

The crystal chemistry of lithium in the alluaudite structure

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Alluaudite is a Na-, Mn-, Fe-bearing phosphate mineral, which is 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). Moore (1971) determined the crystal structure of alluaudite in the $C2/c$ space group and derived the general structural formula, $X(2)X(1)M(1)M(2)_2(PO_4)_3$, with $Z = 4$.

During the past decade, alluaudite has been subject to numerous experimental studies. Antenucci (1992) and Antenucci *et al.* (1993 and 1995) inserted exotic cations in the alluaudite structure, such as Cd, In, Ga and Cr, thus demonstrating the unexpected versatility of this structure type. Hatert *et al.* (2000) proposed a new structural formula for alluaudite, which takes into account the presence of new crystallographic sites in the channels of the structure: $[A(2)A(2)'] [A(1)A(1)'A(1)''_2] M(1)M(2)_2(PO_4)_3$.

In the environment of rare-element pegmatites, in which the formation of alluaudite takes place, the geochemical role of lithium is essential. Since alluaudite is a key mineral in the genetic evolution affecting the Fe-Mn-bearing phosphates, it is of interest to investigate the crystallochemical role of lithium in the alluaudite structure. With this goal in mind, we decided to study the $(Na_{1-x}Li_x)MnFe^{3+}_2(PO_4)_3$ (Hatert *et al.*, 2000; Hermann *et al.*, 2002), $(Na_{1-y}Li_y)CdIn_2(PO_4)_3$ (Hatert *et al.*, 2002), and $(Na_{1-z}Li_z)_{1.5}Mn_{1.5}Fe^{3+}_{1.5}(PO_4)_3$ (Hatert, 2002) solid solutions of alluaudite-like compounds.

The phosphates have been synthesized by solid state reactions in air, between 900 and 950°C. The X-ray powder diffraction patterns show the presence of $Li_3Fe^{3+}_2(PO_4)_3$ as impurity, for $x = 0.95$ to 1.00, and for $z = 0.75$ to 1.00. For $y = 0.60$ to 1.00, $Li_3In_2(PO_4)_3$ crystallizes as supplementary phase.

Single-crystal structure refinements were performed on the $(Na_{1-x}Li_x)MnFe^{3+}_2(PO_4)_3$ solid solution ($x = 0.00$ and 0.50), whereas X-ray Rietveld refinements were performed on the $(Na_{1-y}Li_y)CdIn_2(PO_4)_3$ ($y = 0.00, 0.25, \text{ and } 0.50$) and $(Na_{1-z}Li_z)_{1.5}Mn_{1.5}Fe^{3+}_{1.5}(PO_4)_3$ ($z = 0.00, 0.25, \text{ and } 0.50$) solid solutions. The refinements indicate that Li is localized in the channels of the structure, on the large A(1) cationic site. Despite its small ionic radius (0.76 Å; Shannon, 1976), Li does not occur on the small M(2) site of the alluaudite structure, as suggested by Moore (1971). This observation constitutes a new example of lithium occurring on large crystallographic sites (Wenger & Armbruster, 1991).

The infrared spectra of $(Na_{1-y}Li_y)CdIn_2(PO_4)_3$ were compared with the spectra of similar compounds synthesized with 6Li replacing 7Li . This replacement implies a frequency shift of one weak band from 432 to 445 cm^{-1} , when natural lithium is replaced by 6Li . This moderate frequency shift of 13 cm^{-1} is lower than that theoretically predicted (Tarte, 1965), thus indicating the probable occurrence of interactions between Li-O vibrations and other internal PO_4 bending vibrations or external modes.