

# Analysis of chemical ordering and fragility for Ge–Se–In glasses

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**Abstract** Decreasing the band gap of a material due to metal impurities has been approved through several studies, and this subject is considered as a major area of interest within the optoelectronic applications. Indium-based chalcogenides have been considered good candidates in nonlinear optics due to their ability to transmit in the infrared region. Hence,  $\text{Ge}_{18}\text{Se}_{82}$  has been alloyed with In. The nature of the chemical ordering of amorphous samples of  $\text{Ge}_{18}\text{Se}_{82-x}\text{In}_x$  ( $x = 0, 2, 4$  and  $6$ ) have been systematically studied. The aim of present investigation is to understand the role of chemical composition and mean-coordination number in determining their structural and physical properties. The compactness,  $\delta$ , of alloyed samples has been calculated from their measured densities, and values obtained have been interpreted using the topological model proposed to describe the atomic arrangements in these alloys. The variation of the glass transition temperature,  $T_g$ , with the average coordination number,  $Z$ , has been investigated. The compositional dependence of the mean atomic volume,  $V_m$ , has also been determined. The free volume percentage,  $FVP$ , in  $\text{Ge}_{18}\text{Se}_{82-x}\text{In}_x$  amorphous samples and their fragility indices,  $m$ , have been determined to examine the relationship with the mean-coordination number. We have also analyzed the obtained results on the basis of average single bond energy and electronegativity.

## 1 Introduction

Chalcogenide multicomponent glasses have attracted significant attention due to their remarkable optical properties and technological applications [1, 2]. They are considered as typical glasses for infrared applications [3, 4] and provide good candidates for photo-structural optical recording [5], acousto-optic devices [6, 7] and advanced IR optical fibers [8]. They also provide solid-state physicists with new solutions for the challenging fundamental problems that relate to the possible technological applications for these glasses [7, 9]. The Ge–Se–In system is of special interest in view of the fact that it forms glasses over a wide domain of compositions extending to about 60–90 at.% of Se atoms and about 15 at.% In, with the Ge atoms as remainder [10–13]. Therefore, it is considered as a suitable model system for the investigation of the variation of certain physical properties with composition or equivalently with the average coordination number [1, 14].

Since the addition of a third alloying element has pronounced effect on the structural and physical properties, we propose in this paper to study the role played by metallic indium on the covalently bonded Ge–Se glasses. Several authors have studied the optical and electrical properties of the formed ternary compounds. Through investigations, researchers have shown the effect of In addition on the structural, physical, electronic, optical and thermal properties of the Ge–Se glasses which create both compositional and configurational disorders in this system [13, 15–18]. So far, however, there has been little discussion about the results of the compactness of the structure of these glasses, the variation of glass transition temperature, the free volume percentage  $FVP$ , the value of the fragility index  $m$  and the other related parameters. Therefore, in the current study, the chemical bond approach has been used to explain the

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correlation between the above-mentioned parameters and the coordination number in the present glassy system, and the observed behavior is interpreted as an indirect evidence of the behavior of their chemical nature [19].

## 2 Experimental method

Bulk  $\text{Ge}_{18}\text{Se}_{82-x}\text{In}_x$  glasses ( $0 \leq x \leq 6$ ) have been prepared by the conventional melt-quenching technique. The samples were prepared from a mixture of high purity Ge, Se, and In (99.999 %). The elemental constituents of the desired stoichiometric ratios have been sealed in evacuated quartz ampoules ( $\approx 10^{-3}$  pa) and heated in an electric furnace at 300 °C for 2 h. Afterwards the temperature of the furnace has been raised to 1000 °C for 15 h with frequent shaking to homogenize the melt. The quenching has been done in ice-cooled water. The ingots have been confirmed to be amorphous using X-ray diffraction (XRD). The homogeneity of the compositions has also been confirmed through density measurements. On the other hand, the composition of the final glassy alloys has been determined using energy-dispersive X-ray spectroscopy (EDX). The thermal behavior has been investigated using a differential thermal analyzer (Shimadzu DTA-50). The glass transition temperature for samples has been obtained by heating them at heating rate 10 °C/min.

