The Effect of Atomic Percentage Selenium Content on the Permittivity and Polarizability of $Ge_{1-x}Se_x$ Thin Films

Zina Al-Shadidi[*1], I.H. Khdayer[2]

[*1]Department of Math. & Phys., Faculty of Education, Aden University, Aden, Yemen
[2]Department of Physics College of Education Ibn-Al-Haithem, University of Baghdad, Baghdad, Iraq
[*1]zabaqer@yahoo.com; [2]emanphd2005@yahoo.com

Abstract-Generally the a.c. conductivity shows a power law in frequency $\sigma(\omega) \propto \omega^s$ where the exponent s ≤ 1. As the frequency goes to zero the conductivity become frequency independent. The a.c. conductivity was studied for the $Ge_{1-x}Se_x$ thin films to see how the selenium contents affect the permittivity and the permeability for the $Ge_{1-x}Se_x$. The thin films prepared by thermal evaporation at room temperature and under vacuum (~2 x10^{-5}toor) using Edward coating unit model 306A. From the relation between ln conductivity and ln w, the effect of selenium contents in $Ge_{1-x}Se_x$ thin films on the exponent value, the relaxation time and the maximum barrier height.

An algebric fitting method for circles and circular arcs was used to find the permittivity and the permeability from cole-cole diagram, and to see how the selenium content affects these parameter values of $Ge_{1-x}Se_x$ thin films.

It was clear that there were direct proportions between the selenium content in the Ge1-x Sex structure and each of the following factors: The exponent S, the barrier height, and the permittivity. It was also possible to note the presence of inverse proportion between the selenium content in the Ge1-x Sex structure and each of the polarizability and the charge carrier relaxation time.

Keywords- a.c. Conductivity; Cole-cole Diagram; Thin Films; Matlab

I. INTRODUCTION

Chalcogenide glasses have received a great deal of attention for the last two decades due to their technological applications namely electronics [1]. The a.c. conduction in chalcogenide glasses and semiconductors depends on frequency through the mathematical relation:

$$\sigma(\omega) = A\omega^s \qquad (1)$$

In Eq. (1), A constant ω represents the angular frequency and s ≤1 is the exponent. This behavior of the semiconductor and chalcogenide is due to the relaxation processes caused by the carriers' movements [2]. M.I. Mohamed et. al., 2002 [3] studied the a.c. electric properties of chalcogenide GexFexSe100-2x (x=2.5,5,10 and 15 at%) thin films and they found that the C.B.H. is the dominant conduction mechanism. Fathy Salman 2003 [4] studied the a.c. conductivity and the dielectric properties of glassy system SexTe79-xGe21 at temperatures of 300-450K and frequencies from 50Hz to 500Hz. He described his experimental results using C.B.H. model. R.D. Gold &S.A. swan, 2003 [5] studied the a.c. conductivity and d.c. conductivity of RF-sputtered Silicon nitride thin films; the a.c. conductivity was observed to depend on frequency and follow the expression $\sigma(\omega) = A\omega^s$. The value of S were found to lie between 0.83-1.31, showing a systematic increase with frequency in the range 100Hz-20Hz, and a decrease with increasing temperature in the range of 173-373K. They decided that this type of behavior was associated with carrier hopping process E. Abd El-Wahab 2005 [6] studied the dielectric constant at zero frequency and the dielectric constant at frequency equals to infinity for Ag33Sb36 chalcogenide glasses ;he found that the a.c(ω) depends on the frequency and temperature. The value of the exponent S and its temperature dependence were described by the C.B.H. model. The values of the a.c. conductivity σac, ϵo, ε_∞ and Wm were found to increase with the increase of annealing temperature.

