

## An analysis of the electrical conductivity of the $\text{Ag}_2\text{SO}_4\text{--K}_2\text{SO}_4$ binary system

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**Abstract.** Electrical conductivity of the  $\text{Ag}_2\text{SO}_4\text{--K}_2\text{SO}_4$  binary system shows three maxima at 20, 70 and 90 mole% of  $\text{K}_2\text{SO}_4$  added to  $\text{Ag}_2\text{SO}_4$ . The first and the third maxima have been explained in the light of intragrain percolation due to lattice distortion, whereas, the second maximum by the surface percolation. The limit of solid solubility has been set at 20 mole% on the basis of evidences obtained from XRD, DTA and SEM techniques.

**Keywords.** Ionic conductivity; solid solubility; lattice distortion.

### 1. Introduction

The study of alkali metal sulphates,  $\text{Li}_2\text{SO}_4$  (Kvist and Lunden 1965),  $\text{Na}_2\text{SO}_4$  (Jacob and Rao 1979) and  $\text{K}_2\text{SO}_4$  (Natarajan and Secco 1975) revealed that they are good ionic conductors with negligible electronic transference number in their high temperature form. Other than alkali metal sulphates, only  $\text{Ag}_2\text{SO}_4$  is a better cationic conductor which is used in  $\text{SO}_2$  sensor (Liu *et al* 1990). Silver sulphate is comparatively a less studied sulphate. The high temperature hexagonal phase is isomorphic with that of the high temperature phase of  $\text{K}_2\text{SO}_4$ . These sulphates have been used in the sulphur dioxide gas sensors (Gauthier and Chamberland 1977). For low temperature electrochemical applications, high ionic conductivity near ambient temperature is a prime requisite. In this regard binary sulphates are known to be more conducting than the mono components. Hence,  $\text{Ag}_2\text{SO}_4\text{--K}_2\text{SO}_4$  binary system is selected to develop from low temperature electrochemical applications, in general, and particularly  $\text{SO}_x$  gas sensor point of view. Kumari and Secco (1983) reported the conductivity only for 25 and 60 mole%  $\text{K}_2\text{SO}_4$  added to  $\text{Ag}_2\text{SO}_4$ . As a continuous effort for the development of sulphate based electrolytes for low temperature electrochemical applications, an investigation on the electrical conductivity over entire range of compositions belonging to  $\text{Ag}_2\text{SO}_4\text{--K}_2\text{SO}_4$  system is reported in this paper.

### 2. Experimental

The initial ingredients  $\text{Ag}_2\text{SO}_4$  and  $\text{K}_2\text{SO}_4$  with purity greater than 99.99% were procured from E Merck, India. An appropriate mole fraction of the well dried chemicals in  $(x)\text{Ag}_2\text{SO}_4\text{--}(1-x)\text{K}_2\text{SO}_4$  (where  $x = 0.1, 0.2, 0.3, \dots, 1$ ) were prepared by melting the mixture in a silica crucible followed by twin roller quenching technique at room temperature (Singh *et al* 1988, 1992). The samples were characterized by X-ray powder diffraction (XRD) and differential thermal analysis (DTA) using Philips PW1700, X-ray powder diffractometer and Perkin Elmer TADS 1700, thermal

analyzer respectively. The microstructures were examined with a Cambridge 250 Mark-III Stereoscan scanning electron microscope (SEM). The details of electrical conductivity measurements are similar to those described previously (Singh *et al* 1992). The reproducibility of the data was ensured by repeating the measurement.

