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Upconversion luminescence of high content Er-doped YAG transparent ceramics

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Abstract

The various high content Er-doped YAG transparent ceramics with excellent transparency up to nearly 84% at the visible band and the near-infrared band were prepared by the solid-state reaction and the vacuum sintering technique. It is found that the samples exhibit pore-free structures and there are no secondary phases both at the grain boundaries and the inner grains. The average grain size of the Er:YAG ceramics is about 30 μm. The green and red upconversion luminescences in the Er:YAG ceramics pumped by a 980 nm LD were observed. The different upconversion mechanisms depending on Er content in the Er:YAG ceramics and the LD power were also discussed.

Keywords: B. Grain size; C. Optical properties; Er:YAG; Transparent ceramics

1. Introduction

Since the first polycrystalline Nd:YAG ceramic laser pumped by the diode laser excitation system was reported in 1995 [1], highly transparent ceramics research has been speeding up due to its various potential applications in many industrial fields. Many recent studies on the diode-pumped solid-state lasers have focused on polycrystalline ceramic lasers [2–4], and diode-pumped Nd:YAG, Yb:YAG, composite YAG/Nd:YAG/YAG ceramics laser experiments have also been successfully performed [5–8] and other garnet structure ceramics (i.e. TmAG [9]) have been fabricated in our group. Among the rare earth doped YAG materials, high content Er-doped YAG crystal is an important laser material to obtain near 2.94 μm lasers, which is widely utilized by the medical community because of the strong absorption by water in this wavelength range, and 960 nm diode-pumped 1-W continuous-wave 50 at.% Er:YAG crystal 3 μm laser has been performed by Chen et al. [10].

In upconversion schemes, population in an excited state with an energy exceeding the energy of the pump photon may be achieved either by excited state absorption (ESA), or by energy transfer upconversion (ETU), or by photon avalanche (PA), according to the excitation conditions and the specific pump wavelengths used [11], and the drift of upconversion luminescence intensity could reflect the main excitation mode. Therefore, the research on upconversion luminescence and processes in Er-doped YAG ceramics is very significant for the 3 μm high content Er:YAG laser experiment.

2. Experimental procedure

High-purity α-Al_2O_3 ($D_{50} \approx 0.38$ μm, Shanghai Wusong Chemical Co., Ltd., Shanghai, China), Y_2O_3 ($D_{50} \approx 3.35$ μm, Shanghai Yuelong New Materials Co., Ltd., Shanghai, China), and Er_2O_3 ($D_{50} \approx 7.2$ μm, Conghua Jianfeng Rare-Earth Co., Ltd., Guangzhou, China) were used as starting materials. These powders were weighed according to the different stoichiometric ratios of the Er:YAG and milled with Al_2O_3 balls for 12 h with ethanol and tetraethyl orthosilicate. After dried and sieved through 200-mesh screen, the powder mixture was dry-pressed at 5 MPa and then isostatically pressed at

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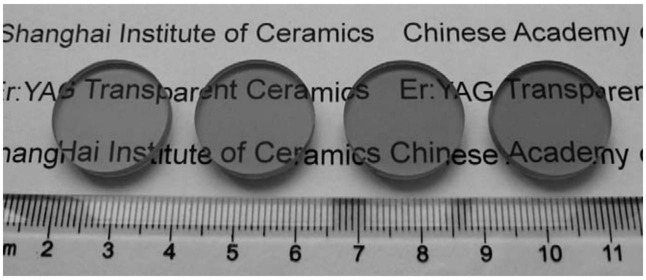

Fig. 1. The mirror-polished Er:YAG ceramics (Er content from the left to the right: 30 at.%, 50 at.%, 70 at.%, and 90 at.%).

250 MPa. The powder compacts were vacuum-sintered at 1780 °C for 20 h under 10^{-3} Pa, then annealed at 1450 °C for 10 h under atmosphere. Before microstructure observation the samples were mirror-polished on both surfaces and thermal-etched at 1500 °C for 2 h.

The microstructures of the samples were observed by the electron probe micro-analyzer (EPMA) (Model JSM-6700, JEOL, Tokyo, Japan). Disk specimens machined to disks (Ø20 mm × 2 mm) and mirror-polished on both surfaces were used to measure optical transmittance (Model U-2800 Spectrophotometer, Hitachi, Tokyo, Japan). For measuring the upconversion fluorescence spectra (Fluorolog-3, Jobin Yvon, Paris, France), the specimens were excited with a 980 nm laser diode (LD).

