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New arsenate minerals from the Arsenatnaya fumarole, Tolbachik volcano, Kamchatka, Russia. II. Ericlaxmanite and kozyrevskite, two natural modifications of $Cu_4O(AsO_4)_2$

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ABSTRACT

Two new minerals, ericlaxmanite and kozyrevskite, dimorphs of $Cu_4O(AsO_4)_2$, were 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, Russia. They are associated with each other and with urusovite, lammerite, lammerite-β, popovite, alarsite, tenorite, hematite, aphthitalite, langbeinite, As-bearing orthoclase, etc. Ericlaxmanite occurs as tabular, lamellar, equant or short prismatic crystals up to 0.1 mm in size, their clusters and pseudomorphs after urusovite crystal crusts up to 1.5 cm × 2 cm in area. Kozyrevskite occurs as prismatic crystals up to 0.3 mm long in clusters and as individual crystals. Both minerals are transparent with a vitreous lustre. They are brittle, with Mohs' hardness ~3½. Ericlaxmanite is green to dark green. Kozyrevskite is bright grass green to light yellowish green; D_{calc} is 5.036 (ericlaxmanite) and 4.934 (kozyrevskite) g cm^{-3}. Both minerals are optically biaxial (−); ericlaxmanite: $\alpha = 1.870(10)$, $\beta = 1.900(10)$, $\gamma = 1.915(10)$, $2V_{meas} = 60(15)^o$; kozyrevskite: $\alpha = 1.885(8)$, $\beta = 1.895(8)$, $\gamma = 1.900(8)$, $2V_{meas.} = 75(10)^o$. The Raman spectra are given. Chemical data (wt.%, electron microprobe; the first value is for ericlaxmanite, the second for kozyrevskite): CuO 57.55, 58.06; ZnO 0.90, 1.04; Fe_2O_3 0.26, 0.12; SiO_2 n.d., 0.12; P_2O_5 0.23, 1.23; V_2O_5 0.14, 0.37; As_2O_5 40.57, 38.78; SO_3 0.17, 0.43; total 99.82, 100.15. The empirical formulae, based on 9 O a.p.f.u., are: ericlaxmanite: $(Cu_{3.97}Zn_{0.06}Fe_{0.02})_{\Sigma 4.05}(As_{1.94}P_{0.02}V_{0.01}S_{0.01})_{\Sigma 1.98}O_9$ and kozyrevskite: $(Cu_{3.95}Zn_{0.07}Fe_{0.01})_{\Sigma 4.03}(As_{1.83}P_{0.09}S_{0.03}V_{0.02}Si_{0.01})_{\Sigma 1.98}O_9$. Ericlaxmanite is triclinic, $P\bar{1}$, $a = 6.4271(4)$, $b = 7.6585(4)$, $c = 8.2249(3)$ Å, $\alpha = 98.396(4)$, $\beta = 112.420(5)$, $\gamma = 98.397(5)^o$, $V = 361.11(3)$ Å^3 and $Z = 2$. Kozyrevskite is orthorhombic, *Pnma*, $a = 8.2581(4)$, $b = 6.4026(4)$, $c = 13.8047(12)$ Å, $V = 729.90(9)$ Å^3 and $Z = 4$. The strongest reflections in the X-ray powder patterns [d Å(I)(hkl)] are: ericlaxmanite: 3.868(46)(101), 3.685(100)(020), 3.063(71)(012), 2.957(58)(0$\bar{2}$2), 2.777(98)($\bar{2}$12, $\bar{2}\bar{1}$1), 2.698(46)($\bar{2}\bar{1}$2) and 2.201(51)(013, 031); kozyrevskite: 3.455(100)(004), 3.194(72)(020, 104), 2.910(69)(022), 2.732(82)(122), 2.712(87)(301) and 2.509(92)(123). Their crystal structures, solved from single-crystal X-ray diffraction data [$R = 0.0358$ (ericlaxmanite) and 0.1049 (kozyrevskite)], are quite different. The ericlaxmanite structure is based on an interrupted framework built by edge- and corner-sharing Cu-centred, distorted tetragonal pyramids, trigonal

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bipyramids and octahedra. The kozyrevskite structure is based on complicated ribbons of Cu-centred distorted tetragonal pyramids and trigonal bipyramids. Ericlaxmanite is named in honour of the Russian mineralogist, geologist, geographer, biologist and chemist Eric Laxman (1737–1796). Kozyrevskite is named in honour of the Russian geographer, traveller and military man Ivan Petrovich Kozyrevskiy (1680–1734), one of the first researchers of Kamchatka.

Keywords: ericlaxmanite, kozyrevskite, new mineral, copper arsenate, crystal structure, fumarolic sublimate, Tolbachik volcano, Kamchatka.

Introduction

This article is the second in a series of coupled papers on mineralogical description and crystal chemistry of new arsenate minerals from the Arsenatnaya fumarole located at the summit 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). General data and mineralogical characteristics of this active, hot fumarole, as well as background information on the arsenate mineralization in volcanic exhalations are given in the first paper of this series (Pekov *et al*., 2014, and references therein).

Here we describe two new mineral species, natural polymorphs of $Cu_4O(AsO_4)_2$ but very different from one another in terms of crystal structure, morphology and physical properties (Table 1). Triclinic ericlaxmanite (Russian Cyrillic: эриклаксманит) is named in honour of the well known Russian mineralogist, geologist, geographer, biologist and chemist, Academician Eric Laxman (1737–1796). He had Swedish roots and was born in Finland; his name in the literature is also spelled as Erik (Ericus) Laxman, Erich Lachsmann or Kirill Gustavovich Laksman. He made significant contributions to the natural history of Siberia and, in particular, discovered several large mineral deposits (of mica, lazurite, etc.) in the Eastern Siberian region. Orthorhombic kozyrevskite (козыревскит) is named in honour of the Russian geographer, traveller and military man (Cossack officer) Ivan Petrovich Kozyrevskiy (1680–1734), one of the first researchers of the geography of Kamchatka and the Kuril Islands. He made the first map of the East Coast of the Kamchatka Peninsula in 1726. The town of Kozyrevsk, the closest settlement to the Tolbachik volcano (40 km), is named after him.

Both new minerals and their names have been approved by the IMA Commission on New Minerals, Nomenclature and Classification (ericlaxmanite: IMA 2013–022, Pekov *et al*., 2013*a*; kozyrevskite: IMA 2013–023, Pekov *et al*., 2013*b*). The type specimens are deposited in the systematic collection of the Fersman Mineralogical Museum of the Russian Academy of Sciences, Moscow, catalogue numbers 94132 (ericlaxmanite) and 94133 (kozyrevskite).

Occurrence and general appearance

Specimens that became the holotypes of ericlaxmanite and kozyrevskite were found by us in the Arsenatnaya fumarole immediately after its discovery in July 2012. In July 2013 we collected more material for studies that gave additional data on the morphology of both new arsenates and their relationships with associated minerals.

Ericlaxmanite and kozyrevskite occur in the same mineral assemblage and are associated intimately with each other (Fig. 1). They are associated closely with the other alkali-free

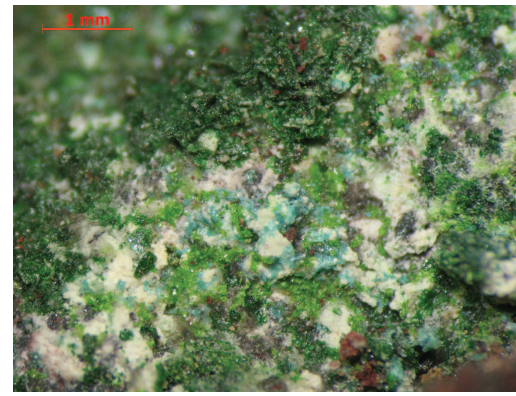

Fig. 1. Partial pseudomorphs of deep green to dark green ericlaxmanite after crystal crusts of urusovite with bright, grass green kozyrevskite, light blue urusovite relics and white crusts of As-bearing orthoclase on volcanic scoria. Field of view: 5.75 mm across. Photo: I.V. Pekov and A.V. Kasatkin.

TABLE 1. Comparative data for ericlaxmanite and kozyrevskite.

