Fabrication of Yb:Lu$_2$O$_3$ Transparent Ceramics by Hot Isostatic Pressing: the Effect of Yb Doping Concentrations

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Abstract: Highly transparent ytterbium doped lutetium oxide (Yb:Lu$_2$O$_3$) transparent ceramics with different Yb doping concentrations (0.5–10 at% Yb) were fabricated from commercial powders by vacuum sintering combined with hot isostatic pressing (HIP) method. The effects of Yb$^{3+}$ doping concentrations on the microstructure, optical performance and the thermal conductivity of Yb:Lu$_2$O$_3$ transparent ceramics were investigated. The grain size of Yb:Lu$_2$O$_3$ ceramics first decreased with Yb doping concentration increasing and then kept nearly unchanged at high Yb doping concentrations. Under 1750°C HIP sintering for 2h, the in-line transmittance of the 5 at.% Yb:Lu$_2$O$_3$ ceramics (3 mm thick) exceeds 81.52% at 1100 nm. And it had the average grain size about 2 μm. As the doping concentrations increase, the overall thermal conductivity decreases slightly. The fluorescence emission spectrum implied high possibility of realizing laser output at 1080 nm by pumping at 980 nm.

1. Introduction
Recently solid-state laser has been applied in many fields (including industry, medicine and military) for its small size, high efficiency and many other excellent performance. As solid-state laser material, single crystal has some disadvantages such as high preparation temperature, complex synthesis process, high cost and cannot realize high concentration doping. Transparent yttrium aluminum garnet (Y$_3$Al$_5$O$_{12}$, YAG) ceramic has been proved to be an excellent laser material owing to its simple synthesis process, high concentration doping and better homogeneity of doping process [1]. Whereas, YAG has the disadvantages of low thermal conductivity and serious thermal expansion, it is necessary to develop a gain material with better performance for solid-state laser. Compared with YAG, the sesquioxides (such as Y$_2$O$_3$, Lu$_2$O$_3$ and Sc$_2$O$_3$) possess better thermal and thermo-optical properties as a gain material for solid-state laser [2]. Among the sesquioxides, Lu$_2$O$_3$ features high thermal conductivity and low phonon energy. The thermal conductivity of Lu$_2$O$_3$ is 12.8 W/mK, and it is weakly dependent on the concentration of rare earth ion. Recent years, researchers have used rare earth ions doped Lu$_2$O$_3$ to produce high quality transparent ceramics. All of the rare earth ion, Yb$^{3+}$ has the similar ionic radii and bonding forces with Lu$^{3+}$, so Yb$^{3+}$ can easily realize high dopant concentration on Lu$_2$O$_3$. Furthermore, Yb$^{3+}$ has high quantum efficiency and simple energy manifolds (the $^2$F$_{7/2}$
ground state and the $^2\text{F}_{5/2}$ excited state), which prevent the excited state absorption and upper level conversion [3]. As a result, Yb:Lu$_2$O$_3$ transparent ceramic is a promising material for solid-state laser.

To fabricate Yb:Lu$_2$O$_3$ transparent ceramics, it is prerequisite to prepare powders with high purity, fine particle size, narrow size distribution, and high sintering activity. There are several methods to prepare Yb:Lu$_2$O$_3$ powders for transparent ceramics including ball milling high-purity commercial powder, sol-gel [4], hydrothermal [5] and co-precipitation [6-10]. Although co-precipitation has been widely used to prepare powders for transparent ceramics, it needs further improvement owing to its low synthetic efficiency, requires a lot of time for a batch preparation. Among them, ball milling is a facile, low cost and efficient technique to fabricate uniform mixing spheroid powders without damaging the original materials, particle distribution and the sintering activity [11]. This method helps us realize the engineering of Yb:Lu$_2$O$_3$ transparent ceramic. It has been demonstrated that Lu$_2$O$_3$ transparent ceramic with laser performance could be prepared by the process of ball milling. In 2015, Qiao et al. [12] fabricated transparent Er:Lu$_2$O$_3$ ceramic with the average grain size of ~2 μm by the ball milling method, and it realized the maximum output power of 189 mW at 2.7 μm with a corresponding slope efficiency of 21.6%. In [13], a 6 at% Yb:(Lu,Y)$_2$O$_3$ ceramic sample was fabricated by means of solid-state sintering of mixed sesquioxide particles under vacuum with a transmission very close to the theoretical limit.

In addition, process of sintering is crucial to achieving the greatest optical transparency in ceramics. The common sintering processes are vacuum sintering [14], atmosphere sintering, hot pressing (HP) [15], hot isostatic pressing (HIP) and spark plasma sintering (SPS) [16]. Recently, a two-step sintering method followed by HIP is used to prepare highly transparent ceramics [17]. In the two-step sintering process, the grain size of the per-sintered sample should be as small as possible to help promote the density during process of HIP [18]. Vacuum sintering is an effective method for preparing small grain size ceramics. In [19], Serivalsatit K. et al. fabricated high optical property Er:Lu$_2$O$_3$ transparent ceramic using vacuum sintering followed by HIP. This two-step process has been a promising method to prepare high quality transparent ceramics.

In this work, the Yb:Lu$_2$O$_3$ powders were prepared by ball-milling high-purity commercial Lu$_2$O$_3$ and Yb$_2$O$_3$ powders with different Yb doping concentrations (0.5–10 at% Yb) in absolute ethyl alcohol and ZrO$_2$ was used as sintering additive. The Yb:Lu$_2$O$_3$ transparent ceramics were fabricated by vacuum sintering combined with HIP method. The effects of Yb$^{3+}$ doping concentration on the microstructure, optical performance and the thermal conductivity of Yb:Lu$_2$O$_3$ transparent ceramics were investigated.

