Effetti delle impurezze sul raffreddamento ottico di fluoruri drogati con terre rare

Alberto Sottile
Università di Pisa

Pisa, 5 Febbraio 2014

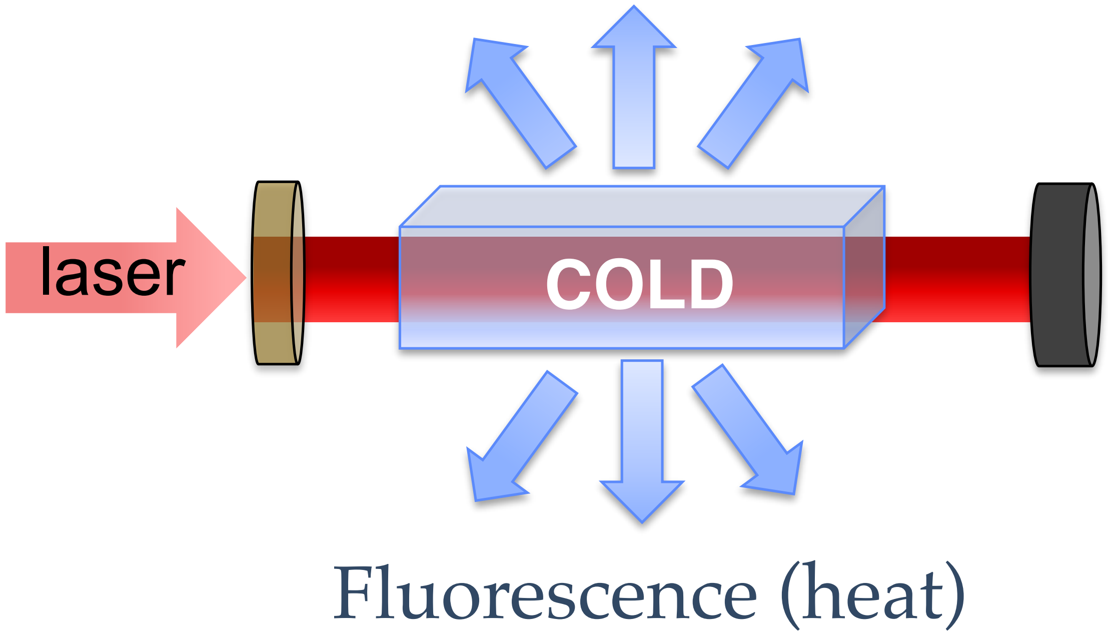
Outline

- Optical refrigeration of solids
- Growth of fluoride crystals
- Refrigeration measurements
- Effects of the impurities

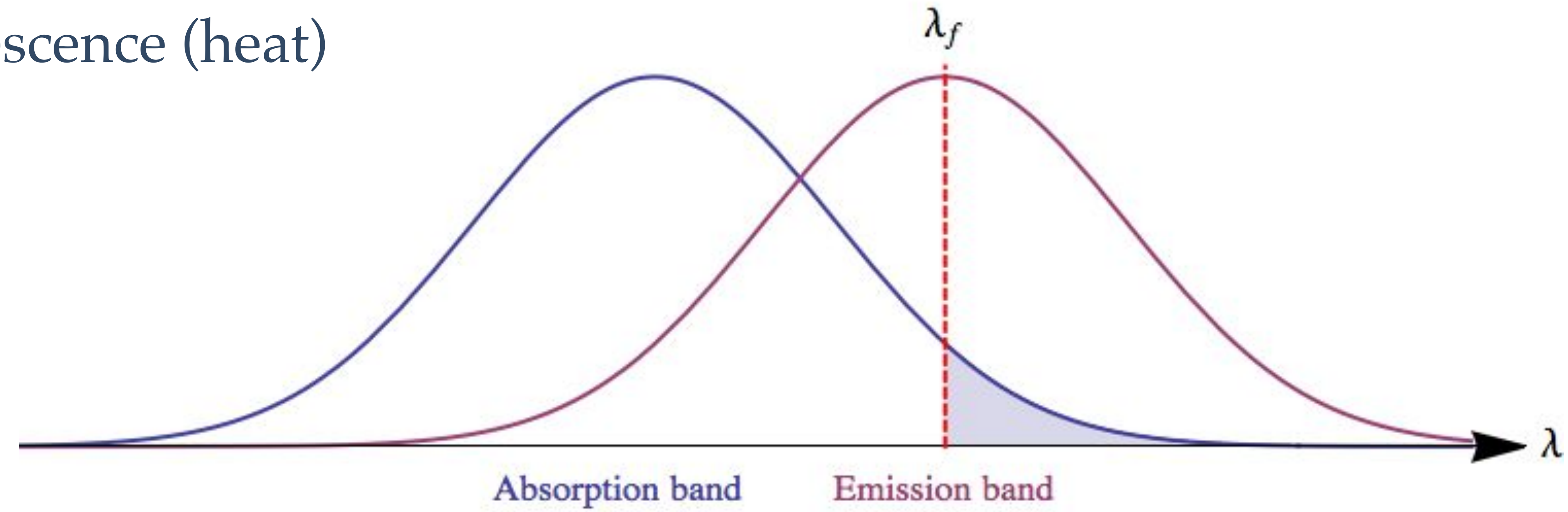
Optical refrigeration

Principle of operation

A solid reduces its temperature when pumped with a laser



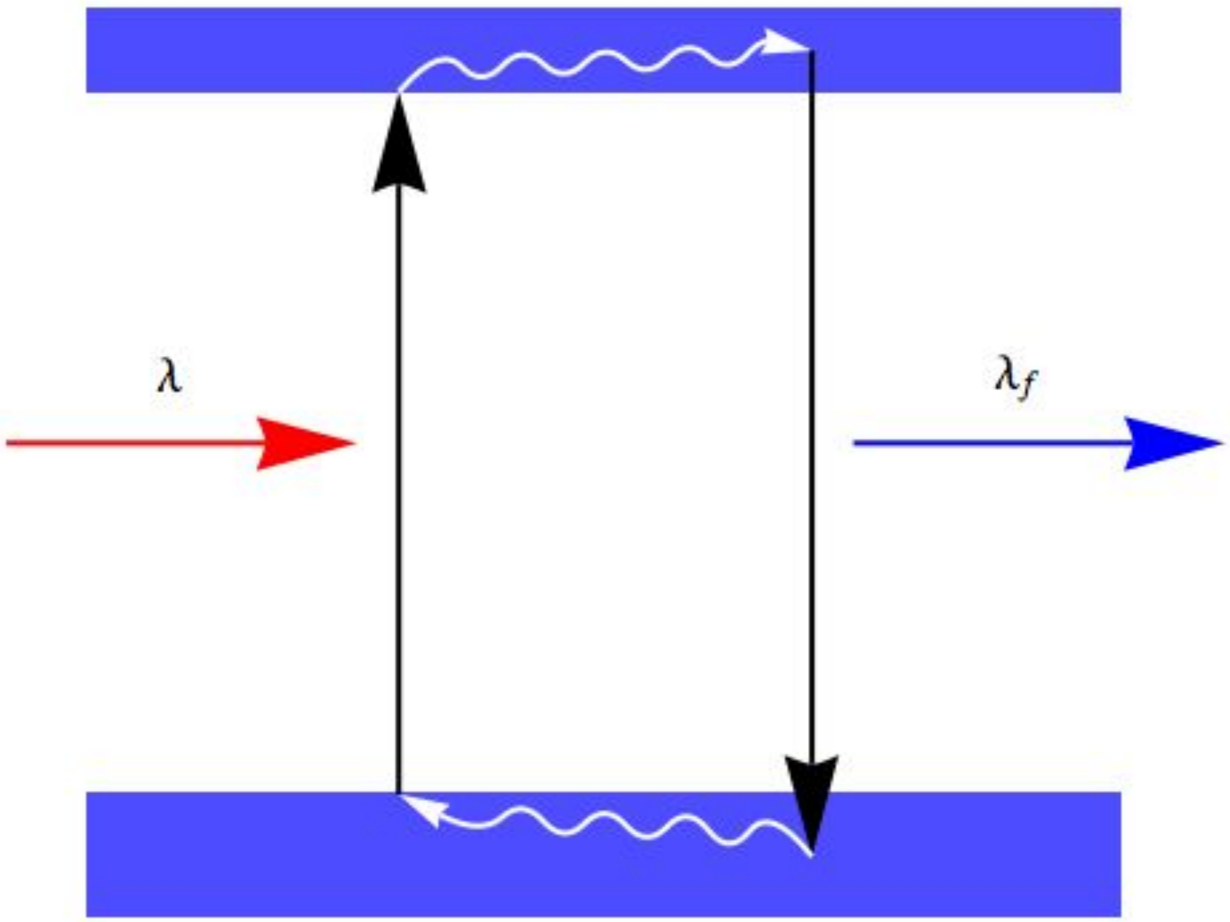
- Proposed in 1929
- Accepted as valid in 1946
- First observation in 1995



Optical refrigeration

Transitions between two broad levels

Theory | Crystals
Cooling | Impurities



The emission subtracts thermal energy from the object

Ideal cooling efficiency:

$$\eta_c = \frac{P_{cool}}{P_{abs}} = \frac{\lambda - \lambda_f}{\lambda_f}$$

Requirement: all the absorbed photons are emitted again as fluorescence photons

Optical refrigeration

Constraints to the ideal model

Two restrictions affect the efficiency

Background absorption (BA):
an incident photon is absorbed and excites the cooling process

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

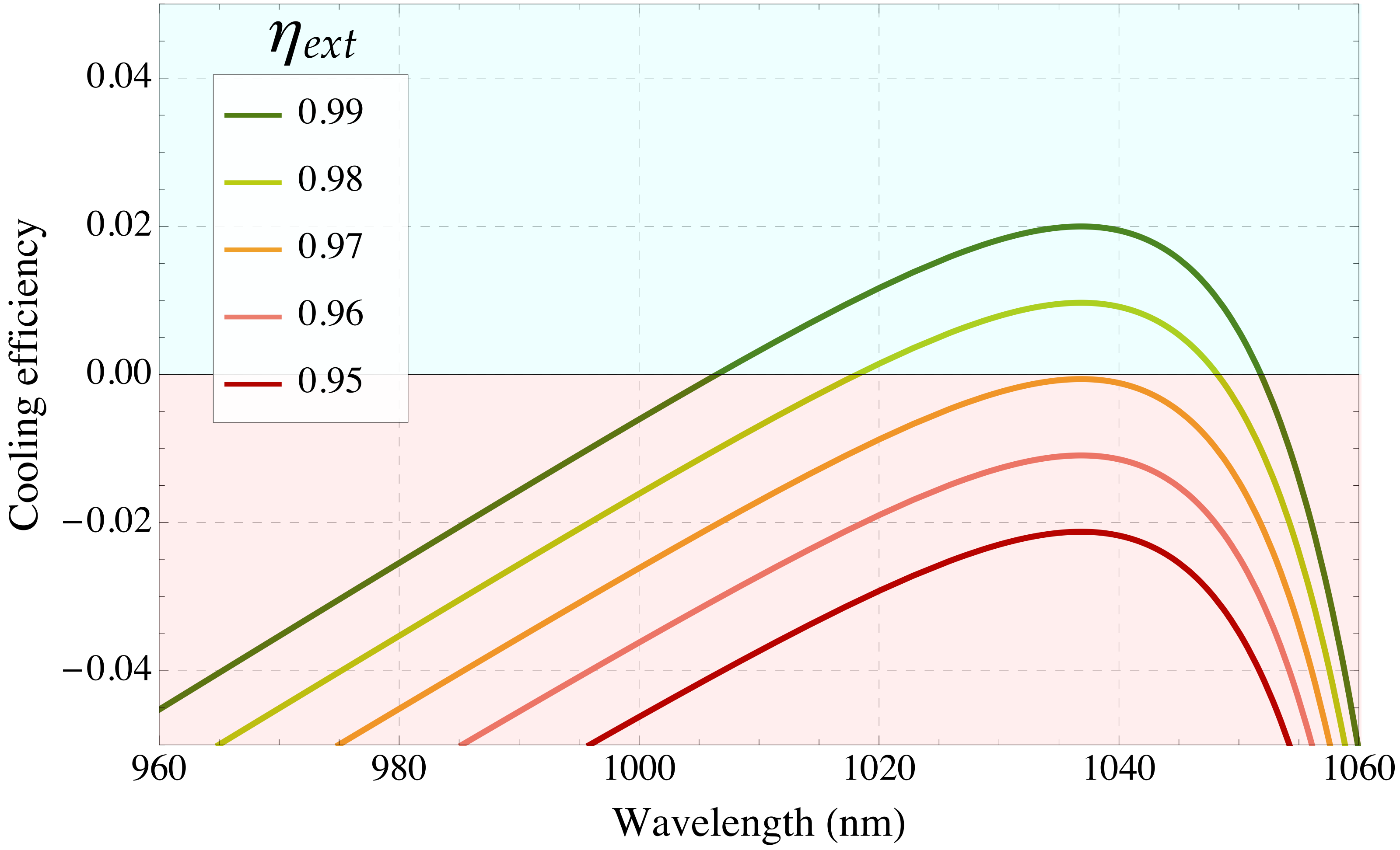
External quantum efficiency (EQE):
an absorbed photon causes a cooling emission that escapes the material

$$\eta_{ext} = \frac{\text{no. of escaping photons}}{\text{no. of absorbed photons}}$$

Optical refrigeration

Cooling efficiency model

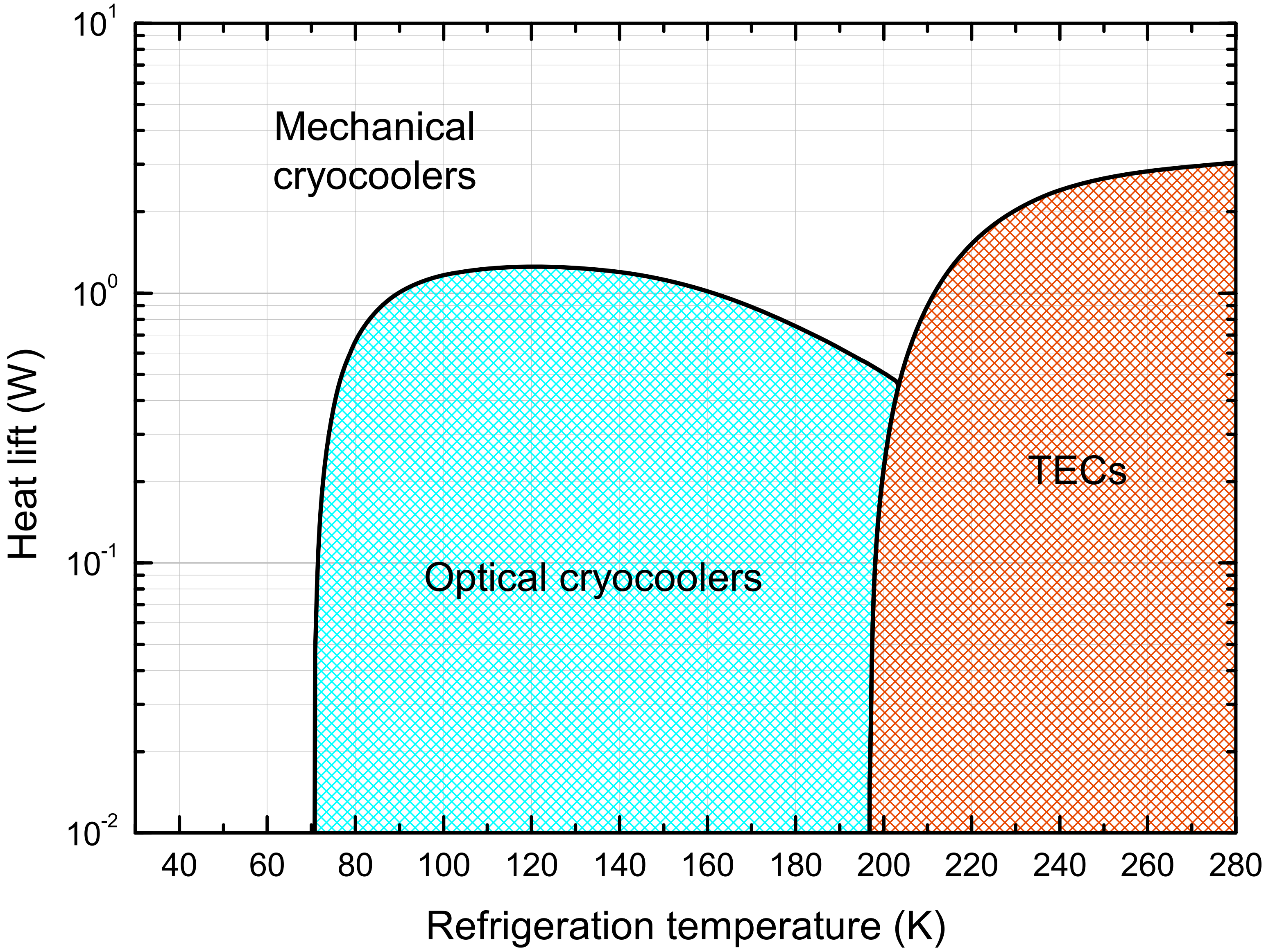
$$\eta_c = \eta_{ext}\left[1+\frac{\alpha_b}{\alpha(\lambda)}\right]^{-1}\left(\frac{\lambda}{\lambda_f}\right)-1$$



- The cooling efficiency is characterized by these two parameters
- The EQE must be higher than 97%!

