

STRUCTURAL and ELECTRICAL STUDIES ON $\text{Ge}_{10}\text{In}_x\text{Se}_{(90-x)}$ CHALCOGENIDE GLASSES

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The Chalcogenide glasses $\text{Ge}_{10}\text{In}_x\text{Se}_{(90-x)}$ system was prepared by usual melt quenching technique (where $x=5, 10, \text{ and } 15$). Structural investigation for the annealing samples by X-ray diffraction and FT Infra-red were carried out at room temperature. X-ray diffraction data for the studied samples indicates their hexagonal structure. The unit cell dimensions (a and c), volume, grain size and density were calculated. The FT infra-red spectra for the investigated samples were examined in the wave number region $150 - 400 \text{ cm}^{-1}$. Three absorption bands at 340 cm^{-1} , 270 cm^{-1} , and 210 cm^{-1} were found, and shifted to higher wave number as In content increase. The change of the electrical conductivity with temperature during heating – cooling cycle was also investigated. A decrease of the electrical conductivity and a corresponding increase of the activation energy of conduction were detected as increasing In content either in the glassy, crystalline and liquid state.

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1. Introduction

The Chalcogenide glasses are of the most widely known families of amorphous materials and have been studied extensively over the past few decades because of their interesting fundamental properties and wide commercial applications. The simple preparation technique of binary and ternary chalcogenide compounds as well as their broad range of band gaps, carrier mobilities, transparency in the IR region and their ability to form various solid state solutions and to accommodate different dopants has led to their emergence as technologically significant device materials [1-3]. Selenium has wide applications, its device application such as rectifiers, photocells, xerography, switching, and memory, etc. made it attractive, but in state its pure sensitivity. To overcome this it has disadvantages because of its short life time and low difficulty, several workers [4-10] have used certain additives (Ge, Te, Bi, Sb, and As, etc.) to make binary and ternary alloys, which in turn gives high sensitivity, a high crystallization temperature, and smaller aging effects. The addition of a third element (In) to the binary alloy such GeSe expands the glass forming area and also creates compositional and configurational disorder in the system.

Infrared and Raman measurements have been made as a useful means of obtaining information about the structure of chalcogenide glasses [11-14]. In this case it is especially important to investigate the vibrational spectra in the fundamental band region.

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The present study reports the effect of replacement of Se by In in $\text{Ge}_{10}\text{In}_x\text{Se}_{(90-x)}$ (where $x=5, 10,$ and 15) system. The study includes measurements of X-ray diffraction, and FT IR spectra in the fundamental band region. The effect of In doping has been also followed through the dc electrical conductivity during heating –cooling consecutive cycle. Interpretation of results in turns of expected chemical bonds.

2. Experimental Techniques

Bulk samples of $\text{Ge}_{10}\text{In}_x\text{Se}_{(90-x)}$ (where $x=5, 10,$ and 15) system were prepared by melt quenching technique. 5N purity elements taken in appropriate atomic percentage were sealed in quartz ampoules at pressure about 10^{-5} torr and heated in a furnace where the temperature was raised at a rate 3-4 K /min up to 925 K and kept around that temperature for (7 -8) hours, the samples were rocked continuously to insure a homogenous mixing of the constituents. The melt was then quenched in iced water. The samples were annealed at 573K for 2hs and then slowly cooled to room temperature. The annealing samples were conformed by using Philips X- ray diffractometer type (PW 1373) with $\text{CuK}\alpha$ radiation ($\lambda= 1.54056 \text{ \AA}$) and a Ni filter. Infrared measurements were done using Beckman 4250 IR spectrometer in the fundamental band region (in the wave number range $150 - 400 \text{ cm}^{-1}$) at room temperature using potassium bromide pellets for the elimination of errors caused by scattering. The dc electrical conductivity measurements were carried out using a special design Pyrex cell supported with two fixed tungsten electrodes. A programmable electrometer model Keithly 617 was used to measure the ohmic resistance of the samples.

