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The Different Phases of Lithium Sulphate and Its Transition at Different Temperature

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ABSTRACT

The present review is focused on Li_2SO_4 salt and its different temperature phases. The enhancement in the conductivity with addition of different compounds in it has been observed by many researchers. Lithium sulphate is a material that has received quite a bit of attention in recent years. It is an ionic salt, presenting a reversible solid-solid phase transition (monoclinic ± FCC) at a relatively high temperature (578°C). The high temperature form of lithium sulfate is a plastic (rotator) phase, presenting an unusually high ionic conductivity, deserving therefore the name of solid electrolyte. From the practical point of view its importance may rest on its application as an electrolyte for high-energy batteries, or as a stable nontoxic material for thermal energy storage.

Keywords : Lithium Sulfate, Phase Transition.

I. INTRODUCTION

The literature survey shows that the lithium sulphate is uniquely interesting among the all types of solid electrolytes system. It has special structural and physical properties which assert high ionic conductivity to this alkali metal sulphate. The FCC phase of the lithium sulphate has very high ionic conductivity about 3 Scm^{-1} close to its melting point with activation energy 0.41 eV, which also shows that it has high mobility of lithium ion [1]. The monoclinic phase of lithium sulphate has low ionic conductivity around 10^{-10} Scm^{-1} at 100°C with activation energy 1.4 eV [2]. The high lithium ion mobility in the FCC phase is due to the sulphate ion which forms the translationally fixed lattice associated with the volume change and large value of latent heat near transition temperature. This leads to considerable orientational disordering of sulphate groups in the cubic phase [3, 4].

The heat capacity measurement at transition temperature [5] suggested that the existence of pre-melting phenomenon [6] gives the evidence of plastic phase, disordered with respect to Li^+ positions and SO_4^{2-} tetrahedra in the α-phase (FCC) are matrix isolated[7].

Though the high temperature phase of lithium sulphate is superionically conducting it is practically impossible to use it in lithium batteries. It is therefore always thought to stabilize α-phase of lithium sulphate at ambient temperature as reported by Balaya M.J.Verkerk et al. [8].

The high latent heat near transition for this salt has provoked the author to add the salts which has high heat content at ambient temperature. This can possibly affect the transition temperature of lithium sulphate by maintaining the disorder in Li^+ and matrix isolation of SO_4-terahedra.The various salts which are added to achieve the goal are given in the chapter-3. The different measurements carried on the prepared samples are also given in the same chapter.

II. X-RAY DIFFRACTION RESULTS SERIES: Li_2S0_4 _ (Li_2O:B_2O_3) _ZrO_2

The room temperature x-ray pattern of samples prepared in this series is shown in figures. 1,3,5,7 and respective h k l planes are shown in fig.2,4,6,8.

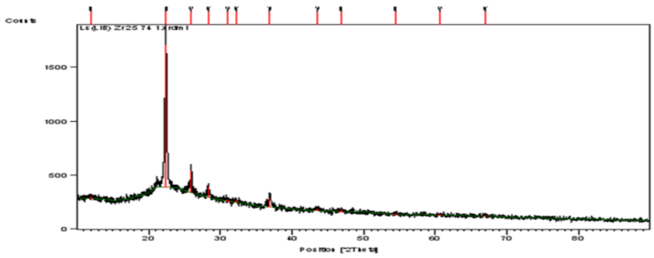

Fig.1.LS_ (LO: BO) _Zr :(25_74_1)

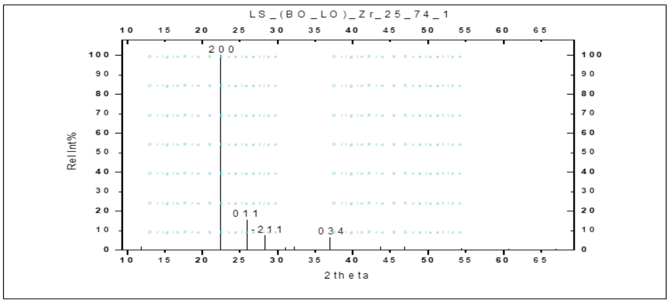

FIG.2.h k l values: LS_(LO:BO)_Zr:(25_74_1)

