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Competing stoichiometric phases $b^{assic solid s}$ and the intermediate phase in Ge_xSe_{1-x} glasses

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Raman and calorimetric studies on $Ge_x Se_{1-x}$ glasses have provided evidence for the existence of the intermediate phase (IP) in chalcogenide and other glasses. *Ab initio* molecular dynamics models of these glasses are discussed, and an atomistic picture of the IP, based upon the models and available experiments, is presented. Analysis of our models reveals that

1 Introduction It is a rare privilege to contribute a paper to a volume that recalls the life of a pillar of our field. Prof. B. T. Kolomiets and his team in Leningrad were the pioneers of the modern understanding of the electronic properties of amorphous materials and glasses. It is easy now to think how "natural" our picture of the electronic structure of these materials is, but in the 1950s, it was the graceful formalism of Bloch, designed for periodic systems that dominated thinking. It was hardly a small leap from this picture to today's image of bands, tails, and gaps in the absence of translational order. The optical gap was seen at the time as a consequence of Bragg reflection, a concept absent in a disordered system. No less a figure than Sir Nevill Mott made a point of emphasizing the role of Prof. Kolomiets in his Nobel Lecture in 1977 [1]. Another great scientist, John Ziman, similarly emphasizes the significance of this problem [2]. So we are honored indeed to offer this paper in Kolomiets' memory.

 $Ge_x Se_{1-x}$ systems are excellent glass formers through a wide range of x. This has enabled the close study of composition-dependent effects. These materials are quite covalent, since Ge and Se have similar Pauling electronegativities. Based on the nature of the bonding in these materials, it is expected that coordination will follow Mott's 8-N rule [3], suggesting that Se should be two-



the IP in $Ge_x Se_{1-x}$ glasses may arise from the competition between amorphous $GeSe_2$ and a polymeric a-Se phase, which gives rise to the non-monotonic evolution of the network parameters through the IP window. A possible electronic signature of the IP in terms of the shift in the conduction edge in the IP range is also observed.

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coordinated and Ge four-coordinated. As x is varied, the network connectivity evolves from a vibrationally floppy network for x near zero, to a rigid tetrahedral glass (network of connected GeSe tetrahedra) for x = 0.33. The former has many low-energy vibrational modes because of the low coordination; the latter is a rigid network glass. It is clear that something interesting must happen as x is varied and the system moves in some fashion from one vibrational regime to the other.

These (and other) considerations led to the application of constraint theory [4–6], which put these concepts on a proper footing and with both simplicity and elegance revealed the nature of the floppy to rigid transition. The transition was predicted to occur when the average number of constraints per atom matches the number of degrees of freedom of the system, following logic treaceable to Maxwell [7] if not Lagrange [8]. Assuming that Mott's rule is satisfied, the floppy-rigid threshold was predicted at $\langle r \rangle = 2.4$, where $\langle r \rangle$ is the mean coordination of the network [6]. For Ge_xSe_{1-x}, the rigidity threshold is expected at x = 0.20.

The field took a very interesting turn when Boolchand and coworkers [9, 10] showed with Raman and calorimetric studies that a *double* rigidity transition occurs in a finite composition window $(0.20 \le x \le 0.25)$. The composition range between the two transitions was named the



intermediate phase (IP). The name originates in the idea that within the window, the system is sandwiched between a floppy and stressed-rigid phase. ¹²⁹I Mössbauer measurements reveal [11, 12] that the variation in the bonding arrangement of Ge and Se sites above $x \approx 0.10$ deviates from a chemically ordered continuous random network (CRN). The existence of the IP implies that some form of ordering or structural correlation is present.

Structural manifestations of the IP have been sought by researchers using diffraction techniques. Studies on the first sharp diffraction peak (FSDP) of the Ge–Se glasses indicated that the inverse peak position and peak area of the FSDP exhibit the telltale "flattening" in the IP composition range [13, 14], as also supported by anomalous X-ray scattering measurements [15]. However, recent work by Shatnawi et al. [16] did not confirm these observations. The latter authors also conducted high-energy X-ray diffraction and extended X-ray absorption fine structure analyses on Ge_xSe_{1-x} , but did not detect structural fingerprints of the IP in the first atomic shell [16].

