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New arsenate minerals from the Arsenatnaya fumarole, Tolbachik volcano, Kamchatka, Russia. III. Popovite, $Cu_5O_2(AsO_4)_2$

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ABSTRACT

The new mineral popovite, $Cu_5O_2(AsO_4)_2$, was found in the sublimates of the Arsenatnaya fumarole at the Second scoria cone of the Northern Breakthrough of the Great Tolbachik Fissure Eruption, Tolbachik volcano, Kamchatka, Russia. It is associated with ericlaxmanite, kozyrevskite, urusovite, lammerite, lammerite-β, johillerite, bradaczekite, tenorite, hematite, aphthitalite, anhydrite, langbeinite, calciolangbeinite, As-bearing orthoclase, etc. Popovite occurs as prismatic or tabular crystals and as grains up to 0.2 mm in size forming clusters up to 1.5 mm in size and as crusts on basalt scoria or on aphthitalite incrustations. Popovite is transparent with a vitreous to greasy lustre. Its colour is olive green to dark olive-green, but fine-grained varieties are light yellow-green. The mineral is brittle, with Mohs' hardness ~3½. Cleavage was not observed and the fracture is uneven. D_{calc} is 5.30 g cm^{-3}. Popovite is optically biaxial (+), $\alpha = 1.84(1)$, $\beta \approx 1.86$, $\gamma = 1.96(1)$, $2V_{meas} = 50(20)^{\circ}$. The Raman spectrum is given. Chemical data (wt.%, electron-microprobe) are CuO 63.28, ZnO 0.56, V_2O_5 0.12, As_2O_5 35.80, SO_3 0.27, total 100.03. The empirical formula, based on 10 O a.p.f.u., is $(Cu_{4.99}Zn_{0.04})_{\Sigma 5.03}(As_{1.95}S_{0.02}V_{0.01})_{\Sigma 1.98}O_{10}$. Popovite is triclinic, $P\bar{1}$, $a = 5.1450(3)$, $b = 6.2557(3)$, $c = 6.2766(4)$ Å, $\alpha = 100.064(5)$, $\beta = 96.351(5)$, $\gamma = 95.100(5)^{\circ}$, $V = 196.47(1)$ Å^3 and $Z = 1$. The strongest reflections in the powder X-ray diffraction pattern [d,Å(I)(hkl)] are 3.715(36)(110, 101), 3.465(43)($1\bar{1}1$), 2.968(90)($0\bar{1}2$), 2.927(100)(111), 2.782(31)($\bar{1}02$), 2.768(67)($\bar{1}20$), 2.513(55)($\bar{1}\bar{2}1$) and 2.462(67)($\bar{2}01$). Popovite has a novel structure type. Its crystal structure, solved from single-crystal X-ray diffraction data ($R = 0.0459$), is based on (010) layers forming an interrupted framework. The layer consists of $Cu(1)O_6$ octahedra with very strong Jahn-Teller distortion and $Cu(2)O_5$ and $Cu(3)O_5$ polyhedra. The linkage between the layers is reinforced by isolated AsO_4 tetrahedra. Popovite is named in honour of the Russian mineralogists Vladimir Anatol'evich Popov (b. 1941) and Valentina Ivanovna Popova (b. 1941), a husband and wife research team working in the Institute of Mineralogy of the Urals Branch of the Russian Academy of Sciences, Miass, Russia.

KEYWORDS: popovite, new mineral, copper arsenate, crystal structure, fumarole sublimate, Tolbachik volcano, Kamchatka.

Introduction

THIS paper continues a series of articles devoted to the mineralogy and crystal chemistry of new

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arsenate species from the Arsenatnaya fumarole located in the top part of the Second scoria cone of the Northern Breakthrough of the Great Tolbachik Fissure Eruption, Tolbachik volcano, Kamchatka Peninsula, Far-Eastern Region, Russia (55º41′N 160º14′E, 1200 m asl). A general description and mineralogical data for this active fumarole were given in the first paper of this series which also contained the characterization of the new mineral yurmarinite, $Na_7(Fe^{3+},Mg,Cu)_4(AsO_4)_6$ (Pekov *et al.*, 2014*a*). In the second article we described ericlaxmanite and kozyrevskite, two natural polymorphous modifications of composition $Cu_4O(AsO_4)_2$ (Pekov *et al.*, 2014*b*).

The present paper concerns the description of another copper arsenate with the idealized formula $Cu_5O_2(AsO_4)_2$. It is named popovite (Russian Cyrillic: поповит) in honour of the Russian mineralogists Vladimir Anatol’evich Popov (born 1941) and Valentina Ivanovna Popova (born 1941), a husband and wife research team working in the Institute of Mineralogy of the Urals Branch of the Russian Academy of Sciences, Miass, Chelyabinsk Oblast, Russia. Popov and Popova have made a great contribution to the mineralogy of the Urals and the Far-Eastern Region of Russia, including the discovery of two new mineral species, nabokoite and atlasovite, from the fumarolic exhalations of the Tolbachik volcano (Popova *et al.*, 1987).

