

Aliovalent substitution in β -Li₂SO₄ towards conductivity enhancement

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Abstract. Aliovalent sulphates were selected for substitution in β -Li₂SO₄ at 6% vacancy concentration. The results show that if the guest ions are substituted on the basis of the criteria given for the formation of a solid solution, then it is possible to achieve a considerable enhancement in conductivity especially in the case of isostructural materials.

Keywords. Aliovalent substitution; conductivity enhancement.

1. Introduction

Solid electrolytes have attracted attention due to their potential use in several technical applications. The prospects for developing an ideal solid electrolyte are good and it is necessary to determine the conditions of the atomic arrangement for this purpose.

The sulphate-based solid electrolytes differ in some respects from the other solid electrolyte materials. An advantage is that many mono- and divalent cations have high mobility in them and thus increasing the choice of anode material in power sources (Heed *et al* 1975).

Amongst all the sulphates studied so far, lithium sulphate is a well-studied solid electrolyte (Benrath and Drekopf 1921; Kvist and Lunden 1965; Kvist 1966, 1967; Heed *et al* 1977). It undergoes a phase transition from a monoclinic to cubic structure at 848 K. Its high temperature form has very high ionic conductivity, comparable to the molten salts (Kvist and Lunden 1965). The effect on the ionic conductivity of substitution of divalent cations Mg²⁺, Ca²⁺ and Zn²⁺ for Li⁺ in the high temperature form of Li₂SO₄ has been investigated (Heed *et al* 1977). Monoclinic Li₂SO₄ has low electrical conductivity at ambient temperatures. Its electrical conductivity has been studied in the monoclinic phase from 550 K to 848 K (Deshpande and Singh 1982).

According to Kimura and Greenblatt (1984), an addition of small quantity of trivalent sulphate enhances the conductivity of β -Li₂SO₄. Similar effect has been reported in Na₂SO₄ (Murray and Secco 1978; Höfer and Esyel 1981; Saito *et al* 1984) and K₂SO₄ (Natarajan and Secco 1975). The maximum conductivity was obtained for 7% vacancy concentration for Na₂SO₄ (Höfer and Esyel 1981). Using the same concept, different vacancy concentrations were calculated for β -Li₂SO₄.

In the present investigation, the effect on the ionic conductivity of the partial substitution of Li⁺ by divalent cations Ca²⁺, Ba²⁺ and Mg²⁺ in β -Li₂SO₄ has been studied to determine whether such a replacement would enhance the ionic conductivity, as a result of the increased vacancies in the cation sublattice described by Li_{2-2x}M_x²⁺□_xSO₄.

2. Experimental

The starting materials Li_2SO_4 , MgSO_4 , CaSO_4 and BaSO_4 with purity greater than 99% procured from AG Fluka, Germany and Sarabhai Chemical, India, were dried at 423 K for 24 hr. Divalent sulphate (6.3 mol%) was added to the lithium sulphate. The mode of sample preparation was the same as reported earlier (Deshpande *et al* 1986). X-ray diffraction results of these samples confirm the solid solubility upto 6.5 mol%.

For electrical conductivity measurements, the specimen was prepared in rectangular shape of dimensions $7 \times 5 \times 3$ mm. Aluminium foils were used to provide a good ohmic contact.

The AC conductivity was measured as a function of frequency (10 Hz to 10 MHz) at various temperatures in the range 740–550 K during the cooling cycle, using an impedance analyzer (Hewlett Packard 4192A) at 5 mV oscillator level.

3. Results and discussion

In the present investigation, $\beta\text{-Li}_2\text{SO}_4$, in quenched form, showed a frequency-independent behaviour of impedance in the frequency range 5 to 13 MHz. Ljungmark (1974) also reported similar results in the case of $\beta\text{-Li}_2\text{SO}_4$. Even after doping, the impedance of $\beta\text{-Li}_2\text{SO}_4$ remained frequency-independent (figure 1).

