Physical Properties Evolution in Network Glasses of Ge–Cd–Se System: A Theoretical Approach

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Abstract

In technology, Ge-Se-Cd is a prototypical chalcogenide system capable of forming glasses on various components. A theoretical analysis was conducted to determine the effect of Ge-addition on the physical parameters of $Ge_xCd_{10}Se_{90-x}$ (x=5, 10, 15, 20 and 25 at. %) glasses systems. The values of the average coordination number, the number of constraints, the average heat of atomization, cohesive energy, density, and packing density were increased with an increase in the Ge content, while the values of lone pair electrons were decreased as the system was moving towards the rigid region. Deviation of the stoichiometry values leads the system to chalcogen-rich regions, except for $Ge_{25}Cd_{10}Se_{65}$ indicating chalcogen-poor composition. A linear correlation was found between the overall mean bond energy and glass transition temperature. Increasing the Ge content leads to an increase in strong heteropolar Ge-Se bonds at the expense of weak homopolar Se-Se bonds, resulting in an increase in network connectivity or the rigidity of the system. The chemical order network model (CONM) was applied to calculate the distribution of the chemical bonds and the cohesive energy of the system. According to the Neffati relation, the theoretical band gap has been calculated. The increase in the energy gap with increasing Ge concentration for all systems except $Ge_{25}Cd_{10}Se_{65}$ suggests that the 2D layered structure generated by the branching of the Se chain is completely established at this composition at <r>=2.6, after that point, the layer structures cross-link, forming a rigid 3D network. Such changes can broaden the lone-pair valence band, reducing the band gap. Physical parameters were sensitive to changes in composition subsequently making this present system suitable for phase change optical recording.

Keywords: The chemical order network model, Ge-Cd-Se glasses,, average coordination number, theoretical band gap, glass transition temperature.

تطـــور الخصـــائص الفيزيائيـــة فــي شـــبكة نظـــام Ge-Cd-Se الزجاجيـــة: نـهجاً نظرياً

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المُلخَّص

مركبات Ge-Se-Cd عبارة عن أنظمة شالكوجينية نموذجية لها العديد من التطبيقات الالكترونية الحديثة وقادرة على التشكل كأشباه موصلات زجاجية بتغيير مكوناتها. لذلك تم إجراء تحليل نظري لتحديد تأثير إضافة الجرمانيوم على الخواص الفيزيائية للشبكة الزجاجية للأنظمة $Ge_xCd_{10}Se_{90-x}$ عند النسب (x=5, 10, 15, 20 and 25 at. %). أظهرت النتائج زيادة قيم متوسط رقم التنسيق، وعدد القيود ، ومتوسط حرارة الانحلال ، وطاقة التماسك ، والكثافة ، وكثافة التعبئة ، بينما انخفضت قيم إلكترونـات الـزوج الوحيد ،الحجم المـولاري، السـالبية الكهربائية مع زيادة محتوى Ge مما يؤكد تحول النظام من النمط المرن إلى النمط الجاسئ، فيما بينت قيم الانحراف عـن التشبع التكـافؤي أن التركيبـات غنيـة بالشـالكوجين، باستثناء $Ge_{25}Cd_{10}Se_{65}$ الذي يشير إلـى تركيبـة فقيـرة بالشالكوجين. تم العثور على ارتباطاً خطياً بين متوسط طاقة الرابطة الكلية ودرجـة حرارة الانتقال الزجاجيـة حيث تـؤدي زيـادة محتوى Ge إلى زيـادة روابط Ge-Se القويـة غير المتجانسـة علـى حسـاب روابط Se-Se الضـعيفة أحادية القطب ، مما يؤدي إلى زيادة ترابط الشبكة و صلابة النظام.

تم تطبيق نموذج شبكة الترتيب الكيميائي (CONM) لحساب طاقة الربط وتوزيعها واستخدام تلك في حساب الطاقة التماسك للنظام. ووفقًا لعلاقة نفاتي ، تم حساب فجوة النطاق النظرية. تشيرا لنتائج المسجلة إلى زيادة في فجوة الطاقة مع زيادة تركيز Ge لجميع الأنظمة باستثناء $Ge_{25}Cd_{10}Se_{65}$ ويعود ذلك إلى أن التركيب ثنائي الأبعـاد النـاتج عـن سلاسـل السـيلينيوم المتفرعـة قد اسـتنفذ في هـذا المركـب ، وتشكيل شبكة صـلبة ثلاثيـة الأبعـاد متشابكة. يمكن لمثل هذه التحولات توسيع نطاق تكافؤ الزوج الوحيد، وتقليل فجوة النطـاق، كمـا نؤكد على قابليـة استخدام هذه المركبات في عملية التسجيل البصري.

الكلمات المفتاحية: نموذج شبكة الترتيب الكيميائي، Ge-Cd-Se الزجاجية، متوسط عدد التناسق، فجوة الطاقة النظرية ، درجة حرارة التحول الزجاجي

1. Introduction

Glassy alloys containing chalcogens were initially studied for their interesting semiconducting properties [1] and more recently for their importance in optical recording [2]. Recording materials must be stable at low temperatures in an amorphous state and have a short crystallization time. Promising materials with these properties have been investigated recently [3-4]. Chalcogenide glasses from Se-based systems such as Ge–Se have recently attracted much attention. This family of chalcogenide glasses can provide an ideal system for investigation. The variation of the Ge–Se structure is reflected in different properties such as the glass-forming regions, glass transition temperature, photoluminescence, IR, Raman spectra, and optical properties [5-7].

Ge-Se-Cd is a prototypical chalcogenide system that forms bulk glasses over many compositions. The glass-forming region in the Ge-Se-Cd system is situated on the selenium-rich Ge–Se side of the Gibbs triangle, where up to 12 at.% Cd can be introduced into the binary $Ge_{20}Se_{80}$ composition without the formation of crystallites [8]. Therefore, it is a suitable model system for the investigation of the variation of the physical parameters with composition. Since very little work is available in the literature on the effect of incorporation of Ge at the expense of Se on the physical properties of Ge-Cd-Se films, the obtained findings may be useful for providing basic knowledge on this composition for a new researcher working in the field of chalcogenide glasses. Incorporating a third element like Ge into Cd-Se binary alloy is expected to change the optical and electrical properties of the host alloy, which play a major role in device preparation. Therefore, in the present study, the effect of Ge-addition on the physical parameters of $Ge_xCd_{10}Se_{90-x}$ has been theoretically investigated. The structural parameters such as average coordination number, Lone pair electron, cohesive energy and heat of atomization, the glass transition temperature, density, compactness, packing density, and molar volume for the examined compositions are calculated. The band gap was also calculated according to the chemical bond approaches. The effect of composition on the structural parameters as well as on the band gap and glass transition temperature was discussed.

