

Influence of other rare earth ions on the optical refrigeration efficiency in Yb:YLF crystals

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Abstract: We investigated the effect of rare earth impurities on the cooling efficiency of Yb³⁺:LiYF₄ (Yb:YLF). The refrigeration performance of two single crystals, doped with 5%-at. Yb and with identical history but with different amount of contaminations, have been compared by measuring the cooling efficiency curves. Spectroscopic and elemental analyses of the samples have been carried out to identify the contaminants, to quantify their concentrations and to understand their effect on the cooling efficiencies. A model of energy transfer processes between Yb and other rare earth ions is suggested, identifying Erbium and Holmium as elements that produce a detrimental effect on the cooling performance.

OCIS codes: (140.0140) Lasers and laser optics; (140.3320) Laser cooling; (160.5690) Rare-earth-doped materials; (300.6280) Spectroscopy, fluorescence and luminescence.

References and links

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1. Introduction

The optical cooling process in solids is based on anti-Stokes fluorescence. Coherent excitation, tuned to wavelengths longer than the mean emission wavelength, results in the

spontaneous emission with average photon energy which is above that of the coherent input. Thermalization of the electronic population within the energy levels requires absorption of lattice phonons to ensure energy conservation. Thermal energy is carried out from the material through fluorescence of blue-shifted photons, leading to a cooling effect.

Since the first observation of laser cooling in solids in 1995, achieved by Epstein *et al.* in a Ytterbium-doped ZBLAN glass [1], optical refrigeration has been obtained in several rare earth doped materials, with ordered and disordered structure [2–4]. Successive research has been devoted to the study of novel materials, as well as to the optimization of the cooling performance. For example, many experiments have been conducted with fluoride hosts, because the low phonon energy strongly reduces multi-phonon emission, a non-radiative process in competition with anti-Stokes fluorescence. The best current result is laser cooling of an Yb:YLF single crystal to 114 K, with cooling power of 750 mW [5].

There are many essential conditions needed in a sample in order to achieve an efficient cooling process, but they can be summarized in two measurable quantities such as the External Quantum Efficiency (EQE) and the background absorption. The EQE defines the radiative efficiency of the transition, taking into account the probability of the competing non-radiative decays and the extraction efficiency, as photons can be trapped inside the material due to reabsorption and total internal reflection. Optical transitions in trivalent rare earth ions embedded in fluorides typically achieve very high external quantum efficiencies due to the weak phonon coupling.

The other fundamental condition necessary to achieve efficient cooling is low background absorption, which essentially means high optical purity of samples. Contaminants embedded inside crystals indeed give spurious absorption bands, leading to either a reduction of the number of pumping photons that can initiate the anti-Stokes process or to trapping and energy down-conversion of the emitted photons. In case of rare earth ions, impurities can also activate non-radiative energy transfers [6]. In order to obtain samples with a low content of impurities, a basic requirement is the high-purity of the starting materials, as well as growth procedure and proper processing in an ultra-clean system [7]. Moreover, structural defects that cause heating processes as scattering of pumping light produce an increase of the parasitic absorption.

Currently, the study of the effect of impurities on the Yb cycle is of large interest to improve the efficiency of the cooling process. Identification of the main sources that influence the anti-Stokes cycle is required for an appropriate preparation and purification of the starting materials [8]. Effects of rare earth ions on optical refrigeration have been recently studied in oxide hosts, such as Yb:YAG [9].

This paper reports differences in the cooling efficiency between two Yb:YLF crystals, doped with the same concentration of Yb, with respect to amount of rare earth ion impurities embedded in the samples. Preliminary data from the first observation of this discrepancy have been previously reported in [10]. In this work, we provide identification of the involved species, obtained both with spectroscopic comparisons and with elemental concentration analyses. We report a qualitative energy transfer model that explains why the refrigeration was altered and which species are more detrimental for the cooling process.

2. Cooling efficiency model

The cooling efficiency η_c of a given material, defined as the ratio between the cooling power (P_{cool}) and the absorbed power (P_{abs}) from a laser source with wavelength λ , can be expressed as [11]:

$$\eta_c(\lambda, T) = \frac{P_{cool}}{P_{abs}} = \eta_{ext} \left[\frac{1}{1 + \alpha_b / \alpha_r(\lambda, T)} \right] \frac{\lambda}{\lambda_f(T)} - 1 \quad (1)$$

where T is the temperature of the material, η_{ext} is the EQE, λ_f is the mean emission wavelength of the cooling transition, and α_b is the background absorption coefficient, representing all parasitic absorption of the material at the wavelength λ . The α_b parameter can be considered temperature-independent [11,12]. Net cooling is achieved only when $\eta_c > 0$.

