



Contents lists available at ScienceDirect

Journal of the European Ceramic Society

journal homepage: www.elsevier.com/locate/jeurceramsoc

Original Article

Rapid fabrication and phase transition of Nd and Ce co-doped $Gd_2Zr_2O_7$ ceramics by SPS

Lan Wang^a, Xiaoyan Shu^{a,*}, Facheng Yi^a, Dadong Shao^b, Kuibao Zhang^a, Haibin Zhang^c, Xirui Lu^{a,*}

^a Fundamental Science on Nuclear Wastes and Environmental Safety Laboratory, Southwest University of Science and Technology, Mianyang 621010, PR China

^b Institute of Plasma Physics, Chinese Academy of Sciences, Hefei 230031, PR China

^c Institute of Nuclear Physics and Chemistry, China Academy of Engineering Physics, Mianyang 621900, PR China

ARTICLE INFO

Keywords:

SPS
Rapid sintering
Co-doping
Nuclear waste forms

ABSTRACT

A series of Nd and Ce co-doped $Gd_{2-x}Nd_xZr_{2-y}Ce_yO_7$ ($0.0 \leq x, y \leq 2.0$) ceramics were rapidly fabricated through spark plasma sintering (SPS) within 3 min. The effects of Nd and Ce contents on the phase composition, lattice parameter, active modes, microtopography and microstructure have been investigated in detail. XRD studies reveal that the compositions corresponding to $0.0 \leq y \leq 1.0$ show a single phase and beyond 1.0 exhibit multiphase. The lattice parameters increase with elevated Nd and Ce content. The grains are densely packed on each other with cube-like shape, and the elements are almost homogeneously distributed in the compound. This synthetic method provides a simple pathway for the preparation of highly densified single phase ceramic at 1600–1700 °C for 3 min under pressure of 80 MPa.

1. Introduction

Crystalline oxides with the general formulation of $A_2B_2O_7$ have received considerable attention in recent years because of its large tolerance and structural flexibility [1–3]. Gadolinium zirconate ($Gd_2Zr_2O_7$) is one such pyrochlore, which has good mechanical properties, low leachability, excellent chemical durability, outstanding thermodynamic stability, as well as high resistance to radiation damage [4,5]. Due to its capability to incorporate certain amount actinides, $Gd_2Zr_2O_7$ is also explored as a promising host for safe disposal of radionuclides containing nuclear wastes. Furthermore, both Gd and Zr sites in $Gd_2Zr_2O_7$ can be simultaneously exchanged by a wide solubility range of long-lived actinides from radioactive wastes [6–9].

The crystalline structure of $A_2B_2O_7$ pyrochlore oxides can be described as a face-centered cubic structure containing eight molecules ($Z = 8$) and four crystallographically nonequivalent sites [10]. The eight-coordinated A cation and six-coordinated B cation occupy at $3m$ ($0, 0, 0$) and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ on $16c$ and $16d$ sites, respectively [11]. These kinds of O atoms lie in $8b$ ($\frac{3}{8}, \frac{3}{8}, \frac{3}{8}$), $8a$ ($\frac{1}{8}, \frac{1}{8}, \frac{1}{8}$) and $48f$ ($x, \frac{1}{8}, \frac{1}{8}$), where O ($8a$) are vacant and O ($48f$) position parameter (x) is the main factor to reflect the disordering degree of oxygen lattice [10,12,13]. For example, the value of O ($48f$) position parameter (x) equals to $\frac{3}{8}$, this material adopts a defect fluorite structure and displays an ideal pyrochlore structure at $x = \frac{5}{16}$ [4,14]. According to Subramanian and

Aravamudan, the phase stability is mainly governed by the cation ionic radius ratio (r_A/r_B) under ambient conditions [15]. For $Gd_2Zr_2O_7$ matrix, the formation of pyrochlore structure requires r_A/r_B ratio lies in the range of 1.46–1.78. When r_A/r_B is less than 1.46, defect fluorite structure is stable. It should be noted that this radius ratio analysis is rather approximate, where high pressure, high temperature synthesis and high radiation dose can also influence the phase structure [11,16].

