

Structural and magnetic phase transition of mixed olivines $\text{Li}_x\text{Fe}_{1-y}\text{Ni}_y\text{PO}_4$ by lithium deintercalation

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The structural and magnetic phase transitions of $\text{Li}_x\text{Fe}_{1-y}\text{Ni}_y\text{PO}_4$ were investigated by x-ray diffraction (XRD), superconducting quantum interference device magnetometry, and Mössbauer spectroscopy. Rietveld refinement of XRD patterns of $\text{LiFe}_{1-y}\text{Ni}_y\text{PO}_4$ ($0.0 \leq y \leq 0.6$) revealed that the lattice parameters $a_0 = 10.328$, $b_0 = 6.007$, and $c_0 = 4.692$ Å for LiFePO_4 changed linearly to $a_0 = 10.154$, $b_0 = 5.923$, and $c_0 = 4.687$ Å for $\text{LiFe}_{0.4}\text{Ni}_{0.6}\text{PO}_4$ with the substitution of Ni ions. Also, the fully lithium-deintercalated $\text{Fe}_{1-y}\text{Ni}_y\text{PO}_4$ ($0.0 \leq y \leq 0.6$) series had enhanced lattice distortions along the c axis compared to $\text{LiFe}_{1-y}\text{Ni}_y\text{PO}_4$ because the Jahn–Teller distortion changed as the unit cell volume decreased due to lithium ion deintercalation. $\text{LiFe}_{1-y}\text{Ni}_y\text{PO}_4$ has an antiferromagnetic order; the magnetic Néel temperature (T_N) decreased from 51 K for LiFePO_4 to 36 K for $\text{LiFe}_{0.4}\text{Ni}_{0.6}\text{PO}_4$. Fully deintercalated $\text{Fe}_{1-y}\text{Ni}_y\text{PO}_4$ has strong antiferromagnetic order; T_N decreased from 114 K for FePO_4 to 62 K for $\text{Fe}_{0.4}\text{Ni}_{0.6}\text{PO}_4$ due to the charge transition of $\text{Fe}^{2+}/\text{Fe}^{3+}$ and $\text{Ni}^{2+}/\text{Ni}^{3+}$, mediated by lithium ion vacancies in an olivine structure. The Mössbauer spectra below the T_N of $\text{Li}_x\text{Fe}_{1-y}\text{Ni}_y\text{PO}_4$ ($x = 0, 1, 0.0 \leq y \leq 0.6$) were fitted with eight asymmetrical Lorentzian functions. The electric quadrupole splitting value (ΔE_Q) of $\text{LiFe}_{1-y}\text{Ni}_y\text{PO}_4$ is larger than that of $\text{Fe}_{1-y}\text{Ni}_y\text{PO}_4$ due to more asymmetric charge distributions around Fe^{2+} ($3d^6$) than Fe^{3+} ($3d^5$) in FeO_6 sites. © 2012 American Institute of Physics. [doi:10.1063/1.3678468]