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A.c. conductivity studies on the silver molybdo-arsenate glassy system

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A new quaternary fast-ion conducting silver molybdo-arsenate [$AgI–Ag_2O–(MoO_3 + As_2O_5)$] (SMA) glassy system has been prepared using the melt-quenching technique for various dopant salt (AgI) concentrations by fixing the formers ($MoO_3 + As_2O_5$) composition and the modifier (Ag_2O) to formers (M/F) ratio. The prepared compounds were characterized by X-ray diffraction. The impedance measurements were made on different AgI compositions of the SMA glasses as a function of frequency (6.5 Hz–65 kHz) and temperature (303–343 K), using the Solatron frequency-response analyser (model 1250). The bulk conductivity and the appropriate physical model (equivalent circuit) of the SMA glass were obtained from the impedance analysis. The a.c. conductivity was calculated for different AgI compositions of SMA glasses at various temperatures and the obtained a.c. conductivity results were analysed using Jonscher's Universal Law. The conduction mechanism for the highest conducting SMA glassy compound has been explained using the diffusion path model.

1. Introduction

Fast-ion conducting compounds are receiving more attention owing to their applications towards solid-state ionic devices [1, 2]. Among the various forms of available fast-ion conducting (FIC) systems, glassy FICs have many advantages over their respective crystalline counterparts, such as isotropic properties, inertness to the atmosphere, high ionic conductivity at ambient conditions, etc. Many types of FIC glassy systems are being synthesized, of which silver-based FIC glasses are found to have higher ionic conductivity, greater ease of preparation, better stability towards temperature and atmosphere, etc., over other FIC glasses [1–5]. The glassy FIC solids have a complex chemical composition, which can be expressed as (a) glass (network) former, (b) glass (network) modifier and (C) dopant salt. The general formula for the ternary oxide-based FIC glassy systems can be written as $MX + M_2O + A_mO_n$, where $MX = AgI$, LiI, NaI, CuI, etc., $M_2O = Ag_2O$, Li_2O, Na_2O, Cu_2O, etc., and $A_mO_n = P_2O_5$, As_2O_5, V_2O_5, Nb_2O_5, B_2O_3, As_2O_3, etc. [6, 7]. Recently, it was found that the addition of one more glass-forming oxides to the ternary compound enhances the conductivity by an order of one or two magnitudes and improves the glass-forming region [2, 6–8]. This is known as the mixed formers effect and the compounds are called quaternary systems. Hence, we have selected a silver-based quaternary FIC system with two glass formers (hexavalent and pentavalent). In our earlier work, we prepared various formers compositions, x, and different modifier to formers ratios (M/F) of compounds for a fixed dopant salt concentration, and electrical conductivity studies were carried out. The formers composition $x = 0.6$ and the ratio $M/F = 1.75$ of the SMA system were found to show the highest conductivity at room temperature and the results are reported elsewhere [9]. In the present paper, we report the a.c. conductivity studies of the quaternary silver molybdo-arsenate (SMA) glassy system. The observed a.c. conductivity results have been analysed by using Jonscher's Universal law [10].

2. Experimental procedure

2.1. Sample preparation

Analar grade of AgI, Ag_2O, MoO_3 and As_2O_5 chemicals were taken according to their molecular weight percentages and mixed in different compositions. The mixtures were melted separately at 500 K and the homogeneous melts were quenched in liquid nitrogen to form glasses. The SMA glasses were prepared for

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different dopant salt (AgI) contents by using the following expression

$$D\%\,\mathrm{AgI} - (100 - D)\%\ [\mathrm{M}\%\,\mathrm{Ag_2O} - \mathrm{F}\%\ (0.6\,\mathrm{MoO_3} + 0.4\,\mathrm{As_2O_5})] \qquad (1)$$

where $D\% = 20\% - 80\%$ in steps of 10, $\mathrm{M} + \mathrm{F} = 100 - D\%$ and $\mathrm{M/F} = 1.75$ values were fixed from previous studies [9].

2.2. Characterization

The obtained bulk SMA compounds were made into fine powders and used for characterization by X-ray diffraction. For all the compositions of SMA compounds, diffractogram spectra were recorded using the Philips X-ray generator (model-1140) with CuK_2 radiation of wavelength, $\lambda = 0.154\,18$ nm for 2θ values between 10° and 70° at a rate of $2°\,\mathrm{min}^{-1}$. The peak-free diffractogram spectra confirm that the prepared SMA compounds, up to 60% AgI, are glassy in nature.

