Conference Paper

Fabrication of YAG:RE (RE = Yb, Nd, Cr) Ceramics Using Divalent Sintering Aids

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Abstract

High-quality YAG:RE (Yb, Nd, Cr) ceramics with CaO and MgO as sintering aids were manufactured by solid state reactive sintering method in vacuum. Influence of annealing temperature on optical properties was studied. This combination of sintering aids requires annealing temperatures at least 1300°C to fully eliminate oxygen vacancies and at least 1400°C to convert Cr^{3+} to Cr^{4+}. It was found that annealing in oxidizing atmosphere creates strong changes in short wavelength transmittance.

Keywords: laser ceramics, Yttrium aluminium garnet, sintering aids

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1. Introduction

Sintering aids play very important role in the process of densification of RE:YAG ceramics [1]. Most commonly used sintering aid is SiO_2 that forms liquid phase by itself or when combined with B_2O_3 [2], but it has an adverse effect of accelerating grain growth and it is not suitable for YAG:Cr^{4+} ceramics because it inhibits Cr^{3+} to Cr^{4+} conversion [3]. In contrast with SiO_2, MgO and CaO additives can inhibit grain growth [4, 5] and assist the conversion of Cr^{3+} to Cr^{4+}[3]. The influence of MgO/CaO ratio on ceramics sintering process for undoped YAG was studied recently [6]. It was found that MgO/CaO ratio of 4/1 is optimal for achieving high optical quality of ceramic. We decided to take this MgO/CaO ratio and apply it to Yb or Nd or Cr-doped YAG because it enables us to make monolithic YAG:Cr/YAG:Nd or YAG:Cr/YAG:Yb composite ceramics without bonding in unified technological process.

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2. Experiment

High purity precipitated yttrium oxide (Lanhit) and commercial alumina (Sumitomo chem.), neodymium oxide (Lanhit), ytterbium oxide (Lanhit), calcium oxide, magnesium oxide and chromium oxide powders were used as starting materials. Stoichiometric amounts of oxide powders were mixed and ball milled for 15 hours with anhydrous alcohol as dispersing medium. After milling and subsequent drying for 48 hours at 50°C, the powders were sieved through 200 mesh sieve, calcined to remove any volatile matter at 1000°C for 5 hours and then compacted. The powders were pressed uniaxially at 200MPa in stainless steel mold (sample groups A–C) or uniaxially at 100MPa in stainless steel mold and then CIPed at 250MPa for 5 minutes (sample group D) to obtain pellets with diameter of 10mm. Green bodies were calcined at 1000°C for 5 hours to remove residual organics and sintered at 1800–1840°C for 5–20 hours in a tungsten mesh heated vacuum furnace under 10^{-6} torr to provide fully dense RE: YAG ceramics. Then, sintered samples were annealed at 1000–1400°C in air to remove oxygen vacancies and/or convert Cr^{3+} to Cr^{4+}. Finally, all RE: YAG ceramics were grinded and mirror polished on both surfaces using diamond slurries, and the thickness of samples after mirror polishing was about 1 mm. In this work, we discuss the influence of divalent sintering aids on sintering and pore formation and elimination processes. To evaluate ceramics quality, transmission spectra and average grain size were measured. Also, the influence of annealing temperature on optical properties was studied.

3. Results

Transmission spectra and general view of samples YAG:0.1% mol Cr ceramic without annealing and annealed in air at different temperatures for 10 hours (sample group A) shown in Figure 1. Samples with 0.1% mol of mixture CaO and MgO with CaO/MgO ratio 1/4 used as sintering aids. Sintering was carried out in vacuum at 1840°C for 5 hours. On this and later figures, only key point lines are shown. It could be found from Figures 1–4 that all samples were fully transparent. As you can see initially, samples are green because Cr ions are in trivalent state and oxygen vacancies generated during vacuum sintering inhibit oxidation of Cr ions from trivalent to tetravalent in Cr:YAG ceramics. These oxygen vacancies would be compensated by oxygen under high temperature and oxygen enriched atmosphere. Accordingly, trivalent Cr ion would be converted into tetravalent to promote charge balance in YAG lattice, when divalent dopants were

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introduced as charge compensators. Average grain size was measured and it is about 8μm. From Figure 1, it can be seen that with increase in the annealing temperatures, the color of the samples changes from green to brown due to conversion of Cr^{3+} to Cr^{4+}. Transmission at 1065nm was measured separately for sample annealed at 1400°C in air for 10 hours and it is 75%. Additional process optimizations are required to enhance Cr^{3+} to Cr^{4+} conversion efficiency.

