

Structures of uranyl peroxide hydrates: a first-principles study of studtite and metastudtite†

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The structures of the only known minerals containing peroxide, namely studtite [(UO₂)O₂(H₂O)₄] and metastudtite [(UO₂)O₂(H₂O)₂], have been investigated using density functional theory. The structure of metastudtite crystallizing in the orthorhombic space group *Pnma* (*Z* = 4) is reported for the first time at the atomic level and the computed lattice parameters, *a* = 8.45, *b* = 8.72, *c* = 6.75 Å, demonstrate that the unit cell of metastudtite is larger than previously reported dimensions (*Z* = 2) derived from experimental X-ray powder diffraction data.

Introduction

Studtite, (UO₂)O₂(H₂O)₄, and metastudtite, (UO₂)O₂(H₂O)₂, are among the important corrosion phases that may form on spent nuclear fuel (SNF) exposed to water.^{1–3} These hydrates of uranyl peroxide, which incorporate (O₂)^{2–} generated by α-radiolysis of water,^{4–6} may play a crucial role in the degradation of nuclear fuel in the context of nuclear reactor accidents or geological repositories.^{7–9} Studtite and metastudtite are also the only two known minerals containing peroxide, and studtite is the only one with a fully elucidated structure.¹⁰ In addition to playing a role for corrosion of SNF, studtite may retain released radionuclides through incorporation into its structure.^{11,12}

The structure of synthetic uranyl peroxide dihydrate, (UO₂)O₂(H₂O)₂, was first characterized by Zachariasen¹³ in 1944 as orthorhombic with unit-cell dimensions *a* = 6.50 ± 0.03, *b* = 4.21 ± 0.02, *c* = 8.74 ± 0.05 Å and uranium positions at (000) and ($\frac{111}{222}$). The X-ray diffraction (XRD) pattern of (UO₂)O₂(H₂O)₂ was published by Ukazi in 1959.¹⁴ In 1961, Sato¹⁵ found that two crystalline modifications of uranium peroxide hydrate exist and that their formation depends on temperature: (UO₂)O₂(H₂O)₄ precipitates below 50 °C following addition of H₂O₂ to an aqueous solution containing uranyl ions, whereas (UO₂)O₂(H₂O)₂ precipitates above 70 °C; a mixture of the two precipitates at 60 °C. Sato also demonstrated that (UO₂)O₂(H₂O)₄ is converted to (UO₂)O₂(H₂O)₂ by drying in air at 100 °C or in vacuum for 24 hours at room temperature. The thermal decomposition of both (UO₂)O₂(H₂O)₄ and (UO₂)O₂(H₂O)₂ was also studied by Cordfunke *et al.* in 1963,^{16,17} while Debets¹⁸ reinvestigated their XRD patterns and

reported unit-cell dimensions for (UO₂)O₂(H₂O)₂: *a* = 6.50 ± 0.02, *b* = 4.211 ± 0.005, *c* = 8.78 ± 0.01 Å (*V* = 240 ± 1 Å³; *Z* = 2) with an orthorhombic body-centered structure (space group *Immm*); and for (UO₂)O₂(H₂O)₄: *a* = 11.85, *b* = 6.785, *c* = 4.245 Å and β = 93°37' with a face-centered monoclinic structure.

The mineral studtite was originally described in 1947 by Vaes¹⁹ as a hydrated carbonate of uranium from a qualitative chemical analysis; however, subsequent chemical and powder XRD investigations by Walenta²⁰ in 1974 demonstrated that studtite is identical to synthetic (UO₂)O₂(H₂O)₄, with monoclinic symmetry (space group *C2*, *Cm* or *C2/m*) and unit-cell dimensions *a* = 11.85, *b* = 6.80, *c* = 4.25 Å and β = 93°51'. Subsequent analyses of studtite from the type locality (Shinkolobwe) confirmed Walenta's unit-cell determination.²¹ *a* = 11.85, *b* = 6.78, *c* = 4.24 Å, β = 93.62°. The structure of studtite was reported in 2003 by Burns and Hughes,²² who showed it to be monoclinic, space group *C2/c*, with unit-cell dimensions *a* = 14.068(6), *b* = 6.721(3), *c* = 8.428(4) Å and β = 123.356(6)° (*V* = 665.6(3) Å³; *Z* = 4), being approximately twice the size of the previously accepted unit-cell volume with *Z* = 2. Burns and co-workers also reported the thermodynamic stability of the peroxide-containing uranyl minerals the same year.⁷

