The Canadian Mineralogist
Vol. 58, pp. 625-636 (2020)
DOI: 10.3749/canmin.2000032

ELEOMELANITE, $(K_2Pb)Cu_4O_2(SO_4)_4$, A NEW MINERAL SPECIES FROM THE TOLBACHIK VOLCANO, KAMCHATKA, RUSSIA

Igor V. PEKOV[§] and Natalia V. ZUBKOVA

Faculty of Geology, Moscow State University, Leninskie Gory, 119991 Moscow, Russia

Atali A. AGAKHANOV

Fersman Mineralogical Museum of Russian Academy of Sciences, Leninskiy Prospekt 18-2, Moscow, 119071 Russia

Nikita V. CHUKANOV

Institute of Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka, Moscow region, 142432 Russia
Faculty of Geology, Moscow State University, Leninskie Gory, 119991 Moscow, Russia

Dmitry I. BELAKOVSKIY

Fersman Mineralogical Museum of Russian Academy of Sciences, Leninskiy Prospekt 18-2, Moscow, 119071 Russia

Evgeny G. SIDOROV

Institute of Volcanology and Seismology, Far Eastern Branch of the Russian Academy of Sciences,
Piip Boulevard 9, 683006 Petropavlovsk-Kamchatsky, Russia

Sergey N. BRITVIN

Department of Crystallography, St. Petersburg State University, University Embankment 7/9, 199034 St. Petersburg, Russia

Anna G. TURCHKOVA and Dmitry Yu. PUSHCHAROVSKY

Faculty of Geology, Moscow State University, Leninskie Gory, 119991 Moscow, Russia

Abstract

The new mineral eleomelanite, $(K_2Pb)Cu_4O_2(SO_4)_4$, was found in the Arsenatnaya fumarole on the Second scoria cone of the Northern Breakthrough of the Great Tolbachik Fissure Eruption, Tolbachik Volcano, Kamchatka, Russia. It is associated with euchlorine, fedotovite, wulffite, chalcocyanite, dolerophanite, dravertite, hermannjahnite, alumoklyuchevskite, klyuchevskite, piypite, cryptochalcite, cesiodymite, anglesite, langbeinite, calciolangbeinite, metathénardite, belomarinaite, aphthitalite, krasheninnikovite, steklite, anhydrite, hematite, tenorite, sanidine, sylvite, halite, lammerite, urusovite, and gold. Eleomelanite occurs as interrupted crusts up to 6 mm across and up to 0.3 mm thick consisting of equant, prismatic, or tabular crystals or grains up to 0.3 mm. It is translucent and black. The luster is oleaginous on crystal faces and vitreous on a cleavage surface. D_{calc} is 3.790 g/cm^3. Eleomelanite is optically biaxial (–), α 1.646(3), β 1.715(6), γ 1.734(6), $2V_{\text{meas.}} = 60(15)°$. The chemical composition (wt.%, electron-microprobe) is K_2O 9.62, Rb_2O 0.49, Cs_2O 0.24, CaO 1.23, CuO 35.28, PbO 19.25, SO_3 34.78, total 100.89. The empirical formula calculated based on 18 O *apfu* is $(K_{1.88}Pb_{0.79}Ca_{0.20}Rb_{0.05}Cs_{0.02})_{\Sigma 2.94}Cu_{4.07}S_{3.99}O_{18}$. Eleomelanite is monoclinic, $P2_1/n$, *a* 9.3986(3), *b* 4.8911(1), *c* 18.2293(5) Å, β 104.409(3)°, *V* 811.63(4) Å^3, and $Z = 2$. The strongest reflections of the powder XRD pattern [d,Å(I)(hkl)] are: 9.07(63)$(\bar{1}01)$ 7.38(44)(101), 3.699(78)(112), 3.658(100)$(\bar{2}04)$, 3.173(40)(211), 2.915(35)(114), 2.838(35)(204), 2.683(36)$(\bar{2}15)$, and 2.576(51)$(310, \bar{1}16)$. The crystal structure was solved using single-crystal XRD data, $R_1 = 4.78\%$. It is based on heteropolyhedral Cu–S–O chains composed of Cu-centered polyhedra with [4+1+1] Cu^{2+} coordination and SO_4 tetrahedra. Adjacent Cu–S–O chains are connected *via* chains

---

[§] *Corresponding author e-mail address*: igorpekov@mail.ru

of (K,Pb)O_8 and KO_{10} polyhedra. Eleomelanite belongs to a novel structure type but has common structural features with klyuchevskite, alumoklyuchevskite, wulffite, parawulffite, and piypite. The name is derived from the Greek ελαιον (*eleon*), oil, and μέλας (*melas*), black, due to its black color and oleaginous luster on crystal faces that are uncommon for sulfate minerals.

Keywords: eleomelanite, new mineral, potassium lead copper sulfate, oxysulfate, crystal structure, fumarole, Tolbachik volcano, Kamchatka.

INTRODUCTION

Natural hydrogen-free alkali-copper oxysulfates form a specific family, in both crystal chemical and genetic aspects, which includes 15 minerals containing additional anion O^{2-} non-bonded to S^{6+}. These are euchlorine, $KNaCu_3O(SO_4)_3$ (Scordari & Stasi 1990); fedotovite, $K_2Cu_3O(SO_4)_3$ (Vergasova *et al*. 1988a, Starova *et al*. 1991); puninite, $Na_2Cu_3O(SO_4)_3$ (Siidra *et al*. 2017); wulffite, $K_3NaCu_4O_2(SO_4)_4$; parawulffite, $K_5Na_3Cu_8O_4(SO_4)_8$ (Pekov *et al*. 2014); cryptochalcite, $K_2Cu_5O(SO_4)_5$; cesiodymite, $CsKCu_5O(SO_4)_5$ (Pekov *et al*. 2018b); klyuchevskite, $K_3Cu_3Fe^{3+}O_2(SO_4)_4$ (Vergasova *et al*. 1989, Gorskaya *et al*. 1992); alumoklyuchevskite, $K_3Cu_3AlO_2(SO_4)_4$ (Gorskaya *et al*. 1995, Krivovichev *et al*. 2009, Siidra *et al*. 2017); elasmochloite, $Na_3Cu_6BiO_4(SO_4)_5$ (Pekov *et al*. 2019); kamchatkite, $KCu_3O(SO_4)_2Cl$ (Vergasova *et al*. 1988b, Varaksina *et al*. 1990, Siidra *et al*. 2017); piypite, $K_4NaCu_4O_2(SO_4)_4Cl$ (Vergasova *et al*. 1984, Effenberger & Zemann 1984); nabokoite, $KCu_7Te^{4+}O_4(SO_4)_5Cl$; atlasovite, $KCu_7Fe^{3+}BiO_4(SO_4)_5Cl$ (Popova *et al*. 1987, Pertlik & Zemann 1988); and, described in the present paper, eleomelanite, $(K_2Pb)Cu_4O_2(SO_4)_4$. These copper oxysulfates occur only in high-temperature (>350–400 °C) oxidizing-type volcanic fumaroles. All 15 minerals are known at the Tolbachik Volcano, Kamchatka, Russia, which is the type locality for 14 of them (euchlorine was first discovered at Vesuvius in Italy). A review of the crystal chemistry of fumarolic copper oxysulfates is given by Pekov *et al*. (2018b, c).

