

A.C. CONDUCTIVITY AND DIELECTRIC PROPERTIES OF AgPO₃ GLASS

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ABSTRACT

Electrical conductivity and dielectric properties of AgPO₃ glass have been measured as a function of temperature (300-400K) and frequency (50-1 MHz). The electrical conductivity was studied by using complex impedance technique and a.c. conductivity. From impedance the bulk conductivity is found to be an activated process with activation energy 0.57eV. An equivalent circuit of a capacitance and resistance in parallel is found for impedance plot for the sample. It was observed that the relaxation time in the sample increases with increasing temperature.

A.C. conductivity expressed in terms of frequency-dependant conductivity shows a dispersive behavior which can be described by a power law with the exponent $s > 1$ at higher frequencies. A nearly constant behavior is found at lower frequencies. The interception of the constant part at $\omega = 0$ is taken as the dc conductivity. The activation energy of the dc conductivity is found to be 0.56eV.

The dependence of the dielectric properties ϵ' and ϵ'' of AgPO₃ on frequency and temperature is also discussed.

Key words:- Ionic conductivity, AgPO₃, A.C. Conductivity, Complex impedance. Dielectric properties.

INTRODUCTION

A number of Li⁺, Na⁺, Ag⁺, and Ca⁺⁺ ion-conductivity glasses which exhibit high ionic conductivity at ambient temperatures are known¹. Ag⁺ ion-conductivity glasses²⁵ have attracted special attention due to their ease of preparation in different forms and their high values of conductivity at room temperature. Silver ion conducting glasses are also interesting from an academic point of view and can be used as model systems for the development of solid state batteries⁶. Therefore, much effort has been devoted to

the preparation of silver based electrolytes⁷⁻⁹.

Study of the A.C. conductivity is one of the useful methods that is applied to ionic materials to characterize the bulk resistance of the prepared sample. Measurement of a.c. conductivity can be done by different techniques. The currently used technique is the complex impedance spectroscopy. This study gives information on electrical properties of materials and interface with electrical conducting electrodes. The complex impedance spectroscopy measurement of a.c conductivity is based on studies made on the measurement of cell impedance over a range of temperatures and

frequencies and analyzing them in complex impedance plane^{10,11}. This is particularly characterized by the measurement and analysis of impedance (Z) and plotting of this function in the complex plane which is known as Nyquist diagrams.

Measurements of the dielectric properties of different substances have been the subject of many researchers and various models have been proposed to interpret the experimental results¹². Dielectric measurements on ionic materials give useful information about dynamical processes involving ionic motion¹³.

The present study aims to throw more light on AgPC-3 glass using complex impedance technique, ac conductivity and dielectric properties.

2. Experimental procedures :

Glassy samples of AgPC-3 were prepared by mixing in stoichiometric proportions of AgPOa (FLUKE, ENGLAND) and $\text{NH}_4 \text{H}_2 \text{PO}_4$ (FLUKE, ENGLAND) in a porcelain crucible and put in a muffle furnace for melting at 600 °C. The melt was held at 600 °C for 6 hours before quenching it into copper moulds kept at room temperature.

Disk shaped samples, with thickness of about 2 mm, were prepared for electrical measurements. Silver paste electrodes were used on both sides of samples. Special care was taken to avoid mechanical stresses. During the measurements the temperature was changed by 1 K/min.

A.C. measurements were carried out by means of PM 6306, FLUKE, DC 1MHz, Programmable Automatic RCL Meter, in the frequency range of 50 Hz to 1 MHz and temperature range of 300 to 405 K.

RESULTS AND DISCUSSIONS

3.1 Complex Impedance Results :

The bulk conductivity for the glass system, AgP03, was estimated using the complex impedance method¹⁴ in the range

between room temperature and 400 K and the frequency range (50Hz-1 MHz). The plots of Z'' , (imaginary part of impedance), against Z' , (real part of impedance), for the glass system, showed a semicircle at each temperature in the whole frequency range, (Figured). The resulting semicircle corresponds to the bulk resistance R_b and geometrical capacitance C_b of the sample. The intersection of the semicircle with Z' axis gives the bulk resistance R_b from which bulk conductivity σ_b can be obtained. The obtained values of σ_b are thermally activated with increasing temperature and obeys Arrhenius equation which can be expressed by the following relation

$$\sigma_b = \sigma_0 \exp (-E_b / KT) \quad (1)$$

where E_b is the apparent activation energy, and T is the temperature. Figure (2) illustrates plot of σ_{b1} versus $10^3/T$. The activation energy is determined by making a least square fit to the data with relation (1) and is found to be 0.57eV.

