A novel approach to the structural distortions of U/Th snub-disphenoids and their control on zircon → reidite type phase transitions of $U_{1-x}Th_xSiO_4$

Sudip Kumar Mondal$^{1,2,6}$, Pratik Kr Das$^{2,3,5,6}$, Nibir Mandal$^2$ and Ashok Arya$^4$

$^1$ Department of Physics, Jadavpur University, Kolkata 700032, India
$^2$ Faculty of Science, High Pressure and Temperature Laboratory, Jadavpur University, Kolkata 700032, India
$^3$ The Centre for Earth Evolution and Dynamics, University of Oslo, Oslo, N-0315, Norway
$^4$ Material Science Division, Bhabha Atomic Research Centre, Mumbai 400085, India

E-mail: pratik@geo.uio.no

Received 1 October 2019, revised 22 November 2019
Accepted for publication 11 December 2019
Published 7 January 2020

Abstract

Coffinite (USiO$_4$) and thorite (ThSiO$_4$) are conspicuous radiogenic silicates in the geonomy. They form $U_{1-x}Th_xSiO_4$ (uranothorite) solid solutions in zircon-type phase. Investigating the phase-evolution of these minerals is of utmost significance in realizing their applicability in the front-as well as at the back-end of nuclear industries. We carried out a systematic study of zircon- to reidite-type (tetragonal I$4_1$/amd to I$4_1$/a) structural transitions of $U_{1-x}Th_xSiO_4$ solid solution, and investigated their mechanical behaviour. We found a unique behaviour of transition pressure with the change in U-Th concentration in the solid solution. The phase transition pressure ($p_t$) is found to be minimum for $x = 0.5$. We develop the necessary formalism and present an efficient method to estimate the longitudinal and angular distortions of U/ThO$_8$-triangular dodecahedra (snub-disphenoids). We have parameterized two new factors: $\delta$ (longitudinal distortions) and $\sigma^2$ (angular distortions) to quantify the polyhedral distortions. A detailed analysis of U/ThO$_8$ snub-disphenoidal distortions is presented to address such variation of $p_t$ with U and Th concentration. We argue that our approach is independent of polyhedral volume and can be used for any AB$_8$ (A: cation, B: anion) type snub-disphenoidal system.

Keywords: phase transition, polyhedral distortion, density functional theory, uranothorite solid solution, mechanical properties, snub-disphenoid

Supplementary material for this article is available online

(Some figures may appear in colour only in the online journal)
1. Introduction

Uranium (U) and thorium (Th) are the most crucial radionuclides in governing a range of processes in the interior of terrestrial planets. However, their modes of occurrence in crystalline phases, especially at high pressure, in terrestrial planetary bodies that contain silicates as the major constituent are yet to be fully explored. Many geophysicists have demonstrated potential high-pressure Mg–Fe silicate phases are capable of housing nominal amount of water [1, 2] to hypothesize the deep-mantle water reservoir in the Earth [3, 4]. But, their lattice structures lack efficiency in hosting these radionuclides owing to their large ionic radii and contrasting valence configurations. This poses a major problem in respect of the residence of U and Th in crustal and mantle mineral phases on geological time scales (million years). Zircon (ZrSiO₄) has been found to be a unique naturally occurring silicate phase, which can substantially house these radionuclides [5–7]. Due to its long-term chemical stability and mechanical durability, zircon is considered as the most competent accessory material for straight disposal of spent nuclear fuel (SNF) and immobilization of vitrified nuclear waste in underground repositories [8, 9]. Zircon structured U-bearing phase, called coffinite (USiO₄) is a natural phase, and also crystallizes as an alternative product of SNF under low temperature silica-rich condition [10]. Its Th-homologue, called Thorite (ThSiO₄) occurs in the Earth’s crust. These two phases are economically viable ores for extraction of nuclear materials and are prospective phases to find immense utility at the front-end of the nuclear fuel cycle. Further, precipitation of coffinite from uranium dioxide (UO₂) under reducing condition [11] can be used to control U (IV) concentration in direct environment and thus serve as viable metallic waste-form towards the back-end of nuclear fuel cycle [12, 13]. They undergo pressure dependent structural transition from zircon- (Space Group: I₄₁/amd) to reidite- or scheelite- type phase (Space Group: I₄₁/a) [14–16]. The accommodation of U and Th in these two phases, their mutual substitution and fluctuations in thermodynamic parameters can largely affect the bonding characteristics and local polyhedral structure around U/Th and induce significant distortion in these coordination polyhedra. It is thus worthwhile to study the local geometrical distortions of U/Th coordination polyhedra, and their effects on the observable physical properties of these phases. In addition, understanding the transformation behaviour of zircon-type U₁₋ₓThₓSiO₄ to reidite-type phase under elevated hydrostatic pressure regime is critical to explore their applicability in nuclear industries as well as fundamental science issues, such as geochronology [17, 18].

Earlier and recent experimental studies focused on the techniques of synthesizing coffinite and the thermochemical problems encountered therein [19–25]. Similar experimental studies were also carried out for synthesizing thorite [26, 27]. Barron the experimental investigation of Bauer et al [15], Zhang et al [14] and the computational study of Bose et al [16], a detailed analysis of the crystal chemistry of coffinite and thorite in high pressure environments is left unattended. Zhang et al [14] reported an irreversible zircon to reidite type phase transition of USiO₄ at 14–17 GPa and inferred the possibility of a pressure-induced electron transfer (U⁴⁺ to U⁵⁺). Bauer et al [15] revisited this transition through high-pressure experiments and established it to be thermodynamically reversible. They identified that this transition is driven by softening of a silent vibrational raman mode. The presence of impurity in the form of UO₂ in coffinite samples used by the former [14] might hinder the reversibility of the phase transition, which was observed in pure samples of the later [15]. Based on a lattice dynamical study, Bose et al [16] predicted such a transition in ThSiO₄ at a pressure >3 GPa. A parallel line of computational study dealt with temperature dependent phase transition of thorite to huttonite (monoclinic), but without accounting the effect of pressure [28]. The same transition was studied employing several different experimental techniques by Estevenon et al [27], Finch et al [29] and Mazeina et al [30]. All these earlier studies showed the phase transition of pure phases, either USiO₄ or ThSiO₄. However, these two phases have a strong tendency to form a solid solution, as reported from natural samples [19, 31–34] and chemical synthesis [22, 24, 35] in zircon-type phase, as initially hypothesized by Goldschmidt [36]. But, none of the studies have so far provided any insight into the phase transition of U-Th solid solutions from experiments or theoretical calculations, and thus it is worthwhile to revisit the phase transition behaviour.

