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Blackburn, L.R. orcid.org/0000-0002-5889-2035, Sun, S., Gardner, L.J. orcid.org/0000-0003-3126-2583 et al. (4 more authors) (2021) Synthesis, structure and characterisation of the thorium zirconolite CaZr1-xThxTi2O7 system. Journal of the American Ceramic Society, 104 (7). pp. 2937-2951. ISSN 0002-7820

https://doi.org/10.1111/jace.17627

This is the peer reviewed version of the following article: Blackburn, L.R., Sun, S.-K., Gardner, L.J., Maddrell, E.R., Stennett, M.C., Corkhill, C.L. and Hyatt, N.C. (2021), Synthesis, Structure and Characterisation of the Thorium Zirconolite CaZr1-xThxTi2O7 System. Journal of the American Ceramic Society, which has been published in final form at https://doi.org/10.1111/jace.17627. This article may be used for non-commercial purposes in accordance with Wiley Terms and Conditions for Use of Self-Archived Versions.

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Synthesis, Structure and Characterisation of the Thorium Zirconolite $CaZr_{1-x}Th_xTi_2O_7$ System

Lewis R. Blackburn[a], Shi-Kuan Sun[a], Laura J. Gardner[a], Ewan R. Maddrell[b], Martin C. Stennett[a], Claire L. Corkhill[a], Neil C. Hyatt[a]

[a]*Immobilisation Science Laboratory, University of Sheffield, Department of Materials Science and Engineering, Sir Robert Hadfield Building, Mappin Street, S13JD, UK*

[b]*National Nuclear Laboratory, Workington, Cumbria, CA14 3YQ, UK*

Corresponding authors – n.c.hyatt@sheffield.ac.uk (N. C. Hyatt); shikuan.sun@sheffield.ac.uk (S.-K. Sun).

Abstract

A series of zirconolite ceramics with composition $CaZr_{1-x}Th_xTi_2O_7$ ($\Delta x = 0.10$) were reactively sintered at 1350 ˚C for 20 h, in air ($0 \leq x \leq 0.60$) and 5% H_2/N_2 ($0 \leq x \leq 0.40$). A sample with composition corresponding to $x = 0.20$ was also produced by hot isostatic pressing (HIP) at 1300 ˚C and 100 MPa for 4 h. Th^{4+} immobilisation was most readily achieved under oxidising conditions, with Th^{4+} preferentially incorporated within a pyrochlore-structured phase in the range $0.10 \leq x \leq 0.50$, yet formation of the zirconolite-4M polytype was not observed. We report the novel synthesis of single phase pyrochlore with nominal composition $CaZr_{0.40}Th_{0.60}Ti_2O_7$ when targeting $x = 0.60$. Th^{4+} incorporation under reducing conditions produced a secondary Th-bearing perovskite, comprising 24.2 ± 0.6 wt. % of the phase assemblage when targeting $x = 0.40$, alongside 8.8 ± 0.3 wt. % undigested ThO_2. Under reducing conditions, powder XRD data were consistent with zirconolite adopting the 3T polytype structure. The sample produced by HIP presented a non-equilibrium phase assemblage, yielding a major phase of zirconolite-2M alongside accessory Th^{4+} bearing phases $ThTi_2O_6$, ThO_2 and perovskite. These data highlight the efficacy of Th^{4+} as a Pu^{4+} surrogate, with implications for the formation of Zr-stabilised Th-pyrochlore phases as matrices for waste with elevated Th^{4+} content.

Keywords:

Zirconolite wasteform; Immobilisation; Plutonium; Thorium surrogate; Pyrochlore.

1 Introduction

The United Kingdom is in the process of consolidating all civil Pu inventories at the Sellafield site, in an effort to satisfy security and proliferation requirements, presenting a significant decommissioning challenge in terms of materials degradation [1]. The Nuclear Decommissioning Authority (NDA), is liable for the management and disposition of all nuclear wastes under UK safeguards, and has commissioned a credible options analysis to identify technically mature reuse and disposition options, one of which is a strategy of immobilisation and disposal [2]. Zirconolite (nominally $CaZrTi_2O_7$) is the proposed candidate ceramic wasteform for the immobilisation of Pu oxides [3]–[7]. The zirconolite-2M parent structure is derived from the anion deficient fluorite unit cell, and is closely related to the $A_2B_2O_7$ pyrochlore structure ($Fd\bar{3}m$) by a compression along the (111) direction. Furthermore, a range of polytypical zirconolite structures (*e.g.* 4M, 3O, 3T) have been reported, the formation of which are controlled by cation substitution and processing conditions [8]–[10]. The zirconolite-2M unit cell is considered the archetype, with observed stability over the compositional range $CaZr_xTi_{3-x}Ti_2O_7$ ($0.8 < x < 1.3$), with a lamellar unit cell crystallising in the space group $C2/c$ [11]. The nomenclature ‘2M’ is reference to the two layer repeating modules that comprise the monoclinic unit cell. In the idealised 2M structure, Ca^{2+} and Zr^{4+} are arranged in CaO_8 and ZrO_7 polyhedra layered between sheets of Ti-O polyhedra. Ti^{4+} sites are arranged in modular symmetry alike to the hexagonal tungsten bronze (HTB) motif. Statistically, one of the octahedra in the HTB layer is collapsed to unusual trigonal bipyramidal symmetry (*i.e.* TiO_5) to satisfy bonding criteria [12]. In the zirconolite-2M structure, adjacent cation layers are layered in a 1:1 along [001], with HTB layers at $z = 0.25$ and $z = 0.75$ positions related by a 180˚ rotation, offset by a stacking vector of approximately 60˚ in the [130] direction; successive HTB layers at $z = 0.75$ and $z = 1.25$ positions are subsequently offset in the [1$\bar{3}$0] direction [8].

