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Electrical resistivity behaviour of Ag–Ge–Te glasses under pressure at different temperatures: the influence of bonding and topological thresholds

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Abstract. The electrical resistivity of melt quenched Ge–Te glasses containing Ag has been studied as a function of pressure at different temperatures in a Bridgman anvil set-up. The samples are found to exhibit a continuous decrease in electrical resistivity with pressure and metallization around 5 GPa. The pressure dependence of conductivity activation energy (ΔE) also confirms the continuous metallization of $\text{Ag}_x\text{Ge}_{15}\text{Te}_{85-x}$ glasses. The variation of ΔE with composition at different pressures has been found to exhibit anomalies at $x = 5$ and $x = 18.5$. A plausible explanation based on the bonding considerations, topological thresholds and density variations with composition has been provided to understand the conductivity activation energy of Ag–Ge–Te and other chalcogenide glasses.

1. Introduction

Bulk Ge–Te [1] glasses exhibit a sharp, discontinuous glassy semiconductor to crystalline metal transition at high pressures around 5 GPa. Further, the composition dependence of parameters such as transition pressure, conductivity activation energy at different pressures etc of Ge–Te glasses are found to show anomalies at compositions at which topological effects take place.

Metallic additives such as Cu, Ag etc enter the structural network of Ge–Te glasses in fourfold co-ordination [2–4]. Consequently, the network becomes rigid and strengthened by the addition of these atoms [2]. The incorporation of the metallic impurities also leads to significant changes in thermal and electrical properties of Ge–Te glasses [2]. The addition of Cu, for example, is found to change the discontinuous metallization of Ge–Te glasses to continuous metallization [5]. Cu–Ge–Te samples are also found to show an anomaly in ΔE at different pressures, at the topological threshold [5]. It is further suggested that the similar atomic radii, electronegativity and coordination of Ge and Cu results in random substitution of Ge by Cu in Ge–Te glasses [6].

The addition of Ag, like the addition of Cu, can have a considerable effect on the properties of glassy germanium tellurides. As the atomic radius and electronegativity of Ag are very different from those of Ge, the addition of Ag should have a higher influence on the structural, thermal and electrical properties of Ge–Te glasses compared to Cu. In the present work, resistivity measurements are carried out under pressure at different temperatures, on Ag–Ge–Te

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glasses, in order to understand the effect of silver on the high pressure behaviour of germanium telluride glasses. The composition dependence conductivity activation energy of Ag–Ge–Te glasses has also been studied.

2. Experiment

$\text{Ag}_x\text{Ge}_{15}\text{Te}_{85-x}$ glasses ($2.5 \leq x \leq 21.5$) have been prepared by melt quenching method. Appropriate amounts of starting materials (approximately 1.2 g) are transferred into flattened quartz ampoules of 6 mm diameter. The ampoules are sealed under a vacuum of 10^{-5} Torr and are heated to 1000°C in a horizontal rotary furnace for 48 hours. Ampoules containing the melt are rotated continuously to ensure the homogeneity of the melt and are subsequently quenched in NaOH+ice–water mixture. The samples are recovered by breaking the ampoules. The amorphous nature of the samples is confirmed by x-ray diffraction.

The room temperature electrical resistivity measurements at high pressures have been undertaken in a Bridgman anvil high pressure set-up [7], using pyrophyllite as the gasket material and steatite as the quasi-hydrostatic pressure transmitting medium. A two probe technique is used to measure the resistance of the samples placed in between the anvils. The variation of electrical resistivity with temperature (down to 77 K) at different pressures has been studied in a Fujii–Nagano [8] type continuous pressure changing system. The pressure is slowly increased at room temperature and locked at a desired pressure. Then the pressure cell is cooled in a controlled manner down to liquid nitrogen temperature using a bath type cryostat. The temperature of the sample is monitored by a T-type thermocouple. For generating high temperature a heater, around the anvil is used and the temperature of the sample is measured by a K-type thermocouple.

