



COVER SHEET

This is the author version of article published as:

Frost, Ray L. and Cejka, Jiri and Bostrom, Thor E. and Weier, Matthew L. and Martens, Wayde (2007) Raman spectroscopic study of the molecular structure of the uranyl mineral zippeite from Jáchymov (Joachimsthal), Czech Republic. *Spectrochimica Acta Part A* 67(5):1220 -1227.

Copyright 2007 Elsevier

Accessed from <http://eprints.qut.edu.au>

Raman spectroscopic study of the molecular structure of the uranyl mineral zippeite from Jáchymov (Joachimsthal), Czech Republic

Ray L. Frost*, Jiří Čejka[†], Thor Bostrom, Matt Weier and Wayde Martens

Inorganic Materials Research Program, School of Physical and Chemical Sciences, Queensland University of Technology, GPO Box 2434, Brisbane Queensland 4001, Australia.

[†] National Museum, Václavské náměstí 68, CZ-115 79 Praha 1, Czech Republic.

Abstract

Raman spectra at 298 and 77 K and infrared spectra of the uranyl sulfate mineral zippeite from Jáchymov (Joachimsthal), Czech Republic, $K_{0.6}(H_3O)_{0.4}[(UO_2)_6(SO_4)_3(OH)_7] \cdot 8 H_2O$, were studied. Observed bands were tentatively attributed to the $(UO_2)^{2+}$ and $(SO_4)^{2-}$ stretching and bending vibrations, the OH stretching vibrations of water molecules, hydroxyls and oxonium ions, and H_2O , oxonium, and δ U-OH bending vibrations. Empirical relations were used for the calculation of U-O bond lengths in uranyl $R = f(\nu_3 \text{ or } \nu_1 (UO_2)^{2+}) \text{ \AA}$. Calculated U-O bond lengths are in agreement with U-O bond lengths from the single crystal structure analysis and those inferred for uranyl anion sheet topology of uranyl pentagonal dipyramidal coordination polyhedra. The number of observed bands supports the conclusion from single crystal structure analysis that at least two symmetrically distinct U^{6+} (in uranyls) and S^{6+} (in sulfates), water molecules and hydroxyls may be present in the crystal structure of the zippeite studied. Strong to very weak hydrogen bonds present in the crystal structure of zippeite studied were inferred from the IR spectra.

Key words: zippeite, potassium uranyl sulfate mineral, chemical formula, infrared and Raman spectroscopy, U-O bond length, O-H...O bond lengths

Introduction

Uranyl sulfates form a group of secondary uranyl minerals typically occurring close to actively oxidizing uraninite and sulfide minerals [1], inclusive uranopilite [2], jáchymovite [3], johannite [4], rabejacite [5], deliensite [6] and a subgroup of zippeite minerals. Characteristic feature of zippeites is their very similar uranyl sulfate sheet topology $[(UO_2)_{2x}(SO_4)_x(O)_y(OH)_z]$ with practically always constant molar ratio $UO_2/SO_4 = 2$. This has been proved on natural and synthetic zippeites [7]. From this reason also rabejacite may be understood as a calcium-member of the zippeite mineral subgroup [8]. Differences are observed in the interlayer, in which mono- (Na, K, NH_4) or divalent (e.g. Mg, Co, Ni, Cd) cations and water molecules are located. Solid solutions are possible especially between zippeites possessing divalent cations in their crystal structures. No such solid solutions are observed between monovalent and divalent cation containing zippeites. Because of the presence of water molecules in the interlayer and/or $(OH)^-$ in the uranyl sulfate sheets, formation of various hydrogen-bonding networks may be expected in the crystal structure of zippeites which may be influenced by different conditions of their origin in nature and in laboratory. There are at least two structurally different subgroups of zippeites [7, 9].

* Author to whom correspondence should be addressed (r.frost@qut.edu.au)

Uranyl sulfate solid state and solution chemistry plays important role in the uranyl chemistry, mineralogy, geochemistry, environmental chemistry with regard to uranium(VI) migration in natural waters and to spent nuclear fuel problems. These compounds may also be significant products of the alteration of nuclear waste in a geologic repository, owing to the presence of sulfur as an impurity in steel used to construct canisters [7].

