

Upconversion luminescence of Er^{3+} in highly transparent YAG ceramics

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Abstract

Transparent Er^{3+} doped YAG ceramic was prepared by the vacuum sintering technique. Scanning electron microscope and transmission electron microscope measurements reveal that the pore volume in our sample is approximately 1 ppm, the average grain size is about 10 μm and the grain boundary width is about 1 nm. With the excitation of a 960 nm laser diode, intense green and red upconversion emissions were observed in our sample. Based on the intensity dependence of the upconversion emissions on the pump power, the upconversion mechanisms were discussed.

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Transparent ceramic laser materials is an aggregate of crystalline grains, each randomly oriented with respect to neighboring grains. The first transparent ceramic laser materials (CaF_2 : Dy^{2+}) was reported in the middle of 1960 s [1]. The second ceramic laser was demonstrated using Nd^{3+} doped Y_2O_3 : ThO_2 [2]. But only in recent years, ceramic laser materials have received much attention due to the developing of highly transparent $\text{Y}_3\text{Al}_5\text{O}_{12}$ (YAG) doped with Ln^{3+} activators [3,4]. The first Nd:YAG ceramic laser was reported in 1995 [5] It is very recently that high power and efficiency Nd:YAG ceramic lasers were performed by our group [6–10], which confirmed that ceramic YAG laser materials have become an attractive alternative to single crystal due to their ease of manufacture, low cost, high doping and scalability.

On the other hand, recent interests in the development of Er-doped solid-state lasers for the high-density 3 μm sources has been fueled predominantly by the medical community because of the strong absorption by water in this wavelength range. Er:YAG, however, has a transition at 2.94 μm fortuitously overlaps one of the few transition bands in the water-vapor spectrum and is therefore useful for meteorological special metrology applications. 960 nm diode-pumped 1-W continuous-wave YAG: 50% Er^{3+} 3 μm laser was reported by Chen et al. [11]. Stoneman et al. [12] obtained a 36% slop efficiency for direct upper-state pumping in Er^{3+} doped gadolinium scandium gallium garnet (GSGG: 30% Er^{3+}). The rather high η for Er^{3+} doped GSGG corresponded to greater-than-unity quantum efficiency, which was attributed to the recycling of population through upconversion out of the lower state. Therefore study on upconversion processes [13,14] in Er^{3+} doped YAG excited at 960 nm is very necessary and valuable for the optimization of 3 μm laser.

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In order to obtain 3 μm YAG ceramic laser, highly transparent YAG:50%Er³⁺ (mol%) ceramic was prepared. 3 μm YAG:50%Er³⁺ ceramic laser experiments are being performed, which will be reported in the future. Until now, upconversion processes in high concentration Er³⁺ (~50%) doped YAG ceramic have not been studied. In this paper, frequency upconversion processes in transparent YAG:50%Er³⁺ (mol%) ceramic were investigated. With the excitation of a 960 nm laser diode, (LD) intense green and red upconversion emissions were observed in our sample. Based on the intensity dependence of the upconversion emissions on the pump power, the upconversion mechanisms were discussed.

Highly transparent YAG:50%Er³⁺ (mol%) ceramic was prepared by the vacuum sintering technique [10], and then sliced and polished to dimensions $\Phi 20 \times 2$ mm for laser experiments. The microstructure after sintering was characterized through a scanned electron microscope (SEM) and transmission electron microscope (TEM), as shown in Fig. 1(A) and (B), respectively. SEM and TEM measurements reveal that the pore volume in our sample is approximately 1 ppm, the average grain size is about 10 μm and the grain boundary width is about 1 nm. Such narrow grain boundary and very low pore volume ensure low scattering in the ceramic materials, which make high power and efficiency

