



# A preliminary investigation of the molten salt mediated synthesis of Gd<sub>2</sub>TiO<sub>5</sub> ‘stuffed’ pyrochlore

D. A. Austin<sup>1</sup> · M. Cole<sup>1</sup> · M. C. Stennett<sup>1</sup> · C. L. Corkhill<sup>1</sup> · N. C. Hyatt<sup>1</sup>

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## Abstract

Refractory ‘stuffed’ pyrochlores such as Gd<sub>2</sub>TiO<sub>5</sub> are of interest for nuclear applications, including as matrices for actinide disposition and as neutron absorbers in control rods. Here, we report the results of a preliminary comparative investigation of the synthesis of Gd<sub>2</sub>TiO<sub>5</sub> by molten salt and conventional solid-state synthesis. We show that synthesis of Gd<sub>2</sub>TiO<sub>5</sub> proceeds from the pyrochlore phase Gd<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> which is first formed as a kinetic product. Molten salt synthesis afforded single phase Gd<sub>2</sub>TiO<sub>5</sub> at 1300 °C in 2 h, via a template growth mechanism, and is effective for the synthesis of these refractory materials. This work demonstrates molten salt mediated synthesis of ‘stuffed’ pyrochlore for the first time.

## Introduction

The fabrication of single phase ceramics is typically achieved through the use of Solid State Synthesis (SSS) methods, wherein a reaction between metal oxides precursors occurs. To enhance the solid-state diffusion necessary to produce single phase products, a combination of repeated milling and reactions at high temperatures for long durations is often necessary [1]. High temperature processing may yield large grain sizes which are an undesirable characteristic for high strength ceramic materials, and lead to non-stoichiometric products, due to the loss of volatile constituents. Issues such as these, along with the time and energy consumption of SSS methods, have motivated the development of alternative synthesis methods such as the co-precipitation, sol–gel or Molten Salt Synthesis (MSS) methods, which proceed at comparatively lower temperature.

The MSS method of synthesis exploits a salt, or a eutectic mixture of salts, which will melt at low temperature to create a liquid medium to assist in the diffusion of reactants [2–4]. MSS has been applied to the synthesis of lanthanide titanate pyrochlores at lower reaction temperatures and in shorter time scales, compared to conventional SSS. In MSS the rapid, low temperature formation of single phase products

is typically achieved through either solution-precipitation or solution-diffusion mechanisms [1, 3]. The relative dissolution rate of the reactants determines which process is dominant. Solution-precipitation is achieved when the dissolution rates of the reactants are comparable, allowing both reactants to dissolve into the molten salt creating a high degree of supersaturation, prior to precipitation of the product phase [1, 5, 6]. Solution-diffusion, also referred to as template growth, involves a mechanism wherein the dissolution rate of one the reactants is significantly higher than that of the other. As the more soluble reactant dissolves into the salt medium it diffuses onto the surface of the less soluble reactant and reacts to form the target product [1]. This mechanism can also be used to control particle morphology and size.

In this preliminary study, we investigate the efficacy of MSS of Gd<sub>2</sub>TiO<sub>5</sub> ‘stuffed’ pyrochlore, to assess the potential advantages over conventional SSS. Gd<sub>2</sub>TiO<sub>5</sub> is one member of the Ln<sub>2</sub>TiO<sub>5</sub> (Ln = La... Lu) system, which are often termed as ‘stuffed pyrochlores’ due to the additional lanthanide incorporated onto the B-site of the parent pyrochlore structure (the composition may be expressed as Ln<sub>2</sub>(Ti<sub>2-x</sub>Ln<sub>x</sub>)O<sub>7-x/2</sub> (x = 0.67)) [7]. Typically, the B site occupancy is within the range 0 ≤ x ≤ 0.67 [8]. This family of titanate ceramics have been proposed as potential waste forms for actinide wastes because of their high tolerance to radiation damage, physical properties and chemical flexibility [9]. Ln<sub>2</sub>TiO<sub>5</sub> ‘stuffed’ pyrochlores exhibit different structures dependant on the size of the lanthanide, temperature and pressure used during synthesis as well as cooling