Frondel et al. [1976] proposed for zippeites containing monovalent cations a general formula $M^+_4[(UO_2)_6(SO_4)_3] \cdot 4 H_2O$, and for zippeites possessing divalent cations a general formula $M^{2+}_2[(UO_2)_6(SO_4)_3] \cdot 16 H_2O$, and to retain the name zippeite for zippeite species containing only K^+ ions [10]. Vochten et al. [1995] reported the single crystal structure of hydrothermally grown zippeite of the composition $K[(UO_2)_2(SO_4)(OH)_3] \cdot H_2O$ [11]. Brugger et al. [12] and Burns et al. [7] made a bond-valence analysis of the structure proposed by Vochten et al. [11]. This analysis leads to the formula $K[(UO_2)_2(SO_4)O_2] \cdot 2 H_2O$, which is not electro-neutral. Meisser proposed for Vochten's zippeite the more correct and electro-neutral formula $K(H_2O)[(UO_2)_2(SO_4)O(OH)](H_2O)$ [13]. Burns et al. published single crystal structure of hydrothermally prepared zippeite with the formula $K_3(H_2O)_3[(UO_2)_4(SO_4)_2O_3(OH)]$ [7].

As a part of our on-going research into secondary mineral formation and the analysis of the molecular structure of these minerals, we report the Raman and infrared spectra of the natural zippeite from the well-known Jáchymov (Joachimsthal) deposit (Czech Republic) and relate the spectra to the mineral structure.

Experimental

Minerals

Two zippeite samples (Registered numbers M25802 and M30643) were obtained from Museum Victoria and originated from the Czech Republic, Jachymov, Bohemia. The samples were analysed by X-ray diffraction and EDX measurements as per below.

X-Ray diffraction

X-ray diffraction (XRD) patterns were recorded using $CuK\alpha$ radiation ($n = 1.5418 \text{ \AA}$) on a Philips PANalytical X' Pert PRO diffractometer operating at 40 kV and 40 mA with 0.125° divergence slit, 0.25° anti-scatter slit, between 3 and 15° (2θ) at a step size of 0.0167° . For low angle XRD, patterns were recorded between 1 and 5° (2θ) at a step size of 0.0167° with variable divergence slit and 0.5° anti-scatter slit.

SEM Analysis

Zippeite samples were coated with a thin layer of evaporated carbon and secondary electron images were obtained using an FEI Quanta 200 scanning electron microscope (SEM). For X-ray microanalysis (EDX), three samples were embedded in Araldite resin and polished with diamond paste on Lamplan 450 polishing cloth using water as a lubricant. The samples were coated with a thin layer of evaporated carbon for conduction and examined in a JEOL 840A analytical SEM at 25kV accelerating voltage. Preliminary analyses of the zippeite samples were carried out on the FEI Quanta SEM using an EDAX microanalyser, and microanalysis of the clusters of fine crystals was carried out using a full standards quantitative

procedure on the JEOL 840 SEM using a Moran Scientific microanalysis system. Uranium oxide was used as a standard for U. The K-K α peak is strongly overlapped by the U-M lines and was deconvolved using a peak strip routine, which gave similar results to a peak fit routine used by the EDAX analysis software. However some uncertainty remains in the quantitative measurements of K in the presence of U. Oxygen was not measured directly but was calculated using assumed stoichiometries to the other elements analysed.

Raman microprobe spectroscopy

The crystals of zippeite were placed and orientated on the stage of an Olympus BHSM microscope, equipped with 10x and 50x objectives and part of a Renishaw 1000 Raman microscope system, which also includes a monochromator, a filter system and a Charge Coupled Device (CCD). Raman spectra were excited by a HeNe laser (633 nm) at a resolution of 2 cm⁻¹ in the range between 100 and 4000 cm⁻¹. Repeated acquisition using the highest magnification was accumulated to improve the signal to noise ratio. Spectra were calibrated using the 520.5 cm⁻¹ line of a silicon wafer. In order to ensure that the correct spectra are obtained, the incident excitation radiation was scrambled. Previous studies by the authors provide more details of the experimental technique. Spectra at liquid nitrogen temperature were obtained using a Linkam thermal stage (Scientific Instruments Ltd, Waterfield, Surrey, England). Details of the technique have been published by the authors [14-17].

Infrared spectroscopy

Infrared spectra were obtained using a Nicolet Nexus 870 FTIR spectrometer with a smart endurance single bounce diamond ATR cell. Spectra over the 4000–525 cm⁻¹ range were obtained by the co-addition of 64 scans with a resolution of 4 cm⁻¹ and a mirror velocity of 0.6329 cm/s. Spectral manipulation such as baseline adjustment, smoothing and normalisation was performed using the GRAMS® software package (Galactic Industries Corporation, Salem, NH, USA).

