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) Li₃PO₄ : x Li₃VO₄ with x = 0.0, 0.33, 0.50, 0.67 and 1.0 and Li₃PO₄ : x Li₃VO₄ with x = 0.0, 0.33, 0.50, 0.67, 1.0, 1.5 and 2.0. The molar magnetic susceptibility \(\chi_m\) and dielectric constant (K) measurements have been performed for the study of phase transition. At phase transition materials undergo from normal to superionic phase. An anomaly appears in \(\chi_m\) and log K vs temperature (T) plots at phase transition. This is also reflected in electrical conductivity (\(\sigma\)) 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\(^{6-12}\). 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) Li₃PO₄ : xLi₃VO₄ and Li₃PO₄ : xLi₃VO₄ 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 Li₃PO₄ and Li₃VO₄ were prepared by mixing Li₂O + P₂O₅ and Li₂O + V₂O₅ respectively in stoichiometric amount. Li₂O (99.99% pure) and P₂O₅ and V₂O₅ (purity 99.99%) were procured from Rare and Research Chemicals, Bombay and Chempure, Calcutta, respectively. The starting materials were taken in required amount, fired at 1100K in air in a silica crucible for 48 h with 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 \(\chi_m\) 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 $\sigma$, $x_M$ and $K$ plots

<table>
<thead>
<tr>
<th>Material with $x$</th>
<th>$T_p$ (K) from the study</th>
<th>$x_M$</th>
<th>$K$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>865</td>
<td>860</td>
<td>865</td>
</tr>
<tr>
<td>0.33</td>
<td>885</td>
<td>880</td>
<td></td>
</tr>
<tr>
<td>0.50</td>
<td>917</td>
<td>920</td>
<td>920</td>
</tr>
<tr>
<td>0.67</td>
<td>930</td>
<td>930</td>
<td>925</td>
</tr>
<tr>
<td>1.0</td>
<td>950</td>
<td>950</td>
<td>950</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Material with $x$</th>
<th>$T_p$ (K) from the study</th>
<th>$x_M$</th>
<th>$K$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>865</td>
<td>860</td>
<td>860</td>
</tr>
<tr>
<td>0.33</td>
<td>870</td>
<td>865</td>
<td>870</td>
</tr>
<tr>
<td>0.50</td>
<td>885</td>
<td>880</td>
<td>890</td>
</tr>
<tr>
<td>0.67</td>
<td>910</td>
<td>900</td>
<td>910</td>
</tr>
<tr>
<td>1.0</td>
<td>917</td>
<td>915</td>
<td>920</td>
</tr>
<tr>
<td>1.5</td>
<td>935</td>
<td>930</td>
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</tr>
<tr>
<td>2.0</td>
<td>945</td>
<td>940</td>
<td>940</td>
</tr>
</tbody>
</table>

Fig. 1: Plots of molar magnetic susceptibility $x_M$ against absolute temperature ($T$) of the system (1-x) $Li_3PO_4 : x Li_3VO_4$

Fig. 2: Plots of molar magnetic susceptibility $x_M$ against absolute temperature ($T$) of the system (1-x) $Li_3PO_4 : x Li_3VO_4$
Fig. 3: Plots of logarithm of dielectric constant (log $K$) against absolute temperature ($T$) of the system $(1-x) \text{Li}_3\text{PO}_4 : x \text{Li}_3\text{VO}_4$

Fig. 4: Plots of logarithm of dielectric constant (log $K$) against absolute temperature ($T$) of the system $(1-x) \text{Li}_3\text{PO}_4 : x \text{Li}_3\text{VO}_4$

Fig. 5: Plots of molar magnetic susceptibility $\chi_m$ against absolute temperature ($T$) of the system $(1-x) \text{Li}_3\text{PO}_4 : x \text{Li}_3\text{VO}_4$

Fig. 6: Plots of molar magnetic susceptibility $\chi_m$ against absolute temperature ($T$) of the system $(1-x) \text{Li}_3\text{PO}_4 : x \text{Li}_3\text{VO}_4$
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$_3$PO$_4$ : x Li$_3$VO$_4$. The $x_M$ variations with temperature ($T$) for this system are shown in Figs. 1 and 2. It is seen from these plots that $x_M$ is 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 $\sigma$T and $S$ vs $T^{-1}$ plots (Table 1).

The variation of molar magnetic susceptibility and dielectric constant of the system Li$_3$PO$_4$ : x Li$_3$VO$_4$ 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 throughout 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$_3$PO$_4$ : 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$_3$PO$_4$ : 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 \((1 - x) \text{Li}_3\text{PO}_4 : x \text{Li}_3\text{VO}_4 \) with \( x = 0.00, 0.33, 0.50 \), \( 0.67, 1.0, \) and 2.0. and \( \text{Li}_3\text{PO}_4 : x \text{Li}_2\text{O} : \text{V}_2\text{O}_5 : \text{P}_2\text{O}_5 \) are ionic compounds and contain no magnetic ions. Thus they are diamagnetic as has been confirmed by the negative value of \( \chi_M \). 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 \( \chi_M \) 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.

**REFERENCES**

24. Muzushima K, Jones P.C. and Goodenough