

3.11 LOCALIZATION OF LITHIUM IN THE CHANNELS OF SYNTHETIC ALLUAUDITE-TYPE PHOSPHATES

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Alluaudite is a Na-, Mn-, Fe-bearing phosphate mineral, which is known to occur in granitic pegmatites. Moore (1) 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 $Z = 4$. Recently, Hatert *et al.* (2) 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 $(Na_{1-x}Li_x)MnFe^{3+}_2(PO_4)_3$ (2, 3), $(Na_{1-y}Li_y)CdIn_2(PO_4)_3$ (4), and $(Na_{1-z}Li_z)_{1.5}Mn_{1.5}Fe^{3+}_{1.5}(PO_4)_3$ 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 $(Na_{1-y}Li_y)CdIn_2(PO_4)_3$ ($y = 0.00, 0.25,$ and 0.50) and $(Na_{1-z}Li_z)_{1.5}Mn_{1.5}Fe^{3+}_{1.5}(PO_4)_3$ ($z = 0.00, 0.25,$ 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), Li does not occur on the M(1) site of the alluaudite structure, as suggested by Moore (1). This observation constitutes a new example of lithium occurring on large crystallographic sites (5).

References

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