### 3. Results and discussion

The XRD patterns of all compositions showed an increase in half width of full height of characteristic peaks (slight potential line broadening) in general; particularly for those samples which are biphasic mixtures. The potential line broadening is also seen for pure quenched samples. Such a line broadening is due to: (i) reduction of grain size resulting from quenching of melt and (ii) the composite nature of the samples under study. These results are in good agreement with the earlier reports (Singh and Bhoga 1990). A comparison of XRD data (a few lines as indicative) with JCPDS values are given in table 1. It is apparent that in case of 10 and 20 mole%  $K_2SO_4$  into  $Ag_2SO_4$ , all the diffracted lines closely match with those due to  $Ag_2SO_4$ . Absence of diffraction lines of  $K_2SO_4$  in these compositions rules out the possibility of  $K_2SO_4$  precipitation into  $Ag_2SO_4$  matrix. A small deviation in the values of  $d$  is, however, due to lattice distortion as a result of the formation of solid solution. Similarly, the solid solubility up to 20 mole% of  $Ag_2SO_4$  into  $K_2SO_4$  is determined. At higher concentrations the diffraction lines due to both the phases are identified whereby we conclude that the intermediate compositions are biphasic mixtures.

The transition temperatures for all samples obtained from onset of endothermic peaks in the thermogram are compared with the earlier reports (Nacken 1907; Kumari and Secco 1983) in table 2. The observed results are in close agreement with those of Nacken (1907). A careful study of phase diagram reported by Kumari and Secco

**Table 1.** Comparison of experimental  $d$  and relative intensity values of AK9, AK8, AK7 and AK7 with JCPDS\* data of pure  $Ag_2SO_4$  and  $K_2SO_4$ .

AK9		AK8		AK7		AK6		JCPDS			
$d$	$I/I_0$	$d$	$I/I_0$	$d$	$I/I_0$	$d$	$I/I_0$	$d$	$I_0I_0$	Phase	$hkl$
4.72	6.3	4.71	6.2	4.72	7.4	4.71	8.7	4.69	10	Ag	111
—	—	—	—	4.19	3.2	4.19	5.4	4.17	28	K	021
4.24	21	4.02	22	4.00	25	4.04	28	3.99	25	Ag	022
—	—	—	—	3.77	4.2	3.75	6.1	3.74	18	K	002
3.19	75	3.18	81	3.18	74	3.18	74	3.17	77	Ag	040
—	—	—	—	3.00	8.4	3.01	14	3.00	77	K	022
2.88	100	2.88	100	2.88	100	2.88	100	2.87	100	Ag	311
2.66	71	2.66	96	2.65	72	2.66	68	2.64	100	Ag	002
2.28	12	2.27	8.3	2.27	9.5	2.27	8	2.27	8	Ag	151
1.92	33	1.92	29	1.92	32	1.93	28	1.92	30	Ag	351
1.71	17	1.71	18	1.71	15	1.72	14	1.71	17	Ag	062
1.59	4.2	1.60	4.8	1.59	6.3	1.59	3.6	1.58	3	Ag	080

AK9-90  $Ag_2SO_4$ :10  $K_2SO_4$ , AK8-80  $Ag_2SO_4$ :20  $K_2SO_4$ , Ag- $Ag_2SO_4$ , AK7-70  $Ag_2SO_4$ :30  $K_2SO_4$ , AK6-60  $Ag_2SO_4$ :40  $K_2SO_4$ , K- $K_2SO_4$

\* JCPDS nos. 27-1403 ( $Ag_2SO_4$ ) and 5-613 ( $K_2SO_4$ ).

**Table 2.** Comparison of solid–solid phase transition temperatures for  $Ag_2SO_4-K_2SO_4$  binary system with the reports of Nacken (1907) and Kumari and Secco (1983).

Composition	Observed	Nacken (1907)	Kumari and Secco (1983)
$Ag_2SO_4:K_2SO_4$			
100:00	415	416	416
90:10	—	300	284
80:20	—	300	284
70:30	302	300	284
60:40	302	300	276
50:50	302	300	283
40:60	301	300	280
30:70	301	300	261
20:80	—	294	261
10:90	—	304	261
00:100	—	555	554

(temperature in °C)

