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REGULAR ARTICLE

Prediction of Physical Behavior of Bi-Modified Se-Ge Chalcogenide System

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Chalcogenide glasses, commonly exhibiting threshold switching, memory switching, and infrared transmission behavior, are investigated intensively for their electrical and optical properties making them useful for versatile potential applications. This work reports the theoretical calculations on the physical parameters of ternary chalcogenide Se-Ge-Bi glasses besides their dependence upon Bi-content. The structure and strength of the material are greatly influenced by the physical parameters. This article attempts to predict the necessary physical characteristics like coordination number, number of lone pair electrons, mechanical constraints, heat of atomization, and cohesive energy for the $Se_{80-x}Ge_{20}Bi_x$ (x = 0, 4, 8, 12 at. %) glass system. The observed variations in the physical parameters are the result of modifications in the covalent char-acter of the glass system.

Keywords: Chalcogenide glasses, XRD, Coordination number, Cohesive energy.

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1. INTRODUCTION

In essence, chalcogenide glasses are amorphous solids that include one or more chalcogen elements from the sixth group of the periodic table. They are fabricated by mixing adequate amounts of the chalcogen group elements, such as sulfur (S), selenium (Se), and tellurium (Te), either together or separately. These glasses, both in bulk and thin film forms, have shown interesting physical properties that make them promising candidates in technological applications and commercial importance for optical memory and switching devices, fiber optics, infrared detection and transmission, photolithography, solar cells, xerography, etc., [1-4].

Depending upon the composition, chalcogenide glasses have excellent chemical inertness and thermal stability against crystallization and aging [4,5]. The capacity of a binary germanium-selenium (Ge-Se) system to form a stable glass composition has been extensively examined for glass stability, and it is predominantly observed in the alloys enriched with Se content and containing 0 – 25 at. % of Ge element [6]. A suitable additive element can be added to the binary system to create a ternary chalcogenide system. The inclusion of a third element i.e., bismuth (Bi) here, by replacing the Se in the binary $Se_{80}Ge_{20}$ in the selective ratios, is an efficient procedure to switch the properties of Se-Ge system.

This paper presents theoretical predictions on the composition-based physical parameters like effective coordination number, mechanical constraints, numbers of lone pair electrons, atomization heat, and cohesive energy for $Se_{80-x}Ge_{20}Bi_x$ (x = 0, 4, 8, 12) glassy system.

2. EXPERIMENTAL DETAILS

$Se_{80-x}Ge_{20}Bi_x$ (x = 0, 4, 8, 12) glassy alloys were prepared from the highly pure (99.9 %) Ge, Se, and Bi elements in the proper weight ratio using the conventional melt quenching technique. These materials were vacuum sealed at 10^{-3} Pa in the well-cleaned quartz ampoules and heated up to 1000 ± 5 °C (at 5 °C/min ramp speed) in a programmable rocking furnace for 24 h. In order to maintain the solid solution melt to be homogeneous, ampules are continuously rotated inside the furnace. After successful heat treatment, these ampoules are rapidly quenched in ice-cold water so that the desired amorphous glass can be achieved. The prepared glassy alloys were washed several times with acetone after ultrasonication to remove the by-products and impurities, further dried in a hot air oven at a temperature 70 ± 5 °C for a period of 36 h, and kept in a vacuum desiccator.

Finally, prepared glass samples ($Se_{80-x}Ge_{20}Bi_x$ where

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$x = 0, 4, 8, 12$) were characterized using PAN-alytical X'pert PRO powder X-ray diffractometer (XRD) having CuKα source, in Bragg-Bretano geometry with a step size of 0.02°, and scanning range of 15° – 60°.

3. RESULTS AND DISCUSSION

Fig. 1, the XRD spectra of the $Se_{80-x}Ge_{20}Bi_x$ ($x = 0, 4, 8, 12$) glassy system demonstrate that there is no sharp XRD peak observed in the prepared alloys. All the samples have a big halo between $2\theta = 20° – 35°$, which implies the amorphous nature and short-range order of the prepared glasses [7]. As the selected composition is rich in Se content and Bi is added in a minute quantity, a slight change in 2θ maximum (24.74° – 25.06°) has been observed which indicates successful amalgamation of Bi in the Ge-Se system.

