

## Magnetic Study on Olivine Compounds

Yoshiki Miwa, Tatsuya Nakamura,

Yoshihiro Yamada, Mitsuharu Tabuchi\* and Hiroyuki Kageyama\*

Department of Electrical Engineering and Computer Sciences, Graduate School of Engineering, Himeji Institute of Technology,  
2167 Shosha, Himeji, Hyogo 671-2201, Japan

Fax: 81-0792-66-8868, e-mail: tm03e036@elct.eng.himeji-tech.ac.jp

\*National Institute of Advanced Industrial Science and Technology, Kansai, 1-8-31 Midorigaoka, Ikeda, Osaka 563-8577, Japan

Fax: 81-727-51-9714, e-mail: m-tabuchi@aist.go.jp

### ABSTRACT

The olivine-type compounds  $\text{LiMn}_x\text{Fe}_{1-x}\text{PO}_4$  ( $x \leq 0.5$ ), where a part of  $\text{Fe}^{2+}$  were substituted by  $\text{Mn}^{2+}$ , was prepared, and both their crystal structure and magnetic properties were studied. In addition, the chemically delithiated  $\text{Li}_{1-y}\text{FePO}_4$  was also investigated. With the increase in the  $\text{Mn}^{2+}$ -substitution degree, the lattice parameters linearly increased and the Neel temperature slightly shifted lower. On the other hand, the delithiation brought about higher Neel temperature. In these compounds, the  $\text{MO}_6$  octahedra are connected with the oxygen in the corner-sharing style and the magnetic properties are attributed to the super-exchange interaction through oxygen anion. From the structural analysis, it was found that the M-O bonding distance and the M-O-M bonding angle played an important role in the cases of the  $\text{Mn}^{2+}$ -substitution and the delithiation, respectively.

Key words: Olivine, delithiation, bonding distance, bonding angle, super-exchange interaction

### 1. INTRODUCTION

$\text{LiFePO}_4$  olivine-type compound has been extensively studied as an attractive cathode material for lithium ion rechargeable batteries. It has the following distinctive advantages: inexpensive, environmentally benign, and a large theoretical specific capacity of 170 mAh/g with a flat charge/discharge profile at 3.4V versus Li metal and good cycle performance [1-6].

However, this olivine compound has only poor electronic conductivity. Although it has high reversible capacity at low current rate, the electrochemical redox at high current rate causes larger polarization effect and it results in poor electrochemical performance. The rate limitation makes it difficult to achieve full utilization of this material. Recently, to overcome this issue, researchers have optimized the synthesis techniques to decrease the particle size and/or have incorporated the conducting additives[7-9]. These approaches have led to some improvement of the cathode performance. For further improvement of this material utilization, the understanding of the electronic state in the olivine compounds is required. In this study, we have studied the magnetic properties of the olivine compounds, since the magnetic study may give us useful information about the electronic state.

### 2. EXPERIMENTAL PROCEDURES

#### 2.1. Sample preparation

First,  $\text{LiFePO}_4$  olivine compound was prepared by the solid-state reaction. The stoichiometric amounts of starting powders,  $\text{LiH}_2\text{PO}_4$  and  $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ , were mixed together by dry milling. The mixed powders were heated in purified  $\text{N}_2$  gas for 10h at temperatures ranging

from 500 to 800°C, followed by furnace cooling. The crystalline structure was identified by powder X-ray diffraction.

Second, the optimum preparation temperature was selected from the above experiment, and the solid solutions of  $\text{LiMn}_x\text{Fe}_{1-x}\text{PO}_4$  ( $x < 0.5$ ) were prepared. With the similar manner as the previous one, the stoichiometric amounts of  $\text{LiH}_2\text{PO}_4$ ,  $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  and  $\text{MnCO}_3$  were mixed together by dry milling, and the mixed powders were heated in purified  $\text{N}_2$  gas for 10h at the optimum temperature. The refinement of their crystal structure was carried out using the Rietveld analysis (RIETAN-2000), and the lattice parameters and the atomic positions were numerically determined. Then, the magnetic susceptibility was measured using the magnetic balance at temperature from 4.2 to 300K.

#### 2.2. Chemical delithiation

The electrochemical charging in the Li-ion battery application means the delithiation from the cathode material. Therefore, in order to investigate the compound in the charged state, the chemical delithiation using bromine was carried out instead of the electrochemical method. In the electrochemical experiment, it is difficult to pick up only cathode material after the electrochemical delithiation, since carbon and/or acetylene black for securing electronic conductivity to the cathode electrode are mixed with the active material to form electrode.

