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Evidence for a critical composition in group-IV–VI chalcogenide glasses

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Experimental evidence for an ideal-glass composition in IV–VI chalcogenide systems is obtained from high-pressure–low-temperature studies of Si-Te glasses. The electrical resistivity of bulk, melt-quenched Si_xTe_{100-x} glasses ($10 \leq x \leq 28$) has been measured up to a pressure of 8 GPa and down to 77 K. All the glasses undergo sharp, discontinuous glassy-semiconductor–crystalline-metal transitions. The properties such as the transition pressure, the room-temperature atmospheric-pressure resistivity, and the activation energy for electrical conduction at different pressures show unusual variations at a composition $x = 20$. The anomalous variations in properties observed at $x = 20$ may be connected with the ideality of the glass occurring at this composition.

Silicon and germanium chalcogenide glasses possess unique physical properties. In particular, anomalous variations in the physical properties of $A_x^{\mathrm{IV}}B_{100-x}^{\mathrm{VI}}$ glasses at a composition $x = 20$ is a feature which concerns us most. Experimental investigations on Ge_xSe_{100-x} glasses reveal that the density as a function of composition shows a maximum at $x = 20$, and the properties like the refractive index, coefficient of linear expansion, optical band gap, dielectric constant, mole polarizability, specific refraction, etc., show a slope change at this composition.[1-5] Raman scattering studies on Ge_xSe_{100-x} glasses show that a discontinuity in the Se_n A_1 band, associated with the stretching of Se chains, occurs at a composition $x = 20$.[6] The acoustic attenuation of $Ge_{20}Se_{80}$ and $Ge_{20}S_{80}$ glasses also exhibits an unusual variation with temperature. Infrared and Raman studies on Ge_xS_{100-x} glasses point out that the S_8 ring fraction sharply increases for $x < 20$, implying that on the average only two S atoms are incorporated between two Ge sites of the network.[7] Recent studies on Ge_xSe_{100-x} glasses show that the Mössbauer site-intensity ratios studied as a function of x exhibit a threshold behavior around $x = 20$.

In the Ge_xTe_{100-x} glassy system, the optical band gap as a function of composition shows a maximum around $x = 20$.[8] ESR studies of this system indicate that glasses with $x \leq 20$ exhibit an ESR signal, while glasses with $x > 20$ do not exhibit any such signal.[9] The thermal crystallization of Ge_xTe_{100-x} glasses shows a marked change in behavior at 20 at.% Ge. Ge_xTe_{100-x} glasses with $x \leq 20$ undergo a double glass transition and double-stage crystallization. On the other hand, glasses with $x > 20$ show only a single glass transition and single-stage crystallization.[10,11] High-pressure studies on Ge_xTe_{100-x} glasses indicate that all glasses in the system undergo pressure-induced glassy-semiconductor to crystalline-metal transitions. The variations of the transition pressure, the room-temperature atmospheric-pressure resistivity, the activation energy for electrical conduction, etc. with composition show anomalies at $x = 20$.[12,13]

Silicon chalcogenide glasses also exhibit the 20% anomaly. The activation energy for electrical conduction in Si_xTe_{100-x} glasses goes through a maximum at 20 at.% Si.[14] The molar volume of Si_xSe_{100-x} glasses shows a minimum at this composition.[15] The thermal crystallization of Si_xTe_{100-x} glasses is similar to that of Ge_xTe_{100-x} glasses. Si_xTe_{100-x} glasses with $x \leq 20$ exhibit a double glass transition and double-stage crystallization, whereas the glasses with $x > 20$ show only single-stage behavior.[16] In this context, it is interesting to study the electrical properties of Si_xTe_{100-x} glasses as a function of composition as well as pressure and temperature. Such studies throw light on the structure and electronic properties of these glasses.[17]

Bulk Si_xTe_{100-x} glasses ($10 \leq x \leq 28$) have been prepared by the conventional melt-quenching technique.[16] Electrical resistivity measurements at pressures up to 8 GPa and temperatures down to 77 K were carried out in a Bridgman anvil system, using steatite as the pressure-transmitting medium. The details of the high-pressure anvil assembly and the pressure-calibration techniques have been reported earlier.[18] A four-probe method was employed to measure the electrical resistivity in the high-pressure anvils. The electrical resistivity at ambient conditions was measured by the Van der Pauw technique.[19]

Samples were also recovered from the pressure cell for structural studies. This was accomplished by using NaCl as the pressure-transmitting medium and dissolving it in distilled water. The structural studies were performed in a Philips x-ray diffractometer with Cu $K\alpha$ radiation.

