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Spectroscopic investigation of a new crystal: Nd^{3+},Yb^{3+}:YVO_4*

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The absorption and emission spectra of the YVO_4 single crystal co-doped with 1 at.% Nd^{3+} and 1 at.% Yb^{3+} are investigated. The efficient $Nd^{3+} \rightarrow Yb^{3+}$ energy transfer and the back transfer ($Yb^{3+} \rightarrow Nd^{3+}$) are observed at room temperature. The fluorescence lifetime of the $^4F_{3/2}$ level of Nd^{3+} in Nd,Yb:YVO_4 is measured under 808 nm laser light excitation. The efficiency of $Nd^{3+} \rightarrow Yb^{3+}$ energy transfer in YVO_4 is determined to be about 34%.

Keywords: Nd,Yb:YVO_4 crystal, energy transfer, luminescence properties
PACC: 7845, 7860

1. Introduction

For many years YVO_4 as a host material for all-solid-state lasers has been widely investigated due to the large absorption and emission cross-sections of rare-earth ions in this material. Moreover, the YVO_4 crystal is a promising Raman medium,[1,2] and Q-switched lasers with Raman self-conversion have been demonstrated.[3,4] Nd^{3+}-doped YVO_4 crystal is considered as one of the most important laser-active materials and has been applied to commercial laser systems. In recent years, crystals doped with trivalent ytterbium ions (Yb^{3+}) has aroused great interest as directly diode-pumped laser materials around 1 μm.[5] As a rare-earth ion with the simply two-level electronic structure, Yb^{3+} has some important advantages such as high efficiency in energy conversion, long fluorescence lifetime and low quantum defect between the pump and the laser wavelengths, etc. Very recently, spectroscopic and laser performances of Yb:YVO_4 crystal have also been reported and femtosecond pulses have been obtained from a diode-pumped Yb:YVO_4 laser.[6,7] However, there exist two problems that have to be solved. One is the difficulty in realizing the laser operation owing to the reabsorption loss of the quasi-three level system and the other is the particular optical treatments that should be applied when the pump and the laser wavelengths are very close to each other. Since the pioneering work of Auzel,[8] it has been accepted that co-doped materials can greatly enhance the efficiency by a clever combination of sensitizer and activator ions.[9−11] Therefore, the $Nd^{3+} \rightarrow Yb^{3+}$ energy transfer has been proposed as a powerful tool for the creation of pump channels in Yb^{3+}-doped laser crystals. Nd^{3+} and Yb^{3+} co-doped laser crystals combine the multiple pump possibilities of Nd^{3+} ions with the well-known good laser properties of Yb^{3+} ions.[12−16] In particular, Nd^{3+} and Yb^{3+} co-doped crystals are very attractive because the Yb^{3+} laser wavelength can be tuned in a broader spectral range and produce even shorter laser pulses than those obtained in the previous singly doped systems. Several preliminary studies on co-doped Nd^{3+} and Yb^{3+} materials have been reported in the cases of $YAlO_3$ and $GdVO_4$ single crystals,[12,13] $YAl_3(BO_3)_4$ nonlinear crystal[14,15] and metaphosphate glass,[16] etc.

In this work, the spectroscopic properties of an YVO_4 crystal co-doped with 1 at.% Nd^{3+} and 1 at.% Yb^{3+} ions are investigated. The efficient $Nd^{3+} \rightarrow Yb^{3+}$ energy transfer is observed with an energy transfer efficiency of 34% and the back transfer ($Yb^{3+} \rightarrow Nd^{3+}$) is also observed at room temperature.

