ILIRNEYITE, Mg$_{0.5}$[ZnMn^{3+}(TeO$_3$)$_3$]·4.5H$_2$O, A NEW MINERAL FROM CHUKOTKA, RUSSIA

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Abstract

The new mineral ilirneyite, ideally Mg$_{0.5}$[ZnMn^{3+}(Te^{4+}O$_3$)$_3$]·4.5H$_2$O, a member of the zemannite structural family, was found at the Sentyabr'skoe Ag-Au deposit, Ilirney ore district, Western Chukotka, North-Eastern Region, Russia. It is associated with gypsum, malachite, azurite, cerussite, anglesite, brochantite, linarite, posnjakite, chlorargyrite, acanthite, gold, goethite, coronadite, paratellurite, raisaite, and xocomecatlite in the oxidation zone of quartz veins with tellurides. Ilirneyite occurs as: (1) long prismatic hexagonal crystals up to 0.15 mm in length and up to 0.01 mm in thickness, typically combined in sprays or open-work chaotic groups; (2) moss-like aggregates consisting of acicular to hair-like crystals up to 0.03 mm in length and up to 2 μm in thickness; and (3) earthy films. Ilirneyite is transparent to translucent, reddish brown, dark brownish-red, brown, or light brown. The luster is adamantine to semi-metallic in crystals and silky in moss-like aggregates. Ilirneyite is brittle; cleavage was not observed. $D_{calc} = 4.205$ g/cm^3. In reflected light, ilirneyite is dark grey. Bireflectance is weak, internal reflections are red-brown. The reflectance values [R_{max}–R_{min}, % (λ, nm)] are: 9.0–7.0 (470), 8.7–7.3 (546), 8.6–7.2 (589), 8.4–7.1 (650). The chemical composition (average of nine analyses, H$_2$O by stoichiometry) is MgO 4.20, MnO 1.25, CuO 0.58, ZnO 11.42, Mn$_2$O$_3$ 7.14, Fe$_2$O$_3$ 0.06, TeO$_2$ 65.06, H$_2$O$_{calc}$ 11.01, total 100.72 wt.%. The empirical formula calculated based on Te$_3$O$_9$ with 4.5 H$_2$O molecules *pfu* is Mg$_{0.56}$[Zn$_{1.03}$Mg$_{0.21}$Mn$^{2+}_{0.13}$Cu$_{0.05}$Mn$^{3+}_{0.67}$Fe$^{3+}_{0.01}$(Te^{4+}O$_3$)$_3$]·4.5H$_2$O. Ilirneyite is hexagonal, $P6_3/m$, a 9.423(1), c 7.669(1) Å, V 589.7(2) Å^3, and $Z = 2$. The strongest reflections of the powder XRD pattern [d,Å(I)(hkl)] are: 8.18(100)(100), 4.088(61)(200), 3.847(14)(002), 3.087(15)(120, 210), 2.977(16)(112), 2.864(24)(121, 211), and 2.796(52)(202). The crystal structure was solved from single-crystal XRD data, $R_1 = 0.045$. Ilirneyite is isotypic with other zemannite-like minerals. It is named after the discovery locality.

Keywords: ilirneyite, new mineral, zemannite, tellurite, crystal structure, oxidation zone of ore deposit, Sentyabr'skoe deposit, Ilirney ore district, Chukotka peninsula.

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Introduction

The zemannite-like minerals are hexagonal tellurites with framework structures and the general formula $Mg_{0.5}[Me^{2+}Me^{3+}(Te^{4+}O_3)_3]\cdot4.5H_2O$. Until recently three mineral species were known in this family, all with $Me^{3+} = Fe$, namely zemannite, $Mg_{0.5}[ZnFe^{3+}(TeO_3)_3]\cdot4.5H_2O$ (Mandarino *et al.* 1976), kinichilite, $Mg_{0.5}[MnFe^{3+}(TeO_3)_3]\cdot4.5H_2O$ (Hori *et al.* 1981), and keystoneite, $Mg_{0.5}[NiFe^{3+}(TeO_3)_3]\cdot4.5H_2O$ (Back *et al.* 1988). The crystal structures of zemannite and kinichilite were first studied by Miletich (1995) and the zemannite structure was later re-investigated by Cametti *et al.* (2017) and Missen *et al.* (in press). A crystal-chemical overview of tellurium oxysalts including these minerals has been published by Christy *et al.* (2016).

