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Raman spectroscopy study of the uranyl oxyhydroxide hydrates becquerelite, billietite, curite, schoepite, and vandendriesscheite

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Abstract

Raman and infrared spectra of five uranyl oxyhydroxide hydrates, becquerelite, billietite, curite, schoepite and vandendriesscheite are reported. Observed bands are attributed to the $(UO_2)^{2+}$ stretching and bending vibrations, U-OH bending vibrations, H_2O and $(OH)^-$ stretching, bending and libration modes. U-O bond lengths in uranyls and O-H…O bond lengths are calculated from the wavenumbers assigned to the stretching vibrations. They are close to the values inferred and/or predicted from the X-ray single crystal structure. The complex hydrogen-bonding network arrangement was proved in the structures of all minerals studied. This hydrogen bonding contributes to the stability of these uranyl minerals.

Key words
Uranyl oxyhydroxide hydrate minerals, becquerelite, billietite, curite, schoepite, vandendriesscheite, Raman and infrared spectra, U-O bond lengths, molecular water, hydroxyl ions, hydrogen-bonding network

Introduction

The knowledge of the crystal structures of uranyl natural and synthetic inorganic phases is important for better understanding the genesis of uranium deposits, interaction of uranium mine and mill tailings with the environment, actinide transport in soils and the vadose zones and the performance of geological repositories for nuclear waste [1]. Uranyl minerals are also observed as products of alteration (hydration-oxidation weathering) of spent nuclear fuel [2]. Uranyl minerals exhibit considerable structural and chemical diversity, and reflects geochemical conditions dominant during their formation [3]. Uranyl oxide hydrates, such as the studied uranyl minerals schoepite, becquerelite, billietite, curite and vandendriescheite, may be understood especially as weathering products of uraninite in the oxidized zone of uranium deposits [4-6].

Crystal structures of these five orthorhombic minerals studied in this work are well known. The structure of becquerelite, $Ca[(UO_2)_6O_4(OH)_6].8H_2O$, contains six symmetrically distinct U^{6+} in the form of nearly linear uranyl, $(UO_2)^{2+}$ Each uranyl is coordinated by five additional anions in its equatorial plane thus forming uranyl pentagonal dipyramids which share equatorial edges and vertices creating $[(UO_2)_6O_4(OH)_6]^{2-}$ sheets parallel to (001). The sheet is based upon the α-U_3O_8 (protasite) anion topology [7]. The symmetrically distinct Ca^{2+} cation is coordinated by four uranyl oxygens and four water molecules in the interlayer. Four other water molecules are also hydrogen bonded in the interlayer [8].

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The crystal structure of billietite, $Ba[(UO_2)_6O_4(OH)_6] \cdot 8H_2O$, contains also six symmetrically distinct U^{6+} in the form of uranyl. There are two different uranyl anion sheets in the billietite structure. The first sheet is formed of uranyl pentagonal dipyramids and tetragonal dipyramids in the ration 4:1 which share edges and vertices while the second sheet is created only of uranyl pentagonal dipyramids. In the interlayer, there is only one symmetrically distinct Ba^{2+} cation coordinated by six uranyl oxygens and four water molecules. The remaining four water molecules are hydrogen-bonded only [6,9]. Pagoaga et al. published a single crystal structure analysis of billietite and assumed that this mineral contains six (OH)⁻ but only four water molecules [10]. Pagoaga's conclusion was recently disproved neither on synthetic billietite [11] nor by single crystal structure analysis of billietite [9]. Protasite sheet anion topology is characteristic for the layer structure of becquerelite and billietite [1,7,12].

The crystal structure of curite, $Pb_{3+x}(H_2O)_2[(UO_2)_4O_{4+x}(OH)_{3-x}]_2$, contains three symmetrically distinct U^{6+} as uranyls, which coordinate in its equatorial plane oxygens or hydroxyls to form uranyl square dipyramids and uranyl pentagonal dipyramids that share edges and corners to form sheets oriented parallel to (100). Two symmetrically distinct Pb^{2+} cations and one water molecule are located in the interlayer. Some variability was observed in the Pb content [13-15]. The structure of schoepite, $[(UO_2)_8O_2(OH)_{12}] \cdot 12H_2O$, contains 8 symmetrically distinct U^{6+} as uranyls forming a neutral $[(UO_2)_8O_2(OH)_{12}]$ sheets of edge- and corner sharing $UO_2(O,OH)_5$ pentagonal dipyramids. The neutral sheets are hydrogen-bonded to each other through interstitial water molecules. The schoepite anion sheets are topologically identical to the sheets found in fourmarierite. In the schoepite structure, there are twelve symmetrically distinct water molecules in the interlayer, forming pentagonal rings with two linking water molecules [1,12,16].

