

Conductivity measurement in Lithium Borate Electrolytes

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ABSTRACT

The Lithium Sulphate being the good solid electrolyte possesses two phases, monoclinic at room temperature and cubic [FCC] above 853°K. The high temperature phase is reported to be a super ionic conductor due to its rotation - like motion of the sulphate ions, which enhances the cation migration and therefore very much useful for battery materials. The trapping of such high temperature phase at lower temperature can give alternative material for the battery. It is well known that fast quenching technique can trap high temperature phase. The Boron Trioxide is glass former and posses many useful properties in its crystallized form, like potential engineering applications and posses many scientific interest like enhance ionic conductivity by suppressing the effects of grain boundaries in ionic conducting crystalline solids. In the present paper the Lithium Sulphate is doped with Boron Trioxide. The Boron Trioxide is added in the molar percentage as 5,7and 10.The samples are prepared using fast quenching technique. The prepared samples are characterized by XRD and electrical conductivity of the sample is measured in the frequency range 20Hz to 2MHz over the temperature range of transition of lithium Sulphate. The variation in the conductivity is explained in the light of XRD and frequency dependence of conductivity.

Keywords: Lithium Sulphate, Boron Trioxide

INTRODUCTION

A Solid electrolyte is characterized by one of its ion species with larger mobility than the other ions present in it [1]. A high temperature phase of solid electrolytes possess large mobility for uni- and divalent cations [2]. The electrical conductivity of Li_2SO_4 was found to be of the order of 0.9S/cm at 823K [3]. This high conductivity is due to enhanced cation mobility observed by a strong coupling of the rotation of the otherwise translationally immobile sulphate ions [1,4]. This motion of sulphate ions is depicted as the paddle wheel or cogwheel model [5,6,4]. The high temperature plastic phase or solid electrolyte possesses grain boundaries. The grain boundaries block the ionic transport and add its resistivity to the bulk resistance. The grain boundary resistance is of several orders of magnitude higher than bulk resistivity [7,8,9]. In present paper the grain boundaries effect on the bulk conductivity of ZrO_2 added Li_2SO_4 is analyzed using impedance.

METHODOLOGY

Unhydrated Li_2SO_4 and B_2O_3 reagent grade materials are the starting compounds. The compositions of $(1-x)\text{Li}_2\text{SO}_4 \cdot x\text{B}_2\text{O}_3$ where $x = 3, 5$ and 7 mol% are mixed in proportion to form 15 gm batches. The homogeneous mixed powders are melted in electric furnace at around 900°C . The homogeneous melts are quenched in stainless steel mould kept at room temperature. The conductivity measurements are performed by complex impedance method using Agilent E 4980A meter in the frequency range from 20 Hz to 2 MHz . The reproducibility of the measurement is verified at least for three times. The temperature range of measurement of conductivity is from 250°C to 550°C .

RESULTS AND DISCUSSION

1. X-Ray Diffraction Results :

The room temperature x-ray pattern of samples prepared in this series is shown in figures. 1, 3, 5 and respective $h\ k\ l$ planes are shown in figures 2, 4, 6.

