



Ziminaite, $\text{Fe}^{3+}\text{VO}_4$, a new howardevansite-group mineral from the Bezmyannyi volcano, Kamchatka, Russia

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Received: 10 June 2017 / Accepted: 16 November 2017 / Published online: 4 December 2017
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Abstract

The new mineral ziminaite, ideally $\text{Fe}^{3+}\text{VO}_4$, was found in fumarole sublimates at the Bezmyannyi volcano, Kamchatka, Russia. Ziminaite occurs as lamellar, tabular or flattened prismatic crystals up to $10 \times 30 \times 50 \mu\text{m}$ typically epitaxially overgrowing koksharovite, and as aggregates (up to 0.15 mm) associated with bannermanite in cavities in volcanic scoria. The mineral is translucent, yellowish-brown with an adamantine luster. The calculated density is 3.45 g cm^{-3} . In reflected light, ziminaite is light grey. Birefractance is weak, internal reflections are deep yellow. The reflectance values [$R_{\text{max}}-R_{\text{min}}$, % (λ , nm)] are: 17.7–16.3 (470), 15.7–14.1 (546), 15.1–13.8 (589), 14.7–13.6 (650). Chemical composition (wt%) is: MgO 2.20, CaO 0.01, Al_2O_3 7.81, Fe_2O_3 27.18, TiO_2 4.50, SiO_2 0.26, P_2O_5 0.09, V_2O_5 57.01, total 99.06. The empirical formula, based on 24 O atoms, is: $(\text{Fe}^{3+}_{3.29}\text{Al}_{1.48}\text{Ti}_{0.54}\text{Mg}_{0.53})_{\Sigma 5.84}(\text{V}_{6.05}\text{Si}_{0.04}\text{P}_{0.01})_{\Sigma 6.10}\text{O}_{24}$ ($Z=1$). Ziminaite is triclinic, $P\bar{1}$, a 8.012(4), b 9.345(5), c 6.678(3) Å, α 106.992(10), β 101.547(8), γ 96.594(11)°, V 460.4(4) Å³, $Z=6$. The strongest reflections of the powder X-ray diffraction pattern [d , Å(hkl)] are: 3.751(17)(1–21, 12–1), 3.539(86)(120), 3.270(67)(01–2), 3.209(100)(2–20), 3.090(20)(2–11, 002), 3.041(18)(03–1, 02–2), 2.934(14)(12–2, 030) and 1.665(24)(023, 12–4). The crystal structure, solved from single-crystal data ($R_1=0.085$), is based upon heteropolyhedral framework built by VO_4 tetrahedra and Fe^{3+} -centred octahedra and five-fold polyhedra. Ziminaite belongs to the howardevansite group being its first member without species-defining uni- or divalent cations and with all large cation sites vacant. The mineral is named after the Zimina volcano situated near the discovery locality.

Keywords Ziminaite · New mineral · Howardevansite group · Fumarole sublimate · Bezmyannyi volcano

Introduction

Vanadium is a typical constituent of fumarolic gases at many volcanoes. An exhalation vanadium mineralization is known at some of them and its character strongly depends, taking into account easy change of V from one valence state to another, on the redox of a mineral-forming fumarole system

(Ostrooumov and Taran 2016). In oxidizing-type fumaroles, where high oxygen fugacity is caused by the mixing of volcanic gases with the atmospheric air (Meniaylov et al. 1980; Taran et al. 2001), vanadates and V^{5+} oxides crystallize. Vanadates are nowadays known in fumarole sublimates at three active volcanoes: Izalco in El Salvador and Tolbachik and Bezmyannyi, both in Kamchatka, Russia. Their diversity is significant: there are 18 valid species, all H-free, namely stoiberite $\text{Cu}_5\text{O}_2(\text{VO}_4)_2$ (Birnie and Hughes 1979), ziesite $\beta\text{-Cu}_2\text{V}_2\text{O}_7$ (Hughes and Birnie 1980), fingerite $\text{Cu}_{11}\text{O}_2(\text{VO}_4)_6$ (Hughes and Hadidiacos 1985), blossomite $\alpha\text{-Cu}_2\text{V}_2\text{O}_7$ (Robinson et al. 1987), lyonsite $\text{Cu}_{3+x}(\text{Fe}^{3+}_{4-2x}\text{Cu}_{2x})(\text{VO}_4)_6$, with $0 \leq x \leq 1$ (Hughes et al. 1987a; Pekov et al. 2013b), mcbirneyite $\text{Cu}_3(\text{VO}_4)_2$ (Hughes et al. 1987b), howardevansite $\text{NaCuFe}^{3+}_2(\text{VO}_4)_3$ (Hughes et al. 1988), leningradite $\text{PbCu}_3(\text{VO}_4)_2\text{Cl}_2$ (Vergasova et al. 1990), averievite $\text{Cu}_6\text{O}_2(\text{VO}_4)_2\text{Cl}_2 \cdot n(\text{K,Cs,Rb})\text{Cl}$ (Vergasova et al. 1998), pseudolyonsite $\text{Cu}_3(\text{VO}_4)_2$ (Zelenski et al. 2011), starovaite $\text{KCu}_5\text{O}(\text{VO}_4)_3$, schäferite $\text{NaCa}_2\text{Mg}_2(\text{VO}_4)_3$

