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Characterization and dielectrical study of AgI – Ag_2O-P_2O_5-Fe_2O_3 glass

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ABSTRACT

Various compositions of silver conducting glasses [AgI – Ag_2O-P_2O_5-Fe_2O_3] were prepared by melt quenching technique. X-ray diffraction (XRD),Mossbauer effect (ME), infrared (IR), differential thermal analysis (DTA) studies were carried. Dielectric measurements have been carried out on (50-x)P_2O_5-xAgI-40Ag_2O-10Fe_2O_3 ,[x=0,5,10,15,20,30] glasses from 50 Hz upto 5MHz.The frequency dependence of the total conductivity is nearly constant at the low frequency, identified with the true dc ionic conductivity σ_{dc} (0) and at high frequencies an additional term increasing in a power law with exponent s<1 corresponds to translational hopping motion.Effect of frequency and temperature on dielectric constants and dielectric loss is studied. The general behaviour of ε" shows a decrease with increasing frequency following a power relation with exponent m>1 and activation energy values of Wm about 0.042-0.016 eV lower than obtained using dc conductivity.

Key words: Dielectric study, silver conducting glassess, different techniques.

INTRODUCTION

Superionic conductors of AgI-Ag_2O- P_2O_5 have drawn particular interest in recent years[1-4]. 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. 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. However, dielectrical property investigations themselves or combined with electrical ones can complement any source of data, giving a useful insight into the mechanism of ion transport. Only a limited number of such investigations have been described in the literature.

Dielectric measurements on ionic materials give useful informations about dynamical processes involving ionic motion[5]. As observed in several ion conducting glasses, the dielectric response, expressed in terms of frequency-dependent conductivity, exhibits a frequency dependence at low frequencies, identified with the true dc ionic conductivity σ_{dc} (0) and at high frequencies an additional term increasing in a power law 6. fashion such that σ_{tot} (ω) = σ_{dc} (0) + σ_{ac} (ω) here σ_{dc} (0) is the dc conductivity and s is the power law exponent which increases slightly with temperature. In addition, ionic conductors exhibit a characteristic enhancement of the dielectric constant and a corresponding dielectric loss. These phenomenological aspects have been studied in AgI–Ag_2O–P_2O_5 glass by dielectric spectroscopy up to 5 MHz. Results have been analyzed in wide frequency and temperature ranges, and discussed in the light of recent models for ion dynamics in glasses

EXPERIMENTAL

The glass system (50-x)P_2O_5-xAgI-40Ag_2O-10Fe_2O_3 x=0,5,10,15,20,30, were prepared by melting mixtures of $NH_4H_2PO_4$, AgI, Ag_2O and Fe_2O_3 in the powder form . The mixture was heated in purceline crucbles at a temperature ranging from 250°C to 350 °C for two hours in order to gas evolution ceased. After that, the temperature was raised gradually to 950 °C and left for 6 hours in order to chemical reaction is completed. Then the melt was shaked several times to ensure the homogenity. The melt was poured on a steel plate kept at (0 °C). Silver paste, which show ohmic contact with glass samples, was used for coating the desired electrode area. The sample before measurements was left at room temperature for about 10 hrs.

Samples of the glass system (50-x)P_2O_5-xAgI-40Ag_2O-10Fe_2O_3 ,x=0,5,10,15,20,30. were characterized by X-ray diffraction (XRD), Mossbauer effect (ME), infrared (IR) and differential thermal analysis (DTA) measurements. Ac measurements have been carried out in the range of frequency from (500 Hz to 5 MHz) by using a programmable automatic RCL meter (HIOK 3532 LCR HITESTER). The density of studied glasses were measured as a function of AgI content.

Characterization

Glass nature of the prepared samples was confirmed from the peaks free XRD patterns. The structure of each glass sample is confirmed by comparing the observed FT-IR spectral results of our glasses with the reports in the literature[7-9]. Glass transition temperature (Tg) and crystallization temperature (T_c) are identified from the measured DTA curves for the prepared samples (Table 1). The obtained ME spectra and parameters show that iron exists as Fe^{3+} occupying both tetrahedral coordination states. It is also found that at high iron oxide content, most of the iron enters the glass network as former while the rest appears as network modifier. In addition a small amount of Fe_2O_3 precipitates which disappears on adding silver oxide.