✉ D. A. Austin  
daaustin1@sheffield.ac.uk

<sup>1</sup> NucleUS Immobilisation Science Laboratory, Department of Materials Science and Engineering, The University of Sheffield, Sheffield S1 3JD, UK

regime.  $\text{Gd}_2\text{TiO}_5$  crystallises in an orthorhombic structure (*Pnma*), comprising a framework of intersecting columns of edge sharing  $\text{LnO}_7$  polyhedra, with Ti cations occupying interstices within the tunnels forming  $\text{TiO}_5$  square pyramids [10]. The range of “stuffing” reported in  $\text{Gd}_2(\text{Ti}_{2-x}\text{Gd}_x)\text{O}_{7-x/2}$  is  $0 \leq x \leq 0.67$  [11]; this work targets the composition with  $x = 0.67$ .

## Experimental procedure

$\text{Gd}_2\text{O}_3$  and  $\text{TiO}_2$  were used as the reagents for MSS and SSS of  $\text{Gd}_2\text{TiO}_5$ . The materials were dried at 800 °C and 180 °C, respectively, overnight. Stoichiometric amounts of the reagents were batched to 10 g. One batch for SSS was planetary ball milled (Pulverisette 6, Fritsch) at 500 rpm, for 15 min, using isopropanol as the carrier fluid (Sialon pot and media). The resulting powder slurry was dried at 80 °C overnight and passed through a 250  $\mu\text{m}$  sieve. 0.5 g samples were then uniaxially pressed as 13 mm pellets (3 tonnes applied for 1 min). Green pellets were reacted at 700–1500 °C, in 100 °C intervals, for 24 h. The heating and cooling rates were 5 °C/min.

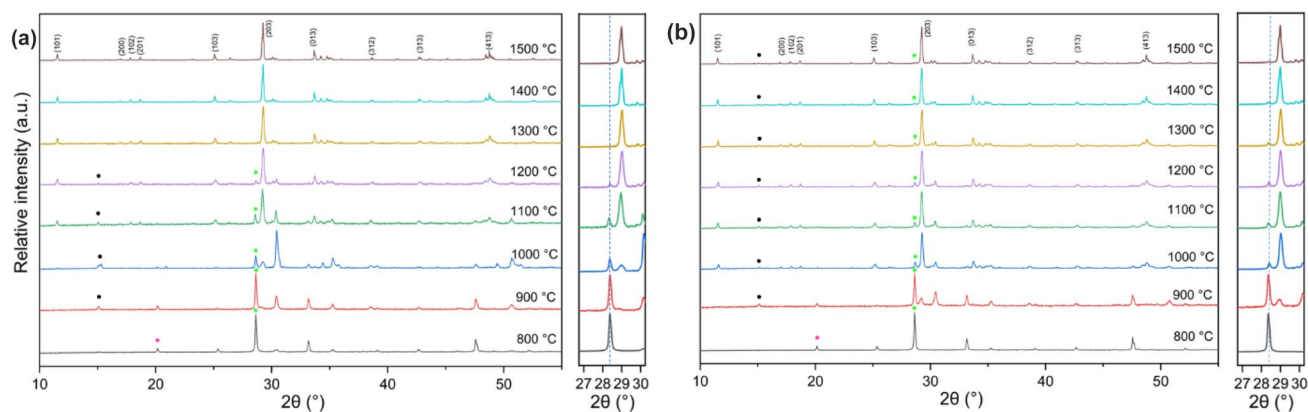
For MSS, the molten salt flux of NaCl:KCl was added at an equimolar eutectic ratio (1:1 mol NaCl:KCl; dried at 110 °C), with a 7:1 mol ratio of molten salt to ceramic precursor, as previously shown to be effective [12]. The salt and precursor mixture were milled together using the same planetary mill as for the SSS feedstock, but at a lower rotational frequency and duration; 250 rpm for 5 min, to minimise size reduction of the reagents. Cyclohexane was used as the carrier fluid. Green pellets were produced as described above and reacted at 700–1500 °C, in 100 °C intervals, for 2 h. The heating and cooling rates were 5 °C/min. The product

was washed with ultrapure water to remove the molten salt medium and the powder collected via vacuum filtration.

