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# A Study on Compositional Dependence on Physical Properties of $(Se_{80}Ge_{20})_{100-x}Bi_x$ System for Phase Change Optical Recording

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**ABSTRACT**

*The investigation of composition dependence of various properties of chalcogenide glasses has been increased in recent years. Since reversible switching phenomenon in certain types of chalcogenide glasses was first reported, a lot of attention has been given to characterization and improvement of the properties of chalcogenide glasses in general and the materials exhibiting the switching phenomenon in particular. In the present work, the effect on the physical properties with the variation in bismuth content has been studied theoretically for $(Se_{80}Ge_{20})_{100-x}Bi_x$ (x=4, 8, 12, 16, 20 at. %) glassy alloys. The glass transition temperature and mean bond energy are calculated by using the Tichy – Ticha approach. It has been found that almost all the parameters, studied here, were increased with the increase in Bi content, thus making this suitable for phase change optical recording and find applications in rewritable optical recording.*

**Keywords:** Chalcogenide Glasses; Average Coordination Number; Lone-Pair Electrons; Glass Transition; Mean Bond Energy.

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## INTRODUCTION

In recent years, chalcogenide glasses have drawn attention because of their technological importance and potential use in photoresist, optoelectronic, microelectronic, holographic applications and especially their ability to transmit light in mid to far infrared region. One of the recent applications of chalcogenide alloys (which contain at least one of the chalcogen elements like S, Se or Te) is in rewritable optical data recording i.e. phase change recording. This technology is based on reversible phase transition between crystalline and amorphous state. Currently, the primary material for phase change recording are based on Sb-Te alloys [1-5], but material research still continues due to the need for increased storage capacity and data recording rates. Now a days the attention is extended over Ge-Se system as possible candidates for this application.

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. In the present work, we have incorporated Bismuth (Bi) in the Ge-Se alloy. The addition of third element will create compositional and configurational disorder in the material with respect to the binary alloys. Chalcogenide glasses in Ge–Se system are used as switching, memory elements and optoelectronic devices and are interesting material for infrared optics too. It has been established that physical properties in this system are highly composition dependent [6 – 9].

Recently, various researchers have synchronized ternary selenide glasses based on Ge-se system with addition of Bi and have considered basic optical and physical parameters in various glass compositions. Normally the binary

material system has poor stability, which may be improved by doping other elements such as Bi, Sb, Pb, As etc. In the present paper higher coordination number of Ge is considered to be effective in forming covalent bonds and reducing the atomic diffusivity, which can provide sufficient amorphous stability i.e. the addition of third element will create compositional and configurational disorder in the material with respect to the binary alloys, which will be useful in understanding the structural properties of these materials. Therefore, the structural studies of Ge-Se alloy doped by Ge with systematic compositional variation can be advantageous for gaining important insight in the structure property relationship for these compounds.

The compositional dependence studies on glassy alloys were reported for Ge-Se, Ge-Se-Ag, Ge-Se-Te, Ge-Se-Sb, Ge-Se-In, Ge-Se-Pb, Ge-Se-As, Ge-Se-Ga [10-15]. 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. Several researchers have studied the effect of Bi on the optical and electrical properties of chalcogenide materials. Addition of third element like Bi to Ge-Se 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 [16-19].

In the present work, we have incorporated Bismuth in the Ge-Se alloy for the compositions belonging to $(Se_{80}Ge_{20})_{100-x}Bi_x$ (x=4, 8, 12, 16, 20 at. %). The addition of third element (Bi) used to create compositional and configurational disorder in the material with respect to the binary alloys. It has been established that physical properties in this system are highly composition dependent [20, 21]. The Ge-Se-Bi 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 60-80 at % Se, with rest being Ge. Therefore we find it a suitable system for investigation of the variation of certain physical properties. 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 and the glass transition temperature etc. for $(Se_{80}Ge_{20})_{100-x}Bi_x$ alloys.

## THEORETICAL STUDIES AND DISCUSSION

**Bonding Constraints & Average Coordination Number**

It may be valuable to consider the transitions in the light of the constraint – counting argument originally proposed by J. C. Phillips for amorphous covalent materials [22]. To explain glass forming tendencies, Phillips gave the mechanical-constraint counting algorithms. 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 average coordination number (Z) is calculated using standard method [23] for the composition $(Se_{80}Ge_{20})_{100-x}Bi_x$, and is given by

$$Z = \frac{xN_{Se} + yN_{Ge} + zN_{Bi}}{x + y + z}$$

where x, y and z are the at. % of Se, Ge and Bi respectively and $N_{Se}(2)$, $N_{Ge}(4)$, $N_{Bi}(3)$ are their respective coordination number [24,25]. Fig 1 shows values of Z increase from 2.424 to 2.52 with increase in concentration of Bi from 4 to 20 using the calculated values of average coordination number for $(Se_{80}Ge_{20})_{100-x}Bi_x$ (x = 4, 8, 12, 16, 20 at. %) system.

