

CHAPTER-III

RESULTS AND DISCUSSIONS

III-1 : D.C electrical conductivity :

Oxide glasses containing transition metal ions (TMI) show semiconducting behaviour due to the presence of TMI in multivalent states in the glasses (e.g V^{+4} and V^{+5} in vanadate glasses). It is generally agreed that the d.c. electrical conduction in these glassy semiconductors takes place by the hopping movement of small polarons between TMI sites of different valence states⁽⁷⁶⁻⁸¹⁾ .

The d.c. electrical conductivity of the vanadium phosphate glasses and the lithium doped glasses sample was studied over the temperature range (300-593 K) .

Fig (III-1) represents semilogarithmic plot of σT against $10^3/T$ for all investigated samples . It is found that the electrical conductivity increases with increasing temperature obeying Mott and Davis relation⁽⁴⁵⁾ ;

$$\sigma = \nu_0 R_s^2 Nc (1-c) / k_B T [\exp (-E / k_B T)] \quad (III-1)$$

where N is the number of TMI sites per unit volume , R is the average TMI site spacing , ν_0 is a jump frequency , c is the ratio of the TMI concentration in the low valency state to the total TMI concentration , (1 - c) represents the fraction of empty sites (V^{+5}), k_B is the Boltzmann's constant and E is the activation energy for conduction processes .

The general behaviour shows two regions in σT versus. $1/T$ relation, one at relatively low temperature range where the other one appears at the higher temperature range . In addition , it shows a transition region at which the conduction process may change . The

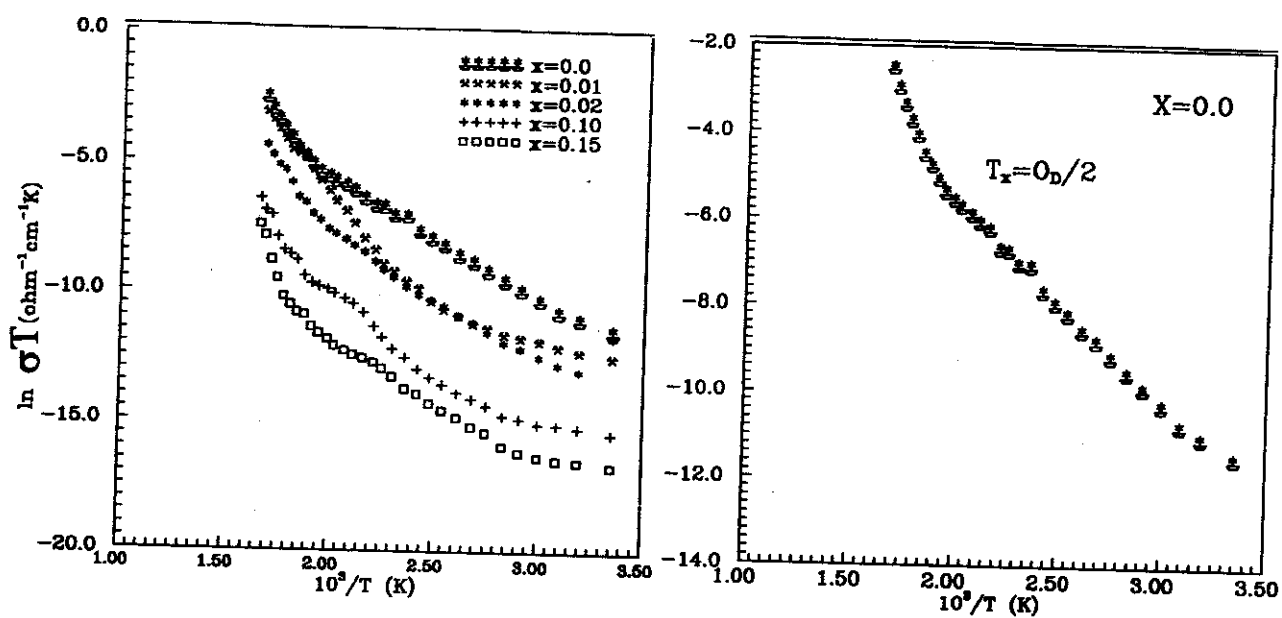


Fig.(III-1):Temperature dependence of d.c. conductivity for $(76\text{V}_2\text{O}_5-24\text{P}_2\text{O}_5)_{1-x}(\text{Li}_3\text{PO}_4)_x$ glasses.

two regions intersect at definite temperature ($T = T_x$), which can be obtained by using equation (III-1) .

$$\sigma_{o1} \exp (-E_1 / k_B T_x) = \sigma_{o2} \exp (-E_2 / k_B T_x) \quad (\text{III-2})$$

where : σ_{o1} , σ_{o2} are fitting parameters .

The obtained values of T_x and subsequently ($\theta_D = 2T_x$) are listed in table(III-1). The transition point (the intersection of both conduction regions) is shifted towards the lower temperature range with increasing the Li_3PO_4 content in the glasses except the case of $0.15\text{Li}_3\text{PO}_4$. This also shows that , the debye temperature is shifted towards the lower temperature range⁽⁸²⁾ .

Auston and Mott⁽⁷⁷⁾ are assumed that a strong electron phonon interaction exists , the activation energy E is the result of polaron formation with binding energy E_H and the energy difference E_D which might exist between the initial and final sites due to variations in the local arrangements of ions , they suggested an expression for activation energy (E) in the small polaron models as :

$$E = E_H + E_D / 2 \quad \text{for } T > \theta_D / 2 \quad (\text{III-3})$$

$$E = E_H \quad \text{for } T < \theta_D / 4$$

where E_H is the polaron hopping energy and θ_D is the characteristic Debye temperature defined by $\hbar\omega = k_B \theta_D$

The obtained values of the activation energy E_1 and E_2 are listed in Table(III-1) .

Table (III-1) The obtained activation energies E_1 , E_2 and T_x as well as θ_D $(76V_2O_5-24P_2O_5)_{1-x}(Li_3-PO_4)_x$ glass sample :

X	E_1 (eV)	E_2 (eV)	T_x (k)	θ_D (K)
0.0	0.3699	0.9816	509.8	1019.6
0.01	0.2115	0.828	409.1	818.2
0.02	0.366	0.848	485.2	970.4
0.10	0.115	1.088	443.9	887.8
0.15	0.129	1.4455	472.5	945

It is noticed that the values of E_2 lie in the range (0.828 – 1.44) eV which refer to the conduction beyond $\theta_D/2$ for the present glasses. In addition they increase with increasing the Li_3PO_4 content. The values of E_1 lie in the range (0.369 – 0.129) eV, these values refer to the conduction at the transition region between $\theta_D/4$ and $\theta_D/2$.

The increase of the activation energies with increasing lithium phosphate content may be caused by an increase of the average distance between pairs of hopping centers. A possible reason for this is the reduction of a part of V^{5+} to V^{4+} by the increase of Li_3PO_4 content ionization of Li atoms, and electron trapping by V^{5+} centers⁽⁸³⁾.

The activation energy for the d.c conductivity should, therefore, exhibit a break in the vicinity of half the Debye temperature as the conduction mechanism changes from the low to high temperature regions. The higher of the activation energies indicate a higher polaronic binding energy due to a greater amount of disorder causing a smaller polaronic radius at the high temperature range (above $T > \theta_D/2$). The mechanism process is dominated by thermally activated nearest-neighbor hopping of small polarons^(11,45).

At the intermediate temperatures (above $\theta_D/4$) the variable range hopping conduction appears.

The addition of lithium phosphate to vanadium phosphate glasses can be understood as follows: (i) An increase of phosphate in glass matrix reduces the vanadium fraction and subsequently the electrical conductivity. (ii) It also enhances the glass hydration

which increases the protonic conduction⁽⁸⁴⁾. (iii) It also leads to an increase of lithium ion contribution in conduction process. and (iv) The increase of Li_3PO_4 content reduces the $\text{V}^{4+} / \text{V}^{5+}$ fraction.

III-2 : I-V Characteristic

In the present section it is interesting to study the influence of applied field on conduction in vanadium phosphate glasses $(76\text{V}_2\text{O}_5-24\text{P}_2\text{O}_5)_{1-x} (\text{Li}_3\text{PO}_4)_x$. The I-V characteristic curves for $(76\text{V}_2\text{O}_5-24\text{P}_2\text{O}_5)$ glass are studied at different temperatures from room temperature to 383 K, see Fig (III-2). It is clear that the general behavior is characterized with a turnover point separates two states, the off state and the negative resistance state. In addition, the voltage and current at the turnover point are defined as the threshold voltage V_{th} and threshold current I_{th} respectively.

The off state extends from zero voltage and zero current to the turnover point (V_{th}, I_{th}) , including two regions, are the quasi-ohmic and the pre-threshold region.

In the case of $(76\text{V}_2\text{O}_5-24\text{P}_2\text{O}_5)$ glass, the values of V_{th} shifts towards lower value with increasing temperature obeying the electrothermal model⁽⁸⁵⁾;

$$V_{th} / T = V_o \exp (E_v / k_B T) \quad (\text{III-4})$$

where V_o is the temperature independent parameter, E_v is an activation energy term concerning the attenuation of conduction path temperature T ($= T_a + \Delta T$), where : T_a is the ambient temperature

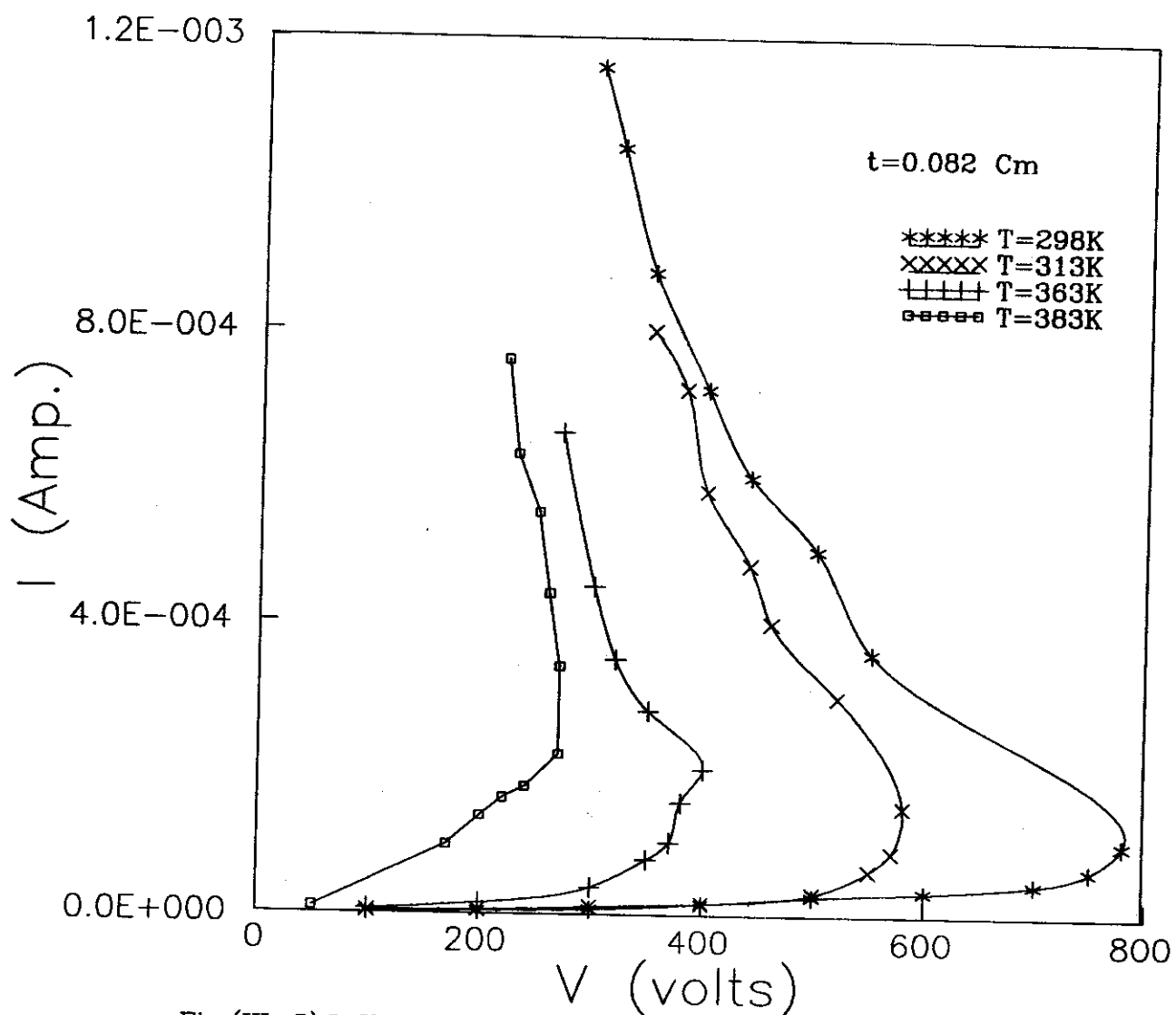


Fig.(III-2): I-V characteristic curves for $(76V_2O_5-24P_2O_5)$ glass sample at different temperatures.

and ΔT is the rise of conduction path temperature due to joule heating⁽⁸⁶⁾,

$$\Delta T = (k_B T_a^2) / (E - k_B T_a) \quad (\text{III-5})$$

where E is the low field activation energy . The calculated values of ΔT are listed in Table (III-2) . Figure (III-3) illustrates a semilogarithmic plot of (V_{th} / T) against $(10^3 / T)$ for $(76V_2O_5-24P_2O_5)$ glass which fits equation (III-4) . The value of $E = 0.162$ eV for vanadium phosphate glass is found to be lower than that obtained at low field ($E=0.369$ eV). This can be attributed to the condition enhacement of both field and self Joule heating . The value of V_{th} is also found to shift towards lower voltage and higher current with increasing temperature for $(76V_2O_5-24P_2O_5)_{1-x}(Li_3PO_4)_x$ glasses obeying the electrothermal model , equation (III-4) .

The semilogarithmic plots of (V_{th} / T) versus $(10^3 / T)$ show straight lines for all compositions . The values of V_o and E_v are obtained and listed in Table (III-3) . It is noticed that , E_v is nearly unchanged in the case of low content of $Li_3 PO_4$, while an irregular variation has been obtained at the higher content of lithium phosphate.

In addition the value of E_v is lower than one half that obtained at low field. This confirms the expectation that the electric field enhances conduction. The values of E_v in the case of 0.1% and 0.15% Li_3PO_4 are closer to that for $E_{d.c}$ obtained at low field . This can be attributed to the influence of Li_3PO_4 as ;

(a) An increase of Lithium ion contribution in the glass matrix .

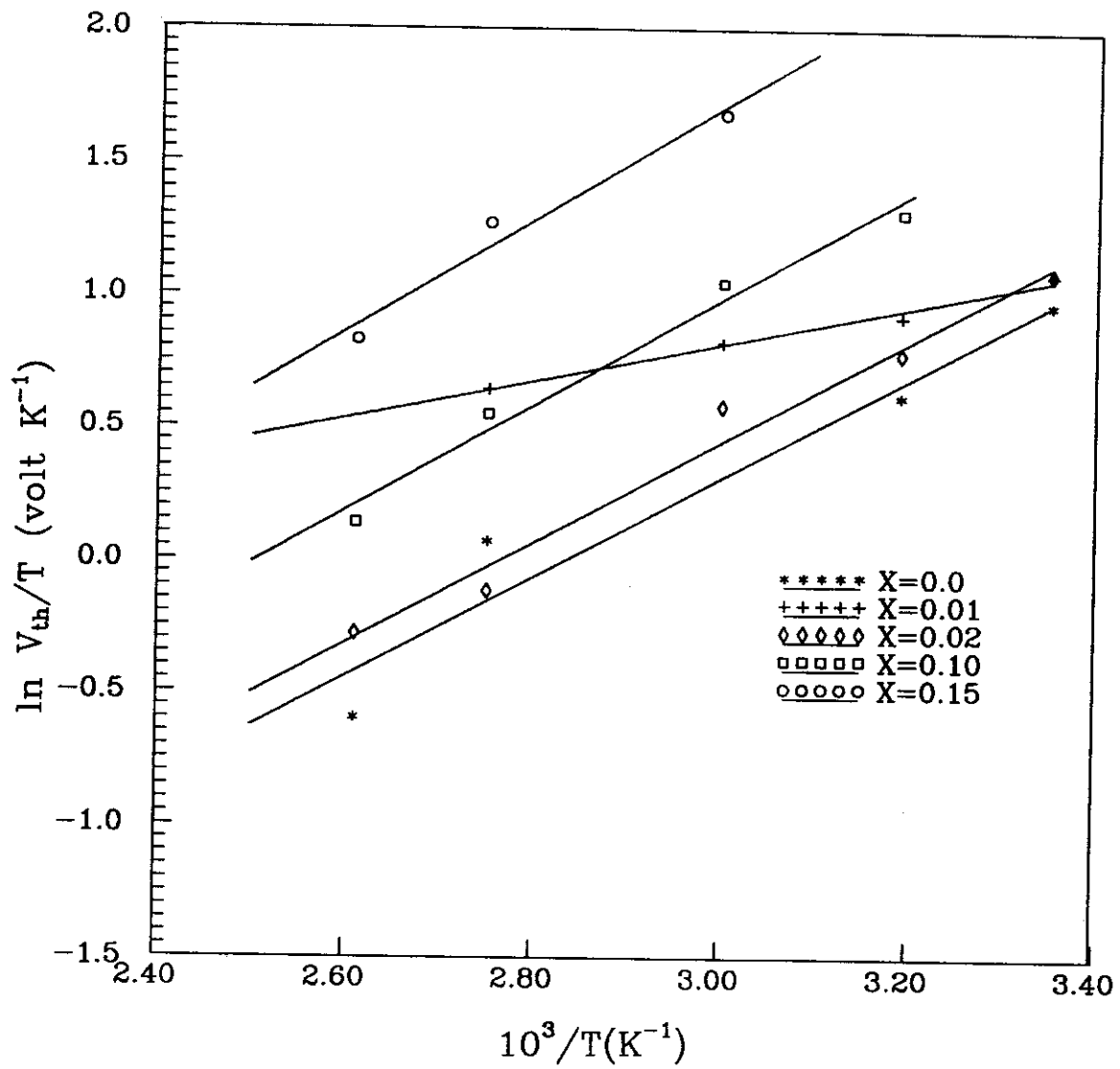


Fig.(III-3): Plots of V_{th}/T against $10^3/T$ for glass samples $(76V_2O_5 - 24P_2O_5)_{1-X} (Li_3PO_4)_X$ ($X=0.0, 0.01, 0.02, 0.10$ and $X=0.15$.)

- (b) An increase of phosphate group (PO_4) in glass matrix which reduces the vanadium fraction, and subsequently V^{4+}/V_{tot} .
- (c) It also enhances the glass hydration which increases the protonic conduction.

The values of conduction path resistance R_{th} ($V_{\text{th}}/I_{\text{th}}$) are obtained at different temperatures for $(76\text{V}_2\text{O}_5-24\text{P}_2\text{O}_5)_{1-x}(\text{Li}_3\text{PO}_4)_x$ glasses.

The results show that R_{th} decreases with increasing temperature obeying Arrhenius relation ⁽¹²⁾;

$$R_{\text{th}} / T = R_0 \exp (E_r / k_B T) \quad (\text{III-6})$$

where R_0 is independent temperature parameter and E_r is the activation energy for conduction processes. The semilogarithmic plots of R_{th} / T versus $10^3 / T$ show straight lines; Fig (III-4). The values of E_r are obtained and listed in Table (III-3). The value of E_r is nearly 65.5% of its initial value. ($\Delta E_r/E_r$) unchanged by increasing the Li_3PO_4 content. But it decreases for the highest concentration of Li_3PO_4 (15%).

Table (III-2) : The switching data as a function of temperature for $(76V_2O_5-24P_2O_5)_{1-x}(Li_3PO_4)_x$ glasses :

X	T _a (K)	ΔT (K)	V _{th} Volt	I _{th} Amp.	P _{th} m. Watt.
0.0	298	22.24	780	8.5×10^{-5}	66.3
	313	25.63	580	1.5×10^{-4}	87
	363	33.54	390	1.8×10^{-4}	70.2
	383	37.53	269	2×10^{-4}	42
0.01	298	41.2	870	8×10^{-5}	69.6
	313	45.76	780	1×10^{-4}	78
	333	52.29	755	8×10^{-5}	83.05
	363	63.03	700	6×10^{-5}	91
0.02	298	22.5	885	7.3×10^{-5}	64.6
	313	24.92	680	8.85×10^{-5}	60.1
	333	28.35	590	9.4×10^{-5}	55.5
	363	33.55	320	2.8×10^{-4}	48
	383	37.98	290	2.20×10^{-4}	63.8
0.10	313	53.83	1140	1.71×10^{-4}	194.9
	333	61.61	940	1.68×10^{-4}	180.5
	363	74.45	633	2.2×10^{-4}	139.3
	383	83.83	400	3.5×10^{-4}	82.5
0.15	333	47.72	1800	8.2×10^{-5}	147.6
	363	57.45	1670	1.2×10^{-4}	200.4
	383	64.51	880	8×10^{-5}	149.6

III-2-1: Influence of lithium phosphate and temperature on the turnover point :

The effect of Li_3PO_4 content in the present glass is also considered . Figure (III-5) illustrate I-V characteristic curves for different Li_3PO_4 content at different temperatures . It is clear that, the behavior is similar to that obtained for vanadium phosphate ($76\text{V}_2\text{O}_5\text{-}24\text{P}_2\text{O}_5$)glass sample .

The turnover point shifts towards higher current and voltage when the lithium phosphate content was increased, the corresponding threshold field E_{th} is obtained (V_{th} / t , Where : t is the sample thickness) and plotted against the Li_3PO_4 content , Fig (III-6). It is noticed that E_{th} increases exponentially with increasing Li_3PO_4 content , obeying the following relation :

$$E_{th} = E_o \exp (f / f_o) \quad (\text{III-7})$$

where E_o is the threshold field ($1.8 \times 10^4 \text{ V/cm}$) at $f = 0$, which is higher than that for the ($76\text{V}_2\text{O}_5\text{-}24\text{P}_2\text{O}_5$) glass . This can be attributed to the effect of sample hydration , f_o is a characteristic concentration equal to 0.074 .

Table (III-3) : The deduced activation energies E_v , E_r and fitting parameters V_o and R_o at the threshold point for $(76V_2O_5-24P_2O_5)_{1-x}(Li_3PO_4)_x$ glasses .

X	V_o	E_v	R_o	E_r
0.0	209.09	0.162	5.28×10^5	0.247
0.01	152.8	0.161	2.5×10^5	0.237
0.02	145.4	0.164	1.15×10^5	0.238
0.10	148.77	0.172	2.62×10^4	0.24
0.15	103.22	0.182	7.7×10^7	0.337

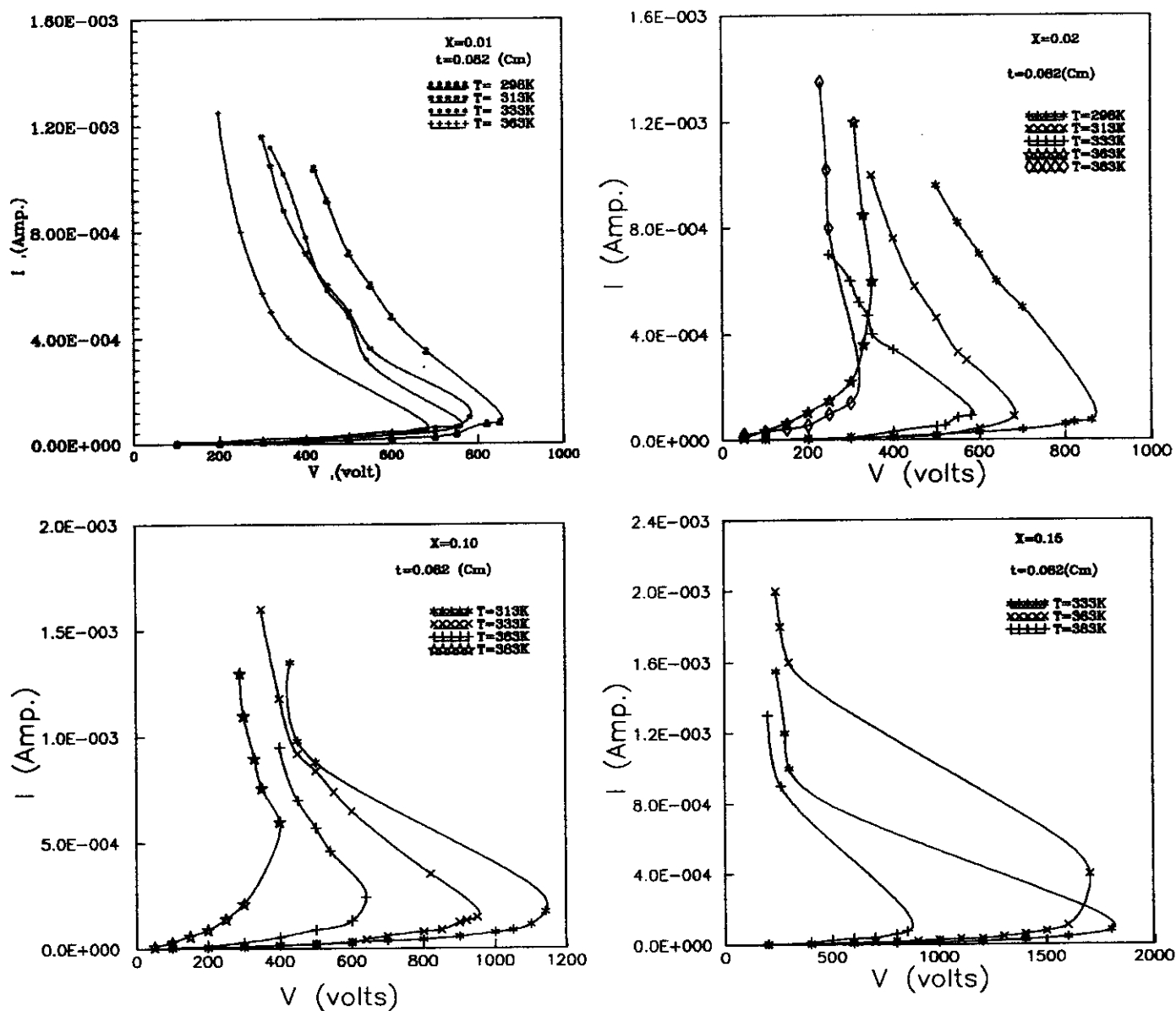


Fig.(III-5): I-V characteristic curves for $(76V_2O_5-24P_2O_5)_{1-x}(Li_3PO_4)_x$ glass samples where $X=0.01, 0.02, 0.10$ and 0.15 at different ambient temperatures.

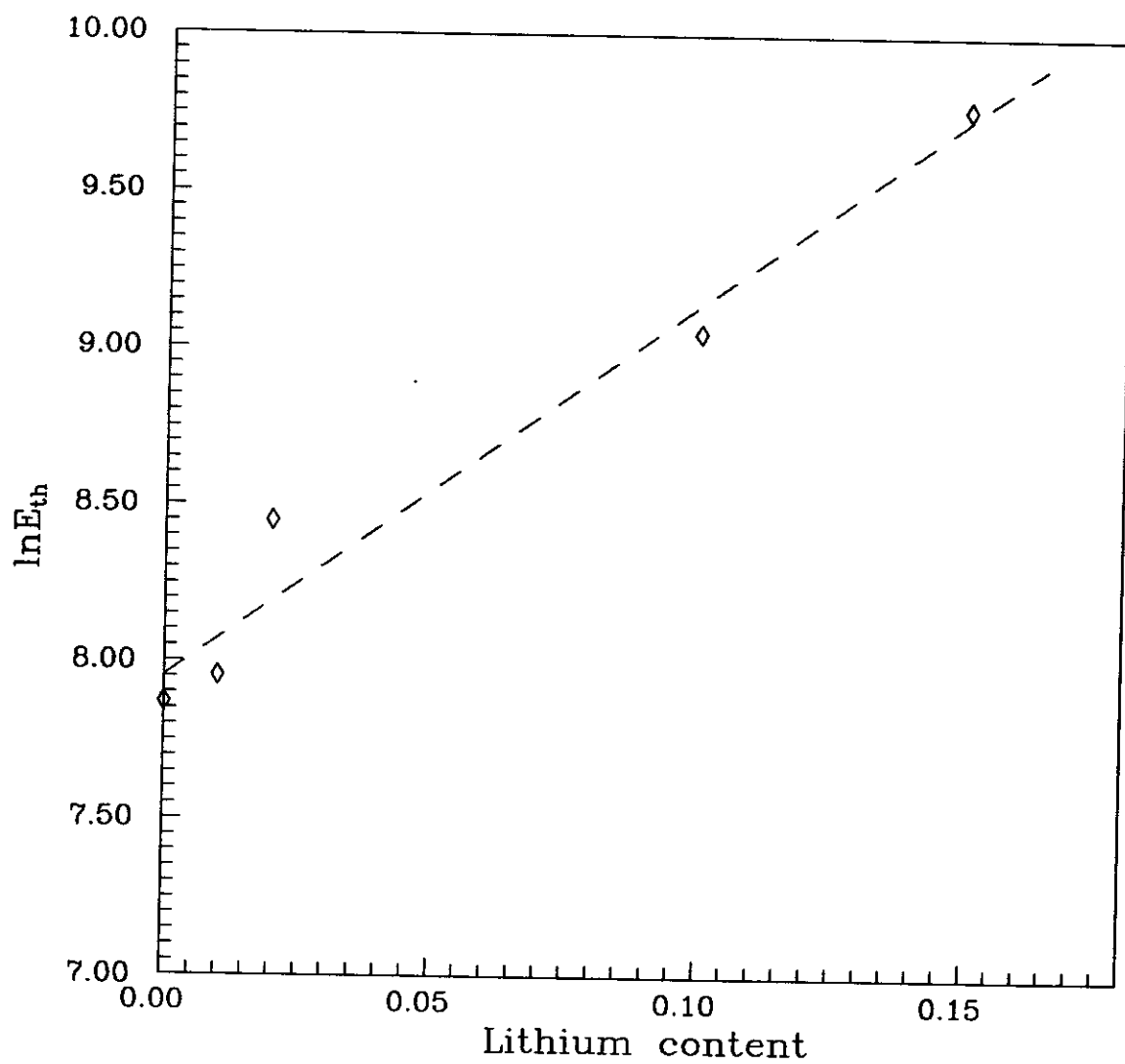


Fig.(III-6): Composition dependence of the threshold field for glass samples $(76\text{V}_2\text{O}_5 - 24\text{P}_2\text{O}_5)_{1-x} (\text{Li}_3\text{PO}_4)_x$

III-2-2: Effect of thickness on I-V characteristic of $(76V_2O_5-24P_2O_5)_{1-x}(Li_3PO_4)_x$ glasses :

The effect of thickness on the I-V characteristic of the investigated samples has been studied at 298 K . All samples showed similar behavior for the convenient I-V characteristic for vanadium phosphate glass , Fig(III-7) . Figure (III-8) shows typical plots for the effect of thickness on the I-V characteristic of the glass samples $(76V_2O_5-24P_2O_5)_{1-x}(Li_3PO_4)_x$.

