A.C. Conductivity and Dielectric Study of doped ZnS Thin Films prepared by chemical spray pyrolysis technique

Mahdi Hasan Suhail, Izzat M. Al Essa, Raoof Ali Ahmed

Abstract— A.C. conductivity[$\sigma_{a.c}(\omega)$] of pure and doped ZnS thin films with 10 % lead ,manganese, and copper prepared by chemical spray pyrolysis technique measured in the frequency range of (0.1- 200) kHz and in the temperature range of (298-473) K. The results reveal that $\sigma_{a.c}(\omega)$ obey the relation $\sigma_{a.c}(\omega)= A\,\omega^s$ and the exponent (s) was found to decrease by increasing the temperature. The values of (s) of the investigated thin films less than one unit. The experimental studies on a.c. conductivity of pure and doped ZnS thin films reveal that correlated barrier hopping (CBH) model is the most suitable model to explain the a.c. conduction mechanism. The activation energies have been calculated for the doped thin films. Values of dielectric constant ε_r and dielectric loss ε_i were found to decrease with frequency and increase with temperatures. Also relaxation time (τ_0), polarizability ('P), and the static dielectric constant (ε_s) were calculated using Cole-Cole diagram and found that the static dielectric constant increasing with increasing the thermal treatment temperature between (298-473) K, but the values of the relaxation time (τ_0) declare a non-systematic variation (increase and decrease) with the increasing of thermal treatment temperatures.

Index Terms— Dielectric Parameters, Nature of Charge Transports, Chalcogenide Semiconductors, A.C. Conductivity

I. INTRODUCTION

zinc sulfide (ZnS) as an important II–VI semiconductor has been researched extensively because of its broad spectrum of potential applications such as in catalysts, cathode-ray tubes (CRT), field emission display (FED) phosphors for a long time. It can also be used for electroluminescent devices and photodiodes [1,2]. Zinc sulfide was one of the first semiconductors discovered and is also an important semiconductor material with direct wide band gaps for cubic and hexagonal phases of 3.72 and 3.77 eV, respectively. It has a high absorption coefficient in the visible range of the optical spectrum and reasonably good electrical properties[3].

The studying of ac-conductivity gives us information about the nature of the conduction mechanisms in a material. This $\sigma_{a.c}(\omega)$ can be represented by the empirical formula which follows a power low of the forms [4]:

$$\sigma_{a.c}(\omega) = A\,\omega^s \qquad \text{.................} \qquad .(1)$$

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Where (ω) is the angular frequency, the frequency exponent lies in the range $0<s<1$.

From equation (1), one can write the exponent (s) as follows:

$$s = d\,\ln\sigma(\omega)\,/d\,\ln(\omega) \qquad \text{.......................} \text{ (2)}$$

A study of the frequency and temperature dependence of dielectric losses should provide information on relaxation processes. In the presence of relaxation effects, the dielectric constant may be given by:

$$\varepsilon^*(\omega)=\varepsilon_r(\omega)+i\varepsilon_i(\omega) \qquad \text{...........................(3)}$$

Where $\varepsilon_r(\omega)$ is the real part of the complex dielectric and $\varepsilon_i(\omega)$ is the imaginary part (dielectric loss factor).

The real part or dielectric constant could give by:

$$\varepsilon_r(\omega)= LC/\grave{A}\,\varepsilon_o \qquad \text{................................(4)}$$

where (L) is the distance between electrodes, (C) is the capacitance of the sample, ($\grave{A}$) is the effective area ($\grave{A}$=width of electrode x thickness of sample), & (ε_o) is permittivity of the space (8.854×10^{-12} F.m^{-1})

The imaginary part is given by[5] :

$$\varepsilon_i(\omega)= \sigma(\omega)\,/\varepsilon_o\,\omega \qquad \text{...............................(5)}$$

We can get $\sigma_{a.c}(\omega)$ by

$$\sigma_{a.c}(\omega) = L/\grave{A}.R \qquad \text{................................(6)}$$

$$\tan\delta= \varepsilon_i(\omega)/\,\varepsilon_r(\omega) \qquad \text{..............................(7)}$$

($\tan\delta$) is the dissipation factor that describes the phase difference between the current and voltage with respect to the applied ac electric field.

The dependence of $\sigma_{a.c}$ on temperature is usually obey the well-known relation [5]:

$$\sigma_{a.c} = \sigma_o\,\exp(-\Delta E\,/\,K_B\,T) \qquad \text{......................(8)}$$

where σ_o, is constant, ΔE is the activation energy, T is the absolute temperature and K_B is Boltzmann constant(1.38×10^{-23} J/k).

