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New arsenate minerals from the Arsenatnaya fumarole, Tolbachik volcano, Kamchatka, Russia. IV. Shchurovskyite, $K_2CaCu_6O_2(AsO_4)_4$ and dmisokolovite, $K_3Cu_5AlO_2(AsO_4)_4$

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ABSTRACT

Two new minerals shchurovskyite, ideally $K_2CaCu_6O_2(AsO_4)_4$, and dmisokolovite, ideally $K_3Cu_5AlO_2(AsO_4)_4$, are found in sublimates of the Arsenatnaya fumarole at the Second scoria cone of the Northern Breakthrough of the Great Tolbachik Fissure Eruption, Tolbachik volcano, Kamchatka Peninsula, Russia. They are associated with one another and with johillerite, bradaczekite, tilasite, melanarsite, tenorite, hematite, aphthitalite, langbeinite, orthoclase, etc. Shchurovskyite occurs as coarse tabular or prismatic crystals up to 0.15 mm in size or anhedral grains forming parallel aggregates and crusts up to 1.5 cm × 2 cm across. Dmisokolovite forms tabular, prismatic or dipyramidal crystals up to 0.2 mm in size, commonly combined in clusters or crusts up to 0.7 cm × 1.5 cm across. Both minerals are transparent with a vitreous lustre. They are brittle, with Mohs' hardness ≈ 3. Shchurovskyite is olive-green or olive drab. Dmisokolovite is bright emerald-green to light green. $D_{calc} = 4.28$ (shchurovskyite) and 4.26 (dmisokolovite) g cm^{-3}. Both are optically biaxial; shchurovskyite: (+), $\alpha = 1.795(5)$, $\beta = 1.800(5)$, $\gamma = 1.810(6)$, $2V_{meas} = 70(15)°$; dmisokolovite: (–), $\alpha = 1.758(7)$, $\beta = 1.782(7)$, $\gamma = 1.805(8)$, $2V_{meas} = 85(5)°$. The Raman spectra are given. Chemical data (wt.%, electron-microprobe; first value is for shchurovskyite, second for dmisokolovite): Na_2O 0.00, 0.83; K_2O 8.85, 10.71; Rb_2O 0.11, 0.00; MgO 0.00, 0.35; CaO 4.94, 0.21; CuO 43.19, 38.67; ZnO 0.42, 0.20; Al_2O_3 0.04, 4.68; Fe_2O_3 0.00, 0.36; P_2O_5 0.59, 0.78; V_2O_5 0.01, 0.04; As_2O_5 40.72, 43.01; SO_3 0.35, 0.00; total 99.22, 99.84. The empirical formulae, based on 18 O a.p.f.u., are shchurovskyite: $K_{2.05}Rb_{0.01}Ca_{0.96}Cu_{5.92}Zn_{0.06}Al_{0.01}P_{0.09}S_{0.05}As_{3.86}O_{18}$; dmisokolovite: $Na_{0.28}K_{2.36}Mg_{0.09}Ca_{0.04}Cu_{5.04}Zn_{0.04}Al_{0.95}Fe^{3+}_{0.05}P_{0.11}As_{3.88}O_{18}$. The strongest reflections of X-ray powder patterns [*d*,Å(*I*)(*hkl*)] are shchurovskyite: 8.61(100)(200, 001), 5.400(32)(110), 2.974(32)($\bar{3}$12, 510), 2.842(47)(003, 020), 2.757(63)($\bar{6}$01, 511), 2.373(36)(512, 420) and 2.297(31)($\bar{4}$21, $\bar{2}$22, 313); dmisokolovite: 8.34(95)(002), 5.433(84)(110), 2.921(66)(510, $\bar{3}$14), 2.853(58)(511, 020) and 2.733(100)(006, 512, $\bar{6}$02). Shchurovskyite is monoclinic, *C*2, $a = 17.2856(9)$, $b = 5.6705(4)$, $c = 8.5734(6)$ Å, $\beta = 92.953(6)°$, $V = 839.24(9)$ Å^3 and $Z = 2$. Dmisokolovite is monoclinic, *C*2/*c*, $a = 17.0848(12)$, $b = 5.7188(4)$, $c = 16.5332(12)$ Å, $\beta = 91.716(6)°$, $V = 1614.7(2)$ Å^3 and $Z = 4$. Their crystal structures [single-crystal X-ray diffraction data, $R = 0.0746$ (shchurovskyite) and 0.1345 (dmisokolovite: model)] are closely related in the topology of the main building units. They are based on a quasi-framework consisting of AsO_4 tetrahedra and polyhedra centred by Cu in shchurovskyite or by Cu and Al in dmisokolovite. K and Ca are located in channels of the quasi-framework. The minerals are named in honour of outstanding Russian geologists and mineralogists Grigory Efimovich Shchurovsky (1803–1884) and Dmitry Ivanovich Sokolov (1788–1852).

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Introduction

This article continues a series of papers on the mineralogy and crystal chemistry of new arsenate species from the Arsenatnaya fumarole at the Second scoria cone of the Northern Breakthrough of the Great Tolbachik Fissure Eruption, Tolbachik volcano, Kamchatka Peninsula, Far-Eastern Region, Russia (55°41′N 160°14′E, 1200 m asl). General characterization of this active fumarole, discovered by us in July 2012, is given in the first paper of the series describing also the new mineral yurmarinite $Na_7(Fe^{3+},Mg,Cu)_4(AsO_4)_6$ (Pekov *et al*., 2014*a*). The second article was devoted to two polymorphous modifications of $Cu_4O(AsO_4)_2$, ericlaxmanite and kozyrevskite (Pekov *et al*., 2014*b*), and the third to popovite $Cu_5O_2(AsO_4)_2$ (Pekov *et al*., 2015).

In this paper, we give mineral data and crystal chemical characteristics for two arsenates chemically and structurally related to one another: shchurovskyite $K_2CaCu_6O_2(AsO_4)_4$ and dmisokolovite $K_3Cu_5AlO_2(AsO_4)_4$. Shchurovskyite (Russian Cyrillic: щуровскиит) was named in honour of the outstanding Russian geologist, mineralogist and specialist in mineral deposits Professor Grigory Efimovich Shchurovsky (1803–1884). At Moscow University, he was a Head and Chair of Mineralogy and Geology in 1835–1861 and Head of the Chair of Geology and Paleontology in 1861–1881 and 1883–1884. Dmisokolovite (дмисоколовит) was named in honour of the famous Russian mineralogist and geologist Dmitry Ivanovich Sokolov (1788–1852), Professor of Mineralogy and Geology at St. Petersburg University, Academician of the Russian Academy of Sciences. He was among the founders of the Russian Mineralogical Society (1817) and one of the founders and first editor of *Gornyi Zhurnal* (*Mining Journal*), the first Russian periodical specializing in geology, mineralogy and mining sciences (1825). Prof. Sokolov wrote the best fundamental textbooks on mineralogy, petrography and geology in the mid-19th century in Russia, namely *Textbook on Mineralogy with Additional Statistical Data on the Most Important Salts and Metals*, 2 vols. (1832), *Course of Geognosy*, 3 vols. (1839) and *Handbook of Geognosy*, 2 parts. (1842). He was also one of first geologists who created volcanology as a science in Russia; his *Handbook of Geognosy* contains the special chapter *On Volcanoes* in which advanced concepts on volcanism phenomena were developed.

Both new minerals and their names have been approved by the IMA Commission on New Minerals, Nomenclature and Classification (shchurovskyite: IMA 2013–078; dmisokolovite: IMA 2013–079). The type specimens are deposited in the systematic collection of the Fersman Mineralogical Museum of the Russian Academy of Sciences, Moscow; the catalogue numbers are 94144, 94145 (shchurovskyite; #94144 is the holotype for which majority of the analytical data given below were obtained) and 94138 (dmisokolovite).

Occurrence and general appearance

Specimens that became the holotypes of shchurovskyite and dmisokolovite were found by us in

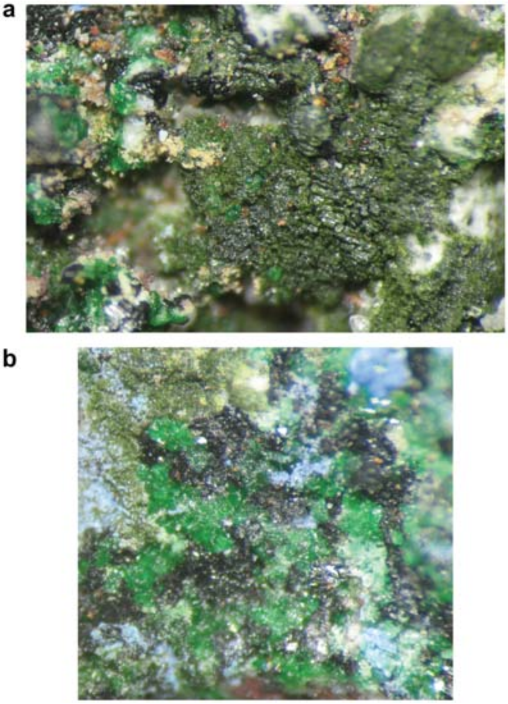

Fig. 1. Association of dark olive green shchurovskyite with emerald green dmisokolovite, blue bradaczekite and black tenorite. They form polymineralic crusts on basalt scoria altered by fumarolic gas. On (*a*) parallel intergrowths of coarse shchurovskyite crystals are shown. Field of view: (*a*) 3.2 mm wide, (*b*) 2.3 mm wide. Photos: I.V. Pekov and A.V. Kasatkin.

