Self-propagating high-temperature synthesis of ZrO_2 incorporated $\text{Gd}_2\text{Ti}_2\text{O}_7$ pyrochlore

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Abstract: In this research, Zr-doped $\text{Gd}_2\text{Ti}_2\text{O}_7$ pyrochlores, with the composition of $\text{Gd}_2(\text{Ti}_{1-x}\text{Zr}_x)_2\text{O}_7$, were firstly synthesized by self-propagating high-temperature synthesis plus quick pressing (SHS/QP) using CuO as the oxidant and Ti as the reductant. To improve the radiation resistance of titanate–pyrochlore, up to 35 at% Zr was incorporated to substitute the Ti site of $\text{Gd}_2\text{Ti}_2\text{O}_7$ pyrochlore ($\text{Gd}_2(\text{Ti}_{0.75}\text{Zr}_{0.35})_2\text{O}_7$). XRD and SEM microstructural characterizations showed the formation of a composite ceramic with the major pyrochlore phase and the minor Cu phase. The generated temperature of samples decreased from 1702 to 1011 °C with increasing Zr content. The effects of sintering temperature and pressure time on phase composition and microstructure were systematically studied. Besides, the influence of thermal transmission on the whole combustion process was also explored. The pyrochlore-based waste form possessed high bulk density of 6.25 g/cm³ and Vickers hardness of 10.81 GPa. The MCC-1 leaching test showed the normalized elemental leaching rates (42 d) of Cu, Gd, and Zr are 1.27×10^{-2} , 1.33×10^{-3} , and 8.44×10^{-7} g·m⁻²·d⁻¹, respectively.

Keywords: self-propagating high-temperature synthesis plus quick pressing (SHS/QP); pyrochlore; thermal transmission; waste form; aqueous leachability

1 Introduction

Nuclear power has been developing rapidly in recent decades around the world thanks to its high efficiency, economic benefits, low carbon, and other advantages. China has built 4 nuclear power plants up to now with

another 10 under construction [1,2]. In such a large scale of nuclear power's service, the study of the by-product of nuclear power, known as nuclear waste, especially on waste liquid separation and immobilization, could be attached great significance. However, because of its strong toxicity and long half-life, high-level radioactive waste (HLW) has been a hard nut to crack for a long time [3–5]. Given that the crying needs of nuclear waste's long-term storage and safely disposal,

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some effective techniques must be developed to meet such an urgent demand. At present, the exclusively preservative materials that have found industrial scale operations are borosilicate and phosphate glasses. However, the low solubility of minor actinides in glass matrix and the metastable nature of glass are the major limitations in the long-term geological disposal [6–9]. On the other hand, synroc is recognized as the second generation waste form for the immobilization of HLW. Pyrochlore, which is an important constituent phase of synroc, is isometric (space group: $Fd3m$), and the general formula is $A_2B_2O_7$ (where A and B are metallic cations) [10–15]. As a derivative of the fluorite structure, the pyrochlore structure-type is common because this isometric structure has a wider choice of A and B cations to satisfy the charge neutrality and ionic radius requirement. The zirconate-pyrochlores are of greatest interest in nuclear waste management because of its high radiation resistance to incorporate trivalent lanthanides and tri- and tetra-valent actinides [16–18].

Recently, we have explored the self-propagating high-temperature synthesis (SHS) of titanate-pyrochlore, $Gd_2Ti_2O_7$ (GTO), which has great chemical durability, and its average leaching rate of Gd is $1.97 \times 10^{-4} \text{ g} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$ [9]. However, Ewing *et al.* [13] have reported that GTO pyrochlores experience a radiation-induced transition from the crystalline to aperiodic state under radiation damage. Contrastively, zirconate-pyrochlore, $Gd_2Zr_2O_7$ (GZO), does not become amorphous, but remain crystalline as a defect fluorite structure-type due to disordering of the A- and B-site cations. According to Sickafus *et al.* [19], the results of calculation and irradiation experiment with heavy ions (Xe), even to very high dose, are perfectly in agreement with Ewing *et al.* [13]. It can be concluded from Sickafus *et al.* that compounds with more similar cation radii are more likely to form as disordered fluorites than ordered pyrochlore. Besides, a particular class of oxides possessing the fluorite crystal structure should accept radiation-induced defects into their lattices far more readily than a structurally similar class of oxides based on the pyrochlore. The r_A/r_B of GTO is higher than that of GZO (1.74 vs. 1.46), namely that the composition $Gd_2(Ti_{1-x}Zr_x)_2O_7$, ranging from GTO to GZO, exhibits radiation improvement with increasing Zr content. In this research, it is hopeful to synthesize $Gd_2(Ti_{1-x}Zr_x)_2O_7$ ($x = 0-0.45$) by SHS plus quick pressing (QP).

