Growth, thermal, and spectroscopic properties of a Cr,Yb,Ho,Eu:YAP laser crystal

Huili Zhang\textsuperscript{a,b}, Dunlu Sun\textsuperscript{a,*}, Jianqiao Luo\textsuperscript{a}, Jiakang Chen\textsuperscript{a,b}, Huajun Yang\textsuperscript{a,b}, Jingzhong Xiao\textsuperscript{c}, Qingli Zhang\textsuperscript{a}, Shaotang Yin\textsuperscript{a}

\textsuperscript{a}The Key Laboratory of Photonic Devices and Materials, Anhui Province, Anhui Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, Hefei 230031, PR China
\textsuperscript{b}University of Chinese Academy of Sciences, Beijing 100049, PR China
\textsuperscript{c}CEMDRX, Physics Department, Universidade de Coimbra, Coimbra P-3004-516, Portugal

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\textbf{A B S T R A C T}

A new Cr,Yb,Ho,Eu:YAlO\textsubscript{3} (YAP) laser crystal was successfully grown by the Czochralski method. Thermal properties were investigated along the a, b, and c crystalline axes. Results indicate that the Cr,Yb,Ho,Eu:YAP crystal has large anisotropic thermal expansion and that the suitable crystal growth direction is the b axis. The Debye temperatures were fitted, and the lattice vibration frequencies were calculated. Spectroscopic measurements show that Cr\textsuperscript{3+} and Yb\textsuperscript{3+} can be used as sensitizers of Ho\textsuperscript{3+} ions, and Eu\textsuperscript{3+} ions can play a role of the deactivator in decreasing the lifetime of laser lower level \textsuperscript{5}I\textsubscript{7} from 8.69 ms to 1.89 ms, which is beneficial in decreasing laser threshold and increasing laser conversion efficiency. All these findings suggest that the Cr,Yb,Ho,Eu:YAP crystal is a new potential candidate for realizing 2.8–3 \textmu m laser output pumped by a 970 nm laser diode or pulsed flash lamp.

\textsuperscript{*} Corresponding author. Tel.: +86 551 65593663; fax: +86 551 65591815.
E-mail address: dlsun@auofm.ac.cn (D. Sun).

1. Introduction

Applications in medical procedures, remote sensing, and pumping source of optical parameter oscillation (OPO) have indicated the need for mid-infrared lasers that operate near 3 \textmu m \cite{1,2}. The Ho\textsuperscript{3+} activator ion \cite{3,4} has been demonstrated to generate lasers in the 2.8–3.1 \textmu m region in various hosts, such as the oxide YAlO\textsubscript{2} (YAP), Y\textsubscript{3}Al\textsubscript{5}O\textsubscript{12} (YAG), and fluoride LiYF\textsubscript{4} (LYF). However, the single-doped Ho\textsuperscript{3+} crystal shows low absorption while pumped by flash lamp or currently well-developed laser diodes (LDs, such as 808, 940, or 970 nm) and leads to a low pumping efficiency. To solve this problem, an effective approach such as co-doping other ions as sensitizers for Ho\textsuperscript{3+} was proposed \cite{5,6}. Yb,Ho:YSGG (Y\textsubscript{3}Sc\textsubscript{2}Ga\textsubscript{4}O\textsubscript{12}) \cite{5} and Cr,Yb,Ho:YSGG \cite{6} were reported to be suitable for pumping by LD and flash lamp, respectively. In particular, in the Cr,Yb,Ho:YSGG crystal, the Cr\textsuperscript{3+}→Yb\textsuperscript{3+}→Ho\textsuperscript{3+} energy transfer process is more efficient than that of Cr\textsuperscript{3+}→Ho\textsuperscript{3+}, and the efficiency in the former case is >90% when the Ho\textsuperscript{3+} concentration is 5 \times 10\textsuperscript{19} cm\textsuperscript{-3}. However, in the YSGG host, the Ga element is volatile and Sc element is expensive, and thus the crystal growth is difficult and the costs become high. However, in the YAP host, no expensive and volatile compositions are needed, and the YAP possesses good thermal and mechanical properties similar to those of YAG. Moreover, the YAP is an excellent laser host because of its natural birefringence and anisotropy, thus the 2.8–3 \textmu m tunable polarization lasers can be generated with the doping of Ho\textsuperscript{3+} activator ions \cite{3}. Nevertheless, the efficiency and output power of 2.8–3 \textmu m Ho\textsuperscript{3+} lasers are still affected because of the long lifetime of the laser lower level \textsuperscript{5}I\textsubscript{7}. Therefore, a method to reduce the lifetime of the laser lower level \textsuperscript{5}I\textsubscript{7} should be adopted by depleting the population of energy level. Diening et al. \cite{5} reported that co-doping 0.1 at.% Eu\textsuperscript{3+} ions in the Yb,Ho:YSGG crystal leads to the decrease in lifetime of \textsuperscript{5}I\textsubscript{7} from 10.4 ms to 6.1 ms. Recently, we demonstrated \cite{7} that in Er,Pr:GYSGG crystal, the threshold decreases from 315 mW to 112 mW and laser slope efficiency increases form 10.1% to 17.4% because of the doping of deactivator Pr\textsuperscript{3+} ions (0.3 at.%). However, no study has reported about the Ho:YAP crystal with sensitizers of double-doping Cr\textsuperscript{3+} and Yb\textsuperscript{3+} ions and a deactivator of Eu\textsuperscript{3+} ions.

