

# Twenty Years of Laser Cooling of Solids

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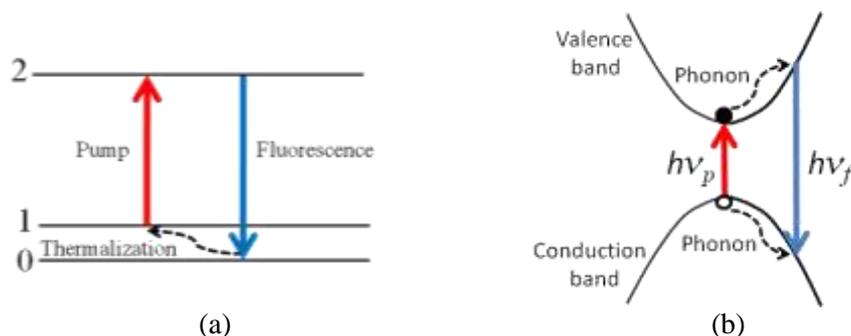
**Abstract.** Laser induced cooling of solids or optical refrigeration is an area of optical science investigating interaction of light with condensed matter. This addresses a very important practical issue: design and construction all optical solid-state cryocoolers, which are compact devices, free from mechanical vibrations, moving parts, or fluids. They are based on reliable diode pump technology and in the most part free from electromagnetic interference in the cooled area. The optical cryocooler has a broad range of applications such as in the development of biomedical sensing, magnetometers for geophysical sensors and other sensors, satellite instrumentations where compactness and the lack of vibration are key parameters. The operation of these devices is based on *anti-Stokes fluorescence* also known as *luminescence upconversion*, in which light quanta in the red tail of the absorption spectrum are absorbed in a material from a pump laser and by adding thermal energy, blue-shifted photons are spontaneously emitted. Laser cooling of solids can be realized in rare-earth doped low phonon energy glasses and crystals as well as in direct band gap semiconductors. Both of these areas are very interesting and important and are discussed in this article.

## 1. Introduction

The term “laser cooling” must not be confused with the cooling of lasers by external means. This type of cooling is *with* a laser. Laser cooling of atoms and ions, for example, Doppler cooling [1] or Sisyphus cooling [2] are well known today. This area of science has progressed immensely in the last two decades facilitating the observation of Bose-Einstein condensates and many related phenomena and resulted in Nobel prizes in physics in 1997 [3] and 2001 [4]. It is worth remembering, that nearly half a century before Doppler cooling of atoms was observed, cooling of solids by anti-Stokes fluorescence was proposed and predicted by Peter Pringsheim in 1929 [5]. It has been shown that some materials emit light at shorter wavelengths than that with which the material is illuminated due to thermal interactions accompanied by phonon absorption with the excited atoms. Typically, this can be realized in rare-earth (RE) doped low phonon energy hosts (figure 1a) as well as in direct band gap semiconductors (figure 1b). Laser cooling of solids is similar to laser cooling of atoms and ions: photons in the red tail of the absorption spectrum are absorbed from a nominally monochromatic



source followed by anti-Stokes fluorescence of blue-shifted photons with higher energy. This process is well known as anti-Stokes fluorescence rather than Stokes fluorescence in which the emitted wavelength is longer than the absorbed one. Since anti-Stokes fluorescence involves the emission of higher energy photons than those which are absorbed, the extra energy has to be extracted from the solid-state lattice in the form of the phonons, the quanta of vibrational energy that generates heat. The net anti-Stokes fluorescence can cause removal of energy from the material illuminated and results in its refrigeration. In the case of laser cooling in RE doped hosts the ground and the first excited manifolds are involved in the cooling cycle. In cooling in semiconductors, the conduction and valence bands of direct band gap semiconductors are involved (figure 1). The idea of cooling solids with anti-Stokes fluorescence stimulated an active discussion between Vavilov and Pringsheim concerning the



