

The NaF–CaF₂–AlF₃ System: Structures of β -NaCaAlF₆ and Na₄Ca₄Al₇F₃₃

A. HEMON AND G. COURBION

*Laboratoire des Fluorures (UA 449), Faculté des Sciences,
Université du Maine, 72017 Le Mans Cedex, France*

Received July 18, 1989; in revised form September 19, 1989

The crystal structure of β -NaCaAlF₆ has been determined from X-ray powder diffraction data ($R_1 = 0.054$, $R_p = 0.102$). The cell is trigonal (Na₂SiF₆-type; SG *P* 321) with $a = 8.9295(9)$ Å, $c = 5.0642(2)$ Å, and $Z = 3$. This compound is isotypical with β -LiMnFeF₆. The α -NaCaAlF₆ phase is indexed in a monoclinic cell ($a = 8.738(3)$ Å, $b = 5.190(3)$ Å, $c = 20.342(9)$ Å, $\beta = 91.451(6)^\circ$). Na₄Ca₄Al₇F₃₃ is cubic (SG *I* $m\bar{3}m$) with $a = 10.781(3)$ Å and $Z = 2$. The crystal structure is refined from 182 reflections to $R = 0.039$ ($R_w = 0.031$). Aluminum and calcium octahedra build up a three-dimensional network [Ca₄Al₇F₃₃]⁴⁻ in which are inserted the Na⁺ ions. Finally, a comparison of the Na₄Ca₄Al₇F₃₃ structure with the Na₅Al₃F₁₄ and Na₃Sr₄Al₅F₂₆ structures is given. © 1990 Academic Press, Inc.

Introduction

Recent works on the NaF–CaF₂–AlF₃ system have been reported by Pfund and Zimmermann (1), Craig and Brown (2), and Baggio and Massiff (3). To summarize, three compounds have been isolated: (I) NaCaAlF₆ (high-temperature form) (1, 2), (II) NaCa_{1.5}AlF₇ (3) (called the NaCaAlF₆ low-temperature form in Refs. (1, 2)), and (III) NaCaAl₂F₉ (2), also formulated as NaCaAl_{1.75}F_{8.25} by Baggio and Massiff (3). As these compounds are difficult to prepare in the pure state no structural information is available. In a recent paper (4), one of us has reported the crystal structure of phase II, called Na₂Ca₃Al₂F₁₄, which exhibits a cubic symmetry ($a = 10.257$ Å, $Z = 4$, SG *I* 2₁3).

In order to obtain more information about phases I and III, the ternary system NaF–CaF₂–AlF₃ was reinvestigated by

means of solid-state synthesis and both hydrothermal and chloride flux growth techniques. In addition to the previously observed phases I and III, a low-temperature form of NaCaAlF₆ was found.

This paper is devoted to the structural determination of the low-temperature form of NaCaAlF₆ (β -form) and to the crystal structure of NaCaAl_{1.75}F_{8.25}, hereafter denoted Na₄Ca₄Al₇F₃₃. In addition cell parameters are proposed for the α -NaCaAlF₆ phase.

Experimental

Preparation

For solid-state synthesis, a mixture of elementary fluorides with the stoichiometric composition (NaCaAlF₆ and NaCaAl₂F₉ or NaCaAl_{1.75}F_{8.25}) was heated in sealed gold tubes with a vertical furnace allowing either

air quenching or natural cooling (about 200°C/hr).

For hydrothermal synthesis, two techniques have been used: (1) a low-temperature ($T < 220^\circ\text{C}$) and low-pressure ($P = 300$ bars) technique using a Teflon vessel in a Paar bomb for acid digestion and (2) a high-temperature ($300^\circ\text{C} < T < 750^\circ\text{C}$) and high-pressure ($P = 2000$ bars) technique using a sealed platinum tube in an autoclave (see Ref. (5) for technical details).

For chloride flux growth (6, 7), a mixture of chlorides and fluorides contained in a platinum crucible was heated, under argon atmosphere, in a vertical furnace and then slowly cooled using an Eurotherm 818 temperature programmer.

NaCaAlF_6 . Various attempts to prepare a phase with the composition NaCaAlF_6 in the solid state are summarized in Table I. It is clear that only the high-temperature form (α) can be prepared (not in the pure state) when the temperature is above 620°C . For temperatures below 620°C , the stable phase $\text{Na}_2\text{Ca}_3\text{Al}_2\text{F}_{14}$ always appears as the main product whatever the cooling mode.

However, in the temperature range 600 – 680°C , the partial substitution of the Ca^{2+} ion by Mn^{2+} ion stabilizes a phase $\text{NaCa}_x\text{Mn}_{(1-x)}\text{AlF}_6$ ($0 < x < 0.85$) related to trigonal Na_2SiF_6 -type, but above $x = 0.85$ a mixture of phases is obtained: mainly $\text{Na}_2\text{Ca}_3\text{Al}_2\text{F}_{14}$, " $\text{NaCa}_{0.85}\text{Mn}_{0.25}\text{AlF}_6$," and α - NaCaAlF_6 . Nevertheless, the evidence

for a low-temperature form of NaCaAlF_6 (β -form) is given and we have used hydrothermal synthesis to stabilize this metastable phase.

At high-temperature and pressure ($T = 350, 630, 720^\circ\text{C}$ and $P = 2000$ bars) crystals or powdered samples of $\text{Na}_2\text{Ca}_3\text{Al}_2\text{F}_{14}$, $\text{Na}_5\text{Al}_3\text{F}_{14}$, and AlF_3 are obtained from the composition NaCaAlF_6 in 40% HF. At low temperature (220°C) and pressure (300 bars), twinned crystals of β - NaCaAlF_6 are synthesized as well as small amounts of $\text{Na}_2\text{Ca}_3\text{Al}_2\text{F}_{14}$, $\text{Na}_5\text{Al}_3\text{F}_{14}$, CaF_2 , and AlF_3 (5 M solution of " NaCaAlF_6 ," in 40% HF for 6 days and then natural cooling of the furnace). Under the same conditions, the addition of a small quantity of MnF_2 (molar ratio $\text{Ca}/\text{Mn} = 78$) gives rise only to powder of β - NaCaAlF_6 , again with small amounts of $\text{Na}_5\text{Al}_3\text{F}_{14}$ and CaF_2 . Change of such experimental parameters as temperature, time, and HF concentration do not improve the last result. Thermal study of β - NaCaAlF_6 by DTA (Netsch 404S, $300^\circ\text{C}/\text{hr}$) shows an endothermic peak at $615(5)^\circ\text{C}$ corresponding to the decomposition of this metastable phase in $\text{Na}_2\text{Ca}_3\text{Al}_2\text{F}_{14}$ and α - NaCaAlF_6 .

