

Ionic conduction in superionic system



VISHALAKSHI SINGH, SATYENDRA SINGH¹ and KANCHAN GAUR

Department of Physics, K.N. Government P.G. College, Gyanpur, Bhadohi (India).

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ABSTRACT

Measurement of electrical conductivity (σ) and Seebeck coefficient (S) of the studied superionic system $\text{Li}_2\text{O}:\text{P}_2\text{O}_5:\text{WO}_3$ have been reported in the temperature range 415K to the melting point 1110K of the solid. All the measurement have been performed on solidified melt. The studied system shows a clear superionic phase. In the temperature range 950K to 1110K, it shows high ionic conductivity ($\sigma_i \sim 90\Omega^{-1}\text{m}^{-1}$ at 1050K) with small (0.38eV) activation energy and almost negligible electronic conductivity. Molar magnetic susceptibility (χ_M) and dielectric constant (K) have also been measured against temperature to confirm anomalies observed in σ and S results.

Key words: Electrical conductivity, seebeck coefficient, superionic system, magnetic susceptibility.

INTRODUCTION

Extensive studies have been done by many workers¹⁻⁷, in the search of lithium ion conducting superionic solids because of their application potentialities in high power miniaturized electrochemical cells⁸⁻¹⁵. We have also been investigating¹⁶⁻²⁰ these solid for the last two decades. This paper presents the study of electrical transport with the molar magnetic susceptibility (χ_M) and dielectric constant (K) measurements.

was then melted, shaken thoroughly and allowed to cool slowly to get solidified melt. X-ray diffraction shows that no unreacted starting material was left and single phase compound is formed. The measurement on electrical conductivity (σ), Seebeck coefficient (S) and dielectric constant (K) were performed on solidified melt whereas molar magnetic susceptibility (χ_M) was performed on powdered sample from 400K to the melting point of the solid. The details of sample holder and measurements have been described elsewhere²¹⁻²³.

MATERIAL

Preparation and experimental technique

To prepare the studied system the base materials Li_2O , P_2O_5 and WO_3 were first procured from Rare and Research Chemical, Bombay and Chempure, Calcutta with stated purity of 99.99 percent. The base materials were taken in stoichiometric amount and mixed thoroughly. The mixed material was then fired around 1050K for 48h with one intermediate grinding. The material

RESULTS AND DISCUSSION

The electrical conductivity (σ_{ac}) as a function of frequency (50Hz, 100Hz, 1kHz, 3kHz and 10kHz) has been measurement at constant temperature. The results are not shown. For comparison σ_{dc} values at corresponding temperature are also given in same figure. It is seen from this figure that there is no difference between σ_{dc} values at different frequencies. Also σ_{dc} is almost same as σ_{ac} . This result indicates that grain-

boundary effects are not very significant in this solid. To investigate the nature of charge carrier σ_{dc} has been measured as a function of time at a constant temperature. This study has been preformed at six widely separated temperatures. The results are shown in Fig. 1. It is seen from this figure that 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 compound is essentially mixed conductor. The value extrapolated to $t=0$ gives total (electronic + ionic) conductivity (σ) where as the value obtained for $t \rightarrow \infty$ gives electronic part of total conductivity. Using the plot of σ_{dc} vs T^{-1} values s_e have been obtained. The ratio (r) is then calculated using equation-1 at five to six widely separated temperature.

$$r = \frac{\sigma_i}{\sigma_e} = \frac{\sigma}{\sigma_e} - 1 \quad \dots(1)$$

The plot of $\log r$ with temperature is shown in Fig.2. It is seen from this figure that r increases with temperature becomes very fast for $T > 890K$ and at higher temperature $T > 1000K$ it tends to decrease with temperature.

σ and S measurements on three to four solidified melts from different lots have been done as a function of temperature. No hysteresis was observed and obtained σ and S values are almost in both heating and cooling cycles. The results are shown as $\log \sigma T$ vs T^{-1} plots in Fig. 3. It is seen from this figure that s values is high being 1.85×10^{-2} at 50K. The material is hygroscopic. The $\log \sigma T$ vs T^{-1} plot is linear between temperature range 415 K to 765K after that there is step and continuous increase of $\log \sigma$ and then conductivity increase slowly till the melting point. 1110K of the solid. The linear region of the plot can be represented by the equation 2.

$$\sigma T = C \exp (-E_a/kT) \quad \dots(2)$$

The values of E_a and C are 0.37 eV and $1.87 \times 10^3 \Omega^{-1} m^{-1} K$ and 0.45 eV and $4.40 \times 10^5 \Omega^{-1} m^{-1} K$ for temperature range 415 K to 765K and 765 K to 1110K respectively. The S vs T^{-1} plot is also linear in the temperature interval 500K to 760K and 770K to 1110K. The linear region can be represented by the equation 3.

$$S = \frac{\eta}{eT} + H \quad \dots(3)$$

The value of η and H in the first region are 0.60 eV and $-0.00m VK^{-1}$ and in the second region- 0.40 eV and $-0.02 mVK^{-1}$. The sign of S in the superionic region indicating that the positive ions are the main entity of charge carrier.

