

LEMANSKIITE, $\text{NaCaCu}_5(\text{AsO}_4)_4\text{Cl}\cdot 5\text{H}_2\text{O}$, A NEW MINERAL SPECIES FROM THE ABUNDANCIA MINE, CHILE

PETR ONDRUŠ AND FRANTIŠEK VESELOVSKÝ

Czech Geological Survey, Geologická 6, CZ-15200 Prague, Czech Republic

ROMAN SKÁLA[§]

*Institute of Geology, Academy of Sciences of the Czech Republic, Rozvojová 269,
CZ-16500 Praha 6 – Lysolaje, Czech Republic*

JIŘÍ SEJKORA

National Museum, Václavské nám. 68, CZ-11579 Prague 1, Czech Republic

RICHARD PAŽOUT

U průhonu 42, CZ-17000 Prague 7, Czech Republic

JIŘÍ FRÝDA AND ANANDA GABAŠOVÁ

Czech Geological Survey, Geologická 6, CZ-15200 Prague, Czech Republic

JOSEF VAJDAK

Pequa Rare Minerals, 342 Forest Avenue, Massapequa, New York 11758-5707, USA

ABSTRACT

Lemanskiite, ideally $\text{NaCaCu}_5(\text{AsO}_4)_4\text{Cl}\cdot 5\text{H}_2\text{O}$, is a new mineral species from the Abundancia mine, El Guanaco mining district, Chile. It is dimorphous with lavendulan and represents the Ca-analogue of zdenekite. It occurs as rosette-shaped aggregates (up to 5 mm) of thin lamellar, subparallel, strongly bent intergrowths ($0.3 \text{ mm} \times 10 \text{ }\mu\text{m}$) or needle-shaped aggregates of 0.8 mm length and 10 μm in thickness. Individual thin tabular crystals (up to 4 mm in length) are invariably bent. It is associated with lammerite, olivenite, mansfieldite, senarmontite, a mineral of the crandallite group, rutile, anatase, and talc. Lemanskiite is dark sky blue, translucent, nonfluorescent with a light blue streak. It is brittle with an excellent cleavage parallel to (001); its luster is vitreous, and its Mohs hardness is $\sim 2\frac{1}{2}$. The mineral displays no parting, and its fracture is uneven. It is optically negative, uniaxial, with indices $\epsilon = 1.647(2)$ and $\omega = 1.749(2)$; its birefringence is 0.102, and the pleochroism is very strong. The compatibility index is superior (0.009). An electron-microprobe analysis revealed the following chemical composition (in wt.%): CaO 5.33(7), Na_2O 3.04(18), CuO 37.76(44), As_2O_5 43.53(59), Cl 3.23(7). The content of H_2O (8.50 wt.%) was determined with a CHN analyzer. The empirical formula based on 22 anions is $\text{Na}_{1.04}\text{Ca}_{1.00}\text{Cu}_{5.01}(\text{AsO}_4)_{4.00}[\text{Cl}_{0.96}(\text{OH})_{0.11}]_{\Sigma 1.07}\cdot 4.93 \text{ H}_2\text{O}$. Crystallographic data were derived from the data on zdenekite. The whole-powder-pattern fitting assuming the tetragonal space-group $P4_122$ (or $P4_322$) gave the following parameters: a 9.9758(4), c 36.714(1) Å, V 3653.6(2) Å³, with $Z = 8$, $D_x = 3.863(5)$, and $D_m = 3.78(1) \text{ g/cm}^3$. The strongest five lines in the X-ray powder pattern [d in Å (hkl)] are: 9.60(9)(101), 9.177(100)(004), 4.588(32)(008), 4.167(10)(108), 3.059(15)(0.0.12). The name honors Chester S. Lemanski, Jr. (b. 1947), mineral collector who built one of the largest privately held collections in the USA. Both the mineral and its name have been approved by the Commission on New Minerals and Mineral Names (IMA 99-037).

Keywords: lemanskiite, lavendulan, zdenekite, new mineral species, electron-microprobe data, unit-cell parameters, infrared spectrum, thermal analysis, secondary mineral, Abundancia mine, Chile.