Mineral	Ericlaxmanite	Kozyrevskite
Formula	$Cu_4O(AsO_4)_2$	$Cu_4O(AsO_4)_2$
Crystal system	Triclinic	Orthorhombic
Space group	$P\bar{1}$	*Pnma*
Unit-cell data:		
a (Å)	6.4271(4)	8.2581(4)
b (Å)	7.6585(4)	6.4026(4)
c (Å)	8.2249(3)	13.8047(12)
α (°)	98.396(4)	
β (°)	112.420(5)	
γ (°)	98.397(5)	
V (Å^3)	361.11(3)	729.90(9)
Z	2	4
Strongest reflections of the X-ray powder pattern: *d* (Å) – *I*	3.868 – 46	3.455 – 100
	3.685 – 100	3.374 – 49
	3.063 – 71	3.194 – 72
	2.957 – 58	3.081 – 50
	2.777 – 98	2.910 – 69
	2.698 – 46	2.861 – 48
	2.449 – 37	2.732 – 82
	2.201 – 51	2.712 – 69
		2.509 – 92
Strongest bands of the Raman spectrum (cm^{-1})	889	875
	863	840
	845	826
	229	445
		216
		112
Optical data:		
α	1.870	1.885
β	1.900	1.895
γ	1.915	1.900
Birefringence	0.045	0.015
Optical sign, $2V_{meas}$	(–) 60°	(–) 75°
D_{calc} (g cm^{-3})	5.04	4.93
Crystal habit	Tabular to lamellar, more rarely equant to short prismatic	Prismatic to long prismatic
Colour	Deep green to dark green	Bright grass green to light yellowish green
Cleavage	One direction of distinct cleavage	Two directions of perfect cleavage

arsenates urusovite, $CuAlO(AsO_4)$, lammerite, $Cu_3(AsO_4)_2$, lammerite-β, $Cu_3(AsO_4)_2$, popovite, $Cu_5O_2(AsO_4)_2$ (IMA 2013–060) and alarsite, $AlAsO_4$, and sometimes with the Na- or K-bearing arsenates johillerite, $NaMg_3Cu(AsO_4)_3$, bradaczekite, $NaCu_4(AsO_4)_3$, shchurovskyite, $K_2CaCu_6O_2(AsO_4)_4$ (IMA 2013–078) and dmisokolovite, $K_3Cu_5AlO_2(AsO_4)_4$ (IMA 2013–079). Other associated minerals are tenorite, hematite, aphthitalite, langbeinite, anhydrite, As-bearing orthoclase, Cu-rich gahnite and, sporadically, 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, $K_2Pb(SO_4)_2$ and OH-free fluoborite, $Mg_3(BO_3)F_3$. All listed minerals form complex, polymineralic, sometimes very rich incrustations up to 0.5 cm 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. We consider that all listed minerals were deposited directly from the gas phase or

were formed as the result of gas–rock interactions at temperatures of not less than 380ºC.

Ericlaxmanite occurs as coarse or, rarely, well shaped, tabular to lamellar, less commonly equant or short prismatic crystals, and irregularly shaped individual grains up to 0.1 mm in size, separate or forming clusters (Figs 2 and 3) up to 1 mm across. Ericlaxmanite also overgrows and/or replaces urusovite that forms clusters or crusts of crude, curved lamellar crystals on scoria. Typical partial pseudomorphs of ericlaxmanite after urusovite crystal crusts are shown in Figs 1 and 4, the surface of such pseudomorphs with coarse tabular crystals of ericlaxmanite in Fig. 5 and a section of ericlaxmannite crust overgrowing urusovite in Fig. 6*a*. The crusts of urusovite partially or, in some cases, almost completely replaced by ericlaxmanite are up to 1.5 cm × 2 cm in area and up to 0.5 mm thick. More complex arsenate aggregates were also observed; there are grains of alarsite overgrown by urusovite and by ericlaxmanite (Fig. 6*b*). The sequence of deposition of these minerals demonstrates an increase of the Cu:Al ratio in arsenates formed in the fumarole system associated probably with a decrease in gas temperature.

Kozyrevskite forms prismatic to long prismatic (elongated along [010]), typically divergent crystals up to 0.02 mm × 0.05 mm × 0.3 mm in size and their radiating, sheaf-, bush- or rosette-like clusters (Figs 1, 7 and 8) up to 0.3 mm across. Abundant crystals and crystal clusters or, rarely, thin crusts (up to 1 mm × 2 mm in area) of the mineral occur on incrustations consisting of langbeinite and As-bearing orthoclase (Fig. 7) or on volcanic scoria. Kozyrevskite is one of the latest copper arsenates in the Arsenatnaya paragenesis, overgrowing not only urusovite and lammerite but also ericlaxmanite.

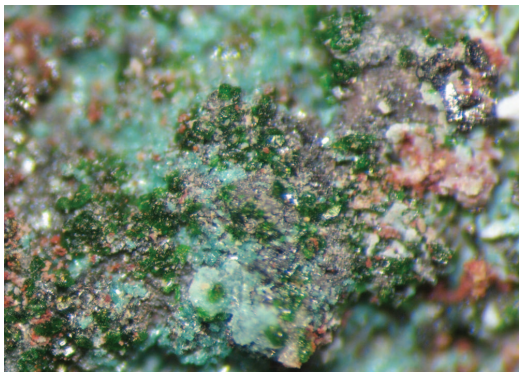

FIG. 2. Numerous deep green tabular crystals of ericlaxmanite on volcanic scoria, with light blue (turquoise) lammerite and dark grey crusts of hematite and tenorite. Field of view: 2.4 mm across. Photo: I.V. Pekov and A.V. Kasatkin.

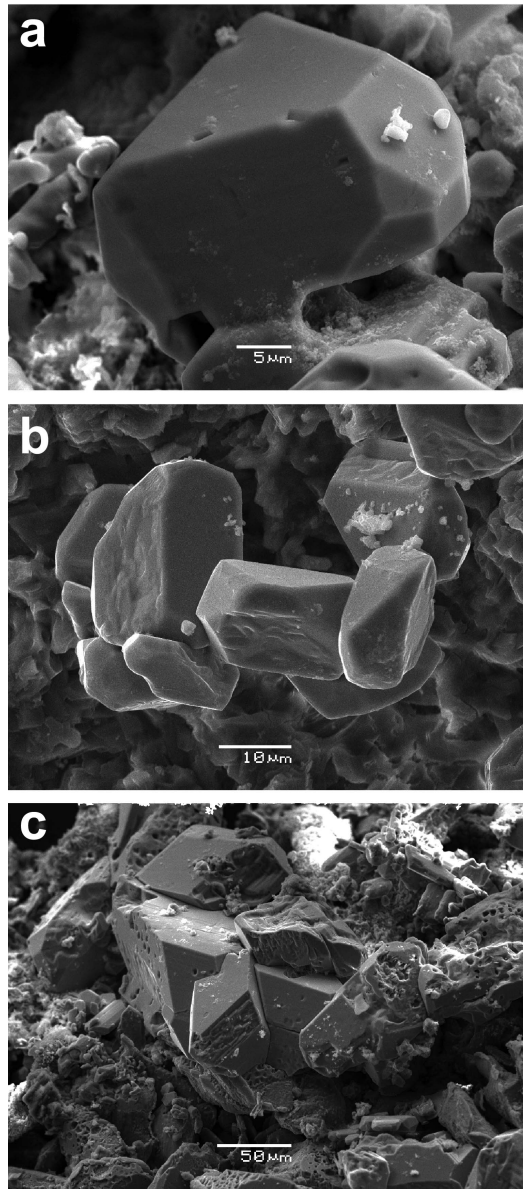

FIG. 3. Well shaped crystal (*a*) and crystal clusters (*b, c*) of ericlaxmanite. Scanning electron microscopy (SEM) secondary electron (SE) images.

