PHYSICAL REVIEW B **73**, 104201 (2006)

Dynamics of Ag^+ ions in Ag_2S-doped superionic $AgPO_3$ glasses

S. Bhattacharya, D. Dutta, and A. Ghosh*

Department of Solid State Physics, Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700 032, India

(Received 11 November 2005; published 2 March 2006)

Dynamics of Ag^+ ions in Ag_2S-doped $AgPO_3$ glasses have been studied in the frequency range 10 Hz to 2 MHz and in the temperature range 93–323 K. The composition dependence of the dc conductivity and the activation energy of these glasses has been compared with that of the AgI-doped $AgPO_3$ glasses. An attempt has been made to explain the comparatively lower conductivity for the present Ag_2S doped glasses than that for the AgI-doped glasses by analyzing the Fourier transform infrared data. The frequency-dependent electrical data have been analyzed in the framework of conductivity formalism. We have obtained the mobile ion concentration and the power-law exponent from the analysis of the conductivity spectra. We have observed that the concentration of Ag^+ ions is independent of temperature and the conductivity is primarily determined by the mobility. It has also been observed that a fraction of the Ag^+ ions in the glass is involved in the dynamic process. Scaling of the conductivity spectra is observed to be independent of temperature and Ag_2S content in the compositions.

DOI: 10.1103/PhysRevB.73.104201 PACS number(s): 61.43.Fs, 66.10.Ed, 78.30.Ly

I. INTRODUCTION

Superionic glasses have attracted many academic activities in recent years because of their possible application in solid state batteries or other electrochemical devices.[1,2] They are important not only for applications but also from an academic point of view. One of the main academic challenges is to explain how the disordered structure of these materials is related to the high ionic conductivity that can be achieved at ambient temperature. The conductivity of AgI-doped glasses has been investigated in recent years in the search for solid electrolytes with superior properties.[1–3] However, the mechanism of the ionic transport in these glasses has still been under debate.[1–5] The conductivity of these glasses has been attributed by some authors to their unique structure, which can be modeled as a mixture of conduction pathways of silver iodides and rigid oxide networks.[3,4] It has been observed[6] that in almost all systems studied, the glassy network structure is unaffected by the addition of AgI. Since the same behavior is found for other properties such as elastic moduli[7] and density,[8] it has been widely suggested[7–10] that the high conductivity pathway in these glasses is through microregions possessing α-AgI structure. It is supposed that there will be more than two kinds of silver cations in the glasses: The first is surrounded by iodide anions only which diffuses very rapidly, the second is strongly bonded to the oxide network to be almost immobile and the third is the intermediate cation coordinating to both iodide and oxygen.[1] It is well known that silver oxide glasses such as Ag_2O-P_2O_5 in combination with AgI offer a group of superionic glasses, such as AgI-$AgPO_3$, exhibiting Ag^+ ionic conductivity of the order of 10^{-5}–10^{-2} Ω^{-1} cm^{-1} at room temperature. $AgPO_3$ glass has low ionic conductivity (10^{-7} Ω^{-1} cm^{-1}) at room temperature. As the amount of AgI in the $AgPO_3$ glass increases, the conductivity increases[11] and the glass transition temperature decreases.[12] In a recent work,[10] it has been shown that the main role of AgI in the AgI-$AgPO_3$ system is to influence the glass structure such as expansion of the $AgPO_3$ network and hence to increase the mobility of Ag^+ ions enhancing the conductivity due to AgI doping.

The present concern has been to examine the effects of Ag_2S doping into the $AgPO_3$ glass and to understand the Ag^+ ion transport mechanism in these systems. This involves insight into both the local structures of the host network and the ways silver cations are coordinated within these glasses. Some structural[13–16] and a few electrical studies[15–18] have been performed for Ag_2S-doped $AgPO_3$ glasses. Some similarities of these properties were observed for an Ag_2S-$AgPO_3$ system with those of the AgI-$AgPO_3$ system. There is no general agreement about the fraction of Ag^+ ions participating in the transport process, which is one of the most critical parameters to explore the transport mechanism in these systems.

