Mineralogical Magazine (2019), **83**, 879–886
doi:10.1180/mgm.2019.33

CAMBRIDGE UNIVERSITY PRESS

Article

New arsenate minerals from the Arsenatnaya fumarole, Tolbachik volcano, Kamchatka, Russia. XII. Zubkovaite, $Ca_3Cu_3(AsO_4)_4$

Igor V. Pekov[1]*, Inna S. Lykova[1], Atali A. Agakhanov[2], Dmitry I. Belakovskiy[2], Marina F. Vigasina[1], Sergey N. Britvin[3], Anna G. Turchkova[1], Evgeny G. Sidorov[4] and Katharina S. Scheidl[5]

[1]Faculty of Geology, Moscow State University, Vorobievy Gory, 119991 Moscow, Russia; [2]Fersman Mineralogical Museum of the Russian Academy of Sciences, Leninsky Prospekt 18-2, 119071 Moscow, Russia; [3]Department of Crystallography, St Petersburg State University, University Embankment 7/9, 199034 St Petersburg, Russia; [4]Institute of Volcanology and Seismology, Far Eastern Branch of the Russian Academy of Sciences, Piip Boulevard 9, 683006 Petropavlovsk-Kamchatsky, Russia; and [5]Institute of Mineralogy and Crystallography, University of Vienna, Althanstrasse 14 (UZA 2), A-1090 Vienna, Austria

Abstract

The new mineral zubkovaite, $Ca_3Cu_3(AsO_4)_4$, was found in 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 anhydrite, svabite, hematite, johillerite, tilasite, fluorophlogopite, sanidine and aphthitalite. Zubkovaite occurs as coarse prismatic crystals up to 0.01 mm × 0.01 mm × 0.2 mm combined in radiating aggregates or crusts. The mineral is transparent, bright sky-blue, turquoise-coloured or light bluish-green, with vitreous lustre. It is brittle, with imperfect cleavage. The Mohs' hardness is *ca* 3. D_{calc} is 4.161 g cm^{-3}. Zubkovaite is optically biaxial (–), $\alpha = 1.747(5)$, $\beta = 1.774(5)$, $\gamma = 1.792(5)$ and $2V_{meas} = 75(10)°$. Chemical composition (wt.%, electron microprobe) is: CaO 19.22, CuO 27.37, As_2O_5 52.54, SO_3 0.67, total 99.80. The empirical formula based on 16 O apfu is $Ca_{2.96}Cu_{2.97}(As_{3.945}S_{0.07})_{\Sigma 4.015}O_{16}$. Zubkovaite is monoclinic, *C*2, $a = 16.836(3)$, $b = 5.0405(8)$, $c = 9.1173(17)$ Å, $\beta = 117.388(13)°$, $V = 687.0(2)$ Å^3 and $Z = 2$. The strongest reflections of the powder XRD pattern [*d*,Å (*I*) (*hkl*)] are: 7.44 (100) ($\bar{2}01$), 3.727 (79) (400, $\bar{2}02$, $\bar{3}11$), 3.334 (92) ($\bar{1}12$), 2.914 (73) (311), 2.765 (50) ($\bar{6}01$, $\bar{6}02$), 2.591 (96) ($\bar{3}13$) and 2.521 (53) (020). The crystal structure is unique for minerals. It was solved from single-crystal X-ray diffraction data to $R = 7.19\%$. The structure contains trimers of Cu^{2+}-centred polyhedra (consisting of one distorted square CuO_4 in the core and two distorted square pyramids CuO_5) and two crystallographically independent $As^{5+}O_4$ tetrahedra playing different roles: As(2)O_4 tetrahedra link neighbouring trimers into ribbons whereas As(1)O_4 tetrahedra link adjacent ribbons into heteropolyhedral layers; Ca cations are located in the interlayer space. The mineral is named in honour of the Russian crystallographer and crystal chemist Natalia Vital'evna Zubkova (born 1976).

Keywords: zubkovaite, new mineral, calcium copper arsenate, crystal structure, fumarole sublimate, Tolbachik volcano, Kamchatka

(Received 14 February 2019; accepted 19 April 2019; Accepted Manuscript published online: 31 May 2019; Associate Editor: David Hibbs)

Introduction

This paper is part of the series of articles containing descriptions of new arsenate minerals from the Arsenatnaya fumarole of the Tolbachik volcano at the Kamchatka Peninsula, Far-Eastern Region, Russia. Fourteen new arsenate species from this fumarole have already been characterised: yurmarinite $Na_7(Fe^{3+},Mg,Cu)_4(AsO_4)_6$ (Pekov *et al.*, 2014*a*), two polymorphs of $Cu_4O(AsO_4)_2$, ericlaxmanite and kozyrevskite (Pekov *et al.*, 2014*b*), popovite $Cu_5O_2(AsO_4)_2$ (Pekov *et al.*, 2015*a*), structurally related shchurovskyite $K_2CaCu_6O_2(AsO_4)_4$ and dmisokolovite $K_3Cu_5AlO_2(AsO_4)_4$ (Pekov *et al.*, 2015*b*), katiarsite $KTiO(AsO_4)$ (Pekov *et al.*, 2016*a*), melanarsite $K_3Cu_7Fe^{3+}O_4(AsO_4)_4$ (Pekov *et al.*, 2016*b*), pharmazincite $KZnAsO_4$ (Pekov *et al.*, 2017), arsenowagnerite $Mg_2(AsO_4)F$ (Pekov *et al.*, 2018*b*), arsenatrotitanite $NaTiO(AsO_4)$ (Pekov *et al.*, 2019*a*), pair of isostructural minerals edtollite $K_2NaCu_5Fe^{3+}O_2(AsO_4)_4$ and alumoedtollite $K_2NaCu_5AlO_2(AsO_4)_4$ (Pekov *et al.*, 2019*b*), and anatolyite $Na_6(Ca,Na)(Mg,Fe^{3+})_3Al(AsO_4)_6$ (Pekov *et al.*, 2019*c*).

In this paper we characterise the new mineral zubkovaite, $Ca_3Cu_3(AsO_4)_4$, (Cyrillic: зубковаит) named in honour of the Russian crystallographer and crystal chemist Natalia Vital'evna Zubkova (born 1976), Associate Professor at the Faculty of Geology of Lomonosov Moscow State University, a specialist in the structural mineralogy. She has studied crystal structures of more than 160 minerals and is a co-author of descriptions of 101 new mineral species approved by the International Mineralogical Association (IMA). Dr. Zubkova has made a significant contribution to the mineralogy of arsenates and the mineralogy of the fumarolic formation. Structures of 34 natural arsenates (including 16 copper-bearing species) have been first solved by Dr. Zubkova, or with her participation as a co-author. She has studied the crystal structures of 64 minerals from fumaroles of the Tolbachik and Bezymyannyi volcanoes at Kamchatka.

