

Crystal Structure of $\text{Sr}_{10}\text{Al}_2\text{F}_{25}\text{Cl}$

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$\text{Sr}_{10}\text{Al}_2\text{F}_{25}\text{Cl}$ is cubic (space group $Fd\bar{3}m$) with $a = 16.4209(3)$ Å and $Z = 8$. The structure is refined from 386 reflections to $R = 0.022$ $R_w = 0.018$. Aluminum ions are in octahedral sites while strontium atoms are in 10- (Sr_1) and 8- (Sr_2) fold coordination. The structure is characterized by two interpenetrated three-dimensional networks: one built from SrF_8 polyhedra and the other from four SrF_{10} polyhedra blocks connected together by aluminum octahedra. The chlorine atoms are octahedrally surrounded by six Sr_2 . © 1989 Academic Press, Inc.

Introduction

During the investigation of the ternary system $\text{NaF}-\text{SrF}_2-\text{AlF}_3$ by means of the chloride flux method (1, 2), single crystals of the chlorofluoride $\text{Sr}_{10}\text{Al}_2\text{F}_{25}\text{Cl}$ were obtained. The crystal structure of this compound is presented here. $\text{Pb}_{10}\text{Al}_2\text{F}_{25}\text{Cl}$ is isotypic.

Experimental

Preparation

Crystals of $\text{Sr}_{10}\text{Al}_2\text{F}_{25}\text{Cl}$ were synthesized using a chloride flux method in a platinum crucible under argon. The best results were obtained from a flux of composition $\text{NaF} + 3\text{SrF}_2 + \text{AlF}_3 + 5.4\text{NaCl} + 3.3\text{ZnCl}_2$ by slow cooling ($6^\circ\text{C}/\text{hr}$) from 700°C . The well-shaped crystals ($<1 \text{ mm}^3$) were obtained in the presence of small amounts of NaSrAlF_6 (3).

The thermal study (ATD Netsch 404S) shows a congruent melting point at $920(3)^\circ\text{C}$ with a heating rate of $300^\circ\text{C}/\text{hr}$.

This compound can be prepared in the solid state at 800°C (17 hr) from a stoichiometric mixture of elementary fluorides and SrCl_2 in sealed gold tubes.

Attempts to prepare new chlorofluorides corresponding to the general formulation $\text{A}_{10}\text{M}_2\text{F}_{25}\text{Cl}$ ($A = \text{Sr}^{2+}, \text{Ca}^{2+}, \text{Pb}^{2+}$ and $M = \text{Al}^{3+}, \text{Cr}^{3+}, \text{Ga}^{3+}$) failed except with $A = \text{Pb}^{2+}$ and $M = \text{Al}^{3+}$. This compound was prepared in the solid state at 550°C in the same way as $\text{Sr}_{10}\text{Al}_2\text{F}_{25}\text{Cl}$ ($a = 16.735(1)$ Å, $\text{mp} = 575(3)^\circ\text{C}$, $\rho_{\text{obs}} = 7.80(16) \text{ g/cm}^3$, $\rho_{\text{cal}} = 7.47 \text{ g/cm}^3$). A study of the $\text{Ba}_{10}\text{M}_2\text{F}_{25}\text{Cl}$ ($M = \text{Al}^{3+}, \text{Tl}^{3+}, \text{V}^{3+}, \text{Cr}^{3+}, \text{Fe}^{3+}$) compounds is in progress.

X-Ray Data Collection, Characterization, and Structure Refinement

The X-ray patterns of both powder and crushed crystals are well indexed with a cubic F cell: $a = 16.424(9)$ Å. The limiting conditions for the reflections observed (h, k, l all odd or even and $0kl, k + l = 4n$) lead to the space groups $Fd\bar{3}m$ or $Fd\bar{3}$.

The crystal selected for X-ray data collection on a Siemens AED2 four-circle dif-

fractometer had an approximate volume of $1.05 \times 10^{-3} \text{ mm}^3$ and was limited by many faces ($0\bar{2}2$, $02\bar{2}$, $1\bar{2}1$, $1\bar{1}4$, $2\bar{2}2$, $2\bar{2}\bar{2}$). The lattice parameter— $a = 16.4209(3) \text{ \AA}$ —was refined from 30 reflections by the double-scan technique. The conditions of the diffraction experiment are summarized in Table I.

