

Långbanshyttanite, a new low-temperature arsenate mineral with a novel structure from Långban, Sweden

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Abstract: The new mineral långbanshyttanite was discovered in a specimen from the Långban mine (59.86°N, 14.27°E), Filipstad district, Värmland County, Bergslagen ore province, Sweden. Associated minerals are calcite, Mn-bearing phlogopite, spinels of the jacobsonite-magnetite series, antigorite and trigonite. The mineral is named after the old name of the mine, smelter and mining village: Långbanshyttan. Långbanshyttanite is transparent, colourless. It occurs in late-stage fractures or corroded pockets, forming soft, radial and random aggregates (up to 1 mm) of acicular crystals up to $5 \times 20 \times 400 \mu\text{m}$. D_{calc} is 3.951 g/cm^3 . The new mineral is biaxial (+), $\alpha = 1.700(5)$, $\beta = 1.741(5)$, $\gamma = 1.792(5)$, $2V$ (meas.) $\approx 90^\circ$, $2V$ (calc.) $= 86^\circ$. Dispersion is strong, $r < v$. The IR spectrum is given. The chemical composition is (electron microprobe, mean of five analyses, wt%): PbO 44.71, MgO 3.79, MnO 13.34, FeO 1.89, P₂O₅ 0.65, As₂O₅ 22.90, H₂O (determined by gas chromatographic analysis of the products of ignition at 1200 °C) 14.4; total 101.68. The empirical formula based on 18 O atoms is: $\text{Pb}_{1.97}\text{Mn}_{1.85}\text{Mg}_{0.93}\text{Fe}_{0.26}(\text{AsO}_4)_{1.96}(\text{PO}_4)_{0.09}(\text{OH})_{3.87} \cdot 5.93\text{H}_2\text{O}$. The simplified formula is: $\text{Pb}_2\text{Mn}_2\text{Mg}(\text{AsO}_4)_2(\text{OH})_4 \cdot 6\text{H}_2\text{O}$. Single-crystal diffraction data obtained using synchrotron radiation indicate that långbanshyttanite is triclinic, $P\bar{1}$, $a = 5.0528(10)$, $b = 5.7671(6)$, $c = 14.617(3) \text{ \AA}$, $\alpha = 85.656(14)$, $\beta = 82.029(17)$, $\gamma = 88.728(13)^\circ$, $V = 420.6(2) \text{ \AA}^3$, $Z = 1$, and is a representative of a new structure type. In the structure, edge-sharing $\text{MnO}_2(\text{OH})_4$ octahedra form zig-zag columns that are linked by isolated AsO_4 tetrahedra. Pb cations having six-fold coordination are located between the AsO_4 tetrahedra. Isolated $\text{Mg}(\text{H}_2\text{O})_6$ octahedra are located in the inter-block space. The strongest lines of the powder diffraction pattern [d , Å (I , %) (hkl)] are: 14.48 (100) (001), 7.21 (43) (002), 4.969 (34) (100, 101), 4.798 (28) (003), 3.571 (54) (112, 1-1-1, 01-3, 11-1), 2.857 (45) (020, 021, 114), 2.800 (34) (11-3). Parts of the holotype specimen are deposited in the Fersman Mineralogical Museum of Russian Academy of Sciences, Moscow, Russia, with the registration number 4032/1 and in the collections of the Swedish Museum of Natural History, Stockholm, Sweden, under catalogue number NRM 20100076.

Key-words: långbanshyttanite, new mineral, new structure type, arsenate, Långban, Bergslagen ore province, Sweden.

1. Introduction

The carbonate-hosted Långban deposit (59.86°N, 14.27°E) is, together with related occurrences in the western part of the Palaeoproterozoic Bergslagen ore province in south central Sweden, characterised by anomalously Pb-As-Ba-Be-Sb-rich, metamorphosed stratabound Fe and Mn oxide ores with associated skarn units, sulphide assemblages, as well as abundant vein and fissure-hosted mineral assemblages (e.g., Flink, 1926; Magnusson, 1930; Moore, 1970; Jonsson, 2004). Particularly the latter types of

assemblages, featuring a multitude of exotic species, have made this into one of the mineralogically most complex and famous localities on Earth.

