ENHANCED LASER COOLING OF ION-DOPED NANOPOWDERS

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ABSTRACT
Enhanced laser cooling performance of rare-earth ion
doped nanocrystalline powders is predicted, using Yb$^{3+}$:Y$_2$O$_3$
as the model material. This is achieved by enhancing the anti-Stokes off-resonance absorption, which is proportional to the
three factors considered in this paper: dopant concentration,
pumping field energy, and anti-Stokes transition rate. The concept of the optimum dopant concentration for cooling is proposed
based on the fact that higher concentration increases absorp-
tion while decreases quantum efficiency. Using the concentra-
tion quenching theory of energy transfer, the optimum concentra-
tion, which gives the maximum cooling power, is found to be
larger than the currently used value, suggesting noticeable en-
hancement effects for laser cooling. The pumping field energy
is enhanced in random nanopowders compared with bulk crys-
tals under the same irradiation, due to the multiple scattering
of photons. Photons are thus localized in the medium and do
not propagate through, increasing the photon absorption of the
pumping beam. This also contributes significantly to laser cool-
ing enhancement. Using molecular dynamics simulations, the
phonon density of states (DOS) of the nanopowder is calculated,
and found to have extended, small tails at low and high frequen-
cies. The second-order electronic transition rate for the anti-
Stokes luminescence is calculated using the Fermi golden rule,
which includes the influence of this phonon DOS, and is shown
to have enhancement effects on the laser cooling efficiency using
nanopowders. Finally, it is concluded that these three en-
hancement mechanisms are exactly equivalent to increasing the
number of the three participating carriers (electron, photon, and
phonon) in the interacting volume.

NOMENCLATURE

$\alpha_{\text{ph}}$ ion-phonon coupling constant
$B_{e,a}$ excitation coefficient (1/(s·J/m$^3$))
$c_0$ speed of light in vacuum (m/s)
$D_p$ phonon density of states (1/m$^3$)
d$_s$ diameter of the solid particle (m)
$E$ complex electric field (V/m)
$E$ energy flow rate (W)
$E_{\text{pump}}$ pumping energy (J)
etr electron charge (C)
$\epsilon_{\text{ph},i}$ energy density of the pumping field (J/m$^3$)
$e_\text{a}$ unit photon polarization vector
$f_{\text{p},ph}$ phonon, photon distribution function
H Hamiltonian (J)
$I$ intensity (W/m$^2$)
k wave vector (1/m), thermal conductivity (W/m-K)
$L$ optical pathlength, (m)
$l$ index of the layers
$M$ interaction matrix
$m_f, m_s$ complex refractive index of fluid, solid
$N$ number of layers
$N_p$ number of phonons
$n_a, n_b$ electronic population at the ground and excited states
(cm$^{-3}$)
$n_d$ dopant concentration, (cm$^{-3}$)
n$_f, n_s$ refractive index of fluid, solid
$Q$ power (W)

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1 INTRODUCTION

The concept of laser cooling (optical refrigeration) of solids dates back to 1929, when Pringsheim recognized that thermal vibrational energy (phonon) can be removed by the anti-Stokes fluorescence, i.e., the photons emitted by an optical material have a mean energy higher than that of the absorbed photons [1]. Initially, it was believed that optical cooling by the anti-Stokes fluorescence contradicted the second law of thermodynamics. Predictions suggested that the cycle of excitation and fluorescence was reversible, and hence the optical cooling would be equivalent to the complete transformation of heat to work [2,3]. This issue was cleared by Landau by assigning entropy to radiation [4].

It was shown that the entropy of a radiation field is proportional to its frequency bandwidth and also to the solid angle through which it propagates. Since the incident laser light has a very small bandwidth and propagates in a well-defined direction, it has almost zero entropy. On the other hand, the fluorescence is relatively broadband and is emitted in all directions, and therefore, it has a comparatively larger entropy. In this way, the second law of thermodynamics is satisfied. A detailed, up-to-date analysis is given in the Appendix for reference.

In Fig. 1(a), the fundamental energy carriers involved in the laser cooling process are shown. There is a host crystal lattice, idealized as transparent to the pumping laser. Some of its atoms are replaced by optically active, doped ions (e.g., Yb$^{3+}$). The ion is represented by an effective transition dipole moment, defined as a quantum mechanical spatial integral of the classical dipole moment $\mu_{e}$, i.e.,

$$\mu_{e} = \int \psi_{f}^{*} e_{e} r \psi_{i} d^{3}r.$$ (1)

where, $e_{e}$ is the electron charge, $r$ is the position vector, and $\psi_{i}$ and $\psi_{f}$ are the initial and final state wave functions of the two level system. The electromagnetic field, which has a polarization vector $e_{\alpha}$, may interact with the ion if the coupling factor $e_{\alpha} \cdot \mu_{e}$ is nonzero (i.e., they are not orthogonal). Shown in Fig. 1(b) are the principles of the photon-electron-phonon interactions which result in the cooling effect in the solid. When the medium is irradiated by laser light with a frequency $\omega_{0}$, that is below the resonance frequency $\omega_{0}$ (10,250 cm$^{-1}$ for Yb$^{3+}$ ion in Y$\text{O}_3$), the electron may be excited by absorbing a photon from the pumping field and a phonon with a frequency $\omega_{p}$ from the host, such that
Figure 1. (a) Three fundamental energy carriers in rare-earth ion doped solids irradiated by laser light: photons from the pumping fields, phonons from the host crystal, and electrons of the doped ions. (b) Principles of laser cooling in rare-earth ion doped crystal. The electron is excited by absorbing a photon and one or more lattice phonons, and then decays by emitting a higher energy photon.

Figure 2. A micrograph of ion-doped nanopowder. The length of shown scale is 100 nm.

the optical transition. Later Djeu and Whitney laser cooled low-pressure CO\textsubscript{2} by 1 K from 600 K by using a CO\textsubscript{2} laser for pumping [6]. In 1995, Epstein et al. [7] reported the first successful experiment of laser cooling in solids. A local temperature decrease in a Yb-doped glass was detected by a photothermal deflection technique, and the cooling efficiencies achieved (up to 2\%) were more than four orders of magnitude greater than those observed in Doppler cooling of gases [9]. The cooling efficiency $\eta_c$ is defined as the ratio between the net cooling power and the absorbed power. Since then, various Yb or Tm doped glasses and crystals have been cooled [8–17]. Solids have been cooled by up to 92 K below room temperature [17].

In the experiments, the pumping wavelength needs to be tuned far from the absorption resonance, since it must be longer than the mean emission wavelength to get cooling. As a result, the laser cooling performance is intrinsically limited by the very low absorption of the pumping photons. Here, we will theoretically explore the possible enhancement of laser cooling by using nanopowders. A micrograph of the nanopowder is shown in Fig.2. Due to the colloidal behavior, the porosity of the nanopowder is rather large, compared to randomly placed larger particles.