2.3. Impedance measurements

A Solatron frequency-response analyser (model 1250) aided with an electrochemical interface (model 1286) and an HP computer (model 9122) were used to measure the impedance in the frequency range 6.5 Hz –65 kHz at room temperature as well as at different temperature (303–343 K) on the pressed pellets of SMA glasses with silver electrodes. For the temperature variation of impedance measurements, the sample was kept inside the furnace with resistive heating, and the temperature was controlled by a temperature controller (Century Instruments, model 806) with an accuracy of ± 1 °C. External effects due to lead connections, etc., were carefully minimized.

3. Results and discussion

3.1. Impedance/admittance analysis

The real, Z', and imaginary, Z'', parts of the impedance data were measured directly for all dopant salt concentrations of SMA glassy samples. Fig. 1 shows the Z'' versus Z' plots plotted on a complex

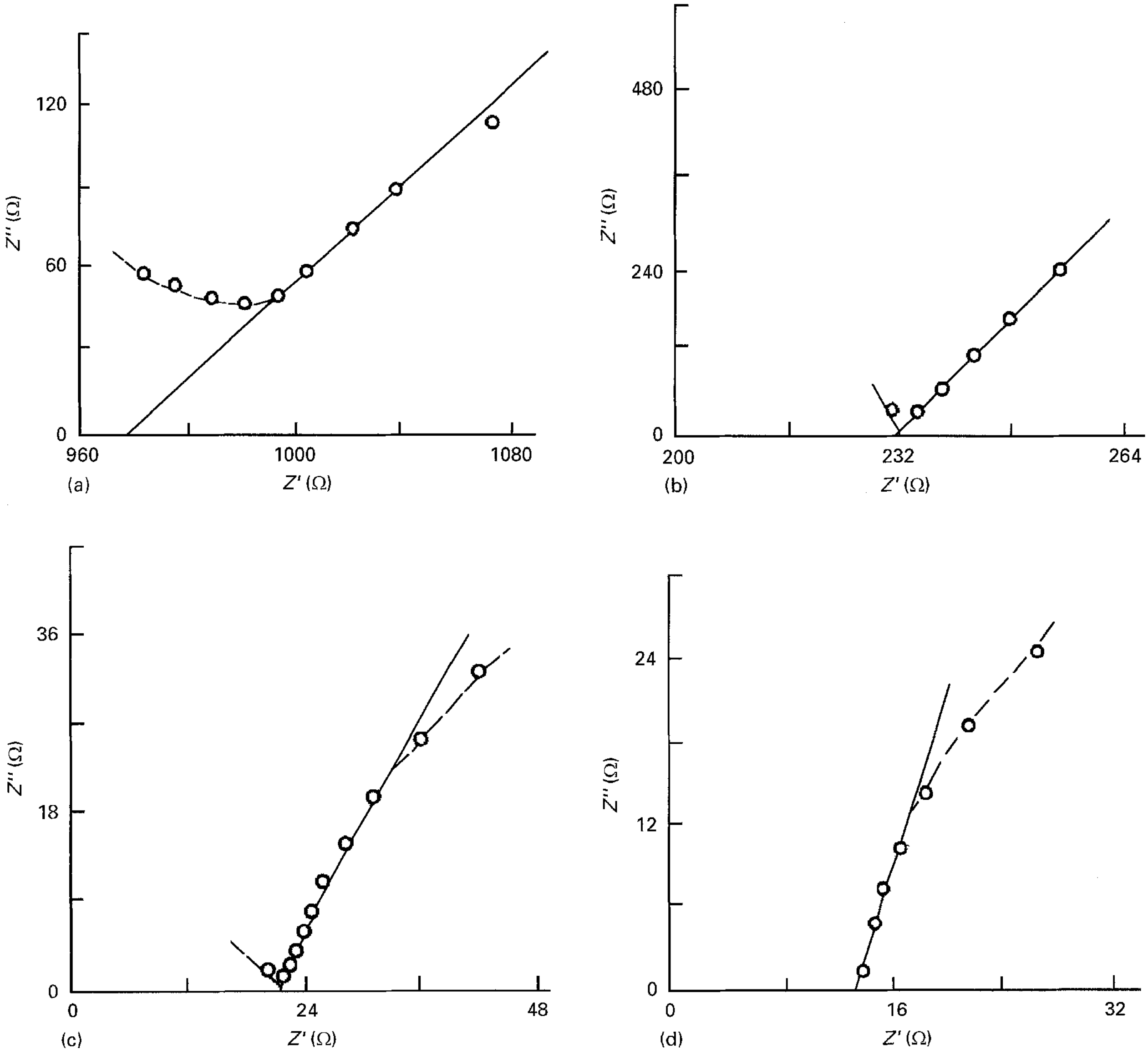

Figure 1 Complex impedance plots (at 303 K) for different AgI contents in the SMA glassy system. (a) 30%, (b) 40%, (c) 50%, (d) 60%.

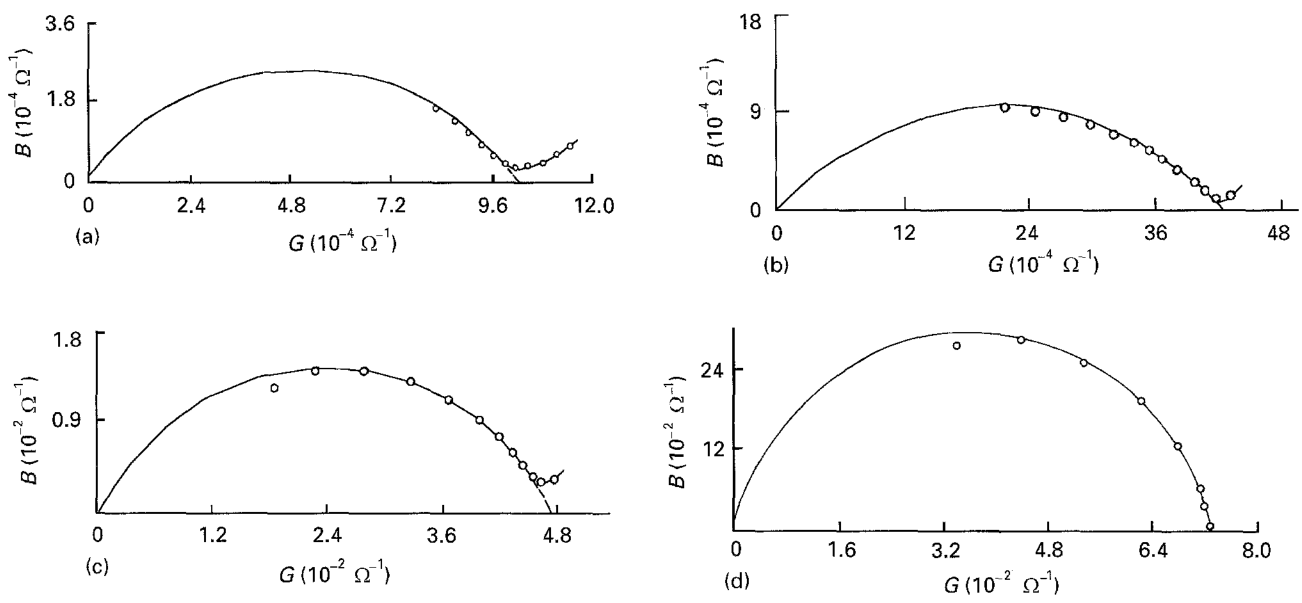

Figure 2 Admittance plots (303 K) for different AgI contents in the SMA glassy system. (a) 30%, (b) 40%, (c) 50%, (d) 60%.

impedance plane for different dopant salt (AgI) concentrations (i.e. low-conducting to high-conducting glasses) of SMA system. The high-conducting samples give a low-frequency straight line in the impedance plot with a slight or no formation of a high-frequency semicircular arc, while low-conducting samples show a low-frequency straight line with a clear formation of high-frequency semicircular arc. The impedance data were transformed into complex admittance, Y^*, using the following expression

$$\begin{aligned} Y^* &= 1/Z^* \\ &= G + jB \end{aligned} \tag{2}$$

where G is conductance and B is susceptance.

