

Pressure Induced Anomalies in an As-Al-Te Glass

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Abstract

The pressure and temperature dependences of the electrical resistance of $\text{As}_{34.4}\text{Al}_4\text{Te}_{61.6}$ and $\text{As}_{16.67}\text{Al}_{16.67}\text{Te}_{66.66}$ glasses have been investigated using an opposed anvil setup. The resistance of the glasses exhibit $\sim 10^6$ fold decrease with increasing pressure up to 7 GPa at 300 K. This behaviour can be traced to the corresponding changes with pressure of the activation energy for electrical conduction, $\Delta E(p)$.

The $\text{As}_{34.4}\text{Al}_4\text{Te}_{61.6}$ glass exhibits pressure induced anomalies at 2 GPa in the pressure variation of $\Delta E(p)$ and the pressure coefficient of electrical resistance. Such an anomaly is not seen for the $\text{As}_{16.67}\text{Al}_{16.67}\text{Te}_{66.66}$ glass. The anomalies point to a pressure induced morphological structural transformation in the $\text{As}_{34.4}\text{Al}_4\text{Te}_{61.6}$ glass.

1 Introduction

Chalcogenide semiconducting glasses are kind of molecular glasses composed of covalent clusters' held together by van der Waals forces. The number of dimensions in which these clusters are extended in the glass is the network dimensionality', D . High pressure experiments on these glasses can probe into the local network dimensionality since compression affects differently^{1,3} the glasses with differing D . In glasses which are locally 1D or 2D, compression preferentially forces the molecular 1D or 2D regions closer together (intermolecular in nature) whereas, in 3D network glasses compression decreases the nearest neighbour distances (intramolecular in nature).

Some interesting high pressure effects on chalcogenide glasses are the semiconductor to metal transition⁴, structural changes^{3,5}, the strong red shift of the absorption edges⁶, cryogenic pressure luminescence studies⁷, and the variation of the electrical resistivity'.

The dependence of the density, the glass transition temperature, T_g , and the average coordination number, Z , on composition have been reported for a large number of compositions of the As-Al-Te system⁸. In this paper, we report the pressure (up to 7 GPa) and temperature (300 to 360K) dependence of the electrical resistance, R , of two glass compositions of the As-Al-Te system. The compositions studied are $As_{34.4}Al_4Te_{61.6}$ (density = 5.493 gcm⁻³, T_g = 390K and Z = 2.54) and $As_{16.67}Al_{16.67}Te_{66.66}$ i.e. $AsAlTe_4$ (density = 5.198 gcm⁻³, T_g = 407K and Z = 2.76) which lie along the As_2Te_3 - $AsAlTe_4$ tie line of the system. The results point to a pressure induced structural transformation in the $As_{34.4}Al_4Te_{61.6}$ composition at pressures around 2 GPa.

2 Experimental

2.1 Sample preparation

The glasses were prepared in fused silica ampoules by the melt-quenching method. As Al reacts with silica at high temperatures, the preparations were done in graphitized ampoules. Appropriate quantities of 99.999% pure As, Te (Atomergic Chemetals Corp., USA) and Al (Johnson Matthey, USA) were weighed (total 6 g) into the graphitized ampoules and sealed under a vacuum of 10⁻⁵ Torr. The ampoules were heated gradually to 1100K, maintained at this temperature for eight hours at the end of which they were quenched in iced water to form the glasses. During heating, the ampoules were continuously agitated in a rotary furnace to obtain homogeneous samples. The amorphous nature of the glass samples was confirmed by recording X-ray diffractograms. All the glass samples used in the present experiments were annealed at one atmosphere at the T_g of the specimen.

