

Low temperature elastic behaviour of As-Sb-Se and Ge-Sb-Se glasses

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Abstract. The ternary glasses of arsenic and germanium with antimony and selenium can be prepared in large sizes for optical purposes. The elastic behaviour of eight compositions of each glass has been studied down to 4.2 K using a 10 MHz ultrasonic pulse echo interferometer. The glasses have a normal elastic behaviour, with the velocities gradually increasing as the temperature is lowered. An anharmonic solid model of Lakkad satisfactorily explains the temperature variations. The elastic moduli of $\text{Ge}_x\text{Sb}_{10}\text{Se}_{90-x}$ glasses increase linearly as the Ge content is increased up to 25 at. % and beyond this the increase is nonlinear. $(\text{AsSb})_{40}\text{Se}_{60}$ glasses show a linear increase in elastic moduli with increasing Sb content. The elastic moduli of $\text{As}_x\text{Sb}_{15}\text{Se}_{85-x}$ glasses exhibit a drastic change near the stoichiometric composition $\text{As}_{2.5}\text{Sb}_{1.5}\text{Se}_{60}$. These behaviours have been qualitatively explained on the basis of the structural changes in glasses.

Keywords. Elastic behaviour; As-Sb-Se glasses; Ge-Sb-Se glasses; low temperature elasticity.

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1. Introduction

Chalcogenide glasses have special electrical and optical properties (Baidkov 1966; Myuller 1966; Savage and Nielsen 1964; Webber and Savage 1976) and are becoming technologically important materials. These glasses can be prepared in large sizes. Their mechanical properties are quite important from the application point of view. In this paper we present the measurement of longitudinal and transverse ultrasonic velocities and elastic constants of two different classes of Ge-Sb-Se and As-Sb-Se glasses as a function of temperature from 300 K down to 4.2 K. In §2 we describe the experimental methods for preparing the samples, the bonding technique and the ultrasonic velocity measurements. Section 3 discusses the results of low temperature elastic constants. These have been fitted to the Lakkad's anharmonic oscillator model. The composition dependence of the low and room temperature elastic constants has been explained using the chemically-ordered network model.

2. Experimental methods

Sample preparation

Samples for ultrasonic measurements should be fairly large in size, homogeneous and free of voids and perforations. Only a few glasses can be prepared with these properties

and chalcogenides are one among them. The Ge-Sb-Se and As-Sb-Se glasses in the form of cylinders (diameter 12 mm, thickness 4–8 mm) were prepared by the melt-quenching technique. As, Sb, Se and Ge (99.99% pure) obtained from Kochlight Company, UK were used. The required amount of materials were placed in a cleaned quartz tube. This is evacuated to a vacuum better than 10^{-3} mm of Hg and sealed in an argon atmosphere. The sealed ampoule is placed in a horizontal rotating furnace, the temperature raised to 1000°C and held at this temperature for 24 hr. The rotation ensures proper mixing of the constituents. The melt is then cooled to 800°C and quenched in water at 90°C. Care is taken to see that the ampoule remains vertical during quenching. The ampoule is annealed at a temperature about 5° lower than the glass transition (T_g) of the glass for an hour and then cooled slowly to room temperature. The quartz tube is broken carefully to remove the glasses without damaging the sample. Preannealing helped in removing the mechanical stress and in obtaining fairly strong samples.

For ultrasonic velocity measurements the two faces of the glasses were polished by handlapping and made parallel to each other (wedge angle better than 0.2 sec). The flatness and parallelism were checked by a dial gauge and the length of the samples was measured with a micrometer at room temperature.

3. Velocity measurements

The longitudinal and shear wave velocities have been measured in these glasses using a pulse echo interferometer which operates at a frequency of 10 MHz (Srinivasan *et al* 1975; Kartha *et al* 1980), and based on the McSkimin pulse superposition technique (McSkimin 1961; Papadakis 1976). Coaxial gold-plated X cut and Y cut quartz transducers (supplied by Bharat Electronics Ltd., Bangalore) of diameter 8 mm are used for generating longitudinal and shear waves. An adhesive from the special cellulose tape (Technical Trade Corporation, USA) has been used as a bonding material.

The bond for the ultrasonic measurements was made as follows. A thin plastic sheet with a circular aperture of about 10 mm diameter is cleaned and the cellulose tape is applied. This is placed on the cleaned surface of the sample and gently pressed uniformly so that the adhesive on the tape sticks to the sample. A drop of water is poured on the tape. After a few minutes the backing of the cellulose tape along with the plastic sheet is carefully peeled off with a sharp razor, leaving behind a thin layer of adhesive on the sample. The transducer is placed on this adhesive and gently pressed uniformly. This bond transfers both the longitudinal and transverse waves quite well and a good echo pattern could be obtained throughout the temperature range of 300 K to 4.2 K.

The ultrasonic velocities at low temperatures have been measured using the cryostat described elsewhere (Padaki *et al* 1985). Measurements were taken while the sample was cooled continuously at a slow rate of 10°C per hour.

4. Results and discussions

4.1 Low temperature elastic constants of Ge-Sb-Se and As-Sb-Se glasses

The ultrasonic longitudinal and transverse velocities have been measured for eight Ge-Sb-Se glasses ($\text{Ge}_{15}\text{Sb}_{10}\text{Se}_{75}$, $\text{Ge}_{20}\text{Sb}_{10}\text{Se}_{70}$, $\text{Ge}_{25}\text{Sb}_{10}\text{Se}_{65}$, $\text{Ge}_{30}\text{Sb}_{10}\text{Se}_{60}$,

