

A note on the composition dependence of elastic properties of Se-P glasses

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Abstract. Longitudinal and shear wave ultrasonic velocities are reported in Se-P glasses over the composition range 0-50 at % P. The glass transition temperatures T_g show maxima at 30 and 50 at % of P, in consonance with earlier data. The bulk modulus shows minima at these compositions, contrary to the expectation of maxima. These are discussed in relation to the formation of compounds at specific compositions and the nature of the covalent bonding in the glasses.

Keywords. Chalcogenide glasses; elastic properties; composition dependence.

1. Introduction

Composition dependent variations of physical properties of co-valently bonded glasses are very interesting in relation to the nature of short range order and bonding in these systems. The structure of co-valently bonded glasses are often well represented by the Zachariasen model (1932) which essentially suggests that a small variation in the bond lengths and bond angles from the ideal crystalline values is the cause for the absence of long range order. It is also known that in co-valently bonded glasses, particularly chalcogenide systems, the total co-ordination at any atom is insensitive to the changes in chemical composition (Mott 1967). Most of the binary chalcogenide systems have a series of congruently melting compounds in the binary phase diagrams. Thus at these compositions, the formation of three-dimensional net work is complete because valency requirements are completed. At non-stoichiometric compositions this is not so easy. This behaviour suggests the possibility of interesting changes in the physical properties of glasses at these compositions.

There is some amount of work on several chalcogenide systems (particularly V b-VI b systems) where such dependences are seen. The thermal expansivity of As-S glasses shows a minimum at 40 at. % As (Tsuchihashi and Kawamoto

1971 ; Novoselova *et al* 1971). At 40 at % As in As-S system, a maximum in ultrasonic velocities is also noticed (Vinogradova *et al* 1967). Minima in the concentration dependence of optical gap, activation energy and thermo-power were also noticed (Hurst and Davis 1974). Maxima were noticed in the electrical conductivity, density and thermal conductivity (Arai *et al* 1972 ; Renninger and Averback 1973 ; Kuriyama 1975). All extrema were at 40 at. % As which corresponds to the compounds As_2Se_3 and As_2S_3 . Similarly the glass transition temperatures of Se-P system show interesting changes as a function of P content up to 50 at % P (Blachnik and Hoppe 1979). A minimum in activation energy at 15 at % P is also reported (Kesatkin and Borisova 1974). We have measured the elastic properties in the Se-P systems as a function of composition.

2. Experiments and Results

The samples of Se-P were produced as suggested by Blachnik and Hoppe by quenching sealed quartz ampoules containing the constituent elements in ice water mixture. The samples produced were cylindrical in shape, 8 mm in diameter and 10-15 mm in length. These were confirmed to be amorphous by DSC and x-ray diffractometry. The ultrasonic velocities were measured at 25°C using an ultrasonic interferometer (Srinivasan *et al* 1975). This uses the McSkimin's pulse superposition technique and proper corrections for bond thickness and the phase angles are made (McSkimin 1961). The results are presented in figure 1. The densities are measured at room temperature and are presented in figure 3. The adiabatic compressibilities are also calculated and are also shown in figure 3. The glass transition temperatures were determined using Perkin-Elmer DSC-2 unit at a heating rate of 20 K/min and are presented in figure 2 along with the data of Blachnik and Hoppe. The T_g values are slightly smaller in our samples but the behaviour is very similar to that of Blachnik and Hoppe. The lower values of T_g could be due to a different quenching rate or due to the use of a different heat rate in DSC. This discrepancy however is not very serious since T_g dependence on the history of sample is well-known. The ultrasonic velocities show minima at 30 and 50 at % P. This behaviour is seen in both the longitudinal and transverse velocities. The behaviour for the density is similar. The adiabatic compressibility has maxima at these compositions.

3. Discussion

The variation of the T_g and the compressibilities are indicated in figures 2 and 3. The changes in T_g have been reported to show peaks at 30 and 50 at % P. Blachnik and Hoppe have correlated such peaks to the formation of P-Se double bond by IR spectroscopy.

As mentioned earlier in the As-S system, a maximum in ultrasonic velocities at 40 at % As is noticed. However we are essentially seeing a contrary trend,

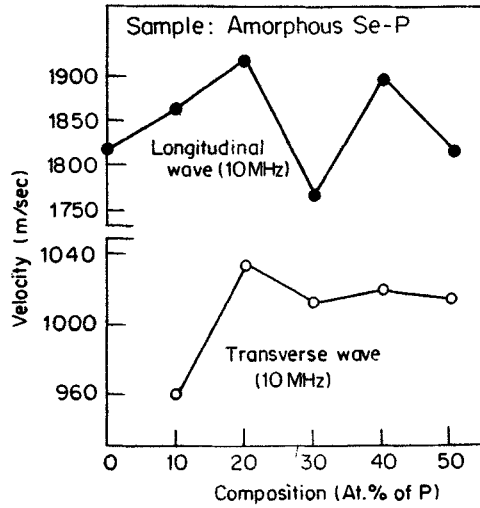


Figure 1. Composition dependence of ultrasonic velocity in amorphous Se-P_x system.

