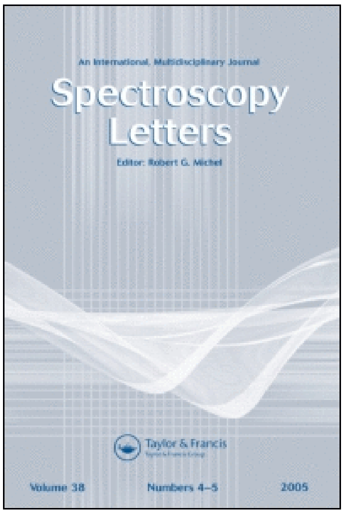

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Photothermally Induced Bistability of Emission of Yb-doped $Ca_4NdO(BO_3)_3$ Single Crystals

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ABSTRACT We report on studies of changes in the emission spectra (excited at 808 nm) of the Yb-doped $Ca_4NdO(BO_3)_3$ single crystals due to the photothermal effects caused by the pulsed Nd:YAG laser. Increase of the sample's surface temperature after laser treatment leads to significant enhancement of the 1040 to 1060 nm emission (ascribed to the Nd^{3+} $^4F_{3/2} \rightarrow {}^4I_{9/2}$, $^4I_{11/2}$ transitions) and simultaneous decrease of the 975 to 1050 nm emission (corresponding to the Yb^{3+} $^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition). We explain such an increase of the Nd^{3+} luminescence by thermally activated $Yb^{3+} \rightarrow Nd^{3+}$ energy transfer.

KEYWORDS Yb–doped crystals, photothermal effects, energy transfer

INTRODUCTION

Intensive search for novel optoelectronic materials, whose properties can be changed by laser light, is focused on the co-doped compounds with efficient energy transfer from one impurity to another. Provided that a proper combination of impurity ions (with closely located energy levels in the spectral region of interest) is chosen, one can get significant enhancement of the emission intensity. The mostly studied materials are new inorganic oxide materials (both glasses and single crystals) co-doped with rare earths ions. In the whole lanthanide series, the Yb^{3+} ions ($4f^{13}$ configuration) are known to be among the most efficient ions with emission in the near infrared spectral range.[1,2] They also have a very simple energy level scheme, which consists of two manifolds only: $^2F_{7/2}$ (the ground state) and $^2F_{5/2}$ (the excited state), located at about $10500\,cm^{-1}$.

From the point of view of luminescence enhancement, a particular interest present the Nd^{3+} and Yb^{3+} co-doped crystals, which earlier were considered as promising materials for luminescent solar concentrators.[3] In crystals doped only with Yb^{3+} ions, there is a single luminescence band at about 1.3 eV,[4–6] which can be excited only directly by the $^2F_{7/2} \rightarrow {}^2F_{5/2}$ absorption transition. With co-doping by Nd^{3+} ions, an additional channel for excitation of the Yb^{3+} luminescence appears. It is related to the 808 nm (1.5 eV) absorption line ($^4I_{9/2} \rightarrow {}^4F_{3/2}$ transition in the Nd^{3+} ion),

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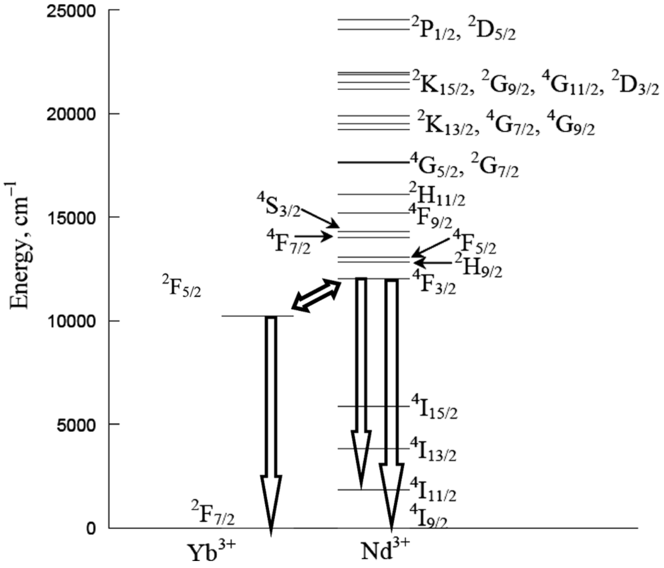

