High-energy, nanosecond pulsed Cr:CdSe laser with a 2.25–3.08 μm tuning range for laser biomaterial processing

MASAKI YUMOTO,¹* NORIHITO SAITO,¹ TAICHEN LIN,²,³ RIE KAWAMURA,⁴ AKIRA AO IKI,⁴ YUICHI IZUMI,⁴ AND SATOSHI WADA¹

¹Photonics Control Technology Team, RIKEN Center for Advanced Photonics, RIKEN, 2-1 Hirosawa, Wako, Saitama 351-0198, Japan
²Department of Dentistry, Chung Shan Medical University Hospital, No. 110, Section 1, Jianguo N. Rd., Taichung 40201, Taiwan
³School of Dentistry, Chung Shan Medical University, No. 110, Section 1, Jianguo N. Rd., Taichung 40201, Taiwan
⁴Department of Periodontology, Graduate School of Medical and Dental Sciences, Tokyo Medical and Dental University (TMDU), 1-5-45 Yushima, Bunkyo-ku, Tokyo 113-8549, Japan
*myumoto@riken.jp

Abstract: We have developed a mid-infrared (mid-IR) tunable Cr:CdSe laser with nanosecond pulse operation. A broad tuning range from 2.25 to 3.08 μm and an output energy exceeding 4 mJ at 2.64 μm were demonstrated. The maximum energy conversion for absorbed energy reached 35% when the pump fluence was 2.1 J/cm². We showed that Cr:CdSe is an attractive laser material for obtaining high-energy pulses in the mid-IR region and that the Cr:CdSe laser has high potential for laser biomaterial processing.

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1. Introduction

Mid-infrared (mid-IR) solid-state pulsed lasers with broad tunability are of significant interest for many applications such as molecular spectroscopy, environmental remote sensing, and materials processing [1–3]. In particular, high-energy mid-IR lasers with the tuning range from 2 to 3 μm are expected to be applied to laser biomaterial processing. Because strong absorption peaks of the water and hydroxide ions (OH⁻) are included in various biomaterials appear in this wavelength range [4,5]. Mid-IR pulsed lasers oscillated at the absorption peaks of water or hydroxide ions can be used for the efficient laser ablation of biomaterials [6,7]. In addition, mid-IR pulsed lasers with wide tunability are also highly advantageous for investigating the wavelength dependence of the ablation effect of various biomaterials.

Cr²⁺-doped chalcogenide materials are effective laser materials for oscillating high-energy pulses in the mid-IR region because of their room-temperature wide tunability, broad absorption bands, and large stimulated-emission cross section [8,9]. In 1996, DeLoach et al. first reported the mid-IR lasing characteristics of Cr:ZnS and Cr:ZnSe [10]. Since then, several Cr²⁺-doped chalcogenide materials, such as Cr:Cd₁₋ₓMnxTe and Cr:CdSe, have been reported as tunable laser materials in the mid-IR region [11–13]. Cr:CdSe is an attractive laser material for direct lasing in the wavelength range from 2 to 3 μm because of its broad fluorescence spectral region and large stimulated-emission cross section [14].

MaKay et al. have demonstrated broadly tunable laser oscillation of a nanosecond pulsed Cr:CdSe laser pumped with a Q-switched Tm,Ho:YLF laser. The laser produced a tuning range of 2.32-2.88 μm and an output energy of 0.35 mJ at 2.5 μm [15]. Akimov et al. have reported a Cr:CdSe laser with a nonselective resonator and an output energy of 17 mJ was obtained around 2.65 μm by pumping with 1.94 μm, 300 μs pulses from a Tm:YAP laser. Using a dispersion prism as a wavelength-selective element, a tuning range of 2.26-3.61 μm was realized and an output energy exceeding 10 mJ was obtained at 2.65 μm [16]. However, a
nanosecond pulsed Cr:CdSe laser with pulse energy exceeding several mJ and broad tuning range in the mid-IR region has not been realized. The realization of the Cr:CdSe laser greatly contributes to further progress in laser biomaterial processing utilizing material absorptions.

We previously developed a 2.01 µm high-energy Q-switched Tm:YAG laser with nanosecond pulse operation [17]. This laser has high potential as a pump source to realize wide tunability and high-energy pulses in a nanosecond pulsed Cr:CdSe laser. In our previous research, Tm:YAG lasers were used as a pump source for Cr:ZnSe, and a nanosecond pulsed Cr:ZnSe laser, which produced a tuning range of 2.12-2.71 µm and an output energy of 7.8 mJ at 2.41 µm, was demonstrated [18]. The use of a Tm:YAG laser as a pump source for Cr:CdSe is expected to accelerate the development of high-energy nanosecond pulsed Cr:CdSe lasers with broad mid-IR tunability.

