Structural, Mechanical and Vibrational Study of Uranyl Silicate Mineral Soddyite by DFT Calculations

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Abstract

Uranyl silicate mineral soddyite, $(\text{UO}_2)_2(\text{SiO}_4) \cdot 2(\text{H}_2\text{O})$, is a fundamental component of the paragenetic sequence of secondary phases that arises from the weathering of uraninite ore deposits and corrosion of spent nuclear fuel. In this work, soddyite was studied by first principle calculations based on the density functional theory. As far as we know, this is the first time that soddyite structure is determined theoretically. The computed structure of soddyite reproduces the one determined experimentally by X-Ray diffraction (orthorhombic symmetry, spatial group $Fddd\ O2$; lattice parameters $a=8.334\ \text{\AA}$, $b=11.212\ \text{\AA}$; $c=18.668\ \text{\AA}$). Lattice parameters, bond lengths, bond angles and X-Ray powder pattern were found to be in very good agreement with their experimental counterparts. Furthermore, the mechanical properties were obtained and the satisfaction of the Born conditions for mechanical stability of the structure was demonstrated by means of calculations of the elasticity tensor. The equation of state of soddyite was obtained by fitting lattice volumes and pressures to a fourth order Birch-Murnahan equation of state. The Raman spectrum was also computed by means of density functional perturbation theory and compared with the experimental

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spectrum obtained from a natural soddyite sample. The results were also found in agreement with the experimental data. A normal mode analysis of the theoretical spectra was carried out and used in order to assign the main bands of the Raman spectrum.

Keywords: Spent nuclear fuel, Soddyite, DFT, Mechanical Properties, Raman Spectroscopy

1. Introduction

The resurgence of the use of nuclear energy is mainly driven by the need of more electricity for increasing populations and consumption, as well as the need of energy sources without CO₂ emissions and other greenhouse gases causing global warming [1-3]. However, the management of nuclear waste is a matter of concern because it can be a source of high ecological damage, in the same way as uranium ore mining [4] and nuclear accidents [5].

High-level nuclear waste, such as spent nuclear fuel (SNF) or reprocessed waste immobilized in a borosilicate glass [6], will be disposed of by burial in an underground geological repository. Contact of this waste with groundwater is expected after a time period of the order of some thousands of years [7] after closure, when the barriers that protect the waste will be breach [3]. The reducing conditions in the deep geological disposal at this time will not be maintained, and oxidized species near the spent fuel surface will increase due to the radiolysis of water caused by the ionizing radiation associated with the SNF [8-12]. Therefore, uranium in the matrix of the spent nuclear fuel, composed by uranium dioxide, U^{IV}O₂, could oxidize to U(VI) and dissolve into the water forming uranyl groups. These uranyl groups can precipitate forming secondary phases, *i.e.* alteration products, on the spent fuel surface depending on the local physico-chemical conditions and concentrations of reactive species present [12]. These secondary phases can reduce the release and environmental impact of the fission products and heavier actinides contents in the SNF to the biosphere [9,13]. The knowledge of the structures of these phases may be a key to evaluate the possible incorporation of fission products and transuranic elements into their crystal structures [13-19].

Uranyl secondary phases are usually studied by analyzing natural minerals containing the uranyl ion [20], $\text{U}^{\text{VI}}\text{O}_2^{2+}$, found as alteration products of uraninite [12], which is a natural analogue of the SNF matrix. The general trend of the temporal sequence of alteration products of natural uraninites at different geochemical conditions was first recognized by Frondel [21], and it is still widely accepted nowadays [12,22-23]. In this sequence, the uranyl oxide hydrates appear at the first place, then the uranyl silicates and, less frequently, the uranyl phosphates; although the specific alteration products depend on the local conditions. Therefore, the study of these uranyl minerals is very important for understanding the long-term performance of a geological repository for nuclear waste.

One of the minerals found very often in nature as alteration product of uraninite is soddyite. Mineral soddyite is a hydrated uranyl nesosilicate which was found in Shinkolobwe Mine (Kasolo Mine), Shinkolobwe, Katanga Cooper Crescent, Katanga (Shaba), Democratic Republic of Congo (Zaire). It was first described by Schoep in 1922 [24]. In nature, soddyite occurs as fine grained pale-yellow aggregates or flat crystals or fibers having a color from greenish to canary yellow [25]. Soddyite, $(\text{UO}_2)_2(\text{SiO}_4) \cdot 2(\text{H}_2\text{O})$, is the unique uranyl silicate mineral known characterized by a 2:1 uranium to silicon ratio [26]. Most uranyl silicate minerals have a 1:1 uranium to silicon ratio and contain sheets [20,26,14], except soddyite [27] and weeksite [17], which have framework crystal structures [14-15,27]. Soddyite is isostructural to the uranyl germanate mineral [26-27] studied by Legros *et al.* [28]. The crystal structure of $\text{Na}_2(\text{UO}_2)_2\text{SiO}_4\text{F}_2$ [29] is structurally related to soddyite. Its structure is very complex and includes 136 atoms in the unit cell, as well as 768 valence electrons. In oxidizing waters that contain uranyl and silicate ions, the solid uranyl orthosilicate may form as a solubility-controlling solid [30]. It has been synthesized in the laboratory, for example,