A glass piece (0.4mm thick) with parallel end faces was prepared from the bulk samples by polishing it on 600 grit emery paper using water as coolant. Pieces, measuring approximately 1mm x 1mm x 0.4mm were cut from this for high pressure experiments. Each experimental sample piece was introduced along with a mixture of talc powder and epoxy into a hole of 1.5mm diameter drilled in a circular talc disc (5mm diameter and 0.4mm thick). The epoxy was then allowed to set, and the sample assembly was thinned down to 0.2mm by polishing both the faces on a fine emery paper (John Oakey and Mohan Ltd., grade 4/0). The samples were crack free when examined under an optical microscope at a magnification of 500.

2.2 High pressure cell and pressure calibration

A pair of tungsten carbide anvils (anvil face diameter 12.7mm) with pyrophyllite gasket (P) and talc (t) as the pressure transmitting medium was used to pressurize the specimen. The details of the high pressure resistivity cell are shown in Fig.1. The cell consisted of three gaskets stacked one over the other. All the gaskets had an o.d. = 12.5mm and i.d. = 5mm; the thicknesses of P_1 , P_2 and P_3 were respectively 0.33, 0.20 and 0.32mm. The diameters of the talc discs were 5mm; the talc disc t_2 containing the sample was 0.2mm thick and the discs t_1 and t_3 were each 0.28mm thick. **AB** and **CD** denote copper wires (0.1mm in diameter) used for electrical contacts. The flattened portions of these wires ensured proper electrical contact with the sample. A chromel-alumel thermocouple was placed close to the sample. The laying of the copper and the thermocouple wires was facilitated by making grooves in the gaskets P_1 and P_3 . The gaskets were held in position with a small quantity of Duco cement along their outer edges.

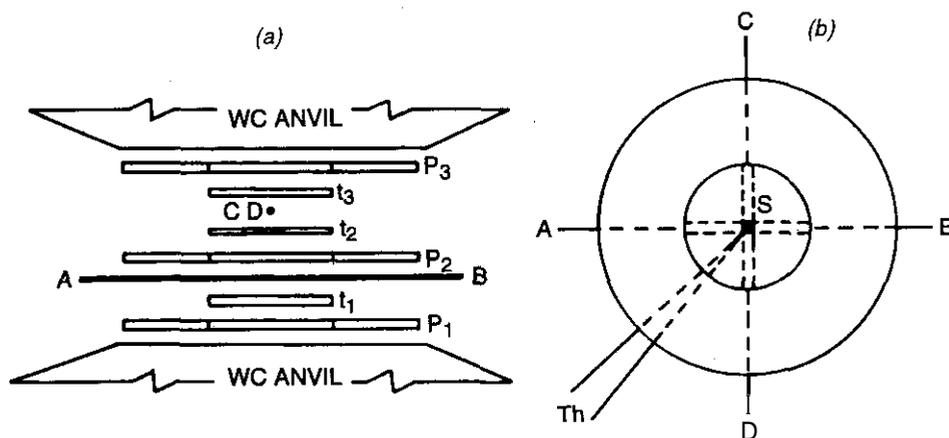


Figure 1: High pressure resistivity cell (a) as viewed parallel to the anvil face and (b) as viewed normal to the anvil face. P_1 , P_2 , P_3 - pyrophyllite gaskets; t_1 , t_2 , t_3 - talc pressure transmitting discs, **AB**, **CD** - electrical leads, *Th* - thermocouple, and *S* - sample.

A tubular heater surrounding the anvils was used to heat the glass sample. The heater tube also served as a guide for the initial alignment of the anvils. The anvils

were powered by a 100-ton hydraulic ram. The oil pressure in the ram was read to an accuracy of 25 psi using a Heise gauge. The hydraulic ram pressure was calibrated in terms of the sample pressure by recording the discontinuities in the electrical resistance of Bi I \rightarrow II (2.55 GPa) and Bi III \rightarrow V (7.7 GPa) transformations. For this, the Bi sample (1 x 1 x 0.2 mm) was cast in the talc-epoxy mixture in the same way as described earlier. The oil pressure-specimen pressure relation was linear. The oil pressure corresponding to the Bi transformations differed by \sim 5 per cent from run to run. The uncertainty in the specimen pressure obtained from the ram pressure-specimen pressure calibration curve was \pm 0.1 GPa in the 2.5 GPa range and \pm 0.3 GPa in the 7 GPa range.

