

Original paper

New data for metakirchheimerite from Jáchymov (St. Joachimsthal), Czech Republic

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Metakirchheimerite was found only on a few samples from the Jan Evangelista vein at the “Adit level” of the Svornost shaft, Jáchymov (St. Joachimsthal) ore district, Krušné Hory/Erzgebirge Mountains, Czech Republic. It forms rare crystalline aggregates consisting of fine tabular crystals reaching 0.1 mm in size, which are very brittle, having light pink to light orange colour, with a high vitreous lustre. Metakirchheimerite crystalline aggregates occur on carbonate gangue with disseminated primary minerals: arsenopyrite, uraninite and skutterudite. Studied metakirchheimerite is a (sub-)recent alteration product of the primary minerals, connected to the old open mine adit environment. According to electron microprobe analyses, the empirical formula of metakirchheimerite can be expressed, based on As + P = 2 *apfu*, as: $(\text{Co}_{0.53}\text{Mg}_{0.25}\text{Ni}_{0.08}\text{Zn}_{0.07}\text{Fe}_{0.05}\text{Ca}_{0.03})_{\Sigma 1.01}(\text{UO}_2)_{2.07}[(\text{AsO}_4)_{1.99}(\text{PO}_4)_{0.01}]_{\Sigma 2.00} \cdot 8\text{H}_2\text{O}$. Metakirchheimerite from Jáchymov exhibits an extensive cationic substitution trend of the metanováčekite component. The X-ray diffraction pattern of metakirchheimerite is consistent with a triclinic symmetry inferred from the single-crystal study of the synthetic metakirchheimerite analogue. Refined unit-cell parameters for the triclinic space group *P*-1 are *a* 7.210(4) Å, *b* 9.771(6) Å, *c* 13.252(9) Å, α 75.39(4)°, β 83.94(6)°, γ 81.88(6)° with unit-cell volume *V* 892(1) Å³. Both infrared and Raman spectra of metakirchheimerite exhibited stretching and bending vibrations of (UO₂)²⁺, (AsO₄)³⁻, (PO₄)³⁻ and H₂O groups. The vibration bands of all these units were tentatively assigned. The U–O bond lengths in uranyl and O–H...O hydrogen bond lengths, which were inferred from the spectra, are consistent with published crystal structure data for a synthetic analogue of metakirchheimerite.

Keywords: metakirchheimerite, X-ray powder data, chemical composition, vibration spectroscopy, uranyl bond lengths, hydrogen bond lengths

Received: 5 October 2009; accepted 18 December 2009; handling editor: M. Novák

The online version of this article (doi: 10.3190/jgeosci.057) contains supplementary electronic material.

1. Introduction

The importance of understanding uranium mineralogy and chemistry is closely connected with the broad issue of spent nuclear fuel (“SNF”) alteration (Finch and Ewing 1992; Wronkiewicz et al. 1992, 1996; Finn et al. 1996; Murakami et al. 1997; Finch et al. 1999; Fayek et al. 2000; Shueneman et al. 2003; Procházka 2007; Procházka et al. 2009), waste management and environmental issues (e.g. Catalano et al. 2004, 2006). Hydrated uranyl arsenates of divalent transition metals are more or less abundant minerals of the secondary origin in the supergene zones of most uranium deposits (Finch and Murakami 1999). A group of hydrated uranyl arsenates and phosphates, with autunite-type sheet containing divalent cations in their interlayer, is represented by a general formula $^{[6]}M^{2+}(\text{UO}_2)_2(\text{TO}_4)_2 \cdot n\text{H}_2\text{O}$ (*T* is P or As), where *n* is 12, 10 and 8 most frequently. Divalent cations including

Co, Ni, Mg, Fe, Mn and Zn occupy six fold-coordinated *M*²⁺ sites (Locock et al. 2004; Locock 2007a, b).

This paper presents new mineralogical data on a rare hydrated cobalt uranyl arsenate – metakirchheimerite, found recently in Jáchymov (St. Joachimsthal), Czech Republic. No recent and detailed data for metakirchheimerite have been published on natural specimens since Walenta’s studies (Walenta 1958, 1964).

2. Previous studies

Metakirchheimerite was described as a new mineral by Walenta (1958) from the dump of the Sophia shaft in Wittichen, Baden, Germany. On the type locality metakirchheimerite forms coatings of tetragonal tabular crystals coming in association with metakahlerite, nováčekite, metaheinrichite and erythrite on weathered uraninite.

These coatings have light pink colour, single crystals are green-yellow to colourless. Metakirchheimerite is non-pleochroic, with pearly lustre on cleavage planes; cleavage is excellent along (001). According to Walenta (1958), metakirchheimerite is optically uniaxial or biaxial, negative, with ω 1.644(2), ε 1.617(2) and $2V$ of 0–20°. The chemical analyses proved Co, U and As as the main constituents of metakirchheimerite, accompanied by minor Fe and traces of Ni. Walenta (1958) proposed the ideal formula $\text{Co}(\text{UO})_2(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$, and assigned metakirchheimerite to metatorbernite group. The mineral is named to honour German geologist and palaeontologist Franz Waldemar Kirchheimer (1917–1984), an author of an important uranium monography (Kirchheimer 1963). Walenta (1964) published powder diffraction data for natural metakirchheimerite and for a synthetic dodecahydrate phase “kirchheimerite” – not approved as (a valid) mineral. Weight loss obtained for metakirchheimerite from thermal analysis corresponds to the sum of 15 wt. %, and the content of 8.59 moles H_2O in its crystal structure. The DTA curve shows endotherms at 115, 195, 300 and 1005 °C, and slight exotherms at > 620 °C. Regarding the powder X-ray diffraction, Walenta (1964) mentioned problem with indexing the powder pattern. He stated that this problem could be solved after doubling the c dimension of the unit-cell and correction of the a parameter. Since Walenta’s times, further scientific papers were based on the study of synthetic metakirchheimerite analogues. Nabar and Iyer (1977) reported preparation of octahydrates of zinc, nickel and cobalt uranylarsenates and their physico-chemical properties. Based on systematic absences in powder diffraction patterns, they assigned synthetic metakirchheimerite to the space group $P4_2/m$, with unit-cell parameters a 6.98(2) Å and c 16.93(2) Å, the unit-cell volume V 825 Å³ and density of 4.042 g · cm⁻³ (measured) and 4.111 g · cm⁻³ (calculated). Vochten and Goeminne (1984) published the synthesis, crystallographic data, solubility products and electrokinetic properties of synthetic metazeunerite, metakirchheimerite and, by that time unknown in natural occurrence, uranylarsenate of nickel (corresponding to new mineral IMA-2008-50 – metarauchite, Plášil et al. 2008; Plášil 2009). Vochten and Goeminne (1984) described synthetic metakirchheimerite as heptahydrate, which is in contrary both to the results of Walenta (1964) and to the currently used definition. Based on X-ray powder diffraction data, they reported that assignment of hkl indices is not reliable, if it is based of unit-cell parameters given by Walenta (1964). Moreover, none of the three published powder diffraction patterns is consistent, differing namely in number of diffractions and intensities (Walenta 1964; Vochten and Goeminne 1984; Nabar and Iyer 1977). Based on the results of thermal analysis, Vochten and Goeminne (1984) described thermal dehydration of the

