Cooperative up-conversion luminescence of ytterbium doped yttrium lanthanum oxide transparent ceramic

C.G. Dou a, Q.H. Yang a,*, X.M. Hu a, J. Xu b,*

a School of Materials Science and Engineering, Shanghai University, Shanghai 200072, China

b Shanghai Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, Shanghai 201800, China

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Abstract

The up-conversion luminescence of Yb\textsuperscript{3+}-doped yttrium lanthanum oxide transparent ceramic was investigated. It was ascribed to cooperative luminescence originated from the coupled states of the Yb\textsuperscript{3+} ion pairs. The proper doping of La\textsubscript{2}O\textsubscript{3} can remove the cooperative luminescence of Yb\textsuperscript{3+} ion. But excessive La\textsubscript{2}O\textsubscript{3} (at least 10 at.%) the cooperative up-conversion of Yb\textsuperscript{3+}:Y\textsubscript{2}O\textsubscript{3} is obtained again, and the intensity of up-conversion luminescence strengthens with the increase of La\textsubscript{2}O\textsubscript{3} content.

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1. Introduction

Yb\textsuperscript{3+} ion doped laser materials have received considerable attention for laser application over the past years [1–3]. The main interest of Yb\textsuperscript{3+} ion lies in its very simple energy level diagram which leads to very low quantum defects, reducing thermal loads and preventing undesired effects such as excited state absorption. Owing to this unique configuration, Yb\textsuperscript{3+} presents remarkable properties. Yb\textsuperscript{3+}-doped Y\textsubscript{2}O\textsubscript{3} material has much broader absorption and emission band widths, which is solve the problem that the fluorescence spectrum bandwidth of Nd doped materials is narrow [4] and greatly limits their applications in the ultra-short pulse laser systems. Unfortunately, the low absorption cross-section of the Yb\textsuperscript{3+}:Re\textsubscript{2}O\textsubscript{3} (Re = Y, Lu, Se) requires quite high Yb\textsuperscript{3+} concentrations. This could induce additional loss mechanisms, such as cooperative processes involving pairs of Yb\textsuperscript{3+} ions. In Y\textsubscript{2}O\textsubscript{3} host material, the cooperative up-conversion luminescence was detected when Yb\textsuperscript{3+} ion concentration reached 5 at.\% [5].

Cooperative up-conversion luminescence is one special type of anti-stokes in which two interacting ions in the excited state return to the ground state simultaneously, emitting a photon. It is a well-studied phenomenon since firstly observed in YbPO\textsubscript{4} by Nakazawa and Shionoya in 1970 [6] and numerous cooperative up-conversion studies such as Yb\textsuperscript{3+}–Er\textsuperscript{3+} ions or Yb\textsuperscript{3+}–Yb\textsuperscript{3+} ions or Ho\textsuperscript{3+}–Yb\textsuperscript{3+} ions have been carried out up to now [7,8]. Meanwhile up-conversion luminescence has many interesting applications, including data-storage, 3-d volumetric display, guard-against-forged applications, sensor, laser imaging and so on.

Y\textsubscript{2}O\textsubscript{3} is a C-type sesquioxide of a \textit{\textit{T}}\textsuperscript{7} cubic crystal and the La\textsubscript{2}O\textsubscript{3} is hexagon structure, and their space groups are \textit{Ia3} and \textit{P3}m1, respectively. But Rhodes [9] and Harris [10] have reported that La\textsubscript{2}O\textsubscript{3}-doped Y\textsubscript{2}O\textsubscript{3} is a C-type cubic limited solid solution. The effect of La\textsubscript{2}O\textsubscript{3} on the spectroscopic properties of transparent Yb:Y\textsubscript{2}O\textsubscript{3} ceramics has been investigated in our previous work [11]. In this

* Corresponding authors. Tel.: +86 21 56331687; fax: +86 21 56332694
E-mail addresses: yangqiuhongcn@yahoo.com.cn (Q.H. Yang), xujun@mail.shcnc.ac.cn (J. Xu).

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paper, the up-conversion luminescence of Yb$^{3+}$-doped yttrium lanthanum oxide transparent ceramics was studied.