Both new mineral and its name have been approved by the IMA Commission on New Minerals, Nomenclature and Classification (IMA2018–008). The type specimen is deposited in the systematic collection of the Fersman Mineralogical

*Author for correspondence: Igor V. Pekov, Email: igorpekov@mail.ru
Cite this article: Pekov I.V., Lykova I.S., Agakhanov A.A., Belakovskiy D.I., Vigasina M.F., Britvin S.N., Turchkova A.G., Sidorov E.G. and Scheidl K.S. (2019) New arsenate minerals from the Arsenatnaya fumarole, Tolbachik volcano, Kamchatka, Russia. XII. Zubkovaite, $Ca_3Cu_3(AsO_4)_4$. *Mineralogical Magazine* **83**, 879–886. https://doi.org/10.1180/mgm.2019.33

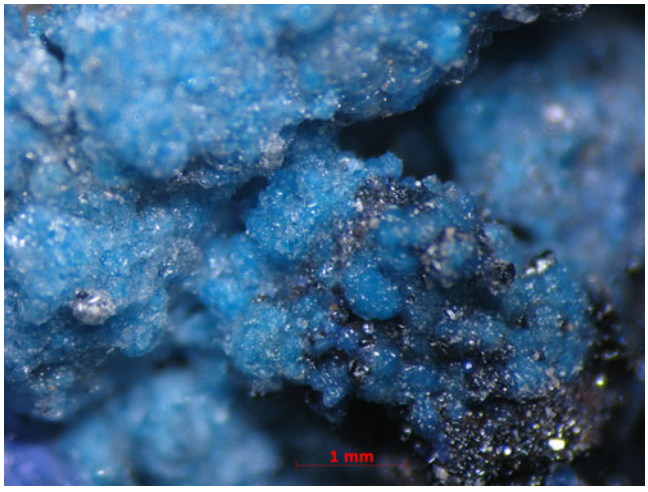

Fig. 1. Blue clusters and interrupted crusts of zubkovaite (intergrown with svabite: see Fig. 3) covered by aqua–transparent, colourless anhydrite coatings and associated with iron-black hematite and minor blue–violet johillerite. The holotype specimen, catalogue number 96202. Field of view width: 5.8 mm. Photo: I.V. Pekov & A.V. Kasatkin.

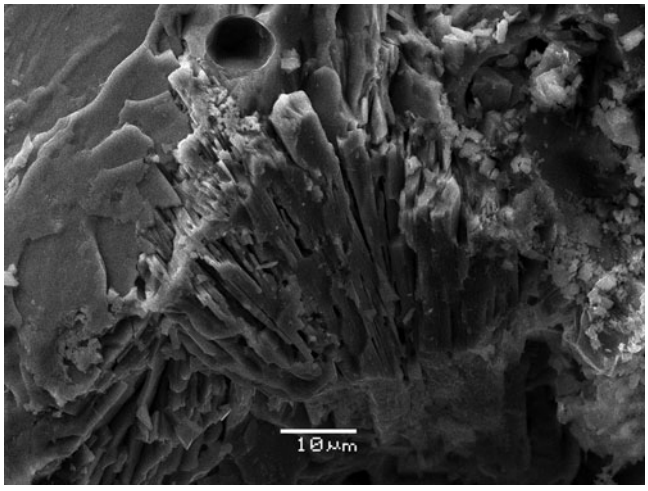

Fig. 2. Radiating aggregate of coarse long prismatic crystals of zubkovaite with massive anhydrite crust (in the left part of the photograph). The holotype specimen, catalogue number 96202. Scanning electron microscopy (SEM) secondary electron (SE) image.

Museum of the Russian Academy of Sciences, Moscow, with the catalogue number 96202.

Occurrence, mineral associations and morphology

The Arsenatnaya fumarole is located at the summit of the Second scoria cone of the Northern Breakthrough of the Great Tolbachik Fissure Eruption (55°41′N, 160°14′E, 1200 m asl). This scoria cone is a monogenetic volcano formed in 1975 (Fedotov and Markhinin, 1983). Arsenatnaya is one of the largest fumaroles at Tolbachik, and is the most interesting for its unique mineralogy. The general description of this active, hot fumarole including the characterisation of zonation in distribution of mineral assemblages is given by Pekov *et al.* (2014*a*, 2018*a*).

The holotype specimen of zubkovaite was found by us in July 2015 at the northern area of the Arsenatnaya fumarole, at the depth of 1.5 m under day surface. The temperature in this area, measured using a chromel–alumel thermocouple at the time of collecting, was ~400°C. Additional samples were collected in July 2018 from another mineral association at the depth of 1 m under day surface. We consider that zubkovaite was deposited directly from volcanic gas as a sublimate or, more likely, crystallised as a result of the interaction between fumarolic gas and basalt scoria at the temperatures not lower than 400°C. Basalt seems the most probable source of Ca which has low volatility in volcanic gases (Symonds and Reed, 1993).

Zubkovaite was found in two mineral assemblages in the polymineralic zone of Arsenatnaya (Pekov *et al.*, 2018*a*). In the holotype material, it is associated closely with anhydrite, svabite, hematite, johillerite, tilasite, fluorophlogopite, As-bearing potassic feldspar and aphthitalite. Zubkovaite occurs here as coarse long-prismatic, sometimes lath-like crystals up to 0.01 mm × 0.01 mm × 0.2 mm, typically slightly split and cavernous. They are combined in radiating clusters, isolated or forming interrupted crusts up to 1 cm × 1.5 cm in area and up to 0.3 mm thick on the surface of basalt scoria altered by fumarolic gas, and typically partially replaced by aggregates of fluorophlogopite, potassic feldspar and hematite. The new mineral commonly forms intimate intergrowths with svabite and aggregates of these arsenates are coated by anhydrite crusts (Figs 1, 2 and 3).

In the samples collected in 2018 zubkovaite was found in association with aphthitalite, johillerite, nickenichite, bradaczekite,

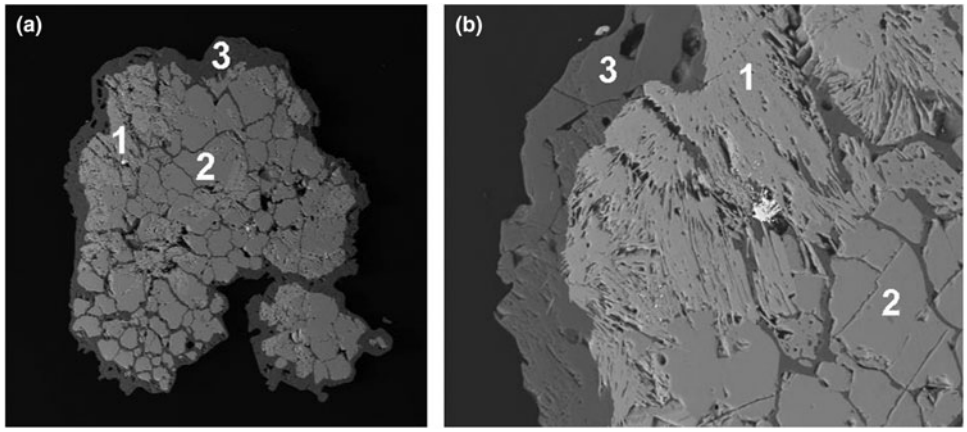

Fig. 3. Clusters of zubkovaite (1) and svabite (2) coated by anhydrite (3); anhydrite crusts (which look like veinlets in the section) are also observed around separate svabite individuals and zubkovaite aggregates: (*a*) polished cross-section; (*b*) its magnified fragment. The holotype specimen, catalogue number 96202. SEM back-scattered electron images. Field of view width: (*a*) 1.5 mm; (*b*) 0.35 mm.

