ELASTIC PROPERTIES OF Ge-Sb-Se GLASSES

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The results of the measurement of transverse and longitudinal sound velocities on eight glass compositions of the Ge-Sb-Se system are reported and their elastic moduli evaluated. While the velocities, elastic moduli and Debye temperature show variation with composition for $Ge_xSb_{10}Se_{90-x}$ glasses, they are essentially constant for the glasses with stoichiometric compositions. The dependence of bulk modulus on mean atomic volume has been analysed. Both the mean atomic volume and the type of bonding are found to be effective in determining the composition dependence of bulk modulus.

1. Introduction

In our earlier communications [1-4], the results of measurements of glass transition temperature, electrical conductivity, density (d) and heat capacity on families of glasses of the Ge-Sb-Se system, with the general formulas $Ge_xSb_5Se_{95-x}$, $Ge_xSb_{10}Se_{90-x}$, and $Ge_xSb_{15}Se_{85-x}$, and also of $Ge_{16.67}Sb_{20}Se_{63.33}$ and $Ge_{12.5}Sb_{25}Se_{62.5}$ were reported and discussed. Glasses with constant atomic percent of Sb were classified as belonging to the same family of the Ge-Sb-Se system, while compositions which fall along the psuedobinary section $(GeSe_2)_{1-C}(Sb_2Se_3)_C$ were referred to as the stoichiometric compositions of the system. The composition dependence of the various properties mentioned above were found to exhibit systematic behaviour for the three families studied. The stoichiometric composition of each family exhibited extrema in the various properties as compared to the other glasses of the corresponding family. A chemically ordered network model for the atomic arrangement in the glasses, wherein the maximum number of heteropolar bonds are formed first and the remaining part of the valence requirement is met with by homopolar bonding at random, was found to account satisfactorily for the observed composition dependence of the several properties mentioned above. Based on this bonding scheme, the structure of glasses of the Ge-Sb-Se system can be pictured to be made up of structural units (s.u) of $GeSe_2$ and Sb_2Se_3 dispersed among excess Ge or Se. The stoichiometric compositions exhibit extrema in the properties because they are made up of cross-linked three-dimensional structural units of $GeSe_2$ and Sb_2Se_3 only with neither Ge nor Se present in excess [1-4].

The results of measurements of the longitudinal (C_l) and transverse (C_t) sound velocities on right glass compositions of the Ge–Sb–Se system are reported here. Four of these form the stoichiometric compositions of the system with 10, 15, 20 and 25 at.% of Sh, while the other four, along with the stoichiometric composition with 10 at.% Sb, belong to the $Ge_xSb_{10}Se_{90-x}$ family. The various elastic moduli have been evaluated and discussed.

2. Experimental

Ge–Sb–Se glasses were prepared (in 12 to 15 g batches) by heating 99.999% pure elements (from Koch Light *Co.*, **U.K.**) in sealed quartz ampoules (about 12 mm diameter) for 24 h at about 1000°C. During heating the ampoule was continuously rotated to ensure homogeneity and cooled to about **700°C** and then quenched in water to form the glasses. Before breaking open the ampoules, they were annealed at about 10°C higher than the respective **glass** transition temperatures. By this preannealing step, it **was** easier to obtain mechanically strong large area samples required lor the ultrasonic measurements. The specimens for sound velocity measurement were prepared by grinding and polishing thr specimens flat (10 mm × 10 mm and **3.5** mm thick) using **a** polishing jig, which rendered the faces parallel. The thickness variation over the entire area was less than **0.2 p.** The pulse superposition technique [5,6] was employed to measure the velocities. An ultrasonic pulse echo interferometer (supplied by Systems Dimensions, Bangalore, Model SDUI-003) in conjunction with a SO MHz Phillips Oscilloscope and frequency/time interval counter (accuracy of one nanosecond) was used for this purpose. Measurements **were** made i t **25°C** using coaxially gold plated 10 MHz, X-cut and Y-cut, 8 mm diameter quartz transducers, bonded to the specimens with phenyl salicilate (Salol) which acted **as** a good bonding material at room temperature. The accuracy of velocity measurements. limited mainly by the thickness measurements was **0.03%**. However, a spread of about **1.5% was** observed in the velocities in different specimens of the **same** composition,

