

Li₂SO₄: LiNbO₃ binary system for solid state battery applications

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Abstract. Different compositions in the Li₂SO₄-LiNbO₃ system have been prepared by adopting the twin roller quenching technique. The electrical conductivity has been measured and the sample with 20 mole% LiNbO₃ exhibited maximum conductivity at 573 K. The results have been explained on the basis of XRD, SEM data and vacancy concentration. A number of solid state electrochemical cells were fabricated by varying the electrolyte composition, using Li-metal and MnO₂ as anode and cathode respectively. The 80 Li₂SO₄:20 LiNbO₃ composition gave the best cell performance.

Keywords. Dispersed solid electrolytes; characterization; cell voltage and current.

1. Introduction

In recent years solid electrolytes have gained importance because of their potential application in many technological devices. Lithium-conducting solid electrolyte is advantageous as it produces a greater cell voltage because of the highly electropositive nature of lithium. In addition, several cathode materials can be employed in lithium-transporting systems, because of their relatively high lithium diffusion coefficient.

Lithium sulphate is a well-known ionic conductor. It undergoes a phase transition from monoclinic (β -phase) to cubic (α -phase) structure at 848 K. In the high temperature α -phase, it has high conductivity, comparable to molten salts (Kvist and Lunden 1965). The high conducting α -phase has a fcc structure (space group F $\bar{4}$ -3m) with sulphate ions situated at the origin and the oxygen atoms rotationally disordered about the sulphur atom. The highly mobile Li⁺ ions, which occupy the $\pm(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ positions in the lattice, are the charge carriers and it has been suggested that the rotational freedom of the sulphate group facilitates cation mobility (Nilsson *et al* 1980; Aronsson *et al* 1981).

β -Li₂SO₄ has a monoclinic structure (space group P2_{1/a}) (Mellander and Nilsson 1983) and exhibits low ionic conductivity (Deshpande and Singh 1982). The phase diagrams of many binary sulphate systems with Li₂SO₄ as one component have been studied (Schroeder and Kvist 1969; Schroeder *et al* 1972; Schroeder 1975). It has been reported that highly conducting phases can be obtained for binary systems of lithium sulphate with Na₂SO₄ and Ag₂SO₄ at a lower temperature (Heed *et al* 1977).

The equilibrium phase diagram of Li₂O:Nb₂O₅ determined by Reisman and Holtzberg (1958) shows that LiNbO₃ exists as a single phase over a narrow range of composition (figure 1). The single phase compound LiNbO₃ crystallizes from the melt at the melting point 1526 K with an exact stoichiometric ratio of atoms at 50 mole% Li₂O.

Charge transport mechanism in single crystals of LiNbO₃ has been investigated at higher temperature ($T > 623$ K) (Jorgensen and Bartlett 1969; Bergmann 1968) and the conductivity at 973 K has been found to be electronic at low oxygen partial

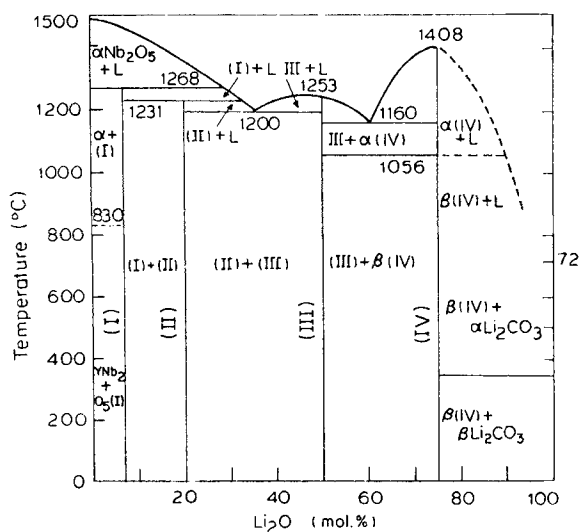


Figure 1. Phase diagram of $\text{Li}_2\text{O}-\text{Nb}_2\text{O}_5$ system.

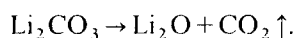
pressure and ionic at one atmosphere of oxygen. They have also reported that ionic conductivity could be increased by a factor of ten by adding Li_2O . Bergmann (1968) also proposed a considerable fraction of ionic conductivity using stoichiometric LiNbO_3 .

