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Carrier density and mobility in AgI-AgPO$_3$ glasses: A NMR study

Piercarlo Mustarelli,* Corrado Tomasi, and Aldo Magistris
Department of Physical Chemistry, CSTE-CNR and INFM, Via Taramelli 16, 27100 Pavia, Italy

Laura Linati
Centro Grandi Strumenti of the University of Pavia, Via Taramelli 16, 27100 Pavia, Italy

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A ^{109}Ag solid state NMR study on $(\mathrm{AgI})_x(\mathrm{AgPO}_3)_{1-x}$ glasses is reported. We demonstrate that, all over the glass formation region $(0<x<0.6)$, the number of Ag carriers is nearly equal to the fraction of silver ions introduced by AgI. The dramatic conductivity changes from $x=0.1$ to $x=0.5$ (more than three orders-of-magnitude) are mainly due to changes of cations mobility. The role of AgI in affecting the transport properties of these glasses is discussed in terms of free volume, mixed oxygen-iodine coordination, and opening of percolative channels, in agreement with modified continuous random network model.

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I. INTRODUCTION

An adequate knowledge of the structure of disordered solids is mandatory to predict their electric, optical, and magnetic properties and, consequently, to develop new materials.[1] $(\mathrm{AgI})_x(\mathrm{AgPO}_3)_{1-x}$ glasses (formation region $0<x<0.6$) have been largely studied because of their high conductivity at room temperature ($\sigma\sim10^{-2}\,\mathrm{Ohm}^{-1}\,\mathrm{cm}^{-1}$),[2] which makes them technologically useful. Moreover, they have gained interest as a model system to understand the complex structure/transport relationships in silver-based amorphous oxysalts.[3] It was early suggested that the dopant salt enters the host AgPO$_3$ glass matrix to form connected pathways of AgI clusters, which somehow resemble the structure of the crystalline fast ion conductor (FIC) α-AgI.[4–7] The clusters dimensions ($\sim$1 nm), as well as medium-range order, were further investigated by means of neutron scattering[8] and diffraction.[9] In the frame of the ''clusters'' approach, a percolative threshold around $x\cong0.3$ was proposed by Mangion and Johari.[10] An ultrasounds study by Bogue and Sladek[11] modelled AgI-AgPO$_3$ glasses in terms of a one-dimensional backbone (the AgPO$_3$ chains) and of an interstitial fluid.

More recently, the ''AgI clusters'' model has been practically disavowed. In Ref. 3 the authors used EXAFS and neutron and x-ray diffraction coupled with a reverse Monte Carlo method[12] to show that the doping salt is completely dissolved in the phosphate matrix, and that silver cations experience a mixed oxygen-iodine coordination. This picture was extended, with some differences, to several silver oxysalt glasses.[13] Both NMR (Refs. 14, 15) and IR (Ref. 16) studies confirmed that Ag$^+$ have oxygen and iodine in their coordination spheres, and that the doping salt does not affect the metaphosphate chain structure, at least for $x<0.5$. The formation of AgI clusters in systems of this kind was considered unlike also on the basis of thermodynamic considerations.[17]

From the point of view of the transport mechanism, the idea is emerging that the added salt is homogeneously distributed in the glass and chiefly acts in order to expand the glass network.[3] This leads to the increase of the accessible free volume for the conduction,[18] and of the number of conduction pathways available for the cations migration, in agreement with the model of Tuller and Button,[19] and also with the modified continuous random network (MCRN) approach.[20] A recent ac conductivity study seemed to support this idea, at least in terms of a general influence of AgI on the glass structure.[21]

However, some relevant points are still unclear, chiefly for what concerns ionic transport and glass connectivity at medium range. Indeed, we do not find a general agreement about what is the Ag$^+$ fraction participating to the conduction, which is the one of the most critical parameter in searching for an adequate transport model. Moreover, full knowledge is lacking on the extent to which the AgPO$_3$ structure is left unaffected by AgI insertion.

In this paper we report an ^{109}Ag solid-state NMR study of the system AgI-AgPO$_3$. Thanks to a careful quantitative analysis of the ^{109}Ag spectra we are able to measure the carriers fraction all over the compositional range $0\leqslant x\leqslant0.9$ and, therefore, to separate the contribution of mobility to the overall ionic conductivity. The modifications in the Ag$^+$ coordination sphere, and the related structural changes, as well as the nature of the percolation threshold, are also discussed in terms of the NMR observables with the help of thermal analysis and impedance spectroscopy techniques.

