The crystal structure of vlodavetsite, $AlCa_2(SO_4)_2F_2Cl{\cdot}4H_2O$

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Absract

The crystal structure of vlodavetsite, $AlCa_2(SO_4)_2F_2Cl{\cdot}4H_2O$, has been determined, space group *I4/m*, a = 6.870(1), c = 13.342(2) Å, Z = 2, D_x = 2.35 g/cm^3. The polyhedron cation chains are parallel to [001] and consist of couples of distorted Ca octahedra alternating with one distorted Al octahedron rotated through 24° with respect to the former. The chains are linked by SO_4-tetrahedra so that all of the four tetrahedron oxygen atoms take part in coordination of Ca atoms to form a distorted octahedron with Cl and F atoms. The Al coordination polyhedron consists of two F atoms and four oxygen atoms belonging to water molecules. There is a specific interaction via hydrogen bonds between oxygen atoms of SO_4-tetrahedra and water molecules.

KEYWORDS: vlodavetsite, crystal structure.

Introduction

VLODAVETSITE is a new mineral of the Tolbachik Main Fracture Eruption volcanic exhalation (Kamchatka, 1975–76). The X-ray single crystal structure determination has been carried out continuing the complex crystallographic investigations of the vlodavetsite crystals (Vergasova *et al.*, 1995).

The mineral is a fine-grained material. The isolated transparent colourless microplates and square plates or rectangular crystals are rarely observed.

Experimental

Weissenberg camera and 4-circle diffractometer 'Syntex P2_1' studies were carried out and gave the following data: 447 unique reflections (Mo-$K\alpha$ radiation, sin θ/λ < 0.903, $I > 3\sigma_I$), tetragonal system, *I-/-* diffraction group, included space groups *I4/m*, *I4*, $I\bar{4}$. The unit cell with a = 6.870(1), c = 13.342(2) Å contains two formula units of vlodavetsite (D_x = 2.35 g/cm^3).

The structure was solved in space group *I4/m* by direct methods and refined by a full-matrix least-squares method with anisotropic thermal parameters to R = 0.046 (R_W = 0.048) using the program complex 'CSD' (Akselrud *et al.*, 1989). The positions of fluorine, chlorine, oxygen and hydrogen atoms were localized on difference Fourier maps. Absorption corrections were made using the program 'DIFABS' (Walker and Stewart, 1983), μ = 18.17 cm^{-1}. The final atomic positions are given in Table 1.*

Discussion

In the crystal structure of vlodavetsite the chains of the cation polyhedra are parallel to the fourfold axis and consist of the couples of distorted Ca-octahedra alternating with one distorted Al-octahedron rotated through 24° with respect to the other. (Figs. 1,2,

* Tables of the calculated and observed crystal structure refinements, atomic parameters and anisotropic parameters are available from the editorial office.

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TABLE 1. Atomic positions and isotropic temperature factors for vlodavetsite

Atom	x/a	y/b	z/c	B
Al	0	1.0	1.0	1.13(9)
Ca	0	1.0	0.7015(1)	1.06(3)
S	0.5	1.0	0.75	1.05(3)
F	0	1.0	0.8688(4)	1.40(9)
Cl	0	1.0	0.5	2.12(6)
O1	0.3372(5)	0.0635(5)	0.6859(2)	1.64(7)
O2	0.0594(8)	1.2727(8)	1.0	1.74(11)
H	0.078(9)	1.327(8)	1.051(4)	1.95(5)

TABLE 2. Bond distances (Å) and angles (degrees) for vlodavetsite

Ca-polyhedron			
Ca–Cl	2.689(3)	Cl–Ca–F	180.0(1)
Ca–F	2.233(6)	Cl–Ca–O1	34.9(1)
Ca–O1	2.366(3)	F–Ca–O1	95.0(1)
		O1–Ca–O1[a]	89.6(1)
		O1–Ca–O1[b]	169.9(1)
Al-polyhedron			
Al–F	1.750(5)	F–Al–F	180.0(2)
Al–O2	1.918(6)	F–Al–O2	90.0(2)
		O2–Al–O2	180.0(2)
		O2–Al–O2	90.0(2)
S-tetrahedron			
S–O1	1.474(4)	O1–S–01	109.1(2)
		O1–S–01	109.7(2)