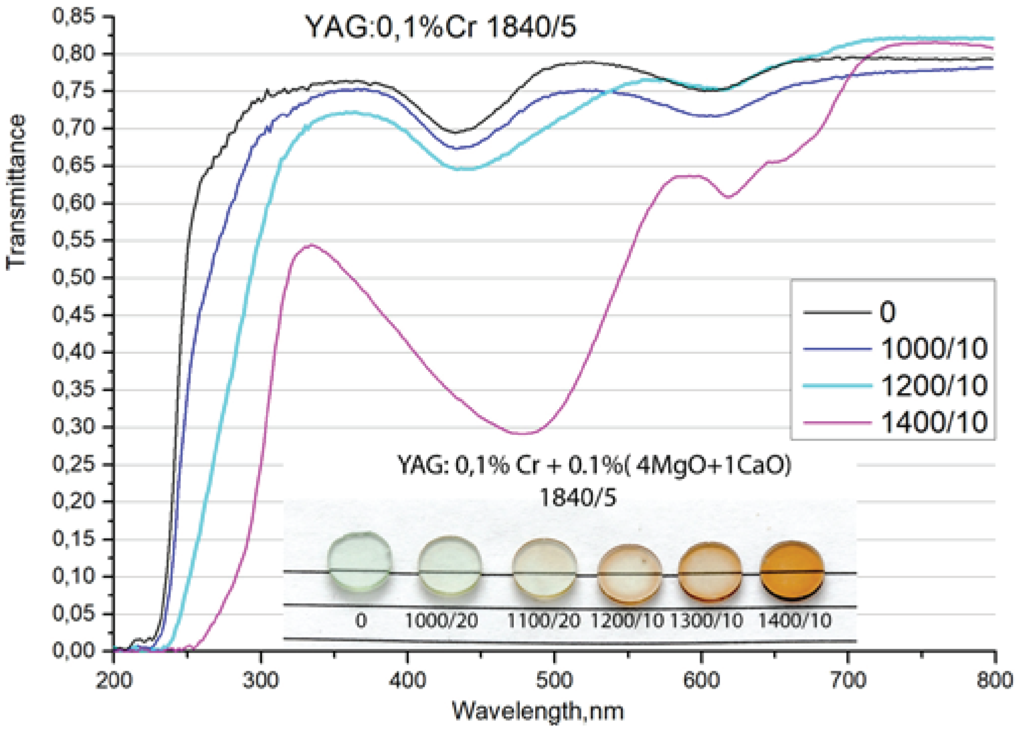

Figure 1: Transmission spectra and general view of samples YAG:0.1% mol Cr ceramic with 0.1% mol of mixture CaO and MgO with CaO/MgO ratio 1/4 as sintering aid sintered in vacuum at 1840°C for 5 hours and annealed at different temperatures for 10 hours. Average grain size about 8μm.

Figure 2 displays transmission spectra and general view of samples YAG:1% mol Nd ceramic with 0.1% mol of mixture CaO and MgO with CaO/MgO ratio 1/4 as sintering aid sintered in vacuum at 1830°C for 8 hours and annealed in air at different temperatures for 10 hours (sample group B). Average grain size was measured and it is about 12μm. From Figure 2, it can be seen that with the increase in the annealing temperatures, color of the samples changes from dark violet to light violet due to the removal of oxygen vacancies. Transmission at 400 nm rises from 70.7% in unannealed sample to 82.6% for sample annealed at 1400°C in air for 10 hours in air which is very close to theoretical limit. It should be noted that transmission in rage of 250 to 350 nm decreases. Possible reasons of this phenomenon may be is formation of color centers [7] or additional nanopores.