The results shows a linear relationship for the dependence of both V_{th} and R_{th} on the sample thickness , fig. (III-9,III-10) .

In addition, the slope of R_{th} against sample thickness is equal to (ρ/A) , where ρ is the sample resistivity and A is the conduction path filament cross-section area , see Table (III-4) . The linearity of R_{th} versus thickness means that the filament cross-section area is the same for the different thicknesses. It is found that the value of ρ/A increases with increasing lithium phosphate content which means an increase of ρ , in agreement with low field study .

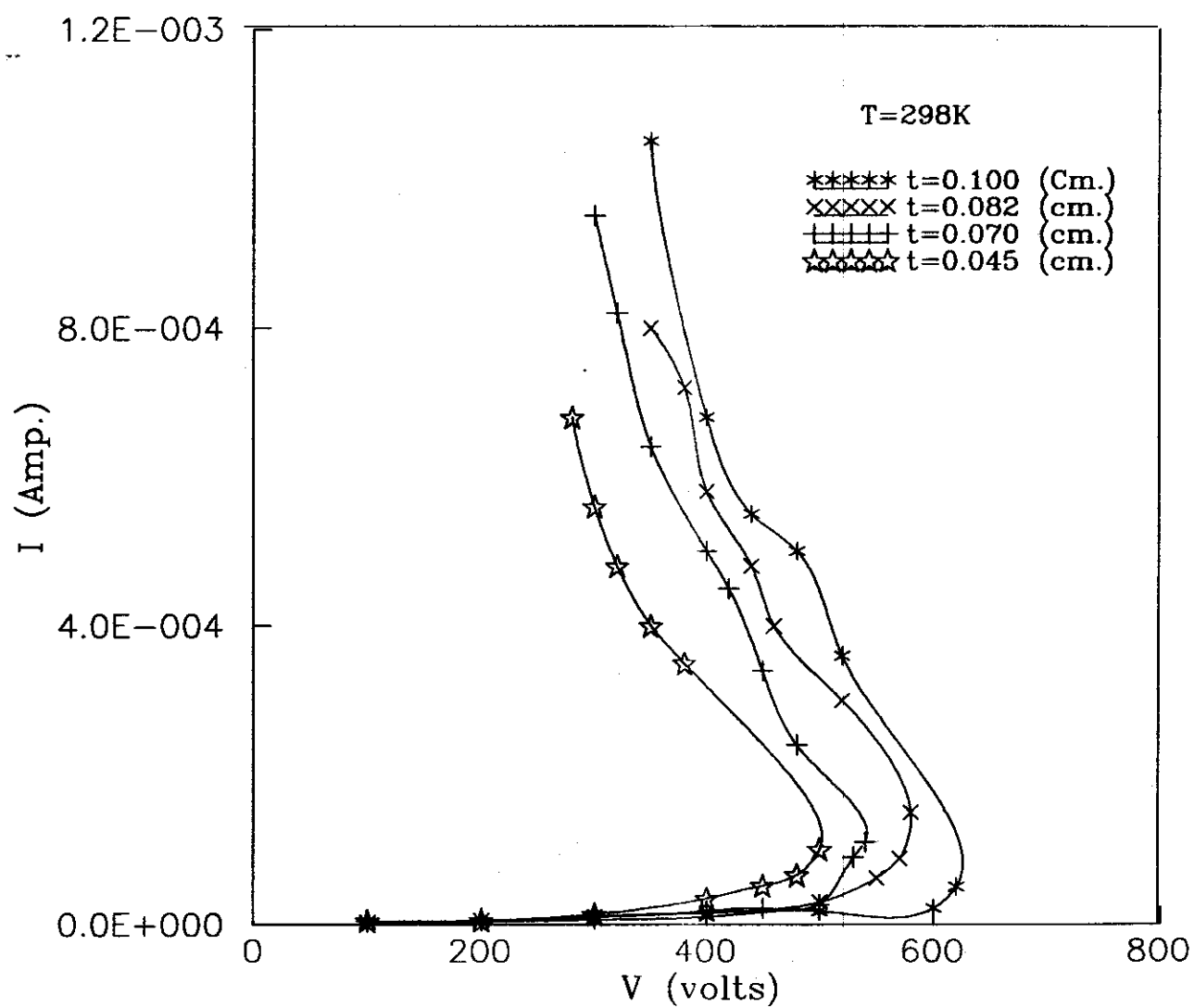


Fig.(III-7):I-V characteristic curves for $(76V_2O_5 - 24P_2O_5)$ glass sample at different thickness

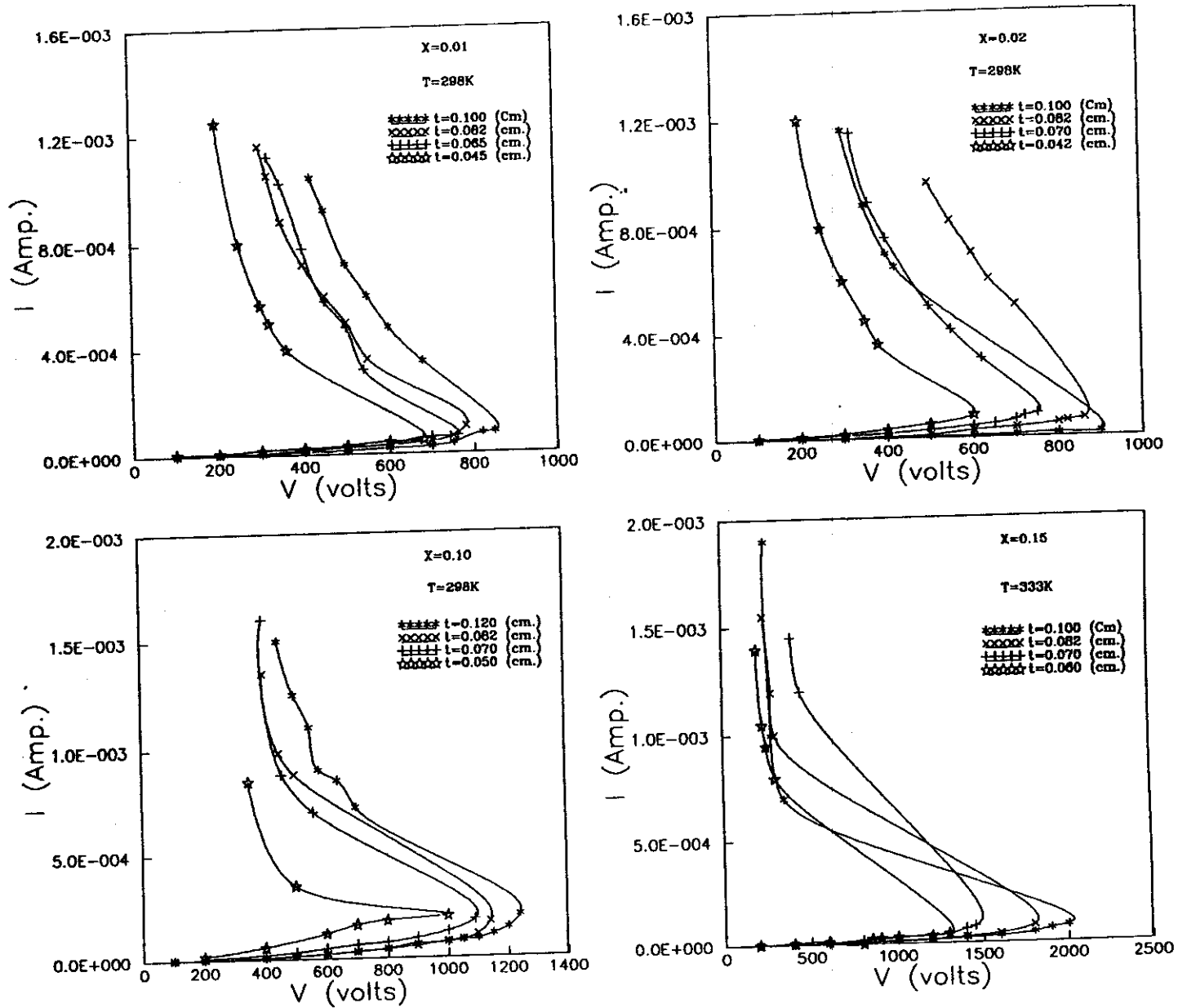


Fig.(III-8): I-V characteristic curves for $(76V_2O_5 - 24P_2O_5)_{1-x}(Li_3PO_4)_x$ where $X=0.01, 0.02, 0.10$ and 0.15 glasses at different thickness.

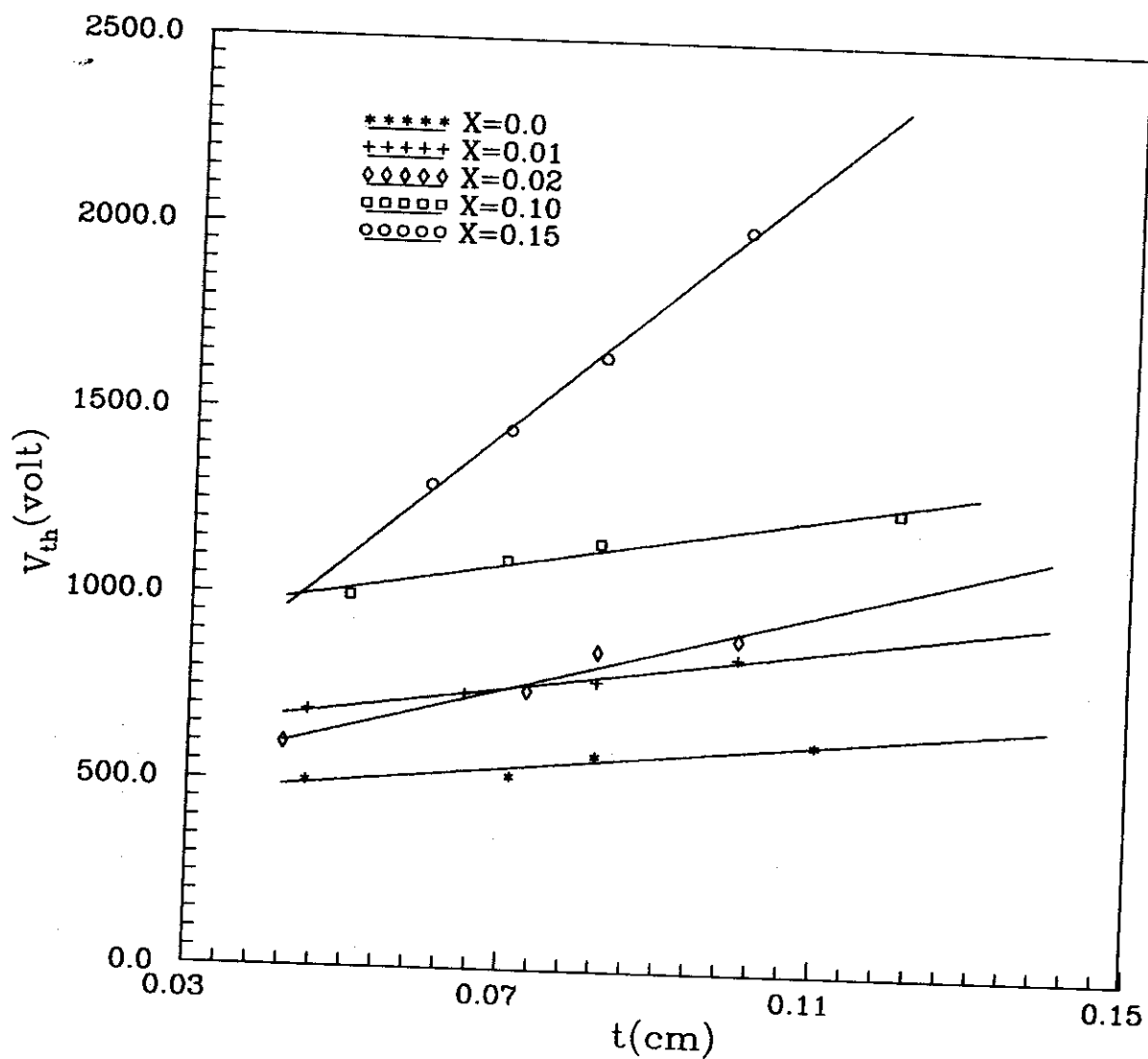


Fig.(III-9): The plot of V_{th} against sample thickness for glass samples $(76V_2O_5 - 24P_2O_5)_{1-x} (Li_3PO_4)_x$ ($X=0, 0.01, 0.02, 0.1$ and 0.15) at 298K.

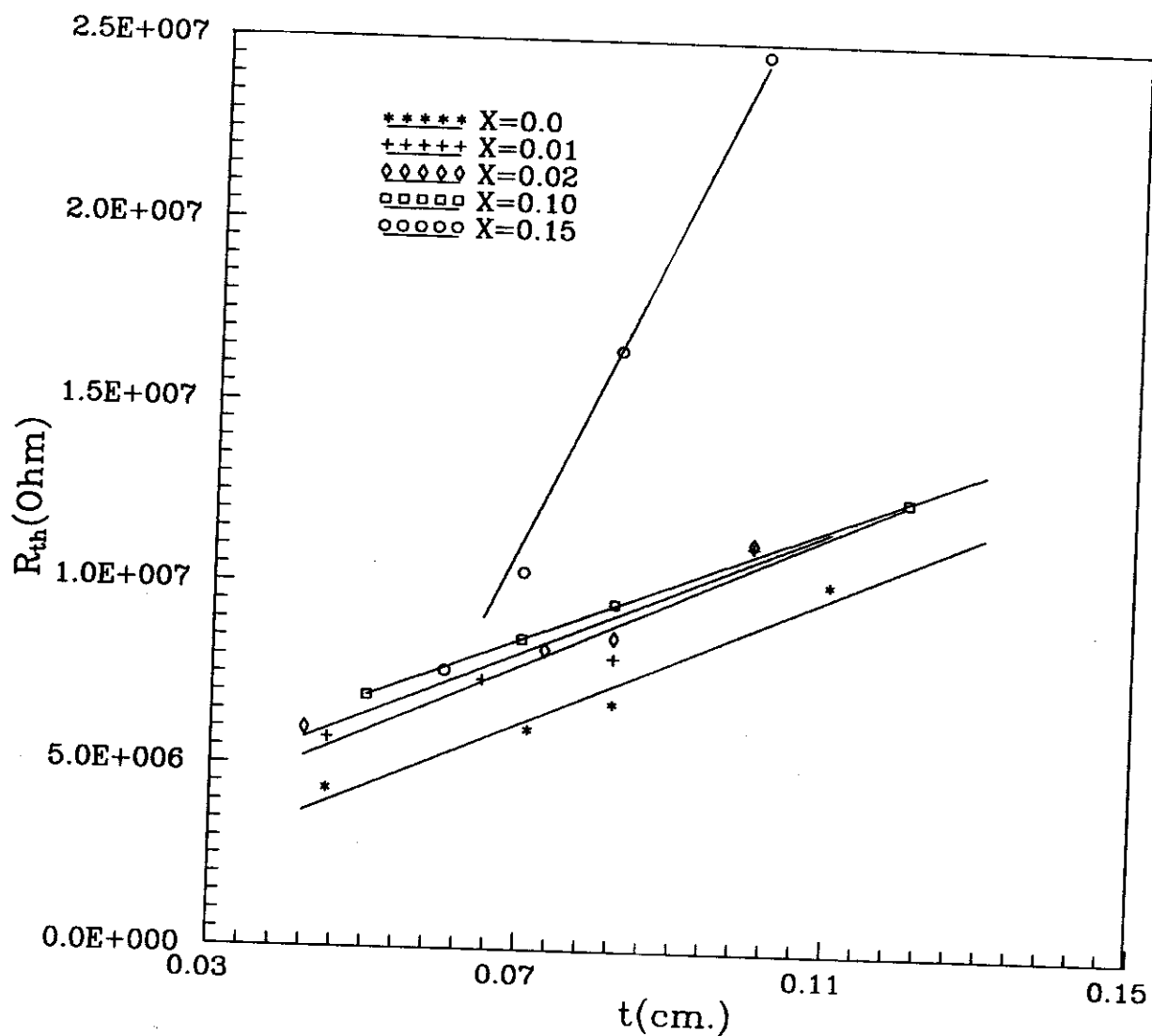


Fig.(III-10):The plot of R_{th} against sample thickness for glass samples $(76V_2O_5 - 24P_2O_5)_{1-X} (Li_3PO_4)_X$ ($X=0, 0.01, 0.02, 0.1$ and 0.15) at 298K.

Table (III-4): The switching data as a function of sample thickness for $(76V_2O_5-24P_2O_5)_{1-x}(Li_3 PO_4)_x$ glasses :

X	t(cm)	V _{th} (volt)	I _{th} (Amp.)	ρ _{th} / A
0.0	0.11	620	5.1×10^{-5}	2.07
	0.082	580	8.78×10^{-5}	
	0.070	520	9.4×10^{-5}	
	0.045	500	1.3×10^{-4}	
0.01	0.10	850	6×10^{-5}	2.01
	0.082	780	1.6×10^{-4}	
	0.065	740	8×10^{-5}	
	0.045	690	1×10^{-4}	
0.02	0.11	900	8×10^{-5}	2.4
	0.082	860	1×10^{-4}	
	0.07	750	1.2×10^{-4}	
	0.042	600	1.15×10^{-4}	
0.10	0.12	1250	2×10^{-4}	2.06
	0.082	1150	2.2×10^{-4}	
	0.07	1100	2.5×10^{-4}	
	0.050	1000	3×10^{-4}	
0.15	0.10	2000	8.1×10^{-5}	2.3
	0.082	1800	9×10^{-5}	
	0.070	1450	1.5×10^{-4}	
	0.06	1300	4×10^{-5}	

III-2-3: Switching mechanism :

The conduction in the off state region (below the turn point) could be divided into two regions . The first region of conduction is ohmic whereas conduction in the second region is field dependent . The later one could be explained according to the field emission of v^{+4} electrons which is based on Pool-Frenkel effect , the voltage dependence of conduction current is given by⁽⁸⁷⁾:

$$I = I_0 \exp (\beta v^{1/2} / k_B T) \quad (\text{III-8})$$

where : $\beta = (e^3 / 4 \pi \epsilon \epsilon_0 d)^{1/2}$, ϵ is the relative permittivity , ϵ_0 is the permittivity of space , and d is the average jumping distance separating filled and empty states .

Semilogarithmic plots of I versus $V^{1/2}$ for the glass samples are shown in Fig(III-11) . It is clear that a linearly of $\ln I$ with $V^{1/2}$ for all samples . Since the onset of emission in semiconductors initiates at field of about 10^6 V/cm , thus this model is considered to explain the non linearity in I-V curves by assuming the electron emission will occur between filled and nearest empty states .

Accordingly, the values of d are obtained using the least square fitting of the above relation (III-8) and listed in Table (III - 5) . It is found that d values lie in the rang $(0.4- 25) \overset{\circ}{\text{A}}$, in agreement with the published data ^(18,87) except the values lower than that of the nearest neighbor distance $(3-4) \overset{\circ}{\text{A}}$.

|nI (Amp.)

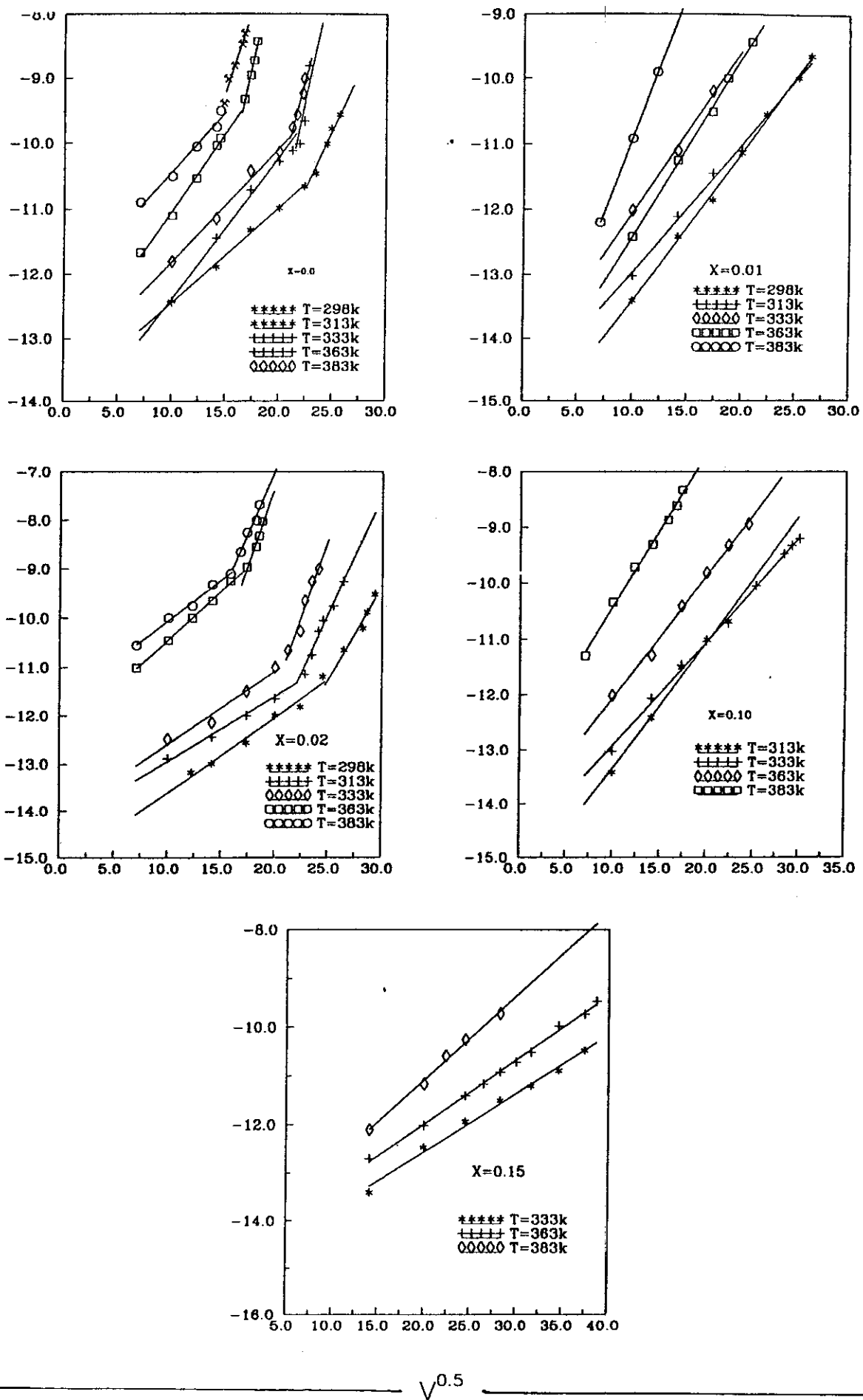


Fig.(III-11): Plots $\ln(I)$ various V^5 for $(76V_2O_5 - 24P_2O_5)_{1-x}(Li_3PO_4)_x$ ($x=0,0.01,0.02,0.1$ and 0.15) glasses at different ambient temperatures.

Table (III-5) The obtained value of $d \text{ (Å)}^{\circ}$ for $(76\text{V}_2\text{O}_5-24\text{P}_2\text{O}_5)_{1-x}$
 $(\text{Li}_3\text{PO}_4)_x$ glasses : at different temperatures .

X	0.0	0.01	0.02	0.10	0.15
T(K)	$d \text{ (Å)}^{\circ}$				
298	1.92	3.35	2.63	-	-
313	2.42	4.05	1.84	25.11	-
333	2.76	2.09	6.75	18.79	15.5
363	1.11	1.29	5.87	12.71	6.06
383	0.93	0.4	2.36	11.05	1.76

The values of d lower than 3 \AA could be attributed to the abnormal large values of the dielectric constant due to both the interfacial and the ionic polarization in the present glasses .

Additionally some deviation in $\ln I - V^{1/2}$ plots is observed as the field approaches the threshold value at the turnover point . This in turn leads to the reduction of conduction path resistance. Resistance will enhance the field emission as the result of the presence of Joule heating . The ultimate conduction is attained when the applied voltage approaches the v_{th} value (zero differential resistance ($\delta v/\delta I=0$)) and then the conduction path switches to the negative differential resistance region . The estimation of the differential negative resistance R_{neg} ($\delta V/\delta I$) showed a strong dependence on both the applied field and the ambient temperature . It was difficult to discuss the variation of R_{neg} with the applied field neglecting the influence of the Joule heating a rises in the conduction path filament .

The dissipated power in the thermally isolated filament plays a significant role in reducing the value of the negative resistance , see Fig (III-12) . This behavior can be described by the following empirical relation ,

$$R_{neg} = R_o (w_o / w)^m \quad (III - 9)$$

where : R_o is the conduction path resistance when $w = w_o$ (the ultimate power initiating the On-state and m is a power .

The values of the power (m) are obtained using the least square fitting of the above relation and listed in Table (III-6) .

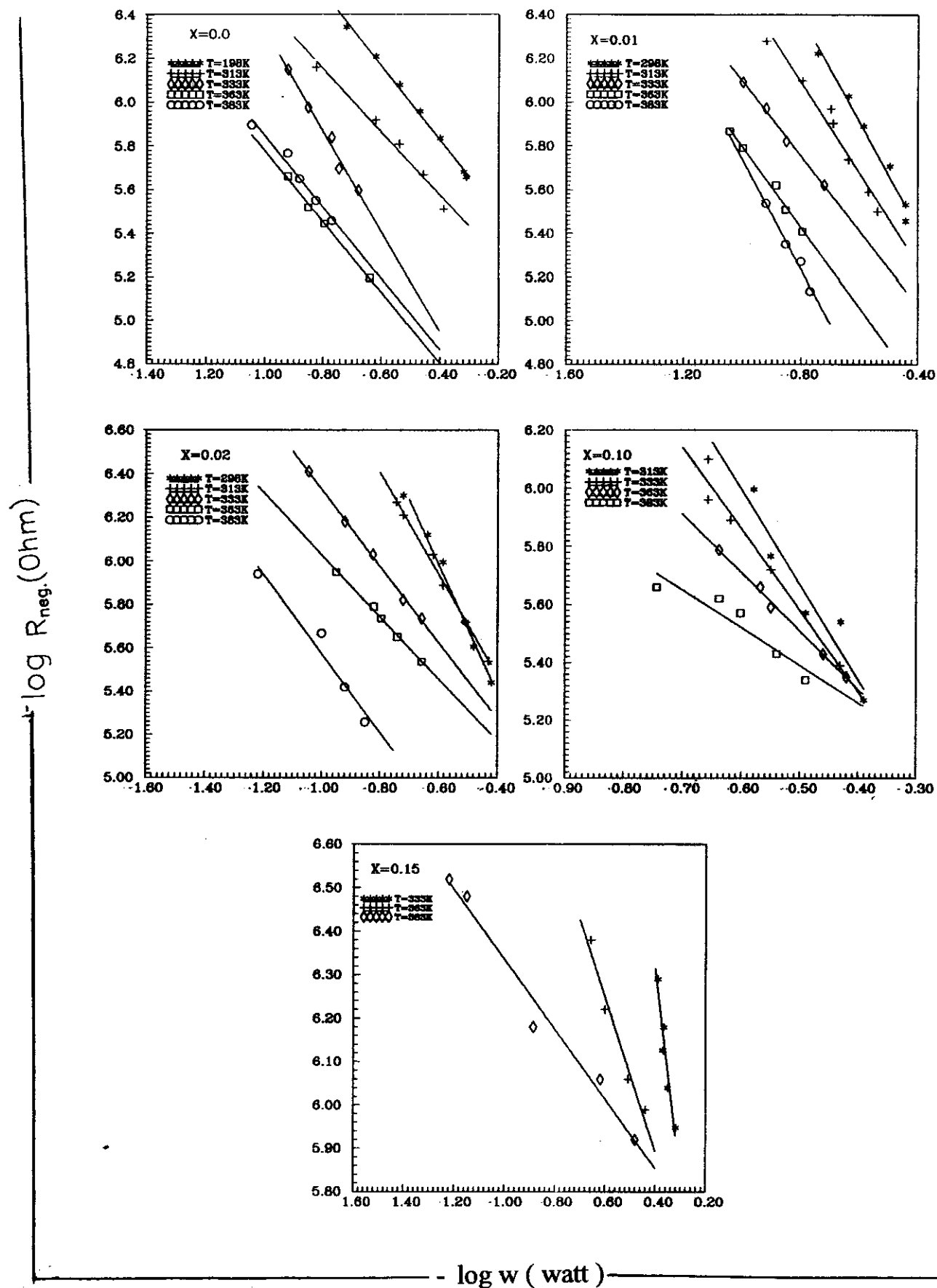


Fig.(III-12): The plots of negative resistance against power for glass sample $(76\text{V}_2\text{O}_5-24\text{P}_2\text{O}_5)_{1-x}(\text{Li}_3\text{PO})_x$ at different temperatures.

Table (III-6): The values of the power (m) obtained at different temperature for $(76V_2O_5-24P_2O_5)_{1-x}(Li_3 PO_4)_x$ glasses :

X	0.0	0.01	0.02	0.10	0.15
T(K)	m				
298	1.6923	2.3685	3.9048	-	-
313	1.4315	2.12751	2.301	3.1617	-
333	2.12191	1.7121	1.7414	2.771	5.463
363	1.60013	1.911	1.3706	2.105	1.737
383	1.6665	2.56	1.8508	1.367	0.798

It is clear , in general , that m is larger than unity indicating that the rise of conduction in the differential resistance region is not due to a simple thermal effects . The conduction level in the mentioned region is greatly influenced by the following ⁽⁸⁸⁾; (i) The temperature of the conduction filament leading to the presence of the phonon to conserve energy required for the electron hopping . (ii) The effective electric field assisting electron hopping , the effect of the electric field (F) is to modify the energy of hop between two sites i and j separated by a distance d_{ij} by an amount “ $eFd_{ij} \cos\theta$ ” , where θ is the angle between F and d_{ij} . (iii) The presence of the negative resistance in the circuit of measurements results in a generation of a very high frequency signals assisting the electron hopping between the localized states at the Fermi level .