2. Experimental setup

Co-doped Nd,Yb:YVO_4 crystal is grown by Czochralski method, containing 1 at.% Nd^{3+} and 1

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at.% Yb^{3+} ions. The test sample used for the measurement of absorption and fluorescence spectra is $5 \times 5 \times 1\,mm^3$ in volume, which is cut along the α-axis from the grown single crystal and polished. All the following experiments are carried out at room temperature. The polarized absorption spectra of the crystal are obtained using a monochromator (SpectraPro-500i, Acton Research Corporation) with two different detectors in the visible and near infrared (IR) regions. For continuous-wave (cw) emission spectrum a tunable Ti:sapphire laser (Spectra-Physics 3900 S) is applied to pumping the crystal. The laser wavelength is tuned to 808 nm and then to 976 nm, corresponding to the $^4I_{9/2} \rightarrow {}^4F_{5/2}$ absorption band of Nd^{3+} and the $^2F_{7/2} \rightarrow {}^2F_{5/2}$ absorption band of Yb^{3+} ions, respectively. The excitation source is π-polarized (E // c) and the pump power is about 200 mW. The unpolarized luminescence is dispersed by the monochromator and detected by an InGaAs (Model ID-441) detector. A tunable optical parametric oscillator (OPO) pumped by the third harmonic wavelength at 355 nm of a Q-switched Nd:YAG laser (NL303G, Eksma) is tuned to 976 nm to pump the Nd,Yb:YVO_4 crystal, and the unpolarized fluorescence spectrum is also recorded by the monochromator. The OPO provides 4 ns pulses with a repetition rate of 10 Hz and the pulse energy is about 0.6 mJ.

The time decay of the $^4F_{3/2}$ level of Nd^{3+} in Nd,Yb:YVO_4 is measured. The excitation source for emission lifetime measurement is the tunable OPO, and the excitation wavelength is 808 nm for Nd^{3+} direct pumping. The fluorescence from the Nd,Yb:YVO_4 samples is separated from the pumping light by a filter (RG 850) and then passes through the monochromator. Signals from the monochromator are recorded by a Si-photodiode (PDA520, Thorlabs) connected with a 500-MHz digital oscilloscope (TDS3052B, Tektronix).

3. Experimental results and discussion

The polarized absorption spectra of the Nd,Yb:YVO_4 crystal in the visible and near IR regions of 450–850 nm and 850–1050 nm, are shown respectively in Figs.1(a) and (b).

The absorption bands in the range of 450–920 nm are associated with Nd^{3+} transitions from the $^4I_{9/2}$ ground state to the different excited states.[17] The broad absorption band around 985 nm, which is similar to the absorption spectra of Yb:YVO_4,[6] is corresponding to the $^2F_{7/2} \rightarrow {}^2F_{5/2}$ transition of Yb^{3+}. The peak absorption coefficient at 985 nm for π-polarization is about $6\,cm^{-1}$, which is lower than that reported in Ref.[6] because of the lower concentration of Yb^{3+}.

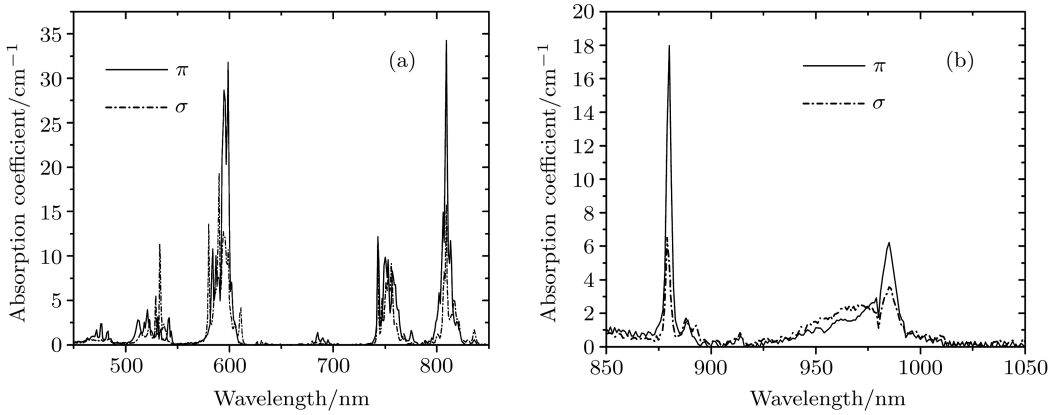


Fig.1. The polarized absorption spectra of Nd,Yb:YVO_4 crystal in the range of (a) 450–850 nm and (b) 850–1050 nm.

Figure 2 shows the emission spectrum in the range of 900–1100 nm under 808 nm cw laser light excitation.