The α - NaCaAlF_6 can also be prepared by dehydration of $\text{NaCaAlF}_6 \cdot \text{H}_2\text{O}$ (Pachnolite (8)) at temperatures above 340°C . This phase remains metastable in the temperature range 340 – 550°C and then decomposes into $\text{Na}_2\text{Ca}_3\text{Al}_2\text{F}_{14}$ and $\text{Na}_4\text{Ca}_4\text{Al}_7\text{F}_{33}$.

TABLE I
PHASES OBTAINED BY HEATING OF THE NaCaAlF_6 COMPOSITION

Temperature range	Main phase	Traces	Cooling mode ^a	Time
480–620°C	$\text{Na}_2\text{Ca}_3\text{Al}_2\text{F}_{14}$	$\text{Na}_5\text{Al}_3\text{F}_{14}$ $\text{Na}_4\text{Ca}_4\text{Al}_7\text{F}_{33}$ CaF_2	Q or NC	2–12 hr
620–730°C (melting point)	α - NaCaAlF_6	$\text{Na}_2\text{Ca}_3\text{Al}_2\text{F}_{14}$ CaF_2	NC Q	2–15 days

^a Q, air quenching; NC, natural cooling of the furnace.

$\text{Na}_4\text{Ca}_4\text{Al}_7\text{F}_{33}$. In the solid state, the Na CaAl₂F₉ or NaCaAl_{1.75}F_{8.25} composition leads to the same cubic phase with a small amount of AlF₃ ($T = 650^\circ\text{C}$ for 60 hr). Therefore this technique does not allow one to choose between the two formulations. Crystals of this phase, with spherical habit, have been obtained by the chloride flux method from a mixture of NaF + CaF₂ + 2AlF₃ + 6NaCl + 3ZnCl₂ cooled at 5°C/hr from 700°C . The following structural determination has allowed us to confirm the formulation $\text{Na}_4\text{Ca}_4\text{Al}_7\text{F}_{33}$.

X-Ray Data Collection and Characterization

NaCaAlF_6 . The X-ray powder diffraction pattern of β -NaCaAlF₆ allows one to identify an isotypic phase of NaMnCrF₆ (SG *P* 321, $Z = 3$, JCPDS diffraction files 29-1242 and 33-1235) related to the Na₂SiF₆ structure. β -NaCaAlF₆ can be indexed on a trigonal cell with $a = 8.9295(9)$ Å and $c = 5.0642(2)$ Å.

For α -NaCaAlF₆, the X-ray powder diffraction pattern is in agreement with JCPDS diffraction files 36-1498 and 38-779. However, some new lines exist in addition to those of the Na₂Ca₃Al₂F₁₄ impurity. Poor quality crystals, achieved by extended heating, allow only a cell characterization. Laue and precession photographs indicate a monoclinic symmetry with the cell parameters $a = 8.75$ Å, $b = 5.20$ Å, $c = 20.34$ Å, and $\beta = 91^\circ$. The observed reflection conditions— $0k0$, $k = 2n$; $00l$, $l = 4n$ —are consistent with the space groups $P 2_1/m$ and $P 2_1$ ($00l$, $l = 4n$, being a fortuitous condition). This proposed cell allows one to index the powder pattern with the following refined parameters: $a = 8.738(3)$ Å, $b = 5.190(3)$ Å, $c = 20.342(9)$ Å, and $\beta = 91.451(6)^\circ$. Table II includes the observed and calculated d spacings.

$\text{Na}_4\text{Ca}_4\text{Al}_7\text{F}_{33}$. The X-ray patterns of both powder and crystals are indexed with a cubic body-centered cell— $a = 10.780(3)$

Å—as reported by Baggio and Craig (JCPDS file 36-1497 and 38-778). The refined cell parameter obtained from 24 reflections by the double scan technique, on the crystal selected for X-ray intensity data collection on an AED2-Siemens Stoe four-circle diffractometer, is $a = 10.781(3)$ Å. The unique condition for the reflections observed ($h + k + l = 2n$) leads to the centric space groups $I m\bar{3}m$ and $I m\bar{3}$, and to the noncentric groups $I \bar{4}3m$, $I \bar{4}32$, $I \bar{2}13$, and $I 23$.

The experimental density of these compounds has been determined with the multi-volume pycnometer 1305 from Micromeritics (see Tables II, III, and V).

Structure Refinement

β -NaCaAlF₆. The structure of β -NaCaAlF₆ was solved from powder diffraction data analyzed by the Rietveld method (9). X-ray intensities were recorded, by step scan, on a Siemens D501 diffractometer with CuK α radiation (back graphite monochromator). A sample holder, described by MacMurdie *et al.* (10), was used to minimize the orientation effects; the conditions of data collection are given in Table III. The atomic coordinates were refined from the NaMnCrF₆ model (11) in the space group *P* 321. However, owing to the absence of the 001 line, observed medium in NaMnCrF₆, two different cationic distributions of Na⁺ and Ca²⁺ ions (close ionic radii) between the 3*e* and 3*f* sites were tested. The reliability factors are as follows:

site 3 <i>e</i> ($z = 0$)	Na ⁺	Ca ²⁺
site 3 <i>f</i> ($z = \frac{1}{2}$)	Ca ²⁺	Na ⁺
R_I	12.52	5.39
R_P	16.62	10.18
R_{WP}	18.98	11.83

The best result corresponds to an inverse distribution in relation to NaMnMF₆ phases ($M = \text{Cr}^{3+}$, Al^{3+} , Fe^{3+}). Table III combines the final positional and thermal parameters