3. Results and discussion

3.1. X-ray Diffraction

The X-ray measurements of the annealed $\text{Ge}_{10}\text{In}_x\text{Se}_{(90-x)}$ system (where $x = 5, 10,$ and 15) are carried out at room temperature. The powder X-ray diffraction patterns for the samples under investigation are given in fig. (1). The inter planer spacing (d) and the relative intensity (I / I_0), for all the samples are given in table (1). Comparison between the experimental (d) values and those of the JCPDS cards shows the absence of some diffraction lines in the composition with $x = 5$ belonging to the elementary In, this insures the complete miscibility of In in the solid solution during samples preparation. The X-ray diffraction patterns for the annealed samples reveal that the addition of In to the binary GeSe keep the structure in the hexagonal phase [15]. The lattice parameters a and c , were calculated and listed in table(2). When the lattice parameters (a and c) are known, it's easy to calculate the expression $\sin^2\theta_{hkl}$ which is a function of $h, k,$ and l . The $\sin^2\theta_{hkl}$ values for hexagonal structure must obey the relation [16]:

$$\sin^2\theta_{hkl} = A (h^2 + h k + k^2) + C l^2 \quad (1)$$

where $A = \lambda^2 / 3 a^2$ and $C = \lambda^2 / 4 c^2$.

The unit cell volume (V) is calculated according to the relation [17]:

$$V = a^2 c \sin 120^\circ \quad (2)$$

The relation between grain size D and X- ray line broadening was calculated according to the following equation:

$$D = A \lambda / \beta \cos \theta \quad (3)$$

Where A is a constant = 0.9, β is the observed diffraction peak width at half maximum intensity and λ is the wave length of X- ray.

The volume of the unit cell, the densities calculated from the X-ray data and the grain size values for the studied samples are calculated and in listed table (2). The calculated lattice parameter (a) shows a slight increase from 7.099 Å for the doped sample with $x = 5$ to 7.123 Å for the doped sample with $x = 15$, and the lattice parameter c shows a gradual decrease from 19.317 Å for the doped sample with $x = 5$ to 19.091 Å for the doped sample with $x = 15$. The corresponding unit cell size follows a gradual decrease with the incorporation of In. This may be explained by the increasing of the bond energy of the system as In content increase.

Table (1): The values of d and I/I_0 for all the studied samples.

Ge ₁₀ In ₅ Se ₈₅		Ge ₁₀ In ₁₀ Se ₈₀		Ge ₁₀ In ₁₅ Se ₇₅		h k l
d	I/I ₀	d	I/I ₀	d	I/I ₀	
-	-	9.351	20.07	9.322	30.13	002
6.144	9.12	6.017	15.52	6.012	24.33	100
5.882	6.40	5.862	12.93	5.700	8.92	101
5.184	20.60	5.187	31.29	5.188	16.92	102
-	-	4.776	10.26	4.788	6.82	004
-	-	4.082	65.99	4.685	68.21	
3.551	100	3.553	100	3.554	100	110
3.219	82.25	3.220	78.20	3.220	74.64	006
3.036	33.53	3.037	22.59	3.020	20.52	201
2.931	32.29	2.929	31.19	2.928	30.88	202
2.793	7.44	2.792	3.81	2.792	3.51	203
2.386	36.45	2.389	38.55	2.387	28.08	116
2.310	13.16	2.311	13.01	2.311	11.92	210
2.264	17.12	2.266	15.06	2.265	13.04	212
2.053	60.69	2.055	52.52	2.053	37.28	300
1.993	11.20	1.996	13.53	1.985	13.26	215
1.901	17.99	1.903	17.46	1.901	15.40	208
1.839	16.96	1.841	9.86	1.842	16.20	119
1.781	22.20	1.780	12.81	1.779	8.24	220
1.733	48.03	1.733	36.99	1.732	26.24	306
1.677	14.45	1.678	14.90	1.678	14.20	218
1.559	3.47	1.558	6.21	1.564	4.74	226

Table (2): Dependence of the lattice parameters, the volume of unit cell (V), density, and grain size on composition.

Composition	Lattice Parameter		V(Å) ³	ρ (gm/cm ³)	D(Å)
	a(Å)	c(Å)			
Ge ₁₀ In ₅ Se ₈₅	7.099	19.317	843.047	4.890	470.041
Ge ₁₀ In ₁₀ Se ₈₀	7.121	19.150	840.947	5.012	460.631
Ge ₁₀ In ₁₅ Se ₇₅	7.123	19.091	838.827	5.135	445.201