David Ayllón 2008 [7] used matlab fitting in regression analysis which is a technique that tries to model numerical data points of a dependant variable and one of more independent variables. The model relates the dependent variable as a function of the independent variables, to find the cole curve in order to use it in the electrical bioimpedance data. S.S Fouad et. al. 2008 [8] studied the a.c. conduction properties of amorphous GexSe100-x semiconductor such as delectric constant and the loss factor and the electric conductivity as function of frequency and temperature. They described their results using the correlated Barrier hopping (C.B.H.) model. N.A. Hegab and H.M. El-Mallah 2009 [1] found that the dielectric constant and the dielectric loss decrease with frequency and increase with temperature. The analysis of dielectric loss leads to determining the barrier height and agrees with that proposed by the theory of hopping of charge carriers over potential barrier between charged defect states. In principle, the dielectric constant at infinite frequency, the static dielectric constant, the relaxation time τ and an

exponent factor S have to be treated as fitting parameters whose values can be retrieved from the best fit to the experimental data. In most of the cases, however, the static dielectric constant and the dielectric constant at infinite frequency cannot be obtained directly from the experimental data since it is difficult to perform the measurements at very low and very high frequencies and to detect the saturated values in the two limits. The cole-cole model has been used successfully to describe the experimental data for the dielectric constant of many materials as a function of frequency.

The movement of a pair of carriers is done under the effect of electric field and it takes one of following types [2].

1) resonance absorption;

2) relaxation process.

Relaxation process must take one of the following two types:

a) Classical hopping for charge carrier over the potential barrier separates two sites of energy；

b) Quantum mechanical tunneling.

In this model, phonons produce a quantum mechanical tunneling through a barrier. Therefore, the conduction mechanisms is classified to three general types, which are:

1- quantum mechanical tunneling QMT;

2- correlated barrier hopping CBH;

3- polaron tunneling.

Any component has an element from the sixth column of the periodic table called chalcogenide glasses. The common feature of these glasses is the presence of localized states in the mobility gap as a result of the absence of long range order as well as various inherent defects [6].

In chalcogenide glasses having selenium in their atomic structures the charge carriers have a very interesting behavior in conducting or optical properties. For this reason great attention must be paid to studying the effect of selenium content in different alloys as in studying GexFexSe1-x [3], Se-Te-Ge [4], Ag7GeSe5 [9], and Se1-xSbx [10].

The electrical properties of Se-based glasses are very interesting, for that materials exhibit effects such as optical memory and photo darkening to which the study of their electrical behavior could shed light [2, 3].

The aim of this study is to report some electrical features, and determine the influence of Selenium content on the electrical conductivity of the Ge-Te-Se system, as well as to shed the light on the structural changes in materials having different atomic content from selenium modified by the bond structure. This modification cases the changes in the a.c. conductivity which is recognizable and measurable.

II. EXPERIMENTAL WORK

The compound was prepared as Ge1-xSex ingots by melting th selenium and germanium of high purity (99.9999%) together with x= 0.5, 0.6, 0.7 or 0.8. A sensitive electric balance type (Mettler H35 AR) was used to weight the elements of the alloys. The stoichiometric proportion of the compositions was loaded into a carefully cleaned quartz tube with water and alcohol respectively, then appropriate weights of Se and Ge were placed in quartz tube attached to the evacuated system, and sealed under (2x10-5) Torr vacuum.

The melting processes were done in an electric furnace of type (Heraeui), the temperature increased gradually to 1523K, which is above the melting point of GeSe. The furnace was still for about 12 h to complete the reaction during this procedure the tube were shaken to ensure the alloy homogeneity. Then, quenching method was used to get the alloy of amorphous structure. The alloys were scanned using an x-ray diffractometer (Phillips –source CuKα radiation, Ni filter) to ensure the amorphous structure.

Every sample was prepared as a Ge1-x Sex sandwich between two aluminum thin films as contact electrodes, which were deposited in vacuum using suitable masks by thermal evaporation. The electrode was circle shaped with 0.5 cm 2 radiuses and 7000Ao thickness.

The Ge1-xSex thin films in the thickness of 4500 Ao were deposited by thermal evaporation onto corning glass substrates kept at room temperature and under vacuum (~2 x10-6Torr) using Edward coating unit model 306A. The source –substrate distance was about 15 cm. A thermocouple was placed in contact with the substrate in order to keep the substrate temperature practically constant during the deposition.

The ac electrical measurements included resistance and capacitance as function of frequency within the range (100Hz-107Hz).

In this technique, the capacitance and the resistance were measured as function of the frequency at fixed voltage and current using a wire connection between the sample and the audio frequency bridge for the multi frequency LRC meter model 4274A (Hewlet-Packard).

