



Reactive spark plasma synthesis of $\text{CaZrTi}_2\text{O}_7$ zirconolite ceramics for plutonium disposition

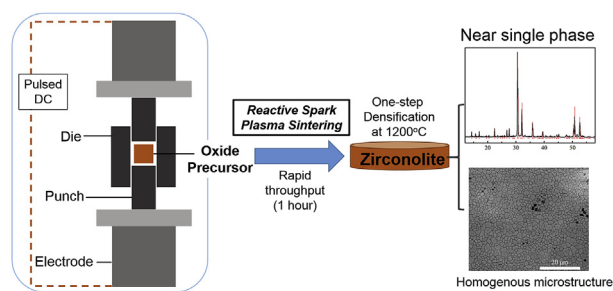
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HIGHLIGHTS

- Rapid fabrication of zirconolite $\text{CaZrTi}_2\text{O}_7$ ceramics was demonstrated by reactive spark plasma sintering (RSPS).
- Zirconolite ceramics could be fully densified at a temperature as low as $1200\text{ }^\circ\text{C}$ in 1h.
- Ceramics were formed with a controlled mean grain size of $1.88 \pm 0.55\text{ }\mu\text{m}$.

GRAPHICAL ABSTRACT



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ABSTRACT

Near single phase zirconolite ceramics, prototypically $\text{CaZrTi}_2\text{O}_7$, were fabricated by reactive spark plasma sintering (RSPS), from commercially available CaTiO_3 , ZrO_2 and TiO_2 reagents, after processing at $1200\text{ }^\circ\text{C}$ for only 1 h. Ceramics were of theoretical density and formed with a controlled mean grain size of $1.9 \pm 0.6\text{ }\mu\text{m}$. The reducing conditions of RSPS afforded the presence of paramagnetic Ti^{3+} , as demonstrated by EPR spectroscopy. Overall, this study demonstrates the potential for RSPS to be a disruptive technology for disposition of surplus separated plutonium stockpiles in ceramic wastefoms, given its inherent advantage of near net shape products and rapid throughput.

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Zirconolite, prototypically $\text{CaZrTi}_2\text{O}_7$, is proposed as an actinide host, for disposal of high level waste from nuclear fuel recycle, as a component of the Synroc composite ceramic, and as a tailored ceramic wasteform for excess civil and military plutonium [1–5]. For this purpose, synthetic and mineral zirconolites demonstrate the requisite stoichiometric flexibility, chemical durability, radiation tolerance, and long term stability in open geochemical environments [5,6].

The fabrication of zirconolite ceramics has been typically achieved by solid state synthesis, with a requirement for sintering at high temperature, typically $1400\text{--}1450\text{ }^\circ\text{C}$ [7]; sintering at $1200\text{ }^\circ\text{C}$, has been shown to yield porous specimens [8]. Zirconolite ceramics of near theoretical density may be produced by hot isostatic pressing (HIPing) at ca. $1250\text{ }^\circ\text{C}$, but with a requirement for containment in a canister e.g. of stainless steel [9].

Fabrication times for ceramic wastefoms produced by conventional sintering and HIPing are typically several hours. In contrast, spark plasma sintering (SPS) is a rapid method for consolidation of ceramics of refractory materials, including UO_2 , UN, and UC nuclear fuels [10–12]. In SPS, the material to be sintered

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is subject to uniaxial pressure, typically within a graphite die, and rapid heating by application of pulsed electric current; the associated electric field may also assist sintering [13–15]. SPS is potentially advantageous for production of ceramic wasteforms since it achieves rapid consolidation of ceramic bodies at lower temperature, potentially reducing the volatilisation of radionuclides, compared to conventional sintering. However, this application of SPS was only recently demonstrated, although in a diversity of examples, including: $\text{CaZr}_{1-x}\text{Ce}_x\text{Ti}_2\text{O}_7$ zirconolite [16]; $\text{Ln}_2(\text{Ti,Zr})_2\text{O}_7$ pyrochlores [17–21]; hollandite-rich ceramics [22]; $\text{CaTh}(\text{PO}_4)_2$, [23]; iodoapatites, [24–26]; and glass-composites [27].

