Experimental minimum of condensed-phase optical refrigeration

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Abstract

Since the first demonstration of optical refrigeration in a rare-earth-doped glass nearly 30 years ago, the nascent field of laser cooling solids has progressed significantly. It is now possible to demonstrate payload cooling to ~91 K using laser-excited ytterbium-doped fluoride crystals. Realizing lower temperatures, however, requires achieving ultrahigh purities in existing rare earth-doped crystals or establishing new cooling media. For the latter, semiconductors are an obvious choice given higher cooling power densities and predicted cooling floors as low as 10 K. This has stimulated a race to demonstrate the optical refrigeration of a semiconductor. It is therefore timely to systematize the necessary and sufficient experimental minimum criteria for reporting optical refrigeration results to elevate the reliability and reproducibility of current and future optical refrigeration claims.

We distill an optical refrigeration Experimental Minimum (EM) that we propose will standardize the reporting of new cooling results. EM tenets fall into the following categories:

- 1) Demonstrations of explicit heating vs cooling: Reports should show reliable and self-consistent transitions between heating and cooling regimes by tuning laser excitation frequencies around mean emission frequencies (\bar{v}_{em}).
- 2) Optical cooling metrics: Two critical quantities, external quantum efficiency (η_{EQE}) and absorption efficiency (η_{abs}), should be measured and reported.
- 3) *Thermodynamic consistency*: Cooling time constants and achieved temperature changes must be consistent with thermodynamic constraints imposed by the cooling environment and sample parameters.
- 4) Reliable temperature measurements: Details of the temperature measurement technique, its calibration procedure, and temperature- as well as time resolution should be reported.

All optical refrigeration claims should demonstrate the above four criteria to ensure their reliability and verifiability. We further propose that the EM serve as a guide for reviewing literature claims in the field.

Introduction

Condensed phase laser cooling is premised on removing thermal energy from a material through its anti-Stokes photoluminescence (ASPL). Since the first 1995 report of ASPL-induced cooling in a Yb³⁺ doped heavy-metal-fluoride glass, numerous experiments now unambiguously confirm condensed phase optical refrigeration as well as cryogenic cooling in rare-earth (RE)-doped glasses and crystals. Of note is a record cooling temperature of 91 K achieved in a Yb³⁺-doped yttrium lithium fluoride crystal. Ongoing efforts in material purification and high-purity crystal growth suggest that 50 K temperatures are within reach for RE-doped systems. One

Unfortunately, the thermal depopulation of higher energy RE atomic levels at low temperatures freezes out their optical cooling cycles. Deep cryogenic applications therefore require changing optical cooling media. To this end, numerous attempts have been made with alternate, condensed phase systems^{8,9} with recent focus shifting to semiconductors^{10,11} where Fermi-Dirac statistics allow laser cooling down to LO-phonon freezeout temperatures around 10 K.¹²

Optical refrigeration has been attempted in bulk, direct-gap semiconductors such as ZnTe 13 and lead-based, hybrid/all-inorganic perovskites such as methylammonium lead iodide (CH₃NH₃PbI₃). ¹⁴ It has also been attempted with low-dimensional semiconductors such as GaAs/InGaP heterostructures 10,11,15 , GaAs quantum wells 16 , CdS nanobelts 17,18,19 , single-layer, two-dimensional Ruddlesden-Popper phenylethylene lead iodide [(C₆H₅C₂H₄NH₃)₂PbI₄] microcrystals 14 , monolayer WS $_2^{20}$, and cesium lead bromide (CsPbBr₃) 21 or core/shell CdSe/CdS 22 nanocrystals. To various degrees, all attempts have been challenged by a combination of factors, originating from the need to produce high-purity, cooling-grade materials.

Crucially, all current semiconductor optical cooling claims are hampered by incomplete experimental details. Often key performance metrics are implied (or assumed), not measured. On rare occasion, results do not conform to known physics.^{23,24} Hence, a need exists to standardize the reporting of optical refrigeration claims to ensure verifiable cooling outcomes.

In what follows, we revisit the tenets of optical refrigeration and distill them into a condensed phase optical refrigeration Experimental Minimum (EM). The EM aims to promote rapid progress in the field by standardizing the reporting of cooling results. We strongly believe that demanding research, especially those which rely on the absolute performance characteristics of advanced materials - be it optical refrigeration, room-temperature superconductivity, light transistors, Majorana fermions, etc... require such standardization. ²⁵ **Figure 1** summarizes optical refrigeration's EM tenets, which are discussed in what follows.

