Fabrication, microstructure and spectroscopic properties of Yb:Lu$_2$O$_3$ transparent ceramics from co-precipitated nanopowders

Qiang Liu[a], Jinbang Li[a,b], Jiawei Dai[b,c], Zewang Hu[b,c], Cong Chen[a,b], Xiaopu Chen[b,c], Yagang Feng[b,c], Jiang Li[b,*]

[a] School of Material Science and Engineering, Jiangsu University, Zhenjiang 212013, China
[b] Key Laboratory of Transparent and Opto-functional Inorganic Materials, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 201899, China
[c] University of Chinese Academy of Sciences, Beijing 100049, China

ABSTRACT

Ytterbium doped lutetium oxide (Yb:Lu$_2$O$_3$) transparent ceramics were fabricated by vacuum sintering combined with hot isostatic pressing (HIP) of the powders synthesized by the co-precipitation method. The effects of calcination temperature on the composition and morphology of the powders were investigated. Fine and well dispersed 5 at% Yb:Lu$_2$O$_3$ powders with the mean particle size of 67 nm were obtained when calcined at 1100 °C for 4 h. Using the synthesized powders as starting material, we fabricated 5 at% Yb:Lu$_2$O$_3$ ceramics by pre-sintering at different temperatures combined with HIP post-treatment. The influence of pre-sintering temperature on the densities, microstructures and optical quality of the 5 at% Yb:Lu$_2$O$_3$ ceramics was studied. The ceramic sample pre-sintered at 1500 °C for 2 h with HIP post-treating at 1700 °C for 8 h has the highest in-line transmittance of 78.2% at 1100 nm and the average grain size of 2.6 μm. In addition, the absorption and emission cross sections of the 5 at% Yb:Lu$_2$O$_3$ ceramics were also calculated.

1. Introduction

Solid-state laser has been successfully used in industrial, military, medical and other fields due to its small size, high efficiency, and excellent performance [1]. In the past decades, rare-earth-doped yttrium aluminum garnet (YAG) as the host material for high-power solid-state lasers has been rapidly developed [2,3]. The sesquioxides such as Sc$_2$O$_3$, Y$_2$O$_3$ and Lu$_2$O$_3$ possess higher thermal conductivity than YAG and have been considered to have significant potential as host materials for high-power and high efficiency solid-state lasers [4–6]. Among them, Yb-doped Lu$_2$O$_3$ stands out as the best host material especially when the dopant concentration of Yb^{3+} ion is high [7]. Because of the similar ionic radii and bonding forces of Lu^{3+} and Yb^{3+} ion, the Yb^{3+} ion can easily substitute for Lu^{3+} ion. In addition, the overall thermal conductivity is almost not affected by the doping concentration, which is due to the negligible scattering of the propagating phonons. Furthermore, Yb^{3+} ion has high quantum efficiency and simple energy manifolds (the $^2F_{7/2}$ ground state and the $^2F_{5/2}$ excited state), which prevent the excited state absorption and upper level conversion [8–10].

The melting point of Lu$_2$O$_3$ is about 2450 °C, which is higher than the melting temperature of iridium crucible [11–13]. Therefore, it is quite difficult to fabricate Lu$_2$O$_3$ single crystals with large size and high optical quality by the conventional melt growth process [14]. The ceramic processing technology provides an alternative way to fabricate transparent Lu$_2$O$_3$ materials since ceramic processing requires 25–30% lower temperature than the melting temperature. Compared with single crystals, transparent ceramics are advantageous in many ways including higher doping concentration, possibility of larger size, and more function design freedom [15].

Powders with high purity, good dispersity and uniform size are the key to obtain high optical quality ceramics [16]. However, commercial Yb^{3+} doped Lu$_2$O$_3$ powders are not common available. Lots of methods have been used to synthesize rare-earth-doped Lu$_2$O$_3$ powders, such as, sol-gel combustion [17], hydrothermal synthesis [18] and co-precipitation methods [7,12,19]. Among these methods, co-precipitation route has been proven to be an effective route to synthesize rare-earth-doped Lu$_2$O$_3$ powders with homogeneous composition and good dispersion. Calcination temperature has a big influence on the purity and agglomeration of the powders [20,21]. Optimization of calcination temperature to obtain highly pure and less-agglomerated Yb:Lu$_2$O$_3$ powders is necessary. In addition, vacuum pre-sintering followed by HIP post-treatment has been employed to achieve Nd: YAG [22] and Y$_2$O$_3$ [23] ceramics with high optical quality. The pre-sintering temperature has a big influence on the optical quality and microstructure of

the final ceramics [24]. As a result, optimization of pre-sintering temperature to obtain highly transparent Yb:Lu$_2$O$_3$ ceramics also needs to be systematically investigated.

