AC conductivity of Se-Ge-As glassy system in relation to rigidity percolation

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Measurements of conductivity (ac & dc) and dielectric constant (ε) have been made for amorphous alloyed samples of $Se_{0.75}Ge_{0.25-x}As_x$ with $x = 0.05$, 0.10, 0.15 and 0.20 at different temperature (289 to 389 K) and various frequencies (10^2 to 10^5 Hz). The conductivity and the dielectric constant of these glasses have been explained on the basis of the correlated barrier hopping (CBH) model. Recent progress in applying percolation theory to explain properties and glass forming ability of chalcogenide glasses is critically reviewed. Percolation theory is shown to be relevant to the liquid-state behavior of glass-forming ability of the $Se_{0.75}Ge_{0.25-x}As_x$ chalcogenide system. The relationship between the optical gap (ΔE_g) and chemical composition is also discussed in terms of the average heat of atomization (H_s) and the average coordination number (r). These findings provide to some extent an important link between experimental and theoretical results.
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1. Introduction

The conductivity of semiconducting glasses is known to be frequency dependent which, as expected is due to conduction in localized state. Measurements of ac conductivity is therefore a powerful experimental method to obtain information about the existence and the location of these states. The ac conductivity, $\sigma_{ac}(\omega)$, of amorphous chalcogenide semiconductors is usually expressed as

$$\sigma_{ac}(\omega) = \sigma_T - \sigma_{dc} = A\omega^s \tag{1}$$

where ω is the angular frequency, A is a constant (s) is the frequency exponent, and σ_T is the total conductivity including the frequency dependent conductivity measured under ac field and σ_{dc} is the dc conductivity. This equation is valid for several low mobility amorphous and even crystalline materials [1]. Various models have been proposed by several investigators [2–7] to explain the behavior of the frequency exponent (s) in the case of chalcogenide glasses. The Quantum-Mechanical Tunneling (QMT) proposed by Pollak and Geballe [2] was the first type of charge transfer for doped crystalline Si, then subsequently applied to the case of amorphous semiconductors by Austin and Mott [7]. According to the QMT the frequency exponent (s) is predicted to be temperature independent, but frequency dependent (s decreases with increasing frequency). The QMT assumes that there is no lattice distortion associated with the carrier whose motion gives rise to the ac conductivity i.e. polaron formation is not considered. Therefore QMT is considered not applicable to chalcogenide glasses. The correlated barrier hopping (CBH) model proposed by Elliott [5] has been applied to the chalco-

genide glassy semiconductors. The CBH model is the most acceptable model used to describe the ac conductivity behavior of amorphous semiconductors. In this model correlated barrier hopping of bipolarons (i.e. two electrons hopping between charged defects D^+ and D^-) has been proposed to interpret the frequency dependence of conductivity in chalcogenide glasses as given in Eq. (1). The theory has explained many low temperature features, particularly the dependence of the A and s parameters on temperature. However, it does not explain the high temperature behavior so well, in the low frequency range. Shimakawa [6] suggested that D° states are produced by thermal excitation of D^+ and /or D^- states, and that single polaron hopping (i.e. one electron hopping between D° and D^+ or D^-) contributes at high temperature Generally the electrical properties of glasses depends on the chemical composition and the structural features. The concept of the average coordination number, r, is useful in describing the cross-linking in such a glass: it is defined as the atom averaged covalent coordination of the constituents. Several structural models describing composition property relationship have been presented for these glasses. Most of these models are based on Phillips constraint theory [8, 9], which predicts a transformation from underconstrained or floppy network to overconstrained or rigid network. This study has two objectives; the first was to study the conduction mechanism of our Se-Ge-As glassy system, and consequently determine its related parameters such as the frequency exponent (s) the frequency dependence of the dielectric constant ε, and the ac activation energy W_m; and the second was to clarify the concept of constraint theory and surface floppy modes for the system under investigation.