Traditionally, pyrochlore was mostly prepared using liquid phase synthesis such as co-precipitation, liquid-mix,

sol-gel [20], and high-temperature solid state reaction [21]. Compared with liquid-phase method, the solid state reaction is relatively convenient and efficient in the industrial field. Tang *et al.* [22] have prepared single phase GZO at 1873 K and 5.2 GPa with 30 min holding time. The whole procedure needs 24–72 h. Lu *et al.* [23] used microwave sintering, 2.45 GHz, to prepare GZO pyrochlore in air at 1400–1500 °C between 10 and 30 min. Spark plasma sintering (SPS) is a rapid sintering technology, and Xu *et al.* [24] used SPS to prepare single phase GZO at 1400 °C for 10 min. The synthesized ceramic was annealed at 800 °C for 2 h under air atmosphere. Although these sintering technologies are excellent for preparing GZO pyrochlore at high temperature, these methods are time consuming, which is the common problem.

Merzhanov firstly proposed SHS in 1967 [25,26]. Once being ignited, the combustion process of SHS reactants will not be suspended because it is an exothermic chemical reaction. This is also an explanation that the activation energy for atomic diffusion comes from the inner chemical reaction rather than the external thermal field, such as thermal radiation furnace. Compared with conventional solid state reaction process, SHS leads to high temperature, low cost, simplified equipment, and convenient handling. According to Yudinsev *et al.* [27], the duration of initiation is 0.05–5 s and the velocity of combustion wave is 1–150 mm/s. In addition, the industrial scale synthesis of actinide-containing pyrochlore will require handling relatively large volumes of materials. Thus, a variety of technologies are under investigation, including SHS method [28,29]. However, SHS also faces its own limitation: the generated high temperature and high reaction speed that may cause this progress hardly to be controlled [8,9,30].

In this study, zirconate-pyrochlore specimens, $Gd_2(Ti_{1-x}Zr_x)_2O_7$, were firstly prepared by SHS/QP using Ti as the reductant and CuO as the oxidant. Gd^{3+} was used as neutron absorber and a surrogate to simulate the trivalent actinides. Up to 35 at% Zr was doped to substitute the Ti site of GTO pyrochlore to improve the radiation resistance. Besides, the whole combustion and densification process took no more than 5 min, which is faster than Laverov *et al.* [31] which needed tens of hours to form a single phase pyrochlore $Gd_2(Ti_xZr_{1-x})_2O_7$ ($x = 0.4$) by solid state sintering. To get highly densified specimen, QP was introduced into the SHS process. In order to make a

distribution of the thermal field uniform, the type of contact between the green body and the tungsten wire was also explored. The effects of sintering temperature and pressure time on phase composition and micro-structure were systematically studied. In addition, the aqueous durability of densified zirconate–pyrochlore waste form was also investigated.

2 Experimental details

All samples were prepared from SHS approach using Ti, TiO_2 , ZrO_2 , Gd_2O_3 , and CuO as the raw materials with granularity less than 10 μm , and were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. Ti was employed as the reductant with CuO as the oxidant. To improve the radiation resistance of titanate–pyrochlore, varied ZrO_2 additions (0, 5, 15, 25, 35, and 45 at%) were incorporated to substitute the Ti site of GTO. The SHS reactions were designed as follows:

The value of x was fixed to be 0, 0.05, 0.15, 0.25, 0.35, and 0.45 (identified as Zr-0, Zr-5, Zr-15, Zr-25, Zr-35, and Zr-45, respectively).

The compositions of raw SHS reactants are list in Table 1. The weight percentages of reductant Ti and oxidant CuO are gradually decreasing. Decreasing from Zr-0 to Zr-15 sample, TiO_2 is completely replaced by ZrO_2 from Zr-25 to Zr-45 sample. Compared with the increment of ZrO_2 from 0 to 15.82 wt%, the weight percentage of Gd_2O_3 maintains about 50 wt%. About 20 g of designed powder reactants were mechanically ground and completely mixed in agate mortar. After desiccation at 60 $^\circ\text{C}$ for 1 h, the homogeneously mixed powders were pressed at 10 MPa using Φ 25 mm stainless mould, which would be used for the next ignition. 100 mesh silica sand was employed as the heat insulator and pressure transmission medium. The reactant was ignited by a tungsten wire, which was located at one side with tight contact of the pellets, and heated by a direct current of about 50 A. As illustrated in Fig. 1, compared with the original position that the axis of the green body is perpendicular to the direction of heat transfer, the new axis of the reactant is parallel to the direction of thermal transmission. In this way, the area of mass transfer is constant and different from the changeable area related to the original position.

