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Sintering of transparent Nd:YAG ceramics in oxygen atmosphere

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Abstract: Yttrium aluminum garnet (YAG) transparent ceramics were fabricated by sintering at oxygen atmosphere. Tetraethyl orthosilicate (TEOS) was added as the sintering additive to control the grain growth and densification. Pores were eliminated clearly at temperature lower than 1700 ºC, while grain size was around 3 μm. The in-line transmittance was 80% at 1064 nm when samples were sintered at 1710 ºC. The effect of TEOS was studied in oxygen atmosphere sintering for Nd:YAG transparent ceramics. At higher temperature like 1710 ºC, the grain growth mechanism was solute drag, while at 1630 and 1550 ºC the grain growth was controlled by liquid phase sintering mechanism. And 0.5 wt.% TEOS was the best adding content for Nd:YAG sintered in oxygen atmosphere.

Keywords: transparent ceramics; YAG; oxygen atmosphere sintering; rare earths

YAG crystal made by the Czochralski method has been the most widely used solid-state laser host during the last five decades with a wide applications in many fields[1,2]. But its fabrication requires expensive equipment and crucible materials. And it is difficult to fabricate high ion doping concentration or large-diameter crystals[3]. YAG transparent ceramics[1,4,5] have received much attention due to its laser performance, mutil-layer doping designing, low cost, short preparation period, large size and high ion doping concentration. In 1995, Ikesue et al.[6–8] reported highly transparent YAG ceramics by solid state reaction sintering method. Doped with Nd^{3+}, its laser slope efficiency was similar to Czochralski grown single crystals. Several years later, Yagi et al.[9] reported high quality YAG laser materials by the sintering of a kind of high active YAG powder. The powder was fabricated by a chemical co-precipitation processed. While solid state reaction was made by a process in which Al_2O_3 and Y_2O_3 powders were mixed in stoichiometric amounts and phase formation occurred during sintering. Many Scientists[10–12] focused on SSR sintering in the fabrication of YAG transparent ceramics. Messing et al.[13] reported that solid state reactive (SSR) sintering was relatively simple compared with solution synthesis processes and it was useful when there were limited quantities of commercial powders available. Pan et al.[14,15] reported good laser output by the SSR sintering. The powder sizes they used are 0.5 and 2 μm, respectively for Al_2O_3 and Y_2O_3. The reported YAG ceramics were always sintered in vacuum. In recent years, many scientists[16–19] have tried different ways to sinter transparent ceramics, like spark plasma sintering (SPS), hot isostatic pressing (HIP) and two-step sintering. In 2011, Stevenson at al.[20] reported Nd:YAG transparent ceramics fabricated by oxygen atmosphere sintering adding with B_2O_3-SiO_2. They reported that B_2O_3-SiO_2 was a good transient liquid phase sintering aid that reduced the sintering temperature of Nd:YAG to 1600 ºC. In 2010, our group[21] reported the possibility of Y_2O_3 transparent ceramics sintered at oxygen atmosphere. In this paper we focused on the sintering of Nd:YAG transparent ceramic at oxygen atmosphere with TEOS adding.

1 Experimental

High-purity α-Al_2O_3 (D=50–0.38 μm, Shanghai Wusong Chemical Co., Ltd., Shanghai, China), Y_2O_3 (D=50–3.35 μm, Shanghai Yuelong New Materials Co., Ltd., Shanghai, China) were used as starting materials. These powders were weighed according to the stoichiometric ratios of YAG and milled with ZrO_2 balls for 12 h with ethanol and 0.5 wt.% TEOS. After being dried and sieved through 200-mesh screen, the powder mixture was dry-pressed at 5 MPa and then isostatically pressed at 250 MPa. Green body was turned to a pellet with a diameter of 18.7 mm, its density was 56% of theoretical density. Oxygen atmosphere sintering was operated at alumina tube furnace (RHTH 120/300/18German, Na-

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bertherm). In this paper, all samples were sintered at oxygen atmosphere except for samples in Fig. 1.