Editorial handling: L. Nasdala

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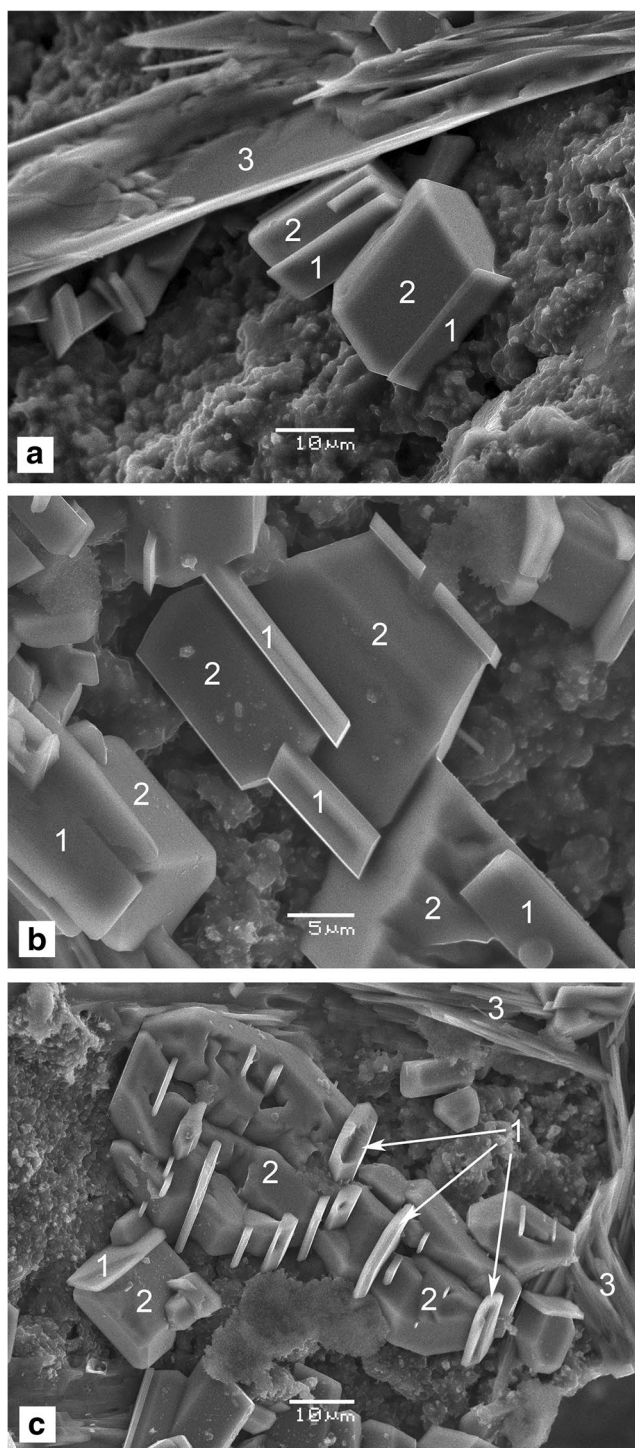


Fig. 1 Crystals of zimaite (marked 1 on the pictures) epitaxially overgrowing koksharovite crystals (2) with bannermanite (3) on the surface of volcanic scoria. Secondary electron images

(Pekov et al. 2013a), yaroshevskite $\text{Cu}_9\text{O}_2(\text{VO}_4)_4\text{Cl}_2$ (Pekov et al. 2013c), grigorievite $\text{Cu}_3\text{Fe}^{3+}_2\text{Al}_2(\text{VO}_4)_6$, koksharovite $\text{CaMg}_2\text{Fe}^{3+}_4(\text{VO}_4)_6$ (Pekov et al. 2014), kainotropite $\text{Cu}_4\text{Fe}^{3+}\text{O}_2(\text{V}_2\text{O}_7)(\text{VO}_4)$ (Pekov et al. 2015), borisenkoite

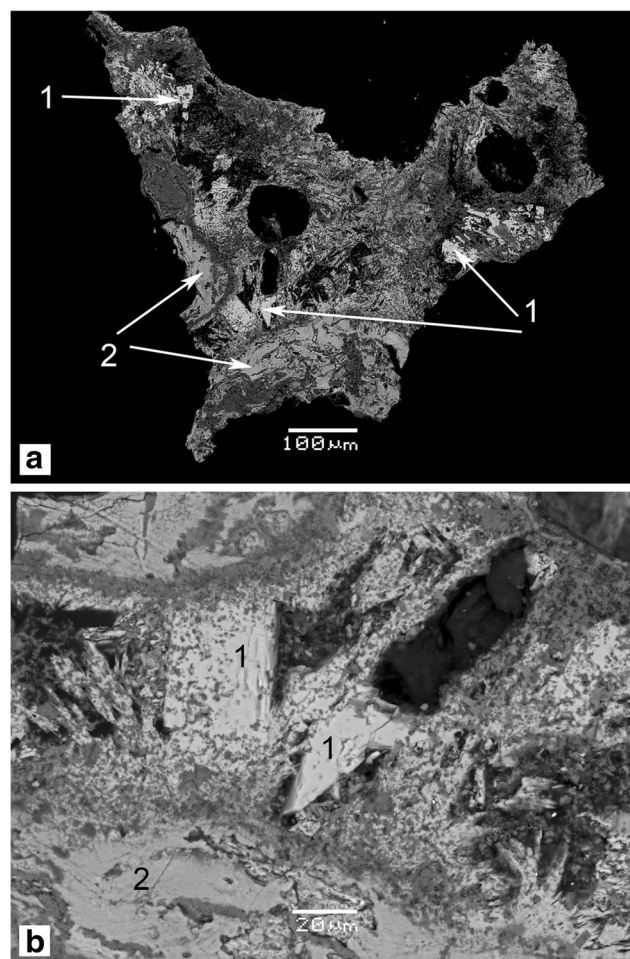


Fig. 2 Polished sections of crystals and aggregates of zimaite (1) and crusts of bannermanite (2) in cavities of porous volcanic scoria altered by fumarole gas: (a) general view; (b) magnified fragment. Backscattered electron images

$\text{Cu}_3[(\text{V,As})\text{O}_4]_3$ (Pekov et al. 2016), and zimaite $\text{Fe}^{3+}\text{VO}_4$. All them are rare minerals endemic in nature for fumarole deposits; some of them were also found in anthropogene objects – burnt dumps of mining enterprises (Witzke and Rüger 1998; Koshlyakova et al. 2017), being formed under the conditions similar to fumarolic ones. Note for comparison that the whole number of H-free vanadate minerals described from all other geological formations is the same: 18 species.

