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CdS bulk crystal growth by optical floating zone method: strong photoluminescence upconversion and minimum trapped state emission

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Abstract. CdS materials have shown promise in optical refrigeration. However, the current success of laser cooling is still limited to nanobelt morphology. It is, therefore, important to explore whether bulk crystal growth technology could provide high-quality materials for laser cooling studies. Herein, we have demonstrated CdS bulk crystal growth by a modified optical floating zone method. The low temperature and continuous displacement of the CdS crystalline zone have resulted in high-quality CdS bulk crystals, which show strong photoluminescence upconversion with the absence of the long-wavelength and broad emission centered ~700 nm that commercial CdS wafers usually exhibit. All these characterizations have confirmed the excellent stoichiometric nature and crystal quality of CdS bulk crystals, which is much better than the commercial counterparts for laser cooling studies. © 2016 Society of Photo-Optical Instrumentation Engineers (SPIE) [DOI: 10.1117/1.OE.56.1.011109]

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1 Introduction

Upconversion photoluminescence (PL) is a light-matter interaction process, in which the mean emission photon energy $h\bar{\nu}_f$ is larger than the pump photon energy $h\nu$, where h is the Planck's constant, $\bar{\nu}_f$ is the mean frequency of emitted photons, and ν is the frequency of the pump photon. In a linear regime, this upconversion process is facilitated by the annihilation of phonons, the quanta of lattice vibration. As a result, the upconversion PL can lead to cooling of the matter. The concept of optical refrigeration was originally postulated by Pringsheim in 1920s,¹ and was experimentally demonstrated by Epstein et al.² in rare-earth doped glasses. The latest laser cooling of a rare-earth system has reached 93 K, approaching liquid nitrogen temperature.³ Recently, net laser cooling in semiconductors was first demonstrated in a CdS nanobelt⁴⁻⁷ and then on perovskite crystals.⁸ Due to the relatively strong Froehlich interaction and multiphonon-assisted processes for cooling at room temperature, the net laser cooling first reported in CdS is not a coincidence.⁹ Nanobelt morphology plays an important role in minimizing photon trapping and reabsorption, but also limits broader applications due to sample variation and scaling challenges, a constraint of current growth strategy. Therefore, it is important to ask whether bulk CdS crystals can provide similar optical quality for laser cooling, which shall have important implications in macroscopic optical refrigeration devices.

As we know, upconversion PL is a classical Pringsheim picture for the laser cooling of solids in which the amount of energy $\Delta E = h\bar{\nu}_f - h\nu$ is removed in each cycle [Fig. 1(a)].¹ In addition to the large energy difference ΔE , the net laser cooling also needs nearly unity external quantum efficiency (EQE) and absorption efficiency according to the Sheik-Bahae/Epstein (SBE) theory.^{10,11} Thus, the trapped state emission contributed by crystalline defects would diminish the laser cooling performance. Unfortunately, the trapped state emission of typically synthesized CdS bulk crystals is considerable, but was not present in the CdS nanobelt used for the laser cooling (comparison will be shown in Fig. 4). This suggests that CdS crystals grown in typical high temperatures contain various kinds of crystalline defects which may lead to emission at long wavelengths. The defect accumulation in the process of CdS bulk crystal growth makes it more difficult to obtain ideal upconversion PL than the nanobelt due to the relative larger size of bulk crystals.

Figure 1(b) shows the nonstoichiometry ranges of CdS.¹² This results from the proportionality between point defect concentration and temperature. A high temperature for crystal growth usually induces a larger concentration of defects in a CdS crystal. Therefore, low-temperature growth can potentially assure stoichiometric crystals with fewer defects. On the other hand, low temperatures may not meet the requirement for bulk crystal growth in traditional methods.

In specific cases, vapor deposition, assisted by chemical transport agent, carrier gas, or plasma, allows crystal growth in relatively low temperatures.¹³ Chemical vapor deposition

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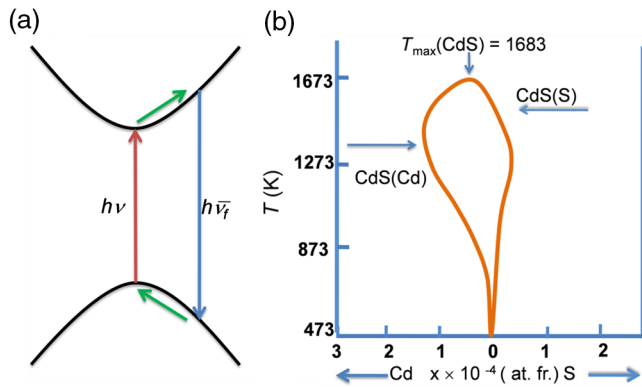