TABLE II
OBSERVED AND CALCULATED d SPACINGS OF α -NaCaAlF₆ (CuK α RADIATION)

h	k	l	d_{obs}	d_{cal}	I_{obs}	h	k	l	d_{obs}	d_{cal}	I_{obs}
1	0	0	8.7334	8.7351	17	2	2	4	2.0325	2.0332	11
0	0	4	5.0866	5.0839	9	1	2	-6	2.0120	2.0123	12
1	0	-4	4.4447	4.4430	19	4	1	1	1.9994	1.9985	9
2	0	0	4.3667	4.3676	76	4	0	4	1.9886	1.9883	3
1	1	-3	3.7589	3.7492	3	2	2	-5	1.9673	1.9667	5
1	1	3	3.7048	3.7049	2	3	2	0	1.9380	1.9372	37
2	0	3	3.6304	3.6298	100	4	1	3	1.9171	1.9174	7
1	1	-4	3.3732	3.3751	41	1	2	-7	1.8953	1.8962	24
2	0	-4	3.3508	3.3552	45	2	1	-9	1.8894	1.8888	36
1	1	4	3.3336	3.3321	47	4	0	-6	1.8575	1.8573	4
2	0	4	3.2734	3.2722	12	3	1	-8	1.8165	1.8167	86
2	1	-3	3.0214	3.0205	8	3	1	8	1.7769	1.7770	14
3	0	0	2.9117	2.9117	34	5	0	0	1.7478	1.7470	5
2	1	-4	2.8168	2.8176	27	2	2	-8	1.6886	1.6876	7
2	1	4	2.7676	2.7679	12	1	3	2	1.6721	1.6725	6
0	2	0	2.5946	2.5949	5	1	2	9	1.6665	1.6665	10
3	0	-4	2.5545	2.5547	2	5	1	0	1.6565	1.6557	10
0	0	8	2.5405	2.5420	2	5	1	-2	1.6402	1.6405	24
3	0	4	2.4980	2.4995	16	5	0	-5	1.6190	1.6201	2
3	1	2	2.4506	2.4510	1	4	1	-8	1.5949	1.5963	13
1	0	8	2.4225	2.4243	10	4	2	4	1.5779	1.5783	7
3	0	-5	2.3976	2.3964	10	2	3	-3	1.5676	1.5682	7
3	1	3	2.3600	2.3609	17	1	0	-13	1.5462	1.5466	2
0	2	4	2.3110	2.3112	5	2	3	-4	1.5378	1.5376	6
3	1	4	2.2521	2.2519	11	2	1	-12	1.5240	1.5233	17
1	2	4	2.2287	2.2280	8	0	1	13	1.4982	1.4977	3
2	2	1	2.2150	2.2144	4	4	2	6	1.4878	1.4872	7
0	2	5	2.1862	2.1876	21	1	1	-13	1.4822	1.4822	9
4	0	-1	2.1772	2.1772	19	5	0	-8	1.4572	1.4571	5
3	1	5	2.1320	2.1329	21	5	1	-8	1.4030	1.4028	16
2	2	-4	2.0527	2.0526	10	1	1	-14	1.3865	1.3865	3
2	1	-8	2.0430	2.0423	16						

Note. $a = 8.738(3)$ Å, $b = 5.190(3)$ Å, $c = 20.342(9)$ Å, $\beta = 91.451(6)^\circ$; density: $d_{\text{obs}} = 2.96(4)$, $d_{\text{cal}} = 2.94$; $Z = 8$.

with the profile parameters and Table IV lists the main interatomic distances and angles. Figure 1 shows the observed and calculated patterns.

$\text{Na}_4\text{Ca}_4\text{Al}_7\text{F}_{33}$. Crystal data and experimental details used during the measurement are reported in Table V. All the calculations were performed using the SHELX-76 program (13). The intensities have been corrected for Lorentz polarization effects as well as for absorption. Aver-

age of equivalents, in the Laue group $m3m$, led to an R_{av} value of 0.051. Atomic scattering factors and dispersion correction factors were taken from Ref. (14). In the absence of heavy atoms, the structure was solved from the Tang option of direct methods in the space group $I m3m$. A solution was found with calcium and two aluminum ions located in $8c$, $2a$, and $12e$ sites, respectively. Successive refinements and Fourier maps located the fluorine and sodium atoms

TABLE III
CONDITIONS OF DATA COLLECTION AND REFINEMENT, ATOMIC, AND THERMAL
PARAMETERS FOR β -NaCaAlF₆

Symmetry	Trigonal				
Space group	<i>P</i> 321 (No. 150)				
Cell parameters	<i>a</i> = 8.9295(9) Å, <i>c</i> = 5.0642(2) Å, γ = 120°, <i>V</i> = 349.7(1) Å ³ , <i>Z</i> = 3				
Density	<i>d</i> _{obs} = 2.88(5); <i>d</i> _{cal} = 2.91				
2 θ range	10–140° ^a				
Step scan increment (2 θ)	0.04				
No. of reflections	444				
No. of structural parameters	30				
Profile parameters ^b	<i>U</i> ₁ = 0.22(2), <i>V</i> ₁ = -0.08(2), <i>W</i> ₁ = 0.144(4), <i>U</i> ₂ = 0.14(3), <i>V</i> ₂ = -0.005(50), <i>W</i> ₂ = 1.44(2), <i>C</i> = 0.006(2), <i>D</i> = -0.310(7)				
Zero point (2 θ)	0.214(2)				
Reliability factors (%)	<i>R</i> ₁ = 5.39, <i>R</i> _p = 10.18, <i>R</i> _{wp} = 11.84, <i>R</i> _E = 3.16				
Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq} (Å ²)
Ca	3 <i>e</i>	0.3720(3)	0	0	1.17(4)
Na	3 <i>f</i>	0.7145(6)	0	$\frac{1}{2}$	1.1 (1)
Al ₁	1 <i>a</i>	0	0	0	1.0 (1)
Al ₂	2 <i>d</i>	$\frac{1}{3}$	$\frac{2}{3}$	0.499(1)	1.4 (1)
F ₁	6 <i>g</i>	0.9136(5)	0.1041(6)	0.796(1)	1.4 (1)
F ₂	6 <i>g</i>	0.5541(5)	0.4101(6)	0.703(1)	2.0 (2)
F ₃	6 <i>g</i>	0.2517(6)	0.7771(7)	0.703(1)	1.3 (1)

^a Four excluded zones; Na₅Al₃F₁₄ and CaF₂ impurity.

^b Definition in (9).