3. Results and discussion

Figs. 1 and *2* and table 1 summarize the **results** obtained. For $Ge_xSb_{10}Se_{90-x}$ **glasses,** the velocities increase with increasing Ge content (fig, 1), the increase being steeper for the Ge-rich glasses **as** compared to the Se-rich glasses. While the velocities show variation **of** about twenty **per** cent across $Ge_xSb_{10}Se_{90-x}$ compositions, they **are** seen to he essentially constant for the four stoichiometric compositions (fig. 2, table I). The elastic **moduli,** namely, the **Young's** modulus *(E)*, **Bulk** modulus *(K)*, Shear modulus (G) and Poisson's ratio (σ) were calculated for these **glasses** using standard expressions. *E*, *K,* and *G* lie in the range of 150–250 kbar, 130–180 kbar and 60–100 kbar, **values** which are
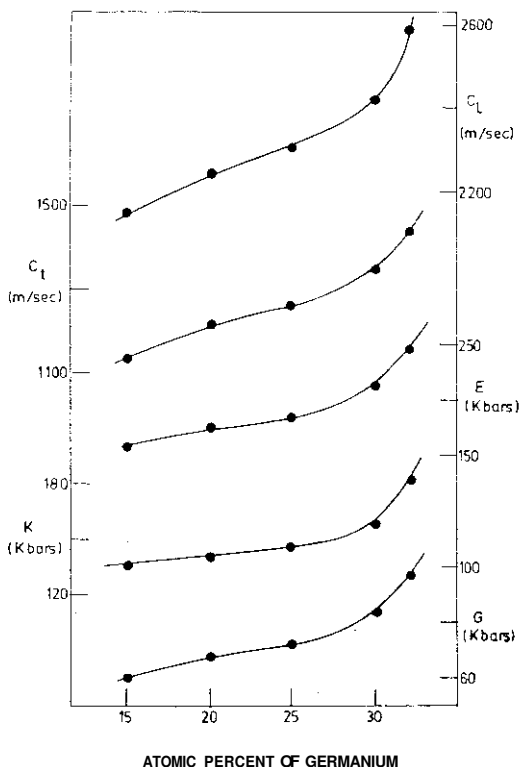
Fig. 1. Variation of C_l, C_t, E, K and G with composition for $Ge_xSb_{10}Se_{90-x}$ glasses

typical of chalcogenide glasses. It is interesting to note that the steep increase in velocities in Ge-rich glasses (fig. 1) is also observed in Ge_xSe_{100-x} and $Ge_xAs_{60-x}Se_{40}$ glasses [7,8].

For isostructural crystalline compounds, a relationship of the form

$$K = \text{constant} \times V_a^{-m} \tag{1}$$

has been found valid between the bulk modulus and the mean atomic volume V_a, with m equal to $\frac{4}{3}$ for a wide range of materials [9,10]; for elements. a change in volume is usually accompanied by a greater change in bulk modulus, with m of the **order** of **4** to **5** [11]. **The** situation is not simple in **glasses** and various types of behaviour have been observed. While **several** alkaline earth silicate **glasses** follow **eq.** (1) with **m** equal to $\frac{4}{3}$ [12], **several** other oxide **glasses** [13] and As–Se glasses [11] have **a value** of **m** of the order of 4. **A value** of $\frac{4}{3}$ **for** **m** of GeO_2–SiO_2 crystals, increases to **6** for the corresponding glassy state of

Table 1
Elastic data for Ge-Sb-Se glasses

No.	Composition Ge:Sb:Se	Longitudinal velocity C_l (m/s)	Transverse velocity C_t (m/s)	d (g/cm³)	Young's modulus E(kbars)	Shear modulus G(kbars)	Bulk modulus K(kbars)	Poisson's ratio σ	Debye temperature Θ_D(K)
a)	15:10:75	2151	1137	4.66	158	60	136	0.308	123
b)	20:10:70	2247	1215	4.60	176	68	142	0.293	130
c)	25:10:65	2312	1260	4.52	185	72	146	0.289	135
d)	30:10:60	2422	1350	4.61	214	84	158	0.275	145
e)	32:10:58	2586	1443	4.65	247	97	182	0.274	155
f)	20.84:15:64.16	2299	1237	4.67	185	71	152	0.297	132
g)	16.67:20:63.33	2306	1240	4.8	191	74	157	0.296	133
h)	12.5:25:62.5	2297	1248	4.94	199	77	158	0.291	134