II. EXPERIMENTAL

Glassy or glass-ceramic samples ($0.0<x\leqslant0.9$) were produced in the following way. Properly amounts of AgI (Aldrich 99%) and glassy AgPO$_3$ were mixed and heated in a Pt crucible at 700 °C, and then the melts held 30 min before pouring into copper moulds kept at room temperature. Glassy AgPO$_3$ was obtained by melt quenching, starting from AgNO$_3$ (Metalli preziosi, bicrystallized) and NH$_4$H$_2$PO$_4$ (Merck >99%), keeping the melt at 700 °C for 6 h before quenching. The cylindrical samples (10 mm length and 9 mm diameter) were kept in desiccator until measurements were performed (generally in a matter of few days after preparation).

^{109}Ag solid-state NMR spectra were acquired on a

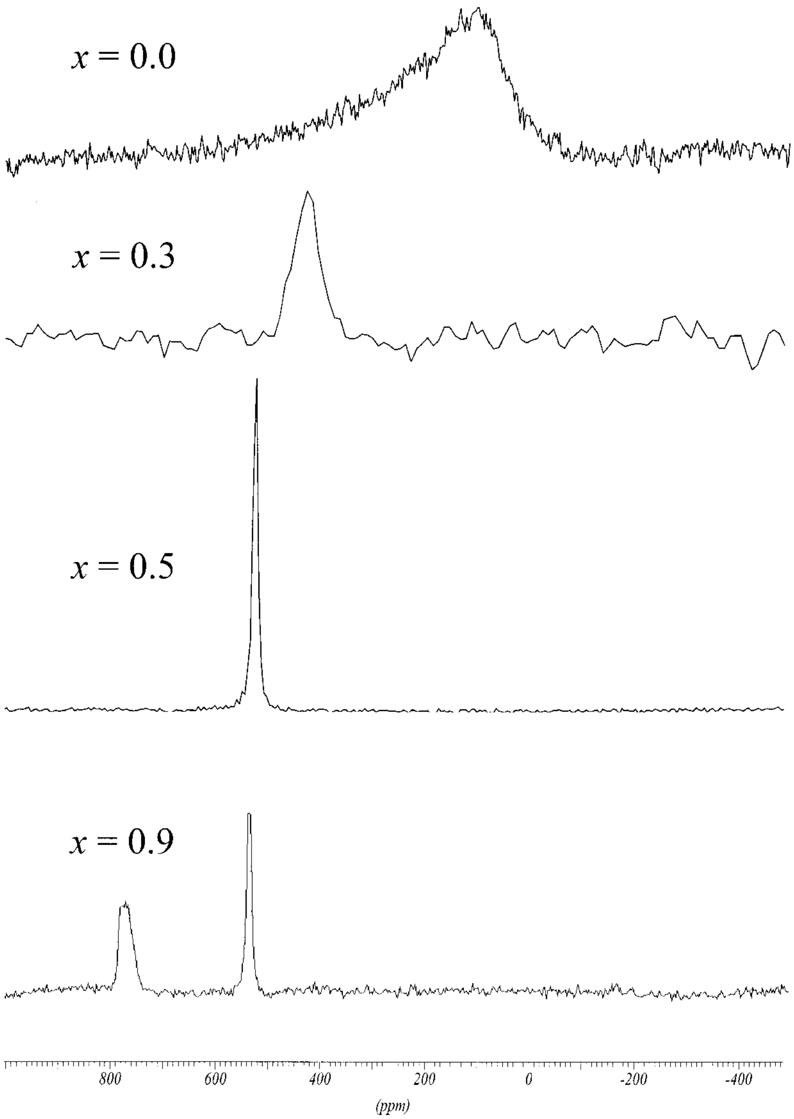

FIG. 1. ^{109}Ag NMR spectra of the samples $x=0.0$, 0.3, 0.5, 0.9. The spectrum of $AgPO_3$ was obtained by averaging over $3k$ acquisitions in order to obtain a satisfactory S/N ratio.

AMX400WB spectrometer (Bruker, Germany), at the Larmor frequency of 18.61 MHz, with a wideline probe (Bruker, Germany). The spectra were referenced to a 10 M aqueous solution of $AgNO_3$. A 90° pulse of 16 μs, a repetition time varying from 100 to 500 s, and a bandwidth of 200 kHz were chosen. 64 accumulations were generally enough to obtain acceptable S/N ratios. Both the glassy samples and the reference solution were kept in standard thin-wall, 10 mm glassy tubes (Bruker). The glassy samples were kept at the center of the NMR coil (19 mm length, 9.5 mm inner diameter). The spectra were obtained both by single-pulse and Hahn-echo sequences. Standard inversion-recovery and Carr-Purcell sequences were employed to estimate T_1 and T_2, respectively. Care was taken to avoid signal saturation and to minimize the baseline distortions. Where not differently specified, the experiments were performed at 297 ± 1 K.

