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Phase evolution and chemical stability of the Nd_2O_3-ZrO_2-SiO_2 system synthesized by a novel hydrothermal-assisted sol-gel process

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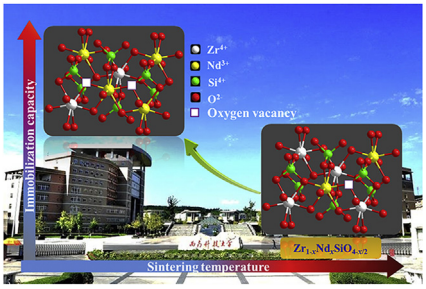
HIGHLIGHTS

- Nd-doped $ZrSiO_4$ can be obtained at low temperature (1723K) and short time (6 h).
- Properties of the ceramics highly depend on sintering temperature and pH.
- Acidity condition is beneficial to phase formation and densification of $ZrSiO_4$.
- Immobilization capacity of Nd can be enhanced by hydrothermal-assisted sol-gel route.
- Immobilization capacity of Nd increases with decreasing sintering temperature.

GRAPHICAL ABSTRACT



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ABSTRACT

A hydrothermal-assisted sol-gel process, a novel method of combining both advantages of sol-gel and hydrothermal processes, was developed to synthesize dense Nd-doped $ZrSiO_4$ ceramics with high Nd (surrogate for trivalent actinides) loading at low sintering temperature (1723 K) and short time (6 h). The evolutions of phase and microstructure of the obtained ceramics with the varying composition, sintering temperature and pH value were investigated. The chemical durability of the ceramics was also evaluated. The results show that the properties of ceramics strongly depend on sintering temperature and pH value. The acidic condition is beneficial to phase formation and densification of $ZrSiO_4$ ceramics. It was found that the maximum immobilization capacity of Nd in the single-phase $ZrSiO_4$ ceramics is highly dependent upon the synthesis method and sintering temperature. With decreasing sintering temperature, the maximum immobilization capacity increases. And the immobilization capacity of Nd in $ZrSiO_4$ ceramics was found to be enhanced by the hydrothermal-assisted sol-gel method. Furthermore, the normalized release rate of Nd in Nd-doped $ZrSiO_4$ ceramics decreases with increasing time and remains almost

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unchanged (~10^{-4} g m^{-2} d^{-1}) after 28 days, and the fractional release of Nd in all samples is about ~10^{-5} wt%, exhibiting high chemical stability.

1. Introduction

Zirconium silicate ($ZrSiO_4$) ceramics have drawn considerable interest due to its high thermal decomposition temperature, excellent chemical stability and low thermal expansion coefficient, as well as the capacity to immobilize actinides in its lattice [1–9]. Therefore, $ZrSiO_4$ ceramics are considered as the promising materials for potential nuclear waste forms [6–10].

Single-phase pure $ZrSiO_4$ ceramics are very difficult to prepare [11]. This is mainly due to the fact that the zircon crystallizes on the interlayer between ZrO_2 and SiO_2 during the preparation, which seems to be a diffusion controlled process [5,12] Generally, in order to obtain a relatively formation efficiency of $ZrSiO_4$ ceramics, high sintering temperature (1773–1973 K) and long holding time (48–72 h) are essential when the conventional solid state method is employed [8,9]. This seriously restricts the application of $ZrSiO_4$ ceramics for the immobilization of radioactive waste. There are many disadvantages when the high sintering temperature and long holding time are used to fabricate the waste forms. On the one hand, the high treatment temperature will cause the low melting point radionuclides to volatilize and produce aerosols, which result in ineffective immobilization of high-level radioactive waste. On the other hand, high sintering temperature and long holding time result high requirement of sintering equipment and lead to high cost. Therefore, development of a relatively fast and efficient method to synthesize $ZrSiO_4$ ceramics waste forms at lower temperatures and shorter times is needed.

