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AC conductivity and dielectric properties of sulphate glasses*

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Abstract. AC conductivity and dielectric properties of sulphate glasses have been studied as a function of temperature, frequency and variation in interalkali concentration. AC conductivity at frequencies well beyond the dielectric loss peaks seems to arise from local motion of alkali ions within the neighbouring potential wells. Activation energies for AC conductivity were found to be very much lower than those for DC conductivity. Further, AC conductivity seems to be independent of interalkali variation, whereas ϵ' and tan δ show a mild degree of mixed alkali effect. The observations made here have been explained on the basis of a structural model earlier proposed by us for these glasses.

Keywords. AC conductivity; sulphate glasses; mixed alkali effect; dielectric studies.

1. Introduction

AC field often produces atomic motions over a short range (Owen 1963) in solids and hence gives rise to AC conductivity. Generally, in an ionic dielectric AC conductivity results from the jumping of ions between neighbouring potential wells. This jumping of ions is characterized by a time constant $\tau = \tau_0 \exp(-E_a/RT)$. In the case of silicate glasses the activation energies (E_a) were found to be similar for both AC and DC conductivities (Taylor 1956). It is not known, however, whether a similar behaviour is exhibited by ionic glasses consisting of discrete anions. Further, a study of dielectric response (and hence AC conductivity) as a function of temperature as well as frequency (sufficiently beyond loss peak frequencies) should result in adequate characterization of transport behaviour of ionic glasses. In this paper we report the AC conductivity (dielectric loss) and dielectric constants measured over a temperature range from ambient to beyond the glass transition temperature and frequencies from 1 to 20 kHz performed on alkali sulphate-zinc sulphate glasses. We have discussed our observations in the light of a structural model proposed earlier for these glasses.

2. Experimental

The glasses were prepared from $ZnSO_4.7H_2O$, K_2SO_4 and Na_2SO_4 (BDH) samples. Sufficient care was taken to eliminate moisture by bubbling dry N_2 gas for several

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hours through the melt. The detailed procedure is described elsewhere (Narasimham and Rao 1978a; Sundar and Rao 1980). Glass discs of $\sim$ 0·5 mm thickness were used for the measurements. Colloidal silver paint was used as electrode material. Measurements were performed on a capacitance bridge (General Radio 1615-A) using external source of frequency and a null detector (General Radio 1232A). Details of the conductivity cell used have also been described previously (Mohan and Rao 1981). Measurements of series equivalent of capacitances and tan δ were made by using the bridge employing a two-terminal sample cell. The dielectric parameters were evaluated from the parallel equivalent of the capacitance and resistance after eliminating lead capacitance. σ_{AC} was calculated by subtracting σ_{DC} from the measured conductivities. The required DC data was taken from our earlier work (Narasimham *et al* 1979a, Rao and Sundar 1980).

3. Results and discussion

3.1 *AC conductivities*

Variation of log σ_{AC} vs T^{-1} for a few frequencies and for a particular glass composition is shown in figure 1. It is representative of the general trend of all the glasses studied here. Log σ_{AC} vs T^{-1} plot shows two linear regions and the point of inflection which corresponds to glass transition temperature is somewhat lower than the T_g obtained from thermal measurements. Inflection temperatures for any particular