Mirror-polished samples were thermal etched at a temperature which was 200 ºC lower than sintering temperature for 30 min. EPMA (Model JXA-8100, JEOL, Japan) was used to determine the grain size, at least 300 grains were measured to get the mean size. The grain sizes were measured by the linear-intercept method and calculated from G=1.5 L, where G is the average grain size and L is the average intercept length. Mirror-polished samples on both surfaces were used to measure the optical transmittance (Model U-2800 Spectrophotometer, Hitachi, Japan).

2 Results and discussion

2.1 Microstructure of YAG ceramics

Since the reported YAG transparent ceramics were always sintered in vacuum. In order to compare the effect of atmosphere, samples sintered from vacuum, argon and oxygen are presented in Fig. 1. Fig. 1 shows the microstructures of Nd:YAG samples sintered in different atmospheres, such as vacuum, oxygen and argon for (a), (b) and (c), respectively. 0.5% TEOS was added in all samples. Same green bodies were used, and all samples reached its limited density at certain atmosphere. The grain size was 6.92, 6.99 and 7.47 μm, the relative density was 99.5%, 99.5% and 98.1%, for vacuum, oxygen atmosphere and argon atmosphere samples, respectively. Few pores were detected in vacuum and oxygen atmosphere samples, but both inner pores and inter pores were detected in argon atmosphere samples. This result was similar to that of alumina reported by Coble[22]. The complete elimination of porosity was possible if the ambient atmosphere was oxygen.

Fig. 2 shows microstructures of Nd:YAG samples sintered in oxygen holding at 1550 (a), 1630 (b) and 1710 ºC (c), respectively. The holding time was 3 h. And 0.5% TEOS was added. Its grain sizes were 1.96 (a), 3.02 (b) and 4.95 μm (c), respectively. There were many small pores in Fig. 2(a) at low temperature. With temperature rising, pores grew bigger, but its number decreased (Seen in Fig. 2(b)). At 1710 ºC, few pores were detected (Seen in Fig. 2(c)) when sintering at oxygen atmosphere for 3 h.

Fig. 3 shows the microstructure evolution of fully densified Nd:YAG samples with and without TEOS. Samples without TEOS were sintered at 1630 ºC, samples with 0.2% TEOS were sintered at 1550 ºC. After 8 h holding, both kinds of samples can reach high density. Few pores could be detected in Fig. 3. With 0.2% TEOS adding, sintering temperature lowered to 1550 ºC for fully densification. Grain sizes of samples without TEOS were 1.18, 3.16 and 5.37 μm for 0, 3 and 8 h, respectively. Grain sizes of samples with 0.2% TEOS were 0.88, 1.38 and 2.09 μm for 0, 2 and 8 h, respectively. TEOS adding lowered the sintering temperature and decreased the grain size for fully densified Nd:YAG ceramics.

Fig. 4 shows microstructures of Nd:YAG samples with different TEOS addings, as 0 (a), 0.2% (b), 0.5% (c) and 1.0% (d), respectively. All samples were sintered at 1550 ºC for 8 h. Many pores were detected in sample with 0 TEOS, its grain size was 1.53 μm. In Fig. 4(b), the microstructure was near densified, but there were still some pores. When the TEOS content raised to 0.5% in Fig. 4(c), few pores were detected and the grain size was

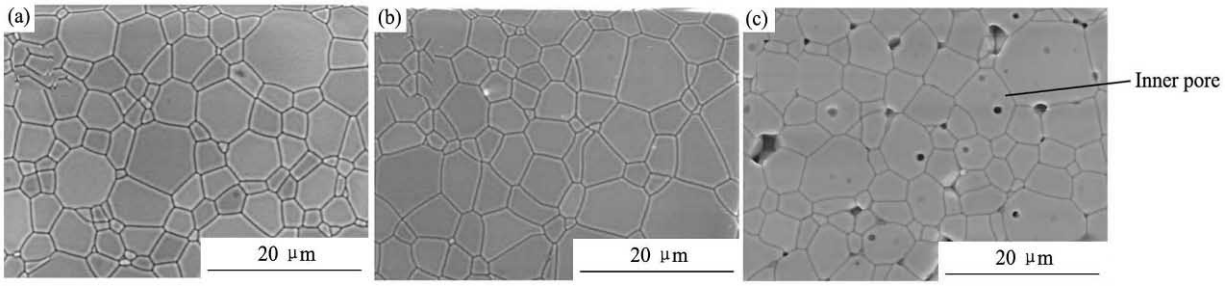

Fig. 1 Microstructures of Nd:YAG samples sintered in vacuum (a), oxygen (b) and Argon (c), respectively (0.5% TEOS was added)