We will focus on the enhanced laser cooling of Yb\textsuperscript{3+}:Y\textsubscript{2}O\textsubscript{3} nanopowder, and compare the predictions to those for bulk crystals. To start, we derive an expression for the total net cooling power in terms of various limiting factors, in order to provide some guidelines for cooling power enhancement. It is found that the off-resonance, anti-Stokes absorption needs to be enhanced, which can be achieved by increasing the number of absorbers, the pumping field energy, and the transition rate. Nanopowders are then proposed to have all these features for the enhanced performance. Using the concentration quenching theory of energy transfer, the optimum concentration is introduced and found to be larger than the currently used value, suggesting noticeable enhancement effects for laser cooling. The pumping field energy

$\omega_{ph,i} + \omega_p = \omega_0$. The electron then decays by emitting a photon with a frequency $\omega_{ph,e}$ and, possibly, phonons. If the average emitted photon frequency $\bar{\omega}_{ph,e}$ is larger than $\omega_{ph,i}$, the medium loses thermal energy and is cooled.

Many attempts have been made to realize radiative refrigeration experimentally, and the associated theoretical interpretations have been discussed. The earliest experiment was performed by Kushida and Geusic on Nd: YAG [5]. Reduced heating other than net cooling was observed, which was conjectured to be a result of the impurities in the crystal and multiphonon decay across
2 Improving Laser Cooling Performance

In Fig. 3, an energy diagram is shown for the laser cooling of nanopowders. The energy entering the control volume is the irradiation power \( Q_{ph,i} \), and those leaving the control volume are the luminescence emission power \( Q_{ph,e} \) and the unabsorbed irradiation power \((1 - \alpha_{ph,i})Q_{ph,e}\). The latter includes the reflected, transmitted, and scattered power. The energy conversion is denoted as \( \dot{S}_{ph-e-p} \). The porosity of the medium is \( \varepsilon \) and the volume is \( V \). The carrier interactions and energy conversions only take place in the volume of the solid phase, which is \( V = (1 - \varepsilon)V \). However, the pores are important in that they affect the photon transport and the phonon DOS, as will be seen in later sections.

In order to relate the absorbed and emitted power, the population dynamics of the ground and excited electronic states needs to be established. Although the rate equation is not suitable for describing atoms with any correlations between them (such as in cooperative interactions or other interatomic couplings), it is correct to describe the population dynamics of statistically independent atoms. In the nanoparticles studied, cooperative effects are negligible [18]. Hence, the rate equation for the two level system shown in Fig.1(b) is

\[
\frac{dn_b}{dt} = -\gamma_{e,d}n_b + \gamma_{e,a}n_a, \quad (2)
\]

where \( n_b \) and \( n_a \) are the populations at the excited and ground states. Here, \( \gamma_{e,d} \) is the total decay rate, contributed by both the radiative decay (includes the spontaneous and stimulated emissions) and nonradiative decay processes. The rate \( \gamma_{e,a} \) is the absorption (or excitation) rate, and is proportional to the energy density of the pumping field, as [19],

\[
\gamma_{e,a} = B_{e,a}e_{ph,i}. \quad (3)
\]

Here, \( B_{e,a} \) is the excitation coefficient, defined as the excitation rate per unit energy density of the pumping field. It describes the photon-electron coupling (may also be phonon assisted) strength. Also, \( e_{ph,i} \) is the energy density of the pumping field inside the nanopowder, given by the following expression for a monochromatic electromagnetic wave [20]

\[
e_{ph,i} = \frac{1}{2}e_{r,\varepsilon}|E|^2, \quad (4)
\]

where \( e_{r,\varepsilon} \) is the real part of the permittivity of the medium, and \( |E| \) is the amplitude of the local electric field. Alternatively, from the particle (photon) point of view, \( e_{ph,i} \) can be written as

\[
e_{ph,i} = \hbar \omega_{ph,i} n_{ph,i}, \quad (5)
\]

where \( n_{ph,i} \) is the number density of the pumping photons. Equations (4) and (5) are equivalent, and clearly show the wave-particle duality of light, which will be seen in later sections playing a central role in understanding the enhancement mechanisms.

At steady state, Eq.(2) becomes

\[
\frac{dn_b}{dt} = -\gamma_{e,d}n_b + \gamma_{e,a}n_a = 0. \quad (6)
\]

Since one excitation transition leads to the absorption of one photon with the energy \( \hbar \omega_{ph,i} \) from the pumping field, the local absorbed power per unit volume is given by

\[
\dot{s}_{ph,a} = \hbar \omega_{ph,i}\gamma_{e,a}n_a = \hbar \omega_{ph,i}B_{e,a}n_a e_{ph,i}. \quad (7)
\]

By definition, the absorption coefficient \( \sigma_{ph,i} \) is given by

\[
\sigma_{ph,i} = \frac{\dot{s}_{ph,a}}{I_{ph,i}} = \frac{\dot{s}_{ph,a}}{\omega_{ph,i}e_{ph,i}}, \quad (8)
\]

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{energy_diagram.png}
\caption{The energy diagram for the laser cooling of a nanopowder. The unabsorbed irradiation power includes the reflected, transmitted, and scattered power.}
\end{figure}
where \( I_{ph,i} \) and \( u_{ph,i} \) are the intensity and speed of the pumping light. Substituting Eq. (7) into Eq. (8), we can write the absorption coefficient in terms of atomistic scale quantities as

\[
\sigma_{ph,i} = \frac{\tilde{h}\omega_{ph,i} B_{e,a} n_a}{u_{ph,i}}. \tag{9}
\]

This indicates that the absorption coefficient \( \sigma_{ph,i} \) is proportional to the excitation coefficient \( B_{e,a} \), and the number density of absorbers \( n_a \), as expected. The total absorbed power is then given by

\[
Q_{ph,a} = \int_{V_s} \dot{S}_{ph,a} dV_s = \tilde{h}\omega_{ph,i} \int_{V_s} \dot{\gamma}_{e,a} n_a dV_s. \tag{10}
\]

The absorptance \( \alpha_{ph,i} \) can then be calculated using

\[
\alpha_{ph,i} = \frac{Q_{ph,a}}{Q_{ph,i}}. \tag{11}
\]

Similarly, one radiative decay transition leads to the emission of a photon with a mean energy \( \tilde{h}\omega_{ph,e} \). The total emitted power is thus given by

\[
Q_{ph,e} = \tilde{h}\omega_{ph,e} \int_{V_s} \dot{\gamma}_{e,d} n_d dV_s. \tag{12}
\]

Here the radiative decay rate \( \dot{\gamma}_{e,d} \) is related to the total decay rate \( \dot{\gamma}_{e,d} \) by

\[
\dot{\gamma}_{e,d} = \eta_{e-ph} \dot{\gamma}_{e,d}. \tag{13}
\]

where \( \eta_{e-ph} \) is the quantum efficiency, defined as the fraction of the decaying electrons that undergo radiative decay. Substituting Eqs. (6) and (13) into Eq. (12), we are able to write the emitted power in terms of the absorbed power as

\[
Q_{ph,e} = \tilde{h}\omega_{ph,e} \eta_{e-ph} \int_{V_s} \dot{\gamma}_{e,d} n_a e_{ph,i} dV.
\]

