Zeitschrift für Kristallographie 194, 221–227 (1991)

The structure of acuminite, a strontium aluminium fluoride mineral

E. Krogh Andersen, G. Ploug-Sørensen

Department of Chemistry, Odense University, DK-5230 Odense M, Denmark

and E. Leonardsen

Institute of Mineralogy, Copenhagen University, Østervoldgade 10, DK-1350 København K, Denmark

Received: May 2, 1990

Mineral / Strontium aluminium fluoride / Crystal structure / Acuminite

Abstract. An X-ray diffraction study of single crystals of acuminite, a strontium aluminium fluoride mineral from Ivigtut, Greenland [$SrAlF_4(OH) \cdot H_2O$, $a = 13.223(1)$ Å, $b = 5.175(1)$ Å, $c = 14.251(1)$ Å, $\beta = 111.61(2)$, $C2/c$, $Z = 8$, $D_m = 3.295$ g cm^{-3}, $D_c = 3.305$ g cm^{-3}] used 2138 diffraction intensities (CAD-4 diffractometer), and was refined to R (unweighted) = 0.069. The strontium ions are 9-coordinated to 7 fluoride ions and 2 water molecules, the aluminium ions have octahedral coordination, 4 fluoride ions and 2 hydroxyl ions. The structure of acuminite is compared with the structure of tikhoenkovite another modification of $SrAlF_4(OH) \cdot H_2O$.

Introduction

The detection of a new strontium mineral in a sample from Ivigtut, Southern Greenland, was published by Pauly and Petersen in 1987. The mineral and the name acuminite have been approved by the Commission for New Minerals and Mineral Names, I.M.A. The material used in this investigation stems from the original sample.

For a full morphological, optical, and chemical description of acuminite the reader is referred to Pauly and Petersen (1987). Here we report only experimental data of importance for the structure determination.

Table 1. Lattice constants of acuminite in Å and degrees, standard deviations in brackets.

From	a	b	c	β
Powder				
Guinier-Hägg	13.223(1)	5.175(1)	14.251(1)	111.61(1)
Single-crystal	13.220(3)	5.163(3)	14.245(2)	111.63(2)

From the results of wet chemical and from thermal analyses the following formula is calculated for acuminite:

$$Sr_{0.98}Al_{1.02}F_{4.07}(OH)_{0.93} \cdot H_2O$$

in close agreement with the ideal formula $SrAlF_4(OH) \cdot H_2O$.

Experimental

The lattice constants of a monocrystal of acuminite were determined from θ values of 25 reflections measured on a single crystal diffractometer. In Table 1 the lattice constants from the single crystal are compared with lattice constants obtained from an indexed Guinier-Hägg powder diffractogram (Cu$K\alpha_1$, quartz calibrated). The lattice constants from powder diagrams were used in all calculations. The intensity data were collected from a crystal with dimensions $0.03 \times 0.06 \times 0.15$ mm^3. The measurements were made on an Enraf-Nonius CAD-4 instrument with graphite monochromatized pulse-height discriminated Mo$K\alpha$ radiation ($\lambda = 0.71069$ Å). In total 2891 reflections ($-23 \leq h \leq 22$, $0 \leq k \leq 9$, $0 \leq l \leq 25$) with $2.5 < \theta < 40°$ were obtained. They were reduced to 2138 unique reflections with $I > 2.5\ \sigma(I)$. The scan mode was $\omega/2\theta$. The 515 reflection was measured every 40 reflections and no decrease in intensity was observed. The data were corrected for background, Lorentz and polarization effects (but not for absorption and extinction). The systematic absences were hkl $(h + k)$ odd, $h0l$ l odd. This leaves two possible space groups $C2/c$ and Cc. The statistical test on normalized structure factors was slightly in favour of a centrosymmetric space group and hence the structure determination was made in $C2/c$.

Structure determination

The positions of the strontium and aluminium ions were found by the direct methods programmes included in SHELX 76 [Sheldrick (1976)]. Alternating structure-factor and electron-density calculations revealed the positions of the fluoride ions, hydroxyl ions, and water molecules (hydrogen atoms were not located).

