Periodic DFT Study of the Structure, Raman Spectrum and Mechanical Properties of Schoepite Mineral

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ABSTRACT

The structure and Raman spectrum of schoepite mineral, $[(\text{UO}_2)_8\text{O}_2(\text{OH})_{12}] \cdot 12 \text{H}_2\text{O}$, was studied by means of theoretical calculations. The computations were carried out by using Density Functional Theory with plane waves and pseudopotentials. A norm-conserving pseudopotential specific for the uranium atom developed in a previous work was employed. Since it was not possible to locate hydrogen atoms directly from X-ray diffraction data by structure refinement in the previous experimental studies, all the positions of the hydrogen atoms in the full unit cell were determined theoretically. The structural results, including the lattice parameters, bond lengths, bond angles and X-ray powder pattern were found in good agreement with their experimental counterparts. However, the calculations performed using the unit cell designed by Ostanin and Zeller in 2007, involving half of the atoms of the full unit cell, leads to significant errors in the computed X-ray powder pattern. Furthermore, Ostanin and Zeller's unit cell contains hydronium ions, H_3O^+ , that are incompatible with the experimental information. Therefore, while the use of this schoepite model may be a very useful approximation requiring a much smaller amount of computational effort, the full unit cell should be used to study this mineral accurately. The Raman spectrum was also computed by means of density functional perturbation theory and compared with the experimental spectrum. The results were also in agreement with the experimental data. A normal mode analysis of the theoretical spectra was performed to assign the main bands of the Raman spectrum. This assignment improved significantly the current empirical assignment of the bands of the Raman spectrum of schoepite mineral. In addition, the equation of state and elastic properties of this mineral were determined. The crystal structure of schoepite was found to be stable mechanically and dynamically. Schoepite can be described as a brittle material exhibiting small anisotropy and large compressibility in the direction perpendicular to the layers, which characterize its structure. The calculated bulk modulus, B , was ~ 35 GPa.

KEYWORDS

Spent nuclear fuel, Schoepite, DFT, X-ray diffraction, Raman Spectroscopy, Mechanical Properties.

I. INTRODUCTION

Hydrated uranyl oxyhydroxide mineral schoepite is a fundamental component of the paragenetic sequence of secondary phases that results from the weathering of uraninite ore deposits.¹⁻⁶ The study of the paragenesis and structure of uranyl oxide hydrates is extraordinarily important, because they not only occur as products of the secondary alteration of uraninite under oxidizing conditions, but are also prominent phases appearing from the UO_2 alteration of the spent nuclear fuel (SNF).⁷⁻¹⁷ Therefore, the study of these minerals is indispensable for understanding the long-term performance of a geological repository for nuclear waste. The knowledge of their structures may be also crucial to evaluate the possible incorporation of fission products and transuranic elements into their crystal structures,¹⁸⁻²¹ thus reducing their release and environmental impact.

Schoepite was originally described by Walker in 1923.²² Its formula was reported in 1932 by Schoep as $3\text{UO}_3 \cdot 7\text{H}_2\text{O}$,²³ subsequently as $4\text{UO}_3 \cdot 9\text{H}_2\text{O}$ ²⁴⁻²⁵ and, finally, as $\text{UO}_3 \cdot 2\text{H}_2\text{O}$ by Christ and Clark²⁶ in 1960. The chemical composition and structure of schoepite have been a matter of discussion over time.^{3-4,27-33,20} The structure solution of schoepite²⁹⁻³⁰ leads to the structural formula of schoepite $[(\text{UO}_2)_8\text{O}_2(\text{OH})_{12}] \cdot 12\text{H}_2\text{O}$, corresponding to the composition $\text{UO}_3 \cdot 2.25\text{H}_2\text{O}$, in agreement with the original one determined by Billiet and de Jong²⁴ from density and unit-cell measurements.

X-ray diffraction studies of synthetic UO_3 hydrates indicate only one schoepite phase. However, infrared spectroscopy and thermogravimetric analysis suggest the existence of a second mineral

phase,³³ named metaschoepite. This related mineral species has a lower water content than schoepite.^{26,32} The composition commonly reported for metaschoepite is $\text{UO}_3 \cdot 2\text{H}_2\text{O}$ ($[(\text{UO}_2)_8\text{O}_2(\text{OH})_{12}] \cdot 10\text{H}_2\text{O}$), and was determined by thermogravimetric analysis (TGA) on both natural and synthetic material.³⁴⁻³⁶ A third related phase, paraschoepite, has remained less well characterized. Paraschoepite, $\text{UO}_3 \cdot 1.9\text{H}_2\text{O}$,²⁵ has not been synthesized, not much being known about its structure. Further dehydration of metaschoepite leads to different phases reported as dehydrated schoepite, $\text{UO}_2\text{O}_{0.25-x}(\text{OH})_{1.25+2x}$,³⁷⁻³⁸ or the related mineral paulscherrerite.³⁸ These dehydrated schoepite phases are related to the α uranyl hydroxide, $\alpha - \text{UO}_2(\text{OH})_2$.³⁹ The distinction between schoepite, metaschoepite, and dehydrated schoepite is still an open issue, because the conversion between the three closely related phases in natural and laboratory settings is easy to occur, the samples being usually present as a mixture.

The chemistry of the hydrated oxides of uranium(VI) is extremely complex and approximately 20 phases have been described in the literature.^{20-21,40-54} All the structures of these materials are composed of polyhedral sheets with composition $(\text{UO}_2)_x\text{O}_y(\text{OH})_z$, consisting of uranyl groups linked by oxide and hydroxide ions. For the higher oxide hydrates, water molecules may be incorporated inside the interlayer space between the sheets.²⁹⁻³² The structures of many of these materials have been described in detail by Finch and coworkers.²⁹⁻³¹ The inter-relationships between these phases have been also studied.³¹⁻³² In particular, the structure of schoepite was investigated in different studies leading to the full structure solution from a naturally occurring sample by Finch *et al.*²⁹ in 1996. The structure of metaschoepite was precisely determined from a synthetic sample by Weller *et al.*³² in 2000.