$\text{LiFePO}_4$  powder (3g) was dispersed in acetonitrile solution (150ml), bromine (30ml) was added to it, and then the suspension was mechanically agitated. Since bromine has a strong volatility and very weakness under the light irradiation, a series of this work was done using

a flask covered with aluminum foil in a draft. After agitating for 2 to 3h, the solid quantity was filtered and dried.

### 3. RESULTS AND DISCUSSION

#### 3.1. Structural results

All products were investigated by powder X-ray diffraction. The specimen prepared at temperature below 700°C consisted of mainly olivine compound with some impurity phases. But, the calcination above 750°C produced a single phase of olivine compound. Fig. 1 shows the X-ray diffraction patterns for the olivine compound  $\text{LiFePO}_4$ , prepared at 750°C, and the refinement of the crystal structure was carried out by Rietveld analysis [10]. From the results, it was found that it had an orthorhombic symmetry with the lattice parameters of  $a=10.3298(2)$  Å,  $b=6.0079(1)$  Å and  $c=4.6921(1)$  Å. These parameters were in good agreement with the values in the previous study [11].

The olivine compounds,  $\text{LiMn}_x\text{Fe}_{1-x}\text{PO}_4$  in which a part of  $\text{Fe}^{2+}$  were substituted by  $\text{Mn}^{2+}$ , were also prepared at the optimum temperature 750°C. The single phase of olivine compounds were obtained in the compositional range of  $X < 0.5$ . The variation of the lattice parameters with the  $\text{Mn}^{2+}$ -substitution degree is shown in Fig. 2. From the figure, the lattice parameters increased almost linearly with the amount of  $\text{Mn}^{2+}$ -substitution. It was likely that the lattice parameter variation was attributed to the ionic radius difference between  $\text{Mn}^{2+}$  and  $\text{Fe}^{2+}$  ions.

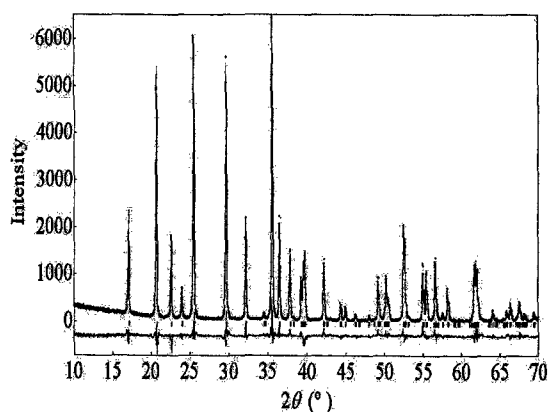


Fig. 1. Rietveld refinement on the powder X-ray diffraction data for  $\text{LiFePO}_4$  sample prepared at 750°C :  $R_{wp}=11.40\%$ ,  $R_p=8.37\%$ ,  $R_R=11.82\%$ ,  $R_e=7.44\%$

It is known that the olivine structure comprises distorted  $\text{FeO}_6$  octahedra and  $\text{PO}_4$  tetrahedra. The corner-sharing of  $\text{MO}_6$  octahedra forms one-dimensional zigzag chains, which is extended in the direction of  $c$  axis (Fig. 3). The zigzag chains are inter-connected in three-dimensional manner through the corner-sharing with  $\text{PO}_4$  tetrahedra. As a result, the networking of  $\text{FeO}_6$  octahedra and  $\text{PO}_4$  tetrahedra produces a two-dimensional pathway for  $\text{Li}^+$  ionic diffusion. In this olivine structure, it is thought that the corner-sharing  $\text{MO}_6$  octahedral chain plays a important role in the electronic conduction. Therefore, the  $\text{MO}_6$  octahedral coordination geometry was examined using the Rietveld

refinement results. Table I shows the variation of the  $\text{MO}_6$  coordination geometry with by the  $\text{Mn}^{2+}$  substitution. Both the longest and the shortest M-O bonding lengths were listed and the ratio of their difference to the average bonding length, which was defined as the distortion ratio, was also included. From the values, it was clear that the  $\text{MO}_6$  octahedra were not regular but strongly distorted, but the distortion degree was almost independent of the  $\text{Mn}^{2+}$ -substitution (the value was 9~10%). It was found that the average value of the M-O bonding length was gradually elongated with the increase in the substitution degree. Moreover, the bonding angle between the transition metal ions through oxygen anion was also almost unchanged (the value was approximately 127°) and insensitive to the  $\text{Mn}^{2+}$ -substitution degree. They implied that the crystal lattice was expanded homogeneously by the ionic radius difference between  $\text{Mn}^{2+}$  and  $\text{Fe}^{2+}$  ions.

