Graduate School of Basic Sciences
"Galileo Galilei" – Physics

Pre-thesis

XXX cycle PhD course

An increasing cooling efficiency in fluoride crystals co-doped Yb-Tm

NPI project between Pisa University and ESA-ESTEC

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Supervisor: **Prof. M. Tonelli**

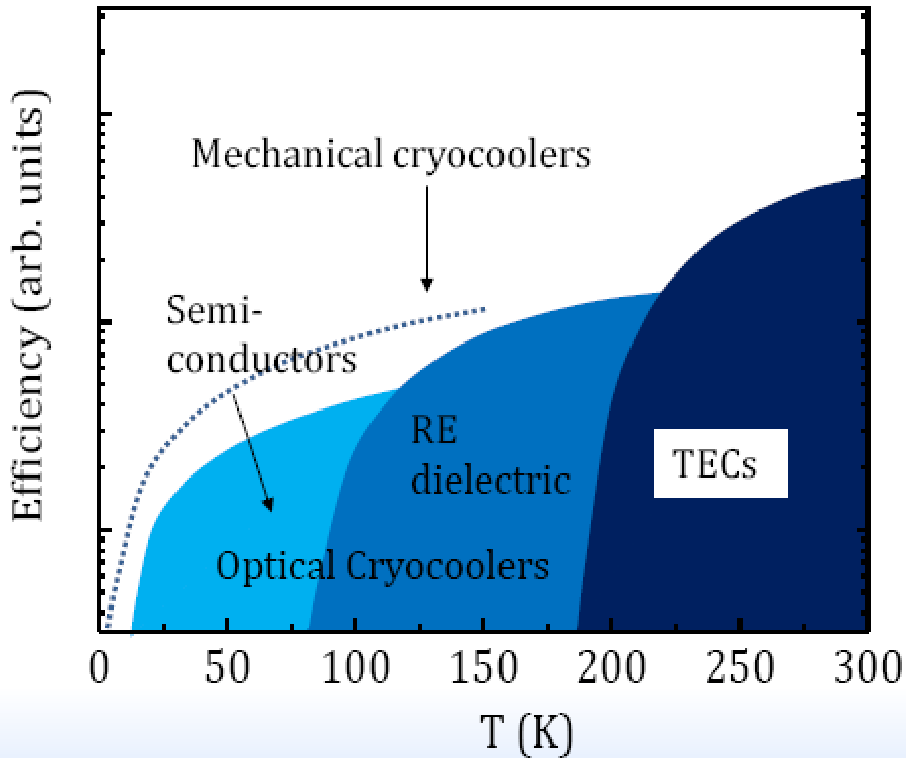
Summary

- Introduction on optical cooling in solids:
  - Anti-Stokes process and cooling efficiency model
    - Yb^{3+} -Tm^{3+} interaction
- G-mat prediction on 5% Yb^{3+} -0,0016%Tm^{3+} :$LiYF_4$
- Crystals grown:
  - First growth:5% Yb^{3+} -50ppmTm^{3+} :$LiYF_4$
  - Second growth:5% Yb^{3+} :$LiYF_4$ and 5% Yb^{3+} -50ppmTm^{3+} :$LiYF_4$
  - Third growth:5% Yb^{3+} :$LiYF_4$ and 5% Yb^{3+} -80ppmTm^{3+} :$LiYF_4$
- Laser cooling tests and chemical analysis
- Conclusion and future work

Advantages of Optical Cryocooling

Perceived advantages of optical cryocooling:

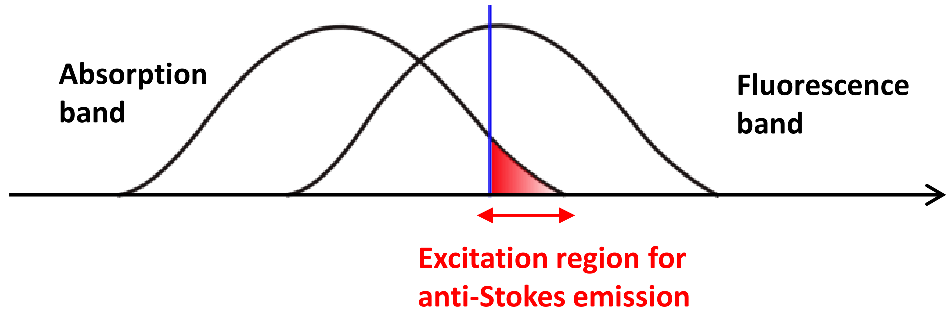
- Accessing the temperature range well below 200 K (TEC cut-off), potentially below 80 K
- No moving parts and *zero* vibration
- potentially smaller, lighter & lower cost compared to mechanical cryocoolers
- Hot and cold parts physically separated
- Enhanced reliability and operational lifetime (robust monolithic design)
- low electromagnetic interference (EMI) and low sensitivity to magnetic fields



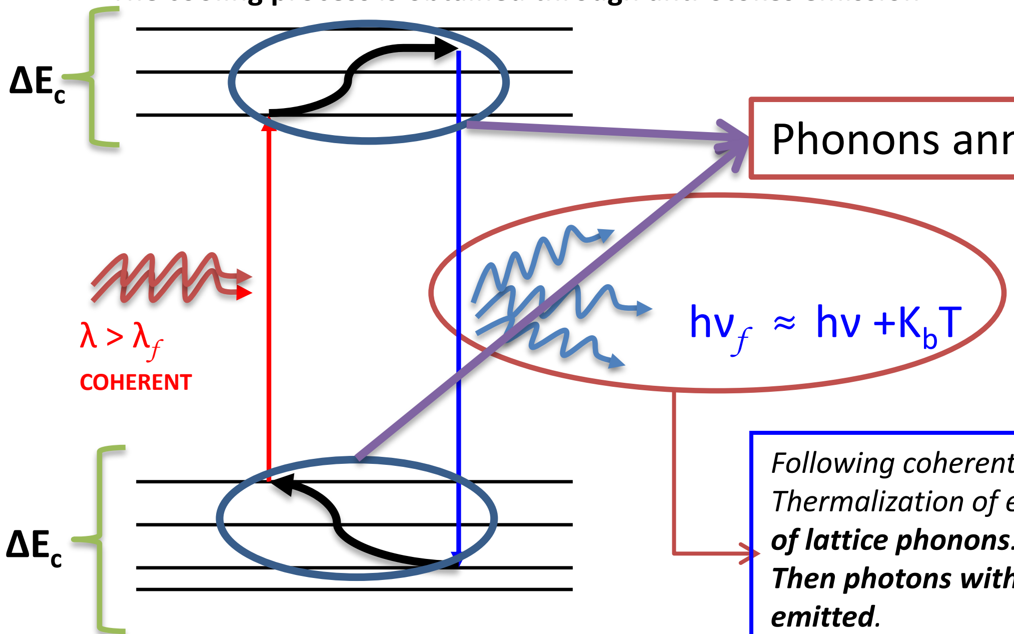
Anti-Stokes process

OPTICAL COOLING: Optical cooling is a process in which laser light is used to lower system energy.
The active element is a dopant ion embedded in a transparent solid (crystal fluoride).

Basic condition: overlap between absorption and fluorescence bands



The cooling process is obtained through anti-Stokes emission



Phonons annihilation allows the cooling performance

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

Cooling efficiency model

- *Ideal efficiency:*

$$\eta_{cool}(\lambda,T) = \frac{P_{cool}}{P_{abs}} = \frac{\Delta E}{h\nu} = \frac{\lambda}{\lambda_f(T)} - 1 \approx \frac{k_B T}{h\nu}$$

$$\Delta E = h\nu_f - h\nu \approx k_B T$$

- *Realistic efficiency:*

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

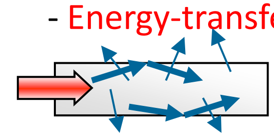
External Quantum Efficiency — **Abs**orption efficiency

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

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

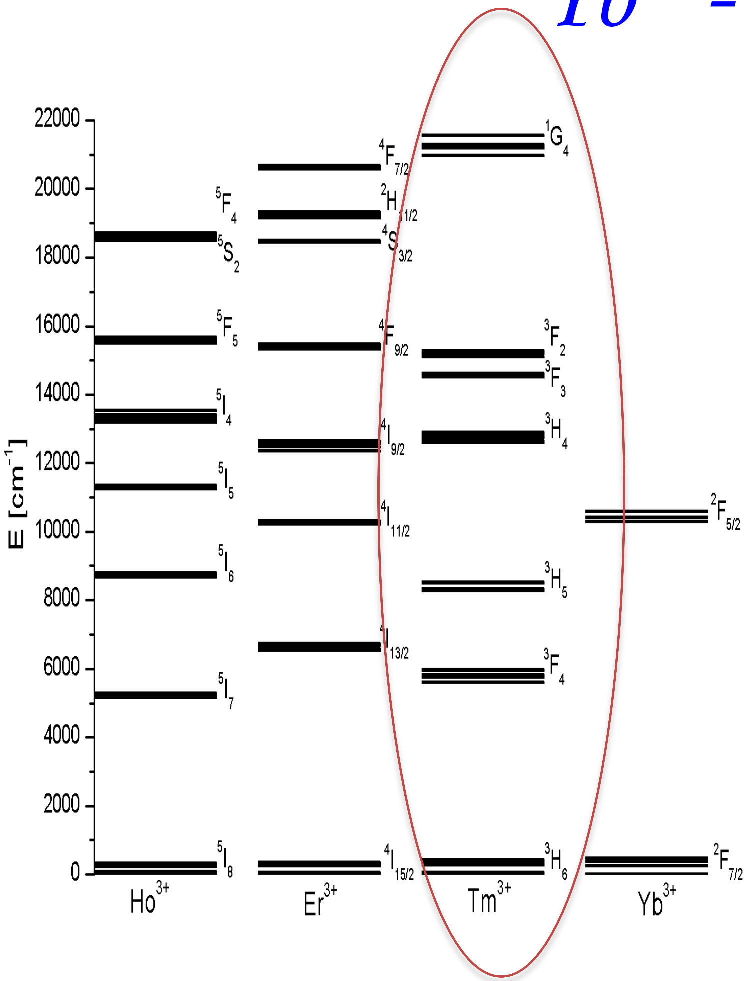
$$\eta_{abs}(\lambda,T) = \frac{1}{1 + \alpha_b/\alpha(\lambda,T)}$$

