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Crystal Structure of $Na_3Sr_4Al_5F_{26}$

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$Na_3Sr_4Al_5F_{26}$ is tetragonal (space group $P4_2/n$) with $a = 10.2679(5)$ Å, $c = 18.373(2)$ Å, and $Z = 4$. The structure is refined, despite a systematic twinning, from 1478 reflections to $R_F = 0.029$ ($R_I = 0.039$). Aluminum ions are in octahedral sites while strontium and sodium atoms are respectively in nine- and eightfold coordination. The structure is characterized by isolated $[Al_5F_{26}]^{11-}$ pentamers. A distorted cube $[Na_{(1)}F_8]^{7-}$ ensures the connection between the octahedra pentamers and builds up $[NaAl_5F_{26}]^{10-}$ chains running along the b-axis at level $z = 0$ and along the a-axis at level $z = \frac{1}{2}$. Strontium ($Sr_{(1)}$ and $Sr_{(2)}$) and sodium ($Na_{(2)}$ and $Na_{(3)}$) are inserted between the chains.

Introduction

The investigation of the ternary system $NaF–SrF_2–AlF_3$ by means of the chloride flux method (*1, 2*) has evidenced three new phases: two fluorides $NaSrAlF_6$ (*3*) on $Na_3Sr_4Al_5F_{26}$ and a chlorofluoride $Sr_{10}Al_2F_{25}Cl$ (*4*). We present here the crystal structure of $Na_3Sr_4Al_5F_{26}$ from single-crystal data.

Preparation

Crystals of $Na_3Sr_4Al_5F_{26}$ were synthesized using a chloride flux method in a platinum crucible under argon atmosphere. They are obtained from the mixture $NaF + 2SrF_2 + 2AlF_3 + 4.5NaCl + 2.75ZnCl_2$ by slow cooling (6°C/hr) from 700°C. $Na_3Sr_4Al_5F_{26}$ crystals, with a stretched octahedron or plate habit (<1 mm^3), are obtained with a small amount of two other phases: $NaSrAlF_6$ (*3*) and an unknown compound whose diffraction pattern is very close to that of Jarlite—$Na_4Sr_{12}Mg_2Al_{12}F_{64}(OH)_4$ (*5*).

The solid-state synthesis of $Na_3Sr_4Al_5F_{26}$ has been achieved, in sealed gold tubes, at 650°C (40 hr) from a stoichiometric mixture of elementary fluorides.

Structural Determination of $Na_3Sr_4Al_5F_{26}$

The crystal selected for X-ray data collection on a Siemens AED2 four-circle diffractometer has an approximate volume of 1.75×10^{-3} mm^3 and is limited by faces (100, 010, 001). The lattice parameters—$a = 10.2679(5)$ Å, $c = 18.373(2)$ Å—were refined from 40 reflections by a double-scan technique. The conditions of the diffraction experiment are summarized in Table I.

The observed reflection conditions—$hk0$, $h + k = 2n$, and $00l$, $l = 2n$—lead to the space group $P4_2/n$. Intensities, corrected from Lorentz—polarization effects as well as for absorption using the correct