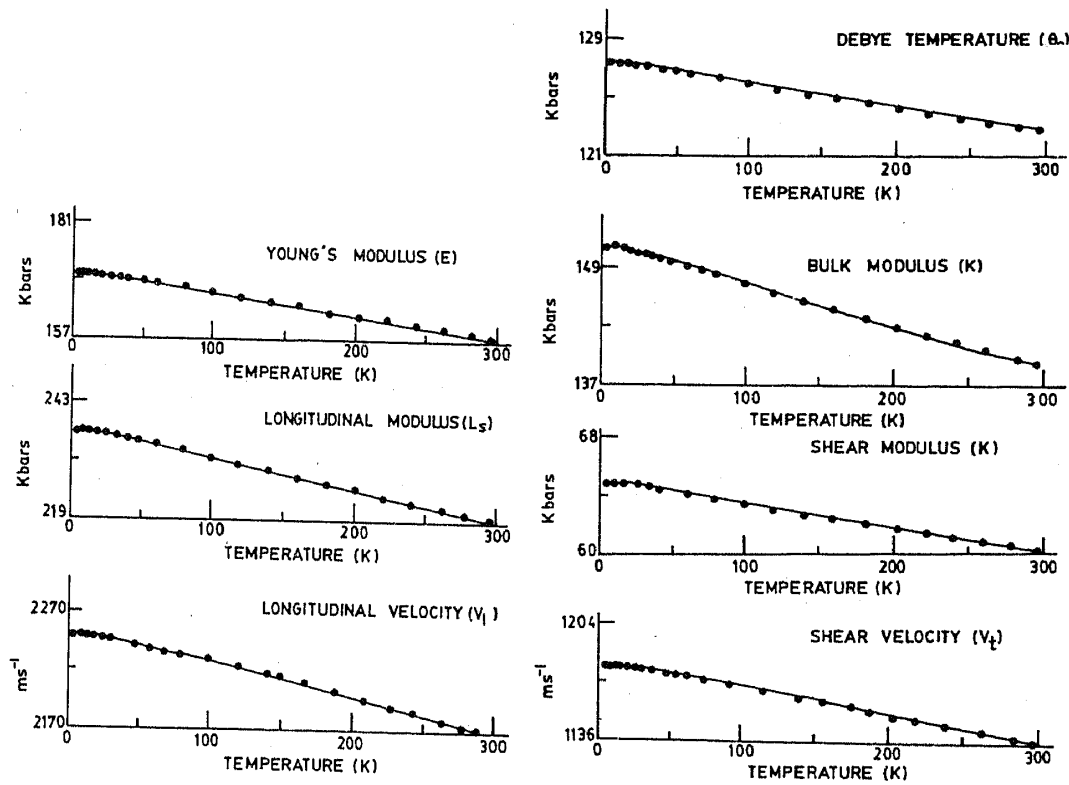


Figure 1. Temperature dependence of the elastic constants of $\text{Ge}_{15}\text{Sb}_{10}\text{Se}_{75}$ glass.

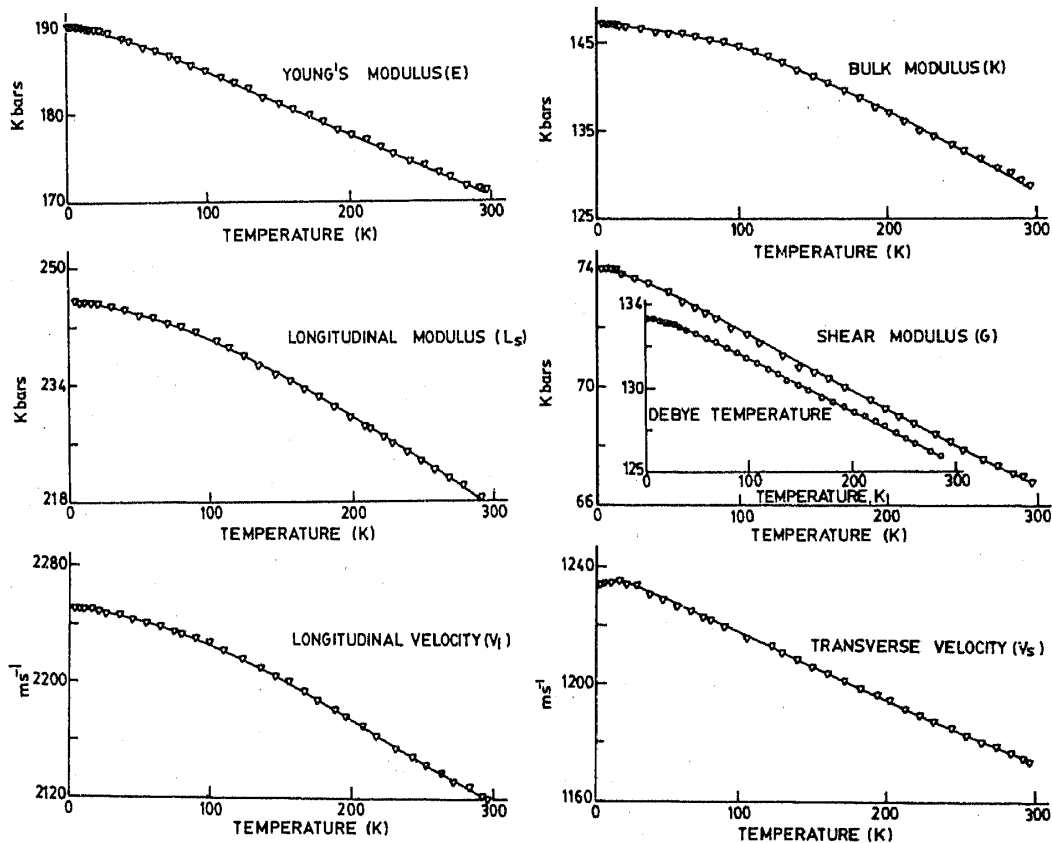


Figure 2. Temperature dependence of the elastic constants of $\text{As}_{10}\text{Sb}_{15}\text{Se}_{75}$ glass.

