Transport Studies on Silver Borotungstate Glasses

R. V. G. K. Sarma and S. Radhakrishna

*Department of Physics, Indian Institute of Technology,
Madras 600 036 India*

The effect of mixing two glass formers, B_2O_3 and WO_3, on the conductivity characteristics was investigated for the silver borotungstate glasses. The dependence of glass transition temperature T_g and conductivity on the composition was presented. The electronic conductivity was measured using Wagner's polarization technique. The glass formation region was established. © 1991 Academic Press, Inc.

Introduction

In recent years, researchers have become increasingly interested in fast ion conducting glasses because of their use in various applications like energy storage, analog memory devices, electrochemical capacitors, and electrochromic displays. Ionically conductive glasses have advantages over their crystalline counterparts (1). The quest for an inorganic vitreous electrolyte with high conductivity and high glass transition temperature has resulted in new types of superionic glasses. This has been achieved by adding more than one glass former to the glass modifier. Though a lot of literature is available on vitreous domain, conductivity characteristics, and glass transition temperatures of ternary glasses, few reports are available on quaternary superionic glasses (which consist of more than one glass former) (2–6).

Recently Chiodelli *et al* (7) reviewed the published data on the relationship between glasses having a single glass former and those having a competitive network formation (having more than one glass former).

The authors conclude that quaternary systems cannot be characterized by the same rules that are applicable to ternary systems. For example, the properties like conductivity and glass transition temperature varied nonlinearly in silver borophosphate systems with the ratio $B_2O_3/B_2O_3 + P_2O_5$.

In the present communication, we present the effect of mixing the two glass formers B_2O_3 and WO_3 on the conductivity characteristics, vitreous domain, and glass transition temperature in the system $AgI–Ag_2O–B_2O_3–WO_3$.

Experimental

Stoichiometric amounts of AgI, Ag_2O, B_2O_3, and H_2WO_4 were taken in an open quartz crucible and heated up to 650°C in a furnace. The open crucible method has been adopted instead of the normal method (in which the compounds are vacuum sealed), because of the more complete formation of glass, as a consequence of the faster quenching rates. The higher quenching rate is achieved because of the melt coming into direct contact with the liquid nitrogen col-

umn. In this process the melt spreads out, resulting in an increased surface area of contact with the coolant. Constant stirring is adopted to have a homogeneous melt. The resulting melt was quenched on a aluminum plate.

The glasses formed by quenching the melt were pulverized and the X-ray studies were performed on these powders using Philiphs Model 1140 X-ray generator using CuK radiation of wavelength $\lambda = 1.5415$ Å at a scanning rate of 2°/min.

The electrical conductivity measurements were performed on the compressed pellets of 1.3 cm diameter pressed at a pressure of 5000 kg/cm² using a Perkin–Elmer hand press. The electrodes were made up of silver powder and the electrolyte mixture in the ratio 1 : 1, to reduce the interfacial resistance, and also to increase the interfacial surface area. The conductivity measurements were performed using a GR 1650 B model bridge at 1 kHz.

Electronic conductivity measurements were carried out on Wagner's polarization cell of the type (−) Ag/sample/ graphite (+) (8). Various dc potentials less than the decomposition potential of the electrolyte were applied and the corresponding currents after the steady state were noticed using a Keithley 610 C electrometer. The glass transition temperature measurements were carried out using a Stanton Redcroft instrument at a heating rate of 10 K/min.

