

Original paper

Uramphite from Nová Ves pod Pleší (Czech Republic), the third world occurrence – description and vibrational spectroscopy

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We have studied the rare ammonium uranyl phosphate mineral, uramphite, from the small uranium occurrence Nová Ves pod Pleší, central Bohemia (Czech Republic). It has been found on a few specimens and forms rare groups up to 1 mm in size in small vugs of limonite veins in altered rocks in association with meta-autunite, metatorbenite and churchite-(Y). Uramphite is pale yellow to light greenish yellow with a pale yellow streak and shows weak fluorescence in a pale yellow hue under 254 nm and 366 nm UV-radiation, respectively. Uramphite crystals are transparent to translucent and have an intensive vitreous luster. The mineral is very brittle and at least one system of perfect cleavage along {001} was observed. The quantitative electron-microprobe chemical analyses of uramphite agree well with the proposed ideal composition and correspond to the following empirical formula $[(\text{NH}_4)_{0.79}\text{Na}_{0.12}\text{K}_{0.07}\text{Ca}_{0.03}]_{\Sigma 1.01}(\text{UO}_2)_{1.00}(\text{PO}_4)_{1.00} \cdot 3\text{H}_2\text{O}$ (on the basis of 1 P atom *pfu*). Uramphite is tetragonal, space group *P4/ncc*, with the unit-cell parameters refined from X-ray powder diffraction data: $a = 7.0292(11)$, $c = 18.092(2)$ Å, $V = 893.9(2)$ Å³. Vibrational (Raman and infrared) spectroscopy documented the presence of molecular water, ammonium, uranyl, and phosphate groups in the crystal structure of uramphite.

Keywords: uramphite, meta-autunite group, chemical composition, Raman spectroscopy, infrared spectroscopy, Nová Ves pod Pleší
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1. Introduction

The so-called *uranium micas*, i.e., members of autunite and meta-autunite groups, belong to the most abundant supergene uranium minerals and represent a very widespread product of weathering of primary uranium minerals (uraninite, coffinite etc.) in weakly acidic and acidic conditions. They are usually formed at greater distances from the primary mineralization and host rocks are the source of phosphorus (Krivovichev and Plášil 2013; Plášil 2014); as less soluble phases may probably control U concentrations in many groundwaters and soils (Finch and Murakami 1999; Fuller et al. 2002).

On the other hand, the ammonium dominant members of the meta-autunite group, minerals uramphite and uramarsite, belong to the rarest uranium supergene minerals. The first mentioned above, uramphite $\text{NH}_4(\text{UO}_2)(\text{PO}_4) \cdot 3\text{H}_2\text{O}$, was described by Nekrasova (1957) from the Tura-Kavak uranium coal deposit, Naryn Region, Kyrgyzstan (Pekov 1998). It has not been found in any other locality for more than 60 years. Recently, concurrently with our research, it was found at the Beshtau uranium deposit in Russia (Gurzhiy et al. 2024). The second, uramarsite $\text{NH}_4(\text{UO}_2)(\text{AsO}_4) \cdot 3\text{H}_2\text{O}$, was found in the supergene zone

of the Bota-Burum U–Mo deposit in southern Kazakhstan (Sidorenko et al. 2007). Later, it was mentioned also from Markey Mine, Utah, USA (Kampf et al. 2018b), Wittichen (Germany) and Darasun mine, Tungokochensky District, Russia (<https://www.mindat.org/min-28919.html>) but without any analytical data.

Both minerals are structurally related to synthetic chernikovite $(\text{H}_3\text{O})(\text{UO}_2)(\text{PO}_4) \cdot 3\text{H}_2\text{O}$ (so-called HUP) and its $\text{M}^+(\text{UO}_2)(\text{PO}_4) \cdot 3\text{H}_2\text{O}$ ($\text{M}^+ = \text{K}^+, \text{Na}^+, \text{Ag}^+, \text{NH}_4^+$) analogs, which are among the best-known fast-proton solid conductors at room temperature and are used in microionic devices such as sensors, supercapacitors, electrochromic display, batteries, etc. (Shilton and Howe 1977, 1980; Morosin 1978; Howe and Shilton 1980; Colomban and Velasco 1983; Fitch and Fender 1983; Pham-Thi and Colomban 1985; Gui et al. 2022; Colomban 2023). This group of compounds is also studied for uranium sequestering from groundwater and industrial wastewaters, as same as for uranium immobilization owing to their low thermodynamic solubility and high chemical stability (Marković et al. 1988; Mehta et al. 2013; Martinez et al. 2014; Baker et al. 2019; Foster et al. 2020).

This paper aims to summarize the results of the complex mineralogical study, including Raman and infrared



Fig. 1 Overgrown remains of the dump of shaft No. 52 Nová Ves pod Pleší; photo J. Kristek (2023).

spectroscopy of rare ammonium uranyl phosphate mineral, uramphite, on the base of new finds of well-crystallized samples at the locality Nová Ves pod Pleší, Czech Republic.

2. Material and methods

2.1. Occurrence and specimen description

Uramphite and associated minerals were found on specimens originating from the remains of the dump of a small

uranium ore occurrence Nová Ves pod Pleší, shaft No. 52 (Fig. 1, GPS coordinates 49°50'26.7"N 14°16'23.7"E), approximately 30 km southwest of Prague, central Bohemia, Czech Republic.

