Identification of parasitic losses in Yb:YLF and prospects for optical refrigeration down to 80K

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Abstract: Systematic study of Yb doping concentration in the Yb:YLF cryocoolers by means of optical and mass spectrosocopies has identified iron ions as the main source of the background absorption. Parasitic absorption was observed to decrease with Yb doping, resulting in optical cooling of a 10% Yb:YLF sample to 114K ± 1K, with room temperature cooling power of 750 mW and calculated minimum achievable temperature of 93 K.

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OCIS codes: (140.0140) Lasers and laser optics; (140.3320) Laser cooling.

References and links
1. Introduction

Optical refrigeration is based on the principle of anti-Stokes fluorescence, where laser photons with energy less than the mean fluorescence energy are absorbed followed by phonon-assisted upconversion fluorescence. When the blue-shifted fluorescence escapes efficiently, photons carry away heat from the material, resulting in cooling [1–5]. Extremely high purity materials with high external quantum efficiency are necessary conditions to achieve cooling. Rare-earth doped solids with low phonon energy, such as fluoride or chloride crystals and glasses, satisfy these conditions [6]. Laser cooling of solids was originally demonstrated in 1995 at Los Alamos National Laboratory, using a Yb$^{3+}$-doped fluorozirconate glass Yb:ZBLAN [5]. Experimental conditions were later optimized [7,8], resulting in cooling to an absolute temperature of 208K by 2005 [8]. Cooling in several rare-earth doped solids has been since demonstrated [8–11, also see recent reviews e.g. 3,12], where ytterbium-doped fluoride crystals (Yb:YLF) have performed particularly well [13,14]. Large inhomogeneous broadening of the rare-earth ion levels in a disordered (glassy) host matrix leads to diminished peak resonant absorption at low temperatures. In comparison, homogeneous splitting of Stark manifolds in a crystalline host matrix results in dramatic improvement in peak absorption cross-section and associated enhancement of the cooling efficiency at a particular pump wavelength [13]. Additionally, high doping concentration in YLF is stoichiometrically allowed, offering a route for further enhancement of the absorption. The increased resonant absorption has recently resulted in bulk cooling of a 5% wt. Yb$^{3+}$-doped yttrium lithium fluoride (Yb:YLF) crystal to 119 K, within less than a degree from the global minimum achievable temperature (gMAT) [14]. This temperature is only limited by heating due to parasitic absorption in impurities. Understanding the cause of this background absorption can guide the research toward realization of 80 K optical cryocoolers, potentially substituting usage of liquid nitrogen in some applications.

In this work we address the question of the nature of the parasitic background absorption by investigating the laser cooling properties of Yb:YLF as a function of systematically varied concentration of the Yb$^{3+}$ ions in multiple samples. Characterization of these samples is accomplished by optical measurements of quantum efficiency and background absorption (Sec. 3) as well as trace elemental analysis (Sec. 4) of their composition. Our central finding is the observation of reduction of background absorption with increase of the Yb$^{3+}$ concentration in the sample, where doping levels up to 10% were investigated. In fact, we observed that a 2-fold increase in the Yb$^{3+}$ has led to a 4-fold improvement in the ratio of background absorption to resonant absorption (Sec. 2) resulting in a new bulk cooling record to 114 K and calculated gMAT of 93 K (Sec. 3). Comparison of optical and mass spectrometry measurements seems to indicate that the presence of Fe ions could be one of the main sources of background absorption, introduced, as data suggests, partly through the YF$_3$ starting material during the crystal growth process.