Dielectric measurements on ionic materials give useful information about dynamical processes involving ionic motion.[19] It is known that the conductivity of glassy materials is frequency dependent, so that the diffusivity of the mobile ions is not entirely characterized by the single steady state parameter σ_{dc} quantifying dc conductivity. Impedance measurements are often used to characterize the response of ionic conductors to a field-induced perturbation.[20] As observed in several ion conducting glasses, the dielectric response, expressed in terms of frequency-dependent conductivity, exhibits a dispersive behavior usually described[20] by a power law with exponent $n<1$, while a further contribution, with exponent $n>1$, is eventually found at higher frequencies.[21] In this article, ion transport at various temperature and frequencies, which often provide valuable suggestive information about the conduction mechanism in glasses, has been studied in detail for Ag_2S-doped $AgPO_3$ glasses. In this approach, we have investigated the conductivity spectra for glasses at different temperatures and estimated Ag^+ ions participating in the transport process. Results have been analyzed in comparison with previous conductivity measurements on silver metaphosphate glasses[11] pure or doped with AgI in wide frequency and temperature ranges,

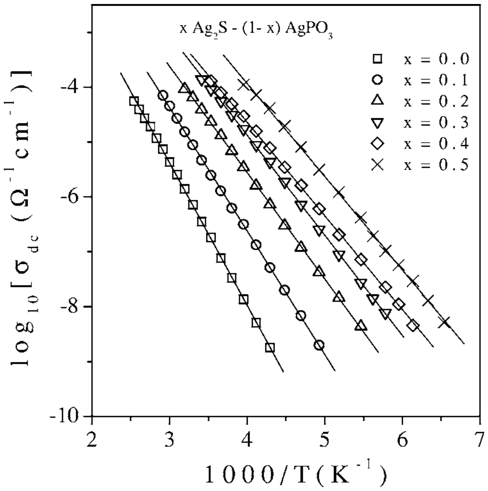

FIG. 1. Arrhenius plots of dc conductivity for $x\mathrm{Ag_2S}-(1-x)\mathrm{AgPO_3}$ glasses for different values of x.

and discussed in light of the power law model for ion dynamics in glasses.

II. EXPERIMENT

Glass samples of compositions $x\mathrm{Ag_2S}-(1-x)\mathrm{AgPO_3}$, where x=0.0,0.1,0.2,0.3,0.4, and 0.5 were prepared in two steps. First, $\mathrm{AgPO_3}$ glass was obtained by melting the $\mathrm{AgNO3_3}$ (Aldrich 99.9%) and $\mathrm{NH_4H_2PO_4}$ (Aldrich 99.9%) at 700 °C for 6 h in a Pt crucible and then quenching the melt in an aluminum mold. In the second step, appropriate amounts of $\mathrm{Ag_2S}$ (Aldrich 99.9%) and $\mathrm{AgPO_3}$ glass were mixed, melted in a Pt crucible at 900 °C for 30 min, and poured in an aluminum mold to get glass samples. Glass formation was confirmed from x-ray diffraction. The density of the samples at room temperature was measured using the displacement method. The Fourier transform infrared (FTIR) spectra of the bulk glass samples in transmission mode were recorded in a Nicolate FTIR spectrophotometer (Magna IR-750, Series II) in the wave number range of 400–4000 $\mathrm{cm^{-1}}$ at a temperature 25 °C and relative humidity of 50–60 %. For electrical measurements, gold electrodes were deposited on both surfaces of the polished bulk samples of diameter ~10 mm. The electrical measurements such as capacitance and conductance of the samples were carried out in the frequency range 10 Hz–2 MHz using the impedance meter (QuadTech, model 7600) interfaced with a computer. The measurements were taken in the temperature range 93–323 K using a closed cycle cryostat (Janis Inc, model-450).