Density measurements on as-prepared samples have been performed by the Archimedes method using distilled water as the immersion liquid. The density,  $\rho$ , has been calculated from the formula,

$$\rho = \left( \frac{W_0}{W_0 - W_L} \right) \rho_L \quad (1)$$

where  $W_0$ ,  $W_L$  and  $\rho_L$  are, respectively, the weight of the sample in air, the weight of the sample in liquid and the density of the reference liquid. The error in the density measurement, and consequently in the compactness, has been estimated to be less than  $\pm 1$  %. The compactness,  $\delta$ , has been calculated using the formula [20–22]

$$\delta = \frac{\sum_i \frac{C_i A_i}{\rho_i} - \sum_i \frac{C_i A_i}{\rho}}{\sum_i \frac{C_i A_i}{\rho}} \quad (2)$$

where  $C_i$ ,  $A_i$ ,  $\rho_i$  and  $\rho$  are the atomic fraction, the atomic weight and the atomic density of the  $i$ th element of the glass, and  $\rho$  is the measured density. The compactness  $\delta$  is a measure of the change in the mean atomic volume  $V_m$  due to chemical interactions of the elements forming the network of a given solid [23].

The polaron concept has been studied in both ordered and disordered solids. For the polaron to be small, the polaron radius,  $r_p$ , must be greater than the radius of the

atom, on which the electron is localized, but less than the distance,  $r$ , separating these sites. The polaron radius has been determined from the relation [24].

$$r_p = \frac{1}{2} \left( \frac{\pi}{6N} \right)^{1/3} \quad (3)$$

where  $N$  is the number of In atoms per unit volume which could be calculated using the Naster–Kingery formula [25, 26]. Moreover, the polarons should decrease in size as the number of atoms increases.

$$N = \frac{\rho_{\text{glass}} P N_A}{AW \times 100} \quad (4)$$

where  $\rho_{\text{glass}}$  is the glass density,  $N_A$  is Avogadro's number,  $AW$  is the atomic weight of the In (in grams), and  $P$  is the weight percentage of In in the glass matrix. In addition, the average spacing of In–In in the glass was calculated from

$$r = \left( \frac{1}{N} \right)^{1/3} \quad (5)$$

## 3 Results and discussion

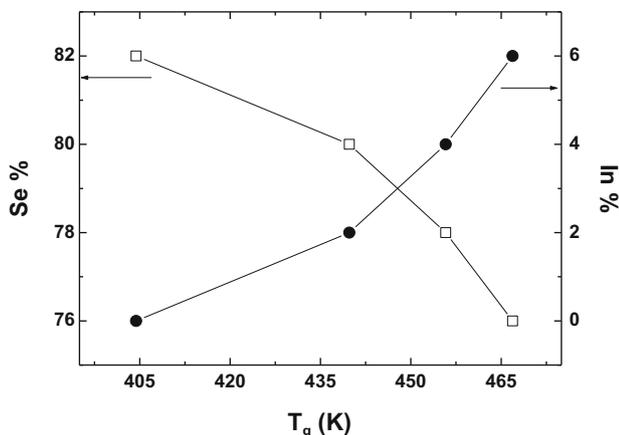
The densities of the investigated compositions, their corresponding compactness values and their respective average coordination numbers are summarized in Table 1. The calculation of the coordination number,  $Z$ , values as suggested by Phillips [27], requires the knowledge of the coordination number values of each element constituting the alloy. For the Ge–Se–In system, the values of the coordination number of Ge and Se generally respect the 8-N rule with  $Z$  for Ge = 4 and for Se = 2. Nevertheless, for In atoms the results obtained by different authors indicate that it is still a subject of controversy. The value of  $Z$  for In = 3 is obtained from extended X-ray absorption fine-structure (EXAFS) measurements from the In K-edge [28]. The values of the coordination number for the investigated compositions have been determined using the following formula [29, 30].

$$Z = [4 \times 18 + 2(82 - x) + 3(x)]/100 \quad (6)$$

The composition variation of the compactness  $\delta$  characterized by  $Z$  for glasses under study is given in Table 1. Figure 1 shows the variation of glass transition temperature,  $T_g$ , with elements percentage in  $\text{Ge}_{18}\text{Se}_{82-x}\text{In}_x$ . We observe that the greater the In content, the larger the  $T_g$  values, while an opposite behavior is obtained for Se content. In spite of the presence of many factors that influence the  $T_g$  obtained for the glasses under study, it is interesting to relate  $T_g$  with  $Z$ . The dependence can be expressed as  $T_g = f(Z)$  in case of adding an element with coordination number greater than 2 to the binary glass.