2. Theoretical analysis

2.1. Average coordination number <r> and number of constraints (N_{cons})

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 [9]. The bonding character in the nearest-neighbor region, i.e. the average coordination number, characterizes the electronic properties of semiconducting materials. Nearest-neighbor coordination in a ternary system is particularly suitable for testing the validity of these topological concepts; because of its large glass-forming region. Based on the average coordination number <r> concept, Philips [10] and Thrope[11] proposed a constraints theory where they looked at a glass as consisting of a network of floppy and rigid regions. It was postulated that a transition will occur when the average coordination number increases and rigidity percolation occurring through the network when <r> passes a value of 2.4. At this value the glass network changes from floppy glass to rigid glass.

Table.1: Some general properties of Ge, Cd and Se elements

Property	Ge	Se	Cd	Reference
Atomic number	32	34	48	
Atomic weight (a.m.u)	72.64	78.96	112.41	
Density(g/cm³)	5.323	4.79	8.65	[12, 13]
Melting point (K)	1211.4	494	594	
Atomic radius (pm)	**125**	**115**	**155**	
Coordination number N^x	4	2	4	[14, 15]
Heat of atomization ‹H_S› **(Kcal/mol)**	377	226.4	111.691	[12, 16]
Electronegativit χ_K	2.01	2.55	1.69	[12, 14, 17,18]
Bond Energy (Kcal/mol)	37.6	44	30.4	[14, 16]
E_g^{opt} **(eV)**	0.95	1.95	0	[18,19, 20, 21]

The average coordination number <r> of the $Ge_xCd_{10}Se_{90-x}$ (x= 5, 10, 15, 20 and 25 at. %) system was calculated using the standard relation [22]:

$$\langle r \rangle = \frac{xN^{Ge} + yN^{Cd} + zN^{Se}}{x + y + z} \tag{1}$$

where N^{Ge}, N^{Cd} and N^{Se} are the coordination numbers of Ge, Cd, and Se respectively, as given in Table1. The *x*, *y*, and z are their respective atomic concentrations in the glassy alloy. The calculated values of <r> for $Ge_xCd_{10}Se_{90-x}$ systems are listed in **Table 2** and plotted in **Fig.1 (a)**, which indicate that <r> increases with the increase of Ge content. It can be seen that the calculated average coordination number <r> values lie in the range

$2.3 \geq$ <r> ≤ 2.7. This increase in coordination number may be correlated with the increased compactness of the structure of the Ge-Cd-Se glassy alloys. This increase in the average coordination number of the system is attributed to the fact that Ge element, with higher coordination number, has been replaced with Se, which has lower coordination number due to the fact that the average coordination number of the system increases.

Table 2: The average coordination number, number of constraints, fraction of floppy modes, valence electrons, number of lone-pair electrons, deviation of stoichiometry, the average heat of atomization, and electronegativity for $Ge_xCd_{10}Se_{90-x}$ (x=0, 10, 15, 20, and 25 at. %) system.

Composition	<r>	N_{con}	f	V	L_p	R	$\overline{H}_s$ (kcal/mole)	χ_{GM}
$Ge_5Cd_{10}Se_{85}$	2.3	2.75	0.0833	5.5	3.2	2.83	222.460	2.418
$Ge_{10}Cd_{10}Se_{80}$	2.4	3.00	0	5.4	3.0	2.00	229.989	2.390
$Ge_{15}Cd_{10}Se_{75}$	2.5	3.25	-0.083	5.3	2.8	1.50	237.519	2.361
$Ge_{20}Cd_{10}Se_{70}$	2.6	3.5	-0.017	5.2	2.6	1.17	245.049	2.336
$Ge_{25}Cd_{10}Se_{65}$	2.7	3.75	-0.25	5.1	2.4	0.93	252.579	2.306
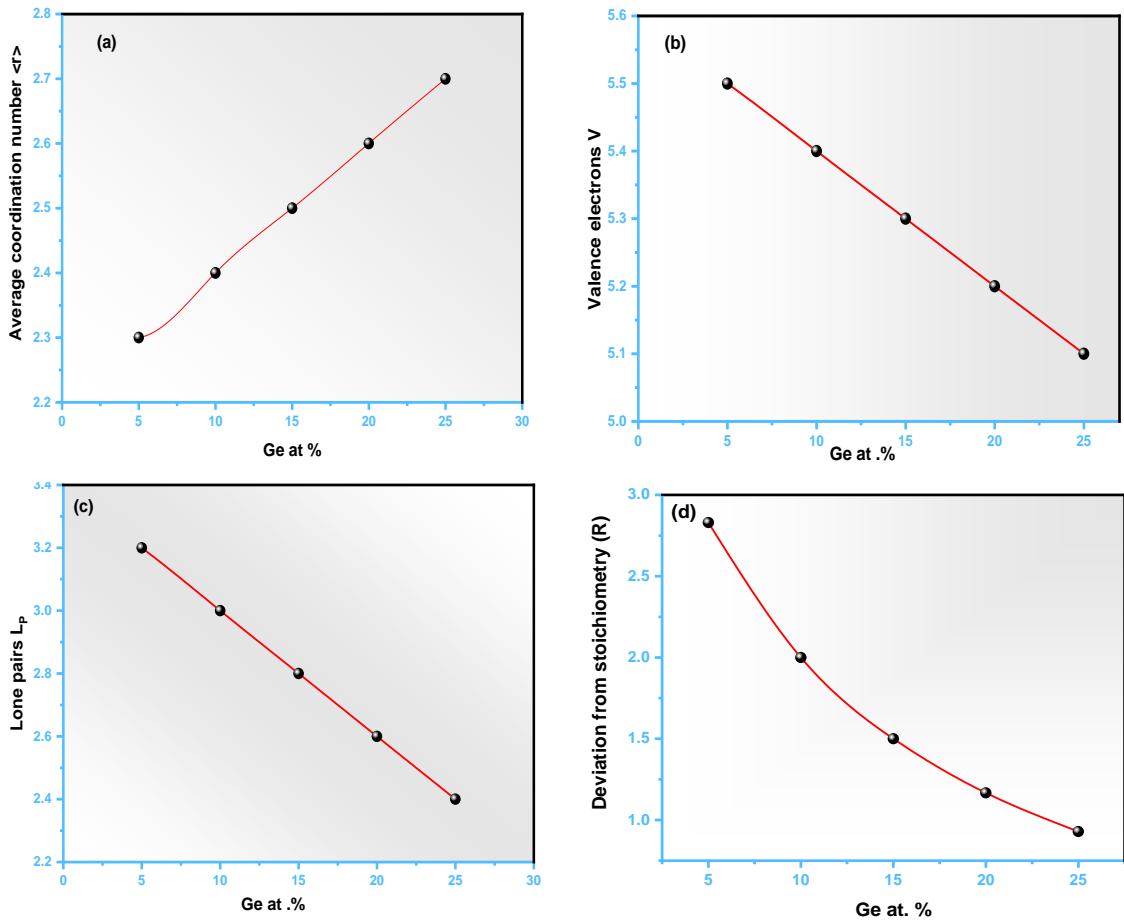
Fig.1: The variation of (a) <r>, (b) V , (c) L_p, and (d) R with the Ge content for $Ge_xCd_{10}Se_{90-x}$ glassy system.