η_{ext} and α_b are the parameters used to characterize the cooling efficiency of a sample, while the resonant absorption α_r and the mean emission wavelength λ_f are spectroscopic parameters of the cooling transition, common to all samples of a specific material.

The α_b parameter is due both to undesired impurities and to scattering effects due to crystal defects. The lower the α_b / α_r ratio, the more efficient is the cooling process. This requires extremely high optical purity and high quality materials. The nature of the background absorption in cooling process is currently under investigation due to its importance for potential improvement of the efficiency of the process. Recent studies have already shown that the parasitic absorption is strongly correlated to the concentration of transition metals, especially Iron [5].

In this work we focused on the effect of rare earth ions impurities on the optical cooling efficiency of Yb:YLF. We studied two 5% at. Yb:YLF samples with slightly different relative amounts of other rare earth ions. The crystals were grown with the Czochralski method in a homemade furnace with resistive heating, optical diameter control and high vacuum cleaning system (with a pressure limit of 10^{-5} Pa). The growth atmosphere was made by argon and CF₄, which prevents the reduction of Yb ions.

The crystals were grown starting from raw materials of LiF, YF₃ and YbF₃ with a guaranteed purity of 99.999% (5N), provided by AC Materials (Orlando, FL, U.S.A.). The growth procedure was the same for the two samples, but different batches of starting materials were used, which caused the small difference in chemical composition. The pulling rate was 0.5 mm/hour, with a rotation rate of 5 RPM, and the growth temperature was between 860 °C and 880 °C. Due to the match between the ionic radii of Y³⁺ and Yb³⁺, the segregation coefficient is expected to be close to unity. The single crystalline structure was checked using a back-scattering Laue technique, which was also employed to identify the crystallographic axes, corresponding to the optical axes for tetragonal structures as YLF. We prepared parallelepiped samples with the optical axes parallel to the edges, for spectroscopy and cooling measurements. All the six facets of the cooling samples were polished to laser grade to enhance their transmission and increase their optical quality.

3. Cooling measurements

Cooling measurements were performed by placing each sample in a custom-made vacuum chamber, and measuring its temperature when irradiated with a laser beam. A detailed layout of the experimental setup is reported in [10]. The chamber is evacuated to pressures of 10^{-3} Pa in order to minimize convective thermal load due to air. The crystal is suspended on two optical fibers of 120 μ m diameter, in order to provide a thermal insulation for the sample, reducing the heating processes due to the conduction. The chamber has four optical windows, suitable for pumping and observing the sample at the same time.

In order to experimentally investigate the dependence of the cooling efficiency on the excitation wavelength, we employed four laser diodes with central emission within the absorption band of Ytterbium: 940 nm, 980 nm, 1030 nm and 1060 nm. All the pumping beams were polarized parallel to the c -axis of the sample to access larger absorption.

Contactless techniques are required to measure the temperature of the crystal, in order to avoid alteration of the heat capacity of the system. We used a thermal camera with a microbolometer sensor (Raytheon 2500AS) to detect temperature differences between the

crystal and the chamber. This sensor was previously calibrated to obtain the proportionality coefficient between temperature difference and pixel brightness. The temperature change was measured monitoring the sample while it was excited with a laser source. From the thermal images acquired, the temperature difference of the sample relative to the environment was calculated for each pumping wavelength. Once the sample reaches the thermal equilibrium with the environment, the temperature stabilizes and we determined the difference with respect of the initial temperature, corresponding to the absence of pumping beam.

Figure 1 shows the results of the cooling measurements for the two samples, along with the model curve, expressed by Eq. (1), used to fit the experimental data. It can be noticed that, despite the same host and Yb doping level, one sample shows a higher cooling efficiency than the other. Furthermore, noticeable difference in the zero-crossing wavelength of the two curves already points to a difference in the EQE of the two samples. We will refer to the sample with higher cooling efficiency as sample *A* and to the other, with lower efficiency, as sample *B*. For sample *A* the results of the fit are $\eta_{ext} = 0.999 \pm 0.001$ and $\alpha_b = (4.2 \pm 0.2)10^{-4} \text{ cm}^{-1}$. For sample *B* we obtained $\eta_{ext} = 0.988 \pm 0.001$ and $\alpha_b = (4.0 \pm 0.2)10^{-4} \text{ cm}^{-1}$. From these values, it is clear that the difference in cooling efficiency could be attributed to a different value of EQE between the two samples.

