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COMPACTNESS IN RELATION TO THE MEAN COORDINATION NUMBER IN GLASSY $Ge_xBi_6S_{94-x}$

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The compactness of the structure of glassy $Ge_xBi_6S_{94-x}$ ($14 \leq x \leq 26$ at %) is determined from the measured densities. The peculiarities observed in the compactness-composition dependence are understood using Phillips'-Thorpe and Tanaka's topological models proposed for the structure of these covalently bonded solids.

Keywords: Chalcogenides, Glasses, Compactness, Mean-coordination number

1. Introduction

Chalcogenide glasses have recently attracted much interest due to mainly two reasons. The first stems from their interesting physical and optical properties and consequently of their potential technological applications. A recent review of all these potential applications appeared in the proceedings of the international workshop on amorphous and nanostructured chalcogenides [1]. These applications include the well-known xerography process with Se or As-Se , lithography with $Ge_{25}Se_{75}$ [2], CD compatible erasable disk with Ge-Te or Ge-Te-Se [3], chemical sensors with As-S(-Se) based alloys [4], long lengths of low loss IR transmitting devices with $As_{40}S_{60-x}Se_x$ [5], the use of memory and switching effects as observed in $Bi_{29}Tl_{35}Se_{36}$ [6] or photodarkening properties as in As_2S_3(-Se_3), Ge-S_2(Se_2) [7,8], and their use for the preparation of electrical memories as in $Al_{23}Te_{77}$ [9]. The second one is linked to the relative ease of their preparation from the melt. The best example is demonstrated by pure Se which is known to be the only element able to give mono-atomic glass [10]. As a consequence, chalcogenide glasses can be used as reference materials in order to develop a better understanding of the glassy state and its specific properties. Moreover, because these materials show a continuous change of their various properties with change in their chemical composition, it is possible to investigate the correlation of the features observed in the property-composition dependence with the structural arrangement in the glass. Such studies on thermal [11], mechanical [12], electrical [13], optical [14] and physicochemical [15] have recently been reported.

The Ge-S-Bi is a prototypical chalcogenide system. The first paper that dealt with the addition of bismuth in a chalcogenide matrix was published by Bowman and Schottmiller [16] in 1968. The goal was the preparation of new infrared photoconductors. At the same time, it was discovered that a small amount of Bi atoms (≈ 7 at% Bi) incorporated in a Se matrix leads to the change of the conductivity type from p to n [17]. More recently, the possibility of making an all chalcogenide glass p-n junction based on this ability of Bi was demonstrated [18,19]. Since the results of [17], many studies were performed to propose an explanation of this specific property that the Bi atom seems to possess. Different atomic configurations were proposed. Most of these works were recently discussed in a review article of Vautier [20]. With regard to this review article, one conclusion was that after three decades of researches and debates on this matter, the origins of this

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specific property are not yet fully understood. Indeed, one of the main problems is the lack of direct structural investigations of the atomic Bi surroundings. Consequently, we have performed Ge K-edge and Bi L_{III}-edge extended x-ray absorption fine structure (EXAFS) measurements on these glasses and EXAFS measurements from Bi L_{III}-edge on crystalline Bi_2S_3 [21]. From these measurements, we have shown that Ge and Bi atoms in these glasses are uniquely coordinated with S atoms with a coordination number (CN) equal to four. The CN of Bi with S in crystalline Bi_2S_3 is found to be three and thus these results allow us to conclude that the presence of Bi_2S_3 microcrystalline inclusions , in the structure of the glasses, is excluded and that these glasses are homogeneous at the microscopic level. Earlier, we reported X-ray photoelectron spectroscopy (XPS) measurements on $Ge_{20}S_{64}Bi_{16}$ glass [22] and concluded that Bi atoms enter the parent glass matrix, $Ge_{20}S_{80}$, as a positive charge centre.

In the present work on Ge-S-Bi glasses, we report the compactness results and discuss them in light of the topological models proposed for their network structure.

