

The expansion ratio analyses on $\text{Zr}_{1-x}\text{Ce}_x\text{SiO}_4$ compounds

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Abstract. In order to investigate the elements doping effects on expansion ratio, a series of $\text{Zr}_{1-x}\text{Ce}_x\text{SiO}_4$ ($0.01 \leq x \leq 0.05$) ceramics were synthesized by high temperature solid state reaction, and the expansion ratio was systematically studied. The results show that the element doping has significant influence on the expansion ratio. The radial, axial and volume expansion ratio of Ce-doped zircon ceramics decrease in the $\text{Zr}_{1-x}\text{Ce}_x\text{SiO}_4$ compounds from $x = 0.01$ to $x = 0.05$. Furthermore, it also found the changes of $\text{Zr}_{1-x}\text{Ce}_x\text{SiO}_4$ ($0.01 \leq x \leq 0.05$) before and after sintering size in detail. At the same time, these results indicated that Ce-doped zircon ceramics good performance in expansion ration.

1. Introduction

In the field of radioactive waste treatment, the geological disposal is complex and the promising material should has good performance in physic property like density, thermal conductivity and expansion. The waste form with low expansion rate means that it has high refractoriness and strong thermal shock resistance, which meets the strict requirements [1, 2]. Therefore, the expansion rate of the material is an important physical property parameter, which represents the length or size of material increased when heated [3]. The expansion rate is also an important factor in the engineering technology for the materials used in the condition of constant temperature fluctuation [4, 5]. The expansion rate is not only the performance of the material, but also the essential parameter in the design of the structure [6, 7]. It is also the main reason for the failure of the materials and components that the large expansion ratio leads to the fatigue propagation of the internal crack [8]. The material has excellent thermal shock resistance due to the smallest thermal stress, when the material with small expansion ratio is subjected to thermal shock. The expansion rate increases the average distance of the material atoms at the certain temperature. With the increase of temperature, the vibration of the solid material is gradually strengthened, which leads to the increase of the average distance of the lattice [9, 10]. The material force between particles and the degree of density about material structure have a great influence on the material expansion ratio than others. Therefore, in this paper, we will study the expansion ratio of the Ce-doped zircon ceramics for waste form in detail.

There are many factors that would influence the expansion ratio of materials, in which the method of doping elements, and the heating would have a great influence on the expansion ratio [11]. In this experiment, we will study the expansion ratio in the field of adding a certain amount of Ce element for the waste form and before and after sintering [12-15]. The doping of tetravalent element Ce was simulated as radioactivity nuclide into zircon ceramic and produce a series of $\text{Zr}_{1-x}\text{Ce}_x\text{SiO}_4$ ($0.01 \leq x \leq 0.05$) samples [16]. The size of $\text{Zr}_{1-x}\text{Ce}_x\text{SiO}_4$ ($0.01 \leq x \leq 0.05$) samples were measured in radius and axial before and after sintering. And the volume was calculated.



2. Experiment

In order to investigate expansion ratio of $Zr_{1-x}Ce_xSiO_4$ ($0.01 \leq x \leq 0.05$) compounds, Ce^{4+} was used as the simulacrum for tetravalent actinides, and the synthesis experiments were heated at 1500 °C for 72 hours, designing specific mole fraction. Table 1 presents the contents of starting materials for synthesizing $Zr_{1-x}Ce_xSiO_4$ ($0.01 \leq x \leq 0.05$). In the experiment, AR grade ZrO_2 , CeO_2 and SiO_2 were selected as the starting materials. A series of $Zr_{1-x}Ce_xSiO_4$ ($0.01 \leq x \leq 0.05$) were prepared by high temperature solid-state reaction method. Before weighing, all the raw powders were heated at 120 °C for 6 hour to remove adsorptive water. Then stoichiometric amounts of the powders in appropriate ratios were weighed, and ground in analytically pure ethanol medium. The dried powders were compacted in a pellet form (12 mm diameter and ~ 4 mm thickness) at a pressure of 10 MPa. The pellets were sintered at 1500 °C for 72 h in air atmosphere to fabricate dense bulk ceramic at a heating ratio of 5 °C/min. The sintered compounds were taken out of the furnace after being naturally cooled to room temperature. After and after sintering, the size of $Zr_{1-x}Ce_xSiO_4$ ($0.01 \leq x \leq 0.05$) samples were measured in radius (r) and high (h). The volume (V) was calculated as the following equation:

$$V = r^2 \cdot h \cdot \pi$$

Where r is the radius of the ceramic (mm), h is the of the ceramic (mm) and π is ratio of the circumference of a circle to its diameter.

