Synthesis and optical characterization of cadmium sulfide (CdS) single crystals for laser cooling effect

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**Synthesis and Optical Characterization of
Cadmium Sulfide (CdS) Single Crystals for
Laser Cooling Effect**

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Summary

In this thesis, the author will describe what he has done in the past two years of his studentship. He will mainly focus on the topic of laser cooling of cadmium sulfide (CdS) single crystals.

The first part of the work is to characterize the laser cooling effect of CdS commercial single crystals. CdS has been proved very promising in laser cooling effect where nanobelts of CdS can be cooled down 40 K from room temperature and 20 K from 100K if excited by certain lasers¹. But large scale is needed instead of nano size in order to make this material useful in real life such as optical refrigerator or self-cooling laser. Hence, the author first characterizes the commercial single crystals of CdS (1 cm² square meters) to see the laser cooling character of large scale CdS. The author also analyzes two different commercial crystals from two industry companies, one from MTI China and one from Semiwafer Taiwan. By analyzing those crystals using optical spectroscopy, the author got the Stokes spectroscopy and anti-Stokes spectroscopy as well as its dependence relationship figure between peak densities and exciting laser power. Through the analysis of the study, it shows that those commercial crystals cannot have the laser cooling effect because of its large defect density which may be caused by anti-sites defect or sulfur vacancies. Those defects will prevent the crystals from having laser cooling effect because those defects may cause the emission of phonons with lower energy which is the opposite of up-conversion laser cooling process. In order to get a higher quality single crystals, the author looks forward to the lab growth of single crystals.

The second part of the work includes the synthesis and characterization of lab grown CdS single crystals. The author tried to grow his own crystals to remove the defects he found in the commercial CdS single crystal. He carried the synthesis of CdS single crystal by physical vapor transport method using cadmium shots and sulfur pieces. Growing condition covers different temperatures and different ratio between Cadmium and Sulfur. From the analysis of optical spectroscopy on those crystals, he concludes that some of the conditions give us a much better quality of crystals in which a higher potential may have to observe laser cooling effect because the defect that he found in commercial crystals no longer exists in his crystals. In the laser cooling experiment he carried out later, laser cooling effect was unfortunately not observed. A thorough comparison is also given between the three crystals: two commercial single

CdS crystals and the best lab grown crystals. Clear improvement of removing the defect can be observed through the comparison.

The third part of the thesis includes an illustration of the device design for optical refrigerator. It's an improvement and detailed explanation of what CdS crystal laser cooling device looks like and how it works based on what we have got so far. It provides an idea to people who are looking forward to step further in semiconductor laser cooling field.

All the three part of the work will be illustrated and explained in details in the following chapters. Moreover, a summary and future plan is clearly stated in the end of the thesis.

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Chapter 1 Introduction and Motivation

1.1 Introduction to Laser Cooling

The concept of laser cooling was first proposed by Pringsheim in 1929². The theory of laser cooling in solids is very straightforward. The average power of the photons emitted by the process of anti-Stokes photoluminescence is less than that absorbed by the material. This process will lead to a difference of the energy power between the absorbed power and emitted power, which is then made up by the energy of phonons which can also be referred to the vibration of lattices. The cooling will finally come from the loss of those phonons. Compared with other traditional cryogenic cooling, solid cooling has advantages of being more robust and non-cryogenic.

Although the theory of laser cooling is proposed about a century ago, laser cooling is not observed until 1995 by Epstein in ytterbium-doped glass materials³. In the following years, reports have shown that by using ytterbium-doped glass materials, the cryogenic temperature as low as 155 Kelvin can be reached⁴. After that, laser cooling of different kinds of rare-earth doped materials have been investigated and observed⁵⁻¹⁴.

However, although rare-earth doped materials have been proved to be effective in laser cooling, it has been regarded not promising in the future use due to the following reasons. First, rare-earth doped material has a very narrow application in the near future, especially in the industry field. Second, its low thermal conductivity and poor thermal contact with semiconductors further prevent its application in further use.

The two reasons above have inspired people looking for substitutions in semiconductor materials in laser cooling application. Compared with rare-earth doped materials, semiconductor industry has been so mature that it affords the wide applications for future use and mass production may lower the cost and confirm the high quality of this technique. Second, semiconductor material has been theoretically proved to exhibit cooling effect at as low as 10 Kelvin¹⁵, which is much lower than rare-earth doped materials. Third, semiconductor material has a better interaction with laser radiation which increases the opportunity for it to be integrated into photonic and electronic devices. Moreover, the laser system may

have a better chance to share a same substrate with laser diode which further increases its compactness, and this part will be illustrated in Chapter 5 of this thesis.

1.2 Motivation

The idea of this thesis comes from the first discovery of laser cooling result in CdS nanobelts in 2013¹. It is the first time ever that laser cooling is observed in semiconductor materials. A temperature drop of 40 Kelvin from 290 Kelvin was achieved by pumping the materials with 514 nanometer laser with a cooling efficiency of 1.4% and a cooling power of 180 microwatts. Under a lower temperature of 100 Kelvin, 15 Kelvin of temperature drop was achieved by pumping with 532 nanometer laser with a cooling efficiency of 2%. According to the author, the net cooling of CdS nanobelt was attributed to the strong coupling between longitudinal optical phonons and excions, together with negligible background absorption and high quantum efficiency. Their findings also give suggestions of the potentials for group II–VI semiconductor materials with strong LOP-excitation coupling in laser cooling.