Optical refrigeration

Vibration-less coolers with extended capabilities



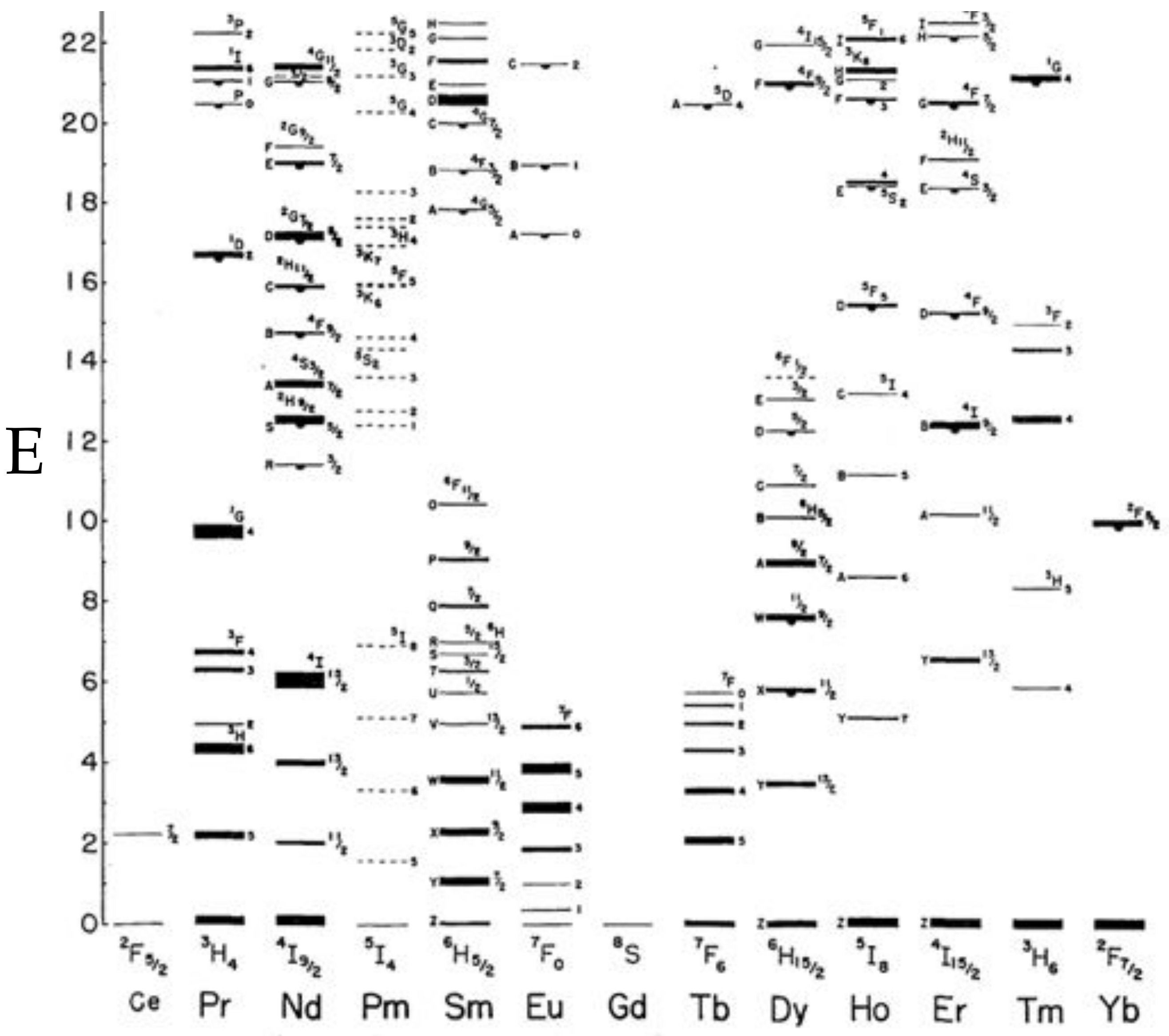
- Insensitivity to electromagnetic fields
- TECs are less efficient for differences larger than 60 degrees
- TECs do not work under 190 K

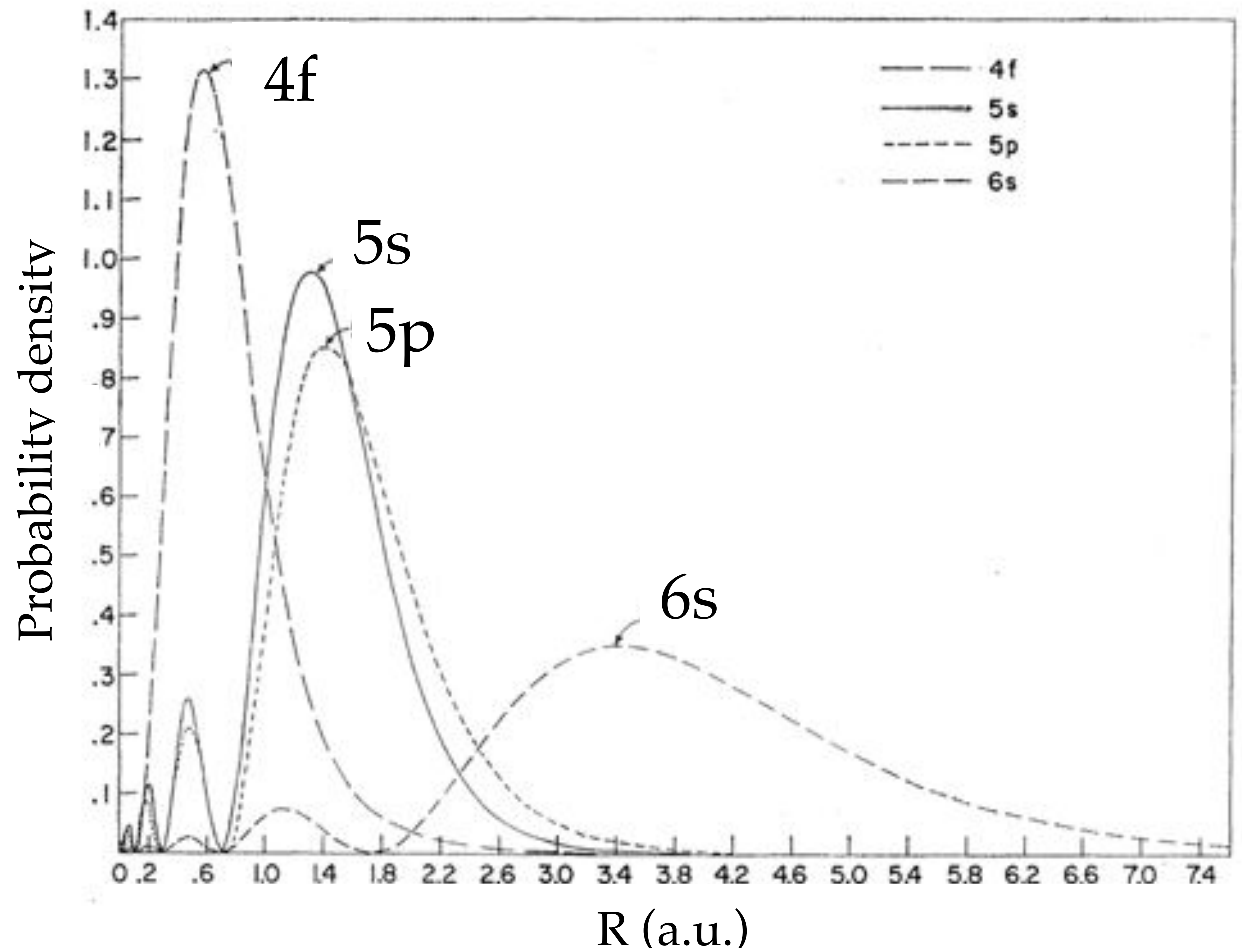
Rare earth trivalent ions

Doping elements for optical applications

From Cerium (58) to Lutetium (71)

RE^{3+} : $[Xe]4f^{n}$ $\qquad n = 1 \div 14$





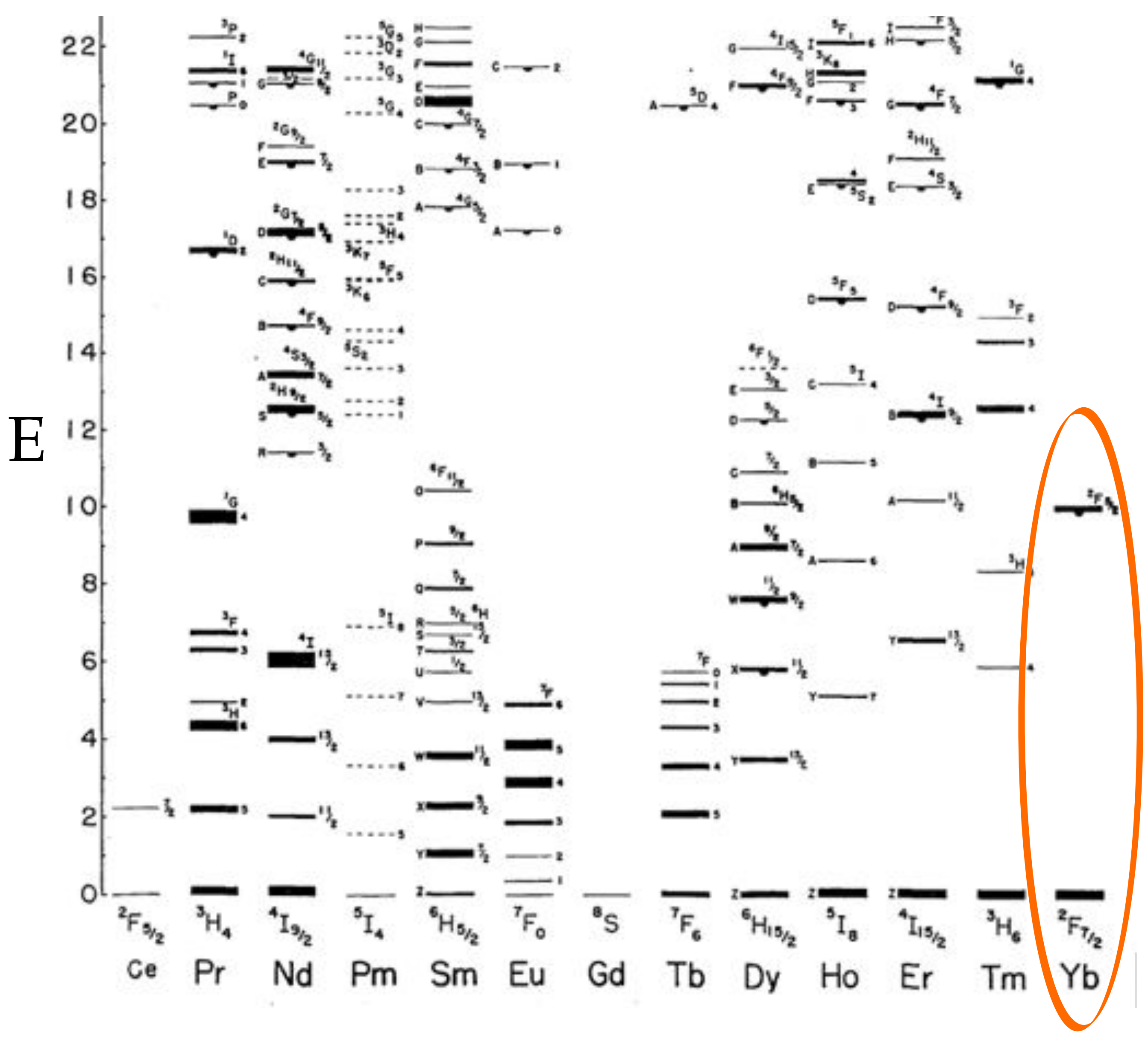
- 4f electrons interact and generate complex structures
- 4f screened by outer orbitals

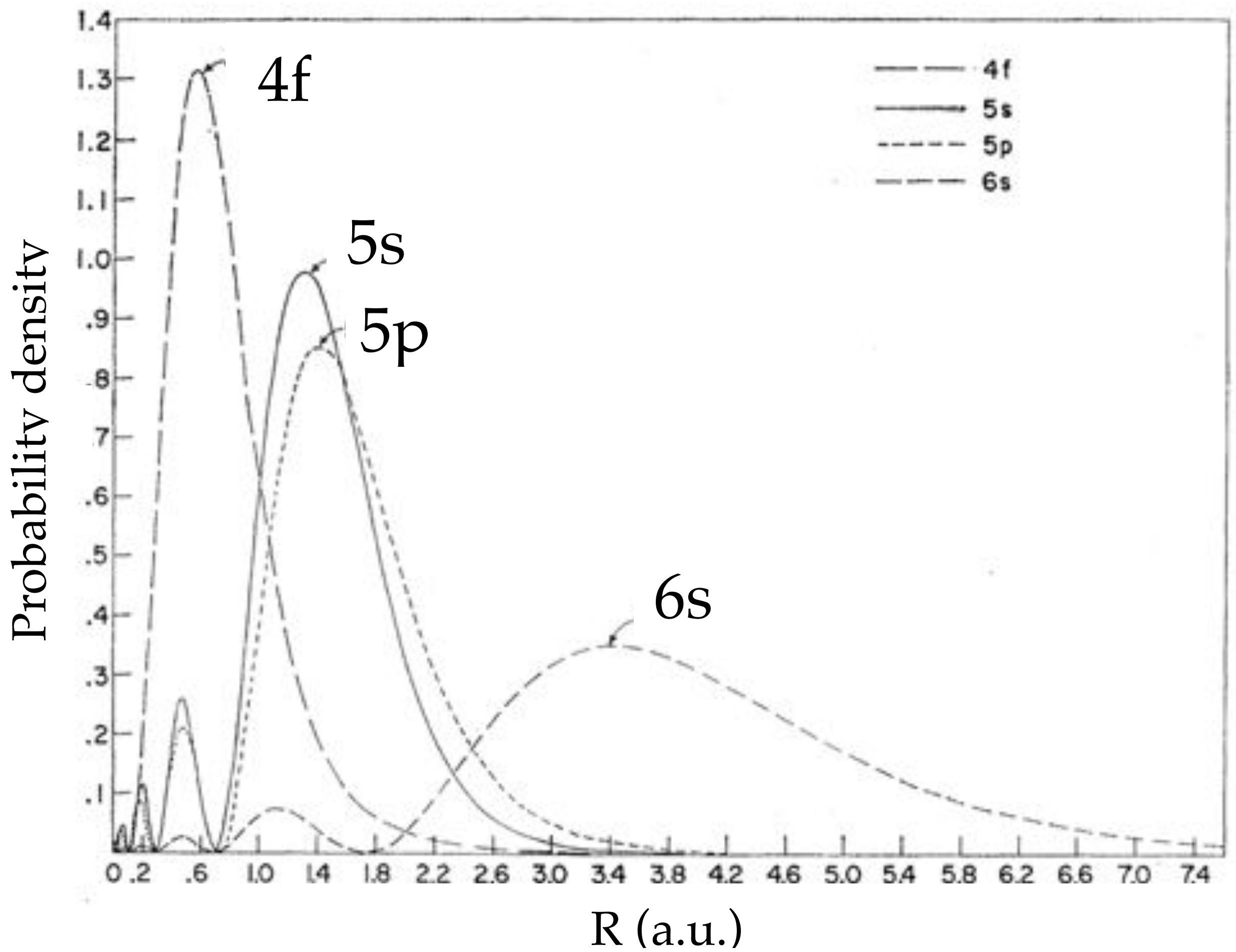
Rare earth trivalent ions

Doping elements for optical applications

From Cerium (58) to Lutetium (71)