by Legros *et al.* [31], Kuznetsov *et al.* [32-33] and Moll *et al.* [30]. The latter synthesized the uranyl orthosilicate with reproducible yields of about 81 %, and phase purity.

The present state of knowledge about the crystal chemistry and bonding of the uranium ion in these systems is very incomplete. As noted by Weck *et al.* [34], the existence of a great amount of information on the formation, thermodynamic stability, and phase transformations of alteration phases formed at the SNF surface is in stark contrast with the paucity of data regarding the mechanical stability and properties of these phases. Saving the theoretical study of Weck *et al.* [34] on the uranyl peroxide hydrates, studtite and metastudtite, no experimental or computational studies have reported the mechanical properties (bulk and shear moduli, stiffness coefficients, anisotropy factors, etc.) of these phases [35]. Furthermore, the conditions of mechanical stability of their structures have not been analyzed. Whereas the lack of the experimental data could be related to the special care needed to handle these radioactive minerals, the computational data are scarce due to the difficulties in the application of theoretical methods to uranium containing solids. The calculations are very computationally demanding, not only due to the great size of the corresponding unit cells, but also to the high level of theory required to describe correctly these systems [36]. For example, there is very few published works on the theoretical vibrational spectra of uranium containing solids [37-40], and none of these works includes a complete determination of these spectra.

Despite the structure of soddyite have been determined by experimental X-ray diffraction techniques, it has never been confirmed by means of theoretical solid state calculations. In this paper, we perform a complete structural characterization of soddyite by theoretical solid state methods, which allow us to confirm the structure obtained

experimentally. From the obtained structure, we had studied the mechanical properties and stability of soddyite structure, based on the elastic constants computed in this study. The elastic constant tensor of an inorganic compound provides a complete description of the response of the material to external stresses in the elastic limit [35]. The analysis of this tensor, which is usually correlated with many mechanical properties, allows to understand the nature of the bonding in the material. Soddyite equation of state is also reported. Besides, although the Raman spectrum of this mineral has been determined by experimental methods [41-44], a precise assignation of the main bands in the spectra is lacking, since they have been characterized incompletely and by using empirical arguments. The theoretical Raman spectrum of soddyite is reported here, including the computation of intensities and the assignment of the vibrational bands. We have performed the assignment of the experimental vibrational Raman bands since theoretical methods provide detailed microscopic scale views of the atomic vibrational motions in the corresponding normal modes. Computations were carried out by means of Density Functional Theory [45] (DFT) based on plane waves and pseudopotentials [46]. A norm conserving relativistic pseudopotential for uranium atom [47] developed in a previous paper [48] was used.

2. Materials and methods

2.1. Experimental

The mineral sample studied in this work [49] is a natural mineral from Sierra Albarrana (Córdoba, Spain) whose structure corresponds to the ideal gummite occurrence [21] (central core black and a yellow surrounding zone, formed by several minerals). The sample contains a mixture of alteration phases of natural uraninite: rutherfordine, soddyite, uranophane and kasolite. Soddyite prevails in the inner part of the sample.

A polished section of the sample was analysed by Raman using a Horiba LabRam HR evolution spectrometer (Jobin Yvon Technology). A red laser of HeNe with a wavelength of 632.81 nm and an operation power of 20 mW was used as excitation source. The laser was focused onto the sample by using 100x objective at the confocal microscope BX4 with confocal 800 mm; the scatter light was collected with the same objective and then dispersed with a Jobin-Yvon spectrometer (600 grooves/mm), and detected with a Peltier cooled CCD detector (256 x 1024 pixel). The spectral resolution was about 1 cm⁻¹ per pixel.

2.2. Theoretical DFT calculations

CASTEP code [50], a module of the Materials Studio package [51], was employed to model soddyite structure. The generalized gradient approximation (GGA) together with PBE functional [52] and Grimme empirical dispersion correction [53], called the DFT-D2 approach, were used. The Grimme dispersion correction was included to describe correctly the hydrogen bonds present in the soddyite structure. The pseudopotentials used for H, O and Si atoms in the unit cell of soddyite mineral were standard norm-conserving pseudopotentials [47] given in CASTEP code (00PBE-OP type). The norm-conserving relativistic pseudopotential for U atom was generated from first principles as shown in a previous work [48].