https://doi.org/10.1180/mgm.2019.33 Published online by Cambridge University Press

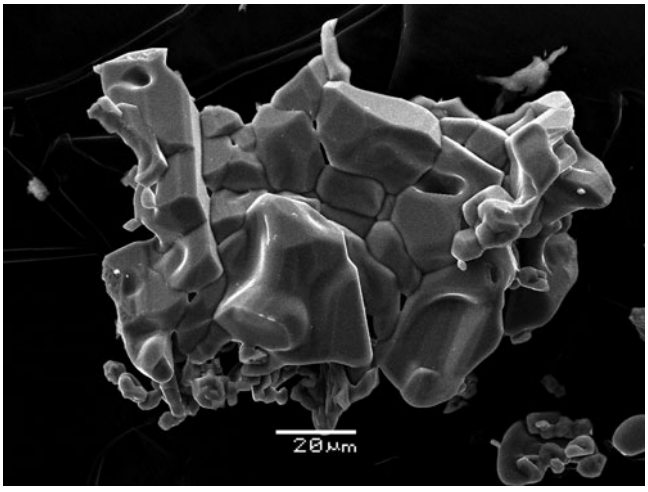

Fig. 4. Aggregate of coarse short prismatic crystals of zubkovaite. SEM (SE) image.

hatertite, tilasite, hematite, cassiterite and As-bearing potassic feldspar. The new mineral forms aggregates (up to 0.5 mm across) consisting of coarse, distorted, sometimes skeletal, short prismatic crystals (Fig. 4) or grains irregular in shape up to 0.05 mm in size. They overgrow bradaczekite and johillerite crystal clusters and usually are embedded in aphthitalite crusts.

Physical properties and optical characteristics

Zubkovaite is transparent, bright sky-blue (the holotype), turquoise-coloured or light bluish-green. Streak is light bluish. Lustre is vitreous. The mineral is brittle. One direction of imperfect cleavage was observed under the microscope. Parting was not observed. The fracture is uneven. The Mohs' hardness is ~3. Density calculated using the empirical formula is 4.161 g cm^{-3}.

Zubkovaite is optically biaxial (–), $\alpha = 1.747(5)$, $\beta = 1.774(5)$ and $\gamma = 1.792(5)$ (589 nm). $2V_{meas} = 75(10)°$ (estimated by the conoscopical figure on the section perpendicular to the optical axis) and $2V_{calc} = 77°$. Dispersion of optical axes is weak with $r > v$. Pleochroism is distinct: Z (blue) > Y (pale blue) > X (very pale bluish, almost colourless).

Raman spectroscopy

The Raman spectrum of the holotype specimen of zubkovaite (Fig. 5) was obtained using an EnSpectr R532 spectrometer with a green laser (532 nm) at room temperature. The output power of the laser beam was ~7 mW. The spectrum was processed using the EnSpectr expert mode program in the range 100 to 4000 cm^{-1} with a resolution of 6 cm^{-1}. The diameter of the focal spot on the sample was ~5 µm. The spectrum was obtained for a randomly oriented crystal.

The strongest bands in the region 750–950 cm^{-1} correspond to As^{5+}–O stretching vibrations of AsO_4^{3-} anions. Bands in the region 380–550 cm^{-1} can be assigned to bending vibrations of AsO_4 tetrahedra and Cu^{2+}–O stretching vibrations. Bands with frequencies lower than 350 cm^{-1} correspond to Ca–O stretching vibrations and lattice modes. The absence of bands with frequencies higher than 950 cm^{-1} (excepting ones belonging to admixed anhydrite: marked with asterisk in Fig. 5) indicates the absence of groups with O–H, C–H, C–O, N–H, N–O and B–O bonds in zubkovaite.

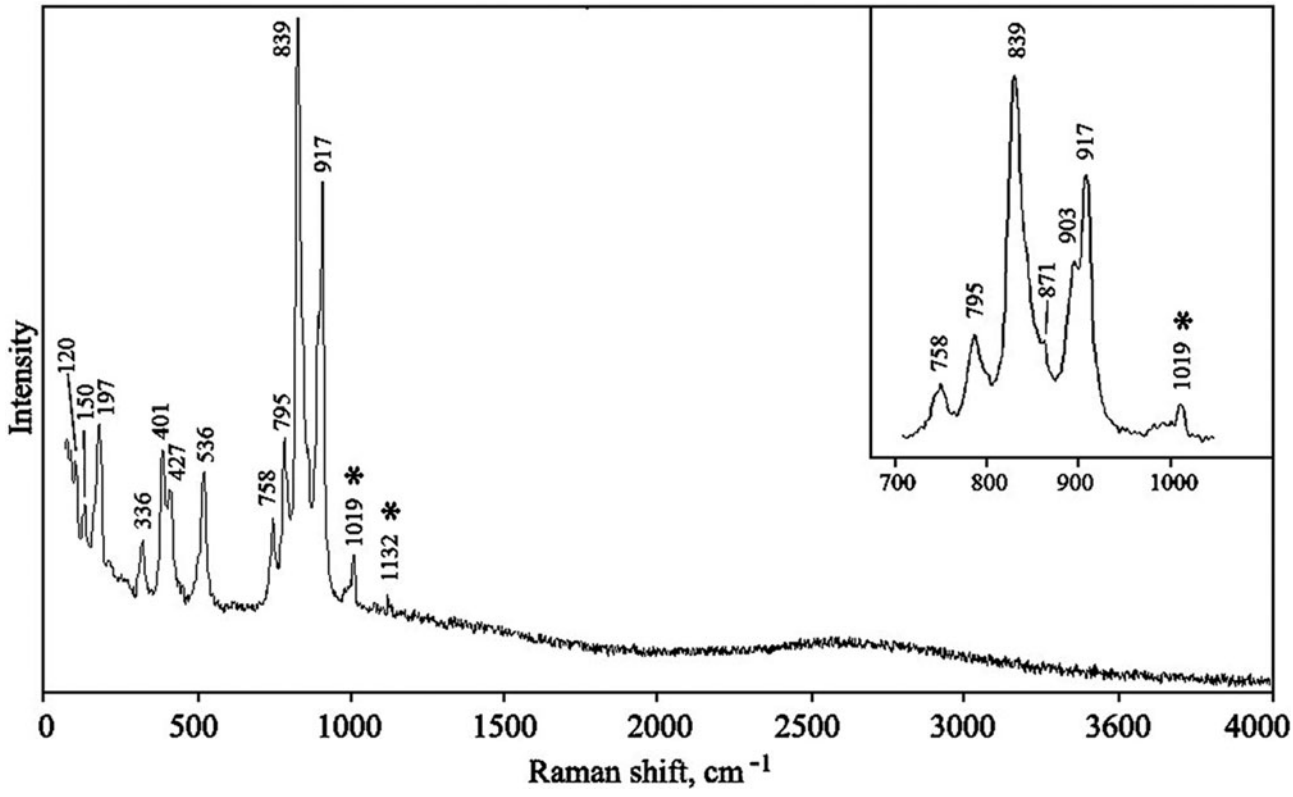

Fig. 5. The Raman spectrum of zubkovaite; bands corresponding to admixed anhydrite are marked with an asterisk.

https://doi.org/10.1180/mgm.2019.33 Published online by Cambridge University Press

Table 1. Powder X-ray diffraction data (*d* in Å) of zubkovaite.

