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ABSTRACT

$\text{Fe}_{1-x}\text{Mg}_x\text{PO}_4$ ($x = 0.01$, 0.05, and 0.1) cathode materials are synthesized by a two-step method, which combines the solid-state reaction method and the chemical lithium deintercalation method. A study was conducted to investigate the structural and the magnetic properties of $\text{Fe}_{1-x}\text{Mg}_x\text{PO}_4$. The crystalline structure of the samples was analyzed by X-ray diffractometer (XRD) using the Rietveld refinement. The magnetic properties of the samples were determined from vibrating sample magnetometer (VSM) and Mössbauer spectroscopy, including their magnetic interactions, Fe ions state, and structural ordering. The Neél temperature ($T_N$) of $\text{Fe}_{1-x}\text{Mg}_x\text{PO}_4$ decreases with the increase of the Mg content due to the weakening of the antiferromagnetic exchange. Furthermore, for $\text{Fe}_{0.9}\text{Mg}_{0.1}\text{PO}_4$, the effective moment value decreases as expected with increasing Mg content. Mössbauer spectroscopy measurements at different temperatures were made. The spectrum at 295 K was fitted with a doublet, which has an isomer shift of $\delta = 0.32 – 0.43$ mm/s ($\text{Fe}^{3+}$). The large value of the electric quadrupole splitting ($\Delta E_Q$ = 0.95 – 1.87 mm/s) is explained by the asymmetric local environment of the Fe ions. Below the $T_N$, the spectra of $\text{Fe}_{1-x}\text{Mg}_x\text{PO}_4$ in the eight resonance absorption lines (including two relatively small intensities) were analyzed. We can obtain a spin value for Fe ions ($S = 5/2$) of $\text{Fe}_{0.9}\text{Mg}_{0.1}\text{PO}_4$ from the Brillouin functional analysis.

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I. INTRODUCTION

Currently, the fastest-growing lithium-ion battery used in energy storage systems is also widely used in portable electronic devices, from wireless communications to mobile computing and electric vehicles.\textsuperscript{1–3} LiFePO$_4$, discovered by the Goodenough group, has been used as a cathode material for secondary lithium batteries, and many research groups have made great efforts to improve its performance.\textsuperscript{4–10}

LiFePO$_4$ is mainly used for high capacity and high-power applications, such as in hybrid vehicles. However, this cathode material has the disadvantage that its energy density is lower than that of LiCoO$_2$ layer and LiMn$_2$O$_4$ spinel cathode materials, which have a discharge voltage of 3.8–4.0 V, because its discharge voltage is in the 3.5 V region.\textsuperscript{11} To overcome this problem, a high voltage olivine material is being actively developed in which Fe is replaced with a transition metal.\textsuperscript{12–15} For example, the substitution of 10% of Fe ions by Mn or Ni ions can improve the discharge capacity value, especially at high rates of charge and discharge.\textsuperscript{11–13} Moreover, it has been shown that the Mg-doped LiFePO$_4$ cathode material can improve the electrochemical performance of the material.\textsuperscript{14,15} In addition to the LiFePO$_4$ cathode, the FePO$_4$ cathode as the delithiated form of LiFePO$_4$ has been of great interest in relation to lithium-ion battery cathodes. Previous studies have reported that olivine-type FePO$_4$ irreversibly transforms into an electrochemically inactive quartz-like structure at about 600 °C, suggesting that the olivine form might be metastable.\textsuperscript{16} However, since the Mg ion is not electrochemically activated, a high capacity can only be obtained when the content is small.\textsuperscript{17} Besides the existing studies on the structural and magnetic properties of LiFe$_{1-x}$Mg$_x$PO$_4$ materials with small amounts of Mg ions, basic studies on the structural and magnetic properties of charged Fe$_{1-x}$Mg$_x$PO$_4$ materials are insufficient.