The temperature dependence of negative resistance is considered at different constant powers . A typical plot of $\ln R_{neg}$ versus $10^3/T$ is shown in Fig (III-13) which obeys an Arrhenious relation :

$$R_{neg} = R_0 \exp (E_n / k_B T) \quad (III-10)$$

where E_n is an activation energy term ; The obtained values of activation energies are listed in Table (III-7) . It is clear that the value of E_n is nearly unchanged with increasing the dissipating power in the case of pure vanadium phosphate glass or the glass having low concentration of lithium phosphate . The value of E_n decreases with increasing dissipating power in the case of higher concentration of lithium phosphate glasses .

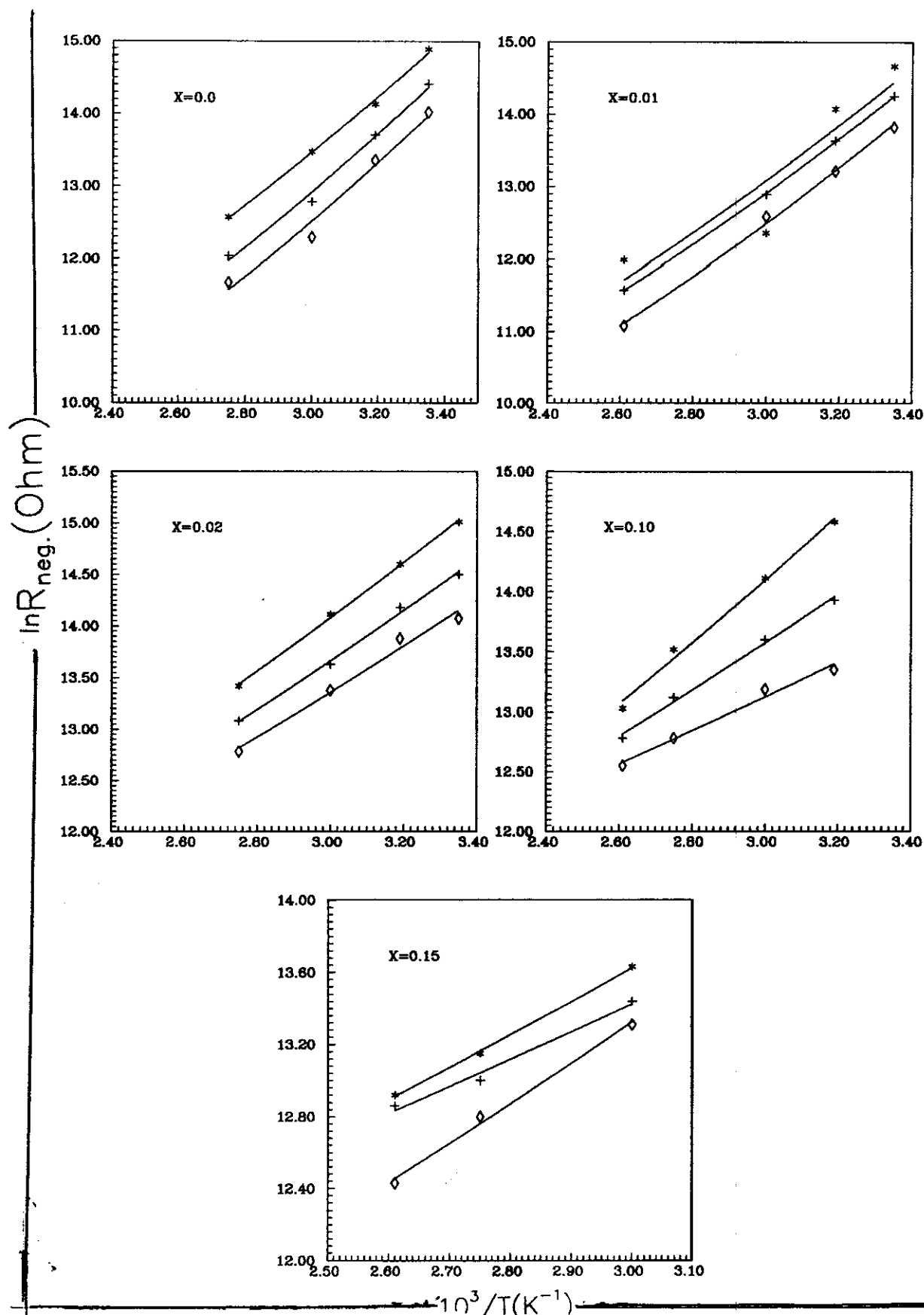


Fig.(III-13) The temperature dependence of negative resistance at different constant power for $(76\text{V}_2\text{O}_5-24\text{P}_2\text{O}_5)_{1-x}$ ($X=0, 0.01, 0.02, 0.1$ and 0.15) glasses.

Table (III-7) The obtained values of power dissipated and activation energy for $(76V_2O_5-24P_2O_5)_{1-x}(Li_3 PO_4)_x$ glasses :

X	0.0		0.01		0.02		0.10		0.15	
	W (watt)	E_n (eV)	W (watt)	E_n (eV)	W (watt)	E_n (eV)	W (watt)	E_n (eV)	W (watt)	E_n (eV)
	0.16	0.328	0.16	0.307	0.17	0.225	0.20	0.228	0.40	0.196
	0.22	0.343	0.19	0.312	0.20	0.209	0.24	0.168	0.430	0.168
	0.28	0.346	0.23	0.317	0.23	0.191	0.28	0.120	0.465	0.156

III-3 : A.C conduction and Dielectric Properties :

In the present section, the dielectric properties have been studied using a.c measurements , analyzing their dependence on temperature and frequency . The total conductivity , σ_{tot} , the dielectric constant , ϵ' , the dielectric loss ϵ'' and the loss tangent , $\tan \delta$ have been studied in the temperature range 293-523 K and frequency range $120- 10^5$ Hz for the glass samples $(76V_2O_5-24P_2O_5)_{1-x}(Li_3 PO_4)_x$ where $(x = 0 , 0.01, 0.02 , 0.10 , 0.15)$.

III-3-1 : Total conductivity :

Figure (III- 14 : 18) illustrate the frequency dependence of total conductivity, σ_{tot} , for the glasses under investigation at different temperature . It is noticed that the general behavior can be divided into two regions .

1)At low frequency range , the conductivity is nearly frequency independent, which refer to the d.c. conductivity of the investigated glass . The low frequency conductivity (σ_{dc}) is found to be strongly dependent on temperature for all investigated samples .

2)At the high frequency range the conductivity to obeye's a power law , relation , $\sigma_{tot}(\omega) = A \omega^s$ (III-11)

where A is a frequency independent parameter and s is a power , which is calculated for all glasses and listed in Table (III-8) .

Thus the total conductivity could be given by :

$$\sigma_{tot} = \sigma_{dc} + A \omega^s \quad (III-12)$$

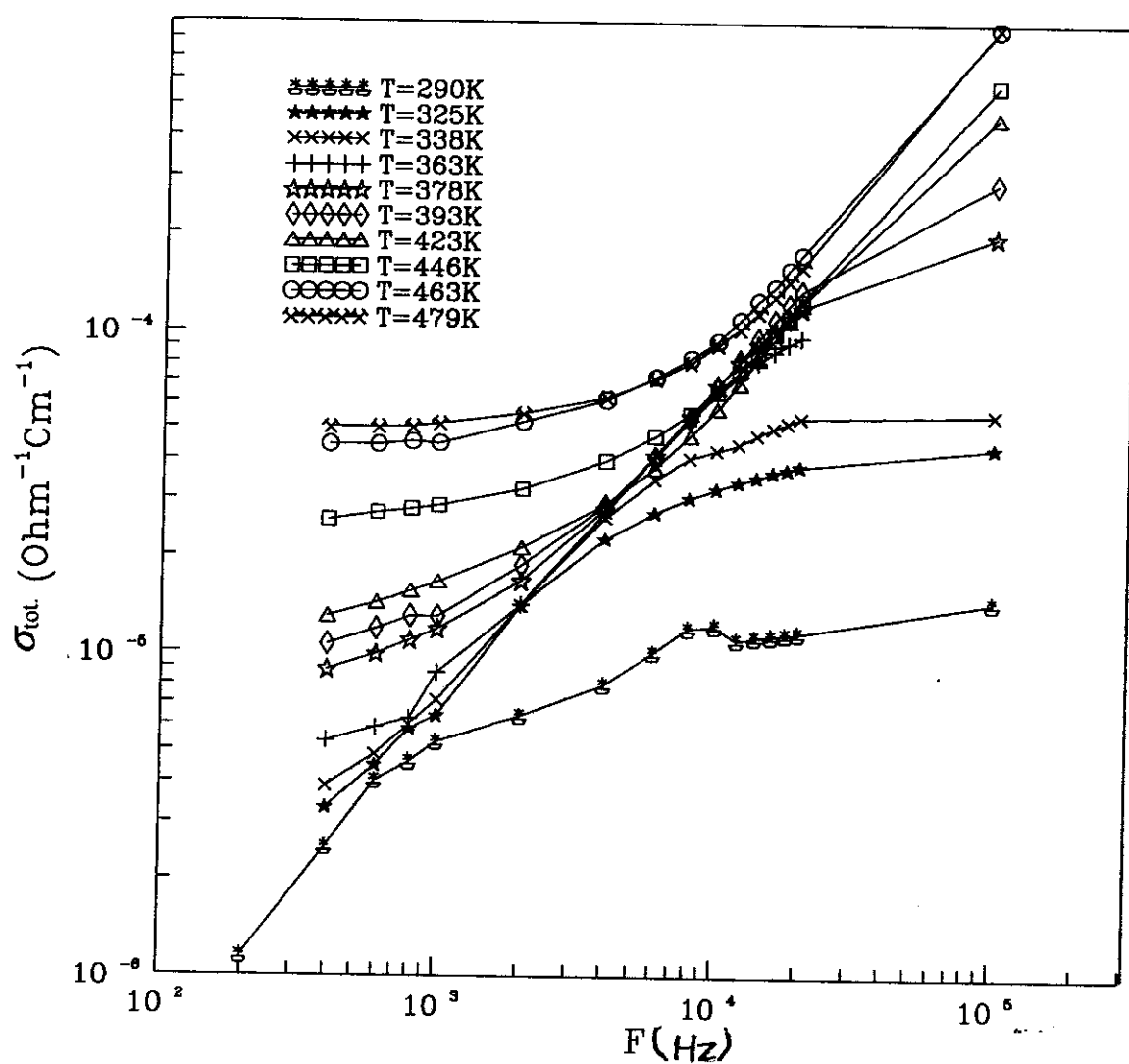


Fig.(III-14): Frequency dependence of the total conductivity for glass sample (76V₂O₅-24P₂O₅) at various temperatures.

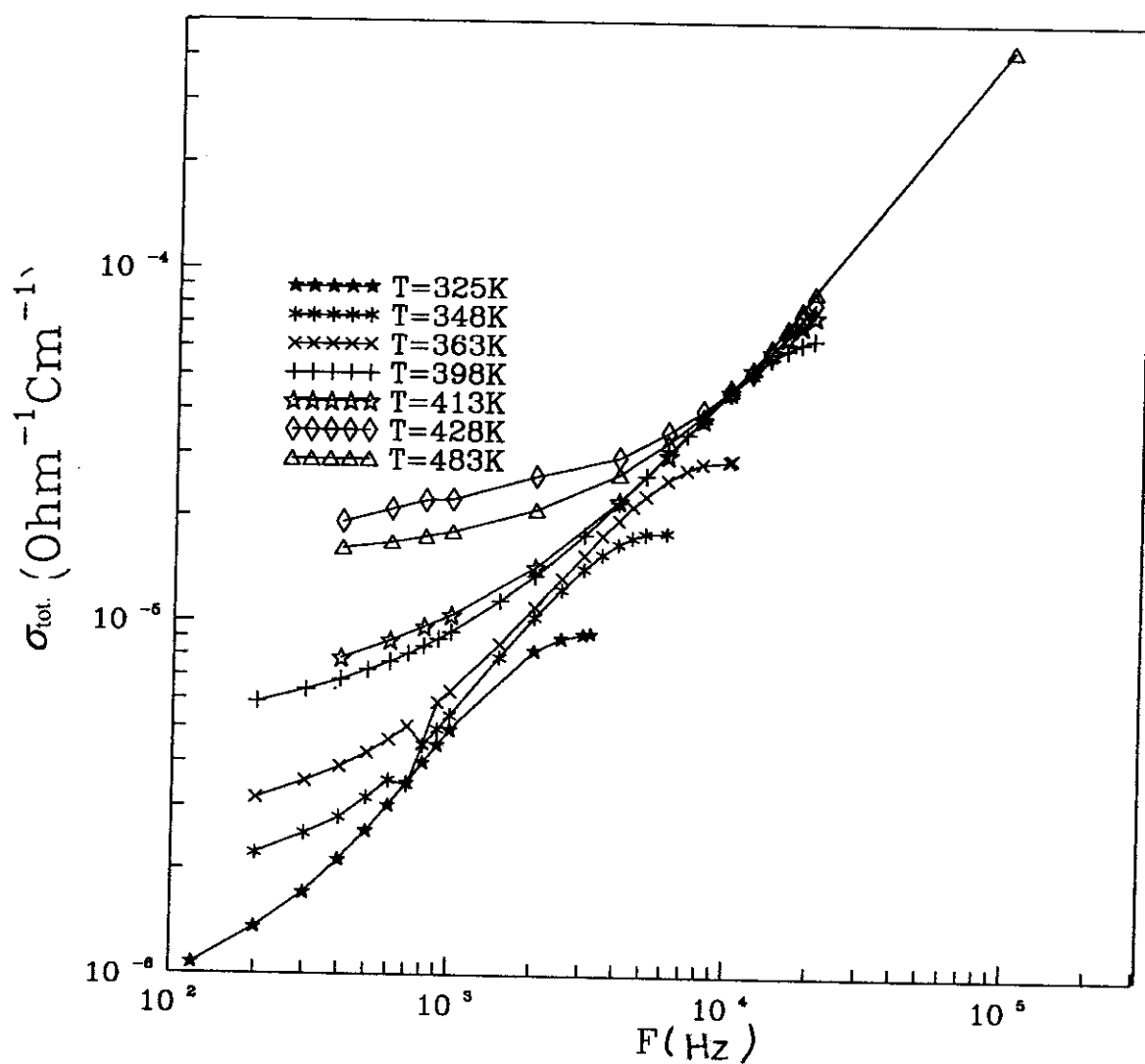


Fig.(III-15): Frequency dependence of the total conductivity for glass sample $(76V_2O_5-24P_2O_5)_{1-x}(Li_3PO_4)_x$ ($x=0.01$) at various temperatures.

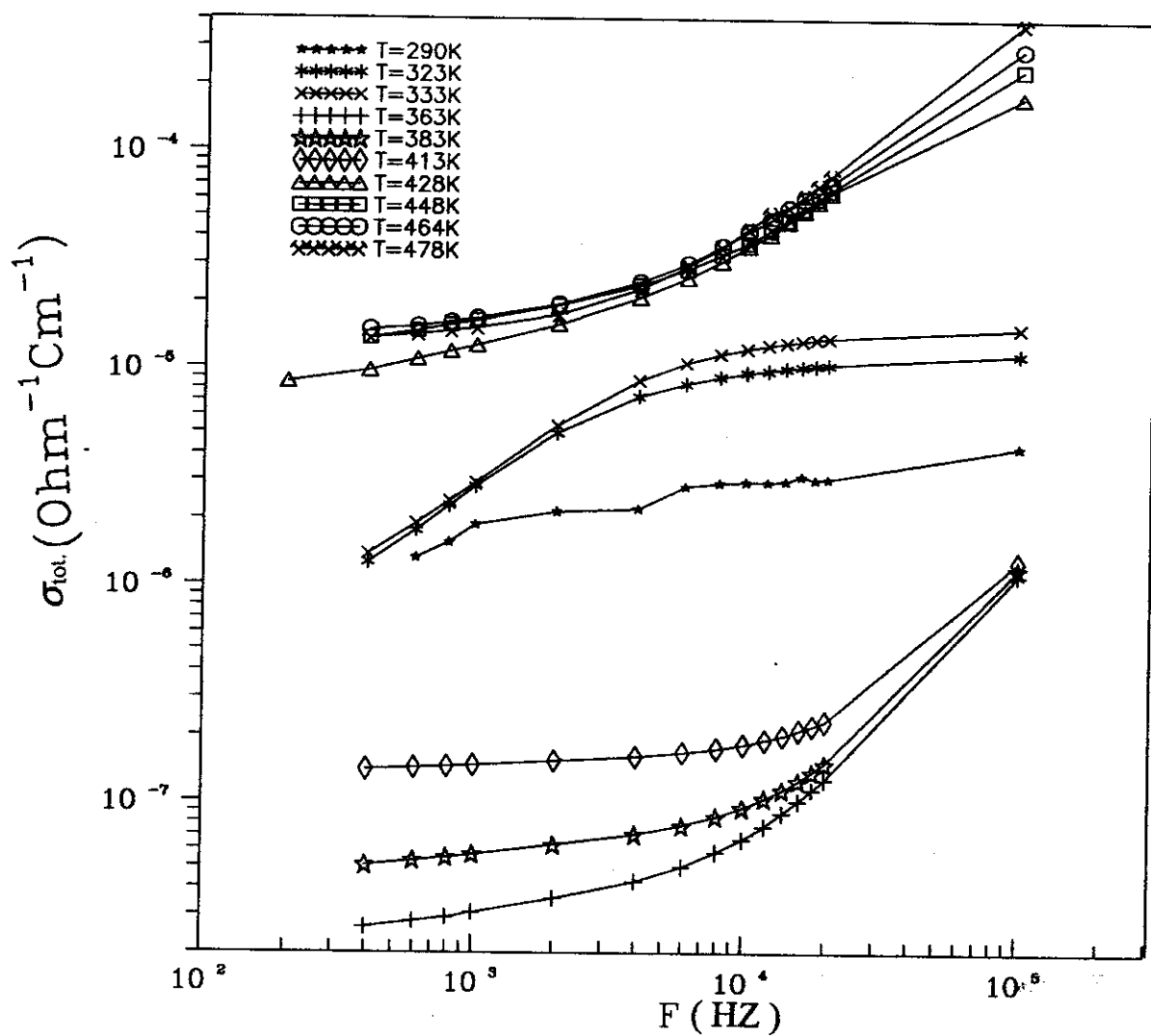


Fig.(III-16): Frequency dependence of the total conductivity for glass sample $(76V_2O_5-24P_2O_5)_{1-x}(Li_3PO_4)_x$ ($x=0.02$) at various temperatures.

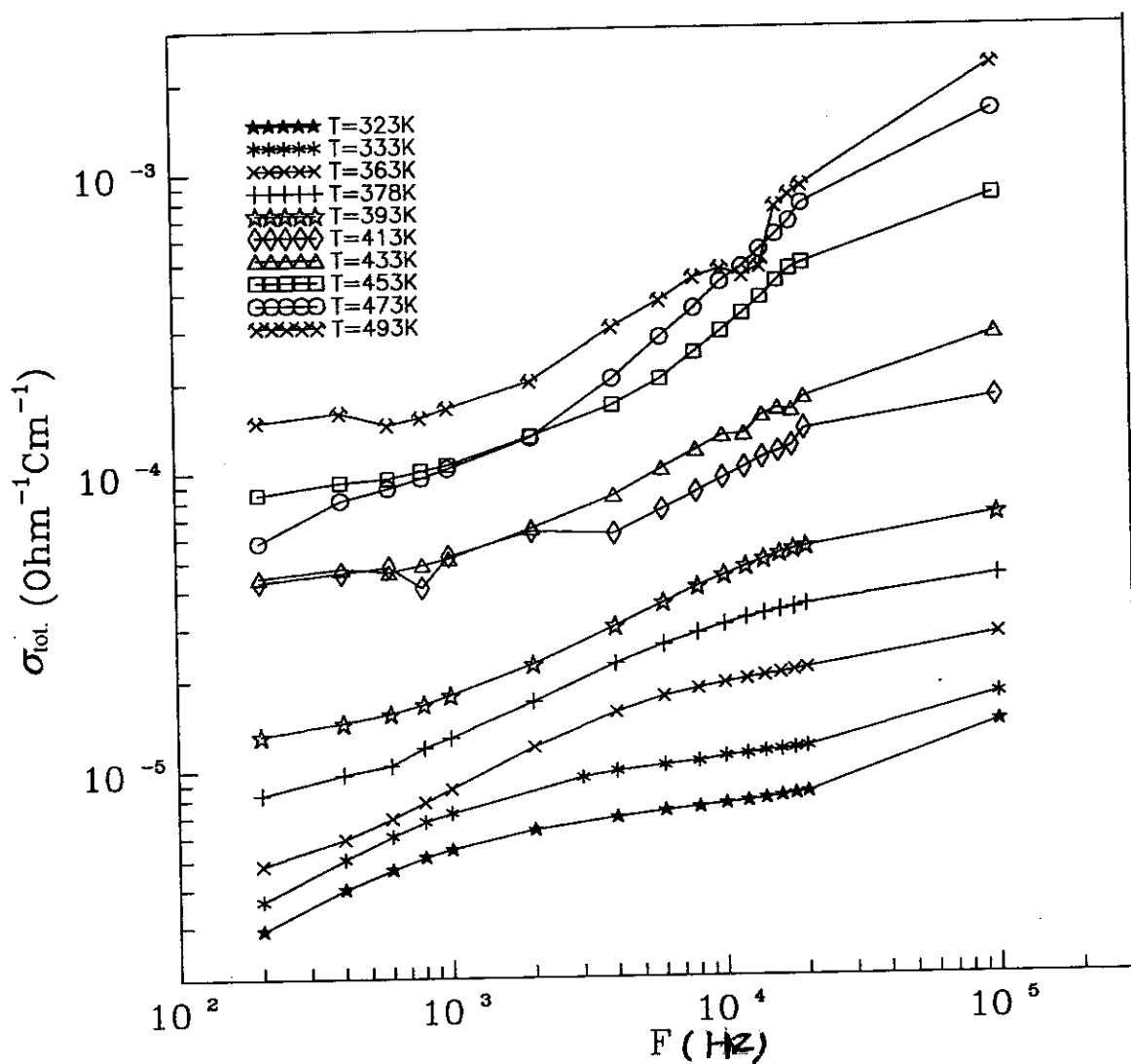


Fig.(III-17) :Frequency dependence of the total conductivity for glass sample $(76V_2O_5-24P_2O_5)_{1-x}(Li_3PO)_x$ ($x=0.10$) at various temperatures.

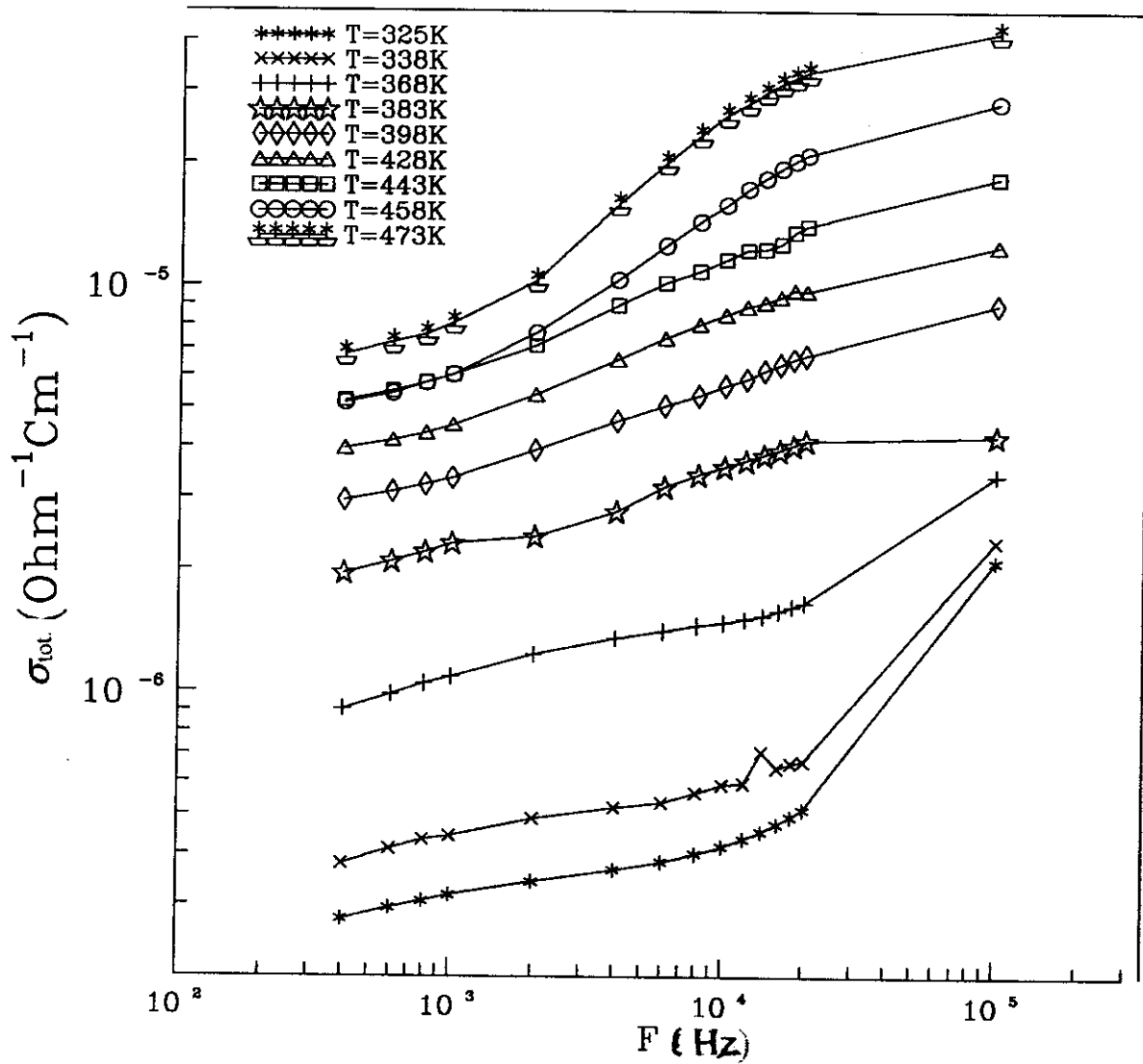


Fig.(III-18): Frequency dependence of the total conductivity for glass sample $(76V_2O_5-24P_2O_5)_{1-x}(Li_3PO_4)_x$ ($X=0.15$) at various temperatures.

Table (III - 8) : The obtain values of the power s at different temperatures for $(76V_2O_5-24P_2O_5)_{1-x} (Li_3 PO_4)_x$ glasses :

X = 0.0		X = 0.01		X = 0.02		X = 0.10		X = 0.15	
T(K)	S	T(K)	S	T(K)	S	T(K)	S	T(K)	S
290	0.911	291	0.82	290	0.90	323	0.32	291	0.384
324	0.88	315.5	0.84	308	0.87	333	0.24	323	0.184
338	0.91	325	0.91	323	0.81	348	0.18	338	0.143
348	0.91	337	0.88	333	0.85	363	0.16	368	0.110
363	0.88	348	0.87	348	0.82	378	0.14	383	0.243
378	0.884	365	0.81	363	0.86	393	0.16	398	0.210
393	0.882	383	0.82	383	0.86	413	0.29	428	0.20
408	0.88	398	0.76	398	0.51	433	0.39	443	0.254
423	0.904	413	0.77	413	0.89	453	0.48	458	0.455
446	0.911	428	0.70	423	0.7	473	0.64	473	0.49
463	0.91	443	0.72	448	0.8	493	0.63		
478	0.92	468	0.82	464	0.83				
		483	0.93	478	0.88				

The values of the power s at different temperatures for the investigated samples lie in the range $0.5 < s < 1$ in the case of vanadium phosphate glass sample and that of low lithium phosphate content, which confirm the expectation of the polaron hopping between V^{4+} and V^{5+} ions⁽⁹⁰⁾. The obtained values of s lie in the range $(0.11 < s < 0.64)$ for samples of high lithium phosphate content $(0.10 - 0.15)$. The obtained values of s less than 0.5 confirms the domination of ionic conductivity in the present glasses.

Mott and Davis⁽¹⁸⁾, interpreted the power law (equation (III-11)) in terms of hopping between pairs of isolated sites close to the Fermi-level and with a random distribution of separation distance R_a from each other and two situations are usually investigated as ;

The carrier hopping occurs under the following considerations :

- (1) The two centers differ in energy by an amount $w \gg k_B T$, in the absence of field, the population of the upper level is $\exp(-w/k_B T)$ and the application of a field changes the population by the factor $\pm(eR_a F/k_B T)$. The carrier then moves between the centers by phonon-assisted quantum – mechanical tunneling when the site energies are brought into equivalence by a suitable phonon.
- (2) Potential minima are separated by an energy barrier of a high (w) in the absence of a field there is equal probability of either being occupied but with the application of a field, the relative energies of the minima change by $\pm(eR_a F/k_B T)$ and their population are

Regarding the general behaviour of $\sigma_{\text{tot}}(\omega)$ there is a critical frequency , ω_p , after which the conductivity obeys the mentioned power relation :

$$\sigma_{\text{tot}}(\omega) = A \omega^s .$$

Almond et. al. ⁽⁹¹⁾ have assumed that , the total conductivity reaches twice its value at a critical frequency ω_p [which is defined as the hopping rate] , and is given by :

$$\omega_p = (\sigma_o / A)^{1/s} \quad (\text{III-13})$$

The values of ω_p are deduced at different ambient temperature for glasses under investigation . Figure (III-19) illustrate the temperature dependence of the hopping rate ω_p for the present glasses. The values of ω_p are found to be thermally activated in the mentioned range of temperature for all glass samples obeying the following Arrhenious relation :

$$\omega_p = \omega_o \exp (-E_\omega / k_B T) \quad (\text{III-14})$$

where E_ω , is an activation energy concerning the shift of ω_p with increasing temperature , and $\omega_o = \omega_p$ at $T = \infty$.

The values of E_ω and ω_o are deduced by using the least square fitting of relation (III-14) and listed in Table (III-9).