The activation of bulk conductivity (σ_b) with increasing temperature can be interpreted by the following structure model which was suggested by Minami¹⁵. This model suggests the occurrence of Ag^+ ions with different nobilities in AgI-based super ionic glasses in three types of Ag^+ ions: (i) Ag^+ ions are bonded to the oxygen atoms of the network, (ii) Ag^+ ions interact weakly with the network oxygen atoms and (iii) Ag^+ ions are surrounded by I^- ions only. Silver ions of the last type have maximum mobility and contribute mostly to ionic conduction. When the temperature is increased to higher values, the conductivity also reaches to higher values because of Ag^+ ions (which interact weakly to the oxygen atoms of the network) may release and contribute in conduction with the Ag^+ ions (which are surrounded by I^- ions) leads to increase the concentration of Ag^+ mobile ions.

The simplest model for an electrode-sample under an applied voltage is a capacitor

and resistor in parallel, Figure 3a. The complex impedance plane plot is shown in Fig.3b. The capacitor is a result of the sample's geometry, while the resistor represents the resistivity of the bulk. For such a circuit, the complex impedance Z is $Z = 1 / (1/R + i\omega C)$ which can be separated into its real, Z' , and imaginary, Z'' , parts to give

$$Z = \frac{R}{1 + (wCR)^2} - j \frac{wR^2}{1 + (wRC)^2} = Z' - iZ'' \quad (2)$$

The time constant of this simple circuit is defined as

$$\tau = RC = \frac{1}{\omega} \quad (3)$$

and corresponds to the characteristic (dielectric) relaxation time of the sample. The relaxation time (τ) is obtained from the impedance analysis at different temperatures making use of relation (3). Figure 4 shows the variation of the relaxation time versus the temperature in the temperature range (300-400K). As one can observe, from the graph, there is a decreasing in the value of the relaxation time as the temperature increases.

3.2. The frequency dependence of the total conductivity:

Figure (5) presents plots of $\sigma_{\text{tot}}(\omega)$ against frequency f in the frequency range (50 Hz -1 MHz) for the glass system AgPO_3 at different ambient temperatures. It is noticed that, the total conductivity is nearly constant at the lower frequency range and obeys a power relation at the higher frequency range. At higher temperature range, $\sigma_{\text{tot}}(\omega)$ is nearly unchanged with increasing frequency over all the frequency range. The variation of $\sigma_{\text{tot}}(\omega)$ with frequency could be expressed by the following relation;

$$\sigma_{\text{tot}} = \sigma_{\text{dc}} + \sigma'(\omega) \quad (4)$$

Where σ_{dc} , the dc conductivity, which is independent of frequency (extrapolation of σ_{tot} at $\omega = 0$) and σ' (ω) is the ac conductivity.

Recently the jump relaxation model of Funke¹⁶ has been used to account for the frequency dependence of the conductivity in disordered systems. Funke proposed that in the case of structurally disordered materials, if an ion performs a hop to neighboring vacant sites, there is high probability for that ion to hop back to its previous position (an unsuccessful hop) but if the neighborhood then becomes relaxed with respect to the ion position, the ion stays on the new site, the initial forward hop has proved successful. In the plateau region, the dc conductivity is determined entirely by the successful hops. In the region above the plateau, many hops are unsuccessful and, as the frequency is increased, the proportion of these unsuccessful hops rises; this change in the ratio of successful to unsuccessful hops results in the dispersive conductivity. The predictions of this jump relaxation model apply to the temperature dependence of the ac conductivity: different activation energies being associated with unsuccessful and successful hopping processes.