Walenta had demonstrated that, when heated to 60 °C, natural studtite transforms irreversibly to the dihydrate, (UO₂)O₂(H₂O)₂, with unit cell parameters *a* = 6.51 ± 0.01, *b* = 8.78 ± 0.02, *c* = 4.21 ± 0.01 Å [*V* = 240.6 ± 1 Å³; *Z* = 2; the *b* and *c* parameters as chosen by Debets¹⁶ were exchanged to comply with the *c* < *a* < *b* recommendation of the International Mineralogical Association (IMA)], and Walenta suggested that the dihydrate may occur as a mineral. Naturally occurring (UO₂)O₂(H₂O)₂ was subsequently reported by Deliens and Piret²³ in 1983, who proposed the name metastudtite, and showed it to be equivalent to the synthetic dihydrate (*a* = 6.51(1), *b* = 8.78(2), *c* = 4.21(1) Å; *V* = 240.6(1.5) Å³, *Z* = 2).

However, to the best of our knowledge, no refined structure of metastudtite has been published to date. Interestingly, Burns and

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Hughes²² suggested that, in light of their structure determination for studtite, it is likely that the $c = 4.21$ Å cell parameter previously reported for metastudtite^{20,23} is probably erroneous, since the repeat length of the chains of polyhedra in studtite is $c = 8.428(4)$ Å and both studtite and metastudtite are expected to contain similar chains of coordination polyhedra. In the absence of well-established crystallographic data for metastudtite, Ostanin and Zeller²⁴ proposed, on the basis of first-principles calculations, an energetically favorable orthorhombic cell with space group D_{2h}^{16} ($Pnma$) and lattice parameters $a = 8.677$, $b = 6.803$, $c = 8.506$ Å ($Z = 4$) and claimed good agreement with experimental XRD data of Deliens and Piret.²³ However, no crystallographic data for the atomic positions of this candidate structure of metastudtite were reported by Ostanin and Zeller and the computed equilibrium volume was $V = 502.06$ Å³ and stated to be 4.3% larger than the experimental estimate.

In this work, the structural properties of studtite and metastudtite have been systematically investigated using density functional theory. The structure of metastudtite crystallizing in the orthorhombic $Pnma$ space group ($Z = 4$) is reported for the first time at the atomic level and the computed lattice parameters suggest that the unit cell of metastudtite is larger than previously reported dimensions ($Z = 2$) derived from experimental XRD data. Particular emphasis is placed here on the determination of an accurate crystal structure of metastudtite needed for thermodynamic properties calculations.

Details of our computational approach are given in the next section, followed by a complete analysis and discussion of our results. A summary of our findings and conclusions is presented in the last section of the manuscript.

Computational methods

First-principles total energy calculations were performed using the spin-polarized density functional theory (DFT), as implemented in the Vienna *ab initio* simulation package (VASP).²⁵ The exchange-correlation energy was calculated using the generalized gradient approximation (GGA), with the parametrization of Perdew and Wang (PW91).^{26,27} The PW91 functional was found in previous studies to correctly describe the geometric parameters and properties of various uranium oxides and uranium-containing structures observed experimentally.^{28–30}

Although theoretical approaches that go beyond standard DFT are needed to account for the strong on-site Coulomb repulsion between U 5f electrons in bulk UO₂, previous studies on studtite and uranyl-organic coordination polymers show that standard DFT is appropriate to describe those systems.^{24,30}

The interaction between valence electrons and ionic cores was described by the projector augmented wave (PAW) method.^{31,32} The U(6s,6p,6d,5f,7s) and O(2s,2p) electrons were treated explicitly as valence electrons in the Kohn–Sham (KS) equations and the remaining core electrons together with the nuclei were represented by PAW pseudopotentials. The KS equations were solved using the blocked Davidson³³ iterative matrix diagonalization scheme followed by the residual vector minimization method. The plane-wave cutoff energy for the electronic wavefunctions was set to a value of 500 eV, ensuring the total energy of the system to be converged to within 1 meV per atom.