2. Experimental details

Four different composition of $Se_{0.75}Ge_{0.25-x}As_x$ chalcogenide glass system with $x = 0.05$, 0.10, 0.15 and 0.20 were synthesized by melting the elemental components of high purity (99.999%) in evacuated silica tubes in an oscillatory furnace according to a technique reported previously in [10]. The proper ingots were confirmed to be completely amorphous using X-ray diffraction given in [11], and differential thermal analysis given in [10, 11]. Polished bulk samples in the form of pellets thicknesses (0.417, 0.409, 0.518 and 0.347 cm) were used for the measurements of ac and dc conductivity. These measurements were made between a temperature range 289–389 K. Total conductivity σ_T was measured on automatic RCL meter (PM 6304 Phillips) and ac conductivity σ_{ac} was calculated by using Eq. (1) where, σ_{dc} (dc conductivity) was measured using a Keithly electrometer (type E 616A). The ac conductivity and the dielectric constant were measured at various frequencies 10^2 to 10^5 Hz. In order to make measurements of conductivity and dielectric constant at given frequncy, separate pellets were used for each temperature cycle. The reproducibility of the results was checked by making many runs at different times over the entire temperature and frequency range. It is observed that the values of the conductivity and the dielectric constant measurements were within $\pm 2\%$ error in different runs. However, only the results of one single run are reported here. No annealing effect on σ_{ac} (ω) and ε was observed for any glass below the glass transition temperature T_g. The dielectric constant ε was calculated by applying the following relation.

$$\varepsilon = (L/A)^*(C_x/\varepsilon_0) \qquad (2)$$

Where C_x, is the capacitance of the sample in (farad), L is the thickness of the pellet (m), A, the area of the sample in (m^2) and ε_0 the permittivity of the free space $(\varepsilon_0 = 8.85 \times 10^{-12}$ f/m).

3. Results
3.1. Temperature and frequency dependence of ac conductivity

Fig. 1 shows the temperature dependence of σ_{ac} (ω) over the investigated frequency for the four different compositions of our $Se_{0.75}Ge_{0.25-x}As_x$ with $x = 0.05$, 0.010, 0.15, and 0.20. It is observed from this figure that, the ac conductivity is independent on temperature in the considered range of temperature except after 353 K, σ_{ac} is very slowly increases with increasing temperature. The overall behavior of the curves is similar for all the compositions under investigation. The measurements of the σ_{ac} conductivity for all the compositions at the same frequency range, measured at room temperature ($RT \approx 289$ K) are reported in Fig. 2. It is clear from the above figure that σ_{ac} (ω) increases with increasing the frequency and decreases with increasing the As content. Fig. 3 represents the dependence of In σ_{ac} (ω) on In(ω) at different frequency and different temperature for $Se_{0.75}Ge_{0.05}As_{0.20}$, as a representative example. Values of the exponent (s) were calculated

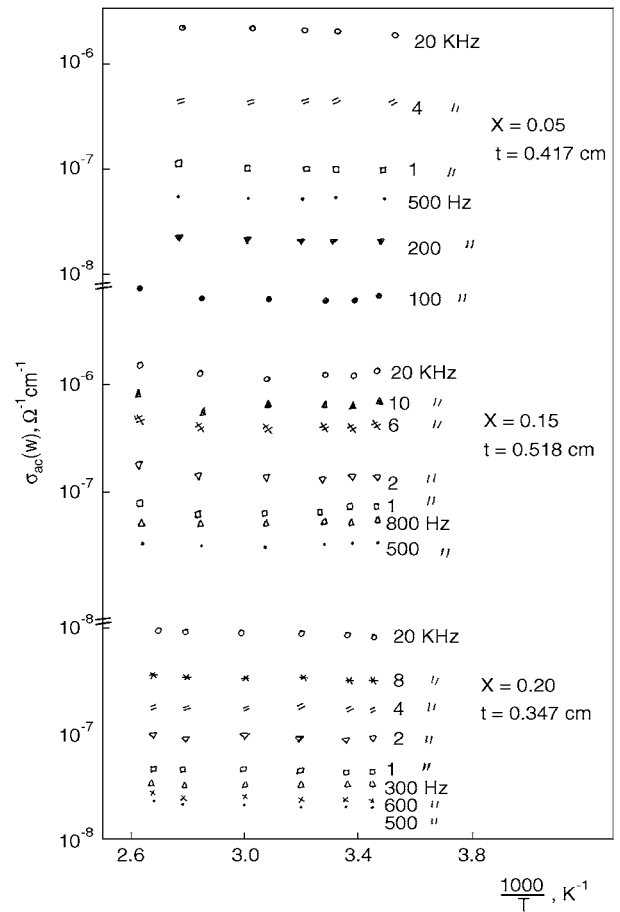*Figure 1* Variation of ac conductivity with temperature at different frequencies for, $Se_{0.75}Ge_{0.25-x}As_x$ at $x = 0.05$, 0.15 and 0.20.