This paper is devoted to a new mineral species of the zemannite structural family, its first representative with Mn^{3+} as a prevailing trivalent cation. The samples with this mineral were collected by two of the authors (EAV and AVA) in 2013 at the Sentyabr'skoe silver and gold deposit situated 110 km ESE of the town of Bilibino in Western Chukotka, North-Eastern Region, Russia (67°41′N, 168°52′E). The mineral was named ilirneyite (Cyrillic: илирнейит) after the discovery locality, near the village of Ilirney; the Ilirney Lakes and Ilirneyveem River are also situated in this area, and the Sentyabr'skoe deposit belongs to the Ilirney ore district.

Both the new mineral and its name have been approved by the IMA Commission on New Minerals, Nomenclature and Classification (IMA 2015-046). The type specimen is deposited in the systematic collection of the Fersman Mineralogical Museum of the Russian Academy of Sciences, Moscow, with the catalogue number 95277.

Occurrence

The Sentyabr'skoe deposit is situated among Lower Cretaceous volcanic rocks, mainly andesites, basaltic andesites, dacites, rhyolites, and tuffs of the Tytyl'veem formation. These are intruded by Upper Cretaceous quartz monzonites, granodiorites, and granitic porphyries belonging to the Ilirney magmatic complex. The deposit consists of numerous hydrothermal veins (up to 0.3 m thick) surrounded by aureoles of propylites and quartz-sericite and quartz-kaolinite rocks. Ores of the Sentyabr'skoe deposit formed at 280–350 °C and 250–380 bar, according to data obtained from fluid inclusions (Nikolaev *et al.* 2013).

Ilirneyite was found in the oxidation zone of sulfide- and telluride-bearing veins consisting mainly of quartz with subordinate carbonates (calcite, dolomite, and ankerite), muscovite, nacrite, and chamosite. Ore minerals are represented by pyrite, chalcopyrite, galena, sphalerite, acanthite, gold, hessite, petzite, altaite, and coloradoite. The secondary supergene mineralization is observed in cracks and small vugs within slightly oxidized upper parts of the veins, close to the surface. The major representatives of the supergene assemblage are gypsum, goethite, malachite, and azurite; secondary gold and acanthite are common. Minor supergene minerals are cerussite, anglesite, brochantite, linarite, posnjakite, chlorargyrite, brucite, coronadite, paratellurite, xocomecatlite, raisaite (Pekov *et al.* 2016), ilirneyite, and insufficiently studied tellurites/tellurates containing Cu, Mg, Fe, and Pb. All the tellurium minerals, both primary and supergene, were examined using electron microprobe, ore microscopy (for tellurides), and/or XRD methods.

Carbonates of the dolomite–ankerite series are an obvious source of Mg and Mn, sphalerite of Zn, and hessite, petzite, and altaite of Te for ilirneyite.

General Appearance, Morphology, Physical Properties, and Optical Data

Ilirneyite occurs, typically in intimate association with later gypsum, in cracks and small cavities in areas of veins enriched by tellurides. Aggregates of the new mineral overgrow quartz, muscovite, hessite, petzite, and gold. Rarely, ilirneyite forms perfect, well-terminated long prismatic hexagonal crystals (up to 0.2 mm in length and up to 0.05 mm in thickness) typically combined in sprays or open-work chaotic groups. The crystal forms are the hexagonal prism {100} and the hexagonal dipyramid {101} (Figs. 1 and 2a). Moss-like, soft, friable aggregates consisting of tiny acicular to hair-like crystals (up to 0.03 mm in length and up to 2 μm in thickness) are more common (Figs. 1 and 2b). Earthy films represent the most typical morphological variety of ilirneyite. Interrupted coatings of the new mineral are up to 1.5 × 2.5 cm in area and usually not thicker than 0.01 mm.