The net cooling power \( \dot{S}_{ph-e-p} \) is then calculated as the difference between the absorbed and emitted radiation, i.e.,

\[
\dot{S}_{ph-e-p} = Q_{ph,a} - Q_{ph,e} = \left(1 - \frac{\dot{\gamma}_{e,d}}{\dot{\gamma}_{e,d}^e \eta_{e-ph}}\right) Q_{ph,a} = \left(1 - \frac{\tilde{h}\omega_{ph,ph} B_{e,a} n_a}{\tilde{h}\omega_{ph,ph} B_{e,a} n_a} \right) \int_{V} e_{ph,i} dV. \tag{15}
\]

This result indicates that a negative value of \( \dot{S}_{ph-e-p} \) represents cooling. As a result, only those \( \lambda_{ph,i} \) larger than \( \lambda_{ph,e} \) may result in cooling, and this range is defined as the cooling regime. Also, the quantum efficiency \( \eta_{e-ph} \) must be larger than \( \lambda_{ph,e} / \lambda_{ph,i} \), which is satisfied in cooling experiments on bulk crystals. Note that we have assumed that the quantum efficiency of nanopowders is the same as that of bulk materials. There are reports of decreased quantum efficiency in nanocrystals, due to surface defects, adsorbed gas molecules, and other quenching centers [21].

The off-resonance absorption in laser cooling experiments is generally very small, and the system can thus be safely assumed to be far from saturation, i.e., the electronic population of the ground state is much larger than that of the excited state. As such, the ground state population can be approximated as the dopant concentration, i.e.,

\[
n_a = n_d. \tag{16}
\]

By defining a total pumping field energy inside the medium as

\[
E_{pump} = \int_{V_s} e_{ph,i} dV_s, \tag{17}
\]

the net cooling power becomes

\[
\dot{S}_{ph-e-p} = \left(1 - \frac{\dot{\gamma}_{e,d}}{\dot{\gamma}_{e,d}^e \eta_{e-ph}}\right) \tilde{h}\omega_{ph,ph} B_{e,a} n_a E_{pump}. \tag{18}
\]

Thus, to enhance the cooling power using the same incident energy, increases in the dopant concentration \( n_d \), the total pumping field energy inside the nanopowder medium \( E_{pump} \), and the excitation coefficient \( B_{e,a} \), are necessary. These effects will be discussed, in the following sections for ion-doped nanopowders.

### 3 Optimum Dopant Concentration

A higher value of \( n_d \), the dopant concentration, is desirable in laser cooling experiments, since more absorbers are available, which will compensate for the low absorption cross section. However, ions will be closer to each other, and the excitation energy may hop around neighboring ions until it finds a quenching center to decay nonradiatively. This energy transfer mechanism leads to a drop in the quantum efficiency \( \eta_{e-ph} \), and is an effect called the concentration quenching. Hence, an optimum dopant concentration, corresponding to a balance between the increase in \( n_d \) and the decrease in \( \eta_{e-ph} \), should exist. However, due to the prior lack of a theory to describe this optimum concentration, arbitrary concentrations of 1 wt.% (corresponding to 2.42 cm\(^{-3}\)) and 2 wt.% have been used in most of the existing experiments. In this section we suggest a criterion for determining the optimum concentration.
In highly pure Yb$^{3+}$-doped crystals, which are preferred in laser cooling experiments, nonradiative processes should be rather weak, and they essentially come from the self-generated quenching processes [22, 23]. In such an event, one excited ion transfers its excitation energy to its identical neighbor at the ground state, through a multiphonon relaxation process, as shown in Fig. 4. As the dopant concentration increases, the radiative decay rate remains unchanged, while the nonradiative decay rate increases due to the increase of the self quenching rate $\gamma_{12}$, and as a result, the total decay rate is increased. This mechanism results in a decrease in both the lifetime of the excited state and the quantum efficiency.

Another mechanism, reabsorption, may also be responsible for a reduction in the quantum efficiency at high concentration. In this case, the luminescent photons are reabsorbed by ions in their ground state, and are then re-emitted. As a result, the effective radiative decay rate is decreased, the nonradiative decay rate remains unchanged, and thus the total decay rate is decreased. In this case, the quantum efficiency will decrease, while the lifetime of the excited state will increase. The former is similar, while the latter is contrary, to the behaviors of energy transfer described in last paragraph. This is very useful to distinct the effects of energy transfer and reabsorption, which both contribute to the observed concentration effect. As the concentration increases beginning from zero, the lifetime first increases, indicating that the concentration effect is dominated by the reabsorption. The lifetime then decreases, indicating that the concentration effect is dominated by the energy transfer [23]. The amount of reabsorption is highly dependent on the geometry of the sample, and can be avoided experimentally by using an optically very thin sample, such as the thin fiber used by Gosnell [11]. In the following discussion, for the sake of simplicity, we assume that the reabsorption effect is absent, and only consider the effect of the self quenching process.

Based on the energy transfer theory, the excited state lifetime as a function of dopant concentration is [22]

$$\tau(n_d) = \frac{\tau(n_d = 0)}{1 + 1.45(n_d/n_{d,c}) \exp(-\beta \Delta E_e/4)},$$

(19)

where $\tau(n_d = 0)$ is the lifetime at extremely low concentration, $n_{d,c}$ is defined as a critical concentration intrinsically dependent on the ion-host coupling, $\Delta E_e$ is the energy gap between the two levels, and $\beta$ is an energy transfer coefficient. Here for Yb$^{3+}$: Y$_2$O$_3$, $\beta$ is given by the following expression

$$\beta = \frac{\ln[4.077/(1 + f_{p,e}^0)]}{\hbar \omega_{p,e}},$$

(20)

where $\omega_{p,e}$ is the effective phonon frequency involved in the self quenching process, and $f_{p,e}^0$ is the equilibrium distribution function of phonon (the Bose-Einstein distribution), given by

$$f_{p,e}^0 = \frac{1}{\exp(h \omega_{p,e}/k_B T) - 1}.$$

(21)

Note that here we made an assumption of involving only one effective phonon mode $\omega_{p,e}$ in the self quenching process. This approximation has proven very useful in understanding the multiphonon radiationless energy transfer processes of many rare-earth-doped solids, especially for systems involving weak coupling like Yb$^{3+}$: Y$_2$O$_3$ considered here. However, it must be noted that the frequency spectrum of phonons for any solid has a significant amount of structure in its DOS, and they may all contribute to the electron-phonon coupling. For physical systems involving strong coupling, the specific structure of the phonon spectra must be taken into account [24].

Equation (19) predicts that the lifetime decreases as the dopant concentration increases. Since the lifetime is the reciprocal of the transition rate, One can rewrite Eq. (19) as

$$\gamma_{e,d}(n_d) = \gamma_{e,d}(n_d = 0)[1 + 1.45(n_d/n_{d,c}) \exp(-\beta \Delta E_e/4)],$$

(22)

where, based on the process shown in Fig. 4, we have

$$\gamma_{e,d}(n_d = 0) = \gamma_r + \gamma_{nr},$$

(23)

and

$$\gamma_{e,d}(n_d) = \gamma_r + \gamma_{nr} + \gamma_{12}.$$

(24)
It is predicted in Eq. (22) that an increase in $n_d$ results in the increase in the total decay rate $\dot{\gamma}_{e,d}$, compared to that for an isolated ion, due to the presence of the self-generated, non-radiative decay rate $\gamma_{12}$.