Table 2). A similar arrangement of an Al-octahedron between two Ca-polyhedra (twelve neighbours) was observed in the structure of woodhouseite (Kato, 1977). The cation chains are disposed in the crystal lattice halfway along the diagonal translation [110] and linked by SO_4-tetrahedra so that all four tetrahedral oxygen atoms take part in the coordination of Ca atoms to form a distorted octahedron with Cl and F atoms exhibiting two nonequal perfect tetragonal pyramids with a common base (Table 2). The stretched pyramid has a Cl atom on top and the flattened one a F atom. The Ca atom is located inside the flattened pyramid. The bond distances Ca–$O_{tetr.}$

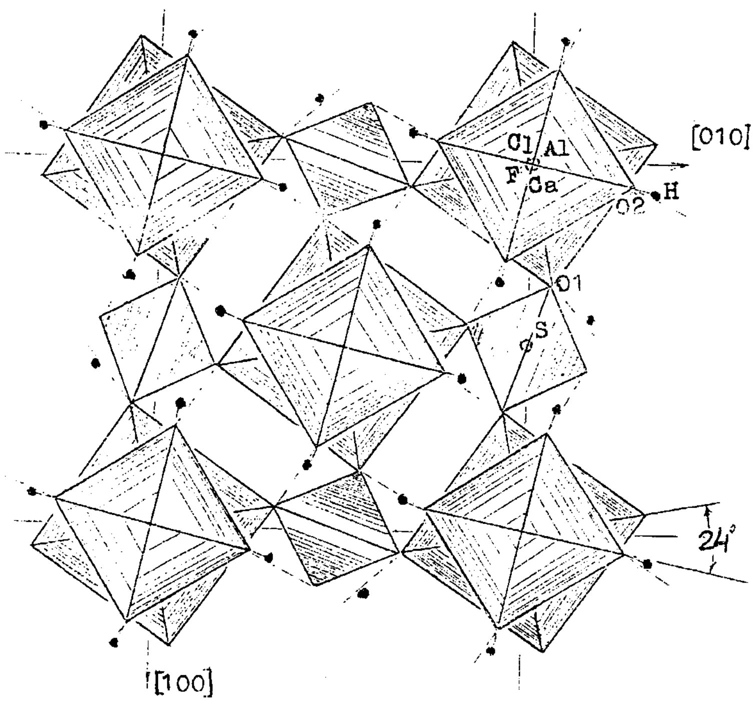

FIG. 1. Projection of the structure on the (001) plane.

