Conference Paper

Problems of High-quality Doped Y_2O_3-ceramics Fabrication

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Abstract

Tm:Y_2O_3, Ho:Y_2O_3 and Yb:Y_2O_3 ceramic samples were fabricated using different heat treatments modes. La_2O_3 (0.5 mol.%) and ZrO_2 (1.5 mol.%) were used as sintering additives. Based on the investigation of structural properties of obtained samples, annealing mode was adjusted, and another set of samples with better optical quality was fabricated. In-line transmittance of the latter samples is 70% at 400nm and 75.6% at 600nm.

Keywords: Y_2O_3, laser ceramics

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1. Introduction

Yttria ceramics is considered to be one of most promising materials for solid-state lasers. Heat conductivity of yttria considerably exceeds corresponding property of yttrium-aluminum garnet, thus yttria ceramics with good optical characteristics would probably increase maximum output of solid-state high-power lasers over YAG-based systems. The obstacle to widespread use of yttria ceramics as a laser material is that producing high-quality laser elements at the moment presents some difficulties. Producing optical ceramics from pure yttria powder demands sintering at very high temperature (over 1900°C). In order to lower sintering temperature and to improve optical properties of the ceramics, one must use sintering additives.

Earlier, in N. P. Ogarev Mordovian State University, our ceramics was used to fabricate laser elements, and lasing was obtained [1]. Maximum output was 2.4W on 1.95μm wavelength, with slope efficiency of 11%. The ceramics from which the laser element was manufactured included lanthanum (0.5 mol.%) and zirconium (1.5 mol.%) oxides as sintering additives. It was noted that improving optical quality of the ceramics might lead to higher maximum output and slope efficiency of the laser.

When deciding which route to take in our attempt to improve optical quality of our ceramics, we thought through few different options. For example, it is known from literature [2, 3] that HIP post-sintering treatment could have positive effect on yttria ceramics transparency. Another possible option was to vary sintering additives composition, for instance, use MgO instead of La_2O_3 [4]. Although these fabrication techniques do increase ceramics quality, we decided to approach the problem from different angle. It was reported previously that reasonably good Y_2O_3 ceramics could be produced by reactive sintering Y_2O_3 with 0.5 mol.% La_2O_3 and 1.5 mol.% ZrO_2 (or 0.7% and 1.6%, respectively, in mass concentrations) [5]. However, while conducting our sintering experiments, we noticed that ceramics of such composition is extremely sensitive to heat treatment mode. Here, some research was conducted in an attempt to better understand processes that take place during Y_2O_3 ceramics annealing.

2. Experiment

High-purity Y_2O_3, Tm_2O_3, Ho_2O_3 и Yb_2O_3 powders made by «Lanhit» were used as starting materials. SEM-image of raw Y_2O_3 powder is shown in Figure 1. Reagent grade ZrO_2 (1.5 mol.%) and high-purity La_2O_3 (0.5 mol.%) were used as sintering additives. Lasing dopant concentrations were: 3.0 mol.% for Tm:Y_2O_3, 0.5 mol.% for Ho:Y_2O_3 and 5.0 mol.% for Yb:Y_2O_3.

Powders were ball-milled in a planetary mill for 15 hours with zirconia balls and isopropanol. Milled powders were dried for 48 hours, sieved through 200 mesh, and then, annealed at 1000–1100°C to remove organic admixtures. Next, 10 and 27 mm-diameter pellets were made in two steps: first, uniaxial pressing (20–50 MPa), and then cold isostatic pressing (200–230 MPa). The thickness of pellets after pressing was in the range of 2–5 mm. Obtained pellets were sintered in vacuum furnace with tungsten heating element at 1800–1860°C with 10–20 hour dwell times and 20–200 degrees per hour heating rate. After sintering, samples were annealed on air at 950–1500°C for 15–30 hours to remove color centers. Complex annealing modes, namely soaking samples at two different temperatures (1000 and then 1450°C, for example) during one heat treatment cycle, were also tried. Produced samples were grinded and polished to mirror finish. Some samples had layers with high porosity (> 100ppm) near the surface. In such samples 500μm-thick layer near each surface was removed during grinding. Residual porosity was measured by taking pictures of samples through optical microscope layer by layer, and then, calculating volume of pores with special