Arsenatnaya in July 2012. In 2013 and 2014 we collected from the same fumarole more material for studies that gave additional data. Shchurovskyite and dmisokolovite occur in the same assemblage and are associated with one another (Fig. 1) and with other arsenates: johillerite $NaMg_3Cu(AsO_4)_3$, bradaczekite $NaCu_4(AsO_4)_3$, tilasite $CaMg(AsO_4)F$, svabite $Ca_5(AsO_4)_3F$, lammerite $Cu_3(AsO_4)_2$, lammerite-β $Cu_3(AsO_4)_2$, urusovite $CuAlO(AsO_4)$, ericlaxmanite $Cu_4O(AsO_4)_2$, kozyrevskite $Cu_4O(AsO_4)_2$, popovite $Cu_5O_2(AsO_4)_2$, alarsite $AlAsO_4$, hatertite $Na_2(Ca,Na)(Fe^{3+},Cu)_2(AsO_4)_3$, yurmarinite $Na_7(Fe^{3+},Mg,Cu)_4(AsO_4)_6$, pharmazincite $KZnAsO_4$ (IMA2013–015), melanarsite $K_3Cu_7Fe^{3+}O_4(AsO_4)_4$ (IMA2014–048) and katiarsite $KTiO(AsO_4)$ (IMA2014–025). Other associated minerals are tenorite, hematite, fluorophlogopite, aphthitalite, langbeinite, calciolangbeinite, krasheninnikovite, steklite, anhydrite, As-bearing orthoclase, Cu-rich gahnite, corundum, wulffite $K_3NaCu_4O_2(SO_4)_4$ (IMA2013–035), arcanite, palmierite, dolerophanite, alumoklyuchevskite, vanthoffite, sylvite and OH-free fluoborite. All these minerals form polymineralic incrustations up to 0.5 cm thick on the surface of basalt scoria altered by fumarolic gas. This mineralization occurs in open fractures and pockets located in the interval from 0.3 to 0.8 m depth below the present surface. The temperature measured by us, using a chromel-alumel thermocouple, inside these pockets immediately after uncovering in July 2013 was 360–380°C. We believe that all the minerals listed were deposited directly from the gaseous phase, as volcanic sublimates, or

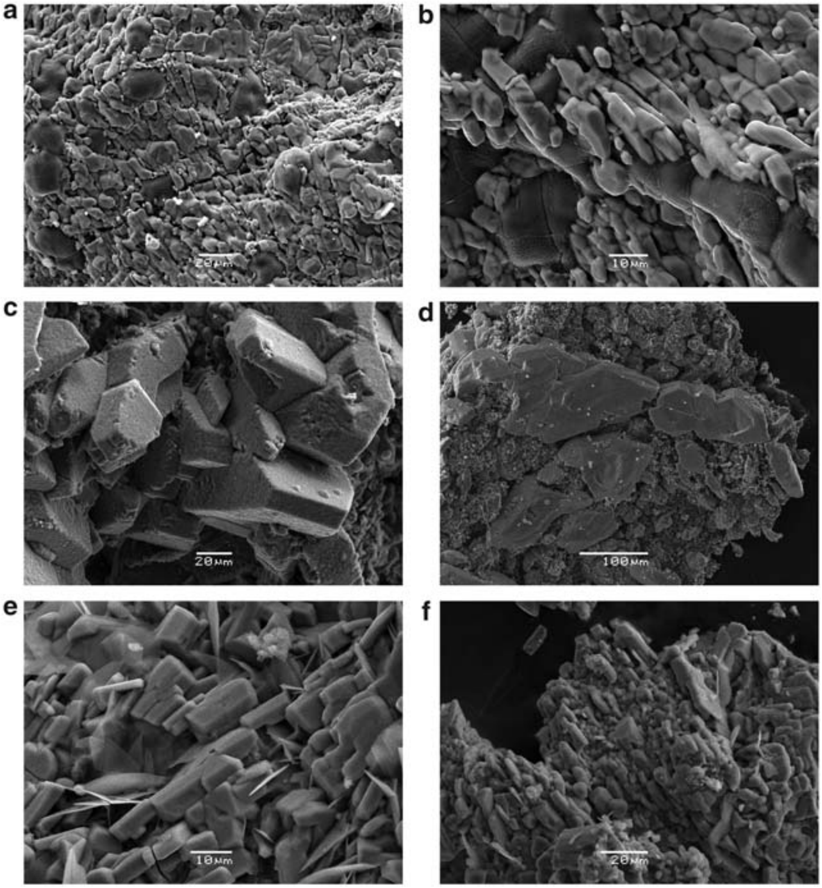

FIG. 2. SEM(SE) images showing the morphology of crystals and aggregates of shchurovskyite (*a*–*b*) and dmisokolovite (*c*–*f*). (*a*–*b*) Numerous coarse tabular to prismatic crystals of shchurovskyite partially cover an aphthitalite crust; (*c*) group of bipyramidal crystals of dmisokolovite; (*d*) tabular crystals of dmisokolovite on a crust of As-bearing orthoclase covering basalt scoria; and (*e*–*f*) near-parallel aggregates of prismatic crystals of dmisokolovite.

were formed in the result of gas-rock interactions (involving low-volatility Ca, Mg, Al and Si from host basalt) at temperatures not lower than 380°C. All the minerals of this assemblage are H free.

Shchurovskyite occurs as coarse tabular to coarse prismatic crystals (usually <0.03 mm, rarely up to 0.15 mm in size) or anhedral grains. The latter form parallel aggregates (up to 1 mm across) and thin, typically interrupted crusts (up to 1.5 cm × 2 cm in area and up to 0.05 mm thick) on basalt scoria and on aphthitalite incrustations (Figs 1 and 2*a*,*b*). Dmisokolovite forms tabular, prismatic or dipyramidal crystals (up to 0.2 mm in size), typically coarse, or equant to flattened grains. They are isolated or, more commonly, combined in groups, parallel or near-parallel aggregates, dense clusters