Here, we demonstrate application of SPS to the rapid fabrication of high quality $\text{CaZrTi}_2\text{O}_7$ ceramics, from commercially available mixed metal oxides, as micron sized powders. Since the target ceramic is produced in a single step, with solid state reaction of reagents and sintering of the product phase occurring in parallel, we refer to this approach as *Reactive Spark Plasma Sintering* (RSPS). We distinguish this from *consolidation* of pre-synthesised powders employed in conventional SPS, as was generally applied in the examples above, including zirconolite ceramics [16]. In contrast, the RSPS approach has not been widely exploited and confined to relatively few examples, such as $\text{Pb}_{10}(\text{VO}_4)_{4.8}(\text{PO}_4)_{1.2}\text{I}_2$, $\text{Gd}_2\text{Zr}_2\text{O}_7$, and $\text{Lu}_2\text{Ti}_2\text{O}_7$ [19,21,24].

The raw materials used were CaTiO_3 (99%, ~325 mesh; Alfa Aesar), ZrO_2 (99%, 5 μm , Aldrich) TiO_2 – anatase ($\geq 99\%$, ~325 Mesh; Aldrich). CaTiO_3 , ZrO_2 and TiO_2 with a mole ratio of 1:1.025:1 were mixed by planetary milling for 20 min using zirconia media and isopropanol as a carrier fluid. The slurry was then dried overnight at 85 °C. An excess of ZrO_2 was utilised, relative to the ideal stoichiometric composition, since, in our experience, this results in near single phase materials.

Reactive Spark Plasma Sintering (RSPS) of zirconolite utilised 3 g of the oxide precursors, loaded into a cylindrical graphite die (diameter 20 mm), with thin graphite foil spacers to obtain a more uniform current flow. An HP-D 1050 SPS system (FCT Systeme GmbH) was used to process materials; samples were ramped to 900–1200 °C, at 50 °C/min followed by a dwell time, under uniaxial pressure of 15 MPa or 50 MPa. The reaction/sintering time was 10 min or 30 min; samples were cooled to room temperature at natural rate. The graphite foil and surface contamination was removed by light grinding with SiC paper.

Solid state synthesis of zirconolite was investigated by reaction sintering of oxide precursors at 900–1300 °C for 10 h under Ar gas (100 ml/min). Conventional sintering of zirconolite powder (from solid state reaction at 1300 °C) was achieved by forming green pellets of 20 mm × 10 mm (diameter × height) under uniaxial pressure of 50 MPa; these were sintered at 1450 °C for 10 h in air. All such processing used a ramp rate of 5 °C/min from/to room temperature.

Microstructures were observed using scanning electron microscopy (SEM; Inspect F50, FEI) on fracture or polished surfaces with a thermal etch (0.25 μm finish using SiC and diamond polishing media; thermal etch at 1100 °C for 1 h in air). Grain size determinations were made on >500 grains, using semiautomatic image analysis to calculate equivalent spherical diameters. The *Span* was calculated by $\text{Span} = (d_{0.9} - d_{0.1})/d_{0.5}$ to represent the width of grain size distribution. The bulk density of ceramics was determined using Archimedes' method by immersion in water. The phase assemblage was determined by X-ray diffraction (XRD; D2 Phaser, Bruker; Cu-K α radiation, Ni-filter). Rietveld quantitative phase analysis (QPA) of XRD data was performed using the GSAS software package [28]. Electron Paramagnetic Resonance (EPR) measurements were carried out on a Bruker EMX-8/2.7 spectrometer operating in the X-band at 9.37 GHz and 1.7 mW, at 77 K; powder samples were contained in Spectrosil tubes.

