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RESEARCH ARTICLE

Synthesis and growth of nonlinear infrared crystal material CdSe via seeded oriented temperature gradient solution zoning method

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Abstract Single crystals of CdSe were grown by using seeded oriented temperature gradient solution zoning (S-TGSZ) method with the sizes of 20 mm in diameter and 80 mm in length. The crystals were characterized with X-ray diffraction, transmission spectrophotometer and infrared microscope. The transmission spectra showed that the infrared transmission is above 65% and the mean absorption was 0.01–0.04 cm^{-1} in the range of 2.5–20 μm. With 2.797 μm Cr,Er:YSGG laser as pumping source, experiments of optical parametric oscillator (OPO) were performed by using fabricated 5 mm×5 mm×30 mm device crystal. The signal and idler wavelengths and the output average power were respectively 4.3 μm, 8 μm and 400 μJ. Optical-to-optical conversion efficiency was obtained by 12%.

Keywords crystal growth, seeded oriented temperature gradient solution zoning (S-TGSZ) method, CdSe, optical parametric oscillator (OPO)

1 Introduction

In recent years, much effort has been focused on some nonlinear infrared crystals which have a wide range of transparency, such as $\mathrm{ZnGeP_2}$, GaSe, CdSe [1], due to their unusual properties and potential applications. Of these crystals, CdSe [2–4] has been more attactive because of its special optical properties, including extremely low optical losses ($< 0.01\ \mathrm{cm}^{-1}$, 1 to 10 μm), long wave tunable efficiency at $\lambda > 8$ μm without multi-phonon absorption. Also, CdSe has small birefringent walk-off, wide band gap and transparency range (E_g = 1.7 keV, 0.75 to 25 μm). These properties make it one of the leading candidates for nonlinear optics devices to achieve high peak power, mid-far (8–20 μm) infrared radiation with 2.797 μm Cr,Er:YSGG laser as pumping source.

However, the wide application of CdSe crystals has been limited for years for the lack of large single crystals with high-quality. The following factors may affect the crystal quality during its growth procedure. First, the melting point of CdSe is very high (1239°C), so the container-quartz crucible is easy to be broken at this temperature. Second, CdSe contains toxic and volatile components at the melting point, equilibrium partial pressures of Cd and Se along the liquids are high, which can induce inhomogeneities in composition, resulting in degradation of the frequency conversion ability [5].

In order to overcome the growth problems described as above, various methods have been used for producing CdSe single crystal. The temperature gradient solution zoning (TGSZ) technology was first described by Steininger [6] and advanced by Burger [7]. The Kolesnikov’s group [8] used high pressure Bridgman (HPVB) and the vertical zone melting (HPVZM) method to grow CdSe. In addition, chemical vapor transport method (CVTM) [9] was also reported.

These are all the important methods to grow CdSe single crystal. Yet, there also exist some limitations of their utilities. Stoichiometric variation, twins, and second phase precipitates are still difficult to be fully avoided during the CdSe growth process. Hence, an effective method to obtain fine optical quality CdSe crystal is urgently required.

In this paper, we report a comparative simple and effective route to grow CdSe crystal with large-size and low defects density. By using a modified growth method —

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seeded oriented temperature gradient solution zoning (S-TGSZ), the high quality CdSe materials with sizes of 20 mm in diameter and 60 mm in length was obtained. The absorption coefficient is as low as 0.01 cm^{-1} in the range of 2.5 to 15 μm.

2 Crystal growth

The typical experimental process was described as follows: first, high purity elements of Se, Cd (EMei Semiconductor Co., Ltd., Sichuan, China) of 5–9's and 6–9's grade were used as starting materials to get CdSe power. The rod-shaped Cd ingots were cleared off the oxide skin, weighed in an inert atmosphere, then mixed with the calculated amount of Se element, placed in carbon-coated quartz ampoules, evacuated (10^{-6} Torr) and sealed. Synthesis was carried out in a two-zone tube furnace. Reaction temperatures of 900°C and soak time exceeding 15 h were utilized. After cooled to room temperature, the synthesized alloy was collected and ground into powder carefully.

