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Na₁₀(Na,Mn)₇Mn₄₃(PO₄)₃₆: a new synthetic fillowite-type phosphateFrédéric Hatert,^{a*} Paul Keller,^b Falk Lissner^c and Thomas Schleid^c^aUniversity of Liège, Laboratory of Mineralogy B.18, B-4000 Liège, Belgium, ^bInstitut für Mineralogie und Kristallchemie, Universität Stuttgart, Pfaffenwaldring 55, D-70569 Stuttgart, Germany, and ^cInstitut für Anorganische Chemie, Universität Stuttgart, Pfaffenwaldring 55, D-70569 Stuttgart, Germany
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Na₁₀(Na,Mn)₇Mn₄₃(PO₄)₃₆ (sodium manganese phosphate) was synthesized hydrothermally at 873 K and 0.35 GPa. The complex crystal structure is almost identical to that of natural fillowite-type phosphates and can be described as a hexagonal packing of three types of rods parallel to the *c* axis. The rods are constituted by an alternation of five- to seven-coordinated Mn sites [average Mn–O = 2.243 (3) Å], of six- to nine-coordinated Na sites [average Na–O = 2.590 (3) Å], of PO₄ tetrahedra [average P–O = 1.548 (3) Å] and of cation vacancies.

Comment

Minerals of the fillowite group are phosphates predominantly of Na, Fe, Mn, Mg and Ca, which occur in rare-element granitic pegmatites (see, for example, Araki & Moore, 1981; Fransolet *et al.*, 1998), in high-grade metamorphic rocks (Livingstone, 1980; Grew *et al.*, 2006) and in meteorites (see, for example, McCoy *et al.*, 1994; Olsen & Steele, 1997). In order to understand better the crystallization conditions of Na–Fe–Mn-bearing phosphates, we decided to investigate the Na–Mn–Fe(+PO₄) ternary system by hydrothermal methods (Hatert, 2002, 2004; Hatert *et al.*, 2006). These experiments produced several fillowite-type phosphates, among which the compound Na₂(Na,Mn)₁₄Mn₄₄(PO₄)₃₆·H₂O, structurally investigated by Keller *et al.* (2006). Starting from the composition NaMn₄(PO₄)₃, hydrothermal synthesis at 873 K and 0.35 GPa produced large colourless-to-pink crystals of the title compound, the structure of which is reported herein.

The crystal structure of the title compound refined in the space group *R* $\bar{3}$ (No. 148) and is similar to that of fillowite from the Branchville pegmatite, Connecticut, USA, with composition Na₁₂Ca₆(Mn,Fe)₄₂(PO₄)₃₆ (Araki & Moore, 1981), and to that of the synthetic compound Na₂(Na,Mn)₁₄Mn₄₄(PO₄)₃₆·H₂O (Keller *et al.*, 2006). In order to facilitate comparison, atom labels were chosen similar to those used by Araki & Moore (1981) and by Keller *et al.* (2006).

The complex structure of Na₁₀(Na,Mn)₇Mn₄₃(PO₄)₃₆ (Fig. 1) can be readily described using the scheme of hexagonal rod-packing proposed by Moore (1981), which consists of three rods parallel to the *c* axis. Rod I develops along the threefold axis, and consists of a sequence of face-sharing polyhedra and a few ordered vacancies (indicated by []): Na21–Na4–Mn5–[]–Mn2–[]–Mn5–Na4–Na21–Mn13–Mn3–[]–Mn1–[]–Mn3–Na13–Na21. Rod II develops along the 3₁ axis and consists of a sequence of corner- and angle-sharing polyhedra: Mn9–Na12–Mn8–Na31–Mn9–Na12–Mn8–Na31–Mn9–Na12–Mn8–Na31–Mn9. Rod III includes all the PO₄ tetrahedra, some coordination polyhedra of Mn, and ordered vacancies: P6–Mn11–P4–Mn6–P1–[]–P5–Mn7–P2–Mn10–P3–[].