X-ray powder diffraction analysis of reagents and products utilised a Bruker D2 Phaser instrument, operating with Cu K $\alpha$  radiation and a Lynxeye solid-state detector (40 mA and 45 kV; step size of 0.02°, counting 1.8 s per step). Diffraction data were analysed for phase identification with the ICDD PDF-4+ database and ICSD sources. The PDF numbers for each phase are as follows:  $\text{Gd}_2\text{O}_3$  (01-074-3085),  $\text{TiO}_2$  (01-076-0317),  $\text{Gd}_2\text{Ti}_2\text{O}_7$  (01-072-9773) and  $\text{Gd}_2\text{TiO}_5$  (21-0342) and the lattice parameters were refined through the use of the DIFFRAC.SUITE TOPAS software [13]. Samples studied through a Scanning Electron Microscope (SEM) were prepared by mixing powder material with acetone in a 7 ml vial. The vials were placed in an ultrasonic bath for 10 min to break up any agglomerates. Samples were withdrawn from the suspension using a disposable Pasteur pipette and dropped onto a carbon sticky pad on an aluminium stub. The solvent was allowed to evaporate prior to being carbon coated. SEM micrographs were obtained with an FEI Inspect F50 operating in secondary electron (SE) mode. The accelerating voltage and spot size ranged were 20 kV and 5.0, respectively. A working distance of approximately 10 mm was used throughout.

## Results and discussion

Figure 1 shows the XRD patterns of the products from MSS after reaction for 2 h at the target temperature. There was no evidence of reflections associated with either NaCl or KCl, indicating that the salt eutectic has been successfully removed. As assessed from the relative intensity of reflections,  $\text{Gd}_2\text{TiO}_5$  and  $\text{Gd}_2\text{Ti}_2\text{O}_7$  (pyrochlore) were formed at



**Fig. 1** XRD patterns of products from **a** MSS for 2 h and **b** SSS for 24 h, at stated temperatures. Labels correspond to reflections associated with a specific phase: Primary diagnostic reflections of reagents and accessory phases are denoted by: Solid green circles— $\text{Gd}_2\text{O}_3$

(222), Solid pink circles— $\text{TiO}_2$  (Rutile) (110), Solid black circles— $\text{Gd}_2\text{Ti}_2\text{O}_7$  (111), Miller indices indicate the major reflections of  $\text{Gd}_2\text{TiO}_5$  (Orthorhombic). The inserts highlight the  $\text{Gd}_2\text{O}_3$  (222) reflections

800–900 °C, with significant residual Gd<sub>2</sub>O<sub>3</sub>. At 1100 °C, Gd<sub>2</sub>TiO<sub>5</sub> was predominant, with Gd<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> and Gd<sub>2</sub>O<sub>3</sub> reflections diminished in relative intensity. At 1300 °C, all reflections were indexed to Gd<sub>2</sub>TiO<sub>5</sub> and the product was apparently single phase. The XRD patterns for materials produced by SSS, Fig. 1, demonstrated a similar phase assemblage as a function of temperature, after reaction at the target temperatures for 24 h. Formation of Gd<sub>2</sub>TiO<sub>5</sub> was first observed at 900 °C after SSS (with Gd<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> and residual Gd<sub>2</sub>O<sub>3</sub>) and was the major phase at 1000 °C. However, trace Gd<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> and Gd<sub>2</sub>O<sub>3</sub> remain present even in specimens heated to 1500 °C, as demonstrated, for example, by the apparent (222) reflection of Gd<sub>2</sub>O<sub>3</sub> ( $2\theta=29^\circ$ ), which is highlighted in Fig. 1, and (111) reflection of Gd<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> ( $2\theta=15^\circ$ ). Evidently, additional heat treatments would be needed to generate a single phase product by SSS, at 1300 °C or higher. In contrast, single phase Gd<sub>2</sub>TiO<sub>5</sub> can be obtained by MSS at 1300 °C for only 2 h. The refined lattice parameters for