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TABLE I

CRYSTAL DATA AND CONDITIONS OF DATA COLLECTION AND REFINEMENT FOR $Na_3Sr_4Al_5F_{26}$

Symmetry	Tetragonal
Space group	$P4_2/n$ (No. 86)
Cell parameters	a = 10.2679(5) Å, c = 18.373(2) Å; V = 1937.06 Å^3; Z = 4
Crystal volume (10^{-3} mm^3)	1.75
Radiation	Mo$K\alpha$ (graphite monochromatized)
Scanning mode	$\omega/2\theta$
Aperture (mm)	3/3
Range registered	
θ_{min}, θ_{max} (°)	2.00, 30.00
h, k, l max	14, 10, 25
Absorption coefficient μ (cm^{-1})	111.54
Absorption correction	Gaussian method
Transmission factors	max: 0.4339 min: 0.2417
Reflections measured:	
Total	6359
Independent ($R_{average}$)	2764, (R = 0.024) in $4/m$ 1696, (R = 0.026) in $4/mmm$
Used in refinement	2409 ($F_o > 6\sigma(F_o)$) in $4/m$ 1478 ($F_o > 6\sigma(F_o)$) in $4/mmm$
Number of refined parameters	75 (with isotropic thermal parameters) 176 (with anisotropic thermal parameters)
Reliability factor	$R_F = (\Sigma\|\|F_o\| - k\|F_c\|\|/\Sigma\|F_o\|)$ $R_I = (\Sigma\|I_o - kI_c\|/\Sigma I_o)$

final composition, were averaged in Laue group $4/m$ and led to an R_{av} value of 0.024.

In the first trial, the structure refinement was performed using the SHELX76 program (*6*). Ionic scattering factors and anomalous dispersion parameters were taken from "International Tables for X-Ray Crystallography" (*7*). The structure was solved from the TANG option of direct methods in the space group $P4_2/n$. Two strontium sites (8g) and one aluminum site (4c) were first located; this led to a reliability factor R_F = 0.42. From successive difference Fourier maps and refinements, the other atoms were easily located but the final R_F value decreased only to 0.21 with isotropic thermal motion. At this stage of refinement the structural formulation obtained was $Na_3Sr_4Al_5F_{26}$ and no new peaks were observed in the difference Fourier map. Moreover all the Al–F, Na–F, and Sr–F distances are realistic. The failure of the structure refinement compelled us to assume a twinning process, involving an increase of the Laue symmetry.

Indeed, when looking at the structure factors for pairs of reflections $hk0/kh0$ and hkl/khl, it appears that the observed F_o obey the Laue symmetry $4/mmm$ instead of $4/m$. Thus, if the space group $P4_2/n$ is the correct one, there is only one solution to this problem: two domains, with a volume ratio near unity, which superpose their hkl and khl reflections.

A structure refinement with the only reflections unaffected by the twinning (hhl and $h0l$) and isotropic temperature factors converges to R_F = 0.06 (406 hkl, 75 refined parameters). This confirms the suggested twin model for our crystal.

In order to solve the structure with a twinned crystal (a limited data collection of two other crystals shows the same twinning) the observed intensities were merged in the $4/mmm$ Laue group (R_{av} = 0.026 for 1696 hkl). Each observed intensity (I_o) was considered to result from two domains (A and B) with equal volume according to the expression $I_o = I_{hklA} + I_{khlB}$. For calculation we have used a local program (unpublished) where the minimized function was $\chi^2 = \Sigma w_i(I_o - kI_c)^2$ with $I_c = F^2_{hklA} + F^2_{khlB}$, $w_i = 1/I_o$ (ponderation scheme) and k = scale factor. Starting from the atomic positions previously obtained, and refining with isotropic temperature factors, the reliability factor fell to R_F = 0.054 (R_I = 0.069) and further to R_F = 0.029 (R_I = 0.039) when applying anisotropic thermal motion. This