Results and discussion

X-ray diffraction

The X-ray diffraction pattern of the Jáchymov zippeite is shown in Figure 1 and the results of the analysis including peak position, peak intensity, peak widths and d-spacing are reported in Table 1. Unit cell parameters of this low potassium content zippeite are a = 8.757(2), b = 13.994(2), c = 17.726(1) Å, β = 102.59(9) °. They are close to the unit cell parameters of natural zippeites described by Ondruš et al. [1997] a = 8.656(2), b = 14.240(4), c = 17.706(5) Å, β = 104.112(4) °, Sejkora et al. [2003] a = 8.740(3), b = 14.157(5), c = 17.722(5) Å, β = 104.28(3) ° and low potassium content zippeite by Frost et al. a = 8.626(0), b = 14.198(3), c = 17.627 (4) Å, β = 102.52(9) °, and also of synthetic zippeites described by Vochten et al. [1995] a = 8.755(3), b = 13.987(7), c = 17.730(7) Å, β = 104.13(3) °, Burns et al. [2003] a = 8.7524(4), b = 13.9197(70), c = 17.6972(8) Å, β = 104.178(1) °, and Čejka [1999] a = 8.698(3), b = 13.856(8), c = 17.760(7) Å, β = 104.17(3) °.

EDX analyses

Figure 1 shows the SEM micrograph of zippeite sample M25802 and Figure 2 zippeite sample M30643. The EDX analysis is reported in Table 2. The two zippeites from Czech Republic, Jachymov, Bohemia, are based upon potassium as the monovalent cation. Only the first mineral sample was used in this work, because the second sample does not correspond to a zippeite-type mineral.

The average atomic ratios (setting S=1) is K : U : S = 0.20 : 2.05 : 1. EDX analyses also proved the presence of low concentrations of divalent cations (Mg, Ca, Fe), SiO₂ and Al₂O₃ which have been omitted. Because of the low K⁺ content, we assume that charge balance may be realized by the presence of oxonium, (H₃O)⁺ ions located in the interlayer. Thus the idealized formula of the zippeite studied is [(K_{0.6}(H₃O)⁺_{0.4}][(UO₂)₆(SO₄)₃(OH)₇]. 8 H₂O. Water content was inferred from the oxygen content and the number of oxygen atoms (39-40) expected in the crystal structure of the zippeite studied. K⁺ ↔ (H₃O)⁺ substitution is possible because ionic radii of these ions are very close.

Frondel et al. [1976] proposed for natural and synthetic zippeite the formula K₄[(UO₂)₆(SO₄)₃(OH)₁₀]. 4 H₂O [10]. Frost et al. described the Happy Jack zippeite having the formula K₂[(UO₂)₆(SO₄)₃O(OH)₆]. 4 H₂O. The formula of the synthetic zippeite presented by Vochten et al. is K[(UO₂)₂(SO₄)(OH)₃] [11]. Bond-valence analysis of the structure of this synthetic zippeite, however, leads to the formula K[(UO₂)₂(SO₄)O₂]. 2 H₂O, which is not neutral [7, 12]. Meisser [2003] assumed the formula of Vochten's synthetic zippeite may be K(H₂O)[(UO₂)₂(SO₄)O(OH)]. H₂O, which is electroneutral [13]. Burns et al. (2003) studied single crystal structure of synthetic zippeite, K₃(H₂O)₃[(UO₂)₄(SO₄)₂O₃(OH)].

Differences in the composition of described natural and synthetic zippeites may be caused by various conditions of zippeite origin and formation in nature and also a variety of conditions of syntheses. Important is the fact, that only small differences may be observed in their uranyl anion (UO₂)²⁺/(SO₄)²⁻/(O)²⁻/(OH)⁻ sheets. This means that all these sheets have very similar uranyl anion topology with the molar ratio (UO₂)²⁺/(SO₄)²⁻ = 2. Coordination polyhedra of uranyls are pentagonal dipyramids, while tetrahedra are typical for sulfate ions [7, 18-20].

Synthetic zippeites possess symmetrically distinct U⁶⁺ and S⁶⁺ { 2 + 2 [11]; 4 + 2 [7] } in their crystal structures. Interpretation of the IR and Raman spectra is therefore done respecting that in the structure of zippeite studied may be present symmetrically distinct U⁶⁺ and S⁶⁺.

Factor group analysis

Factor group analysis of zippeite has been based upon the structure as proposed by Vochten for a synthetic zippeite [11]. This is an assumption as the formulae for the synthetic zippeite differs from that of natural zippeite. Whether the assumption is true or not remains to be proven. The FGA for zippeite is given in Tables 4-6 based upon z=8. The irreducible representation is given by $\Gamma = 43A_g + 43B_g + 42A_u + 41B_u$. This means there are 249 vibrations for the unit cell; 32 for the UO₂, 36 for the SO₄, 12 for H₂O and 169 for the lattice modes making a total of 249 vibrations.

Infrared and Raman spectroscopy

The IR (298 K) and Raman spectra (298 and 77 K) of the Jachymov zippeite studied are shown in Figures 4-7 and the results of the band component analyses reported in Table 7. From the X-ray single crystal structure analysis of synthetic zippeites it may be inferred that symmetries of free uranyl ($D_{\infty h}$) and sulfate (T_d) are lowered. All vibrations may be therefore IR and Raman active and their number enhanced because of the presence of symmetrically distinct (UO_2 in UO_2O_5) and (SO_4) groups in the crystal structure, splitting of degenerate vibrations, and also respecting the factor group analysis.

