Densification of zirconia doped yttria transparent ceramics using co-precipitated powders

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ABSTRACT

Ho:Y_2O_3 ceramics were prepared using co-precipitated powders, with ammonium sulfate as dispersant. Y^{3+} was co-precipitated together with Ho^{3+} and Zr^{4+} to produce precursors, which were calcined at 1100–1400 °C to produce yttria-based powders. At calcination temperatures of ≤ 1300 °C, agglomeration of powders was not observed. When the temperature was increased to 1400 °C, severe agglomeration was detected. Densification was closely related to the calcination temperature: a lower calcination temperature resulted in a faster densification of ceramics to the relative density of 99.7%. The ultimate densification to ~100% was also closely related to powders' impurity level and agglomeration. Grain growth was mainly determined by sintering temperature, but not by the initial crystallite size of powders. The optimal calcination temperature was 1300 °C, at which the obtained Ho:Y_2O_3 powder was free from agglomeration. Using this powder, the resultant Ho:Y_2O_3 ceramics showed pore-free microstructure and good optical transparency.

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1. Introduction

Since the first neodymium-doped yttrium aluminum garnet (Nd:YAG) transparent ceramics were fabricated and their laser oscillation was demonstrated by Ikesue [1,2], transparent ceramics acting as the gain media for solid state lasers have been extensively studied. Compared with single crystals, transparent ceramics are considered to be better host materials, because of their high yield, short fabrication period and ease of making large sizes [3,4]. In fact, the 100 kW level of the solid state lasers have been achieved by using the Nd:YAG ceramics as the gain media and amplifiers [5], implying the great potential of ceramics for high power laser applications. Recent studies indicated that sesquioxide ceramics, such as Y_2O_3, Lu_2O_3, and Sc_2O_3, are excellent host materials for high power laser applications, primarily because of their lower thermal expansion coefficient and higher thermal conductivity than those of YAG [6–9].

Commercial sesquioxide raw powders generally have large particle size and severe agglomeration, which are difficult to be sintered to uniform microstructures with fully densification.

Various methods, including alkalide reduction [10], sol–gel [11], combustion [12], and chemical co-precipitation methods [13–20], have been developed to synthesize the powders with better quality. Among them, chemical co-precipitation method is more favored, due to its capability of synthesizing powders with high uniformity, low degree of agglomeration and large scale production [19]. For example, high quality Yb:Y_2O_3 and Yb:Lu_2O_3 transparent ceramics were developed by using co-precipitated powders at the Konoshima company, with promising laser properties [21–24]. Using co-precipitated nanocrystalline powders, Ballato and his colleagues [20,25] fabricated submicrometer-grained Sc_2O_3 transparent ceramics, with the combination of two-step sintering process followed by the hot isostatic pressing (HIP) treatment. The ceramics exhibited very small grain size (~300 nm) and showed transmittance close to the theoretical value in the near-infrared wavelength range. The reduction of the grain size resulted in significant improvement in microhardness and fracture toughness of the transparent ceramics, which made them more applicable to high-energy laser systems [18]. The obtaining of the highly transparent submicrometer-grained ceramics should be attributed to the precise control of the sintering process and more importantly, to the successful synthesis of the nano powders with better sinterability.

On the other hand, to obtain highly transparent sesquioxide ceramics, ultra-high purity of raw powders is necessary. It is

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known that impurities, such as transition metals and some non-metal inclusions, even at ~10 wt ppm, would influence the sintering behavior and degrade the optical quality of the ceramics [19,26]. For example, Yagi and Yanagitani [26] found that it is difficult to obtain highly transparent Y_2O_3 if the amount of Si exceeds 10 wt ppm. For this reason, Kim and Sanghera et al. developed an additional purifying process before the subsequent precipitation process, i.e., recrystallization treatment [19,27]. After that, the total concentration of the foreign metal impurities (Mg, Al, Si, Ca, Fe, Co, Ni et al.) in the co-precipitated powders was decreased to be below 10 wt ppm. Using these powders, highly transparent $Ho:Lu_2O_3$, $Yb:Lu_2O_3$ and $Yb:Y_2O_3$ ceramics were fabricated and their laser oscillation was also achieved successfully [19,27,28]. No matter what process is utilized, there is a consensus among researchers, that is, to fabricate transparent ceramics with high optical quality, the agglomerated-free or soft-agglomerated powders should be used [29].

During the synthesizing of sesquioxide precursors, SO_4^{2-} has been widely utilized as an inorganic dispersant [14,17,30]. The presence of the SO_4^{2-} is helpful for producing monodispersed particles with more isotropic surfaces [14], and also it is helpful to decrease the agglomeration of both the precursors and the final oxide powders. However, the complete dissociation of sulfate from the final powders was difficult. Therefore, in order to minimize the nonmetal impurities, such as SO_4^{2-}, NO_3^- and CO_3^{2-}, high calcination temperatures of above 1000 °C are generally required [14,17]. Actually, it has been reported that there still be 100 wt ppm of sulfur remains in the sulfate doped yttria powders even after calcining at 1200 °C [14]. It is well known that these kinds of undecomposed by-products tend to reduce the final sintered density of ceramics [31]. However, a high calcination temperature would inevitably lead to the increase in crystallite size, which, according to the Herring's Scaling Law [32], will cause the decline in sinterability of the powders. Another worse disadvantage is that 'necks' between particles could be formed during the high temperature calcination, to form hard agglomerates [33]. Therefore, the calcination temperature should be rightly controlled in this respect. Although there have been reports on the influence of precursor calcination temperature on morphology of powders and early densification of ceramics [14,15], such a relationship has not been systematically studied, especially that with detailed microstructural evolution and densification of ceramics in the final-stage sintering. As the final-stage sintering process contributes to the ultimate densification of ceramics, it is worth clarifying how the densification and microstructure of ceramics were evolved with sintering temperature, and what factors affect the ultimate densification of ceramics in this stage.