Successive zirconolite polytypes (the crystal structures of zirconolite-2M, zirconolite-3T and pyrochlore are displayed in **Fig. 1**) are stabilised through progressive substitution within Ca^{2+}, Zr^{4+} and Ti^{4+} sites, and characterised according to variation in stacking sequence of adjacent Ca/Zr and HTB planes. The accommodation of dopants within zirconolite has been shown to produce a phase transition to the pyrochlore structure, generally *via* the zirconolite-4M structure with increasing dopant concentration, either by extensive M^{4+} substitution within the Zr^{4+} site (*e.g.* U, Ce, Pu) [13]–[15], or isovalent accommodation of M^{3+} within the Ca^{2+} and Zr^{4+} site (*e.g.* Y, Gd, Nd) [16]–[18]. The zirconolite-4M polytype is thus considered an admixture of zirconolite-2M and pyrochlore modules, with a fourlayer repeating sequence and subsequent doubling of the unit cell along c^* due to cation ordering [8]. Further doping of tri- and tetravalent species within the Ca^{2+} and Zr^{4+} sites in zirconolite produces a transformation to the pyrochlore structure (ideally $A_2B_2O_7$ – space group $Fd\bar{3}m$, where A^{3+} and B^{4+} are typically rare earth and transition metal elements, respectively). The pyrochlore supergroup of minerals encompasses a wide range of compositions (> 500 reported) and is considered a suitable matrix for the immobilisation of actinides. The pyrochlore structure is related to that of the ideal fluorite structure, with one eighth of the oxygen anions removed, resulting in two distinct cation sites [19]. Extensive doping within the zirconolite structure produced a phase transformation to the pyrochlore structure in the work of Vance *et al*. for which the $CaZr_{1-x}U_xTi_2O_7$ system stabilised the pyrochlore structure at $x > 0.60$ [13]. Begg *et al*. reported the same solid solution limit for pyrochlore formation in the $CaZr_{1-x}Pu_xTi_2O_7$ system [15]. Zirconolite-3T is the trigonal polytype of zirconolite, however detailed structural characterisation of the 3T phase is rarely reported in the literature. The 3T polytype typically occurs in natural specimens with extensive substitution of REE^{3+}, Fe, Hf, Th, Nb, such as those reported by Zubkova *et al* [20]. Nevertheless, there are solid solution regimes that have been reported to form the zirconolite-3T polytype, such as the $Ca_{1-x}Pu_xZrTi_{2-2x}Fe_{2x}O_7$ system, for which Gilbert *et al*. reported the stabilisation of the 3T polytype between $0.30 \leq x \leq 0.40$ [21]. Despite this, the zirconolite-3T phase was not produced at the same compositional level in the $Ca_{1-x}Ce_xZrTi_{2-2x}Cr_{2x}O_7$ suggesting that the formation of the 3T polytype structure is sensitive to both the different redox and/or site occupancy behavior between Ce/Pu, and/or ionic radii of Cr/Fe as charge compensators [22]. The synthesis and structural characterization of synthetic zirconolite-3T was reported by Grey *et al*., with single crystal X-ray diffraction data produced for $Ca_{0.80}Th_{0.15}Zr_{1.30}Ti_{1.35}Al_{0.40}O_7$ indexed to the space group $P3_121$, with excess Zr accommodated on the Ca and Ti sites [10]. In order to predict the long-term stability and overall performance of zirconolite-rich wasteforms, it is essential to fully understand the structure of the target polytype, and characterise any polytypical transitions that may occur due to cation substitution. It is currently not yet determined whether any manifestations of the zirconolite structure (*i.e.* 2M, 4M, 3T) exhibit superior properties that may contribute to improved radiation tolerance and aqueous durability.

The aim of the current work was to characterise the structural transitions accompanying the substitution of Th^{4+} (as a surrogate for Pu^{4+}) within the Zr^{4+} site in zirconolite, under oxidising and reducing conditions, as this system has not been systematically investigated. We have recently demonstrated that the phase assemblage of $CaZr_{1-x}Ce_xTi_2O_7$ was controlled by the processing atmosphere during the synthesis process, with Ce acting as a structural simulant for Pu [23]. It was revealed that synthesis under oxidising conditions produced a phase transformation to the zirconolte-4M polytype with progressive Ce accommodation (in the compositional interval $0.10 \leq x \leq 0.20$), however this was not observed under reducing conditions, for which Ce^{3+} was preferentially accommodated in an accessory perovskite phase. We acknowledge that a truly representative study of the zirconolite system, producing reliable data that may be transferred to Pu active trails, must utilise several surrogate species in conjunction. Although Ce is commonly deployed as a Pu surrogate, the tendency of Ce to partially reduce to Ce^{3+} under oxidative sintering environments is a behaviour not representative of Pu. Hence, as Th remains stable in the Th^{4+} configuration under oxidising conditions, we consider this to be an effective choice of surrogate. Understanding the effects of compositional modification and subsequent phase transitions that may occur is essential to underpin the safe and effective immobilisation of plutonium. Hence, the data presented here allow a direct comparison of ThO_2 and CeO_2 surrogates in the zirconolite system, $CaZr_{1-x}M_xTi_2O_7$ (M = Ce or Th).

2 Experimental Methodology

2.1 Materials Synthesis

All compositions targeting $CaZr_{1-x}Th_xTi_2O_7$ ($0 \leq x \leq 0.60$, $\Delta x = 0.10$) were produced by a mixed oxide route between $CaTiO_3$, ZrO_2, TiO_2 (Sigma Aldrich, 99.9% trace metals basis) and ThO_2 (ABSCO Ltd.). Samples were batched according to desired composition and homogenised by planetary milling at 400 rpm for 20 min, with isopropanol added as a carrier fluid and ZrO_2 milling media. Slurries were dried at 80 ˚C overnight. Approximately 0.5 g of each composition was pressed into the walls of a 10 mm stainless steel die and compressed under 3 t of uniaxial pressure. Pellets were then sintered at 1350 ˚C for 20 h in air (muffle furnace) or flowing 5% H_2/N_2 (BOC, Al_2O_3 tube furnace), representing oxidising and reducing conditions, respectively. A sample with nominal composition $CaZr_{0.80}Th_{0.20}Ti_{2.00}O_7$ was also produced by Hot Isostatic Pressing (HIP). Milled precursor powder from the x = 0.20 batch was calcined in air at 600 ˚C in air for 12 h to remove adsorbed water and volatiles prior to HIP. The powder was then pressed into the walls of a stainless steel HIP canister (Grade 310 stainless steel) under uniaxial pressure. The canister was heated at 300 ˚C under vacuum until a suitable pressure was achieved (~ 7 Pa). The canister was then hermetically sealed, placed into an AIP 630-H HIP unit, and processed at 1300 °C for 4 h at 100 MPa. The HIPing of radioactive materials was made possible through the use of the active furnace isolation chamber (AFIC) plug-in component, unique to the University of Sheffield, protected under patent number WO 2018/009782 A1 [24]. The AFIC is capable of processing a single HIP canister loaded with U/Th-containing wasteforms whilst providing a multi-layered protection approach, preventing dispersion of radioactive material to the HIP pressure vessel and surrounding workspace in the event of a canister breach.