However, it was not possible to locate H atoms directly from X-ray diffraction data by structure refinement and difference-Fourier maps for such highly absorbing materials as the uranium oxy-

hydroxy-hydrate minerals. This is unfortunate because the H bonding must be the mechanism whereby the sheets of the structural unit are linked. Furthermore, the similar physical and crystallographic properties of schoepite and metaschoepite^{26,55} suggest that these structures are distinguished primarily by differences in their arrangements of the interlayer H-bonding. Despite these problems, an idea of the H atom positions and interlayer H-bonding in schoepite may be obtained from the locations of the O atoms of the H₂O groups and from the stereochemical characteristics of H₂O groups and their associated networks of H bonds.²⁹ The resulting scheme of H bonds in schoepite structure, described in detail by Finch *et al.*,²⁹ is nearly that predicted by our calculations. The same is not true for the structure calculated by Ostanin and Zeller in 2007⁵⁶ using Molecular Dynamics (MD) from the half unit cell. Furthermore, this structure shows the presence of hydronium ions, H₃O⁺, which are not consistent with the proposed interlayer structure of Finch and coworkers.²⁹ Therefore, although the use of this schoepite model may be a very useful approximation requiring a much smaller amount of computational effort, the full unit cell should be used to study this mineral accurately. This should be taken into account if theoretical calculations are performed using this model since only semiquantitative results can be expected. For example, first-principles GIPAW (Gauge Including Projector-Augmented Wave) chemical shift calculations were carried by Alam *et al.*⁵⁷ out using Ostanin and Zeller unit cells of schoepite and metaschoepite.

The theoretical calculations of schoepite are very computationally demanding, not only due to the large size of the corresponding unit cell (344 atoms are involved), but also to the high level of theory required to describe correctly uranium atom containing systems.⁵⁸⁻⁵⁹ There is a very small number of works about the theoretical vibrational spectra of uranium containing solids in the literature since only recently a norm conserving pseudopotential⁶⁰ for uranium atom appropriate

for this purpose was developed,⁶¹⁻⁶² which has been used extensively for the research of the structural, mechanical, thermodynamic and spectroscopic properties of other uranyl containing materials.⁶¹⁻⁶⁹

The hydrogen atom positions in the structure of schoepite were not determined by experimental X-ray diffraction techniques. In this paper, we performed a complete structural characterization of schoepite by theoretical solid-state methods, which allowed us to obtain a full unit cell structure in agreement with that obtained experimentally. Besides, although the Raman spectrum of this mineral has been recorded experimentally,^{70-72,49} a precise assignment of the main bands in the spectra is lacking, since they have been characterized incompletely by using empirical arguments. The theoretical Raman spectrum of schoepite is reported here, including the computation of intensities and the assignment of the vibrational bands. This has been possible because the theoretical methods provide detailed views at the microscopic scale of the atomic vibrational motions in the corresponding normal modes. The equation of state and mechanical properties of schoepite are also given. Computations were performed by means of Density Functional Theory⁷³ (DFT) based on plane waves and pseudopotentials.⁷⁴

II. METHODS

CASTEP code,⁷⁵ a module of the Materials Studio package,⁷⁶ was employed to model schoepite structure. The generalized gradient approximation (GGA) together with PBE functional⁷⁷ and Grimme empirical dispersion correction,⁷⁸ called the DFT-D2 approach, were used. The Grimme dispersion correction was included to describe correctly the dense network of hydrogen bonds present in the schoepite structure. The pseudopotentials used for H and O in the unit cell of schoepite mineral were standard norm-conserving pseudopotentials⁶⁰ given in CASTEP code

(00PBE-OP type). The norm-conserving relativistic pseudopotential for U atom was generated from first principles as shown in previous works.⁶¹⁻⁶² Whereas our uranium atom pseudopotential includes scalar relativistic effects, the corresponding pseudopotentials used for H and O atoms do not include them.

Geometry optimization was carried out by using the Broyden–Fletcher–Goldfarb–Shanno optimization scheme^{74,79} with a convergence threshold on atomic forces of 0.01 eV/Å. Schoepite structure was optimized in calculations with increasing values of the kinetic energy cut-off parameter. At the end, the optimization performed with a cut-off of 900 eV and a K mesh⁸⁰ of $1 \times 1 \times 1$ gave a well converged structure, which was used to obtain the final results.

For the calculations of vibrational properties, the linear response density functional perturbation theory (DFPT),⁸¹⁻⁸³ implemented in the CASTEP code, was used in the same way as in previous works.⁶¹⁻⁶⁷ Since the unit cell of schoepite involves a very large number of atoms (32 U, 168 O and 144 H, giving a total number of atoms of 344 and 1032 vibrational normal modes to be considered), the computation of the vibrational Raman spectrum was performed using a smaller kinetic cutoff of 750 eV. The calculated frequencies have not been scaled to correct for anharmonicity and remaining errors of the theoretical treatment employed, such as incomplete treatment of electron correlation and basis set truncation.⁸⁴ They correspond to the harmonic approximation of the force field. The scale factor should be near to unity because the effects of these defects tend to cancel out.

The full unit cell of schoepite material has been employed in most of the calculations performed in this work. For comparison, the geometry optimization was also performed by using Ostanin and Zeller⁵⁶ unit cell (involving only 172 atoms). We greatly acknowledge to S. Ostanin for providing us with their calculated unit cell. A larger kinetic cut-off of 950 eV (and the same K mesh) was

selected for the calculations. Even with this increased cutoff, the results obtained using this unit cell were worse than those obtained by using the full unit cell, as it will be shown below.

The elastic modulus of schoepite and its derivatives with respect to pressure were calculated by fitting the lattice volumes and associated pressures to a fourth-order Birch-Murnahan equation of state.⁸⁵ The lattice volumes near the equilibrium geometry were determined by optimizing the structure at several applied pressures with values within -1.0 and 12 GPa, where negative pressure values mean traction or tension. EOSFIT 5.2 code⁸⁶ was then used to fit the results to the selected equation of state.

In order to calculate the mechanical properties and to study the mechanical stability of the crystal structure of schoepite, the required elastic constants were obtained from stress-strain relationships. The finite deformation technique is employed in CASTEP for this purpose. In this technique, finite programmed symmetry-adapted strains⁸⁷ are used to extract the individual constants from the stress tensor obtained as response of the system to the applied strains. This stress-based method appears to be more efficient than the energy-based methods and the use of DFPT technique for the calculation of the elasticity tensor.⁸⁸

III. RESULTS AND DISCUSSION

III.1. Crystal structure

The computed structure of schoepite is displayed in Figure 1 (see also Figure 2). There are eight symmetrically distinct uranium sites in space group $P2_1ca$ (See Figure 1.B). All U atoms are coordinated by seven anions in pentagonal bipyramidal arrangements. Each pentagonal bipyramid, referred to as UO_7 below, consists of two apical O^{2-} anions and five equatorial anions O^{2-} or OH^- . While the uranium atoms U2 and U6 (See Figure 1.B) have a coordination environment of

$\text{UO}_2(\text{OH})_5$, the coordination for the remaining uranium atoms is $\text{UO}_2\text{O}(\text{OH})_4$. The most stable configuration around a UO_2^{2+} group has a pentagonal arrangement of equatorial anions as predicted by Evans in 1963.⁸⁹ The apical O^{2-} anions are designated as uranyl-O atoms: O(u).