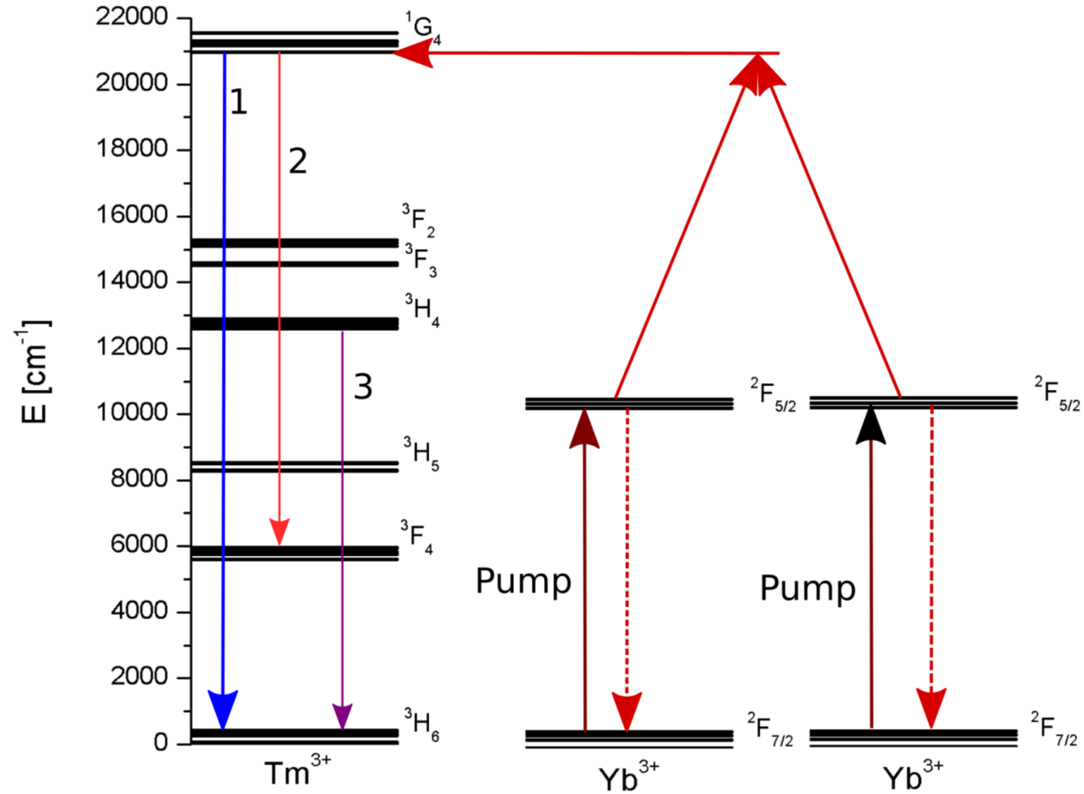
- ***Impurities:*** - Spurious absorption bands
  - Energy-transfer processes
- ***Defects***



CRITICAL PARAMETER: ***Background absorption coefficient***

Yb^{3+}-Tm^{3+} interaction



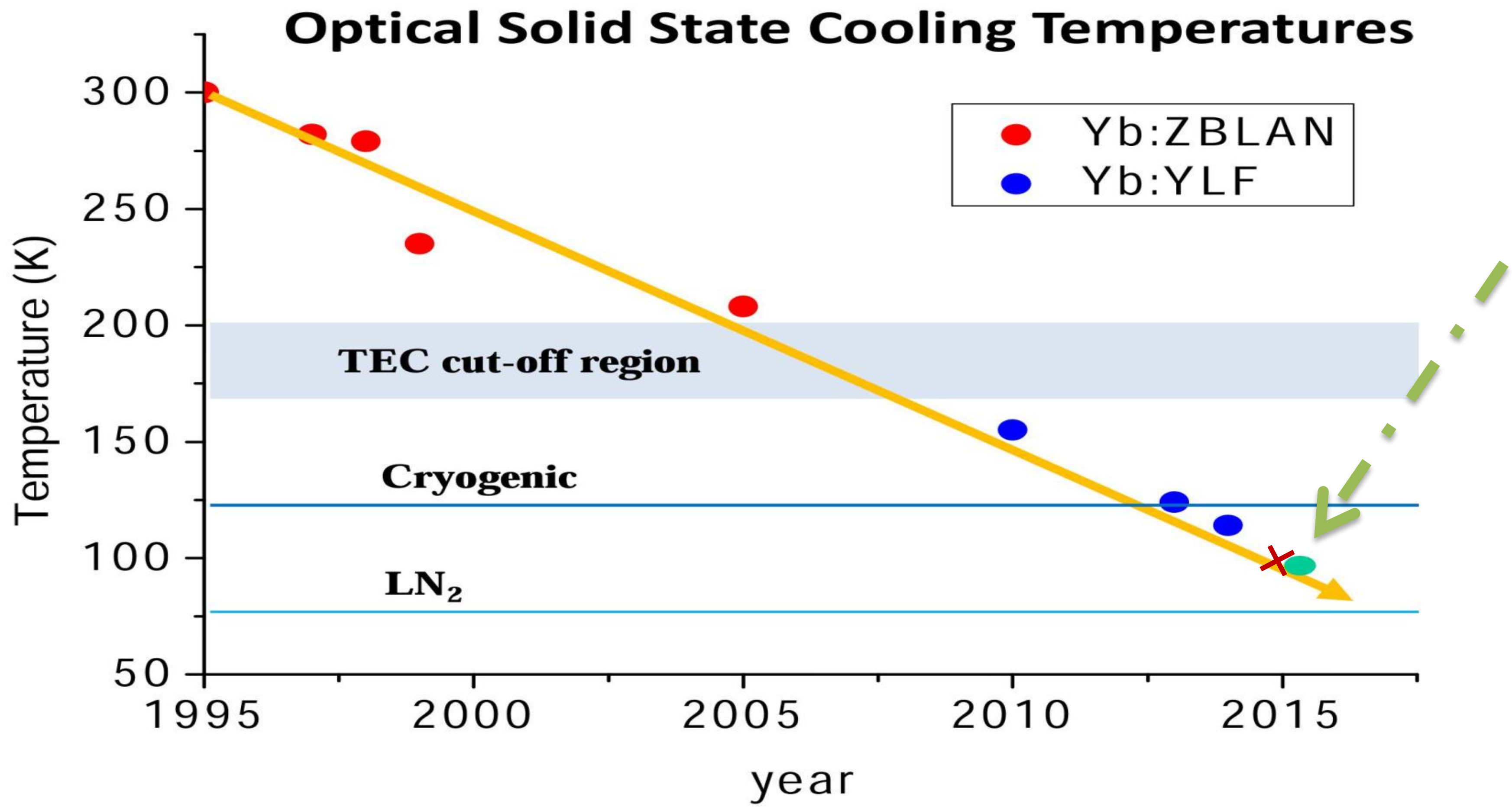


The balance of all the processes involved in the Yb-Tm energy transfer must not be exothermic, i.e. must not involve net phonons emission

The blue emission from $^1G_4$ manifolds is mostly due to a two photon process(ET):

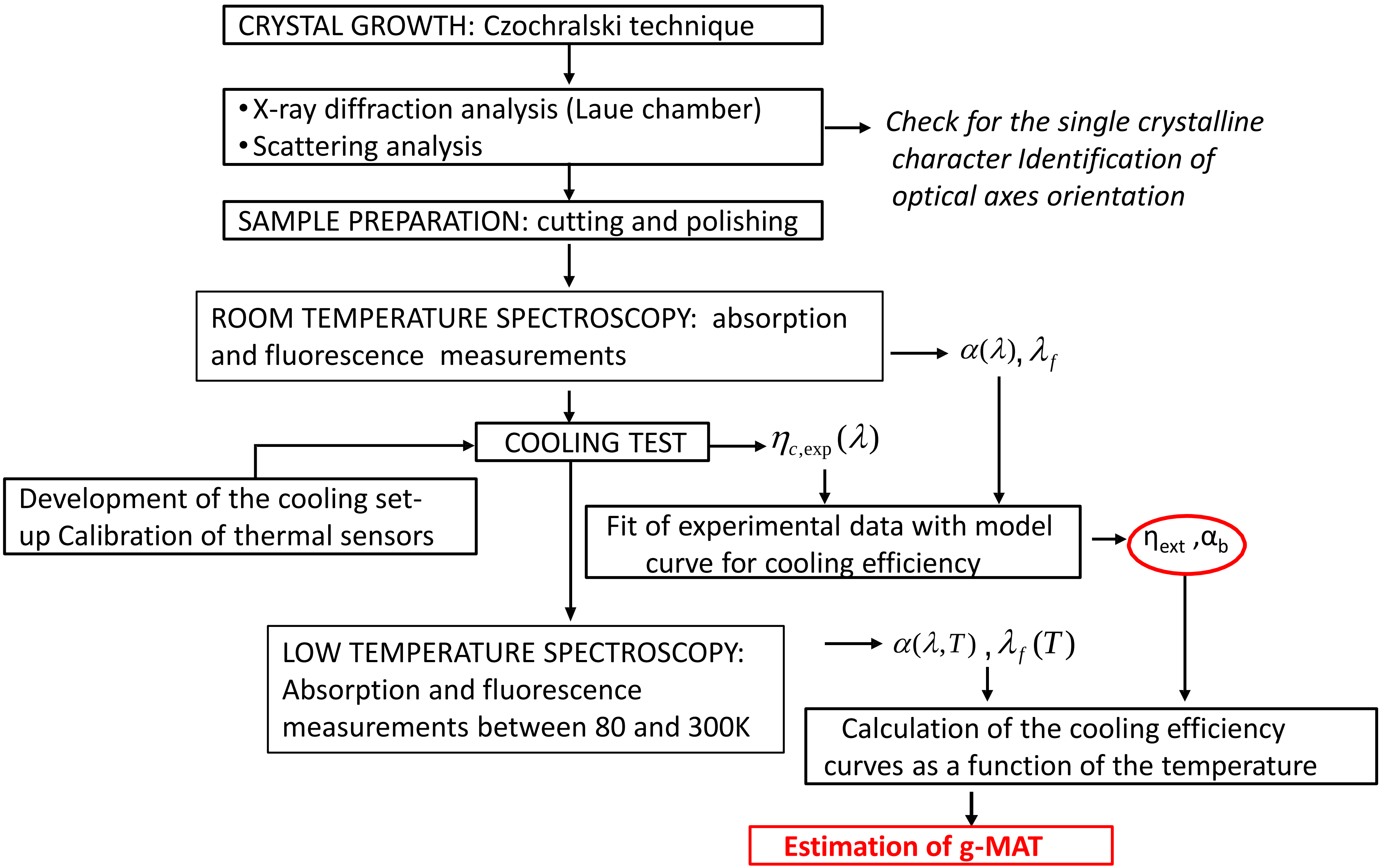
- **COOPERATIVE SENSITIZATION (CS) Yb-Tm:** Yb ($^2F_{5/2}$)+Yb($^2F_{5/2}$)→Tm($^1G_4$) → phonons annihilation
- **Tm up-conversion (UC)**: ($^3F_4$, $^3F_4$)→ ($^3H_6$, $^3H_4$) → phonons annihilation