Ilirneyite is transparent in perfect crystals and translucent in aggregates. Its color is reddish brown to dark brownish-red; friable moss-like aggregates are brown to light brown. The streak is brown. The luster is adamantine to semi-metallic in crystals and silky in aggregates consisting of hair-like individuals. Ilirneyite is brittle, cleavage or parting was not observed, and the fracture is uneven (observed under the scanning electron microscope). The mean Vickers Hardness Number (VHN) is 132 and the range is 122–142 kg
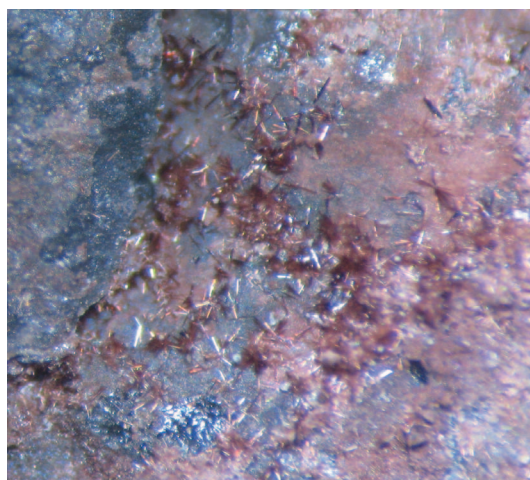
FIG. 1. Two morphological varieties of ilirneyite – groups of reddish-brown long prismatic crystals (see Fig. 2a) and light brown friable, moss-like aggregates consisting of tiny acicular to hair-like individuals (see Fig. 2b) – on the surface of a rich telluride ore mainly composed of quartz, hessite, and petzite. FOV width: 1.9 mm. Photo: I.V. Pekov & A.V. Kasatkin.
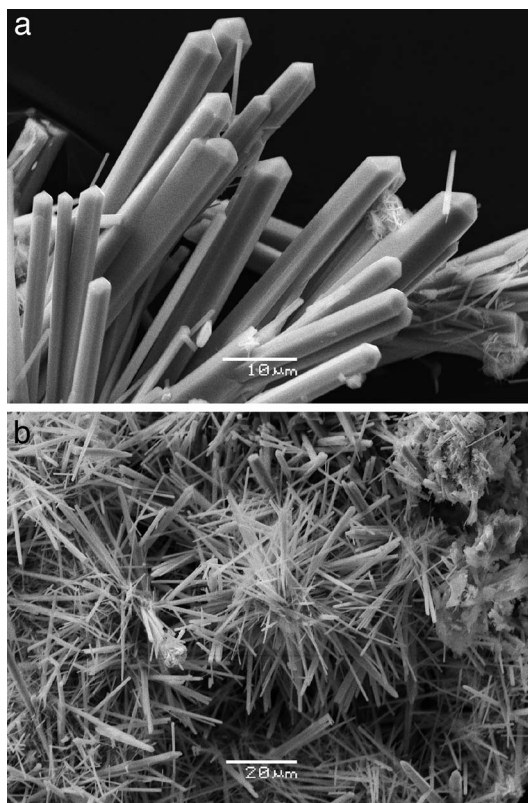

FIG. 2. Group of long, prismatic, well-terminated crystals (a) and open-work aggregate of acicular to hair-like crystals (b) of ilirneyite. SEM (SE) images.

mm^{-2} (load 20 g). Mohs hardness could not be determined because of the tiny size of the crystals and the open-work or friable character of the aggregates; the Mohs hardness value calculated from the VHN is *ca.* 3. Density was not measured because the crystals are small, and the aggregates are open-work or friable. The density calculated based on the empirical formula is 4.205 g cm^{-3}.

Under the microscope in reflected light, ilirneyite is dark grey; pleochroism was not observed. Bireflectance is weak, $\Delta R = 1.3\%$ (589 nm). Anisotropism is weak. Distinct red-brown internal reflections are observed. The reflectance values measured in air by means of the MSF-21 microspectrophotometer (LOMO company, Russia) using the SiC standard (Zeiss, No. 545) are given in Table 1.

