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Phase transition studies of sodium deintercalated $Na_{2-x}FePO_4F$ ($0 \le x \le 1$) by Mössbauer spectroscopy

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The phase transition in sodium deintercalated $Na_{2-x}FePO_4F$ ($0 \le x \le 1$) polycrystalline samples was studied by x-ray diffraction and Mössbauer spectroscopy. Sodium deintercalated samples were obtained by chemical deintercalation of pure Na_2FePO_4F. From the refined x-ray diffraction patterns, the crystalline structure of Na_2FePO_4F was determined to be orthorhombic with the space group *Pbcn*. The structure of fully sodium deintercalated $NaFePO_4F$ is identical to that of pure Na_2FePO_4F, differing only in the cell parameters. The changes in the unit cell parameters and atomic positions in $Na_{2-x}FePO_4F$ ($x=0$, 1) samples originated from a Na_2 ion deficiency in the interlayer spaces. The room-temperature Mössbauer spectra of $Na_{2-x}FePO_4F$ ($x=0$, 1) were fitted with one set of the $Fe^{2+/3+}$ doublets. A decrease in the absorption area of Fe^{2+} in Na_2FePO_4F with increasing sodium deintercalation was observed in the Mössbauer spectra of $Na_{2-x}FePO_4F$, whereas the area of the Fe^{3+} doublet in $NaFePO_4F$ increased. The large value of ΔE_Q for the Fe^{2+} doublet phase was due to the asymmetric charge distribution of FeO_4F_2 arising from different lattice and valence state contributions. [doi:10.1063/1.3561798]