State of art

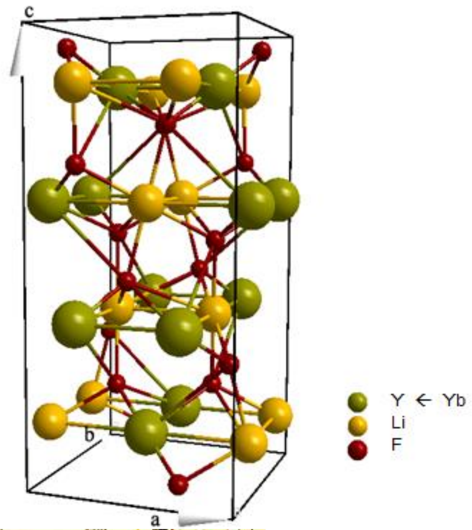


- Yb, Tm :YLF (preliminary result)
  - T= 87 K with clamshell at 278 K → ΔT ~ 190 K **New Record!**
- 10%Yb :YLF
  - T=91 K with clamshell at 270 K → ΔT ~ 180 K

Experimental method

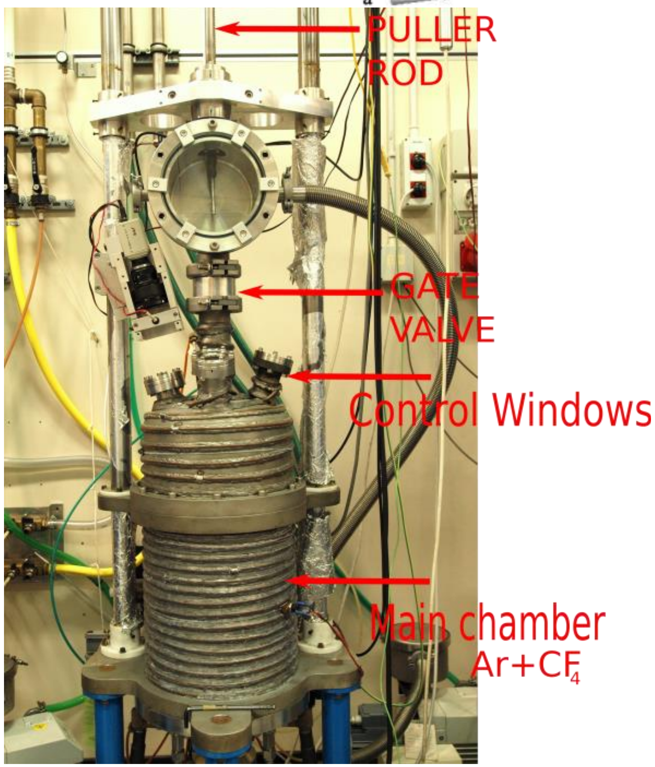


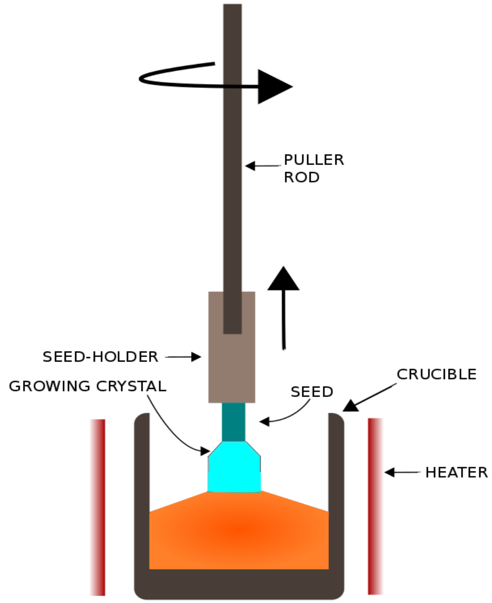
Oriented single crystal of YLF



Lattice parameters	a=5.197Å c=10.735Å
Crystal structure	$I_{41/a}$ symmetry
Density (g/cm³)	3,99
Phonon energy(cm^{-1})	450
Thermal conductivity (W/mK)	a axis: 5.3 (300K) c axis: 7.2 (300K)
Refractive index	n_o= 1.453 (640nm) n_e=1.475(640nm)
Thermal expansion (10^{-6}/K)	a axis: 14.31 (300K) c axis: 10.05 (300K)
Hardness (Mohs)	4-5

Main optical and physical properties of YLF crystal

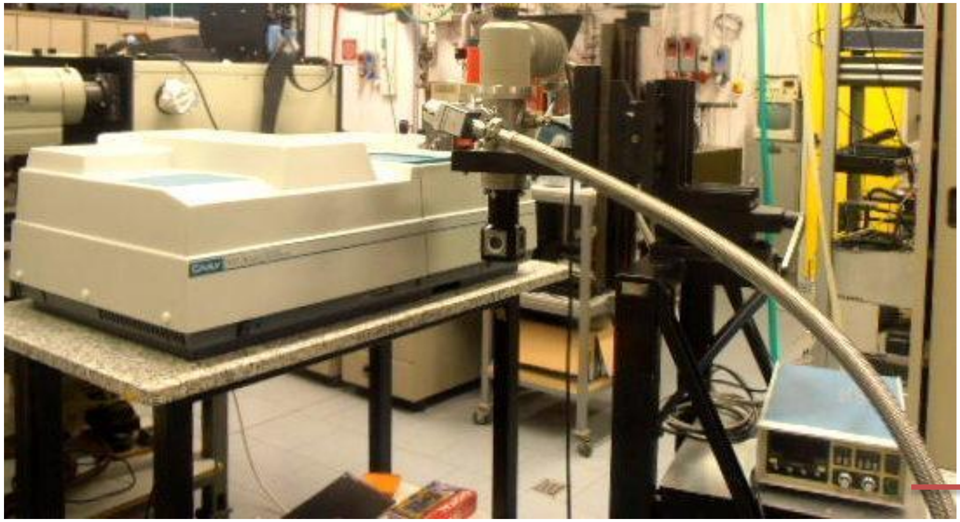




- Pt crucible (99.99%)
- Growth atmosphere: High purity (5N) Ar and CF_4
- Pulling rate: 0.5mm/h (5rpm)
- Resistive heating: graphite resistance (1300°C)
- High vacuum system (10^{-7} mbar)
- Optical system for diameter control
- High purity (5N) powders of LiF, YF3 , YbF3 and TmF3 as raw materials
- Seed: YLF undoped oriented along the a-axis
- Melt temperature: 860-880 °C

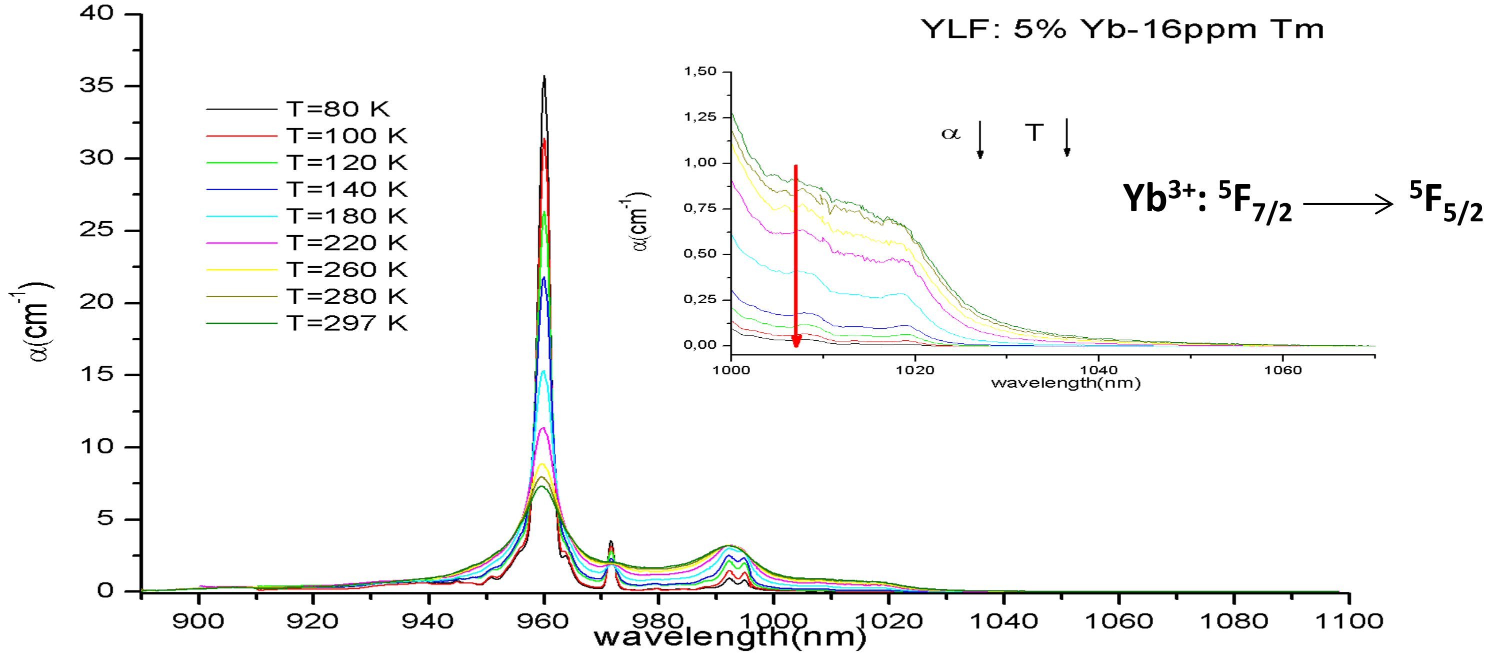
Measurements as function of temperature on $5\%Yb^{3+}$-$0{,}0016\%Tm^{3+}$: $LiYF_4$

