Effect of Compositional Dependence on Physical Parameters of New Quaternary Ge$_{10}$Bi$_x$Se$_{80-x}$Te$_{10}$ Chalcogenide Glasses

Manish Saxena  
Associate Professor, ASH  
Moradabad Institute of Technology  
Moradabad, U.P., INDIA  
manishsaxena67@yahoo.co.in

Shilpa Gupta  
Assistant Professor, ASH  
Moradabad Institute of Technology  
Moradabad, U.P., INDIA  
shilps_2010@yahoo.co.in

Atul K. Kukreti  
Assistant Professor, ASH  
Moradabad Institute of Technology  
Moradabad, U.P., INDIA  
aatul_kukreti@yahoo.com

ABSTRACT

The investigation of composition dependence of various properties of chalcogenide glasses has been increased in recent years. The physical properties of chalcogenide glasses (high refractive index, low phonon energy, high nonlinearity) also make them ideal for incorporation into lasers and other active devices. In the present work, the effect on the physical properties with the variation in bismuth content has been studied theoretically for Ge$_{10}$Bi$_x$Se$_{80-x}$Te$_{10}$ ($x=3, 6, 9, 12, 15, 18, 21, 24$ at. $\%$) chalcogenide glasses. It has been found that almost all the parameters, studied here, vary linearly with the increase in Bi content, thus making this suitable for phase change optical recording. The phase change can be reversibly switched between the amorphous and crystalline state and find applications in rewritable optical recording.

Keywords: Chalcogenide Glasses, Average Coordination Number; Glass Transition; mean bond energy.

I. INTRODUCTION

Recently, chalcogenide glasses have attracted much attention amongst researchers due to their vast applications in various fields. These glasses are based on the chalcogen elements S, Se, and Te. These are formed by the addition of other elements such as Ge, As, Sb, Ga, etc. These glasses are optically highly non-linear and could therefore be useful for all-optical switching (AOS). Chalcogenide glasses are sensitive to the absorption of electromagnetic radiation and show a variety of photo-induced effects as a result of illumination. Chalcogenide glasses have drawn prodigious attention because of their potential use in photo-resist, microelectronic, optoelectronic, holographic applications and especially their ability to transmit light in the mid to far-infrared region [1-5].

Some chalcogenide materials experience thermally driven amorphous crystalline phase changes, enabling the encoding of binary information on thin films of chalcogenides, forming the basis of rewritable optical discs and non-volatile memory devices. Chalcogenide glasses are the most promising materials for a wider range of wavelengths, near and mid-infrared. In general, there are two main sources of infrared absorption in chalcogenide glasses, affecting the transmittance near 10.6 $\mu$m wavelength. As selenium exhibits the unique property of reversible phase transformation and also applications like photocells, xerography, memory switching etc., it seems attractive, but pure selenium has disadvantage like short life time and low photo sensitivity. To overcome this problem, some impurity atoms like Ge, In, Bi, Te, Sb, Ag, etc. can be used to make alloys with Se, which may enhance sensitivity, crystallization temperature and reduce ageing effects [6].

The compositional dependence studies on glassy alloys were reported for the alloys based on the materials like Ge, Sb, Ag, As, Pb, Ga, Sn, Bi, Se, Te etc. [7-12]. The structure of chalcogenide glasses, however, cannot be described by means of a continuous random network which is isotropic in three dimensions, as in the case of amorphous silicon for example. As$_x$S$_y$, As$_x$Se$_y$, Ge$_x$S$_y$, and GeSe$_x$ can be locally layer-like, while pure S and Se are chain like. Ge atoms act as bond modifiers thus they strengthen the average bond by cross-linking the Se chain structure, thereby enhancing the properties like glass transition temperature and resistivity. Ge-Se system is a widely studied system and glass formation in this system occurs predominantly in alloys enriched with Se and containing 0-25 at % of Ge. Some charged additives like Pb, Bi which changes the ratio of valence-alternation pairs to such an extent that the Fermi energy could become unpinned. When the concentration of charged additives exceeds that of valence-alternation pairs, the chalcogenide glasses can exhibit carrier-type reversal. $p$-$n$ transition as has been observed in Ge-Se and In-Se glasses, with
the addition of Bi and Pb. Addition of an element like Bi to Ge-
Se-Te system expands the glass forming region and also creates
compositional and configurational disorder in the system as well
as induce large effect on their structural, physical, optical,
electronic and thermal properties [13-16].