Långbanshyttanite is a new hydrated Pb-Mn-Mg arsenate mineral from the long disused Långban mine, further testifying to the abundance of unusual Pb-bearing phases in this classical deposit. The mineral and its name have been approved by the IMA Commission on New Minerals, Nomenclature and Classification (IMA no. 2010-071). The name is for Långbanshyttan, which is the old name of both the mine, mining village and smelter that in more recent

times has been known plainly as “Långban” (Långbanshyttan actually means “Långbans smelter” or “Långbans furnace”; *cf.* also Holtstam & Langhof, 1999).

No minerals or synthetic compounds chemically and structurally closely related to långbanshyttanite have been found in the literature and databases. Parts of the holotype specimen of långbanshyttanite are deposited in the collections of the Fersman Mineralogical Museum of the Russian Academy of Sciences, Moscow, Russia, registration number 4032/1, and in the collections of the Swedish Museum of Natural History, Stockholm, Sweden, catalogue number NRM 20100076.

2. Occurrence, general appearance and physical properties

Långbanshyttanite occurs as a very late, low-temperature species in the deposit. It crystallized in the so-called late D-period (Magnusson, 1930; Jonsson, 2004), *i.e.*, during the last stage of hydrothermal activity involving metal remobilization in the Långban system, post-dating regional metamorphism of the volcanic-hydrothermal ores and their host rocks. Based on existing evidence, these minerals formed at very low temperature and pressure, in this case most likely below 70 °C, as suggested by fluid-inclusion studies (Jonsson & Broman, 2002). The mineral formed in fractures and corrosion-veinlets, post-dating calcite, in a Mn-oxide-bearing Mn-silicate-rich rock. Associated late-stage minerals are calcite, antigorite, sparse euhedral trigonite and a few microscopic aggregates of a so far unidentified As-bearing mineral. Typically, both calcite and antigorite exhibit evidence of being partly corroded away prior to långbanshyttanite formation. Trigonite, coeval with långbanshyttanite, occurs as sparse, euhedral crystals. The groundmass to the veinlets or fractures mainly consists of reddish brown, fine to medium-grained Mn-bearing phlogopite with disseminated subhedral grains of jacobsonite–magnetite series spinel.

The sample studied was most likely collected at Långban during, or immediately prior to 1926. It was noted by Gustaf Flink, a famous mineralogist who actively studied Långban and related deposits in the area, as number 319 in his list of inadequately studied mineral samples from Långban (Flink, 1926). Judging from his notes, it is likely, although not clearly stated, that the sample could originate from the “Amerika” workings in the mine. For a comprehensive summary and description of the minerals of the Långban deposit, see Nysten *et al.* (1999).

Långbanshyttanite forms unoriented, felty to distinctly radial, hemispherical white aggregates up to 1 mm in size composed of acicular, lath-like crystals, mostly occurring on a groundmass of partly corroded, pinkish to pale beige antigorite, often in direct association with corroded remnants of calcite. The exceedingly soft and brittle nature of the mineral prevented isolation and study of crystals or single crystal fragments larger than $5 \times 10 \times 120 \mu\text{m}$ (Fig. 1). Långbanshyttanite is transparent, colourless, with vitreous lustre. The streak is white. It shows perfect cleavage