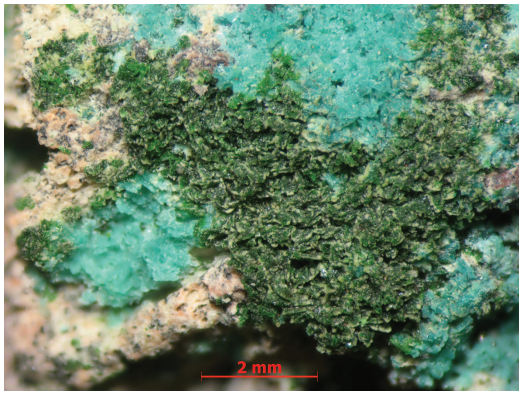

FIG. 4. Partial pseudomorph of green ericlaxmanite after light blue (turquoise) urusovite forming a crystal crust on volcanic scoria. Field of view: 9 mm across. Photo: I.V. Pekov and A.V. Kasatkin.

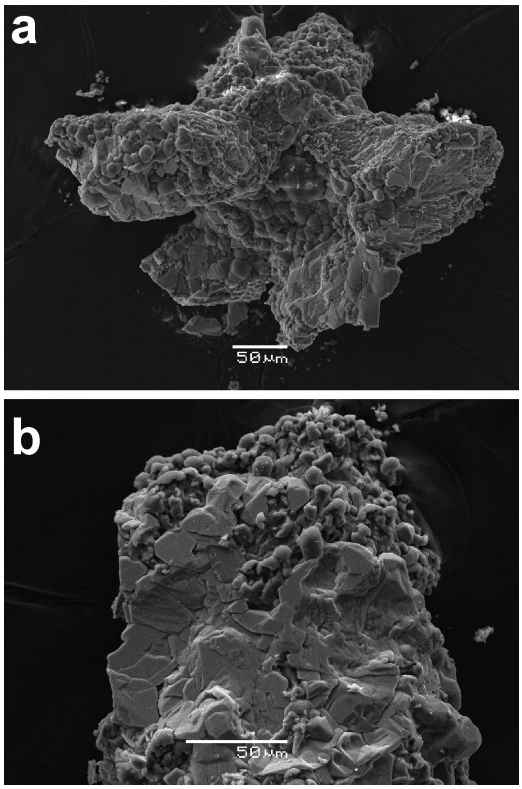

FIG. 5. Pseudomorphs of ericlaxmanite after urusovite: (*a*) fragment of urusovite crystal crust replaced by ericlaxmanite; (*b*) lamellar crystals of ericlaxmanite on the surface of a pseudomorph. SEM (SE) images.

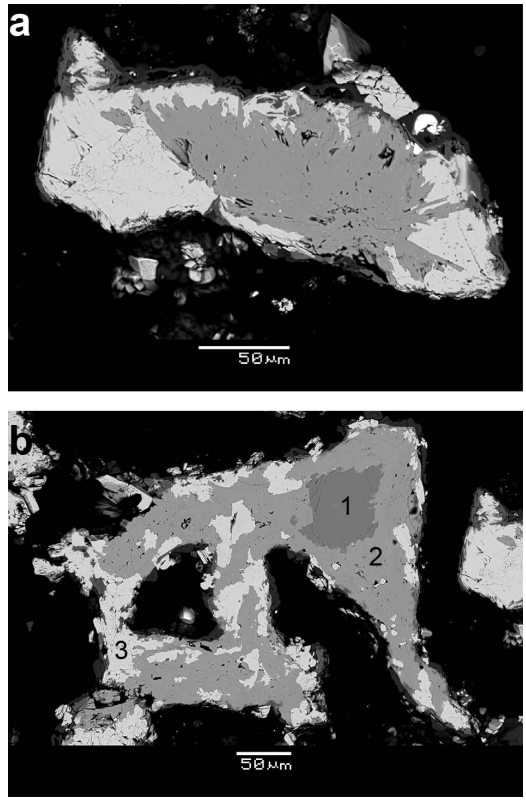

FIG. 6. (*a*) Overgrowth of a crystal cluster of urusovite (grey) by an ericlaxmanite crust (white) and (*b*) overgrowth (with partial replacement) of alarsite (1) by urusovite (2) and later ericlaxmanite (3). Polished sections, SEM (BSE) images.

Physical properties and optical data

Both new minerals are transparent with a vitreous lustre. Ericlaxmanite is green to dark green, with light green streak. Kozyrevskite is bright grass green to light yellowish green; its streak is very light green. Both are brittle, with Mohs' hardness ~3½. Ericlaxmanite shows one direction of distinct cleavage (observed under the microscope) and an uneven fracture. Kozyrevskite has (100) and (001) perfect cleavage and stepped fracture. Density was not measured because of the paucity of pure material for volumetric methods and lack of heavy liquids of the necessary density. Density values calculated from the empirical formulae are 5.036 g cm^{-3} for ericlaxmanite and 4.934 g cm^{-3} for kozyrevskite.

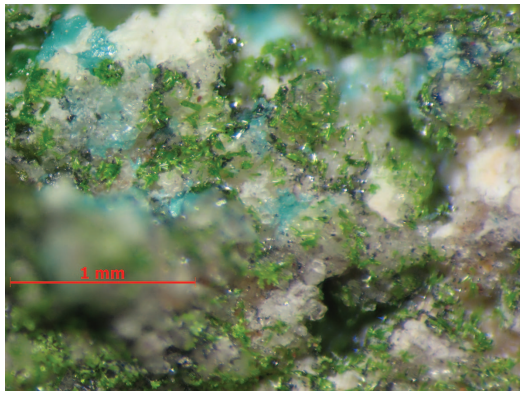

FIG. 7. Numerous grass-green prismatic crystals and crystal clusters of kozyrevskite with light blue urusovite and iron-black hematite on a crust consisting of colourless langbeinite and white As-bearing orthoclase. Field of view: 2.8 mm across. Photo: I.V. Pekov and A.V. Kasatkin.

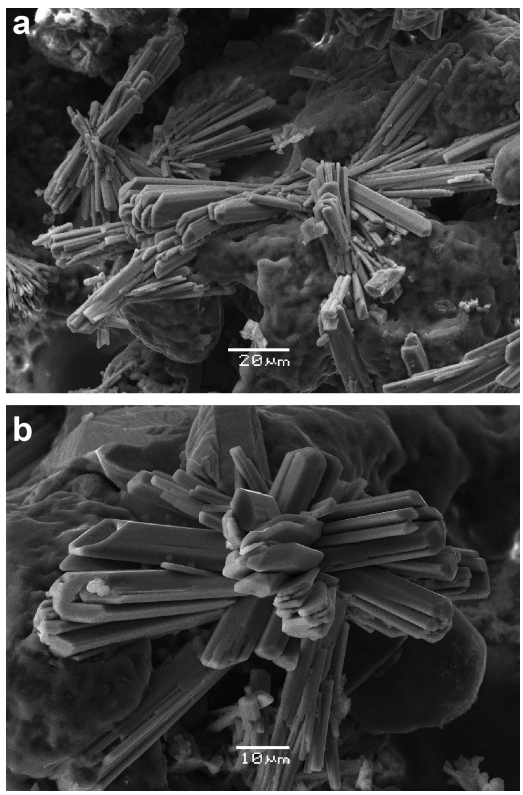

FIG. 8. Sheaf-like (*a*) and bush-like (*b*) clusters of kozyrevskite crystals. SEM (SE) images.

Ericlaxmanite is optically biaxial (−), α = 1.870(10), β = 1.900(10), γ = 1.915(10) (589 nm), $2V_{meas}$ = 60(15)º, $2V_{calc}$ = 70º. Dispersion of optical axes is weak, $r > v$. Pleochroism is strong, with the absorption scheme Z (bright green) > Y (green, with medium saturation of colour) > X (very pale green). Kozyrevskite is biaxial (−), α = 1.885(8), β = 1.895(8), γ = 1.900(8) (589 nm), $2V_{meas}$ = 75(10)º, $2V_{calc}$ = 70º. Dispersion is strong, $r > v$. Extinction is straight, elongation is negative. Orientation is $X = b$. Pleochroism is distinct with X (green) > Y, Z (yellowish green).

