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# Generation of 320 mW at 10.20 $\mu m$ based on CdSe long-wave infrared crystal



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#### ABSTRACT

CdSe single crystal, with the sizes of ~54 mm in diameter and ~25 mm in length, was grown by a high pressure vertical gradient freeze (HPVGF) technique using (0 0 1)-oriented seed. The CdSe crystal was characterized with transmission spectrophotometer. The transmission spectra showed that the infrared transmission was above 68% and the mean absorption coefficient was 0.041 cm<sup>-1</sup> in the range of 2.5–20  $\mu$ m. Using fabricated CdSe crystal with the dimensions of 6 mm × 10 mm × 44 mm, we demonstrated an optical parametric oscillator (OPO) pumped by a 2.05  $\mu$ m Ho:YLF laser at a pulse repetition frequency of 5 kHz. Up to 320 mW output was obtained at the idler wavelength of 10.20  $\mu$ m with a pump power of 18.06 W. 320 mW at 10.20  $\mu$ m, to our knowledge, was the highest power obtained with a 2.05  $\mu$ m laser-pumped CdSe OPO.

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#### 1. Introduction

Coherent long-wavelength infrared laser sources from 8 to 12 µm are significant because of the strong absorption of various molecules and broad atmospheric transparency windows. The long-wavelength infrared laser sources are promising to a wide scope of both military and civilian applications, such as directional infrared countermeasures (DIRCM), ranging and targeting, standoff detection, trace gas monitoring, spectrum analysis and wireless communications [1,2]. However, due to the absence of a direct gain medium to obtain long-wavelength infrared laser, nonlinear optical (NLO) frequency down-conversion, like optical parametric oscillator (OPO), difference frequency generation (DFG), optical parametric amplification (OPA), optical parametric generation (OPG), is regarded as an effective method for producing the longwavelength infrared radiation by using NLO crystals [3,4]. Because the performance of oxide-based NLO crystals is seriously influenced by multi-phonon absorption starting from about 4 µm, non-oxide NLO crystals can be used to produce long-wavelength infrared laser, including unary (Se, Te), binary (CdSe, GaSe), ternary (ZnGeP<sub>2</sub>, AgGaSe<sub>2</sub>, CdGeAs<sub>2</sub>, etc.) and quaternary (AgGaGeS<sub>4</sub>,  $Cd_xHg_{1-x}Ga_2S_4$ , etc.) compounds [5,6]. Although the effective nonlinear coefficient of CdSe is modest ( $d_{31} = 18 \text{ pm/V}$ ), which is about 5 times lower than that of  $ZnGeP_2$  (d<sub>36</sub> = 75 pm/V), CdSe single

tion [7,8]. Therefore, Herbst and Byer [9] demonstrated the OPO based CdSe single crystal in 1972. They have obtained a resonant signal near 2.2  $\mu$ m and a resonant idler from 9.8  $\mu$ m to 10.4  $\mu$ m using a Q-switched Nd: YAG laser operating at 1. 833 µm. In 2003, the tunable output in the range of 9.1–9.7 µm and output powers of 70 mW under the pump power of 800 mW were achieved by a synchronously pumped optical parametric oscillator (SPOPO) [10]. Zakel [11] have demonstrated a intracavity CdSe OPO using Cr:ZnSe laser pumping source, showing the signal and idler are tunable from 3.2 to 3.8 µm and 8.2 to 8.5 µm respectively and total output power is 3 W. Using 5 mm  $\times$  5 mm  $\times$  30 mm CdSe crystal, Wu [12] revealed the output average energy of 400  $\mu$ J at 4.3 µm and 8 µm with 2.797 µm Cr, Er:YSGG laser as pumping source. Yao [13,14] presented a CdSe OPO pumped by a 2.09 µm Ho:YAG laser. The tuning range of the idler was from 10.24 to 12.07 µm. Up to 140 mW and 170 mW output were obtained at the idler wavelength of 10.28  $\mu$ m and 12.07  $\mu$ m, respectively. In this paper, we obtained a large size CdSe single crystal by

crystal, with a wide transparency range from 0.7 to 18 μm, excellent mechanical and chemical stability, high laser damage thresh-

old and long crystals with high optical quality, is still identified as the good candidate for producing long-wavelength infrared radia-

HPVGF technique, with the sizes of ~54 mm in diameter and ~25 mm in length. Using the 6 mm × 10 mm × 44 mm CdSe crystal, we demonstrated an optical parametric oscillator (OPO) pumped by a 2.05  $\mu$ m Ho:YLF laser at a pulse repetition frequency of 5 kHz. As high as 320 mW at the idler wavelength of 10.20  $\mu$ m are generated under a pump power of 18.06 W.





