December 2009 Volume 5 Issue 4

Trade Science Inc.

Materials Science

An Indian Journal

Full Paper

MSAIJ, 5(4), 2009 [469-478]

Investigation of the dielectric properties and thermodynamic parameters of (50-x)P_2O_5 –xAgI -40Ag_2O -10Fe_2O_3 [x= 0,15,20,25,30,35,40 and 45] ionic glass

S.Abouelhassan

Physics Department, Faculty of Science, Banha University, Banha, (EGYPT)

Received: 2nd March, 2009 ; Accepted: 12th March, 2009

ABSTRACT

Fast ion conducting glasses in the form (50-x)P_2O_5-xAgI-40Ag_2O-10Fe_2O_3 [where x= 0,15,20,25,30,35,40,45 mole %]were prepared by the melt quenching technique. The influence of AgI addition on the dielectric properties and thermodynamic parameters of the investigated system has been discussed in terms of the suitable models. The effect of frequency and temperature on the dielectric parameters such as the dielectric constant ε', dielectric loss ε", and the dielectric loss tangent (tan δ) have been studied in the temperature range 300-413°K and in the frequency range 0.5-100 kHz. The thermodynamic parameters such as the free energy of activation (ΔF), the enthalpy of activation (ΔH) the entropy of activation (ΔS) and the activation energy of relaxation (ΔE_r) have been calculated.

KEYWORDS

Super ionic glasses;
Dielectric properties;
Thermodynamic parameters.

INTRODUCTION

Super ionic materials are class of materials which verify the ionic conduction as compared with the ionic conductivity of the molten salts. This type of materials has a value of conductivity reach to 1 $(\Omega cm)^{-1}$, while most of solids has ionic conductivity reach to the value 10-8 $(\Omega cm)^{-1}$. Therefore the studies on the fast ionic conducting glasses are increasing due to their potential application in various electrochemical devices[1-5] such as solid state batteries, coulometer timers, fuell cell, electrochromic and memory devices[6].

The ion conducting glasses have a number of advantages due to their isotropic nature, the absence of grain boundaries , the ease of their preparation in various bulk forms, powders and thin films, the good possibilities for selection of appropriate components and the possibility of varying the working characteristics over a wide range by changing the chemical composition[7–11].

The studies on silver ion conducting super ionic solids in glassy or vitreous phase have attracted widespread attention over recent years mainly due to different reasons, where they exhibit very high ionic conductivity at room temperature[12]. The dielectric properties of the super ionic conducting glasses have been early studied[12-19] because of the more information about the conduction mechanism that can be obtained. Many fast ionic conducting glasses have been synthesized in the from of binary, pseudo binary and binary composition to obtain high ionic conductivity. The effects of adding one or more component to the ternary system, which are called quaternary fast ionic conducting glasses, have been studied[20,21].

Our aim is to investigate the effect of adding AgI on the expense of P_2O_5 on the dielectric properties and the thermodynamic parameters of the glassy system (50-x)P_2O_5-xAgI-40Ag_2O-10Fe_2O_3, [x= 0,15,20,25,30,35,40 and 45].

EXPERIMENTAL TECHNIQUE

Preparation of samples

The glassy system(50-x)P_2O_5-xAgI-40Ag_2O-Fe_2O_3,[x=0,15,20,25,30,35,40 and 45] 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 porcelain crucibles 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 shacked several times to ensure the homogeneity. 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. The solid electrolyte glass 20P_2O_5-30AgI-40Ag_2O-10Fe_2O_3 was pulverized into very small grain sizes. The solid electrolyte powder was pressed under the desired pressure to obtain pellet of 12 mm diameter and 1 mm thickness. The blocking electrode material Ag_2S was mixed with electrolyte glass powder in a weight ratio of 2 : 3. It was pressed together with the solid electrolyte layer into two-layered pellet. Silver paste, which showed an Ohmic behavior with solid electrolyte layer, was used to coat the surface of the solid electrolyte layer as a negative electrode.

A.C. measurements

The ac measurements have been carried out in the range of frequency from (500Hz to 5 MHz). The values of impedance(Z),capacitance(C),Resistance(R), and phase angle (ϕ) are directly read by using a programmable automatic RCL meter (HIOK 3532 LCR HITESTER). The dielectric parameters ε'(real part of dielectric constant), ε''(imaginary part of dielectric constant) and tan δ (dielectric loss tangent), were calculated by using the data of Z, C, R, ϕ at any frequency.

The dielectric constant ε' of the sample is calculated using the following relation;

$$\varepsilon` = \frac{t}{A} \cdot \frac{c}{\varepsilon_o} \tag{2.1}$$

Where C is the capacitance of the sample, t is the thickness of the sample, A is the cross-sectional area of the sample and ε_o is the free space permittivity equal to 8.85 x 10^{-12} F/m.