**Figure 1.** Cooling cycles in a RE doped host (a) and in a semiconductor (b) with  $h\nu_p$  absorbed energy followed by emission of an up-converted luminescence photon at  $h\nu_f$ .

thermodynamic aspect of this process. Vavilov believed [6, 7] that optical cooling of solids by anti-Stokes fluorescence contradicts the second law of thermodynamics. Vavilov argued that the cycle, which includes excitation and fluorescence, is a reversible one and the energy yield of greater than unity would be equivalent to the complete transformation of heat to work. Pringsheim contended [8] that in anti-Stokes cooling, a monochromatic and unidirectional input beam transforms into isotropic broadband fluorescence, and therefore this process must be irreversible, akin to Feynmann's experiment with a water sprinkler [9]. In 1946, Landau [10] concluded this controversy by providing a thermodynamic theory of the process by considering the entropy of the incident and scattered light. He has proved that the fluorescence carries much higher entropy than the beam of the pump laser; it is possible for the energy yield to exceed unity.

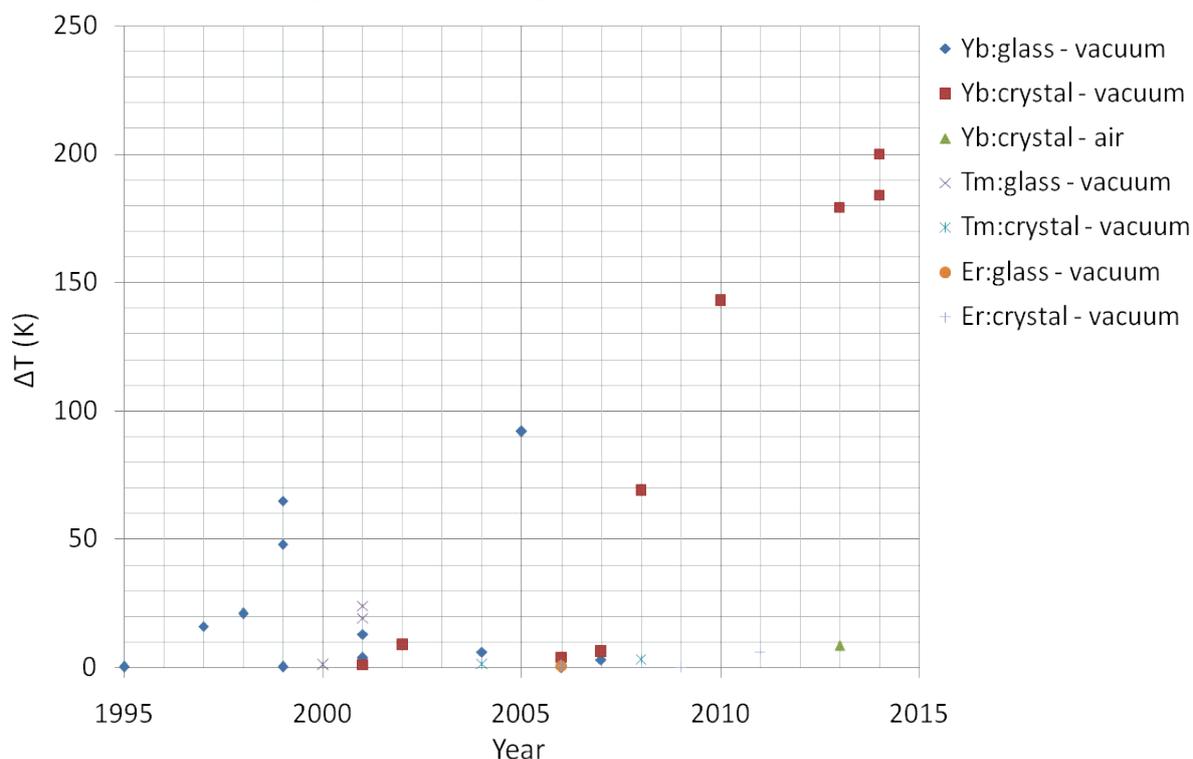
## 2. Laser cooling in rare earth doped low phonon glasses and crystals