In this study, we report on high-energy-pulse oscillation in the mid-IR region using Cr:CdSe pumped with a Q-switched Tm:YAG laser. We investigate the laser-induced damage threshold (LIDT) of Cr:CdSe to avoid optical damage on the Cr:CdSe surface and design a Cr:CdSe laser cavity to obtain a large fundamental-mode beam radius (~0.6 mm) on the surface for damage-free operation. The Cr:CdSe laser produced a maximum output energy of 4.4 mJ at 2.64 µm with nanosecond pulse operation. To the best of our knowledge, this is the highest output energy ever reported for a nanosecond pulsed Cr:CdSe laser. A tuning range from 2.25 to 3.08 µm was demonstrated. In addition, we applied the Cr:CdSe laser to the ablation of hard dental tissues and also demonstrated the potential use of the Cr:CdSe laser for laser biomaterial processing.

2. Laser-induced damage test on Cr:CdSe

We investigated the LIDT of Cr:CdSe for utilization in laser cavity design. The setup for the damage test is shown in Fig. 1(a). We used a Cr:CdSe single crystal (Institute of Solid State Physics Acad. / 3photon) without an optical coating. The crystal length was 2 mm and the doping concentration of Cr²⁺ was approximately $0.7 \times 10^{18}$ cm$^{-3}$, which was grown by high-pressure vertical zone melting method [19]. A laboratory-built Q-switched Tm:YAG laser was prepared to induce optical damage on the sample surface. The Tm:YAG laser operated at a wavelength of 2.01 µm with a repetition rate of 10 Hz. A maximum pulse energy of 25 mJ was obtained with a pulse width of 300 ns. The output beam of the Tm:YAG laser was focused on the sample surface using a planoconvex lens (f = 1000 mm). The beam radius on the sample surface was set at 300 µm, allowing the input fluence on the sample surface to be controlled from 0 to 8.8 J/cm². The beam radius was defined by the intensity at 1/e² from peak intensity. We performed S-on-1 damage tests. Six hundred shots were input to the sample during a radiation time of 60 s, which means the Tm:YAG laser operated at the repetition rate of 10 Hz. The input energy was gradually increased until optical damage occurred on the sample surface. The occurrence of optical damage was confirmed by monitoring the spatial profile of the transmitted beam from the sample. The beam quality deterioration of the transmitted beam indicated the optical damage generated on the sample surface. Following the above procedure, six damage tests were performed and the average damage threshold was found to be ~3.93 J/cm² when the Tm:YAG laser was used as a pump source. We must design a Cr:CdSe laser cavity under the condition that pump fluence on the Cr:CdSe surface is below the damage threshold.
3. Design of the Cr:CdSe laser cavity

A schematic diagram of the Cr:CdSe laser cavity constructed with a Z-fold configuration is shown in Fig. 2. The same Tm:YAG laser as that used in the Cr:CdSe optical damage test was used as a pump source. The laser cavity consists of an output coupler (M1), two folding mirrors (M2, M3), a total reflector (M4), and a 10-mm-long Brewster-cut Cr:CdSe crystal (3 Photon. Inc.). The Brewster angle is 67.9° for the refractive index of 2.46 and the doping concentration of Cr²⁺ is approximately 0.7 × 10¹⁸ cm⁻³. The output coupler and the total reflector are flat and their reflections are 70% and 99.5% in the wavelength range from 2.2 to 3.5 μm, respectively. The folding mirrors are concave mirrors with a curvature radius of 1000 mm and a high reflection (HR) coating for the wavelength range from 2.2 to 3.5 μm. Here, the Cr:CdSe was placed at the midpoint between M2 and M3. The distance between the Cr:CdSe and M2 (M3) was set to 65 mm, and L was the length between M1 (M4) and M2 (M3). The cavity folding angle was set at about 25°. For the wavelength-tuning operation, the total reflector was replaced with a grating (Thorlabs Inc., GR25-0616). The blaze wavelength and the groove density were 1.6 μm and 600 grooves/mm, respectively. The diffraction efficiency was more than 90% in the wavelength range from 2.0 to 3.2 μm.