TABLE IV
MAIN INTERATOMIC DISTANCES (Å) AND ANGLES (°) IN β -NaCaAlF₆

Ca octahedron (symmetry 2)		
Ca-F ₂ = 2 × 2.280(5)	F-Ca-F _{min} = 63.0(3)	F-F _{min} = 2.461(9)
Ca-F ₃ = 2 × 2.289(5)	F-Ca-F _{max} = 110.3(2)	F-F _{max} = 3.743(4)
Ca-F ₁ = 2 × 2.353(5)		
(Ca-F) = 2.308		
Na octahedron (symmetry 2)		
Na-F ₁ = 2 × 2.149(4)	F-Na-F _{min} = 66.5(2)	F-F _{min} = 2.518(8)
Na-F ₃ = 2 × 2.272(5)	F-Na-F _{max} = 104.7(3)	F-F _{max} = 3.403(5)
Na-F ₂ = 2 × 2.319(4)		
(Na-F) = 2.247		
Al ₁ octahedron (symmetry 32)		
Al ₁ -F ₁ = 6 × 1.801(6)	F-Al ₁ -F _{min} = 86.1(4)	F-F _{min} = 2.461(7)
	F-Al ₁ -F _{max} = 93.3(3)	F-F _{max} = 2.619(6)
Al ₂ octahedron (symmetry 3)		
Al ₂ -F ₂ = 3 × 1.793(6)	F-Al ₂ -F _{min} = 88.5(2)	F-F _{min} = 2.518(7)
Al ₂ -F ₃ = 3 × 1.814(6)	F-Al ₂ -F _{max} = 90.7(2)	F-F _{max} = 2.551(10)
(Al ₂ -F) = 1.803		

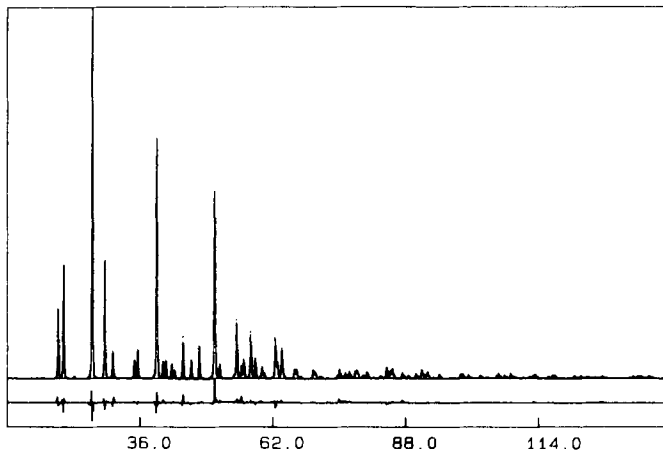


FIG. 1. Comparison of observed (····) and calculated (—) intensities for β -NaCaAlF₆. The difference pattern appears below at the same scale.

and led to $R = 0.12$ ($R_w = 0.11$) with isotropic thermal motion. At this stage of refinement, the structural formulation “Na₆Ca₄Al₇F₃₃” was not in agreement with neutral charge and the sodium atom had a ther-

mal motion factor of 4.16 \AA^2 ; moreover, in the difference synthesis, no new peaks appeared. However, the refinement of the occupation ratio of Na atom led to 0.084 instead of 0.125 and to a thermal motion of

TABLE V
CRYSTAL DATA AND CONDITIONS OF DATA COLLECTION AND
REFINEMENT FOR Na₄Ca₄Al₇F₃₃

Symmetry	Cubic
Space group	$I m\bar{3}m$ (No. 229)
Cell parameter	$a = 10.781(3) \text{ \AA}$, $V = 1253.07 \text{ \AA}^3$, $Z = 2$
Density	$d_{\text{obs}} = 2.83(4)$; $d_{\text{cal}} = 2.83$
Crystal volume (10^{-3} mm^3)	0.61
Radiation	MoK α (graphite monochromatized)
Aperture (mm)	4×4
Scanning mode	$\omega/2\theta$; 40 steps of $\Delta\omega^\circ$; $0.027 < \Delta\omega < 0.032$; time per step: 2 s
Profile fitting data analysis (12)	Isotropic linewidth, $\omega = (1.01 + 0.055 \tan \theta)^\circ$
Range registered	$2\theta_{\text{min}}-2\theta_{\text{max}}$: 5–60°; hkl_{max} 8 10 14
Absorption correction	Gauss method, $\mu = 13.94 \text{ cm}^{-1}$; $t_{\text{min}} = 0.85$, $t_{\text{max}} = 0.95$
Reflections measured:	
Total	2457
Independent	214 ($R_{\text{average}} = 0.051$) in $m\bar{3}m$
Used in refinement	182 ($F_0 > 9\sigma(F_0)$)
Number of refined parameters	21
Weighting scheme	$\omega = 22.76(\sigma^2(F))$
Maximum height in final Fourier difference map	$0.10e^{-}/\text{\AA}^3$

TABLE VI
 ATOMIC COORDINATES, ANISOTROPIC TEMPERATURE FACTORS ($U_{ij} \times 10^4$), AND $B_{eq}(\text{\AA}^2)$ FOR Na₄Ca₄Al₇F₃₃

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	$B^{eq}(\text{\AA}^2)$
Na ^a	12d	$\frac{1}{2}$	0	$\frac{1}{2}$	208(19)	254(14)	254(14)	0	0	0	1.88(12)
Ca	8c	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	109(3)	109(3)	109(3)	1(3)	1(3)	1(3)	0.86(2)
Al ₁	2a	0	0	0	82(7)	82(7)	82(7)	0	0	0	0.65(5)
Al ₂	12e	0.3298(1)	0	0	85(8)	97(5)	97(5)	0	0	0	0.73(5)
F ₁	6b	0	$\frac{1}{2}$	$\frac{1}{2}$	108(25)	376(19)	376(19)	0	0	0	2.26(16)
F ₂	48k	0.1159(1)	0.1159(1)	0.3363(2)	293(7)	293(7)	633(16)	103(7)	103(7)	-169(9)	3.21(8)
F ₃ ^b	48k	0.0239(5)	0.0239(5)	0.1633(4)	224(42)	224(42)	113(22)	-11(15)	-11(15)	-60(27)	1.48(28)

^a Refined occupation ratio: 0.084(1)/0.125.

^b Occupation ratio: 0.125/0.5.

