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Two- and three-photon upconversion of LaOBr:Er^{3+}

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Abstract

In this work, the LaOBr:Er^{3+} (0.1%) powders were prepared by solid state reaction. The structural properties of LaOBr:Er^{3+} were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR) and Raman spectroscopy. The results show that LaOBr:Er^{3+} has low phonon energy, which indicate that LaOBr:Er^{3+} may have high luminescent efficiency. Under excitation into $^4I_{11/2}$ level of Er^{3+} ions by 980 nm laser, the two- and three-photon upconverted luminescence of LaOBr:Er^{3+} were recorded. The most intense emissions were come from the $^2H_{11/2}$, $^4S_{3/2} \rightarrow {}^4I_{15/2}$ transitions. The upconversion mechanisms were studied in detail through laser power dependence, and results show that excited state absorption is responsible for the upconversion. The upconversion properties indicate that LaOBr:Er^{3+} may be used in upconversion phosphors.

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Keywords: LaOBr:Er^{3+}; Upconversion; 980 nm; Excited state absorption

1. Introduction

There has been an intense interest in the investigation of upconversion luminescence these years for a wide range of applications, including all-solid compact laser devices operating in the violet–blue–green region, upconversion phosphors, infrared quantum counter detectors and fluorescent labels for biomolecules, etc [1–26]. Trivalent rare earth ions such as Er^{3+}, Tm^{3+}, Pr^{3+} and Ho^{3+} are doped as emission centers in these materials. Among these rare earth ions, the Er^{3+} ion is the most popular as well as one of the most efficient ions for upconversion because the metastable level $^4I_{11/2}$ of Er^{3+} can be conveniently populated by commercial low-cost high-power 980 nm laser diodes [8–12].

The upconversion performance of a material could be enhanced significantly by suitable selection of host matrix [12]. Numerous host matrixes, such as Y_2O_3 [9], Gd_2O_3 [6,7], ZrO_2 [12,19,23], TiO_2 [11], $BaTiO_3$ [11] and fluoride [1–3,14] have been investigated as host matrix for upconversion phosphors due to their low vibrational frequencies.

LaOBr has unique and excellent characteristics in electrical, magnetic, optical and luminescent properties [27–30]. Especially, the luminescent properties make it a well-known host matrix in luminescent materials. For example, Tb^{3+} and Tm^{3+} activated LaOBr phosphors are very efficient X-ray phosphors for radiation image intensifying screens [28–31]. In addition, its vibrational frequency is quite low, which makes it suitable for host matrix as upconversion phosphors. But the study on upconversion luminescence of rare earth ions doped LaOBr is only focused on 785 nm and 514.5 nm excitation [24,25]. To the best of our knowledge, there is no upconversion properties of LaOBr:Er^{3+} under 980 nm excitation.

In this present work, the LaOBr:Er^{3+} (0.1%) powders were prepared by solid state reaction. The structural properties of LaOBr:Er^{3+} were characterized by XRD, FT-IR and Raman spectroscopy. Under excitation into $^4I_{11/2}$ level

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of Er^{3+} ions by 980 nm laser, the two- and three-photon upconverted luminescence of LaOBr:Er^{3+} were recorded. The upconversion mechanisms were studied in detail through laser power dependence, and results show that excited state absorption is responsible for the upconversion.

2. Experimental

The LaOBr:Er^{3+} powder samples were prepared by solid state reaction [24,25]. Briefly, stoichiometric proportions of La_2O_3 (99.99%) and Er_2O_3 (99.99%) were dissolved by hot hydrochloric acid (AR). Hot oxalis acid solution was added into above solution to form $Re_2(C_2O_4)_3$ precipitation, where Re = La and Er. Then $Re_2(C_2O_4)_3$ precipitation was decomposed into Re_2O_3 at 850 °C in air. Finally, the Re_2O_3 obtained was mixed with an excess of NH_4Br (AR) and KBr flux and fired at 1250 °C. After post-treatment white LaOBr:Er^{3+} powders were obtained. In this present work, Er^{3+} to La^{3+} ratio is 0.1%.

X-ray diffraction was carried out on a MAC Science Co. Ltd. (Japan) MXP18AHF X-ray diffraction apparatus with Cu Kα radiation. The Raman spectra was measured and analyzed by using a Jobin-Yvon LABRAM-HR confocal laser microraman spectrometer system equipped with an Ar^{+} ion 514.5 nm laser. The infrared spectra were recorded in the range of 4000–400 cm^{-1} with a Magna-IR 750 Fourier transform infrared spectrometer.