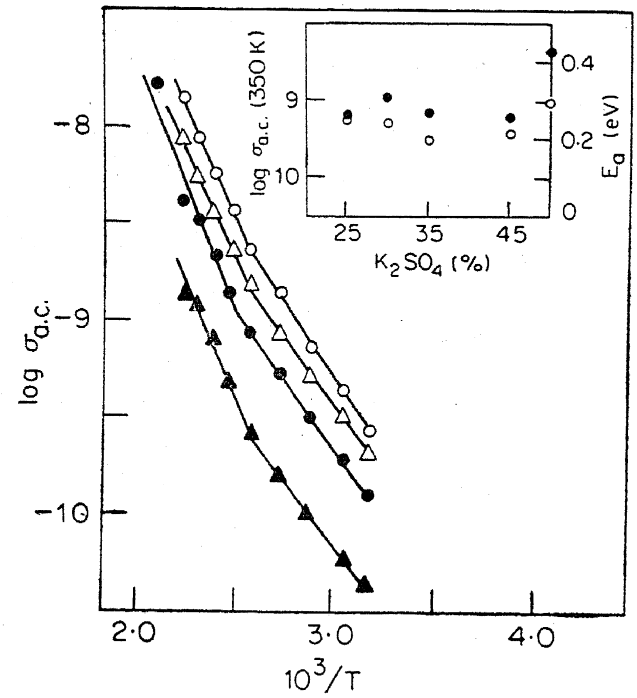

Figure 1. Variation of log σ_{AC} as function of T^{-1} for 50 Zn: 25 K: 25 Na glass at 1 kHz (▲), 5 kHz (●), 10 kHz (Δ) and 20 kHz (O). Inset shows the variation of log σ_{AC} (O) and E_a (●) as a function of composition in 50 $ZnSO_4$ × K_2SO_4. (50 − X) Na_2SO_4 glass.

glass composition are little different from one another within the frequency range employed in these studies. Behaviour of log σ_{AC} (323K) and E_a for the glassy region are shown in the inset of figure 1 as a function of composition (interalkali variation). Both σ_{AC} and E_a are almost independent of interalkali variation. A log-log plot of σ_{AC} vs f is given in figure 2. The activation energies in the glassy region are not sensitive to frequency though the conductivity itself increases with frequency as shown in figure 2. More important, the magnitudes of these activation energies are considerably lower (less than 50 %) than the activation energies for DC conductivity (~1 eV). This clearly suggests that AC conductivity arises from the jumps of alkali ions among potential energy wells which have considerably lower energy barrier than those involved in DC conductivity (discussed further in § 3.3). The behaviour of log σ_{AC} vs log f in figure 2 suggests that in general,

$$\sigma_{AC} = \omega^s$$

is obeyed such that $0{\cdot}25 \leqslant s \leqslant 0{\cdot}75$ for all the glasses. s itself varies with temperature as shown in the inset of figure 2. Also shown in the inset is the behaviour of σ_{DC}/σ_{AC} The implications of the variation shown in the inset plot are discussed in a later section.

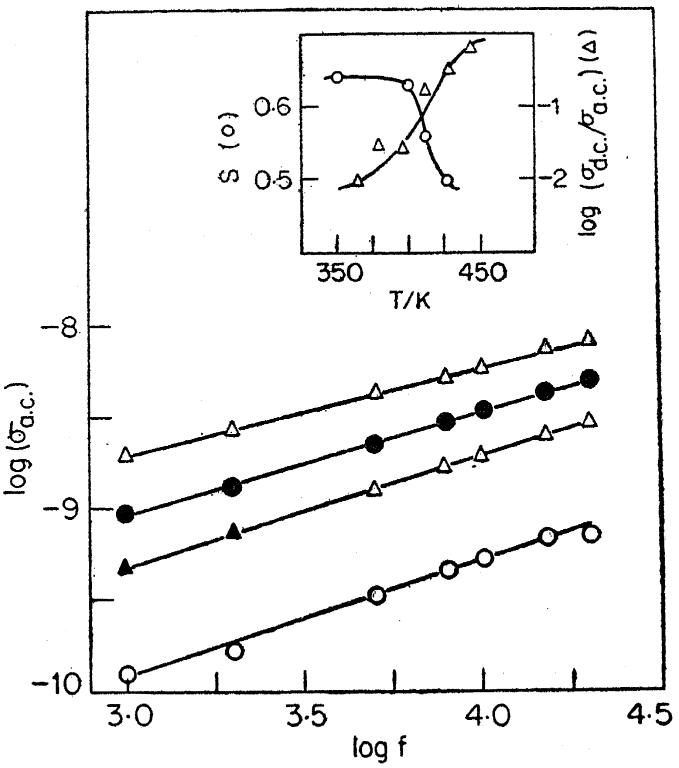

Figure 2. Behaviour of log σ_{AC} as a function of frequency for 50 Zn: 35 K: 15 Na sulphateglass at 350 K (O), 397 K (▲), 428 K (●) and 413 K (Δ). Inset shows dependence of s and log $\sigma(_{DC}/\sigma_{AC})$ on temperature.

3.2 *Dielectric properties*

Real and imaginary parts of dielectric constant, ϵ' and ϵ'', are shown in figure 3 as a function of temperature for two glass compositions. The variation of log tan δ as a function of temperature is shown in figure 4. ϵ' varies very little at lower temperatures but increases rapidly towards T_g. The rapid rise is likely to arise from other sources of polarization possibly from enhanced electrode polarization as the temperature approaches T_g (Narasimham and Rao 1979). The variation of ϵ'' is even more drastic towards T_g due to the combined variations in ϵ' and tan δ. From figure 4 it is evident that in general the relation tan $\delta = K \exp(\alpha T)$ is obeyed (Moore and DeSilva 1952) by these glasses. This behaviour is common to many alkali containing glasses.

