



A consistent approach towards Bi doping mechanism in chalcogenide glasses from C_p measurement in Ge–Se–Te–Bi system

N. Asha Bhat*, K.S. Sangunni

Department of Physics, Indian Institute of Science, Bangalore 560 012, India

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Abstract

In this paper, we are proposing a consistent approach to understand the mechanism of Bi doping in Ge–Se glasses by carrying out specific heat (C_p) measurement in $\text{Ge}_{20}\text{Se}_{70-x}\text{Te}_{10}\text{Bi}_x$ system for $0 \leq x \leq 11$. The two softening temperatures exhibited by heat-treated samples are explained on the basis of ‘microscopic phase separation’. The minimum in ‘configurational heat capacity’ (ΔC_p) at $x = 7.5$ for as-prepared glasses is related to be a feature of chemical threshold. A supporting evidence for three-fold coordination for Bi in line with the earlier structural studies is deduced. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

A carrier type reversal (CTR) from p to n by doping Bi or Pb to a few glassy systems like Ge–Se [1,2], Ge–Se–Te [3,4] and Se–In–Pb [5] has drawn the attention of various researchers in the recent past. Due to its special nature, Bi doping in Ge–Se–Bi and Ge–Se–Te–Bi systems has been a subject of persistent controversy due to two approaches used to explain different experimental results [6–11] discussed briefly as follows.

Many researchers consider Ge–Se–Bi and Ge–Se–Te–Bi glasses to be ‘microscopically phase separated’ with c-Bi₂Se₃ like clusters embedded in the rest of the matrix [9,10,12]. The reasons attributed to this are the strong n-type nature of c-Bi₂Se₃ and observation of two crystallization and melting temperatures. This naturally leads them to assume a coordination number (CN) of six for Bi like in c-Bi₂Se₃ [13]. The CTR was therefore explained to be the resultant of an increase in Bi[−] defects that disturbs the equilibrium between the charged chalcogen defects (C_3^+ and C_1^-).

However, the EXAFS studies carried out by Elliot and

Steel on these glasses support a CN of three for Bi with a positive charge contradicting the assumptions mentioned earlier [6,14]. According to this model, the CTR is due to the suppression of C_3^+ defects by Bi⁺ defects. The fact that this model does not account for the evidences for ‘phase separation’ and the presence of GeSe_{4/2} and BiSe_{3/2} like structural units brought out in recent experiments [7,8] leave the ambiguity unresolved.

In the present paper, we have made an attempt to develop a consistent approach towards Bi doping mechanism by measuring specific heat (C_p) in as-prepared and heat-treated $\text{Ge}_{20}\text{Se}_{70-x}\text{Te}_{10}\text{Bi}_x$ glasses for $0 \leq x \leq 11$.

2. Experimental

Glasses in $\text{Ge}_{20}\text{Se}_{70-x}\text{Te}_{10}\text{Bi}_x$ system for $0 \leq x \leq 11$ are prepared by taking appropriate amount of 5N purity elemental Ge, Se, Te and Bi in 8-mm dia round quartz ampoules and sealed under a vacuum of 10^{-5} torr. The sealed ampoules are heated to a temperature of 1273 K. The melts at this temperature are homogenized by continuous rotation for 24 h before quenching in a mixture of NaOH and ice water. X-ray diffraction and differential scanning calorimetry (DSC) are used to verify the amorphous and

* Corresponding author.

E-mail address: asha@physics.iisc.ernet.in (N. Asha Bhat).