In the present study, the Cr,Yb,Ho,Eu:YAP crystal was successfully grown by the Czochralski method. We investigated its thermal properties, such as thermal expansion, thermal conductivity, and Debye temperature. The optical parameters related to the laser performance, such as absorption, fluorescence, lifetime, and energy transferring among the ions were also studied.

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2. Experimental details

2.1. Crystal growth

Using the Czochralski method, the Cr,Yb,Ho,Eu:YAP crystal was grown from a melt of congruent composition containing 1 at.% Cr\(^{3+}\), 10 at.% Yb\(^{3+}\), 1 at.% Ho\(^{3+}\), and 0.1% Eu\(^{3+}\). The structural formula can be written as \(\text{Cr}_{0.01}\text{Yb}_{0.01}\text{Ho}_{0.01}\text{Eu}_{0.001}\text{Y}_{0.883}\text{Al}_{0.99}\text{O}_{3}\). The chemicals used initially were Cr\(_2\)O\(_3\) (4 N), Yb\(_2\)O\(_3\) (4 N), Eu\(_2\)O\(_3\) (5 N), Ho\(_2\)O\(_3\) (5 N), Y\(_2\)O\(_3\) (5 N), and Al\(_2\)O\(_3\) (4 N) powders. The crystal was grown in a JGD-60 furnace (CETC26th, China) at 7 rpm and 1 mm/h pulling rate. A high optical quality Cr,Yb,Ho,Eu:YAP crystal with a dimension of \(\Phi\) 28 mm \(\times\) 90 mm was obtained. A photograph of the as-grown Cr,Yb,Ho,Eu:YAP crystal is shown in Fig. 1. The Cr,Yb,Ho,Eu:YAP crystal was annealed in the flow H\(_2\) atmosphere at 1400 °C for 2 h.

2.2. Thermal measurements

Thermal expansion behavior of crystals (12 mm \(\times\) 12 mm \(\times\) 2 mm) with \(a\), \(b\), and \(c\) crystalline axes were measured in the temperature range of 273–893 K using a DIL-402C thermal dilatometer under 5 K/min heating rate. The samples (\(\Phi\) 5 mm \(\times\) 2 mm) with \(a\), \(b\), and \(c\) crystalline axes and surfaces coated with a carbon layer were used for thermal diffusivity and specific heat measurements using a Laser Flash Apparatus (LFA457 Netzsch).

