



Review Paper

Analysis of physicochemical properties in covalent network chalcogenide glasses (ChGs): critical review of theoretical modeling of chemical bond approach

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Abstract

The Group 16 elements are frequently named as chalcogens ('ore builders'). From the geographical point of view, they are known as chalcophiles which are the soft elements (keeping in mind the terminology of the hard/soft acids and bases concept). In the geographical sense, chalcophiles preferably form minerals with sulfur (S), selenium (Se) and tellurium (Te). However, oxygen (O) tends to bind preferably to lithophiles, which are hard elements such as the alkali metals, early transition metals, and silicon. The special position of oxygen amongst the chalcogen elements is its association with its very high electronegativity, which in turn correlates with its high ionization energy and the small atomic radius; which makes it difficult for oxygen to act as a central atom in electron-rich multicentre bonds. In the present script, we have reviewed the models for theoretical prediction of some significant physical parameters i.e. coordination number, constraints, density, molar volume, cohesive energy and heat of atomization etc. for the three generations of Se rich multi-component glasses are presented. The present theoretical study of the multi-component chalcogenide glasses reveals that there is a significant change in the structural environment of the three generations (binary, ternary and quaternary systems) due to rigidity percolation.

Keywords Glass · Ternary and quaternary alloys · Mean coordination number · Chemical ordered network model

1 Introduction

Amongst the non-oxygen chalcogens discussed in this review, both the atomic and covalent radii are raised steadily from sulfur to tellurium, while the electronegativities of sulfur and selenium are exceptionally similar and only tellurium is markedly less electronegative [1]. The presence in the latter of the filled $3d^{10}$ subshell is responsible for the resemblance of ionization energies and electronegativities of sulfur and selenium. The $4s$ and $4p$ ionization energies of selenium are increased to values close to those of the smaller sulfur atom since the 10 electrons in the $3d$ shell screen the $4s$ and $4p$ valence shell improperly from the supplementary 10 positive nuclear charges [1]. The consequence is that there is a strong match between S and

Se isologues, whereas these vary from the corresponding O/Te derivatives.

When the metallic additives are incorporated in disordered systems, they play the role of chemical modifiers in order to create the distinct effects on their physicochemical properties by altering their structure. For diverse impurities, the effects are extensively different and such outcomes depend on the concentration of impurities. The analysis of the influence of impurities on the structure in terms of increasing the disorderliness corresponding to enhanced defects produced is now a subject matter of thorough studies. Phillips [2] and Thorpe [3] reported a significant breakthrough in understanding the structure of covalent glasses of chalcogens at fundamental level

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appeared when they [2, 3] separately proposed the elementary postulates of the constraint theory.

Building elements may be classified into two components when investigating the amorphous structure of covalent glasses. One of these components is the standard bonding structure that possesses the covalent bonds having a density number of $\sim 10^{22}$ – 10^{23} cm^{-3} . This component can be characterized by chemical and topological natures. Another component is related to the role of the defects in the structure e.g., impurities, dangling bonds, valence–alternation pairs, and wrong bonds (homo-polar bonds in stoichiometric alloys). The density of defective bonds is, generally, less than 10^{-2} of that for the covalent bonds. Consequently, the structural behavior is determined frequently by the normal configuration. Further, these defects are mainly accountable for such electronic properties (e.g., the band-gap energy) that are derived from them in contrast to gap states. Thus the fruitful ideas may be achieved by concerning the characteristic defects in the glasses using topological concepts. Theoretical prediction of different physical properties of chalcogenide glasses is a significant study for the understanding of the nature and origin of the various phenomena in these materials where the structure plays the role of a new variable [4–7].

The concept of building elements can be well understood by taking particular examples of Se and Ge which are traditional elements of the two main classes of amorphous semiconductors i.e., the tetrahedrally bonded semiconductors and chalcogenides. The two pairs of outer electrons (i.e., valence electrons) in Ge atom occupy the $4s$ states and the $4p$ states in the atom. Subsequently, by hybridization, four equivalent highly directional sp^3 hybrid orbitals are constructed which are divided into bonding (σ) and anti-bonding states (σ^*). When they form solid, the molecular states σ and σ^* takes place. Consequently, the valence and conduction bands are formed due to their extension. Similar to the tetrahedral Ge, the CB in Se also originates from the σ^* states, but the highest VB is formed from the non-bonding or LP-states instead of σ states. Since the LP bond determines the conduction properties of chalcogenides, they are also called lone-pair semiconductors [8].

Recently, Sharma et al. [9] studied the variation of the physical properties in a-Ge-Se-In glassy semiconductor. Sharda et al. [10, 11] reported a physical analysis of structural transformation in Ge incorporated a-Sb_xSe_{100-x} and Sb-Se-Ge-In systems. Saffarini and Saiter [12] reported the compositional dependence of compactness in terms of the mean coordination number in glassy Ge_xBi₆S_{94-x}. George et al. [13] reported the effect of indium content of the optical and other physical characteristics of As-Te glassy system. The relationship between the optical gap and chemical compositional in Sb_xSe_{100-x} system has been

observed by Fouad et al. [14]. Modgil and Rangra [15] reported the study of the theoretical parameters of GeSn substituted Pb based quaternary chalcogenide glasses at their rigidity percolation threshold. Fadel [16] reported the physical properties and the chemical bond approach for Se-Ge-As amorphous chalcogenide glasses.

Physical properties of chalcogenide glasses in the As_xSe_{1-x} system have also been studied by Yang et al. [17]. They observed that the evolution of a wide range of physical properties is consistent with this sharp structural transition and suggests that there is no intermediate phase in these glasses at room temperature. Mao et al. [18] prepared some ChGs of BaSe-Ga₂Se₃-GeSe₂ system and studied the composition dependence of their physical properties. Saxena and Gupta [19] studied a comparison on physical properties of Ge-Se-Bi based ChGs. Saraswat et al. [20, 21] reported the theoretical prediction of some physicochemical parameters in glassy Se-Te-Sb and Se-Te-Cd alloys.

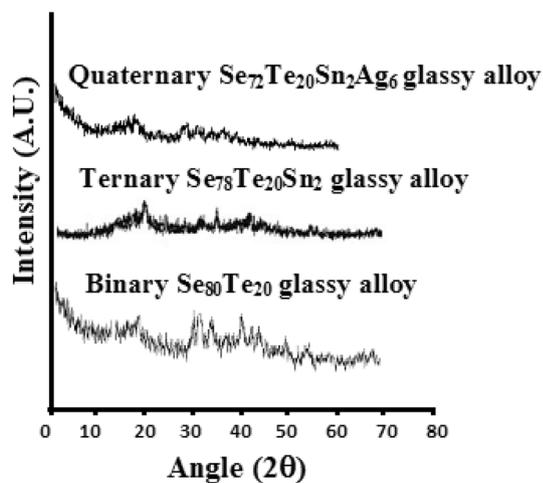
From the literature one can see that the effect of additives, on a variety of physicochemical properties in Se based binary, ternary and quaternary alloys has been studied by various workers by changing the composition; but no efforts have been made to perform a series of such theoretical study for a series of a large number of multi-component glasses in these materials. This was one of the main motivations in undertaking to execute a theoretical study in multi-component glasses of binary, ternary and quaternary systems. The physicochemical properties predicted theoretically in the present review form the basis to disclose structural information which, in effect, can be useful for the perceptive of the various possible applications as well.