For an isolated Yb$^{3+}$ ion in Y$_2$O$_3$ host, the nonradiative decay rate $\gamma_{nr}$ is negligible compared to the radiative decay rate $\gamma_e$, below the room temperature ($< 300$ K). Thus we can make an approximation

$$\frac{\dot{\gamma}_e}{\dot{\gamma}_e + \dot{\gamma}_{nr}} \approx 1.$$  \hspace{1cm} (25)

This indicates that the total decay rate at low concentration is taken as the radiative decay rate, and all nonradiative decay events come from the energy transfer processes.

Using Eqs. (22)-(25), the quantum efficiency $\eta_{e-ph}$ can be written as a function of the concentration as

$$\eta_{e-ph} = \frac{\dot{\gamma}_e}{\dot{\gamma}_{e,d}(n_d)} = \frac{\dot{\gamma}_e}{\dot{\gamma}_e + \dot{\gamma}_{nr}} \approx \frac{\dot{\gamma}_e}{\dot{\gamma}_{e,d}(n_d)} = \left[1 + 1.45(n_d/n_{d,c}) \exp(-\beta \Delta E_e/4)\right]^{-1}. \hspace{1cm} (26)$$

It is predicted in this relation that the quantum efficiency decreases as the dopant concentration and temperature increase, as expected. The temperature effect is due to that more phonons are excited and participate in the nonradiative processes. The total cooling power given by Eq. (15) is now written as a function of the concentration, i.e.,

$$\dot{S}_{ph-e-p} = \left(1 - \frac{\omega_{ph,e}}{\omega_{ph,i}} \right) \left[1 + 1.4 \frac{n_d}{n_{d,c}} \exp(-\beta \Delta E_e/4)\right]^{-1} \hspace{1cm} (27)$$

The maximum cooling power is reached when

$$\frac{\partial \dot{S}_{ph-e-p}}{\partial n_d} = 0,$$  \hspace{1cm} (28)

which yields the optimum concentration

$$n_{d,o} = n_d = A \left(1 - B\right)^{1/2},$$  \hspace{1cm} (29)

where $A$ and $B$ are

$$A = \frac{1}{1.45} \exp(\beta \Delta E_e/4), \quad B = \frac{\lambda_{ph,e}}{\lambda_{ph,i}}.$$  \hspace{1cm} (30)

Figure 5. (a) Variation of the quantum efficiency as a function of dopant concentration. (b) Variation of the normalized cooling power as a function of dopant concentration. The Gosnell $n_{d,c}$, critical $n_{d,c}$, optimum $n_{d,o}$, and transition $n_{d,t}$ dopant concentrations are shown.

It is evident in Eq. (29) that the critical concentration $n_{d,c}$ is the only parameter that needs to be specified before the optimum concentration can be determined. Note that $n_{d,c}$ is an intrinsic property depending on the ion-dopant pair and the temperature, and may be calculated using quantum mechanics. Here, we use a more practical approach, namely, fitting Eq. (19) or Eq. (26) to experiments, as reported in [22].

In an experiment [11], a Yb$^{3+}$ doped ZBLANP fibre was cooled by 65 K from the room temperature, with a concentration $n_d = 2.42 \times 10^{20}$ cm$^{-3}$, and a measured quantum efficiency $\eta_{e-ph} = 0.998$. Using Eq. (26), the critical concentration is readily calculated to be $n_{d,c} = 2.51 \times 10^{20}$ cm$^{-3}$. Then, by using Eq. (26), the variations of the quantum efficiency is plotted as a
function of the concentration, for three temperatures, as shown in Fig.5(a). The results show that the quantum efficiency $n_{q-ph}$ decreases monotonically with the dopant concentration and temperature. By using Eq. (27), the variation of the normalized cooling power is plotted as a function of the concentration in Fig.5(b). The results show that the cooling power first increases and then decreases, as $n_d$ increases. At an optimum concentration $n_{d,opt} = 1.13 \times 10^{21}$ cm$^{-3}$, which is three times higher than that used by Gosnell [11], the maximum cooling power is achieved and is 2.6 times that obtained in that investigation [11]. Note that if the concentration becomes higher than a transition value $n_{d,tr}$, which is $2.05 \times 10^{21}$ cm$^{-3}$, the cooling effect is eliminated (See Fig.5(b)). This is expected, due to the resulting low quantum efficiency.

To examine the dependence of the optimum concentration on temperature, we use Eq. (29) and the results are shown in Fig.6. Since the quantum efficiency increases as the temperature decreases, we expect the optimum concentration to also increase. This is true, as shown in Fig.(29), if we assume that the mean emission wavelength $\lambda_{ph,e}$ is not dependent on temperature. However, in reality the mean emission wavelength $\lambda_{ph,e}$ increases as the temperature decreases, since the electrons in the excited state are more likely to reside in the lowest sublevels, resulting in emission photons with lower energy and longer wavelength. An experimental study was performed on the relation between $\lambda_{ph,e}$ and $T$ [25], and the data are fitted by us using an empirical relation, which reads $\lambda_{ph,e} = 1003 + (996 - 1003) \times (300 - T) / (100) \times (T - 100)$ nm. Taking into account this dependence, the variation of the optimum concentration with temperature is shown in Fig.(29). Interestingly, it first increases, but then decreases, as the temperature decreases. The reason is that, at very low temperatures, the mean emission wavelength increases, leading to a reduction of the cooling ability per ion. As a result, the cooling effect is more likely to be destroyed by the nonradiative decays which can be caused by large concentrations. This variation of the optimum concentration with the temperature reflects the competition and balance between the quantum efficiency and the mean emission wavelength.

4 Enhanced Total Pumping Energy by Photon Localization

In this section, we will discuss how to use the unique photon transport properties of nanopowders to enhance $E_{pump}$, the total pumping energy inside the medium. Shown in Fig.7 are different regimes of photon scattering in nanopowders [26]. When the photon mean free path $l_m$ is much larger than the laser wavelength, photons may experience a single scattering event and the transport is diffusive [27]. As $l_m$ decreases, photons begin to undergo multiple scattering events. When $l_m$ is comparable to or smaller than the laser wavelength, recurrent scattering takes place, i.e., photons return to the original place after being scattered many times. In this case, photons don’t propagate through the medium, but are confined in a small spatial region, forming a cavity. This phenomenon, termed photon localization, is the counterpart of the electron localization suggested by Anderson [28]. The electromagnetic field of the localized light, as shown in Figure 7(d), can be orders of magnitude higher than the incident field [29]. As a result, photon absorption can be enhanced considerably, due to this high photon density (or alternatively, electromagnetic field energy density $e_{ph,s}$).