TABLE II

ATOMIC PARAMETERS, ANISOTROPIC TEMPERATURE FACTORS[a] $U_{ij} \times 10^4$ AND B_{eq} ($Å^2$) FOR $Na_3Sr_4Al_5F_{26}$

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	B_{eq}
Sr_1	8g	0.2821(0)	0.9974(1)	0.8254(0)	59(0)	75(0)	152(0)	−8(0)	−14(0)	−14(0)	0.75
Sr_2	8g	0.2873(0)	0.9970(1)	0.1944(0)	66(0)	72(0)	84(0)	−12(0)	16(0)	−9(0)	0.58
Al_1	4c	0	0	0	112(11)	48(11)	77(0)	−112(21)	9(9)	−3(9)	0.62
Al_2	8g	0.5155(2)	0.7555(2)	0.8727(1)	5(11)	64(5)	65(0)	−4(5)	18(9)	1(9)	0.35
Al_3	8g	0.2523(2)	0.5098(3)	0.6339(1)	48(5)	101(11)	73(0)	0(5)	4(9)	19(9)	0.59
Na_1	4d	0	0	$\frac{1}{2}$	181(21)	438(27)	188(17)	−107(48)	29(19)	−124(19)	2.12
Na_2	4f	$\frac{1}{4}$	$\frac{1}{4}$	0.9978(0)	192(43)	389(48)	68(17)	262(32)	0	0	1.71
Na_3	4e	$\frac{3}{4}$	$\frac{1}{4}$	0.9959(3)	25(48)	763(80)	154(34)	−171(48)	0	0	3.07
F_1	8g	0.1266(4)	0.0093(6)	0.7056(2)	117(16)	139(21)	120(17)	11(21)	38(9)	3(19)	0.99
F_2	8g	0.3361(6)	0.1192(6)	0.6710(3)	160(27)	246(32)	291(34)	−91(21)	0(29)	−86(29)	1.83
F_3	8g	0.6673(6)	0.1132(5)	0.6720(3)	165(27)	133(27)	171(17)	59(21)	1(19)	−9(19)	1.24
F_4	8g	0.3232(5)	0.8760(6)	0.6947(3)	192(27)	165(27)	137(17)	80(21)	−57(19)	29(19)	1.30
F_5	8g	0.4513(5)	0.3695(5)	0.0602(3)	176(27)	149(21)	188(17)	−37(21)	−9(19)	96(19)	1.35
F_6	8g	0.1392(5)	0.3560(5)	0.0879(2)	139(27)	128(27)	103(17)	−59(16)	9(19)	3(19)	0.97
F_7	8g	0.3630(5)	0.8513(5)	0.0943(2)	149(27)	117(27)	120(17)	37(16)	−57(19)	−38(19)	1.02
F_8	8g	0.5031(6)	0.1226(4)	0.1975(2)	117(21)	80(16)	120(17)	37(21)	−7(19)	38(9)	0.83
F_9	8g	0.1574(4)	0.9958(6)	0.9636(2)	112(16)	203(21)	171(17)	11(21)	29(19)	2(19)	1.28
F_{10}	8g	0.3951(5)	0.8402(5)	0.9255(3)	80(27)	171(27)	154(17)	11(21)	57(19)	−9(19)	1.06
F_{11}	8g	0.3742(5)	0.9537(6)	0.5661(3)	128(21)	208(27)	171(17)	5(16)	95(19)	−9(19)	1.33
F_{12}	8g	0.3429(5)	0.3968(6)	0.5786(2)	149(27)	181(27)	137(17)	59(21)	29(19)	−38(19)	1.23
F_{13}	8g	0.3728(6)	0.3242(5)	0.1872(2)	155(27)	160(27)	137(17)	80(21)	−7(19)	−38(19)	1.19

Note. Numbers in parentheses indicate esd's.

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

result, obtained without any major deviation for the atomic coordinates, well confirms the twinning of our crystal. Table II lists the positional and thermal motion parameters and Table III gives the main interatomic distances and angles. A table of I_o and I_c can be obtained on request to the authors.

Structure Description

The main feature of the $Na_3Sr_4Al_5F_{26}$ structure corresponds to the existence of isolated pentamers $[Al_5F_{26}]^{11-}$ built up from five aluminum octahedra. In these pentamers (Fig. 1) the central $Al_{(1)}$ octahedron is corner-connected to four other octahedra in such a way that the $Al_{(2)}$ octahedra (and also $Al_{(3)}$) are always in *trans*-position. These entities are parallel to the (b, c) plane at level $z = 0$ and are rotated by 90° around the c-axis at level $z = \frac{1}{2}$ (Fig. 2).