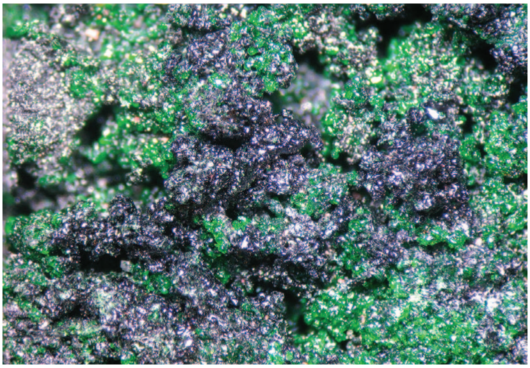

FIG. 1. Black aggregates of eleomelanite on a green euchlorine crust with (in the left upper part of the picture) dark steel-grey tenorite. FOV: 1 cm. Photo: I.V. Pekov & A.V. Kasatkin.

The name of the new mineral, eleomelanite (Cyrillic: элеомеланит), is derived from the Greek ελαιον (*eleon*), oil, and μέλας (*melas*), black, due to its black color and oleaginous luster on crystal faces that are uncommon for sulfate minerals: the surface looks oiled.

Both the new mineral and its name have been approved by the IMA Commission on New Minerals, Nomenclature and Classification (IMA No. 2015–118). The type specimen is deposited in the systematic collection of the Fersman Mineralogical Museum of the Russian Academy of Sciences, Moscow with the catalogue number 95347.

OCCURRENCE, GENERAL APPEARANCE, AND MORPHOLOGY

The new mineral was found in specimens collected by our team in July 2015 from the active Arsenatnaya fumarole located at the apical part of the Second scoria cone of the Northern Breakthrough of the Great Tolbachik Fissure Eruption (NB GTFE), Tolbachik Volcano, Kamchatka Peninsula, Far-Eastern Region, Russia (55°41′N 160°14′E, 1200 m asl). This scoria cone, which emerged in 1975, is a monogenetic volcano about 300 m high and approximately 0.1 km^3 in volume (Fedotov & Markhinin 1983). Many oxidizing-type fumaroles, in which volcanic gas mixes with heated atmospheric air (Zelenski *et al*. 2011), are still active there. The Arsenatnaya fumarole was described by Pekov *et al*. (2018a).

Eleomelanite was recovered at a depth of 0.6–0.8 m from the surface. The temperature, measured using a chromel-alumel thermocouple at the time of collecting, was about 350 °C. This part of the Arsenatnaya fumarole is strongly enriched in alkali and copper sulfates. Eleomelanite is associated with euchlorine, fedotovite, wulffite, chalcocyanite, dolerophanite, dravertite, hermannjahnite, alumoklyuchevskite, klyuchevskite, piypite, cryptochalcite, cesiodymite, anglesite, langbeinite, calciolangbeinite, metathénardite,

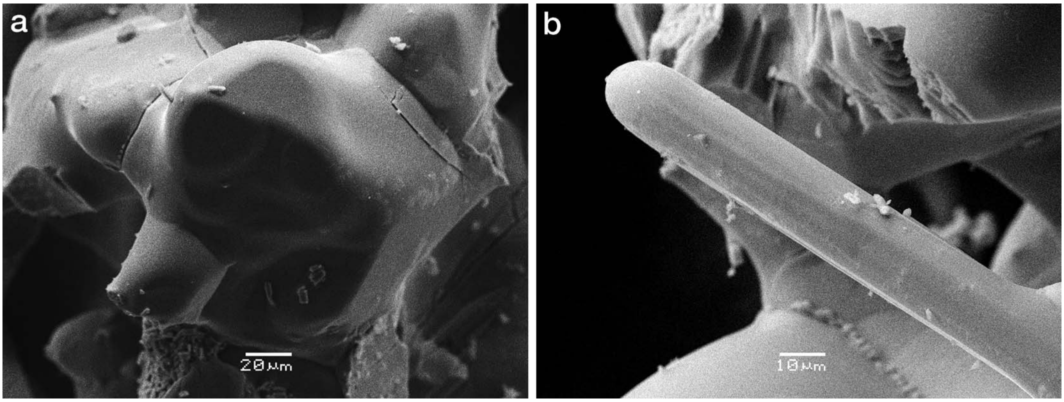

FIG. 2. (a) Crude, equant crystals and (b) polygonal prismatic crystal of eleomelanite. SEM (SE) images.

belomarinaite, aphthitalite, krasheninnikovite, steklite, anhydrite, hematite, tenorite, pseudobrookite, sanidine, sylvite, halite, lammerite, lammerite-β, urusovite, and gold.

The new mineral occurs as interrupted, typically open-work crusts up to 6 mm across and up to 0.3 mm thick overgrowing bright green crystal crusts of euchlorine (Fig. 1). Eleomelanite aggregates usually consist of crude, equant, prismatic or tabular crystals or grains up to 0.3 mm in size (Fig. 2a). Rarely, euhedral polygonal crystals, prismatic (Fig. 2b) or tabular, are observed. A close association of the new mineral with tenorite is common (Fig. 1).

PHYSICAL PROPERTIES AND OPTICAL DATA

Macroscopically, eleomelanite is translucent and black. In very thin fragments it is dark green. The streak is dark green. The luster is strongly oleaginous on crystal faces (the surface looks oiled) and strongly vitreous on cleavage surfaces. The mineral is brittle. One direction of perfect cleavage is observed, presumably on (001) (this direction is assumed based on the structure data), and the fracture is stepped. The Mohs hardness is *ca*. 3. Density was not measured because of the small size of solid individual crystals and the open-work character of aggregates. The density value calculated from the empirical formula is 3.790 g/cm^3.

In plane-polarized transmitted light, eleomelanite is strongly pleochroic $Z \approx Y$ (dark green with brown hue, almost black in thicker grains) $> X$ (green). It is optically biaxial (–), $\alpha = 1.646$ (3), $\beta = 1.715$ (6), $\gamma = 1.734$ (6) (589 nm), $2V_{\text{meas.}} = 60$ (15)° (estimated from the curve of the conoscopic interference figures on sections perpendicular to the optical axes), $2V_{\text{calc.}} = 54°$. Dispersion of the optical axes was not observed. In terms of orientation, *XZ* is coplanar to

TABLE 1. CHEMICAL COMPOSITION (wt.%) OF ELEOMELANITE

Constituent	Mean	Range	Standard deviation	EMPA standard
K_2O	9.62	9.48–9.91	0.14	Microcline
Rb_2O	0.49	0.35–0.64	0.09	$Rb_2Nb_4O_{11}$
Cs_2O	0.24	0.00–0.48	0.23	$Cs_2Nb_4O_{11}$
CaO	1.23	0.96–1.52	0.18	Wollastonite
PbO	19.25	18.50–19.70	0.35	$PbTiO_3$
CuO	35.28	34.88–35.78	0.33	Cu
SO_3	34.78	34.42–35.49	0.31	ZnS
Total	100.89			