2. Experiment

2.1. Preparation process

Commercial Lu$_2$O$_3$ (purity: 99.995%), Yb$_2$O$_3$ (purity: 99.99%) and ZrO$_2$ (purity: 99.99%) were used as raw materials. The raw materials were mixed with the chemical formula of xYb:Lu$_2$O$_3$ (x=0.5 at%, 1.0 at%, 5.0 at% and 10.0 at%), amount of ZrO$_2$ was 3 at% molar ratio to Lu$_2$O$_3$. The mixed raw materials were ball milling with ZrO$_2$ balls for 24h at the speed of 200r/min, and dried for 12h at 70°C. Then the dried powders were passed through a 100-mesh sieve, the sieved powders were dry-formed to prepare a square sample of 10×10mm and subjected to cold isostatic pressing under a pressure of 200MPa to be more compact. The green bodies were vacuum sintered at 1780°C for 10h, then further hot isostatic pressed at 1750°C in an argon atmosphere for further densification. The sintered compact samples were annealed at 1500°C for 8h to remove internal stresses. Samples were polished on both surfaces to obtain a ceramic sample with the thickness of 3mm.

2.2. Characterization

The phase compositions of the ceramics were identified by X-ray diffraction (XRD) using Cu-Kα radiation at 40 kV and 30 mA (DX–1000CSC, Tongda Co. Ltd). The $2\theta$ for all the data ranged from 10° to 90° with the scan speed of 0.3°/s and 0.05° step size. The optical transmittance was measured by a
UV-VIS-NIR spectrometer (Lambda950, PerkinElmer) in the range of 200–1200 nm. The morphologies of the polished surface were examined using FESEM (JSM-6700, JEOL, Japan). The fluorescence spectrum was measured at room temperature using an FLS920 Edinburgh Analytical Instruments Fluorescence Spectroscopy Life Spec PS Spectrophotometer.

3. Results and discussion

Figure 1 shows XRD patterns of the Yb:Lu$_2$O$_3$ ceramics with different Yb doping concentrations. It can be seen that all characteristic peaks of the ceramics correspond well to the standard card of the Lu$_2$O$_3$ cubic crystal structure (JCPDS 43-1021) and no secondary phase or impurity phase appears. With the doping concentration of Yb$^{3+}$ increasing, no lattice distortion occurs due to the similar ionic radii and bonding forces with Lu$^{3+}$, indicating that Yb$^{3+}$ could be doped in the Lu$_2$O$_3$ lattice and form a uniform ceramic solid solution.

Figure 1. XRD patterns of the Yb:Lu$_2$O$_3$ ceramics with different Yb concentrations.

![Figure 1](image1.png)

Figure 2. FESEM micrographs of the thermal etched ceramics surface with different Yb concentrations: (a) 0.5at% (b) 1.0at% (c) 5.0at% (d) 10.0at%.

![Figure 2](image2.png)
FESEM micrographs of the thermal etched ceramics surface with different Yb doping concentrations are shown in figure 2. All of the ceramics after HIP are non-porous structure and no impurities at grain boundaries are found. Figure 2 (a) and (b) shows the non-uniform distribution of grains which would form scattering sources at the grain boundaries. It can be seen that with increasing of Yb$^{3+}$ doping concentration, the average grain size of ceramics decreases from about 4 $\mu$m to 2 $\mu$m and then keep nearly unchanged at high Yb doping concentrations. It indicates that when Yb$_2$O$_3$ is highly doped the grain growth could be limited.

Figure 3 displays in-line transmittance and photographs of polished ceramics with different Yb doping concentrations. All of the ceramics are transparent. The in-line transmittance of ceramics increases as the doping concentration of Yb increases and keep high transmittance at high Yb doping concentrations. The transmittance of 5.0 at% Yb:Lu$_2$O$_3$ reaches 81.52% @ 1100nm. A photo of the ceramic samples is shown in figure 3, the words underneath all of the transparent ceramics samples can be seen clearly.

The room-temperature emission spectrum at 980nm laser excitation of the 5.0 at% Yb:Lu$_2$O$_3$ ceramics is shown in figure 4 (a). There are two emission peaks located at 1033nm and 1080nm and the intensity of peak at 1033nm is the strongest. Both of the emission peaks are responding to transition radiation of Yb$^{3+}$ between the $^2F_{7/2}$ excited state and the $^2F_{5/2}$ground state. The fluorescence emission spectrum implies high possibility of realizing laser output at 1080 nm by pumping at 980 nm.

Figure 4 (b) shows the thermal conductivity curve of ceramics with different Yb concentrations. It can be seen that as Yb doping concentration increases, the thermal conductivity decreases from 12.545W/mK to 11.664W/mK, which indicates the thermal conductivity of Lu$_2$O$_3$ is weakly dependent on the doping concentration of Yb.
4. Conclusions
Highly transparent Yb:Lu$_2$O$_3$ transparent ceramics with different Yb doping concentrations (0.5–10 at% Yb) were fabricated from commercial powders by vacuum sintering combined with HIP method. Results showed that the Yb concentration had effects on microstructure, optical performance and thermal conductivity of Yb:Lu$_2$O$_3$ transparent ceramics. With increasing of Yb concentration, the average grain size of ceramics decreased from about 4 μm to 2 μm and then kept nearly unchanged at high Yb doping concentrations; in-line optical transmittance of transparent ceramics increased from 71% to 81.52% at 1100nm; the thermal conductivity decreased with increasing of Yb doping concentrations slightly; the fluorescence emission spectrum implied high possibility of realizing laser output at 1080 nm by pumping at 980 nm. These results provide a great guidance for preparation of transparent Yb:Lu$_2$O$_3$ ceramics with high optical quality.

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