In the Raman spectrum, the $\nu_1 (SO_4)^{2-}$ symmetric stretching mode is complex with three bands observed at 1014, 1007 and 1000 cm^{-1} at 298 K, and two bands at 1016 and 1008 cm^{-1} at 77 K. It is proposed that there is more than one type of sulfate unit in this zippeite mineral. This agrees with single crystal structure of synthetic zippeite [7, 11], IR and Raman spectroscopy of Happy Jack zippeite, and also published IR spectra of zippeites [for details see Čejka [9]]. Only one band at 1007 cm^{-1} , observed in the IR spectrum, may be attributed to the $\nu_1 (SO_4)^{2-}$.

Two bands observed in the Raman spectrum at 1138 and 1096 cm^{-1} (298 K) and at 1097 and 1068 cm^{-1} (77 K) and five bands in the IR spectrum at 1161, 1139, 1106, 1068 and 1048 cm^{-1} are attributed to the split triply degenerate $\nu_3 (SO_4)^{2-}$ antisymmetric stretching vibrations. The positions of these bands received from the deconvolution process appear to somewhat differ from those previously published [9, 11]. This difference is accounted for by the difference in the samples. The spectra in this work were obtained from natural sample whereas the published data originated from the spectra from synthetic samples and have been previously stated considerably variation in the spectra results because of the variations in the structure of the mineral which results from different method of preparation or origin in nature.

In the Raman spectrum of the zippeite studied, the spectral pattern in the 800 to 850 cm^{-1} region shows complexity. Four intense bands are observed at 849, 838, 826 and 814 cm^{-1} (298 K) and at 847, 838, 829 and 833 cm^{-1} (77 K), while only one band at 840 cm^{-1} was observed in the IR spectrum. These bands are assigned to the $\nu_1 (UO_2)^{2+}$ symmetric stretching vibrations. The complexity of this spectral region may be accounted for the non-equivalence of the $(UO_2)^{2+}$ units or non-equivalence of the U-O (uranyl) bonds, and FGA for zippeite. Observed wavenumbers of bands attributed to the $\nu_1 (UO_2)^{2+}$ vibrations are used for the calculation of the U-O bond lengths in uranyl [21]. Inferred R_{U-O} bond lengths (Å) are : 1.763 (849 cm^{-1}), 1.773 (838 cm^{-1}), 1.785 (826 cm^{-1}), 1.797 (814 cm^{-1}), and 1.765 (847 cm^{-1}), 1.773 (838 cm^{-1}), 1.782 (829 cm^{-1}), 1.789 (822 cm^{-1}), respectively. The band at 840 cm^{-1} in the infrared spectrum corresponds to 1.771 Å.

In the IR spectrum, a broad band is observed centered upon 875 cm^{-1} . The spectral profile can be curve resolved in two components at 911 and 873 cm^{-1} . No intensity is observed in this spectral region in the Raman spectra. The bands at 911 and 873 cm^{-1} attributed to the $\nu_3 (UO_2)^{2+}$ antisymmetric stretching vibrations. Calculated R_{U-O} bond lengths (Å) in uranyls using two empirical relations are 1.777 (911 cm^{-1}) and 1.805 (873 cm^{-1}) [21], and 1.776 (911 cm^{-1}) and 1.797 (873 cm^{-1}) [22]. This doubling of the $\nu_3 (UO_2)^{2+}$ also may support the conclusion that structurally (symmetrically) distinct uranyl groups are present in the crystal structure of zippeite studied. Calculated U-O bond lengths agree with data from single crystal structure analyses of synthetic zippeites – 1.77(3) Å [11] and 1.7805 (1.726-1.815) Å [7], and also with 1.79(4) Å for uranyl pentagonal dipyramidal coordination polyhedra in uranyl anion sheet topology of uranyl synthetic and natural compounds [18-20].

The IR and Raman spectra of the 1250 to 1750 cm^{-1} region are shown in Figure 5. The intensity in the Raman spectra in this spectral region is very weak. Bands at 1530, 1420 and 1410 cm^{-1} are assigned to the δ U-OH bending vibrations. Two infrared bands, found at 1684 and 1620 cm^{-1} are attributed to the δ H₂O bending vibrations. The observation of a band at high wavenumber (1684 cm^{-1}) shows that some water molecules are very strongly hydrogen bonded. However, this band may be connected with the ν_4 (H₃O)⁺ doubly degenerate bending vibrations. A weak Raman band is also observed at 1633 cm^{-1} in the 298 K spectrum which splits into two bands at 1686 and 1611 cm^{-1} in the 77 K spectrum. These bands correspond to the two infrared bands observed above and are assigned to the δ H₂O bending vibrations.

