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Upconversion cooling of Er-doped low-phonon fluorescent solids

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We report on a mechanism for laser cooling of fluorescent solids based on infrared-to-visible upconversion often found in rare-earth-doped low-phonon materials. This type of optical cooling presents some advantages with regard to conventional anti-Stokes cooling. Among them, it allows us to obtain cooling in a broader range of frequencies around the barycenter of the infrared emitting band.

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The demonstration by Epstein *et al.*[1] of laser-induced fluorescent cooling of an Yb-doped fluoride glass generated a surge of interest in this phenomenon because it could provide the means to fabricate the next-generation all-solid-state compact optical cryocoolers for aerospacial applications[2–5] and for the development of radiation-balanced lasers[6,7] that are amenable of multiple applications in the fields of optical telecommunications and medicine. In this regard, it would be extremely useful being able to use optical cryocoolers made of active materials doped with different rare-earth (RE) ions that could be selected according to the targeted application. Unfortunately, in spite of more than two decades after the first experimental demonstration of this effect, only a small number of ions could be used for this purpose. In particular, anti-Stokes laser cooling has been demonstrated in a small number of crystal and glass host materials[8] doped with Yb,[1] Tm,[9] and Er (Ref. 6) due to the inherent characteristics of the absorption and emission processes in rare-earth ions. Two are the main reasons that hinder the cooling efficiency: on the one hand, the presence of nonradiative transitions between the energy levels of the RE ion and, on the other hand, the presence of impurities in the host matrix that gives rise to parasitic absorptions that generate heat. Traditionally, host materials with very small phonons, so that the quantum efficiency of the electronic levels involved in the fluorescent transition is almost unity, with as few impurities as possible have been used in order to overcome these two limitations. However, even in the optimal case, the bulk cooling efficiency is still very small.[6,9] In order to enhance the optical cooling efficiency—most crucial for developing practical applications—a number of ingenious innovations have been suggested, such as using a multipass configuration, increasing the active medium length by using optical fiber,[10] or taking advantage of additional cooling channels, such as cooling in the super-radiance regime,[11] energy-transfer fluorescent cooling,[12] or using nanocrystalline powders doped with RE ions.[13]

In this Brief Report, we present a pathway to efficient anti-Stokes laser cooling based on infrared-to-visible upconversion in RE-doped host materials that we will term from now on *upconversion cooling*. This mechanism makes use of the efficient ir-to-visible upconversion phenomena that are often found in RE-doped low-phonon host materials because of the reduced multiphonon transition rates that make possible for the pump level to act as an intermediate photon reservoir from which additional upconversion processes take place. This is the case, for example, of Er-doped low-phonon potassium lead halide crystals $\mathrm{KPb_2}X_5$, (X=Cl, Br)—such as the one we recently employed to demonstrate anti-Stokes laser cooling in an Er-doped crystal—where extremely efficient ir-to-visible upconversion has been demonstrated.[14,15]

The upconversion cooling process is summarized in Fig. 1 by using the experimental energy levels of an Er-doped $\mathrm{KPb_2Cl_5}$ crystal as a guiding example: upon cw pumping below the barycenter of the $^4I_{9/2}$ level, an electronic population reservoir is created in this level due to its long lifetime (2.4 ms). Part of this population decays spontaneously to the $^4I_{15/2}$ level—emitting infrared photons—by means of a direct $^4I_{9/2} \rightarrow {}^4I_{15/2}$ transition or through a sequential $^4I_{9/2} \rightarrow {}^4I_{13/2} \rightarrow {}^4I_{15/2}$ one. In any case, an anti-Stokes cycle occurs in which the energy of the fluorescent photons is slightly larger than the incident ones and, thus, a small amount of thermal vibrational energy (temperature) is removed from the system. Apart from this conventional laser cooling mechanism, in this system there can also exist additional emissions—in the visible range—due to the presence of upconversion processes.[15] These can be of two types: on the one hand, there is the possibility of sequential absorption by an electron