The UO_7 pentagonal bipyramids share edges to form dimers, which in turn, link by sharing edges to form staggered ribbons along the [100] direction. Then, these ribbons cross-link in the [010] direction by sharing edges and corners of the polyhedra. This results in a strongly bonded sheet of stoichiometry $[(\text{UO}_2)_8\text{O}_2(\text{OH})_{12}]$ parallel to plane {001}. This sheet constitutes the structural unit of schoepite, which stacks along the [001] direction. As the sheets are neutral, they are linked together by H-bonding only, through a complex network of H-bonding involving interlayer H_2O groups and O(u) atoms and OH^- groups in the structural sheet. This explains the perfect {001} cleavage parallel to the sheets. The sites are approximately superimposed when they are viewed along [001] direction, which is a feature of all uranyl oxide hydrate minerals.⁴⁰⁻⁴⁴ No staggering of U sites perpendicular to the sheets is observed, as for most high temperature uranates.⁴⁵

The network within the uranium oxide hydroxide layers is basically the same in schoepite,²⁹ metaschoepite³² and many other uranium(VI) complex oxides, such as fourmarierite $\text{Pb}[(\text{UO}_2)_4\text{O}_3(\text{OH})_4] \cdot 4\text{H}_2\text{O}$.⁴¹ While most equatorial O^{2-} or OH^- groups are shared as vertices of three UO_7 polyhedra, the O atom in hydroxyl groups OH7 and OH4 bridge two uranyl polyhedra alone. The corresponding sections of the layers not occupied by the pentagons of the UO_7 groups have a bow-tie-like motif (see Figure 1.B) connected centrally at the bridging hydroxyl.

There are twelve H_2O groups in schoepite interlayer and are referred to as W(i) ($i = 1, \dots, 12$). Finch *et al.*²⁹ found that the H_2O groups are located at the apices of two distorted pentagons and the remaining two H_2O groups (W(5) and W(11)) are not members of the pentagonal rings and are located between the pentagonal rings. The pentagonal rings vertices are nearly at the positions

of the equatorial anions in the U1 and U7 polyhedra from the two adjacent sheets. The general hydrogen bond structure described by Finch *et al.*²⁹ is reproduced by present theoretical calculations, confirming the suggested structure. Besides, our results provide approximate locations for the hydrogen atoms in the full unit cell, which have been never precisely obtained by either theoretical or experimental methods. The calculated atom positions resulting from our calculations are given as Supporting Information in an independent file of CIF (Crystallographic Information File) type.

Figure 1. Structure of schoepite mineral: A) View of the full unit cell from [100]; B) View of a schoepite sheet from [001] direction. Colour code: U-Blue, O-Red, H-Yellow.

Figure 2. Structure of schoepite mineral: Optimized Ostanin and Zeller⁵⁶ unit cell from [010] direction. As it can be seen this unit cell involves the formation of hydronium ions, H_3O^+ . Colour code: U-Blue, O-Red, H-Yellow.

As it has been mentioned, the structure of schoepite was determined in calculations with increasing complexity. The final lattice parameters, volumes and densities obtained are given in Table 1 where they are compared with the experimental ones from Finch *et al.*²⁹⁻³⁰, the theoretical and experimental results being in good agreement. Our calculated volume and density have errors of about 2.2%. The second row, corresponds to the geometry optimization carried out using Ostanin-Zeller's unit cell.⁵⁶ The calculated cell was then doubled so that lattice parameters, volume and density, shown in Table 1, are comparable with the corresponding experimental values.

Table 1. Lattice parameters

Parameters	a (Å)	b (Å)	c (Å)	α	β	γ	Vol. (Å ³)	Dens. (g/cm ³)
This work	14.2740	16.8076	14.4841	90.0	90.0	90.0	3474.91	4.993
DFT ⁵⁶	14.2782	16.7523	14.7026	90.0	90.0	89.50	3516.62	4.934
Exp. ²⁹⁻³⁰	14.3370	16.8130	14.7310	90.0	90.0	90.0	3550.88	4.886

Table 2 gives a comparison of the more important geometric parameters (bond distances) obtained with the corresponding experimental data of Finch *et al.*²⁹. As it has been said, schoepite has eight structurally (symmetrically) identical U^{6+} ions in its crystal structure. In the pentagonal

bipyramids, the two apical O^{2-} anions are separated of the central uranium atom by distances in the range 1.74-1.83 Å (calculated 1.78-1.81 Å), and the corresponding separation for the five equatorial anions O^{2-} or OH^- are in the range 2.17-2.78 Å (calculated 2.25-2.83 Å). The large difference in efficiencies in X-ray scattering of U and O atoms makes the short U – O(u) distances among the least accurately determined interatomic distances in the structures of uranyl compounds determined by X-ray diffraction.²⁹ The U – O(u) bond lengths determined for schoepite are comparable to those reported for other uranyl-oxy-hydroxide compounds.⁴⁰⁻⁴¹ The differences between the experimental and average equatorial distances are quite small (0.01-0.04 Å) as observed in Table 2. The calculated bond distances between the uranium atom and the oxygen atoms in the three nearest water molecules are also shown in Table 2 and compared with the corresponding experimental values and are also well reproduced by our calculations.

Table 2. Bond distances (in Å).