These findings in CdS nanobelts provide us great confidence in applying them into real use. However, the size has restricted the application of CdS nanobelts. That is why and when this idea comes out. The idea is to find out what it is like for CdS bulk crystals in laser cooling effect.

Starting from the success in CdS nanobelts, it is believed in this thesis that CdS can be a more promising material which may be further applied into future use. A single CdS crystal is worth being investigated to find out is laser cooling potentials. Furthermore, based on the mature industry in semiconductor industry, we decided to start from the commercial products and then continue the investigation step by step.

1.3 Objectives

The objective of the research described in this thesis contains the following three part.

The first objective is to investigate into the commercial crystals in laser cooling characteristics. Optical spectroscopy will be the main tool to test and analyze the real condition for those commercial crystals. Conclusion should also be given to judge the commercial crystals.

The second objective is to grow the CdS crystals using lab furnace based on the application for laser cooling. Tailored condition should be found for optimized crystals and spectroscopy should also be carried out to see the difference and improvement. Laser cooling experiment is also necessary if optimized crystals that are suitable for laser cooling can be grown.

The third objective is to give a solution or a design illustration to what has already been found. This solution should be based on the real application of optical refrigerator for future use.

Chapter 2 Literature Review

2.1 Basic Mechanism of Solids Laser Cooling

The idea of laser cooling of solids due to optical radiation accompanied by anti-Stoke emission was first proposed by Pringsheim a century ago in 1929² (Figure 1). In solid state, the thermal energy is mainly confined in vibration of lattices, which can also be called phonons. Laser cooling is regarded as the extraction of extra energy from the lattice phonons by the process called anti-Stoke up-conversion. Up-conversion means when the material absorbs the energy of a photon, a spontaneous emission of photon with a higher energy will emit. At the same time, it will bring out the thermal energy from the material itself. This process of cooling can also be called “anti-Stoke fluorescence” and “luminescence up-conversion” cooling. Figure 1b depicts the laser cooling process for a two level system with broadened excited and ground state. To explain the process, the photons from the light sources (usually lasers) excite an atom from the top of the ground state to the bottom of the excited state. Then those phonons will be absorbed by the materials to help the atoms reach the quasi-equilibrium with the lattice. Finally, spontaneous emission follows with higher photon energy than that of the light source.

Figure 1 (a) It is suggested by Pringsheim that solid could be cooled through anti-Stoke fluorescence².

In this process, the substance absorbs a photon and then emits one with a higher energy. The energy

difference is made up by the phonon which thermal energy is confined. (b) Broadened two energy levels for laser cooling process. The atom is excited from the top of the ground energy level with a light source having energy $h\nu$. Then the excited atoms reach higher states by absorbing phonons in order to reach quasi-equilibrium. After that, fluorescence will happen in which a photon with a higher energy $h\nu_f$ emits from the atom. In this process, ν is smaller than ν_f , which finally leads to the cooling of the substance.

In the simple laser cooling model mentioned above, the cooling efficiency for a single photon absorbed can be simply written as

$$\eta_c = \frac{h\nu_f - h\nu}{h\nu} = \frac{\lambda}{\lambda_f} - 1 \quad (2.1)$$

Where λ_f is the mean wavelength of the fluorescence while ν_f is the corresponding mean frequency of the fluorescence. However, in this simple model, two challenges were ignored including the radiate recombination of optical excitations and the parasitic heating due to the unwanted impurities. Also, the radiation trapping of the materials is ignored in this model. Radiation trapping is the one that we usually refer to the spontaneous emitted photons being trapped by the material itself and being reabsorbed.¹⁶ The details of radiation trapping will be discussed in Chapter 5

In semiconductor materials, the effect of radiation trapping is critical because semiconductor materials usually have high refractive index and are very easy to generate total internal reflection. So we further need to include the quantum efficiency in this model which usually can be understood as the fraction of the atoms that may be able to decay to the ground state by the preferred radiative process. And quantum efficiency can be written as

$$\eta_q = \frac{W_{rad}}{W_{rad} + W_{nr}} \quad (2.2)$$

Where W_{rad} is the radiative decay rate and W_{nr} stands for the non-radiative decay rate. By including the fluorescence escape efficiency η_e , the external quantum efficiency can be defined as

$$\eta_{ext} = \eta_e \times \frac{W_{rad}}{\eta_e \times W_{rad} + W_{nr}} \quad (2.3)$$

Also, to describe the fraction of photons which are engaged in the laser cooling process, the absorption rate is defined as

$$\eta_{abs} = \frac{\alpha_r}{\alpha_r + \alpha_b} , \quad (2.4)$$

Where α_r is the resonant absorption coefficient and α_b refers to the parasitic absorption which may reduce the cooling effect. The cooling efficiency can be redefined by all of the abovementioned effects as a new equation

$$\eta_c = \eta_{ext} \times \eta_{abs} \times \frac{\lambda}{\lambda_f} - 1 , \quad (2.5)$$

The equation above also suggests that the process of laser cooling can only occur in those materials with high purity, high quantum efficiency and appropriate spaced energy levels. So far, laser cooling of solids is only observed in glasses and crystals doped with rare-earth doped materials ^{6-14,17-19} and II–VI semiconductor nanoribbons ¹.

