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# Spectral and luminescence properties of $\text{Cr}^{4+}$ and $\text{Yb}^{3+}$ ions in yttrium aluminum garnet (YAG)

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## Abstract

In this paper, the spectral and luminescence properties of (Cr,Yb):YAG crystal, Yb:YAG crystal and Cr:YAG crystal are reported. In the absorption spectra of (Cr,Yb):YAG crystal, there are two absorption bands at 937 and 968 nm, respectively, which are suitable for InGaAs diode laser pumping; and there is an absorption band of  $\text{Cr}^{4+}$  near 1030 nm, which is suitable for passive Q switch laser output at 1.03  $\mu\text{m}$ . The luminescent spectra of (Cr,Yb):YAG and Yb:YAG show that the luminescent center of (Cr,Yb):YAG is at 1029 nm, but the intensity is lower than Yb:YAG. The luminescent lifetimes of (Cr,Yb):YAG and Yb:YAG are 0.3 and 1.4 ms, respectively. This Cr–Yb-codoped crystal is a potential material for a compact, efficient, highly stable, diode laser pumped, passive Q-switched solid-state laser. © 2000 Elsevier Science B.V. All rights reserved.

*Keywords:* Laser crystal; (Cr,Yb):YAG crystal; Czochralski (CZ) method; Spectrum properties; Self-Q switched laser crystal

## 1. Introduction

Diode-pumped Q-switched solid-state lasers have been demonstrated to have high efficiency, high average power, and high energy per pulse compared to non-Q-switched solid-state lasers. The applications of Q-switched lasers are well known: lidars, remote sensing, pollution detection, non-linear-optical processes, and material processing. Passive Q switching of solid-state lasers is usually accomplished with organic dyes or color centers as the saturable absorbers [1,2]. Organic dyes, however, have several shortcomings: they show poor thermal stability and tend to degrade

rapidly and, to operate as a Q-switch in a periodically pulsed or cw-pumped laser, they require a cooling circulation system. Color centers, such as the color-center LiF crystal, exhibit a fading phenomenon that may limit the duration of reliable operation. Recently, chromium-doped host crystals, such as yttrium aluminum garnet (YAG), gadolinium scandium gallium garnet (GSGG), and forsterite, are reported to exhibit color-center-like saturable absorption at the  $\text{Nd}^{3+}$  laser wavelength at 1064 nm [3–6]. The absorption now is believed to depend on codoped saturable absorbers, such as  $\text{Cr}^{4+}$  [6,7]. By using the laser host crystal codoped with saturable absorbers, such as  $\text{Cr}^{4+}$ , the functions of a gain medium and a saturable absorber are combined into one. This can lead to the development of monolithic Q-switched solid-state lasers. Thus,  $\text{Cr}^{4+}$ :YAG crystal may be the ideal

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passive Q switch material of choice for high power and high repetition rate solid-state lasers. Cr–Nd-codoped YAG is a good passive Q switch material [3,4,8].

Recent advances in high performance strained layer diode lasers, with a wavelength between 0.9 and 1.1  $\mu\text{m}$ , have stimulated interest in diode pumped  $\text{Yb}^{3+}$  lasers [9,10]. Payne and Krupke of the Lawrence Livermore National Laboratory foresaw that the output power of  $\text{Yb}^{3+}$  laser will be 10 kw in five years [11]. The recent introduction of InGaAs laser diodes allowed the effective coupling of pump light into the gain medium, so as to permit efficient room temperature operation of Yb:YAG. Furthermore, a diode-pumped Yb:YAG laser has several advantages relative to Nd:YAG laser: such as low thermal load, long upper state lifetime, large absorption width around the InGaAs laser emission range, relative large emission cross-section, high thermal conductivity, easy growth of high quality and high concentration crystals without concentration quenching, and strong energy-storing capacity. Therefore, growth of Yb–Cr-codoped YAG crystal will combine the advantages of the gain medium,  $\text{Yb}^{3+}$ , and the saturable absorber,  $\text{Cr}^{4+}$ , potentially providing a passive Q-switched laser crystal which is better than Cr–Nd-codoped YAG. This crystal has potential for compact, efficient, high stable, light-weight diode-pumped solid-state laser devices.

