Universita` di Pisa

Graduate School of Basic Sciences
“Galileo Galilei” – Physics

XVIII cycle PhD course

Pre-thesis

Cooling effect on fluoride crystals

NPI project between Pisa University and ESA-ESTEC

Azzurra Volpi

Supervisor: *Prof. M. Tonelli*
Prof. A. Di Lieto

23rd October 2014

Outline

- **Optical cooling in solids: background and thesis plane**
  - Anti-Stokes process
  - Cooling efficiency model
  - Trivalent rare earth ions in fluoride crystalline hosts
  - State of the art: major results
  - Applications
  - Thesis work: roadmap

- **Investigation of the optical cooling process in Yb in $LiYF_4$ single crystals**
  - Details of Czochralski growth and sample preparation
  - Spectroscopic analysis
  - Cooling test: cooling efficiency measurements
  - Low temperature spectroscopy: cooling power estimation

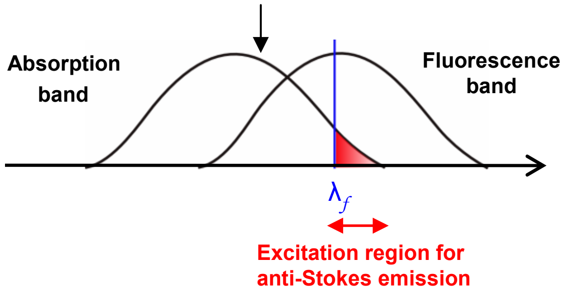
- **Novel scheme for optical cooling in solids: investigation of Yb-Tm codoping**
  - Czochralski growth, spectroscopic analysis and cooling test: YLF:5%Yb-0.0016%Tm
  - Model for efficiency enhancement based on Yb-Tm energy-transfer

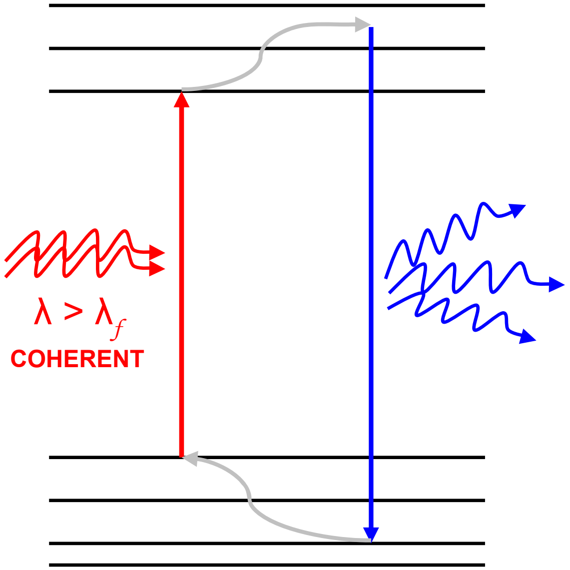
Optical cooling in solids: anti-Stokes process

OPTICAL COOLING: process by which a system cools down through interaction whit laser light.

The active element is a dopant ion embedded in a transparent solid, the cooling process is achievable through anti-Stokes emission.

Basic condition: overlap between absorption and fluorescence bands





$h\nu_f \approx h\nu + K_bT$

*Following coherent excitation at $\lambda > \lambda_f$, **photons with higher energy than those absorbed are spontaneously emitted**. Thermalization of electronic population within the manifolds occur via **annihilation of lattice phonons**.*
→Thermal energy (and entropy) is carried out from the material trough radiative emission, resulting in a net cooling process.

- *P. Pringsheim, Z. Physik 57, (1929)* → **PREDICTION:** cooling matter via anti-Stokes luminescence
- *L. Landau, J. Phys. (Moscow) 10, (1946)* → **THEORY (thermodynamics):** assignment of entropy to light
- *A. Kastler, J. Phys. Radium 11, (1950)* → **PREDICTION:** anti-Stokes cooling in **solids** by using **RE^{3+} ions**
- *R.I. Epstein et al. Nature, 377 (1995)* → **FIRST EXPERIMENTAL DEMONSTRATION:** Yb-doped ZBLAN glass
- 2010-2014: **CRYOGENIC RESULTS**

LiYF$_4$:10%Yb COOLED TO 114K (ΔT=180K)
S.D. Melgaard et al. Opt.Exp. 22 (2014)

Cooling efficiency model

- *Ideal efficiency:* $\Delta E = h\nu_f - h\nu \approx k_B T$

$$\eta_c = \frac{P_{cool}}{P_{abs}} = \frac{\lambda}{\lambda_f} - 1 \approx \frac{k_B T}{h\nu}$$

- *Realistic efficiency:*
  - EQE
  - Impurities mediated processes

→ $p(\lambda, T) = \eta_{ext}\eta_{abs}$

$$\boxed{\eta_c(\lambda, T) = \frac{P_{cool}}{P_{abs}} = \eta_{ext}\eta_{abs}\frac{\lambda}{\lambda_f(T)} - 1}$$

EQE

$$\eta_{ext} = \frac{\eta_e W_{rad}}{\eta_e W_{rad} + W_{nr}} \uparrow \Leftrightarrow W_{nr} \downarrow, \eta_e \uparrow$$

- ***Non radiative-decay rate*** -Multiphonon decay
  - Energy-transfer due to impurities
- ***Extraction efficiency*** - TIR
  - Reabsorption

$$\eta_{abs}(\lambda, T) = \frac{\alpha(\lambda, T)}{\alpha(\lambda, T) + \alpha_b} \uparrow \Leftrightarrow \alpha(\lambda, T) \uparrow, \alpha_b \downarrow$$

Background absorption coefficient

CRITICAL PARAMETER

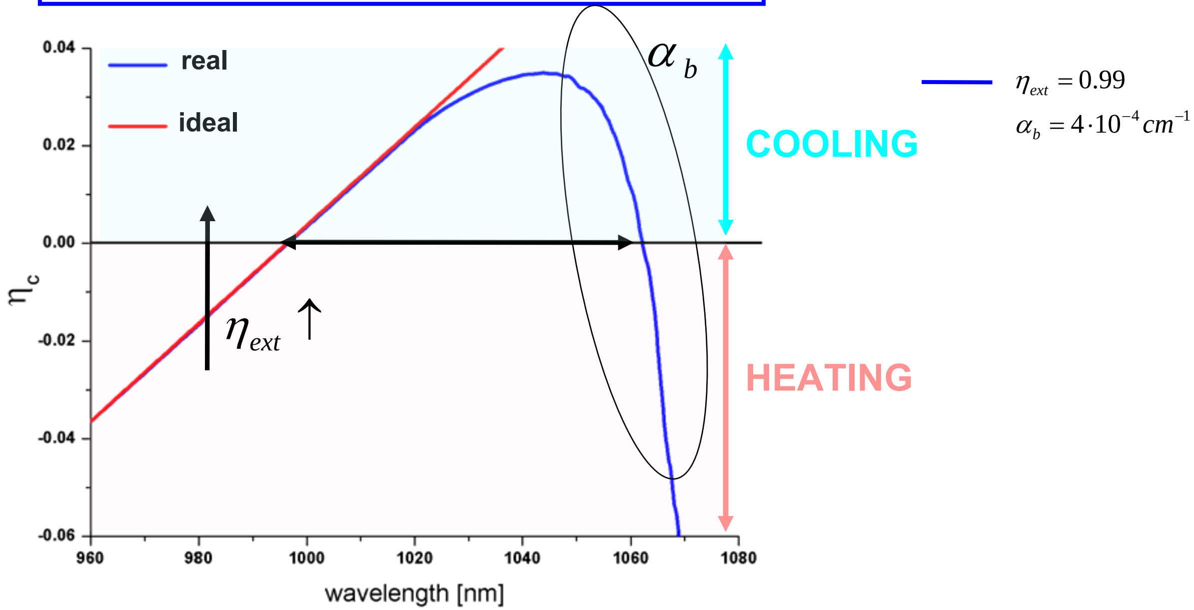
- ***Impurities*** - Absorption bands
  - Energy-transfer processes
- ***Defects***

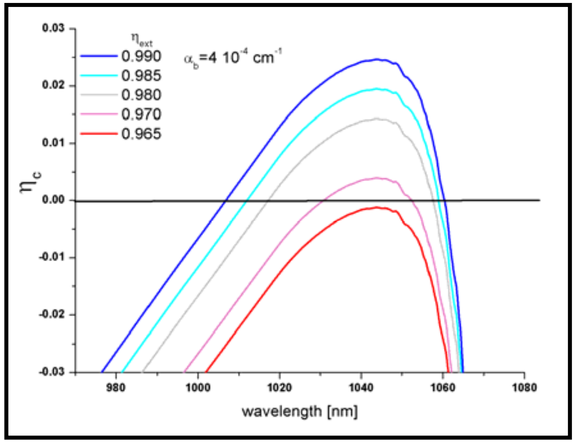
1) **HIGH OPTICAL PURITY** ← open problem
2) **LOW** W_{nr} → RE^{3+} in fluoride crystalline hosts

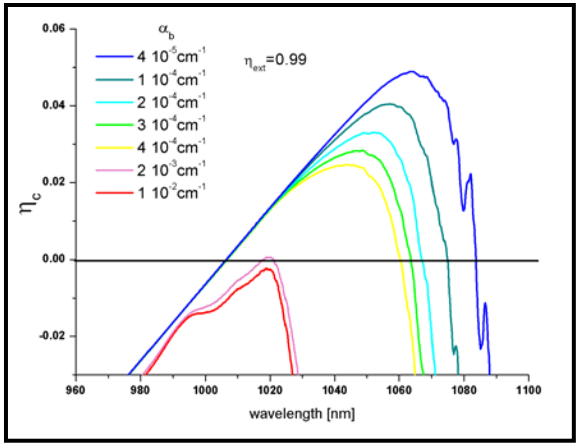
3) **Study on sample geometry and surface polishing technique:** $\eta_e \uparrow$

Cooling efficiency model

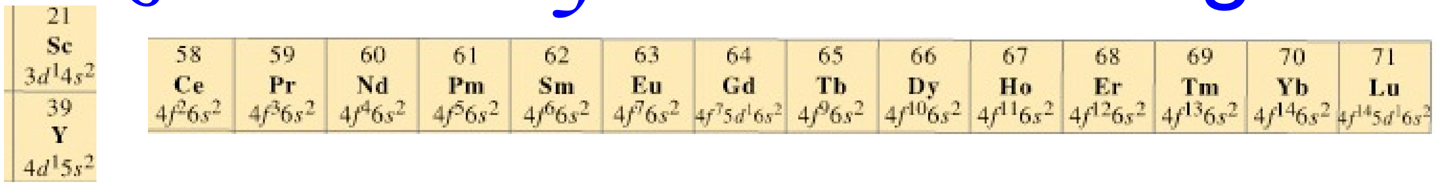
$$\eta_c(\lambda,T) = \frac{P_{cool}}{P_{abs}} = \eta_{ext}\eta_{abs}\frac{\lambda}{\lambda_f(T)} - 1$$







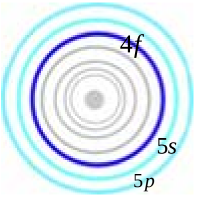
RE^{3+} ions in fluoride hosts: high EQE