Although many solid state electrochemical cells have been reported, attempts to use lithium sulphate-based solid electrolytes are few. Kanda *et al* (1982) tried a composition of 80.8 Li_2SO_4 :19.2 LiNbO_3 in Li/MnO_2 solid state cell. Their cell of 0.8 mm thickness gave an open circuit voltage of 2.65–3.4 V. It may be useful to identify the composition with maximum conductivity in the solid solution series. With this in view, the present investigation was aimed at the study of electrical conductivity of the Li_2SO_4 : LiNbO_3 binary system, and the composition with the highest conductivity was used in an electrochemical cell.

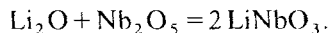
2. Experimental

2.1 Material preparation

The compounds used were Li_2SO_4 , Li_2CO_3 and Nb_2O_5 (99% pure) procured from A G Fluka, Germany. These initial ingredients were dried in a platinum crucible. Dried Li_2CO_3 and Nb_2O_5 (used to grow single crystals of LiNbO_3) were mixed and ground in an agate mortar. The mixture was taken in a 50 ml flat bottom platinum crucible covered with a platinum lid. The mixture was heated in the Gallenkamp furnace. The temperature of the furnace was raised at the rate of 313 K per hour up to 1073 K after which the lid was removed. Then the temperature was raised at the same rate to 1173 K where the mixture was sintered for about 12 hr. During sintering, Li_2CO_3 decomposes and gives CO_2 to produce Li_2O according to the reaction



The temperature was further raised at the same rate to 1573 K which is well above the melting point of Li₂CO₃. LiNbO₃ is formed according to the reaction



The melt kept at this temperature for 12 hr was then cooled at a slow rate of 278 K per hour to the eutectic temperature of 1433 K. During cooling, there was spontaneous nucleation of the melt at many points so that a number of crystals were formed at the surface on solidification. From 1433 K the crystals were cooled at a faster rate of 313 K per hour to 1373 K and at this temperature, the crystals were annealed in atmosphere. It has been noticed that approximately square-shaped crystals were formed on the surface in the central region of the crucible. The crystals were clear, colourless and transparent, but in the outer regions they were pale yellow in colour.

The crystals mechanically taken out from the central region were about 2 × 2 × 1 mm in dimension. The extent of LiNbO₃ formation was determined by the X-ray diffraction technique.

The single crystals of LiNbO₃ were ground in an agate mortar under acetone and dried well at around 393 K. This powder was further used to prepare the Li₂SO₄: LiNbO₃ pseudo binary compositions.

The weighed quantity of Li₂SO₄ and LiNbO₃ of compositions 100:00, 95:5, 90:10, 80:20, 70:30, 50:50 and 30:70 mole% were ground separately. Later, the LiNbO₃ powder was taken in platinum crucible and introduced in an electric furnace at 1533 K. It was kept at this temperature for an hour. After this, the well ground Li₂SO₄ powder was added to the melt of LiNbO₃. The crucible was maintained at 1533 K for 10 to 15 min. After shaking, the melt was poured on the line contact of twin rollers made of stainless steel.

Thin flakes were obtained from the quenched liquid. Other compositions were similarly prepared. The samples were characterized by X-ray diffraction technique.

2.2 *Electrical conductivity*

The samples were obtained in the form of thin flakes and hence could not withstand the pressure of the sample holder. Therefore, these flakes were finely crushed and pelletized at 10 ton/cm² and these pellets were used for electrical conductivity measurements. To ensure good ohmic contact, thin aluminium foils were used before loading the sample in the sample holder (Deshpande and Singh 1982). The a.c. electrical conductivity was measured in air as a function of frequency (10 Hz–13 MHz) at various temperatures in the range 393–753 K during the cooling cycle, with the Hewlett Packard 4192A1.F impedance analyser at 5 mV oscillator level. The temperature was controlled to 273 ± 1 K with Eurotherm (UK) temperature controller.

2.3 *Electrochemical cell*

The solid state electrochemical cells were fabricated by pressing together the compounds sequentially at room temperature in 1.2 cm dia. stainless steel die. A weighed amount of cathode powder was pressed at about 10 ton/cm². A weighed amount of Li₂SO₄: LiNbO₃ (80:20) powder was dispersed on the surface of the pre-

pressed cathode, levelled and pressed at about the same pressure as mentioned above. Finally, a thin lithium foil of appropriate dimension was pressed against the pellet as an anode in a glove bag filled with argon gas. The cell thus obtained was placed in a stainless steel cell holder (figure 2).