The Nová Ves pod Pleší uranium occurrence was first opened in 1957 by the exploration shaft No. 52 (in the close northern vicinity of Nová Ves pod Pleší village) following a submeridional zone NV-1 containing uranium ores to the depth 27 m (Fig. 2). Nearby main shaft No. 56 explored one carbonate vein containing uranium ores as an in-depth continuation of the ore zone and another

six carbonate veins without uranium ores 100 m under surface. The prospection was finished in 1959 (Zikmund and Kotek 1962). Geologically, the deposit is located in contactly metamorphosed Neo-Proterozoic rocks of the Teplá–Barrandian unit in exocontact of the Central Bohemian Plutonic Complex. The shaft No. 52 is situated in rhyolite and dacite tuff and tuffite of the Kralupy–Zbraslav volcano–sedimentary group.

Uramphite has been found on few specimens and forms rare

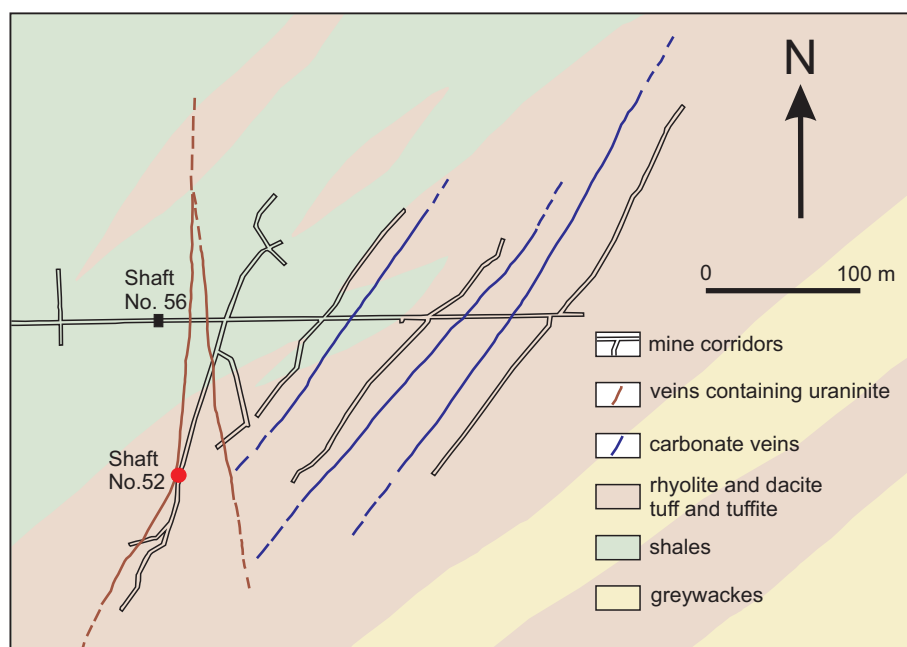


Fig. 2 Geological scheme of the small uranium occurrence Nová Ves pod Pleší; the position of the shaft No. 52 marked by red point; modified after Kaňka (1959).



Fig. 3 Pale yellow tabular crystals of uramphite from Nová Ves pod Pleší in limonite vein. Horizontal field of view 2.5 mm; photo P. Škacha.

groups of tabular crystals (Fig. 3) up to 1 mm in size in small vugs of *limonite* veins in altered rocks in association with meta-autunite, metatorbenite and churchite-(Y). The mineral is pale yellow to light greenish yellow with a pale yellow streak. The fluorescence of uramphite is weak, in pale yellow hues, under 254 nm and 366 nm UV-radiation, respectively. Crystals are transparent to translucent and have an intensive vitreous luster. Studied mineral is very brittle and shows at least one system of perfect cleavage along {001}.

2.2. Electron-probe microanalysis

Samples of uramphite were analyzed with a Cameca SX-100 electron microprobe (National Museum, Prague) operating in the wavelength-dispersive mode with an accelerating voltage of 15 kV, a specimen current of 2 nA, and a beam diameter of 8 μm . The following lines and standards were used: $K\alpha$: albite (Na), BN (N), fluorapatite (Ca, P), sanidine (K) and $M\alpha$: UO_2 (U). Peak counting times (CT) were 200 s for nitrogen and 20 s for other 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 and Pichoir 1985) matrix-correction algorithm. The contents of Al, As, Ba, Bi, Cl, Co, Cr, Cu, F, Fe, Mg, Mn, Mo, Ni, Pb, Si, Sr, V, Y and Zn were also measured, but always found to be below the detection limits (about 0.05–0.20 wt. %). The collected data were manually corrected for the partial overlap of the $NK\alpha$ peak with an unidentifiable U line (U N4–N6 according to Kampf et al. 2018a); pure UO_2 standard generated false content of 2.15 wt. % $(\text{NH}_4)_2\text{O}$. Overlap $KK\alpha$ - $UM\beta 1$ was corrected automatically (standard used: UO_2 , intensity 3.54 cps/nA). Water

content could not be analyzed directly because of the minute amount of material available. The H_2O content was confirmed by infrared spectroscopy and calculated by the stoichiometry of the ideal formula. The slightly increased totals could result from H_2O loss under vacuum in the EPMA chamber.

