

# Self-propagating synthesis of $Y_{2-x}Nd_xTi_2O_7$ pyrochlores using CuO as the oxidant and its characterizations as waste form

Kuibao Zhang<sup>a,c,\*</sup>, Zongsheng He<sup>a</sup>, Jiali Xue<sup>a</sup>, Wenwen Zhao<sup>a</sup>, Haibin Zhang<sup>b</sup>

<sup>a</sup> State Key Laboratory Cultivation Base for Nonmetal Composite and Functional Materials, Southwest University of Science and Technology, Mianyang, Sichuan, 621010, China

<sup>b</sup> Institute of Nuclear Physics and Chemistry, China Academy of Engineering Physics, Mianyang, 621900, China

<sup>c</sup> National Defense Key Discipline Lab of Nuclear Waste and Environmental Safety, Southwest University of Science and Technology, Mianyang, 621010, China

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## ABSTRACT

In this study,  $Y_2Ti_2O_7$  pyrochlore waste forms were rapidly prepared by self-propagating high-temperature synthesis plus quick pressing (SHS/QP) using CuO as the oxidant and Ti as the reductant. As the surrogate of trivalent actinides, Nd was introduced to substitute the Y site with nominal formulation of  $Y_{2-x}Nd_xTi_2O_7$ . Highly densified Nd-bearing  $Y_2Ti_2O_7$  pyrochlore waste forms were readily synthesized within 5 min from this process. The pyrochlore phase was generated as the exclusive ceramic phase within  $x \leq 1.0$ , while higher  $Nd_2O_3$  incorporation ( $x > 1.0$ ) results in impurity phases. Phase separation can be detected in the ceramic matrix, which is actually composed of Nd-rich and Y-rich pyrochlore solid-solutions. The representatively selected waste form ( $Nd_{0.5}$ ) demonstrates promising aqueous durability as the 42 days normalized leaching rates of Cu, Y and Nd are measured to be  $4.67 \times 10^{-2}$ ,  $4.42 \times 10^{-5}$  and  $3.17 \times 10^{-5} \text{ g m}^{-2} \text{ d}^{-1}$ .

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## 1. Introduction

The disposal of high-level radioactive wastes (HLW) has long been a great challenge in nuclear industry [1,2]. Advanced materials can improve the performance of nuclear waste matrices with elevated design flexibility and safety margins [3]. Traditionally, borosilicate or phosphate glasses were considered as generic waste product forms, which hold the capability to immobilize fission products, activation products and actinide nuclides. Because of the low thermodynamic stability, vitrious waste forms can undergo devitrification with time when it is irradiated or hydrated. The maximum tolerable amount of actinides to be incorporated in glass is about 5 wt.%. In recent decades, highly stable matrices of naturally existed minerals or ceramics have been proposed as an alternative strategy over vitrious waste forms [4–7]. Contrary to glass, ceramics exhibit much higher stability and can incorporate higher amount of actinides without significant degradation of the matrix

properties.

According to the previous reports, many naturally existed mineral phases were recognized as promising host materials for HLW immobilization, such as zirconolite ( $CaZrTi_2O_7$ ), pyrochlore ( $A_2B_2O_7$ ), perovskite ( $CaTiO_3$ ), monazite ( $CePO_4$ ), apatite ( $Ca_5(PO_4)_3(F,Cl,OH)$ ), zircon ( $ZrSiO_4$ ), sphene ( $CaTiSiO_5$ ), hollandite ( $BaAl_2Ti_6O_{16}$ ), rutile ( $TiO_2$ ) et al. [8–14]. Zirconolite and pyrochlore based materials are the most important hosts of actinides among these ceramic waste matrices. Zirconolite and pyrochlore in titanate ceramics are in closely related structure and derived from anion-deficient fluorite structure. Furthermore, multi-phase pyrochlore-based ceramics were chosen for the immobilization of excess weapon grade plutonium in the United States [15]. For the cubic titanate pyrochlore with empirical formulation of  $A_2Ti_2O_7$ , the A-site is 8-coordinated and  $Ti^{4+}$  site is 6-coordinated, which can accommodate many metallic cations over a wide range of valence states and ionic radius [16,17]. Thus, pyrochlore-based waste forms usually possess high loading capacity and radiation tolerance for the immobilization of long-life actinides.

