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Dynamics of Ag^+ ions in binary tellurite glasses

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We have reported the ionic relaxation for different compositions of $x\mathrm{Ag_2O}-(1-x)\mathrm{TeO_2}$ conducting glasses in wide temperature and frequency ranges. We have explained the composition dependence of the conductivity and the activation energy in terms of composition-dependent network structure of these glasses. We have compared the results for silver tellurite glasses with those for the alkali (Li,Na) tellurite glasses and observed that the migration of Ag^+ ions in glasses, in general, appears to be anomalous. We have analyzed the frequency-dependent electrical data in the framework of the power-law conductivity formalism. We have explained the decreasing trend of the relaxation time with increasing Ag_2O content in terms of structural transformation of tellurite network. Interestingly, we have observed that the concentration of mobile Ag ions is less than the concentration of total Ag ions and decreases with the increase of silver oxide content in the compositions, while the conductivity increases. We have shown that the scaling of the conductivity spectra is independent of temperature, but depends on composition.

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I. INTRODUCTION

Oxide glasses formed with TeO_2 as a network former possess many interesting physical properties such as low melting point, high chemical durability, high refractive index, and good IR transmittivity, which make them attractive not only from the fundamental point of view, but also for practical applications.[1] The role of modifier oxides in the vitreous transition of tellurite melts is extremely important unlike traditional glass formers such as P_2O_5, SiO_2, etc.[2] Recent studies of alkali tellurite glasses[3–6] reveal that, when alkali oxides are introduced into the tellurite network, different structural units are formed at different alkali oxide contents. The glasses with low alkali content consist of a continuous random network constructed by sharing corners of TeO_4 trigonal bipyramids and TeO_{3+1} polyhedra having one nonbridging oxygen. For glasses with low alkali oxides in the range 20–30 mol %, TeO_3 trigonal pyramids having nonbridging oxygen permeate the whole network. Above 30 mol % of alkali oxides, the glass network consists of TeO_{3+1} polyhedra and TeO_3 trigonal pyramids along with other structural units.[3] Ionic conductivity in alkali tellurite glasses has also been studied.[7–9] These studies indicate high ionic conductivity of the alkali tellurite glasses. Comparatively, silver tellurite glasses have been paid little attention.[10,11] These few studies reveal that, similar to alkali tellurite glasses, silver tellurite glasses also exhibit structural transition from TeO_4 trigonal bipyramids to TeO_3 trigonal pyramids through TeO_{3+1} polyhedra with increasing silver oxide content.[11]

In general, a large number of studies on ionic conductivity and relaxation in alkali oxide glasses have been reported.[12–17] However, no clear consensus on the process has emerged so far. In order to determine the mechanism of ionic conductivity in glasses, it is necessary to separate the contribution of ionic concentration and mobility.[18] Unfortunately, it has not been possible to determine ambiguously the contributions of these two terms separately, although a few methods have been suggested.[19–23] The dependence of the relaxation mechanism on the ionic concentration is another interesting problem. Contradictory results have been reported in the literature.[24–29] In this paper, we have reported the results of electrical measurements for different compositions of the Ag_2O-TeO_2 glasses to shed some light on these problems. Interestingly, we have observed that the mobile Ag ion concentration is less than the total Ag ion concentration and that it is almost independent of temperature, but it depends slightly on composition.

II. EXPERIMENTAL PROCEDURE

Binary glass samples of compositions $x\mathrm{Ag_2O}-(1-x)\mathrm{TeO_2}$, where $x=0.15-0.35$ (mole fraction), were prepared from the reagent grade chemicals $AgNO_3$ and TeO_2 (Aldrich Chem. Co.). The appropriate amounts of $AgNO_3$ and TeO_2 powders were thoroughly mixed and preheated in a platinum crucible at 450 °C for 1 h for calcination and then were melted in the temperature range from 800 to 850 °C depending upon composition. After homogenization for 20 min, the melts were finally quenched between two aluminum plates. Transparent glass samples of thickness ~1 mm were obtained for $x=0.15-0.35$. Density of the glasses was measured using Archimedes' principle. Glass formation was confirmed from x-ray diffraction studies (Rich Seifert, model 3000P). For electrical measurements, gold electrodes were deposited on both surfaces of the polished samples of diameter ~10 mm. The measurements of capacitance and conductance of the samples were carried out in the frequency range 10 Hz–2 MHz using a RLC meter (Quad Tech, model 7600) and in the temperature range 333–493 K.