Substitution of Th in USiO₄ phase or vice-versa can cause significant geometric distortions in coordination polyhedra of their unit cells, which in turn manifest themselves through convoluted behavior of various physical properties. Such geometric distortions can also be a consequence of variations in thermodynamic environment. Existing literature presents two geometrical methods in quantifying such distortions. Robinson et al [37] proposed that the degree of distortion of coordination polyhedra in terms of quadratic elongation (λ) and angular variance (σ²). Alternatively, Makovicky et al [38] expressed the distortions considering the volume ratio of polyhedra and their circumscribed sphere for their real and ideal geometry, keeping the number of coordinated atoms fixed. However, both the approaches adhere to some limitations in terms of their applicability. Robinson’s [37] consideration provides with excellent numerical estimates for two cases of regular, convex and uniform polyhedra (tetrahedra (Z = 4), octahedra (Z = 6)) and can be generalized to cube, dodecahedron (Z = 8) and icosahedron (Z = 12). Later studies [38] improved the analysis by incorporating distortion of an additional set of four polyhedra with Z = 12 as cuboctahedra, anti-cuboctahedra, icosahedron and maximum-volume hexagonal prism. These methods, however, fail to deal with the distortions of polyhedra, which display strongly irregular and/or non-uniform geometry. To overcome this hurdle, Mursic et al [39] provided an alternative approach to quantify the distortions of ZrO₄-tringular dodecahedra or snub-disphenoids in zircon (ZrSiO₄). He treated the ZrO₄-polyhedron as two interpenetrating ZrO₄-tetrahedra, constructed by four edge sharing and four corner sharing oxygen respectively. Based on this formulation, Marques et al [40] calculated the geometry of ZrO₄-snub-disphenoid in zircon and reidite phases.
However, his calculations suffer from a major shortcoming as ZrO8-polyhedra in the reidite phase lack edge sharing O atoms. Furthermore, configuring a dodecahedron in terms of two tetrahedra leads to a volume incompatibility. To meet this gap, it demands an entirely new approach to quantify the longitudinal and angular distortion of 8-coordinated snub-disphenoids without manipulating their original geometry.

Using density functional theory (DFT) calculations this present study aims to understand the mechanism of zircon- to reidite-type phase transformations under hydrostatic pressure conditions in coffinite, and thorite and their solid solutions (U1−xThxSiO4, where, x = 0.25, 0.50, 0.75), accounting the effects of local polyhedral geometry. We develop a novel approach to numerically estimate the polyhedral (AB8; A: cation, B: anion) distortions. The observed nonlinear variation of phase transition pressures with U:Th ratio is then correlated with the distortions of U/Th coordination polyhedra for the two participating phases.

2. Computational methodology

We carried out atomistic calculations within the framework of DFT as implemented in Quantum ESPRESSO suite [41–43]. Spin-polarized simulations were performed using projector augmented-wave (PAW) method [44]. The exchange-correlation effects of the electrons were treated using PBE-GGA, as parametrized by Perdew et al [45]. For U, Th, Si, O atoms the following orbitals were treated as valence states: U (6s27s26p66d1.5f2.5), Th (6s27s26p66d15f1), Si (3s23p2), O (2s22p2). The core cut-off radii for them are 2.1 a.u., 2.1 a.u., 1.9 a.u. and 1.1 a.u. respectively. The remaining core electrons along with the nuclei were treated by scalar relativistic PAW pseudopotentials incorporating a non-linear core correction [46]. The kinetic energy cut-off for each individual members of the solid solution was kept at 1700 eV. The BFGS (Broyden–Fletcher–Goldfarb–Shanno) [47, 48] algorithm was used for geometrical optimization to find the ground state electronic structure under strict convergence criteria. In both cases the convergence threshold for energy and forces were set to 10−8 Ry and 10−6 Ry/bohr, respectively. For the zircon- and reidite-type phases, the brillouin zones were sampled by 7×7×8 and 7×7×4 Monkhorst-Pack [49] k-point grid respectively, which gave rise to 50 and 99 irreducible k-points in their brillouin zone.

Hubbard-U factor in terms of strong Coulomb-like Hartree–Fock electrostatic potential is introduced to the system to handle d and f electrons of U and Th. We tried to determine U self-consistently. A set of simulations for the U0.5Th0.5SiO4 configuration were performed with Hubbard-U varying from 1 to 5 eV, for both uranium and thorium. But no changes were observed in the orbital occupancy. It also underestimated the lattice constants which are incommensurate with experimental data. Thus, the Hubbard-U were not accounted for our further simulations.

3. Results and discussions

3.1. Structural parameters

The tetragonal unit cells of coffinite (USiO4), thorite (ThSiO4) and compositionally varying members (U1−xThxSiO4) contain 24 atoms in their conventional cell, both in zircon- and reidite-type phases. Both have 4 formula units per conventional cell. The former phase crystallizes in Laue group 4/mmm with I41/amd space group, whereas the later crystallizes in Laue group 4/m, but with different space group (I41/a). The positions of Si and U/Th atoms are fixed by symmetry: they are located at (0, 1/4, 3/8) and (0, 3/4, 1/8) on the 4b and 4a Wyckoff sites,
respectively. The 16h Wyckoff sites (0, u, v) are occupied by the O-atoms, where u and v are the internal parameters. Here we restrict our discussion on the crystal structure of zircon (ZrSiO₄) which has been extensively studied [16, 39, 50, 51]. In contrary, our attention focuses upon the different structures between the two types of cationic polyhedra, forming a compact tetragonal cell. In contrast, their high-pressure phase (reidite-type) display only corner sharing between neighbouring actinide polyhedra and SiO₄ tetrahedra (figure 1).