CHEMICAL COMPOSITION

The chemical composition of ilirneyite was studied using a Jeol JSM-6480LV scanning electron microscope equipped with an INCA-Wave 500 wavelength-dispersive spectrometer (Laboratory of Analytical Techniques of High Spatial Resolution, Department of Petrology, Moscow State University), with an acceleration voltage of 20 kV, a beam current of 10 nA, and a 5 μm beam diameter. The following standards were used: diopside (Mg), $MnTiO_3$ (Mn), $CuFeS_2$ (Cu, Fe), ZnSe (Zn), and PbTe (Te).

TABLE 1. REFLECTANCE DATA (*R*, %) FOR ILIRNEYITE

λ (nm)	R_{max}	R_{min}	λ (nm)	R_{max}	R_{min}
400	8.2	7.1	560	8.6	7.3
420	8.8	7.7	580	8.6	7.2
440	9.1	7.9	**589**	**8.6**	**7.2**
460	9.0	7.8	600	8.5	7.2
470	**9.0**	**7.8**	620	8.5	7.1
480	8.9	7.7	640	8.4	7.1
500	8.8	7.6	**650**	**8.4**	**7.1**
520	8.8	7.5	660	8.3	7.0
540	8.7	7.4	680	8.2	7.0
546	**8.7**	**7.3**	700	8.2	6.9

Data for wavelengths recommended by the IMA Commission on ore microscopy (COM) are marked in bold.

The chemical composition of ilirneyite (average of nine spot analyses, ranges in parentheses) is: MgO 4.20 (3.72–4.84), MnO 1.25, CuO 0.58 (0.04–1.65), ZnO 11.42 (7.07–14.85), Mn_2O_3 7.14, Fe_2O_3 0.06

TABLE 2. POWDER X-RAY DIFFRACTION DATA FOR ILIRNEYITE

I_{obs}	d_{obs} (Å)	I_{calc}*	d_{calc}** (Å)	h, k, l
100	**8.18**	100	8.141	100
2	5.608	1	5.578	101
4	4.721	6	4.700	110
61	**4.088**	98	4.070	200
14	**3.847**	20	3.829	002
3	3.612	1	3.594	201
7	3.476	6	3.465	102
15	**3.087**	7, 8	3.077, 3.077	120, 210
16	**2.977**	19	2.968	112
24	**2.864**	10, 28	2.855, 2.855	121, 211
52	**2.796**	99	2.789	202
1	2.722	1	2.714	300
7	2.564	12	2.558	301
3	2.440	2	2.435	103
5	2.403	1, 6	2.398, 2.398	122, 212
10	**2.356**	21	2.350	220
3	2.264	1, 1	2.258, 2.258	310, 130
6	2.218	9	2.214	302
5	2.173	1, 6, 2	2.166, 2.166, 2.162	311, 131, 203
2	2.038	4	2.035	400
5	2.006	11	2.003	222
2	1.970	1, 2	1.964, 1.964	213, 123
2	1.951	1, 1	1.945, 1.945	312, 132
2	1.918	5	1.914	004
4	1.870	2, 3	1.868, 1.863	230, 104
5	1.819	2, 7	1.814, 1.814	321, 231
7	1.804	14	1.797	402
4	1.781	3	1.776	140
9	1.739	12, 9	1.732, 1.731	204, 411
3	1.698	7	1.691	133
2	1.632	2, 3	1.628, 1.625	500, 214
2	1.615	4	1.611	412
3	1.598	6	1.593	501
2	1.568	1, 2	1.567, 1.564	330, 304
2	1.541	1, 1	1.538, 1.538	420, 240
7	1.511	10, 4	1.507, 1.507	233, 323
3	1.487	4	1.484	224
4	1.462	1, 4	1.460, 1.458	134, 413
4	1.441	4	1.436	151
4	1.431	3, 3	1.428, 1.428	422, 242
3	1.399	3	1.394	404
4	1.375	3, 2, 2	1.373, 1.371, 1.371	503, 215, 125
2	1.367	1, 3	1.366, 1.366	512, 600
2	1.343	1, 1	1.338, 1.337	430, 234
3	1.321	5	1.318	431
1	1.305	1	1.302	414
3	1.290	3, 2	1.285, 1.285	251, 521
2	1.240	1, 1	1.240, 1.234	504, 252
1	1.188	1	1.185	433
2	1.163	1, 3, 2	1.161, 1.161, 1.160	523, 253, 415
1	1.152	1	1.150	701
2	1.123	2	1.122	226
1	1.083	1	1.081	406

