PŮVODNÍ PRÁCE/ORIGINAL PAPER

New data on uranyl sulphate mineral shumwayite from Jáchymov - a Raman spectroscopy study

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Abstract

Jáchymov (Czech Republic) is the second locality of hydrated uranyl-sulphate mineral shumwayite in the world. Shumwayite occurs as rich dark orange crystalline coatings composed of crystals - thin elongated blades up to 100 μm in size, but usually as thin tables only of about 20 μm in size, on strongly weathered fragment of gangue. It is associated with rietveldite, rozenite and as yet unnamed Al-uranyl sulphate, uranyl phosphate and Fe-Zn uranyl sulphate-vanadate. Individual shumwayite crystals are translucent to transparent with vitreous lustre. It does not exhibit fluorescence under either long- or short-wave ultraviolet radiation. The quantitative chemical composition of shumwayite sample is in line with the ideal stoichiometry of UO_2:SO_4 = 1:1; but also minor contents of Fe and Zn were identified. Shumwayite is monoclinic, the space group $P2_1/c$, with the unit-cell parameters refined from X-ray powder diffraction data: *a* 6.738(2), *b* 12.482(5), *c* 16.865(6) Å, *β* 91.00(3)° and *V* 1418.3(7) Å^3. Raman spectroscopy documented the presence of both $(UO_2)^{2+}$ and $(SO_4)^{2-}$ units in the crystal structure of shumwayite. Multiple bands connected with vibrations of water molecules suggest that molecular water is involved in different coordination environments in the structure of shumwayite with distinct hydrogen-bond strengths.

Key words: *shumwayite, uranyl sulphate, unit-cell parameters, chemical composition, Raman spectroscopy, Jáchymov ore district*

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Introduction

Uranyl sulphates are common supergene alteration products formed by oxidation–hydration weathering of uraninite (Plášil 2014) associated with sulphides, such as pyrite or chalcopyrite (Finch, Murakami 1999; Krivovichev, Plášil 2013). More specifically, in old mining workings, oxidative weathering of sulphides generates acid solutions that react with primary uraninite to form the uranyl sulphates (Fernandes et al. 1995; Brugger et al. 2003; Plášil et al. 2014).

Shumwayite, $[(UO_2)(SO_4)(H_2O)_2]_2 \cdot H_2O$, has been described recently by Kampf et al. (2017a) as a new mineral from the Green Lizard and Giveaway-Simplot mines, Red Canyon, San Juan County, Utah (USA). The chemical compound had been known before as synthetic one (Van der Putten, Loopstra 1974; Vlček et al. 2009). At type localities, shumwayite forms transparent pale greenish-yellow elongated prismatic crystals up to 0.3 mm in length with bright greenish white fluorescence under both long- and short-wave ultraviolet radiation (Kampf et al. 2017a).

A detailed study of historical specimens labelled „*zippeite*“ from the Jáchymov ore district, deposited in the mineralogical collections of the National Museum in Prague, has brought many new information for mineralogy of uranium, including description of new minerals, such as jáchymovite (Čejka et al. 1996) or rietveldite (Kampf et al. 2017b). This paper aims to summarize results of the complex mineralogical study including Raman spectroscopy of new determined occurrence of shumwyaite from the second locality in the world, Jáchymov (Czech Republic).

Occurrence and specimen description

Shumwyaite was identified on one historical museum specimen from the Jáchymov ore district (formerly St. Joachimsthal), Krušné hory Mountains. Jáchymov lies approximately 20 km to the north from Karlovy Vary, northwestern Bohemia, Czech Republic. The Jáchymov ore district is a typical example of Ag+As+Co+Ni+Bi and U vein-type hydrothermal mineralization. The ore veins cut a complex of medium-grade metasedimentary rocks of Cambrian to Ordovician age, in the envelope of a Variscan Karlovy Vary granite pluton. The majority of the ore minerals were deposited during Variscan mineralization cycle from mesothermal fluids (Ondruš et al. 2003a,b,d). Primary and supergene mineralization in this district resulted in extraordinarily varied mineral associations; more than 440 mineral species have been reported from there (Ondruš et al. 1997a,b and 2003c,d; Hloušek et al. 2014).

