ON THE IRREVERSIBLE PHASE TRANSITION IN LITHIUM PHOSPHATE; THERMAL ANALYSIS, X-RAY DIFFRACTION AND IONIC CONDUCTIVITY MEASUREMENTS

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In the search for new solid electrolytes with high Li^+ ion conductivity, the solid solubility of lithium carbonate and lithium tungstate in the high conducting phase of lithium sulfate has been reported by Dissanayake and Mellander (1) and Gunawardene et al. (2). A similar limited solid solubility of lithium phosphate in lithium sulfate has also been suggested by Kimura and Greenblatt (3) though there appear to be no reported phase diagram of the system lithium sulfate-lithium phosphate. This has encouraged us to study phase transitions and electrical conductivity of lithium phosphate over the temperature range, 150 - 650°C.

The solid-solid phase transition of lithium phosphate from phase V to phase IV was studied using DSC and X-ray measurements. The electrical conductivity measurements in these two phases were done with pellet samples. The V to IV phase transition shows characteristics of both continuous and martensitic transformations and is not reversible under normal conditions (4). Hence the phase IV is often present at ambient temperature. These phases may be described by orthorombic unit cells where phase IV can be derived from phase V by doubling the b parameter (5-8).

In the present DSC experiments this transition was detected as a distinct peak at 501°C on heating while no peak appeared on cooling or reheating. The enthalpy change at the phase transition was 1.8 KJ/mol. The earlier reports that this transition occurred over a wide temperature range, 340 to 410°C (4) and 440 to 520°C (7) was thus not confirmed. The irreversible nature of this transition was confirmed by X-ray measurements. The X-ray powder diffraction patterns obtained agreed well with the literature values (3). In the electrical conductivity measurements, the phase transition was detected at 500°C on heating. The conductivity values found were $6.56\times10^{-}$ S/cm at 400°C (phase V) and 6.81×10^{-5} S/cm at 600°C (phase IV). The activation energy was 1.3 ev for both phases. For phase V this value is in good agreement with the earlier reported values (3). For phase IV no activation energy value was found in the literature.

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