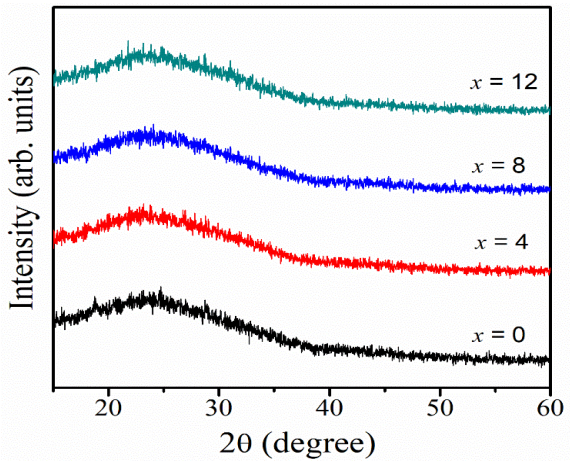

Fig. 1 – XRD Spectra for $Se_{80-x}Ge_{20}Bi_x$ ($x = 0, 4, 8, 12$) glassy system

3.1 Effective Coordination Number, Mechanical Constraints, and Lone Pair Electrons

The elemental cross-linking in the chalcogen glasses can be explained with the help of effective coordination number (<z>) and is evaluated using the formula given below

$$<z> = \frac{pZ(Se) + qZ(Ge) + rZ(Bi)}{p + q + r} \quad (1)$$

where the values of distinct coordination numbers i.e., Z for elements Se, Ge, and Bi are 2, 4, and 3 whereas p, q, and r are elected atomic weight percentage (at. %) of these elements respectively [8]. The estimated value of <z> was found to increase with the increase of bismuth (Bi) content (Table 1) which pro-motes an increase in the cross-linking of chains be-tween atoms of the present Se-Ge system with the ac-cumulation of Bi content. Since the obtained value of <z> in this case lies between 2.40 to 2.52 therefore, it can be said that the Se-Ge-Bi system under study be-come a good glass former. Thorpe asserts that every system should have both rigid and floppy areas in the range of glass-forming compositions [11, 12]. Further-more, a transition from floppy glass to rigid glass occurs at the percolation threshold of the $Se_{80}Ge_{20}$ composition, which corresponds to an average coordination of $<z> = 2.4$. In an amorphous glass alloy system, the bond stretching, ($N_\alpha = <z>/2$) and bond bending, ($N_\beta = 2<z> – 3\beta$) are the mechanical constraints that are counted to understand the stability of the system [8,12]. For an atomic species like a desired glass composition, the average number of mechanical constraints (N_c) are estimated using $N_c = N_\alpha + N_\beta$. It has been analyzed that the value of these constraints in this ternary glass system increases with sthe increase in Bi concentration (Table 1).

The number of lone pair electrons (L) for the $Se_{80-x}Ge_{20}Bi_x$ glassy system has been estimated by the relation, $L = V – <z>$ where V is the amount of valence electrons [8,12]. It has been observed that as the Bi concentration increases in the chosen Se-Ge system, the formation of lone pairs decreases. This might be because of the interaction between the Bi atoms and the lone pair atoms of the Se-Ge system's bridging sections. This might be the result of the interaction between Bi atoms and lone pair atoms of the Se-Ge system's bridging sections. As a result of this interaction in the present system, these lone pair electrons play a smaller role in the formation of glass. As proposed by Zhenhua for all ternary systems, the values of L are always greater than 1, and this is also confirmed in the current system [13]. Fig. 2 also shows that the effective coordination number and the lone pair electrons have linear relationships with the concentration of Bi element

Table 1 – The values of the coordination number (<z>), bond stretching (N_α), bond bending (N_β), average number of constraints (N_c), valance electrons (V), and lone pair electrons (L) for the $Se_{80-x}Ge_{20}Bi_x$ system

x	<z>	N_α	N_β	N_c	V	$L = V – <z>$
0	2.40	1.20	1.80	3.00	5.60	3.20
4	2.44	1.22	1.88	3.10	5.58	3.12
8	2.48	1.24	1.96	3.20	5.52	3.04
12	2.52	1.26	2.04	3.30	5.48	2.97

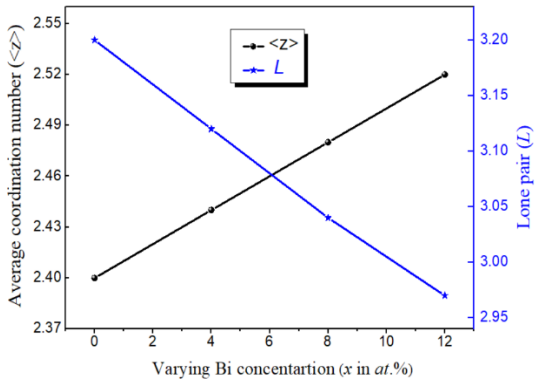

Fig. 2.1 – Plot for the variation of <z> and L of the $Se_{80-x}Ge_{20}Bi_x$ glassy system

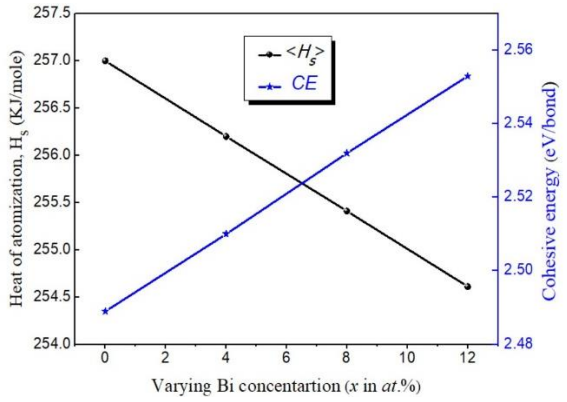

Fig. 2.2 – Plot for the variation of <*z*> and *L* of the $Se_{80-x}Ge_{20}Bi_x$ glassy system