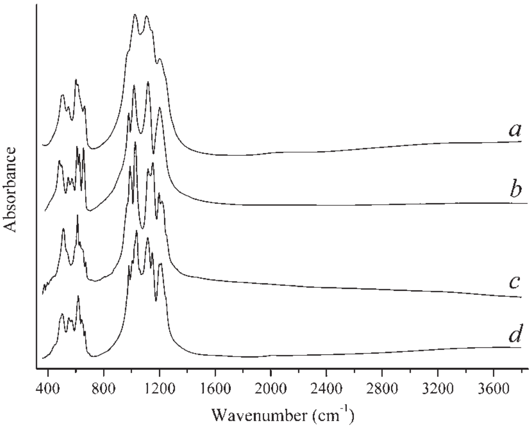

FIG. 3. The IR spectra of (a) eleomelanite, (b) piypite, (c) wulffite, and (d) parawulffite from the Tolbachik volcano, Kamchatka, Russia. For wavenumbers of maxima of spectral bands see Table 3.

TABLE 2. COMPARATIVE DATA FOR ELEOMELANITE AND RELATED MINERALS

Mineral	Eleomelanite	Wulffite	Parawulffite	Piypite*	Klyuchevskite	Alumoklyuchevskite**
Formula	$(K_2Pb)Cu_4O_2(SO_4)_4$	$K_3NaCu_4O_2(SO_4)_4$	$K_5Na_3Cu_8O_4(SO_4)_8$	$K_8Cu_9O_4(SO_4)_8Cl_2$	$K_3Cu_3Fe^{3+}O_2(SO_4)_4$	$K_3Cu_3AlO_2(SO_4)_4$
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Tetragonal	Monoclinic	Monoclinic or triclinic
Space group	$P2_1/n$	$Pn2_1a$	$P2/c$	$I4$	$I2$	$I2$ or $P\bar{1}$
a (Å)	9.399	14.281	13.904	13.60–13.67	18.667	18.772
b (Å)	4.891	4.948	4.977		4.94	4.967
c (Å)	18.229	24.113	23.586	4.94–4.98	18.405	18.468
β (°)	104.41		90.21		101.5	101.66
V (Å^3)	812	1704	1632	921–923	1663	1686
Z	2	4	2	1	4	4
Strongest reflections of the powder XRD pattern: *d* (Å) – *I*	9.07 – 63 7.38 – 44 3.699 – 78 3.658 – 100 3.173 – 40 2.683 – 36 2.576 – 51	9.27 – 100 7.16 – 22 3.125 – 16 2.882 – 16 2.780 – 33 2.725 – 14 2.472 – 20	9.06 – 100 7.00 – 26 5.903 – 12 3.096 – 12 2.736 – 33 2.492 – 24 2.321 – 26	9.63 – 100 6.79 – 40 4.305 – 20 3.039 – 70 3.006 – 30 2.666 – 20 1.924 – 20	9.17 – 95 9.03 – 100 7.20 – 35 4.502 – 25 3.762 – 55 3.678 – 23 3.409 – 28	9.15 – 84 9.04 – 100 7.20 – 52 4.509 – 15 3.781 – 37 3.757 – 33 2.786 – 21
Optical data						
α	1.646	1.582	1.585	ω 1.583–1.598	1.549	1.542
β	1.715	1.610	not determined		1.550	1.548
γ	1.734	1.715	1.717	ε 1.695–1.711	1.680	1.641
optical sign, 2*V*	(–), 60°	(+), calc. 58°	(+), not determined	(+)	(+), calc. 11°	(+), calc. 30°
$D_{calc.}$ (g/cm^3)	3.79	3.19	3.32	3.0–3.22	2.98	2.95
Sources	This work	Pekov *et al.* (2014)		Vergasova *et al.* (1984); Clark *et al.* (1984); Effenberger & Zemann (1984)	Vergasova *et al.* (1989); Gorskaya *et al.* (1992)	Gorskaya *et al.* (1995); Krivovichev *et al.* (2009); Siidra *et al.* (2017)

* In some papers published in 1980s the same mineral was described as "caratiite" (Clark *et al.* 1984; Effenberger & Zemann 1984). This was because it was discovered at both Tolbachik (piypite: Vergasova *et al.* 1984) and Vesuvius (caratiite: Clark *et al.* 1984) at about the same time. Subsequently the priority of piypite was recognized by the International Mineralogical Association (Filatov & Vergasova 1989).

** The monoclinic unit-cell parameters from Krivovichev *et al.* (2009) are given.

TABLE 3. ABSORPTION BANDS AND ASSIGNMENTS IN THE IR SPECTRA OF ELEOMELANITE AND RELATED SULFATES (cm^{-1}; s – STRONG BAND, sh – SHOULDER)

Mineral				
Eleomelanite	Piypite	Wulffite	Parawulffite	Assignment
1235sh	1211s	1250sh	1212s	$\nu_3(F_2)$ – antisymmetric stretching vibrations of SO_4^{2-} anions
1202s	1123s	1123	1202s	
1145s	1018s	1198	1149s	
1108s		1153s	1116s	
1080sh		1118s	1060sh	
1025s	981s	1026s	1036s	$\nu_1(A_1)$ – symmetric stretching vibrations of SO_4^{2-} anions
975sh		989s	1025sh	
		970sh	1006s	
			981s	
662	650	671	690	$\nu_4(F_2)$ – bending vibrations of SO_4^{2-} anions
615	624	645sh	665	
601s	606s	630	650sh	
547	567	612s	642	
			618s	
			572	
			550	
508	543	535sh	503	Stretching vibrations of shorter bonds in Cu-centered polyhedra with [4+1] and [4+1+1] Cu^{2+} coordination and the $\nu_2(E)$ bending mode of SO_4^{2-} anions
500sh	497	511	490sh	
	480		450sh	

the cleavage plane, such that if the cleavage plane is (001) then $Y = c$.

CHEMICAL DATA

Chemical data for eleomelanite were obtained using a Jeol 733 electron microprobe instrument operated in WDS mode with an accelerating voltage of 20 kV, a beam current of 20 nA, and a beam diameter of 3 μm. The chemical composition (average of nine spot analyses) is given in Table 1. Contents of other elements with atomic numbers higher than that of carbon are below detection limits.

The empirical formula of the new mineral calculated on the basis of 18 O *apfu* is $(K_{1.88}Pb_{0.79}Ca_{0.20}Rb_{0.05}Cs_{0.02})_{\Sigma 2.94}Cu_{4.07}S_{3.99}O_{18}$. The simplified formula is $(K_2Pb)Cu_4O_2(SO_4)_4$ which requires K_2O 9.86, PbO 23.35, CuO 33.29, SO_3 33.50, total 100 wt.%.

Eleomelanite hydrolyses (becomes dull and blue) after one hour and slowly dissolves in H_2O at room temperature.

