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Phase transition study in some superionic systems

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ABSTRACT

The study of phase transition has been done in the temperature range 500 K to the melting point of the studied materials of the systems (1-x) Li_3PO_4 : x Li_3VO_4 with x = 0.0, 0.33, 0.50, 0.67 and 1.0 and Li_3PO_4 : x Li_3VO_4 with x = 0.0, 0.33, 0.50, 0.67, 1.0, 1.5 and 2.0. The molar magnetic susceptibility x_M and dielectric constant (K) measurements have been performed for the study of phase transition. At phase transition materials under go from normal to superionic phase. An anomaly appears in x_M and log K *vs* temperature (T) plots at phase transition. This is also reflected in electrical conductivity (σ) and Seebeck coefficient (S) studies. All the studied material remains diamagnetic throughout the measurement.

Keywords: Phase transition, magnetic susceptibility, dielectric constant.

INTRODUCTION

In recent years[1-5] lithium ion conducting superionic solids have been of interest because of their application potentialities in high power solid state batteries[6-13]. Most of the superionic solids undergo phase transition from normal to superionic phase. The critical study of phase transition has been done by many workers[14-22]. Rice et al[16] have discussed the phenomenon of phase transition in superionic solids from ordered normal phase to cationically disordered superionic phase. The nature of phase transition is, however, not similar in all kinds of superionic solids and has been the subject of theoretical and experimental investigation. Theoretical progress is very fast but experimental situation which can confirm these results has not been very satisfactory till recent times. Fortunately a lot of experimental data has started coming in[23-31] and is expected that mystery of phase transition in superionic solids will be resolved soon by well founded theoretical models. Normally all physical parameters of these materials show anomaly at phase transition temperature (T_p) and any of these can be used to look at the nature of phase transition. This paper reports the study of phase transition of the materials of the systems (1-*x*) Li_3PO_4 : xLi_3VO_4 and Li_3PO_4 : xLi_3VO_4 where x = 0.0, 0.33, 0.50, 0.67 and 1.0 and 0.0, 0.33, 0.50, 0.67, 1.0, 1.5 and 2.0 respectively.

Material preparation and experimental technique

The materials of the studied systems were prepared in the laboratory. The starting materials Li_3PO_4 and Li_3VO_4 were prepared by mixing Li_2O + P_2O_5 and Li_2O + V_2O_5 respectively in stoichiometric amount. Li_2O (99.99% pure) and P_2O_5 and V_2O_5 (purity 99.99%) were procured from Rare and Research Chemicals, Bombay and Chempure, Calculta, respectively. The starting materials were taken in required amount, fired at 1100K in air in a silica crucible for 48 h withare intermediate grinding, melted and cooled slowly to room temperature. The analysis of X-ray diffraction pattern shows that no unreacted starting material was left and single phase compound was formed. The measurement of molar magnetic susceptibility (χ_M) and dielectric constant (K) have been performed on solidified melt. The details of measurements together with sample holder have been described elsewhere[32-33].

RESULT AND DISCUSSION

The phase transition study has been done by molar magnetic susceptibility (x_M), Seebeck coefficient (S) and dielectric constant (K) measurements. Measurement of x_M is free from electrode, grain boundaries, shape and size of the sample. Similarly in S measurement no current flows through the sample and thus it is a zero current process. Hence it is also free of electrode electrolyte contact problem, grain boundaries, air pores, shape and size of the sample. S data also provides information about the nature of charge carriers. Hence the result of S data has been utilized in deciding electrical conduction mechanism in the materials of the studied system.

Table 1: Values of T_p for the system (1 - *x*) Li_3PO_4 : *x* Li_3VO_4 from σ, x_M and K plots

Material with *x*	T_p (K) from the study		
	σ	x_M	K
0.0	865	860	865
0.33	885	885	880
0.50	917	920	920
0.67	930	930	925
1.0	950	950	950

Table 2: Values of T_p for the system Li_3PO_4 : *x* Li_3VO_4 from s, X_M and K plots

Material with *x*	T_p (K) from the study		
	σ	x_M	K
0.0	865	860	860
0.33	870	865	870
0.50	885	880	890
0.67	910	900	910
1.0	917	915	920
1.5	935	935	930
2.0	945	940	940