The ratio of ionic electronic conductivities at different temperatures have been evaluated from time dependence study of σ_{dc} . Using these values we have separated ionic (σ_i) and electronic (σ_e) parts of electrical conductivity. Plot of $\log \sigma_i T$ vs T^{-1} is shown in Fig. 3. by dotted line. It is seen from this figure that there is almost no difference between σ_i and σ at higher temperature ($T > 800K$). However, they differ to some extent in lower temperature range. In the second region σ is very high ($\sim 100 \Omega^{-1} m^{-1}$). The ratio r is of the order of 10^3 and essentially $\sigma_i = \sigma$. Thus this compound is pure ionic conductor. Thermo electric power in this range is negative indicating cations to be the mobile charge carrier. Thus from the value of σ and ionic nature of conductivity we can say that the compound is a good solid electrolyte. The span of superionic phase is $160K$ (950-1110K). The transition to superionic phase takes place at 950K. The linear regions of $\log \sigma T$ and S vs T^{-1} plots can be represented by the relation.

$$\dots(4)$$

$$\dots(5)$$

The values of Q and h_m are 0.42 eV and 0.47 eV with a value of σ_i at 1040K as $35 \Omega^{-1} m^{-1}$. Thus h_m is slightly larger than Q . The difference is of the order of polaronic binding energy¹⁸.

Such as result is predicted by Extended ionic gas model. In the lower temperature range of electronic contribution is small (from 20 to 10 present). Thus there is dominance of ionic conductivity. The sign of S in this temperature range is positive. Hence current carries are negatively charged. This can happen when either cation vacancies or anions are mobile in this temperature

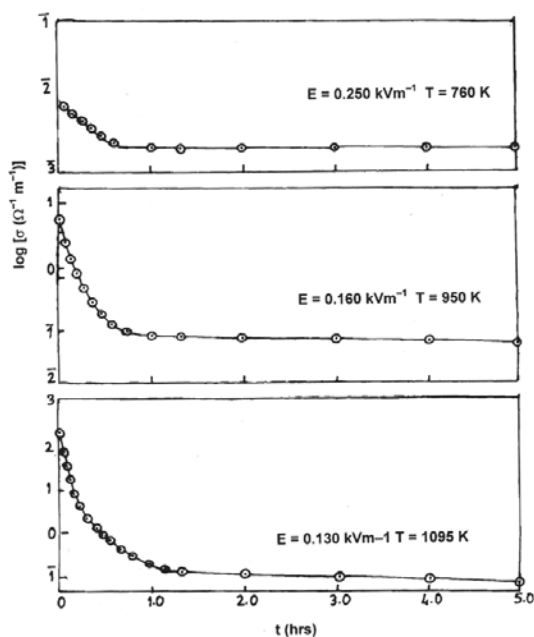


Fig. 1: Plot of Logarithm of conductivity ($\log \sigma$) Vs Time (t) of the system $\text{Li}_2\text{O}:\text{P}_2\text{O}_5:\text{WO}_3$

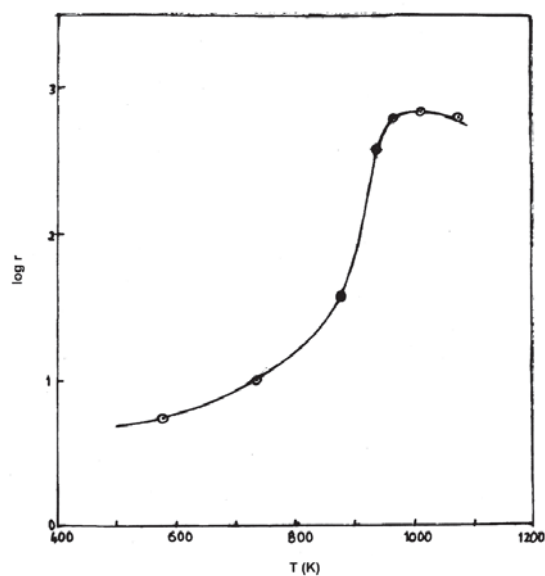


Fig. 2: Plot of Logarithm of Ionic or Electronic conductivity ($\log r$) Vs Absolute Temperature (T) of the system $\text{Li}_2\text{O}:\text{P}_2\text{O}_5:\text{WO}_3$