Besides, whether the thermal field distribution might be uniform, as suggested for curve in Fig. 1, needs to be determined by the area of mass transfer. The quality of specimens and the measurement of temperature are also influenced by the area of mass transfer.

Because this is an exothermic chemical reaction, the SHS reactants were ignited and combusted instantly under high-temperature radiation of tungsten wire. Before pressure exertion, the reaction temperature of Zr-0 to Zr-45 specimen was measured by a W/Re 5/26 thermocouple placed at the center of the green body. The temperature tendency was recorded by an XME 2000/U paperless recorder connected with the thermocouple. The unpressed samples were ground into powders for XRD analysis using an X'Pert PRO X-ray diffractometer. Qualitative phase identification was executed by matching powder diffraction patterns with those retrieved by the standard powder diffraction database [32].

After the temperature and XRD analyses, new samples were employed for subsequent SHS and compression process. In order to optimize the pressurizing parameter and obtain the most compact specimen, 5 pressure gradients were designed: 18, 20, 22, 24, and 26 s, respectively. The red hot sample was compressed at 50 MPa by a hydraulic press with 60 s dwelling time. The whole combustion and densification process took no more than 5 min. After cutting and polishing, the

Table 1 Weight percentage of the raw SHS reactants

Sample number	Weight percentage of reactants (wt%)					Total (wt%)
	Ti	CuO	TiO_2	ZrO_2	Gd_2O_3	
Zr-0	10.07	33.48	5.60	0	50.85	100
Zr-5	10.01	33.27	4.46	1.72	50.54	100
Zr-15	9.89	32.88	2.20	5.09	49.94	100
Zr-25	9.77	32.49	0	8.39	49.35	100
Zr-35	8.67	28.81	0	12.02	50.50	100
Zr-45	7.51	24.96	0	15.82	51.71	100

Fig. 1 Schematic diagram of the sample and the direction of heat transfer; comparison of the area at which the green body transfers the mass for the old and new models.

bulk density of these samples was measured by Archimedes drainage method using water as the immersion medium. Micro hardness of these samples was tested using a Vickers hardness tester (HXD-100 TMC/LCD). The microstructure characterization and elemental distribution were analyzed using a field-emission scanning electron microscopy (Zeiss Ultra-55, Germany), which was equipped with an energy-dispersive X-ray spectroscopy (EDX) attachment. Aqueous durability of the monolithic specimen was evaluated according to the standard MCC-1 method. The testing bars were suspended by a Cu wire and immersed in 80 mL deionized water (pH = 7) with PTFE container. The measurement was made at 90 °C for 1–42 days. In this study, the value of SA/V is about 3.76 m^{-1} , which conforms to the size requirement ($0.5\text{--}10 \text{ m}^{-1}$) of the MCC-1 standard [33,34]. The leachate concentrations (C_i) of Gd, Zr, and Cu were measured by inductively coupled plasma-mass spectrometry (ICP-MS) and inductively coupled plasma (ICP) using PerkinElmer SCIEX and Thermo-Fisher iCAP6500 spectrometer, respectively. The normalized elemental leaching rates (LR_i) were calculated as follows:

$$LR_i = \frac{C_i \times V}{SA \times f_i \times \Delta t} \quad (2)$$

where f_i is the mass fraction of element i in the sample, SA is the geometric surface area, V is the volume of the leachate, and Δt is the interval soaking duration in days.

3 Results and discussion

3.1 Temperature and powder XRD analysis

With the increment of ZrO_2 , the center temperature of Zr-5, Zr-15, Zr-25, Zr-35, and Zr-45 samples shows a decreasing trend, which decreases from 1702 to 1011 °C, as shown in Fig. 2. According to Helean *et al.* [35], X-ray diffraction data suggested structural changes with increasing Zr content due to the gradual disordering of A- and B-site cations (i.e., cation antisites) to a defect fluorite structure. All compositions are stable with respect to their constituent oxides, and the enthalpy of formation becomes more endothermic with increasing Zr content in $\text{Gd}_2(\text{Ti}_{1-x}\text{Zr}_x)_2\text{O}_7$. Thus, more heat will be absorbed during the whole sintering process, and the center temperature presented is lower than the previous one [14]. Besides, the heat released by SHS is decreasing due to the gradual reduction of

