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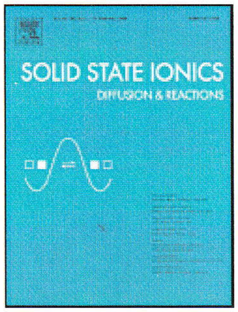

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Ion conductivity commensurate with lattice distortion in Ag_2SO_4

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Abstract

The ionic conductivity of $(1-x)Ag_2SO_4(x)M_2SO_4$ (where $x=0$ to 0.07 and M = Li, Na, K, Rb and Cs) has been systematically investigated by using complex impedance spectroscopy. The solid solubility limits up to 3 mol% of M_2SO_4 in β-Ag_2SO_4 has been set with X-ray powder diffraction and scanning electron microscopy techniques. The transport number obtained at different temperatures using Wagners d.c. polarization method shows negligible electronic contribution. The conductivity behaviour appears to be strongly dependent on the magnitude of difference in ionic radii of host and guest. The lattice structure related term has been correlated to ionic conductivity to explain the results.

Keywords: Ion conductivity; Lattice distortion; Impedance spectroscopy

1. Introduction

Ag_2SO_4 undergoes a phase transition from high temperature highly conducting hexagonal (α) phase to low temperature moderately conducting orthorhombic (β) phase at 416°C. Use of Ag_2SO_4 based solid electrolyte in electrochemical applications, such as SO_x electrochemical gas sensors, is common due to its many fold advantages like (i) the inconvenient reference gas electrode can be replaced by Ag/Ag_2SO_4 (metal/metal sulphate) reference electrode [1,2] and (ii) workable in ambient and SO_x environment [3].

According to Höfer et al. [4] aliovalent cation doping gives enhancement in ionic conductivity irrespective of size, while our earlier preliminary investigations [5,6] reveal that in addition to valency the ionic size and electronic configuration of dopant ions do play an important role in ion migration through the solid in low temperature phases. Though the conduction mechanism in such systems is important, a well defined theory is lacking very much. All above factors have invoked interest to undertake a systematic study on the influence of lattice distortion on ion conductivity, while developing an apt solid electrolyte for SO_x sensor application. The partial substitution of Ag^+ by isovalent M^+ (where M = Li, Na, K, Rb and Cs) has been made with the view to distort the lattice without creating extrinsic vacancies. The local lattice expansion due to ion mismatch is expected to open the doorways for the mobile ions. On the other hand, lattice contraction hinders the silver ion mobility.

2. Experimental

The initial ingredients Ag_2SO_4 and M_2SO_4 (where M = Li, Na, K, Rb and Cs) with assay more than the 99.99% were procured from Aldrich (USA). Initial

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[*] Corresponding author.

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ingredients with mole fraction $(1-x)Ag_2SO_4(x)M_2SO_4$ (where $x = 0$, 0.005, 0.01, 0.03, 0.05, 0.07) were prepared as discussed elsewhere [7]. Thus, prepared samples were characterized by X-ray powder diffraction (XRD) (Philips, PW 170 diffractometer attached with PW 1710 controlling unit) using Cu Kα radiation and scanning electron microscope (SEM) (Cambridge, Mark-III stereoscan electron microscope).

For electrical characterization, the specimens were obtained in the form of circular discs of 9 mm diameter and 2 mm thick by pressing the powder with the help of specac (UK) SS die-punch and hydraulic press. Finally the pellets were sintered at 500°C for 24 h. A good ohmic contact was ensured by putting a quality silver paint onto both opposite parallel surfaces of the pellet, followed by baking at 200°C for 2 h. The ionic transference number of the specimens was measured by Wagners d.c. polarization method from 400 to 300°C using Keithley SMU 236. Prior to a.c. electrical conductivity measurements, the spring loaded samples were heated to 450°C for 2 h so as to homogenize the charge carriers. The impedance of the sample was measured as a parametric function of frequency in the range from 5 Hz to 13 MHz and temperature from 450 to 150°C during the cooling cycle, using hp 4192A if impedance analyzer, hp 16048 test leads were used for electrical connections from sample to analyzer so as to avoid any otherwise parasitic impedance due to improper connecting cables. The temperature of the furnace was controlled to ±1°C using a Eurotherm 810 PID temperature controller.

