Annealing effect on Cr,Yb:YAG laser crystal

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The absorption spectra, fluorescence spectra, and lifetimes of as-grown and annealed Cr,Yb:YAG crystal grown by Czochralski technique have been measured. The broad absorption bands in the visible region increase in intensity and shift to long wavelength after annealing, and the additional absorption around 482 nm may be possibly due to new octahedral Cr$^{4+}$ center in the crystal, and the increase in the infrared (IR) region is due to the increase of Cr$^{4+}$. The increase of Cr$^{4+}$ also results in the ground state absorption and the concentration quenching of Yb$^{3+}$ in Cr,Yb:YAG crystal after annealing, the fluorescence intensity is reduced to 75% and the emission lifetime is shortened from 1.40 to 0.44 ms.

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In recent years, diode-pumped Q-switched solid-state lasers have attracted a great deal of attention. The saturable absorbers which have been successfully used for passively Q-switched lasers include Cr$^{4+}$-doped crystals$^{[1]-[3]}$, dye$^{[4]}$, and LiF:F$^-$ color center crystals$^{[5]}$. Dyes show poor thermal stability and tend to degrade rapidly and require a cooling circulation system. Color centers exhibit a fading phenomenon that may limit the period of reliable operation. Cr$^{4+}$-doped crystals developed in recent years such as Cr$^{4+}$:YAG$^{[6]}$, Cr$^{4+}$:Mg$_2$SiO$_4$$^{[2]}$, Cr$^{4+}$:GSGG$^{[3]}$, Cr$^{4+}$:YSO$^{[3]}$, and so on, have the advantages of good photochemical and thermal stability, large absorption cross-section, low saturable intensity, and high damage threshold. In addition, Cr$^{4+}$ and Nd$^{3+}$ can be doped into YAG crystal to form a self-Q-switched laser crystal and this crystal combines the advantages of both the gain medium, Nd$^{3+}$, and the saturable absorber, Cr$^{4+}$.$^{[7]}

Recent advances in high-performance InGaAs laser diode (LD) with a wavelength around 1 m have stimulated interest in developing LD-pumped Yt$^{3+}$:doped lasers$^{[8]}$. The Yt$^{3+}$ ion has only two electronic states, the $2F_{7/2}$ ground state and $2F_{5/2}$ excited state. Some deleterious effects such as excited state absorption, up-conversion, and concentration quenching are absent in Yb$^{3+}$ lasers. At the same time, the broad emission band centered at 1030 nm of Yt$^{3+}$ couples well with the saturation absorption of Cr$^{4+}$:YAG, and passively Q-switched Yb$^{3+}$ lasers using Cr$^{4+}$:YAG as saturable absorber have been demonstrated$^{[9]}$. Self-Q-switched Cr:Yb:YAG laser has also been demonstrated$^{[10]}$. Yb:YAG laser crystal has many advantages over Nd:YAG such as small quantum defect (8.6%) between the pump and the laser photons resulting in low thermal loading (fractional heating of less than 1%), long radiative lifetime of the upper laser level (1.3 ms), broad absorption bandwidth, etc. So Cr:Yb:YAG self-Q-switched laser crystal has the advantage over Cr,Nd:YAG, it will be a potential self-Q-switched laser material used for generating sub-nanosecond laser pulses.

In this paper, we have grown Cr,Yb:YAG crystal co-doped with 0.05 at.-% Cr and 10 at.-% Yb by Czochralski method. The spectroscopic properties of Cr:Yb:YAG crystal and the effect of annealing on them were investigated.

Cr,Yb:YAG crystal was grown by the Czochralski method. The 99.999% pure raw materials were appropriately preheated and weighed according to a specific molar ratio. After the compounds were ground and mixed, they were pressed into pieces and put into an aluminum crucible. The pieces were heated to 1550 °C for 24 hours. The charge was then loaded into an induction crucible for crystal growth. During the growth the pulling rate was 1 mm/h, the rotation rate was 10–20 rpm, and the growth atmosphere was nitrogen. The as-grown boules had a blue-green coloration and became brown after annealing in oxygen at 1400 °C.

Samples for spectroscopic measurements were cut out of the boules and surfaces perpendicular to the (111) growth axis were polished. A JASCO V-570 UV/VIS/NIR Spectrophotometer was employed for acquisition of the absorption spectra at room temperature and the thickness of the sample was 1 mm. The fluorescence spectra were acquired by a TRIX 550 spectrophotometer with InGaAs LD as the pump source (excited at 940 nm). The decay time was measured by a computer controlled transient digitizer. The thickness of the sample for fluorescence measurement was below 0.5 mm.

Figure 1 shows the absorption spectra of Cr,Yb:YAG crystal as-grown and after annealing at room tempera-

Fig. 1. The absorption spectra of Cr,Yb:YAG crystal.
tured. In the wavelength range from 850 to 1200 nm, each absorption peak of Cr:Yb:YAG crystal increased in intensity and the absorption coefficients at 941 and 1090 nm increased from 10.75 to 12.40 cm⁻¹ and 1.56 to 3.39 cm⁻¹ respectively after annealing. The concentration of Cr³⁺ ions increased, and the absorption peaks of as-grown Cr:Yb:YAG superimposed in new Cr⁴⁺ absorption. The band centered at 1030 nm is believed to be caused by the 3A₂ → 3T₁ transition of Cr⁴⁺ ions. The absorption cross-section at 941 nm is 0.81 × 10⁻²⁰ cm² and the full-width at half-maximum (FWHM) is 21 nm. A large absorption cross-section is in favor of LD pumping and a wide FWHM means that the laser crystal is less sensitive to diode wavelength specification and the output power of the laser keeps stable.

