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THERMOPOWER AND ACTIVATION ENERGY OF SILVER IODIDE BASED SUPERIONIC MATERIALS

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Abstract

Silver iodide based glasses, $60AgI\text{-}20Ag_2O\text{-}20B_2O_3$, $60AgI\text{-}20Ag_2O\text{-}20MoO_3$ and $60AgI\text{-}20Ag_2O\text{-}20WO_3$, all in the mol% ratio, were prepared by rapidly quenching the melts of the chemicals in a stainless steel container kept in a liquid nitrogen bath. The glassy nature of the as-quenched materials was confirmed by X-ray diffraction (XRD). The electrical conductivity of the glasses was measured at various temperatures ranging from 30 to 70 °C using an impedance bridge operating in the frequency range between 40 Hz to 100 kHz. The plot of ln σT versus 1000/T for each glassy material obeys Arrhenius law and the activation energy obtained is between 0.2 to 0.3 eV. Thermopower measurement was also carried out in the same temperature range as the conductivity measurement to obtain the heat of transport.

Theory

A good conductor of electricity has small resistance. The resistance of a material is dependant on its length, L and cross-sectional area A and can be written as

$$R = \frac{\rho L}{A} \qquad (1)$$

where ρ is the resistivity of the material. The reciprocal of ρ is conductivity, σ. Like resistivity, the conductivity of the conducting species inside a material is temperature dependant and can be written as

$$\sigma = (\sigma_o/T) \exp(-E_A/kT) \qquad (2)$$

where E_A is known as the activation energy. This equation reflects the fundamental condition of nature that motion requires energy which is manifested as the activation energy. *What makes up the activation energy?*

The conducting species for superionic solids are ions. We can think of an ion at the bottom of a square well potential. In order for the ion(s) to be free, it must have a minimum energy of E_b to get out of the well. For the ion(s) to move throughout the conductor, it must then have the energy for migration, E_m. So the activation energy can be written as

$$E_A = E_b + E_m \qquad (3)$$

The activation energy can be calculated from the slope of Eqn(2), if the plot of ln σT versus 1/T obeys Arrhenius rule. It may not be possible to measure E_m but if E_b, i.e. the static barrier energy is equivalent to the transport energy of the conducting ion, one can then obtain E_b by thermopower measurements. If $E_A \approx E_b$ then the ions are in a free state and out of the potential well. In this work, we perform thermopower and conductivity-temperature measurements on three types of superionic glasses viz., silver molybdate, silver tungstate and silver borate glasses.

Experimental

The starting materials AgI, Ag_20, MoO_3, WO_3 and B_2O_3 were all AnalaR (AR) grade. These materials were weighed in the required mol % stoichiometric ratio to form 60AgI-20Ag_2O-20MoO_3, 60AgI-20Ag_2O-20WO_3 and 60AgI-20Ag_2O-20B_2O_3. The chemicals were melted in a furnace and the melts were then quenched at liquid nitrogen temperature.

The glassy nature of the solid phases was confirmed by X-ray diffraction using the Philips PW1840 diffractometer. The wavelength of the X-radiation was 154.2 pm. The X-ray source was operated at 40 kV 20 mA.

The electrical conductivity in this work was performed using the impedance spectroscopy technique. The HIOKI 3520-01 LCR HiTester was used and the impedance was measured in the frequency range 40 Hz to 100 kHz. The bridge was interfaced to a microcomputer using a IEEE 488 multifunction card. A software was written to calculate the real and imaginary impedance. The temperature of the material was controlled by wrapping the sample container in a disposable glove and immersing them in a water bath. The temperature of the water bath was controlled between room temperature and 70°C.

For thermopower measurement, the powdered materials were pelletised and cut to form a square of size 1 cm X 1 cm and a cell of the configuration

Ag/ glass /Ag

was constructed. This was then placed in a conductivity mount. The upper electrode of the conductivity mount was heated so as to maintain a temperature gradient between the upper and lower electrode. A thermocouple was used to determine the temperature of the upper and lower electrodes. The conductivity mount was then placed in a "home-made" furnace in order to vary the ambient temperature of the sample. The difference in temperature between the upper and lower electrodes was maintained constant. A digital voltmeter was used to measure the thermally induced voltage. The ratio of this induced voltage for a fixed temperature difference gives the thermopower which can be written as

$$\theta = - \frac{\Delta V}{\Delta T} \qquad (4)$$

where θ is the thermopower. θ can be obtained for every temperaure T and the θ-T relationship can be expressed as

$$\theta = \frac{-q^*}{eT} + H \qquad (5)$$

Here q* is called the heat of transport and H is a constant.