**Table 1** Values of densities,  $\rho$ , compactness,  $\delta$ , and coordination number,  $Z$ , of the four glassy compositions

Sample composition			Density $\rho$ (g cm <sup>-3</sup> )	Compactness $\delta$	$Z$
Ge (%)	Se (%)	In (%)			
18	82	0	4.416	-0.0982	2.36
18	80	2	4.432	-0.1040	2.38
18	78	4	4.461	-0.1070	2.40
18	76	6	4.497	-0.1087	2.42



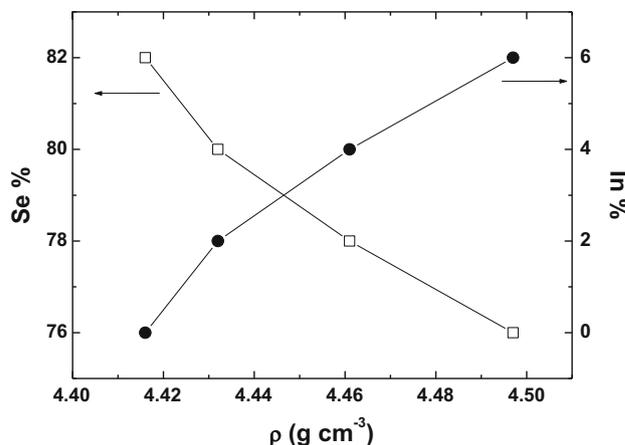
**Fig. 1** Effect of varying both the Se and In percentages on the glass transition temperature

**Table 2** Values of molar volume,  $V_m$ , the concentrations of In atoms per unit volume,  $N$ , the average spacings of In atoms,  $r$ , the small polaron radii deduced from the density,  $r_p$ , and the glass transition temperatures,  $T_g$ , for the four studied compositions

Composition	$V_m$ (cm <sup>3</sup> )	$N \times 10^{22}$ (cm <sup>-3</sup> )	$r$ (Å)	$r_p$ (Å)	$T_g$ (K)
Ge <sub>18</sub> Se <sub>82</sub>	17.62	–	–	–	404.4
Ge <sub>18</sub> Se <sub>80</sub> In <sub>2</sub>	17.72	2.027	3.667	1.478	439.8
Ge <sub>18</sub> Se <sub>78</sub> In <sub>4</sub>	17.77	2.060	3.648	1.470	455.8
Ge <sub>18</sub> Se <sub>76</sub> In <sub>6</sub>	17.78	2.094	3.628	1.462	466.9

Therefore, an increase in the  $T_g$  values is obtained with increasing additive element percentage (cf. Table 2). Hence, we interpret the variation of  $T_g$  observed with increasing In content due to the dependence of  $T_g$  on the connectivity which is in agreement with Saiter et al. [31].

Figure 2 shows the density of the glassy system Ge<sub>18</sub>Se<sub>82-x</sub>In<sub>x</sub> at room temperature as a function of Se and In concentrations. The density increases with increasing In content and decreasing Se content as well. The density,  $\rho$ , and the molar volume,  $V_m$ , of glasses are governed by both the atomic mass and the structure of the components. By knowing the chemical compositions of our glasses, the density variation could be attributed to a change in their structural units' arrangement.



**Fig. 2** Densities of the four compositions as a function of both Se and In concentrations

The molar volume,  $V_m$ , for studied glasses (i.e., the volume occupied by 1 g—molecule of the glass) has been calculated using the following formula [32].

$$V_m = \left(\frac{1}{\rho}\right) \sum_i x_i M_i \tag{7}$$

where  $x_i$  represents the atomic fraction of component  $i$ ,  $M_i$  is its atomic mass, and  $\rho$  represents the experimentally determined density. The values determined for  $V_m$  are listed in Table 2. Figure 3 shows the variation of  $V_m$  with the Se and In contents. The increase in  $V_m$  is observed with increasing In and decreasing Se percentages. By comparing our results with Saffarini et al. [32], we conclude that the variation of  $V_m$  is achieved as a result of new arrangement in the basic structural units.

The free volume percentage ( $FVP$ ) in the glass has been calculated using the relation,

$$FVP = \frac{(V_m - V_T)}{V_m} 100 \% \tag{8}$$

where  $V_T$  is the theoretical molar volume. The calculation of  $V_T$  for the compositions Ge<sub>18</sub>Se<sub>82-x</sub>In<sub>x</sub> has been performed using the following additive formula.

$$V_T = 18V(\text{Ge}) + (82 - x)V(\text{Se}) + xV(\text{In}) \tag{9}$$

where  $V(\text{Ge})$ ,  $V(\text{Se})$  and  $V(\text{In})$  are the atomic volume of elements Ge, Se and In. The obtained results are shown in

Fig. 4. The observed behavior has been confirmed earlier by Kumar et al. [33], in which they found that at lower concentration of In (<8 at.%), In atoms replace Se atoms in these compositions as their chemical bond parameters at