2 Experimental technique for the synthesis of multi-component ChGs

Multi-component glasses of binary, ternary and quaternary systems were prepared by the melt-quenching method. The details of sample preparation are given in Table 1. The necessary quantities of the elements were weighed using an electrical sensitive balance with the least count of 0.1 mg. The weighed materials were placed in a well clean and evacuated silica tube (sealed under a pressure of 10^{-5} Torr), which is also known as the quartz ampoules (length ~ 5 cm and internal diameter 8 mm). This tube was then put in a furnace with a constant appropriate temperature by means of temperature-controller for 8 h. For sealing of the tubes, a high vacuum pumping system (Hindhivac, Model: VS65D) was employed. The temperature of the furnace was increased slowly at a rate of 3–4 °C/min. The temperature of furnace is kept at a temperature higher than fusion temperatures of the constituent elements sealed in the quartz tube. The glass tubes were rocked continuously during heating in order

Table 1 Details of compositions of various multi-component glasses of binary, ternary and quaternary systems and their parent alloy studied in present studies

Binary alloys with parent Se	Ternary alloys $\text{Se}_{78-x}\text{Te}_{20}\text{M}_x$ ($x = 2, 4, 6$) with parent $\text{Se}_{80}\text{Te}_{20}$	Ternary alloys $\text{Se}_{75-x}\text{Te}_{20}\text{M}_x$ ($x = 5, 10, 15$) with parent $\text{Se}_{80}\text{Te}_{20}$	Quaternary alloys with parent $\text{Se}_{78}\text{Te}_{20}\text{Sn}_2$
$\text{Se}_{95}\text{Te}_5$	$\text{Se}_{78}\text{Te}_{20}\text{Cd}_2$	$\text{Se}_{75}\text{Te}_{20}\text{Cd}_5$	$\text{Se}_{76}\text{Te}_{20}\text{Sn}_2\text{Cd}_2$
$\text{Se}_{95}\text{Ge}_5$	$\text{Se}_{76}\text{Te}_{20}\text{Cd}_4$	$\text{Se}_{70}\text{Te}_{20}\text{Cd}_{10}$	$\text{Se}_{74}\text{Te}_{20}\text{Sn}_2\text{Cd}_4$
$\text{Se}_{95}\text{In}_5$	$\text{Se}_{74}\text{Te}_{20}\text{Cd}_6$	$\text{Se}_{65}\text{Te}_{20}\text{Cd}_{15}$	$\text{Se}_{72}\text{Te}_{20}\text{Sn}_2\text{Cd}_6$
$\text{Se}_{90}\text{Te}_{10}$	$\text{Se}_{78}\text{Te}_{20}\text{Sb}_2$	$\text{Se}_{75}\text{Te}_{20}\text{Ag}_5$	$\text{Se}_{76}\text{Te}_{20}\text{Sn}_2\text{Ag}_2$
$\text{Se}_{90}\text{Ge}_{10}$	$\text{Se}_{76}\text{Te}_{20}\text{Sb}_4$	$\text{Se}_{70}\text{Te}_{20}\text{Ag}_{10}$	$\text{Se}_{74}\text{Te}_{20}\text{Sn}_2\text{Ag}_4$
$\text{Se}_{90}\text{In}_{10}$	$\text{Se}_{74}\text{Te}_{20}\text{Sb}_6$	$\text{Se}_{65}\text{Te}_{20}\text{Ag}_{15}$	$\text{Se}_{72}\text{Te}_{20}\text{Sn}_2\text{Ag}_6$
$\text{Se}_{85}\text{Te}_{15}$	$\text{Se}_{78}\text{Te}_{20}\text{Ge}_2$	$\text{Se}_{75}\text{Te}_{20}\text{Sb}_5$	$\text{Se}_{76}\text{Te}_{20}\text{Sn}_2\text{Sb}_2$
$\text{Se}_{85}\text{Ge}_{15}$	$\text{Se}_{76}\text{Te}_{20}\text{Ge}_4$	$\text{Se}_{70}\text{Te}_{20}\text{Sb}_{10}$	$\text{Se}_{74}\text{Te}_{20}\text{Sn}_2\text{Sb}_4$
$\text{Se}_{85}\text{In}_{15}$	$\text{Se}_{74}\text{Te}_{20}\text{Ge}_6$	$\text{Se}_{65}\text{Te}_{20}\text{Sb}_{15}$	$\text{Se}_{72}\text{Te}_{20}\text{Sn}_2\text{Sb}_6$
$\text{Se}_{80}\text{Te}_{20}$	$\text{Se}_{78}\text{Te}_{20}\text{Ag}_2$	$\text{Se}_{75}\text{Te}_{20}\text{Ge}_5$	$\text{Se}_{76}\text{Te}_{20}\text{Sn}_2\text{Bi}_2$
$\text{Se}_{80}\text{Ge}_{20}$	$\text{Se}_{76}\text{Te}_{20}\text{Ag}_4$	$\text{Se}_{70}\text{Te}_{20}\text{Ge}_{10}$	$\text{Se}_{74}\text{Te}_{20}\text{Sn}_2\text{Bi}_4$
$\text{Se}_{80}\text{In}_{20}$	$\text{Se}_{74}\text{Te}_{20}\text{Ag}_6$	$\text{Se}_{65}\text{Te}_{20}\text{Ge}_{15}$	$\text{Se}_{72}\text{Te}_{20}\text{Sn}_2\text{Bi}_6$

**Fig. 1** XRD patterns of representative binary, ternary and quaternary glassy alloys

to ensure homogeneity. The melts were quenched in ice-cooled water. Glassy nature of alloys was confirmed by using XRD technique. The copper target was used as a source of X-rays with $\lambda = 1.54 \text{ \AA}$ ($\text{Cu K}_{\alpha 1}$) at 30 kV and 20 mA. The XRD patterns of some as-prepared samples are shown in Fig. 1. The absence of any sharp peak confirms their glassy nature. Similar XRD patterns were observed for other samples.

3 Phenomenology of glass formation and structure of ChGs

3.1 Glass formation criteria

The cooling rate of a material in the melt stage is the main factor that plays the dominant role in determining

the vitrification of the material. This is a key parameter to decide whether a particular material will be crystallized upon cooling or will be converted into glass. According to this description, it seems theoretically that almost all materials can be prepared in a glassy state if cooled fast as much as necessarily possible.

The rapidness of the cooling rate will depend on the material under consideration. Vitrification of some materials in glassy form is simple. Most S-based and Se-based chalcogen rich materials belong to this class and form glasses even at cooling rates as low as a few Kelvins per second. Some materials can be made amorphous only under tremendous conditions such as an additional high cooling rate. Te-based chalcogenides belong to this class since they can be obtained in the amorphous phase if the minimum cooling rate is of the order of 108 K/s. Such a high cooling rate is quite hard to attain experimentally.

There is no recognized theory in the long history of glass science that could guess whether a particular material is a good glass former or poor glass former. The credit goes to Zachariassen [22] for the first unbeaten attempt in determining essential conditions for glass formation. He proposed that good glass former possess an internal energy in the amorphous state that is just slightly larger than that in their crystalline counterparts. His approach suggests that the deviations in the bond angles are mainly responsible for the non-periodic arrangement of atoms.

Further, it was recommended that a prerequisite of the covalent nature of bonding in the melt may be a more suitable formulation because of a strong connection between glass forming ability of a semiconducting glass and the directional or covalent bonds [23]. The efforts have also been done to find a correlation between a good glass former and the electronic structure of its ingredient elements.

Specifically, it was argued that a material having good glass-forming ability must acquire a high concentration f of lone-pair electrons as compared to the total number of valence electrons ($f=0.5 \div 0.66$) [24].

3.2 Structure of glassy Se, Se–Te and cross-linking of metallic additives

Chalcogenide glasses are frequently known as lone pair semiconductors. Lone pair electrons represent the pairs of valence electrons that do not participate in forming covalent bonds with the neighboring atoms. The characterization of the chemical bonds associated with lone pair electrons is done by their flexible nature. The deformation of a bond consisting of the lone pair electrons is much effortless as compared to a bond which has no non-bonding pair. By raising the number of lone pair electrons, the strain energy in a system decreases. The structure of a solid having a huge number of non-bonding electrons supports its vitrification.

In the last seven decades, an extensive investigation of the structure and properties of amorphous selenium (a-Se) has been done [1, 2]. But still the debates about its molecular structure are on-going. Extensively, it was assumed that the structural elements long selenium chain (Se_n) and the selenium 8-ring (Se_8) are mixed together as the constituents of the amorphous phase. The idea of this model was put forward with the information that the crystalline phase of selenium consists of α -monoclinic Se (α -Se) phase and trigonal Se (γ -Se) phase. The Se_8 rings and the Se_n chains are the building block in the former and the later phases respectively. It is therefore plausible that we can think about a structure for the amorphous phase which is made of a mixture of ring and chain members. However, the polymeric chains of selenium atoms have indecisive lengths. In addition, it is indistinct whether the cyclic structure or rings are the prime members of a-Se. In the current decade, the structural investigation of chalcogenide glasses is the topic of the enhanced interest because of their fascinating applications. The limited molecular order is shown in Fig. 2 for a typical selenium chain. This figure depicts that there are two kinds of segments. One kind of segments is described by the recurrence of the identical dihedral angle ("chain-like" in the sense of trigonal Se), while the alternating dihedral angle ("ring-like" in the sense of Se_8 molecule) are used for the characterization of other kind of segments.