The method of displaying Debye type relaxation is by drawing a Cole-Cole plot, Cole and Cole suggested that the real part of dielectric constant ε_r as a function of imaginary part of dielectric constant ε_i gives important information about the distribution of relaxation times. In the case the center of a circular arc lies below the horizontal axis, the plot is symmetrical about the vertical line through the point $\varepsilon_r(\omega)= [(\varepsilon_s + \varepsilon_\infty)/2]$ when ε_i is a maximum at frequency [6]:

$$f = [\,2\,\pi\,\tau_o\,(1+2\,\sin\pi\,\text{'P})\,]^{-1} \qquad \text{..........................(9)}$$

where (f) is the measuring frequency of the applied ac electric field (Hz) , 'P : is the polarizability and τ_0 :is the relaxation time

II. EXPERIMENTAL

The spray pyrolysis technique is a simple technology in which an ionic solution containing the constituent elements of a compound in the form of soluble salts is sprayed onto over-heated substrates using a stream of clean, dry air. The pure and doped ZnS thin films with Pb, Mn, and Cu of ratio

10% were prepared by spraying an aqueous solution of zinc acetate [Zn(CH$_3$COO)$_2$.2H$_2$O] as zinc ion source, thiourea [CS(NH$_2$)$_2$] as sulfide ion source for pure ZnS film and with lead acetate [Pb(CH$_3$COO)$_2$.3H$_2$O], manganese chloride [MnCl$_2$.4H$_2$O], and copper chloride [CuCl$_2$.2H$_2$O] as lead ion , manganese ion, and copper ion sources respectively for doped ZnS films with molarities (0.1) on a glass substrate kept at 275 ± 10 ^{0}C. The atomization of the chemical solution into a spray of fine droplets is effected by the spray nozzle, with the help of compressed air as the carrier gas. The spray rate of about 2 cm^3/min through the nozzle ensures a uniform film thickness. The substrates are Corning 1737 glass 1 x 2.5 x 0.1 cm, and are placed in a fitted socket at the surface of a substrate heater when sprayed. The heater is a cylindrical stainless steel block furnace, electrically controlled to an accuracy of $\pm1\%$ ^{0}C. The other spray parameters were kept constant. Electrodes were formed by deposition of aluminum electrodes on both electrodes of the samples.

To study the effect of frequency of the applied electric field and heat treatment in the range (298-473)K on the A.C conductivity $\sigma_{ac}(\omega)$, real (ε_r), imaginary part (ε_i) of dielectric constant, of pure and doped ZnS films, the (LRC) meter (model LCR-821) is used. Three dielectric parameters were measured directly from LCR-meter total resistance (R), total capacitance (C) and dissipation factor tanδ with an accuracy of 0.1% in the frequency range of(0.1-200)KHz. Constant

voltage of (0.1) Volt was applied in all frequency range and temperature as indicated in this work.