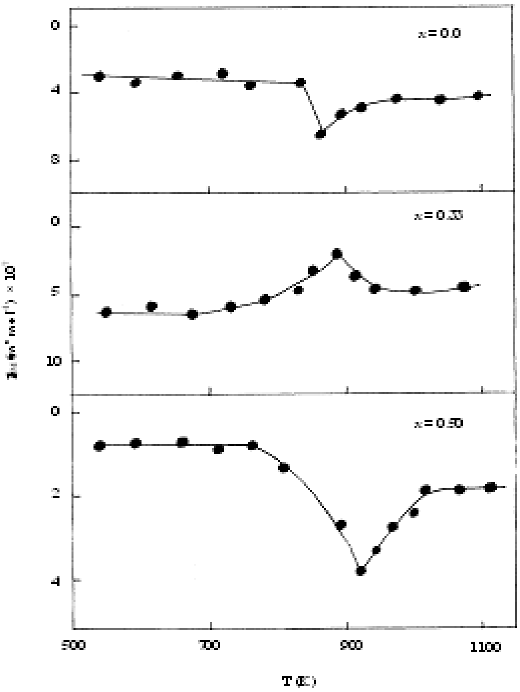

Fig. 1: Plots of molar magnetic usceptibility x_M against absolute temperature (T) of the system (1-x) Li_3PO_4 : x Li_3 VO_4

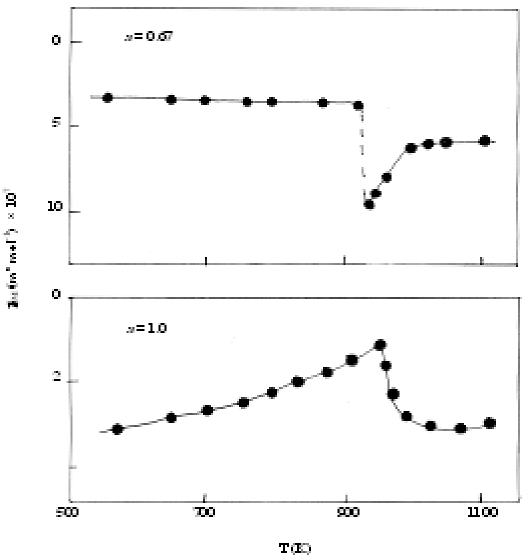

Fig. 2: Plots of molar magnetic susceptibility x_M against absolute temperature (T) of the system (1-x) Li_3PO_4 : x Li_3 VO_4

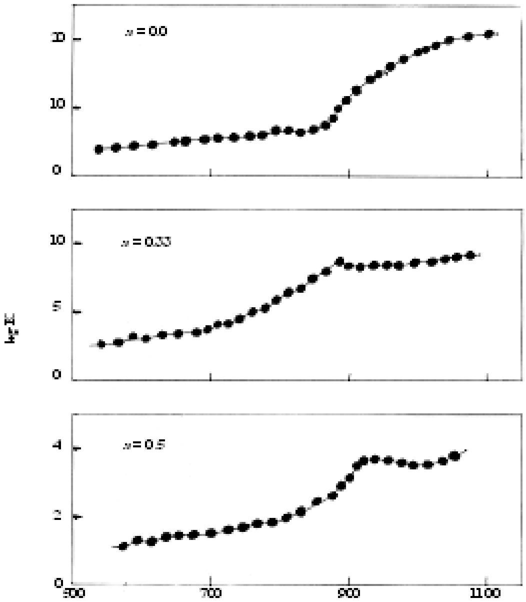

Fig. 3: Plots of logarithm of dielectric constant (log K) against absolute temperature (T) of the system (1-x) Li_3PO_4 : x Li_3 VO_4