It is known from the preparation of the glass samples (50-x)P_2O_5-xAgI-40Ag_2O-10Fe_2O_3 , x = 0 , 5 , 10 , 15, 20, 30. that , AgI increases and P_2O_5 decreases gradually in molecular weight % . This means that, the number of the oxygen decreased gradually when Ag and I are increased. This result confirms the supposition that at low AgI content, the excess oxygen form large non-bridging oxygens as well as the formation of some phosphrous double bond oxygens (P=O)[10]. The disappearance of this bond confirm also the decrease of non-bridging oxygen due to the difficiency of the oxygen anions. In addition , most of iron ions occupy the network forming positions as concluded from both IR and Mossbauer (ME) techniques. Consequently, most of Ag cations prefer to occupy the network modifying positions in the present glass. Increasing AgI content on the expense of P_2O_5 indicates the approximate gradual decrease in the ratio of (P+Fe)/(O+I), since Fe acts as a network former. This reavels that , the non-bridging oxygen may decrease while the Ag–P bonds increase. The addition of AgI (increasing silver cations and introducing I anions) may also increase the dangling bonds between I and P or Fe atoms of the form PO_3–I or FeO_3–I. In addition some silver cations may appeared as an isolated (AgI_4) groups.

The density of studied glasses were measured as a function of AgI content . It showed increasing trend in the range from 0 to 20 mole % AgI and appeared to be stable until 30 % AgI. The molar volume (Vm) is calculated. Table (1) shows the change in the obtained molar volume values as a function of the AgI content . It is noticed that , as the AgI increased from 0 to 20 mole %, the molar volume decreased linearly, while in the range 20 to 30 mole % AgI, it seems to be stable[12].

According to the density and the molar volume , the change in their values in the range up to 20 mol % appeared to be small which may reflect the formation of some AgI_4 clusters . The stability of the density and molar volume in the range 20 and 30 % AgI may reflect the stability of the glass network in this range and the increase in silver cations as AgI was gradually increased may lead to increase the P–Ag bonds. The formation of these bonds reflect no change in the network structure of these glasses. This stability was confirmed in agreement with the results of both line width (LW) and quadrupole splitting (QS) values concluded from ME.

From the IR interpretation , the P=O bond at1200 cm^{-1} apperead in the samples contianing AgI from 0 to 10 mole % and disappeared completely in the samples contianing AgI from 15 to 30 mole % . This result confirm the above supposition that at low AgI content , the excess oxygen form large non-bridging oxygens as well as the formation of some phosphrous double bond oxygens (P=O)[11]. The disappearance of this bond confirm also the decrease of non-bridging oxygen due to the difficiency of the oxygen anions

AC conduction and dielectric study

The frequency dependence of the total conductivity

Fig. 1&2 illustrates the logarithmic plots of $\sigma_{tot}(\omega)$ against frequency f in the frequency range (50 Hz - 5 MHz) for the glass system (50-x)P_2O_5-xAgI-40Ag_2O-10Fe_2O_3 , x = 0,10. as an example, at different ambient temperatures. It is noticed that, the total conductivity is nearly constant at the lower frequency range for the glass samples of the xAgI content (x = 0,5,10) but it obeys a power relation at the higher frequency range and at the higher temperatures, it nearly unchanged with increasing frequency over all the frequency range. The variation of $\sigma_{tot}(\omega)$ with frequency could be expressed by the following relation[6]:

$$\sigma_{tot} = \sigma_{dc} + \sigma'(\omega) \qquad ...(1)$$

where σ_{dc} , the dc conductivity which is independent of frequency (extrapolation of σ_{tot} at w = 0) and $\sigma'(\omega) = A\,\omega^S$ is the ac conductivity. In line with the model predictions, the frequency dependences of the conductivity of the ionic glasses studied can be fitted , as shown in Fig. 1&2. The values of the exponent s have been estimated by means of the least square method at different temperatures. The obtained values of power s are given in Table 2. It is noticed that, the exponent s<1 corresponds to the translational hopping motion and its values does not depend on the AgI content of these glasses.