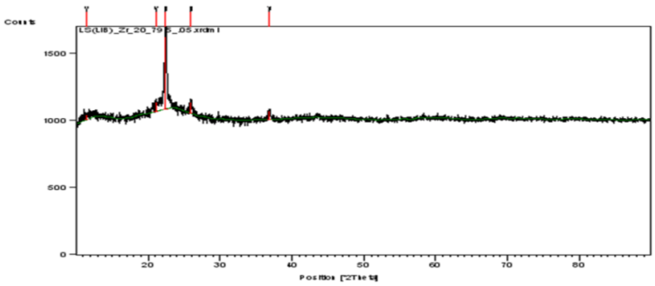

FIG.3. LS_(LO:BO)_ZrO2:(20_79.5_0.5)

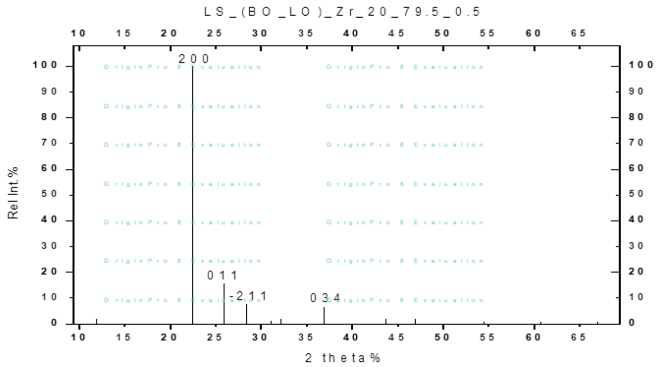

FIG.4..LS_(LO:BO)_ZrO2:(20_79.5_0.5)

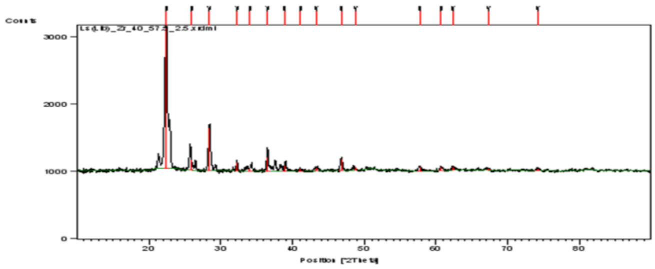

FIG.5. LS_(LO:BO)_ZrO_2:(40_57.5_2.5)

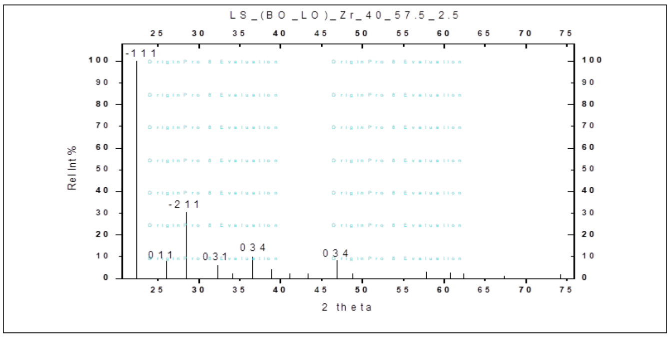

FIG.6.h k l Values: LS_(LO:BO)_ZrO_2:(40_57.5_2.5)

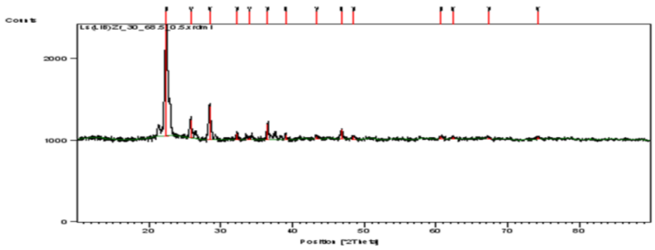

FIG.7. LS_(LO:BO)_ZrO_2:(30_68.5_1.5)

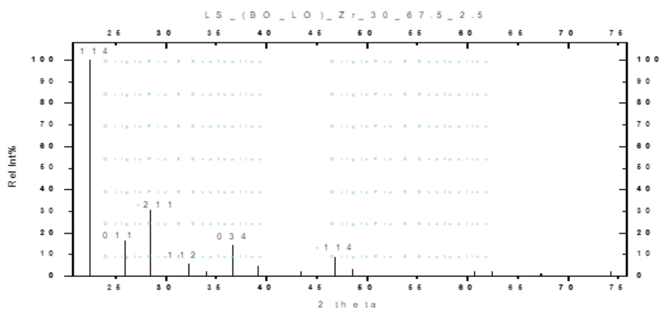

FIG.8. LS_(LO:BO)_ZrO_2:(30_68.5_1.5)

