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Elastic properties of As-Sb-Se glasses

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Abstract. Results of measurement of elastic modulii on As-Sb-Se glasses are reported and their composition dependence discussed. The Young's and the shear modulii lie in the range of 170–210 and 65–80 kb respectively. These values are typical of chalcogenide glasses. For (As, $Sb)_{40}Se_{60}$ glasses, the modulii increase monotonically with increasing Sb_2Se_3 content. The observed composition dependence of the moduli for the $As_xSb_{15}Se_{85-x}$ glasses is examined in terms of the chemically ordered structural units in the glasses.

Keywords. As-Sb-Se glasses; elastic properties; CONM model.

1. Introduction

The results of measurement of glass transition temperature (T_g), electrical conductivity and density (d) on glasses of the As-Sb-Se system were reported earlier (Giridhar and Sudha Mahadevan 1982). The study covered two groups of glasses: (i) those whose composition could be represented by (As, $Sb)_{40}Se_{60}$ and (ii) those whose composition could be represented by $As_xSb_{15}Se_{85-x}$. The (As, $Sb)_{40}Se_{60}$ glasses fall along the (As_2Se_3) (Sb_2Se_3) pseudobinary section and represent the so-called 'stoichiometric' compositions of the As-Sb-Se system. The T_g, electrical conductivity and d of these glasses showed a monotonic increase with increasing Sb_2Se_3 content. In the $As_xSb_{15}Se_{85-x}$ glasses, with the stoichiometric $As_{25}Sb_{15}Se_{60}$ composition as reference, glasses with more than 60 at. % of Se were referred to as Se-rich glasses and those with less than 60 at. % of Se as As-rich glasses of this family. The As_xSe_{100-x} and $Ge_xSb_{15}Se_{85-x}$ glasses show an extremum in T_g and d at the respective stoichiometric compositions (Myers and Felty 1967; Mohan *et al* 1981; Narasimham *et al* 1981; Giridhar *et al* 1981). The composition dependence of T_g and d of the $As_x Sb_{15} Se_{85-x}$ glasses exhibit an interesting feature, namely, that the T_g and d of the As-rich glasses of this family are higher than those of the $As_{25}Sb_{15}Se_{60}$ composition (Giridhar and Sudha Mahadevan 1982).

The results of measurements of elastic properties on eight glass compositions are reported in this paper. Four of these compositions can be represented by (As, $Sb)_{40}Se_{60}$, while the other four belong to the $As_xSb_{15}Se_{85-x}$ family.

2. Experimental

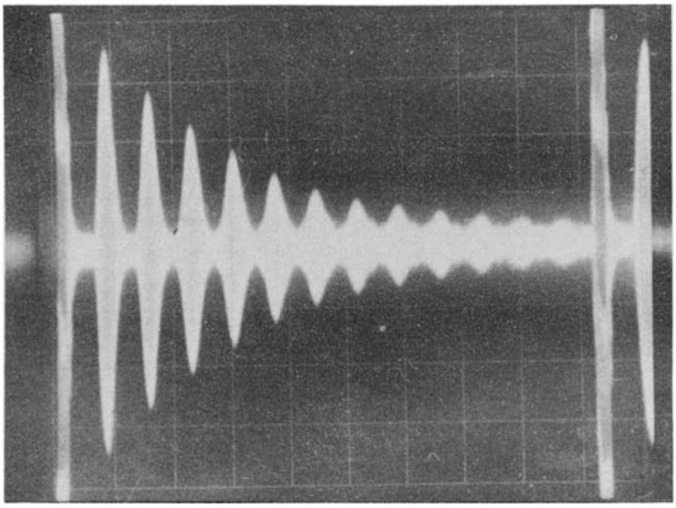
The cylindrical samples (about 12 mm in diameter and 6 mm in length) suitable for ultrasonic sound velocity measurements were obtained by the following procedure.