Regarding to the general behaviour of $\sigma_{tot}(\omega)$ against frequency, it consistes of two regions discribed by equation (1). There is a critical frequency ω_p after which the conductivity obey the mentioned power relation. This is the frequency of peak of dielectric loss and increases with temperature.The crossover frequency from dc to the dispersive region, ω_p, increases with temperature.Almond *et al*[13] have assumed that, the total conductivity reaches twice σ_{dc} at such critical frequency ω_p which is defined as the ionic hopping rate, and is given by,

$$\omega_p = [\sigma_{dc}/A]^{1/S} \qquad ...(2)$$

The values of ω_p are deduced at different ambient temperatures for the glass system under investigation, it is noticed that ω_p values lie in the same range of those obtained by Almond *et al*[13] for silver iodoarsenate ionic glasses (10^3-10^6 Hz). The temperature dependence for the hopping rate ω_p for the all glass samples is plotted (not shown here). The values of ω_p are found to be thermally activated for all glass samples obeying following Arrhenius relation; $\omega_p = \omega_o \exp(-E_\omega / kT)$ where E_ω is an activation energy concerning the variation of w_p with temperature, and $\omega_p = \omega_o$ at $T = \infty$ K. The values of E_ω and ω_o are deduced and listed in table (3). The observed activation of ω_p 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 (50-x)P_2O_5-xAgI-40Ag_2O-10Fe_2O_3 , x = 0 , 5 , 10 , 15, 20, 30. were studied in the temperature range from room temperature up to 500 K, Fig. 2. The temperature dependence of dc conductivity in the whole temperature range can be discribed by the Arrhenius relation[14]. It is noticed that, the general behaviour is the activation of conductivity with increasing temperature. Also there are one region in $\sigma_{dc}(T)$-$10^3/T$ relation appears and the conductivity increases with the increasing xAgI content. The obtained values of the activation energy E_{dc} are listed in table (3). It clears that, E_{dc} lie in the range (0.21 - 0.42 eV) and show regular variation with the increasing xAgI content.

The high dc conductivity with increasing temperature may be attributed to the fast diffusion

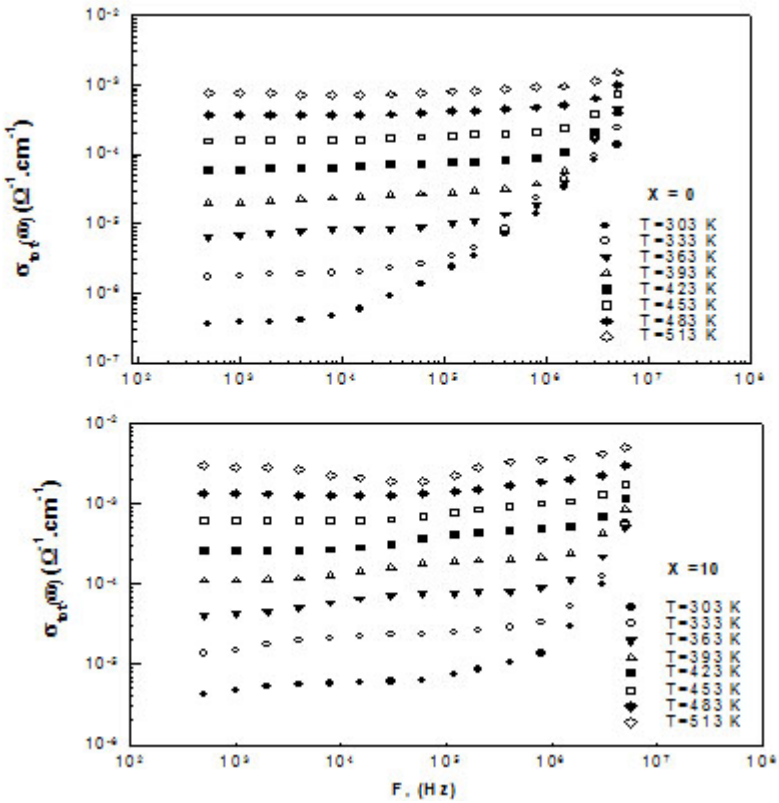

Fig. 1&2: The frequency dependence $\sigma_{tot}(\omega)$ for glass system (x=0,10) at different temperatures

