

# INTERMAG AMERICAS 2020

## ABSTRACTS BOOK



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#### AS-04. The magnetic phase transition of manganese substituted maricite- $\text{NaFe}_{1-x}\text{Mn}_x\text{PO}_4$ .

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**INTRODUCTION** Maricite- $\text{NaFePO}_4$  crystals have gained attention in recent years owing to their excellent thermal stability, electrochemical capacity, low cost, and reduced environmental impact.[1, 2] Sodium has a redox potential of  $-2.71$  V, which is  $0.3$  V above that of lithium, energy penalty to be consumed. However, it has a lower energy density compared to other materials.[3] To compensate such effect, transition metal ion substitution of phosphate is an effective way to improve the performance of cathode material and can be used as an alternative to Na-ion batteries. Recently, research results have been reported to increase the energy density by improving the electrical conductivity by substituting Mn ions for Fe ion sites.[4] The higher possibility of  $\text{Na}^+$  intercalating with  $\text{NaFe(Mn)PO}_4$  is determined by the redox properties of the  $\text{Fe(Mn)}^{2+} / \text{Fe(Mn)}^{3+}$  ion couple.[5, 6] The chemical redox coupling in these materials affects their structure and magnetic properties, where the charge state of Fe ion affects the charge-discharge electrochemical mechanism. In this study, we have investigated the hyperfine interaction of Fe-ion, the crystal structure, and the magnetic phase transitions of  $\text{NaFe}_{1-x}\text{Mn}_x\text{PO}_4$ . **EXPERIMENT PROCEDURES** The Mn-doped Maricite- $\text{NaFe}_{1-x}\text{Mn}_x\text{PO}_4$  ( $x = 0.1, 0.2, 0.3, 0.4$ , and  $0.5$ ) samples were synthesized by the solid-state reaction method. After starting materials were mixed in the ratio of  $1 : 1-x : x : 1$ , the mixture was ground and then dried under vacuum for  $1$  h at  $60^\circ\text{C}$ . These were first calcined at  $350^\circ\text{C}$  for  $3$  h under Argon flow and pressed into cylindrical pellets at  $5000$  N/cm<sup>2</sup>. The pellets were sintered at  $675^\circ\text{C}$  for  $10$  h under Argon flow in a quartz tube. The crystal structure of the synthesized  $\text{NaFe}_{1-x}\text{Mn}_x\text{PO}_4$  samples was obtained by X-ray diffractometer (XRD) with Cu- $K\alpha$  radiation ( $\lambda = 1.5406$  Å) and measured by a step scanning mode in the range of  $10 - 80^\circ$  with a scan speed of  $4^\circ/\text{min}$ . To analyze the XRD patterns, we carried out Rietveld refinement using FullProf software. The temperature-dependence of the magnetization values below  $100$  Oe was investigated between  $4.2$  and  $295$  K by a vibrating sample magnetometer (VSM). The obtained Mössbauer spectra of  $\text{NaFe}_{1-x}\text{Mn}_x\text{PO}_4$  series was recorded at various temperatures. **RESULTS AND DISCUSSION** Rietveld refinements of the XRD patterns confirm that the Maricite- $\text{NaFe}_{1-x}\text{Mn}_x\text{PO}_4$  ( $x = 0.1, 0.2, 0.3, 0.4$ , and  $0.5$ ) is an orthorhombic structure with the space group  $Pmn2_1$ . The lattice constant was found to increase with increasing Mn substitutions due to the larger ionic radius of  $\text{Mn}^{2+}$  ( $0.80$  Å) compared to the ionic radius of  $\text{Fe}^{2+}$  ( $0.74$  Å). In addition, it was confirmed that as the substitution of Mn ions increases, the number of interactions of Fe ions decreases, thereby increasing the bond length of Fe(Mn)-O ions. The temperature-dependent magnetization curves obtained by VSM under an applied field of  $100$  Oe at various temperatures. From the magnetization curve, the Néel temperature ( $T_N$ ) of  $\text{NaFe}_{1-x}\text{Mn}_x\text{PO}_4$  was confirmed that the  $T_N$  decreased with higher Mn substitutions owing to the weak Fe-O-Mn superexchange interactions because of Mn ions on the antiferromagnetic order. (Fig. 1). To determine the Curie-Weiss temperature ( $\theta_{CW}$ ) of  $\text{NaFe}_{1-x}\text{Mn}_x\text{PO}_4$ , we used a modified Curie-Weiss law for the inverse magnetic susceptibility curves at temperatures above  $T_N$ . The Mössbauer spectra at  $295$  K was fitted with one doublet, whereas the antiferromagnetic region ( $T < T_N$ ) contained diagonalizing  $4 \times 4$  magnetic and quadrupole Hamiltonian matrixes for the  $^{57}\text{Fe}$  nucleus and eight Lorentzian lines at  $4.2$  K, as shown Fig. 2. The morphology of the Mössbauer spectrum was asymmetrical owing to the dipole magnetic and electric quadrupole interactions caused by the strong crystalline fields of the distorted octahedral structure of  $\text{FeO}_6$ , suggesting that the electric quadrupole interaction is more powerful. The interval between the first- and eight-line positions decreased with an increase in temperature. The magnetic hyperfine field ( $H_{hf}$ ) reached zero at  $14$  K for  $x = 0.1$ , indicating antiferromagnetic behavior due to magnetic transitions. These results were found to be in good agreement with the  $T_N$  measured by VSM. The charge state in  $\text{NaFe}_{1-x}\text{Mn}_x\text{PO}_4$  was determined to be  $\text{Fe}^{2+}$  from isomer shift ( $\delta$ ), which is between  $1.08$  and  $1.24$  mm/s in all temperature ranges and the existence of  $\text{Fe}^{2+}$  ion is associated with redox potential. The value of  $H_{hf}$  at  $4.2$  K decreased by increasing Mn substitution from  $165.36$  kOe for  $x = 0.1$  and  $153.45$  kOe for  $x = 0.5$ .