The Bezmyannyi volcano (55°58'N 160°36'E) is the type locality of three fumarolic minerals, all with species-defining V^{5+} : shcherbinaite V_2O_5 (Borisenko 1972), koksharovite (Pekov et al. 2014), and described in this paper a new vanadate zimaite (Cyrillic: зими́наит) named after the picturesque Zimina volcano situated 12 km south of Bezmyannyi. Both the new mineral and its name have been approved by the IMA Commission on New Minerals, Nomenclature and Classification (IMA2014-062). The type specimen of zimaite is

Table 1 Reflectance data for ziminaite

λ (nm)	R_{\min} (%)	R_{\max} (%)
400	19.4	20.8
420	18.5	19.9
440	17.6	19.0
460	16.7	18.1
480	15.8	17.2
500	15.1	16.6
520	14.6	16.1
540	14.2	15.8
560	14.0	15.5
580	13.8	15.2
600	13.7	15.0
620	13.7	14.9
640	13.6	14.7
660	13.6	14.7
680	13.5	14.6
700	13.5	14.6

deposited in the systematic collection of the Fersman Mineralogical Museum of the Russian Academy of Sciences, Moscow, with the catalogue number 94996.

Occurrence and general appearance

Ziminaite was found in a single specimen collected in 1985 by one of the authors (PMK). This is the same sample in which koksharovite was earlier discovered. Ziminaite occurs as lamellar, tabular or flattened prismatic crystals, sometimes skeletal, up to $10 \times 30 \times 50 \mu\text{m}$ (usually from 5 to 20 μm) in size. Typically they epitaxially overgrow crystals of chemically and structurally related koksharovite located on the surface of volcanic scoria (Fig. 1). Ziminaite was also found as separate crystals (usually cavernous, with numerous inclusions of particles of scoria) and their groups or as

Table 2 Powder X-ray diffraction data for ziminaite

I_{obs}	d_{obs} (Å)	I_{calc}^a	d_{calc} (Å) ^b	hkl
9	6.46	15	6.414	1–10
6	6.18	3	6.190	001
5	4.454	2	4.429	011
12	3.880	7	3.857	200
17	3.751	7, 4	3.771, 3.739	1–21, 12–1
86	3.539	100	3.545	120
7	3.466	5	3.460	111
67	3.270	52	3.270	01–2
100	3.209	98	3.207	2–20
12	3.154	14	3.153	10–2
20	3.090	13, 11	3.100, 3.095	2–11, 002
18	3.041	10, 9	3.057, 3.035	03–1, 02–2
14	2.934	11, 1	2.940, 2.928	12–2, 030
5	2.750	2	2.753	1-1-2
13	2.655	9, 9	2.661, 2.656	012, 102
6	2.599	3	2.601	3–10
9	2.524	16, 6	2.530, 2.528	2-1-2, 22–2
7	2.216	10, 1, 1	2.223, 2.217, 2.214	1–40, 11–3, 022
4	2.167	1, 3, 1, 2, 1	2.172, 2.171, 2.168, 2.161, 2.161	12–3, 01–3, 202, 14–1, 3-1-2
4	2.097	3, 2, 8	2.107, 2.092, 2.085	2–32, 21–3, 2–41
6	1.875	1, 7, 5	1.882, 1.881, 1.871	23–3, 103, 4-2-1
5	1.844	3	1.846	30–3
24	1.665	2, 23	1.671, 1.665	023, 12–4
13	1.641	1, 1, 16	1.643, 1.641, 1.640	312, 34–2, 34–1
5	1.613	1, 3	1.615, 1.614	13–4, 3-2-3
7	1.571	4, 1, 1, 4	1.573, 1.570, 1.567, 1.565	42–3, 5–10, 042, 4–41
6	1.549	2, 1, 1, 1, 1, 6	1.551, 1.551, 1.550, 1.549, 1.548, 1.548	1–61, 5-2-1, 4–22, 123, 5–20, 004
3	1.500	1, 5	1.501, 1.499	2–61, 30–4
3	1.482	2, 1, 1	1.483, 1.482, 1.479	2–53, 421, 16–2
2	1.424	1	1.426	4–51

^aFor the calculated pattern, only reflections with intensities ≥ 1 are given

^bFor the unit cell parameters calculated from single-crystal data

Table 3 Crystal data, data collection information and structure refinement details for ziminaite