2.2 Materials Characterisation

Post synthesis, a representative portion of each sample was finely ground in an agate pestle and mortar with isopropanol prior to powder X-ray diffraction (XRD) analysis. For the HIPed sample, this involved the use of a Buehler IsoMet 1000 Low Speed Saw; the canister was sectioned and a representative portion was removed. XRD was performed using a Bruker D2 Phaser (Cu Kα, λ = 1.5418 Å, Ni filter), fitted with a Lynxeye position sensitive detector. Data were acquired in the range $5^\circ \leq 2\theta \leq 80^\circ$ with a step size of 0.02° s^{-1}. XRD data were refined by the Rietveld method using the GSAS package with EXPGUI interface [25]. Prior to analysis by scanning electron microscopy (SEM), samples were sectioned and a representative section of each composition was mounted in cold setting resin, with a curing time of 24 h. Samples were polished to a 1 μm optical finish using incremental grades of SiC grinding paper and diamond suspension. Surfaces were also coated with carbon and conductive Ag-based paint to reduce surface charging effects. SEM analysis was performed using a Hitachi TM3030, operating at 15 kV accelerating voltage, at a working distance of 8 mm. This was also fitted with a Bruker Quantax Energy Dispersive X-ray Spectrometer (EDS) for compositional analysis. Semi-quantitative cation compositions of observed zirconolite phases were determined based on 10 independent EDS data points, normalised to seven oxygen atoms.

3 Results

3.1 Synthesis Under Oxidizing Conditions

3.1.1 Phase Assemblage

Powder XRD data for $CaZr_{1-x}Th_xTi_2O_7$ compositions reacted in air are displayed in **Fig. 2**. When targeting x = 0.00, phase pure zirconolite-2M (space group C2/*c*) was observed. Rietveld refinement of the powder diffraction profile for x = 0.00 produced lattice parameters that were in excellent agreement with previously reported unit cell dimensions for undoped $CaZrTi_2O_7$ [26]: ***a*** = 12.44808(11) Å, ***b*** = 7.27366(6) Å, ***c*** = 11.37383(1) Å, ***β*** = 100.5782(7) ° and ***V*** = 1012.321(16) $Å^3$. It should be noted that the reported precision of the lattice dimensions presented here represent the uncertainty associated with parameter fitting in the Rietveld refinement analysis. The diffraction data for the undoped x = 0.00 composition is indexed to the zirconolite-2M structure in **Supplementary Fig. S1**. For x = 0.10, a mixture of zirconolite-2M and a pyrochlore-structured phase was confirmed by XRD analysis. The unit cell parameters for zirconolite-2M and pyrochlore phases are summarised in **Table 1**. The existence of the pyrochlore phase (space group $Fd\bar{3}m$) was rationalised by the appearance of diagnostic supercell reflections at 2θ = 15.2°, 29.2°, 35.4°, 38.7°, and 46.5°, corresponding the (111), (113), (004), (133) and (115) reflections, respectively. As the nominal Th^{4+} concentration was increased to x = 0.10 and x = 0.20, the relative intensity of these reflections increased relative to the diagnostic 2M reflections, suggesting a greater phase fraction. Close inspection of the powder diffraction profile also revealed the presence of a perovskite ($CaTiO_3$) impurity, identified by a weak reflection at 2θ = 33.1°, although only comprising 1.1 ± 0.5 and 1.3 ± 0.5 wt. % of the overall phase assemblage for x = 0.10 and 0.20, respectively, however the lattice dimensions for this impurity were not included in the refinement output. Rietveld refinement of the powder XRD data confirmed that the relative fraction of the pyrochlore phase increased linearly as a function of Th^{4+} incorporation. In the compositional interval $0.10 \leq x \leq 0.50$, the phase assemblage evolved such that pyrochlore became the dominant phase at $x \geq 0.40$. For x = 0.60, powder XRD were consistent with phase assemblage being comprised of phase pure pyrochlore with nominal composition $CaZr_{0.4}Th_{0.6}Ti_2O_7$. We are not aware of this phase being reported elsewhere. This will be discussed later in **Section 3.1.3**. We note that this would correspond approximately to 33.5 wt. % Pu for the corresponding $CaZr_{0.4}Pu_{0.6}Ti_2O_7$ composition.

