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Sintering of nanostructured Sc_2O_3 ceramics from sol–gel-derived nanoparticles

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Abstract

Sol–gel route was used to synthesize scandium oxides nanopowders. Oxohydroxide nanoparticles were first prepared in solution using $ScCl_3 \cdot xH_2O$ as precursor. The influence of pH and reflux time on particle size and shape was studied. Sc_2O_3 nanoparticles were then obtained after water dialysis and ScOOH sol drying. Depending on pH, 40–1000 nm size ScOOH particles can be obtained. At a given pH, reflux time also influences the ScOOH particles size, which can vary from a few nanometers to 1 μm.

The ScOOH sol can be used to prepare very pure Sc_2O_3 nanopowders. Results indicate a strong relation between nanoparticle size and the transformation temperature of γ-ScOOH to Sc_2O_3. A direct correlation between the Sc_2O_3 powder and the original ScOOH nanoparticle shapes has also been observed. From the TEM studies, it is likely that the crystallization from the phase ScOOH into Sc_2O_3 one is isomorphic.

Spark plasma sintering test highlights a very good sinterability of the Sc_2O_3 powder. Nearly fully dense ceramics can be obtained at 1400 °C. Microstructure is very homogeneous with ultrafine grains, with size in the range of 25–225 nm.

Keywords: Sc_2O_3 nanoparticles; Sol–gel synthesis; Spark plasma sintering; Nanostructure

1. Introduction

The high melting-point cubic sesquioxide crystals (Ln_2O_3 with $Ln = Y^{3+}$, Lu^{3+} and Sc^{3+}) are attractive laser matrices due to their favorable properties, such as high transparency in a large frequency range, high thermal conductivity and the possibility of doping with rare earth ions. The short cation–cation distance and a very high density of cationic sites available for doping, allow the Sc_2O_3 system to be attractive to laser emission schemes, in particular to the energy transfer driven processes [1]. Laser operation of sesquioxides crystals doped with various RE^{3+} (Ho, Tm, Er, and Yb) ions has been demonstrated [2]. Due to its high melting point (2420 °C), the Sc_2O_3 crystal growth from melt is complex. Furthermore, the single crystal samples are limited in size, and are difficult to produce at an industrial level.

Transparent ceramic materials are good alternatives to single crystals [3]. Scandium oxide ceramics have already attracted considerable interest due to their promising applications in optical components and solid state lasers such as high thermal conductivity, lower costs than single crystals, and good transparency. The preparation of doped and undoped transparent scandium oxide ceramics have already been reported [4–10]. Transparent Sc_2O_3 ceramics are usually obtained by vacuum sintering at high temperature (1700–1840 °C for 5–20 h). In these conditions, microstructures exhibit large grains in the range of 10–100 μm [11–13]. Bravo et al. observed the influence of the powder processing on the sintering of Yb-doped Sc_2O_3 ceramics. Their results show that nanoparticles obtained by wet chemical routes are more effective for the fabrication of transparent ceramics. Nevertheless, it is possible

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to achieve good transparency from solid state reaction derived powders, but high energy ball milling and addition of sintering aids are required [12]. Jiang et al. obtained fully dense Sc_2O_3 ceramics with huge grains (> 100 μm) at 1840 °C with CaO as sintering aid [14].

Futami et al. obtained translucent Sc_2O_3 ceramics with grain size between 1 and 3 μm by using the spark plasma sintering technique (SPS) [15]. Sintering parameters are not specified. But it is well known that SPS allows achieving full densification at lower temperature and shorter time than by conventional sintering. This technique was already successfully used for the fabrication of rare-earth sesquioxide ceramics with high transparency [16–18].

One of the keys to obtaining highly dense Sc_2O_3 ceramics (> 99%) is the control of inter-grain pore density. Furthermore, it is well known that decreasing powder size can lead to lower sintering temperature. Indeed, in a densification process governed by solid state diffusion, the densification kinetic is inversely proportional to the particle radius. These parameters determine the degree of transparency. In consequence, particle shape, size and agglomeration state control is essential.