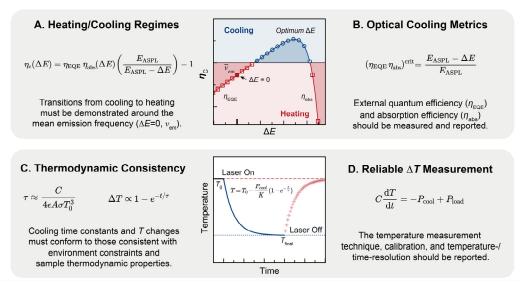


Figure 1. Schematic summary of a condensed phase optical refrigeration Experimental Minimum.

Modeling optical refrigeration

In optical refrigeration, net cooling power density, P_{cool} ($P_{\text{cool}} > 0$ represents cooling by the chosen sign convention), is expressed as¹

$$P_{\text{cool}} = P_{\text{em}} - P_{\text{abs}} \tag{1}$$

where $P_{\rm abs} = (\alpha + \alpha_{\rm b})I_0$ is the absorbed power density for an incident, excitation laser irradiance of I_0 . α is a resonant, semiconductor absorption coefficient at frequency ν_0 and $\alpha_{\rm b}$ is a "parasitic" absorption coefficient that accounts for unwanted light absorption, which ultimately leads to heat generation. In RE-doped solids the origin of $\alpha_{\rm b}$ is believed to be due to trace amounts of transition metal ions, such as ${\rm Co^{2+}/Co^{3+}}$ and ${\rm Fe^{2+}/Fe^{3+}}$, 26,27 some of which has been confirmed at the ppm level. For GaAs heterostructures, it has been suggested that $\alpha_{\rm b}$ stems from defects at GaAs quantum well/InGaP heterojunctions. 7

In Equation 1, the emitted photoluminescence (PL) power density is

$$P_{\rm em} = \alpha I_0 \eta_{\rm EQE} \left(\frac{E_{\rm ASPL}}{E_{\rm ASPL} - \Delta E} \right) \tag{2}$$

where $\eta_{\rm EQE}$ is the material's external quantum efficiency [also referred to as quantum yield (QY) in the semiconductor nanocrystal community] and $E_{\rm ASPL}$ is the average energy at the mean emission frequency ($\bar{\nu}_{\rm em}$) of the PL. The subscript ASPL reflects the anti-Stokes PL obtained in the laser cooling regime. $E_{\rm ASPL}$ approximately corresponds to the band gap absorption energy, $E_{\rm g}$, of a direct-gap semiconductor. It can, however, be redshifted relative to it due to excitonic effects or the existence of absorption/emission Stokes shifts 28,29,30 , associated with dark exciton 31,32 or optically passive emitting states. To illustrate, in CsPbBr3 nanocrystals with edge lengths between 13 and 4 nm, absorption/emission Stokes shifts range from 20-82 meV, respectively. 29,30 The difference $E_{\rm ASPL} - \Delta E$ thus reflects the detuning (ΔE) of the pump laser into the optical gap relative to the material's mean emission (not absorption) energy.

By combining **Equations 1** and **2**, a cooling efficiency,

$$\eta_{\mathbf{c}} = \frac{P_{\text{cool}}}{P_{\text{abs}}} = \eta_{\text{EQE}} \eta_{\text{abs}} \left(\frac{E_{\text{ASPL}}}{E_{\text{ASPL}} - \Delta E} \right) - 1,$$
(3a)

arises where

$$\eta_{\rm EOE} = \eta_{\rm e} W_{\rm r} / (\eta_{\rm e} W_{\rm r} + W_{\rm nr}) \tag{3b}$$

and

$$\eta_{\rm abs} = \alpha/(\alpha + \alpha_{\rm b}).$$
(3c)

In **Equation 3b**, η_{EQE} is defined in terms of band edge, interband radiative (W_r) and non-radiative (W_{nr}) recombination rates with η_e a photon escape efficiency that accounts for light trapping in semiconductors due to refractive index differences with the surrounding medium. ¹² For nanocrystals that behave as dipole emitters, $\eta_e \approx 1$.