2. Experimental

The glasses with the compositions $Ge_xBi_6S_{94-x}$ ($14 \le x \le 26$ at %) were fabricated from high purity elements by the usual melt quenching technique. Appropriate amounts of Bi pellets, S pieces and Ge chunks (total 1.5 g) were loaded into a cylindrical (length 100 mm, internal diameter 8 mm) quartz capsule. Each capsule was then evacuated to a pressure of 10^{-5} Torr, sealed, and transferred to an electric furnace. The temperature of the furnace was then raised to 900 °C and the capsule was kept at this temperature for 72 h. During this time, the capsule was continuously shaken to guarantee the complete mixing of the various constituents. The glass was finally obtained by quenching the capsule to 0 °C in an ice-water mixture.

The Archimedes method was used for the measurement of the density of as-prepared glasses. The weight of a piece of the Ge-S-Bi glassy alloy was measured in air and in distilled water using an electrical balance, as w_1 and w_2, respectively. The density of the glassy alloy could thus be determined from the formula

$$\rho = \left[\frac{w_1}{w_1 - w_2}\right]\rho_{water} \tag{1}$$

Five separate determinations were made on each glass composition and the average of them was taken as the measured density of it. The experimental uncertainties of the density measurement was better than ± 0.5%. The compactness, δ, of the structure of the glass was calculated according to the formula [23-25]

$$\delta = \rho\left(\sum_i x_i A_i \rho_i^{-1} - \rho^{-1}\sum_i x_i A_i\right)\left(\sum_i x_i A_i\right)^{-1} \tag{2}$$

where x_i, A_i, and ρ_i are the atomic fraction, the atomic weight, and the atomic density of the ith element of the glass and ρ is the measured density of the glass. Thus, δ is a measure of the normalized change of the mean atomic volume due to chemical interactions of the elements forming the network of a given solid [26] and, therefore, is associated with the free volume and the flexibility of the network. The compactness can assume negative values, which correspond to larger free volumes and flexibilities.

3. Results and discussion

The composition of the glassy alloy is represented by its mean coordination number, <r>, which has been widely used for the description of the structure of network glasses [27-30] and which is indiscriminate of the type of atomic species in a covalent bond [31]. It is defined as the mean number of bonded neighbours per atom in the structure and represents the rigidity of the structural units [31]. The <r> values for the investigated $Ge_xBi_6S_{94-x}$ glassy alloys are calculated using the normal procedure [32-34] and cover the range between 2.46 to 2.64. The details of the calculation are given elsewhere [35]. Prepared samples with higher <r> were partially crystalline and therefore their results are not included here. The chief result of this work is depicted in Fig. 1.

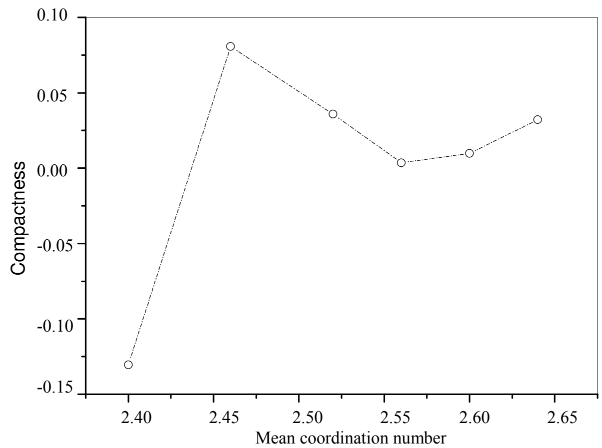

Fig. 1. Variations of the compactness with the mean coordination number in $Ge_xBi_6S_{94-x}$ glasses. Lines through data points are drawn to guide the eye.

The prominent features observed in this figure are a maximum at <r>= 2.46 and a minimum at <r>= 2.56 which are explained in the following paragraphs.

