

The crystal structure of kamchatkite, a new naturally occurring oxychloride sulphate of potassium and copper

T. V. VARAKSINA, V. S. FUNDAMENSKY, S. K. FILATOV

Department of Crystallography, Leningrad State University, USSR,

AND

L. P. VERGASOVA

Institute of Volcanology, Academy of Sciences of the USSR, Petropavlovsk-Kamchatsky

Abstract

The crystal structure of the new mineral kamchatkite, $a = 9.741(5)$, $b = 12.858(6)$, $c = 7.001(3)$ Å, space group $Pna2_1$, $Z = 4$, has been determined through direct methods using 1430 intensities and refined to a final discrepancy index $R = 0.055$. It contains (SO_4) tetrahedra and Cu octahedra interconnected by oxygen atoms to form an electrostatically neutral three-dimensional arrangement of formula $Cu_3O[SO_4]_2$ which contains channels parallel to $\{001\}$. The channels are not empty but house KCl molecules.

KEYWORDS: kamchatkite, crystal structure, Kamchatka, USSR.

Introduction

KAMCHATKITE, $KCu_3OCl(SO_4)_2$, is a new mineral (Vergasova *et al.*, 1988) which was found in products of fumarolic activity of the 1975–1976 Tolbachik Main Fracture eruption, Kamchatka, USSR (Fedotov, 1984), in association with ponomarevite, tolbachite, hematite, etc. The mineral forms intergrowths and aggregates of yellow-brown crystals. Its crystallochemical formula is $(K_{1.06}Na_{0.03})_{\Sigma 1.09}(Cu_{2.92}Zn_{0.04})_{\Sigma 2.96}O_{1.04}Cl_{0.84}(SO_4)_{2.03}$. The mineral is biaxial positive; pleochroism is absent. Hardness 3.5; cleavage is perfect along (011) and (100); fragile. Kamchatkite is unstable in air, hydrating in a few weeks.

Preliminary investigation of a single crystal by Weissenberg photographs revealed Laue symmetry mmm and two possible space groups $Pnam$ or $Pna2_1$.

Cell parameters refined on the basis of X-ray powder data are $a = 9.741(5)$, $b = 12.858(6)$, $c = 7.001(3)$ Å, $V = 877(1)$ Å³ at 20°C, $Z = 4$, $D_x = 3.58$ g/cm³. A total of 1490 independent reflections was recorded up to $\sin \theta/n \leq 0.81$. All the X-ray intensity measurements were made by a ω -scan on an automatic four-circle Syntex P2₁ single-crystal diffractometer with Mo-K radiation

and graphite monochromator. For these measurements a natural crystal was mounted parallel to the Z axis, coincident with its elongation direction. This crystal was 0.30 mm long and had a cross-section of 0.15×0.07 mm². Data collection was carried out avoiding weak reflections. Integrated intensities were converted to structural factors by correcting for polarization and Lorentz factors and for long-duration drift of the diffractometer. The number of reflections having $F < 2\sigma F$ was 56; thus, 1434 reflections were considered as being observed. The independent set used in the refinement contains 1379 reflections with $F > 4\sigma F$.

The solution obtained was in space group $Pna2_1$. After the refinement of atomic coordinates and isotropic temperature factors, the data were corrected for absorption resulting from the crystal shape, using the computer program DIFABS (Walker and Stuart, 1983). The linear absorption coefficient for kamchatkite is 87.3 cm⁻¹. The final refinement in anisotropic approach converged to $R = 0.055$. All calculations were made on a CM-4 computer using the computer program complex CSD (Akselrod *et al.*, 1989). Structure factor lists have been deposited with the editor of *Mineralogical Magazine* and are available on request. Final atomic coordinates and anisotropic

Table 1. Fractional atomic coordinates and equivalent anisotropic temperature factors (\AA) for kamchatkite with the significant figures of the estimated standard deviations in parentheses

	x/a_0	y/b_0	z/c_0	B_{eq}
Cu1	0.1520(1)	0.14914(9)	0.8363(0)	0.97(2)
Cu2	0.2221(1)	0.90739(9)	0.8353(14)	0.95(2)
Cu3	-0.0012(8)	-0.0009(7)	0.0811(12)	0.88(2)
S1	0.1694(2)	0.8542(2)	0.3394(26)	0.81(3)
S2	0.0710(2)	0.2097(2)	0.3353(19)	0.92(4)
K	0.1346(3)	0.5745(2)	0.8472(25)	2.19(5)
O1	0.1759(33)	0.9250(25)	0.5069(41)	1.0(5)
O2	0.0455(8)	0.7907(6)	0.3188(41)	1.03(13)
O3	0.2065(7)	0.2930(5)	0.8423(49)	1.32(12)
O4	0.1722(33)	0.9221(25)	0.1645(41)	1.7(3)
O5	0.0793(8)	0.7888(6)	0.8458(45)	1.1(4)
O6	0.1287(33)	0.1569(22)	0.4991(35)	1.6(2)
O7	0.1154(7)	0.3211(6)	0.3509(47)	1.35(14)
O8	0.1171(33)	0.1540(23)	0.1623(36)	0.9(2)
O9	0.0797(8)	1.0101(6)	0.8227(51)	0.7(3)
Cl	0.1344(2)	0.5586(2)	0.3396(25)	1.68(5)