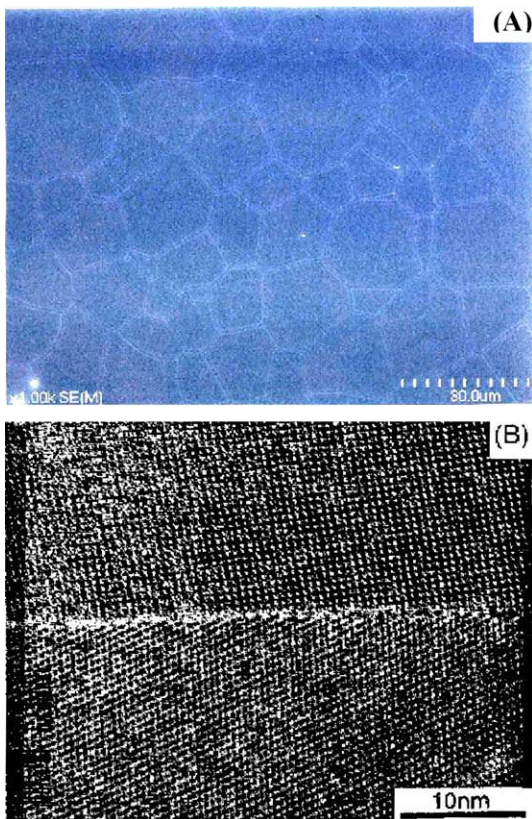


Fig. 1. (A) SEM and (B) TEM image of the YAG ceramic.

laser easily obtained. Optical absorption was carried out using an ANDO AQ-6315A optical spectrum analyzer with an ANDO AQ-4308B white light source as the excitation source. A 960 nm LD was focused on the sample by a object lens ($\times 20$), the upconversion emission spectra were measured with the ANDO AQ-6315A optical spectrum analyzer with the spectral resolution of 1 nm. The electric current of the 978 nm LD was numerate on the controller, which was used to modulate the pump power of the LD.

Fig. 2 shows the absorption spectrum of transparent YAG:50%Er³⁺ (mol%) ceramic. The band assignments are also indicated in the figure. The Judd–Ofelt intensity parameters Ω_t , determined by using a least-square fitting approach, were found to be $\Omega_2 = 0.28 \times 10^{-20} \text{ cm}^2$, $\Omega_4 = 0.77 \times 10^{-20} \text{ cm}^2$ and $\Omega_6 = 0.55 \times 10^{-20} \text{ cm}^2$, which is nearly the same as that ($\Omega_2 = 0.39 \times 10^{-20} \text{ cm}^2$, $\Omega_4 = 0.69 \times 10^{-20} \text{ cm}^2$ and $\Omega_6 = 0.55 \times 10^{-20} \text{ cm}^2$) of Er³⁺ doped YAG crystal [15]. The small differences of Ω_t between ceramic and crystal are attributed to the distortion of the local structure coupled with Er³⁺ ions at the grain boundary in our ceramic sample, as shown in Fig. 1(B).

Room temperature Raman spectra of undoped YAG single crystal and ceramic sample are measured (as shown in Fig. 3), which indicates that the phonon properties of the ceramic is nearly the same as that of the crystal and the highest cut-off phonon energy is about 850 cm^{-1} in YAG:50%Er³⁺ (mol%) ceramic.

Fig. 4 presents the room temperature upconversion spectrum of transparent YAG:50%Er³⁺ (mol%) ceramic excited at 960 nm. The observed emissions correspond to transitions of Er³⁺ ions from excited states to ground state. Intense green and red emissions located at around 521, 561 and 679 nm are attributed to the $^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$, $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ and $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$ transitions, respectively.

For high concentration Er³⁺ doped samples, energy transfers (ET) between Er³⁺ ions should be the dominant mechanism to produce visible luminescence [16,17]. So with the excitation of a 960 nm LD, green upconversion emissions in YAG:50%Er³⁺ (mol%) ceramic should mainly come from the following excited state absorption (ESA): $^4\text{I}_{15/2} \rightarrow ^4\text{I}_{11/2} \rightarrow ^4\text{F}_{7/2}$ and ET: $^4\text{I}_{11/2} \rightarrow ^4\text{I}_{15/2}$; $^4\text{I}_{11/2} \rightarrow ^4\text{F}_{7/2}$,

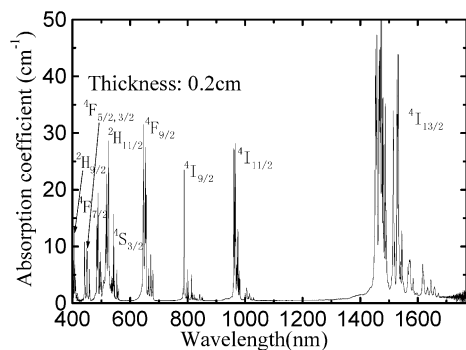


Fig. 2. The absorption spectrum of transparent YAG:50%Er³⁺ (mol%) ceramic.