3. Results and discussion

A comparison of experimental d and relative intensity values, I/I_o with those of JCPDS data is given in Table 1. It is clearly evident that in the case of 3 mol% M_2SO_4 added to Ag_2SO_4, the d values in XRD patterns are slightly deviated from JCPDS data of β-Ag_2SO_4. This small deviation in experimental d values can be attributed to the partial replacement of Ag^+ by wrong size M^+. Further, no decomposition appears from the XRD data. The absence of any line corresponding to either M_2SO_4, $AgMSO_4$ or any other intermediate phase for 3 mol% M_2SO_4 added to Ag_2SO_4 indicates solid solubility. The appearance of a few meagre lines corresponding to M_2SO_4 in the case of 5 mol% of M_2SO_4 added to Ag_2SO_4 indicates precipitation following its in situ dispersion of M_2SO_4 in host the Ag_2SO_4 matrix. A closer look at the Table 1 reveals that, in general, there is a slight shift (negative) in d values for the systems where the dopant ion size is smaller than that of

Table 1
XRD data for 3 mol% added M_2SO_4 (M = Li, Na, Rb and Cs)) in Ag_2SO_4 and lattice constants a, b, c and cell volume are given in A.U. and $(A.U.)^3$.

Experimental data								JCPDS data		
Ag:Li 3 mol%		Ag:Na 3 mol%		Ag:Rb 3 mol%		Ag:Cs3 mol%				
d	I/I_0	d	I/I_0	d	I/I_0	d	I/I_0	d_{JCPDS}	(I/I_0)	JCPDS $[hkl]$
4.694	7.85	4.702	8.33	4.698	7.03	–	–	4.669	10	AS [111]
3.987	19.63	3.985	11.40	3.995	19.90	–	–	3.994	25	AS [220]
3.171	100.0	3.171	100.0	3.178	100.0	3.177	100	3.177	70	AS [040]
2.871	59.21	2.873	9.16	2.875	68.35	2.878	59.0	2.873	100	AS [311]
2.642	48.64	2.648	31.14	2.646	54.60	2.647	54.9	2.644	90	AS [022]
2.415	22.65	2.418	11.62	2.421	24.20	2.425	31.7	2.421	30	AS [311]
1.926	16.91	1.923	16.00	1.927	25.78	2.420	28.1	1.926	30	AS [351]
1.708	13.89	1.713	8.55	1.711	19.50	–	–	1.712	17	AS [062]
a = 10.221		10.227		10.241		10.267		10.269		
b = 12.682		12.686		12.714		12.737		12.706		
c = 05.753		05.750		05.853		05.841	05.818			
Vol = 745.87		746.18		764.20		766.92		759.25		

AS: Orthorhombic Ag_2SO_4. JCPDS card No. 27-1403.

Ag^+, such as Li^+ and Na^+, whereas shift is positive in d values for systems with relatively bigger size cations, such as K^+, Rb^+ and Cs^+. The local distortions caused by the 'wrong' size substitutions were further investigated to detect the magnitude of distortion. The cell volume undergoes a continuous contraction for Na and Li. On the other hand, it undergoes a continuous expansion for K, Rb and Cs substitution (Table 1). The results are in complete agreement with the concept that lattice distortion (expansion and contraction) is directly governed by the 'distortion factor' $(1 - r_g/r_h)$ within the solid solubility region.

The formation of solid solubility is further supported by the evidence obtained by characterizing the samples using scanning electron microscopy, which reveals that the grain morphology of the host material is more or less unaffected by addition up to 3 mol% of Rb_2SO_4; moreover traces of second phase and precipitation are invisible for samples with 5 mol% Rb_2SO_4 in Ag_2SO_4. Similar results are found for other monovalent sulphate added to Ag_2SO_4 systems. These results very well suggest that a complete solid solution can be ensured up to 3 mol% of M_2SO_4 in Ag_2SO_4 at room temperature.

All compositions under investigation obey the Arrhenius law, $\log(\sigma T) = (\sigma T)_o \exp - (E_a/kT)$. The values of $\log(\sigma T)_o$, E_a and $\log(\sigma)$ obtained by least squares method are presented in Table 2. The concentration dependent conductivity for all the series displayed in Fig. 1 shows that the conductivity for M = K- and Rb-doped series exhibits a maximum at 3 mol% and decreases thereafter. The increase in conductivity followed by a minimum at 5 mol% may be due to dispersion of second a precipitated phase in Ag_2SO_4 (solid solution) matrix. It is worth mentioning here that, at lower temperature, the doping effect is more prominent than that at higher temperature. On the other hand, a continuous decrease in conductivity is seen for M = Na and Cs. While in the case of the Li^+ ion, despite lattice contraction taking place, the presence of the Li^+ ion increases the mobility of Ag^+ and vice versa [8]. These results are discussed in the light of influence of ionic size of the dopants on the bulk ionic conduction.