Table 2. Bond lengths (\AA) and angles ($^\circ$) in kamchatkite together with their standard deviations

Cu1–O2	2.080(8)	O2–Cu1–O3	84.1(8)	Cu3–O1	2.03(3)	O1–Cu3–O6	84.7(1)
O3	1.929(7)	O2–O6	80.6(9)	O4	2.04(3)	O1–O8	93.6(1)
O6	2.37(2)	O2–O8	84.9(9)	O6	2.43(3)	O1–O9A	93.7(1)
O8	2.31(3)	O2–O9	90.2(8)	O8	2.37(3)	O1–O9B	85.3(1)
Cl	2.388(3)	O3–O6	90.4(9)	O9A	1.98(3)	O4–O6	95.1(1)
O9	1.928(8)	O3–O8	89.6(9)	O9B	1.86(3)	O4–O8	86.4(1)
		O3–Cl	103.2(7)			O4–O9A	88.1(1)
		O6–Cl	96.5(7)			O4–O9B	92.8(1)
		O6–O9	37.4(10)			O6–O9A	92.7(1)
		O8–Cl	97.5(8)			O6–O9B	87.2(1)
		O3–O9	91.1(10)			O8–O9A	87.9(1)
		Cl–O9	32.2(7)			O8–O9B	92.0(1)
Note. The transformation of the atomic parameters given for O9 atom is as follows: O9A $x, -1+y, -1+z$; O9B $-x, 1-y, -\frac{1}{2}+z$.							
Cu2–O1	2.35(3)	O1–Cu2–O5	88.7(10)	S1–O1	1.48(3)	O1–S1–O2	117.0(2)
O4	2.36(3)	O1–O7	105.4(10)	O2	1.467(9)	O1–O3	106.7(2)
O5	2.069(8)	O1–Cl	92.6(8)	O3	1.445(8)	O1–O4	106.5(2)
O7	1.940(8)	O1–O9	75.5(10)	O4	1.50(3)	O2–O3	112.7(1)
Cl	2.401(3)	O4–O5	83.4(9)			O2–O4	105.0(1)
O9	1.921(8)	O4–O7	99.1(10)	S2–O5	1.468(8)	O3–O4	108.2(2)
		O4–Cl	92.4(3)	O6	1.44(3)	O5–S2–O6	110.7(1)
		O4–O9	80.8(10)	O7	1.503(8)	O5–O7	105.7(1)
		O5–O7	97.1(8)	O8	1.48(3)	O5–O8	110.5(1)
		O5–O9	91.4(9)			O6–O7	106.2(1)
		O7–Cl	89.3(7)			O6–O8	107.6(2)
		Cl–O9	82.0(7)			O7–O8	115.8(1)
		K–O1	2.89(3)				
		O4	3.00(3)				
		O5	2.814(8)				
		O6	2.75(3)				
		O7	2.785(8)				
		O8	2.93(3)				
		Cl	3.56(3)				
		ClA	3.45(3)				
		ClB	3.136(4)				

Note. The transformation of the atomic parameters given for Cl atom is as follows: ClA $x, y, 1+z$; ClB $-x, 1-y, \frac{1}{2}+z$.

equivalent thermal vibration factors are given in Table 1. A full list with anisotropic thermal parameters can be obtained from the editor. Interato-

mic distances and bond angles are compiled in Table 2.

