

Electrical conductivity studies in K_2SO_4 - $ZnSO_4$ glasses

P S L NARASIMHAM, SUDHA MAHADEVAN and K J RAO*
Materials Science Division, National Aeronautical Laboratory, Bangalore 560 017
* Present address : Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560 012

MS received 31 October 1978

Abstract. The d.c. conductivities of K_2SO_4 - $ZnSO_4$ glasses have been measured over a wide range of temperature. It has been found that two different subglassy activation energies are present which may be associated with K^+ and Zn^{++} ions. Also a conductivity maximum occurs as a function of composition. These features have been discussed in the light of the random close packed model of sulphate glasses.

Keywords. Sulphate glasses; model structure; conductivity.

1. Introduction

Glasses are formed over wide range of compositions in the potassium sulphate-zinc sulphate system. Several physical properties characterising these glass systems such as densities, refractive indices, microhardnesses elastic properties and glass transition temperatures have already been reported from this laboratory (Narasimham and Rao 1978a). Optical absorption spectra of sulphate glasses doped with transition metal ions have also been investigated (Narasimham and Rao 1978b). These glasses conform to random close packing model of sulphate units in potassium sulphate rich compositions and to that of oxygen ion random close packing in zinc sulphate rich compositions (Narasimham and Rao 1978a). From spectroscopic studies it appears that zinc ions always retain an octahedral coordination (Narasimham and Rao 1978b).

So in the intermediate compositions where both octahedrally coordinated zinc ions and tetrahedrally coordinated potassium ions are present it should be interesting to investigate the nature of electrical transport in these highly ionic glass systems. Further, conductivity studies in purely ionic glass-forming systems seem to have been confined to the region above glass transitions such as in $Ca(NO_2)_2$ - KNO_3 systems (see Angell *et al* 1969; Bose *et al* 1970). In this paper, we report the d.c. conductivity measurements performed on these glasses over a sufficiently wide range of temperature. The behaviour of activation energies as a function of composition in different regions of temperature has been discussed

in the light of the structure of these glasses proposed by the authors earlier (Narasimham and Rao 1978a).

2. Experimental

The preparation of these glasses from K_2SO_4 and $ZnSO_4 \cdot 7H_2O$ has already been discussed (Narasimham and Rao 1978a). For the conductivity measurements they were obtained as thin slices not more than a millimeter in thickness so that conductivity measurements could be performed over a sufficiently wide range of temperature. The conductivity cell and the measuring technique have been discussed elsewhere (Sudha Mahadevan *et al* 1977). The resistances were calculated by measuring the current 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. The direction of the current was also altered periodically. The low temperature limit for our measurements was set by the sample resistances exceeding 10^{12} ohms. Conductivities were measured beyond the glass transition up to temperatures where either the samples deformed or crystallized.

3. Results and discussion

The conductivity variations with temperature of six different compositions of sulphate glasses are shown in figure 1. In general the conductivities of the samples vary by more than six orders of magnitude in all these cases over an accessible temperature range of about 200 K. The $\ln \sigma$ vs $1/T$ behaviour is nonlinear and in all the cases appear to fall into three distinguishable linear regions; the first two being just above and below the glass transition temperatures and the third well below the glass transition temperature. In the inset of figure 1 these three regions have been delineated for a particular case.

The conductivities of these glasses were found to relax considerably (to much lower values) on annealing. In K_2SO_4 rich glasses the relaxations were much more than in zinc sulphate rich glasses in contrast to the behaviour of volume relaxation (Narasimham and Rao 1968a). The conductivity plots in figure 1 represent the data of completely annealed glasses when no changes were observed on further annealing. However, it was noted that annealing did not alter the general three-region feature of the conductivity plots.