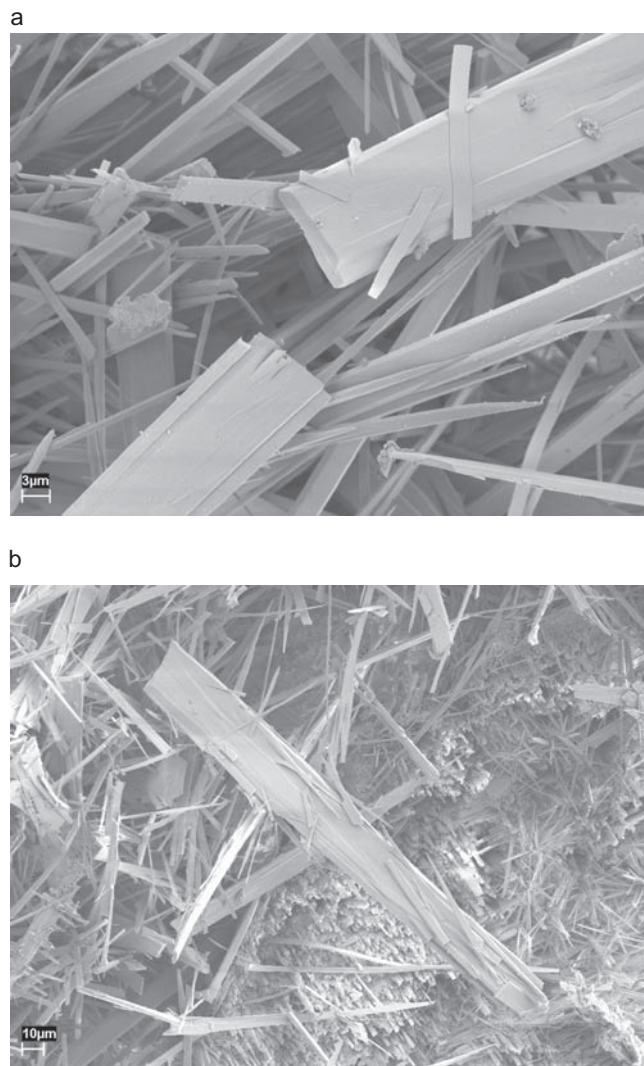


Fig. 1. (a,b) SEM images of representative aggregates of långbanshyttanite crystals. The substrate in Fig. 1b is antigorite.

on (001). Hardness could not be measured because the crystals are very thin, brittle and loosely aggregated. Calculated density is 3.951 g/cm^3 . Minute crystal fragments immersed in dilute hydrochloric acid rapidly decompose to a white mass, with generation of a few small gas bubbles.

Optically, the new mineral is biaxial (+), $\alpha = 1.700(5)$, $\beta = 1.741(5)$, $\gamma = 1.792(5)$, $2V$ (meas.) $\approx 90^\circ$, $2V$ (calc.) = 86° . Dispersion is strong, $r < v$. Orientation: $X \approx c$, the angle between Z and elongation direction is 16° . Under the microscope, långbanshyttanite is colourless, nonpleochroic. No response could be observed in short and long wave ultraviolet light.

3. Chemical data

The electron-microprobe analyses (Table 1) were performed using a fully computer-controlled scanning electron microscope VEGA TS 5130MM equipped with energy dispersive

Table 1. Analytical data for långbanshyttanite (mean of 5 point analyses).

Constituent	wt%	Range	Probe standard
PbO	44.71	42.67–46.48	PbCO ₃
MgO	3.79	2.86–4.53	Diopside
MnO	13.34	13.03–13.68	MnTiO ₃
FeO	1.89	1.11–2.50	Fe
P ₂ O ₅	0.65	0–1.44	LaPO ₄
As ₂ O ₅	22.90	21.69–24.06	Adamite
H ₂ O	14.4	14.2–14.6	
Total	101.68		

X-ray (EDX) microanalyser with an INCA Energy semiconductor Si(Li) detector, at an operating voltage of 15.7 kV and a beam current of 0.5 nA. The electron beam was rastered over an area $2 \times 2 \mu\text{m}^2$. The correctness of Mg and As determination was proved using talnessite as a test sample. Na, K, Ca, Sr, Ba, Zn, Ni, V, Sb, Al, Ti, Si, S, Cl, and F were below detection limits.

H₂O was determined by gas chromatography of the products of ignition at 1200 °C. CO₂ was not analyzed because of absence of bands corresponding to C–O vibrations in the IR spectrum (see below).

The empirical formula of långbanshyttanite based on 18 O atoms is: Pb_{1.97}Mn_{1.85}Mg_{0.93}Fe_{0.26}(AsO₄)_{1.96}(PO₄)_{0.09}(OH)_{3.87}·5.93H₂O.

The simplified formula is Pb₂Mn₂Mg(AsO₄)₂(OH)₄·6H₂O, which requires PbO 44.53, MgO 4.02, MnO 14.15, As₂O₅ 22.93, H₂O 14.38, total 100.00 wt%.

The Gladstone-Dale compatibility index calculated from the empirical formula is $1 - (K_p/K_c) = -0.040$ (*good*).

