JOURNAL OF SOLID STATE CHEMISTRY 45, 309–316 (1982)

Ionic Conductivity of and Raman Spectroscopy Investigation in Binary Oxosalts $(1 - x)AgPO_3$–xAg_2SO_4 Glasses

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Received April 1, 1982; in revised form June 21, 1982

$(1 - x)AgPO_3$–xAg_2SO_4 homogeneous glasses obtained by quenching of a melt of the two salts are pure ionic Ag^+ conductors. The RT conductivity is increased from 2.5×10^{-7} to 4×10^{-6} $(\Omega\ cm)^{-1}$ when the ratio of Ag_2SO_4 is increased from 0 to 0.3. Raman spectroscopy shows that no modifications of the $(PO_3)\infty$ chain skeleton occur by adding Ag_2SO_4. The low-frequency Raman band lying at about 55 cm^{-1} is quantitatively correlated to Ag^+ oscillations, the hopping distance decreasing from 3.0 to 2.7 Å if a jump process between regular Ag^+ sites is considered.

1. Introduction

The use of glassy solid electrolytes in electrochemical devices presents many fundamental as well as technological advantages. Generally vitreous materials have a poor electrical conductivity so they are of restricted practical interest. Kunze (*1*) was the first to find a vitreous superionic conductor at room temperature. Some similar materials have been discovered, and many of them are silver conductors and contain AgI (*2–6*). Studies carried out in the laboratory on solid vitreous electrolytes with silver metaphosphate have shown that it is possible to obtain glasses with a high ionic conductivity over a large composition domain by "dissolution" of the silver halide in a support glass having a low ionic conductivity (*7, 8*).

The substitution of AgX by Ag_2SO_4 was carried out to make a better definition of the parameters which govern conductivity variations in this type of material. In this paper we will analyze, within the glass formation region, the structural and electrical properties of the pseudobinary $AgPO_3$–Ag_2SO_4 system. The results will be compared with the $AgPO_3$–Ag_2O glasses.

2. Experimental

2.1 Glass preparation. The $(1 - x)$ $AgPO_3$–xAg_2SO_4 glasses were prepared by melting, followed by a quenching of silver sulfate and silver metaphosphate mixtures; the silver metaphosphate preparation is described elsewhere (*2*). Fusion was carried out at a temperature close to 700°C in silica tubes sealed under primary vacuum. The melts were repeatedly stirred and kept at 700°C for an hour before being rapidly brought to room temperature. The samples of glasses are obtained in the form of cylinders ($\theta \simeq 10$ mm and $e \simeq 5$ mm) and are then annealed at 150°C, about 10–30°C lower than the glass transition temperature T_g determined by DTA.

0022-4596/82/150309-08$02.00/0

The extent of the glass-forming range was determined by X-ray diffraction patterns, which were nearly structureless; it corresponds to a molar ratio x less than 0.3; for higher Ag_2SO_4 concentrations ($x > 0.3$) an inhomogeneous system appears in which Ag_2SO_4 microcrystals are dispersed in the saturated glass.

2.2 Electrical measurements. Electrical measurements were usually performed on molded disks covered with evaporated silver or sputtered platinum. The total conductivity was determined under nitrogen atmosphere using a symmetric Ag/glass/Ag cell. Most of the dc-conductivity data were obtained by complex plane analysis in the frequency range 10^2–10^5 Hz (*9, 10*). A dissymmetric Ag/glass/Pt cell was used for the electronic conductivity measurements by Wagner's polarization technique (*11*). A potential E lower than the decomposition potential of the electrolyte (Δe) is applied to this cell, the platinum electrode acting as "blocking" electrode.

2.3 Raman spectroscopy investigation. The Raman experiments were performed with a 90° scattering geometry and the 514.5-nm line of a vertically polarized Ar^+ laser; the laser power was limited to 100 mW on the sample, the scattered light being analyzed by a double holographic grating of a Jobin Yvon HG 25 spectrometer. The polarization measurements were obtained from the intensities of the Stokes Raman lines in the I_{VH} and I_{VV} configurations ($\rho = I_{VH}/I_{VV}$).

The spectra shown in this paper are the reduced spectra I_R obtained from I_{VV} spectra by the transformation $I_R = \omega I_{VV}/(1 + n)$, where n is the Bose–Einstein term $1/[\exp(\hbar\omega/kT) - 1]$ (*12*). This reduced form is particularly convenient to compare low-frequency spectra at different temperatures because the thermal occupation is eliminated so that the reduced intensity can be related to the density of vibrational states and allows quantitative correlations.

