Effects of Nd^{3+} concentration on properties of yttrium lanthanum oxide transparent ceramics

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The effects of Nd^{3+} concentration on the visible fluorescence spectroscopic properties of Nd:(Y$_{0.9}$La$_{0.1}$)$_2$O$_3$ transparent ceramics are investigated. Under 270 nm excitation, three emission peaks are observed at 396, 426, and 633 nm. When the Nd^{3+} concentration is increased, intensities of the peaks at 396 and 426 nm increase while the 633 nm peak become weak due to the fluorescence re-absorption effect. Broad luminescence band centered at 426 nm is observed from the fluorescence spectrum stimulated at 358 nm. The emission intensity increases with the increase of Nd^{3+} ion content firstly, then decreases owing to the concentration quenching of Nd^{3+} ions.

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In recent years, Nd^{3+}-doped solid-state laser materials have attracted much attention as high efficient light sources with the widespread use of laser diodes (LD)[1,2]. The Nd^{3+}-doped laser hosts with four-level system have low laser threshold, large stimulated emission cross section, and strong absorption peak at 808 nm, which matches the emission of commercial LD[3]. Among all host materials for Nd^{3+} ions, cubic Y$_2$O$_3$ is an ideal laser host media because it has high thermal conductivity, good thermal, chemical and mechanical properties[4]. However, the high melting point (2 430 °C) and the structural phase transition from cubic to hexagonal system at ~2 350 °C make it extremely difficult to fabricate a high quality Y$_2$O$_3$ crystal by conventional growth methods[5]. Therefore, many recent studies have focused on polycrystalline ceramic lasers since the first report of laser oscillation in Nd:YAG ceramics in 1995[6]. Compared with single crystals, ceramic laser materials have many advantages such as ease of fabrication, low cost, and mass production in a large size. Nowadays, Nd:Y$_2$O$_3$ transparent ceramics have been fabricated by nanocrystalline method and vacuum sintering technology at a relatively low sintering temperature of 1 700 °C, which is about 700 °C lower than its melting point[7].

Our previous works showed that the sintering temperature of Y$_2$O$_3$ transparent ceramic could be further decreased by doping La$_2$O$_3$ as an additive in Y$_2$O$_3$ to form (Y$_{1-x}$La$_x$)$_2$O$_3$ ceramic[8]. (Y$_{1-x}$La$_x$)$_2$O$_3$ is a solid solution of Y$_2$O$_3$ and La$_2$O$_3$ with cubic glass-like structure[9], which makes it possible to have broad absorption and emission bandwidth. It is of great benefit to lower dependency on temperature control of a diode laser and widely tunable laser output. In 2009, output power of 62 mW was obtained from a 1.5-at.-% Nd:(Y$_{0.9}$La$_{0.1}$)$_2$O$_3$ ceramic[10]. Very recently, by using 1 at.-% Nd:(Y$_{0.9}$La$_{0.1}$)$_2$O$_3$ ceramic as the gain medium, a maximum output power up to 1.38 W was obtained at 1 079.5 nm[11], which is the highest power ever achieved from Nd-doped sesquioxides ceramic laser to the best of our knowledge.

In this work, (Nd$_x$Y$_{0.9-x}$La$_{0.1}$)$_2$O$_3$ (x=0.005~0.04)

transparent ceramics were fabricated by solid-state reaction method. The visible fluorescence spectra of Nd-doped yttrium lanthanum oxide ceramics under different wavelengths excitation and the effects of Nd^{3+} concentration on the properties of (Nd$_x$Y$_{0.9-x}$La$_{0.1}$)$_2$O$_3$ ceramics were investigated.

The starting materials Y$_2$O$_3$, La$_2$O$_3$, and Nd$_2$O$_3$ powders with purity of 99.99% were weighed according to the desired composition (Nd$_x$Y$_{0.9-x}$La$_{0.1}$)$_2$O$_3$ (x=0.005~0.04) and mixed in absolute ethyl alcohol for 24 h with zirconia balls. The mixtures were dried and calcined at 1 100~1 200° for 10 h in air, followed by 5-h ball-milling in anhydrous alcohol, dried and sieved. Finally disks with 23 mm in diameter and 6 mm in thickness were isostatically pressed at 200 MPa and sintered at 1 600~1 650° for 40~50 h in H$_2$ atmosphere.