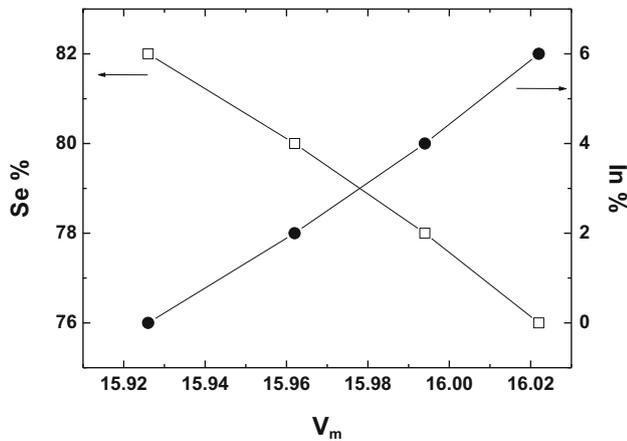


Fig. 3 Molar volume as a function of varying the Se and In percentages

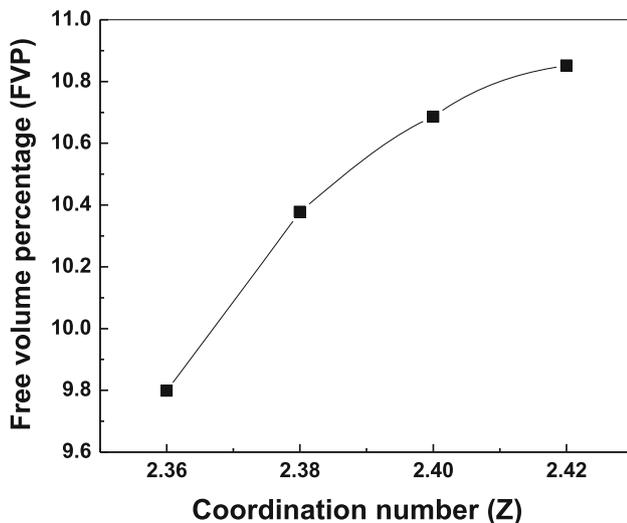


Fig. 4 Free volume percentage as a function of average coordination number

**Table 3** Values of lone-pair electron ( $L$ ); total number of mechanical constraints ( $N_t$ ), constraints due to bond-stretching forces ( $N_\alpha$ ) and bond-bending force ( $N_\beta$ ); cohesive energy ( $CE$ ) Kcal/mol; the parameter  $R$ ; mean bond energy  $\langle E \rangle$  eV/atom; glass transition

$x$	$L$	$N_\alpha$	$N_\beta$	$N_t$	$CE$	$R$	$\langle E \rangle$ (eV)	$T_g^{\text{th}}$ (K)	$E_g^{\text{th}}$ (eV)	$H_s$	$H_s/Z$	$\chi$
0	3.28	1.18	1.72	2.90	46.37	2.28	2.29	431.56	1.77	56.71	24.03	2.44
2	3.24	1.19	1.76	2.95	46.81	2.05	2.34	448.36	1.73	56.88	23.89	2.43
4	3.20	1.20	1.80	3.00	47.26	1.86	2.41	465.61	1.70	57.05	23.77	2.41
6	3.16	1.21	1.84	3.05	47.74	1.69	2.45	483.30	1.66	57.22	23.65	2.40

higher concentration might enter into  $\text{GeSe}_{4/2}$  tetrahedra by adopting Ge–In bonds [33]. According to Sharda et al. [10], it is concluded that the compositional dependence of  $FVP$  of their data is caused by the mechanical and chemical thresholds, respectively.

In order to establish the interdependence between the chemical compositions and the physical properties of the studied ternary Ge–Se–In compounds, the values of the glass density,  $\rho$ , the molar volume,  $V_m$ , the small polaron radius,  $r_p$ , the average space,  $r$ , of the In atoms and the glass transition temperature,  $T_g$ , for the four compositions are determined and shown in Tables 1 and 2. As seen,  $\rho$  and  $V_m$  depend on the In concentration. The changes in  $V_m$  may be due to the change in the composition structure that might have been caused by the variation in interatomic spacing. This could be attributed to the change in the number of bonds per unit volume in the glassy network.

As shown in Table 2, the  $V_m$  values of the ternary compositions are higher than those of the binary  $\text{Ge}_{18}\text{Se}_{82}$  glass. From the changes in the molar volume  $V_m$ , it is clear that the corresponding structural units with its surrounding space increase by introducing In into the glassy composition. It has also been observed that the glass transition temperature  $T_g$  increases with increasing In content (cf. Tables 2, 3). This may indicate a tendency for stronger bonding in In-rich glasses. This can also be correlated with the increasing value of the mean bond energy with In content (cf. Table 3).