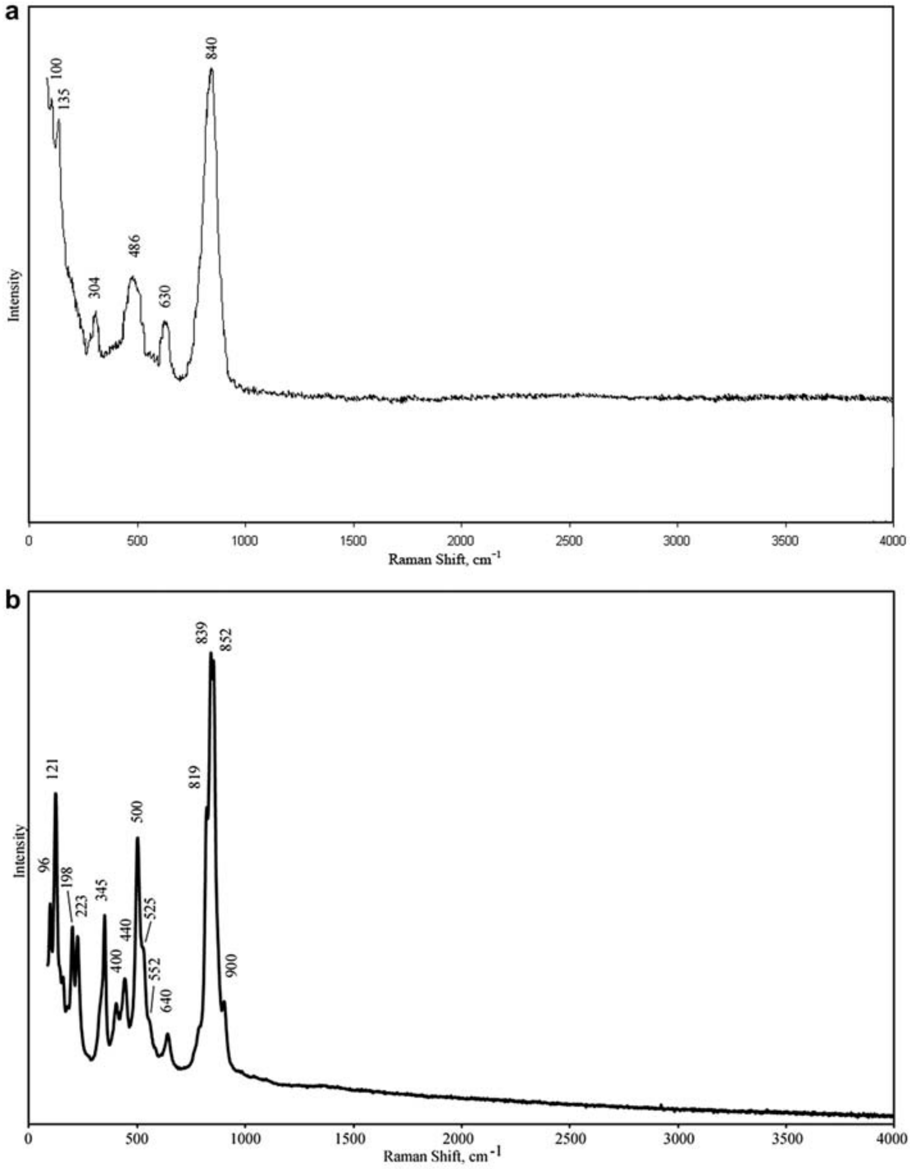

FIG. 3. The Raman spectra of shchurovskyite (*a*) and dmisokolovite (*b*).

(up to 1 mm across) and interrupted crusts (up to 0.7 cm × 1.5 cm in area and up to 0.2 mm thick) overgrowing basalt scoria and aggregates of aphthitalite and tenorite (Figs 1 and 2*c–f*).

Physical properties and optical data

Both new minerals are transparent with a vitreous lustre. Shchurovskyite is olive-green to dark olive-green, typically with a grey hue, or olive drab, with a pale greenish streak. Dmisokolovite is bright emerald-green to light green, sometimes with a bluish hue; its streak is light green. Both are brittle, with Mohs' hardness ≈ 3. Dmisokolovite shows one direction of imperfect cleavage (observed under the microscope) while for shchurovskyite no cleavage or parting was observed. Both have an uneven fracture. Density was not measured because of a paucity of pure material for volumetric methods (massive, without caverns or inclusions, particles of both minerals are too small) and a lack of heavy liquids of necessary density. Density values calculated from the empirical formulae are 4.28 g cm^{-3} for shchurovskyite and 4.26 g cm^{-3} for dmisokolovite.

Shchurovskyite is optically biaxial (+), $\alpha = 1.795(5)$, $\beta = 1.800(5)$, $\gamma = 1.810(6)$ (589 nm), $2V_{meas} = 70(15)°$, $2V_{calc} = 71°$. Dispersion of optical axes is not observed. Pleochroism is weak, with the following absorption scheme: $Z \geq Y$ (grass-green) $> X$ (yellowish green).

Dmisokolovite is biaxial (–), $\alpha = 1.758(7)$, $\beta = 1.782(7)$, $\gamma = 1.805(8)$ (589 nm), $2V_{meas} = 85(5)°$, $2V_{calc} = 88°$. Dispersion is strong, $r > v$. Under the microscope, the mineral is pale green and nonpleochroic.

Raman spectroscopy

Raman spectra of shchurovskyite (Fig. 3*a*) and dmisokolovite (Fig. 3*b*) were obtained using an EnSpectr R532-50 instrument (Dept. of Mineralogy, Moscow State University) with a green laser ($\lambda = 532$ nm) at room temperature. The spectra were recorded from 100 to 3800 cm^{-1} using a diffraction grating (1800 mm^{-1}) and with a resolution of ~6 cm^{-1}. The diameter of the focal spot on the samples was about 10 μm for shchurovskyite and 15 μm for dmisokolovite. The backscattered Raman signal was collected with a 20× objective; signal acquisition time for a single scan of the spectroscopic range was 1500 ms for shchurovskyite and 1000 ms for dmisokolovite; the signal was averaged over 70 scans for shchurovskyite and over 50 scans for dmisokolovite. The spectra were obtained for randomly oriented crystals of both minerals.

The Raman spectra of shchurovskyite and dmisokolovite, are different but have some common features (Fig. 3). In both spectra strong bands in the region 750–950 cm^{-1}, with a maximum at ~840 cm^{-1},

TABLE 1. Chemical composition (wt.%) of shchurovskyite and dmisokolovite.*

	Shchurovskyite	Dmisokolovite	Probe standard
Na_2O	bdl	0.83 (0.61–1.00 / 0.17)	albite
K_2O	8.85 (8.03–9.41 / 0.59)	10.71 (10.51–10.91 / 0.17)	orthoclase
Rb_2O	0.11 (0.00–0.42 / 0.11)	bdl	$Rb_2Nb_4O_{11}$
MgO	bdl	0.35 (0.29–0.47 / 0.09)	olivine
CaO	4.94 (4.53–5.24 / 0.30)	0.21 (0.00–0.50 / 0.21)	$CaWO_4$
CuO	43.19 (42.43–44.11 / 0.83)	38.67 (37.96–39.07 / 0.51)	$CuFeS_2$
ZnO	0.42 (0.00–0.66 / 0.29)	0.20 (0.00–0.40 / 0.20)	ZnS
Al_2O_3	0.04 (0.00–0.10 / 0.04)	4.68 (3.98–5.73 / 0.78)	Al_2O_3
Fe_2O_3**	bdl	0.36 (0.00–0.60 / 0.27)	$CuFeS_2$
P_2O_5	0.59 (0.00–0.99 / 0.42)	0.78 (0.50–1.34 / 0.38)	GaP
V_2O_5	0.01 (0.00–0.05 / 0.01)	0.04 (0.00–0.12 / 0.04)	V
As_2O_5	40.72 (39.96–41.93 / 0.85)	43.01 (42.51–43.65 / 0.51)	FeAsS
SO_3	0.35 (0.00–1.39 / 0.35)	bdl	$CuFeS_2$
Total	99.22	99.84	

*Average values from four spot analyses are given for each mineral; ranges / standard deviations are in parentheses. Contents of other elements with atomic numbers higher than carbon are below detection limits (bdl). **Fe in dmisokolovite 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*).

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

I_{obs}	d_{obs}	I_{calc}*	d_{calc}**	*h k l*
100	8.61	52, 100	8.631, 8.562	200, 001
16	6.25	25	6.242	$\bar{2}01$
3	5.865	1	5.927	201
32	5.400	51	5.387	110
12	4.530	19	4.527	111
9	4.318	14	4.316	400
10	3.918	15	3.916	$\bar{2}02$
28	3.759	40	3.759	202
3	3.598	4	3.603	311
16	3.328	28	3.326	112
6	3.122	12	3.121	$\bar{4}02$
32	2.974	42, 14, 23	2.992, 2.964, 2.948	$\bar{3}12$, 402, 510
47	2.842	29, 56	2.854, 2.835	003, 020
63	2.757	46, 9, 73	2.771, 2.752, 2.751	$\bar{6}01$, $\bar{2}03$, 511
10	2.684	5, 4, 4, 2	2.694, 2.692, 2.686, 2.669	220, 021, 601, 203
9	2.586	17	2.581	$\bar{2}21$
26	2.539	52	2.539	$\bar{1}13$
11	2.443	11, 6	2.447, 2.439	$\bar{6}02$, $\bar{4}03$
36	2.373	31, 37	2.380, 2.370	512, 420
31	2.297	26, 20, 15	2.301, 2.297, 2.292	$\bar{4}21$, $\bar{2}22$, 313
16	2.263	3, 2, 16	2.267, 2.264, 2.261	421, 222, 710
3	2.140	4	2.141	004
5	2.098	8, 1	2.103, 2.097	$\bar{2}04$, $\bar{5}13$
5	2.041	10	2.040	$\bar{7}12$
7	2.019	8	2.019	620
7	1.981	11, 2, 1, 1	1.982, 1.978, 1.976, 1.975	$\bar{6}21$, 114, 603, $\bar{2}23$
3	1.944	6	1.943	223
3	1.922	8	1.920	$\bar{3}14$
5	1.876	8, 2	1.879, 1.879	404, 130
5	1.859	8, 6	1.864, 1.852	314, $\bar{6}22$
3	1.798	1, 9, 1	1.801, 1.798, 1.795	622, 423, $\bar{9}11$
3	1.763	5, 2, 7	1.766, 1.761, 1.760	$\bar{8}03$, $\bar{6}04$, 911
2	1.751	2	1.752	331
2	1.727	4, 2	1.726, 1.724	10.0.0, $\bar{1}32$
3	1.717	5, 5	1.717, 1.717	820, 132
3	1.705	1, 10	1.708, 1.697	024, $\bar{8}21$