3. Results and discussion

When Li_2SO_4 (LS) and LiNbO_3 (LN) were melted together and quenched rapidly, LN remained separated at the bottom of the crucible. Since LS and LN are not isostructural, this system is pseudobinary. The melting point of LN (1526 K) is much higher than that of LS (1133 K). Thus when (90:10) LS:LN was melted together, the LN-rich phase was obtained due to the evaporation of LS which was confirmed by XRD (table 1a). For this composition, the conductivity was quite low due to the increased phase separation. Thus in the case of 80:20 (LS:LN), LN was melted first at 1526 K and then LS was added to the melt. To overcome evaporation losses, the melt was thoroughly shaken before rapid quenching.

Figure 3 depicts the plots of $\log \sigma T$ vs $10^3/T$ for pure LS, LN and different binary compositions. In general, the conductivity increases with rise in temperature. The conductivity of LS is higher than that for LN. This is due to the lower melting point and phase transition temperature ($T_c = 848$ K) of LS as compared to LN ($T_c = 1483$ K).

The functional dependence of $\log \sigma T$ on mole% of LN at 553 K (figure 4) shows maximum conductivity at 20 mole% of LN. It is seen from XRD data (tables 2 and 3) that only a few peaks of LN appear. SEM study (figure 5) revealed the presence of finely dispersed LiNbO_3 in the Li_2SO_4 matrix. This in turn gives rise to more interfacial area between the grains probably contributing to the conductivity. The present results are similar to the results of the composite solid electrolyte system such as $\text{AgI}-\text{Al}_2\text{O}_3$ (Liang 1973; Chowdhary *et al* 1985; Poulsen 1985). A conductivity maximum has also been found for the two-phase regions in the system with two ionic conductors $\text{AgI}-\text{AgBr}$ (Shahi and Wagner 1980, 1984; Maier 1985) $\text{Li}_2\text{SO}_4:\text{CaSO}_4$ (Careem and Dissanayake 1986) and $\text{Li}_2\text{SO}_4:\text{Li}_2\text{CO}_3$ (Dissanayake and Mellander 1986). The increase in conductivity in these cases had been attributed to conduction in the interface region between the two phases.

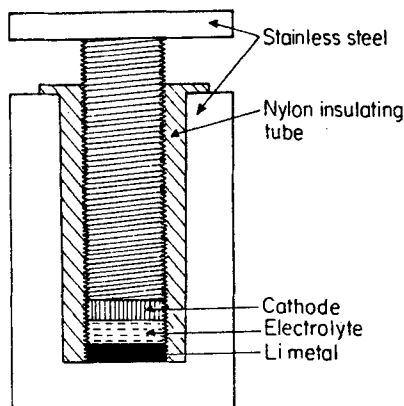
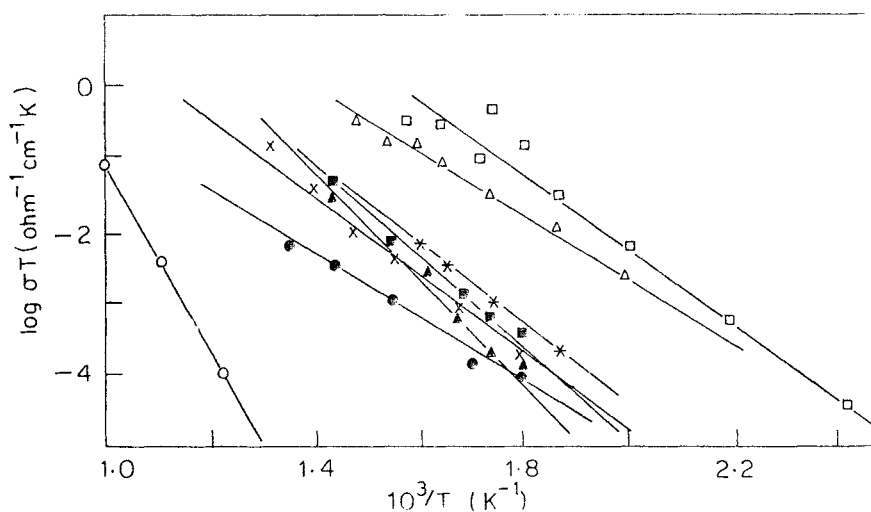


Figure 2. Solid state electrochemical cell assembly.