Little is known of possible electronic features of the IP. Taniguchi et al. [17] have reported photoemission (PES) and inverse photoemission (IPES) studies on these glasses. They observed a splitting of the conduction band at the first rigidity threshold with the major peak shifting toward lower energies. Recently, Novita et al. [18] have observed a slight increase in the conductivity of solid electrolyte glasses $(AgI)_x(AgPO_3)_{1-x}$ in the IP range relative to stressed rigid phase. In the floppy range, the conductivity is found to increase linearly.

Thorpe et al. [19] advanced the first micropscopic concept of the IP, in which they invoked the notion of "self-organization". They argued that the inclusion of extra bonding constraints in a floppy network gives rise to a rigid but stress-free bonding network, before the network transforms into an over-constrained stressed-rigid phase. Later Micoulaut and Phillips [20] introduced the size increasing cluster approximation (SICA) and showed that a stress-free network can be thermodynamically stable. Chubynsky et al. [21] studied rigidity percolation in model systems and demonstrated that a form of IP was possible, and potentially generic near the rigidity percolation threshold. These theories have done much to reveal the underlying nature of the IP.

Recently, we have presented *ab initio* MD models of these glasses over a wide composition range including the IP window [22]. In these models, the evolution of structural parameters such as mean coordination, and concentrations of corner-sharing (CS) and edge-sharing (ES) tetrahedra show a non-monotonic behavior as a function of *x*. These parameters deviate from what one would expect for a chemically ordered CRN, and saturate in the composition range which coincides with the IP window. In this paper, we are led to conjecture that the IP in $\text{Ge}_x\text{Se}_{1-x}$ glasses is a consequence of phase separation and competition between the GeSe_2 phase and the polymeric Se phase. To a significant degree our work supports the picture of Micoulaut and Phillips [20],

inferences of Boolchand et al. [10], and suggests the nature of the self-organization described in Ref. [19].

Atomistic models of the IP were obtained using the approximate ab initio density functional code FIREBALL [23]. We generated a sequence of 500-atom models with x = 0.15, 0.18, 0.22, 0.23, and 0.25. Atoms were randomly placed in a cubic cell with fixed volume and experimental density, and equilibrated above the melting point at 1500 K for about 3.5 ps. Then they were cooled to 400 K over 4.5 ps, using velocity rescaling. Finally they were steepest-descent quenched to obtain relaxed conformations. The models reproduce the measured pair-correlation functions obtained from X-ray diffraction [22]. Models for x = 0.10, 0.20, and 0.33 are from Refs. [24, 25]. These models are reasonably large by the standards of density-functional MD. Besides glass models, we also generated a long (75 ps) molecular dynamics trajectory of liquid GeSe₃ composition consisting of 96 atoms at 1200 K using the plane-wave ab initio code VASP [26] (Vienna ab initio simulation package) at constant volume and temperature.

Structural analysis of the models reveals interesting features in the IP range. Topological parameters like the concentration of CS and ES tetrahedra and number of rings show a flattening or saturation in the IP window. As the building blocks of the Ge–Se network are $Ge(Se_{1/2})_4$ tetrahedra and Se chains, the evolution of the network from a-Se to $GeSe_2$ glass can be described in terms of three types of Se neighbors Ge_mSe_{2-m} , where m = 0, 1, and 2. We have analyzed our models in terms of the SICA, and find that there is a maximum in the concentration of m = 1 units near the IP (Fig. 8 of Ref. [22]), and that the tendency to ordering (non-stochastic network evolution) is significant for m = 1 and 2.

