

Dielectric studies of As-Se glasses†

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Abstract. Dielectric constants and loss tangents of As-Se glasses have been measured between 300 K and the respective glass transition temperatures and between 1 kHz and 20 kHz. The variation of dielectric constants has been interpreted in terms of both heteropolarity of bonds and average bond energies employing a chemically ordered network model. Various contributions to total molar polarizations have been estimated. Rapid rise of loss tangent in the vicinity of glass transitions has been interpreted in terms of rapid increase; of d.c. conductivity.

Keywords. As-Se glasses; dielectric constant; loss factor.

1. Introduction

Dielectric properties of amorphous selenium and arsenic selenide have been reported in the literature (Lakatos and Abkowitz 1971). But the agreement in the reported values of dielectric constant for As_2Se_3 (Crevecoeur and de Wit 1971; Lakatos and Abkowitz 1971; Kolomiets 1964; Marianni *et al* 1973; Shimakawa *et al* 1977; Goyal and Srivastava 1978) is poor. Further, no systematic studies of the dielectric properties of As-Se glasses have been reported in the literature. We have, therefore, considered it important to examine the dielectric behaviour of As-Se glasses, both as a function of temperature and of composition at various frequencies. In this paper we report the dielectric properties of As-Se glasses and discuss the dependence of dielectric constants on composition using a chemically ordered network model. We have also examined dielectric losses in them in the light of their conductivity behaviour.

2. Experimental

Glasses were prepared from 5 N purity materials (Koch-Light, Co., U.K.) and the method of preparation has been described elsewhere (Mohan *et al* 1980). Specimens for dielectric measurements were prepared by cutting into rectangular

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blocks of glass ($8 \times 8 \times 0.7 \text{ mm}^3$), whose parallel faces were polished smooth with rouge powder. Silver paint electrodes were used and measurements of dielectric constant were done on a General Radio 1615-A Capacitance Bridge using external source of frequencies and General Radio 1232-A Null Detector. Temperature dependence of dielectric constants and losses were determined using a special cell shown in figure 1. Temperature was controlled to $\pm 0.5^\circ$ using a temperature controller. The ambient humidities were generally very low and no special precautions were taken to avoid moisture in the cell. Measurements were performed from 300 K up to the respective glass transition temperatures (T_g) and in some cases slightly beyond. The frequency range employed was 1 to 20 kHz.

3. Results and discussion

The measured values of ϵ' , real part of dielectric constant for various compositions are shown in figure 2. The error bars represent estimates obtained from considering uncertainties in thickness measurements, temperature measurements and average of several measurements. The variation of loss factor, $\tan \delta$, for different compositions at 1 kHz is shown in figure 3, as a function of temperature. In the inset of figure 3, variation of $\sigma_{d.c.}/\sigma_{a.c.}$ with temperature has been shown for three compositions $\text{As}_{30}\text{Se}_{70}$, $\text{As}_{40}\text{Se}_{60}$ and $\text{As}_{50}\text{Se}_{50}$. In figures 4a and b, variation of ϵ' and $\tan \delta$ corresponding to 1 kHz and 298 K are given as a function of composition. In figure 5, variation of $\tan \delta$ as a function of frequency for three compositions $\text{As}_{10}\text{Se}_{90}$, $\text{As}_{40}\text{Se}_{60}$ and $\text{As}_{80}\text{Se}_{20}$ are shown.

Figure 2 indicates that between room temperature and their respective T_g 's, ϵ' of these glasses are essentially independent of temperature. Figure 4a shows

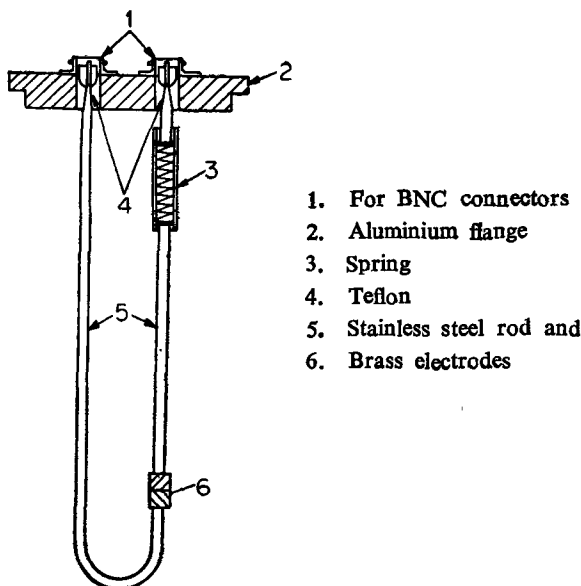


Figure 1. Schematic diagram of the cell for capacitance measurement.

