

Effect of Replacing V_2O_5 by ZnO or PbO on the Electrical Conductivity and Dielectric Properties of Some (V_2O_5 - SrO - FeO) Glasses

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Some SrO. FeO. V_2O_5 glasses containing either ZnO or PbO were prepared by the conventional melt quenching technique. The Ac conductivity and dielectric parameters were thoroughly investigated. The frequency and temperature dependence of dielectric constant (ϵ') and loss (ϵ'') were also studied in the frequency range from 100 Hz to 5 MHz and in the temperature range from 300 up to 500 K. Dielectric dispersion was observed in all samples and the obtained results were explained on the basis of the Debye type relaxation. It is also observed that the activation energy increased when Zn or Pb cations were gradually increased, which was attributed to the decrease in the density of states as well as the decrease of the disorder at the mobility edge. The dielectric modulus approach was used to analyze the complex relative permittivity, where a single relaxation time was observed.

1. Introduction:

It was known early that transition metal ions containing glasses based on conventional network formers [as P_2O_5 , GeO_2 , SiO_2 ... etc], are of interest and they have been studied extensively [1, 2]. Recently, unconventional oxide glasses based on transition metal oxides as glass network formers [as V_2O_5] have become now of much interest [3–5]. These glasses exhibit many technological applications in memory switching, electrical threshold, and optical switching devices ... etc [6-8]. They show also semiconducting properties that arise from the presence of more than one valence state characterizing all TMI's and they usually exhibit mixed electronic and ionic conduction. These glasses have also many applications in electrochemical devices such as batteries, chemical sensors and smart windows [9, 10].

The existence of binary glasses based on V_2O_5 as a major component is well established and their structure have been studied, but until now there is no clear picture to the exact nature of the oxygen polyhedra surrounding vanadium ions. Also the role played by the second component is still unclear. Even in case of pure V_2O_5 glass, it has been reported that V^{5+} ions appeared either in the four- or in the five- fold coordination state which is related to the sample preparation conditions [10]. It was reported also that the structure of vanadate glasses depends on the nature of both the network former and the network modifier cations that form the glass network [3 – 5, 11].

This article aims to investigate the effect of replacing V_2O_5 by ZnO or PbO on the electric and dielectric properties of some iron strontium vanadate glasses and to compare the obtained electrical parameters of both the studied glass systems.

2. Samples Preparation and Experimental Techniques:

Chemically pure materials were used to prepare two glass systems obeying the following molecular formula, $[(70-x)V_2O_5 \cdot xRO \cdot 10SrO \cdot 20FeO]$, where RO represents ZnO or PbO and $(0 \leq x \leq 15)$ by using the conventional melt quenching method. The finely mixed batches were melted in porcelain crucibles in an electrically heated muffle furnace at about 1300 K. The duration of melting was 2 hour, and the melts were swirled several times to ensure complete homogeneity as well as to obtain bubble free melts. The solid glass samples were obtained by pressing the melt between two pre-cooled stainless steel plates. The obtained samples were annealed at 500 K over night under a decreasing temperature rate of about 1K / 3.5 min, in order to remove stress and strain.

For electrical measurements, the annealed glasses were polished to obtain disk shape samples with 2mm thickness and 7mm diameter. Good electrical contact was achieved by painting the faces of the disks with an air drying silver paste. A digital thermometer was used to control the sample temperature during the electrical properties measurements.

The Ac conductivity $\sigma(\omega)$, dielectric constant (ϵ') and dielectric loss (ϵ'') were all measured by using Hioki 3532 LCR bridge in the frequency range from 100 Hz to 5 MHz and in the temperature range from 300 to 500 K. This Bridge can measure directly the angular frequency (ω), capacitance (C), impedance (Z), phase angle (Φ), and Dissipation factor ($\tan\delta$). The dielectric constant (ϵ') and dielectric loss (ϵ'') were then calculated using the following relations [12]:

$$\varepsilon' = Cd / (\varepsilon_0 A) \quad (1)$$

$$\varepsilon'' = \sigma_{(\omega)} / (\omega \varepsilon_0) \quad (2)$$

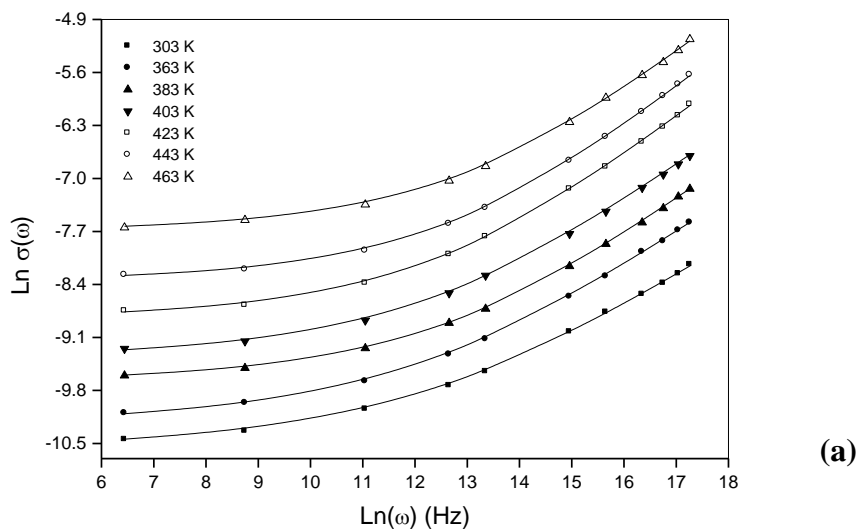
where d is the sample thickness, A is the cross-sectional area, $\sigma_{(\omega)}$ is the Ac conductivity, and ε_0 is the permittivity of free space ($= 8.854 \times 10^{-12}$ F/m).

