

Letter to editor

Crystal structure refinement of pseudojohannite, $\text{Cu}_3(\text{OH})_2[(\text{UO}_2)_4\text{O}_4(\text{SO}_4)_2](\text{H}_2\text{O})_{12}$, from the type locality – Jáchymov, Czech Republic

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The crystal structure of pseudojohannite from the type locality, Jáchymov (Western Bohemia, Czech Republic), was solved by charge-flipping method from single-crystal X-ray diffraction data and refined to an $R = 0.0385$ against 2072 unique observed reflections. Pseudojohannite from Jáchymov is triclinic, $P\bar{1}$, with $a = 8.6653(4)$, $b = 8.8499(5)$ Å, $c = 9.9908(6)$, $\alpha = 72.103(6)$, $\beta = 70.512(5)^\circ$, $\gamma = 76.070(5)^\circ$, $V = 679.12(7)$ Å³ and $Z = 1$. The structural formula derived from the refinement and bond-valence considerations is $\text{Cu}_3(\text{OH})_2[(\text{UO}_2)_4\text{O}_4(\text{SO}_4)_2](\text{H}_2\text{O})_{12}$, confirming previous structure determination on the material from Widowmaker mine, Utah, USA. Contrary to other members of the zippeite-group, the interstitial metal sites in pseudojohannite (populated by Cu^{2+}), are fully occupied and the structure tends to be fully ordered with no important departure from the ideal stoichiometry.

Keywords: pseudojohannite, uranyl sulphate, zippeite group, crystal structure, Jáchymov

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1. Introduction

Pseudojohannite is one of two known copper-bearing uranyl sulfates formed from oxidation–hydration weathering of uraninite in the presence of copper sulphide minerals as chalcopyrite or tennantite (Krivovichev and Plášil 2013; Plášil 2014). It was first described by Ondruš et al. (1997, 2003) as a new mineral from Jáchymov (St. Joachimsthal), Western Bohemia, Czech Republic. Originally it was reported to be triclinic, $\text{Cu}_5(\text{UO}_2)_6(\text{SO}_4)_3(\text{OH})_{16}(\text{H}_2\text{O})_{14}$, with $a = 13.754(2)$, $b = 9.866(1)$, $c = 8.595(2)$ Å, $\alpha = 103.84(2)^\circ$, $\beta = 90.12(2)^\circ$, $\gamma = 106.75(2)^\circ$, and $V = 1081.3(4)$ Å³. Brugger et al. (2006) concluded that pseudojohannite is a member of the zippeite group, based on the characteristic U:S ratio 2:1 (Burns 2005; Krivovichev and Plášil 2013), and they revised chemical formula of pseudojohannite accordingly to $\text{Cu}_{6.5}[(\text{UO}_2)_4\text{O}_4(\text{SO}_4)_2](\text{OH})_5(\text{H}_2\text{O})_{25}$. The final conclusion that pseudojohannite is a member of the zippeite-group of minerals was documented by the full crystal structure solution presented by Plášil et al. (2012) on the material from Widowmaker mine, White Canyon, Utah, USA. According to them, pseudojohannite is triclinic, $P\bar{1}$, with $a = 8.6744(4)$, $b = 8.8692(4)$, $c = 10.0090(5)$ Å, $\alpha = 72.105(4)^\circ$, $\beta = 70.544(4)^\circ$, $\gamma = 76.035(4)^\circ$, and $V = 682.61(5)$ Å³, and its chemical formula is $\text{Cu}_3(\text{OH})_2[(\text{UO}_2)_4\text{O}_4(\text{SO}_4)_2](\text{H}_2\text{O})_{12}$, $Z = 1$. Nevertheless, the structure of pseudojohannite from the

type locality, Jáchymov, has never been disclosed. In the paper of Plášil et al. (2012) the results of Rietveld refinement on the powder data for pseudojohannite are given; however, only positions of the uranium atoms could be refined from the data. Here we present a short report on the crystal structure refinement of pseudojohannite from the type locality, providing similar results as for pseudojohannite from USA, showing no discrepancies or inconsistencies. This suggests that these structures tend to be ordered, in contrast to other members of the zippeite group (see e.g., Burns et al. 2003).