Ge_{20.84}Sb₁₅Se_{64.16}, Ge_{16.67}Sb₂₀Se_{63.33}, Ge_{12.5}Sb₂₅Se_{62.5} and Ge₃₂Sb₁₀Se₅₈) and eight As-Sb-Se glasses (As₂₀Sb₁₅Se₆₅, As₂₅Sb₁₅Se₆₀, As₃₀Sb₁₅Se₅₅, As₃₀Sb₁₀Se₆₀, As₃₅Sb₅Se₆₀, As₂₂Sb₁₈Se₆₀, As₃₅Sb₁₅Se₆₀ and As₁₀Sb₁₅Se₇₅) as a function of temperature from 300 K to 4.2 K. Although a lot of data could be presented we give only representative data for each glass (Ge₁₅Sb₁₀Se₇₅ and As₁₀Sb₁₅Se₇₅) (figures 1 and 2). All the elastic constants for all the glasses increase as the temperature is lowered. They reach a flat value around 4.2 K.

The low temperature elastic moduli can be explained using the quasi-harmonic model of Claytor and Sladek (1978). To compute the elastic moduli using this model, one needs the variation of specific heat and thermal expansion at all temperatures which are not available for these glasses. Instead we follow the Lakkad's anharmonic oscillator model which is simple and does not need other parameters. Lakkad (1971) derived a simple expression to estimate the temperature dependence of the elastic constants using the anharmonic oscillator model. In this model if one knows the elastic moduli at two different temperatures along with the Debye temperature one can predict the elastic moduli at any other temperature.

Following Lakkad (1971) we get an expression for any elastic moduli E at a temperature T as

$$E = E_1 + \frac{(E_1 - E_2)}{(T_2 - T_1)} (T_1 - T), \quad (1)$$

in the high temperature limit, $\theta_D \ll T$.

$$E = E_1 + \frac{E_1 - E_2}{T_2^4 - T_1^4} (T_1^4 - T^4), \quad (2)$$

in the low temperature limit $\theta_D \gg T$, where E_1 and E_2 are the elastic constants at temperatures T_1 and T_2 . Equation (1) has been used for temperatures greater than 20.5 K while equation (2) has been used in the range 20.5 K and 4.2 K.

Figures 3 and 4 clearly show the fit of the experimental data points to the Lakkad's model, for both Ge-Sb-Se and As-Sb-Se glasses. Hence we can conclude that the low temperature elastic constants for the Ge-Sb-Se and As-Sb-Se glasses can be predicted by Lakkad's model.

4.2 Composition dependence of the elastic constants of Ge-Sb-Se glasses

The longitudinal velocity (V_L), shear velocity (V_t), longitudinal modulus (L_s), Young's modulus (E), bulk modulus (K) and shear modulus (G) for the Ge_{*x*}Sb₁₀Se_{90-*x*} glasses as the content of germanium is increased is shown in figure 5a, at room temperature. The velocities and the elastic constants increase linearly up to 25 at. % of Ge and beyond this the changes are nonlinear, and the increase is steeper. Various properties like glass transition temperature (T_g), electrical conductivity, activation energy (ΔE), and density (d) (Savage *et al* 1978; Giridhar *et al* 1980, 1981; Narasimham *et al* 1981; Sudha Mahadevan *et al* 1983, 1984) also exhibit extrema at Ge₂₅Sb₁₀Se₆₅ composition. Since this nonlinear behaviour indicates a change in the basic structure of the glass Giridhar *et al* (1980, 1981) explained the properties on the basis of chemically oriented network model (CONM).

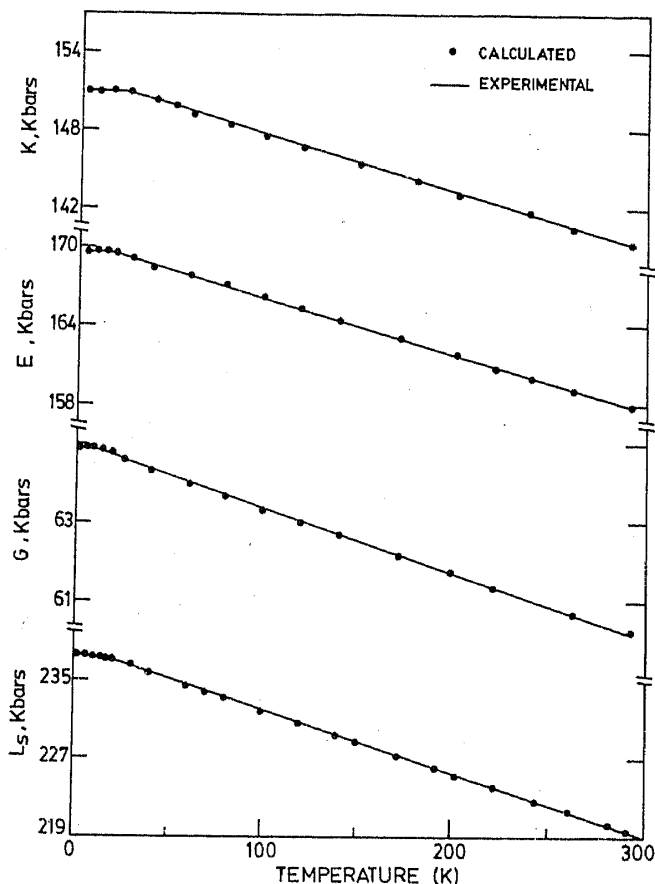


Figure 3. Temperature dependence of the calculated and experimental elastic constants of $\text{Ge}_{15}\text{Sb}_{10}\text{Se}_{75}$ glass.

The composition $\text{Ge}_{25}\text{Sb}_{10}\text{Se}_{65}$ can be written as $(\text{GeSe}_2)_{25}(\text{Sb}_2\text{Se}_3)_5$. Thus the glass structure can be pictured to be made up of cross-linked three-dimensional structural units of GeSe_2 and Sb_2Se_3 with Se or Ge in excess. At stoichiometric composition the bonds are heteropolar. If the Ge content is <25 at.%, some of the original $\text{GeSe}_2/\text{Sb}_2\text{Se}_3$ units are replaced by Se. Since Se is found in two-fold co-ordination, the strength of the resulting lattice would be lower than that of the stoichiometric composition.

