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Feature article

Synthesis and characterization of nanometric gadolinia powders by room temperature solid-state displacement reaction and low temperature calcination

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ABSTRACT

Nanometric-sized gadolinia (Gd_2O_3) powders were obtained by applying solid-state displacement reaction at room temperature and low temperature calcination. The XRD analysis revealed that the room temperature product was gadolinium hydroxide, $Gd(OH)_3$. In order to induce crystallization of Gd_2O_3, the subsequent calcination at 600 ~ 1200 °C of the room temperature reaction products was studied. Calculation of average crystallite size (D) as well as separation of the effect of crystallite size and strain of nanocrystals was performed on the basic of Williamson-Hall plots. The morphologies of powders calcined at different temperatures were followed by scanning electron microscopy. The pure cubic Gd_2O_3 phase was made at 600 °C which converted to monoclinic Gd_2O_3 phase between 1400° and 1600 °C. High-density (96% of theoretical density) ceramic pellet free of any additives was obtained after pressureless sintering at 1600 °C for 4 h in air, using calcined powder at 600 °C.

1. Introduction

Gadolinium oxide (Gd_2O_3), a rare-earth oxide possesses chemical durability, thermal stability, large band gap, high refractive index and high dielectric constant [1–3]. Due to the high magnetic moment of Gd^{3+} ion resulting in an intense magnetic interaction with external magnetic fields, enable Gd_2O_3 to be used as magnetic resonance imaging (MRI) contrast [4,5]. Besides being developed for MRI contrast enhancement and multimodal imaging, Gd_2O_3 also have been considered as a potential material in tumor therapy by thermal neutrons irradiation [6]. Gadolinium has the highest neutron absorption cross-section and already has an application as an additive in UO_2 fuel rods for nuclear reactors [7]. Gadolinia exhibits hydrophobicity due to the inhibition of hydrogen bonding with interfacial water molecules and therefore can be used as coatings under extreme conditions [8,9].

Several methods have been used to fabricate pure or rare-earth doped Gd_2O_3, such as combustion synthesis using different fuels [10,11], solid state reaction method [12,13], template method [14], hydrothermal routine [15], precipitation reaction [16], sol-gel method [17], facile synthesis route [18], and spray pyrolysis [19]. Among these methods, solid-state displacement reactions could be an attractive method because of the advantages of simplicity, high efficiency, energy saving and uniform morphology [20–24]. No research has been done on synthesis of Gd_2O_3 using this method.

The objective of this work was to reduce the reaction temperature, to achieve a small particle size of high quality Gd_2O_3 powder and to investigate the phase evolution during thermal treatment and sinterability of the obtained power.

2. Experiment procedure

2.1. Materials and synthesis

Starting reactants used in the experiments were gadolinium nitrate powder (Merck, in the form of hexahydrate), and sodium hydroxide granule. Amounts of Gd-nitrate and NaOH were calculated according to the nominal composition of the final reaction product. Preparation of Gd_2O_3 powder was performed according to the reaction:

$$2[Gd(NO_3)_3{\cdot}6H_2O] + 6NaOH \rightarrow Gd_2O_3 + 6NaNO_3 + 15H_2O + (1/2)O_2 \quad (1)$$

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The calculated fractions of starting chemicals were hand-mixed in an alumina mortar for about 5 min. In order to remove nus-product $NaNO_3$, the reaction mixture was centrifuged in distilled water three times and in alcohol two times at 3500 rpm (Centurion 1020). Duration of each washing run was 10 min.

The powder calcined at 800 °C is formed by a uniaxial pressure of 20 MPa, and then cold-isostatically pressed at 200 MPa by means of Riken Power press (Riken Seiki Co. Ltd, Japan). Prepared green bodes were cylindrical shape with a radius of 10 mm and height of 12 mm. Sintering was done at 1600 °C for 4 h in statistic air atmosphere.

2.2. Characterization

Thermal analysis of obtained powder at room temperature was conducted employing a NETZSCH STA 449 simultaneous DTA-TG thermoanalyzer. The experiment was run from room temperature to 1400 °C with heating rate of 10 °C/min.

The calcination duration of the obtained powders at temperatures from 600 to 1200 °C was 60 min long. All powders were characterized by means of X-ray diffraction (XRD) using RIGAKU Ultima IV diffractometer. Crystal structure was identified by XRD using filtered Cu Kα radiation (1.54178 nm) in the 2θ range from 20 to 80°.

Phase analysis was done by using the PDXL2 software (version 2.0.3.0) [25], with reference to the patterns of the International Centre for Diffraction Data (ICDD) [26], version 2012.

The average crystallite size (D) was calculated on the basis of the full-width at half-maximum intensity (FWHM) of the 222, 400, 440 and 622 reflections of cubic Gd_2O_3 by applying Scherrer's formula [27]:

$$D_{hkl} = K\lambda/(\beta \cdot \cos\theta) \quad (2)$$

where λ is the wavelengths of the X-ray used, θ is diffraction angle, β is corrected half-width for instrumental broadening $\beta = (\beta_m - \beta_s)$, β_m and β_s are observed half-width and half-width of the standard cubic Gd_2O_3 sample, respectively, and K is a Scherrer's constant (~0.9).