The variation with pressure of the electrical resistivity of bulk Si_xTe_{100-x} glasses ($10 \leq x \leq 28$) is shown in Fig. 1, indicating that the electrical resistivity of Si_xTe_{100-x}

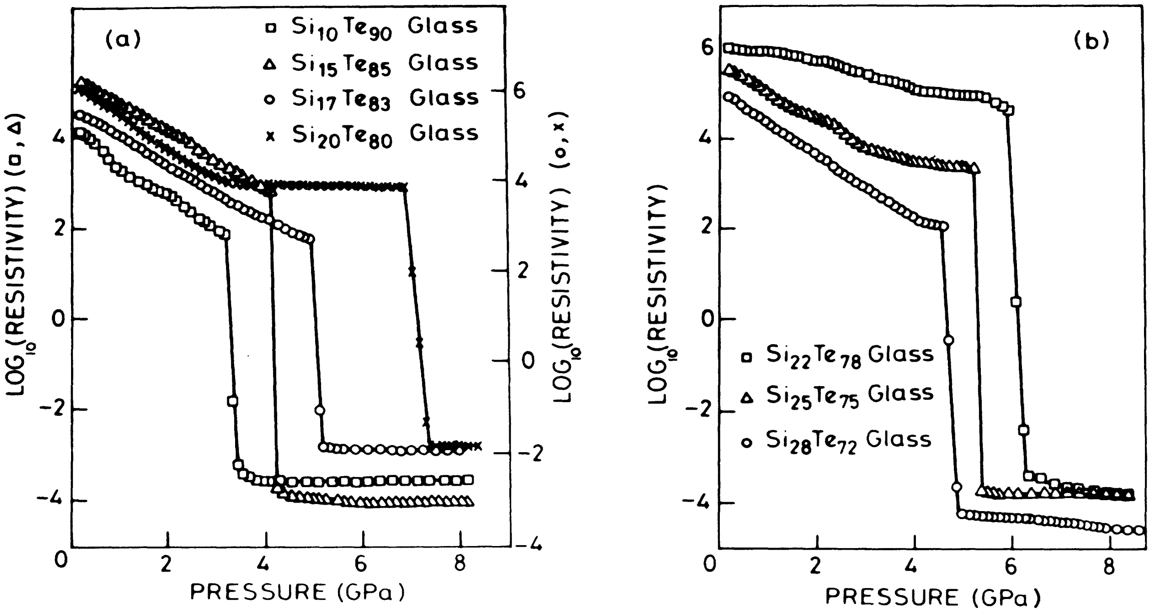


FIG. 1. The variation of electrical resistivity with pressure for Si_xTe_{100-x} glasses. (a) $x=10$, 15, 17, and 20. (b) $x=22$, 25, and 28.

glasses decreases with increasing pressure up to a certain pressure P_T. At P_T, there is a sharp, discontinuous fall in the resistivity by about six orders of magnitude, indicating a semiconductor-to-metal transition. The electrical resistivity of the samples remains constant after the transition.

The variation of the transition pressure P_T and the logarithm of the room-temperature atmospheric-pressure resistivity (ρ_0) of Si_xTe_{100-x} glass as a function of composition is shown in Fig. 2. It is seen from Fig. 2 that P_T and $\log_{10}(\rho_0)$ as a function of composition show well-defined maxima at $x=20$.

The temperature dependence of the dc conductivity of Si_xTe_{100-x} glasses at different pressures below and above P_T has been measured. The electrical conductivity of all the Si_xTe_{100-x} glasses below P_T is thermally activated, with a single activation energy ΔE in the temperature range of investigation. The composition dependence of the activation energy ΔE at different pressures below P_T is shown in Fig. 3. It is interesting to note that ΔE as a function of x at various pressures shows a maximum at $x=20$.

X-ray diffraction studies of Si_xTe_{100-x} samples recovered from high pressures above P_T indicate that the glasses crystallize during the semiconductor-metal transition. The high-pressure crystalline phases all have hexag-

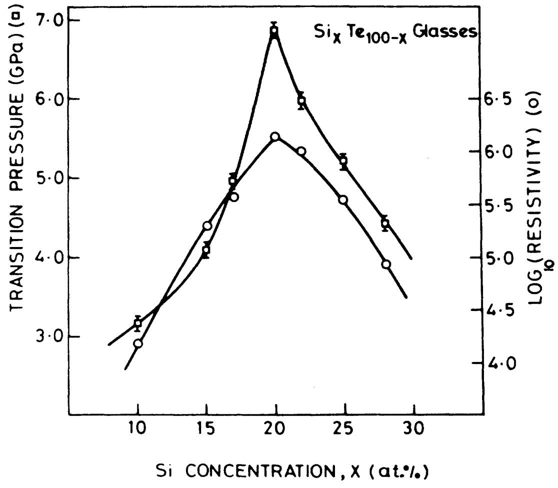


FIG. 2. The variation of transition pressure and room-temperature atmospheric-pressure resistivity with composition for Si_xTe_{100-x} glasses.

