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Čejkaite, the triclinic polymorph of $Na_4(UO_2)(CO_3)_3$—a new mineral from Jáchymov, Czech Republic

PETR ONDRUŠ,[1,*] ROMAN SKÁLA,[1] FRANTIŠEK VESELOVSKÝ,[1] JIŘÍ SEJKORA,[2] AND CECILIA VITTI[3]

[1]Czech Geological Survey, Klárov 3/131, P.O. Box 85, CZ-118 21 Prague 1, Czech Republic
[2]National Museum, Václavské náměsti 68, CZ-115 79 Prague 1, Czech Republic
[3]Dipartimento di Scienze della Terra, Via Laterina, 8, I-53100 Siena, Italy

ABSTRACT

Čejkaite, a new mineral from Jáchymov, NW Bohemia, Czech Republic, forms a thin earthy efflorescence over a calcite vein associated with disintegrated uraninite. The color is pale yellow to beige, the streak is light yellow, and the luster is vitreous. The broad secondary mineral association includes andersonite and schröckingerite. Chemical analysis (by ICP-MS and TG) gave (in wt%): Na_2O = 21.39, MgO = 0.15, FeO = 0.53, UO_3 = 53.93, and CO_2 = 24.00 (calculated by difference). The simplified chemical formula is $Na_4UO_2(CO_3)_3$. The mineral is triclinic, space group $P1$ or $P\bar{1}$, a = 9.291(2), b = 9.292(2), c = 12.895(2) Å, α = 90.73(2), β = 90.82(2), γ = 120.00(1)°, V = 963.7(4) Å^3, Z = 4, D_{meas} = 3.67(1) g/cm^3, and D_{calc} = 3.766(5) g/cm^3. The strongest seven lines in the X-ray powder-diffraction pattern [d in Å(I)(*hkl*)] are: 8.022(92)($1\bar{1}0$, 010, 100), 5.080(57)($\bar{1}02$, $0\bar{1}2$), 5.024(60)($\bar{1}12$, $1\bar{1}2$), 4.967(68)(012, 102), 4.639(100)($1\bar{2}0$, $2\bar{1}0$, 110), 3.221(63)(004), 2.681(60)($3\bar{3}0$, $\bar{1}14$, 030, 300). Optical data could not be measured due to the extremely small grain size, but the calculated mean refractive index is 1.5825. Crystal size varies from 0.2 to 0.6 μm and shows an indistinct hexagonal outline. Thermal decomposition of synthetic čejkaite proceeds in three main steps. DTA endotherm at 430 °C corresponds to the decomposition of the uranyl tricarbonate groups. IR spectrum of čejkaite confirms the presence of crystallographically nonequivalent $(CO_3)^{2-}$ groups and the absence of water. The average U-O bond length in $(UO_2)^{2+}$, calculated from ν_3 = 848 cm^{-1}, is $R_{U\text{-}O}$ ~ 1.81 Å. A model based on the crystal structure of trigonal $Na_4(UO_2)(CO_3)_3$ was adopted and applied to solve the čejkaite crystal structure by the Rietveld method (7238 unique reflections, R_p = 0.076, R_{wp} = 0.104). Uranium is eight-coordinated, and forms a $[UO_2O_6]$ skeleton with almost linear O-U-O that is roughly perpendicular to an irregular cycle formed by six O atoms that, in turn, belong to three more-or-less regular and planar CO_3 groups. Atoms Na1, Na1a, and Na2 are octahedrally coordinated, whereas Na3 is pentagonally coordinated. The mineral name honors Jiří Čejka for his notable contributions to the crystal chemistry of U minerals.

INTRODUCTION

In the course of work on the project *Study of secondary minerals in the Jáchymov ore district* (Ondruš et al. 1997b, 1997c), thirty new naturally forming inorganic phases were recognized and studied. This paper describes one of these, čejkaite, which is triclinic $Na_4(UO_2)(CO_3)_4$, in detail. Because čejkaite was observed at Jáchymov as an extremely rare species, we prepared a synthetic analog of this new mineral in our laboratory, which allowed us to study this phase in more detail. Triclinic $Na_4UO_2(CO_3)_3$ was synthesized according to the following method: a solution containing $2 \cdot 10^{-3}$ *M* uranyl nitrate was added slowly with constant stirring to a solution of $6 \cdot 10^{-3}$ *M* sodium carbonate. A yellow precipitate formed and was decanted three times using distilled water.

To compare the physical and chemical properties and crystal structure parameters of čejkaite to its trigonal polymorph, we also prepared synthetic trigonal $Na_4(UO_2)(CO_3)_3$. The latter was synthesized from synthetic triclinic $Na_4(UO_2)(CO_3)_3$ powder by recrystallization in sealed silica glass tubes under hydrothermal conditions at a pressure of about 20 MPa and a temperature of 135 °C for 3 days (Císařová et al. 2001).

Under hydrothermal conditions at about 200 °C, čejkaite recrystallizes to trigonal $Na_4UO_2(CO_3)_3$, whose crystal structure has been characterized by Douglass (1956), Čejka (1999), Císařová et al. (2001), and Li et al. (2001a). Koglin et al. (1979) summarized the basic structural motif of the $UO_2(CO_3)_3$ complex. Burns (1999) listed twenty-three uranyl phases that have known crystal structures based on a finite cluster of polyhedra of higher bond valence (Burns et al. 1996), but only six of these are recognized as minerals. One may expect that this finite cluster should also occur in uranyl-carbonate minerals in which the crystal structure has not yet been solved (rabbittite, widenmannite, znucalite, and many others).

The holotype material of čejkaite is deposited in the mineralogical collection of the National Museum, Prague, Czech

* E-mail: ondrus@cgu.cz

Republic (the acquisition number is P1p 17/99). The new mineral and mineral name have been approved by the Commission on New Minerals and Mineral Names of the IMA in 1999 (99-045).

The name is in honor of Jiří Čejka, D.Sc. (b.1929) for his numerous contributions to the crystal chemistry of U minerals. His professional record encompasses over 200 scientific papers, 10 Czechoslovakian patents, and 59 unpublished research reports (mainly focused on IR spectroscopy and TG analysis of U compounds and minerals). He previously published a study on the thermal decomposition of the synthetic analog of this new mineral (Čejka 1969). Jiří Čejka was a Director of the Museum of Natural History of the National Museum in Prague, Czech Republic, from 1991 to 2001.

DEPOSIT CHARACTERISTICS

The Jáchymov ore district coincides with the spatial area within the town and its immediate close surroundings. The town of Jáchymov (also known as St. Joachimsthal) is located on the southern slope of the Krušné hory Mountains (Erzgebirge), approximately 20 km north of Karlovy Vary, NW Bohemia, Czech Republic. The location, geological setting, and mineralization of the Jáchymov ore district are described by Ondruš et al. (2002).