2 Competing phases hypothesis The clustering of Ge tetrahedra can be inferred from the temperaturedependence of the A₁ tetrahedral breathing Raman mode in liquids, which shows a sudden increase in intensity, suggesting the nucleation of Ge tetrahedra [27]. To study the formation of clusters of tetrahedra in liquid phase, we analyzed a 75 ps simulated trajectory x = 0.25 at 1200 K. The Ge–Se–Ge configuration (m = 1 unit) can be understood to be the building block [28] of $GeSe_2$ phase, so we quantify the GeSe₂ phase (region A) by calculating the concentration of these units in the system. The clustering of Ge tetrahedra can roughly be quantified by the average number of second neighbor Ge sites to each Ge atoms (n_{Ge-Ge}) in region A. For the pure GeSe₂ phase, the quantity $n_{\text{Ge-Ge}}$ assumes a value of about 4.0 depending upon the concentration of ES tetrahedra. Fig. 1a shows the correlation between the fraction of m = 1 unit and $n_{\text{Ge-Ge}}$. Such nucleation is energetically favorable (Fig. 1b). The cohesive energy of the system tends to increase in the fraction of m = 1 unit. This suggests that even in the liquid phase, there is a propensity to form GeSe tetrahedra that could yield phase separation near the glass transition.



Figure 1 (online color at: www.pss-b.com) (a) The quantity $n_{\text{Ge}-\text{Ge}}$ (see text) plotted against the fraction of m = 1 (Ge–Se–Ge) units. (b) Variation of the cohesive energy of the system with the increase in m = 1 unit. Straight lines are the linear fit to the data. All the quantities are extracted from 75 ps trajectory of liquid phase of GeSe₃ at 1200 K.

3 Network evolution with composition and selforganization Returning to the glass, we note that our models could be understood as consisting of three regions. Region A (as above) consists of clusters of Ge–Se tetrahedra (CS/ES tetrahedral units), region B consists of short Se_n chains, where n = 2-5 are the number of Se in the chain, joining the Ge sites and region C consisting of the rest of Se background which represent the a-Se phase. Figure 2 shows the variation of Ge and Se sites in the three regions. Rapid increase of the Ge content in region A (Fig. 2a) shows the tendency of Ge tetrahedra to form clusters rather than dispersing uniformly in the network. The Ge content in region A shows saturation in the IP range after rapid increase in the Se rich compositions. The saturation suggests that the



Figure 2 (online color at: www.pss-b.com) (a) Variation of concentration of Ge sites in region A. (b) The variation of Se sites in the three regions. Region A, GeSe₂ fragments; B, short Se chains; C, long Se chains (see text). The dotted lines represent the IP range [10].



Figure 3 (online color at: www.pss-b.com) (a) The concentration of short Se_n (n = 2-5) chains plotted against Ge content. (b) Variation of $n_{\text{Ge-Ge}}$ (see the text) with Ge content. The apparent saturation between x = 0.20 and 0.23 reflects the "delay" in the growth of the clusters of Ge tetrahedra.

clustering of Ge tetrahedra does not increase monotonically through the IP window.

Se sites in region B (short Se chains) reach a maximum concentration inside the IP window (Fig. 2b). The concentration of short Se_n chains is shown in Fig. 3a. Variation of Se sites in the three regions suggests that in the IP window most of the background a-Se phase is consumed by regions A and B. Above the IP range the concentration of Se sites in region A increases at the cost of region B.

The compositions in the IP range are characterized by clusters of Ge tetrahedra and short Se_n chains. To detail the growth of region A with the increase in the Ge content, we plot $n_{\text{Ge-Ge}}$ versus the Ge concentration x (Fig. 3b). The increase in $n_{\text{Ge-Ge}}$ indicates the expansion of region A. As suggested by Fig. 2a, n_{Ge-Ge} saturates in the IP window. This shows that in the IP range, the system tends to resist the percolation of GeSe₂, leading to the apparent "flattening" in the evolution of structural parameters like CS/ES tetrahedra. Such a behavior suggests and identifies self-organization in the connectivity of the network [19]. The evolution of the topology of regions A and B is shown in Fig. 4. Note the obviously non-random nature of the positions of the GeSe tetrahedra, especially the clear tendency for the tetrahedra to cluster, even for small x. The short Se chains appear at the boundaries of GeSe₂ clusters. In the IP window, between 0.20 and 0.23, the density of region A seems to saturate, as suggested by Fig. 3b until it covers the whole cell at x = 0.33.