(1983) and Nacken (1907) reveals two phase mixtures in entire binary system below 300°C. Above 300°C, they form a complete solid solution. Furthermore, the XRD results discussed above also predicted that the compositions in the range 30 to 70 mole%  $K_2SO_4$  are two-phase mixtures of  $Ag_2SO_4$  and  $K_2SO_4$ . Hence, the observed endothermic peak in thermogram is due to formation of a solid solution at that temperature. The absence of endothermic peak around 300°C in cases of 10, 20, 80 and 90 mole% of  $K_2SO_4$  confirms the solid solubility. These results indicate that, during cooling of the melt of intermediate compositions, two phases ( $Ag_2SO_4$  and  $K_2SO_4$ ) separate out at 302°C and forms the biphasic mixtures at room temperature. Figures 1a and 1b display the microphotographs of 80:20 and 50:50 ( $Ag_2SO_4:K_2SO_4$ ) samples respectively. 80  $Ag_2SO_4:20 K_2SO_4$  (figure 1a) shows a uniform grain morphology indicating a single phase compound. Similar microstructures are also observed for 10, 80 and 90 mole%  $K_2SO_4$  incorporated  $Ag_2SO_4$  and of pure components. On the other hand, 50  $K_2SO_4:50 Ag_2SO_4$  (figure 1b) shows the presence of two distinguishable phases. The microstructures of other remaining compositions also indicated the formation of biphasic mixtures.

The increased solid solubility limit (up to 20 mole%) obtained from XRD, DTA and SEM data is due to rapid quenching of the melt. The increased solid solubility limit as a result of quenching has also been observed in the case of a number of divalent sulphate doped lithium sulphates (Singh and Bhoga 1990).

The bulk conductivity, obtained from complex impedance analysis as discussed earlier (Singh *et al* 1992) is plotted as a function of  $K_2SO_4$  concentration at two different temperatures in figure 2. Three conductivity maxima at 20, 70 and 90 mole% of  $K_2SO_4$  are clearly seen. In order to discuss the concentration and temperature dependent conductivity behaviour of the system, entire investigated compositional range is divided into two groups: (i) group I includes the results of solid solutions 0 to 20 and 80 to 100 mole%  $K_2SO_4$  and (ii) group II covers the compositions ranging from 30 to 70 mole%  $K_2SO_4$  which are biphasic mixtures. Figure 3 illustrates the Arrhenius plots for the first group. Over the entire temperature range of investigation,