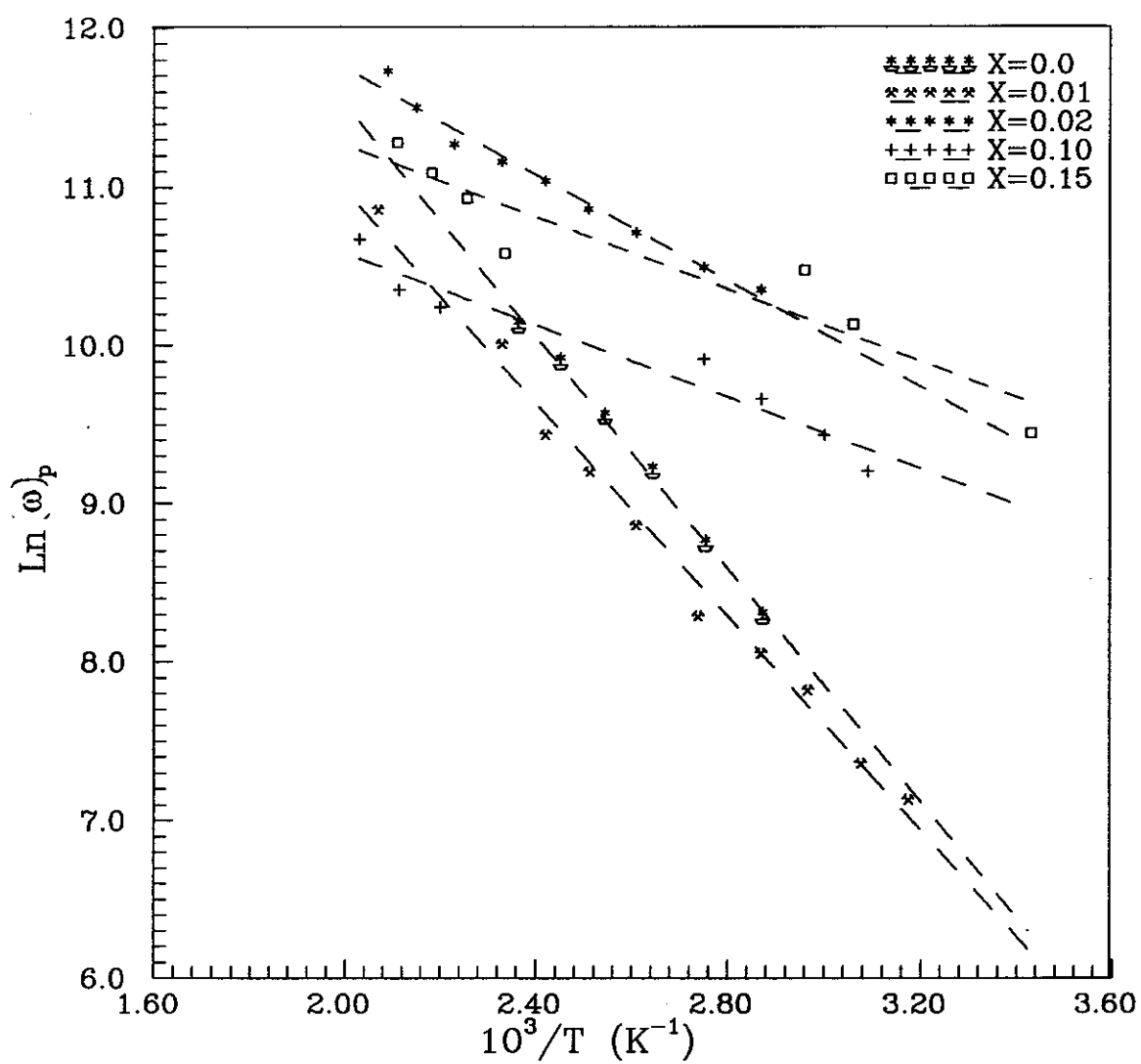


Fig. (III-19): Temperature dependence of hopping rate for glass samples $(^{76}\text{V}_2\text{O}_5-24\text{P}_2\text{O}_5)_{1-x}(\text{Li}_3\text{PO}_4)_x$

Table (III-9): The obtained values of E_{ω} , ω_o and R'_{\circ} for $(76V_2O_5-24P_2O_5)_{1-x}(Li_3 PO_4)_x$ glass sample :

X	$E_{\omega}(eV)$	$\omega_o (Hz)$	$R'_{\circ} (\text{\AA})$
0.0	0.316	1.55×10^5	55.00
0.01	0.291	5.28×10^7	60.75
0.02	0.176	1.37×10^7	67.50
0.10	0.098	3.86×10^5	85.40
0.15	0.098	1.75×10^5	89.00

It is noticed that ω_o , appears to be much lower than the expected values of the phonon frequency (10^{13} Hz) .

The values of the activation energy, E_o , can be explained as follows : The increase of ambient temperature means an increase of the d.c conductivity of the glasses which compites the influence of the polarization conductivity and leads to a shift to the behaviour towards high frequency range.

Long et al ⁽⁹²⁾ have pointed out that electron loss processes involve transitions between states which the glass network distorts , creating a polaron well (the overlapping of electron wave functions has been considered) , from which ω_o could be given by :

$$\omega_o = \omega_{opt} \exp (2\alpha R'_o) \quad (III-15)$$

where ω'_{opt} is the optical phonon frequency α is the decay function . By using the estimated value of the characteristic phonon frequency $\omega_{opt} = 10^{13}$ Hz in vanadium phosphate glasses ⁽⁶³⁾ and the localization distance $1/\alpha = 10 \text{ \AA}$ ^(18,88) . The optimum hopping distance R'_o are obtained and listed in Table (III-9) . It is noticed that R'_o are much greater than the distance of the nearest neighbour distance ($\overset{\circ}{=} 4 \text{ \AA}$) . This means that the electron hopping may occur between the separated sites by R'_o .

III-3-2 : Temperature dependence of the total conductivity :

Figure (III - 20 : 24) shows the total conductivity as a function of reciprocal temperature at different fixed frequencies (0.2 , 10 , 20 and 100 kHz) for the glass samples under investigation . It is noticed that the conductivity , $\sigma_{\text{tot}}(\omega)$, increases with increasing temperature obeying the following relation : $\sigma_{\text{tot}}T = A \exp (-E/k_B T)$ (III-16)

The plot of $\sigma_{\text{tot}}T$ versus $10^3 / T$ illustrates straight line , from which the activation energy of conduction in these glasses are calculated and listed in Table (III-10) .

It is clear that , one region in σ_{tot} versus $1/T$ relation observed for the different glass compositions in addition , the obtained activation energies are comparable with those obtained from temperature dependence of the d.c conductivity . Besides , the activation energy varies irregularly with both frequency and glass composition of lithium phosphate content .

III-3-3: Effect of Frequency and Temperature on dielectric constant ϵ' :

Figures (III-25:29) show the frequency dependence of the dielectric constant ϵ' for the glassy samples $(76V_2O_5-24P_2O_5)_{1-x}(Li_3PO_4)_x$ in the frequency range (0.2 – 100 kHz) at different temperatures (300 to 473 K) . It is noticed that the dielectric constant ϵ' decreases with increasing frequency for all samples . A slight decrease of ϵ' is observed at low frequency range whereas a rapidly decrease at the higher frequency range is observed .

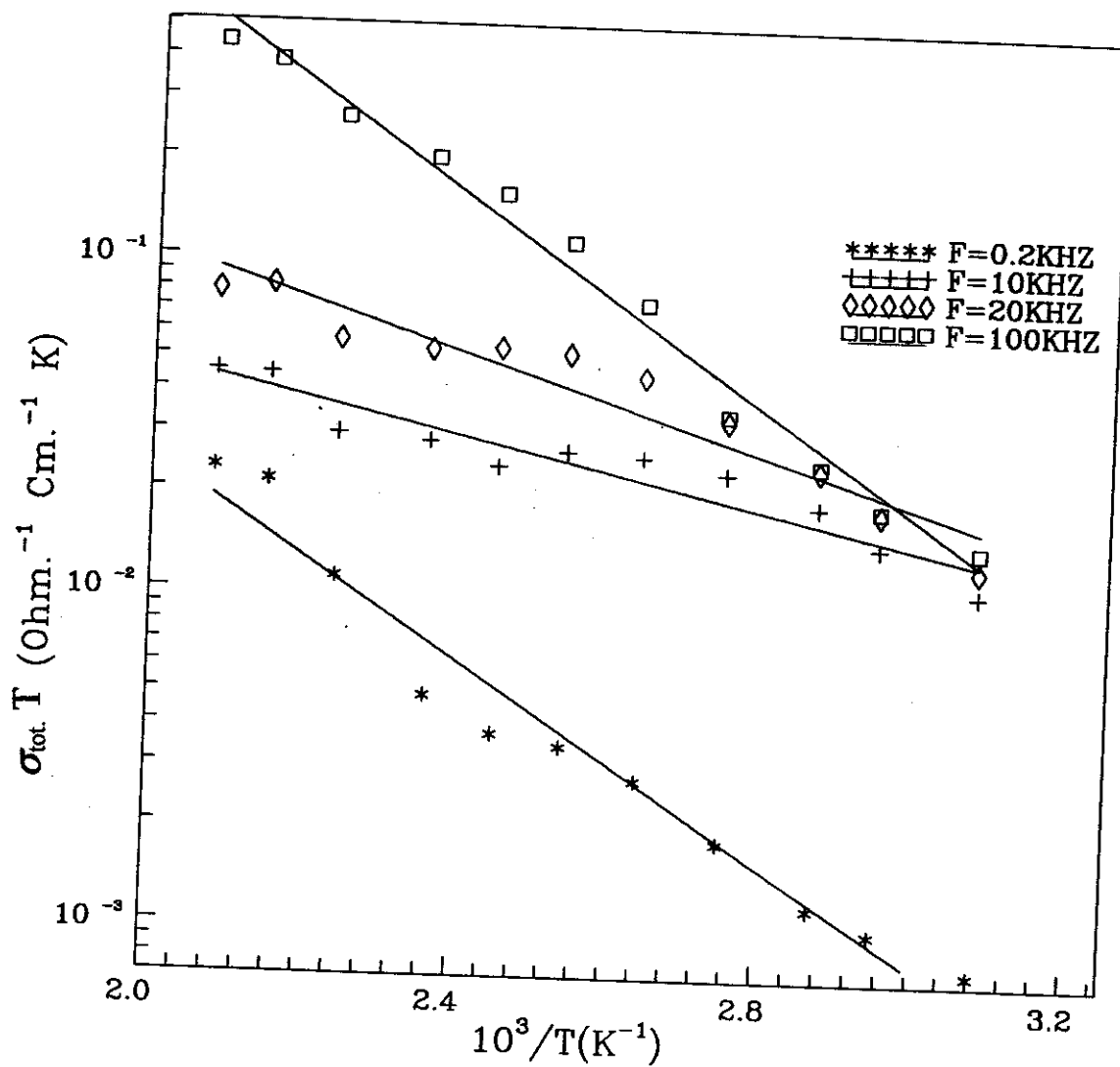


Fig.(III-20): Temperature dependence of the total conductivity for glass sample (76V₂O₅-24P₂O₅) at various frequency

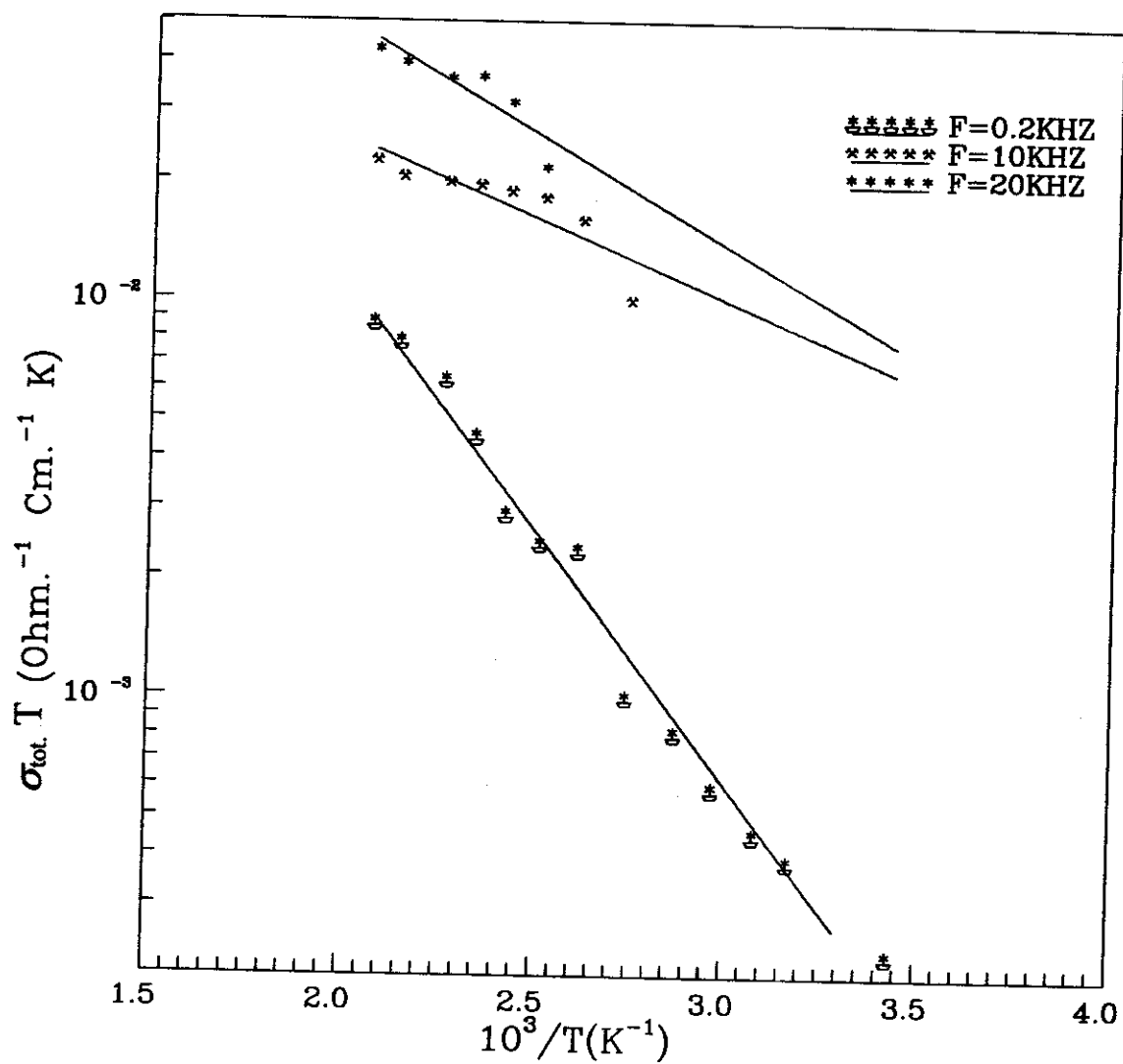


Fig.(III-21): Temperature dependence of the total conductivity for glass sample $(76V_2O_5-24P_2O_5)_{1-x}(Li_3PO_4)_x$ ($X=0.01$) at various frequency.

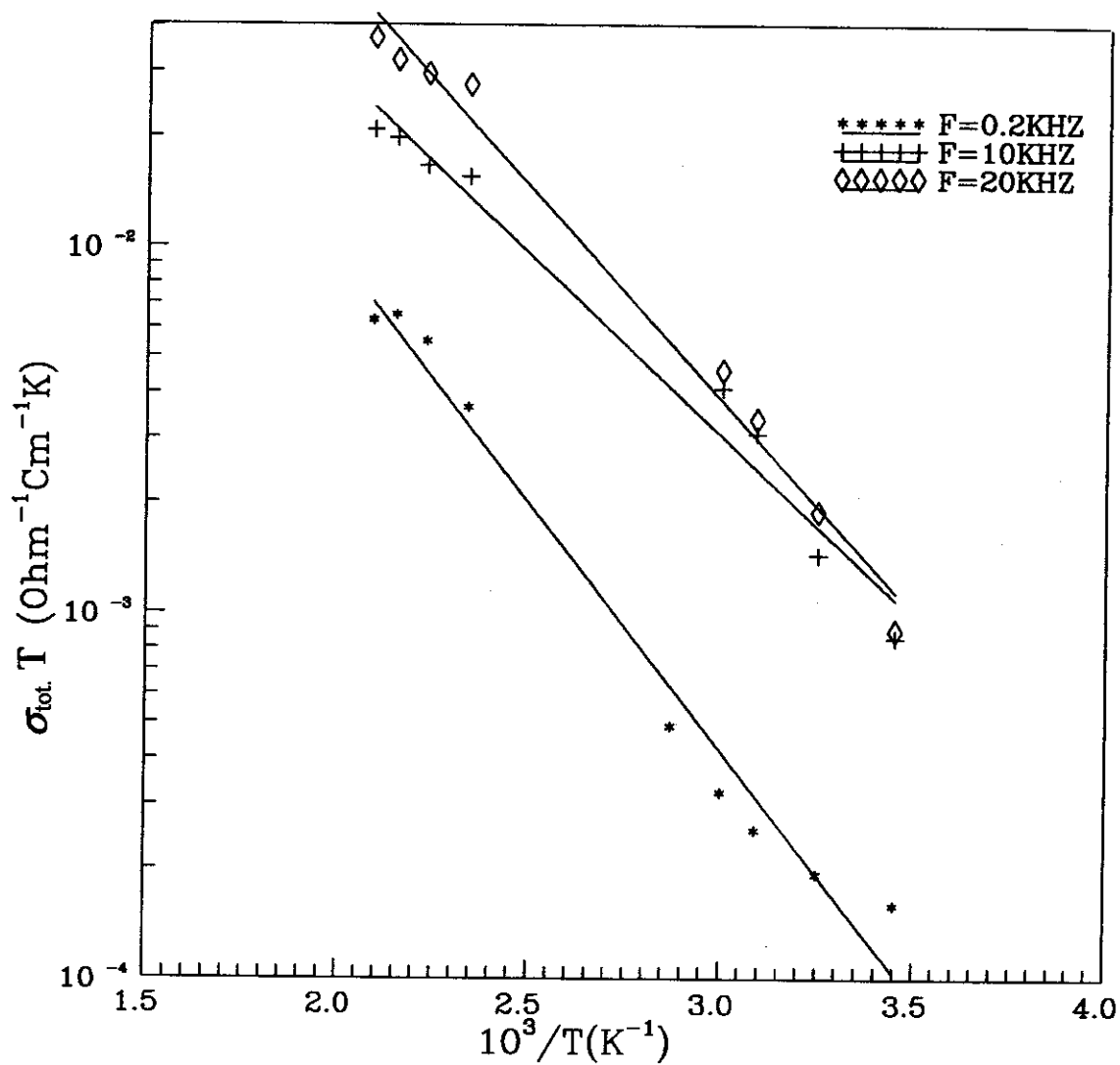


Fig.(III-22): Temperature dependence of the total conductivity for glass sample $(76V_2O_5-24P_2O_5)_{1-x}(Li_3PO_4)_x$ ($X=0.02$) at various frequency.

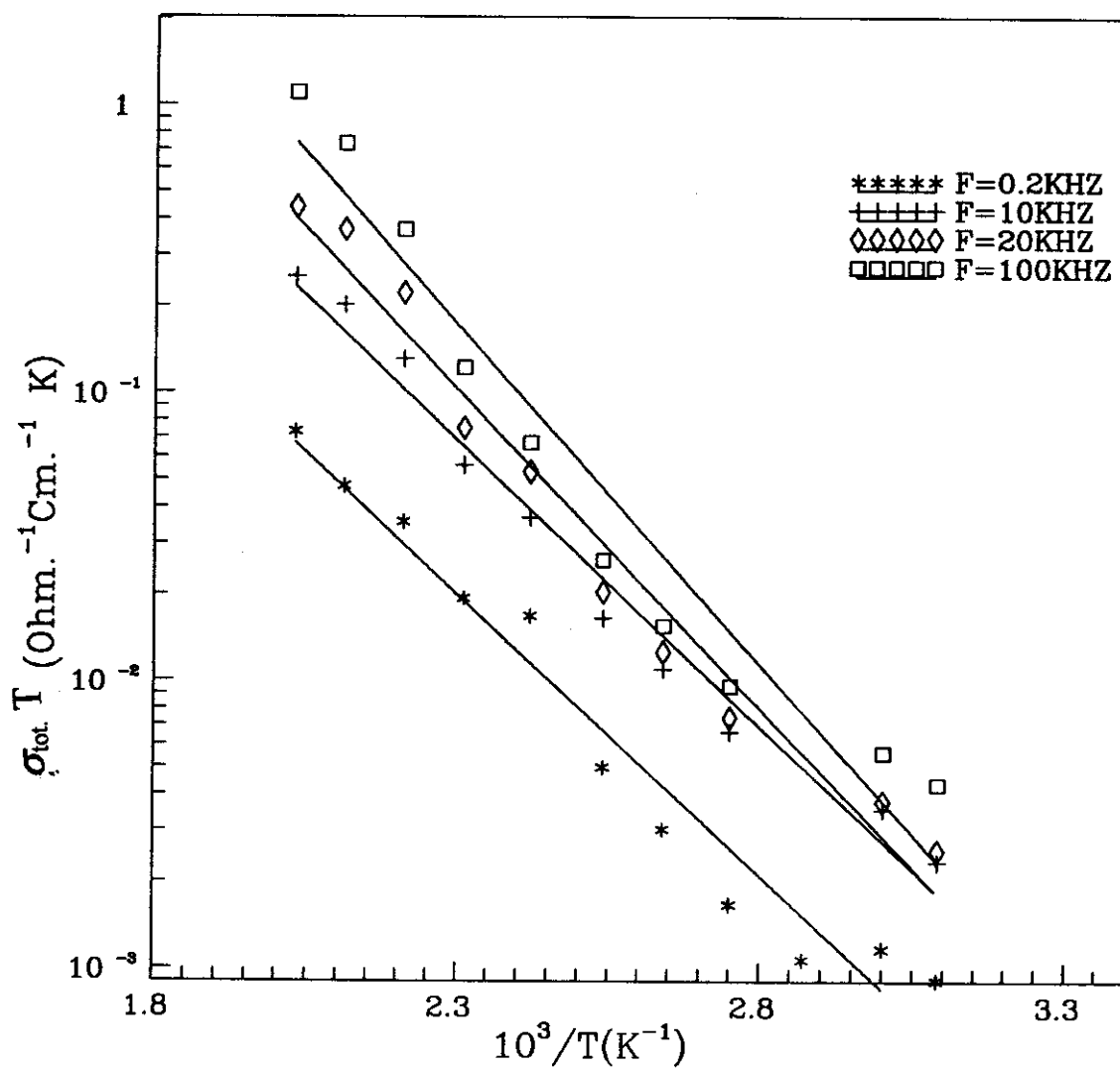


Fig.(III-23): Temperature dependence of the total conductivity for glass sample $(76V_2O_5-24P_2O_5)_{1-x}(Li_3PO_4)_x$ ($X=0.10$) at various frequency.

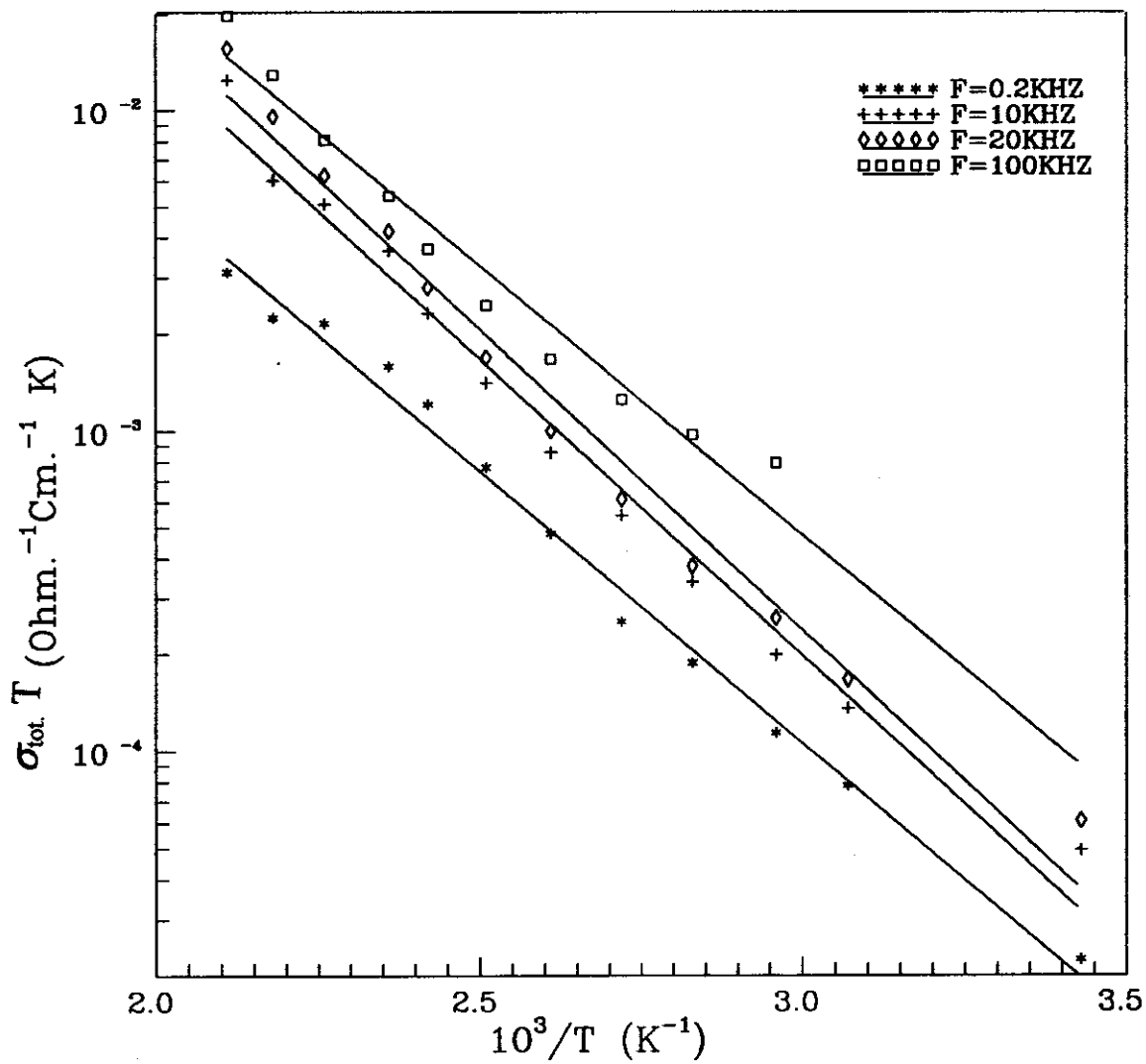


Fig.(III-24) : Temperature dependence of the total conductivity for glass sample $(76V_2O_5-24P_2O_5)_{1-x}(Li_3PO_4)_x$ ($X=0.15$) at various frequency.

Table (III-10): The obtained values of activation energy for $(76V_2O_5-24P_2O_5)_{1-x}(Li_3 PO_4)_x$ glass samples at different frequencies :

Freq.	0.2 (kHz)	10 (kHz)	20 (kHz)	100 (kHz)
X	E (eV)	E (eV)	E (eV)	E (eV)
0.0	0.299	0.106	0.149	0.317
0.01	0.249	0.081	0.112	-
0.02	0.267	0.196	0.230	-
0.10	0.388	0.395	0.440	0.469
0.15	0.337	0.367	0.372	0.274

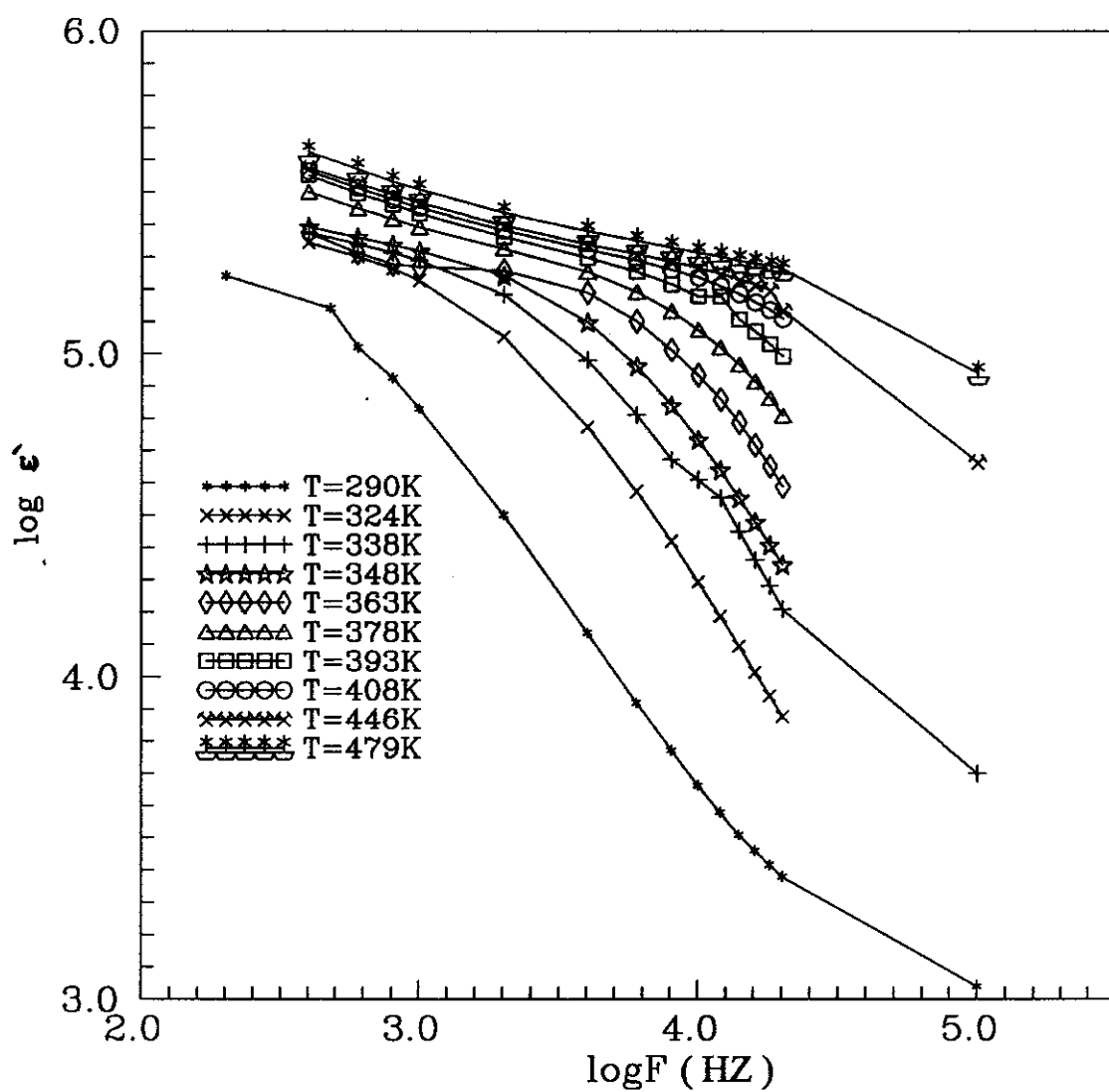


Fig.(III-25): Frequency dependence of the dielectric constant for glass sample (76V₂O₅-24P₂O₅) at various temperatures.

