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An extended application of β -Ga₂O₃ single crystals to the laser field: Cr⁴⁺: β -Ga₂O₃ utilized as a new promising saturable absorber

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Considering their easy growth and doping in bulk crystal growth, and good crystalline quality, β -Ga₂O₃ single crystals, a very important wide-bandgap semiconductor, are now also considered to be a promising optical crystal candidate. In this work, a Cr⁴⁺: β -Ga₂O₃ single crystal has been grown successfully by the edge-defined film-fed growth method. The thermal conductivity of Cr⁴⁺: β -Ga₂O₃ has been measured along the *a** direction at room temperature obtaining 16.2 W m⁻¹ K⁻¹, and it was much larger than that of the usually used Cr⁴⁺-doped crystals, such as Y₃Al₅O₁₂ (YAG) or YVO₄. The Raman spectrum indicated that the cutoff phonon energy of the β -Ga₂O₃ crystal was 767.8 cm⁻¹. A passively Q-switched nanosecond pulsed Nd:YAG laser based on a Cr⁴⁺: β -Ga₂O₃ saturable absorber was experimentally demonstrated for the first time to our knowledge and its mechanism is explained by first-principles calculations. By inserting the Cr⁴⁺: β -Ga₂O₃ crystal into the Nd:YAG laser cavity, a Q-switched laser operation was obtained with a maximum average output power of 50 mW. The corresponding pulse repetition rate, pulse width, and pulse energy were determined to be of 421.5 kHz, 235.2 ns and 0.12 μ J, respectively.

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Introduction

Highly efficient ultra-fast lasers have attracted much attention in the fields of communication, material processing, medicine, etc.¹ Q-Switching is one of the most important and major techniques for generating short laser pulses on micro- and nano-second time scales. There are two types of Q-switching: active and passive ones. Compared with the active one, passive techniques can significantly simplify the operation, improve the compactness, reliability and efficiency, and reduce the cost of laser sources. The saturable absorber (SA) is the key element for a passive Q-switched laser. Many SAs have been studied such as color centers,² transition-metal ion doped crystals^{3–5} and semiconductors.^{6,7}

Transition-metal ions, in tetrahedral coordination, with 3d^N configuration are identified as a class of important active ions for SAs.^{8,9} For example, many crystals such as Cr⁴⁺:YAG,⁴ V³⁺:YAG,¹⁰ Cr⁴⁺:Gd₃Ga₅O₁₂,¹¹ Cr²⁺:ZnS,¹² Co²⁺:LaMgAl₁₁O₁₉

(ref. 13) have been extensively studied as SAs. Among these crystals YAG is a typical host crystal due to its favorable chemical and physical properties especially the good thermal conductivity and high damage threshold, which are beneficial for realizing high power laser output. So far the Cr⁴⁺:YAG single crystal is the most common SA around 1 μ m.⁴ However, the maximum phonon energy of YAG (about 857 cm⁻¹) is relatively high, which is unfavorable for high power laser since it will easily lead to multi-phonon process.^{14,15} Therefore, the exploration of new SA crystals with good physical properties, especially with high thermal conductivity and low phonon energy, has always attracted a lot of attention.⁹

β -Ga₂O₃ crystal is a sesquioxide which belongs to the monoclinic family (space group: *C2/m*). The gallium ions are located at tetrahedral and octahedral sites.¹⁶ So far this host was at the center of a large research work, being an ultra wide-bandgap semiconductor.¹⁷ Wide-bandgap materials are challenging in the field of high voltage field-effect transistors, Schottky barrier diodes and ultraviolet photoelectric devices.^{18–21} The β -Ga₂O₃ crystal presents steady chemical and physical properties. Its thermal conductivity is about 27 W m⁻¹ K⁻¹ along *b* axes,²² which is much larger than that of YAG (12.9 W m⁻¹ K⁻¹).²³ This indicates that β -Ga₂O₃ crystal could be favorable as an SA for the laser pulses of high peak power and high repetition rate. On the other hand, in recent years, large size bulk β -Ga₂O₃ crystals have been grown by various melt-

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growth methods, for example: Czochralski method,²⁴ floating zone technique,²⁵ Bridgman method,²⁶ edge-defined film-fed growth (EFG) method²⁷ and so on. Therefore, the access of high quality and large-sized β -Ga₂O₃ crystals makes it possible to be applied in laser field. However, there is still no report on exploiting the capabilities of β -Ga₂O₃ crystal in laser field until now.