In glasses with a small content of germanium, the three-dimensional tetrahedral $\text{GeSe}_{4/2}$ and trigonal $\text{SbSe}_{3/2}$ units are statistically distributed among the chains of extra selenium. When the germanium content in the glass increases, the excessive chains of selenium become gradually connected and the three-dimensional network of the glass develops due to increase of $\text{GeSe}_{4/2}$ units. This results in the strengthening of the glass framework and an increase of ultrasound velocity and elastic moduli as well as in the decrease of adiabatic compressibility. The selenium chains gradually degenerate into bridges of two selenium atoms -Se-Se-, while the increase of germanium over 15–20 at.% leads to their disappearance. The glass network in this part of compositions begins to build up from tetrahedrons $\text{GeSe}_{4/2}$ and pyramids $\text{SbSe}_{3/2}$ directly bonded to one another. This is completed in the glass containing 25 at.% of germanium, which lies on the pseudobinary section $\text{GeSe}_2\text{-Sb}_2\text{Se}_3$ and in which there is no excess selenium. The disappearance of bonds type -Se-Se-, that contribute to more advantageous space-

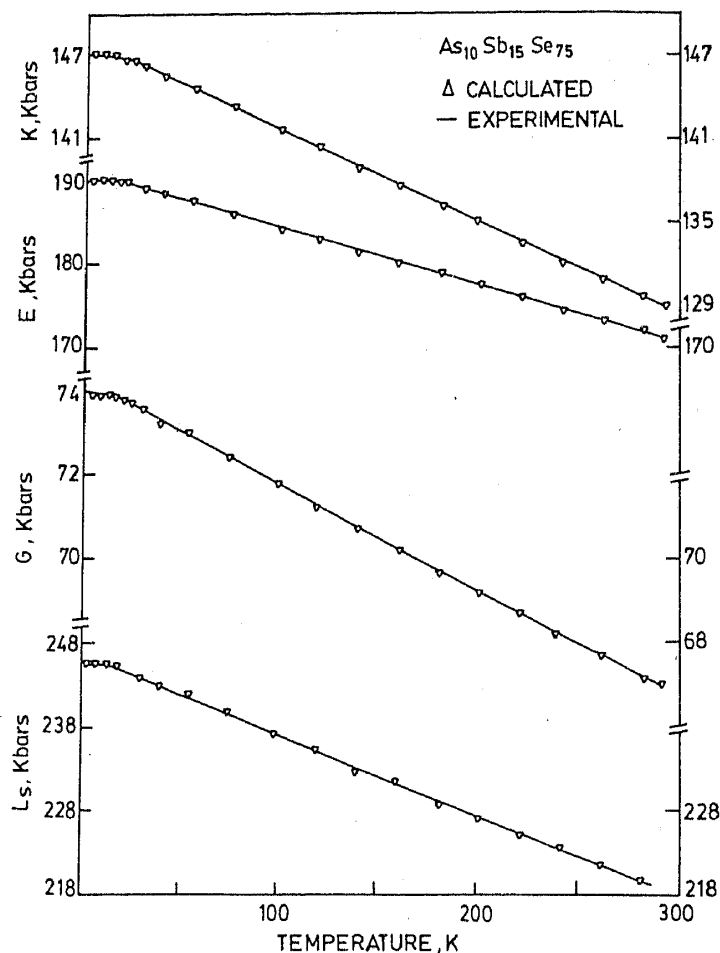


Figure 4. Temperature dependence of the calculated and experimental elastic constants of $\text{As}_{10}\text{Sb}_{15}\text{Se}_{75}$ glass.

packing of three-dimensional $\text{GeSe}_{4/2}$ and $\text{SbSe}_{3/2}$ units, result in the loosening of the structure and a decrease of density. The increase of germanium content over the stoichiometric relationship both in the binary system Ge-Se and in Ge-Sb-Se leads to an increased density; hence the moduli of elasticity rise again. Further $\text{Ge}_x\text{Se}_{100-x}$ and $\text{Ge}_x\text{As}_{60-x}\text{Se}_{40}$ glasses (Ota *et al* 1978; Tille *et al* 1977) exhibit a steep rise in velocities and elastic properties for Ge-rich glasses.

At room temperature the stoichiometric Ge-Sb-Se glasses with Sb = 10, 15, 20 and 25 have almost constant velocities and elastic constants as seen in figure 5b.

The bulk modulus (K) is related to mean atomic volume (V_a) by $K = \text{constant} \times V_a^{-m}$, $m = 4/3$ for a wide range of materials including alkaline earth silicate glasses and $m = 4$ for oxide and As-Se glasses. Glasses behave like crystals in showing an increase in bulk modulus with a decrease in volume. This trend is reversed in GeS_2 - GeSe_2 (Ota *et al* 1978) and As_2S_3 - As_2Se_3 glasses (Ota *et al* 1973; Thompson and Bailey 1978). Variation of ΔE , $\log \sigma$, T_g with atomic percent of Ge for Ge-Se-Sb glasses and $\log K$ vs $\log V_a$ for $\text{Ge}_x\text{Sb}_{10}\text{Se}_{90-x}$, $\text{Ge}_x\text{As}_{20}\text{Se}_{80-x}$ and $\text{Ge}_x\text{Se}_{100-x}$ containing Ge and Se as common elements are shown in figure 6. Taking the stoichiometric composition as reference in the $\text{Ge}_x\text{Sb}_{10}\text{Se}_{90-x}$ system an increase in Se content reduces both mean atomic volume and bulk modulus. This may be due to weakening of structure due to an increase in chains. However the relation $K = \text{const} \times V_a^{-m}$ predicts that a decrease in