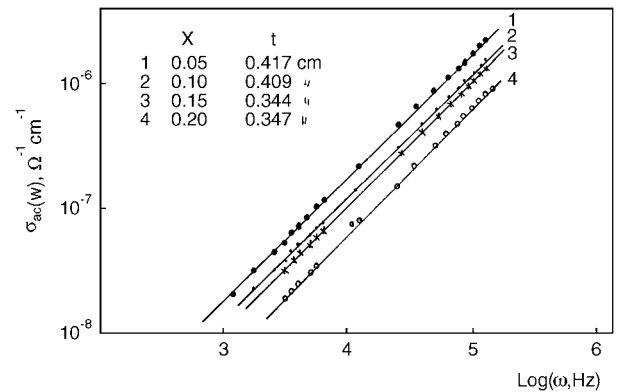*Figure 2* Frequency dependence of ac conductivity in glassy $Se_{0.75}Ge_{0.25-x}As_x$ ($x = 0.05$, 0.10, 0.15 and 0.2) at room temperature.

from the slopes of these lines, for the composition under test.

3.2. Temperature and frequency dependence of the dielectric constant

Fig. 4 shows the frequency dependence of the calculated values of the dielectric constant ε for the four alloys of our $Se_{0.75}Ge_{0.25-x}As_x$ system at constant temperature ($RT \approx 289$ K). The dielectric constant is approximately constant with increasing frequency and decreases with increasing the As contents, as shown in Fig. 4, while according to Fig. 5, the relation between the dielectric constant with temperature, and at a fixed frequency
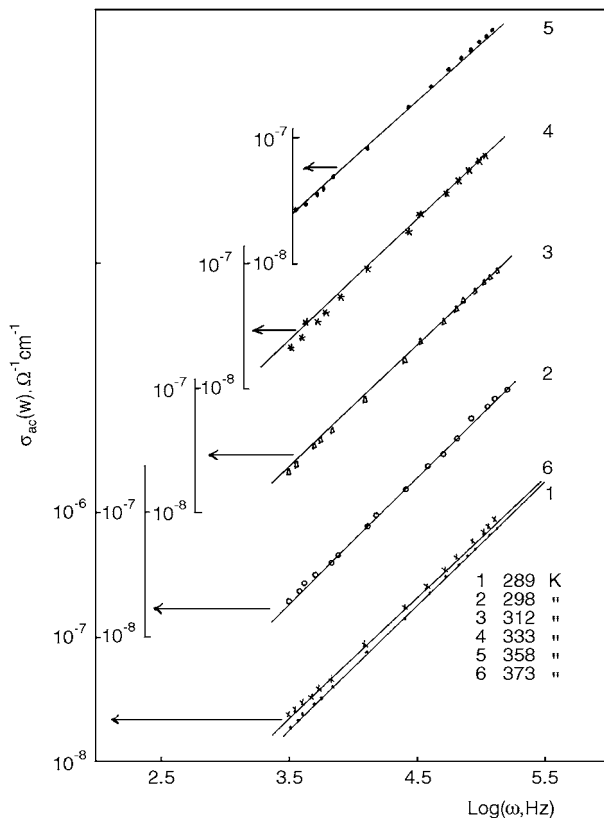
Figure 3 Frequency dependence of ac conductivity σ_{ac} (ω) in glassy $Se_{0.75}Ge_{0.25-x}As_x$ at various temperatures.
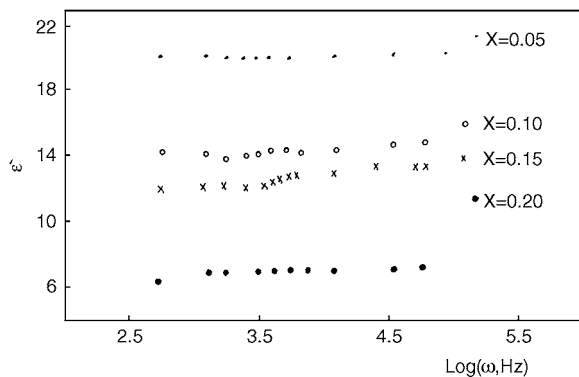
1	289	K
2	298	"
3	312	"
4	333	"
5	358	"
6	373	"