Both the new mineral and its name have been approved by the International Mineralogical Association Commission on New Minerals, Nomenclature and Classification (IMA 2013-060, Pekov, 2013). The type specimen is deposited in the systematic collection of the Fersman Mineralogical Museum of the Russian Academy of Sciences, Moscow, catalogue number 94135.

Occurrence and general appearance

The specimen that became the holotype of popovite was found by the authors (IVP and DIB) in July 2012. Additional material was collected in July 2013. Its examination provided more data on the mineral and showed that popovite is not very rare in the Arsenatnaya fumarole.

Popovite occurs in the same assemblages as the majority of arsenates in this fumarole. In all cases it is intimately associated with the other copper arsenates ericlaxmanite and kozyrevskite, both $Cu_4O(AsO_4)_2$, lammerite and lammerite-β, both $Cu_3(AsO_4)_2$, urusovite $CuAlO(AsO_4)$ (Fig. 1) and/or alluaudite-group members belonging to the series bradaczekite, $NaCu_4(AsO_4)_3$ – johillerite, $NaMg_3Cu(AsO_4)_3$. Other closely associated minerals are tenorite, hematite, aphthitalite, As-bearing orthoclase (abundant), anhydrite, langbeinite, calciolangbeinite ($K_2Ca_2(SO_4)_3$), arcanite (K_2SO_4), wulffite ($K_3NaCu_4O_2(SO_4)_4$; IMA 2013-035), krasheninnikovite ($KNa_2CaMg(SO_4)_3F$), steklite ($KAl(SO_4)_2$), palmierite ($K_2Pb(SO_4)_2$), tilasite ($CaMg(AsO_4)F$), svabite ($Ca_5(AsO_4)_3F$), alarsite ($AlAsO_4$), Cu-rich gahnite and OH-free fluoborite

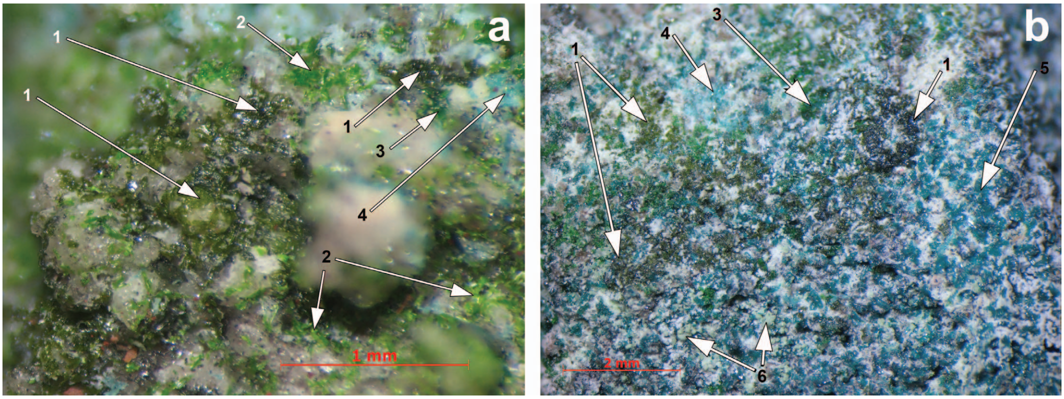

FIG. 1. Typical associations of copper arsenates overgrowing crusts of colourless aphthitalite covering basalt scoria in the Arsenatnaya fumarole: 1 – olive-green to dark olive-green popovite, 2 – grass-green kozyrevskite, 3 – deep-green ericlaxmanite, 4 – light-blue urusovite, 5 – deep turquoise-blue lammerite, 6 – pale greenish lammerite-β. Field of view: 2.8 mm (*a*: the holotype specimen) and 9.1 mm (*b*). Photos: I.V. Pekov and A.V. Kasatkin.

(subordinate). All these sublimate minerals form complex incrustations, typically no thicker than 1 mm, rarely up to 5 mm thick, on the surface of basalt scoria in open pockets uncovered in the interval from 0.3 to 0.8 m deep under the present-day surface. The temperature measured inside these pockets during collecting in July 2013 was 360−380ºC. In our opinion, all these minerals crystallized directly from fumarolic gas or were formed as a result of gas−rock interactions at temperatures of not less than 380ºC.

Popovite occurs as prismatic, tabular or, rarely, lamellar crystals, crude or well formed, complex in shape (Fig. 2*a*−*c*), typically up to 0.03 mm, rarely up to 0.2 mm across. Elongated or flattened anhedral grains of the same size are also typical. Both crystals and irregularly shaped grains form clusters up to 1.5 mm or almost monomineralic crusts (Figs 1 and 2) up to several mm^2 in area and up to 0.1 mm thick on basalt scoria or on aphthitalite incrustations. Thin, interrupted polymineralic crusts consisting mainly of arsenates, with popovite as the major constituent, and tenorite cover areas up to 3 cm × 4 cm. In such crusts, popovite is represented by a fine-grained variety (Fig. 2*d*) of yellow-green colour.