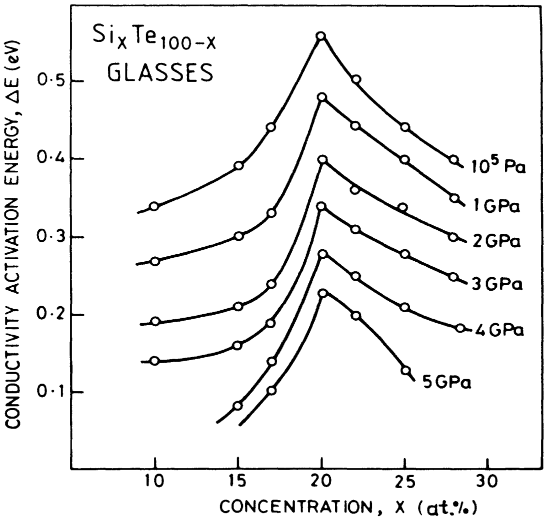


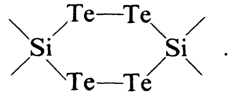
FIG. 3. The composition dependence of the activation energy for electrical conduction at different pressures.

onal structures. The lattice parameters are as follows: $c = 4.74$ Å and $a = 6.42$ Å for $10 \leq x \leq 17$; $c = 6.0$ Å and $a = 4.0$ Å for $x = 20$; $c = 11.58$ Å and $a = 6.06$ Å for $22 \leq x \leq 28$.

The present investigations of Si-Te glasses and the earlier observations[1–16,20,21] suggest that the $x = 20$ glass of the $A_x^{\rm IV}B_{100-x}^{\rm VI}$ chalcogenide glassy systems should possess salient structural features. Substantial progress has been made recently in interpreting the $x = 20$ anomaly on the basis of a constraint model.[20,22] According to the Phillips constraint theory, the $x = 20$ glass of the $A_x^{\rm IV}B_{100-x}^{\rm VI}$ system is an ideal glass in which the number of operative constraints equals the number of degrees of freedom. Glasses with $x < 20$ are undercrosslinked and the glasses with $x > 20$ are overconstrained. The constraint theory has been further extended by Thorpe, with the idea of rigidity percolation.[23–25] According to Thorpe, in the range of glass-forming compositions, the system should contain rigid and floppy regions. The $x = 20$ composition of the $A_x^{\rm IV}B_{100-x}^{\rm VI}$ systems, corresponding to an average coordination $Z = 2.4 = Z_c$, is a percolation threshold at which the transition from a floppy polymeric glass to a rigid amorphous solid takes place. He and Thorpe[26] have further predicted that the elastic moduli of covalent glasses are zero for $Z < Z_c$ and increase with Z as $a(Z - Z_c)^{1.5}$ for $2.4 \leq x \leq 4$. The threshold behavior in physical properties of covalent glasses, occurring at $Z = 2.4$, can be connected with a percolation transition. However, the experimental evidence in terms of a threshold behavior of the elastic constants at $Z_c = 2.4$, favoring the percolation theory, is not clear. Halfpap and Lindsay[27] have found evidence in favor of the percolation theory from the measurement of elastic constants C_{44} and C_{11} of Ge-As-Se glasses. These elastic constants have a finite, constant value for $Z < Z_c$ and increase abruptly around $Z = 2.4$. The finite value of the elastic constants below Z_c has been attributed to the contribution of noncentral forces. The very recent experiments of Tanaka,[28] on the other hand, contradict the predictions of the percolation theory. According to Tanaka, the bulk modulus of covalent glasses has a finite constant value of about 10 GPa for values of $Z \leq 2.7$. The abrupt increase in the bulk modulus occurs only around $Z = 2.7$. There is no threshold behavior exhibited at $Z = 2.4$. Hence it is unclear at the present moment whether the percolation transition is the origin of threshold behavior at $Z = 2.4$ or not.

Our measurements have mainly been of electrical properties, and our observation that the activation energy for electrical conduction and the low-high conductivity transition pressures have a maximum at $x = 20$, cannot be simply interpreted in terms of a rigidity percolation model. One could naively argue that for $x < x_c$, the medium being floppy, localized electronic states will be shallower and the activation energy smaller, whereas in the rigid regime ($x > x_c$), deeper trap states can form so that the activation energy should rise. This is not what we observed. The enhanced stability of electronic defects (larger binding or activation energy) at $x = 20$ is consistent with the maximum density of stable structural units such as that suggested by Feltz and Pfaff[29] for $x = 20$.

The present results are more readily interpreted on the basis of the local network structures, of the type proposed by Feltz and Pfaff[29] who suggest the presence of $\mathrm{Ge(Se_2)_2}$ structural units in the $\mathrm{Ge_xSe_{100-x}}$ glasses. In the present case, ditelluride bonds are possible at $x = 20$ giving the stable structural units



Such a network being stable, one readily understands the maxima in Figs. 2 and 3. A higher pressure is required to drive this relatively stable glassy network into a crystalline form. The reduction in the number of unsatisfied bonds leads to a maxima in the resistivity. There will also be an opening of the activation gap as obtained in Fig. 3. Moreover, the networks are likely to be compact without too much entanglement among the different network regions. This would explain a minimum in T_g as observed at $x = 20$.[16] A specified search for spectroscopic or other local probe evidence for the ditelluride bridges is suggested as a profitable route to study the problem further.

Note added. It has been recently pointed out to us[30] that, as compared to the glasses prepared under high vacuum conditions, the glasses prepared in an atmosphere of argon gas containing traces of oxygen and other impurities may show slight differences. The impurities may stabilize the glass slightly, leading to minor differences in the values of the parameters connected with the electrical transport, glass transition temperature, crystallization temperature, etc. This has to be investigated.

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