Table 1. Comparison of the experimentally obtained d values with that of the ASTM data for 90 mole% Li₂SO₄ and 10 mole% LiNbO₃.

| Observed | | | ASTM | | Observed phase | hkl |
|-----------|--------|---------|--------|---------|---------------------|--------------|
| 2θ | d | I/I_0 | d | I/I_0 | | |
| 22.0 | 4.0401 | 100.00 | 4.04 | 100 | LS | 002 |
| 25.35 | 3.5201 | 14.54 | 3.520 | 04 | LS·H ₂ O | 111 |
| 28.0 | 3.1866 | 39.35 | 3.18 | 30 | LS | 112 |
| 32.7 | 2.7385 | 43.24 | 2.730 | 64 | LN | 100 |
| 33.4 | 2.6067 | 17.14 | 2.603 | 6 | LS·H ₂ O | 200, 003 |
| 34.7 | 2.5851 | 43.24 | 2.5801 | 37 | LN | 110 |
| 36.1 | 2.4830 | 21.38 | 2.479 | 20 | LS | 020 |
| 36.8 | 2.3799 | 27.14 | 2.377 | 06 | LS·H ₂ O | $\bar{2}$ 12 |
| 37.4 | 2.4044 | 11.16 | 2.402 | 10 | LS | $\bar{3}$ 11 |
| 38.6 | 2.3324 | 4.93 | 2.339 | 16 | LS·H ₂ O | $\bar{1}$ 13 |
| 39.1 | 2.3037 | 7.40 | 2.300 | 7.3 | LN | 006 |
| 40.7 | 2.2168 | 9.35 | 2.211 | 2.0 | LS | 121 |
| 42.6 | 2.1222 | 28.57 | 2.120 | 18.4 | LN | 202 |
| 46.4 | 1.9569 | 9.35 | 1.950 | 2 | LS·H ₂ O | 004 |
| 48.3 | 1.8842 | 16.36 | 1.884 | 4 | LS | $\bar{4}$ 03 |
| 55.9 | 1.6447 | 9.74 | 1.641 | 36 | LN | 122 |
| 61.0 | 1.5166 | 7.79 | 1.514 | 21 | LN | 241 |
| 62.2 | 1.4924 | 14.80 | 1.491 | 4 | LS | $\bar{4}$ 05 |

**Figure 3.** Variation of $\log \sigma T$ vs $10^3/T$ for Li₂SO₄:LiNbO₃. —●— 100:00; —×— 95:05; —▲— 90:10; —□— 80:20; —△— 70:30; —■— 50:50; —*— 30:70; —○— 00:100.

Li/MnO₂ cells using different electrolytes have been fabricated. From table 4 it is evident that the 80 Li₂SO₄:20 LiNbO₃ system, giving maximum conductivity in the series, offered better electrochemical cell performance compared to other solid electrolytes developed in our laboratory. In spite of the higher conductivity exhibited

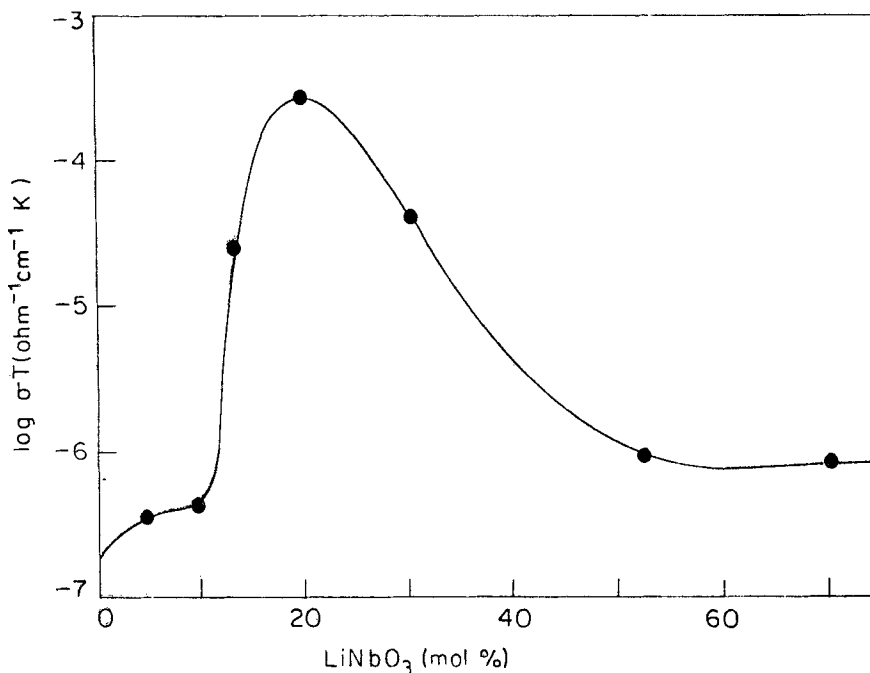


Figure 4. Functional dependence of $\log \sigma T$ vs mol. % of LiNbO_3 .

