

FAST Na⁺ ION TRANSPORT IN Na₂SO₄(I):CeO₂ COMPOSITE SOLID ELECTROLYTE

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The present investigation on Na₂SO₄(I):CeO₂ composite has been performed in order to stabilize the Na₂SO₄(I) phase. A maximum enhancement of 1000 times is achieved for 4 mole% CeO₂ at room temperature. At 548 K the σ attains a maximum value of 1.213×10^{-4} and at 677 K an order of magnitude increase has been observed. The phase examination proves that the addition of an "inert" phase into a crystalline matrix is a viable option for the development of Na⁺ ion conducting solid electrolyte materials for all solid state batteries.

Keywords: Composite solid electrolytes and sodium Sulfate.

INTRODUCTION

Anticipating a potential use of Na⁺ based solid fast-ion conductors as electrolyte in Solid State Electrochemical devices, hitherto a large number of efforts have been devoted in the branch of Solid State Ionics.

The room temperature structure has been characterized by an orthorhombic symmetry which transforms into hexagonal symmetry at 514 K designated as Na₂SO₄(I) [1]. Across this temperature regime, it undergoes several stable as well as metastable transformations. The electrical conductivity of Na₂SO₄(I) is due to the mobile sodium ions and various studies are available in the open literature [2,3]. Recently many workers have attempted unsuccessfully to improve the room temperature conductivity by the addition of other cationic species and rare earth materials [4,5]. The present study has been aimed and attempted to achieve and or improve the fast ion conductivity of Na₂SO₄ down to ambient by way of addition of ceramic oxide filler, for instance CeO₂.

EXPERIMENTAL

Reagent Grade Na₂SO₄ and CeO₂ were procured from E.Merck (India). The various compositions of Na₂SO₄ and

CeO₂ were prepared by grinding the requisite mixtures and quenching on a clean aluminium plate from the melting temperature of Na₂SO₄. The phase analysis of these composite mixtures has been carried out using XRD technique with Cu-K_α radiation (JEOL JDX 8030, X-ray diffractometer, Japan) at room temperature.

The conductivity measurements have been carried out with pellets obtained by pressing the fine powdered samples under the pressure of 15 tons/cm² using a stainless steel die and a hand-operated hydraulic press. To minimize the electrical contact problems, the flat faces of pellets were coated with quick drying graphite aquadag (Dag # 154, Acheson, Holland) on both sides as electrodes.

Such pellets are then stacked between stainless steel electrode, in order to ensure proper electrical contact. For electrical conductivity measurements, fixed frequency (1.5 kHz) a.c. impedance technique has been employed (Wayne Kerr auto balance bridge B 331, England). Measurements are made isothermally on heating cycle only. The temperature range covered was 300 K - 677 K.

