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Electrical permittivities and subglassy relaxations in sulphate glasses

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Abstract. The dielectric behaviour of K_2SO_4-$ZnSO_4$ glasses have been investigated. These glasses exhibit subglassy relaxations close to glass transition temperature. The relative dielectric permittivities exhibit sharp rise near T_g which may be due to loosening of glass constituents leading to ionic dipolar or electrode polarisation contributions.

1. Introduction

Glasses are easily formed in the mixed sulphate system, K_2SO_4–$ZnSO_4$ over a wide range of compositions. Several investigations of these glasses have already been reported from this laboratory (Narasimham and Rao 1978a, 1978b; Narasimham *et al* 1979). The important structural features of this glass system are (a) it corresponds to random close packing SO_4^{--} ' spheres ' in K_2SO_4 rich compositions and random close packing of O^{--} ions in the $ZnSO_4$ rich compositions : (b) K^+ ions are tetrahedrally coordinated to SO_4^{--} ions while Zn^{++} ions are always octahedrally coordinated (Narasimham and Rao 1978a). These features seem to adequately account for the d.c. conductivity behaviour of these glasses (Narasimham *et al* 1979) also.

It is now generally believed that most glass forming systems show subglassy-relaxations (Goldstein 1969). These so-called β-relaxations seem to occur at rather low temperatures in KNO_3^+–$Ca(NO_3)_2$ glasses (Johari and Goldstein 1970, 1971). Since no other purely ionic glass seems to have been thus far investigated with a view to characterising these β-relaxations we considered it interesting to examine the sulphate glasses.

In this short communication we report some of our preliminary results of dielectric measurements performed on a few glass compositions at a fixed frequency (1 kHz) and varying temperatures.

2. Experimental

The glasses were prepared from BDH samples of sulphates by a procedure described earlier (Narasimham and Rao 1978a). Sufficient care was taken to eliminate water thoroughly by bubbling dry nitrogen for longer durations through the melt. The transparent glass discs (typically 0·7 mm thick and 3 cm diameter) were coated on both sides with conducting silver paint using a circular mask such that the electroded areas overlap. Contacts to the silver paint were made through spring-loaded metal disc electrodes. The assembly was then immersed in an oil bath which enabled measurements upto 530 K. The temperature of the heated oil bath was controlled to an accuracy of ± 0·5 K. Measurements of capacitances and dielectric losses were made using a GR 1656 impedance bridge. Lead capacitances were determined using mica of known thickness in place of the glass in an identical configuration. Lead capacitances were subtracted out from measured capacitances of the glasses before evaluating dielectric permittivities (ε_r). The lead capacitances did not vary significantly over the range of temperatures of measurement reported here. The loss angle, tan δ were directly measured from the bridge.

3. Results and discussion

The dielectric loss measurements performed on glasses of different compositions are shown in figure 1. In all these cases the loss peaks appear at about 25° to 35° below the glass transition temperatures. However, in the case of glass containing 60% K_2SO_4, the loss peak appeared at substantially lower temperature