In this work, Cr⁴⁺: β -Ga₂O₃ single crystal has been successfully grown by EFG method. The bivalent Mg²⁺ ion was co-doped into the crystal to increase the ratio of Cr⁴⁺/Cr³⁺. The thermal conductivity and maximum phonon energy have been measured. Moreover, the laser operation has been demonstrated with the SA of Cr⁴⁺: β -Ga₂O₃ crystal and the mechanism of saturable absorption phenomenon is also explained by the first-principles calculation. We believe that this work may provide some reference for future research of β -Ga₂O₃ in laser.

Experimental section

Crystal growth

The Cr⁴⁺: β -Ga₂O₃ single crystal was grown by using a RF-heating EFG furnace. Powder raw materials of β -Ga₂O₃ (purity 99.99%), MgO (purity 99.99%), Cr₂O₃ (purity 99.5%) were adequately mixed and pressed into tablets. The prepared tablets were loaded into the Ir crucible (Φ 60 \times 60 mm³) with an Ir die. The size of the die top and the width of the slit were 4 \times 25 mm² and 0.5 mm, respectively. Then the materials were heated to the melting temperature of β -Ga₂O₃. The molten materials rose through the slit due to capillary action and spread over the top of the Ir die. A pure β -Ga₂O₃ seed crystal with (010) orientation was slowly moved down to touch the top surface of the die under a suitable temperature, at which the seed would neither melt nor expand significantly. After ten minutes stabilization, the seed was pulled up at a speed of 10 mm h⁻¹. The heating power was gradually adjusted to narrow the seed, namely necking. After the necking process, the pulling speed was gradually decreased to 6 mm h⁻¹. The temperature was also decreased in order to extend the crystal spreading out on the whole top section of the die. The crystal was grown under the atmosphere of 98% Ar, plus 2% O₂ in order to suppress the decomposition and evaporation of Ga₂O₃ at high temperature. After the growth, the crystal was cooled down to room temperature at a rate of 20–30 °C h⁻¹. To further increase the ratio of

Cr⁴⁺/Cr³⁺, the crystal was annealed at 1400 °C for 50 h in air. The annealed (100)-faced sample used as an SA in the following laser operation is shown in Fig. 1.

Thermal properties

The thermal conductivities of the Cr⁴⁺: β -Ga₂O₃ and YAG crystals were measured using a Netzsch Nanoflash model LFA 457 apparatus by laser pulse method. The plate samples of 4 \times 4 \times 1 mm³ in dimensions were cut from the bulk crystals. The larger faces were (100) plane for Cr⁴⁺: β -Ga₂O₃, and (010) plane in the case of YAG. The samples coated with graphite on both square faces, were heated using a short light pulse over the temperature range of 25–700 °C. The specific heat was measured using a differential scanning calorimeter (Perkin-Elmer Diamond model DSC-ZC) over the temperature range of 20 °C to 300 °C with a heating rate of 5 °C min⁻¹. The accuracy of calorimetry and temperature for the instrument are less than 0.1% and \pm 0.01 °C, respectively. A sample weighing 90.3 mg was used during this measurement.

Raman spectroscopy and absorption spectrum

Room temperature Raman spectrum of β -Ga₂O₃ single crystal was measured by a Horiba Jobin Yvon LabRAM HR Raman spectrometer equipped with a Ge detector cooled by liquid N₂. A solid state laser at 633 nm with the power of 150 mW was used as excitation source. The absorption spectrum of Cr–Mg co-doped crystal grown by EFG method was measured by using a Varian Cary 500 spectrophotometer in the range of 190–1700 nm with a resolution of 1 nm.