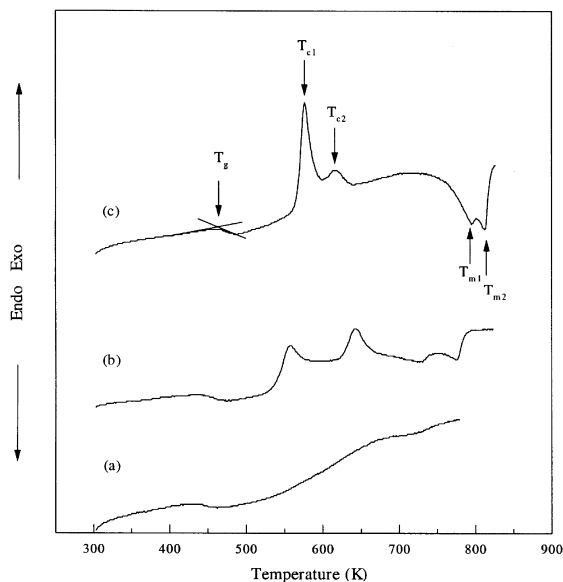


Fig. 1. DSC traces in as-prepared $\text{Ge}_{20}\text{Se}_{70-x}\text{Te}_{10}\text{Bi}_x$ glasses for (a) $x = 2.5$, (b) $x = 5$ and (c) $x = 10$ with 20 K/min heating rate. Also shown are the glass transition (T_g), crystallization (T_c) and melting (T_m) temperatures.

glassy nature. Thermal crystallization studies for $x \geq 5$ are carried out by annealing the samples at their respective crystallization temperatures (T_c).

A conventional differential scanning calorimeter (DSC 1500 model, Stanton Redcraft, UK) interfaced to a PC is used to determine C_p values for all the samples. The Al_2O_3 powder is taken as the reference material [15]. Small pieces crushed from the original samples are sealed in an aluminum crucible by taking enough care to keep the influence of sample size and morphology on C_p at minimum. The reference and sample masses are selected to be around 12 mg and 16 mg, respectively. For heat treatment studies, as-prepared samples heated up to $(T_g - 20)$ K with 20 K/min heating rate and cooled subsequently to room temperature are used. Specific heat values for every 1 K in the temperature range of 323–523 K are calculated using the ratio method [16]. The estimated error in the calculation of C_p is less than $\pm 5\%$. The reliability of the data is confirmed by repeated measurements.

3. Results and discussion

Fig. 1 shows the DSC traces of as-prepared samples for $x = 2.5, 5$ and 10. All compositions exhibit single glass transition (T_g) followed, for $x \geq 5$, by two crystallization (T_{c1} and T_{c2}) and two melting (T_{m1} and T_{m2}) temperatures. The thermal crystallization studies carried out for $x \geq 5$ (shown for $x = 5$ in Fig. 2) at T_{c1} and T_{c2} show that the crystallizing phases are Bi_2Se_3 and GeSe_2 , respectively.

The C_p vs. temperature (T) profiles for as-prepared and heat-treated samples are shown in Figs. 3 and 4. An interesting trend for as-prepared samples is an exothermic effect or a decrease in C_p for T just below T_g , which disappears for heat-treated samples. In addition to this, only the heat-treated samples show two distinct T_g s for $x \geq 9$.

A drop in C_p looks unusual as it is generally accepted that below T_g , C_p vs. T variation of melt-quenched glasses resembles that of their crystalline counterparts. However, there are some reports indicating the dependence of heating and cooling rate on volume and/or specific heat near the T_g region [17,18]. The exothermic effect can therefore be explained as follows. In the present study, the as-prepared samples when quenched from 1273 K were subjected to very high cooling rate roughly taken as a few hundreds of Kelvin per second introducing thermal stresses and strains in the glassy matrix. When the same samples are taken to a temperature near glass transition, energy gets released with the removal of strain and stress, the causes for exothermic effect.