3	1.678	10, 2	1.677, 1.676	$\bar{6}23$, 604
4	1.666	4, 4	1.666, 1.663	$\bar{3}32$, 224
2	1.647	7	1.644	912
8	1.621	1, 10, 4, 13	1.624, 1.621, 1.621, 1.620	115, 623, $\bar{4}05$, 531
4	1.595	14	1.597	$\bar{3}15$
4	1.575	12, 2	1.573, 1.572	$\bar{1}33$, 822
7	1.565	5, 1, 2, 9	1.568, 1.567, 1.565, 1.564	$\bar{9}13$, 424, 133, 405
3	1.534	13, 1	1.533, 1.531	532, $\bar{3}33$
8	1.514	15, 2	1.512, 1.512	11.1.0, $\overline{10}.0.3$
12	1.503	1, 8, 18, 2	1.506, 1.500, 1.499, 1.496	$\bar{6}05$, 730, $\bar{8}23$, $\bar{6}24$
3	1.464	1, 6	1.466, 1.464	025, $\overline{10}.2.1$
9	1.443	3, 9, 5, 3, 6	1.445, 1.444, 1.443, 1.439, 1.439	823, 10.0.3, 10.2.1, 605, 12.0.0
8	1.419	4, 3, 2, 9	1.420, 1.420, 1.418, 1.418	$\bar{9}14$, $\bar{2}06$, 533, 040
6	1.407	10	1.407	$\bar{4}25$
4	1.374	5, 1, 2	1.376, 1.375, 1.375	$\bar{8}05$, 10.2.2, 116
4	1.367	3, 3, 3, 1	1.370, 1.367, 1.365, 1.365	425, $\bar{8}24$, 334, $\overline{11}.1.3$
3	1.331	2, 5	1.333, 1.326	$\bar{2}42$, 242
4	1.312	4, 3, 2, 3, 5	1.313, 1.312, 1.311, 1.310, 1.309	824, $\overline{12}.0.3$, 10.0.4, 11.1.3, 805
2	1.285	4, 2	1.287, 1.283	10.2.3, 12.2.0
3	1.271	3, 1, 1, 2, 1	1.271, 1.270, 1.269, 1.269, 1.269	932, 043, $\bar{2}26$, $\bar{1}35$, 13.1.1
4	1.262	4, 6	1.262, 1.260	$\bar{6}41$, $\bar{2}43$
4	1.254	5, 2, 5, 1	1.255, 1.253, 1.253, 1.252	$\overline{13}.1.2$, 606, 226, 243
2	1.245	3	1.249	$\bar{3}35$
1	1.227	2, 3, 1	1.229, 1.227, 1.226	335, $\bar{6}42$, $\bar{4}43$
2	1.207	4	1.207	11.3.0

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*For the calculated pattern, only reflections with intensities ≥1 are given; ** for the unit-cell parameters calculated from single-crystal data.

TABLE 3. Powder X-ray diffraction data for dmisokolovite.

I_{obs}	d_{obs}	I_{calc}*	d_{calc}**	*h k l*
95	8.34	100	8.263	002
40	6.034	43	6.029	$\bar{2}02$
84	5.433	97	5.423	110
13	5.119	6	5.138	111
34	4.519	42	4.514	112
22	4.263	26	4.269	400
21	3.870	8, 7	3.883, 3.846	$\bar{1}13$, $\bar{4}02$
30	3.774	33	3.763	$\bar{2}04$
22	3.657	23, 5	3.676, 3.656	204, $\bar{3}12$
45	3.274	61	3.271	114
31	3.015	39	3.014	$\bar{4}04$
66	2.921	48, 12, 45	2.932, 2.925, 2.918	510, 404, $\bar{3}14$
58	2.853	14, 38, 8, 3	2.874, 2.859, 2.856, 2.846	511, 020, 314, 600
100	2.733	41, 94, 53	2.754, 2.741, 2.716	006, 512, $\bar{6}02$
10	2.585	2, 7	2.584, 2.584	$\bar{3}15$, $\bar{2}22$
9	2.565	2, 6	2.569, 2.561	222, 513
4	2.537	1	2.538	023
47	2.451	42, 50	2.465, 2.446	$\bar{1}16$, 116
45	2.366	10, 29, 39, 9, 10	2.377, 2.376, 2.362, 2.357, 2.351	$\bar{6}04$, 420, 514, $\bar{4}21$, 024
34	2.284	23, 3, 26, 3	2.293, 2.284, 2.277, 2.273	$\bar{4}22$, 406, $\bar{2}24$, 422
25	2.248	4, 18, 20	2.257, 2.253, 2.244	224, 316, 710
6	2.175	7	2.172	$\bar{1}17$
4	2.156	1, 2	2.157, 2.151	117, 712
11	2.076	1, 8, 1, 5	2.087, 2.082, 2.075, 2.066	225, $\bar{8}02$, $\bar{4}24$, 008
26	2.004	12, 5, 11, 17	2.017, 2.010, 2.007, 1.995	620, $\bar{6}06$, $\bar{6}21$, $\bar{7}14$
7	1.943	5	1.945	$\bar{4}25$
6	1.925	8	1.924	118
10	1.853	14	1.855	$\bar{3}18$
10	1.825	2, 12, 2	1.828, 1.823, 1.821	$\bar{6}24$, 318, 027
8	1.800	4	1.799	$\bar{3}31$
9	1.791	1, 3, 1	1.793, 1.790, 1.789	$\bar{1}33$, 133, $\bar{2}27$
8	1.781	2, 2	1.785, 1.784	911, 426
4	1.765	2, 1	1.770, 1.769	$\bar{9}12$, $\bar{3}32$
15	1.711	3, 3, 6, 6, 3	1.713, 1.712, 1.710, 1.710, 1.708	333, $\bar{8}06$, 820, $\bar{5}18$, 10.0.0
10	1.687	5, 10	1.685, 1.683	$\bar{3}19$, $\bar{8}22$
11	1.652	2, 1, 2, 4	1.654, 1.651, 1.649, 1.649	531, $\bar{2}28$, $\bar{7}17$, 608

14	1.643	2, 3, 14, 1	1.646, 1.645, 1.644, 1.641	$\bar{1}$35, $\bar{8}$23, $\bar{6}$26, 135
6	1.611	3, 19	1.613, 1.611	2.0.10, 626
14	1.581	8, 18, 1	1.585, 1.580, 1.577	$\bar{1}$.1.10, 335, 1.1.10
6	1.565	3, 2, 3	1.572, 1.567, 1.563	$\bar{4}$28, 824, $\bar{1}$36
3	1.541	3	1.541	$\bar{3}$.1.10
5	1.531	6	1.534	$\bar{8}$25
4	1.524	3, 1, 7, 3	1.527, 1.527, 1.526, 1.518	$\bar{9}$16, $\bar{2}$29, 4.0.10, 3.1.10
15	1.495	19, 3, 7	1.498, 1.496, 1.493	11.1.0, $\overline{11}$.1.1, 731
13	1.468	10, 11, 3	1.471, 1.469, 1.467	$\overline{10}$.0.6, $\bar{8}$26, 11.1.2
12	1.458	12	1.456	$\bar{5}$.1.10
15	1.441	2, 9, 1, 5, 6	1.442, 1.442, 1.441, 1.438, 1.437	733, $\bar{3}$37, $\bar{7}$19, 826, 10.2.2
18	1.428	4, 8, 4, 4, 2, 3, 4, 6	1.434, 1.432, 1.431, 1.430, 1.429, 1.424, 1.424, 1.423	$\bar{5}$36, 10.0.6, 0.2.10, 040, 337, 041, 5.1.10, 12.0.0
16	1.415	6, 3, 17	1.417, 1.415, 1.411	$\bar{2}$.2.10, 536, 6.0.10
6	1.378	11, 3	1.377, 1.377	0.0.12, $\bar{9}$18
7	1.371	2, 4, 1, 3	1.371, 1.370, 1.368, 1.367	10.2.4, 827, $\bar{2}$43, $\bar{4}$.2.10
4	1.351	2, 1	1.352, 1.351	$\bar{4}$41, $\bar{5}$.1.11
6	1.338	2, 1, 1	1.338, 1.338, 1.336	931, $\bar{1}$.1.12, $\overline{10}$.0.8
7	1.331	2, 5, 1, 1	1.332, 1.332, 1.332, 1.330	244, $\overline{11}$.1.6, $\bar{9}$32, 0.2.11
6	1.325	2, 3, 1	1.328, 1.326, 1.323	10.2.5, $\bar{8}$.0.10, 5.1.11
6	1.301	1, 6, 2, 1	1.302, 1.300, 1.300, 1.299	828, 11.1.6, 933, 4.0.12
6	1.294	3, 1, 2	1.294, 1.292, 1.292	$\bar{3}$39, $\bar{6}$.2.10, $\bar{4}$44
4	1.281	1, 1, 3	1.282, 1.281, 1.280	$\overline{11}$.1.7, 10.2.6, $\overline{12}$.0.6
5	1.275	2, 2	1.275, 1.274	$\bar{6}$41, 12.2.0
5	1.271	1, 1, 1	1.272, 1.271, 1.269	641, 934, 046
5	1.262	4, 1, 2	1.265, 1.260, 1.260	6.2.10, $\overline{10}$.2.7, 13.1.2
6	1.257	3, 2	1.258, 1.255	$\bar{4}$45, $\bar{9}$35

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*For the calculated pattern, only reflections with intensities ≥1 are given; **for the unit-cell parameters calculated from single-crystal data.

