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Theoretical and experimental study of the conduction mechanism in Sb_2 Se_3 alloy

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To understand the nature of Sb_2 Se_3 semiconductor as a bulk sample, the X-ray diffraction study was carried out to identify the sample structure. Dc and ac electrical properties measured in the temperature range 290–370 K, and frequency range 10^2–10^5 Hz were the subject of the present work. Properties such as dielectric constant $\zeta^{\backslash}$, loss function tanδ, and electrical conductivities σ_{ac} as a function of both frequency and temperature are reported. Different models of electrical conduction in semiconductor materials have been used to explain the observed results. A trail has been made to correlate the results of this paper with the average heat of atomization H_S and the average coordination number M. The experimental and theoretical investigation is in accordance with Liang criterion.

1. Introduction

Antimony selenide Sb_2 Se_3 owing to its good photconducting properties and high thermoelectric power [1] has wide applications to optical devices and thermoelectric cooling devices [2]. Many attempts have been made to investigate the electrical and optical properties [3–5] of Sb_2 Se_3 and other glasses [6], but observations were not consistent enough for the exact carrier mechanism to be ascertained. Works on the ac conductivity and the dielectric properties of Sb_2 Se_3 have not been considered in any extend way for separate studies of its electrical properties. Generally the electrical property of semiconductors depends on the chemical composition and the structural features. In fact the chemical bond approach was very useful in predicting the semiconductor properties of different compounds having polycrystalline structure [7]. This paper offers a critical analysis on the basis of experimental and theoretical results. The investigations of the (ac & dc) conductivities as well as the dielectric constants provide a fundamental method for studying the hopping processes involved in conduction. The results have been interpreted in terms of some theoretical calculations, which seems to explain the experimental results in greater depth.

2. Experimental technique

Antimony selenide in a bulk form was synthesized by melting the elemental components of high purity (99.999%) in evacuated silica tube (10^{-5} Torr) in an oscillatory furnace according to a technique reported previously in [4, 5] The proper ingot was confirmed to be crystalline nature using X-ray diffraction given in [4]. Polished bulk sample in the form of pellet thickness 2.72×10^{-3} m and an area 9.56137×10^{-6} m^2 was used for the measurements of ac and dc conductivity. These measurements were made between a temperature range (290–370 K). The total conductivity σ_{tot} was measured on automatic RCL meter (PM 6304 Phillips) and ac conductivity. The $\sigma_{ac}(\omega)$ was calculated by using Equation 1, where σ_{dc}(dc conductivity) was measured using a Keithly electrometer (type E 616A). The measurements were made by using a simple electrical circuit provided with a digital electrometer and a micro digital multimeter (TE 924), to measure the respective potential drop and the current passing through the sample. Also, the circuit was provided with a heater for sample heating and a thermocouple for measurements of temperature. The dielectric constants ($\zeta^{\backslash}$, $\zeta^{\backslash\backslash}$), the dielectric loss tangent (tan $\delta = D$) and ac conductivity σ_{ac} as a function of temperature (290–370 K) and frequency (500 H-100 KH) were measured using a programmable automatic RCL meter which measures the impedance z, the capacitance C_x and (tan δ) directly.

The ac conductivity $\sigma_{ac}(\omega)$ is determined by the relation [8]

$$\sigma_{ac}(\omega) = \sigma_{tot}(\omega) - \sigma_{dc} \qquad (1)$$

where σ_T (ω) is the total conductivity which calculated from the relation

$$\sigma_T(\omega) = (d/A)(1/Z) \qquad (2)$$

Where d, A, Z are the thickness, the cross-sectional area of the parallel surface and the total impedance of the sample respectively and σ_{dc} is the dc conductivity, which is related to the electrical resistance (R) by the relation

$$\sigma_{dc} = d/RA \qquad (3)$$

The dielectric constant $\zeta^{\backslash}$ (real part) was calculated using the relation

$$\zeta^{\backslash} = C_x d/\zeta_o A \qquad (4)$$

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where ζ_o is the permitivity of the free space having the value 8.85×10^{-12} F/m.

