

The Role of Water and Hydroxyl Groups in the Structures of Stetindite and Coffinite, $M\text{SiO}_4$ ($M = \text{Ce}, \text{U}$)

Andrew C. Strzelecki,[◆] Thomas Barral,[◆] Paul Estevenon, Adel Mesbah, Vitaliy Goncharov, Jason Baker, Jianming Bai, Nicolas Clavier, Stephanie Szenknect, Artaches Migdisov, Hongwu Xu, Rodney C. Ewing, Nicolas Dacheux, and Xiaofeng Guo*



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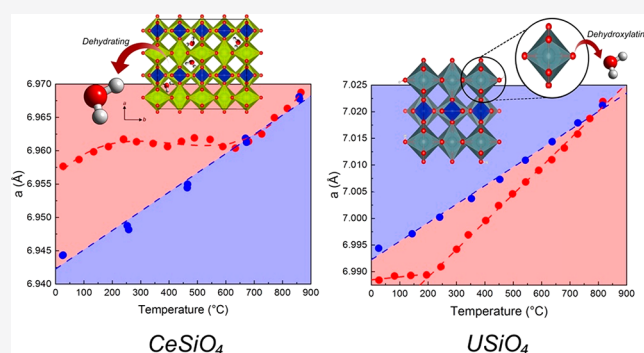


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ABSTRACT: Orthosilicates adopt the zircon structure types ($I4_1/amd$), consisting of isolated SiO_4 tetrahedra joined by A-site metal cations, such as Ce and U. They are of significant interest in the fields of geochemistry, mineralogy, nuclear waste form development, and material science. Stetindite (CeSiO_4) and coffinite (USiO_4) can be formed under hydrothermal conditions despite both being thermodynamically metastable. Water has been hypothesized to play a significant role in stabilizing and forming these orthosilicate phases, though little experimental evidence exists. To understand the effects of hydration or hydroxylation on these orthosilicates, *in situ* high-temperature synchrotron and laboratory-based X-ray diffraction was conducted from 25 to ~ 850 °C. Stetindite maintains its $I4_1/amd$ symmetry with increasing temperature but exhibits a discontinuous expansion along the a -axis during heating, presumably due to the removal of water confined in the [001] channels, which shrink against thermal expansion along the a -axis. Additional *in situ* high-temperature Raman and Fourier transform infrared spectroscopy also confirmed the presence of the confined water. Coffinite was also found to expand nonlinearly up to 600 °C and then thermally decompose into a mixture of UO_2 and SiO_2 . A combination of dehydration and dehydroxylation is proposed for explaining the thermal behavior of coffinite synthesized hydrothermally. Additionally, we investigated high-temperature structures of two coffinite-thorite solid solutions, uranothorite ($\text{U}_x\text{Th}_{1-x}\text{SiO}_4$), which displayed complex variations in composition during heating that was attributed to the negative enthalpy of mixing. Lastly, for the first time, the coefficients of thermal expansion of CeSiO_4 , USiO_4 , $\text{U}_{0.46}\text{Th}_{0.54}\text{SiO}_4$, and $\text{U}_{0.9}\text{Th}_{0.1}\text{SiO}_4$ were determined to be $\alpha_V = 14.49 \times 10^{-6}$, 14.29×10^{-6} , 17.21×10^{-6} , and 17.23×10^{-6} °C⁻¹, respectively.



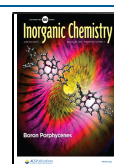
1. INTRODUCTION

The role of water is integral to both the thermodynamics and structures of many mineral systems and synthetic compounds.^{1,2} In some systems the hydration and dehydration of the associated chemical components result in distinct minerals or phases, such as gypsum-anhydrite, polyhalite-anhydrite, studtite-metastudtite, and rhabdophane-monazite.^{3–8} However, hydration and dehydration processes do not necessarily result in an obviously different atomic structure.^{9–12} Subtle changes to the structure pose a challenge for correctly characterizing the state of water and its role during dehydration or mineral formation. Coffinite (USiO_4) is one such mineral where the role of water is much debated.^{13–16} Three different types of water can be associated with coffinite and other zircon structure-type phases: (i) molecular water adsorbed onto the surface, (ii) molecular water that is internally confined in the structure¹² (e.g., the [001] channel), and (iii) structural water or hydroxyl-substituting O^{2-} in the SiO_4^{4-} tetrahedra.^{11,12} Previously, both Fourier transform infrared spectroscopy (FTIR) and powder X-

ray diffraction (PXRD) elucidated that water had no structural role in coffinite,^{13,14,17–21} while Janeczek hypothesized that water may be confined in the structural channel.²¹ Additionally, high-temperature calorimetric studies suggested that water associated with coffinite included a fraction of water molecules that are adsorbed onto the mineral surface and another portion more strongly bonded within the structure.²² This plays an important role in the formation of coffinite, by lowering the overall enthalpy required for its natural formation. Likewise, uranothorite ($\text{U}_x\text{Th}_{1-x}\text{SiO}_4$) and stetindite (CeSiO_4), which are isostructural to coffinite ($I4_1/amd$, Figure 1), exhibit similar

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hydration dependencies that again were revealed by calorimetry.^{23,24}

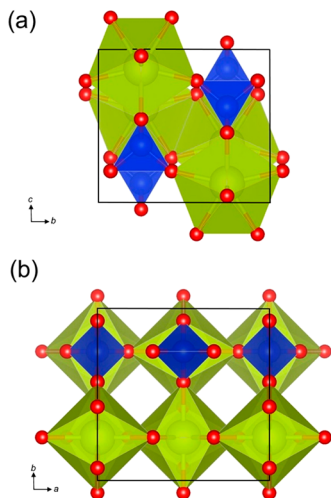


Figure 1. Projections of the structure of stetindite down to various crystallographic axes. In both (a) and (b) the yellow dodecahedra are the CeO_8 , the blue tetrahedra are the SiO_4 , and the red spheres are oxygen. (a) Representation of the structure along [100]. (b) Illustration of the structure along [001] showing clearly the channels where water may reside.

Investigations into the structural and thermodynamic properties of coffinite, uranothorite, and stetindite have also significant implications outside the fields of geochemistry and mineralogy, because these mineral phases are considered as potential ceramic waste forms for the immobilization of actinides.^{25–30} Indeed, zircon (ZrSiO_4) has demonstrated advantages of extreme chemical and physical durability across geologic time,^{31–36} implying considerable durability as an actinide host. While it has been shown that a zircon doped with 10 wt % ^{239}Pu would become fully amorphous after only 1400 years,³⁷ preliminary calculations have shown that very little Pu would be ultimately released over a 500 000 year time span due to the relatively short half-life of ^{239}Pu as well as the low solubility of amorphous zircon.^{25,27} Thus, as uranium is the main component of spent nuclear fuel^{25,27,38–40} and cerium constitutes a useful surrogate for plutonium,^{41–44} these minerals are also representative of how long-lived actinides will behave when incorporated into the zircon structure. These actinide-loaded crystalline waste forms would then be permanently disposed of in either a mined geologic repository or deep borehole.^{32,45–47}

However, any potential immobilization matrix disposed of in either of the geologic disposal strategies will encounter elevated temperatures, ranging between 70 and 350 °C, as a result of the radiogenic decay heat mainly generated by short-lived radionuclides.^{48–52} Thus, a fundamental understanding of the thermal behavior of such ceramic waste form is needed. A previous thermogravimetric analysis (TGA) coupled with differential scanning calorimetry (DSC) on stetindite performed by Strzelecki et al. (2020)²³ showed a sluggish dehydration from room temperature to 900 °C.²³ However, the structural information accompanying the dehydration process and beyond, which dictates the measured mass and energetic events are largely lacking. Similarly, the calorimetric studies reported by Guo et al.²² and Reynolds et al.⁵³ showed that there may be two water-bonded sites associated with coffinite. The first one is

associated with rapidly released water near 150 °C, while the more strongly bonded water was removed at temperatures ranging from 275 to ~600 °C. The first release is associated with weakly bonded water that was adsorbed onto the surface of the sample.^{22,53} Conversely, the origin of the second release is still unclear, suggesting that some water is strongly interacting with the sample either as confined molecular water and/or attached hydroxyl groups (OH^-). Indeed, the zircon structure type can have structurally incorporated water^{13,54–56} and OH^- .^{14,19,56,57} More recent studies discussed the mechanism of hydroxylation in the zircon structure and the impact from these groups on the material properties.^{11,58–61} However, the exact proportion and origin of attached hydroxyl ions is debated; these include whether such incorporation is an indirect result of radiation-induced amorphization of natural zircon.^{59,60,62} Nasdala et al.⁶² proposed three crystallographic models for the location of hydroxyl groups in crystalline zircon: (i) association with Si-vacant tetrahedra, (ii) occupying SiO_4^{4-} tetrahedra with or without (iii) a neighboring zirconium vacancy. Each of these cases can explain a different part of the results obtained by spectroscopy and thermal analysis in their study.⁶² Interestingly, the nature of “embedded” water may have some impacts on the coffinite matrix, resulting in distinct thermal signatures and stabilities. Either natural or synthetic coffinite thermally degrades between 400 and 500 °C,^{63,64} at which temperature it undergoes a complete decomposition into amorphous SiO_2 , UO_2 , and U_3O_8 in air atmosphere.^{22,65}

Here, we report the high temperature behaviors and structural parameters of a series of zircon structure types with hydrothermal origins: stetindite, coffinite, and uranothorite solid solutions up to ~850 °C by performing *in situ* high-temperature synchrotron and laboratory-based X-ray diffraction studies implemented with Rietveld analyses. During heating, all of these zircon structure types exhibited temperature-dependent anisotropic thermal expansion behavior and discontinuous thermal expansion of the *a*-axis, from which we derived critical information about the “strongly bonded” water and its role in dehydration and hydration processes. For stetindite, the discontinuous expansion of the *a*-axis was interpreted to be confined molecular water along the [001] channel and offered an explanation to the “energetically strongly associated” water discussed by Strzelecki et al.,²³ whereas for coffinite, the discontinuous expansion of the *a*-axis during heating, in conjunction with a larger unit cell after being cooled, was attributed to a combination of dehydration and dehydroxylation, consistent with their “strongly bonded” features characterized by Guo et al.²² In addition, for the first time we report the coefficients of thermal expansion (CTEs) for each of these minerals.

2. EXPERIMENTAL METHODS

Caution! Uranium and thorium present radiotoxicity hazards. All work has been performed in radiological laboratories licensed for actinides at Institut de Chimie Séparative de Marcoule, National Synchrotron Light Source II, and Washington State University, equipped with established radiological safety protocols, personal protective equipment (PPE) for handling actinides, proper radioactive sample containment, radiation shielding, and monitoring equipment.

2.1. Sample Synthesis. CeSiO_4 samples were synthesized by a hydrothermal method from Ce(III)-silicate solid precursor ($\text{A-Ce}_2\text{Si}_2\text{O}_7$) according to the protocol described by Estevenon et al.⁶⁶ A stoichiometric mixture of CeO_2 (Sigma-Aldrich, particle size <5 μm) and SiO_2 (Sigma-Aldrich, 10–20 nm) was mechanically milled (30 Hz, 1 h) in a Retsch MM 200 vibration mill mixer using a tungsten carbide

milling vessel. This mixture was pelletized by uniaxial pressing under 5 MPa at room temperature and then heated at 1350 °C under a reducing atmosphere (Ar–4% H₂) to prepare the Ce(III)-silicate solid precursor, A-Ce₂Si₂O₇ (space group: *P*₄₁). A-Ce₂Si₂O₇ (200 mg) was then placed in contact with 4 mL of a 0.75 M HNO₃ solution (prepared by dilution of ACS grade 70% HNO₃, Sigma-Aldrich). The pH of that solution was adjusted to 7.0 ± 0.1 with a freshly prepared NaOH solution (from ACS grade NaOH pellets, Sigma-Aldrich). This mixture was then hydrothermally treated for 7 d at 150 °C under air atmosphere in 23 mL Teflon-lined Parr autoclaves. The final product was separated from the aqueous solution by centrifugation, washed twice with deionized water and once with ethanol, and then finally dried overnight at 60 °C.