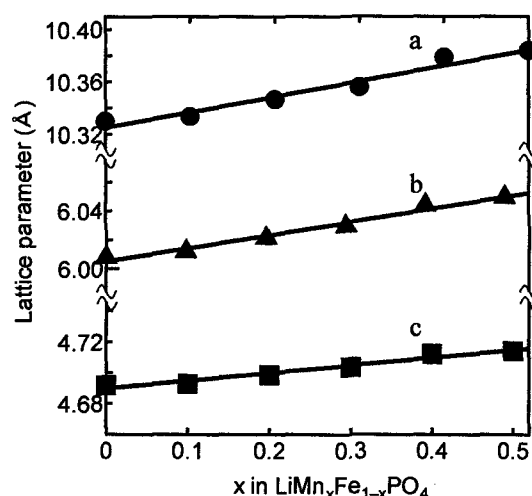


Fig. 2. Variation of lattice parameters with the Mn-substitution degree.

Next, we examined the structure of the chemically delithiated compound. From the Rietveld analysis on the chemically delithiated compound, the chemical delithiation led to the mixture of  $\text{FePO}_4$  and  $\text{LiFePO}_4$ , the fraction of which were estimated as 88% and 12%, respectively. It was thought that this result corresponded with the fact that the electrochemical reaction of the olivine compound proceeded with two-phase reaction : two phase coexistence of end members  $\text{LiFePO}_4$  and  $\text{FePO}_4$ . From the structural refinement of the delithiated phase  $\text{FePO}_4$ , it was found that the delithiated compound also had orthorhombic symmetry with the lattice parameters  $a=9.8143(3)$  Å,  $b=5.7884(2)$  Å and  $c=4.7821(2)$  Å. It figured out that the unit cell dimensions were reduced with keeping the original olivine framework. This was because the transition metal ion was oxidized from  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  and the ionic radius became smaller. Moreover, it was detected that the  $\text{MO}_6$  octahedral coordination geometry was greatly influenced. The coordination geometry was listed in Table 1. The configuration of  $\text{MO}_6$  octahedron was furthermore distorted by delithiation : the distortion ratio reached approximately 13%. In addition, it was seen that the average value of the M-O bonding length was extremely shortened. On the other hand, it was detected

that the bonding angle of M-O-M coupling was widened to  $132^\circ$  on the delithiation process. Therefore, the decrease in the ionic radius of transition metals and the shortening of the M-O bonding length led to the reduction in the cell dimensions along both a and b-directions. However, the lattice parameter c was elongated on the delithiation. The crystallographic c-direction is parallel to the one-dimensional zigzag chain of  $\text{MO}_6$  octahedra. Hence, the spread of the M-O-M bonding angle may bring about a slight elongation of the lattice in c-direction.

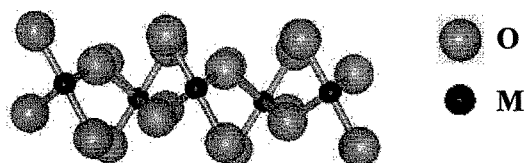


Fig. 3.  $\text{MO}_6$  octahedral coordination geometry projected on ac-plane.

### 3.2. Magnetic properties

For all products, the magnetic susceptibility was measured at temperature range from 4.2 to 300K. The results are shown in Fig. 4. From this figure, it was found that the olivine compounds  $\text{LiMn}_x\text{Fe}_{1-x}\text{PO}_4$  were anti-ferromagnetic materials. The Neel temperature was determined as the temperature where the magnetic susceptibility took a cusp. Further, the asymptotic Curie temperature was estimated by numerical fitting of high-temperature magnetic susceptibility to the Curie-Weiss law [10]. Their variations with the  $\text{Mn}^{2+}$ -substitution degree are plotted in Fig. 5.

