Effect on Physical Parameters of Ge-Se-Bi Chalcogenide Glasses due to Addition of Te

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Abstract— The physical properties of chalcogen based glasses make them ideal for incorporation into lasers and other active devices. In the present article, physical parameters of Ge-Se-Bi chalcogenide glasses with the variation in bismuth content has been studied theoretically with the addition of Te. Some physical parameters for ternary (Ge20Se80-xBix) as well as quaternary (Ge10Se80-xBixTe10) composition, studied here, were found to vary linearly with the variation in Bi content with x = 3, 6, 9, 12 and 15 atomic %, which suggest the system suitable for phase change optical storage and find applications in rewritable optical storage media.

Key words: Chalcogenide Glasses, Average Coordination Number, Lone pair, Mean Bond Energy

I. INTRODUCTION

Chalcogenide glasses generate an important class of amorphous solids. These glasses contain one or more chalcogen elements like S, Se or Te from the 6th group of the periodic table. These glasses have very interesting physical properties. They can be prepared in the bulk or thin film forms. The potential technological applications of these glasses are optical memory switching, xerography, IR detection, transmission and inorganic photo resist etc. There exist various kinds of amorphous chalcogenides. Even then, there is a lot of scope left, in the understanding of various states in the chalcogenide glasses. The absence of rigidity of the structure makes the chalcogenides suitable for a number of applications. Selenium is generally used due to its wide range commercial importance. The addition of Bi used to increase the chemical durability and also broadens the IR transparency region [1].

Ternary chalcogenide glasses can be prepared by adding a suitable additive element in a binary matrix. As Bi–Bi, Bi–S and Bi–Se bonds are formed from Bi - rich glasses, so Se-rich glasses must also have Bi–S, Bi–Se, and Se–Se bonds and S-rich glasses Bi–S, Bi–Se, and S–S bonds. The selenium rich chalcogenide glasses exhibit enhanced electrical, long achievability, better hardness, high resistivity, physical and optical properties with good working performance. Some researchers have reported that ternary glasses have certain drawbacks thus implying the limitation in applications [2, 3].

In the present work, we have taken one ternary combination (Ge20Se80-xBix) and one quaternary combination (Ge10Se80-xBixTe10) composition with x = 3, 6, 9, 12 and 15 atomic % to study the compositional variation on some important physical parameters. We have studied the physical properties, viz.: electro-negativity, average coordination number, glass transition temperature etc., by varying bismuth content from x = 3 to x = 15 atomic % and hence subsequently by decreasing selenium content in order to check the importance of the compositions of Ge-Se-Bi based glass system for optical memory devices. As far as the quaternary composition (Ge10Se80-xBixTe10) is concerned, the Ge content has been reduced from 20 to 10 atomic % by incorporating the Te at 10 atomic % to study the effect of increasing the net chalcogen portion in the combination.

II. MATERIALS AND METHODS

A. Ionic Character of Covalent Bond:

Chalcogenide glasses are formed from materials like sulphur, selenium, arsenic, germanium, and tellurium which have predominantly covalent bonds; the degree of covalency in the bond of amorphous glass under investigation can be calculated by using the Pauling relationship [4]

\[
\text{Amount of covalent character} = e^{-0.25(\chi_A - \chi_B)}
\]

where \((\chi_A - \chi_B)\) is the difference in the electro negativities of atoms A and B.

The Ionicity of a bond may be calculated using the Pauling formula.

\[
\text{Percentage of ionic character} = 1 - e^{-0.25(\chi_A - \chi_B)}
\]

A direct connection between bond strength and the glass formations has been recognized by a number of investigators [5].

B. Average Coordination Number:

Phillips proposed the idea, well supported by Thorpe, of studying the properties of network glasses in terms of the average coordination number [6, 7]. The average coordination number \(Z\) has been calculated by using standard method [8] for these compositions of Ge-Se-Bi system \(Z\) is given by following relations.

For ternary composition

\[
Z = \frac{a N_{Ge} + b N_{Se} + \gamma N_{Bi}}{a + b + \gamma}
\]

For quaternary composition

\[
Z = \frac{a N_{Ge} + b N_{Se} + \gamma N_{Bi} + \delta N_{Te}}{a + b + \gamma + \delta}
\]

Where \(a, b, \gamma\) and \(\delta\) are the atomic % of Ge, Se, Bi, and Te respectively, while NGet(4), NSe(2), NBi(3) and NTe(2) are their respective coordination number.