The aim of this work was to obtain new data on the influence of delithiated FePO$_4$ doping with Mg ion, Fe$_{1-x}$Mg$_x$PO$_4$ ($x = 0.01$, 0.05, and 0.1), on the structure and magnetic properties of the study material.
II. EXPERIMENTS

First, Mg-doped LiFePO₄ was synthesized using the conventional solid-state reaction method. Li₂CO₃, Fe₂O₃, 2H₂O, NH₄H₂PO₄, and (CH₃COO)₂Mg·4H₂O were used as reactants. Different amounts of Mg were used to obtain 1, 5, and 10% of LiFe₁₋ₓMgₓPO₄. These were then calcined at 350 °C for 3 h under argon flow. The powder was pressed into pellets and heated under argon flow at 700 °C for 10 h. A chemical oxidation to obtain Fe₁₋ₓMgₓPO₄ was performed by chemical delithiation using NO₂BF₄ as the oxidizing reagent. Lithium extraction was achieved by stirring LiFe₁₋ₓMgₓPO₄ powder with NO₂BF₄ in an acetonitrile solution. The solution was stirred for 1 day at room temperature, then filtered and washed with acetonitrile to remove LiBF₄, and finally dried overnight.

The crystalline structure was characterized using powder X-ray diffractometer (XRD, Rigaku Ultima IV diffractometer) using Cu-Kα radiation operating at 40 kV and 30 mA. The Rietveld refinement of the XRD patterns was performed using the FullProf program. Magnetic susceptibility measurements were performed using a vibrating sample magnetometer (VSM) in the 4.2-295 K temperature range. After recording the magnetic susceptibility measurements, the samples were shown in Fig. 1. Rietveld refinement was carried out showing that crystal phases of the Fe₁₋ₓMgₓPO₄ samples are orthorhombic structure with space group of Pnma. The lattice constant of Fe₁₋ₓMgₓPO₄ slightly increased from a₀ = 9.816, b₀ = 5.789, and c₀ = 4.780 Å for x = 0.01 to a₀ = 9.854, b₀ = 5.805, and c₀ = 4.780 Å for x = 0.1. Furthermore, the volume (V) of the unit cell increased from 271.63 (x = 0.01) to 273.38 Å³ (x = 0.1). The Bragg factor R₀ and structure factor R₀ indicate a good structural refinement. The lattice parameters are listed in Table I. As illustrated in Figure 2a, the crystalline structure of delithiated Fe₀.₉Mg₀.₁PO₄ is composed of FeO₆ octahedra and PO₄ tetrahedra. The refinement was achieved by considering that the Fe, Mg, and P ions are found at distinct sites, which have O1 and O2 in sites 4c, 015, and O3 in positions 8d. The FeO₆ octahedra, Fe(O1O2O3)₄ units and are linked via common O3 vertices, has an asymmetric octahedral structure. Fe–O bond lengths of Fe₀.₉Mg₀.₁PO₄ are shown in Fig. 2b. The lattice parameters of Fe₁₋ₓMgₓPO₄ Rietveld refinements, the Fe–O bond length increased with increasing lattice constants.