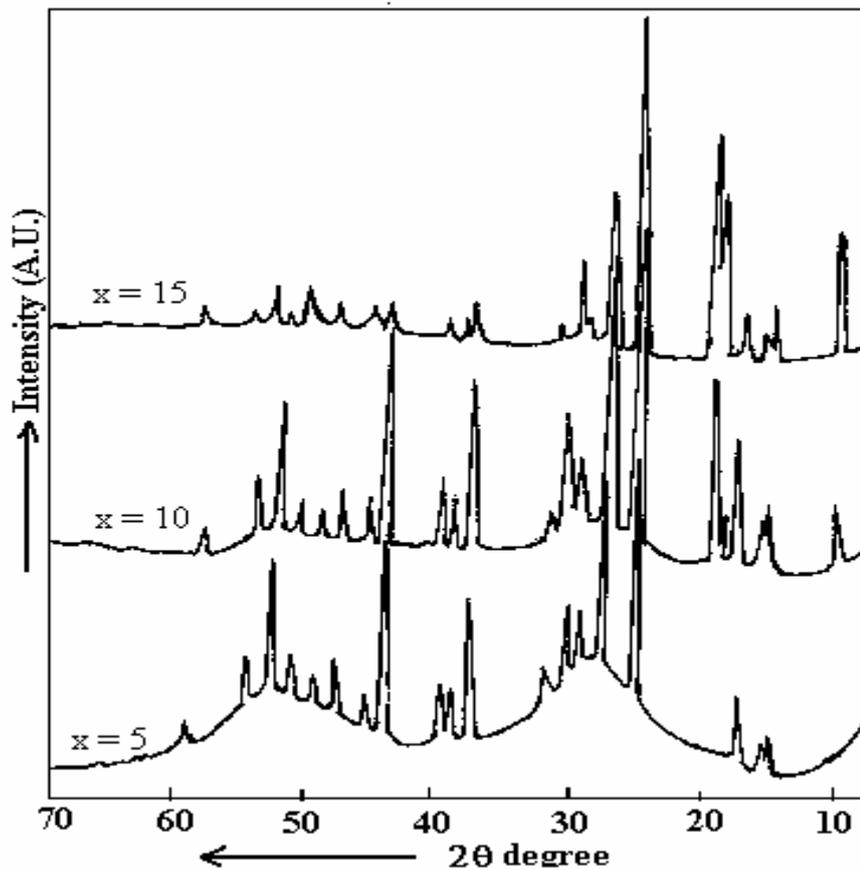


Fig. (1): X-ray diffraction patterns all the studied for samples.

3.2. Hydrostatic Density

Densities for all the annealed samples calculated from X-ray data show a good agreement with the densities values calculated theoretically. A comparison between the densities calculated from X-ray data and the densities values calculated theoretically are given in table (3). The results show that the density increase as the In content increase. The increase of density is related to the molecular weight and atomic volume of elements [18].

3.3. Infra-red Spectra

Fig (2) shows the IR spectra of $\text{Ge}_{10}\text{In}_x\text{Se}_{(90-x)}$ glasses with $x = 5, 10,$ and 15 . Inspection of the spectra for the samples under investigation shows that these spectra are different as In content increase. In the binary Ge Se there are two shoulders bands appear at 307 and 278 cm^{-1} and a separated band appears at 195 cm^{-1} [19]. The addition of In shifted some of bands in the binary Ge Se to higher wave numbers in the ternary samples. In Fig (2) there are three absorption bands at 340 cm^{-1} , 270 cm^{-1} , and 210 cm^{-1} . The band at 340 cm^{-1} increase in its intensity without change in its position as In content increase. The band at 270 cm^{-1} increase in its intensity and also shifted to higher wave number as In content increase. The band at 210 cm^{-1} increase in its intensity as In increase and split to two separate bands in samples with $x=10$ and 15 .

In the binary GeSe, Ge is four-fold, tetrahedrally coordinated [20]. GeSe_4 tetrahedral molecules have four fundamental modes ($\nu_1, \nu_2, \nu_3, \nu_4$) [21], where ν_1 is the symmetric stretching vibrational mode, ν_2 and ν_4 are the bending vibrational modes and ν_3 is the anti-symmetric stretching vibrational mode. Although only ν_3 and ν_4 modes are infrared active in GeSe_4

molecules, it is expected that all fundamental modes appear in infrared absorption spectra because of the breakdown of selection rules in glassy materials.

In the present work, with the addition of In the band at 307 is appear at 340 cm^{-1} , this band can be assigned to anti-symmetric stretching vibrational mode ν_3 . This shift may be due to that the addition of In make the Se-Ge bond more strongly. The band at 270 cm^{-1} which is due to the symmetric stretching vibrational mode ν_1 is shifted to higher wave number as In content increase, this is also due to the stronging of this band as In increase. In the same way the band at 220 which is due to bending mode is also strengthen as In content increase. From these we can see that the system of Ge Se strengthened as In added to it.