X-ray diffraction studies have been performed using a Phillips powder diffractometer with Cu target ($\lambda = 1.5418 \text{ \AA}$) on samples recovered from the anvil after releasing the pressure. The recovery of samples is accomplished using NaCl as the pressure transmitting medium and dissolving the NaCl in distilled water.

3. Results and discussion

3.1. Semiconductor–metal transition in Ag–Ge–Te glasses

Figures 1(a) and (b) show the variation of normalized electrical resistivity of $\text{Ag}_x\text{Ge}_{15}\text{Te}_{85-x}$ glasses with pressure at room temperature, which indicate a continuous decrease in resistivities of these samples under pressure. The normalized resistivity $\log(\rho/\rho_0)$ at room temperature is obtained by dividing the resistance values (ρ) by the atmospheric pressure resistance (ρ_0) value. In low temperature measurements at various pressures, ρ_0 is taken as the starting resistance at the respective pressures ($\approx 300 \text{ K}$). The typical resistances of the samples range from $1.5 \text{ M}\Omega$ to $800 \text{ k}\Omega$ (for $2.5 \leq x \leq 21.5$). The resistivities fall by about six orders of magnitude at pressures around 5 GPa, suggesting a continuous semiconductor–metal transition in Ag–Ge–Te glasses at high pressures. Upon releasing the pressure the samples are found to attain resistance values close to their starting resistance values at atmospheric pressure. The resistance of the pressure released samples is always less than that of the starting resistance of the samples which can be attributed to the densification of the samples under pressure. It should be mentioned that the gaskets enclosing the sample undergo a plastic deformation under pressure and they do not retain their original thickness after releasing the pressure.

Figures 2(a) and (b) show the temperature dependence of electrical resistivity of representative $\text{Ag}_5\text{Ge}_{15}\text{Te}_{80}$ and $\text{Ag}_{20}\text{Ge}_{15}\text{Te}_{65}$ glasses at different pressures. It is seen that

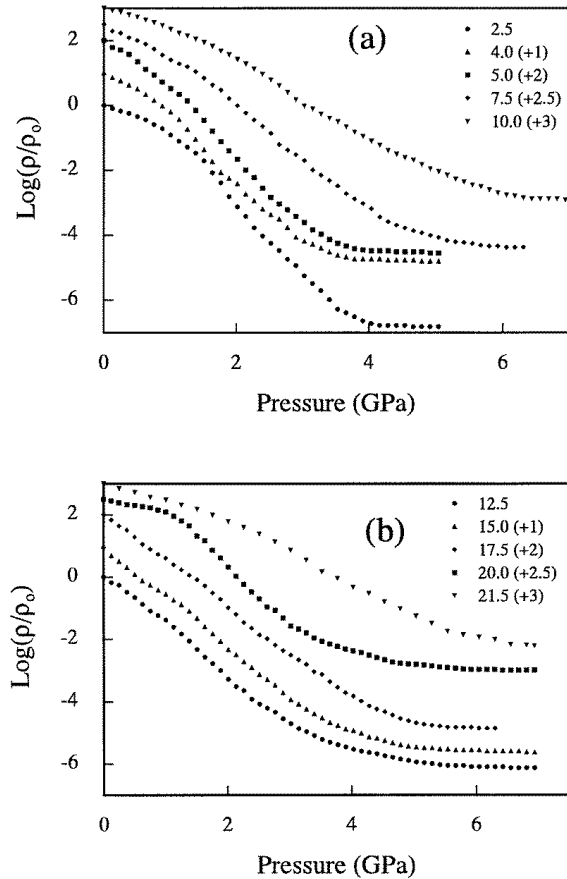


Figure 1. Pressure dependence of the electrical resistivity of Ag_xGe₁₅Te_{85-x} glasses at room temperature: (a) $2.5 \leq x \leq 10$ and (b) $12.5 \leq x \leq 21.5$. For the sake of presentation the $\log(\rho/\rho_0)$ versus pressure plots are shifted by the numbers indicated in the brackets for the respective compositions.

