Mechanical and Chemical Thresholds in IV-VI Chalcogenide Glasses

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It has been possible to identify two critical compositions in the IV-VI chalcogenide glassy system Ge_xSe_{100-x} by the anomalous variations of the high-pressure electrical resistivity behavior. The first critical composition, the chemical threshold, refers to the stoichiometric composition. The second critical composition, identified recently as the mechanical percolation threshold, is connected with the structural rigidity of the material.

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The current interest in chalcogenide glassy semiconductors is the anomalous behavior in physical properties of these materials exhibited at certain specific compositions. Unusual variations in physical properties may be expected for a composition at which a stoichiometric crystalline compound occurs. The critical composition corresponding to the stoichiometric crystalline compound is commonly known as the chemical threshold of the glass. The chemical threshold occurs in the Ge_xSe_{100-x} system at $x=33$, in Ge_xTe_{100-x} at $x=50$, and in As_xTe_{100-x} at $x=40$. Anomalous variations in many different physical properties have been observed at these compositions.[1-3]

The recent studies in various chalcogenide glassy systems like Ge_xSe_{100-x}, etc., reveal the possibility of a second critical composition known as the mechanical threshold, connected with the structural rigidity of the material.[4-9] In any network glassy system, the mean coordination number $\langle m \rangle$ changes with the composition. For a $A_x(Z_1)B_{100-x}(Z_2)$ glassy system, $\langle m \rangle$ is given by $\langle m \rangle = [Z_1(x)+Z_2(100-x)]/100$, where Z_1 and Z_2 are the coordination numbers of the A- and B-type atoms, respectively. It had been first realized by Phillips and Thorp[10-12] that the glassy networks having a mean coordination number $\langle m \rangle$ less than a critical value $\langle m_c \rangle$ are under coordinated. These under-coordinated networks are elastically floppy, as they are easily deformed under a shearing force. On the other hand, over-coordinated (or over-constrained) networks, corresponding to $\langle m \rangle > \langle m_c \rangle$ are visualized to be elastically rigid because such networks resist a change in shape under a shearing force. These ideas of Phillips and Thorpe[10-12] have further led to the suggestion that at the critical coordination $\langle m_c \rangle$ (corresponding to the critical composition x_c), a glassy network constrained by the bond bending and stretching forces sits at a mechanical critical point in which rigid regions are thought to percolate in a mean-field sense. Consequently, at x_c, the mechanical threshold, one may expect anomalous variations in physical properties. The mechanical threshold, determined only by the coordination numbers of the constituents, occurs at $x=20$ for a IV_xVI_{100-x} glassy system and at $x=40$ for a V_xVI_{100-x} glassy system.

Among the well-known network glassy systems such as Ge_xSe_{100-x}, Ge_xTe_{100-x}, Si_xTe_{100-x}, and As_xTe_{100-x}, the Ge_xSe_{100-x} system is the most suitable candidate for probing the mechanical and chemical thresholds. The very wide composition range of bulk glass formation in the Ge_xSe_{100-x} system ($0 \leq x \leq 45$) enables us to investigate both of the critical compositions. In Ge_xTe_{100-x} and Si_xTe_{100-x} systems, the glass-forming range ($10 \leq x \leq 28$) allows us to study only the mechanical threshold. In a V_xVI_{100-x} glassy system like As_xTe_{100-x}, the chemical and mechanical thresholds coincide (at $x=40$), thereby disallowing an independent probing of these compositions.

Bulk Ge_xSe_{100-x} glasses (or thirteen compositions in the range $0 \leq x \leq 45$) are prepared by the melt-quenching technique. Appropriate amounts of the con-

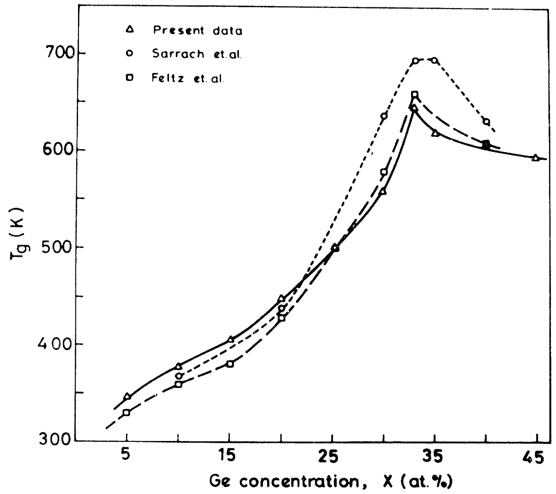

FIG. 1. The variation of glass transition temperature with Ge content for Ge_xSe_{100-x} glasses. The data from Sarrach, de Neufville, and Howarth (Ref. 14) and Feltz, Haust, and Blayer (Ref. 15) are given for comparison.

