1532 nm sensitized luminescence and up-conversion in Yb,Er:YAG transparent ceramics

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ABSTRACT

Luminescent properties of Yb,Er:YAG transparent ceramics containing 5 at% Yb^{3+} and 0.5, 1 and 1.5 at%, respectively, Er^{3+} ions have been studied. It has been found that increasing of erbium ions concentration increases both efficiency of nonradiative energy transfer $Yb^{3+} \rightarrow Er^{3+}$ (which reaches 72% for 1.5 at% Er^{3+}) and the luminescence in the range of 650—700 nm associated with $^4F_{9/2, 11/2} \rightarrow {}^4I_{15/2}$ transitions of Er^{3+} ions. It was also determined that the concentration quenching of sensitized luminescence of Er^{3+} ions at 1532 nm is associated with secondary excitation of metastable energy level of Er^{3+} followed by up-conversion emission.

1. Introduction

$Y_3Al_5O_{12}$ transparent ceramics co-doped with Yb^{3+} and Er^{3+} ions (Yb,Er:YAG) possess potential application in solid-state lasers and up- and down light convertors. Yb^{3+}-Er^{3+} co-doped materials have been most commonly used systems mainly owing to the large absorption cross section of Yb^{3+} ions at ≈ 980 nm, the relatively long lifetime of Er^{3+} energy levels, as well as the good match between energy levels of these rare-earth (RE) ions. Most of the co-doped systems studied include powders, glasses and single-crystalline materials [1—8]. In contrast to single crystals, transparent ceramics are easy to make and they have better mechanical and thermo-optical properties than glasses. With ceramic technology optical elements of complex shapes and different sizes with large doping concentration and doping profile can be obtained. Among the potential crystalline candidate hosts, superior thermal conductivity, optical quality and mechanical strength of YAG

present significant comparative advantages [8].

The luminescent properties of Yb,Er:YAG system are determined by the energy transfer efficiency from Yb^{3+} to Er^{3+} ions which depends on their both absolute and relative concentration in crystalline matrix [9—12] (Fig. 1). While increasing the Yb/Er ratio, energy transfer Yb→Er can decrease owing to the migration of energy between Yb^{3+} ions. Increasing of Er concentration leads to concentration quenching of luminescence due to energy transfer between Er^{3+} ions [1,2]. Laser emission at "eye-safe" wavelength range of 1.6 μm with Yb,Er:YAG ceramics (5% Yb, 0.5% and 1.0% Er) were demonstrated recently [13,14], but there is still no common view about optimal doping concentrations in YAG ceramics. In this article Yb,Er:YAG transparent ceramics with different Yb/Er concentrations were fabricated by solid-state reactive sintering and their luminescent properties were studied.

2. Experimental

Al_2O_3 (purity > 99.99%, Baikowski; d~0.15—0.30 μm); Y_2O_3 (purity >99.999%, Alfa Aesar; d~3—5 μm), Yb_2O_3 (purity >99.99%, Alfa Aesar; d~5—10 μm), Er_2O_3 (purity >99.99%, Alfa Aesar; d~5—10 μm)

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commercial powders were used as starting materials. Tetraethyl orthosilicate (TEOS, ≥99.999%, Alfa Aesar) in amount of 0.5 wt% (0.14 wt% SiO_2) was used as sintering aid. Powders were mixed according to YAG stoichiometry with 5 at% Yb and 0, 0.5, 1, 1.5 at.% Er, both replacing corresponding amount of yttrium (($3-x-y$) $Y_2O_3 \cdot x Yb_2O_3 \cdot y Er_2O_3 \cdot 5Al_2O_3$, $x = 0.15$, $y = 0.015$, 0.03, 0.045). The obtained mixtures were ball-milled with ethanol as dispersant in polyamide jar with Al_2O_3 balls for 15 h using a Pulverisette 5/4 (Fritsch GmbH, Germany) planetary ball mill. After ball milling the effective fragmentation of polycrystalline aggregates into submicron and nano-sized particles was observed. The rotation speed was 140 rounds per minute (rpm). The obtained slurries were dried for 24 h at 60 °C and screened through a 200-mesh sieve. The green bodies for vacuum sintering were prepared by uniaxial pressing of powder mixtures under a pressure of 250 MPa and annealed in air at 800 °C to eliminate organic impurities. The sintering was performed using a furnace with tungsten heating elements at 1800 °C under vacuum (6×10^{-3} Pa) for 10 h. Ceramic samples were cut using a horizontal cutting machine with diamond disk, and then fine polished on both surfaces by a precision lapping machine using lint-free cloth with diamond micro powders slurries. Finally, the obtained ceramics were annealed in air at 1300 °C for 15 h to recover the oxygen stoichiometry and to change ytterbium valence state to Yb^{3+} and completely remove residual stress.