synthetic metakirchheimerite in a following way: phase containing 7 H_2O → (45 °C) phase with 6 H_2O → (122 °C) phase with 2.5 H_2O → (275 °C) anhydrous phase. The authors did not assign the vibration bands for the spectra of the individual phases and confined themselves to the statement that vibrational properties of hydrated Ni and Co uranyl arsenates are practically identical (Vochten and Goeminne 1984). Ondruš et al. (2003c) published a short notice about metakirchheimerite from the Jan Evangelista vein in the Jáchymov ore district, without any further details.

Locock et al. (2004) reported solved crystal structure for a synthetic analogue of metakirchheimerite (named as “CoUAs8”) and also for synthetic dodecahydrate, corresponding to up to now species with doubtful status, “kirchheimerite”. In the asymmetric part of the synthetic metakirchheimerite unit-cell, two structurally non-equivalents U atoms, two non-equivalent As atoms, a single Co atom, and 20 O atoms are present. The crystal structure (Fig. 1) consists of the uranyl tetragonal bipyramids (UO_2O_4) linked by arsenate tetrahedra along (011), resulting in sheets of the autunite topology. Cobalt-based octahedra in the interlayer are formed by five H_2O groups and one shared uranyl-apical oxygen atom that links the octahedron directly to the structural sheets. In addition, three non-equivalent H_2O molecules are located in the interlayer, held only by hydrogen bonding.

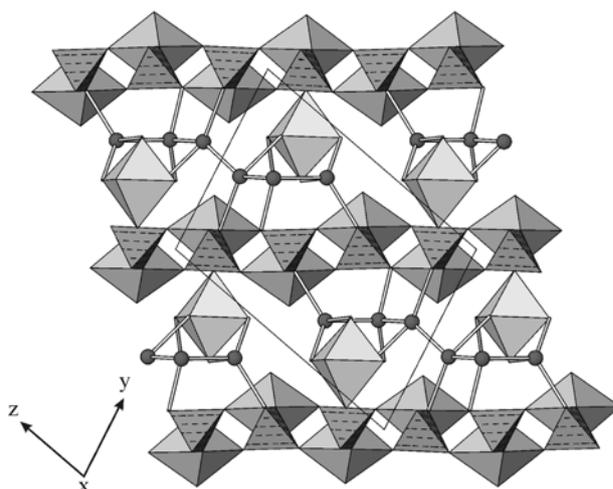


Fig. 1 The crystal structure of synthetic metakirchheimerite – “CoUAs8” (Locock et al. 2004) in projection along [100]. The uranyl arsenate sheets are parallel to (011). Uranyl tetragonal bipyramids are grey, arsenate tetrahedra are dark grey and stippled, cobalt-based octahedra are light-grey and groups of molecular water are dark grey spheres. Donor–acceptor (O...O) distances (<3.0 Å) corresponding to probable hydrogen bonds are shown as rods (Locock et al. 2004, the picture courtesy of Andrew Locock).

3. Occurrence

Samples containing the later identified metakirchheimerite originate from the Jan Evangelista (Johannes Evangelist) vein at the “Adit level” of the Svornost shaft, the Jáchymov ore district, Krušné Hory Mts., Bohemia, Czech Republic. The Jan Evangelista vein is one of the most important in the Svornost mine-area, carrying both Ag–As–Bi–Co–Ni and U mineralization, which were intensively mined since 16th till 20th century. Detailed geological settings and characteristics of the veins and mineralization were described mainly by Ondruš et al. (2003a–d).

Two samples, represented only by fragments approximately 1×1×1.5 cm in size, consist of the carbonate gangue (dominantly calcite and minor dolomite) with disseminated small grains of primary mineralization, represented mainly by skutterudite, uraninite and arsenopyrite. The surfaces of these fragments are coated by small crystals and crystal aggregates of metakirchheimerite



Fig. 2 Aggregates of metakirchheimerite on a surface of altered gangue from Jáchymov. Width of photograph is 4 mm. Photo by J. Sejkora (Nikon SMZ 1500).

(Fig. 2). The aggregates are up to 2 mm long, consisting of fine tabular crystals, maximally up to 0.1 mm (Fig. 3). The crystals are of light pink to grey-pink colour, with a pearly lustre. Crystals are very brittle with excellent cleavage, corresponding with pinacoid (011) (Fig. 4).

4. Results

4.1. X-ray powder diffraction

A hand-picked sample of metakirchheimerite was prepared for the X-ray powder diffraction experiment using the continuous mode of the PANalytical X'Pert Pro

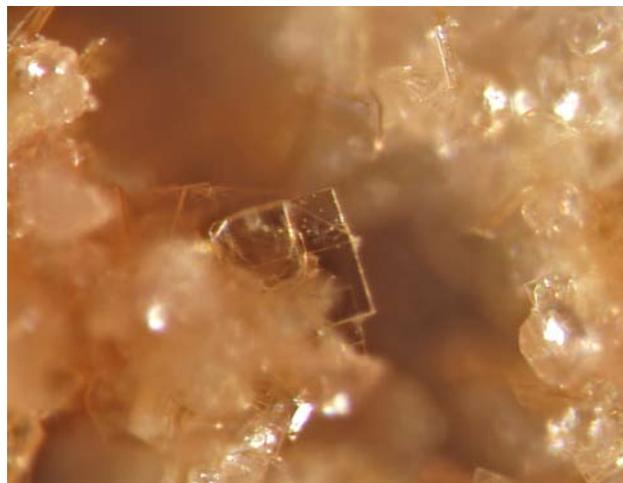


Fig. 3 Detail of thin tabular, translucent crystal of metakirchheimerite. Width of photograph is 0.1 mm. Photo by J. Sejkora (Nikon SMZ 1500).