The elemental components (5N purity, from Koch Light Co.) in appropriate proportions were sealed in a quartz ampoule (12 mm in diameter) under a vacuum of 10^{-3} torr. The contents of the ampoule were melted in a rotary furnace at about 950°C for 24 hr. The melt was then cooled to 800°C and quenched in water at 90°C. Care was taken to see that the ampoule stayed in a vertical position during the quenching operation. Quenching in hot water rather than in cold water was found essential to prevent any cracking or shattering of the cylindrical sample during further processing. The ampoule was then introduced into a tubular furnace where the glass was annealed at a temperature of about 5° higher than T_g for 1 hr and then brought to room temperature by slow cooling. Just before breaking open, the ampoule was chilled in an ice bath for 15 min to facilitate retrieval of the specimen from the ampoule. The faces of the cylindrical samples thus obtained were rendered flat and parallel (the wedge angle being better than 0·2 sec) using a lapping-polishing jig specially designed and fabricated for this purpose. Using Salol (phenyl salicilate) as the bonding material the longitudinal and transverse velocities in the samples were measured (at 25°C) by using 10 MHz X-cut and Y-cut transducers, by McSkimin's pulse superposition technique (McSkimin 1961; McSkimin and Andreatch 1962). As already indicated (Sudha Mahadevan *et al* 1983), an ultrasonic pulse echo interferometer (supplied by Systems Dimensions, Bangalore, model SDUI-003) in conjunction with a 50 MHz Philips oscilloscope and frequency/time interval counter (accuracy of one nsec) was used for this purpose. The accuracy of velocity measurements limited mainly by thickness measurements (for which a Mitutoyo height master transfer stand combination was used), was 0·03 %; A spread of about 1·5 % was observed in the velocities in different specimens of the same composition. The typical quality of the echo pattern obtained in our set up is shown in figures 1–3. A train of 10–12 echoes could be obtained in most cases (figure 1); this is because of the high parallelism of the faces. The measurement of the delay time was facilitated by the good resolution obtained in the amplitude of the expanded echoes (figures 2 and 3).

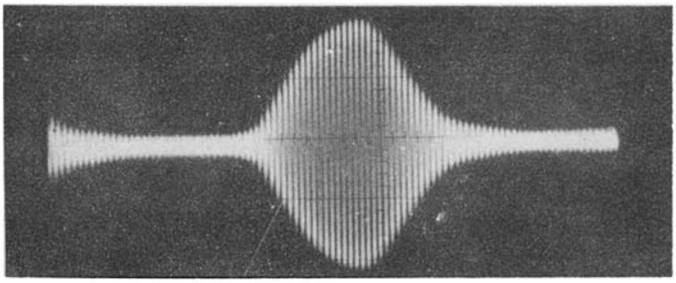
3. Results and discussion

3.1 (As, Sb)$_{40}$Se$_{60}$ glasses

The results for these glasses are summarised in figure 4 and table 1. The shear (G), the Young's (E), the bulk (K) modulii and the Poisson's ratio (σ) of (As, Sb)$_{40}$Se$_{60}$ glasses increase monotonically with increasing Sb_2Se_3 content (figure 4). Extrapolation of G, E, K and σ values (figure 4) of these glasses to zero Sb_2Se_3 content, which corresponds to As_2Se_3, gives the values of modulii which agree well with one set of reported values for As_2Se_3 (Thompson and Bailey 1978). The other values (Hilton and Hayes 1975; Soga and Kunugi 1973) fall slightly away from the extrapolated data. Also shown in figure 4 is the variation of the mean atomic volume with composition. For isostructural crystalline compounds, the bulk modulus increases with decrease in volume (Anderson and Nafe 1965). However, in our discussion (Sudha Mahadevan *et al* 1983) of the variation of K with mean atomic volume of several chalcogenide glass systems, namely Ge-Sb-Se, Ge-As-Se, Ge-Sb-S and Ge-Se, it was seen that the mean atomic volume is not the only factor determining the bulk modulus of these glasses. Besides volume, other factors such as the nature of the type of bonding could also be effective in



(1)