[§] E-mail address: skala@gli.cas.cz

SOMMAIRE

La lemanskiite, de formule idéale $\text{NaCaCu}_5(\text{AsO}_4)_4\text{Cl}\cdot 5\text{H}_2\text{O}$, est une nouvelle espèce minérale découverte à la mine Abundancia, district minier de El Guanaco, au Chili. Elle possède une relation dimorphique avec la lavendulane et représente l'analogie calcique de la zdenekite. Elle se présente en agrégats en forme de rosettes atteignant 5 mm contenant des lamelles subparallèles minces et courbes en intercroissances ($0.3 \text{ mm} \times 10 \text{ }\mu\text{m}$) ou bien des agrégats aciculaires ayant 0.8 mm de long et $10 \text{ }\mu\text{m}$ en épaisseur. Les minces cristaux individuels, atteignant 4 mm en longueur, sont courbes. Lui sont associés lammerite, olivénite, mansfieldite, senarmontite, un minéral du groupe de la crandallite, rutilite, anatase, et talc. La lemanskiite est bleu ciel foncé, translucide, nonfluorescente avec une rayure bleu pâle. Elle est cassante avec un excellent clivage parallèle à (001); son éclat est vitreux, et sa dureté de Mohs est d'environ $2\frac{1}{2}$. Le minéral ne montre aucun plan de séparation, et sa fracture est inégale. Il est optiquement négatif, uniaxe, avec les indices $\varepsilon = 1.647(2)$ et $\omega = 1.749(2)$; sa biréfringence est égale à 0.102, et son pléochroïsme est frappant. L'indice de compatibilité est supérieur (0.009). Une analyse avec une microsonde électronique révèle la composition chimique suivante (en proportions pondérales): CaO 5.33(7), Na_2O 3.04(18), CuO 37.76(44), As_2O_5 43.53(59), Cl 3.23(7). La teneur en H_2O (8.50%) a été établie au moyen d'un analyseur CHN. La formule empirique fondée sur 22 anions est $\text{Na}_{1.04}\text{Ca}_{1.00}\text{Cu}_{5.01}(\text{AsO}_4)_{4.00}[\text{Cl}_{0.96}(\text{OH})_{0.11}]_{\Sigma 1.07}\cdot 4.93 \text{ H}_2\text{O}$. Les données cristallographiques ont été dérivées des données sur la zdenekite. Une simulation du spectre de diffraction sur poudre en supposant le groupe spatial tétragonal $P4_122$ (ou $P4_322$) a donné les paramètres suivants: a 9.9758(4), c 36.714(1) Å, V 3653.6(2) Å³, avec $Z = 8$, $D_x = 3.863(5)$, et $D_m = 3.78(1) \text{ g/cm}^3$. Les cinq raies les plus intenses du spectre de diffraction, méthode des poudres [d en Å (hkl)] sont: 9.60(9)(101), 9.177(100)(004), 4.588(32)(008), 4.167(10)(108), et 3.059(15)(0.0.12). Le nom honore Chester S. Lemanski, Jr. (b. 1947), collectionneur de minéraux qui a monté une des collections privées les plus impressionnantes des États-Unis. Le minéral et son nom ont été approuvés par la Commission des Nouveaux Minéraux et des Noms de Minéraux (IMA 99-037).

(Traduit par la Rédaction)

Mots-clés: lemanskiite, lavendulane, zdenekite, nouvelle espèce minérale, données de microsonde électronique, paramètres réticulaires, spectroscopie infra-rouge, analyse thermique, minéral secondaire, mine Abundancia, Chili.

INTRODUCTION

Lemanskiite, ideally $\text{NaCaCu}_5(\text{AsO}_4)_4\text{Cl}\cdot 5\text{H}_2\text{O}$, is a secondary mineral belonging to a group of Cl-bearing hydrated Na–Cu arsenates or phosphates containing Ca or Pb. Lemanskiite is dimorphous with lavendulan, and is the Ca-analogue of zdenekite. It was found on dumps of the abandoned Abundancia mine, El Guanaco mining district, Region II, Antofagasta Province, Chile.

The new mineral species is named after Chester S. Lemanski, Jr. (born 1947), in recognition of his mineralogical activities; he has built up one of the largest privately held mineralogical collections in the USA. He was the first to recognize the material as a new mineral species, and provided it to the authors for study. The new species and its name were approved by the Commission on New Minerals and Mineral Names of the International Mineralogical Association (IMA 99-037). The holotype sample has been deposited in the mineralogical collection of the National Museum, Prague, Czech Republic (acquisition number P1P 14/99).

Our objectives here are to provide a complete description of the new species, and to explore its relationship to lavendulan and related species.

The lavendulan–lemanskiite problem

During our study of secondary minerals of the Jáchymov (Joachimsthal) ore district, in western Bohemia, Czech Republic (Ondruš *et al.* 1997a, b, c, 2004, Hybler *et al.* 2003), we discovered that laven-

dulan represents rather a complex group of distinct phases with similar color and chemical composition, but distinct structures, and thus not a single mineral. In many cases, we found that material with a composition and a color corresponding to lavendulan does not contain this mineral.

Lavendulan was originally described and named by Breithaupt (1837) as a mineral containing As, Co and Ni (qualitative analysis done by H. Plattner). The problem of the definition of lavendulan is complicated because its holotype, deposited in the Mining Academy, Freiberg, Germany, does not correspond to the mineral lavendulan as defined now. This holotype originates from the type locality, Galliläusche Wirtschaft mine in Annaberg. According to the label, written and signed by Breithaupt in 1835, he obtained this material from mining official von Fromberger (Hofmann 1992). This holotype is represented by several fragments of vitreous zoned material of grayish blue color up to 5 mm long, similar to chalcedony. Our X-ray study of this material shows that it is completely amorphous and contains mainly As, Zn, and minor Cu, Co, and S.

Vogl (1853a, b) described lavendulan as a blue coating from Jáchymov. Foshag (1924a) published a detailed description of lavendulan from Jáchymov, and reported two indices of refraction [$\beta = 1.715(5)$, $\gamma = 1.725(3)$]. In his next paper, Foshag (1924b) described a new mineral species, "freirinite", from the Blanca mine, San Juan, Department of Freirini, Chile. Its indices of refraction ε and ω were found to be 1.645 and 1.748, respectively. He gave the chemical formula as $\text{Na}_6\text{Ca}_{1.5}\text{Cu}_{4.5}(\text{AsO}_4)_4\text{O}_4\cdot 6\text{H}_2\text{O}$. Guillemin (1956) determined by

X-ray diffraction that “freirinite” from San Juan and lavendulan from Jáchymov are identical.