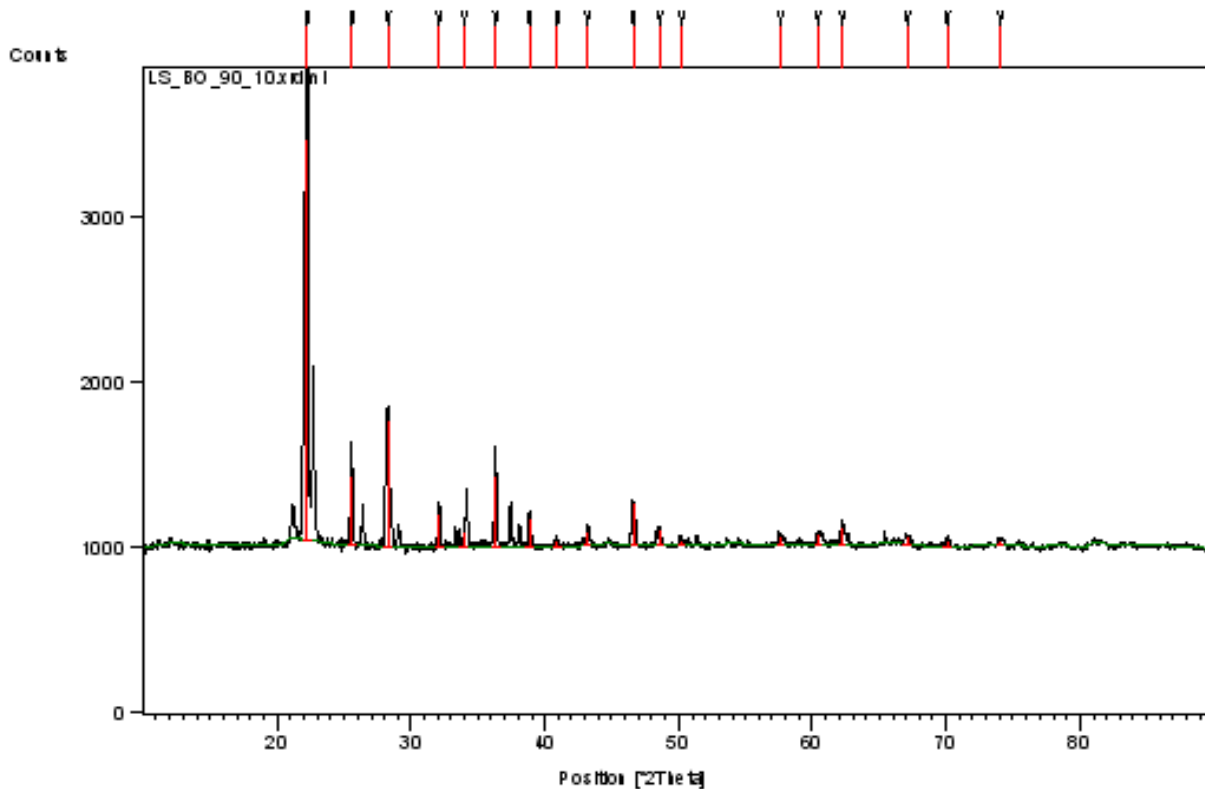


Fig.1. $\text{Li}_2\text{SO}_4 \cdot \text{B}_2\text{O}_3$: (90%_10%)