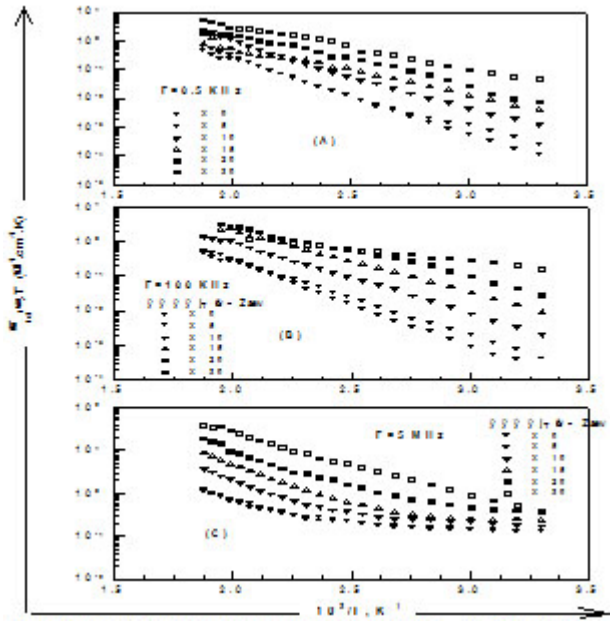

Fig. 3: Temperature dependence $\sigma_{tot}(\omega)$ for glass system (x=0,5,10,15,20,30) at different frequencies

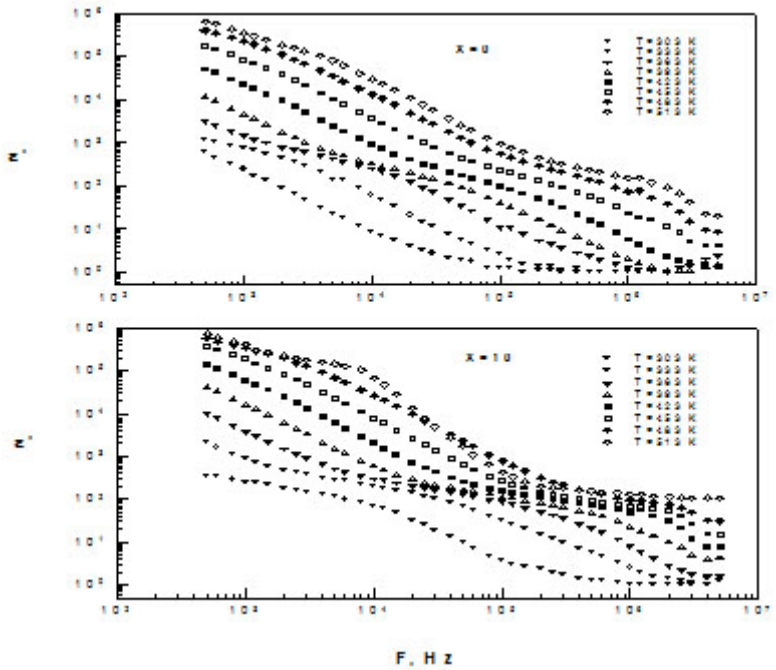

Fig. 4: The frequency dependence of ε for glass system (x=0,10) at different temperatures

