Molar volume and compactness versus mean coordination number in Ge-Se-Fe glasses: observation of a threshold behavior

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Abstract. Molar volumes, V, and compactness values, α, of 34 glassy compositions of the Ge-Se-Fe system have been obtained using their measured densities. The property–composition dependences are examined in light of the models proposed for the structure of these network glasses.

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Chalcogenide glasses have recently drawn much interest due to their use as materials for infrared optical fibers, photoconductors, optoelectronic circuits, optical memories [1–6] and for the preparation of electrical memories [7]. In addition to their technological importance and because chalcogenide glasses show a continuous change of various properties with change in 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.

There are only few studies, to our knowledge, on the properties of chalcogenide glasses containing Fe. This is probably due to its metallic behavior where a small amount of Fe can be incorporated in glass formation. Therefore, it is interesting to investigate the property–composition dependence for glasses from the Ge-Se-Fe system. In the present work we report and discuss the compositional dependence of the molar volume, V, and the compactness, α, for the glasses having the chemical composition $Ge_xSe_{100-x-y}Fe_y$ ($y = 2, 4$ and 6 at. %).

1 Experimental details

High-purity starting elements, in the appropriate atomic proportions, were batched in cylindrical (8 mm in diameter)

quartz ampoules. The ampoules, containing 1.5 g of the material, were evacuated (10^{-5} Torr) and sealed. The ampoules were then heated in an electric furnace to a temperature of 310 °C and left at this temperature for 5 days. After this period, the temperature of the ampoules was raised to 590 °C and left for 1 day. Then the temperature was further raised to 900 °C and the ampoules were continuously agitated, over a period of 3 h, to ensure the homogenization of the samples. Subsequently, the ampoules were quenched from 900 °C to 0 °C in ice–water. However, the above-described procedure did not produce good glasses as evidenced from X-ray diffraction and inspection by an optical microscope. Therefore, the ampoules were cut open, the substances were ground in a glove box, filled in quartz ampoules and sealed under vacuum. The heating cycle used was as follows: the temperature of the ampoules was raised to 600 °C and stayed at this temperature for 1 h. Then the temperature of the ampoules was raised stepwise to 900 °C at the rate 100 °C/h. To obtain the glasses, the ampoules were quenched from this temperature in ice–water.

Density measurements, accurate to less than ±1%, were performed by the Archimedes method using carbon tetrachloride (CCl_4) as the immersion liquid. The molar volume, V, for a given composition, was obtained by dividing the average molecular weight by its measured density.

The compactness, α, of the structure of the glass was calculated via the relation [8–10]

$$\alpha = d \left(\sum_i A_i x_i \varrho_i^{-1} - d^{-1} \sum_i A_i x_i \right) \left(\sum_i A_i x_i \right)^{-1} \quad (1)$$

where x_i, ϱ_i and A_i stand, respectively, for the atomic concentration, atomic density and atomic weight of the i-th element and d is the measured density. Both V and α are influenced by the changes in the structure of the glass network arising from interactions between elements forming the network. Therefore their behavior with composition should shed light on the structure of the glass.

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2 Results and discussion

Coordinations of 4, 2 and 2 for Ge, Se and Fe, respectively, were used in the evaluation of the mean coordination number of the glasses examined. For the composition $Ge_xSe_{100-x-y}Fe_y$ the mean coordination number, $\bar{r}$, is given by [11, 12]:

$$\bar{r} = 2 + 0.02x,$$

where x is the atomic concentration of Ge in the glass composition. The compositions prepared covered a wide range of $\bar{r}$ values from 2.00 to 2.80, 2.04 to 2.80 and 2.04 to 2.76 for compositions with 2, 4 and 6 at. % Fe, respectively.