TABLE 4. Crystal data, data collection information and structure refinement details for shchurovskyite and dmisokolovite.

Mineral	Shchurovskyite	Dmisokolovite*
Formula (refined)	$K_2CaCu_6O_2(AsO_4)_4$	$K_2(K_{0.6}Na_{0.4})Cu_5(Al_{0.9}Fe_{0.1})O_2(AsO_4)_4$
Formula weight	1087.20	1046.10
Temperature, K	293(2)	
Radiation and wavelength, Å	Mo*K*α; 0.71073	
Crystal system, space group; Z	Monoclinic, *C*2; 2	Monoclinic, *C*2/*c*; 4
Unit-cell parameters, Å/°	$a = 17.2856(9)$ $b = 5.6705(4)$ $c = 8.5734(6)$ $\beta = 92.953(6)$	$a = 17.0848(12)$ $b = 5.7188(4)$ $c = 16.5332(12)$ $\beta = 91.716(6)$
V, Å^3	839.24(9)	1614.7(2)
Absorption coefficient μ, mm^{-1}	16.190	15.532
F_{000}	1016	1956
Crystal size, mm	0.04 × 0.10 × 0.13	0.03 × 0.05 × 0.07
Diffractometer	Xcalibur S CCD	
θ range for data collection, °	3.26–26.35	3.38–28.28
Index ranges	$-21 \le h \le 21$ $-7 \le k \le 7$ $-10 \le l \le 10$	$-22 \le h \le 22$ $-7 \le k \le 7$ $-22 \le l \le 22$
Reflections collected	5994	12,046
Independent reflections	1707 ($R_{int} = 0.0857$)	2000 ($R_{int} = 0.2821$)
Independent reflections with $I > 2\sigma(I)$	1598	850
Structure solution	Direct methods	
Refinement method	Full-matrix least-squares on F^2	
No. refined parameters	98	99
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0746$ $wR_2 = 0.1450$	$R_1 = 0.1345$ $wR_2 = 0.2968$
Goof	1.208	1.010
Largest diff. peak and hole, e/Å^3	1.688 and –1.565	4.171 and –2.380

*Taking into account the relatively high value of $R_1 = 13.45\%$, we consider the structural data on dmisokolovite as a model (see text). $R_1 = \Sigma||F_o|-|F_o|| / \Sigma|F_o|$. $wR_2 = \Sigma w(|F_o|^2-|F_c|^2)^2 / \Sigma w|F_o|^2)^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (0.0590P)^2 + 13.9460P]$ for shchurovskyite and $w = 1/[\sigma^2(F_o^2) + (0.1410P)^2 + 0.00P]$ for dmisokolovite; $P = ([\max \text{ of } (0 \text{ or } F_o^2)] + 2F_c^2)/3$.

correspond to As^{5+}–O stretching vibrations of AsO_4 anionic groups. Bands with frequencies <700 cm^{-1} correspond to As^{5+}–O bending vibrations and Cu^{2+}–O stretching vibrations. Strong bands with maxima at 486 cm^{-1} (shchurovskyite) and 500 cm^{-1} (dmisokolovite) presumably correspond to the Cu^{2+}–O stretching modes. An absence of bands with frequencies >950 cm^{-1} indicates the absence of groups with O–H, C–H, C–O, N–H, N–O and B–O bonds in both minerals.

Chemical composition

Chemical data for shchurovskyite and dmisokolovite 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.

The empirical formulae calculated on the basis of 18 O a.p.f.u. are: shchurovskyite: $K_{2.05}Rb_{0.01}Ca_{0.96}Cu_{5.92}Zn_{0.06}Al_{0.01}P_{0.09}S_{0.05}As_{3.86}O_{18}$; dmisokolovite: $Na_{0.28}K_{2.36}Mg_{0.09}Ca_{0.04}Cu_{5.04}Zn_{0.04}Al_{0.95}Fe^{3+}_{0.05}P_{0.11}As_{3.88}O_{18}$.

The idealized formulae require the following contents of constituents (wt.%):

shchurovskyite, $K_2CaCu_6O_2(AsO_4)_4$: K_2O 8.66, CaO 5.16, CuO 43.90, As_2O_5 42.28, total 100.00; dmisokolovite, $K_3Cu_5AlO_2(AsO_4)_4$: K_2O 13.46, CuO 37.89, Al_2O_3 4.86, As_2O_5 43.79, total 100.00.

TABLE 5*a*. Atom coordinates, isotropic displacement parameters (Å^2), Wyckoff positions and bond-valence sums (Σs) for shchurovskyite. Parameters for bond-valence calculations were taken from Brese and O'Keeffe (1991).

Atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq}/ U_{iso}	Wyckoff position	Σs
As(1)	0.35388(8)	0.0693(3)	0.14994(17)	0.0065(4)	4*c*	4.99
As(2)	0.40966(8)	0.5747(4)	0.65110(18)	0.0096(4)	4*c*	5.20
Cu(1)	0.67760(11)	0.5302(4)	0.0231(2)	0.0093(5)	4*c*	1.92
Cu(2)	0.58492(10)	0.5836(4)	0.7281(2)	0.0108(4)	4*c*	1.94
Cu(3)	½	0.3685(6)	0	0.0089(7)	2*a*	2.04
Cu(4)	½	0.8547(6)	0	0.0104(8)	2*a*	2.22
Ca	½	0.1113(9)	½	0.0121(10)	2*b*	0.79
K	0.7073(3)	0.0635(12)	0.3153(9)	0.067(2)	4*c*	1.80
O(1)	0.2843(7)	0.908(2)	0.0556(15)	0.013(3)*	4*c*	1.94
O(2)	0.3217(6)	0.346(2)	0.1811(14)	0.005(2)*	4*c*	2.10
O(3)	0.4833(7)	0.395(2)	0.7127(15)	0.012(3)*	4*c*	1.96
O(4)	0.4371(8)	0.850(3)	0.6560(17)	0.023(3)*	4*c*	2.01
O(5)	0.3858(7)	0.934(2)	0.3131(15)	0.014(3)*	4*c*	1.80
O(6)	0.5714(5)	0.6224(19)	0.9502(11)	0.002(2)*	4*c*	2.00
O(7)	0.4258(6)	0.105(2)	0.0235(12)	0.011(2)*	4*c*	2.13
O(8)	0.3846(7)	0.469(2)	0.4701(16)	0.018(3)*	4*c*	1.88
O(9)	0.3312(6)	0.535(2)	0.7518(13)	0.011(2)*	4*c*	2.05

*U_{iso}

X-ray diffraction data

Powder X-ray diffraction data for shchurovskyite (Table 2) and dmisokolovite (Table 3) were collected using a STOE IPDS II diffractometer equipped with an Image Plate area detector, using the Gandolfi method (Mo*K*α radiation; detector-to-sample distance = 200 mm). The parameters for monoclinic unit cells refined from the powder data are shchurovskyite: $a = 17.279(9)$, $b = 5.671(2)$, $c = 8.571(6)$ Å, $\beta = 93.00(5)°$ and $V = 839(1)$ Å^3; dmisokolovite: $a = 17.078(8)$, $b = 5.717(3)$, $c = 16.547(8)$ Å, $\beta = 91.65(4)°$ and $V = 1615(2)$ Å^3. Single-crystal X-ray studies of both minerals were carried out using an Xcalibur S diffractometer equipped with a CCD detector. The data were corrected for Lorentz and polarization effects. Unit-cell parameters are given in Table 4. Crystal structures of both new minerals were studied based on single-crystal X-ray data. Experimental details are given in Table 4. An absorption correction was applied according to the shape of the crystals. The structure models were obtained by direct methods and refined to $R = 0.0746$ for shchurovskyite and to $R = 0.1345$ for dmisokolovite with the use of the *SHELX* software package (Sheldrick, 2008). The electron density residuals for shchurovskyite are located near As(2) [1.69 *e* Å^{-3} at 0.96 Å from

TABLE 5*b*. Anisotropic displacement parameters (Å^2) for cations in shchurovskyite.

