The NaF-CaF₂-AIF₃ System: Structures of β -NaCaAIF₆ and Na₄Ca₄AI₇F₃₃

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 m3m*) 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 Na₃Sr₄Al₃F₂₆ 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) $NaCa_{1.5}AlF_7$ (3) (called the $NaCaAlF_6$ low-temperature form in Refs. (1, 2), and (III) NaCaAl₂ F_9 (2), also formulated as Na $CaAl_{1.75}F_{8.25}$ 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 $Na_2Ca_3Al_2F_{14}$, 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 ($T < 220^{\circ}$ C) and low-pressure (P = 300bars) technique using a Teflon vessel in a Paar bomb for acid digestion and (2) a hightemperature (300° C $< T < 750^{\circ}$ C) and highpressure (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 NaCaAlF₆ 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 Na₂Ca₃Al₂F₁₄ always appears as the main product whatever the cooling mode.

However, in the temperature range 600– 680°C, the partial substitution of the Ca²⁺ ion by Mn²⁺ ion stabilizes a phase NaCa_x Mn_(1-x)AlF₆ (0 < x < 0.85) related to trigonal Na₂SiF₆-type, but above x = 0.85 a mixture of phases is obtained: mainly Na₂Ca₃Al₂F₁₄, "NaCa_{0.85}Mn_{0.25}AlF₆," and α -NaCaAlF₆. Nevertheless, the evidence for a low-temperature form of NaCaAlF₆ (β -form) is given and we have used hydrothermal synthesis to stabilize this metastable phase.

At high-temperature and pressure (T =350, 630, 720°C and P = 2000 bars) crystals or powdered samples of $Na_2Ca_3Al_2F_{14}$, $Na_5Al_3F_{14}$, and AlF_3 are obtained from the composition NaCaAlF₆ in 40% HF. At low temperature (220°C) and pressure (300 bars), twinned crystals of β -NaCaAlF₆ are synthesized as well as small amounts of Na₂Ca₃Al₂F₁₄, Na₅Al₃F₁₄, CaF₂, and AlF₃ (5 M solution of "NaCaAlF₆" 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 Ca/Mn = 78) gives rise only to powder of β -NaCaAlF₆, again with small amounts of Na₅Al₃F₁₄ and CaF₂. Change of such experimental parameters as temperature, time, and HF concentration do not improve the last result. Thermal study of β -Na CaAlF₆ by DTA (Netsch 404S, 300°C/hr) shows an endothermic peak at 615(5)°C corresponding to the decomposition of this metastable phase in Na₂Ca₃Al₂F₁₄ and α -NaCaAlF₆.

The α -NaCaAlF₆ can also be prepared by dehydration of NaCaAlF₆ · H₂O (Pachnolite (8)) at temperatures above 340°C. This phase remains metastable in the temperature range 340–550°C and then decomposes into Na₂Ca₃Al₂F₁₄ and Na₄Ca₄Al₇F₃₃.

Temperature range	Main phase	Traces	Cooling mode ^a	Time
480-620°C	Na ₂ Ca ₃ Al ₂ F ₁₄	Na ₅ Al ₃ F ₁₄	Q	
		Na ₄ Ca ₄ Al ₇ F ₃₃	or	2-12 hr
		CaF_2	NC	
620-730°C (melting point)	α -NaCaAlF ₆	$Na_2Ca_3Al_2F_{14}$	NC	2–15 days
		CaF ₂	Q	

TABLE I Phases Obtained by Heating of the NaCaAIE, Composition

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

 $Na_4Ca_4Al_7F_{33}$. 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 ($T = 650^{\circ}$ 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 Na₄Ca₄Al₇F₃₃.

X-Ray Data Collection and Characterization

NaCaAlF₆. 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 Na₂ SiF₆ 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.

 $Na_4Ca_4Al_7F_{33}$. 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 fourcircle 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 m3m and I m3, and to the noncentric groups $I \overline{43m}$, I 432, $I 2_13$, and I23.