There are three main emission peaks, two of which have the wavelengths centred separately at 1064.5 nm and 1085.5 nm that are associated with the $^4F_{3/2} \rightarrow {}^4I_{11/2}$ of Nd^{3+} ions. The broad fluorescence around 990 nm is associated with the $^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition of Yb^{3+} ions. The presence of Yb^{3+} emissions un-

der Nd^{3+} absorption is a clear evidence that efficient $Nd^{3+} \rightarrow Yb^{3+}$ energy transfer occurs. To obtain a full understanding of these emission spectra, a schematic diagram of the energy-level of Nd^{3+} and Yb^{3+} ions in YVO_4 is shown in Fig.3.

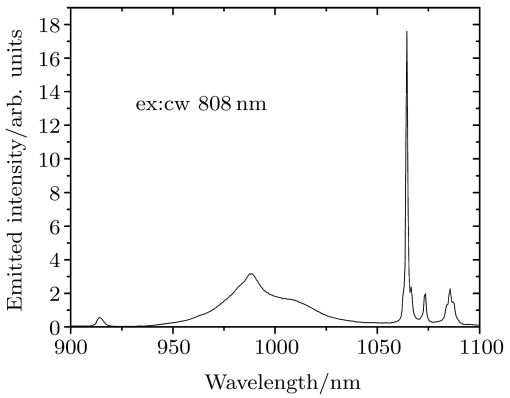


Fig.2. The emission spectrum of Nd,Yb:YVO_4 crystal under 808 nm cw excitation.

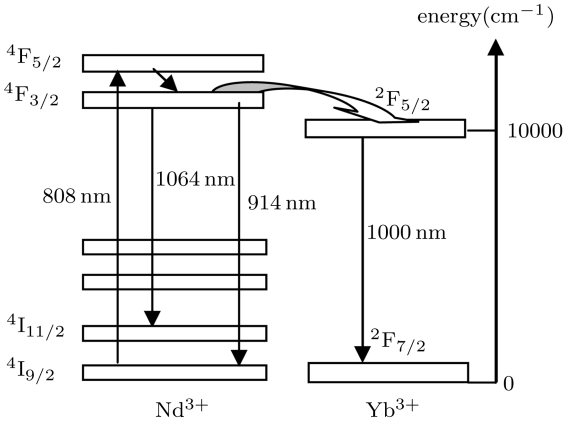


Fig.3. Schematic diagram of the energy-levels of Nd^{3+} and Yb^{3+} ions in YVO_4.

As for other Nd^{3+}; Yb^{3+} co-doped crystals and glasses there is an energy gap ΔE between the $^4F_{3/2}$ (Nd^{3+}) and $^2F_{5/2}$ (Yb^{3+}) metastable excited states. As a consequence, resonant energy transfer is not possible. The energy transfer between the Nd^{3+} and Yb^{3+} ions has been reported in several crystals and glass hosts, and it is attributed to the $^4F_{3/2}$, $^2F_{7/2} \rightarrow {}^4I_{9/2}$, $^2F_{5/2}$ phonon-assisted process.[12,14,16] Based on low-temperature fluorescence spectra,[18] the lowest crystal field component of the $^4F_{3/2}$ multiplet of Nd^{3+} is located at 11372 cm^{-1}. The energy of the highest crystal field component of the $^2F_{5/2}$ multiplet of Yb^{3+} cannot be determined precisely but it should be more than 10152 cm^{-1} from the absorption spectra. Consequently, the energy mismatch will not exceed 1220 cm^{-1}. The rich Raman spectrum[19] of YVO_4 single crystal at room temperature provides the possibility of non-radiative energy transfer from the Nd^{3+} ions to the Yb^{3+} ions by the creation of one or more phonons. The energy mismatches for $^4F_{3/2} \rightarrow {}^4I_{11/2}$ (Nd^{3+}) and $^2F_{7/2} \rightarrow {}^2F_{5/2}$ (Yb^{3+}) are similar in magnitude but opposite in sign, hence phonon annihilation is required for energy conservation. Although the oscillator strength for Nd^{3+} transitions from $^4F_{3/2}$ to $^4I_{11/2}$ is greater than from $^4F_{3/2}$ to $^4I_{9/2}$, energy transfer involving the former should be important only at very high temperatures.

