

First experimental evidence of alluaudite-like phosphates with high Li-content: the $(\text{Na}_{1-x}\text{Li}_x)\text{MnFe}_2(\text{PO}_4)_3$ series ($x = 0$ to 1)

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Abstract: Members of the $\text{Na}_{1-x}\text{Li}_x\text{MnFe}_2(\text{PO}_4)_3$ series, with the alluaudite structure type, were synthesized by solid-state reaction in air. The crystal structure refinement of the $\text{NaMnFe}_2(\text{PO}_4)_3$ end-member (space group $C2/c$, $Z = 4$, $a = 12.018(2)$, $b = 12.565(3)$, $c = 6.415(1)$ Å, $\beta = 114.33(3)^\circ$), a synthetic compound with a chemical composition corresponding to the idealized composition of the Buranga alluaudite, was carried out to $R_I = 0.026$. The following cationic distribution was observed: $\text{Na}^+ + \square$ in A(1) and A(2)' (\square denotes lattice vacancies), Mn^{2+} in M(1), $\text{Fe}^{3+} + \text{Fe}^{2+}$ in M(2). The A(2)' site exhibits a distorted gable disphenoid morphology and is found at the $(0, y, 1/4)$ ($y \approx 0$) position in channel 2 of the alluaudite structure. The crystal structure of $\text{Na}_{0.5}\text{Li}_{0.5}\text{MnFe}_2(\text{PO}_4)_3$ (space group $C2/c$, $Z = 4$, $a = 11.988(2)$, $b = 12.500(3)$, $c = 6.392(1)$ Å, $\beta = 114.67(3)^\circ$), refined to $R_I = 0.034$, leads to the cationic distribution: $\text{Li}^+ + \text{Na}^+ + \square$ in A(2)', $\text{Na}^+ + \square$ in A(1), Mn^{2+} in M(1), $\text{Fe}^{3+} + \text{Fe}^{2+}$ in M(2). Thus, the substitution mechanism involved in the replacement of Na by Li in the $\text{Na}_{1-x}\text{Li}_x\text{MnFe}_2(\text{PO}_4)_3$ alluaudite-like compounds corresponds to $\square + \text{Na} \rightarrow \text{Li} + \square$, with x ranging from 0.00 to 0.90.

Key-words: $\text{Na}_{1-x}\text{Li}_x\text{MnFe}_2(\text{PO}_4)_3$, alluaudite structure type, solid-state reaction synthesis, crystal structure refinement, lithium crystal chemistry.

Introduction

Alluaudite designates a Na-, Mn-, Fe-bearing complex phosphate mineral, which is known to occur in granitic pegmatites, particularly in the beryl-columbite-phosphate subtype of the rare-element pegmatites, according to the classification of Černý (1991).

Moore (1971) determined the crystal structure of alluaudite in the monoclinic $C2/c$ orientation and derived the general structural formula $X(2)X(1)M(1)M(2)_2(\text{PO}_4)_3$, with $Z = 4$. The mineral displays chemical compositions varying between the two end-members, $\text{Na}_2\text{Mn}(\text{Fe}^{2+}\text{Fe}^{3+})(\text{PO}_4)_3$ and $\square\text{NaMnFe}^{3+}_2(\text{PO}_4)_3$, with Mn or some Ca re-

placing Na in the X(1) site, Fe^{2+} in M(1), and Mg or Mn in M(2), where \square represents a lattice vacancy in X(2). Depending on the cations found in the M(1) and M(2) sites, several mineral species have been defined and are included in the alluaudite mineral group (Moore & Ito, 1979).

During the past decade, many synthetic phosphates (Antenucci, 1992; Antenucci *et al.*, 1993 and 1995; Warner *et al.*, 1993; Leroux *et al.*, 1995 a and b; Lii & Ye, 1997; Korzenski *et al.*, 1998) and arsenates (Keller *et al.*, 1981; Riffel *et al.*, 1985; Khorari *et al.*, 1995; Lii & Ye, 1997; Khorari *et al.*, 1997a, b and c; Khorari *et al.*, 1998) with the alluaudite structure type have been reported in the literature, demonstrating the unex-

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Table 1. Unit cell parameters of the synthetic alluaudite-like compounds $\text{Na}_{1-x}\text{Li}_x\text{MnFe}_2(\text{PO}_4)_3$, calculated from their X-ray powder diffraction patterns.

<i>X</i>	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	β (°)	<i>Vol.</i> (Å ³)
0.00	12.001(2)	12.538(2)	6.405(1)	114.45(1)	877.3(2)
0.25	11.989(3)	12.516(3)	6.397(2)	114.56(2)	873.0(2)
0.50	11.983(4)	12.488(3)	6.390(2)	114.70(2)	868.6(3)
0.75	11.976(4)	12.467(3)	6.388(2)	114.86(2)	865.5(3)
0.85	11.975(3)	12.465(3)	6.388(2)	114.93(2)	864.7(2)
0.95 (*)	11.979(4)	12.468(4)	6.389(2)	114.95(3)	865.1(4)
1.00 (*)	11.977(4)	12.470(3)	6.386(2)	114.97(2)	864.5(3)

(*) : Alluaudite + $\text{Li}_3\text{Fe}^{2+}_2(\text{PO}_4)_3$.

pected versatility of the alluaudite framework. However, no synthesis of alluaudite-like phosphates containing Li has been reported to date, except the compound obtained by Fontan *et al.* (1973) by heating a natural ferrisicklerite. As a consequence, the crystallochemical role of Li in these compounds is still problematic.

In the environment of rare-element pegmatites, in which the formation of natural alluaudite takes place, the geochemical role of Li is essential. Taking into account the pegmatitic phosphates in particular, it must be emphasized that Li represents a significant component of some primary phases such as, for instance, the isomorphous triphylite-lithiophilite series $\text{Li}(\text{Fe},\text{Mn})\text{PO}_4$. Since alluaudite is a key mineral in the genetic evolution affecting the Fe-Mn bearing phosphates (Moore, 1971; Huvelin *et al.*, 1972; Fransolet, 1975; Fontan, 1978), it is of interest to investigate the

crystallochemical role of Li in the alluaudite structure. With this goal in mind, we decided to study the synthetic solid solution $(\text{Na}_{1-x}\text{Li}_x)\text{MnFe}_2(\text{PO}_4)_3$, starting from the pure end-member $\text{NaMnFe}_2(\text{PO}_4)_3$, a synthetic compound with a chemical composition corresponding to the idealized composition of the Buranga alluaudite (Fransolet, 1980).

Experimental procedure

Compounds of the $(\text{Na}_{1-x}\text{Li}_x)\text{MnFe}_2(\text{PO}_4)_3$ series were synthesized by solid-state reaction in air. Stoichiometric quantities of NaHCO_3 , Li_2CO_3 , MnO , $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{NH}_4\text{H}_2\text{PO}_4$ were dissolved in concentrated nitric acid, and the resulting solution was evaporated to dryness. The dry residue was progressively heated in a platinum crucible, at a heating rate of 500 °C/hour, to the

Table 2. Wet chemical analyses of synthetic alluaudite crystals.

	$\text{Na}_{1-x}\text{Li}_x\text{MnFe}_2(\text{PO}_4)_3$							
	<i>X</i> = 0.00		<i>X</i> = 0.25		<i>X</i> = 0.50		<i>X</i> = 0.75	
	1	2	1	2	1	2	1	2
P ₂ O ₅	44.41	3.001	44.17	2.975	44.49	2.972	44.39	2.957
Fe ₂ O ₃	30.05	1.805	30.17	1.807	30.96	1.838	30.87	1.828
FeO	3.62	0.242	3.53	0.235	3.81	0.251	3.29	0.217
MnO	15.93	1.077	16.74	1.128	16.02	1.071	17.51	1.167
Na ₂ O	6.11	0.945	4.71	0.727	3.11	0.476	1.60	0.244
Li ₂ O	-	-	0.78	0.250	1.59	0.505	2.28	0.722
Total	100.12		100.10		99.98		99.94	

1 : Weight %. Analyst : J.-M. Speetjens. 2 : Cation number calculated on the basis of 12 oxygens per formula unit.

congruent fusion temperature of was maintained for 15 to 20 crystals were obtained by quering in air.