Foshag’s indices of refraction for “freirinite” are in fact identical with those of lemanskiite. But the reliability of his data is questionable because the indices of refraction of lavendulan do not correspond to his measured values for lavendulan from Jáchymov mentioned above. It was impossible to redetermine the optical constants on Foshag’s original material, deposited in Smithsonian Institute in Washington. As a result, we do not know what mineral phase was determined by Foshag.

Lavendulan-like minerals from Jáchymov represent a group of mostly unknown minerals. Apart from lavendulan, several other phases were identified, containing, for example, K instead of Na, Pb instead of Ca, and there are also several structural variants of phases fitting the nominal composition of lavendulan.

For the purpose of this article, samples from various localities worldwide labeled as lavendulan were tested: Talmessi in Iran, San Juan, Blanca mine in Chile, and Postrama Murcia in Spain. The X-ray-diffraction patterns of material from all these localities confirm that all samples are not lavendulan but in fact lemanskiite. On the contrary, samples of lavendulan from Jáchymov and from Laurion, in Greece, were confirmed to be lavendulan. The identification of lavendulan from Laurion was confirmed, but the material powdered for X-ray analysis transformed to lemanskiite after several days. It seems that lemanskiite is more stable than lavendulan, although lavendulan from Jáchymov never did change into lemanskiite once pulverized.

The properties of lemanskiite, lavendulan and zdenekite are summarized in Table 1.

TABLE 1. COMPARISON OF CRYSTAL DATA, PHYSICAL AND OPTICAL PROPERTIES OF LEMANSKIITE, ZDENEKITE, AND LAVENDULAN

	lemanskiite	lavendulan	zdenekite	
formula	$\text{NaCaCu}_3(\text{AsO}_4)_4\text{Cl}\cdot 5\text{H}_2\text{O}$	$\text{NaCaCu}_3(\text{AsO}_4)_4\text{Cl}\cdot 5\text{H}_2\text{O}$	$\text{NaPbCu}_3(\text{AsO}_4)_4\text{Cl}\cdot 5\text{H}_2\text{O}$	
reference	this work	Guillemin (1956), Chiappero (1997)	Prem <i>et al.</i> & Sarp (1995)	* Zubkova <i>et al.</i> (2003)
crystal system	tetragonal	monoclinic	tetragonal	monoclinic
space group	$P4_122$ or $P4_222$	$P2_1/n$	$P4_122$ or $P4_222$	$P2_1/n$
a [Å]	9.9758	10.009	10.066	10.023
b [Å]		19.467		19.55
c [Å]	36.714	10.059	39.390	10.023
β [°]		90.31		90.02
V [Å ³]	3653.6	1959.9	3991.4	1964.6
Z	8	4	8	4
n_u (e)	1.647	1.661	1.710	
n_b (o)	1.749	1.734	1.770	
n_z		1.734		
\bar{n}	1.715	1.710	1.750	
D_m [g/cm ³]	3.78	3.54	4.10	4.08
D_x [g/cm ³]	3.863	3.60	4.08	4.16

* See notes on the crystal structure in the section on Crystallography.

Location, occurrence and paragenesis

The Abundancia gold mine, El Guanaco mining district, is located south of Cerro La Estrella, about 95 km east of Taltal on the Pacific Coast, and about 53 km east of the Panamerican Highway, near the railway station East Catalina, Region II, Antofagasta Province, Chile (Fig. 1). Very little is known about this small vein-type Au deposit in Chile. The quartz veins contain several sulfides, mostly enargite. Vuggy silica zones are followed outward by pyrophyllite – alunite – kaolinite zones, and finally by propylitic alteration.

Lemanskiite occurs in quartz veins. It is associated with coarse grains or crystals of dark green lammerite. The other associated minerals include dark green crystals of olivenite, light bluish gray mansfieldite, small grains of whitish senarmontite, a mineral of the crandallite group, and a grayish brown mixture of rutile, anatase and talc. The new mineral is of secondary origin, derived from unknown primary minerals.

Its intergrowths with lammerite indicate very acid conditions of origin (Williams 1990), characteristic of epithermal deposits.



FIG. 1. Sketch map displaying the geographic location of the El Guanaco mining district, in northern Chile.

Physical properties

Lemanskiite forms massive nodules up to 5 cm long or fills veinlets in quartz (Figs. 2, 3). Two modes of occurrence have been observed. Firstly, there are rosette-shaped aggregates of thin, lamellar, subparallel intergrowths ($0.3 \text{ mm} \times 10 \text{ }\mu\text{m}$) with strongly bent and extremely thin individual domains $0.1 \text{ }\mu\text{m}$ or less in thickness (Fig. 4). Also, there are needle-shaped aggregates 0.8 mm in length and $10 \text{ }\mu\text{m}$ in thickness. These needles are also composed of extremely thin platelike individuals and strongly bent crystals.

Individual thin tabular crystals of lemanskiite are up to 4 mm in length. The crystals are not straight but invariably bent, which caused problems in the determination of both optical and structural properties of single crystals. The typical shape of lemanskiite crystals is shown in Figure 4, in which the crystals are oriented perpendicular to a glass slide.