III. RESULTS AND DISCUSSION

Figure (1) shows the dependence of Ln ($\sigma_{a.c}$) on Ln(ω) for pure ZnS and Zn$_{1-x}$S:Pb$_x$, Zn$_{1-x}$S:Mn$_x$, and Zn$_{1-x}$S:Cu$_x$ thin films at x=10% in the frequency range of (0.1 - 200) kHz at different temperature (298-473) K .All samples follow a common pattern where $\sigma_{a.c}$ increases with increasing of angular frequency. Obtained data reveal that the A.C. conductivity follows the relation in equation(1) . The phenomenon has been ascribed to relaxations caused by the motion of electrons or atoms. Such motion can involve hopping or tunneling between equilibrium sites [6]. The behavior of the exponent (s) with temperature can help in determining the possible of conduction mechanism and can be estimate from the slope of the curves plotted between Ln$\sigma_{a.c}(\omega)$ versus Ln (ω) as declared in Figure (2). The exponent (s) was found to be less than unity for all prepared films and decreases with increasing of temperature. That means the exponent (s) fits C.B.H. model given by Elliott [7] from which A.C. conductivity occurs between two sites over the barrier separating between (D$^+$D$^-$) defect centers in the band gap. This leads to greater loss in the dielectric and $\sigma_{a.c}(\omega)$ is dominating.
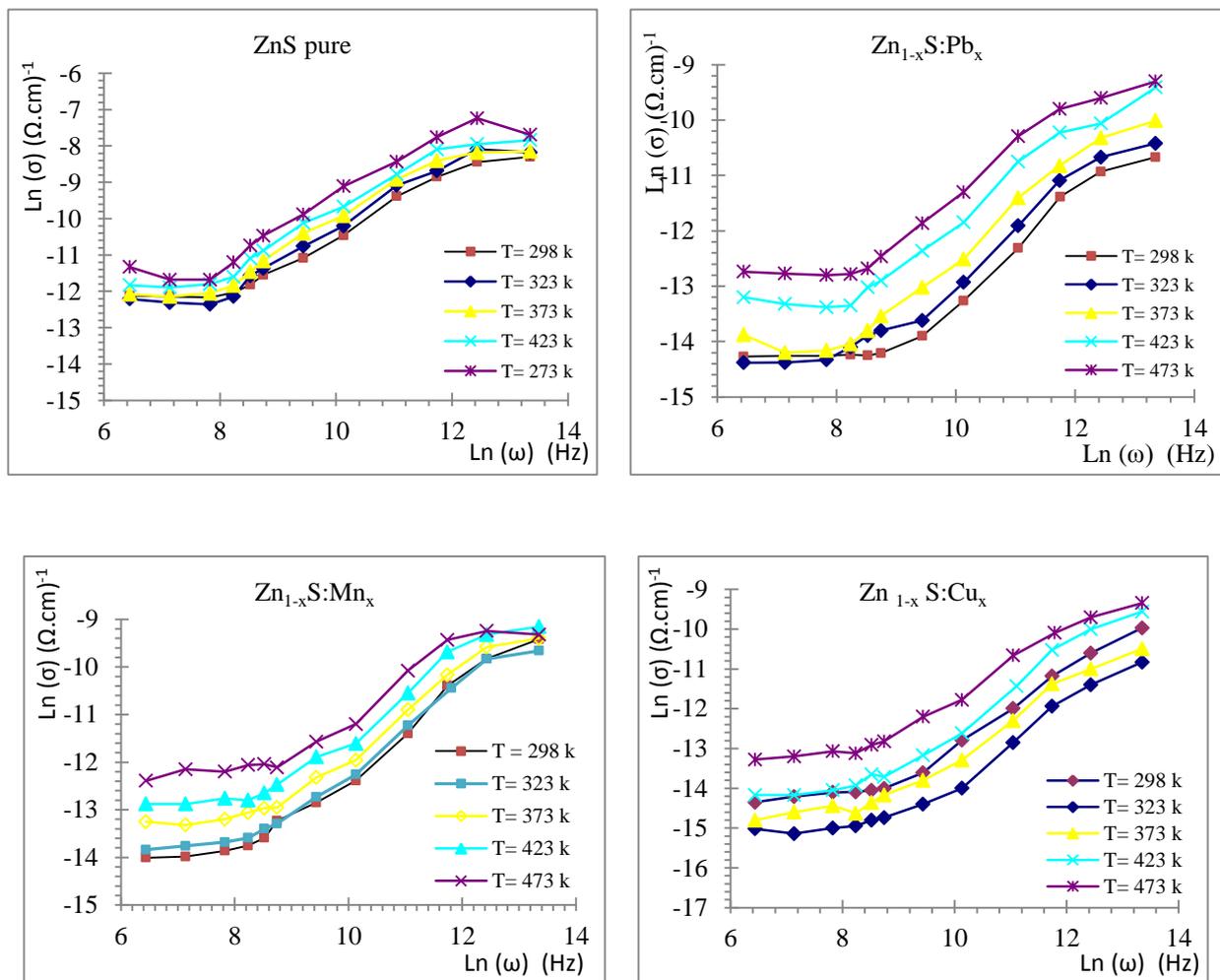
Fig.(1): Frequency dependence of A.C. Conductivity ($\sigma_{a.c.}$) for pure and doped ZnS thin films at x=10% with different frequency and temperature .
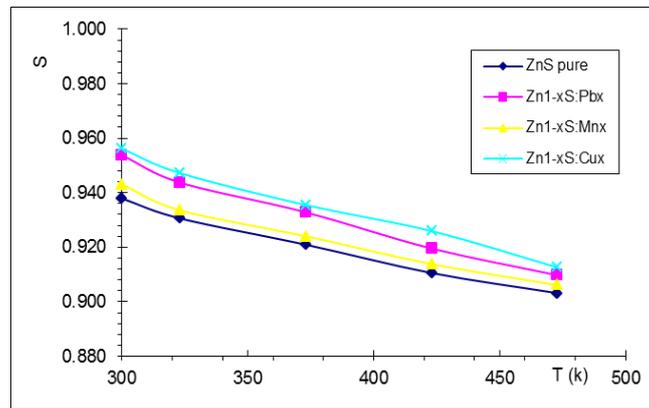
Fig.(2): Temperature dependence of the exponent (s) for pure and doped ZnS thin films at x=10%.

