



# Low-temperature reactive hot-pressing of cerium-doped titanate composite ceramics and their aqueous stability

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## Abstract

Reactive hot-pressing was scarcely applied to fabricate titanate ceramic waste forms designed for immobilizing high-level radioactive waste (HLW). However, compared with non-reactive processes, there is an advantage of producing high-density ceramics at reduced temperatures by reactive hot-pressing.  $\text{Ce}^{\text{IV}}$ -doped titanate composite ceramics with relative densities in excess of 99% were prepared by reactive hot-pressing at temperature as low as 1150 °C and pressure of 30 MPa for 1–4 h. The results show that low-temperature densification of the composite ceramics might be attributed to the plastic deformation under hot-pressing condition. In addition, aqueous stability testing was carried out using the standard MCC-1 static leach test method. The results demonstrate that the normalized elemental leach rate of Ca, Ce and Zr were fairly constant in a low value below  $5 \times 10^{-2} \text{ g m}^{-2} \text{ d}^{-1}$ ,  $7 \times 10^{-6} \text{ g m}^{-2} \text{ d}^{-1}$  and  $6 \times 10^{-6} \text{ g m}^{-2} \text{ d}^{-1}$  after 21 d.

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## 1. Introduction

Synroc-A and -B were first developed by Ringwood et al. for immobilization of high-level radioactive waste (HLW) from nuclear fuel reprocessing.<sup>1</sup> Since then, various Synroc, such as Synroc-C, -D, -E and -F, has been extensively studied as potential candidates for immobilization of a range of different fission products,<sup>2–12</sup> especially Synroc-C.<sup>12–15</sup> In the past, the main research work focused on the zirconolite or monazite for immobilization of different actinide (Ac) or rare earth (RE).<sup>16–23</sup> However, few studies were carried out for immobilization of Ac or RE enter into each phases in multi-component composite material.

A novel titanate composite material was presented firstly in our group.<sup>24</sup> The titanate composite materials were prepared by solid-state reaction method at 1230 °C for 30 min using inexpensive natural zirconite as raw materials. Due to close ionic radius, analogous ion type, alike coordination geometries and similar chemical property,  $\text{Ce}^{\text{IV}}$  is used to simulate

tetravalence actinides, such as U, Pu, Np, Am and Cm.<sup>16,25,26</sup> Research shows that  $\text{Ce}^{\text{IV}}$  can incorporate into the Zr or Ca sites in zirconolite ( $\text{CaZr}_{1-x}\text{Ce}_x\text{Ti}_2\text{O}_7$ ,  $x=0-0.4$ ), sphene ( $\text{Ca}_{1-2y}\text{Ce}_y\text{TiSiO}_5$ ,  $y=0-0.2$ ) and perovskite ( $\text{Ca}_{1-2z}\text{Ce}_z\text{TiO}_3$ ,  $z=0-0.1$ ), respectively.<sup>16–19,27,28</sup>

Low-temperature densification has already become one of the focuses to fabricate ceramic materials.<sup>29–33</sup> Reactive hot-pressing is good method to synthesize low-temperature densification ceramics.<sup>34,35</sup> Ac-doped zirconolite ceramic prepared by hot-pressing a reactive  $\text{CaO-ZrO}_2\text{-TiO}_2\text{-AcO}_x$  precursor at 1250 °C and 18 MPa for 2 h has been reported.<sup>16</sup> However, the research studies dealing with reactive hot-pressing of titanate composite ceramics have been quite few. In this paper, we used Ce to simulate quadrivalence actinides incorporated in the titanate composite ceramic which was fabricated by reactive hot-pressing.