The sodium and strontium atoms are respectively in eight- and ninefold coordination. The NaF_8 (Na_I) polyhedron, which looks like a distorted cube, is also shown in Fig. 1. These polyhedra establish the connection between the $[Al_5F_{26}]^{11-}$ blocks and build up $[NaAl_5F_{26}]^{10-}$ chains running either along the b-axis at level $z = 0$ (Fig. 3) or along the a-axis at level $z = \frac{1}{2}$ (Fig. 4). The

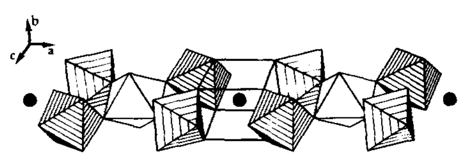

FIG. 1. Perspective view of $[Al_5F_{26}]^{11-}$ pentamers and $[Na_{(1)}F_8]^{7-}$ polyhedra.

TABLE III

MAIN INTERATOMIC DISTANCES (Å) AND ANGLES (°) IN $NaSr_4Al_5F_{26}$[a]

	Sr_1^{2+} polyhedron [9]	
	Sr_1–F_2 = 2.393(6)	
	Sr_1–F_3 = 2.422(6)	
	Sr_1–F_8 = 2.561(5)	
	Sr_1–F_1 = 2.583(4)	
	Sr_1–F_{12} = 2.681(5)	
	Sr_1–F_{10} = 2.709(5)	
	Sr_1–F_1 = 2.722(3)	
	Sr_1–F_4 = 2.737(5)	
	Sr_1–F_9 = 2.844(3)	
	⟨Sr_1–F⟩ = 2.628	
	Sr_2^{2+} polyhedron [9]	
	Sr_2–F_4 = 2.449(6)	
	Sr_2–F_{13} = 2.468(6)	
	Sr_2–F_7 = 2.494(2)	
	Sr_2–F_8 = 2.565(5)	
	Sr_2–F_{13} = 2.582(2)	
	Sr_2–F_6 = 2.584(8)	
	Sr_2–F_8 = 2.609(5)	
	Sr_2–F_1 = 2.618(5)	
	Sr_2–F_3 = 2.743(9)	
	⟨Sr_2–F⟩ = 2.568	
	Al_1^{3+} octahedron	
Al_1–F_9* = 2 × 1.749(4)	F_9–Al_1–F_5 = 2 × 90.2(4)	F_9–F_5 = 2.520(6)
Al_1–F_5 = 2 × 1.808(6)	F_9–Al_1–F_5 = 2 × 89.8(4)	F_9–F_5 = 2.512(6)
Al_1–F_{11} = 2 × 1.836(3)	F_9–Al_1–F_{11} = 2 × 90.2(4)	F_9–F_{11} = 2.540(6)
⟨Al_1–F⟩ = 1.798	F_9–Al_1–F_{11} = 2 × 89.8(4)	F_9–F_{11} = 2.531(6)
	F_5–Al_1–F_{11} = 2 × 87.4(5)	F_5–F_{11} = 2.518(7)
	F_5–Al_1–F_{11} = 2 × 92.6(5)	F_5–F_{11} = 2.634(7)
	Al_1–F_5–Al_2 = 152.8(1)	
	Al_1–F_{11}–Al_3 = 153.2(3)	
	Al_2^{3+} octahedron	
	Al_2–F_{13}* = 1.788(4)	
	Al_2–F_6* = 1.789(4)	
	Al_2–F_{10}* = 1.796(4)	
	Al_2–F_3* = 1.801(4)	
	Al_2–F_8* = 1.807(8)	
	Al_2–F_5 = 1.812(10)	
	⟨Al_2–F⟩ = 1.799	
	Al_3^{3+} octahedron	
	Al_3–F_2* = 1.744(10)	
	Al_3–F_4* = 1.796(2)	
	Al_3–F_{12}* = 1.801(3)	
	Al_3–F_7* = 1.808(8)	
	Al_3–F_1* = 1.822(6)	
	Al_3–F_{11} = 1.838(7)	
	⟨Al_3–F⟩ = 1.802	

