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An X-ray Rietveld and infrared spectral study of the $Na_2(Mn_{1-x}M^{2+}_x)Fe^{2+}Fe^{3+}(PO_4)_3$ (x = 0 to 1 and M^{2+} = Mg, Cd) alluaudite-type solid solutions

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ABSTRACT

Compounds of the $Na_2(Mn_{1-x}M^{2+}_x)Fe^{2+}Fe^{3+}(PO_4)_3$ (M^{2+} = Mg, Cd, Ca, Ni, Zn) alluaudite-type solid solutions were synthesized by hydrothermal techniques at 1 kbar, between 400 and 600 °C, and were investigated by X-ray powder diffraction and infrared spectroscopy. The site occupancy factors of the $Na_2(Mn_{1-x}Cd_x)Fe^{2+}Fe^{3+}(PO_4)_3$ compounds, obtained from the Rietveld refinements of the X-ray powder patterns, indicate that the replacement of Mn by Cd mainly takes place on the M1 site. Small amounts of Cd were also detected on the A1 site, compensated by small amounts of Na occurring on M1. The cationic distributions in the $Na_2(Mn_{1-x}Mg_x)Fe^{2+}Fe^{3+}(PO_4)_3$ solid solution show a partially disordered distribution of Fe and Mg over the M1 and M2 crystallographic sites. The unit-cell parameters increase significantly when Mn is replaced by Ca or Cd, and decrease significantly when it is replaced by Ni, Mg, or Zn. The infrared spectra show the displacement of two absorption band at ca. 405–445 cm^{-1} and 595–610 cm^{-1}, which are assigned to the vibrations of the M^{2+} cations localized on the M1 and M2 sites, respectively. This assignment is confirmed by the excellent correlations between the average ionic radius of the cations occurring on the M sites, and the energy of the absorption band.

Keywords: Crystal chemistry, divalent cation, alluaudite structure, Na-Mn-Fe-phosphate