3.2 Atomization Heat and Cohesive Energy

The mean atomization heat is the amount of heat energy needed to convert one mole of an element in its standard state (at 298 K) to gaseous atoms. Atomization heat, H_s, for the present ternary system formed by the atoms Se, Ge, and Bi at standard temperature and pressure, is determined as

$$H_s = \frac{\alpha H_s^{Se} + \beta H_s^{Ge} + \gamma H_s^{Bi}}{\alpha + \beta + \gamma} \qquad (2)$$

The values of H_s for different compositions are obtained from the standard heat of atomization values which are 226.4 kJ/mol for Se, 334 kJ/mol for Ge, and 207.36 kJ/mol for Bi [12]. It has been observed (Fig. 3, Table 2) that the increase in Bi content from 0 to 12 at. % causes the mean atomization heat to decrease in the current glass system.

Table 2 – Values of atomization heat (H_s) and cohesive energy (CE) for the ternary $Se_{80-x}Ge_{20}Bi_x$ glassy system

x	*Hs (kJ/mol)*	*Hs/<z>*	*CE (eV/atom)*
0	257.00	107.08	2.489
4	256.20	105.00	2.510
8	255.41	102.99	2.532
12	254.61	101.04	2.553

The chemical bond approach states that bonds are generated in a glass system till the available valence of atoms is gratified in a series of decreasing bond energy. The analysis has been done to estimate the cohesive energy (CE) of the present glass system which is the stabilization energy per atom, for all prepared samples using the formula [12]

$$CE = \frac{\sum C_j D_j}{100} \qquad (3)$$

where C_j and D_j represent the anticipated amount of chemical bonds and their respective energies.

Se and Bi atoms are strongly bound to each other, whereas Se atoms also completely cover the valence shells of the Ge atoms. Even after all of these bonds have been created, there are still excess bonds with Se valence that need to be supplied by creating Se-Se homopolar links. We can estimate the cohesive energy, CE, if we continue to believe that the binding energy is cumulative (Table 2, Fig. 3), which is the stable energy of each atom for an infinite set of materials. The cohesive energy of the $Se_{80-x}Ge_{20}Bi_x$ system is observed to increase linearly by the addition of Bi content from 0 to 12 at. % (Fig. 3). In this study, it has been found that the Ge-Se-Bi system has a higher density than the $Ge_{20}Se_{80}$ system, and the partial substitution of Bi atoms, for Se atoms in the concentration range of 2 to 12%, results in a densification of the structural system. Additionally, it might be related to a compositional shift in favor of the Se-rich region.

4. CONCLUSION

The present article theoretically described the physical characteristics of the ternary $Se_{80-x}Ge_{20}Bi_x$ ($x = 0, 4, 8, 12$) glass system including the effective coordination number, presence of mechanical constraints, lone pair electrons, the heat of atomization, and cohesive energy. Bi atoms can cause crossover chain links and support to make the glassy system, examined here, flexible. It has been observed that as the Bi concentration in the Se-Ge-Bi system increases, the effective coordination number of the system also rises, which in turn causes a rise in the number of mechanical constraints. However, the number of lone pair electrons decreases as the Bi concentration increases which supports the amorphous state in the present glass system. Additionally, it is observed that the atomization heat is inversely proportional while the cohesive energy is directly proportion-al to the increase in bismuth content that tends to densify the glass system. It is evident from this analysis that most of the parameters directly depend upon the rise in content of Bi ranging from 0 to 12 at. % in the ternary $Se_{80-x}Ge_{20}Bi_x$ glass system.

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Прогнозування фізичної поведінки модифікованої вісмутом халькогенідної системи Se-Ge

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Халькогенідні скла, що зазвичай демонструють порогове перемикання, перемикання пам'яті та інфрачервону прозорість, інтенсивно досліджуються через їхні електричні та оптичні властивості, що робить їх перспективними для різних застосувань. У цій роботі представлені теоретичні розрахунки фізичних параметрів потрійних халькогенідних стекол Se-Ge-Bi та їх залежність від вмісту Bi. Фізичні параметри мають значний вплив на структуру та міцність матеріалу. У статті розглядається прогнозування ключових фізичних характеристик, зокрема: координаційного числа, кількості неспарених електронів, механічних обмежень, теплоти атомізації, когезійної енергії для скляної системи $Se_{80-x}Ge_{20}Bi_x$ ($x = 0, 4, 8, 12$ ат. %). Спостережувані зміни фізичних параметрів зумовлені модифікацією ковалентного характеру скла.

Ключові слова: Халькогенідні скла, XRD, Координаційне число, Когезійна енергія.