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Electrical transport in the system Li_2SO_4–mLi_2MoO_4–$2mLi_3VO_4$

H. B. LAL, KANCHAN GAUR, A. J. PATHAK
Department of Physics, University of Gorakhpur, Gorakhpur (UP) India

The measurement of electrical conductivity (σ) and thermoelectric power (S) of three compounds (namely m = 0, 0.5 and 1) in the system Li_2SO_4–mLi_2moO_4–$2mLi_3VO_4$ has been reported from 500° C to melting point of each solid. All the three solids show superionic phase just below their melting point. In this phase σ value decreases but activation energy and span of superionic phase increases for compounds with larger m. Further the phase transition temperature (T_p) from normal to superionic phase decreases with m. Below T_p the order of σ is reversed, it increases with m but in all cases it becomes mixed with dominant ionic part.

1. Introduction

Superionic solids are primarily of interest due to their potential applications in electrochemical devices. For high power batteries Li^+ ion active superionic solids have been thought to be better than others and therefore have been of recent interest [1–8]. We have been investigating the electrical transport in superionic solids for the last two decades [9–14] and have also investigated some Li^+ ion active superionic solids in recent years [15–19]. This paper is a part of that activity and reports the study of the Li_2SO_4–mLi_2MoO_4–$2mLi_3VO_4$ system.

2. Material preparation and experimental technique

To prepare the compounds of studied system we have used Li_2SO_4, Li_2MoO_4 and Li_3VO_4. Out of these three salts Li_2SO_4 with stated purity of 99.99% was procured from M/S Rare and Research Chemicals, Bombay, India and the later two compounds were prepared by us in the laboratory. Li_2MoO_4 was prepared using Li_2O and MoO_3. The stoichiometric amount of these materials, properly powdered and dried, was mixed and fired in air around 740 K for 48 h with one intermediate grinding after 24 h. The starting materials for the preparation of Li_3VO_4 were Li_2O and V_2O_5. These materials in stoichiometric amount were mixed and fired in air at around 1100 K for 48 h with one intermediate grinding. It has been inferred from XRD patterns of the prepared compounds that no unreacted starting material is left in the compound and solid state reaction is complete. The materials Li_2O, MoO_3 and V_2O_5 each with stated purity of 99.99% were procured from M/S Rare and Research Chemicals, Bombay, India. The compounds of the system Li_2SO_4–mLi_2MoO_4–$2mLi_3VO_4$ were prepared by mixing the required amount of Li_2SO_4, Li_2MoO_4 and Li_3VO_4. The mixture was melted in a tube, shaken thoroughly and slowly solidified. The melting points for compounds with m = 0, 0.5 and 1.0 were determined as (1133 ± 5), (1110 ± 5) and (1090 ± 5) K, respectively. The solidified melt has been used for the measurements of electrical conductivity and thermoelectric power. The details of σ and S measurements have been the same as described in earlier papers of our group [11, 20, 21]. The overall error in σ measurement has been about 2%. Temperature could be recorded with an accuracy of ±1 K. The error in S measurement depends upon the sample resistance and varies from ±10% for high resistive sample ($R > 10^6\,\Omega$) to ±5% for low ($R \sim 1\,\Omega$) resistive sample.

3. Results and discussion

Electrical conductivity (σ) and thermoelectric power (S) of the system Li_2SO_4–mLi_2MoO_4–$2mLi_3VO_4$ have been measured as a function of temperature. The results of σ and S measurements are shown in Figs 1 and 2 as log σT against T^{-1} and S against T^{-1} plots. The errors in the measurement wherever required are shown by error bars. No hysteresis has been observed and σ values are almost the same in heating and cooling cycles. It is seen from Fig. 1 that plots for all three studied materials are similar. Below a certain temperature T_1 these materials show a linear log σT against T^{-1} plot and then non-linear variation between temperatures T_1 and T_2. In the case of Li_2SO_4 a hump appears in the plot around its phase transition temperature of 846 K [22] and above this temperature there is steep rise in the values of log σT. However, in case of compounds with m = 0.5 and m = 1.0, an upward bending in the curve occurs which becomes steeper with the increase of temperature. All these materials show a flat but linear region above temperature T_2. The linear variation of σ with T can be expressed by equation

$$\sigma T = C \exp(-E_a/kT) \quad (1)$$

where C is pre-exponential factor and E_a is the activation energy. The values of T_1, T_2, C and E_a are given in Table I. The results of thermoelectric power with temperature are shown as S against T^{-1} plot in Fig. 2. From the plot it is clear that S is positive at lower