Shumwayite occurs on a strongly supergene altered gangue in association with rietveldite (Kampf et al. 2017b), rozenite and as yet unnamed Al-uranyl sulphate, uranyl phosphate and Fe-Zn uranyl sulphate-vanadate. Shumwayite forms rich dark orange crystalline coatings (Fig. 1) composed of crystals (Figs. 2 - 3); thin elongated blades up to 100 μm in size (Fig. 4) but usually thin tables only about 20 μm in size (Fig. 5). Individual crystals are translucent to transparent with vitreous lustre. It does not exhibit fluorescence under either long- or short-wave ultraviolet radiation.

The observed differences in color (greenish yellow vs. dark orange), crystal shapes (prismatic vs. thin tables and blades) and fluorescence under UV radiation (bright-greenish white from the type locality vs. absence of fluorescence in case of Jáchymov) of shumwayite from type locality and studied sample from Jáchymov may be caused by minor Fe and Zn contents determined in the Jáchymov sample (see below).

Fig. 1 *Orange crystalline coatings of shumwayite on strongly altered gangue, Jáchymov, field of view 1.6 mm, photo J. Sejkora.*

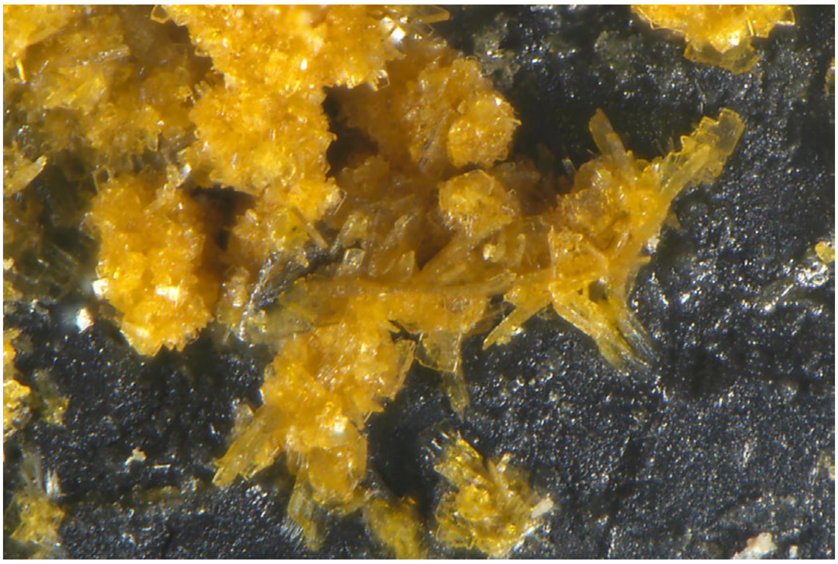

Fig. 2 *Orange thin elongated blade crystals of shumwayite on strongly altered gangue, Jáchymov, field of view 0.4 mm, photo J. Sejkora.*

Fig. 3 *Crystalline coatings of shumwayite on strongly altered gangue, Jáchymov, field of view 0.7 mm, BSE photo L. Vrtiška and L. Váchová.*

Electron microanalysis

Samples of shumwayite were analysed with a Cameca SX-100 electron microprobe (Masaryk University, Brno) operating in the wavelength-dispersive mode with an accelerating voltage of 15 kV, a specimen current of 2 nA, and a beam diameter of 10 μm. The following lines and standards were used: *K*α: almandine (Fe), gahnite (Zn), sanidine (Si), $ScVO_4$ (V), spessartine (Mn), $SrSO_4$ (S) and fluorapatite (P); *M*α: uranophane (U). Peak counting times (CT) were 20 s for main elements and 60 s for minor elements; CT for each background was one-half of the peak time. The raw intensities were converted to the concentrations automatically using the *PAP* (Pouchou, Pichoir 1985) matrix-correction software. The elements Al, As, Ba, Ca, Co, F, K, Mg, Na, Ni and Pb were sought, but found to be below the detection limit (about 0.05-0.10 wt. %). Water content could not be analysed directly because of the minute amount of material available. The H_2O content was confirmed by Raman spectroscopy and calculated by stoichiometry of ideal formula.

Chemical composition of shumwayite sample (Table 1) basically agree to stoichiometry UO_2:SO_4 = 1:1. Lower analytical totals reflect an instability of this phase under the electron beam, similarly as Kampf et al. (2017a) described for sample from type locality. The observed minor contents of Fe (up to 0.25 *apfu*), Zn (up to 0.19 *apfu*) and Mn (up to 0.05 *apfu*) are to be discussed; besides their possible incorporation as a part of the crystal structure of shumwayite they can be caused by intimate intergrowths with other uranyl sulphates (e.g. rietveldite). The anion sites are dominated by S and only partly subsituted by Si, V and P up to 0.07 - 0.14 *apfu*.