### 2.1. Short history of laser cooling in RE-doped hosts

An effort to realise experimentally optical refrigeration of solids has a long history. In 1950, Kastler [11] and in 1961, Yatsiv [12] suggested the use of RE doped solids for optically cooling for the first time. The main advantage of RE ions is the optically active  $4f$  electrons shielded by the filled  $5s$  and  $5p$  outer shells, which limit interaction with the lattice surrounding the RE-ion and suppress non-radiative decay. Hosts with low phonon energy such as fluoride glasses or crystals can provide high quantum efficiency by diminishing non-radiative decay. In 1968, Kushida and Geusic [13] in an attempt to cool a  $\text{Nd}^{3+}$ :YAG crystal observed a reduction of heating.

For the first time *net* laser cooling of solids with anti-Stokes fluorescence was realized experimentally only in 1995 by Epstein's research team at Los Alamos National Laboratory (LANL). In this proof-of-concept experiment, an ytterbium-doped fluorozirconate  $\text{ZrF}_4\text{-BaF}_2\text{-LaF}_3\text{-AlF}_3\text{-NaF-PbF}_2$  (ZBLANP) glass sample of volume  $43 \text{ mm}^3$  was cooled by only 0.3 K below room temperature [14]. Since the first experimental observation optical refrigeration has been realized also with  $\text{Yb}^{3+}$ ,

$\text{Tm}^{3+}$  and  $\text{Er}^{3+}$  ions doped in the wide variety of low phonon energy glasses and crystals (see for e.g. reviews [15-17]). The record temperature drop for thulium ions is 24K in a  $\text{Tm}^{3+}$ :ZBLAN sample starting from room temperature [18]. In this experiment the transition between  $^3\text{H}_6 \rightarrow ^3\text{F}_4$  levels of  $\text{Tm}^{3+}$  ions was involved in the cooling cycle. The record for the temperature drop for the erbium ions is only 6K starting from room temperature in  $\text{Er}^{3+}$ : $\text{Cs}_2\text{NaYCl}_6$  [19]. In this experiment the transition between  $^4\text{I}_{15/2} \rightarrow ^4\text{I}_{9/2}$  levels of  $\text{Er}^{3+}$  ions was used in the cooling cycle. Ytterbium ions are the most suitable for laser cooling applications. They have only one excited manifold free from excited state absorption, which can be a source of undesirable heat generation in the system. It is not surprising that the today's record temperature of optical refrigeration of  $93\text{K} \pm 1\text{K}$  starting from room temperature is reached with ytterbium ions. This temperature has been achieved with 10%  $\text{Yb}^{3+}$ :YLF sample in 2014 [20]. All these experiments have been done within vacuum chambers with only a radiative heat load. In 2013,  $\text{Yb}^{3+}$ :YAG sample was cooled in air for the first time with a temperature drop 8.8K starting from room temperature [21]. The progress in laser cooling of RE-doped glasses and crystals is summarized in figure 2. As seen in figure 2, considerable progress has been made in recent years in laser cooling of RE-doped crystals. The long-range order in crystals in comparison with glasses results in a decrease in the inhomogeneous broadening and increases the quantum efficiency of cooling.



**Figure 2.** Progress in laser cooling of rare earth doped glasses and crystals.  $\Delta T$  is the temperature drop starting from room temperature.

### 3. Laser cooling in direct band gap semiconductors

As shown in the previous part of the paper, the progress in laser cooling of RE-doped glasses and crystals has been slow but good; however, laser cooling of semiconductors is more attractive in a number of applications. Indistinguishable charge carriers in the Fermi-Dirac distributions allow semiconductors to be cooled to lower temperatures than RE-doped materials. Due to Boltzmann distribution, the population of the highest energy levels of the ground manifold in the RE-doped systems decreases dramatically as soon as the temperature is lowered. The cooling cycle in RE-doped

hosts ceases when the Boltzmann constant times the lattice temperature,  $k_B T$ , becomes comparable to the width of the ground state manifold. No such limitation exists in undoped semiconductors where temperatures as low as 10K may be achieved [22]. Semiconductor coolers provide more efficient absorption of the pump radiation. The radiative recombination rates in semiconductors are much faster than in RE ions. Optical cryocoolers based on a semiconductor can be easily integrated with electronic and optical devices. However, significant challenges remain, since the high refractive index of semiconductors leads to energy trapping within the solid causing reabsorption and unwanted heating.