Results and Discussions:

Fig. (1) exhibits the obtained Ac conductivity ($\sigma_{(\omega)}$) values for the samples containing 10 mol% of (a) ZnO and (b) PbO as a function of frequency at different temperatures, where it was found that $\sigma_{(\omega)}$ increased gradually with the increase of both frequency and temperature. Therefore, it could be supposed that the conduction in these glasses is a thermally activated hopping process. It could be observed also that the conductivity of the sample containing Pb cations is higher than that of the sample containing Zn cations. The points in this Figure represent the experimentally obtained values and the solid lines represent the fitting applying the following equation,

$$\begin{aligned} \sigma_{(T)} &= \sigma_{(dc)} + \sigma_{(\omega)} \\ \sigma_{(T)} &= \sigma_{(dc)} + A \omega^s \end{aligned} \quad (3)$$

where $\sigma_{(\omega)}$ is the Ac conductivity, $\sigma_{(dc)}$ is the dc conductivity, ω is the angular frequency, A is a constant and s is the exponent factor [13 – 15]. It is worth to state that all samples exhibit similar behavior, and it could be seen that good fitting between the experimental values and those obtained theoretically was clearly observed.



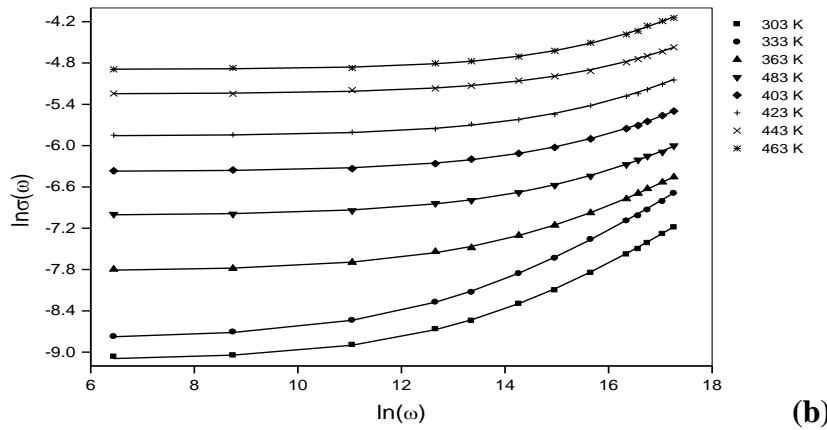


Fig. (1): Frequency dependence Ac conductivity (σ_{ω}) at various temperatures for:
 (a) The sample containing 10 mol% ZnO.
 (b) The sample containing 10 mol% PbO.

The frequency exponent (s) was computed from the following equation:

$$S = d(\ln \sigma_{(\omega)}) / d(\ln \omega) \tag{4}$$

The obtained values of s were plotted -for some samples- versus temperature. Fig. (2- a) exhibits the variation of s with temperature for the samples containing low ZnO content (0 and 5 mol%), where it was observed that s increases with temperature up to a maximum value of about 0.25. Fig. (2- b) exhibits the variation of s with temperature for the samples containing high ZnO content (10 and 15 mol%), where it was seen that s decreases when the temperature was gradually increased. It is worth to state that all other samples (containing ZnO) showed a temperature dependence of s .

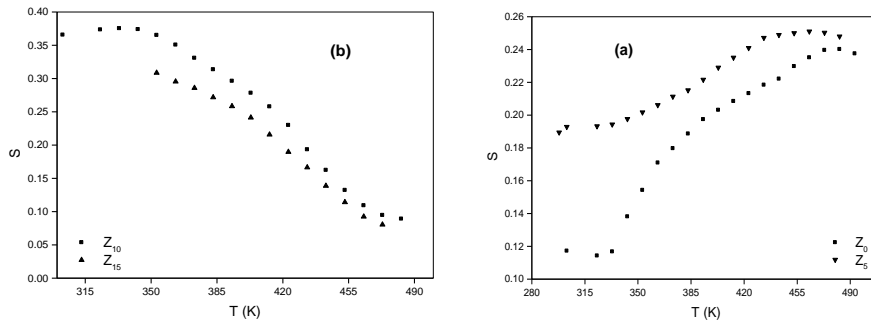


Fig. (2): The frequency exponent (s) as a function of temperature for:
 (a) The samples containing 0 and 5 mol% of ZnO.
 (b) The samples containing 10 and 15 mol% ZnO.

From another point of view, Fig. (3) shows the change of s as a function of temperature for the samples containing 5, 10 and 15 mol % PbO. The samples exhibit gradual decrease of s with temperature and the maximum value of s was found to be about 0.6, while the minimum value was found to be about 0.06 for the sample containing 15 mol% PbO.

It can be supposed here that when ZnO or PbO concentration was gradually increased, there is a corresponding decrease in vanadium. That is ZnO or PbO may behave like a network former.

