Fabrication of Transparent Yb:Sc$_2$O$_3$ Ceramics by Hot Isostatic Pressing Without Sintering Additive

Mingzhen Ma$^1$, Linlin Dong$^1$, Wei Jing$^2$*, Tao Xu$^3$, Bin Kang$^2$, Feng Hou$^1$*

$^1$Key Laboratory of Advanced Ceramics and Mechanical Technology of Ministry of Education, School of Materials Science and Engineering, Tianjin University, Tianjin 300072, China

$^2$Institute of Chemical Materials, China Academy of Engineering Physics, Mianyang 621900, China

* jingwei@caep.cn; # houf@tju.edu.cn

Abstract. Highly transparent Yb:Sc$_2$O$_3$ ceramics were successfully fabricated using commercially powders without any sintering additive by a hot-isostatic-press (HIP) method. The ceramics were sintered at 1700°C in vacuum followed by HIP at 1680°C to obtain a relatively high transmittance. The effects of Yb doping concentrations on the microstructure and transmittance were investigated, respectively. The samples with a doping concentration of 10 at% achieved the highest transmittance, which showed 79.4% at a wavelength of 800 nm. The fluorescence emission spectroscopy suggests that it is promising to achieve laser output at around 1080 nm. These results may afford a enchiridion for comprehending the microstructural development of transparent Yb:Sc$_2$O$_3$ ceramics without sintering additive.

1. Introduction

Yb:Sc$_2$O$_3$ is considered to be an ideal gain medium for high power laser applications due to its high thermal conductivity (17W/mK at 300 K) and large splitting of the electronic states in sesquioxides such as Y$_2$O$_3$, Lu$_2$O$_3$ and Sc$_2$O$_3$ [1-3]. Compared with the Yb:Sc$_2$O$_3$ single crystal [4-7], the polycrystalline Yb:Sc$_2$O$_3$ transparent ceramic can possess similar optical properties at a lower preparation temperature. Moreover, it is possible to achieve large size and uniform doping at a high concentration. Therefore, it is easier to select a suitable Yb doping concentration for laser oscillation compared with single crystal [8-11].

To obtain transparent ceramic with high optical quality, it is vital to eliminate the scattering centers such as pores and secondary phases as much as possible [12-14]. Many attempts have been made to remove the pores and improve the laser quality of the Yb:Sc$_2$O$_3$ transparent ceramics. The one hand is the preparation of nano-powders with high sintering activity, many efforts have been carried out by wet chemical method, such as co-precipitation [15, 16], sol–gel process [9], self-propagating high-temperature synthesis [17] and so on. The powders prepared by these methods can be with high sinterability. However, these processes are complicated and exhausting, resulting in cost too much, very low efficiency and very hard to achieve actual production. Ball milling is a simple and efficient way to obtain homogeneous ultrafine powders compared to these intricate methods. In 2011, C. Gheorghe et al. [18] successfully fabricated Tm:Sc$_2$O$_3$ ceramics with 75% transmittance using powders prepared by solid-state reaction. On the other hand, sintering aids were widely used in the
sintering of transparent ceramics to promote the progress of densification and lower the sintering temperature. For example, Jiang et al.[1] prepared 1 at%Yb:Sc2O3 ceramics by vacuum sintering method with CaO as sintering aids. Russia D. A. Permin et al. [17] obtained 2% Yb:Sc2O3 with a transmittance of 78% by hot-press sintering with LiF as sintering aids. But the introduction of sintering additive can easily cause excessive grain growth and the formation of impure phases[14], which is not conductive to the mechanical and optical properties of the ceramics. As the advent of hot isostatic pressing with high-efficiency sintering ability[19], such as YAG can be achieved without any sintering additive. However, there are very few articles about the efficient preparation of Yb:Sc2O3 ceramics without sintering aids.

In this paper, we reported on an efficient way to fabricate high transparent Yb:Sc2O3 ceramics without any sintering additive, via a vacuum sintering plus hot isostatic pressing method using accessible commercial powders. The effects of Yb doping concentrations on the microstructure and optical properties were investigated. It would help understanding the microstructural development of Yb:Sc2O3 transparent ceramics without sintering additive.

2. Experiment
High-purity Yb2O3 (99.99%) and Sc2O3 (99.99%) powders were used as starting materials. Both powders were mixed according to the formula (Sc(1-x)Ybx)2O3 (x=0, 0.02, 0.03, 0.05, 0.07, 0.10). Then the mixture was ball milled for 24 h in Teflon jars with a speed of 200 r/min. After drying the slurry at 80°C for 24 h, the powders were sifted with a 200-mesh screen and calcinated at 400°C for 4 h. The green ceramic samples were dry pressed into a disk with diameter of 15 mm at 20 MPa, and further cold isostatically pressed at 200 MPa to increase the density. Before the densification sintering, the specimens were calcining at 1000°C for 10h to remove organic impurities and residual carbon. And then, the Yb:Sc2O3 disks were vacuum sintered at 1700°C followed by hot isostatic pressed at 1680°C and 200 MPa in argon atmosphere for 2 h. Next, the obtained Yb:Sc2O3 ceramics were annealed at 1500°C for 8 h in air to remove oxygen vacancies. Finally, the transparent Yb:Sc2O3 ceramics were obtained by mirror-polished into 2.0mm thickness for measurement.

