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MATERIALS CHARACTERIZATION

Comparison study on the high-temperature phase stability of CaO-doped zirconia made using different precipitants

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Abstract

CaO-doped zirconia was synthesized by a traditional sol–gel method using both NaOH and ammonia solutions as precipitants. The high-temperature phase stability was investigated following calcining at 1000 °C for 2 h. XRD and Raman spectra were used to characterize the crystal form of the zirconia. The results indicate that the concentration of OH^- introduced into the ZrO_2 lattice is the main factor controlling the crystal form of nanosized zirconia using NaOH solution as the precipitant. CaO-doped zirconia synthesized using an ammonia solution as the precipitant can maintain the tetragonal phase after calcining at 1000 °C for 2 h.

Keywords: Cubic; Tetragonal; Zirconia; High-temperature phase stability; Sol–gel

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1. Introduction

Zirconia has become one of the most industrially important high-temperature structural materials because of good hardness, high strength, toughness, etc. [1–5]. Pure zirconia exhibits three different phases: monoclinic (m-ZrO_2), which is stable below 1170 °C; tetragonal (t-ZrO_2), which is stable between 1170 °C and 2370 °C; and cubic (c-ZrO_2), stable from 2370 °C to its melting temperature of 2680 °C [6]. Besides m-ZrO_2, metastable t-ZrO_2 can also be stable at room temperature by controlling the preparation conditions [6]. Stabilized t-ZrO_2 is considered an important structural ceramic because of its excellent mechanical properties such as fracture toughness, high strength and hardness [7]. However, a phase transformation from t-ZrO_2 to m-ZrO_2 prevents it from a broader application temperature range because of the volume change that occurs [7]. Over the past few years, phase stability studies have attracted many researchers' attention. Alkaline earth doping methods [8–11] and rare earth doping methods [12–18] have been widely examined at present.

In this paper, we have studied the differences in the high-temperature phase stability of CaO-doped zirconia using either an ammonia solution or a NaOH solution as the precipitant by the traditional sol–gel method. The results indicate that the NaOH solution precipitant can improve the high-temperature phase stability of CaO-doped t-ZrO_2 and the ammonia solution precipitant can

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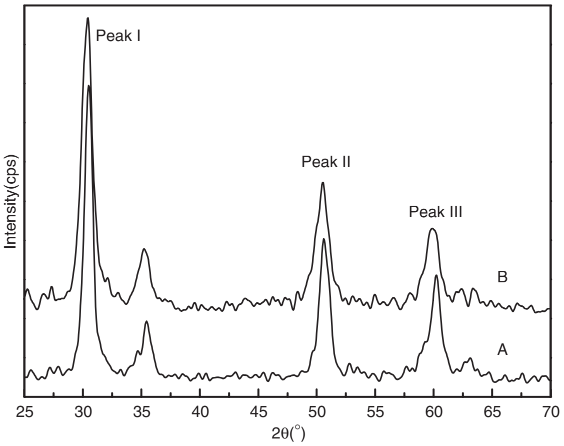

Fig. 1. XRD patterns of the samples of A1 and B1.

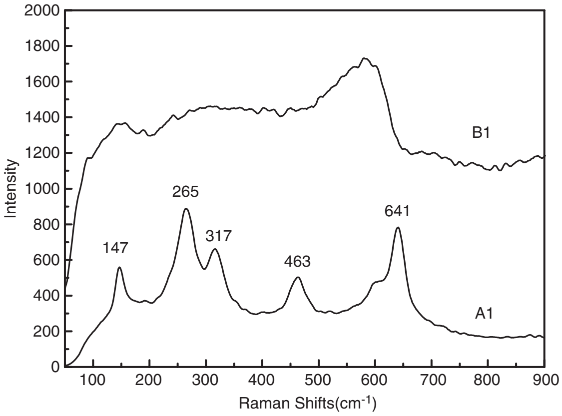

Fig. 2. Raman spectra of the samples of A1 and B1.

improve the high-temperature phase stability of CaO-doped c-ZrO_2.

2. Experimental

2.1. Materials

For these experiments, the starting materials zirconium oxychloride, hydrochloric acid and *n*-butanol were purchased from China National Medicine Group Shanghai Chemical Reagent Company. Ammonia, ethanol and calcium carbonate were purchased from Nanjing Chemical Reagent No. 1 Factory; polyethylene glycol 400 (PEG400) and polyethylene glycol 2000 (PEG2000) were purchased from Beijing Yili Chemistry Co. Ltd.

2.2. Preparation

A 0.5 M $CaCl_2$ aqueous solution was prepared by the reaction of HCl and $CaCO_3$, in stoichiometric ratio. Then, 20 ml of a $ZrOCl_2$ aqueous solution (0.8 M) was mixed with 6.4 ml of $CaCl_2$ aqueous solution (0.5 M) and 170 ml absolute ethanol using a magnetic stirrer; to this was added 1.0 g PEG2000 and PEG400 to form a clear solution. A 1.0 M ammonia solution was added to the solution at a rate of 60 drops/min under 500 rpm continuous to attain a pH 8–9. This reacted solution was aged for 24 h under static conditions to form a precipitate, which was washed several times with distilled water until no Cl^- could be detected by a $AgNO_3$ aqueous solution. Finally, the precipitate was washed using absolute ethanol, dissolved into 100 ml *n*-butanol under continuous vigorous stirring at a rate of 1500 rpm for 10 min and heated to boiling at 117–118 °C. Heating of the solution was continued until the *n*-butanol volatilized completely to form a white powder, designated as Powder A. Powder B was prepared using the same preparation conditions except that a NaOH solution was used as the precipitant. Both the A and B powders were calcined at 650 °C for 2 h to form the samples identified as A1 and B1, respectively. The A1 and B1 samples were further calcined at 1000 °C for 2 h to form the samples A2 and B2, respectively.

2.3. Instruments

X-ray diffraction (XRD) was carried out on a Bruker D8 Advanced X-ray diffraction instrument using Cu Kα radiation); the diffraction angle (2θ) from 20 to 70° was

Table 1
Diffraction data of the samples of A1 and B1

Sample	Peak I				Peak II			Peak III	
	2θ (°)	d (Å)	D (nm)	2θ (°)	d (Å)	D (nm)	2θ (°)	d (Å)	D (nm)
A1	30.51	2.9279	11.2	50.64	1.8011	8.9	60.29	1.5352	11.2
B1	30.50	2.9286	8.9	50.52	1.8050	7.2	59.93	1.5422	9.0