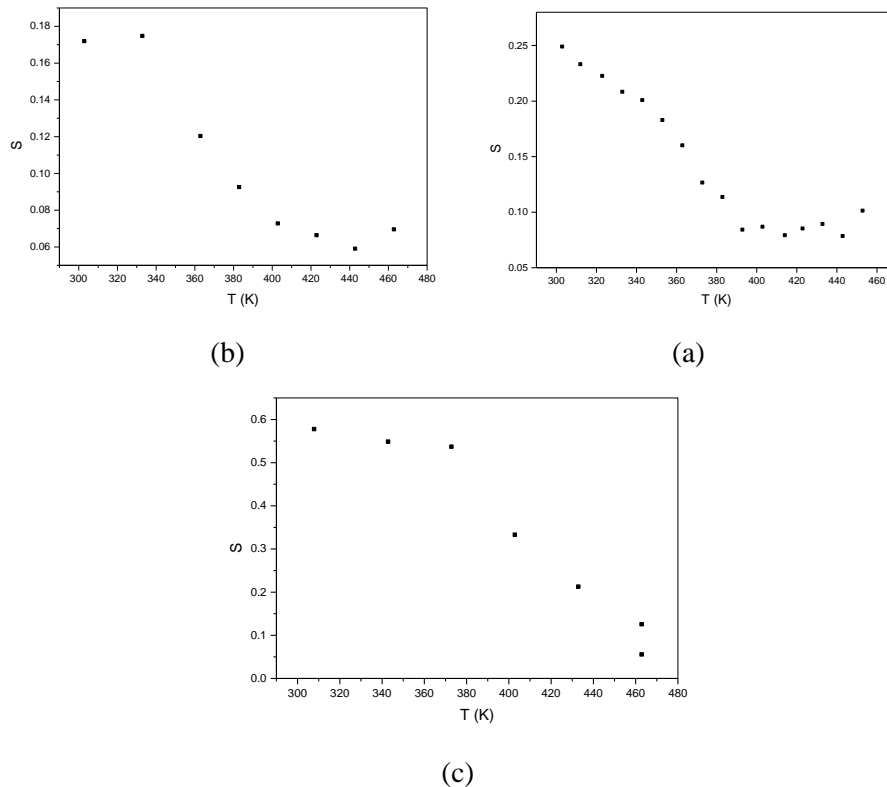


Fig. (3): The frequency exponent s as a function of temperature for the samples containing (a) 5, (b) 10 and (c) 15 mol% PbO.

In most amorphous materials a polaron is formed due to the inhomogeneous lattice distribution [16]. If a small polaron formed the tunneling model predicts a decrease in s factor with the decrease in temperature [Fig. (2- a)]. On the other hand, if an overlapping large polarons formed, the tunneling model predicts a decrease in s with the increase in temperature up to a certain value, but with further increase in temperature an increase in s takes

place [Fig. (2- b)]. From the Ac models, it can be stated that these results nearly agree with the CBH model for the samples containing high ZnO content (10 and 15 mol%) as well as the sample containing 15 mol% PbO. But for the samples containing low ZnO (0 and 5 mol%), s agree well with the small polaron hopping (SPH) model, while for the samples containing low and moderate PbO (5 and 10 mol%) the results agree well with the overlapping large polaron (OLP) model.

It is known that the hopping between two energetically favorable sites over a potential barrier may take place in TM oxide glasses. The CBH model for Ac loss was first introduced by pike [17] for single electron and it was extended by Elliott [18] for two electrons hope simultaneously. This model assumes that the charge carrier hopes between a pair sites over the potential barrier separating them. For neighboring sites at a separation R, the coulomb wells overlap, resulting in lowering of the effective barrier height from W_m to a value W which is given by the following equation [18]:

$$W = W_m - (e^2 / \pi \epsilon \epsilon_0 R) \quad (5)$$

where, W_m is the energy required to remove the electron completely from a site (inside the extended states). The frequency exponent s for this model is temperature – dependent, that is s decreases from unity with increasing temperature.

The dielectric constant ϵ' (real part) and dielectric loss ϵ'' (imaginary part) of the complex dielectric were calculated from relations 1 and 2, and their temperature dependence was thoroughly investigated for all glasses. The data were also analyzed using the electrical modulus formalism [12]. The real (M') and imaginary (M'') parts of the complex electrical modulus ($M^* = 1/ \epsilon^*$) were obtained from ϵ' and ϵ'' values using the following relations [12],

$$M' = \epsilon' / (\epsilon'^2 + \epsilon''^2), \quad (6)$$

$$M'' = \epsilon'' / (\epsilon'^2 + \epsilon''^2) \quad (7)$$

The variation of the real (ϵ') and the imaginary (ϵ'') parts of the complex dielectric with temperature for the Zn and Pb free sample at different frequencies is shown in Fig. (4). In all the studied samples, it was observed that:

- 1- The dielectric constant (ϵ') and the dielectric loss (ϵ'') increase with increasing temperature in a different way for different frequencies.

- 2- Dielectric dispersion can be clearly observed from about 300 K.
- 3- The variation of the dielectric constant (ϵ') and the dielectric loss (ϵ'') with temperature is larger at lower frequencies.

It is of importance to state that all the other samples of the two systems exhibit similar behavior.