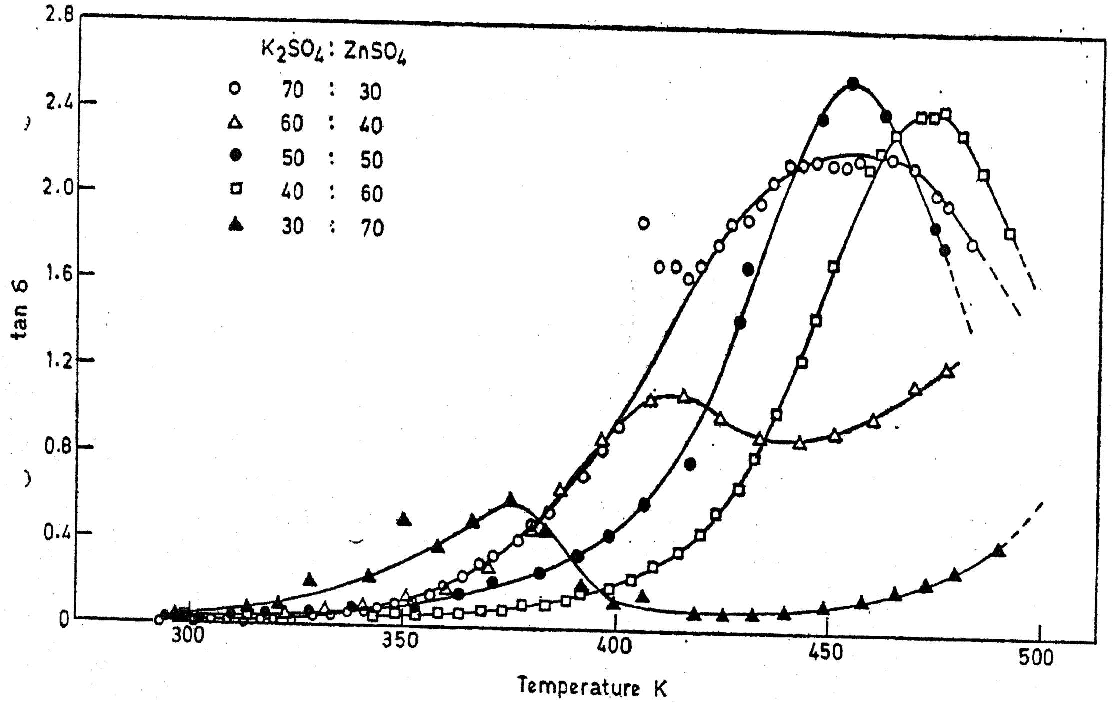

Figure 1. Behaviour dielectric loss at 1 kHz as a function of temperature glasses of various compositions.

(around 410 K) and in the glass containing 70% $ZnSO_4$ a smaller loss peak occurs at even lower temperature (370 K). But it appears from the trends in tan δ, that in both these cases an additional loss peak is likely to occur just above the glass transition temperature (see figure 1). For the potassium-rich compositions the loss peak around 450 K appears to be broader and increase of zinc in the glass seems to decrease the width of the loss peak.

Annealing had very moderate effect on the dielectric loss behaviour. A typical case is shown in figure 2 for a 50 : 50 glass, in which at the end of each heating sufficient time (~ 1 hr) was allowed for annealing to take place. The magnitude, shape and temperature of the loss peak shifts rather insignificantly on annealing as seen in figure 2.

The appearance of these loss peaks seem to indicate the occurrence of β-relaxation in sulphate glasses. It is probable that these loss peaks arise from the field-response of potassium ions which jump from one tetrahedral void to another. By virtue of higher charge and co-ordination, it is unlikely that zinc ion movements contribute to the observed loss peaks. The slight broadening effect which is seen in higher K_2SO_4 glasses may be a consequence of greater variations in the environments of tetrahedral voids (larger and smaller average distances from zinc ions result in differences in coulombic fields and hence, the slight broadening of the energy spectrum of tetrahedral voids). The origin of the loss peaks which appear at much lower temperature in two of these compositions is however not clear at present. It may not be due to incomplete elimination of water in these glasses.

The variation of the dielectric constants as a function of temperature is shown in figure 3. While they remain generally constant almost upto the glass transi-