The variation of isothermal conductivities as a function of composition indicated a maximum. In figure 2 this variation has been shown for three different temperatures representing the three different regions of the conductivity plots. It is interesting to note that this maximum occurs around 50 mole% of zinc sulphate. The activation energies calculated for the three different temperature regions for various compositions are shown in figure 3. In the inset of figure 3 the energies of activation have been plotted as a function of the densities of the bulk glasses. The two activation energies for the subglassy regions do not seem to be sensitive to composition variations. However, the activation energies above the glass transition temperature increase rapidly with the concentration

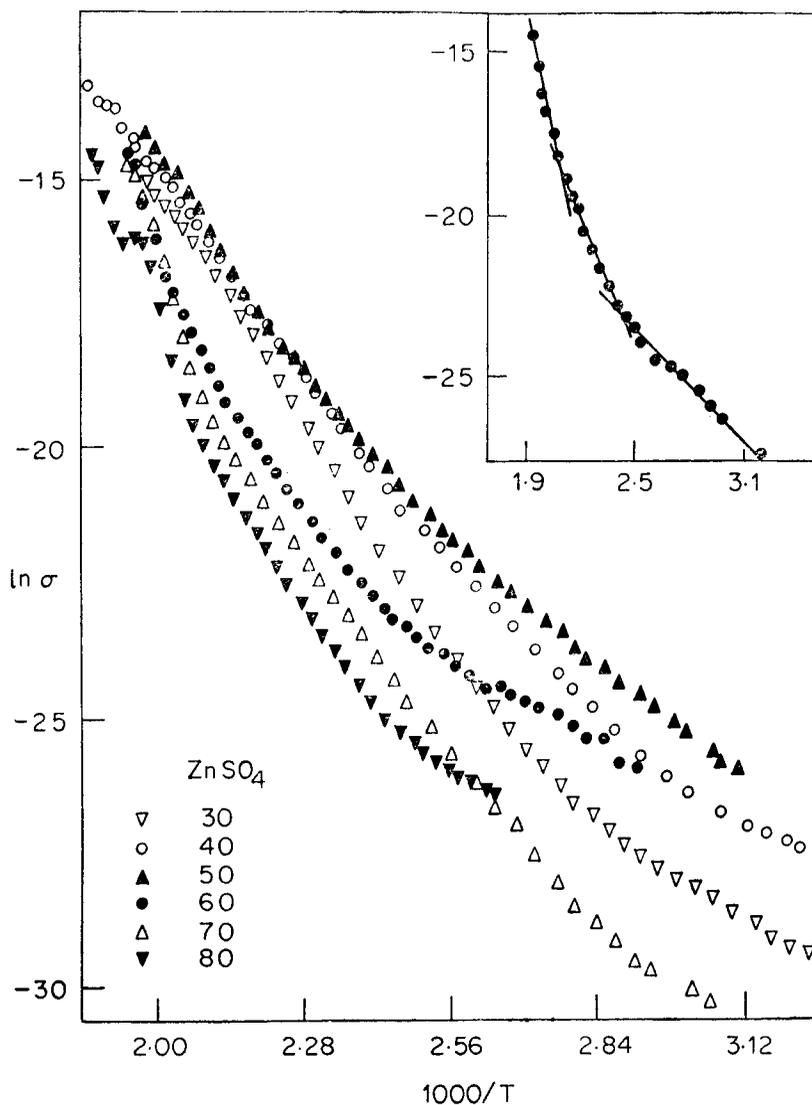


Figure 1. Variation of $\ln \sigma$ as a function of $(1/T)$. The inset is a similar plot for 60% ZnSO_4 glass where the three linear regions of $\ln \sigma$ are delineated.

of zinc ions. The T_g evaluated from the conductivity plots are in quite good agreement with those from thermal measurements (Narasimham and Rao 1978a).

The two different subglassy regions seem to be caused by the dominance of either K^+ or Zn^{2+} ions both of which contribute to conductivity. K^+ ions can be expected to have a lower activation barrier since it is singly charged and since its surroundings have a net lower density because it seems to correspond to loose random close packing of sulphate spheres (Narasimham and Rao 1978a). Therefore, a slight rearrangement or rotation of sulphate groups may be expected to enable K^+ ion migration. Zn^{2+} ions, however, carry a higher charge and also correspond to a more tightly packed environment in this structural model. It