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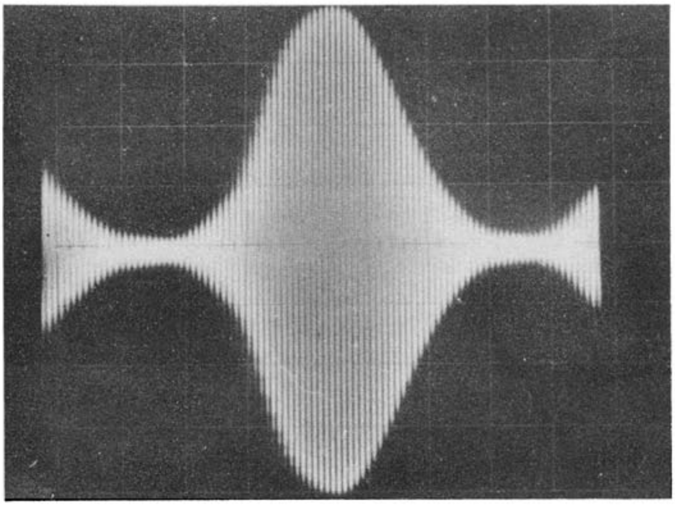

(3)

Figures 1–3 **1.** Typical exponential echo train for a $As_{10}Sb_{15}Se_{75}$ sample for longitudinal waves. **2.** Expanded echo wave form for pulse superposition for $p = 2$, minimum amplitude. **3.** Expanded echo wave form for pulse superposition for $p = 2$, maximum amplitude.

determining the bulk modulus. In $(As, Sb)_{40}Se_{60}$ glasses, (figure 4) the bulk modulus increases with increasing Sb_2Se_3 content while the corresponding volume has also increased. Therefore, the type of bonding, rather than the volume has greater influence in determining the bulk modulus of these glasses.

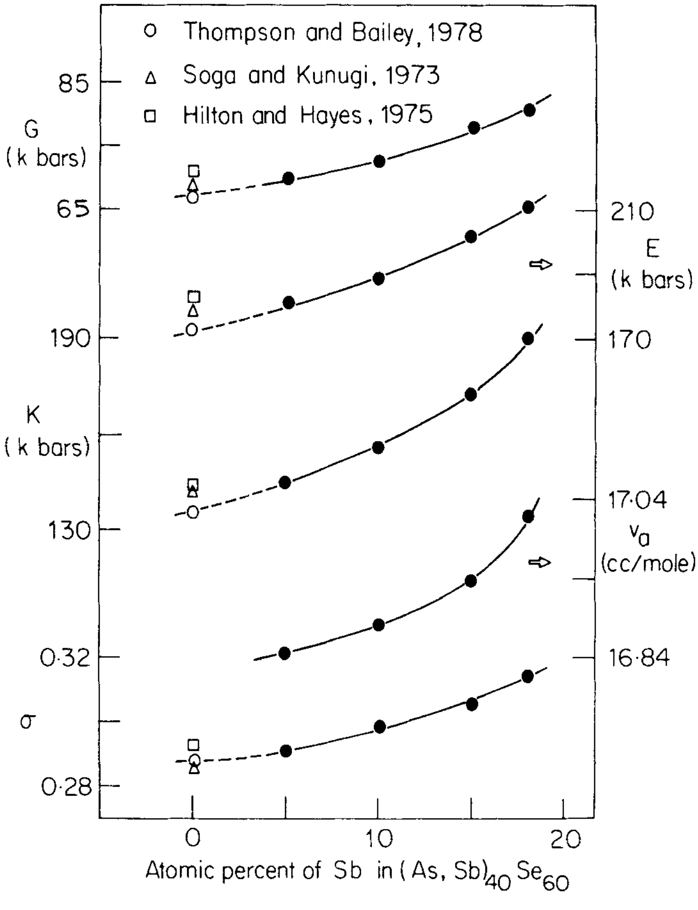

Figure 4. Variation of elastic modulii and mean atomic volume for $(As, Sb)_{40}Se_{60}$ glasses shown as a function of Sb content. Data for As_2Se_3 are from literature.