Grain size distribution and average grain size of ceramics were calculated by the linear intercept method using SEM-images of thermally etched surface of ceramics [15,16]. At least 300 grains were analysed for each measurement. The phase composition was investigated by X-ray diffraction (XRD) using a Siemens D-500 diffractometer (Siemens AG, Germany) with Cu $K\alpha$ radiation ($\lambda = 1.5406$ Å). Phases were identified using the PDF-1 JCPDS X-ray database of the EVA survey system, a component of the diffractometer software. The room temperature transmittance spectra of Er,Yb:YAG samples were measured over a range from 0.2 to 1.6 μm using a Cary 5000 UV-VIS-NIR spectrometer (Varian, USA). The emission spectra of ceramics were recorded at 300 K using a Jarell Ash (model 78–460) monochromator. The spectrometer detection chain is equipped with S1 photomultiplier, Ge photodiode, and Lock-in amplifier connected with computer. The emission spectra were obtained under the excitation at $\lambda = 975$ nm of a CW laser diode from Coherent (USA), with the same detection system as for absorption. The lifetime measurements were carried out using 940 nm pulsed laser radiation generated by a tunable OPO-IR

pumped by the third harmonic of a Q-switched Nd:YAG laser (Rainbow from Quantel, France).

Yb:YAG (5 at%) transparent ceramics fabricated and studied in details in Ref. [17] were used as reference in some experiments during present study.

3. Results and discussion

3.1. Structural analysis of YAG:Yb,Er sintered ceramics

To study $Yb^{3+} \rightarrow Er^{3+}$ energy transfer efficiency, Yb,Er:YAG ceramics with 5 at% Yb and 0.5, 1, and 1.5 at% Er were fabricated by reactive vacuum sintering method. Polished ceramics are shown in Fig. 2a. According to XRD analysis, the obtained ceramics consist of 100% garnet phase (Fig. 2b).

Grain size distribution in fabricated ceramic samples containing 5 at% Yb and 0.5–1.5 at% Er are shown at Fig. 3. All samples demonstrate single-modal grain size distribution, which indicates the prevalence of normal recrystallization during sintering. Average grain size of these samples is almost independent of Er^{3+} ions concentration within the measurement accuracy. Thus, Er content in ceramics has practically no effect on the reactive sintering trajectory and the final microstructure. This is connected with a relatively low concentration of Er^{3+} ions and their similarity in key physical and chemical properties (ionic radius, diffusion mobility, electronegativity) with Y^{3+} ions replaced by erbium ions in the structure of YAG. Consequently, the sintering conditions previously optimized by authors for obtaining of Yb:YAG ceramics [16], can be also applied to produce good quality Yb,Er:YAG ceramics.

In-line optical transmittances of Yb,Er:YAG ceramics are shown in Fig. 4a. The samples measured were 1.5 mm thick, uncoated. Transmittance of all samples at 1.5 μm wavelength range was >82%,
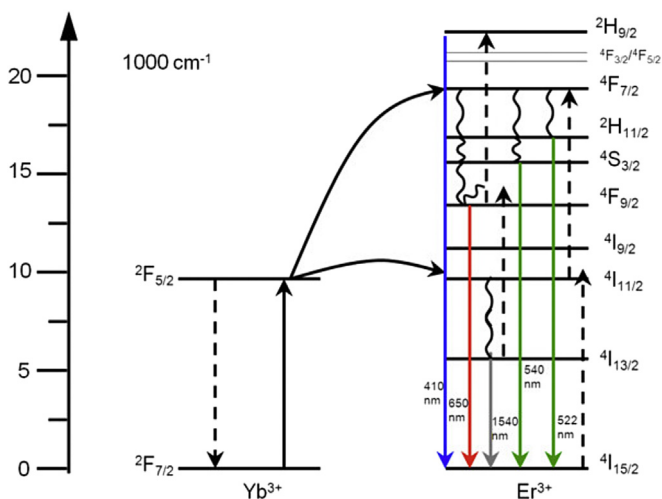

(a)

(b)
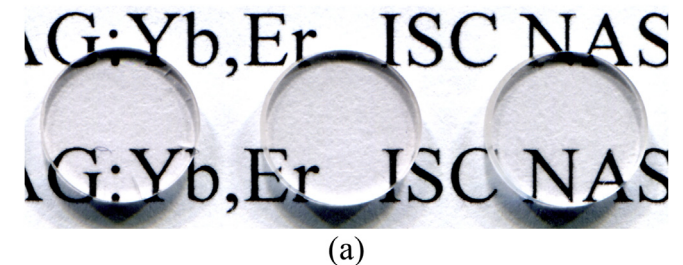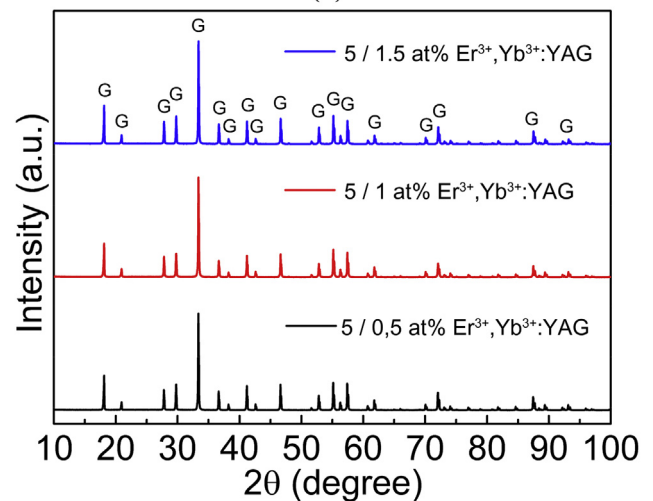
Fig. 2. Photo of obtained Yb,Er:YAG ceramics (a) and their XRD patterns (b).

Fig. 1. Energy level diagram of Yb^{3+}-Er^{3+} pairs (ET - energy transfer, ESA - excited state absorption) [12].