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## 2. Experimental

In present work, CdSe single crystal was fabricated through high pressure vertical gradient freeze (HPVGF) technique using (0 0 1)oriented seed. After a high quality cylindrical CdSe single crystal with (0 0 1) orientation, obtained by spontaneous nucleation, was put into a PBN crucible as seed. The high purity CdSe (6N, CNBM Optoelectronic Materials Co., Ltd.) was used as starting materials, which was settled in a PBN crucible in vertical induction furnace. After the chamber was initially evacuated to a pressure below 0.01 Pa, high-pure Ar gas (99.999%) was introduced into the chamber during the heating process. The growth interface was controlled to be stable with a temperature gradient of 10-20 °C/cm. After 7–10 days, the PBN crucible was cooled slowly to room temperature. An integral and crack-free CdSe single crystal was obtained finally. After the [0 0 1] and [1 1 0] crystal orientation of CdSe single crystal



Fig. 1. (a) Photograph and (b) XRD pattern of CdSe single crystal.



**Fig. 2.** (a) UV–Vis–NIR spectrum, (b) transmission spectrum without coating, (c) absorption coefficient without coating, (d) transmission spectrum with coating of the 4 mm thick CdSe crystal. The inset is photograph of 4 mm thick CdSe crystal with coating.

were determined by a X-ray diffractometer, the CdSe crystals with dimensions of 10 mm  $\times$  10 mm  $\times$  4 mm and 6 mm  $\times$  10 mm  $\times$  44 mm were cut at  $\theta$  = 75° (±0.5°) and  $\varphi$  = 0° in order to meet the requirement for type II phase matching (o  $\rightarrow$  e + o).

X-ray diffraction (XRD) was detected by a D8 advanced X-ray diffractometer (Bruker, Germany) with CuK $\alpha$  radiation ( $\lambda$  = 1.5418 Å) at a scan rate of 8°/min in the 2 $\theta$  range of 10–90°. UV–Vis–NIR spectra at wavelength from 300 nm to 2500 nm were collected with a UV–Vis–NIR spectrophotometer (UV-3600, Shimadzu, Japan). Transmittance spectra were recorded on a Bruker vertex70 spectrophotometer at room temperature model. The idler spectrum was recorded by a spectrometer (iHR550, HORIBA Jobin Yvon) with a liquid-nitrogen cooled detector.

## 3. Results and discussion

The integral and crack-free CdSe, with the sizes of  $\sim$ 54 mm in diameter and  $\sim$ 25 mm in length, are shown in Fig. 1a. X-ray diffraction pattern of the products is shown in Fig. 1b. It is seen that all diffraction peaks of the XRD pattern can be well indexed to the standard pattern of hexagonal CdSe (JCPDS Card No. 65-3415, space group  $P6_3/mc$ ).

Shown in Fig. 2(a–b), the UV–Vis–NIR spectrum and transmission spectrum of 4 mm thick CdSe crystal without coating indicate that the short cut-off wavelength of CdSe crystal is about 740 nm and the infrared transmission was above 68% in the range of 2.5–20  $\mu$ m.

The transmittance absorption coefficients could be calculated according to Eq. (1):

$$\alpha = -\frac{1}{L} \ln \left( \left\{ \left[ \frac{(1-R)^2}{2TR^2} \right]^2 + \frac{1}{R^2} \right\}^{1/2} - \frac{(1-R)^2}{2TR^2} \right)$$
(1)

where L is the thickness of the sample, T is the transmission, and  $R = (n - 1)^2/(n + 1)^2$  is the Fresnel power reflection coefficient [12].

The calculated values, shown in Fig. 2c, reveal that the mean absorption coefficient is  $0.041 \text{ cm}^{-1}$  in the range of  $2.5-20 \,\mu\text{m}$  and the absorption coefficient at  $2.05 \,\mu\text{m}$ ,  $2.56 \,\mu\text{m}$ ,  $10.28 \,\mu\text{m}$  were measured to be  $0.069 \,\text{cm}^{-1}$ ,  $0.055 \,\text{cm}^{-1}$ ,  $0.014 \,\text{cm}^{-1}$ , respectively. The insert image in Fig. 2d exhibits photograph of 4 mm thick CdSe cystal with coating. The transmission was greatly improved after the 4 mm thick CdSe crystal was anti-reflection coated for pump, signal, idler light (Fig. 2d).

The schematic diagram of the OPO system is shown in Fig. 3a. The pump source of the CdSe OPO is an Q-switched Ho:YLF laser operating at a pulse repetition frequency (PRF) of 5 kHz.



Fig. 3. (a) Schematic diagram of the OPO system, (b) Output powers of the idler, (c) Spectrum of the idler with the peak at 10.20 µm.

Table 1	
The transmission and absorption coefficient at 2.05 $\mu m$ , 2.56 $\mu m$	, 10.28 $\mu m$ of CdSe crystal with dimensions of 6 mm $\times$ 10 mm $\times$ 44 mm.

Wavelength ( $\mu m$ )	Transmittance (%)			Absorption coefficient (cm <sup>-1</sup> )	
	Тор	Middle	Bottom	Mean	Mean
2.05	77.1	75.5	73.4	75.3	0.064
2.56	83.6	81.5	79.7	81.6	0.046
10.28	92.2	89.6	94.1	92.0	0.019

The CdSe crystal with dimensions of 6 mm  $\times$  10 mm  $\times$  44 mm was AR coated on both surfaces for pump, signal and idler wavelength bands. Using laser method, the absorption coefficient of the 6 mm  $\times$  10 mm  $\times$  44 mm CdSe crystal at 2.05 µm, 2.56 µm, 10.28 µm was measured as shown in Table 1, which is consistent with the results of transmission spectrum (Figure (a-b)).