The structure of vandendriesscheite, chemical formula sample studied by Burns [17] is $Pb_{1.57}[(UO_2)_{10}O_6(OH)_{11}] \cdot 11H_2O$, contains ten symmetrically distinct U^{6+} in the form of uranyls coordinating five equatorial oxygen and hydroxyl anions to form uranyl pentagonal dipyramidal coordination polyhedra. The uranyl polyhedra link by sharing equatorial edges to form sheets parallel to (001). In the interlayer, there are two symmetrically distinct Pb^{2+} cations coordinated by uranyl oxygens and water molecules and eleven symmetrically distinct water molecules. The Pb(1) cation is coordinated by nine anions, six are oxygen atoms and three are water molecules. The Pb(2) cation is coordinated by eight anions – five are uranyl oxygens and three are water molecules. The remaining water molecules are held in the crystal structure by hydrogen bonds only [17]. From the uranyl sheet anion topology point of view, the structure of curite is classified as containing sheet based upon anion topologies with triangles, squares and pentagons [1,18]. According to Burns [1] the structures of other studied uranyl minerals are characterized by sheets based upon anion topologies containing triangles and pentagons [1]. However, in the structure of billietite, there are two types of uranyl anion sheets one containing uranyl pentagonal dipyramids and one with pentagonal and tetragonal dipyramids [9].

Hydrogen-bonding network arranged in the structures of these minerals plays an important role in the formation and stability of these minerals as discussed generally by Hawthorne and Schindler and Hawthorne [19-21]. Wheeler et al. [22] and Hoekstra and Siegel [23] [and references therein] mentioned the "memory effect" connected with the formation of phases in the UO_3-H_2O system and concluded that minor differences in structure, e.g. arrangement of hydroxyl groups or water molecules must determine e.g. the decomposition route to be followed even though these differences are not apparent in the X-ray powder

patterns. The variations in $UO_3.2H_2O$ spectra studied by Wheeler et al. [22] support this conclusion. Frost et al. [24] discussed this problem in relation to selected uranophanes. This may be also the case of minerals studied in this paper.

Čejka [11] [and references therein] reviewed infrared spectra of becquerelite, billietite, schoepite, curite and synthetic vandendriescheite-type phases. Wavenumbers of infrared bands of becquerelite, billitetite, curite and schoepite without any detailed assignment were published by Povarenykh [25]. Čejka et al. [11,26,27] presented infrared spectra of becquerelite, billietite and curite, and synthetic becquerelite, billietite and protasite. Amayri et al. [28] recently published the infrared spectrum of synthetic becquerelite. Infrared and Raman spectra of synthetic phases in the UO_3-H_2O system were reviewed in detail by Hoekstra and Siegel [23] [and references therein]. The infrared spectrum of schoepite was partly mentioned also by Allen et al. [29], who found two bands at 885 and 930 cm^{-1} and assigned them to the $(UO_2)^{2+}$ stretching vibrations. In the both papers no relation was established between chemical formula of schoepite (its simplified formula is $UO_3. 2.25H_2O$) [30,31] and synthetic $UO_3. 2H_2O$ (synthetic metaschoepite) the crystal structure of which was determined by Weller [32]. Maya and Begun discussed Raman spectrum of schoepite in the band region of the ν_1 $(UO_2)^{2+}$ symmetric stretching vibrations [33]. They observed two bands at 840 and 860 cm^{-1}.

