Crystal structure and physical properties of sophiite, $Zn_2(SeO_3)Cl_2$, a new mineral

T. F. Semenova, I. V. Rozhdestvenskaya,* S. K. Filatov and L. P. Vergasova†

Department of Crystallography, Leningrad State University, C.I.S.

Abstract

The crystal structure of sophiite, $Zn_2(SeO_3)Cl_2$ ($a = 10.251(4)$, $b = 15.223(2)$, $c = 7.666(5)$ Å, $Z = 8$) was solved in space group $Pccn$ from single crystal X-ray data, and refined to $R = 0.053$ for 666 $F_o > 4\sigma_{F_o}$. The mineral belongs to layer compounds. The threefold coordinated Se atom is at the apex of a pyramid, the base of which is formed by three O atoms; Se–O = 1.69 Å. Zn cations occupy two positions with distorted tetrahedral and octahedral coordinations. In the tetrahedra, Zn cations are surrounded by two O (2.02 Å) and two Cl (2.224 Å) atoms. Zn octahedra contain four O atoms (2.07 Å) and two Cl atoms (2.701 Å). The atomic arrangement is characterized by rings containing two Se pyramids linked by their corners to two Zn tetrahedra. The rings are linked by their edges and corners to Zn octahedra to form layers parallel to (010). The layers are interconnected by residual Van der Waals bonds.

Experimental results on thermal phase transformations and deformations, crystal optics and other physical properties of sophiite are presented. A structural aspect of their anisotropy is discussed.

KEYWORDS: sophiite, crystal structure, Tolbachik volcano, Kamchatka.

Occurrence and paragenesis

SOPHIITE is the first selenium-bearing mineral occurring as a result of fumarolic activity of the Tolbachik Main Fracture Eruption, Kamchatka, Russia (Fedotov, 1984). The mineral occurs at a temperature of 180–230 °C on lava flows in the second slag cone of the North Break as well as in a fumarolic field of a slag cone of the South Break (Vergasova *et al.*, 1989). Associated minerals are cotton-like hygroscopic emanations bearing zinc and chlorine which, together with sophiite, fill small fractures and interstices between clasts of igneous rocks. Besides sophiite and white cotton-like emanations, in products of fumarolic activity confined to linear subsidences in the second cone, tenorite, CuO, cotunnite, $PbCl_2$ (Semenova *et al.*, 1988), ponomarevite, $K_4Cu_4OCl_{10}$ (Vergasova *et al.*, 1988; Semenova *et al.*, 1989), halite with sylvite and rare very fine flakes of native gold (Vergasova *et al.*, 1982) have been found to occur.

The mineral forms aggregates of perfect tabular to micaceous crystals. They are pseudohexagonal with developed faces of {010} pinacoid; {100}

pinacoid and {101} prism are less developed (Fig. 1). Tabular crystals are often elongated parallel to *c*, but prism faces are unequally developed which results in an asymmetric pseudo-
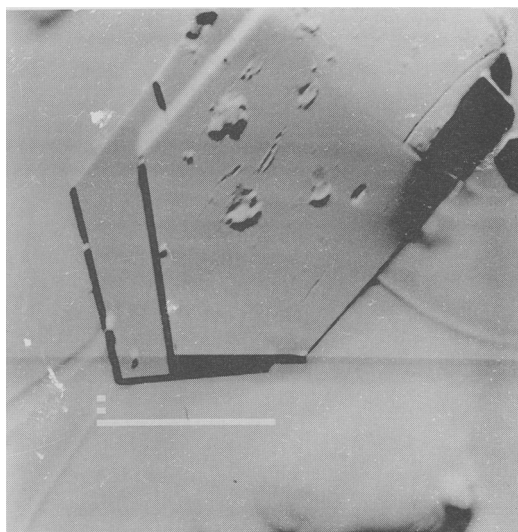

FIG. 1. Sophiite crystals. Secondry electron photomicrograph. A Camebax microprobe (×210).