Fig. 1 (a) Laser cooling cycle by upconversion PL in a semiconductor ($h\nu_f$ is the emission photon energy; $h\nu$ is the pump photon energy).¹⁰ (b) Nonstoichiometry ranges of CdS, the point defect density in thermodynamic equilibrium is higher at an elevated temperature.¹²

(CVD) used in nanomaterials' fabrication is a typical example of such a low-temperature method. As a result, the CdS nanobelts grown by CVD could exhibit low-defect concentration with good stoichiometry. Nevertheless, physical or chemical vapor transport used in CdS bulk crystal growth always induces some defects due to the high temperature or impurity of the transport agent. Therefore, developing a low-temperature method for bulk crystal growth without the trapped state emission is the first challenge to study laser cooling property in CdS bulk crystal. Success of controlling the defects during crystal growth could also benefit the other applications of CdS including solar cell component,¹⁴ laser materials,¹⁵ and waveguides,¹⁶ in which defects in the materials would impair the performance of the related device, such as emission stability and life span of devices.¹⁷

Herein, to ensure the high purity of CdS crystals, we have devised a modified optical floating zone method. The source materials are sealed inside a quartz ampoule without an additional transport agent. The illustration of the method is included in Fig. 2. CdS is evaporated from the hot optical focus and condensed on a much colder part of CdS rod a few millimeters away from the focal point. The conditions for crystal growth have been optimized. Furthermore, the comparison of PL spectra of different CdS sources has been discussed.

2 Synthesis of CdS Bulk Crystal in Optical Floating Furnace

The selected CdS rod of around $4 \times 4 \times 20 \text{ mm}^3$ from the commercial CdS pieces [Alfa Aesar Company with 99.999% purity (metal basis)] was placed inside a quartz tube with a 13-mm external diameter. A quartz tube around 10 cm in length was sealed with an Ar atmosphere inside. Then the ampoule was fixed in the center of a fused silica tube in the optical floating zone (Crystal Systems Corporation, FZ-T-4000-H-VII-VPO-PC) [Fig. 2(a)]. The lamps are $1500 \text{ W} \times 4$. A typical experimental set was 0.2 h for 0% to 40%, 0.5 h at 40%, and 0.1 h for 40% to 0%. The maximum lamp power shown in the computer was 36.6% (0.547 kW) (73.5 V, 11.54 A). The rotation and vertical speed of displacement were set as 30 rpm and 10 mm/h, respectively. In the optical floating zone, the temperature was not directly measured. However, the process was observed through the monitor connected to the camera inside

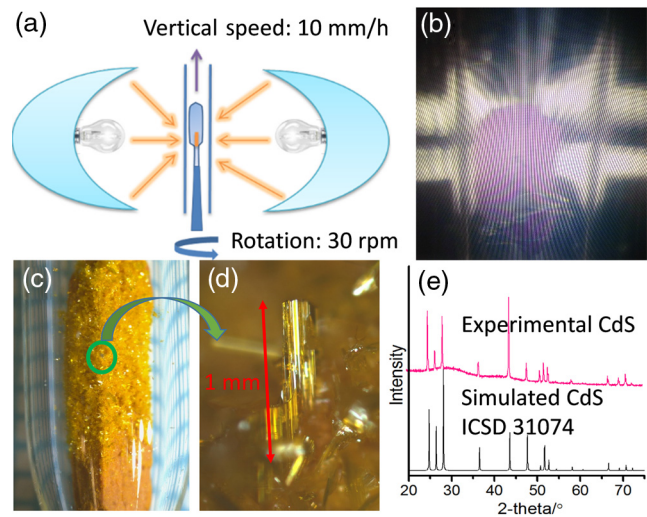


Fig. 2 (a) Schematic diagram of optical floating zone for CdS crystals growth. (b) The photo of CdS rod in the optical floating furnace. (c) The CdS rod with bulk crystals on the surface after optical floating heating. (d) The synthesized CdS bulk crystals. (e) PXRD of the CdS crystals.

the system. The power of the lamp was increased gradually until the color of the CdS rod changed due to the evaporation and condensation of the source material. A pink CdS rod was observed by a digital camera from the reflected light of halogen lamps and the emitted light of CdS [Fig. 2(b)]. After 30 min heating, the power of the lamps was gradually decreased. Then the CdS rod covered with CdS small bulk crystals was obtained [Figs. 2(c) and 2(d)]. The CdS crystal had a wurtzite structure in the $P6_3mc$ space group confirmed by powder x-ray diffraction using Bruker D8 Advance diffractometer $\text{CuK}\alpha$ (1.54178 \AA) radiation at room temperature [Fig. 2(e)]. The crystal structure was the same as the nanobelts used for laser cooling.⁵ Though the crystals were grown in the optical floating furnace, this method was different with the traditional crystal growth in an optical floating zone. No seed crystal and liquid zone were in our process, which was more similar to physical vapor transport.