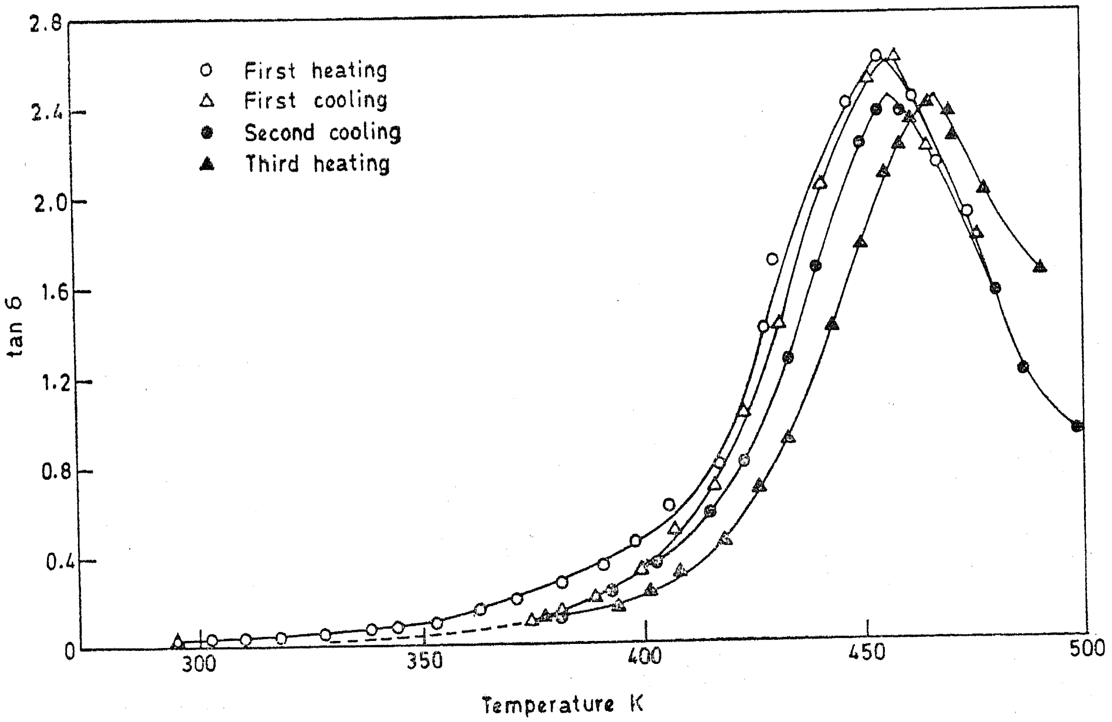

Figure 2. Effect of annealing on the behaviour dielectric loss curves in 50 : 50 : : K_2SO_4 : $ZnSO_4$ glass at 1 kHz.