* LNPO 'Burevestnik', Leningrad, C.I.S.
† Institute of Volcanology, Academy of Sciences of the C.I.S., Petropavlovsk-Kamchatsky.

hexagonal habit. Crystals of sophiite are colourless and transparent. The lustre is vitreous to greasy and satin-like with cleavage (010), perfect and (201) less perfect.

Chemical composition

An analysis using a Camebax electron microprobe (Vergasova *et al.*, 1989) gave ZnO 47.83, SeO$_2$ 34.48, CuO 0.19, PbO 0.35, Cl 22.26, less O = Cl − 5.02, total 100.09 wt.%, which yields the empirical formula (Zn$_{1.92}$Cu$_{0.01}$Pb$_{0.01}$)$_{1.94}$-(Se$_{1.02}$O$_{2.94}$)Cl$_{2.06}$ (caculated for O + Cl = 5). This corresponds to the ideal formula Zn$_2$(SeO$_3$)Cl$_2$. The chemical composition varies only slightly with copper and zinc as permanent minor impurities. Mineral-forming elements are regularly distributed within the lamellae.

Preparation of the sample

Selecting a crystal suitable for data collection was difficult. Tabular crystal habit and perfect cleavage on (010) pinacoid and (201) prism made it impossible to obtain a spherical sample. Because of this, crystals with complete extinction and without layer growth were selected under the microscope. Because of the instability of the compound it was necessary to coat the sample with a protective epoxy film.

Due to common (100) twinning and layer growth, further selection of the material continued with the use of X-ray single crystal techniques and a Weissenberg goniometer. The single crystal selected for intensity measurements was tabular, elongated in the *c* direction, and measured 0.55 × 0.15 × 0.25 mm.

Experimental

Intensity data were collected for 666 reflections with $I > 1.96\sigma_I$ on a computer-controlled $P2_1$ diffractometer using ω-scan technique with varying 3–30° 2θ/min scan speed (MoKα radiation, (sin θ/λ)$_{max}$ = 0.702 ÅMg/$^{-1}$, μ = 156.3 cm^{-1}, h_{max} = 14, k_{max} = 20, l_{max} = 10).

Lattice parameters derived from X-ray powder data and refined by a least-squares procedure are a = 10.251(4), b = 15.223(2), c = 7.666(5) Å (Vergasova *et al.*, 1989). They are close to the lattice parameters obtained from single crystal data: a = 10.238(5), b = 15.226(9), c = 7.658(5) Å. Laue, rotation and Weissenberg photographs showed that the crystal of sophiite is orthorhombic; point group *mmm*, space group *Pccn*, Z = 8, D_x = 3.64 g/cm^3.

The data were corrected for Lorentz and polarization effects. The trial structure was solved by Patterson and Fourier difference techniques (XTL programs, a NOVA-1200 computer). Final cycles of the structure refinement were computed with anisotropic thermal parameters and resulted in R = 0.053 (R_w = 0.059). They were taken over 666 reflections with $F_o > 4\sigma F_o$ and were computed on a CM-4 computer with CSD programs (Akselrud *et al.*, 1989). The following weighting scheme was used: $-(1/W) = \sigma_{F^2} + 0.01F^2$. In the final stage of refinement the data were corrected for the absorption effect according to the DIFABS program (Walker and Stuart, 1983). The refinement of a cation position indicated that cation content is close to 1. The final atomic positions and isotropic thermal parameters are given in Table 1. A full listing of observed and calculated structure factors together with anisotropic thermal parameters are given in Appendices 1* and 2. Interatomic distances and bond angles are given in Table 2.

Description of the structure

In the scientific literature there are no data on crystal structures of minerals with similar composition. By its structure, the mineral belongs to layer compounds (Filatov *et al.*, 1989). Layers consist of Se pyramids, Zn tetrahedra and octahedra shearing corners and edges.

The threefold coordinated selenium atoms occur at the apex of a pyramid, the base of which is formed by three oxygen atoms (Figs. 2 and 3). Se–O separations vary from 1.68 to 1.70 Å with O–Se–O angles varying from 91.3 to 100.9°. The average values of 1.69 Å and 97.3° are common for selenites.

