Luminescence behavior of Yb\(^{3+}\) heavy-doped yttrium lanthanum oxide transparent ceramics

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Abstract

Yb\(^{3+}\) heavy-doped yttrium lanthanum oxide transparent ceramics were fabricated and their spectroscopic properties were investigated. The absorption bands of (Yb\(_x\)Y\(_{0.9-x}\)La\(_{0.1}\))\(_2\)O\(_3\) (x = 0.05–0.15) ceramics are broad at wavelength of 900–1000 nm. The absorption cross-sections centered at 974 nm and the emission cross-sections at 1031 nm of Yb\(^{3+}\) ion are 0.89–1.12 \(\times\) 10\(^{-20}\) cm\(^2\) and 1.05 \(\times\) 10\(^{-20}\) cm\(^2\), respectively. The up-conversion luminescence intensity of Yb\(^{3+}\)-doped yttrium lanthanum oxide ceramics increased firstly, then decreased with the increase of Yb\(^{3+}\) ion content.

Keywords: Optical materials; Transparent ceramics; Sintering; Optical properties; Luminescence

1. Introduction

Recently, Yb\(^{3+}\)-doped laser materials have attracted considerable attention due to the development of high-power and high-efficient laser diode. Yb\(^{3+}\) ions have a very simple electronic structure with only two manifolds separated by about 10 000 cm\(^{-1}\). Owing to perceptible electron–phonon interaction, Yb\(^{3+}\)-doped materials have broad absorption in near-IR which is suitable for laser diode (LD) pumping [1–3]. The broad luminescence band \(^2\)F\(_{5/2}\)–\(^2\)F\(_{7/2}\) is also attractive for ultrashort pulse generation. Unfortunately, the relative low absorption cross-section of the Yb\(^{3+}\) ion requires high Yb\(^{3+}\) concentrations and this could induce additional loss mechanisms, such as cooperative processes involving pairs of Yb\(^{3+}\) ions. In cubic sesquioxides Ln\(_2\)O\(_3\) (Ln = Y, Lu, Sc) materials [4], the cooperative up-conversion luminescence was detected when Yb\(^{3+}\) ion concentration reached 5 at%.

The effect of La\(_2\)O\(_3\) on the spectroscopic properties of transparent Yb\(^{3+}\):Y\(_2\)O\(_3\) ceramics has been investigated in our previous work [5]. In this paper, the spectroscopic properties of Yb\(^{3+}\) heavily-doped yttrium lanthanum oxide ceramics were investigated.

2. Experimental

The starting materials Y\(_2\)O\(_3\), La\(_2\)O\(_3\) and Yb\(_2\)O\(_3\) powders with purity of 99.95% were weighed according to the desired composition (Yb\(_x\)Y\(_{0.9-x}\)La\(_{0.1}\))\(_2\)O\(_3\) (x = 0.05–0.15) and mixed in absolute ethyl alcohol for 24 h with zirconia balls. Specimens were synthesized by conventional solid-state processing, calcined at 1100 °C for 5 h in air atmosphere. Disks with 15 mm in diameter and 5 mm in thickness isostatically pressed at 200 MPa were sintered at 1500–1600 °C for 25 h under H\(_2\) atmosphere without pressure, then the specimens were cut and double polished with 1 mm in thickness for spectral analysis.

The absorption spectra were measured with a spectrophotometer using Xe light as pump source (Model V-570, JASCO) at room temperature. The fluorescence spectra and fluorescence lifetime of the ceramics excited with 940 nm LD were measured with a spectrofluorimeter (Fluorolog-3, Jobin Yvon Spex, France) at room temperature. Microstructures were observed with optical microscopy (Model BX60, OLXPMUS).

3. Results and discussion

(Yb\(_x\)Y\(_{0.9-x}\)La\(_{0.1}\))\(_2\)O\(_3\) transparent ceramics (x = 0.05) have high transparency, as shown in Figs. 1 and 2.

Fig. 3 shows microscopic photograph of (Yb\(_{0.05}\)Y\(_{0.85}\)La\(_{0.1}\))\(_2\)O\(_3\) ceramics sintered at 1500 °C. There are almost no pores between the grain boundaries.