Geometry optimization was carried out by using the Broyden–Fletcher–Goldfarb–Shanno optimization scheme [54,46] with a convergence threshold on atomic forces of 0.01 eV/Å. The kinetic energy cut-off and k-point mesh [55] was adopted to ensure good convergence for computed structures and energies. Soddyite structure was optimized in calculations with increasing complexity by increasing these parameters. The optimization performed with a cut-off of 930 eV and a K mesh of 3 x 2 x 1 gave a well converged structure, and it was used to determine the final results.

Elastic constants, used for the calculation of mechanical properties and to study the mechanical stability of soddyite crystal structure, were calculated from stress-strain methodology. With this purpose, finite deformation technique is employed in CASTEP. In this technique, finite programmed symmetry-adapted strains [35] are applied to the equilibrium conformation generating a set of distorted structures. The individual elastic constants are then extracted from the stress tensor obtained as response of the system to the applied strains. For the calculation of elastic tensor, this stress-based method appears to be more efficient than the energy-based methods and the use of DFPT [56].

Bulk modulus and its pressure derivatives were also calculated by fitting the lattice volumes and pressures to an equation of state. In the present study, the lattice volumes around the equilibrium were calculated by optimizing the structure at several different pressures -1.0, -0.75, -0.50, -0.25, 0.0, 0.25, 0.50, 0.75, 1.0, 1.5, 2.0, 3.0, 4.0, 5.0, 7.0, and 9.0 GPa, where negative pressure values mean traction or tension. The results were then fitted to a fourth-order Birch-Murnaghan equation of state [57] using EOSFIT 5.2 code [58].

For the calculations of vibrational properties, the linear response density functional perturbation theory (DFPT) [59-61], implemented in the CASTEP code, was used in the same way as in previous works [48,62].

3. Results and discussion

The unit cell parameters and internal atomic positions were first optimized using an initial atomistic model based in the atomic coordinates given by Demartin *et al.* [27] From the optimized structure, we have obtained both the structural parameters as well as the X-Ray powder pattern. The elastic tensor was calculated, for the optimized equilibrium structure, from the stress-strain relationships by using the finite deformation technique implemented in CASTEP. From the elastic tensor, mechanical properties such

as elastic modulus, shear modulus, Vickers hardness and anisotropy index were then computed. Besides, the soddyite equation of state was obtained by fitting lattice volumes and pressures to a fourth order Birch-Murnahan equation of state. Finally, the vibrational Raman spectrum was predicted as a list of wavenumbers and intensity values for each normal mode [61]. Experimental Raman spectrum was then compared with the computed one, and the assignment of main fundamental band frequencies was carried out.

3.1. Structure

Stohl and Smith [26] categorized the naturally occurring uranyl silicates according to the uranium to silicon ratio, which in part determines the structure of these minerals. Most uranyl silicate minerals, as uranophane and boltwoodite, are sheet silicates with a 1:1 uranium to silicon ratio [20,26,14]. The sheets are composed of $[(\text{UO}_2)_2(\text{SiO}_4)_2]^{4-}$ units bound at the equatorial edges. Charge compensating cations, as calcium in uranophane and potassium in boltwoodite, lie in the interlayer space between the sheets. Soddyite [27] and weeksite [17] have uranium to silicon ratios of 2:1 and 2:5, respectively, and their structure involve frameworks of U^{6+} polyhedra [14-15,27]. In soddyite, charge compensation for the uranyl silicate groups is not required as the basic building unit is neutral $[(\text{UO}_2)_2(\text{SiO}_4)]$ [63].

The computed structure is shown in Figure 1. Figure 1.A, shows a view of the unit cell from [001]. Figure 1.B is a view of a 2 x 2 x 1 supercell along [110]. Fig 1.C is a view of the latter cell where only a subset of atoms is retained in order to show a clearer view of the soddyite structure. As can be seen, U atoms display pentagonal bipyramid coordination, $\text{UO}_6(\text{H}_2\text{O})$, and Si atoms present tetrahedral coordination, SiO_4 . The U bipyramids are connected by sharing two non-adjacent edges of the equatorial plane to form zigzag chains (see Figure 1.C). The single unshared equatorial vertex of the

bipyramid is occupied by H₂O. The chains are parallel to [110] plane and are cross bonded through two opposite edges of the SiO₄ tetrahedra; *i.e.* adjacent uranyl silicate chains are directly linked as each tetrahedron shares two edges with bipyramids from two different chains. Moreover, the cohesion of the structure is enhanced by a pattern of hydrogen bonds involving the water molecules and the uranyl O atoms.