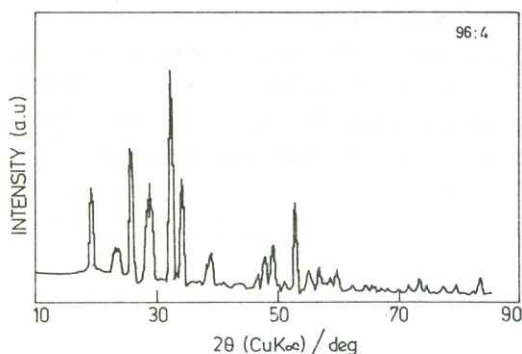


Fig. 1: X-ray diffractogram of 96:4 Na₂SO₄(I) : CeO₃ composites

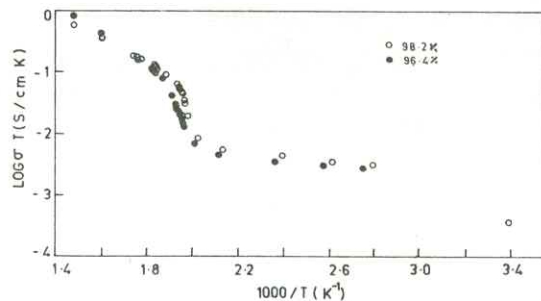


Fig. 3: Arrhenius plot for 98:2 and 96:4 Na₂SO₄(I) : CeO₂ composites

RESULTS AND DISCUSSION

XRD Studies

Various compositions of Na₂SO₄:CeO₂ mixtures have been examined by using XRD technique at room temperature. The typical X-ray diffractometer corresponding to 98:2 and 50:50 compositions of Na₂SO₄:CeO₂ are shown in Figs. 1 and 2. A close examination of the above diffractometer shows the existence of patterns corresponding to both Na₂SO₄ and CeO₂, which rules out the possibility of any global chemical reaction between them, eventhough the composite product is obtained by quenching the metals of the binary mixtures of Na₂SO₄ and CeO₂. The product resulting out of mixing the above two component is, therefore, a biphasic composite matrix of CeO₂ dispersed into Na₂SO₄ matrix.

Electrical conductivity studies

The ionic conductivity of the different composite mixtures of Na₂SO₄:CeO₂ has been measured from room temperature up to 677 K.

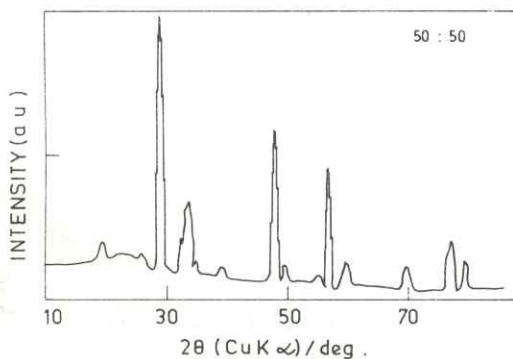


Fig. 2: X-ray diffractogram of 50:50 Na₂SO₄(I) : CeO₂ composites

Electrical Conductivity Versus Temperature

The Arrhenius plots of the various composite mixtures is shown in the Figs. 3 and 4. The σ variation upon increasing the temperature in the presence of insoluble "inert" additive, CeO₂, may be explained invoking the space charge model. However, while observing the overall trend the defect induced conductivity has also been evident. Besides σ enhancement due to the presence of inert phase particles, it must be emphasized that both extrinsic and intrinsic regions are also responsible for the conduction with respect to temperature. This is evident by a sharp discontinuity in σ at or near the Na₂SO₄ hexagonal phase transformation (T_c) as shown in Figs. 3 and 4.

In the present study, CeO₂ has been added in to the Na₂SO₄ matrix as in the case of Liang's LiI-r-Al₂O₃ system [6]. The pronounced changes in the behaviour is observed at all temperatures besides room temperature. At room temperature, a marked improvement in σ (2.5×10^{-6} S/cm) has been observed for 4 mole% addition of CeO₂. The σ enhancement at room temperature (300 K) is about 1000 times higher than pure Na₂SO₄. Similarly at high temperatures, prominent variations with significant

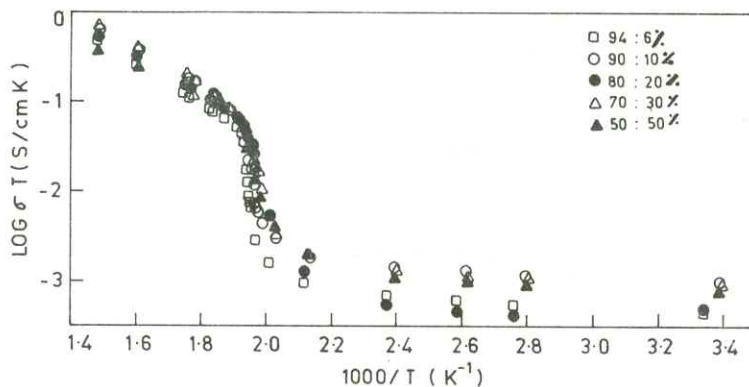


Fig. 4: Arrhenius plot for 94:6, 90:10, 80:20, 70:30 and 50:50 Na₂SO₄(I) : CeO₂ composites

