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Aldean, I., Sun, S.-K., Wilkins, M.C.D. et al. (6 more authors) (2022) Synthesis and characterisation of Ce-doped zirconolite  $\text{Ca}_{0.80}\text{Ce}_{0.20}\text{ZrTi}_{1.60}\text{M}_{0.40}\text{O}_7$  ( $\text{M} = \text{Fe}, \text{Al}$ ) formed by reactive spark plasma sintering (RSPS). MRS Advances. ISSN 2731-5894

<https://doi.org/10.1557/s43580-022-00221-6>

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# Synthesis and characterisation of Ce-doped zirconolite $\text{Ca}_{0.80}\text{Ce}_{0.20}\text{ZrTi}_{1.60}\text{M}_{0.40}\text{O}_7$ (M = Fe, Al) formed by reactive spark plasma sintering (RSPS)

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Received: 29 November 2021 / Accepted: 27 January 2022  
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## Abstract

Reactive spark plasma sintering has been utilised as a high-throughput processing route for the synthesis of two simulant zirconolite wastefrom materials, targeting  $\text{Ca}_{0.80}\text{Ce}_{0.20}\text{ZrTi}_{1.60}\text{M}_{0.40}\text{O}_7$  (M =  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$ ). Materials were processed under 15 MPa uniaxial pressure, with heating/cooling rates of 100 °C/min to 1320 °C, maintained under vacuum. Despite moderate yield (> 80 wt%) of zirconolite-2M, a considerable Ce-rich perovskite phase was formed in both formulations, attributed to complete reduction of the Ce inventory to  $\text{Ce}^{3+}$ , as determined by Ce L<sub>3</sub>-edge XANES analysis. The composition charge balanced with  $\text{Al}^{3+}$  was favoured on the basis of lower accompanying perovskite fraction.

## Introduction

A strategy combining reuse, immobilisation and disposal has been proposed as a long-term solution for at least some portion of the United Kingdom civil  $\text{PuO}_2$  inventory, which is forecast to reach ~ 140 teHM (tonnes equivalent heavy metal) once domestic reprocessing operations cease [1]. Prior to placement alongside the existing HLW inventory in a geological disposal facility (GDF) Pu must first be immobilised at the atomic scale in a high-durability matrix, to confer passive safety and improve handling properties. Fundamentally, the primary driver for immobilisation is to prevent Pu migration into the near-field environment over geological timescales such that the overall activity of the waste package at the time of failure is similar to the U ore from which it was derived. On the basis of high chemical durability and radiation stability, crystalline titanate materials (including hollandite, pyrochlore, perovskite, brannerite and zirconolite) are suitable phases for the sequestration of partitioned

actinides (Pu, Am, U) and fission products (Cs, Sr) present in many nuclear waste streams. The zirconolite phase (ideally  $\text{CaZrTi}_2\text{O}_7$ ) is considered to be the most suitable matrix for the immobilisation of Pu [2]. The zirconolite-2M parent structure is a derivation of an anion-deficient fluorite superstructure, composed of layered  $\text{TiO}_6/\text{TiO}_5$  polyhedra, arranged in a hexagonal-tungsten-bronze (HTB)-type motif interspaced with layers of  $\text{CaO}_8/\text{ZrO}_7$  polyhedra, with the overall structure crystallising in the space group C2/c ( $Z=8$ ,  $\rho=4.47 \text{ g/cm}^3$ ) [3]. The chemical flexibility of the zirconolite phase is one of the primary drivers towards its use as a wastefrom as there are five distinct cation receptor sites that are capable of accommodating actinides, neutron poisoning additives (typically  $\text{Gd}^{3+}$  and  $\text{Hf}^{4+}$  on the basis of compatible oxidation state and ionic radius) and charge compensating species. Typically, larger waste cations such as  $\text{Pu}^{3+/4+}$  are most suitably accommodated within the  $\text{Ca}^{2+}$  site on the basis of ionic radii, with lower valence charge balancing cations (typically  $\text{Fe}^{3+}$  or  $\text{Al}^{3+}$ ) co-substituted in an appropriate molar ratio within the  $\text{Ti}^{4+}$  sites. Substitution of tetravalent cations on the  $\text{Zr}^{4+}$  site produces a transformation to zirconolite-4M, a superstructure composed of alternating layers of zirconolite-2M and pyrochlore-type modules, resulting in a doubling of the unit cell along the c-axis [4–6]. Substitution on the  $\text{Ca}^{2+}$  site has been observed, in some instances, to promote the formation of the trigonal variant zirconolite-3T; a number of such solid solutions have been reported in the literature [4, 7–9]. In the present study,

