Measuring the anti-Stokes luminescence of CdSe/ZnS quantum dots for laser cooling applications

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ABSTRACT

The first demonstration of laser cooling of solids was of an ytterbium doped fluorozirconate glass. While this groundbreaking work successfully showed that it is possible to cool solids using laser cooling, rare-earth materials are governed by Boltzmann statistics limiting their cooling ability to about 100 K. Direct-bandgap semiconductors, on the other hand, are governed by Fermi-Dirac statistics, which allows for a theoretical cooling limit of 10 K as well as higher cooling efficiencies. Recently, it was demonstrated that it is possible to cool CdS nanoribbons by 40 K. That success was attributed to CdS strong electron-phonon coupling, which makes it possible to resonantly annihilate more than one longitudinal optical phonon during each up conversion cycle. To further increase the cooling power, large external quantum efficiency is required. A nanostucture is preferred because it creates confined excitons of tunable wavelength and reduces the self-absorption of the anti-Stokes fluorescence owing to the shorter path length for photons to escape the crystal. However, organically passivated quantum dots have a low quantum yield due to surface related trap states. A core-shell nanostructure alleviates this problem by passivating the surface trap states and protecting against environmental changes and photo-oxidative degradation. As such, we chose to investigate CdSe/ZnS core shell structure for laser cooling applications. This article highlights the measurement of the anti-Stokes luminescence, the dependence of the laser wavelength on the anti-Stokes emission of colloidal quantum dots, and the successful incorporation of CdSe/ZnS into polymers.

Keywords: Optical cooling; optical refrigeration; nanomaterial applications; laser cooling of solids;

1. INTRODUCTION

In 1929, the German physicist Peter Pringsheim proposed that anti-Stokes emission can lead to the cooling of bulk matter [1-3]. Anti-Stokes emission results in photons of shorter wavelength (higher photon energy) than that of the exciting light due to thermal absorption [2-3]. In solids, the thermal energy is mostly due to the vibrational modes (phonons) of the lattice. Thus, using lasers to cool a solid, one has to irradiate a sample with laser light in the red tail of the absorption spectrum. The material to be cooled would then absorb a photon and absorb extra energy from a phonon to emit a blue-shifted photon of higher energy. By removing these phonons, the material is cooled.

Today, this technique is known as laser cooling of solids or optical refrigeration. It can be used to achieve an all-solid-state cryocooler that is compact, contains no moving parts, has a high reliability, and does not require the use of cryogenic fluids [2,4-8]. Laser cooling also allows for the possibility of portable lasers that require no or smaller external cooling systems because the pump wavelength can be adjusted such that spontaneous anti-Stokes luminescence cooling compensates for the stimulated quantum defect heating. A thermally balanced laser such as this would not suffer from thermal defocusing or heat damage; therefore, such solid-state-lasers could achieve higher output powers [4]. Unfortunately, for cooling to occur in solids, the quantum efficiency of the material must be high and nearly all the anti-Stokes luminescence must leave the material without being reabsorbed.

Epstein and his team achieved the first net laser cooling of solids with a ZBLANP glass sample [9]. Later in 2009, cryogenic temperature was first attained using a LiYF₄:Yb³⁺ crystal [10]. To date, laser cooling has been mostly limited to glasses and crystals doped with rare-earth elements [2]. Fluorescence in rare-earth ions involve 4f electrons that are shielded by the filled 5s and 6s outer shells. This shielding limits interactions with the surrounding lattice so that nonradiative decay caused by multiphonon emission is suppressed. However, the cooling of rare-earth doped solids are governed by Boltzmann statistics. According to Boltzmann statistics, the lower energy levels in a manifold are more
populated than higher levels. As the temperature falls and $kT$ (Boltzmann’s constant times the lattice temperature) becomes small compared to the energy width of the ground state manifold, the upper levels become depopulated, which leads to an increased transparency in the red tail of the absorption spectrum; thus, the cooling efficiency approaches zero.

As such, research has expanded to semiconductors. They provide more efficient pump light absorption, the potential for lower temperatures, and the ability to directly integrate the material into electronic and photonic devices [2]. However, while the cooling transition of rare-earth doped materials occurs in localized donor ions within the host material, in direct-bandgap semiconductors the transition occurs between the extended valence and conduction bands. Moreover, indistinguishable charge carriers in Fermi–Dirac distributions may allow semiconductors to get much colder than rare-earth materials. It may then be possible to achieve temperatures as low as 10 K [2,11-13].