2. Experimental

High purity Y$_2$O$_3$ (>99.99 wt.%), La$_2$O$_3$ (>99.95 wt.%) and Yb$_2$O$_3$ (>99.95 wt.%) powders were used as starting materials. (Yb$_{0.05}$Y$_{0.95-x}$La$_x$)$_2$O$_3$ ($x = 0–0.16$) ceramic were fabricated by weighing the starting materials according to the desired composition. The specimens were sintered at 1300–1750 °C for 5 h under hydrogen atmosphere, then 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 fluorescent lifetime of the ceramics excited with 940 nm LD were measured with a spectrofluorimeter (Fluorolog-3, Jobin Yvon Spex, France) at room temperature.

3. Results and discussion

Fig. 1 is the photograph of transparent (Yb$_{0.05}$Y$_{0.95}$La$_{0.05}$)$_2$O$_3$ ceramics (2 mm thick). The specimen has high transparency and the letters under the ceramic can be seen distinctly.

Fig. 2 shows the transmittance of transparent (Yb$_{0.05}$Y$_{0.00}$La$_{0.05}$)$_2$O$_3$ ceramics. The highest transmittance reaches about 65.4%.

Fig. 3 presents the typical absorption and emission spectrum of (Yb$_{0.05}$Y$_{0.95-x}$La$_x$)$_2$O$_3$ ($x = 0.1$) transparent ceramic, which are similar to those of Yb:Y$_2$O$_3$ [12]. The main absorption peaks are centered at 904, 948 and 974 nm, attributing to Yb$^{3+}$ ion $^2F_{7/2}$–$^2F_{5/2}$ transition. Two obvious emission peaks located at 1031 nm and 1076 nm are corresponding to transition between the sublevel of $^2F_{5/2}$ and the ground state $^2F_{7/2}$.

The fluorescent lifetime of (Yb$_{0.05}$Y$_{0.95-x}$La$_x$)$_2$O$_3$ ($x = 0$) ceramic at 1031 nm is 0.84 ms, which is consistent with Yb:Y$_2$O$_3$ [13]. However, when La$_2$O$_3$ was used as an additive, the lifetimes at 1031 nm of (Yb$_{0.05}$Y$_{0.95-x}$La$_x$)$_2$O$_3$ ceramics are remarkably enhanced by 45–60%, as shown in Fig. 4. The maximum value is 1.34 ms with

![Fig. 2. The transmittance of (Yb$_{0.05}$Y$_{0.95}$La$_{0.05}$)$_2$O$_3$ transparent ceramic.](image1)

![Fig. 3. Absorption and emission spectrum of transparent (Yb$_{0.05}$La$_{0.1}$Y$_{0.95}$)$_2$O$_3$ ceramic.](image2)

![Fig. 4. Fluorescent lifetimes of (Yb$_{0.05}$Y$_{0.95-x}$La$_x$)$_2$O$_3$ transparent ceramics.](image3)
La\(^{3+}\) concentration of 4 at\(^\%\). Yttria (Y\(_2\)O\(_3\)) is a sesquioxide crystal with a cubic bixbyite structure. The crystal contains 32 octahedrally coordinated Y\(^{3+}\) dopant sites per unit cell, 24 distributed at C\(_2\) symmetry and 8 distributed at C\(_3\) symmetry. Triply ionized rare-earth ions enter these sites at random during the ceramics-sintered process [14]. In the Y\(_2\)\(_{1-x}\)La\(_2\)O\(_3\) structure, there are two sites (C\(_2\), C\(_3\)) for the Yb\(^{3+}\) cation which are the sites statistically occupied by Y\(^{3+}\) ion and La\(^{3+}\) ion. Due to the difference between the atomic radius values of Y\(^{3+}\) and La\(^{3+}\) (90.0 pm and 103.2 pm, respectively), it is indeed clear that a disordered occupation of the sites is expected. Absorption bands broadening of Nd doped yttrium lanthanum oxide transparent ceramics for the disordered occupation of the sites has been investigated in our previous work [15], which is similar to property of Nd doped glasses, of the same cause, the fluorescent lifetimes of (Yb\(_{0.05}\)Y\(_{0.95}\)\(_{1-x}\)La\(_x\))\(_2\)O\(_3\) are enhanced obviously, such as Yb doped glasses have longer luminescence lifetimes than Yb doped crystals. The long fluorescent lifetimes are advantageous for energy storage and make it suitable for high power laser output.