Electronic relaxation was performed with the conjugate gradient method accelerated using the Methfessel–Paxton Fermi-level smearing³⁴ with a Gaussian width of 0.1 eV.

Ionic relaxation was carried out using the quasi-Newton method and the Hellmann–Feynman forces acting on atoms were calculated with a convergence tolerance set to 0.01 eV Å⁻¹. A periodic unit cell approach was used in the calculations. Structural relaxation was performed without symmetry constraints. The Brillouin zone was sampled using the Monkhorst–Pack k -point scheme³⁵ with k -point meshes of $2 \times 5 \times 3$ and $5 \times 3 \times 3$ for studtite and metastudtite, respectively. In structural relaxation calculations, the monoclinic structure with space group $C2/c$ ($Z = 4$) reported by Burns and Hughes²² was used as the starting geometry for studtite and a candidate structure crystallizing in the space group $Pnma$ ($Z = 4$), with twice the length of the experimental c dimension, was built for metastudtite based on the information reported by Ostanin and Zeller²⁴ and the suggestion of Burns and Hughes.²²

Results and discussion

Crystal structure of studtite

Consistent with XRD data,²² the computed equilibrium structure is monoclinic and crystallizes in the space group $C2/c$ ($Z = 4$; cf. Fig. 1). The calculated cell dimensions $a = 13.93$, $b = 6.84$, $c = 8.55$ Å and $\beta = 122.7^\circ$ ($V = 685.6$ Å³; $b/a = 0.49$, $c/a = 0.61$) are in close agreement with the XRD parameters of Burns and Hughes,²² *i.e.*, $a = 14.068(6)$, $b = 6.721(3)$, $c = 8.428(4)$ Å and $\beta = 123.356(6)^\circ$ ($V = 665.6$ Å³; $b/a = 0.48$, $c/a = 0.60$). The computed equilibrium volume is 3.0% larger than the experimental estimate, due to the fact that GGA calculations tend to overestimate the bond distances³⁶ and that standard DFT cannot account accurately for long-range intermolecular forces between adjacent chains.³⁷ However, this computed equilibrium volume is in better agreement with experiment than previous GGA calculations²⁴ predicting a volume of $V = 690.1$ Å³, *i.e.* 3.7% larger than experiment.

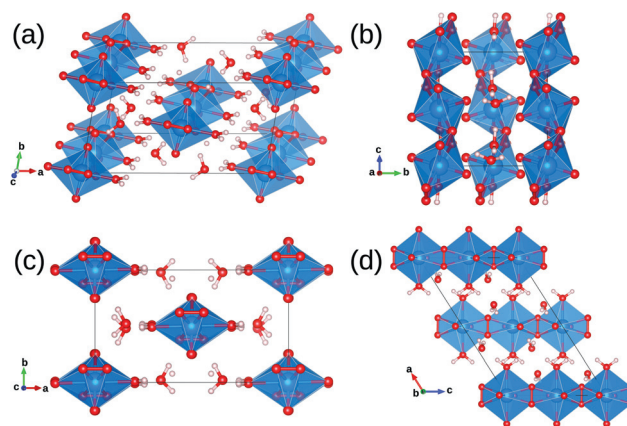


Fig. 1 Crystal unit cell of studtite (UO₂)O₂(H₂O)₄ (space group $C2/c$, $Z = 4$) relaxed with DFT at the GGA/PW91 level of theory. (a) View of the packing of chains showing the uranium coordination polyhedra. Views along the directions: (b) [100], (c) [001] and (d) [010]. Color legend: U, blue; O, red; H, white.