III. RESULTS AND DISCUSSION

The dc conductivity for different temperatures was computed from the ac complex impedance plots. The variation of the dc conductivity with reciprocal temperature for several

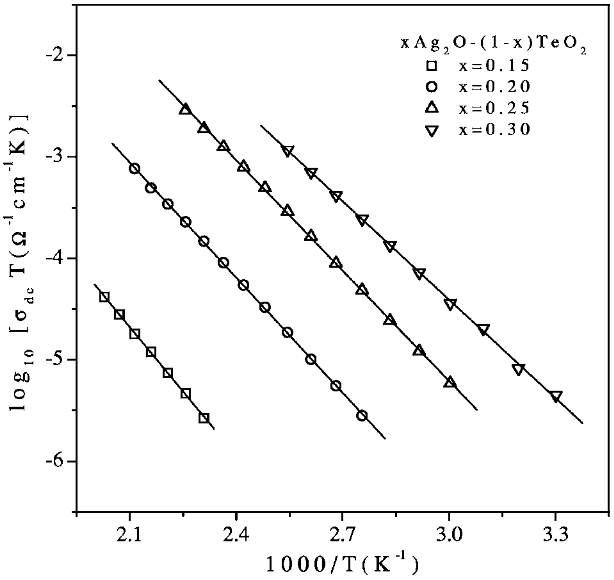

FIG. 1. The dc conductivity shown as a function of the reciprocal of temperature for different compositions (shown) of $x\mathrm{Ag_2O}-(1-x)\mathrm{TeO_2}$ glasses. The solid lines are the least-squares straight-line fits.

compositions of silver tellurite glasses are shown in Fig. 1, which shows that the dc conductivity obeys the Arrhenius relation $\sigma_{dc}T=\sigma_0\exp[-E_\sigma/kT]$. The values of the activation energy obtained from the least-squares straight-line fits are shown in Table I for different glass compositions. The dependence of the dc conductivity at 473 K on the silver oxide content is shown in Fig. 2(a). For comparison, σ_{dc} for alkali (Li,Na) tellurite glasses[9,10] is also included in the figure. It is noted in Fig. 2(a) that the conductivity of silver tellurite glasses is higher than those for the alkali tellurite glasses.[9,10] A comparison of the data for borate and phosphate glasses[30–32] also indicates that silver borate and silver phosphate glasses exhibit higher conductivity compared to those for alkali borate and alkali phosphate glasses, respectively. However, the effect is stronger in tellurite glasses than in borate or phosphate glasses. It is also noteworthy that the silver tellurite glasses exhibit higher conductivity compared to that of silver borate or silver phosphate glasses.[30] Thus, the migration of $\mathrm{Ag^+}$ ions in oxide glasses appears, in general, to be anomalous when crystalline radius is considered.

