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Spectral variations and energy transfer processes on both Er^{3+} ion concentration and excitation densities in Yb^{3+}–Er^{3+} codoped LaF_3 materials

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Abstract

In comparison with the up-conversion spectra of Yb^{3+}–Er^{3+} codopded systems reported previously, the interesting intensity changes of up-conversion luminescence between the violet, the blue, the green and the red on the both Er^{3+} ion concentration and excitation density with 978 *nm* laser diodes as an excitation source were observed in Yb^{3+}–Er^{3+} codopded LaF_3 powders. In order to clarify the change mechanisms, the up-conversion spectra of LaF_3: 10 mol% Yb^{3+}, 0.5 *m*ol% Er^{3+} and LaF_3: 10 mol% Yb^{3+}, 1 mol% Er^{3+} were investigated and the results indicated that the cross-relaxation processes between Er^{3+} ions and the thermal population of the $^2H_{11/2}$ level play significant roles.

Keywords: Up-conversion luminescence; Cross-relaxation; Near-violet enhancement

1. Introduction

As one of the available approaches searching for short-wavelength solid-state laser, the effect of frequency up-conversion on certain rare-earth ions in different matrix has been investigated widely in past two decades. At present, all practical miniaturized solid-state lasers from ultraviolet to green spectral range have attracted much attention because of a wide range of applications in the fields of high-density optical data storage, all color displays, optical fiber communications, biomedicine and infrared sensors. However, for the realization of short-wavelength solid-state lasers, the first drawback was the laser materials themselvies.

Er^{3+} was the first ion showing up-conversion and APTE (sequential two-photon energy transfers) effect has been demonstrated to be a main way for Er^{3+} up-conversion in earlier time. By excitation of laser in near-infrared wavelength region, all kinds of up-conversion emissions and various energy-transfer processes [1–3] have been presented and investigated. Furthermore, the realization of Yb^{3+}-sensitized mechanism has made up-conversion efficiency of Yb^{3+}–Er^{3+} codoped materials improved greatly [4] and the cross-relaxation processes on a single type of Er^{3+} ions [5–8] with a more efficient up-conversion luminescence have been shown in codoped system. More recently, a detailed review involving Er^{3+} on up-conversion processes in solid has been reported by Auzel [9]. Though it can be seen from those that numerous previous investigation results have concluded the picture of many up-conversion properties with Er^{3+}, some investigations with improved functionality related to Er^{3+} still appear as

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a more active area and, in particular, the search for effective up-conversion laser devices with Er^{3+}, with the availability of efficient laser diodes (LD) in near-infrared range, has been renewed [10,11] due to the relatively small multiphonon decay rates in fluoride matrix leading to a long level lifetimes that enhance the energy-transfer processes between ions [12,13]. Here, we paid a special interest to the materials of Yb^{3+}–Er^{3+} codoped LaF_3 matrix and, in converting 978 nm pump radiation to violet and visible light in Yb^{3+}–Er^{3+} codoped LaF_3 matrix, it was noticed that the energy-transfer processes became so intricate for overall populations of Er^{3+} levels that the existing models were not able to explain the up-conversion spectra observed in the materials. By analyzing the dependences of the populations of $^4F_{9/2}$, $^4S_{3/2}$ $^2H_{11/2}$, $^2H_{9/2}$, $^2G_{7/2}$, $^2K_{15/2}$, and $^2G_{9/2}$ on both the Er^{3+} concentration and the excited density, we found that, except for the cross-relaxation processes considered, the transformation of populations between $^4S_{3/2}$ and $^2H_{11/2}$ level, which were induced by thermal effect with a higher excitation density, played important roles for the spectral changes.

2. Experiments

The experiment was carried out using Er^{3+}/Yb^{3+}-codoped samples of both 89.5 LaF_3-10 YbF_3-0.5 ErF_3 (sample 1) and 89 LaF_3-10 YbF_3-1 ErF_3 (sample 2). Two basic samples were synthesized in Al_2O_3 crucibles at about 900°C under a reduced atmosphere and present the thermal stability. Due to the phonon energy [14] in the materials, it was expected to present significantly lower nonradiative decay rates as compared with other materials. With F-4500 spectrophotometer and a diode-laser up to 2 W of CW radiation at 980 nm, the up-conversion spectra were recorded.