In addition, the dielectric loss ε'' was calculated from the following relation:

$$\varepsilon`` = \varepsilon` \tan \delta \tag{2.2}$$

Where tan δ is the dielectric loss tangent which was calculated from the following formula;

$$\tan \delta = \omega R C \quad , \quad \omega = 2\pi f \tag{2.3}$$

RESULTS AND DISCUSSIONS

Frequency and temperature dependence of the dielectric constant (ε')

Figure (1) shows the frequency and temperature dependence of the real part of the dielectric constant (ε') for the glassy system (50-x)P_2O_5-xAgI-40Ag_2O-10Fe_2O_3,[x= 0,15,20,25] in the temperature range 300–413°K. The complex permittivity (ε) is defined by[21]:

$$\varepsilon = \varepsilon` - j\varepsilon`` \tag{3.1}$$

Where`ε is the real part of the dielectric constant and is given by:

$\varepsilon' = \varepsilon_\infty + [(\varepsilon_s - \varepsilon_\infty) / (1 + \omega^2 \tau^2)]$ and ε'' is the imaginary part of the dielectric constant of material ε_s and ε_∞ are the static and infinite dielectric constant. From the figures it can be noticed, for all compositions, that ε' decreases with the increasing in the applied frequency where a dispersion phenomena can be observed at the low frequency range. The attenuation of the dielectric constant with frequency could be attributed to the formation of a space charge region at the electrolyte interface[5,15,22] which is familiarly know as ω^{n-1} variation or the non-Debye type of behavior. The behavior of the real part of the dielectric constant at the low and high frequency range can be explained as follows:

The decreasing of ε' at low frequency region may be attributed[23-27] to the contribution of charge accumulation at the interface. For polar materials ε' depends on the contribution of multi components of polarizability deformational (electronic, and ionic) and relaxation (oriential and interfacial) polarization. The former type of polarization is depend on the electrons and ions while the latter one depends on orientational or interfacial effect. The high value of ε‘, in low frequency region, is due to the presence of metallic or blocking electrodes which do not permit the mobile ions to transfer into the external circuit. As a result mobile ions pile up near the electrodes and give a large bulk polarization in the material. The increasing in frequency leads to a decrease in orientational polarization, since this take more time than electronic and ionic polarization. Such a decrease tends to reduce the value of ε‘ with increasing frequency, reaching a constant value at higher frequency. The general behavior of ε‘ with frequency was related to the applied filed which enhance the electron jumping between filled and empty sites in the amorphous matrix. This will lead to the electronic component in the observed dielectric dispersion. The observed continuous decreasing in ε‘ with frequency, may be attributed to that the dipoles will no longer be able to begin to lay behind the applied field.

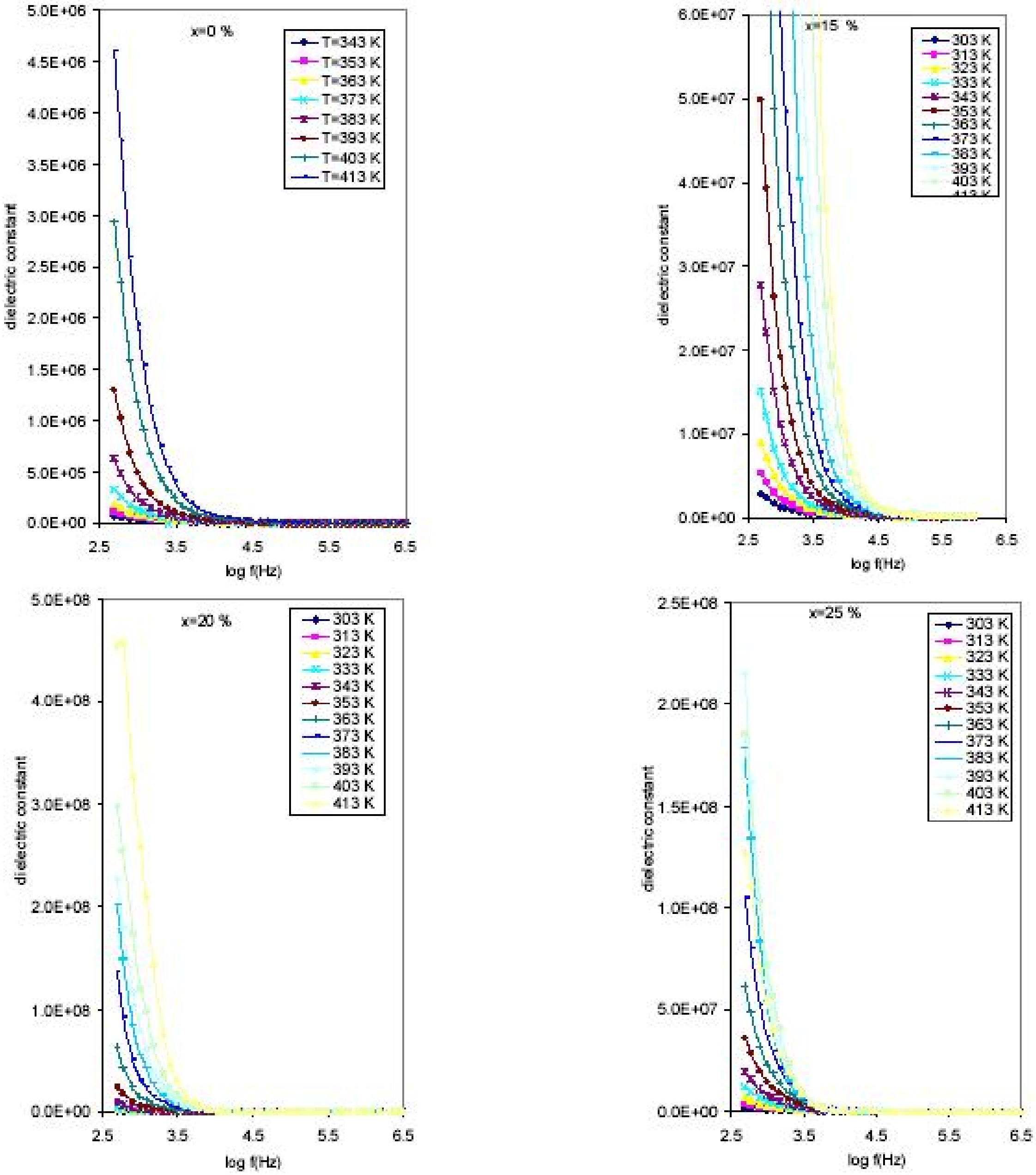

Figure 1: The frequency dependence of the dielectric constant for the sample: (50-x)P_2O_5-xAgI-40Ag_2O-10Fe_2O_3[Where x= 0,15,20,25].