The synthesis techniques and the consequent sample treatments affect the structural as well as physical properties of amorphous alloys of chalcogenides but in a fewer sensitive way as compared to their crystalline counterparts. In several cases, the preliminary structures

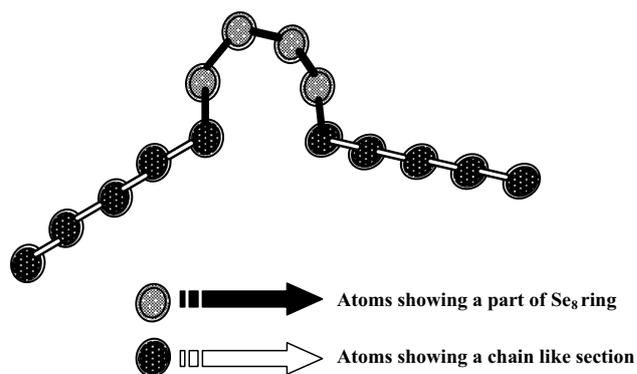


Fig. 2 Local molecular order in a selenium chain

of the amorphous films are dissimilar from those of well-annealed films or their bulk-glass counterparts. Consequently, the noteworthy irretrievable structural modifications take place under the influence of band-gap illumination or annealing. These respective modifications are well known as light-induced and thermal-induced variations.

Various research groups have studied the structure of amorphous Se (a-Se) [25–28] and the consequence of alloying Te into glassy Se [29–32]. The outcome of their research work demonstrates that the widespread polymeric chains and eight-membered rings of Se are present in a-Se in diverse proportions. The dissociation of these structural units takes place due to incorporation of Te in glassy Se. Consequently, the alloys of Se–Te become more significant because of their fascinating advantages (elevated photosensitivity, better hardness, and slighter aging effects) over the pure glassy Se. These advantages makes them useful as recording layer materials in optical phase change (PC) technique [33, 34]. However, some noteworthy troubles are found in these alloys for their use in this kind of application. The two severe troubles are the restricted reversibility [35] and low values of the glass transition and crystallization temperatures. The addition of a third foreign element in Se–Te alloys plays the role of the chemical modification to remove these troubles.

3.3 Chalcogenides as lone-pair semiconductors

First of all, Kastner identified [36] the significant role of lone-pair electrons in the chemistry of chalcogenides. Particularly, he mentioned the difference between tetrahedrally bonded semiconductors such as Si or Ge and the chalcogens (S, Se, Te). The hybridized sp_3 orbitals split into bonding (σ) and anti-bonding (σ^*) molecular states in Si or Ge. On other hand, the σ and σ^* states are consequently expanded into the valence and conduction bands, respectively, in the solid. On the other hand, the s states

lie well below the p states and require not be considered in S, Se, and Te. Thus, chalcogens are twofold coordinated elements because only two of the three p orbitals can be utilized for bonding. Consequently, one non-bonding electron pair (i.e., lone pair electrons) is found in chalcogens. Consequently, the formation of forming a lone pair (LP) band near the original p -state energy takes place in chalcogens and chalcogens rich solids. With respect to this reference energy, the bonding (σ) and anti-bonding (σ^*) bands are split symmetrically. Therefore, chalcogenides are also known as lone-pair semiconductors in Kastner's theory because the role of bonding band is played by the lone-pair band as the bonding band is no longer at the top of the valence band (see Fig. 3).

4 Chemical bond approach

The glasses in which the nature of the bonding is primarily covalent follow this approach. The following assumptions are the basis of this model:

- (1) The first assumption suggests the existence of a preferred coordination number " n " for the covalent structure of every element. The respective values of n numbers are 2, 3 and 4 for the elements of VIB, VB and IVB groups of the periodic table. These values of n obey the ' $8 - N$ ' rule (here N denotes the number of s -valence and p -valence electrons). According to this rule, the coordination numbers is greater than 4 for the elements of the IB–IIIB groups of the periodic table. For a glassy material having the covalently bonded structure, this condition is not feasible. To explain this dilemma for the elements from group IB–IIIB, Liu and Taylor [37] postulated that formal charge transfer takes place either from the chalcogen elements or non-chalcogen elements of the group VB elements. Consequently, the tetrahedral coordination takes place for the group IB–IIIB elements and enlarged coordination for the group VIB or VB elements. Thus, if we consider n as the number of valence electrons formally assigned to the elements then the elements obey the comprehensive ' $8 - n$ ' rule

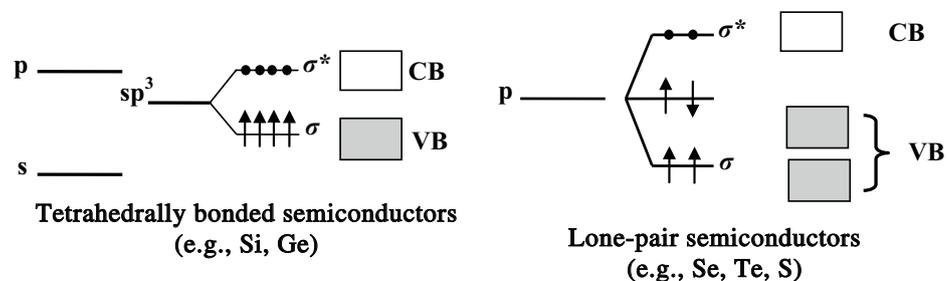
[37]. This new rule proposed a following formula for the determination of the mean coordination number (Z):

$$Z = 8 - n = 8 - N$$

Here $\langle n \rangle$ is the mean number of formal valence electrons per atom in the glass composition. $\langle n \rangle$ equals to the average number of valence electrons per atom (N) in the glass composition.

- (2) Heteronuclear bonds are preferred to homonuclear bonds in Se and Se–Te glasses having a high content of Se [22]. The chemical ordered network model (CONM) may be used to clarify this postulation to some extent. This model suggests that the creation of the heteropolar bonds gets privilege as compared to the homopolar bonds in the covalent network of glass under consideration. In the covalent network of Se–Te–M system, a variety of covalent bonds are involved such as Se–Se, Te–Te, Se–Te, M–Se, and M–Te. The strength of Te–Te bond is smaller than that of Se–Se bonds. The electronegativity of Te is also less than that of Se. The pioneering results established by the Pauling theory [38, 39] also suggest that M–Te bonds are found to be weaker than M–Se bonds. Consequently, one can expect that the metallic additives (like Ag, Cd and Sb) are combined conveniently with Se as compared to Te. The experimental results of x-ray spectroscopy of glassy alloys $\text{Se}_{80}\text{Te}_{10}\text{M}_{10}$ [40] also supports this assumption.
- (3) Bonds are created in the succession of diminishing bond enthalpy (bond enthalpies are defined positive) until the saturation of all accessible formal valences of the atoms. Consequently, mean coordination number (Z) takes the value $\langle Z \rangle = 2$ corresponding to the division of the entire number of bonds by the number of atoms.
- (4) With the help of the Pauling's relation, we can correlate the heteronuclear bond enthalpies and the homonuclear bond enthalpies. Since Pauling did not provide the covalent bond enthalpies for bonds with the group IB–IIIB elements, an alternative approach is used to obtain a consistent set of bond enthalpies [41].

Fig. 3 Bonding descriptions in tetrahedrally bonded and lone-pair semiconductors



5 Result and discussion

5.1 Topological considerations

Keeping in the mind the concept of average coordination number ($\langle r \rangle$), the structural adjustments in the host multi-component glasses of binary, ternary and quaternary systems may be explained smoothly. For the multi-component glasses of binary, ternary and quaternary systems, the average coordination number $\langle r \rangle$ can be calculated using the formula [3–6].

$$\langle r \rangle = \frac{\alpha N_{Se} + \beta N_M}{\alpha + \beta} \text{ (For binary systems)} \quad (1a)$$

$$\langle r \rangle = \frac{\alpha N_{Se} + \beta N_{Te} + \gamma N_M}{\alpha + \beta + \gamma} \text{ (For ternary systems)} \quad (1b)$$

and

$$\langle r \rangle = \frac{\alpha N_{Se} + \beta N_{Te} + \gamma N_{Sn} + \delta N_M}{\alpha + \beta + \gamma + \delta} \text{ (For quaternary systems)} \quad (1c)$$

For binary systems described by Eq. (1a), α and β are the atomic percentages of elements Se and M (M = Te, Ge and, In) and N_{Se} and N_M are the coordination numbers of Se and M (M = Te, Ge and, In) respectively. For ternary systems described by Eq. (1b), α , β and γ are the atomic percentages of elements Se, Te and M (M = Cd, Sb, Ge and Ag) and N_{Se} , N_{Te} and N_M are the coordination numbers of Se, Te and M (M = Cd, Sb, Ge and Ag) respectively. For quaternary systems described by Eq. (1c), α , β , γ and δ are the atomic percentages of elements Se, Te, Sn and M (M = Cd, Sb, Bi and, Ag) and N_{Se} , N_{Te} , N_{Sn} and N_M are the coordination numbers of Se, Te, Sn and M (M = Cd, Sb, Bi and, Ag) respectively.