2. Sample

The crystal of pseudojohannite investigated by single-crystal X-ray diffraction was recovered from the specimen originating from the Červená vein, Rovnost mine in Jáchymov, Czech Republic. The specimen was already studied in course of the detailed mineralogical study by Plášil et al. (2014a). The crystal aggregate was recovered from a rich specimen, of the size $6 \times 4 \times 1.5$ cm, representing a fragment of the ore-vein, containing U- and Cu- ore mineralization (uraninite, chalcopyrite, tennantite and chalcocite). Pseudojohannite forms well-developed crystals up to 0.2 mm across. They have a typical lens or half-lens shape, characteristic of the zippeite-group minerals (cf., Plášil et al. 2010, 2014a).

3. Single-crystal X-ray crystallography

A tiny plate-like greenish crystal of pseudojohannite, with dimensions $0.14 \times 0.05 \times 0.02$ mm, was selected under the optical stereomicroscope. The intensity data were collected using Oxford Diffraction Gemini single-crystal diffractometer equipped with an Atlas CCD detector and using monochromated MoK_α radiation from conventional sealed X-ray tube (55 kV, 45 mA), collimated with fiber-optics Mo-Enhance collimator. The unit cell was refined by a least-squares algorithm using the CrysAlis Pro Package (Agilent Technologies 2014) from 2818 reflec-

tions and provided triclinic unit cell with $a = 8.6653(4)$, $b = 8.8499(5)$ Å, $c = 9.9908(6)$, $\alpha = 72.103(6)$, $\beta = 70.512(5)^\circ$, $\gamma = 76.070(5)^\circ$, $V = 679.12(7)$ Å³ and $Z = 1$. From the total of 4779 measured diffractions, 2550 were independent and 2072 classified as observed [$I_{\text{obs}} > 3\sigma(I)$]. Data were corrected for background, Lorentz and polarization effects, and an analytical correction for absorption was applied (Clark and Reid 1995), leading to R_{int} of the merged data equal to 0.042.

Crystal structure was solved from X-ray diffraction data by the charge-flipping algorithm (Palatinus and Chapuis 2007), independently from the previous structure solution (Plášil et al. 2012). Obtained model was refined by the full-matrix least-squares of the Jana2006 program (Petříček et al. 2006, 2014). All atoms were found from the structure solution, except of several O sites, belonging to the H₂O molecules in the interlayer of the structure; those atoms were localized later by the difference-Fourier syntheses. Careful inspection of the diffraction frames revealed presence of reflections that could not be indexed based on the single domain; therefore, second crystal-domain was introduced into the refinement. Their relation is expressed by the twin-matrix given in the Tab. 1. In total, 565 reflections were discarded from the fit, since they were detected as fully or partially overlapping. The final refinement including all atoms refined with anisotropic displacement parameters converged quickly to an $R_1 = 0.0385$, $wR_2 = 0.0818$ with a GOF = 1.30 for 2072 unique observed reflections. No cell of higher symmetry was found using LePage and ADDSYM (Spek 2003, 2009). Details of the data collection and miscellaneous crystallographic and structure refinement parameters are listed in Tab. 1. Final atom coordinates and their displacement parameters are given in Tab. 2. The CIF file, containing

Tab. 1 Crystallographic data and refinement details for pseudojohannite from Jáchymov

