

# Magnetic Properties of Phospho-Olivine $\text{Li}(\text{Fe}_{1-x}\text{Mn}_x)\text{PO}_4$ Investigated With Mössbauer Spectroscopy

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The crystalline structure of the  $\text{Li}(\text{Fe}_{1-x}\text{Mn}_x)\text{PO}_4$  ( $x = 0.0, 0.2$ ) samples was determined to be olivine-type orthorhombic with  $Pnma$  space group. The contraction of unit cell volume from  $\text{LiFe}_{0.8}\text{Mn}_{0.2}\text{PO}_4$  ( $V = 293.296 \text{ \AA}^3$ ) to  $\text{LiFePO}_4$  ( $V = 291.445 \text{ \AA}^3$ ) can be explained by the different ionic radii of high-spin  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$ . The temperature-dependent magnetic susceptibility and Curie-Weiss fitted reciprocal susceptibility curves of  $\text{Li}(\text{Fe}_{1-x}\text{Mn}_x)\text{PO}_4$  indicates that there are antiferromagnetic ordering with different values of magnetic Néel temperature and effective moment between  $\text{LiFe}_{0.8}\text{Mn}_{0.2}\text{PO}_4$  ( $T_N = 49 \text{ K}$ ,  $\mu_{\text{eff}} = 5.66\mu_B$ ) and  $\text{LiFePO}_4$  ( $T_N = 51 \text{ K}$ ,  $\mu_{\text{eff}} = 5.37 \mu_B$ ). From the Mössbauer analysis, The distribution of the  $\text{Mn}^{2+}$  ( $3d_5$ ) ions in  $M_2$  magnetic sites can lead to the reduction of magnetic hyperfine field ( $H_{\text{hf}}$ ) of  $\text{LiFe}_{0.8}\text{Mn}_{0.2}\text{PO}_4$  in  $\text{Fe}^{2+}$  ( $3d_6$ ) sites. Also, the isomer shift ( $\delta$ ) and electric quadrupole splitting ( $\Delta E_Q$ ) values, increasing with  $\text{Mn}^{2+}$  substitution, can be attributed to the decrease of charge density at Fe nucleus  $\rho_A(0)$  due to the  $3d$ -electron penetrating closer to the Fe nucleus with asymmetric charge distribution by the presence of  $\text{Mn}^{2+}$  ions on the  $\text{FeO}_6$  octahedral sites.

*Index Terms*—Antiferromagnetism, lithium-ion battery, Mössbauer spectroscopy, olivine.