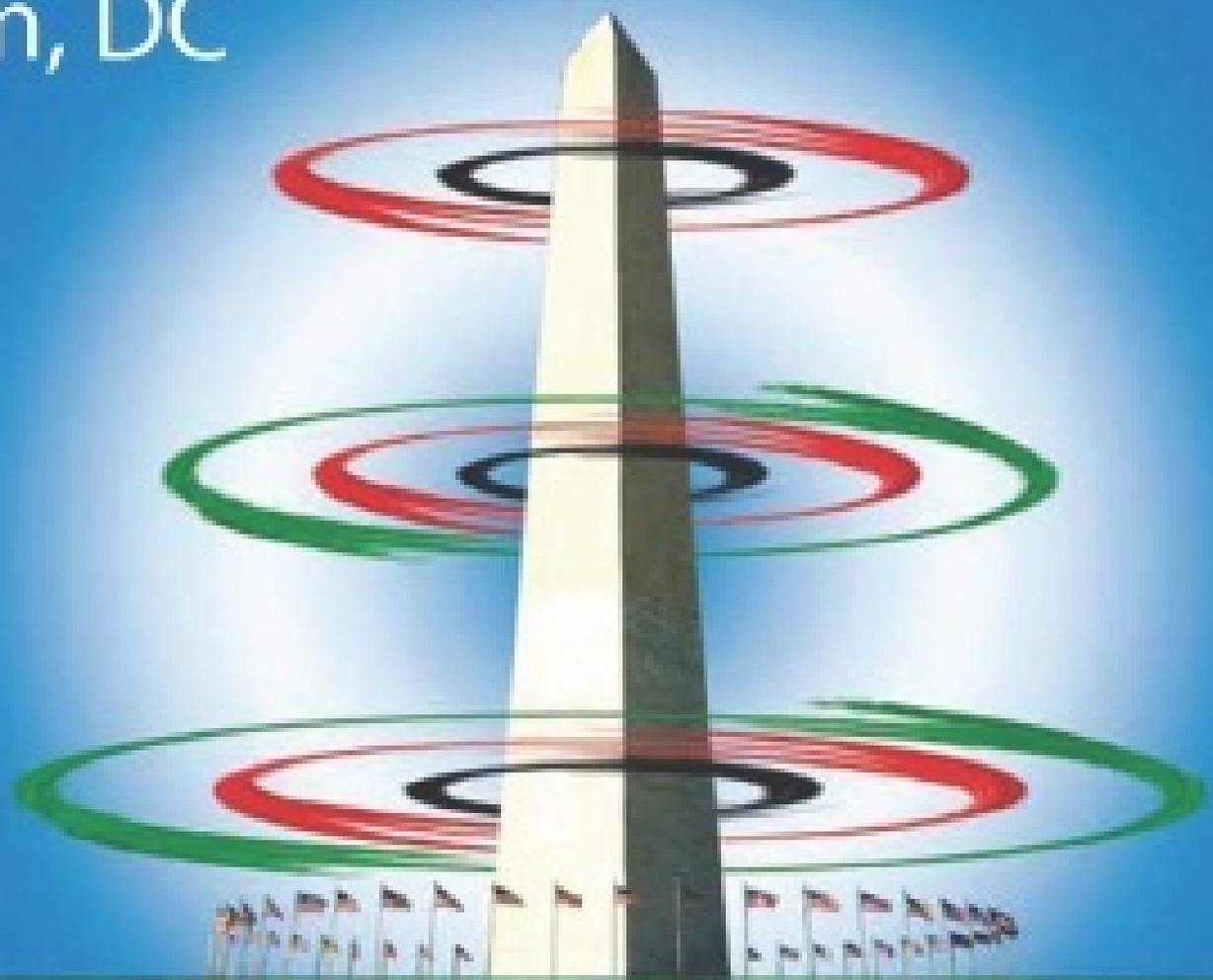
11TH JOINT MMM–INTERMAG CONFERENCE

January 18–22, 2010
Washington, DC

DIGESTS



BV-07

Temperature dependent valence state and magnetic property of lithium delithiated $Li_{0.59}FePO_4$

I. Lee, I. Shim, C. Kim
Department of Physics, Kookmin University, Seoul, Korea, South

Introduction

Rechargeable lithium ion battery is the most promising energy storage device for plug-in hybrid electric vehicles (PHEV). The lithium iron phosphate is a member of the phospho-olivine Li*M*PO_4 (*M* = Fe, Mn Co, Ni) family which is attractive candidate as positive electrode materials for lithium ion batteries. Among the phospho-olivine family, lithium iron phosphate has fascinating properties such as high capacity, high voltage, environmental friendly, and good thermal and chemical stability. Recently, numerous researches have been focused on the delithiated lithium iron phosphate for trying to understand the mechanism of charge/discharge process [1, 2].

In this paper, we have studied temperature dependent valence state and magnetic property of lithium delithiated $Li_{0.59}FePO_4$ by x-ray diffraction, inductively coupled plasma-atomic emission spectrometer (ICP-AES), superconducting quantum interference device (SQUID) and Mössbauer spectroscopy.