$$RE^{3+} : [Xe]4f^n \qquad n = 1 \div 14$$



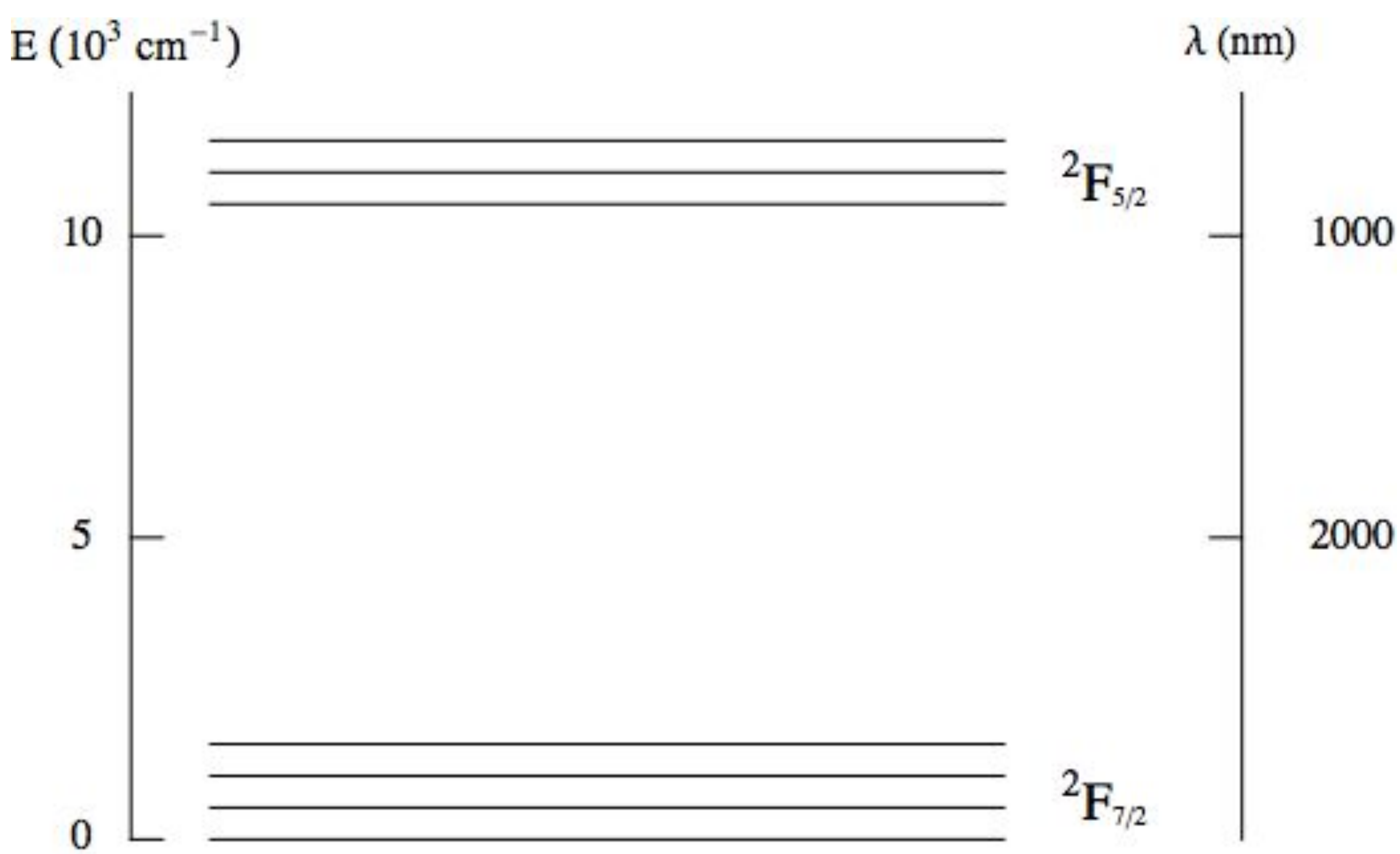


- 4f electrons interact and generate complex structures
- 4f screened by outer orbitals

Rare earth trivalent ions

Ytterbium trivalent ion levels inside a host

The simplest level structure among the rare earth ions



Yb^{3+} : $[Xe]4f^{13}$

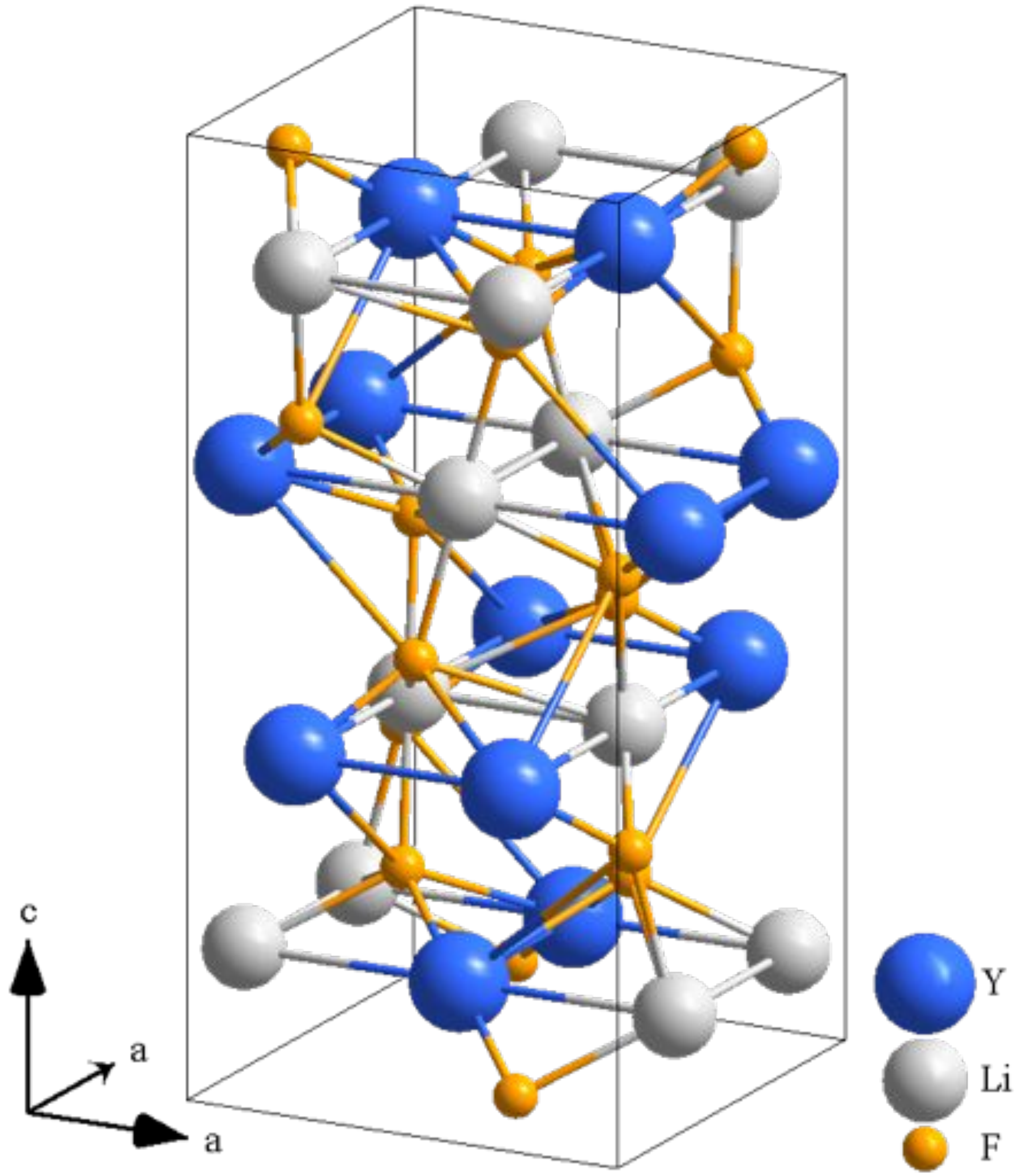
- Large overlap between absorption and emission
- No higher excited states
- Large separation between the manifolds

Fluoride crystals

Yttrium Lithium Fluoride (YLF) as rare earth host

Formula: $LiYF_4$

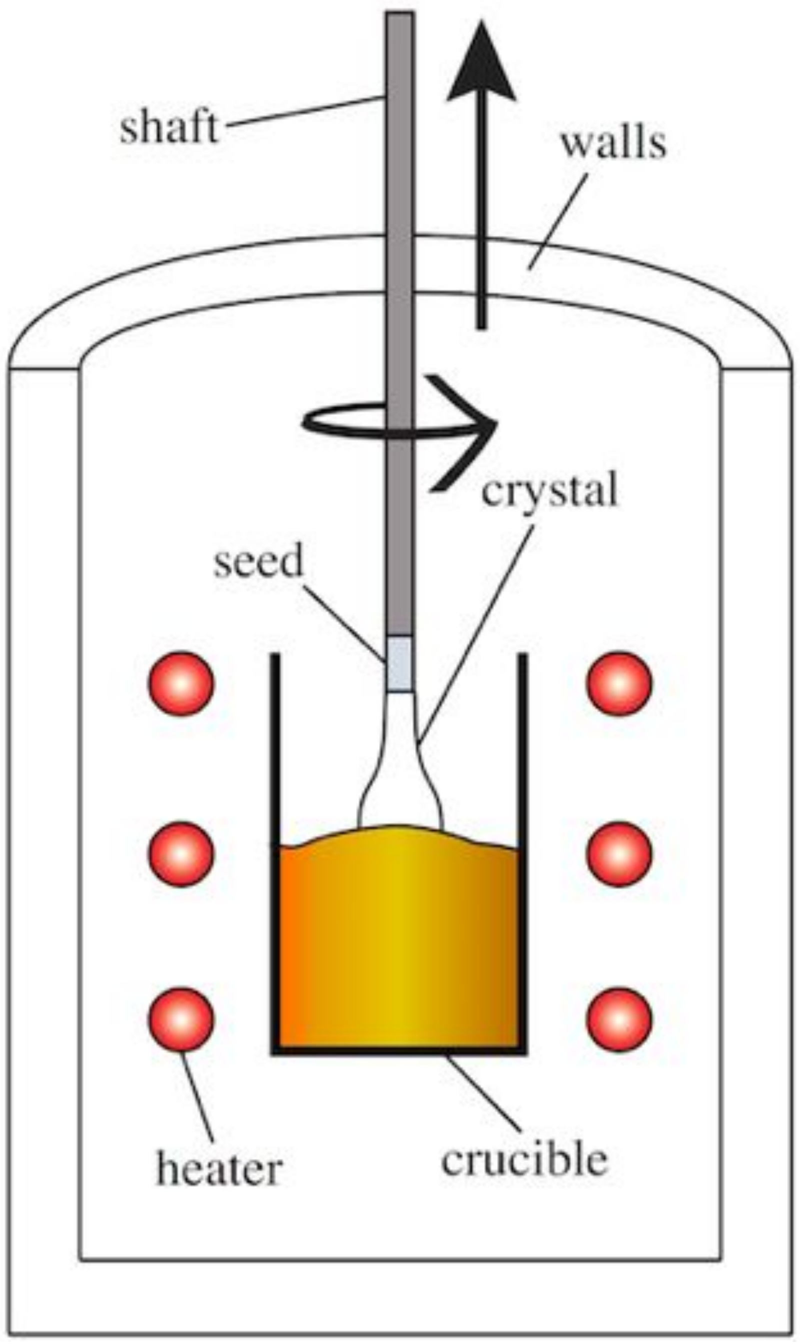
- High performances as solid-state laser medium
- Low phonon energy
- Wide transparency window
- High thermal conductivity
- Yttrium can effectively be replaced by rare earth ions
- Tetragonal structure



Crystal growth

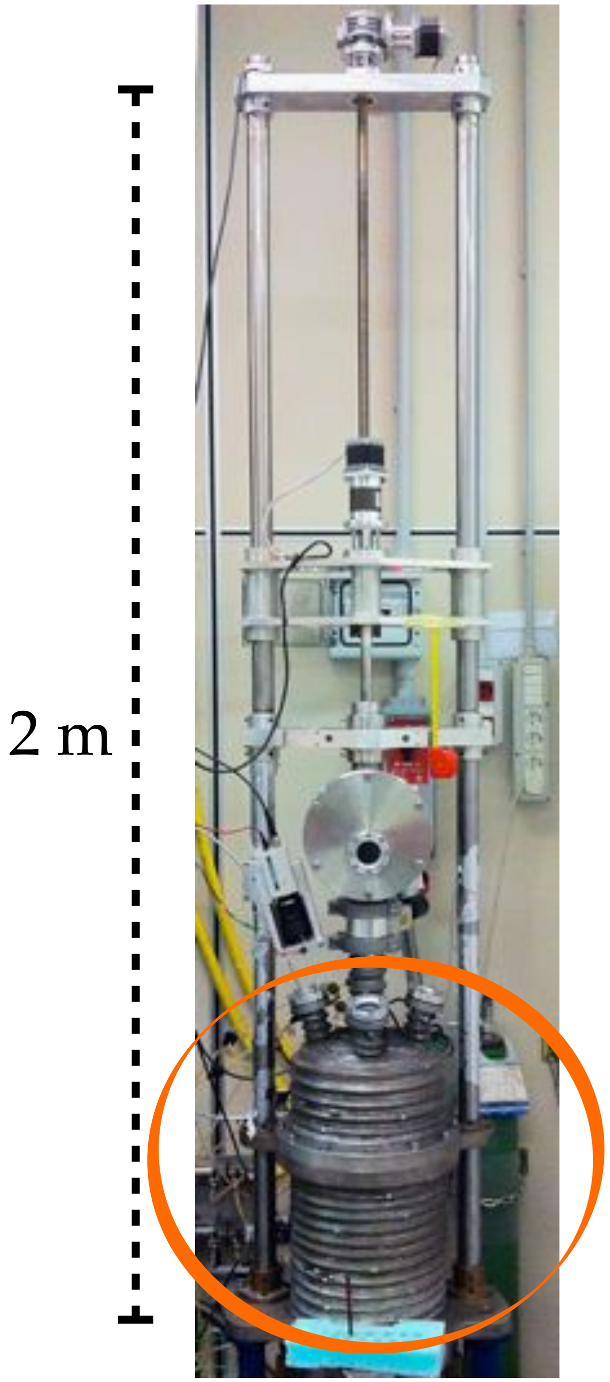
The Czochralski method

- Simultaneous pulling and rotation of the crystal
- Powders are brought to an undercooled phase
- Produces single crystals
- Melt temperature affects the diameter during the growth