X-ray powder diffraction

Powder X-ray diffraction data were collected on a Bruker D8 Advance diffractometer (National Museum, Prague) with a solid-state 1D LynxEye detector using CuK_α radiation and operating at 40 kV and 40 mA. The powder patterns were collected using Bragg-Brentano geometry in the range 3 - 60° 2θ, in 0.01° steps with a counting time of 30 s per step. Positions and intensities of reflections were found and refined using the Pearson VII profile-shape function with the ZDS program package (Ondruš 1993) and the unit-cell parameters were refined by the least-squares algorithm implemented by Burnham (1962). The experimental powder pattern was indexed in line with the calculated values of intensities obtained from the crystal structure of shuwayite (Kampf et al. 2017a), based on Lazy Pulverix program (Yvon et al. 1977).

Fig. 4 *Thin elongated blade crystals of shumwayite on strongly altered gangue, Jáchymov, field of view 230 μm, BSE photo L. Vrtiška and L. Váchová.*

Fig. 5 *Tiny thin tabular crystals of shumwayite on strongly altered gangue, Jáchymov, field of view 90 μm, BSE photo L.Vrtiška and L. Váchová.*

Table 1 Chemical composition of shumwayite from Jáchymov (wt. %)

	mean	1	2	3	4	5
FeO	1.33	0.90	1.90	1.43	1.24	1.20
MnO	0.20	0.00	0.18	0.35	0.25	0.22
ZnO	0.93	0.38	1.63	1.41	0.78	0.46
SiO_2	0.28	0.00	0.39	0.89	0.14	0.00
P_2O_5	0.27	0.02	0.34	0.23	0.19	0.55
V_2O_5	0.34	0.00	0.22	0.23	0.31	0.93
SO_3	16.29	17.70	15.97	14.90	16.82	16.06
UO_3	63.20	63.82	63.18	61.15	68.14	59.74
H_2O*	9.71	9.97	9.60	9.31	9.84	9.85
total	92.55	92.78	93.41	89.88	97.70	89.02
Fe	0.172	0.113	0.247	0.192	0.158	0.153
Mn	0.026	0.000	0.024	0.047	0.032	0.028
Zn	0.106	0.042	0.188	0.167	0.088	0.052
Σ	0.304	0.156	0.459	0.407	0.278	0.234
Si	0.044	0.000	0.061	0.143	0.021	0.000
P	0.035	0.002	0.045	0.031	0.024	0.071
V	0.034	0.000	0.023	0.025	0.031	0.093
S	1.887	1.998	1.871	1.801	1.924	1.836
Σ	2.000	2.000	2.000	2.000	2.000	2.000
UO_2	2.050	2.017	2.072	2.069	2.181	1.911
H_2O	4.999	5.002	4.998	5.002	5.002	5.003

Mean of 5 point analyses; 1-5 point analyses; *apfu* on the base Si+P+V+S = 2; H_2O* contents were calculated on the basis of 5 H_2O molecules in ideal formula.

The experimental powder-data set given in Table 2 agrees well with the X-ray pattern calculated from the single-crystal data for shumwayite and of the natural sample from Green Lizard mine (Kampf et al. 2017a). The refined unit-cell parameters of shumwayite are compared in Table 3 with published data.

Raman spectroscopy

The Raman spectra of studied sample were collected in the range 4000–80 cm^{-1} using a DXR dispersive Raman Spectrometer (Thermo Scientific) mounted on a confocal Olympus microscope. The Raman signal was excited by an unpolarised red 633 nm He-Ne gas laser and detected by a CCD detector. The experimental parameters were: 100x objective, 30 s exposure time, 100 exposures, 50 μm pinhole spectrograph aperture and 4 mW laser power level. The spectra were repeatedly acquired from different grains in order to obtain a representative spectrum with the best signal-to-noise ratio. The eventual thermal damage of the measured point was excluded by visual inspection of excited surface after measurement, by observation of possible decay of spectral features in the start of excitation and checking for thermal downshift of Raman lines. The instrument was set up by a software-controlled calibration procedure using multiple neon emission lines (wavelength calibration), multiple polystyrene Raman bands (laser-frequency calibration) and standardized white-light sources (intensity calibration).