Bond	Exp. ²⁹	Calc.	Bond	Exp. ²⁹	Calc.
U1			U5		
U1 – O1	1.773	1.783	U5 – O9	1.754	1.778
U1 – O2	1.793	1.778	U5 – O10	1.769	1.783
U1 – O17	2.284	2.253	U5 – O18	2.167	2.361
U1 – OH2	2.382	2.358	U5 – OH8	2.388	2.243
U1 – OH6	2.389	2.373	U5 – OH12	2.417	2.374
U1 – OH7	2.464	2.454	U5 – OH1	2.466	2.455
U1 – OH3	2.653	2.796	U5 – OH9	2.775	2.833
Aver. U – O _{eq.}	2.434	2.447	Aver. U – O _{eq.}	2.443	2.453
U1 – W(2)	3.937	3.797	U5 – W(8)	3.863	3.788
U1 – W(7)	3.965	3.870	U5 – W(12)	3.983	3.870
U1 – W(6)	3.986	3.893	U5 – W(1)	3.988	3.876
U2			U6		
U2 – O3	1.737	1.783	U6 – O12	1.778	1.791
U2 – O4	1.787	1.794	U6 – O1	1.796	1.791
U2 – OH10	2.286	2.265	U6 – OH4	2.306	2.275
U2 – OH11	2.424	2.405	U6 – OH12	2.369	2.451
U2 – OH2	2.468	2.472	U6 – OH5	2.421	2.396
U2 – OH6	2.507	2.436	U6 – OH8	2.484	2.441
U2 – OH7	2.611	2.576	U6 – OH1	2.494	2.559
Aver. U – O _{eq.}	2.459	2.431	Aver. U – O _{eq.}	2.415	2.424
U2 – W(10)	4.092	4.092	U6 – W(1)	3.971	3.902

U2 – W(6)	4.129	4.129	U6 – W(12)	4.074	4.148
U2 – W(11)	4.130	4.130	U6 – W(4)	4.115	4.056
U3			U7		
U3 – O5	1.757	1.805	U7 – O13	1.784	1.789
U3 – O6	1.803	1.793	U7 – O14	1.805	1.805
U3 – O17	2.225	2.233	U7 – O18	2.280	2.247
U3 – OH4	2.327	2.357	U7 – OH7	2.362	2.452
U3 – OH3	2.427	2.399	U7 – OH10	2.370	2.347
U3 – OH1	2.525	2.434	U7 – OH9	2.456	2.400
U3 – OH5	2.718	2.697	U3 – OH11	2.562	2.684
Aver. U – O _{eq.}	2.444	2.424	Aver. U – O _{eq.}	2.406	2.426
U3 – W(1)	4.035	4.044	U3 – W(9)	4.009	4.073
U3 – W(3)	4.042	3.990	U3 – W(7)	4.090	4.137
U3 – W(4)	4.253	4.181	U3 – W(10)	4.187	4.119
U4			U8		
U4 – O7	1.766	1.804	U8 – O15	1.737	1.801
U4 – O8	1.833	1.801	U8 – O16	1.791	1.806
U4 – O17	2.198	2.222	U8 – O18	2.285	2.227
U4 – OH5	2.362	2.411	U8 – OH9	2.399	2.374
U4 – OH3	2.430	2.382	U8 – OH12	2.420	2.459
U4 – OH6	2.472	2.444	U8 – OH11	2.532	2.412
U4 – OH2	2.558	2.611	U8 – OH8	2.629	2.596
Aver. U – O _{eq.}	2.404	2.414	Aver. U – O _{eq.}	2.453	2.414
U4 – W(5)	4.157	4.045	U8 – W(9)	3.995	4.031
U4 – W(3)	4.188	4.043	U8 – W(12)	4.082	4.044
U4 – W(2)	4.240	4.296	U4 – W(11)	4.132	4.031

III.2. X-ray powder pattern

The X-ray powder diffractogram of schoepite was calculated from the computed structure using software REFLEX included in Materials Studio package⁷⁶ with CuK_{α} radiation ($\lambda=1.540598$ Å). The results are compared in Figure 3 with the experimental X-ray diffractogram from the record 100188 of the RRUFF database,⁹⁰ which corresponds to a natural schoepite mineral from Shinkolobwe mine, Katanga, Congo. The agreement of the computed and experimental diffractograms is very good.

Figure 3. X-ray powder pattern diffractogram of schoepite using $\text{CuK}\alpha$ radiation: a) X-Ray powder pattern computed from calculated geometry; b) Experimental pattern from the RRUFF database⁹⁰ (record 100188).

To obtain a precise comparison of the computed and experimental X-ray powder patterns of schoepite, we also derived the corresponding patterns from the experimental²⁹ and computed structures.⁹¹ The spectra derived directly from the structures is free of interferences, as the experimental conditions, or possible artefacts, as the presence of impurities, since both are determined under identical conditions. The agreement in line positions and intensities is very good, as reflected in Table S.1. of the Supporting Information.

The X-Ray powder pattern was also computed from the optimized geometry obtained using the cell of Ostanin and Zeller.⁵⁶ The results, given in Table 3, were compared with an experimental pattern from the PDF-2 database⁹² (pattern 50-1601, which corresponds to the natural schoepite sample studied by Finch *et al.*²⁹⁻³⁰). As it can be seen, the use of the Ostanin and Zeller's unit cell leads to some undesirable features. In the first place, the reflections with non-zero Miller index l are doubled (for example the reflection [242] splits into two equally intense [242] and [-2-42]

reflections). Secondly, some reflections absent in the experimental pattern, as [-240], [-242] and [-248], have appreciable intensities. Finally, many important observed reflections appear with a much smaller intensity in the calculated pattern (for example: [242], [402] and [244]).

Table 3. Main reflections in the X-Ray powder pattern of schoepite: a) X-Ray powder pattern computed from calculated geometry using Ostanin and Zeller unit cell,⁵⁶ b) Experimental pattern from PDF-2 database⁹² (pattern 50-1601).

Theoretical (Ostanin and Zeller ⁵⁶ unit cell)				Experimental (PDF-2 ⁹² : 50-1601)		
2 Θ	d(Å)	I (%)	[hkl]	2 Θ	d(Å)	I (%)
12.029	7.3513	100.0	[002]	12.02	7.357	100.0
24.194	3.6756	22.117	[004]	24.16	3.681	15.0
24.531	3.6260	19.641	[240]	24.54	3.624	27.0
24.720	3.5986	18.848	[-240]	-	-	-
24.926	3.5694	16.996	[400]	24.82	3.584	13.0
27.404	3.2519	15.046	[242]	27.40	3.252	41.0
“	“	“	[-2-42]			
7.575	3.2321	14.138	[-242]	-	-	-
“	“	“	[2-42]			
27.761	3.2109	12.611	[402]	27.66	3.222	19.0
“	“	“	[-402]			
34.724	2.5813	4.638	[244]	34.70	2.583	12.0
“	“	“	[-244]			
34.863	2.5714	5.175	[-248]	-	-	-
“	“	“	[2-48]			
35.013	2.5607	4.345	[404]	34.90	2.569	7.0
“	“	“	[-404]			
43.545	2.0767	5.407	[640]	43.54	2.077	6.0
44.594	2.0303	3.722	[246]	44.54	2.032	8.0
“	“	“	[-2-46]			
45.342	1.9985	3.134	[642]	45.32	1.999	8.0
“	“	“	[-6-42]			
50.432	1.8081	2.098	[644]	50.40	1.809	6.0
“	“	“	[-6-44]			
51.903	1.7602	2.302	[484]	51.90	1.760	4.0
“	“	2.302	[-4-81]			

III.3. Raman spectrum and band assignment

The theoretical Raman spectrum is compared with the experimental one⁷⁰ in Figure 4. Both spectra are quite similar. The theoretical spectrum was computed at T=298 K, $\lambda=532$ nm,

FWHM=20 cm^{-1} . Pictures of the atomic motions in the Raman active vibrational modes are depicted in Figure S.1 of Supporting Information.