Jáchymov is a classical deposit of Ag + As + Co + Ni ± Bi and U mineralizations. The ore district is bounded by several faults, including the major northern fault zone. The fault pattern and location of several of the main veins is shown in Ondruš et al. (1997b).

Occurrence and paragenesis

Čejkaite occurs as an extremely rare species due to its inherent instability under even slightly acidic conditions. The mineral was found on a single specimen from the Geschieber vein of the Svornost mine, at Jáchymov. The thin earthy efflorescence covers a calcite vein with associated (disintegrated) uraninite in an area of about 2 × 5 cm. The broad secondary mineral association with čejkaite includes andersonite and schröckingerite; however, čejkaite is not in direct contact with any other secondary phase.

The mineral has formed recently in a relatively dry environment with rapid precipitation, most probably due to a change of acidity of sodium-carbonate solutions. In contrast to the more common uranyl-carbonates found at Jáchymov (Ondruš et al. 1997a, 1997b), gypsum is characteristically absent from the čejkaite mineral assemblage.

The formation of the $[UO_2(CO_3)_3]^{4-}$ complex, as well as its mobility, is limited to a relatively narrow range of pH values. The $[UO_2(CO_3)_3]^{4-}$ anion is stable in the pH range 6.5 to 11.5 (Finch and Murakami 1999), which indicates that čejkaite is not stable in an acidic environment as typically found at the Jáchymov ore district.

Physical and optical properties

The size of čejkaite crystals ranges from 0.2 to 0.6 μm, and individual crystallites display indistinct hexagonal morphology in TEM images. The color of earthy sprays of čejkaite is pale yellow to beige, the streak is light yellow, and the luster is vitreous. The mineral displays a weak yellow to yellow-green fluorescence in short and long UV light wavelengths. The specific gravity of powder aggregates by weighing in toluene is 3.67(1) g/cm^3 and the calculated density (for $Z = 4$) is 3.766(5) g/cm^3 based on ideal formula. Other physical properties, as well as optical data, could not be characterized due to the extremely small grain size. The mean refractive index derived from Gladstone-Dale calculations (Mandarino 1979) is 1.5825, which is consistent with the measured mean refractive index for the trigonal polymorph of čejkaite (Douglass 1956). Čejkaite is readily soluble with reach effervescence in diluted acids and even in water with pH < 6.5.

Chemical composition

Qualitative spectral chemical analysis of čejkaite indicates only Na and U. Magnesium and Fe were detected in concentrations below 0.6 wt%. Quantitative chemical analysis was carried out using a combination of ICP MS method and thermal analysis and the results are summarized in Table 1. The empirical formula of čejkaite, calculated on the basis of 11 O atoms per formula unit, is $(Na_{3.77}Fe_{0.04}Mg_{0.02})(UO_2)_{1.03}(CO_3)_{2.98}$, which results in the simplified formula $Na_4UO_2(CO_3)_3$.

The quantitative determination of CO_2 could not be achieved due to equipment limitations. CO_2 continued to evolve above 1000 °C, which is the upper threshold of the instrumentation. The CO_2 content was therefore calculated by difference.

Thermal data

TG and DTA curves (Fig. 1) were recorded with a Stanton Redcroft TG 750 thermobalance (TG = heating rate 10 °C/min, dynamic air atmosphere), and a Blažek DTA instrument (DTA = heating rate 10 °C/min, static air atmosphere, Al_2O_3 reference sample). Because the mass of natural material is miniscule, the synthetic analog of triclinic čejkaite and the synthetic trigonal polymorph of $Na_4UO_2(CO_3)_3$ were used as appropriate materials for study. Sample weights were as follows (TG, DTA): synthetic čejkaite (6.47, 80 mg), trigonal $Na_4UO_2(CO_3)_3$ (6.36, 60 mg).

Tentative assignment and interpretation of the TG, DTA curves of synthetic čejkaite (Čejka 1969, 1999) is given in Table 2. Decomposition of synthetic čejkaite in the temperature range of 20–950 °C is assumed to proceed in three main steps:

I. $2Na_4UO_2(CO_3)_3 \rightarrow Na_2U_2O_7 + 3Na_2CO_3 + 3CO_2$

II. $Na_2U_2O_7 + 3Na_2CO_3 \rightarrow 2\ Na_2UO_4 + 2Na_2CO_3 + CO_2$

III. $Na_2UO_4 + Na_2CO_3 \rightarrow Na_4UO_5 + CO_2$

Two CO_2 molecules are gradually liberated in several steps between 50–765 °C. The first two reactions listed above represent this process. Release of the third CO_2 molecule, which is

TABLE 1. Chemical analysis (wt%) and formula of čejkaite from Jáchymov

Constituent	Wt%		Cations per 11 O
Na_2O	21.39	Na	3.77
MgO	0.15	Mg	0.02
FeO	0.53	Fe	0.04
UO_3	53.93	U	1.03
CO_2	24.00*	C	2.98
Total:	100.00		

* Calculated by difference (content measured below 1000 °C is about 22 wt%).

TABLE 2. Thermal analyses of synthetic triclinic čejkaite and trigonal $Na_4(UO_2)(CO_3)_3$

Synthetic čejkaite			Trigonal $Na_4(UO_2)(CO_3)_3$		
Temperature range (°C)	Mass decrease (wt%)	Assignment	Temperature range (°C)	Mass decrease (wt%)	Assignment
20–550	13.9	1.76 CO_2	20–650	12.4	1.54 CO_2
550–910	4.6	0.59 CO_2	650–890	4.1	0.51 CO_2
Sample weight 6.47 mg			Sample weight 6.36 mg		
DTA endotherms:			DTA endotherms:		
430, 680, 780, 860, 930, 970 °C			455, 785, 855, 930, 960 °C		

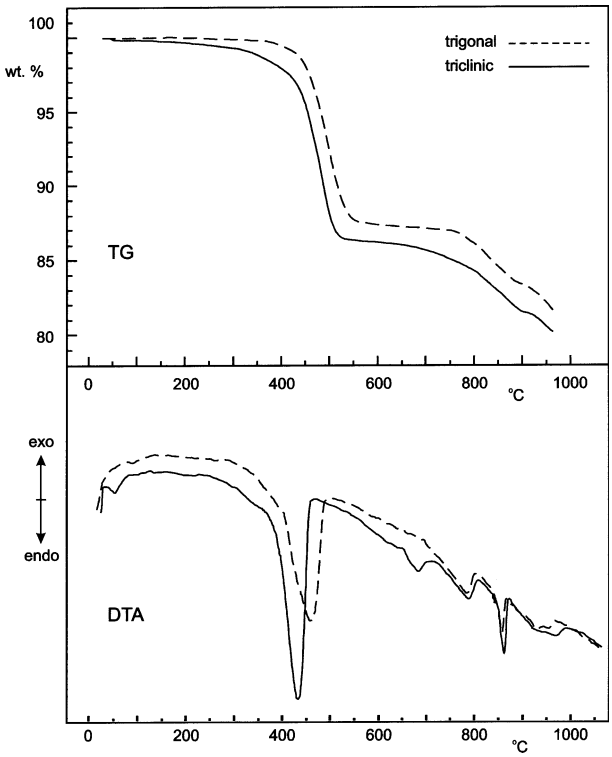

FIGURE 1. TG (upper) and DTA (lower) curves of synthetic triclinic čejkaite and its trigonal polymorph.

characterized by the last reaction listed above, starts at 765 °C and continues up to and beyond 1000 °C.