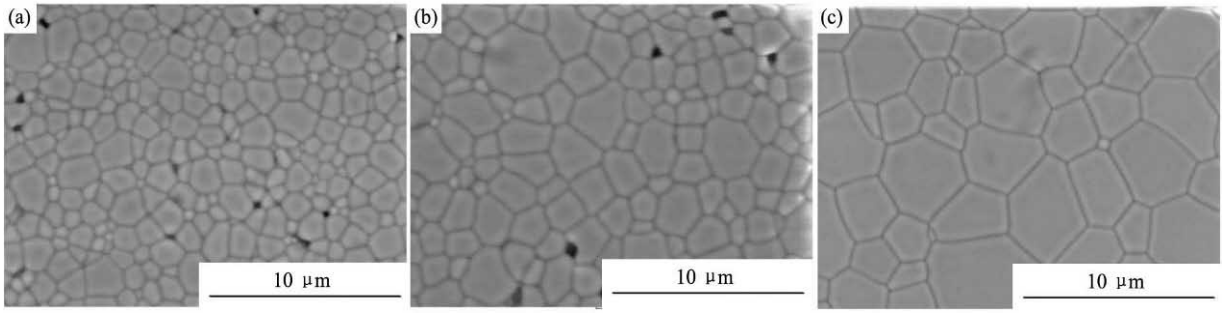

Fig. 2 Microstructures of Nd:YAG samples sintered in oxygen holding for 3 h (0.5% TEOS was added)
(a) 1550 ºC, 1.96 μm; (b) 1630 ºC, 3.02 μm; (c) 1730 ºC, 4.95 μm

