Investigation of absorption spectra of (Cr\textsuperscript{4+}, Yb\textsuperscript{3+}):YAG crystal

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ABSTRACT

In this paper, the absorption spectra characters of the (Cr, Yb): YAG, Cr:YAG and Yb:YAG crystals are reported. In the absorption spectra of the (Cr, Yb): YAG crystal, there are two absorption bands at 937 nm and 968 nm respectively, which are suitable for InGaAs diode laser pumping; and there is an absorption band of Cr\textsuperscript{4+} near 1030 nm, which is suitable for passive Q switch laser output at 1.03 \mu m. This Cr-Yb-codoped crystal may be a potential material for compact, efficient, high-stable diode laser pumped passive Q-switched solid-state laser.

Keywords: laser crystal, (Cr,Yb):YAG crystal, Czochralski (CZ) method, spectrum characters, self-Q switched laser crystal

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 process, and material processing. The saturable absorbers which have been successfully used for passive Q-switched lasers include dye\textsuperscript{[1]}\textsuperscript{[11]}, LiF:F\textsubscript{2} color center crystals\textsuperscript{[2]}, Cr\textsuperscript{4+}-doped crystals\textsuperscript{[3-7]}, etc. Among them, Cr\textsuperscript{4+}-doped crystals developed in recent years such as Cr\textsuperscript{4+}:YAG, Cr\textsuperscript{4+}:GSGG, and Cr\textsuperscript{4+}:Mg\textsubscript{2}SiO\textsubscript{4} 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\textsuperscript{4+} can be doped into gain medium to form self-Q-switched laser\textsuperscript{[9,10]}. As a result of the above advantages, Cr\textsuperscript{4+}-doped crystals become the most promising saturable absorbers for passively Q-switched laser\textsuperscript{[3,4,8]}.

Recent advances in high performance strained layer diode lasers, with a wavelength between 0.9 and 1.1 \mu m have stimulated interest in diode pumped Yb\textsuperscript{3+} laser\textsuperscript{[9,10]} S. A. Payne and W. F. Krupel of the Lawrence Livermore National Laboratory foresaw that the output power of Yb\textsuperscript{3+} laser will be 10 Kw in 5 years\textsuperscript{[11]}. Furthermore, 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, relative 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 Cr,Yb:YAG crystals co-doped with 10 at % Yb and 0.1at % Cr were grown by standard Czochralski (CZ) method and an annealing process was performed. The absorption spectra of the crystals were studied, and the effects of annealing on the absorption spectra characters were studied as well.

2. EXPERIMENTAL SETUP

Cr-Yb-codoped YAG single crystals were grown by using the Czochralski (CZ) method. Starting materials of Y\textsubscript{2}O\textsubscript{3}, Al\textsubscript{2}O\textsubscript{3}, and Yb\textsubscript{2}O\textsubscript{3} were weighed and mixed in stoichiometric composition. The initial charge concentration of CaCO\textsubscript{3} and Cr\textsubscript{2}O\textsubscript{3} are 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 a 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 <111> 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 30mm in diameter and 100mm in length. All crystals were brown, free from inclusions and precipitation. 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, the annealing is necessary. The annealing process involves an oxygen atmosphere where the crystal was fired at 1400 °C for 50h, and then cooled to room temperature at the rate 10 °C/h.

Samples for spectroscopic measurements were cut out of boules and the surfaces perpendicular to the <111> growth axis were polished. The absorption spectra were measured using a Lambda Perkin-Elmer 9 UV/VIS/NIR spectrometer.

3. THE ANALYSIS OF ABSORPTION SPECTRA

The room temperature absorption spectra of Cr,Yb:YAG, Cr:YAG and Yb:YAG crystals are shown in Fig.1 and Fig.2 respectively, where all the following figures are corrected for Fresnel loss from the sample surfaces. In Fig.1, solid line shows the absorption spectrum of Cr,Yb:YAG crystal after annealing at room temperature. The absorption feature in the visible region is similar to the absorption spectrum of Cr:YAG measured (solid line in Fig.2). The broad absorption bands centered at 440nm and 605nm are attributed to the $^4A_2 \rightarrow ^4T_1$ and $^4A_2 \rightarrow ^4T_2$ transitions of Cr$^{3+}$. The bands centered at 937 nm and 965nm are attributed to the $^2E_{7g} \rightarrow ^2F_{5g}$ transition of Yb$^{3+}$, embodying the absorption spectrum of Yb:YAG crystal (dotted line in Fig.2). From the spectra of Cr:YAG (solid line in Fig.2), the band centered at 1064nm is believed to be caused by the $^1A_2 \rightarrow ^3T_1$ transition of Cr$^{3+}$ ions. When we superimposed the spectrum of Yb:YAG over the spectrum of Cr:YAG, the absorption characteristics of the Yb and Cr were combined into one (dotted line in Fig.1). From Fig.1, we can see the shapes of two curves are almost the same and the absorption coefficients are slightly different only near the 940nm, the intensity of the dotted line is higher than the solid line. The cause of this difference may be due to the Cr-Yb-codoped YAG crystal field having been slightly changed. Fig.1 shows that the spectrum of Cr,Yb:YAG crystal combines the absorption features of the Cr and Yb into one.