The imaginary part of the dielectric constant $\zeta^{\backslash\backslash}$ was calculated using the relation [8]

$$\zeta^{\backslash\backslash} = \zeta^{\backslash}(\tan\delta) \quad (5)$$

3. Results and discussion

3.1. Experimental part

The dielectric constants, the ac conductivity at different frequencies in the range 10^2–10^5 Hz, in the temperature range 290–370 K are reported in Figs 1–5. The dielectric constant decreases with increasing frequency as shown in Fig. 3b and increases with increasing temperature as shown in Fig. 3a. These values of the dielectric constant could be explained qualitatively by assuming a decrease in the bond energies. The origin of this behavior will be discussed later. In the low frequency range, $\sigma(\omega)$ does change slightly as shown in Fig. 1. In contrast, at low temperature the ac conductivity tends to be weakly temperature dependent. However, at higher temperatures the dependence of the ac conductivity on temperature becomes strong.

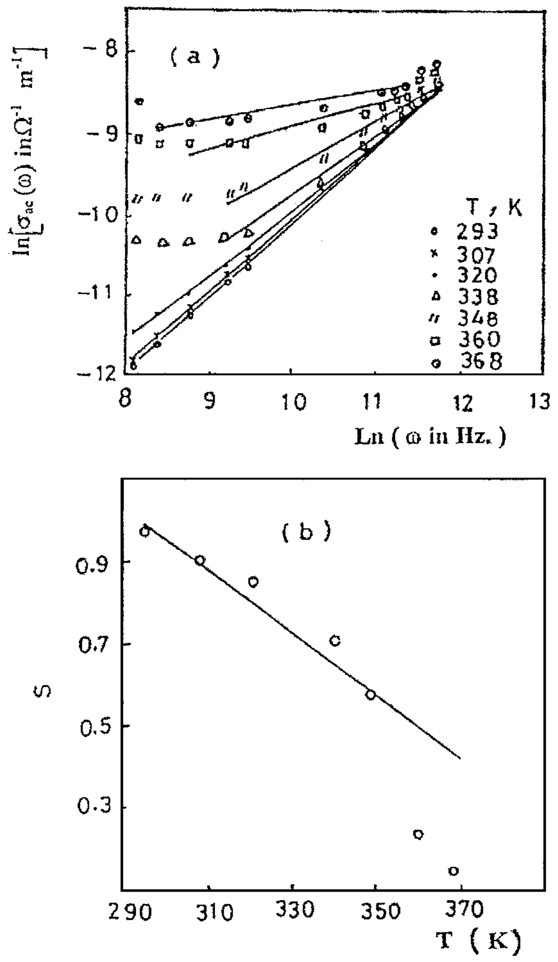

Figure 2 (a) Frequency dependence of $\sigma_{ac}(\omega)$ at different temperature and (b) The frequency exponent s as a function of temperature for Sb_2 Se_3 bulk sample.

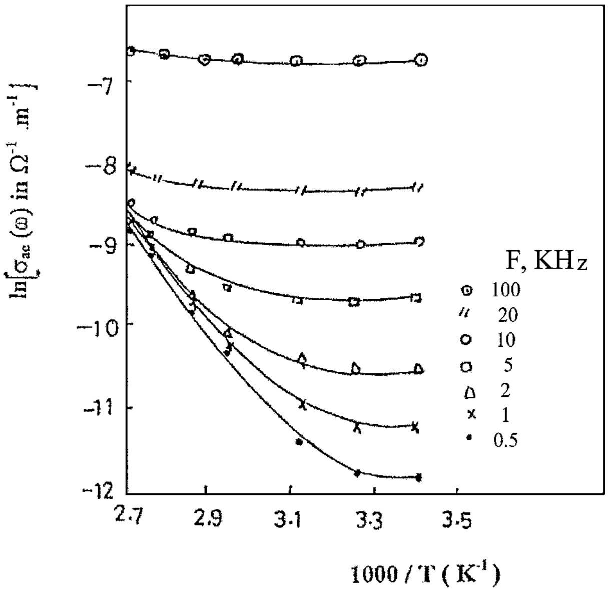

Figure 1 Ac electrical conductivity as a function of $1000/T$, in the temperature range 290–370 K for Sb_2 Se_3 bulk sample at different frequencies.