In line with the model predictions, the frequency dependences of the conductivity of the ionic glasses studied can be fitted, -as shown in Figure (5) using a power law¹⁷

$$\sigma'(\omega) = A \omega^s \quad (5)$$

where A is temperature-dependence parameter and ω is the angular frequency. The values of the exponent s have been estimated from relation (5) by means of the least square method at different temperatures. The obtained values of power s are plotted in Figure (6a). It is noticed that, the exponent $s > 1$ corresponds to the translational hopping motion.

Regarding the general behavior of $\sigma_{\text{tot}}(\omega)$ against the frequency (Fig. 5), it consists of two regions described by equation (4). There is a critical frequency ω_p after which the

conductivity obeys the mentioned power relation. The crossover frequency from the dc to the dispersive region, cop , increases with increasing temperature. Almond *et al.*¹⁸ have assumed that, the total conductivity reaches twice σ_{dc} at such critical frequency cop [which is defined as the ionic hopping rate], and is given by,

$$\text{cop} = [\sigma_{dc}/A]^{1/5} \quad (6)$$

The values of cop are deduced at different ambient temperatures for the glass system under investigation. It is noticed that cop values lie in the same range of those obtained by Almond *et al.*¹⁸ for silver iodoarsenate ionic glasses (10^3 - 10^6 Hz). Figure (6b) illustrates the temperature dependence for the hopping rate cop for all glass samples, obeying the following Arrhenius relation ;

$$\omega_p = \omega_0 \exp (-E_\omega/KT) \quad (7)$$

where E_ω is an activation energy term concerning the variation of cop with temperature, and $\omega_p = \omega_0$ at $T = \infty$. The value of E_ω is deduced by making a least square fitting of relation (5) and is found to be 0.57eV. The observed activation of cop with increasing temperature can be explained as follows. The increase of ambient temperature leads to an increase of the dc conductivity of the glasses which competes the influence of the polarizing conductivity leading to the apparent shift of $\sigma_{tot}(\omega)$ - f curves up right.

The temperature dependence of dc conductivity for the glass system AgPO_3 were studied in the temperature range from room temperature to 400 K, Figure (7). The temperature dependence of dc conductivity in the whole temperature range can be described by the following relation:

$$\sigma_{dc} = \sigma_0 \exp (-E_{dc}/KT) \quad (8)$$

where E_{dc} the apparent activation energy.

It is noticed that the general behavior is the activation of conductivity with increasing temperature. The obtained value of the E_{dc} is 0.55eV.

3.3 Effect of frequency and temperature on the dielectric constant :

Figure 8(a) presents the plot of real part of dielectric constant ϵ' against frequency for the glass system AgPCh at different ambient temperatures. It is noticed that, the general feature is the decrease of ϵ' with increasing frequency to asymptotic value. The attenuation of dielectric constant ϵ' with increasing frequency can be explained as follows; When the frequency is increased, the dipoles will no longer be able to rotate sufficiently rapidly so that their oscillations begin to lag behind the field. It is also noticed that the observed large values of ϵ' at lower frequency over the whole temperature range is due to interfacial polarization effect^{19,21}.

The dielectric constant ϵ' of the glass system AgPCh was studied in the temperature range between room temperature and 400 K at different fixed frequencies, Figure 8(b). It is noticed that, in general, ϵ' increases with increasing temperature.

The dielectric properties in ion conductive glasses mainly arise from the ionic motions. The free energy barriers impeding the ionic diffusion, however, can be expected to vary from site to site, so there are different ionic motions in glasses²². The first is the rotation of ions around their negative sites, the second is short-distance transport, *i.e.* ions hop out of sites with low free-energy barriers and tend to pile up at sites with high free-energy barriers in the electric field direction in dc or low frequency electric field or oscillate between the sites with high free-energy barriers in an ac electric field. Both the first and the second motions make a contribution to the dielectric constant ϵ' of glasses. The third ionic motion is that the ions with higher energy can penetrate the glasses, *i.e.* conduct electricity and cause the dielectric loss ϵ'' . In the case