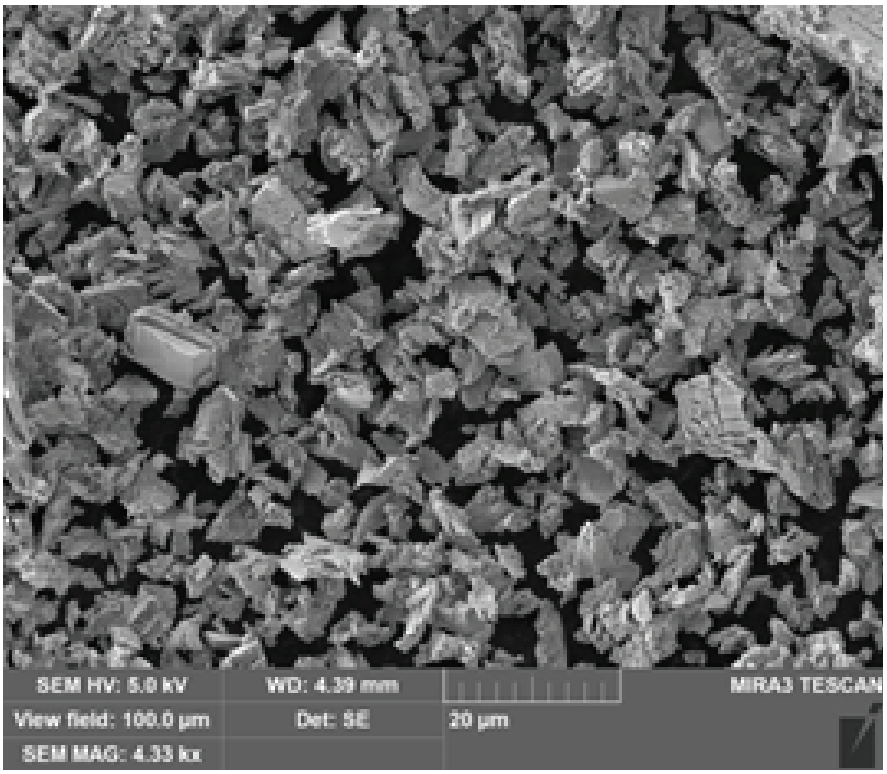

Figure 1: SEM-image of Y_2O_3 powder used as starting material.

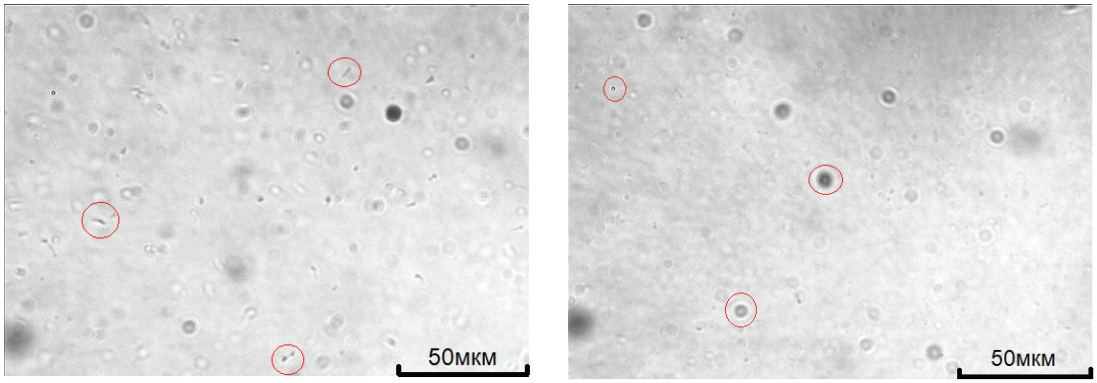

Figure 2: Pore pictures. Left: annealing at 1100°C; right: at 1300°C. Sintering temperature: 1800°C for both.

computer program. Transmittance spectra were recorded using Lambda 950 Perkin Elmer spectrophotometer.