Coffinite and uranothorite samples were prepared by the protocol developed by Mesbah et al.⁶⁷ through modification of the previous procedure proposed by Fuchs and Hoekstra.^{63,64} The reagents of Na₂SiO₃, NaOH, and NaHCO₃ were supplied by Sigma-Aldrich and were of analytical grade. The uranium(IV) chloride solution was prepared by following the methodology developed by Dacheux et al.,^{68,69} which required dissolving U metal chips, obtained from Commission d'ETablissement des Méthodes d'Analyses (CETAMA), CEA Marcoule, France, in 6 M HCl. The thorium(IV) chloride solution was prepared by dissolving thorium nitrate pentahydrate in 6 M HCl and performing several cycles of evaporation and dissolution in 4 M HCl in order to remove all traces of nitrates in the solution.⁷⁰ The final concentrations of the uranium chloride and thorium chloride solutions were determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES). The syntheses were performed under inert atmosphere (argon). It consisted of first dissolving Na₂SiO₃ (0.81 g, 6.66 mmol) in water and then slowly adding the corresponding amounts of uranium and thorium, always keeping an excess of 10 mol % of silicate in order to ensure the complete complexation of the actinides. The pH of the mixture was adjusted to 11.3 ± 0.1 by a dropwise addition of 8 M NaOH. The solutions were then buffered to a pH of 8.7 ± 0.1 through the addition of NaHCO₃. The resulting green gelatinous mixtures were then transferred into 23 mL Teflon-lined Parr autoclaves and placed into an oven at 250 °C for 7 d. The final products were separated by centrifugation and washed twice with deionized water and finally once with ethanol. The solids were then dried overnight in air at room temperature. As previously reported,⁶⁷ the synthesis led to the formation of a mixture of Th_{1-x}U_xSiO₄, Th_{1-x}U_xO₂, and amorphous SiO₂. Therefore, to obtain pure coffinite and uranothorite samples, the resulting powders were purified through the protocol reported by Clavier et al.⁷¹ With this aim, 100 mg of powdered samples was put in contact with 50 mL of 0.01 M HNO₃ for 3–5 d, followed by washing in deionized water, then the remaining solid was placed in 50 mL of 0.01 M KOH solution for 3–5 d. The remaining coffinite or uranothorite samples were contacted again with deionized water and then subsequently recovered by centrifugation. This sequence was repeated, until the samples were fully purified.

2.2. Vibrational Spectroscopies. Both stetindite and coffinite were characterized spectroscopically through a combination of Raman spectroscopy and FTIR. The Raman spectra were recorded with a Horiba-Jobin Yvon Aramis device equipped with an edge filter and Nd:YAG laser (532 nm). The laser beam was focused on the sample with an Olympus BX 41 microscope with an X50LMP objective, with a spot area of 1 μm². Prior to the analysis, the apparatus was calibrated with a silicon wafer, using the first-order Si line at 520.7 cm⁻¹. *In situ* high-temperature Raman spectroscopy was performed on the stetindite sample utilizing the same spectroscopic setup previously described but differed in that the sample was placed in a platinum crucible and inserted into a Linkam TS-1500 heating device. A heating rate of 10 °C/min was applied until the desired temperature (100, 200, 300, 400, 600, 800 °C) was reached with 5 min of idle time between reaching each temperature point and acquisition of the spectrum in order to ensure thermal equilibrium. A separate Raman spectrum for stetindite was collected at room temperature after calcination at 1000 °C. *In situ* high-temperature Raman spectroscopy was not possible for coffinite or uranothorites as a result of the inability to have a controlled atmosphere over the sample during the *in situ* heating. The spectra for stetindite are presented as the average of five scans, while the reported spectrum for

coffinite is an average of four scans, which was done in order to minimize the measurement error; both had an acquisition time of 10 s.

The FTIR spectra of both stetindite and coffinite were recorded with a PerkinElmer FTIR Spectrum 100 device, where powdered samples were directly deposited onto the surface of an attenuated total reflectance (ATR) crystal without any prior preparation. Spectra of stetindite were recorded in the 300–4000 cm⁻¹ range, with a resolution of 2 cm⁻¹, whereas the spectrum collected of coffinite was recorded in the 400–4000 cm⁻¹ range, with a resolution of 4 cm⁻¹. To collect *ex situ* high-temperature FTIR spectra of stetindite, the samples were heated to the desired temperatures (100, 200, 300, 400, 600, 800, and 1000 °C) prior to being analyzed overnight and analyzed the following day upon cooling to room temperature.

2.3. *In Situ* High-Temperature Powder X-ray Diffraction (HT-PXRD). *In situ* HT-PXRD of coffinite and stetindite was conducted at the Sector 28-ID-2 (XPD) of the National Synchrotron Light Source-II (NSLS-II) at Brookhaven National Laboratory. The wavelength of the X-ray beam was 0.1949 Å. The X-ray beam was delivered by a sagittally focusing double Laue crystal monochromator. The beam size at the sample was 0.60 mm (horizontal) × 0.20 mm (vertical). The two-dimensional (2D) XRD images were recorded with a PerkinElmer XRD 1621 Digital Imaging Detector. Stetindite powder was put in a silica glass capillary with one side opened to the air, while coffinite powder was sealed in a double-walled silica-glass capillary filled with Ar gas. The capillary was then inserted into a custom-built, Kanthal coil-based furnace under standard atmosphere for heating and cooling. A K-type thermocouple was mounted near the center of the heating coil and was used to monitor and to control the temperature. The sample temperature was calibrated by measuring the CTE of a standard ceria powder at different temperature points, with a heating rate of 20 °C/min. Data were collected every 50 °C during heating from RT to 865 °C and every 200 °C during cooling. Approximately 3 min of idle time was used between reaching each temperature point and data collection in order to ensure thermal equilibrium. All collected 2D images were calibrated, masked, and integrated through the use of Dioptas.⁷² The obtained XRD patterns of stetindite and coffinite were analyzed through a Rietveld method using General Structure Analysis System software version II (GSAS-II),⁷³ where the instrument parameters were obtained using a CeO₂ standard. The background was modeled by the Chebyshev function with 8 and 20 coefficients, respectively. The above Rietveld refinement procedures on HT-PXRD were also stated previously elsewhere.^{74–77}

In situ HT-PXRD of two uranothorites (*x* = 0.46 and *x* = 0.90) were collected using a Bruker D8 advance diffractometer equipped with a Lynx-eye detector and using Cu Kα_{1,2} radiation (λ = 1.541 84 Å). The PXRD patterns were collected by packing the powder in an alumina boat (0.8 mm of depth), which was placed inside an Anton-Paar high-temperature chamber under a flow of He/H₂ (4%) to reduce the risk of the uranium oxidation. PXRD data were collected every 100 °C from room temperature to 1000 °C with a heating rate of 5 °C/min and a holding time of 15 min before each measurement. Each PXRD pattern was collected for ~1 h in the 2-θ range (10° ≤ 2θ ≤ 100°). The obtained XRD patterns of the uranothorites were also analyzed via the Rietveld method but were performed using the Fullprof suite package.⁷⁸ Before the refinements, pure silicon was used to determine the instrumental function. The crystal structure was refined by allowing multiple parameters to vary, such as the zero shift, unit cell parameters, and isotropic atomic displacement, but the atomic coordinates were kept fixed because of the limited quality of our laboratory XRD data. Moreover, the microstructural effect was modeled using anisotropic size and strain functions in agreement with the Laue group of the zircon structure type.

2.4. Sample Characterization. The morphology of the samples was characterized by scanning electron microscopy (SEM) with an FEI Quanta 200 Environmental Scanning Electron Microscope using a backscattered electron detector (BSED) or secondary electron detector (SE) under vacuum conditions, at room temperature and with a low acceleration voltage of 3 kV for coffinite and 8 kV for stetindite in order to obtain high-resolution images. The samples were always directly analyzed without any additional preparation step such as metallization.

High-Temperature Environmental Scanning Electron Microscopy (HT-ESEM) experiments were performed using the same apparatus equipped with an HT1400 stage. The samples were heated with a 5 °C/min heating rate from room temperature to 600 °C and then with a 10 °C/min rate from 600 to 800 °C. The primary energy of the electron beam was 10 kV, and the partial pressure in the ESEM chamber was 70 Pa. Images were recorded continuously during the experiment using the accumulation mode. More details are provided on Podor et al. (2019),⁷⁹ the results of which are supplied at the end of the [Supporting Information](#). In addition, stetindite was previously characterized by extended X-ray absorption fine structure (EXAFS) and X-ray adsorption near edge structure (XANES)⁶⁶ for the Ce oxidation state and local structures and by thermogravimetric analysis coupled with differential scanning calorimetry (TGA-DSC) for its initial water content (0.43 mol of H₂O per formula unit of CeSiO₄).²³

3. RESULTS

3.1. High-Temperature Synchrotron XRD of Stetindite. The resulting refinements for stetindite yielded R_{wp} values ranging from 3.5% to 4.9% (Table S1). A representative fitted pattern of stetindite is shown in Figure 2. The refined unit cell parameters of stetindite are listed in Table S1 and gathered in Figure 3.

The obtained U_{iso} values are listed in Table S1 and shown in Figure 4. The HT-PXRD patterns of stetindite (Figure S1) show its phase stability from RT to 865 °C under a standard air atmosphere. No phase transition or decomposition was observed during heating or cooling. This is in agreement with HT-ESEM observations for which no significant morphological changes were evidenced (Figures S10–S23). However, a phase transition may occur at higher temperatures. For instance, the isostructural mineral thorite (ThSiO₄)¹³ undergoes a thorite ($I4_1/amd$) → huttonite ($P2_1/n$) transition above 1350 °C at 1 atm,^{80–82} which has not been observed for stetindite. Although stetindite is thermally stable across the entire temperature range during heating, the high-temperature behavior of stetindite can be separated into three regimes: (i) 25–240 °C, (ii) 240–634 °C, and (iii) 634–865 °C. Such division is based on the nonlinear expansion along the *a*-axis with temperature, where a plateau from 240 to 634 °C occurs between two linear-expansion regimes (Figure 3a). However, this discontinuity is much less pronounced along the *c*-axis, which exhibits a nearly linear thermal expansion (Figure 3b). When stetindite is cooled from 865 °C to room temperature, the contractions along the *a*- and *c*-axes both follow linear trends (Figure 3) as an extrapolation from that established in the third stage. The unit cell of stetindite upon returning to room temperature after being heated is smaller ($a = 6.9443$ Å and $c = 6.1988$ Å) than before being heated ($a = 6.9576$ Å and $c = 6.2068$ Å) (Table S1).

