

## The Influence of Ga Content on Physical Topology of Amorphous Chalcogenide $\text{Ge}_{25-x}\text{Ga}_x\text{Se}_{75}$ System with Compositional Variations

<sup>1</sup>S.M. Salem, <sup>1,2</sup>A.M. Salem, <sup>3</sup>M.B.S. Osman, <sup>4</sup>H.M. Hashem and <sup>1</sup>H.A. Saleh

<sup>1</sup>Electron Microscopy and Thin Films Department, National Research Center, Cairo, Egypt.

<sup>2</sup>University College-Umm Al-Qura University-Saudi Arabia Kingdom, Cairo, Egypt.

<sup>3</sup>University College for Art, Science and Education, Ain Shams University, Egypt.

<sup>4</sup>Physics Department, Faculty of Science, Helwan University, Cairo, Helwan, Egypt.

Received: 25 January 2016 / Accepted: 28 February 2016 / Publication date: 20 April 2016

### ABSTRACT

Summary In current years, , tons interest has been paid to amorphous chalcogenide semiconductors as they may be very promising materials for optoelectronic applications. Stoichiometric bulk ingot materials of the ternary mixture  $\text{Ge}_{25-x}\text{Ga}_x\text{Se}_{75}$  [ $5 \leq x \leq 20$ ] were prepared by direct fusion of high purity constituent elements in vacuum sealed silica tubes. They have been used as source materials to produce thin film samples using the thermal evaporation method. The transition temperature “T<sub>g</sub>” of the samples was recorded at the usage of differential scanning calorimeter DSC. Its miles determined that the values of “T<sub>g</sub>” lower with increasing “Ga” content. The discovered lower in the “T<sub>g</sub>” values with “Ga” content material may be explained on the premise of chemically ordered network version. The impact on the physical characteristic viz. mean bond energy, [ the mean bond energy of the average section linking per atom ( $E_{cl}$ ), the average bond energy per atom ( $E_{rm}$ ), the average coordination number ( $Z$ ), mechanical constraints ( $N_{con}$ ), the deviation of stoichiometry “R”, the average heat of atomization “H<sub>s</sub>” and the optical band gap “E<sub>g</sub>”], with the variation in Gallium content had been studied in the existing article for  $\text{Ge}_{25-x}\text{Ga}_x\text{Se}_{75}$  [ $5 \leq x \leq 20$ ] system. Tichy-Ticha approach has been used to investigation the transition temperature and mean bond energy. The difference between “T<sub>p</sub>” and “T<sub>g</sub>” which is an indication of the thermal stability of films towards crystallization. The physical almost all the parameters of the ternary mixture  $\text{Ge}_{25-x}\text{Ga}_x\text{Se}_{75}$  under consideration as studied below.

**Key words:** Chalcogenide thin films, thermal , mean bond energy, thermal stability.

### Introduction

Development of modern technology led to the appearance of new family of munitions. Chalcogenide glass semiconductors are this kind of these families due to their delightful properties. Thin amorphous chalcogenide films are exciting materials, which can potentially be used for integrated planar optical circuits and their components for routing, amplifying or generating of optical signal, , in addition to for diffractive optics, photoresists, holography, optical memories and other optoelectronic applications (Nemec *et al.*, 2002). The amorphous chalcogenide films are relevant as optical recording media the usage of the results of reversible adjustments in the optical parameters [absorption, reflection coefficient and refractive index] during illumination or thermal treatment. The glass transition temperature “T<sub>g</sub>” is symmetrical to another material parameters [such as the average coordination number, optical band gap, over all mean bond energy, and average heat of atomization] which consist on the cohesive forces or the rigidity of the glassy network. Selenium primarily based binary and ternary chalcogenide glasses are considered as the most significant semiconductors due to their applications in various technological fields (Imran and Lafi, 2011). The research of composition dependence of various characteristic of chalcogenide glasses has been increased during last decade. As selenium reveals the unique assets of reversible phase transformation and also implementation like photocells, xerography, memory switching and many others., it seems appealing, but pure selenium has disadvantage like quick existence time and occasional photo sensitivity. To triumph over this hassle, a few impurity atoms like Ge, In, Bi, Te, Ga, Sb, Ag, etc. May be used to make alloys with Se, which might also enhance sensitivity, crystallization temperature and decrease getting older results, Ge atoms act as bond modifiers consequently they strengthen the average bond via cross-linking the Se chain structure, thereby improving the homes like glass transition temperature and resistivity (Saxena *et al.*, 2012). The compositional dependence studies on glassy alloys were reported for Ge-Se, Ge-Se-Te, Ge-Se-In, Ge-Se-Bi GeSe-As, Ge-Se-Sb, Ge-Se-Ag, (Maeda *et al.*, 2007; Sharma *et al.*, 2008; Saxena *et al.*, 2012; Sharda *et al.*, 2012 and Saxena *et al.*, 2013).