The main results are summarized in Figs. 1 to 4. It is worth noting that, for any given composition, the molar volume decreases as the amount of Fe content in the glass is increased. The substitution of Fe, which has a covalent radius of 1.17 Å, for Ge with a covalent radius of 1.22 Å, can be responsible for this decrease in molar volume. For example, V at $\bar{r} = 2.4$ decreases from 16.880 to 16.063 cm^3 as the Fe at. % is varied from 2 to 6. At r_c this value (the composition with 20 at. % Ge), the $V - \bar{r}$ dependence reveals a minimum while the $\alpha - \bar{r}$ dependence reveals a maximum.
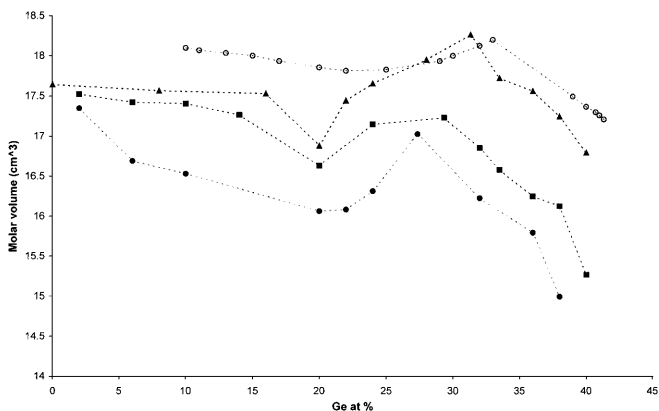

Fig. 1. The molar volume, V, of $Ge_xSe_{100-x-y}Fe_y$ glasses plotted as a function of the Ge content of the glass: ▲, $y = 2$ at. %; ■, $y = 4$ at. %; ●, $y = 6$ at. %. The results for binary Ge_xSe_{100-x}(O) are reproduced from [24] for the reader's reference
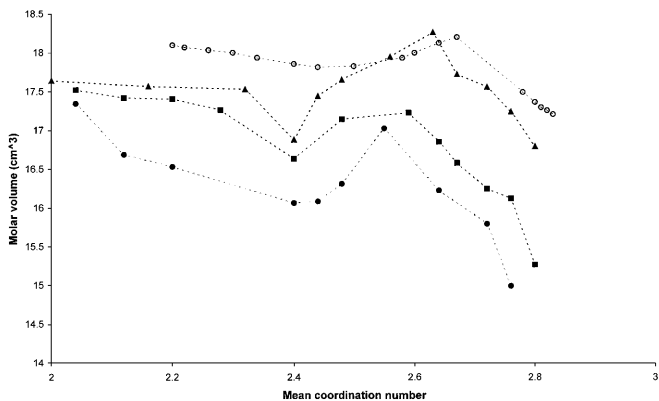
Fig. 2. The molar volume, V, of $Ge_xSe_{100-x-y}Fe_y$ and Ge_xSe_{100-x} glasses vs. mean coordination number, $\bar{r}$. The key to the data symbols is the same as in Fig. 1.
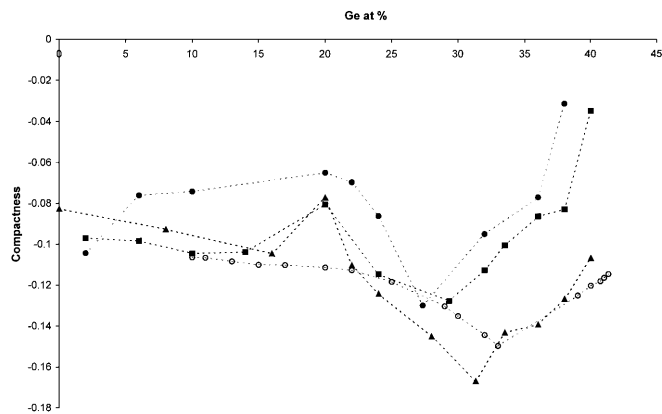
Fig. 3. The compactness, α, of $Ge_xSe_{100-x-y}Fe_y$ and Ge_xSe_{100-x} glasses as a function of the Ge content of the glass. The data of the binary was generated from [24] for the reader's reference. The key to the data symbols is the same as that of Fig. 1
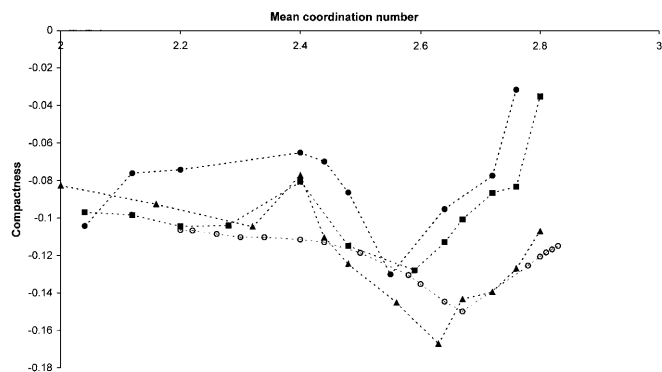
Fig. 4. The compactness, α, of $Ge_xSe_{100-x-y}Fe_y$ and Ge_xSe_{100-x} vs. mean coordination number, $\bar{r}$. The key to the data symbols is the same as in Fig. 1