Table 1. Elastic data for As-Sb-Se glasses

Composition (As:Sb:Se)	d(g/cc)	Long. vel. C_l (m/sec)	Trans. vel. C_t (m/sec.)	Shear mod. G (kbars)	Young's mod. E (kbars)	Bulk mod. K (kbars)	Poisson's ratio σ
35:15:50	4·990	2302	1253	78·34	202·05	159·97	0·2895
30:15:55	4·983	2294	1245	77·24	199·46	159·21	0·2912
25:15:60	4·980	2358	1248	77·56	202·30	173·26	0·3054
20:15:65	4·920	2243	1208	71·80	186·05	151·78	0·2957
10:15:75	4·850	2121	1170	66·39	170·14	129·66	0·2813
35: 5:60	4·730	2245	1218	70·17	181·24	144·80	0·2914
30:10:60	4·860	2281	1222	72·57	188·50	156·07	0·2987
22:18:60	5·040	2429	1263	80·40	211·40	190·14	0·3147

3.2 $As_xSb_{15}Se_{85-x}$ glasses

The data for $As_xSb_{15}Se_{85-x}$ glasses are shown in figure 5 and table 1. With the stoichiometric composition $As_{25}Sb_{15}Se_{60}$ as reference, the G and E of As-rich glasses are seen to be essentially constant while those of the Se-rich glasses show a decrease with increasing Se-content. The bulk modulus exhibits a maximum for the stoichiometric composition (figure 5). Also shown in figure 5 is the variation of the mean atomic volume with composition. Based on the decrease of the mean atomic volume with increasing As content in the As-rich glasses, an increase of bulk modulus is expected, while it is seen that the bulk modulii of these glasses have decreased (figure 5).

In Ge-Sb-S and Ge-Sb-Se systems (Hayes *et al* 1974; Hilton and Hayes 1975; Sudha Mahadevan *et al* 1983) the Poisson's ratio (σ) increases with increasing chalcogen content. As σ denotes the ratio of transverse to longitudinal strains which arise from a single tensile stress, its increase with increasing chalcogen content has been attributed to a change in glass structure from an essentially network to a chain-like form (Hilton and Hayes 1975). However, in the $As_xSb_{15}Se_{85-x}$ glasses studied presently, σ exhibits a maximum for the stoichiometric composition and there is a decrease of σ for the Se-rich glasses in contrast to the expected increase.

The chemically-ordered network model (CONM) wherein the maximum number of

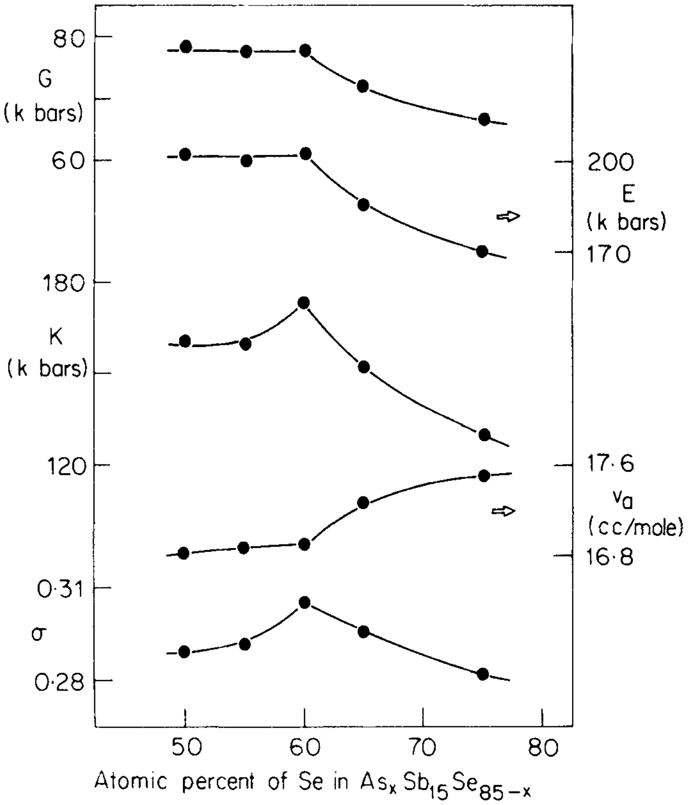

Figure 5. Variation of elastic modulii and mean atomic volume with composition for $As_xSb_{15}Se_{85-x}$ glasses.

