

THEORETICAL OBSERVATION ON THE EXPERIMENTAL DATA OF Ge-Se-Tl SYSTEM

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Understanding of the effect of addition Tl on glassy Ge-Se have been experimentally and theoretically investigated. The correlation between the optical gap E_g^{opt} , the activation energy ΔE_σ , the pre-exponential factor σ_o and theoretical calculations has greatly improved with the advent of several structural and chemical models which predict the influence of such an addition, in terms of the average number of constrains N_{con} , the effective average coordination number $\langle r_{eff} \rangle$, the average heat of atomization H_s , the glass forming ability and the number of Lone-pair (LP) electrons. The decrease in ΔE_σ and σ_o with increasing Tl content has been discussed on the basis of structural changes in Ge-Se which leads to a readjustment in the local environment. Thallium is supposed to form states different from the valence states of elements interacting with Ge-Se according to the octet rule (8-N). A correlation has been found between the Ge-Se-Tl glassy system and the number of LP electrons. The stable vitreous state can be obtained only if enough lone-pair electrons exist in the structure of the glassy system. A simple criterion for computing the ability of a semiconductor system to retain its vitreous state is proposed. Investigation of the experimental data of the Ge-Se-Tl glassy system revealed that N_{con} and $\langle r_{eff} \rangle$ has a strong effect on these properties and this supports the above analysis.

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1. Introduction

The glasses of the system Ge-Se-Tl are among the new generation of chalcogenide glasses. Chalcogenide glasses have been intensively investigated because of their technological properties. Structural, electrical and optical properties as a function of addition of Tl on the Ge-Se system has been studied by several authors [1-16]. Chalcogenide glassy semiconductors have several useful properties that show a continuous change in physical properties with change in chemical composition. Chemical bonds determine the structures and all the properties of a body in any state of aggregation. Therefore, it should be clear that the most complete and general results will be obtained by adopting this course. Another consequence of the consideration above, is the effect of the chemical ordering in determining the structure as compared to the influence of mechanical forces such as, strain associated with bond distortions, bond-stretching forces acting as mechanical constrains are present in Ge, Se and Tl, bond-bending constraints are also important in Ge, Se and Tl, it is this fact which make Ge-Se-Tl a useful glass system to study. In the present work, an attempt has been made to evaluate the correlation between the previously published experimental data with the chemical bonds in some detail based on bond-bending N^b , bond-stretching N^s , average number of constrains N_{con} , average effective coordination number $\langle r_{eff} \rangle$ and other related parameters.

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2. Experimental

The samples of the Ge-Se-Tl system were prepared by direct mono-temperature synthesis in evacuated at 1.33×10^{-3} Pa silica ampoules. The starting components were of purity (5N) for Ge, Se and Tl. The final synthesis temperature was 1000 °C for 6 h with continuous rotation for furnace to ensure the homogenization of the composition. The ampoules were then quenched in icy water. The chemical composition of both bulk and thin film material was monitored by carrying out quantitative analysis energy dispersive spectroscopy, (EDX) on a Jeol 6400 scanning electron microscope with a link-exl EDS detector. The data was processed through a ZAF correction program contained with the link-exl package. These measurements were used to obtain the correct composition as tabulated in Table 1 [1].

The structure of the quenched ingots were confirmed to be amorphous by both X-ray in powder and thin film diffraction (XRD) and differential thermal analysis (DTA) [1] (see Table 1).

Samples in the form of thin films were prepared by evacuating the synthesized material thermally at a base pressure of 2×10^{-5} Torr onto precleaned corning glass 7059 substrate using Edwards E-306A coating unit. Film thickness measurements after preparation were obtained by using multiple beam Fizeau fringes method [17]. For electrical conductivity measurements, the film resistance was measured with a digital electrometer (Keithley type E 616A) in sandwich configuration using Al metal for electrodes. The spectral distributions of the transmittance (T) and reflectance (R) were recorded as a function of the wavelength range (200-2600 nm) by using (UV - 3101 PC) spectrophotometer from Shimadzu Japan [12].