Our calculated values of lattice parameters, c/a ratios and unit-cell volumes are presented in table 1 and compared with previous theoretical and experimental studies. For coffinite, we obtain a good match with the experimental data [22], showing a negligible difference (0.02%). They are also in consistent with the theoretical results of Shein et al [28] and other experimental values from computational study of Bauer et al [15] and experimental studies [15, 21–23]. For the thorite end member also, our results (a = 7.1839 Å and c = 6.3511 Å) hold a good match with the experimental data [22], showing a negligible difference (0.02%). They are also in consistent with the theoretical results of Shein et al [28] and other experimental results [19, 22, 24, 27, 30, 52]. Our calculations for the reidite-type phase of coffinite yield cell parameters: a = 4.9794 Å, c = 11.2318 Å, closely tracking (~0.58%) experimental values from computational study of Bauer et al [15] and experimental studies [15, 21–23]. For the thorite end member also, our results (a = 7.1839 Å and c = 6.3511 Å) hold a good match with the experimental data [22], showing a negligible difference (0.02%). They are also in consistent with the theoretical results of Shein et al [28] and other experimental results [19, 22, 24, 27, 30, 52].

| Phase (Sp. Gr.) | x     | a (Å)       | c (Å)       | c/a | Volume (Å³) | Bulk modulus (GPa) | Transition pressure (GPa) |
|----------------|-------|-------------|-------------|-----|-------------|---------------------|--------------------------|
| Zircon (I4₁/amd) | 0.00  | 7.0303      | 6.2872      | 0.8942 | 310.75      | 181.30              | —                        |
|                |       | 7.0135 [21] | 6.2669 [21] | —    | —           | —                   | —                        |
|                |       | 6.981 [19]  | 6.250 [19]  | —    | —           | —                   | —                        |
|                |       | 6.9862 [15] | 6.2610 [15] | 305.58 [15] | 181 [15]  | —                   | —                        |
|                |       | 6.9842 [22] | 6.2606 [22] | 305.38 [22] | —          | —                   | —                        |
|                |       | 6.9904 [24] | 6.2610 [24] | 305.94 [24] | —          | —                   | —                        |
|                |       | 6.9936 [14] | 6.2614 [14] | —    | 188 [14]   | —                   | —                        |
|                | 0.25  | 7.0758      | 6.2997      | 0.8904 | 315.41      | 174.49              | —                        |
|                |       | 7.0105 [22] | 6.2680 [22] | 308.06 [22] | —          | —                   | —                        |
|                |       | 7.007 [19]  | 6.275 [19]  | —    | —           | —                   | —                        |
|                | 0.50  | 7.1181      | 6.3180      | 0.8876 | 320.11      | 167.57              | —                        |
|                |       | 7.039 [19]  | 6.294 [19]  | —    | —           | —                   | —                        |
|                | 0.75  | 7.1553      | 6.3320      | 0.8849 | 324.19      | 173.60              | —                        |
|                |       | 7.0949 [22] | 6.3194 [22] | 318.10 [22] | —          | —                   | —                        |
|                |       | 7.071 [19]  | 6.314 [19]  | —    | —           | —                   | —                        |
|                | 1.00  | 7.1839      | 6.3511      | 0.8841 | 327.75      | 178.20              | —                        |
|                |       | 7.1816 [22] | 6.2946 [22] | 324.66 [22] | —          | —                   | —                        |
|                |       | 7.1568 [24] | 6.3152 [24] | 323.46 [24] | —          | —                   | —                        |
|                |       | 7.133 [28]  | 6.319 [28]  | —    | —           | —                   | —                        |
|                |       | 7.1439 [27] | 6.3183 [27] | 322.46 [27] | —          | —                   | —                        |
|                |       | 7.129 [30]  | 6.319 [30]  | 321.15 [30] | —          | —                   | —                        |
|                |       | 7.128 [19]  | 6.314 [19]  | 321.48 [52] | —          | —                   | —                        |
|                  | 7.1328 [52] | 6.3188 [52] | 321.15 [52] | —    | —           | —                   | —                        |
| Reidite (I4₁/a) | 0.00  | 4.9974      | 11.2318     | 278.49 | 239.05      | 8.52                | —                        |
|                |       | 4.9502 [15] | 11.0750 [15] | 271.39 [15] | 212 [15]  | 15 [15]            | —                        |
|                |       | 4.8654 [14] | 11.0316 [14] | 2.2557 | 261.14 [14] | 14–17 [14]         | —                        |
|                | 0.25  | 4.9915      | 11.3389     | 2.2717 | 282.51      | 233.60              | 7.67                     |
|                |       | 5.0053      | 11.4308     | 2.2837 | 286.18      | 230.00              | 6.82                     |
|                | 0.50  | 5.0157      | 11.5241     | 2.2976 | 289.92      | 227.30              | 7.92                     |
|                | 0.75  | 5.0251      | 11.6072     | 2.3099 | 293.10      | 225.64              | 8.68                     |
|                | 1.00  | 5.0251      | 11.6072     | 2.3099 | 293.10      | 225.64              | 8.68                     |
The results presented above suggest that the calculated cell parameters for U-Th solid solution phases and their high pressure polymorphs would remain valid, even if the results could not be verified due to lack of experimental data.