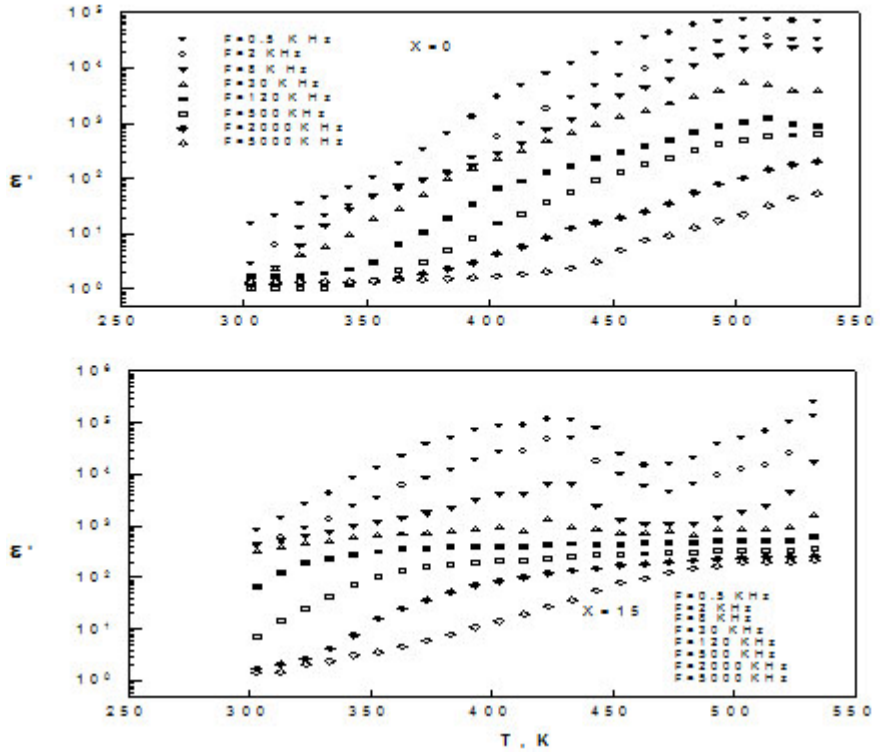

Fig. 5: Temperature dependence of ε' for glass system (x=0,5,10,15,20,30) at different frequencies

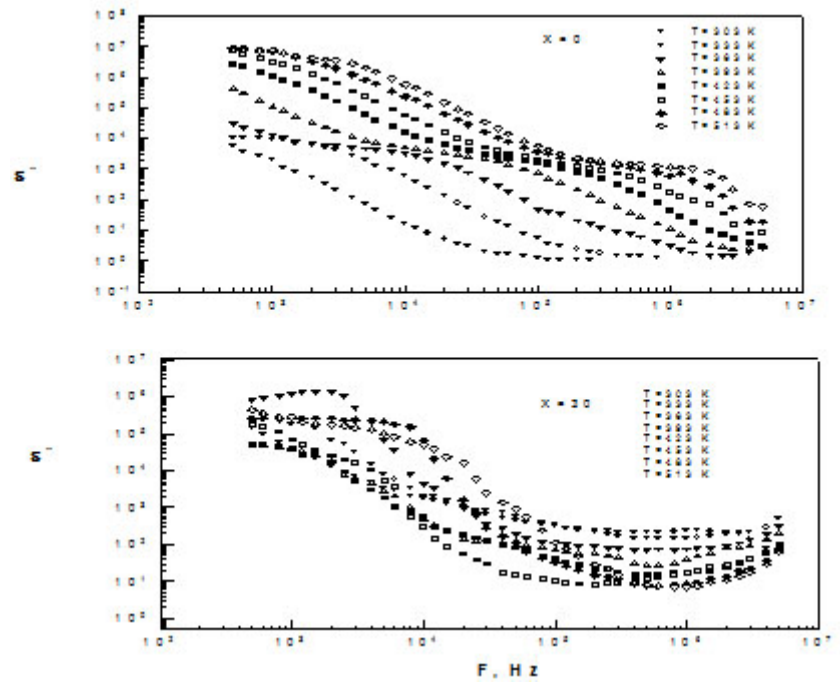

Fig. 6: The frequency dependence of ε" for glass system (x=0,10) at different temperatures

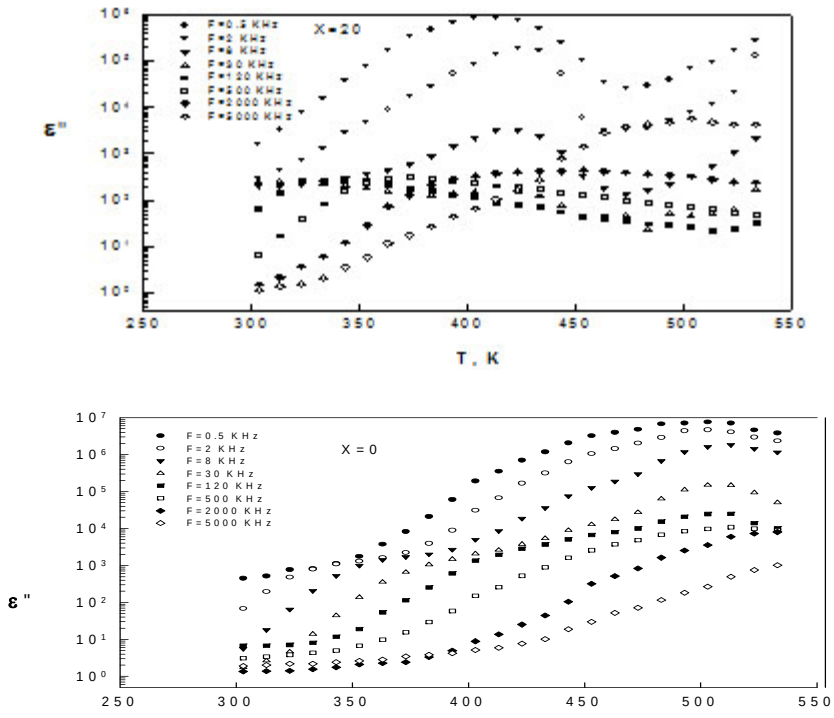

Fig. 7: Temperature dependence of ε" for glass system (x=0,5,10,15,20,30)at different frequencies