Computational detail

In order to better understand the effect of Cr⁴⁺-doping on β -Ga₂O₃ crystal, the first principles calculations were performed based on density functional theory with the projector-augmented wave (PAW) method, as implemented in the Vienna ab initio simulation package (VASP).²⁸ The generalized gradient approximation (GGA) functional of Perdew, Burke and Ernzerhof (PBE)²⁹ was used to approximate the exchange and correlation interactions. A cutoff energy of 400 eV for the plane-wave basis set and a Monkhorst–Pack mesh of 4 \times 6 \times 4 for the Brillouin zone integration were employed.

Pulse laser operation measurements

The laser experimental set-up is shown in Fig. 2. A simple concave-plano cavity was used to investigate the passive Q-switching Nd:YAG laser performance by using the Cr⁴⁺: β -Ga₂O₃ single crystal as the SA. The pump source was an 808 nm fiber-coupled diode laser with a core diameter of 200 μ m and a numerical aperture (N.A.) of 0.22. The pump beam was reimaged into the crystal by a 1 : 1 focusing system. M1 was a concave mirror with radius of curvature of 250 mm, which was anti-reflection (AR) coated at 808 nm on the entrance face, high-reflection (HR) coated at 1.06 μ m and high-transmission (HT) coated at 808 nm on the other face. M2 was a flat mirror with transmission of 5% at 1.06 μ m and HT coated at 808 nm. An

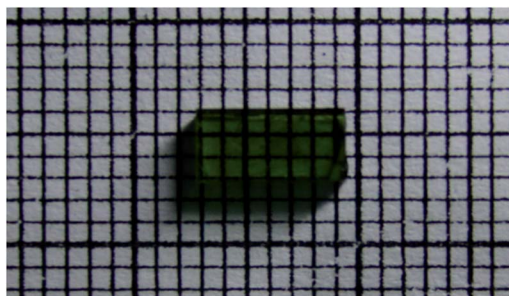


Fig. 1 Polished (100)-faced Cr⁴⁺: β -Ga₂O₃ crystal sample after being annealed at 1400 °C for 50 h in air.



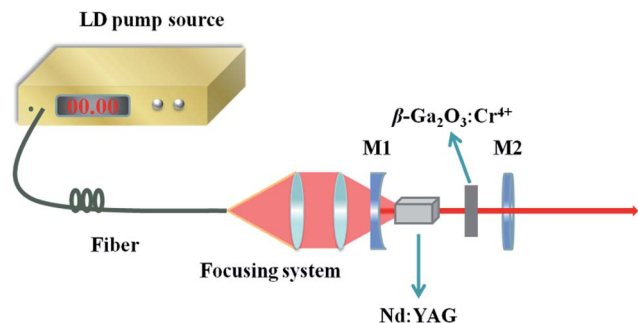


Fig. 2 Schematic diagram of the experimental laser setup.

uncoated and polished Nd:YAG crystal with dimensions of $4 \times 4 \times 7 \text{ mm}^3$ was used as the gain medium. In order to alleviate the thermal lensing effect, the Nd:YAG crystal was wrapped with an indium foil and mounted in a water-cooled copper holder maintained at a temperature of 16°C . A polished (100)-faced $\text{Cr}^{4+}:\beta\text{-Ga}_2\text{O}_3$ crystal with the dimensions of $3 \times 6 \times 1 \text{ mm}^3$ was used as the SA without water cooling. The output power was measured by a power meter (POWERMAX 500D, Molectron Inc.), and the temporal behaviors of the Q-switched lasers were recorded by a 1 GHz bandwidth and 5.0 Gs per s sampling rate digital oscilloscope (DPO7104, Tektronix Inc.).