Spectral manipulations were performed using the Omnic 9 software (Thermo Scientific). Gaussian/Lorentzian (pseudo-Voigt) profile functions of the band-shape were used to obtain decomposed band components of the spectra. The decomposition was based on the minimization of the difference in the observed and calculated profiles until the squared correlation coefficient (r^2) was greater than 0.995.

Shumwayite, $[(UO_2)(SO_4)(H_2O)_2]_2 \cdot H_2O$, is a monoclinic uranyl-containing mineral, the space group $P2_1/c – C^5_{2h}$, $Z = 4$. In the asymmetric part of the unit cell, there are two U sites, occupied by U^{6+}, two S sites, occupied by S^{6+} and five symmetrically independent water molecules bonded by hydrogen bonds. The crystal structure of shumwayite contains UO_7 pentagonal bipyramids (two short apical bonds of the bipyramid constitute the uranyl ion, UO_2^{2+}) and SO_4 tetrahedra that link by sharing corners to form $[(UO_2)(SO_4)(H_2O)_2]$ chains along [100]. These chains and isolated H_2O groups between them are linked together by hydrogen bonds, only (Kampf et al. 2017a).

Table 2 *X-ray powder diffraction data of shumwayite from Jáchymov*

h	*k*	*l*	$d_{obs.}$	$I_{obs.}$	$d_{calc.}$	*h*	*k*	*l*	$d_{obs.}$	$I_{obs.}$	$d_{calc.}$
0	1	2	6.988	37	6.987	-2	1	3	2.833	6	2.836
1	1	0	5.932	22	5.929	0	0	6	2.812	26	2.810
0	2	1	5.849	12	5.853	-2	2	2			2.810
-1	1	1	5.614	49	5.620	0	1	6	2.745	9	2.742
1	1	1	5.575	20	5.567	-2	2	3	2.641	23	2.639
-1	0	2	5.299	7	5.309	2	2	3	2.609	6	2.606
1	0	2	5.213	54	5.219	-2	3	1	2.595	9	2.592
0	1	3	5.128	100	5.125	2	3	1	2.580	14	2.582
0	2	2	5.016	35	5.016	-1	4	3	2.536	32	2.536
-1	1	2	4.891	23	4.885	1	4	3	2.522	11	2.521
1	1	2	4.816	27	4.815	-1	3	5	2.4536	5	2.4531
-1	2	1	4.431	19	4.432	-2	2	4	2.4400	4	2.4426
1	2	1	4.406	24	4.405	1	3	5	2.4295	10	2.4307
0	2	3	4.172	9	4.177	1	5	0	2.3407	18	2.3409
0	3	1	4.039	42	4.039	-2	4	1	2.2745	8	2.2720
0	3	2	3.735	32	3.731	-1	1	7	2.2442	17	2.2438
-1	0	4	3.601	10	3.602	0	5	4	2.1493	8	2.1480
1	0	4	3.547	15	3.546	3	1	2	2.1214	9	2.1291
1	3	0	3.537	34	3.540	-2	3	5	2.0851	7	2.0818
-1	1	4	3.454	91	3.461	-3	0	4	1.9971	9	1.9966
1	1	4	3.411	17	3.411	0	2	8			1.9970
2	0	0	3.369	49	3.369	3	3	0	1.9755	11	1.9763
-1	2	4	3.112	13	3.120	0	4	7	1.9068	18	1.9069
1	2	4	3.074	20	3.083	-1	5	6	1.8020	10	1.8041
0	4	1	3.064	17	3.068	2	1	8	1.7575	10	1.7554
2	1	2	3.023	3	3.017	-3	4	3	1.7435	7	1.7412
0	2	5	2.962	28	2.967	3	4	3	1.7277	12	1.7268
0	3	4			2.961						

Table 3 *Unit-cell parameters for shumwayite (for monoclinic space group $P2_1/c$)*

		a [Å]	*b* [Å]	*c* [Å]	*β* [°]	*V* [Å^3]
Jáchymov	this paper	6.738(2)	12.482(5)	16.865(6)	91.00(3)	1418.3(7)
Green Lizard mine	Kampf et al. (2017a) SXRD	6.7475(2)	12.5026(3)	16.903(1)	90.919(6)	1425.8(1)
Green Lizard mine	Kampf et al. (2017a) PXRD	6.726(6)	12.493(7)	16.888(7)	91.01(4)	1419(1)
synthetic	Vlček et al. (2009)	6.7260(1)	12.4210(2)	16.8270(3)	90.781(1)	1405.66(4)