Crystal growth

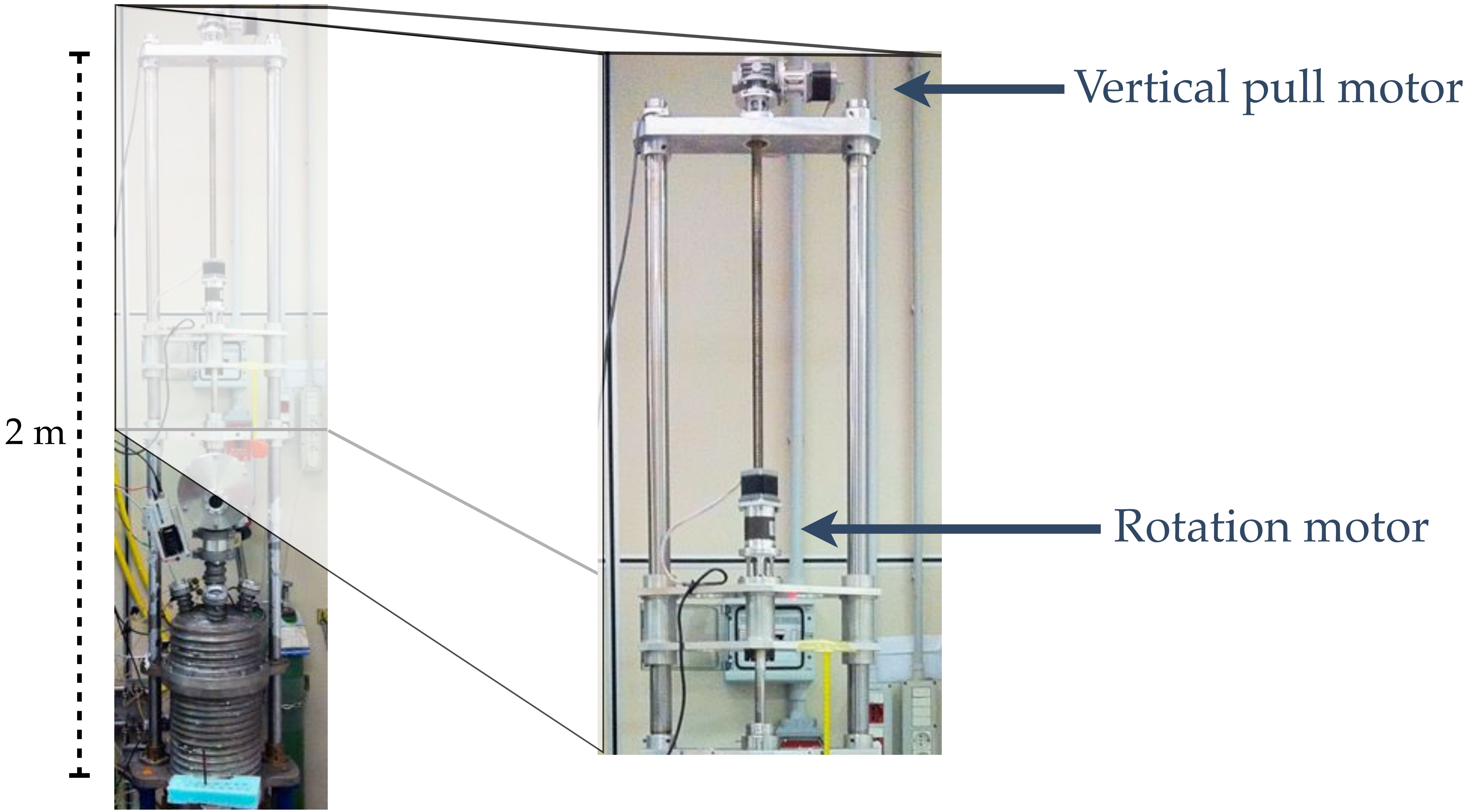
The Czochralski furnace at NMLA laboratories



Main chamber

Crystal growth

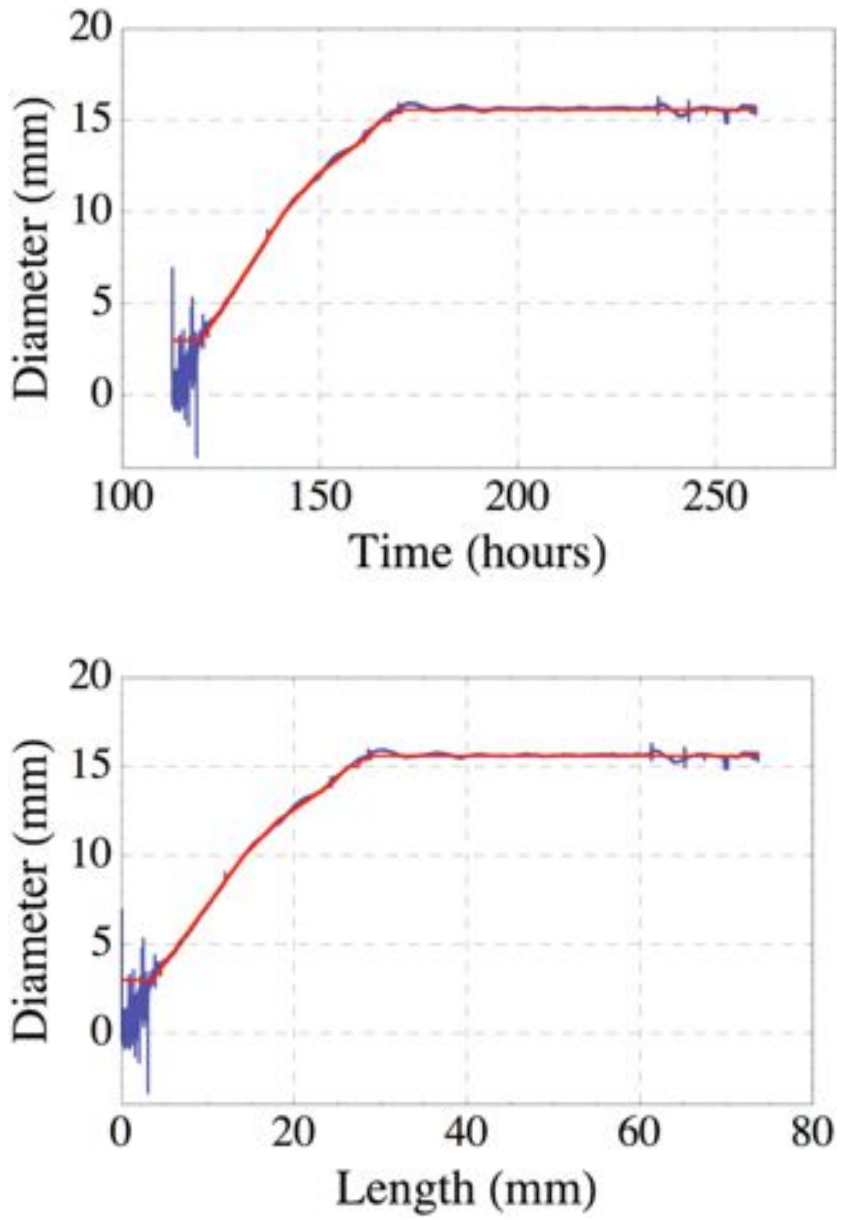
The Czochralski furnace at NMLA laboratories



Crystal growth

Ytterbium-doped growth highlights

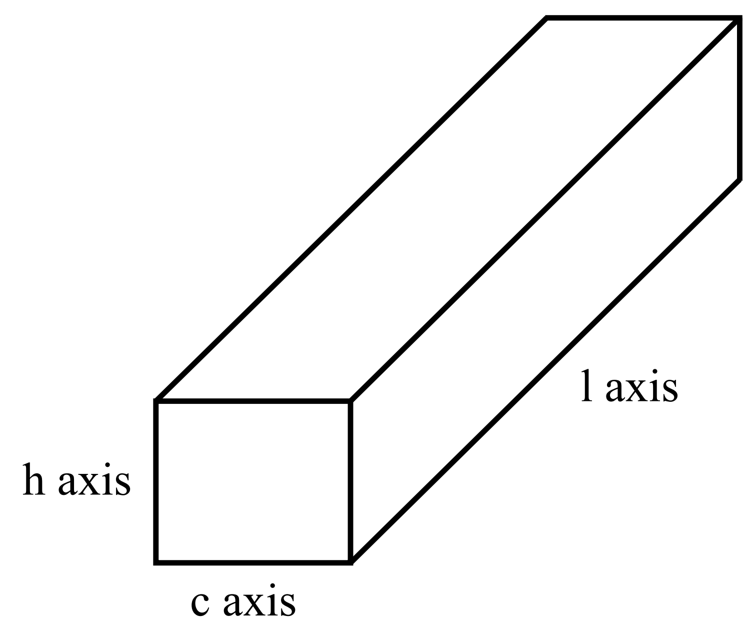
- 99.999% pure materials
- Doping chosen by powder mixture
- Pulled at 0.5 mm/hour
- Rotated at 5 RPM
- Typical growth time of 300 hours (~12 days)



Crystal growth

Two growths prepared for experiments

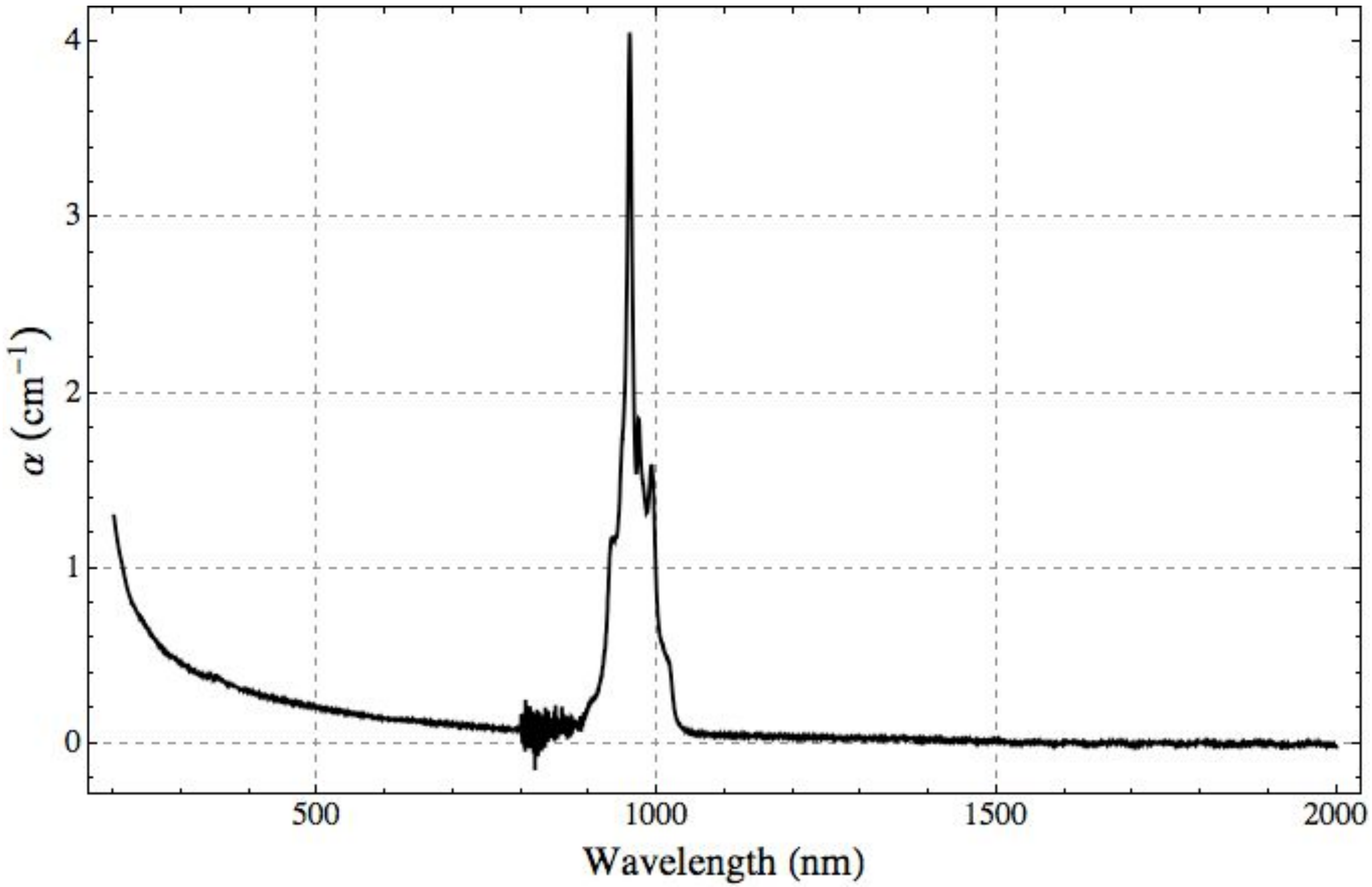
- Same doping level
- Li - $Y_{0.95}Yb_{0.05}$ - F_4 or 5% at. Yb:YLF
- Sample 77 - powders of 2006
- Sample 134 - powders of 2012



Absorption spectra

Overall absorption spectrum

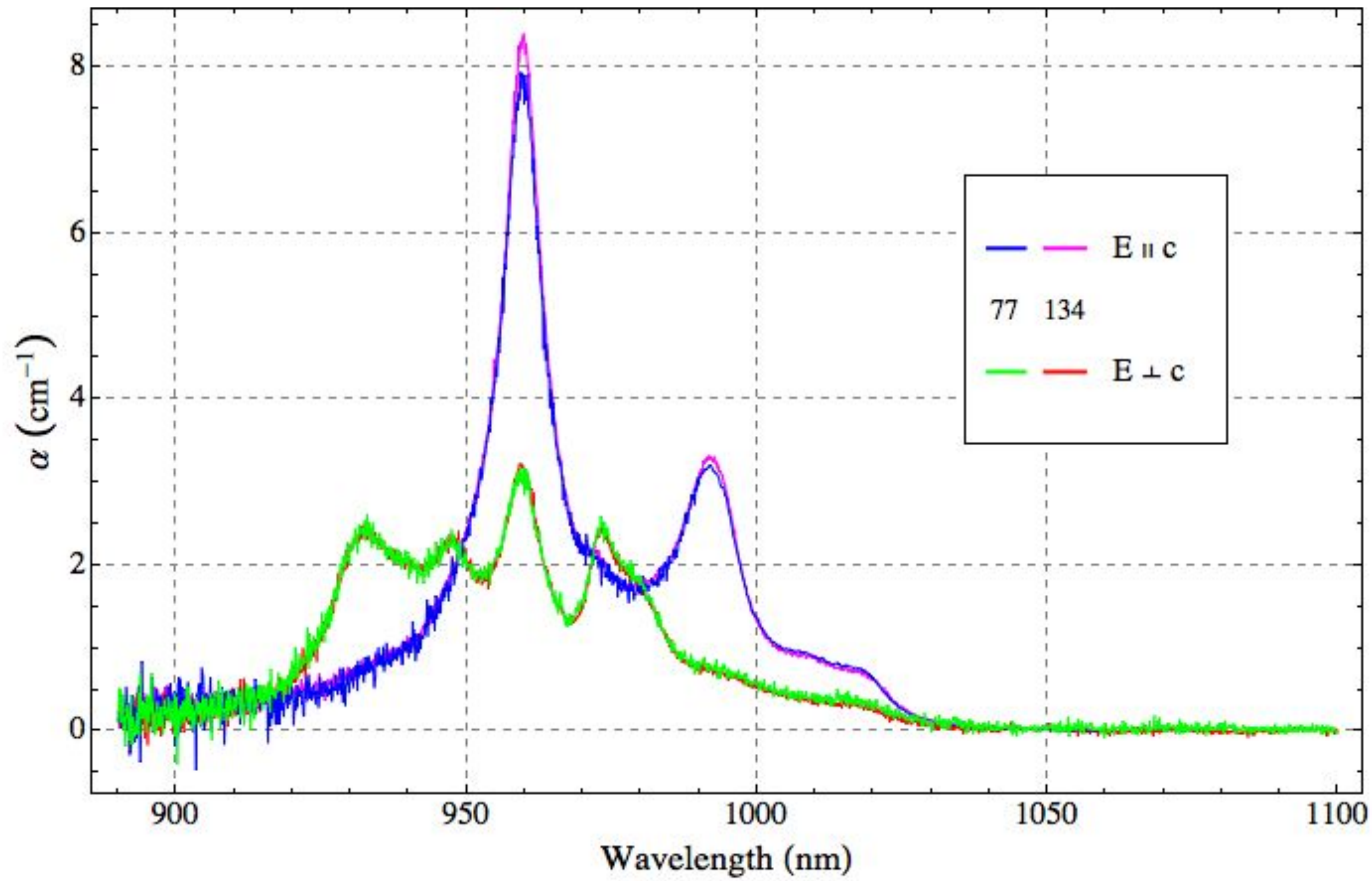
Measured with a Varian Cary 500 integrated spectrophotometer