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with Ce utilised as a surrogate for Pu, reactive spark plasma sintering (RSPS) has been deployed as a high-throughput synthesis route to fabricate zirconolite ceramics with the formulation  $\text{Ca}_{0.80}\text{Ce}_{0.20}\text{ZrTi}_{1.60}\text{M}_{0.40}\text{O}_7$  where  $\text{M} = \text{Fe}^{3+}$  or  $\text{Al}^{3+}$ . RSPS is a potentially attractive route for the ceramic immobilisation of actinides, given the throughput that can be achieved. A detailed review discussing the application of spark plasma sintering in the context of phosphate waste-form development was recently published [10]. The simultaneous synthesis and consolidation of ceramic materials via RSPS are achieved by rapid DC current pulsing through a compressed powder compact, maintained under uniaxial pressure. This allows the production of monoliths of near theoretical density, even in short processing times, due to heating/cooling rates typically of the order  $100\text{ }^\circ\text{C}/\text{min}$  [11]. The process has previously been demonstrated as suitable for the effective immobilisation of  $^{129}\text{I}$  in lead vanadophosphate iodoapatite  $\text{Pb}_{10}(\text{VO}_4)_4.8(\text{PO}_4)\text{O}_{1.2}\text{I}_2$  [12], Cs in hollandite (nominally  $\text{BaAl}_2\text{Ti}_6\text{O}_{16}$ ) [13], and more recently Ce in zirconolite [9].

## Experimental methodology

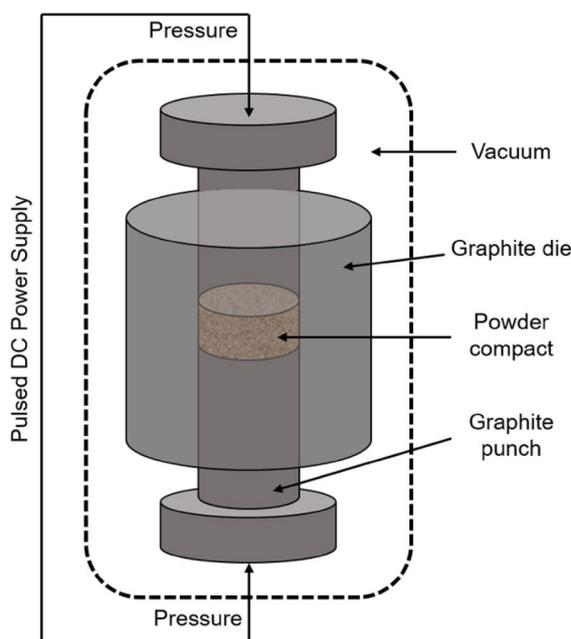
### Materials synthesis

Oxide powders  $\text{CaTiO}_3$  (99.9%, Sigma Aldrich),  $\text{ZrO}_2$  (99.9%, Sigma Aldrich),  $\text{CeO}_2$  (99.9%, Acros Organics),  $\text{TiO}_2$  (anatase, 99.9%, Sigma Aldrich),  $\text{Al}_2\text{O}_3$  (99.9%, Sigma Aldrich), and  $\text{Fe}_2\text{O}_3$  (99.9%, Sigma Aldrich) were calcined

at  $800\text{ }^\circ\text{C}$  for 12 h, prior to addition to a  $\text{ZrO}_2$ -lined milling vessel, in stoichiometric ratios according to the formulations  $\text{Ca}_{0.80}\text{Ce}_{0.20}\text{ZrTi}_{1.60}\text{Al}_{0.40}\text{O}_7$  and  $\text{Ca}_{0.80}\text{Ce}_{0.20}\text{ZrTi}_{1.60}\text{Fe}_{0.40}\text{O}_7$ . The mixtures were homogenised using a Fritsch P7 planetary ball mill, with  $\text{ZrO}_2$  milling media and isopropanol, at 400 rpm for a total of 20 min. Samples were recovered and dried at  $80\text{ }^\circ\text{C}$  to evaporate excess solvent. Approximately 5 g of each batch was measured and transferred to a 20 mm graphite die, with graphite foil spacers to promote uniform current flow, and compressed under 3 t for approximately 5 min to form loosely bound green bodies. The die was then loaded into a HP-D 1050 SPS system (FCT Systeme GmbH) and ramped at  $100\text{ }^\circ\text{C}/\text{min}$  to  $1320\text{ }^\circ\text{C}$ , with a constant uniaxial pressure of 15 MPa maintained throughout. A simplified illustration of this configuration is provided in Fig. 1, alongside a photograph of a typical product.