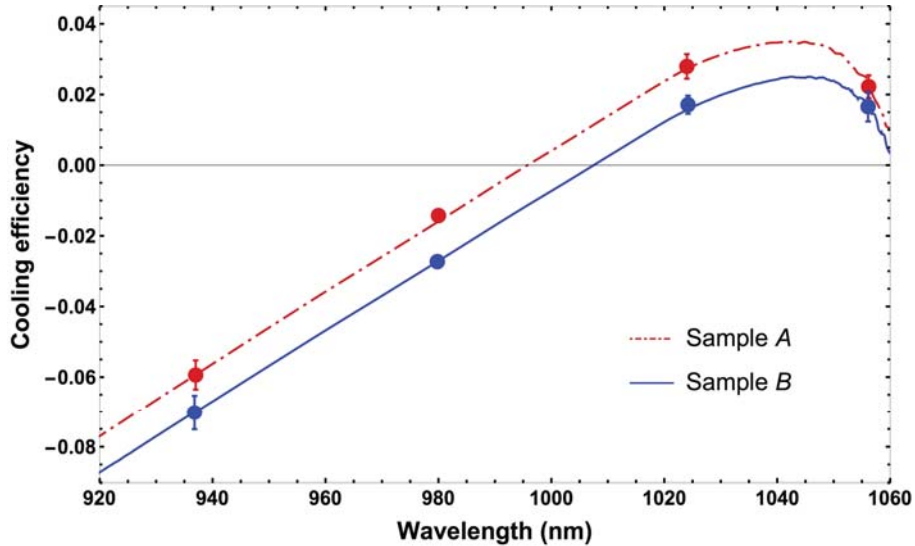


Fig. 1. Cooling efficiency data points and corresponding fits, as functions of the incoming wavelength, for samples *A* and *B*.

4. Spectroscopy and identification of impurities

To gain further insight into the nature of the observed difference between the two samples, we performed their optical characterization, starting from the absorption coefficient and the steady state fluorescence spectrum of the Yb band.

Absorption spectra were collected using a Varian Cary 500 spectrophotometer, between 890 nm and 1100 nm, with a resolution of 0.3 nm. The spectra overlap almost perfectly, with the only exception of the highest peak at about 960 nm, in which the small difference is caused by instrument errors at large absorbance values [10].

Fluorescence spectra of the Yb ions were measured by exciting the samples with a 940 nm laser diode delivering ~300 mW. Wavelength of the pump was selected to avoid reabsorption issues and exclude the excitation laser from the sampled fluorescence. The emission, collected perpendicularly to the pump beam to reduce spurious scattering, is focused on an

entrance slit of a monochromator with a 600 groove/mm diffraction grating, and sampled in the with an InSb detector, feeding a lock-in amplifier. A Glan-Thompson polarizer is placed at the input port of the monochromator to select the incoming polarization state. A custom holder is used to place the crystal exactly in the same position, ensuring measurement repeatability. Also in this case, no noticeable differences have been detected between the spectra of the two crystals [10].

From the similarity of these measurements we conclude that the discrepancy in the cooling efficiency appears to be unrelated to the absorption and emission properties of the Yb in the two samples. This motivated us to perform additional investigations to determine the cause of that difference. We focused our research on the optical emission of other possible rare earth ions contaminants, outside the band of Yb. Therefore, we investigated fluorescence emission from the crystals in the green region, between 535 nm and 560 nm, and in the near infrared (NIR) region, between 720 nm and 860 nm. We employed the same 940 nm pump laser diode, the monochromator with a 1200 groove/mm diffraction grating and a PMT detector with an almost flat spectral response between 350 nm and 800 nm.

Figure 2 shows the results of the measurements in the green spectral region for the two samples under the same excitation conditions. The spectra are close in shape, but dissimilar in magnitude, indicating that emission is coming from the same source, but that the concentration of the emitter is different in the two samples. The fact that sample *B* is emitting with higher intensity than sample *A*, leads to the conclusion that sample *B* contains more impurities than sample *A*. The observed emission in both samples is anti-correlated with the EQE measurement, suggesting that the source of the emission likely participates in the non-radiative quenching of the Yb^{3+} fluorescence.