A free uranyl cation, $(UO_2)^{2+}$, $D_{\mu h}$ point-group symmetry, is, in general, characterized by three fundamental vibration modes: the ν_1 symmetric stretching vibration, Raman active (900-750 cm^{-1}), the ν_2 (δ) doubly degenerate bending vibration, infrared active (300 - 200 cm^{-1}), and the ν_3 antisymmetric stretching vibrations, infrared active (1000 - 850 cm^{-1}). The lowering of the ideal symmetry (due to crystal field and so on) may cause splitting of the ν_2 (δ) vibration and Raman and infrared activation of all three vibrations (Čejka 1999; Nakamoto 2009). A free sulphate anion, $(SO_4)^{2-}$, T_d point-group symmetry, is characterized by four fundamental modes: the ν_1 symmetric stretching vibration, Raman active (~983 cm^{-1}), the ν_2 (δ) doubly degenerate bending vibration, Raman active (~450 cm^{-1}), the ν_3 triply degenerate antisymmetric stretching vibration, Raman and infrared active, (~1105 cm^{-1}), and the ν_4 (δ) triply degenerate bending vibration (~611 cm^{-1}). T_d symmetry lowering may cause splitting of degenerate vibrations and Raman and infrared activation of all vibrations (Čejka 1999; Nakamoto 2009).

Infrared and Raman spectra of shumwayite were recently published by Kampf et al. (2017a). The Raman spectrum of shumwayite sample from Jáchymov, recently studied, is close to the Raman spectra of both shumwayite from Green Lizard Mine (Kampf et al. 2017a) and to its synthetic analogue (Vlček et al. 2009). Our new Raman spectrum, however, offers a better resolution and includes also the region of vibrations of water molecules.

The full-range Raman spectrum of the studied mineral shumwayite is given in Figure 6, wavenumbers with assignments are given in Table 4. Bands of the very low intensity, located at 3521, 3421 and 3230 cm^{-1} (Fig. 7) are connected with the ν OH stretching vibrations of hydrogen-bonded water molecules. According to the empirical relation between energy of vibration and the corresponding bond length (Libowitzky 1999), O-H×××O hydrogen-bond lengths vary approximately in the range from 2.94 to 2.71 Å. This is close to the data 3.01 - 2.72 Å inferred from the X-ray structure analysis by Kampf et al. (2017a). A very weak band at 1624 cm^{-1} (Fig. 8), is attributed to the ν_2 (δ) bending vibrations of water molecules.

Weak bands at 1185 and 1158

Table 4 *Tentative assignment of Raman spectrum of shumwayite from Jáchymov*

position	*FWHH*	*$I_{rel.}$*	*$I_{rel.}$*	*Red Canyon**	*synth.***	*tentative assignment*
[cm^{-1}]	[cm^{-1}]	[height]	[area]	[cm^{-1}]	[cm^{-1}]	
3521	106	0.9	8.0			ν OH (hydrogen bonded H_2O)
3421	190	0.9	12.2			
3230	212	0.6	12.1			
1624	49	0.6	3.4			ν_2 H_2O
1185	27	3.0	7.7	1185 w	1181	ν_3 $(SO_4)^{2-}$
1158	27	3.6	8.9	1155 w	1158	
1127	24	1.8	4.1			
1094	28	11.0	28.7	1100 ms	1099	
1073	16	26.5	39.7	1073 s	1073	
1053	20	20.5	37.6	1050 ms	1052	
1034	13	17.3	21.3	1035 ms	1034	ν_1 $(SO_4)^{2-}$
1024	15	10.9	14.8			
1010	17	15.4	23.6	1015 w		
959	9	1.6	1.4		956	ν_3 $(UO_2)^{2+}$
931	21	1.1	2.6	930 vw	931	
865	11	100.0	100.0	865 vs	863	ν_1 $(UO_2)^{2+}$
852	20	16.7	31.4	850 s	853	
840	15	33.2	47.7			
825	21	16.3	32.2			libration modes of H_2O
808	23	5.0	10.5			
659	26	3.4	9.1			ν_4 $(SO_4)^{2-}$
646	22	1.0	2.1	645 w	646	
611	20	1.8	3.0	615 w	614	
600	10	1.5	1.4		600	
547	18	0.6	1.0			libration mode of H_2O
474	30	2.7	6.3	470 w	470	ν_2 $(SO_4)^{2-}$
458	18	2.1	3.3		457	
431	39	5.4	16.9	430 w	446, 431	
392	27	5.2	13.1			
366	32	6.4	20.9			
250	27	8.6	20.0	255 ms	255	ν_2 $(UO_2)^{2+}$
217	24	13.2	31.4	210 s		
205	9	1.9	1.5			ν U-O_{eq}-*ligand*
197	21	17.9	35.0	200 s		
183	24	15.1	37.0			lattice modes
150	17	6.8	8.6	160, 150 w		
121	17	0.2	0.3			
101	29	1.6	4.3			
87	15	3.6	5.9			