<p align="center">III. RESULTS AND DISCUSSION</p>

A. a.c. Conductivity and Frequency Dependence

Thin films were measured in the frequency range (of 100 - 106) Hz .The dependence of ln σa.c. on ln ω is shown in Fig. 1, 2, 3, 4, for the Ge0.5Se0.5, Ge0.4Se0.6, Ge0.3Se0.7, and Ge0.2Se0.8 respectively.

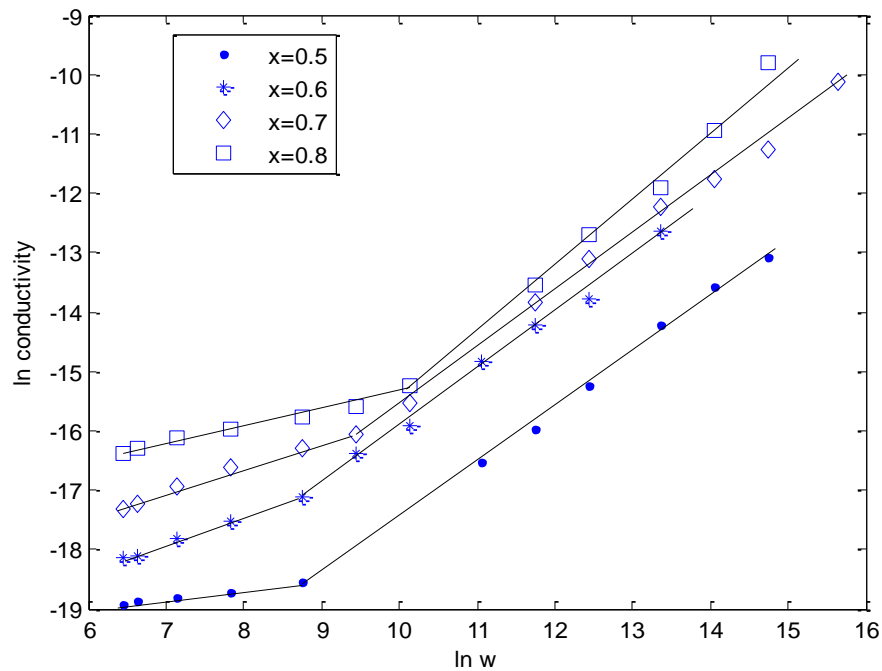All the samples follow a common pattern where ln σa.c. increases with increasing ln ω according to Eq. (1).

<p align="center">Fig. 1 The dependence of ln $\sigma_{a.c.}$ on lnω for Ge$_{1-x}$Se$_x$ thin films</p>

From Fig. 1, the flip point in each curve was obtained to get the value of ln ω, from which the relaxation time for the charge carriers can be obtained and it was decreasing with increasing selenium atomic percentage in the Ge1-xSex alloy. The figure presents the tow straight lines in each curve. According to Mott and Davis [11], at low frequencies the carrier mobility is related with the d.c. and a.c conductivities and its obeying the equation:

$$\sigma_{total} = \sigma_{a.c.} + \sigma_{d.c.} \tag{2}$$

In Eq. (2), σ_{total} is the total conductivity, and at low frequencies the d.c. conductivity $\sigma_{d.c.}$ is the dominant part, while at higher frequencies σ(ω) is the conductivity related with carrier mobility where σd.c. equal to zero. With increasing frequency, a critical point occurs, at which the conductivity dependence on frequency $\sigma_{d.c.}$ become stronger. For this reason more accurate values can be obtained for the exponent s from the slope of the straight lines after flip points.

It is clear from Fig. 1 that σ(ω) increases linearly with frequency according to Eq. (1). The S value suggested by the CBH model for most of chalcogenide glasses at room temperature nearly equal one [12]. In addition, from Fig. 1 and as is listed in Table 1, the value of the exponent S ranged between 0.939 to 0.988, which is in good agreement with the theoretical values for S suggested by Elliot 1985 [12]. It is obvious that the S values increases slightly with increasing selenium atomic percentage.

On the other hand, the increase of conductivity with increasing ω can be attributed to the contribution of the multicomponent of polarizability, the deformational component that concerns with the charge carriers (electrons or ions) and the relaxational components [6], concerns with the orientational and the interfacial [13, 6]. Increasing the applied frequency tends to decrease the orientational polarization since it takes more time than that for the electronic and ionic polarization [13].