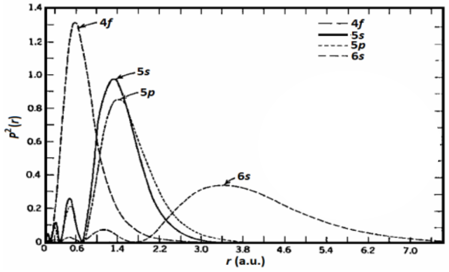


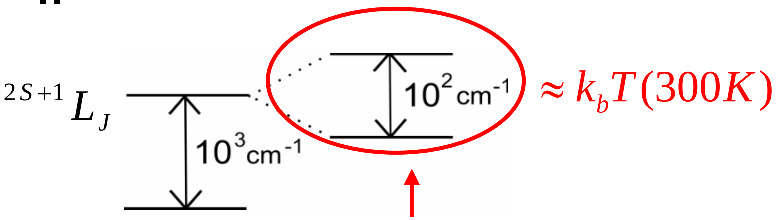
21	39
Sc	**Y**
$3d^1 4s^2$	$4d^1 5s^2$

58	59	60	61	62	63	64	65	66	67	68	69	70	71
Ce	**Pr**	**Nd**	**Pm**	**Sm**	**Eu**	**Gd**	**Tb**	**Dy**	**Ho**	**Er**	**Tm**	**Yb**	**Lu**
$4f^2 6s^2$	$4f^3 6s^2$	$4f^4 6s^2$	$4f^5 6s^2$	$4f^6 6s^2$	$4f^7 6s^2$	$4f^7 5d^1 6s^2$	$4f^9 6s^2$	$4f^{10} 6s^2$	$4f^{11} 6s^2$	$4f^{12} 6s^2$	$4f^{13} 6s^2$	$4f^{14} 6s^2$	$4f^{14} 5d^1 6s^2$

RE^{3+} : $[Xe]4f^n \quad n = 1-14$ → **optical transition 4f - 4f**







Stark splitting (crystal field)

Shielding of valence electron 4f by the outermost filled 5s and 5p shells from the interaction with crystal field

→ **LOW** W_{nr}

→ **Spectra "atomic-like" in crystal host** :sharp lines→ $\alpha \uparrow$

The optical transition 4f-4f are partially allowed by crystal field mixing.→ **METASTABLE LEVELS**

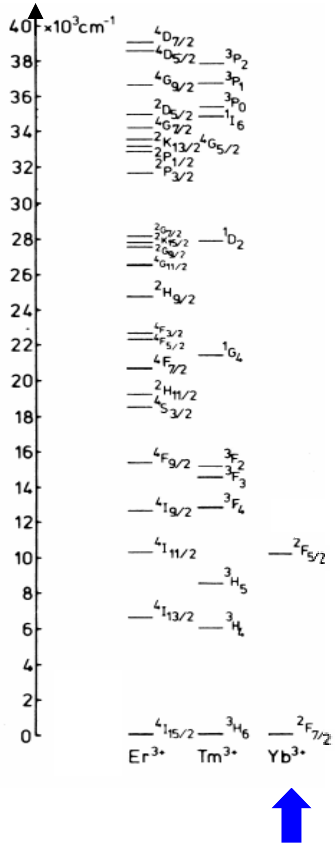
FLUORIDE CRYSTALLINE HOST: Low phonon energy (300-500cm^{-1}) → LOW W_{nr}

- Low inhomogeneous broadening with respect of glass → $\alpha \uparrow$
- Non hygroscopic
- Good thermal conductivity (4-7 W/mK)
- Good hardness (3-5 Mohs)
- Low refractive index
- Gap ~ 5eV→ Transparence window from UV (200-300nm) to IR (6-7µm)

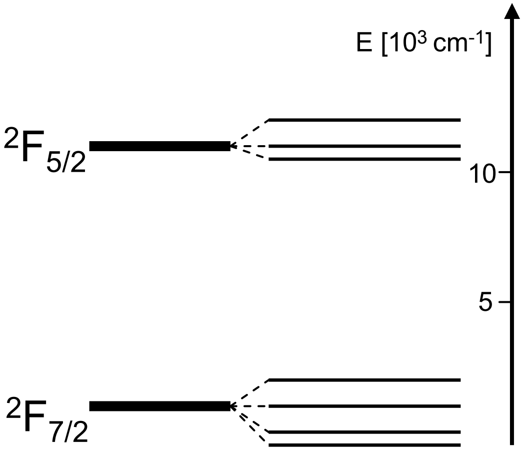
Yb^{3+}

How to choose the best transition?

- *Ground state transition* → $W_{rad} \uparrow$
- $\eta_{c,id} = \frac{\lambda - \lambda_f}{\lambda_f}$
- *Gap width* → W_{nr} *, pumping sources*
- *Energy-transfer processes (phonons assisted)*
- *Overlap width* → *width of excitation region*



Yb³⁺: $[Xe]4f^{13}$ → **Simplest energy level structure among RE³⁺**



- **No higher excited state** → Energy-transfer Yb-Yb prevented
- **1 µm transition** → Multiphonon decay rate negligible in fluoride hosts
  → High-power pumping laser readily available
- **Large overlap** between absorption and fluorescence bands.

$$\eta_{ext}\eta_{abs} > 1 - \frac{k_b T}{h\nu_f} \approx 98\% \quad (Yb, 300K)$$

$$1\mu m \leftrightarrow h\nu_f \approx 1.24eV$$

State of the art: major results

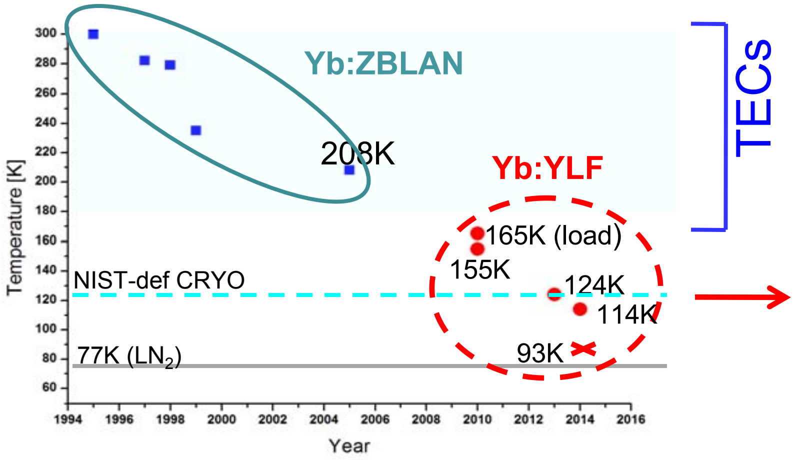
- Optical cooling of **YLF:5%Yb** down to **155K** with estimated steady-state cooling power of **120mW** (pump: **thin disk diode-pumped Yb:YAG, 9W @ 1023nm, multi-pass cavity)**
  D.V. Seletskiy, S.D. Melgaard, S. Bigotta, A. Di Lieto, M. Tonelli, M. Sheik-Bahae, Nature Photonics, 4 161 (2010)

- Optical cooling of a **semiconductor load** (GaAs/InGaP) to **165K** using **YLF:5%Yb** (**20mW)**
  D.V. Seletskiy, S. Melgaard, A. Di Lieto, M. Tonelli, M. Sheik-Bahae, Optics Express 18, 18061 (2010)

- Optical cooling **of YLF:5%Yb** down to **124K** (**50mW**) and sequentially to **119K** (**18mW**) lowering the copper holder temperature to 210K
  (pump: **custom-designed Yb fiber laser 50W @ 1020nm, multi-pass cavity**)
  S.D.Melgaard, D.S.Seletskiy,A. Di Lieto, M. Tonelli, M. Sheik-Bahae, Optics Letters, 38, 1588 (2013)

- **RECORD RESULT**: **YLF:10%Yb** cooled to **114K** (ΔT=180K)
  S.D.Melgaard, D.S.Seletskiy, V. Polyak, Y. Asmerom and M. Sheik-Bahae, Optics Express, 22, 7756 (2014)

- Optical cooling of **YLF:10%Yb** to **93K** lowering the copper holder temperature to 270K (ΔT=180K)
  S.D. Melgaard, A. Albrecht, M. Hehlen, D.V. Seletskiy and M.Sheik-Bahae CLEO 2014, OSA, paper FTh4D.4



Yb-doped $LiYF_4$ single crystals allowed to achieve CRYOGENIC TEMPERATURES (till ~100K)

Applications: cooling for space

Today the **implementation** of a **first generation** of **optical all-solid state cryocooler** can be considered in earnest and is highly appealing especially for **space applications (ideal solution** for many missions).

- **Zero-vibration**
- No moving parts
- Compactness
- Long lifetime
- Enhanced reliabilty (solid state design)
- Low electromagnetic interference

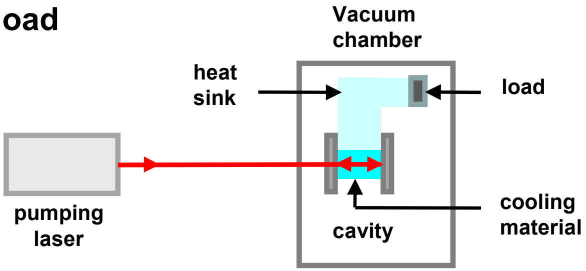
→ ***Significant improvements in high precision space-based technologies:***

- *IR detectors for imaging (focal plane cooling)*
- *Ultra-stable laser for atomic clocks and gravitation wave detectors*

- ***Access to temperatures below the cut-off for TECs (~180K),*** *where no other vibration-free technologies are available at moment* → ***Substitution of TECs between 180 and 90K***

Components of a device:

- **cooling material: generation of cooling power by anti-Stokes process** ← **Thesis work**
- **laser system → absorption enhancement**
- **heat sink: connection between the cooling material and the load**



Thesis work: Optical cooling in fluoride crystals

PURPOSE: **Optimization of the cooling material** for the development of a **first generation of optical all-solid cryocooler**.

CONTENT: Investigation of the **optical cooling process** for three different **Yb-doped fluoride crystalline host** (**$LiYF_4$, $LiLuF_4$, KYF_4**) with doping level varying between **5** and **10%wt.**.

$$d\uparrow \Rightarrow \alpha(\lambda,T)\uparrow \Rightarrow \eta_{abs} = \frac{1}{1+\alpha_b/\alpha(\lambda,T)}\uparrow$$

The increase of doping level provides a route to decrease the $\alpha_b/\alpha(\lambda,T)$ ratio.

