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Densification and microstructure evolution of Cr^{4+},Nd^{3+}: YAG transparent ceramics for self-Q-switched laser

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Abstract

Transparent 0.1 at.% Cr, 1.0 at.% Nd:YAG ceramics were fabricated by solid-state reaction and vacuum sintering using commercial Y_2O_3, α-Al_2O_3, Cr_2O_3 and Nd_2O_3 as raw materials. CaO and tetraethoxysilane (TEOS) were used as charge compensator and sintering aid, respectively. The powders were mixed in ethanol and doped with TEOS, dried and pressed. Pressed samples were sintered from 1450 to 1800 °C for 10 h. The relative density increased from 68.8% to 99.4% at the sintering temperature from 1450 to 1700 °C. Grain size increased with increase of sintering temperature and obvious grain growth occurred between 1650 and1700 °C. For the Cr,Nd:YAG ceramics sintered at 1750 and 1800 °C for 10 h, nearly pore-free microstructures with average particle size of ~10 μm were obtained. The optical transmittance of the 1800 °C sintered sample was ~70% in the infrared wavelength.

Keywords: Cr,Nd:YAG ceramic; Solid-state reaction; Densification; Microstructure

1. Introduction

Laser diode (LD) pumped passively Q-switched lasers have the advantages of simplicity, compactness, low cost, and high efficiency. Therefore LD pumped passively Q-switched lasers have attracted a great deal of attention in recent years. Cr^{4+}:YAG single crystal is one of the developed absorbers, which has specific advantages such as photochemical and thermal stability, high damage threshold, large absorption cross-section, and low saturation intensity at the lasing wavelength. In addition, Cr^{4+} can be doped into a gain medium such as Nd:YAG crystal to form self-Q-switched lasers [1–10]. However, single crystal growth suffers from the disadvantages such as time consuming, high cost, doping concentration and size limitation. For example, the doping concentration in the grown crystal varies in the axial direction, which results in a highly strain core region and other symmetrical inhomogeneities. These defects result in optical birefringence and wave front distortion [11].

Since 1995, polycrystalline YAG ceramic laser materials have received much attention because the optical quality has been improved greatly and highly efficient laser oscillations could be obtained that comparable in efficiency with YAG single crystals [12–19]. Compared with YAG single crystal laser materials, polycrystalline YAG ceramics have several prominent advantages: (1) easy fabrication; (2) scalability in size; (3) high doping concentration; (4) better homogeneity of the doping ions; (5) ease of achieving composite structure and so on. Ceramic technology also makes it easier to incorporate several dopant ions into the YAG material compared with singles grown from a melt and the defects leading to optical birefringence and wave front distortion can be circumvented. A Cr^{3+},Nd^{3+}:YAG transparent ceramic was fabricated by a solid-state reaction method [20], and the optical properties of this ceramic were investigated by Ikesue et al. Most recently, Yagi et al. [21] fabricated a 0.1 at.% Cr^{3+}, 1.0 at.% Nd^{3+}:YAG transparent ceramic by the vacuum sintering and nanocrystalline technology, and the laser performance of the ceramic was reported. Considering Cr^{4+},Nd^{3+}:YAG transparent ceramic, which combines the gain media and the saturable absorber as one, may be a more potential self-Q-switched laser material used for generating sub-nanosecond laser pulses relative to