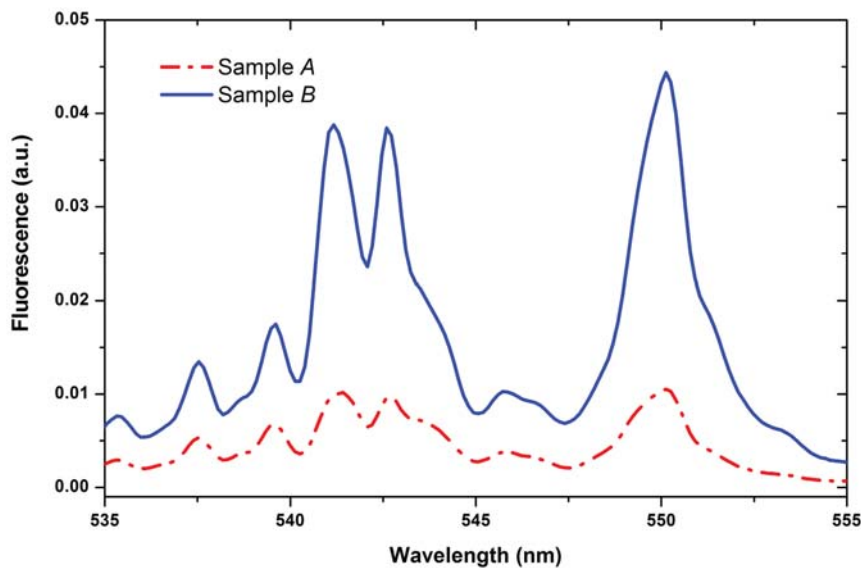


Fig. 2. Spectra of the green fluorescence collected from the Yb:YLF samples.

To identify the elemental source of this emission, we considered fluorescence spectra of YLF crystals doped with other rare earth ions. The same measurements were carried out on a database of fluoride crystals, previously grown in our laboratories. The best match between the spectral features was observed with an Erbium-doped YLF crystal and a Holmium-doped YLF crystal, excited with a 532 nm diode pumped solid-state laser. Acquired spectra from

these crystals in the green region are shown in Fig. 3, together with the unknown emission from the Yb:YLF samples (here sample *B*). As can be seen from the plot, excellent agreement is found between the combined emission of the two test samples and the green emission observed in the cooling crystals. Hence, we can directly conclude that the emission in the green region is predominantly caused by the Erbium and Holmium impurities embedded in the Yb:YLF samples and, combined with the first observation, conclude that these impurities can assist in lowering the external quantum efficiency of the cooling process in Yb:YLF.

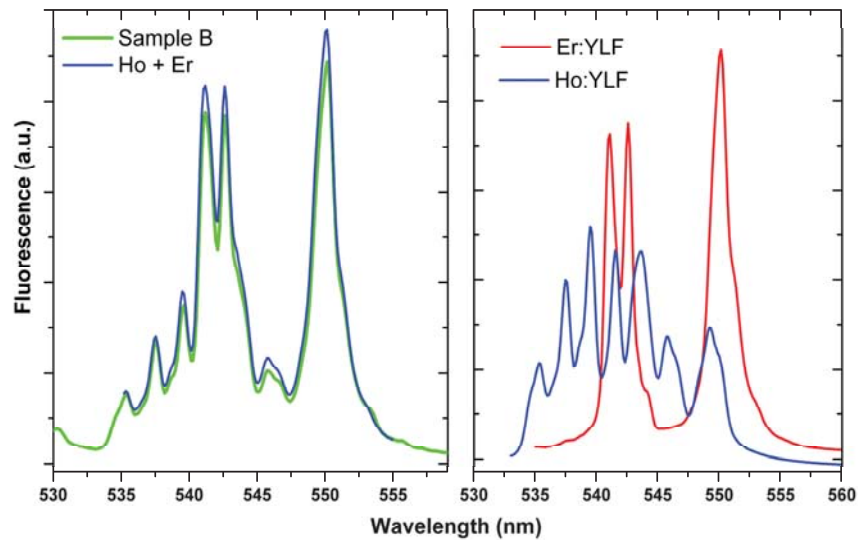


Fig. 3. Left: Spectrum of the fluorescence in the green region from sample *B*, superimposed with a balanced sum of fluorescence spectra from the Erbium- and Holmium-doped test samples. Right: Fluorescence spectra from Erbium- and Holmium-doped test samples (in arbitrary units).

Figure 4 shows the result of NIR spectroscopy on the cooling samples. Also in this case, the spectra are different in counts but not in shape, suggesting that sample *B* contains more impurities. Three distinct areas can be identified in the spectrum, corresponding to the emission from three different ions. As before, we identified the responsible source ions by sampling the fluorescence from other YLF crystals doped with other rare earth ions.