The aim of this paper which is the part of a systematic vibrational spectroscopy studies of minerals from the oxide zone (secondary minerals) inclusive the uranyl minerals, is to present and discuss Raman spectra of becquerelite, billietite, curite, schoepite and vandendriesscheite, to compare them with their infrared spectra, to use wavenumbers of the ν_1 and ν_3 $(UO_2)^{2+}$ for calculation of U-O bond lengths in uranyls and to infer shortly the hydrogen-bonding network in the structure of the studied minerals. The observed data are compared with those from X-ray single crystal structure analysis. Interpretation of the Raman and infrared spectra was made on the basis of the theses by Perrin [34] and Dothée [35] and especially in two published papers by Dothée et al. [36-38]. Dothée attributed the bands in the Raman and infrared spectra of synthetic compreignacite, $K_2[(UO_2)_6O_4(OH)_6]. 8H_2O$, and its deuteroanalogue and discussed the assignment in detail, inclusive of vibrations of $U_3(OH)$, $U_3(O)$ and $U_2O(OH)$ units which may participate in the crystal structure of the studied minerals and also of some other uranyl oxide hydrates. This assignment was also used in the infrared spectroscopy studies of some uranyl oxide hydrates and their synthetic analogues [11,27].

Experimental

Minerals

The minerals used in this work originated from Museum Victoria and are chiefly from Australian mineral deposits. The minerals, where possible, were analysed for phase purity by powder X-ray diffraction and for chemical analysis by EDX techniques.

Raman microprobe spectroscopy

The crystals of uranyl oxyhydroxide hydrates were placed 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 [39-42].

Infrared absorption 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).

Spectroscopic manipulation such as baseline adjustment, smoothing and normalisation were performed using the Spectracalc software package GRAMS (Galactic Industries Corporation, NH, USA). Band component analysis was undertaken using the Jandel 'Peakfit' software package, which enabled the type of fitting, function to be selected and allows specific parameters to be fixed or varied accordingly. Band fitting was done using a Lorentz-Gauss cross-product function with the minimum number of component bands used for the fitting process. The Lorentz- Gauss ratio was maintained at values greater than 0.7 and fitting was undertaken until reproducible results were obtained with squared correlations of r2 greater than 0.995. Further details of the band fitting procedure has been published. [43-45]

Results and discussion

Raman bands of the vibrations of the U-O and U-OH units
(infrared bands are given in parentheses)

The linear $(UO_2)^{2+}$ group, point group $D_{\infty h}$, has four normal vibrations but only three fundamentals: the Raman active ν_1 symmetric stretching vibration, the infrared active ν_2 (δ) doubly degenerate bending vibration, and the infrared active ν_3 antisymmetric stretching vibration [24,46-49]. The decrease of uranyl group symmetry may result in the splitting of the ν_2 $(UO_2)^{2+}$, and in activation of the ν_1 $(UO_2)^{2+}$ in the infrared spectrum and of the ν_3 $(UO_2)^{2+}$ in the Raman spectrum. Excluding the possibility of the Fermi effect and lattice vibrations, the splitting the uranyl stretching vibrations may be inferred because of the formula number in the unit cell and factor group – correlation analysis [see the references [50-53]. As mentioned above, there are six distinct U^{6+} in ther structure of becquerelite (space group Pn21a = C2v9; Z = 4), billietite (space group Pbn21 = C2v7; Z = 4), three symmetrically distinct U^{6+} in the structure of curite (Pnam = D2h16; Z = 2), eight symmetrically distinct U^{6+} in the structure of schoepite (space group P21ca = C2v5; Z = 4), and ten symmetrically distinct U^{6+} in the structure of vandendriesscheite (space group Pbca = D2h15; Z = 8).

The two empirical relations by Bartlett and Cooney [54] used in this paper for the calculation of the U-O bond lengths in uranyls from the wavenumbers of the $(UO_2)^{2+}$ stretching vibrations are $R_{U-O} = 106.5[\nu_1(UO_2)^{2+}]^{-2/3} + 0.575$ Å, and $R_{U-O} = 91.41[\nu_3(UO_2)^{2+}]^{-2/3} + 0.804$ Å. Bands related to the ν_1 $(UO_2)^{2+}$ symmetric stretching vibrations and calculated U-O bond lengths in uranyls are given: 838.3/1.773, 831.1/1.780 and 813.7/1.797; (836/1.775, 806/1.805 and 798/1.813) cm^{-1}/Å (becquerelite), ~830/1.7805, 810/1.801, 800.3/1.811 and 794.6/1.816 ; (850/1.762, 829/1.782 and 804/1.807) cm^{-1}/Å (billietite), 803/1.808 and 791/1.820 ; (848/1.764 and 795/1.816) cm^{-1}/Å (curite), 855.4/1.818 , 838.7/1.773, 826.2/1.785, 817.1/1.794 and 802.3/1.808 cm^{-1}/Å (schoepite), and 852.3/1.760, 840.6/1.771, 831.9/1.779, 819.4/1.791; (791/1.820) cm^{-1}/Å (vandendriesscheite). These values are in close agreement with the average U-O bond lengths from the X-ray single crystal structure analysis becquerelite 1.7939 Å [8], billietite 1.8014 Å [9] curite 1.84 Å [55], 1.792 Å [56], 1.844 Å [57], schoepite 1.779 Å [31], and vandendriesscheite 1.7955 Å [17]. Some bands may be attributed to the δ U-OH bending vibrations. A coincidence of the ν_1 $(UO_2)^{2+}$ and δ U-OH bending vibrations in this region is also possible.