### Materials characterisation

Post-sintering, pellets were sectioned and prepared for powder X-ray diffraction (XRD) using a Bruker D2 Phaser diffractometer, fitted with Lynxeye position sensitive detector utilising  $\text{Cu-K}\alpha$  radiation ( $\lambda = 1.5418\text{ \AA}$ , Ni filter). Data were collected in the range  $10^\circ \leq 2\theta \leq 80^\circ$ . Rietveld analysis of powder XRD data was achieved using the Bruker TOPAS package [14]. The true density of each composition was determined by He-gas pycnometry, with material in the powder form. Density measurements were taken using an AccuPyc 1340 II pycnometer, with a total of 20 cycles performed for each specimen under



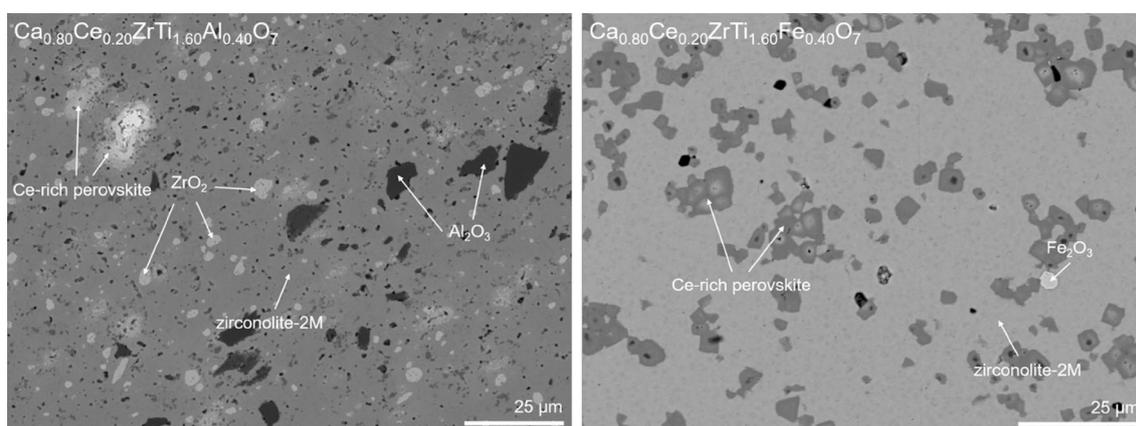
**Fig. 1** Simplified illustration of RSPS configuration (left) and photograph of a typical ceramic product (right)