Table 1. The contents of starting materials for synthesizing $Zr_{1-x}Ce_xSiO_4$ ($0.01 \leq x \leq 0.05$)

Target compounds	Additive amount of raw materials /g		
	ZrO_2	CeO_2	SiO_2
$Zr_{0.99}Ce_{0.01}SiO_4$	1.9884	0.0281	0.9793
$Zr_{0.98}Ce_{0.02}SiO_4$	1.9683	0.0561	0.9793
$Zr_{0.97}Ce_{0.03}SiO_4$	1.9363	0.0837	0.9733
$Zr_{0.96}Ce_{0.04}SiO_4$	1.9163	0.1115	0.9733
$Zr_{0.95}Ce_{0.05}SiO_4$	1.8963	0.1394	0.9733

3. Results and discussion

The value of radius, high and volume are taken as the radial, axial and volume of the samples. The effect of doping Ce element on the expansion ratio of samples is also studied [17, 18]. Due to other factors also affect the expansion ratio of samples, these samples were put in the same processing method, processing environment and measuring method. So other factors were ignored, and the sintering heating ratio and other factors are the same. We minimized other factors affecting the expansion ratio of the sample [19].

Table 2. Tested expansion of $Zr_{1-x}Ce_xSiO_4$ ($0.01 \leq x \leq 0.05$) compounds

Target compounds	Before sintered			After sintered			Expansion ratio /%		
	r_0/m m	h_0/m m	V_0/mm^3 3	r/m m	h/m m	V/mm^3 3	radia l	axial	volum e
$Zr_{0.99}Ce_{0.01}SiO_4$	6	4.1	463.69 9	6	4.3	486.31 8	0	4.878	4.878
$Zr_{0.98}Ce_{0.02}SiO_4$	6	4.1	463.69 9	5.99	4.22	475.68 1	-0.16 7	2.927	2.584
$Zr_{0.97}Ce_{0.03}SiO_4$	6	4.1	463.69 9	5.89	4.22	459.93 1	-1.83 3	2.927	-0.813
$Zr_{0.96}Ce_{0.04}SiO_4$	6	4.1	463.69 9	5.75	4.2	436.24 9	-4.16 7	2.439	-5.920
$Zr_{0.95}Ce_{0.05}SiO_4$	6	4.1	463.69 9	5.70	4.2	428.69 6	-5.00 0	2.439	-7.549

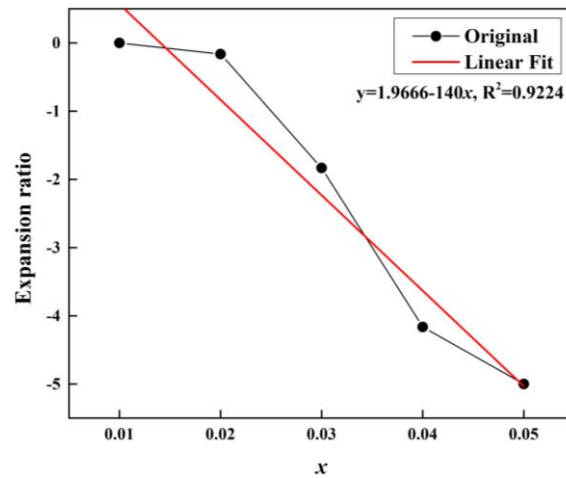


Figure 1. The radial expansion ratio of $Zr_{1-x}Ce_xSiO_4$ ($0.01 \leq x \leq 0.05$) compounds.

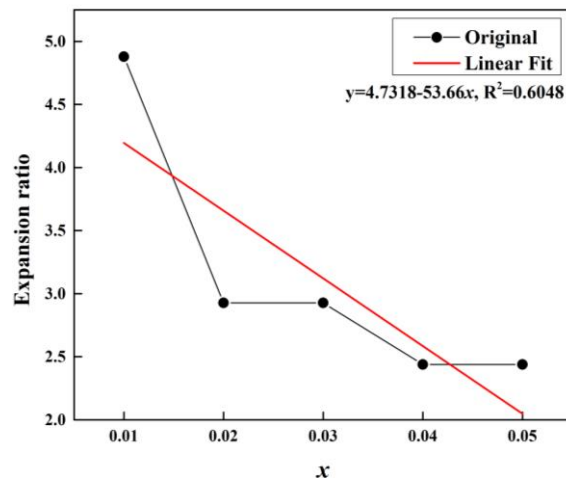


Figure 2. The axial expansion ratio of $Zr_{1-x}Ce_xSiO_4$ ($0.01 \leq x \leq 0.05$) compounds.