I_{obs}	d_{obs}	I_{calc}*	d_{calc}**	*hkl*
100	**7.44**	**2, 100**	**7.474, 7.463**	**200, $\bar{2}$01**
36	4.771	34	4.776	110
8	4.532	3, 3	4.547, 4.540	201, $\bar{2}$02
12	4.401	14	4.407	$\bar{1}$11
4	4.198	2	4.209	$\bar{4}$01
38	4.036	31	4.048	002
9	3.869	6	3.872	111
79	**3.727**	**26, 20, 40**	**3.737, 3.732, 3.725**	**400, $\bar{4}$02, $\bar{3}$11**
5	3.543	3	3.544	310
92	**3.334**	**95**	**3.339**	**$\bar{1}$12**
29	3.017	14, 13	3.024, 3.020	202, $\bar{2}$03
73	**2.914**	**5, 2, 71**	**2.920, 2.915, 2.915**	**401, $\bar{4}$03, 311**
11	2.883	9	2.886	112
48	**2.789**	**46**	**2.790**	**$\bar{5}$11**
50	**2.765**	**26, 19**	**2.766, 2.764**	**$\bar{6}$01, $\bar{6}$02**
3	2.705	1, 2	2.709, 2.699	$\bar{5}$12, 003
96	**2.591**	**93**	**2.595**	**$\bar{3}$13**
30	2.571	30	2.571	510
53	**2.521**	**69**	**2.520**	**020**
11	2.390	7, 1, 9	2.394, 2.388, 2.388	$\bar{5}$13, 220, $\bar{2}$21
6	2.320	8	2.317	312
37	2.229	29, 6	2.231, 2.229	203, $\bar{2}$04
3	2.166	4	2.166	$\bar{7}$12
8	2.124	4, 6	2.129, 2.123	$\bar{7}$11, 601
9	2.088	1, 7	2.089, 2.088	420, $\bar{4}$22
4	2.071	4	2.074	$\bar{3}$14
2	2.055	2	2.057	$\bar{7}$13
6	2.036	1, 4	2.038, 2.036	$\bar{8}$01, $\bar{8}$03
7	2.022	1, 7	2.027, 2.024	$\bar{5}$14, 004
2	1.967	2	1.966	710
15	1.936	13, 6	1.936, 1.935	222, $\bar{2}$23
3	1.908	3, 2	1.908, 1.906	421, $\bar{4}$23
44	**1.865**	**7, 15, 10, 19**	**1.869, 1.866, 1.863, 1.862**	**800, $\bar{8}$04, $\bar{6}$21, $\bar{6}$22**
7	1.820	8	1.823	$\bar{4}$05
7	1.753	5, 1	1.759, 1.751	$\bar{9}$12
1	1.732	2	1.731	$\bar{9}$13
3	1.707	3	1.708	$\bar{5}$15
3	1.695	1, 3	1.697, 1.694	$\bar{3}$15, $\bar{9}$11
3	1.689	3, 2	1.688, 1.687	422, $\bar{4}$24
16	1.671	3, 19, 2	1.674, 1.671, 1.670	$\bar{1}$0.0.3, 223, $\bar{2}$24
9	1.639	8, 2	1.639, 1.635	$\bar{9}$14, $\bar{7}$15
2	1.623	3	1.623	621
15	1.609	14, 3, 4, 1	1.608, 1.608, 1.607, 1.606	10.0.1, $\bar{3}$31, $\bar{1}$15, $\bar{1}$0.0.4
10	1.577	5, 6, 1, 9	1.578, 1.578, 1.576, 1.572	024, 910, 513, $\bar{1}$32
2	1.552	3	1.552	314
9	1.533	14	1.532	712
5	1.522	7	1.520	331
4	1.518	1, 3	1.516, 1.516	132, 603
4	1.513	3, 1	1.513, 1.512	$\bar{6}$06, 404
16	1.501	9, 6, 14	1.502, 1.501, 1.500	$\bar{5}$31, 820, $\bar{8}$24
18	1.468	7, 23, 9, 8	1.469, 1.469, 1.465, 1.463	115, $\bar{3}$33, 530, $\bar{1}$1.1.3
7	1.457	1, 1, 7, 1, 2	1.460, 1.457, 1.457, 1,456, 1.455	802, 622, $\bar{8}$06, $\bar{6}$25, $\bar{5}$16
4	1.442	5	1.442	$\bar{2}$25
5	1.438	5	1.435	911
4	1.430	1, 5	1.431, 1.429	$\bar{7}$16, $\bar{5}$33
3	1.427	1, 1	1.428, 1.426	$\bar{1}$1.1.4, $\bar{3}$16
2	1.414	4	1.413	332
4	1.397	2, 2	1.397, 1.395	$\bar{1}$1.1.1, $\bar{1}$0.2.3
1	1.386	1, 1, 1	1.388, 1.387, 1.383	133, 821, $\bar{1}$2.0.2
11	1.357	1, 2, 12	1.360, 1.356, 1.356	$\bar{1}$0.0.6, $\bar{1}$1.1.5, $\bar{1}$0.2.1
10	1.351	1, 2, 14, 3	1.352, 1.352, 1.351, 1.347	$\bar{3}$34, 514, $\bar{1}$16, $\bar{7}$33
3	1.343	4	1.342	713
3	1.320	1	1.320	730

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

Chemical composition

The chemical composition of zubkovaite was determined using a Jeol 733 electron microprobe instrument (wavelength-dispersive spectroscopy mode, acceleration voltage of 20 kV, a beam current of 20 nA and a 3 μm beam diameter). The following standards were used: wollastonite (Ca), Cu (Cu), InAs (As) and ZnS (S).

https://doi.org/10.1180/mgm.2019.33 Published online by Cambridge University Press

Table 2. Crystal data, data collection information and structure refinement details for zubkovaite.

Crystal data	
Formula	$Ca_3Cu_3(AsO_4)_4$
Crystal size (mm)	0.01 × 0.01 × 0.03
Crystal system, space group	Monoclinic, *C*2
Temperature (K)	293(2)
a, *b*, *c* (Å)	16.836(3), 5.0405(8), 9.1173(17)
β (°)	117.388(13)
V (Å^3)	687.0(2)
Z	2
Calculated density (g cm^{-3})	4.161
Absorption coefficient μ (mm^{-1})	15.375
Data collection	
Crystal description	Coarse prismatic, sky-blue
Diffractometer	STOE StadiVari
Radiation type, wavelength (Å)	Mo*Kα*, λ = 0.71073
θ range (°)	2.52–32.54
No. measured, unique and observed [$I > 2\sigma(I)$] reflections	3068, 1756, 1085
R_{int}	0.0931
h, *k*, *l* range	$-24 \le h \le 23$, $-7 \le k \le 7$, $-13 \le l \le 9$
Refinement	
R_1	0.0719
$wR_{2all}(F^2)$	0.2210
GoF	1.020
Number of refined parameters	120
Weighting scheme	$1/[\sigma^2(F_o^2) + (0.1312P)^2 + 0.0000P]$, $P = [\max(F_o)^2 + 2(F_c)^2]/3$
$\Delta\rho_{max}$ /$\Delta\rho_{min}$ (e$^-$/Å^3)	2.022 / −2.006

Contents of other elements with atomic numbers higher than carbon are below detection limits.