Observation of two softening temperatures in Fig. 4 can be explained on the basis of some earlier reports [10,19,20]. One of the possibilities is the presence of different types of structural units left behind during glass formation which will evolve into separate glassy phases when subjected to proper heat-treatment. The phases thus evolved can undergo glass transition at different temperatures. Therefore based on the evidence in Refs. [7,8] and the crystallization of Bi_2Se_3 and GeSe_2 phases for $x \geq 5$ (Fig. 2) two T_g s observed in Fig. 4 may be attributed to $\text{BiSe}_{3/2}$ and $\text{GeSe}_{4/2}$ like structural units. It is difficult at this stage to distinguish between the two structural units while assigning to T_{g1} and T_{g2} . Can then the glassy phase containing Bi be related to $c\text{-Bi}_2\text{Se}_3$? The discussion on this is given in the last section while developing a consistent approach for Bi doping mechanism.

In Fig. 5, the jump in specific heat at T_g s (ΔC_p) is plotted vs. composition x for as-prepared samples. We observe a small value of ΔC_p at $x = 7.5$, which indicates minimum number of configurations available for this composition. The possibility of some threshold effects being responsible for the observed minimum is explored with a discussion of two different models proposed to understand the property–composition dependence in chalcogenide glasses.

The first one known as mechanical threshold (MT) explains compositional variation of physical properties by bringing *average coordination number* $\langle r \rangle$ into picture [21,22]. According to this model at $\langle r \rangle = 2.4$, the glass network changes from an elastically floppy to a rigid structure whereas at $\langle r \rangle = 2.67$, a transition from two-dimensional to three-dimensional network occurs. The second threshold model known as chemical threshold (CT) takes into account the effects of chemical ordering and proposes threshold at compositions for which the bonds between like atoms start disappearing. The latter model suggests the possibility of threshold behavior anywhere

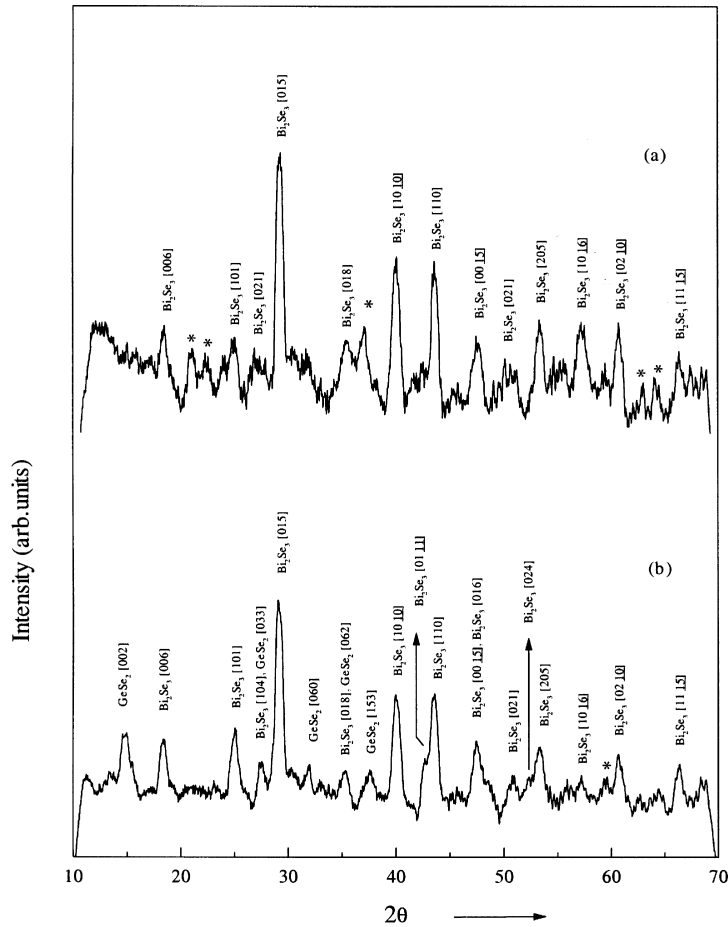


Fig. 2. XRD patterns for $\text{Ge}_{20}\text{Se}_{65}\text{Te}_{10}\text{Bi}_5$ glass annealed at (a) T_{c1} and (b) T_{c2} . The peaks marked by * could not be indexed.