at lower pressures (≤ 4 GPa), the electrical resistivity is thermally activated, obeying the relation $\rho = \rho_0 \exp(\Delta E/kT)$, with a single activation energy (ΔE) in the temperature range of investigation (300–77 K). The temperature dependence of electrical resistivities of representative Ag₅Ge₁₅Te₈₀ and Ag₂₀Ge₁₅Te₆₅ glasses at 5 GPa pressure is shown in figures 3(a) and (b), which indicate the metallic behaviour.

The variation with pressure of ΔE , estimated from the slope of $\log(\rho/\rho_0)-1/T$ plots at different pressures, is shown in figure 4 for representative Ag₅Ge₁₅Te₈₀ and Ag₂₀Ge₁₅Te₆₅ glasses; ΔE exhibits a continuous decrease with pressure, becoming zero around 4–5 GPa which also confirms the continuous semiconductor–metal transformation in Ag–Ge–Te samples. It is interesting to note from the present results that the addition of Ag changes the discontinuous metallization of Ge–Te [1] glasses to a continuous semiconductor–metal transition. However, there is no appreciable reduction in the pressures required for the metallization of these glasses.

X-ray diffraction studies of Ag–Ge–Te samples recovered from the high pressure cell reveal that Ag–Ge–Te samples do not crystallize when they undergo metallization at high

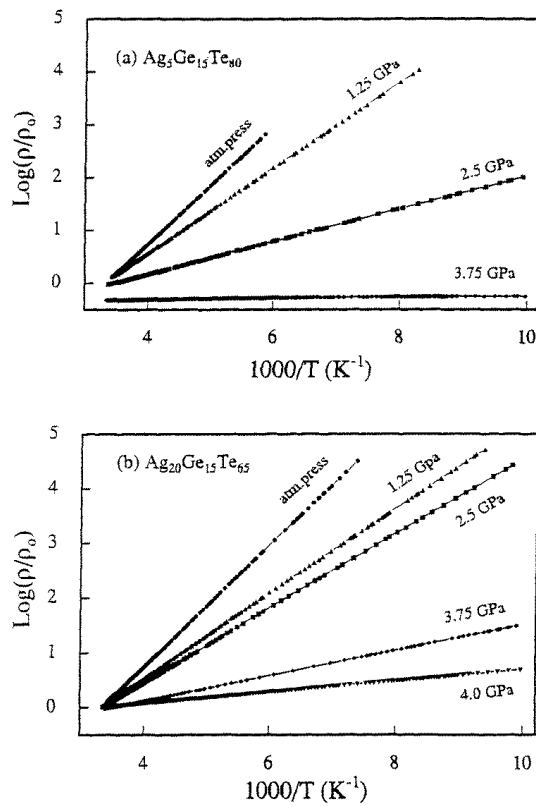


Figure 2. Variation of $\log(\rho/\rho_0)$ with $(1000/T)$ of (a) $\text{Ag}_5\text{Ge}_{15}\text{Te}_{80}$ and (b) $\text{Ag}_{20}\text{Ge}_{15}\text{Te}_{65}$ glasses at various pressures.

pressures. Figure 5 shows the x-ray diffraction patterns of representative $\text{Ag}_5\text{Ge}_{15}\text{Te}_{80}$ and $\text{Ag}_{20}\text{Ge}_{15}\text{Te}_{65}$ samples recovered from 5 GPa pressure, indicating the amorphous nature of the samples. For comparison the x-ray patterns of as-prepared $\text{Ag}_5\text{Ge}_{15}\text{Te}_{80}$ and $\text{Ag}_{20}\text{Ge}_{15}\text{Te}_{65}$ samples are also given in figure 5. Ge–Te samples crystallize as and when they exhibit discontinuous metallization under pressure [1]. The addition of Ag to Ge–Te glasses not only changes the discontinuous metallization to a continuous one, but also retards the crystallization of the material under pressure.