1.85 \AA^2 , the reliability factor being $R = 0.10$ ($R_w = 0.09$). There are then eight Na atoms ($Z = 2$) and the compound formulation is finally Na₄Ca₄Al₇F₃₃, as reported by Baggio. The refinement leads to the reliability factors $R = 0.039$ and $R_w = 0.031$ when applying anisotropic thermal motion, the Na atoms filling at random two-thirds of the crystallographic site. The results are not absolutely satisfactory because of short interatomic distances and high thermal mo-

tion. Indeed the Al₁-F₃ = 1.762 \AA distance is smaller than the sum of the ionic radii—1.820 \AA —(15) as well as the Al-F distances observed in the other fluoaluminates and the thermal motion of the F₃ fluorine atom is very high— $B_{eq} = 6.0 \text{\AA}^2$. This probably indicates a structural disorder. Indeed, the final Fourier difference map shows a maximum peak of $0.25e^-/\text{\AA}^3$ (position: 0.038, 0.038, 0.16) around the F₃ fluorine atom; it corresponds to a fragmentation of site 12e

TABLE VII
 MAIN INTERATOMIC DISTANCES (\AA) AND ANGLES ($^\circ$) IN Na₄Ca₄Al₇F₃₃

Ca octahedron (symmetry $3m$)		
Ca-F ₂ = 6 × 2.246(1)	F ₂ -Ca-F ₂ = 6 × 83.17(7)	F ₂ -F ₂ = 2.982(2)
	F ₂ -Ca-F ₂ = 6 × 96.83(7)	F ₂ -F ₂ = 3.362(2)
	F ₂ -Ca-F ₂ = 3 × 180.0	
Al ₁ octahedron (symmetry $m\bar{3}m$)		
Al ₁ -F ₃ ^a = 6 × 1.798(4)	$\langle F_3\text{-Al}_1\text{-F}_3 \rangle = 12 \times 90.0$	$\langle F_3\text{-F}_3 \rangle = 2.543(8)$
	F ₃ -Al ₁ -F ₃ = 3 × 180.0	
Al ₂ octahedron (symmetry $4mm$)		
Al ₂ -F ₁ = 1.835(1)	F ₁ -Al ₂ -F ₂ = 4 × 87.73(8)	F ₁ -F ₂ = 2.497(1)
Al ₂ -F ₂ = 4 × 1.768(1)	F ₂ -Al ₂ -F ₃ = 4 × 89.91(5)	F ₂ -F ₂ = 2.499(3)
Al ₂ -F ₃ = 1.832(4)	$\langle F_2\text{-Al}_2\text{-F}_3 \rangle = 4 \times 92.22(6)$	$\langle F_2\text{-F}_3 \rangle = 2.595(5)$
$\langle Al_2\text{-F} \rangle = 1.790$	Ca-F ₂ -Al ₂ = 153.2(2)	
	Al ₂ -F ₁ -Na = 90.0	
	$\langle Al_1\text{-F}_3\text{-Al}_2 \rangle = 180.0$	
Na polyhedron (symmetry $42m$): bicapped cube		
	Na-F ₁ = 2 × 2.695(0)	
	Na-F ₂ = 8 × 2.601(1)	
	$\langle Na\text{-F} \rangle = 2.619$	

^a The F₃ atom fills at random on one-quarter of crystallographic site 48k.

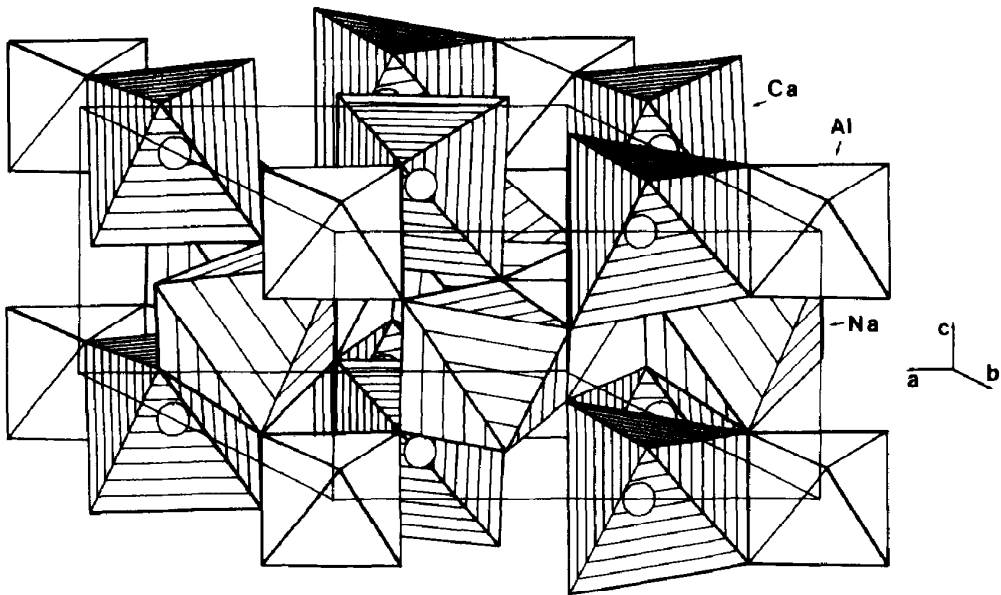


FIG. 2. Perspective view of β -NaCaAlF₆.

in a site 48k. The refinement of this proposal leads to a reliability factor lowering ($R = 0.033$, $R_w = 0.026$), to an interatomic distance Al₁-F₃ of 1.798(4) Å, and to a thermal motion of 1.48 Å² for the F₃ atom. The disorder of F₃ fluorine leads to the delocali-

zation of the other neighboring atoms but the attempts of refinement fail. The present structure must then be considered as an average structure for which final atomic and anisotropic thermal parameters are given in Table VI. Table VII lists the interatomic

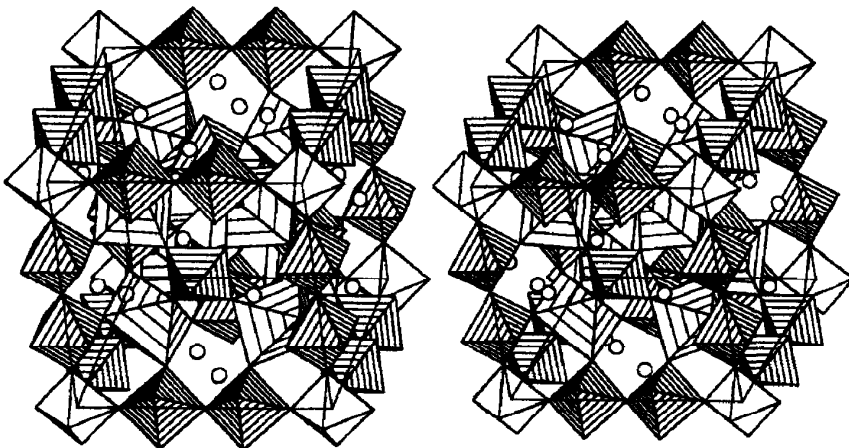


FIG. 3. Stereoview of the Na₄Ca₄Al₇F₃₃ structure (circles correspond to Na⁺ ions; Al octahedra are heavily shaded and unshaded; Ca octahedra are medium shaded).

distances and angles whereas Table VIII gives the mean Al-F distances for recent crystal structure determination of fluoaluminates. A list of F_O/F_C values can be obtained from the authors on request.

