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Sintering of Yb^{3+}:Y_2O_3 transparent ceramics in hydrogen atmosphere

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Abstract

Highly transparent Yb^{3+}:Y_2O_3 ceramics with doping concentration up to 40.0 at.% had been fabricated successfully via hydrogen atmosphere sintering, where the raw powders were synthesized by co-precipitation method. The sintering temperature is about 600 °C lower than its melting temperature. SEM investigation revealed the average grain size of Yb^{3+}:Y_2O_3 ceramics sintered at 1850 °C for 9 h was about 7 μm. The highest transmittance of as-prepared 1 mm thickness samples around wavelength of 1050 nm reached 80%, which is close to the theoretical value of Y_2O_3. The optical spectroscopic properties of Yb^{3+}:Y_2O_3 transparent ceramics have also been investigated, which shows that it is a very good laser material for diode laser pumping and short pulse mode-locked laser.

Keywords: Sintering; Spectroscopy; Optical properties; Y_2O_3; Transparent ceramics

1. Introduction

Cubic Y_2O_3 crystal has been investigated for a long time as a laser-host material due to its high thermal conductivity, broad range of transparency, good chemical stability, strong Stark-splitting and relatively low phonon energies.[1–4] However, it is extremely difficult to grow large-size Y_2O_3 single crystal with good optical quality because of its very high melting point (≈2430 °C) and structural phase transition at ≈2280 °C.[5–6] By using ceramic fabrication technology, it is possible to get optical transparent Y_2O_3 ceramics, at same time with big size and complex structure.

In order to produce good optical quality polycrystalline ceramics, porosity-free microstructure of the sintered ceramics must be achieved. During the past 40 years, many methods have been tried to fully remove the pore. In 1966, Brissette et al. succeeded in obtain transparent Y_2O_3 for the first time in the world by using thermomechanically deforming cold pressed powder compacts.[7] But neither pressure nor temperature conditions were given in their report. Then in the late of 1960s, transparent polycrystalline Y_2O_3 ceramics were prepared by hot pressing method without additives or with addition of LiF that causes the formation of a liquid phase.[8–10] But, due to the limitation of the mold that used in hot-pressing, it is rather difficult to get Y_2O_3 transparent ceramics with complex shape and good optical quality. In 1970s, GE company succeeded in fabricating laser quality transparent Y_2O_3 ceramics by pressureless sintering, which using ThO_2 as the sintering aid to control the grain growth and thus enhance the densification.[11–15] Another effective pressureless sintering method is to form a liquid-phase or transition secondary phase by adding some amount of ZrO_2, Al_2O_3, BeO or La_2O_3 into Y_2O_3.[3,11–12,16] In addition, transparent Y_2O_3 ceramics can also be prepared by pressureless sintering without any additives but it requires very high temperature.[17] In 2002, by combination of nanocrystalline powder technology and vacuum sintering method, Konoshima Company get great progress in fabricating laser quality transparent YAG ceramics. By using very similar manufacturing method, highly transparent Nd^{3+} and Yb^{3+} doped Y_2O_3 ceramics were developed, and their laser properties were also reported.[5–6,18–20]

Compared with vacuum sintering, H_2 atmosphere sintering is also a good way to enhance densification. A study shows that the densification rate and grain growth rate will be greatly increased during the final-stage sintering, when the H_2 atmosphere was applied for the fabrication of alumina ceramics.[21] Actually, since many years ago, dry or wet H_2 atmosphere sintering method has been employed to massively produce ceramic scintillators and translucent alumina tubes. It was also reported that transparent yttrium aluminum garnet (YAG) ceramics can also be

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fabricated successfully in wet H_2 atmosphere.[22] In present research, different doping concentrations of Yb^{3+}:Y_2O_3 ceramics were successfully sintered into transparent in flow dry H_2 atmosphere by using nanocrystalline powders which synthesized by co-precipitation method.