3.2. Composition dependence of conductivity activation energy

In chalcogenide glasses, the variation with composition of ΔE is determined by the composition dependence of three major factors, namely, the bond strengths, the network connectivity and density. From a chemical approach [9], it can be realized that an increase in the bond strength causes a larger splitting between σ (bonding–valence) and σ^* (antibonding–conduction) orbital, which results in an increase in the band-gap. The increase in the network connectivity can lead to an increased interaction between the atomic species, which in turn can widen the separation between σ and σ^* bands. Further, the width of σ and σ^* orbitals is decided by N , the number of atoms/unit volume. It follows from the above that the increase in bond strength and network connectivity will increase the gap (and ΔE),

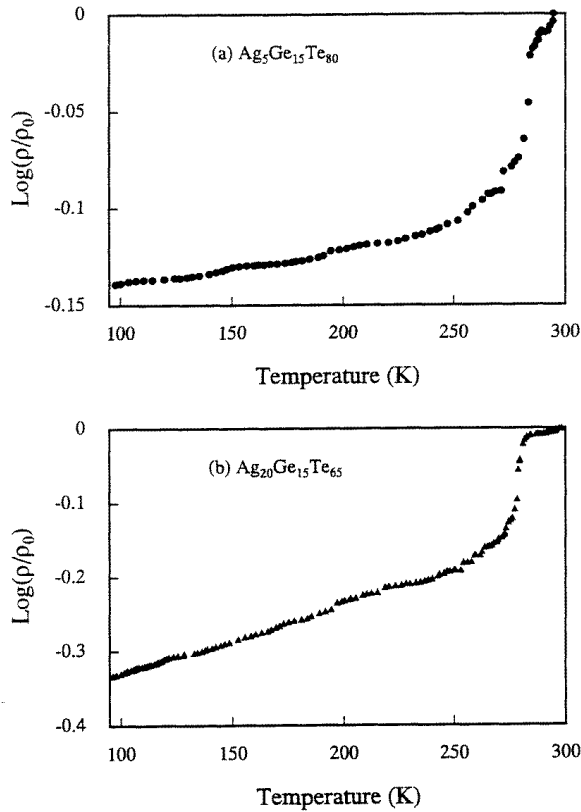


Figure 3. Temperature dependence of electrical resistivity of (a) $\text{Ag}_5\text{Ge}_{15}\text{Te}_{80}$ and (b) $\text{Ag}_{20}\text{Ge}_{15}\text{Te}_{65}$ samples at high pressures, showing the metallic behaviour.

whereas the increase in N can lead to a reduction in the gap.

Let us now consider the two archetypal binary glasses, $\text{Ge}_x\text{Te}_{100-x}$ ($15 \leq x \leq 28$) and $\text{Ge}_x\text{Se}_{100-x}$ ($0 \leq x \leq 45$), in order to understand the influence of bond energy, network connectivity, etc, on the composition dependence ΔE of glassy chalcogenides.

The conductivity activation energy of $\text{Ge}_x\text{Te}_{100-x}$ glasses [1] is found to increase with Ge content, exhibiting a maximum at a composition $x = 20$. In this system, with the addition of Ge (up to 33 at.%), there is a progressive replacement of weaker Te–Te bonds (259 kJ mol^{-1}) [10] by stronger Ge–Te bonds (456 kJ mol^{-1}) [10]. Further, with the increase in Ge content, the network connectivity also increases. These two effects augment each other and account for the increase in the band-gap and ΔE of $\text{Ge}_x\text{Te}_{100-x}$ glasses, in the composition range $15 \leq x \leq 20$.