In this work, 5 at% Yb:Lu$_2$O$_3$ transparent ceramics were successfully fabricated by vacuum sintering combined with hot isostatic pressing from carbonate co-precipitated nano-powders. The influence of calcination temperature on the phase composition, particle size and morphology of the powders was systematically investigated. In addition, the influence of pre-sintering temperature on the densities, microstructures and optical quality of the ceramics was also studied. Finally, the absorption and emission cross-sections of the 5 at% Yb:Lu$_2$O$_3$ ceramics were also calculated.

2. Experimental procedure

The rare earth raw materials used in the experiment were Lu$_2$O$_3$ (99.999%, Zhongkai New Materials Co., Ltd., Jining, China) and Yb$_2$O$_3$ (99.99%, Alfa Aesar, USA). Lu(NO$_3$)$_3$ solution and Yb(NO$_3$)$_3$ solution were prepared by dissolving Lu$_2$O$_3$ and Yb$_2$O$_3$ in nitric acid at 80 °C, respectively. Then the solutions were filtered to remove any undissolved particles and impurities with 0.3 μm filter paper. Lu^{3+} and Yb^{3+} concentrations of the nitrate solutions were assayed by chemical analysis. Lu(NO$_3$)$_3$ solution and Yb(NO$_3$)$_3$ solution were mixed together in stoichiometric proportions of Yb$_{.05}$Lu$_{.95}$O$_3$ (5 at% Yb:Lu$_2$O$_3$). (NH$_4$)$_2$SO$_4$ (99.0%, Sinopharm Chemical Reagent Co., Ltd, china) as the dispersant was added to the mixed metal ion solution. The molar ratio of (NH$_4$)$_2$SO$_4$ to metal ion was 1:1. Finally the solution was diluted with deionized water, and the concentration of Lu^{3+} was set to 0.2 mol/L. Precipitant solution was obtained by dissolving Ammonium hydrogen carbonate (AHC) (Aladdin Industrial Corporation, China) in deionized water with a concentration of 1 M. The Yb:Lu$_2$O$_3$ precursor was prepared by adding 360 mL AHC solution at a speed of 3 mL/min into 500 mL mixed metal solution under stirring. After aging for 3 h, the resulting precipitate was washed for three times with deionized water and alcohol, respectively, and then dried at 70 °C for 48 h in an oven. Then, the precipitate was sieved through a 200-mesh screen and calcined at 600–1200 °C for 4 h in air. The nano-powders calcined at 1100 °C were uniaxially pressed into pellets of 18 mm in diameter at 25 MPa and then cold isostatically pressed under 250 MPa. For ceramic fabrication, the green pellets were pre-sintered at 1450–1750 °C for 2 h in a vacuum furnace (10^{-5} Pa) and subsequently hot isostatic pressed at 1700 °C in an Ar pressure of 100 MPa for 8 h. The sintered ceramics were annealed in air at 1350 °C for 10 h to remove oxygen vacancies. At last, the samples were double-side polished with 1 mm thick for the transmittance test.