Figure 1. Structure of soddyite mineral: A) View of the unit cell from [001]; B) View of a 2 x 2 x 1 supercell from [110]; C) View of a 2 x 2 x 1 supercell from [110], retaining only a subset of atoms (a single chain of U bipyramids cross bonded to other chains through two opposite edges of the SiO₄ tetrahedra is shown). Colour code: U-Blue, Si-Brown, O-Red, H-Yellow.

As mentioned, the structure of soddyite was determined in calculations with increasing complexity. Table 1 gives the final lattice parameters, volumes and densities obtained compared with the experimental ones from Demartin *et al.* [27]. As it can be seen, theoretical and experimental results are in good agreement. The computed volume and density differ from the corresponding experimental values by about 0.3%.

Table 1. Lattice parameters

Parameter	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	α	β	γ	Vol. (Å ³)	Dens. (g/cc)
Calc.	8.0780	11.4253	18.8380	90	90	90	1738.6	5.104
Exp. [27]	8.334	11.212	18.668	90	90	90	1744.4	5.088

Tables A.1 and A.2 of Appendix A of the Supplementary Information give a comparison of the more important geometric parameters (bond distances and angles) obtained with the corresponding experimental data of Demartin *et al.* [27]. Soddyite has only one structurally (symmetrically) identical U⁶⁺ ion and one structurally (symmetrically) identical Si⁴⁺ ion in its crystal structure. The two O atoms in the uranyl group, UO₂²⁺ (O1 and its symmetry related companion), are in apical positions of the pentagonal bipyramids at a distance of 1.781 Å. The calculated value is 1.801 Å. The remaining five O atoms (four O2 and OW) lie in the equatorial plane which U-O distances which range from 2.313 to 2.424 Å (calculated 2.312 to 2.436 Å). The distances between adjacent O atoms range from 2.462 to 3.126 Å (calculated 2.467 to 3.166 Å), the shortest values corresponding to the shared edges with other U centered bipyramids and SiO₄ groups. The SiO₄ tetrahedron is markedly irregular, the O-Si-O angles ranging from 98.0 to 119.0 degrees (calculated 98.1 and 119.6 degrees). The O-O distances range from 2.462 to 2.811 Å (calculated 2.487 and 2.846 Å). The Si-O distances, 1.631 Å, are within the normal range, the calculated value being of 1.647 Å. The geometry and orientation of the plane of water molecule is mainly determined by

the hydrogen bond interaction, directed towards O1. The OW-H-O1 angle determined experimentally is 156 degrees, which is satisfactorily reproduced in our calculations, 149 degrees.

The X-Ray powder diffractogram of soddyite was computed from the experimental [27] and computed structures [64] using CuK α radiation ($\lambda=1.540598$ Å). The most intense lines ($I > 10\%$) are compared in Figure 2. As it can be seen, the agreement in line positions and intensities is very good. The use of spectra derived directly from the experimental and computed structures allows for a fair comparison of the results free of interferences and possible artefacts, as the presence of sample impurities, because both are determined under the identical conditions. Nevertheless, the use of an experimental pattern also leads to an excellent agreement. Computer program X Powder [65] using the PDF-2 database [66] recognizes the computed spectrum as that of soddyite (pattern 77-0604, which corresponds to synthetic soddyite sample, see Nozik and Kuznetsov [33]). The values of the main reflections are given in Table A.3 of Appendix A of the Supplementary Information.

Figure 2. X-Ray powder pattern of soddyite using CuK α radiation: a) Experimental pattern (pattern 77-0604 in the PDF-2 database); b) X-Ray powder pattern computed from experimental geometry [27]; c) X-Ray powder pattern computed from calculated geometry.

3.2. Mechanical properties and stability

Elastic tensor, used for the calculation of mechanical properties and for analysing the mechanical stability of soddyite crystal structure, was calculated for the optimized equilibrium structure, from the stress-strain relations by using the finite deformation technique implemented in CASTEP. Crystals with orthorhombic symmetry have 9 non-degenerate elastic constants in the symmetric stiffness matrix [34-35], which may be written as:

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

Here, we use 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 precise values of these constants obtained in our computations are given in Table 2.

Table 2. The nine independent elastic constants in the stiffness matrix for the orthorhombic lattice structure of soddyite. All values are given in GPa.

C_{11}	C_{22}	C_{33}	C_{44}	C_{55}	C_{66}	C_{12}	C_{13}	C_{23}
81.65	120.92	161.54	40.99	25.93	42.14	35.61	22.59	49.84

For orthorhombic crystals, the necessary and sufficient Born criteria for mechanical stability are [34,67]:

$$C_{11} > 0 \ (i = 1,4,5,6)$$

$$C_{11}C_{22} - C_{12}C_{12} > 0$$

$$C_{11}C_{22}C_{33} + 2C_{12}C_{13}C_{23} - C_{11}C_{23}C_{23} - C_{22}C_{13}C_{13} - C_{33}C_{12}C_{12} > 0$$

Since the above conditions are fulfilled by the elastic constants of soddyite reported in Table 2, its mechanical stability can be inferred. The generic necessary and sufficient Born criterion that all eigenvalues of the C matrix be positive [67] was also checked. The C matrix was diagonalized numerically, and all eigenvalues were found to be positive, as expected. The lowest eigenvalue was about 0.026, so that the soddyite structure is far from instability.

