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# Study of the effects of Cr ions on Yb in Cr,Yb:YAG crystal

Jun Dong <sup>\*</sup>, Peizhen Deng, Jun Xu*Shanghai Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, P.O. Box 800-216, Shanghai 201800, China*

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## Abstract

The absorption and fluorescence spectra of Cr,Yb:YAG crystal were measured. There are two absorption bands at 940 nm and 968 nm although the absorption coefficient is lower than that of the absorption peak of Yb:YAG superimposed in Cr:YAG absorption peak. The emission peak intensity is 4 times lower than that of Yb:YAG, which may be caused by the existence of the ground state absorption of Cr<sup>4+</sup> which quenches the Yb<sup>3+</sup> emission intensity. Although the emission peak of Cr,Yb:YAG is lower than that of Yb:YAG, there is an advantage of this crystal which combines the saturable absorber and gain medium into one and can be a self-Q switching laser crystal if Cr,Yb:YAG crystal is pumped with high energy power. © 1999 Published by Elsevier Science B.V. All rights reserved.

*Keywords:* Cr,Yb:YAG crystal; Self-Q-switching laser; Absorption and fluorescence spectra

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## 1. Introduction

Diode-pumped Q-switching solid-state lasers have been demonstrated to have high efficiency, high average power and high energy per pulse. It is well known that Q-switching lasers can be applied widely in lidar, remote sensing, pollution detection, non linear-optical processes, and material processing. The saturable absorbers which have been successfully used for passive Q-switched lasers include dye [1], LiF:F<sub>2</sub> color center crystals [2], Cr<sup>4+</sup>-doped crystals [3–6], etc. Among them, Cr<sup>4+</sup>-doped crystals developed in recent years such as Cr<sup>4+</sup>:YAG [3], Cr<sup>4+</sup>:GSGG [4], Cr<sup>4+</sup>:YSO [5], and Cr<sup>4+</sup>:Mg<sub>2</sub>SiO<sub>4</sub> [6] and so on, have the advantages of good photo-

chemical and thermal stability, large absorption cross-section, low saturable intensity and high damage threshold. In addition, Cr<sup>4+</sup> can be doped into the gain medium to form a self-Q-switched laser [7]. As a result of the above advantages, Cr<sup>4+</sup>-doped crystals become the most promising saturable absorber for passively Q-switched lasers.

Recent advances in high performance strained layer diode lasers, with a wavelength between 0.9 and 1.1 μm have stimulated interest in diode pumped Yb<sup>3+</sup> lasers [8,9]. Further more, diode-pumped Yb:YAG lasers have several advantages relative to Nd:YAG lasers, such as low thermal load, long upper state lifetime, large absorption width around the InGaAs laser emission range, a relatively large emission cross section, high thermal conductivity, easy growth of high quality and moderate concentration crystal without concentration quenching, and strong energy-storing capacity. So the Cr,Yb:YAG

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<sup>\*</sup> Corresponding author. Fax: +86-21-59928755; e-mail: d\_jun@kali.com.cn

crystal codoped with 0.1 at.% Cr and 10 at.% Yb was grown by standard Czochralski (CZ) method and the effect of annealing on the Cr and Yb was studied. The effects of Cr ions on the absorption and emission properties of Yb was studied as well.

## 2. Experiments

Cr,Yb:YAG single crystals codoped with 0.1 at.% Cr and 10 at.% Yb were grown using the standard Czochralski (CZ) method. The growth parameters and absorption properties have been reported [10].  $\text{Cr}^{4+}$  is regarded to be substituted into tetrahedral Al site, therefore a charge compensator is required and 0.2 at.%  $\text{CaCO}_3$  was added to as a charge compensator. Samples for spectroscopic measurements were cut out of boules and the surfaces perpendicular to the  $\langle 111 \rangle$  growth axis were polished. The absorption spectra were measured using a Lambda Perkin-Elmer 9 UV/VIS/NIR spectrometer.  $\text{Yb}^{3+}$  fluorescence spectra were recorded through a 0.25 m monochromator and detected with a PbS cell. A lock-in amplifier was used to improve the S/N ratio. The excitation source was a cw Ti-sapphire laser. For the convenience of comparison, the samples were the same thickness and used the same pumping source, the same energy and the same setup.  $\text{Yb}^{3+}$  fluorescence lifetime under pulse excitation at 968 nm was recorded with a sampling oscilloscope (Tektronix TDS 420) and detected with a InGaAs cell where time constant was approximately equal to 1  $\mu\text{s}$ .

