

The crystal structure of fedotovite, $\text{K}_2\text{Cu}_3\text{O}(\text{SO}_4)_3$

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Abstract

The crystal structure of fedotovite, $\text{K}_2\text{Cu}_3\text{O}(\text{SO}_4)_3$ has been determined, space group $C2/c$, a 19.037(6), b 9.479(2), c 14.231(5) Å, β 111.04(3)°, $Z = 8$, $D_x = 3.09 \text{ g/cm}^3$. The main units of the fedotovite structure are formed around two additional oxygen atoms and consist of edge-sharing $[\text{OCu}_4]$ tetrahedra and four $[\text{SO}_4]$ tetrahedra attached to them. The units are further connected by two $[\text{SO}_4]$ tetrahedra, building distinct layers parallel to the yz plane. These layers are interconnected by potassium atoms. In the fedotovite structure, the three kinds of copper atoms are fivefold (4 + 1) coordinated to oxygen atoms with a strong Jahn-Teller effect. The coordination polyhedra of Cu1 and Cu2 atoms are distorted and flattened orthorhombic pyramids with Cu–O distances varying from 1.912 to 2.333 Å, the sixth neighbour of the both atoms is the copper atom lying at 2.975 and 2.981 Å for Cu2 and Cu1 respectively. The coordination environment of the Cu3 atom is a distorted elongated orthorhombic pyramid with four Cu–O distances from 1.943 to 1.961 Å, a fifth at 2.558 Å, and further sixth and seventh neighbours (oxygen and copper atoms) at 2.809 and 2.806 Å, respectively.

KEYWORDS: fedotovite, crystal structure.

Introduction

THE X-ray crystal structure determination of fedotovite has been carried out by means of the single crystal method, continuing the investigation of fedotovite, $\text{K}_2\text{Cu}_3\text{O}(\text{SO}_4)_3$ (Vergasova *et al.*, 1988), which is a new mineral from sublimates of the Tolbachik fissure eruption, 1975–1976, Kamchatka (Fedotov, 1984).

Structure

Blue–green tabular crystals of fedotovite are monoclinic, space group $C2/c$, which differs from the formerly reported space group $P2_1/n$ (Vergasova *et al.*, 1988). Few reflections do not correspond to the $C2/c$ space group, all having intensities which slightly exceed that of the background (the 031 reflection is the strongest). The remaining 2819 reflections recorded on the automatic

'Syntex P2₁' diffractometer (Mo- $k\alpha$ radiation, $I \geq 3\sigma_1$, $\sin\theta/\lambda \leq 0.80 \text{ \AA}^{-1}$) fit the $C2/c$ space group. In the unit cell with a 19.037(6), b 9.479(2), c 14.231(5) Å, β 111.04(3)° are eight formula units of fedotovite ($D_x = 3.09 \text{ g/cm}^3$).

The structure was solved by direct methods and refined by full-matrix least-squares methods with anisotropic thermal parameters to $R_w = 0.070$ by using the program system complex 'CSD' (Acsehrud *et al.*, 1989). Absorption corrections were made using the program 'DIFABS' (Walker and Steward, 1983), $\mu = 64.2 \text{ cm}^{-1}$. The population factors refined for the reflections with $\sin\theta/\lambda \leq 0.3$ are close to 1.0. The final atomic positions are given in Table 1.

The crystal structure of fedotovite is a distorted three-layer close-packing of oxygen atom in the xz plane. The cavities are occupied by different atoms in different layers: at $y \approx 0.0$ copper atoms (Cu1 and Cu2) and sulphur atoms (S2 and S3)