2.3 Data recording

The electrical resistances of the samples were measured by two different methods. In the pressure region where the glass samples exhibited a high resistance (10^3 - 10^5 ohms), the resistance of the sample was measured to an accuracy of one part in 10^4 using an autoranging digital multimeter (Keithley model 196 system). When the resistance of the sample under pressure dropped below 10^3 ohms, a four probe measurement was made. For this, an appropriate value of current (in the range 10 - 100 mA) was passed through the sample, and the resulting voltage across it was recorded using a Rikadenki R-50 strip chart recorder (accuracy of 1 part in 10^3).

The sequence of steps in actual experiments was as follows. For obtaining the pressure dependence of electrical resistance of the specimen at room temperature, the specimen was loaded at a rate 0.1 GPa per minute to desired pressures. The resistance of the specimen was noted after a waiting period of one minute at each pressure step. The resistance of the specimen decreased with time at each pressure and became constant within this waiting period. Typical decrease in resistance for one minute waiting was \sim 10% at 1 GPa and \sim 1% at 5 GPa.

The temperature dependence (from 300K to 360K) of electrical resistance of the glass sample at different pressures was obtained in the following way. The specimens were pressurized to a desired value at a rate of 0.1 GPa min^{-1} . The decrease in the resistance of the sample was continuously recorded. A waiting period of 15 minutes was allowed after reaching the desired pressure. The sample was heated to 360K (well below the T_g) at a rate of 5 - 10K min^{-1} . The output of the thermocouple and the voltage across the sample (for a constant current of 10 - 100 mA) were constantly

recorded. Then, the sample was cooled at a rate 5K min^{-1} to room temperature. The thermocouple output and the voltage across the sample were recorded also during the cooling run. The resistance values were noted at intervals of 5K from these records. The hydraulic pressure was maintained constant (within 10 psi) at the desired value during the heating and cooling runs using a gas accumulator connected in series with the hydraulic ram. After the specimen cooled to the room temperature, it was re-loaded to the next value of desired pressure, and the resistance - temperature data (R - T data) were obtained in a similar manner.

The temperature of 360K up to which the samples have been heated to obtain the R - T data at higher pressures is 30 to 60K below the T_g of these glasses at 1 atmosphere. As the T_g of the glasses increases with increasing pressure, the temperature of 360K is well below the T_g s of these glasses at high pressures.

3 Results and discussion

3.1 Resistance-pressure data at room temperature

The $[R(p)/R(0)] - p$ data (at 300K) of the glasses are shown in Fig.2. The atmospheric pressure resistance, $R(0)$, values of both the glasses were obtained by extrapolating the $R(p) - p$ data to $p = 0$. The $R(p)$ of the glasses decreases with increasing p ; the decrease is about six orders of magnitude for a pressure increase of 7 GPa . However, subtle differences are seen in the $R(p) - p$ behaviour of these glasses. For $\text{As}_{34.4}\text{Al}_4\text{Te}_{61.6}$ glass, R decreases slowly upto 1 GPa , rapidly in the pressure region $1 - 3.5\text{ GPa}$ and slowly again with further increase of pressure. The decrease in R with p for the $\text{As}_{16.67}\text{Al}_{16.67}\text{Te}_{66.66}$ glass is fairly uniform in the pressure region $1 - 4\text{ GPa}$ and becomes slower beyond 4 GPa .

The differences in the p dependence of $R(p)$ are seen clearly in the magnitude of the instantaneous pressure coefficient of resistance (PCR) versus p plots (inset Fig.2). The PCR of $\text{As}_{34.4}\text{Al}_4\text{Te}_{61.6}$ exhibits a maximum at $p \approx 2\text{ GPa}$. The PCR of the $\text{As}_{16.67}\text{Al}_{16.67}\text{Te}_{66.66}$ glass sample is nearly constant in the pressure region $1-4\text{ GPa}$. The Z values (of 2.54 and 2.76) of these glasses indicate that their structural arrangements are different'. As discussed later, the differences in the PCR - p behaviour can be traced to the differences in their structural arrangement.

