



# Effects of pre-treatment of starting powder with sulfuric acid on the fabrication of yttria transparent ceramics

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## Abstract

The effects of pre-treating a nano-sized  $Y_2O_3$  powder with sulfuric acid were studied. Both the structural evolution and sintering behavior as a function of  $SO_4^{2-}$ -ion concentrations were investigated. The surface morphologies and aggregation state of particles were notably affected by the sulfuric acid-based treatment. The powder untreated revealed particle of flat surfaces and sharp edges, whereas the powders with sulfate dosage were composed of round particles of isotropic surfaces after calcination. Dispersive  $Y_2O_3$  nanopowder with excellent sintering property was obtained by calcinating the powders treated with 7 mol% sulfuric acid. The optimum sulfate dosage can be well correlated with a single layer coverage of  $SO_4^{2-}$ -ions over the particle surfaces, protecting particles from forming hard agglomerates by contributing to mass transportation mechanisms leading to particle coarsening upon calcination. All the ceramics prepared using treated-powders were transparent after vacuum sintering at 1700 °C, whereas it was opaque for the sample without sulfate dosage.

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**Keywords:** Yttria; Transparent ceramics;  $SO_4^{2-}$ -ion; Sintering; Powder

## 1. Introduction

Recently, yttria transparent ceramic material has been extensively studied, because of its promise for a number of optical applications, such as luminous pipes for high-intensity-discharge lamps, heat-resistive windows, missile domes, host materials for scintillators and solid lasers, etc. [1–3]. In order to achieve a high degree transparency in yttria ceramics, internal porosity of samples should be completely removed [4]. One of the key technologies for fabricating highly dense ceramics is the synthesis of ceramic powders with excellent sintering activity, generally possessing such powder characteristics as low agglomeration state, ultrafine particle size (~100 nm), narrow particle size distribution, and spherical particle shape [5,6]. Thus, the past two decades have witnessed tremendous efforts endeavored in the synthesis of high quality yttria nano powders through

different processing methods, such as precipitation methods [7–9], hydrothermal synthesis [10], emulsion synthesis [11], spray-drying [12], sol–gel synthesis [13,14], and combustion synthesis [15]. Among which, precipitation synthesis routes are attractive because of their accessibility.

Most developed precipitation methods for synthesizing sinterable yttria powders always involve the addition of  $SO_4^{2-}$ -ions [7,8,16–21]. It was found that the morphology, microstructure and sinterability of the calcined powders are highly affected by the  $[SO_4^{2-}]/[Y^{3+}]$  molar ratios. Similar results have also been shown when the precipitation methods were used for the synthesis of  $Al_2O_3$  [22,23],  $Sc_2O_3$  [5,24,25] and YAG [6,26–31] powders by doping  $SO_4^{2-}$ -ions. The doping by  $SO_4^{2-}$ -ions can be realized in several different ways when ammonium sulfate is used as  $SO_4^{2-}$ -ion sources. The ammonium sulfate can be added into reaction mixture during precipitation [19,27,30] during aging [7,17], or the resulting precipitant can be rinsed by ammonium sulfate solution [16]. Alternatively,  $SO_4^{2-}$ -containing substances can be used as a starting material in the reaction [5,25,28,29].

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Previously, an amount of investigations have been performed to reveal the mechanisms of doped  $\text{SO}_4^{2-}$  ions on precursor and calcined powders [5–9,25,26]. Ammonium sulfate was proved to be a regulator, mediating the nucleation and growth of precursors [8,9]. Among common inorganic anions,  $\text{SO}_4^{2-}$  has a higher coordination capability than  $\text{NO}_3^-$  and  $\text{Cl}^-$  and shows stronger complexing effects [25]. The addition of the ammonium sulfate directly into reaction mixture gives rise to a local change of solution chemistry and consequently variations of chemical composition of resulted precursor powders [26]. It has been indicated that even a trace amount of  $\text{SO}_4^{2-}$  decreased the monodispersity of the carbonate particles obtained via homogeneous precipitation with urea [8]. When ammonium sulfate was added into reaction mixture during aging, or the resulting precipitant was rinsed by ammonium sulfate solution, on the other hand, the morphological features of precursor particles were less frequently affected [7].

With respect to calcined powders, although it was generally accepted that doping a certain amount of  $\text{SO}_4^{2-}$ -ions promotes formation of monodispersed spherical powders upon calcination, the influence mechanisms were not clearly verified. The reasons may be two-folds. On one hand, the high-temperature calcination process results in both the dissociation of precursor and the desulfurization of sulfate; the consecutive occurrence of two thermal decomposition procedures complicated the analysis aimed at understanding the mechanism of doped sulfate on calcined powders [24,26]. On the other hand, previous synthetic methods involving sulfate addition are not amenable to precise control of the amount of the doped sulfate in the precursors; it should be noted that the precursors produced by precipitation method are repeatedly washed to remove impurities such as  $\text{NH}_4^+$  and  $\text{NO}_3^-$ , resulting in a lot of sulfate added being washed away. As a consequence, the optimum sulfate dosage was significantly varied in different reaction systems [30,31]. And a correlation between powder property and the exact amount of doped sulfate was not always established.