III. RESULTS AND DISCUSSION

The dc conductivity was obtained from the complex impedance plots for different glass compositions and is shown in Fig. 1 in an Arrhenius fashion. We note that the plots for all compositions are linear indicating thermally activated hopping conductivity. The activation energy for different compositions was obtained from the least-square straight line fits. In Figs. 2(a) and 2(b) we have presented a composition dependence of the measured dc conductivity at T=303 K and the activation energy E_σ, respectively, for all the glass compositions. For comparison, the data for AgI-doped $\mathrm{AgPO_3}$ glasses[11] are included in Figs. 2(a) and 2(b). We note that the conductivity increases and the activation energy decreases with the increase of the dopant salt content for both these glass systems. However, it may be noted that the conductivity for the equimolar glass compositions for the $\mathrm{Ag_2S}$-doped $\mathrm{AgPO_3}$ glasses is lower and the activation energy is higher than those for the AgI-doped $\mathrm{AgPO_3}$ glasses.[11]

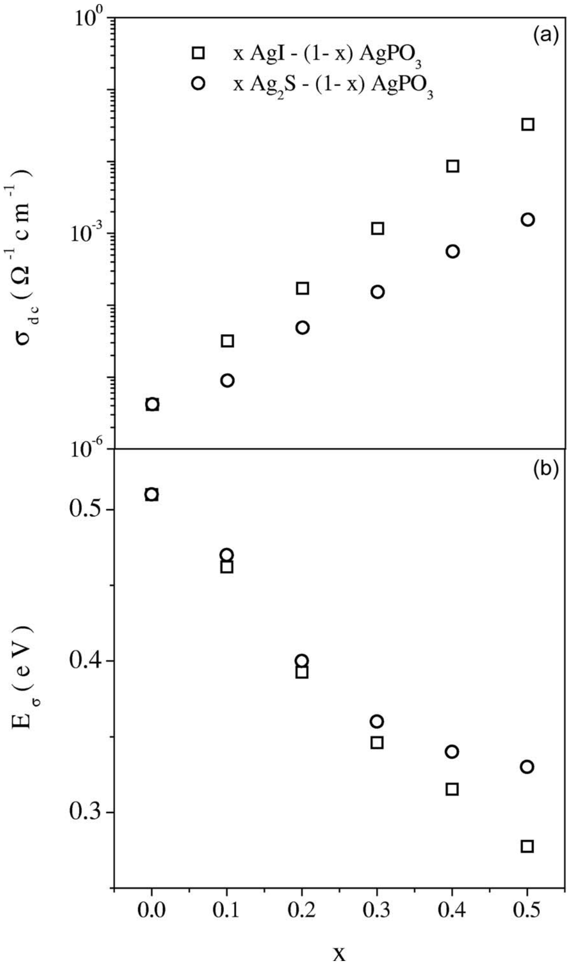

FIG. 2. (a) Compositional variation of the dc conductivity at T=303 K of $x\mathrm{Ag_2S}-(1-x)\mathrm{AgPO_3}$ glasses along with $x\mathrm{AgI}-(1-x)\mathrm{AgPO_3}$ glasses.[11] (b) The dc activation energy of the same glass compositions as shown in Fig. 2(a).

The ac conductivity spectra for the $0.5\mathrm{Ag_2S}$-$0.5\mathrm{AgPO_3}$ glass composition is shown in Fig. 3 for different temperatures. An almost frequency independent plateau region, followed by a high-frequency dispersion is observed for the conductivity spectra at each temperature. The high-frequency dispersive behavior in the investigated frequency range is generally expressed in the form[22]

$$\sigma'(\omega) = \sigma_{\mathrm{dc}} + A\omega^n, \tag{1}$$

where σ_{dc} is the dc conductivity and n lies in the range $0 < n < 1$. It has been suggested[29] that the dc conductivity σ_{dc}