Cations with equal valence, similar ionic radius and extra-nuclear electron orbit could be incorporated in both Gd and Zr sites, which has been reported as one of the most significant advantages of $Gd_2Zr_2O_7$. To investigate the solubility of americium and plutonium in $Gd_2Zr_2O_7$, Lu's group has successfully introduced Nd^{3+} in Gd site and Ce^{4+} in Zr site as surrogates of Am^{3+} and Pu^{4+} in the pyrochlore matrix. However, their preparation by conventional route consumes a substantial amount of time (~ 72 h) [17–19]. Wang's team has obtained $(Gd_{1-x}Nd_x)_2(Zr_{1-x}Ce_x)_2O_7$ ($0 \leq x \leq 1$) pyrochlore ceramics by flux method for 10 h [20]. Ouyang et al. have synthesized the specimens with chemical-coprecipitation and calcination method after 10 h [21]. Nomura et al. have calcined more than 15 h to obtain the sample [22]. Spark plasma sintering (SPS) is known as an electric field-assisted sintering technique (FAST) with rapid heating and short holding time in vacuum. The materials prepared by SPS can obtain high density and compactness in a few minutes. Those advantages meet the severe demands for the rapid disposal of nuclear wastes in several minutes [23].

* Corresponding authors.

E-mail addresses: shuxiaoyanmvp116@163.com (X. Shu), luxiruimvp116@163.com (X. Lu).

<https://doi.org/10.1016/j.jeurceramsoc.2018.02.024>

Received 21 December 2017; Received in revised form 13 February 2018; Accepted 13 February 2018
0955-2219/ © 2018 Elsevier Ltd. All rights reserved.

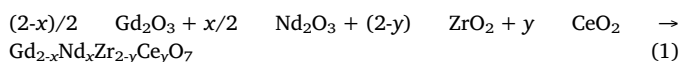
Our previous work has successfully fabricated $Gd_2Zr_2O_7$ waste form by SPS for only one step in 3 min [24]. Therefore, it is possible to employ SPS in preparing co-doped $Gd_2Zr_2O_7$ nuclear waste forms in several minutes.

In this study, we explored to fix simulated radioactive nuclides Nd and Ce simultaneously at both Gd and Zr positions in $Gd_2Zr_2O_7$ matrix through SPS route. The influences of simulated radioactive nuclides at A and B sites on phase composition, vibration mode, microtopography and microstructure were investigated with help of XRD, Raman spectrum, SEM and TEM characterization.

2. Experimental details

2.1. Experimental design

Due to the isovalent nature, the Gd and Zr sites in $Gd_2Zr_2O_7$ matrix can be suitably substituted by Nd^{3+} and Ce^{4+} respectively [2,3]. Moreover, Nd^{3+} and Ce^{4+} are chosen as the simulated actinide elements of Am^{3+} and Pu^{4+} due to their similar ionic radius, outer shell electron distribution and valence state. So the simulated nuclear waste forms can be employed as the following reaction:



In the $Gd_{2-x}Nd_xZr_{2-y}Ce_yO_7$ ($0.0 \leq x, y \leq 2.0$) compounds, the values of x and y are set as 0.0, 0.5, 1.0, 1.5 and 2.0. The detail compound designs are listed in Table 1.

2.2. Fabrication process

AR grade Gd_2O_3 (Tianjin Alfa Aesar Co. Ltd., purity of 99.99%), ZrO_2 (Shanghai Aladdin Co. Ltd., purity of 99.99%), Nd_2O_3 (Shanghai Aladdin Co. Ltd., purity of 99.95%) and CeO_2 (Shanghai Aladdin Co. Ltd., purity of 99.99%) were employed as the raw materials. Before weight, all the raw powders were heat-treated at 120 °C for 6 h to remove adsorptive water and other volatile impurities. Subsequently, stoichiometric amount of the starting reagents were weighed according to Table 1, and sufficiently wet milled in analytically pure alcohol

Table 1
Compound design of $Gd_{2-x}Nd_xZr_{2-y}Ce_yO_7$ ($0.0 \leq x, y \leq 2.0$).