The quantitative estimation of the mobile silver ions was obtained by comparing the areas of their peaks ($T_1\sim1$ s at room temperature) with that of a known volume of the $AgNO_3$ 10 M solution. Several experimental conditions were varied to check the reliability of the quantitative analysis: (i) the solution volume was changed from 1 cm^3 (i.e., roughly the volume of the glassy samples), kept at the coil center, to 2.25 cm^3 in order to evaluate the borders distortions of the rf pulse B_1; (ii) several repetition delays for the solution $[T_1>1$ min (Ref. 22)$]$ up to 25 min were compared to avoid signal saturation; (iii) a $AgNO_3$ solution with added 0.25 M $Fe(NO_3)_3$ was also prepared in order to reduce T_1 of silver; (iv) different aliquots of the same glass were measured and the results were compared. By combining the errors evaluations obtained by these tests we estimated a maximum error of 20% for $x\leqslant0.3$, and of less than 10% for $x>0.3$. The difference is due to the better S/N ratio that was obtained for $x>0.3$ (see Fig. 1). No quantitative estimations were tried for the peaks attributed to AgI (see below) because of the long T_1 $(\sim1\text{ h})$.[14,23]

Differential scanning calorimetry (DSC) measurements were run with a 2910 DSC controlled by a TA 2000 system (TA Instruments). All experiments were performed on powdered samples, in crimped silver pans, at a rate of 10 °C/min under dry N_2 purge. The temperatures of the thermal phenomena are affected by an uncertainty of ±2 °C. The instrument was previously calibrated with standard indium.

Impedance Spectroscopy measurements were carried out with a 1255 HF frequency response analyzer, connected with a SI 1287 electrochemical interface by Solarton (Schlumberger) between 1 and 10^6 Hz, by using a voltage amplitude of 100 mV. Disk-shaped samples (10 mm diameter, ~1 mm thickness) were carefully polished, covered by a graphite layer and kept between stainless-steel electrodes. Powder x rays diffraction patterns were taken on a Philips PW 1710 powder diffractometer, equipped with a Philips PW 1050 vertical goniometer and a graphite crystal monochromator (Cu$K\alpha$ radiation).

III. RESULTS

Figure 1 shows the ^{109}Ag NMR spectra of the samples $x=0.0$, 0.3, 0.5, 0.9. $AgPO_3$ shows a broad pattern of chemical shift anisotropy ($\Delta\sigma \sim 375$ ppm) that is attributed to a fraction of silver ions that are only relatively mobile.[14] The isotropic chemical shift can be estimated to fall near 120 ppm. We stress that mobile Ag^+ in $AgPO_3$ must be considered as ''defects:'' our quantitative analysis gives us an estimate of $\sim 6.0\times 10^{19}$ ions cm^{-3} (see Fig. 5). The remaining Ag^+ fraction of $AgPO_3$ is ''immobile,'' and smeared out below the baseline. Glass $x=0.3$ displays a broad Gaussian peak at ~420 ppm. Sample $x=0.5$ shows a single and narrow peak [full width at half height (FWHH)$\cong$10 ppm] at 520 ppm. Sample $x=0.9$ shows (i) the peak of mobile Ag^+ nearly at the same position seen for $x=0.5$ and (ii) a broad peak at ~770 ppm, which is attributed to β-AgI.[23] We stress here that β-AgI was always observed by routine x rays diffraction for $x\geqslant 0.6$. In the composition range $0.6\leqslant x\leqslant 0.7$ we found two peaks likely due to mobile ions, which point towards subliquidus immiscibility, as already observed in AgI-Ag_2MoO_4 glasses.[24] This fact is not treated here, and will be discussed in a future work on the metastability and the approach towards the equilibrium phase diagram. The presence of two glass phases is accompanied by an anomalously low AgI nucleation (see following).

Figure 2 summarizes the chemical shift positions of all the peaks we observed in glasses and glass-ceramic samples. Black circles correspond to the mobile Ag^+ ions belonging to the glass phase(s), while open circles are due to β-AgI. As far as concerns the region $0.6\leqslant x\leqslant 0.7$, where subliquidus immiscibility exists between two glassy phases, black circles represent the center-of-mass of this portion of the NMR spectrum.