The Stokes emission spectra were measured by a FS920 Spectrofluorometer (Edinburgh Instruments) with a Xe-cw-source (450 W) and RR928P photomultiplier for signal detection. Two- and three-photon upconversion emissions, excited by a 980 nm diode laser, were recorded with a Jobin-Yvon HRD1 double monochromater equipped with a Hamamatsu R456 photomultiplier. The output was analyzed by an EG&G 7265 DSP lock-in amplifier and stored into computer memories. All the measurements were carried out at room temperature.

3. Results and discussion

3.1. Structural properties

The XRD patterns and Raman spectra [24,25] show that LaOBr:Er^{3+} samples have tetragonal PbFCl-type structure with low phonon energy (phonon cutoff = 450 cm^{-1}).

The upconversion efficiency is governed principally by the non-radiative process of the upconversion phosphor materials. The multi-phonon non-radiative decay rate is given by the well-known energy gap law [31]:

$$W_n = W_0[1 - \exp(-hv/kT)]^{-n} \quad (1)$$

where W_n is the rate at temperature T, W_0 is the rate at 0 K, $n = \Delta E/hv$, ΔE is the energy gap between the levels involved, v is the relevant phonon's frequency. When ΔE is equal to or less than 4–5 times the high-energy phonons, the multi-phonon non-radiative relaxation with the emission of a few high-energy phonons becomes competitive with the radiative processes.

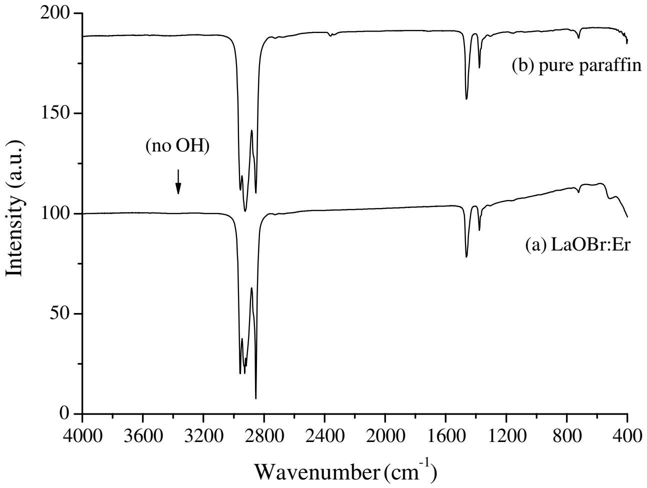

Fig. 1. FT-IR spectra of LaOBr:Er^{3+} (0.1%) in paraffin pellets (a) and (b) pure paraffin as a reference.

Atomic groups with high vibrational frequency, such as OH and CO groups, in materials will increase the multi-phonon non-radiative relaxation rate and hence decrease the upconversion efficiency. FT-IR spectra were used to detect the existence of these groups in LaOBr:Er^{3+} powders.

Fig. 1 presents the FT-IR transmission spectra of LaOBr:Er^{3+} (a) in paraffin pellets and pure paraffin (b) as a reference. It is clear that there are no absorption bands of OH groups (around 3400 cm^{-1}) and CO groups (around 1500 cm^{-1}) in FT-IR spectra of LaOBr:Er^{3+}, which implies that LaOBr:Er^{3+} samples may have higher upconversion luminescence efficiency.

3.2. Stokes emission spectra

Fig. 2(a) shows the Stokes emission spectra of LaOBr:Er^{3+} samples under 261 nm excitation at room temperature. The spectra exhibit six emission bands corresponding to the radiative transitions from some excited states of the Er^{3+} ions. According to the energy level structure of Er^{3+} ions and previous works [6,7,24,31], the assignment can be easy made. The bands in the blue region 400–412 nm and 463–482 nm are assigned to the transitions $^2P_{3/2} \rightarrow {}^4I_{13/2}$ and $^2P_{3/2} \rightarrow {}^4I_{11/2}$ of Er^{3+} ions, respectively. The bands in the green region 516–539 nm and 539–570 nm are associated with the transitions $^2H_{11/2} \rightarrow {}^4I_{15/2}$ and $^4S_{3/2} \rightarrow {}^4I_{15/2}$ of Er^{3+} ions, respectively. The transitions in the red region can be assigned as follows: $^2P_{3/2} \rightarrow {}^4I_{9/2}$ (604–638 nm) and $^4F_{9/2} \rightarrow {}^4I_{15/2}$ (642–683 nm) of Er^{3+} ions.

Fig. 3(a) presents the energy level scheme describing the Stokes emission transitions upon excitation with 261 nm. Under 261 nm excitation, the Er^{3+} ions were excited to the $^4D_{5/2}$ level and then decay non-radiatively to the luminescent levels such as $^2P_{3/2}$, $^2H_{11/2}$, $^4S_{3/2}$ and $^4F_{9/2}$ and give emissions at these levels.