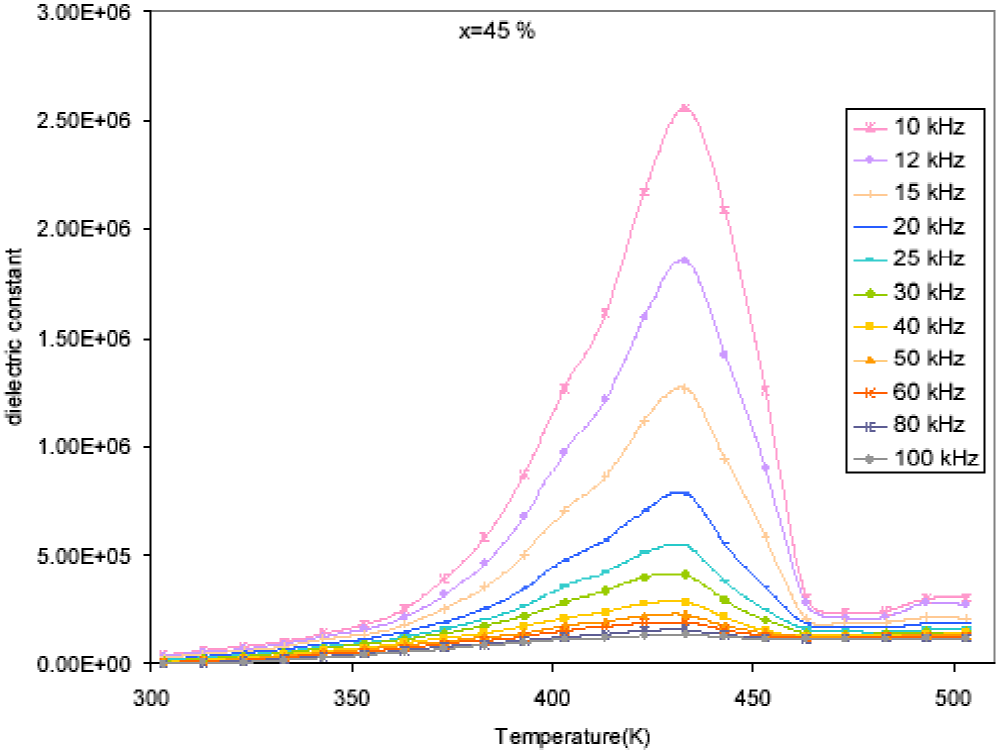

Figure 2: The temperature dependence of the dielectric constant for the sample $5P_2O_5$-45AgI-$40Ag_2O$-$10Fe_2O_3$

The temperature dependence of the dielectric constant is shown in figure (2) as a representative one. The general feature of the observed behavior is the presence of a principle peak. It has been considered[28] that the orientational polarization is connected with the thermal motion of molecules since dipoles cannot orient themselves at low temperature. Therefore as the temperature is increased, the orientation of dipoles is facilitated and thus increases the orientational polarization which in turn increases the dielectric constant.

The increasing in ε‘ with temperature may be attributed[24,29,30,31] at low temperature, to the small contribution of the electronic and ionic component while the orientational component can be neglected. As the temperature increases the ionic and electronic polarization sources start increasing to higher values in addition to the electronic and ionic polarizability contribution at higher temperatures. This behavior continued up to certain temperature then a decreasing behavior of ε‘ with temperature can be noticed. The observed peaks for all samples were found to be in the range of the glass transition temperature of the investigated samples which are studied elsewhere. From the conduction mechanism point of view, it has been considered that there exist three different ionic motions in the ionic conductive glasses, which are leading to the increasing in the dielectric properties in these glasses, they are as follow:-

a -The rotation of ions around their negative sites.

b -The short – distance transport. The 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 the dc or low frequency electric field or oscillate between the sites with high free energy barriers in an ac electric field.

c -The ions with higher energy can penetrate the glasses i.e. conduct electricity and cause the increasing in the dielectric constant. Due to the weak electrode polarization at blocking electrode or the domain interface one can conclude that as the temperature increases the glass network relaxation and the ionic motion become easier. The ions have more time to participate in the ionic conduction, so the ionic conduction at the low frequency range increase gradually on the expense of the dielectric properties, therefore the dielectric constant decreases.

Fequency and temperature dependence of the dielectric loss (ε“)

The variation of the dielectric loss with frequency for the investigated samples is shown in figure (3) as a representative one. It can be noticed that the dielectric loss decreases with increasing in frequency, where a strong dispersion phenomena was observed at lower frequencies and higher temperatures.