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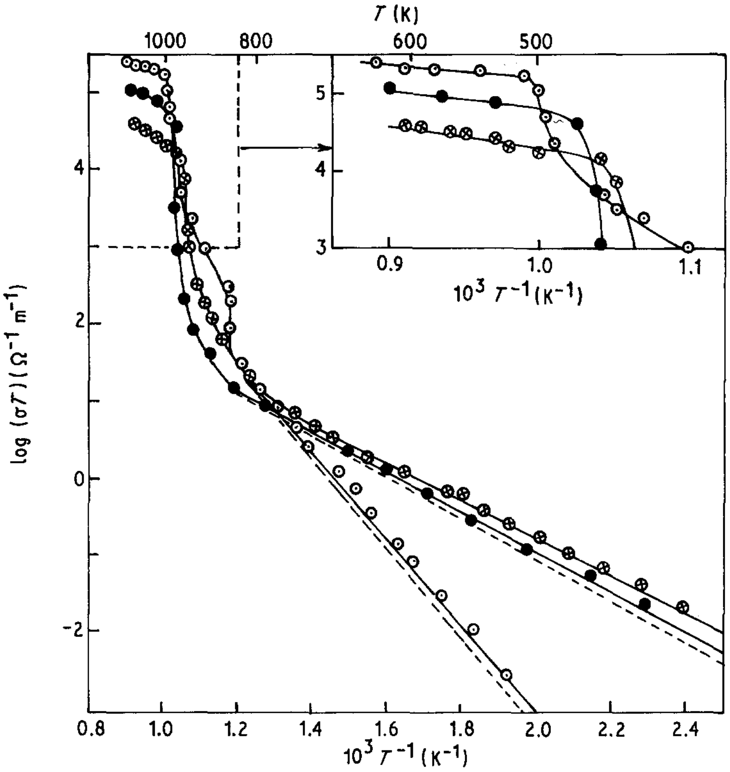

Figure 1 Plot of log σT against T^{-1} for the compounds of the studied system. (⊙ $m = 0$, ● $m = 0.5$, ⊗ $m = 1.0$, σ ——, σ_i - - -).

temperature and changes sign from positive to negative at a certain temperature T_s. All of them show linear S against T^{-1} plots below a temperature T_1' and above T_2'. The linear variation of the S against T^{-1} plot can be represented by

$$S = \eta/eT + H \qquad (2)$$

where η and H are constants for a particular compound. The values of T_1', T_s, T_2', η and H for all solids are given in Table II.

The nature of charge carriers in these solids has been investigated by performing time dependence study of σ_{dc} at constant electric field and temperature and is shown in Fig. 3. It is seen from this figure that for any of the studied compounds σ_{dc} decreases with time and tends to attain a constant value after a long time. This time of constancy becomes small at lower temperature. This indicates that the studied solids are essentially mixed conductors. The value extrapolated to $t \to 0$ gives total (electronic + ionic) conductivity (σ) and value obtained for $t \to \infty$ gives the electronic part (σ_e) of the total conductivity. σ has also been measured at a few a.c. frequencies and fixed temperatures. The results are shown in Fig. 4. It is seen from this figure that σ_{ac} is independent of a.c. frequencies. Further $\sigma_{ac} \simeq \sigma_{dc}$ ($t \to 0$). This indicates that σ_{dc} for $t \to 0$ is the bulk value of σ and grain boundary and air pores are considerably minimized. This is an expected result because the solidified melt of the compounds were used for the measurements. Using the plot of σ_{dc} against time at fixed temperature, σ and σ_e have been obtained. The ratio r is then calculated using the relation

$$r = \frac{\sigma_i}{\sigma_e} = \frac{\sigma}{\sigma_e} - 1 \qquad (3)$$

The values of r have been obtained using the above procedure at five or six temperatures. Using these

TABLE I Summarized results of electrical conductivity of the studied compounds of the system Li_2SO_4–mLi_2MoO_4–$2mLI_3VO_4$

m	Lower temperature range			Higher temperature range		
	E_a (eV)	C (Ω^{-1} m^{-1} K)	T_1 (K)	T_2 (K)	E_a (eV)	C (Ω^{-1} m^{-1} K)
0	1.12	2.11×10^8	840	1000	0.41	1.85×10^7
0.5	0.53	2.46×10^4	800	975	0.42	8.74×10^6
1.0	0.38	1.91×10^3	770	950	0.47	4.48×10^5