Figure 4 Frequency dependence of the real part of permittivity ε temperature (RT) for $Se_{0.75}Ge_{0.25-x}As_x$ ($0.05 \leq X \leq 0.2$) glassy system.

Figure 5 Temperature dependence of the real part ε for $Se_{0.75}Ge_{0.15}As_{0.1}$ (at 100 Hz and 100 KHz), $Se_{0.75}Ge_{0.1}As_{0.15}$ and $Se_{0.75}Ge_{0.05}As_{0.2}$ at 100 Hz.

(see Fig. 5 group a). This behavior is similar to those of semiconducting glasses.

3.3. Structural role of lone pair electrons in relation to rigidity percolation

The idea of overconstrained and underconstrained glasses was introduced by Phillips [8, 9], then developed by Thorpe [13, 14]. According to Thorpe investigation, a phase transition takes place when the average coordination number, r, of the matrix increases such that rigidity percolates the network. In calculating, r, there are several implicit assumptions; (i) each atom should have its full complement of nearest neighbors, and the coordination number follow the 8-N rule [14] where N is valence (hence Ge, As and Se are 4, 3, and 2-fold coordinated respectively); (ii) there should be no voids surfaces; (iii) density/homogeneity of sites should be approximately uniform; (iv) the number of dangling bond, should be negligible in proportion to the number of satisfied covalent bonds and (v) the chemical identity of the matrix is submerged and topological consideration are dominant. This final assumption leads to a method of constraint counting which depends on assuming that stretching and bending forces constants of covalent bonds are the major forces of the chemical network while other, weaker intermolecular, forces are ignored. For an atomic species with coordination number, r, (given in this case by $r = 2X\,Se + 4X\,Ge + 3X$ As, where X is the mole fraction) the number of constraints per atom arising from bond-bending is $N^\beta = 2r - 3$ and from bond stretching is $N^\alpha = r/2$. The total number of constraints N_{con} is the summed of the bond-bending and the bond-stretching. These constraints are summed across a matrix which has $3N$ degrees of freedom (N is the total number of atoms). The fraction of floppy modes, f, is [$3N$-constraints/$3N$] and can be rewritten in the compact form as:

$$f = 2 - (5/6)r \qquad (3)$$

At the floppy-to-rigid transition where $f = 0$, then $r_t = 2.4$, where r_t is the average coordination number of the glass composition at the theoretical percolation

