Luminescence Nanothermometry with Lanthanides: Principles, Applications and Challenges

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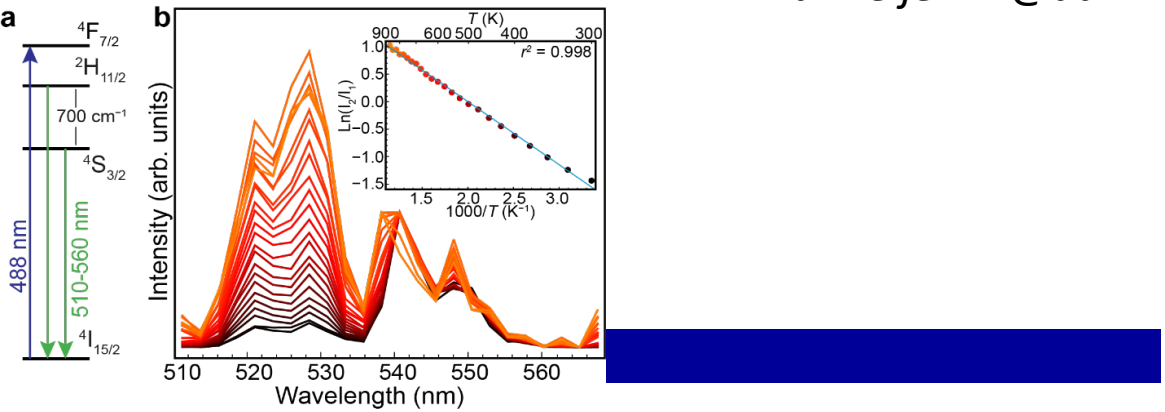