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
As(1)	0.0014(7)	0.0075(8)	0.0105(7)	–0.0024(9)	–0.0008(5)	–0.0010(8)
As(2)	0.0076(7)	0.0118(9)	0.0094(8)	–0.0031(9)	–0.0001(6)	–0.0013(8)
Cu(1)	0.0035(9)	0.0153(13)	0.0089(10)	–0.0040(9)	–0.0021(7)	0.0017(8)
Cu(2)	0.0106(9)	0.0142(11)	0.0075(9)	0.0019(11)	–0.0001(7)	–0.0006(11)
Cu(3)	0.0020(15)	0.0069(15)	0.0177(19)	0.000	–0.0010(13)	0.000
Cu(4)	0.0022(15)	0.0078(16)	0.022(2)	0.000	0.0063(14)	0.000
Ca	0.015(2)	0.008(3)	0.013(2)	0.000	0.0007(18)	0.000
K	0.038(3)	0.023(3)	0.146(6)	0.003(4)	0.052(3)	0.004(3)

Table 6*a*. Atom coordinates, isotropic displacement parameters (Å^2), Wyckoff positions and bond valence sums (Σs) for dmisokolovite. Parameters for bond valence calculations were taken from Brese and O'Keeffe (1991).

Atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq}/U_{iso}	Wyckoff position	Σs
As(1)	0.34898(15)	0.0501(5)	0.33237(13)	0.0171(8)	8*f*	4.89
As(2)	0.58912(15)	0.5261(6)	0.91002(14)	0.0207(8)	8*f*	5.31
Cu(1)	0.32150(18)	0.5861(7)	0.24700(16)	0.0222(10)	8*f*	1.98
Cu(2)	0.91387(18)	0.9556(7)	0.89875(17)	0.0220(9)	8*f*	2.07
Cu(3)	0	0.7427(9)	¾	0.0210(12)	4*e*	1.94
Al**	½	0.732(2)	¾	0.024(3)	4*e*	2.96
K(1)	0.7869(5)	0.5042(14)	0.0681(6)	0.052(2)	8*f*	0.83
K(2)***	0	½	0	0.082(6)	4*b*	1.54
O(1)	0.0498(10)	0.751(3)	0.3583(9)	0.015(4)*	8*f*	1.89
O(2)	0.6664(12)	0.581(3)	0.3695(11)	0.028(5)*	8*f*	2.19
O(3)	0.0184(11)	0.820(4)	0.9210(10)	0.025(4)*	8*f*	2.20
O(4)	0.8772(12)	0.863(4)	0.0024(11)	0.030(5)*	8*f*	2.15
O(5)	0.3647(11)	0.786(3)	0.9153(10)	0.025(4)*	8*f*	1.82
O(6)	0.9354(10)	0.522(3)	0.2822(10)	0.015(4)*	8*f*	2.16
O(7)	0.0718(9)	0.010(3)	0.2157(9)	0.009(3)*	8*f*	1.91
O(8)	0.2880(10)	0.197(3)	0.2673(9)	0.015(4)*	8*f*	1.87
O(9)	0.1789(9)	0.726(3)	0.6506(8)	0.013(3)*	8*f*	2.11

*U_{iso}

** Refined as $Al_{0.9}Fe_{0.1}$. *** Refined as $K_{0.6}Na_{0.4}$; this position is overbonded probably due to the presence of admixed of Cu, Mg or Zn.

As(2) and –1.57 e Å^{-3} at 0.82 Å from As(2)] while for dmisokolovite the highest difference peak (4.17 e Å^{-3}) and hole (–2.38 e Å^{-3}) are at 0.96 Å from Cu(1) and 0.73 Å from Cu(2), respectively. Atom coordinates and equivalent isotropic displacement parameters are given in Table 5*a* for shchurovskyite and in Table 6*a* for dmisokolovite. Anisotropic displacement parameters were used only for cations in both structures (Table 5*b* for shchurovskyite and Table 6*b* for dmisokolovite) whereas all oxygen atoms were refined isotropically. Bond distances in the structures of both minerals are presented in Table 7. Unfortunately even the best of many tested single crystals of dmisokolovite showed low quality because of a slightly divergent character that caused divergent reflections. As a result, a rather high final *R* value was obtained: 13.45%. Thus, we consider our results for dmisokolovite only as its structure model. However the reasonable values of thermal displacement parameters (Table 6*a*,*b*) and interatomic distances (Table 7), as well as good agreement between the measured and calculated X-ray powder-diffraction patterns (Table 3) show that the model is correct.

Table 6*b*. Anisotropic displacement parameters (Å^2) for cations in dmisokolovite.

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
As(1)	0.0103(13)	0.035(2)	0.0055(11)	0.0000(10)	–0.0031(9)	0.0012(11)
As(2)	0.0125(14)	0.041(2)	0.0082(11)	0.0003(11)	–0.0020(9)	0.0023(12)
Cu(1)	0.0142(16)	0.046(3)	0.0058(13)	–0.0023(13)	–0.0027(11)	–0.0004(16)
Cu(2)	0.0136(16)	0.044(3)	0.0079(13)	0.0044(13)	–0.0038(11)	0.0017(15)
Cu(3)	0.013(2)	0.036(3)	0.0145(19)	0.000	0.0026(16)	0.000
Al	0.012(5)	0.053(9)	0.006(4)	0.000	–0.005(3)	0.000
K(1)	0.036(5)	0.042(6)	0.080(6)	0.013(4)	0.027(4)	0.002(4)
K(2)	0.063(12)	0.109(17)	0.074(12)	0.029(10)	0.011(10)	0.017(11)

Crystal structure: description and discussion

Shchurovskyite, ideally $K_2CaCu_6O_2(AsO_4)_4$, and dmisokolovite, ideally $K_3Cu_5AlO_2(AsO_4)_4$, demonstrate a relationship to one another in terms of both chemistry and crystal structure (Tables 1–3; Figs 4–5). At the same time, to our knowledge and also according to an Inorganic Structure Database investigation (ICSD, 2014) no other natural or synthetic compound structurally related to these minerals is known; both shchurovskyite and dmisokolovite represent novel structure types.

The crystal structure of shchurovskyite (Fig. 4*a*) is based upon the (001) layers formed by Cu-centred polyhedra (Fig. 5*a*). Each layer consists of the columns of the alternating edge-sharing $Cu(3)O_6$ octahedra with Jahn-Teller distortion running along the *b* axis [four short distances lie in the range of 1.957(11)–1.988(13) Å and two elongated bonds of 2.470(13) Å] and $Cu(4)O_4$ squares. The basis of the structure of dmisokolovite (Fig. 4*b*) is the (001) heteropolyhedral layer consisting of the Cu- and Al-centred polyhedra (Fig. 5*b*) that form heteropolyhedral columns of the alternating edge-sharing $Cu(3)O_4$ squares and AlO_6 octahedra running along the *b* axis. The Cu(3)-centred polyhedra in dmisokolovite could also be considered as octahedra with very strong Jahn-Teller distortion, with four short distances in the range of 1.958(18)–1.966(16) Å and two Cu(3)···O(3) distances of 2.869(16) Å (given in italics in Table 7). For better clarity, in Figs 4*b* and 5*b* Cu(3)-centred polyhedra are presented as flat squares. In the structures of both minerals the columns [consisting of $Cu(3)O_6$ octahedra and $Cu(4)O_4$ squares in shchurovskyite and of $Cu(3)O_4$ squares and AlO_6 octahedra in dmisokolovite] are linked via zig-zag chains of composition $Cu(1)O_5$ (distorted square pyramids sharing corners). $Cu(2)O_5$ trigonal bipyramids also participate in the cationic layer sharing edges with the Cu(1)-centred polyhedra to form dimers (Figs 5*a*,*b*). Two crystallographically independent As atoms centre tetrahedra which play different roles. The $As(1)O_4$ tetrahedra reinforce the linkage between the alternating zig-zag chains of the $Cu(1)O_5$ polyhedra and columns formed in shchurovskyite by the $Cu(3)O_6$ and $Cu(4)O_4$ polyhedra (Fig. 4*a*) and in dmisokolovite by the $Cu(3)O_4$ and AlO_6 polyhedra (Fig. 5*a*). Thus, the $As(1)O_4$ tetrahedra form together with the Cu-centred polyhedra (and Al-centred octahedra in dmisokolovite) a heteropolyhedral layer. The $As(2)O_4$ tetrahedra link neighbouring layers to form a three-dimensional heteropolyhedral Cu(Al)–As–O quasi-framework.