The phase compositions of the ceramics were identified by X-ray diffraction (XRD) using CuKα radiation at 40 kV and 30 mA (DX–1000CSC, Tongda Co. Ltd). The 2θ for all the datas ranged from 20° to 65° with the scan speed of 10°/min and 0.05° step size. Morphologies of the powders and the ceramics were examined using field emission scanning electron microscopy (SEM, Inspect F, FEI). The average grain size of the sintered ceramic was estimated by Nano measurement software[14] using SEM images. The optical transmittance was measured by a UV-VIS-NIR spectrometer (Lambda950, PerkinElmer) in the range of 200–1100 nm. The fluorescence spectrum was measured at room temperature using an FLS920 Edinburgh Analytical Instruments Fluorescence Spectroscopy Life Spec PS Spectrophotometer.

Figure 1. XRD patterns of (Sc(1-x)Ybx)2O3 transparent
3. Results and discussion

The XRD patterns of the Sc$_2$O$_3$ ceramics with different Yb concentrations HIPed at 1680°C were shown in Figure 1(a). The characteristic peaks of all samples were consistent with the pure Sc$_2$O$_3$ crystal structure (PDF#84-1880), and almost no impurity phase or other impurity peaks were found, which means that Yb$^{3+}$ were solid-dissolved in the Sc$_2$O$_3$ lattice to form a uniform ceramic solid solution. Since Yb$^{3+}$ (0.868Å) replaced Sc$^{3+}$ (0.745Å), lattice distortion occurred, and its unit cell parameter increased from 9.8443 to 9.9332Å. All characteristic peaks shifted to a small angle, which is caused by the increase of the interplanar spacing, as is shown Figure 1(b). Similar results had been appeared in the Y$_2$O$_3$[20] and YAG[21] ceramic systems.

Figure 2 (a) ~ (f) illustrates SEM image of the thermal etched surfaces of Yb:Sc$_2$O$_3$ transparent ceramics. All samples are found to exhibit a pore-free structure and the grains are tightly bound to each other except for Figure 2 (a) and (b). In addition, there is no grain boundary phase observed. These tight microstructures are inseparable from hot isostatic pressing. The high pressure existing during the sintering process may promotes the mass transfer of the grains, effectively lowers the sintering temperature and holding time, thereby increasing the density of the ceramic and not causing excessive grain growth[13, 22]. As shown in Figure 2 (g), with the increasing of Yb doping amount, the grain size continues to decrease, ranging from 8.4 µm for undoped sample to 1.96 µm for 10at%Yb doped sample, which indicates the addition of Yb$^{3+}$ will inhibit the growth of crystal grains. This phenomenon may be caused by the partial poly of Yb$^{3+}$ at the grain boundaries. And fine grain size helps to improve the mechanical properties and thermal shock resistance of ceramics.

![Figure 2](image)

**Figure 2.** SEM micrographs of (Sc$_{1-x}$Yb$_x$)$_2$O$_3$ transparent ceramics after double-sided polishing: (a) x=0 (b) x=0.02 (c) x=0.03 (d) x=0.05 (e) x=0.07 (f) x=0.1and (g) grain size change chart.

Figure 3 shows the photograph and the in-line transmittance spectrum of the Yb:Sc$_2$O$_3$ transparent ceramics (2 mm thick). It can be seen from the Figure 3 (a) that the transmittance of samples increases as the growth of Yb concentrations. The main reason for limiting the transmittance of ceramics is the pores between grains as shown in Figures 2(a) and (b). In order to reduce the porosity and improve the light transmittance, it may be a good choice to adjust the sintering process. The transmittance of 10at% Yb:Sc$_2$O$_3$ transparent ceramic is the highest, reaching 79.4% at 800 nm, and the corresponding average grain size is the smallest (1.96 µm), which is in accordance with the light-scattering model[23]. The absorption peaks of all samples are approximately 890~1000nm, which is consistent with the transition between $^7F_{5/2}$ and $^5F_3$ energy levels of Yb$^{3+}$. And as the Yb concentrations increase, the absorption peaks become more pronounced.

Figure 4 shows the room-temperature fluorescence spectrum of the Yb:Sc$_2$O$_3$ transparent ceramics under excitation at 980 nm. Two obvious emission peaks located at 1044 and 1094 nm, which
corresponds to the energy transfer between $^2F_{7/2}$ and $^2F_{5/2}$ of Yb$^{3+}$. Analogous phenomena have been reported in the Yb$^{3+}$ ions doped Lu$_2$O$_3$[24], Y$_2$O$_3$[25], and YAG[26] ceramics. The full-width at half-maximum (FWHM) of the emission peak at 1044 nm is about 20.4 nm, which is greater than the FWHM of previous Yb:Sc$_2$O$_3$ ceramics[1]. And the wide emission band benefits for ultra-short pulse laser operation[8].

Figure 3. (a) Pictures of the mirror-polished (Sc$_{(1-x)}$Ybx)$_2$O$_3$ ceramics. From left to right: x=0, 0.02, 0.03, 0.05, 0.07, 0.1. And (b) in-line transmittances of (Sc$_{(1-x)}$Ybx)$_2$O$_3$ ceramics.

Figure 4. Fluorescence spectrum of the 10at% Yb:Sc$_2$O$_3$ transparent ceramics pumped at 980 nm.

4. Conclusion
High optical quality and fully dense Yb:Sc$_2$O$_3$ ceramics have been successfully fabricated using commercial powders without sintering additive by vacuum sintering plus HIP. The effects of Yb doping concentrations on their microstructure and optical properties have been investigated, respectively. The results indicate that Yb ions are solid-dissolved in the Sc$_2$O$_3$ lattice to form a solid solution and the increase of Yb doping concentrations lead to the decrease of grain size and the improvement of transmittance. The 10at% Yb:Sc$_2$O$_3$ ceramics after HIP have an in-line transmittance...
of 79.4% at 800 nm and an average grain size of 1.96µm. These results may provide guidance for the efficient preparation of high optical quality Yb:Sc₂O₃ ceramics.

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