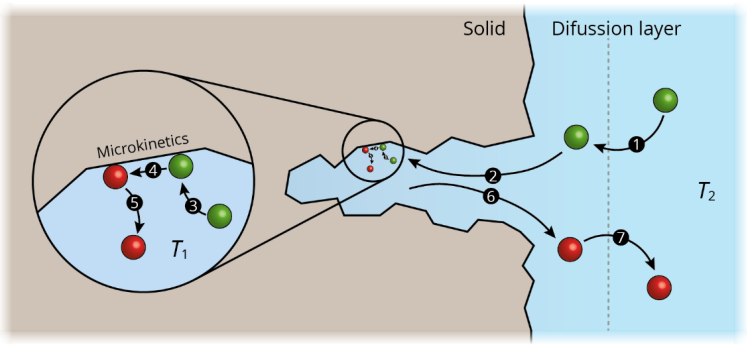

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NanoTBtech

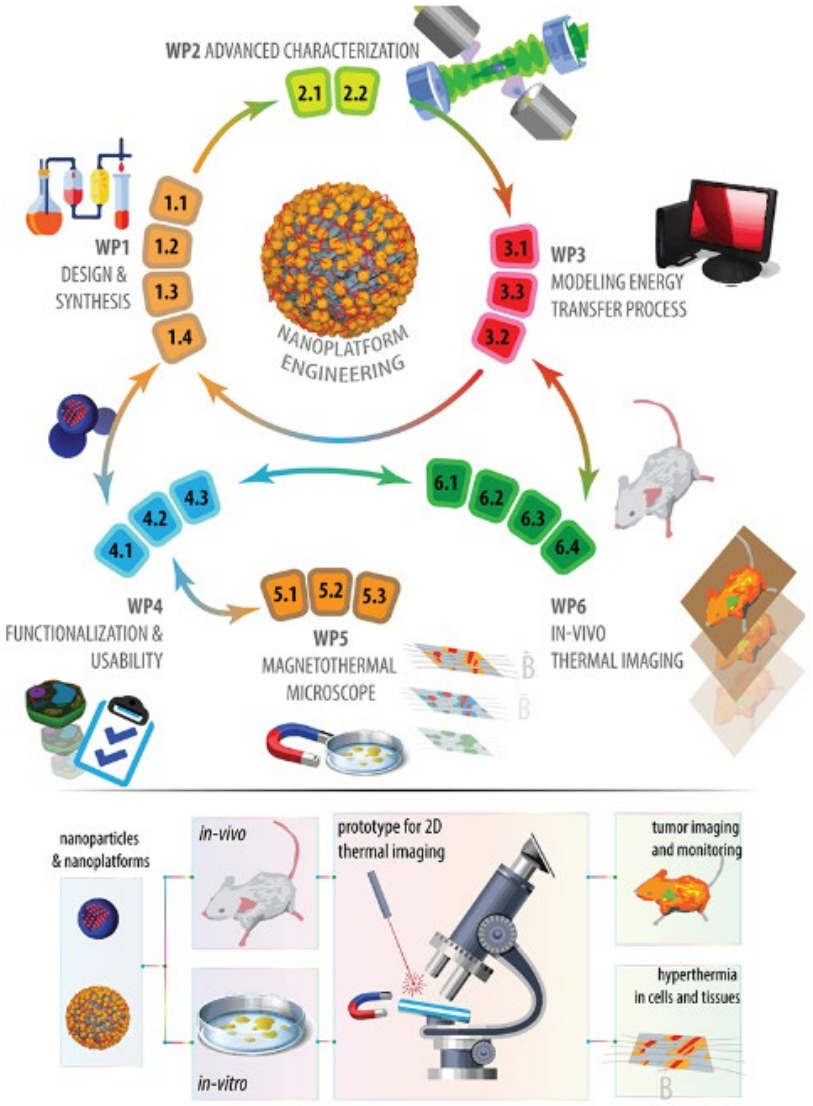
- *NanoTBtech* is a EU-funded *Future and Emerging Technologies-Open* (FET-Open) project (grant agreement no.: 801305)

- Goal: development of novel **2D thermal bioimaging techniques** using **luminescence thermometry** as a key technique.

- Check out the website:

  http://www.nanotbtech.eu/

Important task: Outreach



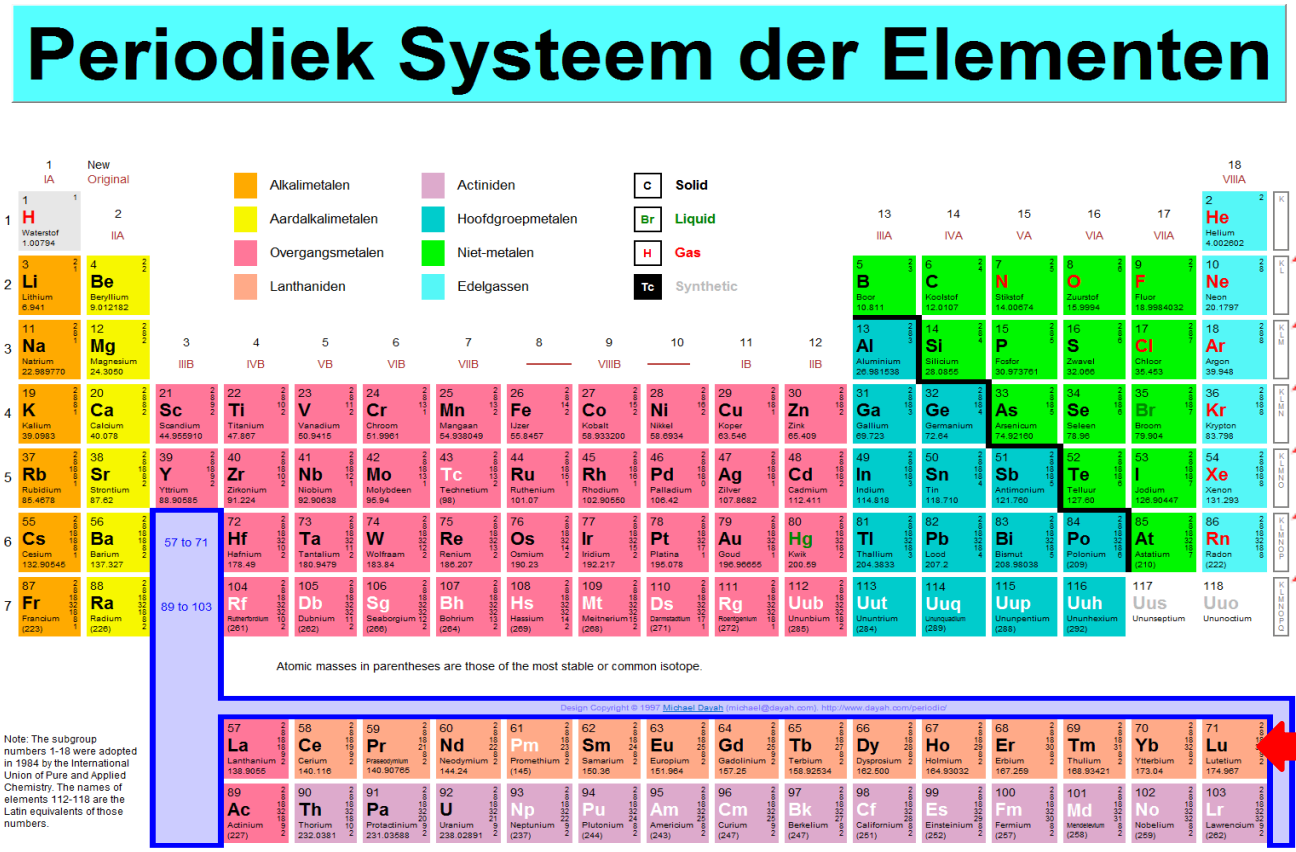
NanoTBtech

- *NanoTBtech* is a EU-funded *Future and*

Ideal for Luminescence thermometry:

Lanthanides

Lanthanides comes from the Greek word “λανθανειν” which means “to lie hidden” – hidden position at the bottom of the periodic table:



Filling the shells with electrons following the Afbau principle::

1s
2s 2p
3s 3p 3d
4s 4p 4d 4f
5s 5p 5d 5f …
6s 6p 6d … … …

Ln – 4f inner shell is filled with electrons

Ln^{3+} $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4f^n 5s^2 5p^6$ n = 0-14

Introduction Lanthanides

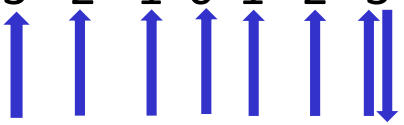
1 – Energy levels lanthanides

Characteristic luminescence properties due to energy levels arising from interaction between 4f-electrons in partly filled 4f-shell, shielded from the surrounding ligands by filled 5s and 5p orbitals.

Example: Tb^{3+} ($4f^8$) – **3003** possible electronic configurations for 8 electrons in 14 orbitals, which can all have different energies. Energy levels are labeled by so-called term symbols:

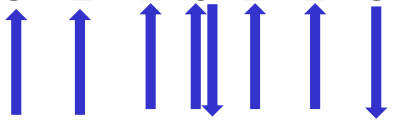
Ground state (Hund's rule):

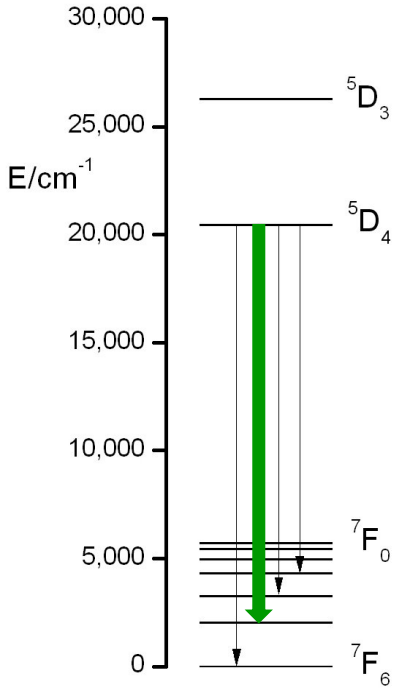
m_l -3 -2 -1 0 1 2 3 $^7F_6$ (term symbol)