$F = 100\,Hz$, tends to be temperature independent below 350 K. Above this degree ε increases with increasing the temperature as expected a dipolar system. The dipolar system have been proposed by Mott *et al.* [12] for chalcogenide glasses. According to their proposal, the states which are formed near the Fermi level in the gap, are due to dangling bonds and when $2D^0 \rightarrow D^+ + D^-$ is exothermic, then only paired defect states are found in the gap. As the temperature increases above 353 K the dipoles slowly attain freedom of rotation. Under such circumstance the σ_{ac} (ω) is expected to become temperature and frequency dependent. If the above assumption is verified then, the measured values of ε should be independent on temperature and frequency at low temperatures, whereas at higher temperatures, ε should increase with increasing temperature as expected in a dipole system and decrease with increasing frequency
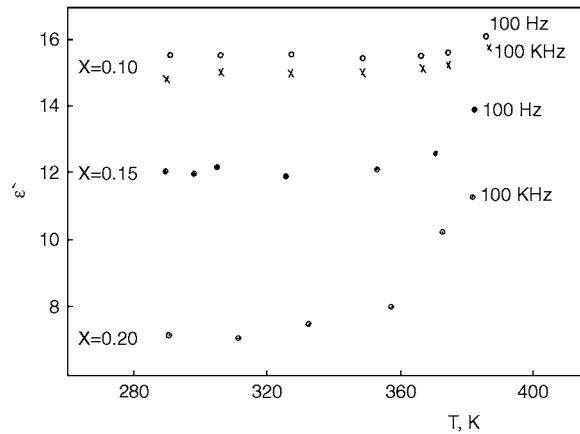
TABLE I Values of the coordination number (r), the constraints (bending N^α, stretching N^β and the total N_{con}) and the floppy (f) for the investigated compositions $Se_{0.75}Ge_{0.25-x}As_x$

Composition $Se_{0.75}Ge_{0.25-x}As_x$	r	N^α	N^β	N_{con}	f	r_t	$r - r_t$
$x = 0.05$	2.45	1.9	1.225	3.125	0	2.393	0.056
$x = 0.10$	2.40	1.8	1.2	3.0	0	2.387	0.0133
$x = 0.15$	2.35	1.7	1.175	2.875	0.042	2.380	−0.03
$x = 0.20$	2.30	1.6	1.15	2.75	0.083	2.373	−0.073

threshold. Table I shows the values of N^β, N^α N_{con} along with, r, and f for different composition of the $Se_{0.75}Ge_{0.25-x}As_x$ glassy system. Mössbauer experiments show that in $Se_{0.75}Ge_{0.25-x}As_x$, As, replaces Ge in the network. The weaker bond-bending forces in, As, allow one can ignore the associated constraints. The addition of As, thus reduces the number of constraints per atom and this allow one to tune the system through the rigidity-percolation threshold, which theory predicts to be at $r_t = 2.4$. As shown also in Table I, at $x = 0.10$, r, is equal 2.4, and the quantity f goes to zero at $r = r_t = 2.4$, of course f can not be negative and so within this simple mean field scheme we have $f = 0$ for $[r > r_t]$. In conclusion, we may say that our $Se_{0.75}Ge_{0.25-x}As_x$ glassy system is divided into two kinds of regions that are designated rigid and floppy as shown in Table I. For $x = 0.05$ and 0.10 were $[r > r_t]$ the network is rigid and we refer to it as an amorphous solids, whereas for $[r < r_t]$, at $x = 0.15$ and 0.20, the network is not rigid and can be macroscopically deformed. This is referred to as a polymeric glass. The previous section deals with the situation of neglecting the presence of dangling bond, an attempt has been made by us to calculate the average coordination number, when the dangling bond is included.

$$r_t = 2.4 - 0.4(n_1/N) \qquad (4)$$

(where n_1 atoms with coordination r ($r = 2, 3,$ or 4), and N is the total number of atoms).

According to our knowledge, there is no existing data for chalcogenide glasses in the literature available for replotting against average coordination number minus average coordination at the percolation there should $[r - r_t]$ to give a large enough range of results, most of the existing data were for chalcohalides [15]. Table I shows a comparison of the average coordination number, r, with the theoretical coordination number r_t for $Se_{0.75}Ge_{0.25-x}As_x$ glassy system A positive value in the final column indicates an overconstrained matrix and a negative value indicates an underconstrained matrix. As shown in Table I, at 10 at% Arsenic, r passes closest to the theoretical percolation threshold r_t, and for large arsenic content the matrix acquires a negative value for $[r - r_t]$ and should be under-constrained. The fact that the minimum fragility occurred at 2.4 rather than at the highest value of, r, as expected was regards by Tatsumisago et al. [16] as evidence of specific chemical effects such as double selenium bridges between germanium centers. In order to understand the above correlation in greater depth, it is necessary to discuss the structural role of lone-pair electrons in achieving the vitreous state. As we know most of the substances that