between $\langle r \rangle = 2.4$ and $\langle r \rangle = 2.7$ depending on the group of the constituent elements [23]. In the present system at $x = 7.5$, $\langle r \rangle$ can be taken to be either 2.475 or 2.7 for the CN of Bi being three or six. Even though both these values lie closer to the ones proposed for mechanical threshold, the basic concepts of floppy to rigid or 2D to 3D transformation are inadequate to explain a minimum in ΔC_p . However, the chemical ordering/threshold idea can be applied to explain the minimum in ΔC_p as follows.

In an attempt to link the relaxational aspects of glass transition and entropy, Adam and Gibbs related a small value of ΔC_p to an Arrhenius-like behavior in viscosity [24]. Based on this and their investigations, Angell and colleagues [25] have classified the glass-forming liquids into two extremes: strong and fragile liquids. Fragile liquids show a large configurational entropy change whereas strong liquids show small ΔC_p during liquid \Rightarrow glass transition. The examples given for strong liquids are SiO_2 , GeO_2 , etc. while those for fragile liquids are $\text{Ca}(\text{NO}_3)_2$, organic glasses etc. Among chalcogenides, the stoichiometric glass As_2Se_3 and $\text{Ge}_{20}\text{Se}_{60}\text{Pb}_{20}$ show a small ΔC_p and fall under strong

liquid category [26,27]. One of the common features observed for strong liquids is their stoichiometric-like composition or a maximum chemical order with least number of bonds between like atoms. In this situation, the different configurations available during the short period of liquid \Rightarrow glass transition might decrease reasonably manifesting a minimum in (ΔC_p) .

To verify the validity of CT for Ge–Se–Te–Bi glasses, we first determine the possible bond distribution at various compositions using chemically ordered network (CON) model [28]. The model assumes that: (a) atoms combine more favorably with atoms of different kinds than with the same and (b) bonds are formed in the sequence of bond energies (Table 1) [29]. Also, we apply the well-known 8-N rule to all the chemical species. The bond distribution based on these assumptions is shown in Fig. 6. As Bi replaces Se, the number of Bi–Se bonds increase at the expense of Se–Se bonds till $x = 8$ around which the Se–Se bonds completely disappear. A further increase in Bi at% leads to a situation wherein the concentration of Se is insufficient to form three-fold coordinated Bi atom. In this case,

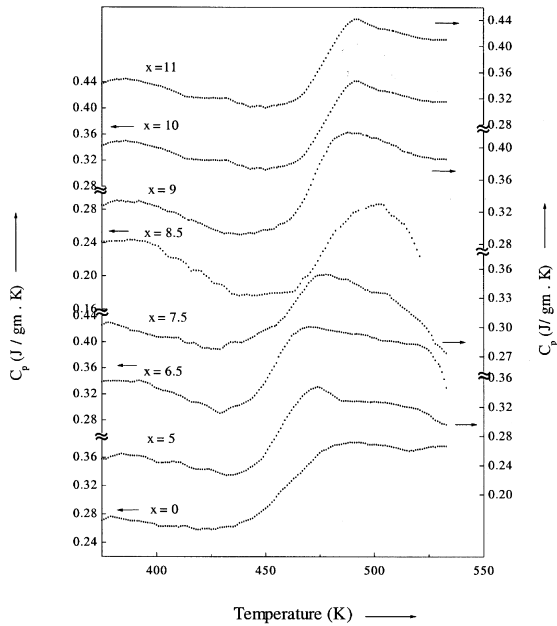


Fig. 3. Specific heat (C_p) vs. temperature (T) for different x in as-prepared $\text{Ge}_{20}\text{Se}_{70-x}\text{Te}_{10}\text{Bi}_x$ glasses with 20 K/min heating rate.