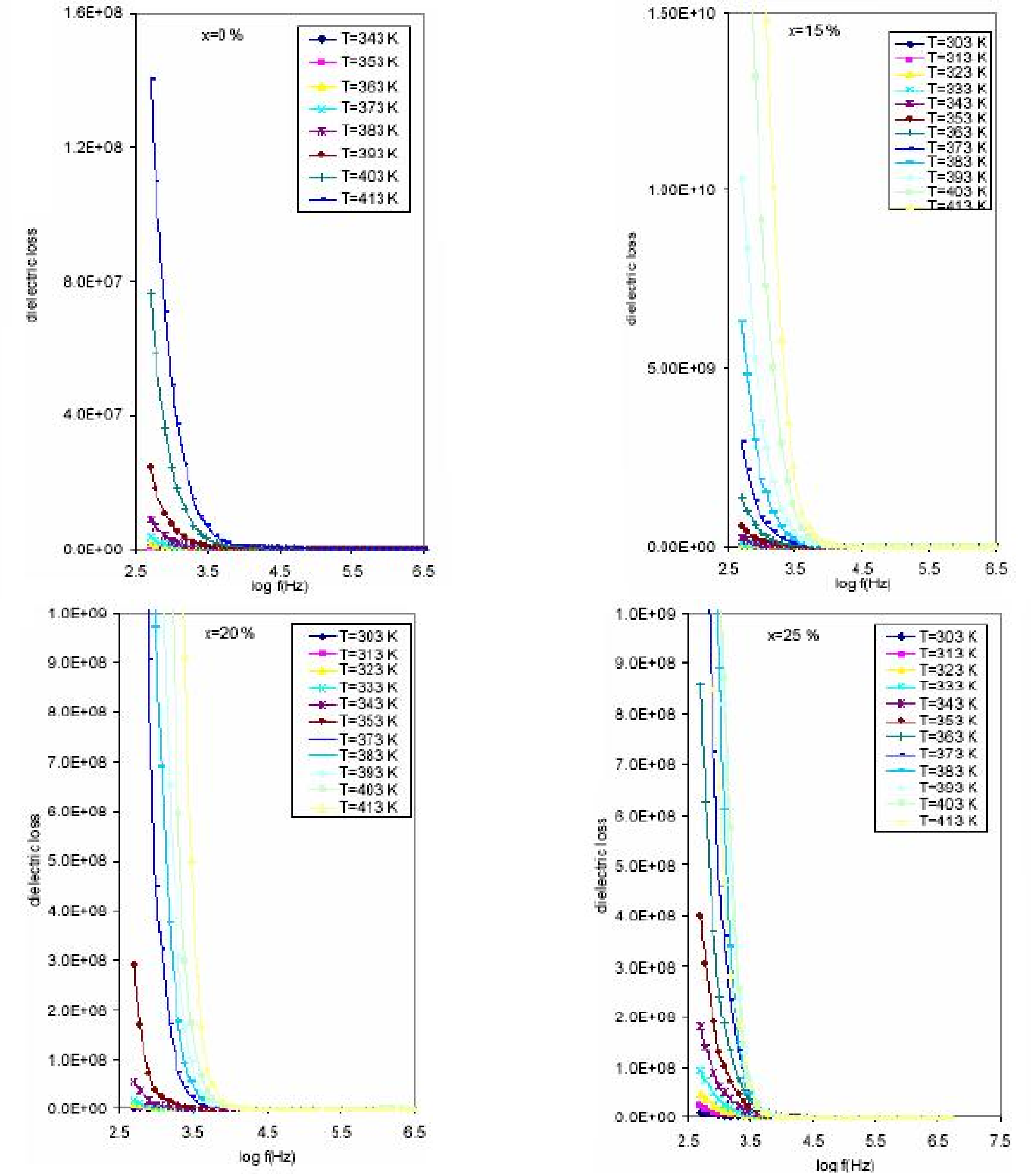

Figure 3: The frequency dependence of the dielectric loss for the sample: (50-x)P_2O_5-xAgI-40Ag_2O-10Fe_2O_3[Where x= 0,15,20,25].

The observed decrease in ε“ with frequency could be attributed to the formation of a space charge region at the electrode and electrolyte interface. The space charge regions with respect to the frequency was explained in terms of ions diffusion[32]

The frequency dependence of ε“ can be divided into two regions, the low frequency region was attributed to the contribution of charge accumulation at the interface[23]. At the high frequency region, due to the high periodic reversal of the field at the interface , the contribution of charge carriers towards the dielectric loss decreases with the increasing in frequency, then ε“ decreases with increasing in frequency.

The variation of ε“ with temperature has been explained[33] according to the types of losses into three parts; the conduction losses, dipole losses and the vibrational losses. At low temperature the conduction losses have a minimum value since they are proportional to (σ/ω). As the temperature increases, σ increases and so the conduction losses increases. This increases the value of ε“ with increasing temperature.