ROADMAP:

1) **$LiYF_4$ (YLF)**
2) **LiLuF4 (LLF)**
3) **KYF4 (KYF)**

- Czochralski growth of single crystals with different Yb doping level: 5%, 7.5%, 10%
- Optical characterization of sample
- Cooling test
- Low temperature spectroscopy (80-300K): MAT, steady-state cooling power at low temperatures
- 10K spectroscopy: Stark structure of Yb in the investigated host

4) **Comparative analysis of samples, study of a preliminary prototype**

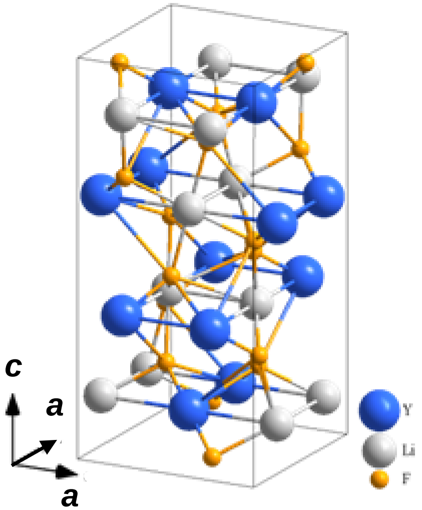
SO FAR:
- Measurements of cooling efficiency in YLF host as a function of Yb doping level (5-10%)
- Novel scheme for optical cooling in fluoride crystals based on **Yb-Tm energy-transfer**: enhancement of cooling efficiency

Investigation of optical cooling in Yb*-doped* YLF *crystals*

Lithium Yttrium Fluoride ($LiYF_4$) crystal

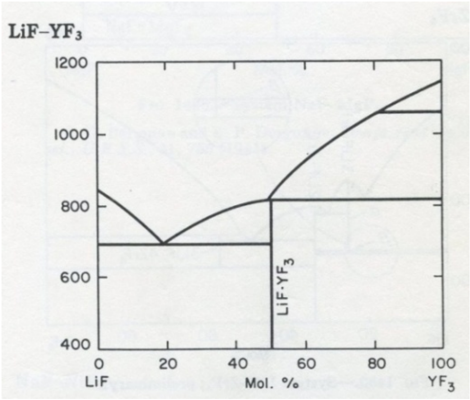
- Excellent laser performances with different RE^{3+} ions
- Best performing material so far in optical cooling of solids

Crystal structure	**TETRAGONAL (uniaxial)**
Point group	$I4_{1/a}$
Density	3.99 (g/cm^3)
Phonon energy	**440 cm^{-1}**
Thermal conductivity (300K)	***a* axis: 5.3 W/mK** ***c* axis: 7.2 W/mK**
Refractive index (640nm)	**n_o= 1.453** **n_e=1.475**
Hardness	**4-5 Mohs**



Unit cell of YLF crystal

Phase diagram LiY-YF$_3$ system



INCONGRUENT MELTING

LiY 53%
YF$_3$ 47%

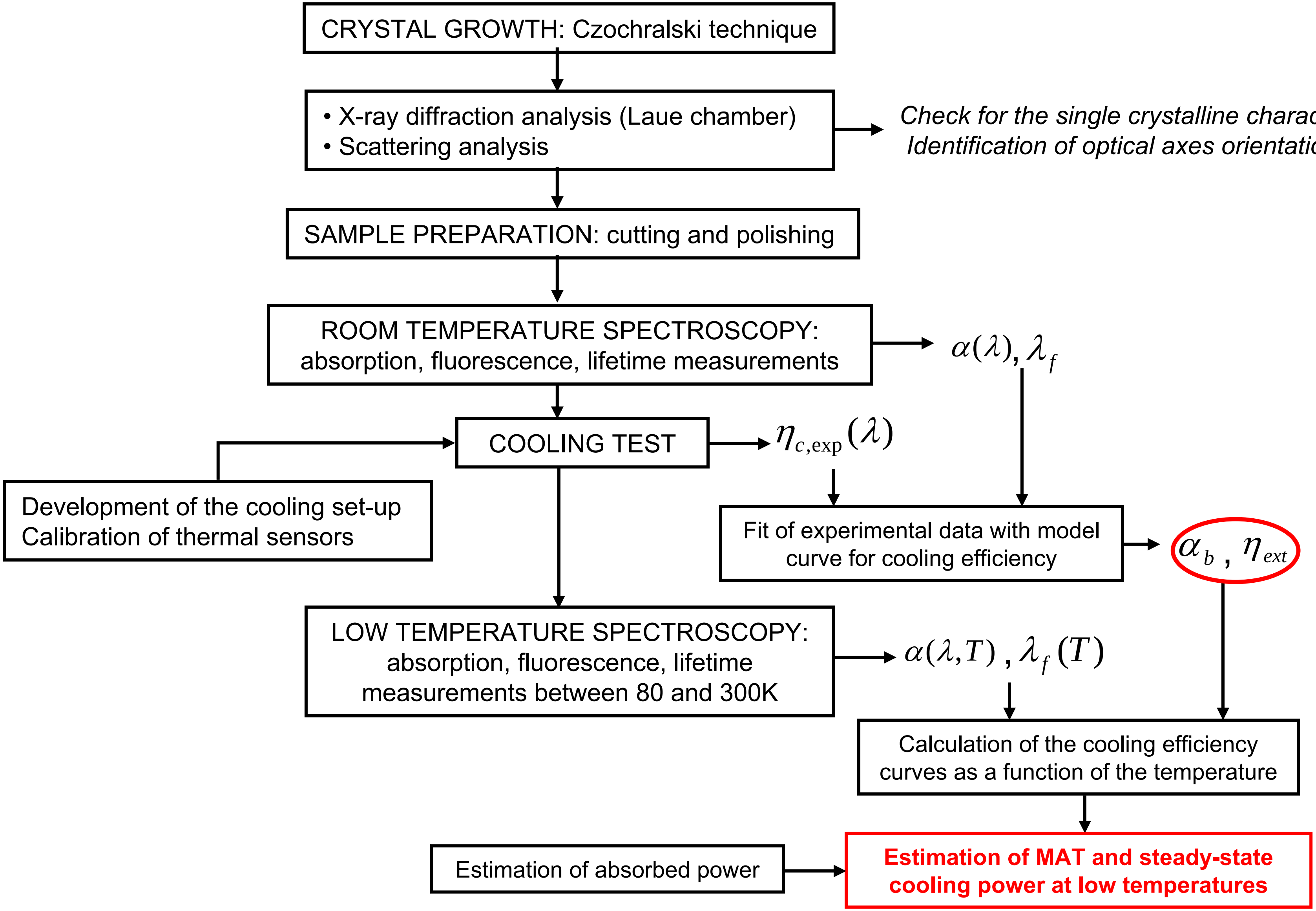
- The **Yb^{3+}** ions **substitutionally** enters the S_4 sites of **Y^{3+}** .

$$R_{Yb} = 1.12\dot{A}$$

$$R_Y = 1.16\dot{A}$$

- YLF:5%Yb
- YLF:7.5%Yb
- YLF:10%Yb

Preparation and characterization of samples



CRYSTAL GROWTH: Czochralski technique

- X-ray diffraction analysis (Laue chamber)
- Scattering analysis

Check for the single crystalline character
Identification of optical axes orientation

SAMPLE PREPARATION: cutting and polishing

ROOM TEMPERATURE SPECTROSCOPY:
absorption, fluorescence, lifetime measurements

$\alpha(\lambda), \lambda_f$

COOLING TEST

$\eta_{c,\exp}(\lambda)$

Development of the cooling set-up
Calibration of thermal sensors

Fit of experimental data with model curve for cooling efficiency

$\alpha_b\ ,\ \eta_{ext}$

LOW TEMPERATURE SPECTROSCOPY:
absorption, fluorescence, lifetime measurements between 80 and 300K

$\alpha(\lambda,T)\ ,\ \lambda_f\,(T)$

Calculation of the cooling efficiency curves as a function of the temperature

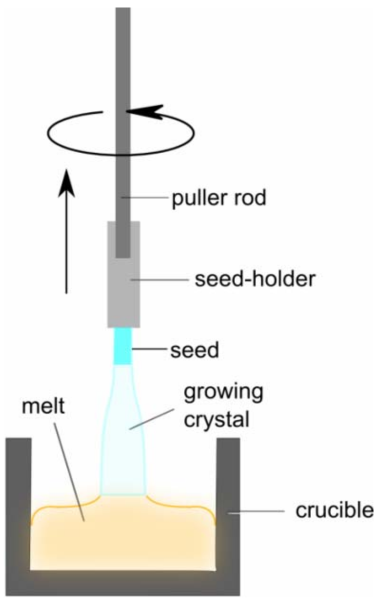
Estimation of absorbed power

Estimation of MAT and steady-state cooling power at low temperatures

Czochralski growth of samples

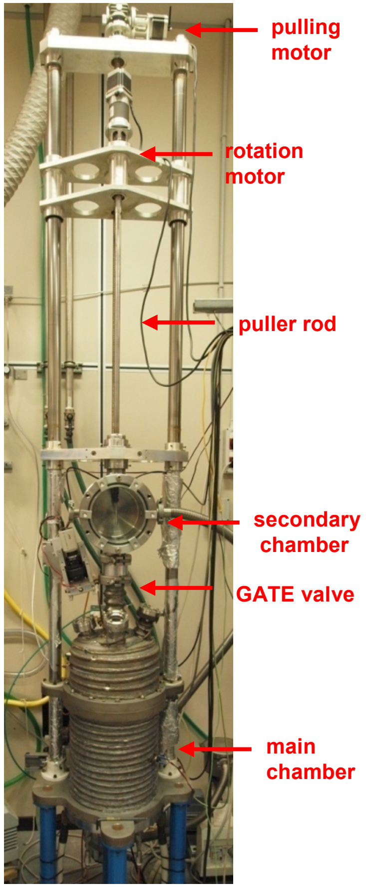
- Growth process ↔ OPTICAL PURITY, STRUCTURAL QUALITY

Principle of Czochralski growth



- Melt growth process
- Growth of laser materials

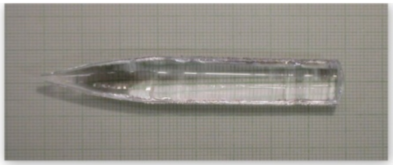
Growth facility



DETAILS OF CZOCHRLAKI GROWTH OF SAMPLES

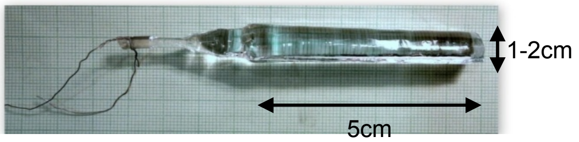
- High purity (**5N**) powders of **LiF**, **YF_3** and **YbF_3** as raw materials
- **Pt crucible** (99.99%)
- Growth atmosphere: High purity (5N) **Ar** and **CF_4**
- Seed: **YLF undoped** oriented along the ***a*-axis**
- Pulling rate: **0.5mm/h** (5rpm)
- Melt temperature: **860-880°C**

YLF:Yb5%



YLF:Yb10%

YLF undoped (seed)