3. Results

Figure 2 shows porosity structure of samples sintered at 1800°C and annealed at different temperatures. Layer by layer, residual porosity measurements of 1mm thick samples are presented in Figure 3. Figure 4 shows cross-sections (plain of the cut is parallel to cylinder axle) of Ho-doped samples, which were all sintered at 1860°C, but

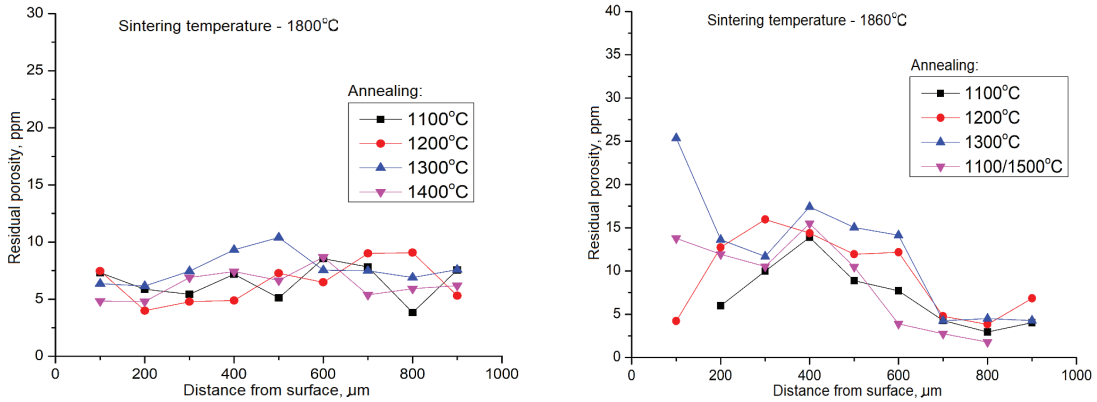

Figure 3: Residual porosity volume measurements of samples annealed at different temperatures. Samples sintered at 1800°C (left) and 1860°C (right) were investigated.

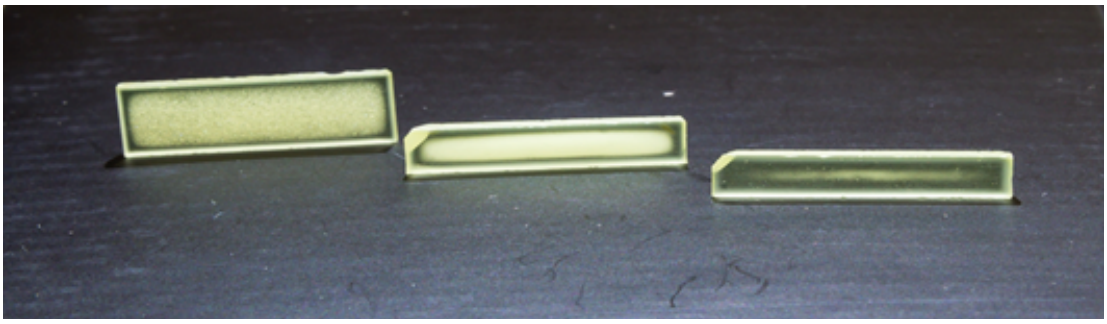

Figure 4: Diameter sections of Ho:Y_2O_3 samples. Left: 4 mm thick sample. Two other samples were annealed at different temperatures. Sample in the middle: 1100/1400°C; on the right: 950/1400°C. Sintering temperature: 1860°C for all three.