Absorption spectra

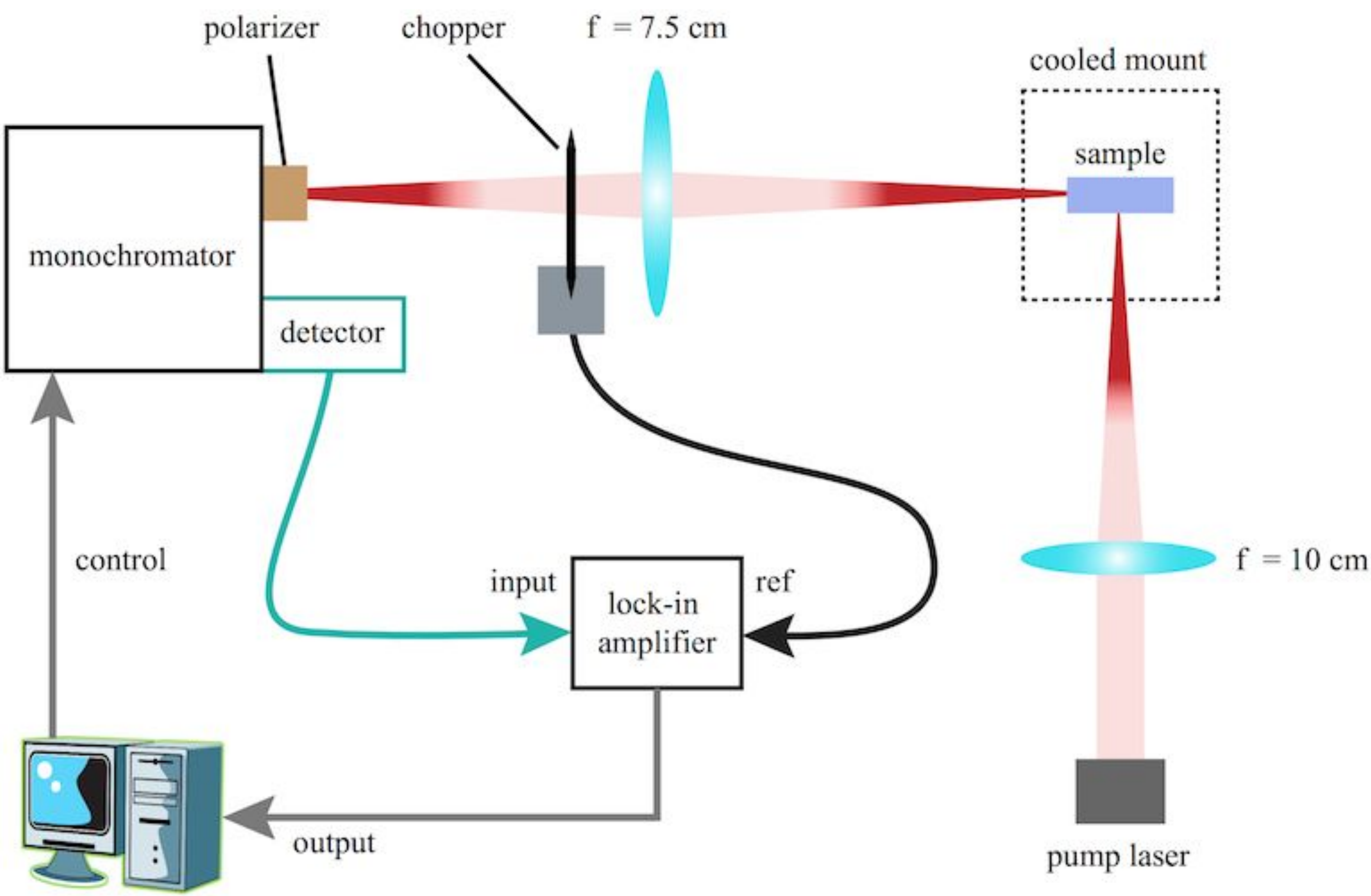
Ytterbium absorption bands

Measured with a Varian Cary 500 integrated spectrophotometer



Fluorescence spectra

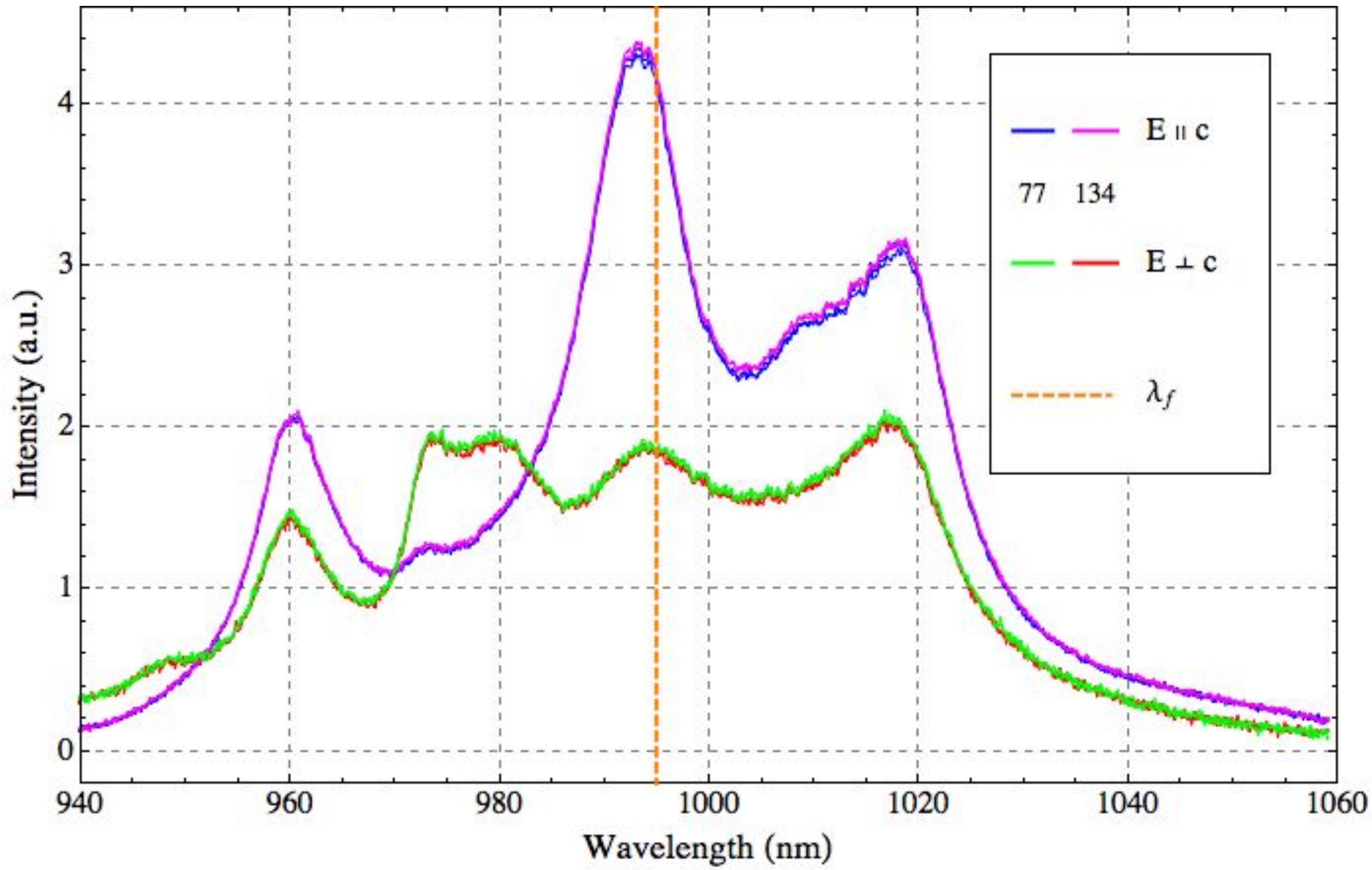
Experimental setup



Fluorescence spectra

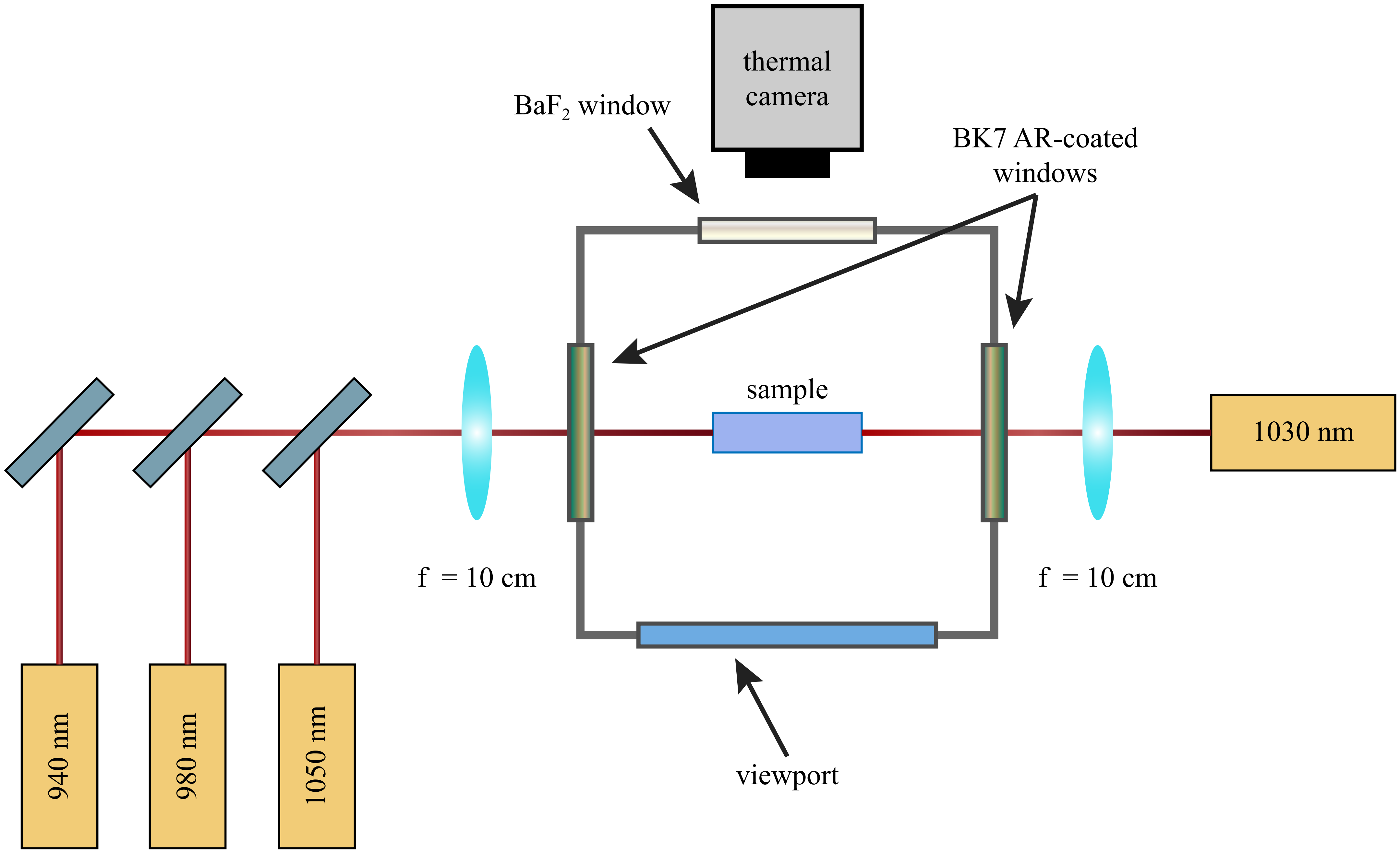
Ytterbium emission bands

Pumped with a 940 nm laser diode - $\lambda_f = 995$ nm



Cooling setup

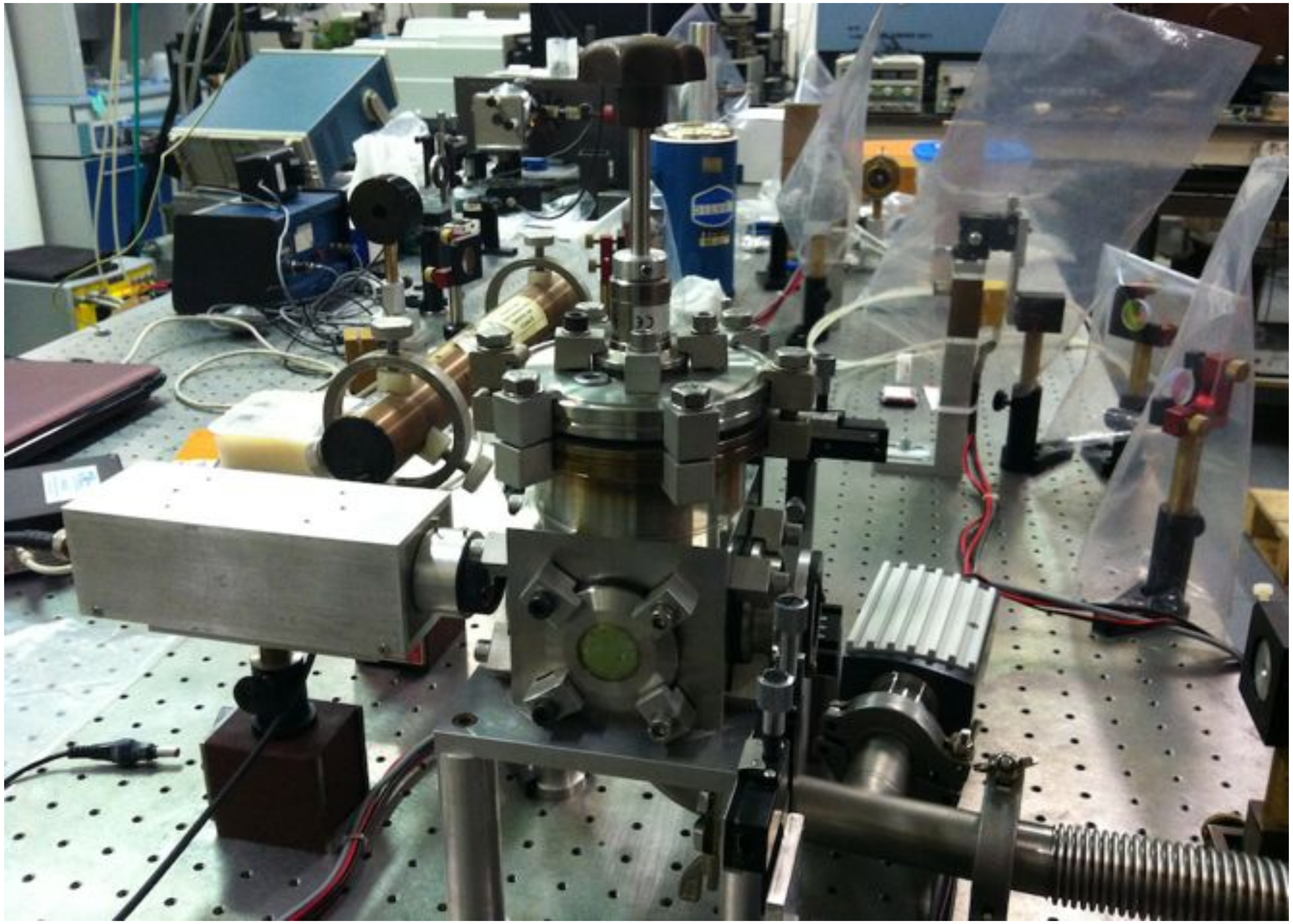
Laser pump and temperature detection layout



Cooling setup

Vacuum chamber design

- Pressures down to 10^{-3} Pa (10^{-5} mbar)
- Four windows to pump and observe the sample at the same time