From these figures, the following things were clarified. The magnetic susceptibility increased and the Neel temperature slightly shifted to lower temperature (from 53 to 47K) as the amount of substitution of  $\text{Mn}^{2+}$  was increased. In addition, the asymptotic Curie temperature had negative values, which indicated that the anti-ferromagnetic interaction was dominant in the olivine

compounds. The asymptotic Curie temperature shifted toward positive direction (from -90 to -68K) with an increase in the  $\text{Mn}^{2+}$ -substitution amount. Considering these modifications in the magnetic properties, it was clear that the anti-ferromagnetic coupling between transition metal ions were weakened by the substitution of  $\text{Fe}^{2+}$  with  $\text{Mn}^{2+}$ . As we already discussed in the previous section, the crystal lattice of the olivine compound was expanded in an isotropic manner by the  $\text{Mn}^{2+}$ -substitution and it resulted in the homogeneous elongation of the distorted  $\text{MO}_6$  octahedra. Taking account of the fact that the magnetic properties of the olivine compound was related to the super-exchange interaction between transition metal ions through oxygen anion, the variation of  $\text{MO}_6$  octahedral coordination geometry may explain the magnetic modifications. It is well known that both the M-O bonding length and the bonding angle of M-O-M coupling are participating in the super-exchange interaction [13]. In the case of the  $\text{Mn}^{2+}$ -substitution, the bonding length was elongated. If the M-O bonding length is elongated, the super-exchange interaction will be reduced. Consequently, it was likely that the weakening of the anti-ferromagnetic coupling was related to the M-O bonding length variation with the substitution.

The chemically delithiated compound  $\text{Li}_{1-y}\text{FePO}_4$  was a mixture of  $\text{LiFePO}_4$  and  $\text{FePO}_4$ , and the Rietveld analysis enabled us to estimate their fractions. Then, the magnetic susceptibility of  $\text{FePO}_4$  compound was numerically calculated by subtracting the contribution of the pristine  $\text{LiFePO}_4$  from the experimentally obtained susceptibility of  $\text{Li}_{1-y}\text{FePO}_4$  compound. The curve of the resulting susceptibility versus temperature exhibited a very broad maximum around 100K, which was considered to be the Neel temperature of this compound. Additionally, the high-temperature susceptibility brought about the asymptotic Curie temperature of approximately -550K. They indicated a significant enhancement of the antiferromagnetic interaction between transition metal ions.

Table I.  $\text{MO}_6$  octahedral coordination geometry in olivine  $\text{Li}(\text{Mn}_x\text{Fe}_{1-x})\text{PO}_4$

X	M-O		Average Bonding Length(Å)	M-O-M Bonding Angle(deg)	Distortion Ratio (%)
	Bonding Length(Å)				
0	2.2502(4)	(max)	2.1563(3)	127.5(1)	8.67
	2.0633(3)	(min)			
0.1	2.2511(4)	(max)	2.1572(4)	127.5(1)	8.65
	2.0645(4)	(min)			
0.2	2.2541(4)	(max)	2.1602(4)	127.5(1)	8.64
	2.0675(4)	(min)			
0.3	2.2566(5)	(max)	2.1624(5)	127.5(1)	8.62
	2.0701(5)	(min)			
0.4	2.2613(5)	(max)	2.1671(4)	127.5(1)	8.60
	2.0748(4)	(min)			
0.5	2.2626(5)	(max)	2.1685(5)	127.5(1)	8.58
	2.0765(4)	(min)			
0.0D*	2.1421(7)	(max)	2.0310(10)	130.2(1)	13.11
	1.8759(6)	(min)			

\*chemically delithiated specimen

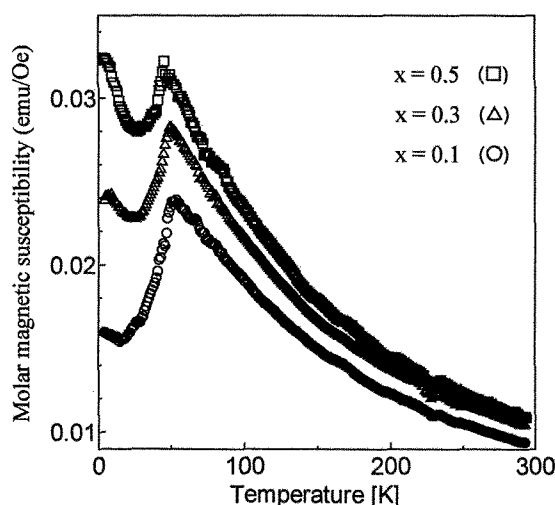


Fig. 4. Temperature variation of magnetic susceptibility of olivine compounds  $\text{LiMn}_x\text{Fe}_{1-x}\text{PO}_4$ .

