



Gd₂Zr₂O₇ and Nd₂Zr₂O₇ pyrochlore prepared by aqueous chemical synthesis

Linggen Kong*, Inna Karatchevtseva, Daniel J. Gregg, Mark G. Blackford, Rohan Holmes, Gerry Triani

Institute of Materials Engineering, Australian Nuclear Science and Technology Organization, New Illawarra Road, Lucas Heights, NSW 2234, Australia

Received 5 March 2013; received in revised form 7 May 2013; accepted 12 May 2013

Available online 13 June 2013

Abstract

Pyrochlore structured Gd₂Zr₂O₇ and Nd₂Zr₂O₇ are produced via complex precipitation processing. A suite of characterization techniques, including FTIR, Raman, X-ray and electron diffraction, TEM, SEM as well as nitrogen sorption are employed to investigate the structural and grain size evolution of the synthesized and calcined powder. Results show that Gd₂Zr₂O₇ with the pyrochlore structure are produced after calcination at 1400 °C for 12 h while Nd₂Zr₂O₇ has already formed the pyrochlore structure at 1200 °C. This method allows the formation of dense materials at relatively low temperature, with bulk densities over 92% of the theoretical values achieved after sintering at 1400 °C for 50 h. This unique aqueous synthetic method provides a simple pathway to produce pyrochlore lanthanide zirconate without using either organic solvent and/or mechanical milling procedures, making the synthesis protocol an attractive potential scale-up production of highly refractory ceramics.

Crown Copyright © 2013 Published by Elsevier Ltd. All rights reserved.

Keywords: Gadolinium zirconate; Neodymium zirconate; Pyrochlore; Soft chemical synthesis; Solid-state structure

1. Introduction

Lanthanide (Ln) zirconate (Ln₂Zr₂O₇) with pyrochlore structure has attracted significant interest in recent years due to its desirable physico-chemical properties such as high thermal stability, high phase stability, high chemical resistance and durability.^{1–13} Ceramics with pyrochlore structure have been identified as potential host materials for the immobilization of actinides present in radioactive waste and as inert matrix materials for actinide transmutation.^{14–18} As waste form ceramics, zirconates are not only chemically durable with release rate typically less than 10^{−5} g/m² d based on zirconium, but they also have remarkable resistance to amorphization under ion beam irradiation.^{9,19} Conversely compositions based on titanates with pyrochlore structures such as Gd₂Ti₂O₇ appear to be susceptible to radiation-induced transformation from crystalline to amorphous state upon ion-beam irradiation at doses

less than 0.5 dpa.^{12,20} However, Gd₂Zr₂O₇ does not amorphize even at doses up to approximately 100 dpa.^{9,21} The Gd₂Zr₂O₇ pyrochlore structure remains crystalline but exhibits a phase transformation related to the defect-fluorite type structure. Further, the pyrochlore structure can incorporate significant amounts of actinides within both its cation sites, depending on the oxidation state of the actinide.⁹

The pyrochlore crystal structure has the general formula A₂B₂O(1)₆O(2) (space group *Fd* $\bar{3}$ *m*) where A and B are cations, for example Ln³⁺ and Zr⁴⁺. It is a superstructure of the fluorite phase (AO₂, space group *Fm* $\bar{3}$ *m*), with the *a*-axis doubled. The A and B cations form a face-centered cubic array and are ordered on two distinct cation sites into rows in the $\langle 1\ 1\ 0 \rangle$ directions. The A ion is coordinated to 8 oxygen atoms and the B ion is coordinated to 6 oxygen atoms. One-eighth of the oxygen anions are absent to maintain charge balance and this oxygen vacancy is also ordered. Two different oxygen sites occur: six oxygen atoms occupy the 48*f* sites, surrounded by two A cations and two B cations, while the seventh oxygen atom occupies the 8*b* site and is surrounded by four A cations. The remaining unoccupied 8*a* site is surrounded by B cations. Finally, the 48*f* anions are shifted toward the smaller B cations by an amount defined

* Corresponding author. Tel.: +61 2 9717 3630; fax: +61 2 9717 9225.

E-mail addresses: lnk@ansto.gov.au, linggen.kong@ansto.gov.au (L. Kong).

by the $x(48f)$ positional parameter. In the ideal fluorite structure, $x=0.375$.^{22–24} The defect-fluorite structure has seven oxygen atoms tetrahedrally coordinated by four random cations, evenly distributed over eight equivalent sites.

The conventional method for the preparation of $Gd_2Zr_2O_7$ and $Nd_2Zr_2O_7$ ceramic is via solid-state mechanical mixing of metal oxide materials.^{25–28} Usually, powders synthesized by solid-state reaction show non-homogeneity of the final phase and large particle size distribution of non-uniform particles, which result in poor ceramic microstructures. Subsequent sintering of these materials typically leads to poor densification of the ceramic. In order to improve the chemical homogeneity and phase assemblage of the system, several wet-chemistry routes have been employed for the preparation of this type of super-structured material. All wet chemistry methods involve mixing of reactant precursors at the molecular level, thus better compositional homogeneity and stoichiometric control is representative of this synthetic strategy. The common methods for the preparation of $Gd_2Zr_2O_7$ and $Nd_2Zr_2O_7$ include sol–gel processing,^{29–32} coprecipitation,^{6,33,34} the Pechini polymeric route,^{29,35–40} gel combustion processing,²⁷ and others.^{31,41,42}