The specimens were cut and double polished for spectral analysis. The absorption spectra of the ceramics were measured with a spectrophotometer using Xe light as pump source (Model V-570, JASCO, Japan). The fluorescence spectra were measured with a spectrofluorimeter (Fluorolog-3, Jobin Yvon Spex, France). All the spectroscopic analyses were made at room temperature.

Figure 1 is the photograph of (Nd$_x$Y$_{0.9-x}$La$_{0.1}$)$_2$O$_3$ (x=0.005~0.04) transparent ceramics. Each pellet is 18 mm in diameter and ~2.5 mm in thickness. All the samples are completely transparent and the letters under the ceramics can be seen distinctly.

Figure 2 shows the room-temperature absorption spectrum of Nd^{3+}-doped yttrium lanthanum transparent ceramics in the ultraviolet (UV) and visible region. For Nd:(Y$_{0.9}$La$_{0.1}$)$_2$O$_3$ transparent ceramic, there are two types of absorption bands with different mechanisms.

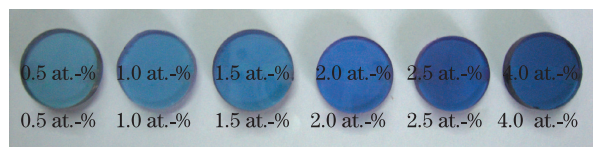Fig. 1. Photograph of (Nd$_x$Y$_{0.9-x}$La$_{0.1}$)$_2$O$_3$ (x=0.005~0.04) transparent ceramics (2.5 mm in thickness).
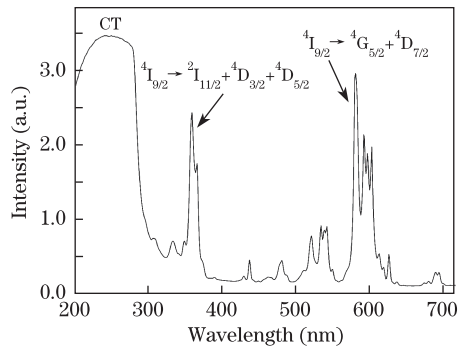
Fig. 2. Room-temperature absorption spectrum of Nd-doped yttrium lanthanum ceramics in the UV and visible region.
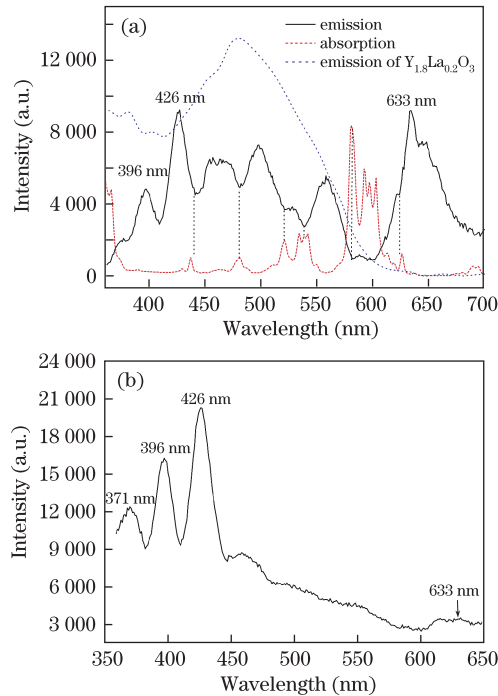

Fig. 3. Room-temperature visible fluorescence spectra of $(Nd_xY_{0.9-x}La_{0.1})_2O_3$ transparent ceramics under 270-nm excitation. (a) $x=0.01$; (b) $x=0.04$.

The absorption shoulder in UV region (from 200 to 300 nm) is assigned to the combination of the charge-transfer (CT) transition of $O^{2-} \rightarrow Y^{3+}$ and $O^{2-} \rightarrow Nd^{3+}$[12]. The other two bands around 358 and 580 nm are corresponded to the f-f transitions of Nd^{3+} ions between the ground state $^4I_{9/2}$ and the mixed higher states of $(^2I_{11/4}+^4D_{3/2}+^4D_{5/2})$ and $(^4G_{5/2}+^2G_{7/2})$, respectively[13].