ATOMIC PERCENT OF ANTIMONY
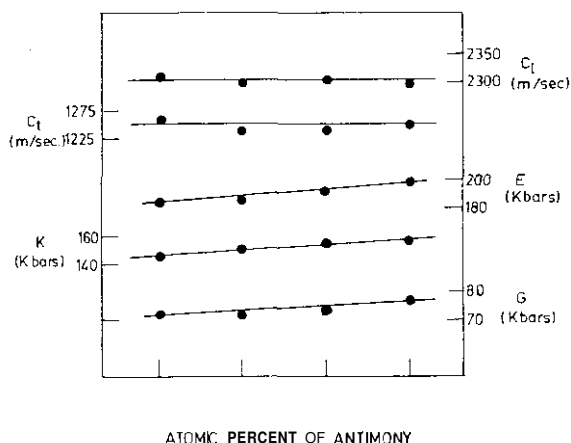
Fig. 2 Variation of C_1, C_t, E, K and G for the stoichiometric glarier $(GeSe_2)_{1-c}(Sb_2Se_3)_c$ of the Ge–Sb–Se system.

the two compounds [7]. Thus these **glasses** behave like crystalline materials **in** that they have a positive value of m indicating an increase in bulk modulus with decrease in volume. However, in several other **glass** systems like GeS_2–$GeSe_2$ [7] and As_2S_3–As_2Se_3 [14,15] the trend **of** the K versus V_a dependence is itself reversed, and glasses of smaller volume have smaller hulk modulus than **glasses** of **larger** volume. Fig. 3 shows the log V_a data for $Ge_xSb_{10}Se_{90-x}$ glasses obtained presently, along with the data for $Ge_xAs_{20}Se_{80-x}$ and Ge_xSe_{100-x} **glasses** [7,8]. **Also** shown in fig. 3 are the corresponding variations of the mean **atomic** volume with composition **for** the three **cases.** With the stoichiometric composition (the composition where the basic s.u. comprising the glass are made **up** of only heteropolar bonds) in each case as reference, addition of Ge is seen to increase the hulk modulus **of** the glasses (as seen for the Ge-rich glasses, fig. 3) while addition **of** Se is **seen** to reduce their bulk modulus. This behaviour is understandable because an increase in Se in Se-rich **glasses** increases the chain-like character which is likely to weaken the structure. The excess Ge in Ge-rich glasses is likely to strengthen the structure by increasing the tetrahedral network arrangement. Further, the log K versus log V_a plots (fig. 3) are not linear. A linear dependence is anyhow not to **be** expected for these compositions because **in** addition to the volume the type of bonding **is** also changing from one composition to another. Some of these features **are** discussed below.

In $Ge_xSb_{10}Se_{90-x}$ glasses (fig. 3a) with the stoichiometric composition as **reference.** it is seen that the hulk modulus decreases with increase of Se **content** for the Se-rich glasses, while the corresponding volume has decreased. Accord-
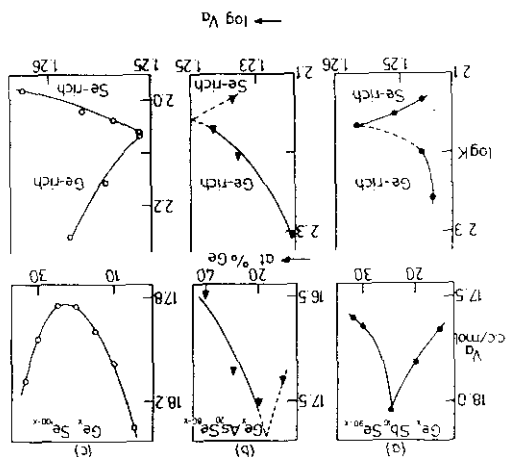
Fig. 3. Log K versus log V_a data for $Ge_xSb_{10}Se_{90-x}$ (●), $Ge_xAs_{20}Se_{80-x}$ (▲) and Ge_xSe_{100-x} (○) glasses. Also shown in the figure are the corresponding volume variations with composition for the three cases. (A value of 4.24 g/cm³ has been used for d of $GeSe_2$ [3] to calculate its mean atomic volume.)