Zinc cations occupy two positions with distorted tetrahedral Zn1 and distorted octahedral Zn2 coordination. In Zn1 tetrahedra, the cation is coordinated by two oxygen (1.99 and 2.05 Å) and

Table 1. Atomic coordinates and equivalent isotropic temperature factors (in Å^2) for sophiite.

Atom	x/a	y/b	z/c	B equiv.
Se	0.4636(1)	0.5909(1)	0.2241(2)	1.22(4)
Zn1	0.4942(2)	0.3850(1)	0.3493(3)	1.71(5)
Zn2	0.7234(2)	0.44691(1)	0.1016(3)	1.84(5)
Cl1	0.2845(4)	0.3778(3)	0.4320(6)	2.13(1)
Cl2	0.5910(5)	0.2976(3)	0.1599(7)	2.87(13)
O1	0.4098(9)	0.5863(8)	0.4320(15)	1.4(3)
O2	0.5473(9)	0.4947(7)	0.2097(14)	1.5(3)
O3	0.3164(9)	0.5575(8)	0.1476(16)	1.4(3)

* Available on request from the editor.

Table 2. Interatomic distances (in Å) and angles (in °) with e.s.d.'s in parentheses for sophiite.

Se PYRAMID

Se–O1	1.68(1)	O1–Se–O2	100.9(5)
–O2	1.70(1)	O1–Se–O3	91.3(5)
–O3	1.69(1)	O2–Se–O3	99.6(5)
mean	1.69	mean	97.3
O1–O2	2.61(2)		
–O3	2.42(2)		
O2–O3	2.59(1)		
mean	2.54		

Zn1 TETRAHEDRON

Zn1–O1	1.99(1)	O1–Zn1–O2	97.3(4)
–O2	2.05(1)	O1–Zn1–Cl1	104.2(3)
mean	2.02	O1–Zn1–Cl2	117.6(4)
		O2–Zn1–Cl1	116.1(3)
Zn1–Cl1	2.244(4)	O2–Zn1–Cl2	91.6(3)
Zn1–Cl2	2.205(5)	Cl1–Zn1–Cl2	126.0(2)
mean	2.224	mean	108.8

Zn2 OCTAHEDRON

Zn2–O1	2.10(1)	O1–Zn2–O3	89.1(4)
–O2	2.02(1)	O1–Zn2–O3	68.6(4)
–O3	1.99(1)	O2–Zn2–O3	104.3(5)
–O3	2.18(1)	O2–Zn2–O3	93.6(4)
mean	2.07	Cl1–Zn2–O1	98.0(3)
		Cl1–Zn2–O2	95.3(3)
Zn2–Cl1	2.420(5)	Cl1–Zn2–O3	98.5(4)
–Cl2	2.982(5)	Cl1–Zn2–O3	99.3(3)
mean	2.701	Cl2–Zn2–O1	94.4(3)
		Cl2–Zn2–O2	72.4(3)
Zn1–Se	3.294(3)	Cl2–Zn2–O3	82.4(3)
Zn2–Se	2.949(2)	Cl2–Zn2–O3	84.3(3)
Zn2–Zn1	3.284(3)	mean	90.05
Zn2–Zn2	3.872(3)		

two chlorine atoms (2.205 and 2.244 Å). Zn2 octahedra contain four equatorial oxygen atoms at the corners of a distorted tetrahedron (Zn–O from 1.99 to 2.18 Å) and two chlorine atoms in trans positions (Zn–Cl 2.42 and 2.98 Å). Significant differences in interatomic distances and bond angles in comparison with the ideal values for zinc polyhedra indicate their strong distortion and displacement of Zn cations from the centres of the polyhedra.

The basic fragment of the crystal structure of sophiite is a centrosymmetric ring containing two Se pyramids attached by their apices to two Zn1 tetrahedra (Fig. 2). These rings lie at $x \simeq 0$ and 0.5. In each tetrahedron two corners occupied by O atoms are linked to Se pyramids, but two other Cl corners are free. The ring radical, $[Zn_2(SeO_3)_2Cl_4]^{4-}$, bears the negative charge which is compensated by Zn^{2+} cations in octahedral coordination, as shown above. Zn2 octahedra shearing O3 atoms form crimped chains running parallel to the c axis (Fig. 3). Chains of octahedra are linked to rings through edges O1–O3 common with Se pyramids (Fig. 3a) and with Zn1 tetrahedra through edges O2–Cl2 and corners (Fig. 3b) to form layers parallel to (010) whose radicals correspond to the chemical formula of the mineral.