Figure 3(a) is the visible fluorescence spectrum of 1 at.-% Nd:$(Y_{0.9}La_{0.1})_2O_3$ transparent ceramic under 270 nm excitation. The absorption spectrum of Nd:$(Y_{0.9}La_{0.1})_2O_3$ and the emission spectrum of undoped $Y_{1.8}La_{0.2}O_3$ ceramic ($\lambda_{ex}=270$ nm) are taken as references. As shown in Fig. 3(a), the fluorescence spectrum of 1 at.-% Nd:$(Y_{0.9}La_{0.1})_2O_3$ ceramic exhibits a large number of emission peaks in the visible region. The strongest two emission peaks at 633 nm and 426 nm are attributed to the $^2H_{11/2}\rightarrow^4I_{9/2}$ and $^2D_{5/2} \rightarrow^4$

$I_{9/2}$ transitions of Nd^{3+} ions, respectively[14]; the weak peak centered at 396 nm is corresponding to the transition of $^2P_{1/2}\rightarrow^4 I_{9/2}^{[14]}$. By comparing the absorption and fluorescence spectrum of Nd:$(Y_{0.9}La_{0.1})_2O_3$ ceramic, it is clear to see that the shapes and positions of the absorption peaks dovetailed well with the mirror images of emission peak valleys in the range from 436 to 625 nm. Moreover, according to the emission spectrum of undoped $Y_{1.8}La_{0.2}O_3$ ceramic, there is a broad emission band of $Y_{1.8}La_{0.2}O_3$ in this spectrum region. Therefore, it can be concluded that the emission peaks at 462, 497, and 557 nm result from the overlapping of $Y_{1.8}La_{0.2}O_3$ fundamental host emission and the absorption of Nd^{3+} ions. They are assigned to be a part of the emission band of undoped $Y_{1.8}La_{0.2}O_3$ actually.

Figure 3(b) is the visible fluorescence spectrum of 4 at.-% Nd:$(Y_{0.9}La_{0.1})_2O_3$ ceramic specimen excited by 270 nm. As the Nd^{3+} concentration is increased, the relative intensities of the two blue emission peaks centered at 396 and 426 nm increased rapidly, while the intensity of the fundamental host emission decreased. At the same time, the 633-nm emission peaks in the red region became very weak. This may be attributed to the fluorescence re-absorption effects, since there is an overlap between the absorption and emission peak of Nd^{3+} ions around 630 nm. The production mechanism of the 371-nm emission peak is not clear, and further studies are still needed.

Figure 4 is the visible fluorescence spectrum of 1 at.-% Nd:$(Y_{0.9}La_{0.1})_2O_3$ transparent ceramic stimulated at 358 nm. A luminescence band centered at 426 nm, which covers a wide wavelength range from 300 to
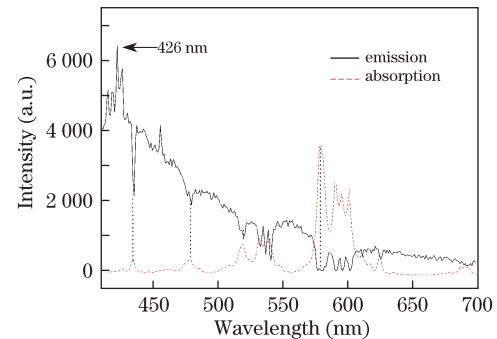

Fig. 4. Room temperature fluorescence spectrum of 1 at.-% Nd^{3+}-doped yttrium lanthanum ceramics stimulated at 358 nm.