In this work, we investigate the effects of doped  $\text{SO}_4^{2-}$ -ions on a commercial  $\text{Y}_2\text{O}_3$  powder by pre-treating the starting material with sulfuric acid. The purpose of the work is to understand the underlying mechanism for the observed morphological changes and sinterability improvement achieved upon sulfate dosage. Both the structural evolution and sintering behaviors as a function of the amount of doped  $\text{SO}_4^{2-}$ -ions were investigated. The direct application of  $\text{SO}_4^{2-}$  to pure yttria, in deed, allows us to discriminate and analyze particle features contributed solely from the doped sulfate. In particular, we show that the optimum sulfate dosage can be well correlated with a single layer coverage of  $\text{SO}_4^{2-}$ -ions over the particle surfaces, protecting particles from forming hard aggregates by contributing mass transportation mechanisms leading to particle coarsening while suppressing the mechanisms giving rise to densification upon calcination. This investigation may provide an insight into more efficient application of anion dopant for manipulating particle features and improving the sinterability of available ceramic powders by a simple sulfate-based pre-treatment.

## 2. Experimental procedure

### 2.1. Preparation process

Commercial  $\text{Y}_2\text{O}_3$  (99.99% pure, Huizhou Ruier Rare Chemical Hi-Tech Co. Ltd., Huizhou, China) powder was used as the starting material. The powder has a BET surface area of  $31.5 \text{ m}^2/\text{g}$ . X-ray diffractometric (XRD) analysis indicated that the  $\text{Y}_2\text{O}_3$  powder was a cubic-structured polymorph and the crystallite size calculated from Scherrer's equation is 19 nm. In a typical processing, 60 g starting  $\text{Y}_2\text{O}_3$  powder was dispersed in ethyl alcohol with the addition of sulfuric acid and 2 wt% of dispersant (ammonium salt of poly(methacrylic acid)), and then the suspensions were ball milled in polyurethane jars filled with  $\text{ZrO}_2$  balls for 8 h. The amounts of added sulfuric acid were expressed as a molar percentage of the  $\text{Y}_2\text{O}_3$  powder basis (mol%). For comparison purpose, the starting  $\text{Y}_2\text{O}_3$  powder without sulfuric acid addition was also ball-milled identically. The resultant suspensions were then dried at  $110^\circ\text{C}$ , followed by sieving through a 200-mesh nylon sieve for pulverization. After sieving, the powder was calcined at  $900\text{--}1200^\circ\text{C}$  for 4 h in furnace in a stagnant air condition. The green compacts were prepared by dry pressing at 100 MPa, followed by hydrostatical isostatic pressing under a pressure of 200 MPa.

### 2.2. Characterization

Powder morphologies were observed by transmission electron microscopy (TEM, Model JEM-2100F, JEOL, Tokyo, Japan). The average particle size ( $d_{\text{TEM}}$ ) was determined from over 200 randomly selected particles with an image analysis software (WinRoof, Mitani Corp., Tokyo, Japan), by assuming a circular shape. The specific surface area of the calcined powders was measured by the BET method (Model TriStar II 3020, Micromeritics Instrument Corp., Norcross, GA) via nitrogen adsorption at 77 K. The equivalent particle size ( $d_{\text{BET}}$ ) was estimated from BET surface area based on the following equation:

$$d_{\text{BET}} = \frac{6 \times 10^3}{\rho S} \quad (1)$$

where  $\rho$  is the theoretical density ( $5.01 \text{ g cm}^{-3}$ ) of  $\text{Y}_2\text{O}_3$  crystal;  $S$  is the specific surface area ( $\text{m}^2/\text{g}$ ) determined by BET measurement.

Thermal analysis of the powders doped with sulfate was performed using a TG/DSC analyzer (Model SETSYS Evolution-16, Setaram, Lyons, France) in flowing oxygen atmosphere ( $40 \text{ mL}/\text{min}$ ). The heating rate was  $10^\circ\text{C}/\text{min}$ .

Fourier transform infrared spectroscopy (FT-IR) (Model Spectrum RXI, Perkin-Elmer, CT, USA) spectra of the yttria powders were recorded by the standard KBr method. The calcined  $\text{Y}_2\text{O}_3$  powder of 0.003 g was grinded and dispersed homogeneously in 0.25 g dried KBr powder using the agate mortar and pestle, and then uniaxially compacted into transparent pellets at 28 MPa. The resultant pellets were dried in the oven before investigation. The quantitative sulfur analysis

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