Fig. 2 Real temperature curve of all samples during SHS reaction.

weight percentage of reductant and oxidant. Because of the fundamental understanding on endothermic and exothermic process, only 35 at% Zr could be incorporated to substitute the Ti site of GTO pyrochlore using SHS method. It is interesting to note that the center temperature of Zr-0 sample is 1551 °C, which is lower than that of Zr-5 (1702 °C) and Zr-15 (1661 °C) samples. The result is in good agreement with previous report that TiO_2 (5.60 wt% TiO_2 in Zr-0 specimen) can regulate the combustion reactivity and generated temperature [9]. Besides, it also can be observed in Fig. 2 that the more ZrO_2 doped into samples, the more time needs to reach the highest center temperature. Compared with Zr-5 sample which needs 10 s to reach the highest center temperature, Zr-45 sample doped with 45 at% ZrO_2 needs 23 s to get the highest one. The reason may be attributed to the decrement of reductant and oxidant, as shown in Table 1.

The products of SHS reaction were analyzed with the XRD patterns presented in Fig. 3. From Zr-5 to Zr-45 specimens, all samples show the same major phase composition as undoped Zr-0 sample, indicating that the increment of ZrO_2 does not change the GTO pyrochlore phase (PDF No. 23-0259). Conforming to the original design, the existence of metallic Cu is also a valuable constituent phase. Because the melting point of Cu is relatively low, the existence of Cu would be beneficial for subsequent densification [8]. However, Zr-45 sample is composed of pyrochlore, Cu, and ZrO_2 , which indicates that ZrO_2 cannot fully react with other SHS reactants. In other words, from the isomorphism substitution theory, Zr can be incorporated into the crystal structure of GTO pyrochlore, and higher occupancy of Ti site by Zr (> 35 at%) is impossible under the present experimental conditions. The subsequent EDX test would further justify this situation.

Fig. 3 (a) XRD patterns of as-prepared samples, (b) amplified view between 29.7° and 31°.

The main pyrochlore peak in Fig. 3(a) located at 29.7°–31° is amplified and presented in Fig. 3(b). This peak exhibits a gradually shifting to the lower angle, from 30.3° of Zr-0 to 30° of Zr-35 sample. According to Bragg equation, this phenomenon can be attributed to the slight increment of lattice parameter, which the ionic radius of Zr^{4+} (0.720 Å) is larger than that of Ti^{4+} (0.605 Å) [18]. However, this peak of Zr-45 specimen does not continually move to the lower angle but shift to the higher one, which also indicates the remaining ZrO_2 exists in Zr-45 sample. Above all, the phase and the diffraction peak intensity of Zr-35 sample are the best one, and 35 at% Zr can be incorporated to substitute the Ti site of GTO pyrochlore.

3.2 Microstructure and mechanical properties

Figure 4(a) shows the BSE image of Zr-45 specimen with pressure time 25 s. The color of “A” region is not the same as that of “B”, i.e., some differences exist between the phases of both regions. The elemental images are presented in Figs. 4(b)–4(f). It can be clearly seen that the “A” region is rich in Zr and O, and the “B” region is rich in Gd, Ti, and O. Zr-45 sample was further investigated using EDX elemental spotting scanning analysis, as shown in Fig. 4(a): “C” and “D”. The results of elemental compositions are demonstrated in Table 2. The chemical formulation of “D” is calculated to be ZrO_2 , which is in good agreement with the XRD pattern of Zr-45 sample (Fig. 3(a)). The existence of Cu is reasonable because there are lots of pores, and the subsequent study would further offer a complete explanation of the ideal place for Cu. If ZrO_2 was completely incorporated into the pyrochlore, the chemical formulation of Zr-45 sample should be $Gd_2(Ti_{0.55}Zr_{0.45})_2O_7$. However, the real chemical formulation of “C” is calculated to be $Gd_2(Ti_{0.85}Zr_{0.19})_2O_{5.76}$ according to

Fig. 4 EDX mapping images of consolidated Zr-45 specimen with pressure time 25 s: (a) representative BSE image of the matrix, (b) mixed elemental mapping image of three elements (Zr: green; Gd: blue; Ti: red), and respective elemental mapping images of (c) Gd, (d) Ti, (e) O, and (f) Zr.