Mn cations are mostly located on octahedral sites [average Mn–O = 2.213 (3) Å], but also occur on five-coordinated [average Mn–O = 2.144 (3) Å] or seven-coordinated sites [average Mn–O = 2.346 (3) Å]. Na atoms occur on large six- to nine-coordinated sites, with average Na–O distances ranging from 2.464 (3) to 2.705 (3) Å, whereas P atoms occur on tetrahedral sites with average P–O distances in the range 1.544 (3)–1.558 (3) Å. Bond-valence sums (BVS) were calculated for each ion using the parameters of Brown & Altermatt (1985). The P-atom BVS are between 4.79 and 4.88, and the O-atom BVS are within the normally acceptable range (1.81–2.09), except for O17, which shows a low BVS of 1.64. Mn-atom BVS are in the range 1.86–2.12, except for Mn13 (BVS = 2.46), whereas Na-atom BVS are in the range 0.86–1.06. The Mn2/Na2 and Na31/Mn31 sites show BVS of 1.50 and 0.94, respectively, thus confirming that the Mn2/Na2 site is occupied

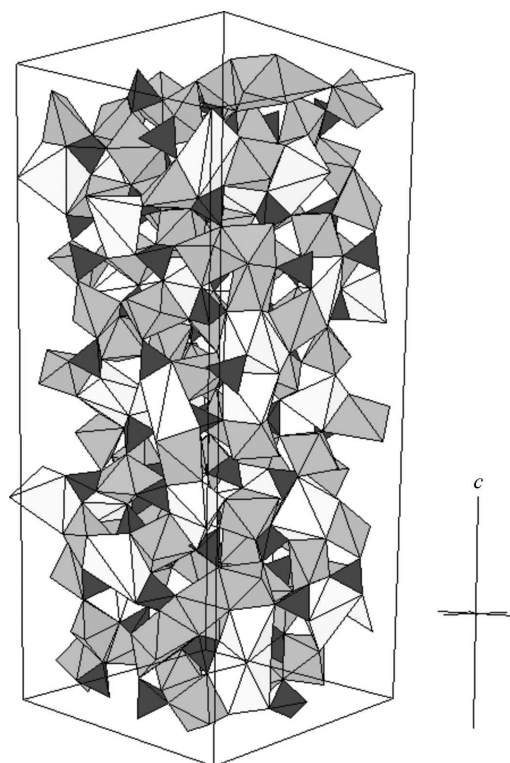


Figure 1
The crystal structure of Na₁₀(Na,Mn)₇Mn₄₃(PO₄)₃₆. NaO_n polyhedra are white, MnO_n polyhedra are light grey, and PO₄ tetrahedra are dark grey.

by both Mn and Na, and that the Na31/Mn31 site is predominantly occupied by Na.

The title compound shows a chemical composition and a crystal structure close to those of the synthetic $\text{Na}_2(\text{Na,Mn})_{14}\text{-Mn}_{44}(\text{PO}_4)_{36}\cdot\text{H}_2\text{O}$ fillowite-type compound reported by Keller *et al.* (2006). However, significant differences in site occupancies exist between the two phosphates: Keller *et al.* (2006) reported Na–Mn miscibility on the Na12, Na13 and Na31 sites and only Mn on the Mn2 and Mn4 sites, whereas the title compound shows Na–Mn miscibility on the Mn2 and Na31 sites and only Na on the Na4 (= Mn4) site. The presence of Na on the Mn2 site has not been reported in the literature, and Na also occurs on the M4 (= Na4, Mn4) site in johnsomervilleite from Loch Quoich, Scotland (Livingstone, 1980). Another difference concerns the presence of H_2O molecules in the phosphate synthesized by Keller *et al.* (2006), which are absent in the title compound.