INFRARED SPECTROSCOPY

In order to obtain infrared (IR) absorption spectra (Fig. 3), powdered samples of eleomelanite and related oxysulfate minerals were mixed with dried KBr, pelletized, and analyzed using an ALPHA FTIR spectrometer (Bruker Optics) with a resolution of 4 cm^{-1}. A total of 16 scans were collected for each spectrum. The IR spectrum of a pellet of pure KBr was used as a reference.

Infrared absorption bands and their assignments for eleomelanite and related minerals (see Table 2) are given in Table 3. Two nondegenerate bands, assigned to symmetric stretching vibrations of SO_4^{2-} anions, are observed in the IR spectrum of eleomelanite at 1025 and 975 cm^{-1}, corresponding to two nonequivalent distorted tetrahedra SO_4. The infrared absorption bands of eleomelanite are broader and more poorly resolved than those in the IR spectra of related sulfates, which may be due to the mixed occupancy of the *A*(1) site containing cations with strongly different atomic numbers, K and Pb (see Discussion). Characteristic bands of BO_3^{3-}, CO_3^{2-}, NO_3^{-}, and hydrogen-bearing groups are absent in the IR spectrum of eleomelanite.

X-RAY CRYSTALLOGRAPHY AND CRYSTAL STRUCTURE DETERMINATION

Powder X-ray diffraction (XRD) data for eleomelanite (Table 4) were collected with a Rigaku R-AXIS Rapid II single-crystal diffractometer equipped with a cylindrical image plate detector (Debye-Scherrer geometry, $d = 127.4$ mm, Co*K*α radiation). Parameters of the monoclinic unit cell calculated from the powder

TABLE 4. POWDER X-RAY DIFFRACTION DATA (d IN Å) OF ELEOMELANITE

I_{obs}	d_{obs}	I_{calc}*	d_{calc}**	*h k l*
63	**9.07**	86	9.061	$\bar{1}01$
14	8.82	18	8.827	002
44	**7.38**	59	7.378	101
26	5.613	32	5.621	$\bar{1}03$
8	4.556	1, 14	4.551, 4.531	200, $\bar{2}02$
5	4.405	4	4.414	004
33	4.304	42, 1	4.309, 4.304	110, $\bar{1}11$
11	4.065	5, 6	4.077, 4.065	111, $\bar{1}12$
3	3.800	1	3.762	013
78	**3.699**	89, 1	3.704, 3.689	112, 202
100	**3.658**	100	3.656	$\bar{2}04$
11	3.605	9	3.609	$\bar{1}05$
7	3.278	12, 2	3.282, 3.277	$\bar{1}14$, 014
40	**3.173**	55, 1	3.171, 3.157	211, $\bar{2}13$
22	3.133	17	3.123	$\bar{3}01$
2	3.041	1	3.046	105
4	3.002	1	3.020	$\bar{3}03$
9	2.942	12	2.943	006
35	**2.915**	51, 4	2.916, 2.904	114, $\bar{1}15$
35	**2.838**	42	2.836	204
32	2.695	38	2.697	213
36	**2.683**	50	2.679	$\bar{2}15$
14	2.654	9	2.650	$\bar{3}05$
34	2.635	42	2.629	$\bar{3}12$
51	**2.576**	32, 69	2.578, 2.575	310, $\bar{1}16$
3	2.520	7	2.521	016
2	2.475	1	2.465	$\bar{3}14$
31	2.444	53, 7	2.446, 2.437	020, $\bar{2}16$
5	2.358	2	2.362	$\bar{1}21$
4	2.284	3, 3	2.289, 2.276	107, 400
18	2.233	5, 3, 16	2.232, 2.231, 2.229	$\bar{3}07$, 206, 215
3	2.213	2	2.214	$\bar{2}08$
14	2.184	20, 4	2.181, 2.169	$\bar{3}16$, $\bar{2}21$
3	2.156	4, 1	2.154, 2.152	220, $\bar{2}22$
4	2.139	5	2.139	024
7	2.107	2	2.105	$\bar{4}11$
4	2.088	9, 6	2.101, 2.082	$\bar{4}13$, 402
6	2.068	3	2.066	$\bar{4}06$
17	2.049	26	2.046	314
12	2.033	4, 13, 2	2.038, 2.033, 2.030	222, $\bar{2}24$, $\bar{3}17$
12	2.026	6, 9	2.024, 2.024	$\bar{1}25$, $\bar{1}09$
5	1.994	7, 6	1.998, 1.987	411, $\bar{4}15$
2	1.949	3, 2	1.950, 1.944	223, $\bar{2}25$
6	1.927	9, 3	1.925, 1.924	$\bar{3}21$, $\bar{3}22$
3	1.906	3, 2	1.907, 1.904	125, 320
6	1.878	4, 6, 4	1.885, 1.881, 1.877	$\bar{3}18$, 026, 118
8	1.866	2, 8, 2	1.862, 1.859, 1.857	321, $\bar{5}01$, $\bar{3}24$
8	1.849	7, 6, 4	1.852, 1.845, 1.844	224, $\bar{2}26$, 404
9	1.826	5, 11	1.828, 1.826	$\bar{4}08$, 109
10	1.821	1, 4	1.823, 1.821	413, 019
3	1.799	10	1.797	$\bar{3}25$
6	1.765	6, 5	1.766, 1.763	0.0.10, 316
7	1.698	13	1.694	$\bar{4}22$
2	1.667	5, 1	1.671, 1.667	127, $\bar{1}28$

TABLE 4. CONTINUED.

I_{obs}	d_{obs}	I_{calc}*	d_{calc}**	*h k l*
2	1.660	4, 2	1.662, 1.661	$\bar{4}24$, 0.1.10
3	1.650	1, 1, 5	1.653, 1.653, 1.648	$\bar{5}16$, $\bar{1}$.0.11, 226
2	1.627	1, 4	1.629, 1.626	415, $\bar{3}$.1.10
10	1.612	1, 2, 15	1.616, 1.615, 1.607	406, $\bar{4}19$, 512
6	1.592	10, 1	1.592, 1.591	$\bar{3}$.0.11, $\bar{1}32$
8	1.568	6, 3	1.570, 1.567	1.1.10, 132
6	1.562	4, 3, 9	1.562, 1.562, 1.559	$\bar{2}$.1.11, $\bar{6}02$, $\bar{1}29$
1	1.538	1	1.534	$\bar{5}18$
3	1.526	2, 2	1.525, 1.525	0.1.11, 318
2	1.520	4	1.518	231
8	1.485	9, 1, 3	1.487, 1.487, 1.486	134, $\bar{3}29$, $\bar{1}35$
7	1.481	10, 1	1.480, 1.480	$\bar{5}21$, 514
6	1.464	5, 11	1.464, 1.463	$\bar{4}28$, 129
3	1.455	8, 5	1.456, 1.455	$\bar{5}25$, 233
2	1.447	2, 6	1.445, 1.445	$\bar{1}$.1.12, $\bar{3}32$
7	1.436	1, 4, 15, 2	1.437, 1.436, 1.436, 1.433	135, 330, $\bar{1}36$, $\bar{4}$.1.11
6	1.418	8, 1	1.418, 1.417	408, 327
2	1.391	2, 3	1.395, 1.387	$\bar{1}$.0.13, $\bar{5}$.0.11
1	1.368	1, 1, 2	1.369, 1.369, 1.366	$\bar{1}$.2.11, 037, 235
4	1.341	1, 1	1.342, 1.340	$\bar{7}03$, $\bar{4}$.2.10
4	1.334	4, 3, 5	1.336, 1.335, 1.334	604, 613, $\bar{3}$.2.11
2	1.322	2	1.321	334
1	1.309	1, 1, 1	1.311, 1.308, 1.308	038, 2.0.12, 431
4	1.294	1, 1	1.294, 1.293	$\bar{7}07$, 2.2.10

* For the calculated pattern, only reflections with intensities $\geq$1 are given; ** for the unit-cell parameters calculated from single-crystal data; the strongest reflections are marked with bold type.

data are $a = 9.396$ (4), $b = 4.895$ (1), $c = 18.219$ (7) Å, $\beta = 104.36$ (3)°, and $V = 811.7$ (7) Å^3.