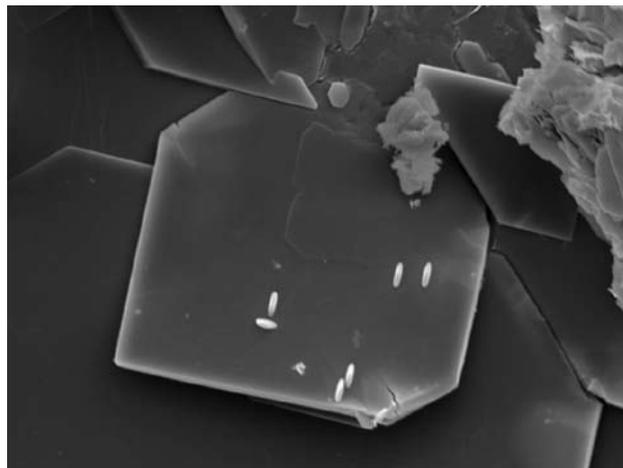


Fig. 4 Detail of metakirchheimerite crystal morphology showing dominating face (011). Other crystal faces suggest symmetry to be lower than tetragonal. Small aggregates on the surface of the crystal are probably scorodite crystals (according to EDS). Width of secondary electron (SE) image is 40 μm. Photo by J. Plášil (JEOL JSM 6380).

powder diffractometer operating at 40 kV and 30 mA, equipped with the X'Celerator detector and the secondary graphite monochromator. The powder diffraction pattern obtained with the Bragg–Bretano geometry exhibited effects of a strong preferred orientation due to the excellent (011) cleavage of metakirchheimerite. This effect was particularly notable as high intensities of the diffraction maxima of the type $0kl$, whereas profiles of other diffractions had a low intensity and were poorly defined. To avoid these problems, experiment with the Debye–Scherrer geometry was undertaken. The effects of the preferred orientation were nearly eliminated, but the chart is characterised by a lower definition of diffraction profiles,

Tab. 1 Powder diffraction patterns for metakirchheimerite from Jáchymov

Calculated from the crystal structure of "CoUAs8"					Jáchymov ¹			Jáchymov ²			Walenta (1964)	
I_{calc}	h	k	l	d_{calc}	I_{obs}	d_{obs}	d_{calc}	I_{obs}	d_{obs}	d_{calc}	I_{obs}	d_{obs}
2	0	1	0	9.39								
100	0	1	1	8.61	100	8.66	8.62	100	8.61	8.61	10	8.75
1	0	-1	1	6.83								
1	1	0	1	6.40								
2	0	0	2	6.39								
1	-1	0	1	6.03								
1	0	1	2	5.99								
5	1	1	1	5.97								
1	1	-1	0	5.35								
12	-1	1	1	5.09								
16	-1	-1	1	5.06	12	5.07	5.05				6	5.08
12	1	0	2	4.93	9	4.95	4.94					
8	1	-1	1	4.80								
17	0	2	0	4.69	9	4.76	4.70				3	4.69
4	-1	0	2	4.59								
8	0	2	2	4.31	15	4.31	4.31	8	4.31	4.31	6	4.32
18	0	1	3	4.28	17	4.29	4.29	2	4.28	4.28		
18	1	2	2	3.98	11	3.97	3.98	<1	3.99	3.98	2	3.99
1	1	-1	2	3.95								
26	0	-1	3	3.57	23	3.57	3.57	<1	3.57	3.57	9	3.58
24	2	0	0	3.55								
20	2	1	1	3.49	14	3.49	3.49					
13	-1	2	2	3.44	10	3.46	3.45	<1	3.44	3.44	6	3.44
16	0	-2	2	3.41	11	3.42	3.41	<1	3.42	3.42		
9	0	3	1	3.22				<1	3.23	3.23	2	3.23
10	0	0	4	3.20	7	3.19	3.20					
7	-2	1	1	3.11	6	3.12	3.12				<1	3.12
3	2	2	0	3.02								
4	1	-2	2	3.02	11	3.02	3.02				5	3.01
3	-2	0	2	3.02								
6	0	2	4	2.995	3	2.997	2.999	<1	2.993	2.994		
2	1	0	4	2.994								
5	2	2	2	2.985								
2	2	1	3	2.922								
3	0	-3	1	2.885								
1	-2	-1	2	2.864								
2	-1	0	4	2.840								
4	1	3	3	2.824				<1	2.824	2.827		
3	1	3	-1	2.769								
3	2	-2	0	2.677	<1	2.684	2.685					
1	0	1	5	2.631								
1	-1	2	4	2.627								
2	1	-3	1	2.586	5	2.583	2.590	<1	2.583	2.586		
2	2	3	1	2.580								
2	-2	1	3	2.577				<1	2.576	2.577		
2	1	1	5	2.558								
1	-2	2	2	2.546								
8	2	-1	3	2.533	8	2.539	2.541	<1	2.534	2.532	5	2.53
7	-2	-2	2	2.528	5	2.518	2.524					
2	-1	3	3	2.524								
6	-2	-1	3	2.503								
2	2	2	4	2.473								
5	2	0	4	2.463	3	2.474	2.470					
2	2	-2	2	2.399								
2	-1	1	5	2.385	3	2.384	2.386					