Compound	Amount of starting materials (g)			
	Gd2O3	Nd2O3	ZrO2	CeO2
Gd2Zr2O7	1.9938	–	1.3554	–
Gd _{1.5} Nd _{0.5} Zr ₂ O ₇	1.4953	0.4626	1.3554	–
GdNdZr ₂ O ₇	1.0150	0.9421	1.3801	–
Gd _{0.5} Nd _{1.5} Zr ₂ O ₇	0.5075	1.4132	1.3801	–
Gd ₂ Zr _{1.5} Ce _{0.5} O ₇	1.9938	–	1.0166	0.4733
Gd ₂ ZrCeO ₇	1.8850	–	0.6407	0.8950
Gd ₂ Zr _{0.5} Ce _{1.5} O ₇	1.7763	–	0.3019	1.2651
Gd ₂ Ce ₂ O ₇	1.7038	–	–	1.6179
Gd _{1.5} Nd _{0.5} Zr _{1.5} Ce _{0.5} O ₇	1.4953	0.4626	1.0166	0.4733
GdNdZr _{1.5} Ce _{0.5} O ₇	0.9969	0.9253	1.0166	0.4733
Gd _{0.5} Nd _{1.5} Zr _{1.5} Ce _{0.5} O ₇	0.4894	1.3627	0.9981	0.4647
Nd ₂ Zr _{1.5} Ce _{0.5} O ₇	–	1.8506	1.0166	0.4733
Gd _{1.5} Nd _{0.5} ZrCeO ₇	1.4138	0.4374	0.6407	0.8950
GdNdZrCeO ₇	0.9425	0.8748	0.6407	0.8950
Gd _{0.5} Nd _{1.5} ZrCeO ₇	0.4803	1.3375	0.6531	0.9122
Nd ₂ ZrCeO ₇	–	1.8506	0.6777	0.9467
Gd _{1.5} Nd _{0.5} Zr _{0.5} Ce _{1.5} O ₇	1.3594	0.4206	0.3081	1.2909
GdNdZr _{0.5} Ce _{1.5} O ₇	0.9425	0.8748	0.3204	1.3425
Gd _{0.5} Nd _{1.5} Zr _{0.5} Ce _{1.5} O ₇	0.4713	1.3122	0.3204	1.3425
Nd ₂ Zr _{0.5} Ce _{1.5} O ₇	–	1.7833	0.3265	1.3684
Gd _{1.5} Nd _{0.5} Ce ₂ O ₇	1.3322	0.4122	–	1.6868
GdNdCe ₂ O ₇	0.9063	0.8412	–	1.7212
Gd _{0.5} Nd _{1.5} Ce ₂ O ₇	0.4531	1.2618	–	1.7212
Nd ₂ Ce ₂ O ₇	–	1.6824	–	1.7212

medium for 1 h twice using agate mortar and pestle by hands. Approximately 1.1 g of the dried powders were loaded in a graphite die (Melson advanced graphite (Kunshan) Co. Ltd.) with three layers graphite paper (Liaoyang Xingwang Graphite Products Co. Ltd.) to wipe off easily, and then put into the SPS apparatus (Sumitomo Coal Mining Co., Japan, Model 320MKII) without other additives. A low internal pressure of 30 MPa was applied before the sintering to adjust the position between graphite dies. Based on our previous studies [24,25], the sintering temperature was chosen as 1600 °C for Ce-doped ceramic while 1700 °C for others. The heating rate is 100 °C/min and dwell time is 3 min. The vacuum condition was added during sintering and a load of 80 MPa was applied at the beginning to the end. Before characterizations, the graphite paper was polishing away from the surface and the samples were treated with ultrasonic conditioning.