Aqueous stability is a very important consideration for chemical durability of waste form when it contact with aqueous solutions in the safe disposal of nuclear waste in a geological repository.<sup>12,18,25,36</sup> At present, the aqueous stability testing was carried out using following methods: the standard product consistency test (PCT)<sup>37</sup> and the Materials Characterization Center (MCC) standard MCC-1, -2, -3 and -4 leach test.<sup>12,18,38,39</sup> The

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results show that the normalized elemental rates of Pu and Zr incorporated in Synroc-C consolidated by hot isostatic pressing are below  $10^{-5} \text{ g m}^{-2} \text{ d}^{-1}$  after 28 d.<sup>12</sup> To evaluate the aqueous stability of the  $\text{Ce}^{\text{IV}}$ -doped titanate composite ceramics, the MCC-1 test was carried out at  $90^\circ\text{C}$  in deionized water in this study.

## 2. Experimental methods

The starting powders were natural zirconite ( $\text{ZrSiO}_4$ , 95.2 wt.%, obtained in Australia), calcium carbonate ( $\text{CaCO}_3$ , AR, Kermel Chemical Reagents Development Center, Tianjing, China), titanium dioxide ( $\text{TiO}_2$ , AR, Sinopharm Chemical Reagents Co., Ltd., Shanghai, China) and cerium oxalate decahydrate ( $\text{Ce}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$ , 98 wt.%, AR, Ai Keda Chemical Technology Co., Ltd., Chengdu, China). They were mixed by ball-milling in ethanol (the mass ratio of powder, ball and ethanol is 1:2:1) at 350 rpm for 10 h using the mass ratio of  $\text{ZrSiO}_4$ ,  $\text{CaCO}_3$ ,  $\text{TiO}_2$  and  $\text{Ce}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$  in 20.76 wt.%, 22.97 wt.%, 33.21 wt.% and 23.06 wt.%, respectively. Ball-milling was carried out by QM-3SP2 (Nanjing University Instrument Plant) planetary ball mill equipment and used  $\text{ZrO}_2$  ball ( $\Phi 8$ ,  $\Phi 5$  and  $\Phi 2$  mm) and PTFE jar ( $\Phi 100$  mm  $\times$  14 mm). The ethanol was removed using dryer at  $80^\circ\text{C}$  and the dried powders were then sieved to 100 meshes. The powders with heat treating at  $1000^\circ\text{C}$  for 30 min in air were sieved to 100 meshes again and mixed PVA with the concentration of 5–10 wt.% for granulation. The mass ratio of starting powder and PVA is about 10:1. In addition, all the mixture powders were heated in air as excess oxygen can maintain cerium in +4 oxidation state.<sup>40</sup> The granules were selected by sieved between 20 and 100 meshes and pressed in a steel mold with diameter of 20 mm at 30 MPa. The extruded articles were heated in muffle furnace for detaching PVA. Lastly, the green body was sintered in graphite die and a pressure of 30 MPa was carried out at period of holding time. Two series samples were prepared: (1) 1100, 1125, 1150, 1175 and 1120  $^\circ\text{C}$  for 0.5 h; (2) 1150  $^\circ\text{C}$  for 0.5, 1, 2 and 4 h. The bulk densities of sintered ceramics were measured using the Archimedes method. The final relative densities were determined as the ratio of experimental bulk densities divides theoretical ones calculated from the rule of mixtures based on the final phase content according to XRD and BSE analysis results. The theoretical densities of 2M- $\text{CaZrTi}_2\text{O}_7$ ,  $\text{CaTiSiO}_5$  and  $\text{CaTiO}_3$  were 4.440, 3.530 and  $4.036 \text{ g cm}^{-3}$ , which obtained from the related JCPDS Card 34-0167 (2M- $\text{CaZrTi}_2\text{O}_7$ ), JCPDS Card 25-0177 ( $\text{CaTiSiO}_5$ ) and JCPDS Card 42-0423 ( $\text{CaTiO}_3$ ).

Phase composition was determined by powder X-ray diffraction (XRD). Powder XRD analysis was conducted with an X'Pert PRO diffractometer using  $\text{Cu K}\alpha$  radiation. The microstructure of polished and fracture surface was observed by backscattered electron (BSE) and scanning electron microscopy (SEM), respectively. The chemical compositions of polished surfaces were then analyzed with energy-dispersive spectroscopy (EDS). BSE and SEM was conducted with an Ultra 55 instrument and fitted with an Oxford IE450X-Max80 EDS system.

