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Synthesis and NIR-to-violet, blue, green, red upconversion fluorescence of Er^{3+}:LaOBr

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Abstract

The Er^{3+}:LaOBr powder were synthesized by a new NH_4Br solid-state reaction, and the structures were studied using XRD and Raman methods. Under 785 nm laser excitation, the upconversion fluorescence spectra in Er^{3+}:LaOBr were recorded and investigated. Four upconverted emission bands centered at about 406 nm (violet), 477 nm (blue), 542 nm (green) and 664 nm (red) were observed. All these upconverted emissions were assigned, and the dominant mechanism was deduced to be excited state absorption. The detailed study of the upconversion processes and the low phonon energy indicate that Er^{3+}:LaOBr would be promising violet and visible upconversion laser materials.

Keywords: Upconversion; Fluorescence; Infrared

1. Introduction

In recent years, the near infrared (NIR) to visible (VIS) and ultraviolet (UV) upconversion luminescence by rare earth (RE) ions doped materials has been investigated extensively, due to the possibility of all-solid-state upconversion lasers operating in VIS and UV spectral domains and the potential applications in areas such as color display, optical data storage, optoelectronics, medical diagnostics, sensor and undersea optical communication [1–6]. Among the RE ion-doped materials that have demonstrated upconversion phenomena, Er^{3+} ion-doped ones have shown efficient NIR to VIS and violet upconversion fluorescence [7–10]. To obtain high upconversion emission efficiency of Er^{3+} ions, most efforts have been spent on fluoride crystals and glasses owing to their lower phonon energies and wide transparent region [11–15]. But as we all know that LaOX (X = Cl, Br) crystal was also a good host material with low phonon energies, and that LaOX:Tb^{3+} and LaOX:Eu^{3+} have been widely used as X-ray intensifying phosphors [16,17]. But the study on upconversion fluorescence of rare earth doped LaOBr materials are very scarce. In the present work, we synthesized the Er^{3+}-doped LaOBr powder using a new NH_4Br solid-state reaction, presented the VIS and UV upconversion fluorescence spectra in Er^{3+}:LaOBr under a 785 nm infrared laser for the first time and investigated in detail the upconversion physical mechanism.

2. Experimental

The LaOBr and Er^{3+}:LaOBr powder samples were prepared by NH_4Br solid-state reaction. The starting materials La_2O_3 and Er_2O_3, are of 99.99% purities. Stoichiometric proportions of rare earth oxides 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. After washing and drying rare earth oxalate $Re_2(C_2O_4)_3$ was decomposed into mixing Re_2O_3 at 850 °C in air. Then the Re_2O_3 obtained was mixed with an excess

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of NH_4Br (AR) and flux and fired at 1250 °C. After post-treatment white Er^{3+}:LaOBr powder was obtained.

The final products were characterized by powder X-ray diffraction (XRD) analysis method using Cu Kα radiation (λ = 1.541838Å) to identify the phases formed in the product. Furthermore, the Raman scattering spectrum for the samples was also measured to get the vibrational modes and phonon energies in LaOBr. For the upconversion study, a semiconductor 785 nm laser (with a maximum power of 1 mW) was employed to excite the Er^{3+}:LaOBr sample. The fluorescence spectra and the Raman spectrum were all measured and analyzed by using a Jobin-Yvon LABRAM-HR confocal laser micro-Raman spectrometer system. All the experiments were performed at room temperature.

3. Results and discussion

3.1. Structures and Raman spectrum

The result of the XRD experiments shows that all the samples have tetragonal PbFCl-type structure (space group P4/nmm–D_{4h}^{7}, $z = 2$). In the RE oxybromide structure, the RE^{3+} ion is coordinated to four oxygen and bromine atoms with C_{4v} point site symmetry [18].

Fig. 1 shows the Raman scattering spectrum of LaOBr polycrystal. Here the excitation light source is 514.5 nm Ar^+ laser. It is found that this spectrum shows five strong peaks corresponding to phonon modes with energy 111.5 cm^{-1}, 129.2 cm^{-1}, 189.8 cm^{-1}, 331.0 cm^{-1} and 430.3 cm^{-1}, which agree well with the previous report in Ref. [18]. As is well known that the host material with low phonon energies would have high upconversion efficiency. Therefore, we can think that LaOBr might be a kind of good upconversion luminescence host material.