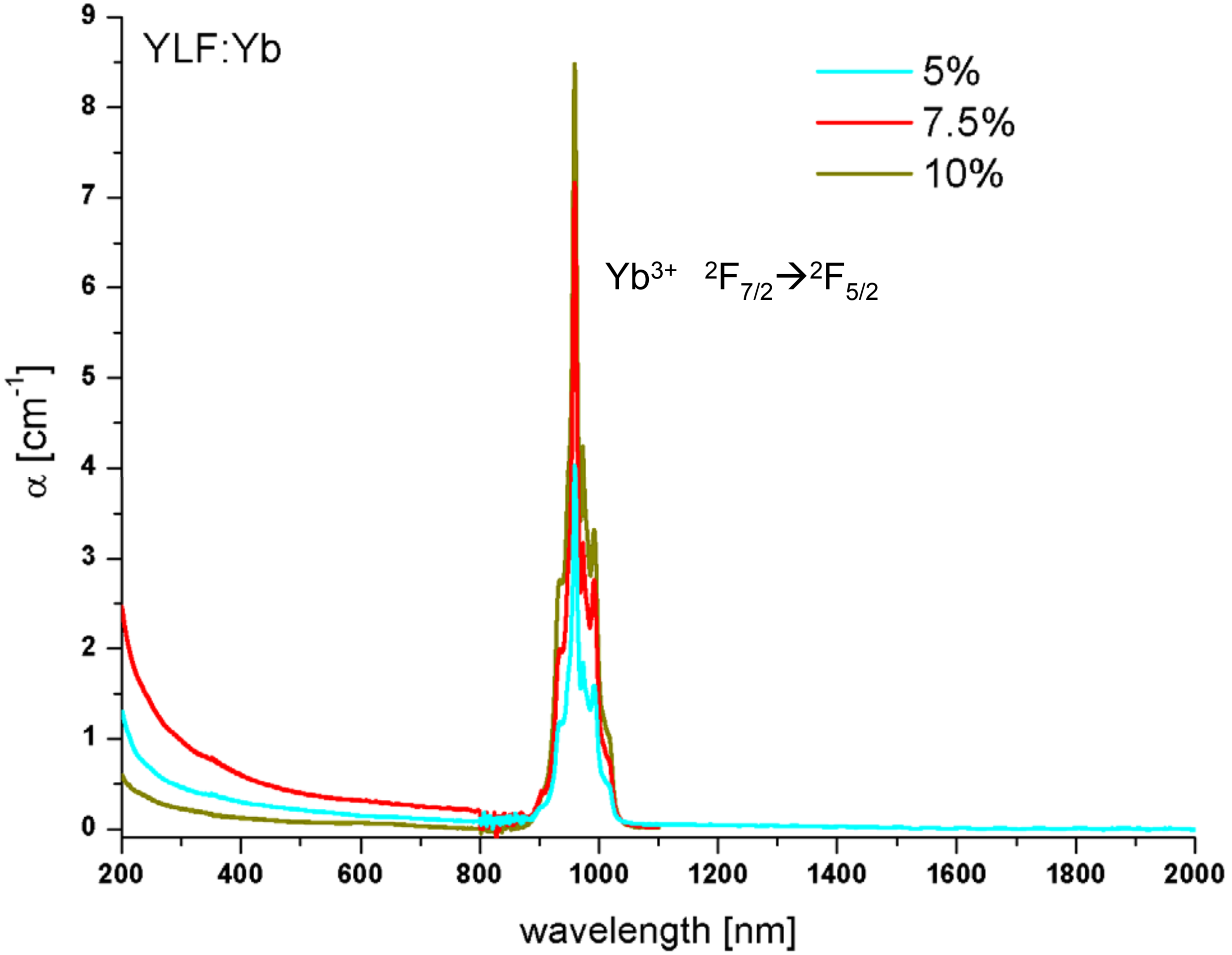


YLF:Yb7.5%

- Resistive heating: graphite resistance (1300°C)
- High vacuum system (10^{-7}mbar)
- Optical system for diameter control

HIGH PURITY(99.999%)
SINGLE CRYSTALS
DEFECT-FREE

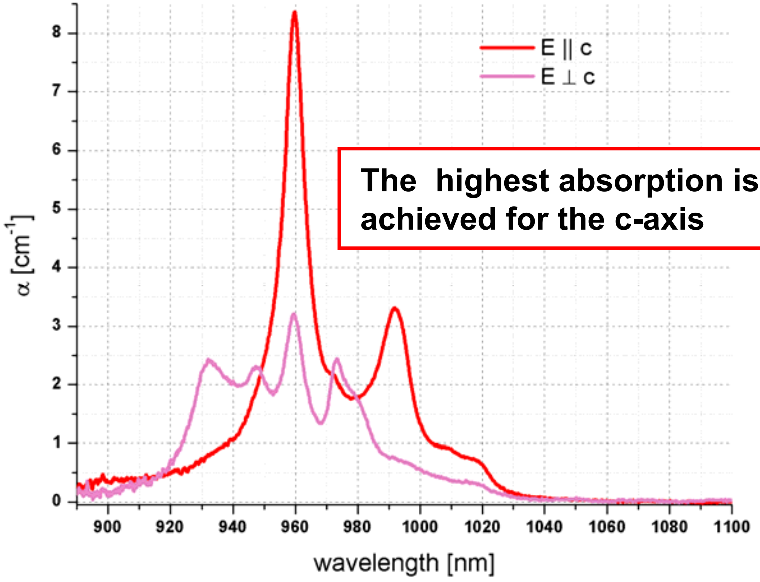
Unpolarized Absorption spectrum UV-NIR: check for pollutants



Absence of spurious absorption bands due to optically active contaminants with concentration higher than 10ppm: no impurities inserted during the growth process.

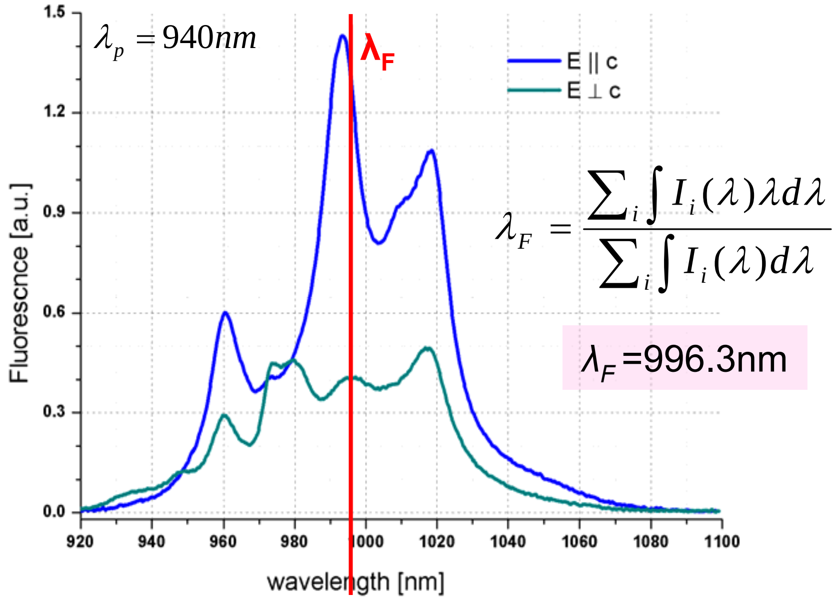
RT spectroscopy: YLF:5%Yb

Absorption spectra: Yb^{3+} $^2F_{7/2} \rightarrow {}^2F_{5/2}$



The highest absorption is achieved for the c-axis

Fluorescence spectra: Yb^{3+} $^2F_{5/2} \rightarrow {}^2F_{7/2}$

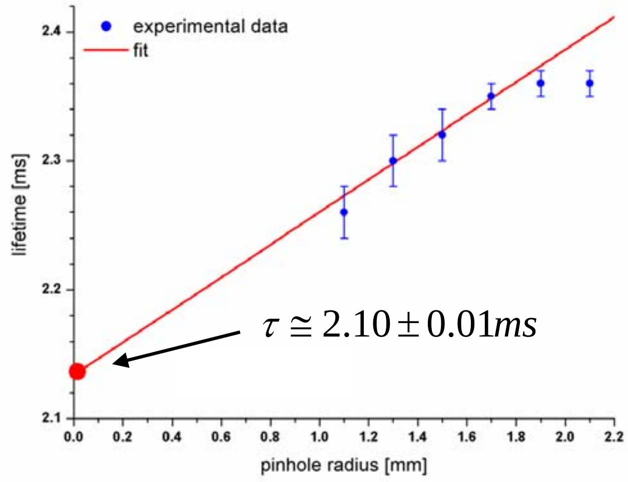


$\lambda_p = 940nm$

$$\lambda_F = \frac{\sum_i \int I_i(\lambda)\lambda d\lambda}{\sum_i \int I_i(\lambda) d\lambda}$$

λ_F=996.3nm

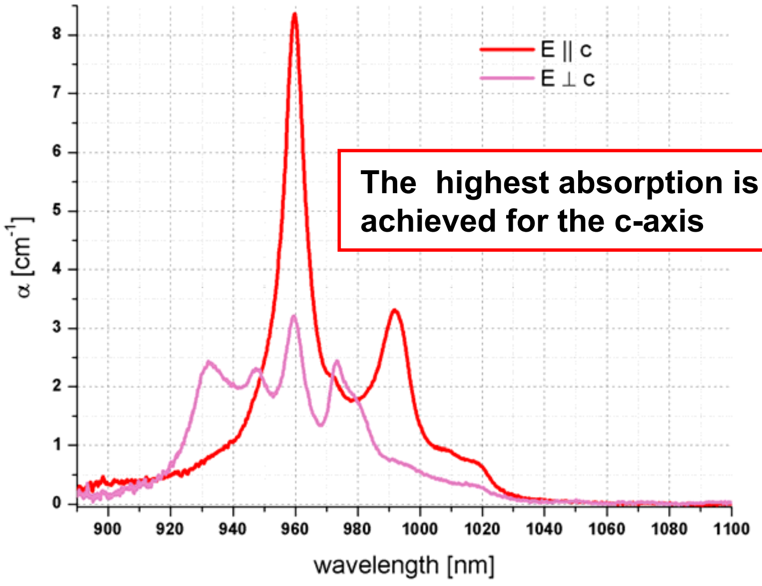
Lifetime measurement of the excited $^2F_{5/2}$ manifold



$\tau \cong 2.10 \pm 0.01ms$

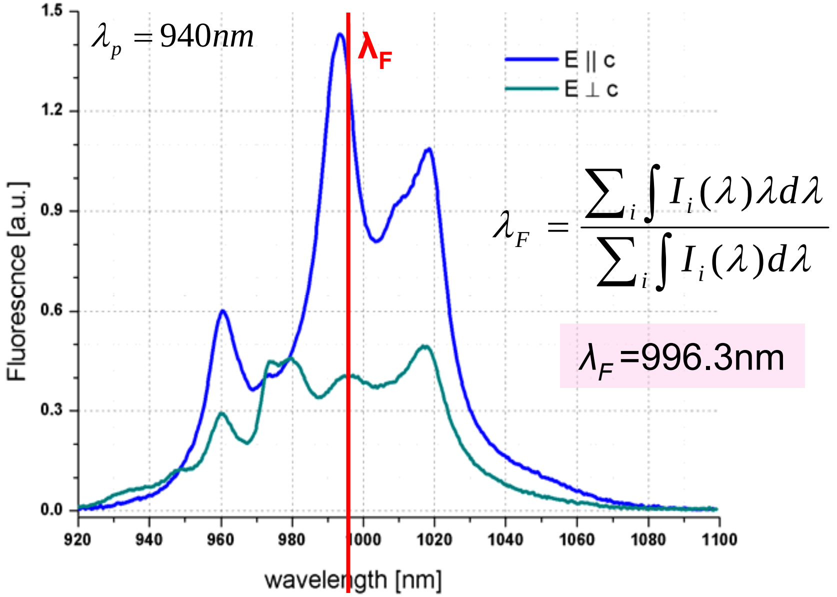
RT spectroscopy: YLF:5%Yb

Absorption spectra: Yb^{3+} $^2F_{7/2} \rightarrow {}^2F_{5/2}$



The highest absorption is achieved for the c-axis

Fluorescence spectra: Yb^{3+} $^2F_{5/2} \rightarrow {}^2F_{7/2}$

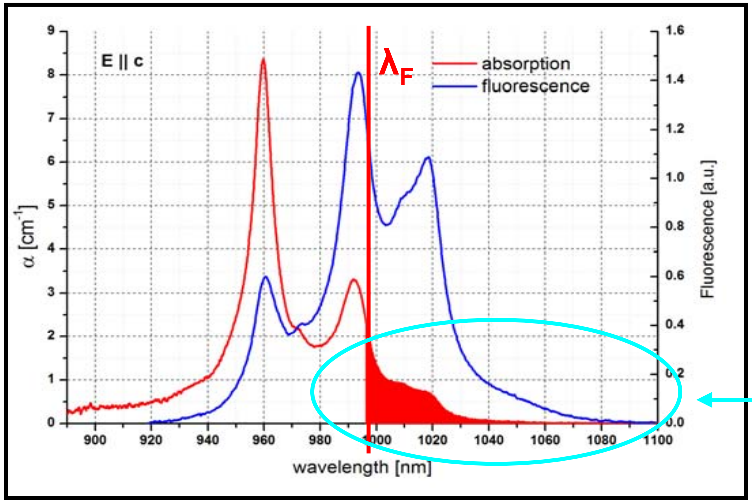


$\lambda_p = 940nm$

$$\lambda_F = \frac{\sum_i \int I_i(\lambda)\lambda d\lambda}{\sum_i \int I_i(\lambda) d\lambda}$$

