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The growth of Cr^{4+} , Yb^{3+} :yttrium aluminum garnet (YAG) crystal and its absorption spectra properties

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Abstract

In this paper, the growth and absorption spectra properties of Cr, Yb:YAG crystal and effect of annealing on the absorption spectra are reported. The growth parameters and annealing conditions were studied; the defects of the crystal were also studied. In the absorption spectra, 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 at 1030 nm, which is suitable for passive *Q*-switch laser output at 1.03 μm . These crystals may be potential materials for compact, efficient, high-stability diode-laser-pumped passive *Q*-switched solid-state lasers. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Diode-pumped *Q*-switched solid-state lasers have been demonstrated to have high-efficiency, high average power, and high energy per pulse. The applications of *Q*-switched lasers are well known: lidars, remote sensing, pollution detection, nonlinear-optical processes, and material processing. Passive *Q* switching of solid-state lasers are 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 period of reliable operation. Recently, the 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 Nd^{3+} laser wavelength at 1064 nm [3–6]. The absorption now is believed to be codoped with saturable absorbers, such as Cr^{4+} [6,7]. By using the laser host crystal codoped with saturable absorbers, such as Cr^{4+} , the functions of the gain medium and the saturable absorbers are combined into one. This can lead to the development of monolithic *Q*-switched solid-state lasers.

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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 μm have stimulated interest in diode-pumped Yb^{3+} lasers [9,10]. Payne and Krupke of the Lawrence Livermore National Laboratory foresaw that the output power of Yb^{3+} laser will be 10 kW in 5 years [11]. The recent introduction of InGaAs laser diodes allowed the effective coupling of pumped light into the gain medium, so as to allow the efficient room temperature operation of $\text{Yb} : \text{YAG}$. Furthermore, diode-pumped $\text{Yb} : \text{YAG}$ laser has several advantages relative to $\text{Nd} : \text{YAG}$ 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 crystal without concentration quenching, and strong energy-storing capacity. Therefore, growth of Yb – Cr -codoped YAG crystal will combine the advantages of the gain medium Yb^{3+} and the saturable absorber Cr^{4+} into one, it may be a more potential passive Q -switched laser crystal relative to Cr – Nd -codoped YAG crystal.

$\text{Yb}, \text{Cr} : \text{YAG}$ crystals codoped with 10 at% Yb and 0.1 at% Cr have been grown by the Czochralski method, and the crystal growth parameter and annealing condition were studied as well. The defects and absorption spectra of the crystal were studied, and the effect of annealing on the absorption spectra properties and the defects were studied as well.

2. Growth of $\text{Cr}, \text{Yb} : \text{YAG}$ crystal

The crystal structure of YAG belongs to cubic system, the space group of YAG is $O_h^{10} - Ia3d$. The difference of lattice constant between Yb and Y is 1.5% [12], thus, most of the Yb substitutes the Y site in the dodecahedron in YAG crystal. Chromium ions in YAG have different valent state: divalent Cr^{2+} , trivalent Cr^{3+} , tetravalent Cr^{4+} , among them, Cr^{3+} is the most stable. When Cr and Ca are introduced into the YAG crystal, there are several valent states. Cr^{3+} is the dominant species

and is substituted at the octahedral Al site, and Cr^{3+} is the most stable valent state among Cr ions and its crystal field stabilization energy is the largest when substituted at an octahedral site. However, Cr^{4+} is a saturable absorber in $\text{Cr}, \text{Yb} : \text{YAG}$ crystal. So, controlling Cr ions valent states is the key step to obtain high Cr^{4+} concentration in Cr – Yb -codoped YAG crystal. Cr^{4+} is regarded to be substituted into tetrahedral Al site, therefore a charge compensation is required, which is accomplished by the substitution of Ca^{2+} into the dodecahedral Y site. Thus, during the growth of $\text{Cr}, \text{Yb} : \text{YAG}$ crystal, CaCO_3 was added to as a charge compensator.

Cr – Yb -codoped YAG single crystals were grown using the Czochralski (CZ) method. Starting materials of Y_2O_3 , Al_2O_3 , and Yb_2O_3 were weighed and mixed in stoichiometric composition. The initial charge concentration of CaCO_3 and Cr_2O_3 are 0.2 and 0.1 at%, respectively. The powders were ball-milled, pressed into rods, and presintered in air. These rods were then crushed, pressed into rod again and sintered at 1400°C for several hours. Then the rods were placed in an iridium crucible of 80 mm in diameter and 50 mm in height. A $\langle 111 \rangle$ oriented undoped single YAG crystal was used as a seed. During growth the crystal was rotated about its axis, pulling rate is 1 mm/h, rotation rate is 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.