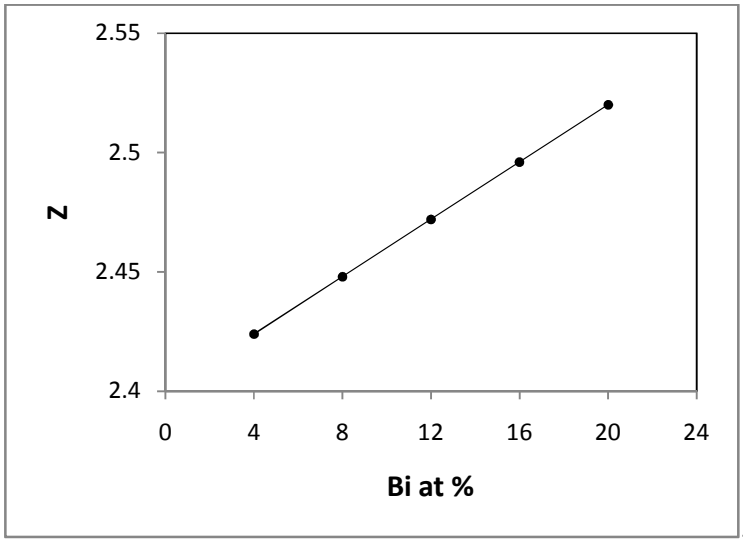


**Fig. 1: Variation of Average Coordination Number with Bismuth content**

The glassy network are influenced by mechanical constraints ($N_c$) associated with the atomic bonding and an average coordination number Z which is also related to $N_c$. There are two types of near-neighbor bonding forces in covalent solids; bond-stretching (α- forces) and bond-bending (β- forces) [26].
The number of Lagrangian bond-stretching constraints per atom is

$$N_\alpha = Z/2$$

and, of bond-bending constraints is

$$N_\beta = 2Z - 3$$

For the case when all α and β constraints are intact and no dangling ends exist in the network, equation implies that the optimum mean coordination number is 2.424 which is known as the regiditty percolation threshold. Highly over-coordinated or under-coordinated structures are not conducive to glass formation and, upon cooling, lead to crystalline solids. The number of floppy modes per atom, f, is rather accurately described by the mean-field constraint count according to the relation [27]

$$f = 3 - N_c \quad (2)$$

This led to the realization that a glass network will become spontaneously rigid when $f \rightarrow 0$, defining a *floppy* to *rigid phase transition* [28].
The total number of constraints is given by

$$N_c = N_\alpha + N_\beta$$

Fig. 2 depicts the variation of $N_c$ with Bi at % for $(Se_{80}Ge_{20})_{100-x}Bi_x$. Here $N_c$ increase from 3.06 to 3.30 with increase in Bi at.% from 4 to 20, which shows in our composition that the number of constraints $N_c$ acting on the network are balanced by the number of degrees of freedom N available from the atoms in the network. This means that network is isostastically rigid, no stress is present i.e. $N_c = N_d$.

The cross-linking density (X) is equal to the average coordination number of cross linked chain less the coordination number of initial chain [29].

$$X = N_c - 2$$

The values of cross linking density (X) are calculated using above mentioned relations. From fig. 3, it is clear that the value X increase with increase in Bi content. Fig.4 shows the variation of molecular weight M with Bi content.