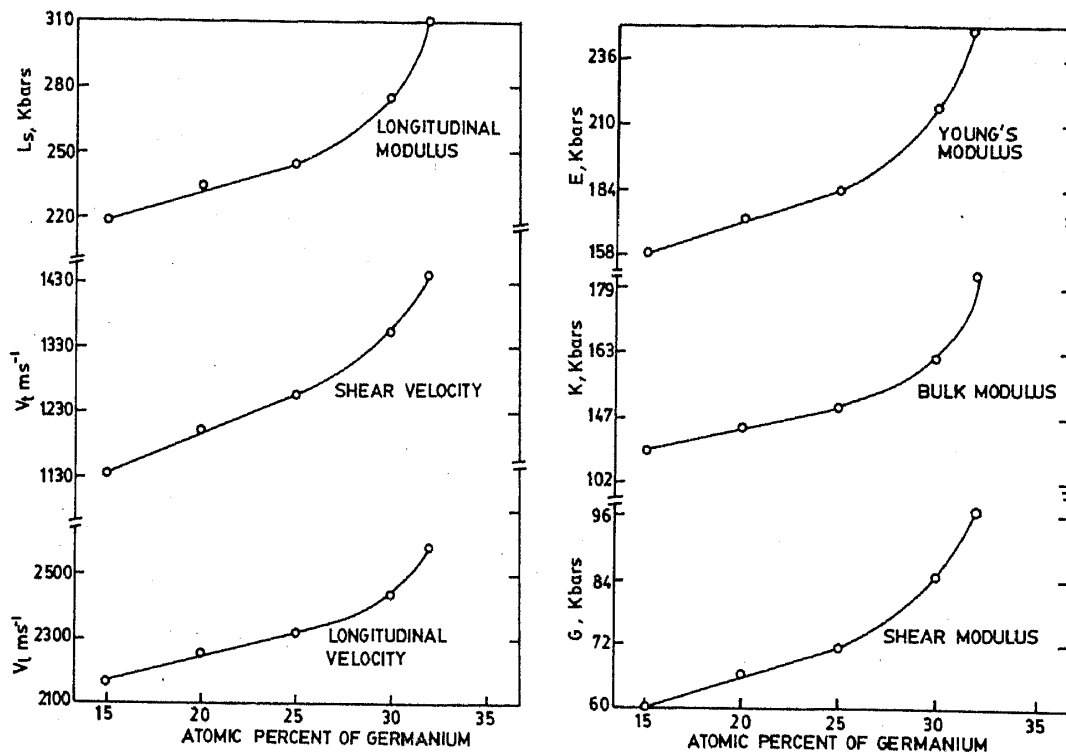


Figure 5. Variation of velocities and elastic moduli of $Ge_xSb_{10}Se_{90-x}$ glasses as Ge content is varied.

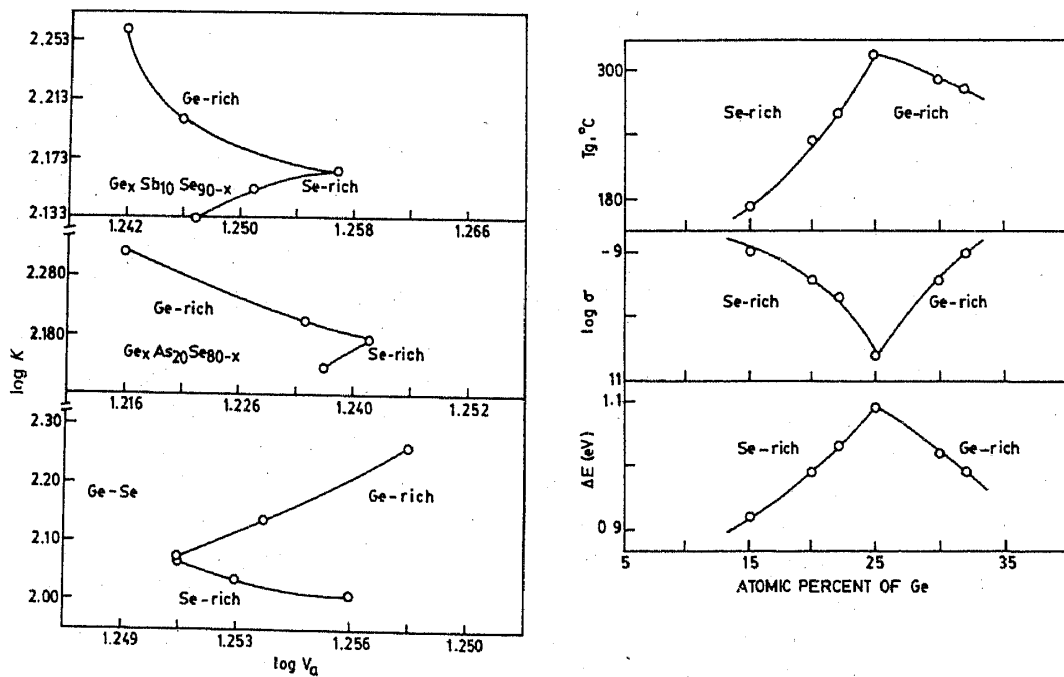


Figure 6. (a) The variation of $\log K$ with $\log V_a$ for $Ge_xSb_{10}Se_{90-x}$, $Ge_xAs_{20}Se_{80-x}$ and Ge_xSe_{100-x} glasses. (b) The variation of ΔE , $\log \sigma$ and T_g with Ge content for Ge-Sb-Se glasses.