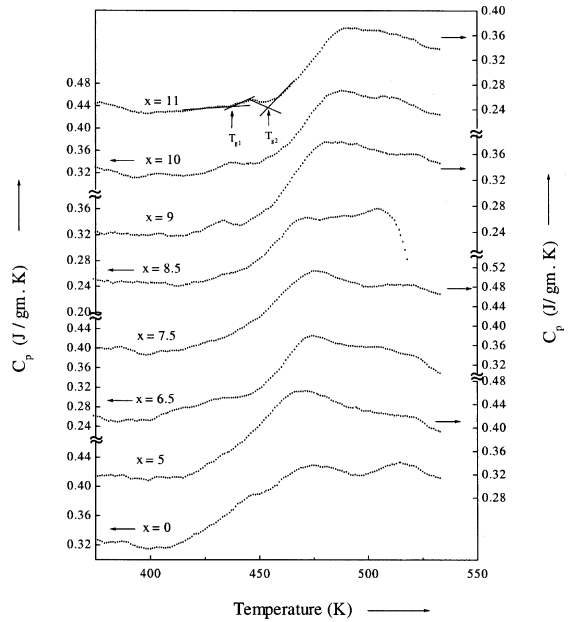


Fig. 4. C_p vs. T for different x in heat-treated $\text{Ge}_{20}\text{Se}_{70-x}\text{Te}_{10}\text{Bi}_x$ glasses. Two different softening temperatures are denoted as T_{g1} and T_{g2} .

either bonds between like atoms start appearing (Ge–Ge, Bi–Bi or Te–Te) or a reduction in the number of Se–Te or Ge–Se bonds occurs to give way for Bi–Se bonds. The first option is disadvantageous for glass formation and is ruled out. In the second option, a reduction in Se–Te bonds leaves some Te atoms unbonded, which will prefer Ge atoms to Bi for bond formation giving rise to a simultaneous reduction in Ge–Se bonds leaving more Se to form Bi–Se bonds. At around $x = 8$, maximum chemical ordering occurs with a crossover from Se–Se bonds to Ge–Te bonds. The difference between our calculations and the one proposed by Tohge et al. [3] (Se–Se bonds start disappearing at around 5 at% of Bi) is understandable if one notes that

CN of 6 is considered for Bi in Ref. [3] whereas it is 3 for our calculations. Keeping in mind the idealistic nature of the model which does not consider the occurrence of dangling bonds and voids, our prediction of the CT at around 8 at.% of Bi appears more suitable to explain the minimum in ΔC_p at 7.5 at% of Bi. The main reason for the minimum in ΔC_p at this composition can therefore be assigned to the maximum chemical ordering with the disappearance of bonds between like atoms and a reduction in number of configurations available. In addition to CT, a simultaneous occurrence of MT at around this composition can not be ruled out, even though $\langle r \rangle$ is different from 2.4 or 2.67 [30].

Table 1
Bond strengths for various types of covalent bonds in Ge–Se–Te–Bi system [29]

Bond type	Bond energy (kcal/mol)
Se–Se	44.0
Ge–Ge	37.6
Bi–Bi	25.0
Te–Te	33.0
Bi–Se	40.7
Bi–Ge	31.53
Bi–Te	29.9
Ge–Se	48.78
Ge–Te	37.5
Se–Te	40.57

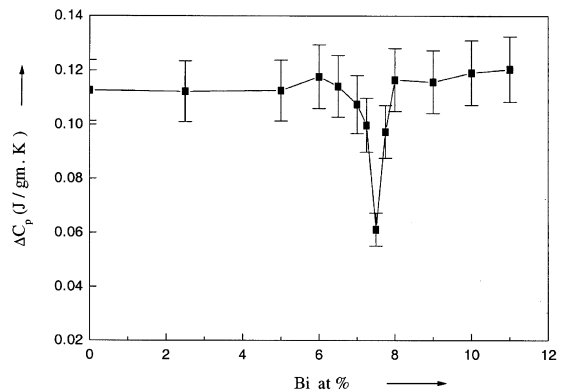


Fig. 5. Compositional dependence of 'configurational heat capacity' ΔC_p for as-prepared $\text{Ge}_{20}\text{Se}_{70-x}\text{Te}_{10}\text{Bi}_x$ glasses.