While much research has been centered on group III-V semiconductors such as GaAs, no net laser cooling in III-V systems has been achieved. Group III-V semiconductors have weak electron-phonon coupling strengths, low anti-Stokes photon escape owing to the large refractive index, and large surface-recombination velocities. Group II-VI semiconductors, on the other hand, have strong electron-phonon coupling, which leads to enhanced anti-Stokes upconversion. In fact, Zhang et al. successfully demonstrated 40 K of cooling of CdS nanoribbons [14]. These ribbons had thicknesses less than half the wavelength of the fluorescent photons, thereby minimizing reabsorption of the anti-Stokes luminescence.

To improve the efficiency and lower the nonradiative recombination, quantum dots (semiconductors that tightly confine electrons or holes in all three spatial dimensions) with a shell of higher bandgap grown around them are used. This type of material is known as a core-shell quantum dot [15]. The shells passivate surface trap sites and reduce non-radiative recombination. To ensure that the emission from the core escapes the QD, the shell material must have a wider bandgap than the core.

Owing to the possibility for near-unity quantum efficiency of CdSe/ZnS [16-21], we have chosen to investigate CdSe/ZnS quantum dots for laser cooling applications. This article discusses anti-Stokes measurements performed on CdSe/ZnS. In addition, the optimum laser excitation wavelength and incorporation of CdSe/ZnS into polymers are explored.

2. EXPERIMENT

2.1 Materials

CdSe/ZnS quantum dots (QSP-630) were purchased from Ocean NanoTech. These quantum dots have an emission spectrum centered at 630 nm and a quantum efficiency of 80% according to the manufacturer. The following chemicals were also used as received without further purification: toluene (Fisher T324 ACS grade), methyl methacrylate (Sigma-Aldrich M55909 99%), and 2,2′-azobis(2-methylpropionitrile) also known as AIBN (Sigma-Aldrich 441090 98%).

2.2 Polymerization of CdSe/ZnS

To ensure uniform dispersion of the CdSe/ZnS quantum dots in the polymer, we based our polymerization method on Pang et al. [22]. First, a desired quantity of quantum dots (between 1 and 8 mg) is dissolved in 1 mL of toluene. In a separate test tube, 3 mL of methyl methacrylate (MMA) and 0.1% AIBN by weight are thoroughly mixed. Then, the quantum dot colloidal solution is poured into the test tube containing MMA and AIBN. This solution is thoroughly mixed and placed in an oven at 90°C for 20 min. Once the solution is uniform in color and suitably viscous, the oven is reduced to 60°C, and the sample is left to polymerize for 20 h. For testing purposes, a sample containing only MMA and AIBN was also polymerized using this same method. Figure 1 is a photograph of the final products.
2.3 Anti-Stokes measurements

The setup to measure the CdSe/ZnS colloidal anti-Stokes spectra used a 2 mg/mL solution of CdSe/ZnS in toluene. The solution was poured into a quartz cuvette and placed in a holder. The cuvette holder was lined up with the entrance port of a SPEX 1680B double monochromator. The entrance and exit slit widths of the SPEX were set to 1.5 mm. One of the following five OBIS lasers was then chosen to excite the colloid: 637, 640, 647, 660, or 685 nm with maximum powers of 140, 100, 120, 100, or 40 mW, respectively. A Hamamatsu HC135 photomultiplier tube (PMT) was used to measure the luminescent spectrum.

A MATLAB program was written to control the SPEX monochromator and Hamamatsu PMT. Typical settings for all anti-Stokes runs were: integration time of 3 s, wavelength range of 560 - 720 nm, laser power of 20 mW, and step size of 0.2 nm.

2.4 Laser cooling setup

Preliminary laser cooling measurements were performed using the 647-nm OBIS laser at 25 mW. Two 4 mL samples were investigated. One contained pure toluene, and the other was a colloidal solution containing 2 mg/mL of CdSe/ZnS to toluene. The temperature was measured using a Type T thermocouple placed inside the solution as shown in Figure 2. The temperatures of the solution were recorded with a Beckman digital temperature thermometer with a resolution of 0.1°C, and the lab temperature was recorded using a standard mercury thermometer. Measurements were recorded every 20 minutes. The toluene levels were also measured before and after the experiment so the amount of evaporation could be determined.

