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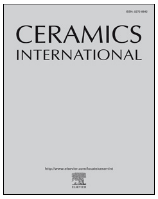

Phase evolution, microstructure and chemical stability of $Ca_{1\text{-}x}Zr_{1\text{-}x}Gd_{2x}Ti_2O_7$ ($0.0 \le x \le 1.0$) system for immobilizing nuclear waste

Yi-Bing Zhang[a,b], Jin Wang[a,b,*], Jun-Xia Wang[a], Yi Huang[a], Ping Luo[a], Xiao-Feng Liang[c], Hong-Bin Tan[a]

[a] School of Materials Science and Engineering, Southwest University of Science and Technology, Mianyang 621010, Sichuan, PR China
[b] Fundamental Science on Nuclear Wastes and Environmental Safety Laboratory, Southwest University of Science and Technology, Mianyang 621010, Sichuan, PR China
[c] Sichuan College of Traditional Chinese Medicine, Mianyang 621000, Sichuan, PR China

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ABSTRACT

In order to ascertain the structural relationship of zirconolite and pyrochlore for their potential application in HLW immobilization, the Gd-doped zirconolite-pyrochlore composite ceramics ($Ca_{1\text{-}x}Zr_{1\text{-}x}Gd_{2x}Ti_2O_7$) were systematically synthesized with $x = 0.0$–1.0 by traditional solid-phase reaction method. The phase evolution and microstructure of the as-prepared samples have been elucidated by XRD and Rietveld refinement, Raman spectroscopy, BSE-EDS and HRTEM analysis. The results showed that zirconolite-2M, zirconolite-4M, perovskite and pyrochlore, four phases were identified in $Ca_{1\text{-}x}Zr_{1\text{-}x}Gd_{2x}Ti_2O_7$ system and could be coexisted at $x = 0.4$ composition. With the increase of Gd^{3+} substitution, the phase evolution was followed by zirconolite-2M→zirconolite-4M→pyrochlore. It is illustrated that the phase transformation from zirconolite-2M to zirconolite-4M was promoted by the preferential substitution of Gd^{3+} for Ca^{2+}. And the solubility of Gd^{3+} in zirconolite-2M, zirconolite-4M and pyrochlore increased in sequence. The chemical stability test was also measured by the PCT leaching method. The normalized elemental release rates of Ca, Zr, Ti and Gd in $Ca_{1\text{-}x}Zr_{1\text{-}x}Gd_{2x}Ti_2O_7$ system were fairly low and in the range of $10^{-6}-10^{-8}\,g\,m^{-2}\,d^{-1}$, which indicated a potential ceramics composite ensemble of $CaZrTi_2O_7$-$Gd_2Ti_2O_7$ system for nuclear HLW immobilization.

1. Introduction

With the development of civilian nuclear power station and the retirement of military nuclear weapons in the last decades, the accumulated high level waste (HLW) needed to be processed urgently. Especially, the treatment and disposal of Pu and minor actinides (MA), such as Np, Am and Cm has become a major concern for the management of HLW because of their long half-lives and high radiotoxicity [1]. So far, separating and immobilizing them in a stable matrix like glass, glass-ceramic composites and ceramics [1–3] is the commonly accepted way. As the radionuclides could be incorporated in the crystal lattice of ceramics, the ceramic is the most stable form among the three above matrices. In addition, the proliferation resistance is also an important attribute of ceramics for immobilizing Pu [4]. Taking this advantage into consideration, the Synthetic Rock (SYNROC) had been proposed by Ringwood as futuristic alternate matrices for HLW immobilization, and many kinds of mineral analogue ceramics such as zirconolite, pyrochlore, perovskite and monazite [5–10] etc. were widely explored and investigated. Particularly, zirconolite and pyrochlore present promising potential for immobilizing Pu and MA [11,12] because their unique structure can incorporate a wide range of ions. Besides, zirconolite and pyrochlore possess superior properties in leaching resistance, radiation and thermal stabilities [6,7,11–17].

Zirconolite ($CaZrTi_2O_7$) structure is consisted of layers of Ti-O, Ca-O and Zr-O polyhedral sheets. This particular layered lattice possess sufficient space and compatibility to accommodate different kinds of radionuclides [17–19]. Zirconolite structure has various polymorphs like zirconolite-2M, zirconolite-3O, zirconolite-4M, et al. [20–22]. Usually, zirconolite-2M is the most common type and it can be transformed to other polymorphs in different situations [22,23]. Similarly, pyrochlore is generally expressed as the formula of $A_2B_2O_7$, in which A and B sites usually present 8- and 6-coordination, respectively [24]. The pyrochlore structure also can accommodate wide range of diversified actinides and MA due to its one-eighth deficiency of anion sites [6,7,17]. Upon the value of r_A/r_B ratio, perovskite related monoclinic type, ordered cubic pyrochlore type and disordered defect-fluorite type structures could be formed [25].

