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$Na_2Ca_3Al_2F_{14}$: A New Example of a Structure with "Independent F^-"—A New Method of Comparison between Fluorides and Oxides of Different Formula

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$Na_2Ca_3Al_2F_{14}$ is cubic (space group $I2_13$) with $a = 10.257(1)$ Å and $Z = 4$. The absolute configuration was determined from 1412 X-ray independent reflections ($R = 0.024$ and $R_w = 0.019$). The structure contains isolated $[AlF_6[^{3-}$ octahedra and an independent fluoride ion, F_3, linked to three Ca^{2+} and one Na^+ ions. The tetrahedra $[FCa_3Na]^{6+}$, linked by Ca^{2+} ions, build up a three-dimensional network in which the octahedral entities $[AlF_6]^{3-}$ are inserted. A structural analysis leading to a comparison with oxide structures is given for compounds containing "independent" fluoride ions and isolated $[MF_6]$ octahedra, despite different chemical formulations for the fluorides and the corresponding oxides.

Introduction

Phase equilibria in the system CaF_2–AlF_3–Na_3AlF_6 have been extensively studied because of their importance to the aluminum industry. The first study of the system CaF_2–AlF_3 was carried out by Fedotieff and Ilyinskii (*1*); more recent work on NaF-containing systems was done by Pfund and Zimmerman (*2*), Craig and Brown (*3*, *4*), and Baggio and Massiff (*5*). Three new compounds have been reported: (I) $NaCaAlF_6$ (high-temperature form) (*2*, *4*, *5*), (II) $NaCa_{1.5}AlF_7$ (*5*) (called the Na $CaAlF_6$ low-temperature form in Refs. (*2*) and (*4*)), and (III) $NaCaAl_2F_9$ (*4*), also formulated as $NaCaAl_{1.75}F_{8.25}$ by Baggio and Massiff (*5*). As these compounds are difficult to prepare in the pure state, only cell parameters have been specified for phases II and III: this is body-centered cubic structure with $a = 10.242(3)$ Å and $10.776(3)$ Å, respectively.

In the absence of structural determinations for these phases, the ternary system NaF–CaF_2–AlF_3 has been reinvestigated. Materials were prepared by solid state reaction and chloride flux growth techniques. In addition to the three compounds previously observed, a low-temperature form of Na $CaAlF_6$ was found.

We present here the first structural paper of the above-mentioned series, dealing with the crystal structure of $NaCa_{1.5}AlF_7$, hereafter denoted $Na_2Ca_3Al_2F_{14}$.

Experimental

Preparation

The compound $Na_2Ca_3Al_2F_{14}$ was prepared in the solid state at 700°C (12 hr) from the elementary fluorides in sealed gold

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TABLE I

CRYSTAL DATA AND CONDITIONS OF DATA COLLECTION (SIEMENS AED2) FOR $Na_2Ca_3Al_2F_{14}$

Space group	$I2_13$ – (Z = 4)
a, V	10.257(1) Å, 1079.1 Å^3
ρ(g/cm^3)	ρ_{obs} = 2.93(3), ρ_{cal} = 2.99
Crystal volume (10^{-3} mm^3)	1.02
Radiation	Mo$K\alpha$ (graphite monochromatized)
Scanning mode	$\omega/2\theta$
Aperture	4/4
Range registered	
θ_{min}, θ_{max} (°)	2.3, 50.0
$h\ k\ l$ min	−20, 20, −20
$h\ k\ l$ max	20, 20, 20
Absorption coefficient μ(cm^{-1})	19.15
Absorption correction	No
Reflections measured: Total	8785
Independent (R average)	833(0.032) in $m3$ 1499(0.030) in 23
Used in refinement	811 ($F_o > 6\sigma(F_o)$ in $m3$ 1412 ($F_o > 6\sigma(F_o)$ in 23

tubes; small amounts of CaF_2 are always present. The thermal study (A.T.D. Netsch 404 S) shows a decomposition into β-Na $CaAlF_6$ (high-temperature form) and CaF_2 at 719(3)°C.

Crystals of $Na_2Ca_3Al_2F_{14}$ were synthesized using a chloride flux method in platinum crucible under argon atmosphere. The best results were obtained from a flux of composition 10 NaCl + 5 $ZnCl_2$ + 2 $CaCl_2$ + 4 NaF + 2 CaF_2 + 2 AlF_3 by slow cooling (5°C/hr) from 650°C. The rounded, well-shaped crystals of $Na_2Ca_3Al_2F_{14}$ (<1 mm^3) are obtained in the presence of small amounts of more birefringent Ca_2AlF_7 crystals with a plate habit.