The measurements began by first aligning the laser using a power meter to ensure that the beam traveled through the center of the cuvette holder as shown in Figure 2. Then a quartz cuvette containing the sample to be investigated was placed into the holder. The cuvette holder has the 4 sides and top clear to ensure that the anti-Stokes luminescence can escape. A beam block was placed at the end of the laser path for safety reasons.
3. RESULTS

Figure 3 plots the conventional Stokes luminescence spectra of the CdSe/ZnS powder, colloid, and polymer. The spectra were obtained using an Ocean Optics JAZ spectrometer with a 405-nm LED light source and bifurcated fiber placed next to the sample. The results were normalized to the colloidal spectrum. As one can see, the medium does not significantly alter the Stokes spectrum. The emission centroid and FWHM are in all three cases approximately 633 and 25 nm, respectively. The only notable difference in the spectra is the phonon sidebands near 680 nm. The CdSe/ZnS powder produces the most intense phonon sidebands, while CdSe/ZnS in toluene has none.

Figure 4 is a plot of the anti-Stokes spectra excited by four different wavelengths from the OBIS laser. The 685-nm anti-Stokes spectrum is not plotted because it is very weak. The optimum laser excitation wavelength for CdSe/ZnS anti-Stokes emission is 647 nm. According to Baranov et al., the longitudinal optical phonon (LO) frequencies of CdSe are near 200 and 400 cm⁻¹ [23]. The difference between the peak frequency of the anti-Stokes emission (near 630 nm) and the pump photon frequency is equal to the frequency of 2LO phonons of CdSe when the pump laser wavelength is 647 nm. Apparently those phonons strongly couple to the laser photons, and thus the anti-Stokes emission is more intense at a pump wavelength of 647 nm than at other pump wavelengths.

Figure 5 plots the laser cooling results where (a) represents the change in temperature of the QD colloid with time, (b) represents the pure toluene under 647-nm irradiation, and (c) represents pure toluene without any laser irradiation. Each result was normalized to the initial temperature measurement. Comparison of plots (b) and (c) show that there is no net laser effect for the pure toluene; the upward drift in both data sets arises from ambient temperature variations in the laboratory. However in plot (a), there is a cooling trend over time which could be attributed to anti-Stokes cooling. Evaporation of 0.1 mL toluene per hour (or 2.5% of the volume per hour) was observed for all solutions; however, plots (b) and (c) show that toluene evaporation does not cool a sample.

The QD colloidal solution exhibits a different trend than that of pure toluene. After the first hour, the temperature of the solution systematically drops by 2.3°C over the course of the next three hours. The temperature then equilibrates to within the ambient drift. The reason for the long laser cooling time may be convection within the solution. The laser beam has a diameter of 4 mm; therefore, the total volume of cooling is only 0.13 mL, i.e., 3% of the entire solution.

Figure 2. Diagram showing the preliminary laser cooling setup. Once the laser is aligned, the sample containing the desired solution is placed inside the sample holder. Then a thermocouple is placed in the laser path of the solution. A thermocouple reader is used to determine the temperature.
Thus, as a small volume of solution is cooled, it sinks and a warmer volume rises into the laser path. This creates a convection current, which slowly circulates the solution around the cuvette. In addition, because the particles in the colloid are undergoing Brownian motion, they are traveling in and out of the laser path randomly. In accord with these two ideas, the temperature of the QD colloid does not rise immediately after shutting the laser off.

Figure 3. Stokes emission of the CdSe/ZnS colloidal solution, polymer, and powder. The spectra were recorded using an Ocean Optics JAZ spectrometer when the samples were irradiated by a 405-nm LED.

Figure 4. CdSe/ZnS anti-Stokes luminescence spectra at excited at various laser wavelengths. The laser power was 20 mW in all cases.
Figure 5. Laser cooling of the QD colloid using a 647-nm laser. The curves represent the changes in temperature with time for (a) the QD colloid, (b) toluene under 647-nm irradiation, and (c) toluene without laser irradiation. All of the results are relative to their starting temperature.

4. CONCLUSIONS

Anti-Stokes emission of CdSe/ZnS in toluene has been measured. The optimum laser wavelength for absorption of optical phonons was found to be 647 nm, which corresponds to thermal excitation of the 2LO phonon of CdSe. The intense anti-Stokes emission from the quantum dots as well as the preliminary 2.3°C reduction in the QD colloidal temperature indicate that this material is a viable candidate for laser cooling.

The QDs have been successfully polymerized and further measurements of their anti-Stokes fluorescence are in progress. The concentration of quantum dots in the polymer has not been optimized. Furthermore, it will be necessary to reduce laser scatter off the surfaces of the sample.

5. ACKNOWLEDGMENTS

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6. REFERENCES