Raman line profiles were fitted by mathematical procedures; we used a Lorentz function modulated by a sinusoidal term,

$$I(\bar{\nu}) = B[\cos \Pi(\bar{\nu} - \bar{\nu}_0)/a]^n \cdot K^2/[K^2 + (\bar{\nu} - \bar{\nu}_0)^2],$$

where B is the maximum amplitude, a is the line foot broadness, $\bar{\nu}_0$ is the maximum frequency, and K the half-width of the Lorentz term. These fittings allow one to display the components of a dissymmetric broad band with the integrated areas A of each of them.

3. Electrical Properties

The Arrhenius plot of the conductivity versus the inverse of temperature for different composition glasses is shown in Fig. 1. In the 25–140°C range the conductivity follows an Arrhenius relation $\sigma = \sigma_0 \exp(-E_c/RT)$. Both σ conductivity and E_c activation energy are strongly dependent on the Ag_2SO_4 ratio: the conductivity is increased with x, the higher value being obtained for

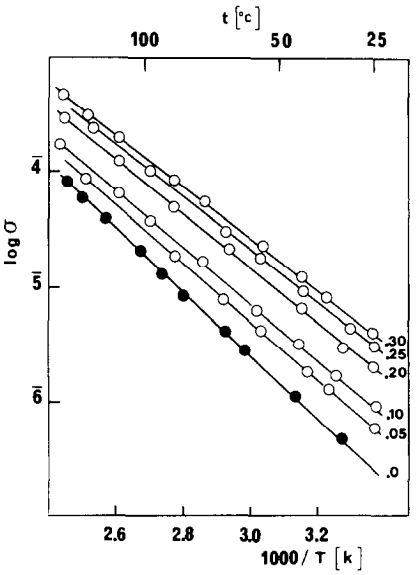

FIG. 1. Temperature dependence of the conductivity $\sigma(\Omega^{-1} \cdot cm^{-1})$ of $(1 - x)AgPO_3$–xAg_2SO_4 glasses.

the saturated glass ($x = 0.3$) ($\sigma = 4 \times 10^{-6}$ Ω^{-1} cm^{-1} at 25°C); for this composition, the activation energy has a minimum value of ≃10 kcal/mole. On the other hand, the pre-exponential term σ_0 remains nearly constant, so the activation energy governs the whole conductivity.

The electronic conductivity value is very low, about 2×10^{-10} Ω^{-1} cm^{-1} at 25°C; so the conduction is of an ionic nature and essentially ensured by Ag^+ cations. The voltage stability window determined by cyclic voltammograms is 1 V, and is limited by the couples O^{2-}/O_2 and Ag^+/Ag.

The dissolution of Ag_2SO_4 in $AgPO_3$ glass gives a large improvement of the ionic conductivity of the host glass; for example, at 25°C, it is 16 times greater for the saturated glass. To display this enhancement, the $\sigma_{25°C}$ dependence on composition is shown in Fig. 2, where, for comparison, the curves we have drawn for $AgPO_3$–Ag_2O glasses are reported (*13, 14*). It must be noticed that the conductivity has the same value for either Ag_2O or Ag_2SO_4 at the same concentrations. There is no linear relation between log σ and x ratio as in $AgPO_3$–AgX glasses.

The conductivity seems to be independent of the nature of the silver solute (oxide or sulfate): this behavior, which has been already observed for other glasses (*15, 16*), suggests that the sulfate anions are inserted in the same way as the oxide ions in the network. For this reason, we looked at whether there are real structural similarities between these two kinds of glasses; this investigation was performed by *in situ* Raman spectroscopy.

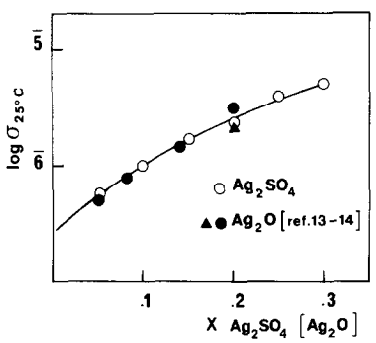

FIG. 2. Composition dependence of $\sigma_{25°C}$ ($\Omega^{-1} \cdot$ cm^{-1}) in Ag_2PO_3–$AgSO_4$ and $AgPO_3$–Ag_2O glasses.

