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# Synthesis, Structure and Characterisation of the Thorium

## Zirconolite $\text{CaZr}_{1-x}\text{Th}_x\text{Ti}_2\text{O}_7$ System

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### **Abstract**

A series of zirconolite ceramics with composition  $\text{CaZr}_{1-x}\text{Th}_x\text{Ti}_2\text{O}_7$  ( $\Delta x = 0.10$ ) were reactively sintered at 1350 °C for 20 h, in air ( $0 \leq x \leq 0.60$ ) and 5%  $\text{H}_2/\text{N}_2$  ( $0 \leq x \leq 0.40$ ). 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.  $\text{Th}^{4+}$  immobilisation was most readily achieved under oxidising conditions, with  $\text{Th}^{4+}$  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  $\text{CaZr}_{0.40}\text{Th}_{0.60}\text{Ti}_2\text{O}_7$  when targeting  $x = 0.60$ .  $\text{Th}^{4+}$  incorporation under reducing conditions produced a secondary Th-bearing perovskite, comprising  $24.2 \pm 0.6$  wt. % of the phase assemblage when targeting  $x = 0.40$ , alongside  $8.8 \pm 0.3$  wt. % undigested  $\text{ThO}_2$ . 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  $\text{Th}^{4+}$  bearing phases  $\text{ThTi}_2\text{O}_6$ ,  $\text{ThO}_2$  and perovskite. These data highlight the efficacy of  $\text{Th}^{4+}$  as a  $\text{Pu}^{4+}$  surrogate, with implications for the formation of Zr-stabilised Th-pyrochlore phases as matrices for waste with elevated  $\text{Th}^{4+}$  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  $\text{CaZrTi}_2\text{O}_7$ ) is the proposed candidate ceramic wastefrom 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  $\text{A}_2\text{B}_2\text{O}_7$  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  $\text{CaZr}_x\text{Ti}_{3-x}\text{Ti}_2\text{O}_7$  ( $0.8 < x < 1.3$ ), with a lamellar unit cell crystallising in the space group  $\text{C}2/c$  [11]. The nomenclature ‘2M’ is reference to the two layer repeating modules that comprise the monoclinic unit cell. In the idealised 2M structure,  $\text{Ca}^{2+}$  and  $\text{Zr}^{4+}$  are arranged in  $\text{CaO}_8$  and  $\text{ZrO}_7$  polyhedra layered between sheets of Ti-O polyhedra.  $\text{Ti}^{4+}$  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.  $\text{TiO}_5$ ) 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  $180^\circ$  rotation, offset by a stacking vector of approximately  $60^\circ$  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  $\text{Ca}^{2+}$ ,  $\text{Zr}^{4+}$  and  $\text{Ti}^{4+}$  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  $\text{M}^{4+}$  substitution within the  $\text{Zr}^{4+}$  site (e.g. U, Ce, Pu) [13]–[15], or isovalent accommodation of  $\text{M}^{3+}$  within the  $\text{Ca}^{2+}$  and  $\text{Zr}^{4+}$  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 four-