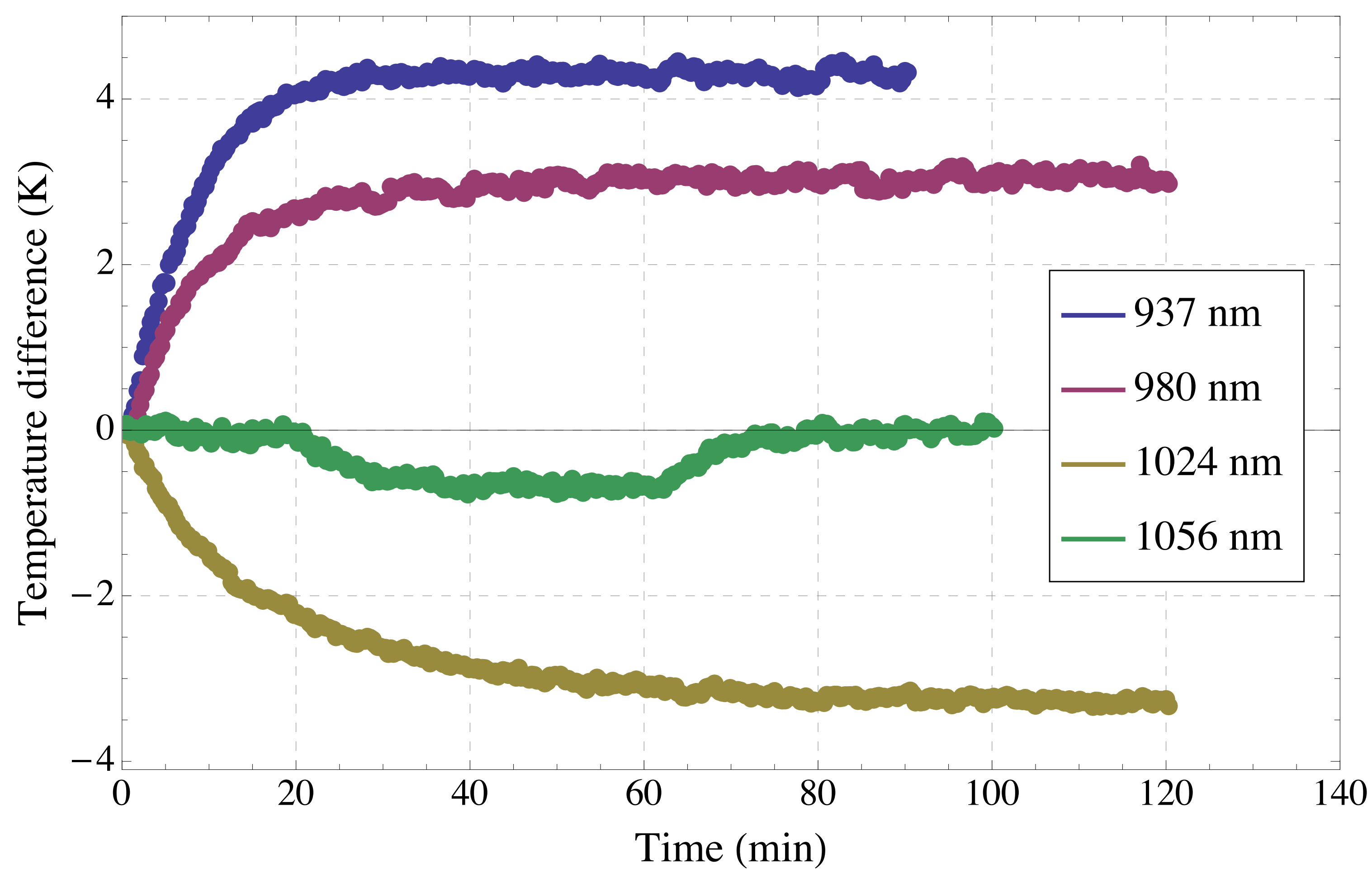


Cooling measurements

Estimation of the cooling efficiency of the samples

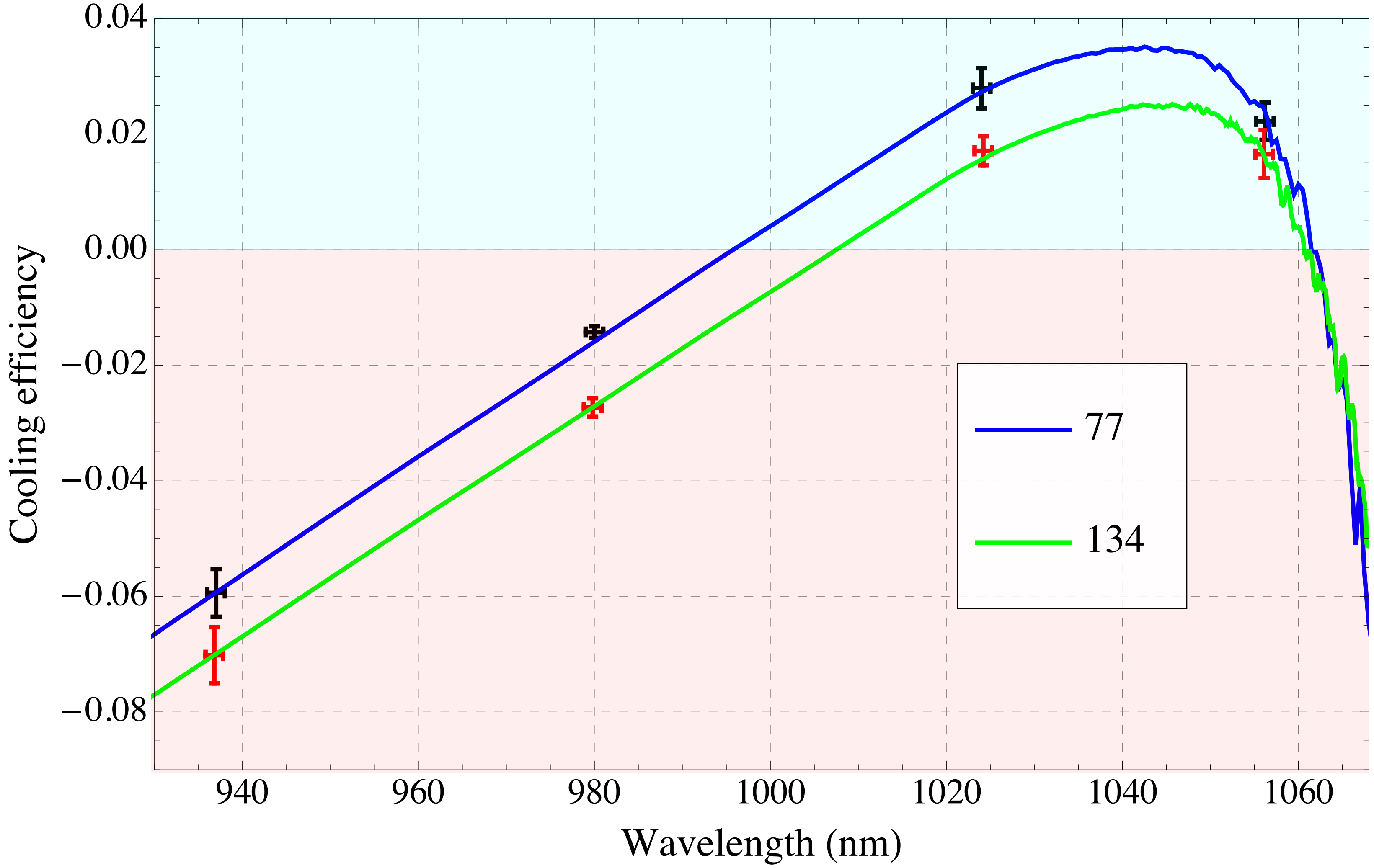
Data collected with the thermal camera - E ∥ c

	Sample no. 77 5% Yb:YLF	
Source	P_{in} (mW)	ΔT (K)
937 nm	42 ± 2	4.2 ± 0.2
980 nm	85 ± 2	3.0 ± 0.2
1024 nm	130 ± 10	-3.2 ± 0.3
1056 nm	800 ± 20	-0.7 ± 0.1



Cooling measurements

Estimation of the cooling efficiency of the samples



- Same spectral features but different cooling efficiencies
- Same value of BA
- Different EQEs

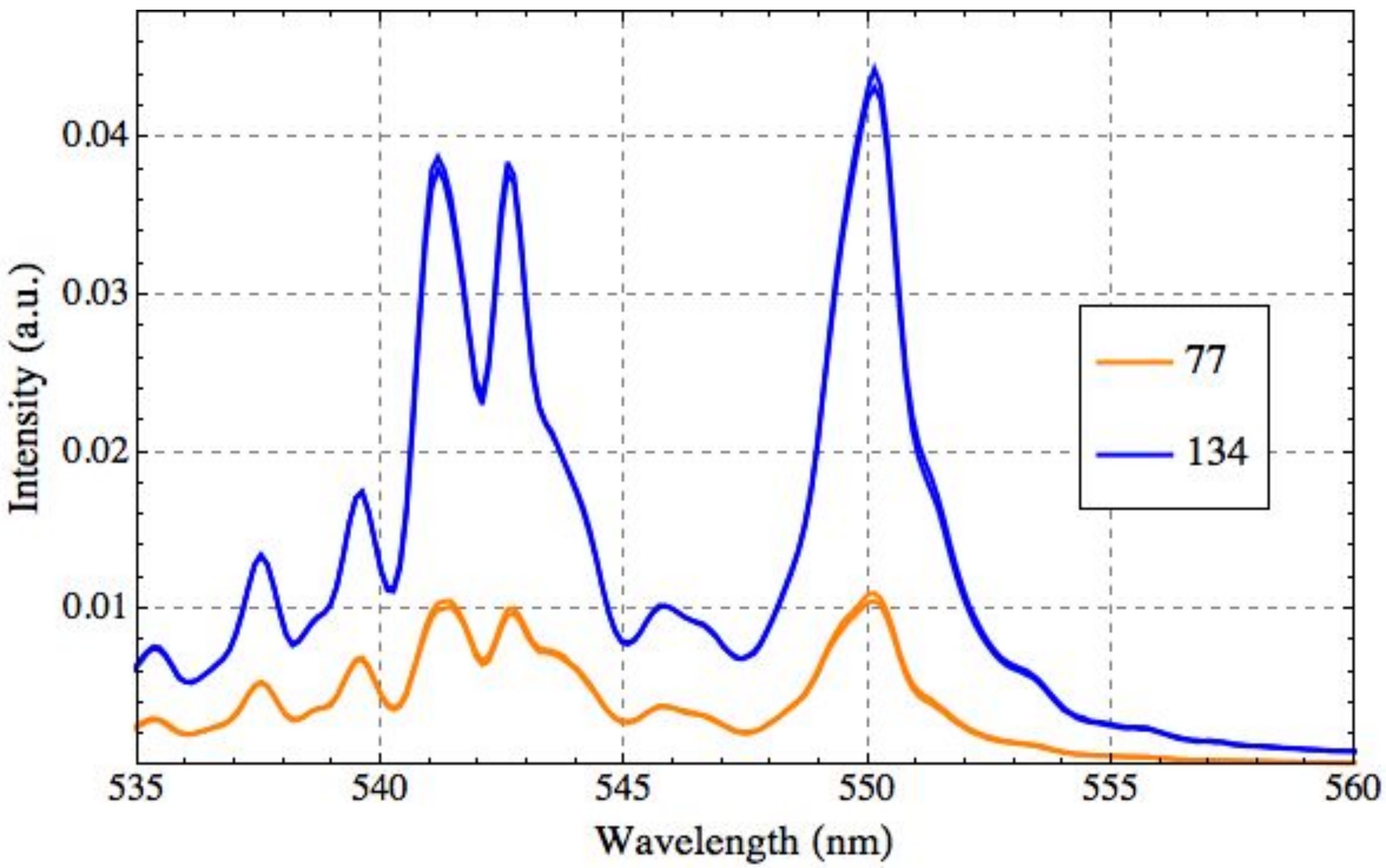
$$\eta_c = \eta_{ext} \left[1 + \frac{\alpha_b}{\alpha(\lambda)}\right]^{-1} \left(\frac{\lambda}{\lambda_f}\right) - 1$$

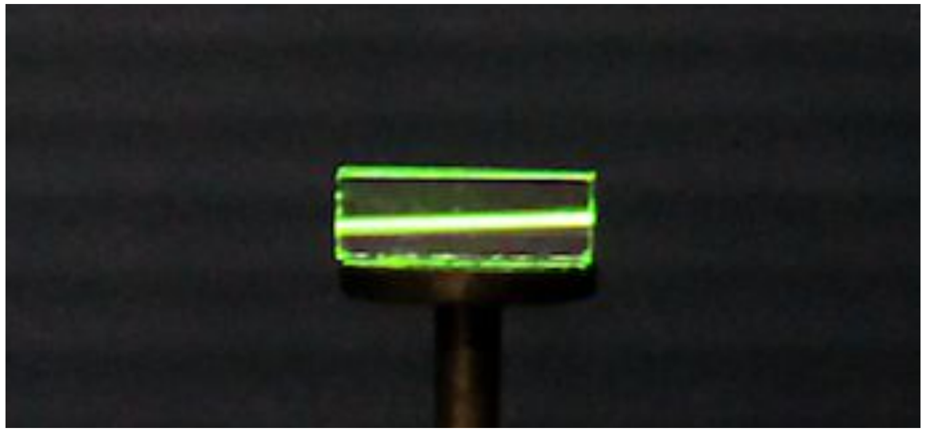
Sample	Doping	α_b $(10^{-4}\,\mathrm{cm}^{-1})$	η_{ext}
77	5 %	4.2 ± 0.2	0.999 ± 0.001
134	5 %	4.0 ± 0.2	0.988 ± 0.001

Effects of impurities

Visible emission in the cooling samples

Pumped with a 940 nm laser diode



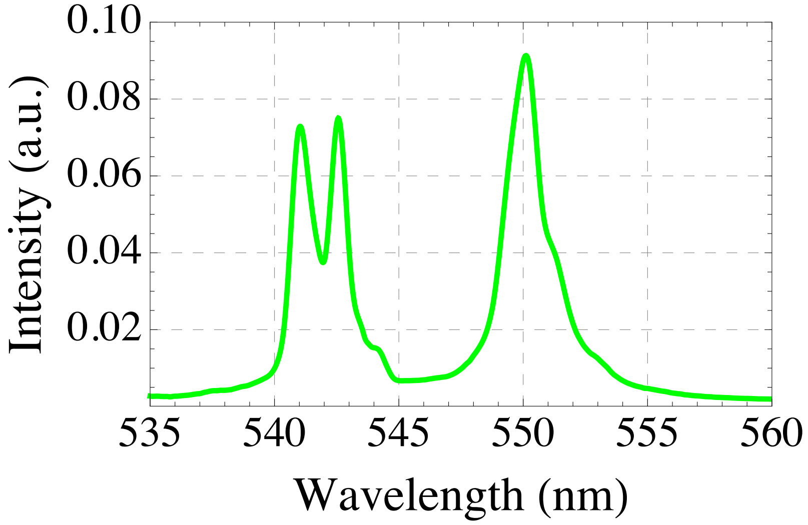


- Different intensities between the two crystals
- Ytterbium cannot cause these emissions
- Identify the elements