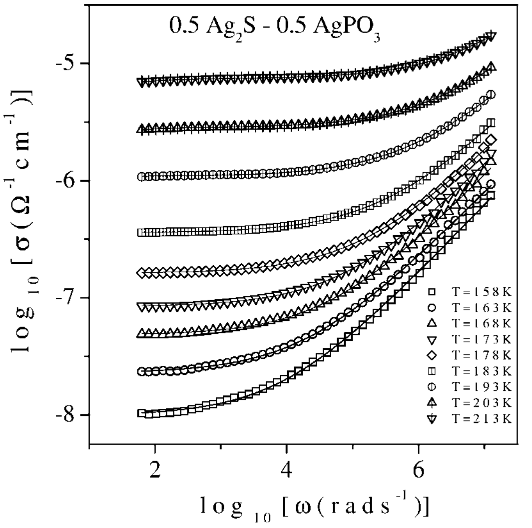

FIG. 3. Frequency dependence of the conductivity at several temperatures (shown) for glass composition $0.5Ag_2S-0.5AgPO_3$. The solid lines are best fits to Eq. (2).

and the parameter A in Eq. (1) are both related by a characteristic macroscopic relaxation frequency ω_c, i.e., the mobile ion hopping rate such that

$$\sigma'(\omega) = \sigma_{\rm dc}[1 + (\omega/\omega_c)^n]. \tag{2}$$

Using the random-walk formulation in the longer time scales for defect transport by isolated jumps with[23] "step of size ξ," the dc conductivity of an ionic conductor can be expressed by the Nernst-Einstein relation as

$$\sigma_{\rm dc} = q^2\xi^2 n_c\omega_c/12\pi kT, \tag{3}$$

where n_c is the mobile ion concentration and T is the absolute temperature.

The conductivity spectra for all compositions were fitted using Eq. (2). In the fitting process, $\sigma_{\rm dc}$, ω_c, and n were varied simultaneously to get the best fits. The quality of the curve fitting is considered good, since the fit and the data agreed to within 2–3 % over the entire frequency range for all temperatures and compositions investigated. In the curve fitting, a systematic variation in the residuals was observed in each parameter and the error in each parameter varied differently with temperature as a result of relative location of the relaxation process within the fixed frequency window of the spectrometer following the procedure reported earlier.[24,25] The parameters obtained from the curve fitting behaved well over the entire temperature range. Figure 4 shows the variation of the Ag$^+$ ion hopping rate ω_c with inverse temperature. It is observed that ω_c is thermally activated as $\omega_c = \omega_0 \exp(-E_c/kT)$, where ω_0 is the attempt frequency and E_c is the activation energy for hopping which is nearly equal to that obtained for the dc conductivity E_σ as shown in Fig. 2(b).

The variation of the power-law exponent n with Ag$_2$S content is shown in Fig. 5 for several glass compositions. In the analysis of the frequency exponent n the window effect[24] has been taken into account using a statistical method, as suggested earlier.[25] In the fitting of the power-law conductivity to the experimental spectra, it has been observed[24] that the value of the frequency exponent n depends on the frequency range considered (window effect). But the statistical analysis removes the dependence of frequency exponent n on the frequency window.[25] The values of the frequency exponent n obtained within the frequency range of our spectrometer without statistical error analysis are also shown in Fig. 5. No significant difference in the values of n, obtained from these analysis, is observed for the present glasses in Fig. 5. We did not observe any temperature dependence of exponent n in the investigated temperature range. Figure 5 indicates that the exponent n is almost independent of Ag$_2$S content also similar to the AgI-doped systems.[11] The values of n indicate three-dimensional conduction pathways in Ag$_2$S-doped AgPO$_3$ glasses.[23]

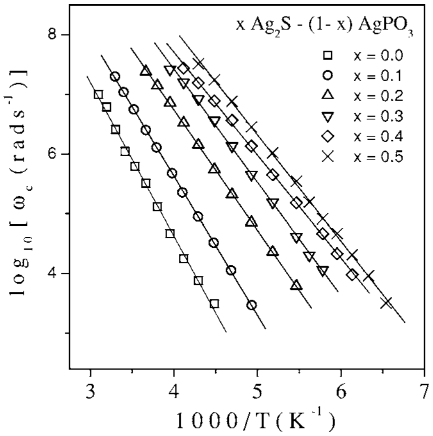

FIG. 4. Arrhenius plots of the hopping frequency for the glass compositions $xAg_2S-(1-x)AgPO_3$ for different values of x. The solid lines are the least square straight line fits of the data.

