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Study of spin–phonon coupling in $LiFe_{1-x}Mn_xPO_4$ olivines

Nguyen Thi Minh Hien,[a] Joo Hee Chung,[a] Xiang-Bai Chen,[b] Woo Jun Kwon,[c] Chul Sung Kim[c] and In-Sang Yang[a]*

$LiFe_{1-x}Mn_xPO_4$ olivines are promising material for improved performance of Li-ion batteries. Spin–phonon coupling of $LiFe_{1-x}Mn_xPO_4$ ($x = 0, 0.3, 0.5$) olivines is studied through temperature-dependent Raman spectroscopy. Among the observed phonon modes, the external mode at ~263 cm^{-1} is directly correlated with the motions of magnetic Fe^{2+}/Mn^{2+} ions. This mode displays anomalous temperature-dependent behavior near the Néel temperature, indicating a coupling of this mode with spin ordering. As Mn doping increases, the anomalous behavior becomes clearly weaker, indicating the spin–phonon coupling quickly decreases. Our analyses show that the quick decrease of spin–phonon coupling is due to decrease of the strength of spin–phonon coupling, but not change of spin-ordering feature with Mn doping. Importantly, we suggest that the low electrochemical activity of $LiMnPO_4$ is correlated with the weak spin–phonon coupling strength, but not with the weak ferromagnetic ground state. Our work would play an important role as a guide in improving the performances of future Li-ion batteries. Copyright © 2015 John Wiley & Sons, Ltd.

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