Laser cooling of solids shows wide advantages including its compactness, cryogen free, less vibration and high reliability. It also provides a wide range of potential applications including athermal lasers (self-cooling lasers), solid-state cryo-coolers and self-cooling lasers. ²⁰

2.2 Laser Cooling of Rare-Earth Doped Glass and Crystals

The potential of rare-earth doped materials for laser cooling application have been suggested by Kastler²¹ and Yatsive²² half a century ago. The main process of transition in this material involves 4f electron which is shielded by outer-shells 5s and 6s. Two outer-shells prevent the interaction with the surrounding lattice. Thus, multi-phonon emission can be suppressed. Moreover, the non-radiative decay is diminished by the low phonon energy and so does the increase of the quantum efficiency.

The first attempt of the laser cooling in rare-earth doped glass is in 1968 by Kushida and Geusic²³. Only reduction of heating was reported instead of net cooling. The first successful cooling experiment in rare-earth doped glass was not observed until in a heavy-metal-fluoride glass (ZBLNAP) doped with trivalent ytterbium ions in 1995³. After that, laser cooling has been achieved in a very wide range of crystals and glasses doped with rare earth materials^{6-14,17-19}. At that period of time, compared with thermoelectric devices, the laser cooling has more efficiency to operate under 170K. Ytterbium- or thulium-doped solids then were proved to be capable of providing such cooling results below 100K.^{7,19,24}

However, there are several disadvantages regarding the rare earth-doped solids in laser cooling application. The first consideration for the choice of the laser cooling medium is the width of the ground state manifold. It is more populated in the lower energy levels than the higher ones according to Boltzmann statistics. As the temperature decreases, the upper levels will be depopulated which finally results in $k_B T$ being close to zero which may finally cause the efficiency down to zero.

The second reason is that since the ideal cooling efficiency may require the pumping with lower energy photons, thulium-doped cooling materials are preferred than ytterbium doped materials since their ground and excited state manifolds are separated by 0.6 eV instead of 1.2 eV²⁵. However, the fact that there are more limits in choices of lasers around 0.6 eV prevent the ideal cooling efficiency from being achieved.

2.3 Laser Cooling of Semiconductors

Although laser cooling of semiconductors has been studied both theoretically^{15,26-32} and experimentally^{17,33-36} in the past decades, net cooling has only been realized in CdS nanobelts in 2013¹. It is regarded the first time in history that laser cooling can be achieved in semiconductor materials. A detailed investigation of the research work of CdS nanobelts will be illustrated in the following paragraphs.

Figure 2 (a) and (d) show the change of the peak position under the excitation of 532nm and 514nm laser. There is a turning back at the point where 532 nm or 514 nm is off. (b) and (e) show the change of temperature in nano-belt according to different wavelength under 290 K and 100 K respectively. (f) gives a theoretical laser cooling efficiency based on absorption, anti-Stokes and photo-current gain.¹

In the experiment described in that work, different lasers were used to excite the CdS sample in different temperatures and the temperature drop of 40 Kelvin and 15 Kelvin were observed from room temperature and 100 Kelvin respectively. 514 and 532 nm laser were proved to be effective in laser cooling at room temperature and 514 nm laser is the only one that proved to be able to lead to net cooling under 100 Kelvin.

A turning off of the laser is conducted in order to distinguish the cooling of the materials from other factors. A turning back of the peak position confirms the net cooling. In the cooling efficiency figure, we can observe that the experimental statistics (pink squares) coincides with the theoretical efficiency curve (blue line), which further confirms the peak position change comes from the net cooling.

Figure 3 (a) represents the SiO₂/silicon platform used to hold the nano-belt. (b) represents where laser shines on the sample. (c) represents how pump probe is carried to measure the temperature change. ¹

In the setup of the experiment, a SiO₂/silicon substrate with holes is used to fix the nanobelts used for laser cooling and isolate it from any heat loss during the cooling process. The cooling process starts from the laser exciting the surface of the nanobelts crossed on the hole. In order to get accurate temperature of the nanobelt, pump probe technique is also implemented while 473 nm laser works as the probe to get the spectroscopy for temperature within 1 s. In this way, the sample may not be heated too much to influence the cooling effect.

Compare with rare earth doped materials, semiconductor materials in laser cooling application show an advantage in the mass production, mature techniques, low operating temperature and its more

opportunity to be integrated into future semiconductor applications.

Chapter 3 Investigation of Commercial Cadmium Sulfide Single Crystals on Laser Cooling Properties

3.1 Background of Commercial CdS Crystals

The idea of investigation of commercial CdS single crystals comes from the realization of net cooling in CdS nanobelts.¹ It is thought in this thesis that CdS single crystals may have a higher chance of getting net cooling than other semiconductor single crystals.