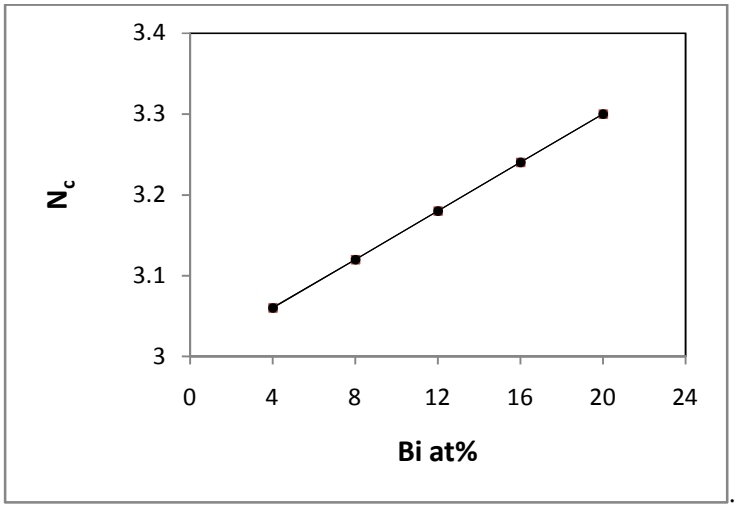


**Fig. 2: Variation of number of constraints with Bi content**

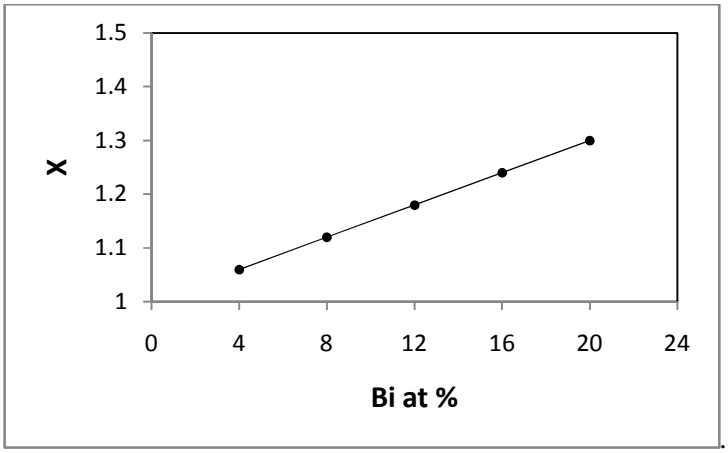


**Fig. 3: Variation of cross-linking density with Bi content**

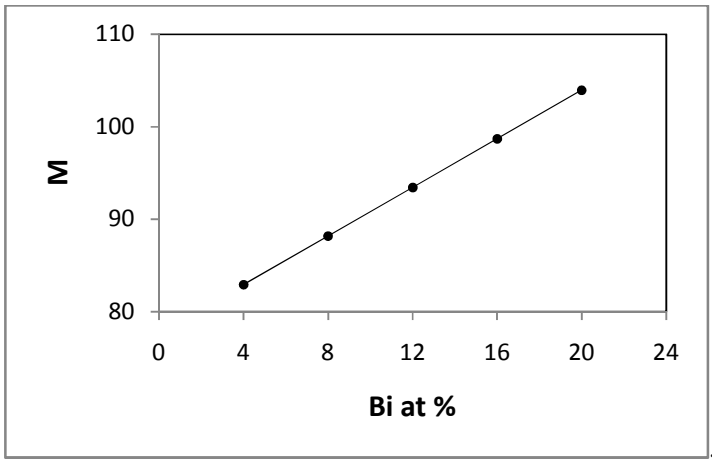


**Fig. 4: Variation of Molecular weight with Bi content**

According to Thorpe, the uncoordinated network having finite fraction of zero frequency normal vibrations modes termed as floppy modes in absence of weak long range forces. The fraction of floppy modes available in a network is given by

$$f = 2 - \frac{5Z}{6}$$

From the values of f and fig. 5 that the value of f becomes more and more negative with increase in Bi content from 4 to 20 at. %. This shows that the system becomes more and more rigid, which corresponds to a strong tendency for making glass.

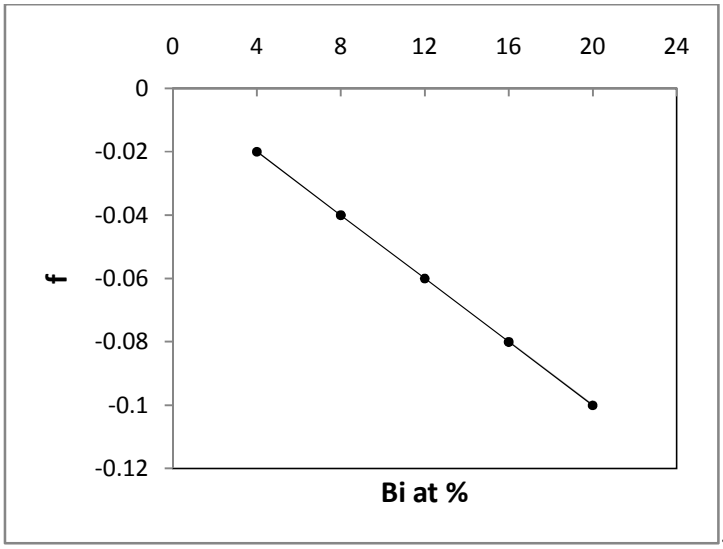


**Fig. 5: Variation of fraction of floppy modes with Bi content**

**Role of Lone Pair Electrons and Glass Forming Ability**

According to Pauling [30], a 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 are calculated by using the relation [31]