The phase compositions of the powders were determined by X-ray diffraction (XRD, Model D/max2200 PC, Rigaku, Japan) in the range of 2 θ = 10–80° using nickel-filtered Cu-Kα radiation. Fourier transform infrared spectrum (FTIR) was performed on an infrared spectrometer (FTIR, Bruker VERTEX 70 spectrophotometer, Ettlingen, Germany) using the standard KBr method in the range of 4000 cm^{-1}–400 cm^{-1}. The specific surface area (S$_{BET}$) of the precursor and calcined powders was performed by Norcross ASAP 2010 micromeritics with N$_2$ as the absorption gas at 77 K. The density of the ceramics was measured by the Archimedes method using deionized water as the immersion medium. The microstructure of the polished samples (thermally etched at 1350 °C for 3 h) was observed by a field emission scanning electron microscopy (FESEM, SU8220, Hitachi, Japan). The average grain sizes of sintered samples were measured by the linear intercept method from SEM images and the average intercept length was multiplied by 1.56 [25]. The in-line transmittance of the samples was measured by a UV–VIS–NIR spectrophotometer (Model Carry-5000, Varian, USA). The pore size of the HIPed ceramics was measured by the optical microscope (BX51, Olympus, Japan).
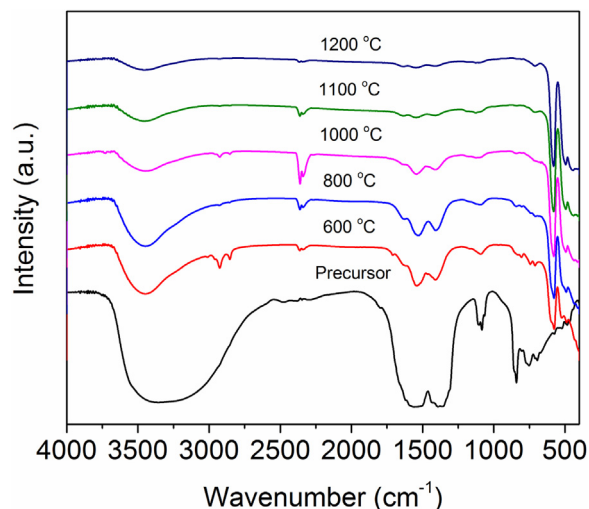

Fig. 1. FTIR spectra of the precursor and the 5at%Yb:Lu$_2$O$_3$ powders calcined at different temperatures for 4 h.

3. Results and discussion

Fig. 1 shows the FT-IR spectra of the precursor and the 5 at% Yb:Lu$_2$O$_3$ powders calcined at different temperatures for 4 h. The wide absorption bands centered at 3450 cm^{-1} are related to O-H stretching of molecular water. The bands at 844 cm^{-1} are assigned to the deformation vibration of C-O in CO$_3^{2-}$, while the bands at 1527 and 1405 cm^{-1} are corresponding to the asymmetric stretch of the C-O bond in CO$_3^{2-}$. The bands at around 1100 cm^{-1} are attributed to SO$_4^{2-}$. The bands at 2360 cm^{-1} are caused by the asymmetric stretch of CO$_2$ absorbed in air. The FT-IR spectrum of the precursor indicates that the precursor contains functional groups such as OH^{-1}, CO$_3^{2-}$ and H$_2$O. With the increase of calcination temperature, intensities of the bands of OH^{-1}, CO$_3^{2-}$, SO$_4^{2-}$ and H$_2$O become weaker. Peaks of CO$_3^{2-}$ and SO$_4^{2-}$ disappear when the calcination temperature is higher than 1000 °C. When the calcination temperature is 600 °C, new band at 575 cm^{-1} related to the stretching of Lu–O bond appears, which results from the crystallization of Yb:Lu$_2$O$_3$ from the precursor [12]. This result is consistent with the results of XRD analysis.

Fig. 2 shows the XRD patterns of the 5 at% Yb:Lu$_2$O$_3$ precursor and the powders calcined at different temperatures for 4 h. It can be seen
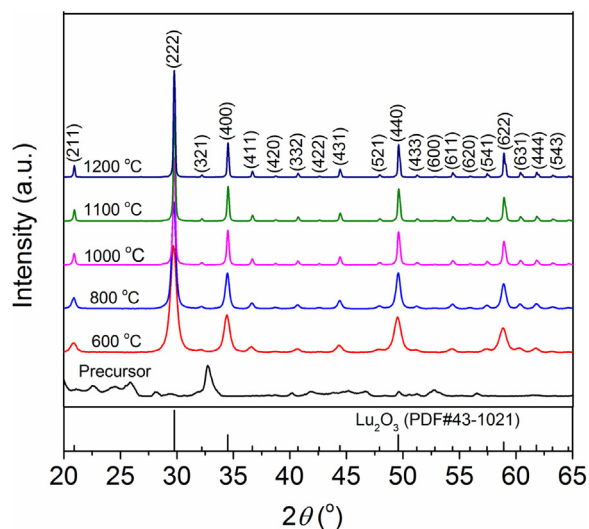

Fig. 2. XRD patterns of the precursor and the 5at%Yb:Lu$_2$O$_3$ powders calcined at different temperatures for 4 h.