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

Structure Refinement

 β -NaCaAlF₆. The structure of β -Na CaAlF₆ 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 $CuK\alpha$ 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 3e and 3f sites were tested. The reliability factors are as follows:

site $3e (z = 0)$	Na ⁺	Ca ²⁺
site $3f(z = \frac{1}{2})$	Ca ²⁺	Na+
R_1	12.52	5.39
R _P	16.62	10.18
Rwp	18.98	11.83

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

HEMON AND COURBION

	Π	Æ	TABL
--	---	---	------

Observed and Calculated d Spacings of α -NaCaAlF₆ (CuK α Radiation)

h	k	1	d _{obs}	$d_{\rm cal}$	Iobs	h	k	l	d _{obs}	$d_{\rm cal}$	Iobs
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: $d_{obs} = 2.96(4)$, $d_{cal} = 2.94$; Z = 8.

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

 $Na_4Ca_4Al_7F_{33}$. 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

THE NaF-CaF₂-AlF₃ SYSTEM

TABLE III

CONDITIONS OF DATA COLLECTION AND REFINEMENT, ATOMIC, AND THERMAL Parameters for β -NaCaAlF₆

Symmetry			Trigonal	Trigonal							
Space grou	up		P 321 (No. 1	P 321 (No. 150)							
Cell paran	neters		a = 8.9295(9)) Å, $c = 5.0642(2$		$V = 349.7(1) \text{ Å}^3, Z = 3$					
Density			$d_{\rm obs} = 2.88(5)$); $d_{cal} = 2.91$	-						
2θ range			10-140° a								
Step scan	increment	(2 <i>θ</i>)	0.04								
No. of ref	lections		444								
No. of str	uctural par	ameters	30	30							
Profile par	ameters ^b		$U_1 = 0.22(2),$	$V_1 = -0.08(2),$	$W_1 = 0.144(4),$						
			$U_2 = 0.14($	3), $V_2 = -0.005($	50), $W_2 = 1.44(2)$	2),					
			C = 0.0060	2), $D = -0.3100$	7)	· · ·					
Zero point	t (20)		0.214(2)		,						
Reliability	factors (%	<i>b</i>)	$R_1 = 5.39, R_P = 10.18, R_{WP} = 11.84, R_E = 3.16$								
	Atom	Site	x	у	z	$\boldsymbol{B}_{eq}(\mathrm{\AA}^2)$					
	Ca	3e	0.3720(3)	0	0	1.17(4)					
	Na	3f	0.7145(6)	0	$\frac{1}{2}$	1.1 (1)					
	Al,	1 <i>a</i>	0	0	0	1.0 (1)					
	Al ₂	2d	$\frac{1}{3}$	23	0.499(1)	1.4 (1)					
	\mathbf{F}_{1}	6 <i>g</i>	0.9136(5)	0.1041(6)	0.796(1)	1.4 (1)					
	F_2	6g	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)					

 $^{\it a}$ Four excluded zones; $Na_5Al_3F_{14}$ and CaF_2 impurity. $^{\it b}$ Definition in (9).