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

(0.00–0.11), TeO_2 65.06 (63.88–65.97), H_2O_{calc} 11.01, total 100.72 wt.%. Contents of other elements with atomic numbers higher than oxygen are below detection limits. Manganese was subdivided into Mn^{2+} and Mn^{3+} by charge balance for the formula based on $Te^{4+}_3O_9$, in accordance with crystal structure

TABLE 3. CRYSTAL DATA, DATA COLLECTION INFORMATION, AND STRUCTURE REFINEMENT DETAILS FOR ILIRNEYITE

Crystal data	
Space group	$P6_3/m$
Unit-cell dimensions	
a (Å)	9.40(2)
c (Å)	7.657(17)
Unit-cell volume (Å^3)	586(2)
Z	2
Absorption coefficient (mm^{-1})	11.002
Crystal size (mm)	$0.05 \times 0.05 \times 0.20$
Data collection	
Temperature (K)	150(2)
Radiation, wavelength (Å)	Mo$K\alpha$, 0.71073
$F(000)$	644
θ range (°)	2.50–22.63
h, k, l ranges	$-8 \rightarrow 10$
	$-10 \rightarrow 10$
	$-6 \rightarrow 6$
Total reflections collected	1415
Unique reflections (R_{int})	250 (0.07)
Unique reflections $F > 4\sigma(F)$	202
Structure refinement	
Refinement method	Full-matrix least-squares on F^2
Weighting coefficients a, b^*	0.0522, 0.0
Data/restraints/parameters	250/6/40
R_1 [$F > 4\sigma(F)$], wR_2 [$F > 4\sigma(F)$]	0.045, 0.103
R_2 all, wR_2 all	0.059, 0.117
Gof on F^2	1.156

data including bond valence calculations for its position (see below); the electron probe compositions calculated with total Mn as Mn_2O_3 average 8.54 (6.16–12.91) wt.%. Minor Fe is considered to be Fe^{3+} by analogy with other zemannite-like minerals containing only trivalent iron.

H_2O was not analyzed because of the paucity of material. The H_2O content was calculated by stoichiometry for 4.5 H_2O *pfu*, based on the crystal structure data. The analytical total including this value for H_2O is close to 100 wt.%, which confirms the correctness of this assumption.

The empirical formula calculated on the basis of $Te^{4+}_3O_9$ with 4.5 H_2O molecules *pfu* is $Mg_{0.77}Mn^{2+}_{0.13}Cu_{0.05}Zn_{1.03}Mn^{3+}_{0.67}Fe^{3+}_{0.01}Te^{4+}_3O_9 \cdot 4.5H_2O$ or, taking into account the structure data (see below), $Mg_{0.56}[Zn_{1.03}Mg_{0.21}Mn^{2+}_{0.13}Cu_{0.05}Mn^{3+}_{0.67}Fe^{3+}_{0.01}(Te^{4+}O_3)_3] \cdot 4.5H_2O$. The idealized formula is $Mg_{0.5}[ZnMn^{3+}(TeO_3)_3] \cdot 4.5H_2O$, which requires MgO 2.72, ZnO 10.99, Mn_2O_3 10.66, TeO_2 64.68, H_2O 10.95, total 100.00 wt.%.

X-RAY CRYSTALLOGRAPHY AND CRYSTAL STRUCTURE DETERMINATION DETAILS

Powder X-ray diffraction data of ilirneyite (Table 2) were collected with a Rigaku R-AXIS Rapid II single-crystal diffractometer equipped with a cylindrical image-plate detector (radius 127.4 mm). The conditions were: Debye-Scherrer geometry, Co$K\alpha$ radiation (rotating anode with VariMAX microfocus optics), 40 kV, 15 mA, and exposure 15 min. The 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 hexagonal unit cell parameters refined from the powder data are a 9.423 (1), c 7.669 (1) Å, and V = 589.7 (2) Å^3.