Crystal data	
Crystal system	Triclinic
Space group	<i>P</i> -1
Unit cell dimensions	
<i>a</i> (Å)	8.012(4)
<i>b</i> (Å)	9.345(5)
<i>c</i> (Å)	6.678(3)
α (°)	106.992(10)
β (°)	101.547(8)
γ (°)	96.594(11)
Unit-cell volume (Å ³)	460.4(4)
Absorption coefficient (mm ⁻¹)	5.892
Crystal size (mm)	0.008 × 0.008 × 0.01
Data collection	
Temperature (K)	296(2)
Radiation, wavelength (Å)	MoK α , 0.71073
θ range (°)	2.319–27.992
<i>h</i> , <i>k</i> , <i>l</i> ranges	–10 → 9 –12 → 12 –8 → 8
Total reflections collected	4508
Unique reflections (R_{int})	2074 (0.0597)
Unique reflections $F > 4\sigma(F)$	1422
Structure refinement	
Weighting coefficients <i>a</i> , <i>b</i> *	0.0764, 30.7816
Restraints/parameters	3/171
$R_1 [F > 4\sigma(F)]$, $wR_2 [F > 4\sigma(F)]$	0.0851, 0.2308
R_2 all, wR_2 all	0.1231, 0.2486
Gof on F^2	1.123

spongy aggregates (up to 0.15 mm across) of irregularly shaped grains filling small cavities in porous volcanic scoria altered by fumarole gas (Fig. 2). The new mineral is closely associated, besides koksharovite, with bannermanite and an insufficiently characterized Ca vanadate; quartz, biotite and Ti- and V-bearing magnetite are earlier minerals.

Ziminaite is a fumarolic mineral. It was deposited directly from volcanic gas as a sublimate or (more probably) was formed as a result of gas-rock interaction. The host rock, a volcanic scoria, seems the most probable source of Al, Mg and Ti, these having low volatilities in fumarole gases (Symonds and Reed 1993).

Physical properties and optical data

Ziminaite is translucent, yellowish-brown with an adamantine luster. The streak is yellow. The Vickers hardness number is 426 with the range 379–495 kgf mm⁻² (load 20 g). The Mohs hardness calculated from the VHN value is approximately 4½. Ziminaite is brittle. According to the data

of observations under the scanning electron microscope, the mineral does not demonstrate cleavage or parting, and its fracture is uneven. Density could not be measured because of the tiny size and cavernous character of grains. The density calculated using the empirical formula is 3.448 g cm⁻³.

In reflected light, ziminaite is light grey, and pleochroism was not observed. Birefractance is weak, $\Delta R = 1.3\%$ (589 nm). Internal reflections are intense, deep yellow. Anisotropism is weak. The reflectance values measured by means of a MSF-21 microspectrophotometer using the SiC standard (Zeiss, No. 545) are given in Table 1.

Chemical composition

The chemical composition of ziminaite was studied using a Jeol JSM-6480LV scanning electron microscope equipped with an INCA-Wave 500 wavelength-dispersive spectrometer. The system was operated at 20 kV acceleration voltage and 20 nA beam current, and the electron beam was focused to a spot with 2 μ m diameter. The following calibrant materials were used: olivine (Mg, Si), CaWO₄ (Ca), Al₂O₃ (Al), FeAsS (Fe), TiO₂ (Ti), GaP (P), and Cu₃VS₄ (V). Contents of other elements with atomic numbers higher than oxygen are below their detection limits. Iron is considered as Fe³⁺ from the crystal structure refinement of ziminaite and on data for all structurally related minerals and synthetic compounds (see below).

The chemical composition of ziminaite (averages of 5 spot analyses; wt%, ranges are in parentheses) is: MgO 2.20 (2.03–2.53), CaO 0.01 (0.00–0.04), Al₂O₃ 7.81 (6.01–9.61), Fe₂O₃ 27.18 (25.30–30.08), TiO₂ 4.50 (3.93–5.15), SiO₂ 0.26 (0.19–0.38), P₂O₅ 0.09 (0.00–0.16), V₂O₅ 57.01 (56.58–57.79), total 99.06.

The empirical formula calculated on the basis of 24 O atoms per formula unit is: (Fe³⁺_{3.29}Al_{1.48}Ti_{0.54}Mg_{0.53}) Σ 5.84(V_{6.05}Si_{0.04}P_{0.01}) Σ 6.10O₂₄ (*Z* = 1). The idealized, end-member formula is Fe³⁺VO₄ (*Z* = 6), which requires Fe₂O₃ 46.75, V₂O₅ 53.25, total 100.00 wt%.

X-ray crystallography

Powder X-ray diffraction data of ziminaite (Table 2) were collected with a Rigaku R-Axis Rapid II single-crystal diffractometer equipped with cylindrical image plate detector using Debye–Scherrer geometry (CoK α radiation, *d* = 127.4 mm). The triclinic unit cell parameters refined from the powder data are: *a* = 8.01(2), *b* = 9.34(3), *c* = 6.67(2) Å, α = 107.00(8), β = 101.58(7), γ = 96.57(8)°, and *V* = 459.6(8) Å³.

A single-crystal X-ray study of ziminaite was carried out using a Bruker SMART diffractometer equipped with an

