Ceramics International 44 (2018) 1812–1816

Contents lists available at ScienceDirect

Ceramics International

journal homepage: www.elsevier.com/locate/ceramint

Preparation and mid-infrared 2.7 µm luminescence property of high content Er^{3+}-doped $(Y_{0.9}La_{0.1})_2O_3$ transparent ceramics pumped at 980 nm

Yan Sun, Qiuhong Yang*, Hongqiang Wang, Qinying Zhang, Yingjie Shao

School of Materials Science and Engineering, Shanghai University, 200444, China

ARTICLE INFO

Keywords:
High concentration Er^{3+} doped
Yttrium lanthanum oxide
Transparent ceramics
Mid-infrared 2.7 µm emission
Up-conversion luminescence

ABSTRACT

High content Er^{3+} doped $(Y_{0.9}La_{0.1})_2O_3$ transparent ceramics have been prepared by conventional ceramic process. Absorption spectra, mid-infrared, up-conversion and near-infrared emission spectra of Er^{3+} pumped at 980 nm have been investigated. The mechanisms of energy transfer processes have been discussed. Large values of Judd–Ofelt parameter Ω_2 (5.73×10^{-20} cm^2) and spectral quality factor X (3.71) have been obtained. The greatly enhanced green up-conversion emission in the high Er^{3+} doped sample is considered important for the applications in up-converters. The much enhanced mid-infrared 2.7 µm and up-conversion emissions, as well as the depressed near-infrared 1.5 µm emission demonstrate the efficient population inversion of Er^{3+}:$^4I_{11/2} \rightarrow {}^4I_{13/2}$ in high Er^{3+}-doped ceramics for the 2.7 µm emission. These results suggest that high Er^{3+}-doped $(Y_{0.9}La_{0.1})_2O_3$ transparent ceramics are promising host materials for the applications of mid-infrared lasers and infrared-to-visible up-converters.

1. Introduction

Recently, mid-infrared (MIR) laser materials operating in the wavelength range of 2.5–3.0 µm have attracted much attention due to their extensive applications in hazardous chemical detection, eye-safe laser radar, remote sensors, pollution monitoring and surgery [1,2]. Numerous researches have been focused on the ~3 µm emission of Er^{3+} ions ($^4I_{11/2} \rightarrow {}^4I_{13/2}$) doped materials for many years owing to the absorption bands of Er^{3+}:$^4I_{15/2} \rightarrow {}^4I_{11/2}$ matched well with the commercial high power 980 nm laser diode (LD) [3]. However, the relative low absorption efficiency in near-infrared (NIR) region of low concentration Er^{3+} ions, and the longer lifetime of Er^{3+}:$^4I_{13/2}$ than that of Er^{3+}:$^4I_{11/2}$ [4] of 2.7 µm emission, lead to the inefficient excitation and emission behavior of Er^{3+}.

Two main methods can be used to overcome this disadvantage: first, recycling the $^4I_{13/2}$ population into $^4I_{11/2}$ states by utilizing an up-conversion (UC) process Er^{3+}:$^4I_{13/2} + {}^4I_{13/2} \rightarrow {}^4I_{9/2} + {}^4I_{15/2}$ [5] through high doping Er^{3+} ions and second, introducing sensitizer ions such as Yb^{3+} [6] ions to enhance the absorption efficiency, Nd^{3+} [7] and Pr^{3+} [8] ions to depopulate the terminal level $^4I_{13/2}$ of 2.7 µm emission. Whereas single doped high concentration Er^{3+} ions provide not only an enhanced absorption but a depopulation of $^4I_{13/2}$ state, and few articles have been reported on 2.7 µm emission in high Er^{3+} single doped transparent ceramics.

The 2.7 µm emission of Er^{3+} requires high chemical and thermal properties of the host materials due to the narrow energy gap between $^4I_{11/2}$ and $^4I_{13/2}$ states. As a good laser host material, Y_2O_3 demonstrates many superior properties such as high thermal conductivity of 13.6 W mK^{-1} and low phonon energy of 591 cm^{-1} (better than ~11 W mK^{-1} and 857 cm^{-1} of YAG, respectively [9]), which makes it a more favorable host material than YAG. Unfortunately, Y_2O_3 crystals are difficult to prepare due to its high melting point at ~2430 °C and structural phase transition at ~2280 °C. Y_2O_3-based transparent ceramics have been developed recently for their excellent properties such as low cost, easy preparation of large-size specimens and the ability to dope high content of rare-earth ions [10], and the sintering temperature of Y_2O_3 could be decreased greatly by adding La_2O_3 to form an yttrium lanthanum oxide without influence on optical property [11]. Since the sample with 10 mol% La_2O_3 shows excellent sintering and optical properties [12], the composition $(Y_{0.9}La_{0.1})_2O_3$ is chosen as host in this study.