Recently, Phillips [27] introduced the concept of viewing the properties of covalent glasses in terms of <r>. In his attempt to explain the glass forming ability of certain covalent glassy alloys and using elegant constraint-counting arguments, he proposed that the network connectivity could be parameterised by simply using <r>. He further proceeded to assume that, for the ideal glass, the number of inter-atomic force-field constraints per atom, N_c, exhausts the number of degrees of freedom per atom, N_d, in three dimensional space. Phillips' balance condition $N_c= N_d$ takes into account both bond stretching α constraints and bond bonding β constraints and led him to conclude that the mechanical stability for the network with the critical coordination number $<r>_c= 2.4$ is optimised. Later on, Thorpe [29,30] recognised that Phillips' balance condition can be formulated as a percolation problem in which the quantity of interest is rigidity. He showed that for a three dimensional network, the number of zero-frequency (floppy) modes per atom, f, is given by

$$f=2-\frac{5}{6}<r> \tag{3}$$

which approaches zero from below when <r> approaches the critical value of 2.4. Networks with <r> less than 2.4 are polymeric glasses (or floppy) in which the rigid regions are isolated. As <r> increases, the network goes through the transition at $<r>= <r>_c$. At this $<r>_c$, the rigidity is said to percolate and the glass transforms to a rigid structure. This $<r>_c$ value is referred to as the rigidity percolation or mechanical threshold. Networks with <r> greater than 2.4 are amorphous solids (or rigid).

The optimised stability of the network with $<r>= <r>_c= 2.4$ is linked with the most tight bonding, shortest bond lengths and consequently with the largest compactness. Therefore, the maximum in δ observed at <r> = 2.46 in these glasses is attributed to the floppy-rigid transition. The <r> value at which the rigidity transition is observed in this work for these glasses is higher than that predicted by the mean field theory [27-30]. Thus, it may be assumed that, in real glasses, this transition occurs in the slightly over-cross-linked regime. The positive shift in the <r> value marking the rigidity transition was noted in <r>-dependencies of various properties of chalcogenide glasses [36-41]. Furthermore, computer simulations of bond-depleted diamond network [42], 2D triangular central force networks [43], and self-organizing networks [44] confirm the existence of this rigidity transition.

The minimum in δ at <r>= 2.56 can be understood by assuming that the structure of this composition ($Ge_{22}S_{72}Bi_6$) is a layered one with a network dimensionality D= 2. For this composition, the interlayer separation is a maximum resulting in the observed minimum in δ.

The idea that D = 2 for structures of <r>≈ 2.5 was previously proposed with structural models based on rafts [27,45] and distorted layers [46,47]. Indeed, Tanaka [31], modified Phillips'-Thorpe balance condition by including intermediate-range order (IRO) interactions and predicted the existence of a threshold at <r>= 2.67. At this <r> value, 2D layered structures are fully evolved and for higher <r> the structure is transformed to a 3D network. Thus, it can be argued that the minimum in δ at <r>=2.56 marks the 2D→3D structural transition in these glasses. The apparent discrepancy between the observed Tanaka's threshold (<r>= 2.56) and the predicted one (<r>= 2.67) could be attributed to the inclusion of the heavy metal Bi into the Ge-S network which, in turn, leads to the formation of partially ionic Bi-S bonds. In this case, Tanaka's threshold derived for purely covalent networks is treated as a reference value. The lower value of <r>, compared to that predicted by Tanaka, at which the 2D→3D transition is observed in these glasses has been reported from mean-atomic volume results in Ge-Se-Ga [48], from surface toughness measurements in Ge-Se-Sb [49], from high pressure resistivity measurements in Ge-As-Te [50], from calorimetric measurements in Ge-S-Sb [51] and from compactness results in Ge-Se-In [52].

4. Conclusions

The compositional dependence of the compactness, δ, for $Ge_xBi_6S_{94-x}$ chalcogenide glasses has been investigated. The observed maximum at <r>= 2.46 and minimum at <r>= 2.56 in the δ-<r> dependence are caused, respectively, by Phillips'-Thorpe floppy-to-rigid and Tanaka's 2D→3D transformations.

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