Lemanskiite is translucent and dark sky blue in color. Its luster is vitreous, and its streak is light blue. It is brittle, and has an excellent cleavage parallel to the largest face visible on crystals, which is (001). The mineral displays no parting and has an uneven fracture. The Mohs hardness is about $2\frac{1}{2}$. The density, measured by flotation in Clerici solution, is $3.78(1) \text{ g/cm}^3$. The calculated density based on the empirical formula, is $3.863(5) \text{ g/cm}^3$. Lemanskiite shows very strong pleochroism: O: dark green-blue, E: light blue-green (light turquoise). Lemanskiite is optically negative and has the following indices of refraction: ϵ 1.647(2) and ω 1.749(2). The birefringence is 0.102. The orientation of the optical and crystallographic directions in lemanskiite crystals is given in Figure 5. The compatibility index [$1 - (K_P/K_C) = 0.009$] is superior. It is nonfluorescent.

Chemical composition

The qualitative and quantitative chemical composition of lemanskiite was measured with a CamScan 4 scanning electron microscope with a LINK eXL energy-dispersion analyzer and a Microspec WDX-3PC wavelength-dispersion analyzer. The following conditions were used for WD analyses: operating voltage 20 kV , sample current 20 nA , and beam size $5 \times 5 \text{ }\mu\text{m}$; lammerite (Cu, As, O), wollastonite (Ca), and halite (Na, Cl) were used as standards. The correction procedure Phi(rho Z) was used for reduction of all quantitative analytical data.

We determined the amount of H_2O quantitatively with a Perkin Elmer 2400 CHN analyzer, and its presence was unambiguously established by infrared absorption spectroscopy and thermogravimetry (Tables 2, 3).

In Table 4, we summarize the results of fifteen analyses and the ideal composition, *i.e.*, the simpli-

fied formula. The empirical formula of lemanskiite, calculated on the basis of 22 anions (O, OH, Cl) per formula unit, is $\text{Na}_{1.04}\text{Ca}_{1.00}\text{Cu}_{5.01}(\text{AsO}_4)_{4.00}[\text{Cl}_{0.96}(\text{OH})_{0.11}]_{\Sigma 1.07} \cdot 4.93 \text{ H}_2\text{O}$, resulting in the ideal formula $\text{NaCaCu}_5(\text{AsO}_4)_4\text{Cl} \cdot 5 \text{ H}_2\text{O}$, which requires Na_2O 2.92, CaO 5.28, CuO 37.45, As_2O_5 43.28, Cl 3.34, H_2O 8.48, sum 100.75, less $\text{O}=\text{Cl}$ 0.75, for a total of 100.00 wt. %.

We heated lemanskiite hydrothermally in a quartz capsule at 200°C for 48 hours, and found that it had transformed to olivenite.

Crystallography

Attempts to collect single-crystal data have been made using a CAD4 MACHIII four-circle diffractometer. However, we failed to acquire such data owing to the unsuitability of the material. All available crystals are significantly bent, and they represent multiple subparallel intergrowths (Fig. 4).

The symmetry, space group and the indexing of the powder pattern are based on the assumption that lemanskiite represents a Ca-analogue of zdenekite and on the close similarity of X-ray powder patterns of the two minerals. Therefore, we adopted the crystallographic model of zdenekite with tetragonal symmetry and space group $P4_122$ or $P4_322$ (Chiappero & Sarp 1995). Though the crystal structure of zdenekite was published recently (Zubkova *et al.* 2003), and shown to have monoclinic (pseudotetragonal) symmetry, we did not use their model for lemanskiite because we found large discrepancies in bond-valence data derived from that refinement. For example, bond valences derived from their structure data gave abnormal values: As3 (3.9), As4 (7.9), O2 (3.0), O7 (3.3), O12 (2.8), O15 (2.8) valence units. These results indicate an incorrect solution of the structure of zdenekite.

Powder-diffraction data were collected using a Philips X'Pert MPD diffractometer. Copper radiation was used with a graphite secondary monochromator. The powder pattern of lemanskiite was collected in the range from 3 to $130^\circ 2\theta$ with a step size of $0.02^\circ 2\theta$ and an exposure of 35 s per step. To minimize the complicated shape of background, the sample studied was placed on a flat low-background silicon wafer.

By application of whole-powder-pattern fitting, we refined the dimensions of the tetragonal unit-cell: a $9.9758(4)$, c $36.714(1) \text{ \AA}$, V $3653.6(2) \text{ \AA}^3$, with $a : c = 0.2717 : 1$. The number of formula units Z per unit cell is 8, and the space group is taken to be $P4_122$ or $P4_322$.

Thermal analysis

Thermal analyses of lemanskiite were carried out with a Stanton Redcroft TG 750 Thermobalance (TG) and a differential thermal analysis apparatus as described by Blazek (1973). The operating conditions

were as follows: TG: sample weight 3.95 mg, heating rate 10°C/min, dynamic air atmosphere 10 mL/min; DTA: sample weight 20.0 mg, heating rate 10°C/min, static air atmosphere and Al₂O₃ reference sample.

A tentative assignment and interpretation of the TG and DTA curves (Fig. 6) are as follows: lemanskiite dehydrates in distinct, partially overlapping steps over the range 20–550°C (a loss of 8.80 wt.% corresponds to ~5 H₂O). This substantiates the presence of structurally nonequivalent molecules of H₂O in the structure of lemanskiite. One weakly bonded H₂O molecule is released in the range 20–65°C, and the other four molecules of H₂O are stepwise released over the range 65–550°C (Table 2). A stepwise loss of weight over the interval 550–820°C may be assigned to oxygen or

chlorine release. An X-ray analysis of the product of the TG analysis of lemanskiite corresponds to a monoclinic NaCu₄(AsO₄)₃ (ICDD PDF card 43–170). Such an observation indicates that the decomposition product does not contain any chloride anions, in agreement with the conclusion concerning the thermal decomposition of lavendulan given by Guillemin (1956). The DTA curve of lemanskiite shows strong endothermic peaks at 70 and 210°C connected with a loss of a part of the H₂O molecules, and a small exothermic peak at 310°C. A small endothermic peak at 520°C corresponds to the last step in the dehydration and indicates that dehydration processes are complete. However, this endothermic reaction probably is related also to the crystallization of a new phase. A strong endothermic reaction at 960°C is connected with melting of the previously formed anhydrous intermediates.