The admittance data plotted as B versus G on a complex admittance plane for various dopant salt content of SMA glasses are shown in Fig. 2. The admittance plots for the high-conducting samples exhibit a clear low-frequency semicircle and slight or no formation of a straight line at the high-frequency side, while for the low-conducting samples, a low-frequency semicircular arc and a high-frequency straight line are observed in the admittance plots.

The bulk resistance, R_b, for all the glassy samples was evaluated from the intersection of the fitted semicircle/straight line in the admittance/impedance plots, respectively. From the deduced R_b values, the conductivity has been calculated for the different AgI concentrations of SMA glasses and Fig. 3 gives the variation of conductivity with AgI content obtained at room temperature for the SMA glass. From Fig. 3, it is observed that the conductivity increases with AgI content, up to 60%, in the SMA glass. Table I gives the AgI composition, bulk conductivity and activation energy for the migration of silver ions in the SMA glassy matrix, obtained from the complex plane analysis. From Table I, it is clear that the conductivity values obtained for different AgI concentrations in the SMA glass are comparable to the conductivity values that are obtained from the fixed frequency measurements [9].

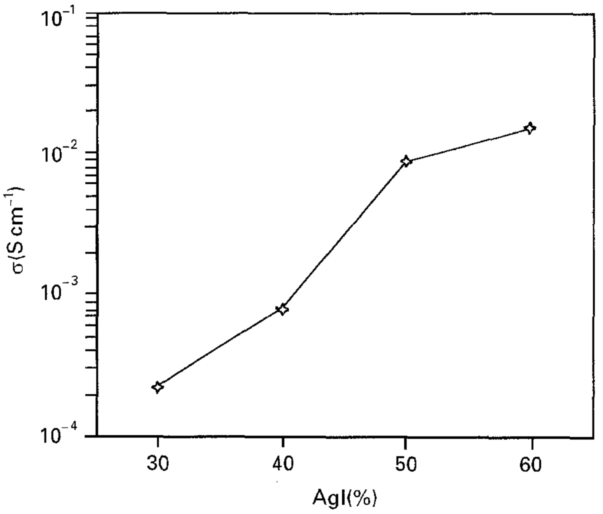

Figure 3 Conductivity obtained from the impedance measurement at room temperature as a function of AgI content in the SMA glassy system.

TABLE I AgI composition, bulk conductivity and activation energy of SMA glassy system

AgI composition (%)	Conductivity at 303 K (S cm^{-1})	Activation energy (eV)
30	2.19×10^{-4} (3.36×10^{-4})[a]	0.38 (0.38)[a]
40	8.01×10^{-4} (6.08×10^{-4})	0.34 (0.36)
50	8.68×10^{-3} (4.00×10^{-3})	0.33 (0.35)
60	1.47×10^{-2} (1.65×10^{-2})	0.30 (0.35)

[a] The values in parentheses were obtained at 1 KHz [9].

From Figs 1 and 2, the high-frequency semicircle in the impedance plot (or a straight line in the admittance plot) is characteristic of a parallel combination of a capacitor and a resistor, respectively, which are bulk capacitance, C_b, and bulk resistance, R_b, of the material [11–14]. The low-frequency straight line in the impedance plot (or a semicircle in the admittance plot) is characteristic of a double-layer capacitance, C_{dl}, at the electrolyte/electrode interface [14, 15]. The glasses are isotropic materials and have almost negligible grain-boundary resistance, R_{gb}, and no capacitance, C_{gb}. It was also reported that the grain size does not affect the bulk conductivity of the FIC glassy materials [8]. Therefore, the present results are worked out by assuming the following equivalent circuit: a parallel combination of C_b and R_b followed by a double-layer capacitance, C_{dl}, in series. The appropriate physical model (equivalent circuit) of the SMA glass is shown in Fig. 4a.

The semicircles of the admittance plots have their centres under the real axis of the complex plane and pass quite close to the origin of the plane. The straight line connecting the origin of the complex plane to the centre of the semicircle formed an angle of about 15°– 20° with the real axis; such distortion is probably due to the existence of asymmetry between the electrode/electrolyte interfaces [15, 16]. This is also visible from the inclination of the low-frequency straight line in the impedance plots. Further, the centres of the high-frequency semicircle of the impedance plots are depressed below the real axis (or the corresponding high-frequency straight line in the admittance plots are inclined at an angle and are not vertical). These results indicate that the relaxation time is not a single value but it is distributed around a mean value [16]. These observations suggest the presence of constant phase elements (CPE), because the properties of the glassy materials are themselves distributed. The CPE at the electrode–electrolyte interface represents the effects of double-layer capacitance, C_{dl}, and other effects [14–16]. Hence, the appropriate physical (equivalent circuit) model of the SMA glassy system is shown in Fig. 4b.