DTA curves show a major endotherm at 455 °C (trigonal polymorph) and 430 °C (synthetic čejkaite), which corresponds to the decomposition of the uranyl tricarbonate groups. The minor endotherm at 680 °C (synthetic čejkaite), which was not observed in the case of the trigonal polymorph, is associated with the formation of $Na_2U_2O_7$ and Na_2CO_3, accompanied by a release of approximately 1.5 CO_2.

A set of endotherms in the 700–1000 °C region is related to the following processes: the $Na_2U_2O_7$ gradually reacts with Na_2CO_3 to form α-Na_2UO_4 (650–750 °C with approximately 0.5 CO_2 released) and, at about 860 °C, the unreacted Na_2CO_3 melts. The irreversible polymorphic transformation of α-Na_2UO_4 to β-Na_2UO_4 takes place between 900–970 °C and lastly, β-Na_2UO_4 reacts with the fused Na_2CO_3 to form Na_4UO_5. This latter process is associated with the release of the last CO_2 molecule and proceeds at temperatures above 1000 °C. There is no DTA evidence for a phase transformation between triclinic and trigonal $Na_4UO_2(CO_3)_3$. This result is not unexpected given that the synthesis of trigonal $Na_4UO_2(CO_3)_3$ (Císařová et al. 2001) could only be achieved in an aqueous environment.

As seen in Figure 1, the TG curves of both phases are similar; however, mass changes proceed at slightly different temperatures. Čejkaite is appreciably less stable upon heating than its trigonal polymorph. Thus, thermal decomposition and formation of transitional phases for synthetic čejkaite proceed at temperatures approximately 50 °C lower than those observed for the trigonal phase.

Infrared-absorption spectra

Infrared-absorption spectra in the 400–4000 cm^{-1} range for čejkaite and its synthetic trigonal polymorph, recorded with a FTIR Nicolet 740 spectrophotometer using KBr pellets, are shown in Figure 2 and interpreted in Table 3. Papers by Čejka (1999), Anderson et al. (1980), and Koglin et al. (1979) were consulted to facilitate interpretation of the IR spectrum of čejkaite.

Absorption bands characteristic of vibrations associated with $(CO_3)^{2-}$ and $(UO_2)^{2+}$ groups were observed in all infrared spectra. The symmetry of the $(CO_3)^{2-}$ group in čejkaite is distinctly lowered; this effect causes IR-activation of the ν_1 symmetric stretching vibration and splitting of the doubly degenerate vibrations, antisymmetric stretching vibration ν_3 $(CO_3)^{2-}$, and in-plane bending vibration ν_4 $(CO_3)^{2-}$. The band at 848 cm^{-1} was assigned to the ν_3 $(UO_2)^{2+}$ antisymmetric stretching vibrations. An intensive band at 832 cm^{-1}, assigned to the out-of-plane bending vibration ν_2 $(CO_3)^{2-}$, strongly overlaps all other weak bands in that region, including the symmetric stretching vibration ν_1 $(UO_2)^{2+}$, which is expected to occur between 770–800 cm^{-1}. The band at 1065 cm^{-1} was assigned to the ν_1 $(CO_3)^{2-}$ antisymmetric stretching vibration; bands at 1349, 1527, 1563, and 1576 cm^{-1} were assigned to ν_3 $(CO_3)^{2-}$ antisymmetric stretching vibrations; and bands at 704 and 737 were assigned to ν_4 $(CO_3)^{2-}$ in-plane bending vibrations. Weak broad bands centered about 1630 and 3400 cm^{-1} may be related to OH stretching and δ bending vibrations of adsorbed H_2O.

The IR spectra of the trigonal polymorph and triclinic čejkaite mainly differ due to splitting of both ν_3 $(CO_3)^{2-}$ bands in the trigonal polymorph into 4–5 distinct ν_3 $(CO_3)^{2-}$ bands in čejkaite. This splitting is fully consistent with the assumption of the presence of crystallographically nonequivalent $(CO_3)^{2-}$ groups in the crystal structure of the triclinic phase.

Wavenumber values of the ν_3 $(UO_2)^{2+}$ vibration may be used to calculate the U-O bond length in an uranyl compound. According to the relationship presented by Glebov (1989) for uranyl carbonates ($R_{U\text{-}O} = 68.2\ \nu_3^{-2/3} + 1.05$ Å), the following U-O bond lengths in $(UO_2)^{2+}$ were calculated: for čejkaite (ν_3 = 848

TABLE 3. Infrared-absorption spectra for čejkaite from Jáchymov and trigonal $Na_4(UO_2)(CO_3)_3$ (measured in KBr disk)

Čejkaite		Trigonal $Na_4(UO_2)(CO_3)_3$		Tentative assignment
3457	mw-b	3447	ms-b	OH stretching vibration
1627	w-sh	1630	w-sh	δ H_2O bending vibration
1576	vs			ν_3 $(CO_3)^{2-}$ antisymmetric stretching vibrations
1563	vs	1568	vs	
1527	sh			
1366	sh	1366	sh	
1349	m	1348	vs	
1065	m	1067	m	ν_1 $(CO_3)^{2-}$ antisymmetric stretching vibrations
		878	m	ν_3 $(UO_2)^{2+}$ antisymmetric
848	s	860	ms	stretching vibrations
832	s	833	ms	ν_2 $(CO_3)^{2-}$ out-of-plane bending vibration
737	s	737	s	ν_4 $(CO_3)^{2-}$ in-plane bending vibrations
		728	m	
704	mw	701	m	

Notes: FTIR spectrophotometer Nicolet 740. Intensity scale: vs = very strong, s = strong, m = medium, w = weak, vw = very weak. Character of absorption maxima: sh = shoulder, b = broad.