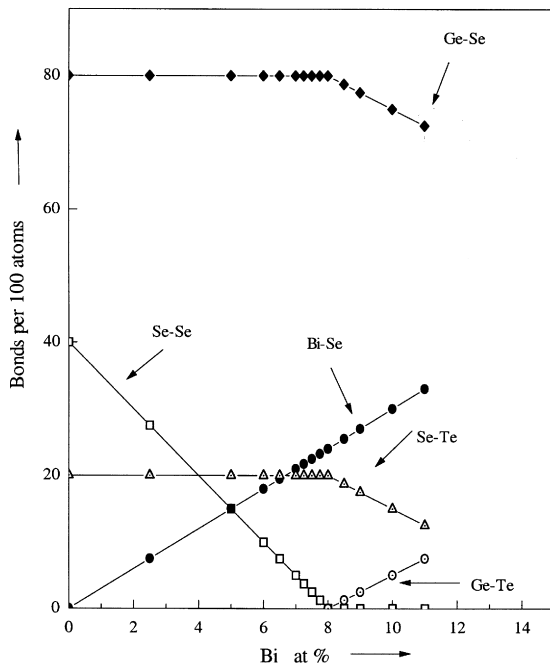


Fig. 6. Calculated number of various covalent bonds per 100 atoms of $\text{Ge}_{20}\text{Se}_{70-x}\text{Te}_{10}\text{Bi}_x$ glasses based on CON model.

The occurrence of two softening temperatures in Ge–Se–Bi glasses in one of the earlier reports and also in our C_p measurements for heat-treated Ge–Se–Te–Bi glasses can be explained by taking into consideration the concept of ‘phase separation’. The question left unanswered in one of the previous sections was — is it necessary to consider the glassy phase having $\text{BiSe}_{3/2}$ like structural units to be analogous to $c\text{-Bi}_2\text{Se}_3$? The necessity occurs when $c\text{-Bi}_2\text{Se}_3$ is the only form of Bi_2Se_3 that can account for $\text{BiSe}_{3/2}$ -like structural units. It can be noted here that the $a\text{-Bi}_2\text{Se}_3$ phase having three-fold coordinated Bi atoms has been known for the last several years [31,32] and hardly been considered in the formulations of phase separation arguments. As and when evidences were found for phase separation the common assumption made in all the earlier studies related the microscopic Bi_2Se_3 glassy phase directly to $c\text{-Bi}_2\text{Se}_3$ to end up in a CN of six for Bi. This assumption does not look satisfactory with the earlier experimental supports for three-fold coordinated Bi atoms in $a\text{-Bi}_2\text{Se}_3$, Ge–Se–Bi systems [6,14]. On the other hand, if we consider $a\text{-Bi}_2\text{Se}_3$ phase in place of $c\text{-Bi}_2\text{Se}_3$, the phase separation issue can be explained without contradicting the experimental evidence for three-fold coordination for Bi in these glasses. The CTR from p to n in chalcogenide glasses can thus be approached with a coherent picture with a CN of 3 for bismuth and $a\text{-Bi}_2\text{Se}_3$ -like structures embedded in the rest of the matrix.

4. Conclusions

In summary, C_p measurements were carried out for Ge–Se–Te–Bi glasses. We observed phase separation taking place for $x \geq 9$ when subjected to heat-treatment. A CN of 3 is found to be appropriate in explaining the minimum in ΔC_p at 7.5 at% of Bi. The difference between the two forms of Bi_2Se_3 with regard to the CN of Bi is brought out and utilized in framing the consistent approach for Bi doping mechanism in chalcogenide glasses.

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