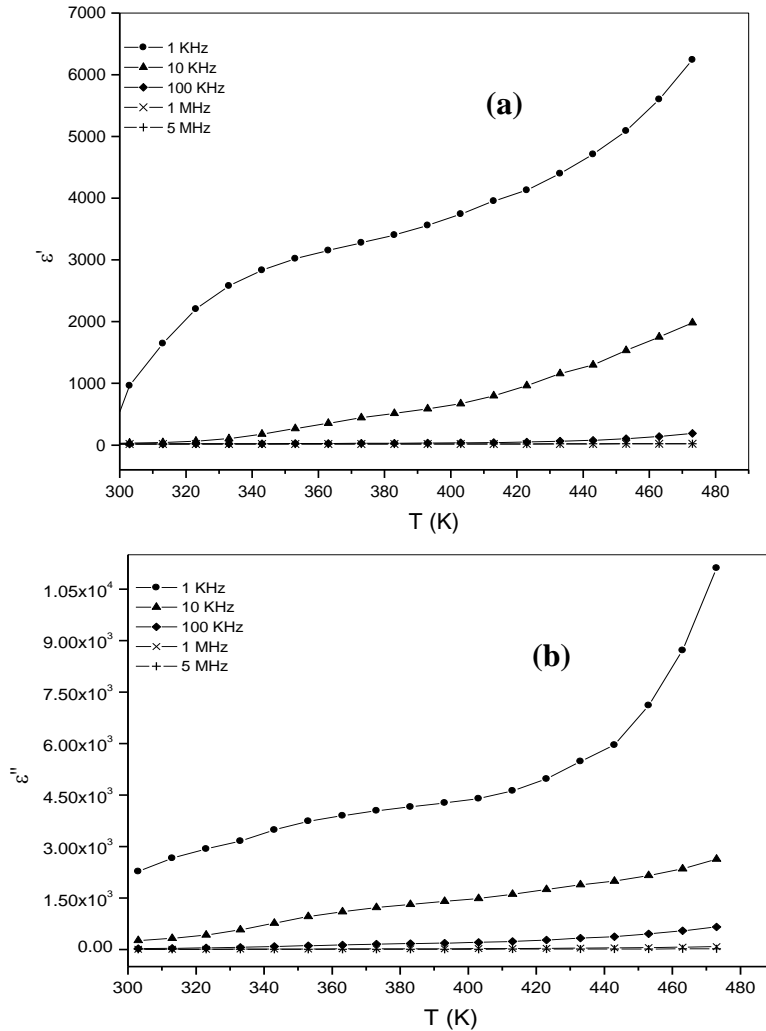


Fig. (4): The variation of (a) dielectric constant (ϵ') and (b) dielectric loss (ϵ'') with temperature for the Zn and Pb free sample at different frequencies.

Fig. (5) shows the frequency response of the dielectric constant and the dielectric loss (ϵ'') at different fixed temperatures for the Zn and Pb free

sample. It is observed that (ϵ') and (ϵ'') decreased with increasing frequency and all other samples show similar behavior.

Figs (6,a and 7,a) show the variation of the dielectric constant (ϵ') with temperature at different frequencies, for the samples containing 10 mol% of ZnO and PbO, respectively. It can be observed that a strong dielectric dispersion is observed at temperatures above 300 K and 340 K for Z₁₀ and P₁₀ respectively. It was observed also that, some peaks appeared in the ϵ' -T curves for different fixed frequencies and these peaks are shifted towards higher temperatures as the frequency was increased.

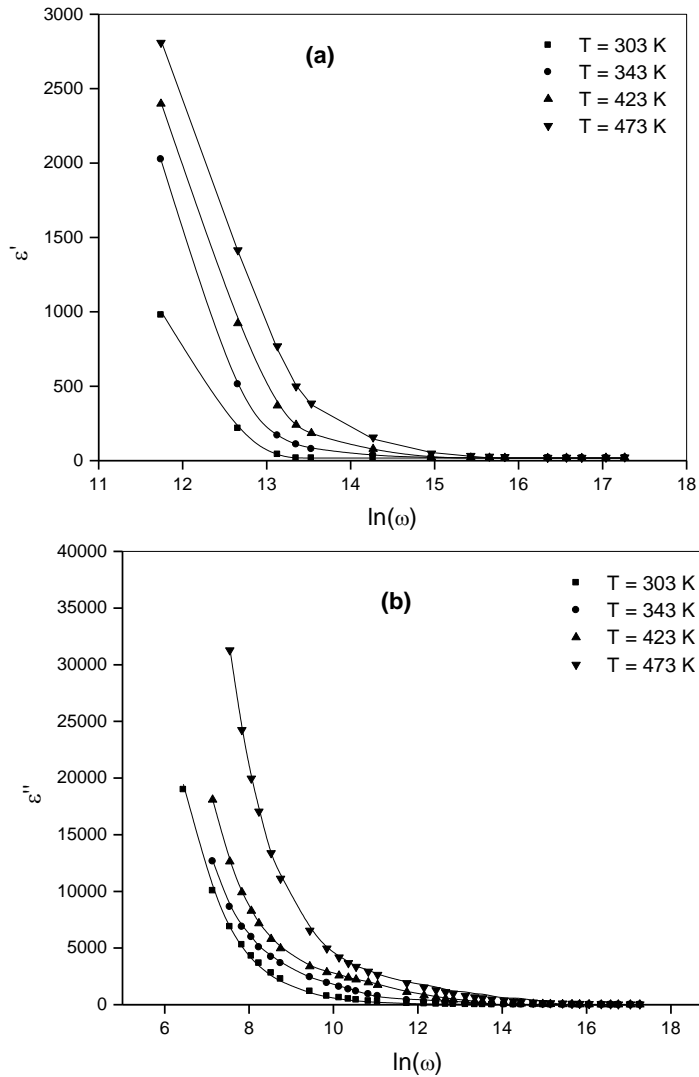


Fig. (5): The variation of (a) dielectric constant (ϵ') and (b) dielectric loss (ϵ'') with frequency for the Zn and Pb free sample at different temperatures.

For the samples containing 5 and 10 mol % of either Zn or Pb cations respectively, it was found that the dielectric constant (ϵ') increased gradually with temperature and this appeared clearly at lower frequencies. Such behavior may be due to the alternating electric field which accompanied by the applied frequencies. Where this field will cause some ordering inside the sample and form an electric dipole moment in the entire volume of the dielectric and in each separate polarized molecule. The molecular dipoles in polar material cannot orient themselves at low temperature. When the temperature raises, the dipoles orientation is facilitated, and this increases the dielectric constant. In slowly varying fields (at low frequency), the dipoles align themselves along the field direction and fully contribute to the total polarization. As the frequency increased, the variation in the field become too rapid for the molecular dipoles to follow so that their contribution to the polarization becomes less with a measurable lag because of the internal frictional forces [19].

Figs (6,b and 7,b) show the variation of the dielectric loss (ϵ'') as a function of both temperature and frequency for the samples that contain 10 mol% of ZnO or PbO, respectively. These Figs illustrate that the dielectric loss (ϵ'') exhibit strong temperature dependence at higher temperatures and lower frequencies. The values of the dielectric loss (ϵ'') increased with temperature when compared with that of Zn and Pb free samples. It was found that all glasses show similar behavior. These results indicate that Zn and Pb cations play an important role in the variation of dielectric parameters with temperature. It was established that, the origins of the dielectric loss (ϵ'') are conduction losses, dipole losses and vibration losses [20]. As the temperature increases, the electrical conduction losses increase which increases the dielectric loss (ϵ'').