Generally the dc & ac conductivities as well as the total conductivity can be studied according to the relations 1, 2 and 3. A common feature to all the semiconductors is that the ac conductivity $\sigma_{ac}(\omega)$ increases with the frequency according to $\sigma_{ac}(\omega) = A\omega^s$ where A is constant and s is the frequency exponent which explain the behavior of chalcogenide glasses [9, 10]. Fig. 2a represents the dependence of Ln $\sigma_{ac}(\omega)$ on Ln(ω) at different temperatures for Sb_2 Se_3 alloy. The values of the exponent (s) were calculated from the slopes of these lines. It has been observed from Fig. 2b that (s) decreases linearly with increasing temperature, and its values are less than unity. The frequency dependence of $\sigma_{ac}(\omega)$, which rises almost linearly with frequency is most likely due to hopping of two electrons between two pairs of localized state at the Fermi Level. The fact that (s) is temperature dependent indicates that the bipolaron conduction is thermally activated process, which is phonon assisted. However, the ac conductivity may be analyzed by assuming the model proposed by Pike [11]. In this model, the carrier's motion is characterized by an activation energy W that is equivalent to height of the potential barrier. Elliott *et al.* [12–14] has given a different theories of ac conduction for chalcogenide materials, based on Pike's model [11], he rules out the possibility of tunneling and considers hopping of carriers between two sites over a barrier separating them. Elliott considered the hopping species to be doubly–occupied, by bipolaron state as envisaged in the work of Mott *et al.* [15] and Kastner *et al.* [7] as well as the theory based on the hopping between the short-range order clusters of crystalline state given by [16]. The real and imaginary parts of the dielectric constants ($\zeta^{\backslash}$, $\zeta^{\backslash\backslash}$) at different frequencies and at different temperature range are reported [9, 17–20]. The real part of the dielectric constant $\zeta^{\backslash}$ at different frequency and temperature are illustrated in Fig. 3 (a&b). The measured values of $\zeta^{\backslash}$ can be explained by assuming a decrease in the bond energies, on the other hand, we can not ignore the effect of temperature on the dipolar system, whereas at higher temperature the dipoles are attaining rotational freedom, and hence the dielectric constant should decrease with increasing frequency and increase with increasing

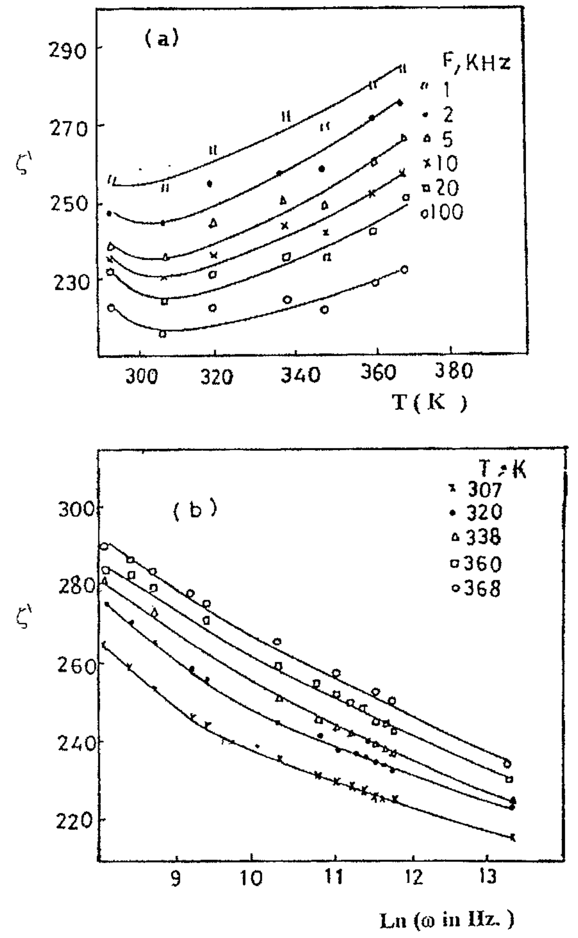

Figure 3 (a) Temperature dependence of the real part of the dielectric constant $\zeta^{\backslash}$ At different frequencies and (b) Frequency dependence of $\zeta^{\backslash}$ at different temperatures for $Sb_2\,Se_3$ bulk sample.