Fig.(3) shows the variation of ln $\sigma_{a.c}(\omega)$ versus 1000/T (K^{-1}) for pure and doped ZnS thin films at different values of frequency. The same behavior was observed in all the samples. From the figure we can deduced that $\sigma_{a.c}(\omega)$ increases non-linearly with temperature especially at a high frequency, i.e., the obtained curves are composed of two regions. One shows weak temperature dependence and other shows strong temperature dependence. The weak temperature dependent mechanism may be attributed to the bipolaron hopping between D$^+$ and D$^-$ centers around the Fermi level [8].
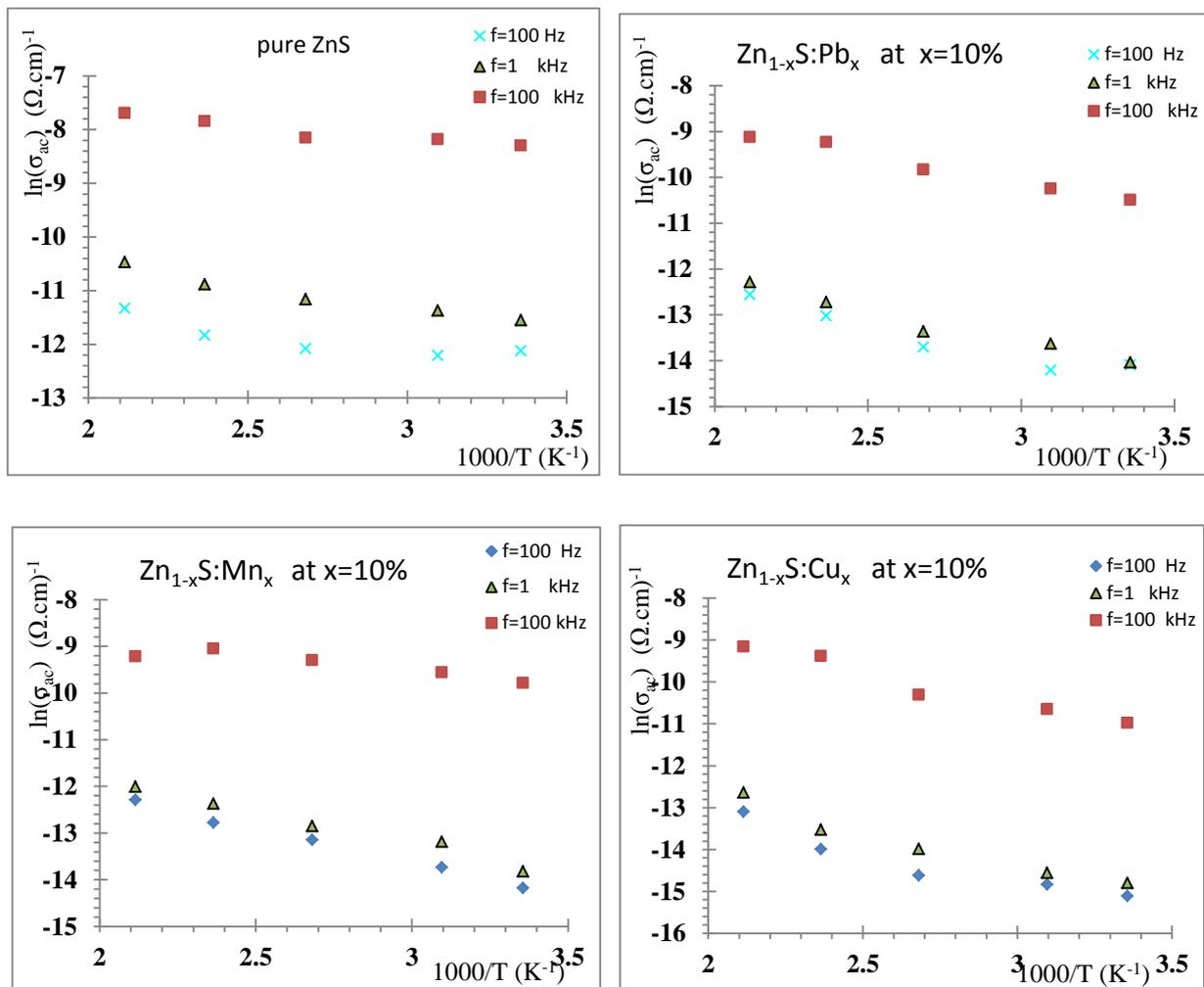
Fig.(3): Variation of ln σ_{ac} (ω) versus 1000/T for pure and doped ZnS thin films at different frequencies

It is clear that at low temperatures and frequencies the conductivity is frequency dependent; however, with increasing temperature the conductivity becomes frequency independent, remaining almost constant throughout the entire frequency range. The strong temperature dependence may be due to the increase of the density of neutral defects D^o (single-polaron states) at a higher temperature. The contribution to σ_{ac} (ω,T) from (CBH) of single polarons exceeds that of bipolarons at a high temperature [9], i.e. the

CBH of single polarons is then the predominant contribution to the AC conduction at higher temperature.

