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Dielectric studies and Cole-Cole plot analysis of silver-ion conducting glasses

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Silver ion conducting glasses are the first solid electrolytes to be used in solid-state electro-chemical devices for low specific energy applications. These glasses represent potential candidates for energy storage devices and solid state batteries. Silver phosphate glasses of the compositions $xAgI – 40Ag_2O-(50-x)P2O5-10Fe_2O_3$ mole% [x=0,5, 10,15, 20, 30] were prepared by quenching method and studied by means of AC measurements in the frequency range (50 Hz-5 MHz) and temperature range (303 -550 K). Dielectric peaks appeared between glass transition T_g and the crystallization temperature T_c. The dielectric peaks change against temperature agree well with the exothermic peak change in DTA results .The study of frequency dependence of both dielectric constant ε' and dielectric loss ε" showed a decrease of both quantities with increasing frequency indicating a normal behavior of dielectrics. Cole-Cole plots are drawn with ε' and ε". From the Cole-Cole plot parameters like optical dielectric constant, static dielectric constant, average relaxation time, and molecular relaxation time are evaluated.

Key words: Dielectric properties, Cole-Cole plot, silver ion conducting glasses.

INTRODUCTION

Superionic conductors of $AgI – Ag_2O – P_2O_5$ have drawn particular interest in recent years (Minami et al., 1980; Takahashi, 1998; Tatsumisago et al., 1993; Krasowski and Garbarczyk,1996). The high mobility of silver ion and the relatively simple structure of the glass network make the materials useful objects for the fast ion transport studies in the glassy phase. These glasses represent potential canadidates for energy storage devices and solid state batteries (Chowdari et al., 1995; Funke, 1993). So far, the main concern has been focused on electrical properties. It is assumed that such investigation is the best way to recognize the details of ion transport.

Dielectric measurements on ionic materials give useful information about dynamical processes involving ionic motion (Funke, 1993). Most of the disordered materials show a dielectric relaxation that cannot be described by an exponential decay with a characteristic single decay time (Debye-like decay). The relaxation times in these materials follow the so called Kohlrausch-William-Watts (KWW) function (Minami, 1987; Pogg and Kohlrausch, 1854).

The aim of this work is to study dielectric properties and to analysis Cole-Cole plots technique for a series of some silver phosphate glasses in which P_2O_5 is replaced by AgI up to 20 mole% to obtain parameters like optical dielectric constant, static dielectric constant, average relaxation time, and molecular relaxation time.

EXPERIMENTAL WORK

Silver phosphate glasses of the compositions xAgI –

$40Ag_2O$-$(50-x)P_2O_5$-$10Fe_2O_3$ mole% [x=0, 10, 20] were prepared using $NH_4H_2PO_4$, AgI, Ag_2O and Fe_2O_3 as starting materials (with purity not less than 99.8%). The practical applications of phosphate glasses are often limited due to their poor chemical durability. It was found that, the chemical durability of this kind of theses glasses increases dramatically with the addition of Fe_2O_3 (Reis et al., 2002). With the addition of Fe_2O_3 into phosphate glasses, the P-O-P bonds are replaced by more chemical durable P-O-Fe^{2+} and / or P-O-Fe^{3+} bonds (Yu, et al.,1997; Baia et al., 2002; Montagne et al., 1996). The raw materials are weighted to the desired concentrations and the batches are mixed well and then melted in porcelain crucibles using an electric furnace at 950°C for 6 h with frequent stirring to ensure complete homogeneity. The melts are quenched between two pre-cooled copper plates to form glass samples. The dielectric measurements are carried out on the silver paste coated pellets by using s programmable automatic RCL meter (Hioki 3532LCR Hi TESTER) in frequency range (50 Hz - 5 MHz) and temperature range (303-550) K. Differential Thermal Analysis (DTA) was performed in static air atmosphere with a constant heating rate of 10 K/min in a temperature range of 298-873K using Shimadzu DT-50. The DTA thermogrames for all samples are shown in Figure 1. The values of the glass transition temperature (Tg) and the crystallization temperature (T_c) for samples under investigation are listed in Table (1).

RESULTS AND DISCUSSION

Dielectric behavior

The dielectric relaxation as a whole is the result of the movement of dipoles (dielectric relaxation) and electric charges (ionic relaxation) due to an applied alternating electric field. Debye relaxation model has been widely employed to describe the response of molecules to an applied field.