Figure 2 shows the variation of unit cell volumes and $c/a$ ratio normalized for members of each phases with respect to the corresponding values of coffinite and its high-pressure reidite polymorph, respectively. Due to their homologous topology, the incorporation of Th by substituting U enforces a linear increase in volume for both the phases, consistent with the Vegard’s law. These increments of volumes are expected as the atomic radius of Th (0.24 nm) is a little larger than that of U (0.23 nm). In particular, the small difference between their atomic radii is chemically desirable aiding to the tolerance of the crystal structure for mixing ions of different sizes in each site and the genesis of the silicate solid solution. On another note, substitution between U and Th preserves the composite electrical neutrality of the crystalline aggregate and is commensurate with the local charge balance through their coordination environment in their crystallographic site. Having said that, the manner of facilitating the volume expansion is markedly distinct for different phases appearing as obvious from the variation of $c/a$ ratio (figure 2). The reidite-type phase undergoes a monotonic gain in $c/a$ whereas the zircon-type phase exhibits a completely antipodal behaviour. This result provide reinforcement to the finding of Dutta et al [50] who showed that the reidite demonstrates a greater compressibility along $c$-axis compared to $a$-axis and vice versa in zircon phases. Our analysis confirms that the increment along $a(c)$ is more administrative in volume change in zircon (reidite) -type phase.

3.2. Characteristics of the phase transitions

We theoretically investigated the effect of hydrostatic pressure on the unit-cell volumes of $\text{U}_1-x\text{Th}_x\text{SiO}_4$ solid solutions in both zircon- and reidite-type phases as a function of U/Th ratio. To obtain the critical hydrostatic pressure for zircon- to reidite-type structural transformation, we have used the formalism of enthalpy crossover of the two phases for a given U/Th ratio. The entire exercise has been performed with the ground state enthalpies of the structures at $T = 0 \text{K}$.

The pressure-homologue rule [53] suggests that the phase with larger cations undergoes structural transition at lower pressures, as compared to those with smaller cations. According to this rule, the transition pressure ($p_t$) for ThSiO$_4$ should be lower than that of USiO$_4$. However, our results predict that $p_t$ for the end-member phases hardly differs from one another. The calculations also reveal an atypical variation of $p_t$ with the radionuclide U and Th concentration (figure 3). Our calculated transition pressure 8.52 GPa for the U-endmember (table 1) decreases to 7.67 GPa as 25 at% of U is replaced by Th. The transition pressure then drops to attain a minimum value of 6.82 GPa when Th and U occur in equal concentration. Further increment of Th reverses the trend of transition pressure variation to reach a value of 8.68 GPa for ThSiO$_4$ phase, which is comparable to that for USiO$_4$ phase. The pressure transmitting media chosen in experiments by Zhang et al [14] and Bauer et al [15] are (16/3/1) methanol/ethanol/water mixture and neon, respectively. Methanol/ethanol/water mixture exhibits signs of nonhydrostacicity at 10–11 GPa, whereas neon does the same at 15 GPa [54]. Close to these pressure ranges and beyond, the media lose their ideal fluid behavior, and start to support shear stress in developing non-hydrostaticity. This non-hydrostatic response might be the
reason behind the apparent disagreement between the results of Zhang et al [14] and Bauer et al [15].

Our theoretical value of the transition pressure differs from the experimental results of Bauer et al [15] and Zhang et al [14] mainly due to two reasons. All our calculations are performed at \( T = 0 \) K, whereas their experiments were carried out at room temperatures (\( T > 0 \) K). The non-zero temperature condition can lead to a significant increase of the transition pressure, as predicted from the positive Clapeyron-slope for a similar phase transition in pure ZrSiO\(_4\) [55, 56]. The cofinite sample used by Zhang et al for in situ x-ray diffraction and IR measurements contained 5–10 wt% of UO\(_2\) mixed with the sample used by Zhang et al for in situ x-ray diffraction and IR measurements. However, our calculated value for pure USiO\(_4\) is kinetically sluggish. Hence, the difference in experimental and theoretical results can be a consequence of the kinetic effects and the associated energy barrier [40]. Cofinite and its high pressure polymorph are isomorphic to zircon and reidite phases, respectively. We thus extrapolate similar effects and the associated energy barrier [40]. Coffinite and theoretical results can be a consequence of the kinetic effects and the associated energy barrier [40].

compressibility in both phases. Note the existence of a maximum value of compressibility in U\(_{0.50}\)Th\(_{0.50}\)SiO\(_4\), sensitive in the solid solution spectrum. This finding allows us to extrapolate that the zircon- type phase of this composition will behave as the most compressible phase, and thereby undergoes structural transition at the lowest hydrostatic pressure in the solid solution series (figure 3). The compressibility of reidite-type phases is always lower than the zircon type for any given U/Th concentration. However, their compressibility increases monotonically with increasing Th content (figure 4).

### 3.3. U/Th polyhedral distortions

An ideal regular polyhedron always contains a unique point inside, equidistant from the vertices. This point represents the position of a cation in the polyhedron, whereas the vertices serve as the positions of anions or the central atoms of ligands. For an ideal regular polyhedron, the distance between this unique point and the vertices defines a longitudinally unique bond. Such a regular arrangement gives rise to a unique angle formed at the centre by any two adjacent vertices in an undistorted polyhedron. This angle can be treated as ideal bond angle. Polyhedral distortions are then quantified in terms of the ideal bond length and bond angles formed at the centre [37]. But it has been observed that, even ideal, but irregular polyhedra can have varying centre to vertex lengths. Thus different bond lengths and bond angles are found to occur with varying multiplicity. Consequently, the existing methods employed in estimating the polyhedral distortions are untenable. This kind of geometrical complexity occurs in many crystalline phases. For example, actinide cantered eight-fold coordination polyhedra with snub-disphenoidal shape can be found in various types of structural symmetry, such as, Monoclinic- Monazite, CuTh\(_3\)(PO\(_4\))\(_2\) [57]; Trigonal- Dugganite [58]; Orthorhombic- Vitusite and CaU(PO\(_4\))\(_2\) [59]; zircon, reidite, wolframite and fargusonite phases; Hexagonal- Rabdophane group of minerals. An analysis of the geometrical peculiarity of snub-disphenoids thus merits a discussion to obtain new structural insights. In this study, we...
In contrast to the zircon type, the reidite type phase shows similar variations, albeit little, of both the bonds on stoichiometric exchange between U and Th (table 2). The relatively open unit cell of reidite phases permits them to accommodate Th in place of U as it does not involve any significant changes in the polyhedral volume and the corresponding bond lengths. The SiO4 tetrahedra, being more rigid than the U-Th polyhedra, do not undergo significant geometrical modifications, leaving Si-O bond lengths virtually intact (1.635 Å to 1.667 Å). This finding is commensurate with the previous studies [15, 22]. In figure 2 we have shown an inverse relation of the c/a ratio with Th content; the relation is opposite for the unit cell volume of zircon type phases. We emphasize that, as the U-Th-O4 bonds lie almost parallel to a and b-axes their length increments have the most effects on increase of the lattice parameters along a and b-axes. On the other hand, the U-O4 bonds have little influence on the lattice parameter along c.