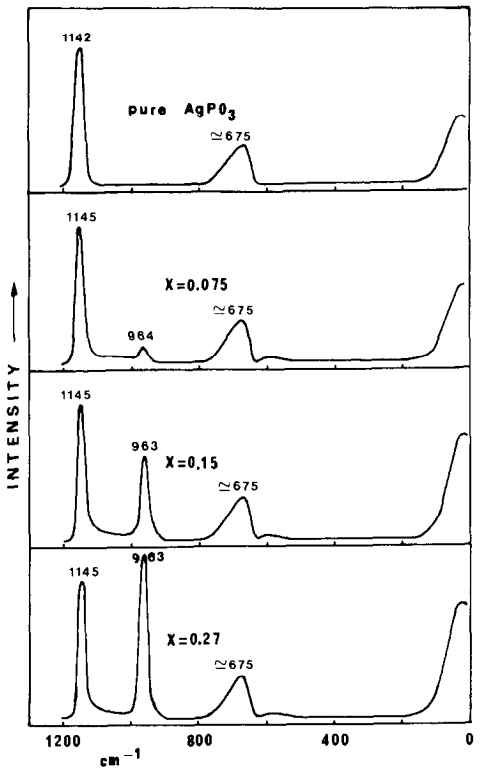

FIG. 3. Raman spectra of $(1 - x)AgPO_3$–(x) Ag_2SO_4 glasses.

4. Raman Investigations

4.1. Assignments of the High-Frequency Spectra ($\bar{\nu} > 200$ cm^{-1})

The following discussion is limited to the three bands appearing very distinctly at about 700, 965, and 1140 cm^{-1} (Fig. 3); some other broad and weak bands can also be observed but they are not interesting for our purpose. The polarization measurements ($\rho = I_{VH}/I_{VV}$) show that these three main bands are very polarized ($\rho < 0.1$) and thus correspond to the symmetric modes of

high-symmetry species (SO_4 and PO_4 tetrahedra). The reference spectra are indeed those of the Ag_2SO_4 and $AgPO_3$ crystalline compounds.

—Polycrystalline Ag_2SO_4 is characterized by one sharp and strong line at 975 cm^{-1} (ν_1SO_4) and three weaker lines at 1180 cm^{-1} (ν_3SO_4), 600 cm^{-1} (ν_2SO_4), and 450 cm^{-1} (ν_4SO_4).

—The infinite chains $(PO_3)_n$ in crystalline $AgPO_3$ (*17*) give rise to two strong lines at 1150 cm^{-1} (ν_3PO_2) and 720 cm^{-1} (ν_sP–O–P) and also to weaker bands.

In $AgPO_3$ glass, two bands are predominant in the Raman spectrum; the 1145-cm^{-1} band is sharp (half-width $\simeq$ 15 cm^{-1}) and is related to the PO_2 stretching mode, while the 720-cm^{-1} band is very broad and dissymmetric; this dissymmetry probably arises from twisted or balled chains, the skeleton POP mode being very sensitive to the configuration of successive linked PO_4 tetrahedra. It must be underlined that this $AgPO_3$ glass spectrum is very similar to that of the MPO_3 alkaline glass (M = Na, Li) (*18–21*), the substitution of cations only giving rise to small frequency shifts of the ν_sPO_2 mode at about 1150 cm^{-1}, which increases when smaller cations are replacing larger ones.

In $AgPO_3$–Ag_2SO_4 glasses, the band at 965 cm^{-1} can be related to the symmetric SO_4 mode. At first sight, it seems there are only a superposition of PO_3 and SO_4 modes without noticeable interactions between them; in particular, the spectrum of the $AgPO_3$ network glass is not modified by Ag_2SO_4 addition since only the intensity enhancement of the SO_4 mode at 965 cm^{-1} can be observed; there is no modification in the half-width and the frequency of this mode for different SO_4 ratios (Table I). The areas of the whole PO_2 and POP bands nearly remain in the same ratio ($A_{PO_2}/A_{POP} \simeq 1.2$) within the glassy range; however, a sharp analysis of their profiles shows the appearance of a shoulder at 1135 cm^{-1} within the ν_sPO_2 band and an increase of the lower-frequency component (675 cm^{-1}) intensity for the ν_sPOP band; the respective areas of the components for these bands are reported in Table I along with their frequencies and half-widths. We are not able, at this time, to give detailed explanations upon these slight perturbations in the structure of $(PO_3)_n$ bands. Nevertheless, this description leads to the assumption that the mixed glasses are built with very long PO_3 chains and SO_4 groups inserted between them. To confirm this hypothesis, we compared these spectra to those of $(1 - x)AgPO_3$–xAg_2SO_4 glasses.