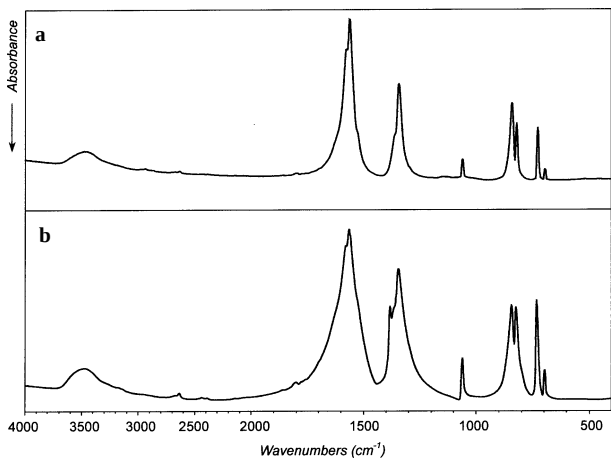

FIGURE 2. The infrared-absorption spectra of čejkaite and its trigonal polymorph. (**a**) čejkaite, (**b**) synthetic trigonal $Na_4UO_2(CO_3)_3$.

cm^{-1}), $R_{U\text{-}O}$ ~1.81 Å; for trigonal $Na_4(UO_2)(CO_3)_3$ (ν_3 = 860 cm^{-1}), $R_{U\text{-}O}$ ~1.80 Å. These values are in agreement with the X-ray structure data (see below).

X-ray powder diffraction and crystal structure

Powder diffraction data were collected using a Philips X'Pert MPD diffractometer equipped with a metallic-ceramic copper tube and operated at 40 kV and 40 mA. A graphite secondary monochromator was used to produce Cu$K\alpha_1\alpha_2$ radiation. The powder data for čejkaite were collected from 3 to 130 °2θ with a step size of 0.02 °2θ and an exposure of 35 s per step. To minimize background, the sample was placed on a flat low-background silicon wafer.

The powder pattern of čejkaite (Fig. 7) superficially resembles that of trigonal $Na_4(UO_2)(CO_3)_3$. Some peaks in the čejkaite pattern, however, are clearly split and form narrow multiplets. This peak splitting is consistent with triclinic symmetry with $P1$ or $P\bar{1}$ as probable space groups (i.e., the 00*l*-type reflections do not split whereas other sets of reflections may split into 3 to 6 reflections). Resolving these split reflections is, however, not usually possible because of extensive peak overlaps. Consequently, the complex čejkaite powder data contains multiplet that cannot be separated unambiguously in a single peak-profile-fitting and indexed correctly. Therefore, we adopted a model of the čejkaite crystal structure derived from the single-crystal structure data for trigonal $Na_4(UO_2)(CO_3)_3$ (Císařová et al. 2001; Li et al. 2001a), and refined the čejkaite unit-cell dimensions applying the Rietveld method. The refined unit-cell parameters are as follows: a = 9.291(2), b = 9.292(2), c = 12.895(2) Å, α = 90.73(2), β = 90.82(2), γ = 120.00(1)°, V = 963.7(4) Å^3, a:b:c = 0.9999:1:1.3878. The powder pattern produced by single-peak profile fitting (Ondruš 1993) and indexed by the Rietveld method is presented in Table 4.

To confirm the symmetry relationship derived from powder studies, due to a lack of either natural or synthetic crystals, selected area electron-diffraction (SAED) experiments were carried out on naturally occurring čejkaite. We used a Philips T400 analytical electron microscope equipped with an EDAX DX4 energy-dispersive system (EDS) operated at 120 kV. The selected area aperture used to acquire diffraction patterns was approximately 1 μm and the camera length was 1150 mm. Images were taken with a 50 μm objective aperture, i.e., with nominal point-to-point-resolution of about 0.4 nm. A qualitative chemical analysis by EDS confirmed the presence of U, Na, C, and O; no other chemical elements were detected. SAED patterns reveal pseudo-hexagonal symmetry (Fig. 3) with approximate unit-cell parameters $a \sim b \sim 9.3$, $c \sim 12.9$ Å, $\alpha \sim \beta \sim 90$ and $\gamma \sim 120°$. Unfortunately, departures from hexagonal symmetry are so subtle in SAED patterns that we are unable to confirm reliably the triclinic symmetry.

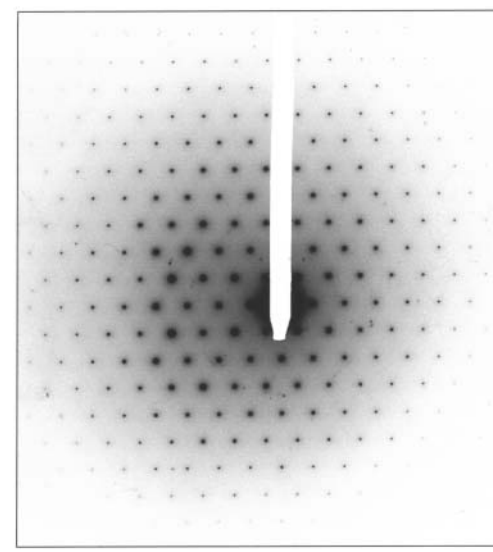

FIGURE 3. Selected area electron-diffraction pattern of čejkaite. *hk*0 reciprocal lattice revealing pseudo-hexagonal symmetry.

TABLE 4. X-ray powder-diffraction pattern of čejkaite from Jáchymov and comparison with synthetic trigonal $Na_4(UO_2)(CO_3)_3$ ($I_{obs} \geq 1\%$, $d_{obs} > 1.75$ Å)