Intensities were corrected for Lorentz-polarization effects as well as for absorption. Average of equivalents in Laue group $m\bar{3}m$ and $m\bar{3}$ led to similar R_{av} values: 0.038 and 0.035, respectively. All the calculations were made with the SHELX76 program (4). Atomic scattering factors and dispersion correction factors were taken from

TABLE I
CRYSTAL DATA AND CONDITIONS OF DATA
COLLECTION AND REFINEMENT FOR $\text{Sr}_{10}\text{Al}_2\text{F}_{25}\text{Cl}$

Symmetry	Cubic
Space group	$Fd\bar{3}m$ (No. 227)
Parameters	$a = 16.4209(3) \text{ \AA}$; $V = 4427.83 \text{ \AA}^3$; $Z = 8$
Density	$\rho_{obs} = 4.37(3)$; $\rho_{cal} = 4.32$
Crystal volume (10^{-3} mm^3)	1.05
Radiation	$\text{Mo K}\alpha$ (graphite monochromatized)
Scanning mode	$\omega/2\theta$
Aperture (mm)	3.5/3.5
Range registered	
θ_{min} , θ_{max} ($^\circ$)	2.15, 45.00
h , k , l max	32, 32, 32
Absorption coefficient μ (cm^{-1})	235.91
Absorption correction	Gaussian method
Transmission factors	max: 0.2428 min: 0.1485
Reflections measured:	
Total	2686
Independent ($R_{average}$)	865 ($R = 0.0383$) in $m\bar{3}m$
Used in refinement	386 ($F_o > 6\sigma(F_o)$) and $2\theta \leq 75.0$
Number of refined parameters	25
Weighting scheme	$w = 1.9033/(\sigma^2(F) + 7 \times 10^{-6} F^2)$
Secondary extinction	$e = 6 \times 10^{-9}$
Maximum height in final Fourier difference map	$0.032 e^-/\text{\AA}^3$

“International Tables for X-Ray Crystallography” (5). The structure was solved from the TANG option of direct methods in the space group $Fd\bar{3}m$. Two strontium sites (32e and 48f) and one aluminum site (16e) were first located. A subsequent Fourier map gave all the remaining atoms, assigned as fluorine atoms. The refinement of atomic parameters and isotropic temperature factors converged to the reliability factor $R = 0.058$ ($R_w = 0.055$). From interatomic distances analyses, it was found that the 8a site was occupied by a chlorine atom ($\text{Sr}-X = 3.196 \text{ \AA}$). Then the residual fell to $R = 0.033$ ($R_w = 0.024$) with isotropic thermal motion and to $R = 0.022$ ($R_w = 0.018$) when applying anisotropic thermal motion. The refinement in the space group $Fd\bar{3}$ led to a larger R value ($R = 0.069$, $R_w = 0.075$ for isotropic temperature factor). Table II lists the atomic coordinates and the thermal motion parameters whereas Table III gives the main interatomic distances and angles. A table specifying the calculated and observed structure factors can be obtained on request to the authors (G.C.).

Description of the Structure

Figure 1 shows a perspective view of one-eighth of the cell, hereafter called the

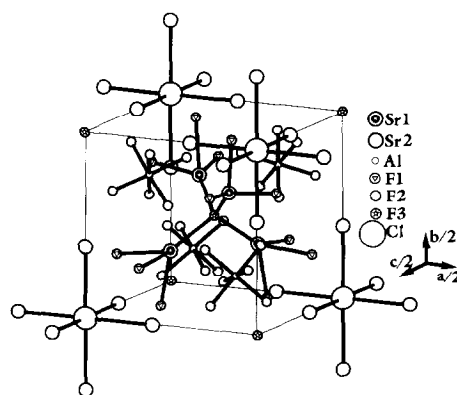


FIG. 1. View of $\text{Sr}_{10}\text{Al}_2\text{F}_{25}\text{Cl}$ structure in an elementary cell ($a/2$).