Then, a slice of high quality CdSe single crystal (8 mm thick, obtained by spontaneous nucleation before this experiment) with certain seed orientation was put into a carbon-coated quartz growth crucible with a cone-shaped bottom. After that, appropriate amount of Se element and CdSe power were placed upon the crystal in succession. Then, the quartz crucible was evacuated and sealed at room temperature. Growth run was carried out in a conventional vertical tube furnace. Single crystal CdSe was grown by using modified TGSZ via seeded growth method. Unlike the simple TGSZ technique, it is not only easy to operate at lower temperatures and pressures, but also suitable for maintaining a constant temperature at the growth surface, especially with the advantage of seeded oriented during crystal growth.

Subsequently, the resistance furnace was set to get a suitable temperature field via three independent heating zones: the upper one was heated to 1100°C at the rate of 40°C/h; the middle one was heated to 1070°C and the lower one was heated to 1000°C, keeping the temperature invariant for 50 h from the beginning of crystal growth. The growth process was performed with a temperature gradient of 15°C/cm typically at the interface. Perhaps the low thermal gradient can minimize thermal stresses associated with the anisotropic thermal expansion of CdSe crystal effectively. Normally, the growth process was finished two weeks later at the rate of 0.4–1.2 mm/h, and then the ampoule was cooled slowly to room temperature. An integral and crack-free CdSe single crystal was obtained finally as is shown in Fig. 1.

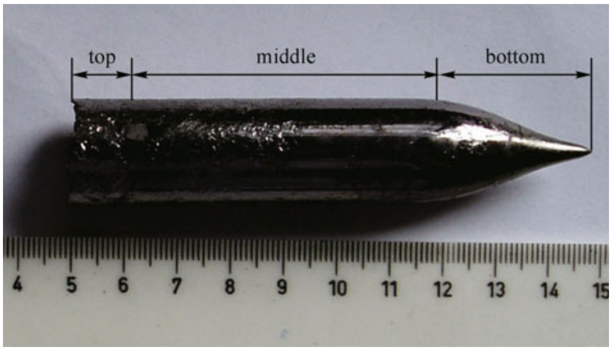


Fig. 1 Photograph of as-grown CdSe boule

The phase and the crystallographic of the products were characterized by X-ray diffraction (XRD) pattern, which was recorded by using a Shimadzu XRD-6000 X-ray diffractometer equipped with Cu Kα radiation (λ = 0.15406 nm). The scanning rate of 0.05°·s^{-1} was applied to record the pattern in the 2θ range of 10°–70°. Transmittance spectra were measured on a Hitachi270-30 spectrophotometer at room temperature model. The visual transmittance morphologies of the sample were observed with a low multiples infrared microscope Shimadzu HG-2 at room-temperature model.

3 Characterization

3.1 XRD analysis

Three little blocks of single-crystal samples were collected, with the positions top, middle and bottom from the whole crystal boule. Then they were ground into powder and their XRD patterns were recorded respectively, as shown in Fig. 2. The strong and sharp reflection peaks indicate that the as-prepared products are well crystallized.

In Fig. 2(b), the main diffraction peaks are labeled and

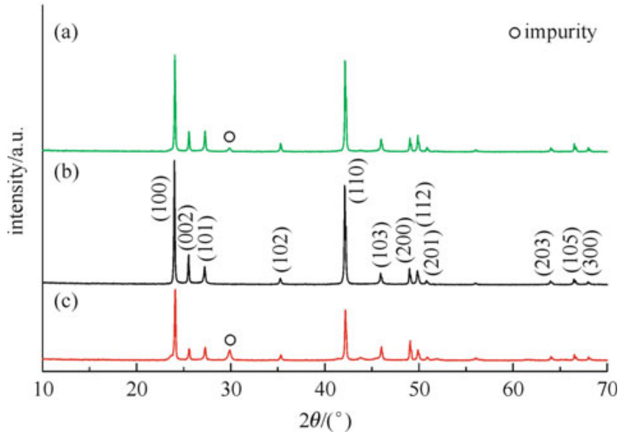


Fig. 2 XRD pattern of as-grown CdSe crystal from different positions: (a) top, (b) middle, and (c) bottom, in which (b) indicates as hexagonal lattice phase of CdSe, (a) and (c) are the mixture of cadmium selenide and selenium