Absorption spectra

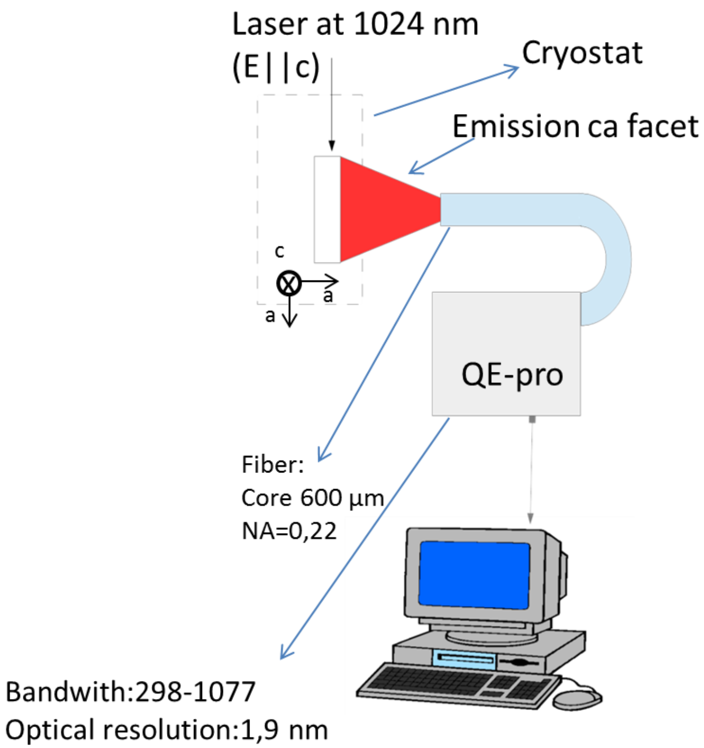


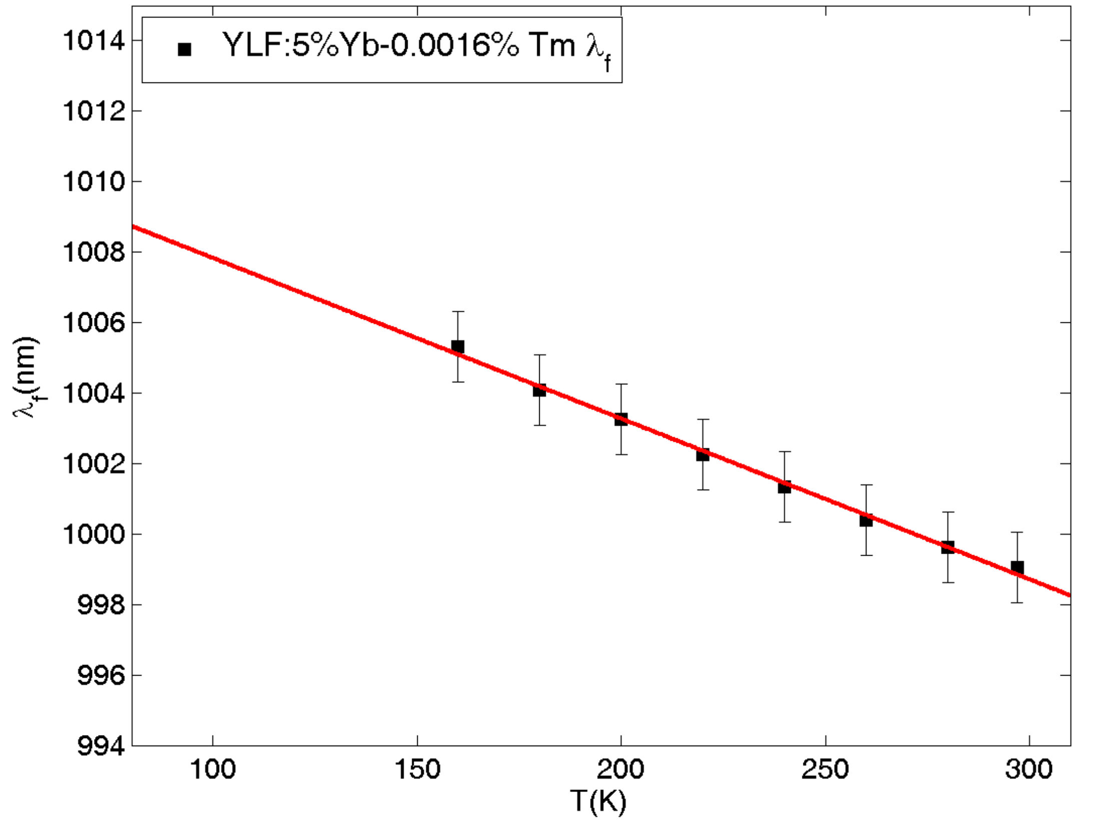
- Twin-beam spectrophotometer
- Working range: λ=175-3300nm
  0-10 A
- UV-VIS: 0.1nm resolution
- NIR: 0.4nm resolution
- Absorbance resolution: 0.001

The temperature of the sample can be varied using a He-cryostat between 10 and 300K



Mean emission wavelength as function of temperature



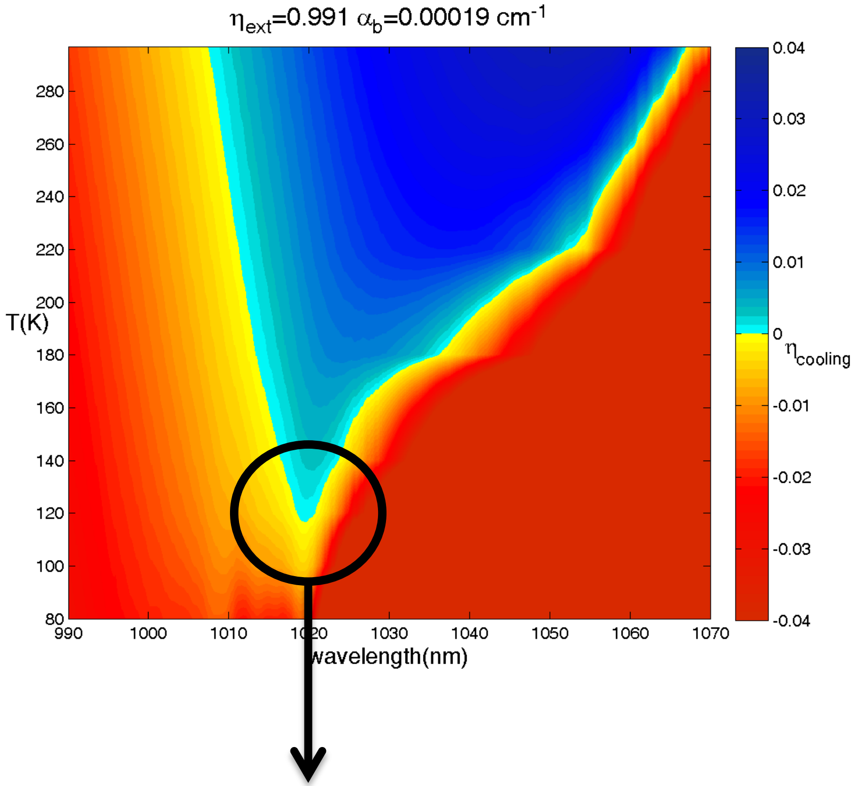


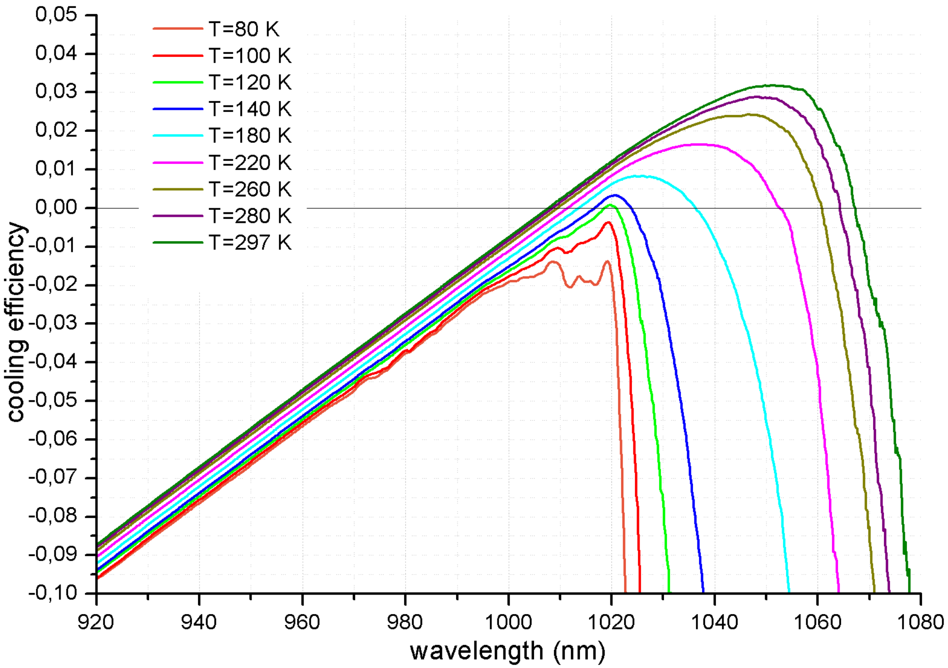
$$\lambda_f(\mathrm{T}) = \frac{\int \lambda \cdot S(\lambda, \mathrm{T})\, \mathrm{d}\lambda}{\int S(\lambda, \mathrm{T})\, \mathrm{d}\lambda}$$