TABLE II
 ATOM PARAMETERS, ANISOTROPIC TEMPERATURE FACTORS^a $U_{ij} \times 10^4$ AND B_{eq} (Å²) FOR Sr₁₀Al₂F₂₅Cl

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	B_{eq}
Sr ₁	32e	0.4146(0)	0.4146(0)	0.4146(0)	76(1)	76(1)	76(1)	-4(1)	-4(1)	-4(1)	0.60
Sr ₂	48f	0.1946(0)	0	0	95(2)	89(1)	89(1)	-15(2)	0	0	0.72
Al	16d	$\frac{5}{8}$	$\frac{5}{8}$	$\frac{5}{8}$	56(4)	56(4)	56(4)	-8(5)	-8(5)	-8(5)	0.44
Cl	8a	0	0	0	149(5)	149(5)	149(5)	0	0	0	1.18
F ₁	96g	0.6032(1)	0.6032(1)	0.2677(1)	130(6)	130(6)	117(9)	0(5)	0(5)	0(5)	0.99
F ₂	96g	0.4470(1)	0.4470(1)	0.6624(1)	115(6)	115(6)	132(9)	-15(5)	-15(5)	-34(8)	0.95
F ₃	8b	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	82(12)	82(12)	82(12)	0	0	0	0.65

Notes. Numbers in parentheses indicate esd's.

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

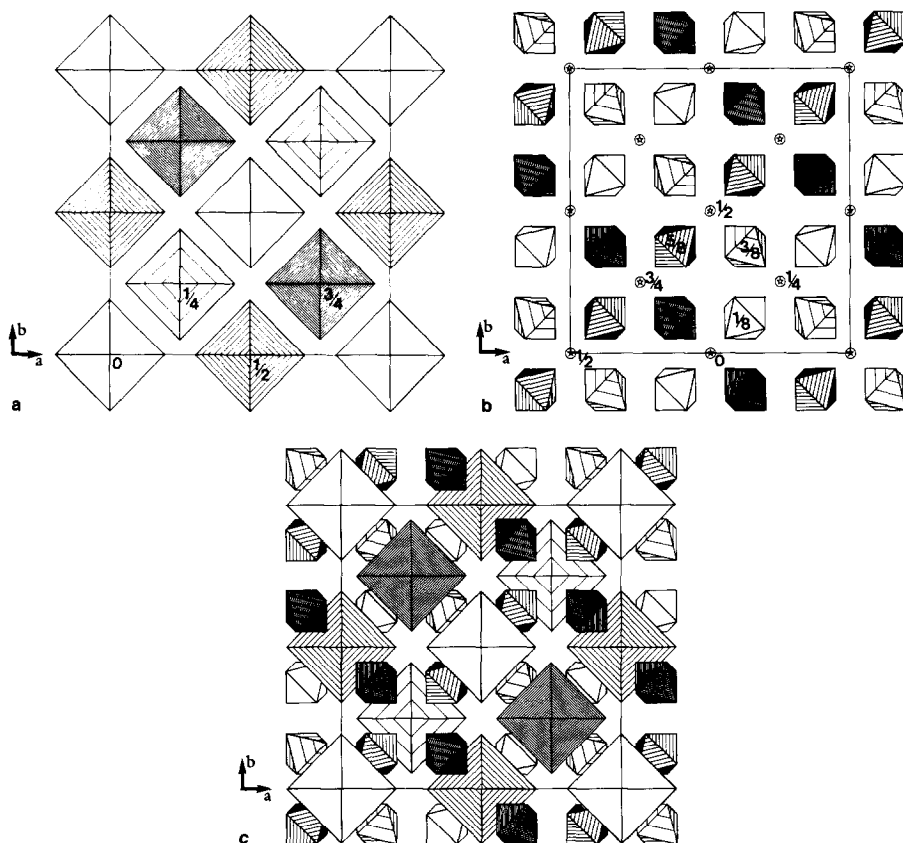


FIG. 2. (a) The ClSr₆ octahedra network related to diamond structure (numbers indicate the *z* coordinate of chlorine atoms). (b) The β-cristobalite network with AlF₆ octahedra and F₃ fluorine atoms. (c) The arrangement of isolated AlF₆ and ClSr₆ octahedra.

