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High Ionic Conductivity of Li₂O:B₂O₃:V₂O₅

Kanchan Gaur and H. B. Lal Department of Physics, University of Gorakhpur, Gorakhpur-273009 (India)

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Lithium ion conducting solids have been of great interest in recent years [1-5]. We have also been active in this direction [6-8]. This paper reports on the electrical transport and phase transition Li₂O:B₂O₃:V₂O₅. The compound was prepared by solid state reaction technique. The measurements of the electrical conductivity (σ), thermoelectric power (S), dielectric constant (K) and molar magnetic susceptibility (χ_M) are performed from 500 to 1110 K. The details of these measurements are described in [9, 10]. The σ and S variations are shown in Fig. 1 as $\log \sigma T$ and S vs. 1/T plots. Both the plots show three linear regions, namely, 500-850 K, 900-960 K, and 980-1110 K. The activation energy (E_a) and heat of transport (Q) for the third temperature range are 0.39 eV and 0.58 eV, respectively. σ jumps by a factor of 180 around 855 K, and again jumps by a factor of 4 around 970 K. Thus this material seems to have two phase transition temperatures: one around 855 K and the other at 970 K. The sign of S indicates that current is carried by positive charge carriers. The time variation of the dc electrical conductivity (the results are not shown) shows that σ is completely ionic in the temperature range 980-1110 K. Ions are also the dominant charge carriers at lower temperatures but in general σ is mixed (ionic and electronic). Lithium seems to be the mobile ion of the solid. σ in the temperature range 980-1110 K is high, being $150 \Omega^{-1} \,\mathrm{m}^{-1}$, and it is totally ionic, hence this is the superionic phase of the solid. The phase transitions around 855 K and 970 K are also reflected in K and $\chi_{\rm M}$ vs. T plots, as shown in Figs. 2 and 3, respectively. The room temperature K value is not high, being about 30 around 300 K. It increases slowly up to 700 K but rises steeply above 855 K and becomes of the order of 3.2×10^7 at 900 K. It drops by a factor of 3 around 970 K and then remains almost constant. It

Reprint requests to Dr. H. B. Lal, Department of Physics, University of Gorakhpur, Gorakhpur 273009/India

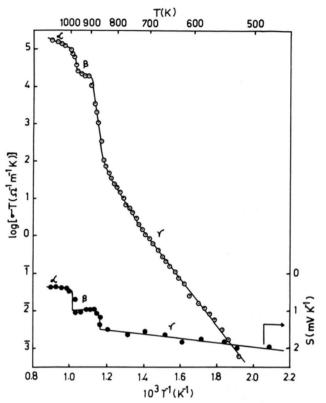


Fig. 1. Plots of $\log \sigma T$ and thermoelectric power (S) against inverse temperature (T^{-1}) .

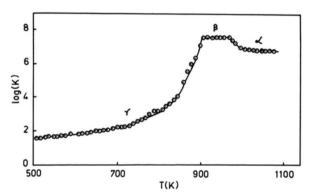


Fig. 2. Plot of logarithm of dielectric constant ($\log K$) against temperature (T).

is seen from the $\chi_{\rm M}$ vs. T plot that $\chi_{\rm M}$ is negative and is almost independent of temperature up to 855 K but shows a downward drop above this temperature. Around 970 K, $\chi_{\rm M}$ jumps abruptly and then increases slowly with temperature. The reason for the negative

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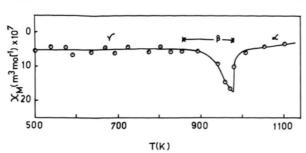


Fig. 3. Plot of molar magnetic susceptibility (χ_{M}) against temperature (T).

value, drop and rise in χ_M is that this material does not contain magnetic ions and χ_M for such solids depends upon their bonding configuration. The onset of disordering at the phase transition disrupts the bonding configuration of the solid. This leads to specific changes in $\chi_{\rm M}$ at this temperature. Q is larger than $E_{\rm a}$ in the superionic phase. This is against the trend $E_a > Q$ observed for Ag⁺ and Cu⁺ active superionic solids. This indicates that the mechanism of ion conduction in this solid differs from that usual ionic solids.

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