they can be indexed as the pure hexagonal lattice phase CdSe with cell constants a = 1.113±0.003 nm, and c = 0.4001±0.004 nm, which are in agreement with the reported data a = 1.114 nm, and c = 0.3981 nm (JCPDS 2-330). In Figs. 2(a) and 2(c), some impurities peaks appear and are pointed as selenium, which might be explained as follows: in the seeded oriented CdSe single crystal growth procession, the temperature gradient creates a concentration gradient across the molten zone and results in the upward diffusion of selenium. At the bottom, the selenium concentration is highly excessive, while the quartz crucible has a narrow cone-shaped bottom, and a small amount of selenium could not be exhausted because of the capillary affection. In the middle part, the diameter of quartz crucible, also the molten zone, satisfied the stabilizing growth condition. While at the top, the excessive selenium has been separated out from the supersaturated solution.

In fact, this is in accordance with the experiment results. The typical photograph of the as-prepared single crystal is presented in Fig. 1. It can be seen that the size of the crystal is about 20 mm in diameter and 80 mm in length. But at the bottom and tail, there are some incompact lumpish crystalloids that may result from poor crystallization.

In order to further confirm the crystallinity of the as-grown CdSe crystal, a cuboid with 5 mm×5 mm×10 mm in size was selected from the middle part and fabricated with (002) plane. The XRD spectrum is shown in Fig. 3(a), in which no peaks except (002), (004) are observed. Figure 3(b) is the typical XRD rocking curve of the as-prepared sample, it can be seen that the intensity of the diffraction peak is high and the shape of the peak is perfectly symmetrical; The FWHM is about 0.055°. All these have demonstrated that the crystal has high crystallinity.

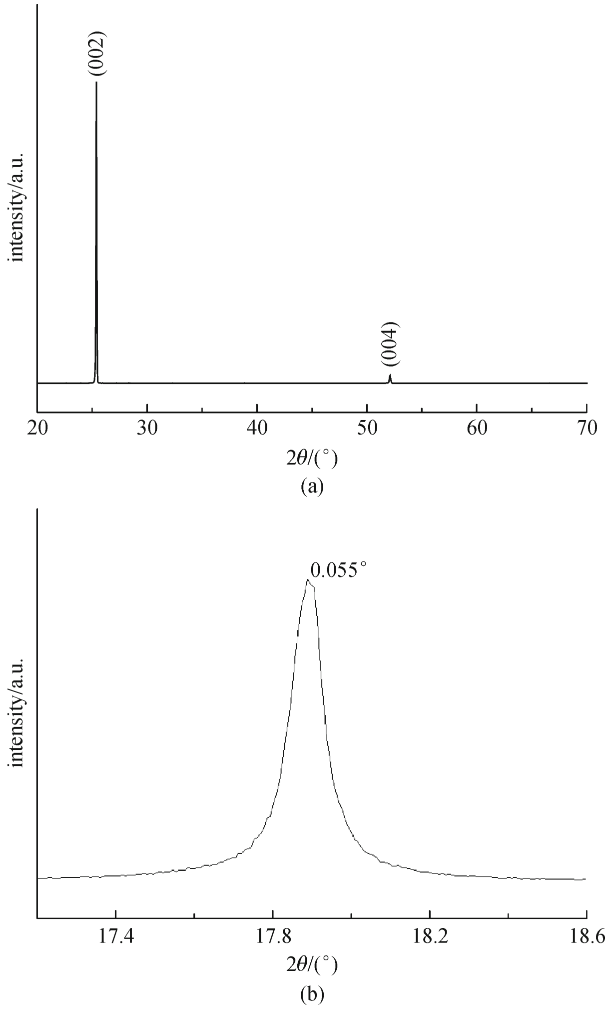


Fig. 3 XRD spectrum of (002) planes (a), and rocking curve of (002) plane (b)

3.2 Infrared microscope inspection and IR transmission tests

The short cut-off wavelength of CdSe crystal is about 0.75 μm, therefore, the opaque crystal's quality can not be judged with naked eyes. Figure 4(a) is a picture of a typical polished CdSe element (sized 5 mm×7 mm×12 mm, from the middle part of the crystal boule) with black color. Figure 4(b) exhibits the image of the above-mentioned crystal with letters "CdSe" under the infrared microscope. We can find that the crystal is free of voids, twins, phase precipitates inside and the characters "CdSe" can be seen clearly.