FIGURE 1 Energy level schemes of free Yb^{3+} and Nd^{3+} ions. Energy transfer between closely located energy levels is shown by a double arrow. The emission transitions are shown by the down-ward arrows.

which is very close to the Yb^{3+} $^2F_{7/2} \rightarrow {}^2F_{5/2}$ absorption transition (Fig. 1). A small energy gap between the $^4F_{3/2}$ level of Nd^{3+} and $^2F_{5/2}$ level of Yb^{3+} can be easily bridged by few host phonons. Such a match of the energy levels opens an opportunity for effective energy transfer, which flows from Nd to Yb and backward and affects the intensity of both Yb and Nd luminescence.

It should be also pointed out that simultaneous incorporation of two kinds of impurity ions into a host crystal may lead to noticeable deformations of the host lattice. One of the possible ways to minimize these unavoidable imperfections and simplify the samples preparation is to consider the crystals, which already contain one of these ions as a part of their chemical formula. Then doping with only one impurity will be needed. With this aim, we have chosen the calcium neodymium oxoborate $Ca_4NdO(BO_3)_3$ (CNOB) doped with Yb^{3+} ions (which naturally occupy the Nd^{3+} positions) and considered how its photoluminescence spectra depend on temperature variations induced by the laser excitation. The study of manifestations of these processes in the emission spectra is the main aim of the present paper.

In a recent publication,[7] we have studied the optical absorption spectrum of this compound (including determination of the Judd-Ofelt intensity parameters for Nd^{3+} ions) and second harmonic generation properties. As a further continuation of the previous research, in the present work we focus our attention on studies of the photoluminescence (PL) spectra and their modifications caused by the photothermal effects.

EXPERIMENTAL METHODS

Samples Preparation

The $Ca_4NdO(BO_3)_3$:Yb^{3+} crystals were grown by Czochralski method in the nitrogen atmosphere with 1.0 vol.% of oxygen. Description of the growth process can be found elsewhere.[7] As a result, violet single crystals with characteristic rhombic cross section 21×24 mm and up to 50 mm in length were obtained (Fig. 2). The ytterbium concentration in crystals was equal to 5 at. %, and the distribution coefficient of ytterbium in CNOB was estimated to be $k \approx 1.1$.

Photothermal Treatment and Photoluminescence Spectra

The obtained samples were illuminated by the 20 ns Nd:YAG pulsed laser ($\lambda = 1064$ nm) with the beam spot diameter of about 0.7 mm. The surface thermoheating was monitored using the laser pyrometer with precision up to 0.2 K. The control of the temperature was done from both sides of the illuminated spot surface. The photoexcitation of the samples was done with cw Ti-sapphire laser tunable from 800 to 920 nm. The optimal treatment (maximal PL output) was observed at 808 nm excitation

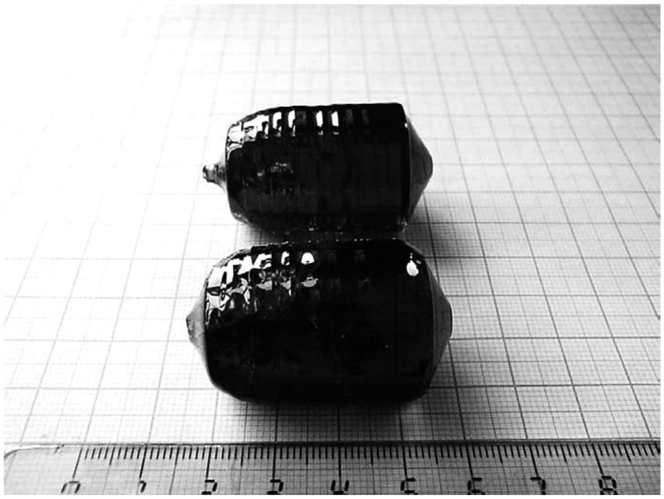

FIGURE 2 Single crystals of $Ca_4NdO(BO_3)_3$ with 5 at.% of Yb.