3.2 Pressure dependence of the activation energy for electrical conduction

The $\ln R$ versus $1000/T$ data for the $\text{As}_{16.67}\text{Al}_{16.67}\text{Te}_{66.66}$ glass at 1.6 GPa and

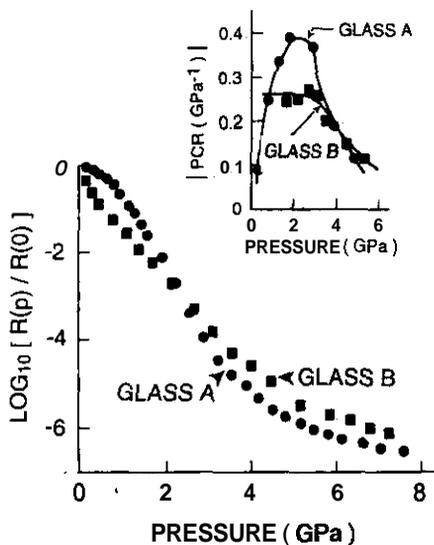


Figure 2: Normalized resistance versus pressure data of the glasses at 300 K; the inset shows the pressure dependence of magnitude of the pressure coefficient of resistance of the glasses. Glass A and glass B denote respectively the $\text{As}_{34.4}\text{Al}_4\text{Te}_{61.6}$ and $\text{As}_{16.67}\text{Al}_{16.67}\text{Te}_{66.66}$ compositions.

5 GPa, typical of the $R - T$ data obtained in the present studies, are shown in Fig 3. Also shown in the figure is the effect of temperature cycling on the $R - T$ data. It is seen that $\ln R$ versus $1000/T$ data are not linear during the first heating. This is probably due to the additional densification of the glass due to heating it under pressure. The data points obtained during the first cooling run lie on a straight line. The data of the first heating run and the subsequent cooling run follow different paths and the R value does not revert to its original room temperature value at the end of the first cooling run. Presumably, the additional densification caused during heating under pressure is retained when the glass is cooled to room temperature