X-Ray Data Collection and Characterization

The X-ray powder diffraction pattern of the crushed crystals agrees with a cubic body-centered cell: a = 10.257(1) Å. The results of the crystallographic study—(i) $h + k + l = 2n$, $00l$ with $l = 2n$, $0kl$ with $k + l = 2n$, and $h00$ with $h = 2n$ and (ii) Laue symmetry m^3—are consistent with the space groups $Im3$, $I2_13$, and $I23$. Taking into account the second harmonic generation signal (frequency doubling level twice as high as quartz), only the noncentric groups $I2_13$ and $I23$ are allowed.

The crystal selected for the structure determination had an approximate volume of 1.02 × 10^{-3} mm^3. Owing to the small value of the absorption factor and to the good agreement within the equivalent intensities, we did not deem it necessary to apply an absorption correction. Table I shows the conditions of the diffraction experiment on a Siemens AED2 four-circle diffractometer.

Structure Refinement

All the calculations were made with the SHELX76 program (*6*). Atomic scattering factors and dispersion correction factors

TABLE II

ATOM PARAMETERS, ANISOTROPIC TEMPERATURE FACTORS[a] $U_{ij} \times 10^4$ AND B_{eq} (Å^2) FOR $Na_2Ca_3Al_2F_{14}$

Atom	Position	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	B_{eq}
Ca	12b	0.4667(0)	0	$\frac{1}{4}$	78(1)	91(1)	78(1)	0(1)	0	0	0.66
Al	8a	0.2482(0)	0.2482(0)	0.2482(0)	75(1)	75(1)	75(1)	−2(1)	−2(1)	−2(1)	0.60
Na	8a	0.0847(0)	0.0847(0)	0.0847(0)	273(2)	273(2)	273(2)	−88(2)	−88(2)	−88(2)	2.16
F_1	24c	0.1387(1)	0.3062(1)	0.1206(1)	114(2)	127(2)	125(2)	25(2)	−29(2)	−7(2)	0.97
F_2	24c	0.3640(1)	0.3627(1)	0.1873(1)	131(2)	147(2)	154(2)	26(2)	−6(2)	−59(2)	1.14
F_3	8a	0.4614(1)	0.4614(1)	0.4614(1)	104(1)	104(1)	104(1)	14(2)	14(2)	14(2)	0.82

Note. Numbers in parentheses indicate esd's.

[a] The vibrational coefficients relate to the expression: $T = \exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})]$.

TABLE III

MAIN INTERATOMIC DISTANCES (Å) AND ANGLES (°) IN $Na_2Ca_3Al_2F_{14}$

Al–F octahedron	
$3 \times$ Al–F_1 = 1.824(1)	F_2–Al–F_2 = 91.4(1)
$3 \times$ Al–F_2 = 1.784(1)	F_1–Al–F_1 = 99.6(1)
F–F_{min} = 2.478(1) F–F_{max} = 2.601(1)	F_1–Al–F_2 = 175.9(1)
⟨Al–F⟩ = 1.804(2)	
Na–F polyhedron [6 + 1]	
$3 \times$ Na–F_1 = 2.367(1)	Na–Al = 2.905(1)
$3 \times$ Na–F_1 = 2.576(1)	Na–Ca = 3.580(1)
$1 \times$ Na–F_3 = 2.191(1)	Na–Na = 3.810(1)
⟨Na–F⟩ = 2.431(2)	
Ca–F polyhedron [8]	
$2 \times$ Ca–F_1 = 2.354(1)	Ca–Ca = 3.890(1)
$2 \times$ Ca–F_2 = 2.326(1)	Ca–Na = 3.580(1)
$2 \times$ Ca–F_2 = 2.489(1)	Ca–Al = 3.392(1)
$2 \times$ Ca–F_3 = 2.324(1)	
⟨Ca–F⟩ = 2.373(2)	
F_3 tetrahedron	
$3 \times$ F_3–Ca = 2.324(1)	$3 \times$ Ca–F_3–Ca = 113.6(1)
$1 \times$ F_3–Na = 2.191(1)	$3 \times$ Na–F_3–Ca = 104.9(1)
F_3–F_3 = 4.408(2)	F_3–Ca–F_3 = 143.0(1)