2.3. Powder X-ray 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 $\text{CuK}\alpha$ radiation and operating at 40 kV and 40 mA. The powder pattern was collected using Bragg-Brentano geometry in the range $2.5\text{--}70^\circ 2\theta$, in 0.01° steps with a counting time of 20 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 pattern obtained from the crystal structure of synthetic $\text{ND}_4(\text{UO}_2)(\text{PO}_4) \cdot 3\text{D}_2\text{O}$ (Fitch and Fender 1983), based on PowderCell2.3 program (Kraus and Nolze 1996).

2.4. Raman and infrared spectroscopy

The Raman spectra of the studied sample were collected in the range $4000\text{--}50\text{ cm}^{-1}$ 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: 100× objective, 10 s exposure time, 100 exposures, 50 µm slit spectrograph aperture, and 2 mW laser power level. The spectra were repeatedly acquired from different grains 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 the excited surface after measurement, observation of possible decay of spectral features at the start of excitation and checking for thermal downshift of Raman lines. The instrument was set up using 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).

The infrared vibrational spectrum of uramphite was recorded by the attenuated total reflection (ATR) method with a diamond cell on a Nicolet iS5 spectrometer. Spectra over the 4000–400 cm^{−1} range were obtained by the co-addition of 64 scans with a resolution of 4 cm^{−1} and a mirror velocity of 0.4747 cm/s. Spectra were co-added to improve the signal-to-noise ratio.

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 minimizing the difference in the observed and calculated profiles until the squared correlation coefficient (*r*²) was greater than 0.995.

3. Results

3.1. Chemical characterization

The chemical composition of the studied sample (Tab. 1) agrees very well with the ideal formula of uramphite (NH₄)(UO₂)(PO₄)·3H₂O and published analyses of this mineral from the type locality (Nekrasova 1957). The cationic site is occupied by dominant NH₄⁺ with mi-

nor contents of Na (up to 0.20 *apfu*), Ca (up to 0.09 *apfu*) and K (up to 0.08 *apfu*). The empirical formula of uramphite (mean of 4 analyses) calculated on the basis of 1 P atom *pfu* is [(NH₄)_{0.79}Na_{0.12}K_{0.07}Ca_{0.03}]_{Σ1.01}(UO₂)_{1.00}(PO₄)_{1.00}·3H₂O. Compared to the type material (Nekrasova 1957), we observed minor Na, Ca and K contents in the currently studied uramphite from Nová Ves pod Pleší.

3.2. Powder X-ray diffraction

The peak positions in experimental X-ray powder patterns (Tab. 2) agree well with data published for uramphite from Beshtau (Gurzhiy et al. 2024), synthetic NH₄(UO₂)(PO₄)·3H₂O (Marković et al. 1988; Foster et al. 2020) as well as with those calculated from the crystal

Tab. 2 X-ray powder diffraction data of uramphite from Nová Ves pod Pleší.

<i>d</i> _{obs}	<i>I</i> _{obs}	<i>d</i> _{calc}	<i>h</i>	<i>k</i>	<i>l</i>
9.0619	100.00	9.0459	0	0	2
5.5581	0.11	5.5505	1	0	2
4.9801	0.11	4.9704	1	1	0
4.5288	5.98	4.5229	0	0	4
4.3632	0.09	4.3561	1	1	2
3.8072	0.61	3.8036	1	0	4
3.5178	0.05	3.5146	2	0	0
3.2788	0.06	3.2760	2	0	2
3.0162	0.15	3.0153	0	0	6
2.9701	0.02	2.9694	2	1	2
2.7878	0.02	2.7876	2	1	3
2.7758	0.19	2.7752	2	0	4
2.7720	0.23	2.7711	1	0	6
2.5796	0.04	2.5813	2	1	4
2.4861	0.05	2.4852	2	2	0
2.3961	0.03	2.3964	2	2	2
2.2614	2.94	2.2615	0	0	8
2.1764	0.02	2.1781	2	2	4
2.1585	0.01	2.1586	3	1	2
2.1526	0.27	2.1528	1	0	8
2.0583	0.13	2.0584	1	1	8
1.9040	0.04	1.9018	2	0	8
1.8348	0.01	1.8358	2	1	8
1.8087	0.97	1.8092	0	0	10
1.7580	0.01	1.7573	4	0	0
1.7528	0.02	1.7521	1	0	10
1.7235	0.01	1.7251	4	0	2
1.6995	0.24	1.7001	1	1	10
1.6085	0.04	1.6086	2	0	10
1.5070	0.29	1.5077	0	0	12
1.4737	0.07	1.4741	1	0	12
1.4419	0.11	1.4416	4	2	5
1.4030	0.02	1.4032	3	1	10
1.3859	0.02	1.3856	2	0	12
1.3096	0.02	1.3104	4	3	5
1.2913	0.05	1.2907	4	2	8

Tab. 1 Chemical composition of uramphite (wt. %).