2. Cooling efficiency model and experimental motivations

At a given laser wavelength $\lambda$ and sample temperature $T$, the ratio of the cooling power ($P_{\text{cool}}$) to the absorbed laser power ($P_{\text{abs}}$) defines the cooling efficiency [15]:
\[ \eta_{\text{ext}}(\lambda, T) = \frac{P_{\text{out}}}{P_{\text{abs}}} = \eta_{\text{ext}} \left[ \frac{1}{1 + \alpha_{\text{r}}/\alpha_{\text{b}}(\lambda, T)} \right] \frac{\lambda}{\lambda_{f}(T)} - 1, \]  

(1)

where \( \eta_{\text{ext}} \) is the external quantum efficiency, \( \lambda_{f} \) is the escaped mean fluorescence wavelength, including effects of reabsorption, and \( \alpha_{\text{r}} \) is the resonant absorption coefficient of the active ion as extracted via reciprocity from calibrated temperature dependent fluorescence spectra [13]. Defined here, positive cooling efficiency denotes sample cooling and negative denotes heating. Parasitic losses are represented by the background absorption coefficient \( \alpha_{\text{b}} \), which is confirmed to be wavelength- and temperature-independent within the experimental conditions [16], also consistent with nearly temperature-independent absorption cross-section of common transition metal impurities [17].

We define the quantity in brackets in Eq. (1) as absorption efficiency (\( \eta_{\text{abs}} \)). The product \( \eta_{\text{ext}} \eta_{\text{abs}} \) is therefore interpreted as the fraction of absorbed photons that escape as fluorescence and hence remove heat from the solid. Thus the cooling requirement (\( \eta_{\text{c}} > 0 \)) is equivalent to the statement that \( \eta_{\text{ext}} \eta_{\text{abs}} \) product has to be as close as possible to unity. It is known that optical transitions in rare-earth ions doped into low-phonon glass and crystal hosts (e.g. fluorides), are typically associated with high external quantum efficiency (\( \eta_{\text{ext}} > 99\% \)) and therefore are naturally strong candidates for host materials. Further improvement of the cooling efficiency is accomplished by the choice of the pump wavelength. The ratio of \( \lambda/\lambda_{f}(T) \) in Eq. (1) suggests that, for a given material, longer pump wavelengths improve cooling efficiency. Under practical conditions, pump detuning is limited to approximately \( k_{B}T \) due to reduced pump absorption caused by the thermal distribution of the ground-state. Additionally, parasitic heating limits the effective range of long wavelength excitations. Pump wavelength corresponding to the E4-E5 Stark manifold transition in \( \text{Yb}^{3+} \) has been identified as the optimal wavelength that maximizes cooling efficiency down to the minimum achievable temperature (MAT) [13].

The cooling efficiency can also be improved by material synthesis targeted to reduce the ratio of background absorption to resonant absorption, \( \alpha_{\text{b}}/\alpha_{\text{r}}(\lambda, T) \). Purification of the starting materials prior to synthesis [18] is one of the direct approaches for reduction of impurities. At the same time, an increase in the doping concentration can improve the ratio, provided heat-producing impurities are not introduced during the doping process.

In this work we set out to answer questions about the nature of background absorption by concentrating on a careful study of the doping dependence. For this purpose we obtain a sample-set with systematically varying doping concentration: un-doped, 1\%, 5\%, 7\% and 10\% wt. \( \text{Yb:YLF} \) (AC Materials, FL, USA). Samples were grown by Czochralski method with minimal time period between the growth runs, to minimize the effect of uncontrolled variations of impurities due to the growth process itself. Such strategy is necessary to single out the intrinsic (doping-dependent) compositional variations. We interrogate the sample set with optical measurements of quantum efficiency and background absorption, together with the elemental analysis. Optical measurements allow us to determine both the external quantum efficiency and the background absorption coefficient. Together with the measurements of resonant absorption and mean luminescence wavelength, these quantities allow us to model the temperature dependence of the cooling efficiency (Eq. (1)), and hence to predict the minimum achievable temperature (MAT) of the samples [16]. Finally, we compare these measurements with the results of elemental analysis in the attempt to correlate optical observations with the chemical composition of the samples.

3. Optical measurements

This section reports measurements of the external quantum efficiency and background absorption coefficient in the sample set of varying concentration of \( \text{Yb:YLF} \). The methodology to fully characterize the laser cooling performance of the sample has been detailed elsewhere [19]. Briefly, each sample is systematically characterized by measuring the four quantities of the cooling efficiency model in Eq. (1) in the \( E||c \) orientation to increase
pump absorption [20]. Absorption and emission spectra were obtained over the temperature range of 80 – 300K for the doped samples. Using a broadly tunable Ti:sapphire laser we perform a laser-induced temperature modulation spectrum (LITMoS) test for each crystal. This test measures the sample fractional heating/cooling as a function of pump photon frequency for a constant (i.e. normalized to the) absorbed power. This temperature change is proportional to, and therefore a relative measure of, the cooling efficiency $\eta_c$ in Eq. (1).