were taken from "International Tables for X-Ray Crystallography" (*7*). The structure was solved from the TANG option of direct methods. A solution was found only for the $I2_13$ space group with calcium, aluminum, and sodium ions located in the 12b and 8a sites, respectively. Successive refinements and Fourier maps located the fluorine atoms and led to $R = 0.045$ ($R_w = 0.039$) for 811 independent reflections in $m3$. The R factor drops to 0.026 ($R_w = 0.020$) when refining the anisotropic thermal parameters. Finally, the absolute configuration of the crystal was determined after averaging equivalent intensities in the Laue subgroup 23, the two enantiomeric forms leading to significantly different R factors: $R_1 = 0.030$ ($R_w = 0.025$) and $R_2 = 0.024$ ($R_w = 0.019$). For the best enantiomorph the weighting scheme was $w = 5.31/\sigma^2(F)$ and the maximum height in the final Fourier difference map was 0.09 $e^- \cdot Å^{-3}$. A table specifying the calculated and observed structure factors can be obtained on request to the authors (G.C.).

Table II lists the atomic coordinates and the thermal motion parameters, whereas Table III lists the main interatomic distances and angles.

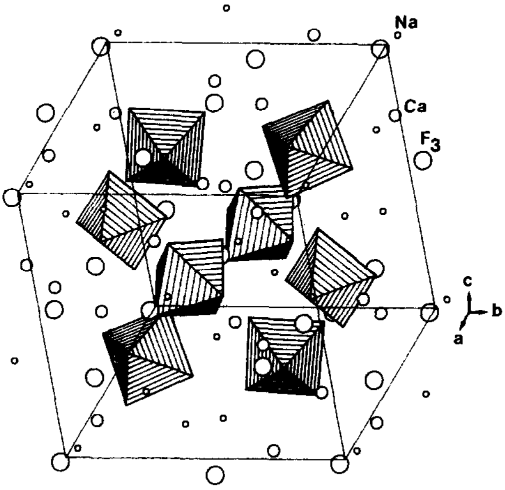

FIG. 1. View of the $Na_2Ca_3Al_2F_{14}$ structure drawn by means of the STRUPLO 84 program (*13*). AlF_6 octahedra are shaded.

Structure Description and Discussion

The main feature of this structure pertains to the existence of an independent fluorine F3, besides those which are bonded to Al^{3+}. There are therefore two ways of describing $Na_2Ca_3Al_2F_{14}$. The first, more conventional, starts from Al^{3+} coordination; the structure may be viewed as consisting of isolated AlF_6 octahedra (Fig. 1) between

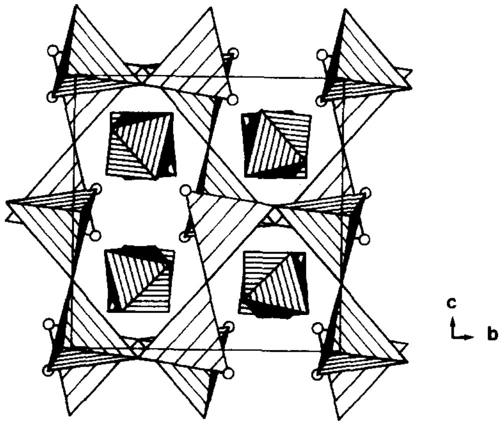

FIG. 2. Projection of the $Na_2Ca_3Al_2F_{14}$ structure on the (100) plane. Tetrahedral entities [FCa_3Na] are drawn (circles correspond to the terminal sodium atoms).

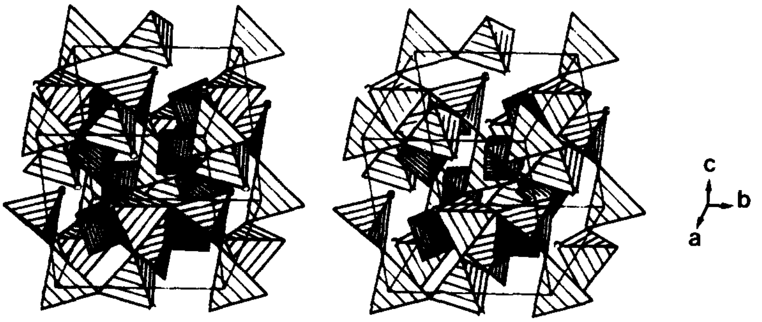

FIG. 3. Stereoview of the $Na_2Ca_3Al_2F_{14}$ structure (circles correspond to Na^+ ions).