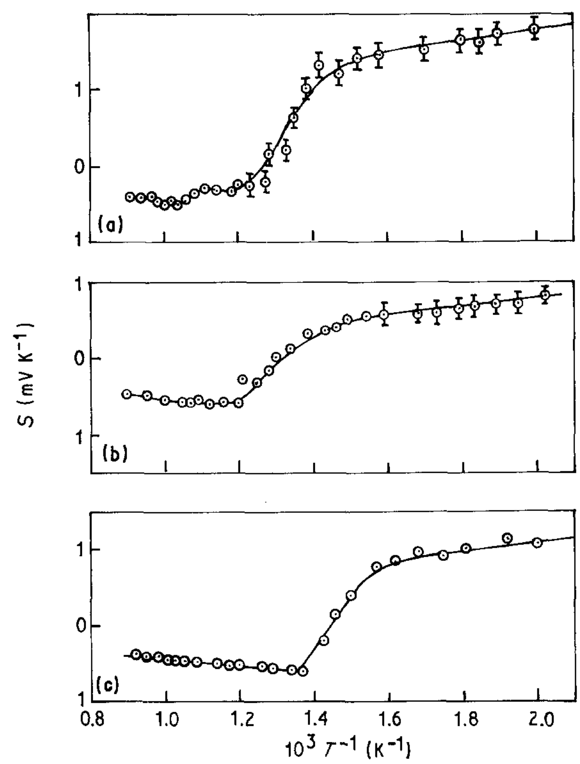

Figure 2 Plot of S against T^{-1} for the compounds of the studied system. (a) $m = 0$, (b) $m = 0.5$, (c) $m = 1.0$.

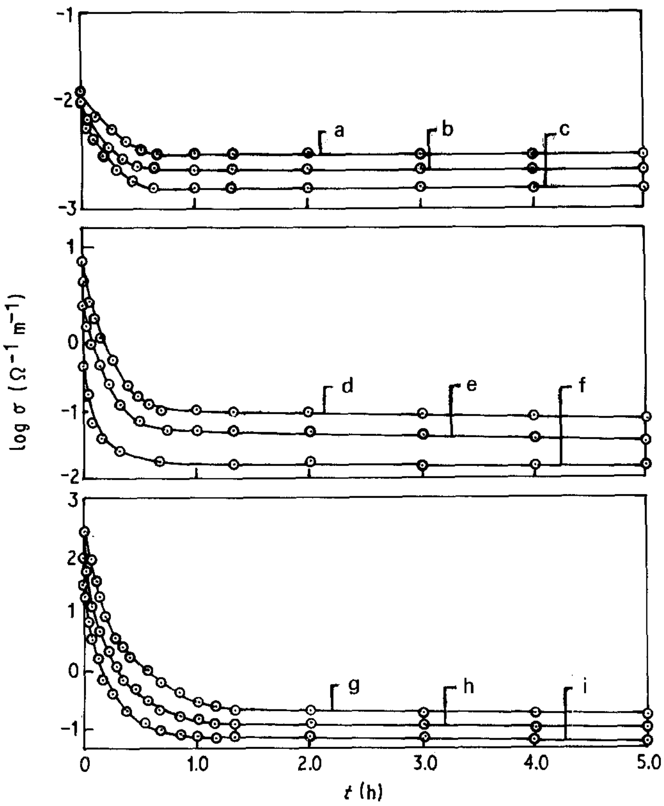

Figure 3 Plot of log σ against time t for the compounds of the studied system.

	m	E (kVm^{-1})	T (K)
a	0	0.270	785
b	0.5	0.270	790
c	1.0	0.265	750
d	0	0.175	925
e	0.5	0.180	930
f	1.0	0.170	952
g	0	0.145	1100
h	0.5	0.150	1110
i	1.0	0.140	1095

values of r we plotted a smooth graph between log r and T. Such plots for all three studied solids are shown in Fig. 5. This plot enables us to get the value of r at any desired temperature. From the known values of r, ionic and electronic contribution to total σ at different temperatures have been estimated using

$$\sigma_i = \left(\frac{r}{r+1}\right)\sigma \quad \text{and} \quad \sigma_e = \left(\frac{1}{r+1}\right)\sigma \qquad (4)$$

