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Thermodynamic, Kinetic, and Conductivity Studies of an Order–Disorder Transition in $Li_4Zn(PO_4)_2$

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Calorimetric measurements by differential scanning calorimetry gave a value of 2.6 kJ/mole for the enthalpy of the order–disorder transition observed in $Li_4Zn(PO_4)_2$ at 445°C. Conductivity measurements gave activation energies of 109 and 203 kJ/mole, above and below the transition temperature, respectively. The difference, 94 kJ/mole, is attributed to the activation enthalpy for the disordering transition. $Li_4Zn(PO_4)_2$ has a low Li^+ ion conductivity, 10^{-5} ohm^{-1} cm^{-1} at 400°C.

Introduction

Crystalline $Li_4Zn(PO_4)_2$ exhibits a phase transition at 445°C that appears to be associated with disordering of Li^+ and Zn^{2+} ions (*1*). This transition is seen by both differential scanning calorimetry (DSC) and ionic conductivity measurements and use of these combined techniques provides a novel means of studying both thermodynamic and kinetic aspects of the order–disorder transition.

$Li_4Zn(PO_4)_2$ is a congruently melting phase that exists in three crystalline modifications, with transition temperatures:

$$\alpha \overset{445}{\rightleftharpoons} \beta \overset{1084}{\rightleftharpoons} \gamma \overset{1360}{\rightleftharpoons} \text{melt}$$

The high temperature γ form cannot be quenched to ambient and nothing is known about its structure. The intermediate temperature β form cannot be preserved in pure form by quenching, since X-ray powder diffraction of quenched material shows small domains of the low temperature α form to be present. The β form can, however, be quenched to ambient in solid solution material in which phosphate has been partially replaced by silicate.

The β form is structurally related to γ-Li_3PO_4, with a similar-sized, orthorhombic unit cell, but a full structure determination is required to show whether they are, in fact, isostructural. The structure probably contains tetrahedrally coordinated cations in an oxide array that may be described as either distorted hexagonal close packed or as distorted tetragonal packed. The specific tetrahedral sites occupied by Li and Zn are not known. The low temperature α form has an orthorhombic unit cell derived from that of the β form by doubling the *a* and *b* axes. It is very likely that the $\beta \rightarrow \alpha$ transition takes place by ordering of Li^+ and/or Zn^{2+} ions.

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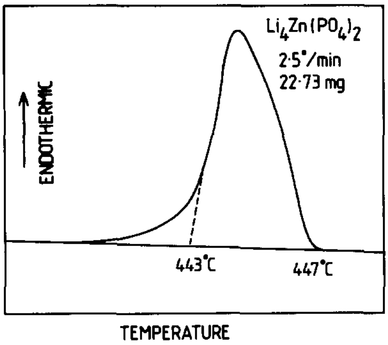

FIG. 1. DSC trace for $Li_4Zn(PO_4)_2$ showing the $\alpha \rightarrow \beta$ transition at 445°C.

Experimental

A sample of $Li_4Zn(PO_4)_2$ was prepared as described previously (*1*) and confirmed to be phase pure by X-ray powder diffraction (Philips Hägg focusing camera, Cu$K\alpha_1$ radiation).

For conductivity measurements, a pellet was cold-pressed and sintered at 1300°C; residual porosity was estimated as 8%. Gold electrodes were formed from organogold paste (Engelhard) which was decomposed and hardened by gradually raising the temperature to 800°C over a period of 3 hr. The pellet was loaded into a conductivity cell and placed inside a tube furnace whose temperature was controlled and measured to within 3°C. Conductivities were measured with a Wayne-Kerr B224 AF bridge over the frequency range 200 Hz to 70 kHz, using a Brookdeal 9473 signal source and Philips PM3232 oscilloscope detector and confirmed subsequently with a Solartron 1250 frequency response analyzer operating over the frequency range 1 Hz to 65 kHz. Conductivities were measured isothermally at temperatures in the range 360 to 850°C; prior to each set of measurements, the furnace and jig were allowed to equilibrate at the set temperature for 2 hr.

DSC measurements used a Perkin-Elmer 2C instrument that had been calibrated previously using In, Pb, and Zn as standards; the heating rate was 2.5°C/min.

Results and Discussion

$Li_4Zn(PO_4)_2$ undergoes an endothermic phase transition on heating at 445°C, as shown previously by differential thermal analysis (DTA) (*1*). DSC measurements were used to determine the enthalpy of this transition; the results are given in Fig. 1 and Table I. The transition enthalpy was evaluated by comparison with three standards and an average value of 8.8 ± 1.1 cal/g obtained. In order to convert this enthalpy to a molar scale, it is necessary to specify the amount of material to which one mole refers.

As a first step, this is assumed to be one mole of Li^+ ions. A value of 2.6 kJ/mole is then obtained.

Conductivity measurements were made on sintered pellets and the ac data analyzed by conventional complex admittance and complex impedance techniques, as used for work on related materials (*2*). These measurements, with blocking gold electrodes, showed the material to be an ionic conductor, with Li^+ ions almost certainly as the principal charge carrier. A typical impedance plot is shown in Fig. 2; an inclined spike is seen with an associated capacitance of 20 μF, calculated using the formula, $Z'' = 1/(2\pi fc)$, where f is the measur-

TABLE I

DSC RESULTS FOR $Li_4Zn(PO_4)_2$

Sample	Weight (mg)	Peak area	ΔH (cal/g)
In	4.48	0.0407	6.80[a]
Pb	10.00	0.0706	5.50[a]
Zn	5.60	0.1800	25.90[a]
$Li_4Zn(PO_4)_2$	22.73	0.2557	8.8 ± 1.1[b]

[a] Standard values provided by Perkin-Elmer.