Calculated from the crystal structure of "CoUAs8"*					Jáchymov ¹			Jáchymov ²			Walenta (1964)	
I_{calc}	h	k	l	d_{calc}	I_{obs}	d_{obs}	d_{calc}	I_{obs}	d_{obs}	d_{calc}	I_{obs}	d_{obs}
2	-2	-3	1	2.355								
2	0	-3	3	2.276								
3	-3	-1	1	2.274	7	2.275	2.274				5	2.27
4	3	0	2	2.273								
4	-1	-2	4	2.272								
2	1	-2	4	2.258								
2	1	3	5	2.256								
2	1	-1	5	2.236								
3	3	2	2	2.231	2	2.235	2.234					
2	3	2	0	2.227								
3	-3	1	1	2.194	1	2.199	2.198					
3	-1	4	2	2.172								
1	1	4	4	2.159	2	2.163	2.161					
4	0	4	4	2.153	10	2.152	2.155	2	2.155	2.154	6	2.15
2	1	-4	0	2.151								
2	2	4	2	2.144	1	2.143	2.143	1	2.148	2.148		
2	-2	2	4	2.142								
3	0	0	6	2.130								
2	1	2	6	2.127								
3	-1	3	5	2.066				<1	2.067	2.066	1	2.05
3	0	-4	2	2.051								
2	3	3	3	1.9901								
1	-1	4	4	1.9738				<1	1.9732	1.9736		
2	-3	2	2	1.9464								
3	1	5	3	1.9046	<1	1.9073	1.9053	<1	1.9075	1.9075		
2	0	1	7	1.8781								
2	3	1	5	1.8615								
2	-2	4	2	1.8453								
2	1	4	6	1.8193				<1	1.8190	1.8203		
4	4	1	1	1.7970	4	1.7990	1.7996					
3	0	-2	6	1.7859	2	1.7852	1.7859				4	1.787
3	0	-3	5	1.7822								
2	4	0	0	1.7754								
2	-2	0	6	1.7724								
1	0	3	7	1.7718	1	1.7748	1.7743	<1	1.7617	1.7624		
2	-1	5	3	1.7621								
1	2	1	7	1.7311							<1	1.726
2	-1	4	6	1.6894	2	1.6904	1.6918	<1	1.6896	1.6890	2	1.687
1	4	3	1	1.6602	<1	1.6596	1.6602					
1	1	-4	4	1.6404	<1	1.6412	1.6419					
2	-4	-2	2	1.6101	3	1.6089	1.6090					
2	-2	-3	5	1.6067	4	1.6047	1.6039				4	1.602
2	2	-2	6	1.6031								
2	4	0	4	1.6005								
2	4	-1	3	1.5975								
1	1	6	4	1.5767	2	1.5771	1.5776				2	1.565
2	1	6	0	1.5695								
2	-3	4	2	1.5686								
2	3	4	6	1.5571								
1	1	5	7	1.5166	<1	1.4915	1.4915				<1	1.516
1	-1	3	9	1.3665	2	1.3687	1.3679					

¹ Debye–Scherrer, 5–100° 2 θ CuK α radiation, integrated step 0.02°/2500 s, rotated sample with a frequency of 1 s⁻¹

² Bragg–Brentano, 5–60° 2 θ CuK α , integrated step 0.02°/2500 s, rotated sample with a frequency of 2 s⁻¹

Walenta (1964) – Debye–Scherrer pattern by Walenta (1964)

* calculated from the structural data of synthetic metakirchheimerite (Locock et al. 2004) Listed are diffractions either observed or with relative intensities higher or equal 2.

a higher background, and a relatively low peak to background ratio. The position of each diffraction maximum in both diffraction patterns was refined using Pearson VII profile shape function by the Xfit software (Coelho and Cheary 1997). The unit-cell parameters were refined with the Celref software (Laugier and Bochu 2002).

The powder diffraction data obtained in the Bragg–Brentano and Debye–Scherrer settings are presented in Tab. 1 together with calculated theoretical values d_{calc} obtained from the crystal structure data for synthetic metakirchheimerite (Locock et al. 2004). In addition, the diffraction data for natural metakirchheimerite published by Walenta (1964) are included in Tab. 1. Compared to the latter, the new diffraction data obtained in the current study are more complete. The refinement of the unit-cell parameters was based on the positions of 39 (Debye–Scherrer) and 21 (Bragg–Brentano) diffraction maxima (Tab. 1) obtained from the profile fitting. Hkl indices were assigned to the observed diffractions on the basis of the theoretical positions, inferred from the crystal structure of synthetic metakirchheimerite (Locock et al. 2004). Both the sets of refined unit-cell parameters (Tab. 2) are approximately the same, varying only in the range of their sigma values, and are consistent with parameters given by Locock et al. (2004) for the synthetic analogue of metakirchheimerite.

Tab. 2 Refined unit-cell parameters for metakirchheimerite from Jáchymov compared with parameters for a synthetic analogue (for triclinic space group $P-1$)

	Jáchymov, this work		Synt., Locock et al. (2004)
	1	2	
a [Å]	7.207(6)	7.199(6)	7.1955(3)
b [Å]	9.773(6)	9.786(1)	9.7715(4)
c [Å]	13.25(1)	13.23(1)	13.2319(6)
α [°]	75.43(6)	75.55(4)	75.525(1)
β [°]	83.89(7)	84.05(7)	84.052(1)
γ [°]	81.83(8)	81.51(6)	81.661(1)
V [Å ³]	892(1)	890(1)	889.08(7)

1 – Debye–Scherrer, mean-squared deviation on refined positions 0.06 °2 θ

2 – Bragg–Brentano, mean-squared deviation on refined positions 0.02 °2 θ

4.2. Chemical composition

Chemical composition of metakirchheimerite was studied using an electron microprobe Cameca SX100 (Laboratory of Electron Microscopy and Microanalysis of the Masaryk University and Czech Geological Survey, Brno, operator R. Škoda). Wavelength dispersive mode and operating voltage of 15 kV, 2 nA current and 20 μ m beam diameter were used. The following analytic lines and crystals were selected to minimize line overlap: K_{α}

lines: P (fluorapatite), Fe (andradite), Mg ($MgAl_2O_4$), Zn (ZnO), Ni (Ni), Co (Co); L_{α} lines: As (InAs); M_{β} lines: U (U metallic). Peak counting times (CT) were 10–20 seconds for major elements, 40–60 seconds for minor to trace elements and counting time on background was $\frac{1}{2}$ CT. The measured intensities were converted to element concentrations using the PAP program (Pouchou and Pichoir 1985).

Chemical composition of metakirchheimerite from Jáchymov (Tab. 3) can be expressed by an empirical formula (mean of 3 analyses, As + P = 2 *apfu*): $(Co_{0.53}Mg_{0.25}Ni_{0.08}Zn_{0.07}Fe_{0.05}Ca_{0.03})_{\Sigma 1.01}(UO_2)_{2.07}[(AsO_4)_{1.99}(PO_4)_{0.01}]_{\Sigma 2.00} \cdot 8H_2O$.