The Debye equation in its simplest form of the complex dielectric constant, assuming a single relaxation time τ_O, is given by

$$\varepsilon^* = \varepsilon' - j\varepsilon'' = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + j\omega\tau_o}$$ (1)

where ε_s is the low frequency of ε' (the static dielectric constant) and ε_∞ is the high frequency of ε' (the optical dielectric constant), ω is the applied angular frequency ($\omega=2\pi f$).

Then we have the real part ε' (dielectric constant) and the imaginary part ε'' (dielectric loss) as follow:

$$\varepsilon' = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + \omega^2\tau_o^2}$$ (2)

$$\varepsilon'' = \frac{(\varepsilon_s + \varepsilon_\infty)\omega\tau}{1 + \omega^2\tau_o^2}$$ (3)

The temperature and frequency dependences of the dielectric constant ε' and the dielectric loss ε'' are studied in the frequency range (50 Hz - 5 MHz) and temperature range (303-523K) for samples with x= 0, 10 and 20.

Figures 2(a, b) illustrate the variation of both dielectric constant ε' and the dielectric loss constant ε'' with temperature at different frequencies (sample x = 20 as an example). In these figures, it is observed that both ε' and ε'' exhibit peaks against temperatures indicating dipolar relaxation character. The comparison of the maximum peaks with the differential thermal analysis (DTA) indicates that the beginning of the maxima corresponding to the glass transition temperature (T_g). These dielectric peaks exist between T_g and T_c temperatures where the crystallization finishes in DTA results. The appeared peaks for samples x = 0, 10, and 20, was noticed at $T_g \approx$ 375, 365, and 360 K respectively.

Figures 3(a, b) illustrates the variation of dielectric constant ε' and the dielectric loss constant ε'' with frequencies (log f) for composition x = 20 at different temperatures. The dielectric constant ε' is higher at low frequencies then decreases sharply with frequency and after that it remains almost constant over the entire frequency range. In the case of ε'', it is very similar nature like of dielectric constant ε', decreases rapidly and becomes almost constant afterwards. This behavior indicates a normal behavior of the dielectric. The decrease of dielectric constants in higher frequency region may be due to the fact that the dipoles cannot follow up the fast variation of the applied field. The higher values of ε' and ε'' at lower frequencies may be due to contribution from all the four types (space charge, dipole, ionic and electronic polarization) of polarizations, but at higher frequencies, only ionic and electronic polarization contribute. Generally, the high value of dielectric constant at low frequencies is attributed to the interfacial ionic polarizations due to localized Ag^+ ion motion within the glass network (Chowdari and Radhakrishnan, 1989). The decrease of dielectric constant ε' , with increasing frequency means that, the response of the permanent dipoles decreases as the frequency increases and the contribution of charge carriers (ions) towards the dielectric constant decreases (Bergo and Pontuschka, 2007; Graca et al., 2003).

Cole-Cole plot analysis

A simple evaluation of the Debye Equations (3) and (4) shows that the relation between ε' and ε'' of the complex dielectric constant (ε^*) is the equation of a circle. By eliminating ($\omega\tau$), these two Equations (2, 3) can be combined and written in the form of a circle:

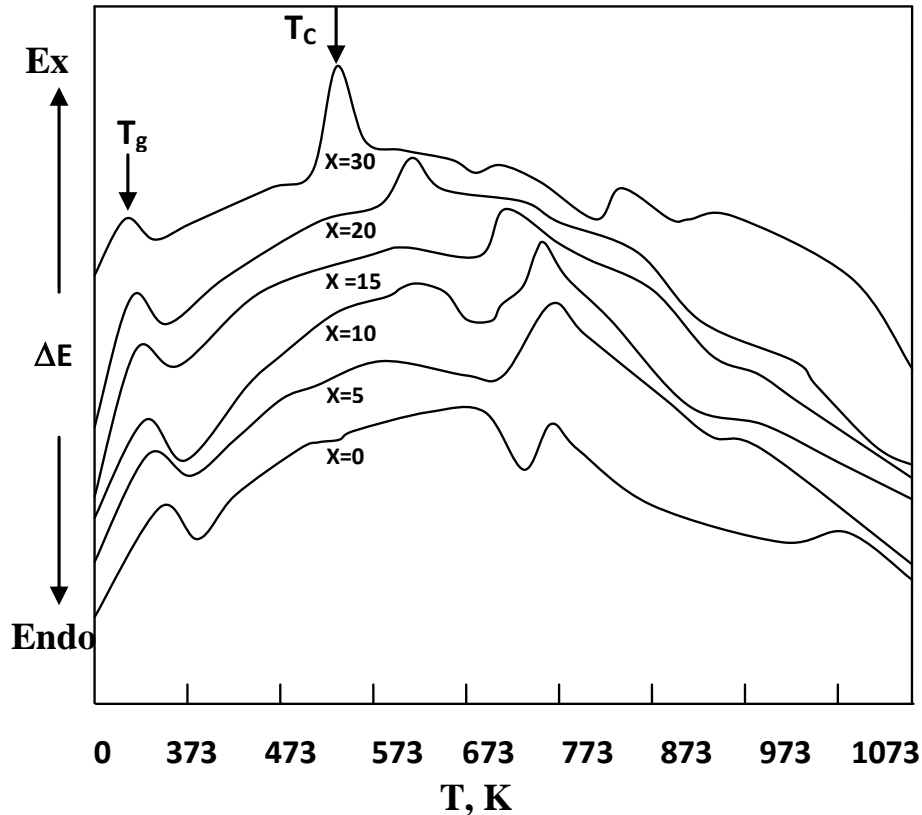**Figure 1.** DTA curves for the glass system (50-x) P_2O_5-xAgI-40Ag$_2$O-10Fe$_2O_3$, [x = 0,5,10,15,20,30].

Table 1. The values Tg, TC for the glass system (50-x)P_2O_5-xAgI-40Ag$_2$O-10Fe$_2O_3$,[x=0,5,10,15,20,30].

x AgI	T_g K	T_C K	ε_s	ε_∞
0	375.89	761.12	-	-
5	371.14	754.96	3	17
10	365.76	725.26	3	35
15	360.27	715.82	3	40
20	359.55	613.32	3	65
30	356.81	528.05	-	-

$$\left(\varepsilon' - \frac{\varepsilon_s + \varepsilon_\infty}{2}\right)^2 + \left(\varepsilon''\right)^2 = \left(\frac{\varepsilon_s - \varepsilon_\infty}{2}\right)^2 \qquad (4)$$

This gives a semicircle plot of ε' against ε'' with a center on the real axis and intersects it at values ε_∞ and ε_s respectively. The top of this semicircle corresponds to $\omega\tau = 1$. This plot confirms Debye theory.

Cole and Cole (Graca et al., 2003) found for a considerable number of liquids and solids that the values of ε'' fell below the semicircle but could be represented by a semicircle arc intersecting the real axis at the values of ε_∞ and ε_s. The center of the circle of which this arc was a part lay below the real axis and the diameter drawn through the center from the ε_∞ point made an angle $\alpha\frac{\pi}{2}$ with the real axis. Cole and Cole suggested that in this case the complex dielectric constant might follow the empirical relation of the form:

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + (j\,\omega\,\tau)^{1-\alpha}} \qquad (5)$$
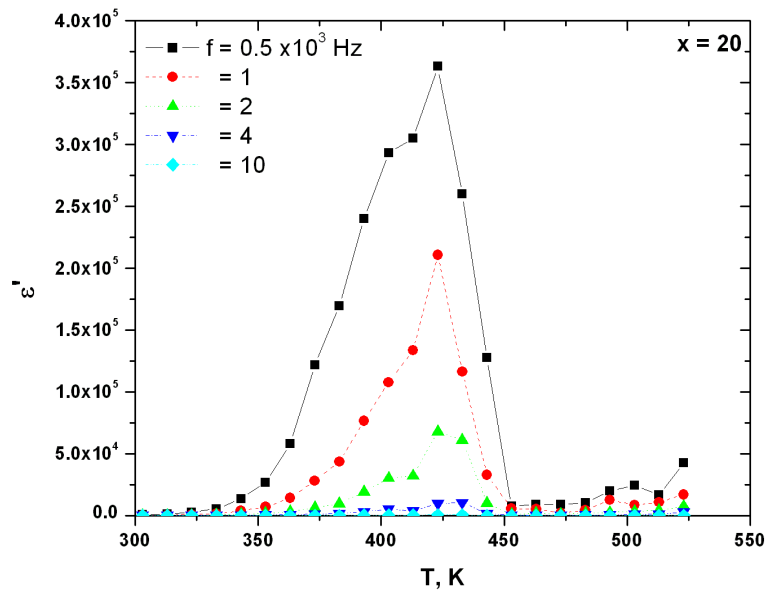
Figure 2a. Temperature dependence of the dielectric constant for sample x=20 at different frequencies.
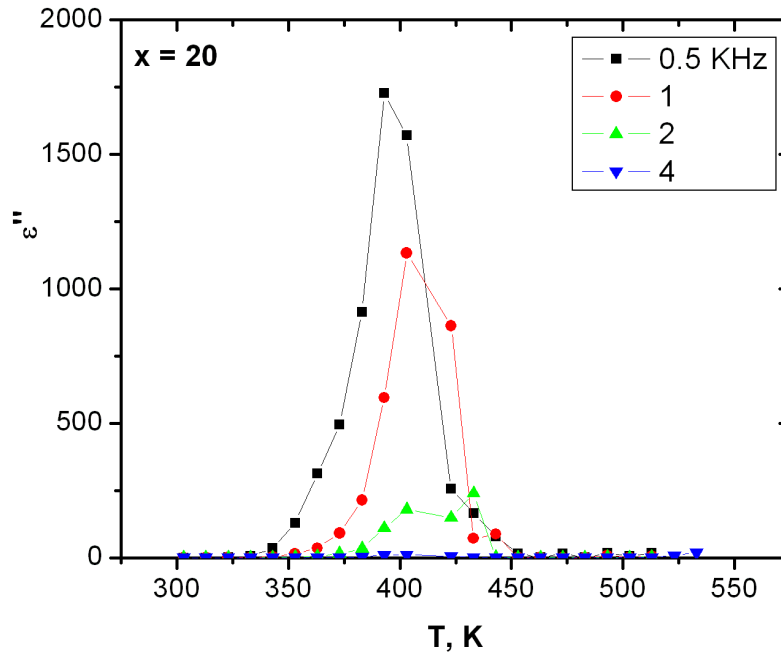

Figure 2b. Temperature dependence of the dielectric loss constant for sample x=20   at different frequencies.

Where τ is the average relaxation time and α is the spreading factor of actual relaxation time τ_o ($0 < \alpha < 1$). When α equals to zero the dielectric has only one relaxation time.