3.2. High-Temperature Synchrotron XRD of Coffinite. The resulting refinements for coffinite yielded R_{wp} values ranging from 3.3% to 9.3% (Tables S2). A representative fitted pattern for coffinite is shown in Figure 2. The refined unit cell parameters of coffinite are tabulated in Table S2 and presented in Figure 5. The associated U_{iso} values are tabulated in Table S2 and presented in Figure 6. The HT-PXRD patterns of coffinite reveal a partial thermal decomposition starting at ~600 °C (Figures 7, 8, and S2). A 10 mol % fraction of UO₂ is identified at 816 °C (Table S3). This could be the result of two possible decomposition reactions: (i) $USiO_4 \rightarrow UO_2 + SiO_2$, in which the formed SiO₂ could remain amorphous and thus invisible from XRD,^{22,53,64,71,83–88} and/or (ii) hydroxylated $USiO_4$ ($U(SiO_4)_{1-x}(OH)_{4x} \cdot nH_2O$) → anhydrous $USiO_4 + UO_2$.¹¹

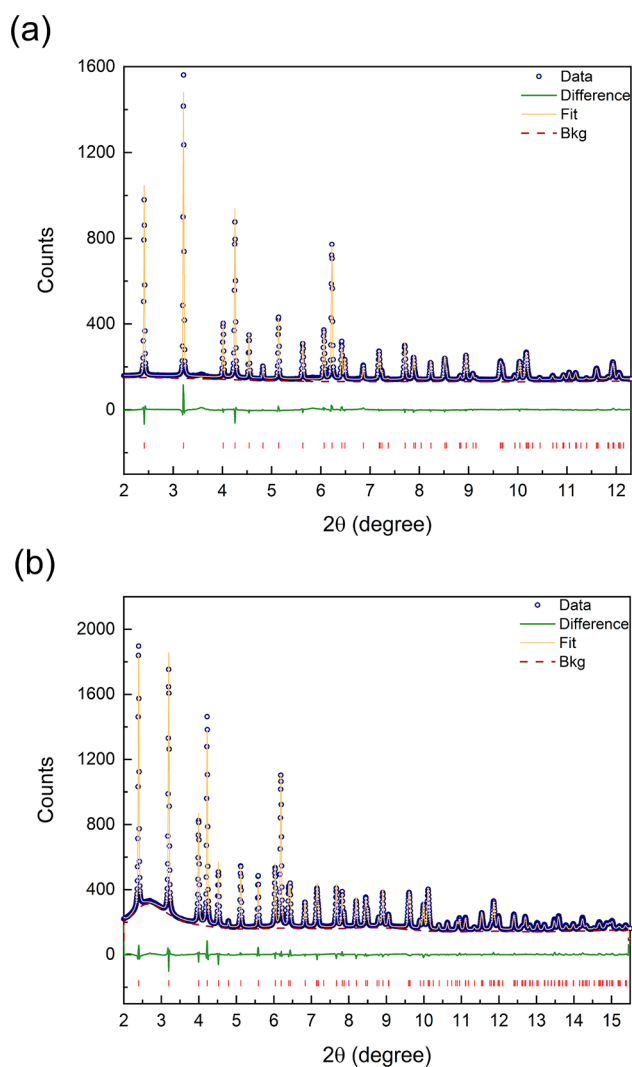


Figure 2. Fitted synchrotron XRD patterns of (a) stetindite at 27 °C and (b) coffinite at 31 °C. Data are shown as open blue circles, and the solid yellow curve is the best fit to the data. The solid green curve represents the difference between the observed and calculated profiles. The red tick marks above the *x*-axis indicate the positions of diffraction maxima.

These two reactions assume different coffinite starting types: the hydrated form, the hydroxylated form, or a combination of both, which will be discussed later. A plateau in the expansion of the unit cell was discovered along the *a*-axis and occurred over the temperature range from room temperature to ~200 °C. At higher temperatures (from 200 to ~450 °C) there was an almost linear unit cell expansion in the structure (5.2×10^{-5} Å/°C for parameter *a*). As coffinite was cooled, the contraction along the *a*-axis followed a linear trend but at a slower rate (4.96×10^{-5} Å/°C). When it reached room temperature, the coffinite unit cell was slightly larger ($a = 6.9944$ Å and $c = 6.2633$ Å) than its original size ($a = 6.9884$ Å and $c = 6.2668$ Å) (Table S2).

3.3. High-Temperature XRD of Uranothorite, the Solid Solution. The refined unit cell parameters of each of the uranothorite solid solutions are listed in Table S4 and reported in Figures S3 and S4. The high-temperature behavior of uranothorite solid solution was similar to that observed for coffinite. There was a partial thermal decomposition of $U_xTh_{1-x}SiO_4$ ($x = 0.46$ and 0.90), leading to a mixture of UO₂, U₃O₈, and amorphous SiO₂ at ~800 °C (Figure S5).

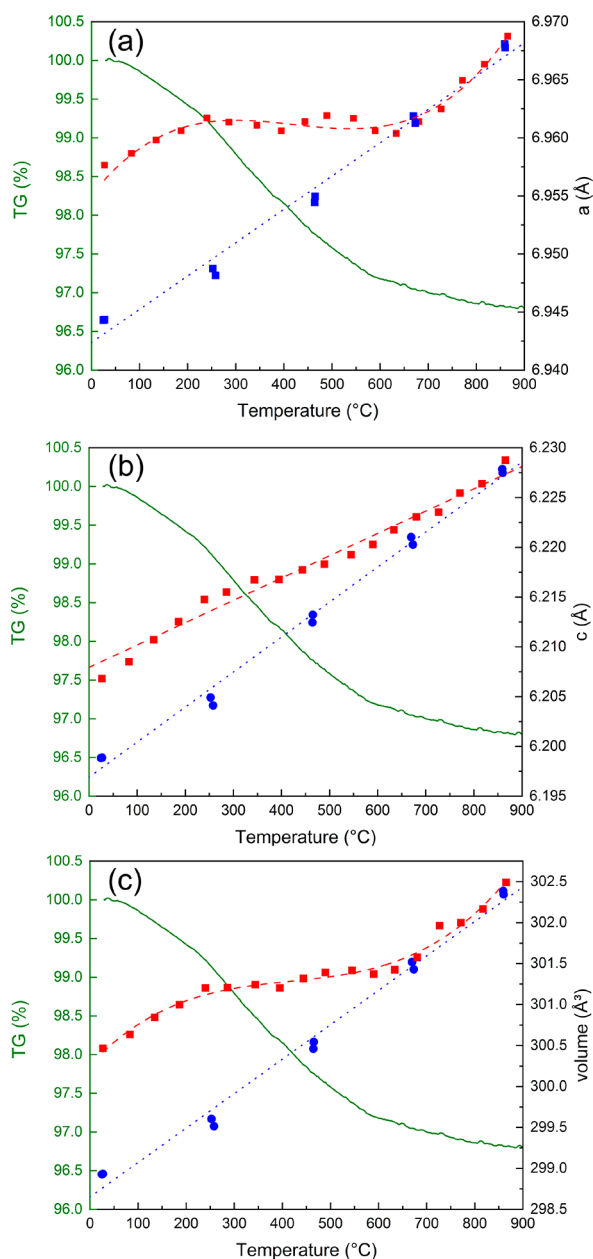


Figure 3. Variation of unit cell parameters for stetindite. Red symbols in (a–c) indicate the data points taken while the sample was heated, and blue symbols indicate data points collected while the sample was cooled. The exhibited TG data in the green curve were published previously.²³

These results are in good agreement with the previous TGA-DSC studies that reported uranothorite to be thermally stable until 800 °C.²⁴ The presence of U_3O_8 as a decomposition product could be related to the possible presence of air as an impurity in the measurement system or to the presence of traces of water in the helium atmosphere used for heating. The phase transition of thorite ($I4_1/amd$) → huttonite ($P2_1/n$) was again excluded, as it occurs at a higher temperature (1200–1225 °C).^{82,89} A nonlinear expansion of the unit cell was once again observed (Figures S3 and S4). For the higher U content (i.e., $x = 0.9$), the high-temperature behavior is unique, showing a sharp decrease of the a parameter followed by a strong increase, coinciding with the opposite behavior of the c parameter (Figure S4). Such changes in the unit cell parameters may result from dynamic compositional changes of uranothorite at high

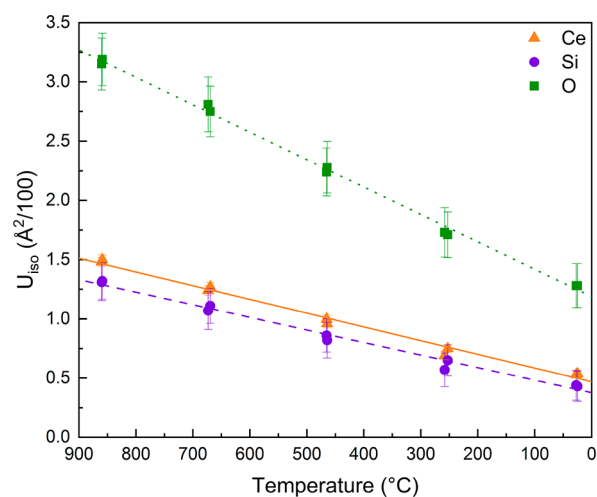


Figure 4. Variation of atomic thermal parameters of stetindite as a function of temperature. Triangles and solid lines represent Ce, circles and dashed lines represent Si, and squares and dotted lines represent oxygen.

temperatures. Uranothorite solid solution was found to have a negative enthalpy and volume of mixing.^{24,90} $U_{0.9}Th_{0.1}SiO_4$ is close to coffinite, which is metastable, and it tends to decompose to a U-depleted uranothorite and surely led the excluded U that crystallized into U_3O_8 , as driven by the energetic downhill toward thorite.²⁴ However, recent neutron diffraction data suggested a minimum unit cell parameter located around $x = 0.8$.⁹⁰ Thus, on the one hand, as the decomposed phase decreased from $x = 0.9$ to lower x values, the resulting unit cell was expected to decrease first until $x = 0.8$, then followed by a continuous increase when $x < 0.8$, in agreement with the above experimental results. On the other hand, $U_{0.46}Th_{0.54}SiO_4$, near the equal molar composition, has the maximum stabilization ($\Delta G = \Delta H - T\Delta S$) from the negative enthalpy of mixing²⁴ and the positive configurational entropic term of U and Th mixing.⁹⁰

3.4. Vibrational Spectroscopy of Stetindite and Coffinite. The $I4_1/amd$ space group has 12 active Raman vibrational modes, based on it being in the D_{4h} point group.^{17,91,92} Of these 12 active modes, seven ($\Gamma_{int} = 2A_{1g} + 2B_{1g} + B_{2g} + 2E_g$)^{91,92} can be assigned to the internal vibrations of the SiO_4 tetrahedron, while the remaining five ($\Gamma_{int} = 2B_{1g} + 3E_g$)^{91,92} can be assigned to the external vibrations of the SiO_4 tetrahedra within the unit cell.^{91–93} Because of the interaction of the SiO_4 tetrahedra with the MO_8 dodecahedra in the unit cell, the SiO_4 tetrahedra cannot be considered a strictly independent unit.⁹⁴ As a result of these interactions, there has yet to be a reporting of a spectra with all 12 of the active Raman modes for materials of the zircon structure type.¹⁷ Similar to what was found by Costin et al.,¹⁷ only seven vibrational bands were presented for the stetindite (Figure 9a,b) and coffinite (Figure S6). Of the seven vibrational bands presented, four belong to the internal vibrational modes and occur near 420, 590, 900, and 920 cm^{-1} , while the three bands at 100, 200, and 300 cm^{-1} are all due to the external vibrational modes. The positions of all the vibrational bands are in excellent agreement with previous Raman spectroscopic measurements on both compounds (Table S5).^{17,66,95}

The *in situ* high-temperature Raman spectroscopy of stetindite revealed that the sample studied in this study was compositionally pure and did not undergo any thermal decomposition, consistent with *in situ* high-temperature XRD.