	Nová Ves pod Pleší this paper		Tura-Kavak Nekrasova (1957)	ideal composition
	mean	range (<i>n</i> = 4)		
(NH ₄) ₂ O	4.75	3.79–6.00	6.64	5.96
Na ₂ O	0.84	0.43–1.42		
K ₂ O	0.72	0.54–0.93		
CaO	0.45	0.08–1.16		
P ₂ O ₅	16.37	15.34–17.17	15.63	16.24
UO ₃	66.05	63.41–69.26	68.70	65.44
H ₂ O*	12.47		11.00	12.37
total	101.65		101.97	100.00

H₂O* calculated on the base of ideal content of three water molecules *pfu*.

structure of synthetic $\text{ND}_4(\text{UO}_2)(\text{PO}_4) \cdot 3\text{D}_2\text{O}$ (Fitch and Fender 1983). The observed significant differences in intensities of individual diffraction maxima are caused by the strong preferred orientation effects due to $\{001\}$ perfect cleavage and other texture effects owing to the small amount of material available for the study. The unindexed X-ray powder data from the Debye camera (86 mm) given for uramphite from Tura-Kavak (Nekrasova 1957) are slightly different in comparison to our pattern and data published for synthetic phases (Fitch and Fender 1983; Marković et al. 1988; Foster et al. 2020). The refined unit-cell parameters of uramphite from Nová Ves pod Pleší for tetragonal space group $P4/ncc$, $a = 7.0292(11)$, $c = 18.092(2)$ Å, $V = 893.9(2)$ Å³, agree very well with data given for synthetic $\text{NH}_4(\text{UO}_2)(\text{PO}_4) \cdot 3\text{H}_2\text{O}$, $a = 7.02(1)$, $c = 18.08(4)$ Å, $V = 891.0$ Å³ (Marković et al. 1988), as well as for synthetic $\text{ND}_4(\text{UO}_2)(\text{PO}_4) \cdot 3\text{D}_2\text{O}$, $a = 7.0221(1)$, $c = 18.0912(3)$ Å, $V = 892.1$ Å³ (Fitch and Fender 1983). Gurzhiy et al. (2024) described uramphite from Beshtau in the space group $P4/nmm$, with twice smaller unit-cell, $a = 6.9971(3)$, $c = 8.9787(9)$ Å, $V = 439.59(6)$ Å³ and $Z = 2$.

3.3. Raman and infrared spectroscopy

Uramphite, $(\text{NH}_4)(\text{UO}_2)(\text{PO}_4) \cdot 3\text{H}_2\text{O}$, is a tetragonal uranyl-containing mineral, the space group $P4/nmm$ or $P4/ncc$, $Z = 2$ or 4 (Gurzhiy et al. 2024; Fitch and Fender 1983). In the asymmetric part of the unit cell, there is one U site, occupied by U^{6+} . Further on, the structure contains one P site, occupied by P^{5+} , four symmetrically independent sites occupied by O or N/O – O(1) and O(2) in the linear uranyl ion, O(3) of slightly distorted phosphate ions and N/O(4) of ammonium ion and water molecules. The crystal structure of uramphite contains infinite sheets formed by linear $(\text{UO}_2)^{2+}$ ions coordinated equatorially by four $(\text{PO}_4)^{3-}$ tetrahedra and separated by a two-level layer with statistically distributed three H_2O molecules and $(\text{NH}_4)^+$ ions (Fitch and Fender 1983; Gurzhiy et al. 2024).

Molecular water (C_{2v} symmetry) is characterized by three fundamental ν_1 (A_1) symmetric stretching OH vibrations (~ 3657 cm⁻¹), ν_2 (δ H_2O) (A_1) bending vibrations (~ 1595 cm⁻¹) and ν_3 (B_1) antisymmet-

ric stretching OH (~ 3756 cm⁻¹) vibrations. All vibrations are Raman and infrared active. Their wavenumbers are influenced by the formation of hydrogen bonds. At wavenumbers lower than 1100 cm⁻¹, libration-modes of water molecules may be observed (Čejka 1999; Nakamoto 2009). A free tetrahedral ammonium group, NH_4^+ (T_d symmetry) is characterized by four normal vibration modes (Nakamoto 2009; Sejkora et al. 2023): the ν_1 symmetric stretching vibration, Raman active (~ 3040 cm⁻¹), the ν_2 doubly degenerate bending vibration, Raman active (~ 1680 cm⁻¹), the ν_3 triply degenerate stretching vibration, Raman and infrared active (~ 3145 cm⁻¹) and ν_4 triply degenerate bending vibration, Raman and infrared active (~ 1400 cm⁻¹).