The output powers of the CdSe OPO are shown in Fig. 3b. The threshold of the CdSe OPO was approximately 9.42 W, corresponding to a pulse energy of ~1.8 mJ and a pump intensity of ~1.9 MW/ cm<sup>2</sup>. The maximum idler output power of 320 mW (~64  $\mu$ J pulse energy) was obtained at a pump power of 18.06 W, corresponding to a slope efficiency of 3.7%. The relationship between output power and incident pump power shows the straight line with two different efficiency slope, including sharp stage (slope efficiency of 6.7%) and smooth stage (slope efficiency of 1.1%), indicating that thermal lens effect influence the out power. The idler spectrum shown in Fig. 3c was measured by a spectrometer with a liquid-nitrogen cooled detector. The peak wavelength of the spectrum was 10.20  $\mu$ m, and the full width at half maximum (FWHM) was around 78 nm.

# 4. Conclusion

Single crystals of CdSe were grown by using seeded high pressure vertical gradient freeze (HPVGF) technique with the sizes of 54 mm in diameter and 25 mm in length. The mean absorption was 0.041 cm<sup>-1</sup> in the range of 2.5–20  $\mu$ m. Using fabricated 6 mm × 10 mm × 44 mm device crystal, we demonstrated a CdSe optical parametric oscillator (OPO) pumped by a 2.05  $\mu$ m Ho: YAG laser, showing as large as 320 mW power output at the idler wavelength of 10.20  $\mu$ m with a pump power of 18.06 W.

#### References

- [1] M. Troccoli, A. Lyakh, J. Fan, X. Wang, R. Maulini, A.G. Tsekoun, R. Go, C.K.N. Patel, Long-wave IR quantum cascade lasers for emission in the  $\lambda$  = 8–12 µm spectral region, Opt. Mater. Express 3 (2013) 1546–1560.
- [2] A. Godard, Infrared (2–12 μm) solid-state laser sources: a review, Comptes Rendus Physique 8 (2007) 1100–1128.
- [3] B. Yao, G. Li, G. Zhu, P. Meng, Y. Ju, Y. Wang, Comparative investigation of longwave infrared generation based on ZnGeP<sub>2</sub> and CdSe optical parametric oscillators, Chin. Phys. B 21 (2012) 034213.
- [4] J. Wang, H. Yu, Y. Wu, R. Boughton, Recent developments in functional crystals in China, Engineering 1 (2015) 192–210.
- [5] S. Wang, S. Dai, N. Jia, N. Zong, C. Li, Y. Shen, T. Yu, J. Qiao, Z. Gao, Q. Peng, Z. Xu, X. Tao, Tunable 7–12 µm picosecond optical parametric amplifier based on a LiInSe<sub>2</sub> mid-infrared crystal, Opt. Lett. 42 (2017) 2098–2101.
- [6] V. Petrov, Parametric down-conversion devices: the coverage of the midinfrared spectral range by solid-state laser sources, Opt. Mat. 34 (2012) 536– 554.
- [7] P.G. Schunemann, Recent advances in nonlinear materials for 5-20 μm wavelength generation, Opt. Soc. Am. (2000) CWN1.
- [8] Z. Lei, C. Zhu, C. Xu, B. Yao, C. Yang, Growth of crack-free ZnGeP<sub>2</sub> large single crystals for high-power mid-infrared OPO applications, J. Cryst. Growth 389 (2014) 23–29.
- [9] R.L. Herbst, R.L. Byer, Singly resonant CdSe infrared parametric oscillator, Appl. Phys. Lett. 189 (1972) 189–191.
- [10] M.A. Watson, M.V. O'Connor, D.P. Shepherd, D.C. Hanna, Synchronously pumped CdSe optical parametric oscillator in the 9–10 mm region, Opt. Lett. 28 (2003) 1957–1959.
- [11] A. Zakel, G.J. Wagner, W.J. Alford, T.J. Carrig, High-power, rapidly-tunable dualband CdSe optical parametric oscillator, Adv. Solid-State Photonics (2005) 433–437.
- [12] Y. Ni, H. Wu, M. Mao, C. Lin, G. Cheng, Z. Wang, Synthesis and growth of nonlinear infrared crystal material CdSe via seeded oriented temperature gradient solution zoning method, Front. Optoelectron. China 4 (2011) 141– 145.
- [13] J. Yuan, X. Duan, B. Yao, Z. Cui, Y. Li, T. Dai, Y. Shen, Y. Ju, Tunable 10 μm to 11 μm CdSe optical parametric oscillator pumped by a 2.1 μm Ho:YAG laser, Appl. Phys. B 122 (2016) 1–4.
- [14] J. Yuan, Y. Chen, X. Duan, B. Yao, T. Dai, Y. Ju, CdSe optical parametric oscillator operating at 12.07 μm with 170 mW Output, Optics Laser Technol. 92 (2017) 1–4.