Tab. 3 Chemical composition of metakirchheimerite from Jáchymov

	Mean	1	2	3
CaO	0.16	0.14	0.22	0.13
MgO	0.93	0.80	0.87	1.13
FeO	0.33	0.29	0.56	0.14
CoO	3.76	3.49	3.22	4.58
NiO	0.55	0.52	0.63	0.50
ZnO	0.55	0.72	0.36	0.57
P_2O_5	0.07	0.03	0.03	0.15
As_2O_5	21.54	21.08	21.51	22.04
UO_3	55.42	58.86	55.15	52.25
H_2O^*	14.01	–	–	–
Total	97.32	85.92	82.55	81.48
Ca	0.031			
Mg	0.245			
Fe	0.049			
Co	0.533			
Ni	0.078			
Zn	0.071			
ΣA site	1.001			
P	0.011			
As	1.989			
ΣT site	2.000			
U	2.056			
H_2O	8.000			

H_2O^* – content of molecular water in wt. % derived from theoretical 8 mol. H_2O in the crystal structure of metakirchheimerite
Mean – based on mean of 3 analyses

Besides slightly dominant Co atoms (0.49–0.63 Co *apfu*) at A site, the presence of several isomorphous components was observed (Fig. 5). These are represented namely by Mg (up to 0.29 *apfu*), Ni (up to 0.09 *apfu*) and Zn (0.10 *apfu*) contents, corresponding to metanováckeite (Mg), metarauchite (Ni) and metalodévíte (Zn) isomorphous components. Only negligible contents (up to 0.02 *apfu*) of $(PO_4)^{3-}$ anions were detected, indicating major prevalence of $(AsO_4)^{3-}$ ions in source fluids. The molecular water content could not have been assessed directly in

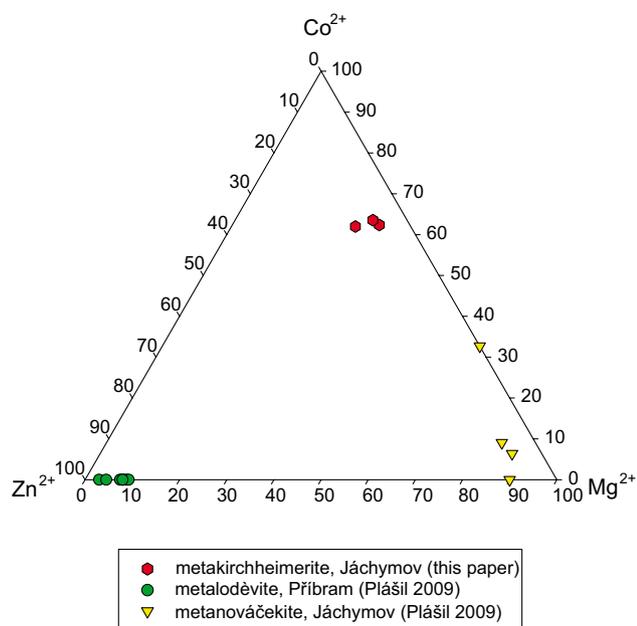


Fig. 5 A ternary plot of the *A*-site occupancy (atomic ratio) for studied metakirchheimerite and related minerals.

the studied material due to small amount of the sample available. Therefore, the water content was inferred based on theoretical value for the synthetic metakirchheimerite, an octahydrate (Locock et al. 2004).

4.3. Vibrational spectroscopy

The infrared spectrum of metakirchheimerite was recorded by DRIFTS method on the Nicolet Magna 760 FTIR spectrometer (range 4000–600 cm^{-1} , resolution 4 cm^{-1} , 128 scans, Happ–Genzel apodization), equipped with Spectra Tech InspectIR micro FTIR accessory. Samples were mixed with KBr without using a pressure, to avoid dehydration or reactions in solid state, and immediately measured. The same KBr was measured as a reference. The Raman spectrum (1100–170 cm^{-1}) was collected with a dispersive Raman spectrometer Labram HR (Jobin Yvon) with a confocal Olympus microscope. The Raman signal was excited by a 730 nm laser and detected with a multichannel air-cooled CCD camera. The laser power was limited to 10 mW. Data processing was performed under Omnic Spectral tools software.

Neither infrared, nor Raman spectra of natural metakirchheimerite have been published yet. Vochten and Goeminne (1984) only mentioned that synthetic uranyl arsenates containing Co, Ni and Cu exhibit the same vibrational characteristics. Chernorukov et al. (2000) published infrared spectra for synthetic metakirchheimerite and not approved “kirchheimerite” with assigned vibration bands. In the study of Plášil (2009), the infrared and

Tab. 4 Tentative assignment of metakirchheimerite infrared and Raman spectra

Assignment	Infrared [cm^{-1}]	Raman [cm^{-1}]
ν O–H stretching	3521 (s–sharp)	–
	3123 (s–broad)	–
ν_2 (δ) bending H–O–H	1622 (w)	–
	1586 (w)	–
ν_3 (PO_4) $^{3-}$	1109 (vw)	–
	1065 (w)	–
	1007 (vw)	–
Overlapping ν_3 (UO_2) $^{2+}$, ν_3 (AsO_4) $^{3-}$, ν_1 (AsO_4) $^{3-}$ and ν_1 (UO_2) $^{2+}$	930 (sh)	–
	908 (sh)	908 (sh)
	–	896 (ms)
	–	883 (sh)
ν_4 (δ) (PO_4) $^{3-}$	830 (vs)	830 (sh)
	819 (sh)	816 (s)
	–	801 (sh)
ν_4 (δ) (AsO_4) $^{3-}$	–	796 (sh)
	–	449 (mw–broad)
ν_2 (δ) (UO_2) $^{2+}$, possible coincidence with U–O _{ligand} vibrations	–	320 (w–broad)
	–	206 (sh)
Lattice modes	–	191 (ms)

Raman spectra of metaloděvite were presented, which seem to be similar with the present assignment of metakirchheimerite spectra (Tab. 4).