The solid electrolytes in which the conductivity does not vary with frequency are considered as ideal solid electrolytes and their properties are simulated by a single parallel resistance capacitance element (Macedo *et al* 1972).

As reported earlier, doping with an aliovalent can help to enhance the ionic conductivity of the host solid electrolytes. Thus, to make a systematic study and to derive conclusions, only those divalents were considered which showed an increase in the conductivity of $\beta\text{-Li}_2\text{SO}_4$ (monoclinic) low conductivity phase.

Here, Ca^{2+} being quite bigger in size (0.99 Å) in comparison with Li^+ (0.67 Å), enhances electrical conductivity in the temperature range 550 to 740 K by an order of magnitude. To understand the role of Ca^{2+} towards increase in conductivity, CaSO_4 was added in different concentration. This effect, illustrated in figure 2, shows that conductivity increases with increasing temperature. This is attributed to the hopping of cations due to thermal energy. Figure 2 also shows that conductivity increases with increasing vacancy concentration upto 6%. This is because of the

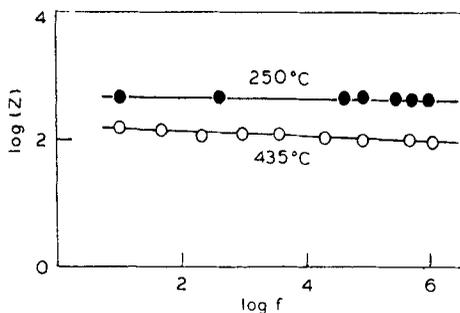


Figure 1. Variation of $\log Z$ vs $\log f$ for 6.3 mol% of CaSO_4 .

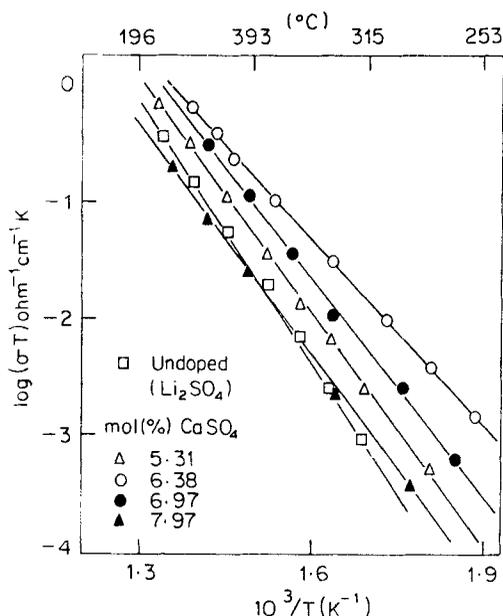


Figure 2. Effect of variation of CaSO_4 content on the electrical conductivity of $\beta\text{-Li}_2\text{SO}_4$.

increasing concentration of cation vacancies in $\text{Li}_{2-2x}\text{Ca}_x\text{SO}_4$ upto the solubility limit and replacement of Li^+ by Ca^{2+} , which in turn, expands the lattice of $\beta\text{-Li}_2\text{SO}_4$. Beyond 6% vacancy concentration, conductivity decreases because at low vacancy concentration, no interactions between mobile ion vacancies take place. At high vacancy concentration, the interaction between the lithium ion vacancies increases decreasing the mobility. With increasing vacancy concentration, greater paths for lithium migration are created. On the other hand the mobility of the ions is reduced by interactions such as cluster formation and ordering in the cation sublattice (Höfer and Eysel 1981). When conductivity attains a maximum at 6% vacancy concentration, these opposite effects cancel each other. Also with increasing concentration of Ca^{2+} , the concentration of vacancies increases whereas the concentration of mobile lithium cations is decreased continuously (here Li^+ ions are considered solely to be mobile ions on account of its smaller size and low equivalent weight compared to Ca^{2+}).

Figure 3 displays the variation of $\log \sigma$ as a function of vacancy concentration. For constant vacancy concentration (6%), conductivity increases with temperature.