Crystal data	
Structure formula	$\text{U}_4\text{Cu}_3\text{S}_2\text{O}_{34}\text{H}_{26}$
Crystal system	triclinic
Space group	$P\bar{1}$
Unit-cell parameters: a, b, c [Å]	8.6653(4), 8.8499(5), 9.9908(6)
α, β, γ [°]	72.103(6), 70.512(5), 76.070(5)
Unit-cell volume [Å ³]	679.12(7)
Z	1
Calculated density [g/cm ³]	4.345
Crystal size [mm]	$0.14 \times 0.05 \times 0.02$
F_{000}	759
Data collection	
Diffractometer	Oxford Diffraction Gemini with Atlas detector
Temperature [K]	293
Radiation, wavelength [Å]	MoK_α , 0.71073 (50 kV, 30 mA)
θ range for data collection [°]	2.87–29.51
Limiting Miller indices	$h = -11 \rightarrow 8, k = -11 \rightarrow 10, l = -12 \rightarrow 9$
Axis, frame width (°), time per frame (s)	$\omega, 1, 350$
Total reflections collected	4779
Unique reflections	2550
Unique observed reflections, criterion	2072, [$I > 3\sigma(I)$]
Absorption coefficient [mm ⁻¹], type	26.34; analytical
$T_{\text{min}}/T_{\text{max}}$	0.514/1
R_{int}	0.042
Structure refinement by Jana2006	
Number of refined parameters, restraints, constraints	198, 0, 0
R, wR (obs)	0.0385, 0.0818
R, wR (all)	0.0476, 0.0865
GOF obs/all	1.30, 1.23
Weighting scheme, weights	$\sigma, w = 1/(\sigma^2(I) + 0.0004F)$
Extinction (Gaussian, Becker and Coppens 1974)	210(30)
Largest diffraction peak and hole (e ⁻ /Å ³)	1.71, -2.81
Twin matrix	$\begin{pmatrix} -1 & 0 & -0.6357 \\ 0 & -1 & -0.5454 \\ 0 & 0 & 1 \end{pmatrix}$
Twin fractions	0.889(5)/0.111(5)

also a block with the reflections, is deposited at the Journal's web page www.jgeosci.org.

4. Results and discussion

The structure of pseudojohannite was described in detail by the previous crystal structure study, including a detailed discussion on the stereochemistry of the interstitial complex and detailed bond-valence considerations (Plášil et al. 2012). The structure of pseudojohannite is layered, consisting of uranyl oxo-sulfate sheets, of the composition $[(\text{UO}_2)_4\text{O}_4(\text{SO}_4)_2]^{4+}$, and alternating interlayer complex $[\text{Cu}_3(\text{OH})_2(\text{H}_2\text{O})_{12}]^{4+}$. These sheets are stacked perpendicular to the c direction. The stacking/interlayer separation of 9.99 Å (which is equivalent to the c parameter), is similar to the interlayer distance e.g. in marécottite (9.47 Å; Brugger et al. 2003); such a distance is typical of structures where interstitial complex is not bonded directly to the adjacent structural layers and is linked by hydrogen bonds only. The topology of the structural sheets found in pseudojohannite is characteristic of the zippeite-group of minerals (Burns 2005; Krivovichev and Plášil 2013). In particular, sheets of the same composition as in pseudojohannite were found e.g., in magnesiozippeite (Plášil et al. 2013), in isostructural synthetic zippeites that contain divalent metal or alkaline-earth metal cations (Burns et al. 2003) and in rabejacite (Plášil et al. 2014b).

The investigated pseudojohannite from Jáchymov (Czech Republic) is more or less identical to the previously studied crystal from the Widowmaker mine, White Canyon (Utah, USA) (Plášil et al. 2012). The two structures can be compared using measures of similarity calculated e.g., by program COMPSTRU (Tasci et al. 2012): degree of lattice distortion (Capillas et al. 2007) $S = 0.001$, arithmetic mean of the distances of paired (symmetrically equal) atoms in compared structures (Orobengoa et al. 2009) $d_{\text{av}} = 0.0152$ Å or the overall measure of similarity (Bergerhoff et al. 1999) $\Delta = 0.004$. The largest deviation in the distances of equivalent atoms (0.0436 Å) was found in case of one O atom site, O9. This is, surprisingly, the oxygen atom shared between two uranyl pentagonal bipyramids. Noteworthy, exactly this atom is protonated in case of both synthetic and natural zippeite (Burns et al. 2003; Plášil et al. 2011a), marécottite (Brugger et al. 2003)

