An X-ray Rietveld, infrared, and Mössbauer spectral study of the NaMn(Fe$_{1-x}$In$_x$)$_2$(PO$_4$)$_3$ alluaudite-type solid solution

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ABSTRACT

Several compounds of the NaMn(Fe$_{1-x}$In$_x$)$_2$(PO$_4$)$_3$ solid solution were synthesized by solid state reaction in air; pure alluaudite-like compounds were obtained for $x = 0.00$ to 1.00. X-ray Rietveld refinements indicate the presence of Na$^+$ at the A1 and A2' sites, Mn^{2+} at the M1 site, and Fe^{2+}, Fe^{3+}, and In^{3+} at the M2 site. The presence of small amounts of In^{3+} at the M1 site, and Mn^{2+} at the M2 site, indicates a partially disordered distribution between these cations. A good correlation was also established between the M1-M2 bond distance and the β angle of the alluaudite-like compounds. The disordered distribution of Fe^{2+}, Fe^{3+}, and In^{3+} at the M2 site is confirmed by the broadness of the infrared absorption bands. The Mössbauer spectra, measured between 90 and 295 K, were analyzed in terms of a model that takes into account the next-nearest neighbor interactions around the M2 crystallographic site. In all cases these spectra reveal the unexpected presence of small amounts of Fe^{2+} at the M2 site, an amount that decreases as the In^{3+} content increases. The Fe^{2+} and Fe^{3+} isomer shifts are typical of the alluaudite structure and vary with temperature, as expected from a second-order Doppler shift. The derived iron vibrating masses and Mössbauer lattice temperatures are within the expected range of values for iron cations in an octahedral environment. The Fe^{2+} and Fe^{3+} quadrupole splittings are also typical of the alluaudite structure and the temperature dependence of the Fe^{2+} quadrupole splitting was fit with the model of Ingalls (1964), which yielded a ground state orbital splitting of ca. 380 to 570 cm^{-1} for the Fe^{2+} sites.