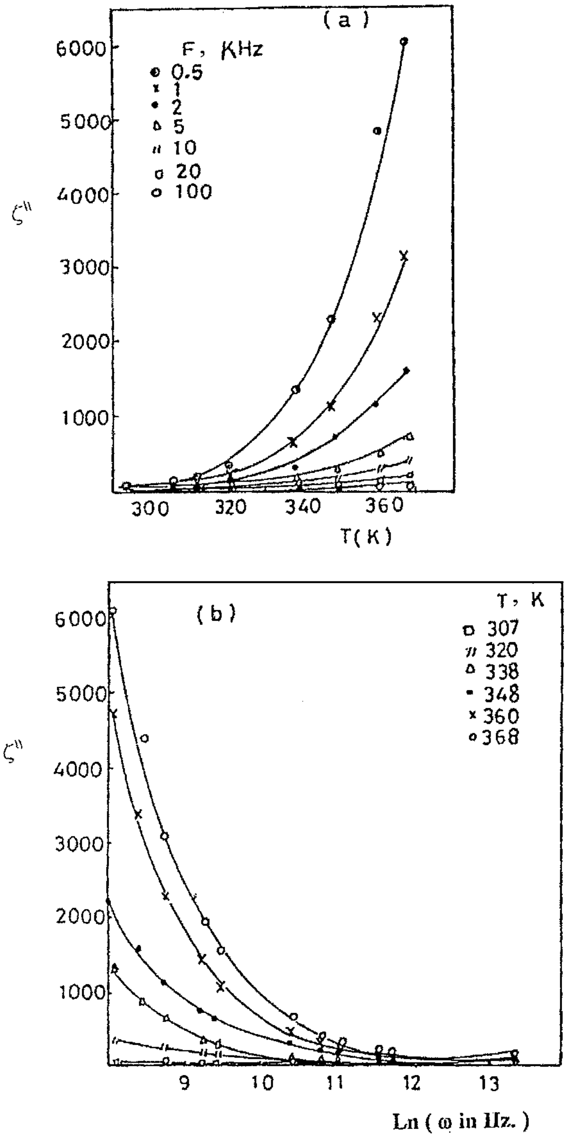

Figure 4 (a) The imaginary part of the dielectric constant $\zeta^{\backslash\backslash}$ as a function of temperature and (b) Frequency dependence of $\zeta^{\backslash\backslash}$ at different temperature for $Sb_2\,Se_3$ bulk sample.

temperature [8, 19]. Also the imaginary part of the dielectric constant $\zeta^{\backslash\backslash}$ can be calculated from Equation 5 and it is plotted against the temperature for different frequencies in Fig. 4a. It is shown that $\zeta^{\backslash\backslash}$ increases as the temperature increases for the considered frequencies. At low temperature (300–320 K), this increases is linear and the variation of $\zeta^{\backslash\backslash}$ with the frequency is small. This linear region extent to higher values of temperature with increasing the frequency, while at higher temperatures (320–360 K), the increases of $\zeta^{\backslash\backslash}$ with temperature is non linear and the variation of $\zeta^{\backslash\backslash}$ is large with increasing the frequency. This behavior can be clarified by plotting $\zeta^{\backslash\backslash}$ against (Ln ω) for various temperatures as shown in Fig. 4b. It was found that $\zeta^{\backslash\backslash}$ follow a power law with frequency according to the relation [20]

$$\zeta^{\backslash\backslash} = A\omega^m \qquad (6)$$

According to Giuntini *et al.* [9, 20], $\zeta^{\backslash\backslash}$ at a particular frequency in the temperature range where dielectric dispersion occurs, is given by:

$$\zeta^{\backslash\backslash}(\omega) = (\zeta_o - \zeta_\infty)2\pi^2 N\left(ne^2/\zeta_o\right)^3 kTt_o^m W_m^4 \omega^m \qquad (7)$$

With $m = -4\pi kT/W_m$, n is the number of electrons that hop, N is the concentration of localized states, ζ_o is the static dielectric constant, ζ_∞ the dielectric constant at "infinitely high" frequencies, k is Boltzmann's constant, T is the absolute temperature, t_o is the characteristic relaxation time, ω is the angular frequency and W_m is the energy required to move the electron from one site to the infinite. The relation between ln$\zeta^{\backslash\backslash}$ and lnω gives straight lines for various temperature for the $Sb_2\,Se_3$ bulk sample are shown in Fig. 5a. The slopes of these lines allow the values of the parameter m as listed in Table I to be determined. Taking into account the expression of m, already calculated, we expect a linear decrease of this exponent with increasing temperature. Fig. 5b shows that the experimental values of m vary