The absorption spectra of (Cr,Yb):YAG crystal as grown and after annealing are also shown in Fig.3. Each absorption peaks increased in intensity by annealing. In the visible region, not only are the intensities of the $^4A_2 \rightarrow ^4T_1$ and $^4A_2 \rightarrow ^4T_2$ 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 440nm to 470 nm and from 605 nm to 610 nm. For the as-grown absorption spectrum, the absorption coefficient is 1.64 cm$^{-1}$ at 1030 nm and 7.07 cm$^{-1}$ at the pumping wavelength of 940 nm. After annealing, the absorption coefficient is 3.64 cm$^{-1}$ at 1030nm and 9.16 cm$^{-1}$ at the pumping wavelength. In Fig.4, the data are actually two curves, 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 after annealing. The near-perfect overlap of the curves indicates that there was essentially no concentration gradient for Cr$^{3+}$ ions and Yb$^{3+}$ ions along the length of the boule and that the distribution coefficient for Cr$^{3+}$ and Yb$^{3+}$ in YAG must be close to unity in the Cr,Yb:YAG boule. This is also demonstrated by x ray fluorescence technique. We analyzed the causes of the changes of the absorption spectra in the point of the crystal field 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 $O_h^{10} = Ia3d$. The difference of lattice constants in YAG crystal between Yb$^{3+}$ and Y$^{3+}$ is 1.5 9\%122, thus, when Yb$^{3+}$ is introduced into YAG, Yb$^{3+}$ is substituted at the dodecahedral Y$^{3+}$ site. When Cr and Ca are introduced into YAG crystal there are several valent states. Cr$^{3+}$ is the dominant spices and is substituted at the octahedral Al sites, 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. The increase of the absorption coefficient after annealing is due to the increase of the
concentration of Cr ions at tetrahedral sites at high temperature oxygen atmosphere. Cr 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,

\[
Cr^{3+} + V_O + \frac{1}{2} O_2 \rightarrow [Cr^{4+}]_{oct}
\]

\[
[Al^{3+}]_{oct} + [Cr^{4+}]_{oct} \rightarrow [Cr^{4+}]_{oera} + [Al^{3+}]_{oct}
\]

Equation (1) is the process of dispersion action of oxygen vacancy \(V_O\) in inter crystal to the crystal surface, and the formation of oxygen vacancy in crystal, combining with a octahedral \(Cr^{3+}\) to form a tetrahedral \(Cr^{4+}\). Equation (2) describes that unstable octahedral \(Cr^{4+}\) disperses into neighbor Al-O tetrahedron and forms a tetrahedral \(Cr^{4+}\) ([Cr4+]oct).

The strong absorption at 940 nm 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 investigation.

4. CONCLUSION

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 100mm in length. Annealing was performed in an oxygen atmosphere at 1400°C for 50h, then the crystals were cooled to room temperature at a rate of 10°C/h. The absorption spectra of Cr, Yb: YAG have five absorption bands. In the visible region, after annealing absorption spectra moved from 440nm and 605nm to 470nm and 610nm, respectively. Absorption intensity increased after samples were annealed. After comparing to the spectra of the Cr:YAG and Yb:YAG crystals, the Cr-,Yb: YAG crystals combine the Yb and Cr absorption characteristics and have a strong absorption band in Yb3 fluorescent wavelength 1030nm, so it can be a saturable absorber as a passive Q switch for Yb3+ in monolithic Cr,Yb:YAG laser crystal.

REFERENCES


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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 spectra of Cr:YAG and Yb:YAG crystal after annealing at room temperature.

Fig. 3 The absorption spectra of (Cr,Yb):YAG crystal as grown and annealing at room temperature.

Fig. 4 The absorption spectra of (Cr,Yb):YAG crystal in the top and bottom at room temperature.