Experiments

Polycrystalline samples of $LiFePO_4$ were prepared by solid-state reaction method. Starting materials were Li_2CO_3 (99.997%), $FeC_2O_4.H_2O$ (99.99%) and $NH_4H_2PO_4$ (99.999%). These were mixed and grinded in an agate mortar. Afterwards, the mixtures were calcined at 400 °C for 3 h. These mixtures were crystallized at 700 °C for 10 h in evacuated quartz tube.

Lithium diffused $Li_{0.59}FePO_4$ was obtained by chemical delithiation process using NO_2BF_4 in acetonitrile solution. After the NO_2BF_4 was dissolved in acetonitrile, powders of $LiFePO_4$ were added, then, the mixtures were stirred at room temperature for 10 h in air. The obtained sample was centrifuged and washed with acetonitrile several times. They were dried at 60 °C in vacuum. The depth of delithiation was controlled by the ratio of $LiFePO_4$: NO_2BF_4 in acetonitrile.

Results and discussion

The x-ray diffraction patterns of $Li_{0.59}FePO_4$ sample shows a two-phase system at room temperature. The sample has the $LiFePO_4$ with lattice constant a_0 = 10.329 Å, b_0 = 6.006 Å, c_0 = 4.698 Å and $FePO_4$ with a_0 = 9.814 Å, b_0 = 5.787 Å, c_0 = 4.783, respectively.

In this study, we wanted to understand the temperature dependence of valence state and magnetic property of $Li_{0.59}FePO_4$. Fig. 1 shows the Mössbauer spectra of $Li_{0.59}FePO_4$ at various temperatures from 4.2 to 114 K. The Mössbauer spectra below 51 K exhibit a 2-set ($LiFePO_4$ / $FePO_4$) of eight Lorentzians by diagonalizing the 4×4 magnetic and quadrupole Hamiltonian matrix to get relative line positions and intensities [3, 4]. Between the 51 and 114 K, spectrum fitted which combines 1-doublet ($LiFePO_4$) and 8-line patterns ($FePO_4$). The zero-field cooled (ZFC) and field cooled (FC) magnetic susceptibility curves of $Li_{0.59}FePO_4$ were taken with a 100 Oe applied field as shown in Fig. 2. With increasing temperature, the magnetic susceptibility increases up to 51 K, and then it shows a decrease, with an abnormal transition point at 114 K. The increase of Néel temperature of heterosite means that the Fe^{3+}-O-Fe^{3+} super-exchange interaction is stronger than Fe^{2+}-O-Fe^{2+} super-exchange interaction which is closely related with the environment of the iron ions. The triphylite with the larger splitting and isomer shift value than that of the heterosite with much smaller splitting and isomer shift. From the results, lithium delithiated lithium iron phosphates are systems where the triphylite $LiFe^{2+}[PO_4]$ and heterosite $Fe^{3+}[PO_4]$ phases are co-existed together which had different valence state of iron ions, and the large value of ΔE_Q for triphylite phase attributed to the distorted FeO_6 octahedra oxygen environment around Fe ions.

[1] C. Delmas, M. Maccario, L. Croguennec, F. L. Cras, and F. Weill, *Nature mater*. **7**, 665 (2008).
[2] S-. I. Nishimura, G. Kobayashi, K. Ohoyama, R. Kanno, M. Yashima, and A. Yamada, *Nature mater*. **7**, 707 (2008).
[3] S. J. Moon, and C. S. Kim, *J. Korean Phys. Soc*. **53**, 1589 (2008).
[4] H. N. Ok and J. G. Mulien, *Phys. Rev*. **168**, 563 (1968).

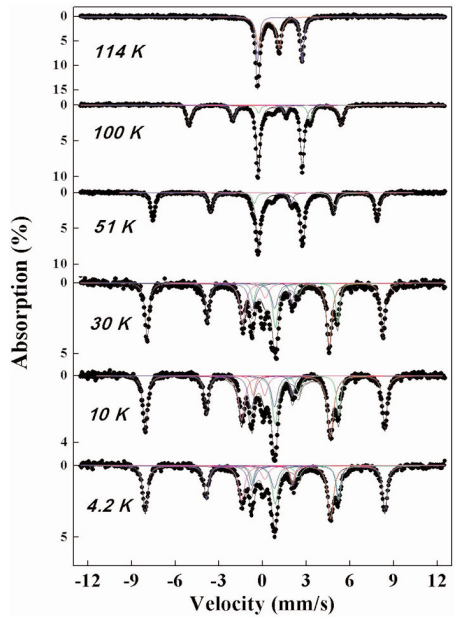


Fig.1 Mössbauer spectra of the $Li_{0.59}FePO_4$ at various temperatures from 4.2 to 114 K.

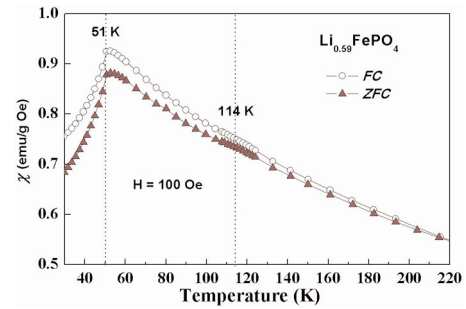


Fig.2 Temperature dependence of magnetic susceptibility χ(T) curves for $Li_{0.59}FePO_4$.