

The crystal structure of klyuchevskite, $K_3Cu_3(Fe,Al)O_2(SO_4)_4$, a new mineral from Kamchatka volcanic sublimates

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Abstract

The crystal structure of klyuchevskite, $K_3Cu_3(Fe^{3+},Al)O_2(SO_4)_4$, was determined in space group I2 using the total of 715 independent reflections up to R 0.12. Klyuchevskite is a structural analogue of piypite (caratiite) $K_4Cu_4O_2(SO_4)_4MeCl$ with the substitution $K^+ + Cu^{2+} \rightarrow (Fe^{3+},Al) + MeCl$. Compared to piypite, the ordering of Cu^{2+} and Fe^{3+} cations in the klyuchevskite structure results in the distortion of the unit cell and in lowering the symmetry of the chains to 1.

This brings about a more compact packing of the chains. The chain-like arrangement of the structure determines physical properties of the mineral, its acicular habit, perfect cleavage, strong anisotropy of optical properties and orientation of optical indicatrix.

KEYWORDS: klyuchevskite, crystal structure, piypite, Tolbachik volcano, Russia.

THE systematic study of the products of fumarolic activity of Tolbachik Main Fracture Eruption (the Kamchatka Peninsula 1975–1976) resulted in the discovery of a series of new minerals. One of them is klyuchevskite (Vergasova *et al.*, 1989). The mineral fills cavities and small joints in the massive sublimates. It forms aggregates of dis-oriented prismatic to acicular crystals intergrown with hematite, ponomarevite, and kamchatkite. The colour is dirty green. The mineral is transparent. Strongly anisotropic. X-olive, Y-green, Z-dark-olive. Klyuchevskite is monoclinic (see Table 1), point group $2/m$, $Z = 4$ (C -cell has $\beta \sim 126^\circ$). According to the symmetry of Patterson maps the solution obtained was in space group I2.

The crystals are prismatic to acicular up to 0.5 mm long (b axis) and <0.01 mm thick. The needles easily split along the b axis that is probably due to the perfect cleavage on (hol).

In the products of fumarolic sublimates occurs another oxysulphate of copper, piypite (Vergasova *et al.*, 1984) and caratiite (Clark *et al.*, 1984), the second finding of piypite (Filatov and Vergasova, 1989), the formula of which is $K_4Cu_4O_2(SO_4)_4.MeCl$, where $Me = Na,Cu$ (Effenberger and Zemann, 1984). The synthetic compound of the structure type of piypite was also

described (Effenberger, 1985*b*). The similarity of crystal chemical formulae, and certain physical properties of piypite and klyuchevskite (Table 1) and their forms of occurrence indicates that these minerals are structurally related. The structural data obtained for klyuchevskite support this assumption.

Originally the chemical formula of klyuchevskite was found to be $K_7Cu_7Fe^{3+}O_3(SO_4)_9$, based on the results of electron microprobe analysis. This formula was approved by CNM IMA. The structural analysis carried out in the period between approval of the mineral and publication of the paper revealed a greater number of O atoms per 3Cu atoms, i.e. 18 instead of 15 as had been stated previously. This is why the paper describing this new mineral gave the formula $K_{3.09}Cu_{3.00}(Fe_{0.046}Cu_{0.15})_{0.61}O_2(SO_4)_{4.00}$ based on $\Sigma O = 18$ (Vergasova *et al.*, 1989).

A problem arose concerning the position of Fe in the structure. According to the results of the chemical analysis, cation occupancy of this site was 0.61, although structural data gave the figure of 0.82(3) (see Table 2). This value shows that there is an element which was not determined by the electron microprobe analysis of the mineral. A new analysis study revealed this element to be

Table 1

Comparison between certain physical properties of klyuchevskite and piypite

Characteristics	Klyuchevskite	Piypite
Crystal chemical formulae	$K_3Cu_3(Fe^{3+}, Al)O_2(SO_4)_4$	$K_4Cu_4O_2(SO_4)_4MeCl$
Chain composition	$[Cu_3(Fe^{3+}, Al)O_2(SO_4)_4]^{3-}$	$[Cu_2O(SO_4)]^{2-}$
Space group	I2	I4
a, Å	18.667(7)	13.60(2) ($a\sqrt{2} = 19.23$)
b, Å	4.94(2)*	
c, Å	18.405(7)	4.98(1)*
β , °	101.5(2)	
z	4	2
D_x , g/cm ³	2.98	2.76
N_g	1.680(1)	1.711(1)
N_m	1.550(1)	
N_p	1.549(1)	1.598(1)

* Direction parallel to the chain axis

Al. In the first study a small amount of Al remained unnoticed in the presence of sulphur. The revised ideal formula becomes $K_3Cu_3(Fe^{3+}, Al)O_2(SO_4)_4$.