Figure 3 shows the temperature-dependent magnetic susceptibility (χ(T)) and inverse susceptibility (χ⁻¹(T)) curve of Fe₁₋ₓMgₓPO₄ in an external magnetic field of H = 100 Oe, measured by VSM. The magnetic behavior for χ⁻¹(T) at high temperatures fits well with the Curie–Weiss law, where χ⁻¹ = T/θ (C-Tθ). The Curie–Weiss temperature (θCW) of Fe₁₋ₓMgₓPO₄ has been determined to be -698, -684, and -678 K for x = 0.01, 0.05, and 0.1. This clearly indicates an antiferromagnetic behavior. Also, with increasing Mg content, the observed experimental effective moment value (μexp) for Fe₁₋ₓMgₓPO₄ is 6.44, 6.26, and 6.10 μB from the VSM measurement, while the calculated value of the spin-only theoretical effective moment (μθCW) is 5.89, 5.77, and 5.63 μB. This high μexp value for the samples is considered to be due to the lack of oxygen generated during the oxidation reaction to remove lithium. The magnetic susceptibility shows a cusp with decreasing temperatures. It shows that the temperature of the cusps corresponds to the Néel temperature (TN). The TN of Fe₁₋ₓMgₓPO₄ with an increasing Mg content decreased from 112, 105, and 98 K for x = 0.01, 0.05, and 0.1. While the magnetization of Fe₁₋ₓMgₓPO₄ decreases with decreasing temperature at below TN, we observed an increase in magnetization below the spin-reorientation temperature (TS) due to spin-orbit coupling. The TS of Fe₁₋ₓMgₓPO₄ was found to be 29, 28, and 26 K for x = 0.01, 0.05, and 0.1, with an increasing Mg content, as shown in Fig. 3. This can be explained by the fact that the temperature of TN and TS decreased gradually due to the strength reduction of the nearest-neighbor's super exchange interaction with the increasing x for Fe₁₋ₓMgₓPO₄. Furthermore, TN and TS can be confirmed either by VSM measurements or by Mössbauer’s study.

### Table I. The lattice parameters of Fe₁₋ₓMgₓPO₄ (x = 0.01, 0.05, and 0.1).

| x   | a (Å) | b (Å) | c (Å) | V (Å³) | R₀ (%) | R₀ (%) | Average Fe–O bond lengths (Å) |
|-----|-------|-------|-------|--------|--------|--------|-----------------------------|
| 0.01| 9.816 | 5.789 | 4.780 | 271.63 | 3.69   | 5.31   | 2.045                       |
| 0.05| 9.830 | 5.795 | 4.780 | 272.47 | 4.20   | 5.08   | 2.060                       |
| 0.1 | 9.854 | 5.805 | 4.780 | 273.38 | 4.03   | 5.30   | 2.073                       |

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The Mössbauer spectra of the samples were taken at different temperatures from 4.2 to 295 K. The spectra are shown in Fig. 4, where the sample with $x = 0.1$ was selected. It was found that the spectrum at 295 K consists of a doublet with the electric quadrupole splitting $\Delta E_Q = 0.95$ mm/s and isomer shift $\delta = 0.32$ mm/s. The $T_N$ has been determined to be 98 K based on an analysis of the Mössbauer spectra. The Mössbauer spectra below $T_N$ show the distorted eight-line shape due to a large electric quadrupole contribution instead of a dipolar magnetic interaction. These spectra were analyzed by adjusting eight Lorentzian using the full Hamiltonian for the $^{57}$Fe and calculating the relative line positions as well as the relative line intensities. The value of $\delta$ (0.32 mm/s $\leq \delta \leq 0.43$ mm/s) shows that the charge states are Fe$^{3+}$ over the entire temperature range. The Mössbauer parameters at different temperatures are summarized in Table II.

Figure 5 shows the temperature dependence of the electric quadrupole splitting for Fe$_{1-x}$Mg$_x$PO$_4$. The quadrupole splitting is the value of the electric field gradient (EFG) acting on the nucleus. The $\Delta E_Q$ value can be expressed as, $\Delta E_Q = (1/2) e'qQ[1+(1/3)\eta^2]^{1/2}$, where $e'qQ$ is the nucleus quadrupole moment of $^{57}$Fe, $eQ \equiv V_{zz}$ is the largest component of the EFG tensor, and $\eta \equiv (V_{xx} - V_{yy})/V_{zz}$ is the asymmetric parameter, which indicates how much the electric potential departs from spherical symmetry. The quadrupole splitting increases with decreasing temperature; however, the quadrupole splitting rapidly decreases below $T_S$. This can be explained by the decrease of the quadrupole splitting under $T_S$ due to spin-orbit coupling and the increase of the quadrupole splitting under $T_N$ due to the distorted FeO$_6$ octahedral structure.