The bond-stretching (α -forces) and bond bending (β -forces) are two types of the near-neighbor bonding forces that are present in the covalent solids. The number of Lagrangian bond-stretching constraints per atom is $n_\alpha = \langle r \rangle / 2$ and bond bending constraints is $n_\beta = 2\langle r \rangle - 3$. The total number of constraints (N_c) is the addition of the bond bending and bond stretching constraints. The effective average coordination number $\langle r_{eff} \rangle$ is determined by using the formula [16]:

$$\langle r_{eff} \rangle = \frac{2(N_c + 3)}{5} \quad (2)$$

The number of constraints was estimated by Thorpe [3] using the Maxwell counting. This procedure was first formulated to find out the stability of a network of rods connected with pivot joints. Each coordinated atom is associated with bond-stretching constraints ($\langle r \rangle / 2$) in this counting. These

constraints appear from the radial force because there are r bonds, each of them are shared by two atoms. In each atom, there are $(2\langle r \rangle - 3)$ bond bending constraints that arrive from the angular forces. When we consider this counting, we get the following formula for the fraction of floppy modes with respect to the degree of freedom [16]:

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

The value of f is reduced to zero when $\langle r \rangle$ approaches the critical value of 2.4. Networks with $\langle r \rangle < 2.4$ are polymeric glasses having a floppy network with the separated rigid regions. As $\langle r \rangle$ increases and it reaches a critical value $\langle r \rangle = \langle r_c \rangle = 2.4$, and thus, the network goes through a transition. The rigidity percolates for this critical value $\langle r_c \rangle$. Consequently, the glass transforms to a rigid structure. This $\langle r_c \rangle$ value is also referred to as the rigidity percolation or mechanical threshold. Networks with $\langle r \rangle > 2.4$ are amorphous solids (or rigid). The calculated values of n_α , n_β , n_γ and f of multi-component glasses of binary, ternary and quaternary systems are shown in respective Tables 2, 3 and 4, respectively.

5.2 Density, molar volume and compactness

Density is an imperative physical parameter and is an assessment of the rigidity of the system. It is also connected to the average coordination number of the system. It can be calculated by using the following relation [42]:

$$\rho = \left(\sum m_i / d_i \right)^{-1} \quad (4)$$

where m_i is the fraction of mass and d_i is the density of i th structural unit.

The values of density (ρ) are given in Tables 2, 3 and 4, respectively for different glassy alloys of binary, ternary and quaternary systems respectively.

Using the value of density obtained from Eq. (4), the molar volume of the system is calculated by using the relation [42]:

$$V_m = \frac{\sum x_i M_i}{\rho} \quad (5)$$

Here x_i represents the atomic fraction of component i and M_i is its atomic mass. The values of V_m are shown in Tables 2, 3 and 4, respectively, for multi-component glasses of binary, ternary and quaternary systems. The plots of density and molar volume against average coordination number are shown in Fig. 4 for particular multi-component glasses of binary, ternary and quaternary systems. From this figures, it is clear that the increasing sequence of molar volume is just opposite

Table 2 Various theoretical physicochemical parameters of multi-component glasses of binary systems

	$\langle r \rangle$	n_a	n_β	n_c	f	Density (g/cm ³)	Volume (cm ³ /mol)	Compactness	LP	R
Se ₁₀₀	2	1	1	2	0.333	4.81	16.41	0	4	∞
Se ₉₅ Te ₅	2	1	1	2	0.333	4.87	16.73	-0.00658	4	∞
Se ₉₅ Ge ₅	2.1	1.05	1.2	2.25	0.25	4.83	16.27	0.000371	3.84	9.5
Se ₉₅ In ₅	2.05	1.025	1.1	2.125	0.292	4.89	16.50	-0.0074	3.8	12.7
Se ₉₀ Te ₁₀	2	1	1	2	0.333	4.92	17.03	-0.01224	4	∞
Se ₉₀ Ge ₁₀	2.2	1.1	1.4	2.5	0.167	4.86	16.13	0.000709	3.6	4.5
Se ₉₀ In ₁₀	2.1	1.05	1.2	2.25	0.250	4.98	16.58	-0.01384	3.6	6
Se ₈₅ Te ₁₅	2	1	1	2	0.333	4.98	17.32	-0.01706	4	∞
Se ₈₅ Ge ₁₅	2.3	1.15	1.6	2.75	0.083	4.88	15.98	0.001013	3.4	2.8
Se ₈₅ In ₁₅	2.15	1.075	1.3	2.375	0.208	5.07	16.64	-0.01954	3.4	3.8
Se ₈₀ Te ₂₀	2	1	1	2	0.333	4.98	17.82	-0.03269	4	∞
Se ₈₀ Ge ₂₀	2.4	1.2	1.8	3	0	4.88	15.92	-0.00361	3.2	2
Se ₈₀ In ₂₀	2.2	1.1	1.4	2.5	0.167	5.07	16.98	-0.04203	3.2	2.7

Table 3 Various theoretical physicochemical parameters of multi-component glasses of ternary (a) Se_{75-x}Te₂₀M_x (x = 2, 4, 6), (b) Se_{75-x}Te₂₀M_x (x = 5, 10, 15) systems

	$\langle r \rangle$	n_a	n_β	n_c	f	Density (g/cm ³)	Volume (cm ³ /mol)	Compactness	LP	R
(a)										
Se ₈₀ Te ₂₀	2	1	1	2	0.333	4.98	17.82	-0.0327	4	∞
Se ₇₈ Te ₂₀ Ag ₂	2.04	1.02	1.08	2.1	0.3	5.10	17.37	-0.0232	3.9	24.5
Se ₇₆ Te ₂₀ Ag ₄	2.08	1.04	1.16	2.2	0.267	5.16	17.42	-0.0253	3.7	12
Se ₇₄ Te ₂₀ Ag ₆	2.12	1.06	1.24	2.3	0.233	5.22	17.33	-0.0272	3.6	7.8
Se ₇₈ Te ₂₀ Cd ₂	2.04	1.02	1.08	2.1	0.3	5.10	17.56	-0.0231	3.9	24.5
Se ₇₆ Te ₂₀ Cd ₄	2.08	1.04	1.16	2.2	0.267	5.12	17.53	-0.0251	3.8	12
Se ₇₄ Te ₂₀ Cd ₆	2.12	1.06	1.24	2.3	0.233	5.18	17.50	-0.0269	3.6	7.8
Se ₇₈ Te ₂₀ Sb ₂	2.03	1.015	1.06	2.075	0.308	5.10	17.70	-0.0226	3.9	28
Se ₇₆ Te ₂₀ Sb ₄	2.06	1.03	1.12	2.15	0.283	5.10	17.72	-0.0241	3.9	13.7
Se ₇₄ Te ₂₀ Sb ₆	2.09	1.045	1.18	2.225	0.258	5.13	17.80	-0.0255	3.8	8.9
Se ₇₈ Te ₂₀ Ge ₂	2.04	1.02	1.08	2.1	0.3	5.05	17.53	-0.0208	3.9	24.5
Se ₇₆ Te ₂₀ Ge ₄	2.08	1.04	1.16	2.2	0.267	5.06	17.50	-0.0206	3.8	12
Se ₇₄ Te ₂₀ Ge ₆	2.12	1.06	1.24	2.3	0.233	5.07	17.41	-0.0204	3.8	7.8
(b)										
Se ₈₀ Te ₂₀	2	1	1	2	0.333	4.98	17.82	-0.0327	4	∞
Se ₇₅ Te ₂₀ Ag ₅	2.1	1.05	1.2	2.25	0.25	5.20	17.37	-0.02630	3.65	9.5
Se ₇₀ Te ₂₀ Ag ₁₀	2.2	1.1	1.4	2.5	0.167	5.34	17.14	-0.0307	3.3	4.5
Se ₆₅ Te ₂₀ Ag ₁₅	2.3	1.15	1.6	2.75	0.083	5.51	17.01	-0.0343	2.95	2.8
Se ₇₅ Te ₂₀ Cd ₅	2.1	1.05	1.2	2.25	0.25	5.16	17.51	-0.0261	3.7	9.5
Se ₇₀ Te ₂₀ Cd ₁₀	2.2	1.1	1.4	2.5	0.167	5.30	17.41	-0.0303	3.4	4.5
Se ₆₅ Te ₂₀ Cd ₁₅	2.3	1.15	1.6	2.75	0.083	5.42	17.30	-0.0336	3.1	2.8
Se ₇₅ Te ₂₀ Sb ₅	2.075	1.037	1.15	2.187	0.271	5.12	17.75	-0.0248	3.875	10.8
Se ₇₀ Te ₂₀ Sb ₁₀	2.15	1.075	1.3	2.375	0.21	5.20	17.90	-0.0278	3.75	5.1
Se ₆₅ Te ₂₀ Sb ₁₅	2.225	1.112	1.45	2.562	0.155	5.27	18.03	-0.0301	3.625	3.2
Se ₇₅ Te ₂₀ Ge ₅	2.1	1.05	1.2	2.25	0.25	5.10	17.44	-0.0205	3.8	9.5
Se ₇₀ Te ₂₀ Ge ₁₀	2.2	1.1	1.4	2.5	0.167	5.10	17.30	-0.0203	3.6	4.5
Se ₆₅ Te ₂₀ Ge ₁₅	2.3	1.15	1.6	2.75	0.083	5.12	17.14	-0.0195	3.4	2.8