In order to prepare sol–gel derived lanthanide zirconate ceramics, synthesis normally requires an organic solvent in order to dissolve the extremely moisture sensitive zirconium alkoxide (e.g. zirconium (IV) butoxide). Once the organic phase containing zirconium alkoxide comes into contact with the aqueous phase, in which the lanthanide nitrates are usually dissolved, the zirconium alkoxide undergoes extremely fast hydrolysis and condensation reaction to produce nanoparticle or nanocluster zirconia. As a result, the lanthanide hydroxide and the condensed transition metal oxide are formed simultaneously, but in a nonhomogeneous manner within a microdomain area (i.e. not a molecular level mixture). So this traditional sol–gel/nitrate route can be seen as a nanoscale oxide reaction during subsequent heating procedures. The Pechini polymeric method ensures the molecular level synthesis, but large amounts of stabilizer (citric acid) and polymerization agent (ethylene glycol) are employed. In the coprecipitation method, various metal hydroxides are mixed after precipitation in base environment; however these hydroxides precipitate at different rates depending on the metal cations and the pH. As a result, the final product is a mechanical mixture of different metal hydroxides. Another issue associated with this method is to ensure that all metal ions are completely precipitated at the same pH.

In this study, a homogeneous (LnZr)-precipitate powder was prepared using an aqueous media with zirconium(IV) bis(diethyl citrato)dipropoxide (Tyzor ZEC) as starting material. Intrinsic to the Tyzor ZEC precursor are stabilizing groups (diethyl citrate), which not only provide alkoxide stability in water, but also decrease the chemical reaction rates. This molecular level synthetic approach promotes homogeneous oxide materials at relatively low temperatures. $Gd_2Zr_2O_7$ and $Nd_2Zr_2O_7$ with the pyrochlore structure were prepared in both powder and pellet form and further characterized using a suite of techniques to investigate its microstructural evolution.

2. Experimental procedure

2.1. Materials and method

Zirconium(IV) bis(diethyl citrato)dipropoxide or Tyzor[®] ZEC containing 12 wt% ethanol and 12 wt% 1-propanol (product of DuPontTM), gadolinium(III) nitrate hexahydrate (99.9%+), and neodymium(III) nitrate hexahydrate (99.9%+) were purchased from Aldrich and used as received. The zirconium content in Tyzor ZEC was determined by gravimetric analysis. All chemicals were A.R. grade, with Milli-Q grade water being used in all experimental procedures.

For a typical synthesis, Tyzor ZEC (15 mmol) was weighed into a glass container and water (150 mL) was subsequently added. The mixture was stirred magnetically and heated at 45 °C for more than 3 h to produce a transparent solution. In the meantime, lanthanide nitrate (15 mmol) was dissolved in water (30 mL), which was then added to the Tyzor ZEC solution with stirring. The pH of the combined solution was titrated to pH=8.0–8.3 by dropwise adding ammonia aqueous solution (1.667 mol/L). The mixture was stirred magnetically for 2 h at room temperature (23 ± 3 °C). After aging, the precipitate was separated from the aqueous phase by centrifugation (10,000 rpm for 15 min), washed twice with water, and dried overnight at 85 °C to form the “as-prepared” powder.

The schematic pathway for this reaction is shown in Scheme 1, and the “as-prepared” powders are designated as (GdZr)- or (NdZr)-precipitate. These powders were further subjected to thermal treatment to produce gadolinium and neodymium zirconates (GdZr or NdZr), and eventually with pyrochlore structure ($Ln_2Zr_2O_7$).

For density analyses the dried powder was calcined at 800 °C for 4 h, pelletized using a uniaxial press at 2.0–2.5 MPa, and sintered at 1200 or 1400 °C for 50 h in air.

2.2. Characterization

Fourier transform infrared spectroscopy (FTIR) spectra were obtained on a Nicolet Nexus 8700 FTIR spectrometer (Thermo Electron Corporation, Madison, WI). Spectra were collected using the Smart iTRTM (Attenuated Total Reflectance) sampling accessory. Spectra were collected from 600 to 4000 cm^{-1} at 4 cm^{-1} resolution with 16 scans acquired for each sample.

Raman spectra were collected on the Renishaw inVia Raman spectrometer equipped with the Argon ion laser (514 nm) and a Peltier cooled CCD detector (Renishaw plc, Old Town, Gloucestershire, UK). Stokes shifted Raman spectra were collected in the static mode with a spectral resolution of 1.7 cm^{-1} for the 1800 l/mm grating. The spot size was approximately 1.5 μm for 50× magnification.

X-ray diffraction (XRD) patterns of powders were collected on a PANalytical X'Pert Pro diffractometer (Almelo, the Netherlands) using $Cu K_{\alpha}$ radiation ($\lambda = 1.5418 \text{ \AA}$) at 45 kV and 40 mA. The data were recorded in an angular range of 10°–80° 2θ in continuous mode with a step size of 0.02° (2θ) and an acquisition time of 2 s per step. Unit cell refinements were carried out using the Le Bail method⁴³ implemented within the

Download English Version:

<https://daneshyari.com/en/article/7899176>

Download Persian Version:

<https://daneshyari.com/article/7899176>

[Daneshyari.com](https://daneshyari.com)