4. X-ray crystallography and crystal structure

X-ray powder-diffraction data for långbanshyttanite were obtained using a Stoe IPDS II image plate diffractometer (Gandolfi geometry) with a detector-to-sample distance of 200 mm. Data (in Å for MoK α) are given in Table 2 (for d_{calc} , only reflections with intensities ≥ 1 are given). Triclinic unit-cell parameters refined from the powder data are as follows: $a = 5.05(3)$, $b = 5.77(4)$, $c = 14.58(9)$ Å, $\alpha = 85.6(1)$, $\beta = 82.1(2)$, $\gamma = 88.7(1)^\circ$, $V = 420(2)$ Å³, $Z = 1$.

A single crystal was studied using synchrotron radiation at the Swiss-Norwegian Beam Lines (SNBL) at the European Synchrotron Radiation Facility (ESRF), Grenoble, France. Diffraction data were collected for a crystal of långbanshyttanite at room temperature using the MAR345 image plate detector, at a wavelength 0.83212 Å. The following results were obtained: långbanshyttanite is triclinic, space group: $P\bar{1}$, $a = 5.0528(10)$, $b = 5.7671(6)$, $c = 14.617(3)$ Å, $\alpha = 85.656(14)$, $\beta = 82.029(17)$, $\gamma = 88.728(13)^\circ$, $V = 420.6(2)$ Å³, $Z = 1$.

The studied crystal was of a poor quality: yet, all diffraction intensities could be indexed by assuming 4 intergrown domains, each possessing the same triclinic lattice.

In the course of the intensity integration, all domains were taken into consideration. 1200 diffraction intensities were integrated for the biggest one using CrysAlis software (Oxford Diffraction, 2006) but the problem of the overlapping intensities did not allow us to obtain the highest-quality experimental data. The data were corrected for Lorentz factor and polarization effects. Absorption correction and scaling of frames for the decaying intensity of the synchrotron beam were performed using SADABS (Sheldrick, 1997a). The structure model was revealed by direct methods and refined using SHELX software package (Sheldrick, 1997b, c). The structure model appears to be correct despite the high value of the final R factor: 0.2307 for 382 unique reflections with $I > 2\sigma(I)$. It is confirmed by very good agreement between measured and calculated X-ray powder diffraction data, as well as between the structure model and the stoichiometry of långbanshyttanite, as determined by the elemental analysis. The good Gladstone-Dale compatibility can be considered as an additional confirmation of the correctness of the structure model.

The atom coordinates, displacement parameters, selected interatomic distances and bond-valence sums for långbanshyttanite (Ferraris & Ivaldi, 1988; Brese & O'Keeffe, 1991; Krivovichev & Brown, 2001) are reported in Tables 3, 4, and 5, respectively. Empirical absorption correction was made using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. ABSPACK does absorption correction and scaling of frames for the decaying intensity of the synchrotron beam at the same time. The transmission factors related to absorption exclusively can not be determined in this procedure. From the ratio of $T_{\text{min}}/T_{\text{max}} = 0.69$ we can conclude that the measurements were not severely affected by absorption.

In the structure of långbanshyttanite (Fig. 2 and 3), isolated zig-zag columns running along the b axis are built up by edge-sharing MnO₂(OH)₄ octahedra with the average Mn–O distance of 2.22 Å. These columns are linked by isolated AsO₄ tetrahedra to form heteropolyhedral block coplanar to (001). Pb cations with six ligands at the distances ranging from 2.28(8) to 2.72(10) Å are located between the AsO₄ tetrahedra. Isolated Mg(H₂O)₆ octahedra with the average Mg–O distance of 2.14 Å are situated in the inter-block space and connected with each other and with O-atoms of the AsO₄ tetrahedra by a system of hydrogen bonds (Table 5). A larger octahedral site (multiplicity = 2) and a smaller one (multiplicity = 1) are considered to be occupied predominantly by Mn and Mg, respectively.

H₂O molecules at the sites O5 and O7 form very strong hydrogen bonds with atoms O8 and O9 of the AsO₄ tetrahedron (the corresponding interatomic distances are: O7–O9 – 2.50(14) Å; O7–O8 – 2.53(14) Å and O5–O9 – 2.56(13); O5–O8 – 2.77(12) Å). As a result, the bonds As–O8 and As–O9 are elongated up to 1.80(9) and 1.84(9) Å respectively (Table 4). This results in the partial protonation of AsO₄ groups (see description of the IR spectrum below). The H₂O molecule at the site O6 forms hydrogen

Table 2. X-ray powder diffraction data of långbanshyttanite.