As major part of SYNROC, zirconolite and pyrochlore show great

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[*] Corresponding author at: School of Materials Science and Engineering, Southwest University of Science and Technology, Mianyang 621010, Sichuan, PR China.
E-mail address: wjin761026@163.com (J. Wang).

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potential application for HLW immobilization. However, the inter-substitution among cations between the two phases is inevitable due to their structural similarity [5,6,24]. Thus, the phase evolution caused by the mutual substitution and the solid solubility limits between the two phases are essential information for their practical applications [26]. At present, only few rare earth (RE, RE = Nd, Sm and Ce) ions and yttrium (Y) ion were used as doping ions to investigate the phase evolution of $CaZrTi_2O_7$-$A_2Ti_2O_7$ system [2,26–28]. In the RE-doped system, the preferential substitution of RE for Ca occurs due to the bigger ionic radii of three RE ions. However, the preferential substitution is not found in Y-doped system [28]. And the existence range of zirconolite-2M phase in the RE-doped system is slightly different [2,26,27].

Similarly, Gd as the trivalent rare earth, the ionic radii of Gd^{3+} is smaller than that of the other three RE^{3+}(Nd^{3+}, Sm^{3+} and Ce^{3+}) while bigger than Y^{3+}, it is worth to be used to investigate the preferential substitution and phase relationship of zirconolite-pyrochlore system. In addition, because of the high neutron capture cross-section of Gd and its widespread applications in nuclear waste immobilization, especially using $Gd_2Zr_2O_7$ and $Gd_2Ti_2O_7$ for immobilizing actinides and MA, it is essential to conduct the phase evolution behavior and the stability of Gd^{3+} in the zirconolite-pyrochlore system. In the present study, Gd^{3+} was employed to simulate the trivalent MA, the Gd-doped zirconolite-pyrochlore composite ceramics ($Ca_{1\text{-}x}Zr_{1\text{-}x}Gd_{2x}Ti_2O_7$) were prepared by traditional solid-phase reaction method. The phase evolution of the as-prepared samples from zirconolite-type $CaZrTi_2O_7$ to pyrochlore-type $Gd_2Ti_2O_7$ structure was investigated systematically by XRD, Rietveld refinement, Raman, BSE-EDX and HRTEM analysis. Moreover, the chemical stability was also evaluated by the PCT leaching method in this manuscript.

2. Experimental

2.1. Preparation of $Ca_{1\text{-}x}Zr_{1\text{-}x}Gd_{2x}Ti_2O_7$ powders and bulk ceramics

The $Ca_{1\text{-}x}Zr_{1\text{-}x}Gd_{2x}Ti_2O_7$ ($0.0 \le x \le 1.0$) composites were synthesized by traditional solid-phase reaction method from AR grade powders of $CaCO_3$, ZrO_2, Gd_2O_3, and TiO_2 (Shanghai Aladdin Co. Ltd., purity ≥ 99.9%). For the pretreatment of raw materials, $CaCO_3$ powder was dried at 200 °C for 4 h and other oxides were heated at 900 °C for 10 h. After that, the stoichiometric amounts of reactants were weighed and mixed by ball milling for 4 h. Then the mixture powders were calcined at 1300 °C for 36 h to synthesize the corresponding compounds. The resultant powders were pressed into pellets with a diameter of 12 mm at 6 MPa of pressure. Finally, the pellets were sintered at 1400 °C for 48 h. The specific formulas and the preparation details of the samples are listed in Table 1.

2.2. Characterization

The crystalline phases of the sintered bulk samples were characterized using a X-ray diffractometer (XRD, X′pert PRO. PANalytical B.V., The Netherlands) with CuKα (λ = 1.5406 Å) radiation over the 2θ range of 10–90° at a step size of 0.03°. The obtained XRD patterns were refined by Rietveld method using Fullprof suite program (a pseudo shape function was chosen in the Rietveld refinement method). Room-temperature Raman spectra were collected with the Renishaw in Via Raman spectrometer (Raman, Renishaw PLC, Gloucestershire, UK) equipped with the Argon ion laser (514 nm). The microstructures and compositions of the ceramics were determined by backscattering scanning electron microscopy (BSE, MAIA3LMU, TESCAN, Czech Republic) with an energy dispersive spectroscope (EDS, Octane Super, AMETEK EDAX, USA) and high-resolution transmission electron microscopy (HRTEM, Carl Zeiss SMT Pte. Ltd., Germany).