Result and discussion

Thermal properties

The thermal properties of crystals are crucial factors to be considered in high power laser. There are a little difference between the reported thermal conductivities of YAG (12.9, 10.7, $10.3 \text{ W m}^{-1} \text{ K}^{-1}$).^{23,30,31} Therefore, the conductivity of undoped YAG was also measured for comparison in our experiment. The thermal conductivities of $\text{Cr}^{4+}:\beta\text{-Ga}_2\text{O}_3$ and YAG crystals were shown in Fig. 3(a). As we can see, the thermal conductivity of $\text{Cr}^{4+}:\beta\text{-Ga}_2\text{O}_3$ along a^* is $16.2 \text{ W m}^{-1} \text{ K}^{-1}$ at room temperature, which is much larger than that of undoped YAG crystal of $11.7 \text{ W m}^{-1} \text{ K}^{-1}$. Although the ion doping usually will induce lattice distortion of the crystals, and lead to a decrease of the thermal conductivity as a result. However, the thermal conductivity of $\text{Cr}^{4+}:\beta\text{-Ga}_2\text{O}_3$ is still much larger than that of undoped YAG crystal. What is more, the thermal conductivities along the b and c axes could be higher than that of a^* axis according

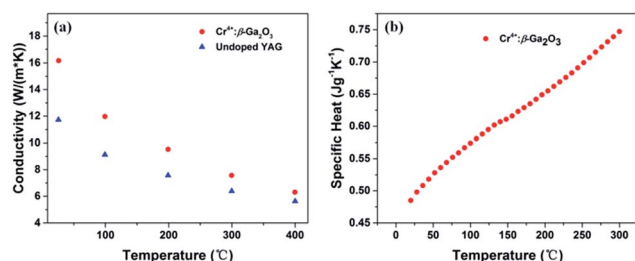


Fig. 3 (a) Thermal conductivities of $\text{Cr}^{4+}:\beta\text{-Ga}_2\text{O}_3$ and YAG, (b) specific heat of $\text{Cr}^{4+}:\beta\text{-Ga}_2\text{O}_3$ crystal.

to previous research.²² The higher thermal conductivity of $\text{Cr}^{4+}:\beta\text{-Ga}_2\text{O}_3$ will provide a better thermal management than of $\text{Cr}^{4+}:\text{YAG}$, which is quite essential especially to high power laser. The specific heat (C_p) of $\text{Cr}^{4+}:\beta\text{-Ga}_2\text{O}_3$ crystal as a function of temperature is shown in the Fig. 3(b). The C_p of $\text{Cr}^{4+}:\beta\text{-Ga}_2\text{O}_3$ increased almost linearly from $0.485 \text{ J g}^{-1} \text{ K}^{-1}$ at 20°C to $0.747 \text{ J g}^{-1} \text{ K}^{-1}$ at 300°C , comparable with the literature value of YAG ($0.603 \text{ J g}^{-1} \text{ K}^{-1}$).²³

Phonon energy

Host materials having low cutoff phonon energy will have a negligible multiphonon process behavior which is beneficial for enhancing the efficiency of laser operation. The phonon energy of laser host materials can be characterized by Raman spectra.³² The Raman scattering spectrum of $\beta\text{-Ga}_2\text{O}_3$ single crystal was shown in Fig. 4. There are 11 peaks ranging from 100 cm^{-1} to 1000 cm^{-1} . The largest Raman shift peak was at 767.8 cm^{-1} which was in good agreement with the calculated value.³³ Therefore, the maximum phonon energy of $\beta\text{-Ga}_2\text{O}_3$ crystal is 767.8 cm^{-1} , which is lower than that of YAG (857 cm^{-1}).^{14,15} This indicates that the $\beta\text{-Ga}_2\text{O}_3$ crystal should be a promising host material for laser applications.

Laser performance

Fig. 5(a) shows the relationship between the average output power and the absorbed pump power of the Q-switched laser. It shows a monotonously linear increase with augmenting the absorbed pump power. In order to protect the crystal from damage, the absorbed pump power was limited to 4.33 W and the maximum output power was 50 mW. No damage was observed on the crystals and mirrors in the laser experiment.