Bands at 879.4/1.800 and 854.4/1.819; (895/1.788) cm^{-1}/Å (becquerelite), 872.6/1.805; (910/1.777, 850/1.762) cm-1/Å (billietite), 886/1.795 (960/1.743, 938/1.758, 912/1.776 and 876/1.802) cm^{-1}/Å (curite), 897.5/1.786, 886.2/1.796, 869.6/1.807 and 855.4/1.818 cm^{-1}/Å (schoepite), and 854.3/1.819 (912/1.776 and 883/1.797) cm^{-1}/Å) (vandendriescheite). Similarly as in the case of the region of the ν_1 $(UO_2)^{2+}$ vibrations, some of the bands observed in this region may be connected with the δ U-OH vibrations. A coincidence of the ν_3 $(UO_2)^{2+}$ and δ U-OH cannot be excluded. Calculated U-O bond lengths in uranyl are also in good agreement with those from the X-ray single crystal structure analysis (see above). Bands at 260.3 and 238.4 cm^{-1} (becquerelite), 259.1 and 244.4 cm^{-1} (billietite), 272 and 250 cm^{-1} (curite), 273.8 and 247.8 cm^{-1} (schoepite) and 273.8 and 247.8 cm^{-1} (vandendriesscheite) are connected with the split doubly degenerate ν_2 (δ) $(UO_2)^{2+}$ bending vibrations.

Bands in the range 560 – 100 may be simply assigned to the ν (U-Oequatorial) (560 – 300 cm^{-1}), ν (δ)$(UO_2)^{2+}$ bending vibrations (274 – 238 cm^{-1}), and molecular deformation and lattice modes (lower than 220 cm^{-1}). However, according to Dothée, a more detailed attribution is possible [36-38]. Bands in the range 560 – 390 (591 – 532) cm^{-1} are assigned to the ν_3 (U_3O) bridge elongation, 370 – 328 cm^{-1} to the ν $U_3(OH)_3$ or $U_2O(OH)$ groups elongation, 321 – 290 cm^{-1} to the γ (U_3O) out-of-plane bending vibrations, 220 – 207 to the γ ($U_3(OH)_3$ out-of-plane bending vibrations, 200 – 193 cm^{-1} to the δ ($U_3(OH)_3$) in-plane bending vibrations, and 171 – 108 cm^{-1} to the $(UO_2)^{2+}$ translations and rotations. Bands in the region 1552 – 1300 (1544 – 1300) cm^{-1} are assigned to overtones or combination bands, however, they may be also attributed to the δ U-OH bending vibrations. Infrared bands in the range 1185 – 960 cm^{-1} may be connected also with the δU-OH bending vibrations. Bands in the range 780 – 702 (784 – 632) cm^{-1} are attributed to the γ U-OH out-of-plane bending vibrations of librations of water molecules.

Bands in the range 2600 – 2000 cm^{-1} may be connected with overtones and/or combination bands.

Raman bands of vibrations of water molecules and hydroxyl ions

(infrared bands are given in parentheses)