The glassy network is influenced by mechanical constraints (N_{con}) associated with the atomic bonding and an average coordination number <r> which is also related to N_{con} [23]. In a covalently bonded glassy network, there are two types of constraints (bond stretching constraints, N^{α}, and bond bending constraints, N^{β}) to be counted [24] . For atomic species with coordination number $\langle r \rangle$, the number of constraints per atom arising from bond bending $N^{\beta}=2\langle r \rangle$-3 and from bond stretching $N^{\alpha}=\langle r \rangle/2$. Knowing the average number of constraints $N_{con}= N^{\alpha} + N^{\beta}$ and the average coordination number $\langle r \rangle$ for different compositions of $Ge_xCd_{10}Se_{90-x}$ (x= 5, 10, 15, 20 and 25 at. %) glassy system, the average number of constraints can be calculated using the formula [25]:

$$N_{con} = \left(\frac{5}{2}\langle r \rangle - 3 \right) \qquad (2)$$

The calculated values of N_{con} of $Ge_xCd_{10}Se_{90-x}$ glasses system are listed in **Table 2**. In our system, the average number of constraints per atom N_{con} exceeds the number of degrees of freedom $N_d = 3$ for the compositions x = 15, 20, and 25 at. %. The non-monotonic behavior of various properties observed in these glasses is explained in terms of the interplay between "mechanical" and "chemical" forces which affect the structure of the glass as a function of $\langle r \rangle$. According to the constraints theory, the value $\langle r \rangle = 2.4$ is known as the rigidity percolation threshold (RPT). At $\langle r \rangle = 2.4$, the number of constraints N_{con} acting on the network is balanced by the degree of freedom N_d available for the atoms in the network, the structure becomes just rigid, and stable glasses can be prepared. In a glass with $\langle r \rangle$ lower than 2.4, the structure is floppy. Above this value, the structure is over constrained, and glass formation becomes difficult [10,11]. In other words, the range of the glass-forming compositions should contain rigid and floppy regions. In the $Ge_xCd_{10}Se_{90-x}$ (x= 5, 10, 15, 20, and 25 at. %) glassy system compositions the average coordination number varies from 2.3 to 2.7. The transition from the floppy mode to the rigid mode occurs at $\langle r \rangle = 2.4$ (the mechanical percolation threshold), which corresponds to $Ge_{10}Cd_{10}Se_{80}$, which is consistent with the theory of constraints.

2.2. Fraction of floppy modes f

In the absence of weak long range forces, uncoordinated networks with a finite fraction of zero frequency normal vibration modes are referred to as floppy modes [11]. The fraction of zero frequency modes, f can be calculated as follows:

$$f = 2 - \frac{5}{6}\langle r \rangle \qquad\qquad (3)$$

The values of f for different Ge-Cd-Se compositions are computed in **Table 2**. The values of the fraction of floppy modes decreased as the Ge concentration in the system increased, indicating that the system's rigidity increased. At the value of <r> =2.4, known as the "ideal" glass matching $Ge_{10}Cd_{10}Se_{80}$, the fraction of zero-frequency modes f is exactly equal to zero.

2.3. Role of Lone pair electrons

Chalcogenide glasses are also called lone pair semiconductors. According to Zhenhua [26] the lone pair of electrons in the structure of a system is a necessary condition for obtaining the system in a vitreous state. The number of lone-pair electrons, L_p in the system under consideration, is computed using the relation [26]:

$$L_P = V - \langle r \rangle \qquad\qquad (4)$$

where <r> is the average coordination number and V is the valence electrons which equals the unshared lone-pair electrons and is generalized as [**26**]:

$$V = \frac{\left(x[V]_{Ge}\right) + \left(y[V]_{cd}\right) + \left(z[V]_{Se}\right)}{\left(x + y + z\right)} \qquad\qquad (5)$$

where V_{Ge}, V_{Cd} and V_{Se} represent the valence electrons for Ge, Cd, and Se elements which are 4, 2 and 6, respectively. The x, y and z are the atomic percentages of Ge, Cd and Se elements respectively. The valence electrons and the numbers of lone pair electrons are listed in **Table 2** and plotted in **Fig.1(b** and **c)**. According to Pauling [27], the lone-pair electrons containing chemical bonds are characterized by their flexibility. Thus it is easier to deform a bond with a lone pair of electrons than a bond with no unshared electrons. Structures with a large number of lone-pair electrons favor glass formation [28]. It is clear from **Table 2** that the lone pair electrons, L_p, decrease continuously with the addition of Ge. That means that the bond deformation decreased with increased Ge content leading to a decrease in the flexibility of the system. Zhenhua [**17**] proposed a simple criterion for a binary and ternary system, i.e for a binary system the value of L_p must be larger than 2.6 and for a ternary system it must be larger than 1. These assumptions lead us to the conclusion that the number of lone pair electrons in a system's structure is necessary for the system to exist in a vitreous state. As the Ge

content rises, our system tends to contain fewer lone pairs, which makes the formation of the glassy structure more difficult.