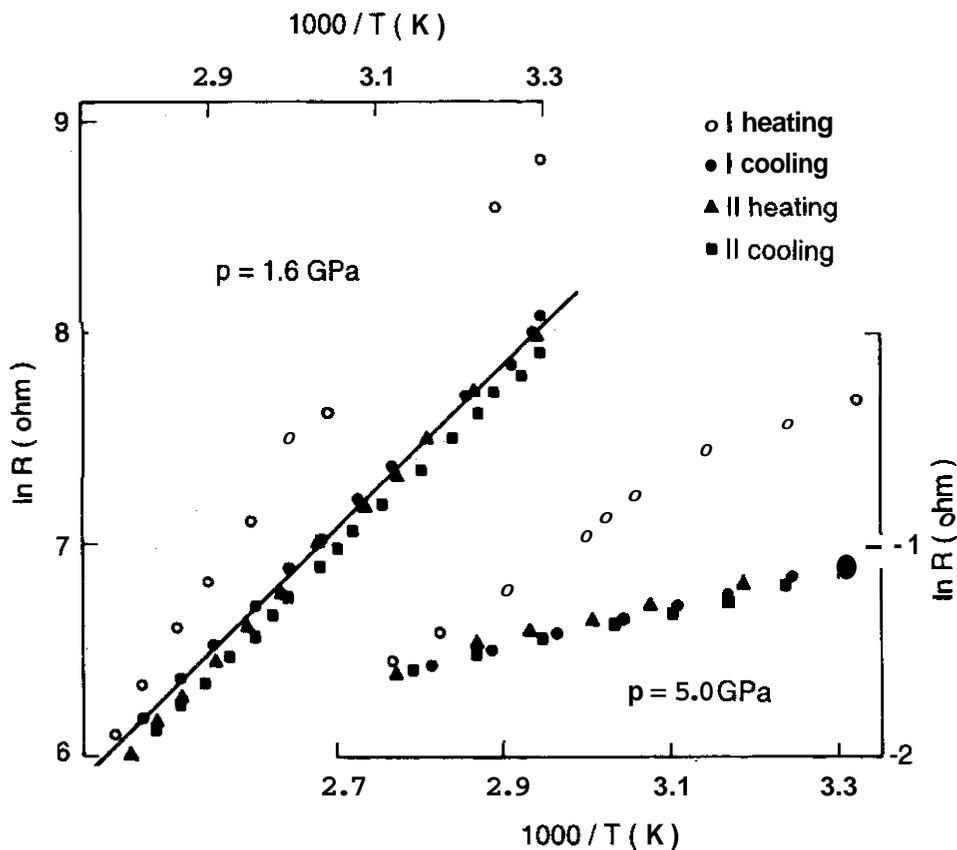


Figure 3: Temperature dependence of the electrical resistance of the specimen at two different pressures.

under pressure. The R - T behaviour is not significantly altered during the subsequent heating and cooling runs due to the stabilization of the glass. In all the cases, AE was calculated using the first cooling data.

The values of AE at different p were obtained by fitting the $\ln R$ versus $1000/T$

data at each p to the standard equation of the form,

$$\ln R = \ln R_0 + \Delta E(p)/kT \quad (1)$$

The $\ln R_0$ values obtained from such fits ranged between -4 to -6.5 for both the compositions; no systematic trend was seen in the variation of $\ln R_0$ with p .

The variation of $\Delta E(p)$ with pressure (up to 5 GPa) for the glasses are shown in Fig.4. The extrapolation of the $\Delta E(p) - p$ data to $p = 0$ gives $\Delta E(0) = 0.38$ eV for the $As_{34.4}Al_4Te_{61.6}$ glass, and $\Delta E(0) = 0.43$ eV for the $As_{16.67}Al_{16.67}Te_{66.66}$ glass. It is interesting to note that these values are in good agreement with the AE values of 0.38 and 0.42 eV respectively determined for these glasses independently from their $R - T$ data at atmospheric pressure. In these studies, AE at higher pressures were determined both by reaching the desired pressure for a sample directly, and by reaching the same pressure after completing the temperature cycles on a sample either at one or more lower pressure values. The data of Fig.4 show that the $\Delta E(p)$ at a specified p does not depend on such temperature cyclings at lower pressure values.

A break in $\Delta E(p)$, corresponding to the maximum in PCR (inset, Fig 2), is seen at 2 GPa for the $As_{34.4}Al_4Te_{61.6}$ glass. Such a feature is not observed for the $As_{16.67}Al_{16.67}Te_{66.66}$ glass.

The following analysis indicates that the $\Delta E(p) - p$ data (Fig.4) reflect corresponding changes in the $R - p$ data at 300K of these glasses (Fig.2). For the $As_{16.67}Al_{16.67}Te_{66.66}$ glass, the linear (up to 5 GPa) $\Delta E(p) - p$ data can be expressed (with a coefficient of determination of 0.994) as,

$$\Delta E(p) = 0.43 - 0.067p \quad (2)$$

here 0.43 eV is the value of AE at one atmosphere and p is in GPa. The $R - p$ data (Fig.2) of this glass (up to 5 GPa) can be expressed (with a coefficient of determination of 0.996) as,