All studied uranyl oxide hydrate minerals are characterized by complex layer (sheet) structures and relatively complicated hydrogen-bonding network. Uranyl oxygens and hydroxyl ions form the layers and water molecules from the interlayers may participate in these hydrogen-bonding network. The Libowitzky's correlation of O-H stretching wavenmumbers and O-H···O hydrogen bond lengths [58] enables to infer the hydrogen bond lengths from the wavenumbers of bands connected with νOH stretching vibrations of water molecules and hydroxyl ions. Bands approximately in the range 3700 – 3500 cm^{-1} may be related to free or very weakly hydrogen-bonded hydroxyls, while bands at lower wavenumbers exhibit stronger hydrogen-bonded water molecules and/or hydroxyls and O-H···O bond lengths ~2.4 – (>3.2) Å. Studies have shown a strong correlation between OH stretching frequencies and both O···O bond distances and H···O hydrogen bond distances [59-63]. Libowitzky [58] showed that a regression function can be employed relating the hydroxyl stretching frequencies with regression coefficients better than 0.96 using infrared spectroscopy. The function is described as: $\nu_1 = (3592 - 304) \times 10^{9 \frac{-d(O-O)}{0.1321}}$ cm^{-1}. Thus OH---O hydrogen bond distances may be calculated using the Libowitzky empirical function.

The values for the OH stretching vibrations listed in Table 1 provide
a)   for becquerelite hydrogen bond distances of 2.989 Å (3546 cm^{-1}), 2.7214 Å (3248.6 cm^{-1}) and 2.7077 Å (3211 cm^{-1});
b)   for billietite hydrogen bond distances of 3.072 Å (3567 cm^{-1}), 2.8775 Å (3486 cm^{-1}), 2.7969 Å (3398 cm^{-1}), and 2.717 Å (3237 cm^{-1});
c)   hydrogen bond distances for schoepite 2.965 Å (3539 cm^{-1}), 2.801 Å (3404 cm^{-1}) and 2.705 Å (3204 cm^{-1});
d)   hydrogen bond distances for vandendriesscheite 2.947 Å (3529 cm^{-1}), 2.864 Å (3475 cm^{-1}), 2.726 Å (3261 cm^{-1}), 2.6295 Å (2904 cm^{-1}), and 2.620 Å (2853 cm^{-1})
e)   hydrogen bond distances for curite 2.949 Å (3531 cm^{-1}), 2.885 Å (3493 cm^{-1}), 2.811 Å (3418cm^{-1}), and 2.527 Å (2102 cm^{-1}); The 2102 cm-1 band is here attributed to a OH stretching vibration. Another assignment may be to an overtone or combination band.

These calculated O-H…O bond lengths are close to the values inferred from the single crystal structure analysis.

The hydrogen bond distances previously established can be used to predict the hydroxyl stretching frequencies. The spectrum of uranyl oxyhydroxides may be divided into two groups of OH stretching wavenumbers; namely 3300–3700 cm^{-1} and 2900–3300 cm^{-1}. This distinction suggests that the strength of the hydrogen bonds as measured by the hydrogen bond distances can also be divided into two groups according to the H-bond distances. An arbitrary cut-off point might be 2.74 Å based upon the wavenumber 3300 cm^{-1}. Thus the bands at positions greater than 3300 cm^{-1} listed above may be described as weak hydrogen bonds and the bands at positions less than 3300 cm^{-1} as relatively strong hydrogen bonds. Such hydrogen bond distances are typical of secondary minerals. A range of hydrogen bond distances are observed from reasonably strong to weak hydrogen bonding. This range of hydrogen bonding contributes to the stability of the minerals.Bands in the range 1675 – 1590 cm^{-1} are assigned to the δ H$_2$O bending vibrations. Some bands especially in the range 800 – 600 cm^{-1} may be attributed to libration modes of water molecules or γ U-OH out-of-plane

bending vibrations. The number of bands assigned to the vibrations of water molecules and hydroxyls proves that structurally non-equivalent units are present in the structure of some of the minerals studied. This is in agreement with the single crystal structure analysis and is also supported by thermal analysis of the minerals studied [see e.g. 25].

Conclusions

(1) Raman and infrared spectra of five uranyl oxyhydroxide hydrates, bequerelite, billietite, curite, schoepite and vandendriesscheite with characteristic sheet structures are studied.
(2) All observed bands were tentatively interpreted and the corresponding $(UO_2)^{2+}$ stretching and bending vibrations, U-OH bending vibrations, H_2O stretching and bending vibrations and libration modes, and $(OH)^-$ vibrations were attributed.
(3) U-O bond lengths in uranyl were calculated from the wavenumbers of the $(UO_2)^{2+}$ stretching vibrations with two empirical relations by Bartlett and Cooney [54] Obtained results are in close agreement with the values inferred from the X-ray single crystal structure.
(4) O-H…O hydrogen bond lengths were calculated using the corresponding bands attributed to the OH stretching vibrations and the empirical correlation by Libowitzky. Calculated distances are close to the values predicted on the basis of single crystal structure.
(5) From the complex arrangement of hydrogen- bonding network may be inferred the contribution of hydrogen bonding to the stability of the minerals. This is in agreement with and supported by the Hawthorne's conception of the important role of water molecules and OH groupings on the origin, formation and stability of minerals.