X-ray powder diffraction patterns were recorded with a diffractometer equipped with a graphite monochromator using $\text{FeK}\alpha$ radiation ($\lambda = 1.937$ Å). The unit cell parameters (Table 1) were calculated by least-squares refinement program (Burnham, 1991), using the d -spacing with an internal standard of Pb

Chemical formula
Space group
a (Å)
b (Å)
c (Å)
 β (°)
Z
Radiation
 μ (mm⁻¹)
Size (mm)

Diffraction method
 $2\theta_{\text{max}}$ (°)
 $h_{\text{min}}, h_{\text{max}}$
 $k_{\text{min}}, k_{\text{max}}$
 $l_{\text{min}}, l_{\text{max}}$
Observed reflections
Unique reflections
 R_{int}
 R_{sigma}
Temperature (°C)
F(000)
Absorption coefficient

Parameters refined
Reflections used
Reflections weak
Extinction
 $R_1(F) (F_0 > 4\sigma)$
 R_1 (all)
 wR_2 (all)
Weighting parameter
GooF
 $(\Delta\rho)_{\text{max}}$ (e/Å³)
 $(\Delta\rho)_{\text{min}}$ (e/Å³)

Table 3. Data collections and single-crystal structure refinements.

Crystal Data		
Chemical formula	NaMnFe ₂ (PO ₄) ₃	Na _{0.5} Li _{0.5} MnFe ₂ (PO ₄) ₃
Space group	C2/c	C2/c
<i>a</i> (Å)	12.018(2)	11.988(2)
<i>b</i> (Å)	12.565(3)	12.500(3)
<i>c</i> (Å)	6.415(1)	6.392(1)
β (°)	114.33(3)	114.67(3)
<i>Z</i>	4	4
Radiation	MoK α	MoK α
μ (mm ⁻¹)	5.32	5.32
Size (mm)	0.3×0.15×0.15	0.4×0.15×0.1
Data Collection		
Diffractometer	Stoe IPDS	Stoe IPDS
2 θ_{\max} (°)	65.8	55.9
<i>h</i> _{min} , <i>h</i> _{max}	-18, 18	-15, 15
<i>k</i> _{min} , <i>k</i> _{max}	-19, 19	-16, 16
<i>l</i> _{min} , <i>l</i> _{max}	-9, 9	-8, 8
Observed reflections	6964	6182
Unique reflections	1584	1050
<i>R</i> _{int}	0.0291	0.0587
<i>R</i> _{sigma}	0.0198	0.0351
Temperature (°C)	20	20
F(000)	916	899
Absorption corrections	X-SHAPE	X-SHAPE
Structure determination and refinement		
Parameters refined	107	109
Reflections used	1458	1050
Reflections with <i>F</i> ₀ >4 σ (<i>F</i> ₀)	1427	894
Extinction	0.0098	0.0076
<i>R</i> ₁ (<i>F</i>) (<i>F</i> ₀ >4 σ (<i>F</i> ₀))	0.022	0.027
<i>R</i> ₁ (all)	0.026	0.034
<i>wR</i> ₂ (all)	0.065	0.066
Weighting parameter	0.0467	0.0446
GooF	1.086	0.980
($\Delta\rho$) _{max} (e/Å ³)	0.49	1.49
($\Delta\rho$) _{min} (e/Å ³)	-0.76	-0.67

congruent fusion temperature of 950 °C at which it was maintained for 15 to 20 hours. Alluaudite crystals were obtained by quenching the product in air.

X-ray powder diffraction patterns of the compounds were recorded with a diffractometer equipped with a graphite monochromator and using FeK α radiation ($\lambda = 1.9373$ Å). The unit cell parameters (Table 1) were calculated with the least-squares refinement program LCLSQ 8.4 (Burnham, 1991), using the *d*-spacings corrected with an internal standard of Pb(NO₃)₂.

The wet chemical analyses of the synthesized alluaudite crystals (Table 2) were performed on 65 to 70 mg of material. Atomic absorption spectrophotometry was used to determine Li, Na, Mn and total Fe, while P was measured by colorimetry. The Ungethüm method (Ungethüm, 1965) was used for the determination of Fe²⁺.

Two single crystals were selected for structure determination, displaying compositions close to NaMnFe₂(PO₄)₃ and Na_{0.5}Li_{0.5}MnFe₂(PO₄)₃ according to the wet chemical analyses (Table 2). The program Siemens SHELXTL, Version 5, was

Table 4. Unit cell parameters for NaMnFe₂(PO₄)₃ and Na_{0.5}Li_{0.5}MnFe₂(PO₄)₃.

NaMnFe ₂ (PO ₄) ₃			
	A	B	C
<i>a</i> (Å)	12.001(2)	12.018(2)	12.004(2)
<i>b</i> (Å)	12.538(2)	12.565(3)	12.533(4)
<i>c</i> (Å)	6.405(1)	6.415(1)	6.404(1)
<i>β</i> (°)	114.45(1)	114.33(3)	114.4(1)
Na _{0.5} Li _{0.5} MnFe ₂ (PO ₄) ₃			
	A	B	
<i>a</i> (Å)	11.983(4)	11.988(2)	
<i>b</i> (Å)	12.488(3)	12.500(3)	
<i>c</i> (Å)	6.390(2)	6.392(1)	
<i>β</i> (°)	114.70(2)	114.67(3)	

A: Refinement of X-ray powder diffraction pattern with program of Burnham (1991). B: Single-crystal analysis. C: Buranga pegmatite, calculated from X-ray powder diagram (Fisher, 1955).

Table 5. Positional (X, Y, Z), isotropic thermal (B) and site occupancy (N) parameters.

NaMnFe ₂ (PO ₄) ₃						
Site	Atom	X	Y	Z	B(Å ²)	N
A(2)'	Na	0	-0.0107(5)	1/4	3.5(2)	0.122(4)
A(1)	Na	1/2	0	0	3.83(6)	0.530(9)
M(1)	Mn	0	0.26237(3)	1/4	0.84(1)	0.484(8)
M(2)	Fe	0.28087(2)	0.65245(2)	0.37081(4)	0.55(1)	0.95(1)
P(1)	P	0	-0.28581(4)	1/4	0.43(2)	0.471(8)
P(2)	P	0.24182(3)	-0.10868(3)	0.13109(7)	0.50(1)	0.95(1)
O(1)	O	0.4533(1)	0.71552(9)	0.5332(2)	0.96(3)	1.00(2)
O(2)	O	0.0998(1)	0.63938(9)	0.2421(2)	1.20(4)	0.98(2)
O(3)	O	0.3289(1)	0.66403(9)	0.1033(2)	1.06(3)	0.99(2)
O(4)	O	0.1224(1)	0.39788(9)	0.3148(2)	1.31(4)	0.99(2)
O(5)	O	0.2251(1)	0.82225(9)	0.3177(2)	1.05(3)	1.00(2)
O(6)	O	0.3127(1)	0.50206(9)	0.3763(2)	1.30(4)	0.97(2)
Na _{0.5} Li _{0.5} MnFe ₂ (PO ₄) ₃						
A(2)'	Li	0	-0.0106(8)	1/4	4.6(4)	0.254(9)
	Na	0	-0.0106(8)	1/4	4.6(4)	0.086(8)
A(1)	Na	1/2	0	0	6.8(3)	0.27
M(1)	Mn	0	0.26410(6)	1/4	0.85(3)	0.454(8)
M(2)	Fe	0.28030(3)	0.65277(3)	0.36868(7)	0.48(2)	0.90(1)
P(1)	P	0	-0.28733(9)	1/4	0.46(4)	0.456(8)
P(2)	P	0.24184(6)	-0.10815(6)	0.1330(1)	0.47(3)	0.91(2)
O(1)	O	0.4525(2)	0.7164(2)	0.5324(4)	0.97(7)	0.97(2)
O(2)	O	0.0987(2)	0.6375(2)	0.2386(4)	1.18(7)	0.95(2)
O(3)	O	0.3284(2)	0.6643(2)	0.1022(4)	1.11(7)	0.95(2)
O(4)	O	0.1221(2)	0.3994(2)	0.3096(4)	1.50(8)	0.95(2)
O(5)	O	0.2244(2)	0.8221(2)	0.3180(4)	0.98(7)	0.94(2)
O(6)	O	0.3148(2)	0.5023(2)	0.3772(4)	1.27(8)	0.94(2)

used for determination and refinement of the crystal structures. Details on the data collection as well as on the structures determination and refinement are given in Table 3.

