Available online at www.sciencedirect.com
SCIENCE DIRECT®
Materials Research Bulletin 41 (2006) 1319–1329
Materials Research Bulletin
www.elsevier.com/locate/matresbu

Influence of synthesis routes on the performance from weakly agglomerated yttria-stabilized zirconia nanomaterials

Xianshuang Xin [a,b], Zhe Lü [a,b], Xiqiang Huang [a,b], Xueqing Sha [a,b], Yaohui Zhang [a,b], Wenhui Su [a,b,c,d,*]

[a] *Center for Condensed Matter Science and Technology, Harbin Institute of Technology, Harbin 150001, China*
[b] *Key Laboratory of the Condensed Matter Science and Technology, Harbin Institute of Technology, HeiLongJiang Provincial Universities, Harbin 150001, China*
[c] *Department of Condensed Matter Physics, Jilin University, Changchun 130023, China*
[d] *International Center for Materials Physics, Academia Sinica, Shenyang 110015, China*

Received 3 September 2005; received in revised form 17 December 2005; accepted 26 December 2005
Available online 2 February 2006

Abstract

Weakly agglomerated nanocrystalline YSZ (yttria-stabilized zirconia) was synthesized by three different routes, namely homogeneous precipitation, ammonium hydroxide-based directly hydrothermal and urea-based homogeneously hydrothermal methods. The XRD and TEM results showed that well-crystallized nanocrystalline YSZ with homogenous and weakly agglomerated assembly was obtained from these processes. The Raman scattering results of the three samples suggested that cubic zirconia was formed as major phase, and consisted of the tetragonal zirconia as minor one. The sintering behavior of the two hydrothermal samples indicated a significant shrinkage at $T < 570$ °C. However, the shrinkage rates of the three samples showed similar at $T > 570$ °C. Impedance spectroscopy was used to determine the ac ionic conductivity. The total and grain boundary conductivities of the sample obtained from ammonium hydroxide-based hydrothermal method were higher than those of the samples obtained from homogeneous precipitation and urea-based homogeneously hydrothermal methods, whereas the total and grain boundary activation energies of the former being slightly lower.

Keywords: A. Nanostructures; A. Oxides; B. Chemical synthesis; D. Electrical properties

1. Introduction

Stabilized zirconia is an important ceramic material for catalyst support, oxygen sensor, electrochemical oxygen pump, thermal barrier coating, and solid oxide fuel cell (SOFC), etc. [1–4]. To acquire better applications about yttria-stabilized zirconia (YSZ), the diverse synthesis methods are still needed for preparing high quality and ultra fine powders with required characteristics in terms of their size, morphology, microstructure, etc. The synthesis conditions must be well controlled to obtain fine powders with narrow particle size distribution that enhance densification and reactivity [5–9].

* Corresponding author. Tel.: +86 451 86418570; fax: +86 451 86412828.
E-mail addresses: xinxianshuang@sohu.com (X. Xin), suwenhui@hit.edu.cn (W. Su).

0025-5408/$ – see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.materresbull.2005.12.014

Homogeneous precipitation process [10–13] has been widely used to produce monodisperse metal oxide particles with various shapes and sizes. If the precipitation agent is added directly by simply pouring one solution into another, then there is little control of the chemistry reaction during precipitation because of the large and inhomogeneous gradients in solution concentration. However, a better control of chemical and morphological characteristics can be achieved if the precipitating ligands are generated simultaneously and uniformly throughout the solution, i.e. a homogeneous precipitation process. Meantime, hydrothermal synthesis [14–17] is an attractive process for the synthesis of nanocrystalline oxide powders. This process involves precipitation from aqueous solution under conditions of elevated temperature and pressure. By controlling reaction, it is possible to produce nanocrystalline powders with controlled particle size, controlled stoichiometry, and in some cases controlled particle morphology. The elimination of any calcinations step significantly reduces the tendency for agglomeration of the powders. Weakly agglomerated powders are needed for both dry powders compaction, and the preparation of stable suspensions in liquids for thin or thick film production [18].

In this study, the urea and ammonium hydroxide used as precipitation agents reacted with soluble Y^{3+} and ZrO^{2+} salts to prepare weakly agglomerated nanocrystalline YSZ by three preparation methods. This work focused on the comparative study about the characterization and electrical properties of the monodispersed nanocrystalline YSZ obtained from three different synthesis processes. Characterizations were performed to investigate the crystalline structure, phase identification, grain size and morphology and the sintering behavior of nanocrystalline YSZ and its precursor. Moreover, for comparison, the resulting electrical properties of YSZ samples prepared by the three different methods were investigated.

2. Experimental

2.1. Samples preparation

Three synthesis routes, referred to as methods A, B and C, were used for preparation of YSZ nanomaterials as described below.

2.1.1. Homogeneous precipitation process (method A)

The raw materials of Y_2O_3 (99.9%) and $ZrOCl_2{\cdot}8H_2O$ (99.0%) were used for the synthesis of YSZ. Y_2O_3 was dissolved into a small amount of nitric acid. $ZrOCl_2{\cdot}8H_2O$ was dissolved into deionized water and mixed with the yttrium nitrate solution. This solution was then added to urea (99.0%) solution and diluted to the ZrO^{2+} concentration of 0.05 mol/l. The stoichiometric solutions (molar ratio 4:23 of Y^{3+}:Zr^{4+}) were transferred to a Teflon cup and put into a stainless steel autoclave. The autoclave was heated to 85 °C for 1 h to form hydrogel precipitation. The hydrogel precipitation was collected by centrifugation and washed with deionized water repeatedly, and then dried overnight in an oven at 85 °C in air, finally calcined at 500 °C for 2 h.

2.1.2. Ammonium hydroxide-based directly hydrothermal method (method B)

The appropriate quantities of Y^{3+} and ZrO^{2+} solutions were dissolved separately in water and mixed. Ammonium hydroxide (4 mol/l) was then added dropwise into the solution under vigorous stirring. The precipitated gels, which were prepared without separating the precipitate from their mother liquor, were sealed into Teflon-lined stainless-steel vessel and hydrothermally treated at 180 °C for 2 h in a thermostatted oven. The oven was quenched from 180 °C to room temperature. The crystallized powder was filtered and repeatedly washed with deionized water and ethanol until no reaction with Cl^- ions (with $AgNO_3$ 1 M) from the filtered solvent, and finally dried at 80 °C for 2 h.

2.1.3. Urea-based homogeneously hydrothermal method (method C)

A mixed solution of ZrO^{2+} salt, Y^{3+} salt and urea in the molar ratio of ZrO^{2+}/Y^{3+}/urea = 1/0.174/15 was poured into a Teflon cup with an inner volume of 1 l held in a stainless steel autoclave. The Teflon cups were used in all experiments to avoid contamination from the reaction vessel. After the autoclave was sealed, it was heated to 85 °C for 1 h, subsequently at 180 °C for another 2 h under autogenous pressure. As the autoclave cooled down to room temperature naturally, the precipitated powders were filtered, washed with deionized water and ethanol to remove the soluble chlorides and to reduce agglomeration, and then dried in an oven at 80 °C for 2 h.