Structure Description and Discussion

β -NaCaAlF₆. β -NaCaAlF₆, of Na₂SiF₆ type, exhibits the same cationic distribution as β -LiMnFeF₆ (28); the bivalent cation fills the 3*e* site at level $z = 0$ whereas the alkaline cation fills the 3*f* site at level $z = \frac{1}{2}$, the smallest cation being in sites 1*a* and 2*d*. In this structure (Fig. 2) all the cations are octahedrally coordinated. One finds alternate layers of composition AlCa₃ at $z = 0$ and Al₂Na₃ at $z = \frac{1}{2}$. For the first layer each AlF₆

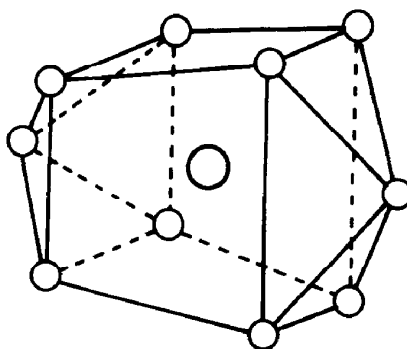


FIG. 4. Sodium polyhedron NaF₁₀: a bicapped cube.

octahedron shares three edges with CaF₆ octahedra to build up the AlCa₃ "clusters" which are not connected to each other. For the second layer, each AlF₆ octahedron

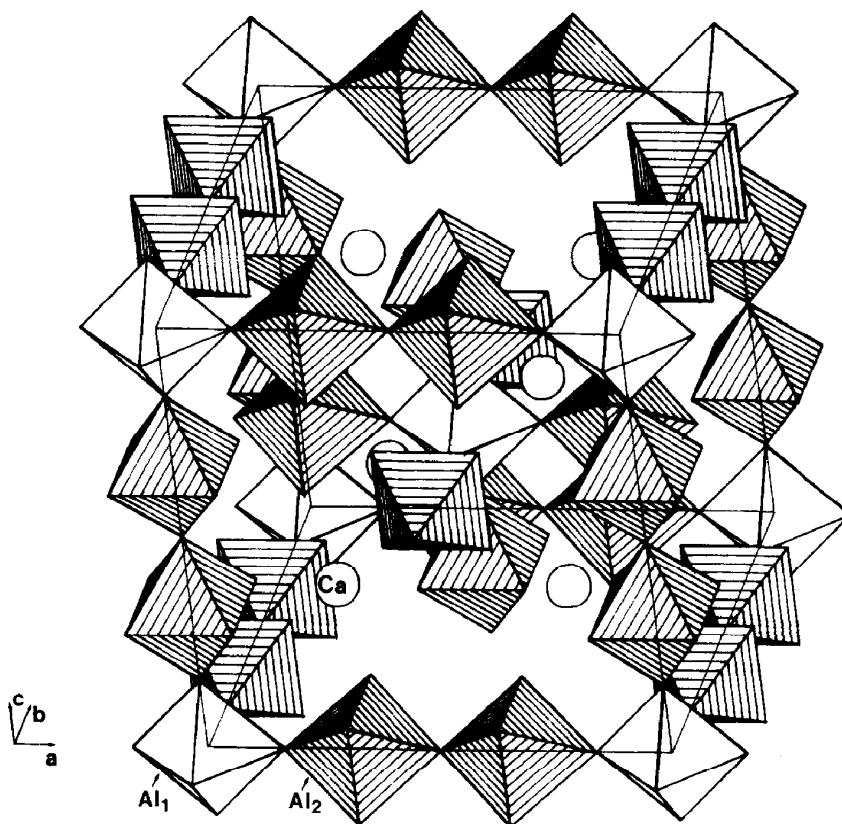


FIG. 5. Perspective view of the $[Al_7F_{33}]^{8-}$ network in Na₄Ca₄Al₇F₃₃.

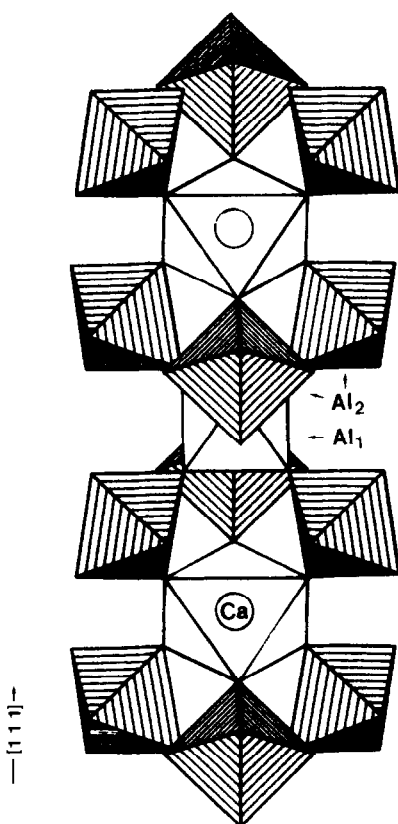


FIG. 6. Connection mode of $[Al_7F_{33}]^{8-}$ blocks by calcium octahedra along $[111]$ direction.

shares three edges with NaF_6 octahedra, each NaF_6 octahedron being connected to two AlF_6 octahedra, thus forming a 2D infinite layer Al_2Na_3 . The cationic distribution, between the $3e$ and $3f$ sites, is the opposite in relation to the compounds $NaMnMF_6$ ($M = Al^{3+}, Cr^{3+}, Fe^{3+}$) where the biggest cation Na^+ always fills the $3e$ site at the least dense level $z = 0$. In β - $NaCaAlF_6$, the sterical effect coming from the difference of ionic radii between M^+ and M^{2+} cations (1.02 and 1.00 Å for Na^+ and Ca^{2+} , respectively) is not significant enough to impose the cationic distribution; this is an electrostatic effect which favors the Na and Ca ordering between the layers (cationic charge +9 in each layer).