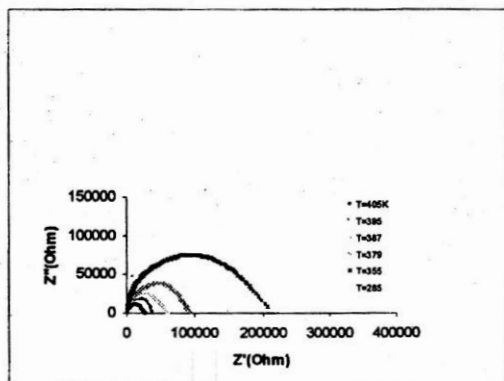


Fig. 1. Complex impedance plot for AgPO_3 at various temperatures.

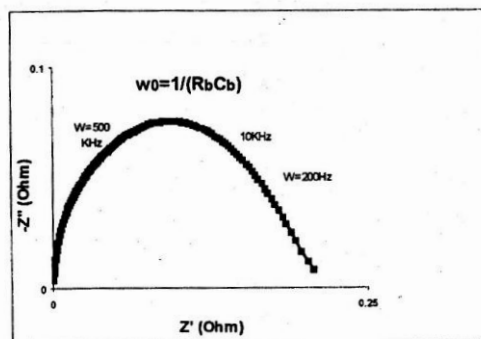


Fig. (3) a. The cole-cole plate for an equivalent circuit, b. an equivalent circuit for the present samples.

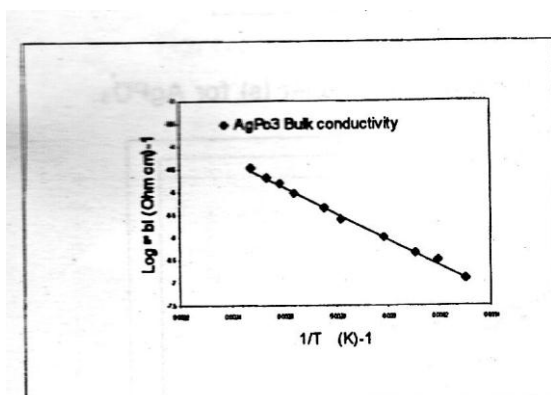


Fig. 2. Variation of bulk conductivity with inverse of temperature.

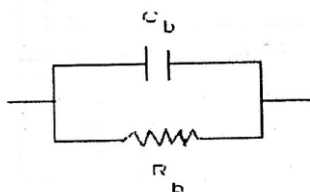


Fig. 3(a)

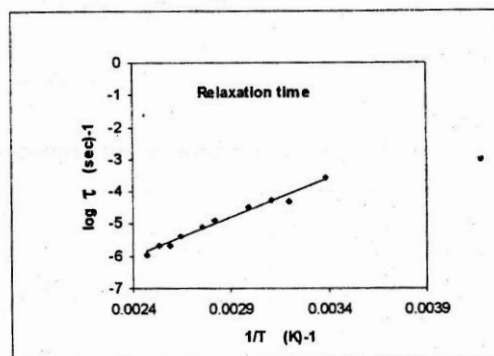


Fig. 4. Inverse temperature dependence of the relaxation time.

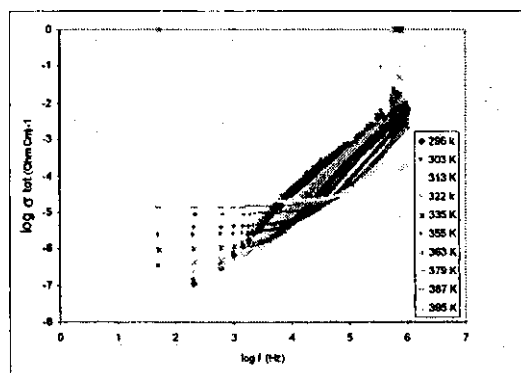


Fig. 5. Frequency dependence of the total conductivity in AgPO_3 at different temperatures.