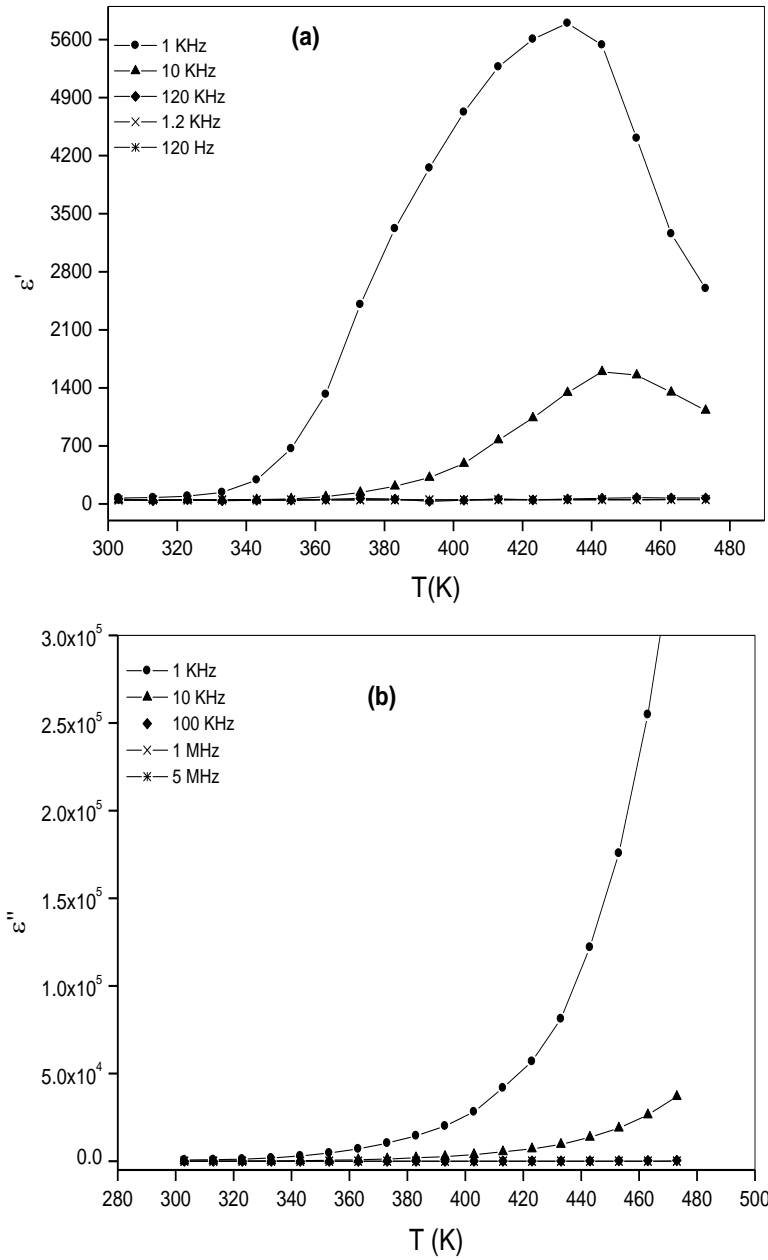


Fig. (6): The variation of (a) ϵ' and (b) ϵ'' , with temperature for the sample containing 10 mol% ZnO, at different frequencies.

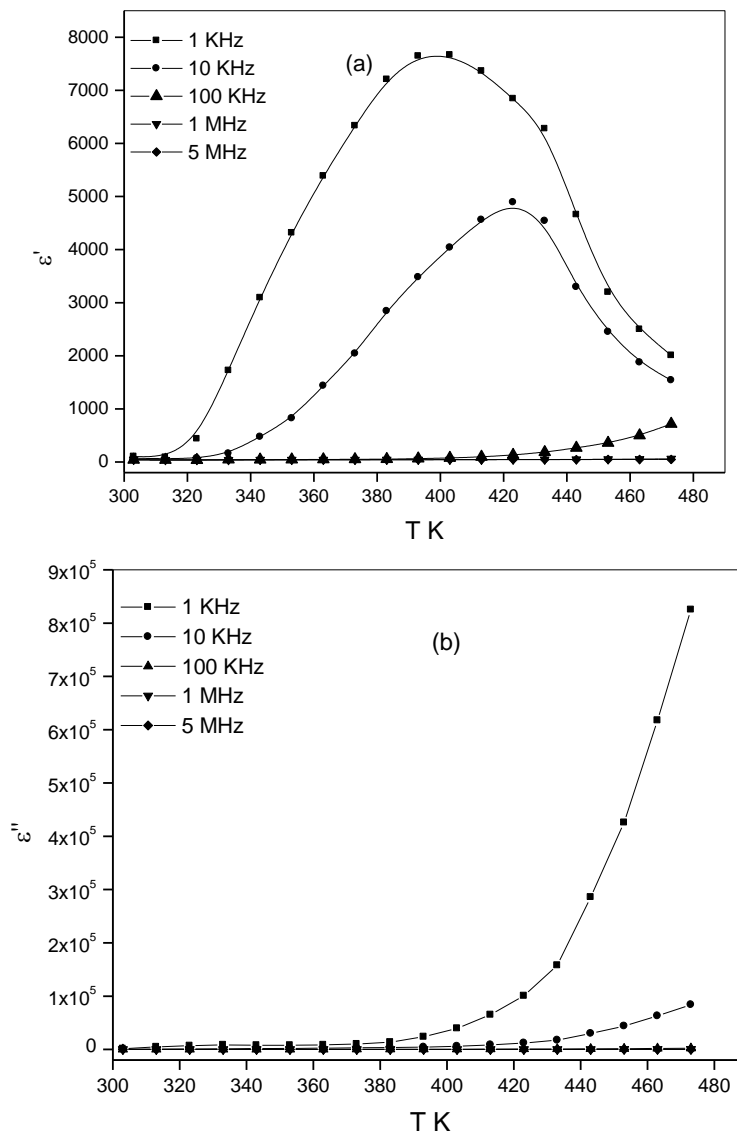


Fig. (7): The variation of (a) (ϵ') and (b) (ϵ'') with temperature for the sample containing 10 mol% PbO, at different frequencies.