The spectral and luminescence properties of Yb,Cr:YAG crystals codoped with 10 at.% Yb and 0.1 at.% Cr, 10 at.% Yb:YAG and 0.1 at.% Cr:YAG were investigated.

## 2. Experimental setup

Cr–Yb-codoped YAG single crystals were grown using the Czochralski (CZ) method. Starting materials of  $\text{Y}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{Yb}_2\text{O}_3$  were weighed and mixed in stoichiometric composition. The initial charge concentration of  $\text{CaCO}_3$  and  $\text{Cr}_2\text{O}_3$  were 0.2 at.% and 0.1 at.%, respectively. The powders were ball-milled, pressed into rods, and presintered in air. These rods were then crushed, pressed into rods again and sintered at 1400°C for several hours. Then the rods were

placed in an iridium crucible of 80 mm diameter and 50 mm in height. A  $\langle 111 \rangle$  oriented undoped single YAG crystal was used as a seed. During growth, pulling rate was 1 mm/h and the crystal was rotated about its axis at 15 r/min. The growth atmosphere was nitrogen. The crystals grown by the CZ method were about 30 mm in diameter and 100 mm in length. All crystals were brown, free from inclusions and precipitations. Cr:YAG and Yb:YAG crystals were also grown with the same method in the same apparatus. Because there are defects such as core and stress striations after growth, annealing is necessary. The crystals were annealed in oxygen atmosphere at 1400°C for 50 h, then cooled to room temperature at the rate of 10°C/h.

Samples for spectroscopic measurements were cut out of the boules and 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 type 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. Yb fluorescence lifetime under pulsed excitation at 968 nm was recorded with a sampling oscilloscope (Tektronix TDS 420) and detected with an InGaAs cell whose time constant was approximately equal to 1  $\mu\text{s}$ .

## 3. The investigation of spectral and luminescence properties of $\text{Cr}^{4+}$ and $\text{Yb}^{3+}$

The room temperature absorption spectra of Cr,Yb:YAG, Cr:YAG and Yb:YAG crystals are shown in Figs. 1–3, respectively. All the following figures are corrected for Fresnel loss from the sample surfaces. In Fig. 1 solid line shows the spectrum of Cr,Yb:YAG crystal after annealing at room temperature. The absorption feature in the visible region is similar to that of chromium-doped YAG [12] and to our measurement of the absorption spectrum of Cr:YAG (Fig. 2). The broad absorption bands centered at 440 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  $\text{Cr}^{3+}$ . The bands centered at 937 and 965

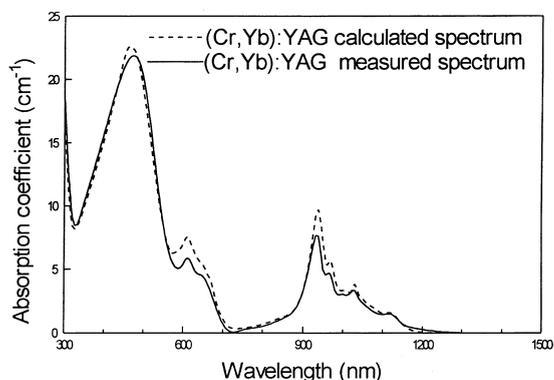


Fig. 1. The absorption spectra of (Cr,Yb):YAG crystal after annealing at room temperature, dotted line shows the figure that superimposed the spectrum of Yb:YAG over the absorption spectrum of Cr:YAG.