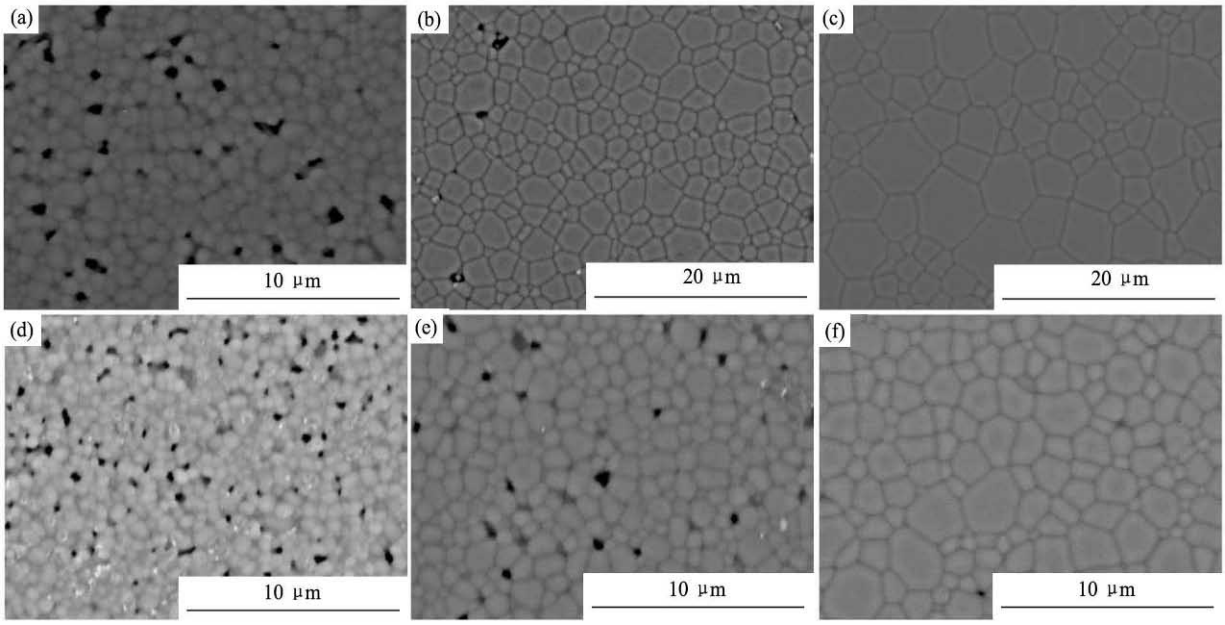

Fig. 3 Microstructure evolution of fully densified Nd:YAG samples with and without TEOS
(a) 0 h–1.18 μm; (b) 3 h–3.16 μm; (c) 8 h–5.37 μm; (d) 0 h–0.88 μm; (e) 2 h–1.38 μm; (f) 8 h–2.09 μm

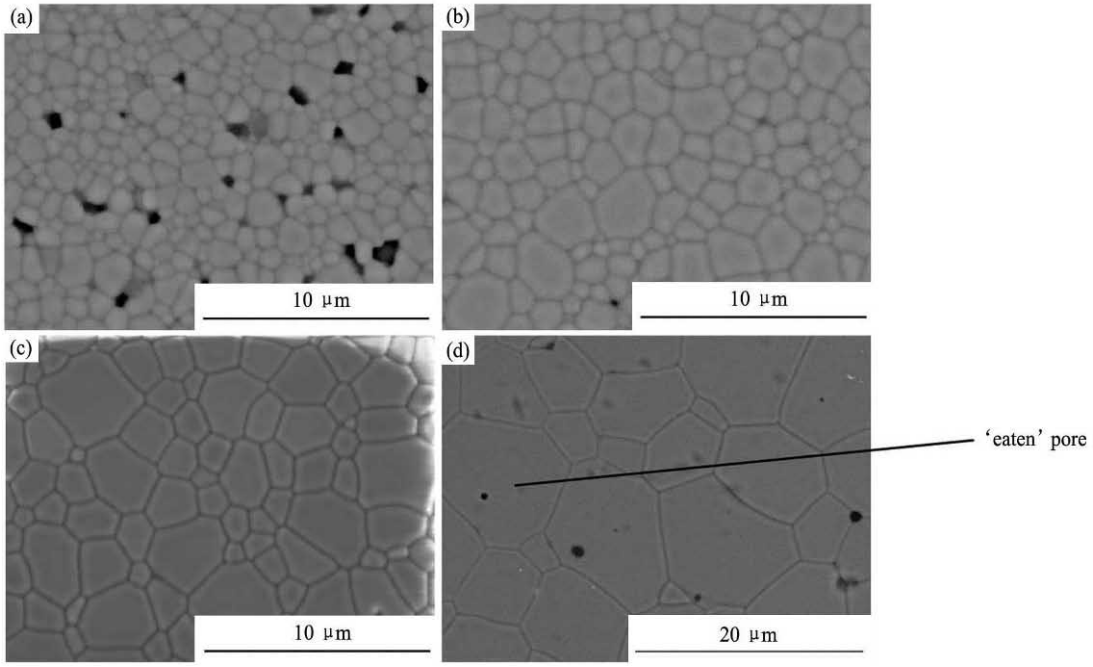

Fig. 4 Microstructures of Nd:YAG samples with different TEOS additions (All the samples were sintered at 1550 ºC for 8 h at oxygen atmosphere)
(a) 0%–1.53 μm; (b) 0.2%–2.09 μm; (c) 0.5%–2.99 μm; (d) 1.0%–9.02 μm

2.99 μm. More TEOS adding like 1.0% in Fig. 4(d) was not good for fully densification. Some inner-grain pores and second phase materials were detected in the micrograph. So 0.5% TEOS adding was optimum for Nd:YAG ceramics sintered at oxygen.