$Na_4Ca_4Al_7F_{33}$. The $Na_4Ca_4Al_7F_{33}$ struc-

ture is made from connected calcium and aluminum regular octahedra which share all their corners to give rise to a $[Ca_4Al_7F_{33}]^{4-}$ three-dimensional network in which the Na^+ ions are inserted (Fig. 3). The NaF_{10} polyhedron, which looks like a bicapped cube, is shown in Fig. 4. The aluminum octahedra build up infinite *trans*-chains running in the directions $[100]$, $[010]$, and $[001]$ with the sequence $Al_1-Al_2-Al_2-Al_1$ (Fig. 5). Thus, each Al_1 octahedron shares its corners with six Al_2 octahedra. These blocks of seven octahedra are connected in the $[111]$ -type direction by means of Ca octahedra as shown in Fig. 6; each Ca octahedra is then surrounded by six Al_2 octahedra (Figs. 6 and 7).

The special arrangement of aluminum octahedra in $Na_4Ca_4Al_7F_{33}$ can be compared to those found in others fluoaluminates structures like $Na_5Al_3F_{14}$ (21, 29) and $Na_3Sr_4Al_5F_{26}$ (30) for which the idealized units are shown in Fig. 8. Indeed, in each of these compounds, there exists a central octahedron, $AlF_{4/2}F_2$ or $AlF_{6/2}$, connected by corners to four or six octahedra rotated by 90° . Starting from isolated pentamers Al_5F_{26}

TABLE VIII

Compounds	SG	Site symmetry	(Al-F)	Refs.
$Na_4Ca_4Al_7F_{33}$	$Im\bar{3}m$	$m\bar{3}m$	1.798	This work
$TlAlF_4$	$P4/mmm$	$4/mmm$	1.82	16
K_2LiAlF_6	$R\bar{3}m$	$\bar{3}m$	1.813	17
		$\bar{3}m$	1.797	
Cs_2NaAlF_6	$R\bar{3}m$	$\bar{3}m$	1.81	18
$Sr_{10}Al_3F_{25}Cl$	$Fd\bar{3}m$	$\bar{3}m$	1.781	19
$RbAlF_4$	$P4/m\bar{b}m$	$4/m$	1.78	16
$KAlF_4$	$P4/m\bar{b}m$	$4/m$	1.795	20
$Na_5Al_3F_{14}$	$P4/nmc$	$4/m$	1.790	21
$Na_4Ca_4Al_7F_{33}$	$Im\bar{3}m$	$4mm$	1.790	This work
NH_4AlF_4	$I4c2$	4	1.80	16
$LiCaAlF_6$	$P\bar{3}1c$	32	1.800	22
$Na_2Ca_3Al_2F_{14}$	$I2_1\bar{3}$	3	1.804	4
$\alpha-AlF_3$	$R\bar{3}$	3	1.794	23
		3	1.801	
$K_2AlF_5 \cdot H_2O$	$Cmcm$	$2/m$	1.805	24
$Rb_2AlF_5 \cdot H_2O$	$Cmcm$	$2/m$	1.817	25
$\beta-AlF_3$	$Cmcm$	$2/m$	1.799	26
$Na_5Al_3F_{14}$	$P4/nmc$	$2/m$	1.80	21
		$2/m$	1.80	
$Cs_2NaAl_3F_{12}$	$R\bar{3}m$	$2/m$	1.80	27

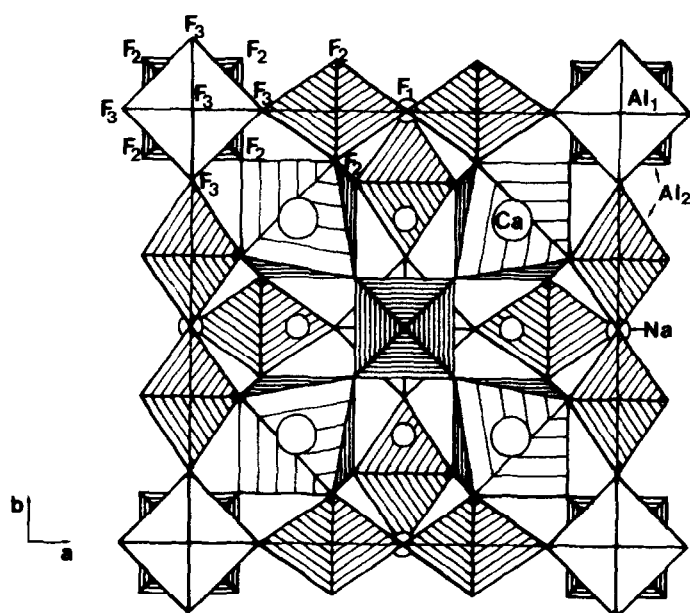
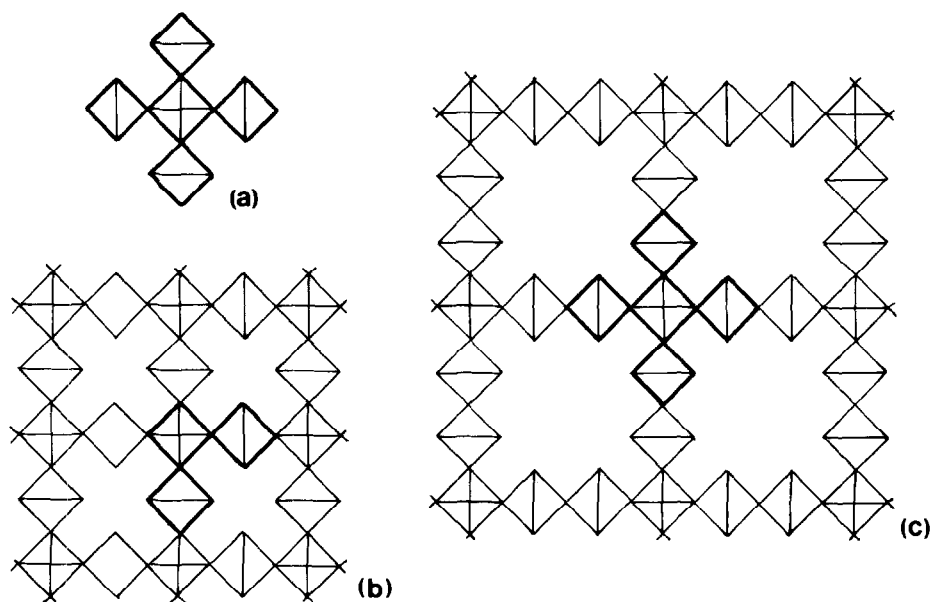
FIG. 7. (001) projection of Na₄Ca₄Al₇F₃₃.