The chemical composition of the holotype sample of zubkovaite (average of 7 spot analyses, in wt.%; ranges are in parentheses) is: CaO 19.22 (18.71–19.74), CuO 27.37 (27.13–27.73), As_2O_5 52.54 (51.26–53.17), SO_3 0.67 (0.00–2.14), total 99.80.

The empirical formula calculated on the basis of 16 O atoms per formula unit is $Ca_{2.96}Cu_{2.97}(As_{3.945}S_{0.07})_{\Sigma 4.015}O_{16}$. The simplified formula is $Ca_3Cu_3(AsO_4)_4$ ($Z = 2$), which requires CaO 19.41, CuO 27.54, As_2O_5 53.05, total 100.00 wt.%.

X-ray crystallography and crystal structure

Powder X-ray diffraction data of zubkovaite (Table 1) were collected with a Rigaku R-AXIS Rapid II single-crystal diffractometer equipped with cylindrical image plate detector (radius 127.4 mm) using Debye–Scherrer geometry, Co*Kα* radiation (rotating anode with VariMAX microfocus optics), 40 kV, 15 mA, and exposure of 12 min. Angular resolution of the detector is 0.045°2θ (pixel size 0.1 mm). The data were integrated using the software package *Osc2Tab* (Britvin *et al.*, 2017). The monoclinic unit-cell parameters calculated from the powder data are: $a = 16.841$ (9), $b = 5.044(1)$, $c = 9.110(5)$ Å, $\beta = 117.33(4)°$ and $V = 687.5(5)$ Å^3.

Single-crystal X-ray studies of zubkovaite (the crystal was separated from the holotype sample) were carried out using a STOE

Table 4. Selected interatomic distances (Å) in the crystal structure of zubkovaite.

As(1)–O(8)	1.623(9)	As(2)–O(5)	1.625(9)
As(1)–O(1)	1.652(15)	As(2)–O(3)	1.653(15)
As(1)–O(6)	1.658(13)	As(2)–O(4)	1.686(13)
As(1)–O(7)	1.731(17)	As(2)–O(2)	1.750(15)
<As(1)–O>	1.666	<As(2)–O>	1.679
Ca(1)–O(8)	2.212(18) ×2	Cu(1)–O(2)	1.919(18) ×2
Ca(1)–O(4)	2.297(14) ×2	Cu(1)–O(3)	1.987(15) ×2
Ca(1)–O(7)	2.48(2) ×2	<Cu(1)–O>	1.953
<Ca(1)–O>	2.330		
		Cu(2)–O(6)	1.903(15)
Ca(2)–O(5)	2.302(17)	Cu(2)–O(4)	1.928(15)
Ca(2)–O(3)	2.315(16)	Cu(2)–O(2)	2.021(16)
Ca(2)–O(1)	2.526(17)	Cu(2)–O(1)	2.150(16)
Ca(2)–O(7)	2.534(15)	Cu(2)–O(7)	2.157(16)
Ca(2)–O(6)	2.69(5)	<Cu(2)–O>	2.032
Ca(2)–O(2)	2.710(18)		
Ca(2)–O(6)	2.77(5)		
Ca(2)–O(5)	2.85(2)		
<Ca(2)–O>	2.587		

Table 5. Bond-valence calculations* for zubkovaite.

	Ca(1)	Ca(2)	Cu(1)	Cu(2)	As(1)	As(2)	Σ
O(1)		0.22		0.28	1.36		1.86
O(2)		0.13	$0.52^{\times 2\downarrow}$	0.40		1.05	2.10
O(3)		0.39	$0.43^{\times 2\downarrow}$			1.36	2.18
O(4)	$0.41^{\times 2\downarrow}$			0.51		1.24	2.16
O(5)		0.40				1.47	1.96
		0.09					
O(6)		0.14		0.55	1.34		2.14
		0.11					
O(7)	$0.25^{\times 2\downarrow}$	0.22		0.27	1.10		1.84
O(8)	$0.52^{\times 2\downarrow}$				1.48		2.00
Σ	2.36	1.70	1.90	2.01	5.28**	5.12	

*Bond-valence parameters were taken from Brese and O'Keeffe (1991); **slight overcharge is probably caused by partial substitution of As^{5+} for S^{6+} (see Table 1).

Table 3. Atom coordinates (*x*, *y*, *z*) and thermal displacement parameters (*U*, Å^2) for zubkovaite.

Site	*x*	*y*	*z*	U_{eq}	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
As(1)	0.34113(11)	0.4774(10)	0.46183(17)	0.0249(4)	0.0237(7)	0.0253(7)	0.0247(6)	−0.002(2)	0.0102(5)	0.0000(19)
As(2)	0.59376(10)	0.9790(9)	0.93510(16)	0.0218(4)	0.0211(7)	0.0209(7)	0.0229(6)	0.002(2)	0.0096(5)	0.0000(18)
Cu(1)	0	−0.0274(17)	0	0.0231(5)	0.0219(11)	0.0177(11)	0.0299(11)	0	0.0120(9)	0
Cu(2)	0.61954(13)	0.9791(14)	0.2945(2)	0.0309(5)	0.0215(9)	0.0440(11)	0.0260(8)	0.001(3)	0.0099(7)	0.002(3)
Ca(1)	½	0.965(3)	½	0.0253(10)	0.0243(19)	0.028(3)	0.0243(16)	0	0.0118(14)	0
Ca(2)	0.2329(2)	−0.029(3)	0.1936(4)	0.0394(10)	0.0270(16)	0.066(3)	0.0266(13)	−0.009(5)	0.0130(12)	−0.007(5)
O(1)	0.354(1)	0.393(3)	0.6466(17)	0.030(3)	0.025(7)	0.021(6)	0.036(7)	−0.004(5)	0.009(6)	−0.004(5)
O(2)	0.5811(10)	0.178(3)	0.0801(17)	0.030(3)	0.022(7)	0.043(9)	0.026(6)	−0.001(6)	0.013(5)	−0.007(6)
O(3)	0.6024(9)	0.669(3)	0.0007(17)	0.027(3)	0.018(6)	0.028(7)	0.035(7)	−0.004(5)	0.013(5)	0.007(6)
O(4)	0.5032(9)	0.032(5)	0.7519(16)	0.039(7)	0.017(5)	0.07(2)	0.027(5)	−0.001(8)	0.012(5)	−0.008(8)
O(5)	0.6844(8)	0.859(4)	0.940(2)	0.050(5)	0.027(8)	0.044(10)	0.055(10)	0.007(7)	0.000(8)	0.010(8)
O(6)	0.2366(9)	0.481(9)	0.3120(15)	0.051(5)	0.021(6)	0.091(13)	0.035(6)	−0.01(2)	0.007(5)	0.00(2)
O(7)	0.3546(11)	0.136(3)	0.4676(18)	0.036(4)	0.029(8)	0.034(9)	0.033(7)	−0.002(6)	0.006(6)	0.001(6)
O(8)	0.4014(14)	0.640(5)	0.396(2)	0.059(7)	0.070(16)	0.069(14)	0.041(9)	−0.039(12)	0.029(10)	−0.025(9)

https://doi.org/10.1180/mgm.2019.33 Published online by Cambridge University Press