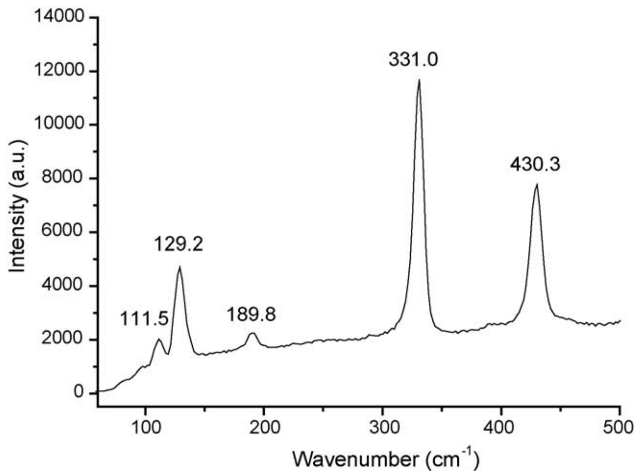

Fig. 1. Raman scattering spectrum in LaOBr polycrystal at room temperature.

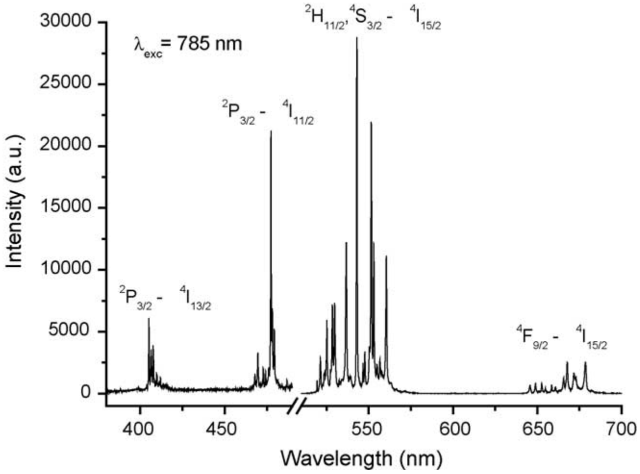

Fig. 2. Upconversion fluorescence spectra of Er^{3+} ions in LaOBr at room temperature pumping with 785 nm laser.

3.2. Upconversion fluorescence of Er^{3+} ions in LaOBr

Fig. 2 shows the observed upconversion luminescence spectrum in LaOBr:1 mol% Er^{3+} under 785 nm laser excitation. This spectrum exhibits four upconversion emission bands centered at about 406 nm (violet), 477 nm (blue), 542 nm (green) and 664 nm (red), respectively. According to the energy level structure of Er^{3+} ions, these four emission bands can be easily assigned as $^2P_{3/2} \rightarrow {}^4I_{13/2}$, $^2P_{3/2} \rightarrow {}^4I_{11/2}$, $^2H_{11/2}$,$^4S_{3/2} \rightarrow {}^4I_{15/2}$ and $^4F_{9/2} \rightarrow {}^4I_{15/2}$ transitions, respectively. Fig. 3 shows the intensity dependence of upconversion emissions versus pump power; the slopes for 406 nm, 477 nm, 542 nm and 664 nm emission bands are 2.64, 2.63,1.83 and 1.82, respectively. This indicates that for the former two emission bands there are three photons participating in the upconversion process, and for the latter two emission bands, the upconversion process involves two photons. In addition, we note that, for our case, energy transfer upconversion (ETU)

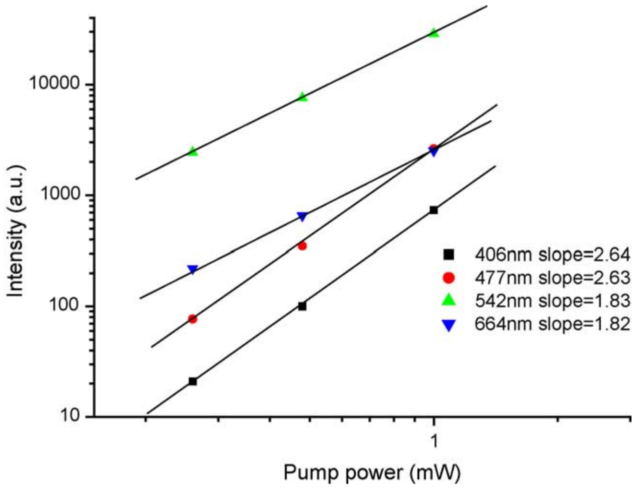

Fig. 3. Power dependence of the upconversion emission intensity pumping with 785 nm laser.