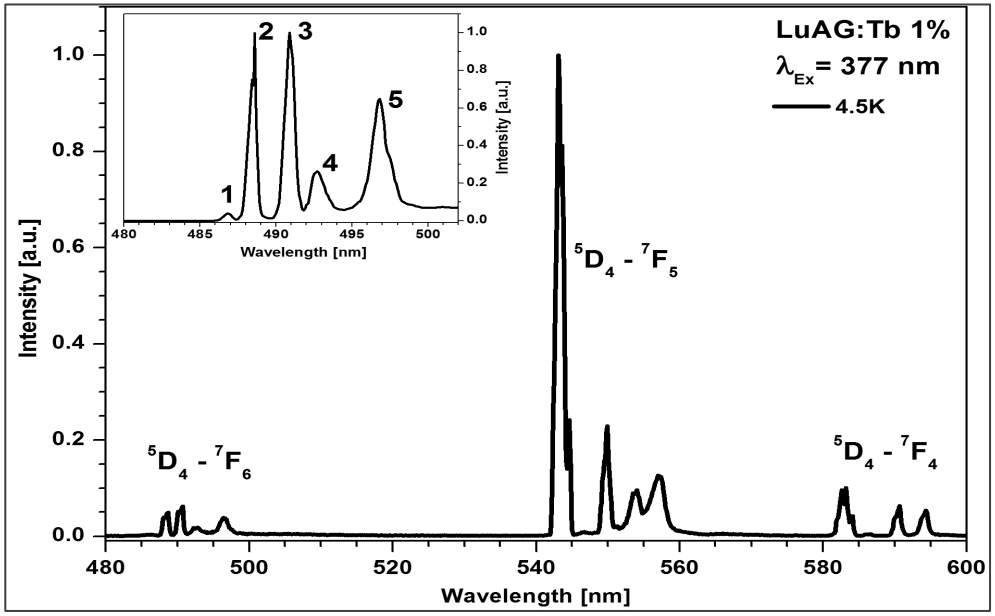
Excited state:

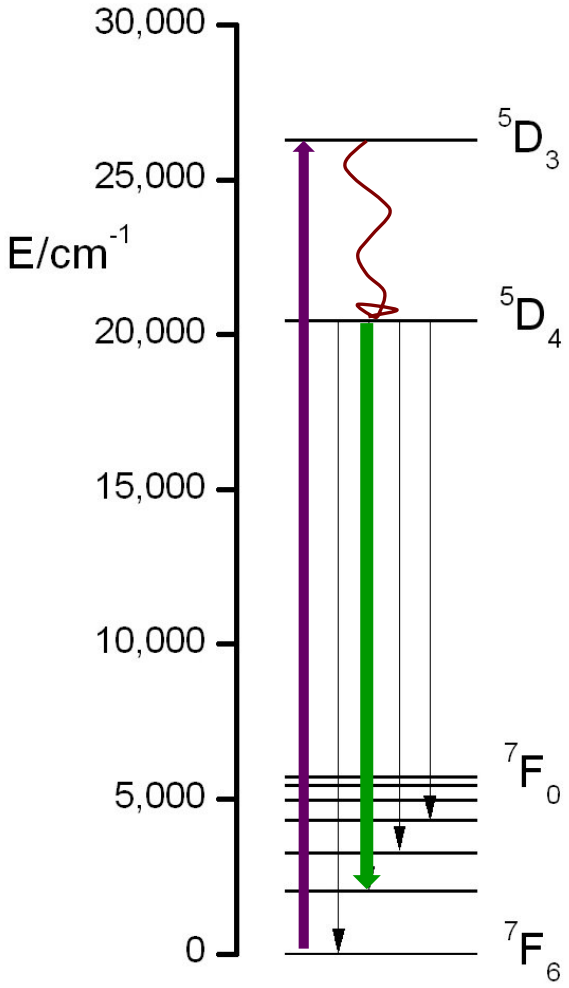
m_l -3 -2 -1 0 1 2 3 $^5D_4$





Emission spectrum Tb^{3+}

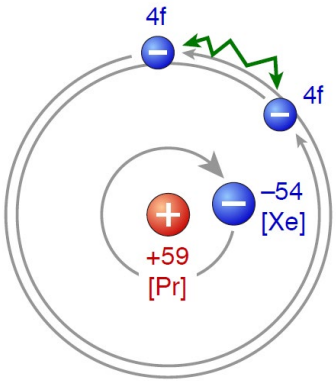


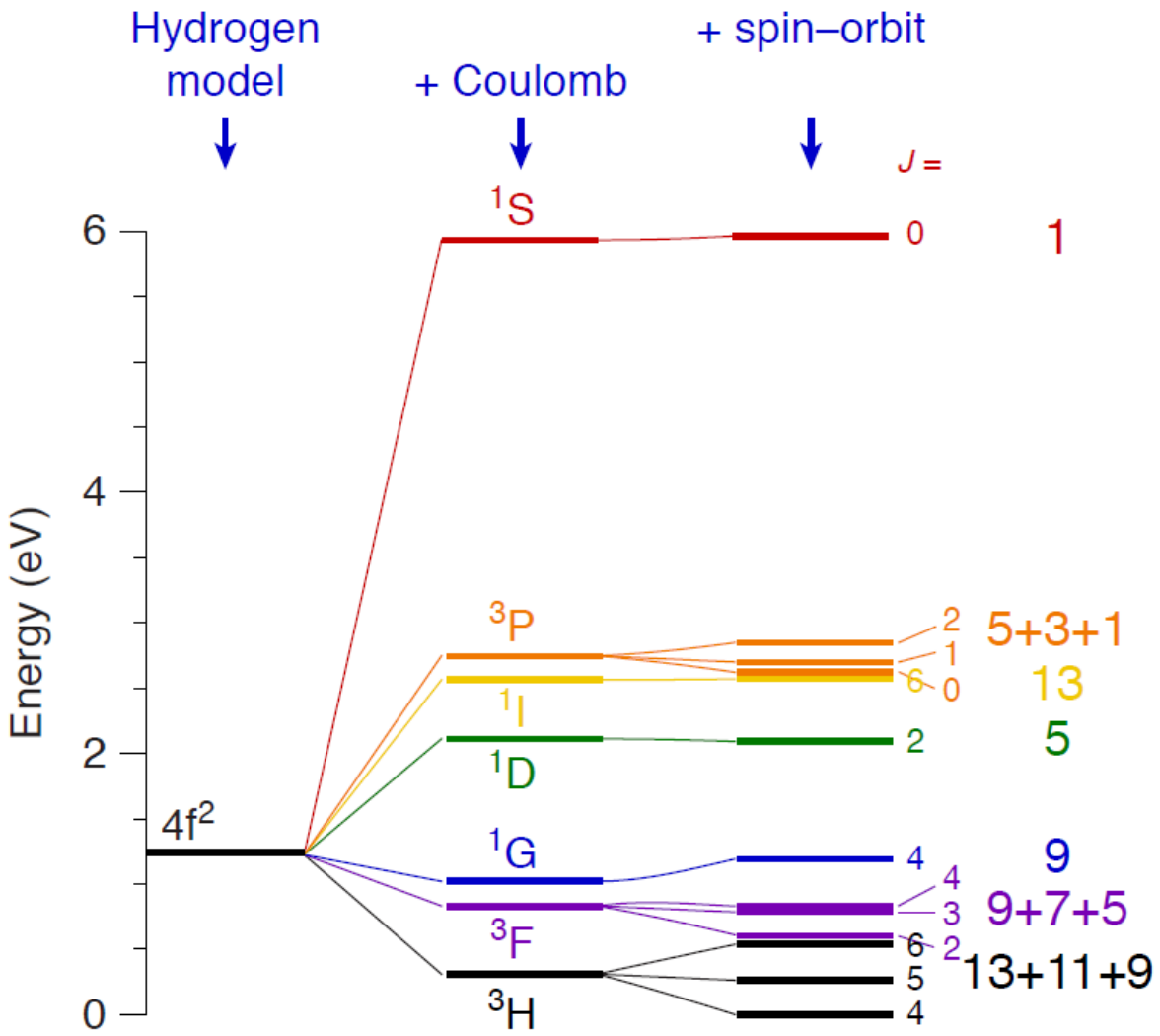


Characteristic f-f luminescence of lanthanides:

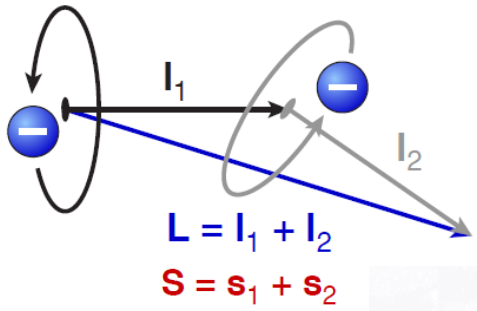
- **Sharp, atomic like, emission lines**
- **Independent of matrix**
- **Long emission life times (ms)**
- **High quantum yield (>90%)**

Origin Energy Levels

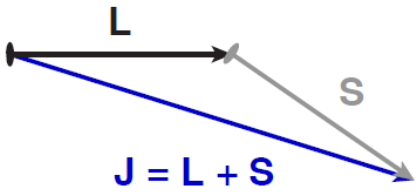