To realize a high-pulse-energy Cr:CdSe laser, high energy pumping of the Cr:CdSe is essential. For instance, assuming an energy conversion efficiency of 20% [15], the Cr:CdSe must be pumped with a pump energy of 25 mJ to obtain an output energy of ~5 mJ. In this case, to avoid optical damage of the Cr:CdSe, the pump beam should be incident with a spot size of more than 0.45 mm at the Cr:CdSe surface. This is because the pump fluence at the Cr:CdSe surface exceeded the damage threshold of 3.93 J/cm² when a pump energy of 25 mJ was focused to a spot size of less than 0.45 mm. To obtain a large fundamental-mode beam radius more than 0.45 mm on the Cr:CdSe surface, we simulated the Cr:CdSe laser cavity mode using the standard ABCD matrix method. The above values of the curvature radius and the distance between the Cr:CdSe and M2 (M3) were used in the simulation. Figure 3 shows the simulation result for the calculated fundamental-mode beam radius at the Cr:CdSe surface and on the surface of M1 (M4) as a function of the distance L. When L was longer than 160 mm, a large beam radius exceeding 0.6 mm was realized at the Cr:CdSe surface. In our experiment, we set L to 160 mm and focused the pump beam to 0.6 mm at the Cr:CdSe surface to realize mode matching between the fundamental-mode beam radius and the pump beam radius at the Cr:CdSe surface. Under this condition, the pump fluence is estimated to be approximately 2.2 J/cm² with a pump energy of 25 mJ. This pump fluence corresponds to less than 60% of the Cr:CdSe damage threshold. According to our cavity design, the Cr:CdSe laser cavity is a stable resonator and allows operation with no laser-induced damage up to a pump energy of 25 mJ.
Figure 4 shows the output energy performance of the Cr:CdSe laser as a function of pump energy. We measured the output energy performances under free-running and wavelength-selected operation. For the free-running operation, a maximum pulse energy of 6.0 mJ was obtained with a pump energy of 24 mJ and the energy conversion efficiency reached 25.0%. The wavelength-selected operation was realized by replacing the total reflector with the grating, and the wavelength of 2.64 μm was selected by rotating the grating. A highest output energy of 4.4 mJ at 2.64 μm was obtained under a pump energy of 24 mJ and the energy conversion efficiency reached 18.2%. Under this pumping condition, the maximum pump fluence was approximately 2.1 J/cm² and optical damage did not occur on the Cr:CdSe surface. Figure 5 shows the energy conversion efficiency at 2.64 μm as a function of a pump energy. As the increasing of pump energy, the conversion efficiency increased to approximately 18%. The maximum conversion efficiency reached 18.2% when the pump energy was 24 mJ (pump fluence ~2.1 J/cm²). Here, the maximum conversion efficiency for the absorbed pump energy was estimated to be 35%. Figure 6 shows the tuning range and spatial beam profiles of the Cr:CdSe laser. The broad tuning range from 2.25 to 3.08 μm was accomplished by rotating the grating inside the laser cavity. The lasing wavelength was measured using a high precision wavelength meter (IR-III WS6-200, HighFinesse). The spatial beam profiles at wavelengths of 2.66 and 2.88 μm were observed using a beam profiling camera (Pyrocam III, Ophir). The spatial beam profile in the TEM_{00} mode was obtained and the beam quality was maintained over the tuning range.
Figure 7 shows temporal profiles of the Cr:CdSe laser pulse and Tm:YAG laser pulse. The Tm:YAG laser pulse had a Gaussian shape with a pulse width of 420 ns (FWHM). The gain-switched pulse of the Cr:CdSe laser was measured at a wavelength of 2.64 μm. The temporal profiles do not have a Gaussian shape and have multiple peaks. Here, the width of the primary peak pulse and the build-up time were 32 and 260 ns, respectively. This pulse behavior is caused by the relaxation oscillation induced by the large stimulated-emission cross section (>110 × 10⁻²⁰ cm²) of Cr:CdSe [20]. When the Cr:CdSe laser was pumped with pulses longer than 100 ns, it is difficult to avoid the oscillation of multiple peak pulses and the temporal dispersion of the pulse energy. Similar phenomena have been reported when using Cr:ZnSe as a laser material [19,21]. The use of an EO Q-switched device inside the laser cavity is one of the means of obtaining Gaussian pulses.

Fig. 4. Output energy characteristics of the Cr:CdSe laser.