The deduced values of activation energy reported in Table (1) for various values of annealing temperature

Table (1): Values of $\Delta E_{a.c}$ (eV) as a function of frequency for pure and doped ZnS thin films.

frequency	$\Delta E_{a.c}$ (ev)		
	0.1 kHz	1.0 kHz	100kHz
pure ZnS	0.112	0.104	0.071
$Zn_{1-x}S:Pb_x$	0.174	0.165	0.111
$Zn_{1-x}S:Mn_x$	0.130	0.128	0.014
$Zn_{1-x}S:Cu_x$	0.229	0.202	0.178

The activation energy decreases with increasing frequency. The low value of the ac activation energy and the increase of $\sigma_{ac}(\omega)$, with the increase of frequency confirm that hopping conduction is the dominant current transport mechanisms. Thus, the increase of the applied frequency enhances the electronic jumps between the localized states; consequently, the activation energy ΔE, decreases with increasing frequency [10,11].

The real part (ε_r) of the dielectric constant of Pure ZnS and $Zn_{1-x}S:Pb_x$, $Zn_{1-x}S:Mn_x$ and $Zn_{1-x}S:Cu_x$ thin films at x=10% are determined by using equation (4) . Figure (4 a, b, c, d) represents the frequency dependence of the dielectric constant ε_r for films at different temperature (298-473) K. It is observed that ε_r decreases with frequency and increases with temperature.
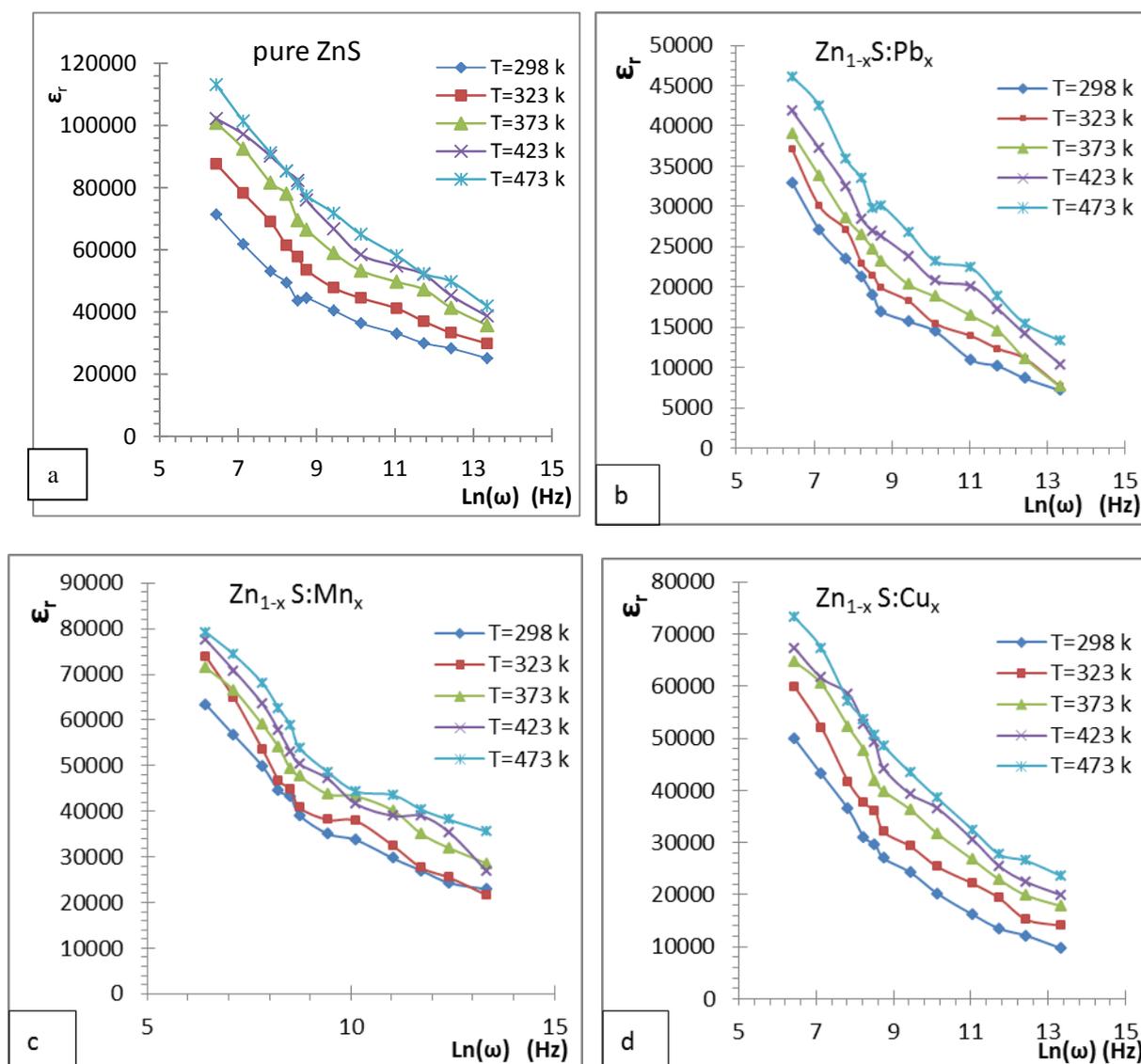
Figure 4(a, b, c & d) Frequency dependence of the (ε_r) of the dielectric constant for Pure ZnS and $Zn_{1-x}S:Pb_x$, $Zn_{1-x}S:Mn_x$ and $Zn_{1-x}S:Cu_x$ thin films at x=10% with different temperature.

