

Na_{1.50}Mn_{2.48}Al_{0.85}(PO₄)₃, a new synthetic alluaudite-type compound

Frédéric Hatert

University of Liège, Laboratory of Mineralogy B.18, B-4000 Liège, Belgium
Correspondence e-mail: fhatert@ulg.ac.be

Received 17 June 2005

Accepted 14 November 2005

Online 10 December 2005

The first hydrothermal synthesis of an Al-rich alluaudite-type compound, namely disodium dimanganese aluminium tris-(phosphate), which has been obtained at 1073 K and 0.1 GPa starting from the composition Na₂Mn₂Al(PO₄)₃, is reported. The crystal structure, which has been refined in the monoclinic *C2/c* space group, is identical to that of natural alluaudite. The structure consists of kinked chains of edge-sharing *M1* and *M2* octahedra, which contain Mn²⁺ and Al³⁺ ions. The chains are stacked parallel to {101} and are connected in the *b* direction by the P1 and P2 tetrahedra. These interconnected chains produce channels parallel to *c*, which contain the large distorted cubic *A1* and *A2'* sites occupied by Na⁺ and Mn²⁺ ions.

Comment

In the natural geological environment of granitic pegmatites, alluaudite-type phosphates generally show chemical compositions comprised between Na₂MnFe²⁺Fe³⁺(PO₄)₃ and NaMnFe₂³⁺(PO₄)₃. The incorporation of significant amounts of aluminium into the crystal structure of these minerals produces a splitting of the *M2* site of alluaudite into the *M2a* and *M2b* positions, thus leading to the more ordered wyllieite-type phosphates (Moore & Molin-Case, 1974; Hatert, Lefèvre *et al.*, 2005). Consequently, the *C2/c* space group of alluaudite transforms into *P2₁/n* in wyllieite, with no significant change in the unit-cell parameters.

During the past 20 years, numerous alluaudite-type phosphates have been synthesized, and the crystal chemistry of this structure type is now well known (Hatert, 2004; Hatert, Rebbouh *et al.*, 2005). Nevertheless, the structural descriptions of natural or synthetic wyllieite-type phosphates are rather scarce (Moore & Molin-Case, 1974; Zhesheng *et al.*, 1983; Brier, 2000; Hatert, Lefèvre *et al.*, 2005). In order to understand better the crystal chemistry of wyllieite-type phosphates, we attempted to obtain a single crystal of wyllieite by hydrothermal synthesis at 1073 K and 0.1 GPa, starting from the composition Na₂Mn₂Al(PO₄)₃ (Hatert, 2002). The synthesized crystals were investigated by single-crystal X-ray diffraction techniques, and a careful examination of systematic absences

indicated the *C2/c* space group, which is characteristic of alluaudite-type phosphates. The crystal structure of this Al-rich alluaudite-type compound is reported here.

The structure is similar to that of natural alluaudite, described by Moore (1971), and consists of kinked chains of edge-sharing octahedra stacked parallel to {101}. These chains are formed by a succession of *M2*–*M2* octahedral pairs, linked by highly distorted *M1* octahedra (Fig. 1). Equivalent chains are connected in the *b* direction by the P1 and P2 phosphate tetrahedra to form sheets oriented perpendicular to [010] (Fig. 2). These interconnected chains produce channels parallel to *c*, which contain both the large distorted cubic *A1* site and the *A2'* site with a morphology of a gabled disphenoid (Fig. 2). The site-occupancy factors indicate the following

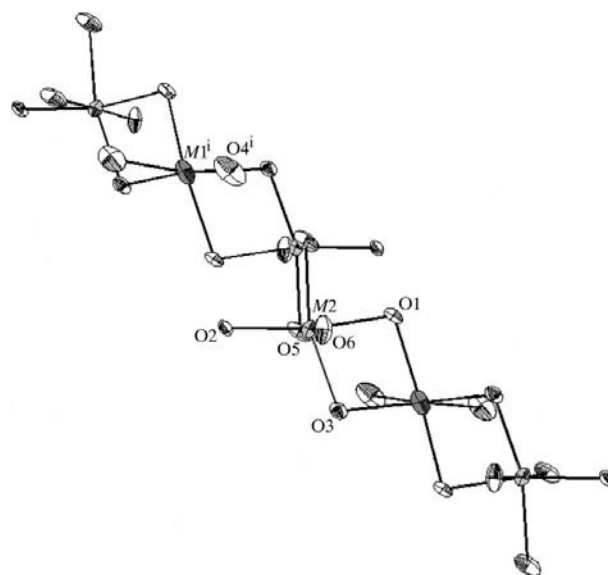


Figure 1
The *M1*–*M2* octahedral chain in Na_{1.50}Mn_{2.48}Al_{0.85}(PO₄)₃, projected along the *b* axis. [Symmetry code: (i) $x - \frac{1}{2}, y - \frac{1}{2}, z$.]