C. Mean Bond Energy:

There are many properties of chalcogenide glasses which are related to overall mean bond energy \(<E>\) [9, 10] The overall mean bond energy is given by

\[
< E >= E_c + E_{rm}
\]

where \(E_c\) is overall contribution towards bond energy arising from strong heteropolar bonds and \(E_{rm}\) is contribution arising from weaker bonds that remains after the strong bonds have been maximized. For GeoSeβBiγ system and GeoSeβBiγTeδ where \((\alpha + \beta + \gamma) = 1\) and \((\alpha + \beta + \gamma + \delta) = 1\), in selenium rich systems (R>1) where there are heteropolar bonds and chalcogen-chalcogen bonds
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\[ E_c = 4\alpha E_{Ge-Se} + 3\gamma E_{Bi-Se} \]

And

\[ E_{rm} = \left[ \frac{2\beta - 4\alpha - 3\gamma}{Z} \right] E_{Se-Se} \]

denotes the average homopolar bonding energy.

\[ E_c = 4\alpha E_{Ge-Se} + 3\gamma E_{Bi-Se} + 2\delta E_{Se-Te} \]

And

\[ E_{rm} = \left[ \frac{2\beta - 4\alpha - 3\gamma - 2\delta}{Z} \right] E_{Se-Se} \]

Where \( \alpha, \beta, \gamma \) and \( \delta \) are the atomic % of Ge, Se, Bi, and Te

D. Glass Transition Temperature:

Tichy and Ticha [9, 10] illustrated an impressive correlation of mean bond energy with glass transition temperature \( T_g \) by the relation

\[ T_g = 311[<E> - 0.9] \]

Where \( T_g \) is in Kelvin and \( <E> \) is in eV/atom

E. Role of Lone Pair Electrons:

According to Pauling [4], an increase in the number of lone-pair electrons decreases the strain energy in the system and structures with large number of lone-pair electrons favours glass formation. The numbers of lone pair electrons are calculated by using the relation [11]

\[ L = V - Z \]

where \( L \) is the number of lone-pair electrons, \( V \) is the valance electrons and \( Z \) is the average coordination number.

III. RESULTS AND DISCUSSIONS

It is clear from the fig. 1 that values of electro negativity, for both ternary as well as for quaternary systems, decreases with increase in concentration of Bi from 3 to 15 at %.

It is clear from fig. 3 that \( <E> \) increases from 2.386 to 2.548 with increase in concentration of Bi from 3 to 15 at %. for Ge20Se80-xBix system. While value of \( <E> \) is found to be increasing from 2.120 to 2.230 for the Ge10Se80-xBixTe10 system.

The variation of \( T_g \) with Bi content is shown in fig. 4, which is clearly depicting the rise in glass transition temperature from 461.99 to 512.5 with increasing the content of Bi from 3 to 15 at. % in Ge20Se80-xBix system and found to be increasing from 378.83 to 413.35 for Ge10Se80-xBixTe10 quaternary composition with increasing the content of Bi from 3 to 15 at. %. This is observed due to the rise in mean bond energy of the glassy system.
Fig. 5: Variation of Cohesive Energy with Bi content (a-Ge20Se80-xBix, b-Ge10Se80-xBixTe10)

A system with large number of lone-pair electrons constitutes a stable state. Chalcogenides with lone-pair electrons are also characterized by flexibility. This flexibility of bonds causes these atoms to readily form amorphous network, either alone or with a variety of other atomic constituents (fig. 5). It is observed that for the glassy system Ge-Se-Bi, that on increasing the Bi content, the number of lone-pair electrons goes on decreasing. This may be due to the interaction between Bi ion and lone-pair of electrons of bridging Se atom.

IV. CONCLUSIONS

In the present work, we have presented the case of two chalcogenide based compositions – one ternary composition (Ge20Se80-xBix) and other one a quaternary composition (Ge10Se80-xBixTe10) composition with x = 3, 6, 9, 12, 15 atomic %. Various physical parameters, viz.: electronegativity, average coordination number, glass transition temperature, Lone pair etc., were calculated theoretically by varying the Bi content from x = 3 to x = 15 atomic %. Ge content was reduced by adding the Te content to study the effect of increasing the net chalcogen portion. The Ge10Se80-xBixTe10 glass system is of special interest as it forms glasses over a wide domain of compositions and subsequently making this present system suitable for phase change optical storage.

REFERENCES