2.4. Deviation from stoichiometry of composition (R).

The deviation from stoichiometry is expressed by the ratio of the covalent bonding possibilities of the chalcogen atom to those of nonchalcogen atom. Values of R were found to be larger than unity for such glasses, which indicate chalcogen-rich materials and less than unity for the glass, which shows chalcogen poor materials. The threshold at R=1 (the point of existence of only heteropolar bonds) marks the minimum chalcogen atom content at which a chemically ordered network is possible without metal- metal bond formation. For $Ge_xCd_ySe_z$ system, the quantity R is defined by [29].

$$R = \frac{zN^{Se}}{xN^{Ge} + yN^{Cd}} \tag{6}$$

where, x, y and z are atomic fraction of Ge, Cd and Se respectively. The calculated values of R for $Ge_xCd_{10}Se_{90-x}$ glasses are listed in **Table 2** and plotted in **Fig.1 d**. For the present investigating system, R values are greater than one, leading the system to chalcogen-rich regions, except for $Ge_{25}Cd_{10}Se_{65}$, where R is less than one, indicating chalcogen-poor composition.

2.5. The average heat of atomization

The average heat of atomization, $\overline{H}_s$ is defined for the compounds in the $Ge_xCd_ySe_z$ glassy system, as a direct measure of the cohesive energy and the average band strength is given by [30]:

$$\overline{H}_s = \frac{xH_s^{Ge} + yH_s^{Cd} + zH_s^{Se}}{x + y + z} \tag{7}$$

where x, y, and z are the atomic percentages of Ge, Cd and Se elements , respectively, whereas the H_s^{Ge}, H_s^{Cd} and H_s^{Se} are their heats of atomization which are given in **Table.1**. The results of the $\overline{H}_s$ for the $Ge_xCd_{10}Se_{9-x}$ system are listed in **Table 2**. It is clear that the value of $\overline{H}_s$ increases with the partial substitution of Ge for Se as shown in **Fig. 2**. This is due to the higher heat of atomization of germanium (377 Kcal /mol) than that of selenium (226.4 Kcal /mol).
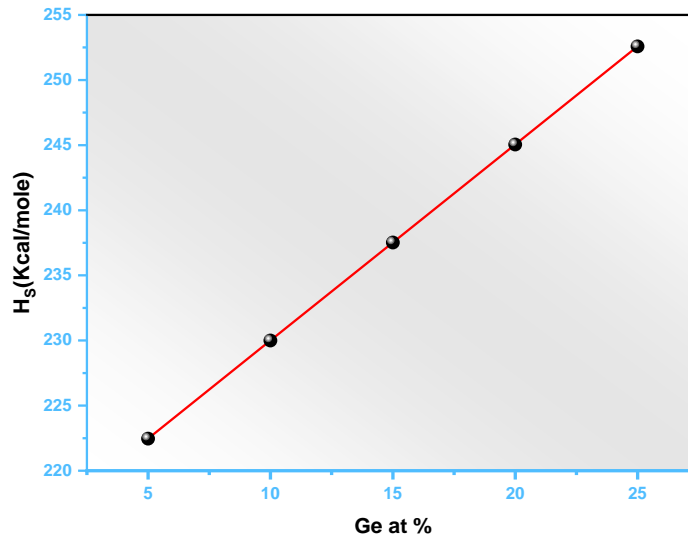
Fig. 2: Plot of the $\overline{\overline{H}}_s$ with Ge content for $Ge_xCd_{10}Se_{90-x}$ glassy system.

2.6. The electronegativity

The study of electronegativity is very useful to understanding many basic properties of materials used in various combinations. The electro–negativity has been defined using different approaches by different investigators. The most commonly predicted approach is given by Linus Pauling, who explains electronegativity as the power of an atom or molecule to attract electrons towards it. The electronegativity of the composition is the geometric mean of all the constituents of that particular composition. The electronegativity, (χ_{GM}) glassy system was obtained using Sanderson's concept [31]. According to this principle, the final molecular electronegativity may be expressed approximately as the geometric mean of the electronegativities of the isolated atoms:

$$\chi_{GM} \approx \left(\prod_{k=1}^{P} \chi_k \right)^{\frac{1}{P}} \tag{8}$$

If the molecule contains P atoms (same or different) and k, where (k = 1, 2,.., p) denotes their isolated atom electronegativities. The computed values of χ_{GM} for $Ge_xCd_{10}Se_{90-x}$ glasses are listed in **Table 2**. It can be seen that the electronegativity values decrease with an increase in Ge content, because Germanium exhibits a lower electronegativity (2.01) than selenium (2.55).

2.7. Density and molar volume

The density is a measure of the rigidity of a system. The change in density is related to the change in the atomic weight and atomic volume of the elements. Since the density of Ge (5.323 g/cm^3) is greater than that of Se (4.79 g/cm^3), the increase in Ge content leads to an increase in the density of the composition Ge-Cd-Se. **Fig. 3.a** shows the linear dependence of the density of the composition Ge-Cd-Se on the ratio extends Ge. As a rule, the linear dependence of the density on the concentration of Ge irrespective of the preparation technique indicates the additive nature of density as a character of the glassy structure. Theoretically, density was calculated by the Fayek relation [32]:

$$\rho^{th} = \left(\sum_i \frac{x_i}{d_i} \right)^{-1} \tag{9}$$

where x_i is the atomic percentage of the same element in the sample and d_i is its density. Another parameter that is related to the density (ρ^{th}), namely the molar volume (V_m), is also calculated from the density data by the equation:

$$V_m = \frac{1}{\rho^{th}} \sum_i x_i M_i \tag{10}$$

where M_i is the molecular weight of the ith component and x_i is the atomic percentage of the same element in the sample. The values of ρth and V_m for the prepared compositions are listed in **Table 3**. As shown in **Fig. 3 b,** that the V_m values decrease continuously with the increase of Ge content. In addition, packing density is defined as a ratio of used space to the allocated space and can be calculated using density values, ($N_A \times \rho_{cal}/M$) where N_A is Avogadro's number and M is molecular weight. The values of packing density are found to increase with the addition of Ge content. It may be said that the increase in glass density results in an increase in packing density (**Table 3**) due to the larger atomic radius of the Ge atom (125 pm) compared with the Se atom (115 pm).

