

Crystal chemistry of the hydrothermally synthesized $\text{Na}_2(\text{Mn}_{1-x}\text{Fe}_x^{2+})_2\text{Fe}^{3+}(\text{PO}_4)_3$ alluaudite-type solid solution

**FRÉDÉRIC HATERT,^{1,2,*} LEILA REBBOUH,³ RAPHAËL P. HERMANN,³ ANDRÉ-MATHIEU FRANSOLET,¹
GARY J. LONG,⁴ AND FERNANDE GRANDJEAN³**

¹Laboratoire de Minéralogie, B18, Université de Liège, B-4000 Sart-Tilman, Belgium

²Institut für Mineralogie, Ruhr-Universität Bochum, Universitätsstrasse 150, D-44780 Bochum, Germany

³Département de Physique, B5, Université de Liège, B-4000 Sart-Tilman, Belgium

⁴Department of Chemistry, University of Missouri-Rolla, Missouri 65409-0010, U.S.A.

ABSTRACT

Several compounds of the $\text{Na}_2(\text{Mn}_{1-x}\text{Fe}_x^{2+})_2\text{Fe}^{3+}(\text{PO}_4)_3$ solid solution have been hydrothermally synthesized at 400 °C and 1 kbar; pure alluaudite-like compounds have been obtained for $x = 0.00, 0.25, 0.50, 0.75,$ and 1.00 . Rietveld refinements of the powder X-ray diffraction patterns indicate the presence of Na^+ at the A1 and A2' sites, Mn^{2+} and Fe^{2+} at the M1 site, and Mn^{2+} , Fe^{2+} , and Fe^{3+} at the M2 site. The presence of small amounts of Na^+ at the M1 site and Mn^{2+} at the A1 site indicates a partially disordered distribution of these cations. An excellent linear correlation has been established between the M1-M2 distance and the energy of the infrared band attributed to the M^{2+} -O vibrations. The Mössbauer spectra, measured between 85 and 295 K, were analyzed in terms of a model which includes the next-nearest neighbor interactions at the M2 and M1 crystallographic sites. Fe^{2+} and Fe^{3+} isomer shifts are typical of the alluaudite structure and exhibit the expected second-order Doppler shift. The derived iron vibrating masses and Mössbauer lattice temperatures are within the range of values expected for iron cations in an octahedral environment. The Fe^{2+} and Fe^{3+} quadrupole splittings are typical of the alluaudite structure, and the temperature dependence of the Fe^{2+} quadrupole splitting was fit with the Ingalls model, which yielded a ground state orbital splitting of ca. 460 to 735 cm^{-1} for the Fe^{2+} sites. The isomer shifts and quadrupole splittings of Fe^{2+} at the M1 site are larger than those of Fe^{2+} at M2, indicating that the M1 site is both larger and more distorted than the M2 site.