Here M represent the foreign element

Table 4 Various theoretical physicochemical parameters of multi-component glasses of quaternary systems

	$\langle r \rangle$	n_α	n_β	n_c	f	Density (g/cm ³)	Volume (cm ³ /mol)	Compactness	LP	R
Se ₇₈ Te ₂₀ Sn ₂	2.04	1.02	1.08	2.1	0.3	5.06	17.70	-0.0217	3.92	24.5
Se ₇₆ Te ₂₀ Sn ₂ Ag ₂	2.08	1.04	1.16	2.2	0.267	5.12	17.60	-0.0237	3.78	12
Se ₇₄ Te ₂₀ Sn ₂ Ag ₄	2.12	1.06	1.24	2.3	0.233	5.17	17.52	-0.0256	3.64	7.8
Se ₇₂ Te ₂₀ Sn ₂ Ag ₆	2.16	1.08	1.32	2.4	0.2	5.24	17.60	-0.0274	3.5	5.75
Se ₇₆ Te ₂₀ Sn ₂ Bi ₂	2.08	1.04	1.16	2.2	0.267	5.11	18.01	-0.0335	3.86	12
Se ₇₄ Te ₂₀ Sn ₂ Bi ₄	2.12	1.06	1.24	2.3	0.233	5.20	18.32	-0.0444	3.8	7.8
Se ₇₂ Te ₂₀ Sn ₂ Bi ₆	2.16	1.08	1.32	2.4	0.2	5.23	18.62	-0.0543	3.74	5.7
Se ₇₆ Te ₂₀ Sn ₂ Cd ₂	2.08	1.04	1.16	2.2	0.267	5.11	17.70	-0.0236	3.8	12
Se ₇₄ Te ₂₀ Sn ₂ Cd ₄	2.12	1.06	1.24	2.3	0.233	5.15	17.62	-0.0255	3.68	7.8
Se ₇₂ Te ₂₀ Sn ₂ Cd ₆	2.16	1.08	1.32	2.4	0.2	5.20	17.60	-0.0272	3.56	5.75
Se ₇₆ Te ₂₀ Sn ₂ Sb ₂	2.07	1.035	1.14	2.175	0.275	5.10	17.75	-0.0231	3.87	12.8
Se ₇₄ Te ₂₀ Sn ₂ Sb ₄	2.1	1.05	1.2	2.25	0.25	5.12	17.81	-0.0245	3.82	8.5
Se ₇₂ Te ₂₀ Sn ₂ Sb ₆	2.13	1.065	1.26	2.325	0.225	5.15	17.87	-0.0257	3.77	6.3

to that of the density. The similar variation of density and molar volume with average coordination number was observed for other binary, ternary and quaternary systems. Theoretically, density is inversely proportional to volume. From the plots shown in Fig. 4 this fact is clearly revealed.

The formula for determination of the compactness (δ) is as follows [43, 44]:

$$\delta = \frac{\sum \frac{C_i A_i}{\rho_i} - \sum \frac{C_i A_i}{\rho}}{\sum \frac{C_i A_i}{\rho}} \quad (6)$$

Here 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. The calculated values of δ are listed in Tables 2, 3 and 4, respectively, for multi-component glasses of binary, ternary and quaternary systems. The compactness of a given glass is an assessment of the normalized alteration of the mean atomic volume as a signature of the chemical interactions of the elements forming the glassy network [5]. Consequently, it is more responsive to alterations in the structure of the glass network over the mean atomic volume.

5.3 Lone pair electron

The formula for the determination of lone-pair electrons (LP) is [42]:

$$LP = V - \langle r \rangle \quad (7)$$

Here LP is the number of lone-pair electrons, V is the valence electron which is equal to unshared lone-pair

electron and $\langle r \rangle$ is the average coordination number. The evaluated values of LP for multi-component glasses of binary, ternary and quaternary systems are tabulated in Tables 2, 3 and 4, respectively.

Zhenhua [45] introduced an easy condition for the computation of the capability of a chalcogenide system to maintain its vitreous state. This condition considers the number of lone-pair electrons which is necessary to achieve the vitreous state of the system. The number of lone-pair electrons must be larger than 2.6 and 1 for binary and ternary systems respectively and so on. This is obvious from the Tables 2, 3 and 4 that the present glassy systems are good glass former. When a huge number of lone-pair electrons are present in a glassy system, its structures support glass formation as a signature of the decreasing strain energy.