TABLE 7. Bond distances (Å) in the structures of shchurovskyite and dmisokolovite.

Shchurovskyite	Dmisokolovite
As(1) – O(5) 1.665(13)	As(1) – O(9) 1.675(17)
– O(1) 1.685(13)	– O(5) 1.677(18)
– O(2) 1.689(12)	– O(8) 1.697(17)
– O(7) 1.703(10)	– O(6) 1.722(17)
As(2) – O(4) 1.630(15)	As(2) – O(2) 1.62(2)
– O(9) 1.660(11)	– O(1) 1.666(17)
– O(3) 1.692(13)	– O(4) 1.667(19)
– O(8) 1.699(13)	– O(3) 1.70(2)
Cu(1) – O(9) 1.944(11)	Cu(1) – O(2) 1.944(19)
– O(1) 1.976(12)	– O(7) 1.956(16)
– O(6) 1.980(10)	– O(8) 1.982(17)
– O(2) 2.040(12)	– O(9) 2.006(15)
– O(1) 2.351(13)	– O(8) 2.325(19)
Cu(2) – O(8) 1.919(13)	Cu(2) – O(4) 1.916(19)
– O(6) 1.943(10)	– O(7) 1.926(15)
– O(3) 2.054(13)	– O(3) 1.97(2)
– O(5) 2.084(13)	– O(5) 2.09(2)
– O(2) 2.213(12)	– O(9) 2.197(16)
Cu(3) – O(6) 1.957(11) × 2	Cu(3) – O(6) 1.958(18) × 2
– O(7) 1.988(13) × 2	– O(7) 1.966(16) × 2
– O(3) 2.470(13) × 2	*– O(3) 2.869(16) × 2*
Cu(4) – O(6) 1.869(10) × 2	Al(1) – O(6) 1.875(19) × 2
– O(7) 1.928(13) × 2	– O(7) 1.943(18) × 2
	– O(1) 1.963(15) × 2
K – O(2) 2.645(13)	
– O(4) 2.796(15)	K(1) – O(2) 2.74(2)
– O(9) 2.808(14)	– O(9) 2.792(18)
– O(9) 3.117(14)	– O(4) 2.81(2)
– O(1) 3.294(14)	– O(5) 3.09(2)
– O(1) 3.310(15)	– O(4) 3.10(2)
– O(8) 3.321(15)	– O(5) 3.148(19)
– O(8) 3.390(14)	– O(1) 3.324(19)
	– O(8) 3.474(18)
Ca – O(4) 2.307(15) × 2	– O(8) 3.512(18)
– O(3) 2.461(13) × 2	– O(2) 3.54(2)
– O(5) 2.675(13) × 2	
– O(8) 2.846(13) × 2	K(2) – O(3) 2.28(2) × 2
	– O(1) 2.896(16) × 2
	– O(5) 2.935(18) × 2
	– O(4) 2.95(2) × 2

Italics indicates two short Cu(3)···O(3) distances.

In shchurovskyite, K cations are located in the wide channels of the quasi-framework forming eight K–O bonds in the range of 2.645(13)–3.390(14) Å. Ca cations occupy narrow channels (Fig. 4*a*) and centre eight-coordinate polyhedra with Ca–O distances in the range 2.307(15)–2.846(13) Å. In dmisokolovite, K(1) atoms are located in wide channels forming ten K–O bonds in the range 2.74(2)–3.54(2) Å while K(2) sites, corresponding

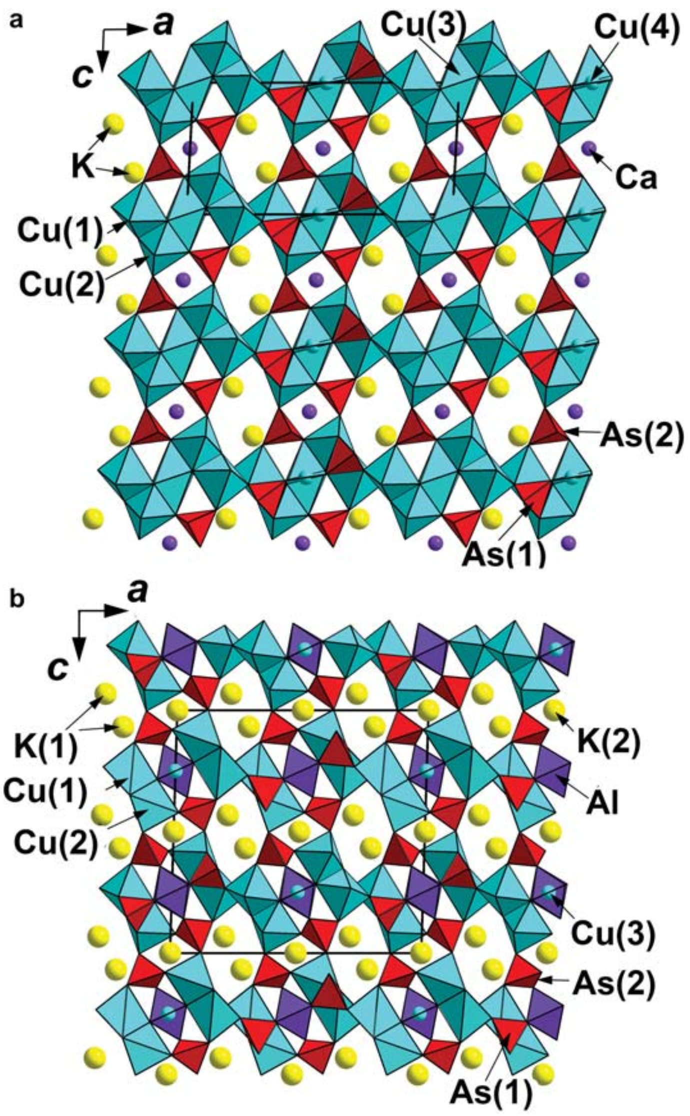

FIG. 4. The crystal structures of shchurovskyite (*a*) and dmisokolovite (*b*). The unit cells are outlined.

to Ca sites in shchurovskyite, occur in narrow channels and centre eight-coordinate polyhedra with K(2)–O distances in the range 2.28(2)–2.95(2) Å (Fig. 5*a*; Table 7). The K(2) site is characterized by shorter K–O distances and a lower number of electrons in comparison with the K(1) site (Tables 6*a* and 7) that is a reason for the conclusion that admixed Na occurs at the K(2) site. Based on the empirical formula of dmisokolovite (see above) with some deficiency of large cations [(K+Na+Ca) = 2.68 a.p.f.u.] and some excess of (Cu+Mg+Zn) = 5.16 a.p.f.u. in comparison with the idealized formula $K_3Cu_5AlO_2(AsO_4)_4$, we assume that the K(2) site can also contain minor amounts of Cu, Mg or Zn and may be partially vacant. This assumption is confirmed by the fact that K(2) is only one site that is strongly overbonded (1.54 vu) (Table 6*a*) and is characterized by shortened K(2)–O distances (Table 7).

Thus, the structures of shchurovskyite $K_2CaCu_6O_2(AsO_4)_4$ and dmisokolovite $K_3Cu_5AlO_2(AsO_4)_4$ have a topologically close main

