Electrical conductivity studies in sulphate glasses and the mixed alkali effect †

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Abstract. Electrical conductivities of alkali sulphate-zinc sulphate glasses have been measured. The variation of conductivity with compositon confirms the presence of the mixed alkali effect. The origin of mixed alkali effect has been explained on the basis of structural considerations reported earlier by us.

Keywords. Ionic glasses ; conductivity ; mixed alkali effect.

1. Introduction

In an earlier paper (Rao and Sundar 1980) on conductivity of sulphate glasses, we reported the mixed alkali effect in K_2SO_4–Na_2SO_4–$ZnSO_4$ glasses. We had attributed the effect to a structural origin using a viable structural model for sulphate glasses. Microscopic strain fields develop around the Na^+ ions and it could account for the observed conductivity minimum. We therefore considered it imperative to examine how other alkali ions behave in mixed alkali compositions of sulphate glasses. In this paper, the observation of the mixed alkali effect for two other alkali pairs is reported and the general conductivity expression suggested earlier is found to be adequate to account for the mixed alkali effect.

2. Experimental

Glasses were prepared using $ZnSO_4 \cdot 7H_2O$, K_2SO_4 (BDH) and Rb_2SO_4 or Cs_2SO_4 (Merck) samples with a minimum purity of 99% as batch materials. Batches weighing 5-10 g were melted in platinum crucibles in an electric furnace and samples suitable for conductivity measurements were obtained as described earlier (Narasimham and Rao 1978, Sundar and Rao 1980). The conductivity cell and the measuring technique have also been discussed earlier (Narasimham *et al*

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1979). The resistances were calculated by measuring the current (with a 610 C Keithley elecetromter) through the sample for a known applied voltage (5 V). The current was passed only for very brief periods (less than 30 sec at a time) in order to avoid polarization. In the present studies also conductivities were measured beyond the glass transition and upto temperatures where the samples either deform under the spring loaded electrodes or crystallised, thus rendering further measurements inaccurate. All the glasses were annealed at a temperature 10 K below T_g before final measurements of σ were made.

3. Results and discussion

The conventional plots of $\log \sigma$ vs T^{-1} are given for various glasses in figure 1. For clarity actual points have not been shown in the conductivity plots. The glasses exhibit an inflection point which corresponds to the glass transition temperature. Variation of conductivity (σ), activation energy (E_a) and the limiting conductivity (σ_0) are plotted separately for Rb and Cs glasses in figures 2 and 3.
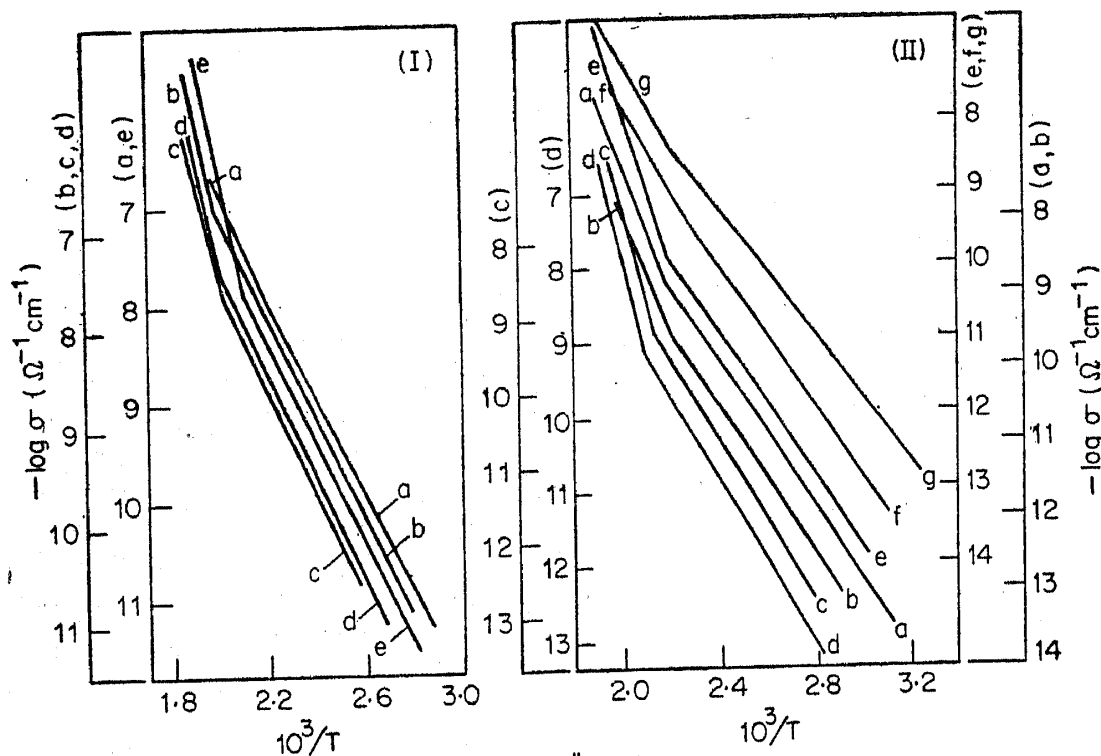

Figure 1. Variation of conductivity with temperature.