Physical properties and optical data

Popovite is transparent with a vitreous to greasy lustre. It is typically olive green to dark olive-green; the fine-grained varieties are light yellow-green, commonly with an olive hue. Streak is light olive-green to light yellow-green. The mineral is brittle, with Mohs' hardness ~3½. Cleavage or parting was not observed and the fracture is uneven. Density was not measured because monomineralic, massive (without voids) particles of popovite are too small for volumetric methods and because of the lack of heavy liquids of necessary density. The density calculated from the empirical formula is 5.30 g cm^{-3}.

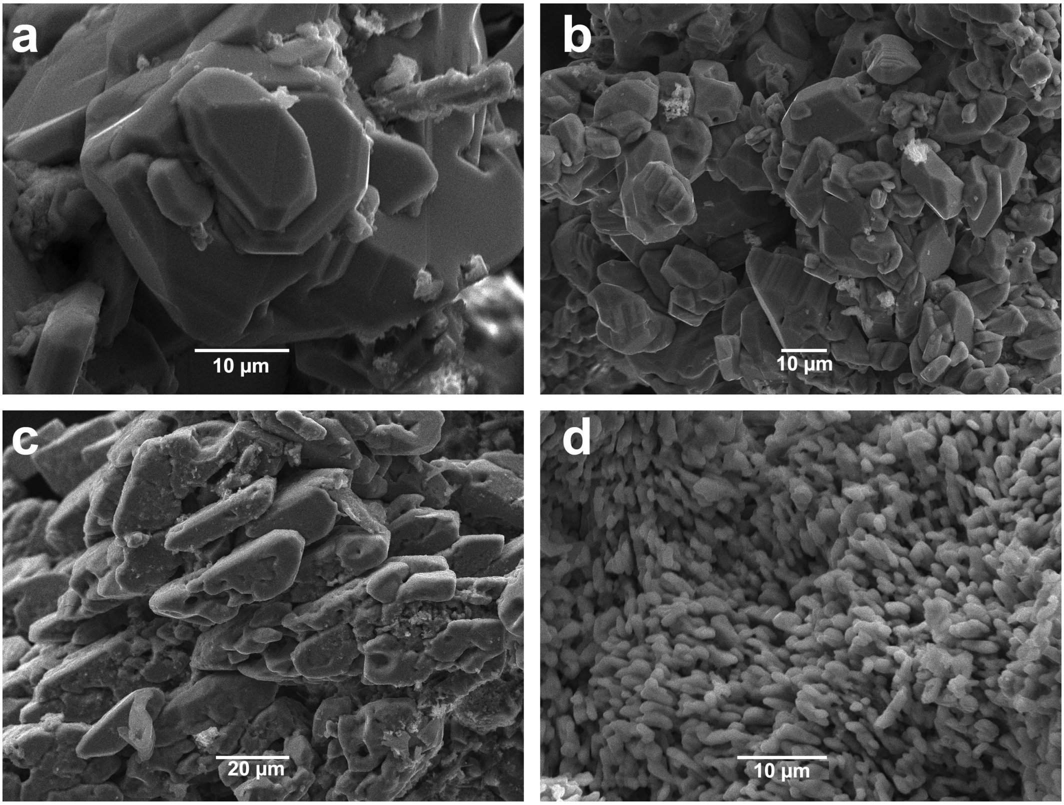

FIG. 2. Typical crystals and crystal crusts of popovite. Scanning electron microscopy - secondary electron images.

TABLE 1. Chemical composition (wt.%) of popovite.

	1	2	3	4	5	6	Probe standard
CuO	63.28 (62.94–63.75)	62.41	62.36	63.77	61.51	63.38	$CuFeS_2$
ZnO	0.56 (0.41–0.72)	0.58	0.63	b.d.l.	1.09		ZnS
Fe_2O_3*	b.d.l.	b.d.l.	0.50	b.d.l.	b.d.l.		$CuFeS_2$
P_2O_5	b.d.l.	0.88	b.d.l.	b.d.l.	b.d.l.		GaP
V_2O_5	0.12 (0.00–0.51)	b.d.l.	b.d.l.	b.d.l.	b.d.l.		V
As_2O_5	35.80 (35.65–36.07)	34.95	35.26	36.61	35.72	36.62	FeAsS
SO_3	0.27 (0.00–0.68)	b.d.l.	b.d.l.	b.d.l.	0.71		ZnS
Total	100.03	98.82	98.75	100.38	99.03	100.00	
Formula calculated on the basis of 10 oxygen atoms							
Cu	4.99	4.96	4.99	5.02	4.86	5.00	
Zn	0.04	0.05	0.05		0.09		
Fe			0.04				
ΣM	5.03	5.01	5.08	5.02	4.95	5.00	
P		0.08					
V	0.01						
As	1.95	1.92	1.96	1.99	1.95	2.00	
S	0.02				0.06		
ΣT	1.98	2.00	1.96	1.99	2.01	2.00	

1 – the holotype specimen (average values from five spot analyses, ranges are in parentheses); 2–5 – other samples; 6 – calculated values for the idealized formula $Cu_5O_2(AsO_4)_2$. Amounts of other elements with atomic numbers higher than carbon are below detection limits (b.d.l.). ΣM = Cu+Zn+Fe, ΣT = As+P+V+S.