## 3. Results and discussions

The room temperature absorption spectra of Cr:YAG, Yb:YAG and Cr,Yb:YAG crystals are displayed in Figs. 1 and 2 respectively. All the following figures are corrected for Fresnel loss from the sample surfaces. Fig. 1 shows the absorption spectra of Cr:YAG (solid line) and Yb:YAG crystals (dotted line) after annealing at room temperature. There are five absorption bands of Cr,Yb:YAG crystal (Fig. 2(a) and Fig. 2(b)). The broad absorption bands centered at 440 nm and 605 nm are attributed to the  $^4\text{A}_2 \rightarrow ^4\text{T}_1$  and  $^4\text{A}_2 \rightarrow ^4\text{T}_2$  transitions of  $\text{Cr}^{3+}$  ions which the absorption features are similar to that of

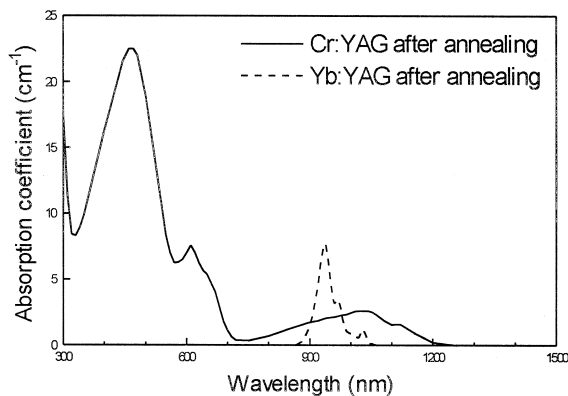


Fig. 1. The absorption spectra of Cr:YAG and Yb:YAG crystal after annealing at room temperature.

Cr:YAG (Fig. 1 solid line). The band centered at 937 nm and 965 nm are attributed to the  $^2\text{F}_{7/2} \rightarrow ^2\text{F}_{5/2}$  transition of  $\text{Yb}^{3+}$ . The absorption band centered at 1030 nm is believed to be caused mainly by the  $^3\text{A}_2 \rightarrow ^3\text{T}_1$  transition of  $\text{Cr}^{4+}$  ions, and at the same time there is the absorption of  $\text{Yb}^{3+}$ . Each absorption peak increased in intensity after annealing. In visible region, not only the intensities of the  $^4\text{A}_2 \rightarrow ^4\text{T}_1$  and  $^4\text{A}_2 \rightarrow ^4\text{T}_2$  transitions absorption peaks of  $\text{Cr}^{3+}$  ions increased after annealing, but also the main band positions moved from 440 nm to 470 nm and from 605 nm to 610 nm. At the same time, the absorption coefficient at 940 nm and 1.03  $\mu\text{m}$  increased from  $7.08 \text{ cm}^{-1}$  to  $9.16 \text{ cm}^{-1}$  and  $1.64 \text{ cm}^{-1}$  to  $3.64 \text{ cm}^{-1}$  after annealing. We superimposed the spectrum of Yb:YAG (dotted line in Fig. 1) over that of Cr:YAG (solid line in Fig. 1) so that the absorption characteristics of the Yb and Cr were combined into one (Fig. 2(c)). From Fig. 2(b) and Fig. 2(c), we can see the shapes of two curves are almost the same and the absorption coefficients are slightly different only near the 940 nm, intensity of Fig. 2(c) is higher than that of Fig. 2(b). This difference may be due to the Cr–Yb-codoped YAG crystal field having slightly changed when the Cr and Ca are introduced into the Yb:YAG crystal.