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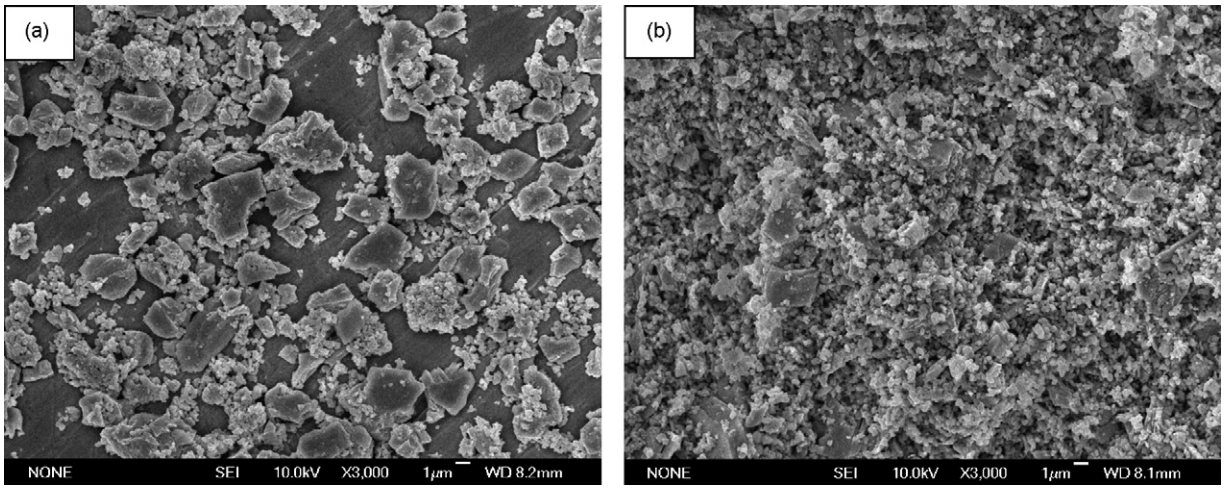

Fig. 1. FESEM micrographs of (a) the α-Al_2O_3, Y_2O_3, Nd_2O_3 and Cr_2O_3 powder mixture after ball milling; (b) the fracture surface of the green from the powder mixture.

Cr^{4+},Nd^{3+}:YAG crystal. Transparent Cr^{4+},Nd^{3+}:YAG ceramics [22] were successfully fabricated by solid-state reaction and vacuum sintering in our previous work. However, the densification and microstructure evolution of the Cr^{4+},Nd^{3+}:YAG ceramics with sintering temperature were seldom discussed. The purpose of this paper is to report how the microstructure changes with densification during sintering.

2. Experimental

High-purity powders of α-Al_2O_3 (Shanghai Wusong Chemical Co. Ltd., 99.99%), Y_2O_3 (Shanghai Yulong New Materials Co. Ltd., 99.99%), Nd_2O_3 (Shanghai Yuelong New Materials Co. Ltd., 99.99%) and Cr_2O_3 (Sinopharm Chemical Reagent Co. Ltd., spectral purity) were used as starting materials. The starting powders were weighed to result in a chemical composition of 0.1 at.% Cr, 1.0 at.% Nd:YAG with CaO (Sinopharm Chemical Reagent Co. Ltd., spectral purity) as a charge compensator and tetraethyl orthosilicate (TEOS, Shanghai Lingfeng Chemical Reagent Co. Ltd., spectral purity) as a sintering aid. All the components were mixed by ball milling with high-purity (99.7%) alumina balls in anhydrous alcohol for 10 h. The slurry was dried at 90 °C for 24 h, sieved through 200-mesh screen, dry-pressed under 100 MPa into Ø20 mm disks and finally cold-isostatically pressed under 250 MPa. The compacted disks were sintered at the temperature from 1450 to 1800 °C in a tungsten mesh-heated vacuum furnace (KZG-110F, Shanghai Chenrong Electrical Furnace Co. Ltd., Shanghai, China) under 3×10^{-3} Pa during holding. The sintered specimens were annealed at 1450 °C for 20 h in air.

Microstructures of the powder mixture and the green body were observed by FESEM (Model JSM-6700, JEOL, Japan). Densities of the sintered specimens were measured by the Archimedes method, using deionized water as the immersion medium. Microstructures of the fractured surfaces were observed by EPMA (Model JXA-8100, JEOL, Japan).