$\lambda_f(\mathrm{T})$ behavior → red shift → cooling efficiency decreasing

G-mat prediction

g-mat (global minimun achievable temperature) is calculated from $\alpha(\lambda,T)$ and λ_f measurements using room temperature variables η_{ext} and α_b





Huge difference between calculated g-mat and experimental data suggests requirement of a new theoretic model including the Tm concentration effects

First growth:
$5\%Yb^{3+}$-$50ppmTm^{3+}$: $LiYF_4$
collocation number 169

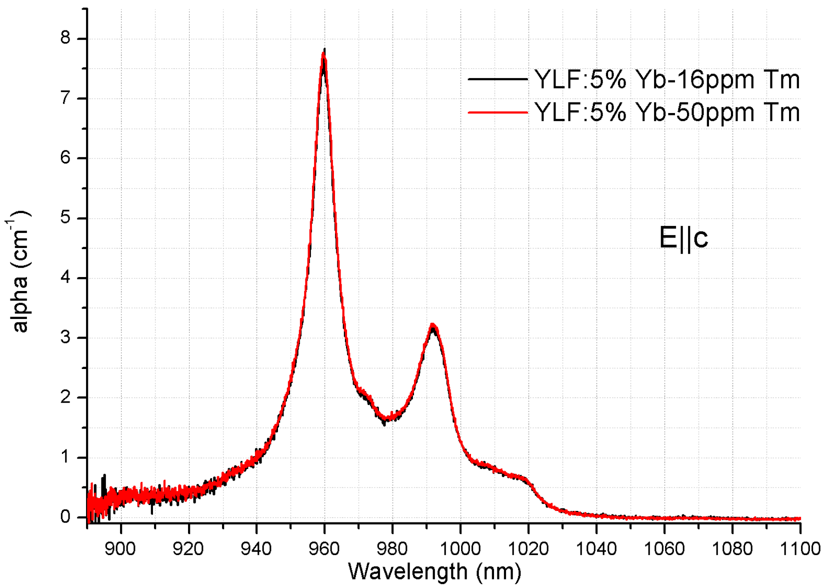
Second growth:
$5\%Yb^{3+}$: $LiYF_4$
$5\%Yb^{3+}$-$50ppmTm^{3+}$: $LiYF_4$

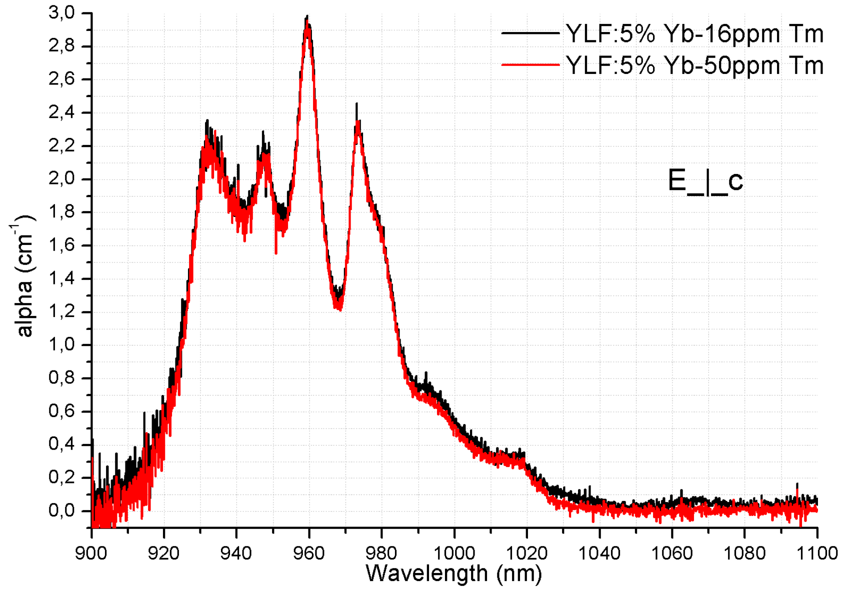
collocation number 173a

collocation number 173b

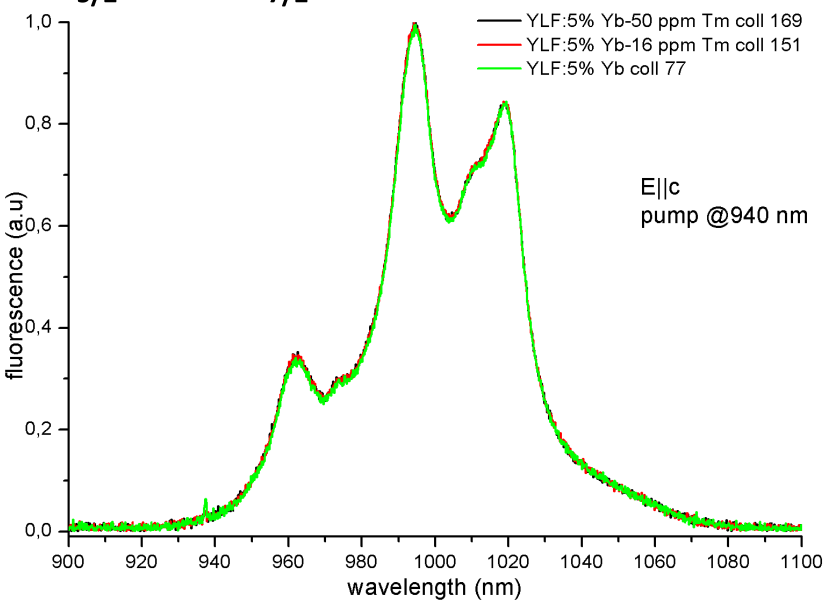
RT-spectroscopy

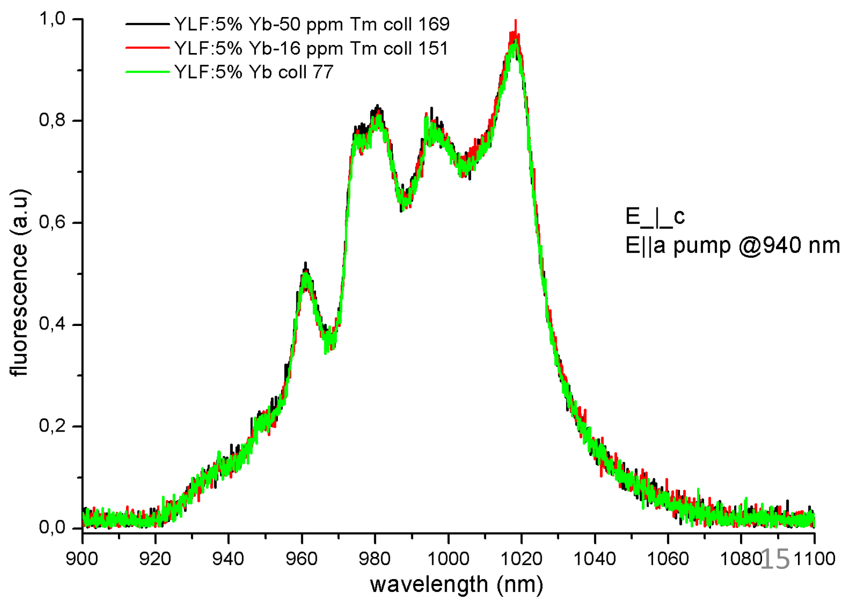
Yb^{3+}: $^5F_{7/2} \longrightarrow {}^5F_{5/2}$



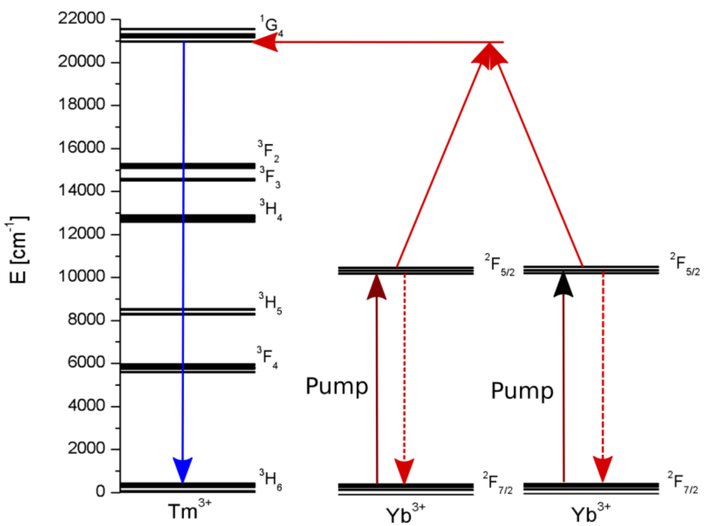


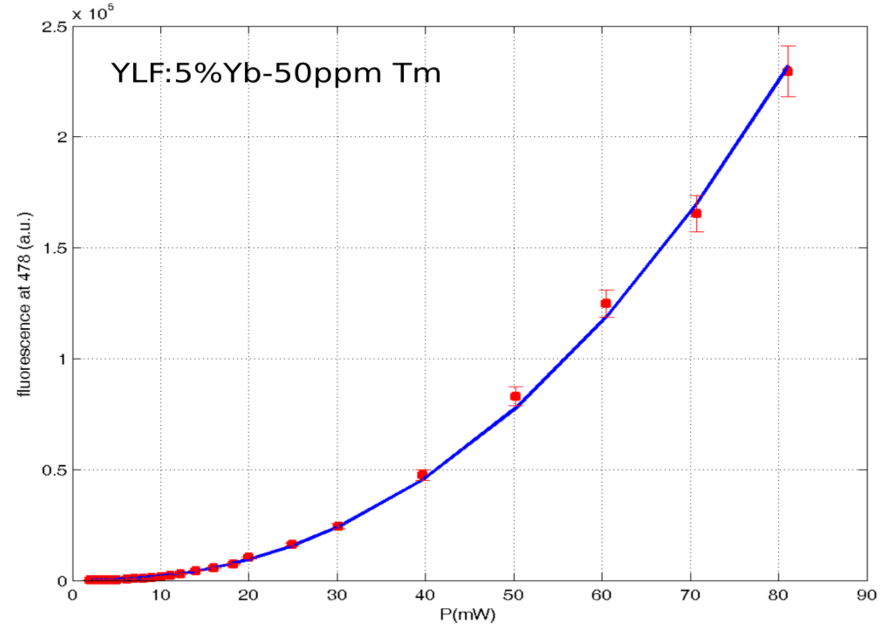
Yb^{3+}: $^5F_{5/2} \longrightarrow {}^5F_{7/2}$