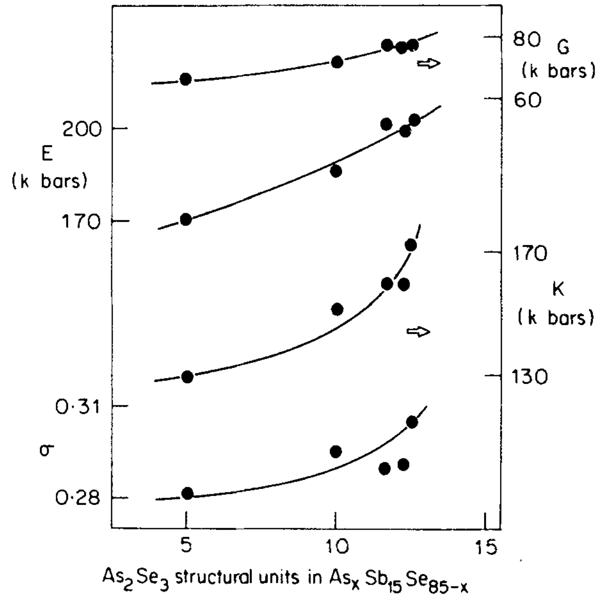

Figure 6. Dependence of elastic modulii on the As_2Se_3 structural units in $As_x Sb_{15}Se_{85-}$ glasses.

heteropolar bonds are formed first and the remaining part of the valence requirement is met with by homopolar bonding at random accounted satisfactorily for the composition dependence of the density of these glasses (Giridhar and Sudha Mahadevan 1982). For a correlation of the elastic properties with composition, the results were examined using the CONM model. A close study of the glass compositions in view of the results of figure 5 indicates the importance of As_2Se_3 content (*i.e.* As-Se bonds) in determining the elastic properties of these glasses, as the observed features in the composition dependence of K and σ can be linked to the As_2Se_3 content in these glasses. It can be seen (figure 6) that the moduli do show in general an increase with increasing As_2Se_3 content in the glasses. Though scatter in the points is seen in the dependence of the moduli on the As_2Se_3 content (figure 6), the increase in these quantities is obvious.

4. Conclusions

Elastic modulii of $(As, Sb)_{40}Se_{60}$ glasses decrease monotonically with decreasing As_2 Se_3 content in the glasses.

In the $As_xSb_{15}Se_{85-x}$ glasses, with the $As_{25}Sb_{15}Se_{60}$ glass as reference, the shear and Young's modulus of As-rich glasses do not vary much with the composition, while those of the Se-rich glasses decrease with increasing Se content. The bulk modulus and the Poisson's ratio of these glasses exhibit a maximum at the stoichiometric composition. An examination of the results indicates that the elastic properties of these glasses are sensitive to the As_2Se_3 content in these glasses.

References

Anderson O L and Nafe J E 1965 *J. Geophys. Res.* **70** 3951

Giridhar A, Narasimham P S L and Sudha Mahadevan 1981 *J. Non-Cryst. Solids* **43** 29

Giridhar A and Sudha Mahadevan 1982 *J. Non-Cryst. Solids* **51** 305

Hayes D J, Rechtin M D and Hilton A R 1974 *Ultrasonics Symp. Proc.* p. 502 (ed.) De Klerk, Institution of Electrical and Electronics Engineers, New York

Hilton A R and Hayes D J 1975 *J. Non-Cryst. Solids* **17** 339

McSkimin H J 1961 *J. Acoust. Soc. Am.* **33** 12

McSkimin H J and Andreatch P 1962 *J. Acoust. Soc. Am.* **34** 609

Mohan R, Panchapakesan T S and Rao K J 1981 *Bull. Mater. Sci.* **3** 29

Myers M B and Felty E J 1967 *Mater. Res. Bull.* **2** 535

Narasimham P S L, Giridhar A and Sudha Mahadevan 1981 *J. Non-Cryst. Solids* **43** 365

Soga N and Kunugi M 1973 *J. Phys. Chem. Solids* **34** 2143

Sudha Mahadevan, Giridhar A and Singh A K 1983 *J. Non-Cryst. Solids* **57** 423

Thompson J C and Bailey K E 1978 *J. Non-Cryst. Solids* **27** 161