I_{obs}	d_{obs}	I_{calc}^a	d_{calc}^a	hkl
100	14.48	100	14.44	001
43	7.21	45	7.218	002
9	5.450	6	5.482	011
34	4.969	26, 13	5.004, 4.943	100, 101
28	4.798	28	4.812	003
11	4.438	2	4.406	102
10	4.297	1	4.345	01–2
4	3.941	1	3.871	10–2
20	3.792	5, 11	3.818, 3.797	111, 110
54	3.571	16, 25, 3, 14	3.594, 3.584, 3.563, 3.407	112, 1–1–1, 01–3, 11–1
10	3.402	12	3.407	1–12
6	3.155	6, 1	3.163, 3.139	014, 104
10	3.027	7	3.042	1–13
45	2.857	16, 8, 26	2.875, 2.860, 2.842	020, 021, 114
34	2.800	29	2.781	11–3
9	2.672	10, 2	2.676, 2.664	1–14, 105
9	2.587	6, 7	2.606, 2.552	02–2, 023
17	2.517	2, 9, 1, 3	2.526, 2.524, 2.506, 2.502	121, 201, 120, 200
14	2.449	5, 4, 3	2.480, 2.446, 2.442	1–20, 1–21, 1–2–1
5	2.352	4	2.356	203
4	2.301	2, 2, 1	2.304, 2.301, 2.295	210, 212, 106
5	2.217	1, 1, 1	2.223, 2.209, 2.203	2–1–1, 1–23, 204
4	2.168	3	2.172	02–4
4	2.147	1	2.146	11–5
5	2.104	7, 1, 2	2.117, 2.102, 2.096	025, 21–2, 214
4	2.051	5	2.062	007
3	1.994	2	1.991	2–1–3
8	1.951	4, 3, 4	1.962, 1.955, 1.941	21–3, 215, 117
12	1.915	8, 1, 1, 1, 3	1.921, 1.917, 1.916, 1.909, 1.905	221, 030, 026, 222, 11–6
14	1.869	6, 7, 4	1.876, 1.874, 1.867	2–20, 2–21, 206
11	1.788	2, 3, 3, 3, 1, 2	1.797, 1.797, 1.794, 1.792, 1.782, 1.782	224, 130, 132, 2–2–2, 02–6, 2–23
6	1.766	1, 1, 2, 1	1.774, 1.771, 1.765, 1.758	1–3–1, 22–2, 1–31, 13–1
4	1.737	1, 1, 1	1.739, 1.737, 1.737	1–3–2, 03–3, 027
5	1.680	2, 1	1.682, 1.681	1–3–3, 22–3
4	1.641	2	1.644	03–4
14	1.609	2, 2, 3, 3	1.615, 1.614, 1.614, 1.611	226, 2–25, 135, 1–3–4
13	1.603	2, 1, 2, 1, 1, 2	1.607, 1.600, 1.597, 1.597, 1.592, 1.592	310, 313, 3–12, 3–10, 109, 1–1–8
5	1.517	2	1.520	31–2
4	1.501	2, 2, 1	1.505, 1.505, 1.498	315, 1–19, 12–7
5	1.458	2, 1, 2	1.463, 1.459, 1.456	1–28, 31–3, 1–2–8
5	1.437	1, 1, 1, 1	1.442, 1.441, 1.441, 1.437	137, 041, 129, 040
2	1.391	2, 1	1.391, 1.390	22–6, 04–2

^aCalculated from single-crystal data. For the calculated X-ray pattern, only reflections with intensities ≥ 1 are given.

bonds only with other H₂O molecules (O5 and O7) with the distances O6–O5 – 2.95(13) Å and O6–O7 – 2.55(16) Å. OH-groups at the sites O3 and O4 form weak hydrogen bonds with atoms O8 and O9 with the corresponding distances O3–O9 – 3.36(13) Å; O4–O8 – 3.34(12) Å.