čejkaite			Trigonal $Na_4(UO_2)(CO_3)_3$			čejkaite			Trigonal $Na_4(UO_2)(CO_3)_3$		
I_{obs}	d_{obs}	*hkl*	I_{obs}	d_{obs}	*hkl*	I_{obs}	d_{obs}	*hkl*	I_{obs}	d_{obs}	*hkl*
92	8.022	$1\bar{1}0$, 010, 100	30	8.080	100	1	2.189	131			
1	6.445	002	5	6.405	002	4	2.183	124, 214			
57	5.080	$\bar{1}02$, $0\bar{1}2$	95	5.022	102	1	2.148	006			
60	5.024	$\bar{1}12$, $1\bar{1}2$				16	2.124	$\bar{3}\bar{1}2$, $\bar{1}\bar{3}\bar{3}2$			
68	4.967	012, 102				16	2.121	$\bar{4}12$, $1\bar{4}2$	41	2.117	312
100	4.639	$1\bar{2}0$, $2\bar{1}0$, 110	52	4.667	110	16	2.112	$\bar{4}\bar{3}2$, $3\bar{4}2$			
40	4.019	$2\bar{2}0$, 020, 200	23	4.043	020	14	2.104	$\bar{3}\bar{4}2$, $4\bar{3}2$			
32	3.446	$\bar{2}02$, $0\bar{2}2$	46	3.419	202	13	2.095	$\bar{1}\bar{4}2$, $4\bar{1}2$			
32	3.410	$\bar{2}22$, $2\bar{2}2$				12	2.091	$\bar{1}\bar{3}2$, $3\bar{1}2$			
31	3.375	022, 202				14	2.087	$\bar{1}06$, $0\bar{1}6$, $\bar{3}04$, $0\bar{3}4$			
63	3.221	004	100	3.205	004	11	2.075	$\bar{1}16$, $1\bar{1}6$			
25	3.039	$2\bar{3}0$, $3\bar{2}0$, $1\bar{3}0$, $3\bar{1}0$, 120, 210	18	3.056	120	25	2.063	016, 106, $\bar{3}34$, $3\bar{3}4$	53	2.065	016
9	3.014	$\bar{1}04$, $0\bar{1}4$				10	2.037	034, 304	8	2.021	400
12	2.990	$\bar{1}14$, $1\bar{1}4$				9	2.011	$4\bar{4}0$, 040, 400, $\bar{1}\bar{3}3$,			
22	2.966	$\bar{1}\bar{2}1$, $1\bar{3}1$, 014, 104, $\bar{3}21$, $2\bar{3}1$, $3\bar{1}1$, 211	46	2.979	104	1	1.9951	$1\bar{4}3$			
23	2.776	$2\bar{1}2$, $1\bar{2}2$				1	1.9924	$\bar{1}\bar{2}5$	6	1.9851	313
23	2.769	$\bar{3}12$, $1\bar{3}2$	53	2.758	122	7	1.9325	215, $\bar{4}02$, $0\bar{4}2$	6	1.9438	116
21	2.760	$\bar{3}22$, $2\bar{3}2$				6	1.9200	$\bar{4}42$, $4\bar{4}2$	12	1.9276	402
20	2.739	$\bar{2}32$, $3\bar{2}2$				12	1.9135	$\bar{2}06$, $0\bar{2}6$			
18	2.731	$\bar{1}32$, $3\bar{1}2$				8	1.9077	$\bar{2}\bar{2}4$, 042, 402			
18	2.722	122, 212				19	1.8955	$\bar{4}24$, $\bar{2}26$, $2\bar{4}4$, $2\bar{2}6$	34	1.8883	206
60	2.681	$3\bar{3}0$, $1\bar{1}4$, 030, 300	38	2.695	030	14	1.8768	026, 206			
6	2.665	$\bar{2}14$, $1\bar{2}4$				7	1.8719	$\bar{2}44$, $4\bar{2}4$			
7	2.630	$\bar{1}24$, $2\bar{1}4$				3	1.8595	$\bar{2}24$	10	1.8548	230
4	2.614	114				12	1.8554	$\bar{3}\bar{1}4$, $\bar{1}\bar{3}4$, $\bar{4}14$			
10	2.543	$\bar{2}04$, $0\bar{2}4$				1	1.8509	$1\bar{4}4$			
11	2.514	$\bar{2}24$, $2\bar{2}4$, $\bar{2}\bar{1}3$				13	1.8454	$3\bar{5}0$, $5\bar{3}0$, $2\bar{5}0$, $5\bar{2}0$, 230, 320			
4	2.497	$\bar{3}13$, $\bar{3}02$, $0\bar{3}2$, $2\bar{3}3$				2	1.8412	$\bar{4}34$			
9	2.486	$0\bar{2}4$, 204				6	1.8395	$3\bar{4}4$	20	1.8370	134
2	2.467	$3\bar{2}3$, $\bar{1}33$				4	1.8312	$\bar{2}\bar{3}1$, $2\bar{5}1$, $\bar{5}31$, $\bar{3}44$			
1	2.451	123				4	1.8282	$4\bar{3}4$, $\bar{3}51$, $5\bar{2}1$			
41	2.322	$2\bar{4}0$, $4\bar{2}0$, 220	32	2.334	220	7	1.8176	321, $\bar{1}44$, $4\bar{1}4$			
6	2.240	$\bar{2}14$, $1\bar{2}4$	17	2.243	130	6	1.8120	$1\bar{3}4$, $3\bar{1}4$			
27	2.231	$\bar{3}14$, $3\bar{4}0$, $4\bar{3}0$, $1\bar{4}0$, $4\bar{1}0$, 130, 310, $1\bar{3}4$				10	1.7861	$\bar{3}\bar{2}2$, $\bar{2}\bar{3}2$			
6	2.221	$\bar{3}24$, $2\bar{3}4$				13	1.7819	$\bar{5}\bar{2}2$, $2\bar{5}2$, $\bar{5}32$	27	1.7817	322
2	2.207	$\bar{3}\bar{1}1$, $\bar{4}11$	26	2.211	214	5	1.7794	$3\bar{5}2$			
2	2.203	$\bar{2}\bar{2}2$, $\bar{2}34$				9	1.7766	$\bar{2}\bar{1}6$, $\bar{1}\bar{2}6$			
2	2.201	$3\bar{4}1$, $3\bar{2}4$				16	1.7690	$\bar{3}16$, $\bar{3}52$, $5\bar{3}2$, $1\bar{3}6$			
1	2.193	$4\bar{3}1$				8	1.7662	$\bar{2}52$, $5\bar{2}2$	31	1.7643	410
2	2.182	$\bar{1}34$				13	1.7615	$\bar{3}26$, 232, 322, $2\bar{3}6$			
2	2.192	$\bar{1}41$, $3\bar{1}4$				46	1.7553	$4\bar{5}0$, $5\bar{4}0$, $1\bar{5}0$, 510, 140, 410	34	1.7507	126

The proposed crystal structure of čejkaite shares the basic structure motif of $UO_2(CO_3)_3$ groups with the chemically similar compounds $(NH_4)_4UO_2(CO_3)_3$ (Graziani et al. 1972), $K_4UO_2(CO_3)_3$ (Anderson et al. 1980), $Tl_4UO_2(CO_3)_3$ (Mereiter 1986), and grimselite (Li and Burns 2001b), despite the fact they are not isotypic. This $UO_2(CO_3)_3$ group shows a pseudo-trigonal outline when viewed along the shortest O-U-O bond pair, and is built up by three planar CO_3 triangles that share one of their edges with the UO_2O_6 polyhedron. In the case of čejkaite and trigonal $Na_4(UO_2)(CO_3)_3$, the U-O bond lengths oriented along the **c** direction are significantly shorter than the U-O bond lengths in the equatorial plane of the UO_2O_6 distorted hexagonal bipyramid polyhedron. The planes of the CO_3 triangles attached to the UO_2O_6 polyhedron are inclined from the 001 plane (Fig. 4). Na1, Na1a, and Na2 atoms are octahedrally coordinated by O atoms. These octahedra are face-sharing and form chains of alternating polyhedra around Na1/Na1a and Na2 atoms that run parallel to the **c** axis and are situated at each unit-cell corner. Na3 atoms are pentagonally coordinated