Such contrasting effects of the two types of bonds explain the inverse relation of c/a with Th content in zircon-type phases. We also found that the U-Th-O4 bond length does not significantly change because the O4 atoms form the edge, shared by both the U/Th and Si-polyhedra. This edge sharing gives rise to a strong connection between the U/Th or Si atoms and O atoms. In contrast, O5 atoms form corner sharing between U/Th-O5 bonds lie almost parallel to a and b-axes and therefore develop, comparatively weaker connections, allowing relatively larger changes in the U-Th-O5 bond lengths (see figure 1). The reidite type phases do not show any preferred orientation of the atomic bonds with respect to the unit cell axes. Both the U-Th-O4 and -O5 bonds increase their lengths with volume increment, associated with enhancement of c/a ratios with increasing Th content.

Table 2 summarizes the calculated values of δU, δTh, σU and σTh, as defined in Equation S2 and S3 see supplemental data (available at stacks.iop.org/JPhysCM/32/145401/mmedia). Our analysis confirms that elemental interchange between U and Th has a dramatic effect on the distortion parameters of the polyhedra, which enables us to explain why the phase transition pressure (p_t) drops down to a minimum at...
U/Th = 1 (figure 3). The variations of these parameters with Th concentration in the unit cell is demonstrated in figure 5. The bond length distortions, $\delta_U$ and $\delta_{Th}$ for the zircon-type phases hold positive relations with Th concentration. But, for the reidite-type phases, they increase to attain a maximum value at U/Th = 1, and then decline with further increase of Th. Interestingly, the presence of such criticality occurs exactly at U/Th = 1 for both $\delta_U$ and $\delta_{Th}$ regressions for the reidite type phases. The corresponding values follow: $\delta_U = 0.12223$ and $\delta_{Th} = 0.11478$. The angular distortion of U–O bonds, $\sigma_U^2$, in the reidite-type phase forms a minimum (94.471 deg²) at U/Th = 1, which exactly coincides with the point of maximum (46.984 deg²) in the regression for the zircon type (figure 5(a)). A similar, although quantitatively different, trend is observed for the zircon type phase transition to occur at the lowest pressure. Therefore, the zircon to reidite-type phase transition occurs at a minimum hydrostatic pressure (6.82 GPa) for the phase with the unique chemical composition: U$_{0.5}$Th$_{0.5}$SiO$_4$. A departure from this unique composition, by either a gain or a loss of Th or U, would widen the gap between $\sigma_U^2$ and $\sigma_{Th}^2$, which acts as a barrier to the structural transition, and requires higher pressures to overcome this barrier. These phase transitions involve a reconstructive mechanism in which the tri-angular dodecahedra break their bonds and reorganize them into another new dodecahedra in the high-pressure phase. This process proceeds through an intermediate transient cubic phase as demonstrated by Smirnov et al [60]. Our theoretical investigations predict that the geometrical difference between the distorted snub-disphenoidal forms in the two states turns to be minimum when U/Th = 1 and facilitates the reconstructive phase transition to occur at the lowest pressure.

Figure 6 provides a quantitative description to show how $\delta_U$ and $\delta_{Th}$ can vary with hydrostatic stresses in the zircon type phases. Both $\delta_U$ and $\delta_{Th}$ hold inverse relations with pressure. However, it is quite interesting to note that $\delta_U$ for USiO$_4$ is the lowest in ambient condition, and it increases as more and more Th is substituted in place of U, suggesting that the larger element Th partly controls the deformation behaviour of U-polyhedra. In case of Th-polyhedra, $\delta_{Th}$ is maximum for pure ThSiO$_4$, and the degree of distortion is reduced with substitution of Th with U in the solid solution phases. In summary, elemental Th has larger influence on the polyhedral distortion than elemental U. Our analysis reveals that pressure-sensitivity of both $\delta_U$ and $\delta_{Th}$ drops with increasing pressure. The lower values of $\delta_U$ and $\delta_{Th}$ at high pressures suggest that hydrostatic pressures counter to the inherent polyhedral distortions, and facilitate the polyhedra to achieve an ideal structure. At the high pressure regime (beyond 8 GPa) the average pressure derivative for $\delta_U$, i.e. $\frac{\Delta \delta_U}{\Delta P}$ in USiO$_4$ and $\delta_{Th}$ in ThSiO$_4$, i.e. $\frac{\Delta \delta_{Th}}{\Delta P}$ are found to be $1.265 \times 10^{-3}$ GPa$^{-1}$ and $1.324 \times 10^{-3}$ GPa$^{-1}$, respectively.

We similarly analyzed the polyhedral distortion for the reidite-type phases as a function of hydrostatic pressure. The distortion parameters, $\delta_U$ and $\delta_{Th}$ exhibit similar pressure-dependent behavior; however, they vary with pressure at much lower slopes, compared to that observed in zircon phases. According to our calculations, an ideal geometry of snub-disphenoid ($\delta_U = 0$ and $\delta_{Th} = 0$) is possible in reidite type phase at a much higher pressure. Secondly, $\delta_U$ and $\delta_{Th}$ for reidite phases are not strongly sensitive to Th content in the solid solution. The absence of edge sharing between the U/Th-polyhedra and Si-tetrahedra and the presence of large amount of empty spaces in the conventional unit cell of reidite phases allows the polyhedra to minimize the distortion, and attain a more ideal shape.