Långbanshyttanite is a representative of a new structure type, it has no natural or synthetic analogues. Topologically, heteropolyhedral blocks in långbanshyttanite are close to that found in the structures of the copper arsenates geminite, Cu(AsO₃OH)·H₂O, (Cooper & Hawthorne, 1995; Prencipe *et al.*, 1996), yvonite, Cu(AsO₃OH)·2H₂O, (Sarp & Cerny, 1998) and lindackerite, (Cu,Co,Ni)Cu₄(AsO₄)₂(AsO₃OH)₂·9H₂O (Hybler *et al.*, 2003). The blocks [Mn₂(OH)₂·(AsO₄)₂]_{∞∞} found in långbanshyttanite can be compared

with heteropolyhedral layers of tsumcorite (Tillmanns & Gebert, 1973) and tsumcorite-type minerals and compounds (Effenberger *et al.*, 2000; Mihajlović & Effenberger, 2004), as well as natrochalcite, NaCu₂(SO₄)₂(OH)·H₂O (Rumanova & Volodina, 1958), and natrochalcite-type compounds including sulphates, selenates, chromates and molybdates with general formula $AMe_2(XO_4)_2[(H_2O)(OH)]$ where $A = \text{Na, K, Rb, Ag, Tl, NH}_4$, $Me = \text{Cu, Co, Ni, Zn}$, $X = \text{S, Se, Mo, Cr}$ (Giester & Zemmann, 1987; Krickl & Wildner, 2007). In the structure of natrochalcite, Cu octahedra share edges to form the columns which are linked by the vertices of SO₄ tetrahedra. As a result the layers $[M_2(OH)H_2O(TO_4)_2]_{\infty\infty}$ (where $M = \text{Mn, Cu}$ and $T = \text{As, S, O}$; $(M + T) = 2.5$) are formed. Thus the heteropolyhedral

Table 3. Atomic coordinates and isotropic atom displacements for långbanshyttanite.

Site	x	y	z	U_{iso}
Pb	0.0769(13)	0.2864(10)	0.3031(4)	0.024(4)
Mn	-0.018(5)	0.246(3)	0.5543(14)	0.010 ^a
As	0.415(3)	0.211(2)	0.7167(9)	0.006(5)
Mg	0.0	0.5	0.0	0.005(17)
O1	0.174(12)	0.346(12)	0.668(5)	0.010 ^a
O2	0.699(9)	0.088(12)	0.675(5)	0.010 ^a
O3	0.225(19)	0.410(14)	0.432(6)	0.010 ^a
O4	0.190(18)	-0.085(14)	0.564(6)	0.010 ^a
O5	0.114(19)	0.724(13)	0.096(6)	0.01(2)
O6	0.28(2)	0.230(15)	0.034(7)	0.02(3)
O7	0.30(3)	0.661(19)	-0.099(8)	0.05(4)
O8	0.206(19)	-0.004(13)	0.787(6)	0.010 ^a
O9	0.56(2)	0.406(15)	0.789(7)	0.02(3)

^aFixed during the refinement.

Table 4. Interatomic distances in långbanshyttanite.

Pb – polyhedron	Mn – octahedron
Pb–O3 2.28(8)	Mn–O1 2.16(6)
–O2 2.44(6)	–O4 2.16(9)
–O4 2.44(9)	–O3 2.19(9)
–O1 2.48(6)	–O3 2.23(9)
–O8 2.72(8)	–O2 2.25(7)
–O9 2.72(10)	–O4 2.30(8)
As – tetrahedron	Mg – octahedron
As–O1 1.648(10)	Mg–O7 2.12(12) × 2
–O2 1.649(10)	–O5 2.12(8) × 2
–O8 1.80(9)	–O6 2.17(10) × 2
–O9 1.84(9)	

blocks of långbanshyttanite can be considered as the characteristic feature of a large, chemically diverse group of minerals and inorganic compounds.

5. Infrared spectroscopy

Långbanshyttanite powder was mixed with anhydrous KBr in the proportion about 1:10³, pelletized, and analyzed using an analogue Specord 75 IR spectrophotometer. The IR spectrum of a pure KBr-disk was subtracted from the overall spectrum. Polystyrene and gaseous NH₃ were used as frequency standards; the precision of frequency measurement is ±1 cm⁻¹; the mean resolution for the range 400–1600 cm⁻¹ is 0.8 cm⁻¹.