The fact that C_{11} , the diagonal component of the C matrix along a direction, is much smaller than either C_{22} or C_{33} , suggests that the thermal expansion of the material will occur predominantly along this direction (contained in the plane of the soddyite chains). C_{33} is the largest diagonal component (along the perpendicular direction to soddyite chains).

If single crystal samples are not available, the measurement of the individual elastic constants cannot be possible. Instead, the polycrystalline bulk modulus (B) and shear modulus (G) may be determined experimentally. The Voigt and Reuss [35] schemes were used to compute the isotropic elastic properties of soddyite polycrystalline aggregates. As shown by Hill [68], 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. Relevant formulae for these approximations may be found in

several sources (see for example Weck *et al.* [34]). The bulk and shear moduli and other mechanical properties computed in these approximations are given in Table 3.

Table 3. Bulk, modulus, shear modulus, Young modulus, Poisson ratio, Pugh's ratio, and Vickers hardness (B , G , E , ν , D , and H) calculated in the Voigt, Reuss, and Hill approximations. Values of B , G and E are given in GPa.

Property	Voigt	Reuss	Hill
B	64.4615	58.4136	61.4375
G	38.8807	36.0015	37.4411
E	97.1164	89.5976	93.3586
ν	0.2489	0.2444	0.2467
D	1.6579	1.6225	1.6409
H	6.4217	6.2374	6.3280

The numerical estimate of the error in the computed bulk modulus given by the CASTEP code is 2.312 GPa, quite similar to the difference of the values in the Hill and Voigt/Reuss schemes, 3.024 GPa. Voigt and Reuss methods yield quite small differences for soddyite. Larger differences are expected for crystalline systems with strong anisotropy, featuring large differences between elastic constants along different directions [34]. The values of the bulk modulus computed by Weck *et al.* [34] for studtite and metastudtite (about 30 and 42 GPa, respectively) are smaller than the value obtained here for soddyite.

In general, a large value of the shear moduli is an indication of the more pronounced directional bonding between atoms. The shear modulus G represents the resistance to plastic deformation, while the bulk modulus represents the resistance to fracture [69]. Young modulus defines the relationship between stress (force per unit area) and strain (proportional deformation) in a material, that is, $E = \sigma/\epsilon$. The individual components of Bulk and Young's moduli may be derived from the elastic compliance matrix components [70,34]. Compliance matrix is the inverse of stiffness C matrix. For

example, the E components along a , b , and c directions can be expressed as $E_a = S_{11}^{-1}$, $E_b = S_{22}^{-1}$ and $E_c = S_{33}^{-1}$. The corresponding values are given in Table 4. As it can be seen, B_c , is larger than either B_a or B_b . Thus, c direction is the least compressible. Also, the component E_c is much larger (stiffer) than E_a and E_b . Thus, the direction perpendicular to the plane containing the chains is the stiffest, in agreement with the results of the stiffness C matrix.

Table 4. Bulk and Young moduli components along the crystallographic axes. All values are given in GPa.

Property	a axis	b axis	c axis
B	105.10	251.92	275.08
E	70.68	95.09	140.12

Pugh [71] introduced the proportion of bulk to shear modulus of polycrystalline phases ($D = B/G$) as a measure of ductility by considering the interpretation of the shear and bulk modulus given above. A higher D value is usually associated with a higher ductility. 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 [70]. The Poisson's ratio, ν , can also be utilized to measure the malleability of crystalline compounds [71], and is related to the Pugh's ratio given above by the relationship $D = (3 - 6\nu) / (8 + 2\nu)$. The Poisson's ratio is close to 1/3 for ductile materials, while it is generally much less than 1/3 for brittle materials. As it can be seen in Table 3, for soddyite we found ratios D and ν about 1.65 and 0.25, respectively. These values are only slightly smaller than 1.75 and 1/3, respectively. Therefore, soddyite corresponds to a brittle material. For comparison, both studtite and metastudtite minerals were found to be ductile [34].

Hardness of these systems was computed according to a recently introduced empirical scheme [72], which correlates the Vickers hardness and the Pugh's ratio ($D = B/G$). Vickers hardness, H , of polycrystalline soddyite is given in Table 3. Its value, about 6.3, corresponds to a material of intermediate hardness. For comparison, we computed the hardness of studtite and metastudtite by using the elasticity data of Weck *et al.* [34]. These systems, characterized by much larger D ratios, have much smaller hardness (smaller than one).