Raman spectroscopy

The Raman spectra of ericlaxmanite (Fig. 9*a*) and kozyrevskite (Fig. 9*b*) were obtained using a HORIBA Scientific XploRA System (Jobin Yvon) with a green laser (λ = 532 nm) at room temperature. The power of the laser beam at the sample was ~1 mW for ericlaxmanite and 3 mW for kozyrevskite. Spectra were processed using the *LabSpec 5* program from 100 to 3800 cm^{-1} with a diffraction grating (1800 mm^{-1}) and with a resolution ~2 cm^{-1}. The diameter of the focal spot on the sample was ~15 µm. The back-scattered Raman signal was collected with 50x objective; signal acquisition time for a single scan of the spectroscopic range was 100 s and the signal was averaged over five scans. Spectra were obtained for crystals oriented randomly.

In both spectra, bands in the region 700−900 cm^{-1} correspond to As^{5+}−O stretching vibrations of AsO_4^{3-} ions and bands with frequencies lower than 550 cm^{-1} correspond to As^{5+}−O bending vibrations and Cu^{2+}−O stretching vibrations. An absence of bands with frequencies greater than 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 new minerals. The Raman spectra of ericlaxmanite and kozyrevskite are quite different (Fig. 9).

Chemical composition

Chemical data for both new minerals were obtained using a Jeol JSM-6480LV scanning electron microscope equipped with an INCA-Wave 500 wavelength-dispersive spectrometer (WDS) (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 2.

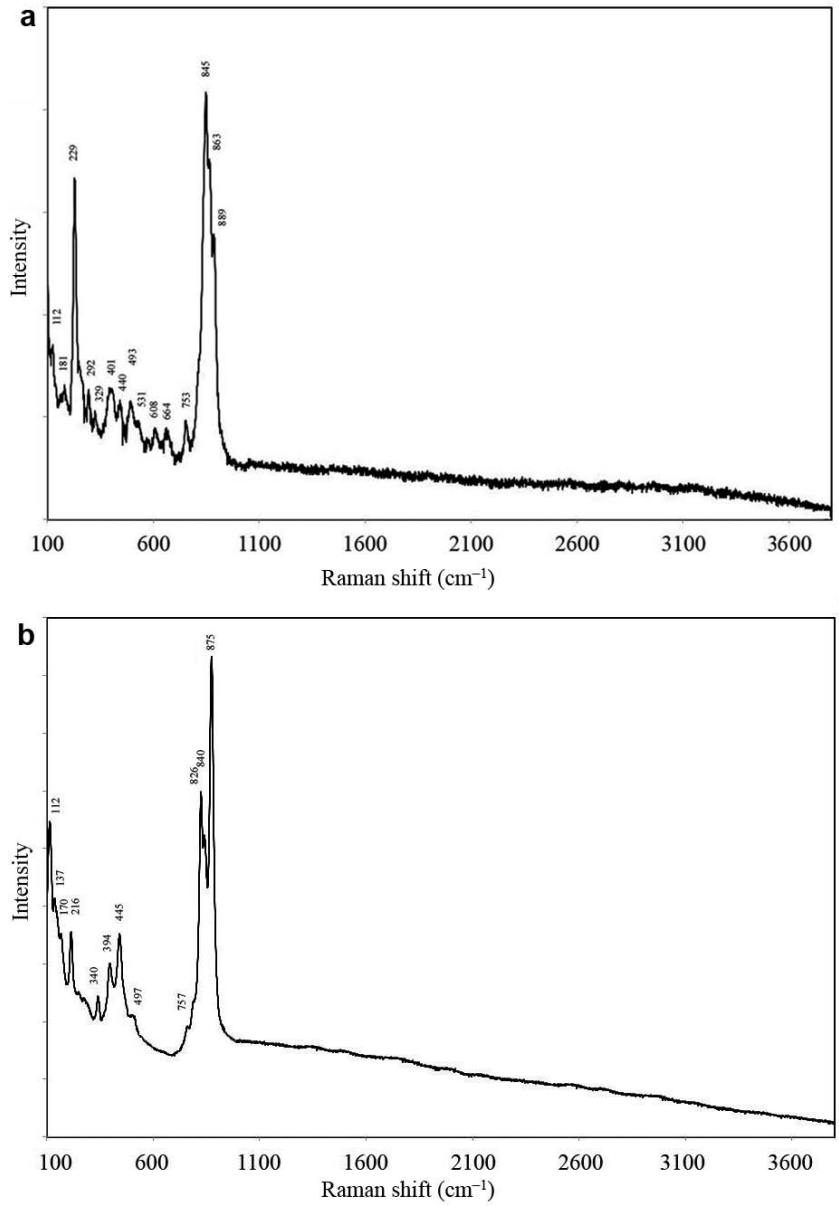

FIG. 9. Raman spectra of ericlaxmanite (*a*) and kozyrevskite (*b*).

The empirical formulae calculated on the basis on 9 O atoms per formula unit are ericlaxmanite: $(Cu_{3.97}Zn_{0.06}Fe_{0.02})_{\Sigma 4.05}(As_{1.94}P_{0.02}V_{0.01}S_{0.01})_{\Sigma 1.98}O_9$; kozyrevskite: $(Cu_{3.95}Zn_{0.07}Fe_{0.01})_{\Sigma 4.03}(As_{1.83}P_{0.09}S_{0.03}V_{0.02}Si_{0.01})_{\Sigma 1.98}O_9$. The idealized formula $Cu_4O(AsO_4)_2$ requires CuO 58.06, As_2O_5 41.94, total 100.00 wt.%.

Powder X-ray diffraction data

Powder X-ray diffraction data for ericlaxmanite (Table 3) and kozyrevskite (Table 4) 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). Unit-cell parameters

TABLE 2. Chemical composition (wt.%) of ericlaxmanite and kozyrevskite.*

	Ericlaxmanite	Kozyrevskite	Probe standard
CuO	57.55 (56.95–57.88)	58.06 (56.67–58.79)	$CuFeS_2$
ZnO	0.90 (0.58–1.27)	1.04 (0.69–1.31)	ZnS
Fe_2O_3*	0.26 (0.00–0.90)	0.12 (0.00–0.49)	FeS
SiO_2	0.00	0.12 (0.00–0.46)	Diopside
P_2O_5	0.23 (0.00–0.49)	1.23 (0.00–2.89)	GaP
V_2O_5	0.14 (0.00–0.43)	0.37 (0.00–0.84)	V
As_2O_5	40.57 (39.54–41.82)	38.78 (36.82–39.58)	FeAsS
SO_3	0.17 (0.00–0.57)	0.43 (0.00–0.86)	ZnS
Total	99.82	100.15	

* Average values from six spot analyses are given for ericlaxmanite and from four for kozyrevskite; ranges are in parentheses. Contents of other elements with atomic numbers greater than that of carbon are below detection limits. Fe is calculated as Fe^{3+} taking into account the strongly oxidizing conditions of the Arsenatnaya fumarole; only minerals of trivalent iron are found there (Pekov *et al*., 2014).

refined from the powder data are as follows. Ericlaxmanite is triclinic, a = 6.43(4), b = 7.66(5), c = 8.23(5) Å, α = 98.4(2), β = 112.5(2), γ = 98.5(2)º and V = 361(1) Å^3; kozyrevskite is orthorhombic, a = 8.257(6), b = 6.406(5), c = 13.80(1) Å and V = 730(2) Å^3.

Single-crystal X-ray diffraction data and crystal structures

Single-crystal X-ray studies of both minerals were carried out using an Xcalibur S diffractometer equipped with a CCD detector. Crystal data and experimental details are given in Table 5. The structure models were obtained by direct methods and refined to R = 0.0358 for ericlaxmanite and to R = 0.1049 for kozyrevskite with the the *SHELX* software package (Sheldrick, 2008). Atom coordinates and displacement parameters are given in Table 6 for ericlaxmanite and in Table 7 for kozyrevskite. Selected interatomic distances in the structures of both minerals are presented in Table 8.