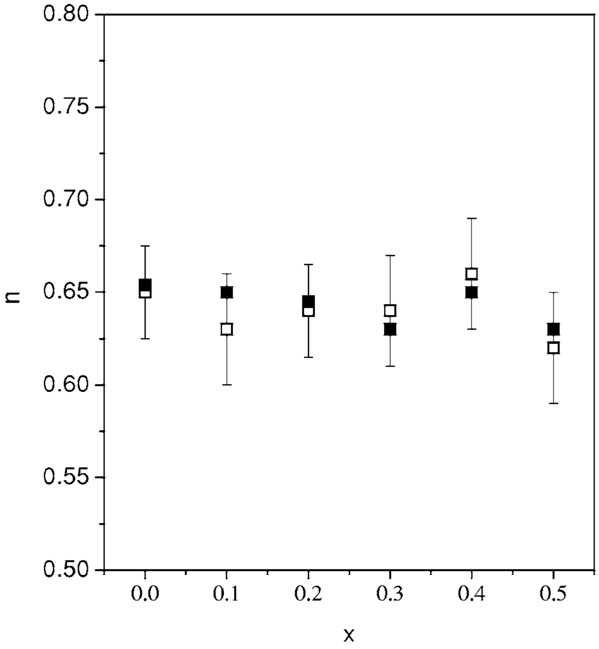

FIG. 5. Frequency exponent n as a function of Ag$_2$S content for $xAg_2S-(1-x)AgPO_3$ glass compositions for different values of x: ☐ represents data obtained with statistical error analysis, while ■ represents the data obtained without error analysis.

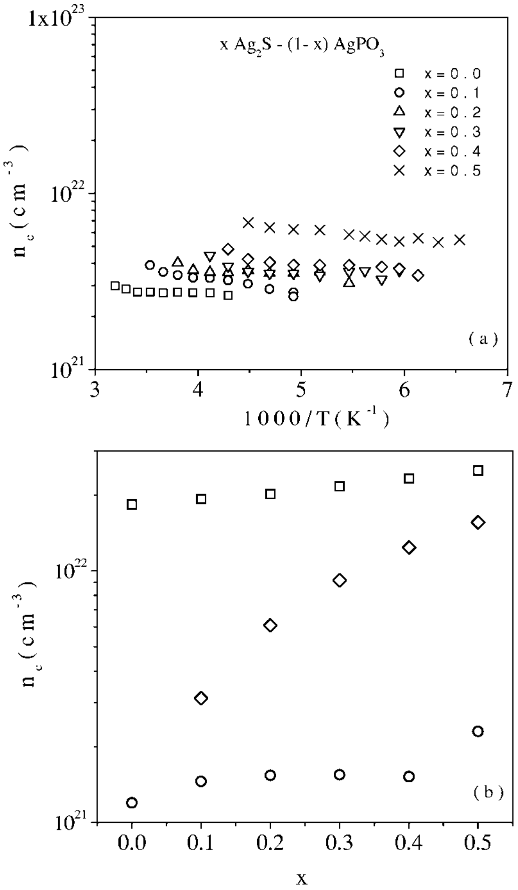

FIG. 6. (a) Arrhenius plots of mobile Ag^+ ion concentration for glass compositions $xAg_2S-(1-x)AgPO_3$ for different values of x. (b) The variation of Ag^+ ion concentration with compositions for $xAg_2S-(1-x)AgPO_3$ glasses. Total Ag^+ ion concentrations are represented by □; Ag^+ ion concentrations contributed by Ag_2S are represented by ◇, and mobile Ag^+ ion concentration n_c for are shown by ∘, respectively.