The absorption spectrum of transparent (Yb\(_{x}\)Y\(_{0.9-x}\)La\(_{0.1}\))\(_2\)O\(_3\) (x = 0.05–0.15) ceramics is shown in Fig. 4. The absorption bands of the specimens are broad with three main absorption peaks located on 904, 948 and 974 nm, respectively. The absorption coefficient increases apparently as the concentration of...
Yb\textsuperscript{3+} ion increases due to more Yb\textsuperscript{3+} ion involving in absorption. Absorption cross-section \((\sigma_{\text{abs}})\) of Yb\textsuperscript{3+} can be calculated as the following formula:

\[
\sigma_{\text{abs}} = \frac{2.303 \log(I_0/I)}{LN}
\]  

where \(\log(I_0/I)\) is optical density, \(N\) is the numbers of active ions per unit volume and \(L\) is the thickness of the sample. The calculated results and the FWHM (Full Width at Half Maximum) are listed in Table 1. The absorption cross-sections of 10 at\% Yb-doped yttrium lanthanum oxide transparent ceramics are a bit smaller than those of 5 at\% and 15 at\% doped samples, which maybe caused from measurement errors. The broad absorption bands of (Yb\textsubscript{x}Y\textsubscript{0.90−x}La\textsubscript{0.1})\textsubscript{2}O\textsubscript{3} \((x = 0.05–0.15)\) ceramics in 900–1000 nm make it suitable to be coupled by LD, hence the temperature control of LD is unnecessary [6].

Fig. 3 shows the emission spectra of transparent (Yb\textsubscript{x}Y\textsubscript{0.90−x}La\textsubscript{0.1})\textsubscript{2}O\textsubscript{3} \((x = 0.05–0.15)\) ceramics. Similar to that of Yb\textsuperscript{3+}:Y\textsubscript{2}O\textsubscript{3} ceramics, three emission peaks corresponding to the transitions from the sublevels of \(^{2}F_{5/2}\) to the compo-
nents of the $^2F_{7/2}$ ground state are located at 976 nm, 1031 nm and 1075 nm. The emission intensity of $(\text{Yb}_x\text{Y}_{0.90-x}\text{La}_{0.1})_2\text{O}_3$ transparent ceramics increases with the increase of Yb$^{3+}$ ion content firstly, then decreases obviously when the concentration of Yb$^{3+}$ reaches 15 at% due to concentration quenching of Yb$^{3+}$ ion.

By assuming a Gaussian-shaped emission band, emission cross-section ($\sigma_{\text{em}}$) of Yb$^{3+}$ ion is estimated from F"uchtbauer–Ladenburg (F–L) formula [7,8]:

$$\sigma_{\text{em}}(\lambda) = \frac{\lambda^4}{4\pi^2c^2\Delta\lambda} \left( \ln \frac{2}{\pi} \right)^{1/2}$$

where $\lambda_c$, $c$, and $\Delta\lambda$ are the center wavelength of the band, the velocity of light, and the FWHM of the emission, respectively. $\tau$ is the emission lifetime. The estimated emission cross-sections of 10 at% Yb$^{3+}$ ion at 1031 nm and 1075 nm are $1.05 \times 10^{-20}$ cm$^2$ and $0.52 \times 10^{-20}$ cm$^2$, respectively, which are close to $1 \times 10^{-20}$ cm$^2$ and $4 \times 10^{-21}$ cm$^2$ at 1030 nm and 1075 nm respectively for both Yb:Y$_2$O$_3$ crystals [9] and ceramics [10].

