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

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MS received 17 July 1981

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 coordination 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 \( Vb-VIb \) systems) where such dependences are seen. The thermal expansivity of As-S glasses shows a minimum at 40 at. % As (Tsuchihashi and Kawamoto

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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 thermal 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 As₅Se₅ and As₅S₅. 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 Tᵩ values are slightly smaller in our samples but the behaviour is very similar to that of Blachnik and Hoppe. The lower values of Tᵩ 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 Tᵩ 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 Tᵩ and the compressibilities are indicated in figures 2 and 3. The changes in Tᵩ 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,
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**Figure 1.** Composition dependence of ultrasonic velocity in amorphous Se-P system.

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

**Figure 3.** Variation of compressibility and density as a function of decomposition.
t.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 $P_3Se_7$ 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.

Acknowledgement

The authors thank CSIR, UGC and DST for financial support.

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