Tab. 2 Atom coordinates and displacement parameters for the crystal structure of pseudojohannite from Jáchymov

Atom	x/a	y/b	z/c	U_{eq}	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
U1	0.09002(5)	0.67634(5)	0.47191(5)	0.01312(18)	0.0094(2)	0.0117(2)	0.0187(3)	-0.00079(16)	-0.00470(16)	-0.00427(18)
U2	0.42813(5)	0.34282(5)	0.46461(5)	0.01266(18)	0.0099(2)	0.0117(2)	0.0170(3)	-0.00097(15)	-0.00450(16)	-0.00413(18)
Cu1	0.5	0	0	0.0196(8)	0.0218(11)	0.0199(12)	0.0193(11)	-0.0062(8)	-0.0087(8)	-0.0023(9)
Cu2	-0.00721(17)	0.1679(2)	-0.00697(18)	0.0228(6)	0.0200(8)	0.0224(9)	0.0241(9)	-0.0031(6)	-0.0014(6)	-0.0085(7)
S1	0.2504(3)	-0.0039(4)	0.5035(3)	0.0146(11)	0.0079(14)	0.0148(15)	0.0217(16)	0.0003(10)	-0.0060(11)	-0.0051(13)
O1	0.5708(10)	0.0789(11)	0.1290(9)	0.024(4)	0.030(5)	0.028(6)	0.020(5)	-0.010(4)	-0.010(4)	-0.009(4)
O2	0.1179(9)	0.0142(11)	-0.1191(9)	0.021(3)	0.020(4)	0.024(5)	0.018(5)	-0.006(3)	-0.001(3)	-0.006(4)
O3	0.4798(9)	0.4238(10)	0.2700(8)	0.017(3)	0.020(4)	0.009(4)	0.013(4)	-0.003(3)	0.000(3)	0.004(3)
O4	0.2050(10)	0.1179(12)	0.1152(9)	0.026(4)	0.033(5)	0.027(6)	0.017(5)	-0.003(4)	-0.009(4)	-0.006(4)
O5	0.3814(9)	0.2372(10)	0.6566(9)	0.018(3)	0.021(4)	0.018(5)	0.014(4)	-0.005(3)	-0.010(3)	0.004(4)
O6	0.4759(9)	-0.2106(11)	0.1359(9)	0.021(4)	0.020(5)	0.020(5)	0.019(5)	-0.005(4)	-0.002(3)	-0.001(4)
O7	0.3140(12)	0.4205(14)	0.0613(12)	0.044(5)	0.054(7)	0.046(8)	0.037(6)	-0.004(5)	-0.029(5)	-0.004(6)
O8	0.1473(9)	0.4095(10)	0.5026(10)	0.020(4)	0.012(4)	0.014(5)	0.034(5)	-0.002(3)	-0.002(3)	-0.010(4)
O9	0.6463(8)	0.4102(10)	0.4982(9)	0.013(3)	0.010(4)	0.012(4)	0.023(5)	0.003(3)	-0.013(3)	-0.008(3)
O10	-0.1609(11)	0.3209(12)	0.1016(10)	0.034(4)	0.042(6)	0.028(6)	0.023(5)	0.005(4)	0.004(4)	-0.017(5)
O11	0.1616(9)	0.7034(11)	0.2748(8)	0.019(3)	0.018(4)	0.027(5)	0.012(4)	0.001(3)	-0.004(3)	-0.008(4)
O12	0.2052(9)	-0.0737(10)	0.4083(9)	0.019(3)	0.022(5)	0.016(5)	0.021(5)	-0.002(3)	-0.010(3)	-0.005(4)
O13	0.3331(9)	-0.1304(11)	0.6016(9)	0.023(4)	0.020(5)	0.026(5)	0.024(5)	0.008(4)	-0.010(3)	-0.014(4)
O14	0.3573(9)	0.1167(10)	0.4077(9)	0.018(3)	0.018(4)	0.016(5)	0.022(5)	-0.003(3)	0.002(3)	-0.014(4)
O15	0.1003(10)	0.3496(12)	-0.1466(10)	0.030(4)	0.028(5)	0.026(6)	0.029(6)	-0.007(4)	0.001(4)	-0.006(4)
O16	0.0167(9)	0.6718(11)	0.6628(9)	0.023(4)	0.018(4)	0.026(5)	0.026(5)	-0.002(4)	-0.005(3)	-0.009(4)
O17	0.1035(9)	0.0748(11)	0.5952(9)	0.021(4)	0.019(5)	0.019(5)	0.023(5)	0.002(3)	-0.006(3)	-0.006(4)