annealed differently (1100°C – center, 950°C – left and right). In both cases, after low temperature annealing was completed, samples were heated to 1400°C to remove remaining color centers. Left sample in Figure 2 is 4.5mm thick, and in this case 950°C annealing doesn't have any positive effect on optical quality. Transmittance spectra of Ho:Y_2O_3, Tm:Y_2O_3 and Yb:Y_2O_3 0.6 mm-thick samples can be seen in Figure 5. These samples were sintered at 1860°C and annealed at 950°C and, then, at 1400°C. Figure 6 allows to compare the transmittance spectra of 0.6 and 2.0 mm-thick Yb:Y_2O_3 samples. Figures 7 and 8 are photographs of 2.0 mm-thick samples. Note that sample in Figure 8 is held few cm above the surface to demonstrate good in-line transmittance.

4. Discussion

It can be seen from Figures 2 and 3 that samples that were annealed at different temperatures have roughly the same volume of pores but somewhat different pore structure. Linear defects are present on the left image of Figure 2, but absent on the

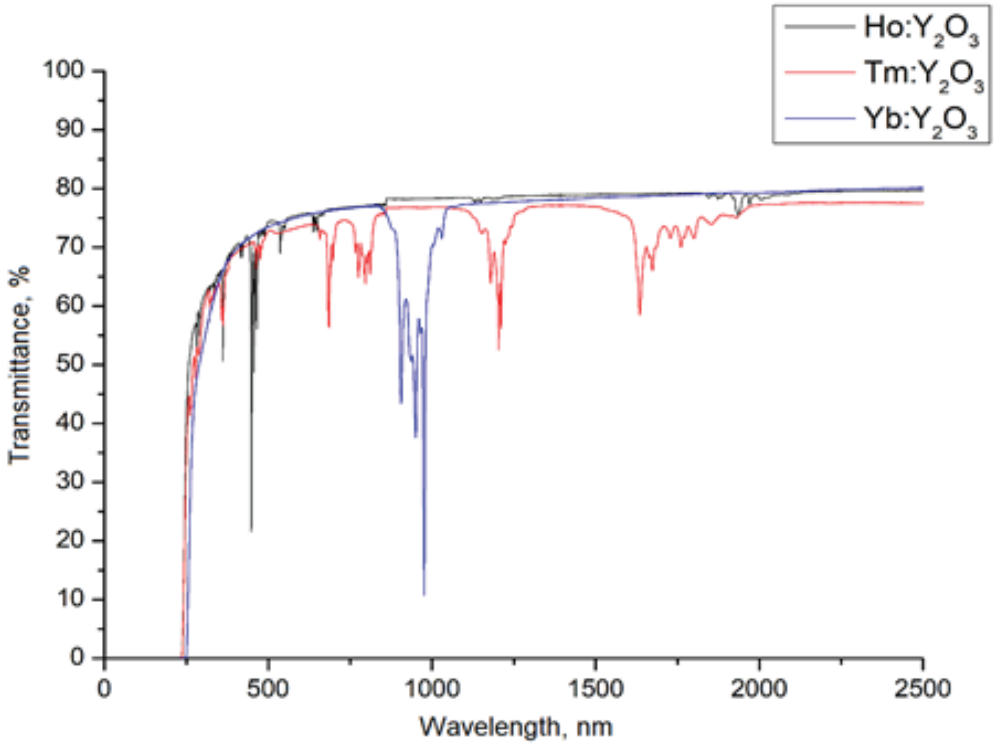

Figure 5: Transmittance spectra of Ho:Y_2O_3, Tm:Y_2O_3, Yb:Y_2O_3 samples. Sample thickness: 0.6 mm. Theoretical transmittance of Y_2O_3 crystal is 81.93% at 1100 nm wavelength.