Table 2 EDX elemental spotting analysis of “C” and “D”

Field	Element (at%)					
	Gd	Ti	Zr	O	Cu	Total
C	28.34	17.34	3.78	58.54	0	100
D	0	0	33.55	60.58	5.87	100

Table 2, which is deficient in Zr. Combined with Fig. 4, the above-mentioned element deficiency is attributed to the formation of ZrO_2 in green area (Fig. 4(b)). Similarly, the element of Ti is ejected from green area and rich in “C” area. Above all, the content of ZrO_2 in Zr-45 specimen (45 at%) is excessive, and up to 35 at% Zr can be incorporated to substitute the Ti site in GTO pyrochlore using SHS method.

Higher relative density, as well as the mechanical properties, is beneficial for the chemical durability regarding to aqueous corrosion [36]. In this research, quick hydraulic pressing was operated to get highly consolidated specimens. After suitable time delay of combustion, the reaction was compacted at 50 MPa with holding time 60 s. Zr-35 sample was selected for the subsequently compression experiment. Five time points (18, 20, 22, 24, and 26 s) were designed to optimize the pressurizing parameter.

The BSE images of Zr-35 samples with different

pressure time (18–26 s) are shown in Figs. 5(a)–5(e). With the delay time increases, the area and amount of pores in samples' surface are decreasing. Figure 5(a) shows lots of big pores in the surface of 18 s sample, and this may be attributed to the CuO grains removed during the polishing step or the early pressure time, namely short reaction time. Combined with Fig. 2, Zr-35 sample's generated temperature reaches to the highest value at 18 s. It is easy for the sample to shape porous structure due to its molten state, when it is instantly supported great pressure. Figure 5(b) shows that a big dark-gray phase is metallic Cu, which was demonstrated by the XRD and subsequent EDX results. With the delay time increases, it is important to note that Cu is squeezed out to the edge of samples with dispersed small particles, which is in good agreement with the results of synthesis GTO in our previous work [9]. As indicated above, due to no big pores or cracks from Fig. 5(e), the best pressurizing parameter is 26 s.

As shown in Fig. 5(f), the bulk density and Vickers hardness keep on a rise with the extension of time. The highest bulk density and Vickers hardness of 26 s specimen are 6.25 g/cm³ and 10.81 GPa respectively, which are higher than that of GTO/Cu composite ceramic prepared in previous work (5.53 g/cm³, 10.48 GPa) [9]. It can be observed in Fig. 2 that the temperature of Zr-35 specimen is about 1150 °C at the time of 26 s, which is lower than the generated temperature point (1206 °C) and higher than the melting temperature of Cu (1083 °C). During this time, the gas escapes from the sample, and highly densified

pyrochlore specimens would be obtained. In this way, not only the porosity decreases, but its density and radiation stability are improved, which lay a solid foundation for the application of the SHS reaction method.

Besides, Zr-35 specimen, with the 26 s pressure time, was also cut and polished to 2000 mesh for the microstructure characterization and elemental distribution analysis. As shown in Fig. 6(a), the light-gray phase is pyrochlore while the dark-gray one is Cu. It is interesting to note that all pores are located in the matrix of Cu, contrarily, and there are no pores in that of compacted pyrochlore. It may be argued that the time required for liquid Cu to cool from high-temperature to low-temperature solid phase is longer than that of pyrochlore during the whole reaction process. Finally, the gas is discharged through the Cu matrix, which is also the last position for gas emergence. This would explain why all pores exist in the matrix of Cu. As shown in Figs. 6(b)–6(f), the equilibrium distribution for Gd, Ti, Zr, and O is in reasonable agreement with the completely reaction for Zr-35 specimen. At least three points of pyrochlore area were characterized to obtain the average element quantities. The EDX spectra and elemental compositions are demonstrated in Figs. 7(a) and 7(b). The chemical formulation of pyrochlore is calculated to be Gd_{2.13}(Ti_{0.67}Zr_{0.34})₂O₇, which is in good agreement with the product we designed (Zr-35, Gd₂(Ti_{0.65}Zr_{0.35})₂O₇). The SEM–EDX results testify that highly compacted zirconate–pyrochlore/Cu multiphase specimen was successfully prepared by SHS/QP with CuO as the oxidant and Ti as the reductant.

Fig. 5 BSE images of Zr-35 samples with different pressure time: (a) 18 s, (b) 20 s, (c) 22 s, (d) 24 s, (e) 26 s and (f) Vickers hardness and bulk density of five samples.

Fig. 6 EDX mapping images of consolidated Zr-35 specimen with pressure time 26 s: (a) representative BSE image of the matrix and elemental mapping images of (b) Gd, (c) Ti, (d) Zr, (e) O, and (f) Cu.

Fig. 7 EDX elemental spotting analysis: (a) representative BSE image of Zr-35 sample, (b) element spotting analysis.