Table 2. Final atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors (Å^2) with standard deviations in parentheses. $B_{eq} = 4/3\ \Sigma b_{ij}\ (a_i a_j)$.

	x	y	z	B_{eq}
Sr	8305(1)	8232(1)	1586(1)	1.11(3)
Al	4024(1)	4020(4)	4203(1)	0.62(9)
O(1)	4891(3)	7063(10)	4557(3)	3.16(28)
O(2)	8986(7)	3251(15)	1617(7)	7.40(77)
F(1)	8042(3)	10371(8)	3068(3)	0.97(21)
F(2)	6648(3)	10977(8)	0930(3)	1.20(23)
F(3)	10236(3)	7910(9)	1577(3)	1.09(22)
F(4)	8174(3)	9601(9)	−0154(3)	1.06(22)

The structure was refined by the CRYLSQ programme [X-RAY 76 system, Stewart et al. (1976)]. In the least-squares calculations $\Sigma(|F_o| - |F_c|)^2$ was minimized.

The positional parameters and anisotropic temperature factors for all atoms (excluding H) and one scale factor were varied in these calculations. In total 73 parameters were refined. All observations were included with equal weight. The atomic scattering factors were taken from the International Tables for X-ray Crystallography (1962). The final $R\,[(\Sigma|F_o| - |F_c|)/\Sigma|F_c|]$ value was 0.069. Coordinates and equivalent isotropic temperature factors are listed in Table 2[1].

Discussion

By the method described by Donnay and Allmann (1970) we have estimated the sum of the valences emanating from the strontium- and aluminium ions and also the sum of the valences received by the fluoride ions and oxygen atoms. These sums were for the strontium- and aluminium ions 2.00 and 3.01, respectively. For the fluoride ions they were in the range 0.85 to 1.07. The valence received by the O(1) and O(2) atoms was 0.83 and 0.35, respectively. The deviation of these values from 1 and 0 indicates the presence of hydrogen bonds; but contributions from such were not included in the calculations. The calculated values for the valence received by the oxygen atoms indicate that O(1) belongs to a hydroxide ion and O(2) to a water molecule. There are two short contacts between oxygen atoms not

[1] A list of structure factors and anisotropic temperature factors may be ordered referring to the no. CSD 53538, names of the authors and citation of the paper at the Fachinformationszentrum Energie-Physik-Mathematik, D-7514 Eggenstein-Leopoldshafen 2, FRG.

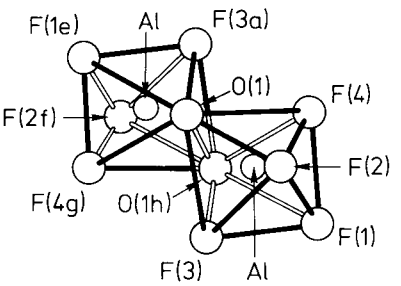

Fig. 1. Two aluminium ions, both octahedrally surrounded by 4 fluoride ions and 2 hydroxide ions. The octahedra are related by a symmetry centre at the midpoint of the O(1)–O(1h) line. The letters a, e, f, g and h refer to the symmetry operations at the bottom of Table 3. The octahedra are viewed almost along the [010] direction.

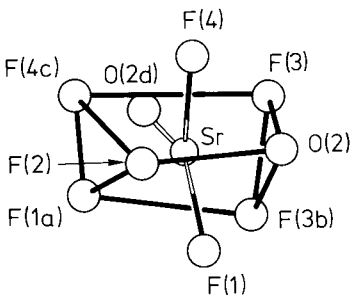

Fig. 2a. The 9-coordination of the strontium ion shown as the addition of an atom beyond the centre of each face of a triangular prism.