λ_F=996.3nm

Overlap between absorption and fluorescence bands

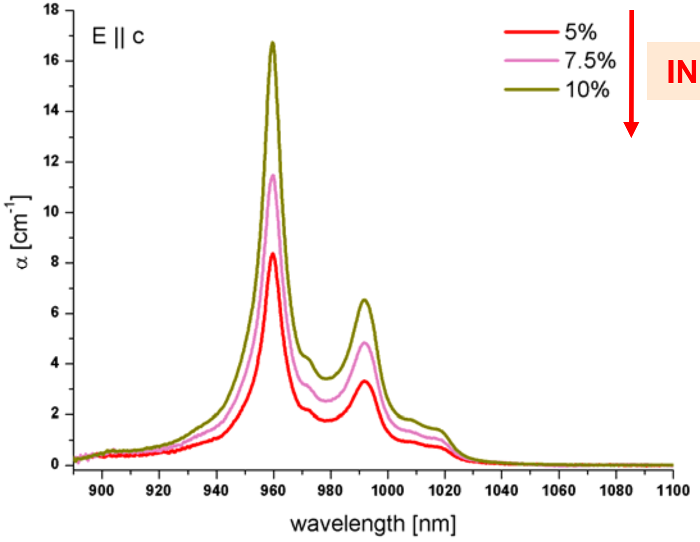


Excitation region for cooling

RT spectroscopy: parameters summary

Summary of spectroscopic parameters that enter the cooling efficiency curve

Absorption coefficient: Yb^{3+} $^2F_{7/2} \rightarrow {}^2F_{5/2}$

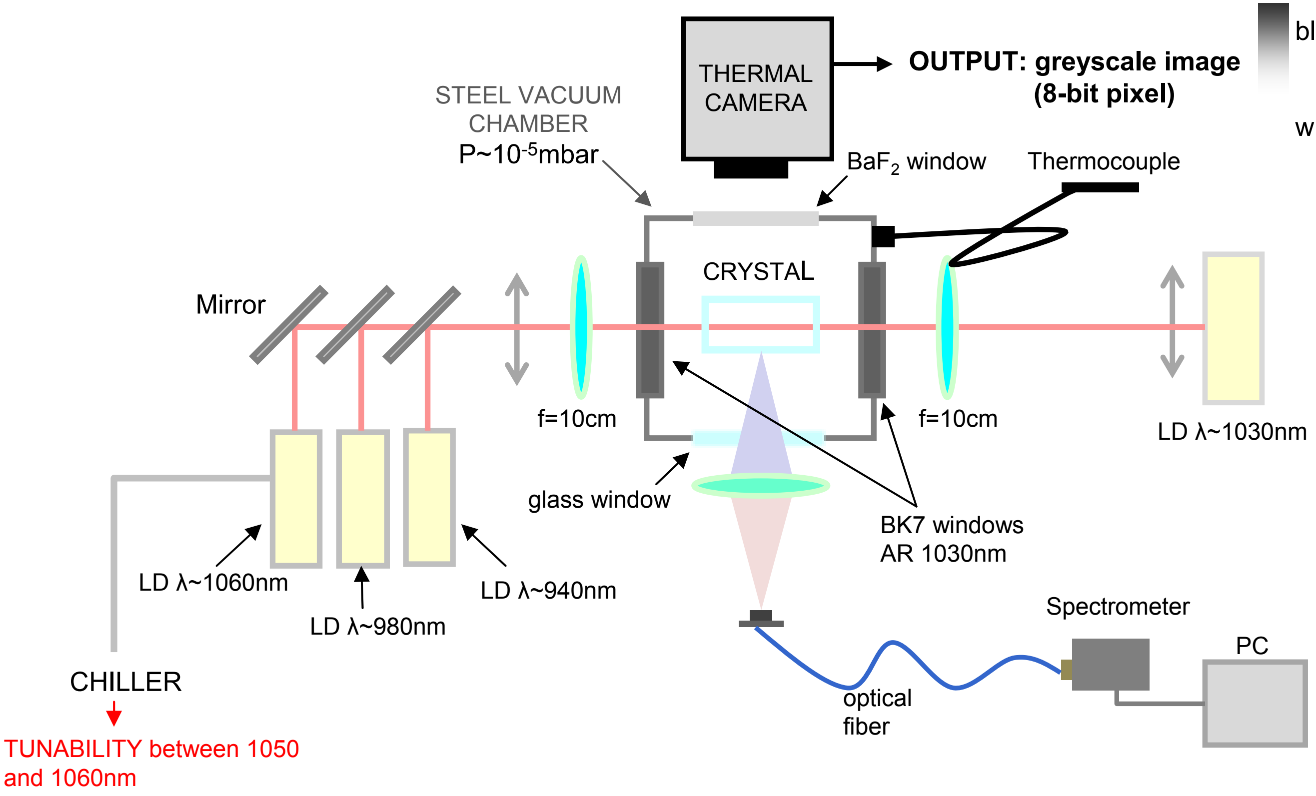


INCREASE

	λ_f
5%	996.3nm
7.5%	996.7nm
10%	997.8nm

RED-SHIFT

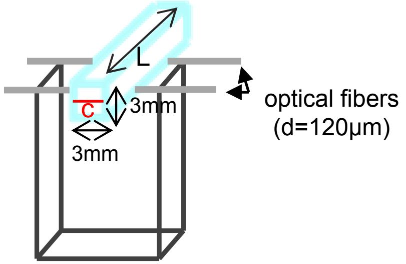
Cooling set-up



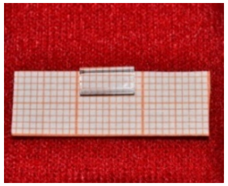
black pixel: 0 (hotter point)

white pixel : 255 (coldest point)

TUNABILITY between 1050 and 1060nm



Sample mounting



cooling sample
YLF:7.5%Yb

CONTACTLESS techniques for temperature measurements:

- **Thermal camera**: Photoconductive sensor (uncooled amorphous silicon microbolometric array)
- **Differential Luminescence Thermometry (DLT):** The difference between integrated areas of fluorescence is used to calculate the temperature change.

Principle of operation

Steady-state conditions: $P_{cool} = P_{load}$

~~CONVECTIVE~~ + ~~CONDUCTIVE~~ + **RADIATIVE (BB)**

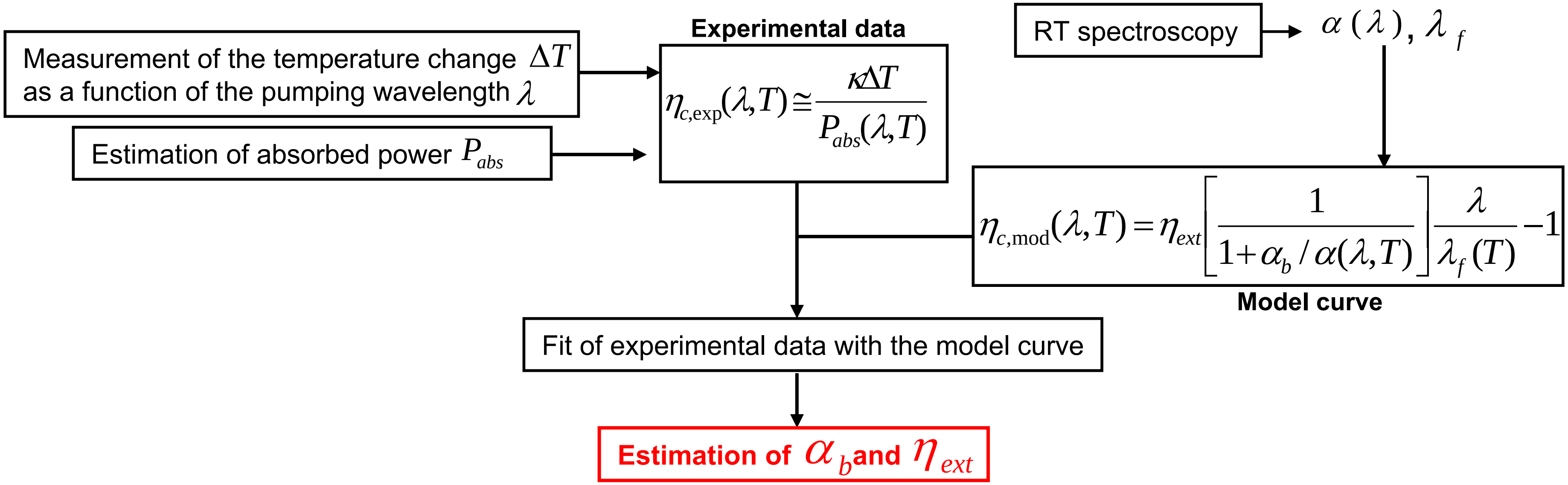
vacuum optical fibers

$$P_{rad} = k(T_c^4 - T^4) \underset{\Delta T \to 0}{\cong} \kappa \Delta T \qquad \Delta T \equiv T_c - T$$

$$k = \frac{\sigma \varepsilon_s A_s}{1+\chi} \qquad \chi = \frac{(1-\varepsilon_c)\varepsilon_s A_s}{\varepsilon_c A_c}$$

$$\kappa = 4kT_c^3$$

$$\eta_c(\lambda, T) \equiv \frac{P_{cool}}{P_{abs}} \qquad \eta_c(\lambda, T) \cong \frac{\kappa \Delta T}{P_{abs}(\lambda, T)}$$



Measurement of the temperature change ΔT as a function of the pumping wavelength λ

Estimation of absorbed power P_{abs}

Experimental data

$$\eta_{c,\exp}(\lambda, T) \cong \frac{\kappa \Delta T}{P_{abs}(\lambda, T)}$$

RT spectroscopy → $\alpha(\lambda), \lambda_f$

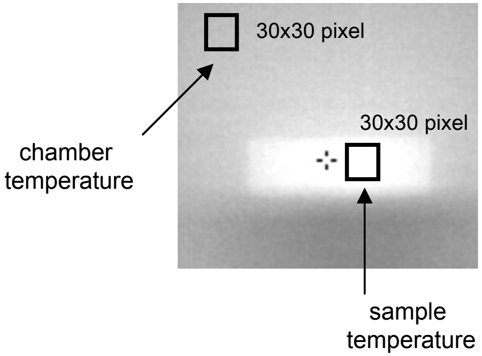
$$\eta_{c,\mathrm{mod}}(\lambda, T) = \eta_{ext}\left[\frac{1}{1+\alpha_b/\alpha(\lambda, T)}\right]\frac{\lambda}{\lambda_f(T)} - 1$$