3.3 Aqueous durability of the Zr-35 sample

As for a nuclear waste form, the most important property is its chemical durability in contact with an aqueous solution. Because the release of radionuclides to the biosphere will certainly occur mainly by contact

and reaction with water followed by transport of dissolved and colloidal radionuclide complexes [13]. The MCC-1 leaching method, which was employed to estimate the aqueous durability of the Zr-35 sample in this study, is a static leaching of monolithic waste forms for the disposal of radioactive waste. This testing method evaluates the relative chemical durability of simulated and radioactive monolithic waste forms such as glasses, ceramics, or cermets in various test solutions and various durations at temperatures $< 100\text{ }^{\circ}\text{C}$, with low surface area to volume ratio (SA/V , $0.5\text{--}10\text{ m}^{-1}$) [30]. Figure 8 shows the normalized elemental leaching rates (LR_i) of Cu, Gd, and Zr in the Zr-35 sample, which was immersed in $90\text{ }^{\circ}\text{C}$ high-purity water with a testing duration of 1–42 days. The LR_i values are substantially based on the geometrical surface area, directly revealing the chemical stability of relevant radioactive nuclide stabilization.

Generally, LR_{Cu} and LR_{Zr} values decrease congruently as the leaching duration prolongs, which remain relatively stable after 14 days. The 1 day LR_{Cu} value shows the highest one ($2.54\text{ g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$) and abruptly declines to $1.29\times 10^{-1}\text{ g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ after 7 days. The elemental leaching becomes steady with the extension of soaking time [37], and the 42 day LR_{Cu} value remains below $1.27\times 10^{-2}\text{ g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$. The 1 day LR_{Zr} value is $3.54\times 10^{-5}\text{ g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$, which subsequently decreases to $5.29\times 10^{-6}\text{ g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ after 14 days. The 42 day LR_{Zr} value ($8.44\times 10^{-7}\text{ g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$) is 4–5 orders of magnitude lower than that of Cu and Gd elements. The very low leaching rates for Zr are thought to reflect the larger bond energies of Zr–O over those of Gd–O in the pyrochlore structure [38]. In contrast to LR_{Cu} and LR_{Zr} , LR_{Gd} value does not decrease, but shows a

Fig. 8 Normalized elemental leaching rates (Zr-35) of Cu, Gd, and Zr using standard MCC-1 method.

slightly rising trend and reaches to the highest one ($3.66 \times 10^{-3} \text{ g} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$) after 7 days. The 42 day LR_{Gd} value shows the lowest one ($1.33 \times 10^{-3} \text{ g} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$). Compared with the GTO/Cu waste form prepared by SHS, the 42 day LR_{Cu} and LR_{Gd} are about an order of magnitude higher in this experiment. Nevertheless, the elemental leaching rates are significantly lower than typical borosilicate glass ($> 1 \text{ g} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$, 90°C). The slightly higher LR_{Gd} value may be associated with the bonding energy of Gd–O (approximately 242.44 kJ/mol) weakened by the doped ZrO_2 [39].

4 Conclusions

In summary, Up to 35 at% Zr was incorporated to substitute the Ti site of GTO pyrochlore using SHS/QP method. The final product is multiphase with the major pyrochlore phase and the minor Cu phase. In comparison to the other sintering processing, SHS can be achieved at relatively low temperature (1206°C), shorter sintering time (5 min), and convenient handling. The generated temperature of samples decreases with increasing Zr content. The axis of the green body is parallel to the direction of thermal transmission, which is beneficial for the uniform thermal field. The $\text{Gd}_{2.13}(\text{Ti}_{0.67}\text{Zr}_{0.34})_2\text{O}_7/\text{Cu}$ composite ceramic shows reasonable high Vickers hardness and very good bulk density, being 10.81 GPa and 6.25 g/cm^3 , respectively. The MCC-1 static leaching demonstrates the normalized leaching rate (42 d) of Gd, Zr, and Cu as low as 1.27×10^{-2} , 1.33×10^{-3} , and $8.44 \times 10^{-7} \text{ g} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$, respectively. This work clearly suggests the possibility of using SHS to fabricate high-quality zirconate–pyrochlore, which is a significant radiation resistance material in the immobilization of high-level nuclear waste.