Due to the mature industry of semiconductor, commercial single crystals of CdS are easily got from different semiconductor companies. Two kinds of CdS single crystals from different semiconductor companies are investigated in this paper, including MTI China and SemiWafere Taiwan.

This chapter will be mainly focus on the characterization of those two kinds of CdS single crystals by optical spectroscopy including its Stokes, anti-Stokes, temperature dependence and power dependence spectroscopy. Its potential for laser cooling will be discussed after the characterization. Further suggestions will also be given in the end of the chapter.

3.2 Calibration of the Crystals from MTI China

The CdS single crystals got from MTI China is with orientation $\langle 0001 \rangle$, N typed and a size of $10 \times 10 \times 1 \text{ mm}$ with two side polished.

Figure 4 In this figure, the Stokes peaks of the CdS crystals show a clear change from 493 nm to 511 nm with a ratio of about 0.07 nm/K. This spectroscopy is designed to investigate the peak change according to different temperatures which is useful for later experiments on laser cooling effect. All the Stokes peaks are collected with 457 nm laser within 0.1, 0.5 or 1 seconds. The final spectroscopy has been normalized.

Stokes spectroscopy is conducted first to see an overall quality of the crystal including its peak position, peak density and existence of defect peaks. Another purpose is to give a calibration of the peak position according to different temperatures. It also serves as a tool of temperature indicator for later laser cooling experiment. The Stokes spectroscopy is conducted under 8 different temperatures from 77 Kelvin to 340 Kelvin. A clear peak position change of 0.07nm / Kelvin is observed in figure 4.

Figure 5 This figure is collected by exciting the crystal with 543 nm laser. Each spectroscopy is collected within 10 to 30 seconds from 77 K to 340 K. The anti-Stokes peak seem not clear. Under 100 K, the DAP peaks seem very strong. There exists a very strong wide range peak between 700 nm to 800 nm.

Anti-Stokes spectroscopy is also conducted using 543nm laser in order to further observe the anti-Stokes peak quality and existence of defect peaks. The anti-Stokes up-conversion process is the basic to laser cooling which shows the importance of this spectroscopy. However, from Figure 5, no strong anti-Stokes peaks is observed before 543nm and only DAP peaks starts to be obvious under 100K which is not helpful to realizing net cooling. Furthermore, unexpected wide range of peaks from 670nm to 820nm dominates the luminance. An emitted photon with a smaller photon energy (higher wavelength) means a heating of the materials, which prevent us from going further to laser cooling.

Figure 6 Those two pictures show the power dependence of the peak intensity under two different temperatures 77 K and 300 K. As the original curve and the fitting curve show, the peak intensity and the power of the laser follow a linear relationship. The fitting curves of 77 K and 300 K are $Y=571X$ and $Y=834X$ respectively.

Although the defect peaks observed in the anti-Stokes spectroscopy have almost prevented the crystals from getting net cooling result, a further study of power dependence is conducted in order to judge the type of up-conversion process.

There are two types of process which may results in up-conversion, including phonon-assisted up-conversion and two photon absorption up-conversion. Both of the process can be observed in the

spectroscopy by having a peak before the laser position. But only phonon assisted up-conversion will lead to the cooling of process according the basic of laser cooling in solids.

To distinguish from those two processes, the relationship between the excitation power and the peak density is the key since the phonon assisted up-conversion follows a linear relationship with the laser power:

$$I_{\text{phonon-assisted}}(P) = I_0 P, \quad (3.1)$$

Where P stands for the excitation power and I_0 is the unit density. Compared with the phonon-assisted up-conversion, two-photon absorption which may cause heating follows a two-time relationship with the laser power:

$$I_{\text{two-photon}}(P) = I_0 P^2, \quad (3.2)$$

The process of two-photon absorption up-conversion contains an absorption of two photons at the same time and emits a photons energy lower than the sum of those two photon energies. In this way, the spectroscopy may seems an up-conversion effect but heat energy which equals to the different between the emitted photon and two absorbed photons will generate during the whole process. Thus, to check whether the anti-Stokes comes from the phonon-assisted up-conversion or the two photon absorption is a big issue for whether we may get laser cooling effect. It can also give a range of the safety power which may not lead to two-photon absorption.

The linear relationship observed in the power dependence curves in figure 6 confirms that the up-conversion anti-Stokes peaks comes from the phonon assisted anti-Stokes process at both 77 Kelvin and 300 Kelvin. It also suggests that if the laser cooling is realizable, laser power of 16 mW can be applicable to achieve that. It is important to notice that if it was not for the limitation of the laser power from the equipment, the range of linear relationship can be more than 16 mW.

3.3 Calibration of the CdS Single Crystals from SemiWafer Taiwan

The CdS single crystals got from SemiWafer Taiwan is with an orientation of $\langle 0001 \rangle$, undoped and a size of $10 \times 10 \times 0.5$ mm with two side polished surface.

The same steps of characterizations are conducted on this single crystal including the Stokes, anti-Stokes, temperature dependence and power dependence spectroscopy.