4 Electronic properties and the intermediate phase Earlier PES and IPES studies [17] on $Ge_x Se_{1-x}$ glasses reveal a shift in the conduction band tail at x = 0.2 in the electronic density of states, while no apparent shift is observed for the valence band tail. Our models also show



1852



Figure 4 (online color at: www.pss-b.com) Two-dimensional projection of the spatial distribution of "region A" (GeSe₂ CS/ES tetrahedra) and B (short Se chains) is shown for different compositions. Red and blue sites represent atoms in regions A and B, respectively. The role of short Se chains as a barrier between GeSe₂ clusters is seen for compositions in the IP window. The black background is polymeric Se. Note the clustering (non-randomness) of the GeSe tetrahedra, even for low Ge concentration.



Figure 5 The shift in the average conduction edge energy $\langle E_c \rangle$ with compositions "*x*."

the shift in the tail states above Fermi level into the band gap in the IP window, with no considerable shift in the valence tail states [22]. Looking for the possible electronic signature of the IP, we obtained the shift in the conduction band edge (Fig. 5) by calculating the average conduction edge energy $\langle E_c \rangle = \int_{cb} \varepsilon \rho(\varepsilon) d\varepsilon$, where $\rho(\varepsilon)$ is the electronic density of states and cb specifies a quadrature range starting at the lowest unoccupied molecular orbital edge, extending 2.0 eV into the conduction band [29]. The flattening of the conduction edge energy in the IP range is apparent. It would be desirable to create an ensemble of models at each composition to enable the inclusion of "error bars" on the theory. This substantial calculation will shortly be undertaken (F. Inam, B. Cai, and D. A. Drabold, unpublished data).

Further insight into the band tails is obtained by projecting the eigenstates in the tails onto the atomic configurations. Figure 6a shows the concentration of atomic sites contributing to the valence and conduction localized states, which lie in the three regions. In the IP range, tail states are mostly localized in region B, which is understandable as this region appears around clusters of tetrahedra due to crosslinking and thus becomes strained as the size of the clusters and the content of this region increases to a maximum in the IP window. Figure 6b shows the average lengths of n = 1 and 2 chains, the strain is apparent in terms of the "bending" of these chains. Since in the IP range the band tail states reside mainly on short Se chains (Fig. 6a), the IP might also be sensitive to the light illuminations as micro-Raman studies suggests [30]. In order to see the effect of the bending of these chains on the electronic spectrum, we studied a toy model consisting of these two chains attached to each other [31]. The decrease in the lengths of these chains show a clear downward shift in the eigenvalues above the Fermi level compared to the relaxed system, which suggests that the antibonding states of

1853



Figure 6 (online color at: www.pss-b.com) (a) Concentration of sites representing the three regions (A, Ge–Se tetrahedra; B, short Se chains; C, long Se chains, see text), which contribute to ten localized states at the valence and conduction tails for different compositions (see text). (b) Variation of the average lengths of n = 1 and 2 chains with the Ge content. Vertical dotted lines indicate the experimental width of the IP.

this system are more sensitive to the bond angles centered on Se atoms.

5 Summary Our work suggests that the IP in the GeSe system is associated with competition between two phases (a-Se and a-GeSe₂). The system evolves in a non-random way as x is varied: the Ge tends to position itself as part of a growing tetrahedral region. We conjecture that the self-organization [19] is this tendency to phase separate. We observe an indication of an electronic signature of the IP. Our work has limitations: We possess only one set of models, hence we cannot estimate the error bars on the results of the simulation. However, it should also be recognized that these calculations are the first based on accurate interatomic interactions, and the tendency to self-organization via phase separation emerges unambiguously from a series of models created from random initial configurations.

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