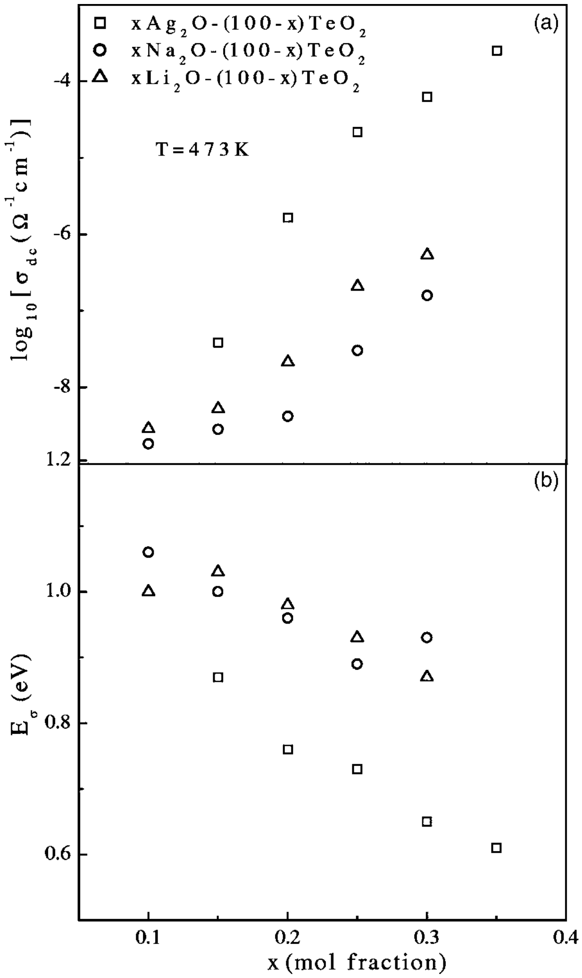

FIG. 2. (a) Comparison of the dc conductivity at 473 K, and (b) dc activation energy of the silver tellurite glasses with those of sodium tellurite (Ref. 9) and lithium tellurite (Ref. 10) glasses for different compositions.

The $\mathrm{Ag^+}$ ions have an apparent radius less than that of $\mathrm{Li^+}$ or $\mathrm{Na^+}$ ions[30] irrespective of glass network formers. Figure 2(b) depicts that the activation energy for silver tellurite glasses is much lower than that for the alkali tellurite glasses[9,10] similar to borate and phosphate glasses.[30–32] Also, the rate of decrease of the activation energy with the increase of $\mathrm{Ag_2O}$ content in the compositions for silver tellurite glasses is

TABLE I. The dc conductivity at 473 K, dc activation energy, ω_h at 473 K, activation energy E_h for ω_h, frequency exponent n for $x\mathrm{Ag_2O}-(1-x)\mathrm{TeO_2}$ glasses.

Mole fraction (x)	$\log_{10}\sigma_{dc}$ at 473 K ($\Omega^{-1}\,\mathrm{cm}^{-1}$) ±(0.01)	E_σ (eV) ±(0.02)	$\log_{10}\omega_h$ at 473 K (rad s^{-1}) ±(0.05)	E_h (eV) ±(0.03)	n ±(0.01)
0.15	−7.41	0.86	4.63	0.82	0.62
0.20	−5.78	0.76	6.43	0.75	0.63
0.25	−4.66	0.73	7.75	0.71	0.64
0.30	−4.20	0.65	8.25	0.63	0.61
0.35	−3.60	0.61	8.92	0.59	0.63

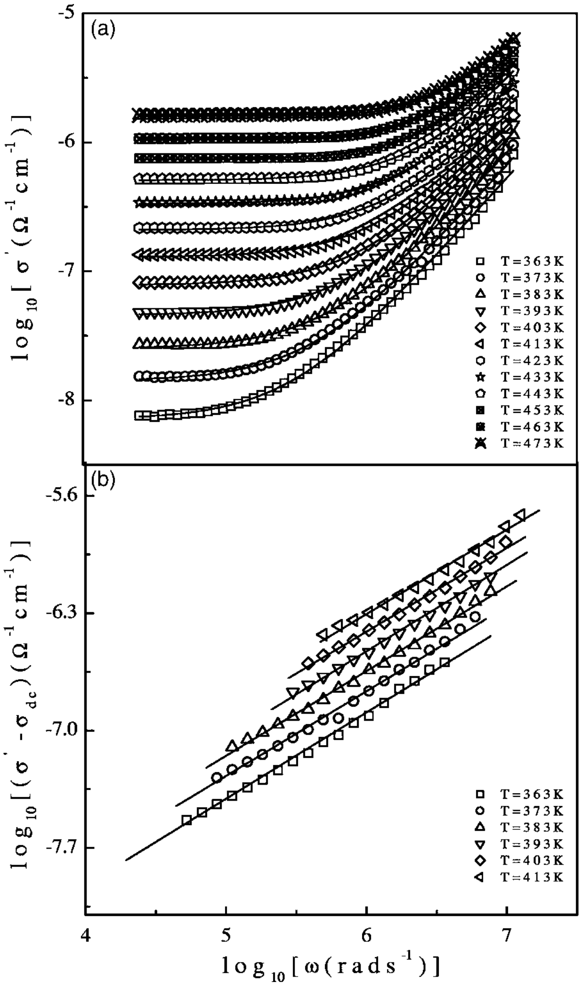

FIG. 3. (a) Conductivity isotherms at different temperatures (shown) for the 0.2 $Ag_2O-0.8$ TeO_2 glass composition as a function of frequency. The solid curves are the best fits to Eq. (1). (b) The dispersive portion of conductivity isotherms obtained for several temperatures by subtracting the dc conductivity from measured total conductivity data.