Single-crystal XRD studies were carried out using an Xcalibur S CCD diffractometer. The structure was solved by direct methods and refined with the use of the SHELX-97 software package (Sheldrick 2008) to $R_1 = 0.0478$ on the basis of 2898 independent reflections with $I > 2\sigma(I)$. Table 5 gives crystal data, data collection information, and structure refinement details; Table 6 reports atom coordinates and displacement parameters; Table 7 gives selected interatomic distances; and Table 8 provides bond-valence calculations.

DISCUSSION

The crystal structure of eleomelanite (Fig. 4) is unique. It is based on heteropolyhedral Cu–S–O chains running along [010] and built of Cu-centered polyhedra with [4+1+1] Cu^{2+} coordination and SO_4 tetrahedra. Two crystallographically independent Cu atoms are involved in the construction of the chains and each of them form four short Cu–O bonds and two elongate Cu–O bonds (Table 7, Fig. 5a). In each [4+1+1] Cu-centered polyhedron, two O atoms forming short Cu–O bonds occur at O(4) and are connected only with Cu cations while two others belong to two SO_4 groups of the same chain. Approximately flat Cu-centered squares involving short Cu–O bonds form two pairs sharing edges: Cu(1)–Cu(1) and Cu(2)–Cu(2). Adjacent pairs have common vertices and are located almost perpendicular to each other. The elongate Cu–O bonds complete coordination of the Cu cations to form octahedra that are significantly distorted due to the Jahn-Teller effect (Fig. 5a). Adjacent chains are connected *via* the polyhedra centered by the large *A* cations. The eight-coordinated *A*(1) site is occupied by K, Pb^{2+}, and Ca in the ratios 0.50:0.35:0.15. Thus, K and bivalent cations are disordered. The 10-coordinated *A*(2) site is also K-dominant with Rb and Cs occurring as minor components, K:Rb:Cs = 0.935:0.050:0.015 (Table 6). Both *A*(1)- and *A*(2)-centered polyhedra form chains running parallel to **b**. They are different in configuration: the $A(1)O_8$ polyhedra share vertices to form double chains whereas the $A(2)O_{10}$ polyhedra share edges and form straight single chains (Figs. 5b, c).

TABLE 5. CRYSTAL DATA, DATA COLLECTION INFORMATION, AND STRUCTURE REFINEMENT DETAILS FOR ELEOMELANITE

Formula	$(K_{1.00}Pb_{0.70}Ca_{0.30})(K_{0.935}Rb_{0.05}Cs_{0.015})Cu_4O_2(SO_4)_4$
Formula weight	909.38
Temperature (K)	293(2)
Radiation and wavelength (Å)	Mo$K\alpha$; 0.71073
Crystal system, space group; Z	Monoclinic, $P2_1/n$; 2
Unit cell dimensions (Å/°)	$a = 9.3986(3)$ $b = 4.89110(10)$ $\beta = 104.409(3)$ $c = 18.2293(5)$
V (Å^3)	811.63(4)
Absorption coefficient μ (mm^{-1})	13.780
F_{000}	854
Crystal size (mm)	0.06 × 0.11 × 0.24
Diffractometer	Xcalibur S CCD
θ range for data collection (°)	3.62 – 34.85
Index ranges	$-14 \leq h \leq 14$, $-7 \leq k \leq 7$, $-28 \leq l \leq 29$
Reflections collected	20947
Independent reflections	3389 ($R_{int} = 0.0406$)
Independent reflections with $I > 2\sigma(I)$	2898
Data reduction	CrysAlisPro, Agilent Technologies, Version 1.171.37.35 (Agilent 2014)
Absorption correction	Gaussian [Numerical absorption correction based on Gaussian integration over a multifaceted crystal model]. Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
Structure solution	direct methods
Refinement method	full-matrix least-squares on F^2
Number of refined parameters	134
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0478$, w$R2 = 0.1187$
R indices (all data)	$R1 = 0.0571$, w$R2 = 0.1245$
GoF	1.097
Largest diff. peak and hole, e/Å^3	3.62 and –1.30

TABLE 6. COORDINATES AND EQUIVALENT DISPLACEMENT PARAMETERS (U_{eq}, in Å^2) OF ATOMS, SITE MULTIPLICITIES (Q), AND SITE OCCUPANCY FACTORS (s.o.f.) FOR ELEOMELANITE

Site	x	y	z	U_{eq}	Q	s.o.f.*
A(1)	0.02219(4)	0.02902(8)	0.23756(2)	0.02123(11)	4	$K_{0.50}Pb_{0.35}Ca_{0.15}$
A(2)	0.5	0.0	0.5	0.0419(4)	2	$K_{0.935}Rb_{0.050}Cs_{0.015}$
Cu(1)	0.85553(6)	0.47283(10)	0.44822(3)	0.01612(13)	4	1
Cu(2)	0.08276(7)	0.02650(10)	0.44327(4)	0.01942(14)	4	1
S(1)	0.24255(13)	0.5278(2)	0.37924(7)	0.0202(2)	4	1
S(2)	0.72731(13)	–0.0094(2)	0.35497(7)	0.0201(2)	4	1
O(1)	0.7184(4)	0.1509(7)	0.4230(2)	0.0240(7)	4	1
O(2)	0.8681(5)	0.0602(10)	0.3380(3)	0.0345(9)	4	1
O(3)	0.8999(6)	0.5501(10)	0.2076(3)	0.0451(12)	4	1
O(4)	–0.0056(3)	0.7495(6)	0.48913(17)	0.0161(6)	4	1
O(5)	0.7807(4)	0.1948(7)	0.1273(2)	0.0275(8)	4	1
O(6)	0.4015(7)	0.5831(17)	0.3988(4)	0.073(2)	4	1
O(7)	0.2060(8)	0.4098(15)	0.3035(3)	0.0652(17)	4	1
O(8)	0.7843(7)	0.6558(11)	0.5627(3)	0.0562(15)	4	1
O(9)	0.1676(7)	0.7943(10)	0.3769(3)	0.0518(15)	4	1

* Occupancy factors for the A(1) and A(2) sites were obtained on the basis of refined numbers of electrons (e_{ref}), analysis of interatomic distances (Table 5), and bond valence calculations (Table 6), also taking into account electron-microprobe data.