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References

- [1] Jing JQ, Luan HW. On the history of world nuclear development and the road for China nuclear development. *Northeast Electric Power Technology* 2008, **29**: 48–52. (in Chinese)
- [2] Ye Q-Z. Studies on the development strategy of China's nuclear power. *Power System and Clean Energy* 2010, **26**: 3–6. (in Chinese)
- [3] International Atomic Energy Agency. *Design and Operation of High Level Waste Vitrification and Storage Facility*. Technical Reports Series No. 339, 1992.
- [4] Ojovan MI, Lee WE. *An Introduction to Nuclear Waste Immobilization*. Elsevier, 2005.
- [5] Barinova TV, Podbolotov KB, Borovinskaya IP, *et al.* Self-propagating high-temperature synthesis of ceramic matrices for immobilization of actinide-containing wastes. *Radiochemistry* 2014, **56**: 554–559.
- [6] Kong L, Zhang Y, Karatchevtseva I. Preparation of $\text{Y}_2\text{Ti}_2\text{O}_7$ pyrochlore glass-ceramics as potential waste forms for actinides: The effects of processing conditions. *J Nucl Mater* 2017, **494**: 29–36.
- [7] Weber WJ, Ewing RC, Catlow CRA, *et al.* Radiation effects in crystalline ceramics for the immobilization of high-level nuclear waste and plutonium. *J Mater Res* 1998, **13**: 1434–1484.
- [8] Zhang K, Wen G, Zhang H, *et al.* Self-propagating high-temperature synthesis of $\text{Y}_2\text{Ti}_2\text{O}_7$ pyrochlore and its aqueous durability. *J Nucl Mater* 2015, **465**: 1–5.
- [9] Peng L, Zhang K, Yin D, *et al.* Self-propagating synthesis, mechanical property and aqueous durability of $\text{Gd}_2\text{Ti}_2\text{O}_7$ pyrochlore. *Ceram Int* 2016, **42**: 18907–18913.
- [10] Fan L, Shu X, Lu X, *et al.* Phase structure and aqueous stability of TRPO waste incorporation into $\text{Gd}_2\text{Zr}_2\text{O}_7$ pyrochlore. *Ceram Int* 2015, **41**: 11741–11747.
- [11] Zhang FX, Wang JW, Lian J, *et al.* Phase stability and pressure dependence of defect formation in $\text{Gd}_2\text{Ti}_2\text{O}_7$ and $\text{Gd}_2\text{Zr}_2\text{O}_7$ pyrochlores. *Phys Rev Lett* 2008, **100**: 045503.
- [12] Jafar M, Sengupta P, Achary SN, *et al.* Phase evolution and microstructural studies in $\text{CaZrTi}_2\text{O}_7$ (zirconolite)– $\text{Sm}_2\text{Ti}_2\text{O}_7$ (pyrochlore) system. *J Eur Ceram Soc* 2014, **34**: 4373–4381.
- [13] Ewing RC, Weber WJ, Lian J. Nuclear waste disposal—pyrochlore ($\text{A}_2\text{B}_2\text{O}_7$): Nuclear waste form for the immobilization of plutonium and “minor” actinides. *J Appl Phys* 2004, **95**: 5949–5971.
- [14] Wan C, Qu Z, Du A, *et al.* Influence of B site substituent Ti on the structure and thermophysical properties of $\text{A}_2\text{B}_2\text{O}_7$ -type pyrochlore $\text{Gd}_2\text{Zr}_2\text{O}_7$. *Acta Mater* 2009, **57**: 4782–4789.
- [15] Fan L, Shu X, Ding Y, *et al.* Fabrication and phase transition of $\text{Gd}_2\text{Zr}_2\text{O}_7$ ceramics immobilized various simulated radionuclides. *J Nucl Mater* 2015, **456**: 467–470.
- [16] Glagovskii EM, Yuditsev SV, Kuprin AV, *et al.* Crystalline host phases for actinides, obtained by self-propagating high-temperature synthesis. *Radiochemistry* 2001, **43**: 632–

