



ELSEVIER

Contents lists available at ScienceDirect

## Materials Research Bulletin

journal homepage: [www.elsevier.com/locate/matresbu](http://www.elsevier.com/locate/matresbu)

# Structural and magnetic properties of lithium cathode materials $\text{Li}_x\text{Fe}_{1/3}\text{Co}_{1/3}\text{Ni}_{1/3}\text{PO}_4$ ( $x = 0, 1$ )



Hyunkyung Choi<sup>a</sup>, Hyung Joon Kim<sup>b</sup>, In-Bo Shim<sup>a</sup>, In Kyu Lee<sup>a</sup>, Chul Sung Kim<sup>a,\*</sup>

<sup>a</sup> Department of Physics, Kookmin University, Seoul 02707, Republic of Korea

<sup>b</sup> Basic Materials & Chemicals R&D Center, LG Chem Research Park, Daejeon 34122, Republic of Korea

## ARTICLE INFO

## Article history:

Received 13 January 2017

Received in revised form 8 May 2017

Accepted 14 May 2017

Available online 17 May 2017

## Keywords:

B. Magnetic properties

B. Phase transitions

C. X-ray diffraction

C. Mössbauer spectroscopy

## ABSTRACT

$\text{LiFe}_{1/3}\text{Co}_{1/3}\text{Ni}_{1/3}\text{PO}_4$  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 method, 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. The crystal structure of  $\text{LiFe}_{1/3}\text{Co}_{1/3}\text{Ni}_{1/3}\text{PO}_4$  is orthorhombic with the space group of  $Pnma$ , which is same as  $\text{Fe}_{1/3}\text{Co}_{1/3}\text{Ni}_{1/3}\text{PO}_4$  during deintercalation. Temperature-dependent magnetization curves of  $\text{Li}_x\text{Fe}_{1/3}\text{Co}_{1/3}\text{Ni}_{1/3}\text{PO}_4$  exhibit the enhancement of antiferromagnetic ordering due to the valence transition of transition metal ions with the increase in the Néel temperature from 35 K for  $x = 0$  to 51 K for  $x = 1$ . The room-temperature Mössbauer spectra shows the valence transition with the  $\text{LiFe}_{1/3}\text{Co}_{1/3}\text{Ni}_{1/3}\text{PO}_4$  exhibiting  $\text{Fe}^{2+}$  doublet whereas fully deintercalated  $\text{Fe}_{1/3}\text{Co}_{1/3}\text{Ni}_{1/3}\text{PO}_4$  showing one  $\text{Fe}^{3+}$  doublet induced by the lithium ion diffusion. Experimental determined effective moment of  $\text{Li}_x\text{Fe}_{1/3}\text{Co}_{1/3}\text{Ni}_{1/3}\text{PO}_4$  was found to be  $5.63 \mu_B$  for  $x = 0$  and  $6.95 \mu_B$  for  $x = 1$ , which can be interpreted as incomplete absence of orbital contribution by crystal field around distorted  $\text{MO}_6$  octahedron.