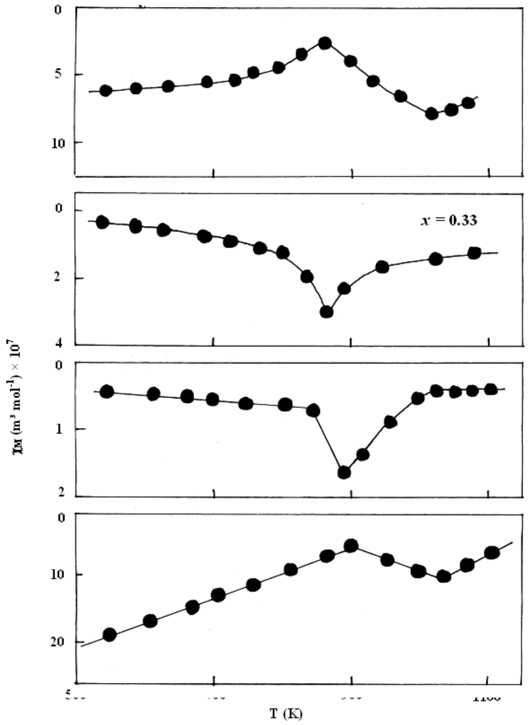

Fig. 5: Plots of molar magnetic susceptibiilty x_M against absolute temperature (T) of the system (1-x) Li_3PO_4 : x Li_3 VO_4

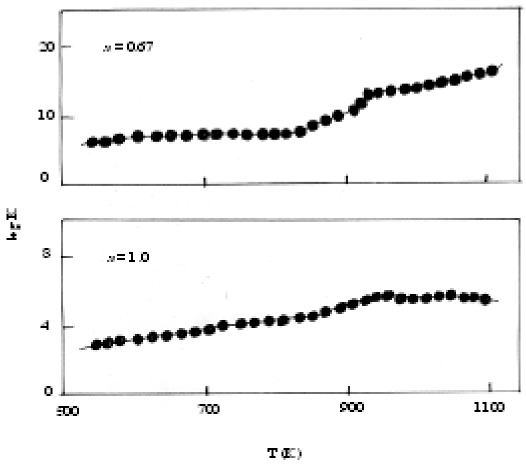

Fig. 4: Plots of logarithm of dielectric constant (log K) against absolute temperature (T) of the system (1-x) Li_3PO_4 : x Li_3 VO_4

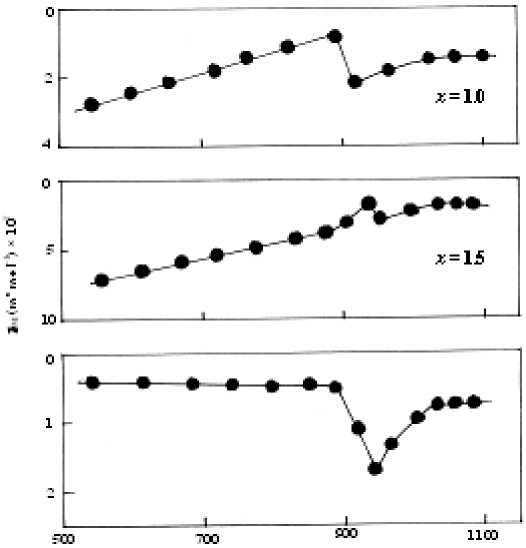

Fig. 6: Plots of molar magnetic susceptibiilty x_M against absolute temperature (T) of the system (1-x) Li_3PO_4 : x Li_3 VO_4

Both the molar magnetic susceptibility (x_M) and dielectric constant (K) studies are performed on two to three samples prepared in different lots from 500 K to 1100 K of the system (1-x) Li_3PO_4 : x Li_3VO_4. The x_M variations with temperature (T) for this system are shown in Figs.1 and 2. It is seen from these plots that x_M negative throughout the study for all the studied materials of the system indicating that the solids are diamagnetic. Initially x_M remains constant with temperature and shows a drop at a particular temperature and then starts increasing for the solids with *x* = 0.0, 0.50 and 0.67. The materials for which *x* = 0.33 and 1.0, x_M vary slowly with temperature, shows a peak and then becomes almost independent of temperature. The log K variations with temperature are shown in Figs. 3 and 4. The value of dielectric constant (K) is small but different for different solids. It increases slowly, shows a peak at a particular temperature and then becomes almost independent of temperature for all the solids but for the solid with *x* = 0.0, dielectric constant increases very slowly but after showing a kink at a particular temperature it rises steeply. The anomalies in x_M and log K against temperature plots are distinctly observed. Break temperatures x_M of and log K against T plots are almost the same as have been observed in log σT and S *vs* T^{-1} plots (Table 1).

The variation of molar magnetic susceptibility and dielectric constant of the system Li_3PO_4 : *x* Li_3VO_4 are shown in Figs. 5 and 6 as X_M vs T and in Figs. 7 and 8 as log K vs T plots. It is seen from x_M plots that the value of molar magnetic susceptibility is negative thought out the study showing that materials are diamagnetic in nature.