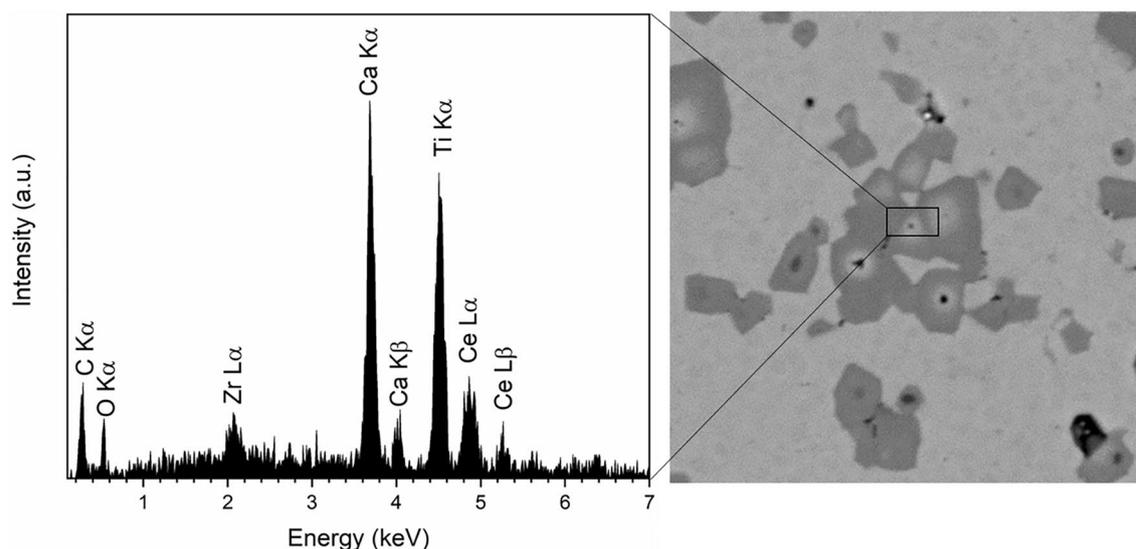
$\beta = 100.368(2)^\circ$  and  $V = 1022.85(7) \text{ \AA}^3$ , yet with a notable increase in unit cell volume. This may be attributed to the ionic radii of  $\text{Al}^{3+}$  (53 pm) and  $\text{Fe}^{3+}$  (63 pm) relative to  $\text{Ti}^{4+}$  (68 pm).

A representative portion of each microstructure is labelled and displayed in Fig. 3. It was clear that both specimens formed with a fine-grained, high-density microstructure. Helium pycnometry determined the true density of the formed products to be  $4.6071 \pm 0.0038$  and  $4.7976 \pm 0.0115 \text{ g/cm}^3$  for  $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$  compositions, respectively. It was clear that when synthesising materials targeting both  $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$  charge compensation, a moderately heterogeneous phase assemblage was formed, with apparent phase distributions consistent with quantitative phase analyses derived from the Rietveld fitting. Upon inspection of the materials

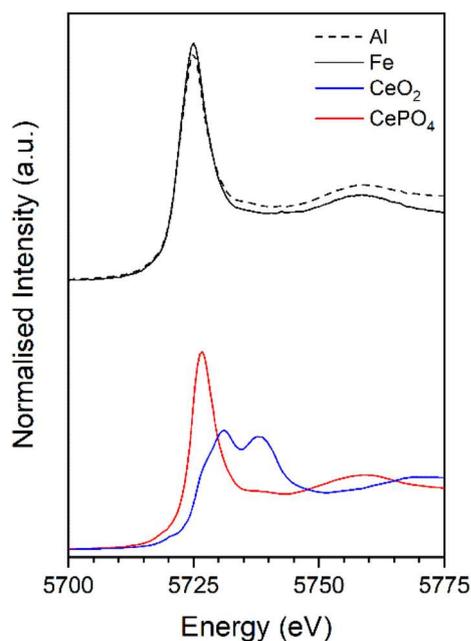
batched as  $\text{Ca}_{0.80}\text{Ce}_{0.20}\text{ZrTi}_{1.60}\text{Al}_{0.40}\text{O}_7$ , clear islands of  $\text{ZrO}_2$  and  $\text{Al}_2\text{O}_3$  were present, with regions of fine-grained Ce-substituted  $\text{CaTiO}_3$  clearly distinguished by complementary EDS phase analysis (not shown). Similar observations were made for the  $\text{Fe}^{3+}$ -substituted sample; it was also clear that the Ce-perovskite occupied a greater proportion of the microstructure, in agreement with the Rietveld analysis of powder diffraction data discussed above. EDS analysis of perovskite grains present in the material batched as  $\text{Ca}_{0.80}\text{Ce}_{0.20}\text{ZrTi}_{1.60}\text{Fe}_{0.40}\text{O}_7$  demonstrated uptake of a significant portion of Ce (Fig. 4). It was clear in early studies on SYNROC (SYNthetic-ROCK) corrosion that perovskite was the least durable phase in the conventional SYNROC-C wastefrom under dissolution conditions [16]. Therefore, partial sequestration of the Pu surrogate fraction within the



**Fig. 3** Backscattered electron micrograph for representative sections of materials batched targeting the compositions  $\text{Ca}_{0.80}\text{Ce}_{0.20}\text{ZrTi}_{1.60}\text{Al}_{0.40}\text{O}_7$  (left) and  $\text{Ca}_{0.80}\text{Ce}_{0.20}\text{ZrTi}_{1.60}\text{Fe}_{0.40}\text{O}_7$  (right)