TABLE I The values of m and S as a function of temperature for $Sb_2\,Se_3$ Alloy

T (K)	m	s
293	−0.526	0.92
307	−0.588	0.89
320	−0.714	0.85
338	−1.000	0.79
348	−0.869	0.70
360	−0.952	0.65
368	−0.952	0.53

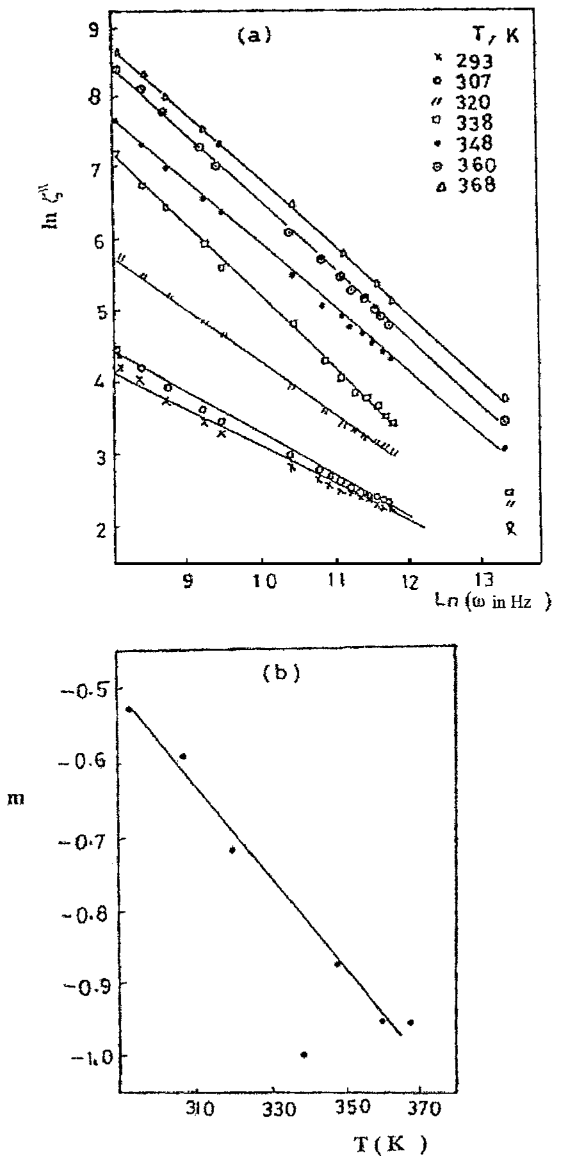

Figure 5 (a) Ln $\zeta^{\backslash\backslash}$ against Ln ω for different temperature and (b) Temperature dependence of the experimental values of m for Sb_2 Se_3 bulk sample.

linearly with T. It can be seen that the experimental study of $\zeta^{\backslash\backslash}$ at variable frequency and temperature of the Sb_2 Se_3 alloy allows a law to be formulated that can be expressed as $\zeta^{\backslash\backslash} = A\omega^m$. The use of some hypotheses coming from a phenomenological theory developed within the study of electrical conductivity [4, 5], led us to propose a simple theoretical model, correctly explaining the experimental results and allowing expression of the empirical law connecting $\zeta^{\backslash}$ and ω to be obtained. Moreover, a new explicit form of the parameter m appears, which acceptably confirms the observed variations as a function of the measuring temperature. In fact, this results is satisfying, if we consider the empirical law [21] $\sigma_{\mathrm{ac}}(\omega) = \omega\zeta(\omega) = A\omega^s$. It is obvious that if s is temperature dependent [12], m should consequently depend on T. According to Fig. 2a the values of s as a function on temperature can be determined and are listed in Table I:

If we assume that s is temperature dependent [18], then it can be written as,

$$s(T,\omega) = 1 - \frac{\nu kT}{w_g + kT\ln(\omega\tau_o)} \tag{8}$$

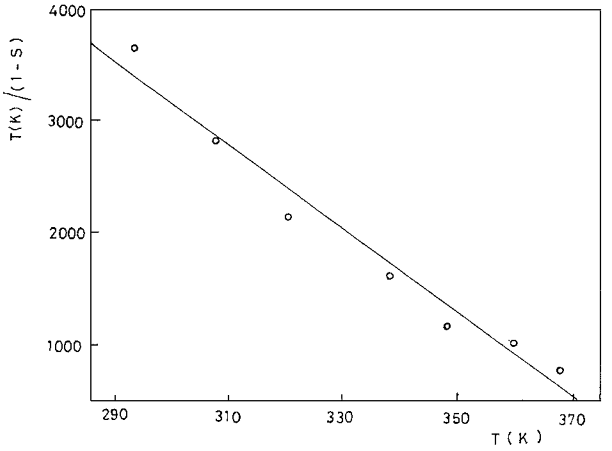

Figure 6 The relation between $T/(1-s)$ against T for the Sb_2 Se_3 alloy.

The gap energy W_g can be obtained by plotting Fig. 6

$$\frac{T(K)}{1-s} f(T) \tag{9}$$

Then W_g occurs to be equal to: $W_g = \gamma$. 1.23 eV. Where γ is a scalar parameter, which characterizes the environment of the potential well in which the charge is trapped.

3.2. Theoretical part

The electronic states of a solid may be considered to first order, as a broadened superposition of the molecular orbital state of the constituent bonds. In the solid, these molecular states are broadened into bonds. 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 [7]. It is therefore interesting to relate the chemical bond energy with three parameters that specify the bonding, the average coordination number M, the number of lone-pair electrons L and the average heats of atomization H_S. Experimental results obtained in standard X-ray diffraction patterns for a non-crystalline system [22] show that the local structural unit in the nearest neighbor coordination sphere for amorphous semiconductors is almost the same as that for crystalline semiconductors. Moreover, Ioff and Regel [23] suggested that the bonding character in the nearest–neighbor region, which means the coordination number, characterizes the electronic properties of semi conducting materials. For a binary system the average coordination number M proposed by Phillips [24] is defined as

$$M = XN_{\mathrm{co(A)}} + (1-X)N_{\mathrm{co(B)}} \tag{10}$$

Where $N_{\mathrm{co(A)}}$ and $N_{\mathrm{co(B)}}$ are the coordination number of A and B atoms, and X is the mole fraction. The coordination number of Sb is five; the large coordination number of Sb makes the coordination number of Se increases from two to three in chalcogenide Sb_2 Se_3. This increase may be the result of the interaction between the Sb ion and the lone-pair electrons of a bridging Se atom.

TABLE II The average coordination number M, the valence electrons V and the lone-pair electron L for $Sb_2\,Se_3$ alloy

System	M	V	L	Ability
$Sb_2\,Se_3$	3.8	5.6	1.8	–

The interaction decreases the role of lone-pair electrons in the glass formation. The observation of the increase of N_{co} of Se from two to three is in agreement with the measurement for the Sn-Ge-Se system given in [24, 25] as well as for Ge-Se-In system given in [26]. The discussion above shows that Lone-pair electrons have an important role in chalcogenide glass formation. In order to calculate the number of lone-pair electrons of a chalcogenide, the unshared lone-pair electrons equal all the valence electrons of the system minus the shared electron i.e.

$$L = V - M \tag{11}$$

where L and V are the lone-pair electrons and valence electrons respectively. The series ($As_2\,Se_3$, $As_2\,Te_3$, $Sb_2\,Se_3$ and $Bi_2\,Se_3$) have the same valence electrons [27]. The number of lone-pair electrons of $Sb_2\,Se_3$ can be obtained according to Equation 11; the results are listed in Table II.

The glass-forming tendency of a compound or a system has a relation with its lone-pair electrons. The stable vitreous state can be obtained only if enough L exists in the system. Liang [28] introduced a simple criterion 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 binary system, the number of lone-pair electrons must be larger than 2.6 [28]. The obtained data given in Table II agrees with the former suggestion given by Liang and was also confirmed by the differential thermal analysis DTA given in [4] and the XRD results [5] which show that the ingot is partially crystalline and hence the ability in the last column in Table II is negative indicating that the system can not form glass at the ordinary rate. According to Pauling [29], the heat of atomization H_S (A – B) at standard temperature and pressure of a binary semiconductor formed from atoms 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 energy of the two atoms [29]

$$H_S(\mathrm{A}-\mathrm{B}) = \Delta H + 1/2\left(H_S^{\mathrm{A}} + H_S^{\mathrm{B}}\right) \tag{12}$$