 $\eta_{\rm abs}$ (**Equation 3c**) is an absorption efficiency, which represents the fraction of the total absorbed pump photons that induce cooling; $1-\eta_{\rm abs}$ is the fraction resulting in heating via impurity absorption. $\eta_{\rm abs}$ can also be defined as an up-conversion efficiency that describes the likelihood that a below-gap absorption event leads to up-conversion and possibly to cooling as opposed to non-radiative relaxation. 33,34,35

Setting $P_{\rm cool}=0$ (alternatively, $\eta_{\rm c}=0$), reveals a critical dimensionless product $(\eta_{\rm EQE}\eta_{\rm abs})^{\rm crit}$ above which the thermal energy removed by up-converted PL exceeds that gained by non-radiative recombination and parasitic impurity absorption. An associated performance threshold is

$$(\eta_{\rm EOE}\eta_{\rm abs})^{\rm crit} = (E_{\rm ASPL} - \Delta E)/E_{\rm ASPL}$$
 (4)

and captures the challenging nature of solid-state optical refrigeration. Namely, **Equation 4** highlights the interrelationship between non-radiative recombination, photon escape efficiency, and absorption/up-conversion efficiency -- all parameters which dictate permissible ΔE -values for realizing optical cooling. An additional complication arises from $\eta_{\rm EQE}$'s carrier-density (N) dependence that leads to optimal values of $N^{\rm opt}$ and correspondingly $\eta_{\rm EQE}^{\rm opt}$. ¹² $\eta_{\rm abs}$ may also depend on N through absorption saturation given sufficient pumping.

For $\eta_{\rm abs}=1$, associated critical $\eta_{\rm EQE}$ -values ($\eta_{\rm EQE}^{\rm crit}$) range from 0.85-0.99.² For GaAs/InGaP heterostructures and CsPbBr₃ nanocrystals with room-temperature optical gaps of 1.42 eV and 2.41 eV, $\eta_{\rm EQE}^{\rm crit}=0.93$ and 0.96 respectively ($\Delta E=100$ meV).² Even realizing $\eta_{\rm EQE}^{\rm crit}$ does not guarantee cooling. To illustrate, despite $\eta_{\rm EQE}>0.99$ in GaAs, cooling has not been achieved due to $\alpha_{\rm b}$ -induced heating. This prevents **Equation 4** from being satisfied so that $P_{\rm cool}<0.^{10}$

Because net laser cooling requires $\eta_c > 0$, η_{EQE} and η_{abs} are important material parameters whose numerical values must be near-unity. That near-unity η_{EQE} and η_{abs} are possible can be seen in RE systems where values of η_c fall in the range 0-0.05.^{5,36} For

semiconductors, near-unity η_{EQE} and η_{abs} require material optimization via a combination of purification, defect passivation, and proper material selection. Systems with large electron-phonon coupling constants are therefore currently believed to be preferential for cooling, as they can possess intrinsically large up-conversion efficiencies.³⁷

EM 1: Demonstrations of explicit heating vs cooling. Reproducible transitions from heating to cooling should be demonstrated as functions of ΔE about a system's mean emission energy.

Equations 3a and 4 reveal that changing ΔE about $\bar{v}_{\rm em}$ transitions a system between its cooling and heating regimes. While this can be used to optimize $\eta_{\rm c}$, more important is that self-consistency requires that a material's cooling and heating regimes be explicitly demonstrated. This can be done in practice using Laser-Induced Thermal Modulation Spectroscopy (LITMoS).⁴²

EM 2: Optical cooling metrics. Critical parameters required to cool should be verified and explicitly reported. Report measurements of $\eta_{\rm EQE}$ and $\eta_{\rm abs}$ together with relevant experimental conditions, such as injected N, ΔE , T, $\alpha_{\rm b}$ etc...

Experimental $\eta_{\rm EQE}$ measurements involve relative, absolute, model-based, and calorimetric approaches.^{2,38} Relative methods involve comparing a specimen's integrated emission spectrum to that of a reference specimen with a known $\eta_{\rm EQE}$. Absolute approaches use an integrating sphere. Model-based approaches such as power-dependent photoluminescence (PDPL)³³ invoke nonlinear I_0 emission intensity ($I_{\rm em}$) dependencies and kinetic models to fit $I_{\rm em}$ from where both a maximum $\eta_{\rm EQE}$ and corresponding $N^{\rm opt}$ can be found.