3. The defects of $\text{Cr}, \text{Yb} : \text{YAG}$ crystals are cores and stress striations

The main defects of $\text{Cr}, \text{Yb} : \text{YAG}$ crystal are core and stress striations. In “deep-interface” growth along growth axis $\langle 111 \rangle$, three $\{211\}$ facet planes forms a core and the core which is formed by three $\{211\}$ facet planes and three stress striations which are formed by radius distributed three $\langle 111 \rangle$ facets separate the crystal cross section into three sections Fig. 1. Cores and facets will cause crystal optical heterogeneity. Using delicate select technique, laser bars can be cut out of boule

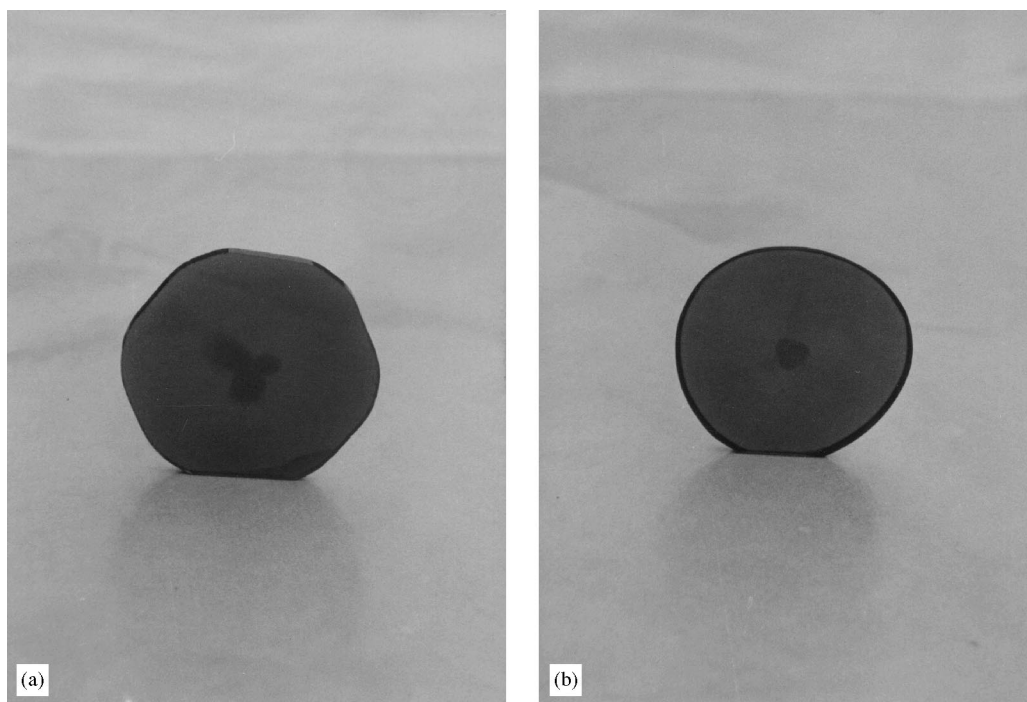


Fig. 1. (a) The photo of the Cr, Yb : YAG crystal as-grown and (b) after annealing.

free from cores and facets. So that we can obtain high-optical homogeneity crystals.

Cr, Yb : YAG crystals grown by CZ method have core and stress striations caused by facets, so that annealing was necessary to reduce these defects. The annealing processing is as follows: in pure oxygen the crystals were fired at 1400°C for 50 h, and cooled to room temperature at a rate of 10°C/h. After annealing, the crystals change from brown to yellowish brown, and the area of core and stress striations is reduced, just shown in Fig. 1a and Fig. 1b. The change of crystal color shows that the Cr^{4+} concentration in the crystal increases after annealing.

4. Absorption spectra

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 and transmittance spectra were

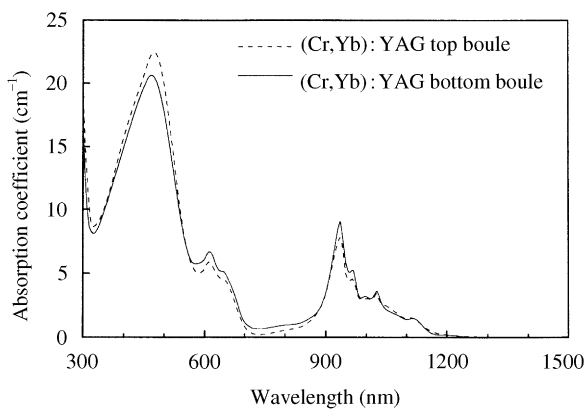


Fig. 2. The absorption spectra of Cr, Yb : YAG crystal from top and bottom boule after annealing at room temperature.