Here, we consider a simple nanostructure model of Yb$^{3+}$-doped Y$_2$O$_3$ particles: parallel solid layers with random thicknesses, as shown in Fig.8(a). The dielectric solid material has a complex refractive index $m_x (= n_x + i k_x)$, while the fluid is assumed to be air and has a refractive index $m_f (= n_f = 1)$. To solve the internal field subject to a normal laser irradiation, we start with the Helmholtz equation

$$\frac{d^2 E(x)}{dx^2} + k_0^2 m_l^2 E(x) = 0,$$  \hspace{1cm} (31)

where $k_0$ is the vacuum wave vector, and $m_l$ is the local complex index of refraction at the incident frequency. This is the electromagnetic wave equation in a source-free medium, and is equivalent to the Maxwell equations in the multilayer system. For the medium shown in Fig.8(a), the solution of Eq. (31) at a particular location $x_l$ in the $l$-th layer is given by

$$E(x) = E_l e^{ik_l(x-x_l)} + E_l^* e^{-ik_l(x-x_l)},$$

$$l = 1, 2, ..., N + 1.$$  \hspace{1cm} (32)

where $k_l = m_l \omega_0 / c_o$ is the wave vector, and $c_o$ is the speed of light in vacuum. The field in the medium is divided into two
components, the forward (transmitted) component $E^+_l$ and the backward (reflected) component $E^-_l$. The boundary conditions require that the tangential electric and magnetic fields be continuous across each interface. Thus the amplitudes of the $l$-th and $(l+1)$-th interfaces are related by a transfer matrix $M$ [29, 30]. Then, the full fields $E$ are solved using this transfer matrix approach, subject to a uniform, normal incident field $E_i$. A detailed solution procedure can be found in [29, 31]. A typical field distribution is shown in Figure 8(b), where the dimensionless electric field $|E|^+$ is normalized against the incident field. The phenomenon of field enhancement is evident, i.e., the peaks of the field distribution inside the medium can be much larger than the incident field, for this realization [29]. Thus, the energy density of the electric field can be two or even more orders of magnitude larger than the incident value. The physical basis of field enhancement is electromagnetic wave interference. In this random multilayer system, the waves will multiply transmit and reflect at all the interfaces, and interfere with each other. At some locations (for some realizations), the interference is so ideally constructive that it results in extremely large fields.

The pumping energy $E_{\text{pump}}$ inside the nanopowder medium is then calculated using Eq. (9), and compared to that for the bulk crystal with the same apparent volume (note however that the volume of the solid phase for nanopowder is smaller than that for the bulk crystal), as shown in Fig.9. Note also that for a model composite given the porosity $\varepsilon$ and the particle size distribution, there are an infinite number of realizations, and hence, the ensemble average of a sufficient number of realizations is taken in calculations, and used for that model composite. The ratio of the total pumping energy, with respect to porosity $\varepsilon$ for different particle mean diameter $\langle d \rangle$, is shown in Fig.9. For high porosities, the ratio may be as large as 1.5 to 1.7, indicating an enhancement of the total pumping energy $E_{\text{pump}}$ by 50% to 70%. Fig.9 also provide the guidelines for the optimum porosity and mean particle size.

In this section, we have used the classical wave theory of light to show its interference effect, which is a signature of the wave nature of light. Quantum theory is also capable of capturing this effect, but the formulation is much more cumbersome than the classical wave theory. However, as electronic transitions are involved, the quantum theory must be used to address the problem correctly. This will be discussed in the next section.

Figure 7. (a) Single, (b) multiple, and (c) recurrent photon scattering trajectories in a system of random scatterers, and (d) a rendering of the electromagnetic field distribution for case (c), i.e., as photon localization takes place [26].

Figure 8. (a) A one-dimensional random multilayer system. The layer thickness follow a uniform distribution between $d_s \pm \Delta d$, and the porosity is prescribed. (b) A typical electromagnetic field distribution, in which a field enhancement up to 7 folds can be seen [31].
Figure 9. Variation of the scaled pumping energy inside the medium (nanopowder to the bulk crystal), with respect to porosity. The total pumping energy of nanopowder can be enhanced by 50%-70%, at high porosities.

5 Enhanced Transition Probability for Nanopowders

5.1 Phonon DOS of the nanopowder

To analyze photon-electron-phonon interactions, the phonon DOS needs to be known. The Debye DOS is often assumed for bulk materials [32]. It shows a parabolic distribution which results from an assumption of an isotropic medium with no dispersion, or effects of optical phonons. The phonon DOS of nanomaterials may, however, deviates from that for bulk crystals, due to quantum size effects [33]. Since the phonon DOS is not available for $Y_2O_3$, it is calculated here using the molecular dynamics simulation.

With molecular dynamics simulations, the phonon DOS may be calculated using three different methods [34]. In the first, the velocity autocorrelation function is calculated for each species and the partial phonon DOS is then obtained by taking the Fourier transforms of this autocorrelation function. In the second, the displacement autocorrelation function is calculated by the equation-of-motion method. In the third, the dynamical matrix is directly diagonalized. The results of these three approaches have been found to agree with one another at low temperatures [34], as expected. However, at high temperature the third method is not suitable since it is harmonic. Therefore, here we use the first method to determine the phonon DOS at 300 K.

In a molecular dynamics simulation, the phase-space trajectory of a system of particles is predicted by solving the Newton equations. The required inputs are an atomic structure and a suitable interatomic potential, which can be obtained from experiments and/or ab initio calculations [35].

The X-ray diffraction [36] and neutron diffraction [37] experiments have shown that $Y_2O_3$ has a face-centered cubic structure, which is retained in nanocrystals [38]. Eight metal ions are in the positions $(1/4, 1/4, 1/4)$; the remaining twenty four occupy the sites $(u,0,1/4)$. The forty-eight oxygen ions are in general positions $(x,y,z)$, arranged in distorted octahedra around the metal ions, the metal-oxygen bonding distances being unequal. The values of $u,x,y,z$ are listed in [36, 37]. The crystal structure is shown in Fig. 10.

The interatomic potential can be assumed to be in the form

$$\phi(r_{ij}) = \frac{q_i q_j}{r_{ij}} + A_{ij} \exp \left( \frac{r_{ij}}{r_{o,ij}} \right) + \frac{C_{ij}}{r_{ij}^6}, \quad (33)$$

where $\phi(r_{ij})$ is the interaction energy of atoms $i$ and $j$, which consists of a Coulomb term and a covalent (short range) contribution, cast into the usual Buckingham form [39]. Here $q_i$ is an effective charge of the $i$th atom, $r_{ij}$ is the interatomic distance between atoms $i$ and $j$, $A_{ij}$, $r_{o,ij}$ and $C_{ij}$ are parameters for covalent interactions. For ionic materials, this Buckingham interatomic potential model has been shown to perform well. The parameters in Eq. (33), obtained from [40, 41], are listed in Table 1. This potential set has been verified to reproduce the bulk
properties (lattice constant, lattice position, bulk modulus, elastic constant, etc) well [42].

<table>
<thead>
<tr>
<th>Atomic charges: $q_Y = 3, q_O = -2$</th>
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<tbody>
<tr>
<td>Atom-Atom</td>
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<tr>
<td>----------</td>
</tr>
<tr>
<td>Y-Y</td>
</tr>
<tr>
<td>Y-O</td>
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<tr>
<td>O-O</td>
</tr>
</tbody>
</table>

To determine the DOS of the bulk crystal, molecular dynamics simulations are carried out in a cubic computation domain which contains $2 \times 2 \times 2 = 8$ unit cells and $N = 640$ atoms (256 Y and 384 O). Periodic boundary conditions are applied in all directions. For the nanopowder, the computation domain is a sphere of diameter $d_s$, which is cut from a much larger bulk crystal, as shown in Figure 11. It should be noted that a nanopowder generated in this way may not be neutral in charge, thus some atoms at the surface may need to be removed accordingly, to eliminate any net charge of the nanopowder. Also, since the center of the sphere can be randomly selected, we have many possible configurations given the diameter. As such, a number of spherical particles with different configurations are considered in this study, and their behaviors are compared. The free boundary condition is used.

