

CHEMISTRY

Crystal Structure of New Native Compound $\text{Cu}_4\text{Al}_3(\text{OH})_{14}\text{F}_3(\text{H}_2\text{O})_2$

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A new mineral, a double aluminum copper hydroxide fluoride, has been found in the Khaidarkan (Kyrghyzstan) mercury–antimony deposit. It occurs in a calcium vein in association with fluorite, malachite, and allophane-like aluminum copper silicate. It forms needlelike, bright blue crystals. In this work, we studied a fine-fiber crystal of dimensions $0.05 \times 0.05 \times 0.8$ mm. Parameters of the monoclinic unit cell were determined and refined on an automated Enraf-Nonius diffractometer (MoK_α radiation, graphite monochromator): $a = 12.326(3)$ Å, $b = 2.907(3)$ Å, $c = 10.369(3)$ Å, $\beta = 97.90(2)^\circ$, $V = 368$ Å³, space group $C2/m$, $Z = 1$, $\rho(\text{calc}) = 3.00$ g/cm³. Comparing these parameters with the parameters of the orthorhombic unit cell of cyanotrichite [1] $\text{Cu}_4\text{Al}_2[\text{SO}_4](\text{OH})_{12} \cdot 2\text{H}_2\text{O}$ ($a = 10.16$, $b = 12.61$, $c = 2.90$ Å), whose structure is unknown, made it possible to assume that both minerals have close chemical compositions with certain differences in anion composition (fluorine was identified in the new mineral). However, X-ray structural analysis showed that the chemical composition of the new mineral differs considerably from that of cyanotrichite. Table 1 presents the data of the repeated chemical analysis of the mineral and its comparison with the composition calculated based on the structural data.

Reflection intensity data were collected on the same diffractometer in a hemisphere of reciprocal space (843 reflections with $I > 2\sigma(I)$, $\sin\theta/\lambda < 0.7$ Å^{−1}, 473 independent reflections with $|F| > 3\sigma(F)$, $R_{\text{merge}} = 0.022$ for 311 groups of equivalents). All calculations were performed by using the AREN program package [2].

The structural fragment solved by the direct methods was used as a starting approximation in the “phase correction” procedure [3]. All non-hydrogen atoms

were located from the ultimate modified synthesis with $R = 18\%$. Refining this model by the least-squares method in isotropic approximation led to $R_{\text{hkl}} = 11\%$. After corrections for absorption were applied (DIFABS [4]), R decreased to 6.2%. However, at one of the two Al positions, the thermal factor remained three times greater than that of the other position. Refining the site occupancy factor of this position revealed a vacancy, and R decreased to 5%. When corrections for extinction ($E = -0.0000112$) were applied, the refinement in anisotropic approximation converged with $R = 3\%$. At this stage, all hydrogen atoms were located from difference syntheses, and the atoms with complete site occupation were refined. The ultimate value $R_{\text{hkl}} = 2.9\%$.

Coordinates of basis atoms and their equivalent thermal factors are listed in Table 2. Interatomic distances and hydrogen-bond geometry are given in Table 3.

The Cu cations have a typical coordination, i.e., a tetragonal bipyramid (or a severely distorted octahedron) with four distances of 1.93–1.99 Å and two longer distances of 2.4 Å. The smaller aluminum cations are in two crystallographically nonequivalent positions. One of them (Al_1) is in a rather regular octahedron with the distances ranging within 1.90–1.93 Å.

Table 1. Chemical composition (%) of the mineral: (1) experimental and (2) calculated from X-ray structural data

Components	1	2
CuO	46.27	47.71
Al ₂ O ₃	23.34	22.94
H ₂ O	22.30	24.29
F	8.05	8.55
SiO ₂	0.47	0
SO ₃	0.10	0
Sum	100.53	103.49
−O=F ₂	3.03	3.48
Sum	97.50	100.01

Note: The Cu, Al, Si, and S contents were determined by X-ray probe analysis (I.P. Laputina). The F and H₂O contents were determined by chemical analysis (V.Yu. Karpenko).

