Observation of Anti-Stokes Fluorescence Cooling in Thulium-Doped Glass

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We report the first observation of anti-Stokes fluorescence cooling in a thulium-doped solid with pump excitation at 1.82 μm < λ < 1.97 μm. At a pump wavelength of 1.9 μm and incident average power of ~3 W, a Tm$^{3+}$:ZBLANP (ZrF$_4$-BaF$_2$-LaF$_3$-AlF$_3$-NaF-PbF$_2$) sample cooled to ~1.2°C from room temperature for a single pass of the pump beam. This corresponds to an absorbed pump power of ~40 mW and a peak temperature change per absorbed power of ~ −30 °C/W from room temperature.

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Parallel to advances in laser cooling of atoms and ions in dilute gas phase, major experimental progress has recently been made in laser cooling of matter in solid and liquid phases [1,2]. Laser refrigeration of solids can potentially lead to the development of an all solid-state cryocooler that can be used for a variety of applications such as cooling sensors and electronics [3]. Since the first observation of optical refrigeration in a solid (ytterbium-doped glass) in 1995 by Epstein et al. [1], researchers have made major strides toward achieving laser induced solid-state cryocoolers [4]. Ytterbium-doped glass has been cooled by more than 50 K below room temperature and has been shown to cool at 100 K [3,5,6]. Progress has been made toward cooling semiconductor materials although no net cooling has yet been observed due to radiation trapping [7,8]. Here we report the first demonstration of laser induced cooling of a thulium-doped glass—the second solid after Yb$^{3+}$-doped glass to exhibit net bulk cooling. These measurements allow us to test material scalability such as the predicted increase in cooling efficiency with decreasing pump photon energy. Moreover, unlike in Yb$^{3+}$-doped systems, these results demonstrate anti-Stokes fluorescence cooling in the presence of excited-state absorption.

We studied a number of Tm$^{3+}$-doped glasses and crystals (CaF$_2$, BaF$_2$, YAlO, LuAG, ZBLANP) but only one, a ZBLANP (ZrF$_4$-BaF$_2$-LaF$_3$-AlF$_3$-NaF-PbF$_2$) sample, exhibited a net cooling effect. This sample consisted of high purity 1 wt % Tm$^{3+}$:ZBLANP cut from a fiber preform. The relevant energy manifolds for Tm$^{3+}$ ions in this host are shown in Fig. 1 [9]. Each level corresponds to a Stark-split manifold of several inhomogeneously broadened levels. We use the transitions between the $^3$H$_6$ and $^3$H$_4$ manifolds for our cooling cycle.

The cooling cycle in anti-Stokes fluorescence cooling involves pump excitation, thermalization, and spontaneous decay. As shown in Fig. 1, laser pump photons excite the dopant ensemble from the top of the ground-state manifold to the bottom of the excited-state manifold. The excitations thermalize within the upper and lower manifolds. The atoms decay through spontaneous emission (fluorescence) with a mean energy of $h\nu_f$, where $\nu_f$ is the mean fluorescent frequency. For each absorbed pump photon of energy $h\nu$, an average energy $h\nu_f - h\nu$ is removed from the thermal vibrations in the glass and carried out of the system. The cooling efficiency can be defined as the ratio of the cooling power to absorbed power and by energy considerations is
\[ \eta_{\text{cooling}} = \frac{\nu_f - \nu}{\nu} = \frac{\lambda - \lambda_f}{\lambda_f}, \quad (1) \]