In the existent occupation, we have incorporated Gallium in the Ge-Se system for the compositions belonging to  $\text{Ge}_{25-x}\text{Ga}_x\text{Se}_{75}$  [ $5 \leq x \leq 20$ ]. The increment of third element used to inspire compositional and

**Corresponding Author:** H.A. Saleh, Electron Microscope and Thin Films Department, National Research Centre, 33 El Bohouth-st. Dokki, Giza, Egypt.  
E-mail: hishamsalehnrc@yahoo.com

configurational disorder in the material with recognize to the binary alloys . It has been established that physical properties in this system are particularly composition structured. The variation of characteristic has been mentioned on the foundation of their compositions. The prevailing paper is concerned with the theoretical prediction of the physical parameters associated with composition, viz. coordination number, constraints, mean bond energy for  $Ge_{25-x}Ga_xSe_{75}$  system. The decrease in the “ $T_g$ ” values with “Ga” import has been explain in terms on the basis of chemically ordered network pattern. In addition ,the optical energy gap has been found to reduction with the increase of the “Ga” content.

### Experimental details:

Series of  $Ge_{25-x}Ga_xSe_{75}$  ingot materials with different composition, “x” was prepared by direct fusion of stoichiometric proportions of high pure [99.999 %] elements [Germanium, Gallium and Selenium].The stoichiometric amounts of the elements were contained in the pre-cleaned silica tube, sealed under vacuum at pressure less than  $10^{-3}$  Pa. The sealed tubes were baked in a high temperature furnace at 1200K for about 48h and were finally water quenched. The fine powder obtained by crushing the bulk ingot was used for the evaporation process. Thin films of  $Ge_{25-x}Ga_xSe_{75}$  were deposited on pre-cleaned glass substrates by conventional thermal evaporation technique using a single source. The substrates were carefully cleaned successively, using hot water, dilute NaOH solution, chromic acid, ethyl alcohol and distilled water. A high vacuum coating unit [type E 306 A, Edwards Co., England] was employed to prepare  $Ge_{25-x}Ga_xSe_{75}$  thin films using the respective bulk composition as a source material. The residual pressure was  $\sim 5 \times 10^{-4}$  Pa. The film thickness and the deposition rate were controlled during evaporation process via quartz crystal thickness monitor [Type Edwards, FTM4]. Several trials were conducted to adjust the evaporation conditions in order to avoid the material spillage or decomposition by overheating during evaporation process. Differential scanning calorimetry [DSC] was carried out on the prepared  $Ge_{25-x}Ga_xSe_{75}$  powdery samples. A wight of about 8.22 mg for powdery sample for such value of “x” was sealed in a platinum cell, and scanned over a temperature range from 50°C to about 700°C at a uniform heating rate of 5 deg/min and in a dynamical nitrogen atmosphere of 30 ml/min.

### Results and Discussion

The thermal firmness and glass forming tendency [GFT] play an crucial role in determining the advantage of chalcogenide alloys as recording substances because of the the fact that phase change optical recording and erasing mechanism are based on the laser prompted thermal amorphization and crystallization of chalcogenide glasses. The descent of the thermal stability and GFT is, consequently, a subject of great service.

Traditional the DSC curves for the inspected  $Ge_{25-x}Ga_xSe_{75}$  powdery samples ( $x = 5, 10, 15$  and  $20$ ) , which were recorded from room temperature to 700 °C, are proven in Fig. 1 with different values of “Ga” content. The figure illustrate the endothermic and exothermic reversal peaks at the glass transitions temperature, “ $T_g$ ”, onset of crystallization temperature, “ $T_p$ ” crystallization temperature, “ $T_c$ ” and melting temperature, “ $T_m$ ” The “ $T_g$ ” and “ $T_c$ ” values were taken as the temperature conformable to the intersection of the two linear portions neighboring the transition below in the DSC traces of endothermic peak [see Fig.1]. The obtained account of the “ $T_g$ ”, “ $T_c$ ”, “ $T_p$ ” and “ $T_m$ ” for the investigated samples are listed in Table1, It has been observed from the figure that the values of “ $T_g$ ” reduction with increasing “Ga” content. The observed reduction in the “ $T_g$ ” values with “Ga” purport can be demonstrate on the basis of chemically ordered network model (March and Mucci, 1993 & Hassanien and Akly, 2015).

According to this model in a multi-component chalcogenide like GeGaSe system, the heteropolar bonds are formed in sequence of their decreasing bond energies. When “Ga” content increases in the system it is expected that the Ga-Se bonds are favourite to formed rather than the Ge-Se bonds. As the bond energy of Ga–Se [179.2 kJ/mol] is lower than the bond energy of Ge–Se [206.8 kJ/mol ] and also than the bond energy of Se–Se [183.92 kJ/mol] the average bond energy of the arrangement goes to decreases and hence the “ $T_g$ ” decreases. Table 2 summerized the possible bond energies occure in the GeGaSe system.