* Fe is calculated as Fe^{3+} taking into account the strongly oxidizing conditions of the Arsenatnaya fumarole; only minerals with trivalent iron are found there (Pekov *et al.*, 2014*a*).

b.d.l.: below detection limit

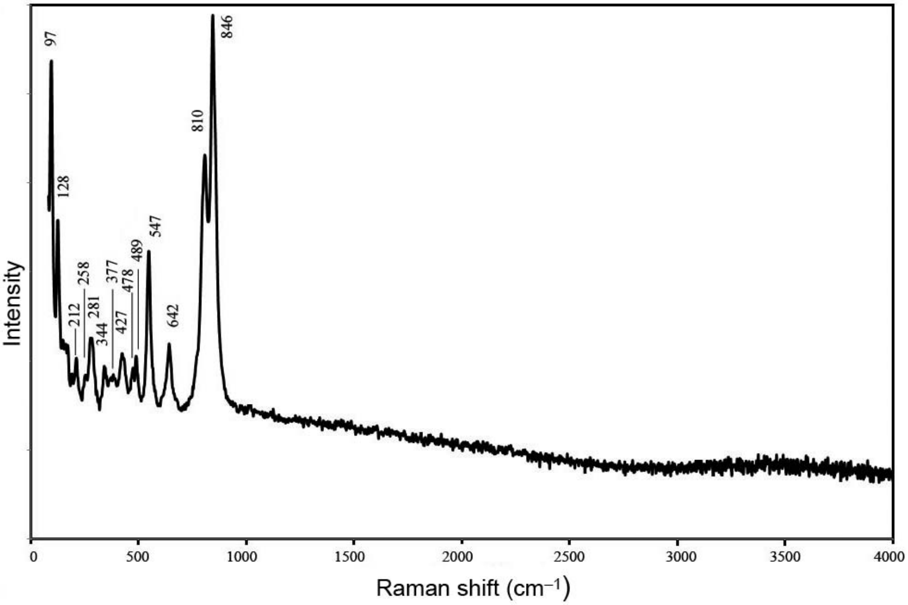

FIG. 3. Raman spectrum of popovite.

TABLE 2. Powder X-ray diffraction data for popovite.

I_{obs}	d_{obs}	I_{calc}*	d_{calc}**	*h k l*
9	4.801	6	4.802	$0\bar{1}1$
36	3.715	29, 8	3.714, 3.686	110, 101
43	3.465	35	3.466	$1\bar{1}1$
26	3.395	12	3.398	$\bar{1}11$
90	2.968	73	2.971	$0\bar{1}2$
100	2.927	100	2.919	111
31	2.782	19	2.788	$\bar{1}02$
67	2.768	56	2.760	$\bar{1}20$
14	2.651	15	2.648	$\bar{1}\bar{1}2$
55	2.513	35	2.514	$\bar{1}\bar{2}1$
28	2.484	7, 3	2.489, 2.487	$1\bar{1}2$, 102
67	2.462	54	2.462	$\bar{2}01$
29	2.239	3, 24	2.247, 2.233	201, $2\bar{1}1$
22	2.190	8	2.183	$\bar{1}\bar{2}2$
8	2.152	4	2.155	112
20	2.046	4, 1, 9	2.054, 2.043, 2.041	$0\bar{3}1$, 003, 030
18	1.997	4, 7, 1	2.005, 2.003, 1.988	211, $\bar{2}\bar{1}2$, 022
21	1.974	6, 4, 8	1.975, 1.971, 1.970	$2\bar{2}1$, $\bar{1}\bar{1}3$, $\bar{1}30$
28	1.842	11, 3, 3, 10	1.848, 1.843, 1.838, 1.836	$1\bar{1}3$, 202, 013, 031
15	1.819	1, 4, 8	1.825, 1.817, 1.816	130, $\bar{1}13$, 103
7	1.766	8	1.765	$1\bar{3}2$
5	1.732	7	1.725	$1\bar{2}3$
9	1.695	3	1.699	$\bar{2}22$
16	1.686	4, 7, 2	1.685, 1.683, 1.681	$\bar{2}30$, 221, $\bar{3}10$
5	1.649	1, 6	1.654, 1.654	$\bar{3}11$, $2\bar{3}1$
21	1.593	5, 3, 18	1.597, 1.591, 1.588	$\bar{2}31$, $3\bar{1}1$, 310
16	1.571	1, 3, 16, 2	1.570, 1.569, 1.569, 1.567	$\bar{1}23$, 023, 032, $\bar{1}32$
31	1.534	14, 5, 19, 9	1.542, 1.533, 1.533, 1.532	$\bar{2}\bar{2}3$, $\bar{1}\bar{3}3$, $\bar{1}\bar{1}4$, 004
25	1.524	5, 1, 1, 17	1.530, 1.522, 1.521, 1.517	040, $\bar{1}04$, $1\bar{4}1$, $\bar{3}21$
12	1.507	4, 7	1.511, 1.501	230, 203
8	1.486	1, 1	1.488, 1.484	$\bar{2}\bar{3}2$, $0\bar{4}2$
7	1.481	4	1.478	311
6	1.454	1, 2	1.454, 1.454	$\bar{1}\bar{4}1$, $\bar{1}\bar{2}4$
11	1.440	3, 4, 8, 4	1.444, 1.442, 1.438, 1.435	$\bar{3}\bar{2}1$, $1\bar{4}2$, 123, $\bar{2}32$
9	1.402	5, 4, 2	1.401, 1.399, 1.399	$\bar{3}22$, 231, $1\bar{2}4$
12	1.349	3, 4, 2, 7, 7	1.353, 1.352, 1.352, 1.350, 1.346	$3\bar{3}1$, $0\bar{3}4$, $0\bar{4}3$, $\bar{3}13$, $2\bar{3}3$
5	1.327	3, 2	1.328, 1.326	$\bar{2}14$, 141
4	1.312	2	1.310	$1\bar{4}3$
4	1.307	3	1.307	$2\bar{4}2$
5	1.283	6, 1, 1	1.287, 1.284, 1.281	$\bar{1}24$, $\bar{1}42$, $\bar{2}\bar{4}1$
6	1.273	7	1.272	$\bar{4}10$
4	1.259	3, 2	1.258, 1.257	$\bar{2}33$, $\bar{2}\bar{4}2$
5	1.251	2, 1	1.251, 1.251	240, 223
5	1.236	1, 4	1.240, 1.235	$\bar{3}\bar{3}2$, $1\bar{5}1$
6	1.231	4	1.231	$\bar{4}02$
6	1.220	1, 2, 1	1.221, 1.219, 1.219	$\bar{1}50$, $\bar{2}24$, $0\bar{2}5$
4	1.197	2, 2	2.000, 1.199	$2\bar{4}3$, $\bar{4}\bar{1}2$
4	1.165	3, 3, 2	1.169, 1.164, 1.163	$\bar{1}\bar{5}2$, $\bar{2}05$, $1\bar{2}5$
5	1.128	3, 1, 2	1.130, 1.128, 1.128	420, 034, 043
3	1.118	1, 1	1.120, 1.118	$\bar{4}31$, $\bar{2}15$
5	1.101	1, 1, 1, 3	1.102, 1.100, 1.100, 1.098	$\bar{3}\bar{4}1$, 151, $\bar{3}42$, 115
7	1.073	1, 1, 2, 1, 3	1.078, 1.077, 1.075, 1.072, 1.071	340, 421, $2\bar{1}5$, $\bar{4}23$, $\bar{2}\bar{3}5$
5	1.050	1, 3	1.050, 1.049	$\bar{3}\bar{4}3$, $\bar{3}50$
7	1.023	2, 1, 1, 2, 3	1.026, 1.025, 1.025, 1.020, 1.020	$\bar{1}\bar{2}6$, $\bar{4}14$, $4\bar{4}1$, 060, 314