Absorption bands in the IR spectrum (Fig. 4) of långbanshyttanite and their assignments (see Miller & Wilkins, 1952; Nakamoto, 1997; Đorđević & Karanović, 2008) are (cm⁻¹, sh – shoulder): 3477 (stretching vibrations of OH groups), 3340, 3090, 2860, 2625 (stretching vibrations of H₂O molecules forming strong hydrogen bonds), 2275, 2000sh (O–H stretching vibrations of acidic hydroxyl groups), 1644, 1600sh (bending vibrations of H₂O molecules), 1060, 1005, 943 (P–O stretching vibrations in PO₄³⁻ anions), 784 (As–O stretching vibrations in AsO₄³⁻ anions),

Table 5. Bond valence calculations for O-sites in långbanshyttanite. Parameters taken from Brese & O'Keeffe (1991), Krivovichev & Brown (2001) and Ferraris & Ivaldi (1988).

	Pb	As	Mn	Mg	Σ	H-bonding	Σ
O1	0.35	1.38	0.37		2.10		2.10
O2	0.38	1.38	0.29		2.05		2.05
O3 = OH	0.52		0.34		1.16	-0.09(O9)	1.07
			0.30				
O4 = OH	0.38		0.37		1.00	-0.09(O8)	0.91
			0.25				
O5 = H ₂ O				0.31 ^{x2l}	0.31	-0.20(O8) -0.32(O9) +0.14(O6)	-0.07
O6 = H ₂ O				0.27 ^{x2l}	0.27	-0.33(O7) -0.14(O5)	-0.20
O7 = H ₂ O				0.31 ^{x2l}	0.31	-0.37(O9) -0.34(O8) +0.33(O6) +0.09(O4) +0.20(O5) +0.34(O7)	-0.07
O8	0.21	0.91				+0.09(O4) +0.20(O5) +0.34(O7)	1.75
O9	0.21	0.82				+0.09(O3) +0.32(O5) +0.37(O7)	1.81
Σ	2.05	4.49 ^a	1.92	1.78			

^aLow value of bond-valence sum on As atom is due to the elongation of As–O8 and As–O9 bonds because of the partial protonation of AsO₄ groups.

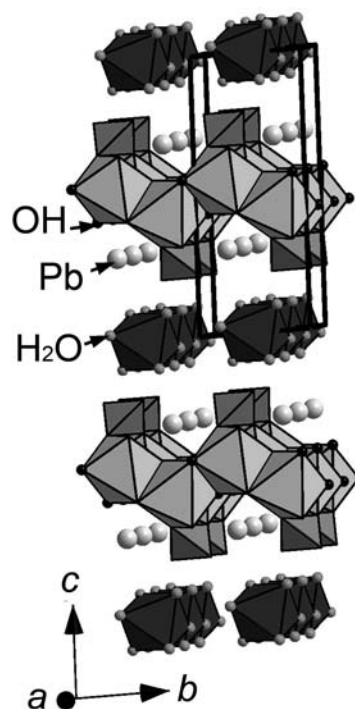


Fig. 2. Crystal structure of långbanshyttanite: general view. AsO₄ tetrahedra are medium-grey, MnO₂(OH)₄ octahedra are light-grey, Mg(H₂O)₆ octahedra are dark-grey.

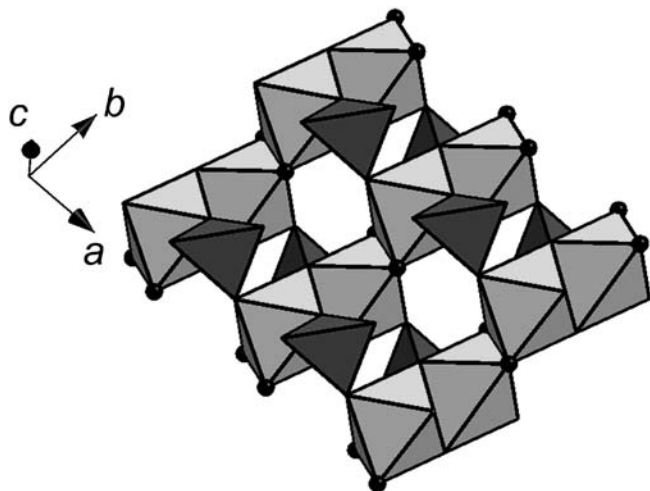


Fig. 3. Heteropolyhedral block in the structure of ląngbanshyttanite.