$$\ln R = 13.3 - 2.5p \quad (3)$$

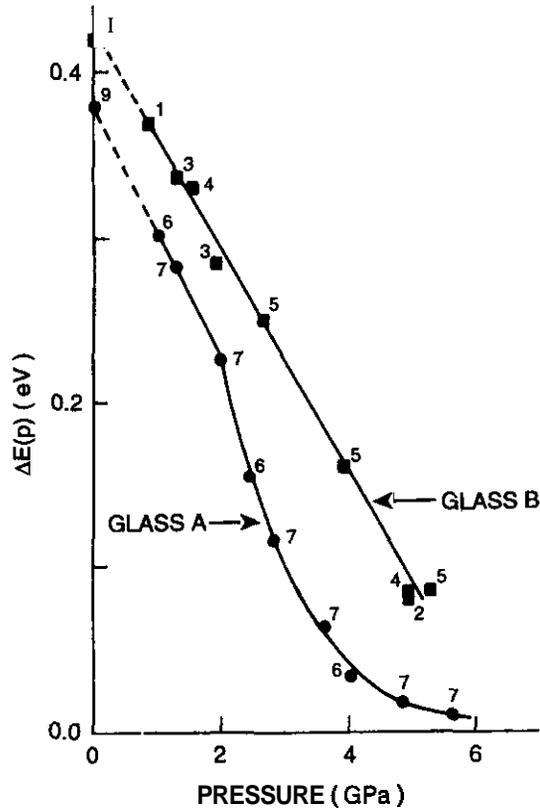


Figure 4: Pressure dependence of the activation energy for electrical conduction in the glasses; the data points designated by the same numeral are obtained in the sequence of increasing pressures on the same specimen after a temperature cycle at each p . Glass A and glass B denote respectively the $As_{34.4}Al_4Te_{61.6}$ and $As_{16.67}Al_{16.67}Te_{66.66}$ compositions.

where R is in ohms and p is in GPa.

Assuming $\ln R_0$ to be independent of p , it is seen from Eq.(1) that,

$$\frac{d \ln R}{dp} = \frac{1}{kT} \frac{d \Delta E(p)}{dp} \quad (4)$$

The values of $d \ln(R)/dp = -2.5 \text{ GPa}^{-1}$ and $d(\Delta E(p))/dp = -0.067 \text{ eV GPa}^{-1}$ from Eqs.(2) and (3) fit very well the Eq.(4). This implies that the decrease of R with increasing p (Fig.2) is essentially accounted for by a corresponding decrease of $\Delta E(p)$ with p . The observed variation of $\ln R_0$ with p does not contribute to the variation of R with p .

The $R(p) - p$ data (Fig.2) extends to 7 GPa while the $\Delta E(p) - p$ data could not be extended to more than 5 GPa because the heating experiments were done using unsupported tungsten carbide anvils. From the $R(p)$ and PCR data of $\text{As}_{16.67}\text{Al}_{16.67}\text{Te}_{66.66}$ glass (Fig.2 and inset), it can be expected that $\Delta E(p) - p$ data also shows curvature similar to that seen in Fig.2 at pressures beyond 5 GPa.

The $R(p) - p$ data of $\text{As}_{34.4}\text{Al}_4\text{Te}_{61.6}$ glass also reflects corresponding changes seen in the $\Delta E(p) - p$ behaviour. For this composition, the curvature seen in the $\Delta E(p) - p$ data is expected to continue beyond 5 GPa.

3.3 Pressure induced structural transformation

The PCR maximum (Fig.2, inset) and the break in $\Delta E(p)$ (Fig.4) at 2 GPa for the $\text{As}_{34.4}\text{Al}_4\text{Te}_{61.6}$ glass are anomalous. Such anomalies are not observed for the $\text{As}_{16.67}\text{Al}_{16.67}\text{Te}_{66.66}$ glass. The varied behaviour of these glasses under pressure can be traced to the differences in pressure effects, arising from different structural arrangements existing in these glasses. The chalcogenide semiconducting glasses are considered to be 2D layer like molecular solids for values of Z lying between 2.40 and 2.67; further, D is known to increase with increasing Z . The glasses undergo a topological structural transformation from 2D layer like structure into the 3D covalent random network structures at $Z = 2.67$. Following this structural assignment for various values of Z , the $\text{As}_{34.4}\text{Al}_4\text{Te}_{61.6}$ glass with a Z of 2.54 is expected to have a layer like structure with the layers being held together by weak van der Waals bonding. On the contrary, the $\text{As}_{16.67}\text{Al}_{16.67}\text{Te}_{66.66}$ glass with a Z value of 2.76 can be expected to have a rigid covalent random network structure.