TABLE 7. SELECTED INTERATOMIC DISTANCES (Å) IN THE STRUCTURE OF ELEOMELANITE

A(1)	–O(3)	2.607(5)	Cu(2)	–O(4)	1.889(3)
	–O(2)	2.607(4)		–O(4)	1.921(3)
	–O(7)	2.620(7)		–O(9)	1.966(4)
	–O(5)	2.752(3)		–O(8)	2.014(5)
	–O(6)	2.765(7)		–O(2)	2.419(5)
	–O(3)	2.793(5)		–O(1)	2.815(4)
	–O(9)	2.813(5)			
	–O(7)	2.895(7)	S(1)	–O(7)	1.456(6)
				–O(8)	1.457(5)
A(2)	–O(6)	2.752(7) × 2		–O(6)	1.472(6)
	–O(1)	2.858(4) × 2		–O(9)	1.477(5)
	–O(8)	3.124(6) × 2			
	–O(6)	3.398(8) × 2	S(2)	–O(3)	1.461(4)
	–O(9)	3.509(7) × 2		–O(2)	1.472(5)
				–O(1)	1.487(4)
Cu(1)	–O(4)	1.899(3)		–O(5)	1.488(4)
	–O(4)	1.917(3)			
	–O(5)	1.959(3)			
	–O(1)	2.014(3)			
	–O(8)	2.510(6)			
	–O(2)	2.870(5)			

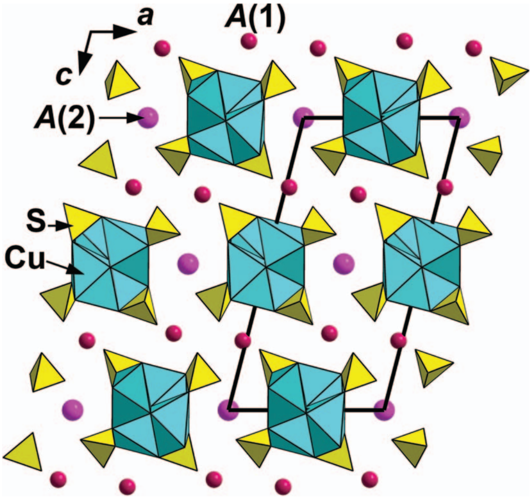

FIG. 4. The crystal structure of eleomelanite in the **ac** projection. The unit cell is outlined.

In terms of stoichiometry and crystal structure, eleomelanite, $(K_2Pb)Cu_4O_2(SO_4)_4$, is close to klyuchevskite, $K_3Cu_3Fe^{3+}O_2(SO_4)_4$ (Gorskaya *et al.* 1992), and alumoklyuchevskite, $K_3Cu_3AlO_2(SO_4)_4$ (Krivovichev *et al.* 2009), which are isostructural to one another. The main structural unit of eleomelanite, the heteropolyhedral Cu–S–O chain, is very similar to those found in these sulfates and in wulffite, $K_3NaCu_4O_2(SO_4)_4$; parawulffite, $K_5Na_3Cu_8O_4(SO_4)_8$ (Pekov *et al.* 2014); and piypite, $K_8Cu_9O_4(SO_4)_8Cl_2 = K_8Cu_8O_4(SO_4)_8{\cdot}CuCl_2$ (Effenberger & Zemann 1984) (Fig. 6). The general comparative characteristics of crystal structures of H-free alkali-copper oxysulfate minerals are given by Pekov *et al.* (2018c).

However, chemical and structural differences between eleomelanite, piypite, wulffite, and parawulffite result in significant differences in the unit-cell dimensions, powder X-ray diffraction patterns, IR spectra, and optical characteristics (Tables 2 and 3). However, the unit-cell parameters of klyuchevskite and alumoklyuchevskite are comparable with the unit-cell parameters of eleomelanite (Table 2).

TABLE 8. BOND-VALENCE CALCULATIONS* FOR ELEOMELANITE

	A(1)	*A*(2)	Cu(1)	Cu(2)	S(1)	S(2)	Σ
O(1)		0.13 $^{\times 2\downarrow}$	0.40	0.04		1.45	2.02
O(2)	0.25		0.04	0.13		1.50	1.92
O(3)	0.25 0.16					1.54	1.95
O(4)			0.55 0.52	0.57 0.52			2.16
O(5)	0.18		0.46			1.44	2.08
O(6)	0.17	0.17 $^{\times 2\downarrow}$ 0.03 $^{\times 2\downarrow}$			1.50		1.87
O(7)	0.24 0.12				1.56		1.92
O(8)		0.06 $^{\times 2\downarrow}$	0.10	0.40	1.56		2.12
O(9)	0.15	0.02 $^{\times 2\downarrow}$		0.46	1.48		2.11
Σ	1.52	0.82	2.07	2.12	6.10	5.93	

* Parameters are taken from Gagné & Hawthorne (2015).

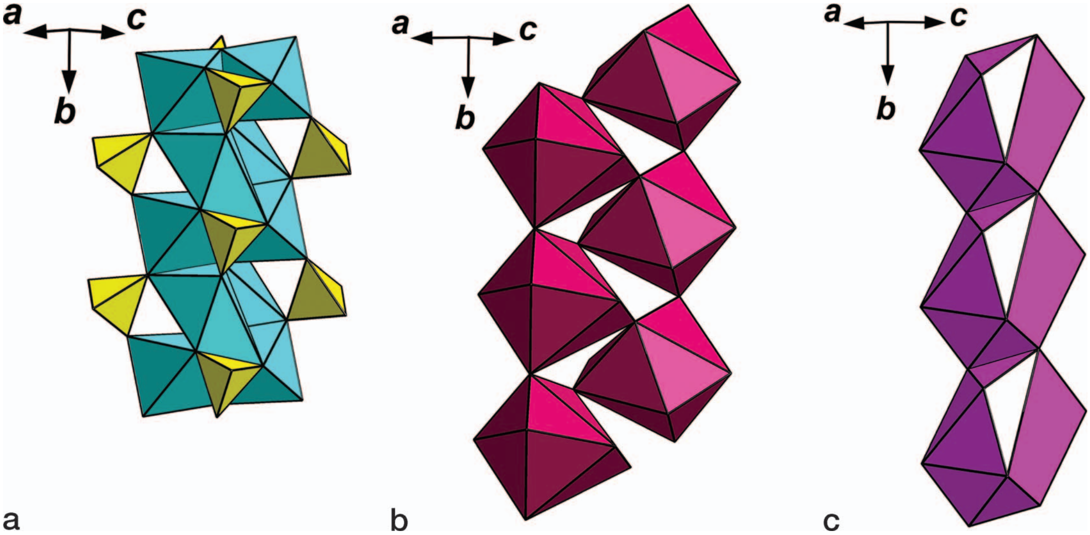

FIG. 5. Fragments of the crystal structure of eleomelanite. (a) A heteropolyhedral Cu–S–O chain, (b) a chain composed of $A(1)$-centered polyhedra, and (c) a chain built of $A(2)$-centered polyhedra.

