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Partial wet route for YAG powders synthesis leading to transparent ceramic: A core–shell solid-state reaction process

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Abstract

Synthesis of $Y_3Al_5O_{12}$ (YAG) powders respectively presents morphology control and chemical stoichiometry problems when employing the solid-state reaction or the wet-chemical route. YAG powder retaining the morphology of Al_2O_3 powder was designed and synthesized via a partial wet-chemical process with yttrium ions precipitating on the Al_2O_3 particles. The formation process of the Y-compound/Al_2O_3 core–shell structure is discussed on the basis of zeta-potential measurements and HRTEM results. Two stages, including direct precipitation at the surface of the Al_2O_3 particles and the assembly of the yttrium precipitate from explosive nucleation onto the yttrium compound-coated Al_2O_3 particles, are proposed. A spherical surface reaction process is illustrated. A pure YAG phase can be realized at a temperature about 300 °C lower than that of the traditional solid-state reaction process.

Keywords: Partial wet route; $Y_3Al_5O_{12}$; Transparent ceramic; Core–shell structure

1. Introduction

Neodymium-doped yttrium aluminum garnet ($Y_{3-x}Nd_xAl_5O_{12}$) is one of the most important materials for laser applications. However, it is impossible to homogeneously dope neodymium at a level above 1 at% as a luminescence element in a YAG single crystal[1] due to the low effective segregation coefficient of elemental neodymium in YAG (about 0.2). Fortunately, based on their high tolerance of defects and the small grain size of ceramics, transparent ceramics are suitable materials to study for increasing the rare earth doping concentration. The first Nd:YAG ceramic laser oscillation was realized with a ceramic obtained by solid state reaction in 1995 by Ikesue et al.[2] Since then, significant progress has been made in the preparation of transparent YAG ceramics and the realization of ceramic lasers.[3,4] By using 2 at% neodymium doped ceramics, dual- and tri-wavelength laser output was achieved.[5–7] To overcome the uncontrollable morphology problem with the conventional solid-state reaction, many kinds of wet chemical synthesis routes have been studied in the preparation of fine powders for ceramics fabrication, such as numerous sol–gel methods,[8,9] homogeneous precipitation,[10,11] co-precipitation methods with ammonium hydrogen carbonate (AHC)[12] or ammonia[13] as precipitant, microwave irradiation,[14,15] solvothermal[16,17] methods and supercritical water synthesis.[18–20] Basically, the wet-chemical routes consist of the process of extracting yttrium and aluminum ions simultaneously from solution. Thus, the precipitate precursor needs to be washed several times respectively with deionized water and alcohol to remove byproducts and to reduce hard aggregation. Due to a preference for the formation of boehmite (AlOOH) or hydrafil ($Al(OH)_3$) at low pH, it is difficult to thoroughly wash the precipitate by filtration. Furthermore, there are many parameters, such as reaction temperature,[21,22] terminal pH value,[23,24] aging duration,[14,25,26] ammonium sulfate dosage,[27] etc., that need to be optimized because they are all interdependent during the formation and

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evolution of the precursor. These parameters have a complex effect on the chemical composition and morphology of the precursor, affecting its final properties, especially for ions with different precipitation properties. This situation limits mass production and causes a stoichiometry problem in the precursor. In our previous study on the reversed titration process, a hollow precursor structure was observed. Although it can be eliminated by calcining at a higher temperature,[22] it is better to obtain a precursor with a solid structure from the outset. Furthermore, dendritic structures are difficult to avoid during the calcination process, resulting in a green body inhomogeneity problem. To solve these problems, a partial wet-chemical process is proposed based on the homogeneous precipitation of the yttria precursor (Y-precursor) with urea. Homogeneous precipitation[11,14] is a very powerful methodology for the synthesis of rare earth oxides such as Y_2O_3. We have achieved the fabrication of a spherical Y-precursor structure with urea as precipitant,[28] and have investigated the dynamics of the formation process.[29] The assembly process of the primary Y-precipitate is unambiguous during the formation of the spherical Y-precursor. Thus, in this work, based on better control of the Y-ion precipitation process, a YAG core–shell precursor was synthesized by using α-Al_2O_3 particles as templates coating them with the Y-precipitate. The YAG phase was obtained at a lower temperature due to the spherical surface reaction, leading to the production of a transparent ceramic.