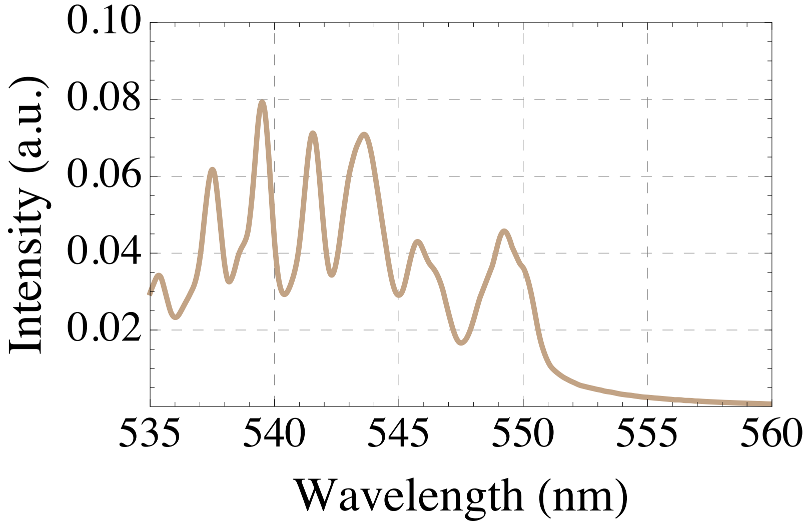
Effects of impurities

Green ray - spectral analysis

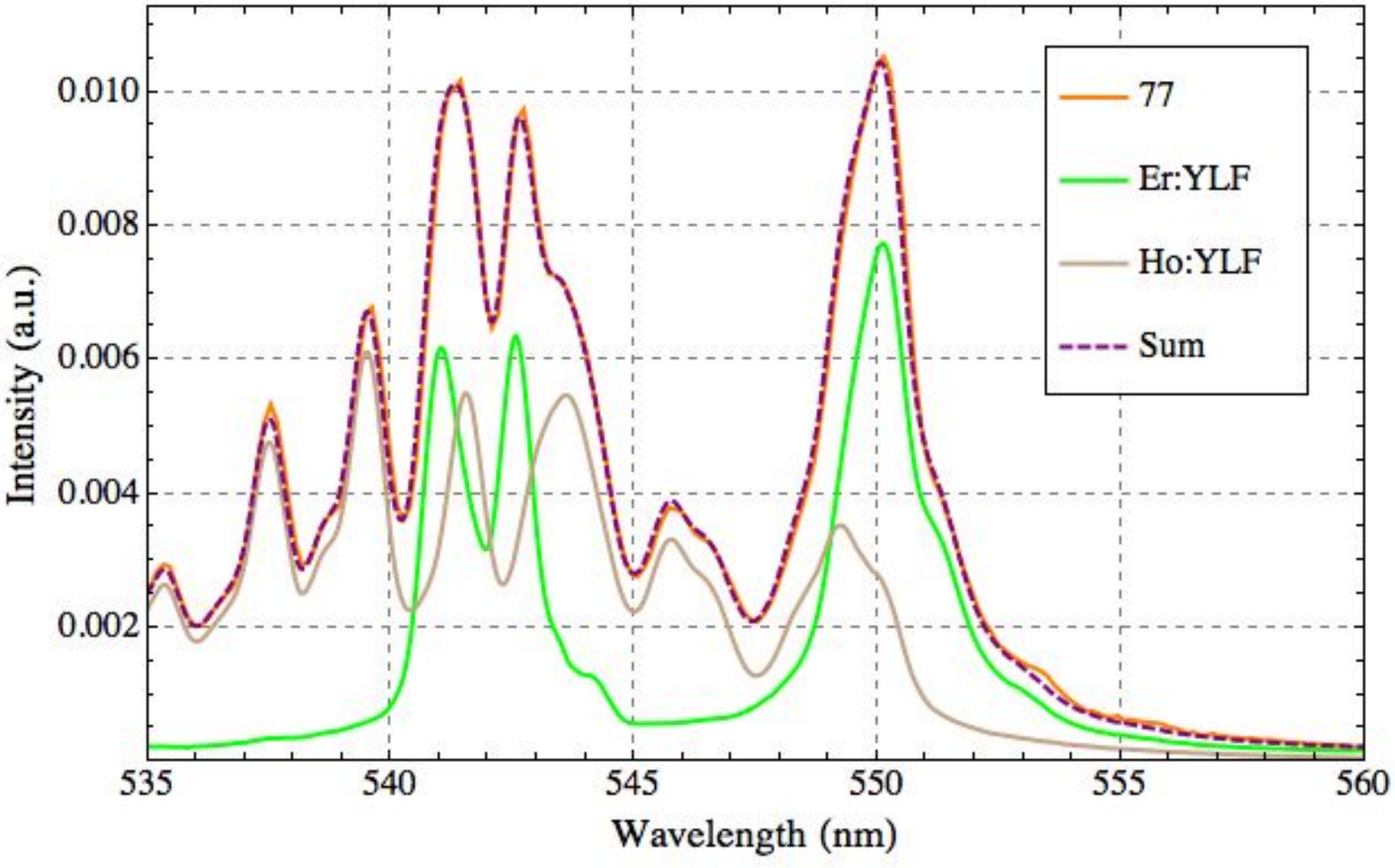
Erbium YLF



Holmium YLF



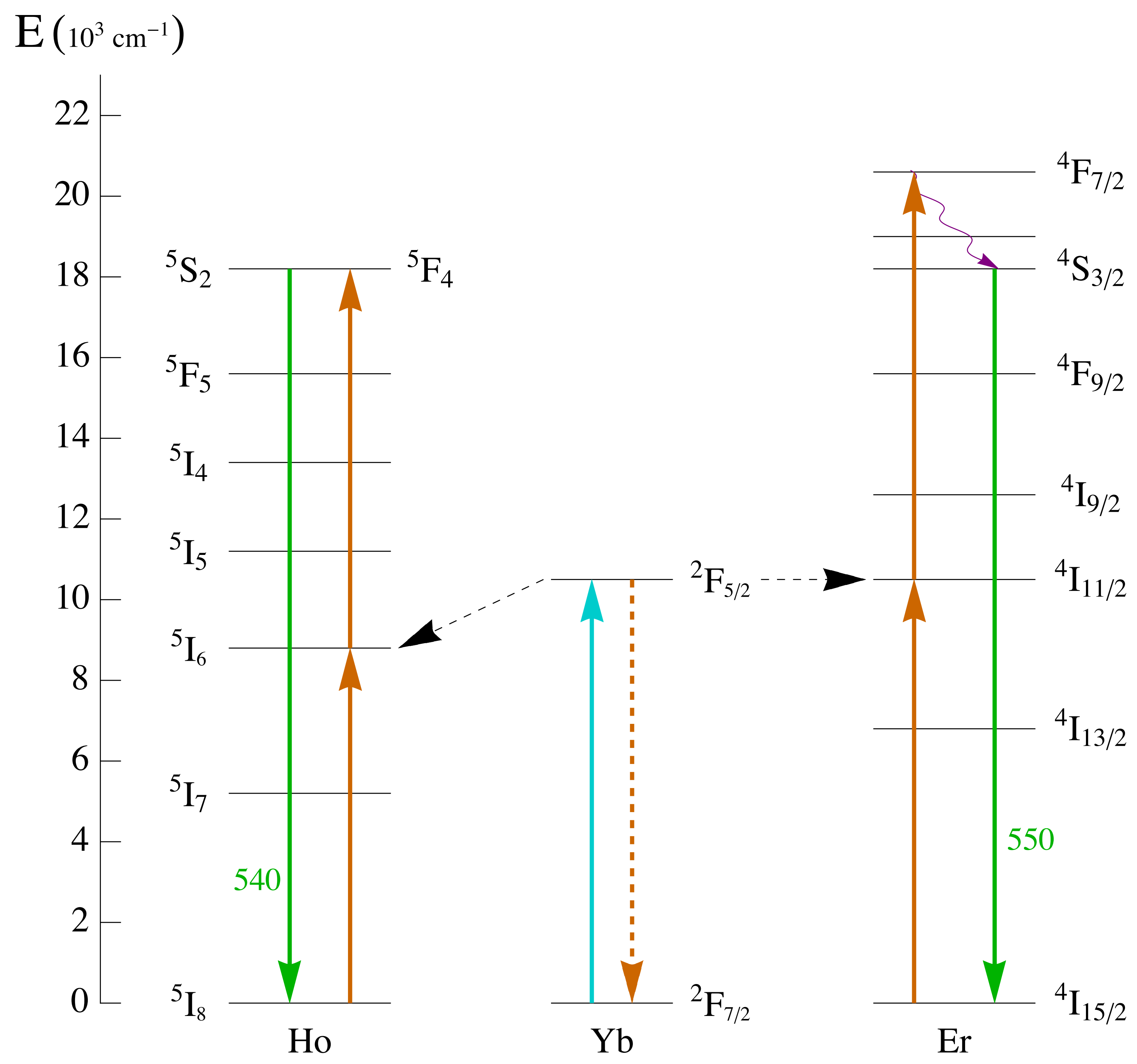
Sample no. 77 - Pumped at 940 nm



Effects of impurities

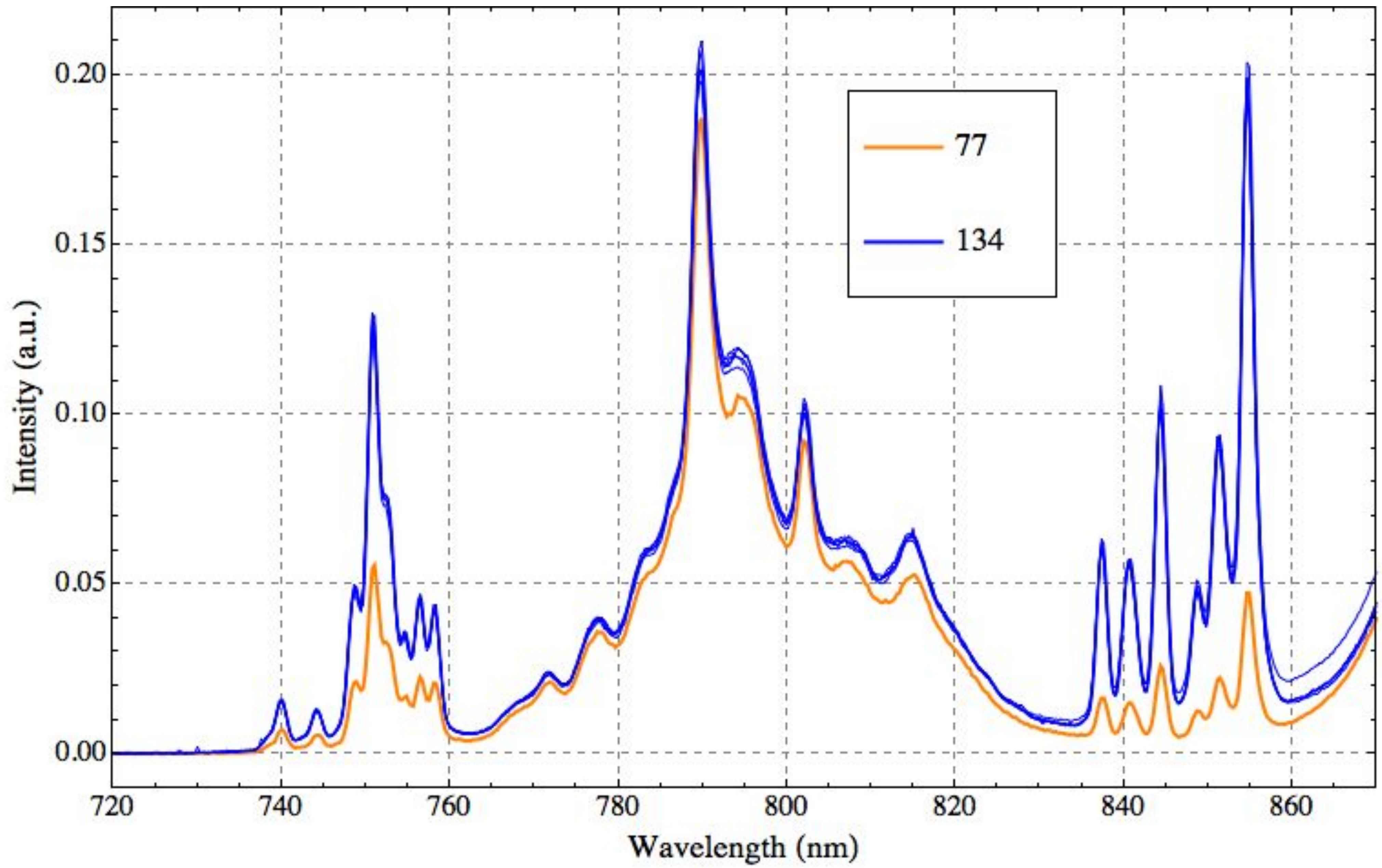
Green ray - energy transfer model

- Contaminants are directly pumped by the Ytterbium ions
- Erbium and Holmium have other emission lines in the NIR region