Calorimetric approaches entail registering the temperature of a sample as a function of the excitation laser frequency, v_0 , such that $\eta_{\rm EQE}$ can be precisely read off from the slope, dT/dv_0 , of measurements in the region where $hv_0 > E_{\rm ASPL}^{36}$, see also **Figure 1**. These temperature measurements commonly employ one or several non-contact techniques, including thermal imaging, calibrated temperature-dependent emission spectra, or photothermal deflection.^{2,39}

A further advantage of calorimetric measurements is simultaneous estimates of α_b when $h\nu_0 < E_{\rm ASPL}$. For CsPbBr₃ nanocrystals, $\eta_{\rm abs} = 0.75$ ($\Delta E = 23$ meV) has been measured via direct measurements of Stokes and anti-Stokes excitation irradiances required to achieve identical Stokes/ASPL emission intensities in conjunction with independent estimates of corresponding Stokes and anti-Stokes absorptances.³⁴ More extensive measurements across a wider range of temperatures and ΔE -values now reveal $\eta_{\rm abs} \sim 1$ in CsPbBr₃ nanocrystals.³⁵

EM 3: Thermodynamic consistency. Cooling results should be explicitly compared to thermodynamically-predicted cooling timescales and final temperatures.

Reported cooling results must furthermore be consistent with thermodynamic considerations of the specimen and its environment⁴⁰ wherein

$$C\frac{dT}{dt} = -P_{\text{cool}}(T) + P_{\text{load}}(T)$$

$$\approx -P_{\text{cool}} + \left[4\epsilon A\sigma T_0^3 + \kappa_{\nu}A + \frac{\kappa_{c}A_{c}}{d_{c}}\right](T_0 - T)$$

$$\approx -P_{\text{cool}} + K(T_0 - T). \tag{5}$$

Equation 5 expresses a material's temperature change due to a competition between optical refrigeration and heating from extrinsic thermal loads (P_{load}). The first bracketed term in P_{load} represents blackbody heating from a specimen's surroundings (e.g., a vacuum chamber). The second and third terms represent environmental convective and conductive loads on the specimen. C is the sample's heat capacity, C is the specimen chamber's emissivity, C is the semiconductor's surface area, C is the Stephan-Boltzmann coefficient, C is an initial temperature, C is a convective heat transfer coefficient, C is a thermal conductivity constant, C is a contact area, and C is a contact point length.

Equation 5 yields a time-dependent temperature (T) and corresponding cooling time constant, τ . In the limit convective and conductive thermal loads are negligible and where $\Delta T = T_0 - T \ll T_0$,

$$T(t) \approx T_0 - {P_{\text{cool}}/K} (1 - e^{-t/\tau}),$$

$$\tau = \frac{c}{\kappa} \approx \frac{c}{4\epsilon A \sigma T_0^3}.$$
(6)

with

Equation 6 can therefore be compared to experimentally-observed cooling timescales to validate their appropriateness. Heating timescale should likewise be consistent with P_{load} .²³ For reference, prior estimates for CsPbBr₃ nanocrystals embedded in an aerogel disk yield $\tau \sim 0.5$ seconds.² For an individual CdS nanobelt suspended in vacuum, a maximum time constant is $\tau \sim 30$ ms.²³

EM 4: Reliable temperature measurements. Details of the temperature measurement technique, its calibration procedure, and temperature- as well as time-resolution should be reported.

Critical to assessing a measurement's conformity with **Equation 6** are accurate time-resolved or steady-state measurements of T. In practice, steady-state measurements are carried out upon reaching thermal equilibrium with achieved final temperatures, $T_{\rm final}$, measured using non-contact (optical) approaches such as up-conversion emission thermometry 41 , differential luminescence thermometry 4 , pump-probe luminescence thermometry 17 or via a calibrated thermal camera. 42 Time-dependent T measurements on sub-millisecond 40 to 10s of picosecond timescales have also been devised, the latter allowing the first observation of transient laser cooling in GaAs at room temperature. 43

Extracted temperatures should ultimately be compared to $T_{\text{final}} = T_0 - \frac{P_{\text{cool}}}{K}$ from **Equation** 6.

In summary, there exists much promise to advance condensed phase optical refrigeration beyond RE systems. Possible semiconductor candidates include GaAs ⁴³ and novel nanostructures that exhibit near-unity up-conversion efficiencies. ^{2,34,35} However, the realization of tangible advances is premised on standardizing reported cooling claims to the above-outlined condensed-phase EM.

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Competing interests

The authors declare no competing interests.

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