In the present work, we have taken a quaternary alloy
comprising of Ge-Bi-Se-Te. Here we have fixed the at % of Ge
and Te at 10 at %, and then studied the variation of various
important physical parameters by varying the concentration of
Bi from 3 – 24 at %. The variation in concentration of Bi element
used to create compositional and configurational disorder in the
material with respect to the ternary alloys [17]. It has been
established that physical properties in this system are highly
composition dependent. The Ge_{10-x}Bi_xSe_{80-x}Te_{10} glass system is of
special interest as it forms glasses over a wide domain of
compositions. The glass formation region in the ternary Ge-Se-
Bi system extends to about 20 at % Bi and about 60-90 at % Se,
with rest being Ge. Adding Te to this increases the chalcogen
concentration in this system. The variation of properties has been
discussed on the basis of their compositions. The present paper
is concerned with the theoretical prediction of some physical
parameters related to composition, viz. coordination number,
mean bond energy, glass transition temperature, etc. for
Ge_{10-x}Bi_xSe_{80-x}Te_{10} (x=3, 6, 9, 12, 15, 18, 21, 24 at. %) alloys.

II. THEORETICAL STUDIES AND DISCUSSION

2.1 Bonding Constraints and Average Coordination Number

J.C. Phillips [18] suggested the mechanical-constraint counting
algorithms to explain glass forming tendencies. The strongest
covalent forces between nearest neighbours serve as Lagrangian
/mechanical) constraints defining the elements of local structure
(building blocks). Constraints associated with the weaker forces
of more distant neighbours must be intrinsically broken leading
to the absence of long-range order. The well known Phillips–
Thorpe approach is based on comparing the number of atomic
degrees of freedom with the number of inter-atomic force field
constraints. If the number of degrees of freedom is greater than
the number of constraints, the network is “floppy”; conversely,
if the network becomes over-constrained, stressed-rigid
structures will percolate throughout the entire network.
According to Phillips, the tendency of glass formation would be
maximum when the number of degrees of freedom exactly equals
the number of constraints.

The average coordination number (Z) was calculated using
standard method [19] for the composition Ge_{10-x}Bi_xSe_{80-x}Te_{10}, Z is
given by

$$Z = \frac{wCN_{Ge} + xCN_{Bi} + yCN_{Se} + zCN_{Te}}{w + x + y + z}$$

(1)

where w, x, y and z are the at % of Ge, Bi, Se and Te
respectively and CN_{Ge} (4), CN_{Bi} (3), CN_{Se} (2), CN_{Te} (2) are their
respective coordination number [20,21]. Figure 1 shows values
of Z increase from 2.23 to 2.44 with increase in concentration
of Bi from 3 to 24 using the calculated values of average
coordination number for Ge_{10-x}Bi_xSe_{80-x}Te_{10} system.

In covalent solids, there are two types of near-neighbour
bonding forces viz: á-forces (bond-stretching) and á-forces
(bond-bending). The determination of average coordination
number Z allows the calculation of total number of constraints
N_{t} = N_{s} + N_{b}. In this quaternary chalcogenide system N_{t} = Z/2 is
the number of bond-stretching constraints and, N_{b} = (2Z - 3) is
the number of bond-bending constraints [22].

The values of N_{t} along with Z for Ge_{10-x}Bi_xSe_{80-x}Te_{10} system
with variation in Bi content are depicted in Figure 2. Here N_{t}
increases with increase in Bi content for Ge_{10-x}Bi_xSe_{80-x}Te_{10} system,
which shows in our composition that the number of constraints
N_{t} acting on the network are balanced by the number of degrees
of freedom N_{s} available from the atoms in the network. In our
system for x = 24, Z = 2.44 and N_{t} = 3.10 indicates that the
system is rigidly stressed and over-constrained. But, as we
decrease the concentration of Bi from x = 24 to x = 3, the value
of Z decreases to 2.23 and hence N_{t} decreases from 3.10 to 2.575.
As a result of which, there is a decrease in the connectivity of
the system. And subsequently makes the system less constrained.

Fig. 1. Variation of Average Coordination Number Z
with Bismuth content

Fig. 2. Variation of Number of constraints N_{t} with Bi content
The cross-linking density \( X \) is equal to the average coordination number of cross linked chain less the coordination number of initial chain [23].

\[
\begin{align*}
X &= N_c - 2 \\
\end{align*}
\]  

(2)

The values of cross linking density \( X \) and molecular weight \( M \) are calculated using above mentioned relation. From Fig. 3 it is clear that the value \( X \) increase from 0.575 to 1.100 with increase in Bi content. Fig. 4 shows the variation of \( M \) with Bi content which is also increasing from 87.13 to 114.43 with the increase in Bi content from 3 to 24 at. %.

\[
\begin{align*}
\end{align*}
\]