$I_{rel.}$ calculated from peak height and band area; * Kampf et al. (2017a); ** Vlček et al. (2009)

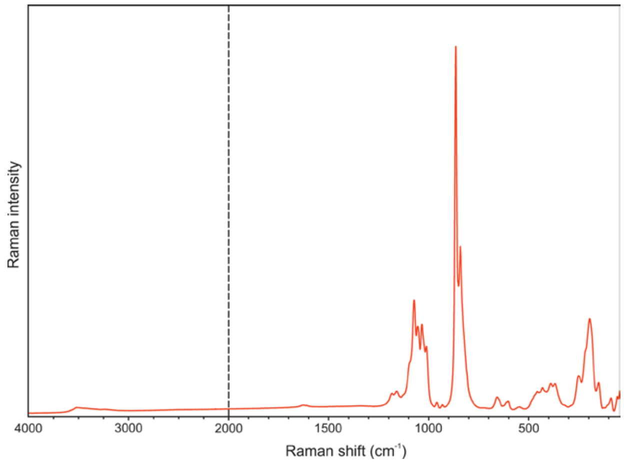

Fig. 6 *Raman spectrum of shumwayite from Jáchymov (split at 2000 cm^{-1}).*

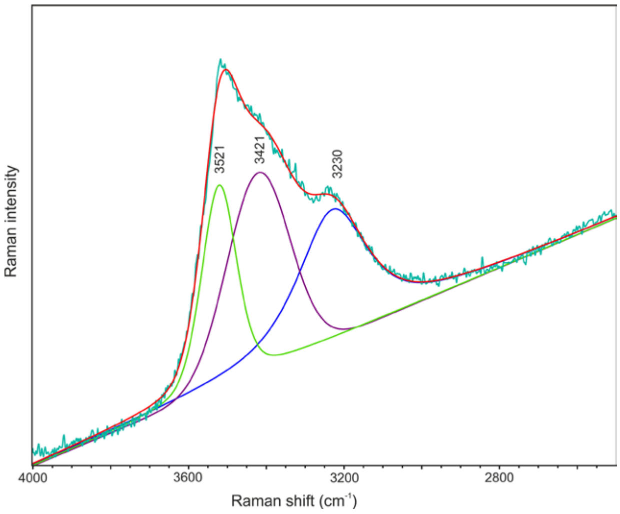

Fig. 7 *Results of the band component analysis in the Raman spectrum of shumwayite from Jáchymov (4000 - 2500 cm^{-1}).*

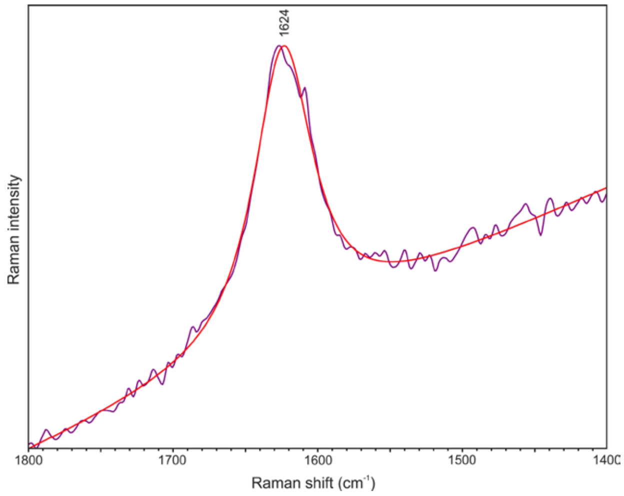

Fig. 8 *Results of the band component analysis in the Raman spectrum of shumwayite from Jáchymov (1800 - 1400 cm^{-1}).*