3. Results and discussion

Fig. 1(a) shows FESEM micrograph of the α-Al_2O_3, Y_2O_3, Nd_2O_3 and Cr_2O_3 powder mixture after ball milling. The larger

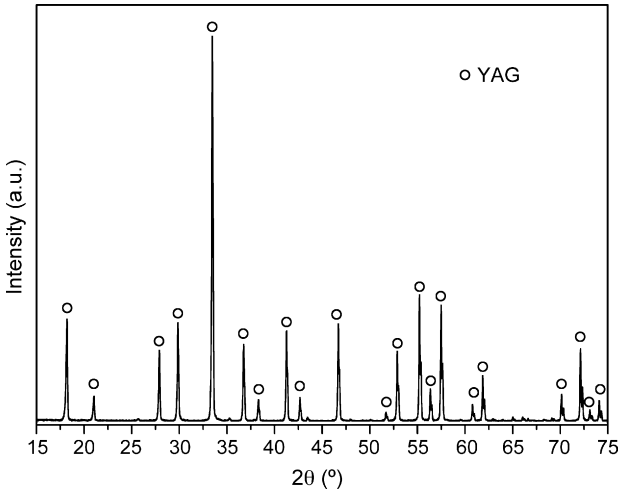

Fig. 2. XRD pattern of 0.1 at.% Cr, 1.0 at.% Nd:YAG after calcination at 1500 °C for 10 h.

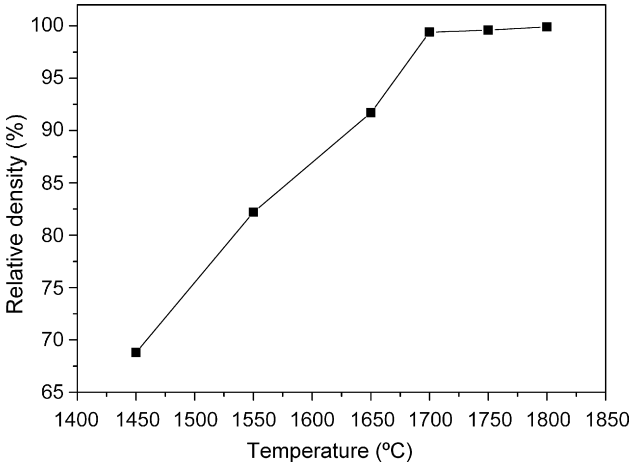

Fig. 3. Relative density of Cr,Nd:YAG ceramics sintered at 1450–1800 °C for 10 h in vacuum.