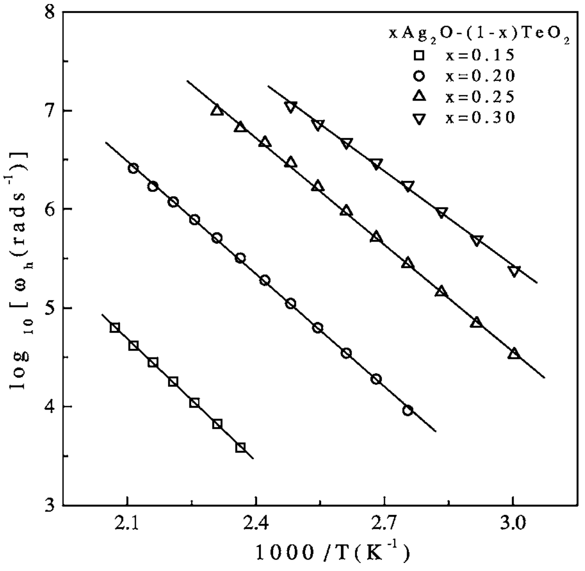

FIG. 4. Reciprocal temperature dependence of ω_h for different compositions (shown) of $x\mathrm{Ag_2O}-(1-x)\mathrm{TeO_2}$ glasses. The solid lines are the least-squares straight-line fits.

lower than the rate of decrease of the activation energy with the increase of alkali oxide content in alkali tellurite glasses. A similar trend was also observed in borate glasses, but not in phosphate glasses.[30,32] It may be noted[3,11,33] that in both tellurite and borate glasses, different structural units exist for different alkali or silver oxide contents. The transformation of the structural units for borate glasses[33] occurs from boroxol to diborate through tetraborate as the alkali or silver oxide content is increased from 0 to 0.30. In the case of tellurite glasses, the transformation occurs from TeO_4 trigonal bipyramids to TeO_3 trigonal pyramids for silver or alkali oxide content between 0 and 0.30.[3,4,11] However, the basic structural units, PO_4 for phosphate glasses, remain the same. It was also observed that the number of nonbridging oxygen increased with increasing alkali or silver oxide content as evinced from the decrease in the glass transition temperature with the increase in alkali or silver oxide contents of these glasses.[8,9] Thus, the structural transformation, as well as the increase in the number of nonbridging oxygen, is responsible for the enhancement of the conductivity with increasing silver oxide content in the tellurite and borate glasses, while the conductivity enhancement for phosphate glasses is solely due to the increasing number of nonbridging oxygen, as no structural transformation occurs for phosphate glasses.

It is well documented[22,23] that in the usual experimental frequency window and temperature range, the overall frequency response of the real conductivity can be described by

$$\sigma'(\omega) = \sigma_{dc}[1 + (\omega/\omega_h)^n], \tag{1}$$

which is the sum of the dc conductivity, σ_{dc}, and a fractional power-law-dependent dispersive conductivity with exponent n. Here ω_h is a characteristic crossover frequency from dc to dispersive conductivity.[22] The exponent n remains temperature independent over a wide temperature range. Both the dc conductivity and the characteristic frequency, above which $\sigma'(\omega) \propto \omega^n$, are thermally activated. However, there is another contribution to the dispersive conductivity, which consists of nearly frequency-independent dielectric loss and corresponds to an almost linear frequency-dependent term of the form $\sigma'(\omega) \propto \omega$ in the real conductivity.[34] At sufficiently high frequencies or low temperatures, the $\sigma'(\omega) \propto \omega$ term dominates over the power-law dependence of $\sigma'(\omega)$ given by Eq. (1). Recently, the above model has been widely used to get an insight into ion dynamics in ion conducting glasses.[34–38]

Typical conductivity isotherms of a glass composition for different temperatures are shown in Fig. 3(a), which exhibits a frequency-independent conductivity (i.e., dc conductivity) at lower frequencies and a dispersive conductivity at higher frequencies. Other glass compositions also showed a similar behavior. The transition from a frequency-independent conductivity to frequency-dependent conductivity indicates the onset of a relaxation phenomenon, which is analyzed here in the framework of the model described above. To ascertain the contribution of the nearly constant loss, we have analyzed the dispersive portion by subtracting the dc conductiv-