A detailed discussion of the atomistic structure of studtite was given by Burns and Hughes.²² As shown in Fig. 1, the studtite structure consists of extended chains propagating along the c axis. The ubiquitous uranyl unit is positioned with uranium on a $4a$ Wyckoff site ($\bar{1}$ symmetry) and coordinated by six equatorial oxygen atoms (on $8f$ Wyckoff sites) donated by symmetry-related pairs of water and peroxy groups. The local environment of the U metal center is hexagonal bipyramidal with two short axial U=O bonds, calculated (measured) to be both at a distance of 1.83 Å (1.769 Å), and a linear O=U=O angle, and with equatorial oxygen atoms at distances of 2.38 Å (2.365 Å) for peroxy oxygen atoms and 2.41 Å (2.395 Å) for water oxygen atoms. The peroxy atoms are μ^2 -bridging between symmetry-related uranium metal centers. The calculated (measured) dihedral angle between equatorial planes of successive uranyl ions along the chains is 0.2° (5.99°); as discussed in previous studies of one-dimensional uranium organic polymers,³⁰ this large deviation, compared to other structural parameters, suggests that interchain forces, which are not accurately described with standard DFT, may play a role in the relative orientation of adjacent uranium coordination polyhedral. Additional information on the computed and measured interatomic distances and angles in studtite is reported in the next section, along with the discussion of the metastudtite structure.

Crystal structure of metastudtite

Structural relaxation calculations predict that metastudtite crystallizes in the orthorhombic space group $Pnma$ ($Z = 4$) with lattice parameters $a = 6.75$, $b = 8.72$, $c = 8.45$ Å ($V = 497.4$ Å³; $b/a = 1.29$, $c/a = 1.25$). Assuming that the length of the experimental c dimension should be doubled,²² those cell dimensions are in good agreement with the corrected XRD parameters given by Deliens and Piret,²³ *i.e.* $a = 6.51(1)$, $b = 8.78(2)$, $c = 8.42(2)$ Å ($V = 481.3$ Å³; $b/a = 1.35$, $c/a = 1.29$). Let us note that the computed equilibrium volume is 3.3% larger than the experimental volume, *i.e.* close to the volume overestimation in the calculation of the studtite structure. The present calculations represent a slight improvement over the previous calculations of Ostanin and Zeller, who predicted lattice parameters $a = 6.803$, $b = 8.677$, $c = 8.506$ Å ($V = 502.1$ Å³; $b/a = 1.27$, $c/a = 1.25$), corresponding to an overestimation of the experimental volume by 4.3%. In order to comply with the IMA recommendation $c < a < b$, a transformation conserving the $Pnma$ symmetry was applied so that the final computed cell dimensions of metastudtite are given as $a = 8.45$, $b = 8.72$, $c = 6.75$ Å. A ball-and-stick representation of the resulting optimized crystal unit cell of metastudtite is shown in Fig. 2.

Using the orthorhombic structure optimized with DFT, the diffraction pattern of metastudtite was simulated using the Mercury³⁸ software and compared with the XRD pattern collected by Debets¹⁸ for synthetic $(\text{UO}_2)\text{O}_2(\text{H}_2\text{O})_2$. Let us note that previous experimental studies showed only minute differences between the XRD powder patterns for synthetic $(\text{UO}_2)\text{O}_2(\text{H}_2\text{O})_2$, natural metastudtite and heated natural studtite.²³ Although simulated and observed diffraction peaks were found to be in overall good agreement, some peak positions appeared slightly shifted due to the larger volume (+3.3%) of the unit cell

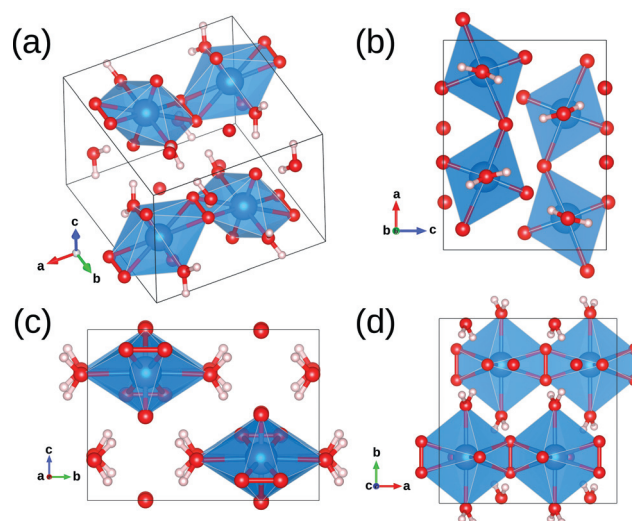


Fig. 2 Crystal unit cell of metastudtite $(\text{UO}_2)\text{O}_2(\text{H}_2\text{O})_2$ (space group $Pnma$, $Z = 4$) relaxed with DFT at the GGA/PW91 level of theory. (a) View of the packing of chains showing the uranium coordination polyhedra. Views along the directions: (b) $[010]$, (c) $[100]$ and (d) $[001]$. Color legend: U, blue; O, red; H, white.