In order to assess the elastic anisotropy of soddyite, shear anisotropic factors were obtained. These factors provide a measure of the degree of anisotropy in the bonding between atoms in different planes, and are very important to study material durability. Shear anisotropic factors for the $\{100\}$ (A_1), $\{010\}$ (A_2), and $\{001\}$ (A_3) crystallographic planes and percentages of anisotropy in compression and shear (A_{comp} and A_{shear}) were computed by using the formulae given by Ravindran *et al.* [69]. For an 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. For percentage anisotropies, a value of 0% represents a perfectly isotropic crystal. For soddyite (see Table 5), the anisotropies grow in the planes $\{100\}$, $\{001\}$, and $\{010\}$ ($A_1 < A_3 < A_2$). The $\{010\}$ plane is shown to be the most anisotropic one. Percentage anisotropies in compression and shear were about 5 and 4 %, respectively.

In the recently introduced universal anisotropy index [73], 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. Thus, A^U represents a universal measure to quantify the single crystal elastic anisotropy. Soddyite is characterized by an anisotropy index of 0.50, which is a rather small value ($A^U = 0$ corresponds to a perfectly isotropic crystal). For comparison, studtite and metastudtite

exhibit much larger anisotropies, the values computed by Weck *et al.* [34] being of 2.17 and 1.44, respectively.

Table 5. Shear anisotropy factors (A_1 , A_2 and A_3), percentages of anisotropy in compression and shear (A_{comp} and A_{shear}), and universal anisotropy index (A^U).

A_1	A_2	A_3	A_{comp} (%)	A_{shear} (%)	A^U
0.8282	0.5674	1.2836	4.9220	3.8449	0.5034

A set of fundamental physical properties may 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 [34]. The values obtained were 2.708 and 4.671 km/s, respectively, by using the calculated crystal density of 5.104 g/cc (see Table 1).

3.3. Equation of state

Lattice volumes around the equilibrium were calculated by optimizing the structure at sixteen different applied pressures. The results are displayed in Figure 3.

Figure 3. Soddyite unit cell volume vs. applied pressure.

The calculated data were fitted to a fourth-order Birch-Murnaghan equation of state [57] (EOS) using the volume at 0 GPa ($1738.6 \text{ \AA}^3$) as V_0 with the EOSFIT 5.2 code [58]:

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

In this equation,

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

and B , B' and B'' are the bulk modulus and its first and second derivatives, respectively, at the temperature of 0 K. The values found for the bulk modulus and its derivatives were $B = 60.07 (\pm 0.67) \text{ GPa}$, $B' = 4.19 (\pm 0.60)$, and $B'' = 0.25 (\pm 0.20) \text{ GPa}^{-1}$ ($\chi^2 = 0.001$). The bulk modulus found agrees very well with those determined from calculated elastic constants given in Table 3. As in other works [74], the agreement is better with the bulk modulus obtained in the Reuss approximation ($B = 58.41 \pm 2.31 \text{ GPa}$). This is due to the fact that values of B obtained from the EOS are generally smaller than those obtained from elastic tensor. The explanation can be found in that in this case the cell shapes are relaxed, whereas the cell shapes are kept fixed in the determinations of the elastic constants [75].

3.4. Raman spectra and band assignment

The theoretical Raman spectrum in the wavenumber range of $3600\text{-}0 \text{ cm}^{-1}$ is compared with the one obtained experimentally in Fig. 4. As can be seen in this figure, the calculated spectrum is quite similar to the experimental one. The theoretical

spectrum was computed at $T=298\text{ K}$, $\lambda=532\text{ nm}$, $\text{FWHM}=20\text{ cm}^{-1}$. Pictures of the atomic motions in the Raman active vibrational modes are given in Appendix B of Supplementary Information (Fig. B.1).

Figure 4. Experimental and calculated Raman spectra of soddyite mineral.

In order to calculate the number of contributions of a given band in the experimental spectrum, we carry out the analysis by using the second derivative method [48-49]. In Fig. 5, we show the experimental and theoretical Raman spectra divided in four regions: (A) OH stretching vibration region from 3800 to 3000 cm^{-1} (Fig. 5.A); (B) H_2O bending region 1800 - 1300 cm^{-1} (Fig. 5.B); (C) uranyl UO_2^{2+} and silicate SiO_4^{4-} fundamental vibrations region from 1400 to 700 cm^{-1} (Fig. 5.C); and (D) low wavenumber region from 700 to 0 cm^{-1} (Fig. 5.D). The wavenumber of both spectra along with the corresponding calculated intensities and assignments are given in Table 6. The Raman shifts and assignments performed by Frost *et al.* [44] are also given in this table for comparison. The results obtained in each region are described in the next paragraphs.