The decrease in (ε_r) with increasing frequency can be attributed to the contribution of the many components of polarization, electronic, ionic, dipolar or orientation and space charge. First, valance electrons relative nucleus. This type of polarization occurs at frequencies up to 10^{16} Hz.

Second, ionic polarization occurs due to the displacement of negative and positive ions with respect to each other. The maximum frequency of ionic polarization is 10^{13} Hz. Third, dipole polarization occurs as a result of the presence of molecules with permanent electric dipole moments that can change orientation into direction of the applied electric filed.

Dipole polarization occurs at frequencies up at about 10^{10} Hz. Finally, space-charge polarization occurs due to impedance mobile charge by interface. Space-charge polarization typically occurs at frequencies between 1 and 10^3 Hz. The total polarization of dielectric material can be represented by the sum of these four polarizations [12].

The imaginary part (ε_i) of the dielectric constant of Pure ZnS and $Zn_{1-x}S:Pb_x$, $Zn_{1-x}S:Mn_x$ and $Zn_{1-x}S:Cu_x$ thin films at

x=10% are determined by using equation (5) . Figure (5 a, b, c & d) shows the frequency dependence of dielectric loss (ε_i) at different temperatures(298-473) K. It can be noticed from the figure that (ε_i) decreases with increasing frequency and increases with temperature throughout the range (100-1000)Hz of frequency and temperature, then the behavior change to inverse behavior.
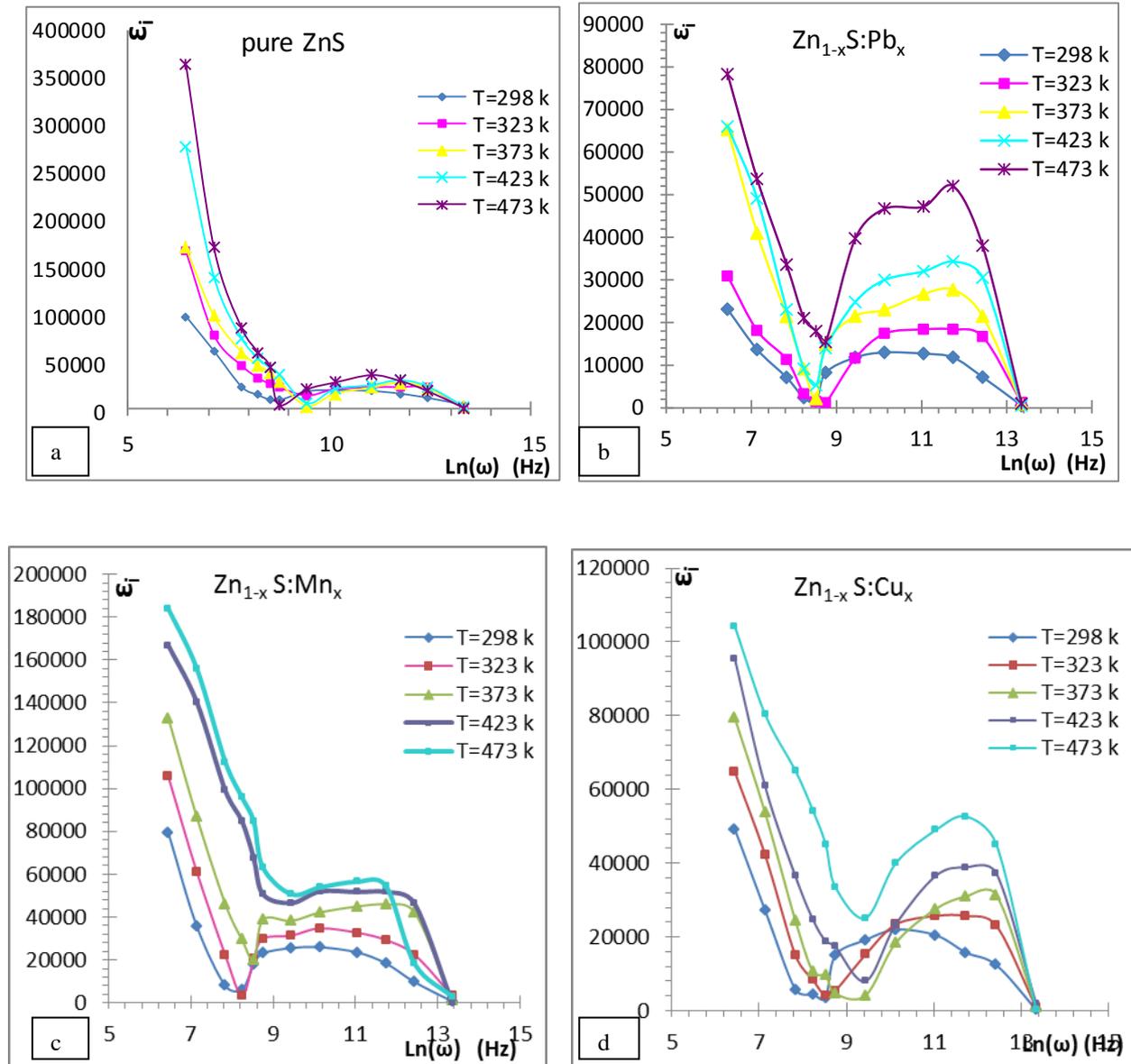
Figure (5 a, b, c & d) Frequency dependence of the imaginary part (ε_i) of the dielectric constant for Pure ZnS and $Zn_{1-x}S:Pb_x$, $Zn_{1-x}S:Mn_x$ and $Zn_{1-x}S:Cu_x$ thin films at x=10% with different temperature.