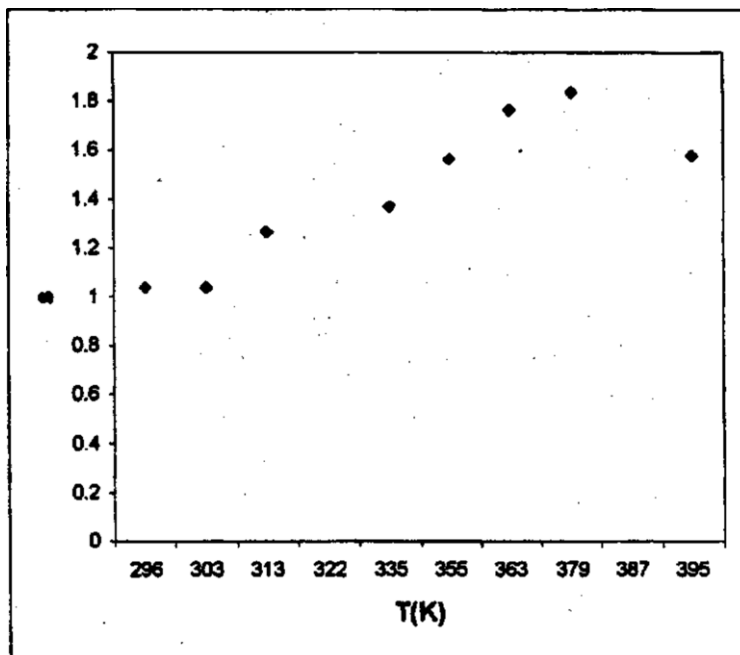


Fig. (6a). Temperature dependence of the power exponent (s) for AgPO_3 .

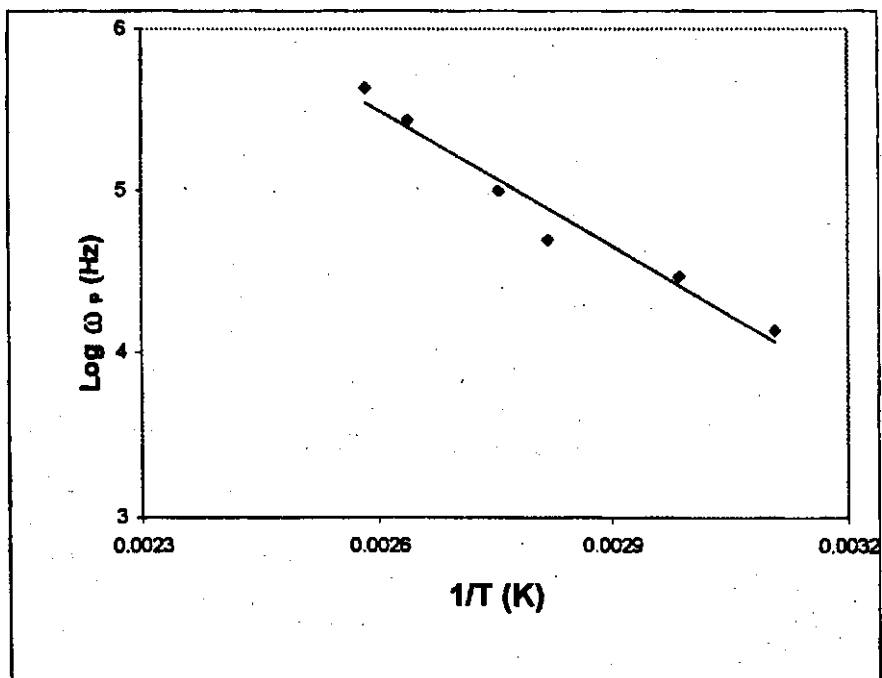


Fig. (6b) Inverse temperature dependence of relaxation frequency.