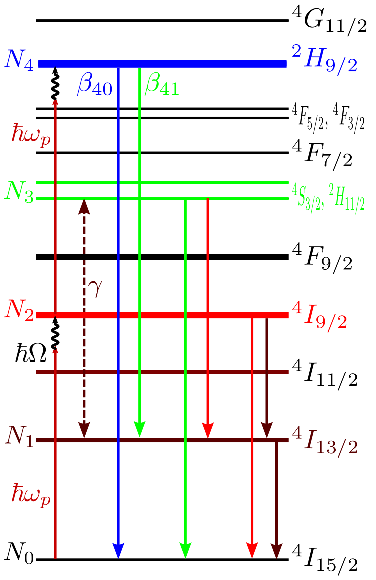

FIG. 1. (Color online) Experimental $\mathrm{Er^{3+}}$ energy levels in a $\mathrm{KPb_2Cl_5}$ host matrix. The straight arrows indicate the possible optical transitions that play a role in the electronic dynamics. The wavy ones represent annihilation of phonons of energy $\hbar\Omega$. The labels used in the rate equations are also indicated.

in the excited state of another pumping photon that promotes it to a higher excited level from where it later decays spontaneously, the so-called excited-state absorption (ESA) upconversion. On the other hand, there can be an energy-transfer upconversion (ETU) process in which two electrons initially in the excited state of two different ions interact with each other and, as a result, one of them decays to the ground state whereas the other one is promoted to a higher excited state, from where it later decays radiatively to the ground state. The population dynamics of the electronic levels taking part in all these processes can be cast in a very simple form by using a simple rate equation formalism,

$$N_{\mathrm{OAI}} = N_0 + N_1 + N_2 + N_3 + N_4, \tag{1}$$

$$\frac{dN_1}{dt} = -W_{10}N_1 + \beta_{21}W_{21}N_2 + \gamma N_2^2 + \beta_{31}W_{31}N_3 + \beta_{41}W_{41}N_4 + (1-\eta_e^{(1)})W_1^{\mathrm{rad}}N_1, \tag{2}$$

$$\frac{dN_2}{dt} = \frac{P_{\mathrm{abs}}^{\mathrm{r}}}{h\nu_p} - \beta_{20}W_{20}N_2 - \beta_{21}W_{21}N_2 - 2\gamma N_2^2 - \sigma_{\mathrm{ESA}}(\nu_p)\frac{I_p(t)}{h\nu_p}N_2 + (1-\eta_e^{(2)})W_2^{\mathrm{rad}}N_2, \tag{3}$$

$$\frac{dN_3}{dt} = -\beta_{30}W_{30}N_3 - \beta_{31}W_{31}N_3 + \gamma N_2^2 + (1-\eta_e^{(3)})W_3^{\mathrm{rad}}N_3, \tag{4}$$

$$\frac{dN_4}{dt} = \sigma_{\mathrm{ESA}}(\nu_p)\frac{I_p(t)}{h\nu_p}N_2 - \beta_{40}W_{40}N_4 - \beta_{41}W_{41}N_4 + (1-\eta_e^{(4)})W_4^{\mathrm{rad}}N_4, \tag{5}$$

where N_i ($i=0,\ldots,4$) is the population of the ith level (see Fig. 1 for the nomenclature of the levels), N_{OAI} is the total population of optically active ions (OAIs) in the sample, $W_{ij}=W_i^{\mathrm{rad}}+W_{i\to j}^{\mathrm{nr}}$ is decay rate from level i to level j that includes both the radiative and the nonradiative (phonon-assisted) decay rates, $\beta_{i0(1)}$ is the branch ratio for the $i\to 0(1)$ transition, γ is the strength of the ETU process in which one electron in level ${}^4I_{9/2}$ decays to the ${}^4I_{13/2}$ level and, at the same time, another electron in a different ion is promoted from the ${}^4I_{9/2}$ level to the ${}^4S_{3/2}$ one, $\eta_e^{(i)}$ is the fraction of photons emitted from the ith level that actually leaves the sample (not reabsorbed), ν_p is the frequency of the pumping laser, $P_{\mathrm{abs}}^{\mathrm{r}}$ is the power absorbed resonantly by the sample at frequency ν_p, σ_{ESA} is the ESA cross section at that same frequency, and $I_p(t)$ is the intensity of the laser beam. This set of equations cannot be solved analytically in the general case. However, it is quite easy to calculate the steady-state populations by using the condition $\frac{dN_i}{dt}=0$, ($i=0,\ldots,4$). Once these populations are known, one can calculate the net power deposited in the sample by using the balance equation,

