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The influence of mechanical and chemical thresholds on the free volume percentage in Ge–Se–(Fe,In) chalcogenide glasses

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Abstract

Assuming that the increase in the volume during melting of a solid is inherent in the amorphous state (supercooled liquid), then the structure of amorphous solids should contain free volume. In the present paper, we determine the free volume percentage (FVP) in Ge–Se–(Fe,In) chalcogenide glasses and examine its relationship with the mean coordination number. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Ge–Se–(Fe,In) glasses; Free volume percentage; Mechanical and chemical thresholds; Mean coordination number

1. Introduction

In the past two decades a great deal of research has been devoted to the investigation of the various properties of chalcogenide glasses as a function of the mean coordination number, n . Researchers studied the mean coordination number dependencies of thermal [1], mechanical [2–4], electrical [5], optical [6,7] and physicochemical [8–12] properties of these materials. However, no account, to the best of our knowledge, of the relationship between the free volume percentage (FVP) and the mean coordination number appeared in the literature. In this paper, an attempt is made to detect whether any unusual features are exhibited in the compositional dependence of the FVP for Ge–Se–(Fe,In) glasses which would serve

as an indirect evidence of the threshold behaviour of mechanical and/or chemical nature.

2. Experimental

Appropriate amounts of high purity elemental Ge, Se and Fe were encapsulated in a quartz ampoule, which was evacuated to a pressure of 10^{-5} Torr, and sealed. The ampoule was then placed in an electric furnace which was heated to 310°C for 120 h. Afterwards its temperature was first raised to 590°C for 24 h and then to 900°C for 3 h. At this temperature the ampoule was rigorously shaken to homogenize the melt. The ampoule was then quenched to 0°C in an ice–water mixture. However, this preparation procedure did not yield the required glasses as was verified from X-ray diffractometry and optical microscopy. Thus, the content of the ampoule was obtained, ground in a glove box, refilled in the

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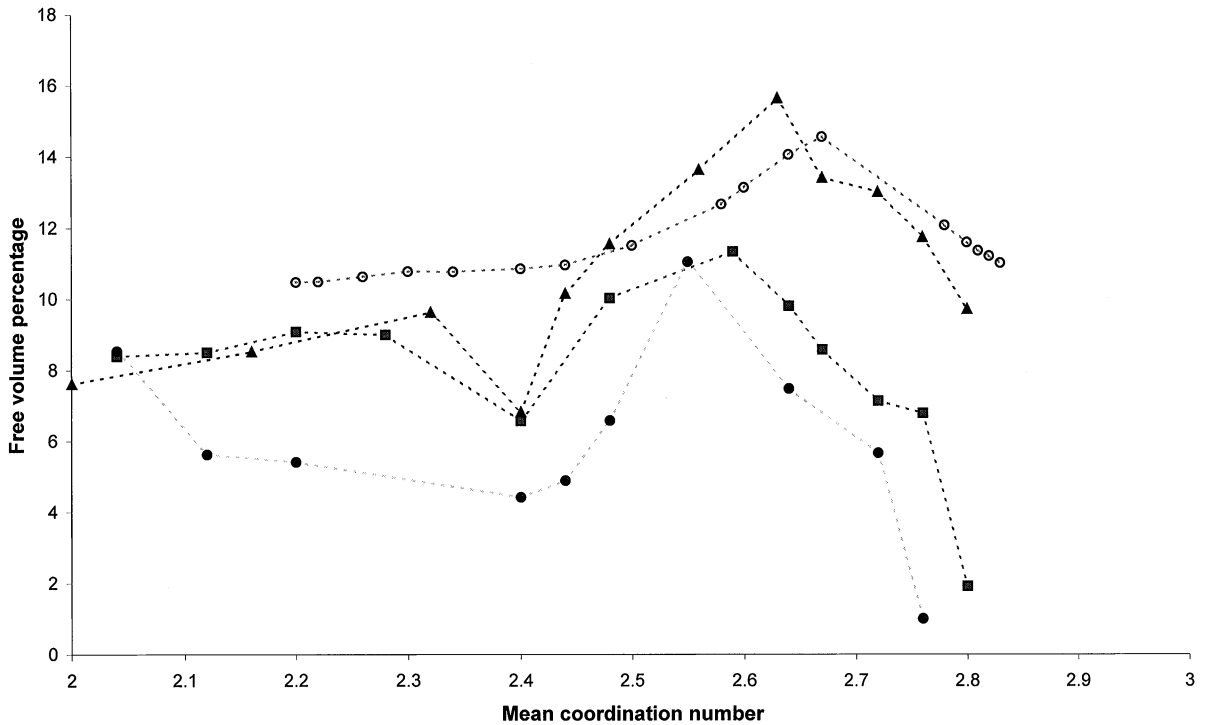


Fig. 1. Dependence of the free volume percentage on the mean coordination number for Ge–Se–Fe glasses. The FVP values for glasses containing 2, 4 and 6 at% Fe are represented, respectively, by triangles, squares and filled circles. The open circles represent the FVP values for the binary Ge–Se system and generated from Ref. [40].

quartz ampoule and sealed under vacuum. The temperature of the ampoule was first raised to 600°C for 1 h and then to 900°C at the rate of 100°C/h. The glasses were then obtained by quenching the ampoule to 0°C in an ice–water mixture.