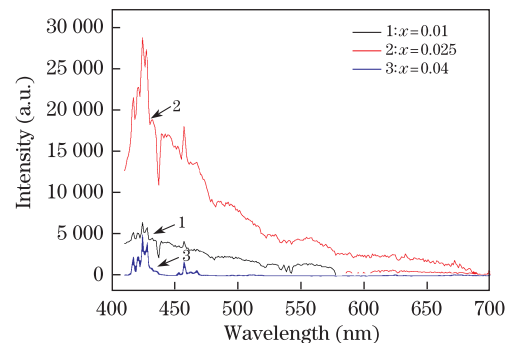Fig. 5. Fluorescence spectra of $(Nd_xY_{0.9-x}La_{0.1})_2O_3$ ($x=0.01$, 0.025, 0.04) transparent ceramics at room temperature ($\lambda_{ex}=358$ nm).
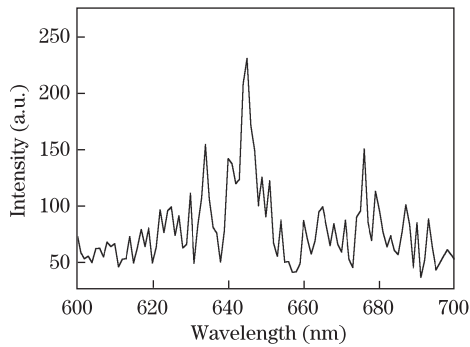
Fig. 6.   Room temperature fluorescence spectrum of Nd:$(Y_{0.9}La_{0.1})_2O_3$ ceramic under excitation at 580 nm.

700 nm, was observed from this spectrum. The edge of this luminescence band is not smooth, there exists four "rift valleys" centered at 436, 480, 541, and 581 nm, which can be attributed to the absorption effect of Nd^{3+} ions by comparing the absorption and fluorescence spectrum of Nd:$(Y_{0.9}La_{0.1})_2O_3$ ceramics. In addition, since there is no absorption peak of $Y_{1.8}La_{0.2}O_3$ fundamental host at 358 nm, no obvious luminescence of $Y_{1.8}La_{0.2}O_3$ host was detected under this condition.

Figure 5 shows the fluorescence spectra of different Nd^{3+} concentration doped $(Y_{0.9}La_{0.1})_2O_3$ transparent ceramics stimulated at 358 nm. All specimens own similar fluorescence spectrum. The emission peak intensity of Nd:$(Y_{0.9}La_{0.1})_2O_3$ transparent ceramics increases with the increase of Nd^{3+} ion content firstly, then decreases obviously when the concentration of Nd^{3+} reaches 4 at.-% due to concentration quenching of Nd^{3+} ions.

The room temperature fluorescence spectrum of Nd^{3+}-doped yttrium lanthanum ceramic under excitation at 580 nm is shown in Fig. 6. In the range from 600 to 700 nm, only a very indistinct red emission peak at about 650 nm can be discerned from the numerous noise peaks of the instrument, which is attributed to the $^2H_{11/2} \rightarrow {}^4I_{9/2}$ transitions of Nd^{3+} ions[14]. This indicates that it is not an effective approach to generating visible luminescence from Nd:$(Y_{0.9}La_{0.1})_2O_3$ transparent ceramics excited by 580 nm light.

In conclusion, $(Nd_xY_{0.9-x}La_{0.1})_2O_3$ (x=0.005~0.04) transparent ceramics are fabricated by solid-state reaction method, and the effects of Nd^{3+} concentration on the visible fluorescence spectroscopic properties are investigated. Under 270-nm excitation, 1 at.-% Nd^{3+}-doped specimen exhibits three emission peaks centered at 396, 426, and 633 nm. The peaks at 462, 497, and 557

nm are caused by the superposition effect of $Y_{1.8}La_{0.2}O_3$ host emission and the absorption of Nd^{3+} ions. When the Nd^{3+} concentration is increased, the emission peak intensities centered at 396 and 426 nm increase while the intensity of the fundamental host emission decreases. At the same time, the 633-nm emission peaks became weak due to the fluorescence re-absorption effect. A broad luminescence band centered at 426 nm is observed from the fluorescence spectrum stimulated at 358 nm. The emission intensity increases with the increase of Nd^{3+} ion content firstly, then decreases obviously when the concentration of Nd^{3+} reaches 4 at.-% due to concentration quenching of Nd^{3+} ions. When the excitation wavelength is set at 580 nm, no visible luminescence is detected.

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