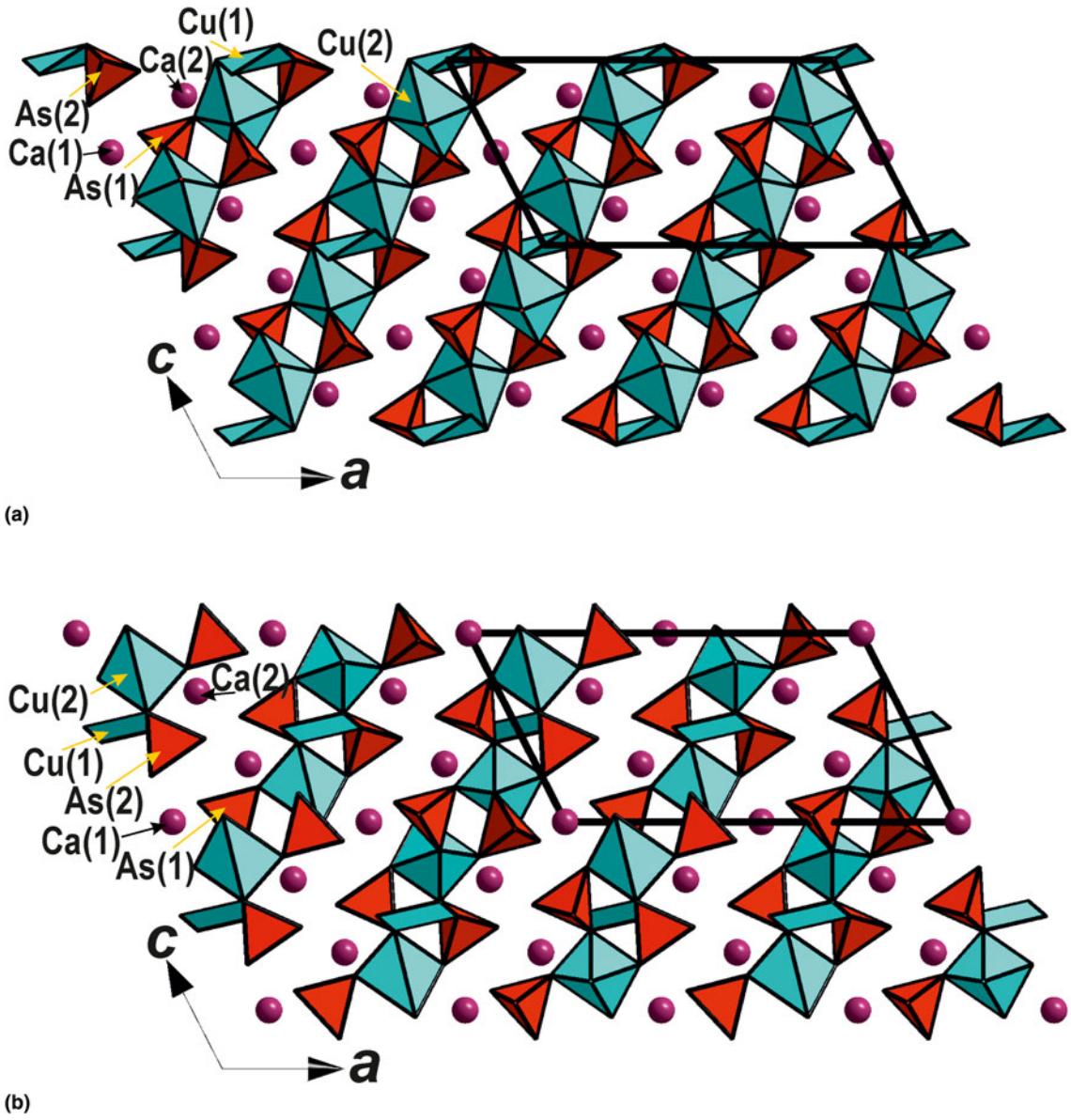

Fig. 6. Crystal structures of zubkovaite (*a*) and synthetic $Ca_3Cu_3(AsO_4)_4$ (*b*, drawn after Osterloh and Müller–Buschbaum, 1994). The unit cells are outlined.

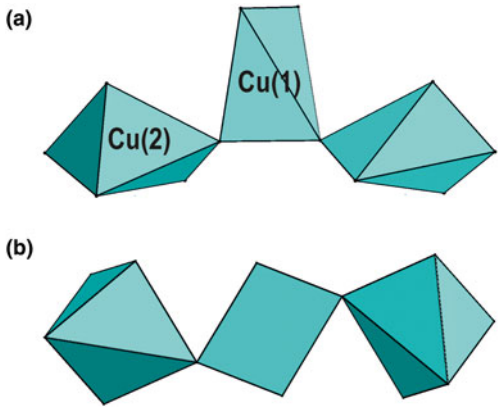

Fig. 7. Trimers of Cu–centred polyhedra in the crystal structures of zubkovaite (*a*) and synthetic $Ca_3Cu_3(AsO_4)_4$ (*b*, drawn after Osterloh and Müller–Buschbaum, 1994).

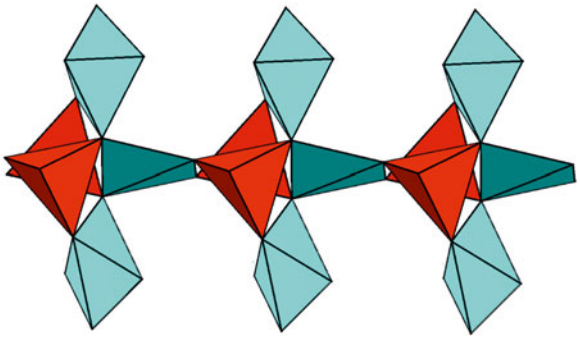

Fig. 8. Ribbon formed by the trimers of Cu-centred polyhedra linked *via* $As(2)O_4$ tetrahedra in the crystal structure of zubkovaite. For legend see Fig. 6.

https://doi.org/10.1180/mgm.2019.33 Published online by Cambridge University Press