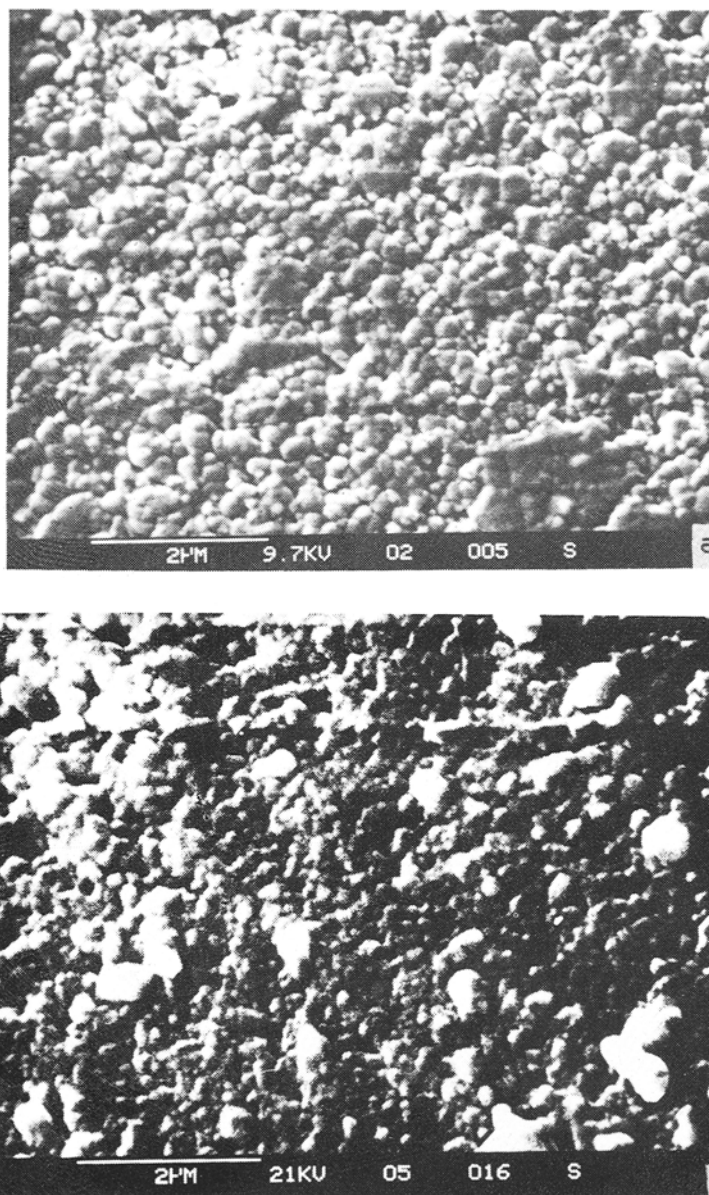


Figure 1. Microphotographs of a. 80 Ag<sub>2</sub>SO<sub>4</sub>:20 K<sub>2</sub>SO<sub>4</sub> and b. 50 Ag<sub>2</sub>SO<sub>4</sub>:50 K<sub>2</sub>SO<sub>4</sub>.

all compositions obey the Arrhenius law:

$$\sigma T = (\sigma T)_0 \exp(-E_a/kT), \quad (1)$$

where  $(\sigma T)_0$  and  $E_a$  are respectively the pre-exponential factor and the activation enthalpy. The values of  $\sigma$ ,  $(\sigma T)_0$  and  $E_a$  obtained using (1) are presented in table 3. The absence of expected change in slope at 302°C (due to formation of solid solution) also indicates an extension of solid solubility to room temperature.

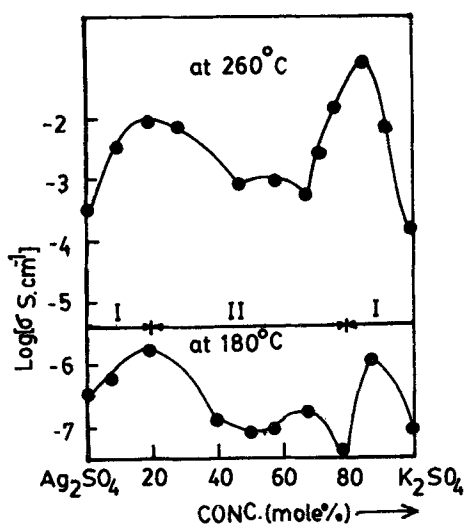
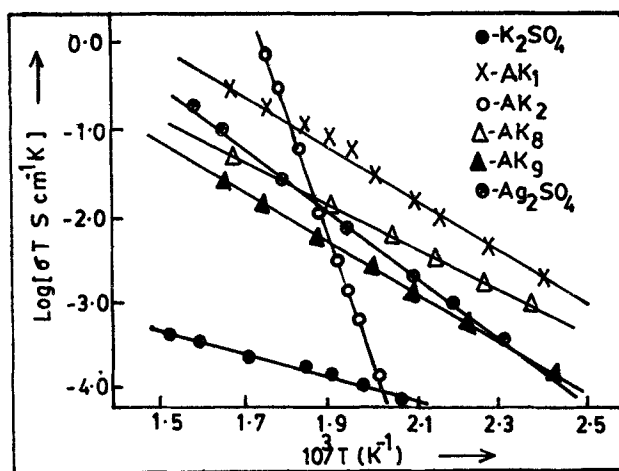
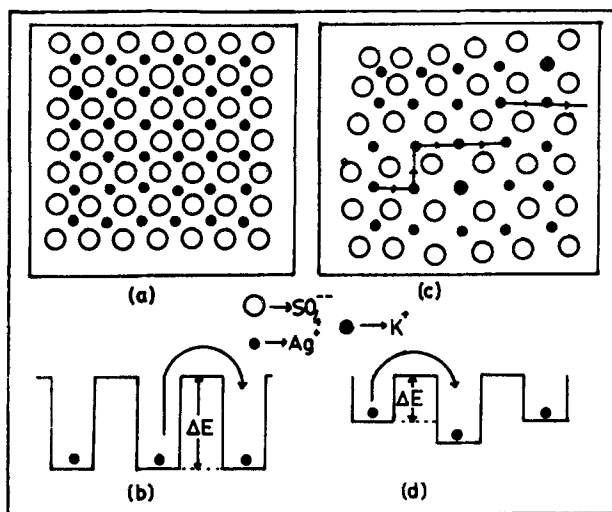