which Na^+ and Ca^{2+}, in seven- and eightfold coordination, respectively, are inserted. However, in this description, only F1 and F2 belong to the octahedra; *F3*, bonded only to Na^+ and Ca^{2+}, can be considered as independent. This peculiarity was already encountered for some other fluorides (*8*). This led us to propose a second description of $Na_2Ca_3Al_2F_{14}$ based on the cationic coordination and these "independent" fluorine atoms.

Indeed, each F3 is surrounded by 3 Ca^{2+} and 1 Na^+ which form a tetrahedron around F. Such tetrahedra build up a three-dimensional network by sharing the vertices occupied by Ca^{2+}, Na^+ being terminal. The large cavities within this arrangement are filled by AlF_6 octahedra (Figs. 2 and 3). The structural formula which corresponds to this description is $[AlF_6]_2[FNaCa_{3/2}]_2$ denoted $A_2B_2X_5$, with $A = AlF_6$, $B = F$, $X =$ Na, Ca, the tetrahedral framework being B_2X_5. This notation suggests a comparison with oxides which exhibit a closely similar crystal chemistry, such as silicates. In our case, the local connection of $FNaCa_3$ tetrahedra appears like that occurring in α-$Na_2Si_2O_5$ (*9*). However, this linkage leads to a layer compound for the latter, but to a framework for $Na_2Ca_3Al_2F_{14}$, which so far seems not to have been reported in mineral compounds.

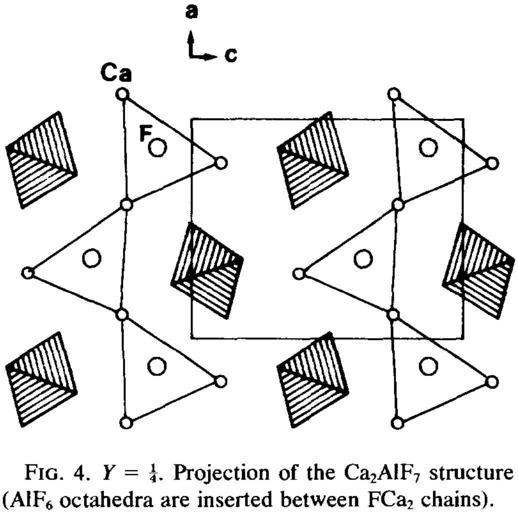

FIG. 4. $Y = \frac{1}{4}$. Projection of the Ca_2AlF_7 structure (AlF_6 octahedra are inserted between FCa_2 chains).

Moreover, this approach of the structure can be extended to other fluorides which exhibit independent F^-, hereafter noted F_{ind}; a first example is provided by Ca_2AlF_7. This structure, described by Domesle and Hoppe (*10*) as built up from isolated AlF_6 octahedra between which Ca^{2+} and supplementary F_{ind} are inserted, can be treated in the same manner. Indeed, each F_{ind} is surrounded by a triangle of Ca^{2+}. These triangles share two of their vertices and form chains running along [100]; AlF_6 octahedra are then inserted between these chains (Fig. 4). The corresponding formulation is thus $[AlF_6][FCa_{2/2}Ca_{1/1}] = [AlF_6][FCa_2]$, and more generally, $A[BX_2]$. This structural arrangement typically exists in $Li\mathit{B}O_2$(I) (*11*).

A second illustration concerns K_3SiF_7 (*12*). This structure exhibits isolated SiF_6^{4-}