3. Results and discussions

By raising Er^{3+} concentration and excitation density, we illustrate the spectral evolution of the up-conversion emission from Er^{3+} ion at a fixed excitation wavelength 980 nm.Sample 2 exhibits up-conversion fluorescence spectra different from sample 1.

For sample 2, the radiation transition (Fig. 1A) from $^4F_{9/2}$ to $^4I_{15/2}$ always dominates the up-conversion spectra under lower excited densities, then, at higher excited densities the spectra (Fig. 1B) evolve into the pattern similar to sample 1. Further, the typical curves of the emission intensities with the changes of excited densities are shown in inset 1 of Fig. 1. The emission enhancement at 520 nm has recently been reported[15] because the sample was heated from room temperature to 155°C. It is obvious that the phonon-assisted anti-Stokes excitation should be responsible for the population transformation between $^4S_{3/2}$ and $^2H_{11/2}$. Therefore, it is possible that the higher excitation densities lead to the same experimental result. In addition, much interesting enhancement from the infrared

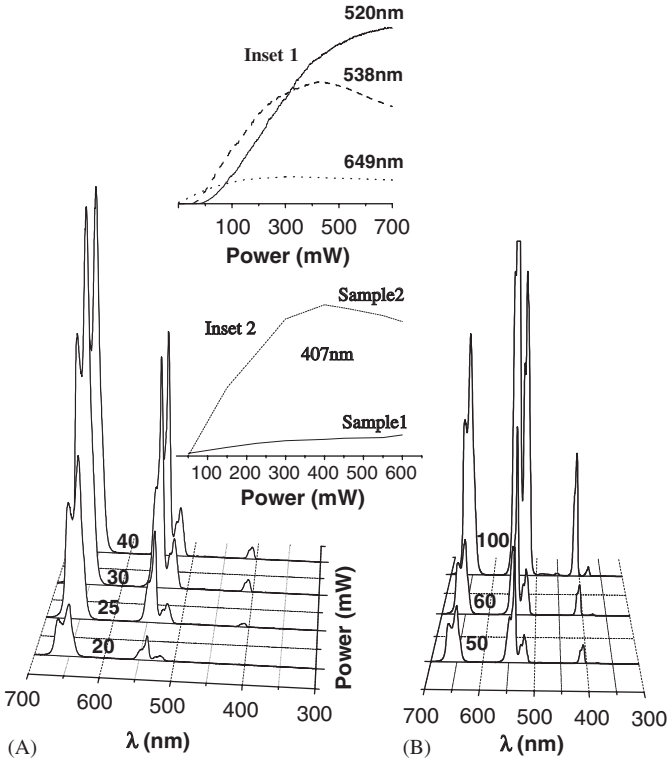

Fig. 1. Upconversion emissions of sample 2 excited at 980 nm from 20 to 100 mW, inset 1 shows the effects from the excitation densities in sample 2 on 649, 538 and 520 nm fluorescence and inset 2 exhibits the evolvements of upconversion luminescence at 407 nm from samples 1 and 2, respectively.

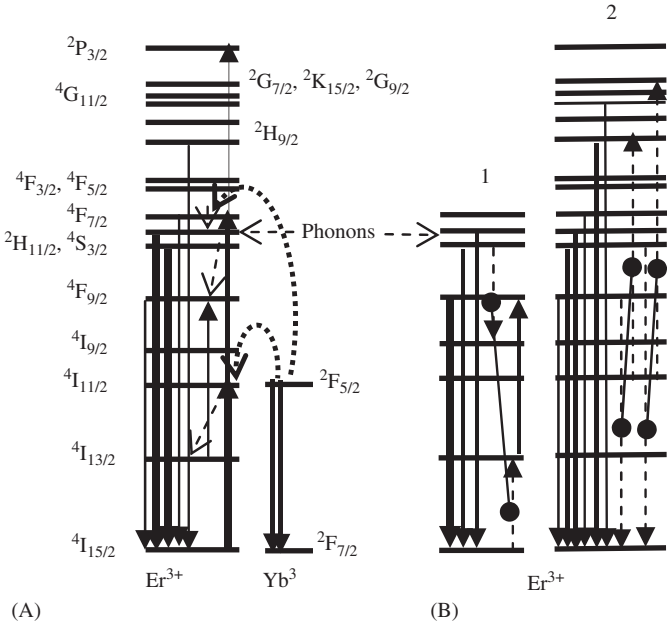

Fig. 2. Er^{3+} energy level. A represents case of sample 1, B displays cases of sample 2.