I 50% ZnSO₄

(a) 45% K₂SO₄ 5% Rb₂SO₄
(b) 35% K₂SO₄ 15% Rb₂SO₄
(c) 25% K₂SO₄ 25% Rb₂SO₄
(d) 20% K₂SO₄ 30% Rb₂SO₄
(e) 15% K₂SO₄ 35% Rb₂SO₄

II 60% ZnSO₄

(a) 35% K₂SO₄ 5% Cs₂SO₄
(b) 30% K₂SO₄ 10% Cs₂SO₄
(c) 25% K₂SO₄ 15% Cs₂SO₄
(d) 20% K₂SO₄ 20% Cs₂SO₄
(e) 15% K₂SO₄ 25% Cs₂SO₄
(f) 5 % K₂SO₄ 35% Cs₂SO₄

The relevant quantities for the pure $K_2SO_4-ZnSO_4$ glasses were taken from earlier work (Narasimham *et al* 1979). The percentages of $ZnSO_4$ in K–Rb–Zn and K–Cs–Zn glasses were 50% and 60% respectively since these formed very stable glasses. The activation energies and log σ_0, values for Zn (Rb, K) SO_4 glass exhibit no variation in the entire composition range. The behaviour of these quantities in Zn (K, Cs) SO_4 glasses exhibited considerable scatter but with an average which had little variation. The conductivity variations in figures 2 and 3 clearly establish the occurrence of the mixed alkali effect in ionic sulphate glasses. In the structural model of sulphate glasses considered in our earlier study K^+ ions are co-ordinated to four sulphate ions. The occupation of K^+ ion sites by smaller Na^+ ions causes a small degree of inward pull of the surrounding ions
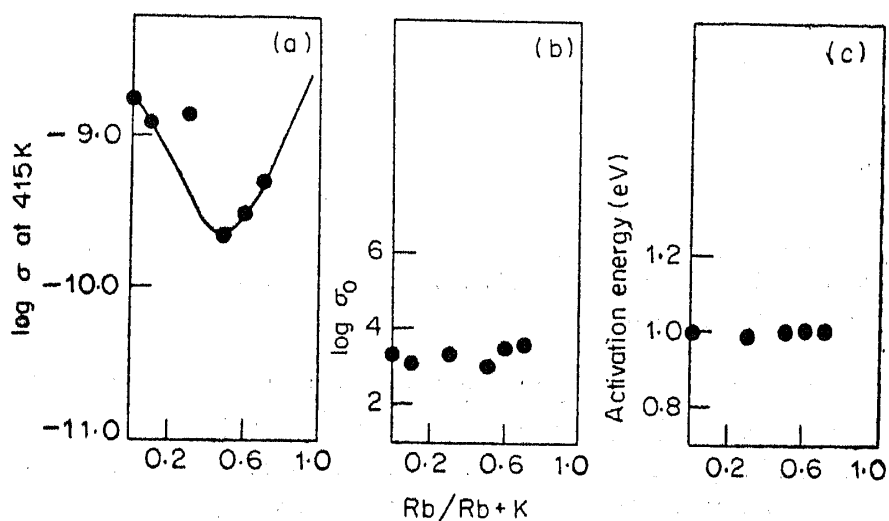

Figure 2. Variation of (a) log σ, (b) log σ_0 and (c) activation energy due to mixed alkali effect in 50 $ZnSO_4 \cdot xK_2SO_4 \cdot (50-x)$ Rb_2SO_4 glasses.
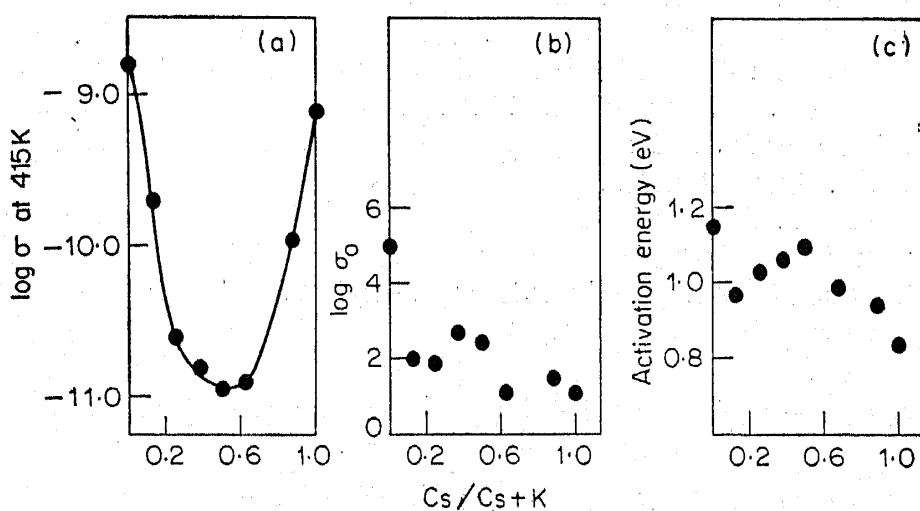