**Table 1:** Values of  $T_g$ ,  $T_c$ ,  $T_p$ , and  $T_m$  for different Ga content.

Exact chemical formula	$T_g$ [°C]	$T_p$ [°C]	$T_c$ [°C]	$T_m$ [°C]
$Ge_{23.85}Ga_{5.97}Se_{70.18}$	134	208	416	644
$Ge_{17.91}Ga_{10.61}Se_{71.48}$	129	198	414	637
$Ge_{12.86}Ga_{17.14}Se_{70.00}$	127	195	413	633
$Ge_{6.14}Ga_{23.95}Se_{69.91}$	125	191	413	628

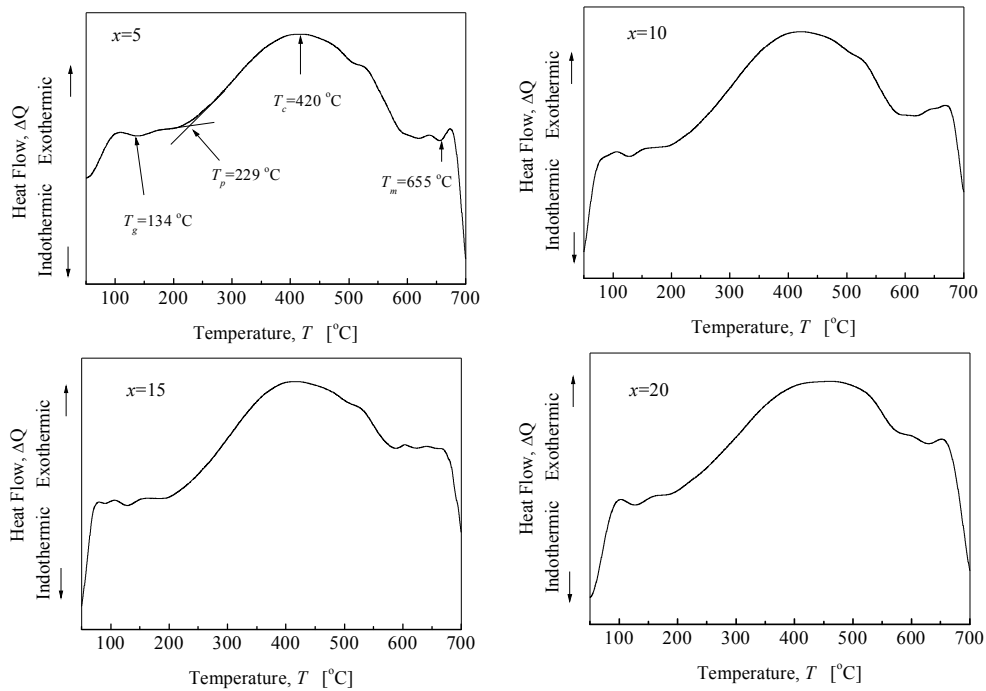


Fig. 1: Shows the DSC curves for powder  $Ge_{25-x}Ga_xSe_{75}$  samples [ $x=5, 10, 15$  and  $20$ ].

Table 2: possible bond energies occur in the GeGaSe system.

$Ge_{x-25}Ga_xSe_{75}$ A-B	Bond Energies D(A-B) KJ Mol <sup>-1</sup>	Ref.
Ge-Ge	157.42	11
Ga-Ga	133.15	11
Se-Se	183.92	11
Ge-Se	206.83	p.w
Ga-Se	179.21	p.w

**Overall mean bond energy of the organized amorphous  $Ge_{25-x}Ga_xSe_{75}$  materials:**

The overall mean bond energy  $\langle E \rangle$  is the basis foundation of the chemical bond technique which was suggested through (Tichy and Ticha, 1995) to investigate various physical characteristic of chalcogenide glasses. According to them the estimate of  $\langle E \rangle$  for any glassy alloy rely upon the bond energy of various bonds which are expected to form a glassy network, the form of bonds, the degree of cross-linking “ $D_{cl}$ ”, and the average coordination number  $\langle Z \rangle$ . For chalcogen-rich glasses, which maintain for the studied glasses, the values of  $\langle E \rangle$  may be evaluated using the following relation (Tichy and Ticha, 1994 & Lafi *et al.*, 2008):

$$\langle E \rangle = \langle E_{cl} \rangle + \langle E_m \rangle \dots\dots\dots (1)$$

where,  $\langle E_{cl} \rangle = D_{cl}.E_{hp}$  is the mean bond energy of the average cross-linking per atom and is calculated from the knowledge of the cross-linking parameter “ $D_{cl}$ ” and the average heteropolar bond energy “ $E_{hp}$ ”. These two parameters are given as in Eqs.2 and 3, respectively (Ioffe and Regel, 1960 & Kumar and Thangaraj, 2006).