stituents (99.99% pure) are sealed in fused silica ampoules which are initially evacuated to 10^{-6} Torr and then filled with argon gas at a pressure of about 5 psi. The sealed ampoules are kept in a furnace at a temperature of 1000 K for about 48 h. The ampoules containing the molten material are also rotated at 10 rpm to homogenize the melt. The melt is subsequently quenched in an ice-water mixture. The glassy nature of the samples is confirmed by x-ray diffraction and differential scanning calorimetry. The electrical resistivity measurements at high pressures are carried out in a Bridgman anvil system up to a pressure of 14 GPa, as described elsewhere.[13]

The variation of the glass transition temperature T_g with composition x for Ge_xSe_{100-x} glasses is shown in Fig. 1, along with the data from the earlier work available in the literature.[14,15] The magnitude of T_g and its variation with x are consistent with the earlier work.

The variation of electrical resistivity with pressure for representative Ge_xSe_{100-x} glasses ($Ge_{10}Se_{90}$, $Ge_{15}Se_{85}$, and $Ge_{20}Se_{80}$) is shown in Fig. 2. The behavior of Ge_xSe_{100-x} glasses with $x < 10$ is similar to that of $Ge_{10}Se_{90}$ glass and the behavior of glasses with $x > 15$ is similar to that of $Ge_{15}Se_{85}$ glass. The electrical resistivity of glasses with $x \leq 10$ decreases with pressure up to a certain transition pressure P_T. At P_T, the samples exhibit a sharp, discontinuous fall in the resistivity, by about 5 orders of magnitude. The resistivity remains a constant after the transition. The magnitude of the fall in the resistivity during the transition and the value of the resistivity after the transition are comparable to those observed in other chalcogenide glassy semiconductors.[6,7,16]

The dc conductivity measurements as a function of temperature, carried out at different pressures before and after the transition, indicate that the transition is from a semiconductor to a metal. The x-ray diffraction studies on the samples recovered from the pressure cell, from pressures above P_T, show that the samples crystallize as they become metallic.

Ge_xSe_{100-x} glasses with $x \geq 15$ show an initial positive pressure coefficient of resistivity. This is followed by a continuous decrease and a sharp, discontinuous glassy semiconductor-crystalline metal transition (Fig. 2). The high-pressure crystalline phases of Ge_xSe_{100-x} glasses are complex and they do not correspond to the equilibrium crystalline compound $GeSe_2$ of the system. This aspect will be described elsewhere.

An interesting outcome of the present experiments is the variation of the transition pressure P_T with composition [Fig. 3(a)]. P_T as a function of x shows a local maximum at the composition $x=20$ (the mechanical threshold) and a minimum at the composition $x=33$ (the chemical threshold). The variation of the conductivity activation energy ΔE with composition shows a distinct slope change at $x=20$ and a well defined maximum at $x=33$ [Fig. 3(b)]. The local maximization of P_T at the mechanical threshold is observed in the related Si_xTe_{100-x} [6] and Ge_xTe_{100-x} [7] glasses also. Further, earlier studies on many different physical properties such

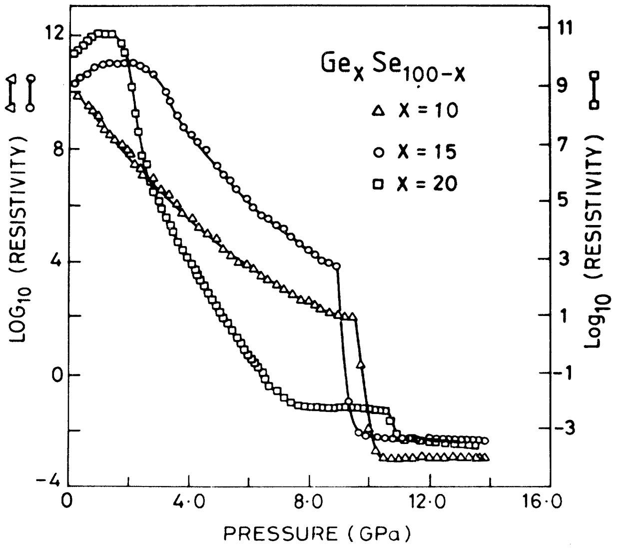

FIG. 2. The variation of electrical resistivity with pressure for $Ge_{10}Se_{90}$, $Ge_{15}Se_{85}$, and $Ge_{20}Se_{80}$ glasses.