Maximum conductivity was achieved by doping $\beta\text{-Li}_2\text{SO}_4$ with CaSO_4 for 6% vacancy and the necessary molar composition of CaSO_4 which was found to be 6.3 mol% was added to study the role of other divalents.

For 6% vacancy concentration, Li_2SO_4 and MSO_4 ($\text{M} = \text{Mg}, \text{Ca}, \text{Ba}$) have been compared (figure 4). It is seen that addition of MSO_4 increases the conductivity of the $\beta\text{-Li}_2\text{SO}_4$ because the presence of the divalent ion increases the cation migration energy (Natarajan and Secco 1975). It is also clear that CaSO_4 -containing specimen shows the highest conductivity. The doping with Mg^{2+} slightly increases the conductivity at lower temperature, but decreases at higher temperature. The higher conductivity of Ba^{2+} -doped Li_2SO_4 sample may be due to its larger ionic size

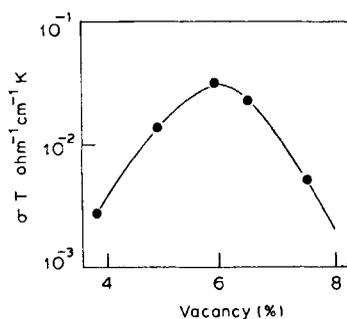


Figure 3. Variation of conductivity with vacancy concentration at 623 K.

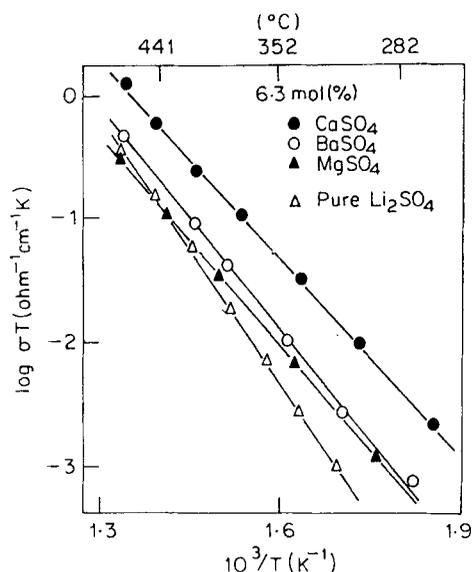


Figure 4. Effect of MSO_4 ($M = \text{Mg}, \text{Ca}$ and Ba) on the electrical conductivity of $\beta\text{-Li}_2\text{SO}_4$.

compared to Mg^{2+} which might be attributed to its attraction towards the dislocation in the salt. Barium ion is mobile along the grain boundaries. Similar effect has been reported in the literature (Ljubnov and Lunden 1966) for K_2SO_4 when added in monoclinic Li_2SO_4 . The larger size of the guest ion leads to an expansion of the lattice and hence the formation of a more open structure giving higher conductivity in the host Li_2SO_4 . At the same time, the highly massive Ba^{2+} ions may obstruct the conduction pathways of mobile cations and hence reduce the conductivity. Thus ionic size might be the predominant factor contributing to the conductivity features of doped Li_2SO_4 . Similar effect has been reported by Natarajan and Secco (1975) which is quite contrary to the reports of Höfer *et al* (1978).

On the basis of the previous discussion it can be concluded that only in the case of CaSO_4 substitution the ionic conduction of substituted $\text{Li}_{2-2x}\text{Ca}_x\text{SO}_4$ phase increased by an order of magnitude in comparison with Li_2SO_4 .

More effective enhancement of the ionic conductivity has been reported in Na_2SO_4 (Höfer *et al* 1978), which is probably due to the structural differences of sodium and lithium host compounds. It is interesting to note that doping does not give considerable importance for the size of ions, but gives special consideration to isostructural compounds, as it is in the present case, that both Li_2SO_4 and CaSO_4 are monoclinic.

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