2. Experimental

The main preparation steps of Yb^{3+} doped Y_2O_3 transparent ceramics were described as following. At first, Yb^{3+} ions doped (0–40 at.%) Y_2O_3 nanocrystalline powders were synthesized via a reverse-strike co-precipitation method using nitrates and ammonia as raw materials. The details of the synthesizing processes have been described in another paper.[23] According to this method, the pure cubic phase of Y_2O_3 will present and the average diameter of particles was in the range of 60–80 nm after calcined at 1000 °C for 2 h. The specific surface area of the powders was measured by BET method using nitrogen absorption on Micromeritics ASAP 2000 analyzer (Micromeritics, Norcross, USA). The main non-rare earth impurities of synthesized pure Y_2O_3 powders were determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES, VARIAN, Palo Alto, CA). The as-prepared nanocrystalline powders were directly cold isostatically pressed (CIP) into 18.5-mm diameter pellets under 200 MPa pressure. For the forming process, no any binder was added. Finally the powder compacts were sintered at 1850 °C for different holding time in flowing dry H_2 atmosphere to get the transparent ceramics. The above sintering process was accomplished in a tungsten-element, molybdenum-shielded furnace, equipped with a rotatory pump. After sintering, no any further annealing treatment was applied on these samples.

The as-sintered surfaces and the fracture surfaces were observed under scanning electron microscope (SEM, JXA-8100, JEOL, Tokyo, Japan). Disk specimens of 14 mm in diameter and 1 mm in thickness, to be used for measuring optical transmittance and emission spectra, were mirror-polished on both surfaces. The inline transmission spectra of as-prepared ceramics were measured over the wavelength region from 300 to 1100 nm, using a spectrophotometer (Model U-3500, Hitachi Co., Tokyo, Japan) with a 0.5 nm slit width and 120 nm/min, scan speed. For emission spectroscopic experiments, a diode laser tuned to 980 nm was used as the excitation source inclined 45° to irradiate the center of the pellets. The laser was focused onto the pellet and the diameter of the exciting beam on the pellet was smaller than 0.2 mm. The emission spectra were recorded by a spectrofluorometer (Fluorolog-3, Jobin Yvon Co., Edision, America) equipped with a Hamamatsu R5509-72 photomultiplier tube. All emission spectra are corrected for the spectral response of the measuring system. The experiments were performed at room temperature.

3. Results and discussion

For laser quality transparent ceramics, high chemical purity, phase purity and agglomerates free or soft-agglomerates powders are essentials for sintering. Nowadays, it seemed that there is an increasing interest of fabricating transparent ceramics from fine powders. However, for this kind powder, it is important to find a suitable processing method. For example, if the specific surface area of the powder is very high, the local sintering activity may be high. But it will be difficult to get whole dense bulk ceramics with the homogenous microstructures, if improperly forming method was applied. For laser ceramics, some of the impurities have the big influence on optical properties. On one hand, they will have the influence on the densification rate during the sintering. On the other hand, some of impurities, especially the transition metal ions will greatly increase the optical loss at specific laser emission wavelength.

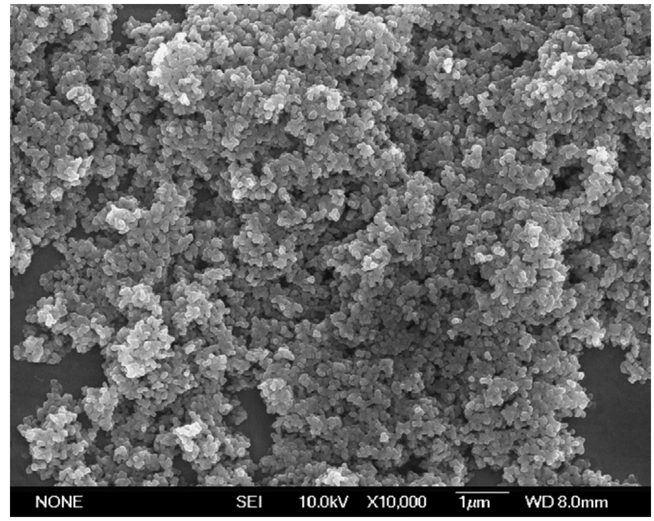

Fig. 1. The SEM morphology of synthesized Yb^{3+}:Y_2O_3 nanocrystalline powders.