TABLE III
MAIN INTERATOMIC DISTANCES (Å) AND ANGLES (°) IN $\text{Sr}_{10}\text{Al}_2\text{F}_{25}\text{Cl}^a$

	Al ³⁺ octahedron	
Al-F ₂ = 6 × 1.781(1)	F ₂ -Al-F ₂ = 6 × 91.0(2)	F ₂ -F ₂ = 2.541(2)
	F ₂ -Al-F ₂ = 6 × 89.0(2)	F ₂ -F ₂ = 2.497(2)
	Cl ⁻ octahedron	
Cl-Sr ₂ = 6 × 3.196(0)	Sr ₂ -Cl-Sr ₂ = 12 × 90.0	Sr ₃ -Sr ₂ = 4.159(0)
	Sr ₁ ²⁺ polyhedron [10]	
Sr ₁ -F ₁ = 3 × 2.447(1)	F ₁ -Sr ₁ -F ₁ = 3 × 75.5(1)	F ₁ -F ₁ = 2.998(2)
Sr ₁ -F ₂ = 6 × 2.655(1)	F ₁ -Sr ₁ -F ₂ = 6 × 69.9(1)	F ₁ -F ₂ = 2.928(2)
Sr ₁ -F ₃ = 2.429(0)	F ₁ -Sr ₁ -F ₃ = 3 × 135.0(1)	F ₁ -F ₃ = 4.505(1)
(Sr ₁ -F) = 2.570	F ₂ -Sr ₁ -F ₂ = 3 × 55.2(2)	F ₂ -F ₂ = 2.462(3)
	F ₂ -Sr ₁ -F ₃ = 3 × 57.2(2)	F ₂ -F ₃ = 2.541(2)
	Sr ₂ ²⁺ polyhedron [8 + 1]	
Sr ₂ -F ₁ = 4 × 2.552(2)	F ₁ -Sr ₂ -F ₁ = 2 × 72.0(1)	F ₁ -F ₁ = 2.998(3)
Sr ₂ -F ₂ = 2 × 2.680(0)	F ₁ -Sr ₂ -F ₂ = 2 × 96.9(1)	F ₁ -F ₂ = 3.820(2)
Sr ₂ -F ₃ = 2 × 2.651(0)	F ₁ -Sr ₂ -F ₃ = 4 × 67.2(1)	F ₁ -F ₃ = 2.897(2)
Sr ₂ -Cl = 3.195(0)	F ₁ -Sr ₂ -Cl = 126.8(1)	F ₁ -F ₃ = 4.793(0)
(Sr ₂ -F, Cl) = 2.674	F ₁ -Sr ₂ -F ₂ = 4 × 85.7(1)	F ₁ -F ₂ = 3.539(2)
(Sr ₂ -F) = 2.609	F ₁ -Sr ₂ -F ₃ = 4 × 66.6(1)	F ₁ -F ₂ = 2.928(2)
	F ₂ -Sr ₂ -F ₂ = 55.3(2)	F ₂ -F ₂ = 2.462(3)
	F ₁ -Sr ₂ -Cl = 4 × 72.1(1)	F ₁ -Cl = 3.424(1)

^a Estimated standard deviations are given in parentheses.

elementary cell: the central fluorine F3 ($\frac{3}{4}, \frac{3}{4}, \frac{3}{4}$) is tetrahedrally surrounded by Sr, Al, and Cl atoms.

One method of description uses the octahedral subnetwork. Indeed, the chloride ions are surrounded by six strontium Sr₂ at

3.196 Å and form a diamond-related structure (Fig. 2a). The [AlF₆]³⁻ isolated octahedra (6 F₂ at 1.781 Å) and the F₃ fluorine describe a β-cristobalite-type network (F₃=Si⁴⁺, [AlF₆]³⁻=O²⁻) (Fig. 2b). The diamond and cristobalite sublattices are

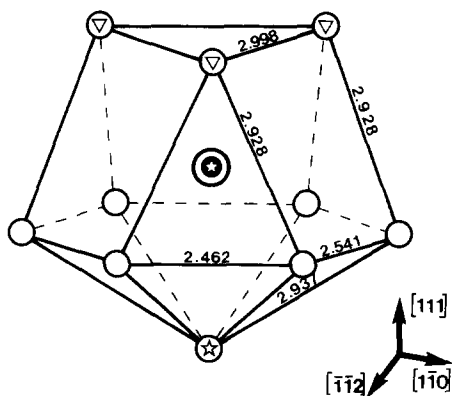


FIG. 3. Sr₁ polyhedron (symmetry 3*m*), legend as in Fig. 1.