Thermoelectric power measurements were carried out on the cell configuration Ag (T)/Electrolyte/Ag (T + Δ T) with T equal to 10 K. The ambient temperature was raised by an external heater and the temperature gradient was maintained by a small subheater. The temperature at the two faces was recorded by an iron constantan thermocouple. The temperature of the sample was taken as the average of the two readings. The readings were taken after a thermo emf was stabilized. Silver wires were connected from the silver disks to the electrometer to
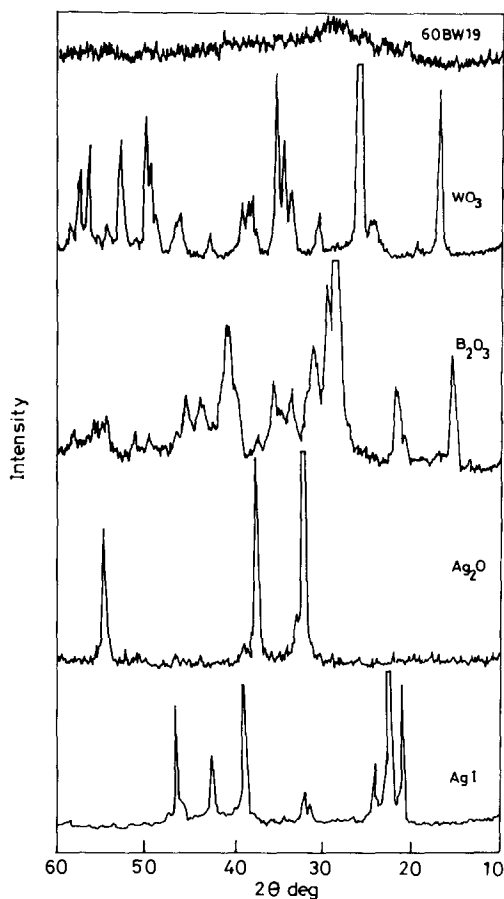

FIG. 1. X-ray diffraction patterns of AgI, Ag₂O, B₂O₃, WO₃, and silver borotungstate glass.

reduce the inhomogeneous contribution to the thermo emf from the leads. The sample holder was kept inside a glass tube which was evacuated to 10^{-2} Torr.

Results and Discussion

The amorphous nature of the compounds has been confirmed by the X-ray diffraction technique. Figure 1. shows the typical X-ray diffraction patterns of AgI, Ag₂O, B₂O₃, WO₃, and silver borotungstate glass. The peak free diffraction pattern in the figure

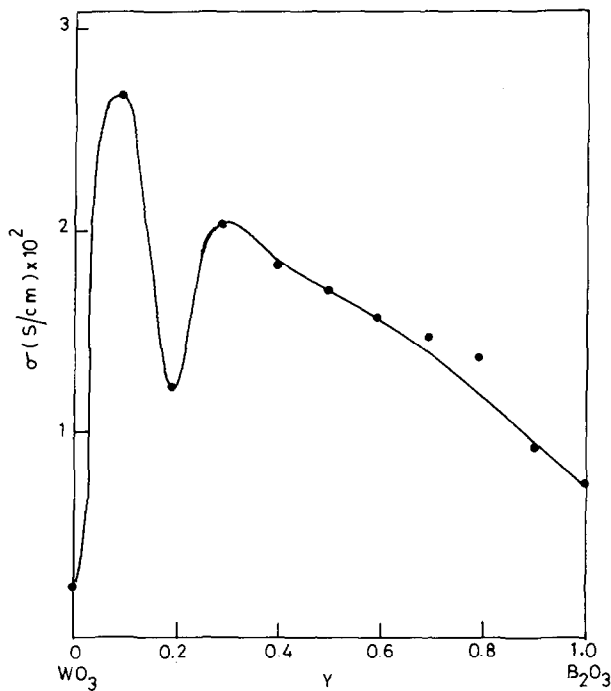Fig. 2. Room temperature conductivity variation with Y for 60 AgI–20 Ag$_2$O–20 [xB$_2$O$_3$–(1 − x)WO$_3$] glasses.

confirms the amorphous nature of the compounds.

Conductivity Studies

To arrive at the maximum conducting composition the following procedure was adopted. The following parameters have been defined for the sake of convenience.