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Table 2. Fractional coordinates, multiplicity (Q), site occupancy factors (q), and equivalent thermal parameters of basis atoms

Atom	x/a	y/b	z/c	Q	q	$B_{eq}, \text{\AA}^2$
Cu	0.1747 (1)	0	0.7085 (1)	4	1	1.21 (3)
Al ₁	0.5	0	0.5	2	1	1.01 (5)
Al ₂	0	0	0	2	0.49 (1)	2.9 (1)
(OH) ₁	-0.0949 (2)	0	0.5228 (3)	4	1	1.3 (1)
(OH) ₂	0.5630 (2)	0	0.6813 (3)	4	1	1.3 (1)
(OH) ₃	0.7780 (3)	0	0.7160 (3)	4	1	1.5 (1)
F	0.5446 (5)	0	0.1108 (5)	4	0.73 (1)	4.8 (2)
W	-0.1528 (6)	0	0.0569 (5)	4	1	4.6 (2)
H ₁	0.146 (9)	0	0.416 (9)	4	1	
H ₂	0.474 (9)	0	0.259 (9)	4	1	
H ₃	0.155 (9)	0	0.220 (9)	4	1	
H ₄	0.168	0.263	0.998	8	0.5	
H ₅	0.235	0	0.956	4	0.5	

Note: W = [(H₂O)_{0.5} (OH)_{0.5}].

Table 3. Interatomic distances (Å) and angles (deg)

Octahedra					
Cu-(OH) ₃	1.926(2) × 2	Al ₁ -(OH) ₁	1.900 (2) × 4	Al ₂ -F	1.887 (3) × 4
(OH) ₂	1.995(2) × 2	(OH) ₂	1.932 (3) × 2	W	2.049 (7) × 2
(OH) ₁	2.463 (3)		⟨1.911⟩		⟨1.941⟩
W	2.484 (6)				
	⟨2.133⟩				
Hydrogen bonds					
(OH) ₁ -H ₁	0.9	H ₁ ... (OH) ₃	1.8	(OH) ₁ -(OH) ₃	2.708 (5)
(OH) ₂ -H ₂	0.8	H ₂ ... F	1.8	(OH) ₂ -F	2.681 (7)
(OH) ₃ -H ₃	0.9	H ₃ ... F	2.2	(OH) ₃ -F	3.006 (5)
W-H ₄	1.0 × 2	H ₄ ... W	2.2	W-W	2.907 (1)
H ₄ -H ₄	1.3	H ₄ ... W	2.3		
W-H ₅	1.0	H ₅ ... W	2.1		
H ₄ WH ₄	106				
(OH) ₁ H ₁ ... (OH) ₃	171				
(OH) ₂ H ₂ ... F	174				
(OH) ₃ H ₃ ... F	138				
WH ₄ ... W	127				
WH ₄ ... W	120				
WH ₅ ... W	129				

The Al₂ atom is in a more distorted octahedron with the distances ranging within 1.89–2.05 Å.

The types of anions that form the above polyhedra were determined based on the local valence balance [5]. The Al₁ octahedron is formed by hydroxide ions, and the Al₂ octahedron is composed of three types of ligands, viz., F, OH, and H₂O. The fluorine position is 25% vacant.

The polyhedra of each type share edges to form columns extended along the b axis, which is the shortest one in the monoclinic unit cell. However, these columns play different crystallochemical roles. The column of Al₁ octahedra share edges with two neighboring Cu columns to form infinite triple bars. They are staggered along the unit cell diagonal. These bars share vertices with the single columns of the Al₂ octahedra to

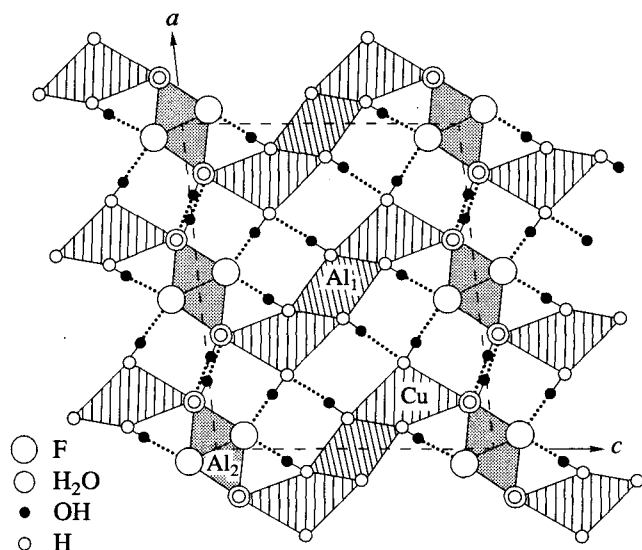


Fig. 1. Projection of the structure of the mineral onto the (010) plane.

form zigzag walls (Fig. 1). Along the a axis, these walls are combined with each other by only hydrogen bonds involving OH groups and H_2O molecules.