Table 4 Atom coordinates and equivalent displacement parameters for ziminaite

Site	Site occupancy	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> _{eq} (Å ²)
<i>M</i> (1)	Fe* _{0.62(2)} Al** _{0.38(2)}	0.6926(4)	0.4069(3)	0.7524(4)	0.0085(6)
<i>M</i> (2)	Fe* _{0.63(2)} Al** _{0.37(2)}	0.3048(4)	0.0098(3)	0.9660(4)	0.0082(6)
<i>M</i> (3)	Fe* _{0.53(2)} Al** _{0.47(2)}	0.8915(4)	0.2155(4)	0.4661(5)	0.0152(7)
<i>V</i> (1)	V	0.9960(3)	0.2548(3)	0.0031(4)	0.0049(5)
<i>V</i> (2)	V	0.6005(3)	0.3420(3)	0.1984(4)	0.0060(6)
<i>V</i> (3)	V	0.2970(4)	0.1224(3)	0.5193(4)	0.0095(6)
<i>O</i> (1)	O	0.4798(17)	0.2504(13)	0.6457(19)	0.022(3)
<i>O</i> (2)	O	0.4396(16)	0.4278(13)	0.254(2)	0.020(3)
<i>O</i> (3)	O	0.6997(16)	0.4246(11)	0.0506(18)	0.015(2)
<i>O</i> (4)	O	0.0999(14)	0.4277(12)	0.1555(17)	0.012(2)
<i>O</i> (5)	O	0.7354(15)	0.3580(12)	0.4520(17)	0.014(2)
<i>O</i> (6)	O	0.8704(14)	0.2644(11)	0.7560(16)	0.009(2)
<i>O</i> (7)	O	0.1215(17)	0.2129(15)	0.524(2)	0.025(3)
<i>O</i> (8)	O	0.8686(14)	0.1785(12)	0.1540(17)	0.011(2)
<i>O</i> (9)	O	0.7305(14)	0.0212(11)	0.3550(16)	0.010(2)
<i>O</i> (10)	O	0.2952(16)	0.0329(13)	0.2592(18)	0.017(2)
<i>O</i> (11)	O	0.1443(15)	0.1486(12)	0.9516(18)	0.015(2)
<i>O</i> (12)	O	0.5230(14)	0.1447(11)	0.0504(17)	0.012(2)

Fe* = Fe + Ti

Al** = Al + Mg

APEX II CCD detector operating with MoK α radiation at 50 kV and 40 mA. The studied crystals were very tiny and diffracted rather poorly. Reported data were obtained from the best acicular fragment of a crystal with size 8 \times 8 \times 10 μ m. This is the reason for the quality of the data: $R_1 = 0.085$. The structure was solved by direct methods and refined on the basis of F^2 for 1422 independent reflections with $F^2 \geq 4\sigma(F^2)$. The twinning matrix [1 0.325 0.613, 0–1 0, 0 0–1] was

employed during the crystal structure refinement. The data were integrated and corrected for absorption using a multi-scan type model using the Bruker programs APEX and SADABS. Ziminaite is triclinic, space group $P\bar{1}$, $a = 8.012(4)$, $b = 9.345(5)$, $c = 6.678(3)$ Å, $\alpha = 106.992(10)$, $\beta = 101.547(8)$, $\gamma = 96.594(11)^\circ$, and $V = 460.4(4)$ Å³. The structure was successfully refined with the use of SHELX software package (Sheldrick 2015). Crystal data, data collection information and

Table 5 Displacement parameters for ziminaite

Site	<i>U</i> ₁₁ (Å ²)	<i>U</i> ₂₂ (Å ²)	<i>U</i> ₃₃ (Å ²)	<i>U</i> ₂₃ (Å ²)	<i>U</i> ₁₃ (Å ²)	<i>U</i> ₁₂ (Å ²)
<i>M</i> (1)	0.0084(15)	0.0079(12)	0.0088(13)	0.0025(10)	0.0020(11)	0.0012(10)
<i>M</i> (2)	0.0059(15)	0.0090(12)	0.0096(13)	0.0036(10)	0.0019(11)	–0.0006(10)
<i>M</i> (3)	0.0165(18)	0.0255(16)	0.0074(14)	0.0062(12)	0.0042(13)	0.0144(14)
<i>V</i> (1)	0.0046(13)	0.0068(11)	0.0037(11)	0.0027(9)	0.0011(9)	–0.0003(9)
<i>V</i> (2)	0.0053(13)	0.0069(11)	0.0044(12)	0.0013(9)	–0.0007(10)	0.0008(10)
<i>V</i> (3)	0.0079(14)	0.0137(12)	0.0071(12)	0.0043(9)	0.0024(10)	–0.0007(10)
<i>O</i> (1)	0.025(8)	0.014(5)	0.019(6)	0.006(5)	–0.005(5)	–0.006(5)
<i>O</i> (2)	0.017(7)	0.017(5)	0.025(7)	0.007(5)	0.005(5)	0.004(5)
<i>O</i> (3)	0.019(7)	0.007(5)	0.017(6)	0.006(4)	0.003(5)	–0.002(4)
<i>O</i> (4)	0.009(6)	0.015(5)	0.014(5)	0.008(4)	0.004(5)	0.006(4)
<i>O</i> (5)	0.015(6)	0.021(6)	0.009(5)	0.010(4)	0.001(5)	0.009(5)
<i>O</i> (6)	0.008(6)	0.007(4)	0.011(5)	0.004(4)	0.000(4)	0.000(4)
<i>O</i> (7)	0.020(7)	0.037(7)	0.022(7)	0.016(6)	0.006(6)	0.005(6)
<i>O</i> (8)	0.007(6)	0.018(5)	0.010(5)	0.009(4)	0.002(4)	0.000(4)
<i>O</i> (9)	0.009(6)	0.011(5)	0.008(5)	0.003(4)	–0.002(4)	–0.003(4)
<i>O</i> (10)	0.018(7)	0.026(6)	0.010(5)	0.012(5)	0.006(5)	0.000(5)
<i>O</i> (11)	0.019(7)	0.021(6)	0.013(6)	0.010(5)	0.008(5)	0.010(5)
<i>O</i> (12)	0.009(6)	0.010(5)	0.014(6)	0.000(4)	0.005(5)	–0.002(4)