The crystal structures were solved in space group C2/c by direct methods, but for the final refinement, position parameters were used that are comparable to the structure determination of alluaudite by Moore (1971).

All structural parameters (Tables 4, 5 and 6), including the anisotropic displacement parameters (Table 7), were refined satisfactorily without contradictions to the *R*-values found in Table 3. It should be noted, however, that for Na_{0.5}Li_{0.5}MnFe₂(PO₄)₃, an electron density of 1.48 e/Å³ was detected on the (0, 0.501(3), 1/4) position. Unfortunately, it was not possible to include this site in the refinement procedure without very strong constraints, either for Li or Na.

Table 6. Selected interatomic distances.

	A
A(2)'-O(6) 2x	2.526
A(2)'-O(6) 2x	2.693
A(2)'-O(1) 2x	2.868
A(2)'-O(3) 2x	2.888
Mean	2.744
M(1)-O(4) 2x	2.175
M(1)-O(1) 2x	2.191
M(1)-O(3) 2x	2.246
Mean	2.204
P(1)-O(2) 2x	1.541
P(1)-O(1) 2x	1.545
Mean	1.543
P(2)-O(4)	1.525
P(2)-O(6)	1.530
P(2)-O(3)	1.553
P(2)-O(5)	1.557
Mean	1.541

The (Na_{1-x}Li_x)MnFe₂(PO₄)₃ compounds consist of green acicular crystals 2 mm in length, with a character-

Fig. 1. Projection of the crystal structure of Na_{0.5}Li_{0.5}MnFe₂(PO₄)₃. The PO₄ tetrahedra are densely shaded. The shaded M(1) octahedra are occupied by Mn, the unshaded M(2) octahedra by Fe. The large circles indicate Na on the A(1) site, and the small circles Li and Na on the A(2) site.

Table 6. Selected interatomic distances (Å) and angles (°). A. NaMnFe₂(PO₄)₃. B. Na_{0.5}Li_{0.5}MnFe₂(PO₄)₃. C. Difference.

	A	B	C		A	B	C
A(2)'-O(6) 2x	2.526(2)	2.491(2)	-0.035	A(1)-O(2) 2x	2.320(1)	2.275(2)	-0.045
A(2)'-O(6) 2x	2.693(2)	2.669(2)	-0.024	A(1)-O(4) 2x	2.333(1)	2.285(2)	-0.048
A(2)'-O(1) 2x	2.868(6)	2.866(9)	-0.002	A(1)-O(4) 2x	2.581(1)	2.587(2)	0.006
A(2)'-O(3) 2x	2.888(5)	2.878(8)	-0.010	A(1)-O(2) 2x	2.979(1)	2.966(2)	-0.013
Mean	2.744	2.726	-0.018	Mean	2.553	2.529	-0.024
M(1)-O(4) 2x	2.175(1)	2.164(2)	-0.011	M(2)-O(6)	1.925(1)	1.922(2)	-0.003
M(1)-O(1) 2x	2.191(1)	2.190(2)	-0.001	M(2)-O(2)	1.991(1)	1.989(2)	-0.002
M(1)-O(3) 2x	2.246(1)	2.249(2)	0.003	M(2)-O(3)	2.029(1)	2.018(2)	-0.011
Mean	2.204	2.201	-0.003	M(2)-O(5)	2.053(1)	2.051(2)	-0.002
				M(2)-O(1)	2.057(1)	2.046(2)	-0.011
				M(2)-O(5)	2.220(1)	2.203(2)	-0.017
				Mean	2.046	2.038	-0.008
P(1)-O(2) 2x	1.541(1)	1.537(2)	-0.004	O(2)-P(1)-O(2)	104.8(1)	104.6(2)	-0.2
P(1)-O(1) 2x	1.545(1)	1.544(2)	-0.001	O(2)-P(1)-O(1) 2x	108.54(7)	108.1(1)	-0.44
Mean	1.543	1.541	-0.002	O(1)-P(1)-O(1)	110.25(9)	109.9(2)	-0.35
				O(2)-P(1)-O(1) 2x	112.31(7)	113.1(1)	0.79
				Mean	108.98	108.9	-0.05
P(2)-O(4)	1.525(1)	1.518(2)	-0.007	O(3)-P(2)-O(5)	107.58(7)	107.1(1)	-0.48
P(2)-O(6)	1.530(1)	1.527(2)	-0.003	O(6)-P(2)-O(3)	108.70(7)	108.4(1)	-0.30
P(2)-O(3)	1.553(1)	1.551(2)	-0.002	O(4)-P(2)-O(5)	108.68(7)	108.9(1)	0.22
P(2)-O(5)	1.557(1)	1.552(2)	-0.005	O(6)-P(2)-O(5)	109.96(7)	109.9(1)	-0.06
Mean	1.541	1.537	-0.004	O(4)-P(2)-O(3)	110.62(8)	110.9(1)	0.28
				O(6)-P(2)-O(4)	111.23(7)	111.6(1)	0.37
				Mean	109.46	109.5	0.01

Results

The (Na_{1-x}Li_x)MnFe₂(PO₄)₃ alluaudite-like compounds consist of green acicular crystals up to 2 mm in length, with a characteristic brownish to

olive green pleochroism in transmitted light under the polarizing microscope.

The powder diffraction patterns show that pure alluaudite-like phases are obtained for x ranging from 0.00 to 0.85. In the range x = 0.95 -

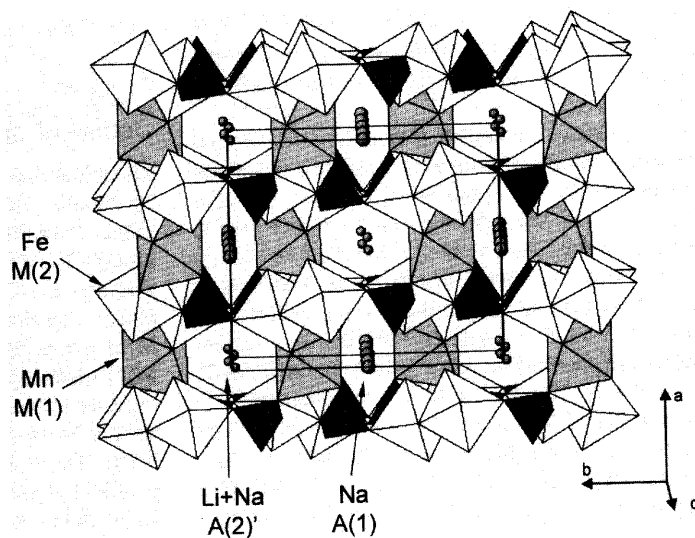


Fig. 1. Projection of the crystal structure of Na_{0.5}Li_{0.5}MnFe₂(PO₄)₃. The PO₄ tetrahedra are densely shaded. The shaded M(1) octahedra are occupied by Mn, the unshaded M(2) octahedra by Fe. The large circles indicate Na on the A(1) site, and the small circles Li and Na on the A(2)' site.

Table 7. Anisotropic displacement parameters (\AA^2).