TABLE 2. THERMOGRAVIMETRIC ANALYSIS OF LEMANSKIITE

Temperature range (°C)	Weight loss (wt.%)	Weight loss (mg)	Interpretation
20 - 65	1.75	0.069	1 H ₂ O
65 - 150	1.05	0.041	0.6 H ₂ O
150 - 190	0.95	0.038	0.5 H ₂ O
190 - 220	0.60	0.024	0.3 H ₂ O
220 - 430	3.40	0.134	2 H ₂ O
430 - 550	1.05	0.041	0.6 H ₂ O
20 - 550	8.80	Σ 0.347	Σ 5 H ₂ O
550 - 820	2.60	0.103	0.9 O ₂ or 0.4 Cl ₂
20 - 820	11.40	Σ 0.450	Σ 5 H ₂ O and 0.9 O ₂ or 0.4 Cl ₂

Endotherms (°C): 70 (strong), 210 (strong), 520 (small), 960 (strong); exotherm (°C): 310 (small).

TABLE 3. INFRARED VIBRATIONAL SPECTRA OF LEMANSKIITE

Frequency, feature	DRIFT	Tentative assignment
3559 s sh		
3521 s sh		
3437 vs	3451 3343	v(OH) stretching vibrations in H ₂ O molecules
3229 m sh		
1630 s sh	1644	δ H ₂ O bending vibrations
1618 vs	1619	
927 m		
902 m sh		v ₃ (AsO ₄) ³⁻ antisymmetric stretching-vibration (may partly overlap with libration modes of H ₂ O)
880 m sh		
839 s		
815 s		v ₁ (AsO ₄) ³⁻ symmetric stretching vibration
789 s		
541 vs		
485 s		v ₄ (AsO ₄) ³⁻ out-of-plane bending vibrations (overlap with Cu–O vibrations possible)
440 s		

Nicolet 740 FTIR spectrophotometer. Intensity and character of absorption bands: vs: very strong, s: strong, m: medium, sh: shoulder. Sample in KBr tablet. Wavenumbers expressed in cm⁻¹.

Infrared vibrational spectra

The infrared vibrational spectra of lemanskiite (Fig. 7) were recorded with a Nicolet 740 FTIR spectrometer using KBr disk (range 4000–400 cm⁻¹) and diffusion-reflection mode (DRIFT) (4000–1400 cm⁻¹). Tentative assignment of the infrared bands of lemanskiite (Table 3) was made on the basis of data published by Ross (1974), Nakamoto (1986), Myneni *et al.* (1998), Frost *et al.* (2002) and Martens *et al.* (2003a, b, 2004).

Bands characteristic of vibrations connected with H₂O and (AsO₄)³⁻ groups are present. The symmetry of the (AsO₄)³⁻ group is lowered from T_d to D₄. This causes a splitting of both triply degenerate vibrations, *i.e.*, the antisymmetric stretching v₃ and the bending vibration v₄ of (AsO₄)³⁻, and also an activation of the v₁ (AsO₄)³⁻ symmetric stretching vibration. Bands and shoulders at 927, 902, 880 and 839 cm⁻¹ may be attributed to the v₃ (AsO₄)³⁻; a coincidence with

TABLE 4. CHEMICAL COMPOSITION OF LEMANSKIITE

	1 wt.%	σ	2 wt.%	3 <i>apfu</i>
Na ₂ O	3.04	0.18	2.92	Na 1.036
CaO	5.33	0.07	5.28	Ca 1.004
CuO	37.76	0.44	37.45	Cu 5.013
As ₂ O ₃	43.53	0.59	43.28	AsO ₄ 4.000
Cl	3.23	0.07	3.34	Cl 0.962
				OH 0.107
H ₂ O	8.50		8.48	H ₂ O 4.929
Sum	101.39		100.75	
-O=Cl	0.73		0.75	
Total	100.66		100.00	

1) average chemical composition and associated standard uncertainties; the amount of H₂O was determined with a CHN analyzer.
2) ideal composition corresponding to the ideal formula, NaCaCu₄(AsO₄)₃Cl·5H₂O.
3) proportions of the constituents recalculated on the basis of 22 (O, OH, Cl).

libration modes of H₂O cannot be excluded, however. Bands at 815 and 789 cm⁻¹ may be connected with the ν_1 (AsO₄)³⁻; the intensity of the two bands is surprisingly high, however. Yet, it should be noted here that the literature data on ν_1 and ν_3 (AsO₄)³⁻ (Ross 1974, Myneni *et al.* 1998, Frost *et al.* 2002, Martens *et al.* 2003a, b, 2004) are conflicting. Bands at 541, 485 and 440 cm⁻¹ may be attributed to the ν_4 (AsO₄)³⁻ vibrations, but overlaps with the Cu–O stretching vibrations cannot be ruled out. The number of bands and shoulders attributed to the (AsO₄)³⁻ stretching and bending vibrations indicates that at least two symmetrically distinct (AsO₄) groups are present in the structure of lemanskiite.