In this work, we reported the fabrication of $Ho:Y_2O_3$ transparent ceramics using chemical co-precipitated powders and the vacuum sintering method. The effects of precursor calcination temperature on morphology and evolution of crystallite size of the powders were examined. In addition, the relationship between initial crystallite size of the powders and the densification and microstructure evolution of ceramics was discussed in detail, particularly in the final-stage sintering. The factors affect the ultimate densification of ceramics were also discussed.

2. Experimental procedure

2.1. Materials processing

Commercial yttrium oxide (Y_2O_3, purity > 99.99%), holmium oxide (Ho_2O_3, purity > 99.99%) and Zirconium oxychloride octahydrate ($ZrOCl_2 \cdot 8H_2O$, purity > 99.5%) were used as the starting
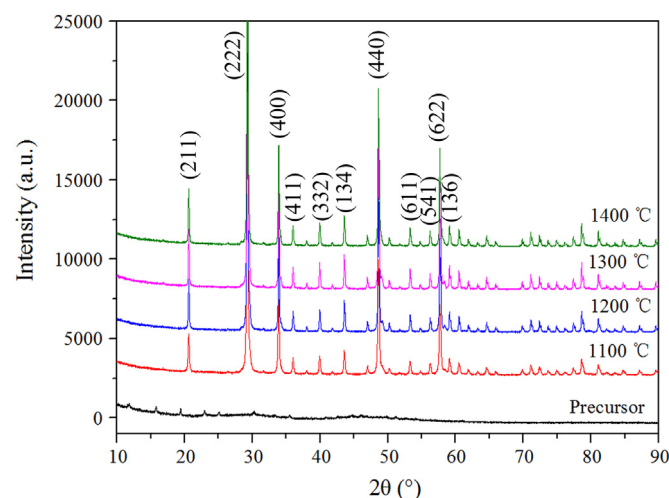

Fig. 1. XRD patterns of the $Ho:Y_2O_3$ precursor and resulted powders after calcined at different temperatures.

materials. First, Y_2O_3 and Ho_2O_3 were dissolved in the diluted nitric acid, while $ZrOCl_2 \cdot 8H_2O$ was dissolved in the ultra-pure water. The obtained nitrate solutions were stoichiometrically mixed according to the chemical formula of $(Y_{0.965}Ho_{0.005}Zr_{0.03})_2O_3$, with Y^{3+} concentration 0.5 mol/L. Then, 5 g $(NH_4)_2SO_4$ was added into 1 l of the above solution. After that, a mixed $NH_4OH + NH_4HCO_3$ precipitant (molar ratio 1:0.9) was dropped into the mother solution at a rate of 6 mL/min under mild agitation (stirring rate 400 rpm) at room temperature. The ultimate pH value of the suspension was kept in the range of 8–9. After being aged for 4 h, the precursor was filtered using a suction filter, washed five times with ultra-pure water and twice with ethanol (99.99% purity; Merck, Darmstadt, Germany), and then dried at 60 °C for 24 h in air. After being crushed, the precursor was calcined in a muffle furnace (Nabertherm LHT 04/17) at 1100–1400 °C for 5 h. The resultant oxide powders were uniaxially pressed into 15 mm diameter pellets at 15 MPa. The green pellets were further cold isostatically pressed (CIPed) at 200 MPa. After CIP, the green bodies were sintered in a vacuum furnace equipped with tungsten mesh as the heating element at vacuum of $\leq 10^{-3}$ Pa for various times at temperatures ranging between 1560 and 1850 °C. Then the ceramics were air annealed at 1400 °C for 10 h in a muffle furnace (Nabertherm LHT 04/17) to remove the color centers. After annealing, they were fine polished on both surfaces, with thickness of around 2.50 mm, using a Hyprez precision lapping machine (Model: EJW400-IN-D, Engis, Japan).

2.2. Characterization

Morphologies of the precursors and calcined powders were observed by using a JEOL JEM-2010 transmission electron microscope (TEM, JEOL JEM-2010, Kyoto, Japan). Phase identification was performed by using a Shimazdu X-ray diffractometer (XRD, Shimazdu, Kyoto, Japan) with CuKα radiation. Scanning speed was 1.5° 2θ per minute. Specific areas of the powders were measured by using the BET method (ASAP, 2020) with N_2 absorption using a Monosorb. Before BET analysis, the powders were degassed at 120 °C for 6 h to eliminate absorbed moisture. Thermo gravimetric analysis (TGA) and differential scanning calorimetry (DSC) of the precursors were conducted on a TGA-DSC analyzer (Q600-SDT, TA Instruments). Bulk densities of the sintered samples were measured by using the Archimedes method. Optical transmittance of the ceramics was recorded using a UV–VIS–NIR spectrometer (Carry 5000, Agilent, Santa Clara, CA, USA). Microstructure of the samples was examined by using a scanning electron microscope