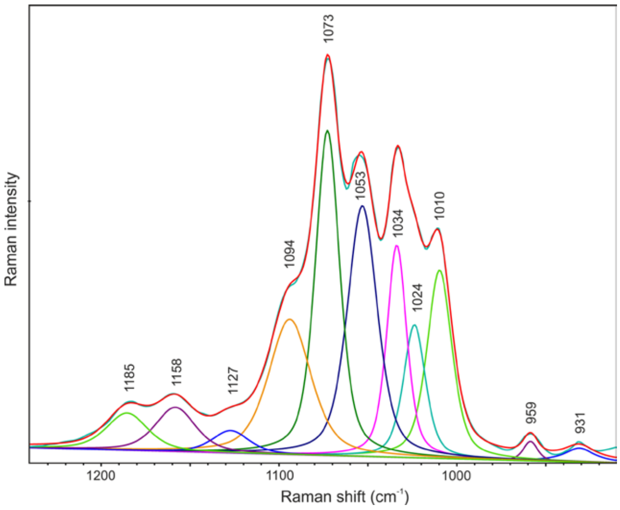

Fig. 9 *Results of the band component analysis in the Raman spectrum of shumwayite from Jáchymov (1240 - 910 cm^{-1}).*

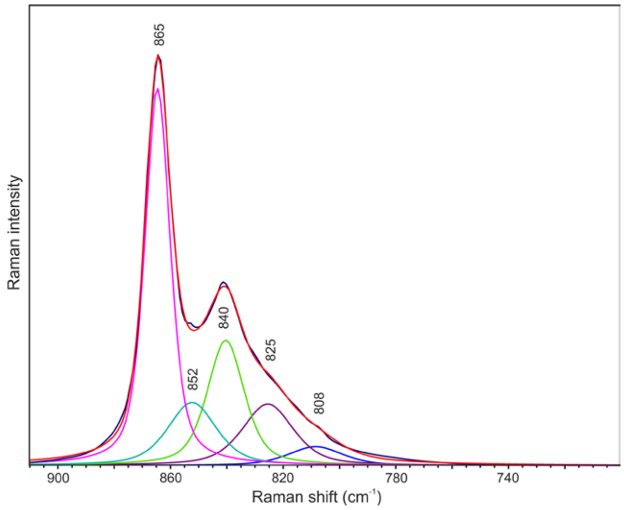

Fig. 10 *Results of the band component analysis in the Raman spectrum of shumwayite from Jáchymov (910 - 700 cm^{-1}).*

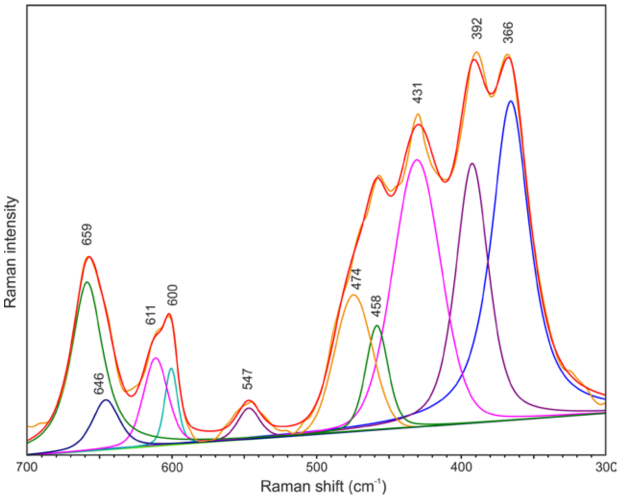

Fig. 11 *Results of the band component analysis in the Raman spectrum of shumwayite from Jáchymov (700 - 300 cm^{-1}).*