The crystal structure of ericlaxmanite (Fig. 10*a*) is based on an interrupted framework built by edge- and corner-sharing Cu-centred

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

I_{obs}	d_{obs}	I_{calc}*	d_{calc}**	*h k l*
6	7.43	1, 4	7.416, 7.390	001, 010
16	5.902	13	5.891	$\bar{1}01$
4	5.140	1	5.144	$\bar{1}10$
32	4.736	1, 37	4.738, 4.721	011, $\bar{1}11$
16	4.509	18	4.500	$\bar{1}\bar{1}1$
24	4.126	18	4.138	110
46	3.868	45	3.860	101
100	3.685	100, 16, 58	3.695, 3.652, 3.643	020, $0\bar{1}2$, $0\bar{2}1$
15	3.493	15	3.483	$\bar{1}20$
15	3.372	24	3.365	$\bar{1}12$
11	3.201	6, 10	3.202, 3.178	$\bar{1}21$, $\bar{2}01$
71	3.063	9, 81, 17	3.063, 3.055, 3.050	$\bar{1}\bar{2}1$, 012, 021
58	2.957	74	2.965	$0\bar{2}2$
98	2.777	55, 85	2.784, 2.775	$\bar{2}12$, $\bar{2}\bar{1}1$
46	2.698	16, 44	2.712, 2.691	$\bar{1}03$, $\bar{2}\bar{1}2$
33	2.605	57	2.607	$\bar{2}21$

polyhedra (Fig. 11*a*). In the structure there are four main crystallographically independent Cu sites. The Cu(2) position is split into Cu(2) and Cu(2′) subsites (Fig. 12) with occupancy factors 0.915(16) and 0.085(16), respectively; the Cu(2)−Cu(2′) distance is 0.65(6) Å. Crystal structure refinement with a fully occupied Cu(2) site showed a relatively intense peak in the

Table 3 (*contd.*).

I_{obs}	d_{obs}	I_{calc}*	d_{calc}**	*h k l*
26	2.517	13, 35	2.517, 2.516	$0\bar{1}3$, 210
37	2.449	24, 25, 31	2.460, 2.441, 2.439	$2\bar{1}1$, $\bar{2}03$, $\bar{1}13$
21	2.367	15, 27	2.376, 2.360	121, $\bar{2}22$
31	2.308	13, 37	2.313, 2.303	$\bar{1}31$, $0\bar{2}3$
51	2.201	49, 46	2.203, 2.197	013, 031
17	2.103	17, 3, 12	2.103, 2.102, 2.091	$\bar{2}31$, $1\bar{3}2$, $\bar{3}01$
6	2.017	4, 11	2.024, 2.015	$\bar{1}04$, $\bar{1}32$
6	2.008	3	1.997	103
6	1.986	6	1.982	$2\bar{3}1$
6	1.973	2, 7	1.975, 1.965	$\bar{3}21$, $\bar{3}\bar{1}2$
4	1.941	2, 6	1.937, 1.936	$\bar{2}32$, 122
5	1.929	3, 4	1.932, 1.926	300, $\bar{3}22$
9	1.898	16	1.900	$0\bar{1}4$
14	1.871	3, 3, 23	1.873, 1.870, 1.868	023, 032, $1\bar{4}1$
11	1.823	3, 14, 8	1.826, 1.822, 1.821	$0\bar{2}4$, $0\bar{4}2$, $\bar{2}\bar{3}1$
19	1.744	1, 21, 11	1.746, 1.743, 1.739	$1\bar{4}2$, $\bar{3}04$, $\bar{1}\bar{4}1$
16	1.710	9	1.710	$\bar{2}41$
18	1.703	7, 3, 6	1.706, 1.701, 1.700	301, 230, $\bar{3}\bar{2}3$
2	1.665	2, 5	1.667, 1.664	$0\bar{4}3$, $\bar{1}24$
10	1.636	10	1.637	$1\bar{1}4$
41	1.605	25, 2, 56	1.608, 1.604, 1.603	$\bar{2}\bar{3}4$, $\bar{1}05$, $\bar{4}12$
20	1.584	19	1.586	203
12	1.552	16, 12	1.553, 1.552	$2\bar{4}2$, 222
12	1.529	12, 2, 8	1.531, 1.528, 1.528	231, $2\bar{3}3$, 024
14	1.520	2, 3, 16	1.524, 1.520, 1.517	$\bar{3}41$, $0\bar{1}5$, $1\bar{3}4$
16	1.499	2, 19, 3	1.500, 1.500, 1.498	$\bar{3}\bar{1}5$, $\bar{3}\bar{3}3$, $\bar{4}\bar{1}3$
14	1.492	8, 2	1.492, 1.491	$\bar{1}\bar{4}4$, $0\bar{5}2$
9	1.475	7	1.473	213
10	1.450	20, 7	1.451, 1.449	$\bar{2}43$, 400
15	1.431	9, 15, 8, 2	1.435, 1.431, 1.431, 1.429	$\bar{4}32$, $\bar{2}\bar{3}5$, $\bar{4}\bar{1}4$, $\bar{3}\bar{2}5$
16	1.424	5, 1, 1, 13	1.424, 1.423, 1.422, 1.422	$\bar{1}\bar{5}2$, $\bar{2}51$, 240, $\bar{2}25$
12	1.393	2, 21, 5	1.396, 1.392, 1.390	015, $\bar{4}24$, $\bar{4}30$
9	1.385	3, 3, 4	1.385, 1.384, 1.382	312, $\bar{1}25$, $\bar{4}33$
3	1.363	3, 2	1.365, 1.362	$1\bar{5}3$, 142
3	1.358	3	1.357	$2\bar{5}2$
5	1.348	2, 1, 2, 4	1.351, 1.348, 1.346, 1.346	$1\bar{1}5$, $\bar{2}52$, $\bar{4}\bar{2}4$, 034
7	1.339	10	1.339	$\bar{4}\bar{2}1$
15	1.327	6, 7, 7, 5, 2	1.328, 1.328, 1.328, 1.325, 1.325	$\bar{1}\bar{2}6$, $3\bar{2}3$, $3\bar{1}3$, $\bar{1}06$, $2\bar{3}4$
5	1.317	3, 2, 1	1.315, 1.314, 1.314	$\bar{3}06$, $\bar{3}\bar{1}6$, $\bar{3}\bar{4}3$
7	1.307	5, 9, 3	1.309, 1.304, 1.304	241, $0\bar{5}4$, $4\bar{3}1$
5	1.288	5, 4	1.287, 1.287	$3\bar{3}3$, 303
9	1.275	2, 6, 10, 8	1.277, 1.277, 1.274, 1.274	$\bar{3}\bar{4}1$, $\bar{3}16$, $1\bar{6}1$, $\bar{3}\bar{2}6$
4	1.267	2, 3	1.267, 1.265	322, $\bar{1}44$
3	1.257	2, 3	1.256, 1.255	214, $\bar{4}43$
3	1.252	2	1.251	411
3	1.237	1, 1, 3, 2	1.238, 1.237, 1.236, 1.236	$\bar{4}\bar{3}4$, $\bar{5}21$, 006, $\bar{2}60$

* For the calculated pattern, only reflections with intensities $\geqslant 1$ are given.
**For the unit-cell parameters calculated from single-crystal data.

TABLE 4. Powder X-ray diffraction data for kozyrevskite.