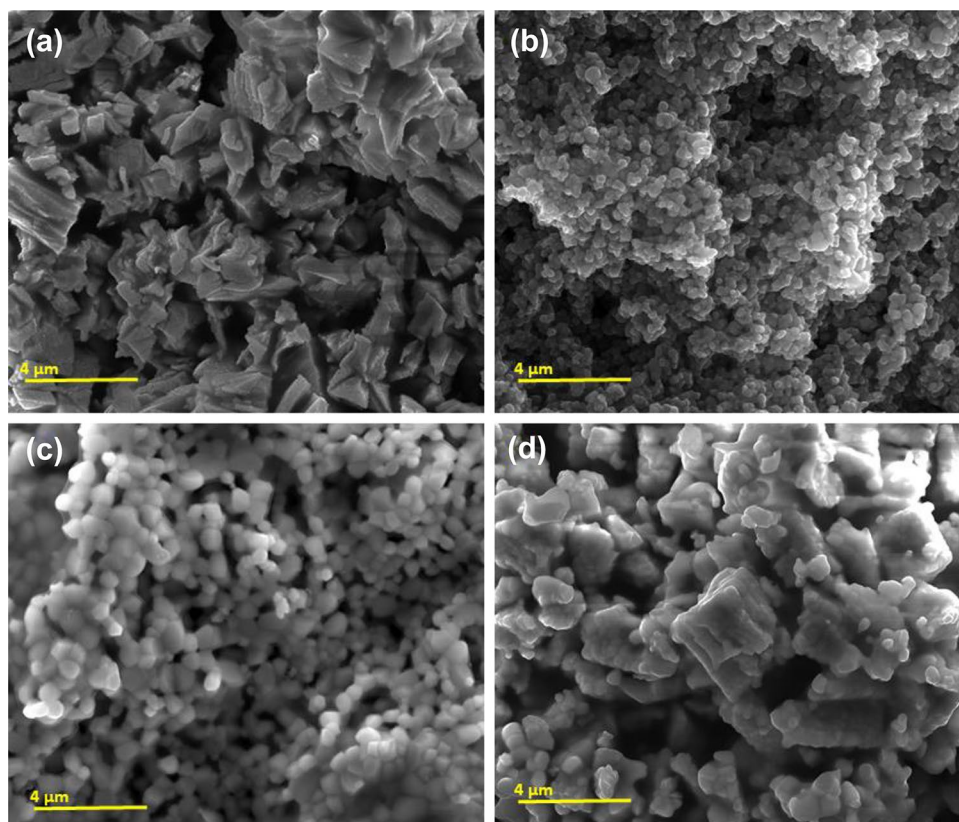
Gd<sub>2</sub>TiO<sub>5</sub>, for both synthesis routes, are in good agreement with literature, Table 1. Additionally, the QPA values confirm the presence of excess Gd<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> and Gd<sub>2</sub>O<sub>3</sub> in Gd<sub>2</sub>TiO<sub>5</sub> (SSS) synthesised at 1500 °C and the absence of either phases in Gd<sub>2</sub>TiO<sub>5</sub> (MSS).

SEM micrographs of Gd<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> reagents, Gd<sub>2</sub>TiO<sub>5</sub> (MSS) and Gd<sub>2</sub>TiO<sub>5</sub> (SSS) are shown in Fig. 2. Inspection of these SEM images show that the TiO<sub>2</sub> and Gd<sub>2</sub>TiO<sub>5</sub> prepared through MSS had an average size of ~1 μm, and, moreover, a similar faceted morphology. In contrast, the Gd<sub>2</sub>O<sub>3</sub> and Gd<sub>2</sub>TiO<sub>5</sub> (SSS) particles were larger, typically 3–4 μm and 2–3 μm, respectively, comprising a more angular morphology. The striking similarity of the particulate morphology and dimensions of the Gd<sub>2</sub>TiO<sub>5</sub> product and TiO<sub>2</sub> reagent, strongly implies a “template growth” mechanism of molten salt mediated synthesis, consistent with that previously reported for closely related Ln<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> pyrochlores [4, 10] The larger size of the Gd<sub>2</sub>TiO<sub>5</sub> particles produced by SSS reflect