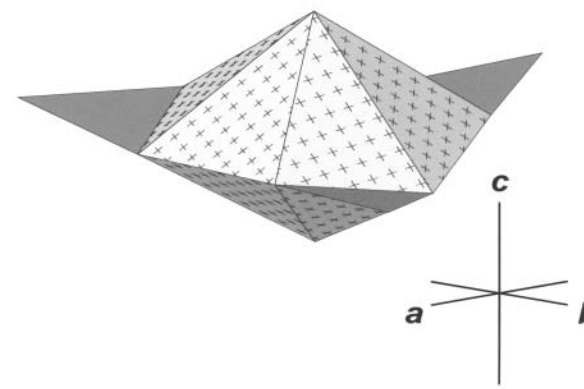

FIGURE 4. The structural motif of $UO_2(CO_3)_3$ group, which is found in both čejkaite and its trigonal polymorph. Hachure and color used: crosses: UO_2O_6 polyhedron; darker gray: planar CO_3 triangles.

and three of these Na3 polyhedra build up edge-sharing triplets (Fig. 5). The shared edge, defined by the O atoms, runs sub-parallel to the **c** axis. Triplets of polyhedra around Na3 atoms share vertices of their common edges with vertices of $UO_2(CO_3)_3$ groups adjacent to them in the [001] direction. These $UO_2(CO_3)_3$ groups, in turn, share medial edges with laterally neighboring Na3 polyhedra that build up two-dimensional sheets sub-parallel to 001. These two-dimensional sheets are stacked along [001] so that the next sheet is rotated by ~60° around [001] with respect to the adjacent one. Finally, each of three apical O atoms of the carbonate triangles from any $UO_2(CO_3)_3$ group is shared by the octahedron around either Na1, Na1a, or Na2 atoms (depending on the height of the sheet along [001] in the unit cell), and also makes a vertex of laterally adjacent polyhedra triplet around Na3 atoms (Fig. 6).

These expectations on the possible crystal structure of čejkaite are supported by the results of atomic-distance-constrained Rietveld refinements carried out on the powder X-ray data using the computer program FullProf (Rodríguez-Carvajal 2000). These Rietveld results are given in Tables 5, 6, and 7. Results of the Rietveld refinement and the comparison to hexagonal pattern are shown in Figure 7. Though the scattering contrast of U vs. O and C does not allow for more reliable

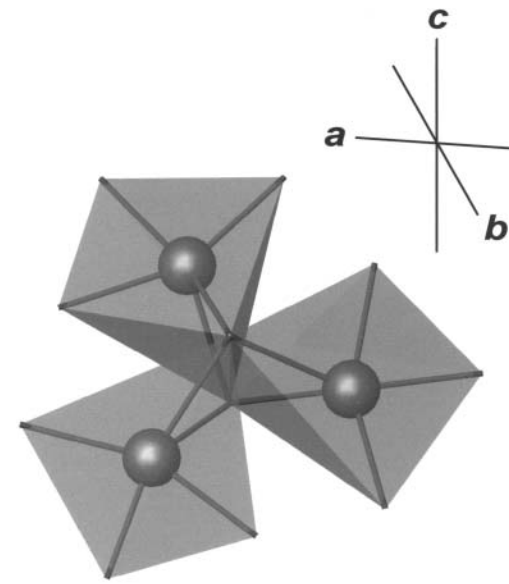

FIGURE 5. Triplets of NaO_5 polyhedra in the čejkaite structure.

TABLE 5. Results of distance-constrained Rietveld crystal-structure refinement carried out on X-ray powder-diffraction data of čejkaite

Atom	x	y	z	CN	ECoN	Δ_{ECoN}	BVS	Δ_{BVS}
U1	0.3268(3)	0.6609(3)	0.1299(3)	8	2.28	–71.5	6.39(4)	6.4
U1a	0.3240(3)	0.6583(3)	0.6279(3)	8	2.30	–71.3	6.39(5)	6.5
Na1	0.0000	0.0000	0.0000	6	6.00	0.0	1.062(4)	6.2
Na1a	0.0000	0.0000	0.5000	6	6.01	0.1	1.062(4)	6.2
Na2	0.0000	0.0000	0.2530(1)	6	6.21	3.5	0.923(4)	–7.7
Na3	0.4318(3)	0.3056(4)	0.1222(3)	5	4.72	–5.6	1.034(9)	3.4
Na3a	0.1148(3)	0.6904(3)	0.3673(3)	5	4.90	–2.1	1.035(7)	3.5
Na3b	0.3176(3)	0.4385(3)	0.3777(3)	5	4.93	–1.4	1.03(1)	3.2
Na3c	0.4284(3)	0.1249(3)	0.6166(3)	5	4.79	–4.1	1.034(8)	3.4
Na3d	0.1251(3)	0.4345(3)	0.8714(3)	5	5.26	5.3	1.031(8)	3.1
Na3e	0.3100(4)	0.8824(3)	0.8784(3)	5	4.77	–4.7	1.036(9)	3.6
O1	0.3348(4)	0.6689(4)	0.2723(2)				2.38(3)	18.9
O1a	0.3332(4)	0.6718(4)	0.7701(2)				2.39(3)	19.5
O2	0.3340(4)	0.6706(4)	0.9892(2)				2.41(3)	20.3
O2a	0.3239(4)	0.6713(4)	0.4871(2)				2.39(3)	19.3
C1	0.0786(9)	0.3229(6)	0.142(2)	3	2.92	–2.8	4.01(6)	0.2
C1a	0.2549(8)	0.9295(8)	0.149(2)	3	2.93	–2.2	3.97(7)	–0.7
C1b	0.3340(8)	0.0751(7)	0.393(5)	3	2.94	–2.1	3.96(7)	–1.1
C1c	0.073(1)	0.7548(7)	0.637(6)	3	2.94	–2.1	4.0(1)	–0.9
C1d	0.2552(7)	0.3169(6)	0.6743(9)	3	2.93	–2.3	3.98(9)	–0.4
C1e	0.3219(7)	0.2568(7)	0.855(2)	3	2.93	–2.2	3.97(6)	–0.8
O11	0.0390(5)	0.4391(5)	0.134(2)				1.89(3)	–5.5
O11a	0.4007(6)	0.9506(5)	0.126(3)				1.90(5)	–5.2
O11b	0.4632(9)	0.0542(7)	0.394(3)				1.91(4)	–4.7
O11c	0.0394(7)	0.6003(3)	0.635(5)				1.90(3)	–5.0
O11d	0.397(2)	0.443(2)	0.647(5)				1.90(8)	–5.0
O11e	0.4520(8)	0.4058(7)	0.865(6)				1.89(4)	–5.3
O12	0.1461(4)	0.7706(6)	0.153(2)				2.01(3)	0.3
O12a	0.2357(7)	0.3768(6)	0.163(1)				2.02(4)	0.8
O12b	0.3865(8)	0.2349(8)	0.395(3)				1.97(3)	–1.5
O12c	0.1526(4)	0.3747(8)	0.672(2)				2.05(3)	2.3
O12d	0.2336(6)	0.8554(4)	0.650(1)				1.98(5)	–0.9
O12e	0.3803(5)	0.1545(7)	0.859(5)				1.96(3)	–1.9
O13	0.2139(3)	0.0338(5)	0.1260(2)				2.06(4)	2.9
O13a	0.0452(5)	0.2216(3)	0.3821(3)				2.05(8)	2.5
O13b	0.1844(4)	0.9671(5)	0.3813(3)				2.04(4)	2.2
O13c	0.2158(3)	0.1865(4)	0.6243(2)				2.06(3)	3.1
O13d	0.0356(5)	0.8211(4)	0.8753(2)				2.09(3)	4.3
O13e	0.1776(4)	0.2155(3)	0.8804(2)				2.05(4)	2.6