$$P_{\mathrm{net}} = P_{\mathrm{abs}}^{\mathrm{r}} + P_{\mathrm{abs}}^{b} - \eta_e^{(2)}W_2^{\mathrm{rad}}h\bar{\nu}_2N_2^{\mathrm{ss}} - \eta_e^{(3)}W_3^{\mathrm{rad}}h\bar{\nu}_3N_3^{\mathrm{ss}} - \eta_e^{(4)}W_4^{\mathrm{rad}}h\bar{\nu}_4N_4^{\mathrm{ss}}, \tag{6}$$

where the frequencies $\bar{\nu}_i$ are the mean fluorescence frequency of the ith emitting band, P_{abs}^{b} is a frequency independent background absorption, and N_i^{ss} is the steady-state population of the ith level. In this expression, the first three terms on the right-hand side account for the standard anti-Stokes absorption cooling mechanism, as described by Hoyt in Ref. 16. The fourth and fifth terms take into account the contribution from the ESA and the ETU processes to cooling, respectively. The sample temperature change can be easily calculated from (6) in the low pump-depletion limit (a reasonable approximation in single pass through the sample experiments)[16] and this quantity can be cast in the form

$$\frac{\Delta T}{P_{\mathrm{in}}} = \alpha_b + \alpha_{\mathrm{r}}\left[1 - \tilde{\eta}_2\frac{h\bar{\nu}_2}{h\nu_p} - \gamma\tilde{\eta}_3\left(\frac{\tilde{\eta}_2\tau_2^{\mathrm{rad}}}{\eta_e^{(2)}}\right)^2\alpha_{\mathrm{r}}\frac{h\bar{\nu}_3}{h\nu_p}\frac{P_{\mathrm{in}}}{h\nu_p} - \tilde{\eta}_4\frac{\tilde{\eta}_2\tau_2^{\mathrm{rad}}}{\eta_e^{(2)}}\frac{\sigma_{\mathrm{ESA}}(\nu_p)}{A}\frac{h\bar{\nu}_4}{h\nu_p}\frac{P_{\mathrm{in}}}{h\nu_p}\right], \tag{7}$$

where α_b is a background absorption coefficient nearly frequency independent,[16] $\alpha_{\mathrm{r}}(\nu_p)$ is the resonant part of the absorption coefficient, P_{in} is the input laser power, and these three quantities are related to the power absorbed by the sample (resonant or nonresonant) through $P_{\mathrm{abs}}^{\mathrm{r,nr}}=P_{\mathrm{in}}\frac{\alpha_{\mathrm{r,nr}}}{\alpha_T}[1-\exp(-\alpha_T L)]$, with $\alpha_T=\alpha_{\mathrm{r}}+\alpha_{\mathrm{nr}}$ and L as the path length of the laser beam in the sample,

$$\tilde{\eta}_i = \frac{\eta_e^{(i)}W_i^{\mathrm{rad}}}{\eta_e^{(i)}W_i^{\mathrm{rad}} + \beta_{i0}W_{i\to 0}^{\mathrm{nr}} + \beta_{i1}W_{i\to 1}^{\mathrm{nr}}}$$

is the generalized quantum efficiency of the ith level when one takes into account the possibility of partial reabsorption of the fluorescence,

$$\tau_i^{\mathrm{rad}} = \frac{1}{W_i^{\mathrm{rad}}}$$

is the intrinsic lifetime of the ith level, and A is the cross-sectional area of the laser beam in the sample. By setting $\sigma_{\mathrm{ESA}}=\gamma=0$, one immediately recovers the standard model for anti-Stokes laser cooling,[9] in which the onset of cooling (the frequency below which cooling occurs) is given by $\nu_0=\frac{\alpha_{\mathrm{r}}}{\alpha_T}\bar{\nu}_2$. However, the full model gives rise to a richer phenomenology. In order to simplify the subsequent discussion, let us assume that the generalized quantum efficiencies are almost unity and that is also the case for the fraction of photons escaping the sample ($\tilde{\eta}_i=\eta_e^{(i)}\approx 1$). The first approximation is well justified in low-phonon materials such as the potassium lead halides mentioned in the introduction for which the multiphonon transition rates are almost negligible. This is further confirmed by photothermal deflection spectroscopy measurements in a number of RE-doped glasses and crystals. The second approximation is more arguable because it depends on a number of factors such as the geometry of sample, its index of refraction, etc. However, with regard to analyzing expression (7), we can always make the substitution

$$\frac{\tau_i^{\text{rad}}}{\eta_e^{(i)}} \to \tilde{\tau}_i^{\text{rad}},$$

where the later lifetime is a renormalized one (that is, a photon escaping fraction smaller than one can be interpreted as a longer intrinsic lifetime of the emitting level), which does not alter any of the following results whatsoever.