The insertion of Ag_2O in $AgPO_3$ glass gives major modifications in the Raman spectra which are already evident for x = 0.1 (Fig. 4). Two new strong lines appear at

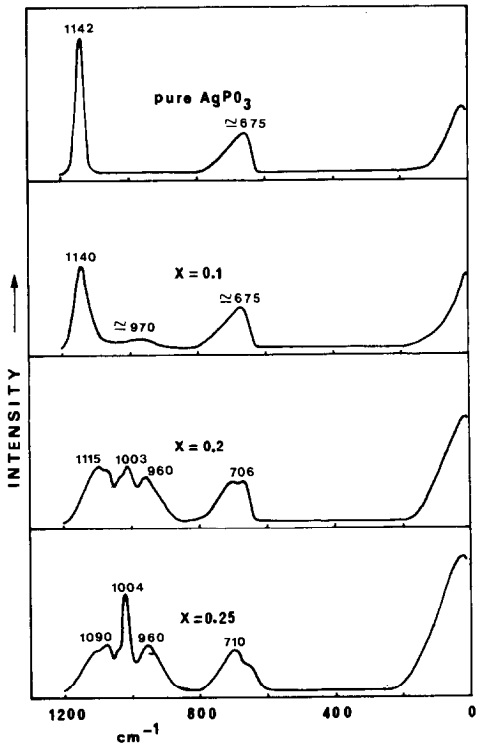

FIG. 4. Raman spectra of $(1 - x)AgPO_3$–$(x)Ag_2O$ glasses.

TABLE I

FREQUENCIES ($\bar{\nu}$), HALF-WIDTHS ($\Delta\bar{\nu}_{1/2}$), AND AREAS RATIO (Av_i/Av_j) OF THE THREE MAIN RAMAN BANDS IN $AgPO_3$–Ag_2SO_4 SYSTEM

	$\nu_s PO_2$ (cm^{-1})					$\nu_s SO_4^2$ (cm^{-1})		$\nu_s POP$ (cm^{-1})					
x	ν_1	$\Delta\bar{\nu}_{1/2}$	ν_2	$\Delta\bar{\nu}_{1/2}$	A_{ν_2}/A_{ν_1}	ν	$\Delta\bar{\nu}_{1/2}$	ν_3	$\Delta\bar{\nu}_{1/2}$	ν_4	$\Delta\bar{\nu}_{1/2}$	A_{ν_3}/A_{ν_4}	Observations
0	1139	6								711	7		$AgPo_3$ polycrystalline
0	1142	16			0			676	37	708	70	0.625	$AgPO_3$ glass
0.075	1145	16	1133	28	0.75	964	20	676	37	707	69	0.71	
0.15	1145	13	1132	28	0.95	963	20	676	34	708	56	1.08	
0.225	1144	14	1132	29	1.02	964	20	674	35	706	69	1.25	
0.3	1144	13	1134	28	1.10	965	19	677	35	710	59	1.40	Vitreous domain limit
0.5	1145	13,5	1134	26.5	1.20	968	17	680	36.5	710	56	1.50	Inhomogeneous glass
1						970	12						Polycrystalline Ag_2SO_4

1004 and 960 cm^{-1} in these glasses along with the splitting of the clump around 720 cm^{-1} into two components; the 710-cm^{-1} one becomes predominant at the limit of the glass homogeneity ($x = 0.25$), which corresponds to the $Ag_5P_3O_{10}$ formulation.

There are many similarities between the Raman spectra of the $x = 0.25$ glass and of $Na_5P_3O_{10}$ crystalline compound that we have recorded. Thus it is clear that short $P_3O_{10}^{5-}$ species are present in this glass, the appearance of shoulders at 1115 cm^{-1} ($\nu_s PO_2$) and 690 cm^{-1} (ν_sPOP) showing that slightly longer chains are mixed with these short ones. The disappearance of the original line at 1145 cm^{-1}, specific of very long chains, is a good test for their absence and for their breakdown in shorter ones (*22*). Consequently, the chains are broken when the Ag_2O ratio increases, the formation of PO_3 terminal groups being easily proved by the appearance of the line at 1004 cm^{-1} ($\nu_s PO_3$).