The Cole-Cole plots is obtained from the dependence ε' on ε'' on the complex plane at temperatures range (303-500K). The Cole-Cole plots method are used to test the effect of compositions $xAgI – 40Ag_2O-(50-x)P_2O_5$-
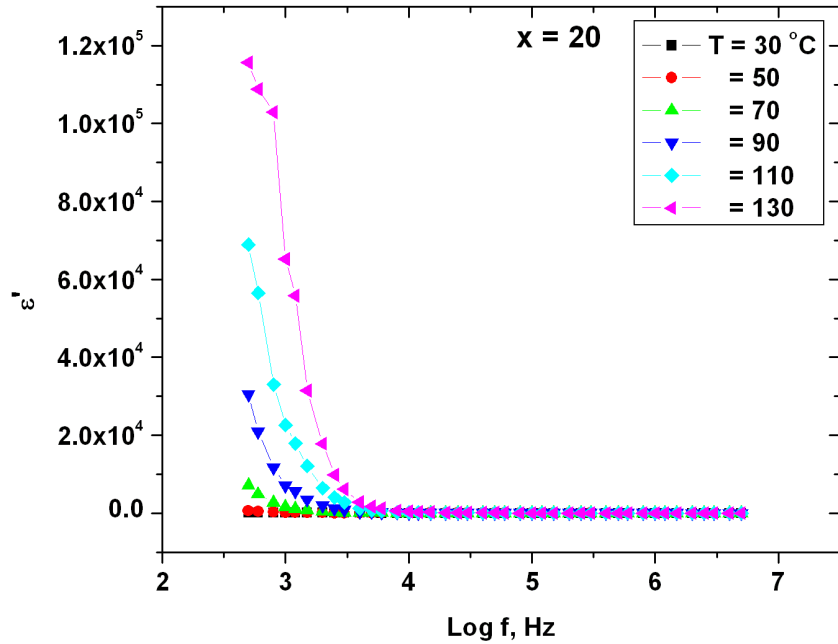
Figure 3a. Frequency dependence of the dielectric constant for sample x = 20 at different temperatures.
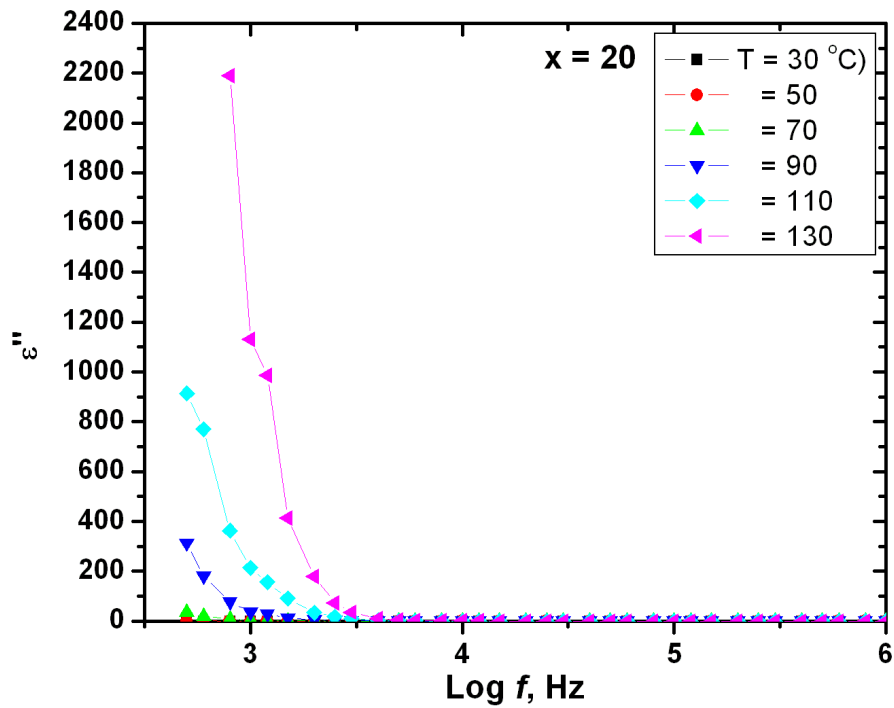

Figure 3b. frequency dependence of the dielectric constant for sample x=20   at different temperatures.

$10Fe_2O_3$ mole% [x = 0, 5, 10, 15, 20] on type of dielectric constant at room temperature (303K), (Figure 4). Each