The analysis of the experimental and theoretical Raman spectra will be divided in four regions: (A) OH stretching vibration region from 3700 to 2800 cm^{-1} (Figure 4.A); (B) H_2O bending region from 1800-1300 cm^{-1} ; (C) uranyl UO_2^{2+} fundamental vibrations region from 950 to 750 cm^{-1} (Figure 4.B); and (D) low wavenumber region from 700 to 100 cm^{-1} (Figure 4.C). Band wavenumbers of both spectra along with the corresponding calculated intensities and assignments are given in Table 4. The Raman band shifts and assignments performed by Frost *et al.*⁷⁰ are also given in this table for comparison.

(A) OH stretching vibrations region

In the hydroxyl stretching region the experimental spectrum shows a broad band which was resolved by Frost *et al.*⁷⁰ into three contributions at about 3538, 3405 and 3204 cm^{-1} . For the first contribution, we found two computed Raman shifts of 3507 and 3495 cm^{-1} . For the second one, we obtained two bands located at 3427 and 3371 cm^{-1} . All these bands were assigned to OH bond stretching vibrations localized in the interlayer water molecules $\nu(\text{OH}) [\text{H}_2\text{O}]$. However, for the third contribution, which is the most intense and very wide, we found a set of six theoretical bands placed between 3182 and 2986 cm^{-1} . Whereas the first of these bands was assigned to a combination of OH bond stretching vibrations localized in the interlayer water molecules and in the equatorial hydroxyl groups of the pentagonal bipyramids, the remaining five bands were attributed to OH bond stretching vibrations in equatorial hydroxyl groups alone (see vibrational mode pictures in the Supporting Information). Frost *et al.*,⁷⁰ however, assigned this whole band to unspecified OH bond stretching vibrations and established a cutoff of 3300 cm^{-1} , the modes with higher wavenumbers being associated to OH bonds localized in weak hydrogen bonds and those

with smaller wavenumber being associated to OH bonds localized in strong hydrogen bonds. Our results show that, in fact, the different assignment of these vibrations may be performed on the basis of the different localization and strength of the corresponding OH bonds. Since the last band associated to OH vibrations localized in the interlayer free water molecules (developing weaker hydrogen bonds) is placed at 3371 cm^{-1} and the first band involving OH vibrations localized in equatorial OH bonds (developing stronger hydrogen bonds) is placed at 3182 cm^{-1} , the criterium and cutoff established by Frost *et al.*⁷⁰ are correct.

Figure 4. Experimental⁷⁰ and theoretical Raman spectra of schoepite mineral: (A) OH stretching region from 3700 to 2800 cm^{-1} ; (B) Uranyl UO_2^{2+} fundamental vibrations region from 950 to 750 cm^{-1} ; (C) Low wavenumber region from 700 to 100 cm^{-1} .

Table 4. Experimental and calculated Raman band wavenumbers, calculated intensities and assignments.

Band Name	Exp. Raman shift (cm ⁻¹) / Assignment ⁷⁰	Calc. Raman shift (cm ⁻¹)	Irr. Rep. (C _{2v})	Int. (Å ⁴)	Assignment (this work)
OH stretching region					
<i>a</i>	3537.8 / ν(OH)	3506.62	A ₁	4726.17	ν(OH) [H ₂ O]
		3494.13	A ₁	4029.09	
<i>b</i>	3404.8 / ν(OH)	3427.47	A ₁	2635.89	
		3371.22	A ₁	1961.80	
<i>c</i>	3203.9 / ν(OH)	3181.83	A ₁	7183.95	ν(OH) [OH, H ₂ O]
		3169.58	A ₁	7165.91	ν(OH) [OH]
		3126.15	A ₁	10515.14	
		3066.21	A ₁	4721.96	
		3018.19	A ₁	11002.60	
		2985.80	A ₁	4488.01	
H ₂ O bending region					
<i>d</i>	1621.0 / δ(HOH)	1623.66	A ₂	27.42	δ(HOH)
		1604.91	B ₁	27.88	
UO ₂ ²⁺ fundamental vibrations region					
<i>e</i>	897.5 / ν ^a (UO ₂ ²⁺)	900.68	A ₁	19.61	δ(UOH)+l(H ₂ O)
<i>f</i>	886.2 / ν ^a (UO ₂ ²⁺)	886.48	A ₁	66.11	
<i>g</i>	869.6 / ν ^a (UO ₂ ²⁺)	875.21	A ₁	72.29	
<i>h</i>	855.4 / ν ^a (UO ₂ ²⁺)	863.89	A ₁	2401.65	
<i>i</i>	838.7 / ν ^s (UO ₂ ²⁺)	857.55	A ₁	3306.03	ν ^s (UO ₂ ²⁺)+δ(UOH)+l(H ₂ O)
		851.95	A ₁	3621.38	ν ^s (UO ₂ ²⁺)+l(H ₂ O)
<i>j</i>	826.2 / ν ^s (UO ₂ ²⁺)	836.48	A ₁	1839.73	ν ^s (UO ₂ ²⁺)+δ(UOH)
<i>k</i>	817.1 / ν ^s (UO ₂ ²⁺)	823.81	A ₁	450.90	ν ^s (UO ₂ ²⁺)+δ(UOH)+l(H ₂ O)
<i>l</i>	802.3 / ν ^s (UO ₂ ²⁺)	808.71	A ₁	1455.65	
Low wavenumber region					
<i>m</i>	554.2 / ν(UO _{eq})	557.62	A ₁	97.77	l(H ₂ O)
<i>n</i>	545.1 / ν(UO _{eq})	522.74	A ₁	115.01	
<i>o</i>	507.8 / ν(UO _{eq})	520.81	B ₁	497.93	
<i>p</i>	460.9 / ν(UO _{eq})	489.42	A ₁	106.99	
<i>q</i>	458.0 / ν(UO _{eq})	452.40	B ₁	175.98	δ(OUO _{eq})+δ(UOH)+l(H ₂ O)
<i>r</i>	402.3 / ν(UO _{eq})	404.95	A ₁	313.03	
<i>s</i>	350.7 / ν(UO _{eq})	362.59	A ₁	204.59	
<i>t</i>	330.3 / ν(UO _{eq})	343.23	B ₁	138.19	
<i>u</i>	304.7 / ν(UO _{eq})	312.85	B ₁	38.34	
<i>v</i>	273.8 / δ(UO ₂ ²⁺)	278.80	B ₁	26.26	
<i>w</i>	247.8 / δ(UO ₂ ²⁺)	243.66	A ₁	38.37	δ(UO ₂ ²⁺)+δ(OUO _{eq})+δ(UOH)+l(H ₂ O)
<i>x</i>	215.6 / Def. Latt.	234.48	A ₁	21.21	
<i>y</i>	194.0 / Def. Latt.	192.30	A ₂	20.71	
<i>z</i>	167.9 / Def. Latt.	166.07	A ₂	27.52	

