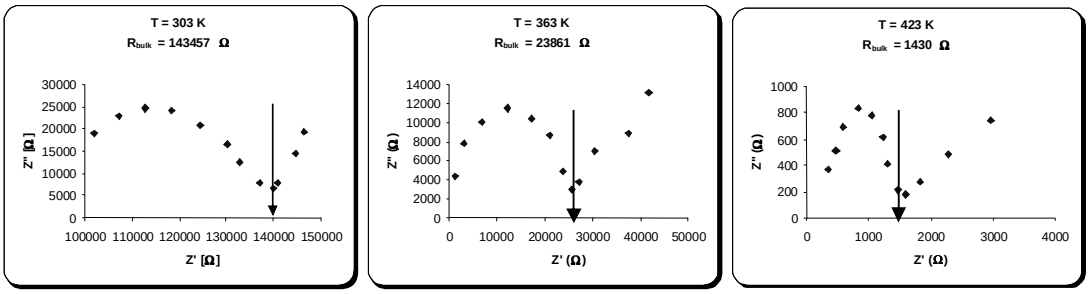

Fig. 3. Complex impedance plots for the determination of conductivities at various temperatures for the glass: $20Ag_2O$-$60MoO_3$-$20P_2O_5$.

The bulk impedance is attributed to the semicircle observed at each temperature, and thus the bulk resistance is identified as the intersection point of the semicircle with the real axis. Similar results were obtained for the other glasses.

Fig. 4 shows the temperature dependence of conductivity for all the glasses in the investigated system.

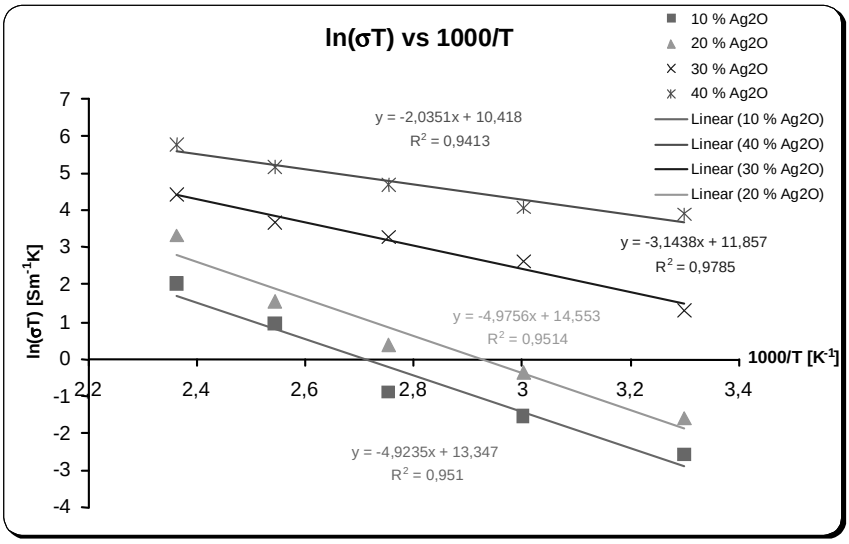

Fig. 4. Temperature dependence of the conductivities of the investigated glasses.

The lines fit the Arrhenius type equation:

$$\sigma T = \sigma_0 e^{-\frac{E_a}{kT}} \tag{1}$$

where T is the absolute temperature, σ_0 the pre-exponential factor, E_a the activation energy for the conduction process and k the Boltzmann constant.

The values of the impedance for the binary glass $80MoO_3$-$20P_2O_5$ were over the impedance-meter scale and therefore cannot be measured. This glass exhibits only electronic conduction, due to the transition of electrons between the Mo^{5+} and Mo^{6+} ions.

Fig. 5 shows the composition dependence of the conductivities at three different temperatures and the activation energy, calculated from equation 1.