To prepare nanocrystalline Sc_2O_3 powders, different routes can be used. The oxalate precipitation technique with pure ethanol enables the preparation of well-dispersed Sc_2O_3 particles with high specific surface area [19]. Another technique recently studied, called propellant synthesis, is based on solution combustion [20,21]. Here, the as-formed scandia samples are constituted of aggregated single crystal particles with non-regular shape, and size distribution usually ranging from 20 to 40 nm. The small voids inside some particles are generated by the large amount of gas produced during the rapid combustion reaction. As a consequence, high combustion reaction temperatures strongly influence the particle shape and consequently the sintering conditions. Sc_2O_3 powders can also be prepared at a lower temperature using other techniques such as electrochemical deposition, reverse-strike precipitation and hydrothermal synthesis [22,24]. Christensen et al. and Milligan et al. reported hydrothermal preparation of ScOOH with boehmite structure (γ-ScOOH) and diaspore structure (α-ScOOH) [25,26].

To elaborate high performance Sc_2O_3 laser ceramics, the synthesis of high quality starting powders is a key point. The morphological characteristics and the purity degree of the starting powders play key factors on the properties of the final materials.

The main objective of this work is to prepare oxohydroxide nanoparticles at 100 °C with controlled size and shape by a sol–gel route, and to dry them at a higher temperature to obtain scandium oxide Sc_2O_3. The objective size is lower than 20 nm with a weak dispersion. The sol–gel process enables the preparation of oxide nanoparticles directly in solution, without additives. Good oxide homogeneity, high purity and shape and size control are some advantages of the solution process. Grosso et al. obtained colloidal particles of ScOOH by the sol–gel method [27]. ScOOH-based platelet-lozenge shape particles of 66 nm length and 37 nm width have been produced from $Sc(acac)_3$ dissolved in alcoholic solution. Li et al. have previously studied the influence of Sc precursor preparation on Sc_2O_3 powder using the wet-chemical route [8,9,28,29]. Monodispersed Sc_2O_3 precursor particles are prepared via homogeneous precipitation from various Sc precursors (nitrate, chloride, and sulfate). NO_3^- and Cl^- lead to ScOOH after precipitation with urea at 90 °C. ScOOH is obtained by the precipitation of scandium nitrate in ammonia whatever be the preparation conditions (reaction temperature up to 70 °C, aging and pH).

In this work, a new route of ScOOH preparation is proposed, with $ScCl_3$ as precursors. ScOOH is produced by precipitation with NaOH and reflux in water at 100 °C at constant volume. In these conditions, no hydrothermal process is necessary, only pH control and reflux-time duration are required. Furthermore, the salt elimination is processed by water dialysis, which, depending on pH and reflux-time, leads to a purer stable ScOOH sol. The influence of pH and preparation time on ScOOH size and shape is clearly shown, as well as the impact of ScOOH preparation conditions on final Sc_2O_3 features.

Finally, the sintering behavior, i.e. densification and final microstructure, of the synthesized powder was investigated by using the spark plasma sintering (SPS) technique. Results are then compared to previous data found in literature.

2. Experimental

The oxohydroxide nanoparticles were produced with scandium chloride hexahydrate (> 99.9% pure, Alfa Aesar) dissolved in water with a molar ratio R=[$ScCl_3$]/[H_2O] around 160. The initial pH of the chlorhydrate aqueous solution was around 3.

The condensation/peptization reaction leading to ScOOH sol was processed by adjusting the pH with 10% NaOH solution at room temperature, and then refluxing the ScOOH solution at 100 °C and pH > 6. Various pH and reflux time have been studied respectively from pH 7 to 11 and 2 to 24 h. pH monitoring was performed during the addition of base as the Point of Zero Charge (PZC) of ScOOH and Sc_2O_3 is respectively close to 5.7 and 6.7 [30]. In each case and before the step reflux, a white precipitate was formed.

After reflux, the resultant suspension was dialyzed in water to remove salts. The dialysis water was changed 4 times. The ScOOH particle size and their distribution were measured by laser granulometry (DLS) (Malvern Nano ZS) after dispersion in an ultrasonic bath for 15 min.

Excess water in the ScOOH sol was further removed by drying at 100 °C in air. The sol was then thermally treated at above 400 °C in a furnace to yield Sc_2O_3 powder. Thermogravimetry and differential thermal analyses (Diamond TG/DTA analyzer) of dried precursor were performed at a heating rate of 10 °C min^{-1}, from room temperature to 1000 °C, using α-Al_2O_3 as reference. The phase identification is performed by X-ray diffractometry with a Rikagu diffractometer in a θ–2θ geometry using Cu-Kα radiation (λ = 1.5406 Å). Powder purity was checked by FTIR analysis (Nicolet, 550 series II spectrometer). The particle morphology was observed by transmission electron microscopy (JEOL 2100, FEG-TEM 200 kV) on a copper grid after dispersion in an alcohol solution.