$ZrSiO_4$ ceramics containing various actinides or actinide surrogates were generally prepared by the solid state method [8,9,13–15]. Compared with solid state method, the sol-gel method, by which the precursor powders could be sufficiently mixed at the molecular level, is viewed as a low temperature and rapid densification technique [16]. $ZrSiO_4$ was synthesized by a sol-gel route at a low temperature with assistance of soft mechano-chemical activation of derived precursors in a high-energy density stirred bead mill [17]. Tu et al. [18] found that Ce-doped zircon ceramics with high formation efficiency and compact structure can be fabricated by sol-gel method at low sintering temperature (1673 K) in short time (10 h). These previous works demonstrated that sol-gel method can be developed as a fast and efficient method to synthesize $ZrSiO_4$ ceramics. However, most of previous studies mainly focus on the synthesis of $ZrSiO_4$ via conventional sol-gel method. A hydrothermal-assisted process method, with the advantages of high purity and good homogeneity, has emerged as a powerful tool for the controlled synthesis of nanostructural or microstructural materials [19–21]. The hydrothermal-assisted process utilizes a solvent under pressures and temperatures above its critical point to speed up reactions [22]. In a sealed vessel, solvents can be brought to temperatures well above their boiling points by increasing pressures resulting from heating. Therefore, the hydrothermal-assisted process has been used for the synthesis of nano-materials because of its simplicity, high efficiency and low cost [23]. As a novel method to prepare oxide powders, the hydrothermal-assisted sol-gel process has the double advantages of both sol-gel and hydrothermal method, and has become attractive in the last decade due to its inherent advantage such as good homogeneity, high purity, good crystallinity, controllable morphology and narrow particle size distribution of the obtained powders [24]. For instance, $KNbO_3$ powder with high electro-optic and nonlinear optical coefficients can be facilely prepared by hydrothermal-assisted sol-gel processing [25]. Zhang et al. [26] prepared Li_2FeSiO_4/C composite materials via a hydrothermal-assisted sol-gel method. Sc and Gd co-doped $BaTiO_3$ nano-crystals can be obtained by a facile hydrothermal-assisted sol-gel process [27]. These early successes with the hydrothermal-assisted sol-gel process suggest it could be an advisable method to synthesize Nd-doped $ZrSiO_4$ ceramics. However, to the best of our knowledge, studies on hydrothermal-assisted sol-gel process synthesis of Nd-doped $ZrSiO_4$ ceramics are limited.

According to our previous work [8], $Zr_{1-x}Nd_xSiO_{4-x/2}$ ($0 \le x \le 0.1$) ceramics could be prepared by sintering at 1823 K for 72 h by solid state reaction method. Neodymium (Nd) was used as surrogate for trivalent actinides [28–30]. In this paper, two main goals were pursued: firstly, investigating the effect of synthesis conditions (sintering temperature and pH value) and Nd immobilization on the phase and structure evolutions of the $ZrSiO_4$ ceramics; secondly, obtaining the first data concerning the isomorphous substitution capacity of $ZrSiO_4$ for Nd and the chemical durability of Nd-doped $ZrSiO_4$ ceramics obtained from hydrothermal-assisted sol-gel process. Nd-doped $ZrSiO_4$ ceramics with $Zr_{1-x}Nd_xSiO_{4-x/2}$ ($0 \le x \le 0.1$) composition were synthesized by hydrothermal-assisted sol-gel process for the first time. The properties of the ceramics obtained by conventional solid state method and hydrothermal-assisted sol-gel process were compared to understand the benefit of hydrothermal-assisted sol-gel process. The effects of composition, sintering temperature and pH value on the phase and microstructures evolutions of the ceramics obtained from hydrothermal-assisted sol-gel process were investigated systematically. Furthermore, the chemical durability of the Nd-doped $ZrSiO_4$ ceramics synthesized by hydrothermal-assisted sol-gel process was evaluated as well.

2. Experimental

2.1. General formula design

According to the theory of isomorphism, we speculate the Zr in $ZrSiO_4$ structure can be substituted by Nd (neodymium, surrogates for trivalent actinides). Moreover, considering the ion charge balance, the chemical general formula $Zr_{1-x}Nd_xSiO_{4-x/2}$ ($0 \le x \le 0.1$) is employed.

2.2. Preparation

All the chemical reagents used in the experiment were of analytical grade and used without any purification. Zirconium oxychloride ($ZrOCl_2 \cdot 8H_2O$), neodymium nitrate ($Nd(NO_3)_3 \cdot 6H_2O$) and ethyl orthosilicate (TEOS, $(C_2H_5O)_4Si$) were used as raw materials to prepare sol-gel precursors. Fig. 1 shows the synthesis route of the Nd-doped $ZrSiO_4$ ceramics through the hydrothermal-assisted sol-gel process synthesis. The mole ratios of $ZrOCl_2 \cdot 8H_2O$, $Nd(NO_3)_3 \cdot 6H_2O$ and TEOS were (0.9–1):(0–0.1):1, and 50% ethanol-water solution was chosen as the solvent. First of all, the TEOS was prehydrolysed in the solvent, then $ZrOCl_2 \cdot 8H_2O$ and $Nd(NO_3)_3 \cdot 6H_2O$ were added into the hydrolyzed solution. The obtained solution was stirred at room temperature while the pH value was adjusted to 4, 7 or 9 using ammonia water. The mixture was subsequently transferred and sealed in a Teflon-lined stainless steel