With these values we plotted graphs of log $\sigma_i T$ against T^{-1} which are shown in Fig. 1 by broken lines. It is seen from this figure that there is almost no difference between σ_i and σ at higher temperature ($T > 800$ K). However, they differ slightly in the lower temperature range. There are three regions in σ_i variation with temperature. These regions are (i) linear region for $T < T_1$ (ii) non-linear region between T_1 and T_2 (iii) linear region for $T > T_2$. In the third region σ is very high ($\sim 100\,\Omega^{-1}\,m^{-1}$) for all three solids. r is of the order of 10^3 and $\sigma_i = \sigma$. Thus they are pure ionic conductors. S in this region is negative indicating that the cation is the mobile charge carrier. Thus from the value of σ and ionic nature of conductivity it can be said that all these solids have become good solid

TABLE II Summarized results of thermoelectric power (S) of the studied compound of the system Li_2SO_4-mL_2MoO_4-$2mLi_3VO_4$

m	Lower temperature range				Higher temperature range		
	η (eV)	H (mVK^{-1})	T_1' (K)	T_s (K)	T_2' (K)	η (eV)	H (mVK^{-1})
0	0.72	0.36	670	800	1000	−0.64	0.16
0.5	0.62	−0.40	665	760	950	−0.50	−0.05
1.0	0.62	−0.00	625	670	950	−0.42	−0.01

TABLE III Relevant data for superionic phase of the studied solids

m	Transition temperature to superionic phase (K)	Span of superionic phase (K)	σ_i at 1050 K ($\Omega^{-1}\,m^{-1}$)
0	1000	133 (1000–1133)	195
0.5	975	135 (975–1110)	85
1.0	950	140 (950–1090)	35

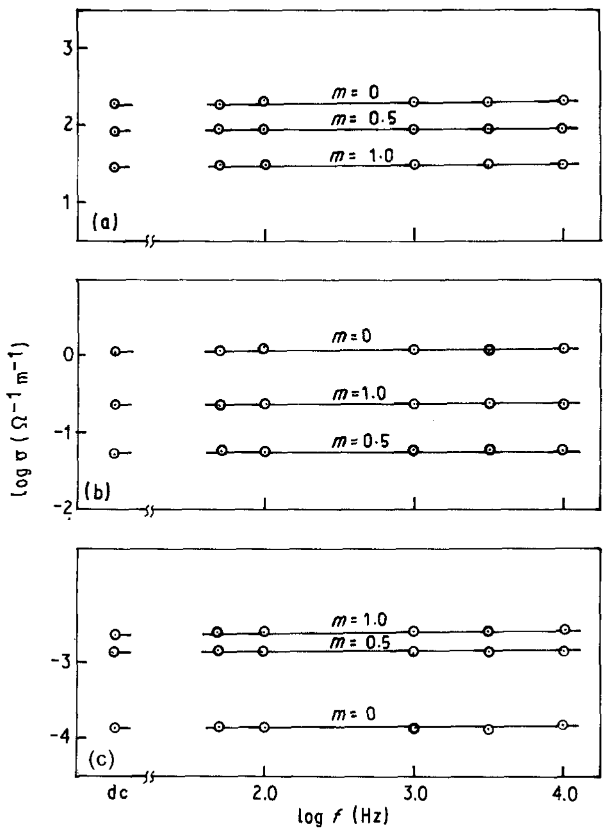

Figure 4 Plot of log σ against log f for the compounds of the studied system.

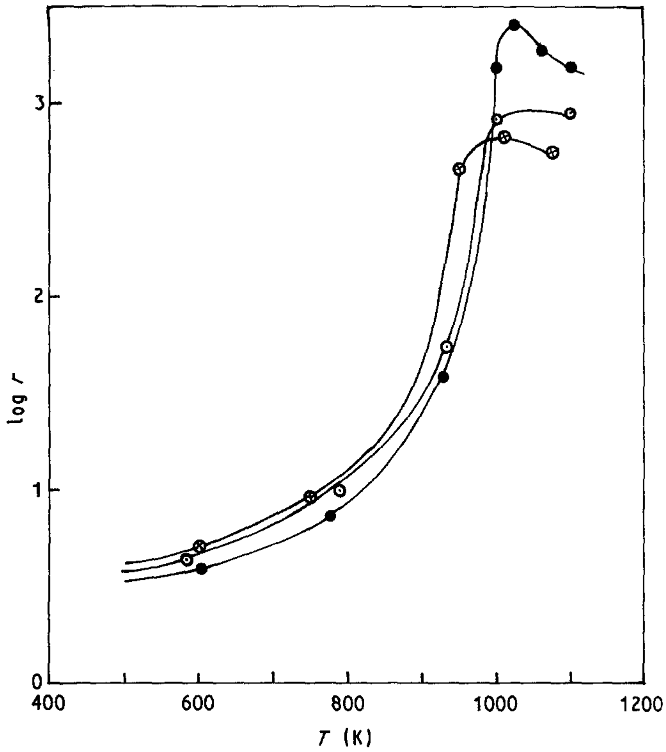

Figure 5 Plot of log r against T for the compounds of the studied system. (● $m = 0$, ⊙ $m = 0.5$, ⊗ $m = 1.0$).