* Only reflections with $I_{calc} \geqslant 1$ are given; **For the unit-cell parameters obtained from single-crystal data.

TABLE 3. Crystal data, data-collection information and structure-refinement details for popovite.

Formula	$Cu_5O_2(AsO_4)_2$
Temperature, K	293(2)
Radiation (wavelength, Å)	MoK_α (0.71073)
Crystal system, space group; Z	Triclinic, $P\bar{1}$; 1
Unit-cell dimensions (Å / °)	a = 5.1450(3) α = 100.064(5)
	b = 6.2557(3) β = 96.351(5)
	c = 6.2766(4) γ = 95.100(5)
V (Å^3)	196.48(2)
Absorption coefficient μ (mm^{-1})	21.715
F_{000}	291
Crystal size, mm	0.03 × 0.03 × 0.05
Diffractometer	Xcalibur S CCD
θ range for data collection (°)	3.32−28.27
Index ranges	$-6 \leqslant h \leqslant 6$, $-8 \leqslant k \leqslant 8$, $-8 \leqslant l \leqslant 8$
Reflections collected	3232
Independent reflections	983 (R_{int} = 0.0688)
Independent reflections with $I > 2\sigma(I)$	815
Structure solution	Direct methods
Refinement method	Full-matrix least-squares on F^2
Number of refined parameters	80
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0459, $wR2$ = 0.0736
R indices (all data)	$R1$ = 0.0634, $wR2$ = 0.0778
Gof	1.111
Largest diff. peak and hole (e Å^{-3})	1.400 and −1.409

Popovite grains used for the optical study seemed transparent and perfect but, under polarized transmitted light, they appeared to be 'fractured' into a number of tiny sub-individuals with irregular extinction; cleavage was not observed. This prevented complete optical data from being obtained. The refractive indexes α = 1.84(1) and γ = 1.96(1) (589 nm) were measured on small grains with higher interference colours. 2V = 50(20)° and $\beta \approx 1.86$ were estimated roughly on the only grain found that showed a conoscopic figure on the section close to perpendicular to the optical axis. Unfortunately this grain could not be extracted from the liquid to mount on the spindle stage. Thus popovite is biaxial (+). Dispersion is strong, $r < v$. The mineral is distinctly pleochroic, with the absorption scheme X (green) > Z (olive green with

TABLE 4. Atom coordinates and equivalent isotropic displacement parameters (Å^2) for popovite.