measured using a Lambda Perkin-Elmer 9 UV/VIS/NIR type spectrometer. The room temperature absorption spectra are shown in Fig. 2. In Fig. 2, the data are actually two curves, one from a 0.19 cm sample cut from the top or first-to-freeze

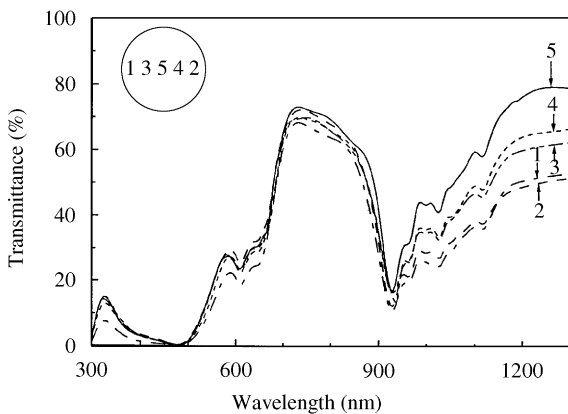


Fig. 3. The transmittance spectra of the Cr, Yb:YAG crystal along the diameter.

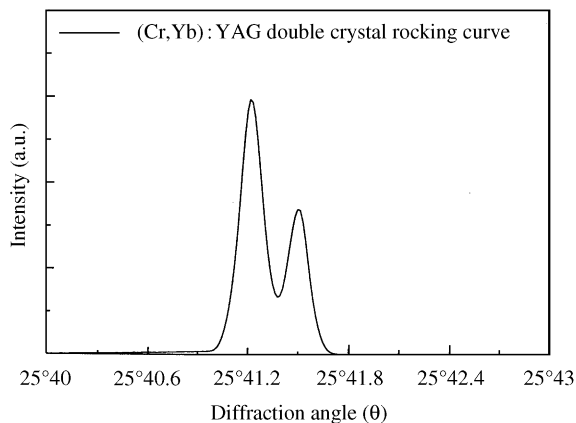


Fig. 4. The double-crystal rocking curve (DCRC) of Cr, Yb:YAG crystal.

end of the Cr, Yb:YAG boule, and the other from a 0.19 cm sample cut from the boule bottom end. The near-perfect overlap of the curves indicates that there was essentially no concentration gradient for Cr^{4+} ions and Yb^{3+} ions along the length of the boule and that the distribution coefficient for Cr^{4+} and Yb^{3+} in YAG must be close to unity. The transmittance spectra of different point along the diameter direction of the (Cr, Yb):YAG crystal were shown in Fig. 3. In Fig. 3, the near-perfect overlap of the transmittance of Cr^{3+} shows that the concentration of Cr^{3+} is near unity; the difference

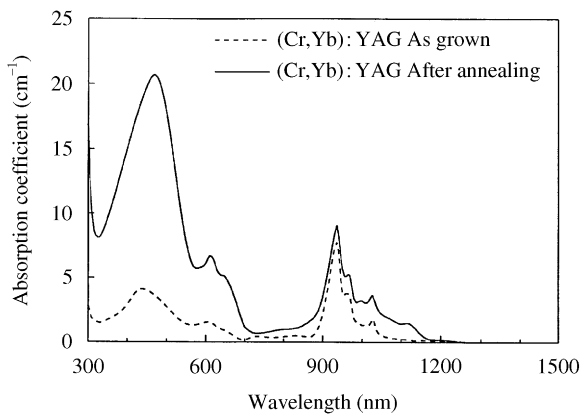


Fig. 5. The absorption spectra of Cr, Yb:YAG crystal as-grown and after annealing at room temperature.

of the transmittance of Yb^{3+} and Cr^{4+} from the core to the periphery of the crystal shows the concentration of Yb^{3+} and Cr^{4+} along the radius not close to the unity. At the same time, the double-crystal rocking curve Fig. 4 of the (Cr, Yb):YAG crystal shows that there may be substructures and segregations in the crystal, so the transmittance spectra of the crystal along the radius of the crystal is shown in Fig. 4. Fig. 5 shows the spectra of Cr, Yb:YAG crystal as-grown and after annealing at room temperature. The absorption feature in the visible region is similar to that of chromium-doped YAG [13]. 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 Cr^{3+} . The bands centered at 937 and 965 nm are attributed to the ${}^2\text{F}_{7/2} \rightarrow {}^2\text{F}_{5/2}$ transition of Yb^{3+} . The band centered at 1025 nm is believed to be caused by the ${}^3\text{A}_2 \rightarrow {}^3\text{T}_1$ transition of Cr^{4+} ions. The absorption band of Cr^{4+} ranges from 900 to 1100 nm. The two absorption bands of Yb^{3+} superimposed over the Cr^{4+} absorption band.