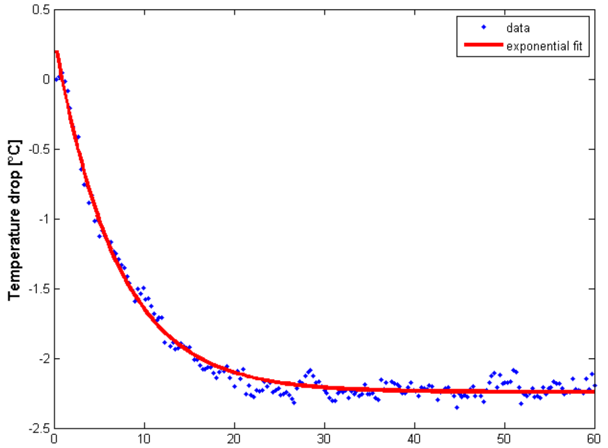
Model curve

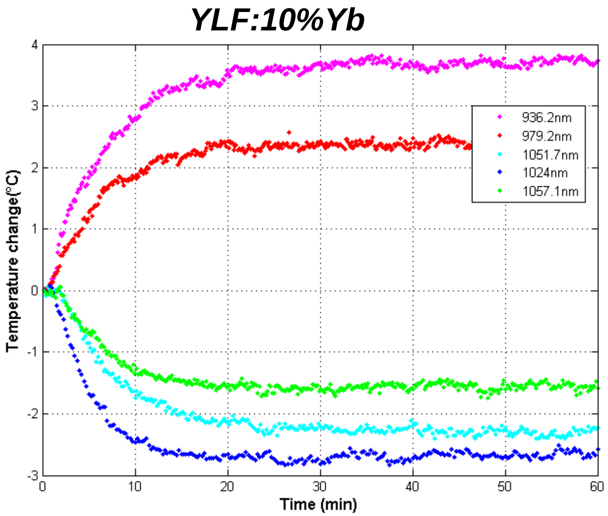
Fit of experimental data with the model curve

Estimation of α_b and η_{ext}

Cooling measurements:details

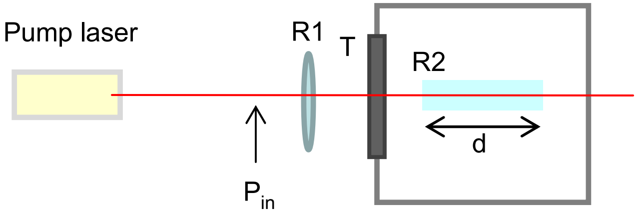






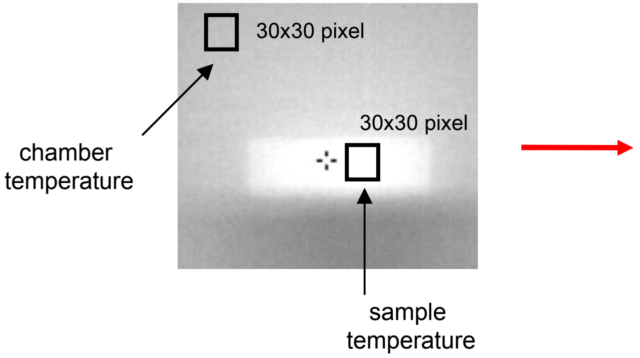
λ	$\Delta T[^oC]$	$P_{in}[mW]$
936.8nm	3.7±0.2	16.5±2
979.6nm	2.4±0.2	16.5±2
1024nm	-2.6±0.2	225±5
1052nm	-2.2±0.2	765±10
1059.5nm	-1.5±0.1	800±10

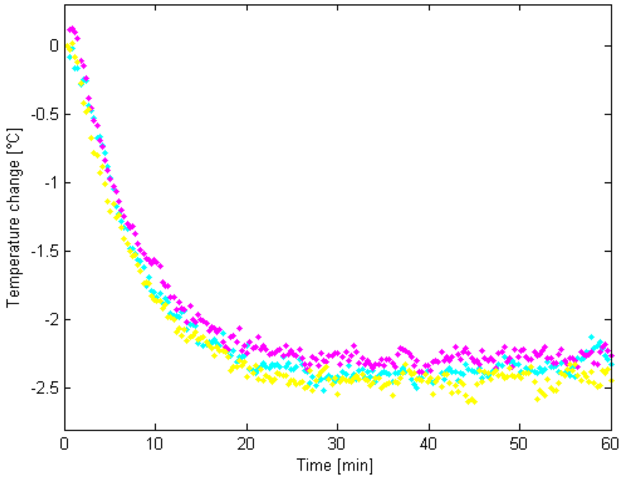
$$P_{abs}(\lambda, T) = AP_{in}(1 - e^{-\alpha(\lambda)\cdot d})$$



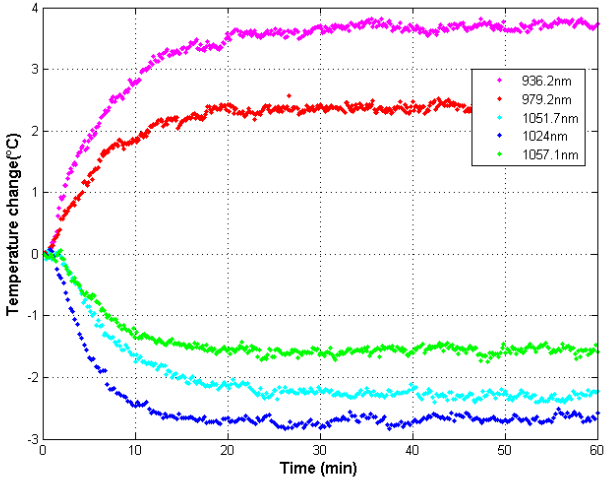
SINGLE-PASS

Cooling measurements:details



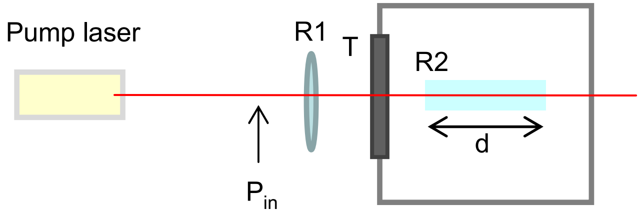


YLF:10%Yb



λ	$\Delta T[^{o}C]$	$P_{in}[mW]$
936.8nm	3.7±0.2	16.5±2
979.6nm	2.4±0.2	16.5±2
1024nm	-2.6±0.2	225±5
1052nm	-2.2±0.2	765±10
1059.5nm	-1.5±0.1	800±10

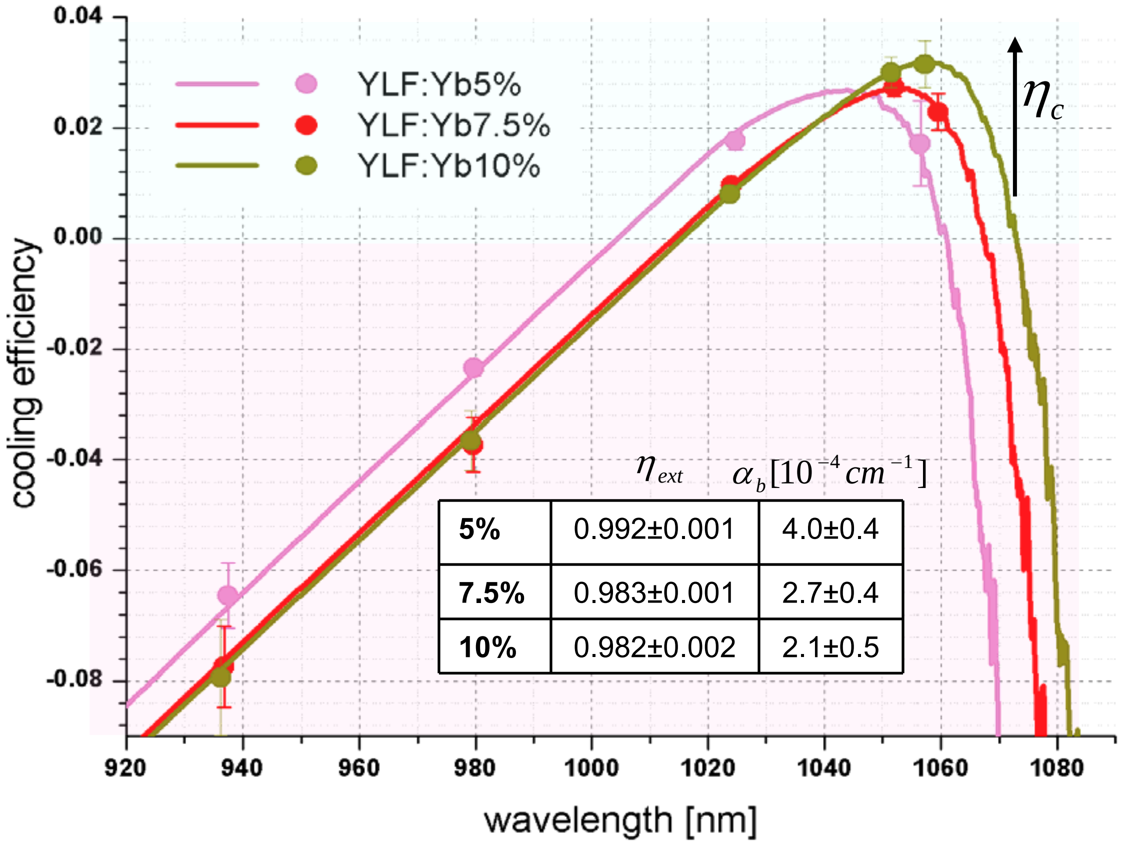
$$P_{abs}(\lambda, T) = AP_{in}(1 - e^{-\alpha(\lambda)\cdot d})$$



SINGLE-PASS

Cooling measurements: YLF:Yb

Measured cooling efficiency for the sample set of YLF:5%Yb, YLF:7.5%Yb and YLF:10%Yb



	η_{ext}	$\alpha_b[10^{-4}cm^{-1}]$
5%	0.992±0.001	4.0±0.4
7.5%	0.983±0.001	2.7±0.4
10%	0.982±0.002	2.1±0.5

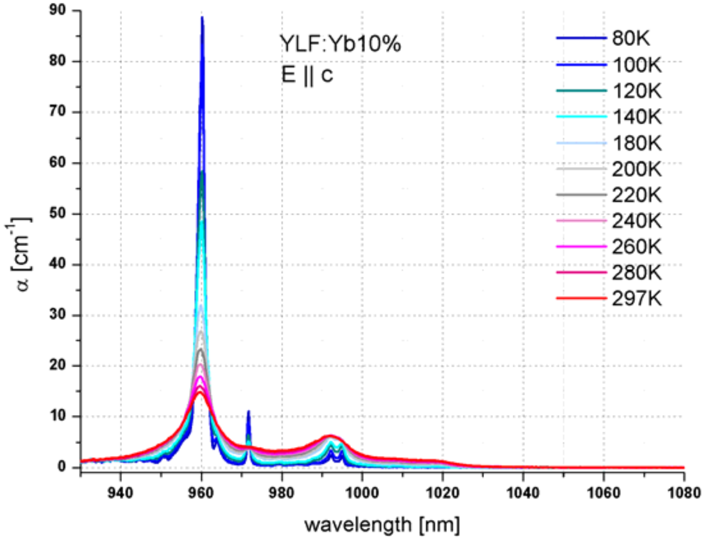
	$\alpha_b[10^{-4}cm^{-1}]$
YLF:5%Yb	4
YLF:10%Yb	2

→ **114K**

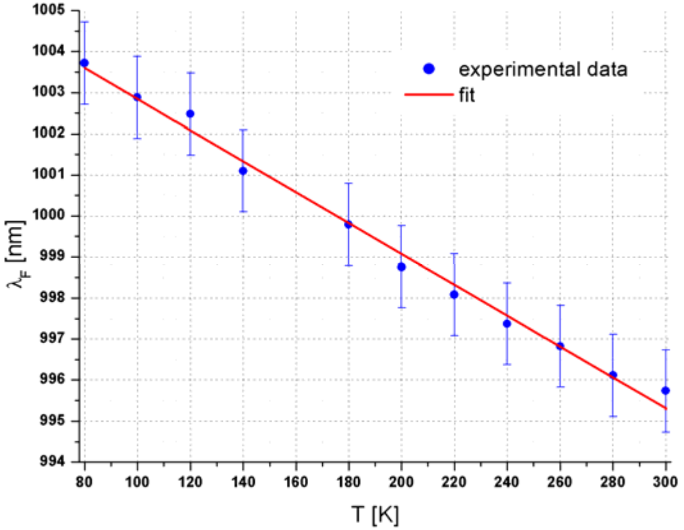
S.D.Melgaard et al.Opt. Expr., 22, (2014)

COOLING EFFICIENCY EHNANCEMENT as the Yb doping level is increased, via a significant **DECREASE** of the **background absorption parameter**.