(B) H₂O bending vibration region

The Raman shift associated to the water bending vibration, $\delta(\text{HOH})$, was found⁷⁰ at about 1621 cm^{-1} , comparable to the calculated wavenumbers of 1624 and 1605 cm^{-1} .

(C) Uranyl UO_2^{2+} fundamental vibrations region

The experimental bands at 897, 886 and 870 and 855 cm^{-1} , correspond to the bands calculated at 901, 886, 875 and 864 cm^{-1} , which were assigned to a combination of UOH bending vibrations and water librations, $\delta(\text{UOH})+\text{l}(\text{H}_2\text{O})$. However, these bands were assigned by Frost *et al.*⁷⁰ to uranyl antisymmetric stretching vibrations, $\nu^a(\text{UO}_2^{2+})$.

The most intense band in the Raman spectrum of this zone is measured experimentally at about 840 cm^{-1} . Amme *et al.*⁷² recorded this band at 843 cm^{-1} . This band corresponds to the pair of calculated Raman shifts of 857 and 852 cm^{-1} . The next experimental bands are those placed at 826, 817 and 802 cm^{-1} , which were reproduced theoretically as 836, 823 and 809 cm^{-1} , respectively. As observed in Table 4 (see also the vibrational mode pictures in the Supporting Information), all these bands can be assigned to combinations of uranyl symmetric stretching vibrations, $\nu^s(\text{UO}_2^{2+})$, UOH bending vibrations, $\delta(\text{UOH})$, and water librations, $\text{l}(\text{H}_2\text{O})$. Frost *et al.*⁷⁰ also assigned these bands mainly to uranyl symmetric stretching vibrations.

Frost *et al.*⁷⁰ noted the possible contribution of UOH bending vibrations to the bands in the region from 900 to 800 cm^{-1} . In fact, as it has been shown, this vibration is very important being the main responsible for the bands located at 897, 886, 870 and 855 cm^{-1} , and making significant contributions to the bands of this region located at lower wavenumbers.

(D) Low wavenumber region

The bands computed at 558, 523, 521 and 489 cm^{-1} are comparable to the experimental bands at 554, 545, 508 and 461 cm^{-1} . They were assigned to water librational vibrations. Similarly, the experimental bands placed at 458, 402, 351 and 330 cm^{-1} correspond to the calculated bands at 452, 405, 363 and 343 cm^{-1} , which are ascribed to combinations of OUO_{eq} and UOH bending vibrations and water librations. Finally, the six observed bands at 305, 274, 248, 216, 194 and 168 cm^{-1} are reproduced theoretically at 313, 279, 244, 192 and 166 cm^{-1} , and are assigned to combinations of uranyl (UO_2^{2+}), OUO_{eq} and UOH bending vibrations and water librations.

Frost *et al.*⁷⁰ proposed an empirical assignment of the bands within the low wavenumber region which is very different from that of this work. They assigned all the bands in the range 560–300 cm^{-1} simply to UO_{eq} (uranium-equatorial oxygen) bond stretching vibrations, $\nu(\text{UO}_{eq})$, the bands within the range 274–238 cm^{-1} to uranyl bending vibrations, $\delta(\text{UO}_2^{2+})$, and finally those having wavenumbers smaller than 220 cm^{-1} to molecular deformation and lattice modes. Although the assignment of the bands at 274 and 248 cm^{-1} mainly to uranyl bending vibrations agrees with present assignment, it must be noted that the bands at 305, 216, 194 and 168 cm^{-1} have also significant contributions from uranyl bending vibrations.

III.2. Equation of state

The lattice volumes near the equilibrium geometry were obtained by optimizing the structure at eighteen different applied pressures. The results are displayed in Figure 5.

Figure 5. Unit cell volume of Schoepite as a function of the applied pressure.

EOSFIT 5.2 code⁸⁶ was then used to fit the calculated volume-pressure data to a fourth-order Birch-Murnaghan⁸⁵ equation of state (EOS) using the computed volume at zero pressure (3474.91 Å^3 , see Table 1) as V_0 :

$$P = 3 B f_E (1 + 2f_E)^{\frac{5}{2}} \left[1 + \frac{3}{2} (B' - 4) f_E + \frac{3}{2} \left\{ B B'' + (B' - 4)(B' - 3) + \frac{35}{9} \right\} f_E^2 \right] \quad (1)$$

In the above equation:

$$f_E = \frac{1}{2} \left[\left(\frac{V_0}{V} \right)^{\frac{2}{3}} - 1 \right] \quad (2)$$

and B , B' , and B'' are the bulk modulus and its first and second derivatives with respect to pressure, respectively, at the temperature of 0 K. The values found for B , B' , and B'' were $B = 35.17 \pm 0.39$ GPa, $B' = 7.39 \pm 0.40$, and $B'' = -1.31 \pm 0.22 \text{ GPa}^{-1}$ ($\chi^2 = 0.001$), respectively.