Internal strain of calcined samples was estimated from the Williamson–Hall plots, using following equation [28]:

$$\beta_{total}\cos\theta = (K\lambda)/D + (4\Delta d/d)\cdot\sin\theta \quad (3)$$

where β_{total} represents full width half maximum of the XRD peak, λ is the incident X-ray wavelength, θ is the diffraction angle, D is the crystallite size and Δd is the difference of the d spacing corresponding to a typical peak. The strain of nanocrystals, Δd/d, can be estimated from the slope of function $\beta\cdot\cos\theta$ vs. sinθ whereas crystallite size, D, can be estimated from the y-intercept.

TEM observation was done using an H-9000 microscope (Hitachi, Japan) operated at an accelerating voltage of 300 kV, with point resolution of 0.19 nm.

The morphology of obtained powders, as-synthesized as well as calcined ones, were observed by field emission scanning electron microscopy (FE-SEM), performed on a JEOL-5200F scanning electron microanalyzer.

For thermal diffusivity measurement, as-synthesized powder was pressed into a pellet and sintered at 1600 °C for 4 h. The experiment was performed by the laser flash technique (LFA427, NET-ZSCH) at room temperature. Prior to measurement, a thin layer of graphite was coated on the Gd_2O_3 sample for thermal absorption of laser pulses. The thermal conductivity was calculated using the following equation:

$$\kappa = \alpha \cdot \rho \cdot C_p \quad (4)$$

Where κ stands for thermal conductivity, α is measured thermal diffusivity, ρ is density and C_p is heat capacity.

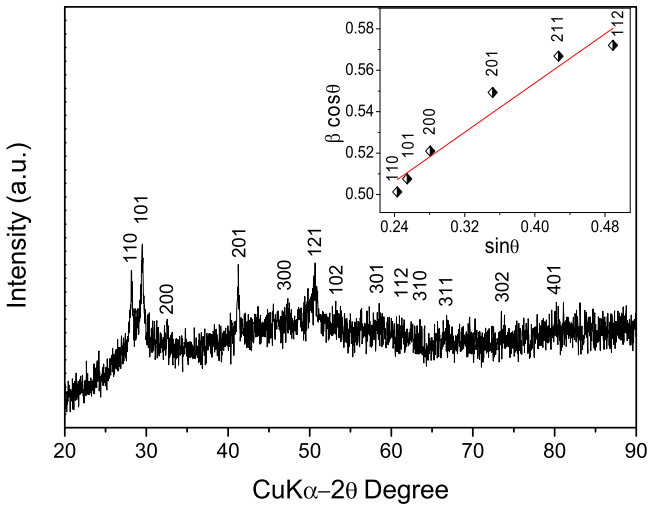

Fig 1. XRD pattern of as-synthesized powder formed at room temperature. Insert is Williamson-Hall plot.

3. Results and discussion

The XRD pattern of the as-prepared sample at room temperature is shown in Fig. 1. The presence of high background and low intensities of the reflections reveals a poor crystallinity of the obtained sample. The X-ray diffraction patterns of the as-prepared powder samples matched with those of the hexagonal phase (space group $P6_3/m$) $Gd(OH)_3$ (JCPDS: 83-2037) well, in good consistency with the literature [29]. This indicates that the solid-state displacement reaction (5) occurred in steady state manner during hand mixing, forming $Gd(OH)_3$:

$$Gd(NO_3)_3\cdot 6H_2O + 3NaOH \rightarrow Gd(OH)_3 + 3NaNO_3 + 6H_2O \quad (5)$$

The average crystallite size estimated from Williamson–Hall plot was 19 nm (Table 1).

DTA and TG curves of the as-synthesized sample are characterized by a several maximum peaks. The first one is endothermic peak at low temperature (≈120 °C) that can be attributed to the lost physically-bonded water. The mass loss at maximum M1 was 3.71%. The endothermic peaks at higher temperatures suggest that the thermal decomposition of the as-prepared powder occurred in two stages at 330 °C (M2) and 450 °C (M3), respectively. The mass losses at M2 and M3 were 7.84% and 4.66%, respectively. These weight losses are in accordance with the theoretical decomposition of $Gd(OH)_3$ via intermediate GdOOH phase. This is in good agreement with the most of the rare earth compounds that dehydrate in two steps [30]:

$$Gd(OH)_3 \rightarrow GdOOH + H_2O \quad (6)$$

$$2GdOOH \rightarrow Gd_2O_3 + H_2O \quad (7)$$

The theoretical mass losses for the reaction (6) and (7) are 8.63% and 4.86%, respectively, what is close to the experimentally obtained data 7.84% and 4.67% for reaction (6) and (7), respectively. These results are coexistent with the dehydration of $Gd(OH)_3$ obtained by wet-chemical route [31]. The maximum at M4 and M5 can be attributed to conversion into Gd_2O_3 phase and its better recrystallization according to reaction (7). No critical change in weight was observed between point M4 and the end of experiment up to 1400 °C, indicating thermal stability of obtained Gd_2O_3 phase (Fig. 2).

XRD patterns of the powders obtained by subsequent heat treatment of the as-synthesized powder at different temperatures for 1 h are presented in Fig. 3. Unlike the as-synthesized powder (Fig. 1),

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