Acknowledgements

References

1. Burns, PC. *Canadian Mineralogist* 2005**; 43**: 1839.
2. Wronkiewicz, DJ, Bates, JK, Wolf, SF, Buck, EC. *Journal of Nuclear Materials* 1996**; 238**: 78.
3. Locock, AJ, Burns, PC. *Journal of Solid State Chemistry* 2004**; 177**: 2675.
4. Frondel, C. *U.S. Geological Survey Bulletin* 1958**; No. 1064**: 400 pp.
5. Frondel, C, Weeks, AD. *Proc. UN Intern. Conf. Peaceful Uses Atomic Energy, 2nd, Geneva, 1958* 1958**; 2**: 277.
6. Finch, R, Murakami, T. *Reviews in Mineralogy* 1999**; 38**: 91.
7. Burns, PC, Miller, ML, Ewing, RC. *Canadian Mineralogist* 1996**; 34**: 845.
8. Locock, AJ, Burns, PC. *Journal of Solid State Chemistry* 2002**; 163**: 275.
9. Finch, RJ, Burns, PC, Hawthorne, FC, Ewing, RC. *Canadian Mineralogist* 2006**; in press**: 0000.
10. Pagoaga, MK, Appleman, DE, Stewart, JM. *American Mineralogist* 1987**; 72**: 1230.
11. Cejka, J, Sejkora, J, Skala, R, Cejka, J, Novotna, M, Ederova, J. *Neues Jahrbuch fuer Mineralogie, Abhandlungen* 1998**; 174**: 159.
12. Burns, PC. *Reviews in Mineralogy* 1999**; 38**: 23.
13. Cejka, J. *Neues Jahrbuch fuer Mineralogie, Monatshefte* 1998: 385.
14. Li, Y, Burns, PC, Gault, RA. *Canadian Mineralogist* 2000**; 38**: 153.
15. Burns, PC, Hill, FC. *Canadian Mineralogist* 2000**; 38**: 163.
16. Finch, RJ, Hawthorne, FC, Ewing, RC. *Materials Research Society Symposium Proceedings* 1996**; 412**: 361.
17. Burns, PC. *American Mineralogist* 1997**; 82**: 1176.
18. Miller, ML, Finch, RJ, Burns, PC, Ewing, RC. *Materials Research Society Symposium Proceedings* 1996**; 412**: 369.
19. Hawthorne, FC. *Zeitschrift fuer Kristallographie* 1992**; 201**: 183.
20. Hawthorne, FC. *Geologiya Rudnykh Mestorozhdenii* 2003**; 45**: 100.
21. Schindler, M, Hawthorne, FC. *Canadian Mineralogist* 2004**; 42**: 1601.
22. Wheeler, VJ, Dell, RM, Wait, E. *Journal of Inorganic and Nuclear Chemistry* 1964**; 26**: 1829.
23. Hoekstra, HR, Siegel, S. *Journal of Inorganic and Nuclear Chemistry* 1973**; 35**: 761.
24. Frost, RL, Weier, ML, Bostrom, T, Cejka, J, Martens, W. *Neues Jahrbuch fuer Mineralogie, Abhandlungen* 2005**; 181**: 271.
25. Povarennykh, AS. *Konstitutsiya i Svoistva Mineralov* 1979**; 13**: 78.
26. Cejka, J, Urbanec, Z. *Casopis Narodniho Muzea v Praze, Rada Prirodovedna* 1983**; 152**: 26.
27. Cejka, J. *Reviews in Mineralogy* 1999**; 38**: 521.
28. Amayri, S, Arnold, T, Foerstendorf, H, Geipel, G, Bernhard, G. *Canadian Mineralogist* 2004**; 42**: 953.
29. Allen, PG, Shuh, DK, Bucher, JJ, Edelstein, NM, Palmer, CEA, Silva, RJ, Nguyen, SN, Marquez, LN, Hudson, EA. *Radiochimica Acta* 1996**; 75**: 47.
30. Miller, ML, Finch, RJ, Burns, PC, Ewing, RC. *Journal of Materials Research* 1996**; 11**: 3048.
31. Finch, RJ, Cooper, MA, Hawthorne, FC, Ewing, RC. *Canadian Mineralogist* 1996**; 34**: 1071.
32. Weller, MT, Light, ME, Gelbrich, T. *Acta Crystallographica, Section B: Structural Science* 2000**; B56**: 577.
33. Maya, L, Begun, GM. *Journal of Inorganic and Nuclear Chemistry* 1981**; 43**: 2827.
34. Perrin, A. Université de Rennes 1976.
35. Dothée, D. Université de Franche-Comté 1980.
36. Dothee, DG, Fahys, BR, Camelot, MM. *Bulletin de la Societe Chimique de France* 1982: 103.
37. Dothee, DG, Camelot, MM. *Bulletin de la Societe Chimique de France* 1982: 97.
38. Dothee, D. Vibrational spectroscopy of hydrated potassium hexauranate for the phase study of the uranium(VI) oxide-potassium chloride-water system; Univ. Besancon,Fr., 1980; pp. 148 pp.
39. Frost, RL, Weier, ML. *Thermochimica Acta* 2003**; 406**: 221.
40. Frost, RL, Weier, ML, Kloprogge, JT. *Journal of Raman Spectroscopy* 2003**; 34**: 760.
41. Frost, RL, Weier, ML. *Journal of Raman Spectroscopy* 2003**; 34**: 776.
42. Frost, RL, Weier, ML. *Thermochimica Acta* 2004**; 409**: 79.
43. Frost, RL, Weier, ML, Martens, W, Cejka, J. *Vibrational Spectroscopy* 2006**; 41**: 205.
44. Frost, RL, Cejka, J, Weier, ML, Martens, W. *Spectrochimica Acta, Part A: Molecular and Biomolecular Spectroscopy* 2006**; 63A**: 305.
45. Frost, RL, Cejka, J, Weier, ML, Martens, W, Kloprogge, JT. *Spectrochimica Acta, Part A: Molecular and Biomolecular Spectroscopy* 2006**; 64A**: 308.
46. Frost, RL, Henry, DA, Erickson, K. *Journal of Raman Spectroscopy* 2004**; 35**: 255.