4.3.1. Stretching O–H, bending H–O...H vibrations

A sharp infrared band at 3521 cm^{-1} (Fig. 6) is assigned to the ν OH stretching vibration of only weakly hydrogen bonded water molecules, whereas a broad infrared band at 3123 cm^{-1} , also attributed to the ν OH stretching vibrations, is connected with more strongly hydrogen bonded water molecules. According to Libowitzky (1999), the tops of these bands are close to the O–H...O hydrogen bonds 2.94 and 2.69 Å, respectively. This proves that structurally non-equivalent hydrogen-bonded water molecules are present in the crystal structure of metakirchheimerite. This interpretation is supported by the fact that three corresponding infrared bands are observed in the region of the ν_2 (δ) H_2O bending vibrations at 1617 (shoulder), 1568 (maximum) and 1526 cm^{-1} (Fig. 6), and also by thermogravimetric analysis (Vochten and Goeminne 1984). The crystal structure analysis of synthetic metakirchheimerite (Locock et al. 2004) proved the presence of three symmetrically distinct H_2O molecules held in the crystal structure only by hydrogen bonding, whereas five other H_2O molecules are coordinated with the interlayer

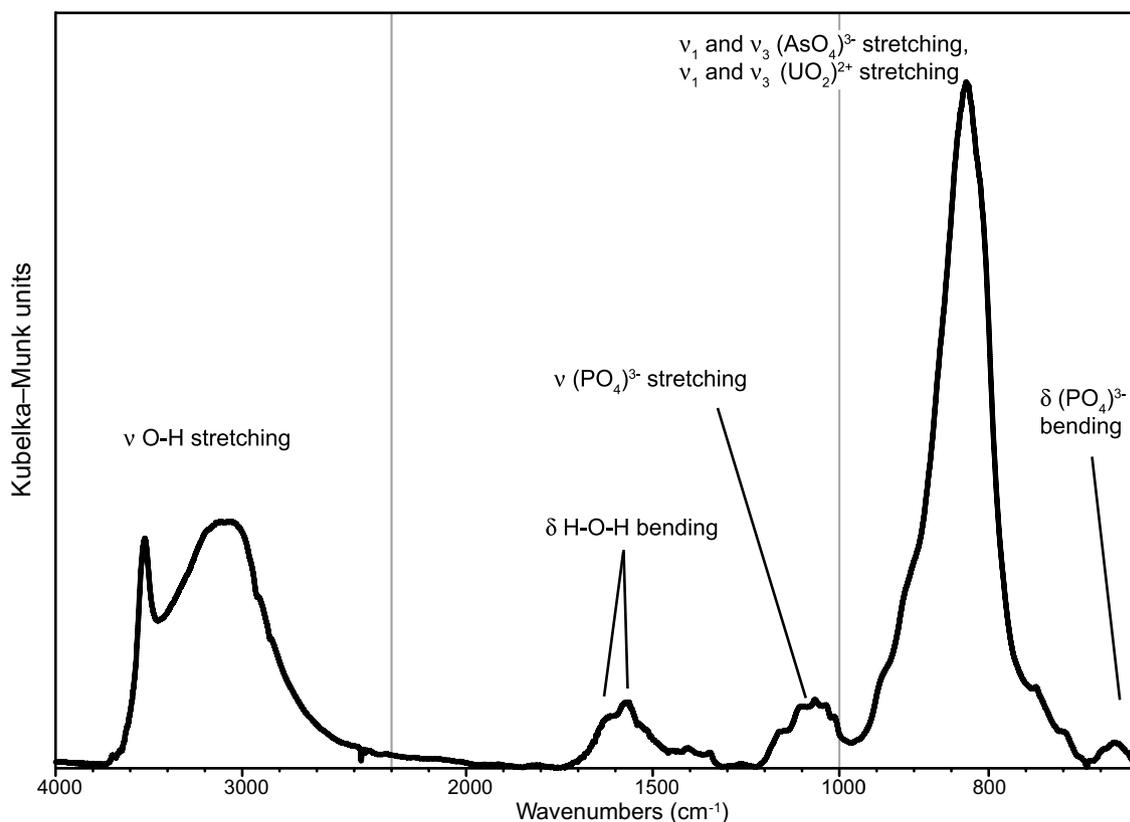


Fig. 6 The infrared spectrum of metakirchheimerite from Jáchymov. The assignments of the vibration bands are displayed for clarity.

Co²⁺ atom. A network of hydrogen bonding was proposed by Locock et al. (2004), based on O··O interatomic distances in the range 2.7 to 3.2 Å (Fig. 1). A band at 735 cm⁻¹ (a shoulder with maximum) was assigned to libration modes of water molecules (Čejka 1999).

5.3.2. Vibrations of the uranyl (UO₂)²⁺ groups and (AsO₄)³⁻/(PO₄)³⁻ polyhedra

The vibration modes assignment of these units is rather difficult due to extensive overlapping of the bands in the region between ca. 950–800 cm⁻¹ (Figs 6–7), regarding stretching modes of AsO₄ groups and uranyl ion. Based on empirical relation given by Bartlett and Cooney (1989) the following U–O bond lengths were obtained from the wavelengths that could correspond to the uranyl stretching vibrations, observed in the both spectra: the infrared bands (Fig. 6) and/or shoulders at 930 cm⁻¹ [ν₃; 1.763], 908 cm⁻¹ [ν₃; 1.779], 830 cm⁻¹ [ν₁; 1.781] and 811 cm⁻¹ [ν₁; 1.800]; the Raman bands (Fig. 7) and/or shoulders at 908 cm⁻¹ [ν₃; 1.779], 896 cm⁻¹ [ν₃; 1.788], 883 cm⁻¹ [ν₃; 1.797], 816 cm⁻¹ [ν₁; 1.795] and 801 cm⁻¹ [ν₁; 1.810]. But all these vibrations may be assigned to (AsO₄)³⁻ stretching modes, too. Chernorukov et al. (2000) observed in the infrared spectrum of a synthetic analogue of metakirch-

heimerite in this region following bands at 952 cm⁻¹ [ν₃; 1.749] (ν₃ UO₂²⁺), 896 cm⁻¹ [ν₃; 1.786] and 812 cm⁻¹ [ν₁; 1.799] [ν AsO₄³⁻]; in the brackets is cited the assignment proposed by Chernorukov et al. (2000). Based on single-crystal study of synthetic metakirchheimerite analogue, Locock et al. (2004) reported average U–O bond length (uranyl) of 1.781 Å [U(1)–O 1.765(3) and 1.809(3) Å, Ø 1.787 Å; U(2)–O 1.774(3) and 1.777(3) Å, Ø 1.755(5) Å]. These values can be compared with those inferred from the Raman and infrared spectra. A comparison of experimental Raman and infrared spectra is displayed in Fig. 8, which can be helpful in understanding the overlapping bands and their assignments. As an approximation, it can be assumed that infrared shoulders at 930 cm⁻¹ and 908 cm⁻¹ are connected with the ν₃ UO₂²⁺ antisymmetric stretching vibration, the strong band at 830 cm⁻¹ (IR) to the ν₃ AsO₄³⁻ triply degenerate antisymmetric stretching vibration overlapping the ν₁ (UO₂)²⁺ and ν₁ (AsO₄)³⁻ stretching bands, that must have lower intensities than antisymmetric modes in the infrared spectrum. The Raman shoulder at 908 and maximum at 896 cm⁻¹ are assigned to the ν₃ (UO₂)²⁺ symmetric stretching vibration. The number of bands is caused by presence of two non-equivalent U atoms in the crystal structure, which is supported by the results of factor group analysis.