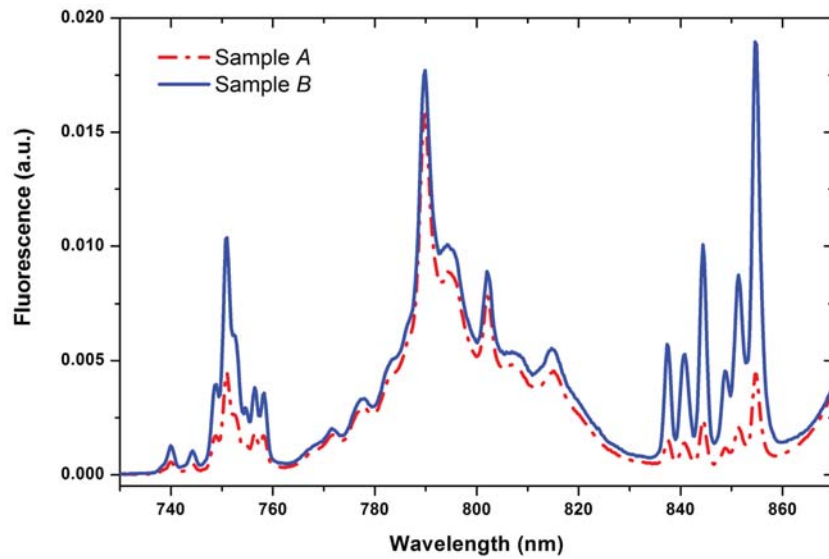


Fig. 4. Spectra of the NIR fluorescence collected from the cooling samples.

Figure 5 shows the spectra acquired from other test samples. Comparing these spectra with those depicted in Fig. 4 allows determining which element was the source of a particular region of the NIR fluorescence of cooling samples. Proceeding in this way, the emission on the left, from 740 nm to 760 nm, is attributed to Holmium ions; the central part, between 780 nm and 820 nm, is emitted by Thulium ions; while Erbium ions are responsible for the emission band between 830 nm to 860 nm.

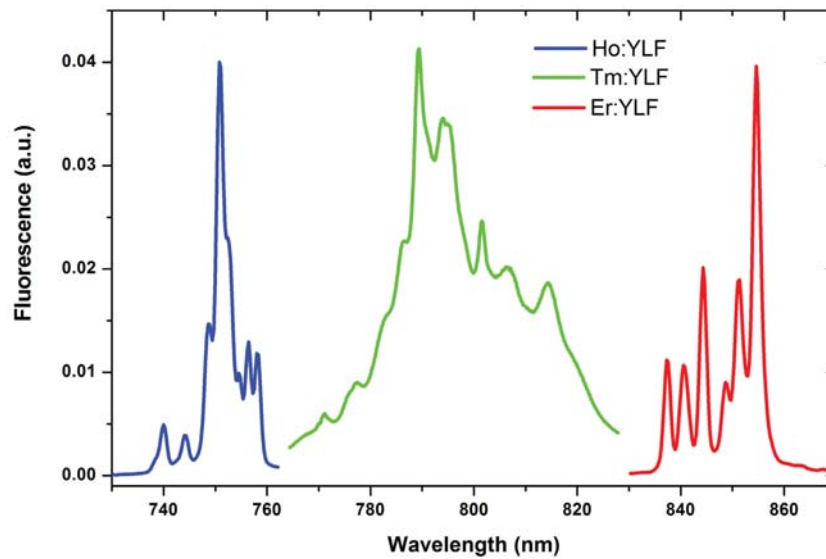


Fig. 5. NIR spectra from test samples, from left to right: Holmium, Thulium and Erbium fluorescence.

By extending the investigation of the fluorescence in the green and NIR region, we confirm the presence of Holmium, Erbium and Thulium as additional contaminants in our

cooling samples. Among the spectroscopic methods employed to investigate the different cooling performances of the two samples, the fluorescence spectra acquired outside the Ytterbium band resulted the most suitable to identify the different amount of impurities embedded inside the crystals as the main source of the discrepancy in cooling efficiency. This technique efficiently allows detecting differences of the order of magnitude of few ppm (parts per million) through the intensities of the fluorescence spectra.