Table 1
Sample preparation details for $Ca_{1\text{-}x}Zr_{1\text{-}x}Gd_{2x}Ti_2O_7$ ($0.0 \le x \le 1.0$) series compositions.

x	Composition	x = (mol)				Temperature (°C)	
		$CaCO_3$	ZrO_2	TiO_2	Gd_2O_3	Powders	Bulks
0.0	$CaZrTi_2O_7$	1	1	2	0	1300	1400
0.2	$Ca_{0.8}Zr_{0.8}Gd_{0.4}Ti_2O_7$	0.8	0.8	2	0.2	1300	1400
0.4	$Ca_{0.6}Zr_{0.6}Gd_{0.8}Ti_2O_7$	0.6	0.6	2	0.4	1300	1400
0.5	$Ca_{0.5}Zr_{0.5}Gd_{1.0}Ti_2O_7$	0.5	0.5	2	0.5	1300	1400
0.6	$Ca_{0.4}Zr_{0.4}Gd_{1.2}Ti_2O_7$	0.4	0.4	2	0.6	1300	1400
0.8	$Ca_{0.2}Zr_{0.2}Gd_{1.6}Ti_2O_7$	0.2	0.2	2	0.8	1300	1400
1.0	$Gd_2Ti_2O_7$	0	0	2	1	1300	1400

2.3. Chemical stability

The chemical stability of $Ca_{1\text{-}x}Zr_{1\text{-}x}Gd_{2x}Ti_2O_7$ (x = 0.2, 0.4, 0.5 and 0.8) bulk ceramics was assessed by the product consistency test method B (PCT, ASTM C1285-14) [29]. The 100–200 mesh powders obtained from the sintered bulk samples were used for leaching test. After been washed by deionized water and absolute ethanol, the powders were sealed in teflon containers with 10 times value of deionized water (ml per gram). Then the containers were put into an oven at 90 °C for 7 days. The amounts of Ca, Zr, Ti and Gd in the leachates were measured by inductively coupled plasma-mass spectrometry (ICP-MS) using an Agilent 7700× spectrometer (Agilent Technologies Inc., Santa Clara, CA, USA). The normalized elemental release rates (NR_i, $g\,m^{-2}\,d^{-1}$) were calculated by the equation below:

$$NR_{\mathrm{i}} = \frac{\mathrm{C_i} \cdot V_{\mathrm{l}}}{\mathrm{f}_i \cdot SA \cdot \Delta \mathrm{t}}$$

Where C_i (g/m^3) represents the leaching concentration of i, f_i (wt%) represents the mass fraction of i in the sample, SA (m^2) represents the geometric surface area of the specimen, V_l (m^3) represents the leachate volume and Δt (d) represents the leaching time.

3. Results and discussion

3.1. XRD analysis

The phase evolution of the $Ca_{1\text{-}x}Zr_{1\text{-}x}Gd_{2x}Ti_2O_7$ ($0.0 \le x \le 1.0$) ceramics was investigated by XRD and the results were shown in Fig. 1. It was found that the zirconolite-2M and zirconolite-4M phases are examined in the range of $0.0 \le x \le 0.4$ and $0.2 \le x \le 0.5$ compositions, respectively. While the cubic ordered pyrochlore phase is formed for $x \ge 0.4$ compositions with the increase of Gd^{3+} substitution.

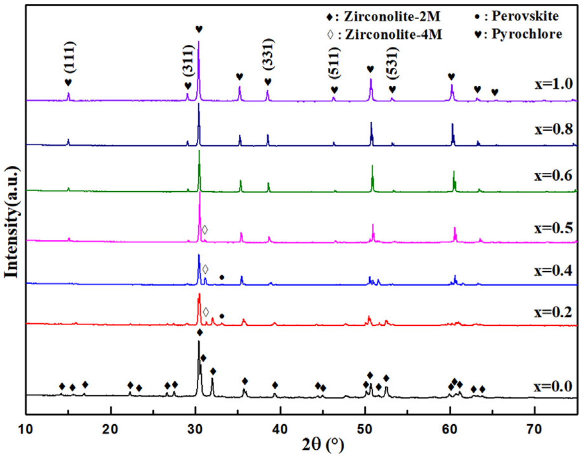

Fig. 1. XRD patterns of $Ca_{1\text{-}x}Zr_{1\text{-}x}Gd_{2x}Ti_2O_7$ ($0.0 \le x \le 1.0$) compositions sintered at 1400 °C for 48 h. The main diagnostic peaks for each phase are indicated.