When trivalent chromium is doped into Yb:YAG, it substitutes for aluminum and normally occupies octahedral sites, the Ca²⁺ substitutes for Y³⁺ leaving a net negative charge, so that chromium ions are forced to the Cr⁴⁺ valence to provide charge compensation at high temperature oxygen atmosphere, and Cr⁴⁺ is regarded to be substituted into tetrahedral Al site. The process[11]

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2\text{Cr}^{3+} + \text{O}_2 + \frac{1}{2}\text{O}_2 \rightarrow 2\text{[Cr}^{4+}]_{\text{oct}} + \text{O}^2-.
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Expression (1) is the process of diffusive action of oxygen vacancies (V₀) in inter crystal to the surface, and the formation of oxygen vacancy in crystal, combining with an octahedral \text{Cr}^{3+} to form an octahedral \text{Cr}^{4+}. Expression (2) describes that unstable octahedral \text{Cr}^{4+} disperses into neighbor Al-O tetrahedron and forms a tetrahedral \text{Cr}^{4+} ([\text{Cr}^{4+}]_{\text{tetra}}).

From Fig. 1, we can also see that in the visible region, there were two obvious absorption bands centered at 425 and 592 nm in as-grown Cr:Yb:YAG crystal. The absorption bands are attributed to the 4A₂ → 4T₁ and 4A₂ → 4T₂ transitions of \text{Cr}^{3+}, respectively. The main band position moved from 425 to 476 nm and from 592 to 611 nm and the absorption peaks increased after annealing. Figure 2 is calculated by subtracting the absorption spectrum of as-grown Cr:Yb:YAG from the absorption spectrum of annealed Cr:Yb:YAG crystal. The absorption in the near infrared (IR) region was due to new Cr⁴⁺ ions in the crystal after annealing and there were also strong absorption bands in the visible region. In the oxidation process at high temperature, the concentration of \text{Cr}^{3+} would not be increased (\text{Cr}^{3+} ions were oxidized to \text{Cr}^{4+} ions). At the same time, the concentration of oxygen vacancy dropped. The bands centered at 482 nm in Fig. 2 are impossibly attributed to \text{Cr}^{3+} and color center, they may be due to \text{3T₁} → \text{3T₂} transition of octahedrally coordinated \text{Cr}^{4+} in the crystal after oxidation[12]. The absorption bands[13] between 614–648 nm belong to \text{3B₁} (\text{3A₂}) → \text{3F}(\text{3T₁}) transition of tetrahedrally coordinated \text{Cr}^{4+}.

The fluorescence spectra of Cr:Yb:YAG crystal as-grown and after annealing at room temperature are illustrated in Fig. 3. The strong emission band is centered at 1030 nm, the emission cross-section at 1030 nm is 2.59 × 10⁻²⁰ cm² and the FWHM is 12 nm. After annealing, the fluorescent intensity at 1030 nm was reduced to about 75%. The great change may be related to the increase of Cr⁴⁺ concentration that results in the ground state absorption and the concentration quenching of Yb³⁺ in Cr:Yb:YAG after annealing. At the same time the fluorescence lifetime of 440 µs of Cr:Yb:YAG after annealing was shortened compared with 1.40 ns of as-grown Cr:Yb:YAG. There is also strong absorption at 1030 nm in Cr:Yb:YAG crystal and the photon emitting from excited state level to ground state level could be absorbed by nearby Yb³⁺ ion. Radiation trapping can easily lead to overestimate in fluorescence lifetime and increase the threshold of the crystal.

As the Cr⁴⁺ concentration increases in Cr:Yb:YAG crystal after annealing, the fluorescence lifetime of the crystal drops quickly. It can be seen that the energy transfer from Yb³⁺ to Cr⁴⁺ is effective. The energy transfer mechanism is as follows. An excited Yb³⁺ ion decays from \text{F₅/₂} to a level of \text{F₇/₂} and simultaneously, a neighboring Cr⁴⁺ ion is excited from its ground state \text{3B₁ (3A₂)} to an intermediate state \text{3A₂ (3T₁)}, because the \text{3A₂ (3T₁)} energy state is metastable and relaxes to the \text{3B₂ (3T₂)} level of Cr⁴⁺ ions very rapidly, the energy is stored in the \text{3B₂ (3T₂)} level until the saturable absorber, Cr⁴⁺, reaches saturation. When the saturable absorber, Cr⁴⁺, is blanches, the energy stored in the cavity will be released instantly, so the high peak power pulses will be generated.

In summary, Cr:Yb:YAG crystal co-doped with 0.05 at.% Cr and 10 at.% Yb was grown using the Czochralski method. The absorption spectra, emission spectrum, and fluorescence lifetime of Cr:Yb:YAG crystal have been investigated at room temperature and the effect of annealing on them were investigated.
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