$$L = V - Z$$

where L is the number of lone-pair electrons, V is the valance electrons and Z is the average coordination number. It is observed that for the glassy system $(Se_{80}Ge_{20})_{100-x}Bi_x$, 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.

Zhenhua [31] proposed a simple criterion for a binary system and a ternary system, i.e., for a binary system the number of lone-pair electrons must be greater than 2.6 while for a ternary system it must be greater than 1.0. In our system $(Se_{80}Ge_{20})_{100-x}Bi_x$, the values of lone-pair of electrons are found to be greater than 1.0 and it is decreasing from 3.20 to 2.96 with the increase in Bi content from 4 to 20 at % as depicted in fig 5. So this explains the fact that the present system under investigation can be obtained in amorphous glassy state. A system with large number of lone-pair electrons constitutes a stable state. Chalcogenides with lone-pair electrons are also characterized by flexibility [32]. This flexibility of bonds causes these atoms to readily form amorphous network, either alone or with a variety of other atomic constituents.

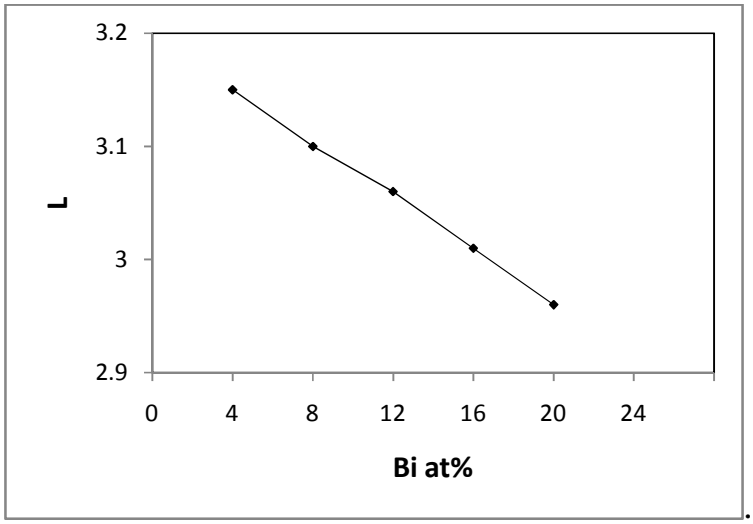


**Fig. 6: Variation of Lone-pair electrons with Bi content**

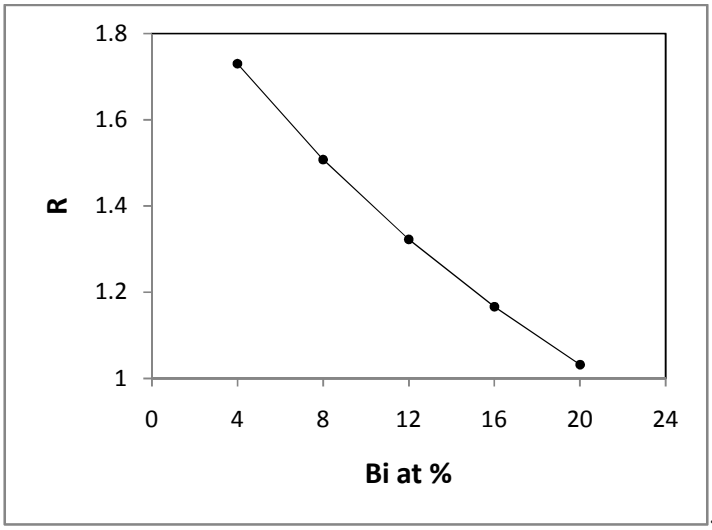


**Fig. 7: Variation of parameter R with Bi content**

**Deviation from the stoichiometery 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 the present $(Se_{80}Ge_{20})_{100-x}Bi_x$ system, the parameter R is given by [33]

$$R = \frac{xCN(Se)}{yCN(Ge) + zCN(Bi)}$$

where x, y, z are atomic frictions of Se, Ge and Bi 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 fig. 7, it is clear that our system is more or less chalcogen rich and turning towards chalcogen poor with the increase in content of Bismuth in the system. As the material is chalcogen rich and so having the high energy lone pair electrons leads to qualitative different electronic densities of states. 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.