Table 6 Selected interatomic distances in the structure of ziminaite

Bond	Distance (Å)	Bond	Distance (Å)
<i>M</i> (1)-O(3)	1.938(11)	<i>M</i> (3)-O(8)	1.977(11)
<i>M</i> (1)-O(1)	1.971(13)	< <i>M</i> (3)-O>	1.915
<i>M</i> (1)-O(2)	1.977(12)	V(1)-O(4)	1.653(11)
<i>M</i> (1)-O(4)	1.994(12)	V(1)-O(11)	1.659(11)
<i>M</i> (1)-O(5)	2.031(11)	V(1)-O(6)	1.785(11)
<i>M</i> (1)-O(6)	2.060(10)	V(1)-O(8)	1.797(10)
< <i>M</i> (1)-O>	1.995	<V(1)-O>	1.724
<i>M</i> (2)-O(12)	1.910(11)	V(2)-O(2)	1.643(12)
<i>M</i> (2)-O(10)	1.924(11)	V(2)-O(3)	1.679(11)
<i>M</i> (2)-O(11)	1.937(11)	V(2)-O(5)	1.772(11)
<i>M</i> (2)-O(8)	1.959(11)	V(2)-O(12)	1.785(11)
<i>M</i> (2)-O(9)	2.033(10)	<V(2)-O>	1.720
<i>M</i> (2)-O(12)	2.103(11)	V(3)-O(1)	1.673(12)
< <i>M</i> (2)-O>	1.978	V(3)-O(10)	1.690(11)
<i>M</i> (3)-O(7)	1.809(13)	V(3)-O(7)	1.723(13)
<i>M</i> (3)-O(6)	1.902(10)	V(3)-O(9)	1.794(10)
<i>M</i> (3)-O(5)	1.938(11)	<V(3)-O>	1.720
<i>M</i> (3)-O(9)	1.950(11)		

structure refinement details for ziminaite are given in Table 3, atom coordinates, and thermal displacement parameters in Tables 4 and 5 and selected interatomic distances in Table 6.

Crystal structure and crystal chemistry: comparative description and discussion

Ziminaite belongs to the howardevansite group (Pekov et al. 2014), which also includes howardevansite, grigorievite and koksharovite. Ziminaite is its first member without species-defining uni- or divalent cations and with all large cation sites vacant (Table 7, Figs. 3 and 4). Ziminaite is isostructural with the synthetic compounds FeVO₄ (Robertson and Kostiner 1972) and AlVO₄ (Dabrowska et al. 2009) and other representatives of the ZnMoO₄ structure type (Reichelt et al. 2000).

Structural similarity of ziminaite to other howardevansite group minerals causes, in particular, epitaxial intergrowths of ziminaite and koksharovite (Fig. 1). However, ziminaite has some distinct differences to howardevansite, grigorievite and koksharovite, obviously caused by the dominating of high-valence cations in all non-tetrahedral cation sites *M*(1), *M*(2) and *M*(3) in the new mineral (Table 4). The crystal structures of howardevansite (Fig. 4a; Hughes et al. 1988), koksharovite and grigorievite (Pekov et al. 2014) are based upon heteropolyhedral frameworks built by VO₄ tetrahedra, *M*(1)O₆ and *M*(2)O₆ octahedra (*M* = Fe³⁺, Al, Mg, Ti) and five-coordinated *M*(3)O₅ polyhedra (*M* = Cu²⁺, Mg, Fe³⁺). This general structural motif is also observed for ziminaite

(Fig. 3a). VO₄ tetrahedra are distorted in the structure of ziminaite, however, average <V-O> bond lengths are identical in all three symmetrically independent VO₄ tetrahedra (Table 6).

M(1)O₆ and *M*(2)O₆ octahedra form isolated, edge-sharing dimeric clusters in the structures of howardevansite, koksharovite and grigorievite. The linkage between the dimers is reinforced by the *M*(3)O₅ polyhedra which results in the formation of the chains depicted in Fig. 4c. *M*(2)O₆ octahedra also form dimers in ziminaite (Fig. 3c), however, the *M*(1)O₆ octahedron is isolated in it. The resulting isles in the structure of ziminaite are shown in Fig. 3c.

Insufficient amount of ziminaite does not allow to carry out Mössbauer spectroscopic study, however, the presence of only (or almost only) trivalent iron in the mineral is undoubted. Fe³⁺ prevails at all *M* sites (Table 4). Since the X-ray scattering power of Fe and Ti atoms differ only moderately, Fe and Ti were regarded as one group with one scattering factor. Fe and Ti atoms were summed to form Fe* in atomic fraction. For the same reason, Al and Mg were assumed to form a species Al*. Bond valences for *M* sites were calculated using the parameters by Brese and O'Keeffe (1991) for Fe³⁺-O bonds. The bond-valence sums at the *M*(1), *M*(2) and *M*(3) sites are 3.19, 3.38 and 3.32 *vu*, respectively. High bond valence sums for cations in the *M*(2) and *M*(3) sites suggest preferable distribution of Ti⁴⁺ in these atomic sites.

The A(1) and A(2) sites occupied by relatively large Na, Ca and smaller Cu²⁺ ions in howardevansite, koksharovite and grigorievite, respectively, are vacant in ziminaite. As a

Table 7 Comparative data of howardevansite-group minerals and synthetic howardevansite-type Fe³⁺VO₄