The first term in Equation 11 is proportional to the square of the difference between the electro negativities χ_A and χ_B of the two atoms A and B,

$$\Delta H \alpha (\chi_{\mathrm{A}} - \chi_{\mathrm{B}})^2 \tag{13}$$

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 is therefore neglected. Hence, H_S (A – B) is given quit well by

$$H_S(\mathrm{A}-\mathrm{B}) = 1/2\left(H_S^{\mathrm{A}} - H_S^{\mathrm{B}}\right) \tag{14}$$

TABLE III The average heat of atomization H_S, the average coordination M, the average heat of atomization per single bond H_S/M and the optical gap E_g for different compositions of Sb Se alloy

Composition	H_S (kcal/ g · atom)	M	H_S/M	E_g (eV) Ref. [30]	$E_g \cdot$ eV Ref. [31]
$Sb_{0.075}\,Se_{0.925}$ [30]	50.35	2.075	24.27	1.75	1.80
$Sb_{0.20}\,Se_{0.80}$ [30]	51.92	2.200	23.60	1.53	1.55
$Sb_{0.40}\,Se_{0.60}$	54.44	3.800	14.32	1.23	1.40

The results of H_S of $Sb_2\,Se_3$ using the values of H_S for Sb and Se are listed in Table III. Where the H_S values used for Sb and Se in kcal/g · atom are 62 and 49.4 respectively.

In order to understand the effect of Sb% in $Sb_2\,Se_3$ on the previously calculated parameters, it is interesting to compare the calculated H_S of the system under test with the previously obtained results of $Sb_{0.075}\,Se_{0.925}$ and $Sb_{0.20}\,Se_{0.80}$ given in Ref [30]. Data listed in Table III reveal that the addition of Sb leads to a change in the considered properties. The increase of Sb leads to the increase in H_S and M where as E_g and H_S/M, decrease. "H_S/M is the average single-bond energy in the alloy". According to Wood *et al.* [31], a linear function of the compositional dependence of the optical gap of $Sb_x\,Se_{1-x}$ films was observed except for the hump near the stoichiometric composition $Sb_2\,Se_3$ (40 at% of Sb). Wood *et al.* [31] suggested that this hump is associated with an ordering in the amorphous phase into molecular units corresponding to the crystalline form [32], but this is not supported by Mössbouer measurement [33]. It can also observed from Table III that there is remarkable changes in H_S, M and H_S/M with the increasing of Sb content. In other word we find that $Sb_x\,Se_{1-x}$ system with higher connectivity, $4 \geq M \geq 3$, depends more strongly on H_S than for lower connectivity, $3 \geq M \geq 2$. We propose the following explanation for this observation. The types of bonds expected to occur in $Sb_x\,Se_{1-x}$ system are Se—Se ($D = 44$ kcal/mol), Sb—Se ($D = 42.9$ kcal/mol) and Sb—Sb ($D = 30.2$ kcal/mol), the addition of Sb—Sb bonds to a stoichiometric compound containing only Sb—Se bonds, leads to the decrease of the average bond strength of the compound. As seen in Table III, H_S/M decreases with the increase of Sb content, it is also predicted that the system exhibits a tendency for chemical ordering which tend to form microscopic molecular species such as $Sb_2\,Se_3$ [33].

4. Conclusions

Conductivity and dielectric constants for $Sb_2\,Se_3$ alloy have been made at various temperature and frequency. Existing theories of ac conduction have been analyzed for interpretation of the present results and it was found that Mott's [15] concept of the hopping carriers between the short range order clusters of crystalline state [16] according to Pike model [11] could explain our experimental results. The theoretical results is also consistent with the experimental ones, where we attributed the high values of dielectric constant, and the overall behavior "the decrease with increasing frequency" by assuming a decrease in the bond energies. This assumption was confirmed by the decrease of H_S/M "the average bond strength of the compound" with the increase of Sb content (see Table III). The magnitude of the average heat of atomization H_S and the average coordination number M, the number of lone-pair electrons can further help us to understand the effect of adding Sb in Sb_x Se_{1-x} composition on theoretical and experimental correlation more deeply.

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