Table 2. Comparison of the experimentally obtained d values with that of the ASTM data for 80 mole% Li_2SO_4 and 20 mole% LiNbO_3 .

| Observed | | | ASTM | | Observed phase | hkl |
|-----------|--------|---------|-------|---------|--------------------------------------|------------------------|
| 2θ | d | I/I_0 | d | I/I_0 | | |
| 21.5 | 4.1329 | 100.00 | 4.133 | 95 | $\text{LS} \cdot \text{H}_2\text{O}$ | 011 |
| 23.2 | 3.8338 | 70.45 | 3.83 | 85 | $\text{LS} \cdot \text{H}_2\text{O}$ | 101 |
| 25.1 | 3.6926 | 95.65 | 3.696 | 35 | $\text{LS} \cdot \text{H}_2\text{O}$ | $\bar{1}02$ |
| 30.4 | 2.9402 | 51.13 | 2.944 | 50 | $\text{LS} \cdot \text{H}_2\text{O}$ | 112 |
| 32.8 | 2.7302 | 55.11 | 2.730 | 64.2 | LN | 014 |
| 33.6 | 2.6671 | 16.47 | 2.666 | 16 | $\text{LS} \cdot \text{H}_2\text{O}$ | $\bar{1}03$ |
| 37.6 | 2.3921 | 7.95 | 2.396 | 10 | $\text{LS} \cdot \text{H}_2\text{O}$ | 112 |
| 38.6 | 2.3324 | 12.72 | 2.339 | 16 | $\text{LS} \cdot \text{H}_2\text{O}$ | $\bar{1}13$ |
| 39.3 | 2.2924 | 15.34 | 2.295 | 20 | $\text{LS} \cdot \text{H}_2\text{O}$ | 210, 013 |
| 40.0 | 2.2539 | 7.95 | 2.254 | 8 | $\text{LS} \cdot \text{H}_2\text{O}$ | $\bar{2}12$ |
| 41.0 | 2.2012 | 9.65 | 2.202 | 12 | $\text{LS} \cdot \text{H}_2\text{O}$ | 122 |
| 45.3 | 2.0018 | 4.54 | 2.001 | 6 | $\text{LS} \cdot \text{H}_2\text{O}$ | $\bar{2}13$ |
| 48.6 | 1.8733 | 12.50 | 1.875 | 6 | LS | 413 |
| 50.8 | 1.7972 | 4.54 | 1.797 | 6 | $\text{LS} \cdot \text{H}_2\text{O}$ | $\bar{1}13, \bar{3}02$ |
| 54.0 | 1.6980 | 7.38 | 1.697 | 2 | LS | 123 |
| 57.0 | 1.6165 | 5.11 | 1.616 | 2 | LS | 130 |
| 59.1 | 1.5631 | 5.68 | 1.565 | 2 | LS | $\bar{4}22, 131$ |
| 78.4 | 1.2068 | 5.11 | 1.206 | 9 | LN | 218 |

by the $\text{Li}_2\text{SO}_4:\text{LiOH}:\text{LiF}$ system, its cell performance is not as good as that of 80 $\text{Li}_2\text{SO}_4:20 \text{LiNbO}_3$. Thus high conductivity is not the only criteria for obtaining a good cell.