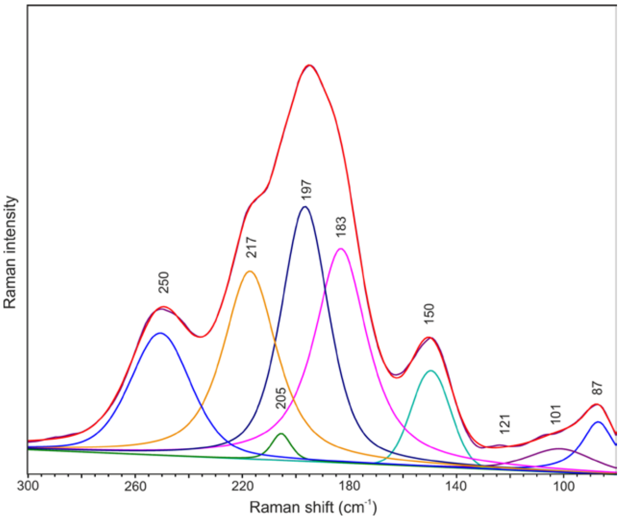

Fig. 12 *Results of the band component analysis in the Raman spectrum of shumwayite from Jáchymov (300 - 80 cm^{-1}).*

cm^{-1} with shoulders at 1127 and 1094 cm^{-1} together with medium strong bands at 1073 and 1053 cm^{-1} (Fig. 9) are assigned to the split triply degenerate ν_3 $(SO_4)^{2-}$ antisymmetric stretching vibrations. Kampf et al. (2017a) presented a set of five bands between 1185 and 1050 cm^{-1}. Medium strong bands at 1034, 1024 and 1010 cm^{1} are attributed to the ν_1 $(SO_4)^{2-}$ symmetric stretching vibrations.

Very weak bands at 959 and 931 cm^{-1} (Fig. 9) are assigned to the ν_3 $(UO_2)^{2+}$ antisymmetric stretching vibrations, corresponding to U–O bond lengths in uranyl 1.75 - 1.77 Å, and very strong and strong bands at 865, 852 and 840 cm^{-1} (Fig. 10) are assigned to the ν_1 $(UO_2)^{2+}$ symmetric stretching vibrations, corresponding to U–O bond lengths in uranyl 1.74 - 1.76 Å (Bartlett, Cooney 1989). The inferrred U–O bond lengths for the uranyl ion are comparable with data derived from the X-ray studies for shumwayite 1.75 - 1.77 Å (Kampf et al. 2017a). Weak shoulders at 825 and 808 cm^{-1} may be associated with the libration modes of H_2O molecules.

Very weak and weak bands at 659, 646 and 600 cm^{-1} with a shoulder at 611 cm^{-1} (Fig. 11) are connected with the split triply degenerate ν_4 (δ) $(SO_4)^{2-}$ bending vibrations. A very weak band at 547 cm^{-1} may be connected with the libration mode of water molecules. Weak and very weak bands at 474, 458, 431, 392 and 363 cm^{-1} are assigned to the split doubly degenerate ν_2 (δ) $(SO_4)^{2-}$ bending vibrations. Kampf et al. (2017a) attributed bands at 645 and 615 cm^{-1} and 470 and 438 cm^{-1} to the ν_4 (δ) and ν_2 (δ) $(SO_4)^{2-}$, respectively.

Medium strong band at 250 cm^{-1} with a shoulder at 217 cm^{-1} (Fig. 12) may be related to the ν_2 (δ) $(UO_2)^{2-}$ doubly degenerate bending vibrations. Kampf assigned a medium strong band at 255 cm^{-1} with a shoulder at 273 cm^{-1} to these vibrations. Some bands between 400 and 197 cm^{-1}, hovever, may be attributed to the ν $(U\text{–}O_{ligand})$ stretching vibrations of the $U\text{–}O_{equatorial}$ bonds in uranyl pentagonal bipyramidal coordination polyhedra (Volod´ko et al. 1981). Weak and very weak bands at 150, 121 and 87 cm^{-1} and a shoulder at 101 cm^{-1} relate to lattice modes. They correspond to weak bands at 160 and 150 cm^{-1} in the Raman spectrum of shumwayite published by Kampf et al. (2017a). These authors assigned the two bands to $-O_{eq}\text{–}U\text{–}O_{eq}$ bending vibrations, according to Ohwada (1976).

Conclusion

Some of the characteristics of the crystal structure of the well-defined sample of shumwayite from Jáchymov (the second world occurrence) have been described using the Raman spectroscopy. It shows the presence of both $(UO_2)^{2+}$ and $(SO_4)^{2-}$ units in the crystal structure of shumwayite. Multiple bands connected with vibrations of water molecules document that molecular water is involved in different coordination environments in the structure of shumwayite due to differing hydrogen-bond strengths.

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