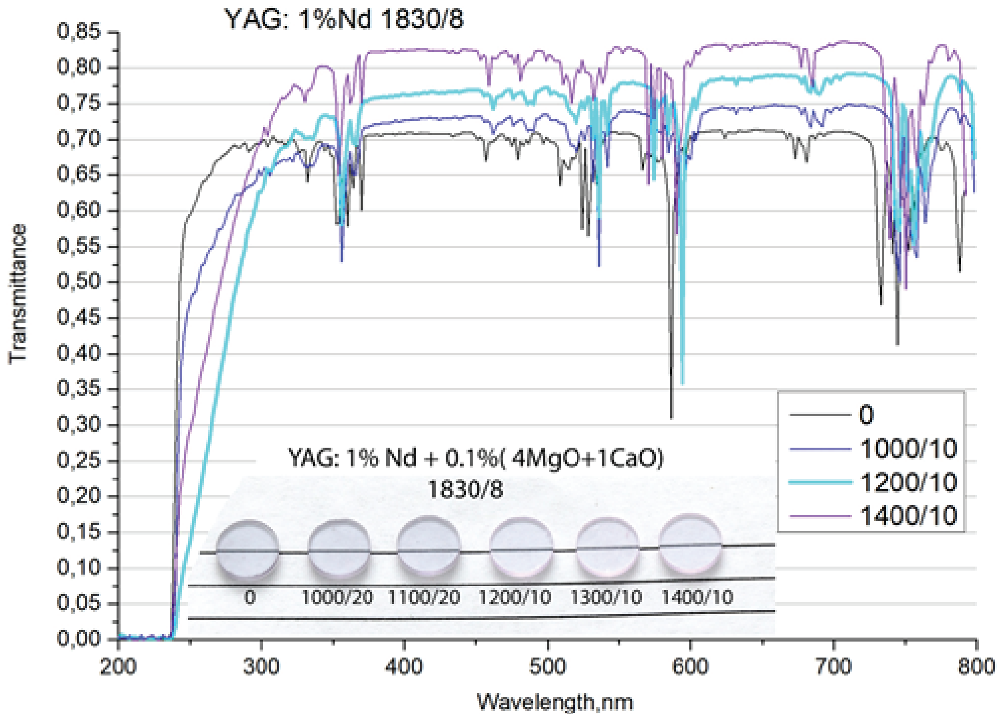

Figure 2: Transmission spectra and general view of samples YAG:1% mol Nd ceramic with 0.1% mol of mixture CaO and MgO with CaO/MgO ratio 1/4 as sintering aid sintered in vacuum at 1830°C for 8 hours and annealed at different temperatures for 10 hours. Average grain size about 12μm.