Substantial studies have been conducted in the past decades to explore the feasibility of using pyrochlore as nuclear waste matrix [18–25]. The synthesis route, phase evolution, waste loading,

\* Corresponding author. State Key Laboratory Cultivation Base for Nonmetal Composite and Functional Materials, Southwest University of Science and Technology, Mianyang, Sichuan, 621010, China.

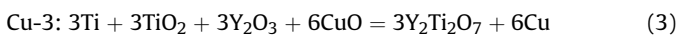
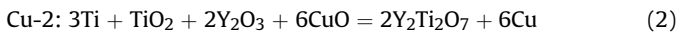
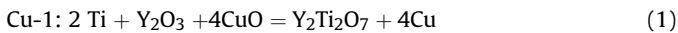
E-mail address: [zhangkuibao@swust.edu.cn](mailto:zhangkuibao@swust.edu.cn) (K. Zhang).

radiation stability and chemical durability have been comprehensively investigated. In the previous studies, pyrochlore-based waste forms were mainly synthesized from solid-state reaction and liquid phase synthesis (such as co-precipitation, liquid-mix and sol-gel) [16]. Muthuraman et al. have proposed an alternative synthesis route, self-propagating high-temperature synthesis (SHS) or combustion synthesis (CS), for the disposal of nuclear wastes [26]. The SHS technique is featured with high reaction speed, low energy consumption, simplified equipment requirement and convenient handling [27]. Because of these advantages, SHS technique was chosen as a candidate approach for environmental protection, such as stabilization of radioactive and toxic wastes [28–32]. For nuclear waste immobilization, SHS is advantageous in some special applications when the implement environment is confined. Thus, it is valuable to explore the feasibility of SHS route as a candidate approach for nuclear waste disposal.

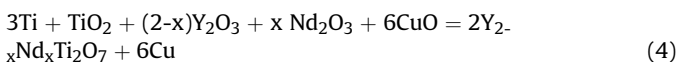
In our previous studies, we have conducted the SHS preparation of zirconolite ( $\text{CaZrTi}_2\text{O}_7$ ) based waste forms using Ti as the reductant [33–35]. The oxidant system and oxidant/reductant fraction were tailored to overcome the inherent faults of SHS technique, such as high reaction speed, low controllability and undesirable impurity phases. Meanwhile, hydraulic quick pressing (QP) was introduced to obtain highly compacted samples. Recently, we have synthesized  $\text{Y}_2\text{Ti}_2\text{O}_7$  pyrochlore by the similar SHS process using  $\text{Fe}_2\text{O}_3$  as the oxidant and Ti as the reductant [36]. In this study, we report the SHS/QP synthesis of  $\text{Y}_{2-x}\text{Nd}_x\text{Ti}_2\text{O}_7$  pyrochlores using CuO as the oxidant. The reaction formulation was firstly optimized for the synthesis of  $\text{Y}_2\text{Ti}_2\text{O}_7$ , where the reactant composition was tailored to obtain desirable temperature and phase composition. Subsequently,  $\text{Nd}_2\text{O}_3$  was incorporated as the surrogate of trivalent actinides according to its crystal chemistry parameters [37]. The phase composition, microstructure and  $\text{Nd}_2\text{O}_3$  immobilization were characterized. Meanwhile, the aqueous durability (Cu, Y and Nd) of selected Nd-bearing waste from ( $\text{Nd}_{0.5}$ ) was evaluated according to ASTM standard leaching test (C1220-68).

## 2. Experimental details

$\text{Y}_2\text{O}_3$ ,  $\text{Nd}_2\text{O}_3$ , Ti,  $\text{TiO}_2$  and CuO with purity higher than 99 wt.% and particle size lower than 200 meshes were purchased as the raw reactants. Firstly, the  $\text{Y}_2\text{Ti}_2\text{O}_7$  pyrochlore was synthesized with optimized phase composition and temperature. The SHS reactions were designed as follows with fixed CuO/Ti ratio of 2:1 and tailored  $\text{TiO}_2/\text{Ti}$  ratios of 0:2, 1:3 and 3:3.