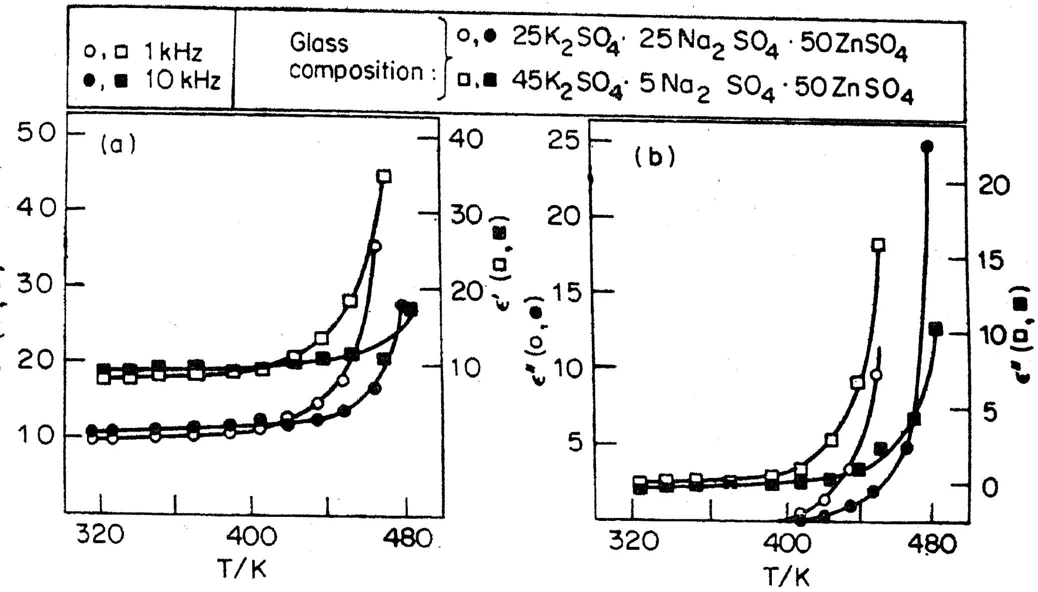

Figure 3. Variation of (a) ϵ' and (b) ϵ'' as a function of temperature.

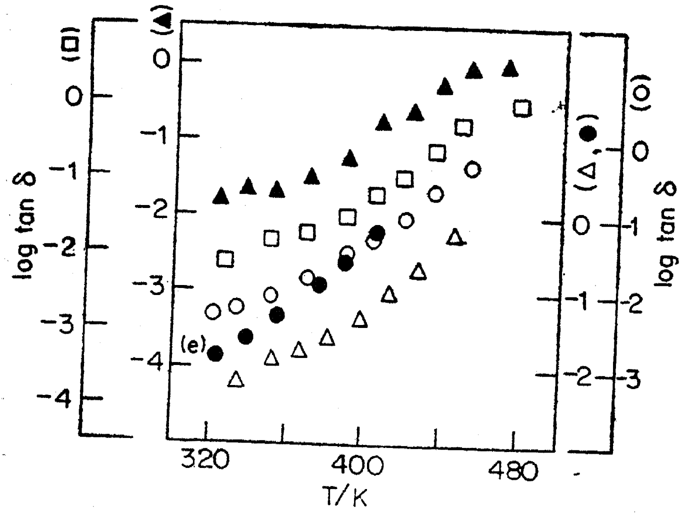

Figure 4. Dependence of log tan δ on temperature for several glasses at 1 kHz. (50 Zn: 25 K: 25 Na) □; (50 Zn: 30 K: 20 Na), Δ; (50 Zn: 35 K: 15 Na), O; (50 Zn: 45 K: 5 Na, ▲; (50 Zn: 50 K), ●.