Fig. 1 shows the morphology of the starting Y_2O_3 powders that prepared from co-precipitation method. The particles are quite uniform in size and most of the particles are nearly spherical. The average diameter of the particles is in the range of 60–80 nm. The powders are only loosely agglomerated. The BET measurements show that the specific surface area of the prepared powders is around 9.5–10.0 m^2/g. After formed by CIP processing, the green body density is in the range of 45–48% of their theoretical density. Table 1 summarizes the ICP-AES analysis results for non-rare earth impurities existed in as-prepared pure Y_2O_3 powders. It can be found from the table that the highly absorptive transition metal impurities, such as Fe, Ni, are substantially low in the synthesized powders.

Table 1
The ICP-AES analysis results of non-rare earth impurities in as-prepared pure Y_2O_3 powders

Non-rare earth impurities	Content (ppm wt)
Fe_2O_3	3.2
SiO_2	15
CaO	5.0
CuO	1.3
ZrO_2	6.2
NiO	2.5
PbO	1.4

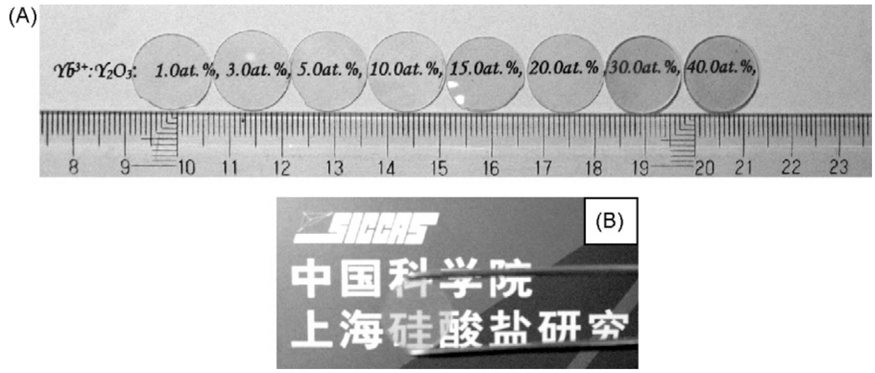

Fig. 2. Visual appearances of the Yb^{3+}:Y_2O_3 ceramics doped with different concentrations (A: Φ15.5 mm × 1.0 mm, placed on the paper; B: kept about 30 cm above the paper).

Fig. 2 shows the pictures of Yb^{3+}:Y_2O_3 ceramics sintered at 1850 °C in flowing dry H_2 atmosphere. It can be seen that Yb^{3+}:Y_2O_3 transparent ceramics doped at different levels all shows very good optical quality. Even when the sample was raised about 30 cm from the paper, the logo of SICCAS can still be clearly resolved. It was reported that the YAG ceramics become grayish if dry H_2 was used during the sintering. This was due to the formation of oxygen vacancies, and the formation of oxygen vacancies is very sensitive to the oxygen partial pressure.[22] But in present research, all of the sintered samples are colorless.

Fig. 3 shows the inline optical transmittance spectrum of 8.0 at.% Yb^{3+}:Y_2O_3 ceramics sintered at 1850 °C for different holding time. With the holding time prolonged from 3 to 9 h, the transmittance of sintered Yb^{3+}:Y_2O_3 ceramics increased gradually. The improvement of the optical quality of as-prepared ceramics is due to the further elimination of residual pores.