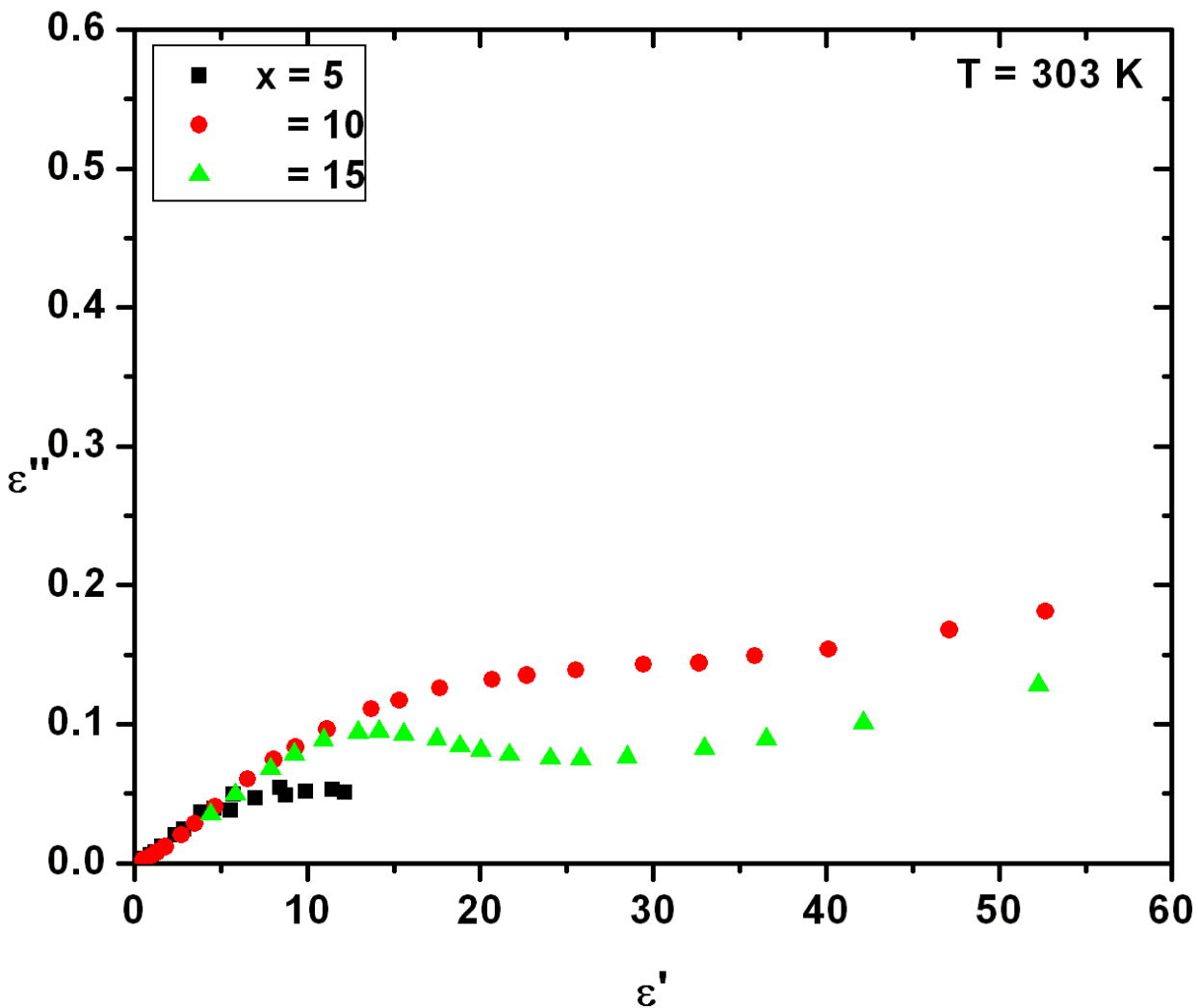plot is represented by a semicircle arc with a centre below ε'-axis. The dielectric parameters ε_∞ and ε_s are

Figure 4. Cole-Cole plots for glassy samples with x=5, 10, and 15 at 303 K.

Table 2. The calculated values of εs, $\varepsilon \infty$ and τ calculated from Cole-Cole plot and τm from Equation (9).

T, °C	F, Hz	ε_s	ε_∞	α	τ, S	τ_m, S
50	8000	49	2	30	2.71E-05	4.24E-02
60	15000	48	2	35	2.19E-05	3.29E-02
70	20000	44	2	38	7.96E-06	1.00E-02
80	30000	42	2	37	4.51E-06	5.18E-03
90	50000	38	2	40	2.63E-06	2.47E-03
100	80000	35	2	47	1.39E-06	1.10E-03
110	120000	32	2	34	8.86E-07	5.86E-04
120	120000	28	2	33	3.12E-07	1.57E-04
130	150000	26	2	33	1.59E-07	6.88E-05
140	250000	25	2	37	1.28E-07	5.13E-05