Fig. (8) shows the variation of the dielectric constant (ϵ') and the dielectric loss (ϵ'') with zinc or lead oxides concentrations at a fixed temperature of 400 K.

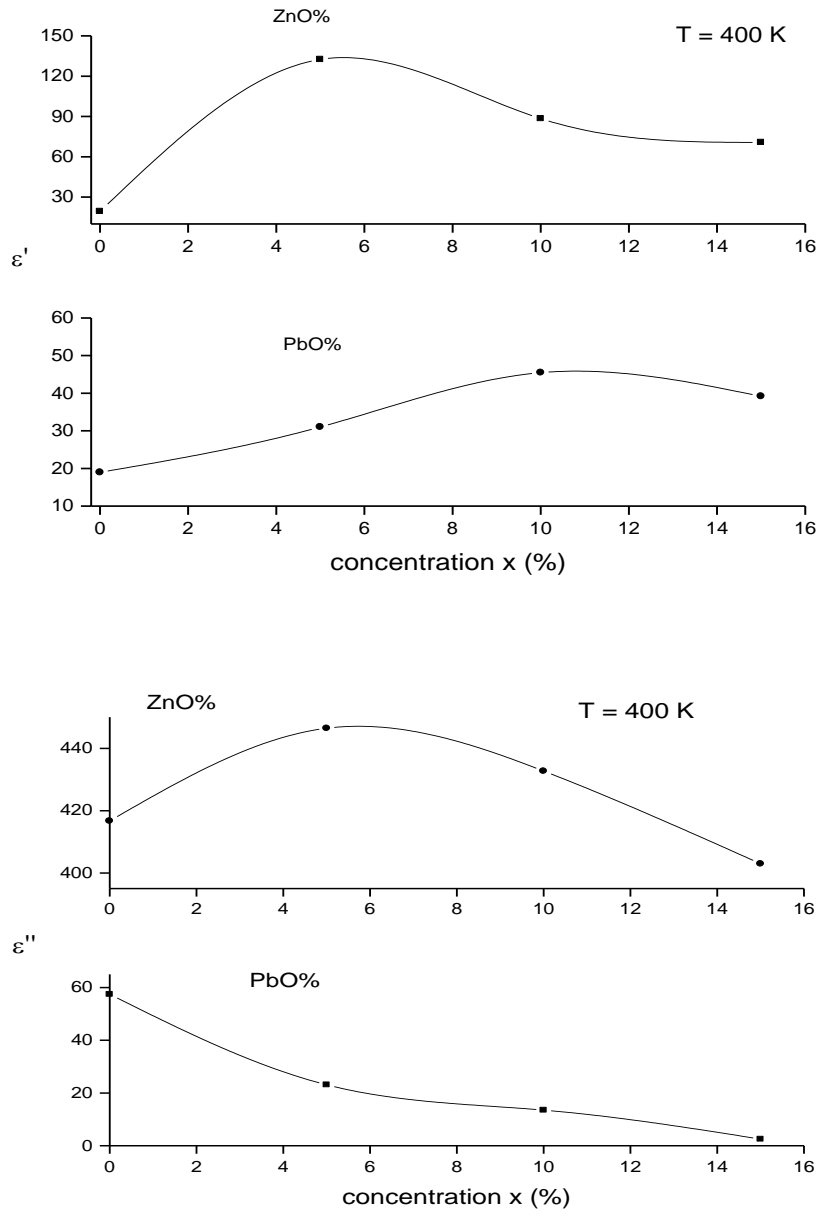


Fig.(8): The variation of (a) dielectric constant and (b) dielectric loss with ZnO and PbO concentrations

Mott and Davis [21] and Kastner et al. [22] have proposed an interesting model for chalcogenide and oxide glasses. They suggest that the states in the gap, near Fermi level are due to the dangling bonds and if the reaction $2D_o \rightarrow D^+ + D^-$ is exothermic, only pair defect states are found in the gap, that is half of the charge carriers (dangling bonds) will be positively charged while the other half will be negatively charged. However the paired states appeared to be analogous to the electric dipoles and hence the entire system may be considered virtually a dipolar system. At low temperature, one would expect a large distribution of relaxation times because of the hindered rotation of these dipoles. Therefore, a Debye-type relaxation may lose its significance at such low temperatures. A very large distribution of relaxation time should give a dielectric loss which would be almost independent of temperature. As the temperature increases, the dipoles slowly attain freedom of rotation and, therefore, a Debye-type relaxation should be observed. Under such circumstances, the dielectric loss was expected to become temperature and frequency dependent.

According to Debye theory of the intrinsic relaxation time, the experimental data of (ϵ') and (ϵ'') was fitted to the following equations [23, 24],

$$\epsilon'(\omega) = \epsilon_{\infty} + (\epsilon_s - \epsilon_{\infty}) / (1 + \omega^2 \tau^2) \quad (8)$$

and

$$\epsilon''(\omega) = (\epsilon_s - \epsilon_{\infty}) \omega \tau / (1 + \omega^2 \tau^2) \quad (9)$$

where ϵ_s and ϵ_{∞} are the static and optical dielectric constants and τ is the relaxation time. All the studied samples exhibit good fitting with Debye theory. The obtained values of ϵ_s , ϵ_{∞} and τ - that drawn from the fitting are given in Table (1).