Since the discovery of zemannite as a new species (Mandarino & Williams 1961) the symmetry of this

TABLE 4. COORDINATES AND EQUIVALENT DISPLACEMENT PARAMETERS (Å^2) FOR ATOMS AND SITE OCCUPANCIES (s.o.f.) IN ILIRNEYITE

Site	Wyckoff site	s.o.f.	b.v.s.**	x	y	z	U_{eq}
Te	6h	1	4.06	0.49883(17)	0.54048(17)	1/4	0.0230(8)
Me	4f	*Me**	2.16	1/3	2/3	−0.0610(6)	0.0267(17)
O(1)	6h	1	1.84	0.5045(16)	0.3445(18)	1/4	0.030(4)
O(2)	12i	1	2.10	0.3448(14)	0.4871(13)	0.4289(18)	0.037(3)
Mg	4e	0.28(4)	2.18	0	0	−0.173(4)	0.005(9)
OW(1)	12i	0.37(4)		0.192(4)	0.135(4)	0.332(4)	0.037(15)
OW(2)	12i	0.36(5)		0.796(4)	0.860(4)	0.012(5)	0.037(15)

* e_{ref} = 26.1 (for the occupancy details see text).
** Bond-valence analysis was calculated using bond-valence parameters taken from Mills & Christy (2013) for the Te^{4+}–O bonds and from Gagné & Hawthorne (2015) for the Mg–O and Zn–O bonds.

TABLE 5. ANISOTROPIC DISPLACEMENT PARAMETERS (Å^2) FOR ATOMS IN ILIRNEYITE

Site	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Te	0.0205(9)	0.0215(10)	0.0261(16)	0	0.000	0.0097(7)
Me	0.0261(17)	0.0261(17)	0.028(4)	0	0.000	0.0130(8)
O(1)	0.015(8)	0.025(8)	0.035(14)	0	0.000	−0.002(6)
O(2)	0.033(6)	0.035(7)	0.035(10)	0.000(6)	0.001(6)	0.012(5)
Mg	0.005(9)	0.005(9)	0.004(15)	0	0.000	0.003(4)

mineral has remained controversial. Until recently, the most commonly used model was the structure of zemannite in the space group $P6_3/m$. We note, however, that as early as Miletich (1995) a number of arguments have been presented in favor of the non-centrosymmetric space group $P6_3$ for zemannite. Recent works indicate a lower symmetry for this mineral (Cametti *et al*. 2017, Missen *et al*., in press). Zemannite-type selenites $K_2[Co_2(SeO_3)_3]\cdot 2H_2O$ and $K_2[Ni_2(SeO_3)_3]\cdot 2H_2O$ crystallize in space group $P6_3/m$ (Wildner 1993).

A crystal of ilirneyite (0.05 × 0.05 × 0.20 mm) was glued to a thin glass fiber and mounted on a Bruker DUO APEX II CCD four-circle diffractometer with a Mo-IµS micro-focus tube (wavelength 0.71073 Å) operating at 50 kV and 40 mA at 150 K. More than a hemisphere of reflections were collected with frame widths of 0.5° in ω and with 45 s spent counting for each frame. The data were integrated and corrected for absorption using an empirical ellipsoidal model using the *APEX* and *SADABS* Bruker programs.

The observed reflection conditions are consistent with space group $P6_3/m$, in agreement with those previously reported for kinichilite (Miletich 1995). Attempts were made to solve the structure of ilirneyite by direct methods in $P\overline{3}$ and $P3$ space groups. Both of the obtained models were transformed into space group $P6_3/m$ using the ADDSYM algorithm incorporated into the *PLATON* program (Le Page 1987, Spek

2003). The $|E^2 - 1|$ parameter was equal to 0.834, which did not clearly indicate the centricity (Marsh 1995) of the ilirneyite crystal structure. The atom coordinates published for kinichilite were used initially and the structure was successfully refined with the *SHELX* software package (Sheldrick 2015) and converged with a residual $R_1 = 0.045$ (Table 3). All of the atoms except intra-channel oxygen sites (OW1 and OW2) were refined anisotropically. Atom coordinates, thermal displacement parameters, and site occupancies are given in Tables 4 and 5 and selected interatomic distances in Table 6.