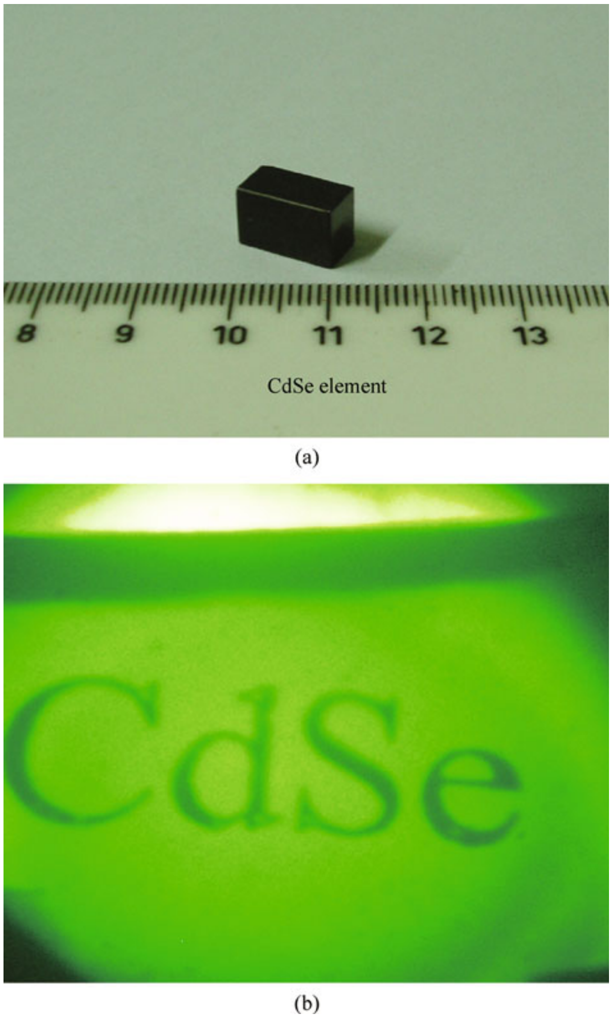
Spectrophotometer was employed to verify the crystal's optical transmission property. Figure 5 expresses the transmittance spectrum of a slice of CdSe with a thickness of 2 mm without any coating. It is found from Fig. 5(a) that the infrared transmission is above 65% in the region from 4000 to 500 cm^{-1}. It has a wide transparent spectral range. The transmittance absorption coefficients could be calculated utilizing the equation [10]:

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

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. The calculated values (Fig. 5(b)) exhibit clearly the absorption coefficients for the crystal (about 0.01–0.04 cm^{-1}), indicating that the crystal has an exceptional optical quality.

4 Optical parametric oscillator

Two CdSe device crystals with different size (A: 7 mm×7 mm×25 mm, B: 5 mm×5 mm×30 mm) were fabricated for the experiments of optical parametric oscillator (OPO). The crystals' cutting angle had been specified at θ = 86°



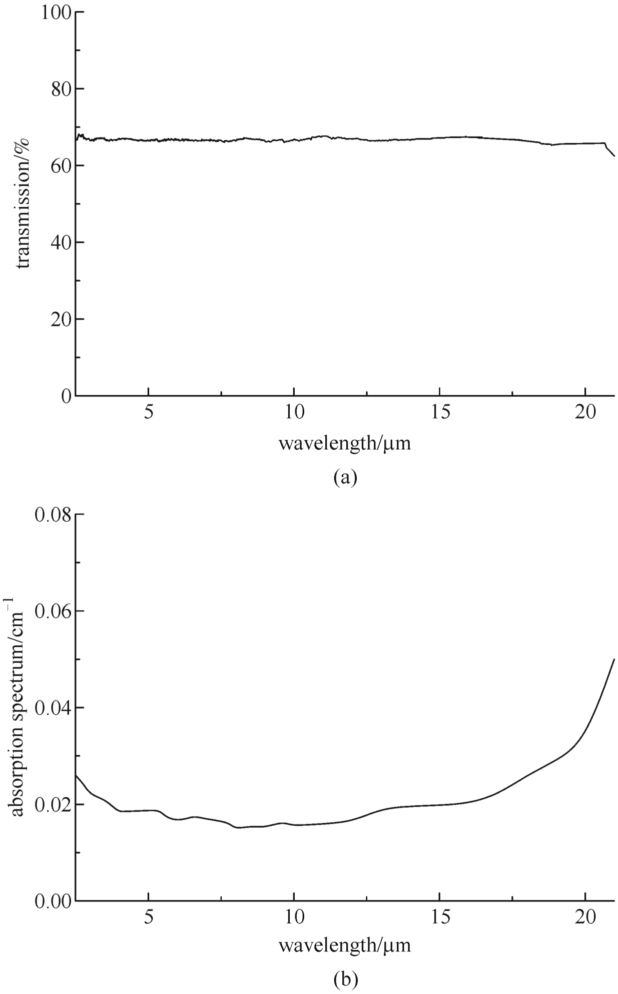
(a)