TABLE III—*Continued*

	Na_1^+ polyhedron [8]	
Na_1–F_{10} = 2 × 2.393(3)	F_{10}–Na_1–F_{12} = 2 × 85.3(4)	F_{10}–F_{12} = 3.255(7)
Na_1–F_{12} = 2 × 2.410(3)	F_{10}–Na_1–F_6 = 2 × 60.3(5)	F_{10}–F_6 = 2.523(8)
Na_1–F_6 = 2 × 2.615(8)	F_{10}–Na_1–F_7 = 2 × 75.3(4)	F_{10}–F_7 = 3.121(6)
Na_1–F_7 = 2 × 2.704(4)	F_{12}–Na_1–F_6 = 2 × 75.6(4)	F_{12}–F_6 = 3.085(6)
⟨Na_1–F⟩ = 2.530	F_{12}–Na_1–F_7 = 2 × 57.8(5)	F_{12}–F_7 = 2.484(9)
	F_6–Na_1–F_7 = 2 × 68.8(4)	F_6–F_7 = 3.007(7)
	Na_2^+ polyhedron [8]	
	Na_2–F_{12} = 2 × 2.270(4)	
	Na_2–F_6 = 2 × 2.285(10)	
	Na_2–F_5 = 2 × 2.663(8)	
	Na_2–F_9 = 2 × 2.848(5)	
	⟨Na_2–F⟩ = 2.517	
	Na_3^+ polyhedron [8]	
	Na_3–F_{10} = 2 × 2.272(4)	
	Na_3–F_7 = 2 × 2.276(10)	
	Na_3–F_{11} = 2 × 2.702(9)	
	Na_3–F_9 = 2 × 2.797(5)	
	⟨Na_3–F⟩ = 2.512	

[a] Estimated standard deviations are given in parentheses.
* Terminal fluorine.

other sodium atoms ($Na_{(2)}$ and $Na_{(3)}$) are inserted between two parallel chains either at level $z \simeq 0$ (Fig. 3) or at level $z \simeq \frac{1}{2}$ whereas the strontium atoms ($Sr_{(1)}$ and $Sr_{(2)}$) are located between the 90° rotated chains (see Fig. 2).

One possible explanation of the easy twinning observed for this compound is il-

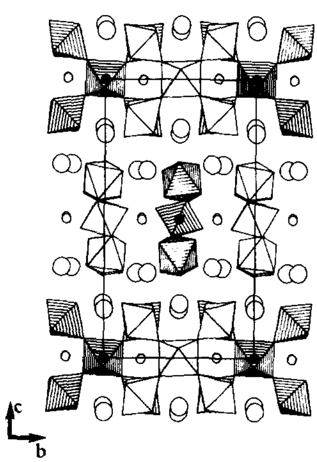

FIG. 2. (100) projection of the $Na_3Sr_4Al_5F_{26}$ structure drawn by means of the STRUPLO program (*8*). Shaded Al_5F_{26} pentamers are those centered at $x = 0$; unshaded ones are centered at $x = \frac{1}{2}$. Na and Sr are represented by small and large circles, respectively ($Na_{(1)}$ black small circles).

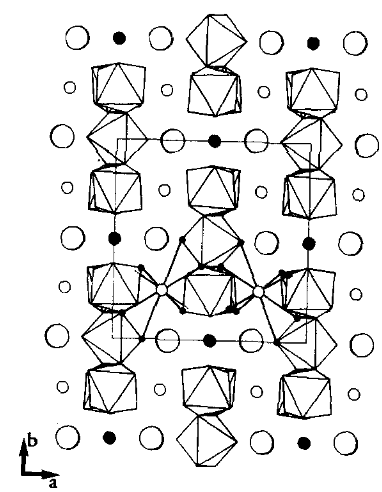

FIG. 3. (001) projection of the $Na_3Sr_4Al_5F_{26}$ structure with $-0.25 < z < 0.25$. Two $Na_{(2)}$ and $Na_{(3)}$ polyhedra are drawn. Na and Sr symbols are defined in Fig. 2.