Grain sizes of Nd:YAG at different sintering conditions are shown in Table 1. It was found that there were two mechanisms in the sintering process. At temperature lower than 1630 ºC, with TEOS content increasing, grain sizes increased. And grain sizes also increased with the holding time and sintering temperature. But at high temperature like 1710 ºC, grain sizes have a trend to decrease with more TEOS. And grain sizes still increased with holding time. According to Messing's recent study[23], SiO_2 would form transit liquid phase during sintering at low temperature. But at high temperature, it would enter into the YAG crystal lattice to form solid solution. So the grain size increasing was caused by liquid phase sintering at low temperature like 1550 and 1630 ºC. At high temperature, the liquid phase sintering phenomena was not obvious. Actually, to some extent, grain sizes decreased with TEOS content increasing. This

Table 1 Grain sizes of Nd:YAG at different sintering conditions

TEOS/wt.%	0 μm	0.2 μm	0.5 μm	1.0 μm
1550 ºC–0 h	0.77	0.88	0.95	1.32
1550 ºC–2 h	1.23	1.38	1.65	5.28
1550 ºC–8 h	1.53	2.09	2.99	9.02
1630 ºC–0 h	1.18	1.14	2.39	4.84
1630 ºC–3 h	3.16	5.04	6.35	10.19
1630 ºC–8 h	5.37	7.16	6.29	14.31
1710 ºC–0 h	2.15	4.62	4.90	5.88
1710 ºC–4 h	5.61	6.23	5.45	5.96
1710 ºC–10 h	8.29	7.68	6.33	6.74

was caused by solute drag effect. For Si^{4+} ion would suppress cation diffusion in Nd:YAG sintering.

Fig. 5 shows the growth map of Nd:YAG sintered from oxygen atmosphere with and without TEOS adding. The grain growth kinetics of Nd:YAG with and without TEOS sintered at different temperatures fit the grain growth model:

$$G^n-G^n_0=kt \quad (1)$$

Where G is the average grain size, G_0 the initial grain size, k a rate constant, and t time. Samples without TEOS are fitter to an n=2 dependence and samples with TEOS are fitter to an n=3 dependence. According to Kochawattana's report[13], a grain growth exponent of 2 means that solid state mass transport is the main mechanism for grain growth, while n=3 means that liquid phase mass transport happened in the sample (for the case of boundary controlled migration), which means that the adding of 0.2% TEOS would transfer the main sintering mechanism for grain growth from solid state mass transport to liquid phase mass transport.

2.2 Relative density and optical property of YAG ceramics

Fig. 6 shows the density map of Nd:YAG with different TEOS addings sintered at 1550 ºC. It was found that higher TEOS adding resulted in higher relative density at 1550 ºC when sintering at oxygen atmosphere.

Fig. 7 shows the in-line transmittance and optical quality of Nd:YAG sample. The sample was sintered at 1710 ºC for 4 h at oxygen atmosphere. Its in-line transmittance at 1064 nm was 80%. And the absorb peak shows the typical Nd^{3+} spectrum.

3 Conclusions

Sintering at oxygen atmosphere is a new route for YAG transparent ceramics. The samples was transparent after sintering at 1710 ºC in oxygen, the grain size was 4.95 μm.

TEOS is a good additive for Nd:YAG sintered at oxygen atmosphere. The optimum content was 0.5 wt.%. At higher temperature like 1710 ºC, the grain growth mechanism was solute drag, while at 1630 and 1550 ºC the grain growth was controlled by liquid-phase-sintering mechanism.