Based on the results and discussion presented above, we now offer an outlook of this study. Many materials undergo sequential phase transitions under hydrostatic pressure, e.g., zircon $\rightarrow$ reidite or reidite $\rightarrow$ wolframite or reidite $\rightarrow$ fergusonite [50]. In these transitions the AOX (A = any cation) polyhedra retain their geometrical shape. Some of the previous studies reported a unique A–O bond length [28]. But our study reveals that the occurrence of such a unique bond

Table 3. Distortions of bond lengths and bond angles of U and Th snub-disphenoids in compositionally different zircon type structures of U$_x$Th$_{1-x}$SiO$_4$ and in their corresponding reidite phase. The subscript in the name of the parameters in heading refers to actinide atomic species at the point X inside the snub-disphenoid as shown in figure S1.

| Phase   | $x$  | $\delta_U$ | $\delta_{Th}$ | $\sigma_U^2$ (deg²) | $\sigma_{Th}^2$ (deg²) |
|---------|------|------------|---------------|---------------------|----------------------|
| Zircon  | 0    | 0.101 98   | —             | 37.982              | —                    |
|         | 0.25 | 0.105 23   | 0.10497       | 40.007              | 38.555               |
|         | 0.50 | 0.111 10   | 0.10824       | 46.984              | 41.707               |
|         | 0.75 | 0.114 41   | 0.11316       | 42.226              | 40.923               |
|         | 1.00 | —          | 0.11468       | —                   | 37.732               |
| Reidite | 0.00 | 0.115 72   | —             | 128.891             | —                    |
|         | 0.25 | 0.118 10   | 0.11215       | 115.069             | 86.555               |
|         | 0.50 | 0.122 26   | 0.11475       | 94.471              | 76.962               |
|         | 0.75 | 0.115 23   | 0.11336       | 104.038             | 82.762               |
|         | 1.00 | —          | 0.11253       | —                   | 91.937               |
length in AO8 polyhedron is not possible due to the geometrical constraint of the polyhedron itself. On the other hand, several other studies [15, 22, 40, 51, 52, 58, 59, 62, 64] have reported one short and one longer A–O bond, but without providing any fundamental explanation for such contrasting bond lengths. Our polyhedral analysis provides a concrete mathematical basis of the two types of bonds, and correlates them with the existence of two distinct types of vertices, occupied by O atoms. The bond lengths are observed to demonstrate a unique ratio (A–O4/A–O5 ≈ 1.374 302), irrespective of the volumes of the polyhedra in ideal geometry. In addition, our analysis explains why the two types of bonds occur with a multiplicity of four. We believe that revisiting the zircon, reidite/scheelite, wolframite, fergusonite and other structures with similar kind of actinide polyhedra can give rise to newer insights into the dynamics of phase transition in terms of polyhedral distortions.

4. Conclusions

Using DFT calculations we have presented a comprehensive analysis of the pressure induced zircon- to reidite-type phase transition of U1−xThxSiO4 (x = 0 to 1 in steps of 0.25) solid solution. This analysis shows that the phase transition pressure varies nonlinearly with increasing Th content in the solid solution to attain a minimum value of 6.82 GPa for x = 0.5. We have also estimated the compressibility of solid solution phases in both ambient and high-pressure conditions. The compressibility of zircon type U0.5Th0.5SiO4 phase is found to be maximum (5.97 × 10−3 GPa−1), implying it as the most pressure sensitive (soft) phase. We have theoretically predicted the structural parameters of the reidite-type polymorphs of the solid solutions, and also enumerated their mechanical properties.

This study provides a new interpretation of the phase transition pressure (p_t) of U1−xThxSiO4, accounting the effects of U/ThO8 polyhedral distortion in the cell structures. We have developed a novel approach to the analysis of the polyhedral distortions of triangular dodecahedra (snub-disphenoids). The following two parameters (δ and σ^2) have been defined to express the longitudinal and angular distortions of highly irregular U/ThO8-triangular dodecahedra. The distortion analysis brings out two kinds of geometrically distinct vertices of the triangular dodecahedra, occupied by oxygen atoms, which explains the occurrence of two types of U/Th-O bonds (U/Th-O4 and U/Th-O5) with contrasting lengths. The bond length ratio (U-O4/U-O5 and Th-O4/Th-O5) remains constant (~1.374 302), irrespective of the triangular dodecahedral volume. It is worthwhile to note that our theoretical framework to quantify the polyhedral distortions of U/Th snub-disphenoids is based entirely on geometrical considerations.
The distortions parameters, δ and σ^2 are independent to the elements occupying the snub-disphenoid space. Also, they are defined without any attribute to external parameters. Thus, we expect that the parameters: δ and σ^2 can be used to calculate the distortion of similar AB₅-type snub-disphenoid in other crystalline phases. Our calculations indicate that the difference in angular distortions (σ₁² and σ₂²) between the zircon- and reidite-type phases becomes minimum when U and Th occur equally in the solid solution. Our study also confirms the highest compressibility of the zircon type phase for U₀.₅Th₀.₅SiO₄. The concurrence of minima of transition pressure and the difference in σ^2 indicates that the polyhedral distortion plays a critical role in dictating the zircono- reidite-type transition.

Acknowledgment

This study was supported by BRNS with a research project (Sanction No. 36(2)/14/25/2016-BRNS), SKM and NM are grateful to DST, India, for providing them with the INSPIRE fellowship and the J C BOSE national fellowship, respectively. PKD thanks the Centre for Earth Evolution and Dynamics (CEED), funded by CoE-grant 223272 from the Research Council of Norway. AA gratefully acknowledges BARC, Mumbai, for giving financial support in this collaborative work.