The details of the sample preparation of Ge–Se–In glasses have already been given elsewhere [9]. The density was measured, to an accuracy of better than $\pm 1\%$, by the Archimedean displacement technique using carbon tetrachloride. The molar volume, V_m , of the glass with the formula $\text{Ge}_x\text{Se}_y\text{(Fe,In)}_z$ ($z = 100 - x - y$) was calculated from the expression

$$V_m = \frac{xM(\text{Ge}) + yM(\text{Se}) + zM(\text{Fe, In})}{\rho}, \quad (1)$$

where $M(\text{Ge})$, $M(\text{Se})$, $M(\text{Fe})$ and $M(\text{In})$ are the molecular weights of Ge, Se, Fe and In, respec-

tively, and ρ is the experimental density. The free volume percentage (FVP) in the glass was obtained using the relation

$$\text{FVP} = \frac{(V_m - V_T)}{V_m} 100\%, \quad (2)$$

where V_T is the theoretical molar volume. The calculation of V_T for the composition $\text{Ge}_x\text{Se}_y\text{(Fe,In)}_z$ was performed using the following additive formula

$$V_T = xV(\text{Ge}) + yV(\text{Se}) + zV(\text{Fe, In}), \quad (3)$$

where $V(\text{Ge})$, $V(\text{Se})$, $V(\text{Fe})$ and $V(\text{In})$ are, respectively, the atomic volumes of elemental Ge, Se, Fe and In. Glasses containing 6 and 12 at% In from the Ge–Se–In system and glasses with 2, 4 and 6 at% Fe from the Ge–Se–Fe system were prepared.

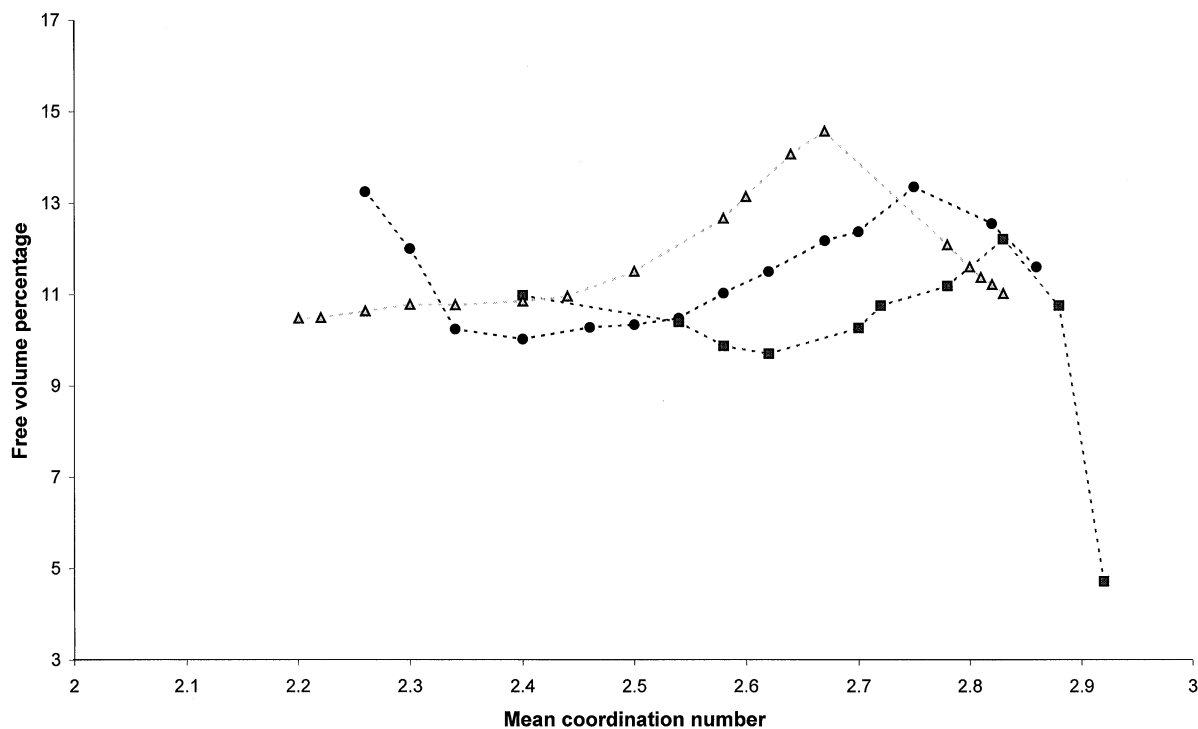


Fig. 2. Dependence of the free volume percentage on the mean coordination number for the binary system Ge–Se generated from Ref. [40] and represented by triangles. The data points represented by circles and squares correspond, respectively, to glasses containing 6 and 12 at% In from the Ge–Se–In system.