[b] Average of values obtained using each standard.

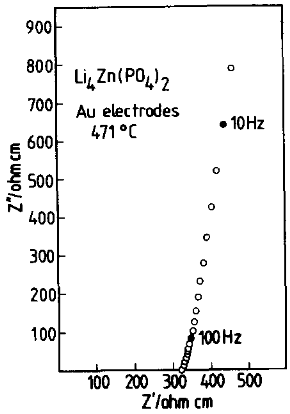

FIG. 2. Complex impedance plane plot showing a steeply inclined spike, attributable to a blocking, double layer capacitance.

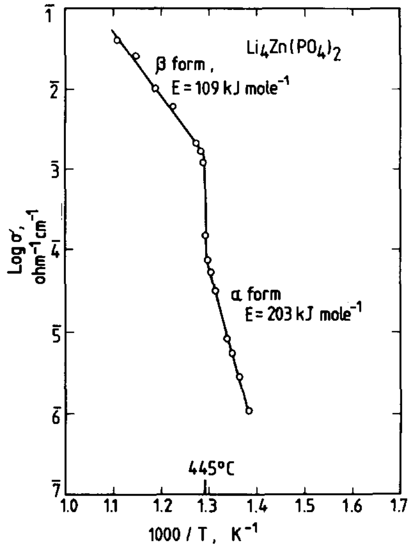

FIG. 3. Conductivity Arrhenius plot.

ing frequency. Such a capacitance value is typical of a double layer capacitance associated with ionic transport and polarization at a blocking electrode/electrolyte interface.

The value of the pellet resistivity is given by the intercept of the spike on the real Z' axis (Fig. 2; viz. 325 ohm cm). From plots such as Fig. 2, the pellet conductivity was determined as a function of temperature and plotted in conventional Arrhenius format (Fig. 3). Two linear regions are seen, separated by a discontinuity at 445°C. Arrhenius parameters for the two regions were obtained by least-squares fitting and are given in Table II.

The $\alpha \rightarrow \beta$ transition, observed at 445°C by both DSC and conductivity measurements, is an order–disorder transition which probably involves both the Li^+ and the Zn^{2+} ions. The DSC measurements yield thermodynamic data on the difference in enthalpy of the ordered and disordered structures. The value given in Table I refers to one mole of Li^+ ions but values could equally well be given, for instance, for one mole of the formula unit $Li_4Zn(PO_4)_2$.

The conductivity measurements yield data on the activation enthalpy for Li^+ ion conduction; in this case, the units (Table II) are also on a molar basis. Since Li^+ ions are the current carrier in both the high and low temperature regions of Fig. 3, and the phase transition is order–disorder in nature, we propose the following interpretation of the data. In the high temperature region, the crystal structure is disordered and the activation enthalpy of conduction is for the migration only of Li^+ ions; the enthalpy of activation for the creation of disordered or mobile Li^+ ions is zero.

In the low temperature region, however, the crystal structure is ordered. The thermodynamic enthalpy of disordering is given by the DSC results, but the kinetic enthalpy

TABLE II

CONDUCTIVITY ARRHENIUS PARAMETERS FOR $Li_4Zn(PO_4)_2$

Temp. range	E (kJ/mole)	log A
453–626°C	109 ± 2	7.9
364–440°C	203 ± 3	13.5

Note. Arrhenius equation $\sigma = A \exp(-E/RT)$.

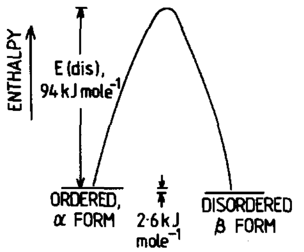

FIG. 4. Schematic enthalpy profile for the $\alpha \rightarrow \beta$ transition.

of disordering, i.e., the activation enthalpy for the disordering process, forms one component of the conductivity activation enthalpy; the other component is the activation enthalpy for migration. Assuming that the activation enthalpy for migration of Li^+ ions is the same in both high and low temperature regions, then the activation enthalpy of the disordering transition is given by the difference in the two conductivity activation enthalpies (viz., 94 kJ/mole).

The key problem, to which we are unable to provide a definitive answer, is how to make a quantitative comparison between the two enthalpy values for the order–disorder transition, the thermodynamic value obtained by DSC and the kinetic value obtained from the conductivity. We suggest that, by quoting the DSC value in terms of one mole of Li^+ ions, the two enthalpies may be compared directly, as shown in a schematic enthalpy profile in Fig. 4. In this case, the difference in enthalpy between ordered and disordered structures is much less than the enthalpy of activation for the disordering transition.

$Li_4Zn(PO_4)_2$ is only a poor conductor of Li^+ ions. For instance, the conductivity at 400°C (ca. 10^{-5} ohm^{-1} cm^{-1}) is several orders of magnitude less than would be required for the material to have applications as a practical solid electrolyte. This low conductivity is consistent with and caused by the high activation enthalpies for conduction (Fig. 3).

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