Results and Discussion

Fig.1 presents the X-ray diffractograms for the three samples. The absence of any crystalline peaks in the diffractograms of the samples confirm their glassy nature. The plot of ln σT versus $10^3/T$ obeys Arrhenius rule and the activation energy, E_A for the glasses in the present work are as tabulated below.

Table 1

Type of glass	Silver Molybdate	Silver Tungstate	Silver Borate
Activation Energy, E_A	0.28 eV	0.20 eV	0.27 eV

The value for activation energy are in good comparison with that reported in the literature [1-3] for silver ion conductors. Fig.2 shows the impedance plots for all glasses at some of the temperatures under investigation and Fig.3 the ln σT versus $10^3/T$ plot.

The plot of thermopower versus $10^3/T$ is as shown in Fig.4. The value for the heat of transport, q* obtained from the gradient of Eqn (4) for all the materials is as tabulated below.

Table 2

Type of glass	Silver Molybdate	Silver Tungstate	Silver Borate
Heat of transport,q*	0.05 eV	0.19 eV	0.25 eV

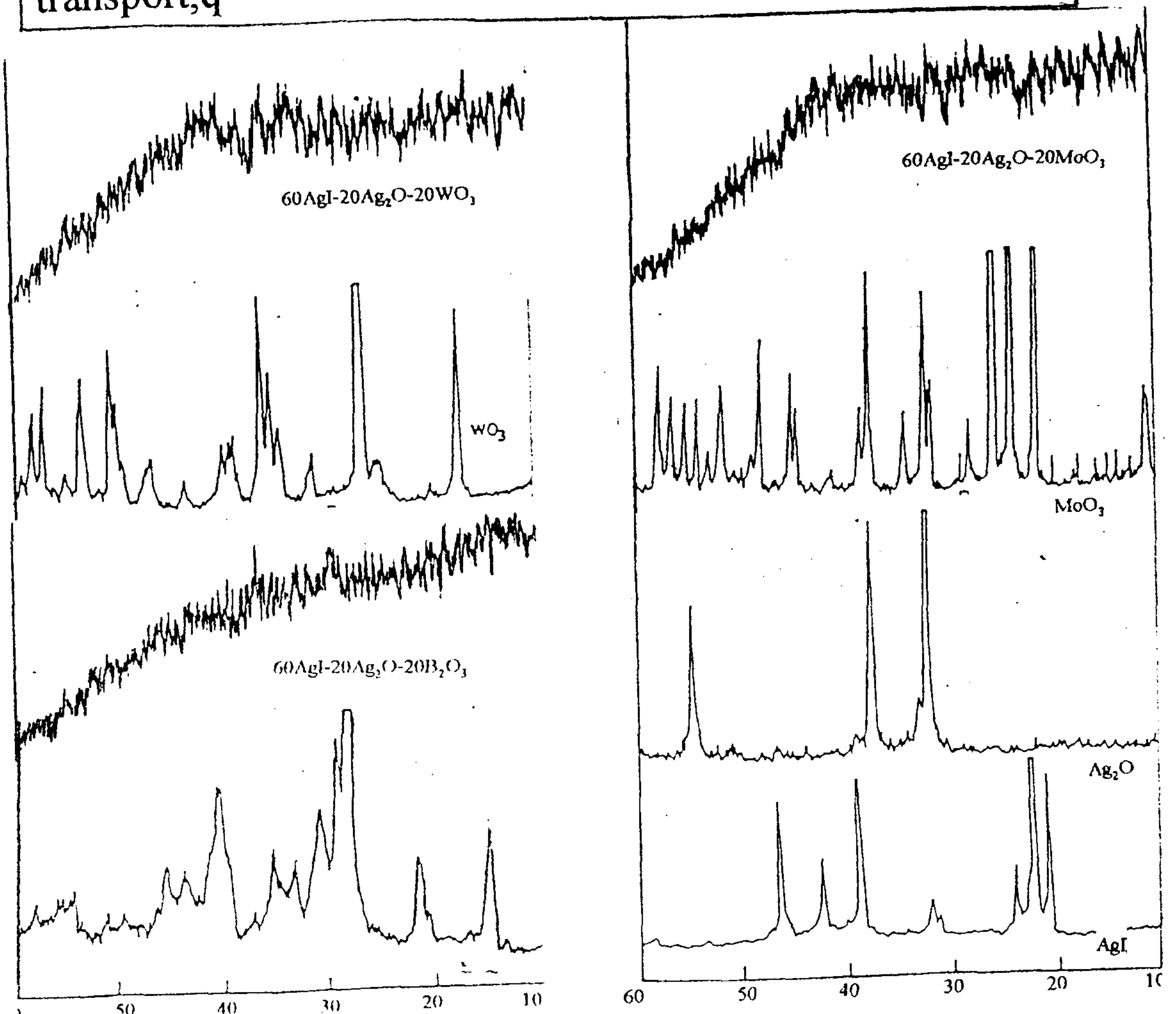

Fig.1 X-ray diffraction patterns of glasses and their chemical constituents.