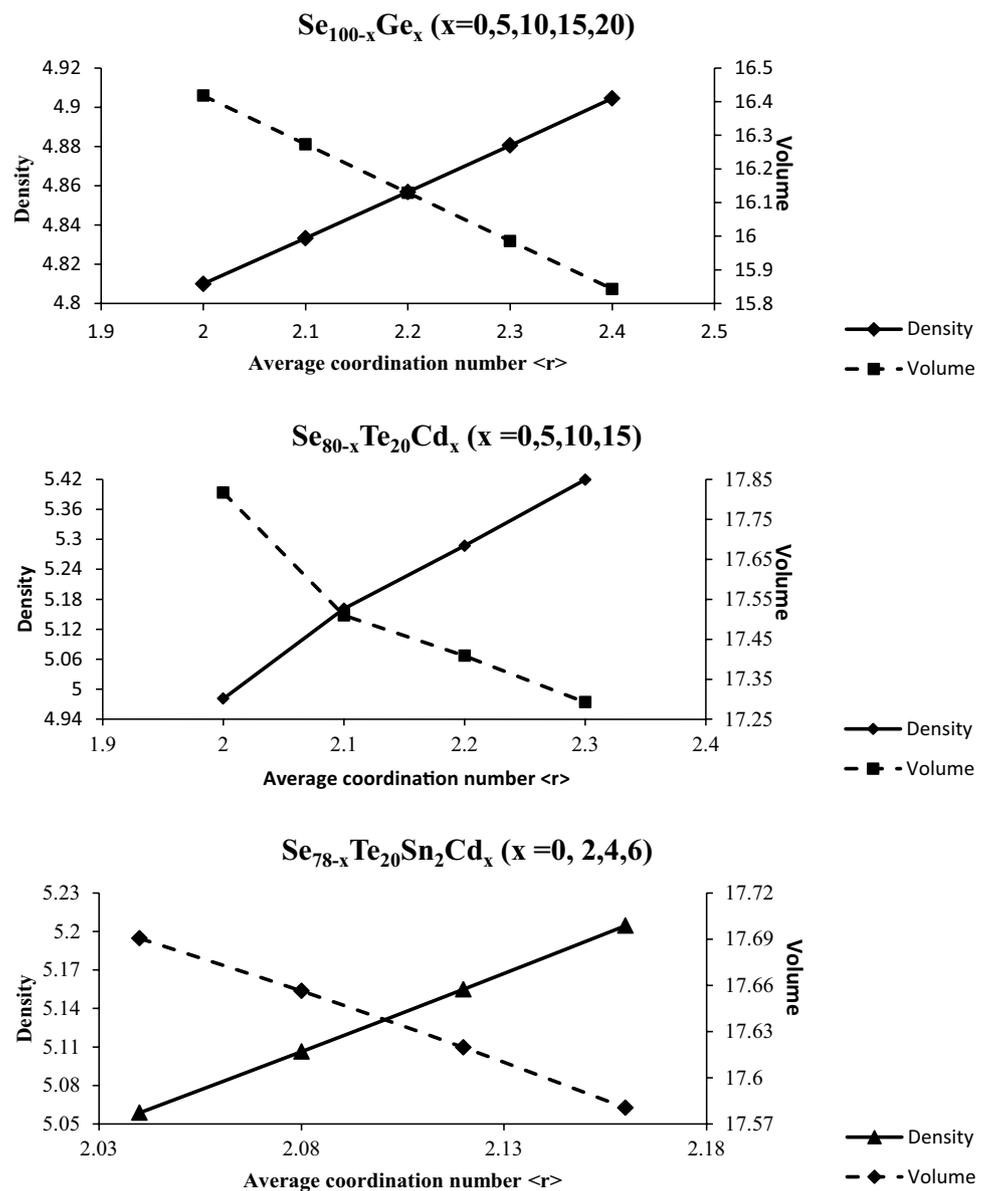
5.4 Parameter R and mean bond energy

The Parameter R signifies the deviation of stoichiometry. It is defined by the ratio of possibilities of the covalent bonding of chalcogen atom to that of a non-chalcogen atom. Here we have described the approach for the determination of R values of ternary alloys but similar approach is applicable for the binary and quaternary alloys.

For glassy Se _{α} Te _{β} and glassy Se _{α} Te _{β} M _{γ} (M = Cd, Sb, Ge, Ag) alloys, the quantity R is defined by [14, 15];

$$R = \frac{\alpha N_{Se} + \beta N_{Te}}{\gamma N_M} \quad (8)$$

Fig. 4 Plots showing the variation of the density and molar volume, respectively, as a function of average coordination number $\langle r \rangle$ for representative three generations (binary, ternary and quaternary ChGs)



Here α , β and γ are the atomic fractions of Se, Te and M ($M = Cd, Sb, Ge, Ag$) and N_{Se} , N_{Te} and N_M are the coordination number of Se, Te and M ($M = Cd, Sb, Ge, Ag$). The values of the overall mean bond energy for the multi-component glasses of binary, ternary and quaternary systems are given in Tables 2, 3 and 4, respectively.

There are three conditions arising for analysis of the parameter R :

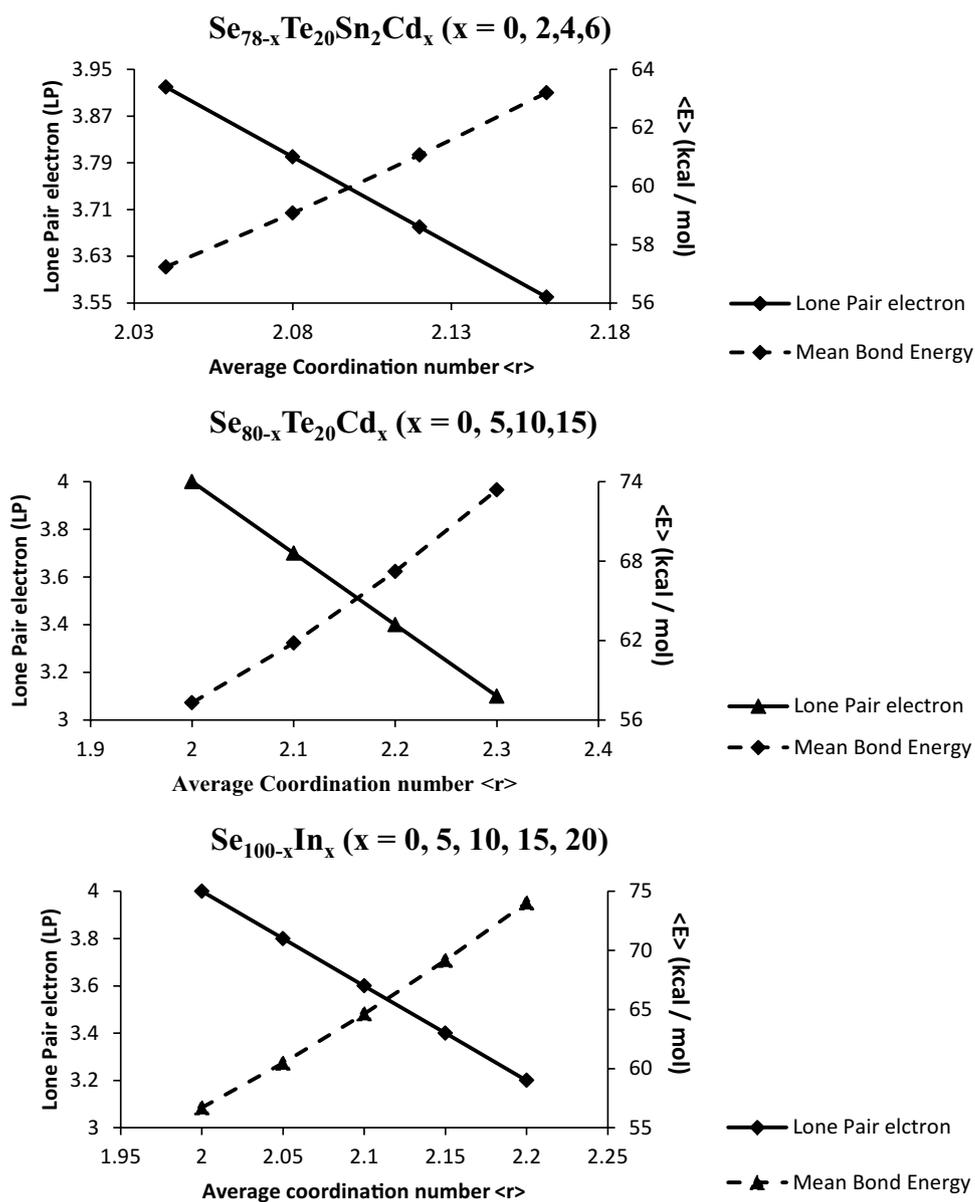
- (1) $R = 1$ symbolizes the stoichiometric composition, consisting only hetero-polar bonds.
- (2) $R > 1$ indicates the existence of both hetero-polar bonds and chalcogen–chalcogen bonds that further indicates that the system is chalcogen rich.

- (3) $R < 1$ represents that the system is selenium poor and so the hetero-polar and metal–metal bonds formed.

For multi-component glasses of three generations (binary, ternary and quaternary systems) studied in the present work, the values of R are greater than 1 (see Table 2, 3, 4). Consequently, each glassy system leads to a network having chalcogen rich regions.

The credit goes to Tichy and Ticha [6] to have drawn attention towards the point that the value of glass transition temperature should not be just related to connectedness of the network (average coordination number $\langle r \rangle$) but should also be linked to the number of connections, i.e. the mean bond energy between the atoms of the network. The substantial difference in the

Fig. 5 Variation of the lone pair electron and mean bond energy, respectively, as a function of average coordination number $\langle r \rangle$ for representative three generations (binary, ternary and quaternary ChGs)



bond energies of the hetero-polar and the homopolar bonds [46] allow us to expect the chemically ordered networks, where the number of hetero-polar bonds is maximized. This means that the hetero-polar bonds are more favorably formed over homo-polar bonds. Since bulk glasses are considered, a chemical bond ordering model is assumed.

The bond energies (E_{AB}) of hetero-polar A-B bonds can be, in first approximation, estimated using Pauling's relation [38]:

$$E_{AB} = 0.5 (E_{A-A} + E_{B-B}) + 23 (\chi_A - \chi_B)^2 \tag{9}$$

Here E_{A-A} and E_{B-B} and χ_A and χ_B are the, respectively, homo-polar bond energies and electro-negativities. The values of these physical quantities are obtained from [47].