The $AgPO_3$–Ag_2SO_4 glasses and the Ag PO_3–Ag_2O glasses have very different structural features. We are sure that neither P–OSO_3 terminal groups nor S–O–S or P–O–S bridges are present in the glasses. SO_3 terminal groups are indeed revealed by a line at 1070 cm^{-1} (*23*) and SO_2 groups give rise to a line at 1270 cm^{-1} (*24*) ($\nu_s SO_2$); none of these modes appears in the Raman spectra.

Thus these $AgPO_3$–Ag_2SO_4 glasses are built from a network of distorted $(PO_3)_n^{n-}$ polyanions, tetrahedral SO_4^{2-} ions, and from Ag^+ cations necessarily coordinated to oxygen atoms of both PO_2 groups and SO_4 ions. We could think that the slight modification in the profile of the $\nu_s PO_2$ band associated to the appearance of the 1135-cm^{-1} component results from a distortion of the O---Ag interactions.

The profile of the SO_4^{2-} ion band at 965 cm^{-1} is not modified by their concentration in the glass. Its integrated intensity A_{SO_4} could be used as an internal standard of SO_4^{2-} species concentration since, as shown in Fig. 5, it rises linearly with the SO_4 concentration. The sum of the areas A_{PO_2} and A_{POP} is a good standard also of the PO_3 concentration. We will use this sum, noted A_{PO_3}, as the internal reference in the following quantitative study in which we shall explain the variations of the very low frequency band intensity versus the Ag_2SO_4 ratio; in particular the A_{SO_4} intensity cannot be used for the pure host glass.

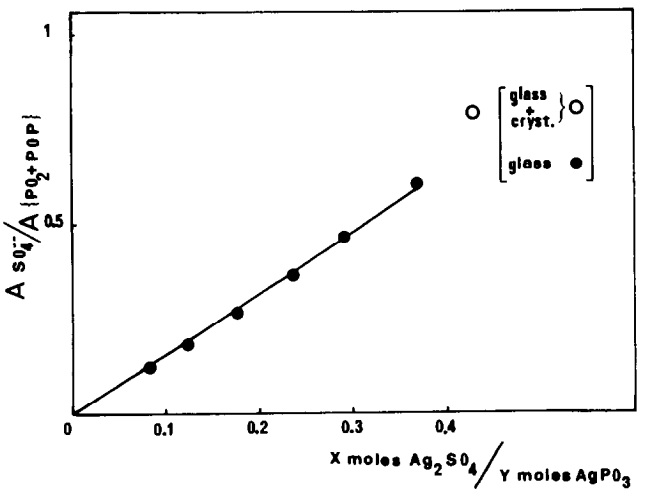

FIG. 5. Linear relationship between the $\nu_1 SO_4$ band intensity and the molar ratio $Ag_2SO_4/AgPO_3$.

4.2. *Characteristics of the Low-Frequency Range* ($\bar{\nu} < 200\ cm^{-1}$)

The reduced spectra (Ir) below 200 cm^{-1} are shown in Fig. 6 with respect to a fixed A_{PO_3} value and for different Ag_2SO_4 ratios. There is a dissymmetric broad band centered at about 55 cm^{-1} and weakly polarized ($\rho \simeq 0.5$) and which is not shifted with x ratio. Its intensity is increasing with the Ag_2SO_4 concentration; the area calculations of this band compared with A_{PO_3} and A_{SO_4} standards allow us to determine that the intensity follows exactly the ratio $(Ag^+)/(PO_3)$; when we report in a plot (Fig. 7) the respective areas ($A_{55\ cm^{-1}}/A_{PO_3}$) versus the fraction $(Ag)/(PO_3)$, the points are aligned near a straight line. This quantitative correlation is a good proof that the low-frequency band is essentially related to Ag^+ oscillations in their potential wells.

In $AgPO_3$–Ag_2O glasses, the intensity of the observed band remains also nearly constant when it is compared to the same Ag^+ concentration. As we have previously seen, there are short chains in these glasses, so many variations in the spectra would be expected if librational modes of these units were the source of this Raman band.

