



Effect of ammonia on the agglomeration of zirconia nanoparticles during synthesis, and sintering by spark plasma sintering



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ABSTRACT

Synthesis conditions have important impacts on the properties of ultrafine nanoparticles; understanding the interdependences of such properties on specific synthetic parameters can lead to controlled and optimized products. Here we discuss the effect of coprecipitation conditions during the synthesis of ultrafine yttria stabilized zirconia (YSZ) nanoparticles and gadolinium doped YSZ. We focused on the effect of ammonia concentration as precipitating agent. Although based on the nucleation theory one expects smaller particle sizes for higher concentrations of NH_4OH , the usage of 1 M or 5 M of NH_4OH lead to similar grain sizes (< 6 nm). However, the more concentrated condition led to highly agglomerated powders. This was attributed to an increase in the ionic force in the precipitating environment that caused particle coagulation. The resultant powders thus showed significantly different densification behaviors during sintering using spark plasma sintering, with the agglomerated powders achieving lower relative densities.

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1. Introduction

In a typical coprecipitation process for the synthesis of oxide nanoparticles, an induced super-saturation allows the decrease in critical radius for nucleation in solution [1]. The basic principle of this super-saturated condition is the reaction between cations and anions from two different solutions to form precipitates of hydroxides which undergo thermal decomposition into oxide nanoparticles. The process can be performed by either a “normal” strike, where the precipitating agent (e.g. OH^-) is added drop wise into the cationic solution; or by a “reverse” strike, where the cationic solution is dropped into the precipitating agent. The reverse strike method is expected to deliver more homogeneous particles [2–4], while ensuring highly super-saturated condition that helps to nucleate very small sized precipitates – exploiting concepts of homogeneous nucleation theory [1]. In this context, it is expected that a high concentration of precipitating agent would lead to smaller nanoparticles.

Here we study the effect of concentration of ammonia as a precipitating agent on the synthesis of yttria stabilized zirconia (YSZ). YSZ nanoparticles are of interest for the lowering of sintering temperature of solid state electrolytes for fuel cells [5,6]. While nanoparticles increases the driving force for densification, sintering is also strongly dependent on the powder's

characteristics [7,8], such as size distribution and surface contaminations [9]. The goal of this work is to understand the dependences of YSZ nanoparticles on the synthesis conditions and impacts on densification. Because of the decrease in activation energy for oxygen vacancy mobility in cubic zirconia caused by the addition of gadolinium [10], we also studied the effect of Gd doping on the microstructure of the synthesized powders and sintering. Sintering of Gd-doped (1–4 mol%) and Gd-free YSZ nanoparticles was studied using spark plasma sintering. This technique enables high heating rates under applied pressures, reducing sintering times and allowing dense samples with reduced grain growth [11–13].

2. Experimental procedures

YSZ (12 mol% Y_2O_3) was synthesized with zirconium oxo-nitrate hydrate [$\text{ZrO}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$] (Aldrich, 99%) and yttrium nitrate hexahydrate [$\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$] (Aldrich, 99.999%) as metal precursors. The nitrates were dissolved in deionized water to form 0.3 M solutions and added drop wise in a solution containing 1.0 M or 5.0 M ammonia (NH_4OH), representing excess of 2.5 and 5.0 times the stoichiometric ratio, respectively. Gadolinium nitrate hexahydrate [$\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$] (Aldrich, 99.999%) was added to achieve 1, 2, 3, and 4 mol% Gd, in 11, 10, 9, 8 mol% Y doped zirconia, maintaining the quantity of trivalent ions in all samples. The precipitates were collected by centrifugation and washed with ethanol. These hydroxide nanoparticles were dried overnight at

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100 °C and grinded before calcination. The calcination temperature was determined by heating the hydroxides in a Differential Scanning Calorimeter (DSC/TG) (Setsys, Setaram Instrumentation) at 1200 °C at a rate of 10 °C/min. Obtained oxide nanoparticles were characterized in terms of chemical compositions, crystalline phase (X-ray diffraction, XRD) and surface area, and transmission electron microscopy, as detailed in Supplemental Materials. The obtained nanopowders were sintered into pellets (5 mm diameter) using spark plasma sintering (SPS) (model 825S, Syntex, Tokyo, Japan) at 950 °C for 5 min with 600 MPa pressure under vacuum. A graphite die with a silicon carbide insert was used to allow high pressures, as detailed elsewhere [14] and then polished and finally re-oxidized in oxidizing atmosphere at 750 °C for 5 h to remove any carbon contaminants. The relative densities for all the pellets were measured using Archimedes method.

3. Results and discussion

Coprecipitation from nitrates is expected to produce hydroxides which in turn need to be calcined to crystallize the oxide phase. The calcination temperature was studied by DSC/TG to determine the lowest temperature to allow oxide formation while avoiding coarsening (Supplemental materials, Fig. S1). The data show 450 °C is enough to induce crystallization. The crystallite sizes of the oxide nanoparticles obtained by calcining the hydroxides precipitated using 1 M or 5 M NH₄OH are listed in Table 1. The XRD patterns from which those data were extracted from are shown in Fig. 1. No impurities or second phases could be detected. All XRD patterns show fluorite structure peaks. There were no significant changes in the patterns in terms of peak position or shape regardless of synthetic condition or Gd content (differences within experimental error, Table S1 shows the lattice parameters). Differences in crystallite sizes were also within experimental deviations, revealing no significant effects of doping or ammonia concentration. Chemical composition analyses showed nominal concentrations as accurate descriptions of the actual composition. Representative data from microprobe for 4 mol% Gd doped YSZ synthesized with 1 M NH₄OH is shown in Table S2.