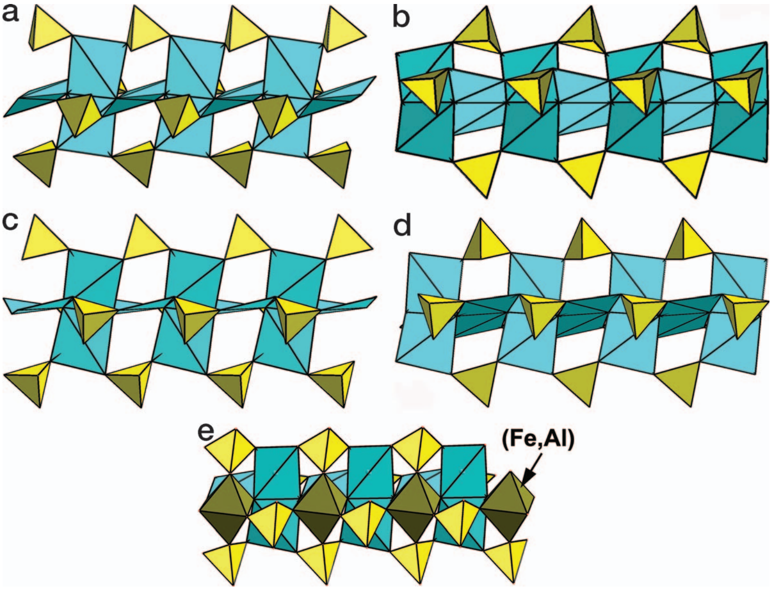

FIG. 6. The heteropolyhedral Cu–S–O chains in (a) eleomelanite, (b) piypite (drawn using data from Effenberger & Zemann 1984), (c) wulffite, (d) parawulffite (both drawn using data from Pekov *et al*. 2014), and (e) the heteropolyhedral Cu–(Fe,Al)–S–O chain in klyuchevskite/alumoklyuchevskite [drawn using data from Gorskaya *et al*. (1992) for klyuchevskite]. Copper-centered polyhedra are blue, SO_4 tetrahedra are yellow.

The crystal structure of eleomelanite could also be described in terms of anion-centered tetrahedra (Krivovichev *et al*. 2013). The O(4) atoms bond only with Cu to form $[O_2Cu_4]^{\infty}$ chains composed of edge-sharing OCu_4 tetrahedra extending parallel to [010] (Fig. 7). Analogous chains were reported in piypite (Effenberger & Zemann 1984); its synthetic sodium analogue, $Na_4Cu_4O_2(SO_4)_2{\cdot}Me$Cl ($Me$ = Na, Cu, ☐)

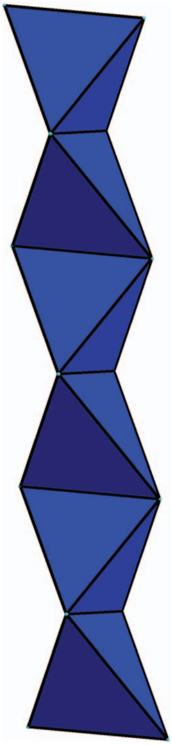

FIG. 7. A $[O_2Cu_4]^{\infty}$ chain composed of oxocentered OCu_4 tetrahedra in the crystal structure of eleomelanite.

(Kahlenberg *et al*. 2000); coparsite, $Cu_4O_2(AsO_4)Cl$ (Starova *et al*. 1998); and wulffite and parawulffite (Pekov *et al*. 2014). In klyuchevskite (Gorskaya *et al*. 1992) and alumoklyuchevskite (Krivovichev *et al*. 2009) topologically identical chains are composed of tetrahedral $[OFe^{3+}Cu_3]$ and $[OAlCu_3]$, respectively.

Eleomelanite is the only one of 15 naturally occurring H-free copper oxysulfates (see Introduction) in which a bivalent cation (Pb) plays an important role among large cations. In the other 14 minerals (see Introduction), only univalent cations of alkaline metals (K, Na, Cs) are significant in the large-cationic part of the structure.

ACKNOWLEDGMENTS

We thank referees Ulf Hålenius and Barbara Nash and Associate Editor Aaron Lussier for their valuable comments. This work was supported by the Russian Science Foundation, grant no. 19-17-00050. A part of this work (IR spectroscopic study) was carried out in accordance with the state task, state registration No. AAAA-A19-119092390076-7. Technical support by the SPbSU X-Ray Diffraction Resource Center for the powder XRD study is acknowledged.

REFERENCES

AGILENT TECHNOLOGIES (2014) CrysAlisPro Software system, version 1.171.37.35. Agilent Technologies UK Limited, Oxford, England.

CLARK, A.M., FEJER, E.E., & COUPER, A.G. (1984) Caratiite, a new sulphate-chloride of copper and potassium, from the lavas of 1869 Vesuvius eruption. *Mineralogical Magazine* **48**, 537–539.

EFFENBERGER, H. & ZEMANN, J. (1984) The crystal structure of caratiite. *Mineralogical Magazine* **48**, 541–546.

FEDOTOV, S.A. & MARKHININ, Y.K., Eds. (1983) *The Great Tolbachik Fissure Eruption*. Cambridge University Press, New York, United States.

FILATOV, S.K. & VERGASOVA, L.P. (1989) Discrediting of caratiite and priority for piypite. *Zapiski Vsesoyuznogo Mineralogicheskogo Obshchestva* **118(3)**, 88–90 (in Russian).

GAGNÉ, O.C. & HAWTHORNE, F.C. (2015) Comprehensive derivation of bond-valence parameters for ion pairs involving oxygen. *Acta Crystallographica* **B71**, 562–578.

GORSKAYA, M.G., FILATOV, S.K., ROZHDESTVENSKAYA, I.V., & VERGASOVA, L.P. (1992) The crystal structure of klyuchevskite, $K_3Cu_3(Fe,Al)O_2(SO_4)_4$, a new mineral from Kamchatka volcanic sublimates. *Mineralogical Magazine* **56**, 411–416.

GORSKAYA, M.G., VERGASOVA, L.P., FILATOV, S.K., ROLICH, D.V., & ANANIEV, V.V. (1995) Alumoklyuchevskite, $K_3Cu_3AlO_2(SO_4)_4$, a new oxysulfate of K, Cu and Al from volcanic exhalations, Kamchatka, Russia. *Zapiski Vserossiiskogo Mineralogicheskogo Obshchestva* **124(1)**, 95–100 (in Russian).

KAHLENBERG, V., PIOTROWSKI, A., & GIESTER, G. (2000) Crystal structure of $Na_4[Cu_4O_2(SO_4)_4]\cdot MeCl$ (Me: Na, Cu, □) – the synthetic Na-analogue of piypite (caratiite). *Mineralogical Magazine* **64**, 1099–1108.

KRIVOVICHEV, S.V., FILATOV, S.K., & CHEREPANSKY, P.N. (2009) The crystal structure of alumoklyuchevskite, $K_3Cu_3AlO_2(SO_4)_4$. *Geology of Ore Deposits* **51**, 656–662.