3 Comparison on Room-Temperature Photoluminescence Spectra of Different CdS Sources

The PL spectra of CdS rod and CdS crystal have been collected. The laser beam (solid-state laser for 473 nm, and Nd:YAG solid-state laser for 532 nm) was collimated and focused through a $100\times$ objective onto the sample surface at room temperature. A confocal triple-grating spectrometer (Horiba-JY T64000) was used to collect the back-scattered spectra.

Two emission bands were usually observed in CdS PL spectra.^{18–21} The higher energy peak is a sharp excitonic emission (around 507 nm) near the band edge, whereas the lower energy band is a broad trapped emission (around 700 nm) in the long wavelength. It is notable that if the PL spectrum is excited by a higher energy than the band edge (2.45 eV) of CdS (i.e., Stokes emission), the trapped state emission may be suppressed by the strong excitonic emission. When the excited energy (such as 532 nm) is lower than the band edge (i.e., anti-Stokes emission), the spectrum could show distinct characteristics of the trapped state emission. The trapped state emission, which is related to the

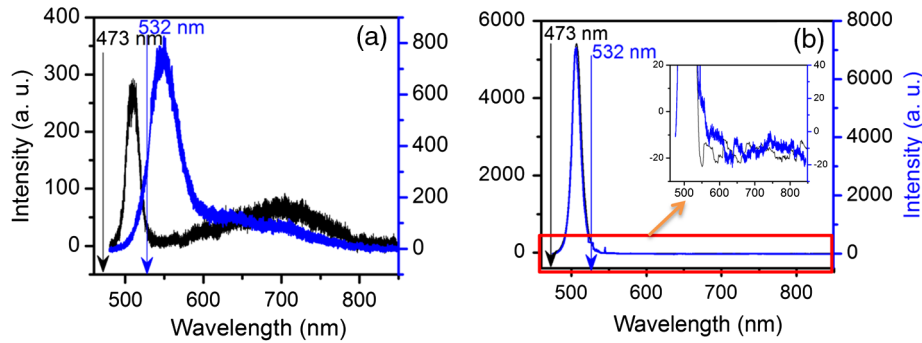


Fig. 3 The PL of the starting CdS rod (a) and the PL of final CdS crystal after optical floating heating (b). The black and blue lines were excited by 473- and 532-nm laser, respectively.

defect signature, could be used to evaluate the quality of the CdS. As shown in Fig. 3(a), the spectra of the CdS rod showed a quite complex trapped level from impurities, which suggested there were a lot of defect levels in the energy band of the CdS rod. The origin of such defect bands is not completely understood, which presumably is a combination of various trap states due to stoichiometric defects (interstitials or vacancies) or surface states.²² In contrast, both Stokes and anti-Stokes emission spectra of an as-grown CdS crystal showed the absence of the long-wavelength defect emission [Fig. 3(b)], whereas the anti-Stokes emission excited by 532-nm laser exhibited a strong PL upconversion, a very important requirement for laser cooling. We can conclude that the CdS bulk crystals grown on the surface of a CdS rod from the optical floating zone has a better stoichiometric nature and quality.

To evaluate the crystalline quality of our CdS crystals, a commercial CdS wafer bought from MTI Corporation was used as a reference. The anti-Stokes PL spectra were measured with the excitation of a 532-nm laser. The spectrum of as-grown crystals showed a strong anti-Stokes emission without any trapped state emission, whereas the commercial CdS wafer had a broad trapped emission around 700 nm [Fig. 4(a)]. The conditions for such a CdS crystal growth have been explored with great efforts. In the beginning, our synthesized crystals with different crystal growth conditions using traditional methods always showed a broad trapped

emission. Then we used the modified optical floating zone method and found that the up-movement effect of the CdS rod played an important role in the defectless crystal growth. As Fig. 4(b) shows, if the CdS rod just kept a rotation without any up-movement, the trapped state emission of the final CdS crystals became larger with a longer heating time as a general trend. However, if the CdS rod kept a rotation with an up-movement simultaneously, no trapped state emission at the long wavelength was found, which indicated that the defect concentration inside the CdS crystal was low. The possible reason is that the up-movement prevents the grown CdS crystals from continuous high-intensity heating around the optical focus, in which the high temperature would induce more stoichiometric defects inside the crystal. However, growing our small bulk crystal into a sufficiently large crystal is still a challenging work for the future.

