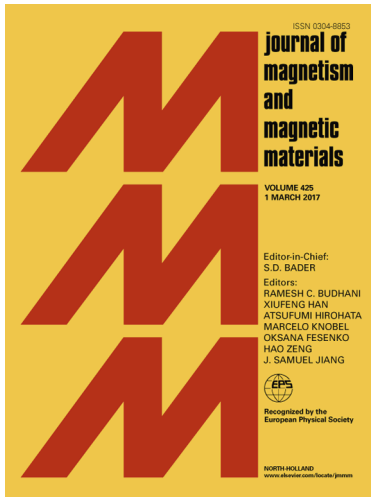


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PII: S0304-8853(16)33226-7
DOI: http://dx.doi.org/10.1016/j.jmmm.2017.02.009
Reference: MAGMA 62465

To appear in: *Journal of Magnetism and Magnetic Materials*

Received Date: 30 November 2016
Revised Date: 12 January 2017
Accepted Date: 8 February 2017

Please cite this article as: H. Choi, M.J. Kim, E.J. Hahn, S.J. Kim, C.S. Kim, Synthesis and magnetic properties of $LiFePO_4$ substitution magnesium, *Journal of Magnetism and Magnetic Materials* (2017), doi: http://dx.doi.org/10.1016/j.jmmm.2017.02.009

# Synthesis and magnetic properties of $LiFePO_4$ substitution magnesium

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**$LiFe_{0.9}Mg_{0.1}PO_4$ 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 *P*nma based on Rietveld refinement method. The effect of Mg substitution in antiferromagnetic $LiFe_{0.9}Mg_{0.1}PO_4$ was investigated using a vibrating sample magnetometer (VSM) and Mössbauer spectroscopy. The temperature-dependence of the magnetization curves of $LiFe_{0.9}Mg_{0.1}PO_4$ shows abnormal antiferromagnetic behavior with ordering temperature. Sudden changes in both the magnetic hyperfine field ($H_{hf}$) and its slope below 15 K suggest that magnetic phase transition associated to the abrupt occurrence of spin-reorientation. The Néel temperature ($T_N$) and spin-reorientation temperature ($T_S$) of $LiFe_{0.9}Mg_{0.1}PO_4$ are lower than those of pure $LiFePO_4$ ($T_N$ = 51 K, $T_S$ = 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 ($\Delta E_Q$) by the spin-orbit coupling effect and the shape of Mössbauer spectrum has provided the evidence for $T_S$ and a strong crystalline field. We have found that Mg ions in $LiFe_{0.9}Mg_{0.1}PO_4$ induce an asymmetric charge density due to the presence of $Mg^{2+}$ ions at the $FeO_6$ octahedral sites.**

*Index Terms*—Lithium battery, Mössbauer spectroscopy, Spin-orbit coupling

## I. Introduction

Lithium iron phosphate ($LiFePO_4$) 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 $LiFePO_4$ [5]. These mixed olivine materials have a strong magnetoelectric effect (ME) observed in the antiferromagnetic phase.

Recently, the rate capability and cyclic stability in Mg-substituted for $LiFePO_4$ were investigated [6-8]. Also, $Mg^{2+}$ 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 $O^{2-}$ ions, shows layers of corner-sharing Fe/Mg octahedra alternating with edge-sharing Li octahedral chains, which are linked by $PO_4$ 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 magnetics structures of Mg-substituted antiferromagnetic $LiFePO_4$ 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.

## II. Experiment Procedures

The $LiFe_{0.9}Mg_{0.1}PO_4$ sample was synthesized by using a solid-state reaction method. The starting materials of $Li_2CO_3$ (99.99 %), $FeC_2O_4 \cdot 2H_2O$ (99 %), $(CH_3COO)_2Mg \cdot 4H_2O$ (99.999 %), and $NH_4H_2PO_4$ (99.999 %) were mixed with the correct stoichiometric ratio. The mixture was calcined at 350 ℃ for 3h under Ar atmosphere and pelletized at 5000 N/cm$^2$. The sample was reheated at 700 ℃ for 8h under Ar atmosphere. The structural characteristics of the prepared sample were analyzed via X-ray diffraction (XRD) measurements with Cu-$K\alpha$ radiation ($\lambda$ = 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

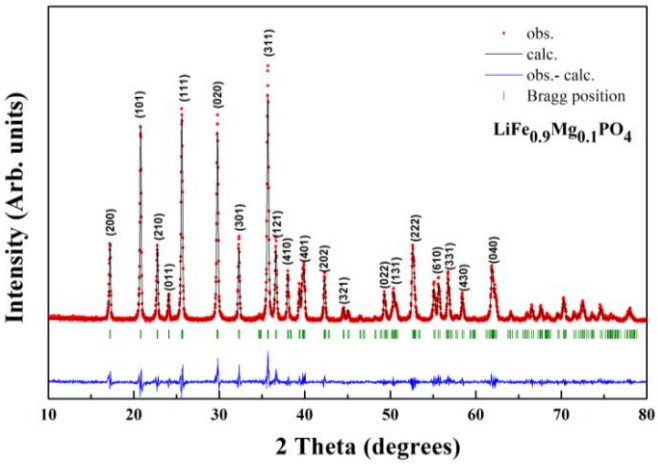


Fig. 1. Refined x-ray diffraction pattern of $LiFe_{0.9}Mg_{0.1}PO_4$ at room temperature.