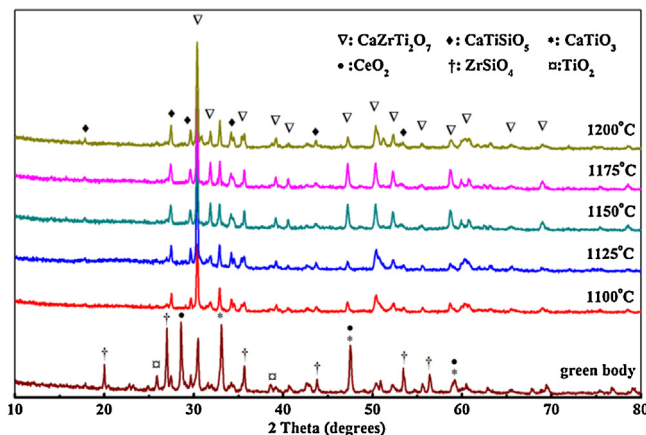


Fig. 1. Powder XRD patterns of the samples sintered at different temperatures.

Quantitative analyses of phases were carried out using Image por Plus 6.0 program.

Leaching test was carried out at  $90^\circ\text{C}$  in deionized water ( $\text{pH} = 7$ ) within PTFE for a series of eight test durations: 0–1, 1–3, 3–7, 7–14, 14–21, 21–28, 28–35 and 35–42 d. The sample sintered at  $1150^\circ\text{C}$  for 1 h was polished, washed and dried. The size of the leaching sample (column) is  $\Phi 20$  mm  $\times$  14 mm. The PTFE was washed by a complex process which is performed on ultrasonic treatment for 30 min immerse in 5 mol/L NaOH, 5 mol/L HCl and deionized water, successively. The leachates were collected for measuring the pH values and the consistence ( $c_i$ ) of Ce and Zr by inductively coupled plasma mass spectrometry (ICP-MS) analysis using an Agilent 7700  $\times$  spectrometer. The normalized elemental leach rate ( $\text{LR}_i$ ) was calculated according to:

$$\text{LR}_i = \frac{c_i \cdot V_l}{f_i \cdot A_s \cdot \Delta t}$$

where  $f_i$  is the mass fraction of element  $i$  in the sample,  $A_s$  is the geometric surface area of the sample,  $V_l$  is the volume of the leachates and  $\Delta t$  is the duration of the experiment in days. In this work, the value of  $A_s/V_l$  is about 0.1 for corresponding to the standard MCC-1 static leach test method.<sup>38</sup>

## 3. Results and discussion

### 3.1. XRD and BSE analyses

Powder XRD patterns of the samples sintered at different temperatures (1100, 1125, 1150, 1175 and 1120  $^\circ\text{C}$ ) for 0.5 h are shown in Fig. 1. The disappearance of  $\text{CeO}_2$ ,  $\text{ZrSiO}_4$  and  $\text{TiO}_2$  diffraction peaks in XRD patterns sintered at  $1100^\circ\text{C}$ , implies that the reaction amongst  $\text{CaTiO}_3$ ,  $\text{CeO}_2$ ,  $\text{ZrSiO}_4$  and  $\text{TiO}_2$  occurred below this temperature. The diffraction peaks of 2M- $\text{CaZrTi}_2\text{O}_7$  (JCPDS Card 34-0167),  $\text{CaTiSiO}_5$  (JCPDS Card 25-0177) and  $\text{CaTiO}_3$  (JCPDS Card 42-0423) are observed in XRD patterns sintered at 1100–1200  $^\circ\text{C}$ , shows that the compositions of primary crystalline phases are 2M-zirconolite, sphene and perovskite in the titanate composite ceramic. On the other hand, the intensities of XRD peaks of sphene and perovskite phases are identified scarcely alteration with the

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