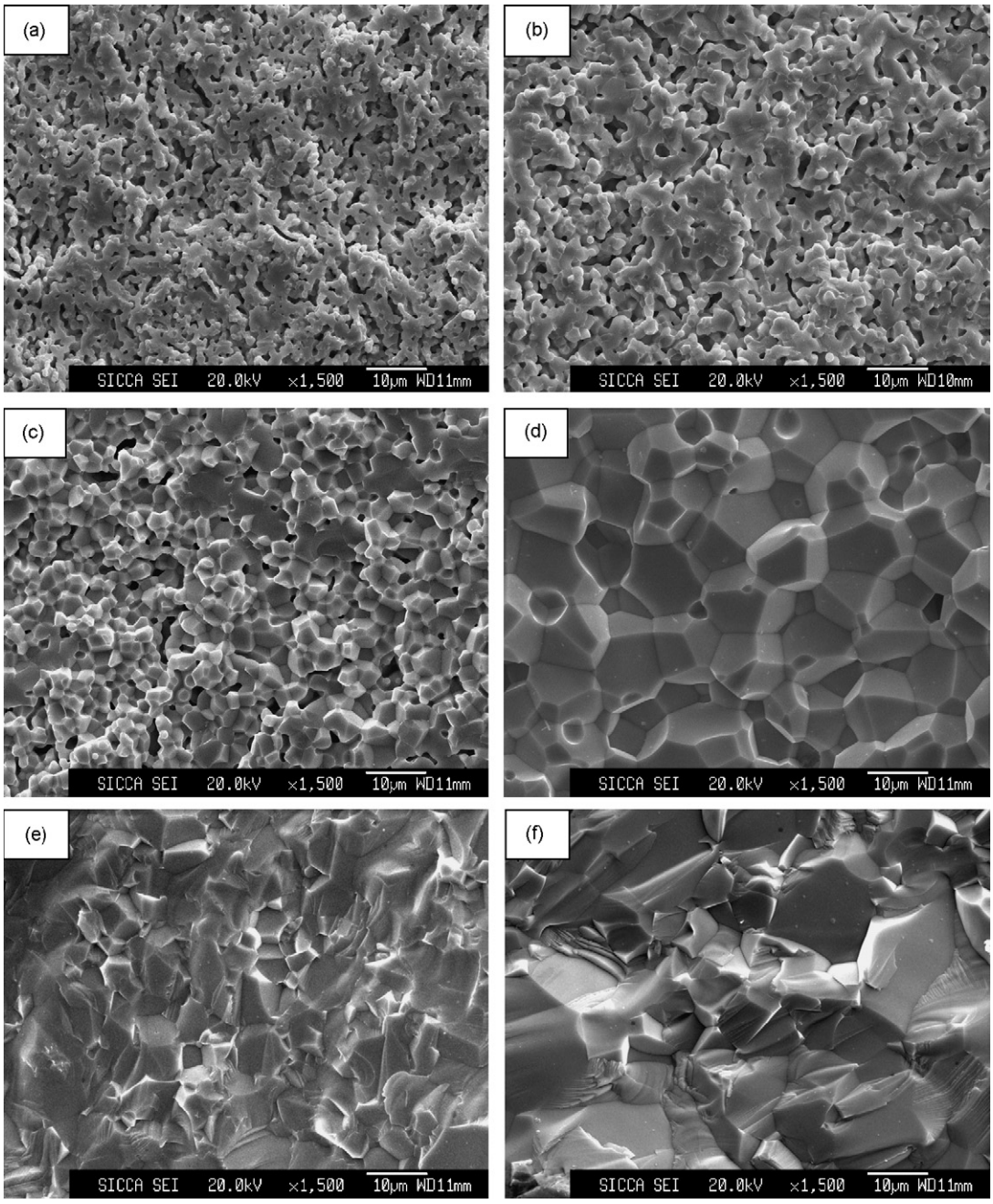

Fig. 4. EPMA micrographs of the fractured surfaces of 0.1 at.% Cr, 1.0 at.% Nd:YAG transparent ceramics sintered at (a) 1450 °C; (b) 1550 °C; (c) 1650 °C; (d) 1700 °C; (e) 1750 °C; and (f) 1800 °C for 10 h.

particles of about 4 μm in diameter are Y_2O_3 and the relatively fine particles of 0.3 μm in diameter are α-Al_2O_3. Fig. 1(b) shows FESEM micrograph of the fracture surface of the green body from the ball-milled powder mixture after dry-pressed. It can be seen that the large particles of Y_2O_3 and the fine particles of α-Al_2O_3 are homogeneously mixed.

Fig. 2 shows the XRD pattern of the ball-milled powder (0.1 at.% Cr, 1.0 at.% Nd:YAG composition) after heating at 1500 °C for 10 h. In the Al_2O_3–Y_2O_3 system, three phases are known, monoclinic phase (YAM, $Y_4Al_2O_9$), perovskite phase (YAP, $YAlO_3$), and cubic phase (YAG, $Y_3Al_5O_{12}$) and the reaction temperature of each phase was reported by Kinsman et al. [23]:

$$2Y_2O_3 + Al_2O_3 \rightarrow Y_4Al_2O_9\,(\mathrm{YAM}) \qquad 900-1100\,^{\circ}\mathrm{C} \quad (1)$$

$$Y_4Al_2O_9 + Al_2O_3 \rightarrow 4YAlO_3\,(\mathrm{YAP}) \qquad 1100-1250\,^{\circ}\mathrm{C} \quad (2)$$

$$YAlO_3 + Al_2O_3 \rightarrow 4Y_3Al_5O_{12}\,(\mathrm{YAG}) \qquad 1400-1600\,^{\circ}\mathrm{C} \quad (3)$$