The crystal structure of ilirneyite was also refined in space group $P6_3$. Only the Te and *Me*1 sites could be refined anisotropically. Moreover, equivalent displacement parameters for the Mg atom were fixed in the final stages of the refinement. Coordination polyhedra of all cations were characterized by the unreliably strong distortions. The Te–O2 bond length in the TeO$_3$ pyramid had a value of 1.79(7) Å, whereas Te–O1 = 1.87(2) and Te–O3 = 1.88(4) Å. The *Me*–O bond lengths in the $P6_3$ structural model are also characterized by large e.s.d. values. The final refinement converged to an agreement index (R_1) of 0.051. Thus, the centrosymmetric $P6_3/m$ model was chosen as most appropriate and is reported below.

CRYSTAL STRUCTURE: DESCRIPTION AND DISCUSSION

Ilirneyite is a new member of the zemannite structural family (Table 7). Crystal structures of these minerals are based upon $[Me_2(TeO_3)_3]^{n-}$ framework formed by Me_2O_9 dimers sharing common corners with pyramidal TeO$_3$ groups with the Te^{4+} cation in the apex pointing into the channel (Fig. 3). Bond valence calculations (Table 4) show that four longer (secondary) bonds [Te–O2 = 2.942(13) ×2 and Te–O2 = 3.223(13) ×2 Å] should be taken into consideration (Christy & Mills 2013). Channels in the ilirneyite framework are filled by chains formed by Mg cations (s.o.f. 0.28: Table 4) and H$_2$O molecules together with lone electron pairs associated with Te^{4+}, which is a typical feature for zemannite-type minerals. Formation of channels and cavities accommodating lone electron pairs associat-

TABLE 6. SELECTED INTERATOMIC DISTANCES (Å) IN THE CRYSTAL STRUCTURE OF ILIRNEYITE

Te–O(1)	1.869(16)
Te–O(2)	1.871(13) ×2
Te–O(2)	2.942(13) ×2
Te–O(2)	3.223(13) ×2
Me–O(2)	2.016(12) ×3
Me–O(1)	2.142(11) ×3
Mg–OW(1)	2.02(4) ×3
Mg–OW(2)	2.10(4) ×3