The absorption spectrum after annealing is also shown in Fig. 2. Each absorption peak increased in intensity by annealing. In the visible region, not only the intensity 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 Cr^{3+} increased after annealing, but also the spectral shape in other wavelength regions also 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 1.6436 cm^{-1} at 1030 nm and 7.0763 cm^{-1} at the pumping wavelength of 940 nm. After annealing absorption coefficient is 3.6363 cm^{-1} at 1030 nm and 9.1635 cm^{-1} at the pumping wavelength. 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 by annealing. These facts show that annealing increased Cr^{4+} concentration dramatically. In this case, we may expect saturable absorber Cr^{4+} as a passive Q-switch for Yb^{3+} in monolithic Cr, Yb : YAG laser crystal. The further research is under study.

5. Conclusions

The Cr, Yb : YAG crystals codoped with 10 at% Yb at 0.1 at% Cr were grown by the CZ method. The crystal was 30 mm in diameter and 100 mm in length. The growth parameter and annealing conditions were studied. Annealing was performed in oxygen at 1400°C for 50 h, then the crystals were cooled to room temperature at a rate of $10^\circ\text{C}/\text{h}$. The defects of the crystal were studied and it was demonstrated that annealing can effectively reduce these defects. The transmittance spectra, absorption spectra and DCRC shows that the concentration of Cr^{4+} and Yb^{3+} along the growth axis is near unity and the concentration of Cr^{4+} and Yb^{3+} along the radius is not near unity. The absorption spectra of Cr, Yb : YAG have five absorption bands. In the visible region, after annealing absorption spectra moved from 440 and 605 nm to 470

and 610 nm, respectively. Absorption intensity increased after samples were annealed. The Cr, Yb : YAG crystals have a strong absorption band in Yb^{3+} fluorescent wavelength 1030 nm, so it can be a saturable absorber as a passive Q-switch for Yb^{3+} in monolithic Cr, Yb : YAG laser crystal.

References

- [1] J.A. Morris, C.R. Pollock, *Opt. Lett.* 15 (1990) 440.
- [2] R. Beach, J. Davin, S. Mitchell, W. Bennett, B. Freitas, R. Solarz, *Opt. Lett.* 17 (1992) 124.
- [3] Y. Gui, G. Yao, T. Ji, Y. Gu, X. Lo, L. Zhang, *Digest of Conference on Lasers and Electro-Optics, Optics Society of America, Washington, DC, 1984*, p. 166.
- [4] A.A. Danilov, V.L. Evstigneev, N.N. Il'ichev, A.A. Malutin, M. Yu, Nikol'shii, A.F. Umyskov, I.A. Shcherbakov, *Sov. J. Quantum Electron.* 17 (1987) 573.
- [5] M.I. Demchuk, V.P. Mikhailov, N.I. Zhavoronkov, N.V. Kuleshov, P.V. Prokoshin, K.V. Yumashev, M.G. Livshits, B.I. Minkov, *Opt. Lett.* 17 (1992) 929.
- [6] S.E. Stokowski, M.H. Randles, R.C. Morris, *IEEE J. Quantum Electron.* 24 (1988) 934.
- [7] V. Petricevic, S.K. Gayen, R.R. Alfano, *Appl. Phys. Lett.* 153 (1998) 2590.
- [8] S. Zhou, K.K. Lee, Y.C. Chen, *Opt. Lett.* 18 (1993) 1418.
- [9] R.M. Kolbas, N.G. Anderson, W.D. Laidig, Y. Sin, Y.C. Lo, K.Y. Hsieh, Y.J. Yang, *IEEE J. Quantum Electron.* 24 (1998) 1605.
- [10] D.P. Pour, D.B. Gilbert, K.B. Fabian, J.P. Bednarz, M. Ertenberg, *IEEE Photon. Technol. Lett.* 2 (1990) 173.
- [11] S.A. Payre, W.F. Krupke, *Opt. Photon. News* 8 (1996) 31.
- [12] A.R. Reinburg, L.A. Riseurg, R.M. Brown et al., *Appl. Phys. Lett.* 1 (1971) 19.
- [13] N.B. Angert, N.I. Borodin, V.M. Garmash, V.A. Zhitnyuk, A.G. Okhrimchuk, O.G. Siyachenko, A.V. Shestakov, *Sov. J. Quantum Electron.* 18 (1988) 73.