Table 1. The EDX data and the glass transition temperature (T_g) of amorphous Ge-Se-Tl films as a function of composition.

Composition	Ge (at %)	Se (at %)	Tl (at %)	T_g , (K)
Ge Se ₇ Tl ₂	10.02	69.94	20.04	412
Ge Se ₆ Tl ₃	10.21	59.7	30.09	400
Ge Se ₅ Tl ₄	10.05	49.9	40.05	373

3. Results and discussion

3.1. Determination of the average number of constraints per atom N_{con} , and the effective average coordination number per atom $\langle r_{eff} \rangle$.

In describing any experimental results, it is interesting to mention that the glassy networks are influenced by mechanical constrains (N_{con}) associated with the atomic bonding, and an average effective coordination number $\langle r_{eff} \rangle$ which is also related to N_{con} as will be explained below. In a covalently bonds glass network two types of constrains, bond-bending N^β , bond-stretching N^α , need to be counted [18], nearest-neighbour coordination in ternary system obeying the so-called 8-N rule, where N is the valency of an atom. According to the previous rule, the average coordination number r in our system is defined by :

$$r = 4X Ge + 2X Se + 5X Tl \quad (1)$$

where X is the mole fraction. For an atomic species with coordination number r , the number of constrains per atom arising from bond-bending is ($N^\beta = 2r - 3$) and from bond-stretching

($N^\alpha = \frac{r}{2}$). Knowing the average number of constraints ($N_{con} = N^\alpha + N^\beta$), and the average coordination number r for different composition of our Ge-Se-Tl glassy system, the effective average coordination number $\langle r_{eff} \rangle$ can be calculated using the formula :

$$\langle r_{eff} \rangle = \left(\frac{2}{5} \right) (N_{con} + 3) \quad (2)$$

Table 2 shows the values of N^β , N^α and N_{con} along with $\langle r_{eff} \rangle$ for Ge-Se-Tl glassy system, these values increase with the addition of Tl.

Table 2. Values of N^β , N^α , N_{con} and $\langle r_{eff} \rangle$ for Ge-Se-Tl glassy system.

Composition	N^β	N^α	N_{con}	$\langle r_{eff} \rangle$
Ge Se ₇ Tl ₂	2.6	1.40	4.00	2.8
Ge Se ₆ Tl ₃	3.2	1.55	4.75	3.1
Ge Se ₅ Tl ₄	3.8	1.70	5.50	3.4

3.2. The average heats of atomization.

According to Pauling [19,20] 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 heats 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 [21] :

$$H_s (A - B) = \Delta H + \frac{1}{2} (H_s^A + H_s^B) \quad (3)$$

The first term in Eq. (3) is proportional to the square of the difference between the electronegativity χ_A and χ_B of the two atoms :

$$\Delta H \propto (\chi_A - \chi_B)^2 \quad (4)$$

In order to extend this idea to ternary and higher-order semiconductor compounds, the average heat of atomization of H_s is defined for a compound $A_\alpha B_\beta C_\gamma$ as a direct measure of the cohesive energy and thus of the average bond strength, as [22,23] :

$$H_s = (\alpha H_s^A + \beta H_s^B + \gamma H_s^C) / (\alpha + \beta + \gamma) \quad (5)$$

In the few materials for which it is known, the amount of the heats of formation ΔH is about 10% of the heat of atomization and therefore can be neglected. Hence, in ternary compounds H_s as give by Eq. (5) is applicable. The values of H_s for Ge, Se and Tl are 90, 49.4 and 43 (Kcal / gm .atom) respectively. The results of Ge-Se-Tl system using the values of H_s for Ge, Se and Tl are listed in Table 3.

Table 3. Values of H_s , E_g^{opt} and $H_s / \langle r_{eff} \rangle$ for Ge-Se-Tl glassy system.