to the near-violet light emitting (Fig. 1B) is observed in sample 2. It can clearly be seen from inset 2 of Fig. 1 that a ten times up-conversion emission enhancement at 407 nm

has been obtained.as the excited density varies from 0 to 700 mW.

In Yb^{3+} and Er^{3+} codoped systems, it is usually known that the excited Yb^{3+} mainly transfers its energy into $^4F_{7/2}$ and $^2P_{3/2}$ levels of a neighbor Er^{3+} ion by APTE named after Auzel [15], as shown in Fig. 2A, the populations of excited-state levels $^2H_{9/2}$, $^4F_{3/2}$, $^4F_{5/2}$, $^4F_{7/2}$, $^2H_{11/2}$, $^4S_{3/2}$, and $^4F_{9/2}$ in Er^{3+} are accomplished through a series of nonradiative relaxation processes. We have shown from sample 1 that the intensities of the red, the blue and the near violet up-conversion luminescences are independent of the excited densities and weaker at all times. It is proved that the red is attributed to the lower nonradiation relaxation rate resulted by the lower phonon energies in fluoride matrix and, for near violet up-coversion emissions, a lower transition probability from $^4F_{7/2}$ to $^2P_{3/2}$ leads to the low-efficiency excited state absorption (ESA). So, the green up-conversion emissions at both 520 and 539 nm become important in sample 1 with the lower Er^{3+} concentration. However, the spectral changes from sample 2 imply that there must be new up-conversion mechanisms. As indicated in Fig. 2B, by considering the interaction between Er^{3+} ions and the thermal population of $^2H_{11/2}$, the spectral differences between samples 1 and 2 can been explained. Firstly, the red enhancement at 649 nm (Inset 1 in Fig. 1) can be depicted by an important cross-relaxation process, $(^4S_{3/2}+{}^4I_{15/2})$ $(^4I_{9/2}+{}^4I_{13/2})$ [16] under a lower excitation densities. With excited power raising, the cross-relaxation process, $(^4F_{9/2}+{}^4I_{11/2})$ $(^4I_{15/2}+{}^2H_{9/2})$ induces the saturation of the red emission, and simultaneously, makes $^2H_{9/2}$ level populated and the up-conversion luminescence at 407 nm enhanced (Fig. 1B). When the excitation densities further increase, the increase of $^2H_{11/2}$ population can be suggested by the transformation of the emission intensities between 520 and 538 nm (Inset 1 in Fig. 1), and this makes the cross-relaxation process, $(^4S_{3/2}+{}^4I_{15/2})$ $(^4I_{9/2}+{}^4I_{13/2})$ disappeared, leading to the obvious decrease of the red and the near ultraviolet emissions (Insets 1 and 2 in Fig. 1).

4. Conclusions

By examining the up-conversion emission on Er^{3+} concentration and excited density in Er^{3+}/Yb^{3+} codoped LaF_3 matrix, it is well known that, for Er^{3+}/Yb^{3+}-codoped systems, higher Er^{3+} concentration is the main reason which the up-conversion emissions with the near ultraviolet and the red are enhanced. For 1 mol% Er^{3+}- and 10 mol% Yb^{3+} doped LaF_3 samples, the result that reveals a tenfold enhancement at 407 nm is observed as the excited density with 980 nm varied from 20 to 700 mW. So it is concluded that, in the codoped systems, the up-conversion spectral changes can be assigned to the efficient cross-relaxation processes and the thermal population of the $^2H_{11/2}$ level induced by the higher Er^{3+} concentration and the higher excitation power, respectively. Especially, it is possible that the enhancement at 407 nm is devoted to the search for all-solid-state near-ultraviolet light sources for applications in high-density optical data reading and storage, undersea communications and optical displays.

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