where \( \lambda \) and \( \lambda_f \) are the pump and mean fluorescent wavelengths, respectively. Figure 2 shows the emission spectrum and mean fluorescent wavelength (\( \lambda_f \)) of a \( \text{Tm}^{3+}:\text{ZBLANP} \) sample after Ref. [10]. Also shown in the figure is the absorptivity of our \( \text{Tm}^{3+}:\text{ZBLANP} \) sample as taken with a Fourier transform infrared spectrophotometer. Equation (1) describes the fundamental limit on the cooler performance. It suggests that, for a given material, longer pump wavelengths produce higher efficiencies. In practice, however, diminished pump absorption at long wavelengths due to the thermal distribution of the ground-state population limits the useful pump wavelength. Moreover, as discussed below, the ever present parasitic absorption due to unwanted impurities in the material further limits the effective range of long-wavelength excitations. The practical range of the energy difference \( h\nu_f - h\nu \) is at most a few times thermal energy \((kT)\) as a consequence of the ground-state Boltzmann distribution. Therefore, with \( h\nu_f - h\nu = \beta kT \), where \( \beta \) is determined by device design and geometries, Eq. (1) indicates that \( \text{Tm}^{3+} \)-doped materials with \( h\nu_f \approx 0.7 \text{ eV} \) have the potential to cool nearly twice as efficiently as \( \text{Yb}^{3+} \)-doped materials with \( h\nu_f \approx 1.25 \text{ eV} \) [1].

Although dopant ions with lower energy gaps can produce more efficient cooling, they will generally be subject to higher nonradiative decay rates that are strongly host dependent. For the relevant energy gaps, multiphonon assisted transition probabilities (rates) increase exponentially with decreasing energy gap. These rates vary greatly from host to host because of the large diversity in phonon energy spectra. Figure 3 is a logarithmic plot of nonradiative decay rate versus energy gap for a number of different hosts [11]. The \( ^3\text{H}_6 \rightarrow ^3\text{H}_4 \) energy gap in a fluorozirconate host such as ZBLANP \((\sim 5000 \text{ cm}^{-1})\) for transitions most important for heating considerations) corresponds to \( \sim 10^{-1} \text{ s}^{-1} \) which is \( \sim 10^{-4} \text{ times the radiative rate of } \sim 160 \text{ s}^{-1} \) [11]. The resultant heating due to nonradiative processes in pure \( \text{Tm}^{3+}:\text{ZBLANP} \) should be insignificant.

The tunable pump source for our experiments was an optical parametric oscillator (OPO) based on periodically poled lithium niobate, synchronously pumped by a 20 W cw-mode-locked Nd:YAG laser (Coherent Antares). The OPO was operated singly resonant and had a maximum average output power of 6.2 W, signal tunability between 1.75–2.05 \( \mu \text{m} \), and a signal output slope efficiency of 42% [12]. The pump beam was focused into the sample \((5 \times 5 \times 9 \text{ mm}^3)\) that rested on thin glass support slides in a vacuum chamber at approximately \( 10^{-3} \text{ Torr} \). An identical reference sample was also placed in the chamber on separate slides out of the beam path. We recorded the net temperature change of the sample relative to the reference sample using a pyroelectric thermal camera (ISI Group). The samples were observed through a CaF\(_2\) window in the chamber for a single pass of the pump beam at a given wavelength after the sample reached thermal equilibrium with its surroundings inside the vacuum chamber. We calibrated the thermal camera by controlling the temperature of a similar glass sample: for a particular aperture of the camera the digitized image yielded an 8-bit value that corresponded to the temperature of the sample as read by a thermocouple.

Figure 4 shows the induced temperature change in the \( \text{Tm}^{3+}:\text{ZBLANP} \) sample versus the pump wavelength.
To investigate the effect of nonradiative decay we generalize Eq. (2) to include fluorescence quenching. This effect is manifested as nonunity quantum efficiency and results in additional heating that follows resonant absorption. Including this, we can express to first order the normalized change in temperature of the sample as

$$\frac{\Delta T}{P_{\text{in}}} = \kappa \left[ \alpha_b + \alpha_r(\lambda) \left( 1 - \eta_q \right) - \alpha_r(\lambda) \eta_q \frac{\lambda - \lambda_f}{\lambda_f} \right],$$

(3)

where $\eta_q$ is the quantum efficiency for the Tm$^{3+}$ ions in the host material. Using Eq. (3) to fit our data we find that the sample has a quantum efficiency of greater than 99%.