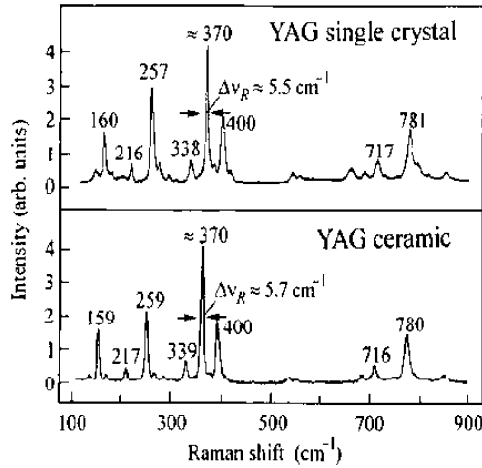


Fig. 3. Room temperature Raman spectra of undoped YAG single crystal and ceramic sample.

followed by fast cascading relaxation to the $^2H_{11/2}$ and $^4S_{3/2}$ states, and red emissions ground state absorption (GSA): $^4I_{15/2} \rightarrow ^4I_{11/2}$, followed by fast relaxation to the $^4I_{13/2}$ state, and then ET: $^4I_{11/2} \rightarrow ^4I_{15/2}$; $^4I_{13/2} \rightarrow ^4F_{9/2}$ (in this case, the direct ESA process: $^4I_{13/2} \rightarrow ^4F_{9/2}$ is invalid due to the large mismatch between the energy gap ($^4I_{13/2} \rightarrow ^4F_{9/2}$, ~ 1100 nm) and the pump light (~ 960 nm)), as shown in Fig. 5. In addition both green and red emissions are two-photon upconversion process.

For unsaturated upconversion, emission intensity, I_s , is proportional to $a(I - I_0)^n$ due to the linear dependence of the pump power on the electric current of LD, where I is the electric current of 960 nm LD, a the modified parameter and the integer n is the number of photons absorbed per upconverted photon emitted [14]. In order to clarify the upconversion mechanisms in YAG:50%Er³⁺ (mol%) ceramic excited at 960 nm, we measured the intensity dependence of the upconversion emissions on the pump power, as shown in Fig. 6(A). At low pump power, $n = 1.69$

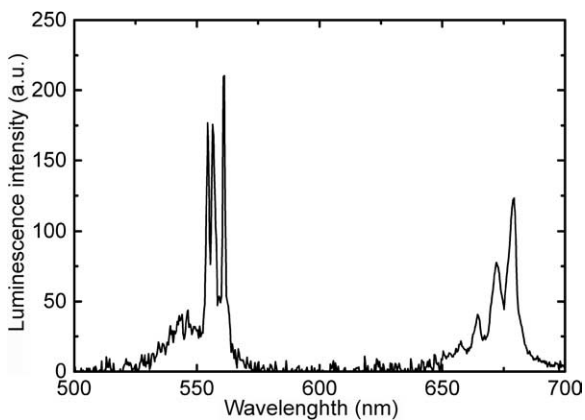


Fig. 4. Room temperature upconversion spectrum of transparent YAG:50%Er³⁺ (mol%) ceramic excited at 960 nm.

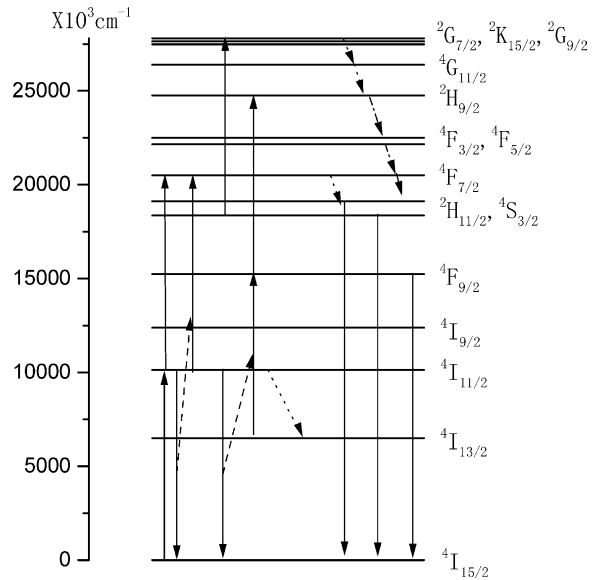


Fig. 5. Upconversion processes in YAG:50%Er³⁺ (mol%) ceramic excited at 960 nm.

for green emissions and 1.56 for red, at high pump power $n = 0.9$ for green emissions and 1.27 for red. The results show that the population of the states $^2H_{11/2}$, $^4S_{3/2}$ and 4F_9 may come from two-photon absorption upconversion process. Decrease in n at high pump power is attributed to the saturation effect of the absorption of Er³⁺ to the pump laser.

