

15. CRYSTAL CHEMISTRY OF THE DIVALENT CATION IN HYDROTHERMALLY SYNTHESIZED ALLUAUDITE-TYPE PHOSPHATES

M. Rondeux and F. Hatert, Laboratory of Mineralogy B.18, University of Liège, B-4000 Liège, Belgium

Keywords: alluaudite, phosphates, divalent cation

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 natural alluaudites, divalent cations are localized in the $A(1)$ (Mn, Ca), $M(1)$ (Mn, Fe^{2+}), and $M(2)$ (Fe^{2+} , Mn, Mg) crystallographic sites (3). The exotic cations Cd and Co^{2+} have also been inserted experimentally in the alluaudite-type compounds $Na_2Cd_2M^{3+}(PO_4)_3$ ($M^{3+} = Fe^{3+}$, Ga, Cr) (4) and $M^+Co^{2+}_3(PO_4)(HPO_4)_2$ ($M^+ = Ag, Na$) (5, 6).

Since alluaudite is a key mineral in the genetic evolution affecting the Fe-Mn-bearing phosphate minerals, it is of interest to investigate the crystal chemistry of the divalent cation in the alluaudite structure. With this goal in mind, we decided to study the $Na_2(Mn_{1-x}M^{2+}_x)Fe^{2+}Fe^{3+}(PO_4)_3$ ($M^{2+} = Ca, Cd, Ni, Zn, Mg$) solid solutions of alluaudite-type compounds.

The phosphates of the $Na_2(Mn_{1-x}M^{2+}_x)Fe^{2+}Fe^{3+}(PO_4)_3$ solid solutions were synthesized hydrothermally between 400 and 600°C at 1 kbar, using horizontally arranged Tuttle-type cold-seal bombs. The powder X-ray diffraction patterns indicate that the Cd-bearing samples are constituted by pure alluaudite for $x = 0$ to 1, whereas the Ca-, Ni-, Zn-, and Mg-bearing compounds contain small amounts of impurities.

The Rietveld refinements of the powder X-ray diffraction patterns show that Cd occurs in the $A(1)$, $M(1)$ and $M(2)$ sites of $Na_2CdFe^{2+}Fe^{3+}(PO_4)_3$, whereas Ca is localized in the $M(1)$ site of $Na_2(Mn_{0.75}Ca_{0.25})Fe^{2+}Fe^{3+}(PO_4)_3$ and Mg is localized in the $M(1)$ and $M(2)$ sites of $Na_2(Mn_{0.25}Mg_{0.75})Fe^{2+}Fe^{3+}(PO_4)_3$. The partially disordered distribution of Cd and Na between the $A(1)$ and $M(1)$ sites results from the similar ionic radii of Cd^{2+} (0.95 Å) and Na^+ (1.02 Å) (7).

References

1. Moore PB (1971). *Am. Mineral.* 56, 1955.
2. Hatert F, Keller P, Lissner F, Antenucci D, Fransolet A-M (2000). *Eur. J. Mineral.* 12, 847.
3. Moore PB & Ito J (1979). *Min. Mag.* 43, 227.
4. Antenucci D (1992). Unpublished Ph. D. Thesis, University of Liège, 259 p.
5. Lii KH & Shih PF (1994). *Inorg. Chem.* 33, 3028.
6. Guesmi A & Driss A (2002). *Acta Cryst.* C58, i16.
7. Shannon RD (1976). *Acta Cryst.* A32, 751.