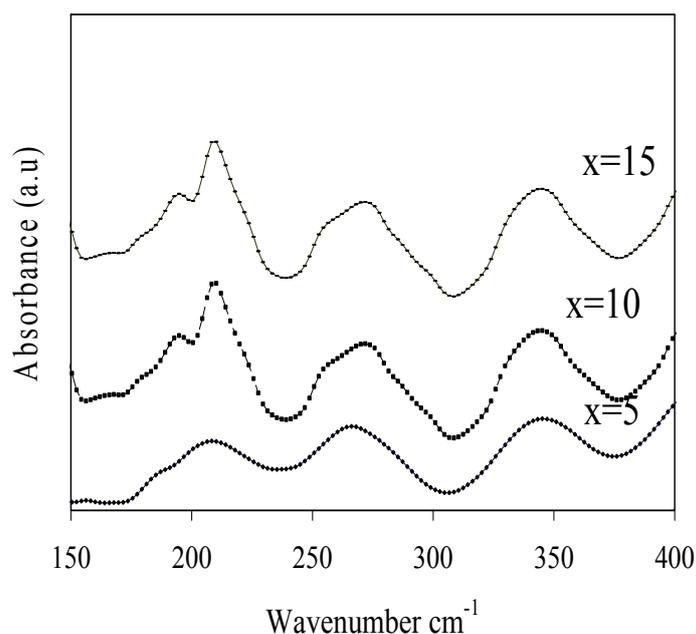


Fig. 2. Infrared absorption spectra of the investigated samples

3.4. The Chemical Bond Determination:

The chemical bond approach is a method that has been used to examine the structure and the properties of various types of chalcogenide glass. In view of this method:

- (a) The atoms of one type combine more favorably with atoms of different types.
- (b) The bonds are formed in the sequence of decreasing bond energy until all the available valences of the atom are filled and
- (c) Each constituent atom is coordinated by $(8-N)$ atoms, where N is the number of the outer shell electrons.

The bond energies (E_{AB}) of heteropolar ($A-B$) bonds can be, in the first approximation, estimated using Pauling relation [22]:

$$E_{AB} = 0.5 (E_{AA} + E_{BB}) + 23 (\chi_A - \chi_B)^2 \quad (4)$$

where E_{AA} , E_{BB} and χ_A , χ_B are homopolar bond energies and electronegativity, respectively, for A and B atoms.

The homopolar bond energies values used are 37.59 for Ge, 29.98 for In and 43.81 for Se [23], and the electronegativity values used are 1.8 for Ge, 1.7 for In and 2.4 for Se [23]. The types of bonds expected to occur together with their bond energies as calculated using

equation (4) are Ge—Se (48.98 K Cal / mol), In—Se (48.17 K Cal/mol) and Se — Se (43.81) K Cal/mol).

Assuming that the bond energies are additive it is possible to estimate the cohesive energy (C.E), by assuming the bond energies over all bonds expected in the material. The (C.E) for the samples was calculated from the following equation [24]:

$$C.E = \sum C_i D_i / 100 \quad (5)$$

where C_i and D_i are the number for the expected chemical bonds, and the energy of each corresponding bond respectively.

As can be seen from table (3), the replacement of Se by In causes an increase in the values of the cohesive energy for all the studied samples.

Table (3): The theoretical density, the density calculated from X-ray, the molecular weight and the cohesive energy (C.E) as a function of composition.

Composition	ρ Theoretical	ρ Calculated from X-ray	Molecular weight	Cohesive energy (C.E)
Ge ₁₀ In ₅ Se ₈₅	4.923	4.890	79.98	2.26
Ge ₁₀ In ₁₀ Se ₈₀	5.012	5.012	81.94	2.34
Ge ₁₀ In ₁₅ Se ₇₅	5.105	5.135	83.74	2.37

3.5. Heat effect of the electrical conductivity of Ge₁₀In_xSe_(90-x) alloys:

To follow the change of the electrical conductivity with temperature (during heating-cooling cycle); the as prepared samples were sealed under vacuum in Pyrex tubes with two fixed tungsten electrodes. The tubes were then heated at 925 K for 7-8 hours and then quenched in cool air to ensure good contact between the sample and the electrodes and to preserve their glassy texture. The experimental results of the variation of the dc conductivity with temperature are displayed for Ge₁₀In_xSe_(90-x) alloys in fig. (3). The curve abcdef represents the change in conductivity during heating while the curve feghi is that during cooling. These obtained curves can be interpreted as follow: The part ab represents a linear relationship corresponding to conduction in the amorphous state according to the general equation:

$$\sigma = \sigma_0 \exp [- \Delta E / k_B T] \quad (6)$$

where σ is the conductivity, σ_0 is the pre- exponential factor, ΔE is the activation energy of conduction, k is the Boltzmann's constant and T is the absolute temperature.