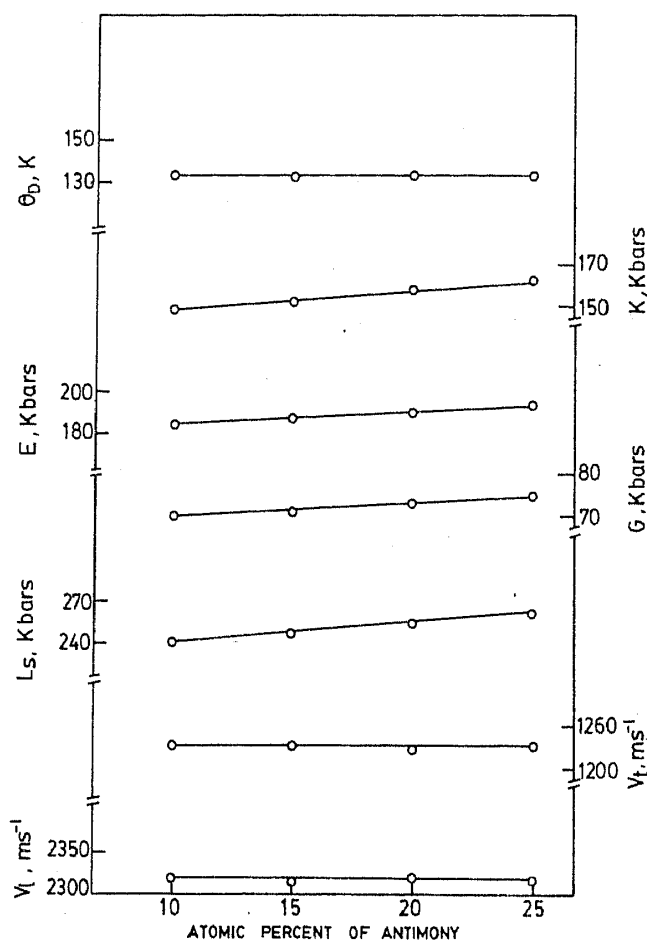


Figure 7. Variation of elastic properties for the stoichiometric $(GeSe_2)_{1-c}(Sb_2Se_3)_c$ glasses of Ge-Sb-Se system.

volume should lead to an increase of bulk modulus (K). Thus the type of bonding seem to play a prominent role in deciding the bulk modulus in addition to volume. For the Ge-rich glasses the bulk modulus increases while the volume decreased; this is due to an increase of tetrahedral network due to excess Ge. The $Ge_xAs_{20}Se_{80-x}$ glass also shows a behaviour of bulk modulus with mean atomic volume similar to the $Ge_xSb_{10}Se_{90-x}$ glass (figure 7). Ge_xSe_{100-x} glasses indicate a complete reversal in the general trend. Here taking $Ge_{20}Se_{80}$ as reference because the glass structure is made up of $GeSe_4$ tetrahedrae for Ge-rich glasses, the mean atomic volume as well as the bulk modulus increase. A similar behaviour is observed for Ge-Sb-S (Hayes *et al* 1974). Hence the type of bonding in the glasses is likely to determine the bulk modulus than increase in volume. For Se-rich region while the volume increases, the bulk modulus decreases. Thus an increase in Se content and volume contributes to a decrease of bulk modulus. The stoichiometric Ge-Sb-Se glasses have almost the same mean atomic volume and bonding leading to a constant bulk modulus. The Poisson's ratio (σ) of Se-rich Ge-Sb-Se glasses is higher than the σ of Ge-rich glass. This may be due to the structure of glass undergoing a change from chain-like to network form.

The Debye temperature (θ_D) is almost constant (133 K), because the mean atomic volume and velocities are constant.

The composition dependence of the low temperature velocities and elastic constants reveals that for $Ge_xSb_{10}Se_{90-x}$ group of glasses, various properties increase smoothly

up to stoichiometric composition $\text{Ge}_{25}\text{Sb}_{10}\text{Se}_{65}$, whereas beyond this there is a steeper rise. In the stoichiometric glasses with $\text{Sb} = 10, 15, 20$ and 25 the parameters are almost constant. It is clear that the composition dependence at low temperatures follows the same pattern as that at room temperature except for an increase in magnitude. Hence the composition dependence can be explained using the CONM model.

In order to examine the role of antimony in the low temperature elastic properties of Ge-Sb-Se glasses, the percentage change of elastic properties between room temperature and 77 K is studied. In the stoichiometric glasses with $\text{Sb} = 10, 15, 20, 25$ at.%, the percentage change in V_L, V_T, L_s, G, E, K and θ_D are respectively $-2.36, -2.49, -4.78, -5.99, -4.05$ and -2.90 and the change is the same for all compositions. This indicates that for stoichiometric glasses of Ge-Sb-Se system, though the Sb content changes, the percentage change in elastic constants is the same. Thus antimony seems to influence very little the elastic behaviour for Ge-Sb-Se glasses.

For $\text{Ge}_x\text{Sb}_{10}\text{Se}_{90-x}$ glasses with antimony kept at 10 at.%, while the content is increased (Se decreased), the elastic constants initially decrease, reach a minimum at $\text{Ge} = 30$ at.% and then increase again. So, we find that only Se or Ge content seems to induce changes in the elastic properties at low temperatures. Hence we conclude that Se or Ge content decides the low temperature elastic behaviour of Ge-Sb-Se glasses.

4.3 Composition dependence of the elastic constants of As-Sb-Se glasses

The As-Sb-Se glasses can be grouped into two categories. (a) Glasses whose composition can be represented as $(\text{AsSb})_{40}\text{Se}_{60}$. These fall along the $(\text{As}_2\text{Se}_3)(\text{Sb}_2\text{Se}_3)$ pseudo-binary section representing the stoichiometric composition of the As-Sb-Se system. (b) Glasses whose composition can be represented as $\text{As}_x\text{Sb}_{15}\text{Se}_{85-x}$. In these glasses, the $\text{As}_{25}\text{Sb}_{15}\text{Se}_{60}$ is taken as a reference stoichiometric composition and the