The admittance data were obtained at different temperatures for all the glassy compounds and Fig. 5 shows the B versus G plots obtained at different temperatures for the highest conducting composition of the SMA glassy system. The temperature dependence of bulk conductivity was calculated for all AgI compositions of compounds and Fig. 6 shows the log (σT) versus $1000/T$ plot for the highest conducting composition of the SMA glassy system. The temperature dependence of bulk conductivity obeys the Arrhenius behaviour i.e. $\sigma = \sigma_0 \exp(-E/KT)$, where σ_0 is the pre-exponential factor, K the Boltzmann constant, T the absolute temperature and E the energy required to migrate the ion. The activation energy was calculated from the log (σT) versus $1000/T$ plot and it was comparable with that obtained by fixed frequency studies (shown in Table I).

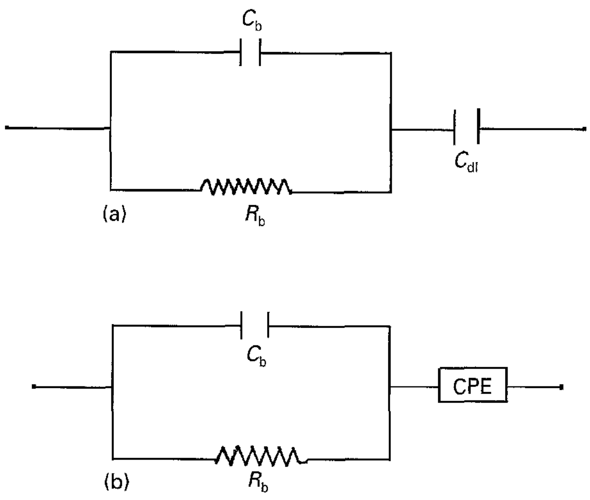

Figure 4 Equivalent circuit for the observed impedance/admittance plots in the SMA glassy system.

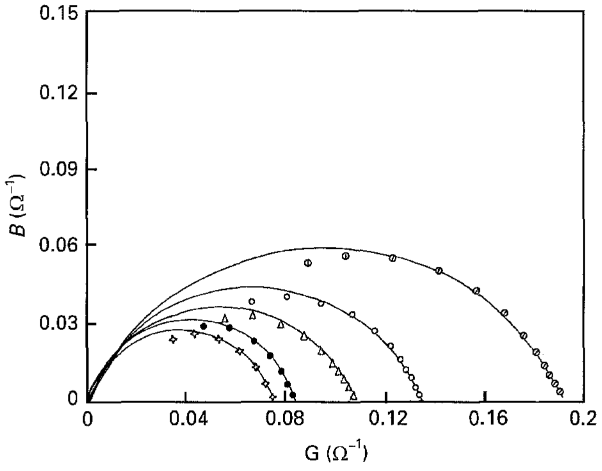

Figure 5 Admittance plots obtained at different temperatures for the high-conducting SMA glassy system. (☆) 303 K, (●) 313 K, (△) 323 K, (○) 333 K, (⦶) 343 K.

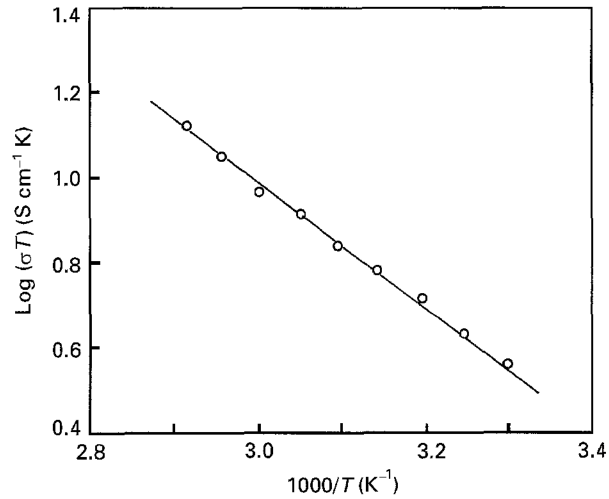

Figure 6 Log σT versus $1000/T$ plot of bulk conductivity for the highest conducting composition of SMA glass.