Mineral / compound	Howardevansite	Koksharovite	Grigorievite	Ziminaite	Synthetic phase ^c
Idealized formula	NaCuFe ³⁺ ₂ (VO ₄) ₃	CaMg ₂ Fe ³⁺ ₄ (VO ₄) ₆	Cu ₃ Fe ³⁺ ₂ Al ₂ (VO ₄) ₆	Fe ³⁺ VO ₄	Fe ³⁺ VO ₄
Crystal system			Triclinic		
Space group			$P\bar{1}$		
Unit-cell data					
<i>a</i> , Å	8.198	8.176	8.022	8.012(4)	8.060(9)
<i>b</i> , Å	9.773	9.829	9.686	9.345(5)	9.254(9)
<i>c</i> , Å	6.651	6.694	6.548	6.678(3)	6.719(7)
α, °	103.82	105.04	103.65	106.992(10)	106.57(8)
β, °	101.99	102.04	102.37	101.547(8)	101.60(8)
γ, °	106.74	106.03	106.28	96.594(11)	96.65(8)
<i>V</i> , Å ³	473.1	476.0	452.6	460.4(4)	462.4(2)
<i>Z</i>	2	1	1	6	6
Structural formula of the end-member (Z=1) ^a	NaNa{Cu ₂ Fe ³⁺ ₂ Fe ³⁺ ₂ (VO ₄) ₆ }	Ca□{Mg ₂ Fe ³⁺ ₂ Fe ³⁺ ₂ (VO ₄) ₆ }	Cu□{Cu ₂ Fe ³⁺ ₂ Al ₂ (VO ₄) ₆ }	□□{Fe ³⁺ ₂ Fe ³⁺ ₂ Fe ³⁺ ₂ (VO ₄) ₆ }	□□{Fe ³⁺ ₂ Fe ³⁺ ₂ Fe ³⁺ ₂ (VO ₄) ₆ }
Locality ^b	Izalco volcano	Bezmyannyi volcano	Tolbachik volcano	Bezmyannyi volcano	–
Reference	Hughes et al. (1988)	Pekov et al. (2014)	Pekov et al. (2014)	Present work	Robertson and Kostiner (1972)

^aOnly constituents prevailing in each site are shown; the composition of the pseudo-framework built by VO₄ tetrahedra and *M*-centred polyhedra is given in braces

^bFor each mineral, only one single locality of occurrence is known thus far

^cHere the unit-cell data are quoted analogous to the mineral data, for better comparison

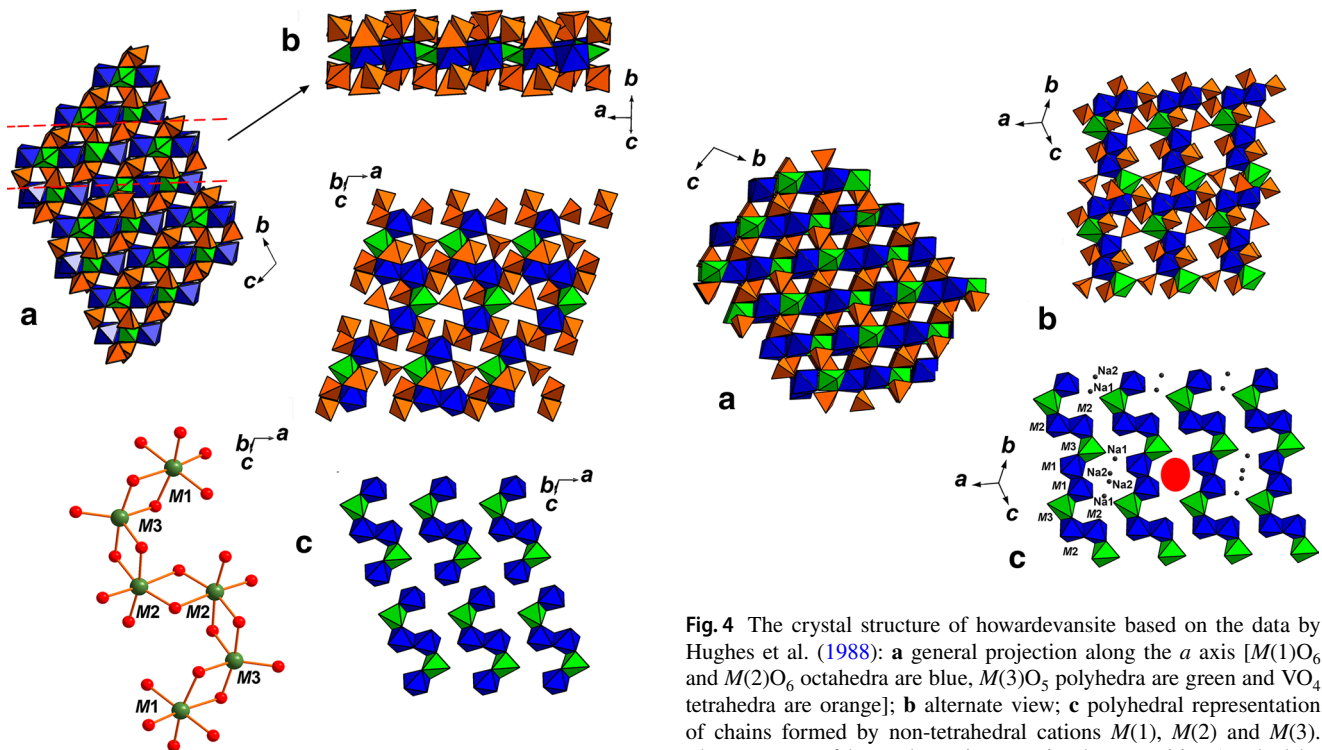


Fig. 3 The crystal structure of ziminaite: **a** general projection along the *a* axis [*M*(1)O₆ and *M*(2)O₆ octahedra are blue, *M*(3)O₅ polyhedra are green and VO₄ tetrahedra are orange]; **b** alternate view; **c** ball and sticks and polyhedral representations of isles formed by non-tetrahedral cations *M*(1), *M*(2) and *M*(3)