Electron microprobe analysis of the specimen of klyuchevskite chosen for crystal data collection gave the following data (average 25 grains, wt.%): K_2O 18.17, Na_2O 0.00, CuO 31.15, SO_3 40.98, Fe_2O_3 7.86, Al_2O_3 1.38, PbO 0.71, ZnO 0.04, Cl 0.13, $O = Cl$ 0.03, total 100.39%. The empirical formula based on $\Sigma O = 18$ is $K_{3.00}(Cu_{3.05}Pb_{0.02})_{3.07}(Fe_{0.77}Al_{0.21})_{0.98}O_2(S_{3.98}O_{16})$.

For crystal structure determination an acicular crystal of klyuchevskite was used $0.14 \times 0.04 \times 0.01$ mm³ in size. A total of 715 symmetrically-independent reflections, having $F_{obs} > 66F$, was collected using a computer controlled $P2_1$ diffractometer (Mo- $K\alpha$ radiation) operating in θ - 2θ scan mode with the scan range $\sin \theta/\lambda < 0.835$. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods and refined by the methods of least squares refinement of structural parameters, including the occupancy of Cu and Fe sites and anisotropic thermal parameters for cation positions using 'XTL' and 'CSD' programmes. On the last cycles of the refinement the data were corrected for absorption resulting from the crystal shape (Walker and Stuart, 1983). The refinement converged to $R = 0.12$. We failed to achieve a

better R value owing to the following circumstances: the small size, acicular crystal habit and instability of the mineral in air which is manifested in the fact that intensities of the standard reflections are approximately ten times lower despite the fact that the crystal was covered with a glue film. For a comparison, a similar refinement was carried out for the transformed data set (146 symmetry independent reflections having $F_{obs} > 66F$, $R = 0.15$) measured during the first two days of data collection (totalling three days). It was assumed that the crystal did not decompose during this period. Refinement of anisotropic thermal parameters gave negative B_{ij} values for some atoms, cation-anion and anion-anion distances being shortened up to the forbidden values. For oxygen atoms, the similar effect was observed even for the refinement of isotropic thermal parameters. Therefore for oxygen atoms $B_{ij} = 1.5$ was fixed and not refined.

Taking into account the results of these refinements we are able to consider the data obtained as a model of the klyuchevskite structure. Position parameters listed in Table 2 were computed by using the Fourier maps.

The comparison between piypite and klyuchevskite structures shows that the basic elements in these structures are chains of copper polyhedra in piypite and copper and iron (with some isomorphous Al) polyhedra in klyuchevskite. In

Table 2

Positional and isotropic thermal parameters of basic atoms in
the klyuchevskite structure

Atom	P_j	x/a	y/b	z/c	B_j
Cu1	1.00(3)	0.186	0.0	0.535	1.5(3)
Cu2	1.04(3)	0.259	0.015	0.410	1.2(3)
Cu3	1.05(3)	0.170	0.485	0.416	1.0(2)
Fe	0.82(3)	0.302	0.528	0.531	0.9(4)
K1		0.5	0.448	0.5	1.47
K2		0.0	0.464	0.5	1.69
K3		0.370	0.503	0.746	1.5
K4		0.429	-0.019	0.28	1.88
S1		0.184	0.535	0.628	1.05
S2		0.329	0.480	0.366	1.32
S3		0.074	-0.022	0.366	0.91
S4		0.407	0.02	0.604	1.23
O1		0.173	0.48	0.708	1.5
O2		0.136	0.334	0.568	1.5
O3		0.16	0.8	0.608	1.5
O4		0.261	0.521	0.62	1.5
O5		0.35	0.507	0.445	1.5
O6		0.39	0.443	0.329	1.5
O7		0.318	0.776	0.356	1.5
O8		0.274	0.233	0.345	1.5
O9		0.005	0.038	0.315	1.5
O10		0.09	0.663	0.363	1.5
O11		0.064	0.027	0.445	1.5
O12		0.134	0.178	0.358	1.5
O13		0.478	0.014	0.575	1.5
O14		0.415	0.052	0.687	1.5
O15		0.391	0.331	0.586	1.5
O16		0.349	0.841	0.553	1.5
O17		0.232	0.755	0.478	1.5
O18		0.226	0.254	0.477	1.5

the piypite and klyuchevskite structures, the chains of cation polyhedra and S-tetrahedra are linked by K atoms to form a three dimensional framework.

Klyuchevskite is a structural analogue of piypite ('caratiite') the b axis in klyuchevskite corresponds to the c axis in piypite (see Table 1). In the klyuchevskite structure chains running parallel to the b axis are formed by Cu and Fe polyhedra coupled in pairs through common edges O17–O18 (Fig. 1a). From outside $(SO)_4^-$ tetrahedra link the base of this chain, additionally connecting Cu and Fe polyhedra inside the chain.