layer 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  $\text{Ca}^{2+}$  and  $\text{Zr}^{4+}$  sites in zirconolite produces a transformation to the pyrochlore structure (ideally  $\text{A}_2\text{B}_2\text{O}_7$  – space group  $Fd\bar{3}m$ , where  $\text{A}^{3+}$  and  $\text{B}^{4+}$  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  $\text{CaZr}_{1-x}\text{U}_x\text{Ti}_2\text{O}_7$  system stabilised the pyrochlore structure at  $x > 0.60$  [13]. Begg *et al.* reported the same solid solution limit for pyrochlore formation in the  $\text{CaZr}_{1-x}\text{Pu}_x\text{Ti}_2\text{O}_7$  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  $\text{REE}^{3+}$ , 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  $\text{Ca}_{1-x}\text{Pu}_x\text{ZrTi}_{2-2x}\text{Fe}_{2x}\text{O}_7$  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  $\text{Ca}_{1-x}\text{Ce}_x\text{ZrTi}_{2-2x}\text{Cr}_{2x}\text{O}_7$  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  $\text{Ca}_{0.80}\text{Th}_{0.15}\text{Zr}_{1.30}\text{Ti}_{1.35}\text{Al}_{0.40}\text{O}_7$  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 wastefoms, 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  $\text{Th}^{4+}$  (as a surrogate for  $\text{Pu}^{4+}$ ) within the  $\text{Zr}^{4+}$  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  $\text{CaZr}_{1-x}\text{Ce}_x\text{Ti}_2\text{O}_7$  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 zirconolite-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  $\text{Ce}^{3+}$  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  $\text{Ce}^{3+}$  under oxidative sintering environments is a behaviour not representative of Pu. Hence, as Th remains stable in the  $\text{Th}^{4+}$  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  $\text{ThO}_2$  and  $\text{CeO}_2$  surrogates in the zirconolite system,  $\text{CaZr}_{1-x}\text{M}_x\text{Ti}_2\text{O}_7$  ( $\text{M} = \text{Ce}$  or  $\text{Th}$ ).

## 2 Experimental Methodology

### 2.1 Materials Synthesis

All compositions targeting  $\text{CaZr}_{1-x}\text{Th}_x\text{Ti}_2\text{O}_7$  ( $0 \leq x \leq 0.60$ ,  $\Delta x = 0.10$ ) were produced by a mixed oxide route between  $\text{CaTiO}_3$ ,  $\text{ZrO}_2$ ,  $\text{TiO}_2$  (Sigma Aldrich, 99.9% trace metals basis) and  $\text{ThO}_2$  (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  $\text{ZrO}_2$  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%  $\text{H}_2/\text{N}_2$  (BOC,  $\text{Al}_2\text{O}_3$  tube furnace), representing oxidising and reducing conditions, respectively. A sample with nominal composition  $\text{CaZr}_{0.80}\text{Th}_{0.20}\text{Ti}_{2.00}\text{O}_7$  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 ( $\sim 7$  Pa). The canister was then hermetically sealed, placed into an AIP 630-H HIP unit, and processed at  $1300\text{ }^{\circ}\text{C}$  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 ( $\text{Cu K}\alpha$ ,  $\lambda = 1.5418\text{ \AA}$ , 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  $0.02^{\circ}\text{ s}^{-1}$ . 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  $1\text{ }\mu\text{m}$  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  $\text{CaZr}_{1-x}\text{Th}_x\text{Ti}_2\text{O}_7$  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  $\text{CaZrTi}_2\text{O}_7$  [26]:  $a = 12.44808(11) \text{ \AA}$ ,  $b = 7.27366(6) \text{ \AA}$ ,  $c = 11.37383(1) \text{ \AA}$ ,  $\beta = 100.5782(7)^\circ$  and  $V = 1012.321(16) \text{ \AA}^3$ . 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  $2\theta = 15.2^\circ$ ,  $29.2^\circ$ ,  $35.4^\circ$ ,  $38.7^\circ$ , and  $46.5^\circ$ , corresponding the (111), (113), (004), (133) and (115) reflections, respectively. As the nominal  $\text{Th}^{4+}$  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 ( $\text{CaTiO}_3$ ) impurity, identified by a weak reflection at  $2\theta = 33.1^\circ$ , although only comprising  $1.1 \pm 0.5$  and  $1.3 \pm 0.5$  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  $\text{Th}^{4+}$  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  $\text{CaZr}_{0.4}\text{Th}_{0.6}\text{Ti}_2\text{O}_7$ . 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  $\text{CaZr}_{0.4}\text{Pu}_{0.6}\text{Ti}_2\text{O}_7$  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  $\text{Th}^{4+}$  was accommodated within both phases in the microstructure, EDS analysis demonstrated that  $\text{Th}^{4+}$  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  $\text{Ca}_{0.98(6)}\text{Zr}_{0.89(8)}\text{Th}_{0.05(2)}\text{Ti}_{2.07(8)}\text{O}_7$ , with the excess  $\text{Th}^{4+}$  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  $\text{Th}^{4+}$  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  $\text{Th}^{4+}$  and rich in  $\text{Zr}^{4+}$  with respect to the pyrochlore phase. It was also evident that grains of zirconolite-2M appeared lath-like in morphology. As the  $\text{Th}^{4+}$  concentration reached  $x = 0.60$ , the microstructure produced for the pyrochlore phase was homogeneous in BSE contrast, consistent with the formation of single phase  $\text{CaZr}_{0.4}\text{Th}_{0.6}\text{Ti}_2\text{O}_7$  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  $\text{ThTi}_2\text{O}_6$  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  $\text{ThTi}_2\text{O}_6$  could be reconciled by XRD analysis.