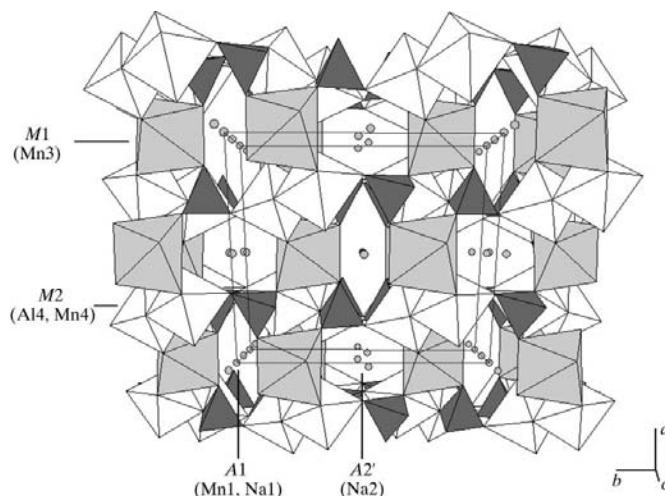


Figure 2
The crystal structure of Na_{1.50}Mn_{2.48}Al_{0.85}(PO₄)₃, projected approximately along the *c* axis.

cationic distribution: 0.891 (10) Na⁺ in A2', 0.619 (8) Na⁺ + 0.381 (7) Mn²⁺ in A1, 0.908 (4) Mn²⁺ in M1, and 0.573 (6) Mn²⁺ + 0.427 (6) Al³⁺ in M2. This cationic distribution is in very good agreement with the chemical composition.

Bond-valence sums were calculated for each ion using the parameters of Brown & Altermatt (1985). The P1 and P2 bond-valence sums are 4.99 and 4.98, respectively, and the O-atom bond-valence sums are within the normal acceptable range (1.89–2.10). For the M1 site, the low bond-valence sum obtained in the preliminary calculations indicates an occupancy by *ca* 0.150 Na⁺ + 0.850 Mn²⁺.

Experimental

The title compound was synthesized under hydrothermal conditions. The starting material was prepared by mixing NaH₂PO₄·H₂O, MnO and Al₂O₃ in the appropriate proportions. A H₃PO₄ solution was added in order to achieve stoichiometry, and the mixture was homogenized in a mortar after evaporation. About 25 mg of the resulting residue was sealed in a gold tube (outer diameter = 2 mm and length = 25 mm), containing 2 mg of distilled water. The gold capsule was then inserted into a Tuttle-type pressure vessel (Tuttle, 1949) and maintained at a temperature of 1073 K and a pressure of 0.1 GPa. After 7 d, the sample, still in the gold tube in the autoclave, was quenched to room temperature in a stream of cold air. The synthesized compounds consisted of colourless needles of the title alluaudite-type compound, together with both irregular colourless crystals of Na₃Al₂(PO₄)₃ and an amorphous matrix. Chemical analysis of the title compound was carried out using a CAMEBAX SX-50 electron microprobe (15 kV acceleration voltage, 20 nA beam current). The standards used were graffonite from Kabira (sample KF16; Fransolet, 1975) (Mn, P), oligoclase (Na) and corundum (Al). The average of six point analyses gives P₂O₅ 45.33, Al₂O₃ 8.27, MnO 37.53 and Na₂O 9.46 wt%, total 100.59 wt%. The chemical composition, calculated on the basis of 12 O atoms, corresponds to Na_{1.453}Mn_{2.518}Al_{0.772}(P_{1.01}O₄)₃.