The ν (OH) stretching vibrations of H₂O molecules are located in the region 3800–2800 cm⁻¹; the δ H₂O bending vibrations are in the range 1650–1600 cm⁻¹. The frequency of these vibrations indicates that some hydrogen bonds may well be involved in the structure of lemanskiite. Considering the correlation of the O–H...O bond lengths with the IR band frequencies given by Libowitzky (1999), it is obvious that both weak and strong H-bonds are present in the structure. Likewise, the results of the thermal analysis and the IR spectroscopy of lemanskiite confirm the presence of at least two types of structurally non-equivalent molecules of H₂O in the structure.



FIG. 2. Gemmy 4–5 mm crystals of lemanskiite in vugs of quartz in a talc matrix. Private collection of Josef Vajdak, photo by Jeffrey G. Weissman.

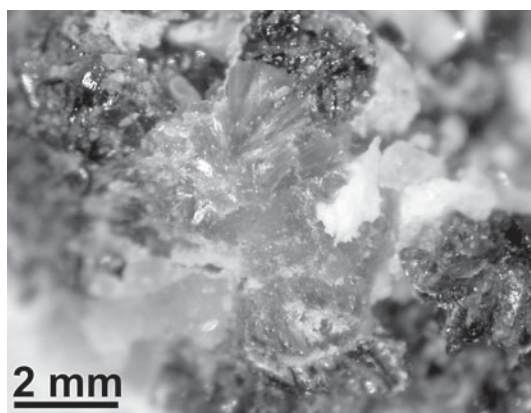


FIG. 3. Rosette-shaped aggregates of lemanskiite on a quartz matrix. Photo by A. Gabašová.

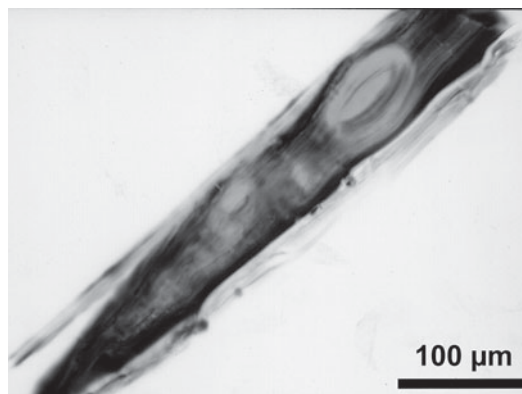


FIG. 4. Aggregate of extremely thin (less than 0.1 μm) and bent tabular crystals of lemanskiite, in subparallel orientation.

TABLE 5. X-RAY POWDER-DIFFRACTION PATTERN OF LEMANSKIITE

<i>h</i>	<i>k</i>	<i>l</i>	<i>d</i> _{obs}	<i>d</i> _{calc}	<i>I</i> _{obs}	<i>h</i>	<i>k</i>	<i>l</i>	<i>d</i> _{obs}	<i>d</i> _{calc}	<i>I</i> _{obs}
1	0	0	9.946	9.976	2	3	1	7	2.698		<1
1	0	1	9.600	9.627	9	3	2	3	2.692		1
0	0	4	9.177	9.179	100	3	0	8	2.688		<1
1	1	0	7.037	7.054	2	1	1	13	2.620		1
1	0	4	6.746	6.754	2	2	0	12	2.606		6
1	0	5	5.908	5.914	<1	3	1	9	2.4915		2
1	1	4	5.584	5.593	1	4	0	2	2.4654		1
2	0	0	4.976	4.988	2	4	1	1	2.4084		<1
1	0	7	4.639	4.642	3	1	0	16	2.2355		<1
0	0	8	4.588	4.589	32	1	1	16	2.1811		<1
2	1	1	4.418	4.429	1	4	2	4	2.1626		<1
2	0	4	4.374	4.383	3	4	1	8	2.1361		<1
1	1	7	4.205	4.209	2	2	0	16	2.0834		<1
1	0	8	4.167	4.169	10	1	1	18	1.9586		<1
2	0	5	4.119	4.126	<1	1	0	20	1.8049		4
2	1	4	4.004	4.012	2	2	0	19	1.8009		1
1	0	9	3.774	3.776	<1	3	1	17	1.7804		<1
1	1	9	3.529	3.531	<1	2	2	18	1.7643		1
2	0	8	3.373	3.377	<1	2	0	20	1.7219		3
3	0	0	3.317	3.325	<1	1	0	21	1.7216		2
3	0	3	3.202	3.209	<1	3	0	19	1.6694		<1
2	2	5	3.173	3.179	<1	5	2	10	1.6506		<1
3	1	1	3.135	3.143	3	1	0	23	1.5758		<1
3	0	4	3.120	3.126	1	0	0	24	1.5294		<1
0	0	12	3.059	3.060	15	3	1	21	1.5280		<1
2	1	9	3.007	3.011	2	5	1	17	1.4479		<1
3	1	4	2.977	2.983	<1	3	0	24	1.3889		<1
2	0	10	2.954	2.957	<1	2	0	27	1.3114		<1
1	0	12	2.924	2.925	5	0	0	28	1.3109		1
3	1	5	2.892	2.898	3	2	2	26	1.3102		4
2	1	10	2.832	2.835	<1	1	0	28	1.2997		1
2	0	11	2.771	2.774	<1	3	0	26	1.2990		1
3	2	1	2.752	2.759	<1	4	2	23	1.2969		<1
1	0	13	2.716	2.717	<1	0	0	32	1.1471		4

$I_{obs} \geq 0.5\%$, $d_{calc} > 1.145 \text{ \AA}$.