### 3.1.3 Initial Refinement of $\text{CaZr}_{0.4}\text{Th}_{0.6}\text{Ti}_2\text{O}_7$

All prominent reflections in the XRD pattern of  $\text{CaZr}_{0.4}\text{Th}_{0.6}\text{Ti}_2\text{O}_7$  could be indexed assuming the structure to be isostructural with that of  $\text{CaUTi}_2\text{O}_7$  (space group:  $Fd\bar{3}m$ ; ICSD 40264, see **Fig. 1**). With the exception of negligible  $\text{ThTi}_2\text{O}_6$  (as indicated in **Fig. 5**) no secondary phases were identified by SEM analysis, and quantitative EDS analyses confirmed the average stoichiometry to be  $\text{Ca}_{1.00(2)}\text{Zr}_{0.33(2)}\text{Th}_{0.54(1)}\text{Ti}_{2.13(2)}\text{O}_7$ , demonstrating an apparent excess of Ti. Structure refinement initially assumed the ideal stoichiometry of  $\text{CaZr}_{0.4}\text{Th}_{0.6}\text{Ti}_2\text{O}_7$  adopting the space group  $Fd\bar{3}m$ , consistent with the published crystal structure of  $\text{CaUTi}_2\text{O}_7$  [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  $\chi^2 = 1.728$  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  $92.4 \pm 0.1$  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  $7.6 \pm 0.3$  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  $11.3 \pm 0.5$  wt. %. Minor reflections at  $2\theta = 27.5^\circ$ ,  $45.7^\circ$  and  $54.2^\circ$  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  $15.4 \pm 0.5$  wt. % and  $0.9 \pm 0.1$  wt. %, respectively. For  $x \geq 0.20$ , 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,  $V = 766.17(3) \text{ \AA}^3$ . These unit cell dimensions were in general agreement with previously reported values for the zirconolite-3T phase when doped with similar levels of  $\text{Th}^{4+}$  [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  $18.9 \pm 0.6$  and  $24.2 \pm 0.6$  wt. %, respectively. The relative quantity of unincorporated  $\text{ThO}_2$  in the microstructure was also further elevated, with an increase from  $0.9 \pm 0.1$  to  $8.8 \pm 0.3$  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  $\sim 67$  wt. %. Hence, the imposition of reducing conditions during the sintering of  $\text{CaZr}_{1-x}\text{Th}_x\text{Ti}_2\text{O}_7$  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  $\text{ThO}_2$  (bright grey). Close inspection of EDS data confirmed that  $\text{Th}^{4+}$  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  $\text{Th}^{4+}$ , relative to the target composition, for all values of  $x$ , coinciding with unincorporated  $\text{ThO}_2$  in the microstructure. In agreement with powder XRD data, the accompanying quantity of perovskite and  $\text{ThO}_2$  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  $\text{Th}^{4+}$  (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  $\text{Th}^{4+}$  within the  $\text{Ca}^{2+}$  site in perovskite would also demonstrate an apparent excess of positive charge, typically necessitating the formation of  $\text{Ti}^{4+}$  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  $\text{Ti}^{3+}$ , providing charge balance by 5 – 10%  $\text{Ti}^{3+}$ . When targeting

$x = 0.40$ , the average composition of the accompanying perovskite phase was calculated from EDS data to be  $\text{Ca}_{0.77(2)}\text{Th}_{0.13(1)}\text{Zr}_{0.09(2)}\text{Ti}_{1.01(3)}\text{O}_3$ , normalised to three oxygen atoms.