TABLE I: Conductivity of Na₂SO₄:CeO₂ composites

Composition (mole %)	Temperature K	σ S/cm
98:2	300	1.22×10^{-6}
	512	6.76×10^{-5}
	515	9.07×10^{-5}
	548	2.37×10^{-4}
	677	8.50×10^{-4}
96:4	300	2.51×10^{-6}
	512	6.20×10^{-5}
	515	6.97×10^{-5}
	548	2.61×10^{-4}
	677	1.26×10^{-3}
94:6	300	1.47×10^{-6}
	512	1.45×10^{-5}
	515	3.33×10^{-5}
	548	1.51×10^{-4}
	677	7.04×10^{-4}
90:10	300	1.20×10^{-6}
	512	5.67×10^{-6}
	515	1.20×10^{-5}
	548	1.62×10^{-4}
	677	8.84×10^{-4}
80:20	300	1.69×10^{-6}
	512	7.15×10^{-5}
	515	8.33×10^{-5}
	548	1.99×10^{-4}
	677	7.59×10^{-4}
70:30	300	1.08×10^{-6}
	512	1.77×10^{-5}
	515	2.88×10^{-5}
	548	1.47×10^{-4}
	677	9.44×10^{-4}
50:50	300	9.46×10^{-7}
	512	1.47×10^{-5}
	515	2.02×10^{-5}
	548	1.15×10^{-4}
	677	4.93×10^{-4}

improvement in the conductivity values of the present composites have also been observed. Table I summarizes the σ values obtained at different temperatures. According to Maier [7], the creation of additional lattice defects can be quantitatively understood by "space charge region" which is induced by an internal absorption of ions at the oxide's

(CeO₂) surface. The present conductivity data suggest that there is an increase in the sodium ion vacancies in the host Na₂SO₄ matrix due to the presence of the dispersed insulating grains which absorb the interface of conducting-non-conducting grain, thereby creating some additional vacancy concentration in the bulk of the host Na₂SO₄ network.

Electrical conductivity versus composition

Fig. 5 shows the variation of conductivity ($\log \sigma$) versus concentration of CeO₂ (mole%) content for various temperatures below and above T_c. The usual behaviour of the conductivity versus concentration of second phase particles is roughly parabolic, increasing sharply as the concentration of CeO₂ content increases and attains a maximum value at 4 mole% of CeO₂, beyond which it falls rapidly. This may be ascribed to the dominant phase of inert particles which may tend to suppress the mass ionic transport behaviour of the host matrix. The above nature has been observed in the present study only for specific compositions. Accordingly, as shown in Fig. 5, at room temperature, the σ increases markedly up to 4 mole% CeO₂ addition and then there is an immediate fall that has been observed up to 10 mole% CeO₂. However, the further addition does not affect the saturation state up to 50 mole% CeO₂ addition. The maximum enhancement in σ occurs for 4 mole% CeO₂ content and the enhancement is the largest for Na₂SO₄ system at room temperature. (see Table I).

Similar nature has also been observed at 548 K and 677 K as depicted in Fig. 5. While at 512 K and 515 K the σ versus

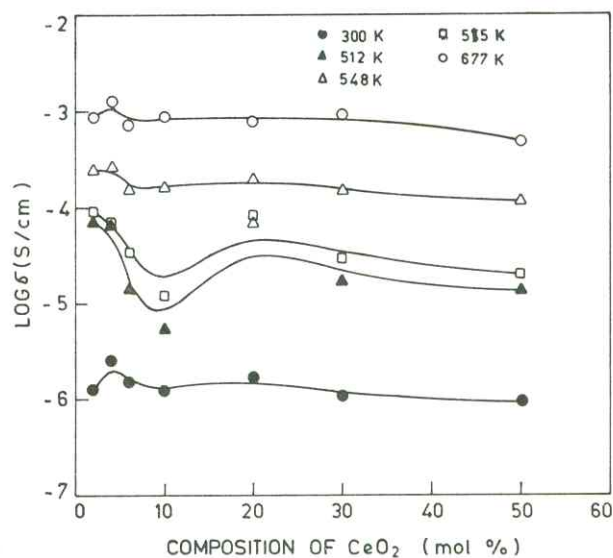


Fig. 5: Conductivity vs composition of CeO₂ dispersion at various temperatures

TABLE II: The extrinsic (region I) and intrinsic (region II) activation energies (E_a^I and E_a^{II} respectively) calculated from the Arrhenius plots of Na₂SO₄:CeO₂ composite mixtures