The surface areas of all nanoparticles are also listed in Table 1. Noticeable differences are found when comparing those calcined from the precipitates from 1 M and 5 M ammonia. For 12YSZ, the surface area for the sample prepared from 1 M was 128 m²/g, more than twice the value of 5 M (52 m²/g). Similar trend is observed for the Gd-doped YSZ nanoparticles regardless of Gd content, suggesting it is an intrinsic synthetic procedural issue.

The fact that the surface area is smaller for the higher ammonia concentration suggests the formation of solid-solid interfaces (hard agglomerates). Note that if the powder is agglomerated, nitrogen cannot penetrate through the agglomeration and thus results in lower surface areas when using BET analysis. This phenomenon is likely related to an increase in ionic force of the

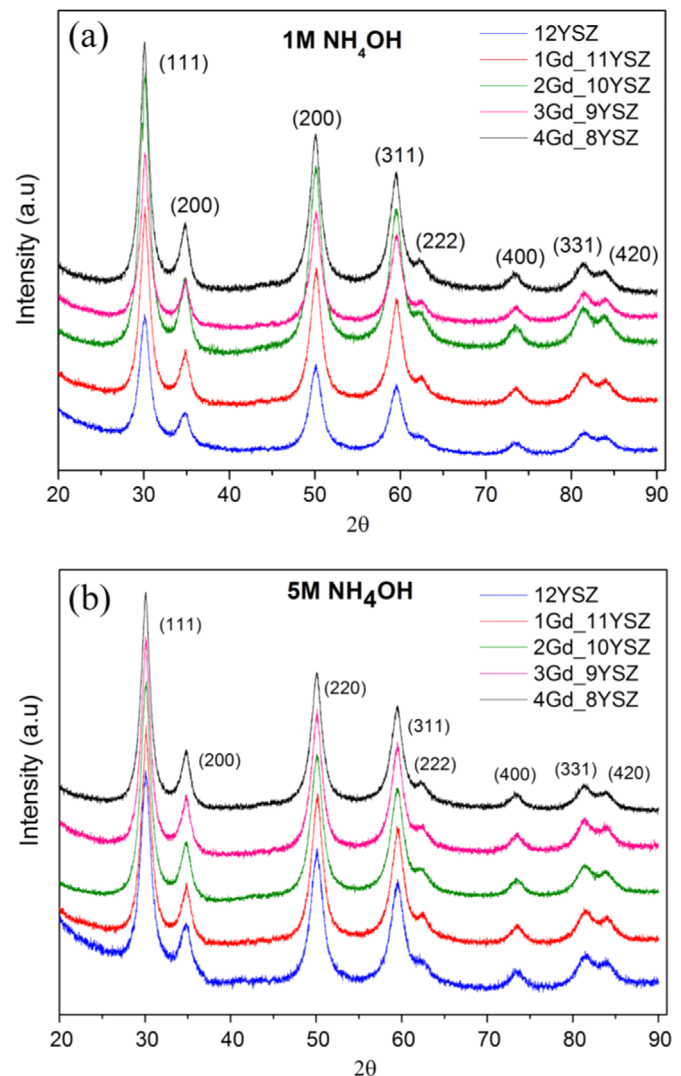


Fig. 1. X-ray diffraction patterns for Gd-free and Gd-doped YSZ nanoparticles synthesized with (a) 1 M NH₄OH or (b) 5 M NH₄OH.

precipitating medium, causing the aggregation of the precipitated hydroxides right after their nucleation. DLVO theory (Derjaguin, Landau, Venvey and Overbeek) establishes that the interaction between approaching particles in solution is the combination of van der Waals attraction and the electric repulsion potentials. If the repulsion energy is higher than the attractive forces, a potential barrier for the agglomeration appears, which if larger than thermal energy shall impede agglomeration. The strength of this repulsive effect can be related to the Debye-Huckel screening length ($1/\kappa$), which is a function of concentration (C_i) and valence (Z_i) of ions in solution [1]:

$$\kappa = \sqrt{\frac{F^2 \sum_i C_i Z_i^2}{\epsilon_r \epsilon_0 R_g T}} \quad (1)$$

Here, F is the Faraday's constant, ϵ_0 is the permittivity of vacuum and ϵ_r is the dielectric constant of the solvent, T is temperature, and R_g the gas constant. The electric potential at the solid surface decreases with increased concentration and valence state of counter ions. Physically, a large number of ions in solution compensate the charges more adjacently to its surface, decreasing the screening length. Higher concentration ammonia would thus result in more agglomerated hydroxides, and consequently agglomerated oxide nanoparticles.

Table 1
Crystallite sizes and surface areas for Gd-free and Gd-doped YSZ nanoparticles prepared by using 1 M or 5 M ammonia.

Sample	5 M ammonia		1 M ammonia	
	Crystallite size (nm)	Surface area (m ² /g)	Crystallite size (nm)	Surface area (m ² /g)
12 YSZ	5.7 ± 0.3	52 ± 0.17	6.4 ± 0.4	128 ± 1.05
1Gd-11YSZ	6.0 ± 0.3	94 ± 0.58	6.1 ± 0.3	128 ± 1.08
2Gd-10YSZ	5.7 ± 0.2	88 ± 0.55	6.0 ± 0.3	124 ± 0.99
3Gd-9YSZ	6.1 ± 0.3	90 ± 0.83	5.8 ± 0.4	125 ± 1.11
4Gd-8YSZ	6.2 ± 0.2	83 ± 0.46	5.6 ± 0.5	126 ± 1.07

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