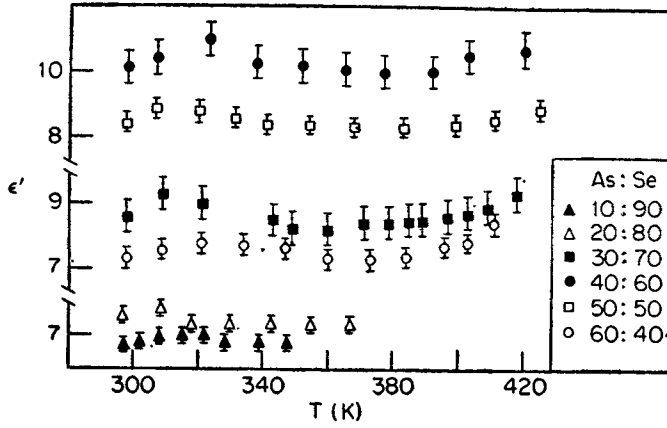


Figure 2. Variation of ϵ' with temperature for various compositions at 1 kHz.

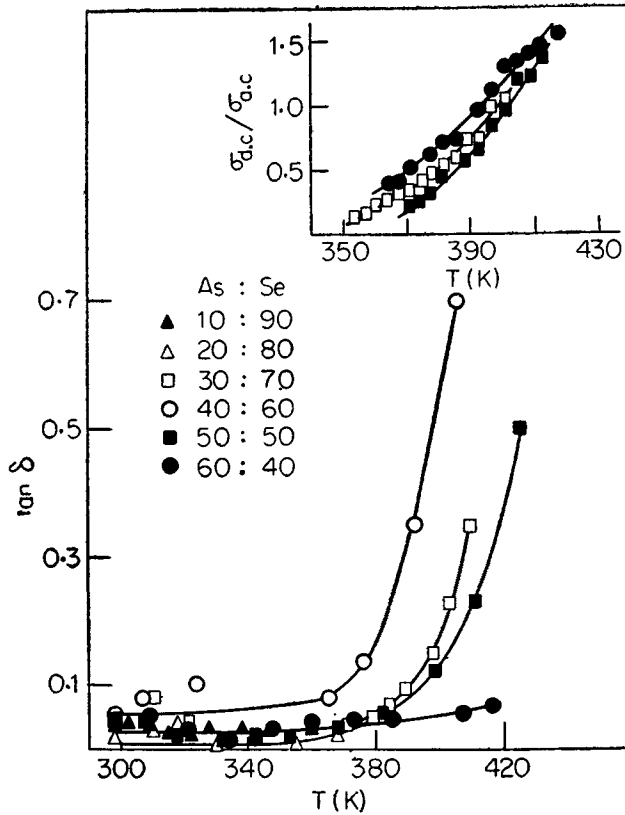


Figure 3. Variation of $\tan \delta$ with temperature at 1 kHz. In the inset, variation $\sigma_{d.c.}/\sigma_{a.c.}$ with temperature has been shown for three compositions; ○, $As_{40}Se_{60}$; □ $As_{50}Se_{50}$; and ■, $As_{50}Se_{50}$.

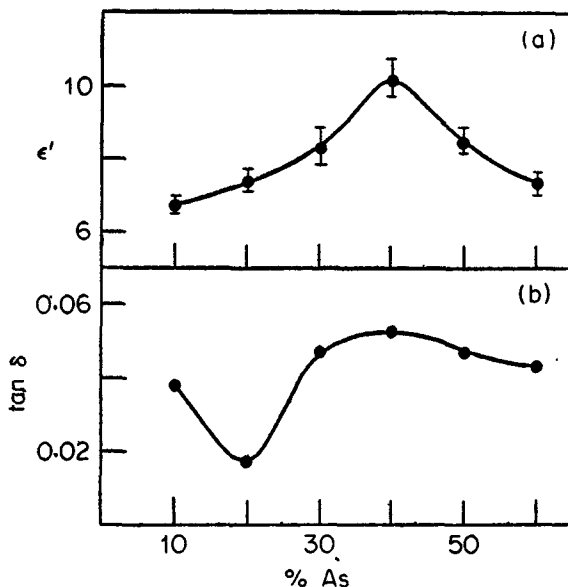


Figure 4. Variation of ϵ' (a) and $\tan \delta$ (b) with composition at 1 kHz and 300 K.