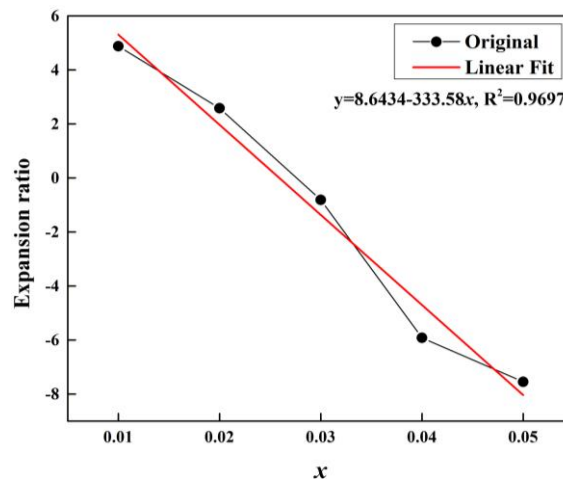


Figure 3. The volume expansion ratio of $Zr_{1-x}Ce_xSiO_4$ ($0.01 \leq x \leq 0.05$) compounds.

Table 2 gives the measured data of radius, high and volume, and calculated the expansion and size of $Zr_{1-x}Ce_xSiO_4$ ($0.01 \leq x \leq 0.05$) compounds before and after sintering. Figures 1 - 3 reflect the trends of the radial, axial and volume expansion ratio of $Zr_{1-x}Ce_xSiO_4$ ($0.01 \leq x \leq 0.05$) samples before and after sintering. The results show that the radial expansion ratio of $Zr_{1-x}Ce_xSiO_4$ ($0.01 \leq x \leq 0.05$) samples ranges from 0 % for $Zr_{0.99}Ce_{0.01}SiO_4$ to -5.000 % for $Zr_{0.95}Ce_{0.05}SiO_4$. The same as the axial

expansion ratio from 4.878 % to 2.439 %. The volume expansion ratio from 4.878 % to -7.549 %. From Figure 1 - 3, it can be clearly seen that with the increase of the amount of Ce, expansion ratio appears to a trend of decreasing gradually. By using the linear equation $y = a + b x$, the expansion ratio can be linear fitted by the x in the sample. The linear relationship is expressed as $y = 1.9666 - 140 x$, $y = 4.7318 - 53.66 x$, $y = 8.6434 - 333.58 x$ in the radial, axial and volume. R^2 value is greater than 0.9224, 0.6048, 0.9697. The R^2 indicates that expansion ratio and the content of Ce directly have a good linear relationship. From the experimental data and mapping can be seen the samples reflected a trend of shrinkage in radial, axial and volume with the tetravalent simulated nuclide Ce increasing. The reason is that the atomic radius of Ce^{4+} is larger than the atomic radius of Zr^{4+} . When Ce^{4+} completely occupied the lattice position of Zr^{4+} , with the simulated nuclides doping, the greater the tendency of the sample to shrink in the radial, axial and volume. Based on the previous study, the density of $Zr_{1-x}Ce_xSiO_4$ ($0.01 \leq x \leq 0.05$) compounds is gradually increased with increasing the tetravalent simulated nuclide Ce doping. Therefore, when the quality of the sample is certain, sample volume will decrease with the addition of tetravalent simulated nuclide Ce in the macroscopic. And the experiments have confirmed that with the increase of the tetravalent simulated nuclide Ce, the size of sample in radial, axial and volume gradually decreases.

4. Conclusions

In order to obtain the data of the expansion ratio of zircon immobilized simulated tetravalent actinides, the samples was measured and analyzed before and after sintering. The quantitative relationship between the amount of nuclide and the expansion ratio was obtained. The main conclusions are as follows: after sintering, the samples have shrinkage in the radial and axial. And it have obvious change in the volume. The axial have changes slightly. With the increase of the doping amount Ce element, the radial expansion ratio changed from 0 % to -5.000 %. The volume expansion ratio of the samples varied from 4.878 % to -7.549 %. The volume of samples had a great change. The doping Ce element has a great influence on the expansion ratio of the samples. Expansion ratio of $Zr_{1-x}Ce_xSiO_4$ ($0.01 \leq x \leq 0.05$) compounds decrease gradually with the increase of Ce content. Expansion ratio and x value has linear fitted as $y = 1.9666 - 140 x$, $y = 4.7318 - 53.66 x$, $y = 8.6434 - 333.58 x$ in the radial, axial and volume. R^2 value is greater than 0.9224, 0.6048, 0.9697.

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