 Figure 2. Functional dependence of conductivity on  $K_2SO_4$  concentration.


Figure 3. Arrhenius plots for region I.

**Table 3.** The values of conductivity  $\sigma$ , pre-exponential factor  $(\sigma T)_0$  and activation energy  $E_a$  for the pure, 10 and 20 mole% of  $K_2SO_4$  doped  $Ag_2SO_4$ .

Sample	$\log(\sigma)$ (S/cm)	$\log(\sigma T)_0$ (SK/cm)	$E_a$ (eV)
$Ag_2SO_4:K_2SO_4$			
00:00	-1.899	-4.626	0.71
90:10	-2.465	-5.192	0.54
80:20	-2.046	-4.772	0.47



**Figure 4.** (a) Schematic representation of a plane through the host  $\text{Ag}_2\text{SO}_4$  lattice, (b) potential well of host lattice, (c) host lattice in which  $\text{Ag}^+$  sites are randomly occupied by relatively larger size  $\text{K}^+$  resulting into local distortion and (d) potential after partial substitution.

Since anions and cations of the  $\text{Ag}_2\text{SO}_4$  and  $\text{K}_2\text{SO}_4$  are of same valency, an increased conductivity in  $\text{Ag}_2\text{SO}_4$  rich region cannot be explained by classical theory of aliovalent doping (Hoffer *et al* 1981). Obviously, the main factor responsible for an enhancement in conductivity is considered to be solely due to lattice distortion caused by the incorporation of the bigger guest  $\text{K}^+$  into the  $\text{Ag}_2\text{SO}_4$  host lattice. A model based on the mobility of ions as a function of lattice distortion was proposed recently (Singh and Bhoga 1992). According to this model although,  $\text{Ag}^+$  and  $\text{K}^+$  possess the same charge, there is a difference in their ionic sizes ( $r_{\text{Ag}^+} < r_{\text{K}^+}$ ). Therefore, the partial replacement of former by latter produces local lattice expansion in the host  $\text{Ag}_2\text{SO}_4$ . A simplest pictorial representation of the model is depicted in figures 4a and c. Such a lattice distortion widens the inter connecting windows and subsequently reduces the height of potential well (figure 4d). Hence, the energy required for surmounting the energy barrier so as to realize a net ion migration from one shallow potential well to nearby one, decreases. This is supplemented by the experimental results presented in table 3, wherein a decrease in activation energy  $E_a$  with the partial substitution of  $\text{K}^+$  for  $\text{Ag}^+$  is seen. Thus a lattice expansion not only opens up the lattice but also reduces the activation energy which, in turn, gives rise to a number of interconnecting percolating pathways between the adjacent interstitial sites. Such percolating pathways increase with increased dopant concentration leading to a rise in conductivity. The maximum conductivity at 20 mole% of  $\text{K}_2\text{SO}_4$  is due to percolation threshold concentration.

Interestingly, the conductivity enhances in spite of the contraction of  $\text{K}_2\text{SO}_4$  lattice due to the partial substitution of smaller  $\text{Ag}^+$  in place of  $\text{K}^+$  (figure 2). This enhancement is attributed to the strong preference for the mobility of  $\text{Ag}^+$  relative to  $\text{K}^+$ , because  $\text{Ag}^+$  needs relatively smaller lattice opening compared to  $\text{K}^+$ . Thus the addition of  $\text{Ag}_2\text{SO}_4$  enhances the mobile ion concentration, in turn, the conductivity.