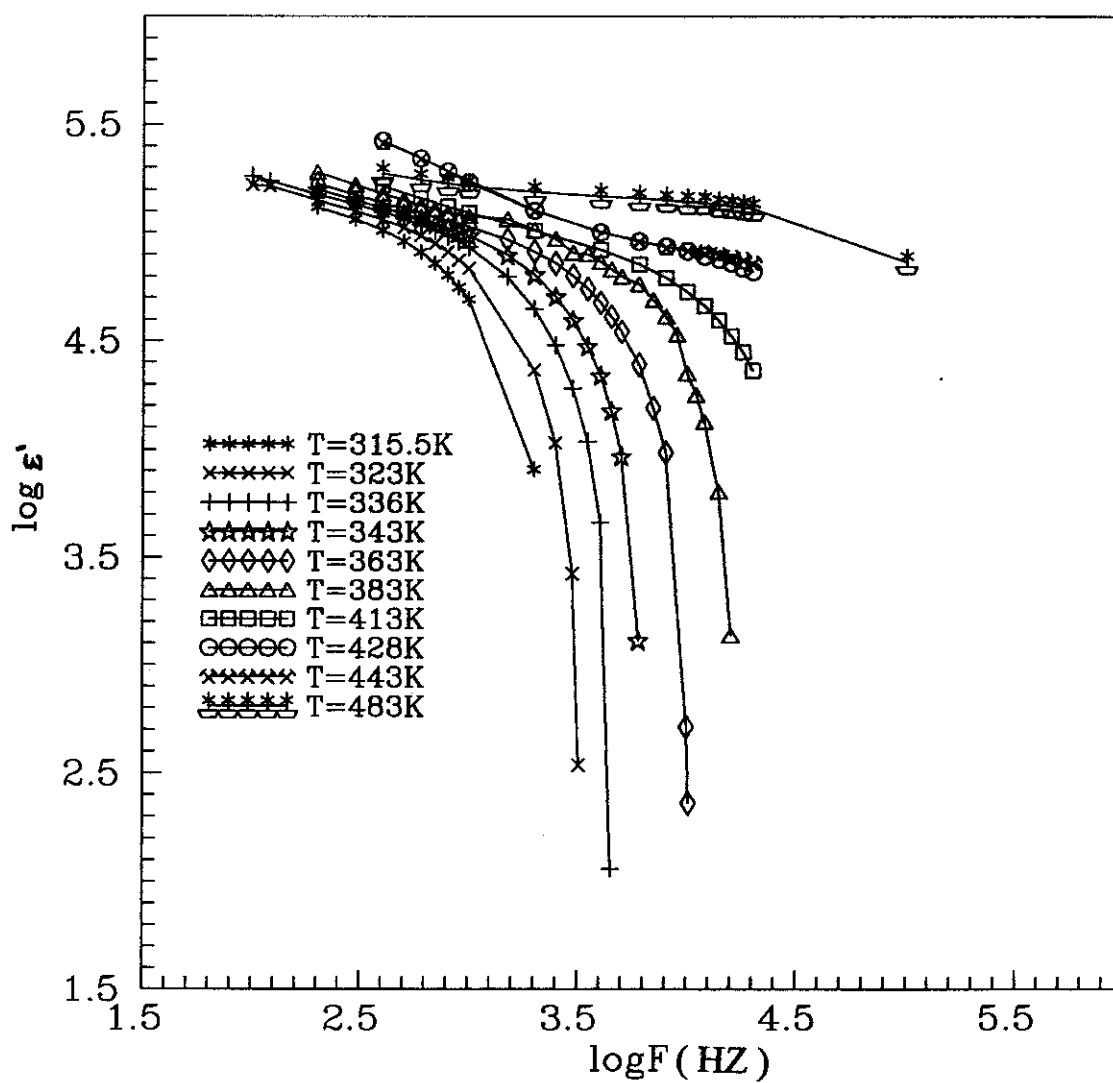


Fig.(III-26): Frequency dependence of the dielectric constant for glass sample $(76V_2O_5-24P_2O_5)_{1-x}(Li_3PO)_x$ ($x=0.01$) at various temperatures.

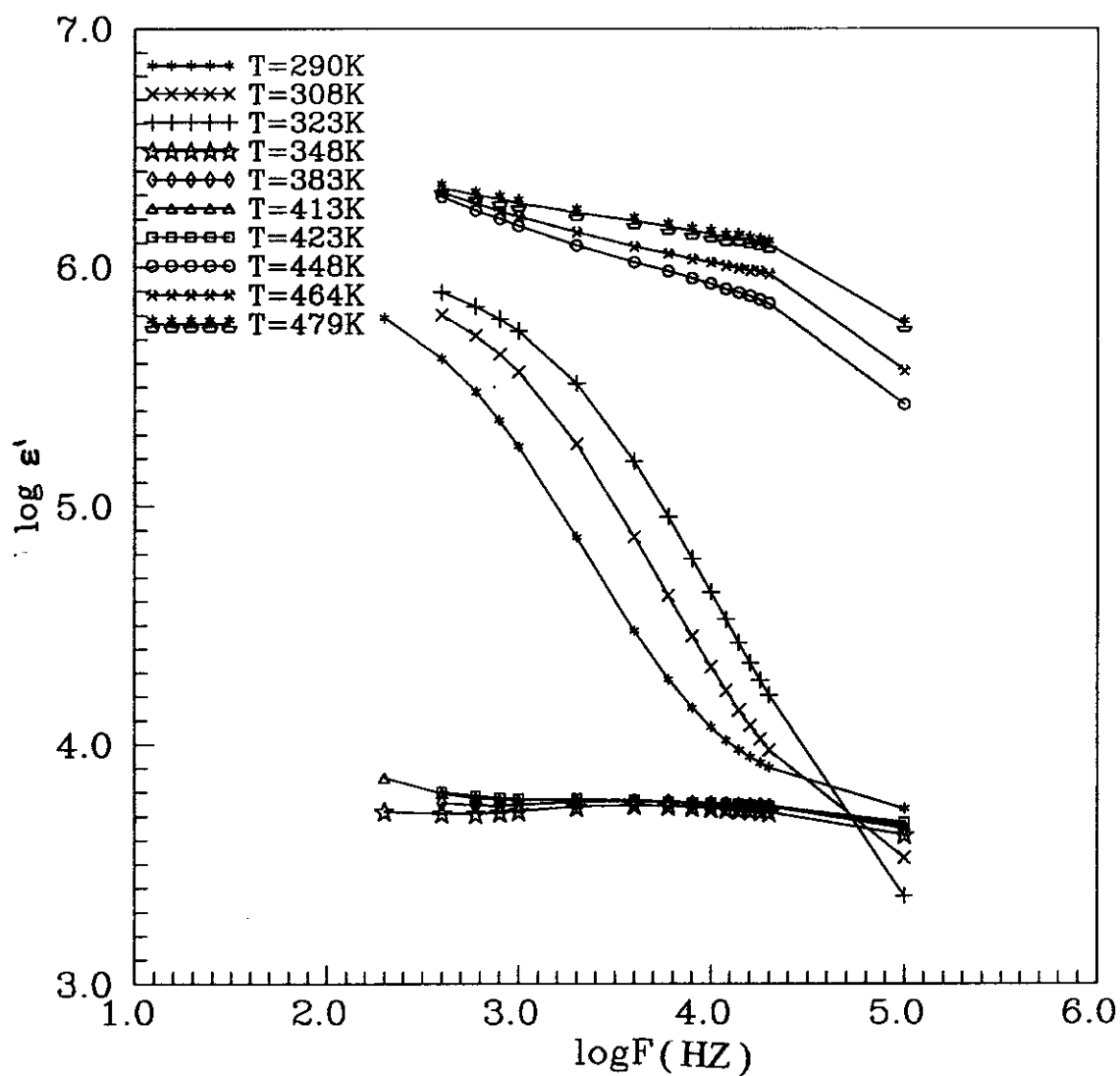


Fig.(III-27): Frequency dependence of the dielectric constant for glass sample $(76\text{V}_2\text{O}_5-24\text{P}_2\text{O}_5)_{1-x}(\text{Li}_3\text{PO})_x$ ($x=0.02$) at various temperatures.

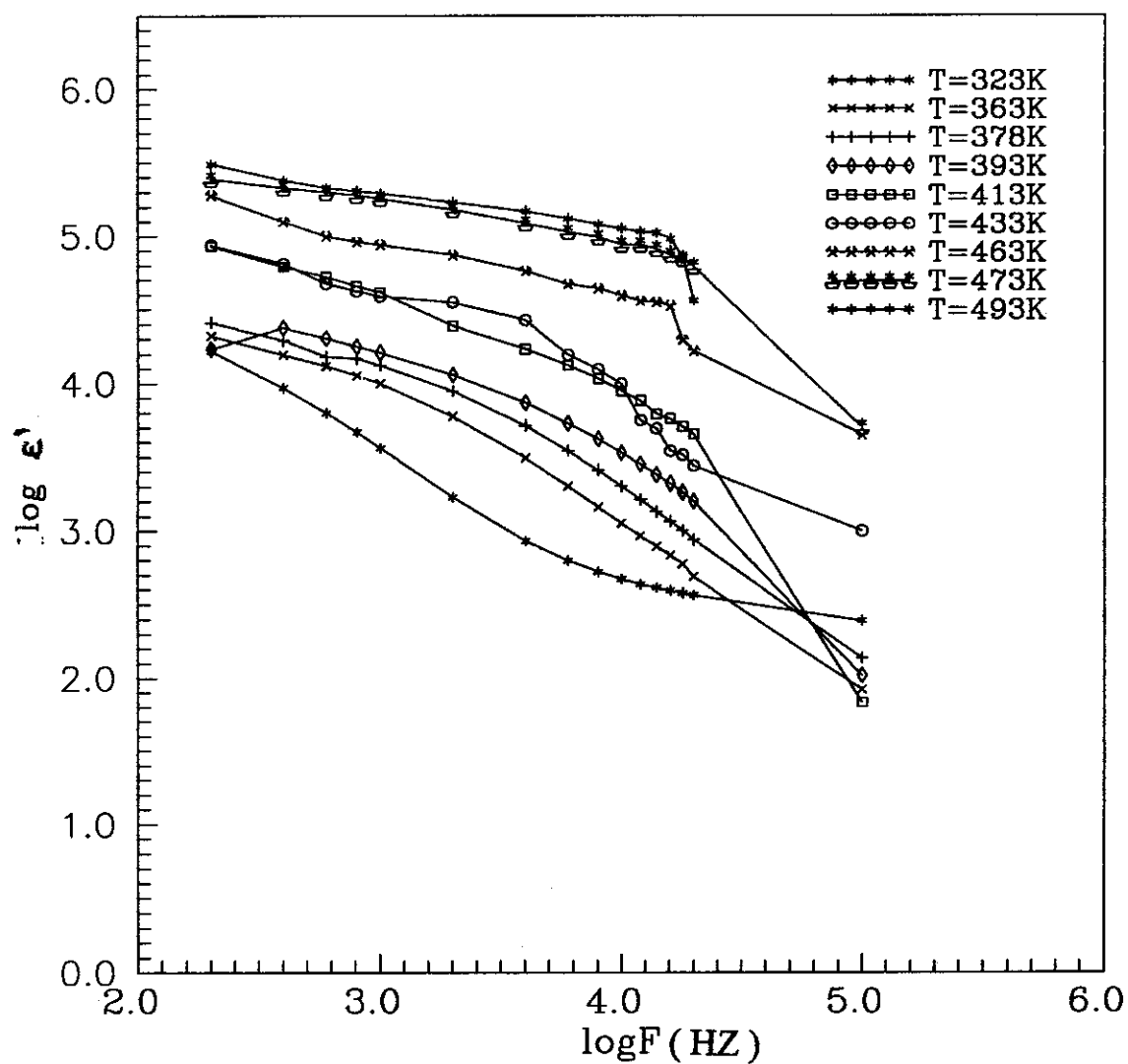


Fig.(III-28): Frequency dependence of the dielectric constant for glass sample $(76V_2O_5-24P_2O_5)_{1-x}(Li_3PO)_x$ ($x=0.10$) at various temperatures.

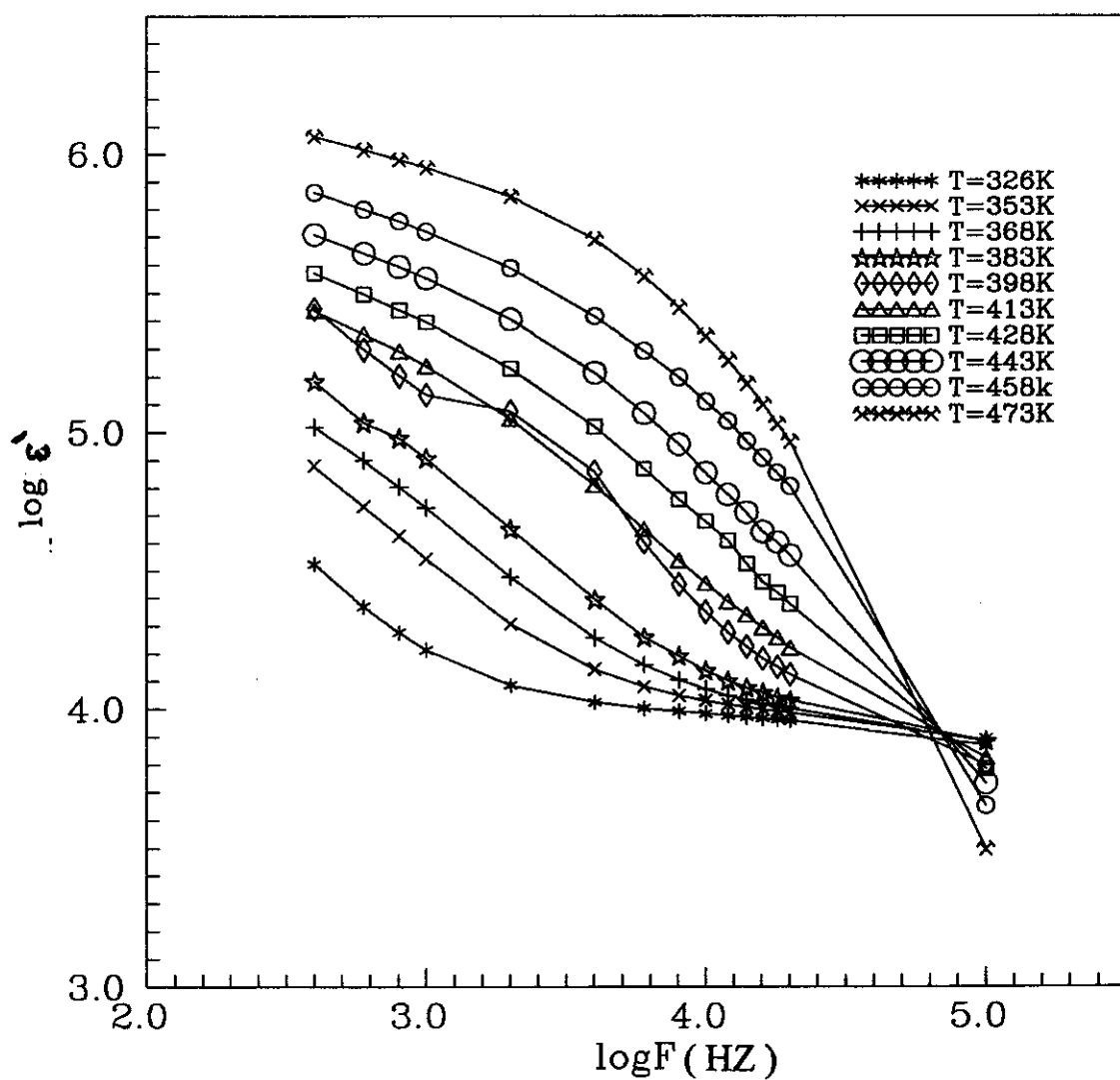


Fig.(III-29): Frequency dependence of the dielectric constant for glass sample $(76V_2O_5-24P_2O_5)_{1-x}(Li_3PO)_x$ ($x=0.15$) at various temperatures.

This behavior can be explain according to the following relation⁽⁹³⁾:

$$(\epsilon' - \epsilon_{\infty})/(\epsilon_0 - \epsilon_{\infty}) = [(1 + \omega\tau)^{1-g} \sin(g\pi/2)]/[1 + 2(\omega\tau)^{1-g} \sin(g\pi/2) + (\omega\tau)^{2(1-g)}]$$

(III – 17)

where τ is the relaxation time , ϵ_0 is the low frequency dielectric constant ($\omega \ll 1/\tau$) , ϵ_{∞} is the infinite frequency ($\omega \gg 1/\tau$) dielectric constants and g is an empirical distribution parameter with values between 0 and 1 . The above relation tends to satisfy Debye equation for single relaxation when $g = 0$.

The behavior of dielectric constant with frequency is related to the application of the field which assists electron jumping between filled and empty sites in the amorphous matrix . This leads to an increase of the electronic component in dielectric dispersion . The other hand , when the frequency is increased the dipoles will no longer able to rotate sufficiently rapid, so that their oscillation will begin to lay behind this field, which explains the observed decrease in dielectric constant ϵ' with increasing frequency .

The dielectric constant ϵ' of the glass samples has been studied as a function of temperature in the range (303 – 473 K) at different fixed frequencies (0.2 , 10 and 20 kHz) , Fig (III- 30 : 34) . It is noticed that the dielectric constant increases slightly with increasing temperature to asymptotic value for the vanadium phosphate glass and those containing lithium phosphate . The mentioned behavior of the dielectric constant ϵ' is found to decrease with increasing the lithium content . This may be due to the decrease of V^{5+} and V^{4+} ions responsible for dielectric relaxation .

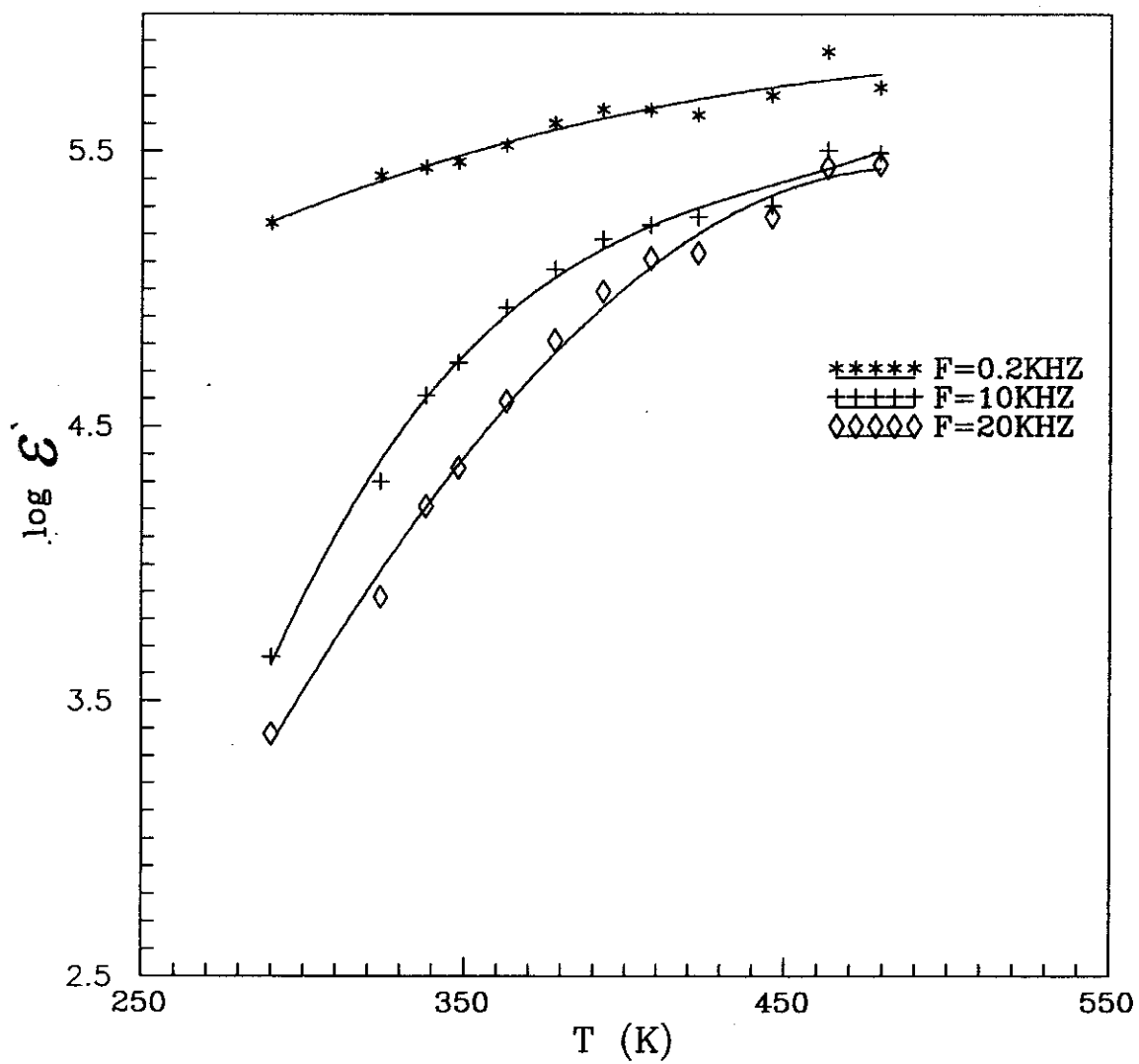


Fig.(III-30): Temperature dependence of the dielectric constant for glass sample (76V₂O₅-24P₂O₅) at various frequency.

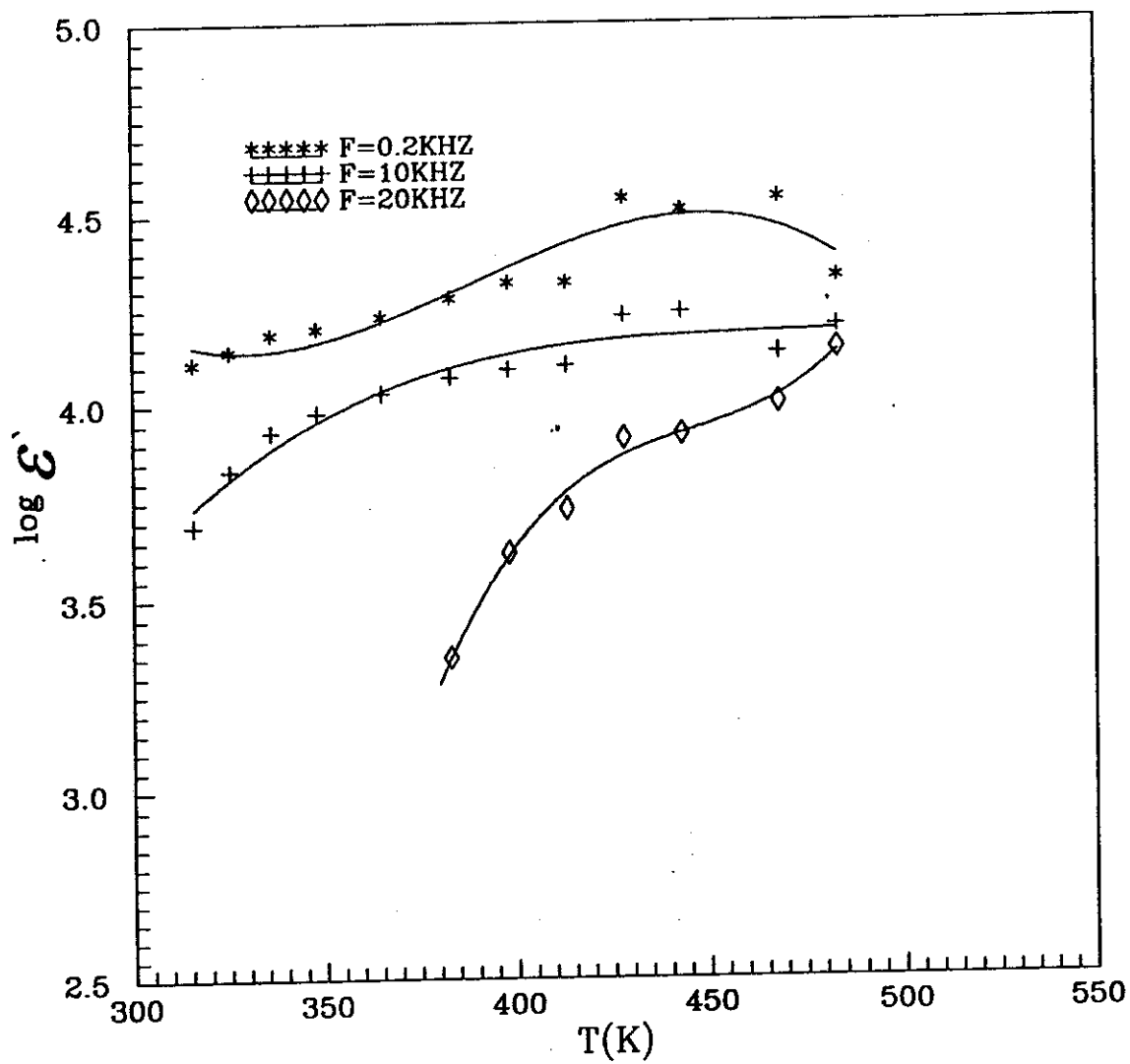


Fig.(III-31): The temperature dependence of the dielectric const. for glassy sample $(76V_2O_5-24P_2O_5)_{1-x}(Li_3PO_4)_x$ ($x=0.01$) at various frequency.

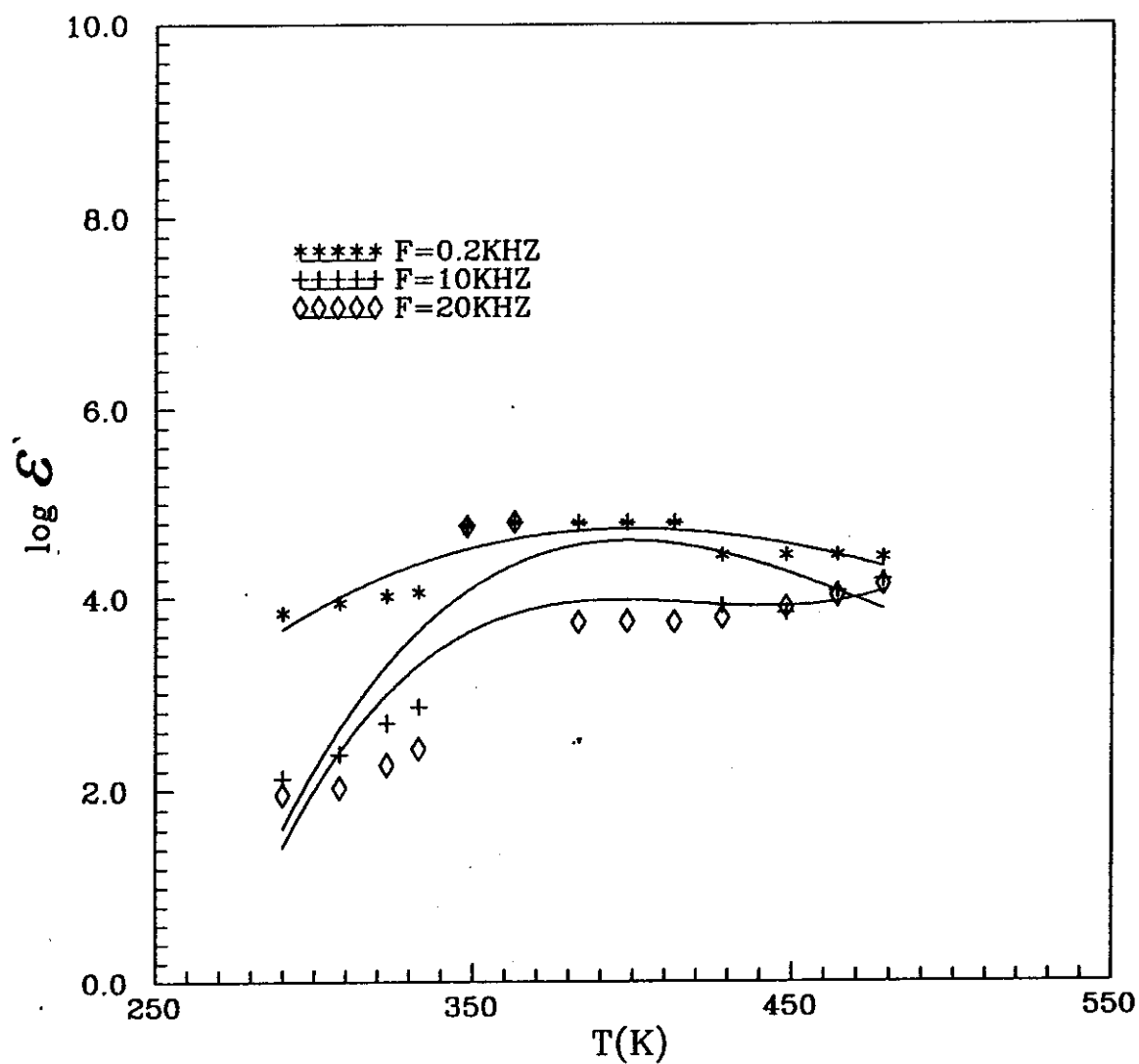


Fig.(III-32): The temperature dependence of the dielectric constant for glassy sample $(76V_2O_5-24P_2O_5)_{1-x}(Li_3PO_4)_x$ ($x=0.02$) at various frequency

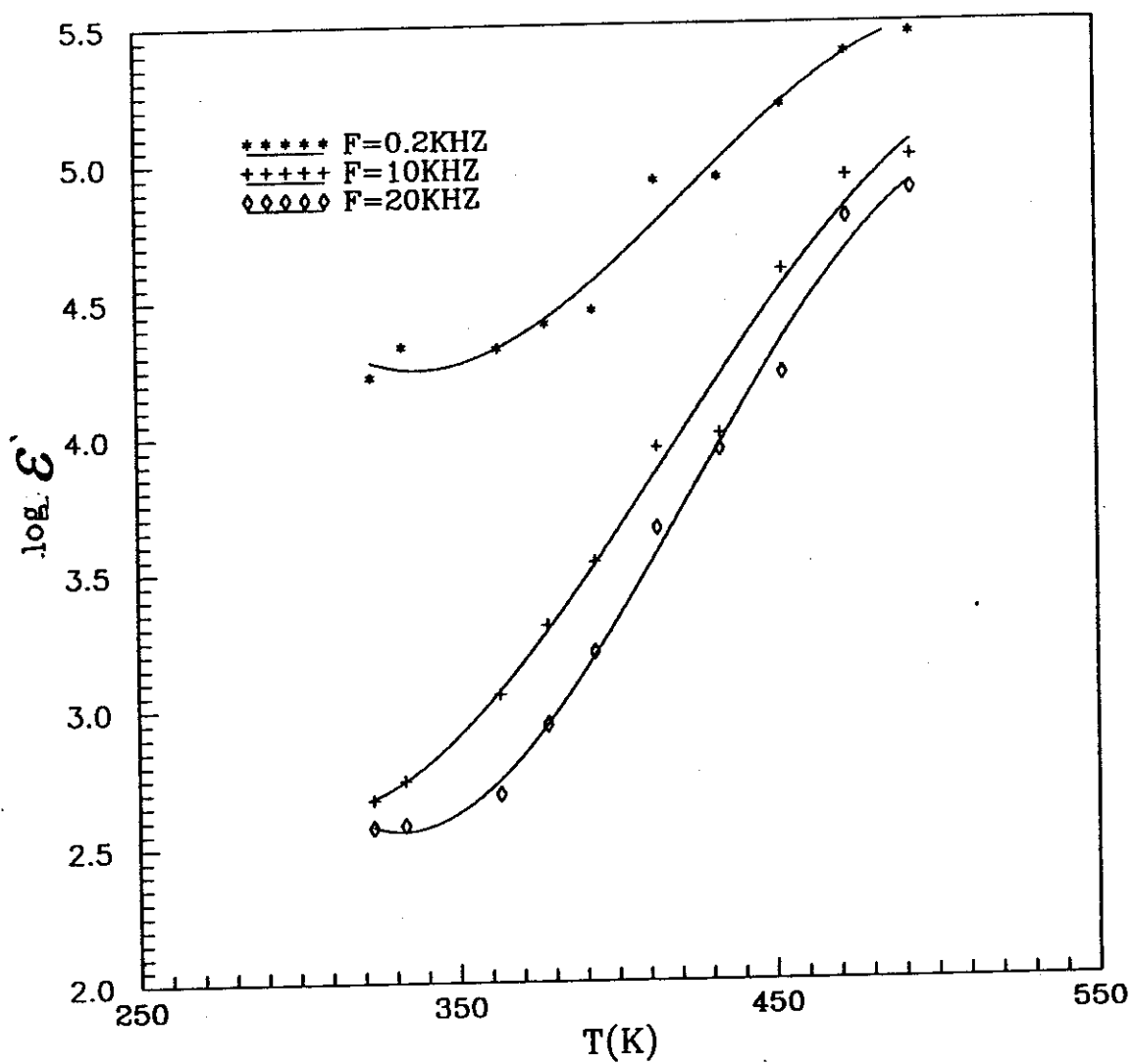


Fig.(III-33): The temperature dependence of the dielectric constant for glassy sample $(76\text{V}_2\text{O}_5-24\text{P}_2\text{O}_5)_{1-x}(\text{Li}_3\text{PO}_4)_x$ ($x=0.1$) at various frequency.