ing to eq. (1) a decrease in volume should lead to an increase in the bulk modulus. The observed decrease in bulk modulus in spite of the decrease in volume shows that in addition to volume, the type of bonding is also important in determining the composition dependence of bulk modulus in these glasses. For the Ge-rich glasses, the bulk modulus increases with increase in Ge con-tent and the corresponding volume has decreased. In this case, the increase in tetrahedral Ge content as well as the reduction in volume could have both contributed to the increase in bulk modulus. The behaviour is similar for the $Ge_xAs_{20}Se_{80-x}$ glasses (fig. 3b). In the Ge_xSe_{100-x} glasses experimental data indicate (fig. 3c) that there is a reversal in the general trend of the dependence of (i) the mean atomic volume on the Ge content and (ii) of bulk modulus on the mean atomic volume, at the composition $Ge_{20}Se_{80}$. At this composition, the glass structure is made up of tetrahedral $GeSe_4$ s.u. [7,16]. Therefore the composition $Ge_{20}Se_{80}$, whose basic s.u. is made up of only heteropolar bonds is taken as the reference composition in this system. With this composition as reference, increase in Ge content is seen to increase the bulk modulus of Ge-rich glasses, while the corresponding volume has increased (fig. 3c). Here again, the type of bonding seems to have a greater influence than the increase in volume in determining the bulk modulus. For the Se-rich glasses on the other hand, (fig. 3c) the increase in Se content and the increase in volume both contribute to the reduction in bulk modulus.

It may be noted that in the Ge–Sb–Se and the Ge–As–Se systems discussed

earlier in this paper, the reference composition consists of $GeSe_2$ and Sb_2Se_3/As_2Se_3 s.u. and all the bonds are heteropolar. In the Ge–Se system also, one can expect another reversal resulting in a decrease of the mean atomic volume and bulk modulus (fig. 3c) for glasses with Ge content greater than 33.33 at.%. However, this cannot be verified experimentally because it is not possible to grow bulk glasses in this system beyond about 33.33 at.% of Ge.

In addition to the systems shown in fig. 3 a close examination of the elastic data of Ge–Sb–S glasses [17] gives examples where (i) increase in Ge-content increases the bulk modulus of the glasses while the corresponding volume has increased, (ii) the effect of increase in Ge-content and increase in volume compensate each other. and (iii) the effect of increase in Ge-content and reduction in volume both contribute to the increase in bulk modulus of the glasses. From these observations, it can be concluded that, while in general the hulk modulus can be expected to increase with the reduction in volume, the change in the type of bonding which occurs when the composition is changed is also an important factor in determining the bulk modulus of these glasses. The relative effectiveness of the two in determining the hulk modulus depends on the detailed nature of the type of bonding in the glasses.

The mean atomic volume of the stoichiometric glasses of the Ge–Sb–Se system is known to be essentially constant [3]. Therefore, their bulk modulus can be expected lo follow mainly the change in the type of bonding. These stoichiometric compositions which can he represented by $(GeSe_2)_{1-c}(Sb_2Se_3)_c$ can be considered to have essentially the same type of bonding. Thus, their hulk modulus can he expected to he nearly constant. Experimentally this is found to be satisfied (fig. 2).

Poisson's ratio gives the ratio of the lateral to longitudinal strains which arises from a single tensile stress. σ, which is 0.315 for pure Se, decreases to 0.265 for glasses with increasing Ge-content [18]. In the Ge–Sb–S system also. S-rich glasses have higher σ compared to Ge-rich glasses [17]. This has been attributed [17,18] to a change of glass structure from chain-like (polymeric) to network form. It can be seen (table I) that in Ge–Sb–Se glasses also, the Se-rich glasses have higher σ wmpared to the Ge-rich glasses.

Also listed in table 1 is the Debye temperature θ, of the glasses calculated using the standard formula

$$\theta_D = \frac{\hbar}{k}\left(\frac{3N_0}{4\pi}\frac{d}{M}\right)^{1/3}C_m,$$

where N_0 is the Avogadro's number and d and M are the density and mean atomic mass of the glass, respectively. C_m, the mean velocity is evaluated from

$$\frac{3}{C_m^3} = \frac{2}{C_t^3} + \frac{1}{C_l^3}$$

The nearly constant mean atomic volume [3] and the velocities (table 1) result in an almost constant value of about 133 K for θ, of the stoichiometric glasses, while the increase in the velocities of $Ge_xSb_{10}Se_{90-x}$ glasses with increasing

Ge-content (fig. 1) is reflected in a corresponding increase of θ_D from 123 K to 156 K for these glasses.

4. Conclusions

Transverse and longitudinal sound velocities have been measured at 10 MHz for eight glass-compositions of the Ge–Sb–Se system and the various elastic moduli and Debye temperatures have been evaluated. While the veloci-ties, Debye temperature and elastic moduli show variations for glasses of the $Ge_xSb_{10}Se_{90-x}$ family, they are found to be essentially constant for the stoichiometric compositions.