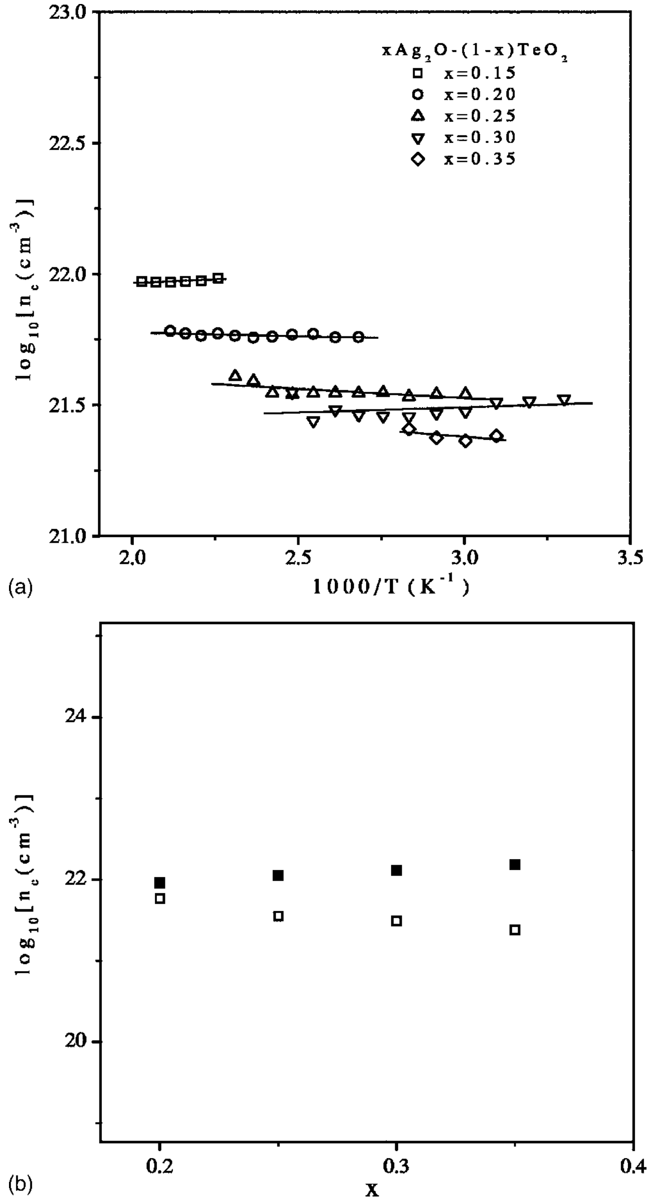

FIG. 5. (a) Reciprocal temperature dependence of concentration of mobile Ag ions for different compositions (shown) of $x\mathrm{Ag_2O}-(1-x)\mathrm{TeO_2}$ glasses. (b) Concentration of mobile Ag ions (open square) and concentration of total Ag ions (solid square) obtained from composition and density shown as a function of composition.

ity from the measured ac conductivity and the results are shown in Fig. 3(b) for several temperatures. We note that in the frequency window of our measurement, the power-law exponent (~0.62) is less than unity and is almost independent of temperature within the experimental errors. Thus, the nearly constant loss region is absent in the investigated frequency and temperature ranges and hence the data can be analyzed by the power-law model given by Eq. (1). We have fitted the frequency isotherms at different temperatures for the different glass compositions to Eq. (1), using σ_{dc}, n, and ω_h as variable parameters. The resulting fits of the data are shown in Fig. 3(a) by solid lines for a glass composition. The quality of curve fitting is considered good, because the fit and the data agreed to within 2% over the entire frequency range for all investigated temperatures. In the curve fitting process, 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.[29] We have noted that the values of the dc conductivity obtained from the fits agreed well with those obtained from the complex impedance plots. The values of ω_h at 473 K are shown in Table I, which shows a decreasing trend in the relaxation time with the increasing $\mathrm{Ag_2O}$ content supported by the structural transformation in tellurite network.[11] For compositions with low $\mathrm{Ag_2O}$ content, a few of the Te-O$^-$ sites are available,[3,11] which makes the $\mathrm{Ag^+}$ ions mobile over a long distance at lower frequencies only, resulting in a large relaxation time. As the content of $\mathrm{Ag_2O}$ is