$$D_{cl} = (4x+3y)/(x+y+z) \dots\dots\dots (2)$$

$$E_{hp} = [4xD(Se-Ge)+3y(Se-Ga)]/((4x+3y)) \dots\dots\dots (3)$$

where  $x, y,$  and  $z$  are the atomic fractions [atomic percentages] of Ge, Ga and Se, while 4, 3, and 2 are their coordination numbers, respectively (Ioffe and Regel, 1960). The estimated of “ $D_{cl}$ ” for the investigated samples were calculated using Eq. 2 and are specified in Table 3. The symbols  $D(Se-Ge)$  and  $D(Se-Ga)$  in Eq. 3 are the heteropolar bond energies which consist on the homopolar bond energies  $D(Se-Se), D(Ge-Ge)$  and  $D(Ga-Ga)$  and the square of the electronegativity difference  $(X_{Se}-X_{Ge})^2, (X_{Se}-X_{Ga})^2$ . The heteropolar bonds can be studied using the Pauling principle (bicerano and ovshinsky, 1985) as given below:

$$D(Se-Ge) = [D(Se-Se)D(Ge-Ge)]^{1/2} + 30(X_{Se}-X_{Ge})^2 \dots\dots\dots (4)$$

$$D(Se-Ga) = [D(Se-Se)D(Ga-Ga)]^{1/2} + 30(X_{Se}-X_{Ga})^2 \dots\dots\dots (5)$$

where,  $X_{Ge}$ ,  $X_{Ga}$  and  $X_{Se}$  are the electronegativities of Ge, Ga, and Se elements of values 2.01, 1.81, and 2.55, respectively. The homopolar bond energy of the constituent elements as given from the literature are 157.42, 133.15 and 183.92 kJ mol<sup>-1</sup> for, Ge-Ge, Ga-Ga and Se-Se, respectively (Saxena *et al.*, 2012). Using these data in the above two equations, the calculated bond energies for Se-Ge and Se-Ga are 206.3 and 172.9 kJ mol<sup>-1</sup>, respectively. The estimate of  $D(Se-Ge)$  and  $D(Se-Ga)$  are now used in Eq. 3 to calculate the value of “ $E_{hp}$ ” which is required to obtain the first condition of Eq.1 i.e.  $\langle E_{cl} \rangle$ . The obtained values of  $\langle E_{cl} \rangle$  for the studied  $Ge_{25-x}Ga_xSe_{75}$  are recorded in Table 3. The second term of Eq.1 is the average bond energy per atom of the residual matrix and given by (Bicerano and Ovshinsky, 1985).

$$\langle E_{rm} \rangle = \frac{2[0.5\langle Z \rangle - D_{cl}]D(Se - Se)}{\langle Z \rangle} \dots \dots \dots (6)$$

where  $\langle Z \rangle$  is the average coordination number given by:

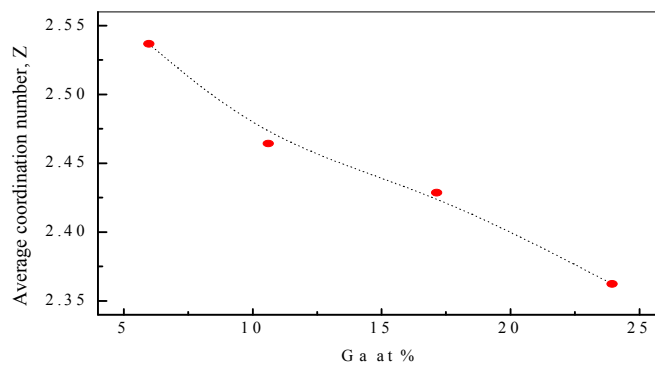
$$\langle Z \rangle = \frac{4 \times \text{atomic fraction of Ge} + 3 \times \text{atomic fraction of Ga} + 2 \times \text{atomic fraction of Se}}{100} \dots \dots \dots (7)$$

The estimated of  $\langle Z \rangle$  for the studied  $Ge_{25-x}Ga_xSe_{75}$  are calculated and are used to obtain  $E_{rm}$ . The values of  $\langle Z \rangle$ ,  $\langle E_{rm} \rangle$ , and the overall mean bond energy  $\langle E \rangle$  for the inspected system are listed in Table 3.

**Table 3:** The values of  $\langle Z \rangle$ ,  $\langle E_{rm} \rangle$ , and the overall mean bond energy  $\langle E \rangle$  for the investigated  $Ge_{25-x}Ga_xSe_{75}$  system

Exact chemical formula	$D_{cl}$	$\langle E_{cl} \rangle$ kJ.mol <sup>-1</sup>	$\langle Z \rangle$	$\langle E_{rm} \rangle$ kJ.mol <sup>-1</sup>	$\langle E \rangle$ kJ.mol <sup>-1</sup>
$Ge_{23.85}Ga_{5.97}Se_{70.18}$	0.95	195.7	2.54	45.54	241.2
$Ge_{17.91}Ga_{10.61}Se_{71.48}$	0.97	190.1	2.46	40.37	230.5
$Ge_{12.86}Ga_{17.14}Se_{70.00}$	1.07	184.5	2.43	21.64	206.1
$Ge_{6.14}Ga_{23.95}Se_{69.91}$	1.11	177.9	2.36	11.39	189.3

Figure 2 shows difference of the average coordination number as a feature of the “Ga” content It is clear that the average coordination number decrease as the “Ga” concentration increases. This finding was attributed due to that the “Ge” element with higher coordination number [ $N_{Ge} = 4$ ] replaced with “Ga” element having lower coordination number [ $N_{Ga} = 3$ ], will reflect decreases in the average coordination number of the system.