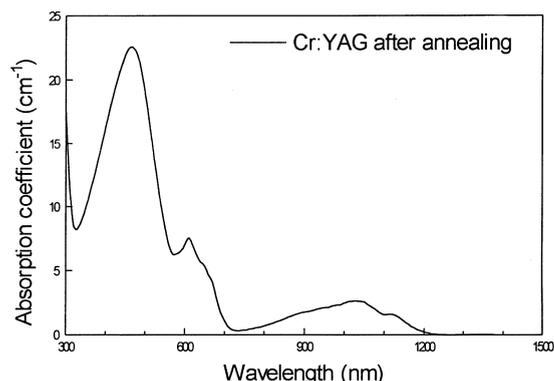


Fig. 2. The absorption spectrum of Cr:YAG crystal after annealing at room temperature.

nm are attributed to the  ${}^2F_{7/2} \rightarrow {}^2F_{5/2}$  transition of  $\text{Yb}^{3+}$ , embodying the absorption spectrum of Yb:YAG crystal (Fig. 3). From the spectra of Cr:YAG (Fig. 2), the band centered at 1064 nm is believed to be caused by the  ${}^3A_2 \rightarrow {}^3T_1$  transition of  $\text{Cr}^{4+}$  ions. We superimposed the spectrum of Yb:YAG over the spectrum of Cr:YAG, and the combined absorption characteristics of the Yb and Cr obtained by this simple method are shown as the dotted line in Fig. 1. From Fig. 1, we can see that the curve (dotted line in Fig. 1) is almost the same as the spectrum obtained from a Cr, Yb:YAG crystal (solid line in Fig. 1). The absorption coefficients are slightly different only near

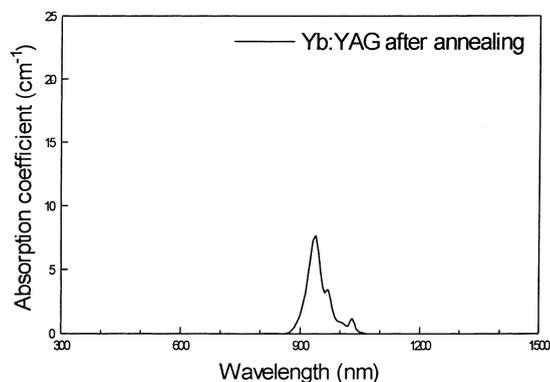


Fig. 3. The absorption spectrum of Yb:YAG crystal after annealing at room temperature.

the 940 nm where the intensity of the dotted line is higher than that of the solid line. The cause of this difference may be due to the Cr–Yb-codoped YAG crystal field having slightly changed. Fig. 1 shows that the spectrum of Cr,Yb:YAG crystal combines the absorption features of Cr and Yb. The two absorption bands of  $\text{Yb}^{3+}$  are superimposed on the  $\text{Cr}^{4+}$  absorption band in the range from 900–1100 nm.

The absorption spectra of (Cr,Yb):YAG crystal as grown and after annealing are shown in Fig. 4. The absorption peaks increased in intensity by annealing. In the visible region, not only the intensity of the  ${}^4A_2 \rightarrow {}^4T_1$  and  ${}^4A_2 \rightarrow {}^4T_2$  transitions absorption peaks of  $\text{Cr}^{3+}$  increased after annealing, but also the spectral shape in other wavelength

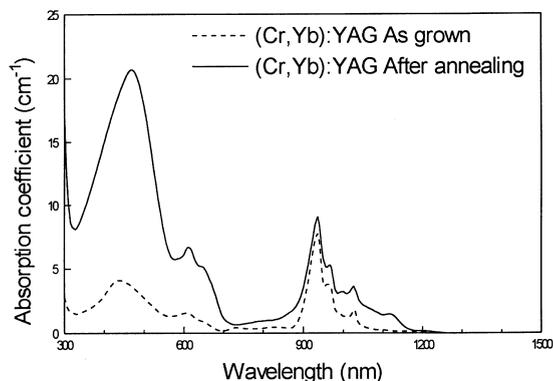


Fig. 4. The absorption spectra of (Cr,Yb):YAG crystal as grown and after annealing at room temperature.