The results of the LITMoS test on the sample set at 300 K are shown in Fig. 1(a). Fits of Eq. (1) (solid lines) for each sample allow determination of both external quantum efficiency and background absorption. Within experimental uncertainty, these results identified the same $\eta_{ext} = (99.6 \pm 0.1)\%$ for all the samples in the set. In contrast, the parasitic background absorption is seen to decrease dramatically with increased doping concentration (Fig. 1(b)), culminating with a record low background absorption of $\alpha_b = 2.0 \times 10^{-4}\text{cm}^{-1}$ in a 10% wt. Yb:YLF crystal. Background absorption of the un-doped sample in Fig. 1(b) is measured by the relative heating as compared to the 1% sample at long wavelengths where resonant absorption goes to zero. We point out that the previous best optical refrigeration sample was a 5% wt. Yb:YLF with measured $\eta_{ext} = (99.5 \pm 0.1)\%$ and $\alpha_b = 4.0 \times 10^{-4}\text{cm}^{-1}$ [13,16] for which a global minimum achievable temperature (gMAT) was verified at 110 K [16]. In contrast to the 5% sample, here we find that doubling of the doping concentration to 10% also results in a factor of two decrease of the background absorption. Thus the background absorption of $\alpha_b = 2.0 \times 10^{-4}\text{cm}^{-1}$, observed in the 10% Yb:YLF sample, is to our knowledge the lowest reported to date. We note that this behavior corresponds to a factor of $4 \times$ improvement in the ratio of $\alpha_b/\alpha_r(\lambda,T)$. Motivated by this dramatic improvement, we model the performance of the 10% sample.

Neglecting temperature dependence of $\eta_{ext}$ and $\alpha_b$, we calculate the cooling efficiency using measured values of $\eta_{abs}(\lambda, T)$ and $\eta_{ext}$ using Eq. (1). Figure 2(a) reveals cooling efficiency as a function of wavelength and temperature, along with a gMAT of $93\text{K}$ at $1020\text{nm}$, corresponding to the transition between E4 and E5 levels of the $^2F_{7/2} - ^2F_{5/2}$ Stark manifold of Yb$^{3+}$. This global minimum achievable temperature corresponds to a strong improvement in comparison with the earlier performance [13,14] and is consistent with previous estimations [19]. Since model prediction of gMAT of 110 K in the aforementioned 5% sample was directly confirmed experimentally [14,16], this reinforces the currently calculated prediction of gMAT to be most probable. To verify this prediction, we investigated cooling performance in a high power cooling setup detailed elsewhere [14]. While currently limited by the pump power trapping efficiency [14], we nonetheless were able to achieve cooling to an absolute temperature of $114 \pm 1\text{K}$, starting from the ambient, with the estimated
cooling power of 750 mW (Fig. 2(b)). This result corresponds to a new low-temperature record for optical refrigeration and indirectly testifies to the correctness of the low gMAT prediction. Further experiments are underway to directly verify the gMAT value but in the remainder of this work, we turn our attention to the study of the nature of the background absorption.