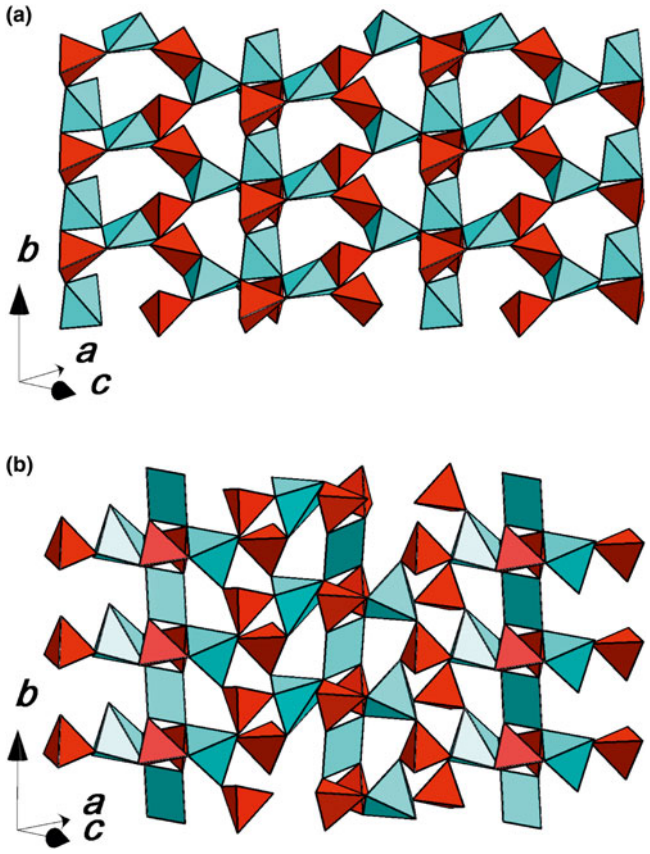

Fig. 9. Heteropolyhedral Cu–As–O layers in the crystal structures of zubkovaite (*a*) and synthetic $Ca_3Cu_3(AsO_4)_4$ (*b*, drawn after Osterloh and Müller–Buschbaum, 1994). For legend see Fig. 6.

StadiVari diffractometer equipped with a Dectris PILATUS 300K pixel detector. The measured crystal was small (0.01 mm × 0.01 mm × 0.03 mm) and irregular in shape (distorted prismatic). The crystal structure was solved by direct methods and refined with the use of *SHELX-97* software package (Sheldrick, 2015) to $R = 0.0719$. The crystal data and the experimental details are given in Table 2, coordinates and displacement parameters of atoms in Table 3, selected interatomic distances in Table 4 and bond-valence calculations in Table 5. The crystallographic information file has been deposited with the Principal Editor of *Mineralogical Magazine* and is available as Supplementary material (see below).

The crystal structure of zubkovaite is shown in Fig. 6*a*. The mineral is monoclinic, space group *C*2; the studied crystal demonstrates twinning by merohedry Class I (Nespolo and Ferraris, 2000), with twin domains ratio 65/35. The structure is based on trimers of Cu^{2+}-centred polyhedra. Each trimer consists of one Cu(1)-centred distorted square CuO_4 [the Cu(1)–O distances lie in the range of 1.919(18)–1.987(15) Å] in the core and two Cu(2)-centred distorted square pyramids CuO_5 [the Cu(2)–O distances lie in the range of 1.903(15)–2.157(16) Å] (Fig. 7*a*). Two crystallographically independent As atoms play different roles: distorted $As^{5+}(2)O_4$ tetrahedra link neighbouring trimers into ribbons running along the *b* axis (Fig. 8) whereas distorted $As^{5+}(1)O_4$ tetrahedra link adjacent ribbons into heteropolyhedral layers coplanar to $(\bar{2}01)$ (Fig. 9*a*). Restraints were applied to the As(1)–O(8) and As(2)–O(5) distances at the final stage of refinement. Ca cations are located in the interlayer space (Fig. 6*a*).

Discussion

Among minerals, zubkovaite is unique in terms of structure. Its synthetic chemical analogue $Ca_3Cu_3(AsO_4)_4$ studied by Osterloh and Müller-Buschbaum (1994) is structurally similar but not identical to the mineral. Both are monoclinic with close unit-cell dimensions but the mineral adopts space group *C*2 whereas the synthetic phase crystallises in space group $P2_1/a$ and has a somewhat denser structure (Table 6). The general motifs of both structures are close, however, details of atomic arrangement in zubkovaite and synthetic $Ca_3Cu_3(AsO_4)_4$ are different, which

Table 6. Comparative data for zubkovaite and synthetic $Ca_3Cu_3(AsO_4)_4$.

	Zubkovaite		Synthetic $Ca_3Cu_3(AsO_4)_4$
Formula	$Ca_3Cu_3(AsO_4)_4$		$Ca_3Cu_3(AsO_4)_4$
Crystal system	Monoclinic		Monoclinic
Space group	*C*2		$P2_1/a$
a (Å)	16.836(3)		16.609(9)
b (Å)	5.0405(8)		5.056(4)
c (Å)	9.1173(17)		8.950(6)
β (°)	117.388(13)		117.08(5)
V (Å^3)	687.0		669.2
Z	2		2
$D_{calc.}$ (g cm^{-3})	4.16		4.30
Strongest reflections of the powder	Measured	Calculated	Calculated*
X-ray diffraction pattern:	7.44, 100	7.463, 100, $\bar{2}01$	7.335, 98, $\bar{2}01$
d (Å), *I*, *hkl*	3.727, 79	3.725, 40, $\bar{3}11$	4.784, 41, 110
	3.334, 92	3.334, 95, $\bar{1}12$	3.705, 51, $\bar{3}11$, 400
	2.914, 73	2.915, 71, 311	3.311, 100, $\bar{1}12$
	2.789, 48	2.790, 46, $\bar{5}11$	2.896, 71, 311
	2.765, 50	2.766, 26, $\bar{6}01$	2.889, 51, 401
	2.591, 96	2.595, 93, $\bar{3}13$	2.768, 50, $\bar{5}11$
	2.521, 53	2.520, 69, 020	2.561, 90, $\bar{3}13$, 213
			2.553, 71, 510
			2.528, 64, 020
Reference	This work		Osterloh and Müller-Buschbaum (1994)

*From JCPDS–ICDD #82-982 – powder diffraction file from the International Centre for Diffraction Data, http://www.icdd.com/

https://doi.org/10.1180/mgm.2019.33 Published online by Cambridge University Press

results in the differences in geometry of the trimers (Fig. 7) and an overall high degree of distortion of the structure of zubkovaite in comparison with that of synthetic $Ca_3Cu_3(AsO_4)_4$ (Figs 6 and 9). Probably this causes merohedral microtwinning of the mineral.

Zubkovaite and its synthetic chemical analogue reported by Osterloh and Müller-Buschbaum (1994) can be considered as two modifications of $Ca_3Cu_3(AsO_4)_4$ related closely structurally. However, they may be distinguished clearly using powder X-ray diffraction data. The measured and calculated powder X-ray diffraction patterns of zubkovaite are very close to one another and differ from that of synthetic $Ca_3Cu_3(AsO_4)_4$ in both positions (d values) and intensities of many reflections (Tables 1 and 6). This difference is the most demonstrative in the position of one of the strongest reflections located in low-angle region, namely $\bar{2}01$: $d_{meas} = 7.44$ and $d_{calc} = 7.46$ Å for zubkovaite and $d_{calc} = 7.335$ Å for synthetic $Ca_3Cu_3(AsO_4)_4$. The refinement of the crystal structure of zubkovaite based on the structure model for synthetic $Ca_3Cu_3(AsO_4)_4$ given by Osterloh and Müller-Buschbaum (1994) proved to be unstable most likely due to the high degree of the structural distortion, which made it impossible for a structure to be solved in a centric space group.

Acknowledgements. We are grateful to Vasiliy O. Yapaskurt for assistance in obtaining SEM (SE) images. We thank Peter Leverett and two anonymous referees for valuable comments. This study was supported by the Russian Foundation for Basic Research, grant no. 17-05-00179. The technical support by the SPbSU X-Ray Diffraction Resource Center in the powder XRD study is acknowledged.