The chemical composition of these chains is based on the radical $[Cu_3(Fe^{3+}, Al)O_2(SO_4)_4]^{3-}$. The symmetry of the chain is 1. The string of a chain is formed by additional oxygen atoms O17 and O18 occurring in tetrahedral coordination $O[Cu_3-(Fe, Al)]$ with bond distances $O-Cu = 1.91$ and $O-(Fe, Al) = 1.97$ Å (mean $O-R = 1.92$ Å) which compare well to $[OCu_4]$ tetrahedra found in inorganic crystal structures (Effenberger, 1985a).

Cu atoms are coordinated by 4 oxygen atoms (two oxygen atoms of the 'string' and two of a sulphate group in the same chain) at $Cu-O = 1.71-2.07$ Å and by one oxygen atom of another

sulphate group in the same chain at Cu–O = 2.48–2.88 Å (Table 3). These five oxygen atoms form an elongated pyramid. The base of the pyramid is an irregular quadrilateral with sides O–O = 2.43–3.09 Å, the Cu atoms being slightly shifted from the centre of the basal quadrilateral towards the apical oxygen. Fe atoms have the six-fold close to octahedral coordination (Fe–O = 1.95–2.08 Å). The central section of the octahedron, similar to the base of the pyramids, is an irregular quadrilateral with sides O–O = 2.39–3.33 Å.

Taking into account the shape of the coordinational polyhedra and the values of occupancy factors for cation sites Cu1–Cu3 and Fe (Table 2) we can suggest that Cu1–Cu3 sites are occupied

only by Cu atoms while Fe sites are occupied by iron and aluminium (~25%) atoms that complies with the chemical data. The location of Fe and Al atoms within the same point system and different coordinations of Cu and (Fe,Al) atoms result in assymetry of the chain compared to that of pipypite (Fig. 1), having the symmetry 4_2 . In due course this results in the distortion of the unit cell and lowers the klyuchevskite symmetry to $I2$ (Fig. 2). In klyuchevskite an extra degree of freedom (β angle) compared to pipypite, results in a more compact packing of the chains and a disappearance of the channels where Me and Cl atoms occur in the pipypite structure.

Interatomic distances (S–O)ave. for S tetra-

Table 3

Interatomic distances in the klyuchevskite structure					
Atoms	Distances, Å	Atoms	Distances, Å	Atoms	Distances, Å
Cu1-02	2.07	Cu2-07	2.00	Cu-010	1.84
-03	1.82	-08	1.71	-012	1.92
-017	1.94	-017	1.94	-017	1.99
-018	1.91	-018	1.92	-018	1.81
Mean:	1.94		1.89		1.89
Cu1-011	2.54	Cu2-012	2.48	Cu3-08	2.88
Fe-015	2.02	S1-01	1.55	S2-05	1.45
-016	1.81	-02	1.63	-06	1.44
-017	1.86	-03	1.47	-07	1.51
-018	2.08	-04	1.48	-08	1.61
-04	1.95	Mean:	1.52		1.50
-05	2.02				
Mean:	1.96				
S3-09	1.48	S4-013	1.53	K1-05	2.74/2/*
-010	1.61	-014	1.58	-013	2.65/2/
-011	1.52	-015	1.62	-013	3.22/2/
-012	1.54	-016	1.56	-015	2.89/2/
Mean:	1.54		1.57		2.86
K2-02	2.68/2/	K3-01	2.91	K4-06	2.99
-011	2.79/2/	-01	2.71	-06	2.64
-011	3.31/2/	-04	2.76	-07	2.93
-010	3.45/2/	-09	2.59	-09	3.23
Mean:	3.06	-014	2.73	-010	2.73
		-03	3.01	-012	2.99
		-014	3.14	-013	2.90
		-015	3.18	-014	2.88
		Mean:	2.88		2.91