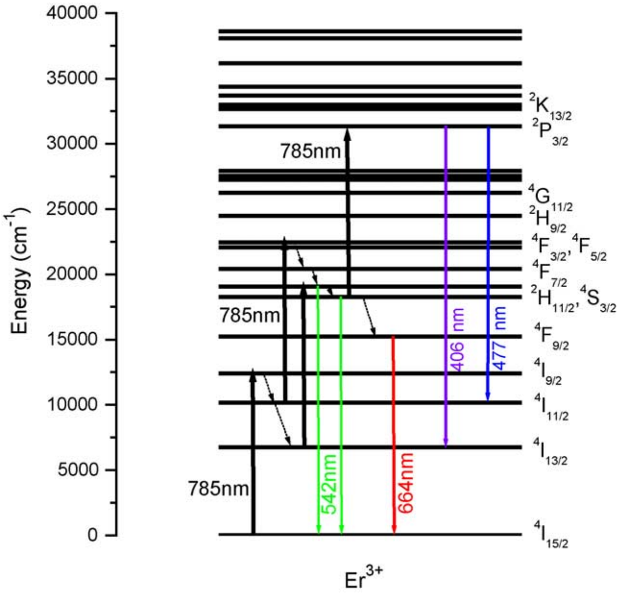

Fig. 4. Upconversion models of Er^{3+} ions in LaOBr under the 785 nm laser excitation. The solid lines stand for the absorption and emission transitions for Er^{3+} ions. The dashed lines stand for the nonradiative relaxations.

process cannot be the dominant upconversion mechanism because the concentration of Er^{3+} ions in LaOBr is low. Therefore, the dominant upconversion mechanism is deduced to be excited state absorption (ESA) (Fig. 4). As is well known that the lifetime of $^4I_{9/2}$ level is comparatively short. Therefore, when $^4I_{9/2}$ level is excited by 785 nm laser excitation, the population will relax quickly to long lifetime $^4I_{11/2}$, as well as the lower $^4I_{13/2}$ level, and then $^4I_{11/2}$ and $^4I_{13/2}$ levels can absorb a second 785 nm photon to $^2F_{3/2,5/2}$ and $^2H_{11/2}$ levels, respectively. Finally, the luminescent levels $^2H_{11/2}$,$^2S_{3/2}$ and $^2F_{9/2}$ all can be populated and the green and red upconversion emission bands (centered at 542 nm and 664 nm) will be seen. So this is a two-photon ESA process.

And for the other two upconversion emission bands centered at 406 nm and 477 nm, Fig. 4 also shows their upconversion mechanism. This is a three photons participant upconversion process. When $^4S_{3/2}$ state are populated, it can absorb the third 785 nm photon and transits to the $^2P_{3/2}$ level, and emit the upconversion luminescence there.

As we all know, the upconversion efficiency is a most important key factor when one solid laser material is used to obtain upconversion laser output. Therefore, for our case, the upconversion efficiency of 406 nm, 477 nm, 542 nm and 664 nm emission bands was estimated and expressed by the ratio of upconverted integrated emission intensity to downconverted integrated emission intensity, since we hardly determine the efficiency of incident laser into upconversion fluorescence. After the quantitative analysis, the ratio of integrated intensities of 406 nm, 477 nm, 542 nm, 664 nm and 966 nm ($^4I_{11/2} \rightarrow {}^4I_{15/2}$) is in the order of 0.00038:0.00068:0.835:0.150:1. From this ratio, it can be seen that the upconversion efficiency of 542 nm and 664 nm emissions is very high. So, we can think that they can be used to get green and red upconversion laser output. And the efficiency for 406 nm and 477 nm upconverted emission bands is low. According to the previous report that the upconverted emission intensity is proportion to P^N (for n photons participant upconversion process, $1 < N \leq n$; P is the pump power) [19], it can be deduced that the reason for low upconversion efficiency is the low pump power (in our experiments, the maximum of the 785 nm laser power is 1 mW). Therefore, we can obtain much higher upconversion efficiency for these two emissions by increasing greatly the pump power P. All these results indicate that, under 785 nm laser excitation, Er^{3+}:LaOBr can be used potentially as violet and blue upconversion laser material in the future.

4. Conclusion

The Er^{3+}:LaOBr luminescent materials are synthesized using a new NH_4Br solid-state reaction and its structures are confirmed. Under 785 nm laser excitation, violet, blue, green and red upconversion fluorescence of Er^{3+} ions in LaOBr is observed and explained successfully. The dominant physical mechanism responsible for green and red upconversion emission bands centered at 542 nm and 664 nm, respectively, is ascribed to be two-photon ESA, and for violet and blue upconversion emission bands (centered at 406 nm and 477 nm, respectively), the dominant mechanism is three photons participant ESA. In addition, the recorded Raman spectrum and the upconversion study in this work show that LaOBr is a very promising host material to obtain violet and visible upconversion laser output.

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