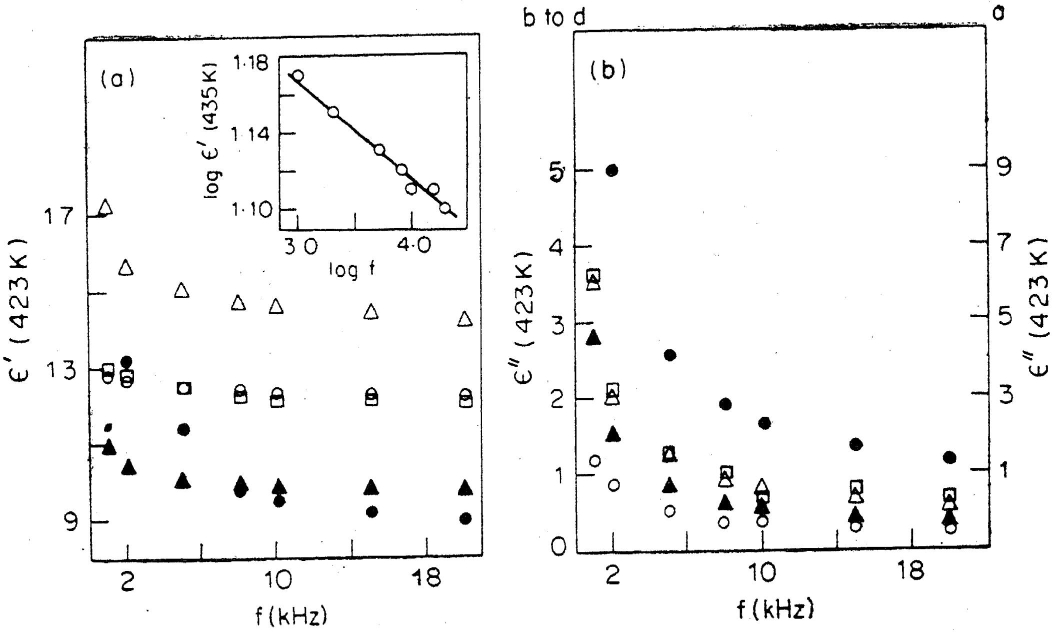

Figure 5. Behaviour of (a) ϵ' and (b) ϵ'' as a function of frequency for several glasses. (50 Zn: 50 K,) ●; (50 Zn: 45 K: 5 Na), ▲; (50 Zn: 35 K: 15 Na), O; (50 Zn: 30 K: 20 Na), △; (50 Zn: 25 K: 25 Na), □. Inset in (a) shows variation of log ϵ' as a function of log f.

A theoretical analysis given by Gevers and DuPre (1946) suggests that it is due to the existence of a distribution of depths of potential energy wells. Variation of ϵ' and ϵ'' as a function of frequency for various glass compositions is shown in figures 5a and 5b. Inset of figure 5(a) shows the dependence of ϵ' on f. The variation of ϵ'' suggests that a loss maximum could possibly occur at still lower frequencies.

3.3 *General discussions*

The possible structure of sulphate glasses has been described elsewhere (Narasimham and Rao 1978a, Sundar and Rao 1980) which is based on the use of a random close packing model. In this model, SO_4^{2-} ions which are " pseudo " spherical are initially random close-packed and structural alterations are allowed to occur around Zn^{2+} ions to render them octahedrally coordinated so as to be consistent with spectroscopic observations (Narasimham and Rao 1978b). The alkali ions are assumed to occupy the tetrahedral voids created by SO_4^{2-} ions. Several physical properties of sulphate glasses are in agreement with such a model. In the ternary glasses the observed mixed alkali effect, is also well accounted for by the model. We need to assume however, that near neighbour Na^+ and K^+ ions are locked up in local strain fields created by the smaller Na^+ ions (Rao and Sundar 1980). The DC electrical conductivity of these glasses, therefore, is largely due to ions which are not thus immobilized and are transported *via* the available tetrahedral voids. The conductivity is characterized by barriers close to ~1 eV. However, the distribution of voids and alkali ions in the immediate vicinity of Zn^{2+} ions are different since the environment around Zn^{2+} ions is modified. We suggest that these voids are separated by much lower barriers. Transport of alkali ions in these voids characterises the AC conductivity. We may note in this context that the activation energies for thermally activated diffusion of ^{7}Li and ^{133}Cs in various glass systems were found to be ~0·2 eV from NMR measurements. This rather low value as compared to the DC conductivity activation barrier (~ 1 eV) was also attributed by Bray and co-workers (Bishop and Bray 1968, Rhee and Bray 1971; Hendrickson and Bray 1972) and by Svanson and Johnson (1970), to such local motions of the alkali ions. We should expect that the concentration of voids which we have suggested as responsible for the observed AC conductivity, should be independent of the interalkali variations and that it should depend only on the concentration of Zn^{2+} ions. Indeed, σ_{AC} was found to be essentially independent of interalkali variation (figure 1 inset). We should however expect Na^{+} and K^{+} ions which are locked up in the strain fields to contribute somewhat differently to the total polarization of the system. In other words, we should expect at least a weak manifestation of mixed alkali effect in tan δ and ϵ'. This has been found to be so as shown in figures 6a and 6b. Since $\sigma_{AC} = \omega \epsilon_0 \epsilon''$, variation of ϵ'' represented in figure 6b is insufficient to cause a demonstrable mixed alkali effect in log σ_{AC} plot (figure 2 inset).