A free uranyl cation, $(\text{UO}_2)^{2+}$, $D_{\infty h}$ 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). In the case of free $(\text{PO}_4)^{3-}$ tetrahedra (T_d symmetry), there are nine normal vibrations, characterized by four fundamental modes of vibrations – ν_1 symmetric stretching vibration, Raman active (~ 938 cm⁻¹), ν_2 (δ) doubly degenerate bending vibration, Raman active (~ 420 cm⁻¹), ν_3 triply degenerate asymmetric stretching vibration, Raman and infrared active (~ 1017 cm⁻¹), and ν_4 (δ) triply degenerate

Tab. 3 Tentative assignment of Raman spectrum of uramphite from Nová Ves pod Pleší.

position	FWHM	$I_{\text{rel.}}$	$I_{\text{rel.}}$	synth. ¹	synth. ²	tentative assignment
[cm ⁻¹]	[cm ⁻¹]	height	area	[cm ⁻¹]	[cm ⁻¹]	
3420	124	0.2	1.6			ν O–H stretch of hydrogen-bonded water molecules
3223	130	0.2	2.1			ν O–H stretch of hydrogen-bonded water molecules
3048	83	0.4	1.9			ν_1, ν_3 N–H stretch of NH_4^+ groups
2911	115	0.5	4.0			
1605	74	3.7	19.0			ν_2 bend of hydrogen-bonded water molecules
1549	182	2.0	27.9			
1332	156	5.7	75.4			ν_4 bend of NH_4^+ groups
1003	28	9.1	17.6			ν_3 asymmetric stretch of $(\text{PO}_4)^{3-}$
994	18	83.2	100.0	990	s	ν_1 symmetric stretch of $(\text{PO}_4)^{3-}$
836	13	100.0	90.5	836	vs	ν_1 symmetric stretch of $(\text{UO}_2)^{2+}$
618	43	1.2	3.6			ν_4 bend of $(\text{PO}_4)^{3-}$
401	13	4.5	4.1	402	w	ν_2 bend of $(\text{PO}_4)^{3-}$
290	13	1.2	1.0	290	w	ν_2 bend of $(\text{UO}_2)^{2+}$
194	20	18.6	29.5	196	w	202
123	9	1.7	1.1			130
114	15	1.7	1.8			102
92	18	4.1	5.0			lattice and other modes
77	13	3.9	3.4			82

$I_{\text{rel.}}$ calculated from peak height and band area; synth¹ – synthetic analog of uramphite (Novitskiy et al. 1981); synth² – synthetic analog of uramphite (Pham-Thi and Colomban (1985). s – strong, vs – very strong, w – weak.

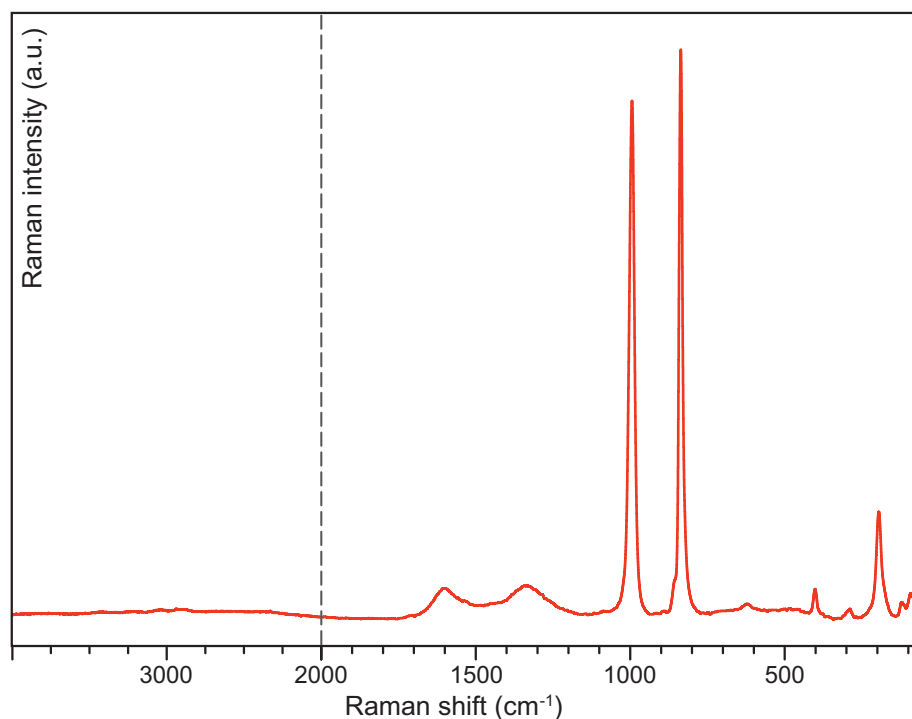


Fig. 4 Raman spectrum for uramphite from Nová Ves pod Pleší (split at 2000 cm^{-1}).

Tab. 4 Tentative assignment of infrared spectrum of uramphite from Nová Ves pod Pleší.