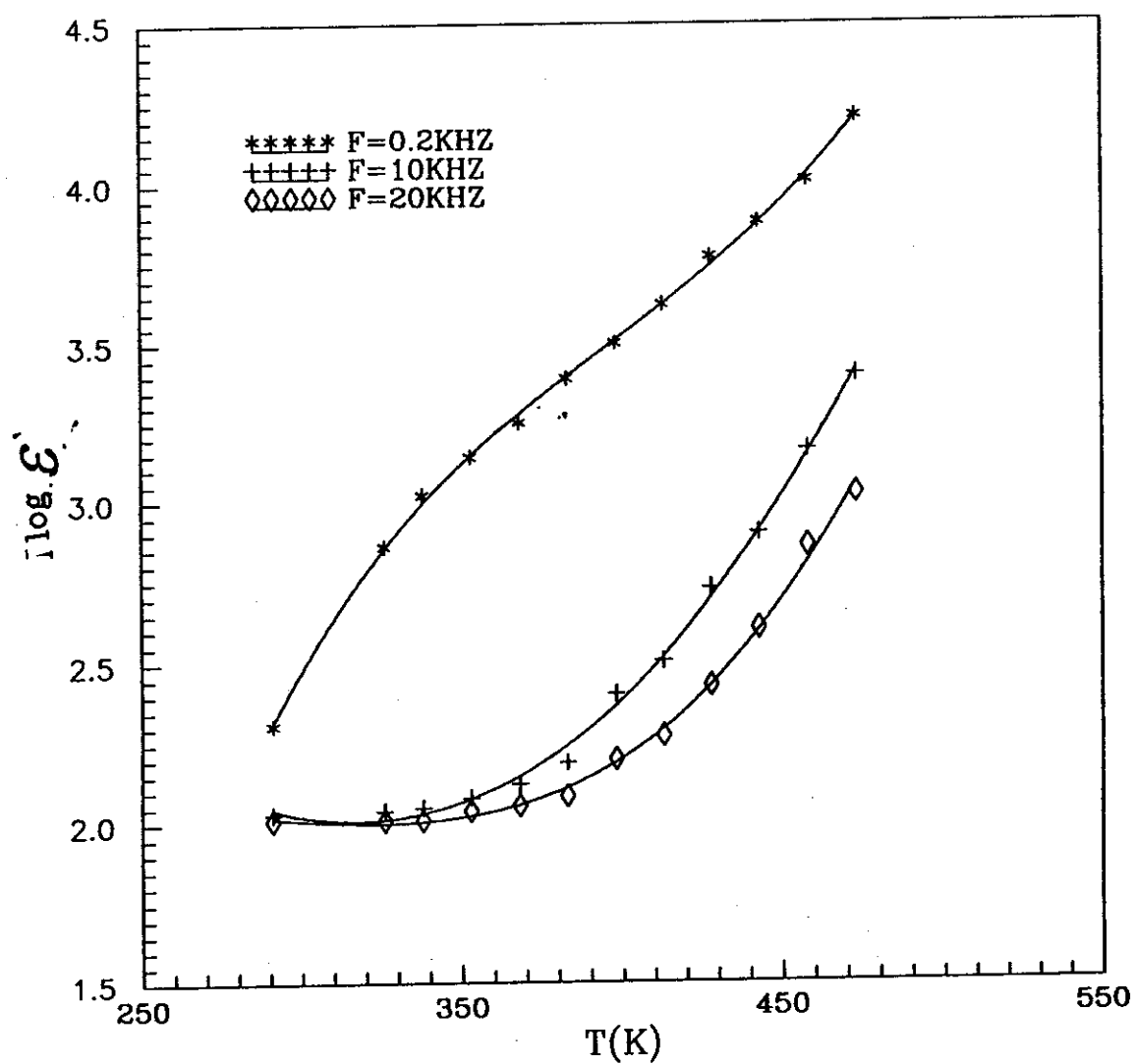


Fig.(III-34): The temperature dependence of the dielectric constant for glassy sample $(76V_2O_5-24P_2O_5)_{1-x}(Li_3PO_4)_x$ ($X=0.15$) at various frequency

In other words , the glassy network relaxes with increasing temperature from which the ionic motion becomes easier . This increase is also expected to be pronounced at low frequencies , since the ions have more time to participate in the motion . These expectations have been repeatedly confirmed for a variety of glasses⁽⁹⁴⁾.

III-3-4: Effect of frequency and Temperature on the dielectric loss ϵ'' of $(76V_2O_5-24P_2O_5)_{1-x}(Li_3PO_4)_x$ glass :

Figures (III - 35 : 39) shows the variation of the dielectric loss ϵ'' with frequency at different ambient temperatures for the investigated glass samples . In general the dielectric loss ϵ'' decreases as the frequency is increased . This behavior can be expressed by the following relation ⁽⁹³⁾ :

$$\epsilon'' / (\epsilon_0 - \epsilon_\infty) = [(\omega\tau)^{1-g} \cos(g\pi/2) (\epsilon_0 - \epsilon_\infty)] / [(1+2(g\tau)^{1-g} \cdot \sin(g\pi/2) + (\omega\tau)^{2(1-g)})] \quad (III-18)$$

This relation also tends to satisfy Debye equation for the single relaxation when $g = 0$. The general behaviour for all investigated glasses show nearly the inverse behaviour of the total conductivity against frequency . A nearly frequency independent of ϵ is observed at low frequency range while a strong dependence appears at higher frequency range followed by a stationary value . The transition point between the nearly independent and that of strong dependence regions shifted towards higher frequency with increasing temperature. (this has been discussed in σ_{tot} against frequency) .

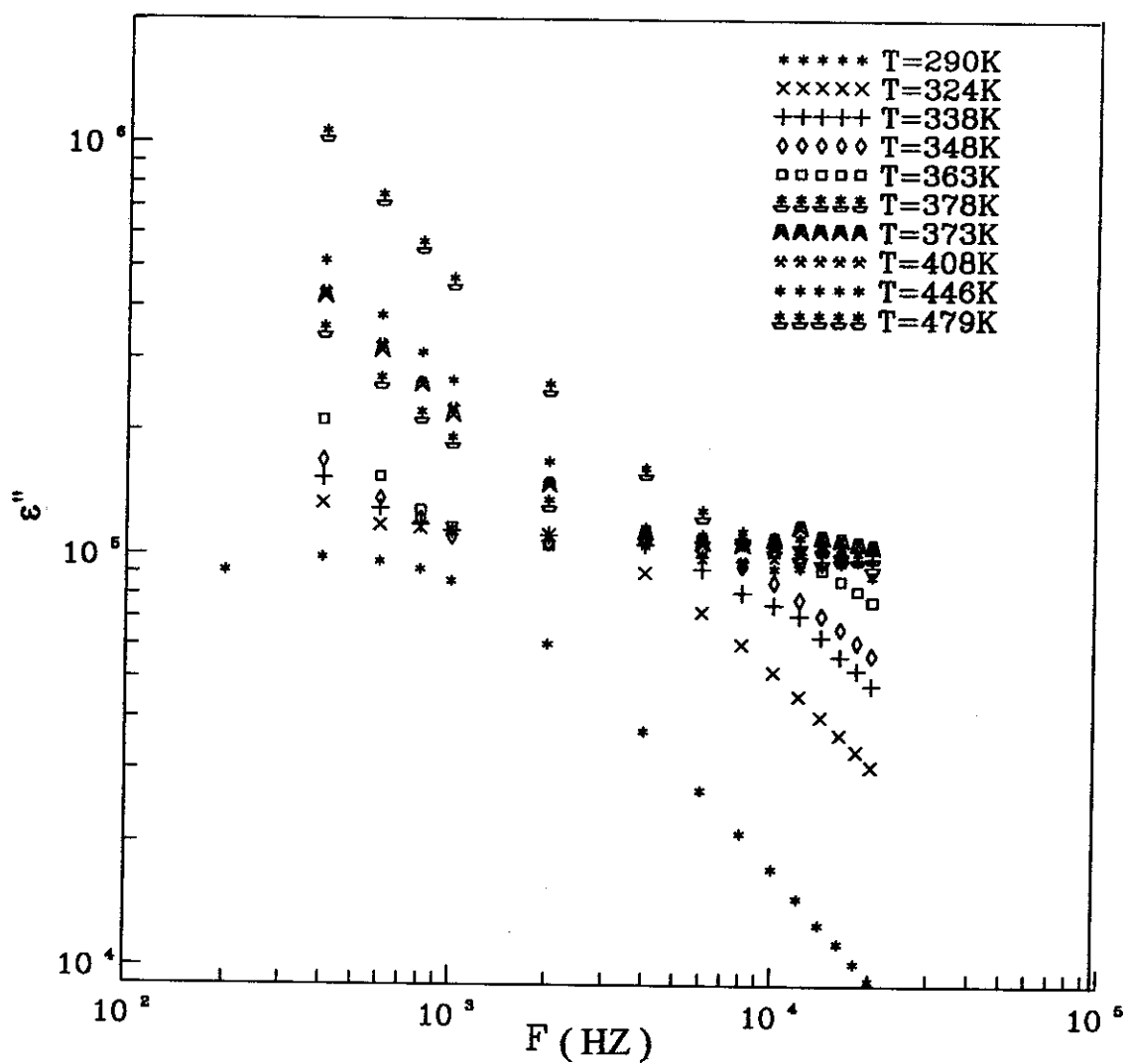


Fig.(III-35):The frequency dependence of the dielectric loss for glass sample (76V₂O₅ 24P₂O₅) at various temperatures.

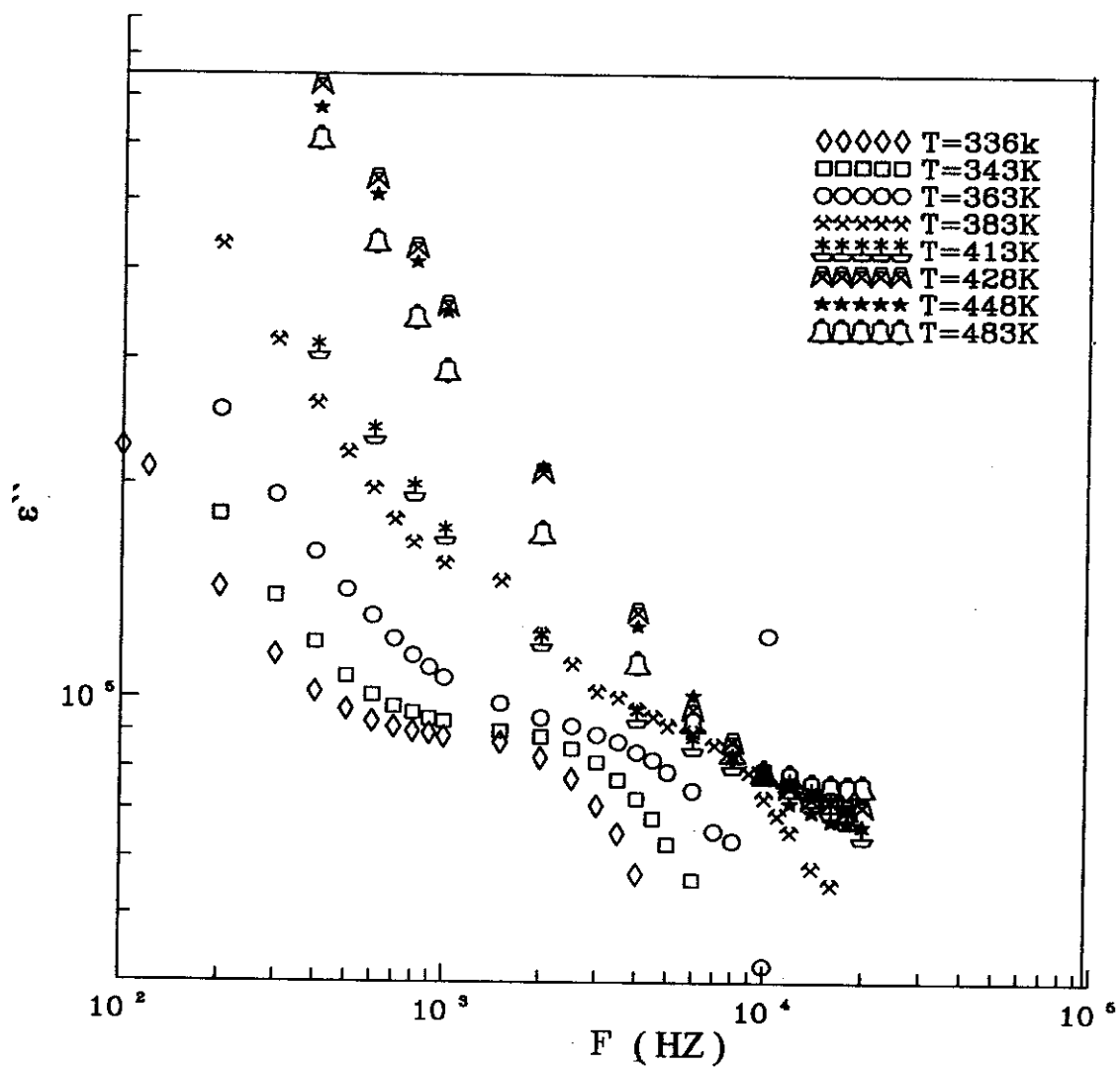


Fig.(III-36):The frequency dependence of the dielectric loss for glass sample $(76V_2O_5-24P_2O_5)_{1-x}(Li_3PO_4)_x$ ($X=0.01$) at various temperatures.

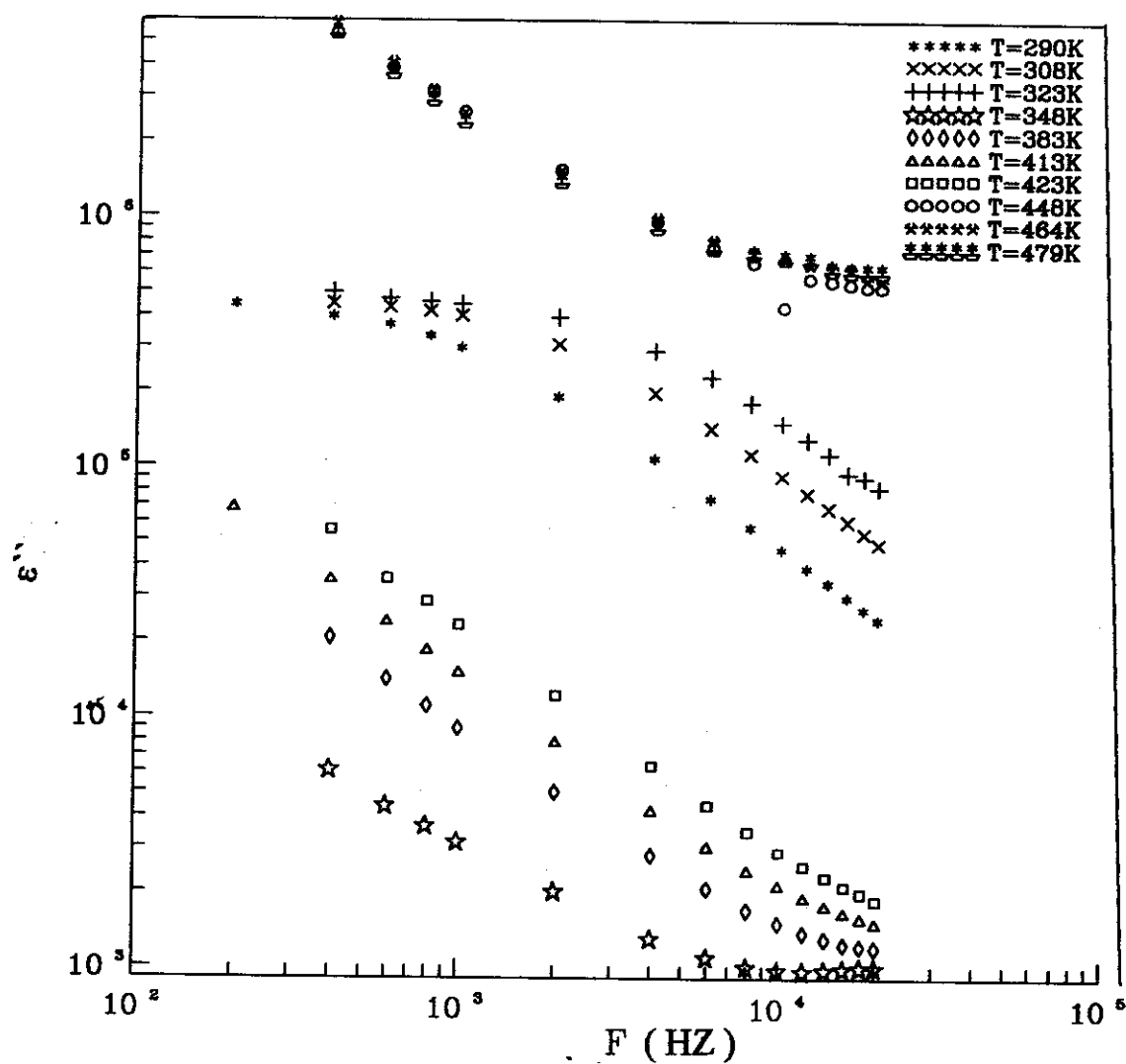


Fig.(III-37):The frequency dependence of the dielectric loss for glass sample $(76V_5O_5 \cdot 24P_5O_5)_{1-x} (Li_3PO_4)_x$ ($X=0.02$) at various temperatures.

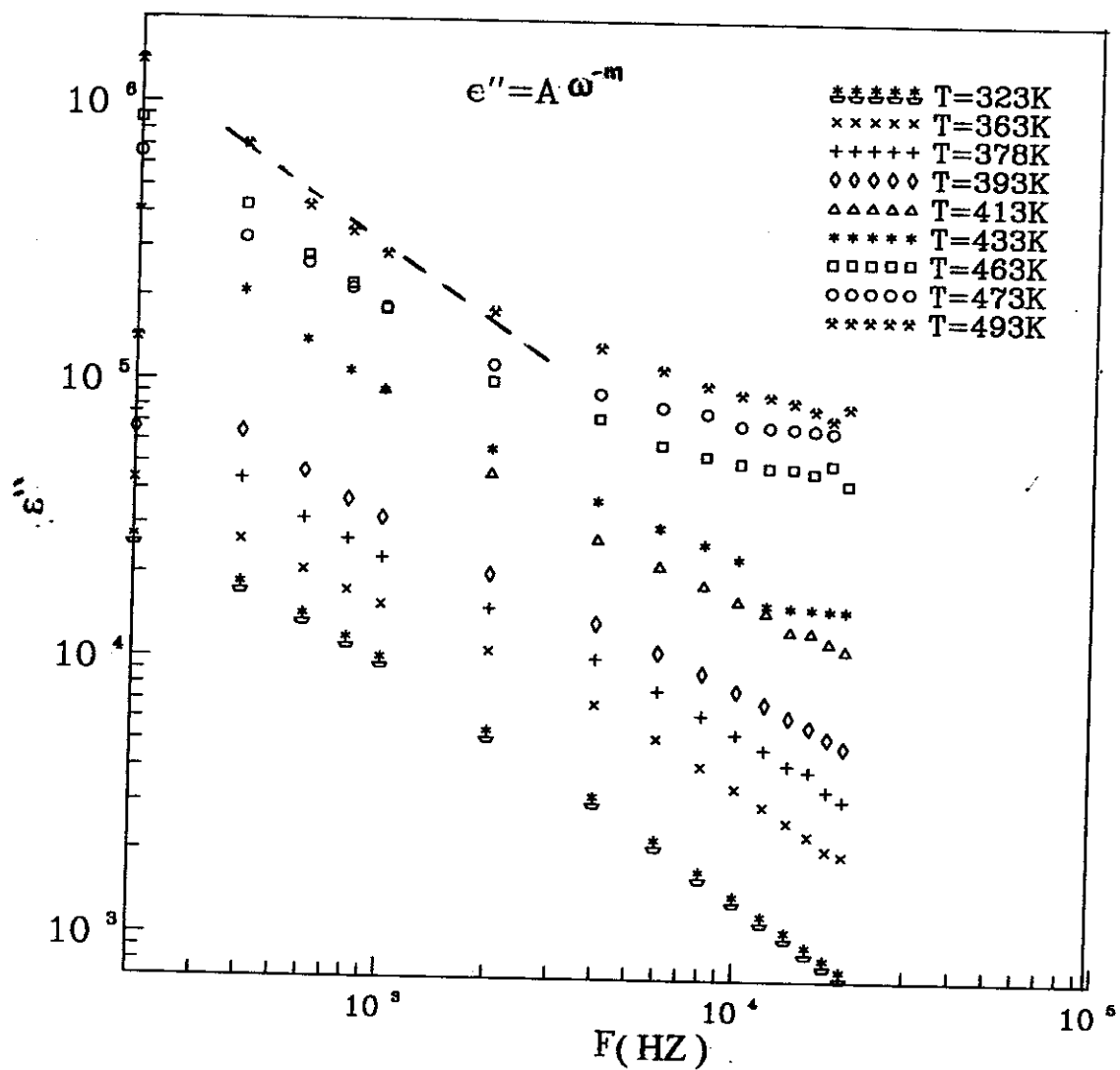


Fig. (III-38): The frequency dependence of the dielectric loss for glass sample $(76V_2O_5-24P_2O_5)_{1-x}(Li_3PO_4)_x$ ($X=0.10$) at various temperatures.

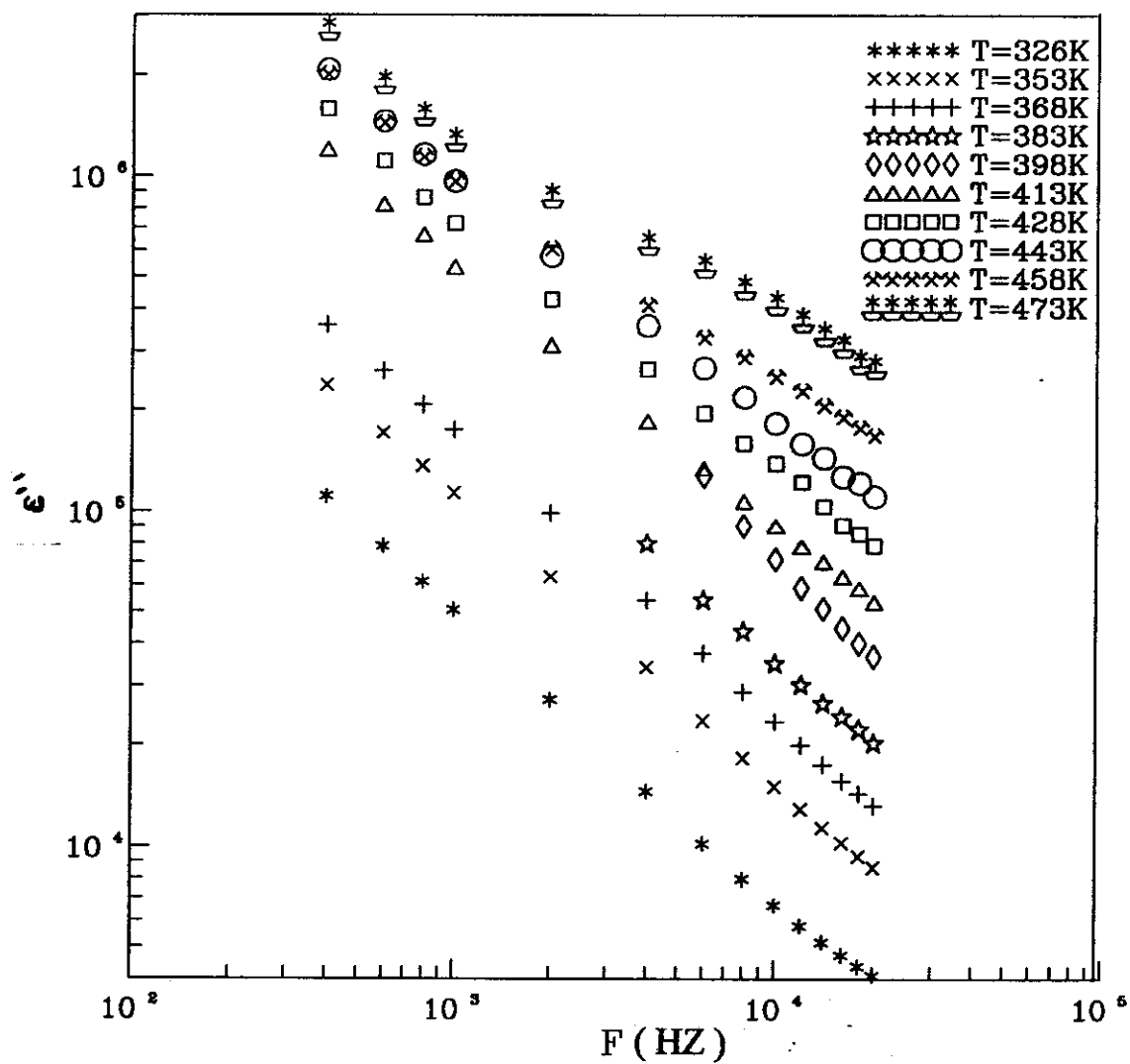


Fig.(III-39):The frequency dependence of the dielectric loss for glass sample $(76\text{V}_2\text{O}_5 - 24\text{P}_2\text{O}_5)_{1-x} (\text{Li}_3\text{PO}_4)_x$ ($X=0.15$) at various temperatures.

The frequency dependence of the moderate range , ϵ'' decreases with frequency increased the following relation⁽⁹⁵⁾.

$$\epsilon''(\omega) = (\epsilon_s' - \epsilon_\infty) 2\pi^2 N (ne^2/\epsilon_s)^3 k_B T \tau_0^m W_M^{-4} \omega^{-m} \quad (\text{III-19})$$

where $m = -4kT/W_M$, n is the number of electron that hop, N is the concentration of the localized states and W_M is the energy required to move an electron from one site to infinity. According to this model the values of W_M are obtained and listed in Table (III-11), the value of W_M lie in the range 0.093 – 0.236 eV and vary irregularly with varying glass composition.

The plots of ϵ'' against ϵ' for $(76V_2O_5-24P_2O_5)_{1-x}(Li_3PO_4)_x$ glasses have been done at different ambient temperature which showed semicircles, having centers lie below the ϵ' axis, Figure (III-40). The intersections with ϵ' axis give the static and infinite dielectric constants respectively (ϵ_s and ϵ_∞). The values of ϵ_s and ϵ_∞ have been obtained at different temperatures. The $(\epsilon_s - \epsilon_\infty)$ is found to be increase exponentially by increasing temperature, in agreement with Sayer and Mansigh⁽⁹³⁾ for the vanadium phosphate glasses. The semilogarithmic plot of $\ln(\epsilon_s - \epsilon_\infty)$ versus $10^3/T$ as in Fig (III-41) shows an straight line obeying the relation :

$$\epsilon_s - \epsilon_\infty = c \exp(E_D/k_B T) \quad (\text{III-19})$$

where : E_D is an activation energy term. The values of E_D for the different compositions are obtained and listed in Table (III-12).