Before we proceed, however, we want to discuss general considerations for the $\alpha_b/\alpha_r(\lambda,T)$ ratio. The objective for efficient laser cooling is to decrease this ratio. In linear approximation, i.e., for low doping levels, doubling of the doping concentration should correspondingly double the resonant absorption, i.e., the denominator of this fraction. To anticipate variation of the background absorption, we have to first remember that a Yb:YLF crystal is grown from three starting materials: YbF$_3$, YF$_3$ and LiF [20]. Scaling of the $\alpha_b$ with doping relies on the exact path by which the impurities can enter the final crystal, during the growth process. For instance, if impurities are introduced through the YbF$_3$ starting material, increasing the doping concentration will also proportionally increase the level of impurities, thus potentially negating the benefit of higher resonant absorption. The observed anti-correlation between background absorption and the doping level (Fig. 1(b)) however does seem to suggest an interpretation where we can rule out YbF$_3$ starting material as the major source of impurities. Furthermore, the anti-correlated behavior of these two quantities suggests that at least some background absorption material is introduced through the YF$_3$ starting material, which is being substituted by YbF$_3$ during the growth. Of course, at high concentrations, linear approximation will fail, due to an increased probability of energy transfer between two neighboring Yb$^{3+}$ ions, as the distance between ions decreases. On average this energy transfer alone does not cause unwanted heating, but instead increases the probability for an excitation to reach an impurity where it will decay non-radiatively, causing heat [17]. This is called concentration quenching [15,21] and sets a limit on the doping concentration, which in turn depends on the impurity levels of the material. The observed linear decrease of the background absorption in our samples with increase of the doping concentration (Fig. 1(b)) however suggests the influence of the concentration quenching up to the 10% is not evident. We also note that while the linear decrease of impurities with doping is highly encouraging (Fig. 1(b)), laser cooling performance will most likely be detrimentally affected by concentration quenching at doping levels in the 10-20% range [21]. Investigation of laser cooling in such heavily-doped samples is currently underway by our group.

Next, elemental analysis is performed for the crystal sample set to draw statistical correlations between impurity elements and the measured background absorption in Fig. 1.

Fig. 2. (A): Cooling efficiency (Eq. (1) for 10% Yb:YLF sample with $\eta_{\text{ext}} = (99.6 \pm 0.1)\%$ and $\alpha_b$, 2-4 cm$^{-1}$. Global minimum achievable temperature of 93 K is obtained at the E4-E5 transition of Yb$^{3+}$ ion (red vertical arrow on inset). (B): Plot of temperature vs. time for 10% Yb:YLF pumped at 1020nm resulting in 114K ± 1K.
4. Trace elemental analysis

Elemental analysis is an ideal tool to identify the constituent elements that produce parasitic heating and hence to understand the observed trend in the optical measurements (Sec. 3). Sample dissolution and subsequent procedures were carried out in a class 100 cleanroom at the Radiogenic Isotope Laboratory, the University of New Mexico. Teflon cleaning and dissolution vials were prepared by boiling in nitric and hydrochloric acids for two 8-hour sessions followed by an additional 8-hour boiling in 18MΩ water. Without a method of dissolution of LiYF₄ crystals available in literature, and only a brief mention of a method of dissolution under development [22], a method was developed for sample preparation, prior to elemental analysis. The details of the procedure are outlined below [23].

The sample powders were prepared using the following procedure:

1. The crystal is cleaned with ultra-pure 18MΩ resistance de-ionized water as a general surface preparation.

2. One of the surfaces is removed and discarded by scraping with a tungsten carbide bit to remove any remaining surface impurities and expose the internal crystal from where the sample is taken. It was found that carbide tipped tool contaminates the sample with iron, so the bit should be made up of entirely tungsten carbide, which did not cause contamination.

3. The dissolution sample is scraped from the exposed internal part of the crystal, taking care to avoid any surface that has not been previously removed. This scraping also serves to finely crush the sample, a necessary step for dissolution. Once ~10mg of material (carefully weighed) is generated, it is placed into a previously leached and weighed Teflon vial.

After completion of this procedure, the sample is ready for dissolution. It is important to note that a finely powdered sample is useful to reduce the time required to dissolve the sample. Particles > 1/4 mm in diameter required 4 – 10 X longer to dissolve. The systematic dissolution method for Yb:YLF used for this work is as follows:

1. The previously prepared powdered sample inside a leached Teflon vial is combined with ~2 ml of 15N HNO₃ and ~2 ml of 6N HCL ultra-pure acids.

2. The Teflon vial with a tightly secured lid is put on hot plate at ~120°C. Boiling commences for at least 4 hours to drive off the fluorine atoms. If vapor escapes additional acid may needed to prevent the sample from drying before it is dissolved. If the sample dries prematurely, a crystalline precipitate is formed which is very difficult to re-dissolve and it was found easiest to begin again with a fresh powdered crystal.