position [cm^{-1}]		Beshtau ¹ [cm^{-1}]		synth ² [cm^{-1}]		synth ³ [cm^{-1}]		tentative assignment
		3550	sh					
3422	ms	3424	s	3440	s	3415	vs	v O–H stretch of hydrogen-bonded water molecules
3290	ms			3320	ms			
3192	ms	3207	ms	3200	s	3160	vs	v O–H stretch of hydrogen-bonded water molecules; v ₃ N–H stretch of NH_4^+ groups
		3120	sh					
3020	ms	3050	sh			3010	vs	
2935	ms	2940	sh					
2882	ms					2880	vw	
		2093	vw	2090	w	2080	vw	combination bands/overtones
1846	vw	1842	vw	1850	w	1840	vw	
1654	w	1638	ms	1650	w	1645	ms	v ₂ bend of hydrogen bonded water molecules
1491	sh	1488	sh			1485	sh	v ₄ bend of NH_4^+ groups
1466	ms	1469	ms			1465	s	
1427	ms	1430	ms	1430	s	1425	m	
1399	sh	1405	sh			1397	s	
1104	ms	1101	s	1115	ms	1112	m	v ₃ asymmetric stretch of $(\text{PO}_4)^{3-}$
989	vs	1008	vs	1000	vs	1000	vs	v ₁ symmetric stretch of $(\text{PO}_4)^{3-}$
915	vs	921	ms	922	ms	918	vs	v ₃ antisymmetric stretch of $(\text{UO}_2)^{2+}$
849	ms			828	w	822	w	v ₁ symmetric stretch of $(\text{UO}_2)^{2+}$
808	w	807	w					libration mode of H_2O
668	w	690	sh	670	w			v ₄ bend of $(\text{PO}_4)^{3-}$
		645	w					
590	ms	602	w	618	w	610	w	
545	vs	543	ms	543	ms	545	vw	libration mode of H_2O
468	w	470	ms	465	w	490	vw	

Beshtau¹ – uramphite from Beshtau (Gurzhiy et al. 2024); synth² – synthetic analog of uramphite (Novitskiy et al. 1981); synth³ – synthetic analog of uramphite (Baran and Botto 1977). s – strong, vs – very strong, ms – medium strong, m – medium, w – weak, vw – very weak, sh – shoulder.

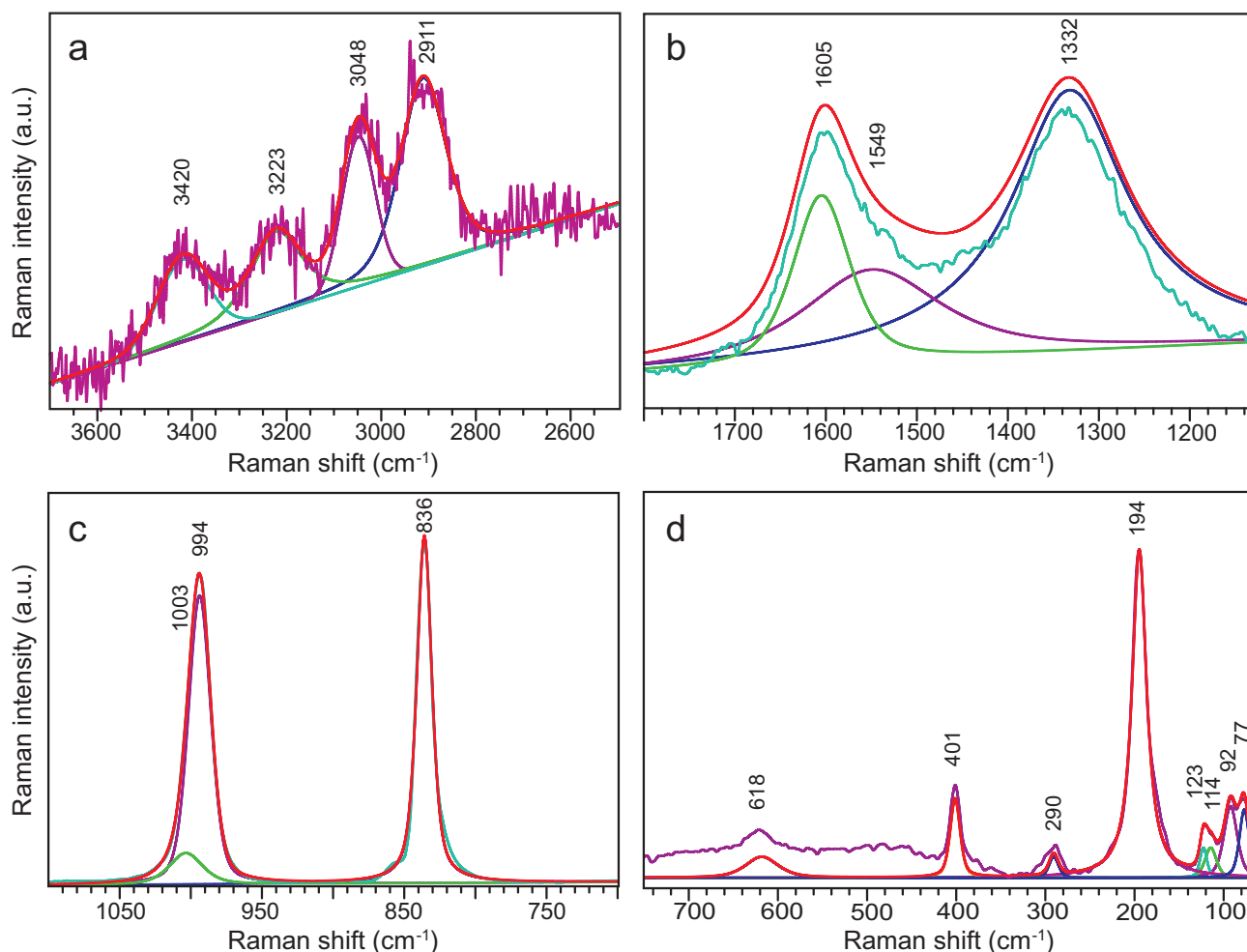


Fig. 5 Results of the band component analysis in the Raman spectrum of uramphite from Nová Ves pod Pleší: **a** – 3700–2500 cm^{-1} ; **b** – 1800–1130 cm^{-1} ; **c** – 1100–700 cm^{-1} ; **d** – 750–65 cm^{-1} .

bending vibration, Raman and infrared active ($\sim 567 \text{ cm}^{-1}$) (Nakamoto 2009). Symmetry lowering $T_d \rightarrow C_{3v}$, C_{2v} , C_1 may be connected with infrared activation of infrared inactive vibrations and splitting of degenerate vibrations.