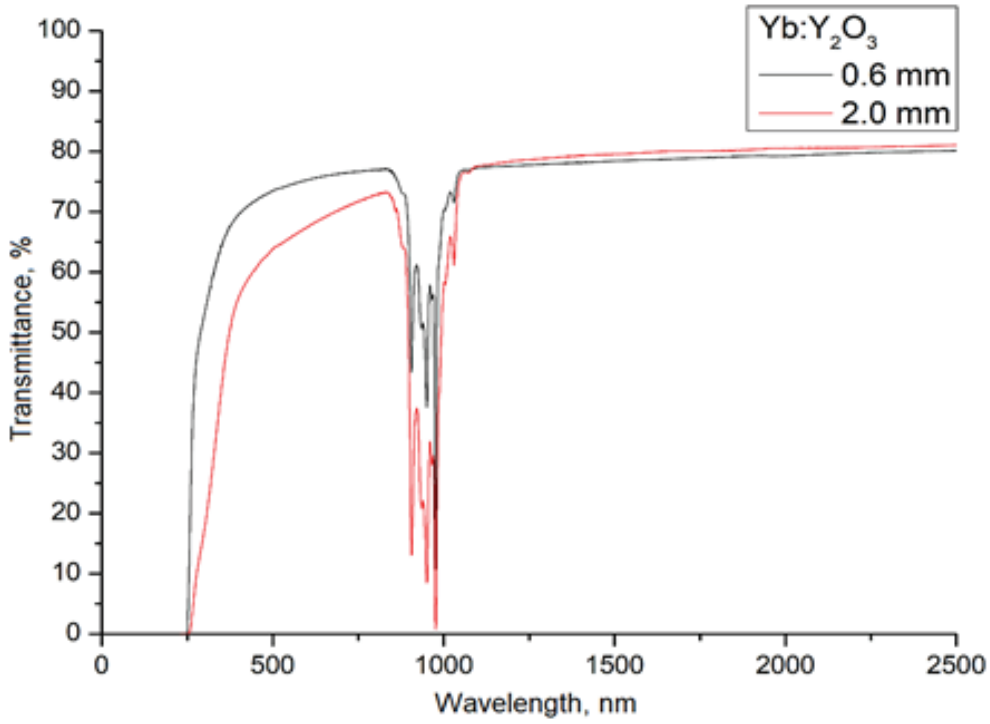

Figure 6: Transmittance spectra of 0.6 and 2.0 mm-thick Yb:Y_2O_3 samples.

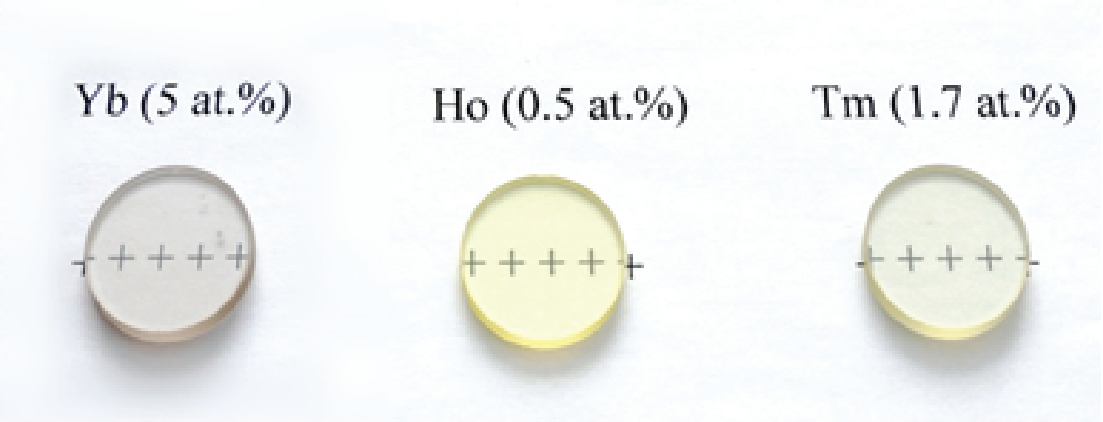

Figure 7: Photo of ceramics samples with different lasing dopants. Diameter: 23 mm; thickness: 2 mm.