Experimental

The title compound was synthesized under hydrothermal conditions. The starting material was prepared by mixing $\text{NaH}_2\text{PO}_4\cdot\text{H}_2\text{O}$ and MnO in 1:4 proportion, and then adding a stoichiometric amount of H_3PO_4 . The resulting solution was reduced by evaporation and the dry residue was homogenized in an agate mortar. The homogenized mixture (about 25 mg) was sealed in a gold tube (outer diameter = 2 mm and length = 25 mm) containing distilled water (2 mg). The gold capsule was then inserted in a Tuttle-type pressure vessel (Tuttle, 1949) and maintained at a temperature of 873 K and an external pressure of 0.35 GPa. After 7 d, the gold tube containing the sample was quenched in the autoclave to room temperature in a stream of cold air. The synthesized products consisted of large colourless-to-pink crystals of fillowite-type phosphate.

The redox conditions encountered in the autoclave, which is made of hard steel, were very close to those controlled by the Ni–NiO buffer (O'Neill & Pownceby, 1993). Such reducing conditions strongly favour the occurrence of Mn^{2+} instead of Mn^{3+} .

A chemical analysis was performed using a CAMEBAX SX-50 electron microprobe (15 kV acceleration voltage, 20 nA beam current, analyst J. Wautier, Louvain-la-Neuve, Belgium). The standards used were graffonite from Kabira (sample KF16, Franolet, 1975) (Mn, P), and oligoclase (Na). The average of nine point analyses gives $\text{P}_2\text{O}_5 = 41.52$, $\text{MnO} = 51.31$, $\text{Na}_2\text{O} = 7.10$, total = 99.93 wt%. The chemical composition, calculated on the basis of 36 P, corresponds to $\text{Na}_{14.10}\text{Mn}_{44.50}(\text{PO}_4)_{36}$, is in fairly good agreement with the composition calculated from the structural data, $\text{Na}_{14.05}\text{-Mn}_{45.31}(\text{PO}_4)_{36}$. These formulae are not charge-balanced, since the total number of cations corresponds only to 141.55 and 142.34 O atoms, respectively. This charge deficit probably indicates the presence of small amounts of Mn^{3+} , which is confirmed by the pink colour of the synthesized crystals.

Crystal data

$\text{Na}_{10}(\text{Na,Mn})_7\text{Mn}_{43}(\text{PO}_4)_{36}$	$Z = 3$
$M_r = 6232.86$	Mo $K\alpha$ radiation
Trigonal, $R\bar{3}$	$\mu = 5.38 \text{ mm}^{-1}$
$a = 15.3053 (7) \text{ \AA}$	$T = 293 \text{ K}$
$c = 43.672 (3) \text{ \AA}$	$0.05 \times 0.04 \times 0.03 \text{ mm}$
$V = 8859.7 (8) \text{ \AA}^3$	

Data collection

Stoe IPDS diffractometer	41372 measured reflections
Absorption correction: ψ scan (XSCANS; Siemens, 1991)	7052 independent reflections
$T_{\min} = 0.773$, $T_{\max} = 0.851$	4405 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.108$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.038$	375 parameters
$wR(F^2) = 0.081$	2 restraints
$S = 0.86$	$\Delta\rho_{\max} = 0.98 \text{ e \AA}^{-3}$
7052 reflections	$\Delta\rho_{\min} = -1.45 \text{ e \AA}^{-3}$

Atomic coordinates similar to those given by Araki & Moore (1981) and by Keller *et al.* (2006) were used during the refinement procedure. The site-occupancy factors indicated, in the early stages of the refinement, that significant amounts of Na^+ occupied the Mn2 site and that significant amounts of Mn^{2+} occupied the Na31 site. Consequently, the site-occupancy factors of both atoms were refined simultaneously on both sites, and the sums of the site-occupancy factors were constrained to be 1.0. The positions of these atoms and their displacement parameters were constrained to be identical using the EXYZ and EADP instructions of *SHELXL97* (Sheldrick, 2008).

Data collection: *DIF4* (Stoe & Cie, 1991); cell refinement: *DIF4*; data reduction: *REDU4* (Stoe & Cie, 1991); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ATOMS* (Dowty, 1993); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FN3021). Services for accessing these data are described at the back of the journal.

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