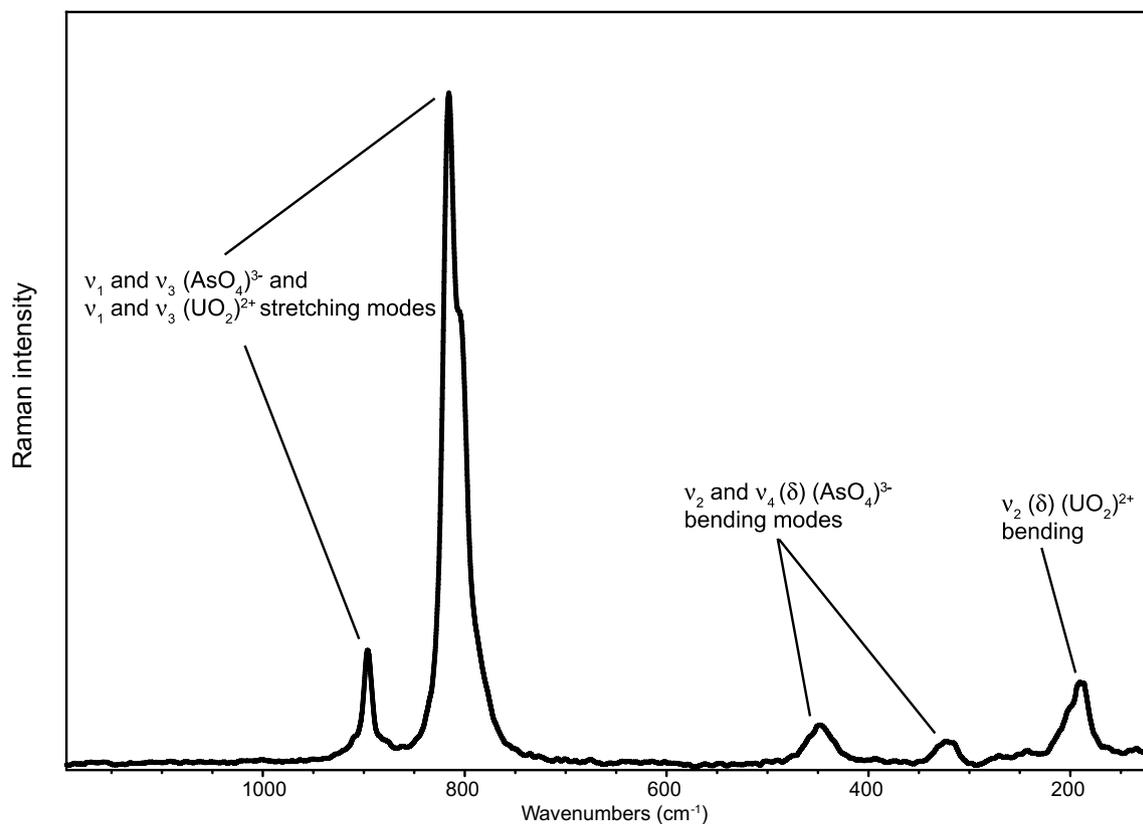


Fig. 7 Raman spectrum of metakirchheimerite from Jáchymov with tentatively assigned vibration bands.

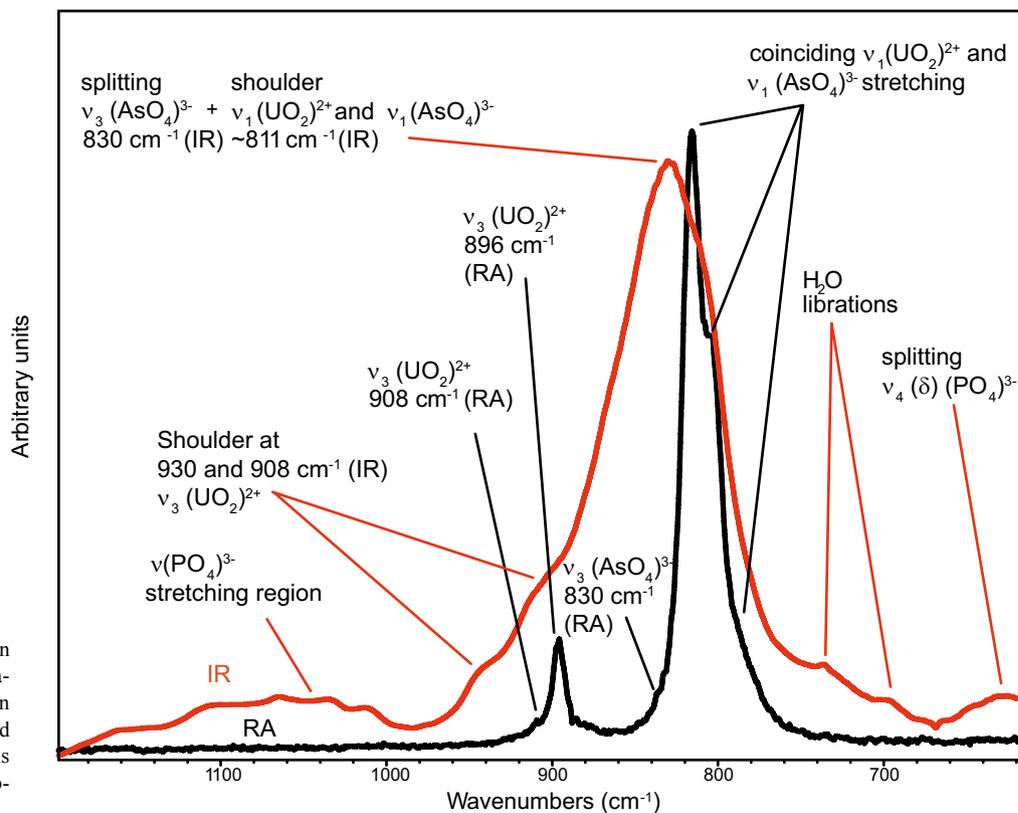


Fig. 8 A comparison of Raman and infrared spectra of metakirchheimerite in the region of the overlapping $(\text{UO}_2)^{2+}$ and $(\text{AsO}_4)^{3-}$ stretching vibrations with tentatively assigned vibration bands.