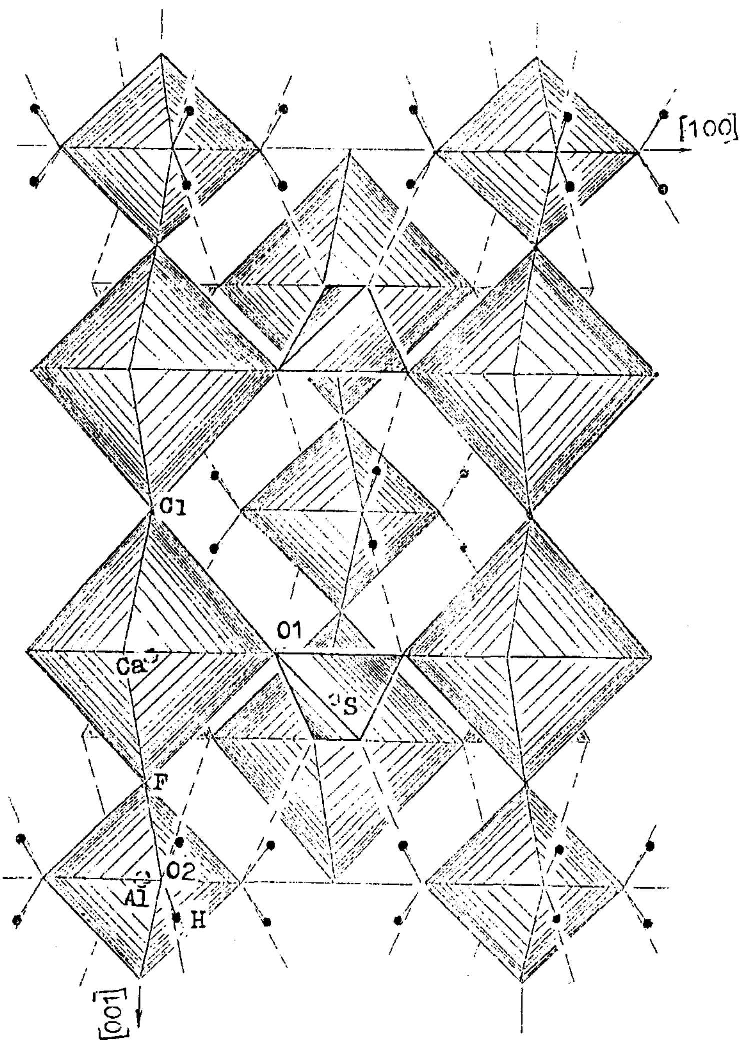

FIG. 2. Projection of the structure on the (010) plane.

are the shortest distances among the sulphate structures where they fluctuate from 2.888(3) Å in woodhouseite (Kato, 1977) to 2.528(2)–2.378(1) Å in gypsum (Cole and Lancucki, 1974).

The Al coordination polyhedron is a flattened perfect tetragonal dipyramid with F atoms at the points, and four oxygen atoms belonging to water molecules in the basal plane (Table 2). The bond distances Al–F and Al–O are identical to those in the khademite structure (Bachet *et al.*, 1981). The Al coordination polyhedron has no direct contacts with the almost ideal SO_4-tetrahedra. However, interatomic distance analysis shows that there are large distances between the oxygen atoms of the water molecules and those of the SO_4-tetrahedra (O1...O2 = 2.815(5) Å) and shortened distances between water molecule hydrogen atoms and tetrahedron oxygen atoms (H..O1 = 2.03(5) Å), which are smaller than their sum of Van der Waals radii. Hence, these atoms have a specific interaction via hydrogen bond ($\angle$ O2HO1 = 170.6(6)°) to penetrate the crystal structure (Figs. 1,2). The hydrogen interaction between the SO_4-tetrahedra and water molecules is typical of hydrosulphate structures and occurs in structures of gypsum (Cole and Lancucki, 1974) and khademite (Bachet *et al.*, 1981).

References

Akselrud, L. G., Grun, Yu. M., Zavalii, P. Yu., Pechsky, V. K. and Fundamensky, V. S. (1989) CSD — Universal program for single crystal ANR/OR POWDER structure data treatment. Collected abstracts of XII European crystallographic meeting, **3**, 155, Moscow, USSR.

Bachet, H., Cesbron, F. and Chevalier, R. (1981) Structure cristalline de la khademite $Al(SO_4)\cdot 5H_2O$. *Bull. Mineral.*, **104**, 19.

Cole, W. F. and Lancucki, C. J. (1974) A refinement of the crystal structure of gypsum $CaSO_4\cdot 2H_2O$. *Acta Crystallogr.*, **B30**, 921.

Kato, T. (1977) Further refinement of the woodhouseite structure. *Neues Jahrb. Mineral. Mh.*, **54**.

Vergasova, L. P., Filatov, S. K., Starova, G. L. and Matusevich, G. L. (1995) Vlodavetsite — a new mineral of volcanic sublimates. *Dokl. Akad. Nauk. Russ.* (in Russian) (in press).

Walker, N. V. and Stewart, D. (1983) An empirical method for correction of diffractometer data for absorbtion effects, 'DIFABS', *Acta Crystallogr.*, **A39**, 158.

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