5. Elemental analysis

To supplement our optical measurements and to quantify the amounts of impurities included into the cooling crystals, as well as to rule out further contaminations from other elements, an elemental analysis on the two Yb:YLF samples was performed by means of Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS) [13]. Results of these measurements are reported in Table 1. Only the contaminants relevant to this work are shown. The analysis confirms the presence of Erbium, Holmium and Thulium ions in both of the cooling crystals, consistent with the optical investigation. In addition to that, the overall concentration of impurities was between 2 and 3 ppm in both samples, considerably lower than the 10 ppm threshold guaranteed by the starting material supplier.

Table 1. Concentration of impurities in the Yb:YLF cooling samples

Element	Sample <i>A</i>	Sample <i>B</i>
	Conc. (ppm)	Conc. (ppm)
Erbium	0.25 ± 0.05	1.1 ± 0.2
Holmium	0.39 ± 0.08	0.72 ± 0.04
Thulium	1.4 ± 0.6	0.7 ± 0.3

Even though the total amount of measured impurities is approximately the same in both samples, the relative concentrations of the elements are not. In particular, sample *B* contains more Erbium and Holmium than sample *A*. The ratios of concentrations of Erbium, Holmium and Thulium in sample *A* over sample *B*, are compared directly in Table 2, calculated from the LA-ICP-MS analysis and from the peak intensities of green and NIR emission spectra, reported in Figs. 2 and 4.

Table 2. Ratios of impurities concentrations from LA-ICP-MS analysis and fluorescence peaks in green and NIR regions

	LA-ICP-MS	Green	NIR
Erbium	4.4 ± 1.0	4.7	4.3
Holmium	1.8 ± 0.4	2.6	2.3
Thulium	0.5 ± 0.3	N/A	1.1

The table clearly indicates that for both Erbium and Holmium, the ratios of the peaks match approximately well between the two evaluation methods and thus give great confidence in the assignment of the spectra and the overall experimental consistency. Although the intensities of Thulium emission are almost the same, the concentrations are different between the two samples. In particular, sample *B* contained about a half the amount of Thulium than sample *A*. Thus, it is clear that an indirect energy transfer mechanism is responsible for emission by the Tm ions. To address this possibility, we propose a qualitative

model of the energy transfer between Yb and the rare earth impurities, detailed in the following section.

6. Energy transfer model

Systems doped with multiple rare earth ions have been extensively studied in recent years. When dealing with materials with a dominant element and some foreign contaminants, the first way to understand relations between different species is to assume direct energy transfers from the pumped abundant ion, in our case Ytterbium, to the other impurities. A scheme of the direct transitions from Ytterbium to Erbium, Holmium and Thulium ions, derived from literature data [14], is reported in Fig. 6.