The optimal reaction was selected for the subsequent  $\text{Nd}_2\text{O}_3$  immobilization, where the SHS reactions were designed as shown in the following equation:



The  $x$  value was adjusted from 0.25 to 2.0 ( $x = 0.25, 0.5, 0.75, 1.0, 1.5, 2.0$ ) to explore the maximum  $\text{Nd}_2\text{O}_3$  incorporation, which also represents the waste loading of trivalent actinides. The SHS/QP experiments were conducted identically as our previous study (illustrated in Fig. 1) [33]. About 15–30 g powder reactants were mixed and cold pressed at 10 MPa using  $\Phi 20$ –30 mm stainless

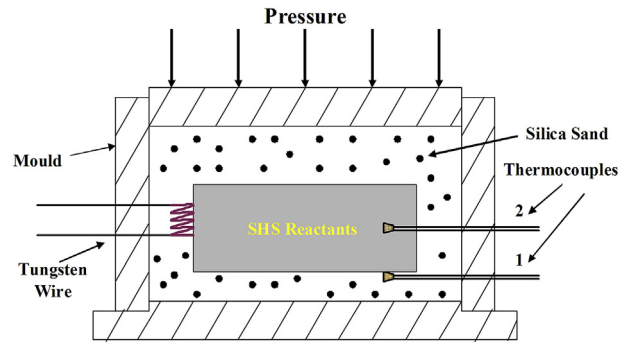


Fig. 1. Schematic diagram of the designed SHS/QP process.

mould. The SHS reactants were ignited by a tungsten wire, which was placed at one side with close contact of the green pellets. The reactants were ignited instantly under the high temperature radiation of tungsten wire. Before compression, the reaction temperatures were measured in advance by W/Re thermocouples located at the bottom and center (thermocouple 1 and 2 in Fig. 1) of the green pellets. On the basis of temperature measurement, the red-hot samples were compressed at about 50 MPa by hydraulic pressing with holding time of 60 s. During this process, 70–100 meshes silica sand was employed as the heat insulator and pressure transmission medium. After cooling, the compacted specimens were cutted and polished to 2000 meshes for the following characterizations.

The SHS-ed specimens were ground to refined powders and characterized by X'Pert PRO X-ray diffractometer (XRD; PANalytical B.V., Netherlands) with Cu  $K\alpha$  radiation. The XRD results were subjected to Rietveld refinement using Fullprof-2k software package. Microstructure and elemental distribution were analyzed using field-emission scanning electron microscopy (FESEM; Zeiss Ultra-55, Oberkochen, Germany) equipped with energy-dispersive X-ray (EDX) spectrometer attachment. Aqueous durability of the monolithic  $\text{Nd}_{0.5}$  specimen was evaluated according to the static standard of materials characterization center (MCC-1) [38,39]. The selected  $x = 0.5$  sample was cutted and grinded to external dimension of  $17.7 \times 6.9 \times 5.8$  mm. The testing bar was suspended by a Cu wire and immersed in 80 ml deionized water ( $\text{pH} = 7$ ) within PTFE container. The containers were subsequently moved into a  $90^\circ\text{C}$  baking oven with testing durations of 1, 3, 7, 14, 21, 28, 35 and 42 days. The leachate concentrations ( $C_i$ ) of Y and Nd were measured by inductively coupled plasma-mass spectrometry (ICP-MS) using an Agilent 7700  $\times$  spectrometer, while the consistency of Cu was obtained by inductively coupled plasma (ICP, iCAP 6500, MA, USA). The normalized elemental leaching rates ( $LR_i$ ) were calculated as follows:

$$LR_i = \frac{C_i \cdot V}{S_A \cdot f_i \cdot \Delta t} \quad (5)$$

where  $f_i$  is the mass fraction of element  $i$  in the sample,  $S_A$  is the geometric surface area,  $V$  is the volume of the leachate and  $\Delta t$  is the interval soaking duration in days. According to the ASTM standard, the  $S_A$  value represents to the contact area between the leaching sample and the immersion leachate. As the selected  $\text{Nd}_{0.5}$  sample was not completely densified, the presence of open pores should be considered for the  $S_A$  calculation. The open porosity was measured to be 5.2% for the tested  $\text{Nd}_{0.5}$  sample. And the  $S_A/V$  value was calculated to be about  $7.33 \text{ m}^{-1}$ , which conforms to the size requirement of ASTM leaching standard ( $S_A/V = 0.5$ – $10.0 \text{ m}^{-1}$ ).

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