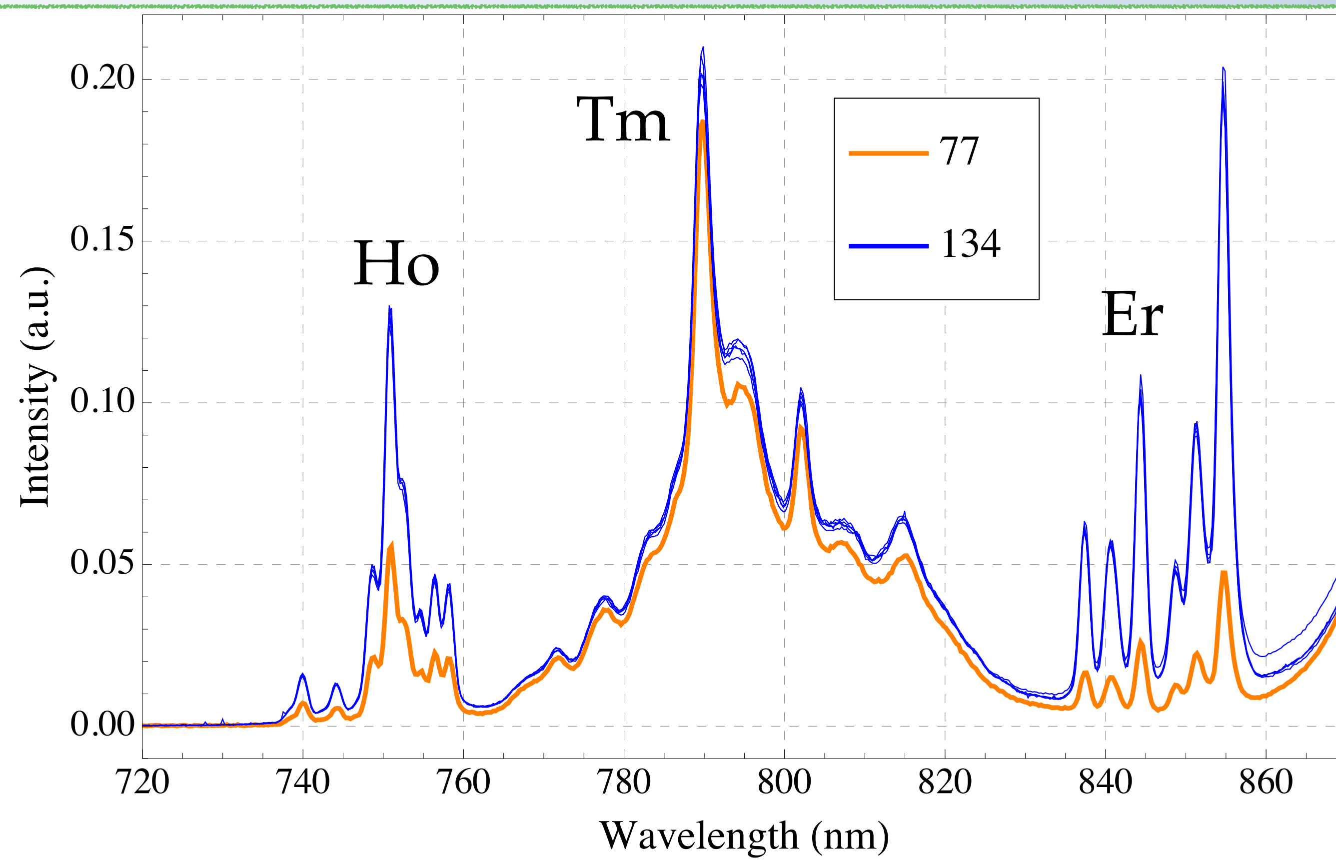
Effects of impurities

Infrared region fluorescence spectra

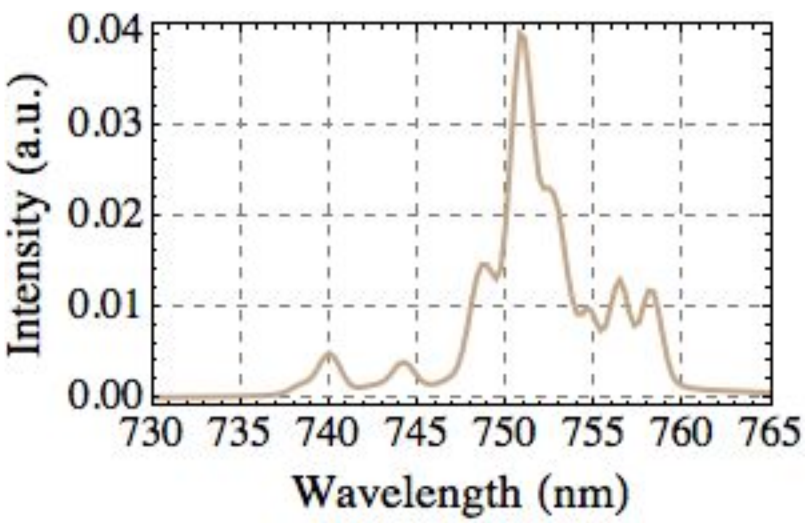


Effects of impurities

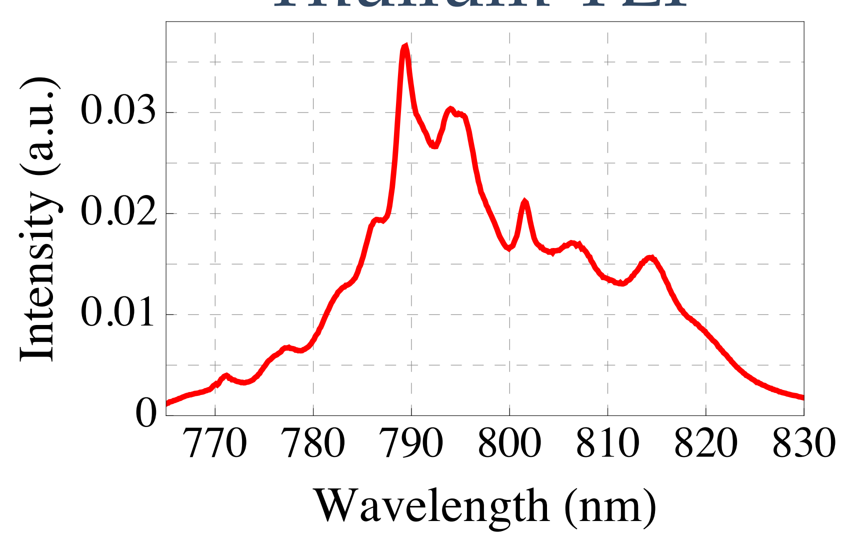
Infrared region fluorescence spectra



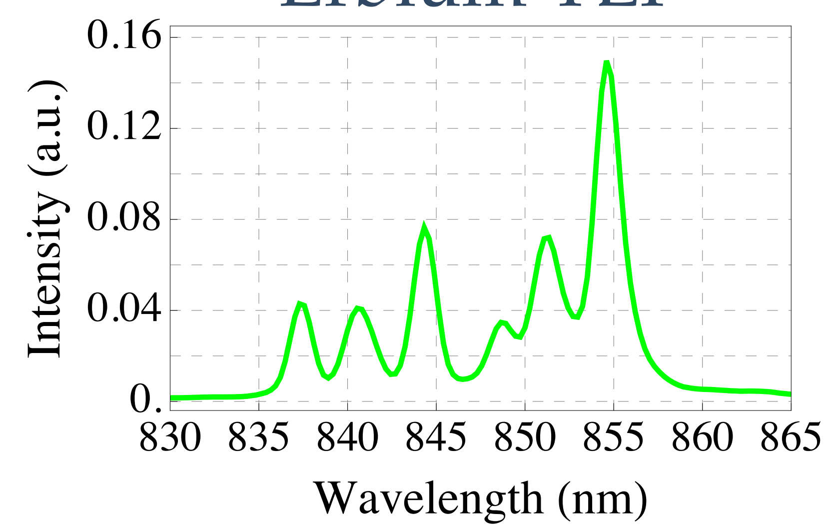
Holmium YLF



Thulium YLF



Erbium YLF



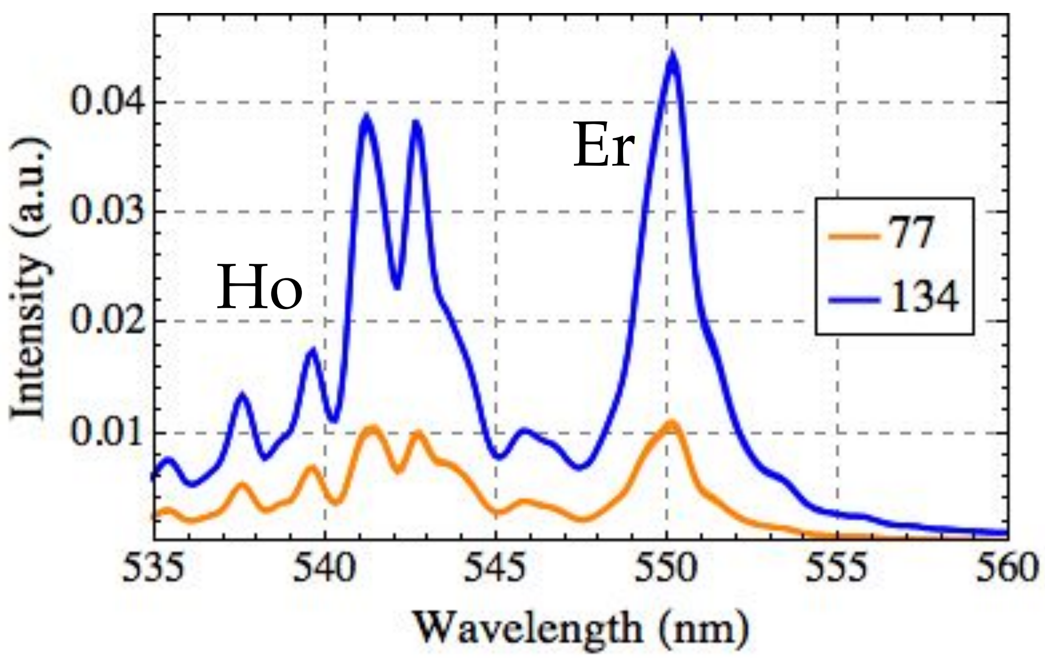
Effects of impurities

Elemental analysis and ratios of the peaks

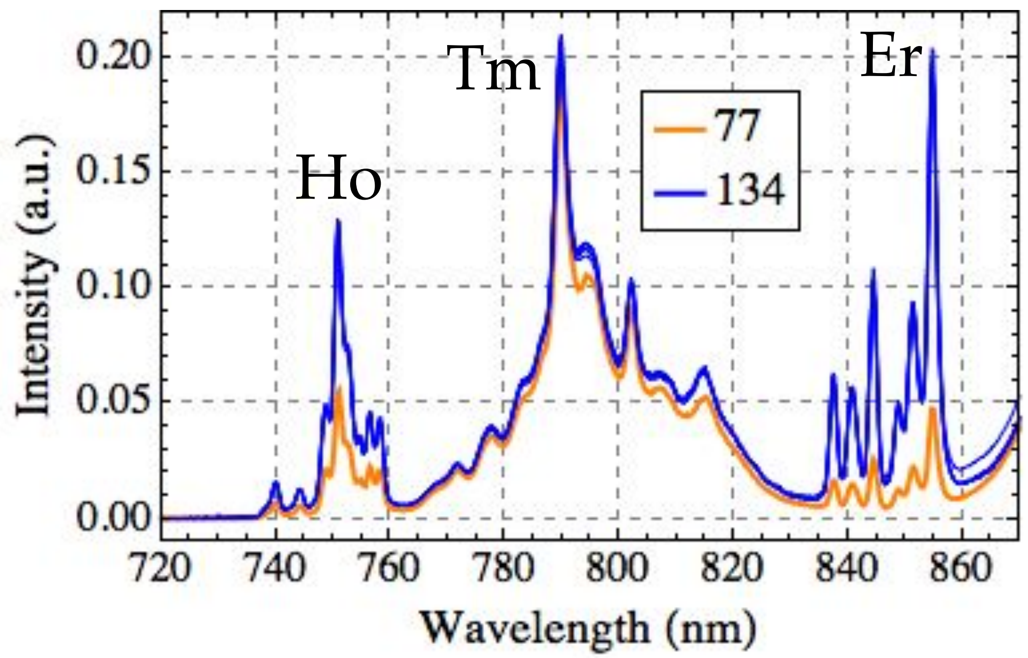
Mass spectrometry

	Sample no. 77	Sample no. 134
Element	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

Green emission



Infrared emission



Peak and amount ratios

	Green	Infrared	Elemental
Erbium	4.7	4.3	4.4 ± 1
Holmium	2.6	2.3	1.8 ± 0.4
Thulium	n.a.	1.1	0.5 ± 0.3

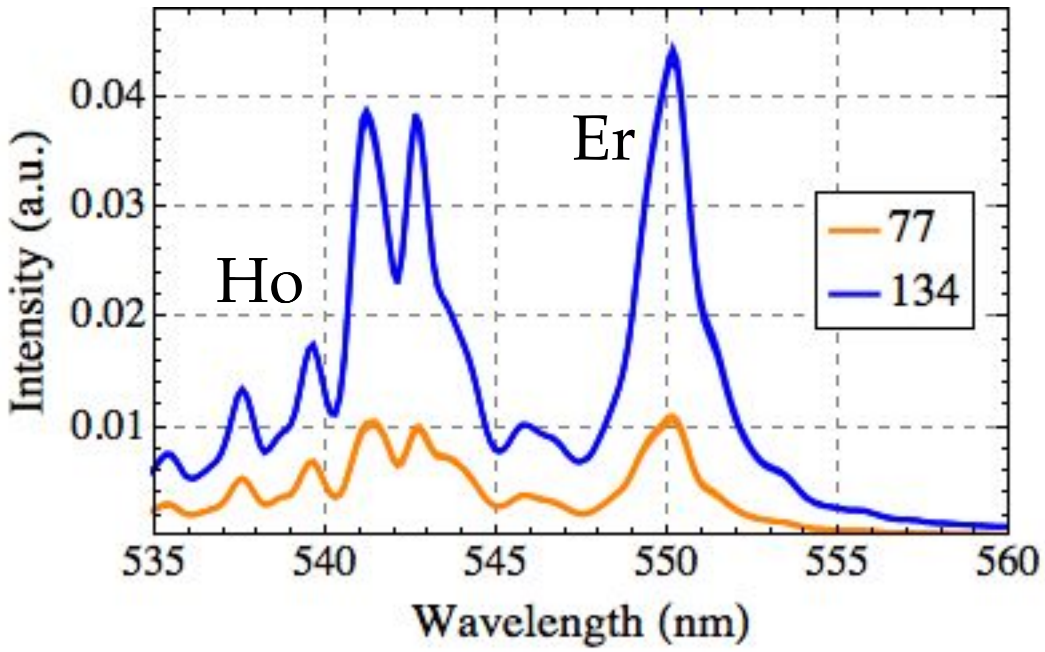
Effects of impurities

Elemental analysis and ratios of the peaks

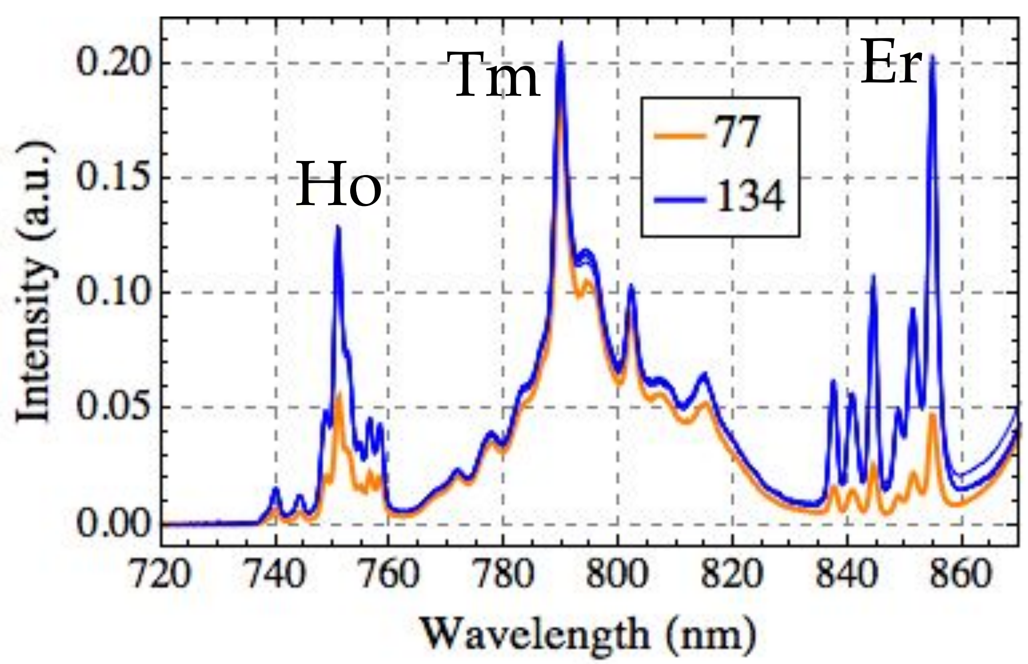
Mass spectrometry

	Sample no. 77	Sample no. 134
Element	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

Green emission



Infrared emission



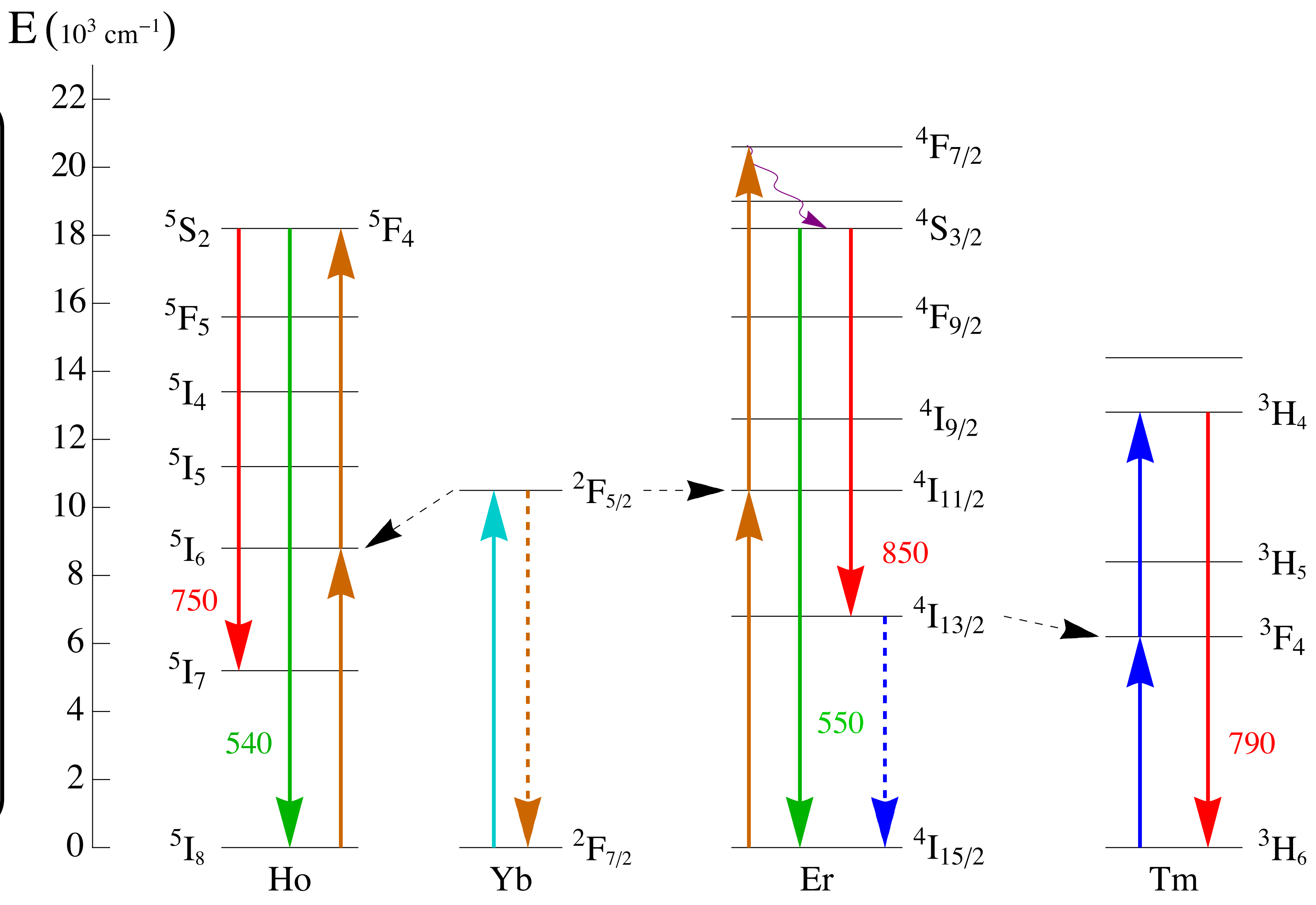
Peak and amount ratios

	Green	Infrared	Elemental
Erbium	4.7	4.3	4.4 ± 1
Holmium	2.6	2.3	1.8 ± 0.4
Thulium	n.a.	1.1	0.5 ± 0.3

Effects of impurities

Er - Ho - Tm energy transfer model

- Thulium gains energy through Erbium impurities
- Only direct transfers subtract ions from the cooling cycle
- Only direct transfers reduce the EQE



Conclusions

- Net cooling requires high efficiencies
- Higher purity needed (ppm level)
- Rare earth ions affect refrigeration
  - Direct transfers decrease the EQE
  - Some elements are worse than others

Thank you for your attention