Further, it increases with temperature, shows a peak and then again increases slowly for the materials with x = 0.0, 0.67, 1.0 and 1.5 whereas the materials for which x = 0.33, 0.50 and 2.0, x_M decreases with temperature, shows a downward

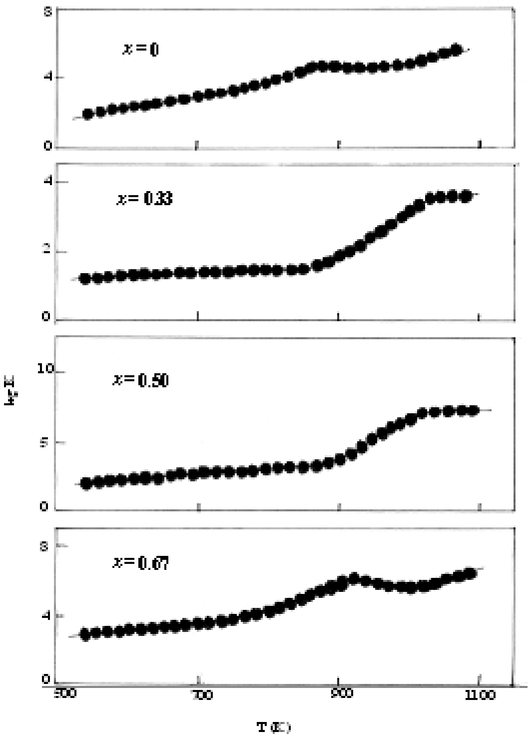

Fig. 7: Plots of logarithm of dielectric constant (log K) against absolute temperature (T) of the system (1-x) Li_3PO_4 : x Li_3 VO_4

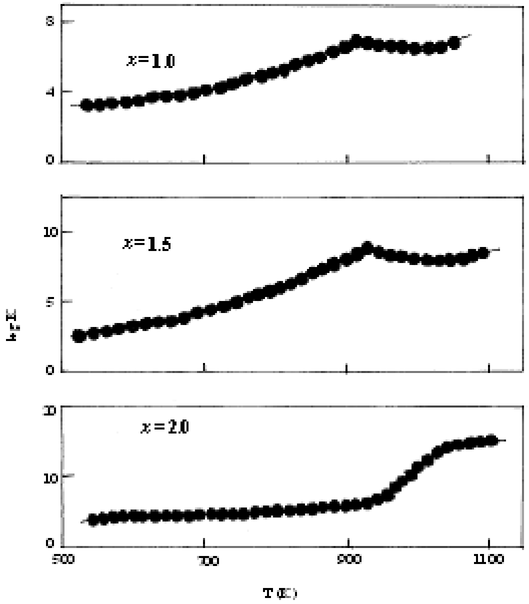

Fig. 8: Plots of logarithm of dielectric constant (log K) against absolute temperature (T) of the system (1-x) Li_3PO_4 : x Li_3 VO_4

drop and then becomes almost independent of temperature. It is seen from Figs. 7 and 8 that dielectric constant increases slowly, shows a small peak and then increases very slowly again with temperature for the materials with x = 0.0, 0.67, 1.0 and 1.5. The log K vs T plot for x = 0.33, 0.50 and 2.0, initially vary very slowly with temperature, shows a knee, then increases and becomes constant. The temperatures at which anomalies are observed in and log K vs T plots are shown in Table 2 together with the break temperatures observed in log sT and S vs T^{-1} plots.

The materials of the studied superionic systems (1 - x) Li_3PO_4 : x Li_3VO_4 with x = 0.00, 0.33, 0.050, 0.67 and 1.0, Li_3PO_4 : x Li_3VO_4 with x = 0.0, 0.33, 0.50, 0.67, 1.0, 1.5 and 2.0 and Li_2O : V_2O_5 : P_2O_5 are ionic compounds and contain no magnetic ions. Thus they are diamagnetic as has been confirmed by the negative value of χ_M. Their diamagnetism depends upon their bonding configuration. The onset of disordering at phase transition disrupts the bonding configuration and leads to an abrupt change in X_M Thus the temperature around which anomaly appears, is the phase transition temperature and is also confirmed by dielectric constant, electrical conductivity and Seebeck coefficient plots.

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