The pulse width and pulse repetition rate were recorded and they are shown in Fig. 5(b). By increasing the pump power, the pulse repetition rate increased from 290.5 to 421.5 kHz, while the pulse width shortened from 287 to 235.2 ns. The pulse trains and single pulse profile were shown in Fig. 6, which were obtained at

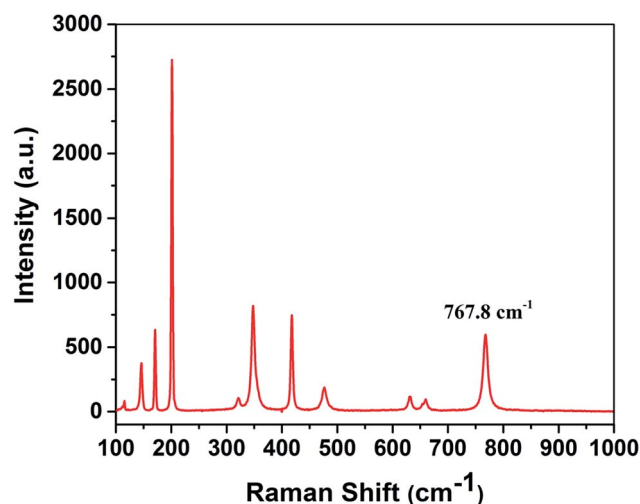


Fig. 4 Raman scattering spectrum of $\beta\text{-Ga}_2\text{O}_3$ single crystal.



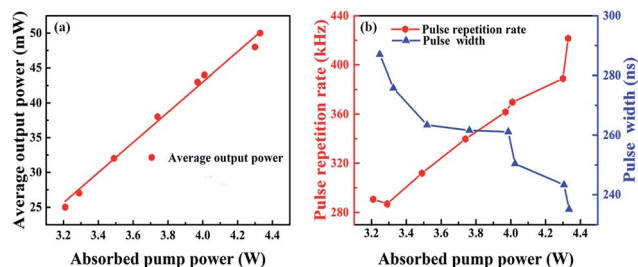


Fig. 5 (a) Average output power versus pump power for the Q-switching regime, (b) pulse width and pulse repetition frequency versus pump power.

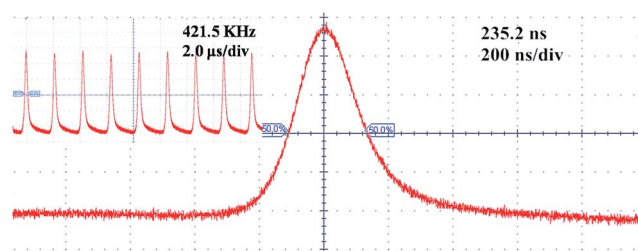


Fig. 6 The pulse train and single pulse profile at the maximum pump power of 4.33 W.

the maximum pump power of 4.33 W. At the maximum pump power the pulse duration and the corresponding pulse repetition rate were measured to be about 235.2 ns and 421.5 kHz, respectively. The maximum single pulse energy was calculated to be 0.12 μJ with a corresponding peak power of 0.51 W.

Mechanism of the saturable absorption

The calculated electronic and optical properties of pure and doped β -Ga₂O₃ are shown in Fig. 7(a). The electronic band gap of pure β -Ga₂O₃ is predicted to be 2.3 eV (Fig. 7(b)), which is consistent with previous calculated results,³⁴ however much smaller than the experimental results, (4.5–4.9) eV, due to the very well-known underestimation on band gap value of DFT-GGA. For Cr–Mg co-doped β -Ga₂O₃, the flat bands are found near the Fermi level in spin up states. Therefore, the band gap is largely decreased to 0.5 eV (Fig. 7(d)). From the partial density of states (PDOS), we note that the flat band states are mainly contributed by Cr atoms but little involved with Mg atoms. In addition, the decreased band gap is expected to be beneficial for long wavelength absorption of the doped β -Ga₂O₃ as excited by light. The optical properties are determined by the dielectric function $\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$, where the imaginary part $\epsilon_2(\omega)$ can be obtained from the momentum matrix elements between the occupied and unoccupied wave functions, and the real part $\epsilon_1(\omega)$ can be evaluated from $\epsilon_2(\omega)$ using the Kramer–Kronig relations.³⁵ The absorption coefficient $\alpha(\omega)$ can be expressed as $\alpha(\omega) = \sqrt{2}\omega \left[\sqrt{\epsilon_1^2(\omega) + \epsilon_2^2(\omega)} - \epsilon_1(\omega) \right]^{1/2}$, which is used to determine the absorption spectrum in the calculation. The measured absorption spectrum of Cr–Mg co-doped crystal