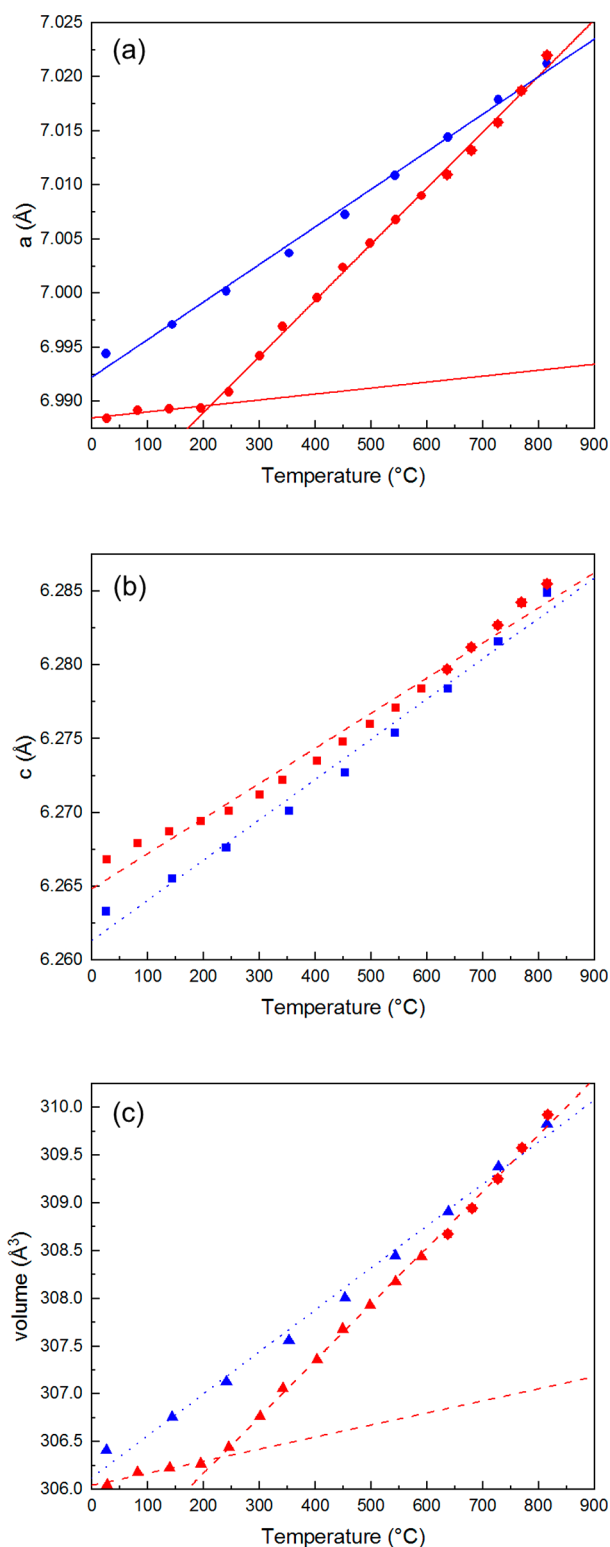


Figure 5. Variation of unit cell parameters for coffinite. Red symbols in (a–c) indicate the data points taken while heating the sample, while blue symbols indicate data points collected while cooling the sample. Red star symbols indicate measurements where USiO_4 was observed to be decomposing to UO_2 starting at 636 °C.

This was confirmed, as there were no observed vibrational peaks at 460 cm^{-1} , which would suggest the presence and/or the formation of CeO_2 . The characteristic H_2O bending mode band around 1600 cm^{-1} and the OH stretching mode bands in the

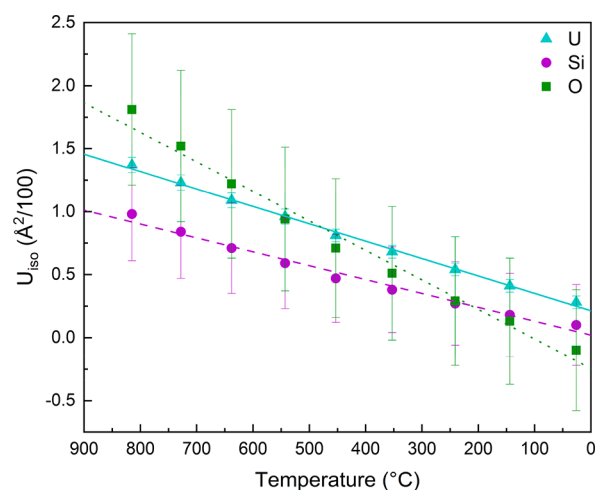


Figure 6. Variation of atomic thermal parameters of coffinite as a function of temperature. Triangles and solid lines represent U, circles and dashed lines represent Si, and squares and dotted lines represent O.

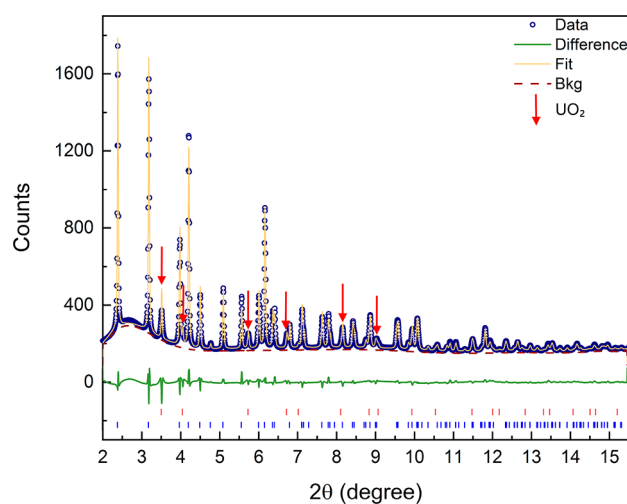


Figure 7. Fitted synchrotron XRD pattern of coffinite at 816 °C. Data are shown as open blue circles. The solid yellow curve is the best fit to the data. The solid green curve represents the difference between the observed and calculated profiles. The blue tick marks above the x-axis indicate the positions of allowed reflections for coffinite, and the red tick marks indicate those for UO_2 .

range of 3500–3200 cm^{-1} are observed on the spectra collected at 200 and 300 °C (Figure 9c). However, the absence of the H_2O bending mode band for spectra obtained at room temperature and 100 °C is not explained yet, and it is not possible to be sure these bands around 3500–2900 cm^{-1} correspond to water only or to both water and hydroxide bonds. This is consistent with the reports of Naslada et al., who suggested that Raman spectroscopy does often present problems in the detection of hydrous species with a zircon structure type due to the low-intensity bands.⁶² Lastly, there was a shift in the silicate bands located at 150, 280, and 920 cm^{-1} for temperatures below 400 °C and a disappearance of the bands located at 380 and 510 cm^{-1} (which could correspond to M–OH bands) in the same temperature range (Figures S7 & S8).

For FTIR spectroscopy, the $I4_1/amd$ space group has seven active FTIR vibrational modes, which was determined again through a factor-group analysis.^{17,91} Similar to Raman spectroscopy, these vibrational modes can be assigned to the internal and

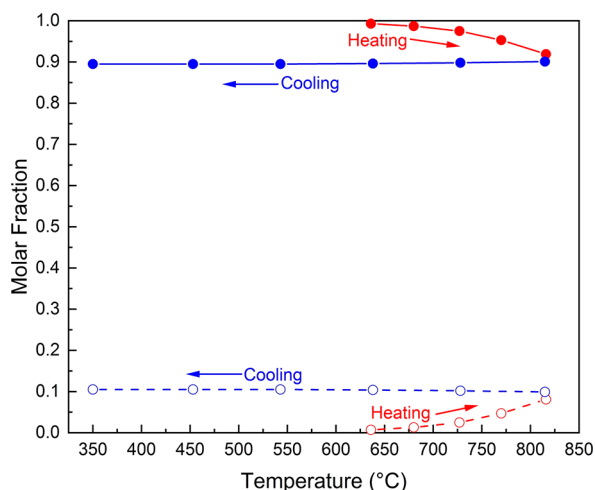


Figure 8. Variation of molar fraction of USiO_4 (solid circles) and UO_2 (open circles) when heated (red) and then cooled (blue).

external vibrations of the SiO_4 tetrahedron. Of the seven vibrational modes, four ($\Gamma_{\text{int}} = 2A_{2u} + 2E_u$) can be assigned to internal vibrational modes and three ($\Gamma_{\text{ext}} = A_{2u} + 2E_u$) can be assigned to external vibrational modes. The four internal modes are presented for all of the calcinated stetindite samples (Figure 10) as well as the pristine coffinite sample (Figure S9). The four internal modes occur near 435, 570, 800, and 980 cm^{-1} . Again, the positions of all the vibrational bands are in excellent agreement with previous FTIR spectroscopic measurements on both compounds (Table S5).^{17,66,95}

In contradiction to Raman spectroscopy, FTIR spectroscopy is often much more sensitive to vibrational modes of both H_2O and OH^- ,⁹⁶ with the recorded FTIR spectra collected for the various calcinated stetindite samples and pristine coffinite sample demonstrating the following. For stetindite, a hydrous component was identified as two different bands. The first is a broad band between 3300 and 3400 cm^{-1} (Figure 10b), while the second is a broad and diffuse minor peak that is centered at 1635 cm^{-1} (Figure 10c). These bands can be attributed to the stretching and bending modes of H_2O , respectively.^{11,62,96} Each of these two vibrational bands was found to disappear as temperature exceeded 400 °C (Figure 10). The FTIR spectra collected for the pristine coffinite sample displays a very broad and diffuse peak in the region from ~ 3700 to ~ 2950 cm^{-1} and also another broad and diffuse minor peak that is centered at 1636 cm^{-1} (Figure S10). Again, each of these peaks can be attributed to the stretching and bending modes of H_2O .^{11,62,96} Interestingly, coffinite does display a peak centered at 1088 cm^{-1} (Figure S9).^{11,17} This vibrational band could indicate that coffinite is partially hydroxylated.

4. DISCUSSION

4.1. Water in Stetindite. The observed three-stage high-temperature behavior of stetindite revealed by XRD (section 3.1) is in excellent agreement with the *in situ* high-temperature Raman spectroscopy, the FTIR spectroscopy performed on the calcinated samples, and the previous TGA-DSC analysis by Strzelecki et al.²³ Indeed, these authors suggested that a portion of water was energetically more strongly associated with stetindite than that of surface-adsorbed water, as it was not fully removed until ~ 700 °C,²³ corresponding well to the first and second regimes (25 to 634 °C) shown by the XRD results (Figure 2a). The high temperature needed for removing this

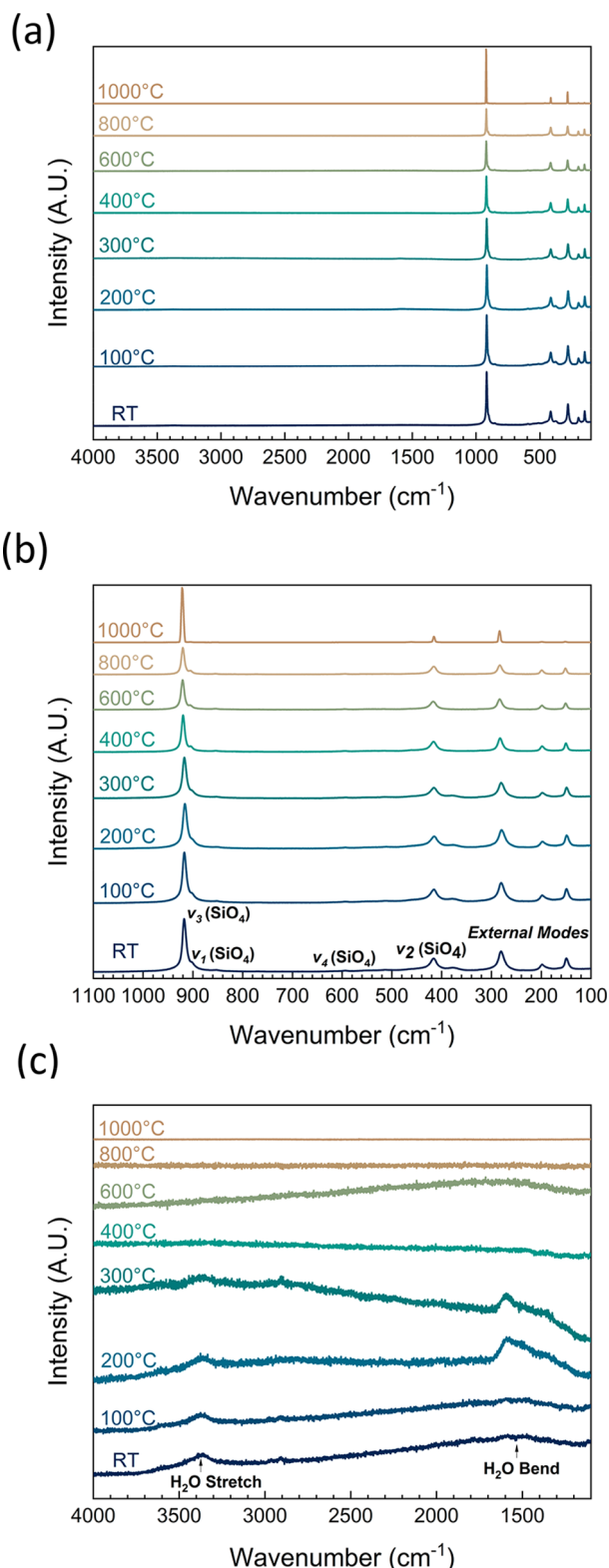


Figure 9. *In situ* high-temperature Raman spectroscopy of stetindite for temperatures ranging from room temperature to 1000 °C in the regions (a) 4000–100 cm^{-1} , (b) 1100–100 cm^{-1} , and (c) 4000–1000 cm^{-1} . Arrows and labels indicate to what the various vibrational bands are attributed. ν_1 , ν_2 , ν_3 , and ν_4 are the four normal internal modes of vibration.