$\begin{array}{l} Ca-F_2 = 2 \times 2.280(5) \\ Ca-F_3 = 2 \times 2.289(5) \\ Ca-F_1 = 2 \times 2.353(5) \\ \langle Ca-F \rangle = 2.308 \end{array}$	Ca octahedron (symmetry 2) $F-Ca-F_{min} = 63.0(3)$ $F-Ca-F_{max} = 110.3(2)$	$F-F_{min} = 2.461(9)$ $F-F_{max} = 3.743(4)$
	Na octahedron (symmetry 2)	
$Na-F_1 = 2 \times 2.149(4)$	$F-Na-F_{min} = 66.5(2)$	$F - F_{min} = 2.518(8)$
$Na-F_3 = 2 \times 2.272(5)$	$F-Na-F_{max} = 104.7(3)$	$F - F_{max} = 3.403(5)$
$Na-F_2 = 2 \times 2.319(4)$		
$\langle Na-F \rangle = 2.247$		
	Al ₁ octahedron (symmetry 32)	
$Al_1 - F_1 = 6 \times 1.801(6)$	$F-AI_1-F_{min} = 86.1(4)$	$F-F_{min} = 2.461(7)$
	$F-Al_1-F_{max} = 93.3(3)$	$F - F_{max} = 2.619(6)$
	AI_2 octahedron (symmetry 3)	
$Al_2 - F_2 = 3 \times 1.793(6)$	$F-Al_2-F_{min} = 88.5(2)$	$F-F_{min} = 2.518(7)$
$Al_2 - F_3 = 3 \times 1.814(6)$	$F-Al_2-F_{max} = 90.7(2)$	$F-F_{max} = 2.551(10)$
$\langle Al_2 - F \rangle = 1.803$		

TABLE IV

Main Interatomic Distances (Å) and Angles (°) in β -NaCaAlF₆



FIG. 1. Comparison of observed (\cdots) 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 "Na₆ Ca₄Al₇F₃₃" was not in agreement with neutral charge and the sodium atom had a thermal motion factor of 4.16 $Å^2$; 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 $Na_4Ca_4Al_7F_{33}$

Cubic
<i>I m3m</i> (No. 229)
a = 10.781(3) Å, $V = 1253.07$ Å ³ , $Z = 2$
$d_{\rm obs} = 2.83(4); d_{\rm cal} = 2.83$
0.61
$MoK\alpha$ (graphite monochromatized)
4 × 4
$\omega/2\theta$; 40 steps of $\Delta \omega^{\circ}$; 0.027 < $\Delta \omega$ < 0.032; time per step: 2 s
Isotropic linewidth, $\omega = (1.01 + 0.055 \tan \theta)^{\circ}$
$2\theta_{\min} - 2\theta_{\max}$: 5-60°; hkl_{\max} 8 10 14
Gauss method, $\mu = 13.94$ cm ⁻¹ ; $t_{min} = 0.85$,
$t_{\rm max} = 0.95$
2457
214 ($R_{\text{average}} = 0.051$) in $m3m$
$182 (F_0 > 9\sigma(F_0))$
21
$\omega = 22.76(\sigma^2(F))$
· · · · · ·
0.10e ⁻ /Å ³

ATOMIC COORDINATES, A	Anisotropic T	EMPERATURE FA	ACTORS $(U_{ii} \times$	10^{4}), AND	$B_{ac}(Å^2)$ FC	R Na ₄ Ca ₄ Al ₇ F ₂
-----------------------	---------------	---------------	-------------------------	-----------------	------------------	--

Atom	Site	x	у	z	U_{11}	U ₂₂	U ₃₃	U_{12}	<i>U</i> 13	U ₂₃	B ^{eq} (Å ²)
Naª	12 <i>d</i>		0		208(19)	254(14)	254(14)	0	0	0	1.88(12)
Ca	8 <i>c</i>	ł	4	Ĩ	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	6b	0	$\frac{1}{2}$	ł	108(25)	376(19)	376(19)	0	0	0	2.26(16)
F_2 F_3^b	48 <i>k</i> 48 <i>k</i>	0.1159(1) 0.0239(5)	0.1159(1) 0.0239(5)	0.3363(2) 0.1633(4)	293(7) 224(42)	293(7) 224(42)	633(16) 113(22)	103(7) -11(15)	103(7) -11(15)	-169(9) -60(27)	3.21(8) 1.48(28)

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

^b Occupation ratio: 0.125/0.5.