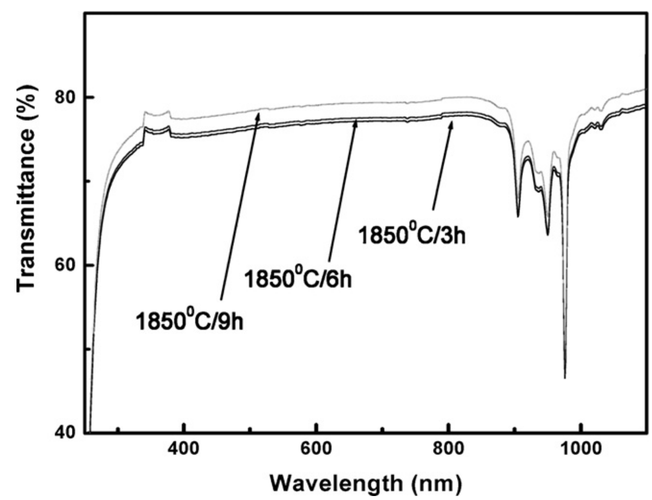

Fig. 3. The inline optical transmittance of 8.0 at.% Yb^{3+}:Y_2O_3 ceramics sintered at 1850 °C for different time.

Fig. 4(A) shows the SEM photograph of the as-sintered surfaces of Yb^{3+}:Y_2O_3 ceramic sintered at 1850 °C for 9 h. It reveled that the microstructure of sintered ceramics is very uniform and the average grain size is about 7 μm. Fig. 4(B) shows the SEM picture of the fracture surface from which it can be seen that there are nearly no pores existed in or between the grains. The microstructure is very dense, which resulted in the high optical quality. In addition, from the fracture surfaces, it was observed that the sintered ceramics are mainly fractured intragranularly.

Fig. 5 shows the inline optical transmittance spectrum of the Yb^{3+}:Y_2O_3 ceramics with different doping concentrations, which were measured in the wavelength region from 300 to 1100 nm. The highest transmission at non-absorption band of

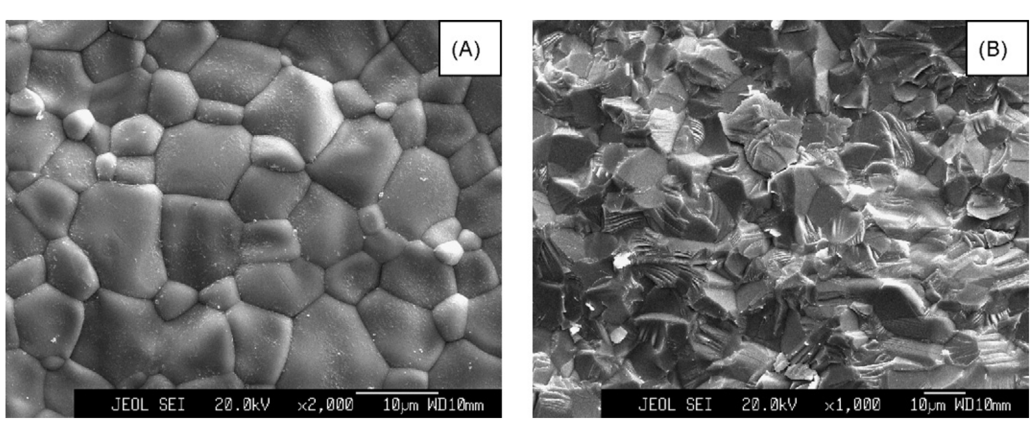

Fig. 4. The microstructure of Yb^{3+}:Y_2O_3 transparent ceramics (A: as-sintered surface; B: fracture surface).

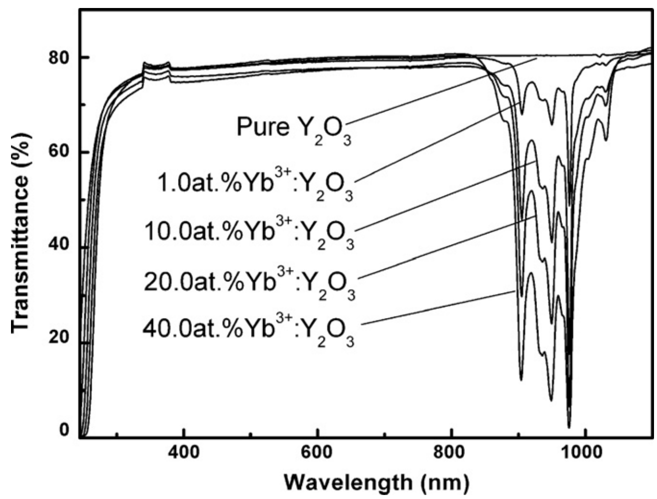

Fig. 5. The inline optical transmittance spectrum of Yb^{3+}:Y_2O_3 ceramics with different doping levels.