* figures in slants indicate the bond multiplicity

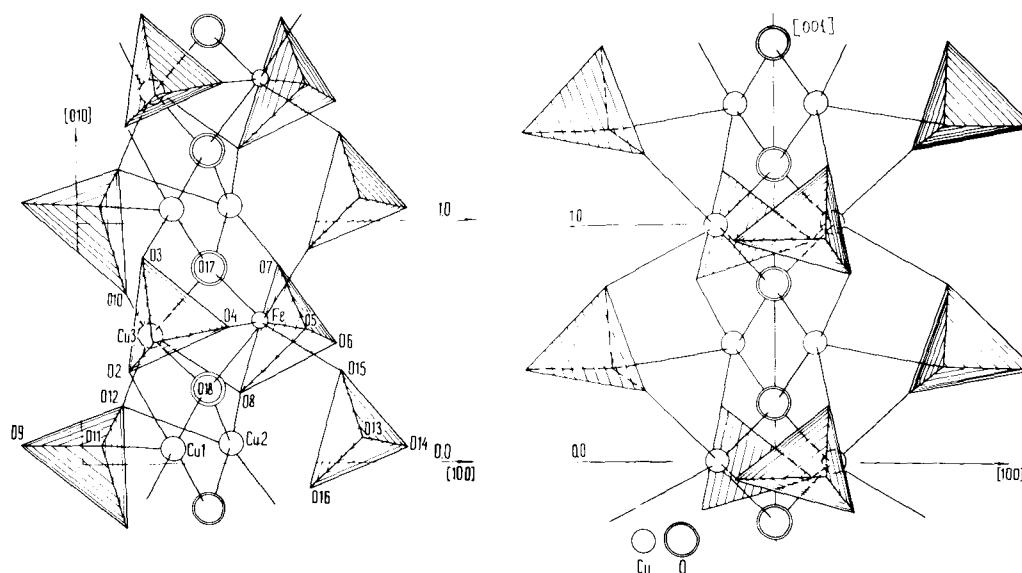


FIG. 1. Projection of the piypite structure onto the (001) plane (a, left) (Effenberger and Zemann, 1984) and the klyuchevskite structure onto the (010) plane (b, right).

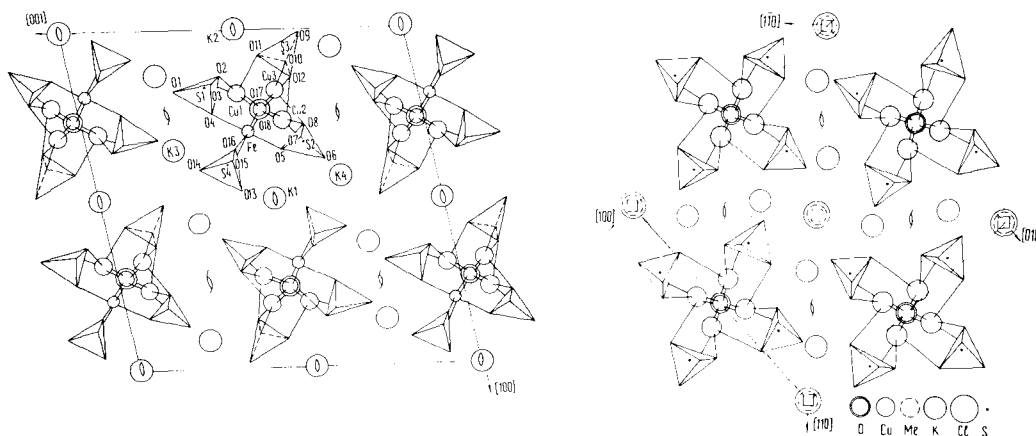


FIG. 2. Projection of the $[Cu_2O(SO_4)_2]^{2-}$ chain in the piypite structure onto the (010) plane (a, left) (Effenberger and Zemann, 1984) and of the $[Cu_3Fe^{3+}O_2(SO_4)_4]^{3-}$ chain in the klyuchevskite structure onto (100) plane (b, right).

hedra are similar in the compared structures: 1.53 and 1.47 Å for klyuchevskite and piypite, respectively.

Electrostatically neutral arrangement of the structure is achieved by K atoms (Fig. 2). Two of them (K1 and K2) are bonded with two chains while K3 and K4 are bonded with three chains. K atoms have an eight-fold coordination (K1-O = 2.65–3.22, K2-O = 2.68–3.31, K3-O = 2.59–3.18, K4-O = 2.64–3.23 Å) assuming the bond distances K-O < 3.45 Å.

K atoms link the chains by relatively weak ionic

bonds K-O which are approximately equal in the *ac* plane. These bonds form weakened zones parallel to (001) and (100) planes (Fig. 2). It may be suggested that perfect cleavage in klyuchevskite parallel to elongation of the needles (*b* axis) corresponds to (001) and (100) planes. Optical properties of klyuchevskite are strongly anisotropic, i.e. $N_g(b \text{ axis})$ coincides with the axis of the chain while a practically circular section of optical indicatrix lies in the *ac* plane ($n_m \approx n_p$, Table 1).

In this paper the results of the crystal structure

the determination of klyuchevskite are reported. Instability of the mineral in air and small crystal size (the crystals are less than 0.01 mm thick) bring about high $R = 0.12$. The studies indicate that klyuchevskite, $K_3Cu_3Fe^{3+}O_2(SO_4)_4$, is a structural analogue of piypite, $K_4Cu_4O_2(SO_4)MeCl$. Ordering of Cu^{2+} and (Fe^{3+}, Al) cations was discovered. The chain-like structure of klyuchevskite determines physical properties of the mineral: acicular habit, perfect cleavage parallel to elongation of the crystals, strong anisotropy of optical properties and orientation of optical indicatrix.

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