It can be seen from Fig. 2 that YAM and YAP are not detected at 1500 °C and only YAG is observed. It is important to point out that full transformation to YAG occurs despite the

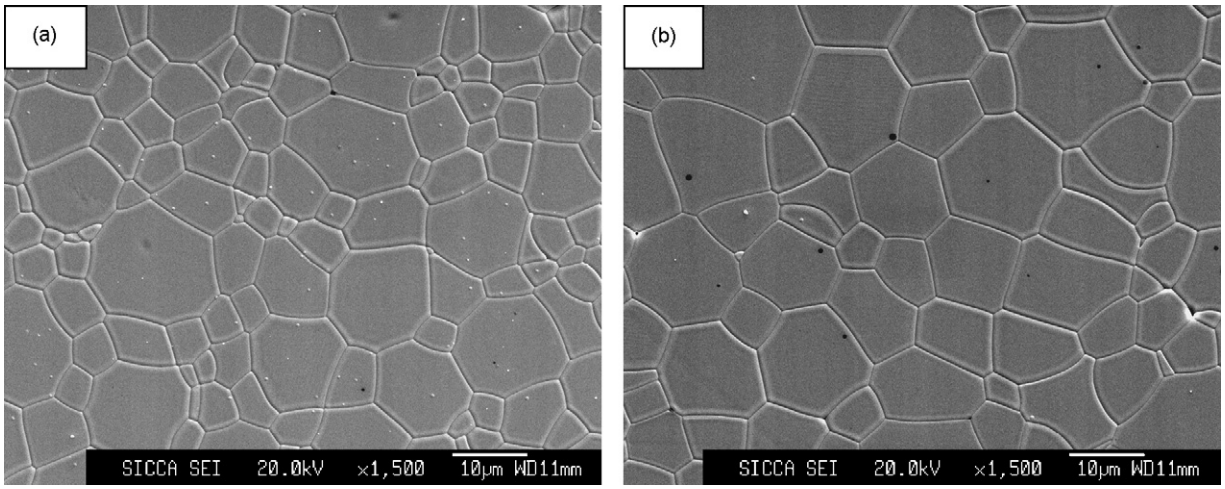

Fig. 5. EPMA micrographs of the mirror-polished surfaces of 0.1 at.% Cr, 1.0 at.% Nd:YAG transparent ceramics sintered at (a) 1750 °C and (b) 1800 °C for 10 h.

significant large size of the Y_2O_3 particles, because the raw materials are well mixed, as shown in Fig. 1.

Fig. 3 shows the relative density of the vacuum sintered Cr,Nd:YAG specimens as a function of sintering temperature. The relative density of the Cr,Nd:YAG ceramic sintered at 1700 °C is 99.4%. As the temperature increased to 1800 °C, the density increased to 99.9% of the theoretical value (4.55 g/cm^3). The density of the specimen sintered at 1450 °C for 10 h is only 68.8%, which indicates that the sample is only in the initial densification stage. At the sintering temperature between 1450 and 1700 °C, the increase of temperature distinctly enhanced densification and the higher sintering temperature only slightly enhanced densification.

Fig. 4 shows the EPMA micrographs of the fractured surfaces of 0.1 at.% Cr, 1.0 at.% Nd:YAG transparent ceramics sintered from 1450 to 1800 °C for 10 h. It can be seen that grain size increases with increase of sintering temperature. Obvious grain growth occurs between 1650 and1700 °C. A dense and nearly pore-free microstructure was observed at or above 1700 °C and there was no obvious grain size increase between 1700 and 1800 °C. The fracture mode of the 1700 °C sintered Cr,Nd:YAG ceramic is mainly intergranular. However, the fracture mode of the 1750 and 1800 °C sintered Cr,Nd:YAG ceramics are mainly transgranular. In our study, it appears that grain growth is an important factor to remove the final pores and to achieve transparent Cr,Nd:YAG ceramic.