For both bulk and nano crystals, an initialization period of $5 \times 10^4$ time steps is used, with the time step being 1.6 fs. The system is run in the $NVT$ (constant mass, volume and temperature) ensemble. To set the temperature for the $NVT$ ensemble, the potential energy of the system is monitored every time step. When it reaches a value within $10\%$ of the desired value, the ensemble is switched to $NVE$ (constant mass, volume and energy), and the system is run until the total number of time steps is $1.5 \times 10^5$.

The normalized velocity-velocity autocorrelation function for the $\beta$th species ($\beta = Y, O$) is

$$
\Gamma_\beta(t) = \left\langle \sum_{i_\beta = 1}^{N_\beta} \mathbf{u}_{i_\beta}(t)\mathbf{u}_{i_\beta}(0) \right\rangle / \left\langle \sum_{i_\beta = 1}^{N_\beta} \mathbf{u}_{i_\beta}(0)\mathbf{u}_{i_\beta}(0) \right\rangle,
$$

with $\beta = Y, O$,  

(34)

where $N_\beta$ is the number of atoms of species $\beta$, $\mathbf{u}_{i_\beta}$ is the velocity of atom $i_\beta$ and $\langle \rangle$ is an ensemble average. The frequency spectrum of the normalized velocity autocorrelation function gives

$$
\text{the partial phonon DOS } D_{p,\beta}(\omega), \text{ as }
$$

$$
D_{p,\beta}(\omega) = \int_0^\infty \Gamma_\beta(t) \cos(\omega t)dt.
$$

(35)

The total phonon DOS is obtained by summing over the partial DOS weighted with the population, i.e.,

$$
D_p(\omega) = \sum_{\beta} c_\beta D_{p,\beta}(\omega),
$$

(36)

where $c_\beta$ is the population of the $\beta$th species in the molecular dynamics system. Here, for $Y_2O_3$ they are $c_Y = 2/5$, and $c_O = 3/5$.

The partial phonon DOS $D_{p,\beta}(\omega)$ of Y and O atoms are calculated for the bulk and nanoparticle $Y_2O_3$ crystals, and are normalized, i.e., $\int_0^\infty D_{p,\beta}(\omega)d\omega = 1$. This normalization is needed to compare the partial and total DOS of MD systems with different number of atoms. The total DOS, calculated using Eq. (36), is then shown in Fig. 12. As mentioned before, there are many different configurations for the nanopowder, each having its own phonon DOS. However, calculations review that they share similar characteristics. Therefore, here we only show the DOS of one representative configuration. It can be seen that the phonon DOS of nanocrystals is distinct from that of the bulk crystal, in its broadened peaks, and extended tails at low and high frequencies. The bulk crystal has sharp, well-defined peaks (or modes) related to the rigorous periodic structure, while these peaks are broadened in the nanocrystal, due to the loss to some extent of this periodicity. The high frequency tail in the nanocrystal phonon DOS.
Consideration is given by the perturbation theory. The Hamiltonian for the physical system is

\[ H = H_{ion} + H_p + H_{ph} + \Phi_{ion-ph} + \Phi_{ion-p}. \tag{37} \]

\( H_{ion} \) is the Hamiltonian of the ion electronic levels, where \( h\omega_{jg} \) is the energy difference between the optically active energy levels of the dopant ion (considered as a two-level ion) and \( a^+(a) \) is the creation (annihilation) operator of an electronic excitation. The second term is

\[ H_p = \sum_p h\omega_p b_p^+ b_p, \tag{39} \]

\( b_p^+(b_p) \) is the creation (annihilation) operator of a phonon in mode \( p \). The third term is

\[ H_{ph} = h\omega_{ph}\epsilon c^+ c, \tag{40} \]

\( \omega_{ph} \) is the phonon frequency and \( \epsilon \) is the dielectric constant of the environment. The fourth term is

\[ \Phi_{ion-ph} = -|e_v| \cdot \mu_v \left( \frac{h\omega_{ph,i}}{2\epsilon_0 V_i} \right)^{1/2} (a^+ + a)(c^+ + c), \]

\[ C_{ph} = \frac{\epsilon_0}{|e_v| \cdot \mu_v} \left( \frac{h\omega_{ph,i}}{2\epsilon_0 V_i} \right)^{1/2}, \tag{41} \]

\( |e_v| \) is the polarization factor of the photon, \( \mu_v \) is the dipole moment of the electronic transition, \( \epsilon_0 \) is the vacuum permittivity, and \( V_i \) is the interacting volume. Note that the term \( \left[ \frac{h\omega_{ph,i}}{2\epsilon_0 V_i} \right]^{1/2} \) is the electric field per photon. The fifth term is

\[ \Phi_{ion-p} = a_{i-p} \left( \frac{h\omega_p}{2\rho u_p^2} \right)^{1/2} a^+(b_p - b_p^+), \]

\[ C_p = a_{i-p} \left( \frac{h\omega_p}{2\rho u_p^2} \right)^{1/2}, \tag{42} \]

\( \omega_p \) is the pumping frequency, and \( u_p \) is the speed of sound in the material. \( \rho \) is the mass density.
The transition rate \( \dot{\gamma}_{e,a} \) is given by the Fermi golden rule [12]

\[
\dot{\gamma}_{e,a} = \sum_f \dot{\gamma}_{e,i,f} = \frac{2\pi}{\hbar p} \sum_f |M_{fi}|^2 \delta(E_f - E_i),
\]

where \( E_i \) and \( E_f \) are the initial and final energies of the system. The \( M_{fi} \) matrix can be expanded as the following series [12]

\[
M_{fi} = \langle f|\Phi_{out}|i \rangle + \sum_m \frac{\langle f|\Phi_{out}|m \rangle \langle m|\Phi_{out}|i \rangle}{E_{f,i} - E_{e,m}} + \sum_{m,n} \frac{\langle f|\Phi_{out}|m \rangle \langle m|\Phi_{out}|n \rangle \langle n|\Phi_{out}|i \rangle}{(E_{f,i} - E_{e,m})(E_{f,i} - E_{e,n})} + \ldots,
\]

with \( \Phi_{out} = \Phi_{ion-ph} + \Phi_{ion-p} \). The summations on \( m \) and \( n \) include all the intermediate phonon and photon states.