### 3.3 Hot Isostatic Pressing of $\text{CaZr}_{0.80}\text{Th}_{0.20}\text{Ti}_{2.00}\text{O}_7$

A specimen with nominal composition  $\text{CaZr}_{0.80}\text{Th}_{0.20}\text{Ti}_{2.00}\text{O}_7$  (*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%  $\text{H}_2/\text{N}_2$  sintered samples, largely due to the increased occupation of perovskite within the phase assemblage (increasing from  $\sim 1$  wt. % to  $\sim 14$  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  $\text{CaZr}_{0.80}\text{Th}_{0.20}\text{Ti}_{2.00}\text{O}_7$ . A reasonable fit was achieved, with the diffraction profile refined to a phase assemblage of zirconolite-2M ( $74.0 \pm 0.3$  wt. %),  $\text{ZrO}_2$  ( $3.1 \pm 0.4$  wt. %),  $\text{ThO}_2$  ( $3.6 \pm 0.1$  wt. %),  $\text{ThTi}_2\text{O}_6$  ( $5.3 \pm 0.3$  wt. %) and  $\text{CaTiO}_3$  ( $14.1 \pm 0.6$  wt. %). The existence of  $\text{ThTi}_2\text{O}_6$  was confirmed by reflections at  $2\theta = 14.3^\circ$ ,  $18.4^\circ$  and  $25.4^\circ$  corresponding to reflections in the (001),  $(20\bar{1})$  and (110) planes in the  $\text{ThTi}_2\text{O}_6$  structure, respectively.

A representative section of the microstructure for the  $\text{CaZr}_{0.80}\text{Th}_{0.20}\text{Ti}_{2.00}\text{O}_7$  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%  $\text{H}_2/\text{N}_2$ ,  $\text{Th}^{4+}$  was also located within this phase, presumably accommodated within the  $\text{Ca}^{2+}$  site. The incorporation of  $\text{Th}^{4+}$  within the more abundant perovskite phase ( $\sim 14$  wt. %) would be considered highly undesirable, as the lower durability of perovskite with respect to the target zirconolite phase may negatively impact the overall performance of the wasteform, resulting in accelerated release of  $\text{Th}^{4+}$  (and Pu, by analogy) from the ceramic phase into solution in the disposal environment [32]. Undigested  $\text{ThO}_2$  was observed in the microstructure, clearly visible in **Fig. 11** as relics with bright contrast, with a clear reaction rim surrounding the  $\text{ThO}_2$  cores. The composition of these reaction rims was consistent with both XRD and EDS analyses as  $\text{ThTi}_2\text{O}_6$  (*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  $\text{ThO}_2$  being prevalent 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  $\text{Th}^{4+}$  within an ancillary phase was generally considered undesirable,  $\text{ThTi}_2\text{O}_6$  is known to be highly durable in aggressive leaching environments, with Zhang *et al.* reporting normalised release rates of  $\text{Th} < 10^{-5} \text{ g m}^{-2} \text{ d}^{-1}$  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 $\text{CaZr}_{1-x}\text{Th}_x\text{Ti}_2\text{O}_7$