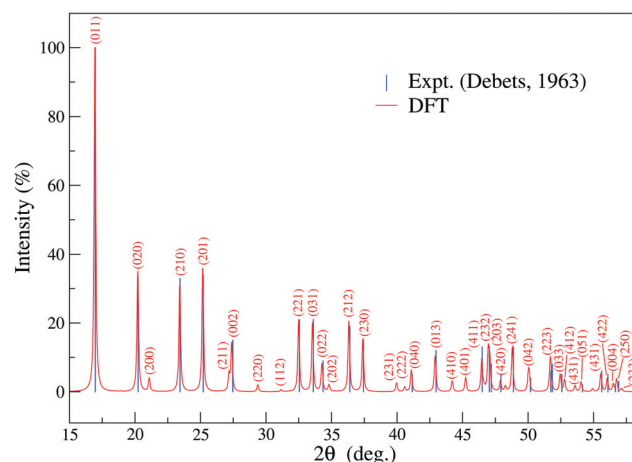


Fig. 3 X-ray diffraction pattern of metastudtite. The experimental powder diffraction pattern for Cu $K_{\alpha 1}$ radiation (Debets, 1963) is represented by blue lines. The diffraction pattern simulated from the orthorhombic structure (space group $Pnma$, $Z = 4$) reported in the present study is shown in red. A full-width at half-maximum (FWHM) parameter of 0.2 2θ was used in the simulation.

relaxed with DFT/GGA compared with the experimentally determined volume. As shown in Fig. 3, excellent agreement between simulated and observed diffraction patterns was ultimately achieved by a simple rescaling of the computed structure to fit experimental unit-cell dimensions, followed by ionic relaxation. The resulting atomic positions and fractional coordinates for the $(\text{UO}_2)\text{O}(\text{H}_2\text{O})$ motif (*cf.* Fig. 4) are reported in Table 1, and the corresponding interatomic distances and bond angles are given in Table 2.

Similar to the studtite structure, metastudtite consists of polymeric chains propagating along the a axis (*cf.* Fig. 2). The uranyl unit is positioned with uranium on a $4c$ Wyckoff site

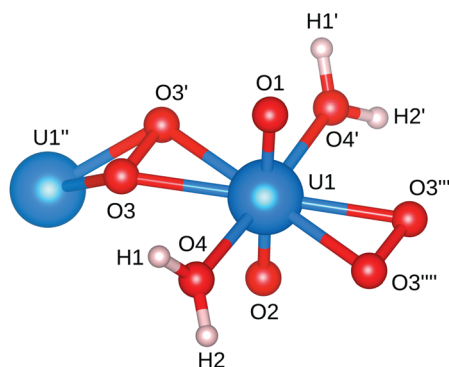


Fig. 4 Ball-and-stick representation of the $(\text{UO}_2)\text{O}(\text{H}_2\text{O})$ complex composing metastudtite. Color legend: U, blue; O, red; H, white. Symmetry codes: ' = $x, 5/2 - y, z$; '' = $-1/2 + x, 5/2 - y, 3/2 - z$; ''' = $1/2 + x, 5/2 - y, 3/2 - z$; '''' = $1/2 + x, y, 3/2 - z$.

Table 1 Atomic positions and fractional coordinates of the $(\text{UO}_2)\text{O}(\text{H}_2\text{O})$ complex composing metastudtite (space group $Pnma$, $Z = 4$; $a = 8.42$, $b = 8.78$, $c = 6.51$ Å)

$\text{UO}_2\text{OH}_2\text{O}$	Wyckoff position	x	y	z
U1	4c	0.150	0.250	0.750
O1	4c	0.227	0.250	0.016
O2	4c	0.080	0.250	0.488
O3	8d	0.599	0.833	0.382
O4	8d	0.150	0.974	0.761
H1	8d	0.127	0.584	0.889
H2	8d	0.190	0.600	0.659