Table 3: The density, compactness, molar volume, and fraction of zero-frequency for the $Ge_xCd_{10}Se_{90-x}$ (x= 5, 10, 15, 20 and 25 at. %) system

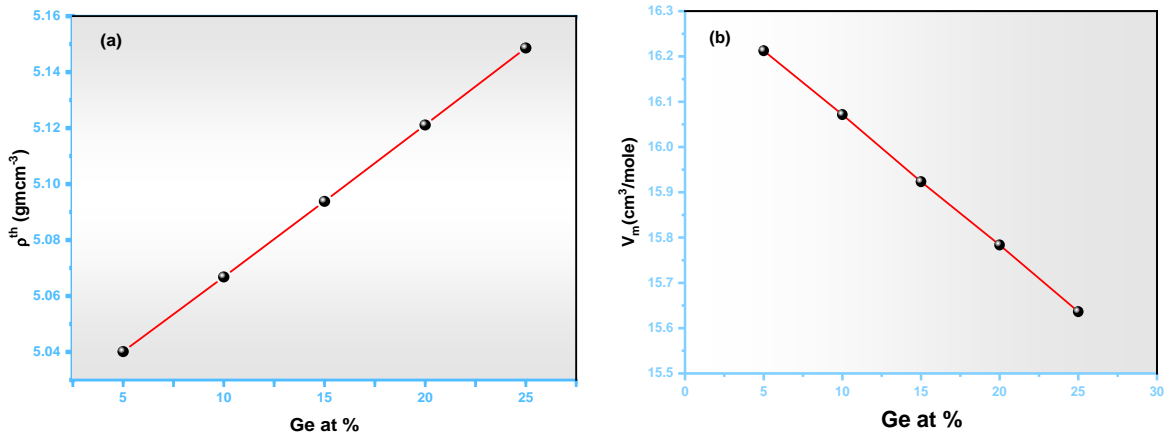| Composition	M (gm)	ρ^{th} (gcm^{-3})	V_m (cm^3 mol^{-1})	δ	Packing density ($\times 10^{20}$ atom/cm^3)
$Ge_5Cd_{10}Se_{85}$	81.989	5.0401	16.2127	-0.0135	370.198
$Ge_{10}Cd_{10}Se_{80}$	81.673	5.0668	16.0717	-0.0137	373.599
$Ge_{15}Cd_{10}Se_{75}$	81.357	5.0938	15.9233	-0.0134	377.049
$Ge_{20}Cd_{10}Se_{70}$	81.041	5.1211	15.7836	-0.0137	380.548
$Ge_{25}Cd_{10}Se_{65}$	80.725	5.1486	15.6364	-0.013	384.089

Fig. 3: The variation of (a) ρ^{th} and (b) V_m with Ge content in the $Ge_xCd_{10}Se_{90-x}$ glassy system.

2.8. Compactness and fraction of zero-frequency modes

The compactness (δ) is a measure of a normalized change in mean atomic volume due to chemical interaction forming the network of given solids [33]. Consequently, it is more sensitive to changes in the structure of the glass network as compared to the mean atomic volume, and thus it is associated with the flexibility and free volume of the network. The compactness (δ) was calculated using the relation [34-36]:

$$\delta = \frac{\sum_i c_i A_i / \rho_i - \sum_i c_i A_i / \rho^{th}}{\sum_i c_i A_i / \rho^{th}} \tag{11}$$

where c_i is the atomic fraction, A_i is the atomic weight; ρ_i is the atomic density of the i_{th} element of the glass and ρ^{th} is the measured density of the glass. From the **Table 3**, we observed that the compactness has negative values, which shows that the given Ge-Cd-Se system has larger free volume and flexibilities, as well as the disturbance in the compactness values associated with atomic arrangements. When Ge enters an Ge-Cd–Se system, it makes a bond with Se, new bonds are forming with longer bond length,

since the bond length of Ge–Se is 2.81 Å and that of Cd-Se is 2.66 Å, at expense of the bond length of Se-Se (2.35 Å) [37].

2.9. Bond energy and cohesive energy CE.

According to Zachariasen [38], atoms combine more with atoms of different kinds than with the same kind. This condition is equivalent to assuming the maximum amount of chemical ordering possible. This means that bonds between like atoms will only occur if there is an excess of a certain type of atom so that it is not possible to satisfy its valence requirements by bonding it to atoms of different kinds alone, so bonds are formed in the sequence of decreasing bond energy until all available valences of the atoms are saturated. The possible bond distribution at various compositions using a chemically ordered network model (CONM) [39].This model suggested that hetero-nuclear bonds are favored over homo-nuclear bonds and they are formed in the sequence of their decreasing bond energy until the available valence of atoms is satisfied and the bond energies are assumed to be additive. The bond energies U_{A-B} for hetero-nuclear bonds between two unlike atoms A and B are calculated using the relation proposed by Pauling [27]:

$$U_{A-B} = \left(U_{A-A} \cdot U_{B-B}\right)^{1/2} + 30\left(\chi_A - \chi_B\right)^2 \tag{12}$$

where U_{A-A} and U_{B-B} are the homo-nuclear energies and $(\chi_A - \chi_B)$ is the difference in Pauling's electro-negativities of the two atoms involved, which is given in **Table.1**. The bonds formed and their energies, along with chemical bond distributions for all compositions, are tabulated in **Table.4**.

Table.4: The cohesive energy, overall mean bond energy, and distribution of chemical bonds for the $Ge_xCd_{10}Se_{90-x}$ (x= 5, 10, 15, 20 and 25 at. %) system according to the chemically ordered network model (CONM).