I_{obs}	d_{obs}	I_{calc}*	d_{calc}**	*h k l*
17	4.109	5, 9	4.129, 4.081	200, 112
34	3.728	30	3.737	013
100	3.455	18, 100	3.470, 4.451	210, 004
49	3.374	8, 24	3.404, 3.365	113, 211
72	3.194	32, 58	3.201, 3.184	020, 104
50	3.081	41	3.073	203
69	2.910	15, 53	2.917, 2.904	121, 022
48	2.861	37	2.851	114
82	2.732	74	2.740	122
87	2.712	69	2.700	301
92	2.509	7, 84, 29	2.530, 2.504, 2.489	220, 123, 221
23	2.370	22	2.362	303
16	2.294	18	2.295	205
36	2.217	38, 6	2.217, 2.216	223, 106
18	2.155	8, 2	2.161, 2.152	215, 304
11	2.096	8	2.094	116
37	2.064	27, 13	2.065, 2.064	400, 321
16	2.038	3, 4, 7	2.042, 2.040, 2.040	401, 224, 314
15	1.957	2, 4	1.965, 1.945	410, 305
17	1.925	4, 9	1.936, 1.918	033, 216
36	1.873	6, 40	1.878, 1.868	231, 026
9	1.771	8, 3	1.773, 1.772	134, 404
28	1.687	5, 22	1.689, 1.683	108, 422
19	1.646	5, 14	1.653, 1.645	405, 127
8	1.630	3	1.633	118
34	1.601	1, 10, 38	1.603, 1.601, 1.601	307, 415, 040
25	1.559	13	1.558	512
11	1.520	5, 3	1.519, 1.515	028, 334
22	1.490	12, 14	1.492, 1.490	019, 504
19	1.451	12, 7	1.452, 1.448	044, 037
27	1.436	2, 4, 31, 6	1.439, 1.438, 1.436, 1.433	335, 209, 522, 327
5	1.412	2, 1	1.417, 1.412	505, 433
25	1.385	36, 3	1.385, 1.384	426, 515
27	1.380	4, 17, 2	1.380, 1.377, 1.376	0.0.10, 341, 600
19	1.338	2, 5, 1	1.342, 1.340, 1.339	506, 309, 611
22	1.328	4, 7, 1	1.330, 1.325, 1.324	328, 343, 138
20	1.313	8, 1	1.313, 1.312	245, 229
21	1.304	6, 1	1.307, 1.303	435, 427
16	1.287	9, 3	1.283, 1.283	532, 2.1.10
14	1.267	2, 3, 7	1.268, 1.266, 1.265	0.2.10, 507, 440
11	1.244	5, 1, 1	1.246, 1.245, 1.244	039, 152, 442
5	1.225	2, 1	1.223, 1.223	428, 250
7	1.210	2, 1, 7	1.212, 1.210, 1.206	2.2.10, 615, 338
8	1.186	1, 2, 1	1.190, 1.188, 1.188	247, 154, 444
8	1.181	1, 2, 1	1.181, 1.181, 1.180	606, 535, 2.1.11
7	1.150	2, 2, 1	1.150, 1.150, 1.149	0.0.12, 445, 429
7	1.142	3	1.144	712
5	1.124	4, 1	1.124, 1.124	2.2.11, 509

* For the calculated pattern, only reflections with intensities $\geqslant 1$ are given. ** For the unit-cell parameters calculated from single-crystal data.

TABLE 5. Crystal data, data collection information and structure refinement details for ericlaxmanite and kozyrevskite.

Mineral	Ericlaxmanite	Kozyrevskite
Formula	$Cu_4O(AsO_4)_2$	
Formula weight	548	
Temperature (K)	293(2)	
Radiation and wavelength (Å)	MoK_α; 0.71073	
Crystal system, space group; Z	Triclinic, $P\bar{1}$; 2	Orthorhombic, *Pnma*; 4
Unit-cell dimensions (Å/º)	a = 6.4271(4)	a = 8.2581(4)
	b = 7.6585(4)	b = 6.4026(4)
	c = 8.2249(3)	c = 13.8047(12)
	α = 98.396(4)	
	β = 112.420(5)	
	γ = 98.397(5)	
V (Å^3)	361.11(3)	729.90(9)
Absorption coefficient μ (mm^{-1})	20.743	20.525
F_{000}	508	1016
Crystal size (mm)	0.05 × 0.11 × 0.12	0.03 × 0.05 × 0.16
Diffractometer	Xcalibur S CCD	
θ range for data collection (º)	2.75–28.28	2.87–24.40
Index ranges	$-8 \leqslant h \leqslant 8$	$-9 \leqslant h \leqslant 9$
	$-10 \leqslant k \leqslant 10$	$-7 \leqslant k \leqslant 7$
	$-10 \leqslant l \leqslant 10$	$-16 \leqslant l \leqslant 16$
Reflections collected	6493	8521
Independent reflections	1787 (R_{int} = 0.0406)	657 (R_{int} = 0.1318)
Independent reflections with $I > 2\sigma(I)$	1616	629
Structure solution	Direct methods	
Refinement method	Full-matrix least-squares on F^2	
Number of refined parameters	148	82
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0358	$R1$ = 0.1049
	$wR2$ = 0.0760	$wR2$ = 0.2484
R indices (all data)	$R1$ = 0.0418	$R1$ = 0.1090
	$wR2$ = 0.0784	$wR2$ = 0.2511
Gof	1.115	1.328
Largest diff. peak and hole, e (Å^{-3})	1.309 and −1.110	4.896 and −2.876

difference Fourier synthesis (4.78 e Å^{-3}) near Cu(2) and R = 0.0433. An attempt to split the Cu(2) site into two subsites was successful, the highest peak in the difference Fourier synthesis is 1.32 e Å^{-3} and R decreased to 0.0358. Cu(1) cations occupy sites in distorted tetragonal pyramids while the Cu(3) cations centre distorted trigonal bipyramids, taking into account elongated distances; each cation forms four short Cu–O bonds [1.936(4)–1.958(4) Å for Cu(1) and 1.901(4)–2.020(4) Å for Cu(3)] and one elongated bond: 2.646(5) Å [Cu(1)–O(8)] and 2.472(5) [Cu(3)–O(7)]. The Cu(4) cations occupy sites in [4+2] octahedra characterized by Jahn–Teller distortion; four Cu(4)–O bonds lie in the range 1.910(4)–2.006(4) Å and two bonds are elongated with distances 2.445(4) and 2.483(4) Å. The Cu(2) polyhedron could also be described as an octahedron distorted due to the Jahn–Teller effect; the Cu(2) cation is located in a distorted square planar environment [the Cu(2)–O distances are in the range 1.906(4)–2.042(4) Å] and forms two elongated bonds, 2.315(6) and 2.777(6) Å. It seems reasonable to include the elongated Cu(2)–O(4) distance [2.777(6) Å] in the primary coordination polyhedron of Cu(2) due to its contribution to bond-valence sums (Table 6) and the participation of an O(4) anion in the Cu(2′) five-fold polyhedra. Moreover, the Cu-layers [coplanar to (010)] consisting of the Cu(1–4) polyhedra are connected, forming the interrupted framework *via*

TABLE 6. Coordinates and equivalent isotropic displacement parameters (in Å^2) of atoms and site occupancy factors for ericlaxmanite.

Atom	*x/a*	*y/b*	*z/c*	U_{eq}	s.o.f.
As(1)	0.13069(10)	0.22820(8)	0.35367(7)	0.00938(16)	1
As(2)	0.50259(10)	0.28742(8)	0.08946(7)	0.00920(16)	1
Cu(1)	0.34652(12)	0.84130(10)	0.54832(9)	0.01140(19)	1
Cu(2)	0.3804(7)	0.6103(3)	0.2540(5)	0.0133(5)	0.915(16)*
Cu(2′)	0.288(8)	0.564(5)	0.186(6)	0.018(7)	0.085(16)*
Cu(3)	0.09419(12)	0.35782(11)	0.73392(9)	0.01450(19)	1
Cu(4)	0.14634(13)	0.87928(10)	0.08430(9)	0.01299(19)	1
O(1)	0.6263(7)	0.4856(5)	0.2516(5)	0.0112(8)	1
O(2)	–0.0032(7)	0.0699(6)	0.1583(5)	0.0118(8)	1
O(3)	0.1941(7)	0.7722(6)	0.2877(5)	0.0104(8)	1
O(4)	0.2337(7)	0.3090(6)	–0.0275(5)	0.0146(9)	1
O(5)	0.3420(7)	0.7207(6)	0.0356(6)	0.0143(9)	1
O(6)	0.5009(7)	0.8858(6)	0.8090(5)	0.0137(9)	1
O(7)	0.1739(8)	0.4347(6)	0.3161(6)	0.0184(10)	1
O(8)	0.3733(7)	0.1730(6)	0.4901(5)	0.0156(9)	1
O(9)	-0.0319(7)	0.2272(6)	0.4727(5)	0.0139(9)	1

The site occupancies for Cu(2) and Cu(2′) were restrained to give a sum of 1.00.

O(4) atoms in the vertices of Cu(2) and Cu(2′) polyhedra. The linkage between the layers is reinforced by isolated AsO_4 tetrahedra centred by two crystallographically independent As atoms. AsO_4 tetrahedra share common vertices with Cu polyhedra of adjacent layers.