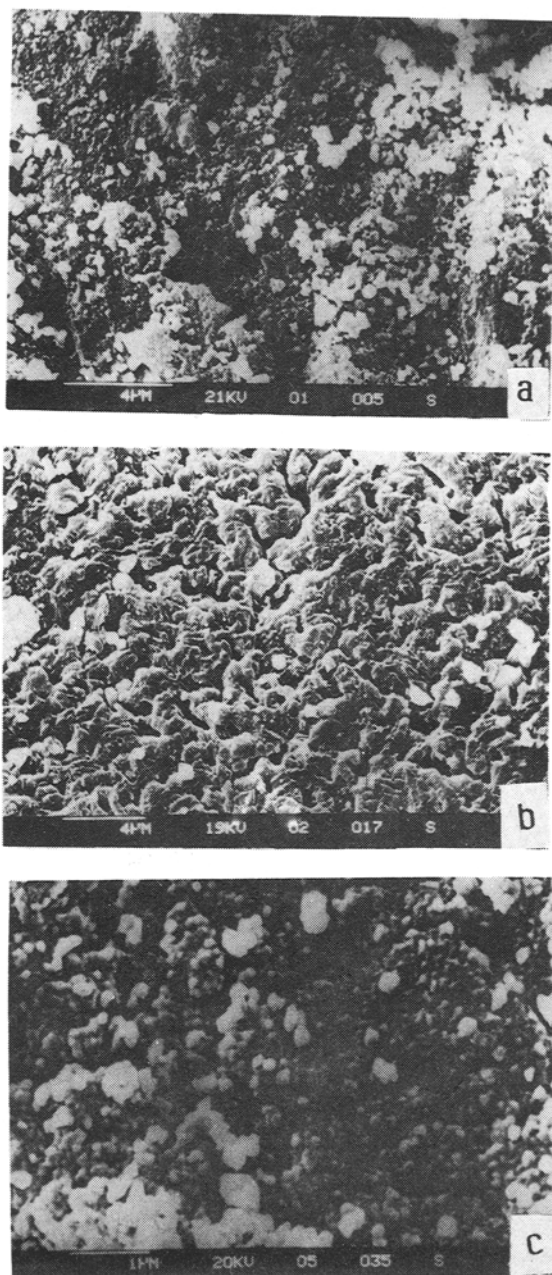


Figure 5. Scanning electron micrographs of LiNbO_3 : Li_2SO_4 system.

Table 3. Comparison of the experimentally obtained d values with that of the ASTM data for 70 mole% Li_2SO_4 and 30 mole% LiNbO_3 .

| Observed | | | ASTM | | Observed phase | hkl |
|-----------|--------|---------|-------|---------|--------------------------------------|-------|
| 2θ | d | I/I_0 | d | I/I_0 | | |
| 23.2 | 3.8338 | 14.34 | 3.837 | 85 | $\text{LS} \cdot \text{H}_2\text{O}$ | 101 |
| 25.0 | 3.5617 | 22.22 | 3.559 | 90 | $\text{LS} \cdot \text{H}_2\text{O}$ | 110 |
| 25.5 | 3.4930 | 7.87 | 3.49 | 20 | LS | 111 |
| 28.2 | 3.1644 | 25.85 | 3.16 | 40 | LS | 201 |
| 29.2 | 3.0532 | 17.57 | 3.049 | 60 | $\text{LS} \cdot \text{H}_2\text{O}$ | 012 |
| 32.7 | 2.7385 | 16.16 | 2.730 | 64.2 | LN | 014 |
| 36.2 | 2.4813 | 6.85 | 2.479 | 16.0 | LS | 020 |
| 42.7 | 2.1175 | 100.00 | 2.120 | 18.40 | LN | 202 |
| 61.9 | 1.4989 | 32.59 | 1.495 | 4.0 | LS | 510 |
| 78.4 | 1.2197 | 7.6147 | 1.217 | 5.5 | LN | 312 |

Table 4. Conductivity and cell performance for various solid electrolytes.

| Cell $\text{Li}/\text{SE}/\text{MnO}_2$ | | | | |
|---|----------------|------------------|---|---|
| Solid electrolyte | Condition | O.C.V. (V) | Short circuit current (μA) | AC conductivity (bulk) at 553 K $\text{ohm}^{-1} \text{cm}^{-1} \text{K}$ |
| Li_2SO_4 | Powder | 3.2 | 0.22 | 2.70×10^{-7} |
| LiNbO_3 | Single crystal | 1.6 | 0.02 | 1.53×10^{-7} |
| 7 Li_2SO_4 : 3 LiNbO_3 | Powder | 3.22 | 0.00 | 3.71×10^{-5} |
| 8 Li_2SO_4 : 2 LiNbO_3 | Powder | 3.55 | 10.00 | 2.74×10^{-4} |
| 8.08 Li_2SO_4 : 1.92 LiNbO_3 * | Powder | 2.65–3.40 (16 h) | — | — |
| 6 Li_2SO_4 : 4 Li_2CO_3 | Powder | 3.60 | 1.4 | 7.19×10^{-4} |
| $\text{Li}_2\text{SO}_4 \cdot \text{LiOH} : \text{LiF}$ | Powder | 3.183 | 0.069 | 2.27×10^{-2} |
| $\text{Li}_2\text{O} : \text{B}_2\text{O}_3 : \text{Ag}_2\text{SO}_4$ | Powder | 2.00 | 0.00254 | 1.2×10^{-3} |

*Kanda *et al* (1982).

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