Figure 3. Variation of (a) log σ, (b) log σ_0 and (c) activation energy due to mixed alkali effect in 60 $ZnSO_4 \cdot xK_2SO_4 \cdot (40-x)$ Cs_2SO_4 glasses.
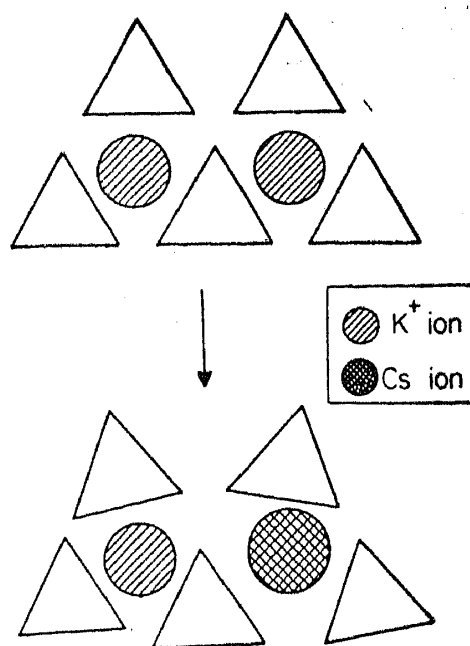
Figure 4. Schematic of possible rearrangement of structure when a K$^+$ ion is substituted by larger Cs$^+$ ion. Note that diffusion outwards is difficult when the larger ion is present.

and hence creates a local strain field. This strain field has the effect of locking up the K$^+$ ions in the neighbourhood which, we assumed, would therefore not contribute to conductivity. Since the substitution of Na$^+$ ions in general leads to a decrease in volume, there is an average enhancement of activation barriers. The contribution of Zn^{2+} ions to conductivity was neglected throughout.

Similar considerations may be applied to the other alkali pairs though we do not have a clear idea of the nature of the co-ordination of Cs$^+$ or Rb$^+$ ions. Substitution of K$^+$ ions by larger ions may not, in general, affect the activation energy since the anions can rearrange with no net strain when pushed outwards. We assume therefore, that the activation energies are unmodified. However, the K$^+$ ions in the immediate neighbourhood of larger (Rb$^+$ or Cs$^+$) ions are still locked up as schematically represented in figure 4 in two dimensions. The fact that activation energies and the pre-exponentional terms are not much affected is borne out in figures 2 and 3.

Hence, the conductivity variation is only due to the locking up of a fraction of dissimilar alkali-ion pairs which are nearest neighbours. We can therefore represent the total conductivity σ_t of a $x\mathrm{ZnSO_4}\,(1-x)\,[f(\mathrm{Rb},\ \mathrm{Cs})_2\mathrm{SO_4}\,(1-f)\ \mathrm{K_2SO_4}]$ glass by the expression,

$$\sigma_t = (1-x)\,A_{\mathrm{zn}^{2+}} \cdot \exp\left[\frac{-E_{\mathrm{zn}^{2+}}}{RT}\right] + 2\,(1-x)\,(1-f)\,A_{\mathrm{K}^+}\exp\left[\frac{-E_{\mathrm{K}^+}}{RT}\right]$$

$$+ 2\,(1-x)\,f\,A_{\mathrm{Rb}^+/\mathrm{Cs}^+} \cdot \exp\left[\frac{-E_{\mathrm{Rb}^+/\mathrm{Cs}^+}}{RT}\right]$$

$$-4\,(1-x)^2\,(1-f)\,f\,A_{\mathrm{K}^+} \cdot \exp\left[\frac{-E_{\mathrm{K}^+}}{RT}\right] \tag{1}$$

A's and E's represent the respective pre-exponential (frequency) factor and activation barriers.

The last term represents the contribution from locked-up K^+ ions whose concentration is governed by the joint probability of the presence of K^+ and the other alkali ion as immediate neighbours. Assuming that

$$A_{Rb^+/Cs^+} \cdot \exp\left[\frac{-E_{Rb^+/Cs^+}}{RT}\right] \cong A_{K^+} \exp\frac{-E_{K^+}}{RT}$$

in view of figure 2. Thus the value of f corresponding to the minimum conductivity may be obtained by differentiating equation (1) with respect to f,

$$\frac{\partial \sigma_t}{\partial f} = 0 \cong \exp\left[\frac{-E}{RT}\right]\{-2(1-x)A + 2(1-x)A$$

$$- 4A(1-x)^2(1-2f)\} = 0$$

or

$$2(1-x)(1-2f) \cong 0; \quad \text{or } f \cong \tfrac{1}{2}$$

The value of f obtained is in agreement with the conductivity behaviour in figures 2 and 3. The unique size ratio of K^+ to O^{2-} is the factor which, while causing significant strain contributions when Na^+ is present, does not affect the activation barriers when larger alkali ions are present. We therefore feel that in ionic glasses the mixed alkali effect is primarily a structural consequence and conductivity is dominantly affected by packing considerations, perhaps unlike in other network and covalently bonded glasses (Isard 1969, Day 1976)

Acknowledgements

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