In this work, high concentration Er^{3+}-doped $(Y_{0.9}La_{0.1})_2O_3$ transparent ceramics have been prepared by conventional ceramic process. The MIR 2.7 µm, NIR and UC emissions have been investigated under the excitation of 980 nm LD, energy transfer mechanisms have been discussed.

2. Experimental procedure

Starting nanopowders Y_2O_3 (99.99 wt%), La_2O_3 (99.99 wt%), Er_2O_3

---

* Corresponding author.
E-mail address: yangqiuhong@shu.edu.cn (Q. Yang).

http://dx.doi.org/10.1016/j.ceramint.2017.10.115
Received 27 June 2017; Received in revised form 17 October 2017; Accepted 17 October 2017

(99.99 wt%), obtained from Rare-Chem. Hi–Tech Co., Ltd., China, were weighed with the composition of $(Er_xY_{0.9-x}La_{0.1})_2O_3$ (x = 1%, 5%, 10%), which are denoted according to the nomenclature E1, E5 and E10 with nominal concentrations of 1, 5 and 10 mol% Er^{3+} ions, respectively. Compounds were milled with ZrO_2 balls in alcohol for 6 h, dried at 80 °C and then calcined at 1100–1200 °C for 9–10 h in air atmosphere. Pellets isostatically pressed under 200 MPa with 10 mm in diameter and 4 mm in thickness were sintered at 1500–1700 °C for 5–20 h in H_2 atmosphere. Each specimen was double-polished with ~1 mm in thickness for spectral analysis.

The absorption and in-line transmittance spectra at room temperature were measured with a spectrophotometer (Model V-570, JASCO, Japan) that used Xe light as the pump source. The emission spectra and fluorescence lifetime of the specimens excited by 980 nm LD were measured with a fluorescence spectrum analyzer (Fluorolog-3, Jobin Yvon Spex, France). Microstructures were observed with an optical microscopy (Model BX60, OLYMPUS, Japan). Phase composition was measured by X-ray diffraction (XRD) with a diffractometer (Model D/MAX-2200, Rigaku, Japan).

3. Results and discussion

3.1. Structural characterization, absorption spectra and Judd–Ofelt analysis

Fig. 1 displays the photographs of Er^{3+}:$(Y_{0.9}La_{0.1})_2O_3$ transparent ceramics E1, E5 and E10 (from left to right). All ceramic samples have high transparency, and the letters under the ceramics can be clearly seen. The in-line transmittance spectra of E1, E5 and E10 transparent ceramics are shown in Fig. 2. Similarly high transparency can be found in these spectra and the maximum transmittance reaches up to 70% in the range of 1600–2000 nm.

Fig. 3 shows the measured XRD patterns of Er^{3+}:$(Y_{0.9}La_{0.1})_2O_3$ transparent ceramics. Single cubic Y_2O_3 phase (JCPDS: 43-1036) can be found in these samples without any secondary phases, suggesting the solid solution has been formed completely from all composition. The microstructure photo of Er^{3+}:$(Y_{0.9}La_{0.1})_2O_3$ transparent ceramics (a) E1, (b) E5 and (c) E10 are depicted in Fig. 4, in which a dense structure and an average grain size around 40 μm can be observed.

The absorption spectra of Er^{3+}:$(Y_{0.9}La_{0.1})_2O_3$ transparent ceramics have been measured in the wavelength region of 400–1800 nm and are shown in Fig. 5. Several absorption bands peaked at 1534, 970, 799, 653, 538, 523 and 489 nm corresponding to transitions of Er^{3+} from ground state $^4I_{15/2}$ to excited states of $^4I_{13/2}$, $^4I_{11/2}$, $^4I_{9/2}$, $^4F_{9/2}$, $^4S_{3/2}$, $^2H_{11/2}$ and $^4F_{7/2}$, respectively, are observed and labeled. The position and lineshape of absorption peaks are independent of the Er^{3+} concentration, indicating homogeneous incorporation of dopant ions into the host. The enhanced absorption bands around 980 nm as a function of Er^{3+} concentration indicate that these samples can be efficiently excited by the 980 nm LD.