III.3. Mechanical properties and stability

Orthorhombic symmetry crystals have 9 non-vanishing independent elastic constants in the symmetric stiffness matrix.^{87,93} In this case the stiffness matrix may be expressed as:

$$C = \begin{pmatrix} C_{11} & C_{12} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{22} & C_{23} & 0 & 0 & 0 \\ C_{13} & C_{23} & C_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{55} & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{66} \end{pmatrix} \quad (3)$$

This equation is written by using the standard Voigt notation for the indices contracting a pair of Cartesian indices into a single integer $1 \leq i \leq 6$: $xx \rightarrow 1$, $yy \rightarrow 2$, $zz \rightarrow 3$, $yz \rightarrow 4$, $xz \rightarrow 5$, $xy \rightarrow 6$. The values of the C_{ij} constants obtained from our calculations are detailed in Table 5.

Table 5. The nine non-vanishing and independent elastic constants in the stiffness matrix for the orthorhombic lattice structure of schoepite. All values are given in units of GPa.

C_{11}	C_{22}	C_{33}	C_{44}	C_{55}	C_{66}	C_{12}	C_{13}	C_{23}
112.36	88.22	52.19	18.69	17.21	28.88	39.55	5.62	13.47

The *necessary* and *sufficient* Born criteria for mechanical stability of crystals having orthorhombic symmetry are:^{94,93}

$$C_{ii} > 0 \quad (i = 1, 4, 5, 6) \quad (4.a)$$

$$C_{11} C_{22} - C_{12}^2 > 0 \quad (4.b)$$

$$C_{11} C_{22} C_{33} + 2 C_{12} C_{13} C_{23} - C_{11} C_{23}^2 - C_{22} C_{13}^2 - C_{33} C_{12}^2 > 0 \quad (4.c)$$

Since these conditions are satisfied by the elastic constants of schoepite (Table 5), its crystal structure is mechanically stable. The high mechanical stability of schoepite structure was suspected from the beginning because all the elastic constants obtained were positive and large, and, therefore, the calculated stiffness matrix was positive definite.⁹⁴ The dynamical stability must also be analyzed to study the stability of the material in a complete form. A necessary and sufficient condition for the dynamical stability of a structure is that all of its phonon modes have positive frequencies for all wave vectors.⁹⁴ Since the satisfaction of this condition was also verified from the phonon calculation employed to determine the thermodynamic properties of schoepite, the crystal structure of schoepite was found to be mechanically and dynamically stable. These thermodynamic properties will be reported in a forthcoming paper.⁹⁵

The thermal expansion of the material should occur predominantly along [001] direction because C_{33} , the diagonal component of C matrix along c direction, is much smaller than both C_{11} and C_{22} components. As expected, this direction is the one perpendicular to schoepite layers (see Figure 1). The diagonal component C_{11} is the largest (along a direction).

If single crystal samples are not available, the measure of the individual elastic constants is not possible. However, the polycrystalline bulk and shear moduli (B and G) may be determined experimentally. The Voigt⁹⁶ and Reuss⁹⁷ schemes were used to compute the isotropic elastic properties of schoepite polycrystalline aggregates. In Voigt method for calculating the elastic moduli, the strain throughout the aggregate of crystals is considered uniform, and the relations expressing the stress are averaged over all possible lattice orientations. While the strain is assumed to be uniform throughout the aggregate of crystals in Voigt's method, Reuss approximation considers the stress to be uniform and the averaging of the relations expressing the strain is carried out. As shown by Hill,⁹⁸ the Reuss and Voigt approximations result in lower and upper limits,

respectively, of polycrystalline constants and practical estimates of the polycrystalline bulk and shear moduli in the Hill approximation can be computed using average formulas. The formulae for these approximations may be found, for example, in the work of Weck *et al.*⁹³. The Reuss scheme provided the best results when the computed bulk modulus was compared with that determined from the equation of state, given in Section III.2, although the differences between the results obtained from these approximations was relatively small. The bulk and shear moduli calculated in these three approximations together with the values obtained for other mechanical properties are given in Table 6. Since CASTEP code gave a numerical estimate of the error in the computed bulk modulus of 2.28 GPa, our final value of the bulk modulus computed from the elastic constants in the Reuss approximation is $B=34.53\pm 2.28$ GPa, which agrees very well with that obtained from the EOS, $B=35.17 \pm 0.39$ GPa.

Table 6. Bulk, modulus, shear modulus, Young modulus, Poisson ratio, Pugh's ratio, and Vickers hardness (B , G , E , ν , D , and H) calculated in the Reuss approximation. Values of B , G and E are given in GPa.

Property	Voigt	Reuss	Hill
B	41.12	34.53	37.83
G	25.90	23.17	24.53
E	64.21	56.80	60.51
ν	0.24	0.23	0.24
D	1.59	1.49	1.54
H	4.81	4.88	4.83

While the elasticity theory is very well understood and mathematically well founded, it is difficult to visualize how the elastic properties vary with the strain orientation, except for the simplest cases of isotropic materials. In order to address this difficulty, the ELAM software of Marmier *et al.*⁹⁹ was used to obtain detailed tridimensional representations of the most important elastic properties calculated in this work, which are shown in Figure 6. In Figure 6.A, the property displayed is the inverse of the bulk modulus (the compressibility) instead of the bulk modulus. As it can be seen in Figure 6.A, the vertical direction (c axis) is the most compressible one in

accordance with the previous discussion on the results of the stiffness matrix C matrix. Also, it must be noted that the corresponding tridimensional representations of the elastic properties of metaschoepite mineral,¹⁰⁰ including those of the shear modulus, are very similar to those reported in Figure 6. This means that although the dehydration from schoepite to metaschoepite leads to a change of space symmetry,³² the transformation is not shear induced, as occurs for the dehydration of studtite to metastudtite.¹⁰¹ This behavior is the expected one, since the structures of schoepite and metaschoepite are very similar, the main changes being the differences in the arrangements of the interlayer water molecules and associated hydrogen bonds.^{31,32}

Figure 6. Schoepite elastic properties as a function of the orientation of the applied strain: (A) Compressibility; (B) Young modulus; (C) Shear modulus; (D) Poisson ratio.