Since quantum efficiency is related to atomic lifetimes, Eq. (3) gives an upper limit on the nonradiative decay rate ($R_{\text{nr}}$) allowed in the cooling process for a given pump wavelength. Quantum efficiency is defined as $(1 + R_{\text{nr}} \tau_{\text{rad}})^{-1}$, where $\tau_{\text{rad}}$ is the radiative lifetime. Assuming no background absorption, by Eq. (3) we see that to observe cooling the material must meet the condition

$$R_{\text{nr}} \tau_{\text{rad}} < \frac{\lambda - \lambda_f}{\lambda_f}.$$  

(4)

With the measured value of $\tau_{\text{rad}} = 6.2$ ms [11], we find $R_{\text{nr}} \lesssim 3$ s$^{-1}$ for $\lambda_f = 1.82$ $\mu$m and $\lambda = 1.86$ $\mu$m. According to Fig. 3, the fluorozirconate host safely meets this criterion while silicate and phosphate do not.

The sensitivity of the expected cooling to wavelength-independent background absorption is shown in Fig. 5, where Eq. (2) is plotted again with four different values of $\alpha_b$. Background absorption corresponding to $\alpha_b > 0.001$ cm$^{-1}$ eliminates net cooling for our sample.
Similarly, the sensitivity of the cooling process to quantum efficiency ($\eta_q$) is shown in Fig. 6, where Eq. (3) is plotted with three different values of $\eta_q$ for $\alpha_0 = 0.0002 \text{ cm}^{-1}$. Quantum efficiencies less than $\sim 97\%$ eliminate cooling for our sample. In other experiments we examined different thulium-doped solids and found no cooling. These solids included Tm$^{3+}$:CaF$_2$, Tm$^{3+}$:BaF$_2$, and another sample of Tm$^{3+}$:ZBLANP. These negative results can be attributed to background absorption or fluorescence quenching by impurities or defects as discussed above.

Similar to the cooling transitions discussed above, excitations to the $^3F_4$ manifold in the Tm$^{3+}$:ZBLANP sample have the potential to produce fluorescence cooling. Along the possible decay paths from this manifold, the $^3F_4 \rightarrow ^3H_3$ and the decays are largely radiative (see Fig. 3). However, the $^3H_3 \rightarrow ^3H_4$ transition is strongly nonradiative. Nevertheless, the branching ratio for the $^3F_4 \rightarrow ^3H_3$ transition of 0.03 [11] indicates that the heat from this nonradiative branch should be small compared to the cooling processes. Since the $^3F_4$ manifold lies 6900 cm$^{-1}$ above the $^3H_4$ level, it can be populated via excited-state absorption (ESA) during illumination by the OPO at $1.82 < \lambda < 1.97 \mu\text{m}$. This was verified by observing fluorescence at $\sim 1 \mu\text{m}$ using a simple silicon-based video camera during our experiments. At the above excitation wavelengths, this ESA process is endothermic and should contribute extra cooling if fluorescence efficiency and background absorption are in the acceptable range. Since our average intensity is far below the saturation intensity of the $^3H_4 \rightarrow ^3F_4$ transition, we expect the population of the $^3H_4$ manifold to be much larger than that of the $^3F_4$ manifold. Therefore any heating or cooling effects from the ESA process should be negligible. We examined the $^3F_4$ manifold further by directly pumping the $^3H_6 \rightarrow ^3F_4$ transition using a Ti:sapphire laser at 790–900 nm. We did not, however, observe any cooling. This may indicate the presence of strong fluorescence quenching at this transition in addition to the background absorption.

In conclusion, we have presented the first observation of optical cooling in a Tm$^{3+}$-doped solid. We used tunable near-infrared light from an OPO to cool a sample by $-1.2 \degree\text{C}$ from room temperature for a single pass of the pump beam. We deduce a peak cooling per absorbed power of $\sim -30 \degree\text{C/W}$, which depends on the thermal load to the sample—this value can be drastically improved by reducing the surface area of the sample and covering the vacuum chamber walls with low thermal emissivity materials [3]. By increasing the absorbed power via pump recycling (as in mirrored samples [3]) and using higher doping concentrations we should be able to approach cryogenic temperatures in this material with our available laser power.

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