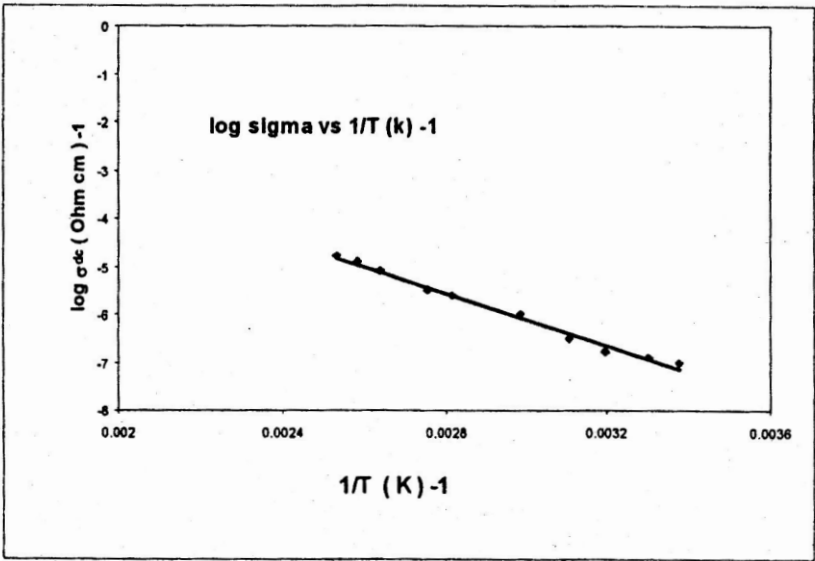


Fig. (7) Inverse temperature dependence of dc conductivity.

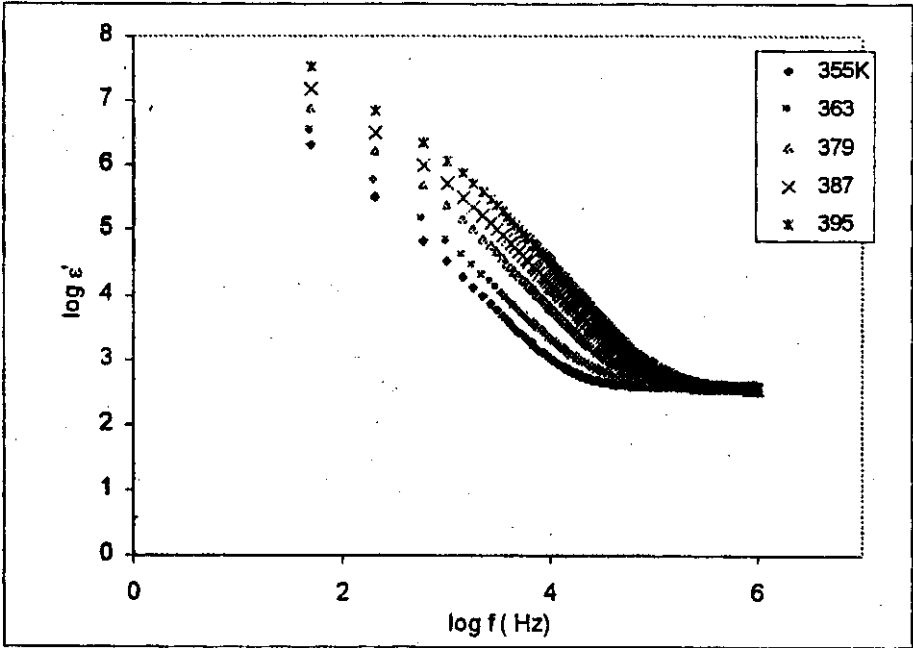


Fig. (8a). Variation of ϵ'' with frequency at different temperatures for AgPO_3 .

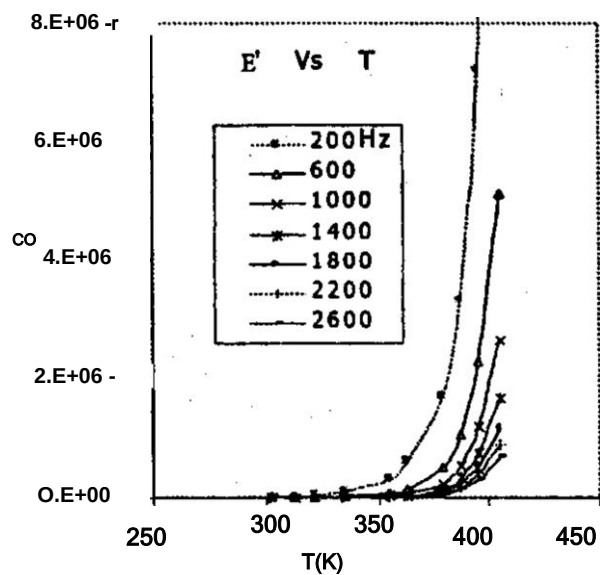


Fig. (8b). Variation of e' with temperature at different frequencies for AgPO_3 .