ORCID iDs

Sudip Kumar Mondal https://orcid.org/0000-0003-4103-3901
Pratik Kr Das https://orcid.org/0000-0001-6446-0389

References

[1] Hae R, Ohtani E, Kubo T, Koyama T and Utada H 2006 Hydrogen diffusivity in wadsleyite and water distribution in the mantle transition zone Earth Planet. Sci. Lett. 243 141–8
[2] Zhao C and Yoshino T 2016 Electrical conductivity of mantle clinopyroxene as a function of water content and its implication on electrical structure of uppermost mantle Earth Planet. Sci. Lett. 447 1–9
[3] Huang X, Xu Y and Karato S 2005 Water content in the transition zone from electrical conductivity of wadsleyite and ringwoodite Nature 434 746–9
[4] Yoshino T, Matsuzaki T, Shatskiy A and Katsura T 2009 The effect of water on the electrical conductivity of olivine aggregates and its implications for the electrical structure of the upper mantle Earth Planet. Sci. Lett. 288 291–300
[5] Lee J K W, Williams I S and Ellis D J 1997 Pb, U and Th diffusion in natural zircon Nature 390 159–62
[6] Reiners P W 2005 Zircon (U-Th)/He thermochronometry Rev. Mineral. Geochem. 58 151–79
[7] Kirkland C L, Smithies R H, Taylor R J M, Evans N and McDonald B 2015 Zircon Th/U ratios in magmatic enivrons Lithos 212-5 397–414
[8] Ewing R C and Lutze W 1995 Zircon: a host-phase for the disposal of weapons plutonium J. Mater. Res. 10 243–6
[9] Ewing R C 2002 Nuclear waste forms for actinides Proc. Natl. Acad. Sci. 96 3432–9
[10] Janecek J and Ewing R C 1992 Dissolution and alteration of uraninite under reducing conditions J. Nucl. Mater. 190 157–73
[11] Amme M, Renker B, Schmid B, Feth M P, Bertagnolli H and Döbelin W 2002 Raman microspectrometric identification of corrosion products formed on UO₂ nuclear fuel during leaching experiments J. Nucl. Mater. 306 202–12
[12] Striefl L R, Stern T W and Sherwood A M 1955 Preliminary description of coffinite-a new uranium mineral Science 121 608–9
[13] Kamieniecki C and Lemire R J 1991 Thorite in fault zones of a granitic pluton, Atikokan, Canada: Implications for nuclear fuel waste disposal Chem. Geol. 90 133–43
[14] Zhang F X et al 2009 Structural transitions and electron transfer in coffinite, USiO₄, at high pressure Am. Mineral. 94 916–20
[15] Bauer J D et al 2014 High-pressure phase transition of coffinite, USiO₄, J. Phys. Chem. C 118 25141–9
[16] Bose P P, Mitral R and Chaplot S L 2009 Lattice dynamics and high pressure phase stability of zircon structured natural silicates Phys. Rev. B 79 174301
[17] Cocherie A and Legendre O 2007 Potential minerals for determining U-Th-Pb chemical age using electron microprobe Lithos 93 288–309
[18] von Blackenburg F 1992 Combined high-precision chronometry and geochemical tracing using accessory minerals: applied to the central-alpine bergell intrusion (central Europe) Chem. Geol. 100 19–40
[19] Fuchs L H and Gebert E 1958 X-ray studies of synthetic coffinite, thorite and uranorthites Am. Mineral. 43 243–8 (https://pubs.geoscienceworld.org/msa/ammin/article/43/3-4/243/541342/x-ray-studies-of-synthetic-coffinite-thorite-and)
[20] Fuchs L H and Hoekstra H R 1959 The preparation and properties of uranium(IV) silicates Am. Mineral. 44 1057–63 (https://pubs.geoscienceworld. org/msa/ammin/article/44/9/1057/541535/The-preparation-and-properties-of-uranium-IV)
[21] Pointeau V, Deditius A P, Miserque F, Renock D, Becker U, Zhang J, Clavier N, Dacheux N, Poinssot C and Ewing R C 2009 Synthesis and characterization of coffinite J. Nucl. Mater. 393 449–58
[22] Labs S, Hennig C, Weiss S, Curtius H, Zänker H and Bosbach D 2014 Synthesis of coffinite, USiO₄, and structural investigations of U₁₋ₓThₓSiO₄ solid solutions Environ. Sci. Technol. 48 854–60
[23] Guo X et al 2015 Thermodynamics of formation of coffinite, USiO₄ Proc. Natl Acad. Sci. 112 6551–5
[24] Guo X, Szenknect S, Mesbah A, Clavier N, Poinssot C, Wu D, Xu H, Dacheux N, Ewing R C and Navrotsky A 2016 Energetics of a uranothorite (Th₁₋ₓUₓSiO₄) solid solution Chem. Mater. 28 7117–24
[25] Mesbah A, Szenknect S, Clavier N, Lozano-Rodriguez J, Poinssot C, Den Auwer C, Ewing R C and Dacheux N 2015 Coffinite, USiO₄, is abundant in nature: so why is it so difficult to synthesize? Proc. Natl Acad. Sci. 102 15719–24
[26] Frondel C and Collette R L 1957 Hydrothermal synthesis of coffinite, USiO₄, at high pressure Am. Mineral. 43 306–15
[27] Estevenon P, Welcombe E, Szenknect S, Mesbah A, Moiuy P, Poinssot C and Dacheux N 2018 Multiparametric study of the synthesis of Th₃SiO₄ under hydrothermal conditions Inorg. Chem. 57 9393–402
[28] Shein I R, Shein K I and Ivanovskii A L 2006 Thorite versus huttonite: stability, electronic properties and x-ray emission spectra from first-principle calculations Phys. Chem. Miner. 33 545
[29] Finch C B, Harris L A and Clark G W 1964 The thorite → huttonite phase transformation as determined by growth of synthetic thorite and huttonite single crystals Am. Mineral. 49 782–5 (https://pubs.geoscienceworld.org/msa/ammin/article/49/5-6/782/539916/ The-thorite-huttonite-phase-transformation-as)

[30] Mazeia L, Usahov S V, Navrotsky A and Boanter L A 2005 Formation enthalpy of ThSiO₄ and enthalpy of the thorite → huttonite phase transition Geochim. Cosmochim. Acta 69 4675–83

[31] Pointer C M, Ashworth J R and Ixer R A 1988 The zircon-thorite mineral group in metamositized granite, Ririwai, Nigeria 2. Geochemistry and metastable solid solution of thorite and coiffine Mineral. Petrol. 39 21–37