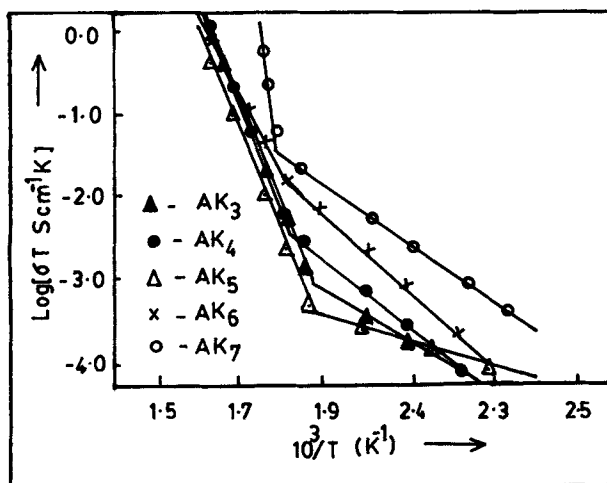


Figure 5. Arrhenius plots for region II.

Arrhenius plots of group II depicted in figure 5 show a change in slope at around  $300^\circ\text{C}$  corresponding to the formation of solid solution. In this group 70 mole% of  $\text{K}_2\text{SO}_4$  added into  $\text{Ag}_2\text{SO}_4$  shows maximum conductivity. The conductivity enhancement in binary system, in general, could be caused by the presence of highly conducting intermediate phase. For the present system, however, this is not true as XRD, DTA and SEM results show the presence of only  $\text{K}_2\text{SO}_4$  and  $\text{Ag}_2\text{SO}_4$  phases. Amongst the existing theories of composite solid electrolytes, the theory proposed recently (Singh 1993) explains an increase in the conductivity in this region. The total ionic conductivity of the specimen of this group is due to the contributions made by: (a) the grains of  $\text{Ag}_2\text{SO}_4$  solid solution, (b) grains of  $\text{K}_2\text{SO}_4$  solid solution and (c) interfacial space charge region between the  $\text{Ag}_2\text{SO}_4/\text{Ag}_2\text{SO}_4$ ,  $\text{K}_2\text{SO}_4/\text{K}_2\text{SO}_4$  and  $\text{Ag}_2\text{SO}_4/\text{K}_2\text{SO}_4$  grains. Interfacial space charge region ( $\text{Ag}_2\text{SO}_4/\text{K}_2\text{SO}_4$ ) formed due to the net transfer of surface cations from  $\text{Ag}_2\text{SO}_4$  to  $\text{K}_2\text{SO}_4$  and *vice versa*. The ion transport parallel to the interface (in the space charge region) is called surface percolation. This surface percolation is of great importance from mass transport view point and provides an increase in overall conductivity of the sample. The maximum conductivity at 30 mole%  $\text{Ag}_2\text{SO}_4$  is due to its optimum dispersion or percolation threshold (Bunde *et al* 1985).

#### 4. Conclusions

An investigation of electrical conductivity of the  $\text{Ag}_2\text{SO}_4\text{-K}_2\text{SO}_4$  system—supported by XRD, DTA and SEM—have shown maxima in conductivity at 20, 70 and 90 mol%  $\text{K}_2\text{SO}_4$ . Intragrain percolation (20, 90 mol%) due to lattice distortion, and, surface percolation (70%) account for these maxima. Rapid quenching has enhanced the limit of solid solubility of  $\text{K}_2\text{SO}_4$  to 20 mol%. The 90–10  $\text{Ag}_2\text{SO}_4\text{-K}_2\text{SO}_4$  composition with highest conductivity is proposed as a candidate for  $\text{SO}_2/\text{SO}_3$  gas sensor.

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