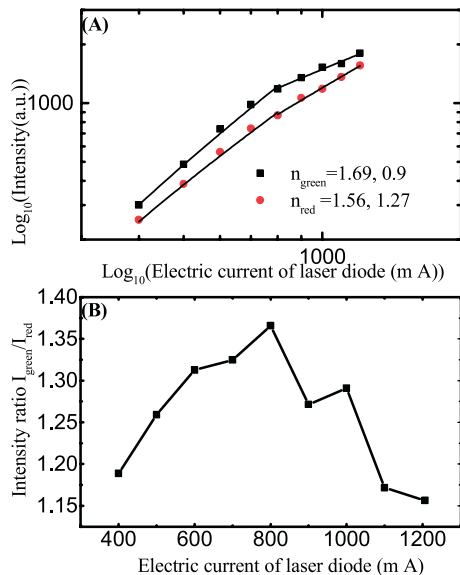


Fig. 6. (A) Intensity dependence of the upconversion emissions on the pump power, (B) the dependence of the upconversion emission intensity ratio I_{green}/I_{red} on the excitation power. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 6(B) shows the dependence of the upconversion emission intensity ratio $I_{\text{green}}/I_{\text{red}}$ on the excitation power. At low pump power, the intensity ratio $I_{\text{green}}/I_{\text{red}}$ becomes larger and larger with increasing the pump power, which is attributed to the effect of the three-photon upconversion processes [18]: GSA: ${}^4I_{15/2} \rightarrow {}^4I_{11/2}$, followed by fast relaxation to the ${}^4I_{13/2}$ state, then ET: ${}^4I_{11/2} \rightarrow {}^4I_{15/2}$: ${}^4I_{13/2} \rightarrow {}^4F_{9/2}$ and ESA: ${}^4F_{9/2} \rightarrow {}^4G_{11/2}$, followed by fast cascading relaxation to the ${}^2H_{11/2}$ and ${}^4S_{3/2}$ states. This three-photon upconversion process would populate the ${}^2H_{11/2}$ and ${}^4S_{3/2}$ states, depopulate the ${}^4F_{9/2}$ level and make $I_{\text{green}}/I_{\text{red}}$ increased. However, at high pump power, the thermal effect [19] induced by the absorption of YAG:50%Er³⁺ (mol%) ceramic to the pump laser would make the following multi-phonon non-irradiative relaxation greatly intensified: ${}^4I_{11/2} \sim {}^4I_{13/2}$ and ${}^4S_{3/2} \sim {}^4F_{9/2}$ due to high cut-off phonon energy ($\sim 850 \text{ cm}^{-1}$), which may populate the ${}^4F_{9/2}$ level by ET: ${}^4I_{11/2} \rightarrow {}^4I_{15/2}$: ${}^4I_{13/2} \rightarrow {}^4F_{9/2}$ and make $I_{\text{green}}/I_{\text{red}}$ decreased. From Fig. 6(A), the saturation effect of the absorption of Er³⁺ to the pump laser will happen at high pump power, which makes the three-photon upconversion processes invalid. In this moment, the thermal effect will dominate and change the dependence of the upconversion emission intensity ratio $I_{\text{green}}/I_{\text{red}}$ on the excitation power, as shown in Fig. 6(B). From above results, we believe that during 3 μm YAG:50%Er³⁺ ceramic laser experiments, the sample must be fully cooled. Otherwise, with the excitation of a high power 960 nm LD, the thermal effect would make the multi-phonon non-irradiative relaxation from ${}^4I_{11/2}$ to ${}^4I_{13/2}$ faster and faster, and diminish the efficiency of 3 μm YAG:50%Er³⁺ ceramic laser greatly.

In conclusion, we have investigated upconversion luminescence properties of Er³⁺ in highly transparent YAG ceramic excited at 960 nm. SEM and TEM measurements reveal that the pore volume in our sample is approximately 1 ppm, the average grain size is about 10 μm and the grain boundary width is about 1 nm. Such narrow grain boundary and very low pore volume ensure low scattering in the ceramic materials. Based on the intensity dependence of the upconversion emissions on the pump power, the upconversion mechanisms were discussed. In addition, from our experimental results, we think that during 3 μm YAG:50%Er³⁺ ceramic laser experiments, the sample must be fully cooled. Otherwise, the thermal effect would diminish the efficiency of a 3 μm YAG:50%Er³⁺ ceramic laser greatly.

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