In addition to the temperature dependence of the hopping rate, the concentration of the mobile ions may also be temperature dependent. In this case the temperature dependence of the dc conductivity would differ from that of the hopping rate. To confirm this we have estimated the concentrations of mobile Ag^+ ions n_c contributing to the transport process by the fitting of the ac conductivity spectra using Eqs. (2) and (3) in a similar way as mentioned above. The value of ξ for the present glasses was taken from an earlier report.[23] Arrhenius temperature dependence of the mobile Ag^+ ions contributing to the transport process is shown in Fig. 6(a). We note that mobile Ag^+ ions are almost independent of temperature. In Fig. 6(b), the mobile Ag^+ ions contributing to the transport process are shown as a function of Ag_2S content in the compositions. In this figure, the total Ag^+ ion density and Ag^+ ions contributed by Ag_2S only, calculated from glass composition and density, are also included. We note that the mobile Ag^+ ions are less than the total Ag^+ ion concentration, i.e., only a fraction of total Ag^+ ions are mobile, which depend little on the Ag_2S doping. It is also noted that this mobile Ag^+ ion concentration is also less than the Ag^+ ion concentration contributed by Ag_2S. Thus, the increase in the conductivity due to the Ag_2S doping is not due to the increase in the mobile Ag^+ ions, but is due to the increase in the mobility of Ag^+ ions for Ag_2S-doped $AgPO_3$glasses.[11] It was also observed that the fraction of total Ag^+ ions which are mobile for Ag_2S doped $AgPO_3$ glasses are almost same as was found for AgI-doped $AgPO_3$ glasses.[11] But the conductivity enhancement with the fraction of the dopant salt is different for the two systems as shown in Fig. 2(a), which is explained below from a structural point of view.

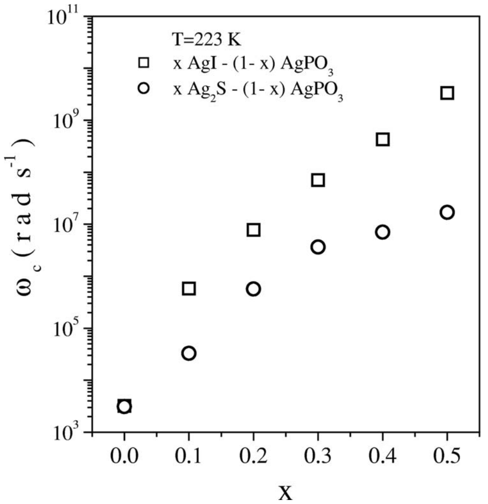

FIG. 7. Compositional variation of hopping frequency of mobile ions ω_c at $T=223$ K for both Ag_2S- and AgI-doped silver metaphosphate glasses.

Figure 7 shows a comparison of the hopping rate ω_c of mobile ions for both the Ag_2S- and AgI-doped $AgPO_3$ glasses at a fixed temperature as a function of the dopant fraction. It is observed that the hopping rate increases with the increase of AgI doping, while for Ag_2S doping the hopping rate is almost independent for the higher dopant content and is smaller than that of the former. It was demonstrated[10,11] that the main role of AgI in AgI-doped $AgPO_3$ glasses is to influence the glass structure such as expansion of the $AgPO_3$ network and hence to increase the mobility of Ag^+ ions enhancing the conductivity due to AgI doping. AgI does not enter the $AgPO_3$ chain structure, but since the phosphate chains are intrinsically one dimensional they are surrounded by AgI.

The above results have been explained by using the FTIR spectra of AgI- and Ag_2S-doped $AgPO_3$ glasses, shown in Figs. 8(a) and 8(b), respectively. The spectrum for $AgPO_3$ glass is included in the figures for comparison. In both the figures the band near 900 cm^{-1}, recognized as to P-O-P stretching vibration,[26] is present for pure $AgPO_3$ glass as well as for the doped glasses. The band near 1270 cm^{-1}, attributed to the P═O vibration,[27] is a clear feature in the spectrum of all metaphosphate chain structures, in which double bonded oxygen has a well-defined existence. It is observed from Fig. 8(a) that the glasses containing AgI have similar spectra as that of $AgPO_3$ itself indicating that the $(PO_4)_n$ infinite chains are not modified by the introduction of silver iodide, which thus acts simply as a plasticizing agent as in polymer-diluent systems.[16]