The composition of sulphate glasses, which we have considered here is fairly complex and we have already seen that at least two dominant barriers to migration of alkali ions should exist in these glasses; the lower barrier being of relevance to the AC response discussed above. It is therefore reasonable to expect that there is a distribution of depths of the potential wells and correspondingly a distribution of relaxation times. If we assume that the distribution of relaxation times corresponds to a Cole-Cole (1941) distribution, we can show that

$$\tan \delta \cong \frac{\Delta\epsilon}{\epsilon'} \tau_0^{-(\alpha-1)} \cos\left(\tfrac{1}{2}\alpha\pi\right).\ \omega^{-(\alpha-1)},$$

where $\Delta\epsilon = \epsilon_0 - \epsilon_\infty$. For $\omega\tau_0 \gg 1$. α in the above equation is a measure of the width of the distribution of relaxation times. Further, since σ_{AC} is equal to $\epsilon_0 \omega \epsilon''$ where ϵ_0 is the permittivity of free space, we have

$$\sigma_{A.C.} = \omega\epsilon'\epsilon_0 \tan\delta = \Delta\epsilon\, \epsilon_0\, \tau_0^{1-\alpha} \cos\left(\tfrac{1}{2}\, \alpha\pi\right) \omega^{\alpha}.$$

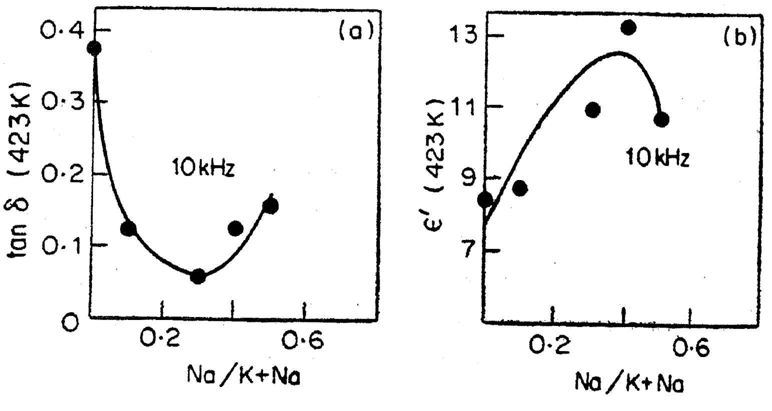

Figure 6. Variation of tan δ and ϵ' for mixed alkali compositions.

α obtained from σ_{AC} behaviour of figure 2 for a 50 Zn : 30 K : 20 Na glass is found to be approximately 0·7 ($\alpha = s$) and represents the width of the distribution of relaxation times.

Rapid variation of s or α with temperature around T_g shown in figure 2 (inset) seems to coincide with rapid rise of σ_{DC}/σ_{AC}. Such a behaviour has been evidenced in other glasses also (Mansingh *et al* 1975). It is probably a consequence of " loosening " of glass structure which may result in a rapid broadening of barrier distribution. Thus the ω dependence changes rapidly in this region with attendant rapid rise in DC conductivity.

4. Conclusions

The AC conductivity and dielectric parameters of ionic glasses are different from the conventional network forming glasses in that the activation energy for AC conductivity is much lower than that for DC conductivity. The exponents of ω for the AC conductivity suggests $\alpha \simeq 0{\cdot}7$ for the possible Cole-Cole distribution function for relaxation times. Mixed alkali effect does not manifest in AC but it is mildly evident in ϵ' and tan δ. The AC response of ionic sulphate glasses are consistent with the structural model proposed for these glasses.

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