3. The lid is removed and dissolution of the powder is verified visually in the remaining liquid, allowing time for any small particles to settle. If dissolved, remaining liquid is evaporated on the hot plate and the sample is ready for step 4. If, however, the sample is not dissolved, the liquid is evaporated to a small quantity, leaving about 1 drop to avoid the crystalline precipitate, and the process is restarted from step 1, except with half of the amount of acids.

4. After remaining liquid has evaporated, either a small amount of easily dissolvable solid or no visible solid should remain. A solution of 3% HNO₃ with 10 ppb indium (¹⁵⁵In) for a dilution of 1:1000, e.g. a15mg of original powder, diluted with 15ml of solution, is added. ¹⁵⁵In is an internal standard used by the instrument to monitor any signal suppression or enhancement from the solution matrix and other instrument variability. Blanks (monitor for trace element contribution from reagents; 3% HNO₃ spiked with 10 ppb indium) were run with the samples; given the purity of our reagents, blank correction was not significant.
A Thermo X-series II quadrupole inductively coupled mass spectrometer (Q-ICPMS) in the Radiogenic Isotope Laboratory was used for the trace elemental analysis. We did an initial semi-quantitative survey followed by 26 elements quantitatively with a concentration range from 1,000 ppt to 100,000 ppt. Elemental standards in the range of the concentration of the elements of interest were used to construct calibration curves. Overall precision ranged from 0.01% to 102% (1σ) including all 26 elements, however by removing 82Se from the set, the precision improved to 0.01% to 17.46% (1σ) and 0.81% to 4.08% (1σ) for Fe.

Without a priori knowledge of which impurities cause heating, it is necessary to analyze as many elements for which calibration samples exist. Analysis of the prepared solutions using the Q-ICP mass spectrometer is then compared with the background absorption measurement obtained from the optical study (Sec. 3).

For a 5-sample set, the full dimensionality of our data set is $5 \times N$, where $N$ is the number of trace elements analyzed. To reduce data set to $I \times N$, we replace the 5-sample column by the correlation coefficient, $r$ [24]. This coefficient represents statistical correlation between quantities A and B and lies on the segment [-1;1], where 0 corresponds to the case of no statistical correlation between A and B, while positive/negative extremum corresponds to perfect correlation/anti-correlation between these quantities. We plot $r$ for correlation between the elemental composition and Yb$^{3+}$ (top) and background absorption (bottom) in Fig. 3. We first note the nearly perfect correlation ($r \approx 1$) of Yb doping (top plot) with concentration of $^{172}$Yb element, which attests to excellent growth calibration as well as great sensitivity of Q-ICPMS. Furthermore, near-unity positive correlation coefficients observed for $^{153}$Eu, $^{159}$Tb, $^{165}$Ho, $^{169}$Tm elements imply that they are introduced together with the Yb through the YbF$_3$ starting material. Additionally, strong anti-correlation ($r < -0.8$) observed for $^{51}$V and $^{56}$Fe suggests that these elements are displaced during the process of Yb doping, in other words these elements most likely belong to the YF$_3$ starting material due to the Y$^{3+}$→Yb$^{3+}$ substitution. Here we would like to note that we have chosen to detect $^{56}$Fe instead of a naturally abundant $^{54}$Fe in order to avoid common isobaric interference in the mass spectrometry of the latter (see e.g [25]). The concentrations of these two iron isotopes are related, thus not affecting the drawn conclusions.