water also indicates that the additional energetic contributions arise from the water-lattice interaction due to confinement that

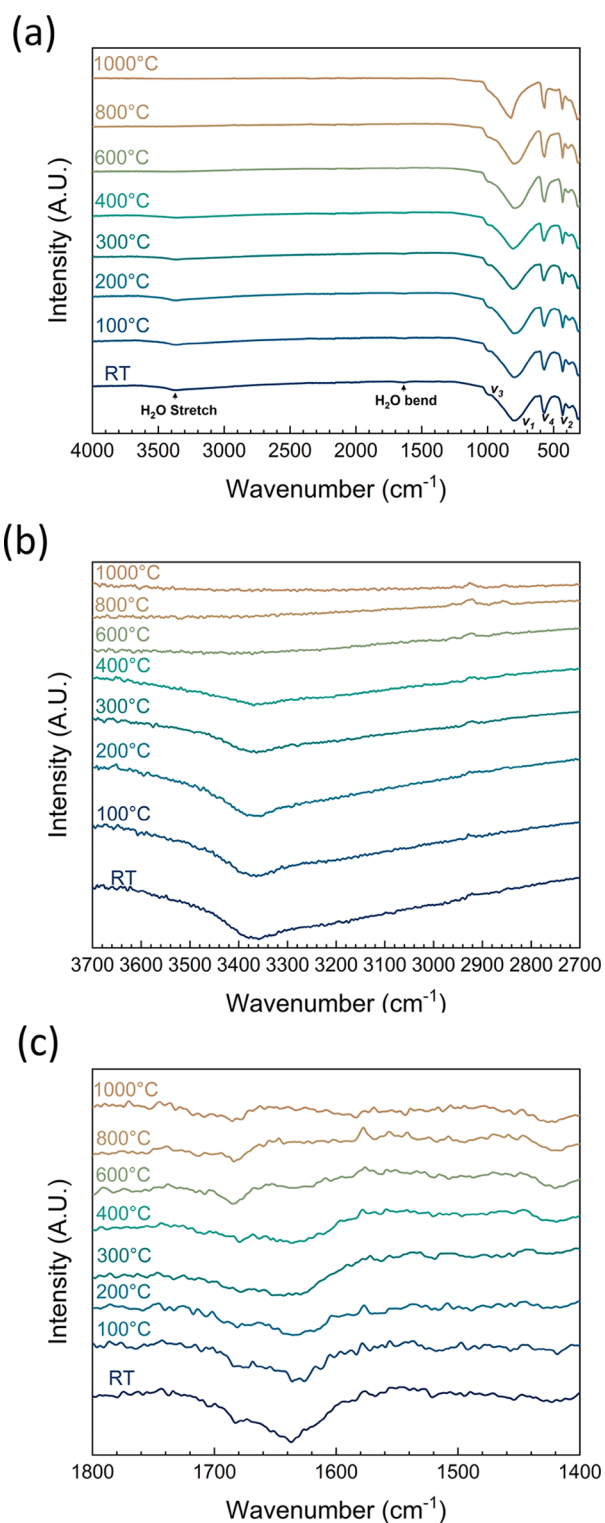


Figure 10. FTIR performed on pristine and calcinated stetindite for temperatures ranging from room temperature to 1000 °C in the regions of (a) 4000–300, (b) 3700–2700, and (c) 1800–1400 cm^{-1} . Arrows and labels indicate to what the various vibrational bands are attributed. ν_1 , ν_2 , ν_3 , and ν_4 are the four normal internal modes of vibration.

helps overcome the enthalpic penalty encountered by the anhydrous phases.²³ The nature of this confined molecular water is further indicated by the Raman spectra, where the presence and persistence of characteristic H₂O bending mode band around 1600 cm^{-1} and the OH⁻ stretching mode bands in the

range of 3500–3200 cm^{-1} up to 400 °C (Figure 9c). The temperature is obviously too high for physically adsorbed water to persist. FTIR further corroborates the existence of “strongly” associated water, as the bending and stretching vibrational bands of water did not disappear until temperatures exceeded 400 °C, as they were absent in the spectra collected for stetindite calcinated at above 600 °C (Figure 10).

Moreover, the removal of such confined water (accounts for ~87% of the water measured by TGA),²³ occurs between ~200 and ~700 °C, which is consistently overlapped with the second temperature regime (240–634 °C) in XRD, where the *a*-axis undergoes a plateau, but the *c*-axis still follows a nearly linear expansion. This strongly suggests that the removal of the confined water preferably impacts the lattice in the direction perpendicular to [001], causing the discontinuity in the expansion along the *a*-axis. Thus, we hypothesized that the confined water resides in the channels parallel to [001] (Figure 1b). Similar hypotheses have been proposed for other zircon structure-type phases,^{13,14,55,56} including the one for coffinite by Janeczek in 1991.²¹ On the basis of this hypothesis, the key structural feature of the confined water is its relative transitional freedom along the *c*-axis while being restrained in the (001) planes.^{96,97} Hence, when thermal energy is provided to the confined water through heating, the thermal motion of the water molecules will gradually promote the breaking of the confinement and the release through the channels. As a result, the structure along the *a*-*b* planes is subject to the competition between the thermal expansion along the *a*-axis (or *b*-axis) and the contraction of [001] channels due to the void formation after water removal, which together leads to the plateau in the unit cell parameter *a* between 240 and 634 °C, while the structure along the *c*-axis receives a smaller impact from the breaking of confinement and thus follows a nearly linear expansion. This is further confirmed by measuring the bond distances constituting the channel size (Figure 11). As the channel is a parallelepiped, the three constituent bonds were selected to measure the height/width, diagonal, and the diagonal depth. The bonds that define the channel size are Ce (0, 3/4, 7/8)–Ce (1/2, 1/4, 5/8) or –Si (0, 3/4, 5/8) for the height/width; Ce (0, 3/4, 7/8)–Si (1/2, 3/4, 5/8) for the diagonal; and Ce (0, 3/4, 7/8)–Ce (1/2, 1/4, 3/8) for the depth. The variation for the size of the channels as a function of temperature (Figure 11) follows a nearly identical trend as observed for the *a*-axis (Figure 2a).

Further evidence supporting the dynamic interplay of confined water in the [001] channel comes from the investigation of the changes in the Si–O bond length and angle of the two sets of O–Si–O comprising the SiO₄ tetrahedron (Figure 12). This is shown by the fact that the Si–O (Si (1,0,0)–O (1,0,0)) bond distance contracts as a function of temperature (Figure 12a). The contraction begins at a gradual rate from room temperature to 394 °C, followed by an acceleration in the contraction rate from 394 to 633 °C, reaching to a reduced Si–O bond length above 633 °C. The longer Si–O bond length near ambient temperature could be a result of decreased electron density due to the formation of hydrogen bond with the same oxygen (Si–O–H) and hydrogen from the [001] confined water. Once the thermal energy was provided for the H₂O to be liberated from the channel, the Si–O bond can then relax and contract. The increase in the rate of contraction occurring over the temperature interval from 394 to 633 °C is again supported by the Raman and FTIR spectroscopic observations.

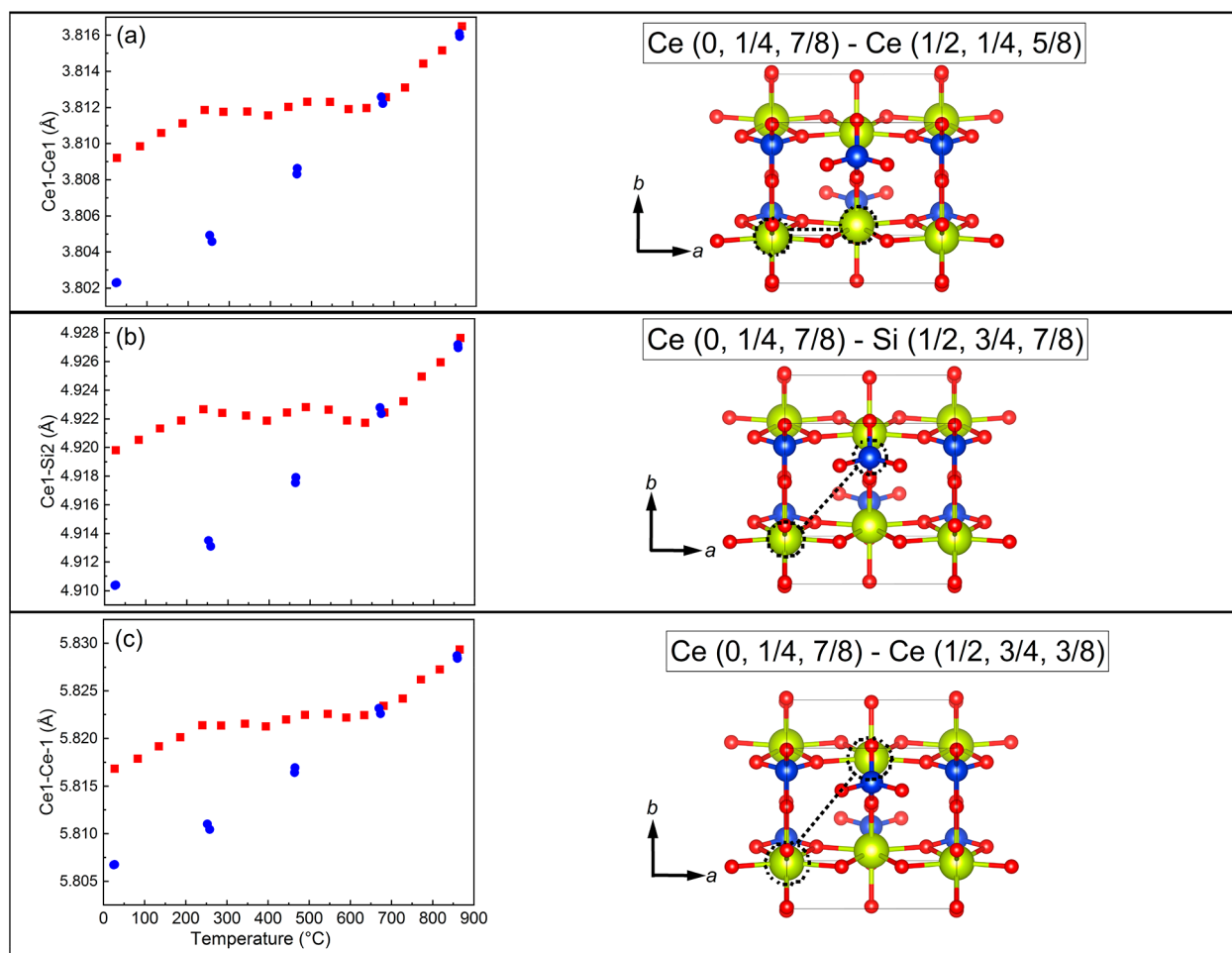


Figure 11. Variation in the measured bond lengths as a function of the temperature of the constituting elements that define the dimensions of (a) height/width, (b) diagonal cross-section, and (c) depth to the [001] channels of CeSiO_4 .