NaMnFe ₂ (PO ₄) ₃							
Site	Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
A(2)'	Na	0.018(3)	0.042(4)	0.036(4)	0	0.001(2)	0
A(1)	Na	0.0430(8)	0.0074(5)	0.0273(7)	-0.0009(4)	-0.0231(6)	0.0004(5)
M(1)	Mn	0.0082(2)	0.0097(2)	0.0093(2)	0	0.0056(1)	0
M(2)	Fe	0.0055(1)	0.0061(1)	0.0055(1)	-0.00128(6)	0.00283(8)	-0.00118(6)
P(1)	P	0.0045(3)	0.0049(3)	0.0029(3)	0	0.0010(2)	0
P(2)	P	0.0060(2)	0.0046(2)	0.0044(2)	-0.0006(1)	0.0022(1)	-0.0006(1)
O(1)	O	0.0091(5)	0.0121(5)	0.0069(6)	-0.0023(4)	0.0027(4)	-0.0002(4)
O(2)	O	0.0093(5)	0.0105(5)	0.0145(6)	-0.0032(4)	0.0033(4)	0.0027(4)
O(3)	O	0.0148(6)	0.0099(5)	0.0065(6)	-0.0014(4)	0.0036(4)	-0.0023(4)
O(4)	O	0.0096(6)	0.0111(6)	0.0078(6)	-0.0001(4)	0.0073(5)	0.0012(4)
O(5)	O	0.0120(6)	0.0128(5)	0.0078(6)	0.0018(4)	0.0053(4)	-0.0010(4)
O(6)	O	0.0161(7)	0.0084(6)	0.0144(7)	0.0022(4)	0.0063(5)	-0.0024(4)

Na _{0.5} Li _{0.5} MnFe ₂ (PO ₄) ₃							
Site	Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
A(2)'	Li	0.030(4)	0.047(6)	0.046(6)	0	-0.002(4)	0
	Na	0.030(4)	0.047(6)	0.046(6)	0	-0.002(4)	0
A(1)	Na	0.065(3)	0.006(2)	0.055(3)	-0.001(2)	-0.052(3)	0.002(2)
M(1)	Mn	0.0090(3)	0.0095(4)	0.0091(4)	0	0.0061(3)	0
M(2)	Fe	0.0059(2)	0.0044(2)	0.0051(2)	-0.0008(2)	0.0031(2)	-0.0007(1)
P(1)	P	0.0056(5)	0.0036(6)	0.0037(6)	0	0.0012(4)	0
P(2)	P	0.0066(4)	0.0036(4)	0.0044(4)	-0.0003(3)	0.0026(3)	-0.0001(3)
O(1)	O	0.011(1)	0.011(1)	0.007(1)	-0.0015(8)	0.0036(8)	-0.0005(8)
O(2)	O	0.009(1)	0.010(1)	0.014(1)	-0.0039(9)	0.0030(9)	0.0010(8)
O(3)	O	0.017(1)	0.009(1)	0.006(1)	-0.0009(8)	0.0036(8)	-0.0019(8)
O(4)	O	0.012(1)	0.012(1)	0.022(1)	-0.001(1)	0.0087(9)	0.0008(8)
O(5)	O	0.011(1)	0.012(1)	0.007(1)	0.0015(8)	0.0045(8)	-0.0008(8)
O(6)	O	0.018(1)	0.007(1)	0.013(1)	0.0010(9)	0.0057(9)	-0.0018(8)

1.00, the alluaudite-type compounds are intimately mixed with Li₃Fe³⁺₂(PO₄)₃, a phase synthesized by Winand *et al.* (1990). Thus, the maximum Li-content of the solid solution (Na_{1-x}Li_x)MnFe₂(PO₄)₃ must be constrained between $x = 0.85$ and $x = 0.95$ (in this study we chose $x = 0.90$).

The unit cell parameters from our single-crystal study compare reasonably well with those calculated from the powder diffraction patterns (Table 1), and with those given by Fisher (1955) for the Buranga alluaudite (Table 4). The atomic coordinates, the interatomic distances and angles, as well as the anisotropic thermal parameters calculated from the single-crystal structure refinements, are presented in Table 5, Table 6, and Table 7, respectively. The comparison of the average P(1)-O and P(2)-O distances with those published by Moore (1971) for the Buranga alluaudite is quite satisfactory, and the O-P(1)-O and O-P(2)-O angles are very close to those of an ideal tetrahe-

dron. Figure 1 shows a polyhedral representation of the crystal structure of Na_{0.5}Li_{0.5}MnFe₂(PO₄)₃, approximately projected along [001].

Discussion

Outline of the alluaudite structure

The alluaudite crystal structure was first described by Moore (1971) for a natural sample from Buranga, Rwanda. This monoclinic structure (space group C2/c) consists of kinked chains of edge-sharing octahedra stacked parallel to the {101} plane. These chains are formed by a succession of M(2) octahedral pairs linked by highly distorted M(1) octahedra. Equivalent chains are connected together in the *y* direction by the P(1) and P(2) tetrahedra to form sheets oriented perpendicular to [010]. These connected sheets produce channels parallel to the *c* axis containing the distorted cubic X(1) site and the 4-coordinated X(2) site.

Table 8. Occupancies of the

Site	A(1)
Position	1/2, 0,
Wyckoff	4b
Channel	1
Coordination	4, 4+ 4+4
NaMnFe ³⁺ ₂ (PO ₄) ₃	Na
Na ₂ Mg ₂ Fe ³⁺ (PO ₄) ₃	Na
Na ₂ Cd ₂ Fe ³⁺ (PO ₄) ₃	Na
Na ₂ Cd ₂ Ga ³⁺ (PO ₄) ₃	Na
Na ₂ Cd ₂ Cr ³⁺ (PO ₄) ₃	Na
NaCdIn ³⁺ ₂ (PO ₄) ₃	Na
Cu _{1.35} Fe ₃ (PO ₄) ₃	□
NaCaCdMg ₂ (PO ₄) ₃	Na, C
NaMn ₃ (PO ₄)(HPO ₄) ₂	□
AgMn ₃ (PO ₄)(HPO ₄) ₂	□
Na ₃ In ₂ (PO ₄) ₃	Na
NaFe _{3.67} (PO ₄) ₃	Fe
NaMnFe ₂ (PO ₄) ₃	Na
Na _{0.5} Li _{0.5} MnFe ₂ (PO ₄) ₃	Na

During the past decade, a number of structural studies have been published for synthetic compounds exhibiting the alluaudite structure. These new studies, summarized by Moore (1995), clearly demonstrate the existence of additional cationic sites not reported by Moore (1971). These sites are localized in the channels of the structure, in addition to those of X(1) and X(2).

In order to avoid the confusion caused by the different sites of wyllieite (Moore & Moore, 1971) and bobfergusonite (Ercit *et al.*, 1995), we decided to use the nomenclature proposed by Leroux *et al.* (1995) for the crystallographic sites of the alluaudite structure. According to this nomenclature, the sites are relabelled A(1) and A(2), respectively. A(1) is localized in channel 1 running parallel to the *c* axis (0, 1/2, *z*), and A(2) lies in channel 2 (0, 0, *z*) and (1/2, 1/2, *z*).

The first of the new cationic sites was described in the alluaudite structure by Leroux *et al.* (1995b) and corresponds to (0, *y*, 1/4) with $y \approx 0$.

Table 8. Occupancies of the A crystallographic sites of phosphates exhibiting the alluaudite structure.

Site	A(1)	A(2)	A(2)'	A(1)'	A(1)''	Reference
Position	1/2, 0, 0	0, 0, 0	0, y, 1/4 (y ≈ 0)	0, y, 1/4 (y ≈ 1/2)	x, y, z	
Wyckoff	4b	4a	4e	4e	8f	
Channel	1	2	2	1	1	
Coordination	4, 4+2, 4+4	2, 4	4+2, 4+4	4	2, 4+2	
NaMnFe ³⁺ ₂ (PO ₄) ₃	Na	□	□	□	□	Moore, 1971
Na ₂ Mg ₂ Fe ³⁺ (PO ₄) ₃	Na	□	Na	□	□	Antenucci, 1992
Na ₂ Cd ₂ Fe ³⁺ (PO ₄) ₃	Na	□	Na	□	□	Antenucci, 1992
Na ₂ Cd ₂ Ga ³⁺ (PO ₄) ₃	Na	□	Na	□	□	Antenucci, 1992
Na ₂ Cd ₂ Cr ³⁺ (PO ₄) ₃	Na	□	Na	□	□	Antenucci, 1992
NaCdIn ³⁺ ₂ (PO ₄) ₃	Na	□	□	□	□	Antenucci <i>et al.</i> , 1993
Cu _{1.33} Fe ₃ (PO ₄) ₃	□	Cu	□	Cu	Cu	Warner <i>et al.</i> , 1993
NaCaCdMg ₂ (PO ₄) ₃	Na, Cd	□	Na, Ca	□	□	Antenucci <i>et al.</i> , 1995
NaMn ₃ (PO ₄)(HPO ₄) ₂	□	□	Na	□	H	Leroux <i>et al.</i> , 1995a
AgMn ₃ (PO ₄)(HPO ₄) ₂	□	□	Ag	□	H	Leroux <i>et al.</i> , 1995b
Na ₃ In ₂ (PO ₄) ₃	Na	□	Na	□	□	Lii & Ye, 1997
NaFe _{3,67} (PO ₄) ₃	Fe	□	Na	□	□	Korzenski <i>et al.</i> , 1998
NaMnFe ₂ (PO ₄) ₃	Na	□	Na	□	□	This work
Na _{0.5} Li _{0.5} MnFe ₂ (PO ₄) ₃	Na	□	Li, Na	□	□	This work

During the past decade, an increasing number of structural studies have been performed on synthetic compounds exhibiting the alluaudite structure. These new studies, summarized in Table 8, clearly demonstrate the existence of three new cationic sites not reported by Moore (1971). They are localized in the channels on different positions from those of X(1) and X(2).