### 3.1. Short history of laser cooling in semiconductors

There are several theoretical approaches for analysing laser cooling in semiconductors. The approach based on a rate-equation theory, in which the effects of nonradiative, radiative and Auger recombination are taken into account, were presented in 1996 by Oraevsky [23]; and in 1997 by Gauck and colleagues [24]. In 1997, Rivlin and Zadernovsly proposed an energy balance theory for semiconductors [25]. The possibility of excitonic luminescence in the limit of vanishing electron-hole pair density was taken into account, but not of excitonic absorption. In 2004, Sheik-Bahae and Epstein extended a rate-equation theory to analyze laser cooling of bulk GaAs based on a microscopic theory for the luminescence and absorption spectra [26]. They took into account the effect of luminescence reabsorption. The main feature of the rate-equation approach is its simplicity. This theory neglects the change of carrier distribution with temperature. It is valid only for a small change in the temperature. In 2004 and 2005, comprehensive theoretical studies of laser cooling of semiconductors was carried out by a research team at Kirkland Air Force Base [27, 28]. The change in the carrier distribution with temperature as well as temperature diffusion of phonons was calculated. It was shown that the lattice and the carriers can have different temperatures varying in space and time.

In 2005, a four-step model for spatially selective laser cooling of carriers in undoped semiconductor AlGaAs/GaAs/AlGaAs quantum wells was developed in a paper [29]. In 2007, Li developed a cooling theory for semiconductor quantum wells at the Hartree-Fock level [30]. In these papers, no indication that quantum wells are better suited to optical refrigeration than bulk semiconductors is found under the assumption of quasi-thermal equilibrium.

In 2008, Eliseev theoretically investigated heavily doped semiconductors [31]. It was shown that the minimum temperature, which can be reached in such a semiconductor, is about 60-120K depending on the dopant concentration.

Most of the papers devoted to laser cooling in semiconductors considered the cooling process with GaAs (group III-V semiconductor). However in 2013, in a surprising but exciting advance, the first *experimental* observation of laser cooling with semiconductor CdS (group II-VI semiconductor) *nanobelts* was announced by Zhang and colleagues [32]. A net cooling by about 40K starting at 290 K was reported. It was shown that strong exciton - longitudinal optical phonon (LOP) coupling in CdS nanobelts permits the resonant annihilation of *multiple* LOPs in the luminescence up-conversion processes, such that in a CdS structure, each cooling cycle can remove more heat from the sample than in a GaAs sample.

### 3.2. Principles of laser cooling in semiconductor nanobelts

Let us consider an undoped semiconductor pumped with a laser at frequency  $\nu_p$ . The rate equation for the electron-hole pair density,  $N$ , is given by the relationship [26]:

$$\frac{dN}{dt} = \frac{\alpha(\nu_p, N)}{h\nu_p} I - AN - BN^2 - CN^3 + (1 - \eta_e)BN^2, \quad (1)$$

where  $\alpha(\nu_p, N)$  is the interband absorption coefficient.  $\eta_e$  is the probability that an emitted photon escapes from the semiconductor without being reabsorbed. The recombination process consists of linear nonradiative recombination with the rate  $AN$ , a “bimolecular” radiative recombination with the rate  $BN^2$ , and an Auger nonradiative recombination with the rate  $CN^3$ .  $A$ ,  $B$  and  $C$  are decay

coefficients, which characterize the fundamental properties of semiconductors. The cooling efficiency can be presented as [26]:

$$\eta_{cool} = \eta_{ext} \frac{\tilde{\nu}_f}{\nu_p} - 1, \quad (2)$$

where  $\eta_{ext}$  is the external quantum efficiency described by the relation:

$$\eta_{ext} = \frac{\eta_e B N^2}{A N + \eta_e B N^2 + C N^3}. \quad (3)$$

Let us take the first derivative of the external quantum efficiency (3) with respect to the electron-hole pair density  $N$ . The optimum electron-hole pair density,  $N_{opt}$ , for the maximum external quantum efficiency can be determined as

$$N_{opt} = \sqrt{\frac{A}{C}}. \quad (4)$$

From (3) and (5) the external quantum efficiency can be obtained at  $N_{opt}$ :

$$\eta_{ext}(N_{opt}) = 1 - 2 \frac{\sqrt{AC}}{\eta_e B}. \quad (5)$$

In relation (5) the nonradiative recombination coefficient,  $A$  and the extraction efficiency  $\eta_e$  are functions of the thickness of the sample. *Surface* nonradiative recombination,  $A_s$ , dominates coefficient,  $A$  [33]. The surface nonradiative recombination  $A_s$  is a function of the thickness of the sample,  $d$ , and the surface recombination rate,  $S$ :

$$A_s = \frac{S}{d}. \quad (6)$$

Following paper [33] and considering  $\eta_e = \eta_0 \exp(-\alpha_{eff} d)$  one can obtain

$$\eta_{ext}(N_{opt}) = 1 - 2 \frac{\sqrt{2SC}}{\sqrt{dB} \eta_0 \exp(-\alpha_{eff} d)}. \quad (7)$$

For CdS with the values  $B = 10^{-11} \text{ cm}^3/\text{s}$ ,  $C = 10^{-30} \text{ cm}^6/\text{s}$ ,  $S = 250 \text{ cm}/\text{s}$ ,  $\alpha_{eff} = 4.6 \text{ } \mu\text{m}^{-1}$ , and  $\eta_0 = 0.996$  the maximum external quantum efficiency can be achieved with a thickness of the sample of 110nm. The source of the decreased external quantum efficiency,  $\eta_{eff}$ , is an increase in the surface nonradiative recombination. A decrease in  $\eta_{eff}$  of the thick nanobalbs is due to the reabsorption process. It is expected that in the near future progress in the development of laser cooling of semiconductors will be associated first of all with cooling of nanosize semiconductor samples.

#### 4. Conclusions

We have reviewed the progress in the very interesting and promising area of laser physics known as *laser induced cooling of solids* or *optical refrigeration*. Recent developments in our understanding of the science stimulated by a number of applications such as an all optical solid state cryocooler, which is free from mechanical vibrations, moving parts and liquids, is progressing fast. A significant advantage of these devices is that they use compact long lived diode pump lasers. Thermoelectrical coolers (TEDs) are free from mechanical vibrations as well, but present day TECs can reach only ~180K; although recent developments may lower this limit if material can be better engineered. Mechanical coolers can reach as low as ~10K, but they are large and cause mechanical vibrations, which are undesirable characteristics for a number of applications. Optical cryocoolers may be beneficial for satellite instrumentation and small sensors, where compactness and the lack of vibrations are important factors. Optical solid state cryocooler have already reached an extremely low temperature of 93K±1K in a small sample of a crystal, but the problem of scaling still remains a

challenge. An optical cooler based on a semiconductor should reach as low as ~10K. The realization of laser cooling with semiconductors is a significantly more difficult task than laser cooling in RE doped glasses or crystals. At the present time only nanobelt semiconductor samples have been cooled. Several methods to improve the cooling process have been proposed. Multipassing of the pump beam with an extra-cavity as well as with the intra-cavity have been proposed [34]. Development of new artificially engineered structures with suitable for laser cooling parameters may prove to be very promising for the future design and implementation of all optical cryocoolers.

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