The XRD patterns for the products after RSPS at various temperatures with a dwell time of 10 min, are shown in Fig. 1. In comparison with the starting materials (Fig. S1 in Supporting Information), no obvious changes could be seen in the product after heat treatment at 900 °C. For the product heat-treated at 1000 °C and 1100 °C, characteristic (221)/(40 $\bar{2}$) and (004) reflections of $\text{CaZrTi}_2\text{O}_7$ (2M phase; C2/c) were apparent at $2\theta = 30.5^\circ$ and 32.0° , respectively. The relative intensity of these reflections increased with increasing temperature, indicating increased yield of zirconolite, however, substantial unreacted CaTiO_3 , TiO_2 , and ZrO_2 remained. Near single phase zirconolite was obtained after heat treatment at 1200 °C, with trace residual CaTiO_3 and ZrO_2 . No other ternary oxides could be identified after reaction at any temperature. The XRD patterns from the powdered bulk material and polished ceramic surface, after removal of the graphite foil, showed no significant difference (Fig. 1d and e, respectively).

For comparison, the solid state synthesis of zirconolite was investigated under argon atmosphere. The phase assemblage, as a function of reaction temperature, was very similar to that to RSPS (compare Fig. S2). In particular, near single phase zirconolite was only obtained at 1200 °C or 1300 °C, and was observed to be in equilibrium with CaTiO_3 , TiO_2 and ZrO_2 at lower temperature; no other ternary oxides were identified. These results are consistent with the phase diagram of the $\text{CaO-ZrO}_2\text{-TiO}_2$ system in air [29] and suggest that the mechanism of the conventional solid state and RSPS reactions are identical. However, inspection of relative reflection intensities in the XRD patterns, showed that the zirconolite yield is reduced at lower processing temperatures in RSPS, compared to solid state synthesis, due to the short processing time and kinetic limitations.

SEM observations (backscattered electron images) of the fracture surface of RSPS zirconolite ceramics processed at 1100 °C and 1200 °C at 15 MPa, are shown in Fig. S3 and Fig. S4. Comparison of these microstructures revealed considerable porosity, observed as black contrast, in the sample processed at 1100 °C, which was all but eliminated after processing at 1200 °C. In these microstructures, the zirconolite phase appeared as mid grey contrast with residual ZrO_2 evident as bright contrast (consistent with XRD and

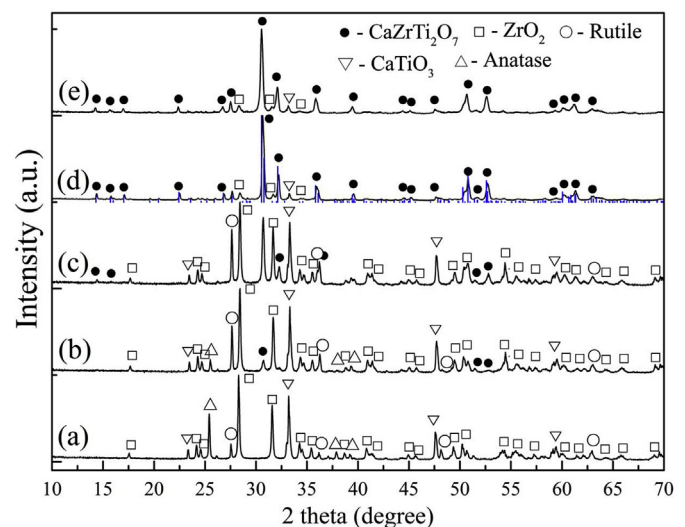


Fig. 1. XRD patterns of the products of RSPS at 900 °C (a), 1000 °C (b), 1100 °C (c), 1200 °C (d and e); patterns (a)–(d) were acquired from bulk powder specimens, whereas (e) was acquired from a polished ceramic surface; vertical blue lines are the reference diffraction pattern for zirconolite from Ref. [4]. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

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