Crystal data

Na_{1.50}Mn_{2.48}Al_{0.85}(PO₄)₃
M_r = 468.76
 Monoclinic, *C*2/*c*
a = 11.9816 (10) Å
b = 12.5387 (13) Å
c = 6.4407 (10) Å
 β = 114.621 (8)°
V = 879.64 (18) Å³
Z = 4
D_x = 3.614 Mg m⁻³

Mo *K*α radiation
 Cell parameters from 34 reflections
 θ = 5.8–12.5°
 μ = 4.31 mm⁻¹
T = 293 (2) K
 Acicular (elongated along the *c* axis), colourless
 0.23 × 0.07 × 0.05 mm

Data collection

Bruker *P4* diffractometer
 Profile data from ω scans
 Absorption correction: ψ scan
 (*XSCANS* in *SHELXTL-Plus*;
 Sheldrick, 1991)
T_{min} = 0.761, *T_{max}* = 0.806
 1271 measured reflections
 1019 independent reflections
 894 reflections with *I* > 2σ(*I*)

R_{int} = 0.024
 θ_{max} = 27.5°
h = -15 → 1
k = -16 → 1
l = -7 → 8
 3 standard reflections
 every 97 reflections
 intensity decay: 2.3%

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.032
wR(*F*²) = 0.075
S = 1.07
 1019 reflections
 100 parameters

$w = 1/[\sigma^2(F_o^2) + (0.0344P)^2 + 2.4705P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.52 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\text{min}} = -0.65 \text{ e } \text{Å}^{-3}$

Atomic coordinates similar to those given by both Moore (1971) and Hatert *et al.* (2000) were used during the refinement procedure. The site-occupancy factors indicated, in the early stages of the refinement, that the M2 site was occupied by Al³⁺ and Mn²⁺ ions, and that A1 was occupied by Mn²⁺ and Na⁺ ions. Consequently, the site-occupancy factors of both atoms were refined simultaneously on each site, and the sums of the site-occupancy factors were constrained to 1.0. The positions of these atoms and their displacement parameters were constrained to be identical using the EXYZ and EADP instructions in *SHELXL97* (Sheldrick, 1997).

Data collection: *XSCANS* in *SHELXTL-Plus* (Sheldrick, 1991); cell refinement: *XSCANS*; data reduction: *SHELXTL-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ATOMS* (Dowty, 1993); software used to prepare material for publication: *SHELXTL-Plus*.

Thanks are expressed to A.-M. Fransolet for constructive comments on the first version of this manuscript, as well as to M.-R. Spirlet, who helped with using the four-circle diffractometer. The author thanks J. Wautier, Louvain-la-Neuve, Belgium, for chemical analysis of the title compound, and also acknowledges the FNRS (Belgium) for a position of Chargé de Recherches and for grant No. 1.5.113.05.F.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1500). Services for accessing these data are described at the back of the journal.

References

- Brier, M. (2000). Diploma thesis, University of Stuttgart, Germany.
 Brown, I. D. & Altermatt, D. (1985). *Acta Cryst.* **B41**, 244–247.
 Dowty, E. (1993). *ATOMS for Windows*. Version 2.3. Shape Software, 521 Hidden Valley Road, Kingsport, TN 37663, USA.
 Fransolet, A.-M. (1975). PhD thesis, University of Liège, Belgium.
 Hatert, F. (2002). PhD thesis, University of Liège, Belgium.
 Hatert, F. (2004). *Mem. Acad. R. Belg. Cl. Sci. Coll. 8° 3eme Ser.* **21**, 1–96.
 Hatert, F., Keller, P., Lissner, F., Antenucci, D. & Fransolet, A.-M. (2000). *Eur. J. Mineral.* **12**, 847–857.
 Hatert, F., Lefèvre, P., Fransolet, A.-M., Spirlet, M.-R., Rebbouh, L., Fontan, F. & Keller, P. (2005). *Eur. J. Mineral.* **17**, 749–759.
 Hatert, F., Rebbouh, L., Hermann, R., Fransolet, A.-M., Long, G. J. & Grandjean, F. (2005). *Am. Mineral.* **90**, 653–662.
 Moore, P. B. (1971). *Am. Mineral.* **56**, 1955–1975.
 Moore, P. B. & Molin-Case, J. (1974). *Am. Mineral.* **59**, 280–290.
 Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
 Sheldrick, G. M. (1991). *SHELXTL-Plus*. Release 4.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
 Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
 Tuttle, O. F. (1949). *Geol. Soc. Am. Bull.* **60**, 1727–1729.
 Zhesheng, M., Nicheng, S. & Zhizhong, P. (1983). *Sci. Sinica Ser. B*, **26**, 876–884.