To our best knowledge, the Raman spectrum of natural uramphite has not yet been published; in the case of its synthetic analog, the Raman spectrum is reported only in regions 1500–150 and 350–50 cm^{-1} , respectively (Novitskiy et al. 1981; Pham-Thi and Colomban 1985). The full-range Raman spectrum of the studied uramphite from Nová Ves pod Pleší is given in Fig. 4, and wavenumbers with assignments in Tab. 3.

A broad band of very low intensity, located at 3420 cm^{-1} (Fig. 5a), is connected with the ν OH stretching vibrations of hydrogen-bonded water molecules; bands at 3223, 3048 and 2911 cm^{-1} along with ν_1 and ν_3 N-H stretching vibration from interlayer NH_4^+ groups. According to the empirical relation between the energy of vibration and the corresponding bond length (Libowitzky 1999), O–H $\cdots$ O hydrogen-bond lengths vary approximately in the range from 2.67 to 2.82 Å, which

correspond to the results (2.78–2.98 Å) of the crystal structure study (Gurzhiy et al. 2024). A weak band with components at 1605 and 1549 cm^{-1} (Fig. 5b) is attributed to the ν_2 bending vibrations of water molecules. A broad band at 1332 cm^{-1} (Fig. 5b) is related to the ν_4 bending vibration of NH_4^+ groups.

A very strong band at 994 cm^{-1} (Fig. 5c) is assigned to the ν_1 (PO_4) $^{3-}$ symmetric stretching vibration; its shoulder is observed at 1003 cm^{-1} is attributable to the ν_3 (PO_4) $^{3-}$ asymmetric stretching vibration. The most intensive band at 836 cm^{-1} (Fig. 5c) is assigned to the ν_1 (UO_2) $^{2+}$ symmetric stretching vibrations, corresponding to U–O bond lengths in uranyl 1.775 Å (Bartlett and Cooney 1989). The inferred U–O bond length for the uranyl ion is comparable with data derived from the X-ray studies for synthetic deuterated analog of uramphite (1.792–1.793 Å, Fitch and Fender 1983) and for uramphite from Beshtau (1.802–1.804 Å, Gurzhiy et al. 2024).

A weak band at 618 cm^{-1} (Fig. 5d) is connected with the triply degenerate ν_4 (δ) (PO_4) $^{3-}$ bending vibrations and another weak one at 401 cm^{-1} to the doubly degenerate

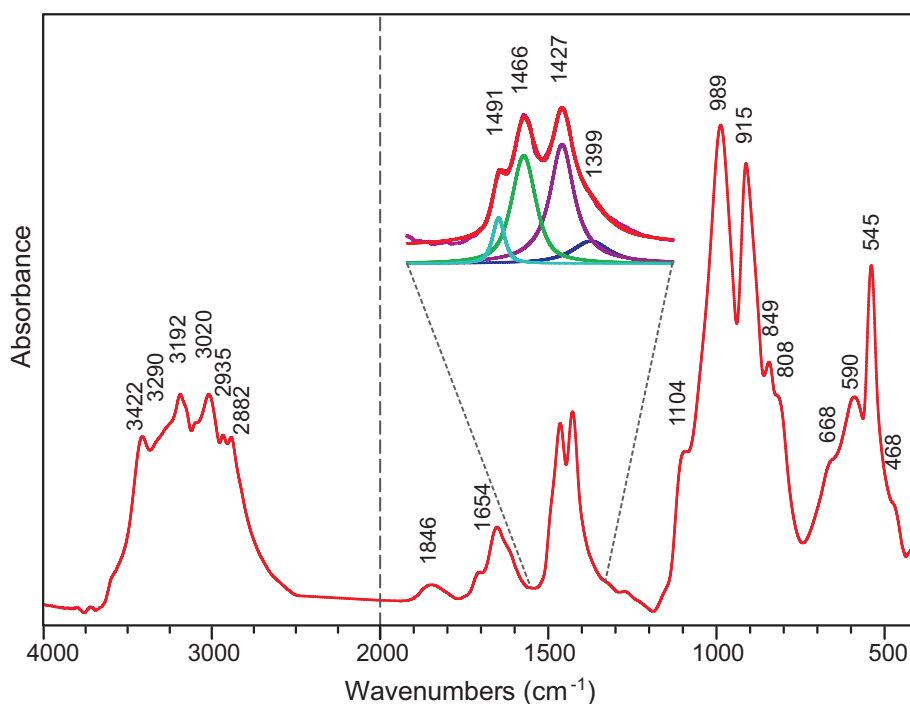


Fig. 6 Infrared spectrum for uramphite from Nová Ves pod Pleší (split at 2000 cm^{-1}) with deconvolution of ν_4 bending vibrations of NH_4^+ groups.