The main factor responsible for change in conductivity by isovalent doping has been considered to cause lattice distortions (increased entropy), due to the incorporation of the wrong size guest ion into the host crystal lattice. The experimental findings suggest that the lattice undergoes contraction and expansion upon partial substitution of respectively smaller and bigger guest ions comparative to host. In contrast to lattice expansion, the contraction of the lattice results in (i) reduction in number of mobile Ag^+ charge carriers and (ii) increased activation energies of defect formation and migration. In addition to these, contraction effect reduces the space available, which in turn hinders mobility of Ag^+.

Table 2
Conductivity $\log(\sigma)$ (at 250°C), pre-exponential factor $\log(\sigma T)_o$, f_p (at 250°C), E_a for $(1-x)Ag_2SO_4(x)M_2SO_4$ $(x=0.03)$

	$\text{Log}(\sigma)$ (S/cm)	$\text{Log}(\sigma T)_o$ (S·K/cm)	f_p (Hz)	$\log(f_p)$ (kHz)	E_a (eV)	E_a^* (eV)
Li	−4.68	3.04	7122	12.7	0.52	0.55
Na	−5.08	2.47	5211	12.0	0.50	0.51
Ag	−4.65	3.45	3331	11.7	0.72	0.77
K	−4.40	4.80	3035	11.5	0.67	0.66
Rb	−3.62	5.04	2685	10.2	0.61	0.62
Cs	−5.54	6.56	5512	14.1	0.97	0.95

E_a^*: Activation energy from peak frequency analysis.
E_a: Activation energy from Arrhenius equation.

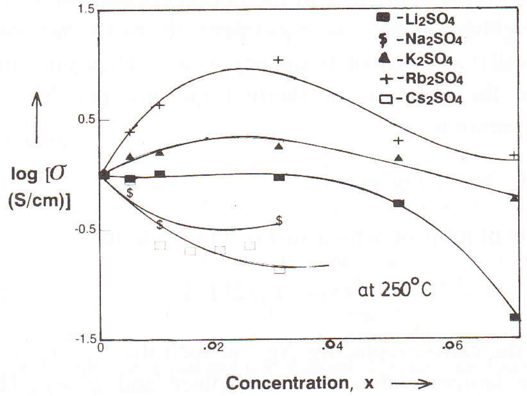

Fig. 1. Variation of $\log(\sigma)$ with x for $(1-x)Ag_2SO_4(x)M_2SO_4$ series.

The concentration of mobile charge carriers in an ionic solid is given by

$$n = (k_f)^{1/2} \exp[(\Delta S_{th} + \Delta S_{cf})/2k] \exp(-E_f/2kT), \tag{1}$$

where k_f, ΔS_{th}, ΔS_{cf} and E_f are respectively mass action constant, thermal entropy, configurational entropy and defect formation enthalpy. If the system under consideration (solid solution of Ag_2SO_4 with M_2SO_4) is assumed to be homogeneous and isotropic, then the term S_{cf} remains invariant with respect to distribution of cations and anions. However, in a M^+ substituted system the immediate ions surrounding M^+ will have a different vibrational frequency (ν') than those at regular undistorted sites (ν). The thermal entropy term ΔS_{th} in Eq. (1) for M^+ doped Ag_2SO_4 will be a consequence of change in frequency of the lattice vibration due to the distortion taking place. Considering the Einstein model [8,9], we may assume that in the doped crystal, each atom neighboring M^+ is equivalent to three harmonic oscillators each of frequency $\nu' \neq \nu$. Then one finds for the increase in thermal entropy per M^+ an expression

$$\Delta S_{th} = 12k \log(\nu/\nu') \tag{2}$$

substitution of which in Eq. (1) leads to

$$n = (k_f)^{1/2}[(\nu/\nu')^6 \exp(-E_f/2kT)]. \tag{3}$$

If the cation replacing Ag^+ is such that $r_g < r_h$, then the lattice contraction takes place and $\nu' > \nu$. This reduces the mobile charge carrier, Ag^+ concentration (n). This is reflected in the conductivity behaviour (a decrease in conductivity) presented in Fig. 1. The opposite behaviour is expected if $r_g > r_h$.