3.1.2 Microstructure Analysis

Fig. 3 shows the microstructure for x = 0.10 and x = 0.20 compositions. Two phases were clearly distinguished by backscattered electron contrast, consistent with zirconolite-2M and pyrochlore in agreement with powder XRD data. Although Th^{4+} was accommodated within both phases in the microstructure, EDS analysis demonstrated that Th^{4+} was preferentially distributed within the bright contrast pyrochlore phase. The zirconolite-2M phase present in the x = 0.10 microstructure had an average composition of $Ca_{0.98(6)}Zr_{0.89(8)}Th_{0.05(2)}Ti_{2.07(8)}O_7$, with the excess Th^{4+} presumably concentrated in the pyrochlore grains, which were too small to accurately measure. The average compositions of the zirconolite-2M and pyrochlore phases produced for $0.10 \leq x \leq 0.60$, calculated from EDS analysis, are listed in Table 2. The occupation of each phase in the microstructure was consistent with the quantitative phase analysis (Table 1); as the level of Th^{4+} substitution was elevated in the interval $0.10 \leq x \leq 0.50$, the pyrochlore phase comprised a greater proportion of the visible microstructure. A representative section of the microstructure corresponding to the composition x = 0.40 is displayed in Fig. 4, alongside the corresponding elemental distribution. EDS data clearly demonstrated that the zirconolite-2M phase was deficient in Th^{4+} and rich in Zr^{4+} with respect to the pyrochlore phase. It was also evident that grains of zirconolite-2M appeared lath-like in morphology. As the Th^{4+} concentration reached x = 0.60, the microstructure produced for the pyrochlore phase was homogeneous in BSE contrast, consistent with the formation of single phase $CaZr_{0.4}Th_{0.6}Ti_2O_7$ as inferred by powder XRD analysis (Fig. 2). A representative section of the microstructure is displayed in Fig. 5. SEM analysis also evidenced grains of a Th-Ti-O rich phase, occasionally distributed across the surface, consistent with $ThTi_2O_6$ from EDS analysis (however, it should be noted that this phase was not detected by XRD). Despite this trace impurity, it was considered that the pyrochlore formed as a single phase at x = 0.60, as no reflections consistent with $ThTi_2O_6$ could be reconciled by XRD analysis.

3.1.3 Initial Refinement of $CaZr_{0.40}Th_{0.60}Ti_2O_7$

All prominent reflections in the XRD pattern of $CaZr_{0.4}Th_{0.6}Ti_2O_7$ could be indexed assuming the structure to be isostructural with that of $CaUTi_2O_7$ (space group: $Fd\bar{3}m$; ICSD 40264, see Fig. 1). With the exception of negligible $ThTi_2O_6$ (as indicated in Fig. 5) no secondary phases were identified by SEM analysis, and quantitative EDS analyses confirmed the average stoichiometry to be $Ca_{1.00(2)}Zr_{0.33(2)}Th_{0.54(1)}Ti_{2.13(2)}O_7$, demonstrating an apparent excess of Ti. Structure refinement initially assumed the ideal stoichiometry of $CaZr_{0.4}Th_{0.6}Ti_2O_7$ adopting the space group $Fd\bar{3}m$, consistent with the published crystal structure of $CaUTi_2O_7$ [27]. Refinements quickly converged yet produced negative isotropic thermal parameters for the Ti site; the fits were, however, improved after setting 0.1 f.u. of Zr occupying the Ti site. In this instance, the refinement quickly converged to a satisfactory fit (displayed in **Fig. 6**) with R_{wp} = 9.72% and χ^2 = 1.728 for 22 variables, including 6 structural parameters. As shown in **Table 3**, the isotropic thermal parameter (U_{iso}) of the Ti_2/Zr_2 cation was significantly larger than that of the Ca cation, inferring the presence of Ti vacancies with charge compensation provided by oxygen vacancies, or Ti reduction to Ti^{3+}. Complimentary structural refinement studies of the specimens studied here are underway.

Pyrochlore compounds with significant U/Ce incorporation, corresponding to compositions $Ca_{1.46}U^{4+}_{0.23}U^{6+}_{0.46}Ti_{1.85}O_7$ and $Ca_{0.93}Ce_{1.00}Ti_{2.04}O_7$ have been previously reported [28]. In contrast, here we hypothesise Th-pyrochlore may be stabilised by the occupation of Zr within the Ti site. Considering the ionic radii of Ca (1.12 Å, CN = 8), Th (1.05 Å, CN = 8 and 0.94 Å, CN = 6), Zr (0.84 Å, CN = 8 and 0.72 Å, CN = 6), and Ti (0.74 Å, CN = 8 and 0.605 Å, CN = 6), the substitution of Ca by Th may be preferable, alongside the reduction in coordination number from 8 to 6, which likely drove zirconolite (C2/c) to a higher symmetry space group ($Fd\bar{3}m$) [29].

3.2 Synthesis Under Reducing Conditions

3.2.1 Phase Assemblage

Powder XRD data for $CaZr_{1-x}Th_xTi_2O_7$ compositions reacted under 5% H_2/N_2 are displayed in **Fig. 7**, quantitative phase analysis data for all compositions sintered under 5% H_2/N_2 are summarised in **Table 4**. When targeting x = 0.00, zirconolite-2M was formed as the major phase, occupying 92.4 ± 0.1 wt. % of the total phase assemblage. The diagnostic reflection at $2\theta = 33.1^\circ$ confirmed that perovskite was also formed as a secondary phase, comprising 7.6 ± 0.3 wt. % of the assemblage (**Table 4**). As the nominal Th^{4+} concentration was increased to x = 0.10, the relative yield of perovskite increased to 11.3 ± 0.5 wt. %. Minor reflections at $2\theta = 27.5^\circ$, 45.7° and 54.2° corresponding to reflections in the (111), (022) and (113) plane for ThO_2 were also visible, indicating incomplete digestion of Th^{4+} within the target zirconolite phase. The intensity of perovskite and ThO_2 reflections were observed to increase when targeting x = 0.20, accounting for 15.4 ± 0.5 wt. % and 0.9 ± 0.1 wt. %, respectively. For x ≥ 0.20, the powder diffraction profiles for zirconolite compositions were consistent with the zirconolite-3T polytype, adopting trigonal symmetry in the space group $P3_121$. The lattice parameters for the zirconolite-3T phase (**Table 5**) corresponding to x = 0.20 were derived from Rietveld fitting: ***a*** = 7.2511(2) Å, ***c*** =

16.826(1) Å, **V** = 766.17(3) Å^3. These unit cell dimensions were in general agreement with previously reported values for the zirconolite-3T phase when doped with similar levels of Th^{4+} [10]. However, as can be seen from the data provided in **Table 5**, there did not appear to be a trend between the zirconolite-3T unit cell parameters and the targeted level of substitution (x). The proportion of the perovskite phase increased linearly, which further increased at x = 0.30 and x = 0.40 to 18.9 ± 0.6 and 24.2 ± 0.6 wt. %, respectively. The relative quantity of unincorporated ThO_2 in the microstructure was also further elevated, with an increase from 0.9 ± 0.1 to 8.8 ± 0.3 wt. % in the interval $0.20 \leq x \leq 0.40$. When targeting x = 0.40, the zirconolite-3T phase, whilst still forming the dominant portion of the phase assemblage, accounted for only ~ 67 wt. %. Hence, the imposition of reducing conditions during the sintering of $CaZr_{1-x}Th_xTi_2O_7$ was not favourable compared to sintering in air.