**Fig. 2:** variation of the average coordination number as a function of the Ga content.

It will known that the glassy network are stimulated by mechanical constraints [ $N_{con}$ ] associated with the atomic bonding and an average coordination number “ $Z$ ” which is also related to [ $N_{con}$ ]. There are two types of near-neighbor bonding forces in covalent solids; bond-stretching [ $\alpha$ -forces] and bond-bending [ $\beta$ -forces] (Saxena *et al.*, 2012). The first type is the number of Lagrangian bond-stretching constraints per atom given by:

$$N_{\alpha} = \frac{Z}{2} \dots \dots \dots (8)$$

While, the 2nd type is the bond-bending constraints given by:

$$N_{\beta} = 2Z - 3 \dots \dots \dots (9)$$

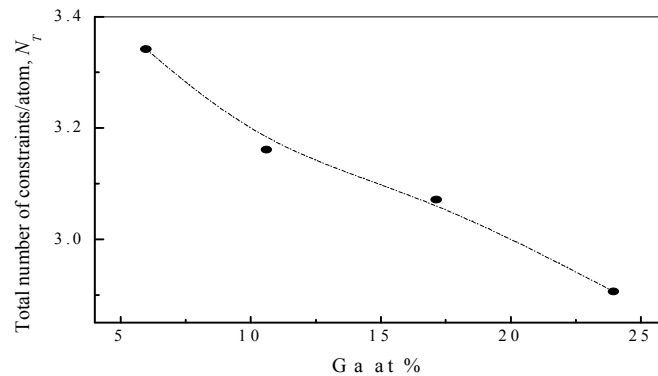
The total number of constraints per atom,  $N_T$  can be given:

$$N_T = N_{\alpha} - N_{\beta} \dots \dots \dots (10)$$

According to constraints theory (Saxena *et al.*, 2012), chalcogenides can be assorted into three groups which are:

- floppy or under-coordinated glasses with  $Z < 2.4$  and  $N_T < 3$ ;
- optimally-coordinated or quixotic glasses with  $Z = 2.4$  and  $N_T = 3$ ;
- stressed-rigid and over-coordinated glasses with  $Z > 2.4$  and  $N_T > 3$ .

Figure 3. depicts the difference of the total number of constraints per atom “ $N_T$ ” with “Ga” at %. It was found that “ $N_T$ ” decrease from to 3.35 to 2.91 as the “Ga” at.% increases from 5.79 to 23.95. This finding reflects that with increasing “Ga” at%, the system tends to manage as floppy or under-coordinated glasses



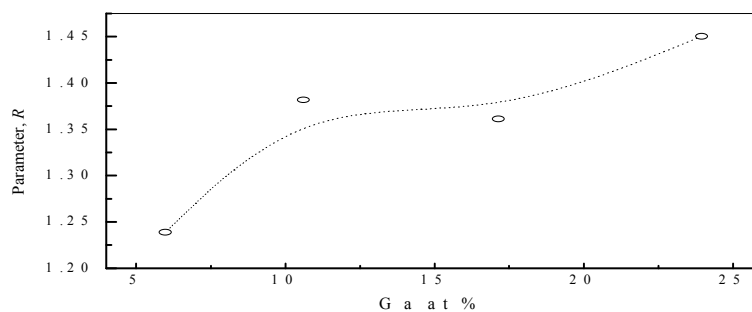
**Fig. 3:** The variation of the total number of constraints per atom  $N_T$  with Ga at %.

**Deviation from the stoichiometry of composition:**

The parameter “R” which describe the deviation of stoichiometry can be expressed by the means of the covalent bonding opportunities of chalcogen atoms to that of non-chalcogen atoms. For  $Ge_{25-x}Ga_xSe_{75}$  system, the parameter “R” is given by:

$$R = \frac{zCN_{se}}{YCN_{Ge} + XCN_{Ga}} \dots\dots\dots(11)$$

where x, y and z are the atomic frictions of Ga, Ge and Se, respectively. The calculated value [the point of existence of only heteropolar bonds] marks the minimum selenium content at which a chemically ordered network is possible without metal–metal bond formation. For  $R > 1$ , the arrangement is chalcogen rich and for  $R < 1$ , the arrangement is chalcogen poor. It has been observed from figure 4. that in the sitting  $Ge_{25-x}Ga_xSe_{75}$  system, the values of “R” is greater than unity leading to that the investigated system has a chalcogen rich.



**Fig. 4:** Variation of the parameter R vs. Ga at %

**Average Heat of Atomization,  $H_a$ , of the  $Ge_{25-x}Ga_xSe_{75}$  system:**

Heat of atomization or the enthalpy of atomization is the enthalpy change that is required for total separation of all atoms in a chemical compound such that the compound bonds are interrupted and component atoms are reduced to individual atoms. It has been adduce that the average heat of atomization,  $\overline{H_a}$  is a useful parameter for correlating the physical residences of semiconducting compounds (Hassanien and Akly, 2015). According to Pauling, the heat of atomization  $H_a(A - B)$  for a binary semiconductor fashioned from atom