The ratio between the glass former to the total glass former content,

$$Y = B_2O_3/B_2O_3 + WO_3.$$

The ratio between the glass modifier to the total glass former content,

$$N = Ag_2O/B_2O_3 + WO_3.$$

Figure 2. shows the variation of room temperature conductivity with Y in the system 60 AgI–20 Ag$_2$O–20 [xB$_2$O$_3$–(1 −

x)WO$_3$]. It is seen from the graph that the conductivity goes through two maxima when $Y = 0.1$ and $Y = 0.3$, with the former peak being more prominent. Conductivity is a nonlinear function of Y, which might be the effect of the structure of the glass on the conductivity. The appearance of the maxima can be explained as follows. The conductivity can be given by

$$\sigma = n\,e\,\mu,$$

where n is the charge concentration, e is the charge of mobile ion, and μ is the mobility. It is already established that silver ions are mobile species in all silver ion conducting glasses (our TEP results also confirms this result) (*9, 10*). Moreover, the carrier concentration is fixed by the amount of AgI present in the vitreous matris. Thus, charge
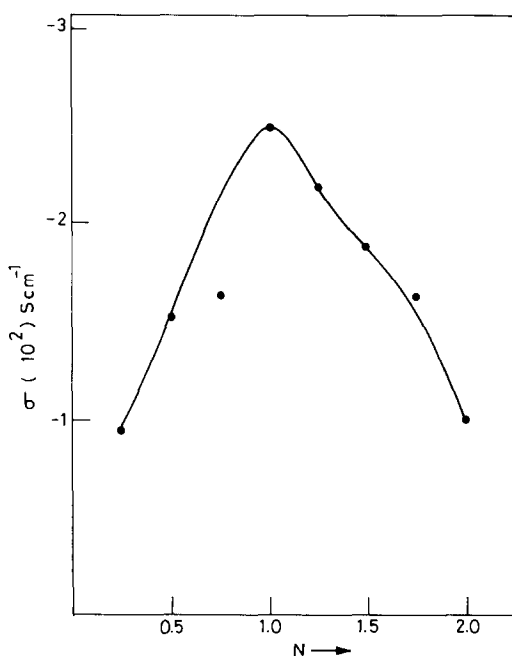
FIG. 3. Room temperature conductivity variation with N for 60 AgI–X Ag$_2$O–(1 − X)(0.1 B$_2$O$_3$–0.9 WO$_3$) glasses.

carriers are practically constant, as is the mobility (since the temperature of measurement is constant). Under these conditions we expect no change in conductivity with change in Y. But we observe two maxima. This might be due to the effect of the structure of glass on the conductivity. The probable explanation for this is that at these two compositions, the glassy matrix is such that it creates open channels for the mobile species to migrate. This causes enhancement in ionic mobility, and in turn the conductivity. The existence of two maxima in conductivity has been reported for oxide glasses (3–5) and also for sulfide glasses (11). Raman spectroscopic study on Ag$_2$O–MoO$_3$–R$_2$O$_5$ glasses revealed the presence of MoO$_4$ and PO$_4$ units in the matrix (12).

Figure 3 shows the variation of room temperature conductivity with N in borotungstate system. It is observed that the

conductivity goes through maxima when N = 1.00. Addition of metal oxide to a glass former involves incorporation of oxygen into the macromolecular chain formed by the network former, thereby introducing ionic bonds into the glass. This incorporation depends mainly on the coordination chemistry of the glass former element. As the glass modifier to glass former content increases, a greater number of oxygen bridges are broken. As the number of nonbridging oxygen atoms (NBO's) increases, the average length of the macromolecular chain decreases. Thus, an increase in the content of Ag$_2$O breaks the bonds and facilitates easy migration of conducting species. Hence, after a particular optimum value of N, the conductivity decreases. After this value, the entire glassy matrix breaks and the randomness increases, which inhibits the motion of the mobile species, and results in 0 decrease in conductivity. Figure 4 shows the variation of room temperature conductivity with mole percentage of AgI in the composition XAgI–(1 − X) (Ag$_2$O–[0.1 B$_2$O$_3$–0.9 WO$_3$]). It is seen that the logarithmic conductivity increases with increase in AgI content up to a particular value. The room temperature conductivity value increases with the addition of AgI and reached a maximum value of 10^{-2} S/cm, which appears to be the limit for all silver ion conducting glasses (3). This high conductivity of silver glasses is often interpreted as evidence that ionic conductivity of doped glasses is essentially due to the presence of some form of clustering of AgI with intercluster connections allowing for fast Ag$^+$ diffusion throughout the glassy matrix. Moreover, many properties in pseudobinary systems with AgI as one component tend to behave as γ-AgI with increasing AgI concentration (13).