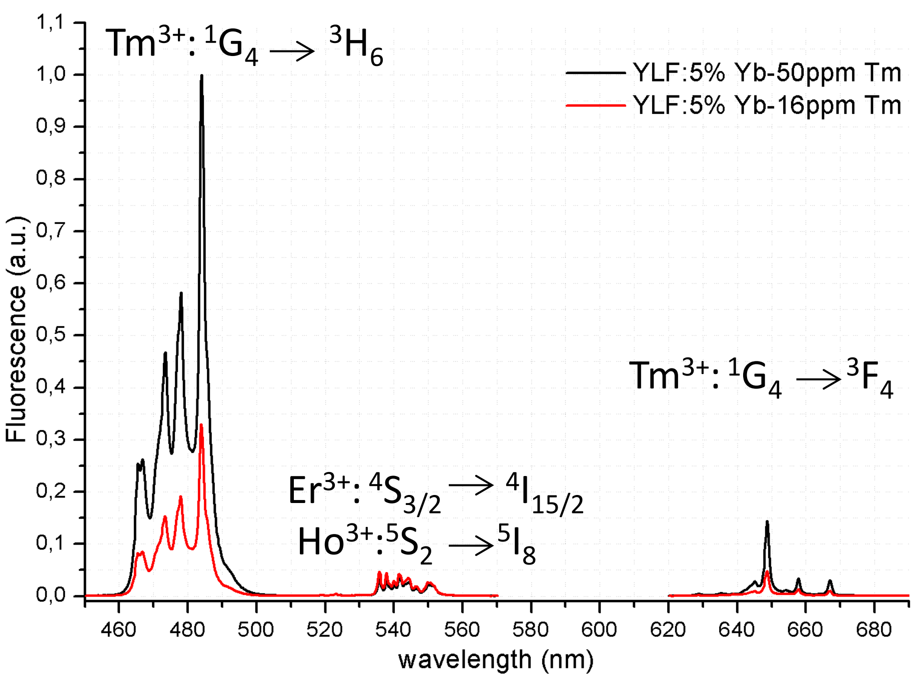


Measurement on Tm-Yb interaction





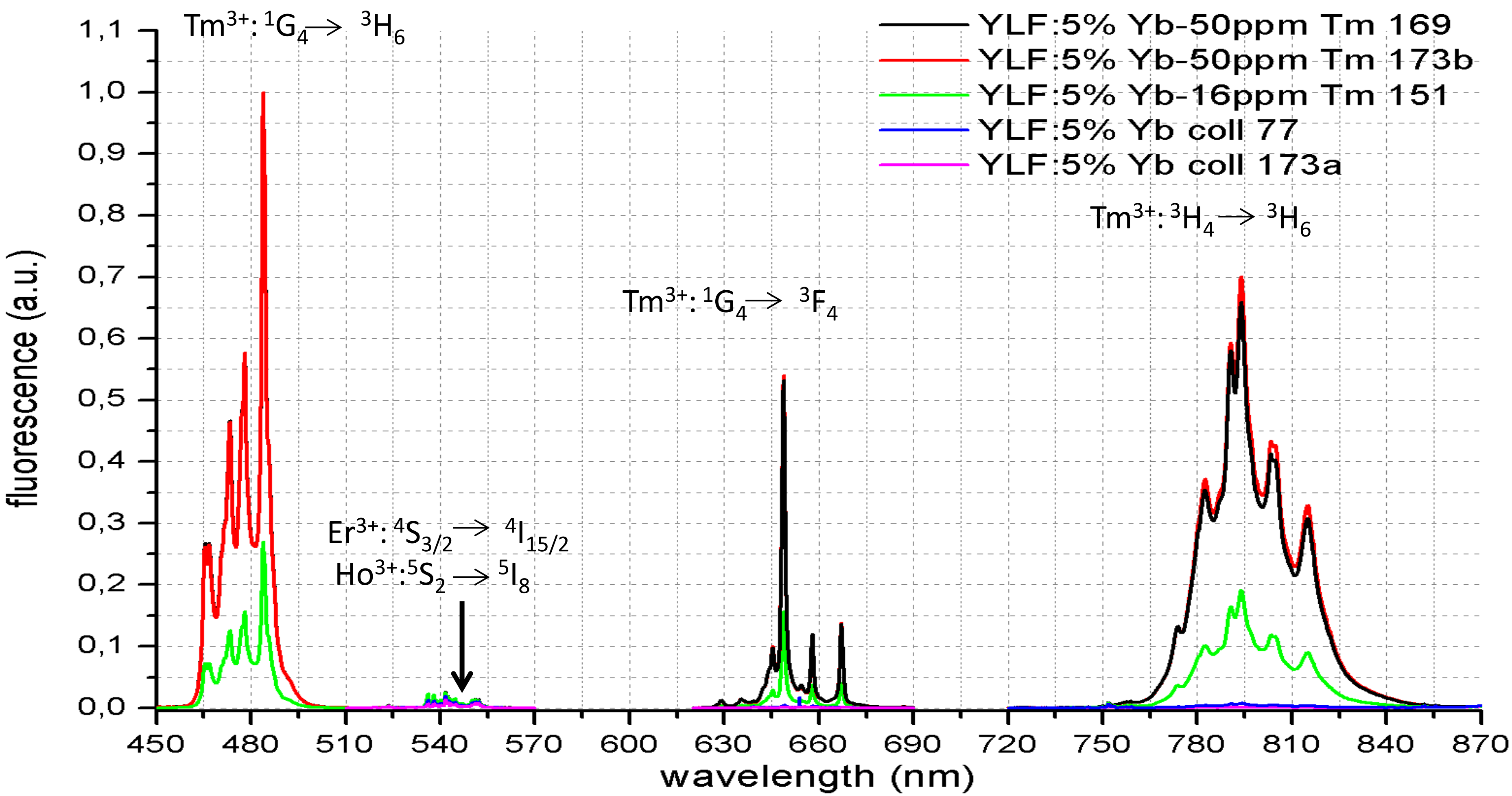
Fit: I ~ P^k **k=2.3±0.1**



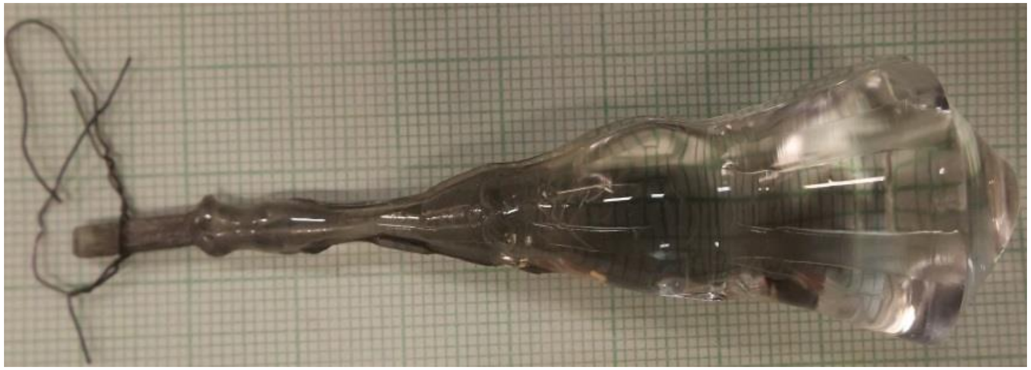
There is no substantial difference between the exponential of YLF:5% Yb-16ppm Tm (b=2,3 ± 0,2)[1] and YLF:5% Yb-50ppm Tm (b=2,3 ± 0,1)

[1] **Azzurra Volpi, Alberto Di Lieto and Mauro Tonelli , 'A novel approach for solid state cryocoolers', Vol. 23, No. 7 | DOI:10.1364/OE.23.008216 | OPTICS EXPRESS 8216**

RT-spectroscopy on Tm^{3+}



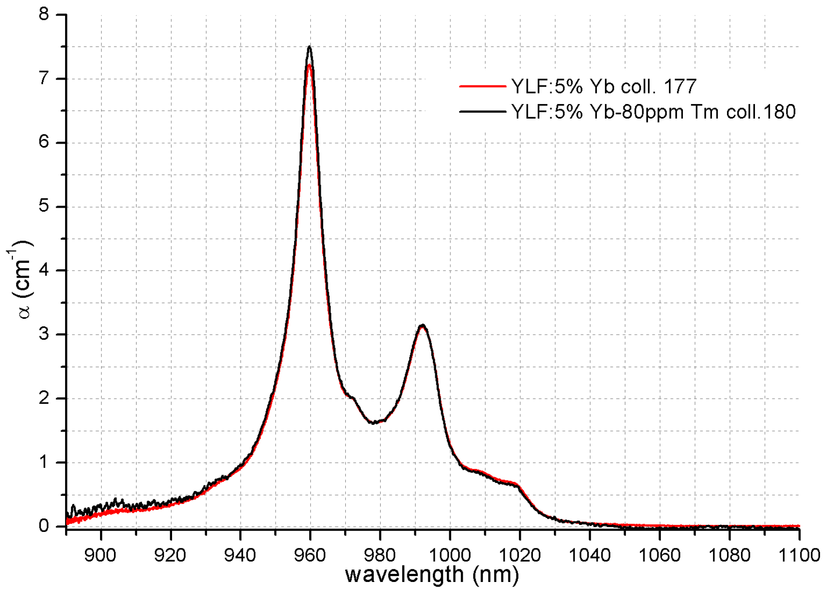
third growth:
5%Yb^{3+}: $LiYF_4$
5%Yb^{3+}-80ppmTm^{3+}: $LiYF_4$

