INTRODUCTION

Recently, studies of sodium-lithium fluorophosphate (AFePO4F, A = Li, Na, M = Fe, Mn, Co) as a cathode material of battery cells have been reported continuously.\[1\] AFePO4F has a two-dimensional intercalation deintercalation pathway for Na⁺ / Li⁺ ion transfer with improved ionic conductivity.\[2\] In addition, Mn-based phosphates have higher redox reduction potential than Fe based phosphates. Therefore, research is being conducted to improve performance by substituting Mn in place of Fe, and it can be used in batteries requiring higher output through high operating voltage.\[3, 4\] In this paper, the crystal structure and temperature-dependent magnetic properties of Na2Fe0.9Mn0.1PO4F were studied. We investigated the charge states of Fe ions, which are important for cathode material applications, by substitute transition metals such as Mn ion.

EXPERIMENTAL PROCEDURES

The sodium iron fluorophosphate Na2Fe0.9Mn0.1PO4F was synthesized by a two-step method. A NaFe0.9Mn0.1PO4 sample was prepared using the ball milling method. The starting materials were Na(CH3COO), FeC2O4·2H2O, MnCO3 and NH4H2PO4; these materials were mixed in a ratio of 1: 0.9: 0.1: 1, and zirconia balls and a 500ml volume stainless steel jar were used in the milling process. The mixture was first calcined at 350°C for 3 h under Ar flow and pressed into pellets at 5000 N/cm². These pellets were sintered at 675°C for 10 h under Ar flow. The as-prepared NaFe0.9Mn0.1PO4 was then mixed with an appropriate amount of NaF, ground in an agate mortar for 1 h, pelletized and annealed at 625°C for 6 h under Ar flow. The crystalline structure of Na2Fe0.9Mn0.1FePO4F was measured by RIGAKU X-ray diffractometer (XRD) with Cu-Kα radiation (λ = 1.5406 Å) and obtained by a step scanning mode in the range of 10 - 80 ° with steps of 0.02 °/s and a scan speed of 4 °/min. The temperature dependence of zero-field-cooled (ZFC) and field-cooled (FC) curves was obtained by Superconducting Quantum Interference Device (SQUID), at 100 Oe from 1.8 to 295 K. The temperature dependence Mössbauer spectra were recorded at temperatures ranging from 4.2 to 295 K by Mössbauer spectrometer. The spectrometer was calibrated with an α-Fe foil and a 57Co γ-ray source.

RESULTS AND DISCUSSION

The XRD patterns of Na2Fe0.9Mn0.1PO4F were experimentally measured and analyzed by the Rietveld refinement method using the FullProf program. The crystal structure was determined to be orthorhombic with the space group Pbnm, the changes in the lattice parameters of a₀ = 5.244 Å, b₀ = 13.873 Å, c₀ = 11.790 Å, and V = 857.860 Å³. The Na2FePO4F has reported two-dimensional (2D) layer structure, which consists of a pair of Fe(Mn)O₄F₂ octahedra through fluorine ion sharing. A six-coordinated Fe²⁺ environment is observed in Na2Fe0.9Mn0.1PO4F with distances ranging from 2.029 to 2.336 Å. Also, it was confirmed Fe(Mn)O₄F₂ octahedral sites and that four O ions and two F ions were asymmetrically distributed around Fe ions. In order to study the magnetic ordering, temperature-dependent magnetization curves measured at temperatures from 1.8 to 295 K under an applied field of 100 Oe. As shown in Fig. 1. The Na2Fe0.9Mn0.1PO4F undergoes a paramagnetic to antiferromagnetic transition, with Néel temperature TN = 2.5 K, resulting in observed that it is less than TN = 3.4 K of Na2FePO4F.\[5\] It is due to the Fe-O–Mn superexchange interaction being lower than the Fe-O–Fe link. The temperature-dependent Mössbauer spectra of Na2Fe0.9Mn0.1PO4F consists of one set of doublet absorption lines at all temperature, as shown in Fig. 2. The resulting values of Mössbauer parameters are electric quadrupole splitting (E_{Q}) = 2.79 mm/s, isomer shift (δ) = 1.24 mm/s at 4.2 K, and E_{Q} = 2.52 mm/s, δ = 1.22 mm/s at 295 K, indicating paramagnetic behavior due to the electric quadrupole interaction only. We also confirmed that the Fe ion is an asymmetric structure having ferrous (Fe²⁺) in octahedral sites of Fe(Mn)O₄F₂.