Further, in the $\text{Ge}_x\text{Te}_{100-x}$ system, the addition of Ge has no appreciable effect on the density, in the entire composition range of glass formation [11]. There should be a significant increase in N with the addition of Ge, in order to maintain the density, due to the large mass difference between Te (127.6) and Ge (72.61) atoms. The increase in N at higher values of x causes the closure of the gap and the observed turnaround in ΔE of $\text{Ge}_x\text{Te}_{100-x}$ glasses.

It is interesting to observe that the reversal in trend in the composition dependence of ΔE in $\text{Ge}_x\text{Te}_{100-x}$ glasses occurs at the composition $x = 20$, which is the rigidity percolation

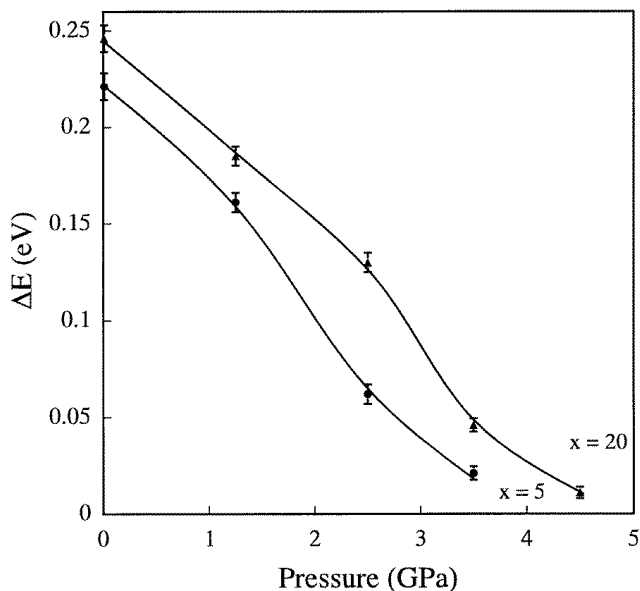


Figure 4. Variation of conductivity activation energy of $\text{Ag}_5\text{Ge}_{15}\text{Te}_{80}$ and $\text{Ag}_{20}\text{Ge}_{15}\text{Te}_{65}$ glasses as a function of pressure.

threshold of the material [1]. At the rigidity percolation threshold, there is a sudden change in the network connectivity of the material and a transformation from an under-cross-linked to an over-constrained network takes place [12, 13]. The occurrence of the ‘turnaround’ in the composition dependence of ΔE at compositions above $x = 20$, is indicative of the saturation of the structural effects and onset of the domination of the band broadening (due to increase in N).

In $\text{Ge}_x\text{Se}_{100-x}$ glasses, ΔE is found to increase with Ge content [14], which is consistent with the bond energy and network connectivity considerations described above. However, there is no maximum in ΔE of $\text{Ge}_x\text{Se}_{100-x}$ glasses, at the percolation threshold ($x = 20$), as in the case of Ge–Te glasses. The ΔE of $\text{Ge}_x\text{Se}_{100-x}$ glasses continues to increase with x above the percolation threshold, with a slight change in slope [14].

Earlier investigations [15] indicate that the density of Ge–Se glasses increases with the Ge content in the composition range $0 \leq x \leq 20$. This can be attributed to the increase in N . It is also interesting to note that the density of Ge–Se glasses exhibits a maximum at $x = 20$, and there is a considerable decrease in density with Ge content in the composition range $20 \leq x \leq 33$ [15]. As the atomic masses of Se and Ge are not widely different (78.96 and 72.61 respectively), the large decrease in density can be accounted only for by a corresponding decrease in N . In Ge–Se glasses, the chemical ordering occurs after the rigidity percolation threshold (at $x > 20$), involving major atomic rearrangements in the network. This eventually leads to a maximally ordered glass having the least density at $x = 33$ (the chemical threshold) [16]. Due to the decrease in N (because of chemical ordering), there is no band broadening and gap closure in $\text{Ge}_x\text{Se}_{100-x}$ glasses at higher values of x (> 20). In fact, ΔE keeps increasing with x , exhibiting a maximum at $x = 33$ [14]. These results also confirm our conjecture that the turnaround in ΔE in $\text{Ge}_x\text{Te}_{100-x}$ samples above $x = 20$ is only because of the increase in N .