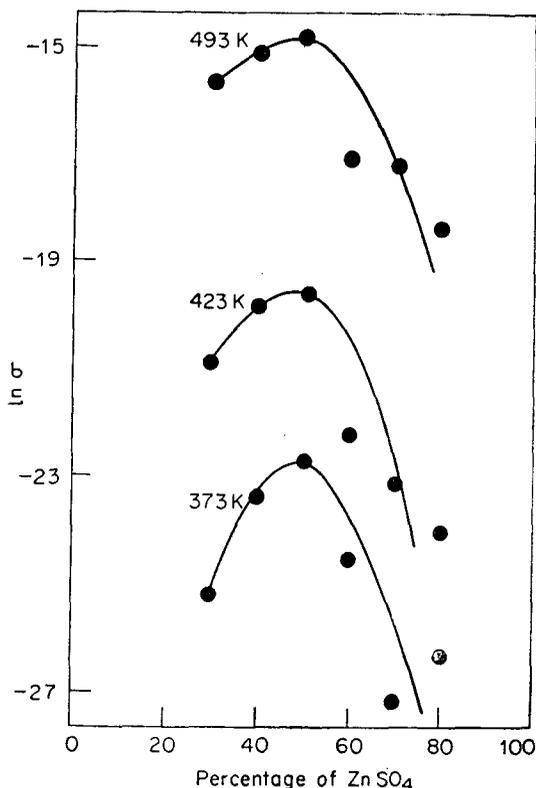


Figure 2. Isothermal variation of σ as a function of composition at three different temperatures.

requires more energetic saddle point rearrangements to allow for the migration of Zn^{++} ions. Hence we associate the lower activation energy with K^+ ions and the higher one with Zn^{++} ions. It may be seen from figure 3 that the activation energies of both Zn^{++} and K^+ ions are fairly constant over the entire composition range in good agreement with the above structural model. Hence it should be expected that these activation energies are independent of bulk densities of the glass which appears to be true as shown in the inset of figure 3.

The total conductivity represents the charge transported by (a) the low charge low activation barrier K^+ ions and (b) the high charge high activation barrier Zn^{++} ions. The activation energy presumably represents the highest barrier that the ions will have to overcome in the conduction process. However, a transport event can occur only when a neighbouring void of sufficient size is available for either the K^+ or Zn^{++} ions to jump into. It should be noted that substitution by zinc decreases the number of larger tetrahedral voids which are presumably essential for the conduction to occur. Further, with increasing concentrations of zinc and decreasing specific volumes of the glasses zinc ions find it increasingly difficult to rearrange their own surroundings and without such a rearrangement they may prefer either to jump back or remain in their original positions. These considerations will influence to a very great extent the pre-exponential factors in

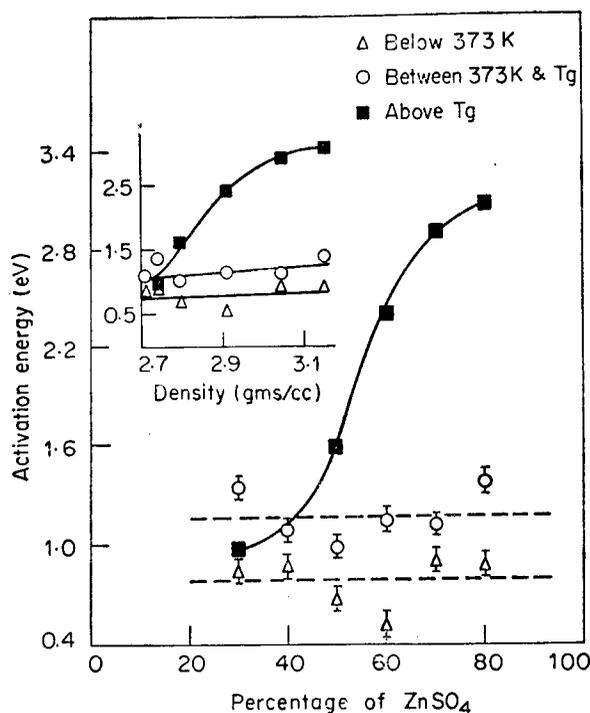


Figure 3. The activation energies for the three regions in figure 1 as a function of composition. The inset is a plot of activation energies as a function of density of the glasses.

conductivity expressions and hence the value of σ . Therefore substitution of K^+ ions by Zn^{++} , though is expected to increase the conductivity by virtue of its larger charge, may also decrease the conductivity because it causes depletion of larger tetrahedral voids. As a result, the conductivity is expected to show a maximum as function of Zn^{++} ion concentration. Assuming that the larger tetrahedral voids play a crucial role in conduction, we can roughly evaluate the concentration of Zn^{++} ions at which the maximum in conductivity occurs in the following manner. The total conductivity σ_t may be written as

$$\begin{aligned}\sigma_t &= \sigma_{K^+} + \sigma_{Zn^{++}}, \\ &= 2(1-x)A_1 \exp(-E_1/kT) + xC_t A_2 \exp(-E_2/kT),\end{aligned}$$

where x is the mole fraction of $ZnSO_4$ and C_t is the concentration of tetrahedral voids. E_1 and E_2 are the activation barriers for K^+ and Zn^{++} ions.