![Fig. 3. Statistical correlation coefficient $r$ of elemental sample composition with the level of Yb$^{3+}$ doping (top) and background absorption (bottom). Strong correlation of $\alpha_b$ with $^{56}$Fe identifies the transition metal as potentially dominant impurity in current optical cryocoolers.](image)

While the top plot of Fig. 3 contains information about the elemental composition of the variously-doped samples, the bottom chart displays correlation of elemental composition with the background absorption coefficient, as measured by the optical means (Sec. 3). It is remarkable to note that $^{56}$Fe exhibits pronounced peak with $r \approx -0.9$. Such indication suggests the presence of iron is the main source of the background absorption, for current accuracy...
levels in the measurements. It should be noted here that further investigation of the oxidation state of Fe is necessary. Previous investigations [17] concerned the oxidation state Fe$^{2+}$, where absorption is strong around 1000 nm corresponding to the mean fluorescence of Yb$^{3+}$. The oxidation state Fe$^{3+}$ absorbs between 700 and 850 nm, and hence could still contribute to background absorption, as being resonant with the higher-energy states of Tm$^{3+}$ unintentional co-dopant. In Yb:YLF, charge compensation is necessary to incorporate Fe$^{2+}$. An electron paramagnetic resonance spectroscopy study is currently underway to verify the oxidation state of Fe in YLF.

Combining these findings with the compositional information (Fig. 3, top), we can draw an additional conclusion that iron impurity is most likely introduced through the YF$_3$ starting material. This is further corroborated by the optical measurements (Fig. 1(b)) and provides direct feedback to the material synthesis in terms of the potential targets for starting materials purification efforts.

To further support the interpretation that iron appears to be one of the main sources of the background absorption in Yb:YLF, we carried out elemental analysis on an additional 5%-doped Yb:YLF sample, grown in a different laboratory and most probably under different growth conditions. Due to the growth variations, this sample cannot be combined with the original 5-sample set to draw compositional conclusions, as above. Nonetheless, the measured background absorption and concentration of iron are in very good agreement with the trend measured from the controlled sample set (Fig. 4). Here the iron concentration has been scaled by the natural isotope abundance ratio of $^{56}$Fe relative to the measured $^{58}$Fe in the mass spectrometer. The observed correlation suggests the generality of our finding that the presence of transition-metal iron in current Yb:YLF cryocoolers limits the performance, by increase in the background absorption and hence in the global minimum achievable temperature value. The calculated gMAT value of 93 K, as currently demonstrated in this work, is observed in correspondence with a 4-fold reduction of the $\alpha_b/\alpha_r$ ratio (Sec. 3). This already is a considerable improvement from the earlier performance [13,14] and in very good agreement with the earlier prediction of the gMAT dependence on the background absorption [19]. With additional factor of 2 reduction of Fe in YF$_3$ starting materials, operation close to 80 K is calculated, promising a bright future for the next generation optical cryocoolers.

5. Conclusion
In this work we carried out a systematic study of the Yb doping concentration in the Yb:YLF cryocoolers. By comparing optical measurements of the background absorption and Q-ICPMS compositional data, we find evidence for iron ions as the main source of the background absorption in the currently-available Yb:YLF crystals. Furthermore, we observe indication
that iron is could be contained in the YF₃ starting material. We were also able to measure
the lowest background absorption in Yb:YLF to date of $\alpha_b = 2.0 \times 10^{-4}\text{cm}^{-1}$, corresponding to the
calculated global minimum achievable temperature of 93 K. Power cooling of this sample has
resulted in a new record of absolute temperature of 114 K and 750 mW cooling power,
corresponding to a 185 K differential temperature drop with respect to the ambient. If present
concentration of Fe in YF₃ can be reduced by an additional factor of 2, under assumption that
all heating is coming from Fe, gMAT near 80 K is predicted. This work outlines a clear path
for the material synthesis efforts in achieving these temperatures.

Acknowledgments

The authors thank Markus Hehlen and Richard Epstein for useful discussions, and AC
Materials (Tarpon Springs, FL) for customized sample growth and preparation. The work at
UNM was supported by DARPA (GRANT 10669320), Thermo Dynamic Films (TDF)
through an STTR Grant, AFRL (FA94531310223). SDM acknowledges the support of a
National Research Council Research Associateship Award at the Air Force Research
Laboratory. DVS acknowledges support by the National Science Foundation under Grant No.
1160764 and partial support by the EU FP7 Marie Curie Zukunftskolleg Incoming Fellowship
Programme, University of Konstanz (Grant No. 291784).