The bulk modulus data of Ge–Sb–Se glasses obtained presently have been analysed along with the data of other chalcogenide glass systems. The analysis indicates that increase of Ge-content (decrease of chalcogen content) and decrease in mean atomic volume both contribute to an increase in bulk modulus of these glasses; the relative effectiveness of the two in determining the bulk modulus depends on the nature of bonding involved in the glass system.

References

[1] A. Girdhar, P.S.L. Narasimham and Sudha Mahadevan, J. Non-Crystalline Solids 37 (1980) 165.

[2] P.S.L. Narasimham, A. Girdhar and Sudha Mahadevan, J. Non-Crystalline Solids 43 (1981) 365.

[3] A. Girdhar, P.S.L. Narasimham and Sudha Mahadevan, J. Non-Crystalline Solids 43 (1981) 29.

[4] P.S.L. Narasimham, A. Girdhar and Sudha Mahadevan, J. Non-Crystalline Solids 43 (1981) 301.

[5] H.J. McSkimin, J. Acoust. Soc. America 33 (1961) 12.

[6] H.J. McSkimin and P. Andreatch, J. Acoust. Soc. America 34 (1961) 609.

[7] R. Ota, T. Yamate, N. Soga and M. Kunugi, J. Non-Crystalline Solids 29 (1978) 67.

[8] U. Tille, G.H. Frischat and K.J. Leers, Fourth Int. Conf. on Non-Crystalline Solids, Zelterfield, 1976, ed., G.H. Frischat (Trans-Tech Publications, New York, 1977) p. 631.

[9] O.L. Anderson and J.E. Nafe, J. Geophys. Res. 70 (1965) 3951.

[10] O.L. Anderson and N. Soga, J. Geophys. Res. 72 (1967) 5754.

[11] N. Soga and M. Kunugi, J. Phys. Chem. Solids 34 (1973) 2143.

[12] N. Soga, H. Yamanaka, C. Hisamoto and M. Kunugi, J. Non-Crystalline Solids 22 (1976) 67.

[13] N. Soga, R. Ota and M. Kunugi, Mechanical Behaviour Materials, Vol. 4, eds., S. Taira and M. Kunugi (Society of Materials Science, Kyoto, 1972) p. 366.

[14] R. Ota, N. Soga and M. Kunugi, J. Soc. Mat. Sci. Japan 22 (1973) 567.

[15] J.C. Thompson and K.E. Bailey, J. Non-Crystalline Solids 27 (1978) 161.

[16] J. Ruska and H. Thurn, J. Non-Crystalline Solids 22 (1976) 277.

[17] D.L. Hayes, M.D. Reckhun and A.R. Hilton, Proc. Symp. on Ultrasonics, 1974, ed., J. De Klerk (IEEE, New York) p. 502.

[18] A.R. Hilton and D.J. Hayes, J. Non-Crystalline Solids 17 (1975) 339.

ELECTRODE EFFECTS ON THE ELECTRICAL PROPERTIES OF CHALCOGENIDE FILMS

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The effect of Al, Ag and Cr metal electrodes on the electrical properties of Ce–Se–Te films was studied. The relative case of the diffusion of metallic atoms and the accompanied tendency to nucleation leads to irreversible changes of the film resistivity while annealing. The recrystallization temperature of the chalcogenide film depends strongly on the type of the metal electrode. The observed increase in the values of resistivity after annealing, was interpreted on the basis of charged dangling bond theory

1. Introduction

Transformations of amorphous films to crystalline phases could he studied using different techniques e.g., optical transmission [1], X-ray diffraction [2], electron beam exposure [3] and electrical conductivity measurements. **Measure-**ment of conductivity is a sensitive tool, hut in this case metal electrodes should he applied to the film specimen. Studies have shown that contact may play a crucial **role** in determining the structure and hence the resistivity of amorphous films [4]. The results of different investigators [5,6] **have** shown that amorphous films crystallize below their normal crystallization temperatures when brought into contact with certain metals.

The mechanism leading to the lowered crystallization temperature **has** been interpreted as due to mass transport at the interface between films [7], or by lowering of the apparent binary eutectic temperature [8].

The glass formation **range** in the system Ce–Se–Te **was** studied for hulk and thin films [9,10]. Studies on Ge_4Se_5Te films showed that the composition as well as the current–voltage characteristics were independent of the film thick-**ness** [11].

The object of the present work is to report the effect of metal contact on the structure and resistivity of $Ge_2Te_5Se_3$ films. The influence of different metal electrodes on the chalcogenide film character during annealing was **also** investigated. **The** electrical changes produced within the chalwgenide film **are** correlated to corresponding structural changes by using X-ray diffraction and