The heat of transport q* and the activation energy, E_A are almost equal for the silver tungstate and silver molybdate glasses. The silver ions in these glasses can be considered to be in a free state, since they have enough energy to overcome the energy barrier for migration. For the silver molybdate glass, some energy is required to overcome the energy barrier for migration while the rest of the energy may be used for migration.

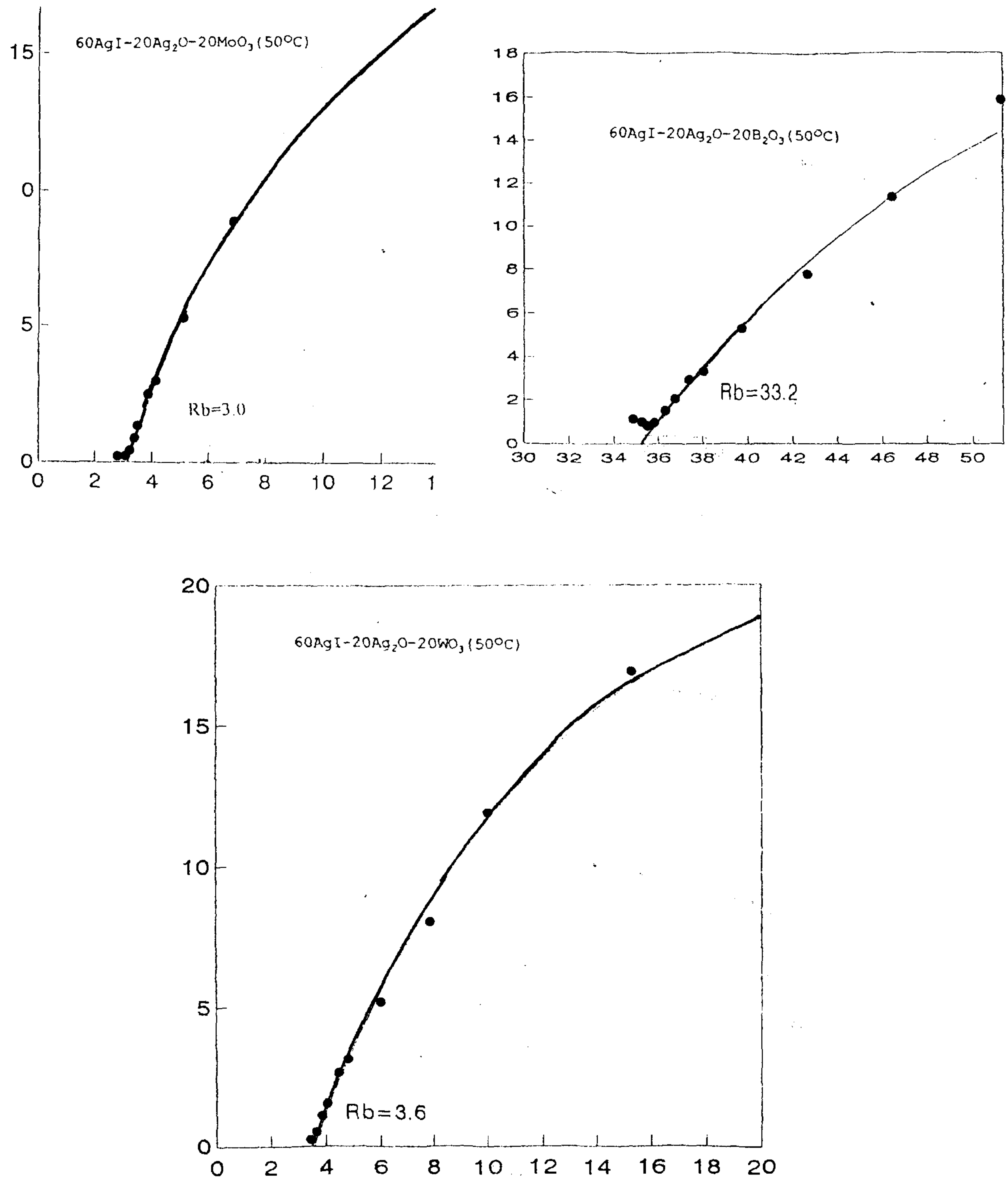

Fig.2 Some Cole-Cole plots for all glasses at some temperatures of investigation.