The shoulder at 830 cm⁻¹ (RA) is connected with the ν_3 (AsO₄)³⁻ antisymmetric stretching vibration. The intensive band with maximum at 816 cm⁻¹ and with shoulders at 801 and 790 cm⁻¹ belongs to the overlapping ν_1 (UO₂)²⁺ and ν_1 (AsO₄)³⁻ symmetric stretching vibration modes.

Infrared weak bands at 1109, 1065 and 1007 cm⁻¹ (Fig. 6) are attributed to the split ν_3 PO₄³⁻ triply degenerate antisymmetric stretching vibration, and those at 650 and 630 cm⁻¹ to the splitting ν_4 (δ) PO₄³⁻ triply degenerate bending vibration. Broad Raman bands at 449 and 320 cm⁻¹ (Fig. 7) are assigned to the ν_4 (δ) AsO₄³⁻ triply degenerate and ν_2 (δ) AsO₄³⁻ doubly degenerate bending vibrations, respectively. A shoulder at 206 cm⁻¹ is attributed to the ν_2 (δ) UO₂²⁺ bending vibration and that at 191 cm⁻¹ may be connected with lattice modes.

5. Notice on the occurrence of metakirchheimerite in the nature

There are only two reported localities of metakirchheimerite worldwide: Sophia Mine in Wittichen, Germany (Walenta 1958) and Jáchymov ore district, Czech Republic (Ondruš et al. 2003c). The reasons of metakirchheimerite rarity are only poorly understood at present. The association of cobalt arsenides with uranium minerals is relatively common in uranium deposits not only in the Czech Republic (e.g., Zálesí near Javorník, Jáchymov ore district) but also e.g. in the Schlemma deposit (Germany) or at Bou Azzer (Morocco). Commonly, within these localities, uraninite occurs on the calcite–dolomite veins. During the alteration of primary mineralization, the local environment is probably highly saturated in Mg from dolomite, which leads to the formation of metanováčekite instead of Ni-Co uranyl arsenates. The observations on the natural samples from Jáchymov indicate that alteration of cobalt arsenides dominantly results in crystallization of erythrite, even in the environment rich in (UO₂)²⁺ ions. In the Jáchymov ore district, a Ni-dominated hydrated uranyl arsenate – metarauchite (IMA 2008-050) (Plášil et al. 2008) is by far more abundant than metakirchheimerite. The chemical similarity of Co and Ni suggests that an analogous behaviour of these elements could be expected in supergene processes. It indicates that under oxidation conditions cobalt and nickel exhibit slightly different behaviour but the problem is actually poorly understood (V. Ettler, person. comm. 2009). On the other hand, the more or less inconspicuous appearance of metakirchheimerite, in contrast to secondary minerals coloured by Co²⁺ (or Ni²⁺), may be an important factor. It is possible that metakirchheimerite remains unnoticed at numerous localities.

Acknowledgements The kind help of Ivan Němec (Charles University, Prague) and Vladimír Machovič (Institute of Chemical Technology, Prague) with spectroscopic measurements as well as the assistance of Radek Škoda (Masaryk University, Brno) with electron microanalyses are highly acknowledged. The valuable comments by Andrew Locock (University of Alberta, Canada) are highly acknowledged, as well as his kind favour in providing us with the schematic picture of the metakirchheimerite crystal structure and reprint permission. Our thanks are due to both anonymous reviewers for their valuable comments as well as *big chief* Vojtěch Janoušek and handling editor Milan Novák. The authors are grateful for the financial support by the Grant Agency of the Charles University in Prague (GAUK no. 17008/2008), the Ministry of Culture of the Czech Republic (DE07P04OMG004) and the Ministry of Education of the Czech Republic (MSM0021620855).

Electronic supplementary material. The GPS coordinates of the studied samples are available online at the Journal web site (<http://dx.doi.org/10.3190/jgeosci.057>).

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Nová data pro metakirchheimerit z Jáchymova (St. Joachimsthal), Česká republika

Metakirchheimerit byl nalezen pouze na několika málo vzorcích pocházejících ze žíly Jan Evangelista na Štolovém patře šachty Svornost v Jáchymově. Metakirchheimerit na vzorcích tvoří krystalické agregáty sestávající z tenkých tabulkovitých krystalů do velikosti 0.1 mm. Krystaly jsou velmi křehké, světle růžové až oranžové barvy a silného skelného lesku. Krystalické agregáty metakirchheimeritu narůstají na karbonátovou žilovinu s vtroušenými primárními minerály – arsenopyritem, uraninitem a skutteruditem. Studovaný metakirchheimerit je produktem sub/recentního zvětvávání primárních minerálních fází vzniklým v prostředí opuštěného důlního díla. Na základě elektronové mikroanalýzy lze chemické složení studovaného metakirchheimeritu vyjádřit empirickým vzorcem $(\text{Co}_{0.53}\text{Mg}_{0.25}\text{Ni}_{0.08}\text{Zn}_{0.07}\text{Fe}_{0.05}\text{Ca}_{0.03})_{\Sigma 1.01}(\text{UO}_2)_{2.07}[(\text{AsO}_4)_{1.99}(\text{PO}_4)_{0.01}]_{\Sigma 2.00} \cdot 8\text{H}_2\text{O}$ (na bázi $\text{As} + \text{P} = 2 \text{ apfu}$). Metakirchheimerit z Jáchymova vykazuje značný podíl izomorfní metanováčekitové komponenty. Rentgenový práškový difrakční záznam metakirchheimeritu odpovídá triklinické symetrii zjištěné studiem syntetického analogu na monokrystalovém difraktometru. Vypřesněné mřížkové parametry pro triklinickou prostorovou grupu $P-1$ jsou a 7.210(4) Å, b 9.771(6) Å, c 13.252(9) Å, α 75.39(4)°, β 83.94(6)°, γ 81.88(6)° s objemem V 892(1) Å³. V infračerveném i Ramanově spektru metakirchheimeritu se projevují valenční a deformační vibrace $(\text{UO}_2)^{2+}$, $(\text{AsO}_4)^{3-}$, $(\text{PO}_4)^{3-}$ a molekulární H_2O . Vibrační projevy jednotlivých molekulárních skupin byly přiřazeny jednotlivým vlnočtům. Vazebné délky U–O v uranylu délky vodíkových vazeb, které byly odvozeny studiem vibračních spekter, jsou konsistentní se strukturálními daty uváděným pro syntetický analog metakirchheimeritu.