3. Results and discussion

The mean coordination number, n , of the investigated glasses was calculated using the standard procedure [13–15]. The results, depicted in Figs. 1 and 2, reveal that the FVP, for Ge–Se–Fe glasses and glasses containing 6 at% In from the Ge–Se–In system, possesses a minimum at $n = 2.4$. This minimum can be understood on the basis of the Phillips’–Thorpe constraint theory proposed for covalent network glasses [16–18]. This theory predicts a transformation from underconstrained floppy network to overconstrained rigid network at the critical mean coordination number $n = 2.40$. At this critical n value, the number of constraints, due to bond stretching and bond bending interactions, exhausts the number of degrees of freedom available for the atoms of the network, and the network attains its maximum mechanical stability. So, glasses with $n < 2.40$ must contain large floppy regions and are loosely connected. The optimised

mechanical stability of the glass with $n = 2.40$, where the transformation from a floppy to a rigid network takes place, is associated with the maximum in the compactness of the structure of the glass [8]. Consequently, the free volume content of the glass with $n = 2.40$ must be a minimum as observed in this work. This mechanical threshold has been reported from binary Si–(Se,Te) [19,20], Ge–(S,Se,Te) [20–24] and As–Te [25]. It has also been noted in ternary As–Se–Te [26], Ge–As–(S,Se,Te) [27–30], Al–As–Te [31], Ge–Se(In,Sb,Te) [4,8,9,23,24,29,32], Ge–Te(Ag,Cu) [1], Ge–Ga–Se [12] and multicomponent Ge–Se–Sb–Te–As [4] systems.

The ideas of Phillips were extended by Tanaka [33] to the case of networks possessing medium-range ordering. He showed that for two-dimensional (2-D) glassy structures, laid in three-dimensional (3-D) space, the mechanical threshold is shifted to $n = 2.67$. In covalent glasses, he envisaged the formation and growth of a layered

structure and its transition to a 3-D network at $n = 2.67$. Tanaka's proposal can be used as an alternative model for explaining the observed minimum in the FVP at $n = 2.62$ for glasses containing 12 at% In from the Ge–Se–In system. At this stage, it must be mentioned that Tanaka's value of the threshold at $n = 2.67$ was obtained for only networks with pure covalent bonding. However, the presence of 12 at% of the heavy element In presumably results in the formation of partially covalent bonds in the glass and, in this case, it might be responsible for the apparent discrepancy between the observed value of the threshold ($n = 2.62$) and that predicted by Tanaka ($n = 2.67$). The aforementioned observation of the threshold, marking the 2-D \rightarrow 3-D transition, at $n < 2.67$, was recently reported for Ge–Sb–S [34,35], Ge–As–S [36], Ge–Sb–Se [3,37], Ge–Ga–Se [12], Ge–In–Se [38] and Ge–As–Te [39].

As can be seen from Figs. 1 and 2, the FVP passes through maximum at $n = 2.63$, 2.59 and 2.55 for glasses containing 2, 4 and 6 at% Fe, respectively, in the Ge–Se–Fe system. The maxima in the FVP for the Ge–Se–In system are observed at $n = 2.75$ and 2.83 for compositions with 6 and 12 at% In, respectively. In these figures, experimental data for the binary Ge–Se system have also been plotted which were generated from Ref. [40]. A maximum for the GeSe₂ composition ($n = 2.67$) is exhibited. These maxima can be traced to effects of chemical origin and are explained by employing the chemical ordered network (CON) model [7]. According to this model, in a chalcogenide glassy system, there exists a critical composition at which only heteropolar bonds are allowed and its structure is assumed to be formed of 3-D cross-linked structural units of the stable chemical compounds of the system. Thus, in Ge–Se–Fe system, this composition can be pictured to be built from 3-D completely cross-linked GeSe₂- and FeSe₂-type structural units and is represented by the formula (GeSe₂) _{β} (FeSe₂)_{1- β} where β and $1-\beta$ are the fractional contents of GeSe₂ and FeSe₂, respectively. This composition is also referred to as the chemical threshold of the system [2]. The chemical threshold, in Ge–Se–In system, is composed of GeSe₂- and In₂Se₃-type structural units. The network with maximum chemical ordering

(chemical threshold) possesses a minimum density [18,41] and compactness [8,42] and consequently a maximum in the FVP. Therefore, the compositions at which the maxima in the FVP are observed for the systems studied, are their chemical thresholds.

4. Conclusions

The compositional dependence of the FVP for the Ge–Se–Fe and Ge–Se–In chalcogenide glasses has been investigated. For both the systems studied, it is concluded that the minima and the maxima observed in the compositional dependence of the FVP are caused by the mechanical and chemical thresholds, respectively.

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