- 638.
- [17] Kulkarni NK, Sampath S, Venugopal V. Preparation and characterization of Pu-pyrochlore: $(\text{La}_{1-x}\text{Pu}_x)_2\text{Zr}_2\text{O}_7$ ($x = 0-1$). *J Nucl Mater* 2000, **281**: 248–250.
 - [18] Zhang KQ, Liu CG, Li FZ, *et al.* Study on the crystal structure of $(\text{Gd}_{2-x}\text{Ce}_x)\text{Ti}_2\text{O}_7$ ($0 \leq x \leq 0.8$) pyrochlore. *Adv Appl Ceram* 2016, **115**: 411–416.
 - [19] Sickafus KE, Minervini L, Grimes RW, *et al.* Radiation tolerance of complex oxides. *Science* 2000, **289**: 748–751.
 - [20] Begg BD, Hess NJ, Weber WJ, R. *et al.* Heavy-ion irradiation effects on structures and acid dissolution of pyrochlores. *J Nucl Mater* 2001, **288**: 208–216.
 - [21] Finch RJ, Bullen DB. Scientific Basis for Nuclear Waste Management XXVI: Symposium Held December 2–5, 2002, Boston, Massachusetts, USA. Warrendale, PA, USA: Materials Research Society, 2003.
 - [22] Tang J, Chen X, Pan S, *et al.* Synthesis of $\text{Gd}_2\text{Zr}_2\text{O}_7$ pyrochlore with cubic structure at high pressure and high temperature conditions. *Atomic Energy Science and Technology* 2010, **44**: 394–399. (in Chinese)
 - [23] Lu X, Ding Y, Dan H, *et al.* Rapid synthesis of single phase $\text{Gd}_2\text{Zr}_2\text{O}_7$ pyrochlore waste forms by microwave sintering. *Ceram Int* 2014, **40**: 13191–13194.
 - [24] Xu Q, Pan W, Wang J, *et al.* Preparation and characterization of $\text{Gd}_2\text{Zr}_2\text{O}_7$ ceramic by spark plasma sintering. *Key Eng Mater* 2005, **280–283**: 1507–1510.
 - [25] Muthuraman M, Dhas NA, Patil KC. Combustion synthesis of oxide materials for nuclear waste immobilization. *Bull Mater Sci* 1994, **17**: 977–987.
 - [26] Merzhanov AG. History and recent developments in SHS. *Ceram Int* 1995, **21**: 371–379.
 - [27] Yudintsev SV, Ioudintseva TS, Mokhov AV, *et al.* Study of pyrochlore and garnet-based matrices for actinide waste produced by a self-propagating high-temperature synthesis. *MRS Proceedings* 2003, **807**, DOI: 10.1557/PROC-807-273.
 - [28] Yudintsev SV, Stefanovskii SV, Kir'Yanova OI, *et al.* Radiation resistance of fused titanium ceramic for actinide immobilization. *Atomic Energy* 2001, **90**: 487–494.
 - [29] Laverov NP, Yudintsev SV, Stefanovsky SV, *et al.* Radiation stability of actinide matrices. *Dokl Earth Sci* 2001, **377**: 175–177.
 - [30] Zhang K, Yin D, Peng L, *et al.* Self-propagating synthesis of Nd_2O_3 -incorporated zirconolite/Mo composites and their aqueous durability. *J Nucl Mater* 2017, **491**: 177–182.
 - [31] Laverov N, Yudintsev S, Lapina M, *et al.* Phases formation rate at synthesis of actinide waste forms. *MRS Proceedings* 2002, **757**, DOI: 10.1557/PROC-757-II3.20.
 - [32] Wong-Ng W, McMurdie HF, Hubbard CR, *et al.* JCPDS-ICDD research associateship (cooperative program with NBS/NIST). *J Res Natl Inst Stand Technol* 2001, **106**: 1013–1028.
 - [33] Smith KL, Lumpkin GR, Blackford MG, *et al.* The durability of synroc. *J Nucl Mater* 1992, **190**: 287–294.
 - [34] ASTM C1220-98. Standard test method for static leaching of monolithic waste forms for disposal of radioactive waste. ASTM International, West Conshohocken, PA, USA, 1998.
 - [35] Helean K, Begg B, Navrotsky A, *et al.* Enthalpies of formation of $\text{Gd}_2(\text{Ti}_{2-x}\text{Zr}_x)\text{O}_7$ pyrochlores. *MRS Proceedings* 2000, **663**, DOI: 10.1557/PROC-663-691.
 - [36] Wen G, Zhang K, Zhang H, *et al.* Immobilization and aqueous durability of Nd_2O_3 and CeO_2 incorporation into rutile TiO_2 . *Ceram Int* 2015, **41**: 6869–6875.
 - [37] McGlinn P, Advocat T, Leturcq G, *et al.* Leaching behaviour of zirconolite in 0.001M citric acid at 90 °C under various flow regimes. *MRS Proceedings* 2006, **932**, DOI: 10.1557/PROC-932-61.1.
 - [38] Yokoi H, Arita Y, Matsui T, *et al.* EXAFS study of $(\text{La}_{1-x}\text{M}_x)_2\text{Zr}_2\text{O}_7$ ($\text{M} = \text{Nd}$ and Ce). *J Nucl Mater* 1996, **238**: 163–168.
 - [39] Kingery WD, Bowen HK, Uhlmann DR. *Introduction to Ceramics*, 2nd edn. New York: John Wiley and Sons Incorporated, 1976.

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