The increase of ε_i with increasing temperature can be interpreted on the basis of the relaxation phenomena, which is divided into three parts; conduction loss, dipole loss and vibration loss. The losses that are attributed to conduction presumably involve the migration of ions over a large distance. This motion is the same as that occurring under direct current conditions. The ions jump over the highest barriers in the network. As the ions move, they impart some of the energy to the lattice as heat and the amount of heat lost per cycle is proportional to $\sigma_{a.c}(\omega)$ [13] . At low temperature

values, conduction losses, dipole losses and vibration losses have minimum values. However, at higher temperatures, conductions, dipole and vibration losses all contribute to the dielectric loss. This will lead to an increase in ε_i with increasing temperature.

The relation between the real part (ε_r) and imaginary part (ε_i) of the dielectric constant was plotted for all samples. Figure (6) represents the variation of ε_r and ε_i for Pure ZnS and $Zn_{1-x}S:Pb_x$, $Zn_{1-x}S:Mn_x$ and $Zn_{1-x}S:Cu_x$ thin films with x=10% at different temperatures. Similar behavior graphs were obtained for all samples.
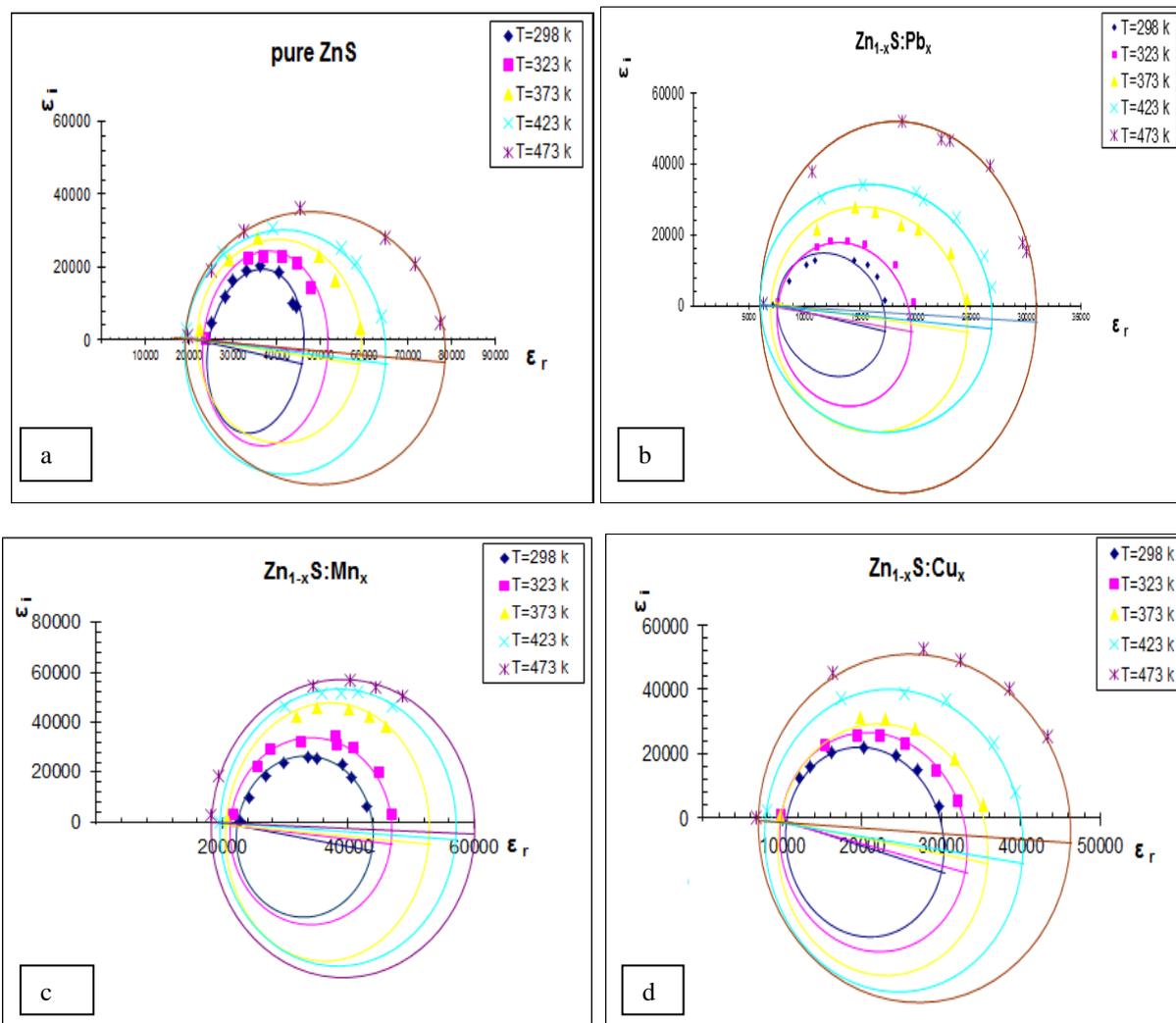
Figure (6 a, b, c & d) Cole-Cole diagram for Pure ZnS and $Zn_{1-x}S:Pb_x$, $Zn_{1-x}S:Mn_x$ and $Zn_{1-x}S:Cu_x$ thin films at x=10% with different temperature.