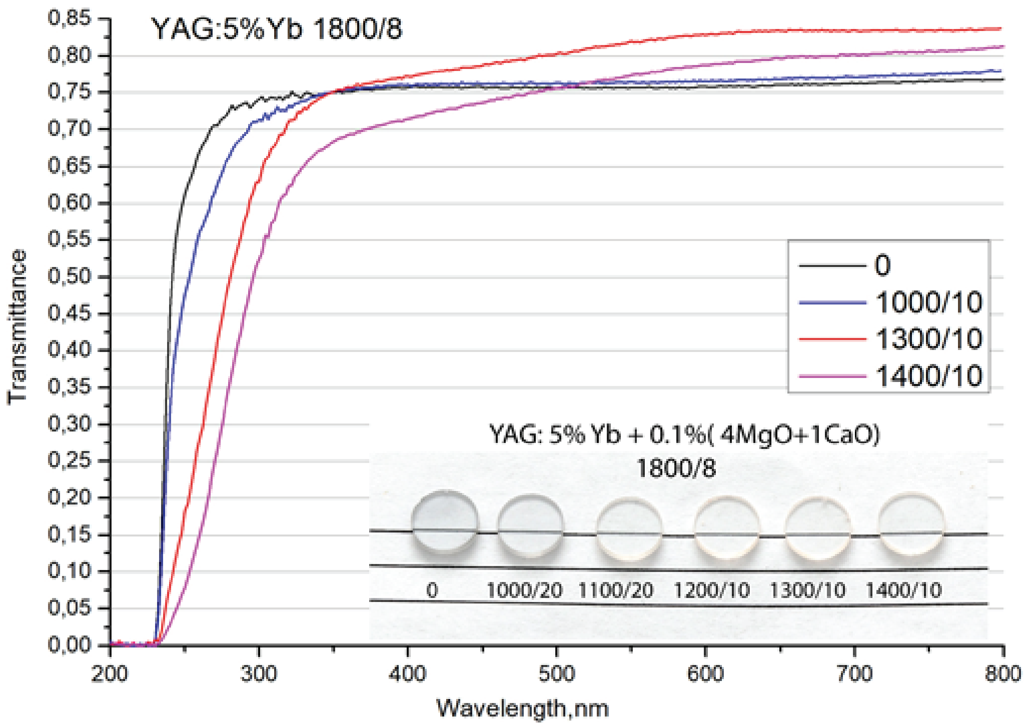

Figure 3: Transmission spectra and general view of samples YAG:5% mol Yb ceramic with 0.1% mol of CaO and MgO mixture with CaO/MgO ratio 1/4 as sintering aid sintered in vacuum at 1800°C for 8 hours and annealed at different temperatures for 10 hours. Average grain size about 8μm.

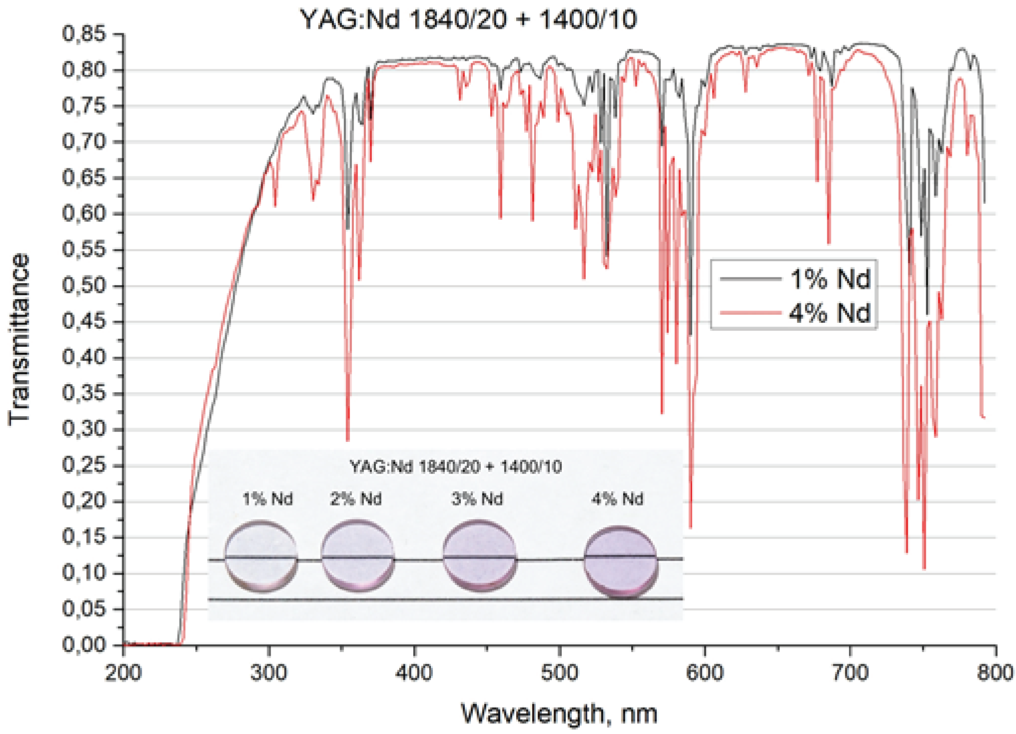

Figure 4: Transmission spectra and general view of samples YAG:Nd ceramic with different concentrations of Nd and 0.1% mol of CaO and MgO mixture with CaO/MgO ratio 1/4 as sintering aid sintered in vacuum at 1840°C for 20 hours and annealed at 1400°C for 10 hours.