The composition dependence of ΔE of $\text{Ag}_x\text{Ge}_{15}\text{Te}_{85-x}$ samples is very different from

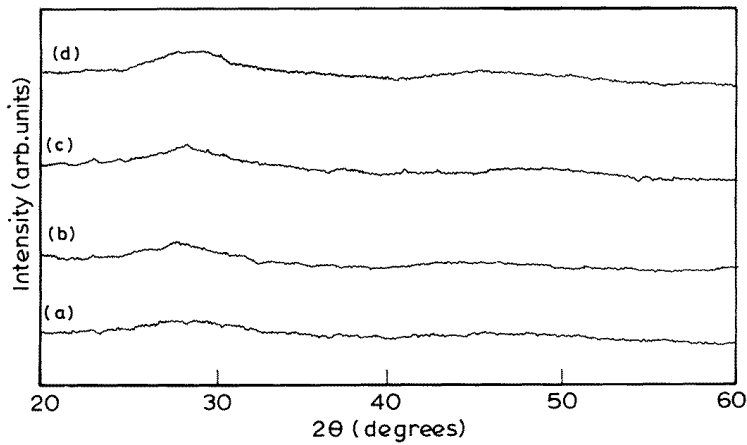


Figure 5. XRD patterns of (a) as-prepared $\text{Ag}_5\text{Ge}_{15}\text{Te}_{80}$ sample, (b) pressure recovered $\text{Ag}_5\text{Ge}_{15}\text{Te}_{80}$ sample, (c) pressure recovered $\text{Ag}_{20}\text{Ge}_{15}\text{Te}_{65}$ sample and (d) as-prepared $\text{Ag}_{20}\text{Ge}_{15}\text{Te}_{65}$ sample. The XRD patterns indicate the reversible nature of the pressure induced metallization in Ag–Ge–Te samples.

that of Ge–Te samples. Figure 6 shows the composition dependence of ΔE of Ag–Ge–Te samples at different pressures. It can be seen that at all pressures, ΔE of Ag–Ge–Te glasses decreases with Ag content and attains a minimum at $x = 5$. Above $x = 5$, there is a slight increase in ΔE with composition up to $x = 18.5$. At $x = 18.5$ a reversal in trend is seen in ΔE , especially at pressures below 1.5 GPa. The variations of glass transition temperature (T_g) and crystallization temperature (T_c) as a function of composition and average coordination number (inset in figure 6) also show distinct changes at the compositions $x = 5$ and $x = 18.5$, which are associated with the percolation threshold and chemical ordering in the Ag–Ge–Te glasses [17].

In metal doped chalcogenide glasses such as As–Se–M and Ge–Se–M ($M = \text{Cu}$ and Ag) Cu and Ag atoms are found to have different coordinations [4, 19]. For example, Ag in As–Se–Ag glasses is generally coordinated by three chalcogen atoms [20]. In contrast to the metal doped arsenic selenides and germanium selenides, Ag atoms in Ag–Ge–Te glasses exist only in tetrahedral coordination [4]. The ionic conductivity in these glasses is found to be absent and the conduction is of electronic type [4].

The fourfold co-ordinated Ag atoms in Ag–Ge–Te glasses enter the structural network, by replacing initially the Te–Te bonds present in the $(\text{Te})_n$ chains by Ag–Te bonds and later by replacing the Ge–Te bonds present in the $\text{GeTe}_{4/2}$ tetrahedral units by Ag–Ge bonds. The bond energies [9] of Ag–Te bonds (195 kJ mol^{-1}) and Ag–Ge bonds (174 kJ mol^{-1}) are less than those of Te–Te bonds (260 kJ mol^{-1}) and Ge–Te (456 kJ mol^{-1}) respectively. Thus, from the bond energy consideration, there will be a decrease in the gap and ΔE with the Ag content in Ag–Ge–Te samples.