3.2.2 Microstructure Analysis

The microstructure for x = 0.10 and x = 0.20 compositions are displayed in **Fig. 8**, with x = 0.40 presented in **Fig. 9**. In all instances, a homogenous mid-grey matrix was observed representative of zirconolite-2M or 3T, with two secondary phases evidenced by variation in backscattered electron contrast. These were consistent with perovskite (dark grey) and ThO_2 (bright grey). Close inspection of EDS data confirmed that Th^{4+} was partitioned between all three phases, contrary to experimental design. The average composition of the zirconolite-2M and zirconolite-3T phases are summarised in **Table 6**. The zirconolite phase(s) were consistently deficient in Th^{4+}, relative to the target composition, for all values of x, coinciding with unincorporated ThO_2 in the microstructure. In agreement with powder XRD data, the accompanying quantity of perovskite and ThO_2 in the microstructure was elevated for x = 0.30 and x = 0.40 samples.

The elemental distribution for the sample with composition x = 0.40 is displayed in **Fig. 9**. EDS analysis of perovskite grains also evidenced incorporation of Th^{4+} (see **Supplementary Fig. S2**). The formation of perovskite in this system is undesirable, and would be considered detrimental to Pu wasteform performance, due to inferior chemical durability with respect to the target zirconolite phase [30]. The accommodation of Th^{4+} within the Ca^{2+} site in perovskite would also demonstrate an apparent excess of positive charge, typically necessitating the formation of Ti^{4+} vacancies (or the co-accommodation of a lower valence charge balancing species, such as in the case of Begg *et al.* where Ce was used as a Pu surrogate [31]). However, in this instance, the imposition of reducing conditions would be considered sufficient to drive the reduction of Ti to Ti^{3+}, providing charge balance by 5 – 10% Ti^{3+}. When targeting x = 0.40, the average composition of the accompanying perovskite phase was calculated from EDS data to be $Ca_{0.77(2)}Th_{0.13(1)}Zr_{0.09(2)}Ti_{1.01(3)}O_3$, normalised to three oxygen atoms.

3.3 Hot Isostatic Pressing of $CaZr_{0.80}Th_{0.20}Ti_{2.00}O_7$

A specimen with nominal composition $CaZr_{0.80}Th_{0.20}Ti_{2.00}O_7$ (*i.e.* x = 0.20) was also produced by HIP, with the view to determine whether the obtained phase assemblage would be greatly disrupted by the in-canister containment necessary for HIP, with respect to conventional sintering processes. Processing *via* HIP appeared to negatively impact the phase assemblage with respect to both air and 5% H_2/N_2 sintered samples, largely due to the increased occupation of perovskite within the phase assemblage (increasing from ~ 1 wt. % to ~ 14 wt. % in the case of the air-sintered composition), and through the production of a non-equilibrium microstructure. Fig. 10 displays the powder diffraction data obtained for $CaZr_{0.80}Th_{0.20}Ti_{2.00}O_7$. A reasonable fit was achieved, with the diffraction profile refined to a phase assemblage of zirconolite-2M (74.0 ± 0.3 wt. %), ZrO_2 (3.1 ± 0.4 wt. %), ThO_2 (3.6 ± 0.1 wt. %), $ThTi_2O_6$ (5.3 ± 0.3 wt. %) and $CaTiO_3$ (14.1 ± 0.6 wt. %). The existence of $ThTi_2O_6$ was confirmed by reflections at $2\theta = 14.3^\circ$, 18.4° and 25.4° corresponding to reflections in the (001), $(20\bar{1})$ and (110) planes in the $ThTi_2O_6$ strucure, respectively.

A representative section of the microstructure for the $CaZr_{0.80}Th_{0.20}Ti_{2.00}O_7$ sample processed by HIP is displayed in Fig. 11. A mid-grey matrix of zirconolite-2M was observed, with several secondary phases identified by variation in backscattered electron contrast. Clusters of perovskite were distributed throughout, with a contrast darker than that of the bulk matrix. Reliable EDS analysis of individual perovskite grains was not possible due to small grain size, yet it is assumed that, similar to the compositions sintered under 5% H_2/N_2, Th^{4+} was also located within this phase, presumably accomodated within the Ca^{2+} site. The incorporation of Th^{4+} within the more abundant perovskite phase (~14 wt. %) would be considered highly undesirable, as the lower durability of perovskite with respect to the target zirconolite phase may negatively impact the overal performance of the wasteform, resulting in accelerated release of Th^{4+} (and Pu, by analogy) from the ceramic phase into solution in the disposal environment [32]. Undigested ThO_2 was observed in the microstructure, clearly visible in Fig. 11 as relics with bright contrast, with a clear reaction rim surrounding the ThO_2 cores. The composition of these reaction rims was consistent with both XRD and EDS analyses as $ThTi_2O_6$ (*i.e.* thorutite), evidencing that the reactions did not reach equilibrium under the imposed conditions (1300 °C dwell temperature maintained for 4 h). This is clear when comparing Fig. 9 and Fig. 11, the former of which does not contain these features, despite ThO_2 being prevelant in the microstructure. In this instance, the difficulty in attaining an equilibrated microstructure through the use of HIP was considered to be the result of variations between HIP (1300 °C, 4 h) and CPS (1350 °C, 20 h) processing parameters, the latter of which provided more suitable equilibrium conditions due to extended dwell time at high temperature. Although the partitioning of Th^{4+} within an ancillary phase was generally considered undesirable, $ThTi_2O_6$ is known to be highly durable in aggressive leaching environments, with Zhang *et al.* reporting normalised release rates of Th $< 10^{-5}$ g m^{-2} d^{-1} over a cumulative time of 60 d, in pH = 2 solution [33]. It should be noted that whilst this microstructure is not representative of a wasteform that would be considered suitable for the disposition of Pu, its inclusion in the present work may serve as a useful comparison for future Ce/U/Pu compositions processed in a similar manner.