In addition to this, lattice expansion opens the lattice in the vicinity of M^+ (Fig. 2c) thereby widening the window (opening) between two tetrahedral sites, through which ions undergo a successive jump from an occupied site to a vacant one. Such a lattice opening offers minimum activation energy (Fig. 2d) facilitating ion mobility. With increase in concentration of (K^+ or Rb^+), a considerable number of localized lattice opening takes place throughout the sample giving rise to continuous interconnecting ion percolating paths, leading to an enhancement in ionic conductivity. The decrease in conductivity beyond threshold concentration is due to the formation of clusters which hinder the mobility of Ag^+. On the other hand, it is worthwhile to note here that the lattice contraction reduces the size of window (Fig. 2e), offering a comparatively larger activation energy (Fig. 2f) resulting in a decrease in conductivity. Nevertheless, in the case of Li_2SO_4 added to Ag_2SO_4 inspite of lattice contraction, the lattice opening of the host is large enough for the added Li^+ that it can move from one site to a nearby vacant one i.e. added Li^+ becomes the mobile charge carrier. Thus with increase in Li_2SO_4 content, the total concentration of mobile charge carries ($Li^+ + Ag^+$) increases leading to a net enhancement in conductivity.

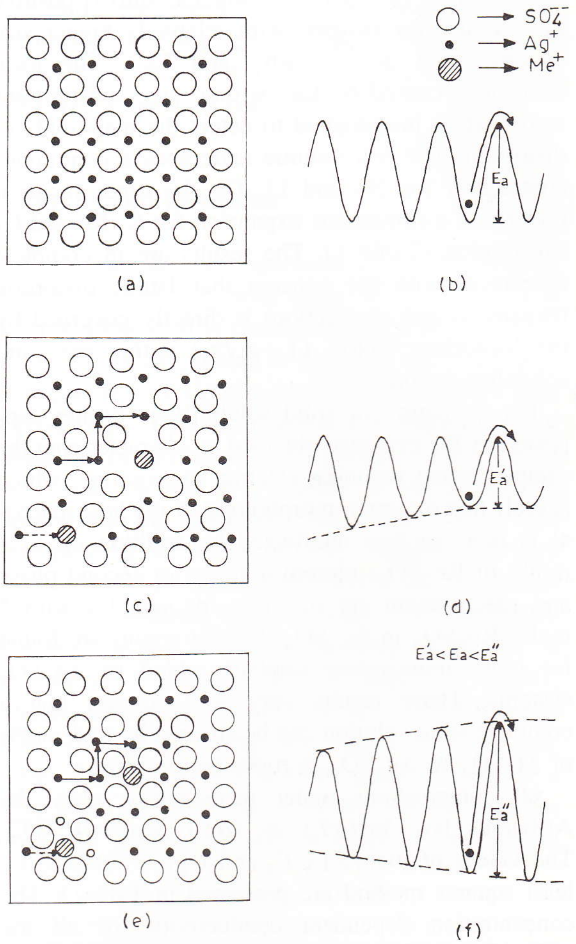

Fig. 2. Schematic representation of plane through (a) normal lattice, (b) energy profile of normal lattice, (c) lattice expansion, (d) energy profile after lattice expansion, (e) lattice contraction and (f) energy profile after lattice contraction.

Fig. 3 reveals the variation of normalized conductivity ($1 - \sigma_d/\sigma_h$) vs. relative ionic radius ($1 - r_g/r_h$). This isotherm clearly is in excellent agreement

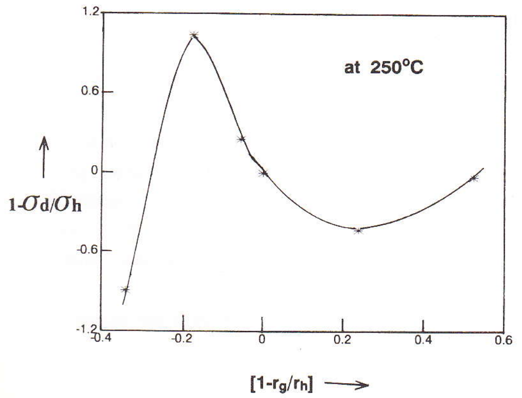

Fig. 3. Variation of normalized conductivity $(1-\sigma_d/\sigma_h)$ vs. lattice distortion factor $(1-r_g/r_h)$.

with the above discussion, and also demonstrates that the ‘right’ size cation selection for enhancing the conductivity by classical doping is an important factor to be considered.

4. Conclusion

The electrical conductivity of $(1-x)Ag_2SO_4$ $(x)M_2SO_4$ has been systematically investigated in the single phase region and solid solubility limits have been set in the orthorhombic phase. The role of lattice distortion functioned by ionic size has correlated with ionic conductivity. To understand the conduction mechanism, a simplistic model based on optimum lattice expansion favoring conductivity enhancement has been proposed. Thus, modifying the lattice by merely substituting a wrong size isovalent cation would not be sufficient, but a proper selection of size is also very important for conductivity enhancement, especially at moderate temperature. Rb_2SO_4-doped composition for $x=0.03$ could be considered in the engineering of new electrochemical SO_2 sensors.

Acknowledgments

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