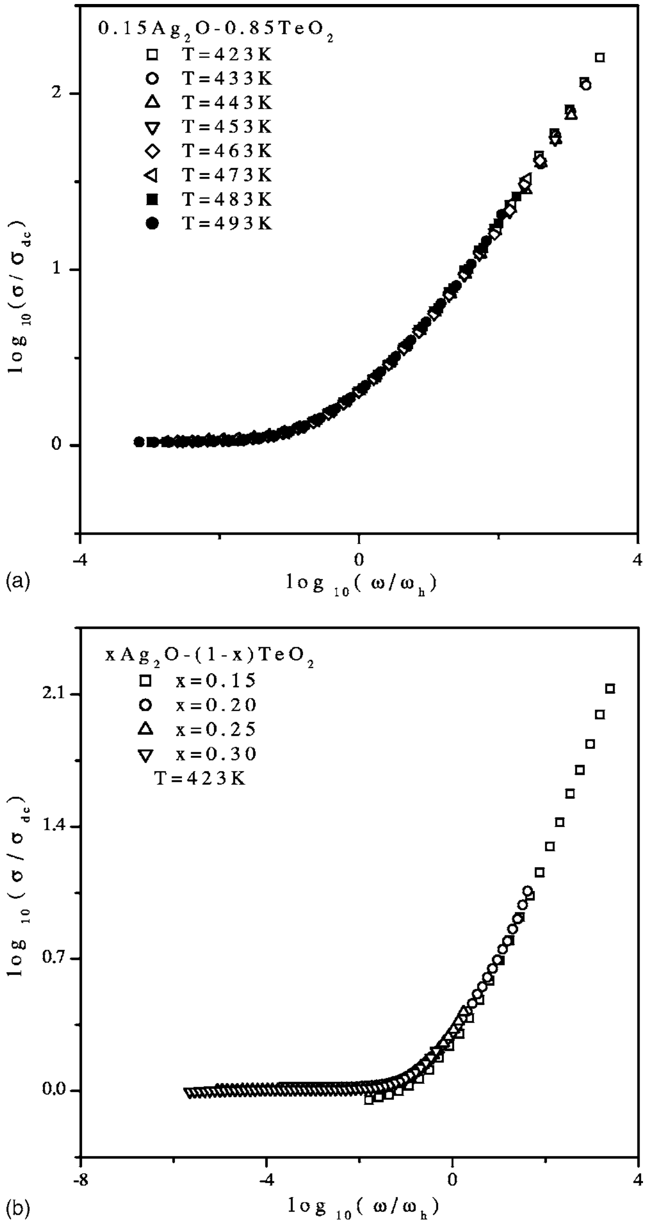

FIG. 6. (a) Scaled conductivity spectra at different temperatures for a glass composition (shown), and (b) scaled spectra at a fixed temperature for different compositions (shown).

increased, more and more nonbridging oxygens are included in the network and consequently the Ag^+ ions remain mobile at higher frequencies making the relaxation time small.

The Arrhenius plots of ω_h obtained from the fits are shown for a glass composition in Fig. 4, which reveals that ω_h is thermally activated. It may be noted that the values of the activation energy E_h (Table I), obtained from the least-squares straight-line fits, are slightly less than the dc activation energy E_σ. It is also noted that the values of the parameter n (Table I) are independent of temperature and composition. Thus the interaction[25] between mobile Ag^+ ions in silver tellurite glasses is almost independent of the silver oxide content in the composition unlike alkali tellurite glasses where an increase of n was observed with the increasing alkali ions.[9,10] We have calculated the concentration of mobile Ag ions in the compositions from the Nernst-Einstein equation