3.2. A.c. conductivity analysis

The frequency dependence of conductivity calculated for different dopant salt (AgI) concentration in the glasses of SMA system is shown in Fig. 7. Over the full frequency range (6.5 Hz–65 kHz), the studied glasses exhibited two regions: (1) a low-frequency dispersive, and (2) a flat high frequency. The frequency dependence of conductivity at different temperatures, calculated for the highest conducting composition of the

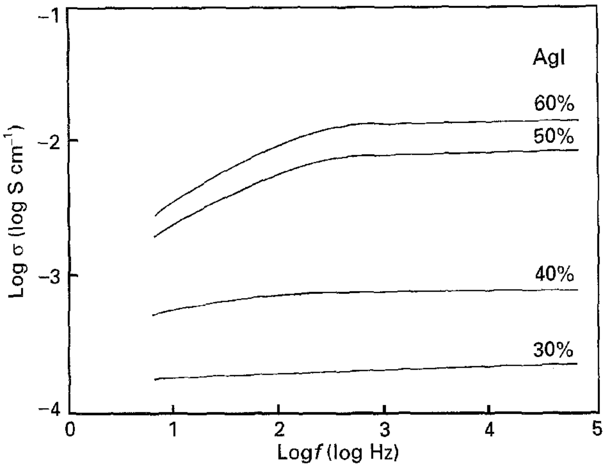

Figure 7 Frequency dependence of conductivity for various dopant salt contents in the SMA glassy system.

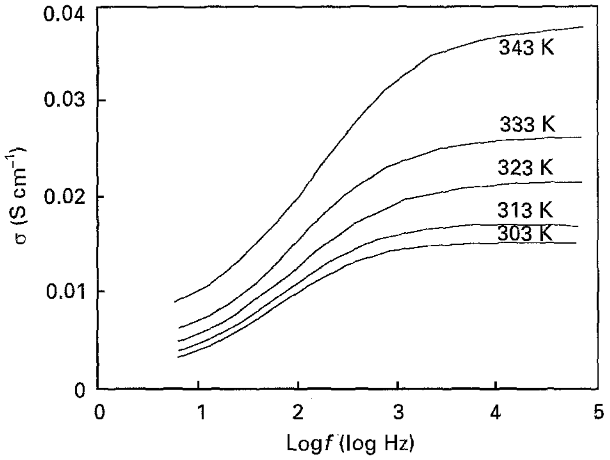

Figure 8 Frequency-dependent conductivity obtained at various temperatures for the highest conducting composition of the SMA glassy system.

SMA glassy system, is shown in Fig. 8. From Fig. 8, it is clear that the frequency dependence of conductivity shows dispersive and flat regions. The phenomenon of dispersion in the a.c. electrical conductivity is discussed below. The dispersion in the a.c. electrical conductivity manifests itself in the following form

$$\sigma(\omega) = \sigma(0) + A\omega^s \quad (3)$$

where, $\sigma(0)$ is the d.c. (or low-frequency) conductivity, A is a constant and s is the power-law exponent (which lies in the range $0 < s < 1$). The above expression is known as the power law of a.c. behaviour. Because the power law of a.c. behaviour is observed in a wide range of materials, Jonscher called it "Universal Behaviour" [10, 17]. In the time domain, the above equation is equivalent to

$$\phi(t) = \exp(-t/\tau)^{1-s} \quad (4)$$

where, $\phi(t)$ is the decay current and τ is the non-Debye-type relaxation time. The above expression is known as a "stretched exponential" or as the Kohlrousch–Williams–Watts (KWW) expression [18, 19].