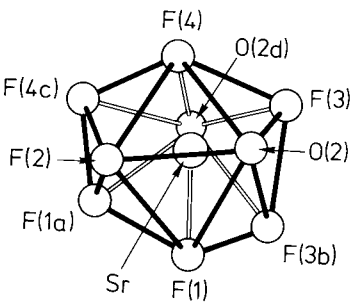

Fig. 2b. Another drawing of the strontium polyhedron. The strontium ion is surrounded by 7 fluoride ions and 2 water molecules [O(2) and O(2d)]. The 2 water molecules are related by the *b* axis translation. Viewed along the [010] direction the O(2) atoms overlap (as in Figure 3a). Here the viewing direction has been shifted so much that the lower O(2d) atom [and also the F(4c)–F(1a) edge] come into sight. The letters a, b, c and d refer to the symmetry operations at the bottom of Table 3.

Table 3. The coordination of strontium and aluminium in acuminite. Distances in Å, standard deviations in brackets.

Sr coordination polyhedron		Al coordination polyhedron	
Sr–F(1)	2.520(5)	Al–F(1)[e]	1.802(4)
Sr–F(1)[a]	2.501(5)	Al–F(2)[f]	1.784(5)
Sr–F(2)	2.487(4)	Al–F(3)[a]	1.823(5)
Sr–F(3)	2.563(4)	Al–F(4)[g]	1.836(5)
Sr–F(3)[b]	2.624(4)	Al–O(1)	1.903(5)
Sr–F(4)	2.523(5)	Al–O(1)[h]	1.905(4)
Sr–F(4)[c]	2.683(4)		
Sr–O(2)[d]	2.744(8)		
Sr–O(2)	2.727(8)		

[a] $\bar{x}+1.5, y-0.5, \bar{z}+0.5$;
[b] $\bar{x}+2, y, \bar{z}+0.5$;
[c] $\bar{x}+1.5, \bar{y}+1.5, \bar{z}$;
[d] $x, y+1, z$;
[e] $x-0.5, y-0.5, z$;
[f] $\bar{x}+1, y-1, \bar{z}+0.5$;
[g] $x-0.5, \bar{y}+1.5, z+0.5$;
[h] $\bar{x}+1, \bar{y}+1, \bar{z}+1$.

belonging to the same polyhedron. These are a O(2)...O(2) contact of 2.92(1) Å and a O(2)...O(1) contact of 2.69(1) Å). These distances may be taken as indication of hydrogen bonds.

Drawings of the surroundings of the aluminium ions and strontium ions are shown in Figure 1, 2a and 2b. The aluminium ions are octahedrally surrounded by 4 fluoride ions and two hydroxyl ions. These octahedra are rather regular [largest deviation is for the O(1)–Al–O(1) angle which is 79.8(2)°]. The strontium ions are 9-coordinated. The configuration of the 9-coordination can best be visualized by adding an atom above the midpoint of each of the square faces of a triangular prism. The strontium polyhedra are fairly regular. Interionic distances are recorded in Table 3. Distances from the strontium and aluminium ions to fluoride and hydroxyl ions and to water molecules are recorded in Table 3.

In the crystal structure of acuminite strontium and aluminium coordination polyhedra are connected to puckered layers parallel to the (010) plane. One such layer is shown in Figure 3a. Due to the short *b* axis, only two atoms belonging to the same polyhedron overlap in this projection, i.e. the oxygen atoms O(2) belonging to the water molecules. Within the layers each strontium polyhedron is bonded to three other polyhedra. To two of them the binding involves common edges. In one along an [F(4)–F(4)′] edge where the two fluoride ions are related by a centre of symmetry; in the other along an [F(3) – F(3)′] edge where the two fluoride ions are related by a twofold axis. To the third the bonding is through a common vertice