A large value of shear modulus is an indication of the more pronounced directional bonding between atoms. The shear modulus represents the resistance to plastic deformation while the bulk modulus represents the resistance to fracture. By considering this interpretation of the shear and bulk modulus, Pugh¹⁰² introduced the proportion of bulk to shear modulus of polycrystalline phases ($D = B/G$) as a measure of ductility of a material. A higher D value is usually associated with higher ductility and the critical value which separates ductile and brittle materials is 1.75, i.e. if $B/G > 1.75$, the material behaves in a ductile manner, otherwise the material behaves in a brittle manner.¹⁰³ Poisson's ratio,¹⁰² ν , can be also utilized to measure the malleability of crystalline compounds and is related to the Pugh's ratio given above by the relation $D = (3-6\nu) / (8+2\nu)$. This ratio is close to 1/3 for ductile materials and, generally, much smaller for brittle materials. Schoepite material is brittle because the ratio D is smaller than 1.75 and Poisson's ratio is much smaller than 1/3 (see Table 6). For comparison, studtite and metastudtite were found to be ductile⁹³ and rutherfordine, uranophane and soddyite were found to be brittle.^{65,67,64}

The recently introduced empirical scheme¹⁰⁴ correlating the Vickers hardness and Pugh's ratio ($D = B/G$) was employed to compute the hardness of schoepite mineral. The value of the Vickers hardness, H , of polycrystalline schoepite is reported in Table 6. Its value, about 4.9, corresponds to material of intermediate hardness. For comparison, studtite and metastudtite^{93,62} have much smaller hardness (smaller than one), and rutherfordine, uranophane and soddyite are characterized by hardness values of 9.5, 6.3 and 6.3, respectively.^{65,67,64}

The elastic anisotropy of schoepite was evaluated by obtaining the corresponding shear anisotropic factors which provide a measure of the degree of anisotropy in the bonding between atoms in different planes. These factors are important to study material durability.¹⁰⁵ Shear anisotropic factors for the $\{100\}$ (A_1), $\{010\}$ (A_2), and $\{001\}$ (A_3) crystallographic planes were

computed using the formulae given by Bouhadda *et al.*¹⁰³. For a perfectly isotropic crystal, the factors A_1 , A_2 , and A_3 must be one, while any value smaller or greater than unity is a measure of the degree of elastic anisotropy possessed by the crystal. The computed values were 0.49, 0.61, and 0.95, respectively. The {001} plane, containing schoepite sheets, is the least anisotropic.

The universal anisotropy index,¹⁰⁶ A^U , was recently introduced to provide a measure of material anisotropy independent of the scheme used to determine the polycrystalline elastic properties, since it is defined in terms of the bulk and shear moduli in both Voigt and Reuss approximations. Thus, A^U represents a universal measure to quantify the single crystal elastic anisotropy. In this scheme, the departure of A^U from zero defines the extent of single crystal anisotropy and accounts for both the shear and the bulk contributions unlike all other existing anisotropy measures. Schoepite is characterized by a computed anisotropy index of 0.78, which is a rather small value ($A^U = 0$ corresponds to a perfectly isotropic crystal). For comparison, studtite, metastudtite, rutherfordine, uranophane and soddyite exhibit anisotropy values of 2.17, 1.44, 8.82, 0.81 and 0.50, respectively.^{93,67,65,64}

A set of fundamental physical properties can be estimated using the calculated elastic constants. For example, V_L and V_T , the transverse and longitudinal elastic wave velocities of the polycrystalline materials may be determined in terms of the bulk and shear moduli.⁹³ The values obtained were 2.217 and 3.759 km/s, respectively, using the calculated crystal density of 4.993 g/cm³ (see Table 1).

IV. CONCLUSIONS

In this work, the full schoepite structure was determined theoretically for the first time. Since in the previous experimental studies of this mineral it was not possible to locate hydrogen atoms

directly from X-ray diffraction data by structure refinement, we optimized the positions of all the hydrogen atoms in the unit cell. An idea of the H atom positions and interlayer H-bonding in schoepite was obtained by Finch *et al.*²⁹ from the locations of the O atoms of the H₂O groups and from the stereochemical characteristics of H₂O groups and their associated networks of H bonds. The general hydrogen bond structure described by Finch *et al.*²⁹ was reproduced by present theoretical calculations, confirming the suggested structure. Structural optimization performed by using the GGA-PBE exchange-correlation functional, taking into account a dispersion correction scheme, has given unit cell lattice parameters, atomic bond distances and angles in good agreement with experimental data. The computed X-Ray powder pattern was also in very good agreement with the experimental pattern.

Despite of the extraordinarily large computational resources required, the Raman spectrum of schoepite was computed and compared with their experimental counterpart. The results were also found in agreement with the experimental data. Similar calculations performed using Ostanin and Zeller's unit cell⁵⁶ produced a computed Raman spectrum which is not in agreement with the experimental spectrum. The normal mode analysis of the theoretical spectra obtained using the full unit cell was carried out and used to assign the main bands of the Raman spectra. This assignment improved significantly the current empirical assignment of the bands of the Raman spectrum of schoepite mineral.

The equation of state and mechanical properties of schoepite were also computed. The crystalline structure was found to be mechanically and dynamically stable. Schoepite is a brittle material characterized by small anisotropy and large compressibility along direction perpendicular to the sheets, which characterize its structure. The computed bulk modulus of schoepite ($B \sim 35$ GPa) is intermediate between the values obtained in previous works for other layered uranyl-

containing materials as rutherfordine ($B \sim 20$ GPa) and uranophane ($B \sim 60$ GPa).^{65,67,62} A large amount of relevant mechanical data of schoepite mineral was reported here, including bulk modulus derivatives, elastic coefficients, shear and Young moduli, Poisson ratios, ductility and hardness indices and elastic anisotropy measures.

SUPPORTING INFORMATION

Supplementary data associated with this article contain the main reflections in the X-Ray powder pattern of schoepite (Table S.1) and pictures of the atomic motions in some of the Raman active vibrational normal modes of this mineral (Figure S.1). Also, the calculated atomic positions resulting from our calculations are given in an independent file of CIF type.

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ACKNOWLEDGEMENT

This work was supported by ENRESA in the project: N° 079000189 “Aplicación de técnicas de caracterización en el estudio de la estabilidad del combustible nuclear irradiado en condiciones de almacenamiento” (ACESCO) and Project FIS2013-48087-C2-1-P. Supercomputer time by the CETA-CIEMAT, CTI-CSIC and CESGA centers is also acknowledged. This work has been

carried out in the context of a CSIC–CIEMAT collaboration agreement: “Caracterización experimental y teórica de fases secundarias y óxidos de uranio formados en condiciones de almacenamiento de combustible nuclear”. We also want to thank Dr. Ana María Fernández and Dr. Rafael Escribano for reading the manuscript and many helpful comments.

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FOR THE TABLE OF CONTENTS GRAPHIC ONLY

Synopsis. Calculated structure and X-ray diffraction patterns of schoepite. The position of all the hydrogen atoms in the unit cell of this material, which could not be determined by using X-ray diffraction techniques, were determined by means of solid-state theoretical methods. The computed pattern agrees in an excellent way with its experimental counterpart.