Table 1. Atomic positions of fedotovite*

| Atom | x/a | y/b | z/c |
|------|------------|------------|------------|
| Cu1 | 0.48071(4) | 1.01816(7) | 0.34265(5) |
| Cu2 | 0.48587(4) | 0.47783(8) | 0.14018(5) |
| Cu3 | 0.42119(4) | 0.74635(7) | 0.20615(6) |
| S1 | 0.50646(9) | 0.7505(1) | 0.4904(1) |
| S2 | 0.64724(9) | 1.0261(2) | 0.3652(1) |
| S3 | 0.35139(9) | 0.4648(1) | 0.2120(1) |
| K1 | 0.32573(9) | 0.7519(2) | 0.4388(2) |
| K2 | 0.1957(1) | 0.7346(2) | 0.1249(2) |
| O1 | 0.5 | 0.8908(5) | 0.25 |
| O2 | 0.4501(3) | 0.8269(5) | 0.4066(3) |
| O3 | 0.5620(3) | 0.6771(5) | 0.4582(3) |
| O4 | 0.4636(3) | 0.6480(4) | 0.5267(3) |
| O5 | 0.5891(3) | 1.0572(6) | 0.4098(4) |
| O6 | 0.4051(3) | 0.4394(5) | 0.3183(4) |
| O7 | 0.3385(3) | 0.6195(5) | 0.2000(4) |
| O8 | 0.2803(3) | 0.3966(5) | 0.2007(4) |
| O9 | 0.5478(3) | 0.8504(5) | 0.5706(3) |
| O10 | 0.6215(3) | 1.0720(6) | 0.2585(4) |
| O11 | 0.3844(3) | 0.4150(6) | 0.1403(4) |
| O12 | 0.5 | 0.6045(5) | 0.25 |
| O13 | 0.6606(3) | 0.8707(5) | 0.3699(4) |
| O14 | 0.7169(3) | 1.0959(5) | 0.4243(4) |

* Thermal parameters may be obtained from the editor or authors

occupy octahedral and tetrahedral cavities respectively; at $y = 0.25$ copper atoms (Cu3) and sulphur atoms (S1) are disposed in octahedral and tetrahedral cavities, and two potassium atoms enter into octahedral cavities and strongly distort a close-packing of oxygen atoms (Fig. 1).

The main unit of the fedotovite structure is formed around two additional oxygen atoms (O1 and O12) and consist of two edge-sharing $[\text{OCu}_4]$ tetrahedra with Cu–O distances from 1.912 to 1.961 Å and Cu–O–Cu angles from 91 to 124° (Table 2) and four $[\text{SO}_4]$ tetrahedra attached to them (Fig. 1). The units are further connected to two $[\text{SO}_4]$ tetrahedra to form distinct layers parallel to the yz plane. The layers are interconnected by potassium atoms (Fig. 2). Similar units formed around additional oxygen atoms by edge-sharing $[\text{OCu}_4]$ tetrahedra and sulphate groups connected with them in such a way that the chains with symmetry 4_2 are formed which were described in pypite (caratiite) (Effenberger and Zemann, 1984).

In the fedotovite structure the three kinds of

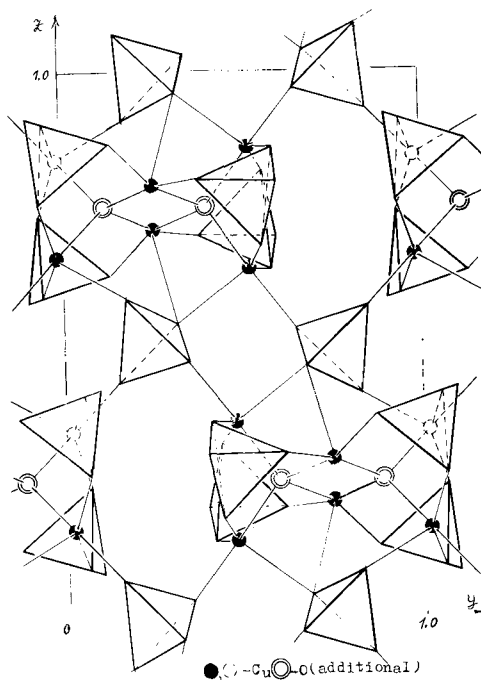


Fig. 1. The projection of the $[\text{Cu}_3\text{O}(\text{SO}_4)_3]^{2-}$ layer on the yz plane.

copper atoms are five fold ($4 + 1$) coordinated by oxygen atoms with strong Jahn–Teller distortion (Table 2). Coordination polyhedra of Cu1 and Cu2 atoms are distorted and flattened orthorhombic pyramids with Cu–O distances varying from 1.912 to 2.333 Å; a sixth neighbour follows at a distance of 2.981 and 2.975 Å for Cu1 and Cu2 respectively. The coordination environment of the Cu3 atom is a distorted orthorhombic pyramid with four Cu–O distances from 1.943 to 1.961 Å, a fifth at 2.558 Å and further sixth and seventh neighbours (oxygen and copper atoms) at 2.809 and 2.806 Å respectively (Table 2).