Figure 7 This figure is received by exciting the sample with 473 nm laser with a laser power of 0.4 mW. The temperature range in which the sample is put is from 77 K to 300 K. Stoke peaks, DAP peaks and defect peaks are all observed in the spectroscopy.

From the Stokes spectroscopy observed in figure 7, clear defect peaks ranging from 560 nm to 650 nm start to dominate from 77 Kelvin to 300 Kelvin.

Figure 8 This figure is a zoom in figure of the previous one with a wavelength from 480 nm to 550 nm. Stokes peaks, DAP peaks can be observed here.

In the zoom-in spectroscopy for the Stokes (Figure 8), blue shift of the Stokes peak from high temperature to low temperature is clear while DAP peaks begin to dominate below 160K.

Figure 9 This figure is obtained by exciting the sample with 543 nm laser. The laser power is 1.4 mW and the temperature range in which the sample is under is from 77 K to 300 K. Anti-Stokes peaks and defect peaks are both observed in the figure.

In the anti-Stokes spectroscopy excited by 543nm laser with a power of 1.4mW, a stronger anti-Stokes peaks can be observed at room temperature and DAP peaks dominates under low temperature. The defect peaks can be clearly seen from this figure with temperatures higher than 140 Kelvin.

Figure 10 This figure is obtained by exciting the CdS single crystal from SemiWafer Taiwan with 532 nm laser. The laser power is 1.3 mW and the temperature range in which the sample is under is from 77 K to 300 K. Anti-Stokes peaks, Defect Peaks are observed in the figure.

In the anti-Stokes spectroscopy excited by 532 nm laser with a power of 1.3 mW, the result is similar to what is gotten by 543 nm laser. A stronger anti-Stokes peaks can be observed at room temperature and DAP peaks dominate in low temperature. The defect peaks can be clearly seen from the figure in temperatures beginning from 180 Kelvin.

Figure 11 This is a zoom-in figure of the anti-Stokes experiment with a wavelength range from 510 nm to 570 nm. The exciting laser is 543 nm with a power of 2.38 mW. Anti-Stokes peaks, 2LO at 601 cm^{-1} , LO at 300 cm^{-1} are assigned in the figure respectively.

Also, after inspecting the details of those Raman peaks in the spectroscopy (Figure 11), we attribute those little peaks to the phonons that assist the process of laser cooling. They are 2LO at 601 cm^{-1} , LO at 300 cm^{-1} assigned in the spectroscopy. Below 140K, those peaks are not clear to see. Those phonons give evidences to the phonon-assisted up-conversion which will be further proved in the power dependence spectroscopy.

Figure 12 This figure is obtained by measuring the peak intensity of the anti-Stokes peaks of the sample excited by 532 nm laser with a power range from 0.6 mW to 5.5 mW. A linear fitting curve is also given in the figure to illustrate its linear relationship between the power and the peak intensity.

By conducting the power dependence characterization of the single crystals, a clear linear relationship between power and peak density shows an evidence of the phonon-assisted up-conversion process. It also indicates a safe power range from 0 to 6 mW.

3.4 Conclusion

In this chapter, two commercial CdS single crystals are examined by analyzing the Stokes and anti-Stokes optical spectroscopy. It is found that the phonon-assisted up-conversion can be observed for both crystals, but defect peaks exist between 600 nm to 800 nm may lead to the heating effect. Laser cooling experiment for two commercial crystals is not necessary because the defect peaks with lower energy emission dominate by observing the anti-Stokes spectroscopy.

So far, the first goal of this thesis has been accomplished by investigation of two different commercial CdS single crystals using optical spectroscopy. In order to solve the problem of defect peaks which prevent us from getting laser cooling, lab grown CdS single crystals are proposed for a better quality and less defects.

Chapter 4 Synthesis and Investigation of Lab Grown CdS Crystals

4.1 Synthesis of Lab Grown CdS Crystals

The synthesis of CdS single crystals have been investigated for over half a century. The method of growing CdS single crystals include physical vapor transport (PVT), chemical vapor transport (CVT) and sublimation method.^{26,37-39}

In this thesis, based on the equipment in lab environment, PVT is chosen for the synthesis of the single crystal of CdS.

Figure 13 This is the illustration of the growing furnace system. The source materials contain Cd and S elements sealed in a quartz ampoule with the size of 10 cm length and 1.5 cm diameter. The temperature profile of the system is also shown above.

PVT method for synthesis of CdS crystals is illustrated in Figure 13. Cd shots with a purity of 99.9995% and S pieces with a purity of 99.9995% are sealed in the quartz ampoule for 5 to 7 days. The temperature is first risen to 500 °C for 20 hours, and then it is set to the growth temperature, usually 750 °C to 975 °C. The crystal will generate at the end with a lower temperature. It will be kept for 5 days at that temperature before it is cooled down. The cooling process usually takes 25 hours to finish

with a cooling speed of 35 °C / hour in order not to generate any unexpected defect during the cooling process.

The crystals are then obtained by breaking the quartz. Usually more than 50 % of the sources will be consumed and different shaped of crystals may exist according to different temperatures and ratios.