The achievement of a bulk CdS crystal without trapped state emission can be attributed to the low crystallization temperature on the CdS rod surface in the optical floating zone. As Fig. 1(b) suggested, a lower temperature for crystal growth would induce a narrower nonstoichiometry.¹² The CdS bulk crystals were grown at low lamp power (36%) on the surface of the CdS rod out of the optical focus. The temperature could decrease dramatically out of the optical focus according to the diagram of temperature distribution in the optical floating zone.²³ Thus, the temperature should be low enough for a good stoichiometry nature [Fig. 1(b)].

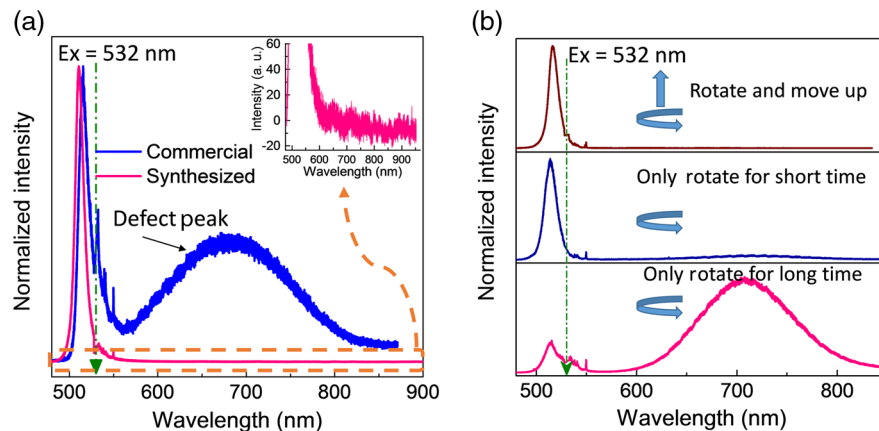


Fig. 4 (a) The comparison of PL between commercial and as-grown CdS crystals excited by 532-nm laser of 8.65 mW. (Inset is the enlarged part of nonnormalized PL of as-grown CdS crystal.) (b) The PL (excited by 532-nm laser) of CdS crystals in different growth conditions (up-movement of sample rods).

In addition, the short time for crystal growth and continuous up-movement can prevent overheating of the CdS bulk crystals, which would induce the high-defect concentration.

In a previous attempt of laser cooling in III–V quantum well structures, the limitation on the achieved net cooling is more likely to have an insufficient extraction efficiency due to parasitic absorption or photon trapping due to the large refractive index. The success in laser cooling CdS nanobelts is an exception, as the nanoribbon morphology prevents photon trapping, in addition to the high-EQE and strong longitudinal optical phonon-assisted PL upconversion. Our as-grown CdS bulk crystals and luminescence spectra have shown the achievement of higher crystalline quality with very minimum stoichiometric defects and trap state emission. This result indicates that high-quality bulk crystals exhibit a potential for achieving laser cooling of macroscopic samples. However, the achievement of net laser cooling may be still limited by the EQE and the absorption efficiency, which have not been investigated for our crystal samples. The nonradiative recombination and background absorption of materials will generate unwanted parasitic heating to prevent the achievement of net cooling, while they can not be reflected in the steady-state PL spectra. Therefore, a further step for our research may focus on the investigation of the nonradiative process in existing as-grown crystals by the optical floating zone method and crystalline samples grown by other methods as well.

4 Conclusion

In conclusion, we have modified the optical floating zone method to synthesize CdS bulk crystals without defect emission at long wavelength, which was attributed to the low crystallization temperature and continuous displacement of the CdS crystalline zone. The steady-state PL has been collected and analyzed. Strong upconversion PL has been achieved with the absence of a trap state emission compared to commercial CdS rod and crystal wafers. Further work needs to be done to investigate the nonradiative process in existing as-grown crystals and grow larger CdS crystals, so that laser cooling properties on bulk crystal can be systematically measured. However, our work has demonstrated that the optical floating heating method can improve the solid CdS stoichiometry and crystallization quality, which has wide potential applications, including the purification of CdS-like materials and heat treatment of CdS-like thin films.

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