The Raman spectra of the low wavenumber region are shown in Figure 6. This region shows the ν_2 doubly degenerate and ν_4 triply degenerate bending regions of the (SO₄)²⁻ units and the ν_2 doubly degenerate bending region of the (UO₂)²⁺ units. No intense bands are observed in this region. Low intensity bands are observed at 668 and 615 cm^{-1} (298 K) and low intensity bands at 670, 606, 559 and 538 cm^{-1} (77 K). Bands (IR) at 668, 621, 603 and 580 cm^{-1} are observed. All these bands may be connected with the ν_4 (SO₄)²⁻ bending modes of the (SO₄)²⁻ units. Bands (Raman) at 492, 463, 424, 414 and 403 cm^{-1} (298 K), and at 509, 483, 462, 426 and 409 cm^{-1} (77 K) are attributed to the ν_2 bending modes of the (SO₄)²⁻ units. Bands at 375 and 353 cm^{-1} (77 K) are ascribed to the ν U-O_{equatorial}, i.e. U-O_{ligand} vibrations. Bands at 274 cm^{-1} (298 K) and 287, 272 cm^{-1} (77 K) are attributed to the ν_2 bending modes of the (UO₂)²⁺ units. Bands with the lowest wavenumbers [203 cm^{-1} (298 K) and 206 cm^{-1} (77 K)] may be connected with molecular deformation and/or lattice modes.

Some coincidences of the bands related to the (SO₄)²⁻ bending vibrations and the H₂O libration modes, and of the (UO₂)²⁺ symmetric stretching vibrations and the (SO₄)²⁻ stretching vibrations and the U-OH bending vibrations cannot be excluded and are possible.

The Raman and IR spectra of the OH stretching region of the Jáchymov zippeite are shown in Figure 7. The mineral has both hydroxyl and water units in the structure. Therefore bands from both these units are expected. The Raman spectrum displays a spectrum with two bands observed at 3500 and 3404 cm^{-1} (298 K). These bands resolve into bands at 3504, 3195 and 3116 cm^{-1} at 77 K. The infrared spectrum shows a broad profile with some features which make the curve resolution somewhat more valid. One possible assignment is that the bands in the Raman spectra are attributed to the (OH)⁻ stretching vibrations as water is a renowned poor Raman scatterer. Thus the bands in the infrared spectrum at 3604, 3553, 3500 and 3402 cm^{-1} may be assigned to the (OH)⁻ stretching vibrations and the remaining broad bands deconvoluted to 3397, 3252, 3192, 3041, 2953, 2922, 2899 and 2852 cm^{-1} to the OH stretching vibrations of water molecules. Vochten et al. [11] and Čejka [9] reported sharp infrared bands for a synthetic zippeite at 3623 and 3540 or 3625 and 3540 cm^{-1} , respectively, and broad bands in the 3350 to 3000 cm^{-1} region. These results for synthetic analogue of zippeite corresponds well with our IR results for Jáchymov zippeite. Crystal structures of zippeites are characterized by complex hydrogen-bonding network. O-H...O bond lengths in the Jáchymov zippeite H-bonding network inferred from the IR and Raman spectra vary from strong to very weak (~ 2.63 to > 3.2 Å) [23].

As mentioned above, the presence of oxonium ions, (H₃O)⁺, partly substituting K⁺ ions in the interlayer of the crystal structure of studied zippeite is supposed. If so, bands at 3192, 1139 or 1161, 3252 or 3192, and 1684 cm^{-1} (IR) may be assigned to the ν_1 symmetric

stretching vibrations, the ν_2 bending vibrations, the ν_3 doubly degenerate antisymmetric stretching vibrations, and the ν_4 doubly degenerate bending vibrations [9, 24]

Conclusions

IR and Raman spectroscopic study of the Jáchymov zippeite, $K_{0.6}(H_3O)_{0.4}[(UO_2)_6(SO_4)_3(OH)_7] \cdot 8 H_2O$, was studied. From this observation and published data on zippeite may be inferred, that zippeite in fact comprises several potassium uranyl hydroxy sulfate hydrates with essentially identical uranyl anion sheet topology and similar uranyl sulfate oxy hydroxy sheet composition with constant $(UO_2)^{2+}/(SO_4)^{2-} = 2$ in all known zippeite type natural and synthetic phases. Differences may be observed especially in the interlayer space, where K^+ , $(H_3O)^+$ [oxonium ions may occupy potassium sites because of close ionic radii of these two cations], and water molecules are located. The arrangement of the interlayer may be influenced by conditions of origin of zippeites in nature and also by various methods (e.g. hydrothermal or under normal temperature) used for their synthesis. Especially hydrogen-bonding network (in the interlayer and also between the sheets and the interlayer) may be strongly influenced by such different conditions of formation. This may cause some rearrangements of the crystal structure and chemistry of natural and also synthetic uranyl sulfates like zippeites. However, IR spectra of natural and synthetic uranyl sulfates may be influenced also by sample preparation, e.g. of KBr disks [Čejka 1999].