4 Discussion

4.1 Influence of Processing Environment on Phase Evolution of $CaZr_{1-x}Th_xTi_2O_7$

There exists a narrow scope of literature concerned with the incorporation of Th^{4+} within the zirconolite structure, making any reasonable comparison with published solid solution data limited. Kesson *et al.* discussed the incorporation of Th^{4+} within the Zr^{4+} site, with compositions corresponding to $CaZr_{0.90}Th_{0.10}Ti_{2.00}O_7$ and $CaZr_{0.80}Th_{0.20}Ti_{2.00}O_7$ fabricated by hot pressing in a graphite die at 1400 ˚C [34]. When targeting x = 0.10, a single phase zirconolite was reported, in contrast to the data presented here for the air-sintered solid solution, with a two phase mixture of zirconolite and a "*fine-grained face centered cubic phase*" produced for x = 0.20 (further Th^{4+} doping was not attempted). However, it is accepted that the discrepancies in solid solution limit on the Zr^{4+} site, with reference to the current work, may be rationalised by the use of a graphite die, which would be expected to yield conditions similar to sintering under a reducing H_2/N_2 mixture, rather than air. By making comparison to the data presented in this work, it may be reasonable to assume that the cubic phase reported by Kesson *et al.* was ThO_2, however as no unit cell parameters were reported, this cannot be confirmed. We are not aware of any other studies that have accommodated Th^{4+} within the Zr^{4+} site of zirconolite.

Sintering the $CaZr_{1-x}Th_xTi_2O_7$ solid solution in air produced a pseudo-binary system comprised of $Ca(Zr,Th)Ti_2O_7$ zirconolite and a pyrochlore-structured phase, requiring mixed Th/Zr occupancy, with the pyrochlore phase favoured with increasing Th-content, without the formation of the expected zirconolite-4M intermediate phase. Replacement of Zr^{4+} by 0.60 f.u. of Th^{4+} stabilised a composition retaining the pyrochlore structure, however targeting a higher Th^{4+} concentration would be expected to destabilise the pyrochlore phase in favour of ancillary phases. This was informed by the work of Vance *et al.*, who reported zero yield of the '$CaThTi_2O_7$' phase when sintering in air between 1300 – 1500 °C, rather a mixture of Th-brannerite and perovskite [35]. Furthermore, McCauley *et al.* attempted to form $CaThTi_2O_7$ by reacting at 1700 ˚C for 8 h in a sealed Pt-Rh tube, yet this failed to yield the pyrochlore structure [36]. The formation of $A_2B_2O_7$ pyrochlores is generally limited by the relative size difference of constituent A and B-site cations (8 and 6-fold coordinated, respectively), with the pyrochlore phase stabilised in the range $1.46 < r_A/r_B < 1.78$; compositions for which $r_A/r_B < 1.46$ crystallise with the defect fluorite unit cell, whilst $r_A/r_B > 1.78$ produces a layered perovskite-type structure with monoclinic symmetry [37]. Considering the relative ionic radii of Ca^{2+}, Th^{4+} and Ti^{4+} in the relevant coordination environment (see **Supplementary Table 1**), the average A-site radius for $CaThTi_2O_7$ is calculated to be 1.085, resulting in $r_A/r_B = 1.79$, hence slightly too large to satisfy the pyrochlore formation criterion. It is logical to conclude the inclusion of Zr^{4+} within the Ca/Th-site reduced the average ionic radius of the A-site, allowing the stabilisation of the pyrochlore phase with 0.4 f.u. Zr^{4+} and 0.60 f.u. Th^{4+}. This is in good agreement with Vance *et al.* when considering the size limitations for $Ca(A)Ti_2O_7$ pyrochlores, who concluded that 0.7 f.u. Th^{4+} could be accommodated on the A site of the titanate pyrochlore, facilitated by co-incorporation of Zr^{4+} [38]. Furthermore, published thermodynamic data for a selection of pyrochlore ceramic phases relevant to the immobilisation of Pu indicate that the $CaThTi_2O_7$ may not be thermodynamically stable [39], [40].

Sintering of the $CaZr_{1-x}Th_xTi_2O_7$ solid solution under flowing 5% H_2/N_2 produced an undesirable phase assemblage due to the presence of a deleterious perovskite phase, expected to be detrimental to the overall wasteform performance due to the inferior aqueous durability of this structure relative to the zirconolite phase. The reduced compositions were comprised of zirconolite (of the 3T polytype structure, space group $P3_121$, above $x \geq 0.20$), undigested ThO_2 and the perovskite phase, accepting Th^{4+} in dilute solid solution. Considering the average compositions of the zirconolite-3T phase *e.g.* $Ca_{0.88(8)}Zr_{0.77(11)}Th_{0.21(4)}Ti_{2.13(7)}O_7$ as calculated for the $x = 0.40$ sample, it is clear that to maintain charge balance, Ti would be partially reduced to Ti^{3+} (5 – 10% Ti^{3+}). The formation of Ti^{3+} is likely under the reductive sintering conditions imposed (5% H_2/N_2), hence it may be inferred that $CaZr_{1-x}Th_xTi_2O_7$ zirconolite-2M is unstable with respect to perovskite and zirconolite-3T under reducing conditions. The