At the same time, there is an increase in the network connectivity and rigidity when Ag replaces Te, which can lead to the widening of the gap and increase in the conductivity activation energy. The present results indicate that the bond energy considerations clearly dominate, resulting in a net decrease in the conductivity activation energy of $\text{Ag}_x\text{Ge}_{15}\text{Te}_{85-x}$ glasses in the composition range $2.5 \leq x \leq 5$ (figure 6). The composition $x = 5$ in $\text{Ag}_x\text{Ge}_{15}\text{Te}_{85-x}$ glasses corresponds to the rigidity percolation threshold of the material [17].

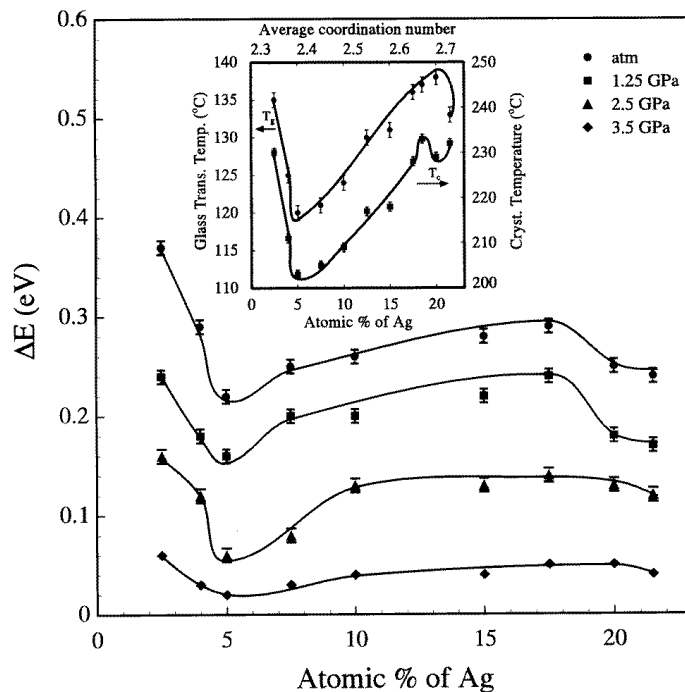


Figure 6. The variation of conductivity activation energy of $\text{Ag}_x\text{Ge}_{15}\text{Te}_{85-x}$ glasses with the concentration of Ag. The inset shows the variation of glass transition temperature (T_g) and crystallization temperature (T_c) as a function of composition and average coordination number.

The increase in ΔE above $x = 5$ can be attributed to the chemical ordering occurring in the glass, beyond rigidity percolation. The conductivity activation energy increases up to $x = 18.5$, the composition around which chemical ordering occurs in Ag–Ge–Te samples [17]. Thus, the variation with composition of ΔE of Ag–Ge–Te glasses is consistent with the bond energy, network connectivity and chemical ordering considerations.

As mentioned earlier, Ag as well as Cu enters the Ge–Te network in fourfold coordination. The addition of both Cu and Ag changes the discontinuous glassy semiconductor to crystalline metal transition in Ge–Te glasses into a continuous metallization. However, there are subtle differences in the composition dependence of ΔE of Cu and Ag alloyed Ge–Te glasses; ΔE of $\text{Cu}_x\text{Ge}_{15}\text{Te}_{85-x}$ glasses increases sharply with x exhibiting a maximum at the rigidity percolation threshold. From the viewpoint of network connectivity, an increase in ΔE can be expected on replacing Te by Cu. This increase is not highly augmented (as in the case of Ge–Te samples) by the bond energy considerations as the energies of Te–Te bonds and Cu–Te bonds are not widely different (259 and 278 kJ mol^{-1} respectively). However, the variation in ΔE with x of $\text{Cu}_x\text{Ge}_{15}\text{Te}_{85-x}$ glasses is as pronounced as in the case of Ge–Te glasses. Thermal crystallization studies on $\text{Cu}_x\text{Ge}_{15}\text{Te}_{85-x}$ glasses [6] provide a clue for understanding this aspect. These studies indicate that there is no elemental Cu or any compounds of Cu with Ge or Te, found in thermally crystallized Cu–Ge–Te samples containing even up to 10 at.% of Cu (limit of glass formation) [6]. Based on this, it has been suggested that Cu randomly substitutes for Ge in the Ge–Te matrix and does not form any distinct species of its own. Thus, the composition dependence of ΔE of Cu–Ge–Te glasses mimics that of the binary Ge–Te samples, whereas Ag–Ge–Te samples are different from Ge–Te samples due to the reasons cited above.