The temperatures in the synthesis cover 750 °C, 800 °C, 850 °C, 900 °C, 950 °C and 975 °C which is the maximum temperature for the furnace. Also, source ratio have been adjusted from 1:1, 1:1.15, 1:1.3 to 1:1.5 (Cd:S).

Every patch of crystals from different conditions have been analyzed using optical spectroscopy including its Stokes, anti-Stokes, temperature dependence and power dependence.

4.2 Investigation of the Lab Grown CdS Single Crystals by optical spectroscopy

An optimized shaped single crystal and an optimized spectroscopy single crystal will be discussed here. The optimized spectroscopy single crystal is the one that is suitable for laser cooling application.

Figure 14 (b) and (d) are the images of the needle like CdS crystal under the microscope. (a) is the Stokes spectroscopy of the sample (b) and (d) excited by 473 nm laser with a laser power of 1.33 mW. (c) is the anti-Stokes spectroscopy of the sample (b) and (d) 7 excited peaks by 532 nm laser with a laser power of 1.37 mW under room temperature. For the images, if you have the scale bar, it will be better.

The optimized shape crystals obtained are needle like crystals with around 1 cm in length and 0.05 cm in width (Figure 14b and 14d). It can be obtained from the patches whose growing temperatures are between 850 °C to 975 °C and ratios are between 1:1 to 1:1.5 (Cd:S). Although it shows a very good shape and uniformity, the Stokes spectroscopy (Figure 14a) and anti-Stokes spectroscopy (Figure 14c) doesn't give a good sign of suitable crystal quality for laser cooling since the defect peaks ranging from 600 nm to 750 nm can be observed both in Stokes and anti-Stokes spectroscopy.

Figure 15 (b) and (d) shows the image of the CdS crystal under the microscope. (a) and (c) is the Stokes and anti-Stokes spectroscopies of the sample (b) and (d) excited by 473 nm and 532 nm laser with a laser power of 0.62 mW and 1.37 mW at room temperature.

The optimized crystal comes from the random shaped crystals with the condition in which the crystals are grown by giving a larger amount of sulfur, usually with a ratio of 1:1.3 between cadmium and sulfur (Figure 15b and 15d). Both the Stokes (Figure 15a) and anti-Stokes spectroscopy (Figure 15c) show a clear sign of defect-free crystals after 550nm. The color of the crystal is also more yellow than what we have got for other crystals with defects.

A good sign of defect-free arouses the attention of its application for laser cooling. Thus, further research is conducted on this crystal including its Stokes and anti-Stokes with temperature change and power dependence spectroscopy, is conducted in the following part.

Figure 16 This figure is obtained by exciting the sample in the vacuum in the temperature range from 77 K to 300 K with a 473 nm laser whose power is 1.37 mW.

The Stokes experiment is for the later use of laser cooling experiment to calibrate the temperature change.

Figure 17 This figure is obtained by exciting the sample with 532 nm laser whose power is 1.37 mW. The sample is sealed in vacuum environment and the temperature range of the sample is from 77 K to 300 K.

The Stokes (Figure 16) and anti-Stokes (Figure 17) experiment at the temperature from 77 Kelvin to 300 Kelvin have further proven that the defects of the crystal have been reduced a lot since no large defect peaks can be seen around 600 to 700 nm while at the same time, the strong anti-Stokes peaks have shown a very good quality as well.

But at lower temperatures, defect peaks still can be observed due to the decrease of the intensity of anti-Stokes peaks. It is attributed to the radiation trapping which will be discussed late in Chapter 5. Also, the anti-Stokes peaks of CdS single crystals decrease a lot which gives a sign of possibility of having laser cooling effect only in high temperature environment.

4.3 Laser Cooling Experiment on Lab Grown CdS Crystals

A further investigation of laser cooling effect is conducted for the optimized CdS single crystals from lab synthesis. The setup of the experiment is slightly different from the setup of the test on the CdS nanobelts.¹

Figure 18 (a) shows the setup of the cooling experiment. The CdS single crystal is sealed under the vacuum environment with a vacuum of 10^{-5} Torr. CdS single crystal stands between two double sided tapes. The setup is fixed on the copper platform. (b) shows the power dependence of the peak intensity excited by 532 nm laser.

In the setup of the laser cooling experiment for CdS single crystals, the CdS single crystals are sealed in a vacuum environment with 10^{-5} Torr in order to free the influence from air. CdS single crystal is fixed between two double sided tapes on the copper platform with a round hole in the middle. The exciting laser that is supposed to cool down the single crystal is 532 nm laser with a power of 1 mW to 2.3 mW, which is within the linear region. Figure 18b is conducted to decide the linear region for the phonon-assisted up-conversion.

Figure 19 (a) shows the peak position change in the cooling experiment done under the linear region of exciting power 0.99 mW. (b) shows the peak position change under the power of non-linear region 9.34 mW.

The results of the cooling experiment are shown in Figure 19. With the exciting power from linear region, the peak position almost remains the same and doesn't show a clear sign of net cooling for the crystals. The second power selection is in the non-linear region which is supposed to heat the crystals. The result also shows a heating of the crystals by observing a red shift of the peak position.