$CaZr_{1-x}Pu_xTi_2O_7$ solid solution sintered in air by Begg *et al.* was annealed in a 3.5% H_2/N_2 mixture at 1200 ˚C for 12 h, and whilst this was sufficient to produce powder XRD data consistent with zirconolite-3T and a perovskite phase, in agreement with the current work, no free PuO_2 was observed [15]. Despite zirconolite-3T occupying a moderate portion of the overall phase fraction at low targeted Th concentration, under reducing conditions, the perovskite and ThO_2 phases occupied more than 30 wt. % of the phase assemblage combined, when targeting $x = 0.40$. We consider this would render the wasteform significantly more susceptible to accelerated dissolution, due to the relatively low chemical durability of the perovskite phase [30] relative to the target zirconolite phase, and indeed ThO_2 [41], [42]. Although it is accepted that relics of unincorporated PuO_2 would be practically unavoidable on a large scale, as a consequence of localised incomplete milling, this would fall within the envelope of the expected wasteform product. In the present work, however, the abundance of ThO_2 throughout the microstructure was considered to be a consequence of the high thermal stability, low redox activity (*i.e.* Th present only as Th^{4+}) and high melting point of the component oxide. In summary, the immobilisation of Th^{4+} in the $CaZr_{1-x}Th_xTi_2O_7$ was best achieved when sintering under oxidising conditions, as whilst the composition favours a pyrochlore structure as the dominant phase for $x \geq 0.4$, no perovskite or undigested ThO_2 remained present in the microstructure.

4.2 Implications for use of Th^{4+} as Surrogate for Pu^{4+} Wasteform Development

The data presented in this study demonstrate the need for careful use of chemical surrogates in the context of wasteform development, as the use of Th^{4+} produced a phase evolution in the $CaZr_{1-x}Th_xTi_2O_7$ system that was inconsistent with respect to closely related analogue solid solutions. Blackburn *et al.* fabricated a series of zirconolite samples targeting $CaZr_{1-x}Ce_xTi_2O_7$ under identical processing conditions with those used in the current work, demonstrating that the progressive accommodation of Ce^{4+} within the Zr^{4+} site, during oxidative sintering, was consistent with a polymorphic transition to the zirconolite-4M polytype in the compositional range $0.10 \leq x \leq 0.20$ [23]. The extension of this solid solution to $x \geq 0.5$ was reported by Li *et al.* to form the pyrochlore structure [43]. Analogous phase fields were reported by Vance *et al.* for the $CaZr_{1-x}U_xTi_2O_7$ solid solution, in which a transition to the zirconolite-4M polytype was observed at $x = 0.15$, with inert Ar gas introduced during the sintering process to maintain U^{4+} [13]. Akin to the Ce system, the U-pyrochlore phase was obtained alongside the 4M phase for $x \geq 0.5$. It is advantageous that for this solid solution there are published Pu data that can provide validation as to the effectiveness of each surrogate. The findings of Begg *et al* [15] confirmed that oxidative sintering of the $CaZr_{1-x}Pu_xTi_2O_7$ solid solution produced a phase transition from zirconolite-2M to pyrochlore, *via* the formation of Pu-rich zirconolite-4M in the compositional interval 0.1 ≤ x ≤ 0.6. Moreover, single phase Pu pyrochlore was obtained at x = 0.60 (*i.e.* corresponding to a nominal composition $CaZr_{0.4}Pu_{0.6}Ti_2O_7$), identical to the present work. The data set presented in the current work provides a notable contribution towards the comparative study of plutonium surrogates in the zirconolite system (a summary of which is provided in **Table 7**), highlighting an important caveat for the application of Th^{4+} as a Pu^{4+} surrogate in the development of zirconolite wasteforms. The zirconolite-4M polytype transformation at higher wasteloading was not observed under oxidising conditions, presumably as a consequence of size restrictions, due to the large ionic radius of Th^{4+}, compared to U^{4+}, Ce^{4+} and Pu^{4+} (1.05 Å vs. 1.00, 0.97 and 0.96 Å, respectively, for 8-fold coordinate species). Nevertheless, these findings may support the deployment of Th as a Pu surrogate on the basis of safety and expediency, considering the specific activity of ^{239}Pu (2.30×10^2 Bq/µg) is significantly greater than that of ^{232}Th, approximately 4.1 Bq/µg. Hence, these data confirm that Th may act as a suitable radioactive surrogate for Pu in the zirconolite system, and indeed would be beneficial for the investigation of the stability and durability of pyrochlore wasteforms.

5 Conclusions

The phase assemblage, microstructure development and substitution boundary of Th^{4+} within the Zr^{4+} site in $CaZrTi_2O_7$ zirconolite was investigated, by sintering the $CaZr_{1-x}Th_xTi_2O_7$ at 1350 °C for 20 h, under oxidising and reducing conditions (air and 5% H_2/N_2, respectively). A specimen with nominal composition $CaZr_{0.80}Th_{0.20}Ti_{2.00}O_7$ was also produced by HIP, with a dwell temperature of 1300 ˚C maintained for 4 h at 100 MPa. Synthesis of $CaZr_{1-x}Th_xTi_2O_7$ compositions in air produced a polycrystalline phase assemblage of zirconolite-2M and pyrochlore in the compositional interval 0.10 ≤ x ≤ 0.50, with no observed formation of zirconolite-4M as an intermediate phase. Single phase pyrochlore with nominal composition $CaZr_{0.4}Th_{0.6}Ti_2O_7$ was stabilised when targeting x = 0.60. The $CaZr_{0.4}Th_{0.6}Ti_2O_7$ pyrochlore may be deployed as a suitable phase for the immobilisation of wastes with a high Th^{4+} fraction, given relative ease of processing with moderate Zr^{4+} content with respect to the $CaThTi_2O_7$ end-member. Although, further analysis is necessary to provide a detailed structural refinement of this phase. Synthesis under reducing conditions produced an undesirable phase assemblage consisting of zirconolite-2M and a perovskite phase in the compositional range 0.10 ≤ x ≤