The degree of cross-linking per atom for chalcogen-rich region, as in the present case, can be expressed as [6]:

$$P_r = \frac{\alpha N_{Te} + \beta N_M}{(a + b + c)} \tag{10}$$

The mean bond energy of average cross-linking per atom (E_c) is given by [6]:

$$E_c = P_r \cdot E_{hb} \tag{11}$$

The mean hetero-polar bond energy is given by [6]:

$$P_{Eb} = \frac{aN_{Te}(E_{Se-Te}) + bN_M(E_{Se-M})}{(aN_{Te} + bN_M)} \tag{12}$$

Table 5 Values of cohesive energy (CE) and average heat of atomization (\bar{H}_5) of various multi-component binary systems and their parent Se

Binary alloys	CE (kcal/mol)	\bar{H}_5 (kcal/mol)
Se	56.7	49.4
Se ₉₅ Te ₅	56.9	49.2
Se ₉₅ Ge ₅	55.9	51.4
Se ₉₅ In ₅	58.6	49.8
Se ₉₀ Te ₁₀	57.0	49.1
Se ₉₀ Ge ₁₀	55.1	53.5
Se ₉₀ In ₁₀	60.6	50.3
Se ₈₅ Te ₁₅	57.2	48.9
Se ₈₅ Ge ₁₅	54.1	55.5
Se ₈₅ In ₁₅	63.0	50.7
Se ₈₀ Te ₂₀	57.4	48.7
Se ₈₀ Ge ₂₀	53.1	57.5
Se ₈₀ In ₂₀	65.6	51.1

Table 7 Values of cohesive energy (CE) and average heat of atomization (\bar{H}_5) of various multi-component quaternary systems and their parent Se₇₈Te₂₀Sn₂

Quaternary alloys	CE (kcal/mol)	\bar{H}_5 (kcal/mol)
Se ₇₈ Te ₂₀ Sn ₂	27.7	49.2
Se ₇₆ Te ₂₀ Sn ₂ Ag ₂	57.6	49.5
Se ₇₄ Te ₂₀ Sn ₂ Ag ₄	58.2	49.9
Se ₇₂ Te ₂₀ Sn ₂ Ag ₆	58.8	50.3
Se ₇₆ Te ₂₀ Sn ₂ Bi ₂	56.4	49.0
Se ₇₄ Te ₂₀ Sn ₂ Bi ₄	55.7	48.9
Se ₇₂ Te ₂₀ Sn ₂ Bi ₆	55.0	48.8
Se ₇₆ Te ₂₀ Sn ₂ Cd ₂	57.5	48.7
Se ₇₄ Te ₂₀ Sn ₂ Cd ₄	55.2	48.3
Se ₇₂ Te ₂₀ Sn ₂ Cd ₆	58.3	47.8
Se ₇₆ Te ₂₀ Sn ₂ Sb ₂	57.6	49.4
Se ₇₄ Te ₂₀ Sn ₂ Sb ₄	58.1	49.7
Se ₇₂ Te ₂₀ Sn ₂ Sb ₆	58.7	49.9

Here the hetero-polar bond energies of Te–Se and M–Se heteropolar bonds are represented as E_{Te-Se} and E_{M-Se} respectively. The mean bond energy per atom of the ‘remaining matrix’, E_{rm} is defined as [6]:

$$E_{rm} = \frac{2(0.5\bar{r} - P_r)(E_{Se-Se})}{\bar{r}} \quad (13)$$

In Eq. (13) E_{Se-Se} is the homopolar bond energy of the Se–Se bond in the chalcogen-rich region.

Finally, the overall mean bond energy is given by [6]:

$$\langle E \rangle = E_c + E_{rm} \quad (14)$$

The values of the overall mean bond energy for the multi-component glasses of binary, ternary and quaternary systems are found between the range 230 kJ/mol to 310 kJ/mol for the all multicomponent glassy systems studied in the present work.

The plots of the lone pair of electron (LP) and overall mean bond energy ($\langle E \rangle$) against average co-ordination number are shown in Fig. 5 for particular binary, ternary and quaternary systems. These plots clearly reveal that the number of lone pair electron (LP) increases with the decrease in the overall mean bond energy on the bonded atom. This may be caused due to the electrostatic repulsion of the lone pair of electrons of the two bonded atoms.

Table 6 Values of cohesive energy (CE) and average heat of atomization (\bar{H}_5) of multi-component ternary systems Se_{75-x}Te₂₀M_x (x = 2, 4, 6) and Se_{75-x}Te₂₀M_x (x = 5, 10, 15) their parent Se₈₀Te₂₀ (Here M represent the foreign element)

Ternary alloys Se _{78-x} Te ₂₀ M _x (x = 2, 4, 6) with parent Se ₈₀ Te ₂₀	CE (kcal/mol)	\bar{H}_5 (kcal/mol)	Ternary alloys Se _{75-x} Te ₂₀ M _x (x = 5, 10, 15) with parent Se ₈₀ Te ₂₀	CE (kcal/mol)	\bar{H}_5 (kcal/mol)
Se ₈₀ Te ₂₀	48.7	57.4	Se ₈₀ Te ₂₀	48.7	57.4
Se ₇₈ Te ₂₀ Ag ₂	49.1	58.0	Se ₇₅ Te ₂₀ Ag ₅	47.6	58.9
Se ₇₆ Te ₂₀ Ag ₄	49.5	58.6	Se ₇₀ Te ₂₀ Ag ₁₀	46.5	60.5
Se ₇₄ Te ₂₀ Ag ₆	49.8	59.2	Se ₆₅ Te ₂₀ Ag ₁₅	45.3	62.4
Se ₇₈ Te ₂₀ Cd ₂	48.3	57.8	Se ₇₅ Te ₂₀ Cd ₅	47.6	58.5
Se ₇₆ Te ₂₀ Cd ₄	47.8	58.2	Se ₇₀ Te ₂₀ Cd ₁₀	46.5	59.6
Se ₇₄ Te ₂₀ Cd ₆	47.4	58.7	Se ₆₅ Te ₂₀ Cd ₁₅	45.3	61.0
Se ₇₈ Te ₂₀ Sb ₂	49.0	57.9	Se ₇₅ Te ₂₀ Sb ₅	49.3	58.7
Se ₇₆ Te ₂₀ Sb ₄	49.2	58.5	Se ₇₀ Te ₂₀ Sb ₁₀	50.0	60.2
Se ₇₄ Te ₂₀ Sb ₆	49.5	59.0	Se ₆₅ Te ₂₀ Sb ₁₅	50.6	62.0
Se ₇₈ Te ₂₀ Ge ₂	49.5	57.1	Se ₇₅ Te ₂₀ Ge ₅	50.7	56.5
Se ₇₆ Te ₂₀ Ge ₄	50.3	56.1	Se ₇₀ Te ₂₀ Ge ₁₀	52.8	55.5
Se ₇₄ Te ₂₀ Ge ₆	51.1	56.3	Se ₆₅ Te ₂₀ Ge ₁₅	54.8	54.3

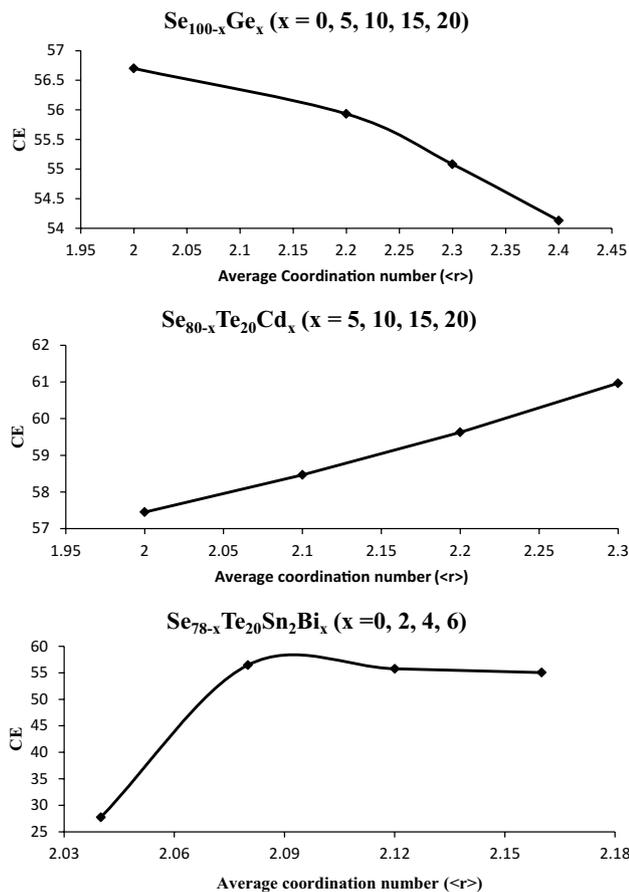


Fig. 6 Plots of cohesive energy (CE) versus average coordination number for representative three generations (binary, ternary and quaternary ChGs)

This is possibly the answer of the question: why LP is increased with decreased along with $\langle E \rangle$? The similar variation of LP and $\langle E \rangle$ with average coordination number was observed for other binary, ternary and quaternary systems.