2. Experimental procedure

A typical synthetic procedure for colloidal precursor particles similar to the synthesis of the Y-precursor[29] was used. A well-dispersed α-Al_2O_3 turbid liquid was added to form $Y_3Al_5O_{12}$. Briefly, $Y(NO_3)_3{\cdot}6H_2O$ (Alfa Aesar, 99.99%) and urea (Sinopharm Chemical Reagent Co., Ltd, Specpure) were dissolved in distilled water to make a transparent solution. The Y^{3+} concentration was kept at 0.015 M while the urea concentration was kept at 0.5 M. The α-Al_2O_3 (Sinopharm Chemical Reagent Co., Ltd, 99.99%) was added into the mixed solution, and dispersed by ultrasonication. The mixed turbid liquid with Y/Al = 3/5 was homogenized by agitation, and then was heated to 90 °C and held at this temperature for 3 h. After cooling down naturally, the resulting precursor material was collected via suction filtration. Byproducts of the reaction were removed by washing the particles with deionized water via suction filtration three times. After rinsing with anhydrous ethanol, the particles were dried in an oven at 100 °C for 24 h and then calcined at various temperatures for 3 h. The pure YAG powder was uniaxially pressed into pellets ($\phi = 13$ mm) under a pressure of 200 MPa. Then it was sintered at 1780 °C for 4 h under a vacuum of 4×10^{-5} Pa in a furnace with a tungsten heating element (712-T, Thermal Technology LLC, USA). Separate Y-precursor material was also synthesized by homogeneous precipitation with urea as the precipitant,[29] in order to investigate its surface chemical state.

A zeta potential analyzer (Zetapals, Brookhaven Instruments Corporation, USA) was used to characterize the electrokinetic properties of the mixed powders. A powder suspension of 0.1 mg/mL concentration was prepared in deionized water and in various concentrations of NH_4HCO_3 for the zeta potential measurement. X-ray powder diffraction (XRD) patterns of the powder were recorded on a Bruker D8 Advance powder X-ray diffractometer with Cu Kα ($\lambda = 0.15406$ nm). A HITACHI S-4800 field emission scanning electron microscope (FESEM) was used to characterize the morphology of the synthesized samples, and the chemical composition of the powder was studied via energy-dispersive X-ray spectroscopy (EDS). The ceramic grains of the new fracture and its polished surface were also studied by FESEM. A JOEL JEM 2100 transmission electron microscope (TEM) was employed to study the core–shell structure.

3. Results and discussion

The zeta potentials of the individual commercial α-Al_2O_3 powder and the synthesized Y-precursor materials obtained by homogeneous precipitation using urea as precipitant were measured as a function of the concentration of NH_4HCO_3. Here, NH_4HCO_3 was chosen as the main environmental ion, because the precipitation and assembly process occurs at a certain concentration of NH_4HCO_3, which hydrolyses from urea. As shown in Table 1, α-Al_2O_3 exhibits a zeta potential value of 50(3) mV in deionized water, where the number in parentheses is the uncertainty in the last significant digit. This value is consistent with perfect dispersive stability in that it did not separate even after being left to stand for 2 days. With NH_4HCO_3 concentration increasing in the system, the absolute value of the zeta potential decreases, and reverses to negative values around −24(3) mV at a NH_4HCO_3 concentration of 10^{-3} mol/L. The zeta potential approaches a maximum value of around −24(3) mV at a NH_4HCO_3 concentration of 0.1 mol/L, and changes little with further increase in the NH_4HCO_3 concentration. The variation of the zeta potentials can be attributed to the alteration of the surface chemical state of the α-Al_2O_3 particles, in which negative ions adsorb onto the Al_2O_3 particles with an increase of the NH_4HCO_3 concentration in the system. The zeta potential of the Y-precursor are measured to be near zero in deionized water. The absolute value increases with an increase of the NH_4HCO_3 concentration in the negative range. Similarly, the zeta potential approaches a maximum value of around −29(2) mV at a concentration of 0.1 mol/L. It indicates that the Y-precursor material has the same surface electric types as the α-Al_2O_3 particles in the precipitation system, and cannot assemble by electrostatic attraction onto the α-Al_2O_3 particles. As is well known, the formation of a spherical Y-precursor is a process of Y-precipitate assembly. Thus, if the α-Al_2O_3 particle can be surface-modified with the Y-precipitate, a similar process could occur, and form the Y-compound/Al_2O_3.

The morphology of α-Al_2O_3 and the as-obtained precursor were investigated by TEM and the results are as shown in Fig. 1. The pure α-Al_2O_3 powder consists of homogeneous particles in sizes of 100–200 nm. The powder is well crystallized with continuous and clear edges (Fig. 1(a)). The as-obtained precursor particles (Fig. 1(b)) exhibit an obvious interface between the core and shell, which corresponds to the different core–shell