Let us start by considering a case in which standard anti-Stokes cooling is negligible when compared with the upconversion channels, i.e., $\tau_2^{\text{rad}} \to \infty$. In this case, there is an input power threshold for cooling, that is, we need to provide a minimum input power to the sample in order to make $\Delta T < 0$. This power threshold is easily calculated to be

$$P_{\text{in}}^{(0)} = \frac{\alpha_T}{\alpha_{\text{r}}} \frac{(h\nu_p)^2}{\tau_2^{\text{rad}}} (h\nu_{up})^{-1}, \tag{8}$$

where

$$h\nu_{up} = \gamma \tau_2^{\text{rad}} \alpha_{\text{r}} L h \bar{\nu}_3 + \frac{\sigma_{\text{ESA}}(\nu_p)}{A} h \bar{\nu}_4. \tag{9}$$

Interestingly, this expression shows that upconversion cooling occurs by means of any of the upconversion channels. This is quite useful in systems where the operating upconversion mechanism can be selected by adequately tuning the pumping frequency, such as it is the case in potassium lead halide matrices.[14,15] If we now go back to the general model, another important conclusion coming out from Eq. (7) is that the onset of cooling, that is, the pumping frequency below which cooling occurs, is larger when upconversion is present. The exact cutoff frequency depends on both $\alpha_{\text{r}}(\nu_p)$ and $\sigma_{\text{ESA}}(\nu_p)$ and, as such, cannot be put in a closed form in the general case. However, near the resonance, where these two functions can be approximated by their values at the maximum—α_0 and σ_0—and the constant background absorption can be neglected, the cutoff frequency can be put in the form

$$\nu_0^{up} \approx \nu_0 + \frac{\nu_{up} \tau_2^{\text{rad}} P_{\text{in}}}{h\nu_0}. \tag{10}$$

It is important to note that $\nu_0^{up} > \nu_0$. This, in fact, is quite reasonable, as one has additional channels for extracting energy from the system when upconversion is present, so that cooling can be more efficient. What is really interesting is the fact that if the pumping beam is very intense or the upconversion process is very efficient ($\nu_{\text{up}} \gg 1$), the onset of cooling could be located above the barycenter of the pumping level, that is, in its Stokes part. Of course, the possibility of these new effects being noticeable rests on the assumption that the amount of energy extracted from the system by means of the upconversion channels is comparable to the amount of energy extracted by means of the conventional anti-Stokes emission channel (in the particular case of the Er-doped potassium lead halides considered in this work, the direct ${}^4I_{9/2} \to {}^4I_{15/2}$ transition). A quantitative estimation of whether that is the case for a particular system requires, mainly, precise measurements of the corresponding excited-state absorption cross sections of the levels involved in the upcoversion processes. In the particular case of the $\text{Er}^{3+}:\text{KPb}_2\text{Cl}_5$, these measurements have been performed by Ferrier *et al.*,[17] who found that σ_{ESA} for the ${}^2H_{9/2} \leftrightarrow {}^4I_{9/2}$ transition is not only comparable but, in some cases, larger than the corresponding ground-state absorption cross section of the ${}^4I_{9/2} \leftrightarrow {}^4I_{15/2}$ transition. Therefore, one can expect that, at least for $\text{Er}^{3+}:\text{KPb}_2\text{Cl}_5$ and, no doubt, some other low-phonon fluorescent solids, upconversion cooling will play a significant role in the global optical cooling process.

In conclusion, we have presented a mechanism for laser cooling based on infrared-to-visible upconversion processes. It has been analyzed by using a simple rate equation formalism from which it is concluded that upconversion cooling presents a number of advantages with regard to standard anti-Stokes cooling. Among these there is the possibility to control the onset of cooling by using the pumping power or to select the active upconversion mechanism by adequately tuning the pumping frequency, which can be very useful for frequency selective applications. We hope that the results presented in this work will encourage other researchers to further investigate the role that upconversion cooling could play in the development of highly efficient solid-state refrigeration applications.

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