Atom	x/a	y/b	z/c	U_{eq}
As	0.40982(16)	0.66287(13)	0.27191(14)	0.0074(2)
Cu(1)	0.0	0.0	0.5	0.0089(3)
Cu(2)	0.1429(2)	0.66303(15)	0.72409(18)	0.0106(3)
Cu(3)	0.7455(2)	0.87429(15)	0.94844(17)	0.0105(3)
O(1)	0.9794(10)	0.0604(8)	0.2159(9)	0.0063(12)
O(2)	0.4194(10)	0.8113(8)	0.0699(10)	0.0085(12)
O(3)	0.2017(11)	0.4393(8)	0.1723(10)	0.0109(13)
O(4)	0.2946(11)	0.8033(8)	0.4891(9)	0.0091(12)
O(5)	0.7176(10)	0.6100(8)	0.3465(10)	0.0097(13)

TABLE 5. Selected interatomic distances (Å) in the structure of popovite.

As−O(3)	1.665(5)
−O(5)	1.679(5)
−O(4)	1.684(5)
−O(2)	1.700(5)
Cu(1)−O(1)	1.880(5) × 2
−O(4)	2.035(5) × 2
−O(5)	2.689(6) × 2
Cu(2)−O(1)	1.884(5)
−O(5)	1.911(5)
−O(4)	2.035(5)
−O(3)	2.043(5)
−O(2)	2.444(6)
Cu(3)−O(1)	1.898(5)
−O(2)	1.955(5)
−O(3)	2.029(5)
−O(1)	2.060(6)
−O(2)	2.226(5)

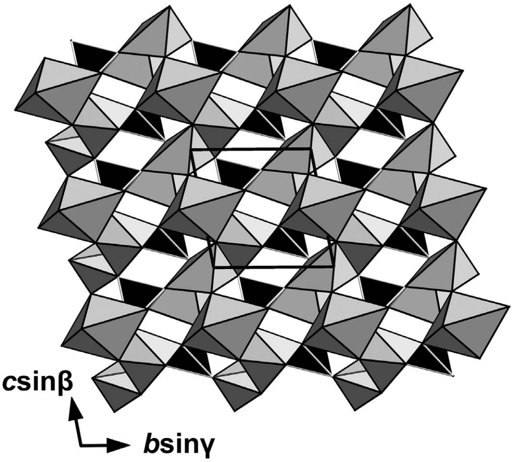

FIG. 4. The crystal structure of popovite projected down the *a* axis. Cu-centred polyhedra are grey, AsO_4 tetrahedra are black. The unit cell is outlined.

greyish hue). It also shows strong pseudo-absorption.

Raman spectroscopy

The Raman spectrum of popovite (Fig. 3) was obtained using an EnSpectr R532-50 instrument with a green laser (λ = 532 nm) at room temperature. The power of the laser beam at the sample was ~9 mW. The spectrum was recorded from 100 to 4000 cm^{-1} with a diffraction grating (1800 mm^{-1}) and resolution ~6 cm^{-1}. The diameter of the focal spot on the sample was ~15 μm. The backscattered Raman signal was collected with a 20 × objective; signal acquisition time for a single scan of the spectral range was 1500 ms and the signal was averaged over 50 scans. The Raman spectrum was obtained from a randomly oriented crystal.

Two strong bands in the region 800−900 cm^{-1} correspond to As^{5+}−O stretching vibrations of AsO_4^{3-} anionic groups. Bands with frequencies less than 700 cm^{-1} correspond to As^{5+}−O bending vibrations and Cu^{2+}−O stretching vibrations, as well as lattice modes. The absence of bands with frequencies higher than 900 cm^{-1} indicates the absence of groups with O−H, C−H, C−O, N−H, N−O and B−O bonds in popovite.

TABLE 6. Bond-valence calculations for popovite.

	As	Cu(1)	Cu(2)	Cu(3)	Σ
O(1)		0.58 ×2↓	0.57	0.55 0.36	2.06
O(2)	1.20		0.13	0.47 0.23	2.03
O(3)	1.32		0.37	0.39	2.08
O(4)	1.25	0.38 ×2↓	0.38		2.01
O(5)	1.27	0.06 ×2↓	0.53		1.86
Σ	5.04	2.04	1.98	2.00	

Parameters are taken from Brese and O'Keeffe (1991).

Chemical composition

Chemical data for popovite were obtained using a Jeol JSM-6480LV scanning electron microscope equipped with an INCA-Wave 500 wavelength-dispersive spectrometer (Laboratory of local methods of matter investigation, Faculty of Geology, Moscow State University). The WDS mode was used, with an acceleration voltage of 20 kV, a beam current of 20 nA, and a 3 μm beam diameter. Analytical data are given in Table 1 and yield the empirical formula $(Cu_{4.99}Zn_{0.04})_{\Sigma5.03}(As_{1.95}S_{0.02}V_{0.01})_{\Sigma1.98}O_{10}$, based on 10 O atoms per formula unit.