Supplementary material. To view supplementary material for this article, please visit https://doi.org/10.1180/mgm.2019.33

References

Brese N.E. and O'Keeffe N.E. (1991) Bond-valence parameters for solids. *Acta Crystallographica*, **47**, 192–197.

Britvin S.N., Dolivo-Dobrovolsky D.V. and Krzhizhanovskaya M.G. (2017) Software for processing the X-ray powder diffraction data obtained from the curved image plate detector of Rigaku RAXIS Rapid II diffractometer. *Zapiski Rossiiskogo Mineralogicheskogo Obshchestva*, **146**, 104–107 [in Russian].

Fedotov S.A. and Markhinin Y.K. (editors) (1983) *The Great Tolbachik Fissure Eruption*. Cambridge University Press, New York, 341 pp.

Nespolo M. and Ferraris G. (2000) Twinning by syngonic and metric merohedry. Analysis, classification and effects on the diffraction pattern. *Zeitschrift für Kristallographie*, **215**, 77–81.

Osterloh D. and Müller-Buschbaum H. (1994) Zur kenntnis eines Calcium-Kupfer-Orthoarsenats: $Ca_{1.5}Cu_{1.5}(AsO_4)_2$. *Journal of Alloys and Compounds*, **206**, 155–158.

Pekov I.V., Zubkova N.V., Yapaskurt V.O., Belakovskiy D.I., Lykova I.S., Vigasina M.F., Sidorov E.G. and Pushcharovsky D.Yu. (2014*a*) New arsenate minerals from the Arsenatnaya fumarole, Tolbachik volcano, Kamchatka, Russia. I. Yurmarinite, $Na_7(Fe^{3+},Mg,Cu)_4(AsO_4)_6$. *Mineralogical Magazine*, **78**, 905–917.

Pekov I.V., Zubkova N.V., Yapaskurt V.O., Belakovskiy D.I., Vigasina M.F., Sidorov E.G. and Pushcharovsky D.Yu. (2014*b*) New arsenate minerals from the Arsenatnaya fumarole, Tolbachik volcano, Kamchatka, Russia. II. Ericlaxmanite and kozyrevskite, two natural modifications of $Cu_4O(AsO_4)_2$. *Mineralogical Magazine*, **78**, 1527–1543.

Pekov I.V., Zubkova N.V., Yapaskurt V.O., Belakovskiy D.I., Vigasina M.F., Sidorov E.G. and Pushcharovsky D.Yu. (2015*a*) New arsenate minerals from the Arsenatnaya fumarole, Tolbachik volcano, Kamchatka, Russia. III. Popovite, $Cu_5O_2(AsO_4)_2$. *Mineralogical Magazine*, **79**, 133–143.

Pekov I.V., Zubkova N.V., Belakovskiy D.I., Yapaskurt V.O., Vigasina M.F., Sidorov E.G. and Pushcharovsky D.Yu. (2015*b*) New arsenate minerals from the Arsenatnaya fumarole, Tolbachik volcano, Kamchatka, Russia. IV. Shchurovskyite, $K_2CaCu_6O_2(AsO_4)_4$, and dmisokolovite, $K_3Cu_5AlO_2(AsO_4)_4$. *Mineralogical Magazine*, **79**, 1737–1753.

Pekov I.V., Yapaskurt V.O., Britvin S.N., Zubkova N.V., Vigasina M.F. and Sidorov E.G. (2016*a*) New arsenate minerals from the Arsenatnaya fumarole, Tolbachik volcano, Kamchatka, Russia. V. Katiarsite, $KTiO(AsO_4)$. *Mineralogical Magazine*, **80**, 639–646.

Pekov I.V., Zubkova N.V., Yapaskurt V.O., Polekhovsky Yu.S., Vigasina M.F., Belakovskiy D.I., Britvin S.N., Sidorov E.G. and Pushcharovsky D.Yu. (2016*b*) New arsenate minerals from the Arsenatnaya fumarole, Tolbachik volcano, Kamchatka, Russia. VI. Melanarsite, $K_3Cu_7Fe^{3+}O_4(AsO_4)_4$. *Mineralogical Magazine*, **80**, 855–867.

Pekov I.V., Yapaskurt V.O., Belakovskiy D.I., Vigasina M.F., Zubkova N.V. and Sidorov E.G. (2017) New arsenate minerals from the Arsenatnaya fumarole, Tolbachik volcano, Kamchatka, Russia. VII. Pharmazincite, $KZnAsO_4$. *Mineralogical Magazine*, **81**, 1001–1008.

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. and Sidorov E.G. (2018*a*) Fumarolic arsenates – a special type of arsenic mineralization. *European Journal of Mineralogy*, **30**, 305–322.

Pekov I.V., Zubkova N.V., Agakhanov A.A., Yapaskurt V.O., Chukanov N.V., Belakovskiy D.I., Sidorov E.G. and Pushcharovsky D.Yu. (2018*b*) New arsenate minerals from the Arsenatnaya fumarole, Tolbachik volcano, Kamchatka, Russia. VIII. Arsenowagnerite, $Mg_2(AsO_4)F$. *Mineralogical Magazine*, **82**, 877–888.

Pekov I.V., Zubkova N.V., Agakhanov A.A., Belakovskiy D.I., Vigasina M.F., Yapaskurt V.O., Sidorov E.G., Britvin S.N. and Pushcharovsky D.Y. (2019*a*) New arsenate minerals from the Arsenatnaya fumarole, Tolbachik volcano, Kamchatka, Russia. IX. Arsenatrotitanite, $NaTiO(AsO_4)$. *Mineralogical Magazine*, **83**, 453–458.

Pekov I.V., Zubkova N.V., Agakhanov A.A., Ksenofontov D.A., Pautov L.A., Sidorov E.G., Britvin S.N., Vigasina M.F. and Pushcharovsky D.Yu. (2019*b*) New arsenate minerals from the Arsenatnaya fumarole, Tolbachik volcano, Kamchatka, Russia. X. Edtollite, $K_2NaCu_5Fe^{3+}O_2(AsO_4)_4$, and alumoedtollite, $K_2NaCu_5AlO_2(AsO_4)_4$. *Mineralogical Magazine*, **83**, 485–495.

Pekov I.V., Lykova I.S., Yapaskurt V.O., Belakovskiy D.I., Turchkova A.G., Britvin S.N., Sidorov E.G. and Scheidl K.S. (2019*c*) New arsenate minerals from the Arsenatnaya fumarole, Tolbachik volcano, Kamchatka, Russia. XI. Anatolyite, $Na_6(Ca,Na)(Mg,Fe^{3+})_3Al(AsO_4)_6$. *Mineralogical Magazine*, **83**, 633–638.

Sheldrick G.M. (2015) Crystal structure refinement with SHELXL. *Acta Crystallographica*, **C71**, 3–8.

Symonds R.B. and Reed M.H. (1993) Calculation of multicomponent chemical equilibria in gas-solid-liquid systems: calculation methods, thermochemical data, and applications to studies of high-temperature volcanic gases with examples from Mount St. Helens. *American Journal of Science*, **293**, 758–864.