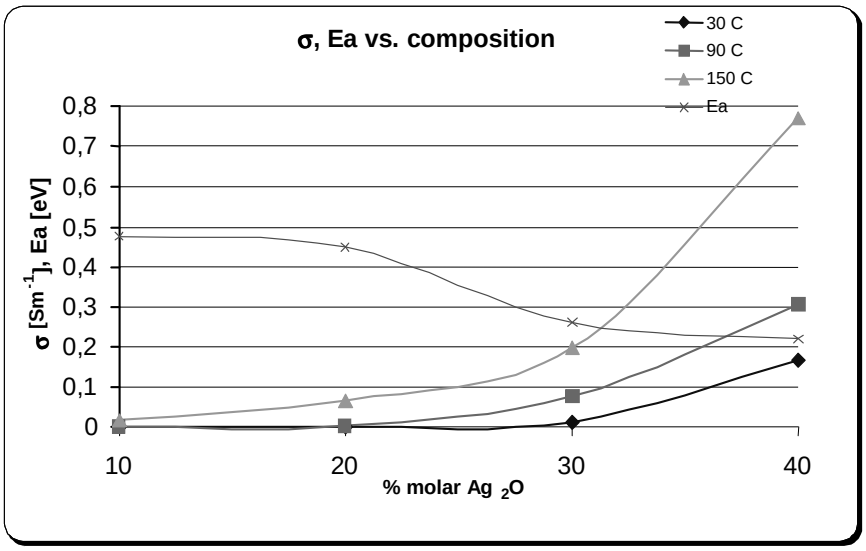

Fig. 5. The composition dependence of the conductivities at 30°C, 90°C and 150°C and the activation energies of the conduction process respectively.

The conductivity of the investigated glasses presents a small increase at lower Ag_2O amounts (P_1 and P_2) and then a more important increase, especially in the last sample, containing 40 mol % Ag_2O. The explanation of this evolution for the conductivity is based on the glass structure. The conduction process is realized by the Ag^+ ions movement across the conduction pathways. At lower MoO_3 contents the structure is more opened and, therefore, a larger number of such pathways exist. The evolution of the activation energy with composition sustains the pathway conduction mechanism.

3.4 DC conductivity measurements

The global conductivity of the investigated glasses was measured in DC current using a standard two electrodes procedure. The electrical conductivities and the activation energies are presented in table 2, compared to the similar AC measurements.

The DC conductivities reflect both the electronic and ionic conduction in the glass. The importance of the ionic conduction upon the total conduction is expressed by the transport number [4]:

$$t = \frac{\sigma_{AC}}{\sigma_{global}} = \frac{\sigma_{AC}}{\sigma_{DC}} \tag{2}$$

Table 2. Electrical parameters for the DC and AC measurements for the xAg_2O-$(80-x)MoO_3$-$20P_2O_5$ glasses.

x (mol %)	Electrical parameters for the DC conduction		Electrical parameters for the AC conduction		Transport number (t) at 303K
	σ_{DC} at 303K	E_a [eV]	σ_{AC} at 303K	E_a [eV]	
0	*	0.581	-	-	-
10	0.00025	0.478	0.000248	0.474	0.992
20	0.00066	0.462	0.000657	0.448	0.995455
30	0.012379	0.271	0.012338	0.262	0.996688
40	0.166276	0.225	0.165895	0.220	0.997709

* The conductivity of the binary glass was under the measurement range.

The values of the transport number, very close to unity shows the major contribution of the ionic conductivity in these glasses. The electronic contribution is negligible; Ag^+ ions moving through the conduction pathways are the charge carriers for the conduction process.

4. Conclusions

The xAg_2O-$(80-x)MoO_3$-$20P_2O_5$ glasses can be considered as fast ion conductors, having Ag^+ ions as charge carriers. The conductivity in these glasses increases with the Ag_2O amount, due to the increase of the number and length of the conduction pathways in the structure. The glass formers are MoO_3 and P_2O_5. The role of the last one is more important as the MoO_3 content decreases. The IR spectra show only the presence of Mo-O-Mo and P-O-P structural bridges, no mixed Mo-O-P bonds can be identified. The composition and, therefore, the structure of the glasses have a very important effect upon the conduction.

The high conduction values of 0.16 S/m at 303 K and low activation energies of 0.22 eV along with a very small electronic contribution to the total conduction suggests the possible application of these electrolytes in solid state ionic devices.

References

[1] T. Minami, Bulletin of the Institute for Chemical Research, Kyoto University **72**, 305 (1994).
[2] P. Znasic, M. Jamnicky, Journal of Non-Crystalline Solids **146**, 74 (1992).
[3] C. P. Varsamis, E. I. Kamistos, N. Machida, T. Minami, J. Physics and Chemistry Bulletin **101**, 3734 (1997).
[4] T. Minami, Journal of American Ceramic Society **71**, 784 (1985).