ACKNOWLEDGEMENTS

We benefitted from the thorough constructive reviews and editorial comments by H. Effenberger, C.M. Gramaccioli, R.F. Martin, J.A. Mandarino and G. Raade. The authors also express their gratitude to J. Čejka, National Museum, Prague, for comments on thermal analysis and infrared spectra of the phases studied, and to K. Rank, Mining Academy, Freiberg, Germany, for providing Breithaupt's type specimen of lavendulan for the study. We also thank the Grant Agency of the Czech Republic and the Ministry of Culture of the Czech Republic (project MK0 CEZ99F020) for support of the research. The study was a part of the research plan of the Inst. of Geology, AS CR, Prague (project AV0 Z30130516).

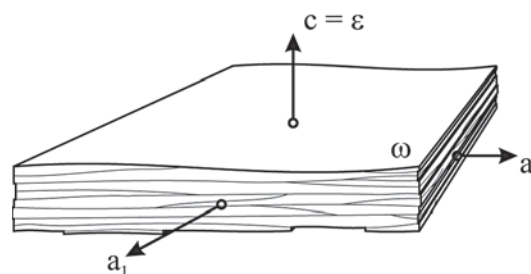


FIG. 5. Optical and crystallographic orientation of lemanskiite.

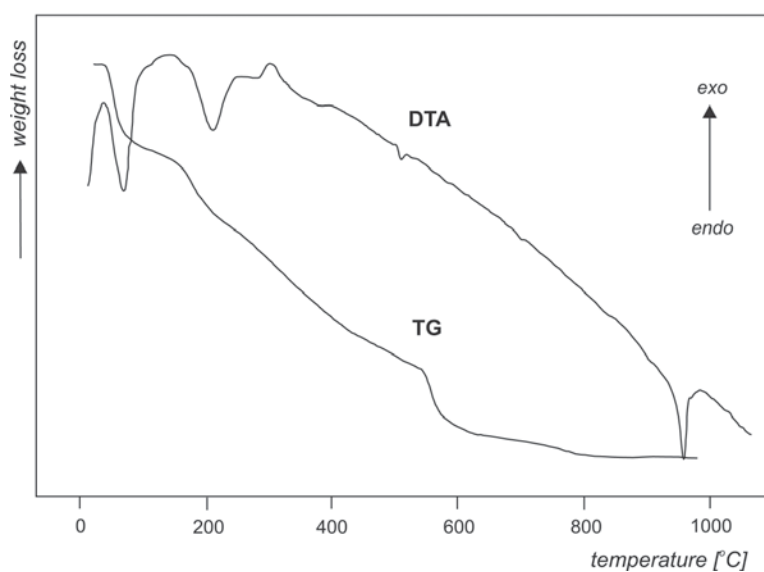


FIG. 6. Thermogravimetric (TG, DTA) curves for lemanskiite.

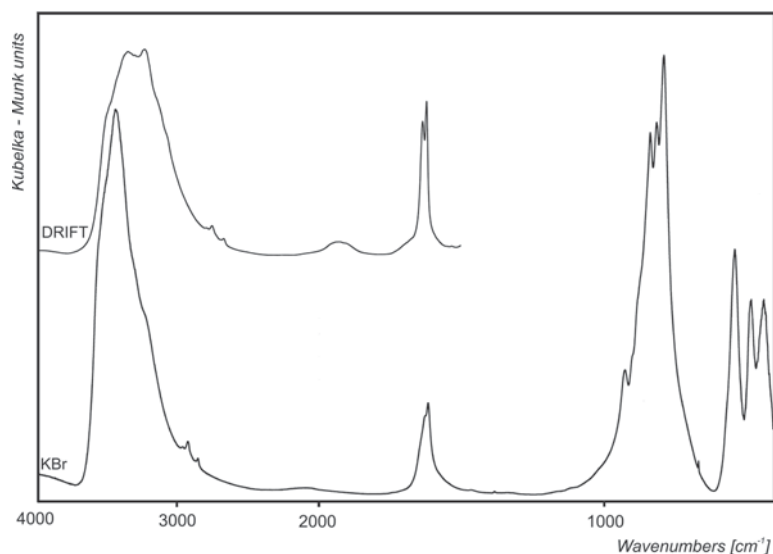


Fig. 7. Infrared absorption spectra (KBr disk, DRIFT) of lemanskiite.