The observed minimum in V and maximum in α at $\bar{r} = 2.4$ are interpreted by using the Phillips–Thorpe (PT) rigidity percolation model [12–15]. In this model, by considering short-range-order structures only, and setting off the number of degrees of freedom in a covalently bonded network glass against the number of constraints due to bond-stretching (ω) and bond-bending (β) interactions, they predicted the occurrence of a threshold at the critical mean coordination number, $\bar{r}_r = 2.4$. For $\bar{r} < \bar{r}_r$, the network is a polymeric glass (or floppy) in which the rigid regions are isolated. As $\bar{r}$ increases, the network goes through a phase transition at $\bar{r} = \bar{r}_r$. At this critical mean coordination number, the rigidity is said to percolate and the glass transforms to a rigid structure. This $\bar{r}_r$ value is referred to as the rigidity percolation or mechanical threshold. Networks with $\bar{r} > \bar{r}_r$ are amorphous solids (or rigid).

The optimized stability of the network with $\bar{r} = \bar{r}_r = 2.4$ is linked with tight bonding, shorter bond lengths and consequently with the smallest molar volume. Therefore, the minima in V observed at $\bar{r} = 2.4$ for the glasses under investigation are attributed to the floppy–rigid transition. As the minima in V correspond to maxima in α, this explains the observed maxima in the $\alpha - \bar{r}$ dependence at the same $\bar{r}$ value.

Ample experimental evidence in support of the existence of this threshold in the property–composition depen-

dence for chalcogenide glasses comes from neutron [16, 17], Mossbauer [18–21], thermal [22–24], electronic [25], vibrational [26–28], mechanical [29] and molar-volume [23, 24] measurements. In addition to this, numerical simulations confirm the existence of such a threshold in the property–$\bar{r}$ dependences for chalcogenide glasses [15, 30, 31].

For the readers' convenience, we reproduce the molar-volume results for the Ge_xSe_{100-x} system [24] and its generated compactness–composition data. The composition $GeSe_2$, for which V passes through a maximum and α through a minimum, is called the stoichiometric composition or the chemical threshold of the Ge_xSe_{100-x} system. The utilization of the chemically ordered network model [32, 33] to explain the presence of anomalies, in the property–composition relationships for chalcogenide glasses, at the chemical threshold is well discussed in the literature [25, 34]. According to this model, the prevalence of heteropolar bonds is suggested and the network of the stoichiometric composition (chemical threshold) is assumed to be composed of three-dimensional (3D) cross-linked structural units consisting of heteropolar bonds only.

The larger volume requirement for the attainment of the completely cross-linked 3D network for $GeSe_2$ as compared with the Ge-rich or Ge-deficient compositions is, therefore, responsible for the observed maximum in V. On the same basis, the maxima in V and minima in α observed in this work at $\bar{r} = 2.63, 2.59$ and 2.55 for compositions with 2, 4 and 6 at. % Fe, respectively, are attributed to chemical ordering effects taking place at these compositions.

3 Conclusions

The mechanical threshold in Ge-Se-Fe glasses ($\bar{r}_r = 2.4$), due to a floppy-to-rigid transition in network glasses, is marked by a minimum in V and a maximum in α. Effects due to chemical ordering are registered by maxima in V and minima in α at the mean coordination numbers of 2.63, 2.59 and 2.55 for glasses containing 2, 4 and 6 at. % Fe, respectively.

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