The luminescence decay curve of $(\text{Yb}_0.05\text{Y}_{0.85}\text{La}_{0.1})_2\text{O}_3$ ($x = 0.05$) are shown in Fig. 6. The lifetimes are calculated to be 1.28 ms, which is longer compared with the lifetime 0.82 ms of Yb:Y$_2$O$_3$ ceramics[11]. Fig. 7 shows the relationship between fluorescent lifetimes of Yb$^{3+}$ at 1031 nm and Yb$^{3+}$ content in $(\text{Yb}_x\text{Y}_{0.90-x}\text{La}_{0.1})_2\text{O}_3$ ($x = 0.05$–0.15) transparent ceramics. Since the radius of La$^{3+}$ ion (101.6 pm) is larger than that of Y$^{3+}$ ion (89.3 pm), the crystal lattice become larger after La$_2$O$_3$ doping into Y$_2$O$_3$, which makes the strength of the Y$_2$O$_3$ crystal field become weaker and result in weaker interaction between Yb$^{3+}$ ions and O$^{2-}$ ions. This results in lengthening the lifetime of Yb$^{3+}$ in $(\text{Yb}_x\text{Y}_{0.90-x}\text{La}_{0.1})_2\text{O}_3$ host. At the same time, the existence of a weak reabsorption at 1031 nm also will result in lengthening the lifetime of Yb$^{3+}$ in $(\text{Yb}_x\text{Y}_{0.90-x}\text{La}_{0.1})_2\text{O}_3$ ceramics, which is similar to that of Yb:Y$_2$O$_3$ ceramic[6]. Moreover, the lifetime has little changes with the increase of Yb$^{3+}$ ion content firstly, then decreases obviously when the concentration of Yb$^{3+}$ reaches 15 at% because of the concentration quenching. Cooperative up-conversion is a well-studied phenomenon since firstly observed in YbPO$_4$ by Nakazawa and Shionoy-ain [12] and numerous cooperative up-conversion researches such as Yb$^{3+}$–Er$^{3+}$ ions or Yb$^{3+}$–Yb$^{3+}$ ions have been carried out [13,14]. Meanwhile up-conversion luminescence has many interesting applications, including data-storage, 3-d volumetric display, guard-against-forgery applications, sensor, laser imaging and so on.

Up-conversion fluorescence spectra of $(\text{Yb}_x\text{Y}_{0.90-x}\text{La}_{0.1})_2\text{O}_3$ ($x = 0.05$–0.15) ceramics excited with a 940 nm LD is shown in Fig. 8. The up-conversion luminescence is caused by the simultaneous radiative transition of the excited Yb$^{3+}$ ion pairs accompanied by the emission of a photon in the following manner: $\text{Yb}^+ (2F_{5/2}) + \text{Yb}^+ (2F_{5/2}) \rightarrow \text{Yb} (2F_{7/2}) + \text{Yb} (2F_{7/2}) + h\nu$, so it is dependent on the coupling property of Yb$^{3+}$ and quantities of Yb$^{3+}$ ion pairs. The main up-conversion luminescence peak is centered at 489 nm and the up-conversion luminescence intensity of transparent ceramics increases with the increase of Yb$^{3+}$.
ion content firstly, then decreases obviously when the concentration of Yb\(^{3+}\) reaches 15 at\%. It becomes easier to form Yb\(^{3+}\) ion pairs with the increase of Yb\(^{3+}\) concentration, so the up-conversion luminescence become stronger. However, the heavy Yb\(^{3+}\)-doped host materials causes concentration quenching [15], which results in Yb\(^{3+}\) ionic energy transfer and the intensity decreases, thus the up-conversion luminescence of 15 at\% Yb\(^{3+}\)-doped concentrations is quite weak.

4. Conclusions

(Yb\(_x\)Y\(_{0.90-x}\)La\(_{0.1}\))\(_2\)O\(_3\) (\(x = 0.05–0.15\)) transparent ceramics sintered at 1500–1600 °C for 25 h have high transparency and their grain sizes are around 20 \(\mu\)m without pores. The absorption cross-sections of the samples at 974 nm are 0.89–1.12 \(\times 10^{-20}\) cm\(^2\). The 10 at\% heavy-doped concentration of Yb\(^{3+}\) ion was achieved without obvious concentration quenching and its emission cross-sections at 1031 nm is \(1.05 \times 10^{-20}\) cm\(^2\), which is close to that of Yb\(^{3+}\):Y\(_2\)O\(_3\). The fluorescent lifetimes of (Yb\(_x\)Y\(_{0.90-x}\)La\(_{0.1}\))\(_2\)O\(_3\) (\(x = 0.05–0.15\)) transparent ceramics has little changes with the increase of Yb\(^{3+}\) ion content firstly, then decreases obviously when the concentration of Yb\(^{3+}\) reaches 15 at\% because of the concentration quenching. The up-conversion luminescence of (Yb\(_x\)Y\(_{0.90-x}\)La\(_{0.1}\))\(_2\)O\(_3\) (\(x = 0.10\)) ceramics are obviously detected and the main up-conversion luminescence peak is centered at 489 nm. But the up-conversion luminescence of 15 at\% Yb\(^{3+}\)-doped yttrium lanthanum oxide ceramic is quite weak due to the concentration quenching.

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References