Table (1): The dielectric relaxation parameters of the studied glasses

Samples	T (K)	ϵ_{∞}	ϵ_s	τ	τ_0	τ from Cole-Cole	α	ΔE
Z ₀	343	45	4100	2.4×10^{-5}	1.16×10^{-9}	3.5×10^{-4}	0.61	0.35
Z ₅	383	35	8300	2.7×10^{-4}	6.67×10^{-12}	4.5×10^{-3}	0.5	0.43
Z ₁₀	383	36	18700	3.3×10^{-4}	2.2×10^{-12}	3×10^{-5}	0.51	0.52
Z ₁₅	433	40	21100	2.5×10^{-4}	1.84×10^{-9}	3×10^{-4}	0.59	0.69
P ₅	373	42	150	5.4×10^{-6}	6.55×10^{-12}	5.2×10^{-2}	0.5	0.48
P ₁₀	403	46	140	3.5×10^{-6}	3.58×10^{-11}	1.35×10^{-4}	0.31	0.53

P ₁₅	383	20	100	1.4 x 10 ⁻³	1.69 x 10 ⁻⁹	3.1 x 10 ⁻⁴	0.60	0.56
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The Ac response of the investigated samples have been examined by the variation of real (M') and imaginary (M'') parts of the dielectric moduli. Fig. (9) exhibits a representative curves for the change of both M' and M'' of the dielectric moduli with temperature at different frequencies. All the studied glasses show similar behavior and a peak can be shown clearly in all the obtained $M'' - T$ curves, and this peak shifts to higher temperatures when the frequency was gradually increased. This reveals that f_c increased when the frequency was gradually increased. The peak positions of M'' give the temperature at which the measuring frequency is equal to the conductivity relaxation frequency (f_c) which can be calculated from the relation [25],

$$f_c = \nu_c \exp(-W_c / k T_m) \tag{10}$$

where ν_c is the characteristic phonon frequency and W_c the activation energy for conductivity relaxation. The values of the characteristic relation time τ_0 ($\nu_c = 1/ \tau_0$) have been evaluated from the plots of $\ln(1/ f_c)$ versus $1/ T_m$, Fig.s (10 and 11) for Zn and Pb system respectively where T_m is the temperature at the peak for certain frequency. The obtained values of τ_0 are given also in Table (1).

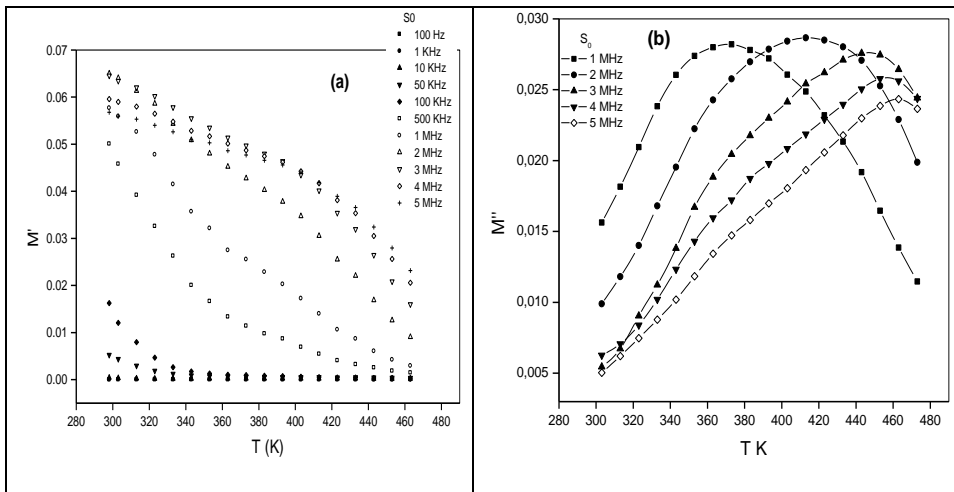


Fig. (9): The variation of (a) real (M') and (b) imaginary (M'') parts of the dielectric modulus with temperature for ZnO and PbO free sample at different frequencies.

Cole and Cole showed that if a dielectric system has a distribution of relaxation time, the curve obtained by plotting M'' versus M' is generally an arc of a circle intersecting the abscissa axis at the values of ϵ_∞ and ϵ_s . However Fig. (12) shows a pseudo Cole – Cole diagram for the sample containing 10

mol% of ZnO, as a representative curve, where all the studied glasses show the same regime.

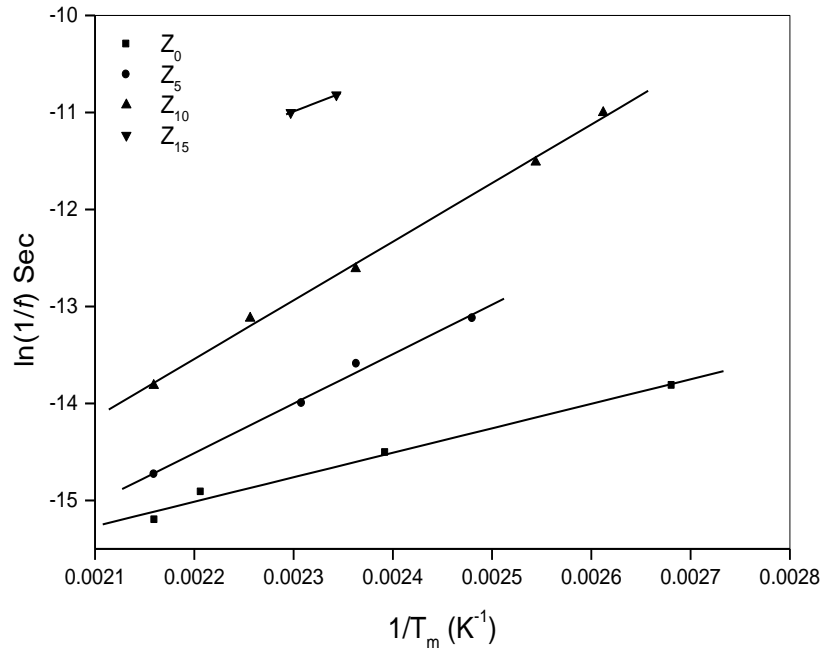


Fig. (10): The variation of the relaxation frequency with $1/T_m$.