Fig. 6. Appearance of mirror-polished 0.1 at.% Cr, 1.0 at.% Nd:YAG transparent ceramics sintered at 1800 °C for 10 h.

Fig. 5 shows the EPMA micrographs of the mirror-polished surfaces of 0.1 at.% Cr, 1.0 at.% Nd:YAG transparent ceramics sintered at 1750 and 1800 °C for 10 h, respectively. Both samples are nearly pore free and there is no evidence of abnormal grain growth. It can be seen that the Cr,Nd:YAG ceramic sintered at 1750 °C displays average grain size of about 10 μm. With increasing of sintering temperature up to 1800 °C, there was comparatively small increase in grain size.

The specimens sintered below 1700 °C were all opaque. At 1750 °C, specimens became translucent. The specimens sintered at 1800 °C for 10 h were all transparent, as shown in Fig. 6. The optical transmittance of 0.1 at.% Cr, 1.0 at.% Nd:YAG sample sintered at 1800 °C for 10 h is shown in Fig. 7(a). The in-line transmittance increases with increasing wavelength till 900 nm, which can be attributed to the existence of scattering centers (mainly pores) in the ceramics. According to the Rayleigh's equation, the scattering intensity increases proportionally with λ^{-4}, where λ is the wavelength. So the scattering intensity increases with the decrease of wavelength [24]. The decrease of optical transmittance from the wavelength

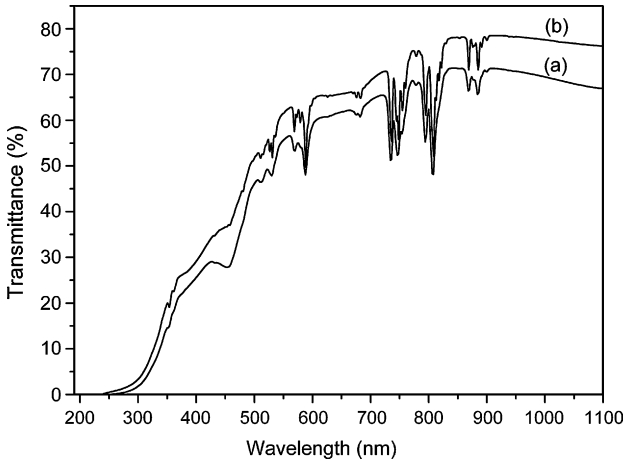

Fig. 7. Optical transmittance of 0.1 at.% Cr, 1.0 at.% Nd:YAG transparent ceramics (specimens thickness 1.0 mm) sintered at 1800 °C for (a) 10 h and (b) 30 h [20].

900–1100 nm is believed to be caused by the absorption of Cr^{4+} ions. The optical transmittance of the 0.1 at.% Cr, 1.0 at.% Nd:YAG ceramic was ~70% in the infrared wavelength. With the holding time increasing up to 30 h, the transmittance increased up to ~78% [20] because of grain growth and further elimination of pores, as shown in Fig. 7(b).

4. Conclusions

Transparent ceramics of 0.1 at.% Cr, 1.0 at.% Nd:YAG were successfully fabricated from commercially available powders by the solid-state reaction and vacuum sintering using high-purity Y_2O_3, α-Al_2O_3, Cr_2O_3 and Nd_2O_3 as raw materials with CaO as a charge compensator and TEOS as a sintering aid. It is interesting to point out that full transformation to YAG occurs at 1500 °C despite the significant large size of the initial Y_2O_3 particles. At the sintering temperature between 1450 and 1700 °C, the increase of temperature distinctly enhanced densification and the relative density increased from 68.8% to 99.4%. Grain size increased with increase of sintering temperature and obvious grain growth occurred between 1650 and 1700 °C. For the Cr,Nd:YAG ceramics sintered at 1750 and 1800 °C for 10 h, both samples were of nearly pore-free microstructures with average particle size of ~10 μm. The optical transmittance of the 1800 °C sintered sample was ~70% in the infrared wavelength, which could be improved by increasing the holding time.

Acknowledgements

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