Composition	H_s (kcal/g.atom)	E_g^{opt} (eV)	$H_s / \langle r_{eff} \rangle$
Ge Se ₇ Tl ₂	52.18	1.62	18.64
Ge Se ₆ Tl ₃	51.54	1.40	16.63
Ge Se ₅ Tl ₄	50.90	1.22	14.97

The relation between the energy gap and the average heat of atomization was discussed by Benoit et al. [24]. According to their study, there exists a linear correlation that can be expressed for the semiconductors of the diamond and Zinc-blend structure by :

$$\Delta E = a (H_s + b) \quad (6)$$

where a and b are characteristic constants. This equation represents the relative bond strength, that in turn are correlated with properties such as energy gap. In order to emphasize the relationship between E_g^{opt} and H_s , we used the optical gap of the Ge-Se-Tl system given in [12] and listed in Table 3, which reveals that the addition of Tl leads to the decrease of H_s as well as E_g^{opt} . The experimental results are interpreted as follow: the bond strengths of the three bonds (Ge-Ge), (Se-Se) and (Tl-Tl) are 37.6, 44 and 15.4 Kcal. mol⁻¹ respectively, by addition Tl to Ge-Se system, the average bond strength of the compound decrease and hence E_g^{opt} will decrease. Furthermore, since correlation between E_g^{opt} and H_s is very important, we compared E_g^{opt} with $(H_s / \langle r_{eff} \rangle)$, the average single-bond energy in the alloy which is easily computed from the value of each composition. In Table 3 one observe that E_g^{opt} is closely correlated to $(H_s / \langle r_{eff} \rangle)$ were E_g^{opt} as well as $(H_s / \langle r_{eff} \rangle)$ decreases with the increase of Tl content. According to the previous discussion, and since the relationship between E_g^{opt} and H_s expressed by Eq. (6) is obtained, we can conclude that our theoretical calculation in comparison with experimental data agrees well with the previous suggestions.

3.3. The relation between glass forming ability and Lone-pair electrons of structure.

The first attempt to correlate glass formation tendency with the structure of the electron shell was that of Winter [25]. She thought that P-electrons were important in glass formation. This idea lead to the rule, according to which, in order to obtain a compound in the vitreous state, it is necessary that the ratio of the number of P-electrons from the component elements to the number of atoms in the molecule is higher than 2. However, the chalcogenide glass forming ability cannot be explained by Winter's rule, because the same group of elements have the same P-electrons but differ in glass forming abilities. The variation of these abilities can be explained, according to the Pauli force model potential, from which Chelikowsky and Phillips [26] obtained the orbitally dependent ionic redii. In discussing the ionic redii of the elements used we are talking of r_s and r_p which are the orbitally dependent ionic redii of S-orbital and P-orbital respectively, the redii of Ge and Tl elements are displayed in Table 4.

Table 4. Se (Tl,S) based chalcogenide glass forming ability and orbitally dependent radii of Ge and Tl elements (radii are given in atomic units).

Element	Maximum content	Ability	r_s (a.u.)	r_p (a.u.)
Ge	52	Very good	0.64	0.92
Tl	50	Very good	0.69	1.16

The previous correlation is given also in terms of the chemical bond approach. The difference of chemical bonds forms by Ge and Tl element with Se atom is given in Table 5.

Table 5. The character of the chemical bonds formed by Ge and Tl selenium atoms.

Bond	Ge-Se	Tl-Se
R_σ^{AB} (a.u.)	0.27	0.50
R_τ^{AB} (a.u.)	0.45	0.64

The R_σ^{AB} and R_τ^{AB} scales correspond to the ionicity and metallicity of an A-B bond respectively, and are defined as [26] :