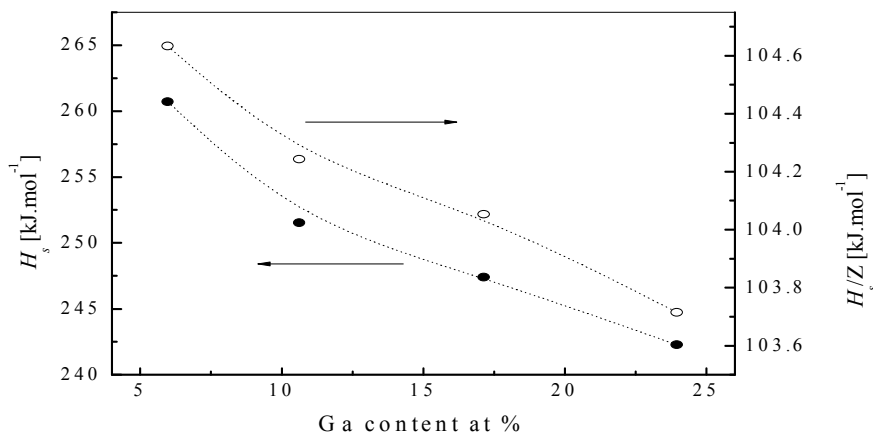
“A” and “B” at gauged pressure and temperature is the sum of heat of formation “ $\Delta H$ ” and average heat of atomization [ $H_s^A$  and  $H_s^B$ ] of the two atoms and is given by the relation.

$$H_s(A - B) = \Delta H + \frac{1}{2}(H_s^A + H_s^B) \dots \dots \dots (12)$$

The term “ $\Delta H$ ” given in Eq. 12 is symmetrical to the square of difference between the electronegativities of the atoms “A” and “B”, i.e.  $\Delta H \propto (\chi_A - \chi_B)^2$ . In case of some substances for which it is found that the heat of atomization “ $\Delta H$ ” is about 10% of the average of the heat atomization, “ $H_s$ ” and hence can be neglected, therefore, in the state of the ternary system  $Ge_{25-x}Ga_xSe_{75}$ , the average heat of atomization,  $\overline{H_s}$  can be written as

$$\overline{H_s} = \frac{YH_s^{Ge} + XH_s^{Ga} + ZH_s^{Se}}{X + Y + Z} \dots \dots \dots (13)$$

where x, y and z are the atomic frictions of Ga, Ge and Se, respectively, and  $H_s^{Ge} = 377$ ,  $H_s^{Ga} = 276$  and  $H_s^{Se} = 227$   $kJ\ mol^{-1}$  are the elements heat of atomization. The graphical difference of the average heat of atomization,  $\overline{H_s}$  of the ternary system  $Ge_{25-x}Ga_xSe_{75}$  as a characteristic of the “Ga” at % is proven in Fig.5. It has been discovered that the average heat of atomization,  $\overline{H_s}$  as well as the average single bond energy [ $\overline{H_s}/Z$ ] which is measure the cohesive energy of prepared system goes to decrease with increasing of “Ga” content [see table 4]. This behaviour can be dissect as follows. As the “Ga” content increases in the  $Ge_{25-x}Ga_xSe_{75}$  system the grist of Ga-Se bonds increase and Ge-Se bonds decreases. Since, the heat of atomization of “Ga” is minimal than that of “Ge”, therefore, the lesser value of “Ga” decreases the total heat of atomization of the network and hence the overall heat of atomization of the arrangement decreases. Inside the other hand, the decrease in the average single bond energy, [ $\overline{H_s}/Z$ ] with the increase of “Ga” content may cause the decrease of optical band gap.



**Fig. 5:** Graphical variation of the average heat of atomization,  $\overline{H_s}$  and average single bond energy,  $\overline{H_s}/Z$  as a function of the Ga at % .

**Table 4:** Values of  $\overline{H_s}$ ,  $\overline{H_s}/Z$ ,  $T_g$ ,  $T_c$ ,  $T_p$ , and  $T_m$  for different Ga content

Exact chemical formula	$\overline{H_s}$ $kJ\ mol^{-1}$	$\overline{H_s}/Z$ $kJ\ mol^{-1}$	$T_g$ [°C]	$T_p$ [°C]	$T_c$ [°C]	$T_m$ [°C]
$Ge_{23.85}Ga_{5.97}Se_{70.18}$	264.9	104.4	134	208	416	644
$Ge_{17.91}Ga_{10.61}Se_{71.48}$	256.3	104.0	129	198	414	637
$Ge_{12.86}Ga_{17.14}Se_{70.00}$	252.2	103.8	127	195	413	633
$Ge_{6.14}Ga_{23.95}Se_{69.91}$	244.7	103.6	125	191	413	628

This motivated us to go for further calculation of the optical band gap of the thin films under study. Generally, the optical characteristic of solid are governed by the interaction between solid and the electric field of the electromagnetic wave. In crystalline materials, the fundamental edge is without delay associated with the conduction and valence band i.e., direct and indirect band gaps, while within the case of amorphous materials a a exclusive form of optical absorption edge is found. The energy difference of the absorption coefficient offers an illustration of the distribution of the density of states in the energy gap. Therefore, the permission of the optical absorption coefficient of a given materials provide us important information about the optical transition and the corresponding energies. The estimate of the optical energy gap “ $E_g$ ” of the