Figure 3 shows the DSC traces of samples $x=0.0$, 0.3, 0.5, 0.9. $AgPO_3$ displays a glass transition above 180 °C, as expected for a glass with $-$OH content lower than 0.4 wt. %.[25] Parallel ^{31}P MAS-NMR standard measurements (not reported here) showed that the average chain length is greater than 100 (PO_4 units); for more details on this technique see Ref. 25. The peaks starting at ~270 and ~450 °C represent sample crystallization and melting of $AgPO_3$ crystal, respectively. The samples $x=0.3$ and $x=0.5$ show only a glass transition, T_g, whose temperature decreases for increasing x. This behavior, already reported in the literature, is attributed to the decrease of the electrostatic forces among phosphate chains caused by interposition of AgI.[26] Finally, the DSC trace of $x=0.9$ shows a small glass transition nearly at the same temperature observed for $x=0.5$, a deep endotherm at 147 °C that is attributed to AgI $\beta\rightarrow\alpha$ phase transition, and a broad endotherm in the range 400–500 °C that represents the attainment of the liquidus. We recall here again that all the samples for $x\geqslant 0.6$ are glass ceramic in nature.

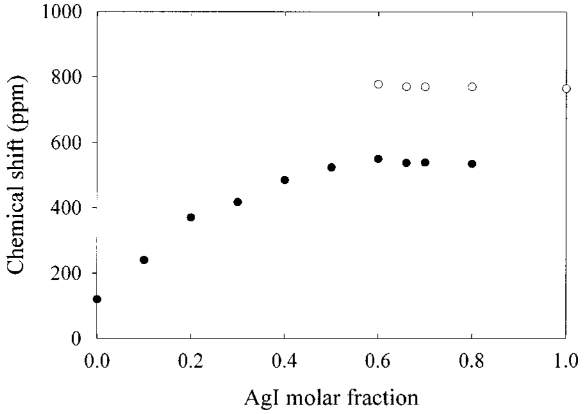

FIG. 2. ^{109}Ag NMR chemical shifts of glasses and glass ceramics. Filled circles: spins belonging to the mobile (glassy) phase. Open circles: β-AgI. The filled points for $x=0.6$, 0.66, and 0.7 are the centers-of-mass of two peaks belonging to different glassy phases. The value for $x=0.0$ is evaluated from the anisotropy parameters of the pattern.

IV. DISCUSSION

Ag^+ mobile spins were observed in the glass formation region of AgI-based borate,[23] phosphate,[14] and molybdate glasses.[24] In all cases, the peaks were shifted towards the paramagnetic direction (downfield) for increasing AgI contents, which is explained in terms of the substitution of oxygens with iodines in the silver coordination sphere. It was early shown in the case of borates[23] that the substitution of the first oxygen accounts for a shift of about 300 ppm. Since the silver coordination number of glassy $AgPO_3$ is ~3.4,[27] if the silver spins are homogeneously distributed we can as-

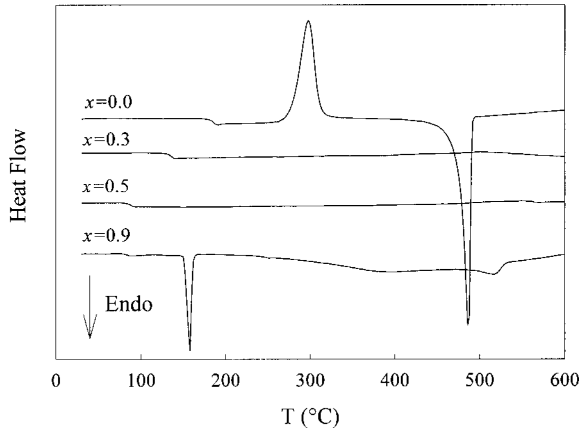

FIG. 3. DSC traces of samples $x=0.0$, 0.3, 0.5, 0.9.