Fig. 5. Optical-optical energy conversion efficiency.
5. Ablation of dental hard tissue with the nanosecond pulsed Cr: CdSe laser

Q-switched Er:YAG and Er, Cr: YSGG lasers have been used for dental hard tissues ablation, and several studies show that the use of the lasers provides effective dental treatment [7, 22-25]. The Er: YAG and Er, Cr: YSGG lasers oscillate at 2.94 and 2.78 µm, respectively. The Cr: CdSe laser can also oscillate the both wavelengths because of its broad tuning range. To demonstrate the potential performance of the Cr: CdSe laser for laser biomaterial processing, we applied the Cr: CdSe laser to the dental hard tissues ablation.

For the ablation of hard dental tissues using the Cr: CdSe laser, with informed consent from patients, we extracted teeth, and prepared human dentin, which was then stored in saline solution at 4°C. Before laser irradiation, the dentin was removed from the saline solution and placed on a motorized translation stage. Mid-IR pulses oscillated from the Cr: CdSe laser were irradiated on the dentin. The surface of the dentin was analyzed using stereomicroscopy and scanning electron microscopy (SEM). The two wavelengths of the Cr: CdSe laser were tuned to the desired wavelengths of 2.78 and 2.94 µm by rotating the grating, and each beam was focused on the dentin surface using a planoconvex lens. The input beam energy and the spot size on the dentin surface were set at 2 mJ and 75 µm, respectively. The input fluence was estimated to be 2.8 J/cm². During laser irradiation, the stage was moved at a velocity of 0.5 mm/s. Figure 8 shows stereomicroscopic and SEM images of dentin surfaces irradiated by mid-IR pulses. The images in (a.1-3) and (b.1-3) represent the ablation results obtained at
2.78 and 2.94 μm, respectively. Cr:CdSe laser irradiation at 2.78 and 2.94 μm clearly produced grooves on the dentin surface with no visible thermal damage such as carbonization. Efficient laser ablation of the dentin was realized at a lower pulse energy than that for laser ablation using conventional Er:YAG lasers or Er,Cr:YSGG lasers [26,27]. This is due to the high peak power of our nanosecond pulsed Cr:CdSe laser as compared to microsecond pulsed operation of conventional Er:YAG lasers and Er,Cr:YSGG lasers. As shown in (a.3) and (b.3), scaly structures with open dentinal tubules were observed, similar to previous reports using conventional Er:YAG lasers and Er,Cr:YSGG lasers [28,29]. The results show that the Cr:CdSe laser has effective ablation ability of dental hard tissues, and the broad tunability in the mid-IR region becomes high advantage for effective laser ablation of various biomaterial.

The Cr:CdSe laser has broad tunability in the mid-IR region, supporting its effectiveness in investigating the dependence on wavelength of the ablation effect. In addition, the Cr:CdSe laser has high potential for achieving oscillation of picosecond and femtosecond mid-IR pulses using mode-locking techniques. The use of mid-IR pulses with various pulse width from nanosecond to femtosecond is highly advantageous for investigating the pulse width dependence of the ablation effect. Future developments of Cr:CdSe pulsed lasers can be expected to make major contributions in mid-IR laser biomaterial processing.

Fig. 8. Stereomicroscopic and SEM images of dentin surfaces after laser irradiation. (a.1-3) and (b.1-3) show the dentin surfaces irradiated at 2.78 and 2.94 μm, respectively.

6. Conclusion

In this study, we have demonstrated high pulse energy and wide mid-IR tunability for a nanosecond pulsed Cr:CdSe laser pumped with a Q-switched Tm:YAG laser. The tuning range of the Cr:CdSe laser was from 2.25 to 3.08 μm, which was realized by using a grating inside the laser cavity. A maximum output energy of 4.4 mJ was obtained at 2.64 μm with a pump energy of 24 mJ. Energy conversion efficiency reached 18.2% and the maximum conversion efficiency for the absorbed pump energy was estimated to be 35%. Spatial beam profiles in the TEM00 mode were observed over the tuning range. We also obtained the LIDT of Cr:CdSe, which will be useful for further energy scaling. These results show that the Tm:YAG laser is an effective pump source for realizing high-pulse-energy Cr:CdSe lasers. In addition to the development of a Cr:CdSe laser, we applied the Cr:CdSe laser to the ablation of dentin surfaces and demonstrated the high potential of the Cr:CdSe laser for laser biomaterial processing.

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Disclosures
The authors declare that there are no conflicts of interest related to this article.

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