The presence of shared edges in the polyhedra brings Se toward Zn2 (2.949 Å) and Zn1 toward Zn2 atoms (3.284 Å). The valency balance indicated that the compensation of positive and negative charges in the layer was satisfactory. The shortest cation–anion separation Zn1–Cl2 (3.792 Å) between adjacent layers is greater than
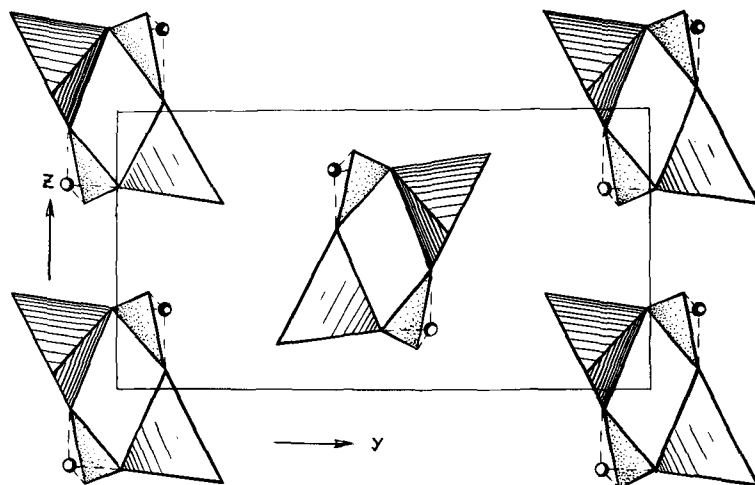
FIG. 2. Arrangement of $[Zn_2(SeO_3)_2Cl_4]^{4-}$ rings in the crystal structure of sophiite ($x \simeq 0.5$).
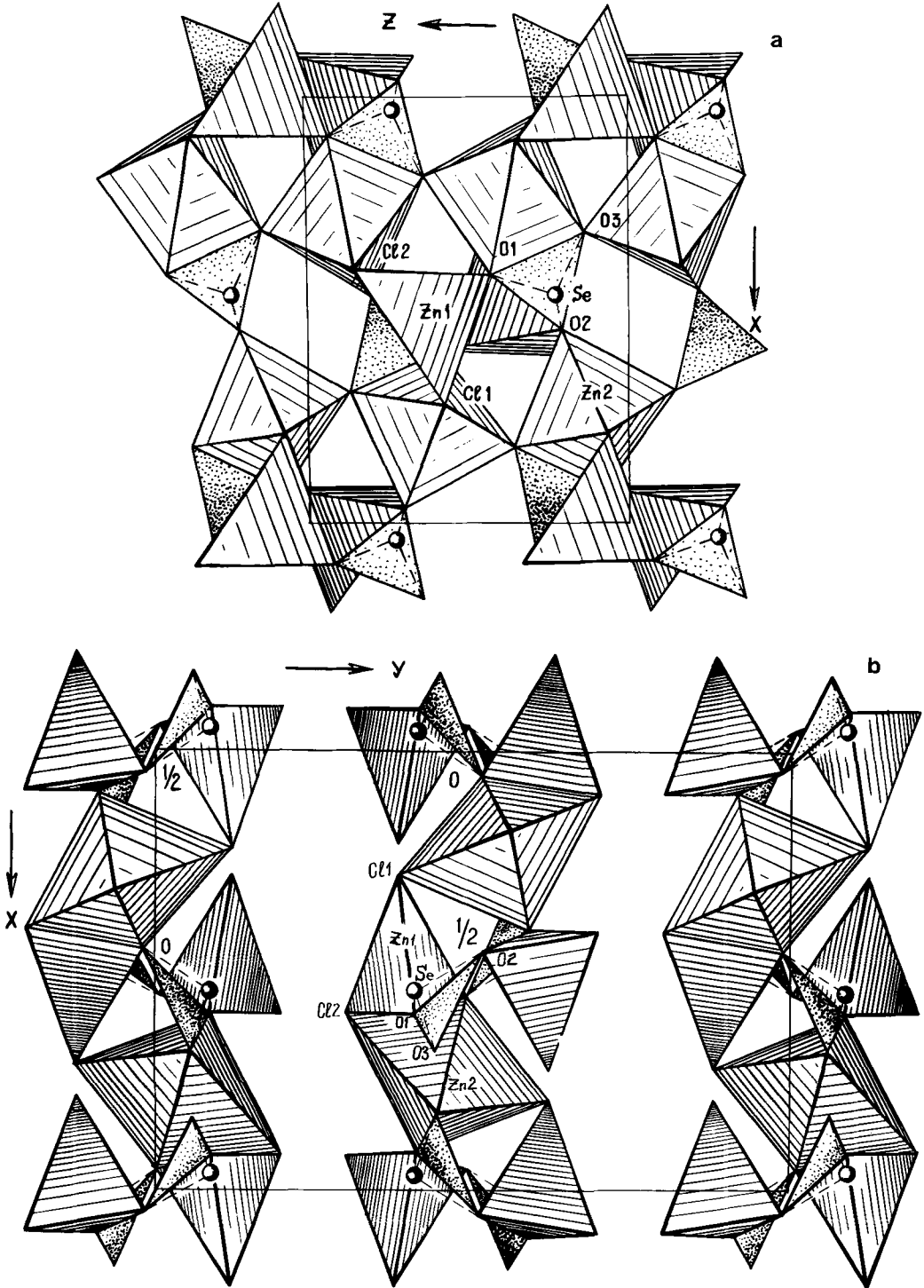
FIG. 3. Projection of the structure of sophiite onto (*a*) the *a–c* and (*b*) the *a–b* plane. Heights of symmetry centres of rings are indicated.