The fragility index or steepness index,  $m$ , has been evaluated using the formula [34, 35]

$$m = \frac{d \log_{10}(\tau)}{d\left(\frac{T_g}{T}\right)} \Big|_{T = T_g} \quad (10)$$

and it presents the dependence of the relaxation time  $\tau$  on temperature around  $T_g$ . The procedures outlined earlier [20, 21] have been used to determine the values of  $m$  for the investigated compositions. The determination of the fragility index,  $m$ , requires a mathematical expression for the relaxation time  $\tau$ . In the present work, the Tool–Narayananaswamy–Moynihan (TNM) expression has been

temperature ( $T_g^{\text{th}}$ ) K; theoretical band gap ( $E_g^{\text{th}}$ ) eV; heat of atomization ( $H_s$ ) Kcal/g atom;  $H_s/Z$  average single bond energy; and electronegativity ( $\chi$ ) for the four compositions studied in detail

chosen to be used from the different expressions in the literature [34–36]

$$\tau = \tau_0 \exp\left(\frac{x\Delta h^*}{\mathcal{R}T}\right) \exp\left(\frac{(1-x)\Delta h^*}{\mathcal{R}T_f}\right) \quad (11)$$

where  $\Delta h^*$  is the apparent activation energy,  $\mathcal{R}$  is the ideal gas constant,  $x(0 < x < 1)$  is the nonlinearity parameter, and  $T_f$  is the fictive temperature which depends on the cooling rate  $q$  applied to the material; it is a characteristic parameter for the material. The fictive temperature can be calculated from

$$T_f = (\Delta T_g/2) + T_{g\min} \quad (12)$$

where  $\Delta T_g$  is the width of the glass transition range and  $T_{g\min}$  is the temperature of the beginning of the glass transition. Moynihan [36] has proposed an experimental way to determine the value of  $\Delta h^*$  from the variation of  $T_f$  with  $q$

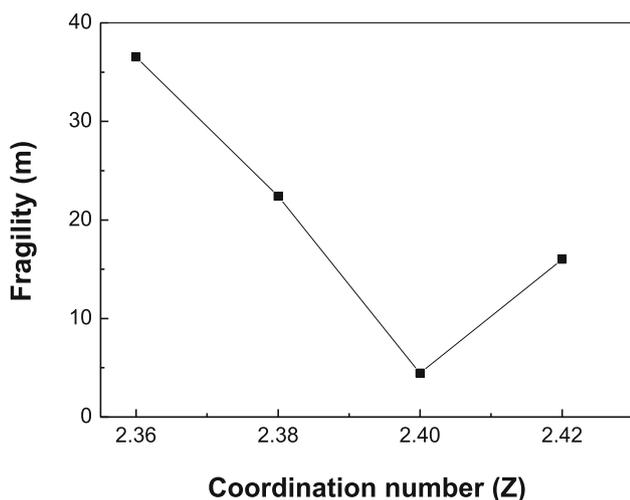
$$\frac{d\ln(q)}{d(1/T_f)} = \frac{-\Delta h^*}{\mathcal{R}} \quad (13)$$

A simple formula of  $m$  can be obtained by introducing Eq. (11) into Eq. (10) [34]

$$m = \frac{\Delta h^*}{\mathcal{R}T_f \ln(10)} \quad (14)$$

Hence, knowing values of  $T_f$ ,  $\Delta h^*$ , and according to Eq. (14), the value of the fragility index,  $m$ , can be evaluated [34].

The dependence of  $m$  on  $Z$  is shown in Fig. 5. It is interesting to note that upon further increase in  $Z$ , the formation of three-dimensional network structures almost freezes the molecular mobility. Therefore, a drastic



**Fig. 5** Fragility variation of the four glassy compositions with the mean-coordination number

decrease in the fragility index has been obtained with the attainment of the strongest composition at the meantime.

The value of  $Z$  of the glassy system is assumed to be comprised of two types of constraints: the first being the bond-stretching constraint ( $N_\alpha$ ) and second the bond-bending constraint ( $N_\beta$ ). The value of  $N_\alpha$  is given by  $Z/2$  and  $N_\beta$  is given by  $2Z - 3$  for a  $Z$ -coordinated system. The total number of mechanical constraints per atom ( $N_t$ ), therefore, is equal to the sum of bond-bending and bond-stretching constraints. The optimum condition for glass formation according to Phillips and Thorpe [37] occurs when  $N_t$  equals the degree of freedom number ( $N_d$ ), i.e., when  $N_t = N_d = 3$ . The value of  $Z$  for this condition has been suggested to be 2.4, where a transition from floppy to rigid mode takes place in the glassy system. The values of  $N_\alpha$  and  $N_\beta$  are given in Table 3, and both of them increase with increasing In content. Hence, an increase in the total number of mechanical constraints from 2.90 for  $x = 0$  to 3.05 for  $x = 6$  is also obtained. The values of  $Z$  for ternary glass system  $\text{Ge}_{18}\text{Se}_{82-x}\text{In}_x$  have been observed to be greater than the binary composition  $\text{Ge}_{18}\text{Se}_{82}$  ( $=2.36$ ). Addition of 4 at.% In causes an abrupt change in  $Z$  value to 2.4, and with further addition of In,  $Z$  increases. According to Phillips and Thorpe [37], at  $Z = 2.4$  there is rigidity percolation and a transition from two-dimensional structural network to three-dimensional structural network takes place.