5.5 Cohesive energy and average heat of atomization

The cohesive energy (CE) of the system is the assessment of the strength of a chemical bond and is defined as the stabilization energy of an infinitely large cluster of material per atom [22]. This permits the evaluation of the number of possible bonds. Zachariasen [22] proposed an assumption that the conjecture is commonly found to be applicable for glass structure; thereby the atoms combine more favorably with atoms of diverse types than with the same type. The condition is correspondent for assuming the maximum quantity that is probable for the chemical ordering. It favors the development of an ageless structure by raising the glass transition temperature T_g . When

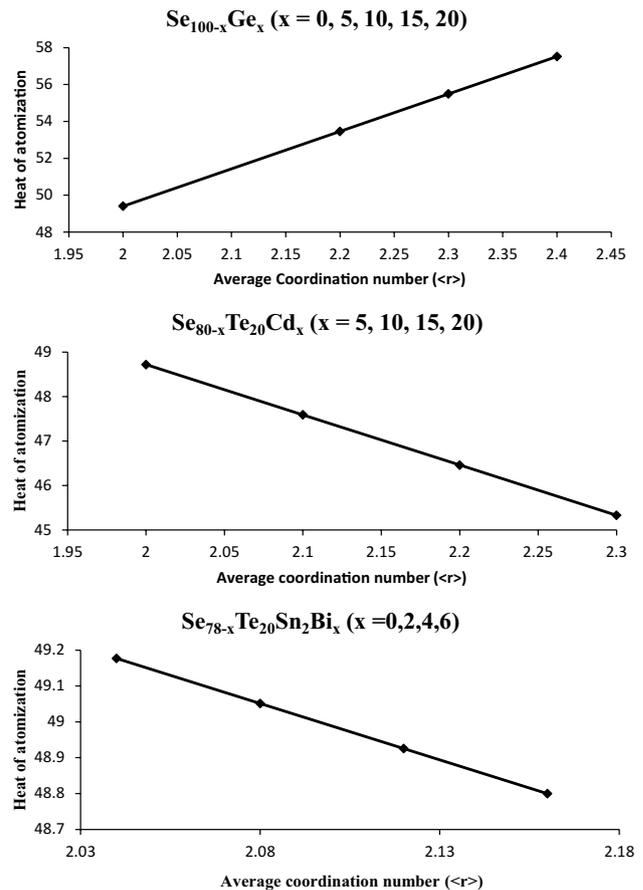


Fig. 7 Plots of average heat of atomization versus average coordination number for representative three generations (binary, ternary and quaternary ChGs)

this postulation is considered, the bond linkages between like atoms occur only if there is a surplus of a certain type of atoms. Bonds are formed in the sequence of decreasing bond energies until all the accessible valences for the atoms are saturated. So Thus, the bond energies are assumed to be additive in accordance with this model. Thus, the cohesive energy is estimated by summing the bond energies over all the bonds predictable in the alloy, using the following expression [22]:

$$CE = \sum \frac{C_i D_i}{100} \quad (15)$$

Here the C_i is the bond probabilities and D_i is the bond energy of the corresponding bond in the glassy system. After all these bonds are formed, there are still unsatisfied Se valences “excess bonds” which must be satisfied by the creation of Se–Se bonds. The values of the Cohesive Energy (CE) for the multi-component glasses of binary, ternary and quaternary systems are given in Tables 5, 6 and 7, respectively. The plot of CE versus average co-ordination number $\langle r \rangle$ is shown in Fig. 6 for particular binary, ternary

and quaternary systems. From these plots is clear that the variation of CE with the average coordination number $\langle r \rangle$ is diversified in nature.

According to Pauling's theory [38], the heat of atomization H_s (A–B) at standard temperature and pressure of a binary semiconductor created from A and B is the addition of heat of formation (ΔH) and the average heats of atomization (H_s^A) and (H_s^B), respectively, that corresponds to the average non-polar bond energy of the two atoms [38]:

$$H_s(A - B) = \Delta H + 0.5(H_s^A + H_s^B) \quad (16)$$

The term (ΔH) in Eq. (16) is proportional to the difference between the electronegativities χ_A and χ_B of the two atoms:

$$\Delta H \propto (\chi_A - \chi_B)^2 \quad (17)$$

In order to pull out this proposal to ternary and higher order semiconductor compounds [23], the mean heat of atomization \bar{H}_s (kcal/g atom) is defined for a compound $A_\alpha B_\beta C_\gamma$ as a straightforward assessment of the cohesive energy and thus of average bond strength, given by [6]:

$$\bar{H}_s = \frac{\alpha(H_s)_{Se} + \beta(H_s)_M}{\alpha + \beta} \quad (\text{For binary systems}) \quad (18a)$$

$$\bar{H}_s = \frac{\alpha(H_s)_{Se} + \beta(H_s)_{Te} + \gamma(H_s)_M}{\alpha + \beta + \gamma} \quad (\text{For ternary systems}) \quad (18b)$$

and

$$\bar{H}_s = \frac{\alpha(H_s)_{Se} + \beta(H_s)_{Te} + \gamma(H_s)_{Sn} + \delta(H_s)_M}{\alpha + \beta + \gamma + \delta} \quad (\text{For quaternary systems}) \quad (18c)$$

For binary systems described by Eq. (18a), α and β are the atomic percentages of elements Se and M (M=Te, Ge and, In) and $(H_s)_{Se}$ and $(H_s)_M$ are the heats of atomization of Se and M (M=Te, Ge and, In) respectively. For ternary systems described by Eq. (18b), α , β and γ are the atomic percentages of elements Se, Te and M (M=Cd, Sb, Ge and, Ag) and $(H_s)_{Se}$, $(H_s)_{Te}$ and $(H_s)_M$ are the heats of atomization of Se, Te and M (M=Cd, Sb, Ge and, Ag) respectively. For quaternary systems described by Eq. (18c), α , β , γ and δ are the atomic percentages of elements Se, Te, Sn and M (M=Cd, Sb, Bi and, Ag) and $(H_s)_{Se}$, $(H_s)_{Te}$, $(H_s)_{Sn}$ and $(H_s)_M$ are the heats of atomization of Se, Te, Sn and M (M=Cd, Sb, Bi and, Ag) respectively. The plot of \bar{H}_s versus average coordination number $\langle r \rangle$ is shown in Fig. 7 for particular binary, ternary and quaternary systems. From these plots, it is clear that \bar{H}_s varies linearly with the average coordination number $\langle r \rangle$. Similar linear correlations were obtained for other glassy systems. The values of \bar{H}_s for the

multi-component glasses of binary, ternary and quaternary systems are given in Tables 5, 6, 7 respectively.

6 Conclusions

The physical behavior of multi-component glasses of binary, ternary and quaternary systems is examined systematically as a function of average coordination number $\langle r \rangle$. Theoretically, it has been revealed that all the glassy samples studied in the present work are flexible. They can be also referred as floppy or under-coordinated with $\langle r \rangle < 2.4$ and $n_c < 3$. The values of density and molar volume are to follow mutually opposite increasing trend with an increase in the average coordination number $\langle r \rangle$. The values of lone pair electron and parameter R show that all the multi-component glasses of present binary, ternary and quaternary systems are the members of chalcogens-rich glassy system. The cohesive energy CE shows the non-linear variation with average coordination number without following any definite relationship. However, the average heat of atomization of present alloys varies linearly with average coordination number $\langle r \rangle$ in all the multi-component glasses of present binary, ternary and quaternary systems.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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