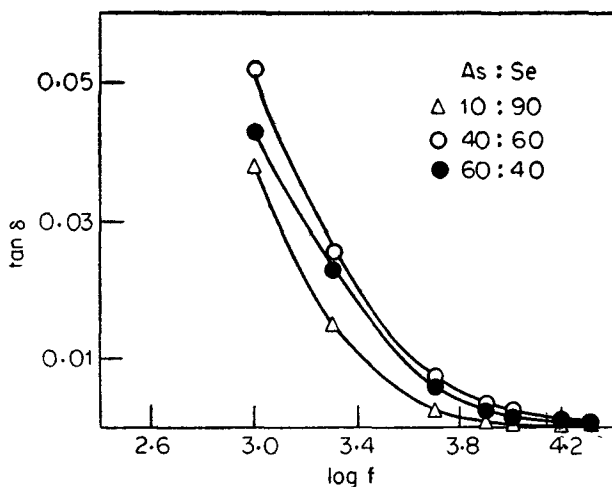


Figure 5. Variation of $\tan \delta$ with logarithmic frequency for three compositions.

that $\text{As}_{40}\text{Se}_{60}$ which corresponds to stoichiometric composition, has the maximum dielectric constant of 10.3 ± 0.5 . This value is midway between those reported by Kolomiets (1964) and Lakatos and Abkowitz (1971) and is in good agreement with that reported by Marianni *et al* (1973). The extrapolated values of ϵ' for Se is in good agreement with the literature value of 6.3 ± 0.3 at this frequency (1 kHz) (Lakatos and Abkowitz 1971).

One possible origin of the large values of dielectric constant and hence of polarization is the dipolar nature of As-Se bonds. However, dielectric constants may be expected to depend upon the bond concentration (number of bonds per cm^3)

and the bond energies (since the latter determines the polarizabilities of bonded electrons) also. The dipolar contributions may be estimated from $\Delta\chi$ values where $\Delta\chi = (\chi_{\text{Se}} - \chi_{\text{As}})$, and χ 's are the electronegativities of the atoms. Further, we know from our earlier studies (Mohan *et al* 1981; Rao *et al* 1981) that these glasses possess chemically-ordered network and therefore, we can estimate the number of bonds which involve $\Delta\chi$. The variation of dielectric constant ϵ' , may therefore be represented as

$$\epsilon' \propto [\Delta\chi \cdot f + C(1 - f)], \quad (1)$$

where C is used as an adjustable parameter. The variation of right side of expression (1) with C = 0.1 is shown in figure 6a (as a line on a scale indicated on the right ordinate). The measured dielectric constants ϵ' are shown as circles on a scale corresponding to left ordinate.

Employing bond concentration and bond energy values, dependence of dielectric constants may be estimated as follows. The polarization may be assumed to be directly proportional to bond densities (number of bonds/cm³) and inversely proportional to the bond energies or in other words, inversely proportional to

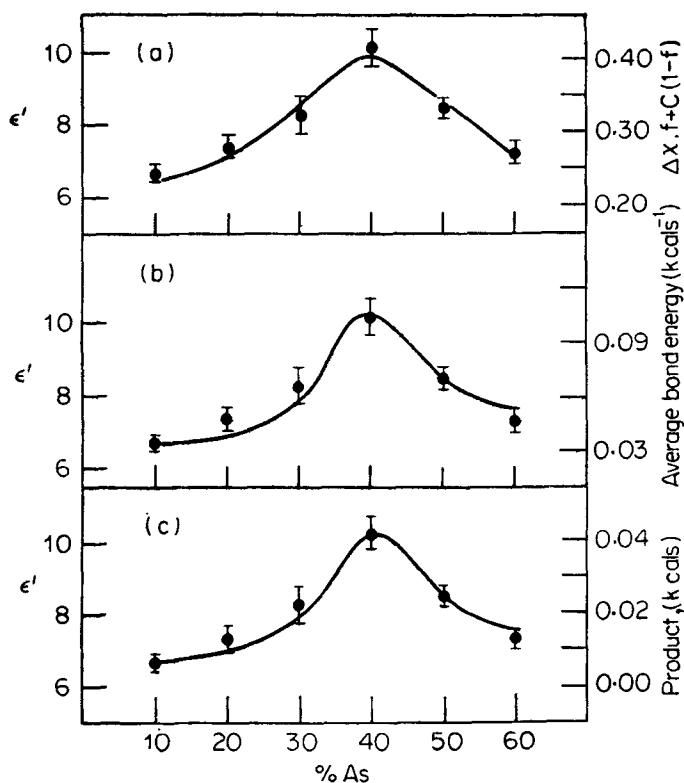


Figure 6. (a) Variation of $[\Delta\chi \cdot f + C(1 - f)]$ with composition is shown as a line along with ϵ' values (closed circles) (see text). (b). Variation of reciprocal of bond energies with composition is shown as a line along with ϵ' values (closed circle) (see text). (c) Variation of the product, $[\{\Delta\chi \cdot f + C(1 - f)\} (\text{av. bond energy})^{-1}]$ with composition is shown as a line along with ϵ' values (closed circles) (see text).