and sejkoraite-(Y) (Plášil et al. 2011b). According to both data sets, the Cu^{2+} cations are perfectly periodically distributed over the two fully-occupied Cu-sites in interlayer without any sign of disorder. Noteworthy, such a perfect match, in terms of isostructurality and behavior of the crystals during diffraction experiments, is seldom encountered for zippeite-group minerals and synthetic compounds. There are neither diffuse scattering nor any streaks on the diffraction frames that might be connected to the disorder of the cations in interlayer.

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References

- AGILENT TECHNOLOGIES (2014) CrysAlis RED, CCD data reduction GUI. Agilent Technologies Ltd., Oxford, UK
- BECKER PJ, COPPENS P (1974) Extinction within the limit of validity of the Darwin transfer equations. I. General formalism for primary and secondary extinction and their applications to spherical crystals. *Acta Cryst A* 30: 129–147
- BERGERHOFF G, BERNDT M, BRANDENBURG K, DEGEN T (1999) Concerning inorganic crystal structure types. *Acta Cryst B* 55: 147–156
- BRUGGER J, MEISSER N, BURNS PC (2003) Contribution to the mineralogy of acid drainage of uranium minerals: marécottite and the zippeite-group. *Amer Miner* 88: 676–685
- BRUGGER J, WALLWORK KS, MEISSER N, PRING A, ONDRUŠ P, ČEJKA J (2006) Pseudojohannite from Jáchymov, Musonoï, and La Creusaz: a new member of the zippeite-group. *Amer Miner* 91: 929–936
- BURNS PC (2005) U^{6+} minerals and inorganic compounds: insights into an expanded structural hierarchy of crystal structures. *Canad Mineral* 43: 1839–1894
- BURNS PC, DEELY K, HAYDEN L (2003) The crystal chemistry of the zippeite group. *Canad Mineral* 41: 687–706
- CAPILLAS C, PEREZ-MATO JM, AROYO MI (2007) Maximal symmetry transition paths for reconstructive phase transitions. *J Phys: Condens Mat* 19: 275203
- CLARK RC, REID JS (1995) The analytical calculation of absorption in multifaceted crystals. *Acta Cryst A* 51: 887–897
- KRIVOVICHEV SV, PLÁŠIL J (2013) Mineralogy and crystallography of uranium. In: BURNS PC, SIGMON GE (eds) *Uranium: From Cradle to Grave*. Mineralogical Association of Canada Short Courses 43: pp 15–119
- ONDRUŠ P, VESELOVSKÝ F, SKÁLA R, CISAŘOVÁ I, HLOUŠEK J, FRÝDA J, VAVŘIN I, ČEJKA J, GABAŠOVÁ A (1997) New naturally occurring phases of secondary origin from Jáchymov (Joachimsthal). *J Czech Geol Soc* 42: 77–107
- ONDRUŠ P, VESELOVSKÝ F, GABAŠOVÁ A, HLOUŠEK J, ŠREIN V (2003) Supplement to secondary and rock-forming minerals of the Jáchymov ore district. *J Czech Geol Soc* 48: 149–155
- OROBENGOA D, CAPILLAS C, AROYO MI, PEREZ-MATO JM (2009) AMPLIMODES: symmetry-mode analysis on the Bilbao Crystallographic Server. *J Appl Cryst* A42: 820–833