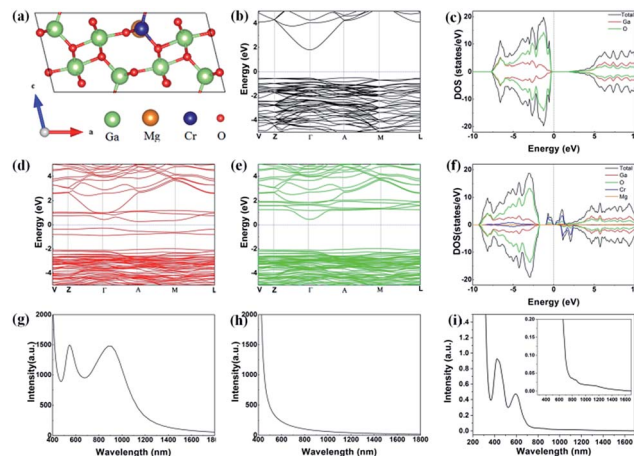


Fig. 7 (a) The optimized structure of Cr–Mg co-doped β -Ga₂O₃. The electronic band structure (b) and PDOS (c) of pure β -Ga₂O₃. Band structures of spin-up (d) and spin-down (e) electrons of Cr–Mg co-doped β -Ga₂O₃. (f) PDOS of Cr–Mg co-doped β -Ga₂O₃. Calculated absorption spectrum of pure (g) and Cr–Mg co-doped (h) β -Ga₂O₃. (i) The measured absorption spectrum of Cr–Mg co-doped crystal.

grown by EFG method was shown in the Fig. 7(i). For comparison, the calculated results are shown in Fig. 7(g) and (h). From Fig. 7(g) we can see that there is no obvious absorption peak of pure β -Ga₂O₃ in the region of wavelength larger than 600 nm apart from the intrinsic absorption peak located at ~ 440 nm. Nevertheless, two distinct absorption peaks individually located at 600 and 1000 nm appear in Cr–Mg co-doped β -Ga₂O₃, which correspond to the electrons transition from the doping states. When doped β -Ga₂O₃ is under strong excitation, the final states may be fully occupied and exhibited saturable absorption. This is also the reason that the experiment observed saturable absorption of Cr–Mg co-doped β -Ga₂O₃ at 1064 nm.

Conclusions and prospect

In this work, the β -Ga₂O₃ crystal has been studied and successfully demonstrated as a laser element for the first time. The Cr⁴⁺-doped β -Ga₂O₃ crystal has been grown by EFG method. Passively Q-switched laser based on Cr⁴⁺: β -Ga₂O₃ SA was experimentally demonstrated. Cr⁴⁺: β -Ga₂O₃ has high thermal conductivity (16.2 W m^{−1} K^{−1}) and favorable maximum phonon energy (767 cm^{−1}). We obtained a Q-switched laser operation with a maximum average output power of 50 mW, a pulse repetition rate of 421.5 kHz, a pulse width of 235.2 ns and a pulse energy of about 0.12 μJ was demonstrated. In conclusion, considering the easy large-scale fabrication of crystal, good thermal properties and low phonon energy, the β -Ga₂O₃ crystal should be a promising laser element crystal, not only used as SAs after doping with Cr or Co transition-metal ions but also as laser crystal, doped with Ti ions in the future.

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