2.3. Characterizations

The phase structures were analyzed using an X-ray diffractometer (D8 ADVANCE, Germany) with Cu radiation ($\lambda = 1.5406 \text{ \AA}$). The data were recorded over an angular range of 10–80° (2θ) at a scanning rate of 2°/min. Based on XRD results, the CHEKCELL program was used to calculate the lattice parameters [26,27]. The Raman spectra measurements were performed with a Raman spectrometer (in Via, Britain) using 785 nm excitation from an argon ion laser. Stokes shifted Raman spectra were collected in the static mode in the range of 100–1000 cm^{-1} and the spectral resolution was $\sim 1 \text{ cm}^{-1}$. The micromorphology of the samples was observed by scanning electron microscope (SEM, Ultra 55, German). In addition, an energy-dispersive X-ray spectroscopy (EDS) attached with the SEM equipment was used to provide a supplementary method for elemental distribution data. The microstructure observations were carried out with transmission electron microscopy (TEM, Libra 200 FE, German).

3. Results and discussion

3.1. Phase evolution and solid solution

3.1.1. Influence of Nd content at Gd site

Powder XRD patterns of various compositions $Gd_{2-x}Nd_xZr_{2-y}Ce_yO_7$ are present in Fig. 1. It could be found in Fig. 1(d) and (e) that the Gd_2O_3 , ZrO_2 , Nd_2O_3 and CeO_2 peaks emerge as y value goes beyond 1.5. Thus, the solubility of Ce at Zr site in $Gd_{2-x}Nd_xZr_{2-y}Ce_yO_7$ lies in the range of 50–75 at %. At $y = 0.0, 0.5$ and 1.0 , the compositions exhibit a single phase. Further observation reveals that $Gd_{2-x}Nd_xZr_{2-y}Ce_yO_7$ shows a fluorite or pyrochlore structure, where the fluorite structure is evidenced by the appearance of main diffraction peaks at 2θ of about 29°, 33°, 47°, 56°, 59°, 67° and 76°, while the pyrochlore structure is clearly evident in superstructure reflections at 2θ of 28°, 37° and 51° [24,25,28]. Moreover, the samples have sharper diffraction peaks with increment of Nd content, indicating the crystallinity degree is elevated.

Fig. 1(a) presents the superlattice peak at 37° (331) gradually emerges with Nd substituting in $Gd_{2-x}Nd_xZr_{1.5}Ce_{0.5}O_7$ ($0.0 \leq x \leq 2.0$). This phenomenon means the degree of structural ordering gradually increase, which is related to the ionic radius ration of A and B cations (r_A/r_B). The ionic radius of Gd^{3+} and Nd^{3+} at A site are 1.05 Å and 1.11 Å, and that of Zr^{4+} and Ce^{4+} at B site are 0.72 Å and 0.87 Å. The average ionic radius of r_A/r_B is estimated as the following equation:

$$r(A) = (2-x) r(Gd) + x r(Nd) \quad (2)$$

$$r(B) = (2-y) r(Zr) + y r(Ce) \quad (3)$$

For $Gd_{2-x}Nd_xZr_{1.5}Ce_{0.5}O_7$ ($0.0 \leq x \leq 2.0$) compounds, the highest r_A/r_B is obtained as 1.4653 for $Nd_2Zr_{1.5}Ce_{0.5}O_7$, and the lowest is obtained as 1.4059 for $Gd_{1.5}Nd_{0.5}Zr_{1.5}Ce_{0.5}O_7$. It clearly indicates that the r_A/r_B gradually increases and the distribution of oxygen ions ordered with the enhancement of Nd content. Therefore, the enhanced Nd

Download English Version:

<https://daneshyari.com/en/article/7898388>

Download Persian Version:

<https://daneshyari.com/article/7898388>

[Daneshyari.com](https://daneshyari.com)