$$\sigma_{dc} = q^2 d^2 n_c \omega_h / 12\pi kT, \tag{2}$$

where n_c and d are the concentration of mobile Ag ions and the jump distance, respectively. Here it has been assumed[23] that the characteristic relaxation frequency ω_h in Eq. (1) is equal to the hopping frequency ω_h in Eq. (2). This approach has been widely used to estimate carrier concentration[23,37,38] and has been verified experimentally recently.[38] Taking the values of d as nearest Ag–Ag distance,[39] the values of the concentration of mobile Ag ions were calculated from Eq. (2). The results are shown in Figs. 5(a) and 5(b), respectively, as a function of reciprocal temperature and composition. The concentration of total Ag ions obtained from glass composition and density is also shown in Fig. 5(b). It is observed in Fig. 5(a) that the concentration of mobile Ag ions exhibits Arrhenius behavior with very small activation energy ($\sim$0.03 eV) compared to the dc activation energy (Table I). Thus the mobility of Ag ions rather than the concentration of mobile Ag ions controls the ion dynamic process. It may be noted in Fig. 5(b) that the concentration of mobile Ag ions is a fraction of the concentration of total Ag ions obtained from the composition and density. Interestingly, it may be further noted that the concentration of mobile Ag ions decreases from 65% to 20% of the total Ag ions as the Ag_2O content is increased from 0.15 to 0.35. It is noteworthy that in alkali tellurite glasses,[9,10] also a fraction of the total alkali ions participate in the dynamic processes. However, the concentration of mobile ions in alkali tellurite glasses is almost constant (about 15%) for all compositions[9,10] and is less than that for the present silver tellurite glasses. These results mean that there are two types of Ag ions in tellurite glasses: one type mobile and the other immobile. The immobile ions are tightly bound to the tellurite networks. The different composition dependence of the mobile ions in these tellurite glasses is not clear at present. Structural studies of these glasses using molecular dynamic simulation can resolve these different behaviors.

Finally, the scaling of the conductivity spectra has been used to get an idea about the dynamics of mobile ions in glasses. We have scaled in Figs. 6(a) and 6(b), respectively, the conductivity spectra at different temperatures for a fixed composition and the same for different compositions at a fixed temperature using the procedure reported earlier.[40] We note that the glasses obey scaling of the conductivity spectra at different temperatures for each composition, indicating that the dynamic process is independent of temperature. However, the scaling of the spectra for different compositions is not valid.

IV. CONCLUSIONS

We have studied the conductivity and relaxation dynamics for different compositions of $x\mathrm{Ag_2O}-(1-x)\mathrm{TeO_2}$ glasses in the frequency range from 10 Hz to 2 MHz and temperature range from 333 to 493 K. The dc conductivity and activation energy of these glasses were compared with those of some alkali (Li,Na) tellurite glasses. The steeper increase of the conductivity with composition for the silver tellurite glass has been explained on the basis of the structural transition from TeO_4 trigonal bipyramids to TeO_3 trigonal pyramids. The decreasing trend of the relaxation time with increasing Ag_2O content was explained in terms of structural transformation of tellurite network. The concentration of mobile Ag ions is less than the total concentration of Ag ions and decreases with the increase of silver oxide content in the compositions. The glasses obey scaling of the conductivity spectra with respect to temperature, but not with respect to composition.

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[1] B. Dubois, H. Aomi, J. J. VIdeau, J. Porter, and P. Hagenmutter, Mater. Res. Bull. **19**, 1317 (1984); C. Prebende, J. F. Cottrani, B. Dubois, J. J. Videau, and J. Porter, Rev. Chim. Miner. **23**, 231 (1986).

[2] S. Noev, V. Kozhukharov, I. Gerasimova, K. Krezhov, and B. Sidzhimov, J. Phys. C **12**, 2475 (1979).

[3] T. Sekiya, N. Mochida, A. Ohtsuka, and M. Tonokawa, J. Non-Cryst. Solids **144**, 128 (1992).

[4] S. Sakida, S. Hayakawa, and T. Yoko, J. Non-Cryst. Solids **243**, 13 (1999).

[5] H. Munemura, K. Mitome, M. Misawa, and K. Maruyama, J. Non-Cryst. Solids **293–295**, 700 (2001).

[6] J. C. McLaughlin, S. L. Tagg, and J. W. Zwanziger, J. Phys. Chem. B **105**, 67 (2001).

[7] G. D. L. K. Jaysinghe, D. Coppo, P. W. S. K. Bandaranayake, and

J. L. Souquet, Solid State Ionics **76**, 297 (1995).

[8] C. S. Sunandana and T. Kumaraswami, J. Non-Cryst. Solids **85**, 247 (1986).