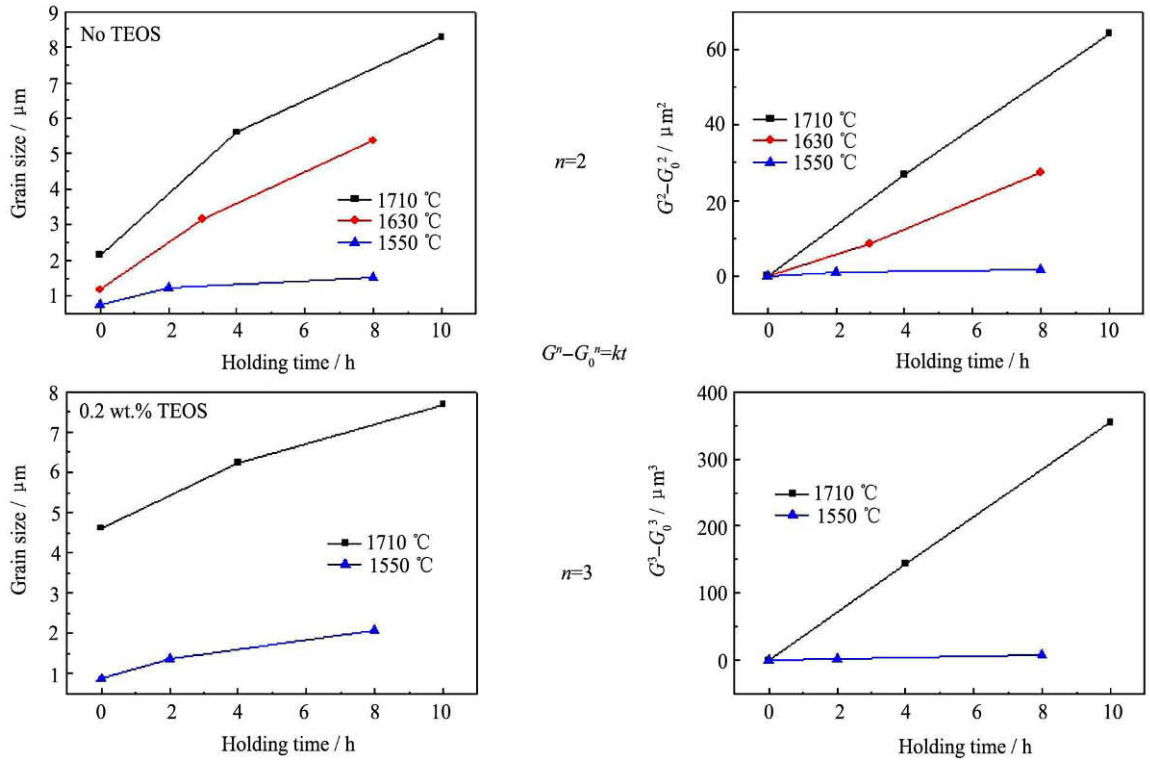

Fig. 5 Grain growth map of YAG with and without TEOS adding sintered in oxygen atmosphere

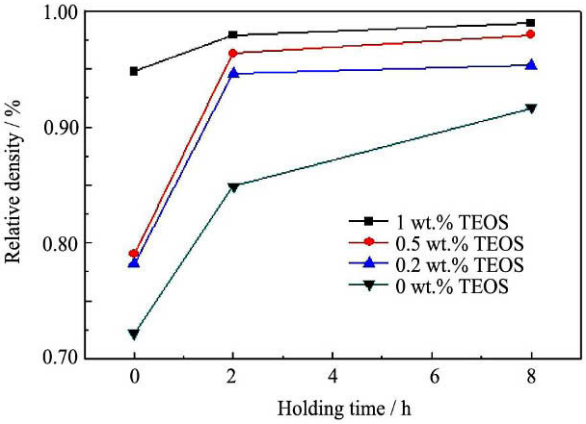

Fig. 6 Density map of Nd:YAG with different TEOS additions sintered at 1550 ℃ in oxygen atmosphere

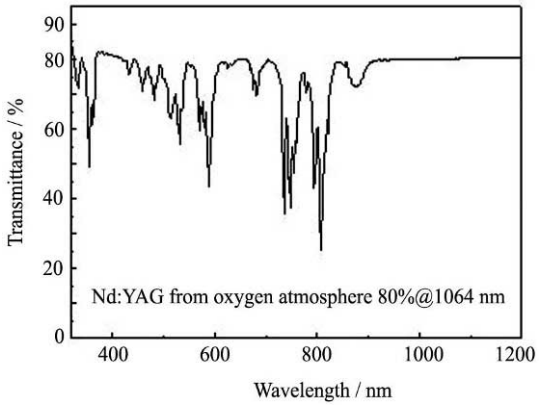

Fig. 7 In-line transmittance of Nd:YAG sample

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