47. Frost, RL, Carmody, O, Erickson, KL, Weier, ML, Cejka, J. *Journal of Molecular Structure* 2004; **703**: 47.
48. Frost, RL, Erickson, KL, Weier, ML, Carmody, O, Cejka, J. *Journal of Molecular Structure* 2005; **737**: 173.
49. Frost, RL, Cejka, J, Weier, ML, Martens, WN. *Journal of Molecular Structure* 2006; **788**: 115.
50. Volod'ko, LV, Komyak, AI, Sleptsov, LE. *Zh. Prikl. Spektroskopii* 1965; **3**: 56.
51. Volod'ko, LV, Komyak, AI, Umreyko, DS *Uranilovye sojedinenija (Uranyl compounds)*: Belorusskogo Universiteta Minsk, 1981; Vol. Vol. 1, Izdat.
52. Parshkov, OM; Saratovskogo Universiteta, 1972.
53. Caville, C, Poulet, H, Mathieu, J-P. *Bull. Soc. Franc. Miner. Crist.* 1973; **96**: 10.
54. Bartlett, JR, Cooney, RP. *Journal of Molecular Structure* 1989; **193**: 295.
55. Mereiter, K. *Tschermaks Miner. Petr. Mitt* 1979; **26**: 279.
56. Taylor, JC, Stuart, WI, Mumme, IA. *J. Inorg. Nucl. Chem.* 1981; **43**: 2419.
57. Li, Y, Burns, PC. *Can. Mineral.* 2000; **38**: 727.
58. Libowitzky, E. *Monatshefte fuer Chemie* 1999; **130**: 1047.
59. Libowitzky, E. *Monatshefte fuer Chemie* 1999; **130**: 1047.
60. Emsley, J. *Chemical Society Reviews* 1980; **9**: 91.
61. Lutz, H. *Structure and Bonding (Berlin, Germany)* 1995; **82**: 85.
62. Mikenda, W. *Journal of Molecular Structure* 1986; **147**: 1.
63. Novak, A. *Structure and Bonding (Berlin)* 1974; **18**: 177.