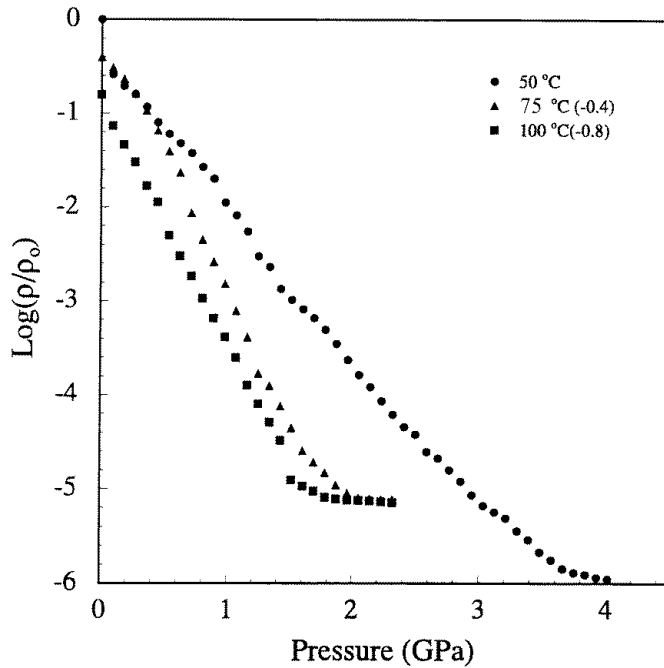


Figure 7. Electrical resistivity of $\text{Ag}_5\text{Ge}_{15}\text{Te}_{80}$ glass as a function of pressure at high temperatures. The $\log(\rho/\rho_0)$ versus pressure plots are shifted by the numbers indicated in the brackets.

3.3. Metallization of Ag–Ge–Te glasses at high pressures and high temperatures

Figure 7 shows the variation of electrical resistivity of a representative $\text{Ag}_5\text{Ge}_{15}\text{Te}_{80}$ glass at 50, 75 and 100 °C. It can be seen that the metallization of the sample occurs around 3.6 GPa at 50 °C. At higher temperatures, the metallization pressures are drastically reduced (2 GPa and 1.5 GPa at 75 °C and 100 °C respectively).

In glasses such as Ge–Te [1] and Si–Te [18], which crystallize during metallization, the decrease in the transition pressure at high temperatures can be accounted for easily. The appreciable decrease in the metallization pressures at high temperatures in samples like Ag–Ge–Te, which remain amorphous during metallization under pressure, is very interesting. The enhancement of the conductivity of the sample at higher temperature may lead to the observed decrease in the metallization pressures. This aspect needs to be investigated in more detail.

4. Conclusions

Ag–Ge–Te glasses are found to undergo a continuous semiconductor—metal transition at high pressures. The composition dependence of conductivity activation energy of Ag–Ge–Te and other related chalcogenide glasses are understood on the basis of bonding considerations, topological thresholds and density variations with composition. The metallization pressures of Ag–Ge–Te glasses are found to be significantly reduced at high temperatures.

Acknowledgments

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