SERIES Li_2S0_4_(Li_2O:B_2O_3)_ZrO_2:

COMPOSITION	d values from XRD with intensity	d values ICCD	Components
Li_2S0_4_(Li_2O:B_2O_3)_ZrO_2 (20%_79.5%_0.5%)	3.96 100 3.43276 15.60 4.21974 12.41 2.43537 11.63	3.96 3.43 4.22 2.43	ZrSO4(O) Li HDROXIDE BORATE(A) Zr(OH)SO4(O) ZrO2(R)
Li_2S0_4_(LI2O:B2O3)_ZrO_2 (25%_74%_1%)	3.96073 100.00 3.44423 15.19 3.15656 21.67 2.43 6.17	3.96 3.44 3.15 2.43	ZrSO4(O) Li HDROXIDE BORATE(A) Zr O2(M) ZrO2(R)
Li_2S0_4_(Li2O:B2O3)_ZrO_2 (30%_68.5%_1.5%)	3.96244 100.00 3.13410 30.07 2.45432 14.51	3.96 3.13 2.45	ZrSO4(O) LI BORATE HYDRATE(M) ZrO2(R)
Li_2S0_4_(Li_2O:B_2O_3)_ZrO_2 (40%_57.5%_2.5%)	3.97069 100.00 3.13978 30.50 2.46279 9.95 1.94160 8.23	3.97 3.13 2.46 1.94	Li-BORATE HYDRATE(X) LIB5O6(M) Zr(H) Li BORATE HYDOXIDE(T)

Table 1

III. DIFFERENTIAL SCANNING CALORIMETRY

The DSC curve for lithium sulphate salt revealed the phase transition as an endothermic peak at 575°C, as shown in figure 9. Moreover no peak for dehydration has been observed in quenched lithium sulphate salt. The figures show the DSC curves for all series prepared in the present work.

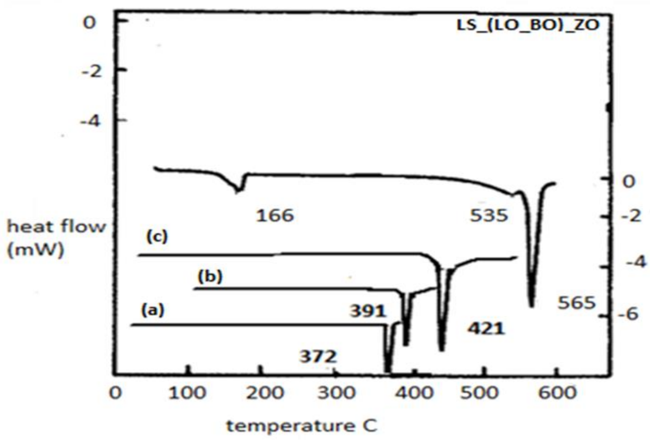

Fig 9

Series	Composition	Eg	Transition temp
	PURE Li2SO4	0.6348eV	574 C
LS_(LO_BO)_ZrO	83%_7%_10% 85%_5%_10% 80%_10%_10%	0.617eV o.44eV 0.566eV	441 C 393 C 490 C

Table 2

IV. CONCLUSION

The series- Li_2S0_4_(Li_2O:B_2O_3)_ZrO_2 is with composition, lithium borate glass and ZrO_2 added lithium sulphate, The minimum transition temperature is 372°C obtained for sample containing 25 mol% of lithium sulphate. The figure 9 shows the Endotherm for different mol % Li_2O-B_2O_3+ZrO_2 added in lithium sulphate also the inset shows the variation in endotherm temperature with Li_2O-B_2O_3+ZrO_2. This variation in endotherm temperature is also given in table 2. It is observed that the increase in the glassy phase due to addition ZrO_2 increases the viscosity of the melt as observed during synthesis, this may restrict the moment of SO_4 ion to support FCC structure of lithium sulphate to get stabilized at lower temperature as observed in earlier series.

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