The fluorescence spectra of Cr,Yb:YAG and Yb:YAG are shown in Fig. 3. From Fig. 3, we can see that the fluorescence intensity of  $\text{Yb}^{3+}$  in Cr,Yb:YAG (solid line) is lower than that of  $\text{Yb}^{3+}$  in Yb:YAG crystal (dotted line). And the fluores-

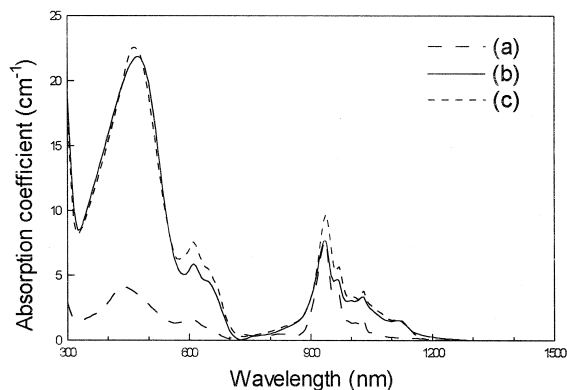
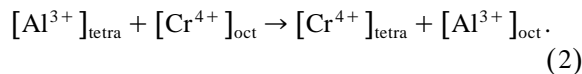
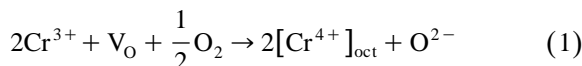


Fig. 2. The absorption spectra of Cr,Yb:YAG crystal at room temperature: (a) as-grown; (b) after annealing; and (c) the measured absorption spectrum of superimposed the spectrum of Yb:YAG over the spectrum of Cr:YAG.

cence lifetime of Cr,Yb:YAG (0.3 ms) is shorter than that of Yb:YAG (1.48 ms) which is seriously radiation trapped. Since Yb<sup>3+</sup> concentration quenching is nonexistent in principle, the decrease of the fluorescence intensity and the measured lifetime of Yb<sup>3+</sup> in Cr,Yb:YAG crystal are attributed to the ground state absorption of Cr<sup>4+</sup> at the emission wavelength at 1.03 μm (Fig. 2).

We analyzed the causes of the changes of the absorption spectra and the decrease of the fluorescence intensity and emission lifetime when the Cr and Ca were introduced into the Yb:YAG crystal. The crystal structure of YAG belongs to cubic system, the space group of YAG is O<sub>h</sub><sup>10</sup> – Ia3d. The difference of lattice constants in YAG crystal between Yb<sup>3+</sup> and Y<sup>3+</sup> is 1.5%, thus, when Yb<sup>3+</sup> is introduced into YAG, Yb<sup>3+</sup> is substituted at the dodecahedral Y<sup>3+</sup> site. When Cr and Ca are introduced into YAG crystal there are several valent states. Cr<sup>3+</sup> is the dominant species and is substituted at the octahedral Al sites, and Cr<sup>3+</sup> is the most stable valent state among Cr ions and its crystal field stabilization energy is the largest when substituted at an octahedral site. The increase of the absorption coefficient after annealing is due to the increase of the concentration of Cr<sup>4+</sup> ions at tetrahedral sites at high temperature oxygen atmosphere. Cr<sup>4+</sup> is regarded to be substituted into tetrahedral Al site, therefore a charge compensator is required, which is

accomplished by the substitution of Ca into the Y site. The process is as following [11],



Eq. (1) is the process of diffusive action of oxygen vacancies (V<sub>O</sub>) in inter crystal to the surface, and the formation of oxygen vacancy in crystal, combining with a octahedral Cr<sup>3+</sup> to form a octahedral Cr<sup>4+</sup>. Eq. (2) describes that unstable octahedral Cr<sup>4+</sup> disperses into neighbor Al–O tetrahedron and forms a tetrahedral Cr<sup>4+</sup> ([Cr<sup>4+</sup>]<sub>tetra</sub>).

Another phenomenon after annealing is that the main absorption band of Cr<sup>3+</sup> shifts to longer wavelength with the increase of the concentration of Cr<sup>4+</sup>. Fig. 4 is one octant of the Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub> unit cell. Cr<sup>3+</sup> ions are regarded to be occupied in octahedral sites. With the increase of the concentration of Cr<sup>4+</sup>, Cr<sup>4+</sup> occupied Al–O tetrahedral sites gradually. Because of Cr<sup>4+</sup> ions substituting in Al<sup>3+</sup> sites, they attract the tetrahedral oxygen ions to center along the arrows in Fig. 4. So the neighbor octants are enlarged, the crystal field is weakened, resulting in the increase of the concentration of Cr<sup>3+</sup>, and the absorption bands shift to longer wavelength. In addition, with the increase of the concentration of Cr<sup>4+</sup>, absorption band of Cr<sup>4+</sup> shifts to longer wavelength is negligible, owing to the Cr<sup>4+</sup>–O tetrahedron is difficult to distort.