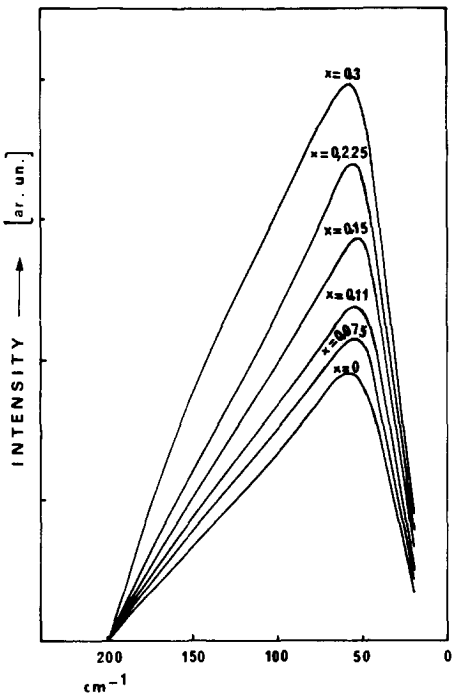

FIG. 6. Low-frequency Raman spectra of $(1 - x)AgPO_3$–$(x)Ag_2SO_4$ glasses.

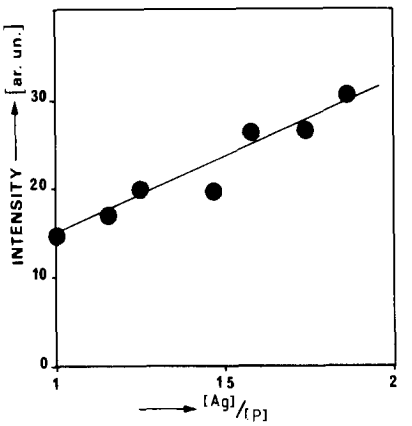

FIG. 7. Linear dependence of the low-frequency Raman band intensity with molar ratio Ag/P for $(1 - x)AgPO_3$–xAg_2SO_4 glasses.

A qualitative explanation of the assignment of this low-frequency band to cation oscillations rather than to librational modes of the PO_3 chains will be discussed in a future paper (*25*), in which the dependence of both frequency and intensity of this band will be discussed with respect to the molar fraction Ag/Na in mixed (Ag–Na) cation phosphate glasses.

4.3. *Raman Conclusions*

The qualitative and quantitative arguments we are going to expand lead us to think that this low-frequency band reflects oscillation modes of Ag^+ cations inside their oxygen cages (probably AgO_4 or AgO_5) and that the attempt-frequency mode lies inside this clump. If we suppose a sinusoidal potential with Ag^+ sites at a mean distance d, the activation energy E_c for a hopping process is given by the relation $E_c = 2\Pi d^2\bar{\nu}^2c^2$ (*26*). But this d value is not known, so we may calculate it by a choice of $\bar{\nu}$ and E_c; a mean length jump of 3 Å is

thus obtained with $\bar{\nu} = 55$ cm^{-1} and $E_c = 12.7$ kcal · mole^{-1}, for glassy $AgPO_3$; it must be noticed that this distance is close to the site-to-site distance between two Ag^+ sites in $AgPO_3$ (*17*).

As this broad band is not shifted when x increases, one may suppose that the hopping distance decreases when going from $AgPO_3$ pure glass to the saturated $0.7(AgPO_3)\ 0.3(Ag_2SO_4)$ glass. Thus a value of 2.7 Å is obtained for this glass, which seems very realistic.

5. Conclusions

Electric measurements and Raman investigations on the vitreous electrolytes $(1 - x)(AgPO_3)$–xAg_2SO_4 $(0 < x < 0.3)$ reveal the following considerations:

—First, the dissolution of Ag_2SO_4 in $AgPO_3$ glass clearly improves the ionic conductivity properties of the host glass without altering either the electronic conductivity or the redox stability range.

—The ionic conductivity of these mixed glasses is the same as that of the $AgPO_3$–Ag_2O glasses when the comparison is made for identical $[Ag^+]/[PO_3^-]$ ratio, though the structures of these two systems are quite different. For $AgPO_3$–Ag_2O glasses the chains of the network are broken, the chains shortening versus the Ag_2O concentration, but for $AgPO_3$–Ag_2SO_4 glasses the network is not modified and the SO_4^{2-} ions are probably lying between the chains without interactions with them. In particular, no insertion of SO_4 group inside the skeleton of a chain occurs.

—The low-frequency band in the Raman spectra is correlated to oscillations of all Ag^+ cations. The attempt frequency is certainly included in this band and gives rise to a mean length jump going from 3 to 2.7 Å when going from the host $AgPO_3$ glass to the saturated 0.7 $AgPO_3$–0.3 Ag_2SO_4 glass.

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