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Concentration quenching in Yb:YAG

Peizhi Yang[a,]*, Peizhen Deng[b], Zhiwen Yin[a]

[a] *Laboratory of Functional Inorganic Materials, Shanghai Institute of Ceramics, Chinese Academy of Sciences, 1295 Dingxi Road, Shanghai 200050, People's Republic of China*

[b] *Shanghai Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, Shanghai 201800, People's Republic of China*

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Abstract

The concentration quenching in Yb:YAG crystals with high Yb^{3+} doping level was demonstrated, and studied as well. The color center and lattice distortion which originated from Yb^{2+} are the main reasons for producing the concentration quenching in unannealed Yb:YAG crystals, and after annealing at 1600°C in oxygen atmosphere for 24 h, Yb^{2+} vanished. Trace impurity ions are also responsible for this phenomenon. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

In recent years, Yb^{3+} doped materials have attracted great interest for application in high-efficiency and high-power diode pumped laser systems [1] with the development of InGaAs laser diode [2]. Among the numerous Yb-doped crystals, Yb:YAG is one of the most promising as a high-power diode-pumped laser gain media [3] due to the small quantum defect between the pump and the laser photons resulting in low thermal loading, long radiative lifetime of the upper laser level, large absorption width, broad emission bands, no excited state absorption and up-conversion loss. Moreover, Yb:YAG also exhibits high thermal conductivity and tensile strength.

Yb^{3+}, the simplest energy level scheme of rare-earth active ion, has only two multiplet manifolds—the $^2F_{7/2}$ ground state and the $^2F_{5/2}$ excited state—which are separated by about 10,000 cm^{-1}. Theoretically, Yb^{3+} doping level in Yb:YAG can be very high without concentration quenching. However, the measured fluorescence lifetime was observed to decrease at higher Yb^{3+} doping concentration [4].

In this paper, we report the concentration quenching observed in Yb:YAG with different doping levels, and study the reason behind this phenomenon.

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*Corresponding author. fax: +86-21-62513903.
E-mail address: pzhyang@hotmail.com (P. Yang).

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2. Experiment

2.1. Sample preparation

The [1 1 1]-oriented Yb:YAG crystals with 5, 10, 20 and 30 at% Yb^{3+} doping level used in the experiment were grown by the CZ method. The detailed growth parameters are shown in Ref. [5]. The samples used in the absorption spectra measurement are 2–3 mm thick, in the IR measurement are 20 mm, and that in the fluorescence lifetime measurement are 0.5 mm.

2.2. Spectral and fluorescence lifetime measurement

A Perkin-Elmer Lambda 9 Spectrophotometer was employed for acquisition of the absorption spectra. IR spectra measurements were performed in a model $2750\sim50$ infrared spectrometer (Hitachi). The fluorescence lifetimes were acquired by exciting the samples with InGaAs LD as the pump source (excited at 970 nm) and detected by an S-1 photomultiplier tube. The fluorescence decay curves were recorded and averaged with a computer controlled transient digitizer.

3. Result and discussion

The fluorescence lifetimes of Yb:YAG crystals with different doping levels are shown in Fig. 1.

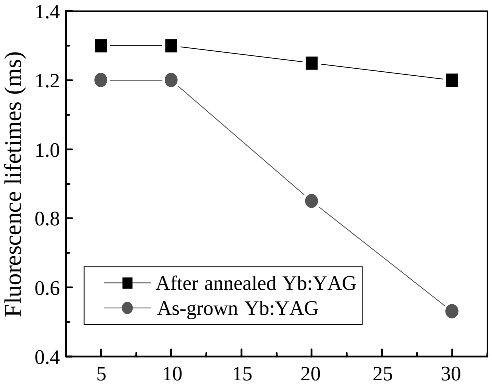

Fig. 1. The fluorescence lifetimes of Yb:YAG with different doping concentration.

The lifetimes of the four as-grown samples are shorter than those of the annealing samples. For as-grown samples with a Yb^{3+} doping level of more than 10 at%, the lifetimes are shorter than the low doping level. Owing to radiative trapping, after annealing, the measured fluorescence lifetimes with different doping levels are longer than theoretic values of 1.08 ms [4].