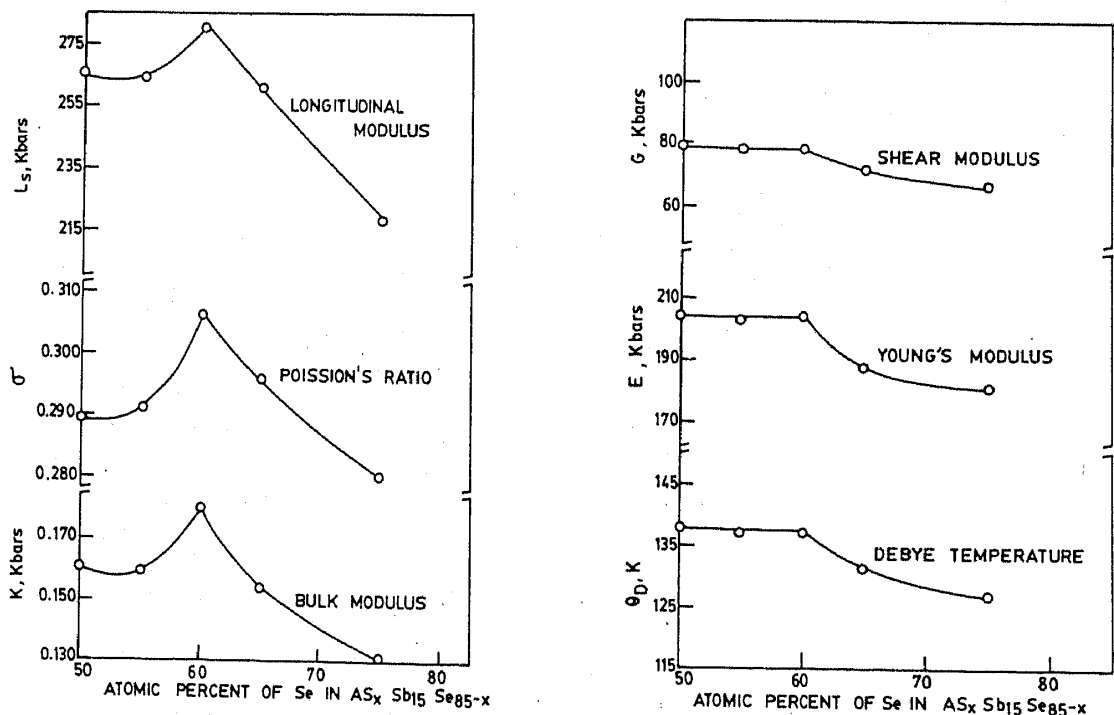


Figure 8. Variation of elastic moduli as a function of Se content for $\text{As}_x\text{Sb}_{15}\text{Se}_{85-x}$ glasses.

glasses with >60 at. % of Se are called Se-rich glasses and glasses with <60 at. % of Se are called As-rich glasses.

The variation of longitudinal modulus (L_s), Poisson's ratio (σ), Debye temperature (θ_D), shear modulus (G), Young's modulus (E) and bulk modulus (K) for the $(As, Sb)_{40}Se_{60}$ glasses as the Sb content is increased is shown in figure 9. It is clear that the elastic moduli increase monotonically smoothly. The room temperature elastic constants are in good agreement with the measurements of Giridhar *et al* (1984). The extrapolated elastic moduli for zero at. % of Sb give the elastic constants for As_2Se_3 which are in good agreement with the measurement of Soga and Kungu (1973) for As_2Se_3 .

The observation of the increase of mean atomic volume in isostructural compounds indicates an increase of bulk modulus (Anderson and Nafe 1965). For these glasses it is seen that the bulk modulus increases with increasing Sb_2Se_3 content while the corresponding volume is also increased. This shows that the type of bonding rather than the volume has a greater influence in determining the bulk modulus of these glasses. Such a dependence has been observed in many other glasses (Sudha Mahadevan *et al* 1983).

The variation of T_g , density have been observed by Giridhar *et al* and the elastic moduli do depend on these parameters. A qualitative explanation can be given for the variation of elastic moduli as follows. The T_g shows a slight increase with the increasing Sb content, indicating the strengthening of glass which is reflected in the increase of elastic moduli. The small increase is because As and Sb are isovalent and replacement of As by Sb does not drastically alter the basic structure of the glass. This is supported by the nearly equal bond energies of 52 kcal/mol and 51 kcal/mol of As-Se and Sb-Se bond (Giridhar *et al* 1982).

The elastic moduli G , E , K , L_s , σ and Debye temperature θ_D for $As_xSb_{15}Se_{85-x}$ glasses as the Se content is increased is shown in figure 8. Taking $As_{25}Sb_{15}Se_{60}$ as the