Composition	Distribution of chemical bond energy				CE (KCal/mole)	$\langle E \rangle$ (KCal/mole)
	Ge-Se 49.45 kcal/mol	Cd-Se 42.34 kcal/mol	Se-Se 44.04 kcal/mol	Ge-Ge 37.6 kcal/mol		
$Ge_5Cd_{10}Se_{85}$	17.39	34.78	47.83	0	57.588	47.7635
$Ge_{10}Cd_{10}Se_{80}$	33.33	33.33	33.33	0	60.872	51.1867
$Ge_{15}Cd_{10}Se_{75}$	48	32	20	0	64.156	55.12
$Ge_{20}Cd_{10}Se_{70}$	61.54	30.77	7.69	0	67.44	59.5046
$Ge_{25}Cd_{10}Se_{65}$	66.67	29.63	0	3.7	69.862	62.5373

On the other hand, the cohesive energy, CE, is the stabilization energy of an infinitely large cluster of the material per atom, and also reflects the average bond

strength. The cohesive energy for the investigated samples has been calculated with the help of the chemical order network model [40].Therefore the cohesive energy was calculated by summing the bond energies of the overall bonds expected in the material. The CE, of the prepared samples is evaluated using the following equation [41] as:

$$CE = \sum C_i D_i / 100 \tag{13}$$

where C_i represents the number of expected chemical bonds, D_i is the energy of each corresponding bond The values of cohesive energy for all the compositions are given in **Table.4**. It is observed that CE increased with increasing Ge content. The amount of Se in Ge-Cd-Se is fixed. Variations in C.E are caused by variations in Ge and Se content. When Ge is increased, it forms a bond with Se with the highest bond energy (49.45 kcal/mol). Meanwhile, Cd–Se and Se–Se bonds with energies of 42.34 and 44.04 kcal/mol decrease. Therefore, the increase in C.E and band gap of the system is caused by the formation of Ge–Se bonds at the expense of Cd–Se and Se–Se bonds [42]. Thus, the chemical bond arrangement seems to have a significant effect on the overall trend of the C.E. and band gap. Both are increasing with increasing Ge content. These increases in C.E imply an increase in bonding strength and, consequently, a decrease in defect states as shown in **Fig. 4.a**. This decrease in defect states is also reflected in the decrease in homopolar Se–Se bonds. The increase in cohesive energy is consistent with the band gap calculated theoretically.

2.10. The overall mean bond energy.

According to Tichy and Ticha [43], the value of glass transition temperature should not be only related to connectedness of the network (which is related to $\langle r \rangle$) but should also be related to the quality of connections, i.e. the mean bond energy between the atoms of the network. Since the difference in the bond energies of hetero-nuclear and homo-nuclear bonds is substantial, so chemically ordered network are expected where the number of hetero-nuclear bonds is maximized i.e. they are more favorably formed than homo-nuclear bonds. Based on this assumption the overall mean bond energy $\langle E \rangle$ is given by [44]:

$$\langle E \rangle = \overline{E}_C + \overline{E}_{rm} \tag{14}$$

where E_c is the mean bond energy of average cross-linking per atoms i.e, the overall contribution towards bond energy arising from strong heteronuclear bonds [45] such that:

$$\overline{E}_C = P_{rich}E_{hb}, \text{R} > 1 \, (\text{chalcogen - rich})$$

$$\overline{E}_C = P_{Poor}E_{hb}, \text{R} < 1 \, (\text{chalcogen - poor})$$

(15)

Where P_{rich} and P_{poor} are the degrees of cross-linking per atom for the chalcogen-rich case and the chalcogen-poor one, respectively given by:

$$P_{rich} = (xN^{Ge} + yN^{cd})/(x+y+z)$$

$$P_{poor} = (xN^{Se})/(x+y+z)$$

(16)

The average heteronuclear bond energy E_{hb} is given by:

$$E_{hb} = \frac{xN^{Ge}E_{Ge-Se} + yN^{cd}E_{Cd-Se}}{xN^{Ge} + yN^{cd}}$$

(17)

where E_{Ge-Se}, E_{Cd-Se} and E_{Ge-Cd} are the hetero-nuclear bond energies of the Ge, Cd, and Se, which are given in **Table.4**. The second term in Eq.(14), E_{rm}, is the average bond energy per atom of the remaining matri, i.e., the contribution arising from weaker bonds that remain after the strong bonds have been maximized [46], which is defined as

$$\overline{\langle E_{rm} \rangle} = \frac{2[0.5\langle r \rangle - P_{rich}]E_{se-se}}{\langle r \rangle}, \text{ R} > 1$$

$$\langle \overline{E}_{rm} \rangle = \frac{2[0.5\langle r \rangle - P_{poor}]E_{\langle \rangle}}{\langle r \rangle}, \text{ R} < 1$$

(18)

where $E_{\langle \rangle}$ is the average bond energy of a "metal-metal" bond in the poor chalogen-poor region in a ternary system.

$$E\langle \rangle = (E_{Ge-Ge} + E_{Cd-Cd} + E_{Ge-Cd})/3$$

(19)

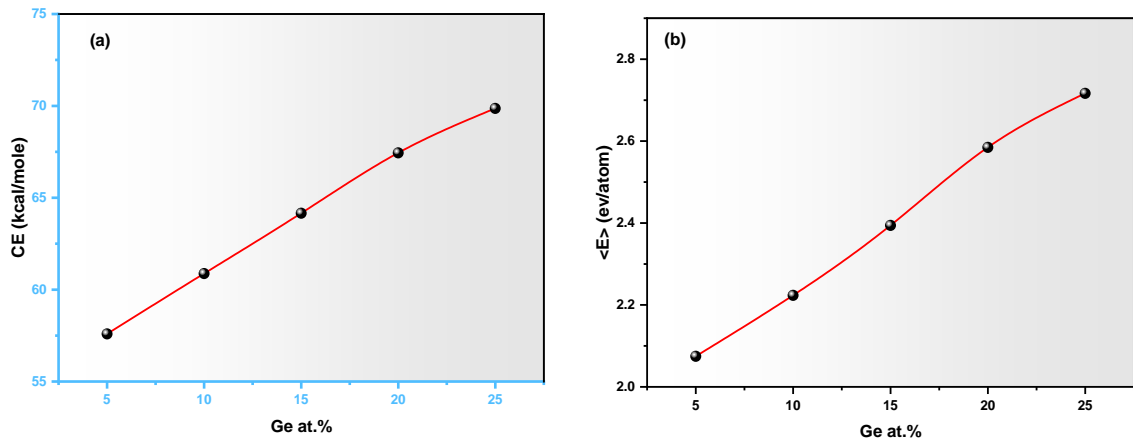Fig. 4. The variation of (a) CE and (b) <E> with Ge content in the Ge$_x$Cd$_{10}$Se$_{90-x}$ glassy

system.