(3)

The variations of \( f \) for \( \text{Ge}_{10} \text{Bi}_x \text{Se}_{80-x} \text{Te}_{10} \) system are shown in Figure 5. It has been observed from Figure 5 that the value of \( f \) becomes more and more negative with increase in Bi content from 3 to 24 at. % . This shows that the system becomes more and more rigid, which corresponds to a strong tendency for making glass [25].

\[
\begin{align*}
\end{align*}
\]

(4)

2.2 Deviation from the Stoichiometry of Composition

The parameter \( R \) that determines the deviation from stoichiometry is expressed by the ratio of content bond possibilities of chalcogen atoms to that of non-chalcogen atoms. For \( \text{Ge}_{10} \text{Bi}_x \text{Se}_{80-x} \text{Te}_{10} \) system, the parameter \( R \) is given by [26].

\[
\begin{align*}
R &= \frac{y \text{CN(Se)} + z \text{CN(Te)}}{w \text{CN(Ge)} + x \text{CN(Bi)}} \\
\end{align*}
\]

(5)

Where \( w, x, y, z \) are atomic frictions of Ge, Bi, Se and Te respectively. The threshold at \( R=1 \) (the point of existence of only heteropolar bonds) marks the minimum selenium content at which a chemically ordered network is possible without metal–metal bond formation. For \( R>1 \), the system is chalcogen rich and for \( R<1 \), the system is chalcogen poor. From Figure 6, it is clear that our system is chalcogen rich and turning towards less chalcogen rich with the increase in content of Bismuth in the system, but still far away from being chalcogen poor. As the material is chalcogen rich and so having the high energy lone pair electrons leads to qualitative different electronic densities of state. The valence band is then non bonding and does not significantly contribute to the cohesive energy. The major limitation of this approach is that it does not account for molecular interactions, which play a vital role in the relaxation process in the glass transition region.
2.3 Mean Bond Energy and Glass Transition Temperature

There are many properties of chalcogenide glasses which are related to overall mean bond energy $<E>$. According to Tichy and Ticha [27,28], the value of glass transition temperature should not only be related to connectedness of the network which is related to $Z$, but should also be related to the quality of connections, i.e., the mean bond energy between the atoms of the network. The overall mean bond energy for the $\text{Ge}_{10} \text{Bi}_{y} \text{Se}_{80-x} \text{Te}_{10}$ system is given by

$$<E> = E_c + E_{\text{hm}}$$  \hspace{1cm} (5)

where $E_c$ is overall contribution towards bond energy arising from strong heteropolar bonds and $E_{\text{hm}}$ is contribution arising from weaker bonds that remains after the strong bonds have been maximized. For $\text{Ge}_y \text{Bi}_x \text{Se}_{10} \text{Te}_z$, where $(w+x+y+z) = 1$, in selenium rich systems ($R > 1$) where there are heteropolar bonds and chalcogen-chalcogen bonds

$$E_c = 4wE_{\text{Ge-Se}} + 3xE_{\text{Bi-Se}} + 2zE_{\text{Se-Te}}$$  \hspace{1cm} (6)

and

$$E_{\text{hm}} = \left[ \frac{2y-4w-3x-2z}{Z} \right] E_{\text{Se-Se}}$$  \hspace{1cm} (7)

denotes the average homo-polar bonding energy. It is clear from Figure 7 that $<E>$ increases from 2.12 to 2.35 with increase in concentration of Bi from 3 to 24 at. % i.e selenium rich region.

An impressive correlation of mean bond energy with glass transition temperature $T_g$ was illustrated by Tichy and Ticha by the relation

$$T_g = 311[<E> - 0.9]$$  \hspace{1cm} (8)

The variation of $T_g$ with Bi content is shown in Figure 8, which is clearly depicting the rise in glass transition temperature from 378.83 to 449.77 with increasing the content of Bi from 3 to 24 at. % due to rise in mean bond energy of the glassy system.

III. CONCLUSION

In the present work, we had considered a quaternary alloy comprising of $\text{Ge-Bi-Se-Te}$. Here Ge and Te have been fixed at 10 at. %, and then studied the variation in various important physical parameters by varying the concentration of Bi from 3 – 24 at. %. It has been established from the above results that physical properties in this system are highly composition dependent. The $\text{Ge}_{10} \text{Bi}_{y} \text{Se}_{80-x} \text{Te}_{10}$ glass system is of special interest as it forms glasses over a wide domain of compositions. Adding Te to this increases the chalcogen concentration in this system. Almost all the parameters, except $f$ and $R$, were found to increase with the variation in Bi content thus making this combination suitable for phase change optical recording.

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