In order to avoid the confusion with the X sites of wyllieite (Moore & Molin-Case, 1974) or bobfergusonite (Ericit *et al.*, 1986), which are more ordered minerals structurally related to alluaudite, we decided to use the nomenclature proposed by Leroux *et al.* (1995b) for the crystallographic sites of the alluaudite structure. According to this nomenclature, X(1) and X(2) are relabelled A(1) and A(2), respectively. A(1) is localized in channel 1 running along (1/2, 0, z) and (0, 1/2, z), and A(2) lies in channel 2 running along (0, 0, z) and (1/2, 1/2, z).

The first of the new cationic sites, recently described in the alluaudite structure, was named A(2)' by Leroux *et al.* (1995b). Its position corresponds to (0, y, 1/4) with y ≈ 0, in channel 2. Large

cations such as Na, Ag, and Ca are able to occupy this site, which exhibits 4+2 (distorted trigonal prism) or 4+4 coordination polyhedra (distorted gable disphenoid) (Antenucci, 1992; Antenucci *et al.*, 1995; Leroux *et al.*, 1995 a and b; Lii & Ye, 1997; Korzenski *et al.*, 1998). A(1)' corresponds to the A(4) site of Keller (1996), and is localized on (0, y, 1/4) with y ≈ 0.5, in channel 1. It contains Cu in a 4-coordinated square-planar environment (Warner *et al.*, 1993). The last A(1)'' site occurs on the general (x, y, z) position in channel 1, and accommodates 2-coordinated H or 4+2-coordinated Cu in a distorted trigonal prism (Warner *et al.*, 1993; Leroux *et al.*, 1995 a and b).

According to these new data, the following crystallochemical formula can be written for alluaudite-type compounds, [A(2)A(2)']₂[A(1)A(1)']₂M(1)M(2)₂[(P,As)O₄]₃. In contrast to the M sites, the A crystallographic sites can be partially or totally empty. The majority of alluaudites contain atoms on A(1) and A(2)', with vacancies on A(2), A(1)' and A(1)'' (Table 8). Nevertheless, when A(1)' or A(1)'' are occupied, as in the protonated alluaudite-like compounds, A(1) is empty

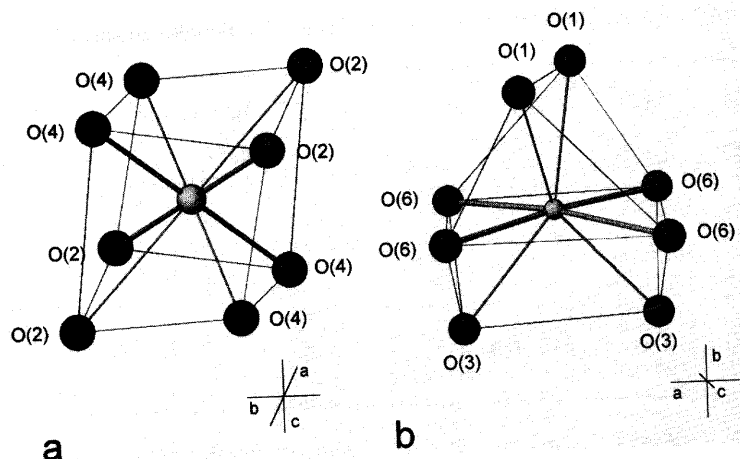


Fig. 2. Morphology of the A(1) (a) and the A(2)' (b) crystallographic sites in the synthetic alluaudite-like compound, $\text{NaMnFe}_2(\text{PO}_4)_3$.

because channel 1 is already filled by A(1)' or A(1)'' atoms (Warner *et al.*, 1993; Leroux *et al.*, 1995 a and b).

Crystal structure of $\text{NaMnFe}_2(\text{PO}_4)_3$

According to the positional parameters (Table 5), the A(2)', A(1), M(1) and M(2) crystallographic sites can be identified in the synthetic alluaudite-like compound $\text{NaMnFe}_2(\text{PO}_4)_3$. The coordination polyhedra morphologies of A(1) (distorted cube, Fig. 2a), M(1) (very distorted octahedron) and M(2) (distorted octahedron) are in good agreement with the data previously published in the literature (Moore, 1971; Antenucci *et al.*, 1995). However, the morphology of the A(2)' coordination polyhedron is rather unusual (Fig. 2b). The bond lengths (Table 6) indicate a (4+4) coordination for this site, with 4 short bonds (2×2.526 and 2×2.693 Å) and 4 long bonds (2×2.868 and 2×2.888 Å). This morphology corresponds to the gable disphenoid described by Moore (1981) in the wyllieite structure. It can be constructed by two trigonal prisms fused at a common square face after a rotation of 90° .

The occupancy factors for A(2)' and A(1) sites (Table 5) lead to the following cationic distribution, idealized for 1.0 Na and 1.0 \square : 0.81 \square and 0.19 Na on A(2)', 0.81 Na and 0.19 \square on A(1). This distribution of Na between A(2)' and A(1) is different from the one suggested by Moore (1971), who considers Na to be only localized on the A(1) site. It is interesting to note, however, that the simultaneous presence of Na on both the

A(2)' and A(1) sites has already been observed in the synthetic alluaudite-like compounds $\text{Na}_2\text{Cd}_2\text{M}^{3+}(\text{PO}_4)_3$, with $\text{M}^{3+} = \text{Fe}^{3+}$, Ga, Cr (Antenucci, 1992) and in $\text{Na}_3\text{In}_2(\text{PO}_4)_3$ (Lii & Ye, 1997).

Concerning the cationic distribution on the M sites, the occupancy factors (Table 5) indicate the presence of Mn on M(1) and of Fe on M(2). This ordered distribution is in good agreement with the M(1)-O and M(2)-O average distances given in Table 6, distances which are very close to the interatomic Mn^{2+} -O (2.23 Å) and Fe^{3+} -O (2.05 Å) distances (Shannon, 1976). The bond valence sums for these sites have also been calculated using the empirical parameters of Brown & Altermatt (1985). According to these authors, the bond valence, s , associated with the bond length, R , is given by the equation: $s = \exp[(R_0 - R)/0.37]$, where R_0 is 1.790 for Mn^{2+} and 1.759 for Fe^{3+} . Ideally, the bond valence sum should equal the mean valence of the cation in the crystallographic site. For pure Mn^{2+} occupation on M(1), the bond valence sum ($\Sigma_s = 1.97$) is very close to the ideal value, but for pure Fe^{3+} on M(2), the bond valence sum ($\Sigma_s = 2.84$) is slightly lower than the expected value. This feature can be explained by the presence of significant amounts of Fe^{2+} on the M(2) site, as detected by the wet chemical analysis (Table 2).

Finally, it is interesting to note that the intense brownish to olive green pleochroism observed in transmitted light probably results from an optically induced intervalence charge transfer between Fe^{2+} and Fe^{3+} in the M(2) octahedra (Burns, 1970).