Figure 5 shows the plots of Log σT versus 1000/T for various compositions in the silver borotungstate system with variation in Y. Conductivity increased with temperature

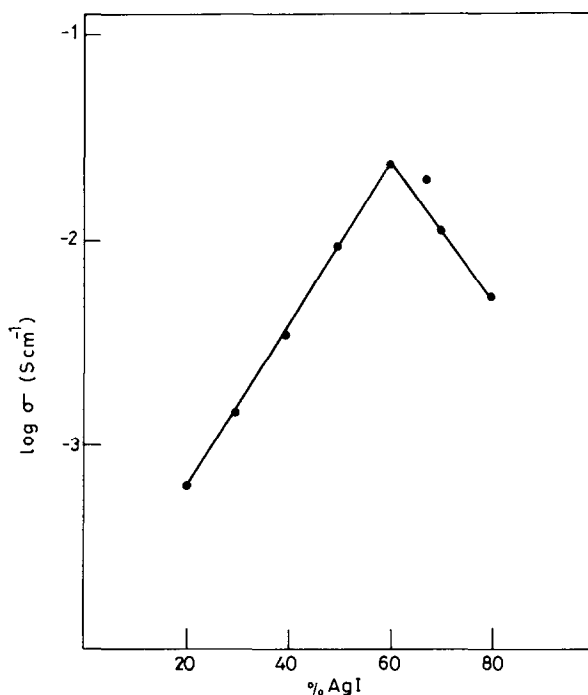FIG. 4. Room temperature conductivity variation with mole percentage of AgI for XAgI–(1 − X) (Ag$_2$O–[0.1 B$_2$O$_3$–0.9 WO$_3$]).

for all the compositions, up to a particular temperature, which is characteristic of that composition (glass transition temperature Tg). Heating beyond this point resulted a decrease in conductivity. At this stage the sample was annealed above this temperature for 2–3 hr and the temperature variation was performed again. It was found that the conductivity decreased by about 1–2 orders of magnitude. This behavior was found in all samples and the conductivity of the unannealed sample was always higher than that of annealed sample. This is due to the fact that above the glass transition temperature amorphous materials transform themselves into polycrystalline, which is an irreversible process.

The temperature variation of conductivity, which was found to be Arrhenius in nature, followed the equation

$$\sigma = \sigma_0/T \exp\left(-E_a/kT\right),$$

where the symbols have their usual meanings. The activation energy for silver ion migration has been calculated from the slopes of the above plots. The highest conducting composition has an activation energy of 0.21 eV.

As is seen from the Fig. 6 Tg is almost independent of Y. Moreover, it varied drastically with mol percentage of AgI. This is because Tg depends mainly on dopant concentration. It was reported in lithium borophosphate glass (7) that the variation of Tg with different B$_2$O$_3$/P$_2$O$_5$ ratios does not follow any rule. Moreover, the presence of two glass formers will increase the presence of a number of units (e.g., BO$_4$ and WO$_4$).