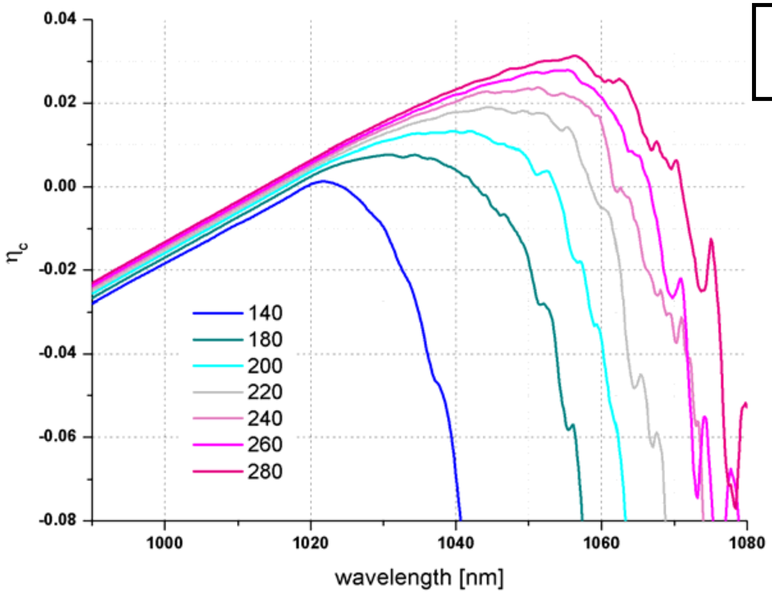
Low T spectroscopy: cooling power estimation



Absorption coefficient VS Temperature



Mean emission wavelength VS Temperature



Estimated cooling efficiency curve VS Temperature

The reduction of $\alpha(\lambda)$ and the red shift of λ_f with decreasing temperature lead to a corresponding decrease in the cooling efficiency.

$$\longrightarrow \quad P_{cool}(\lambda,T)=\eta_{cool}(\lambda,T)P_{abs}(\lambda,T)$$

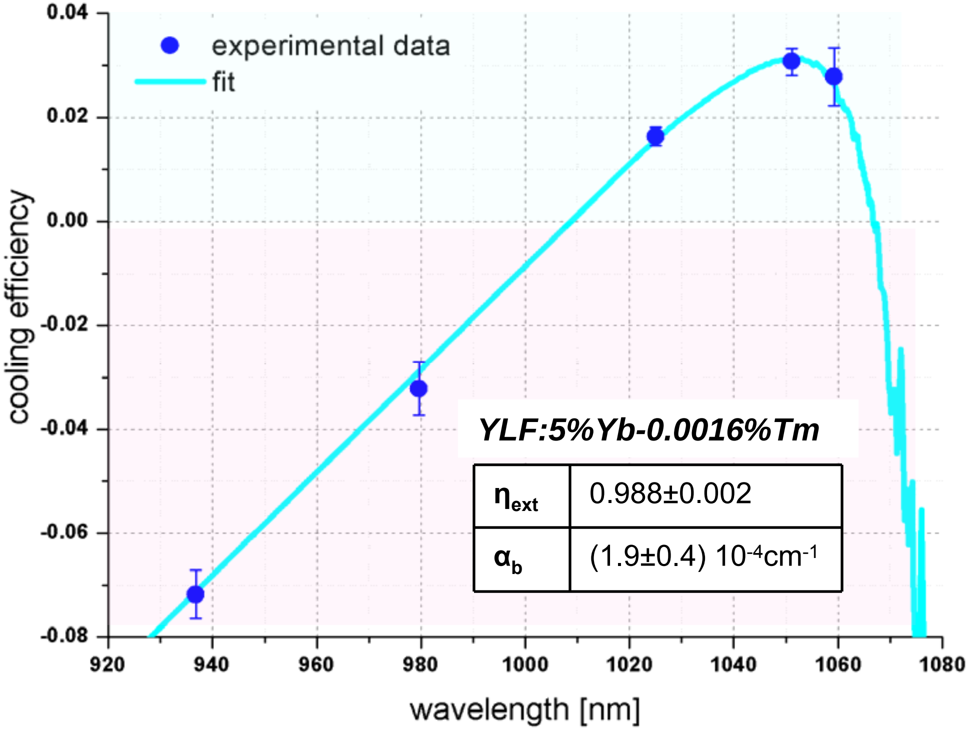
ABSORPTION ENHANCEMENT

- Multi-pass cavity
- Intracavity

Novel scheme : Investigation of Yb-Tm *codoping*

Investigation of Yb-Tm codoping

Motivated by previous studies on the effect of rare earth impurities on the efficiency of Yb anti-Stokes process we have grown a sample of ***YLF single crystal doped Yb at 5%*** *with a* ***controlled Tm doping of 16ppm*** *to investigate the effect of* ***Yb-Tm codoping****.*



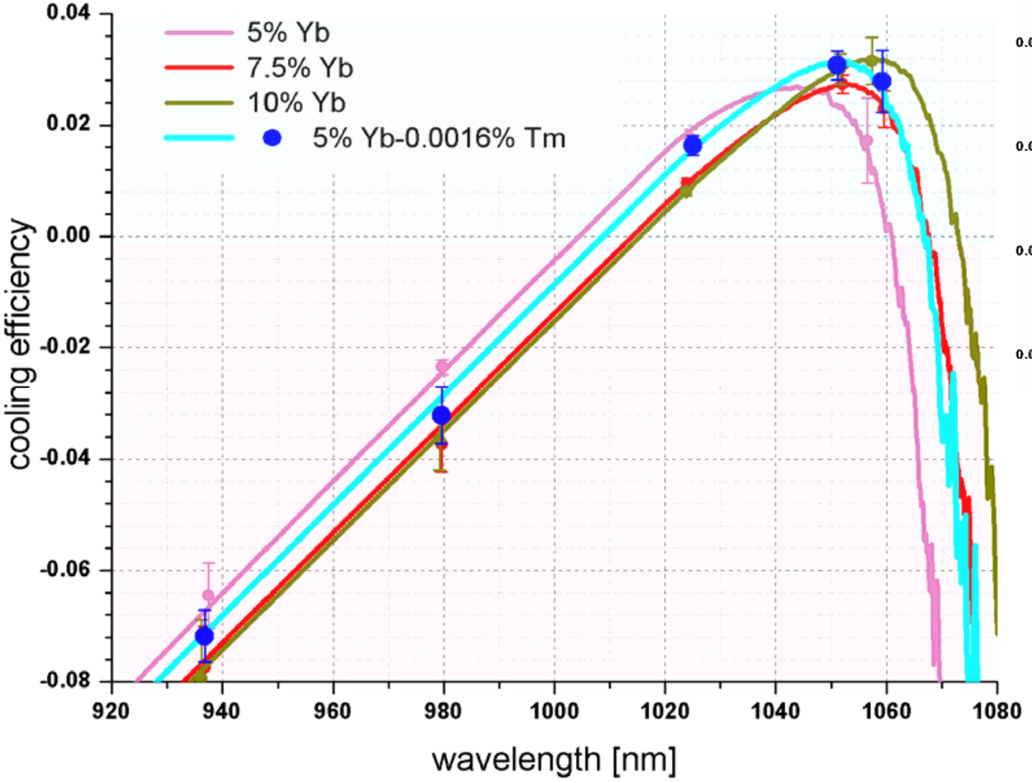
YLF:5%Yb-0.0016%Tm

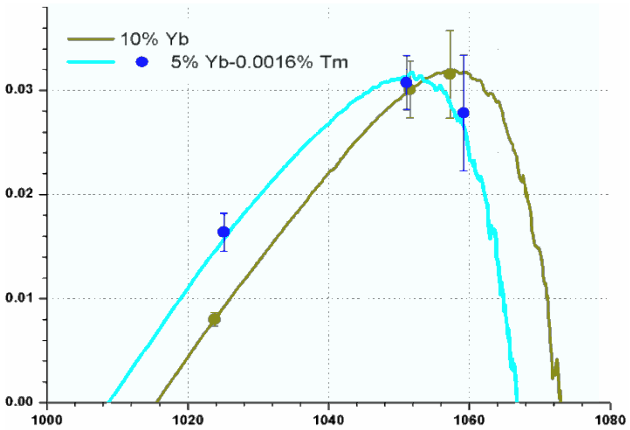
η_{ext}	0.988±0.002
α_b	$(1.9\pm0.4)\ 10^{-4}\text{cm}^{-1}$

The addition of **Tm DOPING** results in **NET INCREASE** of the overall cooling efficiency, via a significant **DECREASE** of the **background absorption parameter**.

Investigation of Yb-Tm codoping

Cooling efficiency comparison between the sample set of YLF doped Yb between 5 and 10% and the YLF codoped Yb(5%)-Tm(0.0016%)



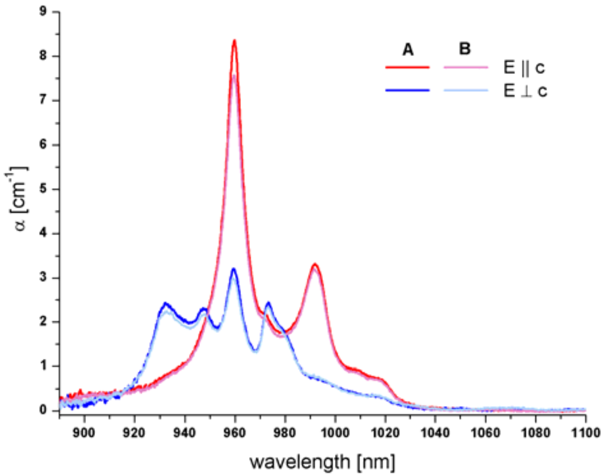


5%	0.992±0.001	4.0±0.4
7.5%	0.983±0.001	2.7±0.4
10%	0.982±0.002	2.1±0.5
Yb-Tm	**0.988±0.002**	**1.9±0.4**

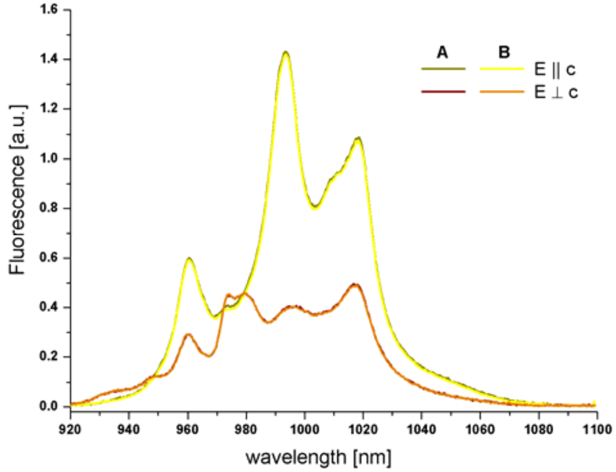
- The addition of **controlled Tm doping** determines a **decrease of α_b** comparable to an **increase** of the **Yb doping level .**
- No reabsorption effects: **lower decrease of η_{ext}** compared to higher Yb doping level.