In general, with the doping concentration increase, the distance between active ions decreases, and when the distance is short enough (<1–2 nm). The interaction between active ions will occur and cause concentration quenching. Thus the lifetimes of upper level decrease. Usually, the concentration quenching may occur through the following channels: (1) Cross-relaxation between active ions. (2) The transference of active energy between ions and in the end transfer to the impurity ions, and then forming the quenching center. (3) The interaction between active ions and host will transfer the energy to lattice defects. (4) A lot of defects such as color center, OH$^-$ and other kinds of defects may trap energy and form the quenching center. Yb^{3+}, the simplest rare earth active ion, is two-level system in nature. Thus, the cross-relaxation between active ions ($^2F_{5/2}+{}^2F_{7/2}={}^2F_{7/2}+{}^2F_{5/2}$) has no effects on ions upconversion in the upper level. The concentration quenching occurs in Yb:YAG crystals mainly through channels (2)–(4).

The absorption spectra of as-grown Yb:YAG and annealed Yb:YAG at 300–800 nm are shown in Fig. 2. Obviously, two absorption bands located at wavelengths 375 and 625 nm, respectively, with increase in doping level, the absorption intensity increases, and after annealing at 1600°C in oxygen for 24 h, the two absorption bands vanish. These two absorption bands degrade intrinsic absorption bands and emission bands of Yb^{3+} in Yb:YAG. The crystals were grown in an inert atmosphere, so it is possible for Yb^{3+} to be reduced to Yb^{2+}, and 375 nm absorption band is attributed to the 4f→5d transition of Yb^{2+} in the YAG host. The experiments on Yb:YAG crystals with different annealing conditions verified that 625 nm absorption band and 375 nm absorption band weakened or disappeared at the same time. As a result the F center perturbed by the rare-earth ion, Yb^{2+} is

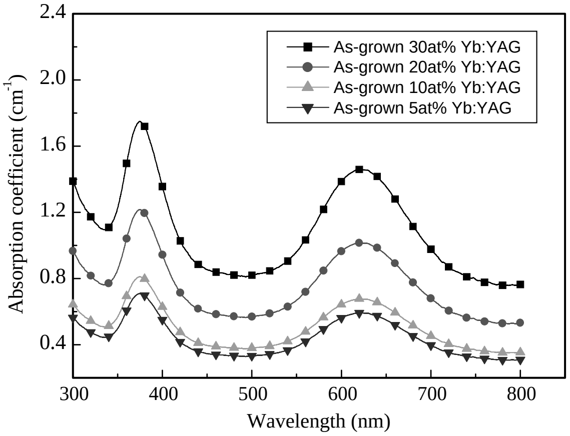

Fig. 2. The absorption spectra of as-grown Yb:YAG with different Yb^{3+} doping levels in the range 300–800 nm.

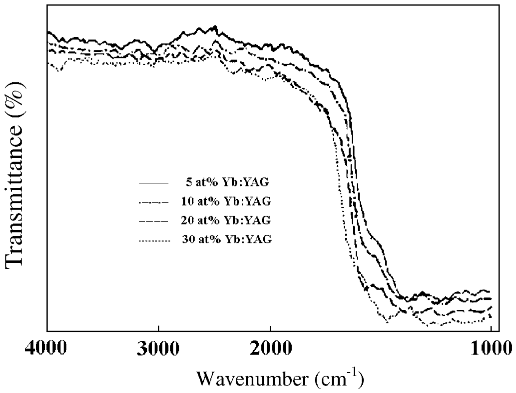

Fig. 3. IR spectra of Yb:YAG with different Yb^{3+} doping concentration.

responsible for the 625 nm absorption band. Therefore, after annealing, $Yb^{2+} \rightarrow Yb^{3+}$, the two absorption bands disappear. The effects of Yb^{2+} on Yb:YAG involved two aspects: one is that the charge needs to be compensated and the Re–F color center is formed; another causes the distortion of lattices due to the discrepancy between ion radius of Yb^{2+} and Y^{3+} in the octahedral structure ($R_{Yb2+} = 1.14$, $R_{Yb3+} = 0.985$, $R_{Y3+} = 1.019$ pm), and then reduces the fluorescence lifetime. Hydroxyl group impurities in YAG and rare-earth-doped YAG are associated with the color center in the IR, visible and some UV spectral region [6], which result in nonequivalent crystal field around doped ion and nonradiative relaxation by the doping ion hydroxyl coupling. From Fig. 3, we can see that there are few hydroxyl groups in the Yb:YAG crystals, and so its effects on concentration quenching may be negligible.