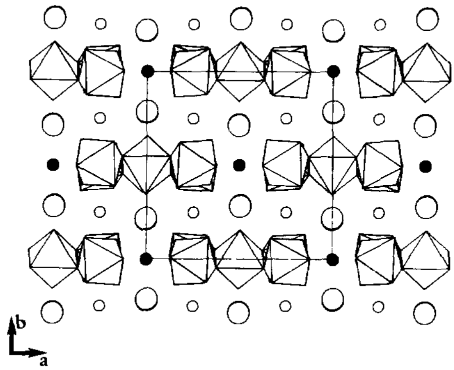

FIG. 4. (001) projection of the $Na_3Sr_4Al_5F_{26}$ structure with $0.25 < z < 0.75$. Symbols as in Fig. 2.

lustrated in Fig. 5. Two crystals can share a common plane perpendicular to the c-axis in which the Al_5F_{26} blocks at $z = 0$ from a domain A become the Al_5F_{26} blocks at $z = \frac{1}{2}$ from a domain B. Such a twinning only involves small shifts of atoms (0.14 Å between $Al_{(2)}$ and $Al_{(3)}$, 0.12 Å between $Na_{(2)}$ and $Na_{(3)}$).

The mean Al–F observed distances (1.80 Å) for the three octahedra are in good agreement and close to the sum of Shannon's radii (*9*) (1.82 Å); the smaller Al–F bonds always correspond to terminal fluorines (see Table III).

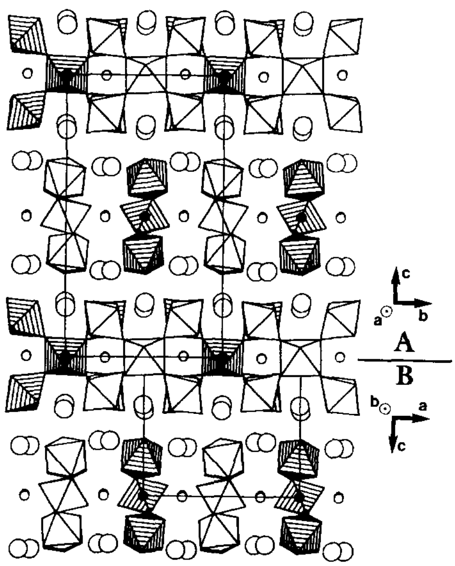

FIG. 5. View of a possible twinning between two crystals A and B. Symbols as in Fig. 2. Shaded Al_5F_{26} blocks are centered at $x = 0$ (A) and $y = 0$ (B); unshaded ones are centered at $x = \frac{1}{2}$ (A) and $y = \frac{1}{2}$ (B).

To our knowledge, the $[Al_5F_{26}]^{11-}$ pentamer has not been encountered in fluoaluminates. However the corner connection mode between the central octahedron and the four others, rotated by 90° (see Fig. 1), is observed in the $[Al_3F_{14}]^{5-}$ layers of the Chiolite structure $Na_5Al_3F_{14}$ (*10, 11*). Indeed, in $Na_3Sr_4Al_5F_{26}$ there exists isolated octahedra pentamers $[Al_5F_{26}]$ = AlF_4 $[Al_4F_{22}]$ where AlF_4 is the central octahedron and in $Na_5Al_3F_{14}$ these octahedra pentamers undergo a condensation by sharing the external octahedra, resulting in a layer $AlF_4[Al_2F_{10}]$ = Al_3F_{14}. A study of the homologous compounds with M^{III} = $3d$ transition metal is in progress.

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