2.3. Spectroscopic measurements

The absorption spectra of the crystals with \(b\) axis were obtained using a spectrophotometer (PE lambda 950) from 320 nm to 3000 nm wavelength range. A fluorescence spectrometer (Edinburgh FLSP920) with an excitation source of 968 nm LD was used to measure the fluorescence spectrum and the fluorescence decay curves excited by OPO (opolette 355I) laser.

3. Results and discussion

3.1. Thermal expansion and density

Thermal expansion has significant effects on both crystal growth and possible applications of the material [8]. Appropriate thermal expansion can reduce thermal lensing effect and improve laser performance. By contrast, if the anisotropy of the thermal expansion is significant, then cracking of the crystal may occur during the growth process. Moreover, given that the thermal expansion of a crystal heated during the laser operation is significant, knowing the thermal expansion coefficients is important to predict the material behavior with the increase in temperature [9].

The thermal expansion coefficient \(\alpha\) of a crystal is a symmetric second-rank tensor [10]. For a crystal, the number of independent constants is consistent with its symmetry. Therefore, in the principal coordinate system, the \([\alpha_{ij}\) of the orthorhombic Cr,Yb,-Ho,Eu:YAP crystal is diagonal

\[
\begin{bmatrix}
\alpha_{11} & 0 & 0 \\
0 & \alpha_{22} & 0 \\
0 & 0 & \alpha_{33}
\end{bmatrix}
\]

where \(\alpha_{11}\), \(\alpha_{22}\), and \(\alpha_{33}\) are three independent thermal expansion coefficients, which represent expansion along \(a\), \(b\), and \(c\) axes, respectively. The coefficients can be determined by measuring the thermal expansion of \(a\), \(b\), and \(c\) oriented crystal samples. The thermal expansion curves of Cr,Yb,Ho,Eu:YAP crystal along three crystallographic directions are shown in Fig. 2. The thermal expansions are almost linear from 300 K to 893 K, and the Cr,Yb,-Ho,Eu:YAP crystal exhibits only positive thermal expansion when heated, which is similar to the Ho:YAP crystal [11].

The average linear thermal expansion coefficients along \(a\), \(b\), and \(c\) axes can be calculated in accordance with the following formula [11]:

\[
\bar{\alpha}(T_0 \rightarrow T) = \frac{\Delta L}{L_0} = \frac{1}{T_0 - T_0}
\]

where \(\bar{\alpha}(T_0 \rightarrow T)\) is the average thermal expansion coefficient from \(T_0\) to \(T\), \(L_0\) is the sample length at \(T_0\), \(\Delta L\) is the length change when the temperature changes from \(T_0\) to \(T\), and \(\Delta T = T - T_0\) is the temperature change. In this case, the average thermal expansion coefficients along \(a\), \(b\), and \(c\) axes are \(1.83 \times 10^{-5}\), \(7.20 \times 10^{-5}\), and \(1.80 \times 10^{-5}\) from 300 K to 893 K, respectively. The thermal expansion coefficients along the \(a\) axis is larger than those of the \(b\) and \(c\) axes, thereby indicating that the Cr,Yb,Ho,Eu:YAP crystal has a large anisotropic thermal expansion. In addition, the thermal expansion coefficient along the \(b\) axis is the smallest. Thus, the Cr,Yb,Ho,Eu:YAP crystal grown along the \(b\) direction could effectively reduce the internal stress and cracking caused by isotropic contraction during cooling. Given that the crystal is grown along the \(c\) direction, anisotropic contraction occurs in the radial plane, and a maximum is found for the hoop stresses along the directions, which belongs to the above type \(ab\) radial plane [12]. Therefore, the \(b\) direction is relatively preferential to be chosen for the crystal.
growth by the Czochralski method to obtain crack-free crystals with high quality.