the average bond energies of these glasses. Average bond energies are evaluated assuming chemical ordering in these glasses; average bond energy of As₂Se₃ is equal to average bond energy per mole of As₂Se₃ (Rao and Mohan 1980; Mohan *et al* 1981) divided by the number of bonds in As₂Se₃ per mol. In figure 6b, the variation of reciprocal of the average bond energies are shown (as a line on a scale indicated on the right ordinate) and dielectric constants are indicated by circles. In figure 6c the behaviour of the product of (i) inverse of average bond energy (from figure 6b) and (ii) the r.h.s. of expression (1) (from figure 6a) is shown as a line (scale; right ordinate) along with measured dielectric constants (circles). This heuristic analysis seems to suggest that the dielectric constants depend both on the average bond energies and the polarities of bonds.

Dielectric constants can be utilised directly to evaluate molar polarization P_t in the audiofrequency range from the Clausius-Mossotti equation. Molar polarization in the optical frequency range P_e is similarly evaluated using the Lorentz-Lorentz equation. The polarization, P_t and P_e so determined represents the total polarization and electronic polarization respectively. The atomic polarization P_a is then easily determined by the relation $P_a = (P_t - P_e)$. Electronic polarization has been evaluated using the refractive index values reported by Nang *et al* (1979). Values of P_a and P_e have been listed in table 1 for the various compositions. P_a includes contributions arising from ionic polarization of the medium also. If we assume that arsenic and selenium carry an effective charge Ze^* , we can employ Szigetti (1950) relations to approximately evaluate the ionic contribution to polarization. The Szigetti relations may be combined to yield

$$\frac{\epsilon_0 - \epsilon_\infty}{(\epsilon_\infty + 2)(\epsilon_0 + 2)} \frac{9V}{8\pi} = \frac{Z^2 e^{*2}}{p}, \quad (2)$$

where $\epsilon_0 = \epsilon'$ and $\epsilon_\infty = n^2$ and n is the refractive index. This quantity has units of polarization and arises from a consideration of vibrations of ions with effective charge Ze^* only. We may, therefore, consider this as the ionic polarization P_i of these glasses; P_i values are listed in table 1. It is interesting to note that P_i is approximately 10–12% of P_a .

The loss factors ($\tan \delta$) exhibit an increase towards lower frequencies as shown in figure 5. The three glass compositions chosen in figure 5, represents stoichio-

Table 1. Molar polarizations of As-Se glasses

Composition	P_e	P_a	$P_i = e^{*2}Z^2/P$
As ₁₀ Se ₉₀	14.6217	0.1754	0.0212
As ₂₀ Se ₈₀	19.4533	0.4884	0.0577
As ₃₀ Se ₇₀	28.9121	1.8086	0.2166
As ₄₀ Se ₆₀	58.2281	5.8100	0.6733
As ₅₀ Se ₅₀	35.3733	1.4896	0.1780
As ₆₀ Se ₄₀	25.9380	0.0780	0.0039

metric ($\text{As}_{40}\text{Se}_{60}$), arsenic excess ($\text{As}_{80}\text{Se}_{40}$) and selenium excess ($\text{As}_{10}\text{Se}_{90}$) glasses. But the loss dependence on temperature shown in figure 3 suggests that a small dispersion in $\tan \delta$ only corresponds to the tail of a very broad absorption peak occurring at very low frequencies. The rise in loss peak in the region of T_g for the various compositions does not follow the same trend as T_g 's themselves. It is likely that the rise in $\tan \delta$ represents a rapid rise in d.c. conductivity (Mansingh *et al* 1980). It may be seen from the inset of figure 3 that $\sigma_{d.c.}/\sigma_{a.c.}$ attains values of the order of unity in the region where the losses increase enormously. However, our interpretation of loss data, on the basis of structural informations is limited by the frequency range covered in these glasses.

The variation of dielectric constants as a function of composition seems to be adequately accounted for assuming a chemically ordered network model for As-Se glasses. Both the dielectric constant and losses are essentially temperature and frequency-independent almost up to glass transition temperature in the audio-frequency range.

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