We will calculate the transition probability \( \dot{\gamma}_e \) between the initial \( |i\rangle = |\psi_i, f_{ph} + 1, f_p + 1 \rangle \) and final \( |f\rangle = |\psi_f, f_{ph}, f_p \rangle \) states of the system, where the first ket element, \( \psi_i \), refers to the ion state, the second one, \( f_{ph} \), to the photon number in the interacting volume \( V_s \), and the third one, \( f_p \), to the phonon distribution function. This type of processes only appears in the second order perturbation expansion of the \( M_{fi} \) matrix, which is [24, 43]

\[
M_{fi,2nd} = \sum_m \frac{\langle f|\Phi_{out}|m \rangle \langle m|\Phi_{out}|i \rangle}{E_{f,i} - E_{e,m}}
\]

\[
= \sum_m \left[ \frac{\langle \psi_f, f_{ph}, f_p | \Phi_{ion-ph} | \psi_m, f_{ph} + 1, f_p \rangle \times}{E_i - (E_m - \hbar \nu \omega_p)} \langle \psi_m, f_{ph} + 1, f_p | \Phi_{ion-p} | \psi_i, f_{ph} + 1, f_p + 1 \rangle \right] \times
\]

\[
+ \frac{\langle \psi_f, f_{ph}, f_p | \Phi_{ion-ph} | \psi_m, f_{ph}, f_p + 1 \rangle \times}{E_i - (E_m - \hbar \nu \omega_p)} \langle \psi_m, f_{ph}, f_p + 1 | \Phi_{ion-p} | \psi_i, f_{ph} + 1, f_p + 1 \rangle \right].
\]

The sum runs over all possible intermediate states of the system. Substituting the expressions for the interaction Hamiltonians into Eq. (45), we have

\[
M_{fi,2nd} \approx \sum_m \frac{\langle \psi_f, f_{ph}, f_p | C_{ph} (a^+ + a)(c^+ + c) | \psi_m, f_{ph} + 1, f_p \rangle \times}{E_i - (E_m - \hbar \nu \omega_p)} \langle \psi_m, f_{ph} + 1, f_p | a_{f-p} C_{ph} a (b_p - b_p^+) | \psi_i, f_{ph} + 1, f_p + 1 \rangle \times
\]

\[
= \sum_m \frac{\langle \psi_f, f_{ph}, f_p | C_{ph} (a^+ + a)(c^+ + c) | \psi_m, f_{ph} + 1, f_p \rangle \times}{E_i - (E_m - \hbar \nu \omega_p)} \langle \psi_m, f_{ph} + 1, f_p | C_{ph} a (b_p - b_p^+) | \psi_i, f_{ph} + 1, f_p + 1 \rangle \times
\]

\[
= \sum_m \frac{\langle \psi_f, f_{ph}, f_p | C_{ph} (a^+ + a)(c^+ + c)^{1/2} | \psi_m, f_{ph}, f_p \rangle \times}{E_i - (E_m - \hbar \nu \omega_p)}
\]

\[
= \sum_m \frac{\langle \psi_m, f_{ph} + 1, f_p | C_{ph} (a^+ + a)^{1/2} | \psi_i, f_{ph} + 1, f_p \rangle \times}{E_i - (E_m - \hbar \nu \omega_p)}
\]

\[
= \sum_m C_{ph}^{1/2} C_{ph}^{1/2} \frac{\langle \psi_f | (a^+ + a) | \psi_m \rangle \langle \psi_m | (a^+ + a) | \psi_i \rangle}{E_i - (E_m - \hbar \nu \omega_p)}.
\]

where, the second term in Eq. (46) has been neglected since the photon energy is much greater than the phonon energy [24].

Since the phonon energy \( \hbar \nu \omega_p \) is much smaller than the energy gap, it cannot by itself induce an electronic transition. In the perturbation theory, the intermediate wave function \( \psi_m \) is then approximated as unperturbed, i.e., \( \psi_m = \psi_i \), and \( E_m = E_i \). Therefore Eq. (46) becomes

\[
M_{fi,2nd} = \sum_{p} C_{ph}^{1/2} C_{ph}^{1/2} \frac{\langle \psi_f | (a^+ + a) | \psi_i \rangle \langle \psi_i | (a^+ + a) | \psi_i \rangle}{E_i - (E_i - \hbar \nu \omega_p)}
\]

\[
= \sum_{p} C_{ph}^{1/2} C_{ph}^{1/2} \frac{1}{\hbar \nu \omega_p}.
\]

Substituting Eq. (47) into Eq. (43), we have

\[
\dot{\gamma}_{e,a} = \sum_f \dot{\gamma}_{e,i,f} = \frac{2\pi}{\hbar p} \sum_{p} \frac{C_{ph}^{1/2} C_{ph}^{1/2}}{\hbar \nu \omega_p} \delta(\hbar \nu \omega_{ph,i} + \hbar \nu \omega_p - \hbar \nu \omega_{e,g}).
\]

In order to perform the summation on the phonon modes in Eq. (48), we must introduce the phonon DOS \( D_{ph}(E_p) \), where \( E_p \) is the phonon energy given by \( E_p = \hbar \nu \omega_{e,g} - \hbar \nu \omega_{ph,i} \). In terms of this distribution function, the transition rate, Eq. (48), becomes

\[
\dot{\gamma}_{e,a} = \frac{2\pi}{\hbar p} C_{ph}^{1/2} \frac{a_{e-p}^2}{2\mu_{ph}^p} \int_{E_{min}}^{E_{max}} dE_p D_{ph}(E_p) \frac{f_{p}(E_p)}{E_p} \delta(\hbar \nu \omega_{ph,i} + E_p - \hbar \nu \omega_{e,g})
\]

\[
= \frac{2\pi}{\hbar p} C_{ph}^{1/2} \frac{a_{e-p}^2}{2\mu_{ph}^p} \frac{D_{ph}(E_p) f_{p}(E_p)}{E_p}.
\]

This result implies that the excitation spectra can be associated with the phonon spectra, as observed in [44]. We here have used the equilibrium distribution functions for phonons. To compare with Eq. (3), we rewrite Eq. (49) as:

\[
\dot{\gamma}_{e,a} = \frac{2\pi}{\hbar p} \frac{C_{ph}^{1/2} \mu_{ph}^{1/2}}{2e_o} \frac{a_{e-p}^2}{2\mu_{ph}^p} \frac{D_{ph}(E_p) f_{p}(E_p)}{E_p} \times
\]

\[
\hbar \nu \omega_{ph,i} \frac{f_{ph}}{V_s}
\]

\[
= \frac{2\pi}{\hbar p} \frac{C_{ph}^{1/2} \mu_{ph}^{1/2}}{2e_o} \frac{a_{e-p}^2}{2\mu_{ph}^p} \frac{D_{ph}(E_p) f_{p}(E_p)}{E_p} e_{ph,i}.
\]
This expression is found to be consistent with Eq. (3), as expected. Therefore, we are able to extract the excitation coefficient \( B_{e,a} \) from Eq. (50), as

\[
B_{e,a} = \frac{2\pi (\varepsilon_{ph,i} \cdot \mu_e)^2}{\hbar_p} \frac{\alpha_{ep}^2}{2\varepsilon_o} \frac{D_p(E_p)f_0^0(E_p)}{2\mu_{ep}^2}.
\]