These figures show a semi-circle diagram, each semi-circle has its center below ε_r –axis. It begins from the origin at the high frequencies and ends at a point on the ε_r –axis at low frequencies. The intersections of the semicircle at lower frequencies with ε_r -axis gives the static dielectric constant (ε_s) which increases with temperature. The observation of dielectric effects in the glasses implies that dipoles exist. It can be seen from Table (2) that (ε_s) has a large value especially at high temperatures. Most of this behavior arises from electrode polarization effects [14]. The polarizability (P) (dispersion parameter) which calculated according to this relation $[P=2\theta/\pi]$,where (θ) the angle between ε_r -axis and the diameter of semi-circle, increases with increasing temperature, because the increase of thermal energy will weaken the forces of intermolecular interaction[15].

The Cole-Cole plots are also useful to confirm the distribution of the relaxation time, which can be determined from the equation (9). From the Table (2) we can notice that the value of (τ_o) declares anon systematic variation (increase and decrease) with the increasing of thermal treatment temperatures, the increase of (τ_o) value attributes to the formation of barrier.

Table (2):Cole-Cole representation parameters for pure ZnS and $Zn_{1-x}S:Pb_x$, $Zn_{1-x}S:Mn_x$ and $Zn_{1-x}S:Cu_x$ thin films at x=10% with different temperature.

T (k)	pure ZnS			$Zn_{1-x}S:Pb_x$			$Zn_{1-x}S:Mn_x$			$Zn_{1-x}S:Cu_x$		
	P	τ_o x10^{-5} sec	ε_s x10^3	P	τ_o x10^{-5} sec	ε_s x10^3	P	τ_o x10^{-5} sec	ε_s x10^3	P	τ_o x10^{-5} sec	ε_s x10^3
298	0.100	3.87	46	0.100	3.87	17	0.111	4.11	44	0.156	4.2	30
323	0.076	0.726	52	0.078	1.56	19.5	0.078	1.56	47	0.139	0.53	32.2
373	0.067	0.812	59	0.056	0.784	24.5	0.067	0.812	53	0.100	0.77	35.4
423	0.050	0.265	65	0.033	0.789	27	0.044	0.806	57	0.089	0.82	40
473	0.033	1.58	78	0.022	0.801	31	0.028	0.531	60	0.044	0.81	46

IV. CONCLUSIONS

The A.C. conductivity for all samples showed strong temperature dependence where the exponent (s) decreases by increasing thermal treatment temperatures and it was related to the correlated barrier hopping type (CBH) mechanism. The activation energy decreases with increasing frequency. The increase of $\sigma_{ac}(\omega)$, with the increase of frequency confirm that hopping conduction is the dominant current transport mechanisms. Both the real part dielectric constant ε_r and the imaginary part dielectric constant ε_r decreased with frequency within the range (100 Hz-100 kHz). From the Cole-Cole diagram that the static dielectric constant (ε_s) increasing with increasing the concentration (x) for all films, (increasing and decreasing) in relaxation time with increasing the concentration (x) for all samples, and the parameter ('P) is less than one unit.

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