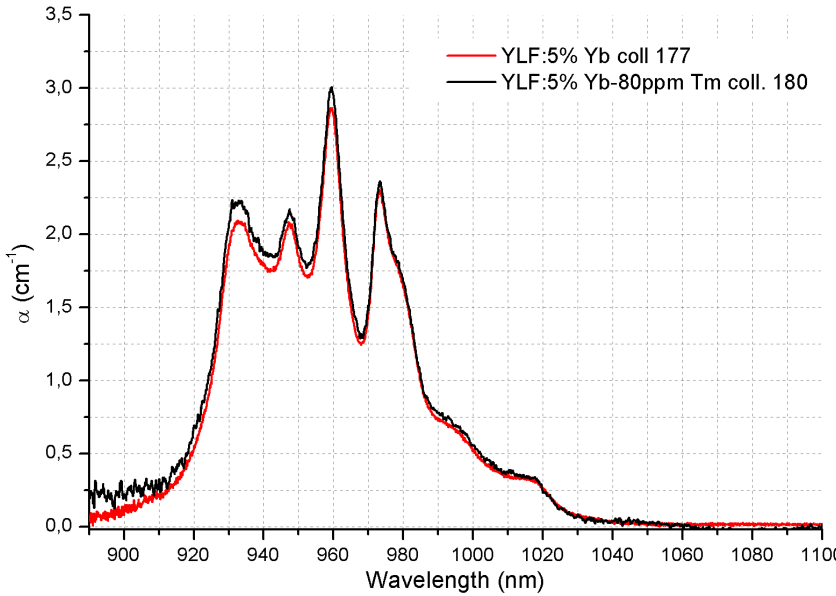


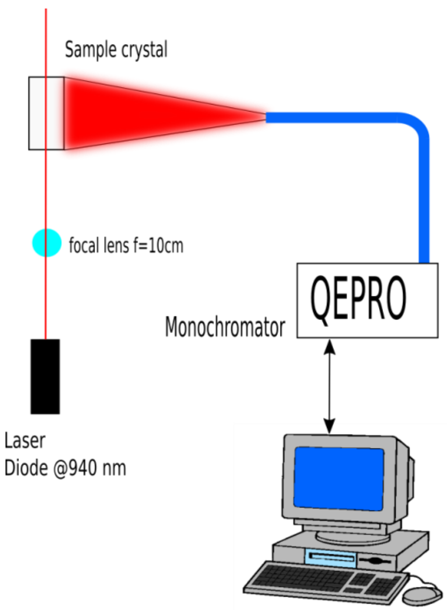
collocation number 177

collocation number 180

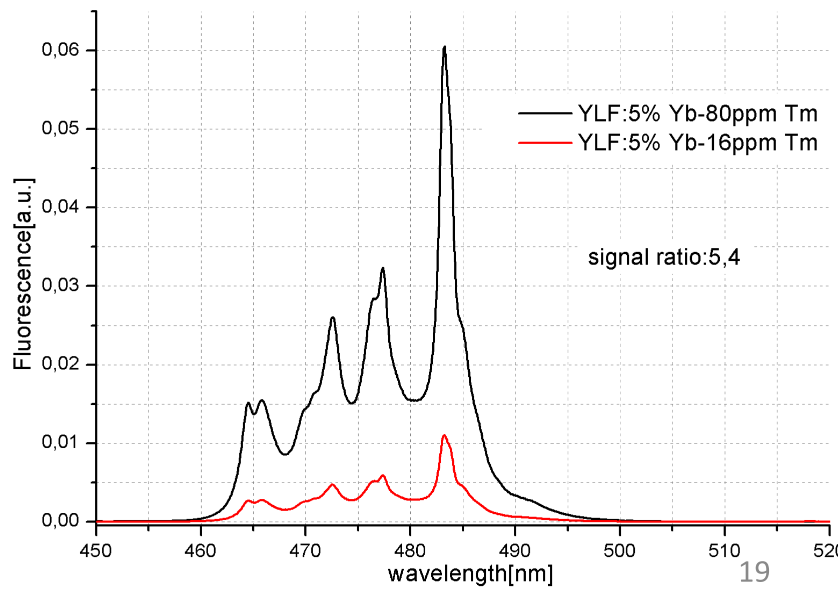
α *and* λ_f measuring



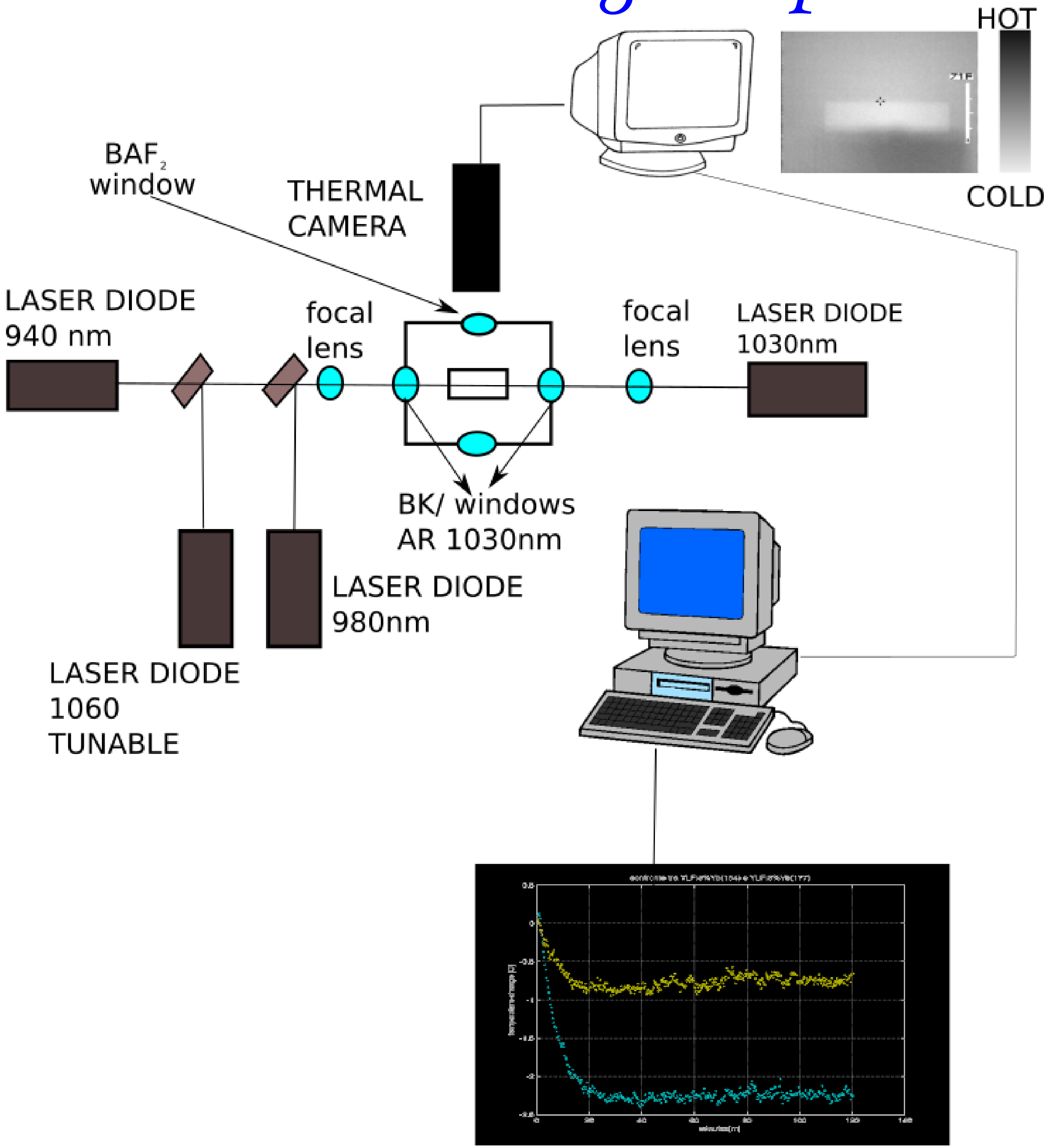




Sample	λ_f(nm)
YLF:5%Yb coll. 177	998,1
YLF:5%Yb-80ppm Tm coll. 180	998,1

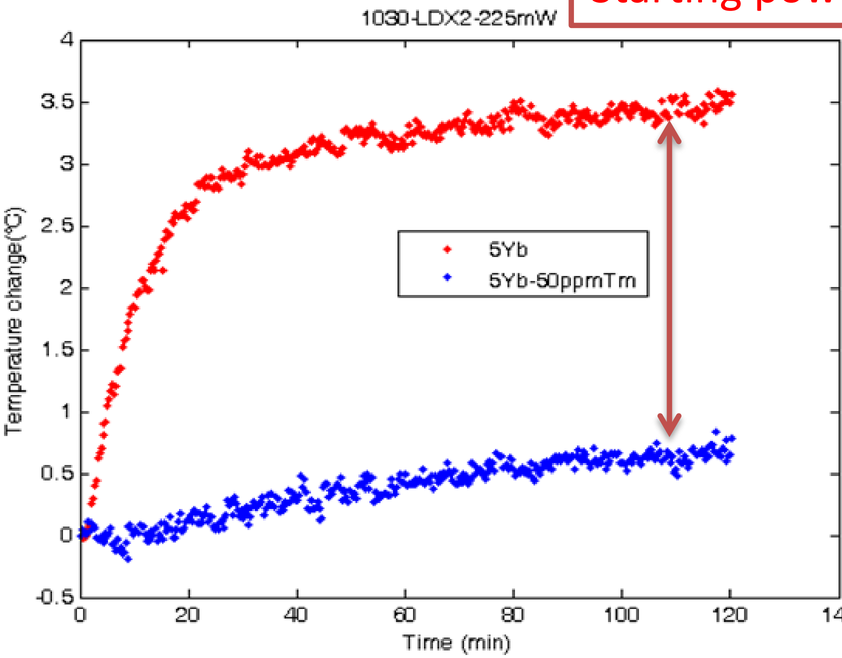


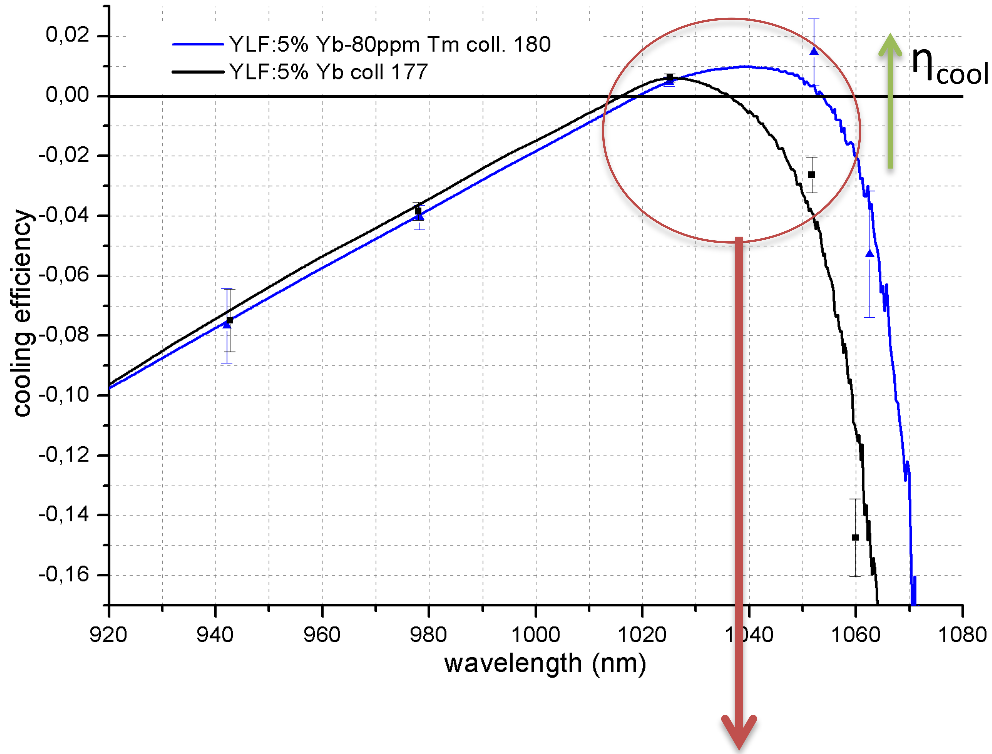
Laser cooling setup

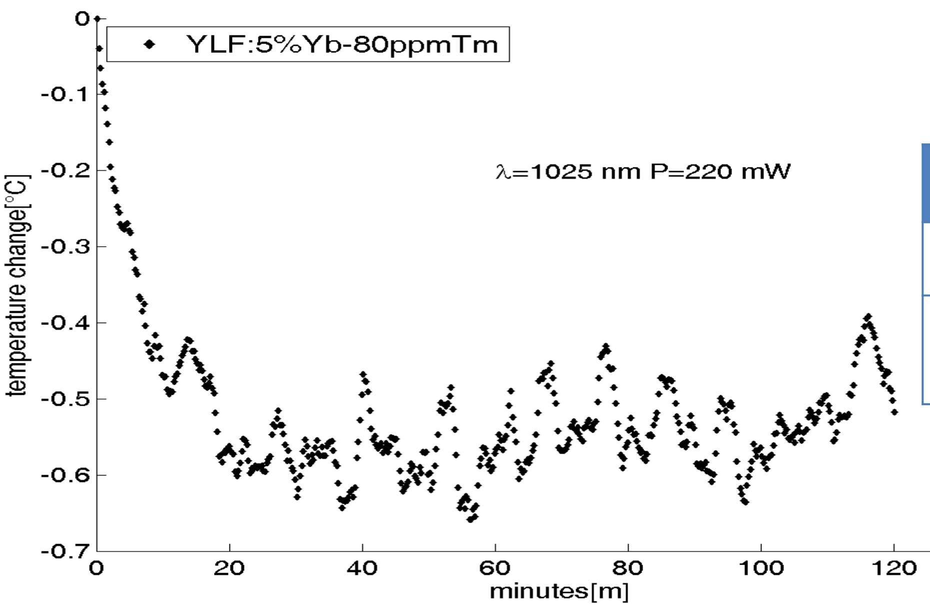


Laser cooling test and performance

Starting powders are the same for each pair





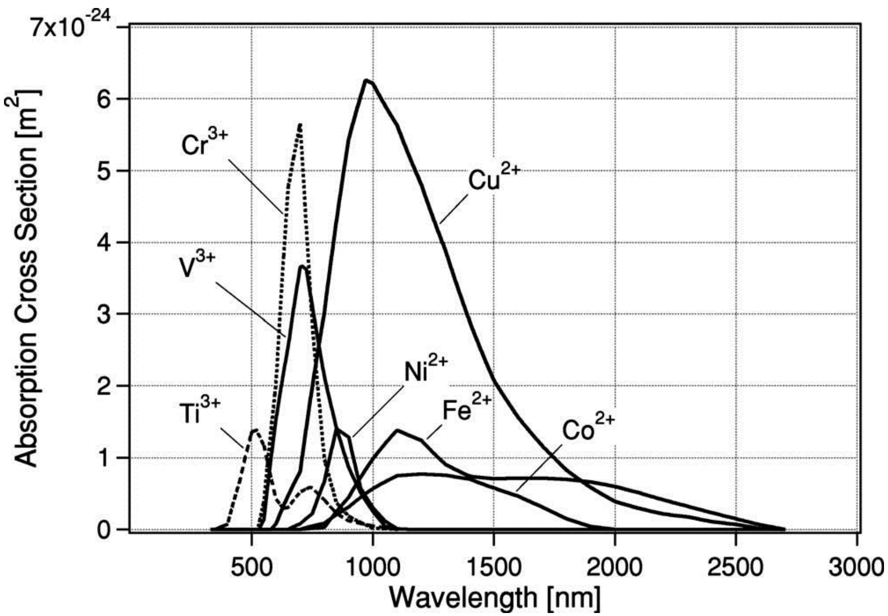


Crystals	η_{ext}	$\alpha_b(cm^{-1})$
YLF:5%Yb coll. 177	0.984 ± 0.001	$(1.28 \pm 0.08) \cdot 10^{-3}$
YLF:5%Yb-80ppm Tm coll. 180	0.980 ± 0.001	$(5 \pm 1) \cdot 10^{-4}$

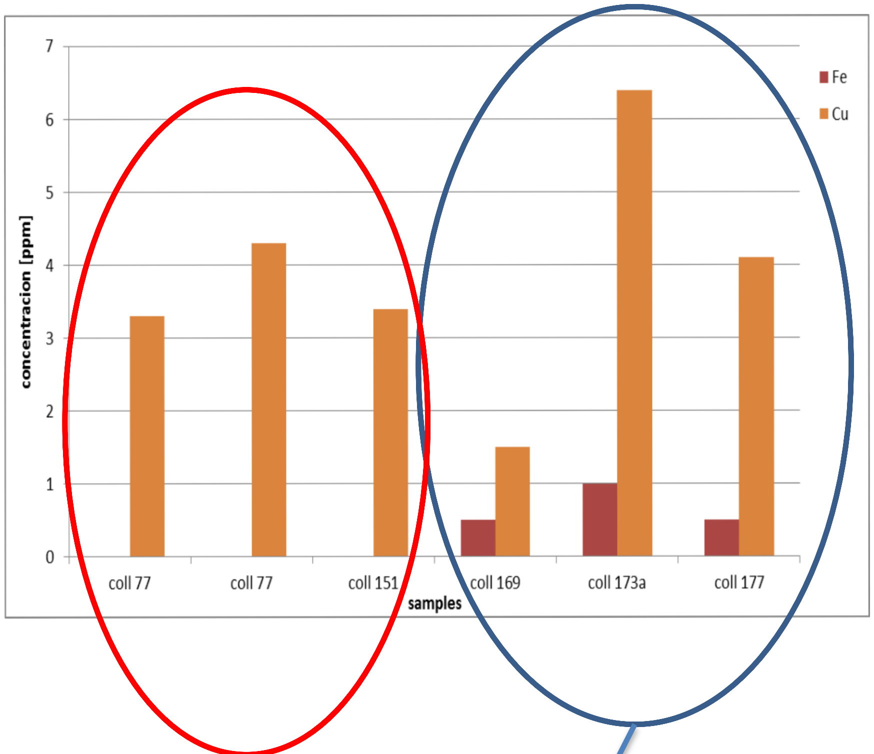
Chemical analysis

Samples sent to SUERC(Scottish University Environment Research Center)

Elements can quench Yb^{3+} transition:



Detection limit:250ppb (part per billion)



Good cooling performance

Sample 177 shows poor cooling and others do not cool

Conclusion and future work

- The result of adding Tm ions is to obtain a redshift of cooling efficiency curve and a reduction of α_b coefficient. A reduction of α_b has a consequence to increase the peak cooling efficiency and hence to improve the performance of the system.

- In future work, we are going to employ 6N purity of starting powders, that means the sum of all impurities is less 1ppm, in order to decrease detrimental concentration of pollutant like Fe^{2+}.

- The next stages of the work will involve the investigation of the optical cooling effect in $LiLuF_4$ and KYF_4 crystalline host as a function of the Tm doping level at fixed Yb level at 5% and a comparative analysis of the cooling performances in connection with material properties