Using the relations \( \omega = 2\pi c_o/\lambda \) and \( E_p = \hbar_p \omega_{e,g} - \hbar_p \omega_{ph,i} \), the above expression for \( B_{e,a} \) can be written as a function of \( \lambda_{ph,i} \) as

\[
B_{e,a} = \frac{2\pi (\varepsilon_{a} \cdot \mu_e)^2}{\hbar_p} \frac{\alpha_{ep}^2}{2\varepsilon_o} \frac{D_p(\hbar_p (\frac{2\pi c_o}{\lambda_{e,g}} - \hbar_p \frac{2\pi c_o}{\lambda_{ph,i}})) f_0^0(\hbar_p (\frac{2\pi c_o}{\lambda_{e,g}} - \hbar_p \frac{2\pi c_o}{\lambda_{ph,i}}))}{\hbar_p (\frac{2\pi c_o}{\lambda_{e,g}} - \hbar_p \frac{2\pi c_o}{\lambda_{ph,i}})}.
\]

Using the resonance wavelength (\( \lambda_{e,g} = 980 \text{ nm} \)) for Yb\(^{3+}\): Y\(_2\)O\(_3\) along with the phonon DOS determined in section 5.1, the variations of the normalized (against the resonance) transition coefficient \( B_{e,a}^* = B_{e,a}(\lambda_{ph,i})/B_{e,a}(\lambda_{ph,i} = 980 \text{ nm}) \), as a function of the pumping wavelength \( \lambda_{ph,i} \), are shown in Fig. 13(a), for bulk and nano crystals. Note that a singularity exists for \( B_{e,a}(\lambda_{ph,i}) \) right on resonance \( \lambda_{ph,i} = 980 \text{ nm} \), so we use the limit \( B_{e,a}(\lambda_{ph,i} = 980 \text{ nm}) = B_{e,a}(\lambda_{ph,i} \rightarrow 980 \text{ nm}) \). The transition coefficients show an exponential decay with the increasing wavelength. Shown in Fig. 13(b) is the ratio of the transition rates for nano- and bulk crystals. The transition rates may be enhanced (the area above the dotted line) or reduced (the area below the dotted line), depending on the pumping wavelength used. However, in the practical cooling range (\( \lambda_{ph,i} = 1,020 \) to 1,030 nm) used in most experiments, more enhancement is observed than reduction.

6 Discussion and Conclusions

We have investigated the enhanced laser cooling of nanopowders, using the optimization of the dopant concentration, the photon localization, and the phonon DOS size effect. Taking a closer look at these three mechanisms, we notice that they all facilitate to increase the carrier number in the interacting volume: optimization of the dopant concentration for higher electron number, photon localization for higher photon number, and phonon DOS size effect for higher phonon number in the desired range. This seems to be natural since the excitation is a photon induced, phonon assisted, electronic absorption. Thinking of an interaction of only one photon, one phonon, and one electron (ion) as the base system, to increase the number of each type of carrier would independently enhance the excitation events proportionally. This is an important yet intuitive finding that more carriers are needed to be put in the same interacting volume, to enhance their interactions. The enhancement effects due to each carrier are summarized in Fig. 14.

The optimum dopant concentration is pursued using the energy transfer theory. Although it is well known that an optimum concentration for maximum cooling performance should exist (since high concentration would result in a low quantum efficiency), a quantitative analysis had been lacking. Here, we apply the energy transfer theory and obtain an analytical expression for the optimum concentration. For high purity doped solids, the concentration quenching is identified as a self-generated multiphonon decay process, allowing to establish a relation between the quantum efficiency and the concentration. The results show

![Image](https://example.com/image.png)
that the optimum concentration gives a 150% enhancement in cooling power, as shown in Fig.14. This enhancement mechanism applies to both the bulk and the nanoparticle crystals doped with Yb\(^{3+}\).

The cooling performance in nanocrystals may also be enhanced compared to that of bulk crystals, due to photon localization. Calculations based on the Maxwell equations show that as the particle size decreases to the order of the pumping wavelength, photons are localized in the interior of the powder media as the particle size decreases to the order of the pumping wavelength. Treating the cooling process as a phonon-assisted transition, a second order extended, small tails at low and high frequencies. Treating the correlation function. The DOS of nanocrystals possesses the broadening of the absorption spectra is taken into account, we can conclude that the phonon size effect would generally enhance the cooling performance.

Considering all these three mechanisms, the cooling power is predicted to be enhanced by about 275%.

Figure 14. Enhancement of laser cooling power by (i) optimization of the dopant concentration, (ii) photon localization, and (iii) phonon DOS size effect. The base line is the experiment of Gosnell [11]. The cooling and heating regimes are shown.

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REFERENCES


7 Appendix: Thermodynamics Limit of Laser Cooling of Solids

The theoretical limits of laser cooling are governed by the second law of thermodynamics. An excellent analysis was given by Mungan [45], in which the ideal cooling efficiency is calculated to be 20%. Here we briefly review the basic concepts and
Consider an example using actual values relevant to laser cooling of Yb$^{3+}$:ZBLANP [45]. The temperatures of the pump laser and the fluorescence are calculated, using Eq. (56), to be $T_o = 7 \times 10^{11}$ K and $T_f = 1,760$ K, respectively. Thus the Carnot efficiency of this optical cooler is about 20% at room temperature, and it diminishes approximately linearly to zero as $T \to 0$. However, the actual cooling efficiency achieved to date is only around 3%, which indicates that much irreversibility has been

Again, for an ideal laser, we have

$$ T_F \approx \frac{h \nu \omega_o}{k_b} f_{ph} \to \infty, \quad \text{as} \quad f_{ph} \to \infty, $$

(57)

which is consistent with the zero entropy at a finite irradiance. It can be further deduced by Eq. (57) that the flux temperature of narrowband radiation propagating in a well-defined direction is higher than that of broadband radiation propagating in all directions.

In laser cooling of solids, according to the first law of thermodynamics, we have

$$ E_{out} = E_{in} + Q. $$

(58)

The cooling coefficient of performance is defined in the usual way for a refrigerator as

$$ \eta = \frac{Q}{E_{in}}. $$

(59)

The maximum value of $\eta$ is the Carnot limit, $\eta_C$, and is determined by the second law of thermodynamics. The entropy carried by the fluorescence cannot be less than the sum of the entropy withdrawn from the cooling sample and the entropy transported in by the pump laser, i.e.,

$$ \frac{\dot{E}_{out}}{T_f} \geq \frac{\dot{E}_{in}}{T_0} + \frac{Q}{T}, $$

(60)

where $T$ is the steady-state operating temperature of the refrigerator, and $T_f$ and $T_o$ are the flux temperatures of the fluorescence and pump radiation, respectively. The reversible Carnot limit is obtained by choosing the equality sign in Eq. (60). By substituting Eqs. (58) and (59) into Eq. (60), we have

$$ \eta_C = \frac{T - \Delta T}{T_f - T}, $$

(61)

where $\Delta T = TT_f/T_o$.
introduced into the process. One might use a longer pumping wavelength to obtain higher cooling efficiency, but the absorption coefficient of Yb$^{3+}$ would become too small. As a result, the trace impurity absorption will dominate over the Yb$^{3+}$ absorption, and the cooling efficiency $\eta$ decreases. To reduce these irreversibilities introduced into this process, the sample should be purified to suppress the trace absorption, and also the Yb$^{3+}$ absorption coefficient should be enhanced.