Glass Formation Region

The glass forming region has been established in the systems by studying the conductivity, glass transition temperature, and
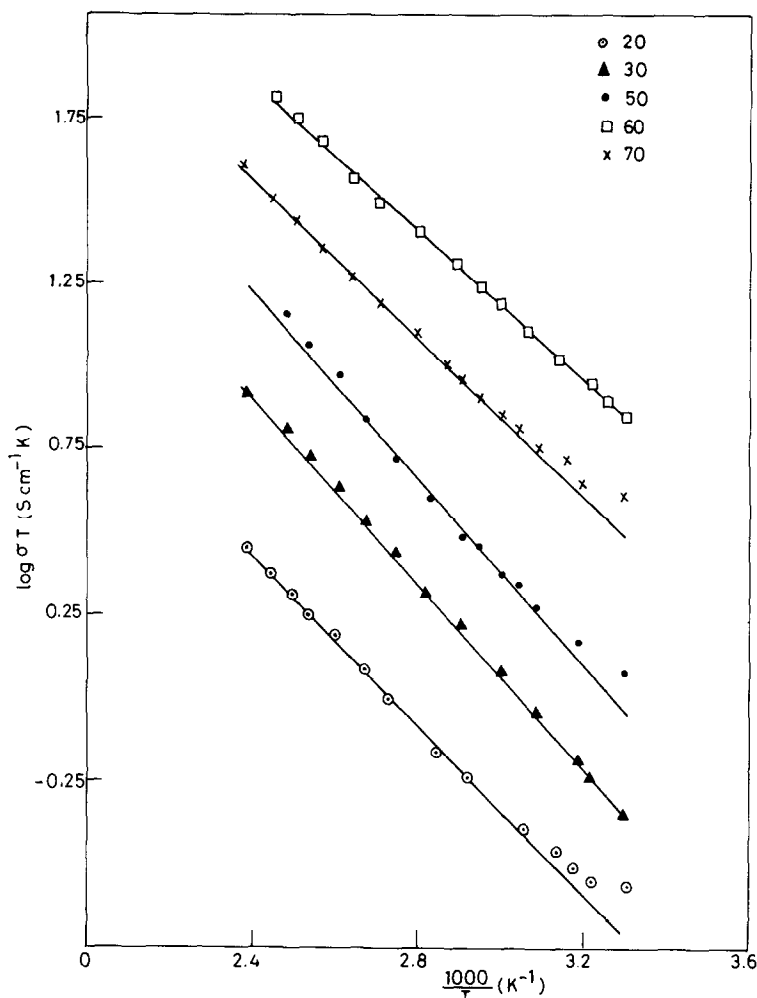
FIG. 5. Temperature variation of conductivity for various compositions with variation in mole percentages of AgI.

amorphous nature of each composition by X-ray diffraction. Figures 7a and 7b represent the glass formation region in the system. Figure 7a represents the glass formation at a constant mole percentage of AgI (60 mole%) and Fig. 7b at a constant value of the ratio between the two glass formers B_2O_3 and WO_3 ($Y = 0.1$). From the figures the limits for the glass forming region can be given as follows:

$$0 \leq Y \leq 1$$
$$0.25 \leq N \leq 1.5$$
$$20 \leq \text{mole } \% \text{ AgI} \leq 70.$$

Though the glass formation is limited to above-mentioned limits, the glass formation region can be extended by using ultrahigh quenching techniques. The quenching rates in the present investigation are around 10^3 K/sec.

Electronic Conductivity Studies

Wagner's dc polarization cell of the type $(-)$Ag/glass/graphite$(+)$ was used to study the electronic contribution to the total conductivity. In the above configuration, the
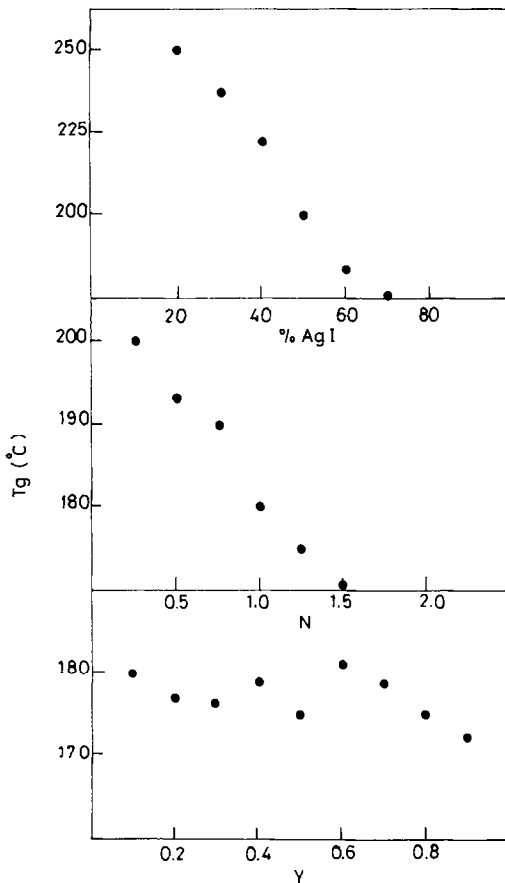
FIG. 6. Variation of glass transition temperature for various glasses prepared.