Notes: CN = coordination number; ECoN = effective coordination number of Hoppe (1979) calculated using the program of Rieder (1993); Δ_{ECoN}(%) = difference of ECoN and CN on percentage scale; BVS = bond valence sum; Δ_{BVS} (%) = difference to ideal BVS value on percentage scale. BVS values calculated by program FullProf.2k (Rodríguez-Carvajal 2000) using default program settings.

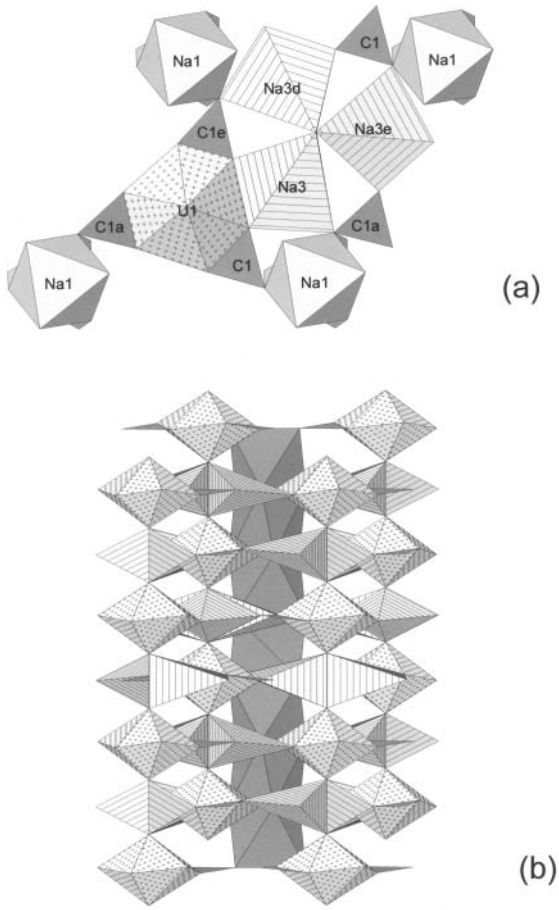

FIGURE 6. Projection of the crystal structure of čejkaite onto the 001 plane (**a**) and the 100 plane (**b**). Note the chain of alternating octahedra around the Na1, Na1a, and Na2 atoms parallel to [001] at the unit-cell edges. Hachure and color used: crosses = UO_2O_6 polyhedra; lines = NaO_5 polyhedron; dark gray = planar CO_3 triangles; light gray = NaO_6 octahedra.

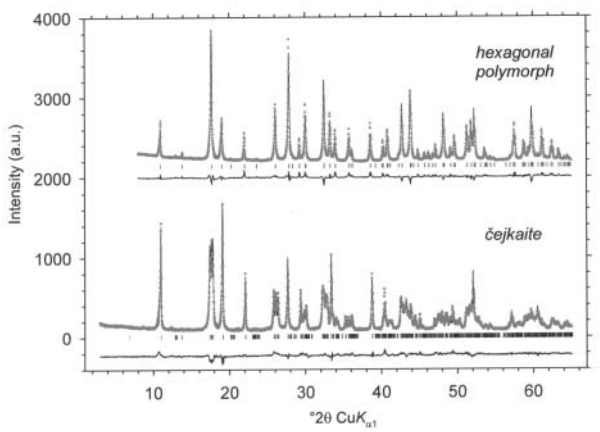

FIGURE 7. Part of the Rietveld plot comparing results of the Rietveld crystal structure refinements for natural čejkaite and its synthetic trigonal polymorph. Splitting of peaks of the trigonal polymorph to the multiplets found in the powder pattern of čejkaite is readily visible.

TABLE 6. Conditions and results of the Rietveld crystal-structure refinement of čejkaite

Formula:	$Na_4UO_2(CO_3)_3$		
Diffractometer:	Philips X'Pert System MPD		
Wavelengths, λ (Å)	1.5405 + 1.5443	V(Å^3)	963.7(4)
2θ range (°2θ)	3–120	Z	4
Step width (°2θ)	0.02	D_x (g/cm^3)	3.766(5)
Counting time (sec.)	35	overall temp. factor (Å^2)	1.53(6)
No. of observations	5851	R_p (%)	7.6
No. of reflections	7238	R_{wp} (%)	10.4
No. of fitted variables	129	R_{exp} (%)	7.7
Space group	$P\bar{1}$	R_B (%)	12.3
Unit-cell parameters:		R_F (%)	7.1
a (Å)	9.291(2)	χ^2	1.83
b (Å)	9.292(2)		
c (Å)	12.895(2)		
α (°)	90.73(2)		
β (°)	90.82(2)	Convergence criterion, ε	0.10
γ(°)	120.00(1)		

Note: Meaning of R_p, R_{wp}, R_{exp}, R_B, R_F, and ε values is described in Rodríguez-Carvajal (2000).

TABLE 7. Summary of selected data for čejkaite and the synthetic trigonal polymorph

	čejkaite	Synthetic trigonal phase (Císarová et al. 2001)
Formula	$Na_4UO_2(CO_3)_3$	$Na_4UO_2(CO_3)_3$
Crystal system	triclinic	trigonal
Space group	$P1$ or $P\bar{1}$	$P\bar{3}c1$
a (Å)	9.291(2)	9.3380(2)
b (Å)	9.292(2)	
c (Å)	12.895(2)	12.8170(3)
α (°)	90.73(2)	
β (°)	90.82(2)	
γ (°)	120.00(1)	
V (Å^3)	963.7(4)	967.89
Z	4	4
n_ε	–	1.531(2)*
n_ω	–	1.645(1)*
$\bar{n}$ (from indexes)	–	1.606
$\bar{n}$ (from Gladstone-Dale)	1.5825	1.5851
D_m (g/cm^3)	3.67	3.715 †
D_x (g/cm^3)	3.766	3.720
Central atom	Mean bond lengths	X-O (Å)
U1^u	1.827(9)	1.810(8)
U1^e	2.40(2)	2.40(2)
U1	2.3(3)	2.3(2)
U1a^u	1.827(6)	
U1a^e	2.40(2)	
U1a	2.3(2)	
Na1	2.4408(4)	2.440(3)
Na1a	2.4407(5)	
Na2	2.4931(6)	2.492(4)
Na3	2.4(1)	2.4(1)
Na3a	2.4(1)	
Na3b	2.4(1)	
Na3c	2.4(1)	
Na3d	2.4(1)	
Na3e	2.4(1)	
C1	1.28(3)	1.28(3)
C1a	1.29(3)	
C1b	1.29(3)	
C1c	1.29(3)	
C1d	1.29(3)	
C1e	1.29(3)	