The pressure effects on these two types of structures can be drastically different in view of the nature of bonding present in them. It has been argued³ that when

glasses with $D = 2$ are subjected to hydrostatic compression to pressures higher than 2 GPa, cross linking between the layered molecular clusters are induced resulting in 3D structures. Following this view, the anomalies at 2 GPa observed in the present studies are likely to be due to a pressure induced morphological structural transformation in $\text{As}_{31.4}\text{Al}_4\text{Te}_{61.6}$ glass from a layered structure to a crosslinked random 3D network structure. Since the effect of pressure on a 3D network (fully cross linked) glass is to merely decrease the nearest neighbour distance (the normal compression effect), the $\text{As}_{16.67}\text{Al}_{16.67}\text{Te}_{66.66}$ glass exhibits a normal behaviour.

It is pertinent at this juncture, to examine other chalcogenide glasses in which similar anomalies at 2 GPa are seen. In the optical gap $\Delta E_0 - p$ data of GeS_2 ($Z = 2.67$) and As_2S_3 ($Z = 2.40$) glasses, a break is seen⁵ at $p = 2$ GPa; the effect is more pronounced for the GeS_2 glass. For the $(\text{GeSe}_2)_x(\text{As}_2\text{Se}_3)_{1-x}$ glasses⁶, ΔE_0 shows a pronounced decrease at 2 GPa for the GeSe_2 composition. This effect gets less pronounced as x decreases, and is absent for compositions with $x \leq 0.7$ i.e. for glasses with $Z \leq 2.56$. From the $AE - p$ data of $\text{As}_{40}(\text{Se},\text{Te})_{60}$ glasses⁷, it can be inferred that a break exists at 2 GPa; eventhough all these glasses have the same value of Z of 2.40, the effect is more pronounced for compositions with higher Se content. The present result for $\text{As}_{31.4}\text{Al}_4\text{Te}_{61.6}$ glass along with these observations confirm a threshold pressure of 2 GPa for the anomalies observed. Interestingly, the occurrence of this feature does not appear to have a direct bearing on the Z value of these glasses. The following aspects are seen from the experimental results summarised above. The anomaly at $p = 2$ GPa was present in As_2S_3 glass⁵ and absent for As_2Se_3 ⁶ and As_2Te_3 ⁸ glasses. It is indicated^{7,8} for the $\text{As}_2\text{S}_3 - \text{As}_2\text{Se}_3 - \text{As}_2\text{Te}_3$ series, that there is a transition from a layer like structure in As_2S_3 glass to a covalent random network structure in As_2Te_3 glass. Accordingly, As_2Te_3 glass is not expected to show this anomaly. In the $(\text{As}_2\text{Te}_3)(\text{As}_2\text{Se}_3)$ system⁷, the anomaly is seen with the introduction of Se to As_2Te_3 glass though it is absent in As_2Se_3 and As_2Te_3 glasses per se. In the present study also, the anomaly is seen in the $\text{As}_{34.4}\text{Al}_4\text{Te}_{61.6}$ glass i.e. the $(\text{As}_2\text{Te}_3)_{0.79}(\text{AsAlTe}_4)_{0.21}$ composition though it is absent in As_2Te_3 ⁸ and AsAlTe_4 (Fig 4, glass B) glasses. The anomalies seen for the intermediate compositions of the system point out that the structural arrangement in these glasses, rather than the value of Z (< 2.67) seems to control the occurrence of this feature.

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