The nearest environment of potassium atoms consists of six oxygen atoms; for the K1 atom they are from 2.497 to 2.835 Å, with a seventh at 3.142 Å; for the K2 atom there are six neighbours from 2.759 to 3.036 Å and seventh at 3.150 Å.

In the structure of fedotovite $[\text{SO}_4]$ tetrahedra are somewhat distorted (Table 2) and interatomic distances in the sulphate groups are the typical values.

The participation of oxygen atoms in coordination polyhedra differs: ten oxygen atoms take part in coordination of copper and sulphur atoms, two oxygen atoms are only connected with sulphur atoms and two oxygen atoms (additional) are bonded to copper atoms only.

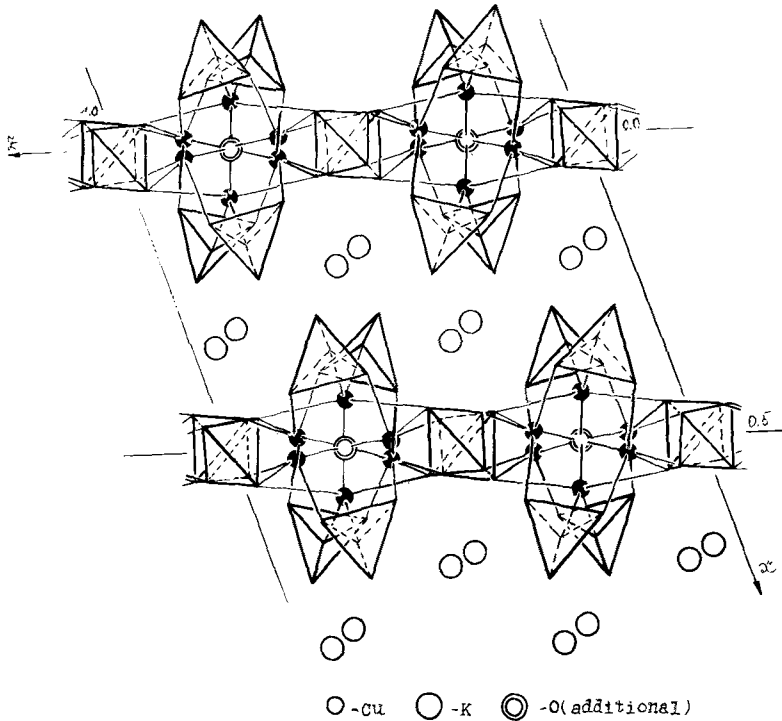


FIG. 2. The projection of the fedotovite structure on the xz plane.