The nonradiation transition by Yb^{3+} ions reacting with YAG host may be considered as a multiphonon relaxation process [7]. The probability of nonradiative energy transfer was depicted as follows:

$$W_{\mathrm{nr}} = \frac{1}{\tau_{\mathrm{m}}}, \tag{1}$$

$$W_{\mathrm{nr}} = W_{\mathrm{o}}\varepsilon_p, \tag{2}$$

$$W_{\mathrm{nr}} = C\exp(-\alpha\Delta E)\,[n(T) + 1]^{p_i}, \tag{3}$$

where ε represents the decay probability of multiphonon, $\varepsilon = W_p/W_{p-1} < 1$; p_i is the order of phonon, $p_i = \Delta E/h\omega$; ΔE is the energy gap of the nearest energy levels, $h\omega$ is the phonon energy, $n(T)$ is the phonon mode, $n(T) = [\exp(h\omega/kT) - 1]^{-1}$, C, α, constants relevant to the hosts. Therefore, nonradiative transition probability of multiphonon process relies first of all on the phonon order, i.e. the energy gap of energy levels, and also on the phonon energy. The former determines the energy level structure of ions, and the latter is dependent on the structure of hosts. For as-grown Yb:YAG crystal boules, with the increase of Yb^{3+} doping level, concentrations of Yb^{2+} increased proportionally, which causes the lattice distortion and affects the energy level structure of Yb^{3+}. As a consequence, the fluorescence lifetime of Yb^{3+} was reduced.

After annealing, the lifetime was reduced to about 4% for 20 at% Yb:YAG and it was reduced to about 9% for 30 at% Yb:YAG. These small changes may be related to the impurity ions in Yb:YAG crystals. Since the raw materials Y_2O_3 and Al_2O_3 used in crystal growth were of 4N5 purity, and Yb_2O_3 was of 3N5 purity, the impurity ions in Yb:YAG mainly come from Yb_2O_3. The impurity ions in Yb_2O_3 were analysed by ICP, and the results are given in Table 1. Usually, energy transfer between Yb^{3+} and impurity ions can take place directly or assisted by phonon, and is a

Table 1
Impurities in Yb:YAG

Impurity	Concentration (wt%)
Er_2O_3	<0.001
Lu_2O_3	<0.001
Fe_2O_3	0.0003
CuO	0.0005
Tm_2O_3	0.001
Y_2O_3	0.001
CaO	0.019
SiO_2	0.001

diffusion-limited relaxation process. The fluorescence lifetime of Yb^{3+} is related to concentrations of Yb^{3+} and other impurity ions by the equation [8]

$$\frac{1}{\tau_f} - \frac{1}{\tau_0} = K_D N_{Yb} N_0, \tag{4}$$

where τ_f is the fluorescence lifetime of Yb^{3+}, τ_0 is the radiative lifetime of Yb^{3+} doped crystal without other impurity ions. N_{Yb} and N_0 are concentrations of Yb^{3+} and other impurity ions for doped system containing other impurity ions.

Obviously, with increase of Yb^{3+} concentration in Yb:YAG, the concentrations of impurity ions increased proportionally. As a consequence, fluorescence lifetime of Yb^{3+} was reduced.

4. Conclusion

In summary, the measurements on fluorescence lifetimes of Yb:YAG with different doping levels demonstrated that there were concentration quenching in Yb:YAG crystal for Yb^{3+} doping concentration of more than 10 at%. This phenomenon is mainly attributed to Yb^{2+}, which results in color center and lattice distortion of Yb:YAG. After annealing at 1600°C in oxygen atmosphere for 24 h, $Yb^{2+} \rightarrow Yb^{3+}$ and the color center and the lattice distortion were eliminated. Trace impurity ions are detected by means of ICP, which are also responsible for the concentration quenching at high Yb^{3+} doping level.

Acknowledgements

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References

[1] T.Y. Fan, IEEE J. Quantum Electron. 29 (1993) 1457.
[2] P. Lacovara, H.K. Choi, C.A. Wang, et al., Opt. Lett. 16 (1991) 1089.
[3] A. Giesen, H. Hügel, A. Voss, Appl. Phys. B 58 (1994) 365.
[4] D.S. Sumida, T.Y. Fan, Opt. Lett. 19 (1994) 1343.
[5] P.Z. Yang, P.Z. Deng, J. Xu, et al., J. Cryst. Growth 216 (2000) 348.
[6] D.P. Devor, R.C. Pastor, L.G. Deshazer, J. Chem. Phys. 30 (1984) 4104.
[7] L.A. Riseberg, M.J. Weber, Proc. Opt. 14 (1976) 91.
[8] B. Peng, T. Izumitani, Opt. Mater. 4 (1995) 701.