All tested single crystals of kozyrevskite showed rather poor quality, being slightly divergent; this is thought to be the cause of the relatively high value of R = 0.1049 even for the best case. Thus we consider our results only as a structure model. During refinement, a restraint was used to refine the As(1)−O(7) distance. A restraint was also used to refine atoms with ADP problems [As(1), As(2), Cu(1), Cu(2), Cu(3), O(4−7)]. However, reasonable values of interatomic distances (Table 8), the close similarity of our results with the structure data obtained for the synthetic analogue of kozyrevskite (Adams *et al.*, 1995), and good accordance of the measured and calculated powder X-ray diffraction patterns (Table 4) confirm our structure model as being correct.

TABLE 7. Coordinates and equivalent isotropic displacement parameters (in Å^2) of atoms and site multiplicities (Q) for kozyrevskite.

Atom	*x/a*	*y/b*	*z/c*	U_{eq}	Q
As(1)	0.1613(4)	¼	0.4141(3)	0.0121(11)	4
As(2)	0.4976(4)	¼	0.6563(2)	0.0074(10)	4
Cu(1)	0.5804(5)	¼	0.4120(3)	0.0143(12)	4
Cu(2)	0.6426(3)	0.0057(4)	0.8450(2)	0.0099(10)	8
Cu(3)	0.3605(5)	¼	0.9480(3)	0.0143(12)	4
O(1)	0.605(3)	¼	0.7595(19)	0.016(6)	4
O(2)	0.598(3)	¼	0.9703(18)	0.013(5)	4
O(3)	0.620(3)	¼	0.561(2)	0.027(7)	4
O(4)	0.407(2)	−0.028(3)	0.8627(12)	0.014(4)	8
O(5)	0.385(2)	0.034(3)	0.6503(12)	0.012(4)	8
O(6)	0.313(3)	¼	0.0882(18)	0.015(6)	4
O(7)	0.3543(14)	¼	0.405(2)	0.034(8)	4

TABLE 8. Selected interatomic distances (Å) in the structures of ericlaxmanite and kozyrevskite.

Ericlaxmanite		**Kozyrevskite**	
As(1)–O(7)	1.660(4)	As(1)–O(7)	1.599(11)
–O(9)	1.683(4)	–O(2)	1.68(3)
–O(2)	1.693(4)	–O(4)	1.683(18) × 2
–O(8)	1.693(4)		
As(2)–O(6)	1.669(4)	As(2)–O(3)	1.65(3)
–O(4)	1.673(4)	–O(5)	1.667(17) × 2
–O(5)	1.686(4)	–O(1)	1.68(3)
–O(1)	1.721(4)		
Cu(1)–O(3)	1.936(4)	Cu(1)–O(7)	1.870(13)
–O(6)	1.940(4)	–O(6)	1.92(3)
–O(9)	1.947(4)	–O(5)	2.034(18) × 2
–O(8)	1.958(4)	–O(3)	2.09(3)
–O(8)	*2.646(5)*	Cu(2)–O(6)	1.914(13)
		–O(4)	1.976(18)
Cu(2)–O(3)	1.906(4)	–O(1)	1.985(16)
–O(1)	1.967(5)	–O(5)	2.010(18)
–O(7)	2.006(5)	–O(2)	2.360(19)
–O(5)	2.042(4)		
–O(8)	2.315(6)	Cu(3)–O(6)	1.97(3)
–O(4)	*2.777(6)*	–O(2)	1.99(2)
Cu(2′)–O(7)	1.834(14)	–O(3)	1.99(3)
–O(5)	1.930(13)	–O(4)	2.169(18) × 2
–O(3)	1.97(2)		
–O(1)	2.23(3)		
–O(4)	2.32(4)		
Cu(3)–O(3)	1.901(4)		
–O(4)	1.940(4)		
–O(1)	1.961(4)		
–O(9)	2.020(4)		
–O(7)	*2.472(5)*		
Cu(4)–O(3)	1.910(4)		
–O(5)	1.976(4)		
–O(2)	1.977(4)		
–O(2)	2.006(4)		
–O(6)	2.445(4)		
–O(4)	2.483(4)		

The crystal structure of kozyrevskite (Fig. 10*b*) is based on complicated ribbons of Cu-centred polyhedra running along the *b* axis (Figs 11*b*,*c*). Each ribbon consists of two zig-zag chains formed by edge-sharing Cu(1)-centred, distorted trigonal bypiramids; the Cu(1)–O distances lie in the range 1.89(5)–2.15(4) Å and Cu(2)-centred square pyramids have four Cu(2)–O distances in the range 1.885(19)–1.99(2) Å with the fifth being 2.37(2) Å. Cu(3) trigonal bypiramids (Cu(3)–O distances are in the range of 1.98(4)–2.17(2) Å) link adjacent chains sharing edges with two Cu(2)-centred polyhedra belonging to the same chain and one Cu(1)-centred polyhedron belonging to another chain. Two crystallographically independent As atoms occupy sites in tetrahedra which play different roles. As(1) tetrahedra link adjacent ribbons of

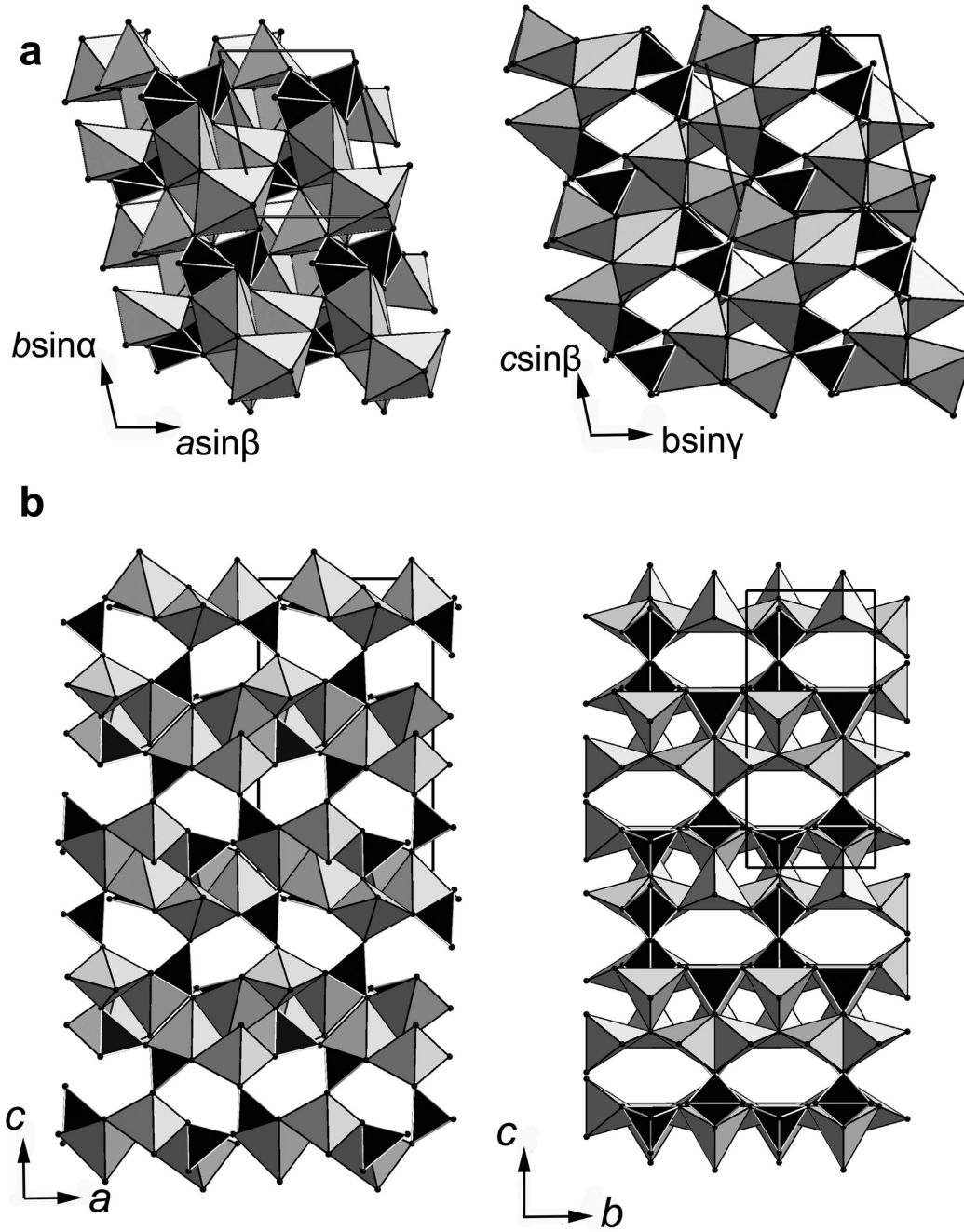

FIG. 10. Crystal structures of ericlaxmanite projected down the *c* and *a* axes (*a*) and kozyrevskite in two projections (*b*). Cu-centred polyhedra are grey, AsO_4 tetrahedra are black.