Composition (mole %)	Activation energy (eV)	Temperature range (K)
98:2	$E_a^I = 0.081$ $E_a^{II} = 0.168$	300-498
96:4	$E_a^I = 0.031$ $E_a^{II} = 0.193$	300-498
94:6	$E_a^I = 0.031$ $E_a^{II} = 0.188$	300-498
90:10	$E_a^I = 0.030$ $E_a^{II} = 0.199$	300-498
80:20	$E_a^I = 0.022$ $E_a^{II} = 0.167$	300-498
70:30	$E_a^I = 0.035$ $E_a^{II} = 0.229$	300-498
50:50	$E_a^I = 0.042$ $E_a^{II} = 0.179$	300-498

composition curves (see Fig. 4) show an anomalous behaviour. That is, at close to T_c (514 K for pure Na₂SO₄(I)) the reverse parabolic trend has been noticed. A pronounced drop in σ has been observed right from 2 mole% CeO₂ onwards. It progresses rapidly upto 10 mole% beyond which it improves and reaches a maximum for 20 mole% CeO₂ content. Further drop in σ , beyond 20 mole% addition reaches a saturation limit. Thus the overall effect both at room temperature and high temperatures with respect to inert phase compositions seems to be unusual.

An immediate explanation in the vicinity of the composite theory as promoted by Wagner and co-workers [8] and Maier [7] is that although the present composite mixtures obey Maier's hypothesis, the observed unusual effect at or near hexagonal transitions deserves a deeper explanation. The drop in σ at or near T_c with respect to the composition of CeO₂ may be due to the increase in host volume across T_c that results in the agglomeration of the second phase inert particles forming the clusters of inert phase particles which in turn dominates the conductivity of the second inert phase

nullifies the total conductivity of the bulk. Further rise in temperature, destroys the clusters and once again the distribution of dispersion begins. This leads to retain the original conducting-non-conducting grain contact in an optimized manner so that σ improves as before. The above observation is in good agreement with the corresponding change in activation energies with respect to CeO₂ composition as summarised in Table II.

CONCLUSION

The present investigations on Na₂SO₄:CeO₂ composite solid electrolytes suggests that considerable enhancement of conductivity can be achieved while mixing CeO₂ with Na₂SO₄ solid electrolytes. A conductivity enhancement of 1000 times is achieved for the 4 mole% CeO₂ addition at room temperature. It improves further beyond 548 K. At 548 K the σ attains a value of 1.513×10^{-4} S/cm and at 677 K an order of magnitude increase has been observed, 1.265×10^{-3} S/cm.

It has been found that the maximum enhancement occurs for 4 mole% of CeO₂ content at all temperatures studied. The phase examination proves that the addition of an "inert" phase into a crystalline matrix of ionic conductor is a viable option for the development of Na ion conducting solid electrolyte materials for all solid state battery applications.

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REFERENCES

1. W Eysel, H H Hofer, K L Keester and T Habn, *Acta Cryst* **B41** (1985) 5
2. A Josefson and A Kvist, *Z Naturforsch*, **249** (1969) 466
3. K Singh and V K Deshpande, *Solid State Ionics*, **13** (1984) 466
4. P W S K Bandaranayake and B-E Mellander, *Solid State Ionics*, **40/41** (1990) 31
5. G Prakash and K Shahi, *Solid State Ionics*, **23** (1987) 151
6. C C Liang, *J Electrochem Soc*, **120** (1973) 1289
7. J Maier, *Ber Bunsenges Physik Chem*, **88** (1984) 1057
8. T Jow and J B Wagner Jr, *J Electrochem Soc*, **126** (1979) 1963