Investigation of Yb-Tm codoping: spectroscopy

Absorption spectra: $Yb^{3+}\ ^2F_{7/2} \rightarrow ^2F_{5/2}$

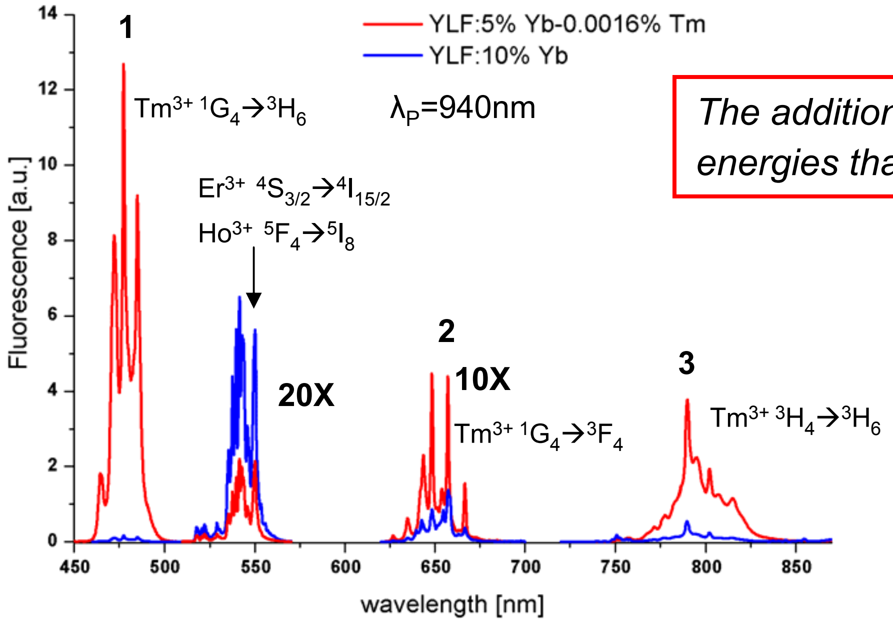


Fluorescence spectra: $Yb^{3+}\ ^2F_{5/2} \rightarrow ^2F_{7/2}$

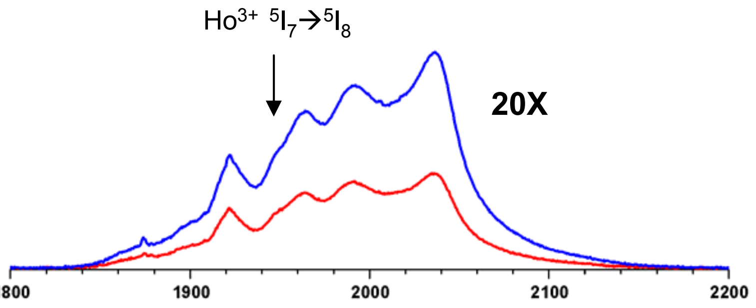


A: YLF:Yb5%
B: YLF:Yb5%-Tm0.0016%

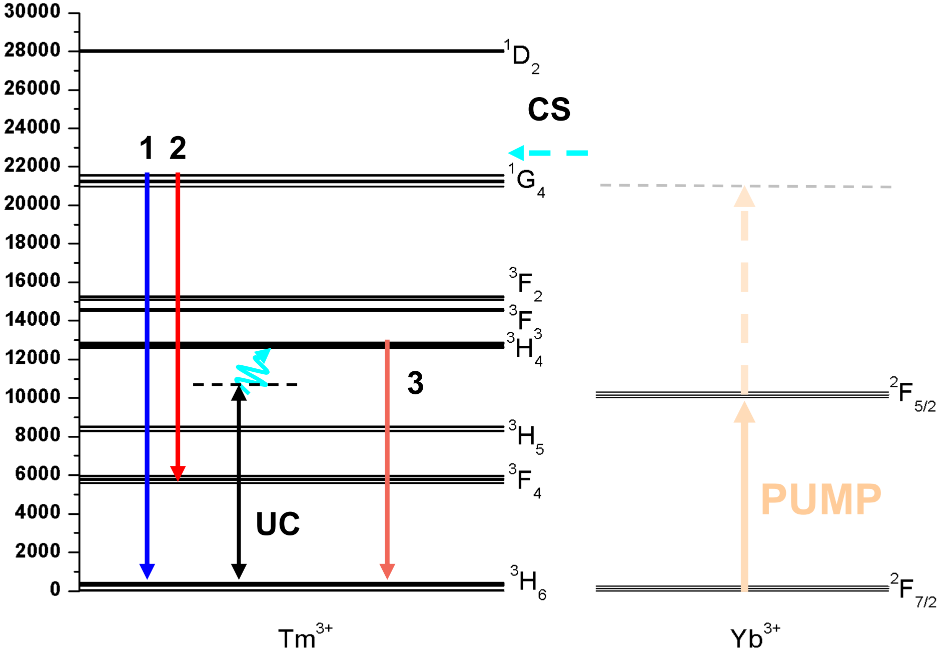
Visible and IR emissions due to Yb-Tm energy transfer

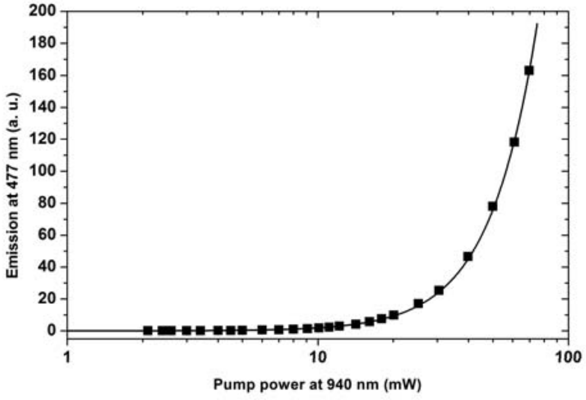


The addition of Tm doping produces emissions at higher energies than the absorbed photons (940nm): 1, 2, 3.



Model for Yb-Tm energy-transfer





Fit: I ~ P^k **k=2.3±0.2**

THE EXCITATION OF THE $^1G_4$ MANIFOLD IS MOSTLY A **TWO PHOTONS** PROCESS

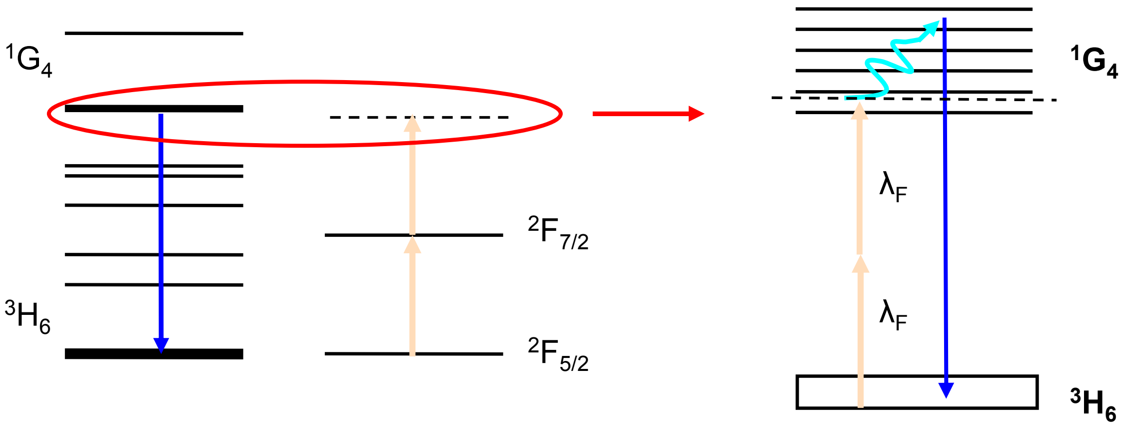
- **COOPERATIVE SENSITIZATION (CS) Yb-Tm:** Yb ($^2F_{5/2}$)+Yb($^2F_{5/2}$)→Tm($^1G_4$) → phonons annihilation
- **Tm up-conversion (UC)**: ($^3F_4$, $^3F_4$)→ ($^3H_6$, $^3H_4$) → phonons annihilation

The Yb-Tm energy-transfer appear to contribute to the Yb cooling process: efficiency enhancement

NOVEL SCHEME FOR OPTICAL COOLING IN SOLIDS

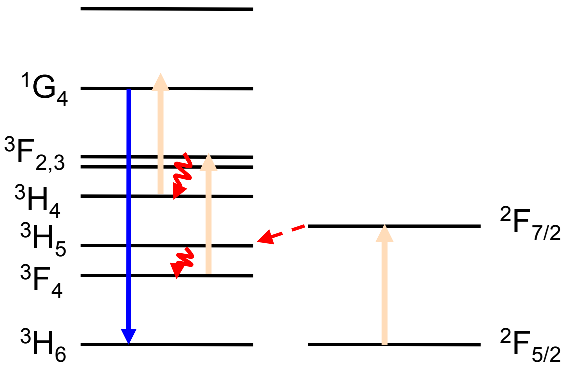
Yb-Tm blue up-conversion

A) Two photons process (COOPERATIVE SENSITIZATION) → phonons annihilation



Donor (Yb) concentration dominant over acceptor (Tm) concentration

B) Three photons process → phonons emission



Practical advantages of Yb-Tm codoping

- **Inhibit a posteriori energy-transfer to detrimental impurities, which involve phonon release in internal processes or in the direct transfer lowering the efficiency of the anti-Stokes process → Less mandatory requirements on the purity of the starting powders.**

- **Substitute of higher Yb doping level to increase the cooling efficiency without limit due to reabsorption phenomena, typical of high doping level.**

Conclusions and future work

- High optical purity YLF single crystals with varying Yb doping level between 5 and 10% of high structural quality have been grown, spectroscopically characterized and tested in a optical cooling experiment measuring the efficiency curve

- The increase of Yb doping level in YLF single crystals produce an increase of the cooling efficiency via a decrease of the background absorption parameter

- A novel approach for laser cooling based on Yb-Tm energy-transfer, has been developed resulting in cooling efficiency enhancement via a significant decrease of the background absorption parameter: novel concept, interesting practical advantages.

- The next stages of the work will involve the investigation of the optical cooling effect in LLF and KYF crystalline host as a function of the Yb doping level and a comparative analysis of the cooling performances in connection with material properties.

- Further investigation of the Yb-Tm copoding will be performed, for different relative concentrations and different host material.