Crystallochemical role of Li

From the crystal structure refinement of the alluaudite-like compound $\text{NaMnFe}_2(\text{PO}_4)_3$ (Table 5), it is evident that Li occupies the 8-fold coordinated A(2)' site, exhibiting a morphology as that of the A(2)' site in the alluaudite-like phase $\text{NaMnFe}_2(\text{PO}_4)_3$. The occupancy factors lead to the following distribution: 0.44 \square , 0.42 Li and 0.14 Na on A(2)', 0.56 \square and 0.44 Na on A(1). Consequently, the substitution $\text{Na} + \text{Na} \rightarrow \text{Li} + \square$ can be considered.

The electron density distribution on the A(2)' site (0.501(3), $1/4$) position can be compared with the A(1)' site, but it was not observed in this site in the refinement procedure.

The cationic distribution in $\text{NaMnFe}_2(\text{PO}_4)_3$ is similar to the distribution observed in the synthetic $\text{NaMnFe}_2(\text{PO}_4)_3$ compound. The occupancy factors for Mn on M(1) and Fe on M(2) are in good agreement with the theoretical value, whereas the occupancy factor for Fe on M(2) is significantly lower, probably indicating the presence of Fe^{2+} on the M(2) site.

A rather unusual feature of the crystal structure is the occurrence of Li on the large 8-fold coordinated A(2)' site. According to Wenger & Armbruster (1991), Li generally occurs on 6-fold coordination. However, it has been pointed out that Li is situated in an 8-fold coordinated site in nambulite, $(\text{Li},\text{Na})\text{MnPO}_4$. The limited occupancy of Li on the A(2)' site is probably due to the very long mean Li-O distance (2.726 Å). This phenomenon has also been observed in other Li-bearing alluaudite-like compounds. The mean Li-O distances in LiMnPO_4 (2.154 Å) (Finger & Rapp, 1991), LiMnPO_4 (2.166 Å) (Finger & Rapp, 1990), are significantly shorter than the mean Li-O distance in ferrisicklerite, LiMnPO_4 (2.222 Å) (Alberti, 1976). The occupancy of Li on the A(2)' site is also in good agreement with the data published by Wenger & Armbruster (1991). They have underlined the preference of Li for the 8-fold coordinated A(2)' site for distorted (4+2)-coordination sites.

Crystallochemical role of Li

From the crystal structure refinement of the alluaudite-like compound $\text{Na}_{0.5}\text{Li}_{0.5}\text{MnFe}_2(\text{PO}_4)_3$ (Table 5), it is evident that Li occupies the (4+4)-coordinated A(2)' site, exhibiting the same morphology as that of the A(2)' site of the alluaudite-like phase $\text{NaMnFe}_2(\text{PO}_4)_3$. The occupancy factors lead to the following idealized cationic distribution: 0.44 \square , 0.42 Li and 0.14 Na on A(2)', 0.56 \square and 0.44 Na on A(1). A comparison with the cationic distribution in $\text{NaMnFe}_2(\text{PO}_4)_3$ suggests a replacement of a vacancy by Li on the A(2)' site, and of Na by a vacancy on the A(1) site. Consequently, the substitution mechanism $\square + \text{Na} \rightarrow \text{Li} + \square$ can be considered.

The electron density detected on the (0, 0.501(3), $\frac{1}{4}$) position can be attributed to Li on the A(1)' site, but it was not possible to include this site in the refinement procedure.

The cationic distribution on the M sites is similar to the distribution observed in the synthetic $\text{NaMnFe}_2(\text{PO}_4)_3$ compound, with Mn on M(1) and Fe on M(2). The bond valence sum for pure Mn^{2+} occupation on M(1) ($\Sigma_s = 1.99$) is close to the theoretical value, whereas the bond valence sum for pure Fe^{3+} on M(2) ($\Sigma_s = 2.89$) is significantly lower, probably indicating the presence of Fe^{2+} on the M(2) site.

A rather unusual feature of this structure is the occurrence of Li on the large, (4+4)-coordinated A(2)' site. According to Wenger & Armbruster (1991), Li generally occurs on sites with a 4, 5 or 6-fold coordination. However, these authors point out that Li is situated in an 8-coordinated polyhedron in nambulite, $(\text{Li},\text{Na})\text{Mn}_4\text{Si}_5\text{O}_{14}\text{OH}$. The limited occupancy of Li on the A(2)' site is probably due to the very long mean interatomic Li-O distance (2.726 Å). This phenomenon has already been observed in other Li-bearing phosphates. The mean Li-O distances in triphylite, LiFePO_4 (2.154 Å) (Finger & Rapp, 1970), and in lithiophilite, LiMnPO_4 (2.166 Å) (Geller & Durand, 1960), are significantly shorter than the mean Li-O distance in ferrisicklerite, $\text{Li}_{1-x}(\text{Fe}^{3+},\text{Mn}^{2+})\text{PO}_4$ (2.222 Å) (Alberti, 1976). The morphology of the A(2)' site is also in good agreement with the data published by Wenger & Armbruster (1991) who have underlined the preference of octahedral Li for distorted (4+2)-coordinated crystallographic sites.

Morphology of the A(1) and the A(2)' (b) crystallographic sites in the synthetic alluaudite-like compound, $\text{NaMnFe}_2(\text{PO}_4)_3$.

has already been observed in alluaudite-like compounds with $\text{M} = \text{Fe}^{3+}, \text{Ga}, \text{Cr}$ (Antenore & Ye, 1992).

The distribution on the M sites (Table 5) indicates the presence of Fe on M(2). This is in good agreement with the bond lengths given in Table 6, which are very close to the values for Fe^{3+} -O (2.05 Å) (Finger & Rapp, 1970). The bond valence sum for Fe^{3+} on M(2) has also been calculated (Finger & Armbruster, 1991) and is lower than the expected value for Fe^{3+} (2.89), which can be explained by the presence of Fe^{2+} on the M(2) site. The wet chemical analysis

shows that the intense dichroism observed in the synthetic alluaudite-like compounds results from an optical charge transfer between the M(2) octahedra (Burns,

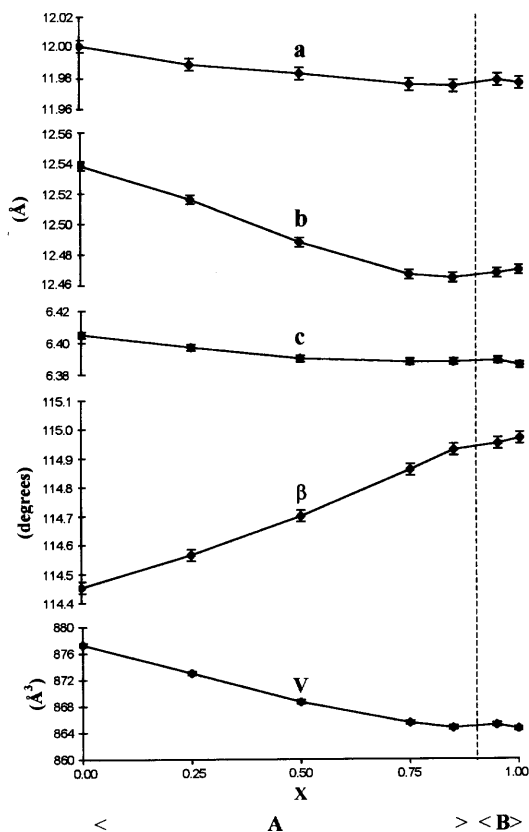


Fig. 3. Variation of the unit cell parameters in the synthetic alluaudite-like compounds, $\text{Na}_{1-x}\text{Li}_x\text{MnFe}_2(\text{PO}_4)_3$. A: pure alluaudite; B: alluaudite + $\text{Li}_3\text{Fe}^{3+}_2(\text{PO}_4)_3$.

Variation of the unit cell parameters

The unit cell parameters of $\text{Na}_{1-x}\text{Li}_x\text{MnFe}_2(\text{PO}_4)_3$ calculated here (Table 1) show a regular decrease versus x , resulting from the replacement of Na by Li in the alluaudite structure (Fig. 3). For $x \geq 0.90$, the constant values of the unit cell parameters indicate that additional Li could not be incorporated in the structure, which implies the crystallization of additional $\text{Li}_3\text{Fe}^{3+}_2(\text{PO}_4)_3$.