U-O bond lengths in uranyl, calculated with some empirical relations from the wavenumbers of the uranyl stretching vibrations are in agreement with the U-O bond lengths inferred from known single crystal structure analysis of synthetic zippeites. Number of the bands assigned to the $(UO_2)^{2+}$ stretching vibrations and $(SO_4)^{2-}$ stretching and bending vibrations supports the conclusion from the single crystal structure analysis that symmetrically distinct uranyl and sulfate units are present in the zippeite crystal structure.

As known also via thermal analysis (Čejka 1999), Raman and IR spectroscopy confirmed that very weakly to strongly hydrogen bonded structurally nonequivalent water molecules and probably also very weakly to strongly hydrogen bonded hydroxyls are present in the crystal structure of zippeite [9]. Participation of the oxonium ions in the crystal structure of the zippeite studied partly substituting K^+ ions is assumed on the basis of corresponding bands observed in the IR spectrum of the zippeite studied.

Acknowledgements

The financial and infra-structure support of the Queensland University of Technology Inorganic Materials Research Program of the School of Physical and Chemical Sciences is gratefully acknowledged. The Australian Research Council (ARC) is thanked for funding.

Mr Dermot Henry of Museum Victoria is thanked for the supply of the zippeite minerals.

References

- [1]. D. K. Smith, Jr., In Uranium Geochemistry, Mineralogy, Geology, Exploration and Resources F. Ippolito, B. Devero & G. Capaldi, eds (1984) 43.
- [2]. P. C. Burns, Canadian Mineralogist 39 (2001) 1139.
- [3]. J. Cejka, J. Sejkora, Z. Mrazek, Z. Urbanec and T. Jarchovsky, Neues Jahrbuch fuer Mineralogie, Abhandlungen 170 (1996) 155.
- [4]. K. Mereiter, TMPM, Tschermaks Mineralogische und Petrographische Mitteilungen 30 (1982) 47.
- [5]. M. Deliens and P. Piret, European Journal of Mineralogy 5 (1993) 873.
- [6]. R. Vochten, N. Blaton and O. Peeters, Canadian Mineralogist 35 (1997) 1021.
- [7]. P. C. Burns, K. M. Deely and L. A. Hayden, Canadian Mineralogist 41 (2003) 687.
- [8]. F. Veselovský and P. Ondruš, Secondary mineralization of Rožná uranium deposit and their comparison with the Jáchymov ore district. In Uranium Deposits (B. Kříbek & J. Zeman, eds.), Czech Geological Survey, Prague, Czech Republic (2002).
- [9]. J. Cejka, Reviews in Mineralogy 38 (1999) 521.
- [10]. C. Frondel, J. Ito, R. M. Honea and A. M. Weeks, Canadian Mineralogist 14 (1976) 429.
- [11]. R. Vochten, L. Van Haverbeke, K. Van Springel, N. Blaton and O. M. Peeters, Canadian Mineralogist 33 (1995) 1091.
- [12]. J. Brugger, P. C. Burns and N. Meisser, American Mineralogist 88 (2003) 676.
- [13]. N. Meisser, (2003).
- [14]. R. L. Frost, D. A. Henry and K. Erickson, J. Raman Spectrosc. 35 (2004) 255.
- [15]. R. L. Frost, Spectrochim. Acta, Part A 60A (2004) 1469.
- [16]. R. L. Frost, O. Carmody, K. L. Erickson, M. L. Weier and J. Cejka, J. Mol. Struct. 703 (2004) 47.
- [17]. R. L. Frost, O. Carmody, K. L. Erickson, M. L. Weier, D. O. Henry and J. Cejka, J. Mol. Struct. 733 (2004) 203.
- [18]. P. C. Burns, M. L. Miller and R. C. Ewing, Canadian Mineralogist 34 (1996) 845.
- [19]. P. C. Burns, R. C. Ewing and F. C. Hawthorne, Canadian Mineralogist 35 (1997) 1551.
- [20]. P. C. Burns, Reviews in Mineralogy 38 (1999) 23.
- [21]. J. R. Bartlett and R. P. Cooney, Journal of Molecular Structure 193 (1989) 295.
- [22]. V. A. Glebov, Khimiya Urana, M. (1989) 68.
- [23]. E. Libowitzky, Monatshefte fuer Chemie 130 (1999) 1047.
- [24]. N. V. Chukanov, D. Y. Pushcharovsky, M. Pasero, S. Merlino, A. V. Barinova, S. Moeckel, I. V. Pekov, A. E. Zadov and V. T. Dubinchuk, European Journal of Mineralogy 16 (2004) 367.