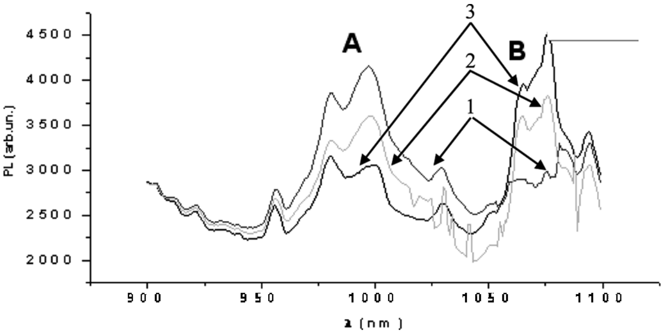

FIGURE 3 Dependence of the $Ca_4NdO(BO_3)_3$:Yb^{3+} PL after illumination by the Nd-YAG 20 ns laser. Curve 1 corresponds to the initially non-illuminated sample. The origin of the A and B peaks is explained in the text. The initial temperature of the samples was 295 K. Curve 2 corresponds to the increase of the illuminated surface temperature – $\Delta T = 30$ K; and curve 3 to $\Delta T = 60$ K. All the spectra are given for the illuminated spot.

wavelength corresponding to the Nd^{3+} absorption from the ground states $^4I_{9/2}$ to the excited manifold $^4F_{3/2}$, which is why we restrict our consideration to this case only. The emitted light was analyzed by a spectrophotometer with spectral resolution $2\,cm^{-1}$ and was detected by a calibrated germanium diode. Additional lock-in was used to enhance the signal to noise ratio. The principal results of the measurements are given in Fig. 3.

RESULTS AND DISCUSSION

The PL excitation was performed at 808 nm, which is the characteristic wavelength of the Nd^{3+} $^4I_{9/2} \rightarrow {}^4F_{3/2}$ absorption transition. The maximal efficiency was observed at excitation power densities about $25\,kW/cm^2$. Emission band B in Fig. 3 corresponds to the superposition of the Nd^{3+} $^4F_{3/2} \rightarrow {}^4I_{9/2}$ and $^4F_{3/2} \rightarrow {}^4I_{11/2}$ transitions, and emission band A is the Yb^{3+} $^2F_{5/2} \rightarrow {}^2F_{7/2}$ intra-center transition. As can be seen from Fig. 3, increase of the surface temperature after the Nd:YAG laser pulse treatment is accompanied by a decrease of the emission band A at 975 nm to 1050 and simultaneously by an enhancement of the emission band B intensity at 1040 nm to 1060 nm. The spectra are presented only for the concentration 3.5 at. % of Yb, because for the lower concentrations the luminescence output was very low. Such a redistribution of intensities suggests effective energy transfer from Yb^{3+} to Nd^{3+} ions.

Comparison of the experimental spectra from Fig. 3 with other Yb^{3+} spectra in matrices like $Sr_{0.6}Ba_{0.4}Nb_2O_6$[8] shows the presence of additional structure of the emission bands studied in the present work. This structure may be of electron-phonon nature because it becomes more pronounced with increased temperature. A particular role may be played here by anharmonic electron-phonon interactions, which are closely related to the thermal effects. It is necessary to add that such kinds of spectral structure are observed only under photothermal treatment, because without thermal and laser treatment no additional structure appeared in the spectra. Since the beam spot diameter is about 0.7 mm, the temperature distribution on the sample's surface is non-homogenous. It should be mentioned here that the temperature distribution is non-homogenous not only in the perpendicular to the surface direction, but also through the cross-section of the beam, which adds more complications to the whole picture.