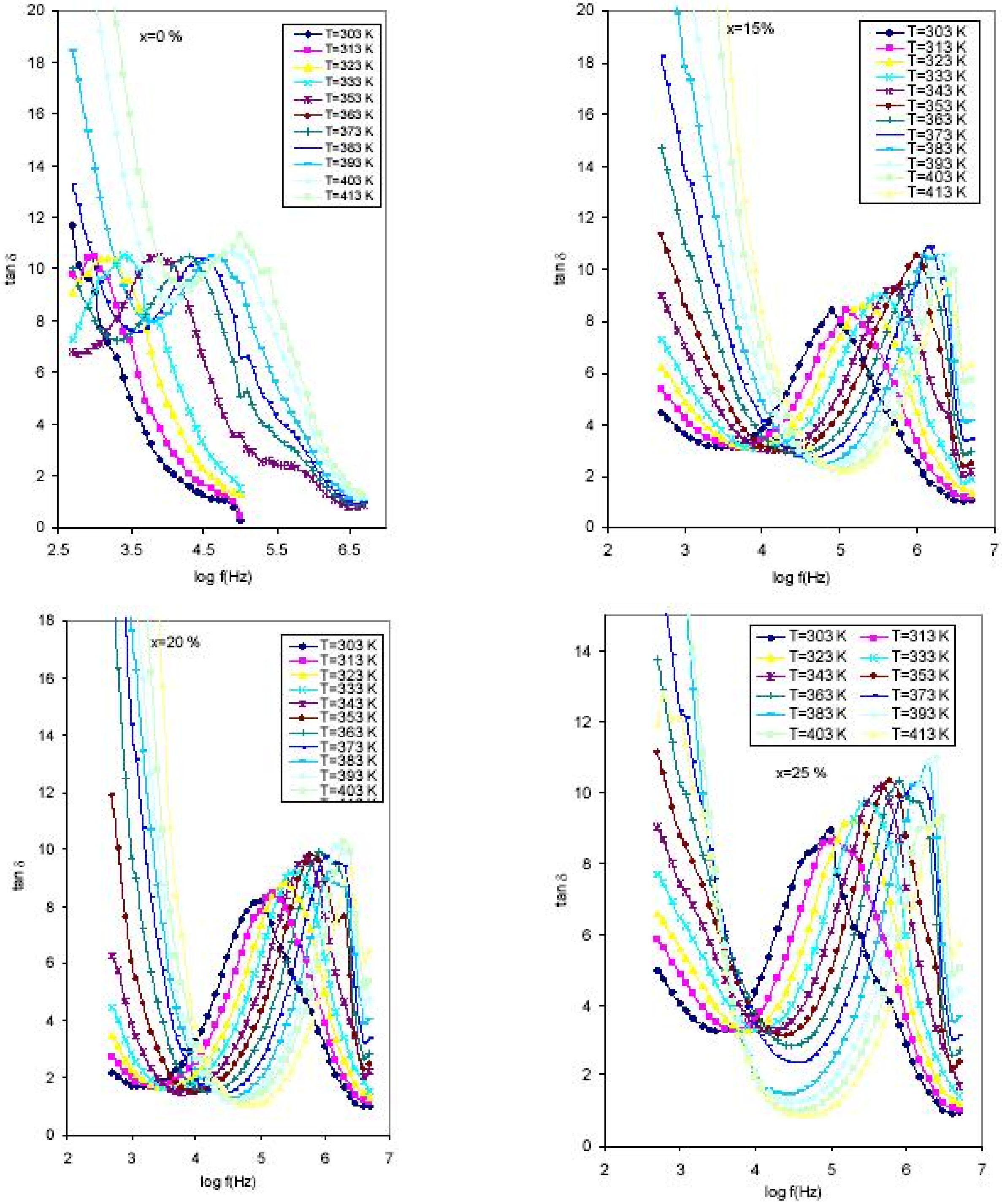

Figure 4: The frequency dependence of the dielectric loss tangent for the sample: (50x)P_2O_5xAgI40Ag_2O10Fe_2O_3[Where x= 0,15,20,25] .

Frequency and temperature dependence of the dielectric loss tangent (tan δ)

The effect of frequency on the dielectric loss tangent at different ambient temperatures for the glasses sample $(50-x)P_2O_5-xAgI-40Ag_2O-Fe_2O_3$,[x=0, 15,20,25,30,35,40 and 45] is shown in figure (4) as a representative one. From the curves it can be noticed that at low and moderate frequencies tan δ decreases fastly, then at high frequency range the decreasing behavior became more slowly which may be attributed to the migration of ions in glasses as the main source of dielectric loss at low frequency[34].

The high values of tan δ at low and moderate frequencies may be attributed to the contribution of ion jump, conduction loss and the electron polarization loss, which the law values may be attributed to the ion vibrations. It is possible to state that at low frequency range most of Ag ions in the glasses matrix contribute to the ionic polarization. As the frequency increases the ionic polarization decreases which leads to the presence of the peak in the curves, which shifts to the higher frequency with increasing in temperature. The observed absorption position and height of tan δ peaks increases and shifts very slightly towards higher frequency temperatures. This behavior is a characteristic one for the ionic glass and coincides with the Debye model of dielectric relaxation.

The frequency (f_m) corresponding to the peak value of tan δ is used to calculate the dielectric loss relaxation time (τ). When the frequency f is lower than (f_m), the charge carriers are mobile over large distances and are associated with the hopping conduction. For $f > f_m$ the charge carriers are spatially confined to their potential wells, being mobile over short distances and associated with the relaxation polarization processes. The peak frequency f_m is an indicative of a transition from long range to short range mobility and is defined by the condition $2\pi f\tau_m = 1$ where τ_m is the conductivity relaxation