Table 1 Peak List of the X-ray diffraction pattern of zippeite

Pos.[°2Th.]	Height[cts]	FWHM[°2Th.]	d-spacing[Å]	Rel.Int.[%]
10.3130	1099.38	0.0590	8.57773	14.36
11.6523	1405.43	0.0590	7.59464	18.36
12.3200	6836.39	0.0984	7.18453	89.32
12.5300	7654.22	0.1181	7.06458	100.00
16.2350	76.92	0.4723	5.45976	1.00
20.7031	315.31	0.1181	4.29043	4.12
23.4200	127.35	0.0787	3.79850	1.66
24.8218	530.16	0.1968	3.58707	6.93
25.2152	844.72	0.1771	3.53199	11.04
25.5919	272.17	0.1378	3.48085	3.56
26.6061	75.47	0.2362	3.35042	0.99
28.5976	173.48	0.2755	3.12147	2.27
31.2574	702.42	0.0984	2.86166	9.18
33.8876	131.53	0.5510	2.64533	1.72
36.2100	28.81	0.4723	2.48082	0.38
38.1910	47.79	0.3149	2.35657	0.62
46.8662	29.75	0.7872	1.93859	0.39
52.4382	31.65	0.5760	1.74353	0.41

Table 2 Table of the EDX analyses of the Jáchymov zippeite (sample M25802)

Analysis	Weight %									
	O*	Mg	Al	Si	P	S	K**	Ca	Fe	U
1. Small crystal	28.65	0.79	0.08	0.13	0.01	4.27	0.65	0.00	0.48	64.94
2. Bright phase	27.88	0.00	0.27	0.08	0.00	4.47	1.26	0.00	0.46	65.57
3. Crystals1 (needle-like)	31.30	0.99	0.17	0.26	0.00	5.04	1.12	0.46	0.24	60.43
4. Crystals2	25.91	0.75	0.25	0.15	0.00	3.52	1.11	0.17	0.14	67.99
<i>Mean:</i>	<i>28.44</i>	<i>0.63</i>	<i>0.19</i>	<i>0.16</i>	<i>0.00</i>	<i>4.32</i>	<i>1.04</i>	<i>0.16</i>	<i>0.33</i>	<i>64.73</i>
<i>Std dev:</i>	<i>2.23</i>	<i>0.44</i>	<i>0.09</i>	<i>0.07</i>	<i>0.00</i>	<i>0.63</i>	<i>0.27</i>	<i>0.22</i>	<i>0.17</i>	<i>3.16</i>
Stoichiometry K : U : S	Atomic %									
	O*	Mg	Al	Si	P	S	K**	Ca	Fe	U
0.12 : 2.05 : 1	79.18	1.44	0.14	0.20	0.01	5.89	0.73	0.00	0.38	12.06
0.23 : 1.98 : 1	78.83	0.00	0.46	0.13	0.00	6.30	1.46	0.00	0.38	12.46
0.18 : 1.62 : 1	89.34	1.66	0.25	0.37	0.00	6.37	1.16	0.46	0.17	10.28
0.26 : 2.53 : 1	77.28	1.47	0.45	0.26	0.00	5.24	1.36	0.21	0.12	13.62
~ 0.20 : 2.05 :										
1	81.16	1.14	0.32	0.24	0.00	5.95	1.18	0.17	0.26	12.11
	5.52	0.77	0.16	0.10	0.00	0.52	0.32	0.22	0.14	1.38

Table 3 UO₂ internal modes

$D_{\infty h}$	C_1	C_{2h}
\sum_g^+		4A _g
\sum_u^+	4A	4B _g
Π_u		4A _u
		4B _u

Table 4 SO₄ internal modes

T_d	C_2	C_{2h}
A ₁	5A	5A _g
E		5A _u
2T ₂	4B	4B _g
		4B _u

Table 5 H₂O internal modes

C_{2v}	C_1	C_{2h}
2A ₁		3A _g
	3A	3A _u
B ₂		3B _g
		3B _u

Lattice vibrations

$$\Gamma = 43A_g + 43B_g + 42A_u + 41B_u$$

$$3n-3$$

$$3*4*21-3$$

$$=249$$

UO ₂	2*16
SO ₄	2*18
H ₂ O	12
Lattice	169
Total	=249

Table 6 Table of the Raman at 298 and 77 K and infrared spectral results of zippeite