1.85 Å², 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 Na₄Ca₄Al₄F₃₃, 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 motion. Indeed the Al₁-F₃ = 1.762 Å distance is smaller than the sum of the ionic radii— 1.820 Å—(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— $B_{eq} = 6.0$ Å². This probably indicates a structural disorder. Indeed, the final Fourier difference map shows a maximum peak of $0.25e^{-}/Å^{3}$ (position: 0.038, 0.038, 0.16) around the F₃ fluorine atom; it corresponds to a fragmentation of site 12e

$Ca-F_2 = 6 \times 2.246(1)$	Ca octahedron (symmetry 3m) $F_2-Ca-F_2 = 6 \times 83.17(7)$ $F_2-Ca-F_2 = 6 \times 96.83(7)$ $F_2-Ca-F_2 = 3 \times 180.0$	$F_2-F_2 = 2.982(2)$ $F_2-F_2 = 3.362(2)$
$Al_1 - F_3^a = 6 \times 1.798(4)$	Al ₁ octahedron (symmetry $m3m$) $\langle F_3 - Al_1 - F_3 \rangle = 12 \times 90.0$ $F_3 - Al_1 - F_3 = 3 \times 180.0$	$\langle \mathrm{F}_3 \mathrm{-} \mathrm{F}_3 \rangle = 2.543(8)$
$\begin{array}{llllllllllllllllllllllllllllllllllll$	$\begin{array}{l} Al_2 \text{ octahedron (symmetry 4mm)} \\ F_1 - Al_2 - F_2 &= 4 \times 87.73(8) \\ F_2 - Al_2 - F_2 &= 4 \times 89.91(5) \\ \langle F_2 - Al_2 - F_3 \rangle &= 4 \times 92.22(6) \\ Ca - F_2 - Al_2 &= 153.2(2) \\ Al_2 - F_1 - Na &= 90.0 \\ \langle Al_1 - F_3 - Al_2 \rangle &= 180.0 \end{array}$	$F_1-F_2 = 2.497(1)$ $F_2-F_2 = 2.499(3)$ $\langle F_2-F_3 \rangle = 2.595(5)$
Na po	lyhedron (symmetry 42 <i>m</i>): bicapped Na-F ₁ = 2 × 2.695(0) Na-F ₂ = 8 × 2.601(1) $\langle Na-F \rangle = 2.619$	cube

TABLE VII MAIN INTERATOMIC DISTANCES (Å) AND ANGLES (°) IN Na4Ca4Al7F33

^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 thermals parameters are given in Table VI. Table VII lists the interatomic



FIG. 3. Stereoview of the $Na_4Ca_4Al_7F_{33}$ 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 CaF_6 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 [Al₇F₃₃]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 NaF₆ octahedron being connected to two AlF_6 octahedra, thus forming a 2D infinite layer Al₂Na₃. The cationic distribution, between the 3e and 3f sites, is the opposite in relation to the compounds NaMnMF₆ $(M = Al^{3+}, Cr^{3+}, Fe^{3+})$ where the biggest cation Na^+ always fills the 3e site at the least dense level z = 0. In β -NaCaAlF₆, 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 Ca²⁺, 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 Na₄Ca₄Al₇F₃₃ struc-

ture is made from connected calcium and aluminum regular octahedra which share all their corners to give rise to a $[Ca_4Al_7F_{33}]^{4-1}$ three-dimensional network in which the Na^+ ions are inserted (Fig. 3). The NaF_{10} polydedron, 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 Al₁ octahedron shares its corners with six Al₂ 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 Al₂ octahedra (Figs. 6 and 7).

The special arrangement of aluminum octahedra in Na₄Ca₄Al₇F₃₃ can be compared to those found in others fluoaluminates structures like Na₅Al₃F₁₄ (21, 29) and Na₃Sr₄Al₅F₂₆ (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}F₂ or AlF_{6/2}, connected by corners to four or six octahedra rotated by 90°. Starting from isolated pentamers Al₅F₂₆