There exists a narrow scope of literature concerned with the incorporation of  $\text{Th}^{4+}$  within the zirconolite structure, making any reasonable comparison with published solid solution data limited. Kesson *et al.* discussed the incorporation of  $\text{Th}^{4+}$  within the  $\text{Zr}^{4+}$  site, with compositions corresponding to  $\text{CaZr}_{0.90}\text{Th}_{0.10}\text{Ti}_{2.00}\text{O}_7$  and  $\text{CaZr}_{0.80}\text{Th}_{0.20}\text{Ti}_{2.00}\text{O}_7$  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  $\text{Th}^{4+}$  doping was not attempted). However, it is accepted that the discrepancies in solid solution limit on the  $\text{Zr}^{4+}$  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  $\text{H}_2/\text{N}_2$  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  $\text{ThO}_2$ , however as no unit cell parameters were reported, this cannot be confirmed. We are not aware of any other studies that have accommodated  $\text{Th}^{4+}$  within the  $\text{Zr}^{4+}$  site of zirconolite.

Sintering the  $\text{CaZr}_{1-x}\text{Th}_x\text{Ti}_2\text{O}_7$  solid solution in air produced a pseudo-binary system comprised of  $\text{Ca}(\text{Zr,Th})\text{Ti}_2\text{O}_7$  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 wastefrom 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

$\text{CaZr}_{1-x}\text{Pu}_x\text{Ti}_2\text{O}_7$  solid solution sintered in air by Begg *et al.* was annealed in a 3.5%  $\text{H}_2/\text{N}_2$  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  $\text{PuO}_2$  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  $\text{ThO}_2$  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  $\text{ThO}_2$  [41], [42]. Although it is accepted that relics of unincorporated  $\text{PuO}_2$  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  $\text{ThO}_2$  throughout the microstructure was considered to be a consequence of the high thermal stability, low redox activity (*i.e.* Th present only as  $\text{Th}^{4+}$ ) and high melting point of the component oxide. In summary, the immobilisation of  $\text{Th}^{4+}$  in the  $\text{CaZr}_{1-x}\text{Th}_x\text{Ti}_2\text{O}_7$  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  $\text{ThO}_2$  remained present in the microstructure.

#### 4.2 Implications for use of $\text{Th}^{4+}$ as Surrogate for $\text{Pu}^{4+}$ 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  $\text{Th}^{4+}$  produced a phase evolution in the  $\text{CaZr}_{1-x}\text{Th}_x\text{Ti}_2\text{O}_7$  system that was inconsistent with respect to closely related analogue solid solutions. Blackburn *et al.* fabricated a series of zirconolite samples targeting  $\text{CaZr}_{1-x}\text{Ce}_x\text{Ti}_2\text{O}_7$  under identical processing conditions with those used in the current work, demonstrating that the progressive accommodation of  $\text{Ce}^{4+}$  within the  $\text{Zr}^{4+}$  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  $\text{CaZr}_{1-x}\text{U}_x\text{Ti}_2\text{O}_7$  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  $\text{U}^{4+}$  [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  $\text{CaZr}_{1-x}\text{Pu}_x\text{Ti}_2\text{O}_7$  solid solution produced a phase transition from zirconolite-2M to pyrochlore, *via* the formation of Pu-rich zirconolite-4M in the compositional interval  $0.1 \leq x \leq 0.6$ . Moreover, single phase Pu pyrochlore was obtained at  $x = 0.60$  (*i.e.* corresponding to a nominal composition  $\text{CaZr}_{0.4}\text{Pu}_{0.6}\text{Ti}_2\text{O}_7$ ), 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  $\text{Th}^{4+}$  as a  $\text{Pu}^{4+}$  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  $\text{Th}^{4+}$ , compared to  $\text{U}^{4+}$ ,  $\text{Ce}^{4+}$  and  $\text{Pu}^{4+}$  (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  $^{239}\text{Pu}$  ( $2.30 \times 10^2$  Bq/ $\mu\text{g}$ ) is significantly greater than that of  $^{232}\text{Th}$ , approximately 4.1 Bq/ $\mu\text{g}$ . 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  $\text{Th}^{4+}$  within the  $\text{Zr}^{4+}$  site in  $\text{CaZrTi}_2\text{O}_7$  zirconolite was investigated, by sintering the  $\text{CaZr}_{1-x}\text{Th}_x\text{Ti}_2\text{O}_7$  at 1350 °C for 20 h, under oxidising and reducing conditions (air and 5%  $\text{H}_2/\text{N}_2$ , respectively). A specimen with nominal composition  $\text{CaZr}_{0.80}\text{Th}_{0.20}\text{Ti}_{2.00}\text{O}_7$  was also produced by HIP, with a dwell temperature of 1300 °C maintained for 4 h at 100 MPa. Synthesis of  $\text{CaZr}_{1-x}\text{Th}_x\text{Ti}_2\text{O}_7$  compositions in air produced a polycrystalline phase assemblage of zirconolite-2M and pyrochlore in the compositional interval  $0.10 \leq x \leq 0.50$ , with no observed formation of zirconolite-4M as an intermediate phase. Single phase pyrochlore with nominal composition  $\text{CaZr}_{0.4}\text{Th}_{0.6}\text{Ti}_2\text{O}_7$  was stabilised when targeting  $x = 0.60$ . The  $\text{CaZr}_{0.4}\text{Th}_{0.6}\text{Ti}_2\text{O}_7$  pyrochlore may be deployed as a suitable phase for the immobilisation of wastes with a high  $\text{Th}^{4+}$  fraction, given relative ease of processing with moderate  $\text{Zr}^{4+}$  content with respect to the  $\text{CaThTi}_2\text{O}_7$  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  $0.10 \leq x \leq$