Note: Subscripts "u" and "e" indicate mean bond lengths in UO_2O_6 bipyramids in uranyl and in equatorial plane of the polyhedron, respectively.
* Douglass 1956.
† This study.

structure data (the Bragg *R*-factor is 12.3%), calculated bond-valence sums (BVS) indicate fair agreement with that obtained from single-crystal data for the trigonal polymorph. Moreover, the departures of BVS from ideal values are mainly due to the highly irregular shape of the octahedrally coordinated U and pentagonally coordinated Na polyhedra. Similar departures have been observed for the trigonal polymorph whose structure was solved from single-crystal data (Císařová et al. 2001). As čejkaite recrystallizes to its trigonal polymorph only under hydrothermal conditions at temperatures higher than 100 °C, the probability of a natural occurrence of the trigonal polymorph is low.

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REFERENCES CITED

Anderson, A., Chieh, Ch., Irish, D.E., and Tong, J.P.K. (1980) An X-ray crystallographic, Raman and infrared spectral study of crystalline potassium uranyl carbonate, $K_4UO_2(CO_3)_3$. Canadian Journal of Chemistry, 58, 1651–1658.

Burns, P.C. (1999) The Crystal Chemistry of Uranium. In P.C. Burns and R. Finch, Eds., Uranium: Mineralogy, Geochemistry and the environment, 38, 23–90. Reviews in Mineralogy, Mineralogical Society of America, Washington, D.C.

Burns, P.C., Miller, M.L., and Ewing, R.C. (1996) U^{6+} minerals and inorganic phases: A comparison and hierarchy of crystal structures. Canadian Mineralogist, 34, 845–880.

Císařová, I., Skála, R., Ondrus, P., and Drábek, M. (2001) Trigonal $Na_4UO_2(CO_3)_3$. Acta Crystallographica, E57, i32–i34.

Čejka, J. (1969) To the chemistry of andersonite and thermal decomposition of dioxotricarbonatouranates. Coll Czechoslov Chem Commun, 34, 1635–1656.

——— (1999) Infrared spectroscopy and thermal analysis of the uranyl minerals. In P.C. Burns and R. Finch, Eds., Uranium: Mineralogy, Geochemistry and the environment, 38, 521–622. Reviews in Mineralogy, Mineralogical Society of America, Washington, D.C.

Douglass, R.M. (1956) Tetrasodium uranyl tricarbonate, $Na_4[UO_2(CO_3)_3]$. Analytical Chemistry, 28, 1635.

Finch, R. and Murakami, T. (1999) Systematic paragenesis of uranium minerals.In P.C. Burns and R. Finch, Eds., Uranium: Mineralogy, Geochemistry and the environment, 38, 91–179. Reviews in Mineralogy, Mineralogical Society of America, Washington, D.C.

Glebov, V.A. (1989) Stretching vibration frequencies and interatomic distances in uranyl compounds. In B.N. Laskorin and D.F. Myasoyedov, Eds., Uranium chemistry, 68–75. Nauka. Moscow. (in Russian).

Graziani, R., Bombieri, G., and Forsellini E. (1972) The crystal structure of $(NH_4)_4UO_2(CO_3)_3$. Dalton Transactions, Inorganic Chemistry, 1972, 2059–2061.

Hoppe, R. (1979) Effective coordination numbers (ECoN) and mean fictive ionic radii (MEFIR). Zeitschrift für Kristallographie, 150, 23–52.

Koglin, E., Schenk, H.J., and Schwochau, K. (1979) Vibration and low temperature optical spectra of the uranyl tricarbonato complex $[UO_2(CO_3)_3]^{4-}$. Spectrochimica Acta, 35A, 641–647.

Li, Y.I. and Burns, P.S. (2001b) The crystal structure of synthetic $K_3Na[UO_2(CO_3)_3](H_2O)$. Canadian Mineralogist, 39, 1035–1039.

Li, Y.I., Krivovichev, S.V., and Burns, P.S. (2001a) The crystal structure of $Na_4UO_2(CO_3)_3$ and its relationship to schröckingerite. Mineralogical Magazine, 65, 297–304.

Mandarino, J.A. (1979) The Gladstone-Dale relationship. Part III: Some general applications. Canadian Mineralogist, 17, 71–76.

Mereiter, K. (1986) The crystal structure of $Tl_4[UO_2(CO_3)_3]$. Acta Crystallographica, C42, 1682–1684.

Ondruš, P. (1993) ZDS—A computer program for analysis of X-ray powder diffraction patterns. Materials Science Forum, Vol. 133–136, pp. 297–300, EPDIC-2. Enschede.

Ondruš, P., Veselovsky, F., and Hlousek, J. (1997a) A review of mineral associations and paragenetic groups of secondary minerals of the Jáchymov (Joachimsthal) ore district. Journal of the Czech Geological Society, 42, 109–115.

Ondruš, P., Veselovsky, F., Hlousek, J., Skála, R., Vavrín, I., Fryda, J., Čejka, J., and Gabasová, A. (1997b) Secondary minerals of the Jáchymov (Joachimsthal) ore district. Journal of the Czech Geological Society, 42, 3–76.

Ondruš, P., Veselovsky, F., Skála, R., Císarová, I., Hlousek, J., Fryda, J., Vavrín, I., Cejka, J., and Gabašová, A. (1997c) New naturally occurring phases of secondary origin from Jáchymov (Joachimsthal). Journal of the Czech Geological Society, 42, 77–108.

Ondruš, P., Skála, R., Císarová, I., Veselovsky, F., Fryda, J., and Čejka, J. (2002) Description and crystal structure of vajdakite, $[(Mo^{+6}O_2)_2(H_2O)_2As^{+3}{}_2O_5].H_2O$—a new mineral from Jáchymov, Czech Republic. American Mineralogist, 87, 983–990.

Rieder, M. (1993) Program HOPPE for calculation of MEFIR, ECoN and mean (plus s.e.m.) from FIRs. Faculty of Science, Charles University, Prague, Czech Republic.

Rodríguez-Carvajal, J. (2000) FullProf.2k.—Rietveld, Profile Matching and Integrated Intensity Refinement of X-ray and/or Neutron Data. A computer program.

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