Figure 4(a) shows the unpolarized emission spectrum of the crystal under 976 nm cw excitation. We can see from the figure that the intensity of the $^4F_{3/2} \rightarrow {}^4I_{11/2}$ emission (1064 nm) of Nd^{3+} ions is very weak and almost neglectable. The unpolarized emission spectrum of the crystal excited by the pulsed OPO is displayed in Fig.4(b).

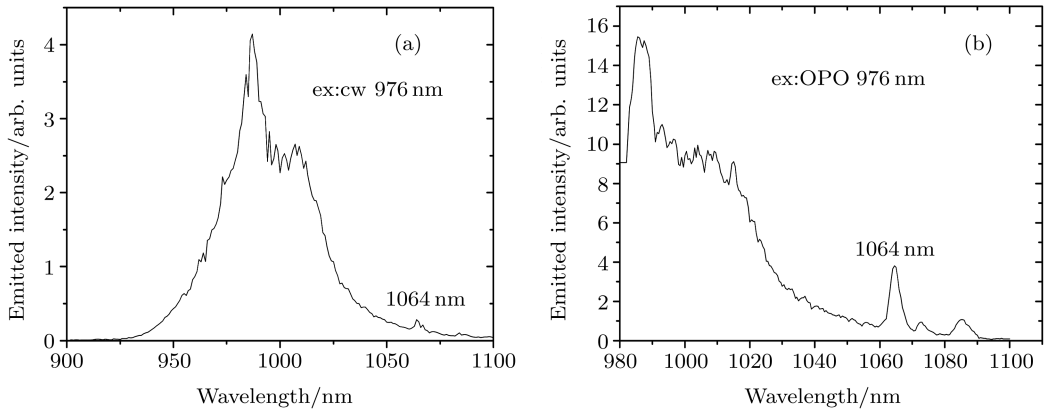


Fig.4. The unpolarized emission spectrum of the Nd,Yb:YVO_4 crystal under the 976 nm (a) cw excitation and (b) pulsed OPO excitation.

When the pulsed OPO is applied as a pump source, the $^4F_{3/2} \rightarrow {}^4I_{11/2}$ emission of Nd^{3+} ions is observed obviously, which is an evidence of the $Yb^{3+} \rightarrow Nd^{3+}$ energy back transfer. The Yb^{3+} emission barycenter (990 nm) and one of the Nd^{3+} absorption barycenters (880 nm) are separated by 1260 cm^{-1} in energy. As a consequence, efficient $Yb^{3+} \rightarrow Nd^{3+}$ energy back transfer requires the absorption of one or more phonons with a total energy close to 1260 cm^{-1}. The crystal heating induced by the pulsed OPO with a peak power of about 150 kW should be much stronger than that induced by the Ti:sapphire (cw) laser, which could be the reason why the $Yb^{3+} \rightarrow Nd^{3+}$ energy back transfer of the former is much enhanced.[15]

The lifetime of the $^4F_{3/2}$ level in Nd:YVO_4 crystal containing 1 at.% Nd^{3+} is about 98 μs,[20] which is reduced to 65 ± 5 μs in the Nd,Yb:YVO_4 sample. The efficiency of the $Nd^{3+} \rightarrow Yb^{3+}$ energy transfer is about 34%, which is given by $\eta_t = 1 - \tau/\tau_{Nd}$. Here τ is the fluorescence lifetime of the $^4F_{3/2}$ level of Nd^{3+} in the presence of Yb^{3+} and τ_{Nd} is the intrinsic lifetime of the $^4F_{3/2}$ level of Nd^{3+} in Nd:YVO_4 crystal. The value obtained for energy transfer efficiency can be compared with those reported for 3.8 at.% Nd^{3+} and 3.6 at.% Yb^{3+} co-doped $GdVO_4$ ($\eta_t = 0.78$),[13] for 2 at.% Nd^{3+} and 1 at.% Yb^{3+} co-doped $YAl_3(BO_3)_4$ ($\eta_t \approx 0.16$),[14] for 1 at.% Nd^{3+} and 1 at.% Yb^{3+} co-doped metaphosphate glass ($\eta_t \approx 0.18$),[16] but it is lower than that reported in Ref.[13], which may be ascribed to the lower concentrations of the Nd^{3+} and Yb^{3+} ions.