Cooperative up-conversion luminescence spectrum of transparent (Yb\(_{0.05}\)Y\(_{0.95}\)\(_{1-x}\)La\(_x\))\(_2\)O\(_3\) (x = 0–0.16) ceramics excited by a 940 nm LD was shown in Fig. 5. The weak cooperative up-conversion luminescence of transparent (Yb\(_{0.05}\)Y\(_{0.95}\)\(_{1-x}\)La\(_x\))\(_2\)O\(_3\) (x = 0) ceramic was detected. But when the value of x is between 0.04 and 0.08, the up-conversion luminescence was not detected. However, the up-conversion luminescence of Yb\(^{3+}\) was detected again after the content of La\(^{3+}\) exceeds 12 at\(^\%\) and the intensity strengthens as the content of La\(^{3+}\) increases. The up-conversion luminescence of Yb\(^{3+}\) ion pairs cooperative luminescence. As a result, the cooperative up-conversion luminescence of Yb\(^{3+}\) ion in (Yb\(_{0.05}\)Y\(_{0.95}\)\(_{1-x}\)La\(_x\))\(_2\)O\(_3\) ceramics disappeared when proper doping of La\(_2\)O\(_3\) (x = 0.04–0.08). Although the lattice constant of Y\(_2\)O\(_3\)-doped with excessive La\(^{3+}\) ion (at least 10 at\(^\%\)) continue to increase, Yb\(^{3+}\) ion pairs cooperative up-conversion luminescence was achieved again and the up-conversion luminescence intensity strengthens with the increase of La\(_2\)O\(_3\) content when excessive La\(_2\)O\(_3\) is doped. This is because the radius of Yb\(^{3+}\) (86.8 pm) ion is close to that of Y\(^{3+}\) ion, Yb\(^{3+}\) primarily substitute the sites of Y\(^{3+}\) ion, which result in the increase of Yb\(^{3+}\) ions concentration in Y\(_2\)O\(_3\) sites, and make it easier to form Yb\(^{3+}\) ions cluster structure in (Yb\(_{0.05}\)Y\(_{0.95}\)\(_{1-x}\)La\(_x\))\(_2\)O\(_3\) transparent ceramics.

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: Yb\(^{3+}\)(2F\(_{5/2}\)) + Yb\(^{3+}\)(2F\(_{5/2}\)) → Yb\(^{3+}\)(2F\(_{7/2}\)) + Yb\(^{3+}\)(2F\(_{7/2}\)) + hv (shown in Fig. 6). The main up-conversion luminescence peak lied at 489 nm in Fig. 5, which is in similarly agreement with the result reported in Ref. [6].

In order to obtain high capacity laser output, the up-conversion luminescence phenomenon must be controlled, so the content of La\(_2\)O\(_3\) must be controlled below 10 at\(^\%\) at transparent Yb\(^{3+}\)-doped yttrium lanthanum oxide ceramics. On the other hand, Yb:Y\(_2\)O\(_3\) ceramic doped with high concentration La\(_2\)O\(_3\) can achieve high efficient up-conversion luminescence.

4. Conclusions

The fluorescent lifetimes at 1031 nm of Yb\(^{3+}\) ion are enhanced greatly due to the disorder in Y\(_2\)\(_{1-x}\)La\(_x\)O\(_3\) ceramics. It was ascribed to cooperative luminescence originated from the coupled states of the Yb\(^{3+}\) ion pairs. The weak cooperative up-conversion luminescence of transparent (Yb\(_{0.05}\)Y\(_{0.95}\)\(_{1-x}\)La\(_x\))\(_2\)O\(_3\) (x = 0) ceramic was detected. But when the value of x is between 0.04 and 0.08, the up-conversion luminescence was disappeared. However, the up-conversion luminescence of Yb\(^{3+}\) was appeared again after the content of La\(^{3+}\) exceeds 12 at\(^\%\) and the intensity strengthens as the content of La\(^{3+}\) increases. The up-con-
version luminescence is deteriorated to obtain high efficiency laser output in IR wavelength, so the content of La$_2$O$_3$ must be controlled below 10 at% at transparent Yb$^{3+}$-doped yttrium lanthanum oxide ceramics. On the other hand, Yb:Y$_2$O$_3$ ceramic doped with high concentration La$_2$O$_3$ can achieve high efficient up-conversion luminescence.

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**References**