Recently, Almond and West [20, 21] have suggested that the power-law behaviour can be expressed as

$$\sigma(\omega) = \sigma(0)\,[1 + (\omega\tau)^s] \quad (5)$$

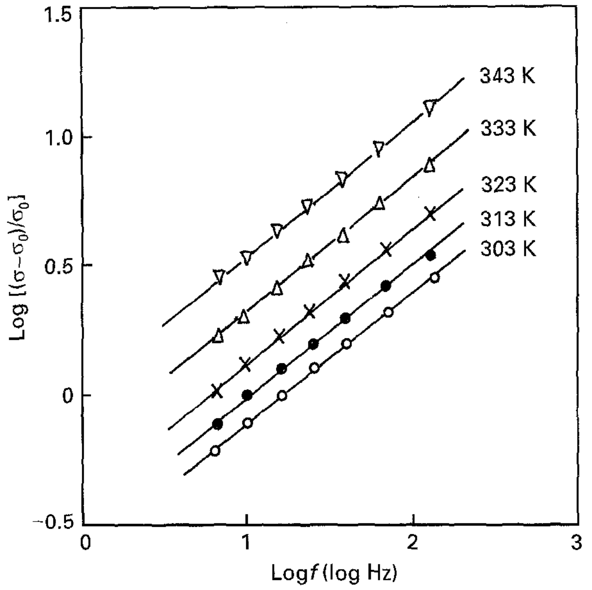

Figure 9 The $[\sigma(\omega) - \sigma(0)]/\sigma(0)$ versus frequency plot of SMA glass.

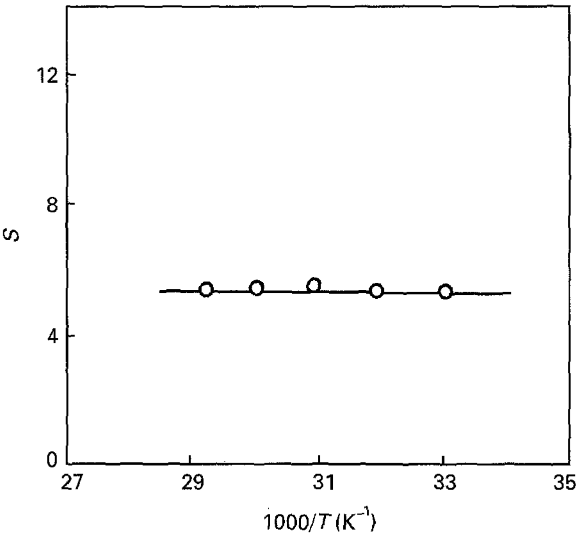

Figure 10 Power-law exponent as a function of temperature of the SMA glassy system.

The above equation was used for the analysis of a.c. conductivity in the present study. In the dispersive regime, relaxation time, τ, is conveniently obtained as the reciprocal of frequency at which $\sigma(\omega) = 2\sigma(0)$. The $\sigma(0)$ value is obtained by extrapolating and conductivity value to the lower frequency side [22]. A plot of $[\sigma(\omega) - \sigma(0)]/\sigma(0)$ versus frequency is shown in Fig. 9. The τ and s values are estimated, respectively, from the intercept and slope of $[\sigma(\omega) - \sigma(0)]/\sigma(0)$ versus frequency plot. The exponent s values thus obtained at different temperatures are shown in Fig. 10 and are found to be almost constant over the temperature range 303–353 K for SMA glasses. The s values for all the compositions of SMA glasses were found to be less than 1.0 and these are in good agreement with the s values reported by Jonscher [10, 17].

The relaxation time, τ, is strongly temperature dependent [23] and exhibits Arrhenius behaviour

$$\tau = \tau_0 \exp(E_\tau/kT) \quad (6)$$

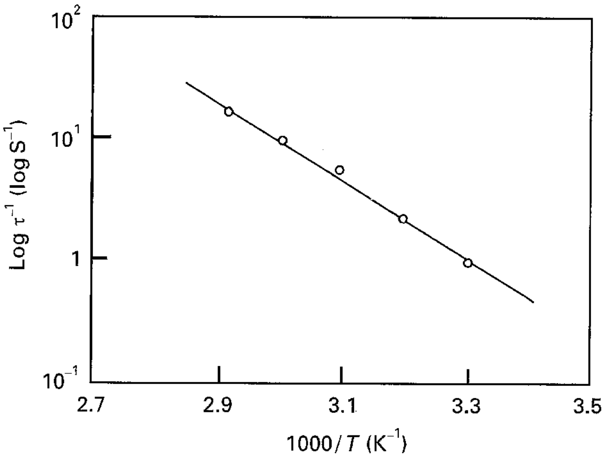

Figure 11 τ versus 1000/T plot of the SMA glass.

where τ_0 is the pre-exponential of the relaxation time and E_τ the activation energy for relaxation. The temperature dependence of the relaxation time is shown in Fig. 11. The activation energy, E_τ, for relaxation and pre-exponential of the relaxation time, τ_0 (hopping rate), are obtained from the log τ versus 1000/T plot. The τ_0 value falls in the range of 10^{-13} s and the order of this value is in good agreement with the hopping rate of Ag^+ ions obtained from many other silver-based systems [23]. Thus, it can be concluded that the Almond and West relation holds good for the glasses studied in the present investigation. The significance of this result appears to be that the a.c. (relaxation effect) and the d.c. conductivities are closely coupled through ion–ion interactions in the hopping process.