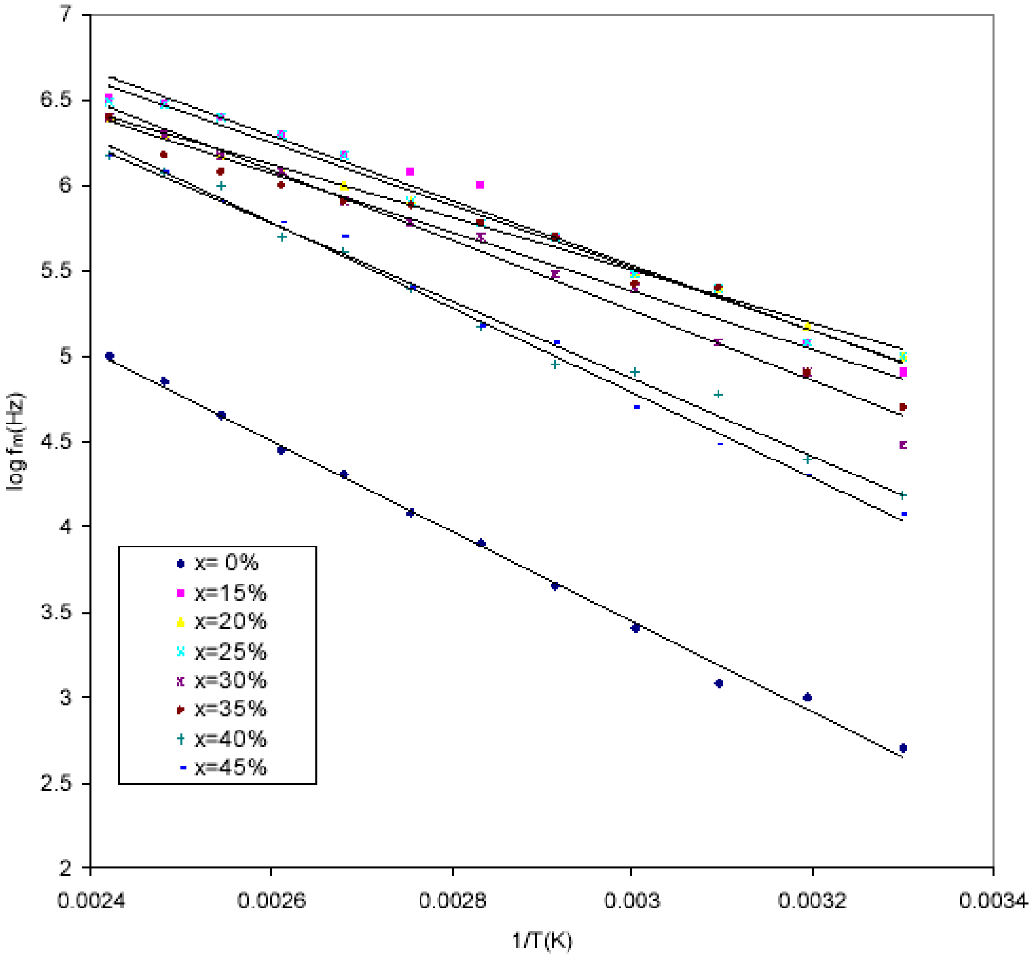

Figure 5: The temperature dependence of the peak frequency of the dielectric loss tangent for the investigated samples.

time. The temperature dependence of the peak frequency obeys the Arrehenius relation:

$$f_m = f_o \exp(-\Delta E_r / KT) \qquad (3.2)$$

Where ΔE_r is the activation energy of relaxation. From the relation between log (f_m) and the reciprocal temperature, at different compositions (figure 5), it can he noticed that a linear forms are obtained and therefore the relaxation process are considered to be thermally activated. The effect of AgI content on the activation energy of relaxation is shown in figure (6).The curves indicate two regions, where in the first one shows a decreasing behavior up to x = 20 % while in the second one an increasing behavior is obtained.

The decreasing behavior in E_r may be attributed to the increasing in the concentration of AgI ions in the glassy matrix which leads to decrease the relaxation time, accordingly the activation energy of relaxation decreases. More addition of "AgI" content leads to a structural relaxation which in turns tends to increase the relaxation time, therefore the activation energy of relaxation increases.

Determination of some thermodynamic parameters

Eyring[35] was the first one whose correlates the dielectric relaxation to the chemical rate theory. According to this theory the following relation was carried out[36,37]:-

$$\tau = (h/kT) \exp(\Delta F/RT) \qquad (3.3)$$

Where DF is the free energy of activation for dipole relaxation, k is the Boltzman's constant and h is the Plank's constant.

The enthalpy of activation (ΔH) is related to (ΔF) and the entropy of activation (ΔS) by the relation:

$$\Delta F = \Delta H - T\,\Delta S \qquad (3.4)$$

Eqs. (3.3) and (3.4) indicate that the plot of log (τ T) versus (1/T) should give approximately a linear relation ship with slope equal to ($\Delta H/R$) from which ΔH can be calculated.

Using equation (3.4) ΔF can be calculated by the relation:

$$\Delta F = 2.303\, RT \log(k\,\tau T/h) \qquad (3.5)$$

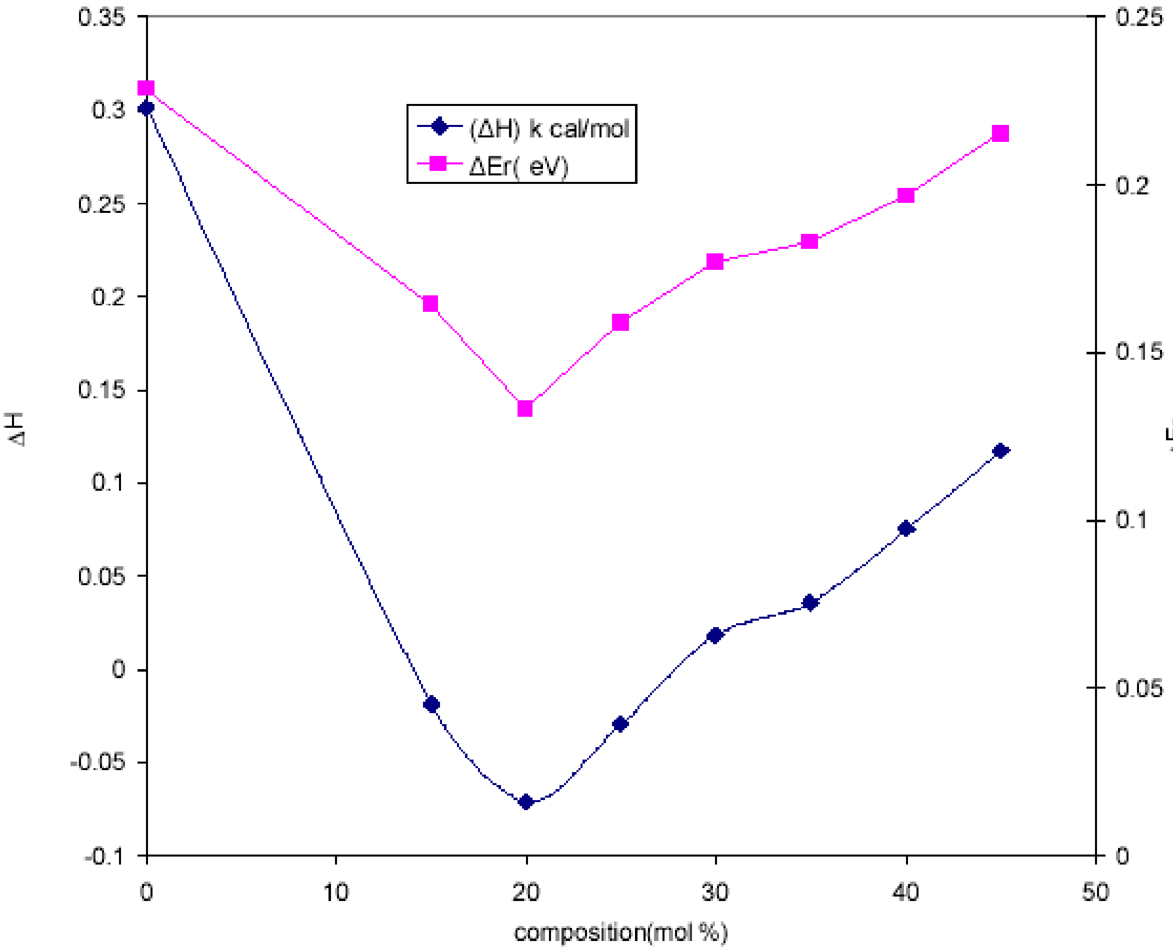

Figure 6: The composition dependence of the enthalpy of activation and the activation energy of relaxation for the investigated samples.

The relation between ΔH and ΔE_r against the AgI content in the composition is shown in figure (6). From the figure it can be noticed that ΔH and ΔE_r decrease gradually until the value of AgI content is attained 20%, then a slowly increase in the curves is obtained.

Figure (7) shows the effect of Ag I addition on the free energy (ΔF) at different ambient temperatures. The decreasing behavior in ΔH, ΔE_r and ΔF with the increasing in AgI content may be explained as follows. In the sample X = 0 % many non-bridging oxygen bonds was found and most of iron ions occupy the network forming positions. Therefore the activation energy was found to be high. 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 may leads to that the non-bridging oxygen decrease and the Ag-p bonds increase, which tends to decrease the activation energy up to X = 0 & 20 % . More addition of AgI may increase the dangling bonds between I and P or Fe atoms of the from Po–I or Feo–I. One can expect that an isolated groups of may appeared, which leads to increase the activation energy ΔE_r or ΔF or ΔH.

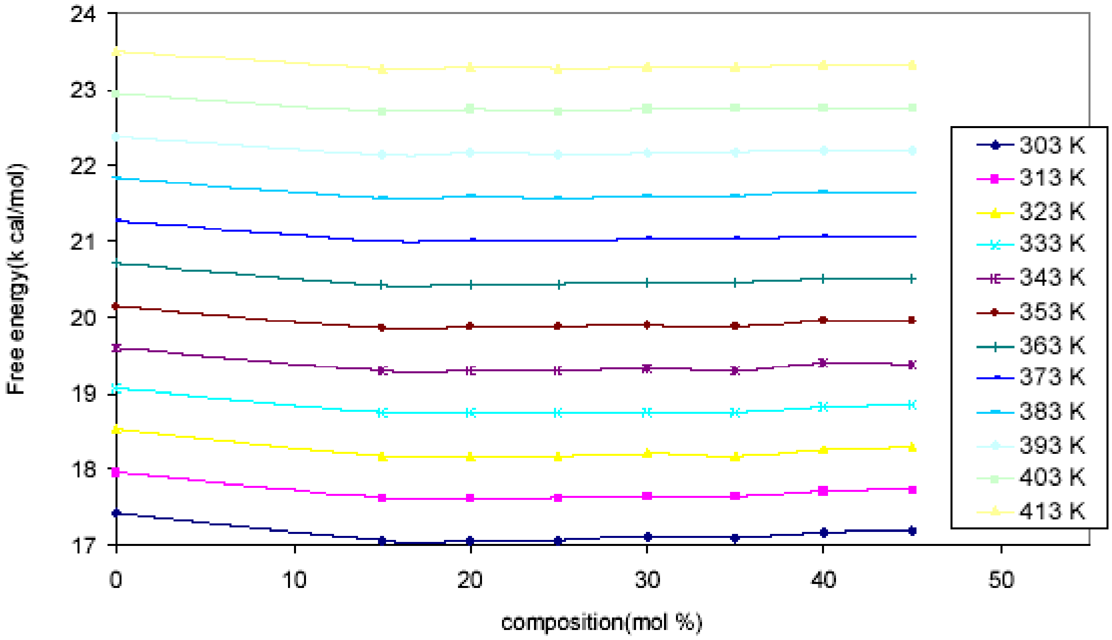

Figure 7: The composition dependence of the free energy of activation for the investigated samples.

