Synthesis and magnetic properties of LiFePO₄ substitution magnesium

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LiFe₀.₉Mg₀.₁PO₄ sample was prepared by using a solid–state reaction method, and the temperature-dependent magnetic properties of the sample were studied. The X-ray diffraction (XRD) pattern showed an olivine-type orthorhombic structure with space group Pnma based on Rietveld refinement method. The effect of Mg substitution in antiferromagnetic LiFe₀.₉Mg₀.₁PO₄ was investigated using a vibrating sample magnetometer (VSM) and Mössbauer spectroscopy. The temperature-dependence of the magnetization curves of LiFe₀.₉Mg₀.₁PO₄ shows abnormal antiferromagnetic behavior with ordering temperature. Sudden changes in both the magnetic hyperfine field (Hhf) and its slope below 15 K suggest that magnetic phase transition associated to the abrupt occurrence of spin-reorientation. The Néel temperature (TN) and spin-reorientation temperature (TS) of LiFe₀.₉Mg₀.₁PO₄ are lower than those of pure LiFePO₄ (TN = 51 K, TS = 23 K). This is due to the Fe–O–Fe superexchange interaction being larger than that of the Fe–O–Mg link. Also, we have confirmed a change in the electric quadrupole splitting (AEQ) by the spin-orbit coupling effect and the shape of Mössbauer spectrum has provided the evidence for TS and a strong crystalline field. We have found that Mg ions in LiFe₀.₉Mg₀.₁PO₄ induce an asymmetric charge density due to the presence of Mg²⁺ ions at the FeO₆ octahedral sites.

1. Introduction

Lithium iron phosphate (LiFePO₄) is promising as for the cathode of Li-ion batteries because it is a low-cost material with possible environmentally friendly large-scale applications, replacing the use of fossil fuels. Olivine is regarded as a stable structure for the charge/discharge process with good cycling [1–3]. However, pure olivine materials have a disadvantage of exhibiting poor performance due to their low electronic conductivity [4]. To compensate this disadvantage, researches aiming at the improvement of their electrochemical characteristics have been carried out by considering substitution, coating and utilizing nano-sized particles in LiFePO₄ [5]. These mixed olivine materials have a strong magneto-electric effect (ME) observed in the antiferromagnetic phase.

Recently, the rate capability and cyclic stability in Mg-substituted for LiFePO₄ were investigated [6–8]. Also, Mg²⁺ substitution has been reported to improve the reaction kinetics of olivine compounds [9–12]. The Mg-substituted olivine structure, which has a close-packed array of O²⁻ ions, shows layers of corner-sharing Fe/Mg octahedra alternating with edge-sharing Li octahedral chains, which are linked by PO₄ tetrahedra [13]. In particular, the effects of iron redox reaction for lithium chemical extraction are very important to improve their electrochemical properties in charge–discharge process.

In this paper, we have investigated the crystalline and magnetic structures of Mg-substituted antiferromagnetic LiFePO₄ via X-ray diffraction, VSM, and Mössbauer analysis. The quenched orbital angular moment due to the strong crystalline field was confirmed in the Mössbauer experiment.

2. Experiment procedures

The LiFe₀.₉Mg₀.₁PO₄ sample was synthesized by using a solid–state reaction method. The starting materials of Li₂CO₃ (99.99%), FeC₂O₄·2H₂O (99%), (CH₃COO)₂Mg·4H₂O (99.999%), and NH₄H₂PO₄ (99.999%) were mixed with the correct stoichiometric ratio. The mixture was calcined at 350 °C for 3 h under Ar atmosphere and pelletized at 5000 N/cm². The sample was re-heated at 700 °C for 8 h under Ar atmosphere. The structural characteristics of the prepared sample were analyzed via X-ray diffraction (XRD) measurements with Cu-Kα radiation (λ = 1.5406 Å) at room temperature. The temperature dependence of zero-field cooled (ZFC) and field-cooled (FC) curves were measured using a vibrating sample magnetometer (VSM) at various temperatures. The Mössbauer