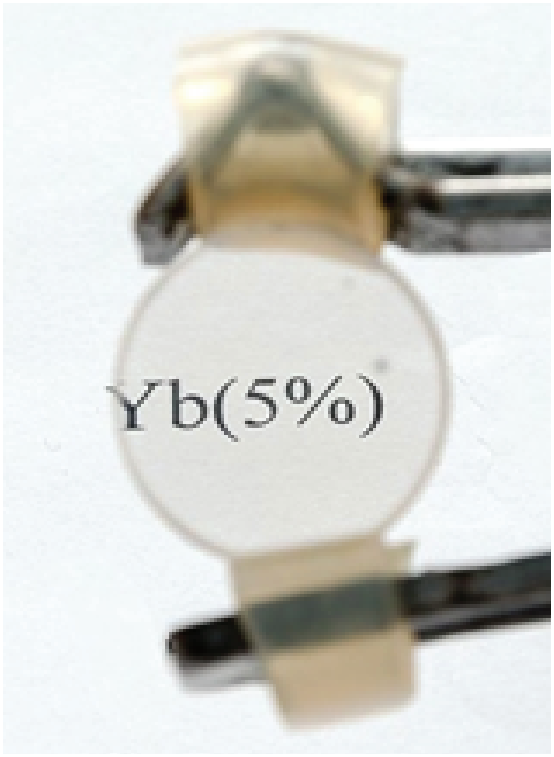

Figure 8: Photo of 2.0 mm-thick Yb:Y_2O_3 sample (the sample is held few cm above the surface).

right one. This led us to the conclusion that even at temperatures as low as 1100–1400°C, diffusion processes other than oxygen vacancies diffusion take place. Possibly, pores reconfigure and fuse together. More detailed research is needed for a better understanding of these processes.

The aforementioned observation strongly suggested trying lower annealing temperatures in order to limit all diffusion except the diffusion of oxygen vacancies. Center sample on Figure 4 annealed conventionally at 1100°C, and the sample on the right

annealed at 950°C. The difference in porosity is clear. It must be noted that relatively coarse structure of raw Y_2O_3 powder used in this research requires low heating rates, long dwell times and high temperatures during sintering, and, therefore, leads to higher concentration of oxygen vacancies. In case of shorter sintering cycle (and raw powder with better sintering ability), this effect, possibly, would be less pronounced. From Figure 3, it can be seen that samples sintered at 1860°C have slightly higher residual porosity than samples sintered at 1800°C. This can be attributed to higher concentration of oxygen vacancies in samples sintered at higher temperatures.

Application of described technique allowed us to produce samples with transmittance in 400–600 nm range that exceeds data in similar investigations [5], and comparable with HIP-ed samples [3]; 70% transmittance at 400 nm wavelength indicates that these samples are practically pore-free.

This experimental data raises the question—what induces such difference in the behavior of Y_2O_3 ceramics when annealing temperature increases by a mere 150°C, while still staying well below the sintering range, where matter diffusion normally occurs? It could be carefully assumed that possible cause of hugely different porosity of samples annealed at 950°C and 1100°C is due to the behavior of the heterovalent sintering aid (ZrO_2) on grain boundaries. Because of this aid, grain boundary diffusion can become prevailing diffusion mechanism of oxygen vacancies at certain temperatures. Some additional research, which would include estimating activation energies for different diffusion mechanisms, is certainly required to answer more specifically.

5. Conclusion

It can be concluded that post-sintering heat treatment substantially affects optical properties of Y_2O_3 ceramics, at least with given sintering additives. Structure of samples, which were fabricated using different heat treatment modes, was investigated. Based on results of this investigation, the annealing mode was adjusted, and samples with good optical characteristics were obtained. While small samples (less than 1 mm thick) show good transmittance (70% at 400nm), manufacturing of thicker samples still presents some difficulties.

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