involving low-energy barriers for the motion of Ag^+ ions in the microdomains of AgI_4 clusters[15] which are embedded in the glass matrix. Also, the total interaction between the Ag^+ and I^- ions including both ionic and covalent bonding in the AgI_4 cluster, is very small. This characteristic electronic state[16] of the Ag^+ ion is one of the causes of the fast movement of Ag^+ ions in AgI-based superionic glasses.In addition, the Ag^+ ion has a $(4d)^{10}$ configuration of electrons and this configuration makes a "soft outer shell" . The outer soft shell of the Ag^+ ion may be distorted and fitted to the conduction pass . This flexibility of the outer shell is belived to be one of the origins of the hight ionic conductivity of AgI related compounds. As the concentration of the xAgI content increases, the concentration of the microdomains increases which leads to increase the conductivity.

Effect of frequency and temperature on the dielectric constant ε'

Fig. 3 illustrates the plot of real part of dielectric constant e' against frequency for the glass system (50-x) P_2O_5-xAgI-40Ag_2O-10Fe_2O_3, x = 0, 5,10, 15, 20, 30. at different ambient temperatures. It is noticed that, the general feature is the decrease of e' with increasing frequency to asympototic value. According to Deby's theory of intrinsic relaxtion time, ε' can be expressed by following relation,

$$\varepsilon' = \varepsilon_\infty + [(\varepsilon_s - \varepsilon_\infty) / (1 + \omega^2 \tau^2)] \quad ...(3)$$

where ε_σ and ε_∞ are the static and infinite dielectric constant respectively. The attenuation of dielectric constant ε' with increasing frequency can be explained as follows. When the frequency was increased, the dipoles will no longer be able rotate sufficiently rapidly so that their oscillations begin to lag behined field. It is noticed also that,the observed large values of e' at lower frequency over the whole temperature range interfacial polarization effect[17-19].

The dielectric constant ε' of the glass system (50-x)P_2O_5-xAgI-40Ag_2O-10Fe_2O_3, x = 0, 5,10,15,20,30. was studied in the temperature range between room temperature and 500 K at different fixed frequencies as shown in Fig. 4 . It is noticed that, ε' increases with increasing temperature for all tested samples up to a maximum peak but it decreases again at certain temperature. The maximum peaks are broaded in samples x = 0,5,10 and defined in samples x = 15,20,30 .The comparison with the differential thermal analysis (DTA) indicates that the beginning of the maxima corresponding to the glass transsition temperature (T_g). The quenched glass samples show a glass transsition before transforming exothermally to a crystalline phase.

The dielectric properties in ion conductive glasses mainly arise from the ionic motions. The free energy barriers impeding the ionic diffution, however, can be expected to vary from site to site, so there are different ionic motions in glasses[20]. 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 of blocking electrodes, Dc 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.

When the temperature was increased the dielectric constant e' increases because of the glass network relaxes and ionic motion becomes easier. This increase is also expected to be more pronounced at low frequencies, since the ions have more time to participate in the motion. At a certain temperature the dc ionic conductivity dominates leading to the appearent decrease of the dielectric constant .

Effect of frequency and temperature on the dielectric loss ε".

The frequency dependence of the dielectric loss ε" is studied for the glass system (50-x)P_2O_5-xAgI-40Ag_2O-10Fe_2O_3, x = 0 , 5 , 10 , 15, 20, 30. at different ambient temperatures, Fig. 5. It is noticed that, the general behaviour shows a

decrease of ε“ with increasing frequency which can be expressed according to Guntini *et al*[21] in the range wt >>1 by the following relation ;

$$\varepsilon\text{“} \ (\varepsilon_\sigma - \varepsilon_\infty)\ 2\pi^2\ N\ [ne^2/\varepsilon_\sigma]^3\ KT\ \tau_0^m\ w_M^{-4}\ \omega^{-m} \quad ....(4)$$

where m = (-4KT /W_M) , W_M being the energy required to librate a carrier, N is the concentration of the charge carriers that hop and N is the concentration of localized sites. However the relation (4) can be reformulated as;

$$\varepsilon\text{“} = A\ \omega^m \quad ...(5)$$

The values of the exponent m are obtained The values of m, W_M is listed in Table 4.