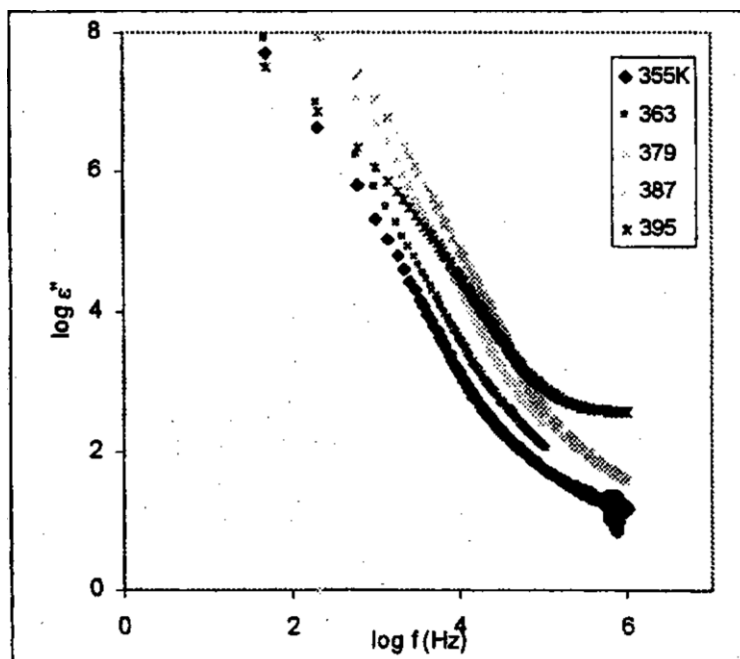


Fig.(9a). Variation of e'' with frequency at different temperatures for AgPO_3 .

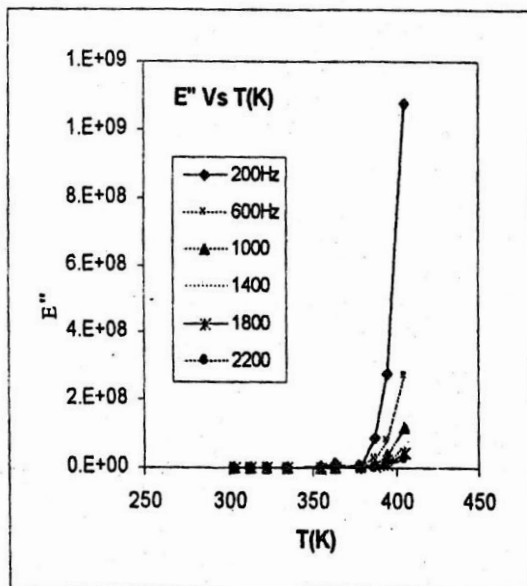


Fig. (9b). Variation of ϵ'' with temperature at different frequencies for AgPO_3

of blocking electrodes and/or domain interface or even low-frequency conduction can easily lead to electrode polarization. Thus, it will not only cause dielectric loss ϵ'' but also lead to a sharp increase of the apparent dielectric constant ϵ' of glasses.

3.4 Effect of frequency and temperature on the dielectric loss:

The frequency dependence of the dielectric loss ϵ'' is studied for the glass system AgPO_3 at different ambient temperatures, Figure 9(a). It is noticed that the general behavior shows a decrease of ϵ'' with increasing frequency.