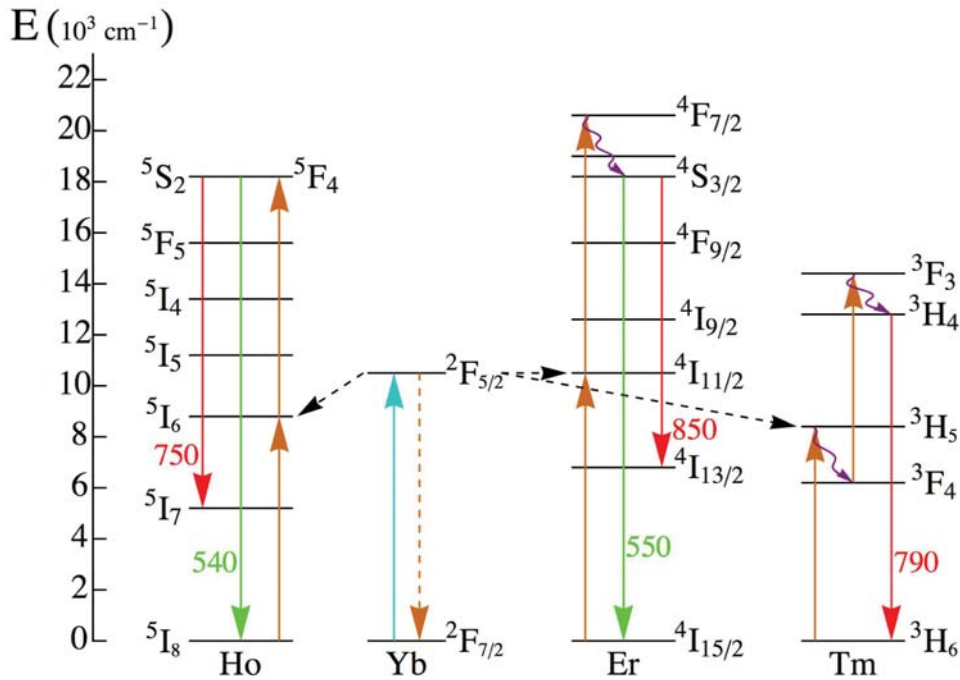


Fig. 6. Direct energy transitions between elements detected in the samples. Laser pump is shown in cyan. Direct transfers from Ytterbium are shown in orange. Dotted lines represent the non-radiative de-excitation of the donor and solid lines represent transitions due to acquired excitations in the acceptor. Radiative emissions are depicted in green or red, according to their color, with the approximate wavelength in nm. Internal non-radiative decays are shown in purple.

However, data obtained from spectroscopic and elemental analyses indicate that Erbium and Holmium impurities emit with intensities proportional to their concentrations, while Thulium ions do not. In addition to that, the presence of Thulium impurities seems not to influence the high external quantum efficiency detected in sample *A*. These results cannot be explained by allowing the transitions shown in Fig. 6. To explain these discrepancies we found in collected data, we propose a different model of the transitions in our cooling samples, reported in Fig. 7.

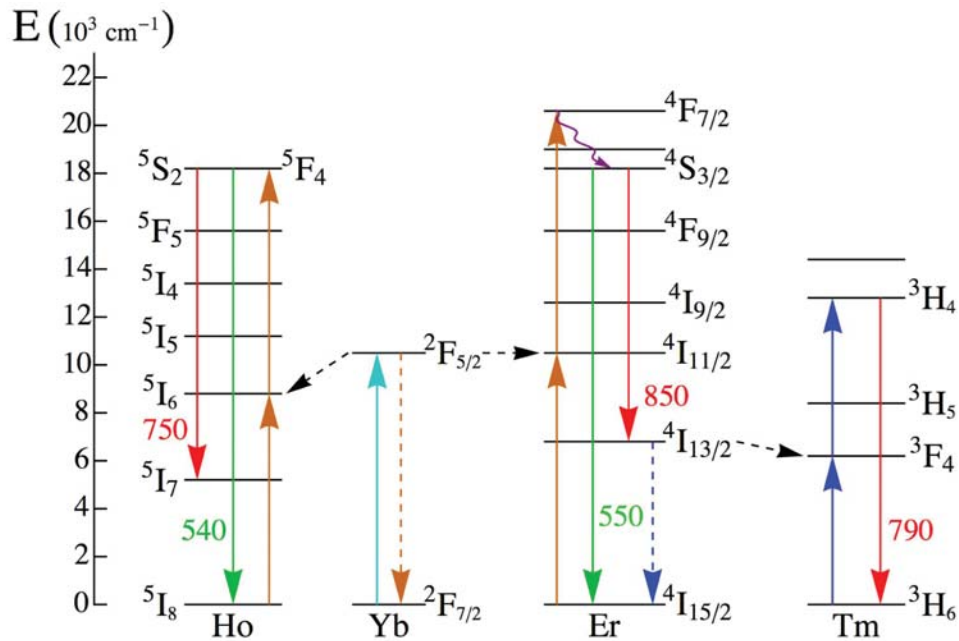


Fig. 7. Qualitative model of the energy transfer mechanisms inside the cooling samples. Transfers from Erbium are shown in blue. All the other colors are detailed in the caption of Fig. 6.

During the cooling process, the laser excites the Ytterbium ions, which, due to the long lifetime of the excited state, have a finite probability to transfer part of their energy to other impurities, instead of radiating through a photon emission. Only photons re-emitted by Ytterbium are capable to subtract thermal energy from the system. Hence, any process that removes ions from the excited level of Ytterbium can reduce the cooling efficiency of the crystal, through an additional probability of a non-radiative transition [7].

Because of the proportionality between fluorescence and concentration ratios, it is reasonable to assume that Erbium and Holmium ions gain energy directly from the excited state of Ytterbium, via the de-excitation of the two ions, as shown in Fig. 7. For Thulium ions, on the other hand, we suggest an indirect energy transfer process that uses excitation states of Erbium ions as an intermediate step in energy relaxation.