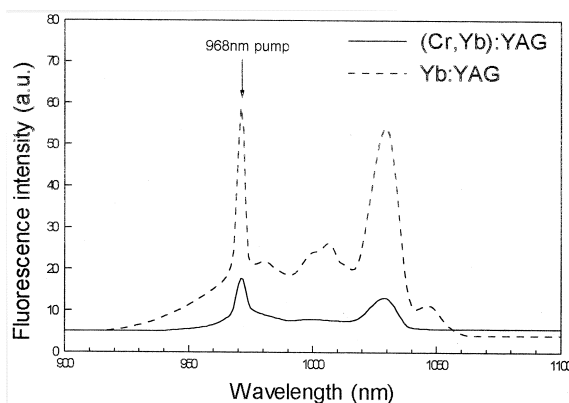


Fig. 3. The fluorescence spectra of Yb<sup>3+</sup> in Yb:YAG and Cr,Yb:YAG crystal at room temperature.

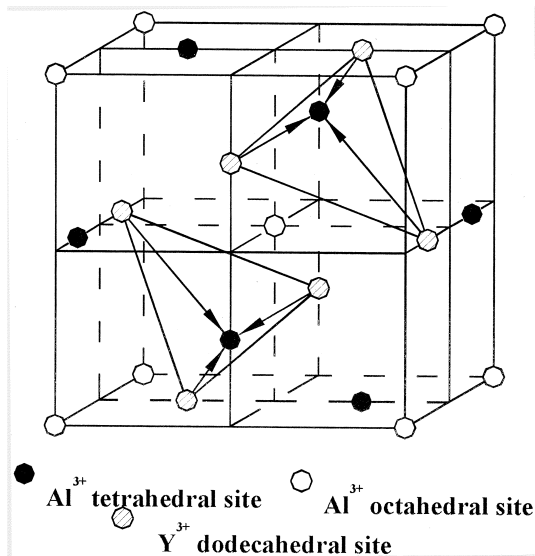


Fig. 4. One octant of the  $Y_3Al_5O_{12}$  unit cell.

The increase of  $Cr^{4+}$  concentration results in the ground state absorption and the concentration quenching of  $Yb^{3+}$  in Cr,Yb:YAG crystal after annealing, the fluorescent intensity is reduced and the emission lifetime is shortened.

Although the fluorescent intensity of Cr,Yb:YAG crystal is lower than that of Yb:YAG crystal at 1030 nm, the absorption and fluorescence spectra show that Cr,Yb:YAG crystal combines the saturable absorber and gain medium into one and it can be a self-Q-switching laser crystal if the crystal is pumped with high power. The further laser experiment is under investigation.

#### 4. Conclusions

The absorption and fluorescence spectra of Cr,Yb:YAG crystal were measured. After annealing, the increase of  $Cr^{4+}$  ions in the Cr,Yb:YAG crystal results in the quenching of  $Yb^{3+}$  in the Cr,Yb:YAG crystal. The emission intensity of  $Yb^{3+}$  in Cr,Yb:YAG crystal is 4 times lower than that of  $Yb^{3+}$  in Yb:YAG crystal and the emission lifetime is also shortened (0.3 ms). The effects of annealing on the Cr,Yb:YAG crystal are weakening the crystal field and increasing the Cr ions. The fluorescence

lifetime of  $Yb^{3+}$  in Cr,Yb:YAG is shorter than that of  $Yb^{3+}$  in Yb:YAG (0.3 ms vs. 1.48 ms) because of the existence of the ground state absorption of  $Cr^{4+}$  ions causing  $Yb^{3+}$  concentration quenching. The decrease of the emission intensity of Yb in the Cr,Yb:YAG crystal is due to the ground state absorption of  $Cr^{4+}$ . The absorption spectra show that there are two absorption bands at 940 nm and 968 nm which are suitable for InGaAs diode laser pumping. And there is an absorption band of  $Cr^{4+}$  near 1.03  $\mu m$  which can be used as a saturable absorber. So, the Cr,Yb:YAG crystal combines the saturable absorber and gain medium into one and can be a self-Q-switched laser crystal if it is pumped with high energy and power.

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