**Table 1** Showing the refined lattice parameters and QPA values of primary and accessory phases for Gd<sub>2</sub>TiO<sub>5</sub> synthesised at 1500 °C through either SSS or MSS routes

Gd <sub>2</sub> TiO <sub>5</sub>	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	<i>V</i> (Å <sup>3</sup> )	Gd <sub>2</sub> TiO <sub>5</sub>		Gd <sub>2</sub> Ti <sub>2</sub> O <sub>7</sub>		Gd <sub>2</sub> O <sub>3</sub>	
					wt%	±	wt%	±	wt%	±
SSS	10.4811 (2)	3.7575 (5)	11.3216 (2)	446.01 (14)	94.47	0.44	3.27	0.33	2.26	0.24
MSS	10.4816 (3)	3.7574 (9)	11.3245 (3)	445.87 (19)	100	–	–	–	–	–
Gd <sub>2</sub> TiO <sub>5</sub> [14]	10.46	3.75	11.31	446.00	–	–	–	–	–	–

**Fig. 2** SEM Micrographs of reagent materials and resultant products collected in secondary electron mode. **a** Gd<sub>2</sub>O<sub>3</sub>, **b** TiO<sub>2</sub>, **c** Gd<sub>2</sub>TiO<sub>5</sub> (MSS: 1300 °C 2 h) and **d** Gd<sub>2</sub>TiO<sub>5</sub> (SSS: 1500 °C 24 h)



the process of solid-state diffusion and growth at comparatively higher temperature. Size reduction was minimised during the milling stage of preparing the MSS samples so as to rule out that the reduction in the size of the larger  $Gd_2O_3$  reagents produced the observed size of the  $Gd_2TiO_5$  particles prepared by MSS. The very low solubility of  $TiO_2$  in alkali chloride salts has been established in several previous studies of the synthesis of ternary titanate materials, leading to a common “template growth” mechanism that has been exploited to produce titanate materials as nanopowders and with rod-like morphologies, directed by the  $TiO_2$  template [15–18]. In the present study, the solubility of  $TiO_2$  is also expected to control the synthesis mechanism by “template growth” resulting in a product with morphological and dimensional characteristics of the  $TiO_2$  reagent.

Comparing the MSS and SSS routes, the pyrochlore phase is the first to be formed below 900 °C, giving way to the ‘stuffed’ pyrochlore  $Gd_2TiO_5$  at 1000 °C as the major phase, with single phase  $Gd_2TiO_5$  achieved at 1300 °C by MSS. The pyrochlore phase is apparently a kinetic product in the synthesis of ‘stuffed’ pyrochlores by MSS and SSS below 1300 °C; subsequent reaction with  $Gd_2O_3$  yields the desired ‘stuffed’ pyrochlore. As far as we are aware, this is the first such mechanistic understanding developed with regard to the synthesis of ‘stuffed’ pyrochlores. It is evident that molten salt mediated diffusion is effective in achieving the synthesis of single phase  $Gd_2TiO_5$  at much lower temperature and time, 1300 °C for 2 h, compared to SSS which did not afford a single phase product even at 1500 °C for 24 h.

## Conclusion

This preliminary investigation has determined that the  $Gd_2Ti_2O_7$  pyrochlore phase forms as the kinetic product in the synthesis of  $Gd_2TiO_5$  ‘stuffed’ pyrochlore. The MSS method effectively yields single phase  $Gd_2TiO_5$  at 1300 °C for 2 h, via a template growth mechanism, in which  $TiO_2$  acts as the initial nucleating substrate. In contrast, SSS failed to yield single phase  $Gd_2TiO_5$  after reaction at 1500 °C for 24 h. Given the highly refractory nature of the  $Ln_2TiO_5$  pyrochlores, and their potential application in nuclear environments, MSS is therefore clearly worthy of further investigation as a route to the synthesis of this family of ceramic materials.

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