The temperature dependence of the dielectric loss ϵ'' is studied for the glass system AgPO_3 at different frequencies, Figure 9(b). It is clear that, the dielectric loss ϵ'' increases with increasing temperature. When the frequency is increased the dielectric loss decreases which can be attributed to the reduction or to the diffusion of silver ions in the glass

matrix with increasing frequency. Consequently, there is a phase lag between the applied field and the polarization of the glass leading to the energy absorbed from the field to the dielectric material. No dispersion relation in studying ϵ'' against frequency were recorded, only a decrease in the value of ϵ'' with frequency which suggested that the relaxation peak shifts towards lower temperature range. The obtained values of $\omega\tau_m$ (0.042 - 0.016 eV) are lower than the activation energies obtained using dc conductivity. This can be attributed to the remarkable contribution of the localized electrons of the amorphous matrix in conduction process.

4. Summary :

Impedance measurements of AgPO_3 were carried out to separate the bulk sample properties from processes at electrode sample interface and the total conductivity activation energy were derived.

Measurements of the a.c. conductivity in the temperature range from 300K to 400K and for frequencies ranging from 50 Hz to 1MHz revealed that the value obtained for the power exponent s and its temperature dependence predict that conduction in AgPO_3 is mainly due to hopping mechanism.

The temperature dependence of the

conductivity of AgPO_3 glass is a semiconductor type with activation energy of 0.55 eV.

The dielectric permittivity $\epsilon(T)$ was calculated from the geometrical capacitance of equivalent circuit model. The temperature dependence of the dielectric permittivity of AgPO_3 glass is discussed.

REFERENCES

1. K. Singh, *Indian J. Pure and Appl. Phys.* **37**, 266 (1994).
2. M.D. Ingram, *Phys. Chem. Glasses* **28**, 215 (1987).
3. C.A. Angell, *Solid State Ionics*, **18/19**, 72 (1986).
4. K.M. Shaju and S. Shandra, *Phys. Stat. Sol.* **B181**, 301 (1994).
5. R.S. Kumar and K. Hariharan, *Bull Electrochem.* **14** (10), 332 (1998).
6. S. S. Shekhon, *Phys. News*, **26**, 80 (1995).
7. V.G. Chandrashekhar, A.M. Sureshini, and S. A. Suthanthiraraj, in: B. V. R. Chowdari (ed.), *Solid state ionics. Materials and Applications*, World Scientific, Singapore, 503 (1992).
8. S. Chandra, K.M. Shaju and Ajay Kumar, in *Solid State Materials and Application*, ed. B.V.R. Chowdari, World Scientific, Singapore p. 487 (1992).
9. S. Radhakrishna, and A.K. Arof, in *Solid State Materials and Application*, ed. B. V. R. J. Chowdari, World Scientific, Singapore p. 269 (1992).
10. J.E. Bauerle, *Phys. Chem. Solids*, **30**, 2657 (1969).
11. J.R. Macdonald (ed.), *Impedance spectroscopy emphasizing solid state materials and systems* (New York: Wiley) National Semiconductor Corporation 2000 Linear IC Data book 33 (1987).
12. S. R. Elliott, *Adv. Phys.* **36** (2), 135 (1987).
13. K. Funke, *Prog. Solid State Chem.* **22**, 1110 (1993).
14. J. E. Bauerle, *J. Phys. Chem. Solids*, **30**, 2657 (1969).
15. T. Minami, *Journal of Non-Crystalline Solids* **56**, 15-26 (1983).
16. K. Funke, *Phil. Mag. A.*, **68**, 711 (1993b).
17. F. Roger, J. Bartholomew, *Non. Cryst. Sol.*, **7**, 221 (1972).
18. D. P. Almond, G. K. Duncan and A.R. West, *Solid State Ionics*, **8**, 58 (1983).
19. M. Cutroni, A. Mandanici, A. Piccolo and C. Tomasi, *Philosophical Magazine B*, **71**, 843 (1995).
20. J.R. Macdonald, *J. Non-Cryst. Solids* **83**, 197 (1996).
21. A.R. Long, J. McMillen, N. Balkan and S. Summerfield, *Philos. Mag.*, **B 58**, 153 (1988).
22. H. Pengnian and H. Xihuai, *Journal of Non Crystalline Solids* **112**, 318 (1989).