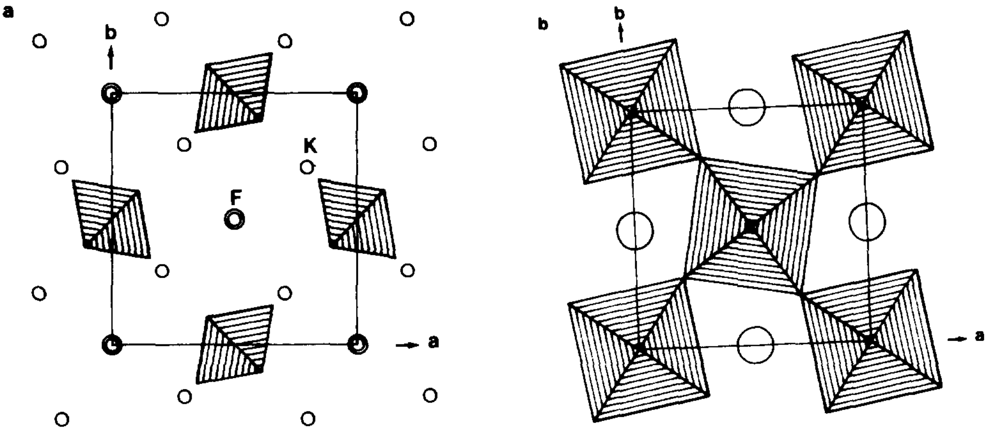

FIG. 5. (a) (001) projection of the K_3SiF_7 structure. SiF_6 octahedra are at $Z = 0$, whereas the F_{ind} with four K^+ are at $Z = \frac{1}{2}$. (b) (001) view of K_3SiF_7 showing the ReO_3-type network from FK_3 ($Z = \frac{1}{2}$) inside which the isolated SiF_6 octahedra (circles) are inserted ($Z = 0$).

octahedra separated by F_{ind}, each surrounded by an octahedron of K^+. The FK_6 octahedra share corners and build up an ReO_3-type sublattice, the SiF_6 octahedra being in the cubooctahedral cavities (Figs. 5a and 5b). Therefore, $K_3SiF_7 = [SiF_6][FK_{6/2}] = ABX_3$ is a perovskite-like compound.

The fluorides with F_{ind} and isolated octahedra may thus be considered from a structural point of view as the "negative" of complex oxides of an equivalent topology, even when the corresponding chemical formulas are completely different. In our description, the oxyanions are replaced by fluocations, and the countercations in the oxides, by octahedral polyanions in the fluorides. Table IV explicitly demonstrates the above correspondence, which considerably enlarges the classical one between CaF_2 and Li_2O (antifluorite structure).

TABLE IV

Fluorides		
Chemical formula	Structural formula	Oxides
$Na_2Ca_3Al_2F_{14}$	$= [AlF_6^{3-}]_2[F_2(Na_2Ca_3)^{6+}]$	$(Na^+)_2[Si_2O_5^{2-}]$
Ca_2AlF_7	$= [AlF_6^{3-}][FCa_2^{3+}]$	$(Li^+)[BO_2^-]$
K_3SiF_7	$= [SiF_6^{2-}][FK_{6/2}^{2+}]$	$(Ba^{2+})[TiO_3^{2-}]$

Finally, it is suggested that this structural analysis can be carried out in reverse: starting from known oxide structures, it may be expected to suggest new formulas and new topologies in the crystal chemistry of fluorides.

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References

1. P. P. FEDOTIEFF AND W. P. ILYINSKII, *Z. Anorg. Allg. Chem.* **129**, 93 (1923).
2. H. PFUND AND H. ZIMMERMANN, *Erzmetall* **25**(11), 564 (1972).
3. D. F. CRAIG AND J. J. BROWN, *J. Amer. Ceram. Soc.* **60**(9–10), 396 (1977).
4. D. F. CRAIG AND J. J. BROWN, *J. Amer. Ceram. Soc.* **63**(5–6), 254 (1980).
5. S. BAGGIO AND G. MASSIFF, *J. Appl. Crystallogr.* **18**(6), 537 (1985).
6. G. SHELDRICK, "SHELX76: A Program for Crystal Structure Determination," University of Cambridge (1976).

7. "International Tables for X-Ray Crystallography," Vol. IV, Kynoch Press, Birmingham (1968).
8. D. Babel and A. Tressaud, "Inorganic Solid Fluorides" (P. Hagenmuller, Ed.), Academic Press, New York, p. 77 (1985).
9. F. Liebau, "Structural Chemistry of Silicates," Springer-Verlag, Berlin (1985).
10. R. Domesle and R. Hoppe, *Z. Kristallogr.* **153,** 317 (1980).
11. W. H. Zachariasen, *Acta Crystallogr.* **17,** 749 (1964).
12. D. L. Deadmore and W. F. Bradley, *Acta Crystallogr.* **15,** 186 (1962).
13. R. X. Fisher, *J. Appl. Crystallogr.* **18,** 258 (1985).