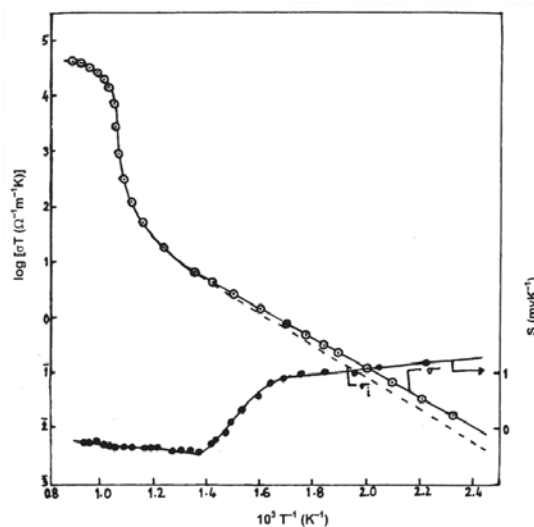


Fig. 3: Plot of logarithm of product of conductivity and Temperature ($\log \sigma T$) and Thermoelectric power (S) Vs Inverse of absolute temperature (T^{-1}) of the system $\text{Li}_2\text{O}:\text{P}_2\text{O}_5:\text{WO}_3$

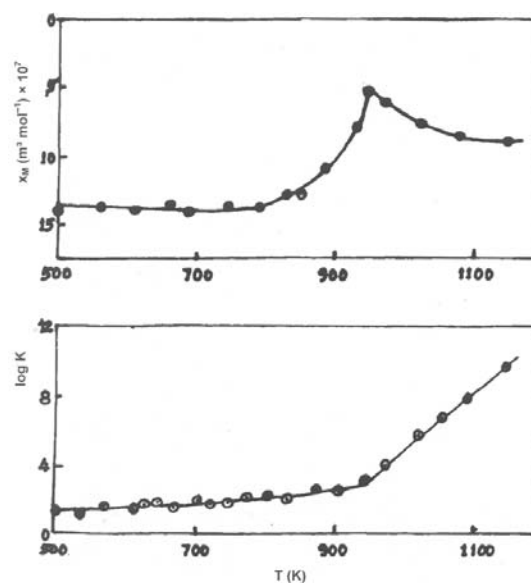


Fig. 4: Plot of Molar magnetic susceptibility (χ_M) and logarithm of dielectric ($\log K$) Vs absolute temperature (T) for the system $\text{Li}_2\text{O}:\text{P}_2\text{O}_5:\text{WO}_3$

range. Motion of anions at lower temperature is less probable. Hence the conduction seems to be dominated by cation vacancies or Schottky type defects.

The $\log \sigma_e T$ vs T^{-1} plot (Fig. 3.) is similar to the plot of $\log \sigma_i T$ vs T^{-1} . σ_e jumps by several order of magnitude around particular temperature. The linear region can be represented by the equation 6.

$$T\sigma_e = \sigma_0 \exp (-W/kT) \quad \dots(6)$$

The value of σ_0 and W are $3.08 \times 10^3 \Omega^{-1} \text{m}^{-1}$ and 0.51 eV.

The χ_M and K studies are performed on two to these samples prepared in different lots. The χ_M

and $\log K$ plots are shown in Fig. 4. It is seen from that χ_M increases very slowly up to 770K, shows a peak at 950K then decreases with increase of temperature. The value of χ_M is throughout negative. Similar trend of variation is observed in $\log K$ vs T . The value of K is 55 at 500K. It increases with temperature up to 950K then decreases slowly indicating an anomaly at 945K as observed in $\log \sigma T$ vs T^{-1} plot. The studied superionic system is ionic compound and contains no magnetic ions. Thus it is a diamagnetic as has been confirmed by the negative value of χ_M . Their diamagnetism depends upon its bonding configuration. The onset of disordering at phase transition disrupts the bonding configuration and leads to an abrupt change in χ_M . Thus the temperature around which anomaly appears is also confirmed by K and σ plots.

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