REFERENCES

[1] K.P.Padmasree, D.K.Kanchan; Material Chemistry and Physics, **9**, 551 **(2005)**.

[2] D.Kunze; in W.Van Gool (ed) Fast Ionic Transport in solids, North Holland, Amsterdam, **(1973)**.

[3] B.V.R.chowdari, S.Radhakrishan; Material for solid state Batteries, world scientific singapore, **(1986)**.

[4] C.Suresh; Superionic solids: Principles and Application, North Holland, Amsterdam, **(1981)**.

[5] M.Venkateswarlu, K.N.Reddy, B.Rambou, N.Satyanarayana; Solid State Ionics, **127**, 177 **(2000)**.

[6] F.A.Fusco, H.L.Tuller; 'Superionic Solids and Solid Electrolytes recent trends' ed, A.L lasker and S.Chandra (New York: Acodemic) 43 **(1989)**.

[7] E.Lefterova, P.Ang dov; Y.Dimitriev and stoynov, Analytical laboratory, **6**, 123 **(1997)**.

[8] P.S.Nicholson, S.M.Whilling, G.Farringtion, W.W.Smeltzer, J.Thomast (ed); Solid State Ionics (Amesterdam: North Holland) 91 **(1992)**.

[9] T.Minami; J.Non-Cryst solids, **56**, 15 **(1983)**.

[10] G.Chiodelli, Campari, G.Vigano, G.Flor, A.Magistris, M.Villa; Solid State Ionics, **8**, 331 **(1983)**.

[11] M.D.Ingram, C.A.Vincent; chem.Soc.Ann.Rep.A, 23 **(1977)**.

[12] R.C.Arawald, R.Kumar; S.Phys.D: Appl.Phys, **27**, 2431 **(1994)**.

[13] K.P.Padmasree, D.K.Kanchan; J.Non-Cryst.Solids, **352**, 3841 **(2006)**.

[14] A.Doi; J.Non-Cryst.Solids, **352**, 469 **(2006)**.

[15] F.E.Salman, N.H.Shash, H.Abouelhaded, M.K.EL-Mansy; J.Physics and Chem.Of solids, **63**, 1957 **(2002)**.

[16] F.Henn, G.G.Belmonte, J.Bisqure, S.Devautour, J.C.Givntini; J.Non-Cryst.Solids, **354**, 3443 **(2008)**.

[17] S.M.Martin, J.Schrooten, B.Meyer; J.Non-Cryst.Solids, **37**, 981 **(2002)**.

[18] M.Cutroni, A.Mandanici, P.Mustarelli, C.Tomasi, M.Fednco; J.Non-Cryst. Solids, **307**, 963 **(2002)**.

[19] J.E.Garharczyk, P.Machowski, M.Machowski; Solids state ionics, **157**, 269 **(2003)**.

[20] A.Chiodelli, A.Magistris; Solid state ionics, **18–19**, 356 **(1986)**.

[21] N.Satyanarayana, A.karthikeyan, Venkateswarlu; J.Mater.Sci., **31**, 5471 **(1996)**.

[22] M.M.Ahmed, E.Yousf, E.Mostafa; Physica B, **371**, 74 **(2006)**.

[23] F.S.Howell, R.A.Base, P.B.Macedo, C.T.Moynahan; J.Phys.Chem., **78**, 639 **(1974)**.

[24] A.M.Farid, H.E.Atyia, N.A.A.Hegab; Va cuum, **80**, 284 **(2005)**.

[25] I.Pd, A.Agarwal, S.Sanghi, A.Sheoran, N.Ahlawat; J.Alloys and compounds, **(2008)**.

[26] T.L.Sidebottom, B.Rolling, K.Funke; Phys.Rev.B., **63**, 24301 **(2001)**.

[27] B.Bergo, W.M.Pontusch, J.M.Prison, C.C.Motta, J.R.Martinelli; J.Non-Cryst Solids, **348**, 84 **(2004)**.

[28] B.Tareev; Physics of dielectric materials, Moscow: Mir Publishers, 107 **(1979)**.

[29] N.Musuhwar, M.A.M.Khan, M.Husain, M.Zulfuquar; Plysica B, **396**, 81 **(2007)**.

[30] N.Mehta, D.sharma, A.Kumar; Plysic B, **391**, 108 **(2007)**.

[31] M.A.Afifi, A.E.Bekheet, E.Abdelwahhab, H.E.Atyia; Vacuum, **61**, 947 **(2001)**.

[32] J.R.Macdonald Editor; Impedance spectroscopy wiley, New York **(1987)**.

[33] J.M.Stevels; The electrical properties of glass (Hantbuch der Phsik), 350 **(1975)**.

[34] M.M.Elkholy, L.M.Sharaf EL-Deen; Mater.Chem and Physics, **65**, 192 **(2000)**.

[35] H.Eyring; J.Chem.Phys., **4**, 283 **(1936)**.

[36] A.E.Stearn, H.Eyring; J.Chem.Phys., **5**, 113 **(1937)**.

[37] S.Glasstone, K.J.Laidler, H.Eyring; The theory of rate process (Mcgraw- Hill, New York), 544 **(1941)**.