regions changed. The main band position moved from 440 to 470 nm and from 605 to 610 nm. The as-grown spectrum, the absorption coefficient is  $1.64 \text{ cm}^{-1}$  at 1030 nm and  $7.08 \text{ cm}^{-1}$  at the pumping wavelength of 940 nm. After annealing absorption coefficient is  $3.64 \text{ cm}^{-1}$  at 1030 nm and  $9.16 \text{ cm}^{-1}$  at the pumping wavelength. Fig. 5 contains data from two samples, one from a 0.19 cm sample cut from the top or first-to-freeze end of the Cr,Yb:YAG boule, and the other from a 0.19 cm sample cut from the boule bottom end, both after annealing. The near-perfect overlap of the curves indicates that there was essentially no concentration gradient for  $\text{Cr}^{4+}$  ions and  $\text{Yb}^{3+}$  ions along the length of the boule and that the distribution coefficient for  $\text{Cr}^{4+}$  and  $\text{Yb}^{3+}$  in YAG must be close to unity in the Cr,Yb:YAG boule. The strong absorption at 940 and 968 nm is suitable for InGaAs diode laser pumping. At the same time, the sample color changed from brown to yellowish-brown during annealing. These facts suggest that annealing increased  $\text{Cr}^{4+}$  concentration dramatically.

The fluorescence spectra of Yb:YAG and (Cr,Yb):YAG are shown in Fig. 6. From Fig. 6, we can see that the fluorescence intensity of  $\text{Yb}^{3+}$  in (Cr,Yb):YAG is lower than that of Yb in Yb:YAG. The fluorescent lifetime of (Cr,Yb):YAG is 0.3 ms, lower than that of Yb:YAG which is 1.4 ms. This implies that the saturation fluence for (Cr,Yb):YAG is higher than that of Yb:YAG and furthermore, that (Cr,Yb):YAG is capable of storing more energy to amplify spontaneous

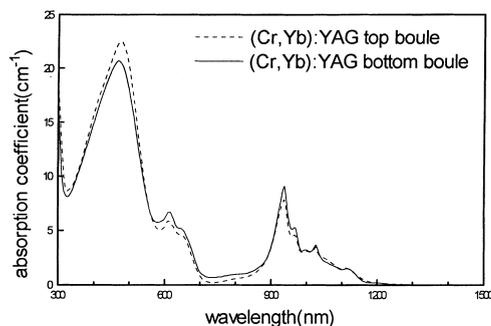


Fig. 5. The absorption spectra of (Cr,Yb):YAG crystal in the top and bottom at room temperature.

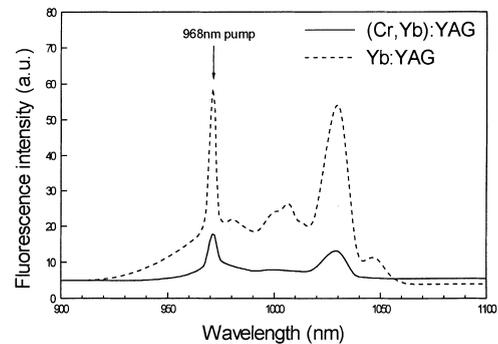


Fig. 6. The fluorescence spectra of  $\text{Yb}^{3+}$  in (Cr,Yb):YAG and Yb:YAG crystal at room temperature.

emission (ASE) and parasitic oscillation in Q-switched lasers.

In this case, we may expect saturable absorber  $\text{Cr}^{4+}$  as a passive Q switch for  $\text{Yb}^{3+}$  in monolithic Cr,Yb:YAG laser crystal. The further research is under investigation.

#### 4. Conclusion

The spectral and luminescence properties of Cr,Yb:YAG crystals codoped with 10 at.% Yb and 0.1 at.% Cr were investigated. The absorption spectra of Cr,Yb:YAG have five absorption bands. In the visible region, after annealing, the absorption spectra moved from 440 and 605 nm to 470 and 610 nm, respectively. The absorption intensity increased after samples were annealed. The Cr,Yb:YAG crystals combine the Yb and Cr absorption characteristics of Cr:YAG and Yb:YAG crystals. A strong absorption band exists at the  $\text{Yb}^{3+}$  fluorescent wavelength 1030 nm, as demonstrated by the fluorescence spectra of Cr,Yb:YAG. Cr,Yb:YAG crystals have potential for self-Q-switched monolithic laser.

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