All the measurements were done at room temperature. Therefore the exponent values have a little difference between each other (as in Table 1 below) which means that the change in the activation energy for the charge carriers come only from the changes in bond types which translate to changes in forces between the negative and positive charges and to changes in carriers energy. In other words the relaxation time also has very small changes with changing selenium atomic percentage as in Table 2 below.

TABLE 1 THE DEPENDENCE OF THE EXPONENT S ON THE SELENIUM ATOMIC PERCENTAGE FOR GE$_{1-x}$SE$_x$ THIN FILMS

Selenium percentage (x)	atomic	The exponent S
0.5		0.939
0.6		0.950
0.7		0.980
0.8		0.988

TABLE 2 THE DEPENDENCE OF RELAXATION TIME ON SELENIUM ATOMIC PERCENTAGE FOR GE$_{1-x}$SE$_x$ THIN FILMS

Selenium atomic percentage(x)	ln w	The relaxation time τ (s)
0.5	8.745	0.00100
0.6	8.745	0.00100
0.7	9.438	0.00050
0.8	10.13	0.00025

Those very small changes refer to the very wide distribution of relaxation time. The wide distribution of relaxation time and the exponent values imply that the mechanism responsible for the transitions between the conduction and the valence band is the correlated barrier hopping CBH. These results agree with the results of Fouad et. Al [8]. According to this model, the maximum barrier height ω_m can be obtained from the following relation:

$$S = 1 - \beta = 1 - \frac{6k_\beta T}{\omega_m} \tag{3}$$

In Eq. (3), kβ is the Boltzman constant, and T is the Kelvin temperature.

TABLE 3 THE DEPENDENCE OF MAXIMUM BARRIER HEIGHT ON SELENIUM ATOMIC PERCENTAGE FOR GE$_{1-x}$SE$_x$ THIN FILMS

Selenium atomic percentage(x)	The maximum barrier height ω_m (J)
0.5	4968×10^{-23}
0.6	6210×10^{-23}
0.7	8280×10^{-23}
0.8	12420×10^{-23}

From the above table, it is obvious that ωm increases with increasing selenium atomic content, which means that there is larger bonding energy. This behavior is due to increasing Ge-Se bonds and Se-Se bonds and these results seem to be very reasonable because the leaning of selenium atom to relate with the other atoms by the very strong covalent bonds. In addition because it has four electrons in its outer orbital, it will relate by four covalent bonds relating each Selenium atom with the others, while the germanium atoms have only two electrons in the outer orbital. For this reason, with increasing selenium atomic percentage we get.

1- increasing value the exponent S.
2- decreasing relaxation time τ.
3- increasing maximum barrier hight ωm.

B. Permettivity and Polarizability

In the case of absence of the electric field each charge carrier has its own place and there is no polarization. On the contrary, the polarization effect is very clear with the presence of the electric field thus the changes in the dielectric constant (or the permittivity) can be detected through the capacitance and resistance changes.

$$\varepsilon''(\omega) = ((t / a)G - \sigma_{d.c.}) / \varepsilon_o \omega \tag{3}$$

$$\varepsilon'(\omega) = (tC / a\varepsilon_o)) \tag{4}$$

In Eqs. (4) and (5) ε'' is the imaginary part of the permittivity, ε' is the real part of the permittivity, t is the film thickness, α is the area of the sample, G represents the conductance of the sample, ε_o is the dielectric constant for vacuum, and C represents the capacitance of the sample.

By plotting ε'' as a function of ε' we get cole-cole diagram, in which the relationship between the imaginary and the real part of the permittivity translates as a part of semicircle. Using Matlab, the code for circular fitting was set in order to get the upper half from the circle and the position of its center, then the angle between the x-axis and the line from the origin to the center of the circle can be measured. This angle equals to $\alpha\pi/2$, where α is the polarizability that represents the capability of the material to separate the negative ions from the positive ions. Moreover the variations of ε_s and ε_∞ with the variation of selenium atomic content can be measured where:

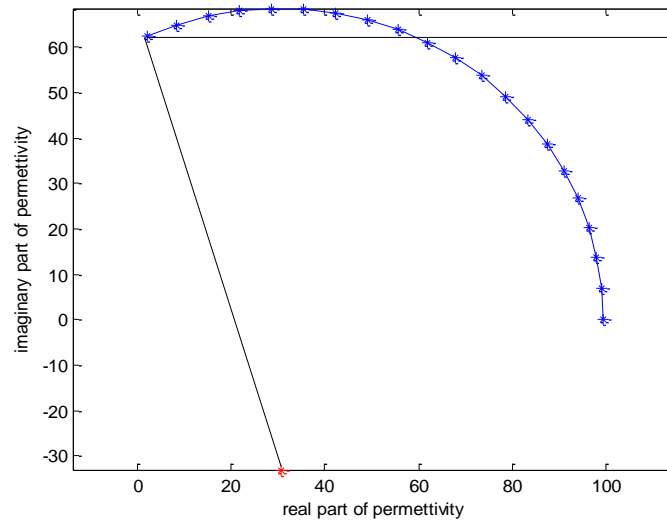ε_s represents the statistical permittivity (at ω=0), and ε_∞ represents the permittivity at infinity (at ω=∞).

Fig. 2 Cole-cole diagram for Ge$_{0.5}$Se$_{0.5}$ thin film
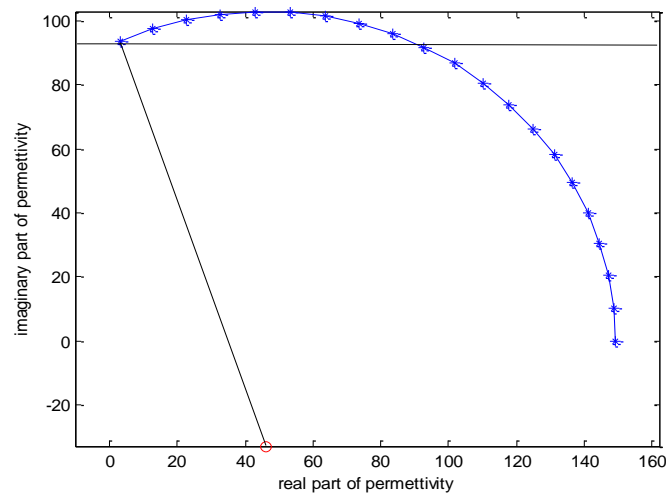

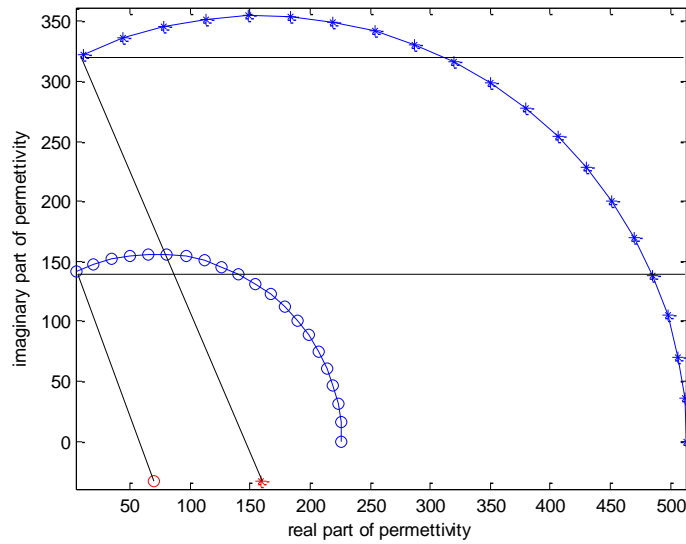Fig. 3 Cole-cole diagram for Ge$_{0.4}$Se$_{0.6}$ thin film

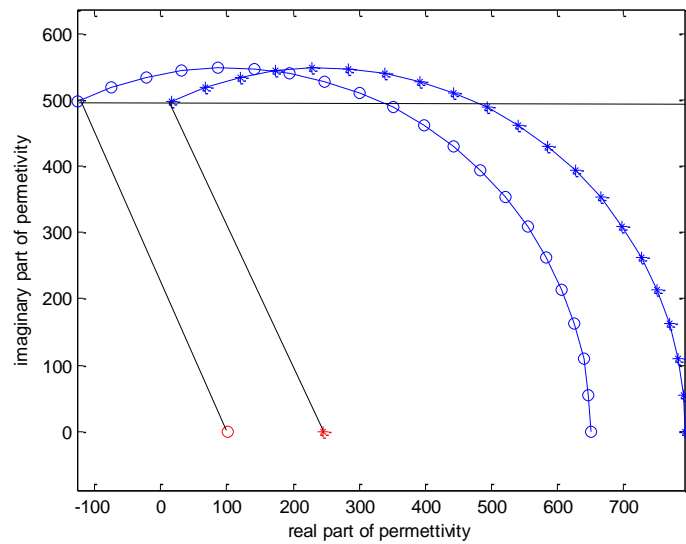Fig. 4 Cole-cole diagram for $Ge_{0.3}Se_{0.7}$ thin film