m25802			m30643		
Raman 298K	Raman 77K	IR	Raman 298K	Raman 77K	IR
Band Centre (cm ⁻¹) / Intensity (%)	Band Centre (cm ⁻¹) / Intensity (%)	Band Centre (cm ⁻¹) / Intensity (%)	Band Centre (cm ⁻¹) / Intensity (%)	Band Centre (cm ⁻¹) / Intensity (%)	Band Centre (cm ⁻¹) / Intensity (%)
3500 / 3.80 3404 / 4.80	3504 / 3.72 3195 / 3.79 3116 / 2.96	3604 / 1.80 3553 / 4.37 3500 / 8.96 3402 / 0.99 3397 / 11.26 3252 / 13.01 3192 / 11.30 3041 / 5.77 2953 / 0.54 2922 / 0.41 2899 / 0.38 2899 / 8.49 2852 / 0.97	3548 / 0.61 3461 / 9.23	3550 / 0.58 3449 / 3.44 3392 / 5.46 3270 / 1.26 3211 / 1.91	3574 / 3.93 3500 / 7.98 3403 / 7.14 3268 / 19.45 3086 / 29.24 2852 / 10.25
		1684 / 0.07 1620 / 2.90 1620 / 0.47 1530 / 0.64			1641 / 1.54 1620 / 2.34 1533 / 1.60
		1420 / 4.07 1410 / 0.19			1431 / 0.73 1377 / 0.49
1138 / 1.79 1096 / 6.43 1014 / 4.23 1007 / 11.37 1000 / 1.82	1097 / 7.15 1068 / 0.16 1016 / 4.86 1008 / 1.15	1161 / 2.43 1139 / 3.13 1106 / 3.82 1068 / 3.53 1048 / 1.79 1007 / 1.68	1143 / 1.41 1117 / 3.89 1097 / 2.60 1010 / 6.39	1151 / 0.91 1127 / 2.12 1116 / 1.14 1099 / 2.56 1012 / 7.07	1171 / 0.92 1140 / 1.05 1119 / 0.84 1099 / 0.83 1075 / 3.07 1000 / 0.17
849 / 0.61 838 / 9.29 826 / 6.95 814 / 16.89	879 / 1.41 847 / 1.12 838 / 11.22 829 / 10.91 822 / 28.49	911 / 1.25 873 / 3.10 840 / 1.58	843 / 20.42 835 / 7.84 832 / 21.98	844 / 27.30 836 / 4.39 834 / 5.93 824 / 6.57	932 / 0.98 911 / 2.09 886 / 2.83 833 / 1.59
797 / 2.13 668 / 0.38 615 / 0.68	670 / 0.40 606 / 0.36 559 / 0.24 538 / 0.40	795 / 0.69 668 / 0.13 621 / 0.08 603 / 0.06 580 / 0.15	663 / 0.45 556 / 5.12 541 / 7.82	667 / 0.35 602 / 0.30 564 / 2.78	777 / 0.50 711 / 0.34 601 / 0.10
492 / 9.55 463 / 5.76 424 / 3.49 414 / 1.88 403 / 2.91	509 / 0.34 483 / 1.31 462 / 1.56 462 / 1.31 427 / 2.51 409 / 6.17		404 / 2.00	548 / 14.08 476 / 0.49 408 / 1.88	
	375 / 0.31 353 / 0.25		319 / 4.03	375 / 0.22 324 / 3.50	
274 / 3.52 203 / 1.72	287 / 1.12 272 / 3.36 206 / 3.42		294 / 1.15 252 / 5.06	298 / 1.36 255 / 2.34 206 / 0.47 194 / 0.88 181 / 0.60	

List of Tables

Table 1 Peak List of the X-ray diffraction pattern of zippeite

Table 2 Table of the EDX analyses of the Jáchymov zippeite (sample M25802)

Table 3 Factor Group analysis of the UO₂ internal modes

Table 4 Factor Group analysis SO₄ internal modes

Table 5 Factor Group analysis H₂O internal modes

Table 6 Table of the Raman at 298 and 77 K and infrared spectral results of zippeite

List of Figures

Figure 1 XRD pattern of zippeite from Czech Republic, Jáchymov, Bohemia.

Figure 2 SEM image of zippeite from Czech Republic, Jáchymov, Bohemia.

Figure 3 EDX analysis of zippeite from Czech Republic, Jáchymov, Bohemia

Figure 4 Raman spectra at 298 and 77 K and infrared spectra of zippeite in the 650 to 1250 cm⁻¹ region.

Figure 5 Infrared spectra of zippeite in the 1250 to 1750 cm⁻¹ region.

Figure 6 Raman spectra at 298 and 77 K and infrared spectra of zippeite in the 100 to 650 cm⁻¹ region.

Figure 7 Raman spectra at 298 and 77 K and infrared spectra of zippeite in the 2500 to 3700 cm⁻¹ region.