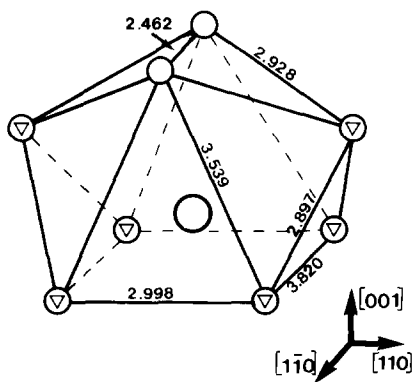


FIG. 4. Sr₂ polyhedron (symmetry 2*mm*), legend as in Fig. 1.

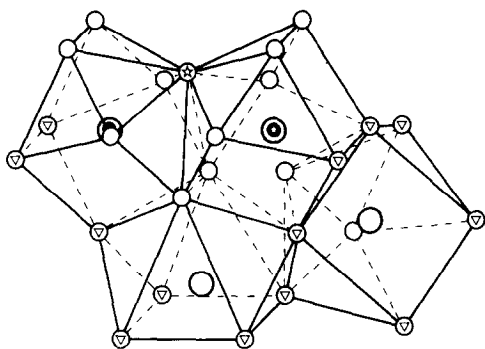


FIG. 5. Connections between Sr_1 and Sr_2 polyhedra, legend as in Fig. 1.

shifted from $a/2$ (Fig. 2c). Each elementary cell is occupied either by a tetrahedron of $[\text{AlF}_6]^{3-}$ octahedra or by a $[\text{ClSr}_6]^{11+}$ octahedron at the center. Within the elementary cell, the strontium Sr_1 and fluorine F_1 atoms are inserted between these isolated octahedra in such a way as to give, once more, a tetrahedral arrangement around fluorine F_3 .

A second method of description is based on the anionic coordination of the cations Al^{3+} and Sr^{2+} . From Table III it is clear that two kinds of strontium polyhedra are present; Sr_1 and Sr_2 have respectively 10- and 8-fold coordination of fluorine atoms.

The Sr_1 polyhedron $[\text{SrF}_{10}]$ (Fig. 3) can be described as having derived from a half

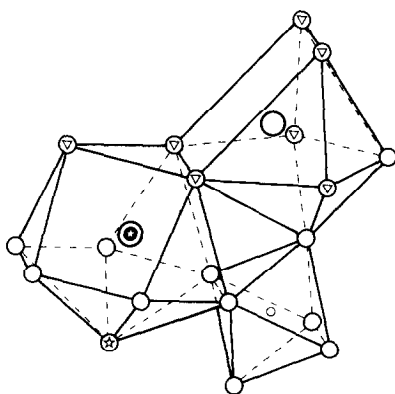


FIG. 6. Connections between Sr_1 , Sr_2 , and Al polyhedra, legend as in Fig. 1.

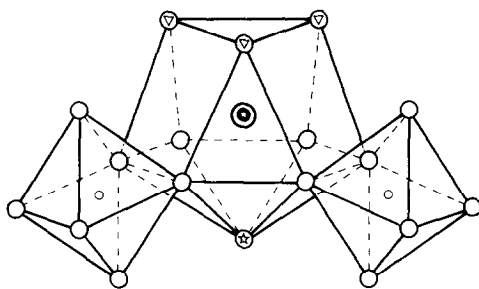


FIG. 7. Connections between Sr_1 and Al polyhedra, atom label as in Fig. 1 (the third AlF_6 octahedron was omitted for clarity).

cubooctahedron capped with a F_3 fluorine. The eightfold coordination of Sr_2 (Fig. 4) can be seen as a distorted square antiprism of fluorines ($8 \langle \text{Sr}_2\text{-F} \rangle = 2.609 \text{ \AA}$).

Each Sr_1 polyhedron is connected to three Sr_1 , six Sr_2 , and three Al polyhedra. The different connection modes are given in Table IV and shown in Figs. 5, 6, and 7. Four Sr_1 polyhedra are linked together in a tetrahedral way to build up an isolated " Sr_4F_{25} " block; these blocks are connected together by aluminum octahedra to ensure a three-dimensional network " $\text{Sr}_4\text{Al}_2\text{F}_{25}$ " for which only a bidimensional view is drawn in Fig. 8.