627 (librational modes of H₂O molecules), 390 (stretching vibrations in MO₆ octahedra). Based on the IR spectroscopic data, featuring the strongest band at 784 cm⁻¹, ląngbanshyttanite is an arsenate, not an arsenite as the absorption maximum of the strongest band of As–O stretching vibrations of the anions (As³⁺O₃)³⁻ in arsenites is observed at wavenumbers below 700 cm⁻¹ (Bahfennea & Frost, 2010).

A relatively weak band at 2275 cm⁻¹ and shoulder at 2000 cm⁻¹ (connected with vibrations of acidic O–H groups, *i.e.* strongly polarized O–H groups) could be due to partial protonation of arsenate anions, in accordance with the equilibrium H₂O + AsO₄³⁻ ↔ OH⁻ + HAsO₄²⁻. This phenomenon is common for hydrous arsenates with very strong hydrogen bonds to H₂O molecules (Pekov *et al.*, 2001; Chukanov *et al.*, 2010).

The following empirical correlations between O–H stretching frequencies in IR spectra of minerals and O · · · O and H · · · O distances (from structural data) were established by Libowitzky (1999):

$$\nu(\text{cm}^{-1}) = 3592 - 304 \times 10^9 \times \exp\left[\frac{-d(\text{O} \cdots \text{O})}{0.1321}\right] \quad (1)$$

$$\nu(\text{cm}^{-1}) = 3632 - 1.79 \times 10^6 \times \exp\left[\frac{-d(\text{H} \cdots \text{O})}{0.2146}\right] \quad (2)$$

It should be noted that at high frequencies (above 3500 cm⁻¹) substantial deviations from the correlations (1) and (2) are possible because O–H stretching frequencies depend not only on O · · · O and H · · · O distances, but also on the nature of cations coordinating O–H groups and H₂O molecules, as well as on the angle O–H · · · O, and the influence of these factors becomes most evident in case of weak hydrogen bonds. The Equations (1) and (2) predict that maximum possible values of O–H stretching frequencies for minerals are 3592 and 3632 cm⁻¹ respectively. However *e.g.* for magnesium serpentines, brucite and kaolinite, observed frequencies are close to 3700 cm⁻¹.

After this *proviso* let us try to establish the connection of observed O–H stretching frequencies to O · · · O distances for hydrogen bonds. IR absorption bands located at 2000, 2275, 2625 and 2680 cm⁻¹ (O · · · O distances calculated from Equation (1) being 2.52, 2.54, 2.585 and 2.59 Å respectively) can be put in correspondence with the distances O7 · · · O9 (2.50 Å), O7 · · · O8 (2.53 Å), O5 · · · O9 (2.56 Å) and O6 · · · O7 (2.55 Å). The wavenumbers of the bands at 3090, 3340 and 3477 cm⁻¹ (O · · · O distances calculated from Equation (1) being 2.67, 2.76, 2.87 Å respectively) should be correlated with O6 · · · O5 (2.95 Å), O4 · · · O8 (3.34 Å) and O3 · · · O9 (3.36 Å). For the latter three bands, the agreement between O · · · O distances calculated from structural data and from IR spectrum is worse, probably for the above-mentioned reasons. An additional reason for the observed discrepancy can be due to high errors in the determination of O · · · O distances for hydrogen bonds.

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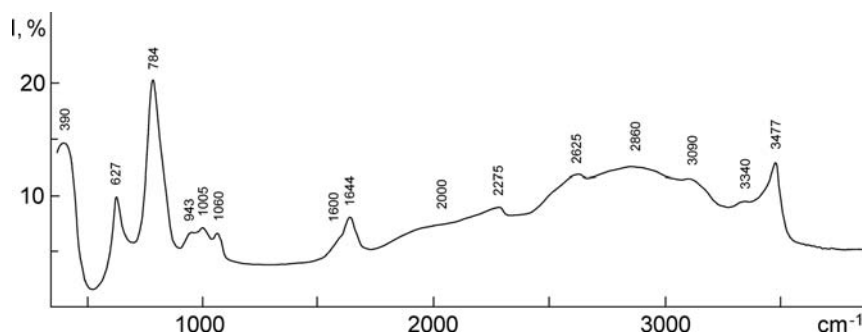


Fig. 4. IR absorbance spectrum of ląngbanshyttanite.

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