ν_2 (PO_4) $^{3-}$ bending vibrations. A weak band at 290 cm^{-1} (Fig. 5d) is related to the ν_2 (UO_2) $^{2+}$ doubly degenerate bending vibrations. A weak band at 114 cm^{-1} is probably connected with (PO_4) $^{3-}$ libration motion (Pham-Thi and Colomban 1985). Other observed bands below 200 cm^{-1} (194, 123, 92 and 77 cm^{-1}) may be attributed to $\text{O}_{\text{eq}}-\text{U}-\text{O}_{\text{eq}}$ bending vibrations (Ohwada 1976), $\nu_{\text{translational}}$ of NH_4^+ groups (Heyns et al. 1987), UO_2^{2+} translations and rotations and external lattice vibration modes (Plášil et al. 2010; Kampf et al. 2018a).

The infrared spectrum of uramphite from Nová Ves pod Pleší corresponds to published spectra of uramphite from Beshtau (Gurzhiy et al. 2024) and synthetic (NH_4) (UO_2)(PO_4) $\cdot 3\text{H}_2\text{O}$ (Baran and Botto 1977; Novitskiy et al. 1981). The experimental full-range spectrum is given in Fig. 6, and its tentative assignment is presented in Tab. 4. Medium strong and broad infrared bands at 3422, 3290, 3192, 3020, 2935, and 2882 cm^{-1} are assigned to the ν O–H stretching vibration of hydrogen-bonded water molecules; part of these bands between 3200–2700 cm^{-1} also to ν_1 and ν_3 N–H stretching vibrations of NH_4^+ group. According to Libowitzky (1999) correlation function, O–H $\cdots$ O hydrogen bond lengths vary approximately from 2.82 to 2.63 Å. A very weak band at 1846 cm^{-1} can be assigned as a combination band/overtone. A weak infrared band at 1654 cm^{-1} is attributed to the ν_2 H_2O bending vibration of water molecules. The medium strong band with components at 1466, 1427 cm^{-1} and shoulders at 1491 and 1399 cm^{-1} is related to the ν_4 triply degenerate bending vibration of NH_4^+ groups in the interlayer. It is worth noticing that Novitskiy et al. (1981) observed for synthetic analog of uramphite only one broad band

(1430 cm^{-1}) in this area, while Baran and Botto (1977) found a band with four components (1485, 1465, 1425, 1397 cm^{-1}). This four-component band Gurzhiy et al. (2024) explained by the resonance splitting of a group of NH_4^+ cations occurring around the four-fold axis at close distances from each other. Sidorenko et al. (2007) and Chukanov (2014) reported a band with distinct four components (1495, 1473, 1433, 1405 cm^{-1}) also for analogous uramarsite (NH_4)(UO_2)(AsO_4) $\cdot 3\text{H}_2\text{O}$.

A very strong infrared band at 989 cm^{-1} is assigned to the ν_1 (PO_4) $^{3-}$ symmetric stretching vibration, its shoulder at 1104 cm^{-1} to the ν_3 (PO_4) $^{3-}$ asymmetric stretching vibration. Strong infrared bands at 915 cm^{-1} and 849 cm^{-1} are attributed to ν_3 (UO_2) $^{2+}$ antisymmetric and ν_1 (UO_2) $^{2+}$ symmetric stretching vibrations, respectively. The uranyl U–O bond lengths 1.773 (ν_3) and 1.762 (ν_1) Å, calculated using the empirical relation given by Bartlett and Cooney (1989), are comparable with bond lengths 1.792–1.793 Å obtained from the X-ray studies for synthetic deuterated analog of uramphite (Fitch and Fender 1983) and 1.802–1.804 Å given for uramphite from Beshtau (Gurzhiy et al. 2024). A shoulder at 808 cm^{-1} is probably related to the libration mode of H_2O molecules (e.g., Plášil et al. 2012; Kampf et al. 2018a). Medium strong infrared band at 590 cm^{-1} with shoulder at 668 cm^{-1} is probably connected with ν_4 (PO_4) $^{3-}$ triply degenerate bending vibration. Baran and Botto (1977) and Čejka (1999) state that this vibration occurs in synthetic analog of uramphite (543 or 545 cm^{-1}) but in comparison with other uranylphosphates (e.g. Čejka 1999) or phosphates (e.g. Frost et al. 2010, 2013) it is clear that infrared bands at 545 and 468 cm^{-1} are instead related to libration modes of H_2O .

4. Conclusions

A rare mineral uramphite, a member of the meta-autunite group containing nitrogen, was determined in the material from Nová Ves pod Pleší (the third-world occurrence) by X-ray powder diffraction and electron microprobe analyses. The molecular structure of this well-defined sample can be better constrained using vibrational spectroscopy. Raman and infrared spectroscopy confirmed the presence of molecular water, ammonium, uranyl, and phosphate units in its crystal structure. Multiple bands related to vibrations of water molecules prove the presence of hydrogen-bonded water molecules bonded in the structure of uramphite with distinct bond strengths.

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