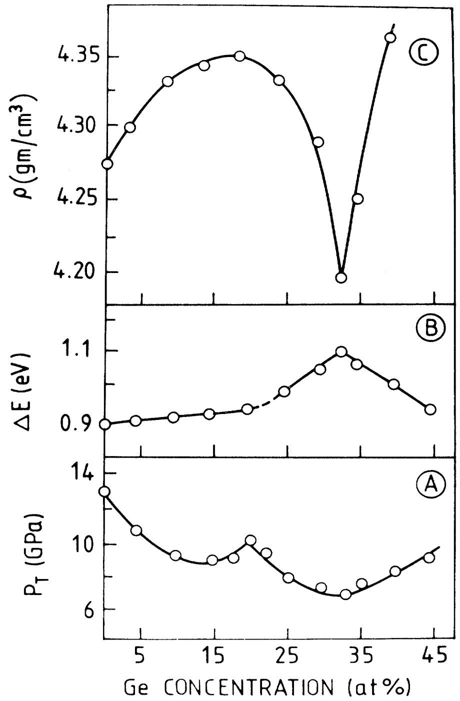

FIG. 3. (a) The composition dependence of glassy semiconductor-crystalline metal-transition pressure (P_T), (b) conductivity activation energy (ΔE), and (c) density (ρ) of Ge_xSe_{100-x} glasses. The density data are from Ota *et al.* (Ref. 1).

as density,[1,17] coefficient of linear expansion,[1] refractive index,[2,3] dielectric constant,[15] mole polarizability,[15] acoustic attenuation,[18] Mössbauer site intensities,[4] etc., also show anomalous variations at the mechanical and the chemical critical compositions. For example, the density of Ge_xSe_{100-x} glasses, measured by Ota *et al.*[1] and shown in Fig. 3(c), exhibits a maximum at $x=20$ and a minimum at $x=33$ consistent with the criticality of these compositions.

The results of the present high-pressure investigations tie up well with the results of the Mössbauer experiments on Ge_xSe_{100-x} glasses by Bresser, Boolchand, and Suranyi.[4] These Mössbauer experiments reveal that a simple linking chain model is valid for Ge_xSe_{100-x} glasses for the compositions $x<15$ only. When the composition x is increased beyond $x=15$, rigid, tetrahedral molecular clusters are nucleated in the glass.[4] As seen from Fig. 2, the addition of Ge to glassy Se only decreases the transition pressure P_T and does not change the overall pressure response of the material for the composition $0 \le x < 15$. At and above $x=15$, Ge_xSe_{100-x} glasses exhibit an initial positive pressure coefficient of resistivity (Fig. 2), which is a very typical behavior of glasses with tetrahedral local structures.[19] This observation supports the proposal of Bresser, Boolchand, and Suranyi[4] that tetrahedral molecular fragments are nucleated in the glass around the $x=15$ composition. It is also interesting to note that the variation of P_T with x also shows a reversal in its trend above $x=15$ [Fig. 3(a)].

As the composition is increased beyond $x=15$, the rigid, tetrahedral $Ge(Se_{1/2})_4$ molecular units, begin to coalesce progressively to give rise to a layerlike molecular fragment.[4,8] The composition range $15<x<20$ physically corresponds to the interval between the homogeneous nucleation and the subsequent growth of the rigid fragments in the glass. At $x=20$, the rigid molecular units contact each other or percolate in the material.[4] The percolation threshold is exhibited in the present investigations by a local maximum in P_T and a slope change in ΔE [Figs. 3(a) and 3(b)].

The chemical effects start dominating beyond $x=20$ with the transition pressure exhibiting a decrease and the activation energy a rapid increase with composition [Figs. 3(a) and 3(b)]. The composition $x=33$ gives rise to the second critical composition (chemical threshold), which is connected with the chemical stoichiometry of the glass. The transition pressure exhibits a minimum at the chemical threshold and the activation energy a maximum [Figs. 3(a) and 3(b)]. The reversal of trend in both P_T and ΔE at $x=33$ indicates that the local structure of the glass changes again at this composition.

However, the above explanations cannot explain quantitatively the specific features such as the maximum in P_T at $x=20$ and a minimum at $x=33$. They appear to be the result of a bulk compaction and change in density superposed on local structural effects of the type observed by Bresser, Boolchand, and Suranyi.[4] Crystallization of the glass involving large-scale rearrangement of the atoms appears to require higher pressures in the glasses with special local structure and bonding, as also seen in Si_xTe_{100-x} [6] and Ge_xTe_{100-x} [7] glasses.

In conclusion, the present high-pressure measurements provide an experimental evidence for the existence of two critical compositions in the Ge_xSe_{100-x} glassy system at $x=20$ and $x=33$. The threshold behavior at $x=20$ is connected with the rigidity percolation proposed by Phillips and Thorpe. The $x=33$ composition is associated with the stoichiometric composition.

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