The obtained results are principally different with respect to the photoinduced changes (Ref. 7), where all investigations were performed with the same laser source for the local thermoheating and excitation (two lasers—one for excitation, one for heating—are used in the present study). Additionally the laser used by Reshak et al.[7] was out of the more efficient band used for excitation of the corresponding Yb^{3+} line.

After the relaxation of temperature or the volume equilibration (which may take several minutes), the PL feature is returned to its beginning state. Jaque et al.[9] demonstrated that in other Nd-Yb co-doped crystal the optically induced thermal treatment could

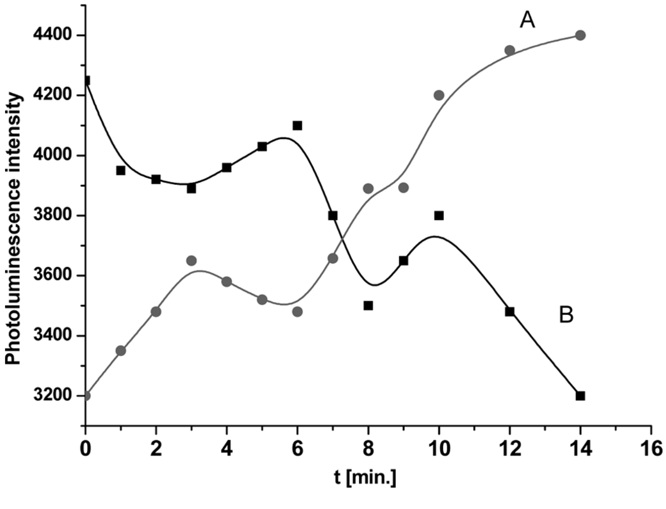

FIGURE 4 Time evolution of the two principal emission peaks A and B (which are the same as in Fig. 3) after switching off the photothermal laser source. The changes of the temperatures are the same as in the Fig. 3.

favor Nd-Yb back energy transfer due to participation of the lattice phonons.

From Fig. 4 one can see that the behavior of two principal spectral bands (A and B) after switching off the external optically stimulated treatment is non-monotonic. These dependences are in antiphase, which may emphasize the principal role of the thermal mechanisms in the processes of the PL changes. Probably all the Nd → Yb transfer processes are determined by the temperature gradients on the surface and in the volume of the samples. Additional role may be played by the temperature gradients appearing due to differences of temperatures on the illuminated sizes of the surfaces and non-illuminated ones. Mathematical modeling of these processes is non-trivial and requires additional investigations.

CONCLUSIONS

Variations of the emission spectra of Yb^{3+}-doped $Ca_4NdO(BO_3)_3$ single crystals under 808 nm excitation were studied using photothermal treatment done by the pulsed Nd:YAG laser. It was established that increase of the surface temperature as a consequence of the laser treatment leads to re-distribution of the PL intensity: the 975 nm to 1050 nm emission (the so called A line, which is the Yb^{3+} $^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition) is more or less quenched, and the 1040 nm to 1060 nm emission (the so called B line, which is due to the Nd^{3+} $^4F_{3/2} \rightarrow {}^4I_{9/2}$ and $^4F_{3/2} \rightarrow {}^4I_{11/2}$ transitions) is enhanced. It was also shown that intensities of these two bands after switching off the external optically stimulated treatment follow a non-monotonic dependence and return to initial situation, when Yb^{3+} emission was more intensive. Their intensities are in antiphase, which indicates principal role of the thermal mechanisms in the processes of the varied PL changes. Probably all the Nd → Yb and Yb → Nd transfer processes are determined by the temperature gradients of the observed processes. Additional role may be played by the temperature gradients appearing due to differences of temperatures on the illuminated sizes of the surfaces and non-illuminated ones.

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