KRIVOVICHEV, S.V., MENTRE, O., SIIDRA, O.I., COLMONT, M., & FILATOV, S.K. (2013) Anion-centered tetrahedra in inorganic compounds. *Chemical Reviews* **113**, 6459–6535.

PEKOV, I.V., ZUBKOVA, N.V., YAPASKURT, V.O., BELAKOVSKIY, D.I., CHUKANOV, N.V., LYKOVA, I.S., SAVELIEV, D.P., SIDOROV, E.G., & PUSHCHAROVSKY, D.YU. (2014) Wulffite, $K_3NaCu_4O_2(SO_4)_4$, and parawulffite, $K_5Na_3Cu_8O_4(SO_4)_8$, two new minerals from fumarole sublimates of the Tolbachik volcano, Kamchatka, Russia. *Canadian Mineralogist* **52**, 699–716.

PEKOV, I.V., KOSHLYAKOVA, N.N., ZUBKOVA, N.V., LYKOVA, I.S., BRITVIN, S.N., YAPASKURT, V.O., AGAKHANOV, A.A., SHCHIPALKINA, N.V., TURCHKOVA, A.G., & SIDOROV, E.G. (2018a) Fumarolic arsenates – a special type of arsenic mineralization. *European Journal of Mineralogy* **30**, 305–322.

PEKOV, I.V., ZUBKOVA, N.V., AGAKHANOV, A.A., PUSHCHAROVSKY, D.YU., YAPASKURT, V.O., BELAKOVSKIY, D.I., VIGASINA, M.F., SIDOROV, E.G., & BRITVIN, S.N. (2018b) Cryptochalcite $K_2Cu_5O(SO_4)_5$ and cesiodymite $CsKCu_5O(SO_4)_5$ – two new isotypic minerals and the K–Cs isomorphism in this solid-solution series. *European Journal of Mineralogy* **30**, 593–607.

PEKOV, I.V., ZUBKOVA, N.V., & PUSHCHAROVSKY, D.YU. (2018c) Copper minerals from volcanic exhalations – a unique family of natural compounds: crystal chemical review. *Acta Crystallographica* **B74**, 502–518.

PEKOV, I.V., BRITVIN, S.N., AGAKHANOV, A.A., VIGASINA, M.F., & SIDOROV, E.G. (2019) Elasmochloite, $Na_3Cu_6BiO_4(SO_4)_5$, a new fumarolic mineral from the Tolbachik volcano, Kamchatka, Russia. *European Journal of Mineralogy* **31**, 1025–1032.

PERTLIK, F. & ZEMANN, J. (1988) The crystal structure of nabokoite, $Cu_7TeO_4(SO_4)_5\cdot KCl$: The first example of a $Te(IV)O_4$ pyramid with exactly tetragonal symmetry. *Mineralogy and Petrology* **38**, 291–298.

POPOVA, V.I., POPOV, V.A., RUDASHEVSKIY, N.S., GLAVATSKIKH, S.F., POLYAKOV, V.O., & BUSHMAKIN, A.F. (1987) Nabokoite $Cu_7TeO_4(SO_4)_5\cdot KCl$ and atlasovite $Cu_6Fe^{3+}Bi^{3+}O_4(SO_4)_5\cdot KCl$. New minerals of volcanic exhalations. *Zapiski Vsesoyuznogo Mineralogicheskogo Obshchestva* **116(3)**, 358–367 (in Russian).

SCORDARI, F. & STASI, F. (1990) The crystal structure of euchlorin, $NaKCu_3O(SO_4)_3$. *Neues Jahrburh für Mineralogie - Monatshefte*, 241–253.

SHELDRICK, G.M. (2008) A short history of *SHELX*. *Acta Crystallographica* **A64**, 112–122.

SIIDRA, O.I., NAZARCHUK, E.V., ZAITSEV, A.N., LUKINA, E.A., AVDONTSEVA, E.Y., VERGASOVA, L.P., VLASENKO, N.S., FILATOV, S.K., TURNER, R., & KARPOV, G.A. (2017) Copper oxosulphates from fumaroles of Tolbachik volcano: Puninite, $Na_2Cu_3O(SO_4)_3$ – a new mineral species and structure refinements of kamchatkite and alumoklyuchevskite. *European Journal of Mineralogy* **28**, 499–510.

STAROVA, G.L., FILATOV, S.K., FUNDAMENSKY, V.S., & VERGASOVA, L.P. (1991) The crystal structure of fedotovite, $K_2Cu_3O(SO_4)_3$. *Mineralogical Magazine* **55**, 613–616.

STAROVA, G.L., KRIVOVICHEV, S.V., & FILATOV, S.K. (1998) Crystal chemistry of inorganic compounds based on chains of oxocentered tetrahedra. II. The crystal structure of $Cu_4O_2[(As,V)O_4]Cl$. *Zeitschrift für Kristallog*raphie **213**, 650–653.

VARAKSINA, T.V., FUNDAMENSKY, V.S., FILATOV, S.K., & VERGASOVA, L.P. (1990) The crystal structure of kamchatkite, a new naturally occurring oxychloride sulphate of potassium and copper. *Mineralogical Magazine* **54**, 613–616.

VERGASOVA, L.P., FILATOV, S.K., SERAFIMOVA, E.K., & STAROVA, G.L. (1984) Piypite, $K_2Cu_2O(SO_4)_2$, a new mineral of volcanic exhalations. *Doklady Akademii Nauk SSSR* **275**, 714–717 (in Russian).

VERGASOVA, L.P., FILATOV, S.K., SERAFIMOVA, E.K., & STAROVA, G.L. (1988a) Fedotovite, $K_2Cu_3O(SO_4)_3$, a new mineral of volcanic exhalations. *Doklady Akademii Nauk SSSR* **299**, 961–964 (in Russian).

VERGASOVA, L.P., FILATOV, S.K., SERAFIMOVA, E.K., & VARAKSINA, T.V. (1988b) Kamchatkite, $KCu_3OCl(SO_4)_2$, a new mineral of volcanic sublimates. *Zapiski Vsesoyuznogo Mineralogicheskogo Obshchestva* **117**, 459–461 (in Russian).

VERGASOVA, L.P., FILATOV, S.K., GORSKAYA, M.G., ANANIEV, V.V., & SHAROV, A.S. (1989) Klyuchevskite, $K_3Cu_3(Fe,Al)O_2(SO_4)_4$, a new mineral from volcanic exhalations. *Zapiski Vsesoyuznogo Mineralogicheskogo Obshchestva* **118(1)**, 70–73 (in Russian).

ZELENSKI, M.E., ZUBKOVA, N.V., PEKOV, I.V., BOLDYREVA, M.M., PUSHCHAROVSKY, D.YU., & NEKRASOV, A.N. (2011) Pseudolyonsite, $Cu_3(VO_4)_2$, a new mineral species from the Tolbachik volcano, Kamchatka Peninsula, Russia. *European Journal of Mineralogy* **23**, 475–481.

Received April 8, 2020. Revised manuscript accepted June 9, 2020.