The number of lone-pair electrons has been calculated using the formula [38, 39]:

$$L = V - Z \quad (15)$$

where  $L$  and  $V$  are the number of lone-pair electrons and valence electrons, respectively. The number of lone-pair electrons ( $L$ ) is assumed for a binary system to be  $L > 2.62$  and for a ternary system  $L > 1$  [38, 39]. It has been observed that the number of lone-pair electrons is  $>1$  for all compositions, and it decreases with increasing In concentration in the glassy system. This may be due to In ion interaction with the electrons of the bridging Se atoms. The presence of lone-pair electrons aids to stabilize the glass formation and to lower the strain on the glassy network. The availability of lone-pair electrons makes it easy to form bonds and extend network [40].

The cohesive energies have been calculated using the chemical bond approach (CBA) [41]. This implies that the atoms of one type combine more favorably with atoms of different types and that the bonds are formed in the decreasing bond energy sequence until all the available valences of the atom are satisfied. The bond energies of heteropolar bond ( $E_{A-B}$ ) have been calculated using the Pauling relation [42]:

$$E_{A-B} = (E_{A-A} \times E_{B-B})^{0.5} + 30(\chi_A - \chi_B) \quad (16)$$

where  $E_{A-A}$  and  $E_{B-B}$  are the homopolar bond energies and  $\chi_A$  and  $\chi_B$  are corresponding electronegativities. Assuming that the bond energies are additive, the cohesive energy has been calculated using the relation [41]:

$$CE = \sum_i C_i E_i \quad (17)$$

where  $C_i$  is the distribution of the chemical bonds and  $E_i$  is the energy associated with the corresponding bond. The values of  $CE$  are listed in Table 3. The results indicate that the  $CE$  increases with increasing In content.

The parameter  $R$  signifies the deviation from the stoichiometric composition and indicates the ratio of covalent bonding possibilities of chalcogen species (Se) to the non-chalcogen species (Ge and In) [15, 41]:

$$R = \frac{bN_{Se}}{(aN_{Ge} + cN_{In})} \quad (18)$$

where  $a$ ,  $b$ ,  $c$  are the atomic fractions and  $Z(\text{Ge}) = 4$ ,  $Z(\text{Se}) = 2$  and  $Z(\text{In}) = 3$  are the coordination numbers of Ge, Se and In, respectively. Although as the In content increases, the value of  $R$  decreases. It has also been observed that  $\text{Ge}_{18}\text{Se}_{82-x}\text{In}_x$  glass system lies in the  $R > 1$  domain (cf. Table 3). The domain  $R > 1$  indicates that the system is chalcogen rich.

The value of glass transition temperature is not only related to the conjugation of the glassy network, i.e., average coordination number, but also related to the quality of the conjugation, i.e., the mean bond energy between the atoms forming the glassy network [23, 43]. Tichy–Ticha [23, 43] has proposed a method for the calculation of mean bond energy  $\langle E \rangle$  which is given by

$$\langle E \rangle = E_c + E_{rm} \quad (19)$$

where  $E_c$  is the total contribution toward bond energy originating from strong bonds and  $E_{rm}$  is the contribution originating from weaker bonds that remains after the strong bonds have been maximized.

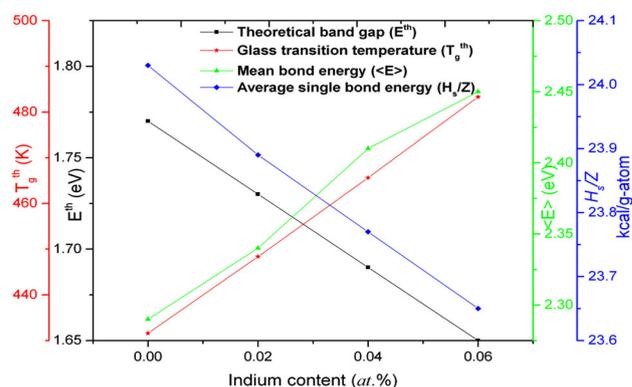
For  $\text{Ge}_a\text{Se}_b\text{In}_c$  system (where  $a + b + c = 1$ ), there are two cases: one the chalcogen (Se) rich, i.e.,  $R > 1$  and second chalcogen poor, i.e.,  $R < 1$ . Since our system is chalcogen rich, therefore the treatment given in references [15, 23, 41, 43] has been used to calculate  $E$ .