It is noticeable that the superexchange interaction via a Fe-O-Mn link is less than that via a Fe-O-Fe link. These values decreased with increasing Mn concentration owing to a decreasing number of interactions between Fe ions.

[1] V. Palomares, *et al.*, Energy Environ., Sci. Vol. 5, p.5884 (2012). [2] Y. Fang, L. *et al.*, Nano Lett., Vol. 14, p.3539 (2014). [3] G. Ali, J. Lee, *et al.*, ACS Appl. Mater. Interfaces, Vol. 8, p.15422 (2016). [4] N. T. M. Hien, *et al.*, J. Raman Spectrosc., Vol. 46, p.1161 (2015). [5] I. K. Lee, S. J. Kim, and C. S. Kim, IEEE Trans. Magn., Vol. 48, p.1553-1555 (2012). [6] C. Masquelier and L. Croguennec, Chem. Rev., Vol. 113, p.6552 (2013).

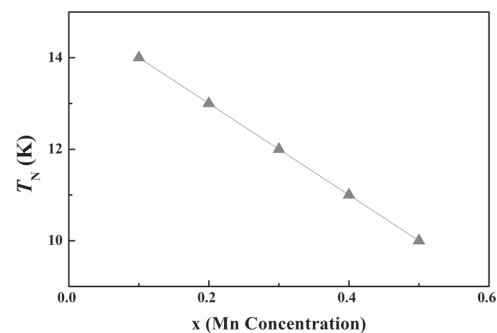


Fig. 1. The Néel temperature ( $T_N$ ) of the Mricite- $\text{NaFe}_{1-x}\text{Mn}_x\text{PO}_4$  ( $x = 0.1, 0.2, 0.3, 0.4$ , and  $0.5$ ).

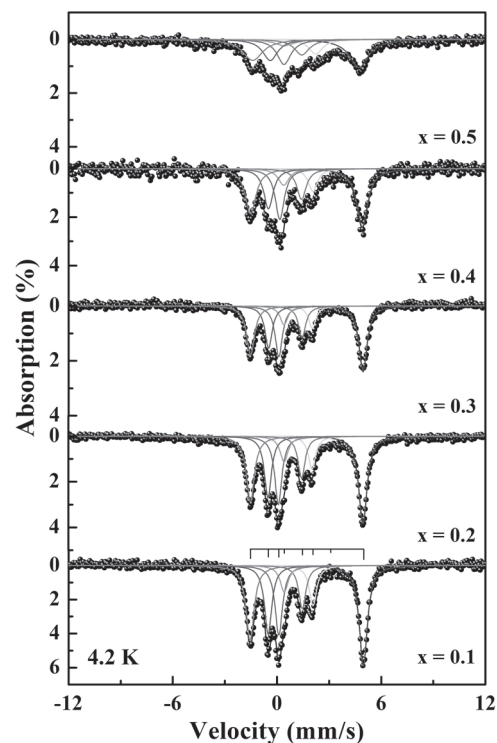


Fig. 2. The Mössbauer spectra of the Mricite- $\text{NaFe}_{1-x}\text{Mn}_x\text{PO}_4$  ( $x = 0.1, 0.2, 0.3, 0.4$ , and  $0.5$ ) at  $4.2$  K.