The basic element of the structure of kamchat-

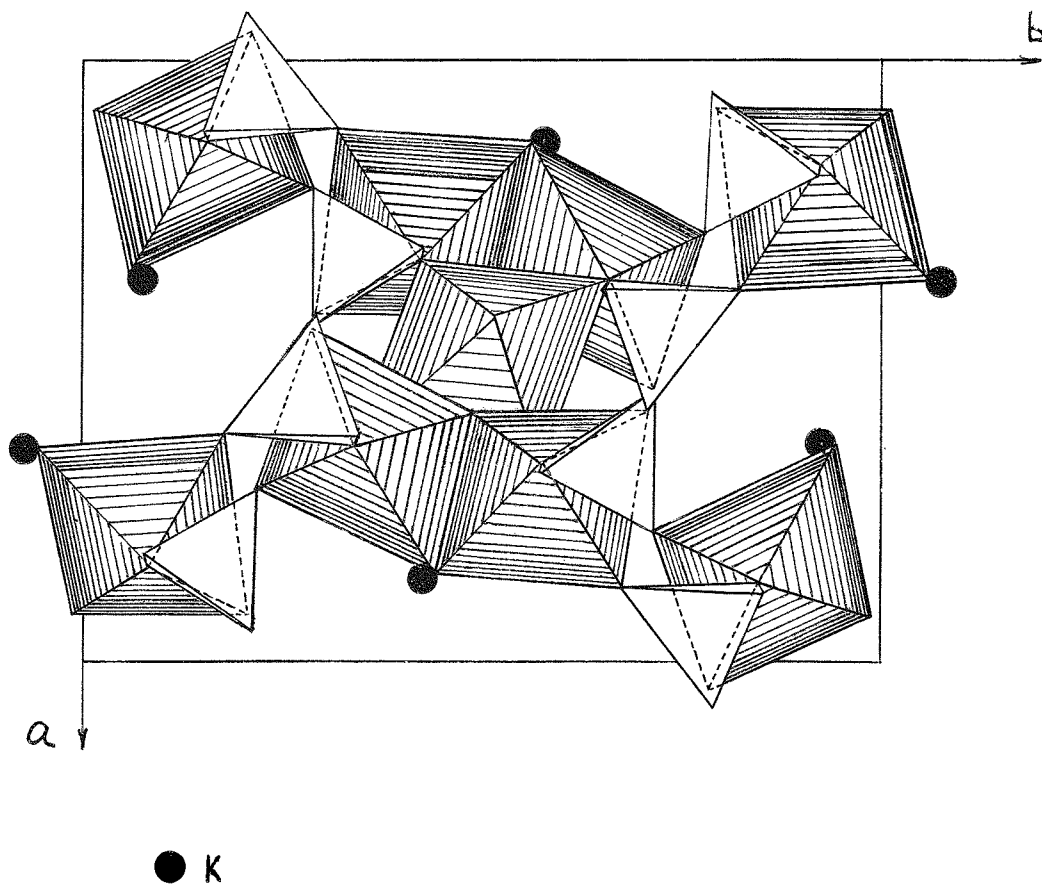


Fig. 1. Projection of the structure of kamchatkite on the ab plane.

kite (Fig. 1) consists of four independent isolated $[\text{SO}_4]^{2-}$ tetrahedra and three independent Cu octahedra. S–O bond lengths in the tetrahedra vary from 1.44 to 1.50 Å and O–S–O angles from 105.0 to 117.0°. Their average values, 1.47 Å and 111.0°, are the typical values found in the sulphate group (Lonsdale, 1962) and they indicate that the tetrahedra are close to ideal. Cu atoms occur in two types of highly distorted octahedra. In one type of octahedra, Cu1 and Cu2, three equatorial O atoms and one Cl atom are situated at the corners of distorted polyhedra in which the Cu–O distance varies from 1.92 to 2.08 Å and Cu–Cl is 2.40 Å. Two axial O atoms occur at distance of 2.31–2.37 Å from Cu atoms. All this shows a rather usual distortion around Cu. In another type of octahedra, Cu3, the Cu atom is situated on the axis z_1 and is surrounded by six O atoms; four equatorial O occur at distances of

1.86–2.04 Å and two axial atoms at 2.37–2.43 Å, revealing a typical Jahn-Teller coordination. Cu3 octahedra are linked with each other by O9 shared by two adjacent Cu3 atoms. Thus, endless columns of Cu3 octahedra run parallel to the 2-fold inversion axis along [001].

Cu octahedra and SO_4 tetrahedra are interconnected by their edges to form an electrostatically neutral three-dimensional framework of formula $\text{Cu}_3\text{O}[\text{SO}_4]_2$ which contains channels parallel to [001]. The channels are not empty but house endless chains of $[\text{KCl}]^\ominus$ molecules; the axes of the molecules are nearly parallel to [001]. Along the chains lies a local 2-fold inversion pseudoaxis. The K–Cl distance in the plane perpendicular to the chain axis is 3.14 Å and is the shortest. Along the chain axis there is a regular alternation of two K–Cl bonds of 3.45 and 3.56 Å, a total of 7.0 Å which is close to the c -parameter. Insofar as the

framework is electrostatically neutral we can expect it existing without KCl molecules and giving $\text{Cu}_3\text{O}(\text{SO}_4)_2$.

References

- Akselrod, L. G., Grun, Yu. N., Zavali, P. Yu., Pecharsky, V. K., and Fundamensky, V. S. (1989) *XII European Crystallographic Meeting, Moscow*. Collected abstracts, **3**, 155.
- Fedotov, S. A., ed. (1984) *The Tolbachik Main Fracture Eruption*. Nauka, Moscow (in Russian).
- Lonsdale, K., ed. (1962) *International Tables for X-ray Crystallography*, **III**. The Kynoch Press, Birmingham.
- Vergasova, L. P., Filatov, S. K., Seraphimova, Ye. K., and Varaksina, T. V. (1988) *Zap. Vses. Mineral. Obshch.* **4**, 459–61 (in Russian).
- Walker, N. and Stuart, D. (1983) *Acta Crystallogr.* **A39**, 158–66.

[Manuscript received 6 October 1989;
revised 7 March 1990]