The values of homopolar, i.e., 37.60 kcal/mol, 44.00 kcal/mol and 29.83 kcal/mol for Ge–Ge, Se–Se and In–In, respectively, and heteropolar bond energies, i.e., 49.40, 54.01 and 35.07 kcal/mol for Ge–Se, Se–In and Ge–In, respectively, are calculated using Pauling's relation (Eq. 16). The calculated values of mean bond energy have been found to be increased with the addition of In content and are given in Table 3. The values of mean bond energy

have been used to calculate theoretically the glass transition temperature ( $T_g^{\text{th}}$ ) [15, 41] using the relation,  $T_g^{\text{th}} = 311[\langle E \rangle - 0.9]$ . The values of  $T_g^{\text{th}}$  are listed in Table 3 and found to increase with increasing indium content. This may be due to the increase in the quality connectivity in the glassy network as envisaged from the mean bond energy.

The band gap for the compositions under investigations has also been computed theoretically using the relation given in Ref. [44] and obtained values are listed in Table 3. Figure 6 shows the relationship between theoretically calculated physical parameters such as mean bond energy  $E$ , glass transition temperature ( $T_g^{\text{th}}$ ), theoretical band gap ( $E_g^{\text{th}}$ ) and average single bond energy  $H_s/Z$  as a function of increasing In content. The values of theoretical band gap decrease with the increasing content of indium which may be correlated with the decrease in average single bond energy in the system (cf. Fig. 6).

Further, the average heat of atomization ( $H_s$ ) for a compound is a straight measure of the cohesive energy and thus for the average bond strength. The average heat of atomization ( $H_s$ ) and average single bond energy ( $H_s/Z$ ) are calculated using the relation given in Ref. [41, 45, 46] and are listed in Table 3. The values of  $H_s$  have the similar behavior as the cohesive energy where both increase with increasing In content, whereas  $H_s/Z$  decreases. Moreover, the decrease in theoretical band gap has also been supported by the decrease in electronegativity values with Indium content. Electronegativity has been calculated using Sanderson's principle [47]; i.e., electronegativity of an alloy is the geometric mean of electronegativity of its constituent elements. It is apparent from Table 3 that band gap decreases as electronegativity decreases with the increasing content of Indium.



**Fig. 6** Plot showing the variation of theoretically calculated some physical parameters with In content

## 4 Conclusions

On the basis of the determined physical parameters presented here, we have seen that In atoms are threefold coordinated with Se atoms in Ge–Se–In glassy alloys. By adding In to the Ge–Se binary system, we change the mean-coordination number of the alloys by varying the number ratio of Ge/Se atoms. An increase has been observed in the density, the molar volume and the glass transition temperature values with increasing In content. The quality connectivity dependence has been confirmed from the compositional dependence of glass transition temperature for the system under study. Theoretically, band gap has been calculated and found to depend on In content, and the variation in it has been correlated with the average single bond energy and electronegativity. The goal of our next investigations is to enhance our understanding of Ge–Se–In system by several experimental parameters.