- PALATINUS L, CHAPUIS G (2007) Superflip – a computer program for the solution of crystal structures by charge flipping in arbitrary dimensions. *J Appl Cryst* 40: 451–456
- PETŘÍČEK V, DUŠEK M, PALATINUS L (2006) Jana2006. The crystallographic computing system. Institute of Physics, Prague, Czech Republic
- PETŘÍČEK V, DUŠEK M, PALATINUS L (2014) Crystallographic Computing System Jana 2006: general features. *Z Kristall* 229: 345–352
- PLÁŠIL J (2014) Oxidation–hydration weathering of uraninite: the current state-of-knowledge. *J Geosci* 59: 99–114
- PLÁŠIL J, BUIXADERAS E, ČEJKA J, SEJKORA J, JEHLIČKA J, NOVÁK M (2010) Raman spectroscopic study of the uranyl sulphate mineral zippeite: low wavenumber and U–O stretching regions. *Anal Bioanal Chem* 397: 2703–2715
- PLÁŠIL J, MILLS SJ, FEJFAROVÁ K, DUŠEK M, NOVÁK M, ŠKODA R, ČEJKA J, SEJKORA J (2011a) The crystal structure of natural zippeite $\text{K}_{1.85}\text{H}^{+}_{0.15}[(\text{UO}_2)_4\text{O}_2(\text{SO}_4)_2(\text{OH})_2](\text{H}_2\text{O})_4$, from Jáchymov, Czech Republic. *Canad Mineral* 49: 1089–1103
- PLÁŠIL J, DUŠEK M, NOVÁK M, ČEJKA J, CISAŘOVÁ I, ŠKODA R (2011b) Sejkoraite-(Y), a new member of the zippeite group containing trivalent cations from Jáchymov (St. Joachimsthal), Czech Republic: description and crystal structure refinement. *Amer Miner* 96: 983–991
- PLÁŠIL J, FEJFAROVÁ K, WALLWORK KS, DUŠEK M, ŠKODA R, SEJKORA J, ČEJKA J, VESELOVSKÝ F, HLOUŠEK J, MEISSER N, BRUGGER J (2012) Crystal structure of pseudojohannite, with a revised formula, $\text{Cu}_3(\text{OH})_2[(\text{UO}_2)_4\text{O}_4(\text{SO}_4)_2](\text{H}_2\text{O})_{12}$. *Amer Miner* 97: 1796–1803
- PLÁŠIL J, FEJFAROVÁ K, ŠKODA R, DUŠEK M, MARTY J, ČEJKA J (2013) The crystal structure of magnesiozippeite, $\text{Mg}[(\text{UO}_2)_2\text{O}_2(\text{SO}_4)](\text{H}_2\text{O})_{3.5}$, from East Saddle Mine, San Juan County, Utah (U.S.A.). *Mineral Petrol* 107: 211–219
- PLÁŠIL J, SEJKORA J, ŠKODA R, ŠKÁCHA P (2014a) The recent weathering of uraninite from the Červená vein, Jáchymov (Czech Republic): a fingerprint of the primary minerals

- geochemistry in the alteration association. *J Geosci* 59: 223–253
- PLÁŠIL J, DUŠEK M, ČEJKA J, SEJKORA J (2014b) The crystal structure of rabejacite, the Ca²⁺-dominant member of the zippeite group. *Mineral Mag* 57: 1249–1263
- SPEK AL (2003) Single-crystal structure validation with the program PLATON. *J Appl Cryst* 36: 7–13
- SPEK AL (2009) Structure validation in chemical crystallography. *Acta Cryst D* 65: 148–155
- TASCI ES, DE LA FLOR G, OROBENGOA D, CAPILLAS C, PÉREZ-MATO JM, AROYO MI (2012) An introduction to the tools hosted in the Bilbao Crystallographic Server. *EPJ Web of Conferences*, 22, 00009, DOI:10.1051/epjconf/20122200009