In the above expression, it is assumed that it is only Zn^{++} ion conductivity which depends on the tetrahedral void concentration and it is so because the K^+ ions will anyway ensure for themselves availability of tetrahedral voids near to them (Narasimham and Rao 1978a). Further, since the number of tetrahedral voids are continuously destroyed by Zn^{++} ions, it is function of x and is given by $C_t = 3(1-x)$ moles. The total conductivity σ_t may be written as

$$\sigma_t = B_1(1-x) + 3B_2x(1-x)$$

where B_1 and B_2 are given by

$$B_1 = 2A_1 \exp(-E_1/kT)$$

and

$$B_2 = A_2 \exp(-E_2/kT).$$

Therefore by equating $(\partial\sigma_i/\partial x)$ to zero, we may expect the maximum in conductivity to occur when

$$x = \frac{3B_2 - B_1}{6B_2}$$

values of B_1 and B_2 may be found out by making use of conductivity values at two different temperatures* and it is found B_1 is generally much less than B_2 so that x is approximately 0.5 quite consistent with the data presented in figure 2.

The activation barrier corresponding to temperatures above glass transition is very interesting. It is sigmoidal in shape and increases rapidly in the intermediate regions. Since it is a function of Zn^{2+} ion concentration it is likely that in super-cooled melts Zn^{2+} ions migrate as charged clusters of much larger sizes (may be a few Zn^{2+} ions with associated octahedra of sulphate ions). One of the reasons why the conductivity value of the zinc sulphate rich compositions drop fairly rapidly above the glass transition temperature may be due to the low mobility of these charged clusters.

Hence the structural model of sulphate glasses, based on the random close packing of sulphate ions seems to provide a reasonable basis to discuss the conductivities of these glasses. It may be noted that in these glasses K^+ and Zn^{++} ions are present in distinct environments of their own. It is the essentially fully ionic nature (as contrasted rigid covalent networks) of these glasses which seems to allow for fairly distinct environments and hence distinct barriers to migration. However once the rigid anion framework of the glass is broken down above the glass transition temperature, the very high ionic potential (charge to radius ratio) allows the Zn^{++} ions to form charged clusters and hence alter the magnitudes of the conduction parameters.

4. Conclusions

The conductivities of sulphate glasses exhibit two linear regions below the glass transition temperature corresponding to the dominance of either K^+ or Zn^{++} ions as the conducting species. The activation barriers for K^+ and Zn^{++} ions below the glass transition temperatures are nearly independent of composition. Above the glass transition temperature activation barriers vary sensitively as a function of composition and it may be due to the formation of large ionic clusters migrating as a group. The behaviour of conductivity both as a function of temperature

* The pre-exponential factors were determined by using the conductivities at 393.6 K and 425.1 K for 60% $ZnSO_4$ glasses. (B_1/B_2) were found to be 6×10^{-6} to 1×10^{-5} in sample cases of 40% and 70% Zn^{++} containing glasses and the value of x was found for all the compositions to be about 0.5.

and composition is consistent with the structural model based on the random close packing of the sulphate ions.

Acknowledgements

The authors are thankful to Prof. S Ramaseshan and Prof. S R Valluri for their kind encouragement.

References

- Angell C A and Moynihan C T 1969 *Molten salts* ed. G Mamantov (New York: Marcel Dekker)
Bose R, Weiler R and Macedo P B 1970 *Phys. Chem. Glasses* **11** 117
Narasimham P S L and Rao K J 1978a *J. Non-Cryst. Solids* **27** 225
Narasimham P S L and Rao K J 1978b *Proc. Indian Acad. Sci.* **A87** 275
Sudha Mahadevan, Giridhar A and Rao K J 1977 *J. Phys.* **C10** 4499