Cu-centred polyhedra forming heteropolyhedral layers coplanar to (001) while As(2) tetrahedra link neighbouring layers to form a three-dimensional *quasi*-framework (Fig. 10*b*).

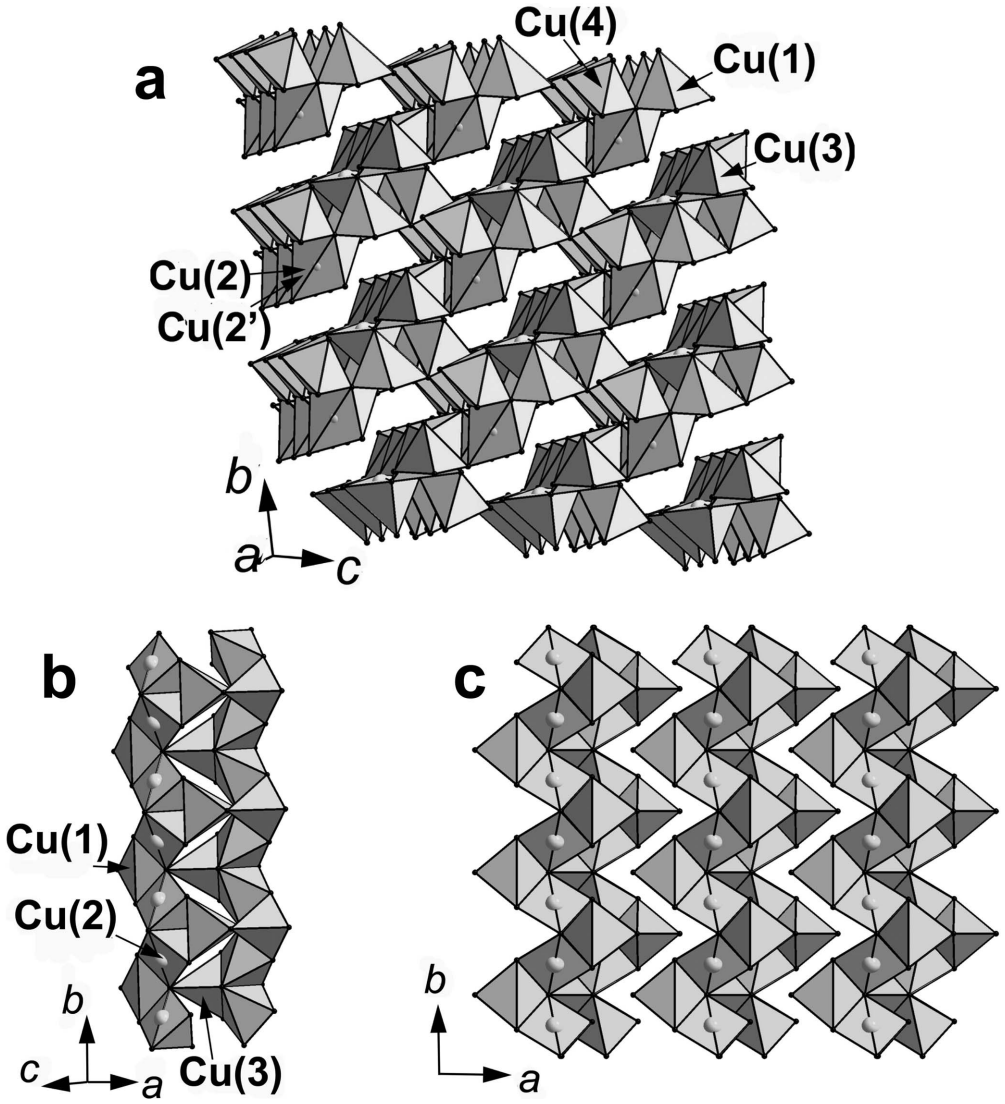

FIG. 11. Motifs of Cu-centred polyhedra in crystal structures of two natural modifications of $Cu_4O(AsO_4)_2$: (*a*) interrupted framework in ericlaxmanite; (*b*,*c*) complicated ribbons in kozyrevskite [*b* – separate ribbon, *c* – the motif in the (001) projection]. For legend see text and Tables 5–6.

Discussion

The crystal structures of the two natural modifications of $Cu_4O(AsO_4)_2$ are quite different, firstly in the topologies of the main building units, cationic copper motifs. In ericlaxmanite Cu-centred polyhedra form an interrupted framework (Fig. 11*a*) whereas in kozyrevskite we observe complicated ribbons (Figs 11*b*, *c*). Copper cations in ericlaxmanite have five-fold and six-fold coordination whereas in kozyrevskite all three crystallographically independent Cu cations centre five-fold polyhedra. The structure of ericlaxmanite is markedly denser than that of kozyrevskite (Table 1). All these structural differences cause significant differences in unit-cell dimensions, X-ray powder patterns, crystal morphology and physical properties (including

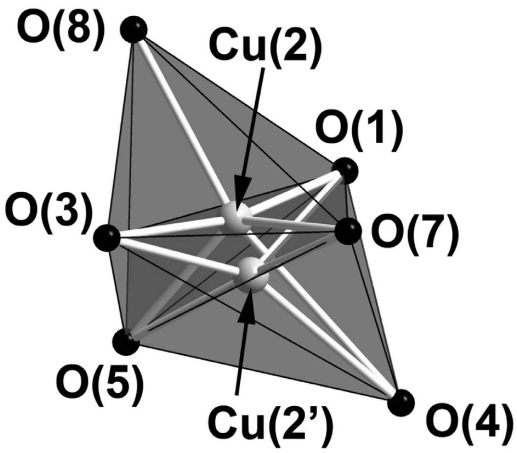

FIG. 12. The oxygen polyhedron around the split Cu(2) position in ericlaxmanite. The Cu(2)−O and Cu(2′)−O distances are given in Table 8.

Raman spectra and optical data) (Table 1; Figs 1, 3, 8 and 9).

No minerals related closely to ericlaxmanite and kozyrevskite in terms of stoichiometry and structure are known but both new species have synthetic analogues. For ericlaxmanite, there is triclinic $Cu_4O(AsO_4)_2$ ($P\bar{1}$, a = 6.4148, b = 7.6549, c = 8.2241 Å, α = 98.521, β = 112.394, γ = 98.378º and V = 360.13 Å^3) reported by Staack and Müller-Buschbaum (1996). The isostructural synthetic phosphate $Cu_4O(PO_4)_2$ has also been studied well (Anderson *et al.*, 1978; Brunel-Laugt *et al.*, 1978). Kozyrevskite is the natural analogue of synthetic orthorhombic $Cu_4O(AsO_4)_2$ (*Pnma*, a = 8.253, b = 6.4122, c = 13.789 Å and V = 729.7 Å^3; Adams *et al.*, 1995) and the orthorhombic modification of $Cu_4O(PO_4)_2$ adopts the same structure (Schwunck *et al.*, 1998). Both synthetic modifications of $Cu_4O(AsO_4)_2$ were prepared from a mixture of powdered CuO and $As_2O_5{\cdot}xH_2O$, an analogue of ericlaxmanite at 1050ºC (Staack and Müller-Buschbaum, 1996) and an analogue of kozyrevskite at 1090ºC in a $BaCO_3$ flux (Adams *et al.*, 1995).

The structures of both new minerals could be described in terms of anion-centred tetrahedra. All these arsenates and phosphates contain isolated OCu_4 tetrahedra, as do fingerite, $Cu_3(Cu_4O)_2(VO_4)_6$ (Finger, 1985) and several synthetic vanadates (Krivovichev, 2009).

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