the cation–cation separation in the layer. This fact indicates the absence of significant contacts between the layers and suggests that the layers in the structure of sophiite are interconnected by residual Van der Waals bonds.

Relationship between the structure and physical properties

From the structural point of view, sophiite is a layer compound whose layers are electrostatically neutral and each layer can be considered as an infinite molecule. The structure of a layer itself is unstable. According to the third Pauling's law, the presence of shared edges in the structure decreases its stability since it results in shorter cation–cation separations. This effect is especially significant for cations bearing a high charge and a low coordination number. The fact that sophiite is unstable in air can be explained from its crystal structure.

Thermal deformations of sophiite were studied by the thermoroentgenographic powder method. The coefficient of volumetric expansion, $\alpha_v = 69.10^{-6}$/deg, is significant and can be explained by weak Van der Waals bonds. Coefficients of thermal expansion for the unit cell dimensions are $\alpha_a = 10$, $\alpha_b = 33$, $\alpha_c = 26$ (10^{-6}/deg). The strongest thermal expansion occurs in directions parallel to the weakest bonds (perpendicular to layers, parallel to the b-axis). Highly anisotropic thermal expansion in the (010) layer can result from its transformation within the limits of the given structure type. In the layer the maximum thermal expansion occurs along the c-axis which coincides with Zn2 octahedra chains (Fig. 3a). The shape of these chains is not fixed by symmetry and they may be straightened, which brings about highly anisotropic thermal deformations in the a–c plane.

A correlation between the axes of thermal deformation tensor and optical indicatrix was found in sophiite. The maximum thermal expansion occurs along the b-axis corresponding to the shorter axis of optical indicatrix, whereas the minimum thermal expansion corresponds to the longer axis.

The layer atomic arrangement in the crystal structure of sophiite brings about a perfect (010) cleavage parallel to the layers. The (201) cleavage is less perfect since it is parallel to prism faces in which zones of Se pyramids are divided by zones with weak bonds (Fig. 3).

Thus, highly anisotropic optical, thermal and other physical properties result from specific features of the crystal structure of sophiite.

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