graphite electrode was maintained at a positive potential with respect to the silver electrode (8). The graphite electrode acts as a blocking electrode and is polarized by applying dc potential in the range 10 to 150 mV. In the glass the silver ions will migrate toward the silver electrode and the electrons toward the graphite electrode. After some time the ionic conductivity is suppressed, because silver ions are not being supplied by the graphite electrode. Then the conduction will be due to the migration of electrons or electron holes across the electrolyte. According to Wagner's analysis, the total electronic current (I) is given by

$$I = I_e + I_h$$
$$= (RTA/LF) \ (\sigma_e[1-\exp(-EF/RT)]$$
$$+ \ \sigma_h[\exp(EF/RT)-1]),$$

where I_e and I_h are the currents due to the electrons and holes, respectively, R the gas constant, T absolute temperature, F the Faraday constant, E the applied voltage, and σ_e and σ_h the conductivities due to the electrons and holes. If $\sigma_e \gg \sigma_h$, the second term will be negligible and I becomes independent of applied voltage. On the other hand, if $\sigma_e \ll \sigma_h$, the first term will be negligible and I increases exponentially with the applied voltage. The saturation of the current with the applied voltages after 70 mV indicates that the current is essentially due to electrons. Figure 8 shows the plot of I versus 1-exp $(-EF/RT)$, which is a straight line passing through the origin. From the slope of the straight line the electronic contribution toward the total conductivity is calculated as 10^{-8} S/cm.

Transport Number Measurement

The transport number of silver ions can be calculated from the total electronic conductivity and was equal to 0.999. It was also calculated from the emf method, by constructing an Ag/glass/I_2 cell and comparing the open circuit voltage (685 mV) of the fabricated cell with the thermodynamically calculated value (687 mV). The slight discrepancy in the values of the transport number calculated from two methods can be explained as follows. In the emf method the actual transfer of ions across the electrolyte is involved, whereas in the previous method the results are obtained by blocking the ions. Moreover, iodine may diffuse into the electrolyte and may induce some electronic conductivity in the electrolyte.

Thermoelectric Power (TEP)

To investigate further into the transport properties, thermoelectric power (TEP) ex-
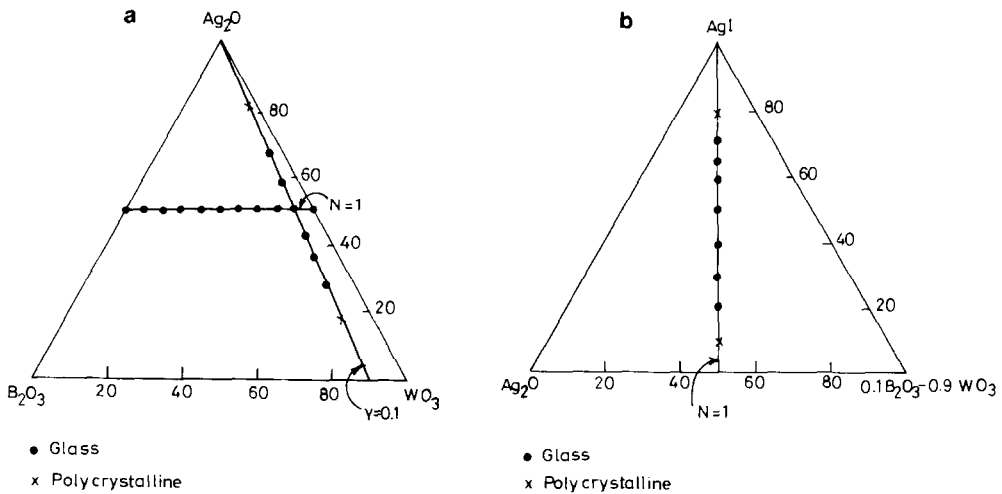
• Glass

x Polycrystalline

• Glass

x Polycrystalline

FIG. 7. Glass formation region in the silver borotungstate system (a) with a constant mole percentage of AgI (60) (b) with a constant mole percentage of Y (0.1).