**Fig. 4** EDS analysis of a perovskite cluster present in the material targeting  $\text{Ca}_{0.80}\text{Ce}_{0.20}\text{ZrTi}_{1.60}\text{Fe}_{0.40}\text{O}_7$ , presenting a signal corresponding to the Ce L $\alpha$  emission line



**Fig. 5** Above: Ce  $L_3$ -edge XANES spectra of materials targeting  $\text{Ca}_{0.80}\text{Ce}_{0.20}\text{ZrTi}_{1.60}\text{Al}_{0.40}\text{O}_7$  (labelled as Al) and  $\text{Ca}_{0.80}\text{Ce}_{0.20}\text{ZrTi}_{1.60}\text{Fe}_{0.40}\text{O}_7$  (labelled as Fe). Below: spectra of the  $\text{CeO}_2$  and  $\text{CePO}_4$  reference compounds

perovskite phase would be expected to significantly decrease the overall durability of such wastefoms, given the lower chemical durability of this phase relative to the targeted zirconolite matrix. In a recent publication, we demonstrated that, when carefully dissolved under aggressive leaching media, the extent to which a Ce surrogate inventory was extracted into solution could be decreased by a factor of 100 through altering the batch formulation to precluding the formation of an ancillary perovskite phase [17].

In order to determine the prevalent Ce oxidation state, Ce  $L_3$ -XANES data were collected alongside the reference compounds  $\text{Ce}^{4+}\text{O}_2$  and  $\text{Ce}^{3+}\text{PO}_4$  (Fig. 5). Both RSPS samples exhibited a single intense asymmetric white line feature consistent with uniform  $\text{Ce}^{3+}$  speciation when compared qualitatively with the  $\text{CePO}_4$  reference compound (in which  $\text{Ce}^{3+}$  is ninefold coordinated to oxygen). No features consistent with  $\text{Ce}^{4+}$  were presented, confirming that the reducing environment imposed by the graphite SPS die was sufficient to completely reduce the available  $\text{Ce}^{4+}$  inventory to  $\text{Ce}^{3+}$ , and subsequently, promote Ce substitution within the perovskite phase. Moreover, linear combination analysis of Ce  $L_3$ -XANES data using the spectra of reference compounds was consistent with 100%  $\text{Ce}^{3+}$  speciation in the ceramic formulations. These data are consistent with previous studies, wherein sintering of Ce-substituted zirconolite under reducing conditions resulted in the formation of a significant perovskite fraction [18].

## Conclusions

Reactive spark plasma sintering has been utilised to synthesise two synthetic zirconolite wasteform materials, targeting  $\text{Ca}_{0.80}\text{Ce}_{0.20}\text{ZrTi}_{1.60}\text{Al}_{0.40}\text{O}_7$  and  $\text{Ca}_{0.80}\text{Ce}_{0.20}\text{ZrTi}_{1.60}\text{Al}_{0.40}\text{O}_7$ , with Ce included as a Pu surrogate. Despite the rapid (< 1 h total processing time per sample) formation of high-density ceramic monoliths, a significant portion of the phase assemblage was composed of Ce-rich perovskite, the stability of which was attributed to the complete reduction of the available Ce inventory to  $\text{Ce}^{3+}$ . These data form a useful contribution towards ongoing efforts to design suitable wasteform compositions for Pu immobilisation and optimisation of processing routes for these materials.

**Acknowledgments** We acknowledge financial support from the Nuclear Decommissioning Authority (NDA) and EPSRC under Grant Numbers EP/S01019X/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 [19]. Collection of the Ce  $L_3$ -edge XAS data was performed under the approval of the Photon Factory Advisory Committee (Proposal No. 2019G586); the support of Yoshihiro Okamoto (Japanese Atomic Energy Agency) and Noriko Usami (The High Energy Accelerator Research Organisation—Kō Enerugi Kasokuki Kenkyū Kikō) during the experiment is gratefully acknowledged.

**Data availability** The data that support the findings of this study are available from the corresponding author upon reasonable request.

## Declarations

**Conflict of interest** 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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