Table (III-11) :The obtained values of exponent (m) and the energy (W_m) for $(76V_2O_5-24P_2O_5)_{1-x}(Li_3PO_4)_x$ glass samples at different temperatures :-

X	0.0		0.01		0.02		0.10			0.15				
	T(K)	m	W_M (eV)	T(K)	\bar{m}	W_M (eV)	T(K)	m	W_M (eV)	T(K)	m	W_M (eV)		
296	1.058	0.096	315.5	-	-	290	1.076	0.093	323	1.052	0.106	326	1.09	0.131
324	0.854	0.131	323	0.797	0.139	308	1.128	0.094	363	0.943	0.133	353	1.078	0.113
338	0.846	0.134	336	0.717	0.162	323	1.131	0.098	378	0.763	0.171	368	1.073	0.118
348	0.685	0.175	343	0.727	0.159	348	0.797	0.151	393	0.771	0.175	383	1.045	0.126
363	0.516	0.234	363	0.926	0.128	383	1.063	0.124	413	1.05	0.134	398	1.056	0.129
378	0.623	0.209	383	0.776	0.170	413	1.151	0.115	433	1.12	0.133	413	0.984	0.145
398	0.716	0.192	413	0.996	0.143	423	1.171	0.125	463	0.974	0.164	428	0.939	0.157
408	0.697	0.202	428	0.968	0.152	448	0.951	0.162	473	0.972	0.168	443	0.923	0.165
446	0.807	0.190	443	0.923	0.164	464	0.976	0.164	493	0.998	0.17	458	0.767	0.206
479	0.985	0.164	483	0.939	0.171	479	0.971	0.170				473	0.690	0.236

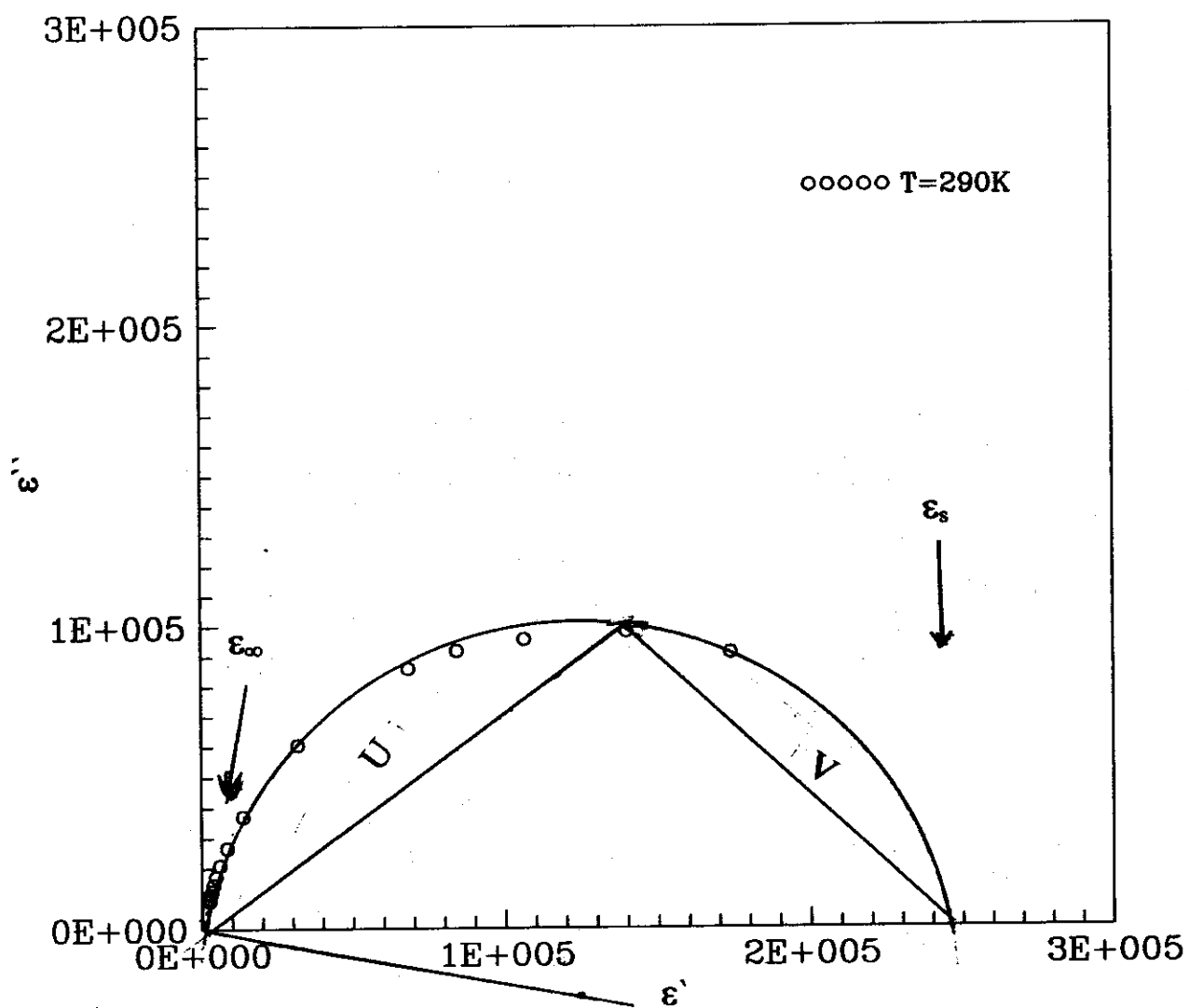


Fig.(III-40):Plots of the dielectric loss against the dielectric constant for glass sample (76V₂O₅ - 24P₂O₅).

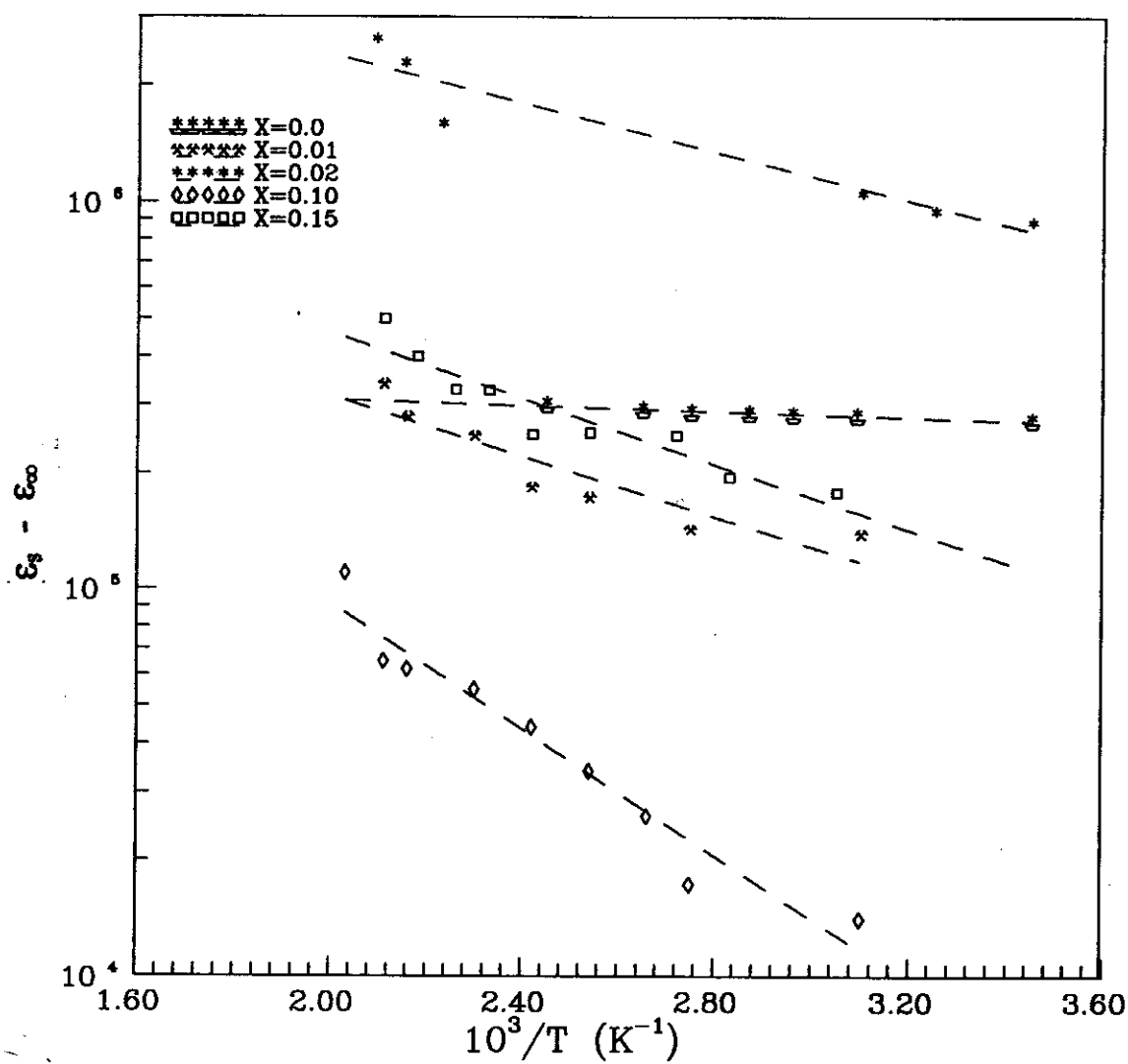


Fig. (III-41): Semilogarithmic plot of $(\epsilon_s - \epsilon_\infty)$ versus $10^3/T$ for glass samples $(76V_2O_5-24P_2O_5)_{1-x} (Li_3PO_4)_x$

Table (III-12): The obtained values of E_D , ΔH and ΔS of $(76V_2O_5-24P_2O_5)_{1-x}(Li_3 PO_4)_x$ glass samples :

X	E_D (eV)	ΔH (eV)	$\Delta S \times 10^3$
0.0	0.048	0.51	1
0.01	0.179	0.725	0.86
0.02	0.144	0.379	1.26
0.10	0.371	0.695	0.94
0.15	0.195	0.461	0.99

It is noticed that E_D changes irregular by increasing $(Li_3 PO_4)$ content for the glasses . It is also noticed that the values of E_D are different from those obtained from d.c conduction referring to a different mechanism .

From Cole and Cole ⁽⁹⁶⁾ diagrams the diameter drawn through the center from ϵ_∞ makes an angle $\alpha\pi/2$ with ϵ' axis , knowing α , one can determine τ_o by using the relation ⁽⁹⁶⁾ :

$$V/U = (\omega \tau_o)^{1-\alpha} \quad (III-20)$$

where τ_o is the macroscopic relaxation time , V is the distance on the Cole-Cole diagram between ϵ_s and the experimental point , u is the distance between the point and ϵ_∞ and ω is the angular frequency . Knowing τ_o , one can estimate the value of the molecular relaxation time (τ) by using the relation ⁽⁹⁷⁾ :

$$\tau = [(2\epsilon_s + \epsilon_\infty) / 3 \epsilon_s] \tau_o \quad (III-21)$$

According to the Eyring's theory⁽⁹⁸⁾ , the molecular relaxation has been expressed by the following relation :

$$\tau = [(h / k_B T) \exp (\Delta F / RT) \quad (III-22)$$

where ΔF is the free energy for dipole relaxation , h is the plank's constant and R is the gas constant, substituting by :

$\Delta F = \Delta H - T \Delta S$, equation (II-22) can be written as:

$$\tau = (h / k_B T) e^{\Delta H/RT} e^{-\Delta S/R} \quad (III-23)$$

where ΔH is the thermal activation for dipole reorientation and ΔS is the entropy of activation .

$\ln \tau T$ against $10^3 / T$ suggest linear relationships, with slope equal to $\Delta H/R$, shown as Fig (III-42).

The values of ΔH and ΔS have been obtained using the least square fitting of relation (III-23) and listed in Table (III-12). It is clear that E_D , ΔH and ΔS vary irregular with varying sample composition. In addition the values of ΔS lies in the range of amorphous solids.

III-3-5: Frequency Dependence of Dielectric loss tangent :

The frequency dependence of the dielectric loss tangent $\tan \delta$ was studied for vanadium phosphate glasses under investigation in the frequency range 100 Hz - 100 kHz at different ambient temperatures. Figures (III- 43 : 47) show the frequency dependence of the dielectric loss tangent $\tan \delta$ at various temperatures. It is noticed that a minimum in $\tan \delta$ is observed at a certain frequency and shifted towards higher frequency when the temperature was increased. In addition, $\tan \delta$ increases with increasing frequency. The appearance of minimum depend on the sample nature, the concentration of the micro domains and their reflection on the interfacial polarization. The temperature dependence of the frequency responding to the minimum in $\tan \delta$ can be described by the following Arrhenious relation :

$$F_{\min} = F_0 \exp (-E_m / k_B T) \quad (III-24)$$

where E_m is an activation energy term concerning the shift of F_{\min} with temperature. Figure (III-48) show the temperature dependence of F_{\min} versus $10^3/T$. The values of E_m and F_0 are obtained by using

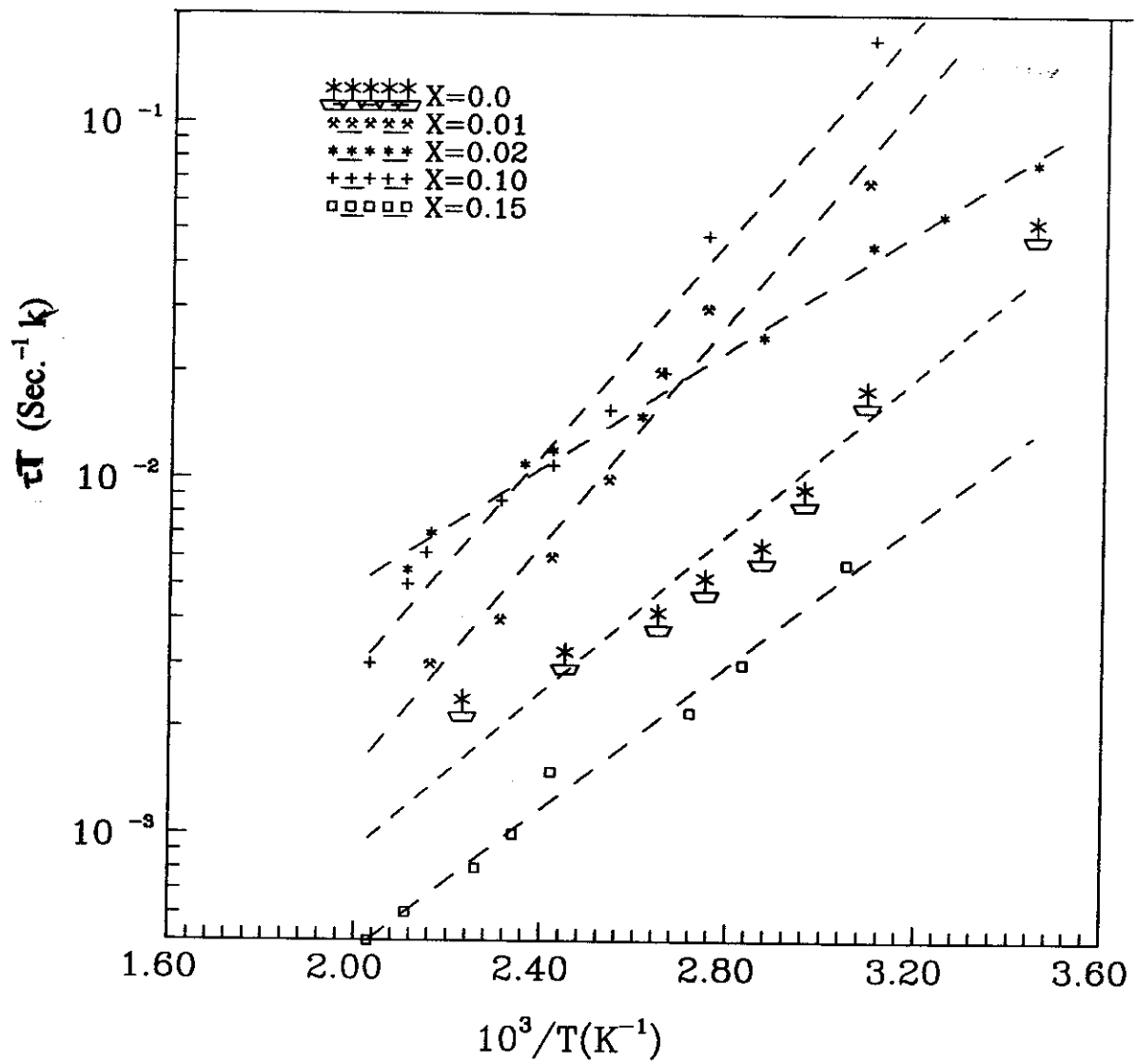


Fig.(III-42): Temperature dependence of the relaxation time for the glass samples $(76V_2O_5-24P_2O_5)_{1-x}(Li_3PO_4)_x$.

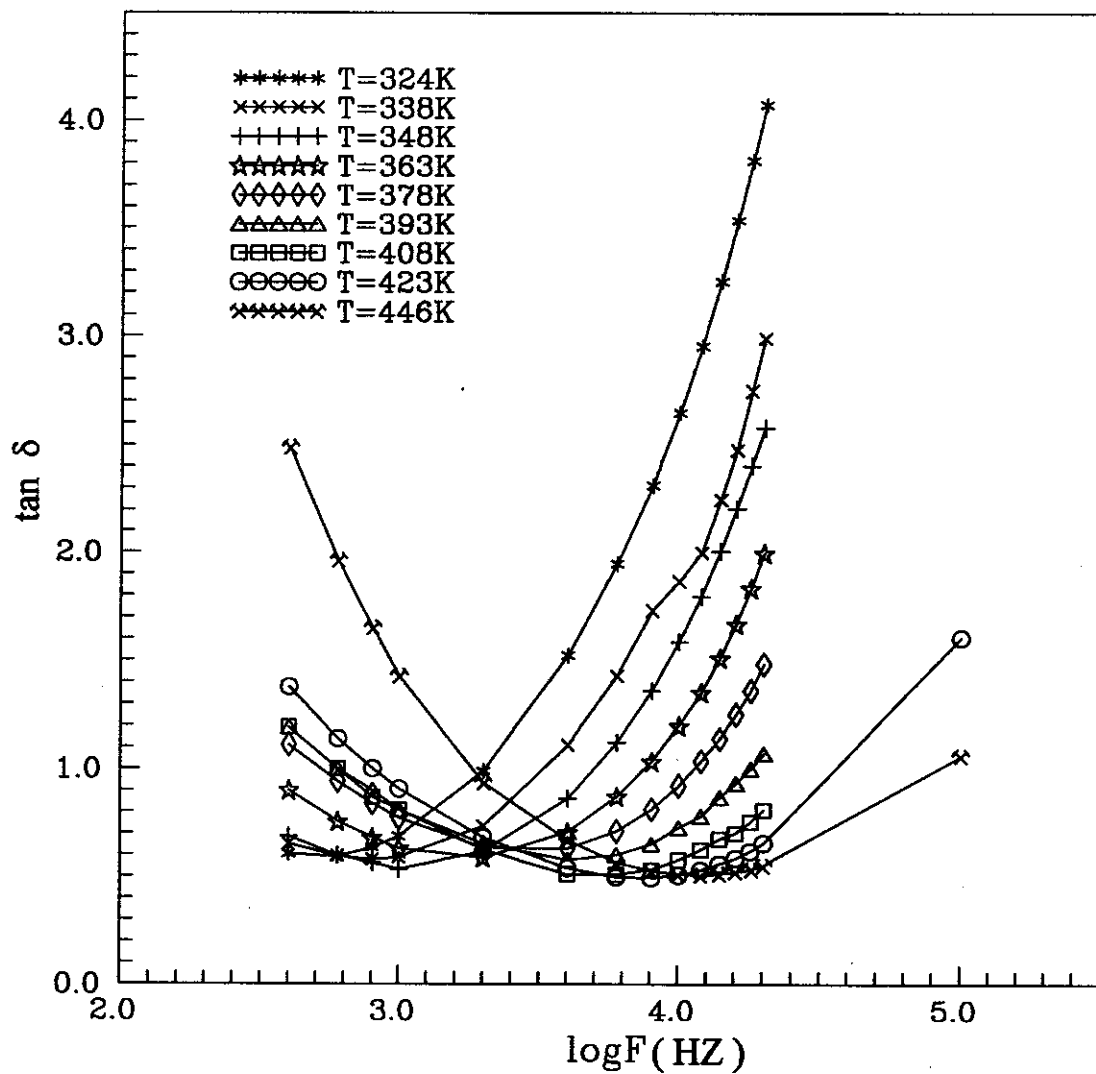


Fig.(III-43):Frequency dependence of the dielectric loss tangent for glass sample (76V₂O₅-24P₂O₅) at various temperatures.

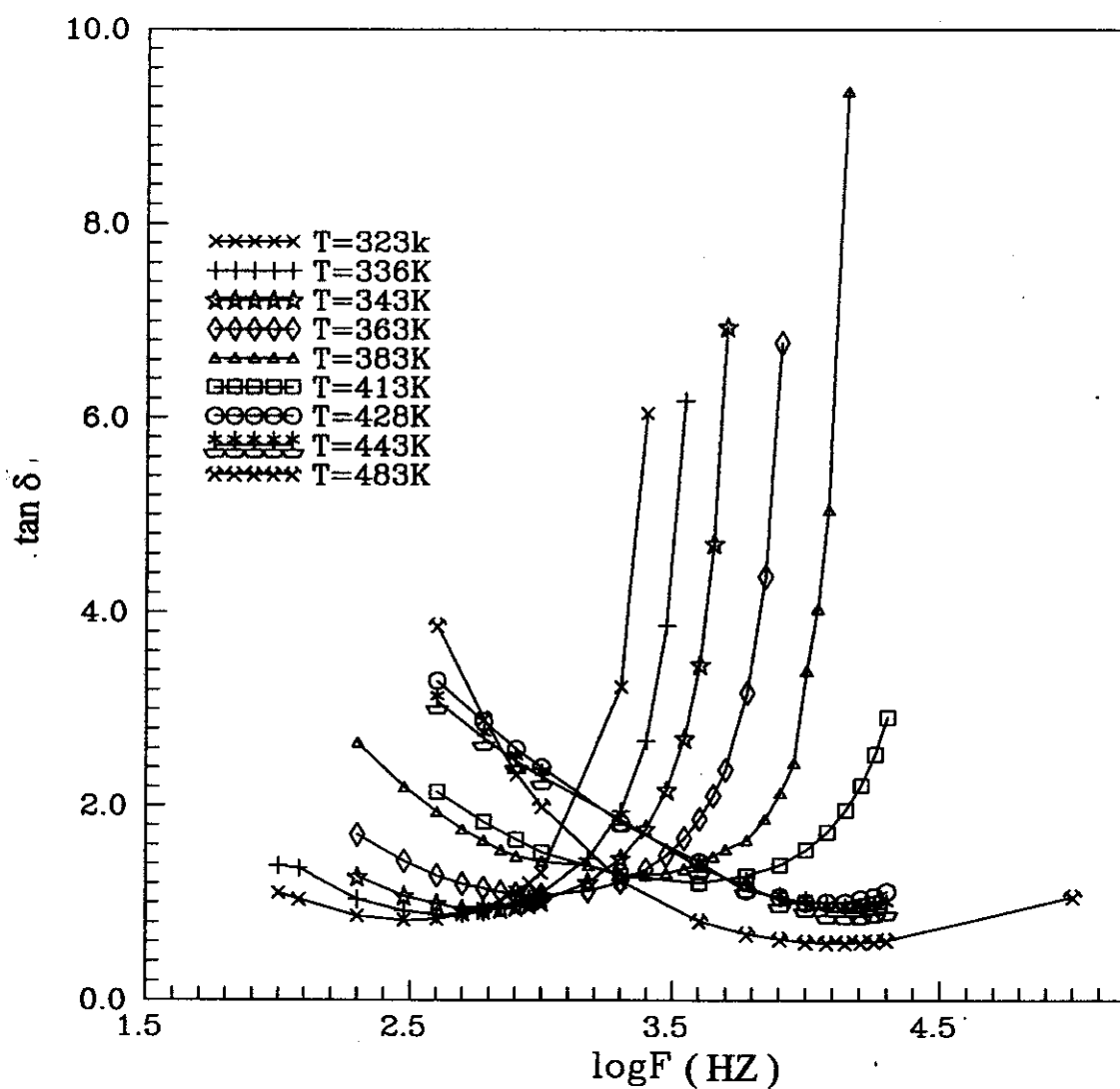


Fig.(III-44):The frequency dependence of the dielectric loss tangent for glass sample $(76V_2O_5-24P_2O_5)_{1-x}(Li_3PO)_x$ ($X=0.01$) at various temperatures.

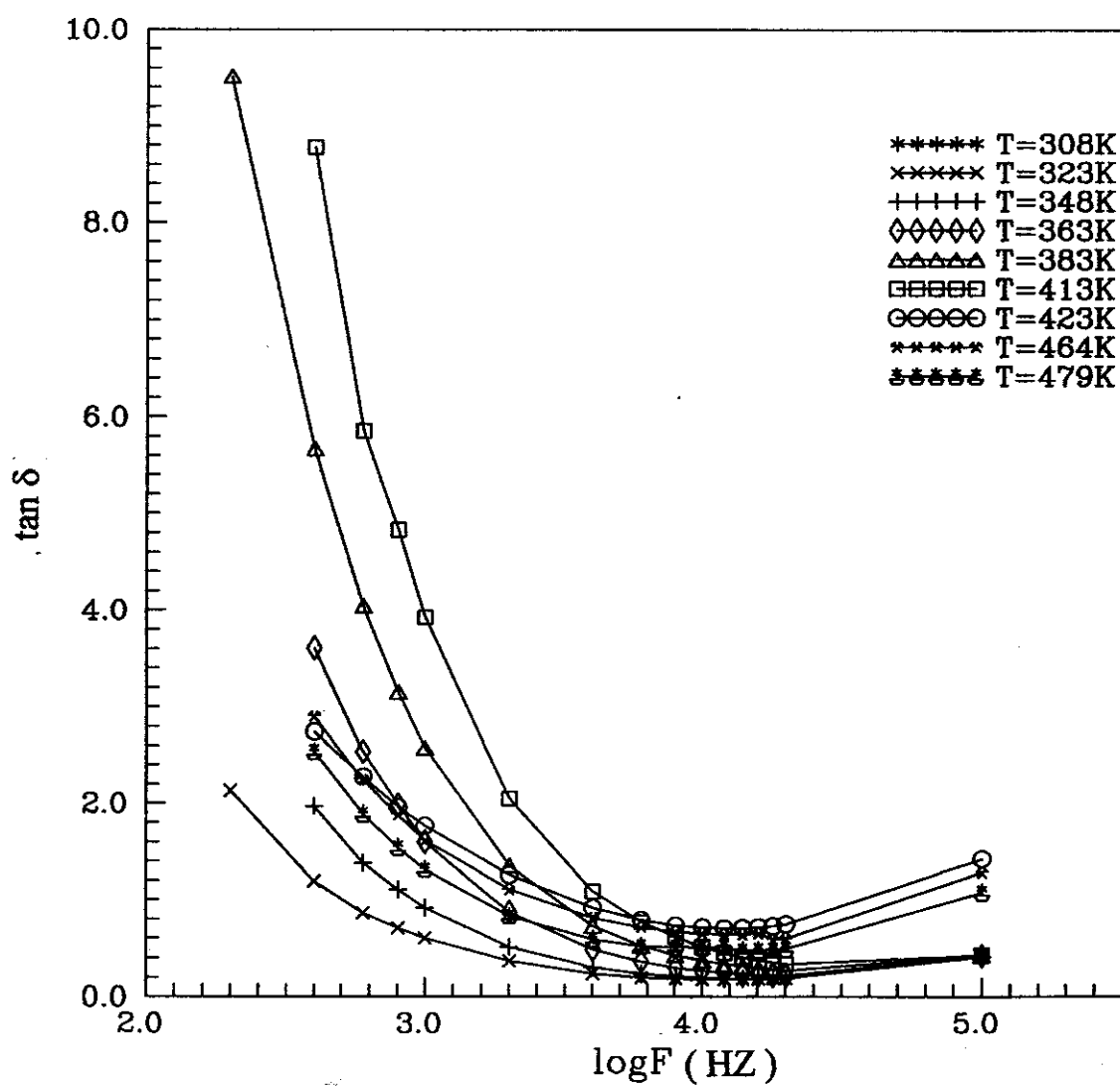


Fig.(III-45):Frequency dependence of the dielectric loss tangent for glass sample $(76V_2O_5-24P_2O_5)_{1-x}(Li_3PO)_x$ ($X=0.02$) at various temperatures.

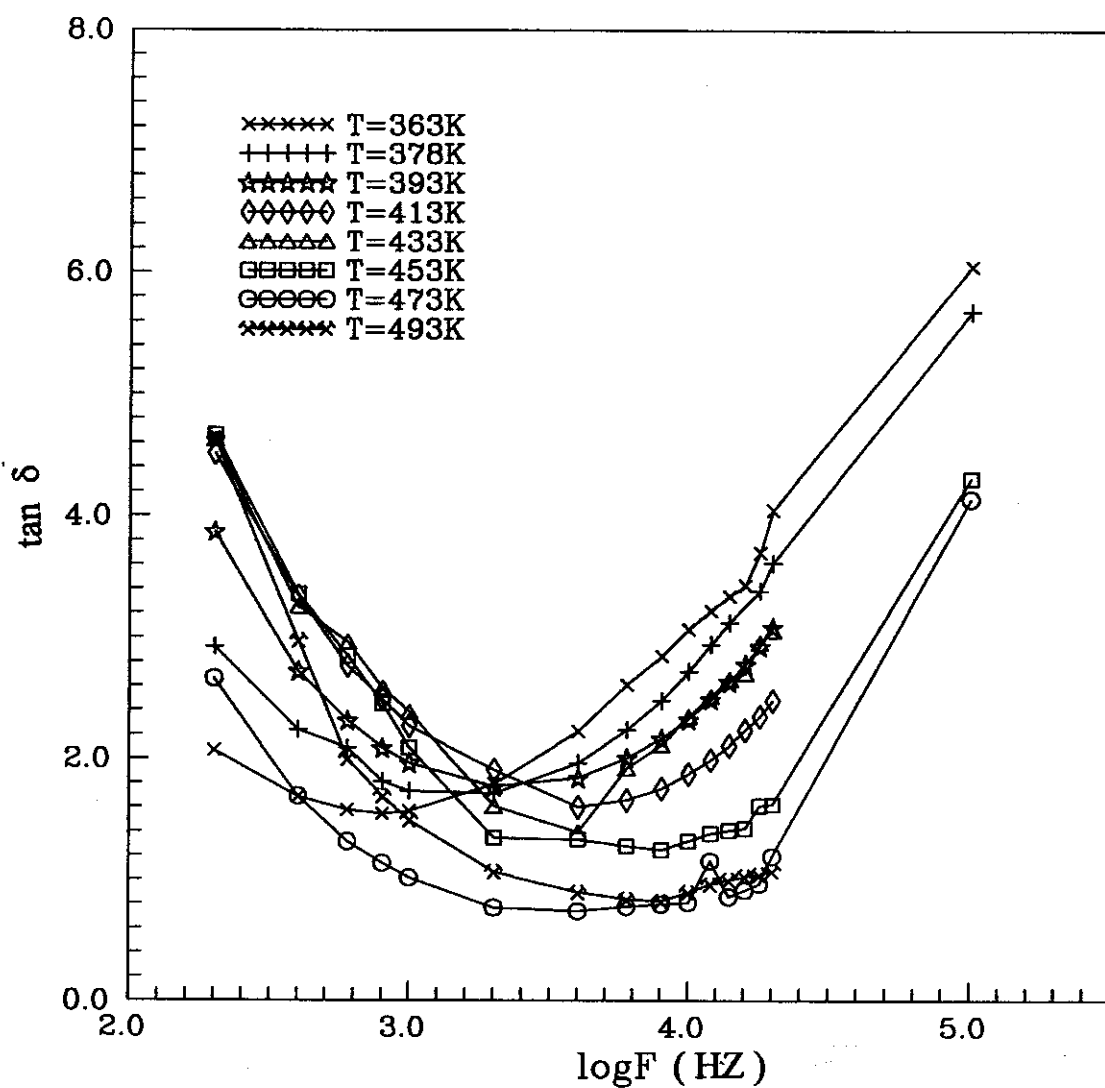


Fig.(III-46):Frequency dependence of the dielectric loss tangent for glass sample $(76V_2O_5-24P_2O_5)_{1-x}(Li_3PO)_x$ ($X=0.10$) at various temperatures.