Table 1: The values of Tg, Tc, Density, Molar volume for the glass system (50-x)P_2O_5-xAgI-40Ag_2O-10Fe_2O_3,[x=0,5,10,15,20,30]

x AgI	Tg K	Tc K	Density experimental gm/cm3	Molar volumeVm
0	375.89	761.12	4.32	51.77
5	371.14	754.96	4.68	47.84
10	365.76	725.26	5.27	42.53
15	360.27	715.82	5.51	40.72
20	359.55	613.32	6.23	36.13
30	356.81	528.05	6.37	35.26

Table 2: The values of Tg, Tc, Density, Molar volume for the glass system (50-x)P_2O_5-xAgI-40Ag_2O-10Fe_2O_3,[x=0,5,10,15,20,30]

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20	359.55	613.32	6.23	36.13
30	356.81	528.05	6.37	35.26

Table 3: The values of the power S and pre-factor A for the glass system (50-x)P_2O_5-xAgI-40Ag_2O-10Fe_2O_3, [x=0,5,10,15,20,30]

x AgI T, K	S	S	S	S	S	S
303	0.58	0.78	1.28	0.86	0.64	0.48
333	0.85	1.05	1.09	0.95	0.95	0.38
363	0.94	0.89	1.04	0.86	0.81	0.41
393	1.01	0.87	0.85	0.60	0.51	0.53
423	0.61	0.92	0.79	0.49	0.49	0.43
453	0.47	1.03	0.51	0.37	0.39	0.70
483	0.59	0.75	0.50	0.36	0.38	0.45
513	0.53	0.56	0.45	0.35	0.39	0.50

The temperature dependence of the dielectric loss e“ is studied for the glass system (50-x)P_2O_5-xAgI-40Ag_2O-10Fe_2O_3 ,x=0,5,10,15,20,30. at different frequencies, Fig. 6. It is clear that, the dielectric loss ε“ increases with increasing temperature for all tested samples but it decreases again at certain temperature for samples of composition x= 15,20,30. In addition, the maximum peak of e“-T relation appears high at relatively low frequency ranges and it appears low at relatively high frequency ranges . When the frequency was increased the dielectric loss decreases which can be attributed to the reduction 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 energy absorbed from the field to the dielectric material. No disperion relation in studing e“ against frequency were recorded, only a decrease in the value of e“ with frequency which suggested that the relaxation peak may be shifted toward lower temperature. The obtaineed values of W_M (0.042 - 0.016 eV) are lower than the activation energies obtained using dc conductivity or relaxation time. This can be attributed to the contribution of localized electrons of the amorphous matrix in conduction process.

Table 4: The values E_w and w_o for the glass system (50-x)P_2O_5-xAgI-40Ag_2 O-10Fe_2O_3, [x=0,5,10,15,20,30]

xAgI	E_{ω},εV	$\omega_{o\ ,\ Hz}$	E_{bl}, εV
0	0.585	7 × 10^12	0.488
5	0.262	8 × 10^8	0.432
10	0.028	9 × 10^5	0.397
15	0.038	8 × 10^6	0.393
20	0.150	3 × 10^7	0.366
30	0.475	5 × 10^8	0.282

Table 5: The parameters A , m , and W_m for the glass system (50-x)P_2O_5-xAgI-40Ag_2O-10Fe_2O_3 , [x=0,5,10]

	X=0		X=5		X=10	
T, K	m	Wm, eV	m	Wm,eV	m	Wm , eV
303	1.903	0.054	1.724	0.060	1.534	0.068
333	1.978	0.058	1.120	0.102	1.281	0.089
363	0.964	0.129	1.224	0.102	1.659	0.075
393	1.712	0.079	1.797	0.075	1.925	0.070
423	1.760	0.082	1.995	0.073	1.859	0.078
453	1.832	0.085	2.004	0.078	1.879	0.083
483	1.825	0.091	2.126	0.078	1.990	0.083
513	1.944	0.091	1.798	0.098	3.285	0.053

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