A continuous rapid increase in $\log \sigma$ is observed at point b till point c, this increase in the conductivity may be attributed to the appearance of the crystalline phase which characterizes the conduction during the part cd. Further increase of temperature causes of $\log \sigma$ over the line ef as a result of conduction in liquid state. Values of the activation energy calculated from the slope of $\log \sigma (1/T)$ for the glassy, liquidous and crystalline states are given in table (4).The table shows also values of the conductivity measured at room temperature σ_{20} and those of the parameter σ_0 for the glassy, and crystalline state. During the subsequent cooling cycle Feghi of the sample, the rapid increase in the conductivity at the point g is attributed to the crystallization form the liquid state. The part hi represents the change in $\log \sigma$ during the crystalline state. Many results can be extracted in table (4).Firstly, for each state (glassy, crystalline or

liquidous), introducing In as a metal dopant decrease the conductivity value by many orders of magnitude. There is also a corresponding increase of the ΔE values. Secondly, the values of ΔE for each composition are nearly the same in the amorphous and liquid states since they correspond to the same disordered network. Thirdly, a sharp decrease of the value of the conductivity as expected is detected for each composition as it undergoes a transition from the amorphous to crystalline state. From table (4), it is clear that the replacement of Se by In in $\text{Ge}_{10}\text{In}_x\text{Se}_{(90-x)}$ leads to increase the activation energy of conduction (ΔE) for these three states which is due to the replacement of the Se—Se bonds (bond energy 43.81K Cal/mol) by In—Se bonds (bond energy 48.17 K Cal/mol). Hence the cohesive energy of the system increase with increasing In content and the condition is not easier, and, hence, ΔE will increase.

Table (4): Electrical parameters of all the studied samples

Composition	Liquid State		Amorphous State			Crystalline State		
	$\Delta E(\text{ev})$	$\log\sigma_s$	$\Delta E(\text{ev})$	$\log\sigma_s$	$\log\sigma_{20}$	$\Delta E(\text{ev})$	$\log\sigma_s$	$\log\sigma_{20}$
$\text{Ge}_{10}\text{In}_5\text{Se}_{85}$	0.67	-4.90	0.40	-2.90	-9.70	0.15	-2.22	-4.8
$\text{Ge}_{10}\text{In}_{10}\text{Se}_{80}$	0.71	1.60	0.58	1.08	-10.3	0.20	-1.50	-5.00
$\text{Ge}_{10}\text{In}_{15}\text{Se}_{75}$	0.84	2.26	0.76	1.54	-11.4	0.25	-0.87	-5.20

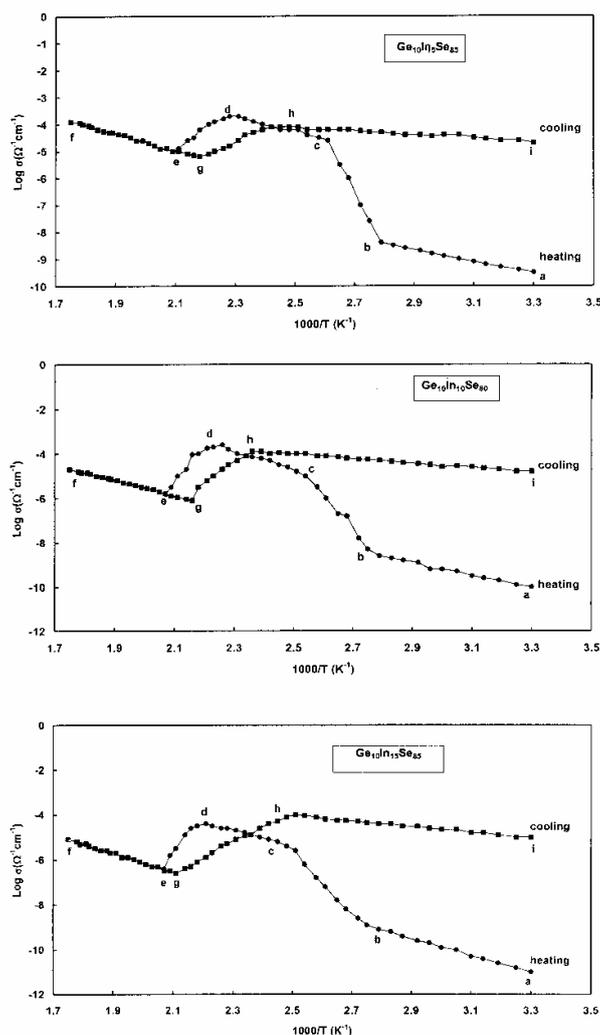


Fig (3): The dependence of $\log \sigma$ as a function of temperature for all the studied samples.