electrolytes. The phase transition temperature and span of superionic phase of all three solids are given in Table III. It is seen from this table that with an increase of m, the phase transition temperature (T_p) is lowered, the span of superionic phase increases and the σ value goes down. The first two are positive and third is a negative aspect for superionic solids. Since σ for all the three compounds remains in the superionic range, a slightly larger or smaller value within the range is immaterial. Hence the two positive aspects obtained for $m = 0.5$ and 1.0 are quite significant. For $m > 1$, σ drops drastically. Therefore we have not studied compounds corresponding to $m > 1$.

In the lower temperature ($T < T_1$) range σ values for both $m = 0.5$ and 1.0 are larger than Li_2SO_4. The values of r, however, remains larger than unity (Fig. 5) indicating the dominance of ionic part in conductivity. The sign of S in this temperature range is positive for all studied solids. This indicates that the current carriers are negatively charged. In this case this can happen when either cation vacancies or anions are mobile in this temperature range. The motion of anions is less probable at lower temperature. Hence the conduction seems to be dominated by cation vacancies or Schottky type defects.

The log $\sigma_e T$ against T^{-1} plots (Fig. 6) are similar to

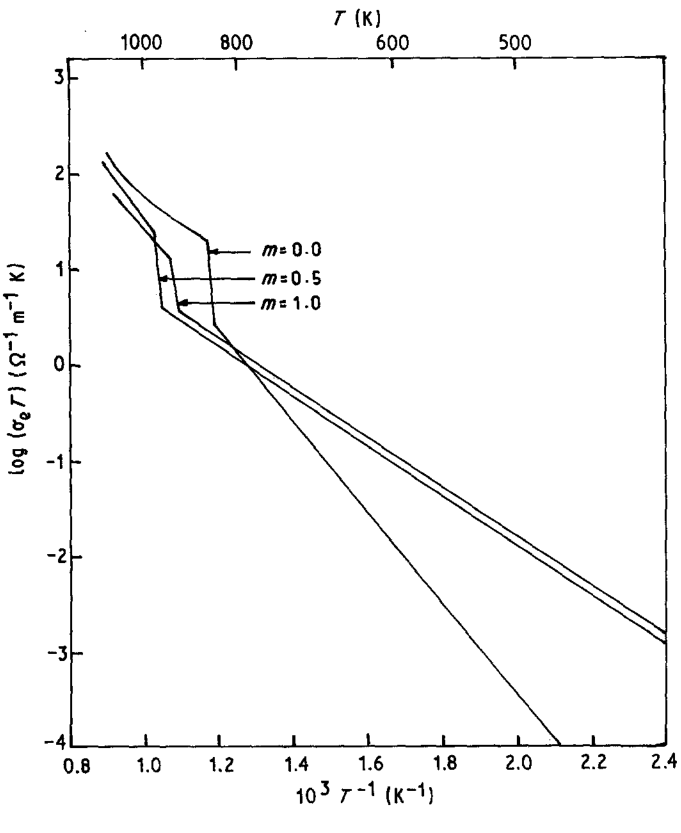

Figure 6 Plot of log $\sigma_e T$ against T^{-1} for the compounds of the studied system.

TABLE IV Summarized results of electronic contribution to the conductivity of studied compounds of the system Li_2SO_4–mLi_2MoO_4–$2mLi_3VO_4$

m	E_a (eV)	C (Ω^{-1} m^{-1} K)	Temperature span (K)
0	0.96	1.68×10^6	475–840
0.5	0.53	3.09×10^3	416–945
1.0	0.52	3.10×10^3	416–910

the plot of log $\sigma_i T$ against T^{-1}. σ_e jumps by several order of magnitude around a particular temperature. Below this temperature log $\sigma_e T$ against T^{-1} plots are linear and can be represented by Equation 1. The values of C and E_a together with the span of linear range are given in Table IV.

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