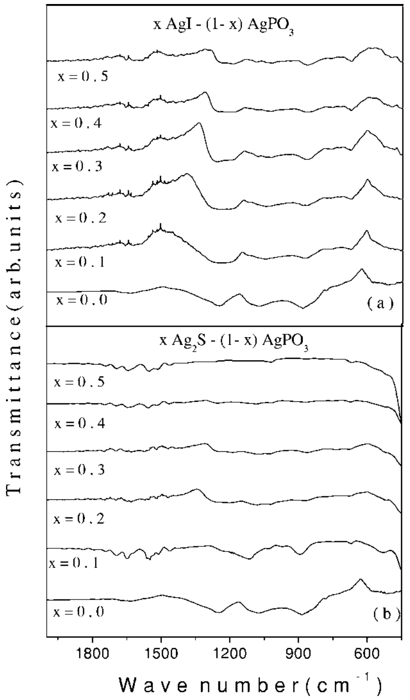

FIG. 8. (a) FTIR spectra for $x\mathrm{AgI}-(1-x)\mathrm{AgPO}_3$ glasses for different values of x. (b) FTIR spectra for $x\mathrm{Ag}_2\mathrm{S}-(1-x)\mathrm{AgPO}_3$ glasses for different values of x.

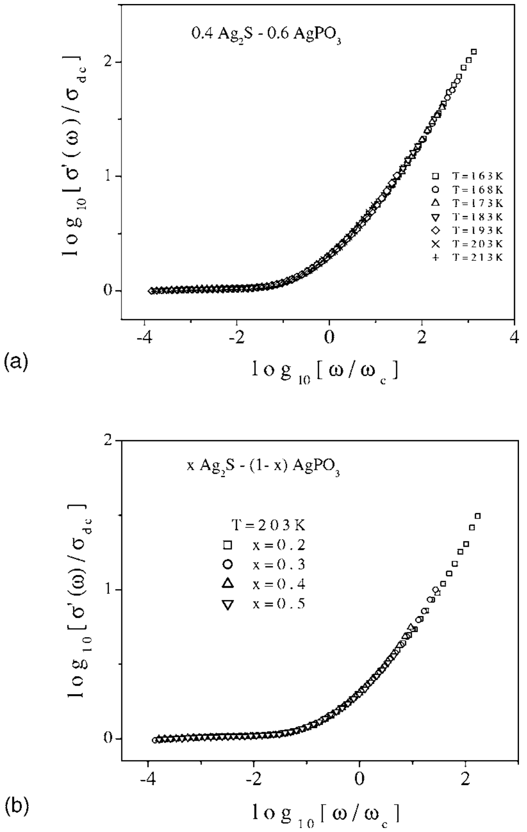

FIG. 9. (a) Scaling of the conductivity spectra with temperature for a glass composition shown in the inset. (b) Scaling of the conductivity spectra at $T=153$ K for $x\mathrm{Ag}_2\mathrm{S}-(1-x)\mathrm{AgPO}_3$ glass compositions for different values of x shown in the insets.

Although crystalline AgI and Ag_2S exhibit behaviors similar to superionic materials, and both have similar crystal structures and similar high ionic conductivity, when dissolved in $AgPO_3$, they behave differently as observed in Fig. 8(b). In these systems the added Ag_2S attacks and depolymerizes the $AgPO_3$ chains, since S^{2-} is a Lewis base unlike I^-. Since in $AgPO_3$ the acid-base process forms an incomplete infinite chains of $(PO_4^{3-})_n$ corner-shared tetrahedra, the P-O-P chain bond breaking will involve the replacement of chain-end oxygen by sulfur. The chain length decreases with increasing content of Ag_2S. The diminished intensity of both the 900 and 1270 cm^{-1} bands is consistent with the drastic shortening of the $(PO_4^{3-})_n$ infinite chains with the addition of Ag_2S in the $AgPO_3$ glass network as shown in Fig. 8(b). At a higher concentration of Ag_2S the composition corresponds to $(O_3P\text{-}O\text{-}PO_2S)^{6-}$ where one out of four P-O links has been replaced by a P-S link and there remains just a set of distinct PSO_3 tetrahedra and no chemical ordering is expected.[27] The band near 1100 cm^{-1} in $AgPO_3$ base glass arises due to the P-O vibration.[26] Diminution in intensity and shift of this bond in the Ag_2S-doped glasses indicates the creation of PSO_3 tetrahedra. The above result has been also clarified by a P-NMR study[15] of Ag_2S-doped $AgPO_3$ glasses showing that the Ag_2S acts both as an interstitial dopant and a network modifier. The magic angle spinning spectra reveal a complex scheme of reactions between the Ag_2S and the metaphosphate.[15]