Transmission spectra and general view of samples YAG:5% mol Yb ceramic with 0.1% mol of CaO and MgO mixture with CaO/MgO ratio 1/4 as sintering aid sintered in vacuum at 1800°C for 8 hours and annealed at different temperatures for 10 hours (sample group C) presented on Figure 3. Average grain size was measured and it is about 8µm. From Figure 3, it can be seen that the addition of divalent sintering aids inhibits reduction of Yb^{3+} (colorless) to Yb^{2+} (dark green) during vacuum sintering [8]. With increasing annealing temperatures, color of the samples changes from grey to yellowish due to the removal of oxygen vacancies and possible formation of color centers [7]. Transmission at 400 nm rises from 75.7% in unannealed sample to 77.3% for sample annealed at 1300°C in air for 10 hours. However, the transmission at 800 nm for this sample is 83.7%. Theoretical limit is 83.8% at 800 nm and 82.9% at 400 nm. Additional process optimizations are required to improve ceramic quality.

Finally, Figure 4 displays transmission spectra and general view of samples YAG:Nd ceramic with different concentrations of Nd (1–4% mol). For all samples in this group 0.1% mol of CaO and MgO mixture with CaO/MgO ratio 1/4 was used as sintering aid. Samples were sintered in vacuum at 1840°C for 20 hours and annealed at 1400°C in air for 10 hours (sample group D). From Figure 4, it can be seen that the color of the samples becomes more saturated with increasing concentration of Nd^{3+} ions. Transmittance at 400 nm is 81.5% for sample with 1% mol Nd and 80.9% for sample with 4% mol Nd. At 650 nm, transmittance is 83.7 and 83.2% for 1% Nd and 4% Nd samples, respectively. Theoretical limit is 83.7% at 650 nm and 82.9% at 400 nm. Decrease of transmittance in short wavelengths may be attributed to the formation of color centers [7].

4. Conclusion

High-quality YAG:RE (RE = Yb, Nd, Cr) ceramics with CaO and MgO as sintering aids were manufactured by solid state reactive sintering method in vacuum. It is necessary to note that annealing in oxidizing atmosphere creates significant changes in short wavelength transmittance. There are two possible reasons of this phenomenon; first, the formation of color centers [7], and second, the formation of additional nanopores. To make a final decision, it is required to continue the research.

References

[1] Kaminskii, A. A., Balashov, V. V., Cheshev, E. A., et al. (2017). High quality $Y_3Al_5O_{12}$ doped transparent ceramics for laser applications, role of sintering additives. *Optical Materials*, vol. 71, pp. 103–108.

[2] Stevenson, A. J. (2010). The effects of sintering aids on defects, densification, and single crystal conversion of transparent Nd:YAG ceramics. PhD Thesis.

[3] Yagi, H., Takaichi, K., Ueda, K.-I., et al. (2006). *Optical Materials*, vol. 29, pp. 392–396.

[4] Guo, W., Cao, Y., Huang, Q., et al. (2011). Fabrication and laser behaviors of Nd:YAG ceramic microchips. *Journal of the European Ceramic Society*, vol. 31, pp. 2241–2246.

[5] Yang, H., Qin, X., Zhang, J., et al. (2011). Fabrication of Nd:YAG transparent ceramics with both TEOS and MgO additives. *Journal of Alloys and Compounds*, vol. 509, pp. 5274–5279.

[6] Zhou, T., Zhang, L., Li, Z., et al. (2017). Toward vacuum sintering of YAG transparent ceramic using divalent dopant as sintering aids: Investigation of microstructural evolution and optical property. *Ceramics International*, vol. 43, pp. 3140–3146.

[7] Lu, Z., Lu, T., Wei, N., et al. (2015). Effect of air annealing on the color center in Yb:Y3Al5O12 transparent ceramics with MgO as sintering additive. *Optical Materials*, vol. 47, pp. 292–296.

[8] Lu, Z., Lu, T., Wei, N., et al. (2013). Novel phenomenon on valence unvariation of doping ion in Yb:YAG transparent ceramics using MgO additives. *Journal of Wuhan University of Technology - Materials Science Edition*, vol. 28, p. 320.