## References

- G. Antipas, E. Mangiorou, E. Hristoforou, *Mater. Res. Express* **1**, 015202 (2014)
- S.S. Fayek, S.S. Fouad, M.R. Balboul, M.S. El-Bana, *Phys. B* **388**, 230–236 (2007)
- A. Herzog, B. Hadad, V. Lyubin, M. Klebanov, A. Reiner, A. Shamir, A.A. Ishaaya, *Opt. Lett.* **39**, 2522–2525 (2014)
- J.A. Brant, D.J. Clark, Y.S. Kim, J.I. Jang, J.-H. Zhang, J.A. Aitken, *Chem. Mater.* **26**, 3045–3048 (2014)
- G. Saffarini, J. Saiter, H. Schmitt, *Opt. Mater.* **29**, 1143–1147 (2007)
- A. Stronski, E. Achimova, A. Paiuk, V. Abaskin, A. Meshalkin, A. Prisacar, G. Triduh, O. Lytvyn, *J. Non-Cryst. Solids* **409**, 43–48 (2015)
- A. Seddon, *J. Non-Cryst. Solids* **184**, 44–50 (1995)
- I.D. Aggarwal, J.S. Sanghera, *J. Optoelectron. Adv. Mater.* **4**, 665–678 (2002)
- S.S. Fouad, *Phys. B* **270**, 360–365 (1999)
- S. Sharda, N. Sharma, P. Sharma, V. Sharma, *J. Non-Cryst. Solids* **362**, 136–139 (2013)
- M. El-Nahass, M. Ali, I. Zedan, *J. Lumin.* **151**, 143–148 (2014)
- Z. Borisova, *Glassy Semiconductors* (Springer, Plenum Press, New York, 1981)
- M. Saxena, A.K. Kukreti, S. Gupta, M.K. Agarwal, N. Rastogi, *Arch. Appl. Sci. Res.* **4**, 994–1001 (2012)
- G.S. Antipas, E. Mangiorou, E. Hristoforou, *Metals* **5**, 102–118 (2015)
- R. Kumar, A. Kumar, V. Rangra, *Optoelec. Adv. Mater.* **4**, 1554 (2010)
- M.S. Kamboj, R. Thangaraj, *Eur. Phys. J. Appl. Phys.* **24**, 33–36 (2003)
- S. Mahadevan, A. Giridhar, *J. Non-Cryst. Solids* **152**, 42–49 (1993)
- G. Saffarini, *Appl. Phys. A* **74**, 283–285 (2002)
- G.S. Antipas, *Mater. Res.* **17**, 1677–1685 (2014)
- M. Vlček, M. Frumar, *J. Non-Cryst. Solids* **97**, 1223–1226 (1987)
- E. Savova, E. Skordeva, E. Vateva, *J. Phys. Chem. Solids* **55**, 575–578 (1994)
- E.R. Skordeva, D.D. Arsova, *J. Non-Cryst. Solids* **192**, 665–668 (1995)
- L. Tichý, H. Ticha, *Mater. Lett.* **21**, 313–319 (1994)
- V. Bogomolov, Y.A. Firsov, E. Kudinov, D. Mirlin, *Phys. Status Solidi (b)* **35**, 555–558 (1969)
- H.H. Naster, W.D. Kingery, in *Proceedings of the Seventh International Conference on Glass, Brussels* (Gordon and Breach, New York, 1965), p. 106
- A. Maged, L. Wahab, I. El Kholly, *J. Mater. Sci.* **33**, 3331–3335 (1998)
- J.C. Phillips, *J. Non-Cryst. Solids* **34**, 153–181 (1979)
- J. Ledru, J. Saiter, G. Saffarini, S. Benazeth, *J. Non-Cryst. Solids* **232**, 634–637 (1998)
- D. Swiler, A.K. Varshneya, R. Callahan, *J. Non-Cryst. Solids* **125**, 250–257 (1990)
- M.R. Balboul, S.S. Fouad, S.A. Fayek, M.S. El-Bana, *J. Alloy. Compd.* **460**, 570–576 (2008)
- J. Saiter, A. Hamou, C. Vautier, *J. Non-Cryst. Solids* **172**, 580–583 (1994)
- G. Saffarini, J. Matthiesen, R. Blachnik, *Phys. B* **305**, 293–297 (2001)
- A. Kumar, M. Husain, S. Swarup, A. Nigam, *Phys. B* **162**, 177–180 (1990)
- A. Saiter, C. Devallencourt, J. Saiter, J. Grenet, *Eur. Polym. J.* **37**, 1083–1090 (2001)
- G. Saffarini, A. Saiter, M. Garda, J. Saiter, *Phys. B* **389**, 275–280 (2007)
- C.T. Moynihan, A.J. Easteal, M.A. Bolt, J. Tucker, *J. Am. Ceram. Soc.* **59**, 12–16 (1976)
- J.C. Phillips, M. Thorpe, *Solid State Commun.* **53**, 699–702 (1985)
- P. Sharma, S. Katyal, *Phys. B* **403**, 3667–3671 (2008)
- L. Zhenhua, *J. Non-Cryst. Solids* **127**, 298–305 (1991)
- N. Sharma, S. Sharda, V. Sharma, P. Sharma, *Chalcogenide Lett.* **9**, 355–363 (2012)
- I. Sharma, S. Tripathi, P. Barman, *Phys. B* **403**, 624–630 (2008)
- L. Pauling, Cornell University, New York, (1976)
- L. Tichý, H. Ticha, *J. Non-Cryst. Solids* **189**, 141–146 (1995)
- I. Sharma, S. Tripathi, P. Barman, *Phil. Mag.* **88**, 3081–3092 (2008)
- M. Yamaguchi, *Philos. Mag. B* **51**, 651–663 (1985)
- S.S. Fouad, E.A.A. El-Shazly, M.R. Balboul, S.A. Fayek, M.S. El-Bana, *J. Mater. Sci. Mater. Electron.* **17**, 193–198 (2006)
- R.T. Sanderson, *J Chem Educ* **29**(1):539–544 (1952)