The decrease of the unit cell parameters can be correlated with the variations of bond distances induced by the incorporation of Li into the alluaudite structure. The differences between the bond lengths of $\text{NaMnFe}_2(\text{PO}_4)_3$ and $\text{Na}_{0.5}\text{Li}_{0.5}\text{MnFe}_2(\text{PO}_4)_3$, presented in Table 6 (column C), clearly show that significant variations in the

bond distances occur for the A(1) and A(2)' crystallographic sites. The most important variations have been observed for the A(1)-O(2) and A(1)-O(4) bonds, forming a square parallel to the *b* axis (Fig. 2a). This feature explains the significant decrease in the *b* parameter (Fig. 3). In the same way, the smaller variation of the *a* and *c* unit cell parameters is related to the shortening of the A(2)'-O(6) bonds, forming a square parallel to (010) (Fig. 2b).

Conclusions

This paper reports the first synthesis of the alluaudite-like compound $\text{NaMnFe}_2(\text{PO}_4)_3$, a compound which is chemically similar to the natural alluaudite from Buranga, Rwanda. The synthesis of solid solutions, with a progressive replacement of Na by Li, leads to a better understanding of the crystallochemical role of Li in the alluaudite structure. Lithium is exclusively localized in channel 2, on the (4+4)-coordinated A(2)' site occurring on a $(0, y, 1/4)$ ($y \approx 0$) position. Despite the unusually long Li-O distances, lithium can be inserted up to 90 atomic % in this site following the substitution mechanism $\square + \text{Na} \rightarrow \text{Li} + \square$.

Finally, it should be pointed out that the morphology of the A(1) and A(2)' distorted crystallographic sites resembles the morphology of the distorted cubic site of the garnet structure. This observation tends to confirm the close relationship between the alluaudite and the garnet structures, as already pointed out by Moore & Molin-Case (1974), and recently demonstrated by the existence of a garnet-alluaudite transition (Khorari *et al.*, 1995).

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References

- Alberti, A. (1976): The crystal structure of ferrisicklerite, $\text{Li}_{1-x}(\text{Fe}^{3+}, \text{Mn}^{2+})\text{PO}_4$. *Acta Cryst.*, **B32**, 2761-2764.
- Antenucci, D. (1992): Synthèse et cristallographie de composés à structure alluaudite. Incidences dans les processus d'altération des phosphates Fe-Mn des pegmatites granitiques. Unpublished Ph. D. Thesis, Univ. Liège, 259 p.
- Antenucci, D., Fransolet, A.-M., Miehé, G., Tarte, P. (1995): Synthèse et cristallographie de $\text{NaCaCdMg}_2(\text{PO}_4)_3$, phosphate nouveau à structure alluaudite sans cation trivalent. *Eur. J. Mineral.*, **7**, 175-181.
- Antenucci, D., Miehé, G., Tarte, P., Schmahl, W.W., Fransolet, A.-M. (1993): Combined X-ray Rietveld, infrared and Raman study of a new synthetic variety of alluaudite, $\text{NaCdIn}_2(\text{PO}_4)_3$. *Eur. J. Mineral.*, **5**, 207-213.
- Brown, I.D. & Altermatt, D. (1985): Bond-valence parameters obtained from a systematic analysis of the inorganic crystal structure database. *Acta Cryst.*, **B41**, 244-247.
- Burnham, C.W. (1991): LCLSQ version 8.4, last-squares refinement of crystallographic lattice parameters. Dept. of Earth & Planetary Sciences, Harvard University.
- Burns, R.G. (1970): Mineralogical applications of crystal field theory. Cambridge University Press, 224 p.
- Černý, P. (1991): Rare-element granitic pegmatites. I. Anatomy and internal evolution of pegmatite deposits. *Geosci. Canada*, **18**(2), 49-67.
- Ercit, T.S., Hawthorne, F.C., Černý, P. (1986): The crystal structure of bobfergusonite. *Can. Mineral.*, **24**, 605-614.
- Finger, L.W. & Rapp, G.R. (1970): Refinement of the structure of triphylite. *Carnegie Inst. Year book*, **68**, 290-293.
- Fisher, D.J. (1955): Alluaudite. *Am. Mineral.*, **40**, 1100-1109.
- Fontan, F. (1978): Etude minéralogique et essais expérimentaux sur des phosphates de fer et de manganèse des pegmatites des Jebilet (Maroc) et des Pyrénées (France). Unpublished Ph. D. Thesis, Univ. Paul-Sabatier, Toulouse, 250 p.
- Fontan, F., Orliac, M., Permingeat, F. (1973): Transformation, par voie thermique, d'une ferrisicklerite en une alluaudite lithique. *C. R. Acad. Sci. Paris, ser. D*, **276**, 877-879.
- Fransolet, A.-M. (1975): Etude minéralogique et pétrologique des phosphates des pegmatites granitiques. Unpublished Ph. D. Thesis, Univ. Liège, 333 p.
- (1980): The eosphorite-childrenite series associated with the Li-Mn-Fe phosphate minerals from the Buranga pegmatite, Rwanda. *Mineral. Mag.*, **43**, 1015-1023.
- Geller, S. & Durand, J.L. (1960): Refinement of the structure of LiMnPO_4 . *Acta Cryst.*, **13**, 325-331.
- Huvelin, P., Orliac, M., Permingeat, F. (1972): Ferrialludaudite calcifère de Sidi-Bou-Othmane (Jebilet, Maroc). *Notes Serv. géol. Maroc*, **32**, 241, 35-49.
- Keller, P. (1996): Strukturbestimmung von neuen Mineralen und anorganischen Verbindungen. in "Fakultät Geo- und Biowissenschaften, Universität Stuttgart", K. Pfizenmaier & H. Seyfried, ed. 47-48.
- Keller, P., Riffel, H., Zettler, F., Hess, H. (1981): $\text{AgCo}_3\text{H}_2(\text{AsO}_4)_3$ und $\text{AgZn}_3\text{H}_2(\text{AsO}_4)_3$. Darstellung und Kristallstruktur. Ein weiterer neuer Arsenat-Strukturtyp. *Z. anorg. Allg. Chem.*, **474**, 123-134.
- Khorari, S., Rulmont, A., Tarte, P. (1995): Structure of the $\text{NaCa}_2\text{M}^{2+}_2(\text{AsO}_4)_3$ (M = Fe, Mn) series: experimental evidence of a new possible polymorphism. *J. Solid State Chem.*, **134**, 273.
- Khorari, S., Rulmont, A., Tarte, P. (1997a): Na $\text{Ca}_2\text{M}^{2+}_2(\text{AsO}_4)_3$ (M = Fe, Mn): evidence of cationic substitution polymorphism. *J. Solid State Chem.*, **134**, 273.
- Khorari, S., Rulmont, A., Tarte, P., Gilbert, B. (1997b): Na $\text{Ca}_2\text{M}^{2+}_2(\text{AsO}_4)_3$ (M = Fe, Mn): the complex arsenate Na $\text{Ca}_2\text{M}^{2+}_2(\text{AsO}_4)_3$ like structure of the $\text{NaCa}_2\text{M}^{2+}_2(\text{AsO}_4)_3$ series. *J. Solid State Chem.*, **134**, 273.
- (1998): Influence of the $\text{NaCa}_2\text{M}^{2+}_2(\text{AsO}_4)_3$ transition on the alluaudite structure. *J. Solid State Chem.*, **134**, 273.
- Korzenski, M.B., Schimek, M., Tarte, P. (1998): Hydrothermal synthesis and characterization of a new phosphate, $\text{NaFe}_{3.67}(\text{PO}_4)_2(\text{HPO}_4)$ alluaudite structure type. *J. Solid State Chem.*, **134**, 273.
- Leroux, F., Mar, A., Payen, A., Piffard, Y. (1995a): $\text{NaMn}_3(\text{PO}_4)(\text{HPO}_4)_2$ alluaudite structure type. *J. Solid State Chem.*, **117**, 240-246.
- Leroux, F., Mar, A., Guyon, J. (1995b): Cation substitution in the alluaudite structure. *J. Solid State Chem.*, **117**, 240-246.
- Lii, K.-H. & Ye, J. (1997): Crystal structure of $\text{Na}_3\text{In}_2(\text{PO}_4)_3$ and its synthetic modifications. *J. Solid State Chem.*, **131**, 298-308.
- Moore, P.B. (1971): Crystal structure type. Contribution to the crystal structure of the garnet-alluaudite transition. *J. Solid State Chem.*, **131**, 298-308.