The cooling experiment is repeated in 10 different part of the chosen crystal. No net cooling has been observed unfortunately. Due to the limitation of the optimized crystals and the preliminary result of cooling, no further cooling experiment is conducted after that so far.

4.4 Comparison between Commercial Crystals and Lab Synthesis Crystals

After the investigation of the lab synthesis crystals, a comparison is carried between three kind of crystals including their Stokes and anti-Stokes spectroscopy.

Figure 20 This figure is the combination of three different Stokes peaks temperature range from 77 K to 300 K experiments of the crystals from TaiWan, the crystals from MTI China and the crystals grown by our own PVT method.

In the comparison of their Stokes spectroscopy between three different kinds of CdS crystals, three separate figures are listed with the temperature dependence. Based on the requirement for laser cooling, the Stokes spectroscopy from lab synthesis crystals shows a perfect one since there is no defect peaks observed from it in different temperatures. Compared with other two commercial crystals, defect peaks have been removed completely according to what have been observed in this figure.

Figure 21 This figure is the combination of three different anti-Stokes experiments of the crystals from TaiWan, the crystals from MTI China and the crystals grown by our own PVT method.

In the comparison of the anti-Stokes spectroscopy, a much clearer sign of removing the defect peaks can be observed from the Figure 21. Other from the removal of the defect peaks, the anti-Stokes peak density is much higher than what have been observed in other two commercial ones.

4.5 Conclusion

In Chapter 4, the synthesis of the CdS single crystals have been carried out to solve the problem found in commercial crystals. PVT method is used for the synthesis and the condition of the synthesis covers different temperatures as well as different ratios of sources. Both fixed shaped and random-shaped crystals are found in different patches of synthesis.

The further characterizations by optical spectroscopy give a better understanding of those crystals. It turns out that fixed shaped crystals such as needle like crystals have very poor quality for laser cooling despite of its shape uniformity. Random shaped crystals with an optimized spectroscopy are further characterized with different temperatures and powers. A laser cooling experiment is also conducted for the optimized crystals.

Although no net cooling is observed in the cooling experiment, we can conclude from the comparison between the synthesis crystals and commercial ones that the defects found in commercial crystals have been mostly removed and it is also believed that the potential of having laser cooling effect for CdS single crystals remains high.

Chapter 5 Device Design of Optical Refrigerator

5.1 Motivation of the Device Design of Optical Refrigerator

Based on the crystals that have been produced in our lab, we can see the big improvement in crystal quality and clearly the potential of CdS in laser cooling application. However, for the use of laser cooling in industry or real life, raw crystals can hardly reach the cooling requirement due to what we call radiation trapping.

In this chapter, attention will be drawn on the basic theory of radiation trapping. A design of optical refrigerator device will be performed based on a patent to solve the problem of radiation trapping⁴⁰. Details of the design and illustration will be given in figures in this chapter.

5.2 Radiation Trapping

Radiation trapping is the phenomenon that most of the fluorescent light leaving the region that has interaction with lasers will be internally reflected due at the boundary of semiconductor materials. Because of the fact that the fluorescent light will exist in the crystal for a longer time, there is a higher chance for reabsorption process. The whole process of repeated absorption, together with fluorescence will heat the cooling materials and overwhelm the cooling effect. That is also why many semiconductor materials haven't achieved net cooling while the up-conversion and other related experiments show a very good proof for laser cooling potentials.

Taking CdS as an example, we know a refractive index for CdS crystals being around 2.4 at 530nm wavelength. By calculating the refractive index we can see that the critical angel for total internal reflection is:

$$\theta_c = \arcsin\left(\frac{n_2}{n_1}\right) \quad 6.1$$

in which n_2 refers to the refractive index of crystal while n_1 refers to the refractive index of air. By using $n_2 = 2.4$ we can get a $\theta_c = 24.64^\circ$ which means 72.6% of the fluorescent light may not come out of the crystal. That is also probably why we cannot get laser cooling effect in section 4.3.

In order to solve the radiation trapping and finally aims at reaching laser cooling effect, a device of optical refrigerator is designed in the following pages.

5.3 Design of Optical Refrigerator for CdS Single Crystal

The design of the optical refrigerator that will be illustrated in this part is based on the US patent by Richard I. Epstein⁴⁰. In my design, each part including the laser will be assigned a detailed material name and type. First of all, here illustrates the basic design of the optical refrigerator.

Figure 22 This is the illustration of the design of optical refrigerator by Richard I. Epstein⁴⁰ including the laser part and the enclosed vacuum box that have the object to be cooled. Two main parts are fixed in the same heat sink.

My design of the optical refrigerator is based on the design of Richard I. Epstein shown in Figure 6.1.⁴⁰ This design has been published in 2002 as a US patent, more than 10 years earlier than the discovery of the laser cooling of semiconductor. But it provides a useful solution to what we are looking for to solve the problem of radiation trapping.

The design in the following will be mostly based on CdS single crystals for laser cooling. Materials type and size will be assigned according to application for CdS crystals.

Figure 23 This figure shows a detailed illustration of what are inside the enclosed box for the laser cooling device. In order to solve the problem of radiation trapping, 8 different parts are stacked in order to serve different purposes.