The density of the Cr,Yb,Ho,Eu:YAP crystal was measured to be 5.395 g/cm³ by the buoyancy method at room temperature. Dong et al. [11] reported that the density of Ho:YAP is 5.3 g/cm³ at 293.15 K. The increased density for Cr,Yb,Ho,Eu:YAP crystal should mainly result from the doping of 10 at.% Yb³⁺ ions. The temperature dependent density curve is shown in the inset of Fig. 2. The density decreases linearly with the increase in temperature, which is due to the linear expansion of Cr,Yb,Ho,Eu:YAP crystal at the three crystalline directions.

3.2. Thermal diffusivity coefficient, specific heat, and thermal conductivity

The thermal diffusivity coefficient and specific heat of the Cr,Yb,Ho,Eu:YAP crystal along the a, b, and c axes were measured from 300 K to 750 K (Fig. 3). The thermal diffusivity coefficients along the above directions decrease with the increase in temperature, and the thermal diffusivity coefficient along the a axis is larger than those of the b and c axes at a constant temperature, which is consistent with the strong anisotropy of the YAP crystalline structure. Furthermore, the thermal diffusivity coefficients along the b and c axes are significantly close to each other, which shows weak anisotropy in the (100) plane. In addition, the specific heat along the b axis is higher than those of the a and c axes and increases almost linearly from 0.72 J g⁻¹ K⁻¹ to 0.89 J g⁻¹ K⁻¹ from 300 K to 750 K. For optical crystals, the damage threshold and the possible applications could be seriously influenced by the specific heat, thereby indicating that the Cr,Yb,Ho,Eu:YAP crystal grown with the b axis can tolerate more thermal load at high temperatures.

To understand the thermal properties of the Cr,Yb,Ho,Eu:YAP crystal, we calculated the thermal conductivity κ using the following equation:

\[ \kappa = \lambda \rho C_p \]

where \( \lambda \), \( \rho \), and \( C_p \) denote the thermal diffusion coefficient, density, and specific heat, respectively. The calculated thermal conductivities along the different crystalline axes are shown in Fig. 4. The phonon mean free paths are reduced with increasing temperature [13], resulting in the decreasing trend of the thermal conductivities of the Cr,Yb,Ho,Eu:YAP crystal along the a, b, and c axes. Moreover, the thermal conductivity along the b axis is larger than those of the other two directions at constant temperature, thereby indicating that the Cr,Yb,Ho,Eu:YAP crystal grown along the b axis possesses better ability to conduct heat and can tolerate more thermal load at high temperature than those along the other axes, thereby making it possible to pump the crystal at high repetition rates. The thermal conductivity of the Cr,Yb,Ho,Eu:YAP crystal is lower than that of the Ho:YAP crystal [11], which should be ascribed to the more dopant ions and high Yb³⁺ doping concentrations (10 at.%) in the Cr,Yb,Ho,Eu:YAP crystal, thereby leading to the decreasing crystal order degree and increasing lattice malformation [13].

3.3. Debye temperature

Debye temperature \( \theta_D \), which is an important thermal parameter to assess crystal properties, represents the characteristic temperature of the atomic vibration inside the crystals. The specific heats were measured directly along the a, b, and c directions, and the Debye temperature \( \theta_D \) can be calculated from the specific heat capacity data based on the Debye model [14],

\[ C_v = 9nR \left( \frac{T}{\theta_D} \right)^3 \int_0^{\theta_D/T} \frac{e^{x^4}x^4}{(e^x - 1)^2} \, dx \]

where \( C_v \) is the specific heat, \( n \) is the atom number in the chemical formula, \( R \) is the gas constant, and \( M \) is the molecular weight. \( C_v \) is directly proportional to the \( T^3 \) when the temperature is under the Debye temperature, while it remains constant (24.943 J mol⁻¹ K⁻¹) when the temperature is higher than the Debye temperature. Assuming that \( a = \theta_D/T \) and \( x = (t + 1)a/2 \), the values of the Debye temperature \( \theta_D \) can be fitted using the least-square method, and the Gauss numerical integration calculation is applied to the equation:

\[ C_v = \frac{9nR}{2\pi^2} \sum A_i \left( \frac{t_i + 1}{2} \right) \]