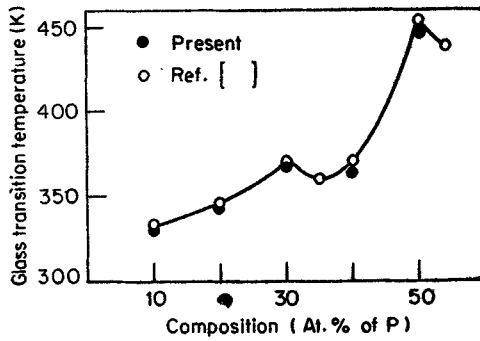


Figure 2. Glass transition temperatures in amorphous Se-P systems.

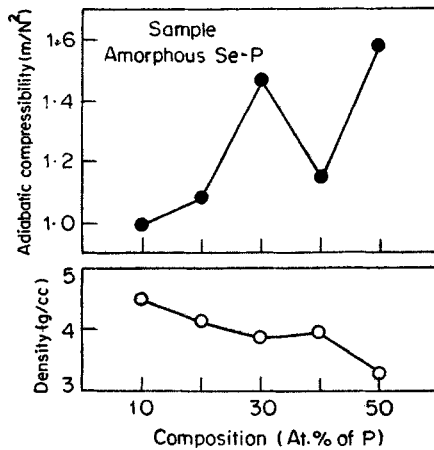


Figure 3. Variation of compressibility and density as a function of decomposition.

i.e. minima for the ultrasonic velocities and maxima in compressibilities are noticed. The basic idea of composition dependent changes in properties of glasses is that congruently melting compounds form at specific compositions and this enhances the stability of the 3-dimensional glass network. Thus, an increase in the elastic constants and a maximum in ultrasonic velocity is expected.

However there are certain basic limitations to this simplistic picture. Blachnik and Hoppe have shown that in As-S system, there is a sharp maximum in T_g at 40 at % As. However in As-Se system there is only a broad maximum. This they attribute to the greater tendency of Se to form polymeric chains. However P-Se system shows maximum in T_g at 30 and 50 at % P. The P-Se binary system forms compounds P_2Se_3 and P_2Se_5 at 30 and 40 at % P (Bailar *et al* 1973; Vanwazer 1958) and the behaviour of P is similar to As. The differences in T_g variations of As-Se and P-Se system is not clear. Also since the P-Se system crystallize easily beyond 50 % P, the results of T_g might be indicating a broad minimum at 40 at % P. But if it is so, the ultrasonic velocities might be said to show a maximum at 20 at % P also. Our experimental results of elastic properties empirically follow the trends in T_g variation. However the basic physical explanation of the behaviour is not clear.

In conclusion, one can state that while in general most physical properties show extrema at some compositions, the underlying causes are not clear. The differences in the behaviour of P-Se and As-Se systems are also not clear. A more precise understanding of local order and its relation to physical properties is apparently needed to resolve the existence of such extrema in the physical properties.

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References

- Arai K, Kawahata T, Namikawa H and Saito S 1972 *Jpn. J. Appl. Phys.* **11** 1080
 Bailar J C, Emeleus H J, Nyholm R and Trotman-Dickenson A F (eds) 1973 *Comprehensive inorganic chemistry* (New York: Pergamon Press) Vol. 2 p. 45
 Blachnik R and Hoppe A 1979 *J. Non-Cryst. Sol.* **34** 191
 Hurst C M and Davis E A 1974 *J. Non-Cryst. Sol.* **16** 343
 Kuriyama U 1975 *J. Am. Ceram. Soc.* **58** 302
 Kesatkin B E and Borisova Z U 1974 *Inorg. Mater.* **10** 1237
 McSkimin H J 1961 *J. Acoust. Soc. Am.* **33** 12
 Mott N F 1967 *Adv. Phys.* **16** 49
 Novoselova N A, Novoselova S K and Baidakov L A 1971 *Russ. J. Appl. Chem.* **44** 2615
 Renninger A L and Averbach B L 1973 *Phys. Rev.* **B8** 1507
 Srinivasan K R, Krishnan S, Sivaraman A, Nagarajan N, Ramakrishna J and Gopal E S R 1975 *Proc. Symp. Transducer Technology, Cochin*, (Cochin: NPOL Press) Vol. 6, p. 283
 Tsuchihashi S and Kawamoto J 1971 *J. Non-Cryst. Sol.* **5** 286
 Vanwazer J R 1958 *Phosphorous and its compounds* (Wiley Interscience) Vol. 1
 Vinogradova G Z, Dembovski S A, Kuzmina T N and Chernov A P 1967 *Russ. J. Inorg. Chem.* **12** 1715
 Zachariasen D H 1932 *J. Am. Chem. Soc.* **54** 3841