can solidify in the vitreous state are found to possess structural "bridges", that give rise to tri-dimensional, bi-dimensional or linear heteropolymeric formation. The existence of bridging atoms with lone-pair electrons can eliminate the stain force caused by the formation of the amorphous polyhedral polymer. This role of lone-pair electrons can be understood in terms of valence shell electron pair repulsion (VSEPR) theory proposed by Gillespic [17]. Because of the electrostatic repulsion and the repulsion caused by the Pauli exclusion principle, the valence electrons tend to avoid one another. If all the valence electrons of a centric atom are used to form bonds, the coordination polyhedral have a strictly symmetrical structure. The configuration of polyhedra with unshared electron pairs are similar to those of polyhedra with only shared pairs in the valence shell, except that the unshared pairs occupy a large volume than the shared pairs. The chemical bonds with lone-pair electrons have a character of flexibility. It is easier to deform a bond with lone-pair electrons than a bond with no unshared electrons. Increasing the number of lone-pair electrons decreases the strain energy in a system and structures with large numbers of lone-pair electrons favor glass formation. In order to calculate the number of lone-pair electrons of a chalcogenide glass system, we must introduce the average coordination number proposed by Phillips [8]. The unshared lone-pair electrons equal all the valence electrons of the system minus the shared electrons, i.e.:

$$L = V - r \qquad (5)$$

where L and V are the lone-pair electrons and the valence electrons, respectively. The number of lone-pair electrons of our $Se_{0.75}Ge_{0.25-x}As_x$ glassy system can be obtained according to equation 5; the results are listed in Table II. It seem from the above table that the number of lone-pair electrons increases continuously with the increase in the content of, As, in the $Se_{0.75}Ge_{0.25-x}As_x$ system. We can conclude from the results given above, that some lone-pair electrons in the structure of a system is a necessary condition for obtaining the system in a vitreous state. Liang [18] introduced a simple criterion

TABLE II Values of (r), valence electron (V) and lone-pair electrons for the system under test

Composition $Se_{0.75}Ge_{0.25-x}As_x$	r	V	L
$x = 0.05$	2.45	5.5	3.1
$x = 0.10$	2.40	5.6	3.2
$x = 0.15$	2.35	5.65	3.3
$x = 0.20$	2.30	5.7	3.4

for computing the ability of a chalcogenide system to retain its vitreous state. The criterion contains the number of lone-pair electrons which is necessary for obtaining the system in its vitreous state, for a ternary system the number of lone-pair electrons must be larger than 1. The obtained data given in Table II agrees with the former suggestion given by Liang.

3.4. The relation between the average heat of atomization the optical gap and the coordination number

According to Pauling [9] the heat of atomization H_s (A-b) at standard temperature and pressure of a binary semiconductor formed from atom A and B is the sum of the heat of formation ΔH and the average of the heats of atomization H_s^A and H_s^B that corresponds to the average non-polar bond of the two atoms [10, 11]

$$H_s(A - B) = \Delta H + (1/2)\left(H_s^A + H_s^B\right) \quad (6)$$

The first term in Eq. (6) is proportional to the square of the difference between the electronegativity χ_A and χ_B of the two atoms:

$$\Delta H \propto (\chi_A - \chi_B)^2 \quad (7)$$

In order to extend this idea to ternary and higher order semiconductor compounds, the average heat of atomization H_S is defined for the compound $A_\alpha B_\beta C_\delta$ as a direct measure of the cohesive energy and thus of the average bond strength, as [12, 13]:

$$H_s = \frac{\left(\alpha H_s^A + \beta H_s^B + \delta H_s^C\right)}{\alpha + \beta + \delta} \quad (8)$$