Moreover, the shifts in the vibrational modes of SiO_4 bring additional information (Figures 9, S7, and S8). The vibrational frequencies of all the vibrational modes either plateau or decrease from room temperature to 200 °C. The symmetric internal stretching (ν_1) and the asymmetric stretching (ν_3) modes both increased to higher frequencies above 200 °C (Figure S7b). While such a trend was not typically expected for high-temperature Raman spectroscopy,⁹⁸ it was what has been found in high-pressure Raman spectroscopy studies of zircon-type materials,^{60,86,99} where the Si–O bond length decreased with increasing pressure, similar to the contraction of Si–O bond distance relating to ν_1 and ν_3 shifting to higher frequencies. The vibrational frequencies of the internal bending modes (ν_2 and ν_4) increased to higher frequencies from 200 to 600 °C and then decreased to lower frequencies from 600 to 1000 °C (Figure S7a). As both the ν_2 and ν_4 vibrational modes were influenced by the vibrations of the Ce cation,⁹² the behavior of these two modes was further complicated. The vibrational modes of all three external modes (Figure S8) were found to increase above 200 °C, again consistent with the decreased Si–O bond length.^{60,86,99} The observed trend that vibrational frequencies either reached a plateau or decreased from room temperature to 200 °C may be due to the disappearance of the bands located at 380 and 510 cm^{-1} , which could correspond to M–OH bands. All of these shifts in both the internal and external vibrational bands (Figures S8 and S9) of the SiO_4

tetrahedron further support the elimination of water inserted in the CeSiO_4 structure and the reorganization of the silicate structure. The changes in the angle of rotation of the two sets of O–Si–O, where set one is comprised of O (0,0,0)–Si (1,0,0)–O (1,0,0) and set two is comprised of O (1,1,1)–Si (1,0,0)–O (1,0,0), are to compensate the change in Si–O bond length (Figure 12b,c). This all further demonstrates that the hypothesized confined molecular water plays a major role in controlling the dynamics of the structural thermal expansion.

4.2. Hydroxyl Group in Coffinite. As it was previously mentioned in the result of *in situ* high-temperature XRD of coffinite (Section 3.2), the coffinite in this study was either of the hydrated form, the hydroxylated form, or a combination of both. This complexity of coffinite comes from its high-temperature behavior, which is different from that of stetindite in the following three points. First, the plateau in the expansion of the unit cell along the *a*-axis occurred in a much lower temperature range, from room temperature to ~200 °C (Figure 5a), compared with that of stetindite. While the plateau corresponds well to water removal characterized by previous thermal analyses (TGA-DSC and mass spectrometry, MS)^{22,53} and the hypothesized water, which resides in the [001] channel, may explain the attenuation of thermal expansion, the relatively low temperature for removing the confined water suggests a weaker water-structure interaction. Second, the expansion of the unit cell at a higher temperature (200 to ~450 °C) is almost linear

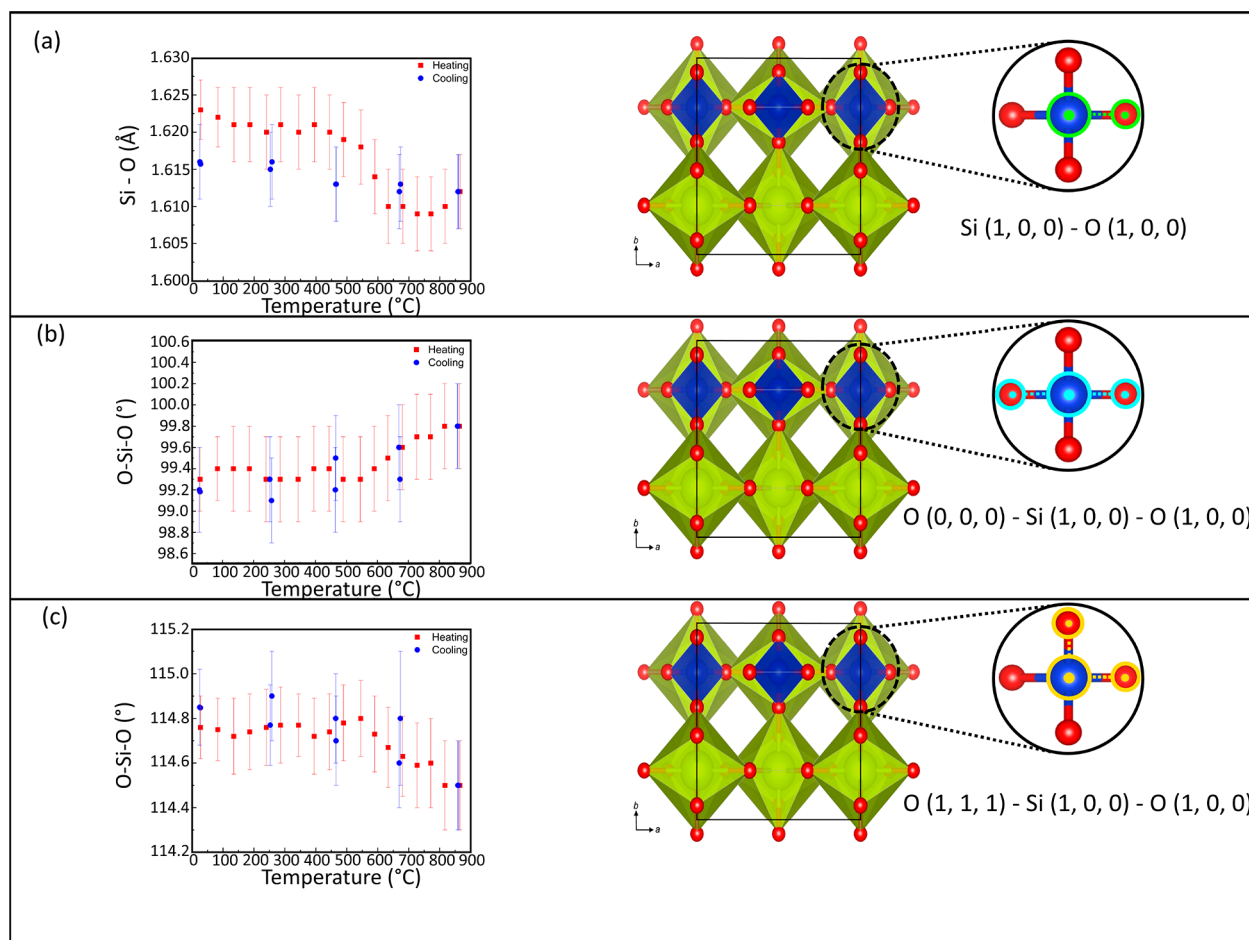


Figure 12. Variation in the measured (a) Si–O bond lengths and (b, c) angles of the O–Si–O bonds as a function of temperature for CeSiO_4 .

($5.2 \times 10^{-5} \text{ \AA}/^\circ\text{C}$ for parameter *a*) (Figure 5c), as a result of the continued liberation of water and/or hydroxyl groups from coffinite as suggested by mass spectrometry.²² This high-temperature structural behavior, different from that observed for stetindite, may be due to the presence of a disphenoidal cluster of four OH^- replacing the SiO_4^{4-} tetrahedron.¹¹ As hydroxylated zircons exhibit a smaller unit cell size,¹¹ loss of OH^- groups would expand the structure. Such a conjecture is further supported by the observation that, at temperatures above 450 °C, the *a*-axis continued a nearly linear expansion at a rate of $5.2 \times 10^{-5} \text{ \AA}/^\circ\text{C}$, as a result of mainly unit cell thermal expansion and possible dehydroxylation. Third, the unit cell of coffinite after being cooled to room temperature has a larger unit cell of $306.05(1) \text{ \AA}^3$ compared to its original size, $306.41(2) \text{ \AA}^3$ (Figure 5c and Table S2), supporting that the starting coffinite was hydroxylated with a smaller unit cell.

The hydroxylation is further supported by the following analysis of Si–O bond length and bond angle (Figure 13). The variance of Si–O bond length as a function of temperature was plotted in Figure 13a. From room temperature to 301 °C, Si–O underwent a slight contraction, probably due to the removal of confined water similar to the Si–O contraction in stetindite (Figure 12). Then Si–O expanded from 301 to 544 °C, nearly coincident with the secondary mass loss observed by the previous TGA-DSC-MS studies.^{22,53} Again, the changes in the angle of rotation of the two sets of O–Si–O are to compensate the change in Si–O bond lengths (Figure 13b,c). The overall observed trend of lengthening of the Si–O bond length further

indicates that the sample was mostly hydroxylated, again in agreement with hydroxylated zircons having a smaller unit cell due to the shorter Si–OH bond length.¹¹

Thus, coffinite in this study is likely to be both partially hydrated and hydroxylated: $\text{U}(\text{SiO}_4)_{1-x}(\text{OH})_{4x} \cdot n\text{H}_2\text{O}$, which is also supported by FTIR analysis, where both water stretching (from ~ 3700 to $\sim 2950 \text{ cm}^{-1}$) and bending (1636 cm^{-1}) modes and an OH^- stretching mode (1088 cm^{-1}) were identified (Figure S10).^{11,17,62,97} Coffinite after dehydration and dehydroxylation was “cleaner”, exhibiting a slightly larger size after heating, which is consistent with Caruba et al.¹¹ reporting an increase in unit cell volume for hydroxylated zircons after being heated to 950 °C. The above observation agrees well with previous reports on synthetic and natural coffinites. The average unit cell values in the literature for synthetic (pristine and thermally treated) coffinite are ($\bar{a} = 6.989 \text{ \AA}$ and $\bar{c} = 6.266 \text{ \AA}$, Table 1),^{22,53,54,60,64,65,83–86} which are, in general, larger than those for natural coffinites ($\bar{a} = 6.951 \text{ \AA}$ and $\bar{c} = 6.263 \text{ \AA}$, Table 1).^{57,64,100,101} Additionally, the complicated interplay between hydration and hydroxylation explains the discrepancy in the reported unit cell parameters for coffinite (Table 1).^{22,52,53,56,62–64,82–85,88,89} Finally, the differences in vibrational band and thermal behavior also indicate that hydrothermally prepared zircon structure-type phases could deviate from one another. Thus, $\text{U}(\text{SiO}_4)_{1-x}(\text{OH})_{4x} \cdot n\text{H}_2\text{O}$ is probable and should commonly represent the phases encountered in nature or prepared via hydrothermal synthesis routes. As the hydroxylated coffinite can be preserved in a low temperature

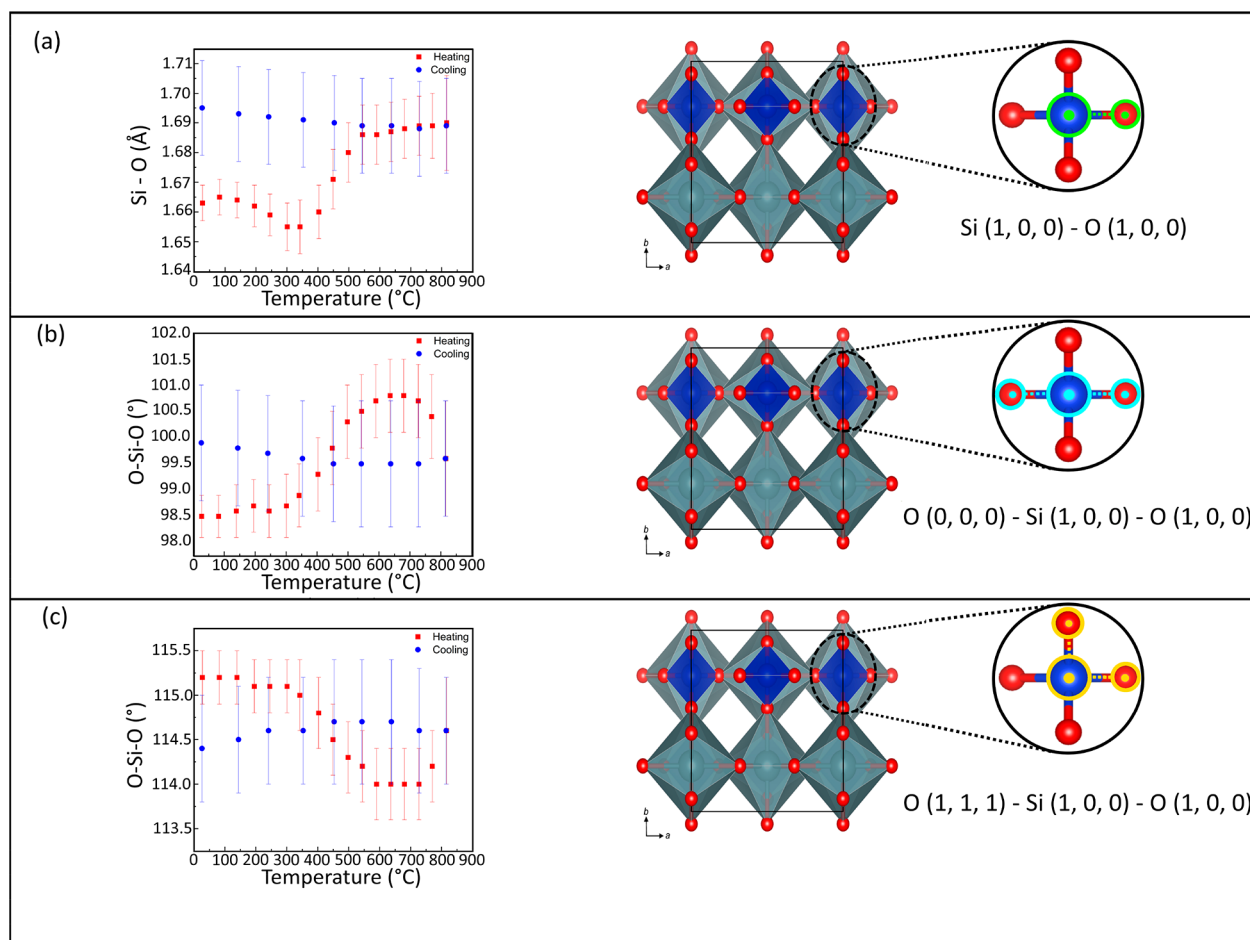


Figure 13. Variation in the measured (a) Si–O bond lengths and (b, c) angles of the O–Si–O bonds as a function of temperature for USiO_4 .