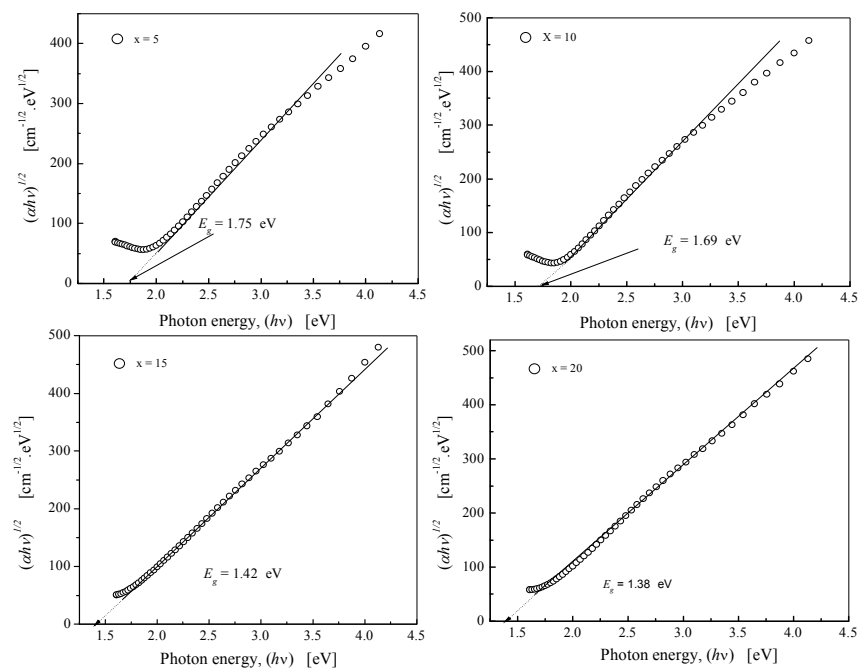
films under investigation are determined in the strong absorption region, where the optical absorption is due to extended state transitions. Since, “ $E_g$ ” is a measurement of the energy gap between valence and conduction band edges. The absorption coefficient extracted from transmittance and reflection spectral are analyzed using the classical relation (Sharma and Katyal, 2007):

$$(\alpha h\nu)^r = A \times (h\nu - E_g) \quad (14)$$

where A is a constant and the exponent  $r$  equal to 1/2, 2, 1/3 or 2/3 for indirect allowed, direct allowed, indirect forbidden and direct forbidden transition, respectively. The approach method used to determine the band gap of the studied films is to plan a graph between  $(\alpha h\nu)^{1/r}$  and photon energy,  $(h\nu)$  and look for that value of “ $r$ ” which bear best linear graph in the band edge region. The present results expose that the best fit of the linear parts for these samples was obtained with  $r = 1/2$  indicates a non direct optical transitions with different estimated of “ $x$ ” as shown in Fig.6. Consequently, Eq.14. can be written in the form:

$$(\alpha h\nu)^{1/2} = A \times (h\nu - E_g) \quad (15)$$

The extrapolation of the linear part of the curves to the photon energy axis as shown in Fig.6, would give the optical band gap. The optical energy gap has been determined to lower with the increase of the Ga content [see Table 5, from 1.75 eV for  $x = 5$  to 1.38 eV for  $x = 20$ ]. It is worth noting that the rate of the optical band gap for the investigated Ge<sub>25-x</sub>Ga<sub>x</sub>Se<sub>75</sub> thin film are in good agreement with that reported in literature for other Ge<sub>z</sub>Ga<sub>x</sub>Se<sub>y</sub> compositions (Nemec *et al.*, 2002).



**Fig. 6:** Plot of  $(\alpha h\nu)^{1/2}$  vs.  $(h\nu)$  for Ge<sub>25-x</sub>Ga<sub>x</sub>Se<sub>75</sub> thin films,  $x=5, 10, 15$  and  $20$

**Table 5:** values of the optical band gap energy for Ge<sub>25-x</sub>Ga<sub>x</sub>Se<sub>75</sub> thin films as well as the values of  $N/m^*$

Film compositions	$E_g$ [eV]	$N/m^* \times 10^{19}$ [cm <sup>-3</sup> .Kg <sup>-1</sup> ]
Ge <sub>23.85</sub> Ga <sub>5.41</sub> Se <sub>70.74</sub>	1.75	3.51
Ge <sub>17.91</sub> Ga <sub>10.61</sub> Se <sub>71.48</sub>	1.69	3.96
Ge <sub>12.86</sub> Ga <sub>20.14</sub> Se <sub>67.00</sub>	1.42	4.47
Ge <sub>04.42</sub> Ga <sub>24.95</sub> Se <sub>70.63</sub>	1.38	7.45

## Conclusions

The physical properties and optical band gap in Ge<sub>25-x</sub>Ga<sub>x</sub>Se<sub>75</sub> thin films [ $x = 5, 10, 15$  and  $20$ ] chalcogenide thin films have been studied. The supplement of “Ga” is found to enhance thermal stability, as indicated by the values of “ $T_g$ ” and “ $T_c$ ”. Further, the decreasing trend of “ $T_g$ ” with “Ga” content reveal the contribution of “Ga” to the cross-linking parameters of the thin films network out of the formation of GaSe<sub>4/2</sub> structural units. Despite the fact that the glass transition temperature will increase with increasing “Ga” content with a sharp increase at an average coordination number  $Z = 2.54$ . Inside the composition range of study, the

structure of the samples under respect still contains some homopolar bond and cross-linking is not completed, as it is apparent from the values of “ $D_{el}$ ” parameter. The “ $T_g$ ” estimated of the studied correlated linearly well with the average coordination number ‘ $Z$ ’, the overall mean bond energy “ $E$ ”, and the average heat of atomization “ $H_s$ ”, but the optical band gap “ $E_g$ ” exhibits an opposite behavior.