(A) OH stretching vibrations region

In the hydroxyl stretching region we found one broad band with two contributions at about 3488 cm^{-1} and 3398 cm^{-1} . The corresponding computed Raman shifts are 3443 and 3353 cm^{-1} . These bands were assigned to antisymmetric and symmetric water stretching vibrations, $\nu^a(\text{OH})$ and $\nu^s(\text{OH})$, respectively. Although the difference of

computed and experimental shifts is quite large, it must be noted that the infrared OH stretching frequencies calculated for uranyl silicate clusters have much larger differences with respect to the experimental data [76]. Note that the low intensity contribution band at wavenumber 3147 cm^{-1} is not found in the calculated spectrum. This band was also found by Frost *et al.* [44] at 3158 cm^{-1} .

(B) H_2O bending vibration region

The Raman shift associated to the water bending vibration, $\delta(H_2O)$, was found to be placed at about 1584 cm^{-1} , comparable to the calculated wavenumber of 1495 cm^{-1} . Note that Frost *et al.* [44] found a shoulder at 1596 cm^{-1} . This was attributed to water absorbed on the sample surface [30].

Figure 5. Experimental and theoretical Raman spectra of soddyite mineral. (A) Region: 3800-3000 cm^{-1} ; (B) Region: 1800-1300 cm^{-1} ; (C) Region: 1400-700 cm^{-1} ; (D) Region: 700-0 cm^{-1} .

(C) Uranyl UO_2^{2+} and silicate SiO_4^{4-} fundamental vibrations region

The experimental band at 1024 cm^{-1} , corresponds to the band calculated at 995 cm^{-1} , which was assigned to the SiO_4^{4-} asymmetric stretching vibration, $\nu^a(\text{SiO}_4)^{4-}$ (see vibrational mode picture in Appendix B of the Supporting Information). Similar wavenumbers were found by Frost *et al.* [44] and Biwer *et al.* [42] (1025 and 1018 cm^{-1} , respectively).

The most intense band in the Raman spectrum is found experimentally at about 830 cm^{-1} , and calculated at 807 cm^{-1} . This band was found to be placed at 824, 830, and 828 cm^{-1} by Biwer *et al.* [42], Amme *et al.* [43] and Frost *et al.* [44]. As it can be observed in the vibrational mode picture in Appendix B, it was assigned to UO_2^{2+} symmetric stretching vibration, $\nu^s(\text{UO}_2)^{2+}$.

It should be noted that in the computed spectrum appears two very close bands at 874 and 873 cm^{-1} . Frost *et al.* [44] also found two bands in this region at 909 and 897 cm^{-1} , which were attributed to the $\nu^a(\text{UO}_2)^{2+}$ vibration. Based in our computed results we think that the band at 909 cm^{-1} corresponds to the calculated vibration at 873 cm^{-1} , which is attributed to the symmetric stretching SiO_4^{4-} vibration. Additionally, Frost *et al.* [44] found a band at 791 cm^{-1} , which was assigned it to water librational vibrations. This band is close to the computed one at 799 cm^{-1} , assigned to $\nu^s(\text{UO}_2)^{2+}$ vibration.

(D) Low wavenumber region

The bands computed at 610 and 579 cm^{-1} are comparable to the experimental value of 592 cm^{-1} . They were assigned to the water librational vibrations (twisting and rocking, respectively). In the experimental work of Frost *et al.* [44], the 591 cm^{-1} band

was assigned to a silicate bending vibration, $\delta(\text{SiO}_4)^{4-}$. This kind of vibration appears in the theoretical spectrum at 431 cm^{-1} , which is comparable to the experimental band at 460 cm^{-1} . The corresponding values found by Biwer *et al.* [42], Amme *et al.* [43] and Frost *et al.* [44], are 457 , 455 and 459 cm^{-1} , respectively. While Biwer *et al.* [42], attribute this band to an equatorial UO stretching vibration, Frost *et al.* [44], assign this band to $\delta(\text{SiO}_4)^{4-}$ vibration in agreement with the data from this work. The free ion value for this vibration is 527 cm^{-1} [77-78].

The bands calculated at 299 , 296 and 295 cm^{-1} were assigned mainly to a silicate translation the first, and the other ones to different silicate deformation vibrations, $t(\text{SiO}_4)^{4-}$ and $\rho(\text{SiO}_4)^{4-}$ (twisting and rocking). They are comparable to the experimental band at about 289 cm^{-1} .

Finally, the band calculated at 50 cm^{-1} can be approximately mapped to the experimental shift of 103 cm^{-1} .