Fig. 4 The crystal structure of howardevansite based on the data by Hughes et al. (1988): **a** general projection along the *a* axis [*M*(1)O₆ and *M*(2)O₆ octahedra are blue, *M*(3)O₅ polyhedra are green and VO₄ tetrahedra are orange]; **b** alternate view; **c** polyhedral representation of chains formed by non-tetrahedral cations *M*(1), *M*(2) and *M*(3). The structure of howardevansite contains large cavities (marked by the red oval) occupied by Na atoms in contrast to the structure of ziminaite in which such cavities are absent and isles formed by cations *M*(1), *M*(2) and *M*(3) are closely packed (compare Fig. 3). Note, different direction of chains elongation in howardevansite in comparison to isles in ziminaite

result, all species-defining cations in the new mineral are highly charged: Fe^{3+} in all M sites and V^{5+} in tetrahedrally coordinated sites. The isles (Fig. 3c) formed by non-tetrahedral cations in ziminaite are rather closely packed compared to chains in other howardevansite-group minerals. Thus, the cavities able to contain large cations such as Na (howardevansite; Fig. 4c) or Ca (koksharovite), or even smaller Cu^{2+} (grigorievite) are in fact absent in the structure of ziminaite. This structural feature of ziminaite results in the different direction of elongation of isles in ziminaite comparing to chains formed by non-tetrahedral cations in howardevansite (Fig. 4c). These differences are also reflected in significantly smaller values of the b and γ unit-cell parameters of ziminaite in comparison with other howardevansite group members (Table 7).

The structural formula of ziminaite can be presented in the form simplified to only species-defining constituents: $^{A(1)}\square^{A(2)}\square^{M(1)}\text{Fe}^{3+} {}_2^{M(2)}\text{Fe}^{3+} {}_2^{M(3)}\text{Fe}^{3+} {}_2(\text{VO}_4)_6$. Further, this formula can be reduced to $\text{Fe}^{3+}\text{VO}_4$. Such idealization of the formula is in agreement with the synthetic analogue of the end-member ziminaite, a compound $\text{Fe}^{3+}\text{VO}_4$ (Robertson and Kostiner 1972; Table 7). Its existence clearly demonstrates that the simple Fe^{3+} orthovanadate can adopt a howardevansite-type structure even without any admixed cation. Thus, the idealized formula $\text{Fe}^{3+}\text{VO}_4$ ($Z=6$) is correct for ziminaite and it is not excluded that its variety chemically close to this hypothetical end-member will be found in nature.

Trivalent state of iron in ziminaite is grounded in four facts: (1) cation–oxygen distances for all Fe-dominant sites (M) are too short for Fe^{2+} (Table 6); (2) general charge balance of the formula; (3) bond valence sums for the M cations (see above); (4) the fact that all known natural (Table 7) and synthetic vanadates with howardevansite-type structures contain only Fe^{3+} but not Fe^{2+} . Synthetic howardevansite-like compounds, besides $\text{Fe}^{3+}\text{VO}_4$ (Robertson and Kostiner 1972), are $\beta\text{-Cu}_3\text{Fe}^{3+} {}_4(\text{VO}_4)_6$ (Lafontaine et al. 1994), $\text{Li}_2\text{Cu}_2\text{Fe}^{3+} {}_4(\text{VO}_4)_6$ (Belik 1999), $\text{Cu}_{2.5}\text{Fe}^{3+} {}_{4.333}(\text{VO}_4)_6$ (Belik et al. 2001), $\text{Zn}_3\text{Fe}^{3+} {}_4(\text{VO}_4)_6$ (Guskos et al. 2005a), $\text{Mn}_3\text{Fe}^{3+} {}_4(\text{VO}_4)_6$, $\text{Co}_3\text{Fe}^{3+} {}_4(\text{VO}_4)_6$ (Guskos et al. 2005b), and $\text{Mg}_3\text{Fe}^{3+} {}_4(\text{VO}_4)_6$ (Beskrovnyi et al. 2006).

In the empirical formula of ziminaite, $(\text{Fe}^{3+} {}_{3.29}\text{Al}_{1.48}\text{T}_{i_{0.54}}\text{Mg}_{0.53})_{\Sigma 5.84}(\text{V}_{6.05}\text{Si}_{0.04}\text{P}_{0.01})_{\Sigma 6.10}\text{O}_{24}$, a slight deficiency of M cations and slight excess of tetrahedrally coordinated components is observed. The most probable cause is common analytical error but we can not exclude the presence of minor part of vanadium in the octahedral M sites as V^{3+} . However, this assumption can neither be confirmed nor refuted because of insignificant amount of vanadium that could be present in the M sites.

Note, polymorphism for synthetic $\text{Fe}^{3+}\text{VO}_4$ is reported. Besides the above-discussed howardevansite-type modification studied by Robertson and Kostiner (1972), $\text{FeVO}_4\text{-II}$,

$\text{FeVO}_4\text{-III}$ and $\text{FeVO}_4\text{-IV}$ belonging to structure types of CrVO_4 , the orthorhombic $\alpha\text{-PbO}_2$ and the monoclinic wolframite-type NiWO_4 , respectively, are known (Oka et al. 1996).

Acknowledgements We thank Gerald Giester and an anonymous referee for their valuable comments and Lutz Nasdala for the editorial work. Chemical composition of ziminaite was studied in Laboratory of Analytical Techniques of High Spatial Resolution, Dept. of Petrology, Moscow State University. Technical support by the St Petersburg State University X-Ray Diffraction Research Resource Center is gratefully acknowledged. This study was supported by the Russian Science Foundation, grant no. 14-17-00048 (mineralogical studies) and St Petersburg State University through the internal grant 3.38.238.2015 (X-ray diffraction studies and crystal structure determination).

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