(m. symmetry) and coordinated by six equatorial oxygen atoms on 8d Wyckoff sites donated by water and peroxy groups. The local hexagonal bipyramidal environment of the U metal center consists of two short axial $\text{U}=\text{O}$ bonds calculated to be 1.80 and 1.85 Å long, with a nearly linear $\text{O}=\text{U}=\text{O}$ angle (178.8°), and with equatorial oxygen atoms at distances of 2.39 Å for peroxy oxygen atoms and 2.42 Å for water oxygen atoms (cf. Fig. 4). The μ^2 -bridging peroxy atoms have a bond distance $\text{O3}-\text{O3}'$ of 1.46 Å, identical to the bond distance in studtite. As shown in Table 2, the predicted bond distances and angles for metastudtite are close to the ones of studtite.

Hydrogen bonds linking the $-y1$ O1 and peroxy O3 oxygen atoms of one chain to the H2 and H1 atoms, respectively, of a neighboring chain are present in metastudtite. The $\text{O1}\cdots\text{H2}-\text{O4}$ and $\text{O3}\cdots\text{H1}-\text{O4}$ contact distances are 1.75 and 1.67 Å, respectively. These distances are comparable to the calculated (measured) hydrogen bonds in studtite ranging from 1.62 to 1.79 Å (1.722 to 1.959 Å). The calculated dihedral angle between equatorial planes of successive uranyl ions along the chains is 0.0° , close to the 0.2° value computed for the relaxed structure of studtite.

Conclusions

The structures of the only known minerals containing peroxide, *i.e.* studtite $[(\text{UO}_2)\text{O}_2(\text{H}_2\text{O})_4]$ and metastudtite $[(\text{UO}_2)\text{O}_2(\text{H}_2\text{O})_2]$, have been investigated using DFT. The detailed structure of metastudtite crystallizing in the orthorhombic space group $Pnma$ ($Z = 4$) is explicitly reported for the first time at the

Table 2 Selected interatomic distances (Å), angles ($^\circ$) in the structures of metastudtite and studtite^a

Parameters	Metastudtite DFT ^b	Studtite DFT ^b	Studtite expt. ^c
U1–O1	1.85	1.83	1.769
U1–O2	1.80	1.83	1.769
U1–O3	2.39	2.38	2.365
U1–O4	2.42	2.41	2.395
U1–U1''	4.21	4.21	4.214
O3–O3'	1.46	1.46	1.464
O4–H1	1.00	1.00	0.978
O4–H2	1.00	1.00	0.975
O1...H2	1.75	—	—
O3...H1	1.67	—	—
H1...OH ₂	—	1.62	1.722
H2...OH ₂	—	1.66	1.959
O3...H ₂ O	—	1.71	1.757
O2...H ₂ O	—	1.79	1.956
O1–U1–O2	178.8	180.0	180.00
O1–U1–O3	88.2	88.8	89.73
O1–U1–O4	88.4	86.5	86.53
O2–U1–O3	92.9	92.3	90.27
O2–U1–O4	91.7	87.7	93.47
O3–U1–O3''	35.5	35.5	36.17
O3–U1–O3''''	179.9	180.0	180.00
O3–U1–O3''''	144.5	144.4	143.83
O3–U1–O4	71.6	71.4	71.32
U1–O3–U1''	123.7	124.0	126.60
O4–U1–O3'	107.0	106.9	107.25
O4–U1–O4'	176.5	180.0	180.00
O1–U1–U1''–	0.0	0.2	5.99
O1''	—	—	—

^a Symmetry codes: ' = $x, 5/2 - y, z$; '' = $-1/2 + x, 5/2 - y, 3/2 - z$; ''' = $1/2 + x, 5/2 - y, 3/2 - z$; '''' = $1/2 + x, y, 3/2 - z$. ^b Experimental cell dimensions were used in the calculations. ^c Burns and Hughes, 2003.

atomic level. Excellent agreement was obtained between the observed XRD powder pattern of metastudtite and the structure predicted in this study, thus demonstrating that the unit cell of metastudtite is actually larger than the previously reported cell dimensions ($Z = 2$) derived from experimental XRD data.

Further first-principles calculations will investigate the thermal stability of studtite and metastudtite, which are of crucial importance to understand the evolution and possible phase transformations occurring in minerals containing peroxide.

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