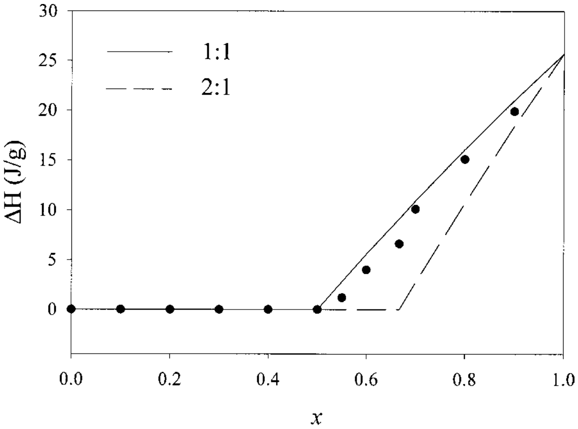

FIG. 4. Excess heat of $\beta \rightarrow \alpha$ AgI transition vs the AgI molar fraction. Filled triangles: experimental points. Full line: calculated excess enthalpy in case of maximum 1:1 AgI:$AgPO_3$ glassy phase formation. Dashed line: calculated excess enthalpy in case of maximum 2:1 glassy phase formation.

sume that for $x \cong 0.29$ nearly each Ag^+ will ''see,'' in average, one iodine in its coordination sphere. This is indeed the case, as demonstrated by the chemical shift change of about 280 ppm from $x=0$ to $x=0.3$.

For $x \geqslant 0.6$ a phase separation takes place, which is accompanied by a leveling off of the chemical shift of the mobile phase. Such a behavior was already observed in AgI-Ag_2MoO_4 glass ceramics,[24] and it was there related to the formation of a glass phase of composition 0.67AgI:0.33Ag_2MoO_4. Under appropriate thermal treatment, that glassy phase gave origin to a metastable 2:1 crystal,[28] in agreement with Angell's model of ''barely stable crystal.''[29] In the case of AgI-$AgPO_3$ we now find a 1:1 limiting glassy phase, as demonstrated by Fig. 4, which shows the behavior vs composition of the enthalpy of AgI $\beta \rightarrow \alpha$ transition at 147 °C, as measured by DSC. The deviation from the theoretical line of 1:1 formation we find for $0.5 < x \leqslant 0.7$ reflects the difficulty of AgI to nucleate also in a region where ''stoichiometrically··· no O-Ag-O cross links could be formed,''[3] and it is a further confirmation that AgI is well distributed in the glass network. A detailed study of the metastable phase diagram and the approach towards the equilibrium, however, is beyond the scope of this paper and will be reported elsewhere.

Figure 5 reports the carriers density vs composition, as evaluated from the NMR spectra, compared with the stoichiometric fractions of Ag ions brought by AgI and $AgPO_3$, respectively, which have been obtained from standard density measurements. In the limits of the experimental errors we can say that, over the entire glass forming region, the number of mobile spins is nearly equal to that of Ag^+ brought by AgI. In the glass-ceramic region, in contrast, it scales as the fraction of $AgPO_3$, that means as the quantity of 1:1 glassy phase that we suppose to be preferentially formed (see Fig. 4). The anomaly for $x=0.6$ is likely related to the presence of the two immiscible glassy phases which somehow hinder excess AgI to fully crystallize, at least in a matter of several weeks. In order to see if the scaling of mobile ions with AgI molar fraction is coincidentally related to the measurements conditions, the behavior of the carriers density against temperature has been checked on the samples $x=0.3$ and $x=0.5$. We found that the number of Ag^+ ions is nearly independent from the temperature in the range 0–80 °C (see inset of Fig. 5). The carriers density of samples $x=0.3$ and $x=0.5$ was also found to be the same after one-year aging at room temperature.

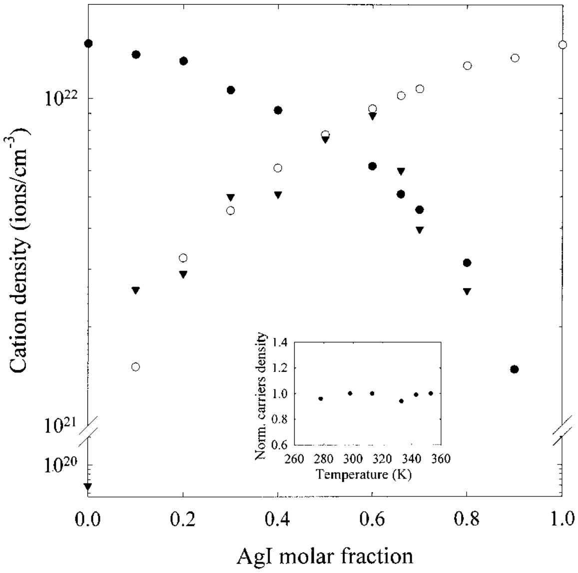

FIG. 5. Open circles: number of Ag^+ carriers as determined by NMR (see text). Filled circles and triangles represent the nominal number of silver atoms carried by $AgPO_3$ and AgI, respectively. The inset shows the behavior vs temperature of the number of mobile carriers (normalized to 1 at $T=298$ K) for the sample $x=0.5$. Similar results were obtained for $x=0.3$.