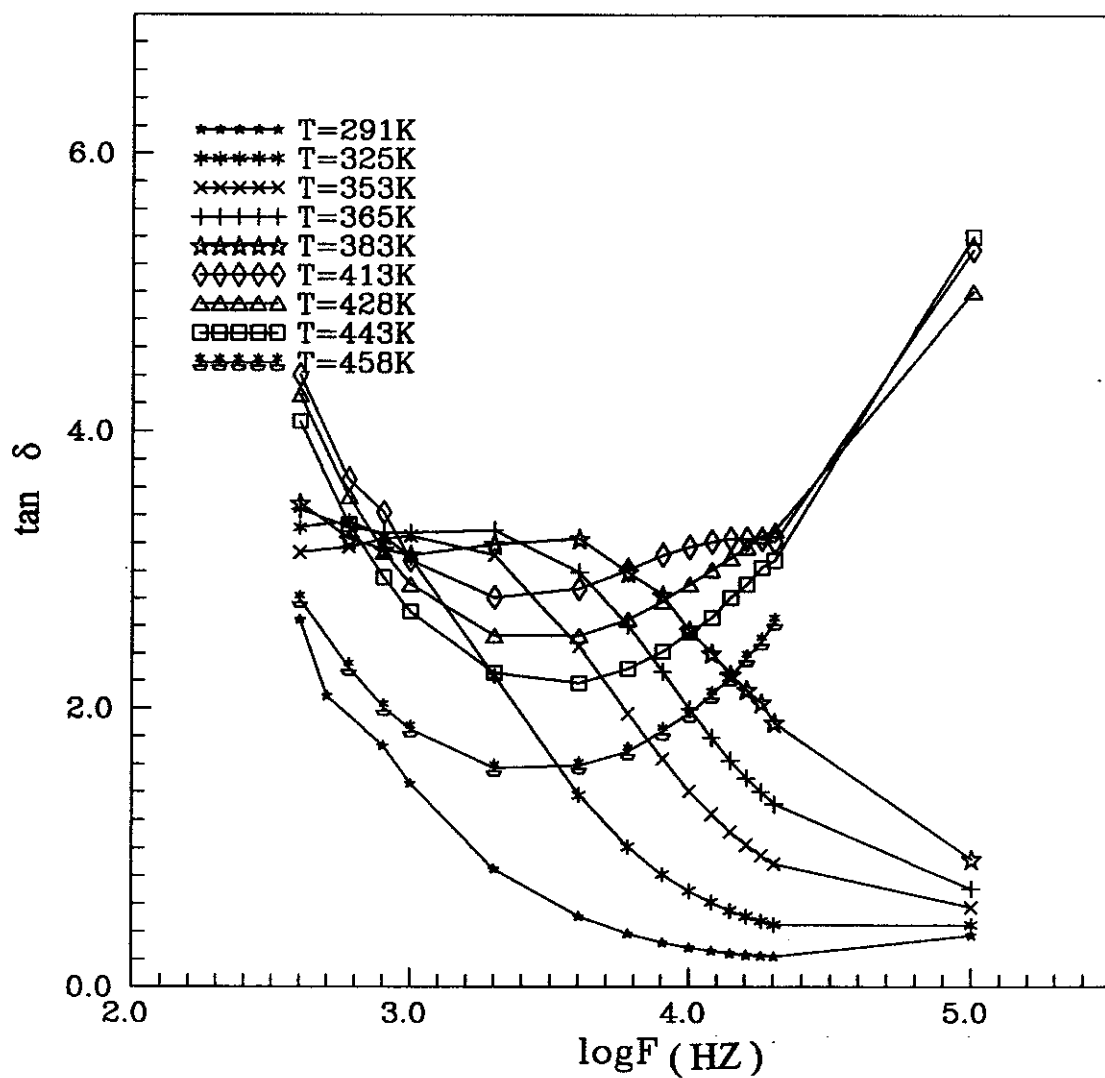


Fig.(III-47):Frequency dependence of the dielectric loss tangent for glass sample $(76V_2O_5-24P_2O_5)_{1-x}(Li_3PO)_x$ ($X=0.15$) at various temperatures.

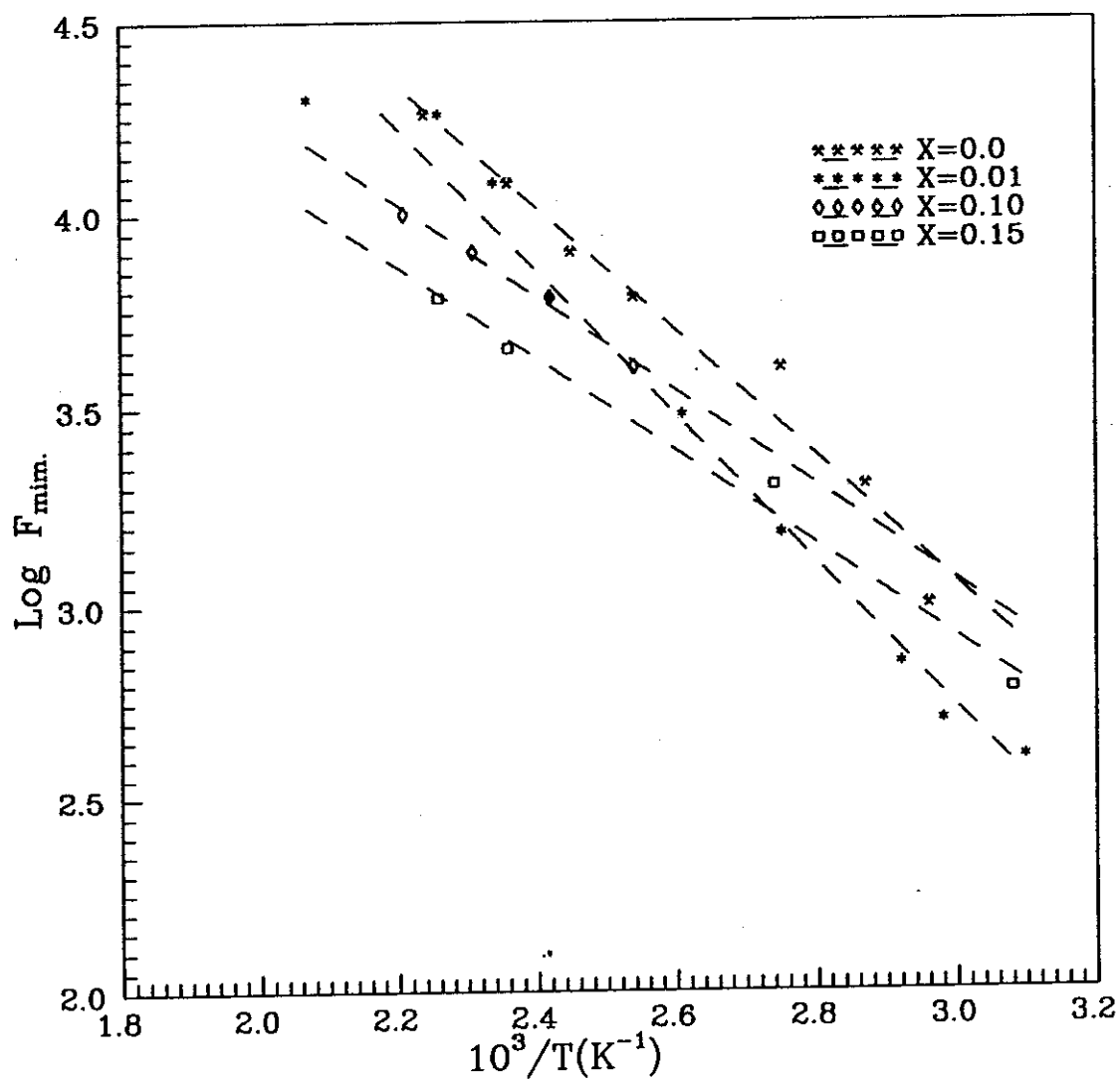


Fig. (III-48): Temperature dependence of F_{\min} for glass samples $(76V_2O_5-24P_2O_5)_{1-X} (Li_3PO_4)_X$

the least square fitting of relation(III-24) and listed in Table (III-13). In general E_m varies irregular with increasing lithium Phosphate content. The obtained value of E_m (0.318eV) is nearly equal to that obtained for E_o (0.316eV).

III-3-6 : Temperature dependence of bulk conductivity for $(76V_2O_5-24P_2O_5)_{1-x}(Li_3PO_4)_x$ glasses :

The complex impedance $z''(z')$ diagrams for the different glass samples are shown in Figs. (III – 49 : 53). The plots show semicircles, with centers lie below Z' axis. The intersection of Z' axis represents the sample bulk resistance R_b (at the infinite frequency). It is also clear that the diameter of the semicircle decreases with increasing temperature referring to the pronounced increase of dc conduction. The appearance of tails at the low frequency range can be attributed to the electrode blocking⁽⁹⁹⁾. The bulk conductivity has been estimated for the glasses which was found to increase with temperature obeying Arrhenious equation ,

$$\sigma_B T = \sigma_{Bo} \exp(-E_B / k_B T) \quad (III-25)$$

where E_B is the activation energy , σ_{Bo} is the pre-exponential factor .

Figure (III-54) show the temperature dependence of the bulk conductivity for the investigated glasses .The values of E_B is obtained and listed in Table (III-14). It is clear that the values of E_B lie in the range 0.348 – 0.448 eV .These values are higher than those obtained for vanadium phosphate glasses (0.035– 0.054eV)⁽⁷²⁾ which can be attributed to the different of V^{+4}/V^{+5} ratio as a result of varying the preparation condition and the glass network .

Table (III-13): Relaxation activation energy for $(76\text{V}_2\text{O}_5-24\text{P}_2\text{O}_5)_{1-x}$
 $(\text{Li}_3\text{PO}_4)_x$ glasses :

X	E_m (eV)	F_o (Hz)
0.0	0.318	7.23×10^8
0.01	0.370	2.14×10^8
0.10	0.239	7.73×10^6
0.15	0.234	2.9×10^6

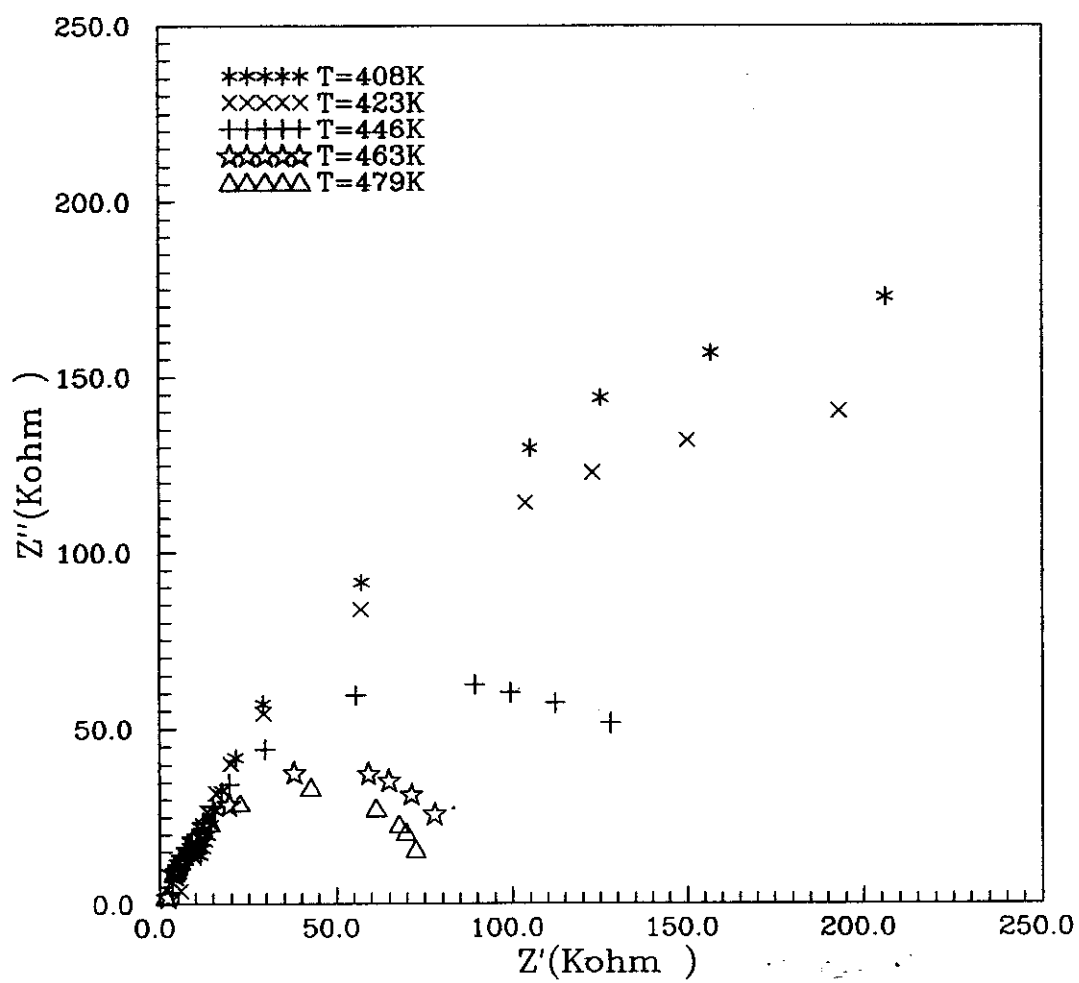


Fig.:(III-49):Impedance plot of Z'' versus Z' for glass sample $(76V_2O_5 - 24P_2O_5)$ at selected temperatures.

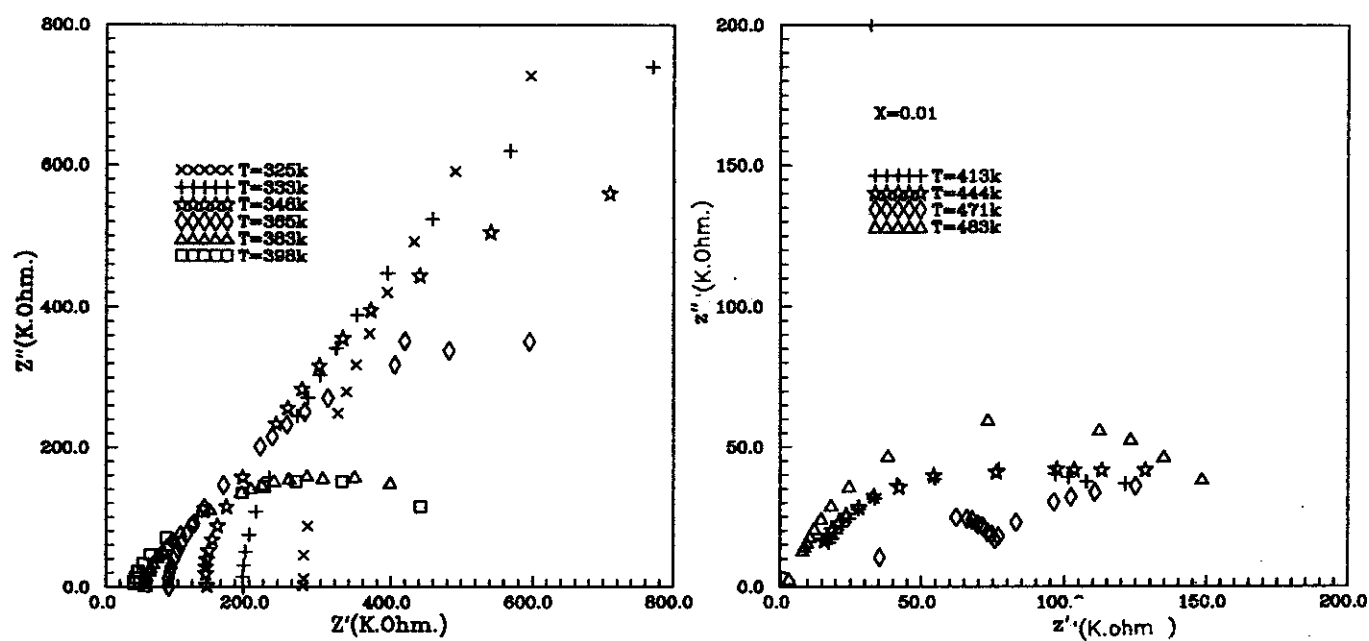


Fig.:(III-50): Impedance plot of Z'' versus Z' for glass sample $(76V_2O_5 - 24P_2O_5)_{1-x} (Li_3PO_4)_x$ ($X=0.01$) at selected temperatures.

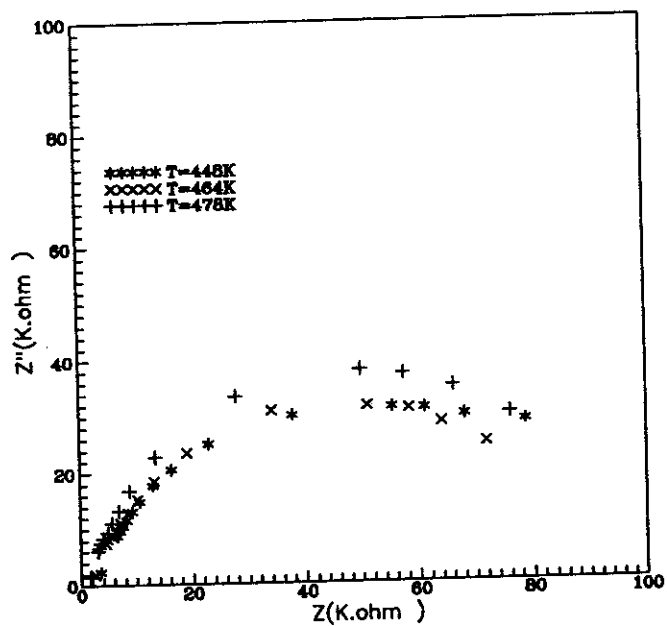
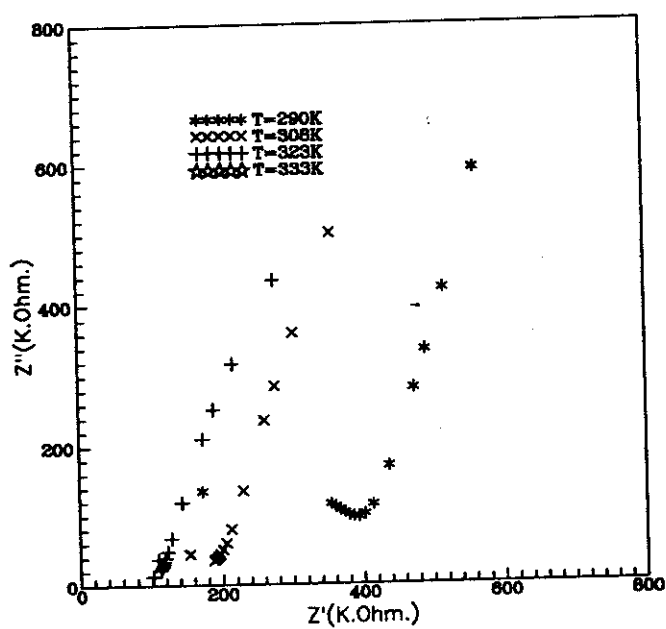


Fig.:(III-51): Impedance plot of Z'' versus Z' for glass sample $(76V_2O_5 - 24P_2O_5)_{1-x} (Li_3PO_4)_x$ ($X=0.02$) at selected temperatures.

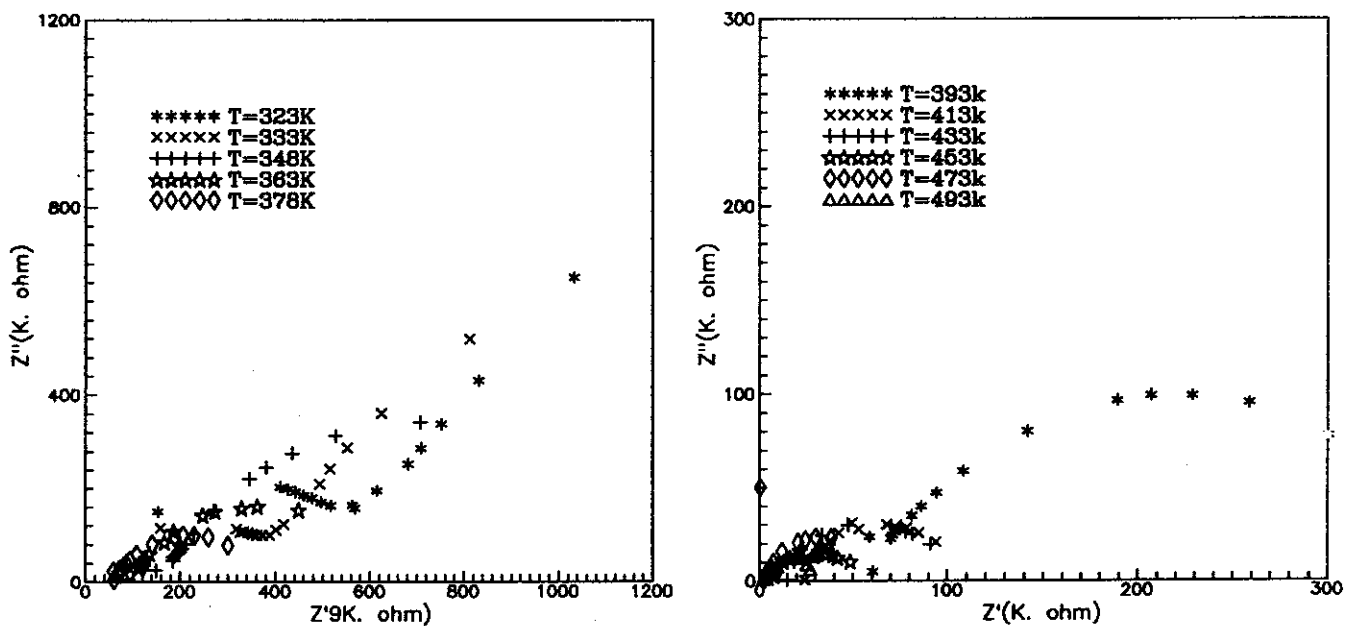


Fig.:(III-52): Impedance plot of Z'' versus Z' for glass sample $(76V_2O_5 - 24P_2O_5)_{1-x} (Li_3PO_4)_x$ ($X=0.10$) at selected temperatures.

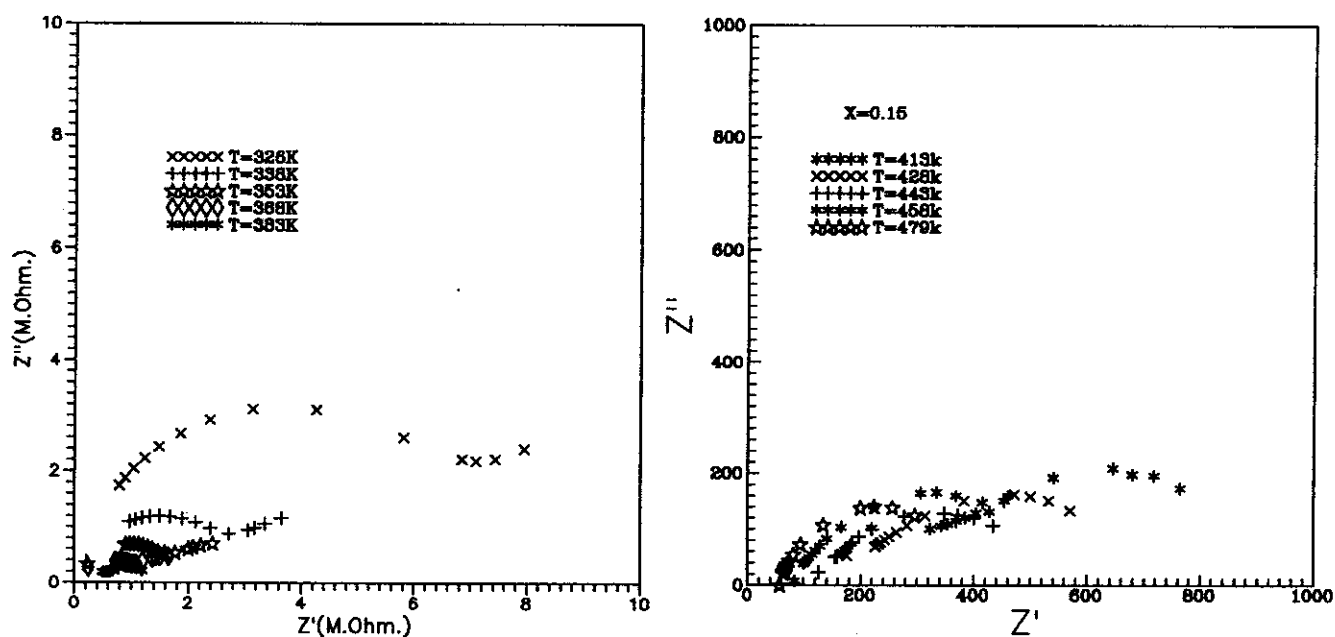


Fig.:(III-53): Impedance plot of Z'' versus Z' for glass sample $(76V_2O_5 - 24P_2O_5)_{1-x} (Li_3PO_4)_x$ ($X=0.15$) at selected temperatures.

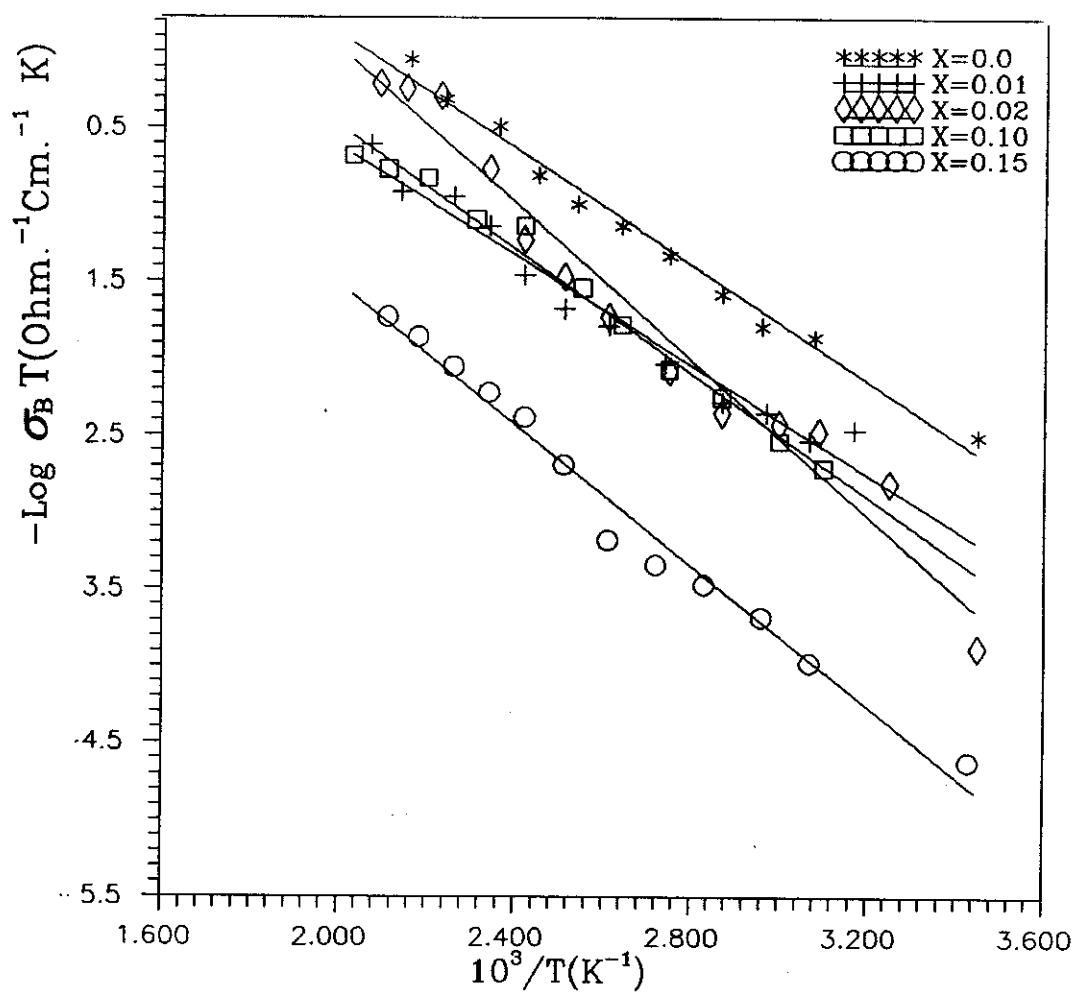


Fig.(III-54):The temperature dependence of the bulk conductivity for glass samples $(76V_2O_5 - 24P_2O_5)_{1-x}(Li_3PO_4)_x$ ($X=0.0, 0.01, 0.02, 0.10$ and $0.15.$)

Table (III-14): The Bulk activation energy for the conduction in $(76\text{V}_2\text{O}_5-24\text{P}_2\text{O}_5)_{1-x}(\text{Li}_3\text{PO}_4)_x$ glasses :

X	E_B (eV)
0.0	0.392
0.01	0.348
0.02	0.448
0.10	0.397
0.15	0.385

The bulk conductivity is found to decrease with increasing the lithium phosphate content in the glasses obeying the following relation

$$\sigma_B = \sigma_{B_0} \exp(-f / f_0) \quad (\text{III-26})$$

where $\sigma_B = \sigma_{B_0}$ at $f = 0$ and F_0 is a characteristic concentration . The values of f_0 are estimated at different tempratures and listed in Table (III-15).A little variation of f_0 is observed .In addition the pre-exponential σ_{B_0} is found to increase with increasing temperature obeying Arrhenious relation :

$$\sigma_{B_0} T = A \exp(-E_0 / k_B T) \quad (\text{III-27})$$

where A is a constant and E_0 is the activation energy . The obtained activation energy equal to 0.454 eV, is larger than E_b (σ_B versus $1/T$), 0.392 eV for the vanadium phosphate glass which can be attributed to the influence of hydration in the presence of lithium phosphate .This ,in turn ,leads to a change of protonic conduction in the sample.

Table (III-15): The obtained value of the characteristic concentration at different temperatures :

T (K)	F _o (wt.%)
323	3.7×10^{-2}
338	4.4×10^{-2}
363	3.9×10^{-2}
393	4.7×10^{-2}
425	4.21×10^{-2}
445	3.95×10^{-2}
473	3.71×10^{-2}