where \( t_i \) and \( A_i \) represent the node and the corresponding coefficient of the Gauss–Legendre numerical integration. The gained Debye temperature \( \theta_D \) of the Cr,Yb,Ho,Eu:YAP crystal along a, b, and c directions are 586, 573, and 573 K, respectively. According to the relationship \( \theta_D = h\nu_{\text{lm}}/(2\pi k_B) \), the lattice vibration frequency \( \nu_{\text{lm}} \) of the three crystalline orientations are 7.66 × 10¹³, 7.49 × 10¹³, and 7.49 × 10¹³ Hz, respectively. The magnitude order of the vibration frequency in the Cr,Yb,Ho,Eu:YAP crystal along the three orientations is 10¹³, which shows that the crystal growths along the above directions have insignificant effect on the vibration frequency.
3.4. Absorption spectra

Fig. 5 shows the absorption spectra of the Ho:YAP, Cr,Yb,Ho:YAP and Cr,Yb,Ho,Eu:YAP crystals in the wavelength range of 320 nm–3000 nm. Compared with the single doped crystal, the Cr$^{3+}$ and Yb$^{3+}$ co-doped crystals exhibit an evidently widened absorption feature in the visible waveband and an additional absorption band in 910 nm to 990 nm. Thus, the Cr,Yb,Ho:YAP and Cr,Yb,Ho,Eu:YAP crystals may be more suitable for pumping by the currently well-developed 940 and 970 nm LD or pulsed flash lamp. The absorption cross-section of Yb$^{3+}$ ions at 970 nm is calculated to be approximately $4.0 \times 10^{-21}$ cm$^2$. The full width at half-maximum of the 970 nm absorption band is approximately 60 nm, which is relatively suitable and desirable for efficient pumping by high-power InGaAs LDs.

3.5. Fluorescence spectrum and level lifetime

The fluorescence spectrum of Cr,Yb,Ho,Eu:YAP crystal excited by 970 nm LD is shown in Fig. 6. The transitions of stark levels from $5I_6$ to $5I_7$ result in a quantity of fluorescence peaks (2.796, 2.816, 2.853, 2.878, 2.918, 2.930, 2.974, and 3.014 $\mu$m) within 2.7–3.1 $\mu$m. In addition, we calculated the stimulated emission cross-section based on the Füchtbauer–Ladenburg equation [15].

$$\sigma_{em}(\lambda) = \frac{I_0 - I_\infty}{8\pi^2 c n^2 \tau_m \int I(\lambda) d\lambda}$$  \hspace{1cm} (5)

where $I_0$ is the fluorescence intensity, $\tau_m$ is the measured lifetime of the upper energy level, $c$ is the velocity of light, $n$ is the refractive index, and $\lambda$ is the emission wavelength. The maximum emission cross-section value at 2853 nm is as high as $1.03 \times 10^{-21}$ cm$^2$ (Fig. 6, inset), which is beneficial in obtaining low-threshold and high-efficiency laser output. The emission cross sections of the other two strong peaks at 2918 and 3014 nm are $6.6 \times 10^{-22}$ and $4.3 \times 10^{-22}$ cm$^2$, respectively.

The fluorescence decay curves of Cr,Yb,Ho:YAP and Cr,Yb,Ho,Eu:YAP crystals show single exponential decay behavior (Fig. 7), corresponding to the lifetimes of upper level $5I_6$ and lower level $5I_7$ at 0.35 and 8.69 ms for Cr,Yb,Ho:YAP crystal, respectively. By contrast, the lifetime of upper level $5I_6$ and lower level $5I_7$ at 0.33 and 1.89 ms for Cr,Yb,Ho,Eu:YAP crystal. The lifetime of lower level $5I_7$ decreases from 8.69 ms in the Cr,Yb,Ho:YAP crystal to 1.89 ms in the Cr,Yb,Ho,Eu:YAP by nearly 5x, whereas the lifetime of $5I_6$ level decreases from 0.35 ms to 0.33 ms (6%). Therefore, the lifetime of the $5I_7$ level decreases significantly quicker than that of the $5I_6$ level in the Cr,Yb,Ho,Eu:YAP crystal, which is due to the energy transfer within Ho$^{3+}$;$5I_6$ → Eu$^{3+}$;$F_6$ (abbreviated as ET$_1$) and Ho$^{3+}$;$5I_7$ → Eu$^{3+}$;$F_6$ (ET$_2$) channels (Fig. 8). We can calculate the efficiency of the energy transfer Ho$^{3+}$ → Eu$^{3+}$ from [16]:

$$\eta_1 = 1 - \frac{\tau_{DA}}{\tau_D}$$  \hspace{1cm} (6)

where $\tau_{DA}$ is the lifetime of the donor in the presence of the acceptor (Cr,Yb,Ho:Eu:YAP) and $\tau_D$ is the lifetime of the donor in
the absence of the acceptor (Cr,Yb,Ho:YAP). According to the Eq. (6) and the lifetimes, the efficiencies of the energy transfer Ho\(^{3+}\) \(\rightarrow\) Eu\(^{3+}\) in ET\(_1\) and ET\(_2\) are evaluated as 5.7% and 78.2%, respectively. The energy transfer rate of ET\(_2\) is more prominent than that of ET\(_1\), which can explain the significantly quicker lifetime shortening of Ho\(^{3+}\):\(^{5}\)I\(_7\) than Ho\(^{3+}\):\(^{5}\)I\(_6\) level in the Cr,Yb,Ho,Eu:YAP crystal compared with the Cr,Yb,Ho:YAP crystal. Therefore, a population inversion between the Ho\(^{3+}\):\(^{5}\)I\(_6\) and \(^{5}\)I\(_7\) levels might be achieved under a lower pumping threshold, and thus the self-termination problem can be suppressed effectively. As a result, the doping of deactivator Eu\(^{3+}\) ions is helpful in reducing the laser threshold and improving the efficiency of 2.8–3 \(\mu\)m lasers in the Cr,Yb,Ho,Eu:YAP crystal. Further studies should focus on realizing 2.8–3 \(\mu\)m laser output by designing appropriate cooling system and cavity structure.

4. Conclusions

We report for the first time the thermal and spectroscopic properties of the Cr,Yb,Ho,Eu:YAP laser crystal grown by the Czochraski method. The thermal results indicate that the Cr,Yb,Ho,Eu:YAP crystal possesses large anisotropic thermal expansion, with average thermal expansion coefficients along the a, b, and c axes are 1.83 \(\times\) 10\(^{-5}\), 7.20 \(\times\) 10\(^{-6}\), and 1.80 \(\times\) 10\(^{-5}\) from 300 K to 893 K, respectively. In addition, the thermal conductivity along the b axis is larger than those along the a and c axes, thereby indicating that the Cr,Yb,Ho,Eu:YAP crystal grown along the b axis possesses good ability to conduct heat and can tolerate more thermal load at high temperature. Furthermore, the Debye temperature \(\theta_D\) of the Cr,Yb,Ho,Eu:YAP crystal is fitted to be approximately 580 K and the lattice vibration frequency \(\omega_{0}\) is approximately \(7.5 \times 10^{13}\) Hz. The spectroscopic measurements show that Cr\(^{3+}\) and Yb\(^{3+}\) can be used as sensitizers of Ho\(^{3+}\) ions, the Eu\(^{3+}\) ions can be the deactivator in decreasing the lifetime of laser lower level \(^{5}\)I\(_7\) from 8.69 ms to 1.89 ms, which is beneficial to the decrease in the laser threshold and the increase in the laser conversion efficiency. In summary, the Cr,Yb,Ho,Eu:YAP crystal is a new potential candidate for realizing the 2.8–3 \(\mu\)m laser output pumped by 970 nm LD or pulsed flash lamp.

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