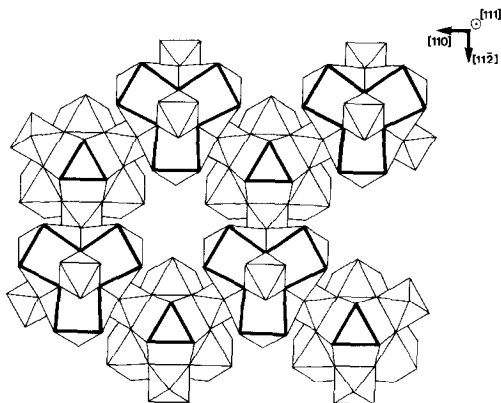


FIG. 8. [111] view of the connection mode between AlF_6 and " Sr_4F_{25} " blocks. Heavy lines correspond to faces which are close to a same level.

TABLE IV
THE DIFFERENT CONNECTION MODES BETWEEN
POLYHEDRA

Polyhedron 1	Polyhedron 2	Connection	
Sr ₁	Sr ₁	Face	F ₂ -F ₃ -F ₂
Sr ₁	Sr ₂	Face	F ₂ -F ₁ -F ₂
Sr ₁	Sr ₂	Edge	F ₁ -F ₁
Sr ₁	Al	Edge	F ₂ -F ₂
Sr ₂	Sr ₂	Edge	F ₁ -F ₁
Sr ₂	Sr ₂	Vertex	F ₁
Sr ₂	Al	Vertex	F ₂

The Sr₂ polyhedra [SrF₈] give rise to a three-dimensional network by means of edge-sharing chains running in the directions [100], [010], [001] along the screw axis 4₁ or 4₃ and one polyhedron belongs to only two perpendicular chains (Fig. 9). In this network the crossing chains lead to the formation of a hexacapped cubooctahedral cavity occupied by a chlorine atom (Fig. 10). So, each chlorine is surrounded by 6 Sr₂ at 3.196 Å and then by 12 F₁ at 3.424 Å. From this description the coordination

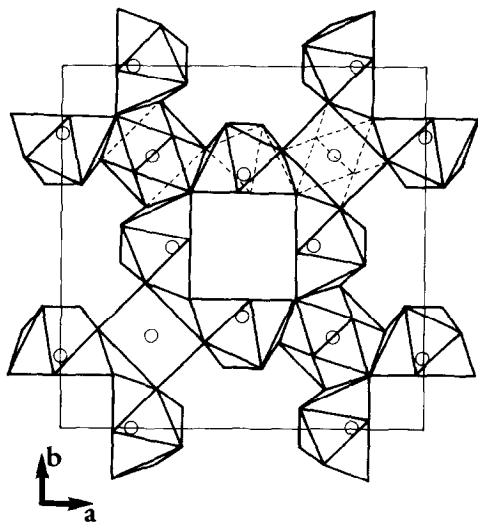


FIG. 9. Cross-linked chains of SrF₈ polyhedra in the (a, b) plane.

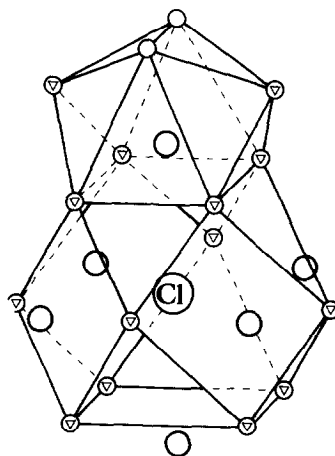


FIG. 10. The chlorine coordination: cubooctahedron ClF₁₂ and octahedron ClSr₆ (Sr₂), legend as in Fig. 1.

number of Sr₂ can be considered to be nine: 8F + 1Cl. A similar ninefold coordination is observed in the alkaline earth chloro-fluorides (4F + 5Cl) with one M-Cl distance shorter than the other four (6).

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References

1. J. NOUET, C. JACOBONI, G. FERREY, J. Y. GERARD, AND R. DE PAPE, *J. Cryst. Growth* **8**, 94 (1971).
2. G. COURBION, Thesis, Le Mans (1979).
3. A. HEMON, A. LE BAIL, AND G. COURBION, *J. Solid State Chem.* **81**, 299 (1989).
4. G. SHELDRIK, "SHELX76: A Program for Crystal Structure Determination," University of Cambridge (1976).
5. "International Tables for X-Ray Crystallography," Vol. IV, Kynoch Press, Birmingham (1968).
6. M. SAUVAGE, *Acta Crystallogr. Sect. B* **30**, 2786 (1974).