Since we have exactly determined the fraction of mobile carriers n we can now estimate spin mobility μ from the simple relationship $\sigma = n\mu e$, where σ is the dc conductivity

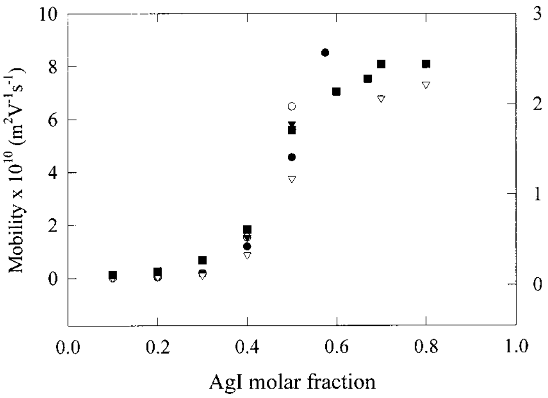

FIG. 6. Comparison on the cations mobility determined by conductivity data, and ^{109}Ag NMR spin-spin relaxation times. Open circles: conductivity data from Ref. 31. Filled down triangles: conductivity data from Ref. 32. Filled circles: conductivity data from Ref. 33. Open down triangles: conductivity data from this work. Filled squares: ^{109}Ag NMR spin-spin relaxation times from this work.

and e is the electronic charge. We make use of conductivity data obtained from our samples, as well as of results taken from the literature. Figure 6 shows the mobility vs composition compared with the behavior of ^{109}Ag NMR spin-spin relaxation time T_2. Both the quantities display a threshold near $x \cong 0.3$, in agreement with the findings of Mangion and Johari based on conductivity measurements.[10] This threshold is indeed related to setting up of long-range diffusion, in fact the narrowing of the ^{109}Ag NMR line (probed by T_2) is due to the average of chemical shift terms of the Hamiltonian,[24,30] which requires the cations to move over several lattice positions. Across the glass formation region, spin mobility spans over more than three orders-of-magnitude, ranging from $\sim 2 \times 10^{-6}\ \mathrm{m^2\,V^{-1}\,s^{-1}}$ at $x=0.1$ to $\sim 7 \times 10^{-3}\ \mathrm{m^2\,V^{-1}\,s^{-1}}$ at $x=0.5$. This substantial variation, which cannot be fully appreciated in the figure because of the linear scale chosen to highlight the threshold, almost entirely accounts for the dramatic change in conductivity observed from $x=0$ to $x=0.5$. Our findings are not in agreement with the results of Clement *et al.*[31] who reported a nearly constant cations mobility in their AgI-$AgPO_3$ glasses by means of Hall effect measurements. Finally, for $x \geqslant 0.6$, where β-AgI and one or more glassy phases appear to coexist, mobility levels off.

V. CONCLUSIONS

Our NMR, thermal and conductivity findings lead to model the structural changes determined by addition of AgI to $AgPO_3$, considered as a quasimonodimensional array of long phosphate chains. For relatively low salt contents ($x < 0.3$) the iodide ions break apart the chains, as demonstrated by the lowering of the T_g,[26] and open channels where the Ag^+ start to move. Only those cations experiencing iodines in their coordination clouds, on the other hand, are so mobile to narrow substantially the NMR line. At $x \cong 0.33$, which means one iodine every two phosphorous atoms, a fully connected migration pathway is likely formed, which corresponds to the electric threshold found by Mangion and Johari,[10] and long-range diffusion takes place. From the percolation threshold to the limit of the glass forming region, indeed, cations mobility increases very strongly due to the combined effect of the free volume,[18] and the increase of the iodine coordination number.[3]

Indeed, a fundamental role in determining the transport properties of these AgI-based glasses is played by the I^- anions, which increase the free volume available for conduction, by creating channels (pathways) as supposed by the MCRN model. We are inclined to think this as a common mechanism in AgI-based oxysalt glasses, as recently shown also by RMC modeling.[34] While the role played by the iodine ions and the number of mobile carriers seemed to point towards the cluster model, our spectroscopic results clearly indicate that, over the timescale of the NMR experiment ($\sim 10^{-5}$–10^{-3} s), the fraction of Ag^+ involved in the conduction is homogeneously distributed all over the glass matrix.

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*Corresponding author. E-mail address: mustarelli@matsci.unipv.it

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