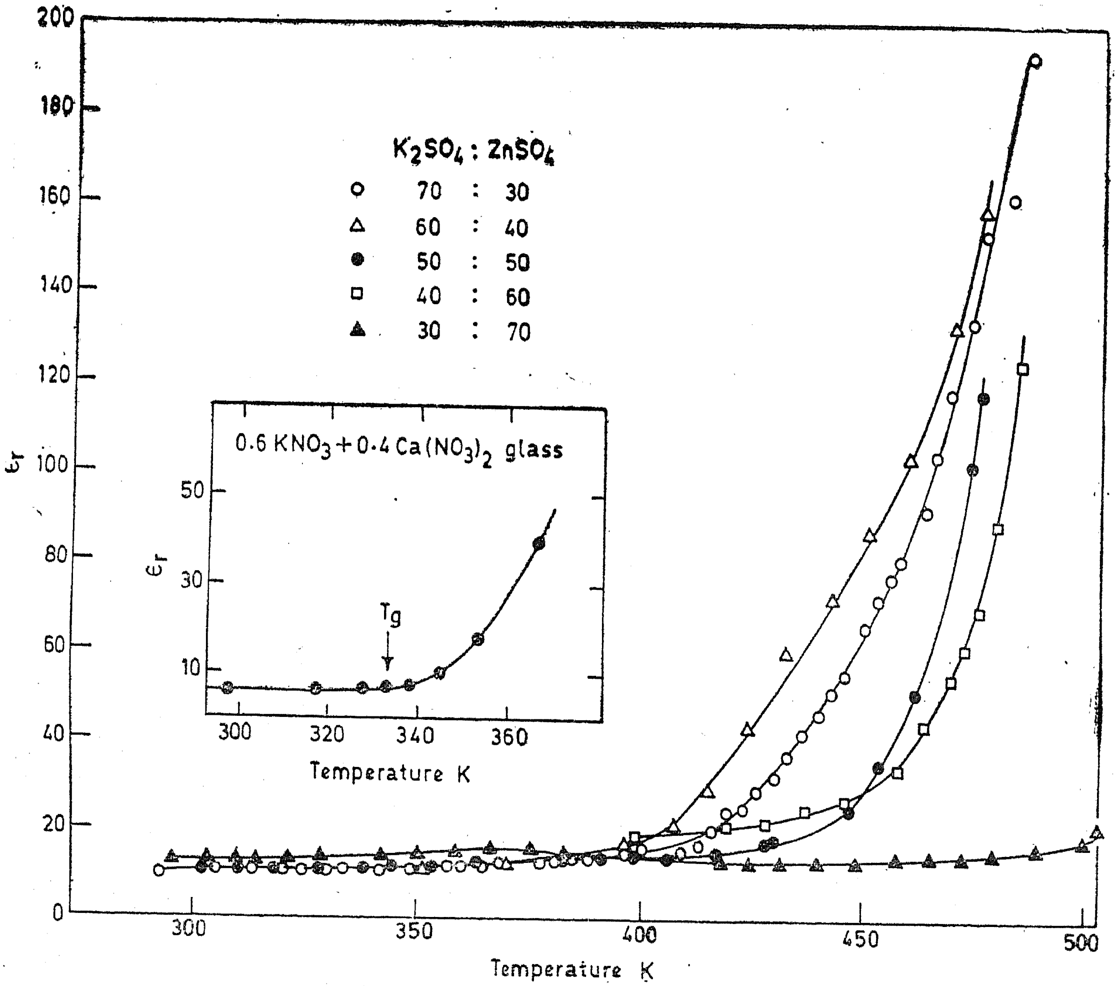

Figure 3. Behaviour of dielectric constant as a function of temperature for different glass compositions at 1 kHz. The corresponding T_g's are 0 : 482 K; △ : 458 K; ● : 488 K; □ : 480 K; ▲ : 463 K. The inset of the figure corresponds to the behaviour ε_r of a KNO_3–$Ca(NO_3)_2$ glass at 1 kHz : data are from Howell *et al* 1974.

tion temperature, they rise to very high values on approaching the glass transition and continue to rise even beyond. From the fact that these are highly ionic glasses, the ion and the dipole polarisation terms (Hench and Schaake 1972) in addition to the electrode polarisation effects should be expected to increase enormously. The very high dielectric permittivities are also a consequence of the fact, that the complex part of the conductivity

$$k = k' + ik'' \quad \text{where} \quad k'' = (\varepsilon_r \, \omega/4\pi)$$

also increases with temperature (Smyth 1955). A similar trend of ε_r is observed in KNO_3-$Ca(NO_3)_2$ glasses studied by Howell *et al* (1974). These results are shown in the inset of figure 3.

The possibility of ferroelectric type of behaviour in glasses has recently been investigated (Glass *et al* 1977). The sulphate glasses can be expected to have small ordered regions of non-centrosymmetric nature constituting the so-called ‘soft local units’. It is indeed interesting that the increase of dielectric constant begins to manifest in the subglassy region. However, it seems more probable that it is only the loosening of the glass matrix and consequent emergence of ionic dipolar or electrode polarisation contributions in these sulphate glasses which cause the substantial rise in dielectric constant. It is consistent with the fact that cluster formation occurs beyond glass transition temperature as evidenced from conductivity studies (Narasimham *et al* 1979).

4. Conclusions

Sulphate glasses exhibit β-relaxations immediately below glass transition temperatures. The relaxations are likely to arise from potassium ions which execute jumps among tetrahedral voids. The dielectric constants increase to high values upon glass transition and is most likely due to emergence of ionic, dipolar or electrode polarisation contributions.

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