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## **$\text{Na}_{1.50}\text{Mn}_{2.48}\text{Al}_{0.85}(\text{PO}_4)_3$ , a new synthetic alluaudite-type compound**

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**Na<sub>1.50</sub>Mn<sub>2.48</sub>Al<sub>0.85</sub>(PO<sub>4</sub>)<sub>3</sub>, a new synthetic alluaudite-type compound**

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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 Na<sub>2</sub>Mn<sub>2</sub>Al(PO<sub>4</sub>)<sub>3</sub>, 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 Mn<sup>2+</sup> and Al<sup>3+</sup> 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 *A1* and *A2'* sites occupied by Na<sup>+</sup> and Mn<sup>2+</sup> ions.

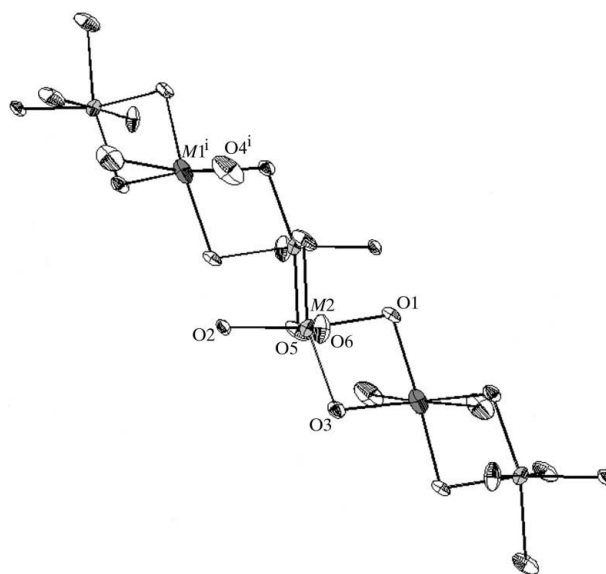
**Comment**

In the natural geological environment of granitic pegmatites, alluaudite-type phosphates generally show chemical compositions comprised between Na<sub>2</sub>MnFe<sup>2+</sup>Fe<sup>3+</sup>(PO<sub>4</sub>)<sub>3</sub> and NaMnFe<sup>3+</sup>(PO<sub>4</sub>)<sub>3</sub>. 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 *P2<sub>1</sub>/n* in wyllieite, with no significant change in the unit-cell parameters.

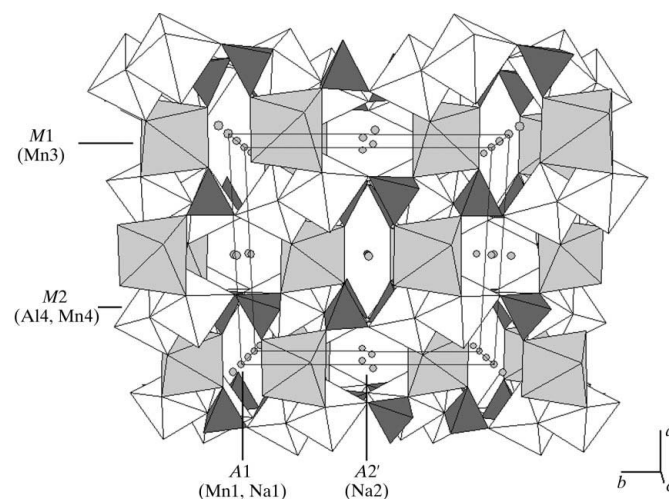
During the past 20 years, numerous alluaudite-type phosphates have been synthesized, and the crystal chemistry of this structure type is now well known (Hatert, 2004; Hatert, Rebbouh *et al.*, 2005). Nevertheless, the structural descriptions of natural or synthetic wyllieite-type phosphates are rather 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 Na<sub>2</sub>Mn<sub>2</sub>Al(PO<sub>4</sub>)<sub>3</sub> (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<sub>1.50</sub>Mn<sub>2.48</sub>Al<sub>0.85</sub>(PO<sub>4</sub>)<sub>3</sub>, projected along the *b* axis. [Symmetry code: (i)  $x - \frac{1}{2}, y - \frac{1}{2}, z$ .]



**Figure 2**  
The crystal structure of Na<sub>1.50</sub>Mn<sub>2.48</sub>Al<sub>0.85</sub>(PO<sub>4</sub>)<sub>3</sub>, projected approximately along the *c* axis.

cationic distribution: 0.891 (10) Na<sup>+</sup> in A2', 0.619 (8) Na<sup>+</sup> + 0.381 (7) Mn<sup>2+</sup> in A1, 0.908 (4) Mn<sup>2+</sup> in M1, and 0.573 (6) Mn<sup>2+</sup> + 0.427 (6) Al<sup>3+</sup> 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<sup>+</sup> + 0.850 Mn<sup>2+</sup>.

## Experimental

The title compound was synthesized under hydrothermal conditions. The starting material was prepared by mixing NaH<sub>2</sub>PO<sub>4</sub>·H<sub>2</sub>O, MnO and Al<sub>2</sub>O<sub>3</sub> in the appropriate proportions. A H<sub>3</sub>PO<sub>4</sub> 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 Na<sub>3</sub>Al<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> 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 P<sub>2</sub>O<sub>5</sub> 45.33, Al<sub>2</sub>O<sub>3</sub> 8.27, MnO 37.53 and Na<sub>2</sub>O 9.46 wt%, total 100.59 wt%. The chemical composition, calculated on the basis of 12 O atoms, corresponds to Na<sub>1.453</sub>Mn<sub>2.518</sub>Al<sub>0.772</sub>(P<sub>1.01</sub>O<sub>4</sub>)<sub>3</sub>.

### Crystal data

Na<sub>1.50</sub>Mn<sub>2.48</sub>Al<sub>0.85</sub>(PO<sub>4</sub>)<sub>3</sub>  
*M<sub>r</sub>* = 468.76  
 Monoclinic, C2/c  
*a* = 11.9816 (10) Å  
*b* = 12.5387 (13) Å  
*c* = 6.4407 (10) Å  
 $\beta$  = 114.621 (8)°  
*V* = 879.64 (18) Å<sup>3</sup>  
*Z* = 4  
*D<sub>x</sub>* = 3.614 Mg m<sup>-3</sup>

Mo *K*α radiation  
 Cell parameters from 34 reflections  
 $\theta$  = 5.8–12.5°  
 $\mu$  = 4.31 mm<sup>-1</sup>  
*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  $\omega$  scans  
 Absorption correction:  $\psi$  scan  
 (XSCANS in SHELXTL-Plus;  
 Sheldrick, 1991)  
*T<sub>min</sub>* = 0.761, *T<sub>max</sub>* = 0.806  
 1271 measured reflections  
 1019 independent reflections  
 894 reflections with *I* > 2σ(*I*)

*R<sub>int</sub>* = 0.024  
 $\theta_{\max}$  = 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*<sup>2</sup>  
*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.032  
*wR*(*F*<sup>2</sup>) = 0.075  
*S* = 1.07  
 1019 reflections  
 100 parameters

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

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 Al<sup>3+</sup> and Mn<sup>2+</sup> ions, and that A1 was occupied by Mn<sup>2+</sup> and Na<sup>+</sup> 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.

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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.

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