The walls of close-packed polyhedra (including octahedra) is a typical feature of the structure of many complex oxides responsible for their layered character. In the structure in question, the walls are nonhomogeneous and composed of different linear fragments (triple and single) alternating along the c axis. Similar fragments occur in some other structures. For example, double columns are the structural building blocks of the hollandite family [6]. A combination of double and triple columns of Mn octahedra forms the structure of psilomelane [7]. However, in both cases, the columns are combined in a three-dimensional framework with bulky channels along a short period of ca. 3 Å. In the new mineral, a combination of single and triple columns occurs. The pseudolayered character of the structure is due to the fact that the bonds within the triple bars are considerably stronger than the interbar bonds. Additionally, the interbar bonds are weakened because of incomplete occupancy of the Al_2 octahedra, which causes the needle habit of crystals.

With regard to the occupancy of the Al_2 position (50%), the Al_2/F ratio is 1/3, which indicates a certain mode of the filling of the Al_2 positions. The possible variants of filling are shown in Fig. 2. In variant I (Fig. 2b) of filling (alternate filling), the Al_2/F ratio would be 1/4. Evidently, the second variant of filling is valid. In this case, pairs of occupied octahedra share the F-F edges, and the vacancies lead to a decrease in the number of anions by 1/3. Given the regular distribution of vacant and occupied octahedra, the b lattice parameter should increase by a factor of 4. In the sample studied, parameter b only tends to be doubled (in terms of the doubled

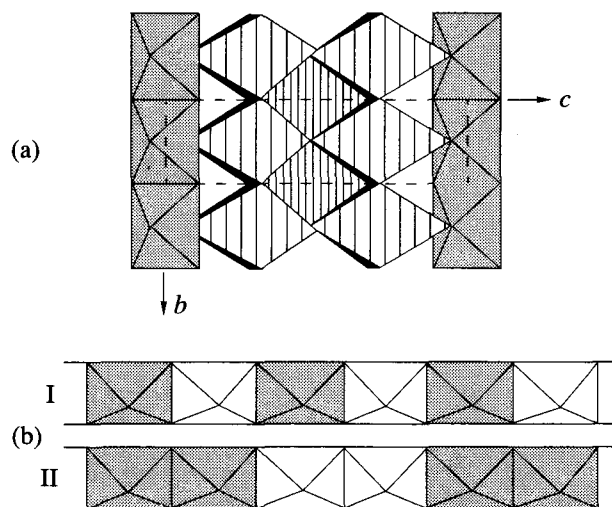


Fig. 2. (a) Projection of the structure of the mineral onto the (100) plane and (b) the schemes of two modes of statistical distribution of vacancies in the Al_2 columns.

unit cell, the experimental array of structure amplitudes contains more than ten reflections sufficiently significant in magnitude with the indices $k = 2n + 1$). This indicates that some other variants of the statistical filling of the columns are also possible.

Because of the vacancies at the Al_2 sites, the common vertex of the Al_2 and Cu octahedra is statistically occupied either by water molecules or by hydroxo groups. This is supported by half-occupancy of the hydrogen positions.

Taking into account the above features, the crystallochemical formula of the mineral, which is refined in the course of X-ray diffraction analysis, can be presented as $Cu_4Al_2(Al\Box)(OH)_{12}F_3[(OH)_2(H_2O)_2]$. This formula is consistent with spectral data. The IR spectrum of the mineral shows two absorption bands of the HOH bending vibrations at 1560 and 1640 cm^{-1} , which proves the occurrence of two types of water molecules. A large portion of the OH groups (both hydroxo groups and those from water molecules) forms strong hydrogen bonds (broad bands at 3190, 3400, and 3495 cm^{-1} in the region of OH stretching vibrations). A narrow band at 3560 cm^{-1} is assigned to weakly bonded OH groups.

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REFERENCES

1. Feklichev, V.G., *Diagnosticheskie konstanty mineralov* (Diagnostic Constants of Minerals), Moscow: Nedra, 1989.

2. Andrianov, V.I., *Kristallografiya*, 1987, vol. 32, no. 1, pp. 228–231.
3. Andrianov, V.I., *Kristallografiya*, 1989, vol. 34, no. 3, pp. 592–597.
4. Walker, N. and Stuart, D., *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 1983, vol. 39, pp. 158–166.
5. Brown, I.D. and Shannon, R.D., *Acta Crystallogr., Sect. A: Cryst. Phys., Diffraction, Theor. Gen. Crystallogr.*, 1973, vol. 29, no. 3, pp. 266–282.
6. Bolotina, N.B., Dmitrieva, M.T., and Rastsvetaeva, R.K., *Kristallografiya*, 1992, vol. 37, no. 3, pp. 598–605.
7. Wadsley, A.D., *Acta Crystallogr.*, 1953, vol. 6, no. 6, pp. 433–438.