$$R_\sigma^{AB} = (r_s^A + r_s^B) - (r_p^A + r_p^B) \quad (7)$$

$$R_\tau^{AB} = (r_s^A - r_s^B) + (r_p^A - r_p^B) \quad (8)$$

The change of R_σ from Ge-Se bond to Tl-Se bond is very important to an understanding of glass-forming ability. As shown in Table 5 the ionicity of Ge-Se bond is less than that of Tl-Se bond. As we know, the σ bonds of P-orbitals have a very marked directivity, which leads to well defined structure that are malleable and makes possible, within certain limits, modifications in bond angles and the rotation of the structural elements around bond axes. These properties of σ bonds are in favor of the glass formation. The lower ionicity of Ge-Se bond means that the σ bond have a preponderance over that of Tl-Se. This means that the small ionicity of Ge-Se bonds is the typical of σ bond. A lone-pair electrons and lower ionicity of Ge-Se bond are the reasons that Ge have better glass forming ability than Tl atom. For the Ge-Se-Tl system, the coordination number of Ge is four and that for Tl is five. The largest coordination number of Tl may be the result of an interaction between Tl ions and the lone-pair electrons of bridging Se atoms. The interaction decreases the role of LP electrons in the glass formation. We also know that most of the substances which 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 Se atoms in glass structure have two pairs of LP electrons. The existence of bridging atoms with LP electrons, can eliminate the strain force caused by the formation of amorphous materials. In terms of the viewpoint proposed by Pauling [20] the chemical bonds with LP electrons have a character of flexibility. Increasing the number of lone-pair electrons decreases the strain energy in a system, and structures with large numbers of LP electrons favor glass formation. The above discussion shows that LP electrons have an important role in glass formation. The chemical environment in the structure has influenced on the rule of LP electrons. If there are cations that have high ionicity and strong electrostatic field in the compound, unshared electrons may interact with the cations because of the electrostatic force and the Vander Waals interaction. This action of cation constrains the LP electrons of bridging atoms, and the flexibility of a chemical bond with lone-pair is decreased. In order to calculate the number of LP electrons of chalcogenide glassy system, the unshared LP electrons equal all the valence electrons of the system minus the unshared electron, i.e.

$$L = V - r \quad (9)$$

Where L , V and r are the number of lone-pair electrons, valence electrons and coordination number respectively. The number of LP of the Ge-Se-Tl glassy system can be obtained according to Eq. (9), the results are listed in Table 6.

Table 6. Lone-pair electrons and glass forming abilities of Ge-Se-Tl system.

Composition	V	r	L	Ability
Ge Se ₇ Tl ₂	5.2	2.8	2.4	+
Ge Se ₆ Tl ₃	4.9	3.1	1.8	+
Ge Se ₅ Tl ₄	4.6	3.4	1.2	+

It is seen from the above table, that the number of LP electrons decreases continuously with the increase in the content of Tl in the Ge-Se-Tl system. This result is caused by the interaction between Tl ion and the LP electrons of a bridging Se atom. The interaction decreases the role LP of electrons in the glass formation as previously mentioned. Liang [27] introduced a simple criterion for computing the ability of a chalcogenide system to retain its vitreous state, the criterion contains the number of LP electrons which is necessary for obtaining the system in its vitreous state for single, binary and ternary systems. For a ternary system the number of LP electrons must be larger than (1) and less than (2.6). The obtained data given in Table 6 agrees with the former suggestion by Liang [27], and was also confirmed by X-ray results [1], and differential thermal analysis measurements (DTA) [12] previously obtained for the system under study.

4. Analysis of results

It has been shown that the optical gap E_g^{opt} is closely correlated with the character of the chemical order in amorphous semiconductors. Two parameters, the average heat of atomization H_s , and the average coordination number r are useful in relating the optical gap to chemical composition. It is interesting to compare the previously obtained results E_g^{opt} , ΔE_σ and σ_o given in Ref. [1,12] for Ge-Se-Tl glassy system, with the calculated theoretical data given in the present work for the same system under study (see Table 7).

Table 7. Values of E_g^{opt} , ΔE_σ , σ_o , N_{con} , r , H_s and L for Ge-Se-Tl glassy system.