4. Conclusions

According to the above results and discussion, we can conclude that:

- (1) X-ray diffraction results indicate that all the annealed samples were in the crystalline state, and have hexagonal crystal structure. The unit cell volume decreases as the (In) content increases.
- (2) Comparison between the bands obtained in the experimental infrared spectra and the bands of the binary GeSe show that the addition of In shifted some of bands to higher wave numbers, and also strengthen the Se — Ge bonds. All the bands at 340, 270, and 220 cm^{-1} are assigned to the vibrations of GeSe_4 tetrahedral units.
- (3) By increasing (In) content, both the density calculated from x-ray data, and the cohesive energy for all compositions increase.
- (4) The activation energy of conduction in both amorphous, liquid and crystalline states increase with increasing In content.

References

- [1] A.B Sedden, *J. of Non cryst. Solids*, **184**, 44 (1995).
- [2] S.Y. Suh, D.A. Synder, and D.L. Anderson, *Appl. Opt.*, **24**, 866 (1985).
- [3] P.F. Carcia, F.D. Kalk, P. Bierstedt, A. Ferretti, G .A. Jones and D.G. SwarizFager, *J. of Appl. Phys.* **64**, 1745 (1988).
- [4] A.S. Abd- Rabo and K.A. Sharaf, *International J. of Pure and Appl. phys*, **1**, 49 (2007).
- [5] S.A. Fayek, *Vacuum*, **72**, 1 (2003).
- [6] S.M. EL Sayed, *vacuum*, **24**(2003)169.
- [7] N. saxena and P.K. Bhathagar, *Bull. Mater. Sci*, **26** (2003)547.
- [8] Z.G. Ivanova and E. Cernoskova, *Thermochimica Acta*, **411**(2004)117.
- [9] K.S. and N.S. Saxena, *Bull.Mater.Sci*, **26**(2003)543.
- [10] S.A. Fayek, *Vacuum*, **172** (2004)17.
- [11] G. Yang, X. Zhang, J. Ren , H. Ma, J.L. Adam, Y. Yang, G. Chen, *J. Am. Ceram. Soc.* **90**(5), 1500 (2007).
- [12] F. Xia, J. Ren , X. Zhang, H. Ma, J.L. Adam, G. Chen, *J. Am. Ceram. Soc.* **89** (7), 2154 (2006).
- [13] D. Zhao, Fa. Xia, G. Chen, X. Zhang, H. Ma, J.L. Adam, *J. Am. Ceram. Soc.* **88** (11) 3143 (2005).
- [14] X. Zhang, H. Ma, J. Lucas, Y. Guimond, S. Kodjikian, *J. Non Crystal. Solids*, **336**, 49 (2004).
- [15] JCPDS- International Centre for Diffraction Data, PCPDWIN, vol. 2.01 (1998).
- [16] H. Lipson, H. Steeple, *Interpretation of X-ray Powder Diffraction Patterns*, Macmillan and Co. LTD (1970).
- [17] V. Azaroff, J. Martin Bverger, *Hand book of X- ray*, Graw Hill Book Company Int., New York, (1958).
- [18] E.A. Mahmoud, *J.Al- Azhar Bull. Sci.* **10**, (1999). 221.
- [19] T .Ohsaka, *J.Non- crystal. Solids*, vol. 19 (1975) 121.
- [20] H. Wang et al, *Ceramics International*, **35**(2009) 83.
- [21] I. Quiroga, C. Corredor, F. Bellido, J. Vazquez, P. Villares, R. Jimenez Garay, *J. Non-crystal. Solids*, vol. 19 **6**(1996) 18.
- [22] L. Pauling, *The chemical Bonds*, Cornell University, New York, (1976)
- [23] A.L. Allured In: S.P. Parker, Editor, *Physical Chemistry Source Book*, McGraw Hill, New York (1987) 186.
- [24] M.I. Mohammed, A. S. Abd- Rabo, and E.A. Mahmud, *J. of Egypt. Soli.* **25** (2002) 49.