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

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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 Ge$_{20}$Se$_{70-2x}$Te$_{10}$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' ($\Delta C_p$) 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.

Keywords: A. Disordered systems; A. Semiconductors; D. Heat capacity; D. Thermodynamic properties

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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-Bi$_2$Se$_3$ 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-Bi$_2$Se$_3$ 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-Bi$_2$Se$_3$ [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$_2^-$ 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$_2^-$ 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 Ge$_{20}$Se$_{70-x}$Te$_{10}$Bi$_x$ glasses for $0 \leq x \leq 11$.

2. Experimental

Glasses in Ge$_{20}$Se$_{70-x}$Te$_{10}$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...
crystallization temperatures (carried out by annealing the samples at their respective
sample size and morphology on C p crucible by taking enough care to keep the influence of
crushed from the original samples are sealed in an aluminum powder is taken as the reference material [15]. Small pieces
used to determine C p using the ratio method [16]. The estimated error in the
1500 model, Stanton Redcraft, UK) interfaced to a PC is
values for all the samples. The Al 2 O 3
is confirmed by repeated measurements.

the removal of strain and stress, the causes for exothermic
temperature near glass transition, energy gets released with
the removal of strain and stress, the causes for exothermic effect.

The first one known as mechanical threshold (MT)
explains compositional variation of physical properties by bringing average coordination number ⟨r⟩ into picture
[21,22]. According to this model at ⟨r⟩ = 2.4, the glass
network changes from an elastically floppy to a rigid structure whereas at ⟨r⟩ = 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

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 $x = 5$ (shown for $x = 5$ in Fig. 2) at $T_{c1}$ and $T_{c2}$ show that the
crystallizing phases are Bi$_2$Se$_3$ and GeSe$_2$, respectively.
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 \( \Delta C_p \). However, the chemical ordering/threshold idea can be applied to explain the minimum in \( \Delta C_p \) as follows.

In an attempt to link the relaxational aspects of glass transition and entropy, Adam and Gibbs related a small value of \( \Delta C_p \) 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 \( \Delta C_p \) during liquid \( \Rightarrow \) glass transition. The examples given for strong liquids are \( \text{SiO}_2, \text{GeO}_2 \), etc. while those for fragile liquids are \( \text{Ca(NO}_3)_2 \), organic glasses etc. Among chalcogenides, the stoichiometric glass \( \text{As}_2\text{Se}_3 \) and \( \text{Ge}_{20}\text{Se}_{40}\text{Pb}_{20} \) show a small \( \Delta C_p \) 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 \( \Delta C_p \).

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,
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 \( \Delta C_p \) at 7.5 at.% of Bi. The main reason for the minimum in \( \Delta C_p \) 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]

<table>
<thead>
<tr>
<th>Bond type</th>
<th>Bond energy (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Se–Se</td>
<td>44.0</td>
</tr>
<tr>
<td>Ge–Ge</td>
<td>37.6</td>
</tr>
<tr>
<td>Bi–Bi</td>
<td>25.0</td>
</tr>
<tr>
<td>Te–Te</td>
<td>33.0</td>
</tr>
<tr>
<td>Bi–Se</td>
<td>40.7</td>
</tr>
<tr>
<td>Bi–Ge</td>
<td>31.53</td>
</tr>
<tr>
<td>Bi–Te</td>
<td>29.9</td>
</tr>
<tr>
<td>Ge–Se</td>
<td>48.78</td>
</tr>
<tr>
<td>Ge–Te</td>
<td>37.5</td>
</tr>
<tr>
<td>Se–Te</td>
<td>40.57</td>
</tr>
</tbody>
</table>

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

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

Fig. 5. Compositional dependence of ‘configurational heat capacity’ \( \Delta C_p \) for as-prepared Ge\(_{20}\)Se\(_{70-x}\)-Te\(_x\)Bi\(_x\) glasses.
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 Bi$_{3/2}$Se$_{3/2}$ like structural units to be analogous to c-Bi$_2$Se$_3$? The necessity occurs when c-Bi$_2$Se$_3$ is the only form of Bi$_2$Se$_3$ that can account for Bi$_{3/2}$Se$_{3/2}$-like structural units. It can be noted here that the a-Bi$_2$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 relates the microscopic Bi$_2$Se$_3$ glassy phase directly to c-Bi$_2$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-Bi$_2$Se$_3$, Ge–Se–Bi systems [6,14]. On the other hand, if we consider a-Bi$_2$Se$_3$ phase in place of c-Bi$_2$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-Bi$_2$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 $\Delta C_p$ at 7.5 at% of Bi. The difference between the two forms of Bi$_2$Se$_3$ 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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