In the few materials for which it is known, the amount of the heat of formation ΔH is about 10% of the heat of atomization and therefore is neglected. Hence, H_s (A-B) is given quite well by:

$$H_s(A - B) = (1/2)\left(H_s^A + H_s^B\right) \quad (9)$$

The results of H_s for $Se_{0.75}Ge_{0.25-x}As_x$ with $x = 0.05, 0.10, 0.15,$ and 0.20 using the values of H_s for Se, Ge and, As (the H_s values used are in units K cal/gm-atom are 49.4 for Se, 90 for Ge and 69 for As) are listed in Table III. As seen from Table III, the value of H_s decreases with the addition of, As. In chalcogenide glasses containing a high concentration of a group VI element, the lone-pair electrons form the top of the valence band and the antibonding band forms the conduction band [24]. It is therefore interesting to relate the optical gap ΔE_g with the chemical bond energy, and the parameters we use to specify the bonding are H_s and, r. The relation between the energy gap and the average heat of atomization was discussed by Aigrain *et al.* [25]. According to their study there exists a linear correlation that can be expressed for the semiconductor of the diamond and Zinc-blend structure by:

$$\Delta E_g = a(H_s - b) \quad (10)$$

TABLE III Effect of heat atomization (H_s), (r) and optical gap (ΔE_g) on investigated system

Composition $Se_{0.75}Ge_{0.25-x}As_x$	H_s Kcal/g-atom	r	H_s/r Kcal/g-atom	ΔE_g (eV)
$x = 0.05$	58.50	2.45	23.87	1.98
$x = 0.10$	57.45	2.40	23.93	1.88
$x = 0.15$	56.40	2.35	24.00	1.81
$x = 0.20$	55.35	2.30	24.06	1.71

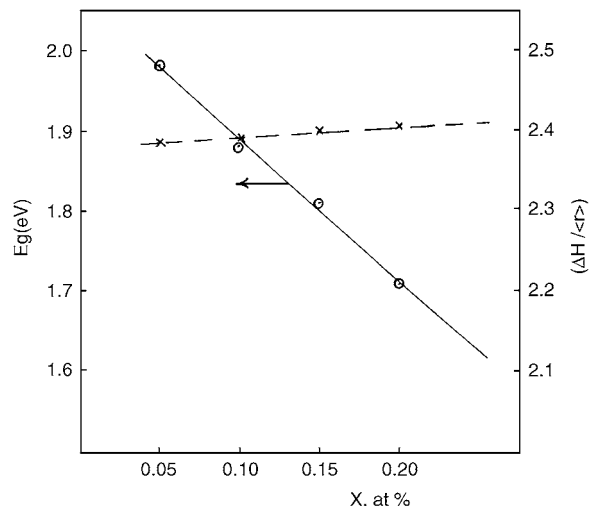*Figure 6* The optical gap E_g and the average heats of atomization per single bond H_s/r in $Se_{0.75}Ge_{0.25-x}As_x$ as a function of the composition parameter x%.

where a and b are characteristic contents. In order to emphasize the relationship between the optical gap ΔE_g and H_s, we used the optical gap of $Se_{0.75}Ge_{0.25-x}As_x$ given in [10] and are listed in Table III. Data listed in Table III reveals that the addition of As leads to the decrease of H_s as well as ΔE_g. Furthermore, since the correlation between ΔE_g and H_s is very important, we compare ΔE_g with $[H_s/r]$, the average single-bond energy in the alloy, which is easily computed from the value of each composition. Fig. 6 represents ΔE_g in the $Se_{0.75}Ge_{0.25-x}As_x$ glassy systems as a function of compositional parameter x%. The relation between $[H_s/r]$, "the dashed curve" for the same system is also plotted as a function of composition parameter x. In the glassy system no pronounced dependence of ΔE_g on x is observed. This to be expected because the strengths of the three bonds Ge-Se, As-Se and Se-Se are nearly in the same order: 49.4, 41.69 and 44 K cal mole^{-1}, respectively [26]. If there is a linear relationship between the bond strength and the average band gaps, and if one allows superposition to describe the compounds, then the addition of (As-Se) to $Se_{0.75}Ge_{0.25-x}As_x$ will affect the average band gap. By adding As to our glassy system, the average bond strength of the compound decreases, and hence E_g will decrease.