4. Conclusions

We report on the spectroscopic properties of Nd^{3+} and Yb^{3+} co-doped YVO_4 single crystal. The $Nd^{3+} \rightarrow Yb^{3+}$ energy transfer and the back transfer $Yb^{3+} \rightarrow Nd^{3+}$ are observed at room temperature. The fluorescence lifetime of the $^4F_{3/2}$ level of Nd^{3+} is measured, and the efficiency of $Nd^{3+} \rightarrow Yb^{3+}$ energy transfer in YVO_4 is determined to be about 34%. In summary, Nd,Yb:YVO_4 crystal is a promising candidate for tunable laser oscillation through one of the multiple pump channels of Nd^{3+} ions by efficient energy transfer.

References

[1] Kaminskii A A, Ueda K, Eichler H J, Kuwano Y, Kouta H, Bagaev S N, Chyba Th H, Barnes J C, Gad M A, Murai T and Lu J 2001 *Opt. Commun.* **194** 201

[2] Lu G W, Xia H R, Meng X L, Liu X S and Yang W B 2002 *Acta Phys. Sin.* **51** 424 (in Chinese)

[3] Chen Y F 2004 *Opt. Lett.* **29** 1251

[4] Kisel V E, Troshin A E, Tolstik N A, Shcherbitsky V G, Kuleshov N V, Matrosov V N, Matrosova T A and Kupchenko M I 2005 *Appl. Phys.* B **80** 471

[5] Krupke W F 2000 *IEEE. J. Sel. Top. Quantum Electron.* **6** 1287

[6] Kisel V E, Troshin A E, Tolstik N A, Shcherbitsky V G, Kuleshov N V, Matrosov V N, Matrosova T A and Kupchenko M I 2004 *Opt. Lett.* **29** 2491

[7] Kisel V E, Troshin A E, Shcherbitsky V G, Kuleshov N V, Matrosov V N, Matrosova T A, Kupchenko M I, Brunner F, Paschotta R, Genoud F M and Keller U 2005 *Opt. Lett.* **30** 1150

[8] Auzel F 1966 *C. R. Académie des Sciences, Paris* **262** 1016

[9] Wang D Y, Xie P B, Zhang W P, Lou L R and Xia S D 2001 *Acta Phys. Sin.* **50** 329 (in Chinese)

[10] Zhang L, Zhang J J, Hu H F and Lin F Y 2001 *Chin. Phys.* **10** 58

[11] Wu Z H, Song F, Liu S J, Cai H, Su J, Tian J G and Zhang G Y 2006 *Acta Phys. Sin.* **55** 4659 (in Chinese)

[12] Weber M J 1971 *Phys. Rev.* B **4** 3153

[13] Zhuang N F, Xu X L, Zhao B, Chen J L, Lin X S and Chen J Z 2004 *J. Crystal Growth* **271** 151

[14] Jaque D, Ramirez M O, Bausa L, Speghini A, Bettinelli M and Cavalli E 2004 *J. Opt. Soc. Am.* B **21** 1203

[15] Ramirez M O, Jaque D, Bausa L E, Martin I R, Lahoz F, Cavalli E, Speghini A and Bettinelli M 2005 *J. Appl. Phys.* **97** 093510

[16] Liegard F, Doualan J L, Moncorge R and Bettinelli M 2005 *Appl. Phys.* B **80** 985

[17] Zhang H J, Meng X L, Zhu L, Wang C Q, Chow Y T and Lu M K 2000 *Opt. Mater.* **14** 25

[18] Sardar D K and Yow R M 2000 *Opt. Mater.* **14** 5

[19] Miller S A, Caspers H H and Rast H E 1968 *Phys. Rev.* **168** 964

[20] Tucker A W, Birnbaum M, Fincher C L and Erier J W 1977 *J. Appl. Phys.* **48** 4907