- le nouveau à structure al-
alent. *Eur. J. Mineral.*, **7**,
- Tarte, P., Schmahl, W.W.,
Combined X-ray Rietveld,
ly of a new synthetic var-
 $\text{Na}_2(\text{PO}_4)_3$. *Eur. J. Mineral.*,
- (1985): Bond-valence par-
systematic analysis of the
are database. *Acta Cryst.*,
- Q version 8.4, last-squares
graphic lattice parameters.
netary Sciences, Harvard
- ogical applications of crys-
ge University Press, 224 p.
ent granitic pegmatites. I.
evolution of pegmatite de-
18(2), 49-67.
- Černý, P. (1986): The crys-
sonite. *Can. Mineral.*, **24**,
- (1970): Refinement of the
arnegie Inst. Year book, **68**,
- ite. *Am. Mineral.*, **40**, 1100-
- minéralogique et essais ex-
osphates de fer et de man-
des Jebilet (Maroc) et des
published Ph. D. Thesis,
ulouse, 250 p.
- mingeat, F. (1973): Transfor-
ique, d'une ferrisicklérite en
C. R. Acad. Sci. Paris, ser.
- tude minéralogique et pétro-
s des pegmatites granitiques.
esis, Univ. Liège, 333 p.
- c-childrenite series associated
osphate minerals from the Bu-
nda. *Mineral. Mag.*, **43**, 1015-
- (1960): Refinement of the
Acta Cryst., **13**, 325-331.
- rmingeat, F. (1972): Ferri-al-
Sidi-Bou-Othmane (Jebilet,
éol. Maroc, **32**, 241, 35-49.
- bestimmung von neuen Min-
hen Verbindungen. in "Fakul-
enschaften, Universität Stutt-
& H. Seyfried, ed. 47-48.
- ettler, F., Hess, H. (1981):
d $\text{AgZn}_3\text{H}_2(\text{AsO}_4)_3$. Darstel-
ktur. Ein weiterer neuer Ar-
anorg. Allg. Chem., **474**, 123-
- Khorari, S., Rulmont, A., Cahay, R., Tarte, P. (1995):
Structure of the complex arsenates
 $\text{NaCa}_2\text{M}^{2+}_2(\text{AsO}_4)_3$ ($\text{M}^{2+} = \text{Mg, Ni, Co}$): first ex-
perimental evidence of a garnet-alluaudite revers-
ible polymorphism. *J. Solid State Chem.*, **118**, 267-
273.
- Khorari, S., Rulmont, A., Tarte, P. (1997a): The arsenates
 $\text{NaCa}_2\text{M}^{2+}_2(\text{AsO}_4)_3$ ($\text{M}^{2+} = \text{Mg, Ni, Co}$): influence
of cationic substitutions on the garnet-alluaudite
polymorphism. *J. Solid State Chem.*, **131**, 290-297.
- Khorari, S., Rulmont, A., Tarte, P., Miehe, G., Antenucci,
D., Gilbert, B. (1997b): Alluaudite-like structure of
the complex arsenate $\text{NaCaCdMg}_2(\text{AsO}_4)_3$. *J. Solid
State Chem.*, **131**, 298-304.
- Khorari, S., Rulmont, A., Tarte, P. (1997c): Alluaudite-
like structure of the arsenate $\text{Na}_3\text{In}_2(\text{AsO}_4)_3$. *J.
Solid State Chem.*, **134**, 31-37.
- – (1998): Influence of cationic substitutions in
 $\text{Na}_3\text{Fe}_2(\text{AsO}_4)_3$: transition from the garnet to the
alluaudite structure. *J. Solid State Chem.*, **137**, 112-
118.
- Korzenski, M.B., Schimek, G.L., Kolis, J.W., Long, G.J.
(1998): Hydrothermal synthesis, structure, and
characterization of a mixed-valent iron (II/III)
phosphate, $\text{NaFe}_{3.67}(\text{PO}_4)_3$: a new variation of the
alluaudite structure type. *J. Solid State Chem.*, **139**,
152-160.
- Leroux, F., Mar, A., Payen, C., Guyomard, D., Verbaere,
A., Piffard, Y. (1995a): Synthesis and structure of
 $\text{NaMn}_3(\text{PO}_4)(\text{HPO}_4)_2$, an unoxidized variant of the
alluaudite structure type. *J. Solid State Chem.*, **115**,
240-246.
- Leroux, F., Mar, A., Guyomard, D., Piffard, Y. (1995b):
Cation substitution in the alluaudite structure type :
synthesis and structure of $\text{AgMn}_3(\text{PO}_4)(\text{HPO}_4)_2$. *J.
Solid State Chem.*, **117**, 206-212.
- Lii, K.-H. & Ye, J. (1997): Hydrothermal synthesis and
structure of $\text{Na}_3\text{In}_2(\text{PO}_4)_3$ and $\text{Na}_3\text{In}_2(\text{AsO}_4)_3$: syn-
thetic modifications of the mineral alluaudite. *J.
Solid State Chem.*, **131**, 131-137.
- Moore, P.B. (1971): Crystal chemistry of the alluaudite
structure type: Contribution to the paragenesis of
pegmatite phosphate giant crystals. *Am. Mineral.*,
56, 1955-1975.
- (1981): Complex crystal structures related to gla-
serite, $\text{K}_3\text{Na}(\text{SO}_4)_2$: evidence for very dense pack-
ings among oxysalts. *Bull. Minéral.*, **104**, 536-547.
- Moore, P.B. & Ito, J. (1979): Alluaudites, wyllieites, ar-
rojadites: crystal chemistry and nomenclature.
Mineral. Mag., **43**, 227-235.
- Moore, P.B. & Molin-Case, J. (1974): Contribution to
pegmatite phosphate giant crystal paragenesis: II.
The crystal chemistry of wyllieite, $\text{Na}_2\text{Fe}^{2+}_2\text{Al-}$
 $(\text{PO}_4)_3$, a primary phase. *Am. Mineral.*, **59**, 280-
290.
- Riffel, H., Keller, P., Hess, H. (1985): Die Kristallstruk-
tur von $\text{AgCu}_3\text{Cu}(\text{AsO}_4)_3$ und ihre strukturellen Be-
ziehungen zu $\text{AgCo}_3\text{H}_2(\text{AsO}_4)_3$ bzw. AgZn_3H_2-
 $(\text{AsO}_4)_3$. *Z. anorg. Allg. Chem.*, **530**, 60-68.
- Shannon, R.D. (1976): Revised effective ionic radii and
systematic studies of interatomic distances in
halides and chalcogenides. *Acta Cryst.*, **A32**, 751-
767.
- Ungethüm, H. (1965): Eine neue Methode zur Bestim-
mung von Eisen (II) in Gesteinen und Mineralen,
insbesondere auch in bitumenhaltigen Proben. *Z. f.
angewandte Geol.*, **11**(9), 500-505.
- Warner, T.E., Milius, W., Maier, J. (1993): Synthesis and
structure of $\text{Cu}_{1.35}\text{Fe}_3(\text{PO}_4)_3$ and $\text{Cu}_2\text{Mg}_3(\text{PO}_4)_3$:
new mixed valence compounds of the alluaudite
structure type. *J. Solid State Chem.*, **106**, 301-309.
- Wenger, M. & Armbruster, T. (1991): Crystal chemistry
of lithium: oxygen coordination and bonding. *Eur.
J. Mineral.*, **3**, 387-399.
- Winand, J.M., Rulmont, A., Tarte, P. (1990): Synthèse et
étude de nouveaux arsénates $(\text{M}^I)_3(\text{N}^{\text{III}})_2(\text{AsO}_4)_3$ et
de solutions solides $(\text{M}^I)_3(\text{N}^{\text{III}})_2(\text{AsO}_4)_x(\text{PO}_4)_{3-x}$ (M
= Li, Na; N = Fe, Sc, In, Cr). *J. Solid State Chem.*,
87, 83-94.

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