| $T$ (K) | $H_{hf}$ (kOe) | $\Delta E_Q$ (mm/s) | $\delta$ (mm/s) | $\eta$ |
|-------|----------------|----------------------|-----------------|-------|
| 4.2   | 495.4          | 1.83                 | 0.43            | 0.75  |
| 10    | 493.6          | 1.84                 | 0.43            | 0.75  |
| 20    | 488.3          | 1.85                 | 0.43            | 0.75  |
| 25    | 482.3          | 1.86                 | 0.43            | 0.78  |
| 26    | 479.6          | 1.87                 | 0.43            | 0.79  |
| 27    | 478.4          | 1.85                 | 0.43            | 0.77  |
| 30    | 477.3          | 1.85                 | 0.43            | 0.78  |
| 50    | 442.4          | 1.80                 | 0.43            | 0.75  |
| 77    | 343.1          | 1.77                 | 0.42            | 0.75  |
| 98    | –              | 1.47                 | 0.35            | –     |
| 295   | –              | 0.95                 | 0.32            | –     |

FIG. 2. (a) Structures and (b) the Fe–O bond lengths of Fe$_{0.9}$Mg$_{0.1}$PO$_4$. The PO$_4$ tetrahedra are represented in magenta, the FeO$_6$ octahedra in cyan, and the oxygen atoms in red.

FIG. 3. Temperature-dependent inverse magnetic susceptibility and magnetic susceptibility (inset) as a function of temperature of Fe$_{1-x}$Mg$_x$PO$_4$.

FIG. 4. Mössbauer spectra of Fe$_{0.9}$Mg$_{0.1}$PO$_4$ at different temperatures.
by the strong crystalline field. With increasing Mg content, the quadrupole splitting was found to decrease monotonically, suggesting a decrease in the electrical order between Fe$^{3+}$ ions due to the increased distortion of the Fe sites.

Figure 6 shows the reduced magnetic hyperfine fields $H_{hf}(T)/H_{hf}(0)$ for Fe$_{1-x}$Mg$_x$PO$_4$ as a function of the reduced temperature $T/T_N$ ($T_N = 98$ K for $x = 0.1$). To derive information on the behavior of the Fe ion spin, the Mössbauer data have been fitted to the Brillouin function on the spin quantum number $S$. The circles and line represent the experimental data and the calculated data, respectively. From the Brillouin functional analysis, it can obtain a spin value for the Fe ions is in high spin state, $S = 5/2$. Therefore, Fe$_{0.9}$Mg$_{0.1}$PO$_4$ consists of high-spin Fe$^{3+}$ with an electronic configuration of (3d$^6$)(3d$^1$)$^5$.

IV. CONCLUSION

Mg-doped FePO$_4$, Fe$_{1-x}$Mg$_x$PO$_4$ ($x = 0.01$, 0.05, and 0.1), was synthesized via a solid-state reaction and chemical oxidation method. The crystalline structure of Fe$_{1-x}$Mg$_x$PO$_4$ has an orthorhombic structure with space groups of Pnma. Fe$_{1-x}$Mg$_x$PO$_4$ samples are strongly affected by the asymmetric FeO$_6$ structure. The lattice constants and Fe–O bond length increased with increasing Mg content. The strength reduction of the super exchange interaction with the increase of the Mg content causes the decrease of $T_N$ and $T_S$. The magnetic susceptibility curves below $T_S$ exhibited abnormal antiferromagnetic behavior due to the spin-orbit coupling. The Mössbauer spectra were analyzed with eight resonance absorption lines below the $T_N$. In addition, below $T_S$, the electric quadrupole splitting in Fe$^{3+}$O$_6$ octahedral sites decreased by spin-orbit coupling. From the reduced magnetic hyperfine field, the spin value of Fe$_{0.9}$Mg$_{0.1}$PO$_4$ is determined to be $S = 5/2$.

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