FIG. 8. (a) Isolated unit $\text{AlF}_4[\text{Al}_4\text{F}_{22}] = \text{Al}_5\text{F}_{26}$ in $\text{Na}_3\text{Sr}_4\text{Al}_5\text{F}_{26}$; (b) layer $\text{AlF}_4[\text{Al}_2\text{F}_{10}] = \text{Al}_3\text{F}_{14}$ in $\text{Na}_5\text{Al}_3\text{F}_{14}$; (c) bidimensional view of the $\text{Na}_4\text{Ca}_4\text{Al}_7\text{F}_{33}$ three-dimensional network (2D formulation: $\text{AlF}_4[\text{Al}_4\text{F}_{20}] = \text{Al}_5\text{F}_{24}$; 3D formulation: $\text{AlF}_3[\text{Al}_6\text{F}_{30}] = \text{Al}_7\text{F}_{33}$).

(Fig. 8a), one can build up a 2D network Al_3F_{14} by condensation of the external octahedra or a " Al_5F_{24} " layer by only four *trans*-corners sharing the external octahedra. The same scheme applied to the hypothetical isolated heptamer " Al_7F_{36} " gives rise to the 3D networks " Al_4F_{18} " or Al_7F_{33} .

Conclusion

In addition to the structure of $\text{Na}_2\text{Ca}_3\text{Al}_2\text{F}_{14}$ (4), this study of the $\text{NaF-CaF}_2\text{-AlF}_3$ system by means of different methods of synthesis allows us to determine the structure of the new fluoaluminate $\text{Na}_4\text{Ca}_4\text{Al}_7\text{F}_{33}$ and to evidence a low-temperature form of NaCaAlF_6 . In these calcium fluoaluminates, the AlF_6 octahedra are either isolated ($\text{Na}_2\text{Ca}_3\text{Al}_2\text{F}_{14}$) or connected with other octahedra to build up a 3D framework ($\beta\text{-NaCaAlF}_6$ and $\text{Na}_4\text{Ca}_4\text{Al}_7\text{F}_{33}$). The special unit Al_7F_{33} , encountered in the last compound, indicates that new octahedra networks like " Al_5F_{24} " and " Al_4F_{18} " can be considered. Toward this aim new syntheses are in progress.

References

1. H. PFUND AND H. ZIMMERMANN, *Erzmetall* **25**(11), 564 (1972).
2. D. F. CRAIG AND J. J. BROWN, *J. Amer. Ceram. Soc.* **65**(5-6), 254 (1980).
3. S. BAGGIO AND G. MASSIFF, *J. Appl. Crystallogr.* **18**(6), 537 (1985).
4. G. COURBION AND G. FERÉY, *J. Solid State Chem.* **76**, 426-431 (1988).
5. F. PLET, J. L. FOURQUET, G. COURBION, M. LEBLANC, AND R. DE PAPE, *J. Crystallogr. Growth* **47**, 699 (1979).
6. J. NOUET, C. JACOBONI, G. FERÉY, J. Y. GERARD, AND R. DE PAPE, *J. Crystallogr. Growth* **8**, 94 (1971).
7. G. COURBION, Thesis, Le Mans (1979).
8. F. C. HAWTHORNE AND R. B. FERGUSON, *Canad. Mineral.* **21**, 561-566 (1983).
9. A. LE BAIL, H. DUROY, AND J. L. FOURQUET, *Mater. Res. Bull.* **33**, 447 (1988).
10. H. F. MC MURDIE, M. C. MORRIS, E. H. EVANS, B. PARETZKIN, W. WONG NG, AND C. R. HUBBARD, *Powder Diffraction* **1**, 40 (1986).
11. G. COURBION, C. JACOBONI, ET R. DE PAPE, *Acta Crystallogr. Sect. B* **33**, 1405-1408 (1977).
12. W. CLEGG, *Acta Crystallogr. Sect. A* **37**, 22 (1981).
13. G. SHELDRIK, "SHELX76: A Program for Crystal Structure Determination," Cambridge Univ., London/New York (1976).
14. "International Tables for X-ray Crystallography," Vol. IV, Kynoch Press, Birmingham (1968).
15. R. D. SHANNON, *Acta Crystallogr. Sect. A* **32**, 751 (1976).
16. J. L. FOURQUET, F. PLET, G. COURBION, A. BULOUE, AND R. DE PAPE, *Rev. Chim. Miner.* **16**, 490 (1979).
17. A. TRESSAUD, J. DARRIET, P. LAGASSIE, J. GRANEC, AND P. HAGENMULLER, *Mater. Res. Bull.* **19**, 983 (1984).
18. N. I. GOLOVASTIKOV AND N. V. BELOV, *Kristallografiya* **23**, 42 (1978).
19. A. HEMON AND G. COURBION, *J. Solid State Chem.* **81**, 293 (1989).
20. J. NOUET, J. PANNETIER, AND J. L. FOURQUET, *Acta Crystallogr. B* **37**, 32 (1981).
21. C. JACOBONI, A. LEBLE, AND J. J. ROUSSEAU, *J. Solid State Chem.* **36**, 297 (1981).
22. W. VIEBAHN, *Z. Anorg. Allg. Chem.* **386**, 335 (1971).
23. R. HOPPE AND D. KISSEL, *J. Fluorine Chem.* **24**, 327 (1984).
24. J. L. FOURQUET, B. BOULARD, AND F. PLET, *J. Solid State Chem.* **81**, 35 (1989).
25. J. L. FOURQUET, F. PLET, ET R. DE PAPE, *Rev. Chim. Miner.* **18**, 19 (1981).
26. A. LE BAIL, C. JACOBONI, M. LEBLANC, R. DE PAPE, H. DUROY, AND J. L. FOURQUET, *J. Solid State Chem.* **77**, 96 (1988).
27. G. COURBION, C. JACOBONI, AND R. DE PAPE, *Acta Crystallogr. B* **32**, 3190 (1976).
28. G. COURBION, C. JACOBONI, AND R. DE PAPE, *J. Solid State Chem.* **45**, 127-134 (1982).
29. C. BROSSET, *Z. Anorg. Allg. Chem.* **238**, 201 (1938).
30. A. HEMON, A. LE BAIL, AND G. COURBION, *J. Solid State Chem.* **81**, 229 (1989).