Fig. 5 Cole-cole diagram for $Ge_{0.2}Se_{0.8}$ thin film

From the above Figs. 2, 3, 4, 5 the following conclusions were deduced:

1) The polarizability decreases with increasing selenium atomic percentage as in the following table:

TABLE 4 THE DEPENDENCE OF THE POLARIZABILITY ON SELENIUM ATOMIC PERCENTAGE FOR $GE_{1-X}SE_X$ THIN FILMS

Selenium atomic percentage(x)	The polarizability (α) (first semicircle)	The polarizability (α) (second semicircle)
0.5	**0.805**	--------
0.6	**0.794**	--------
0.7	**0.777**	**0.755**
0.8	**0.733**	**0.738**

2) On the other hand, increases in the permittivity values ε_s and ε_∞ were seen with increasing Selenium atomic percentage.

TABLE 5 THE DEPENDENCE OF THE PERMITTIVITY ON SELENIUM ATOMIC PERCENTAGE (X) FOR $ge_{1-x}se_x$ THIN FILMS

Se atomic percentage	The static permittivity at $\omega=0$		The permittivity at $\omega=\infty$	
	ε_{s1}	ε_{s2}	$\varepsilon_{\infty1}$	$\varepsilon_{\infty2}$
0.5	58.32	------	1.66	--------
0.6	88.8	------	3.88	--------
0.7	306.6	146.2	10	0
0.8	476.4	329.4	29.4	-123.5

The permittivity increased with increasing Selenium atomic percentage because of changing type and strength of bonding present in the compound. The observed change in electrical properties resulted from the local change in the chemical bonding [8]. Fouad et. al. [14] explained the effect of changing atomic percentage for the semiconductor glasses on the cohesive energy because of the changes in the average bond strength. Chalcogenide glasses are often called lone-pair semiconductor due to the fact that the lone pair electrons (4p for Se) do not participate in the bonding [8], hence the chemical environment in the structure has influence on the role of lone pair electrons. These results can be attributed to the fact that Selenium atom relates with other atoms by four covalent bonds. These bonds are strong enough to catch its electrons, preventing them from being free and keeping the electrons related with its positive ions, which means that increasing selenium atomic percentage indicates increasing localized states in the alloy. For this reason, the polarizability will decrease and the permittivity will increase. These conclusions are consistent with the results of K. shimkawa [15], for the Ge_xSe_{1-x} which he noted through the structural representation of IR and Raman Spectra. It has been demonstrated that there are Ge-Se bonds in the Se-rich region but no Ge-Ge bonds that follow the smaller binding energy of Ge-Ge bonds compared with those of Se-Se.

A detailed analysis of the atomic content and the thin films structure was conducted based on the x-ray diffraction analysis given in [16].

When the Selenium atomic percentage exceeds the value 0.7 two circles exist in the cole-cole diagram and this means there are two values for α, two values for ε_s and two values also for ε_∞. This means that there are two groups of carriers, each having different value of the energy required to split it from the atomic knitting. This behavior is because of the existence of two types of carriers in the alloys having higher values of (x) (bonded carriers & unbounded carriers). In other words there are electrons with different energy levels. Therefore two values of each (α, ε_s, and ε_∞) were obtained.

IV. CONCLUSIONS

1- An easy method for circular fitting was established and used to plot the cole-cole diagram and to determined α, ε_s and ε_∞, this is the least square method.

2- The relaxation time for the charge carriers decreases with increasing selenium atomic percentage (x).

3- The value for the exponent S was obtained and it increased with increasing selenium atoms and varied from 0.939 to 0.988.

4- The relaxation time also had very small changes with changing selenium atomic percentage. These results implied that the mechanism responsible for transitions between the conduction and the valence band was the correlated barrier hopping CBH.