0.20. Sintering under reducing conditions also resulted in considerable unincorporated ThO<sub>2</sub>, 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 ≤ x ≤ 0.4 were consistent with zirconolite adopting the 3T polytype. At x = 0.40, the perovskite phase and residual ThO<sub>2</sub> accounted for 24.2 and 8.8 wt. % of the total phase fraction, respectively. EDS analysis of perovskite inclusions confirmed partial Th<sup>4+</sup> incorporation, with charge balance presumably facilitated by the formation of Ti<sup>3+</sup>. The phase assemblage formed by HIP was similar to the counterpart synthesised in 5% H<sub>2</sub>/N<sub>2</sub>, with a major phase of zirconolite-2M, alongside 3.6 ± 0.1 wt. % ThO<sub>2</sub>, 5.3 ± 0.3 wt. % ThTi<sub>2</sub>O<sub>6</sub> and 14.1 ± 0.6 wt. % perovskite. It was concluded that the immobilisation of Th<sup>4+</sup> in the Zr<sup>4+</sup> 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<sup>4+</sup> acted as an effective surrogate for Pu<sup>4+</sup>. Due to the absence of the trivalent Th species (*i.e.* Th<sup>3+</sup>), Th<sup>4+</sup> could not accurately reproduce the behavior of Pu<sup>4+</sup> under reducing conditions. The work presented hitherto demonstrates the need for multi parametric approach to wastefrom development, utilising several surrogates in conjunction.

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## Table Captions

**Table 1)** Unit cell dimensions and quantitative phase analysis (QPA) of  $\text{CaZr}_{1-x}\text{Th}_x\text{Ti}_2\text{O}_7$  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  $\text{CaZr}_{0.40}\text{Th}_{0.60}\text{Ti}_2\text{O}_7$  (here  $\sigma$  represents one standard deviation from the mean)

**Table 4)** Quantitative phase analysis for  $\text{CaZr}_{1-x}\text{Th}_x\text{Ti}_2\text{O}_7$  ( $0 \leq x \leq 0.40$ ) compositions reacted at 1350 °C for 20 h in 5%  $\text{H}_2/\text{N}_2$

**Table 5)** Unit cell dimensions of zirconolite-2M and zirconolite-3T from *Rietveld* refinement of powder X-ray diffraction profile of  $\text{CaZr}_{1-x}\text{Th}_x\text{Ti}_2\text{O}_7$  ( $0 \leq x \leq 0.40$ ) reacted at 1350 °C for 20 h under 5%  $\text{H}_2/\text{N}_2$

**Table 6)** Observed compositions for zirconolite phase in  $\text{CaZr}_{1-x}\text{Th}_x\text{Ti}_2\text{O}_7$  compositions reacted under flowing 5%  $\text{H}_2/\text{N}_2$  at 1350 °C for 20 h, calculated by EDS analysis, normalized to seven oxygen.