evaluated as the high- and low-frequency intercepts of experimental ε' with the real axis of Cole-Cole plot (Table 2). At higher frequencies, all the data at different compositions converge in one point that represents a
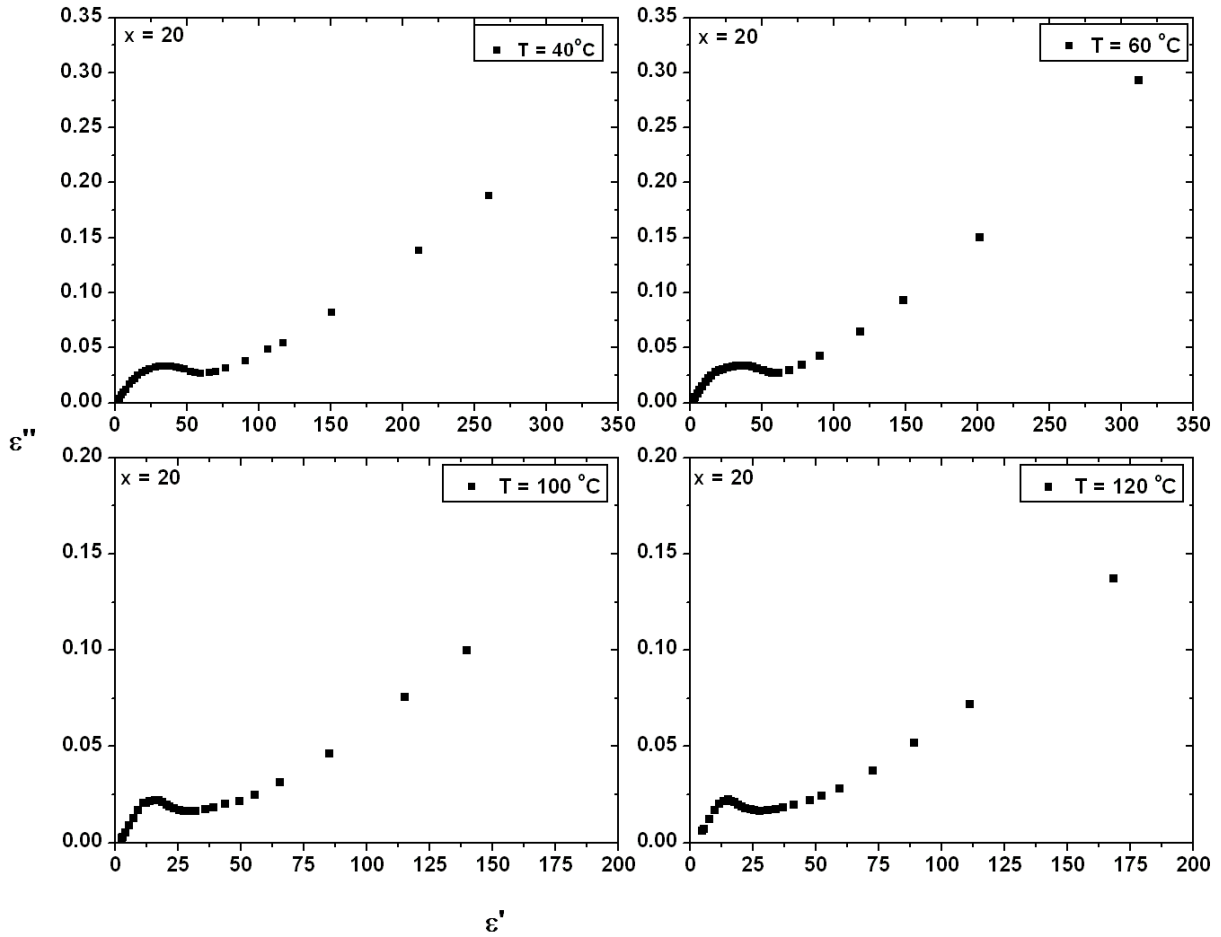
Figure 5. Cole-Cole plots for sample x=20 at different temperatures.

unique value of optical dielectric constant ε_∞. The reason for ionic value of ε_∞ is that the alternating field oscillates to rapidly for the dipole to follow and so the dipole remains essentially stationary and consequentially the dipolar polarization vanishes. The low frequency intercepts ε_s shift to a higher value as P_2O_5 is replaced by the AgI up to 20 mol%. This means that the increasing of AgI concentration in the glassy system is to increase silver ion in the glass matrix and excess ionic jumps at lower frequency in the field direction.

The Cole-Cole analysis (Figure 5) is also used to obtain the relaxation time of relaxation process. The average relaxation time may be calculated from the relation:

$$\frac{v}{u} = \left(\omega\tau\right)^{1-\alpha} \tag{6}$$

Where v is the distance on the Cole-Cole plot between ε_s and an experimental point, and u is the distance between

the experimental point and ε_∞. From the Cole-Cole plot the parameters like optical dielectric constant ε_∞, static dielectric constant ε_s, average relaxation time τ, molecular relaxation time τ_m are evaluated and listed in Table (2). The average relaxation time τ is plotted against temperature for studied glasses (Figure 6). The relaxation time is thermally activated and follows closely the Arrhenius relation; $\tau_m = \tau_o\, e^{-\left(Em/KT\right)}$, with values of activation energies listed in Table (2).