REFERENCES

- BLAZEK, A. (1973): *Thermal Analysis*. Van Nostrand Reinhold, London, U.K.
- BREITHAUP, A. (1837): Bestimmung neuer Mineralien. 1. Symplischer Diatom oder Symplisit. *J. prakt. Chem. (Erdmann)* **10**, 501-512.
- CHIAPPERO, P.-J. & SARP, H. (1995): Zdenekite, $\text{NaPbCu}_5(\text{AsO}_4)_4\text{Cl}\cdot 5\text{H}_2\text{O}$, a new mineral from Cap Garonne mine, Var, France. *Eur. J. Mineral.* **7**, 553-557.
- FOSHAG, W.F. (1924a): Note on lavendulan from Joachimstal, Bohemia. *Am. Mineral.* **9**, 29-30.
- FOSHAG, W.F. (1924b): Freirinite: a new mineral species. *Am. Mineral.* **9**, 30-31.
- FROST, R.L., MARTENS, W.N. & WILLIAMS, P.A. (2002): Raman spectroscopy of the phase-related basic copper arsenate minerals olivenite, cornwallite, cornubite and clinoclase. *J. Raman Spectrosc.* **33**, 475-484.
- GUILLEMIN, C. (1956): Contribution à la minéralogie des arsénates, phosphates et vanadates de cuivre. *Bull. Soc. fr. Minéral. Cristallogr.* **79**, 7-95.
- HOFMANN, F. (1992): Die Minerale des Annaberger Reviers im sächsischen Erzgebirge. *Lapis* **17**(12), 24-33.
- HYBLER, J., ONDRUŠ, P., ČISAŘOVÁ, I., PETŘÍČEK, V. & VESELOVSKÝ, F. (2003): Crystal structure of lindackerite, $(\text{Cu,Co,Ni})\text{Cu}_4(\text{AsO}_4)_2(\text{AsO}_3\text{OH})_2\cdot 9\text{H}_2\text{O}$ from Jáchymov, Czech Republic. *Eur. J. Mineral.* **15**, 1035-1042.
- LIBOWITZKY, E. (1999): Correlation of OH stretching frequencies and O-H...O hydrogen bond lengths. *Monatsh. Chem.* **130**, 1047-1059.
- MARTENS, W.N., FROST, R.L. & KLOPROGGE, J.T. (2003a): Raman spectroscopy of synthetic erythrite, partially dehydrated erythrite and hydrothermally synthesized dehydrated erythrite. *J. Raman Spectrosc.* **34**, 90-95.
- MARTENS, W.N., FROST, R.L. & WILLIAMS, P.A. (2003b): Molecular structure of the adelite group of minerals – a Raman spectroscopic study. *J. Raman Spectrosc.* **34**, 104-111.
- MARTENS, W.N., KLOPROGGE, J.T., FROST, R.L. & RINTOUL, L. (2004): Single-crystal Raman study of erythrite, $\text{Co}_3(\text{AsO}_4)_2\cdot 8\text{H}_2\text{O}$. *J. Raman Spectrosc.* **35**, 208-216.
- MYNENI, S.C.B., TRAINA, S.J., WAYCHUNAS, G.A. & LOGAN, T.J. (1998): Experimental and theoretical vibrational spectroscopic evaluation of arsenate coordination in aqueous solutions, solids, and at mineral – water interfaces. *Geochim. Cosmochim. Acta* **62**, 3285-3300.
- NAKAMOTO, K. (1986): *Infrared and Raman Spectra of Inorganic and Coordination Compounds*. J. Wiley and Sons, New York, N.Y.
- ONDRUŠ, P., VESELOVSKÝ, F., GABAŠOVÁ, A., HLOUŠEK, J. & ŠREIN, V. (2004): Supplement to secondary and rock-forming minerals of the Jáchymov ore district – Jáchymov Issue II. *J. Czech Geol. Soc.* **48**(3-4), 149-156.
- ONDRUŠ, P., VESELOVSKÝ, F. & HLOUŠEK, J. (1997c): A review of mineral associations and paragenetic groups of second-

- ary minerals of the Jáchymov (Joachimsthal) ore district. *J. Czech Geol. Soc.* **42**(4), 109-114.
- ONDRUŠ, P., VESELOVSKÝ, F., HLOUŠEK, J., SKÁLA, R., VAVŘÍN, I., FRÝDA, J., ČEJKA, J. & GABAŠOVÁ, A. (1997a): Secondary minerals of the Jáchymov (Joachimsthal) ore district. *J. Czech Geol. Soc.* **42**(4), 3-76.
- ONDRUŠ, P., VESELOVSKÝ, F., SKÁLA, R., ČÍSAŘOVÁ, I., HLOUŠEK, J., FRÝDA, J., VAVŘÍN, I., ČEJKA, J. & GABAŠOVÁ, A. (1997b): New naturally occurring phases of secondary origin from Jáchymov (Joachimsthal). *J. Czech Geol. Soc.* **42**(4), 77-108.
- PREM, M., LENGAUER, C., & TILLMANN, E. (1997): ICDD PDF2 Card No. 49-1857. Univ. of Vienna, Austria, ICDD Grant-in-Aid.
- ROSS, S.D. (1974): Phosphates and other oxy-anions of group V. *In* The Infrared Spectra of Minerals (V.C. Farmer, ed.). The Mineralogical Society, London, U.K. (383-422).
- VOGL, J.F. (1853a): Drei neue Mineral-Vorkommen von Joachimsthal. *Jahrb. K.-kön. geol. Reichsanstalt* **4**, 221-223.
- VOGL, J.F. (1853b): Lindackerit, eine neue Mineralspecies, und Lavendulan von Joachimsthal, nebst Bemerkungen über die Erzführung die Gänge. *Jahrb. K.-kön. geol. Reichsanstalt* **4**, 552-557.
- WILLIAMS, P.A. (1990): *Oxide Zone Geochemistry*. Ellis Horwood, Chichester, U.K.
- ZUBKOVA, N.V., PUSHCHAROVSKY, D.YU., SARP, H., TEAT, S.J. & MACLEAN, E.J. (2003): Crystal structure of zdenekite $\text{NaPbCu}_5(\text{AsO}_4)_4\text{Cl}\cdot 5\text{H}_2\text{O}$. *Crystallogr. Rep.* **48**, 939-943.
- Received January 19, 2004, revised manuscript accepted November 15, 2005.*