[32] Pointer C M, Ashworth J R and Ixer R A 1988 The zircon-thorite mineral group in metamositized granite, Ririwai, Nigeria 1. Geochemistry and metastable solid solution of thorite and coiffine Mineral. Petrol. 38 245–62

[33] Iffil R O, Cooper W C and Clark A H 1996 Mineralogical and process controls on the oxidative acid-leaching of radioactive phases in Elliot Lake, Ontario, uranium ores: II—brannerite and allied titaniferous assemblages CIM Bull. 89 93–103 ISSN 0317-0926 (https://store.cim.org/ en/mineralogical-and-process-controls-on-the-oxidative-acid-leaching-of-radioactive-phases-in-elliot-lake-ontario-uranium-ores-ii-brannerite-and-allied-titaniferous-assemblages)

[34] Förster H J 2006 Composition and origin of intermediate solid solutions in the system thorite-xenotime-zircon-cofinettite Lithos 88 35–55

[35] Clavier N, Szenknect S, Costin D T, Mesbah A, Poinssot C and Dacheux N 2014 From thorite to coiffine: a spectroscopic study of Th₂₋ₓUₓSiO₄ solid solutions Spectrochim. Acta A 118 302–7

[36] Anon 1956 Geochemistry. By the late V. M. Goldschmidt. Edited by Alex Muir, Clarendon Press, 1954 Q. J. R. Meteorol. Soc. 82 547

[37] Robinson K 1971 Quadratic elongation: a quantitative measure of distortion in coordination polyhedra Science 172 567–70

[38] Makovicky E and Ibañez-Zúñiga T 1998 New measure of distortion for coordination polyhedra Acta Crystallogr. B 54 766–73

[39] Mursic Z, Vogt F and Frey F 1992 High-temperature neutron powder diffraction study of ZrSiO₄ up to 1900 K Acta Crystallogr. B 48 584–90

[40] Marquès M, Flórez M, Recio J M, Gerward L and Olsen J S 2006 Structure and stability of ZrSiO₄ under hydrostatic pressure Phys. Rev. B 74 014104

[41] Giannozzi P et al 2009 Quantum espresso: a modular and open-source software project for quantum simulations of materials J. Phys.: Condens. Matter 21 395502

[42] Giannozzi P, Andreussi O, Brumme T, Bunau O, Nardelli M, Ushakov S V., Navrotsky A and Boatner L A 2001 First-principles study of structural, electronic, dynamical, and dielectric properties of zircon Phys. Rev. B 63 104305

[43] Ewing R C ; T M 1978 The crystal structures of the ThSiO₄ polymorphs: huttonite and thorite Acta Crystallogr. B 34 1074–9

[44] Zhong X, Herrmann A, Wang Y and Ma Y 2016 Monoclinic high-pressure polymorph of Al₂O₃ predicted from first principles Phys. Rev. B 94 224110

[45] Klotz S, Chervin J C, Munsch P and Le Marchand G 2009 Hydrostatic limits of 11 pressure transmitting media J. Phys. D: Appl. Phys. 42 075413

[46] Timms N E, Erickson T M, Pearce M A, Cavosie A J, Schneider M, Tohver E, Reddy S M, Zanetti M R, Nemchin A A and Wittmann A 2017 A pressure-temperature phase diagram for zircon at extreme conditions Earth Sci. Rev. 165 185–202

[47] Knittle E and Williams Q 1993 High-pressure Raman spectroscopy of Zr₂SiO₄: observation of the zircon to scheelie phase transition at 300 K Am. Mineral. 78 245–52 (https://pubs.geoscienceworld.org/msa/ammin/article/78/3-4/245/42721/High-pressure-Raman-spectroscopy-of-ZrSiO4)

[48] Louër M, Bouroch L, Louër D, Arsalane S and Ziyad M 1995 Structure determination of Ca₂Th₂(PO₄)₃ Acta Crystallogr. B 51 908–13

[49] Yu H, Young J, Wu H, Zhang W, Rondinelli J M and Halasymanski P S 2016 Electronic, crystal chemistry, and nonlinear optical property relationships in the dugganite AₓBₓCD₄O₄ family J. Am. Chem. Soc. 138 4984–9

[50] Dusausoy Y, Gherrmani N-E, Peder R and Cuneo M 1996 Low-temperature ordered phase of CaₓU(PO₄)₂; synthesis and crystal structure Eur. J. Mineral. B 8 667–74

[51] Smirnov M B, Mirgordosky A P, Khazimirov V Y and Guinebretière R 2008 Bond-switching mechanism for the zircon-scheelite phase transition Phys. Rev. B 78 94109

[52] Errandonea D et al 2005 High-pressure structural study of the scheelite tungsates Ca₂WO₄ and Sr₂WO₄ Phys. Rev. B 72 1–14

[53] Zheng C, Zhang Z, Dai R C, Wang Z P, Zhang J W and Ding Z J 2010 High-pressure raman and luminescence study on the phase transition of GdV₂O₅·Eu⁺ microcrystals J. Phys. Chem. C 114 18279–82

[54] Errandonea D, Kumar R, López-Solano J, Rodríguez-Hernández P, Muñoz A, Rabie M G and Sáez Puch P 2011 Experimental and theoretical study of structural properties and phase transitions in YASO₄ and YCrO₄ Phys. Rev. B 83 134109

[55] Panchal V, Garg N, Poswal H K, Errandonea D, Rodríguez-Hernández P, Muñoz A and Cavalli E 2017 High-pressure behavior of CaMoO₃ Phys. Rev. Mater. 1 043605

[56] Errandonea D and Garg A B 2018 Recent progress on the characterization of the high-pressure behaviour of AVO₄ orthovananades Prog. Mater. Sci. 97 123–69

[57] Errandonea D, Kumar R S, Achary S N and Tyagi A K 2011 In-situ high-pressure synchrotron x-ray diffraction study of CeVO₃ and Th₂VO₄ up to 50 GPa Phys. Rev. B 84 224121