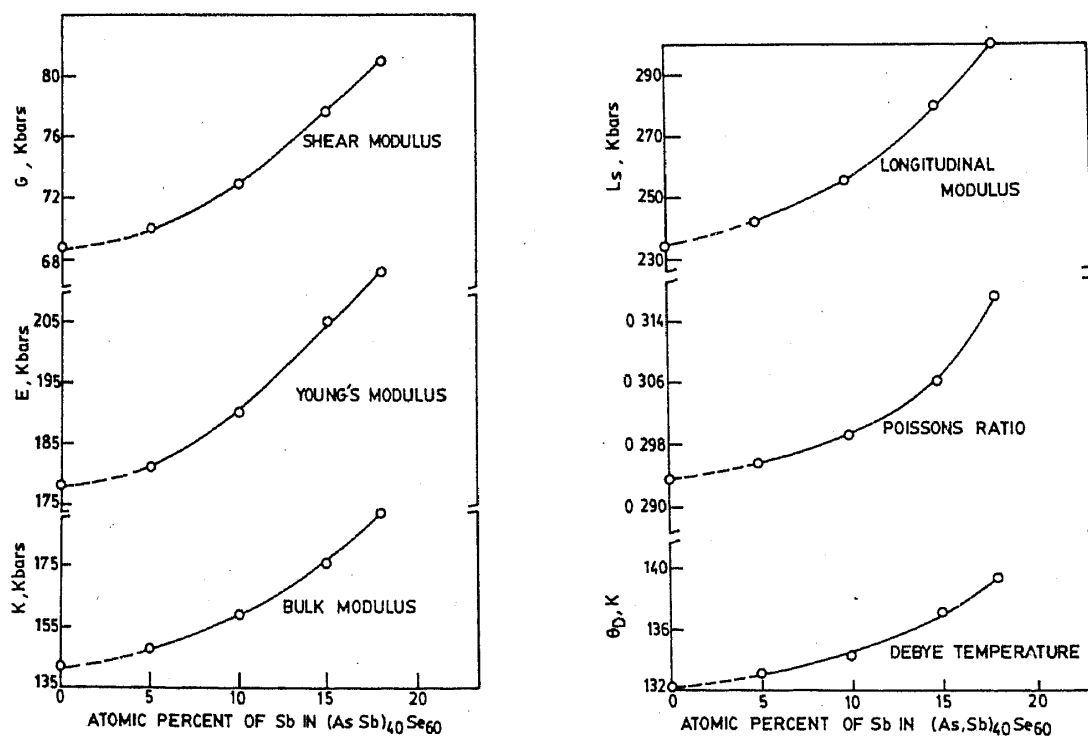


Figure 9. Variation of elastic moduli for $(As, Sb)_{40}Se_{60}$ glasses as a function of Sb content.

reference stoichiometric composition it is seen that the elastic moduli G , E and Debye temperature (θ_D) for As-rich glasses are constant whereas for Se-rich glasses they decrease sharply. These observations are in good agreement with the idea that higher the Se content lower the elastic moduli. The elastic moduli K , L_s and Poisson's ratio σ on the other hand show a decreasing trend on either side of the stoichiometric composition both for As as well as Se-rich glasses, with a steeper decrease on the Se-rich side compared to the As-rich side.

Using the CONM model and following the discussion for Ge-Sb-Sb glasses, we try to give a qualitative explanation for the observed behaviour of elastic moduli. The $As_{2.5}Sb_{1.5}Se_{6.0}$ glass can be thought of as made up of completely crosslinked three-dimensional structural units of As_2Se_3 and Sb_2Se_3 only with either As or Se in excess. For As-rich glasses some of the original AsSe units are replaced by As which does not drastically alter the resulting atomic arrangement. The As-As bond energy is 46 kcal/mol which is slightly less than the As-Se bond energy. However, with decreasing Se content in As-rich glasses the Sb_2Se_3/As_2Se_3 ratio progressively increases which slightly increases T_g . For the Se-rich glasses some of the original As_2Se_3 units are replaced by Se. Since Se is generally found in two-fold co-ordination, the T_g for these glasses can be expected to show a deep decrease. With increase in the Se content, the Sb_2Se_3 units would increase for Se-rich glasses which would increase T_g . But the lower the coordination number of Se can make T_g fall continuously for these glasses and hence the elastic moduli. The composition dependence of K and σ can be linked with the As_2Se_3 content, and As-Se bonds decide the elastic properties of these glasses. All the elastic properties show a general increase with increasing As_2Se_3 content. The Debye temperature θ_D is similar to that of selenide glasses (Sudha Mahadevan *et al* 1983). θ_D shows a variation with composition for both $(As, Sb)_{40}Se_{60}$ and $As_xSb_{1.5}Se_{8.5-x}$ series of glasses. Hence the As-Sb-Se system is relatively weakly bonded, with particularly low ultrasonic velocities and Debye temperature.

The low temperature elastic constants for various compositions of As-Sb-Se glasses at 77 K can be discussed now. It is seen that for $As_xSb_{1.5}Se_{8.5-x}$ glasses the elastic constants remain constant as the Se content is increased up to 60 at.%, and beyond the stoichiometric composition $As_{2.5}Sb_{1.5}Se_{6.0}$ they decrease drastically. This is similar to what has been observed at room temperature. So, the composition dependence can be explained using the CONM model. For the $(As, Sb)_{40}Se_{60}$ group of glasses, there is a smooth increase of elastic constants, and the percentage change in the elastic constants over the temperature range 296.4 K to 77 K is appreciable. For $As_xSb_{1.5}Se_{8.5-x}$ glasses in the As-rich range, the percentage change in elastic constants is almost constant. For selenium-rich glasses beyond stoichiometric composition, even a small addition of selenium induces a large percentage change in elastic constants. Hence, it could be concluded that selenium content plays a dominant role in deciding the low temperature elastic behaviour of As-Sb-Se glasses. In the case of $(As, Sb)_{40}Se_{60}$ glasses, the percentage changes in elastic constants are again almost constant indicating that although the As-Sb content is changing, it does not very much affect the elasticity of these glasses because the selenium content is constant. We therefore conclude that selenium plays a key role in deciding the elastic behaviour of As-Sb-Se glasses both at room and low temperatures.

A comparison of the elastic behaviour of the Ge-Sb-Se and As-Sb-Se glasses reveals that they have a negative temperature coefficient of elastic constants for all the glasses studied. A comparison can also be made of the two glasses, $Ge_{30}Sb_{10}Se_{60}$ and $As_{30}Sb_{10}Se_{60}$ in which only Ge has been replaced by As. This clearly shows that Ge-

based glasses are much tougher than As-based glasses, which is clearly indicated by the higher elastic moduli in Ge-based glasses. It also shows that the Ge-based glasses are less sensitive to temperature than As-based glasses.

5. Conclusions

(i) The elastic moduli of both Ge-Sb-Se and As-Sb-Se glasses smoothly increases as the temperature is decreased down to 4.2 K. (ii) The temperature dependence of low temperature elastic constants can be explained with Lakkad's anharmonic oscillator model for both the glasses. (iii) The composition dependence of elastic moduli both at low and room temperatures can be explained using the chemically ordered network model. (iv) The germanium-based glasses are much harder and less sensitive to the temperature than arsenic based glasses.

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