Table 6. Experimental and calculated Raman band wavenumbers, calculated intensities and assignments. Raman shifts and assignments performed by Frost *et al.* [44] are also given in this table for comparison.

Band Name	Exp. Raman shift (cm^{-1}) (This work)	Exp. Raman shift (cm^{-1}) (Frost <i>et al.</i> [44]) shift/assignment	Calc. Raman shift (cm^{-1})	Irr. Rep. (D_{2h})	Int. ($\text{\AA}^4$)	Assignment
OH stretching region						
a	3488	3516/ $\nu(\text{OH})$	3443	B_{2g}	3229.1	$\nu^a(\text{OH})$
b	3398	3414/ $\nu(\text{OH})$	3353	A_g	27818.8	$\nu^s(\text{OH})$
c	3147	3158/ $\nu(\text{OH})$	-	-	-	-
H₂O bending region						
d	1584	1584,1596/ $\delta(\text{H}_2\text{O})$	1495	A_g	433.8	$\delta(\text{H}_2\text{O})$
UO₂²⁺ and SiO₄⁴⁻ fundamental vibrations region						
e	1024	1025/ $\nu^a(\text{SiO}_4)^{4-}$	995	B_{1g}	750.1	$\nu^a(\text{SiO}_4)^{4-}$
	-	909,897/ $\nu^a(\text{UO}_2)^{2+}$	874	B_{2g}	53.5	$\nu^a(\text{UO}_2)^{2+} + \rho(\text{H}_2\text{O})$
			873	A_g	583.7	$\nu^s(\text{SiO}_4)^{4-}$
f	830	838,828,820/ $\nu^s(\text{UO}_2)^{2+}$	807	A_g	8054.0	$\nu^s(\text{UO}_2)^{2+}$
	-	791/ $\nu(\text{H}_2\text{O})$	799	B_{1g}	387.3	$\nu^s(\text{UO}_2)^{2+}$
Low wavenumber region						
g	592	591/ $\delta(\text{SiO}_4)^{4-}$	610	A_g	168.6	$t(\text{H}_2\text{O})$
			579	B_{2g}	138.4	$\rho(\text{H}_2\text{O})$
h	460	459/ $\delta(\text{SiO}_4)^{4-}$	431	A_g	323.3	$\delta(\text{SiO}_4)^{4-}$

i	289	310	299	B_{1g}	54.8	$T(\text{SiO}_4)^{4-}$
			296	A_g	39.6	$t(\text{SiO}_4)^{4-}$
			295	B_{3g}	308.3	$\rho(\text{SiO}_4)^{4-}$
j	103	111,102	50	B_{2g}	54.5	$\delta^{\text{op}}(\text{U-OH}_2)$

4. Conclusions

In this work, soddyite structure was determined theoretically for the first time. The calculations have been performed by using the CASTEP module of Materials Studio software. The pseudopotentials used for H, O and Si atoms in the unit cell of soddyite mineral were standard norm-conserving pseudopotentials, whereas the pseudopotential for U atom was generated from first principles in a previous paper [48].

These calculations, based on density functional theory, show the role of water in the structural and vibrational properties of the uranyl silicate mineral soddyite. Water molecules enter in the structure of soddyite as structural water forming part of the coordination structure of uranium atom, that is, within the pentagonal bipyramids, $\text{UO}_6(\text{H}_2\text{O})$. 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 excellent agreement with experimental data. The computed X-Ray powder pattern was also in very good agreement with the experimental pattern.

Elastic tensor was calculated from stress-strain relationships by using the finite deformation technique implemented in CASTEP for the optimized equilibrium structure. The analysis of the calculated elasticity stiffness tensor has revealed that the soddyite structure satisfies properly the mechanical stability conditions. Furthermore, mechanical properties of this mineral, for which there are not experimental data to compare with, were predicted. Mechanical data reported here include the bulk modulus,

elastic coefficients, shear and Young moduli, Poisson ratios, ductility and hardness indices and elastic anisotropy measures.

Soddyite equation of state was obtained by fitting lattice volumes and pressures to a fourth order Birch-Murnahan equation of state.

Raman spectrum was also computed and compared with their experimental counterpart. The normal mode analysis of the theoretical spectra was carried out and used to assign the main bands of the Raman spectra. It should be also noted that some bands, as that placed at 3147 cm^{-1} , were not found in the theoretical spectrum. Thus, they may correspond to other phases present in the natural mineral under study.

This work verifies that the DFT method is a reliable tool to analyse the structure, mechanical properties and vibrational spectra of uranyl silicate minerals.

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SUPPLEMENTARY DATA

Supplementary data associated with this article contain two appendices. Appendix A contains additional details about the optimized soddyite structure. Pictures of the atomic motions in the Raman active vibrational modes of soddyite mineral are given in Appendix B.

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