Table 2. Bond distances (Å) and angles (degrees) of fedotovite

| Cu - polyhedra | | | | S - tetrahedra | | | | | | | | |
|----------------|----------|-----------------|----------|----------------|----------|---------------|----------|----------|----------|---------|-----------|--|
| Cu1 - O1 | 1.918(3) | Cu2 - O3' | 2.333(4) | Cu3 - O1 | 1.961(4) | S1 - O2 | 1.476(5) | S2 - O5' | 1.489(6) | S3 - O6 | 1.4795(5) | |
| O2 | 2.198(5) | O4' | 1.928(4) | O3 | 2.558(5) | O3 | 1.470(5) | O10 | 1.484(5) | O7 | 1.490(5) | |
| O5 | 1.973(5) | O6' | 1.978(6) | O7 | 1.959(5) | O4 | 1.477(5) | O13 | 1.492(5) | O8 | 1.447(6) | |
| O9' | 1.963(5) | O11 | 2.036(6) | O12 | 1.943(4) | O9 | 1.474(5) | O14 | 1.447(6) | O11 | 1.458(6) | |
| O10' | 2.026(5) | O12 | 1.912(3) | O13' | 1.943(5) | | | | | | | |
| Cu1' | 2.981(1) | Cu2' | 2.975(1) | O2 | 2.809(4) | | | | | | | |
| | | | | Cu3' | 2.806(1) | | | | | | | |
| O1 - Cu1 - O2 | 84.8(2) | O3' - Cu2 - O4' | 94.4 | O2 - S1 - O3 | 112.1(3) | O5 - S2 - O10 | 110.8(3) | | | | | |
| O1 | O5 | 91.5(2) | O5' | O8' | 118.1(2) | O2 | O4 | 105.9(3) | O5 | O13 | 108.5(3) | |
| O3 | O9' | 175.2(2) | O3' | O11 | 94.6(2) | O2 | O9 | 110.0(3) | O5 | O14 | 109.2(3) | |
| O1 | O10' | 92.4(2) | O3' | O12 | 83.8(2) | O3 | O4 | 110.3(3) | O10 | O13 | 108.8(3) | |
| O2 | O5 | 109.5(2) | O4' | O6' | 91.6(2) | O3 | O9 | 107.5(3) | O10 | O14 | 111.1(3) | |
| O2 | O9' | 95.1(2) | O4' | O11 | 84.9(2) | O4 | O9 | 111.1(3) | O13 | O14 | 108.4(3) | |
| O2 | O10' | 99.9(2) | O4' | O12 | 175.7(2) | | | | | | | |
| O5 | O9' | 93.1(2) | O6' | O11 | 147.4(2) | O6 - S3 - O7 | 106.8(3) | | | | | |
| O5 | O10' | 150.2(2) | O6' | O12 | 92.7(2) | O6 | O8 | 110.2(3) | | | | |
| O9' | O10' | 82.9(2) | O11 | O12 | 91.3(2) | O6 | O11 | 109.1(3) | | | | |
| | | | | | | O7 | O8 | 106.7(3) | | | | |
| | | | | | | O7 | O11 | 108.0(3) | | | | |
| | | | | | | O8 | O11 | 112.0(3) | | | | |
| | | | | K - polyhedra | | | | | | | | |
| O1 - Cu3 - O3' | 99.9(1) | | | K1 - O2 | 2.665(6) | K2 - O3'' | 2.910(5) | | | | | |
| O1 | O7 | 162.6(2) | | O4 | 2.658(5) | O5' | 3.036(6) | | | | | |
| O4 | O12 | 88.1(1) | | O5' | 2.835(5) | O7 | 2.762(6) | | | | | |
| O1 | O13 | 97.9(2) | | O8' | 2.649(6) | O8' | 2.814(6) | | | | | |
| O3' | O7 | 99.5(2) | | O11' | 3.145(5) | O9' | 2.759(6) | | | | | |
| O3' | O12 | 77.3(1) | | O14' | 2.497(6) | O10' | 3.150(6) | | | | | |
| O3' | O13 | 89.1(2) | | O14' | 2.772(5) | O13' | 3.001(6) | | | | | |
| O7 | O12 | 96.1(2) | | | | | | | | | | |
| O7 | O13 | 83.0(2) | | | | | | | | | | |
| O12 | O13 | 166.1(2) | | | | | | | | | | |

Coordinates of generated atoms: O3' 0.4380, 0.6671, 0.0418; O4' - 0.4636, 0.3520, 0.0267; O5' - 0.4109, 0.9428, 0.5902; O6' - 0.5949, 0.4394, 0.1817; O8' - 0.2197, 0.8986, 0.2993; O9' - 0.4522, 1.1496, 0.4394; O10' - 0.3785, 1.0720, 0.2415; O11' - 0.3844, 0.5890, 0.6430; O13' - 0.3394, 0.8707, 0.1301; O14' - 0.2169, 0.5952, 0.4243; O3'' - 0.0620, 0.8229, 0.0418; O6'' - 0.0949, 0.9394, 0.1817; O9'' - 0.0478, 0.6496, 0.0706; O10'' - 0.2215, 0.5720, 0.2585; O14'' - 0.2831, 0.9048, 0.5757; Cu1' - 0.51929, 1.01818, 0.15735; Cu2' - 0.51413, 0.47763, 0.35982; Cu3' - 0.57881, 0.74635, 0.29385

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