**Table 7)** Summary of reported phase fields for  $\text{CaZr}_{1-x}\text{M}_x\text{Ti}_2\text{O}_7$  zirconolites in the compositional range  $0.10 \leq x \leq 0.60$  ( $\text{M}^{4+} = \text{Ce}/\text{U}/\text{Th}/\text{Pu}$ , \*denotes single phase)

## Figure Captions

**Fig. 1)** Crystal structure of zirconolite 2M, 4M and 3T polytypes, alongside  $\text{CaUTi}_2\text{O}_7$  pyrochlore.

**Fig. 2)** Powder XRD analyses of  $\text{CaZr}_{1-x}\text{Th}_x\text{Ti}_2\text{O}_7$  ( $0 \leq x \leq 0.60$ ) 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  $1350\text{ }^{\circ}\text{C}$  for 20 h in air.

**Fig. 4)** EDS analysis of  $x = 0.40$  microstructure reacted at  $1350\text{ }^{\circ}\text{C}$  for 20 h in air.

**Fig. 5)** Representative BSE micrograph for single phase Th-rich pyrochlore with nominal composition  $\text{CaZr}_{0.4}\text{Th}_{0.6}\text{Ti}_2\text{O}_7$  reacted at  $1350\text{ }^{\circ}\text{C}$  for 20 h in air.

**Fig. 6)** Rietveld refinement of powder diffraction profile for  $\text{CaZr}_{0.4}\text{Th}_{0.6}\text{Ti}_2\text{O}_7$  reacted in air at  $1350\text{ }^{\circ}\text{C}$  for 20 h. Bragg positions of the pyrochlore structure are labelled by vertical indices.  $R_{\text{wp}} = 9.72\%$ ,  $\chi^2 = 1.728$ .

**Fig. 7)** Powder XRD analyses of  $\text{CaZr}_{1-x}\text{Th}_x\text{Ti}_2\text{O}_7$  ( $0.00 \leq x \leq 0.40$ ) reacted under flowing 5%  $\text{H}_2/\text{N}_2$  at  $1350\text{ }^{\circ}\text{C}$  for 20 h. Zirconolite-3T reflections are indexed by appropriate  $(hkl)$  indices.  $\text{ThO}_2$  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  $1350\text{ }^{\circ}\text{C}$  for 20 h under flowing 5%  $\text{H}_2/\text{N}_2$ .

**Fig. 9)** EDS analysis of  $x = 0.40$  microstructure reacted at  $1350\text{ }^{\circ}\text{C}$  for 20 h under flowing 5%  $\text{H}_2/\text{N}_2$ .

**Fig. 10)** Refined powder XRD data for  $\text{CaZr}_{0.80}\text{Th}_{0.20}\text{Ti}_{2.00}\text{O}_7$  processed by HIP at  $1300\text{ }^{\circ}\text{C}$  at 100 MPa for 4 h. Zirconolite-2M reflections are highlighted by  $(hkl)$  values (black).  $\text{ThTi}_2\text{O}_6$  reflections are highlighted by  $(hkl)$  values (red).  $\text{ThO}_2$  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  $\text{CaZr}_{0.80}\text{Th}_{0.20}\text{Ti}_{2.00}\text{O}_7$  processed by HIP at  $1300\text{ }^{\circ}\text{C}$  at 100 MPa for 4 h.