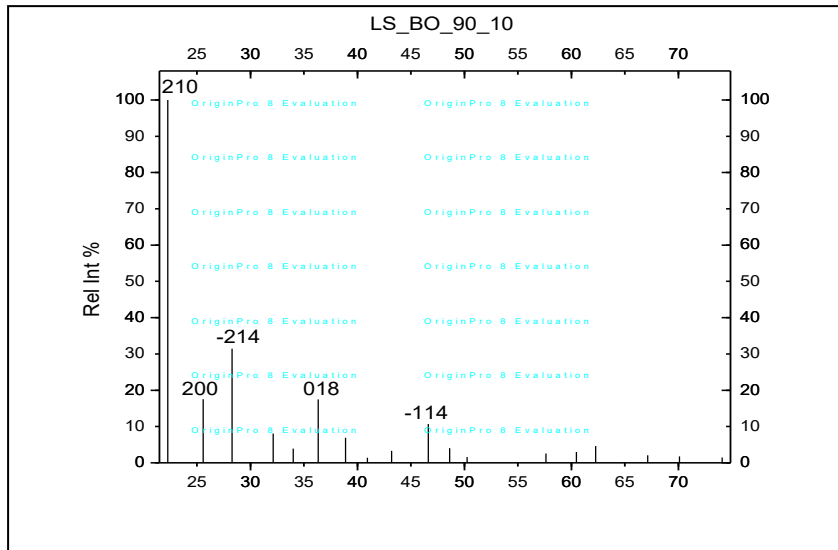


Fig2 .h k l values $\text{Li}_2\text{SO}_4\text{-B}_2\text{O}_3:(90_10)$

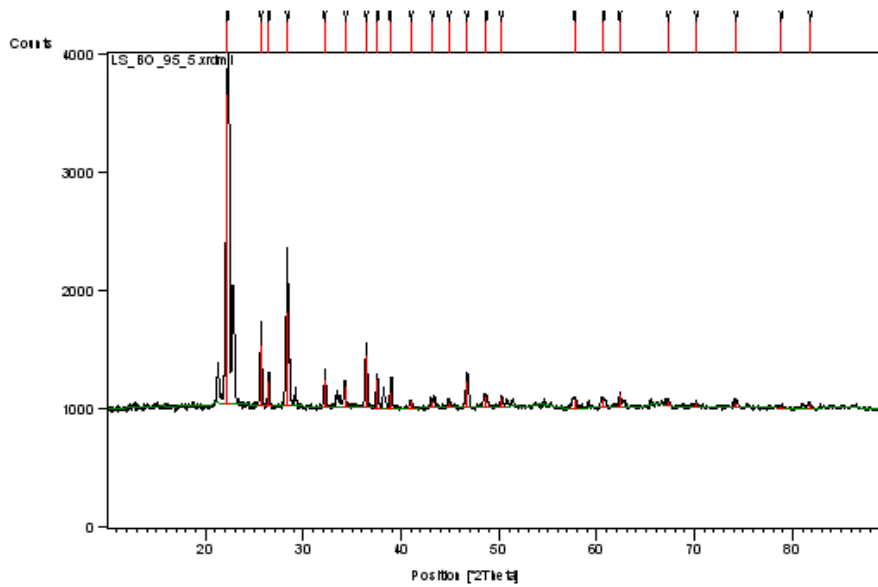


Fig.3. $\text{Li}_2\text{SO}_4\text{-B}_2\text{O}_3:(95\%_5\%)$

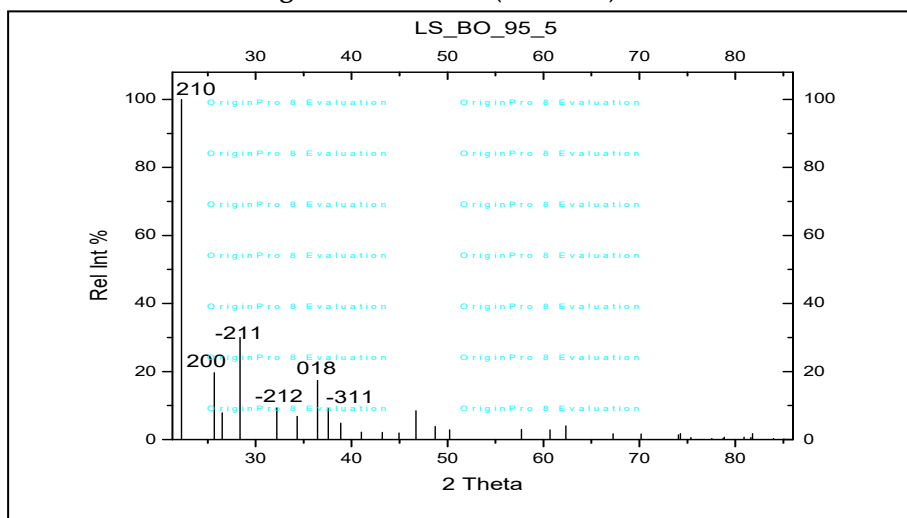


Fig.4. h k l values $\text{Li}_2\text{SO}_4\text{-B}_2\text{O}_3:(95\%_5\%)$

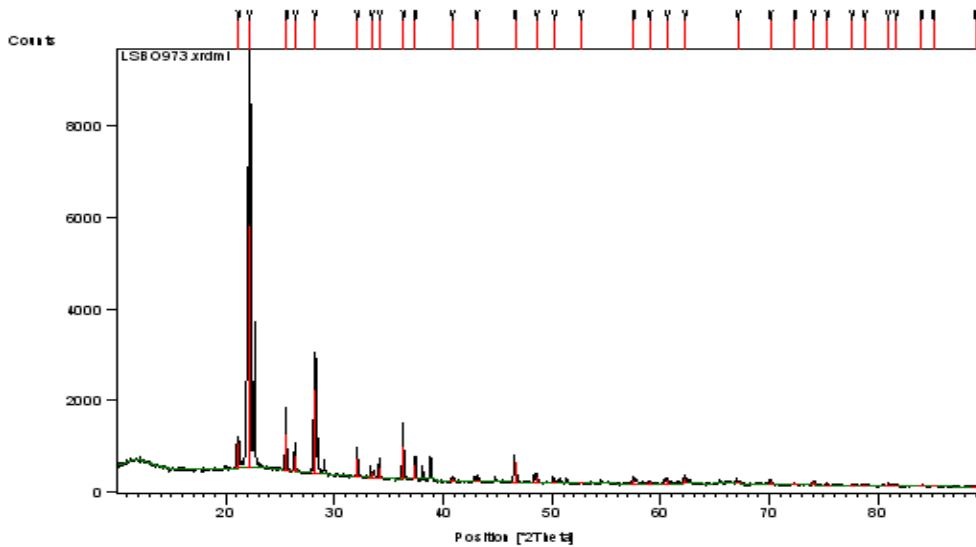


Fig.5. $\text{Li}_2\text{SO}_4\text{-B}_2\text{O}_3$: (95%_5%)

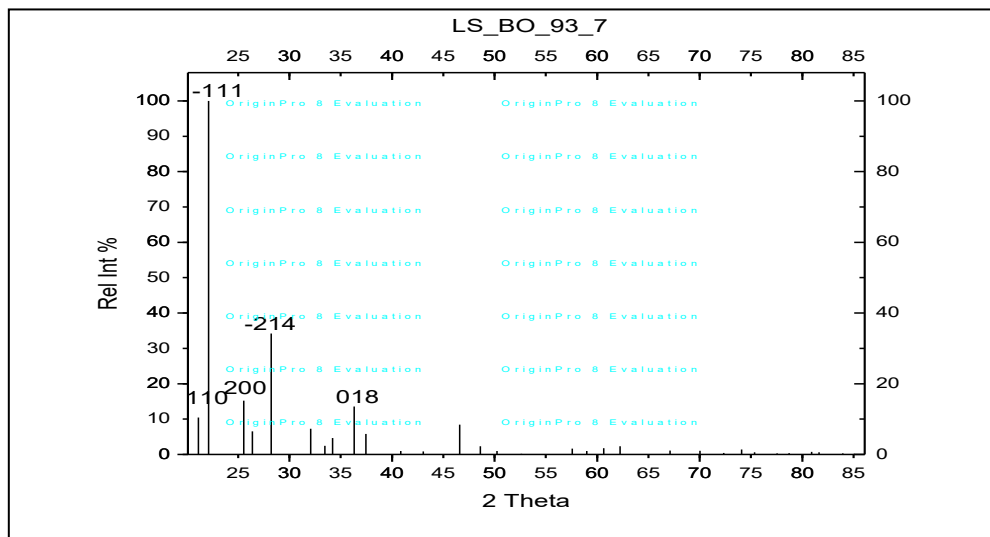


Fig.6. $\text{Li}_2\text{SO}_4\text{-B}_2\text{O}_3$: (93%_7%)

CONCLUSION

The activation energies for LS_BO: 5mole % calculated to be 0.44 eV as shown in table 1. These values are very close to the earlier published values of 0.43 eV by Lunden A. and Dissanayake [10,11] for crystalline α - Li_2SO_4 , but much lower compared to 1.2 eV observed by Singh k. and Deshpande V. [12] and 1.4 eV observed by Kimura N. for the monoclinic phase [13]. It is important to note that the high conductivity achieved by quenching is not due to the Composite formation of two phases. Supported by observations by Maier J. and Dudney N. [14, 15]. Chryssikos et al.[16] have studied lithium sulphoborate system using IR and Raman spectra.

	Composition	Eg	Transition temp
	Pure LS	0.634eV	574 °C
LS_BO	93%_7%	0.617eV	441 °C
	95%_5%	0.44eV	393 °C
	90%_10%	0.566eV	490 °C

The one of the important result observed in the X-ray pattern is the intensity of the components of the samples remain same irrespective of its contain. The Li_2SO_4 monoclinic phase may accommodate the Boron oxide in its matrix. The remaining components of Boron oxide of sample thus seen in the X-ray pattern. The comparison of a, b, c lattice values of lithium

sulphate with Boron oxide gives the justification that how open the structure of L_2SO_4 to occupy the component salts

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Conflicts of interest: The authors stated that no conflicts of interest.

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