The indirect energy transfer pathway leading to Thulium excitation shown in Fig. 7 has a higher probability than the corresponding direct transfer reported in Fig. 6, because the energy difference between the $^4I_{13/2}$ level of Erbium and the 3F_4 level of Thulium is smaller than the gap between the same Thulium level and the excited state of Ytterbium. This transition, besides being energetically favorable, explains also why the fluorescence intensity of Thulium was approximately the same in samples *A* and *B*. The larger concentration of Erbium in sample *B* compensated for the lack of Thulium, by increasing the amount of transferred energy. The apparent balance of these two effects at this Yb^{3+} concentration is a plausible cause for nearly the same fluorescence intensity from Thulium in the two crystals.

Both these models provide an estimation of the fraction of energy converted into heat by excited impurities. Erbium and Holmium contribute in the same way in the two mechanisms, emitting about 3000 cm^{-1} of thermal energy each when pumped. If we consider Thulium ions in the direct pumping scheme shown in Fig. 6, we have to account two non-radiative decays, plus the energy gap between Ytterbium and Thulium described above, leading to a total dissipated energy of about 10000 cm^{-1} . On the other hand, in the indirect model proposed in Fig. 7, the energy mismatch crossed to pump Thulium from Erbium is lower and there are no

non-radiative decays, thus the thermal energy dissipated is about 800 cm^{-1} , more than one order of magnitude lower than in direct pumping, and an order of magnitude lower than Erbium and Holmium impurities. Thus, these calculations indicate that our indirect model is in better agreement with data than the direct transfer model.

Moreover, the model we suggest also qualitatively explains the discrepancy in the external quantum efficiency between the two samples. We note that in cases of possible transfers of Yb excitation to Holmium and Erbium ions, non-radiative recombination pathways may be activated (see Fig. 7). Thus, detection of green or NIR Holmium and Erbium up-conversion signals implies parasitic heating. For large external quantum efficiencies $\eta_{\text{ext}} = W_r / (W_r + W_{nr}) \approx 1 - W_r / W_{nr}$, where W_r is the external radiative rate and W_{nr} is the non-radiative recombination coefficient. Taking radiative recombination rate the same for both samples, we obtain the following ratio $(1 - \eta_{\text{ext},B}) / (1 - \eta_{\text{ext},A}) = W_{nr,B} / W_{nr,A} = (0.012 \pm 0.001) / (0.001 \pm 0.001) \approx 12 \pm 12$. This fraction appears in agreement with the product of the ratio of Erbium and Holmium concentrations in samples *B* and *A* (from Table 2): $(4.4 \pm 1) \cdot (1.8 \pm 0.4) \approx 8.5 \pm 3.5$. While it is early to draw quantitative conclusions, this agreement does scale with our qualitative model.

Namely, both Erbium and Holmium impurities can reduce the number of Ytterbium ions involved in the cooling cycle, while Thulium did not affect it. Transfers to Erbium and Holmium shrink the ratio between the number of blue-shifted photons escaping from the crystal and the number of absorbed photons and hence the EQE of the sample, due to the increased probability of non-radiative relaxation pathways. By comparing this statement with concentration data reported in Table 1, it can be inferred that the EQE was larger in sample *A* than in sample *B* due to the lower amount of Erbium and Holmium impurities, while Thulium had no apparent influence on the cooling efficiency.

We point out that further studies are needed to evaluate the effect of rare earth contaminants more precisely. In particular, the efficiency of the transfers would depend on the concentration of the ions, thus our current results are only applicable for the stated amounts of impurities and for the 5% Yb³⁺ doping level. Further studies with other contaminant concentrations and as a function of Yb doping should be carried out to verify this model and quantitatively evaluate the effect of the rare earth contaminants on cooling.

7. Conclusions and perspectives

In this work we characterized the optical refrigeration efficiency of two 5% Yb-doped YLF crystals with slightly different concentrations of other rare earth ions impurities. This discrepancy caused a lower value of the EQE in one of the cooling samples. Both the spectroscopic study and the elemental analysis identify traces of Erbium, Holmium and Thulium in the cooling samples, with a global concentration of about 2 ppm.

We provide a model of the energy transfer processes inside the crystals that explains which elements are responsible for the reduction of cooling performance. This model is supported quantitatively both by the fluorescence spectra and by the results of the elemental analysis. According to the model, Erbium and Holmium ions are directly excited by relaxation of Ytterbium, while Thulium impurities gained energy through de-excitation of Erbium ions. We identified Erbium and Holmium as primary causes of reduction of the EQE in one sample with respect to the other. Furthermore, our observations suggest that Thulium impurity does not show detrimental effects on cooling, at least within the range of our experimental parameters. We suggest reduction of Erbium and Holmium in the starting materials as a possible way to potentially enhance future performance of optical refrigeration in fluoride crystals.

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