Hurst and Davis [27] explained these results by suggesting that when the bond energies in the alloy are not very different, the increase in disorder associated with deviation from stoichiometry will tend to push the mobility edges further into the bonds (Anderson transition) thereby increasing ΔE_g. Furthermore, comparing ΔE_g

TABLE IV The ac conductivity σ_{ac} (ω), the activation energy (ε), the barrier height (W_m) with glass transition for the compositions under test

Composition $Se_{0.75}Ge_{0.25-x}As_x$	σ_{ac} (ω) $(\Omega cm)^{-1}$	ε	W_m (eV)	r	H_s Kcal/g-atom	T_g (C°)
$x = 0.05$	1.1×10^{-7}	20.2	2.66	2.45	58.50	273
$x = 0.10$	7×10^{-8}	14.8	1.726	2.4	57.45	248
$x = 0.15$	6.2×10^{-8}	13.3	1.684	2.35	56.40	165
$x = 0.20$	4×10^{-8}	7.2	1.682	2.3	55.35	148

with H_s given in Table III, we can find a decrease in ΔE_g with H_s on increasing $x\%$ of our $Se_{0.75}Ge_{0.25-x}As_x$ system. But according to [28], ΔE_g for overconstrained materials with higher connectivity $4 \geq r \geq 3$, depends more strongly on H_s than for glasses with lower connectivity $3 \geq r \geq 2$. These results suggest that the parameter H_s/r has a very small effect on ΔE_g, which was confirmed in our study "see dashed curve in Fig. 6", since H_s/r is approximately constant with x and ΔE_g has no pronounced dependence also with the composition parameter $x\%$.

4. Analysis of results
The present values of σ_{ac} (ω) are considered to be temperature independent, however it has a linear variation with the frequency as observed in the present results of our Se Ge As glassy system. The dependence of the frequency exponent (s) on temperature shown in Fig. 3 indicates that the values of the exponent (s) decreases from 1.02 to 0.94, these results are consistent with Elliott's general features, concerning the amorphous semiconductor nature. The observed behavior of $s(T)$ may be analyzed by assuming that ac conduction mechanism is the correlated barrier hopping (CBH) model, which allow us to consider, according to Elliott [5] that, the hopping species to be double-occupied bipolaron states as investigated in the work of Mott *et al*.[12]

It is interesting to note that also the dielectric constant according to Figs (4 and 5) are temperature independent on temperature below 353 K, and above the previously mentioned degree ε starts to increase, this behavior appear to be influenced considerably by the effect of dangling bonds. This idea have been applied to amorphous semiconductors by Mott *et al*. [12, 29, 30]. The temperature dependence of (s) is also consistent with the following law proposed by Long [30]

$$1 - s = (6kT)/W_m \qquad (11)$$

where k is the Boltzmann's constant, T is the temperature in K and W_m is the energy required to move the electron from site to infinity.

The calculated values of W_m are given in Table IV for all the different compositions of our Se Ge As glassy system, in comparison with σ_{ac}, ε, H_s, r, and T_g. The data listed in Table IV reveal that the addition of As and hence the submission of Ge leads to a decrease in all the parameters mentioned above. In this respect T_g is related to the coordination number r, since r indicates the average number of bonds that need to be broken in order to obtain fluidity, a decrease in r, leads to a de-

crease in T_g. Thorpe and co-workers [13, 14] suggested that glasses having a higher chalcogen content are mechanically soft, these glasses can be compressed easily without costing much energy. Also the decrease of σ_{ac}, ε, as well as W_m with the increase of As content could be explained qualitatively by assuming a decrease in the bond energy, which was discussed in Section 3–4 and consequently confirmed by the decrease of H_s with the increase of As content, and as we know H_s is defined for a compound as a direct measure of the cohesive energy and thus of the average bond strength and hence we suppose that this contribution of H_s is relevant to the covalent bond approach and is proportional to some overall mean bond energy. We believe that the agreement between the theoretical and experimental results is excellent, even when the dangling bonds are included in a very simple way and adjusted to bring the coordination number to the correct coordination r_t. In conclusion we can say that the discussion given above helps us to understand the correlation between the theoretical and experimental results more deeply.

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