Layer 1 in figure 23 stands for the device to be cooled in the whole system. Layer 3 in Figure 23 stands for the laser cooling material, in this case, CdS single crystal. The size of the crystals should be very thin to approximately less than 1mm in order not to have fluorescent photons reabsorbed when passing through this layer.

Layer 2 which covers the upper and lower part of CdS single crystal is called the passivating layer, which is the key to solve the problem of radiation trapping. The passivating layer, in this case, is made of semiconductor material such as GaN ($n = 2.45$) or GaS ($n = 2.66$). Both of the materials has a higher refractive index than CdS which prevent the total internal refractive in the layer 3. At the same time, they form a waveguide that confirm the laser radiation to the layer 3.

Layer 5 is called the radiation transmission thermal barrier. The purpose of this layer, as its name says, is to help to pass through the fluorescent light while preventing the thermal conduction. This layer, in the case of CdS, can be made of amorphous aluminum dioxide. A substitute of this layer can be made

of vacuum gap which serves the similar purpose but has worse photon conduction.

Layer 6 is called the absorbing layer made of Ge. Below it is the layer 7 made of gold. Layer 7 serves as a preventing layer because gold has an emissivity for thermal radiation of about 2%. Layer 6 is also transparent to thermal radiation which finally leads to the fact that layer 6 and layer 7 helps the whole system to reduce 98% of the heat produced by the fluorescent photons. Layer 8 is the heat sink that may be made of any cheap metals that works of heat absorption materials.

Layer 4 is an omni-directional mirror which is in the middle of the device to be cooled and the passivating Layer 2. It reflects back the up-coming fluorescent light to the passivating layer but has good thermal conductivity.

The whole process of the laser cooling comes as following. The laser excites the cooling material CdS, the fluorescent light will come out both upward and downward. The upward fluorescent light will be reflected back to the lower part of passivating layer. When fluorescent light passes through the lower passivating layer, it will pass through the radiation transmission thermal barrier, and finally be absorbed by the absorption layer. The thermal barrier layer will prevent the heat generated in the absorption layer back to upper layers. The gold layer will carry away 98% of the heat to the heat sink and finally got absorbed by heat sink. The cooling effect will be passed through the upper passivating layer to the device that is to be cooled in the very upper of the whole system.

Figure 24 This is a complete system of the cooling part of the device including all the part listed in Figure 22 and Figure 23. New layer anti-reflection layer 9 is also listed in this figure.

To complete the design, an anti-reflection layer is added in the surface of each absorption Layer 6 to prevent any reflection of fluorescent light. Also gold Layer 7 is added to the every corner of the enclosed system.

Also, there are some restrictions to the design. The inside part of the system should be under vacuum environment in case of airflow interference.

5.4 Summary

In this chapter, a careful design of CdS single crystal optical refrigerator is illustrated based on the patent of Richard I. Epstein⁴⁰. The tailored details are added to each part of the design based on the crystals that are grown in Chapter 4.

The design solves the problem radiation trapping which is the most important obstacles in laser

cooling by adding the two passivating layer (GaN and GaS in this case) together with other absorption parts. Although this design only gives an illustration and an idea of what it looks like for laser cooling of semiconductor crystals in the near future, it may lead research and industry to further investigate into the manufacturing and design of the optical refrigerator.

Chapter 6 Conclusion and Recommendations

6.1 Conclusion

In conclusion, this thesis has reached the goal of investigation of CdS single crystals on its laser cooling characteristics.

In this thesis, we investigate the CdS single crystals from both commercial and lab grown ones. After the found of defect in commercial crystals, the lab grown crystals produced by the author successfully solve the problem of defect that have been observed in commercial ones. Further laser cooling experiment has also been done to test the laser cooling effect of lab grown crystals. Although no net cooling has been observed, a detailed design of the device of optical refrigerator base on CdS single crystal is made at the end of the thesis to further give an idea and possibility of realizing laser cooling effect in CdS single crystals.

The methods used in the whole research process includes the optical spectroscopy characterization, the analysis and calculations of those spectroscopies, growing crystals using furnace and laser cooling experiment set up. All those experiments done so far have not only helped to push forward the research progress, but also help the author to improve himself day by day in thinking, working and studying.

It is much better to say that this thesis is a complete process of finding a problem, solving that problem by hand and giving an idea to the future. It would be a great treasure in the author's life.

6.2 Recommendations for Future Work

There are a few recommendations for those who want to follow the research work in this thesis.

1. In the growth, it is important to repeat the growth of optimized CdS single crystals with optimized spectroscopy using the condition given in this thesis. At the same time, larger crystals are required if there is a need for further manufacturing.
2. In the growth part, it is also a good chance to get better and larger crystals trying the sublimation method or CVT method. There is a chance of improving the crystals quality and size by other ways of furnace growth.
3. In the aspect of materials choice, other II–VI semiconductor crystals like CdSe, ZnS, ZnSe etc. should be investigated at the same time since they also have a bigger chance of being found having laser cooling effect.
4. In the aspect of laser cooling experiment, it is a good chance to get laser cooling if one can adjust the crystals by tailoring the size and thickness, or even realize the device depicted in this thesis.

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