On the molecular level, the molecular relaxation time τ_m can be estimated by employing the following Equation (Montagne et al., 1996) by substituting the value of τ:

$$\tau_m = \left[\frac{\left(2\varepsilon_s + \varepsilon_\infty\right)}{3\,\varepsilon_s}\right]\tau \tag{7}$$

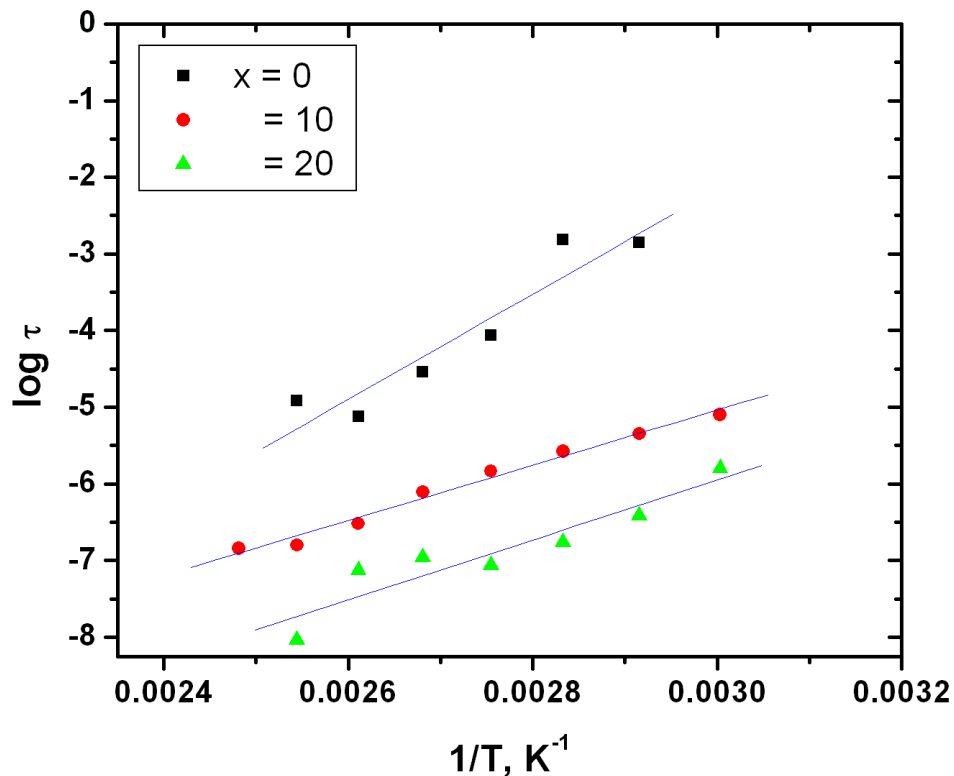The obtained molecular relaxation time is listed in Table

Figure 6. Temperature dependence of the relaxation time for samples.

2. According to this Table, values of the relaxation times of the studied glasses are very near to that of amorphous bulk chalcogenide semiconductors and oxide glasses (Chowdari and Radhakrishnan, 1989; Bergo and Pontuschka, 2007; Graca et al., 2003). The relaxation time is fast at high temperatures and increases dramatically at low temperatures, suggesting a freezing of electric dipoles at low temperatures (Ahmad and Yamada, 2007).

Conclusions

Silver phosphate glasses of the compositions xAgI – 40Ag$_2$O-(50-x)P$_2$O$_5$-10Fe$_2$O$_3$ mole% [x=0, 5, 10, 15, 20, 30] was prepared using melt-quenching technique. The glass transition temperature (T$_g$) changes with silver iodide concentration increasing reflecting the formation of the most opened network structure. It has been observed that both ε$_\infty$ and ε$_s$ decrease with increasing frequency indicating a normal behavior of dielectrics. It is noticed from Cole-Cole plots that the increasing of AgI concentration in the glassy system is to increase the static dielectric constant which may act as electric dipoles. From the Cole-Cole plot parameters the average relaxation time and molecular relaxation time are

evaluated. The relaxation time is found to be fast at high temperatures and increases dramatically at low temperatures, suggesting a freezing of electric dipoles at low temperatures.

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