## References

- Bicerano, j. and S.R. Ovshinsky, 1985. chemical bond approach to the structures of chalcogenide glasses with reversible switching properties. *Journal of Non-Crystalline Solids*, 74: 75-84.
- Hassanien, A.S. and A.A.A. kl, 2015. Estimation of some physical characteristics of chalcogenide bulk  $Cd_{50}S_{50-x}Se_x$  glassy systems. *Journal of Non-Crystalline Solids*, 428: 112-120.
- Imran, M.M.A. and O.A. Lafi, 2011. Glass transition kinetics and optical band gap in  $Se_{85-x}Sb_{15}Sn_x$  ( $x = 10, 11, 12.5$  and  $13$ ) chalcogenide glasses. *Materials Chemistry and Physics*, 129: 1201-1206.
- Ioffe, A.F. and A.R. Regel, 1960. Semiconductivity in Pyrite, Marcasite and Arsenopyrite Phases. *Progress Semicond*, New York, 4: 239.
- Kumar, K. and R. Thangaraj, 2006. Glassy state and structure of Sn–Sb–Se chalcogenide alloy. *Journal of Non-Crystalline Solids*, 352: 2288-2291.
- Lafi, O.A., M.M.A. Imran and M.K. Abdullah, 2008. Chemical bond approach to glass transition temperature and crystallization activation energy in  $Se_{90}In_{10-x}Sn_x$  ( $2 \leq x \leq 8$ ) semiconducting glasses. *Mater. Chem. Phys.* 108: 109.
- Maeda, K., T. Sakai, K. Sakai, T. Ikari, M. Munzar, D. Tonchev, S.O. Kasap and G. Lucovsky, 2007. Effect of Ga on the structure of Ge–Se–Ga glasses from thermal analysis, Raman and XPS measurements. *J Mater Sci: Mater Electron*, 18: 367-370.
- March, N.H. and J.F. Mucci, 1993. *Chemical Physics of free Molecules*. Springer Science, Business Media, New York, (1993), 1st Edition.
- Nemec, P., M. Frumar, J. Jedelsky, M. Jelinek, J. Lancok and I. Gregora, 2002. Thin amorphous chalcogenide films prepared by pulsed laser deposition. *Journal of Non-Crystalline Solids*, 299(302): 1013-1017.
- Saxena, M., S. Gupta, A. Agarwal, S.C hawla, 2013. A Topological Study on Physical Properties of Ge-Se-Bi Glass System for Phase Change Optical Storage. *MIT International Journal of Electronics and Communication Engineering*, 3(2): 76-82.
- Saxena, M., A.K. Kukreti, Sh. Gupta, M.K. Agarwal and N. Rastogi, 2012. Theoretical Predictions of Physical Parameters in Glassy  $Ge_xSe_{80-x}Te_{20}$  Alloys. *European Journal of Applied Engineering and Scientific Research*, 1(4): 160-166.
- Saxena, M., M.K. Agarwal, A.K. Kukreti and N. Rastogi, 2012. Effect on physical properties of  $Ge_{20}Se_{80-x}Ga_x$  glass system with compositional variations. *Advances in Applied Science Research*, 3(3): 1440-1448.
- Sharda, S., N. Sharma, P. Sharma and V. Sharma, 2012. Basic physical analysis of new Sb-Se-Ge-In chalcogenide glassy alloys by predicting structural units. theoretical approach, *Chalcogenide Letters*, 9(9): 389 – 395.
- Sharma, A., N. Mehta and A. Kumar, 2011. Dielectric relaxation in  $Se_{80-2x}Te_{20}Sn_x$  chalcogenide glasses. *J Mater Sci.*, 46: 4509-4516.
- Sharma, P. and S.C. Katyal, 2007. Optical study of  $Ge_{10}Se_{90-x}Te_x$  glassy semiconductors. *Thin Solid Films*, 515: 7966-7970.
- Sharma, P. and S.C. Katyal, 2008. Effect of tellurium addition on the physical properties of germanium selenide glassy semiconductors. *Physica B*, 403: 3667-3671.
- Tichy, L. and H. Ticha, 1994. On the chemical threshold in chalcogenide glasses. *Materials Letters*, 21: 313-319.
- Tichy, L. and H. Ticha, 1995. Covalent bond approach to the glass-transition temperature of chalcogenide glasses. *Journal of Non-Crystalline Solids*, 189: 141-146.