TABLE 7. COMPARATIVE DATA FOR MINERALS BELONGING TO THE ZEMANNITE STRUCTURAL FAMILY

| Mineral	Ilirneyite	Zemannite	Kinichilite	Keystoneite
Idealized formula	$Mg_{0.5}[ZnMn^{3+}$ $(TeO_3)_3]\cdot4.5H_2O$	$Mg_{0.5}[ZnFe^{3+}$ $(TeO_3)_3]\cdot4.5H_2O$	$Mg_{0.5}[MnFe^{3+}$ $(TeO_3)_3]\cdot4.5H_2O$	$Mg_{0.5}[NiFe^{3+}$ $(TeO_3)_3]\cdot4.5H_2O$
Crystal system	Hexagonal	Hexagonal	Hexagonal	Hexagonal
Space group	$P6_3/m$	$P6_3/m$ or $P6_3$	$P6_3/m$	$P6_3/m$ or $P6_3$
Unit cell data:				
a, Å	9.423 (1)	9.40–9.42	9.42–9.45	9.344
c, Å	7.669 (1)	7.64–7.66	7.67–7.69	7.607
V, Å^3	589.7 (2)	585–588	589–595	575
Z	2	2	2	2
Strongest	8.18–100	8.11–100	8.15–90	8.12–90
reflections of	4.088–61	4.07–80	4.079–100	4.05–80
the powder	3.847–14	2.96–60	3.824–35	2.95–50
XRD pattern:	3.087–15	2.845–60	2.966–30	2.84–50
d, Å $- I$	2.977–16	2.778–90	2.861–50	2.77–100
	2.864–24	2.345–50	2.790–85	1.720–60
	2.796–52	1.726–60	1.735–20	1.498–50
D_{calc}, g cm^{-3}	4.205	4.18–4.19	4.11	4.40
Source	this work	Mandarino *et al.* (1976), Miletich (1995), Cametti *et al.* (2017), Missen *et al.* (in press)	Hori *et al.* (1981), Miletich (1995)	Back *et al.* (1988)
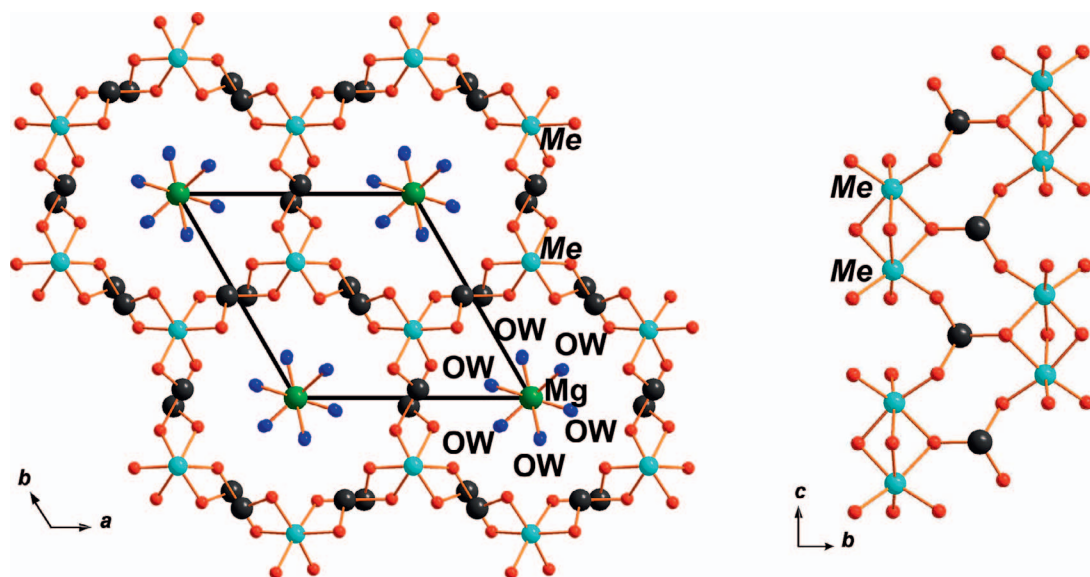
FIG. 3. General projection of the crystal structure of ilirneyite along the **c** axis (left) and fragment of the $[Me_2(TeO_3)_3]^{n-}$ framework along the **a** axis (right). Tellurium atoms are shown as black spheres and O atoms belonging to tellurite anions as red spheres. Channels in the framework are filled by Mg cations, H_2O molecules, and lone electron pairs associated with Te^{4+}. The unit cell is outlined.

ed with Te^{4+} is typical for tellurites in general (Markovski *et al.* 2016). There is one symmetrically independent *Me* site in the structure of ilirneyite. This site has a mixed occupancy of Me^{2+} and Me^{3+} cations. The refined number of electrons (e_{ref}) for the *Me* site in ilirneyite is 26.1, which is in excellent agreement with the value of 26.2 calculated on the basis of averaged chemical data corresponding to the following empirical formula: $Mg_{0.56}[Zn_{1.03}Mg_{0.21}Mn^{2+}_{0.13}Cu_{0.05}Mn^{3+}_{0.67}Fe^{3+}_{0.01}(Te^{4+}O_3)_3]\cdot4.5H_2O$. Note, the Mg content in the framework channel is given in accordance with the Mg site occupancy (Table 4). The bond-valence sum for the *Me* site is 2.16 *vu* (calculated using the Zn^{2+}–O bond-valence parameters in Gagné & Hawthorne 2015). The presence of a significant amount of trivalent cations (species-defining Mn^{3+}) at the *Me* site in ilirneyite is confirmed by the following observations: (1) general charge-balance requirements in the formula, (2) agreement between calculated and refined number of electrons, and (3) relatively high b.v.s. value.

The reported crystal structure of ilirneyite was refined in the centrosymmetric space group $P6_3/m$. The small size of the studied crystal resulted in a relatively small number of observed $[I > 2\sigma(I)]$ reflections (202). This is less than half of that reported (1248) for zemannite by Missen *et al.* (in press). Measurements of the SHG signal of ilirneyite could be of interest to future studies. The question of the space group choice remains a debate for some zemannite-type minerals.

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