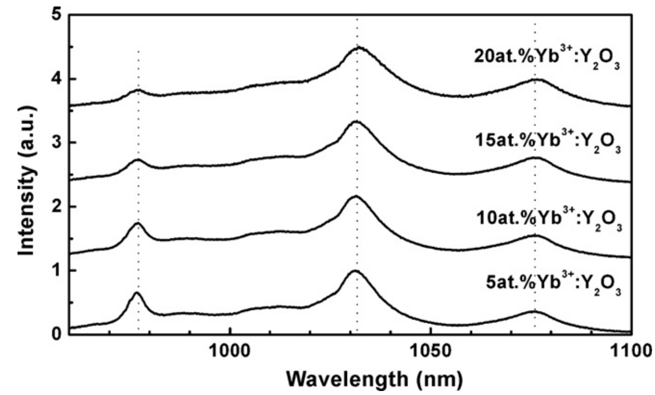

Fig. 6. The emission spectrum of Yb^{3+}:Y_2O_3 ceramics with different doping levels under the excitation of a 980 nm diode laser.

1 mm thick Y_2O_3 ceramics is about 80%, which reaches 98% of the theoretic transmittance value of Y_2O_3 at this wavelength. It seemed that the transmittance is almost independent of doping concentration of Yb^{3+} ions, even when the doping concentration increased to 40.0 at.%. The very strong absorption band in the range of 850–1050 nm is due to the absorption transition of Yb^{3+} ions. Such broad absorption band makes Yb^{3+}:Y_2O_3 ceramics much suitable for being pumped by laser diode arrays which the emission band is larger than that of single laser diode.[5] When Yb^{3+}:Y_2O_3 is pumped by a 940 nm LD, temperature control of the LD is not necessary because of its broad absorption spectrum around 940 nm.[19] This is important for the practical applications. In addition, from the transmittance spectrum, it can be found that there are no any other optical absorption appeared in the visible region. The reducing environment does not result in strong optical absorption in the visible region in our cases. So it is not necessary to perform the further annealing treatment on these samples.

Granger succeeded in fabricating transparent Y_2O_3 ceramics by commercial available fine Y_2O_3 powders, combined with slip-casting and hot isostatic pressing (HIP) technologies.[24] From their results, it seemed that small amount of the ZrO_2 additives will have big positive influence on improving the optical transmittance, especially in the visible range. From our unpublished results, when 900 ppm ZrO_2 was adopted as the sintering aid, the same optical transmittance can be achieved at the lower sintering temperature.[25]

Fig. 6 shows the emission spectrum of Yb^{3+}:Y_2O_3 ceramics. Under the excitation of the 980 nm diode laser, there are two main emission peaks, which centered at 1030 and 1075 nm wavelength, respectively. With the doping concentration of Yb^{3+} ions increased from 5.0 to 20.0 at.%, nearly no peak shift can be observed. The emission bandwidths around 1030 and 1075 nm are as broad as 12 and 17 nm, respectively. Because of the very broad emission spectra, femtosecond pulse laser could be obtained by using mode-locking technologies. And also because of the broad emission band, it is quite possible to get the tunable laser with the emission range from 1025 to 1080 nm.

4. Conclusions

Using nanocrystalline Yb^{3+}:Y_2O_3 as the starting materials, highly transparent Yb^{3+}:Y_2O_3 ceramics were fabricated successfully in flowing dry H_2 atmosphere. After sintered at 1850 °C, very uniform microstructure presents and the average grain size of sintered Yb^{3+}:Y_2O_3 ceramic is about 7 μm. By optimizing the processing parameters, the laser quality transparent Yb^{3+}:Y_2O_3 ceramics will be expected to obtain.

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