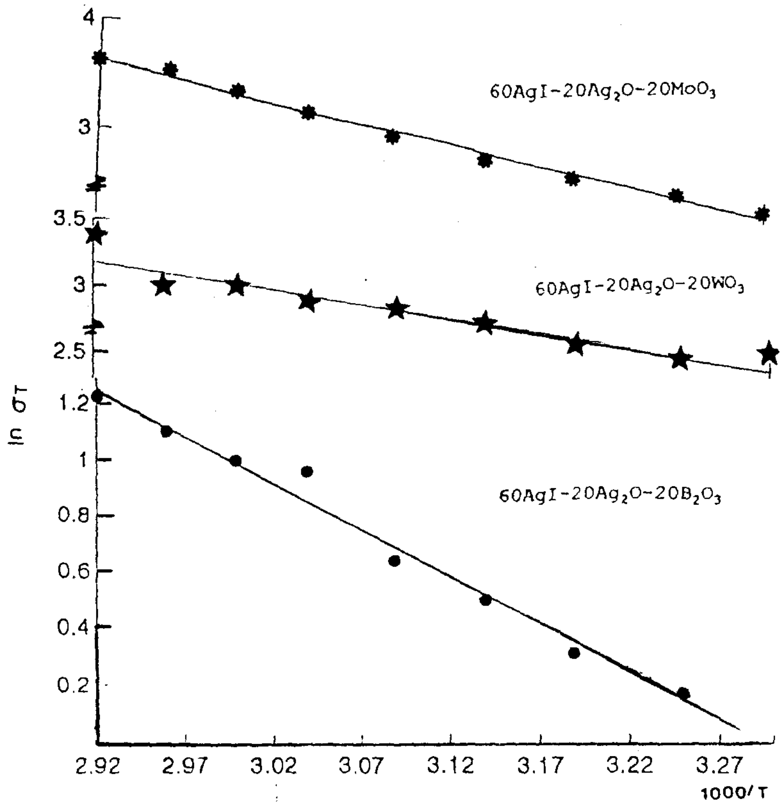

Fig.3 Arrhenius plots for all glasses.

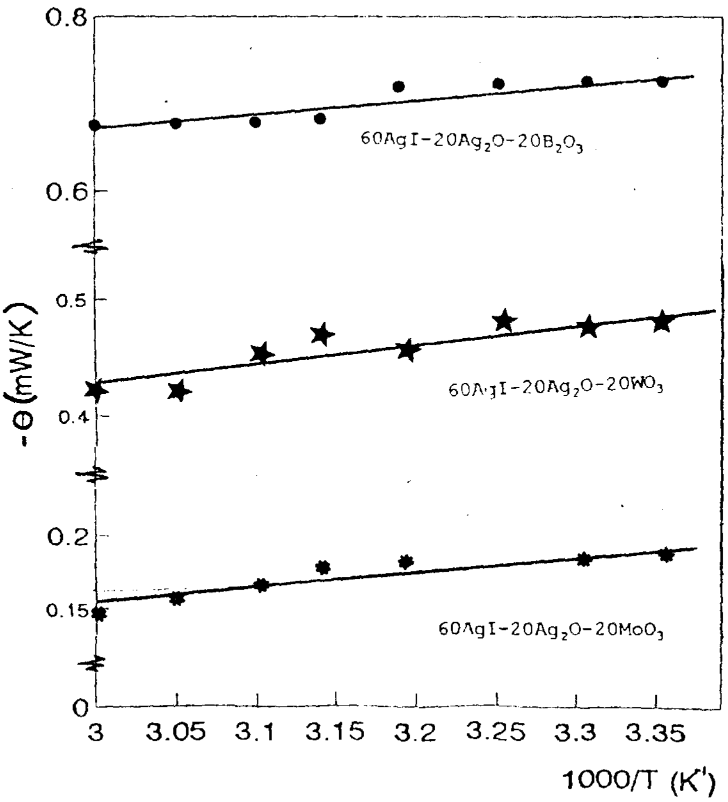

Fig.4. Thermopower versus temperature plots for all glasses.

Conclusions

The thermopower and activation energy relationship for the tungstate and borate glasses seems to follow the Rice and Roth theory. It is not understood from this work why the silver molybdate glass have a very low heat of transport.

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