periments were carried out on the highest conducting sample. For the thermocell configuration already discussed, the expression for the TEP has been worked out to be (14)

$$\theta = -q^*_{Ag^+}/eT + H,$$

where $q^*_{Ag^+}$ is the heat of transport for Ag^+ ions, e the charge on the mobile species, and H the correction term due to electrode contact potential effects, which for thermocells constructed with reversible electrodes is almost temperature independent and constant. So TEP should vary linearly with $1/T$ and the slope of the plot should be equal to $q^*_{Ag^+}$. Figure 9 shows the plot of TEP $(-\theta)$ versus the reciprocal of temperature. It is clear that plot is a straight line and can be expressed by the equation

$$-\theta = [0.218 (1000/T) - 0.030] \text{ mV/K},$$

giving a slope of 0.218, which agrees closely with the activation energy for the migration of silver ions. For materials possessing average structure, the mobile ions can jump from one site to another of equal energy. Thus the distinction between interstitial Ag^+ ions

and Ag^+ ions at the normal site is lost. Hence, the heat of transport, which is equal to the barrier height for ion hopping, is expected to approach the activation energy of Ag^+ ion migration.
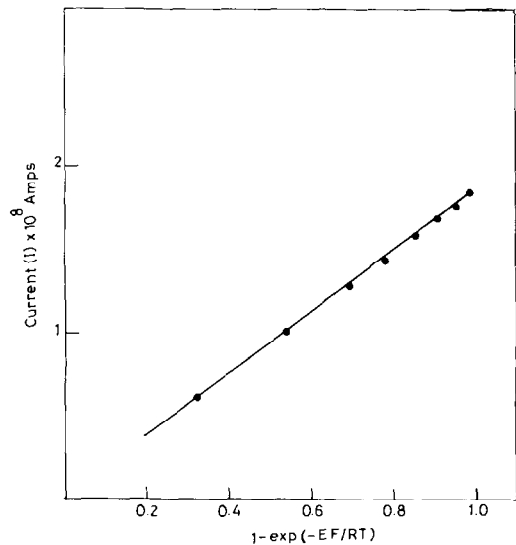

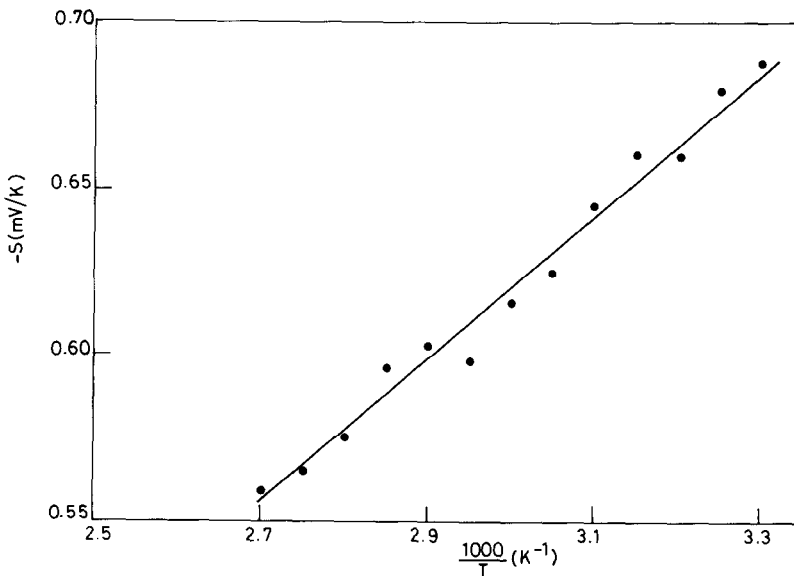FIG. 8. Plot of I versus exp $(-EF/RT)$ for the best conducting composition.

FIG. 9. Plot of thermoelectric power ($-\theta$) versus $1000/T$.

Conclusions

The mixed former effect has been observed in the quaternary silver borotungstate system. The ionic conductivity in these glasses has attained a maximum of 10^{-2} S/cm. TEP measurements confirmed that only silver ions are mobile species. The glass formation region has been established in the above system.

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