0.20. Sintering under reducing conditions also resulted in considerable unincorporated ThO_2, occupying 3.9 ± 0.1 and 8.8 ± 0.3 wt. % of the phase assemblage, respectively. XRD data of the reduced solid solution for which $0.2 \leq x \leq 0.4$ were consistent with zirconolite adopting the 3T polytype. At $x = 0.40$, the perovskite phase and residual ThO_2 accounted for 24.2 and 8.8 wt. % of the total phase fraction, respectively. EDS analysis of perovskite inclusions confirmed partial Th^{4+} incorporation, with charge balance presumably facilitated by the formation of Ti^{3+}. The phase assemblage formed by HIP was similar to the counterpart synthesised in 5% H_2/N_2, with a major phase of zirconolite-2M, alongside 3.6 ± 0.1 wt. % ThO_2, 5.3 ± 0.3 wt. % $ThTi_2O_6$ and 14.1 ± 0.6 wt. % perovskite. It was concluded that the immobilisation of Th^{4+} in the Zr^{4+} site in zirconolite was best accommodated by synthesis under oxidising conditions, although a deviation from the expected phase evolution was observed, insofar as the zirconolite-4M intermediate phase was not produced. Nevertheless, the zirconolite-2M to pyrochlore phase transformation was reproduced in the same solid solution range as for Pu, hence under oxidising conditions Th^{4+} acted as an effective surrogate for Pu^{4+}. Due to the absence of the trivalent Th species (*i.e.* Th^{3+}), Th^{4+} could not accurately reproduce the behavior of Pu^{4+} under reducing conditions. The work presented hitherto demonstrates the need for multi parametric approach to wasteform development, utilising several surrogates in conjunction.

6 Acknowledgements

We acknowledge financial support from the Nuclear Decommissioning Authority (NDA) and EPSRC under grant numbers EP/201019X/1, EP/N017870/1 and EP/R511754/1. This research utilised the HADES/MIDAS facility at the University of Sheffield established with financial support from EPSRC and BEIS, under grant EP/T011424/1 [44]. The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Table Captions

Table 1) Unit cell dimensions and quantitative phase analysis (QPA) of $CaZr_{1-x}Th_xTi_2O_7$ compositions reacted at 1350 ˚C for 20 h in air (* indicates phase purity)

Table 2) Average composition of zirconolite-2M and pyrochlore phases determined from EDS analyses, assuming complete oxygen stoichiometry, reacted at 1350 ˚C for 20 h in air, normalised to seven oxygen atoms (* - *composition determination not possible due to grain size*).

Table 3) Refined structural parameters for $CaZr_{0.40}Th_{0.60}Ti_2O_7$ (here σ represents one standard deviation from the mean)

Table 4) Quantitative phase analysis for $CaZr_{1-x}Th_xTi_2O_7$ ($0 \leq x \leq 0.40$) compositions reacted at 1350 ˚C for 20 h in 5% H_2/N_2

Table 5) Unit cell dimensions of zirconolite-2M and zirconolite-3T from *Rietveld* refinement of powder X-ray diffraction profile of $CaZr_{1-x}Th_xTi_2O_7$ ($0 \leq x \leq 0.40$) reacted at 1350 ˚C for 20 h under 5% H_2/N_2

Table 6) Observed compositions for zirconolite phase in $CaZr_{1-x}Th_xTi_2O_7$ compositions reacted under flowing 5% H_2/N_2 at 1350 ˚C for 20 h, calculated by EDS analysis, normalized to seven oxygen.

Table 7) Summary of reported phase fields for $CaZr_{1-x}M_xTi_2O_7$ zirconolites in the compositional range $0.10 \leq x \leq 0.60$ (M^{4+} = Ce/U/Th/Pu, *denotes single phase)

Figure Captions

Fig. 1) Crystal structure of zirconolite 2M, 4M and 3T polytypes, alongside $CaUTi_2O_7$ pyrochlore.

Fig. 2) Powder XRD analyses of $CaZr_{1-x}Th_xTi_2O_7$ ($0 \leq x \leq 0.60$) reacted in air at 1350 ˚C for 20 h. Pyrochlore reflections are labelled by *(hkl)* indices.

Fig. 3) Representative BSE micrographs for x = 0.10 (left) and x = 0.20 (right) microstructures reacted at 1350 ˚C for 20 h in air.

Fig. 4) EDS analysis of x = 0.40 microstructure reacted at 1350 ˚C for 20 h in air.

Fig. 5) Representative BSE micrograph for single phase Th-rich pyrochlore with nominal composition $CaZr_{0.4}Th_{0.6}Ti_2O_7$ reacted at 1350 ˚C for 20 h in air.

Fig. 6) Rietveld refinement of powder diffraction profile for $CaZr_{0.4}Th_{0.6}Ti_2O_7$ reacted in air at 1350 ˚C for 20 h. Bragg positions of the pyrochlore structure are labelled by vertical indices. $R_{wp} = 9.72\%$, $\chi^2 = 1.728$.

Fig. 7) Powder XRD analyses of $CaZr_{1-x}Th_xTi_2O_7$ ($0.00 \leq x \leq 0.40$) reacted under flowing 5% H_2/N_2 at 1350 ˚C for 20 h. Zirconolite-3T reflections are indexed by appropriate (*hkl*) indices. ThO_2 reflections are highlighted with open circles. Perovskite reflections are highlighted with closed circles.

Fig. 8) Representative BSE micrographs for x = 0.10 (left) and x = 0.20 (right) microstructures reacted at 1350 ˚C for 20 h under flowing 5% H_2/N_2.

Fig. 9) EDS analysis of x = 0.40 microstructure reacted at 1350 ˚C for 20 h under flowing 5% H_2/N_2.

Fig. 10) Refined powder XRD data for $CaZr_{0.80}Th_{0.20}Ti_{2.00}O_7$ processed by HIP at 1300 ˚C at 100 MPa for 4 h. Zirconolite-2M reflections are highlighted by (*hkl*) values (black). $ThTi_2O_6$ reflections are highlighted by (*hkl*) values (red). ThO_2 reflections are highlighted by open circles. Perovskite reflections are highlighted by filled circles.

Fig. 11) Backscattered electron micrograph detailing a representative section of the microstructure for $CaZr_{0.80}Th_{0.20}Ti_{2.00}O_7$ processed by HIP at 1300 ˚C at 100 MPa for 4 h.