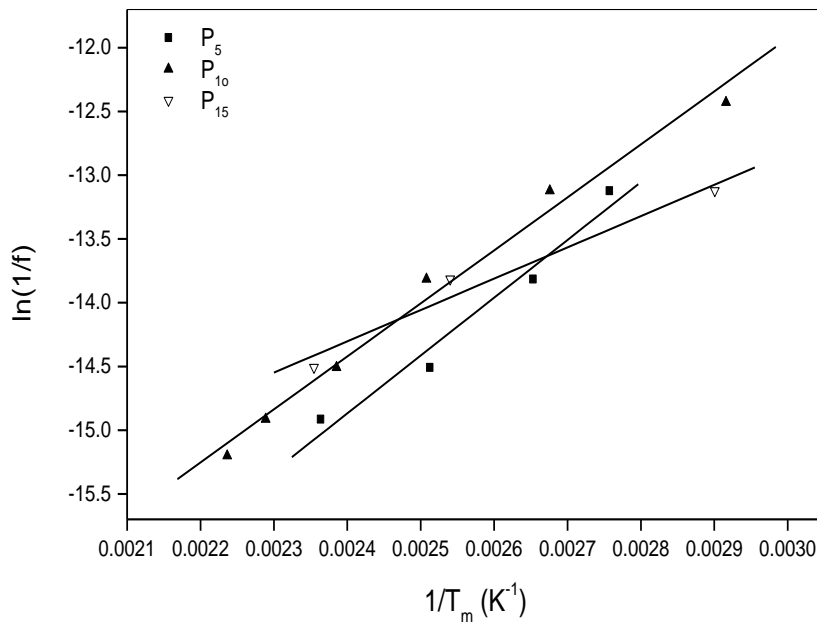


Fig. (11): The variation of the relaxation frequency with $1/T_m$.

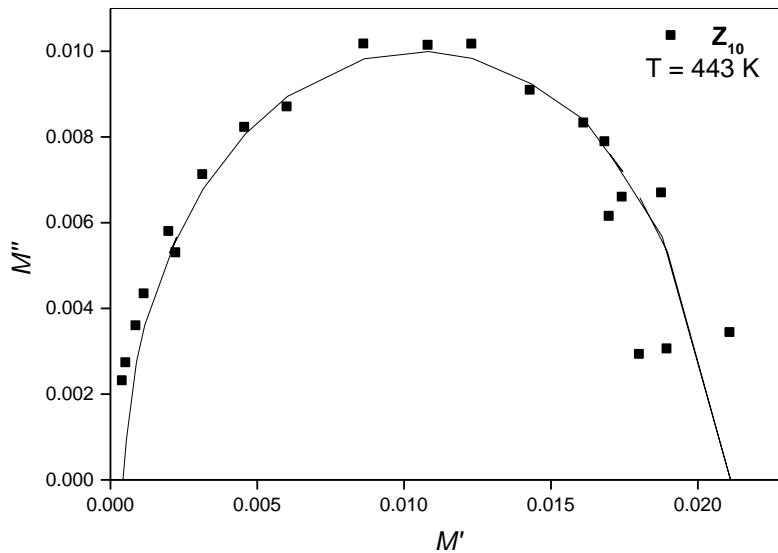


Fig. (12): Pseudo Cole – Cole diagram of the sample containing 10 mol% ZnO.

The dielectric constant and loss data of samples ($x = 0, 5, 10$ and 15% mole ZnO or PbO) were fitted to Cole-Cole functions [26], at $T = 473$ K (the following relations),

$$\epsilon' = \epsilon_{\infty} + \frac{[(\epsilon_0 - \epsilon_{\infty}) (1 + (\omega\tau)(1-\alpha) \sin(\alpha\pi/2))]}{[1 + 2(\omega\tau)(1-\alpha) \sin(\alpha\pi/2) + (\omega\tau)^2(1-\alpha)]} \quad (11)$$

and

$$\epsilon'' = \epsilon_{dc} + \frac{[(\epsilon_0 - \epsilon_{\infty}) ((\omega\tau)(1-\alpha) \cos(\alpha\pi/2))]}{[1 + 2(\omega\tau)(1-\alpha) \sin(\alpha\pi/2) + (\omega\tau)^2(1-\alpha)]} \quad (12)$$

where α is the Cole-Cole distribution parameter having values between 0 and 1. The parameters τ and α are given in Table (1). The agreement between the theoretical and the experimental values appeared to be good at high – frequency tail regime for all temperatures of measurements.

Conclusion:

The dielectric parameters and the electrical properties of the studied glass systems were found to be temperature and frequency dependent. A dielectric dispersion was found to occur in these two systems. Such dispersion was supposed to be due to the conduction loss as well as to the dipolar type of

the defects in the studied samples. The dielectric constant and the dielectric loss show slight increase with the addition of ZnO until it reached a maximum value in the sample containing 10 mol% but on adding PbO to the vanadate network, they show a decrease to reach its smallest value at 15 mol% PbO. A possible explanation for glasses containing ZnO is given in terms of hopping of charge carriers over a potential barrier between charged defect states. The increase of the dielectric parameters with zinc oxide concentration can be understood in terms of the decreased density of defect states. In glasses containing PbO, it can be stated that the density of defect states increased when lead oxide concentration was increased.

On increasing the concentrations of zinc or lead oxides, an increase in the activation energies was observed, which may be due to the decrease of the density of defect states and/or to the decrease of the disorder at the mobility edge. Complex relative permittivity data have been analyzed using the dielectric modulus (M' and M'') approach where a single relaxation process was observed.

The dielectric constant and loss data of all glasses were fitted to Cole – Cole functions, where the parameter α was found to be less than unity, and the relaxation time τ varies between 3×10^{-5} and 4.5×10^{-3} s for glasses containing zinc, while it varies between 1.35×10^{-4} and 5.2×10^{-2} s for glasses containing lead.

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