The Judd–Ofelt (J–O) theory [13,14] is the most effective method to analyze the important spectroscopic and luminescence parameters of rare earth ions. Based on the absorption spectrum, the experimental oscillator strength of transitions can be calculated as

$$f_{exp} = \frac{2.303mc^2}{\pi N d e^2 \bar{\lambda}^2} \int OD(\lambda)\mathrm{d}\lambda \tag{1}$$

where m is the mass of electron, e is the charge of electron, c is the velocity of light in vacuum, d is thickness of sample, $N = \rho/M_w m_{mol} N_A$ is the number of dopant ions per unit volume (ρ is the density of sample, M_w is molar mass, m_{mol} is molar concentration of dopant ions, $N_A = 6.02 \times 10^{23}$ is Avogadro number), $\bar{\lambda}$ is the mean wavelength of transition photon, and $OD(\lambda)$ is the measured absorption coefficient at wavelength λ. The theoretical oscillator strength of the induced electric-dipole $4f \rightarrow 4f$ transition from an initial J manifold $|(S, L)J\rangle$ to a final J' manifold $|(S', L')J'\rangle$ can be calculated by following equation:

$$f_{cal}(J;J') = \frac{8\pi^2 mc}{3h(2J+1)\bar{\lambda}} \times \frac{(n^2+2)^2}{9n} \times \sum_{t=2,4,6} \Omega_t \left|\langle 4f^N(S, L)J \| U^t \| 4f^N(S', L')J'\rangle\right|^2 \tag{2}$$

where h is Planck constant, n is the refractive index of the $(Y_{0.9}La_{0.1})_2O_3$ host ceramics, and its value is ~2 [15], the terms

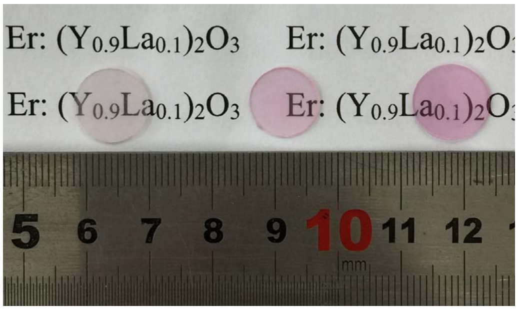

Fig. 1. Photographs of Er^{3+}:$(Y_{0.9}La_{0.1})_2O_3$ transparent ceramics E1, E5 and E10 (from left to right).

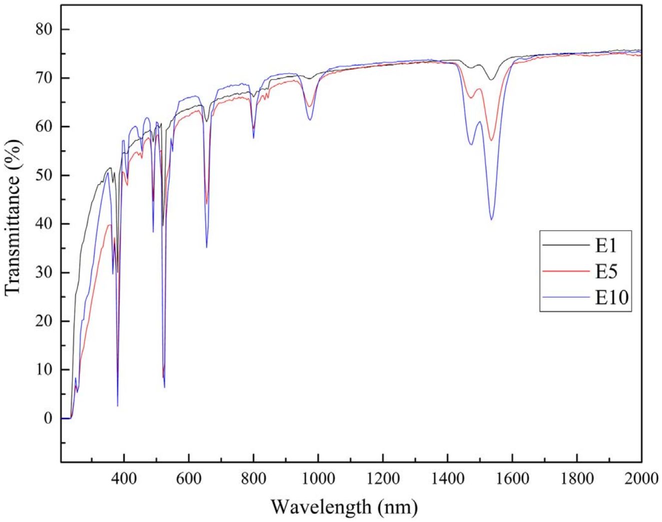

Fig. 2. In-line optical transmittance spectra of E1, E5 and E10 transparent ceramics.

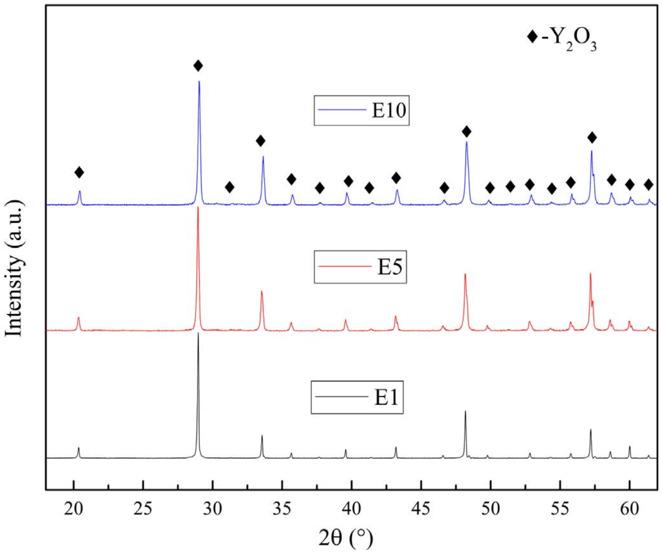

Fig. 3. XRD patterns of Er^{3+}:$(Y_{0.9}La_{0.1})_2O_3$ transparent ceramics.