X-ray diffraction data

Powder X-ray diffraction data for popovite (Table 2) were collected using a STOE IPDS II diffractometer equipped with an Image Plate area

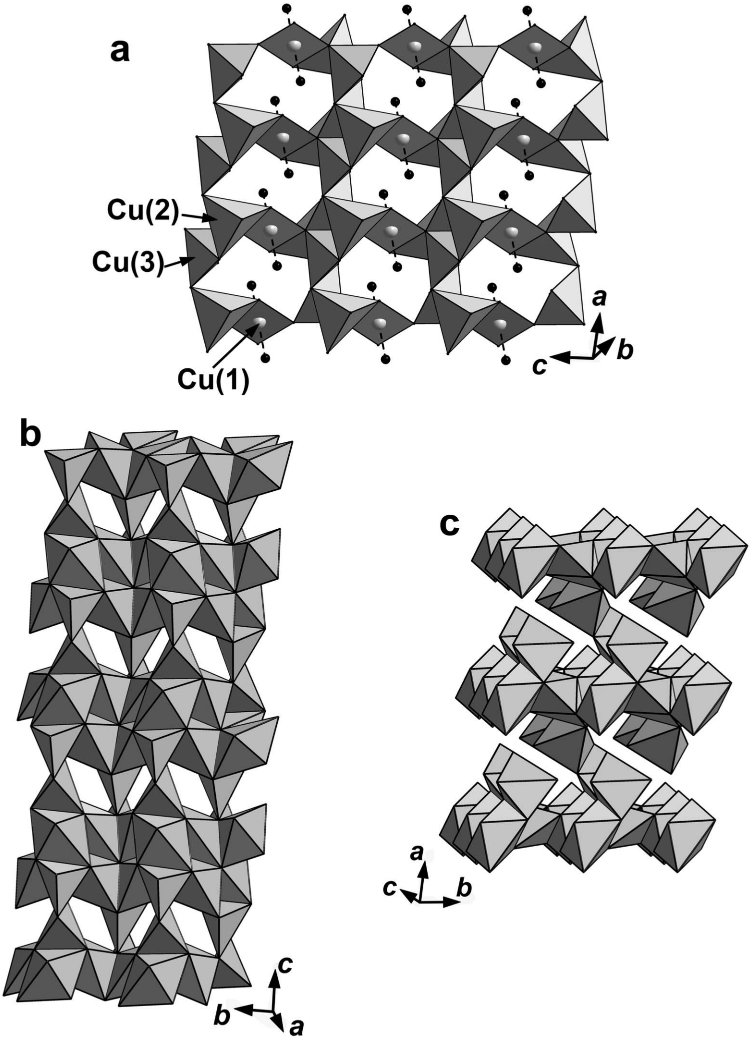

Fig. 5. Motifs of Cu-centred polyhedra: (*a*) layer formed by $Cu(1)O_4$ squares and $Cu(2)O_5$ and $Cu(3)O_5$ polyhedra in popovite [the O(5) sites that transform Cu(1)-centred polyhedra to octahedra with very strong Jahn-Teller distortion are shown by black circles]; (*b*) complex layer in stoiberite after Shannon and Calvo (1973); and (*c*) interrupted framework in $Cu_5O_2(PO_4)_2$ after Brunel-Lauegt and Guitel (1977).

detector, using the Gandolfi method (Mo$K\alpha$ radiation; detector-to-sample distance 200 mm). The triclinic unit-cell parameters refined from the powder data using *WinX^{Pow}* software (STOE & Cie, 2002) are: a = 5.15(1), b = 6.26(1), c = 6.27(1) Å, α = 100.00(5), β = 96.31(5), γ = 95.16(5)° and V = 196.4(3) Å^3.

Single-crystal X-ray studies of popovite were carried out using an Xcalibur S diffractometer equipped with a CCD detector. An absorption correction was applied according to the shape of the crystal. The structure of popovite was solved by direct methods and refined with *SHELX-97* (Sheldrick, 2008) to R = 0.0459. The unit-cell parameters and the experimental details are presented in Table 3, atom coordinates and displacement parameters in Table 4, selected interatomic distances in Table 5 and bond-valence calculations in Table 6.

Crystal structure: description and discussion

Popovite is characterized by a novel structure type. The asymmetric unit contains one As, three Cu and five O atoms; only one Cu atom is located in a special position (0, 0, ½). The crystal structure (Fig. 4) is based on (010) layers formed by Cu(1)O_4 squares and Cu(2)O_5 and Cu(3)O_5 polyhedra (Fig. 5). Each layer is formed by complex ribbons of edge-sharing Cu(2)- and Cu(3)-centred polyhedra running along the a axis (Fig. 6). Adjacent ribbons are connected by Cu(1)O_4 squares *via* common edges. Cu(1)-centred polyhedra can also be considered as CuO_6 octahedra with very strong Jahn-Teller distortion; four Cu(1)–O bonds lie in the range 1.880(5)–2.035(5) Å and two bonds are elongated with distances of 2.689(6) Å (Fig. 5*a*). It seems reasonable to include the elongated Cu(1)–O(5) distances in the primary coordination polyhedron due to their contribution to bond-valence sums (Table 6). In this case the neighbouring Cu–O layers are connected forming an interrupted framework. The linkage between the layers is reinforced by isolated, somewhat distorted, AsO_4 tetrahedra [As–O = 1.665(5)–1.700(5) Å].

