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

FRÉDÉRIC HATERT,1,* RAPHAËL P. HERMANN,2 GARY J. LONG,3 ANDRÉ-MATHIEU FRANSOLET,1 AND FERNANDE GRANDJEAN2

1Laboratoire de Minéralogie, B18, Université de Liège, B-4000 Sart-Tilman, Belgium
2Institut de Physique, B5, Université de Liège, B-4000 Sart-Tilman, Belgium
3Department of Chemistry, University of Missouri-Rolla, Missouri 65409-010, U.S.A.

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, Mn2+ at the M1 site, and Fe2+, Fe3+, and In3+ at the M2 site. The presence of small amounts of In3+ at the M1 site, and Mn2+ 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 Fe2+, Fe3+, and In3+ 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 Fe2+ at the M2 site, an amount that decreases as the In3+ content increases. The Fe2+ and Fe3+ 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 Fe2+ and Fe3+ quadrupole splittings are also typical of the alluaudite structure and the temperature dependence of the Fe2+ 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 Fe2+ sites.

INTRODUCTION

The alluaudite mineral group consists of Na-Mn-Fe-bearing phosphates that are known to occur in granitic pegmatites, particularly in the beryl-columbite-phosphate subtype of the rare-element pegmatites, according to the classification of Černý (1991). Wyllieite and bobfergusonite are two pegmatite phosphates homeotypic with alluaudite.

Moore (1971) determined the crystal structure of alluaudite in the monoclinic C2/c space group and derived the general structural formula X2X1M1M22(PO4)3, with Z = 4. The structure consists of kinked chains of edge-sharing octahedra stacked parallel to [010]. These chains are formed by a succession of M2 octahedral pairs linked by highly distorted M1 octahedra. Equivalent chains are connected in the b direction by the P1 and P2 phosphate tetrahedra to form sheets oriented perpendicular to [010]. These interconnected sheets produce channels parallel to c, channels that contain the distorted cubic X1 site and the four-coordinated X2 site.

The past decade has seen an increasing number of structural studies of synthetic phosphates with the alluaudite structure. These papers (Yakubovich et al. 1977; Antenucci 1992; Warner et al. 1993; Antenucci et al. 1995; Leroux et al. 1995a, 1995b; Lii and Ye 1997; Korzenski et al. 1998; Hatert et al. 2000; Chouaibi et al. 2001) clearly demonstrate the existence of three cationic sites in the alluaudite structure, sites that were not reported by Moore (1971). These sites are located in the channels at crystallographic positions different from X1 and X2. Based on detailed structural studies, Hatert et al. (2000) proposed a new general formula, (A2A2')(A1A1'A1''2)M1M22(PO4)3, for alluaudite-type compounds.

In granitic pegmatites, alluaudite displays chemical compositions mainly varying between the two end-members, Na3Mn(Fe2+Fe3+)2(PO4)3 and [NaMnFe3+]2(PO4)3, with Mn3+ or some Ca2+ replacing Na+ at the A1 site, Fe3+ replacing Mn2+ at the M1 site, and Mg2+ or Mn2+ replacing Fe at the M2 site, where □ represents a lattice vacancy at the A2’ site. Because of the complex chemical compositions of natural alluaudite minerals, pure alluaudite-like compounds have been synthesized in order to better understand the crystal chemistry of the alluaudite structure. Whereas the crystalchemical role of lithium was investigated by Hatert et al. (2000, 2002) and Hermann et al. (2002), the crystal chemistry of the trivalent cation has only been briefly investigated by Antenucci (1992) who synthesized Na3Cd3Mg(PO4)3, where M is Fe2+, Cr3+, or Ga3+. A large number of indium-bearing alluaudite-like compounds have also been synthesized, i.e., NaCdIn2(PO4)3 (Antenucci et al. 1993), Na2In2(PO4)3 (Lii and Ye 1997), and Na3In3(AsO4)3 (Lii and Ye 1997; Khorari et al. 1997). The similarities between In3+ and the trivalent transition metal cations led to the synthe-