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$\text{Li}_{1-x}[\text{Fe}_{1-y}\text{M}_y]\text{PO}_4$  ( $x=0, 1$ ;  $\text{M}=\text{Co}, \text{Ni}$ )



## Magnetic and structural phase transition properties of the lithium ion battery materials $\text{Li}_{1-x}[\text{Fe}_{1-y}\text{M}_y]\text{PO}_4$ ( $x=0, 1$ ; $\text{M}=\text{Co}, \text{Ni}$ )

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Lithium transition-metal phospho-olivines,  $\text{LiMPO}_4$  ( $\text{M}=\text{Fe}, \text{Co}, \text{Ni}$ ) compounds occupies an important position in the large-scale energy-storage systems (ESSs) as positive electrode materials for rechargeable lithium-ion cells [1]. In this work, the study on structural and magnetic phase transition of  $\text{Li}_{1-x}\text{Fe}_{1/3}\text{Co}_{1/3}\text{Ni}_{1/3}\text{PO}_4$  ( $x=0, 1$ ) solid-solution system carried out using x-ray diffraction (XRD), magnetization measurement and Mössbauer experiment.  $\text{LiFe}_{1/3}\text{Co}_{1/3}\text{Ni}_{1/3}\text{PO}_4$  and its fully deintercalated  $\text{Fe}_{1/3}\text{Co}_{1/3}\text{Ni}_{1/3}\text{PO}_4$  compounds were prepared by the vacuum-sealed solid-state reaction and chemical-oxidation process with reaction of  $\text{LiFe}_{1/3}\text{Co}_{1/3}\text{Ni}_{1/3}\text{PO}_4$  and  $\text{NO}_2\text{BF}_4$  in acetonitrile. From the analyzed XRD patterns, the intercalated  $\text{LiFe}_{1/3}\text{Co}_{1/3}\text{Ni}_{1/3}\text{PO}_4$  compound crystallized in orthorhombic with the Pnma space group, which is same structure with deintercalated  $\text{Fe}_{1/3}\text{Co}_{1/3}\text{Ni}_{1/3}\text{PO}_4$ . The lattice parameter of both materials were determined to be  $a_0=10.1994 \text{ \AA}$ ,  $b_0=5.9396 \text{ \AA}$ ,  $c_0=4.6957 \text{ \AA}$  and  $V=284.47 \text{ \AA}^3$  for  $x=0$ ;  $a_0=10.0498 \text{ \AA}$ ,  $b_0=5.8648 \text{ \AA}$ ,  $c_0=4.7333 \text{ \AA}$  and  $V=278.98 \text{ \AA}^3$  for  $x=1$  which can be originated by structural phase transition with Li-ion diffusion. Temperature dependent magnetization curves of the  $\text{Li}_{1-x}\text{Fe}_{1/3}\text{Co}_{1/3}\text{Ni}_{1/3}\text{PO}_4$  samples exhibits enhancement of antiferromagnetic ordering due to the valence transition of transition metal ions with the increase of the Néel temperature ( $T_N$ ) from 35 K for  $x=0$  to 51 K for  $x=1$ . The room temperature Mössbauer spectrum of the  $\text{LiFe}_{1/3}\text{Co}_{1/3}\text{Ni}_{1/3}\text{PO}_4$  exhibits one  $\text{Fe}^{2+}$  doublet with the measured value of  $\delta=1.10 \text{ mm/s}$ , whereas fully deintercalated  $\text{Fe}_{1/3}\text{Co}_{1/3}\text{Ni}_{1/3}\text{PO}_4$  shows the one  $\text{Fe}^{3+}$  ( $\delta=0.32 \text{ mm/s}$ ) doublet induced by the lithium ion diffusion and valence transition. Mössbauer spectra below the  $T_N$  analyzed with eight Lorentzian which indicates that different antiferromagnetic ordering with different  $T_N=35 \text{ K}$  for  $x=0$  and  $51 \text{ K}$  for  $x=1$ . The measured value of  $H_{\text{hf}}=120 \text{ kOe}$ ,  $\Delta E_Q=3.05 \text{ mm/s}$ ,  $\delta=1.22 \text{ mm/s}$  for  $x=0$  and  $H_{\text{hf}}=505 \text{ kOe}$ ,  $\Delta E_Q=1.51 \text{ mm/s}$ ,  $\delta=0.43 \text{ mm/s}$  for  $x=1$  at 4.2 K, respectively. From these results, we concluded that the magnetic phase transition originated from the change of the magnetic super exchange-interaction between each  $\text{Fe}^{2+}/\text{Fe}^{3+}$  ions in  $\text{Li}_{1-x}\text{Fe}_{1/3}\text{Co}_{1/3}\text{Ni}_{1/3}\text{PO}_4$ .

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[1] H. Gwon, D.-H. Seo, S.-W. Kim, J. Kim, and K. Kang, *Adv. Funct. Mater.* **19**, 1 (2009).