(b)

Fig. 4 (a) Typical polished CdSe element; (b) element's image under infrared microscope with letters "CdSe"

with respect to the optical axis, which allows for type-II phase matching. The end faces of the crystals were optically polished and coated with certain films, both of which were pumped by 2.797 μm Cr,Er:YSGG lasers (repetition 5 Hz, energy 3 mJ, pulse width about 0.2 ns). The signal and idler wavelengths and the output power from CdSe OPO were registered with a 20 cm grating monochromator and a mercury cadmium telluride detector.

However, no matter how high the input power, even the CdSe crystal's surface was damaged, crystal A could not emit the signal and idler wavelengths. When we replaced crystal A with crystal B and kept other experimental parameters invariables, the peak wavelengths of 4.3 and 8 μm appeared with a total average power of 400 μJ. As shown in Fig. 6, we observed that phase-matching angle (86.2°) is very close to the ones which are theoretically predicted by Bhar [11]. Crystal A could not output certain light because of probably the fact that its nonlinear optical (NLO) coefficient d_{31}= 18 pm, which is rather small, the length of crystal is essential under this condition.



(a)

(b)

Fig. 5 (a) Transparency measured with unpolaried light of CdSe slice with thickness of 2 mm in region of 2.5–21 μm; (b) optical absorption spectrum in region of 2.5–21 μm

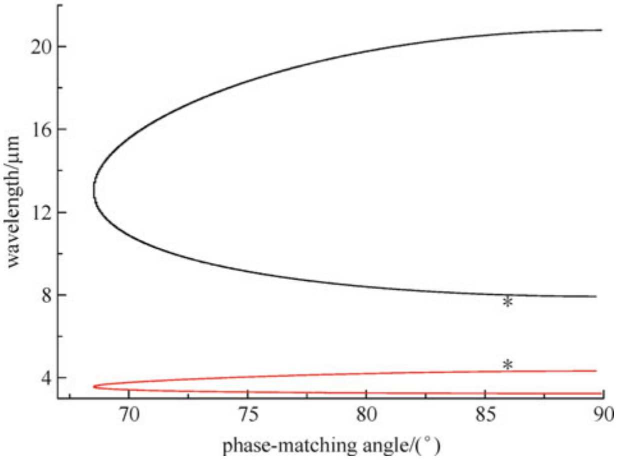


Fig. 6 Angular tuning characteristics for type II phase-matching OPO tunable laser radiation (2.797 μm) in crystal CdSe (* are our experimental data)

5 Conclusions

Single crystal CdSe with size of 20 mm×80 mm has been successfully grown by using S-TGSZ method. Under carefully controlled and adjusted thermal conditions, the cracking of crystal was avoided by modifying the Bridgman furnace and optimizing the growth parameters.

Transparency of the as-grown crystal was quite good; device crystal with such sizes as 5 mm×5 mm×2 mm was obtained with the absorption in the range of 0.01–0.04 cm^{-1}.

The results of OPO experiments with 5 mm×5 mm×30 mm device crystal imply that crystals have a potential in long wavelength ($> 8\ \mu\text{m}$), high-power applications by using long interaction crystal length due to its broad transparency range.

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