The values of the overall mean bond energies for the compositions under investigation are given in **Table.4**. In **Fig. 4 b**, the overall mean bond energy <E>, as a function of composition, increases with increases Ge contents. This behavior in <E> can be interpreted according to the chemical approaches that explain it as the energy of bonds occurring in the system. Increasing the Ge content leads to an increase in strong heteropolar Ge-Se bonds at the expense of weak homopolar Se-Se bonds, resulting in increased system rigidity and increased <E>.

2.11. The overall electronegativity difference.

Since the glassy network is considered a giant macromolecule, we can calculate its overall electronegativity in order to estimate the degree of iconicity or covalency of the whole compound. In fact, the ionicity or the electronegativity is very important for estimating to what degree electrons are itinerant as well as the degree of stretching and/or bending of the chemical bonds. This concept was introduced first by Pauling [27] for single chemical bonds in molecules and also was used by Philips [47] for crystalline structures. The overall electronegativity difference $\Delta\chi$ can be estimated from the electronegativity difference between the heteropolar bonds weighted by the proportion of each bond present as follows:

$$\Delta\chi_{th} = P_{A-B}\left|\chi_A - \chi_B\right| + P_{B-C}\left|\chi_B - \chi_C\right| + P_{A-C}\left|\chi_A - \chi_C\right| \tag{20}$$

where χ_A, χ_B and χ_C are the electronegativity of A, B and C elements, respectively. The obtained values of the $\Delta\chi$, which can be used for calculating the energy gap theoretically, are given in **Table 5.**

Table 5: The overall electronegativity difference, the theoretical energy gap and the glass transition temperature according toTichy and Ticha, and Gibbs-Marzio relations of $Ge_xCd_{10}Se_{90-x}$(x=0, 10, 15, 20, and 25 at. %) system.

Composition	$\Delta\chi$	E_g^{the}	T_g(K) By Tichy and Ticha	T_g^{the} (K) By Gibbs-Di Marzio Law
$Ge_5Cd_{10}Se_{85}$	0.393	1.599	365.3006	381.93
$Ge_{10}Cd_{10}Se_{80}$	0.467	1.7198	411.5774	446.63
$Ge_{15}Cd_{10}Se_{75}$	0.534	1.8157	464.6962	496.87
$Ge_{20}Cd_{10}Se_{70}$	0.597	1.8919	523.9417	559.86
$Ge_{25}Cd_{10}Se_{65}$	0.615	1.8916	564.9315	641.00

2.12. Theoretical prediction of band gap

According to Kastner [48], the valence band (σ-bonding) in chalcogenide glasses is constituted by the lone-pair band and the conduction band by the antibonding (σ^*) band. In a multicomponent glass like Ge-Cd-Se, the position of the conduction band and valence band edges and thus the energy gap largely depends upon the relative number of various possible bonds and thus the average bond energy. The band gap for $Ge_xCd_{10}Se_{90-x}$ system was calculated by using the Neffati relation, which adds very local atomic contributions, via a correction given by the introduction of the overall electronegativity difference $\Delta\chi$ of the compound [18]:

$$E_g^{the} = \sqrt{3.72.\Delta\chi.[x.E_g(Ge) + y.E_g(Cd) + z.E_g(Se)]} \qquad (21)$$

where $E_g(Ge)$, $E_g(Cd)$ and $E_g(Se)$ are the band gaps of the individual elements (listed in **Table.1**) and x, y and z are their volume fractions. The values of the $E_g^{the.}$ for all the compositions are tabulated in **Table 5** and are plotted in **Fig. 5** as a function of Ge at.%. It can be concluded that an increase of $E_g^{the.}$ with increasing Ge content is due to an increase in average stabilization energy. The increase in CE of the Ge-Cd-Se system tends to increase the energy of the conduction band edge causing a broadening in the gap between bonding (σ) and anti bonding (σ^*) orbitals and thus resulting in an increase in the band gap. Additionally, the heat of atomization and the overall electronegativity difference increase with an increase in germanium content, which is thought to contribute to the increase in the energy gap. It is noteworthy that the maximum value of energy gap is attained when the average coordination number reaches 2.6. It was argued that the 2D layered structure formed through the branching of the Se chain is fully developed at this composition. When **<r>** >2.6, the system attains a rigid 3D structure. The cross linking of the layer structures and the formation of a 3D network occur when **<r>.**> 2.6 changes the interactions between the lone-pair p electrons. Such changes can broaden the lone-pair valence band causing a decrease in E_g [49].
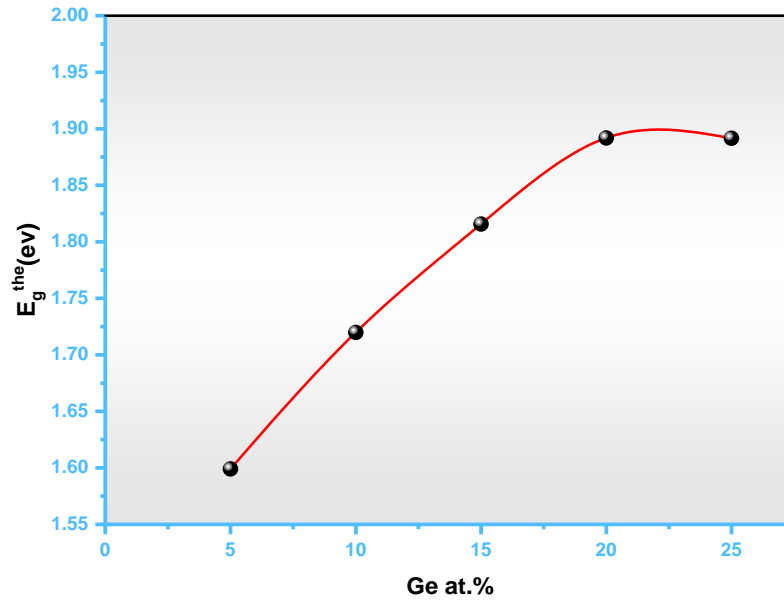
Fig. 5: Plot of the theoretical values of the energy gap with Ge content in the $Ge_xCd_{10}Se_{90-x}$ glassy system.