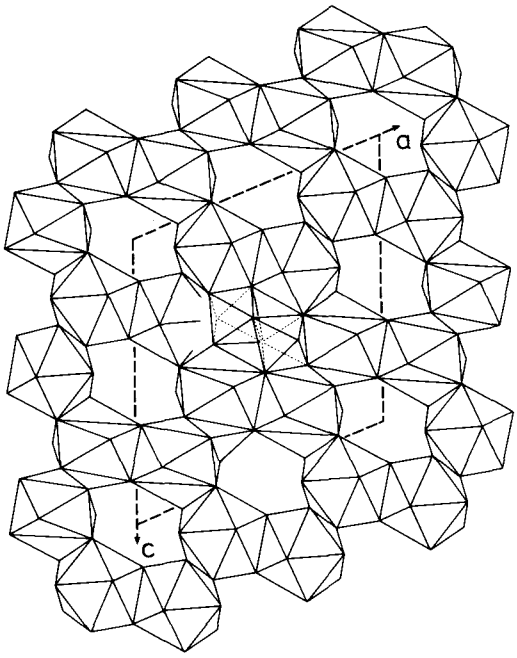

Fig. 3a. A layer of polyhedra parallel to the (010) plane. Only two aluminium octahedra are shown. For atom labelling see Figure 3b.

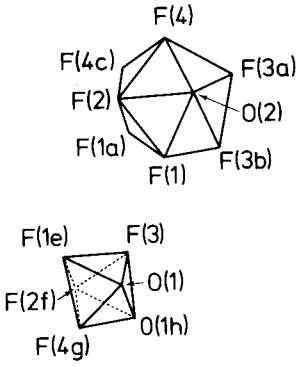

Fig. 3b. The labelling of atoms in the strontium nonahedra and aluminium octahedra. The polyhedra are shown in the same orientation as in Figure 3a. The letters a through h refer to the symmetry operations at the bottom of Table 3.

at F(1). It is worth noticing that the lines between two F(1) ions in Figure 3a is not an edge common to two polyhedra. It is the projection of separate edges formed by F(1) ions related by the twofold screw axes.

Two aluminium octahedra fill the space between six strontium polyhedra. They share an edge [O(1) – O(1)′].

Each of them also share an edge F(1) – F(4) with one strontium polyhedron, an edge F(1) – F(3) with another and a vertice that belongs to a strontium polyhedron in an adjacent layer. This arrangement leads to a bond between the layers. Another bond between adjacent layers is the sharing of O(2) vertices. The cleavage that Pauly and Petersen (1987) report along (001) finds no support in our interpretation of the structure.

The structure of tikhonenkovite, another mineral with the composition $SrAlF_4(OH)$, H_2O, was determined by Pudovkina and Pyatenko (1967). The structures of tikhonenkovite and acuminite are similar. They agree, with respect to the coordination of strontium- and aluminium ions, not only in coordination numbers but also in dimensions and shape of the polyhedra. The major difference concerns the connection between the strontium polyhedra in the puckered layers. In both structures each strontium polyhedron (within a layer) is in contact with three strontium polyhedra. In tikhonenkovite the contacts are one by sharing an edge and two by sharing apices. In acuminite two of the three contacts are by edge sharing and the third is by sharing an apex. Another difference is that, while the hydroxide ions are only part of the aluminium octahedra in acuminite, they also take part in the coordination of strontium ions in tikhonenkovite.

References

Donnay, G., Allmann, R.: How to recognize O^{2-}, OH^- and H_2O in crystal structures determined by X-rays. Am. Mineral. **55** (1970) 1003 – 1015.

International Tables for X-ray Crystallography, Vol. III, 201 – 209. Birmingham: Kynoch Press (1962).

Pauly, H., Petersen, V. O.: Acuminite, a new Sr-fluoride from Ivigtut, Southern Greenland. Neues Jahrb. Mineral. Monatsh. **11** (1987) 502 – 514.

Pudovkina, Z. V., Pyatenko, Y. A.: Crystal structure of tikhonenkovite. Dokl. Akad. Nauk SSSR **174** (1967) 193 – 196.

Sheldrick, G. M.: SHELX 76. Programme for crystal structure determination. Univ. of Cambridge, England (1976).

Stewart, J. M., Machin, P. A., Dickinson, C. W., Ammon, H. L., Heck, H., Flack, H.: The X-RAY 76 system. Tech. Rep. TR-446. Computer Science Center, University of Maryland, College Park, Maryland (1976).