at which both synthetic and natural coffinites form, what we learned from coffinite in this study should closely reflect its alteration at elevated temperature in nature. These above discoveries could be generalized toward other zircon structure types (e.g., thorite, hafnon (HfSiO_4)) that have hydrothermal origins.^{23,80,102,103}

4.3. Thermal Response of Metal Orthosilicates. The mismatch in the a -parameter before and after the heating appears to be a unique feature of the synthetic stetindite and coffinite prepared by hydrothermal routes, which could be more generalized for other zircon structure types with hydrothermal origins.^{80,102,103} Metal orthosilicates synthesized from the dry routes, the usual method for preparing zircon, hafnon (HfSiO_4), and thorite, do not show such a sluggish thermal response, suggesting the absence of confined water or structural OH^- . Note that the high-temperature solid-state routes^{54,104–108} are possible for zircon, hafnon, and thorite (but not for coffinite or stetindite), because they all have an energetically favorable enthalpy of formation ($\Delta H_{f, \text{ox}}$) from binary oxides ($\text{MO}_2 + \text{SiO}_2$).^{24,104} In contrast, stetindite and coffinite are both energetically metastable with respect to their binary oxides and thus require hydrothermal synthetic techniques to obtain the pure phases,^{22,23,66,95} in which water and/or OH^- play significant roles in stabilizing the formed silicates. Thus, although all of these zircon-type materials crystallize in the same long-range structure, the hydration and hydroxylation introduced during their formation can greatly modify their material signatures, high-temperature behaviors, and thermody-

amic properties.^{22–24} This conclusion can be generalized to other natural metastable minerals having hydrothermal origins, such as the dichotomy pairs of rhabdophane-monazite or xenotime-churchite.^{3,9,109,110}

For this reason, to compare the high-temperature structural data of stetindite and coffinite with other metal orthosilicates, such as zircon, hafnon, and thorite reported in the studies of Mursic et al.,¹¹¹ Ding et al.,¹¹² and Knyazev et al.⁸⁹ (Table 2),^{89,111–115} we used the XRD data obtained during cooling, where samples were fully dehydrated or dehydroxylated. In addition, we normalized all the data by taking the relative change in unit cell parameters (a/a_0 and c/c_0) as a function of temperature (Figure 14). This shows that both stetindite and coffinite followed a similar thermal response of the c -axis in zircon, hafnon, and thorite. However, when the thermal response of the a -axis is observed, stetindite and coffinite deviate slightly (by $\sim 0.1\%$) from the group.

4.4. Coefficients of Thermal Expansion. As it is evident from the previous section that the hydrous and anhydrous forms expanded differently in response to thermal energy, here we present two sets of coefficients of thermal expansion (CTEs) for the two forms. The mean CTEs for hydrous stetindite and hydroxylated coffinite are presented in the Supporting Information. Note that the CTEs of hydrated phases are strongly dependent on the nature of the starting material and susceptible to the synthesis conditions; therefore, the CTEs of hydrated phases may not be representative.

Table 1. Unit Cell Parameters of Synthetic Coffinite Compared to Those Published for Synthetic and Natural Coffinite^a

reference	publication date	<i>a</i> (Å)	<i>c</i> (Å)
Hoekstra and Fuchs ⁶³	1956	6.977	6.307
Fuchs and Gebert ⁵³	1958	6.981(4)	6.250(5)
Guo et al. ²²	2015	6.983(3)	6.263(4)
Laboratories et al. ⁸³	2014	6.9842(3)	6.2606(3)
Szenknect et al. ⁸⁴	2016	6.9856(2)	6.2582(2)
Mulak ⁸⁵	1977	6.986(2)	6.268(2)
Bauer et al. ⁸⁶	2014	6.9862(2)	6.2610(4)
pristine coffinite (this study)	2021	6.9884(1)	6.2668(1)
coffinite after heating (this study)	2021	6.9944(2)	6.2633(3)
Guo et al. ²²	2015	6.990(1)	6.261(1)
Zhang et al. ⁶⁰	2009	6.9936(4)	6.2614(6)
Reynolds ⁵²	2013	6.9980(2)	6.2720(2)
Pointeau et al. ⁶⁵	2009	7.0135(4)	6.2669(6)
average values \bar{a} and \bar{c} (Å) ^a		6.989	6.266
Stieff et al. ⁵⁷	1956	6.94	6.31
Hansley and Fitzpatrick ⁸⁹	1989	6.946(1)	6.268(2)
Darnley et al. ⁹⁰	1965	6.95(2)	6.26(3)
Darnley et al. ⁹⁰	1965	6.98(2)	6.19(3)
Hoekstra and Fuchs ⁶³	1956	6.937	6.285
average values \bar{a} and \bar{c} (Å)		6.951	6.263

^aThe data above and below the solid line are associated with synthetic and natural coffinite, respectively.

The CTEs for anhydrous phases are considered as the standard values. Stetindite was found to be fully dehydrated above 634 °C. The following linear relations of unit cell parameters for anhydrous stetindite were then derived by fitting the data obtained during the heating from 634 to 865 °C and the full cooling data from 860 to 25 °C ($R^2 > 0.987$).

$$a(\text{Å}) = 6.9421 + 2.9244 \times 10^{-5}T(^\circ\text{C})$$

$$c(\text{Å}) = 6.1967 + 3.6518 \times 10^{-5}T(^\circ\text{C})$$

$$V(\text{Å}^3) = 298.63 + 4.33 \times 10^{-3}T(^\circ\text{C})$$

Table 2. Thermal Expansion Coefficients of Orthosilicate Compounds Crystallizing in the Zircon Structure

compound	$\alpha_a (\times 10^{-6}/^\circ\text{C})$	$\alpha_c (\times 10^{-6}/^\circ\text{C})$	α_c/α_a	<i>T</i> range (°C)	reference
ZrSiO ₄	3.05	6	1.97	31–885	Mursic ¹¹¹
ZrSiO ₄	3.2	5.4	1.69	20–520	Bayer ¹¹³
ZrSiO ₄	3.4	5.6	1.65	20–1020	
ZrSiO ₄	3.5	6	1.71	20–800	Subbarao ¹¹⁴
ZrSiO ₄	3.8	6.5	1.71	25–1000	
ZrSiO ₄	4.3	6.5	1.51	25–1500	
ZrSiO ₄	3.9	6	1.54	25–500	
HfSiO ₄	3.0	4.9	1.63	20–520	Bayer ¹¹³
HfSiO ₄	3.1	5.1	1.65	20–1020	
HfSiO ₄	2.77	6.09	2.20	25–1200	Ding ¹¹²
HfSiO ₄	3.11	5.97	1.92	100–1250	
HfSiO ₄	3.2	6.1	1.91	25–800	Varghese ¹¹⁵
CeSiO ₄ anhydrous	4.21	5.89	1.40	25–885	this study
USiO ₄ dehydroxylated	4.96	4.35	0.88	31–815	this study
(U _{0.46} Th _{0.54})SiO ₄	4.65	7.93	1.71	400–800	this study
(U _{0.9} Th _{0.1})SiO ₄	4.71	7.81	1.66	200–600	this study
ThSiO ₄	2.5	5.3	2.12	25–500	Subbarao ¹¹⁴
ThSiO ₄	3.5	5.1	1.46	25–900	Knyazev ⁸⁹

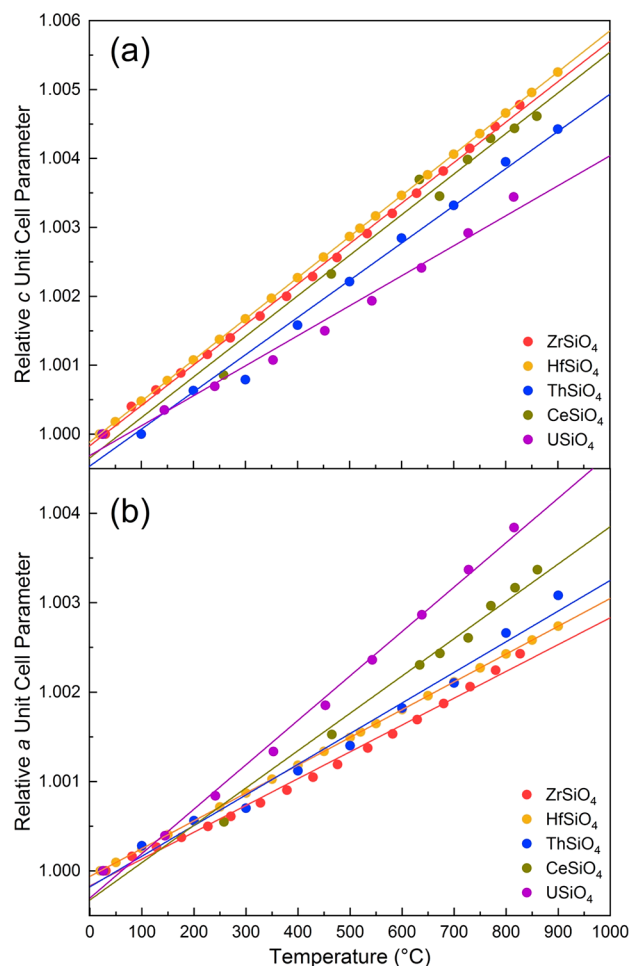


Figure 14. Comparison of the thermal expansion obtained for unit cell parameters (a) *a* and (b) *c* for several anhydrous MSiO₄ compounds (data from this study for M = Ce, U and data from the literature for M = Zr, Hf, Th).^{89,111,112}

The derived mean CTEs of anhydrous stetindite are $\alpha_a(\text{stetindite-anhyd}) = 4.21 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$, $\alpha_c(\text{stetindite-anhyd})$