5- The maximum barrier height ω_m increase with increasing selenium atomic content. On the other hand, it was obvious that with increasing selenium atomic percentage, the relaxation time will be smaller because of the larger frequency, which means that there is larger bonding energy. This means that the change in the activation energy for the charge carriers come only from the changes in bonds type, which translate to changes in forces between the negative and positive charges and to changes in carriers' energy.

6- The polarizability decrease with increasing selenium atomic percentage.

7- The permittivity values ε_s and ε_∞ increase with increasing Selenium atomic percentage.

8- Increasing Selenium atomic percentage leads to the existence of two groups of electrons, each group having different energy level. Therefore two values of (α, ε_s, and ε_∞) were obtained.

REFERENCES

[1] N.A Hegaab and H.M Mallah, "A.c. conductivity and dielectric properties of Amorphous Te42As36Ge10Si12 glasses," Acta physica Polonica A, vol. 116, no. 6, pp. 1048-1052, 2009.

[2] Z.A. Al Shadidi, "Studying the transition mechanism in CdTe thin films," MSc thesis, Baghdad university, College of science,

department of physics, Baghdad, Iraq, 1995.

[3]   M.I. Mohammed, A.S. Abd-rabo, and E.A. Mahmoud, "A.c. conductivity and dielectric behavior of chalcogenide $Ge_xFe_xSe_{100-2x}$ thin films," Egypt. J. Sol., vol. 25, no. 1, pp. 49-56, 2002.

[4]   F Salman, "A.c. conductivity and dielectric study of chalcogenide glasses of Se-Te-Ge system," Turk J phys, vol. 28, pp. 41-48, 2003.

[5]   R.D. Gold, and S.A. Aswan, "Dielectric properties of RF-sputtered silicon nitride thin films with gold electrodes," Thin Solid Films, vol. 433, pp. 309-314, 2003.

[6]   E. Abd El-Wahabb, "Effect of heat treatment on the a.c. conductivity and dielectric properties of $Ag_{33}Sb_{31}Se_{36}$ thin films," Acta physica Polonica A, vol. 108, no. 6, pp. 985-995, 2005.

[7]   David Ayllon, "Methods for cole parameter estimation from bioimpedance spectroscopy Measurements," Master degree thesis, University of Boras, School of engineering, Sweden, 2008.

[8]   S.S. Foud, M. Fadel, and E. Abd El Wahab, "A detailed comparison between the hopping conductivity and theoretical data of the Ge_xSe_{100-x} glassy system," Journal of Ovonic Research, vol. 4, no. 3, pp. 51-60, 2008.

[9]   R. Belin, A. Zerouale, A. Pradel, M. Ribes, "Ion dynamics in the argyrodite compound Ag_7Ge_5I: non-Arrhenius behaviour and complete conductivity spectra," Solid state ionics, vol. 143, pp. 445-45, 2001.

[10] R.S. Tiwari, N. Mehta, R.K. Shukla, and A. Kumar, "Glassy $Se_{1-x}Sb_x$ Alloys," Turk J. Phys.,vol. 29, pp. 233-241, 2005.

[11] N.F. Mott and E.A. Davis, "Electronic process in non crystalline materials," Clarendon, Oxford, UK, 1979.

[12] S.R Elliot, "A.c. conduction in amorphous chalcogenide and pnictide semiconductors," Advances in Physics, vol. 36, no. 2, pp. 135-218, 1987.

[13] J.M. Stevels, "The electrical properties of glasses," Hand book of physics, Ed. Flugged, springer, Berlin, 1975.

[14] S.S. Foud, S. Fayek and M.E. El Oker, "The effect of chemical bonding on the physical behavior of the amorphous Ge_xSe_{1-x} system," J. Phys. D., vol. 28, no. 4, p. 755, 1995.

[15] K. Shimakawa, "On the Compositional Dependence of the Optical Gap in Amorphous Semiconducting Alloys," J. Non- cryst. Solids, vol. 43, p. 229, 1981.

[16] I.H. Khdayer, "the study of charge transport mechanism and optical band of $Ge_{1-x}Se_x$ films," MSc thesis, Baghdad university, College of science, department of physics, Baghdad, Iraq, 1995.