[9] A. Pan and A. Ghosh, Phys. Rev. B **59**, 899 (1999).

[10] A. Pan and A. Ghosh, Phys. Rev. B **60**, 3224 (1999).

[11] J. Dexpert-Ghys, B. Piriou, S. Rossignol, J. M. Reau, B. Tanguy, J. J. Videau, and J. Portier, J. Non-Cryst. Solids **170**, 167 (1994); M. Dimitrova-Pankova, Y. Dimitriev, M. Arnandov, and V. Dimitrov, Phys. Chem. Glasses **30**, 260 (1989).

[12] C. A. Angell, Chem. Rev. (Washington, D.C.) **90**, 523 (1990).

[13] S. R. Elliott and A. P. Owen, Ber. Bunsenges. Phys. Chem. **B95**, 987 (1991).

[14] A. Bunde, M. D. Ingram, and P. Maass, J. Non-Cryst. Solids **172–174**, 1222 (1994).

[15] D. L. Sidebottom, P. F. Green, and R. K. Brow, J. Chem. Phys. **108**, 5870 (1998).

[16] K. Funke, Solid State Chem. **22**, 111 (1993).

[17] P. Maass, M. Meyer, and A. Bunde, Phys. Rev. B **51**, 8164 (1995).

[18] K. L. Ngai, J. Non-Cryst. Solids **203**, 232 (1996).

[19] M. D. Ingram, M. A. Mackenzee, W. Muller, and M. Torse, Solid State Ionics **28–30**, 677 (1988).

[20] Y. Moyamoto, M. Itoh, and K. Tanaka, Solid State Commun. **92**, 895 (1994).

[21] H. J. Scutt, Solid State Ionics **70–71**, 505 (1996).

[22] D. P. Almond, G. K. Duncan, and A. R. West, Solid State Ionics **8**, 159 (1983); Solid State Ionics **9–10**, 277 (1983).

[23] E. F. Hairetdinov, N. F. Uvarov, H. K. Patel, and S. W. Martin, Phys. Rev. B **50**, 13259 (1994).

[24] J. M. Senegas, J. M. Reau, H. Aomi, P. Hagenmuller, and M. Poulain, J. Non-Cryst. Solids **85**, 315 (1985).

[25] H. K. Patel and S. W. Martin, Phys. Rev. B **45**, 10292 (1992).

[26] H. Kahnt, Ber. Bunsenges. Phys. Chem. **95**, 1021 (1991).

[27] K. L. Ngai and S. W. Martin, Phys. Rev. B **40**, 10550 (1989).

[28] K. L. Ngai, J. N. Mundy, H. Jain, O. Kanert, and G. Balzer-Jollenbeck, Phys. Rev. B **39**, 6169 (1989).

[29] D. L. Sidebottom, Phys. Rev. B **61**, 14507 (2000).

[30] R. F. Bartholomew, J. Non-Cryst. Solids **12**, 321 (1973).

[31] S. A. Schtchukares and W. L. Muller, Z. Phys. Chem. Abt. A **150**, 439 (1930).

[32] S. W. Martin and C. A. Angell, J. Non-Cryst. Solids **83**, 185 (1986).

[33] J. Krogh-Moe, Phys. Chem. Glasses **6**, 46 (1965).

[34] W. K. Lee, J. F. Liu, and A. S. Nowick, Phys. Rev. Lett. **67**, 1559 (1991).

[35] D. L. Sidebottom, P. F. Green, and R. K. Brow, Phys. Rev. Lett. **74**, 5068 (1995).

[36] C. Leon, A. Rivera, A. Varez, J. Sanz, J. Santamaria, and K. L. Ngai, Phys. Rev. Lett. **86**, 1279 (2001).

[37] M. Sural and A. Ghosh, Phys. Rev. B **61**, 8610 (2000).

[38] M. M. Ahmad, K. Yamada, and T. Okuda, Solid State Ionics **167**, 285 (2004).

[39] J. Swenson, L. Borjesson, R. L. McGreevy, and W. S. Howells, Phys. Rev. B **55**, 11236 (1997).

[40] A. Ghosh and A. Pan, Phys. Rev. Lett. **84**, 2188 (2000).