Composition	E_g^{opt} (eV)	ΔE_σ (eV)	σ_o $\Omega^{-1} \cdot \text{cm}^{-1}$	N_{con}	r	H_s (kcal/g.atom)	L
Ge Se ₇ Tl ₂	1.62	0.82	5.06×10^4	4.00	2.8	52.18	2.4
Ge Se ₆ Tl ₃	1.40	0.69	2.99×10^3	4.75	3.1	51.54	1.8
Ge Se ₅ Tl ₄	1.22	0.59	1.80×10^3	5.50	3.4	50.90	1.2

An increase in Tl leads to an increase in N_{con} and r . On the other hand E_g^{opt} , ΔE_σ , σ_o , H_s and L decrease. To account for the observed results, one should consider the type and strength of bonding. According to Mott and Davies [28], the intercept σ_o is related to the density of localized states, as σ_o decreases the density of localized states increases. Thus the Ge-Se-Tl system is found to be a more disorder solid than Ge-Se. It is likely that the Ge-Se network is gradually modified by Tl concentrations with respect to, interatomic distances, coordination numbers and bond-strengths, since Tl is found to replace Se-sites. Such effects in other systems have been reported in the literature [29-31]. The increase in coordination number and corresponding modification in the chemical bond should directly affect the optical and electrical properties of the Ge-Se-Tl glassy system. It is proposed that the observed changes in the optical gap result from the local changes in the chemical bonding. So the decrease in E_g^{opt} , ΔE_σ and σ_o should be associated with a decrease in H_s and H_s / r where H_s represents the relative bond-strength and H_s / r is the average single-bond energy in the alloy, which is easily computed from the value of each composition (see Table 3). Mott and Davis [28] have suggested that, when values of σ_o are in the range 10^3 - $10^4 \Omega^{-1} \cdot m^{-1}$, “our case”, the electrical conduction takes place predominantly in the extended states. Lower values of σ_o indicate greater participation of localized states in the conduction process. The feature of the Ge-Se-Tl glassy system is reflected in the continuous decrease of E_g^{opt} , ΔE_σ and σ_o as well as H_s and H_s / r with increasing Tl concentration from 20 to 40 at%. Sanghera et al. [32] have shown that the addition of Tl to GeSe₂ glass shifts the binding energy of the bridging Se to lower energies (for the addition of 30 mol% Tl the shift is 3.6 eV). Sanghera et al. attributed this phenomenon to the presence of non-bridging selenium, which influenced the electron density around the bridging selenium that makes up the vitreous network. Theoretical support for the above discussion is supplied by lone pair analysis where L decrease with increasing the Tl content. According to Zope et al.[6] the energy E_{LP} of lone-pair electrons of chalcogen bounded by a normal σ -bond with an atom of Tl will be higher than that of chalcogen bonded with chalcogen or Ge owing to the coulombian interactions between the LP states and the higher electron density at the Tl atoms. On the other hand the energy $E_{LP} < U_{LP}$, where U_{LP} is the repulsive energy of the lone-pair states of chalcogen. The above process is responsible of the decrease of the activation energy with the increase of Tl concentration. Our theoretical results are in accordance with the reported results previously published in [1,12] for the system under study. The network-dimensionality approach may further help us to understand the effect of adding Tl to Ge-Se composition on theoretical and experimental correlation more deeply.

5. Conclusions

The paper tried to understand the decrease in ΔE_σ and σ_o in Ge-Se-Tl glasses with increasing Tl content on the basis of structural changes in Ge-Se which leads to a readjustment in the local environment. Thallium is supposed to form states different from the valence states of elements interacting with Ge-Se according to the octet rule (8-N). A correlation has been found between the Ge-Se-Tl glassy system and the number of LP electrons. The stable vitreous state can be obtained only if enough lone-pair electrons exist in the structure of the glassy system. A simple criterion for computing the ability of a semiconductor system to retain its vitreous state was proposed. Investigation of the experimental data of the Ge-Se-Tl glassy system revealed that N_{con} and $\langle r_{eff} \rangle$ has a strong effect on these properties and support the above analysis.

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