No natural or synthetic compound related to popovite in terms of structure is known. It is interesting that compounds $Cu_5O_2(T^{5+}O_4)_2$ show three quite different structure types and unit-cell dimensions when T = P, V or As. Stoiberite $Cu_5O_2(VO_4)_2$ is monoclinic (space group $P2_1/n$, a = 15.654, b = 6.054, c = 8.385 Å, β = 102.29°, V = 776 Å^3 and Z = 4), as is its synthetic analogue (Birnie and Hughes, 1979). The main building unit of its structure is a complex layer of Cu-centred distorted octahedra and trigonal bipyramids (Fig. 5*b*); these layers are connected by VO_4 tetrahedra (Shannon and Calvo, 1973). Synthetic $Cu_5O_2(PO_4)_2$ is triclinic (space group $P\bar{1}$, a = 7.603, b = 5.304, c = 5.200 Å, α = 111.66, β = 90.19, γ = 82.56°, V = 193.0 Å^3 and Z = 1). Its structure is based on an interrupted framework (Fig. 5*c*) formed by Cu-centred trigonal bipyramids and squares which could be viewed as octahedra strongly distorted by Jahn-Teller effects, taking into account two elongated Cu–O distances of 3.01 Å (Brunel-Lauegt and Guitel, 1977). Both the vanadate and phosphate are topologically different from each other and from the arsenate popovite.

Other known H-free arsenates with only copper as a species-defining metal cation and with additional oxygen atoms are represented only by the two polymorphs of $Cu_4O(AsO_4)_2$ (triclinic ericlaxmanite, orthorhombic kozyrevskite (Pekov

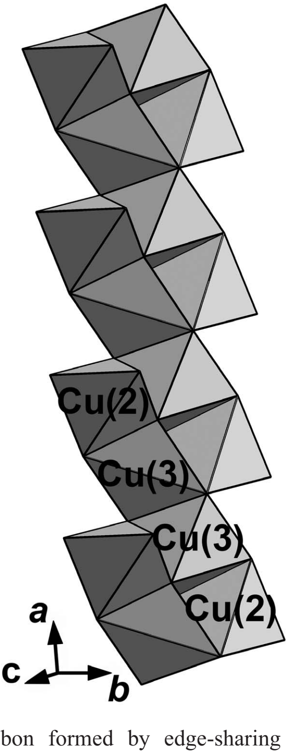

FIG. 6. Ribbon formed by edge-sharing Cu(2)- and Cu(3)-centred five-fold polyhedra in popovite.

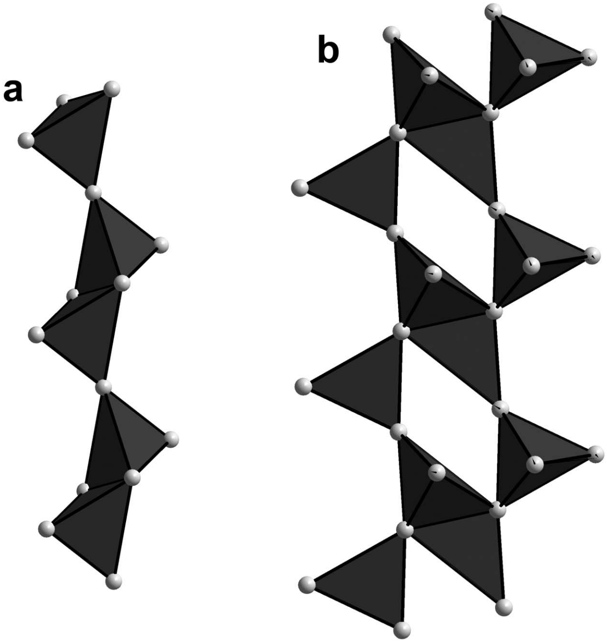

FIG. 7. Chains formed by oxocentred tetrahedra OCu_4 in popovite (*a*) and stoiberite (*b*).

et al., 2014*b*) and their synthetic analogues), very different from popovite in terms of structure.

The structure of popovite can also be described in terms of anion-centred $[OCu_4]$ tetrahedra (Krivovichev *et al.*, 1999*b*). The $[O_2Cu_5]^{\infty}$ chains running along the *c* axis are formed by O(1)-centred tetrahedra with alternating corner [Cu(1)] and edge [Cu(3)–Cu(3)] linkages (Fig. 7*a*). Topologically close complexes of $[OCu_4]$ tetrahedra were found in georgbokiite and parageorgbokiite, two polymorphs of $Cu_5O_2(SeO_3)_2Cl_2$ (Krivovichev *et al.*, 1999*a*, 2007), and in synthetic $Cu_5O_2(PO_4)_2$ (Brunel-Lauegt and Guitel, 1977). Note that these compounds show the same stoichiometry as popovite, $Cu_5O_2(AsO_4)_2$. The oxocentred tetrahedral chain in stoiberite $Cu_5O_2(VO_4)_2$ (Fig. 7*b*) could be considered as merging of two *zweier* $[OCu_3]$ chains by edge-sharing between tetrahedra (Krivovichev, 2009).

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