Thus from the above discussion it is clear that the gradual expansion of $AgPO_3$ network due to the incorporation of AgI as observed in the previous studies[10,11] is not expected in that extent due to incorporation of Ag_2S in the $AgPO_3$. This leads to a decrease in the mobility or in other words the hopping rate of the mobile ions in comparison to the AgI-doped glasses as shown in Fig. 7. An almost composition independent hopping rate, observed in Fig. 7, for the Ag_2S-doped $AgPO_3$ glasses due to the completeness of the network modification, such as the P-O-P chain breaking due to presence of S^{2-} ions above $x=0.3$ (Ref. 14). Here the composition corresponds to Ag_3PSO_3 and there remains just a set of distinct PSO_3 tetrahedra above $x=0.3$.

The temperature and composition independence of the power law exponent which was observed in these $x\mathrm{Ag}_2\mathrm{S}-(1-x)\mathrm{AgPO}_3$ system is highly significant and this leads to the composition and temperature independence of the scaling of the conductivity spectra. Scaling is an important feature in any data evaluation. The ability to scale different conductivity isotherms so as to collapse all to one common curve indicates that the process can be separated into a common physical mechanism modified only by temperature scales. An attempt has been made to scale the conductivity spectra for the present systems. Depending upon the type and composition range of the glasses, the appropriate scaling parameters have been considered by different workers[28–30] in different forms. In our approach as suggested by Ghosh and Pan[30] the hopping frequency (ω_c) and dc conductivity (σ_{dc}) was considered as the scaling parameters. The selection of the parameters appears quite justified as the change in hopping length with composition is manifested in the change in the hopping frequency which takes into account the correlation effects between successive hops through the Haven ratio. The results of the scaling of the conductivity spectra at different temperatures is shown in Fig. 9(a) for a glass composition. Figure 9(b) depicts the scaling of the conductivity spectra at a fixed temperature for different glass compositions. The perfect overlap of the spectra for different temperatures and compositions indicates that the ion dynamics is independent of temperature and glass composition in consistence with the temperature and composition independence of the power law exponent. Previously, a scaling law was applied to ionic glasses, in which it was assumed that the mobile ion concentration was proportional to the cation concentration.[28] The present results indicate that such assumption is not valid for the presently studied glasses.

IV. CONCLUSIONS

We have reported the Ag^+ ion dynamics in some Ag_2S-doped silver metaphosphate glasses. The dc conductivity and activation energy of these glasses have been compared with those of the AgI-doped silver metaphosphate glasses. An insight for the comparatively lower conductivity and higher activation energy for the present system than those of the AgI-doped glasses is given by studying the FTIR spectra. From the conductivity spectra we have obtained the concentration of mobile ions and the power low exponent. It is observed that the Ag^+ ion concentration is temperature independent and the conductivity is primarily determined by the mobility. The mobile Ag^+ ion concentration is less than both the total Ag^+ ion concentration as well as the Ag^+ ion concentration estimated from the Ag_2S component. The perfect overlap of the scaled conductivity spectra obtained for different temperatures and compositions indicates that the nature of ion dynamics for these glasses is independent of temperature and Ag_2S content in the compositions.

ACKNOWLEDGMENTS

The financial support for the work by the DAE, India (Grant No. 2002/37/32/BRNS) is thankfully acknowledged.

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*Email address: sspag@iacs.res.in

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