INTERMEDIATE-RANGE ORDER IN BINARY AND TERNARY GLASSES*

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Abstract

Intermediate-range order in binary and ternary chalcogenide glasses is discussed, with special reference to GeSe_2 and $\text{Ag}_4\text{Ge}_3\text{Se}_9$. A signature of this order is provided by the first sharp diffraction peak, which occurs in these glasses at $Q \sim 1 \text{ \AA}^{-1}$ and shows anomalous behavior in several ways. It is strongly depressed by the addition of Ag to the GeSe_2 glass. The addition of Ag also leads to a softening of the vibrational spectrum.

Key words: Glass, chalcogenide, intermediate-range order.

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1. Introduction

While glasses are, by definition, solids which possess no long-range order, they possess both short-and intermediate-range order. The former is conventionally taken to mean the regularity in bond distances and angles between neighboring atoms, while the latter represents the way in which the short-range configurations are brought together to build up the network structure of the glass. A striking signature of the intermediate-range order is often given by a first sharp diffraction peak (FSDP) in the glass [1]. This appears at a wave vector Q given approximately by $Qr_1 \sim 2.5$, where r_1 is the nearest neighbor distance in the glass, and has a full width at half maximum ΔQ given by $\Delta Q \cdot r_1 \sim 0.6$, indicating a correlation length for the intermediate-range order of $r_2 \sim 2\pi/\Delta Q \sim 10 r_1$, a remarkably long range in a material that has by definition no long-range order.

The FSDP is remarkably sensitive to variables such as temperature, pressure, and thermal treatment [1]. It may also be a strongly varying function of composition, for

example rising out of a smoothly varying background when silicon [2] or phosphorus [3] is added to selenium glass. The addition of a third component may have a reverse effect in attenuating or even suppressing the FSDP. Figure 1 shows the effect on the structure factor of g-GeSe₂ of adding 25 atom % silver [4], which attenuates the FSDP to about 25% of its original value. This result is supported by anomalous X-ray scattering on bulk glass of the same composition [5] and by glancing-angle X-ray diffraction from g-GeSe₂ films into which Ag has been photo-diffused [6].

The nature of the intermediate-range ordering in chalcogenide glasses, and of the structural elements giving rise to the FSDP, remain controversial. Several crystalline analogs of chalcogenide glasses, such as As₂Se₃ and GeSe₂, exhibit layered structures giving rise to Bragg reflections at $Q \sim 1 \text{ \AA}^{-1}$, and it has been proposed that the glasses are made up of interconnected sections of such layers [7]. On the other hand, it has been shown that the FSDP has a similar appearance in glasses which have dimensionalities different from each other, for example in

P_4Se_3 , $SiSe_2$, $GeSe_2$, and SiO_2 whose crystalline analogs have dimensionality 0, 1, 2, and 3 respectively [8,9]. Also, it is easy to show that a sharp peak at a low wave vector Q_1 can be produced by the random packing of structural units which have dimensions on the order of $2\pi/Q_1$ [1], and that a layered or two-dimensional structure is not required. Finally, the persistence of the FSDP into the liquid state argues against a crystalline analog for this feature.

Figure 2 shows the diffraction pattern in glassy and liquid $GeSe_2$ [10]. The position Q_1 and full-width at half maximum ΔQ_1 are essentially unchanged on going through the glass transition, the principal effect being a decrease in intensity of $\sim 10\%$ in going from low temperature to above the glass transition (having reached a maximum at an intermediate temperature in the glass). The width of the peak implies a correlation length $2\pi/\Delta Q_1$ of 27 Å in both glass and liquid. Pronounced FSDP's are also found in liquid semi-conductors consisting of equiatomic binary mixtures of alkali and polyvalent metals [11].

Information about the structural changes in GeSe₂ glass due to the addition of silver may be inferred from the radial distribution function obtained from Fourier transformation of the data in Fig. 1. In Fig. 3 we show the radial distribution functions for GeSe₂ and Ag₄Ge₃Se₉, the latter case being shown for two experimental situations, one with isotopic ¹⁰⁷Ag (middle curve) and the other with natural Ag (lower curve). From an intercomparison of these curves, it is clear that the first peak at 2.38 Å in all three samples is due to Ge-Se correlations, with the coordination number of Se about Ge essentially unchanged at the value of 3.9 ± 0.2 . This implies that the basic structural unit of Ge(Se_{1/2})₄ tetrahedra is appropriate for both systems.

The second peak at 2.69 Å in the Ag-doped glasses is ascribed to Ag-Se correlations, by analogy with crystalline β-Ag₂Se and β'-Ag₈GeSe₆, which have Ag-Se bonds in the range 2.6 - 2.8 Å. On this basis the coordination of Se about Ag is 3.1 ± 0.5 . This value is consistent with anomalous X-ray scattering results on GeSe₂ films with photodiffused Ag [6] and on bulk Ag₄Ge₃Se₉

glass [5], which yield values in the ranges 3.5 - 4.1 and 3.3 - 4.6, respectively. It is also reasonable by analogy with the crystalline compounds referred to above, where Ag is tetrahedrally and triangularly coordinated. From these results we infer that at least some of the Ag ions are modifying the GeSe_2 covalent network by bonding to the Se atoms, with the effect of breaking up the larger ring structures and hence reducing the intensity of the FSDP.

Dynamical probes such as Raman scattering and inelastic neutron scattering (INS) also provide information about the intermediate-range order. Figure 4 compares the density of states of g-GeSe_2 and $\text{g-Ag}_4\text{Ge}_3\text{Se}_9$. The breathing mode of the $(\text{GeSe}_{1/2})_4$ tetrahedra at 26 meV remains well defined in the Ag-doped glass, confirming the fact that these tetrahedra remain the basic structural unit. The population of the stretching modes at the high-energy end of the spectrum, 30-40 meV, is depleted in favor of a significantly increased population at lower energies, 15-22 meV, possibly due to breathing modes associated with 3- or 4-coordinated silver.

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Figure Captions

1. Structure factor $S(Q)$ for GeSe_2 (upper curve) and $\text{Ag}_4\text{Ge}_3\text{Se}_9$ (lower curve) glasses, measured at 10 K. The upper curve is displaced 1 unit.
2. Structure factor $S(Q)$ for GeSe_2 glass at 10 K and liquid at 1084 K. The upper curve is displaced 0.75 units.
3. Radial distribution functions $n(r)$ for GeSe_2 glass (upper curve) and $\text{Ag}_4\text{Ge}_3\text{Se}_9$ glass with isotopic ^{107}Ag (middle curve) and natural Ag (lower curve). Successive curves are displaced 5 units.
4. One-phonon effective density of states $G(E)$ for GeSe_2 and $\text{Ag}_4\text{Ge}_3\text{Se}_9$ glass at 13 K.