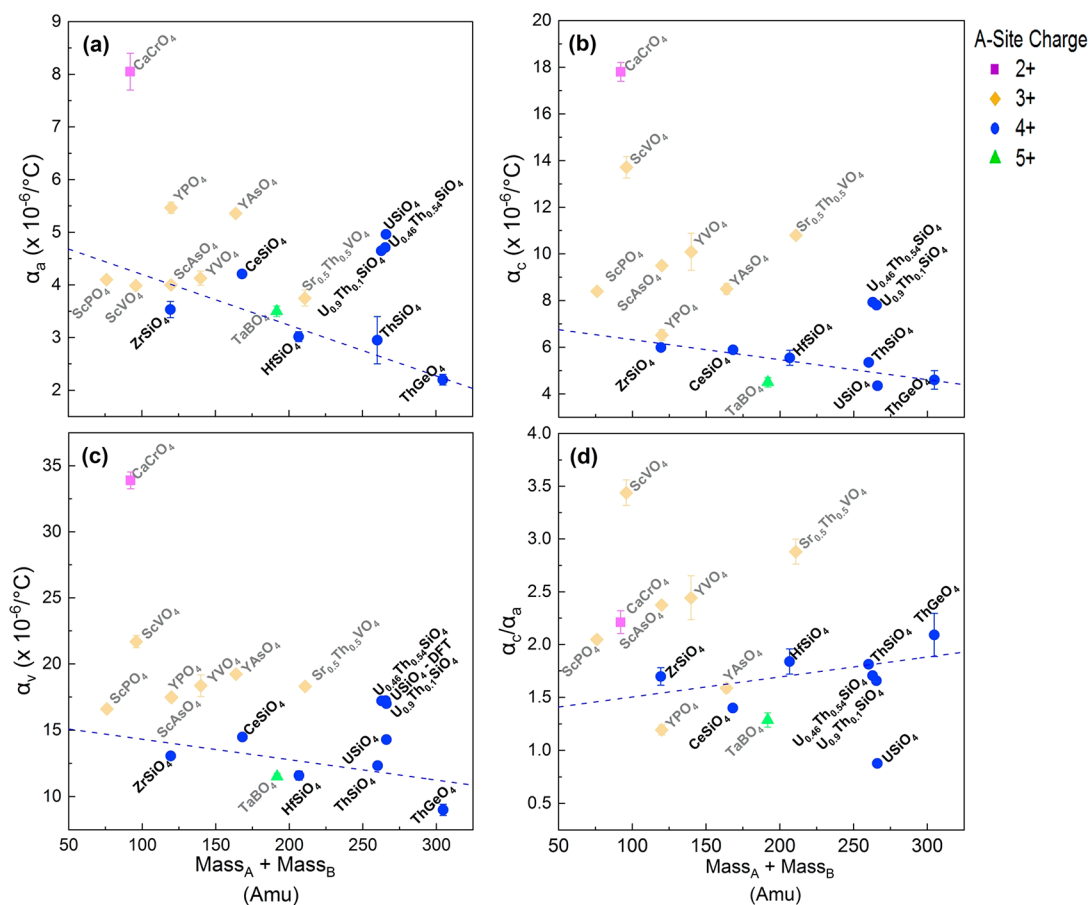


Figure 15. Comparison of the coefficients of thermal expansion of various zircon-type materials as a function of sum of the mass of the A- and B-cations. The dashed blue trend line describes only the $A^{4+}B^{4+}O_4$ zircon structure types. A detailed description of the source of the data points is provided in the Supporting Information (Tables S6–S8).^{89,111–115}

$= 5.89 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$, and $\alpha_V(\text{stetindite-anhyd}) = 14.49 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$.

For dehydroxylated coffinite, only the unit cell parameters during cooling from 815 to 31 $^\circ\text{C}$ were used to fit the CTEs to linear relations ($R^2 > 0.986$).

$$a(\text{\AA}) = 6.9923 + 3.4732 \times 10^{-5}T(^\circ\text{C})$$

$$c(\text{\AA}) = 6.2613 + 2.7283 \times 10^{-5}T(^\circ\text{C})$$

$$V(\text{\AA}^3) = 306.12 + 4.39 \times 10^{-3}T(^\circ\text{C})$$

The derived mean CTEs of dehydroxylated coffinite are $\alpha_a(\text{coffinite-dehyd}) = 4.96 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$, $\alpha_c(\text{coffinite-dehyd}) = 4.35 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$, and $\alpha_V(\text{coffinite-dehyd}) = 14.29 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$. Previously, $\alpha_V(\text{coffinite})$ has been calculated via density functional theory by Fleche¹¹⁶ to be $17.0 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$, disagreeing with our experimental value by 19%. Coffinite exhibited anisotropic expansion, with the a -axis expanding at a rate 1.14 times faster than that of the c -axis. However, the inverse anisotropic expansion was found in stetindite, thorite, hafnon, zircon, and both compositions of uranothorite investigated in this study, with all the materials exhibiting a faster expanding rate along the c -axis (Table 2).^{89,111–115} The anisotropic behavior can be explained from the perspective of arrangement of TO_4 tetrahedra and MO_8 dodecahedra, which can be also depicted as two intersected disphenoidal MO_4 forms: edge-sharing MO_4 alternating with TO_4 along the c -axis, and MO_2 corner-sharing with another MO_4 tetrahedra forming a zigzagging chain along

the a -axis (Figure 1).^{13,55,90} Thus, the zircon structure is more flexible along the a -axis due to the higher freedom of corner-sharing MO_2 tetrahedra and can relax the structure during expansion, which results in a smaller change along the a -axis compared to the c -axis, along which the TO_4 is more incompressible.^{90,117} Consequently, because of the higher repulsion experienced due to the edge-sharing over corner-sharing, the c -axis expands at a faster rate than that of the a -axis.

However, coffinite exhibits inverse anisotropic expansions (Figures 14 and 15, Table S6), when compared to other zircon-type orthosilicate phases. One possible cause for the inverse anisotropic expansion with a greater change of α_a is the unique bonding feature of U^{4+} in the eight-coordination environment, which allows for more orbital overlap between $\text{U } 5f$ and $\text{O } 2p$ orbitals to form hybridization,^{90,118–121} thereby contributing to partial covalent characters,^{90,121} particularly along the a - b planes.⁹⁰ A covalent bond is easier to be compressed or stretched than an ionic bond, thus having a larger variance in bond length of $\langle \text{U}-\text{O} \rangle$ and size of UO_4 tetrahedra during thermal expansion. Such expansion in addition to the unit cell expansion leads to a larger change in α_a than α_c . This explanation is also applicable to uranothorite, though its chemistry is more complicated because of the internal polyhedral distortion due to the mixing of U and Th .⁹⁰ After all, all other potential reasons (vacancies, local ordering, or oxidation of U^{4+} to U^{6+}) can only lead to the decrease in the expected α_a or affect only the uranothorite solid solutions.

Many thermodynamic variables of isostructural inorganic materials are able to be studied through the existence of different empirically derived relationships.^{122–131} These empirically derived relationships link the specific thermodynamic variables to the varying components of the isostructural materials and allow the study of the periodicity of said variable. Subbarao et al.¹¹⁴ found one such way to study CTEs of zircon-type phases was by plotting the CTEs for several zircon structural materials versus the sum of the atomic weights of the A-site and B-site cations. We employed such a methodology (Figure 15)^{89,111–115} to explore the uniqueness of coffinite. Subbarao et al.¹¹⁴ reported that CTEs of $M^{4+}T^{4+}O_4$ zircon-type phases decrease with increasing the overall mass of the A- and B-site cations. When Figure 15 is viewed, it can be seen that coffinite has an α_a value that severely deviates from the trend in Figure 15a,^{89,111–115} but α_c and α_v comply with the trend in Figure 15b,c,^{89,111–115} respectively. As a result, the anisotropic behavior of coffinite also shows a large deviation from other zircon structure-type compositions (Figure 15d).^{89,111–115} Uranothorite solid solution deviates from all of these trends, as both compositions consistently have a higher CTE than would be expected for the corresponding A + B site mass.

5. CONCLUSIONS

The thermal behaviors of stetindite and coffinite were investigated by *in situ* high-temperature synchrotron powder XRD, *in situ* high-temperature Raman spectroscopy, and *ex situ* high-temperature FTIR spectroscopy (on calcined samples) up to 900 °C. Stetindite was found to maintain its $I4_1/amd$ symmetry across the entire temperature gradient investigated. Coffinite, however, thermally decomposed to a mixture of UO_2 and SiO_2 at 600 °C. We also identified hydrous stetindite and hydroxylated coffinite, both of which showed nonlinear expansions along the *a*-axis with increasing temperature. The removal of molecular water from the [001] channels in the zircon structure type explained the discontinuous thermal expansion of hydrous stetindite. A combination of dehydration and dehydroxylation was proposed for synthetic coffinite, which exhibited a similar, yet less dramatic, thermal expansion. Additionally, uranothorite had a similar high-temperature behavior to that of coffinite, with a notable difference in thermal stability, controlled by the interplay of its negative enthalpy of mixing and volume of mixing. Lastly, the CTEs of $CeSiO_4$, $USiO_4$, $(U_{0.9}Th_{0.1})SiO_4$, and $(U_{0.46}Th_{0.54})SiO_4$ were determined for the first time. Interestingly, $USiO_4$ showed a different anisotropic expansion than other zircon structure types in that the *a*-axis expanded at a faster rate than the *c*-axis. Such an inverse in anisotropic expansion may be due to the directionality of partial covalent characteristics along the *a*-*b* planes as a result of U 5f–O 2p hybridization in the UO_8 dodecahedra.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c02757>.

PXRD, CTE analyses, FTIR, *in situ* high-T Raman, high-T ESEM, and additional information about hydrated and hydroxylated phases (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Xiaofeng Guo – Department of Chemistry, Alexandra Navrotsky Institute for Experimental Thermodynamics, and Materials Science and Engineering Program, Washington State University, Pullman 99164, Washington, United States; orcid.org/0000-0003-3129-493X; Email: x.guo@wsu.edu

Authors

Andrew C. Strzelecki – Department of Chemistry, Alexandra Navrotsky Institute for Experimental Thermodynamics, and Materials Science and Engineering Program, Washington State University, Pullman 99164, Washington, United States

Thomas Barral – Department of Chemistry and Alexandra Navrotsky Institute for Experimental Thermodynamics, Washington State University, Pullman 99164, Washington, United States; ICSM, Univ Montpellier, CNRS, CEA, ENSCM, Site de Marcoule 30207, Bagnols sur Cèze, France

Paul Estevenon – ICSM, Univ Montpellier, CNRS, CEA, ENSCM, Site de Marcoule 30207, Bagnols sur Cèze, France; CEA, DES, ISEC, DMRC, Univ Montpellier, Site de Marcoule 30207, France

Adel Mesbah – ICSM, Univ Montpellier, CNRS, CEA, ENSCM, Site de Marcoule 30207, Bagnols sur Cèze, France; orcid.org/0000-0002-6905-2402

Vitaliy Goncharov – Department of Chemistry, Alexandra Navrotsky Institute for Experimental Thermodynamics, and Materials Science and Engineering Program, Washington State University, Pullman 99164, Washington, United States; Earth and Environmental Sciences Division, Los Alamos National Laboratory, Los Alamos 87545, New Mexico, United States

Jason Baker – Earth and Environmental Sciences Division, Los Alamos National Laboratory, Los Alamos 87545, New Mexico, United States

Jianming Bai – National Synchrotron Light Source II, Brookhaven National Laboratory, Upton 11973, New York, United States; orcid.org/0000-0002-0575-2987

Nicolas Clavier – ICSM, Univ Montpellier, CNRS, CEA, ENSCM, Site de Marcoule 30207, Bagnols sur Cèze, France

Stephanie Szenknect – ICSM, Univ Montpellier, CNRS, CEA, ENSCM, Site de Marcoule 30207, Bagnols sur Cèze, France; orcid.org/0000-0003-3691-3621

Artaches Migdisov – Earth and Environmental Sciences Division, Los Alamos National Laboratory, Los Alamos 87545, New Mexico, United States

Hongwu Xu – Earth and Environmental Sciences Division, Los Alamos National Laboratory, Los Alamos 87545, New Mexico, United States

Rodney C. Ewing – Department of Geological Sciences, Stanford University, Stanford 94305, California, United States

Nicolas Dacheux – ICSM, Univ Montpellier, CNRS, CEA, ENSCM, Site de Marcoule 30207, Bagnols sur Cèze, France; orcid.org/0000-0003-1636-1313

Complete contact information is available at:

<https://pubs.acs.org/10.1021/acs.inorgchem.0c02757>

Author Contributions

◆(A.C.S. and T.B.) These two cofirst authors have equal contribution.

Notes

The authors declare no competing financial interest.

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