TABLE VIII

Compounds	SG	Site symmetry	(Al-F)	Refs.
Na ₄ Ca ₄ Al ₇ F ₃₃	Im3m	m3m	1.798	This work
TIAIF ₄	P4/mmm	4/ <i>mmm</i>	1.82	16
K ₂ LiAlF ₆	R3m	$\frac{\overline{3}}{3}m$	1.813 1.797	17
Cs ₂ NaAIF ₆	R3m	<u>3</u> m	1.81	18
Sr ₁₀ Al ₂ F ₂₅ Čl	Fd3m	$\overline{3}m$	1.781	19
RbAlF₄	P4/mbm	4/m	1.78	16
KAlF₄	P4/mbm	4/m	1.795	20
$Na_3Al_3F_{14}$	P4/nmc	4/m	1.790	21
Na ₄ Ca ₄ Al ₇ F ₃₃	Im3m	4mm	1.790	This work
NH ₄ AIF ₄	I4c2	4	1.80	16
LiCaAlF ₆	$P\overline{3}1c$	32	1.800	22
Na2Ca3Al2F14	I2 <u>1</u> 3	3	1.804	4
α-AlF3	R3	3	1.794	23
		3	1.801	
$K_2AIF_5 \cdot H_2O$	Cmcm	2/m	1.805	24
$Rb_2AlF_5 \cdot H_2O$	Cmcm	2/m	1.817	25
β-AlF3	Стст	2/m	1.799	26
Na5Al3F14	P4/nmc	2/m	1.80	21
		2/m	1.80	
Cs ₂ NaAl ₃ F ₁₂	R3m	2/ <i>m</i>	1.80	27



FIG. 7. (001) projection of $Na_4Ca_4Al_7F_{33}$.



FIG. 8. (a) Isolated unit $AlF_4[Al_4F_{22}] = Al_5F_{26}$ in $Na_3Sr_4Al_5F_{26}$; (b) layer $AlF_4[Al_2F_{10}] = Al_3F_{14}$ in $Na_5Al_3F_{14}$; (c) bidimensional view of the $Na_4Ca_4Al_7F_{33}$ three-dimensional network (2D formulation: $AlF_4[Al_4F_{20}] = Al_5F_{24}$; 3D formulation: $AlF_3[Al_6F_{30}] = Al_7F_{33}$).

(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 Na₂ $Ca_3Al_2F_{14}$ (4), this study of the NaF-CaF₂-AlF₃ system by means of different methods of synthesis allows us to determine the structure of the new fluoaluminate Na4 Ca₄Al₇F₃₃ and to evidence a low-temperature form of NaCaAlF₆. In these calcium fluoaluminates, the AIF₆ octahedra are either isolated $(Na_2Ca_3Al_2F_{14})$ or connected with other octahedra to build up a 3D framework (β -NaCaAlF₆ and Na₄Ca₄Al₇ F_{33}). The special unit Al₇ F_{33} , encountered in the last compound, indicates that new octahedra networks like "Al₅F₂₄" and "Al₄F₁₈" can be considered. Toward this aim new syntheses are in progress.

References

- 1. H. PFUND AND H. ZIMMERMANN, Erzmetall 25(11), 564 (1972).
- D. F. CRAIG AND J. J. BROWN, J. Amer. Ceram. Soc. 65(5-6), 254 (1980).
- S. BAGGIO AND G. MASSIFF, J. Appl. Crystallogr. 18(6), 537 (1985).
- 4. G. COURBION AND G. FEREY, 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. FEREY, 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).
- H. F. MC MURDIE, M. C. MORRIS, E. H. EVANS, B. PARETZKIN, W. WONG NG, AND C. R. HUB-BARD, *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. SHELDRICK, "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. BULOU, AND R. DE PAPE, *Rev. Chim. Miner.* 16, 490 (1979).
- A. TRESSAUD, J. DARRIET, P. LAGASSIE, J. GRANNEC, AND P. HAGENMULLER, Mater. Res. Bull. 19, 983 (1984).
- N. I. GOLOVASTIKOV AND N. V. BELOV, Kristallographiya 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).
- 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).