3.3. Conduction mechanism

The observed variation of conductivity with the AgI content in the SMA glass can be explained as follows. In the present SMA system, the M/F ratio and the glass formers composition are fixed and only the dopant salt (AgI) concentration is varied. While varying the dopant salt (AgI) content in the SMA glass, the conductivity changes are observed for about three orders of magnitude, as shown in Fig. 3. Further, the activation energy obtained from the slopes of log(σt) versus 1000/T plot for the migration of Ag^+ ions decreases with AgI content in the SMA glass and it is found to be minimum for the highest conducting composition. The Ag^+ ion concentration due to AgI, Ag_2O and the total Ag^+ are calculated with AgI content in the glass [9, 13]. While increasing the AgI content, the Ag_2O content is decreased in the compound and hence, the Ag^+ ion concentration due to AgI increases, whereas that from Ag_2O decreases. Although, the total Ag^+ ion concentration is found to be almost constant with the AgI variation, a change in conductivity of three orders of magnitude is observed. This suggests that the increase in conductivity is not governed by the total Ag^+ ion concentration in the glass.

Further, the infrared structural studies of the SMA and other silver-based glasses showed that the glassy network is not significantly modified by the addition of dopant salt (AgI) [24, 25]. Hence, it is confirmed that the dopant salt is only dispersed in between the glass network in a disorderly manner. Based on the observed results, the variation of conductivity with the AgI content in the SMA glass could be explained qualitatively using the diffusion path model [26].

In the diffusion path model, the fact that only a fraction of the Ag^+ ions contribute to the conduction and the mobility depends on glass composition, can be explained in terms of the coexistence of two types of anion potentials, namely iodide and oxide. Hence, two distinct populations of Ag^+ ions exist in the glass, i.e. mobile Ag^+ ions associated with the iodine anion, and immobile Ag^+ ions bonded to the non-bridging oxygen (NBO) anions. Further, the interaction of Ag^+ ions with the iodide anions will form shallow and wide potentials and the interaction of the Ag^+ ions with the non-bridging oxygens (NBOs) will form deep and narrow potentials. Hence, mobile ions require less energy to migrate from one potential to another, whereas, immobile ions require a higher energy for the migration of silver ions. From Table I it is observed that the activation energy obtained for the highest conducting composition of the SMA glass is found to be minimum. Thus, the carrier concentration must depend on how many Ag^+ ions are located in the shallow wells and the mobility must depend on how long the shallow wells are connected. When the shallow wells are connected for a long period, they form a path favorable for ion transport with less activation energy. Thus, the mobile Ag^+ ions easily diffuse through the shallow potential paths. Such paths are referred to as diffusion paths. Hence, the conduction mechanism for the observed highest conducting composition of the SMA glass could be well explained qualitatively, using the diffusion path model.

4. Conclusion

X-ray diffraction spectra confirmed that only 30%–60%, in steps of 10%, of AgI content of SMA compounds prepared from the melt-quenching method were glassy in nature. The true bulk conductivity and the appropriate physical (equivalent circuit) model of the SMA glass were obtained from the impedance/admittance analysis. The 60% AgI–25.45% Ag_2O–14.55% ($0.6MoO_3 + 0.4As_2O_5$) composition of the SMA glassy compound was found to have the highest conductivity. The activation energy for the mobile charge carriers was estimated for all the AgI compositions and it was found to be minimum for the highest conducting composition of the SMA glass. The frequency dependence of conductivity could be analysed well using Jonscher's Universal Law and the modified expression given by Almond and West. The observed results suggested that the prepared SMA glasses exhibit a non-Debye type of relaxation. Finally, the conduction mechanism for the highest conductivity composition of the SMA glass could be explained on the basis of diffusion path model.

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