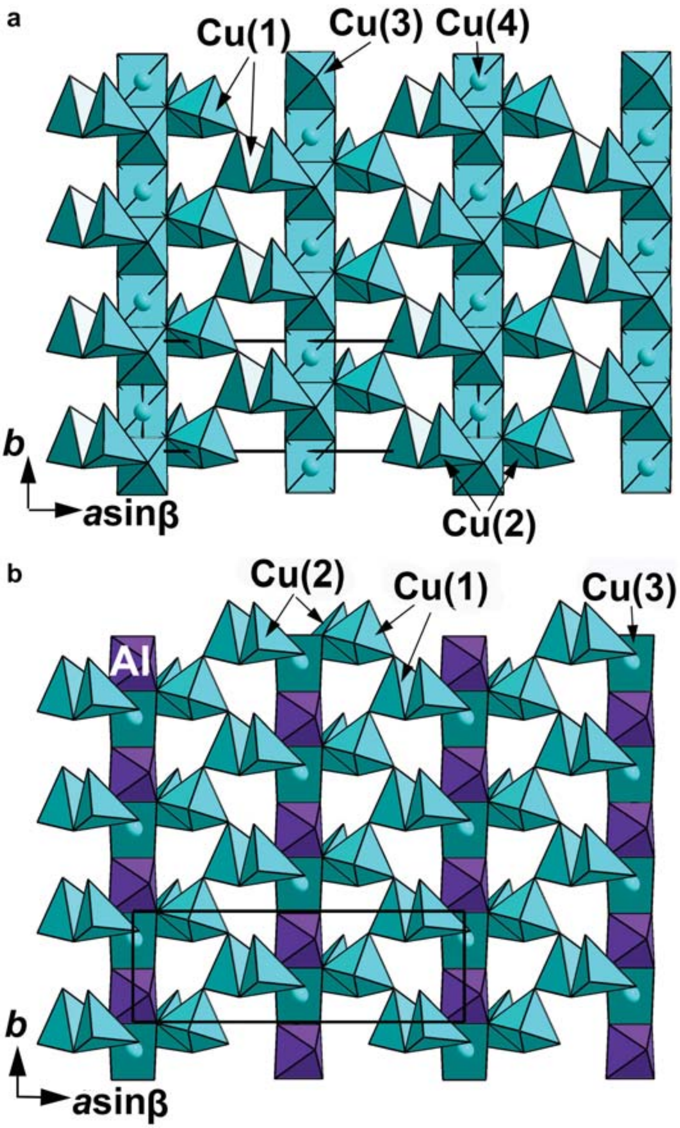

FIG. 5. Cationic layers formed by Cu-centred polyhedra in shchurovskyite (*a*) and by Cu- and Al-centred polyhedra in dmisokolovite (*b*) projected on the plane perpendicular to *c* axis. The unit cells are outlined.

structural unit, the (001) layer formed by the Cu- and Al-centred polyhedra in dmisokolovite (Fig. 5*b*) and by Cu-centred polyhedra in shchurovskyite (Fig. 5*a*). At the same time, there are some differences in the construction of the layer. In dmisokolovite, the AlO_6 octahedra participate in the layer while in shchurovskyite the same site is occupied by the $Cu(4)O_4$ square [another two Cu(4)–O distances are 3.090(15) Å, too long to be included in the primary coordination polyhedron]. The $Cu(3)O_6$ polyhedra in both minerals could be considered as octahedra with Jahn-Teller distortion, but in dmisokolovite this distortion is much stronger. The most important difference between the structures of these minerals is in the orientation of $Cu(1)O_5$ distorted square pyramids forming zig-zag chains (and, correspondingly, the orientation of the dimers formed by Cu(1)- and Cu(2)-centred polyhedra) in the adjacent layers. In shchurovskyite the neighbouring (001) layers have the same orientation

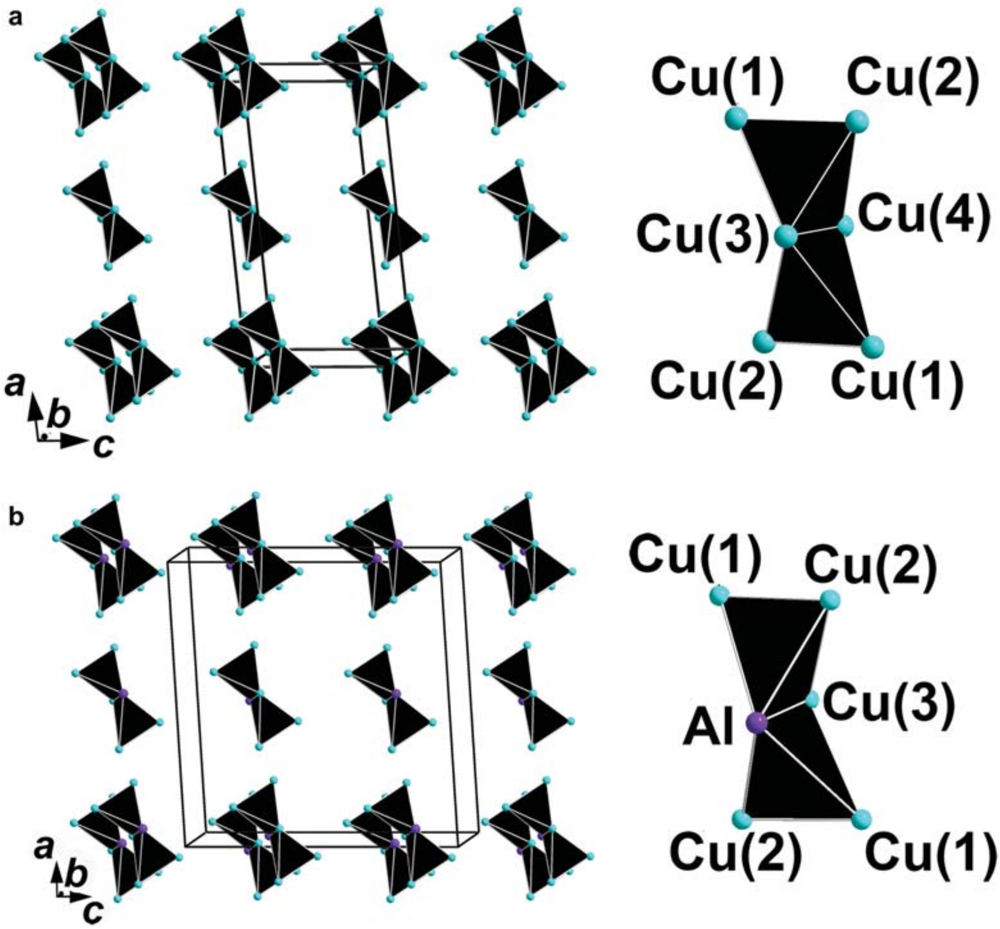

FIG. 6. Oxocentred tetrahedral motifs (*a*; the unit cells are outlined) and the dimers formed by the oxocentred tetrahedra (*b*) in shchurovskyite (upper drawings: the [O_2Cu_6] dimers) and in dmisokolovite (lower drawings: the [O_2Cu_5Al] dimers).

as these polyhedra (Fig. 4*a*) while in dmisokolovite in the neighbouring layers their orientation is opposite (Fig. 4*b*). In dmisokolovite, the AlO_6 octahedra are located under the Cu(3)O_4 squares, or under the Cu(3)O_6 octahedra with very strong Jahn-Teller distortion, of the next layer while in shchurovskyite the Cu(3)O_6 octahedra, as well as the Cu(4)O_4 squares, are located under the equivalent units of the adjacent layer (Fig. 4). This causes the doubling of the unit-cell parameter *c* of dmisokolovite in comparison with shchurovskyite (Table 4; Fig. 4). The role of AsO_4 tetrahedra in both structures is the same. The large cations have a similar arrangement; K cations are located in the wider channels of the quasi-framework in both while narrow channels are occupied by (K,Na) in dmisokolovite and by Ca in shchurovskyite (Fig. 4).

Note that the Jahn-Teller distortion of Cu^{2+}-centred polyhedra is observed widely in natural copper oxysalts. Among anhydrous arsenate and vanadate minerals known in the fumarolic exhalations at Tolbachik, strong Jahn-Teller distortion of CuO_6 octahedra was reported, e.g. for lammerite and lammerite-β, both $Cu_3(AsO_4)_2$ (Hawthorne, 1986; Starova *et al.*, 2012), bradaczekite, $NaCu_4(AsO_4)_3$ (Krivovichev *et al.*, 2001), pseudolyonsite $Cu_3(VO_4)_2$ (Zelenski *et al.*, 2011), grigorievite, $Cu_3Fe^{3+}_2Al_2(VO_4)_6$ (Pekov *et al.*, 2014*c*), ericlaxmanite, $Cu_4O(AsO_4)_2$ (Pekov *et al.*, 2014*b*) and popovite, $Cu_5O_2(AsO_4)_2$ (Pekov *et al.*, 2015).

The simplified structural formula of dmisokolovite can be written as $K_2(K,Na)[Cu_5AlO_2][AsO_4]_4$ whereas that of shchurovskyite is $K_2Ca[Cu_6O_2][AsO_4]_4$. Thus, the structures of both new minerals could also be described in terms of anion-centred tetrahedra (Krivovichev, 2009). In dmisokolovite, two $[OCu_3Al]$ tetrahedra are linked via a common Cu–Al edge forming $[O_2Cu_5Al]$ dimers. In shchurovskyite, such dimers are formed involving only Cu cations, $[O_2Cu_6]$ (Fig. 6). The same $[O_2Cu_6]$ complexes were found in the structures of euchlorine, $NaK[Cu_3O](SO_4)_3$ (Scordari and Stasi, 1990), fedotovite, $K_2[Cu_3O](SO_4)_3$ (Starova *et al*., 1991), and both triclinic and monoclinic modifications of synthetic $Cu[Cu_3O](SeO_3)_3$ (Effenberger and Pertlik, 1986). Unlike these, in dmisokolovite Al is involved in these dimers.

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