3. Results and discussion

Fig. 1 shows the photographs of the mirror-polished Er:YAG ceramics with the thickness of 3 mm. All the specimens are deep pink due to the light absorption of Er^{3+} at the visible band (shown in Fig. 3). According to the EPMA photographs shown in Fig. 2, it is found that the specimens are very compact and almost without pores. There are no secondary phases observed both at the grain boundaries and the inner grains. The average grain size of the Er:YAG ceramics is about 30 μm. Depending on the poreless microstructure, the highly Er-doped YAG ceramics possess excellent transparency up to nearly 84% at the visible band and the near-infrared band, as shown in Fig. 3. With the increase of the Er^{3+} content, the absorption peaks are enlarged and amplified comparatively. In this case the absorption saturation will be achieved easier.

The upconversion process mechanism (shown in Fig. 4) of the Er-doped materials has been studied [12]. The atoms at the ground state $^4I_{15/2}$ can be excited to $^4I_{11/2}$ pumped by the LD through the ground state absorption (GSA), then through ESA: $^4I_{11/2} \rightarrow {}^4F_{7/2}$ and ET: $^4I_{11/2} \rightarrow {}^4I_{15/2}$, $^4I_{11/2} \rightarrow {}^4F_{7/2}$, followed by fast cascading relaxation from $^4F_{7/2}$ to the $^2H_{11/2}/^4S_{3/2}$ states, and the green light appears through $^2H_{11/2}/^4S_{3/2} \rightarrow {}^4I_{15/2}$. The red light emission process is firstly GSA: $^4I_{15/2} \rightarrow {}^4I_{11/2}$, followed by the fast cascading relaxation to $^4I_{13/2}$, and then ET: $^4I_{11/2} \rightarrow {}^4I_{15/2}$, $^4I_{13/2} \rightarrow {}^4F_{9/2}$, and finally $^4F_{9/2} \rightarrow {}^4I_{15/2}$.

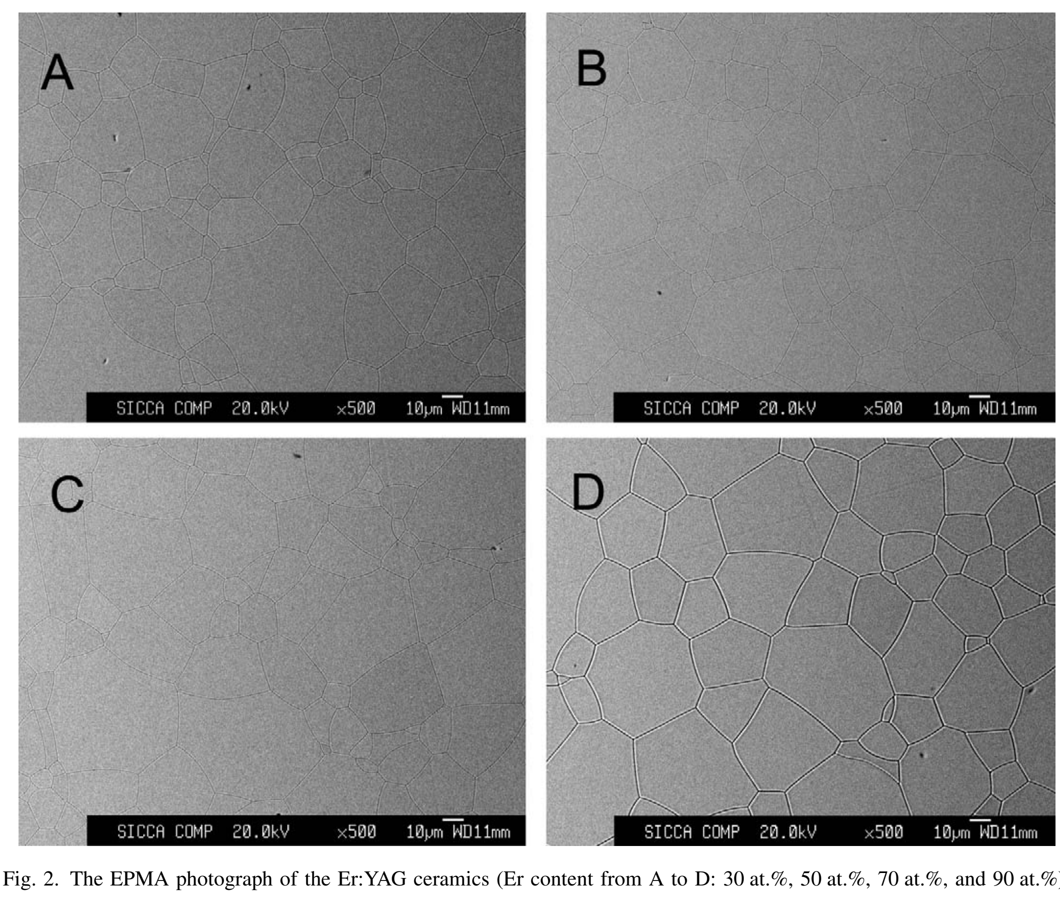

Fig. 2. The EPMA photograph of the Er:YAG ceramics (Er content from A to D: 30 at.%, 50 at.%, 70 at.%, and 90 at.%).