2.13. The Glass transition temperature (T_g^{the}) and the mean bond energy <E>.

The covalent bond approach of Tichy and Ticha [33,50] may be considered as a first approximation in the case of chalcogenide glass. The glass transition temperature is considered to be proportional to the mean bond energy <E>, which depends on factors like mean coordination number, degree of cross linking, bond energy and the nature of bonds. Taking account of all these factors they have examined 186 chalcogenide glasses with T_g^{the} ranging from ~320K to 760K, and obtained a good correlation between T_g^{the} and <E> in the form

$$T_g^{the} = 311[\langle E \rangle - 0.9]$$
(22)

The T_g^{the} was calculated by applying the Tichy and Ticha model of the $Ge_{10}Cd_{10}Se_{80}$ system using the well-known mean bond energy energies and summarized in **Table 5** It can be seen that the T_g^{the} is directly proportional to mean bond energy <E>. When Ge content increases, T_g^{the} of the system increases with the increases in mean bond energy <E> as shown in **Fig. 6** The increase in glass transition temperature values with increasing Ge content in glass-forming alloys may be due to the enrichment of the three-dimensional structural units $GeSe_2$ and CdSe and the reduction of chain content and the formation of excess selenium. The experimental and estimated values of T_g^{the} are very close.

2.14. Relation between T_g^{the} and connectivity

The glass transition temperature T_g^{the} is one of the important parameters that represent the strength and rigidity of glass structure. The variation of T_g^{the} with composition is generally understood in terms of the evaluation of network connectivity with the composition [51]. T_g^{the} has been calculated using Sreeram's model [52,53] based on Gibbs and Di-Marzio's work. In this model the authors assume that glasses are formed by a chain of twofold coordinated atoms (S, Se, or Te) in chalcogenide glasses. They assumed that T_o, which equals T_g^{the} for the ideal chalcogenide glasses (pure element) where<r>equals 2. Considering thus the average coordination number<r>, T_g is ruled by the following law;

$$T_g^{the} = \frac{T_o}{1 - 0.7(\langle r \rangle - 2)}$$

(23)

where $T_0=245$ K is the glass transition temperature of selenium element in pure case. [54,55]. The values of the glass transition temperature T_g^{the} for $Ge_xCd_{10}Se_{90-x}$ glasses are given in **Table 5**. The increase in T_g^{the} with increasing the Ge content is suggestive of an increase in network connectivity or rigidity of the system.
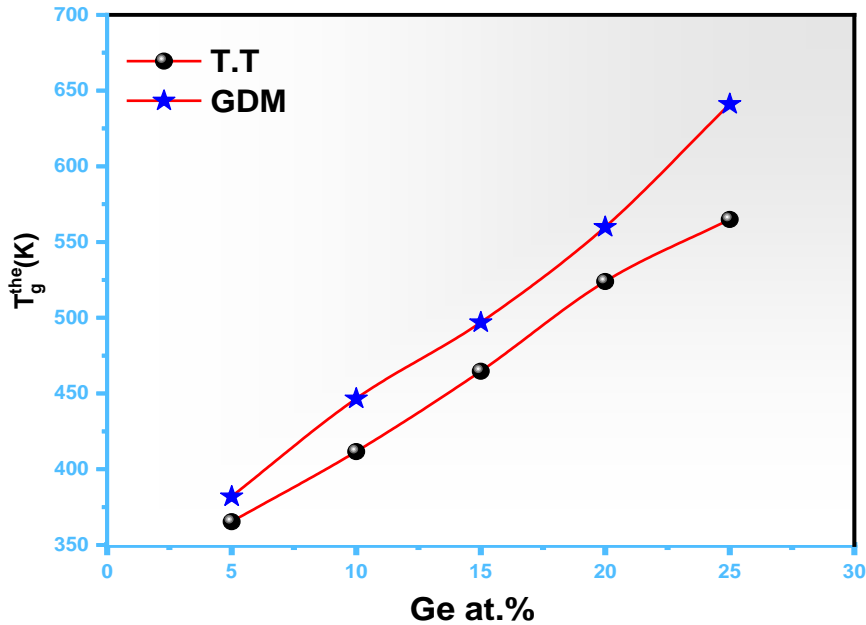

Fig. 6. Plot of T_g^{the} with Ge content for $Ge_xCd_{10}Se_{90-x}$ glassy system.

3. Conclusion

Various physical parameters have been calculated theoretically for the $Ge_xCd_{10}Se_{90-x}$ (x=5, 10, 15, 20 and 25 at. %) chalcogenide glasses. The following conclusions can be drawn from the present analysis:

- The average coordination number, number of constraints, the average heat of atomization, cohesive energy, density, and packing density increase whereas lone-pair of electrons, valence electrons, deviation from stoichiometry and molar volume decrease with increasing Ge content

- Deviation of the stoichiometry values leads the system to chalcogen-rich regions, except for $Ge_{25}Cd_{10}Se_{65}$ indicating chalcogen-poor composition.

- The distribution of the chemical bonds was determined in terms of the chemical order network model (CONM).

- A linear correlation was found between the overall mean bond energy and glass transition temperature. Increasing the Ge content leads to an increase in strong heteropolar Ge-Se bonds at the expense of weak homopolar Se-Se bonds, resulting in an increase in network connectivity or rigidity of the system.

- The increases in the values of cohesive energy and average heat of atomization imply that bonding strength increase with the addition of Ge content and this reflects the cause of increase in the band gap values of all systems except $Ge_{25}Cd_{10}Se_{65}$ the transformation from a 2D layered structure to a rigid 3D network led to a decrease in their value.

- Physical parameters were sensitive to changes in composition subsequently making this present system suitable for phase change optical recording.

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