**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 [34], 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 $(Se_{80}Ge_{20})_{100-x}Bi_x$ system 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 $Se_x\ Ge_y\ Bi_z$ system, where (x + y + z) = 1, in selenium rich systems (R>1) where there are heteropolar bonds and chalcogen-chalcogen bonds

$$E_c = 4yE_{Ge-Se} + 3zE_{Bi-Se}$$

and

$$E_{rm} = \left[\frac{2x-4y-3z}{Z}\right]E_{Se-Se}$$

denotes the average homopolar bonding energy. It is clear from fig. 8 that <E> increases with increase in concentration of Bi from 4 to 20 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

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

The variation of $T_g$ with Bi content is shown in fig. 9, which is clearly depicting the rise in glass transition temperature with increasing the content of Bi due to rise in mean bond energy of the glassy system.

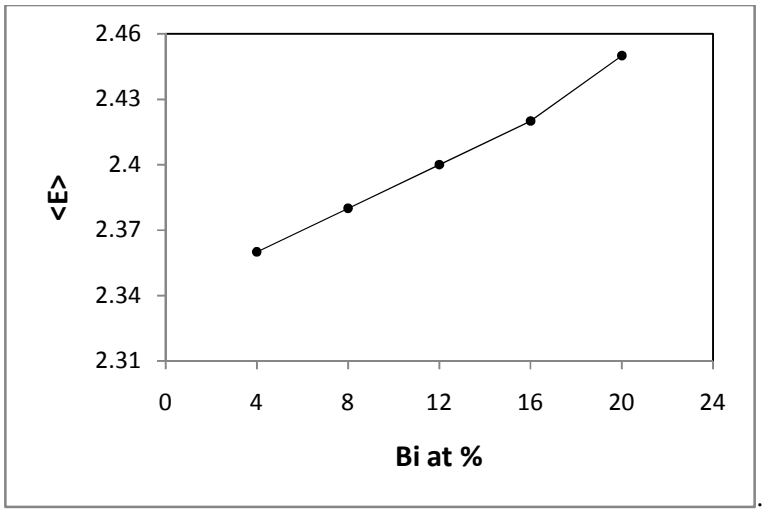


**Fig. 8: Variation of overall mean bond energy with Bi content**

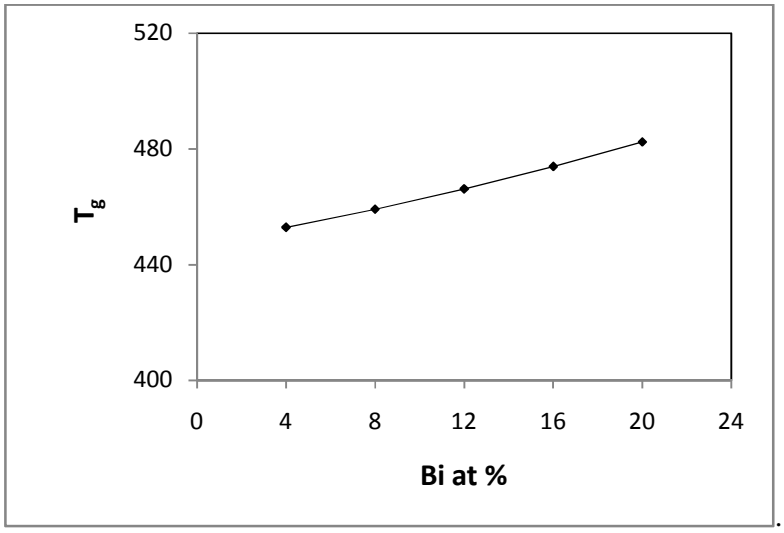


**Fig. 9: Variation of glass transition temperature $T_g$ with Bi content**

## CONCLUSION

The influence of Bi content on physical and optical parameters of Ge-Se glassy alloys has been investigated here. The addition of Bi to Ge-Se glassy alloys leads to change from floppy to intermediate or rigid region. In the present work almost all the parameters were found to increase with the increase in content of Bi. With the addition of Bi, number of lone-pair electrons decreases continuously, which are caused by the interaction between Bi ion and lone-pair of electrons of bridge Se atom. It has been found that mean bond energy <E> is proportional to glass transition temperature and both increases with the increase in content of Bi.

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