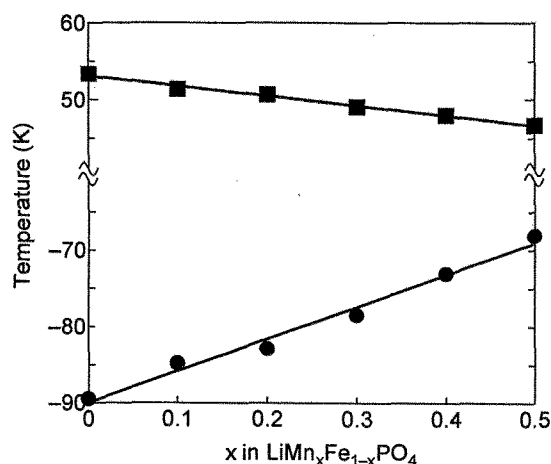


Fig. 5. Variation of Neel and asymptotic Curie temperatures with the Mn-substitution degree.

It was possible that the magnetic modification with the delithiation was also explained from the view-point of  $\text{MO}_6$  coordination geometry. From the discussion of in the previous section, it was clear that the delithiation led to anisotropic lattice deformation, where the M-O bonding length was shortened and the M-O-M bonding angle was spread. It is known that that these two geometrical variations enhance the super-exchange interaction between transition metal ions through oxygen anion. Accordingly, the enhancement of the anti-ferromagnetic interaction by the delithiation was also attributed to the modification of  $\text{MO}_6$  octahedral coordination geometry.

#### 4. CONCLUSION

We prepared the olivine compounds  $\text{LiMn}_x\text{Fe}_{1-x}\text{PO}_4$  ( $x < 0.5$ ) by the solid state reaction, and the chemically delithiated compound  $\text{Li}_{1-y}\text{FePO}_4$  using bromine and acetonitrile. In the  $\text{Mn}^{2+}$ -substitution, the ionic radius difference led to the shortening of the lattice parameters and homogeneous expansion of the olivine lattice. The

lattice expansion caused in the weakening of the super-exchange interaction and it resulted in the lowering of the Neel temperature. In contrast, the chemical delithiation brought about anisotropic change in the olivine lattice. The spread of the M-O-M coupling angle in the zigzag chain running along the crystallographic c-axis enhanced the anti-ferromagnetic super-exchange interaction between transition metal ions. Consequently, the chemical delithiated compound had higher Neel temperature than the lithiated one. In this work, it became clear that, in the olivine compound, the  $\text{MO}_6$  coordination geometry had a great influence on the magnetic property. It was thought very meaningful to study the cathode materials from both electrochemical and magnetic aspects.

#### REFERENCES

- [1] A. K. Padhi, K. S. Nanjundaswamy, C. Masquelier, S. Okada and J. B. Goodenough, *J. Electrochem. Soc.*, **144** (1997) 1609.
- [2] A. Yamada and S. Chung, *J. Electrochem. Soc.*, **148** (2001) A960.
- [3] S. Okada, S. Sawa, M. Egashira, J. Yamaki, M. Tabuchi, H. Kageyama, T. Konishi and A. Yoshino, *J. Power Sources*, **97-98** (2001) 430.
- [4] P. P. Prosini, M. Lisi, D. Zane and M. Pasquali, *Solid State Ionics*, **148** (2002) 45.
- [5] G. Li, H. Azuma and M. Tohda, *J. Electrochem. Soc.*, **149** (2002) A743.
- [6] M. Takahashi, S. Tobishima, K. Takei and Y. Sakurai, *Solid State Ionics*, **148** (2002) 283.
- [7] A. Yamada, S. C. Chung and K. Hinokuma, *J. Electrochem. Soc.*, **148** (2001) A224.
- [8] P. P. Prosini, M. Carewska, S. Scaccia, P. Wisniewski, S. Passerini and M. Pasquali, *J. Electrochemical Society*, **149** (2002) A886.
- [9] F. Croce, A. D'Epifanio, P. Reale, L. Settini and B. Scrosati, *J. Electrochemical Society*, **150** (2003) A576.
- [10] F. Izumi and T. Ikeda, *Mater. Sci. Forum*, 321-324 (2000) 198-203.
- [11] A. S. Anderson, B. Kalska, L. Haggstrom and J. O. Thomas, *Solid State Ionics*, **130** (2001) 41.
- [12] D. Jiles, *Introduction to Magnetism and Magnetic Materials*, Chapman & Hall (1991) pp. 185.
- [13] J. B. Goodenough, *Magnetism and the Chemical Bond*, Wiley, New York (1963).

(Received October 8, 2003; Accepted February 16, 2004)