Coulomb Interaction



Spin-Orbit Coupling



LS-coupling: Russell Saunders Term symbols

+ SO Coupling

Term symbols $^{2S+1}L_J$

Crystal Field Splitting

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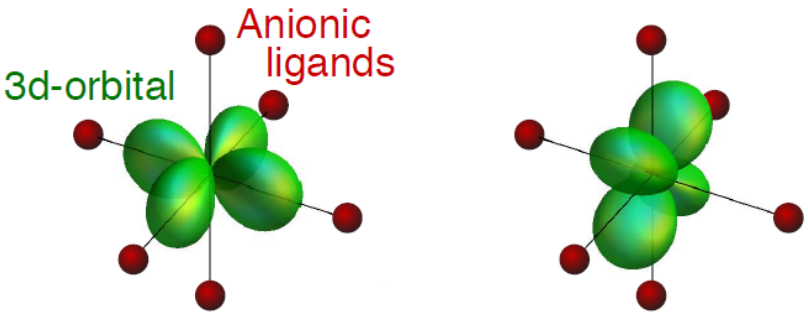
Term symbols $^{2S+1}L_J$ Degeneracy is $2J + 1$

Further splitting into (maximum) 2J+1 (*n*=even) or (2J+1)/2 (*n*=odd) crystal field components. Origin crystal field splitting similar to 3d CF splitting, but 100x smaller:

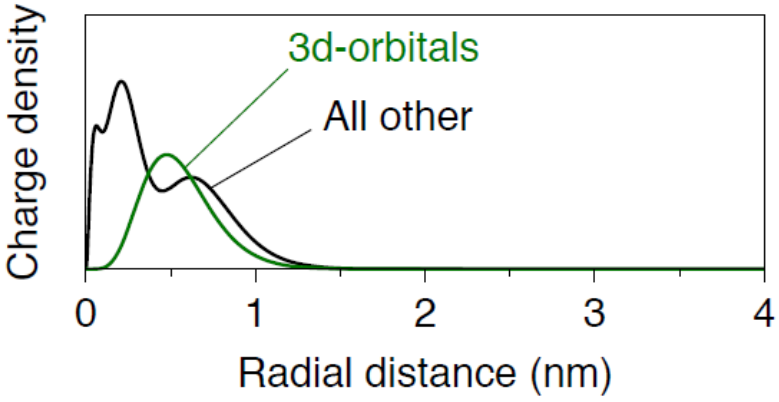


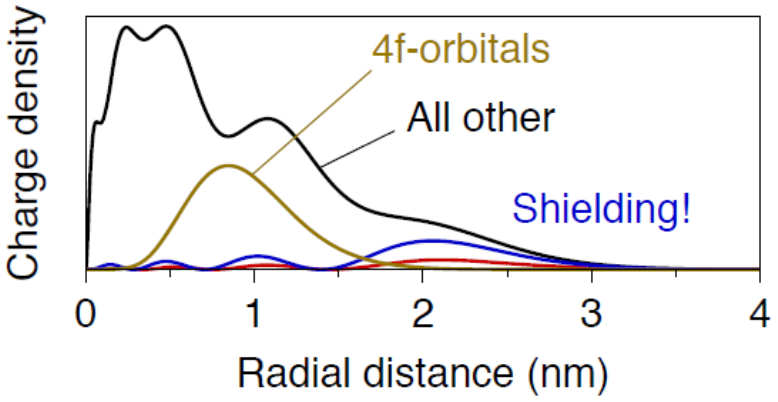
More repulsion

Less repulsion

Δ_{CF} ~ 10 000 cm^{-1}

Δ_{CF} ~ 100 cm^{-1}





Shielding 4f orbitals = No influence surrounding ligands for energy levels lanthanides (different from 3d transition metals)

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$Co^{2+} = 3d^7$

$CoCl_2$

$CoCl_2.6H_2O$

$Cr^{3+} = 3d^3$

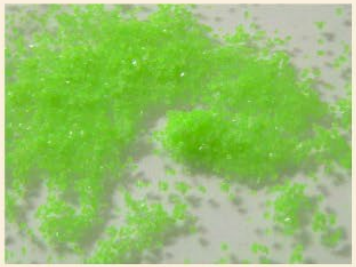
$Al_2O_3:Cr^{3+}$

$Be_3Al_2(SiO_3)_6:Cr^{3+}$

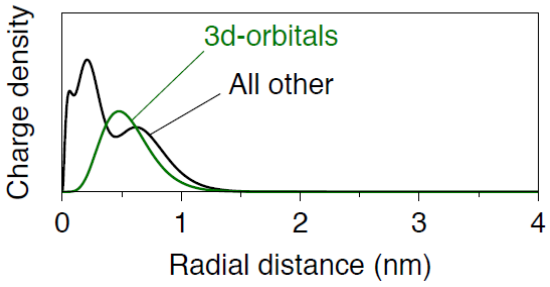
$Pr^{3+} = 4f^2$

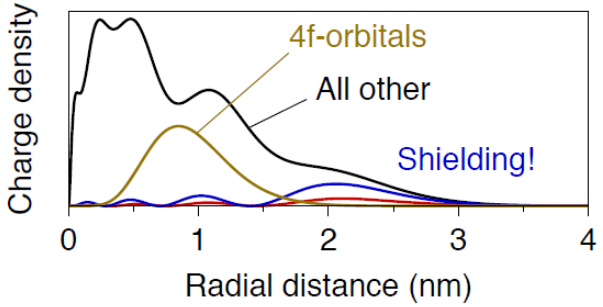
PrF_3

$Pr_2(CO_3)_3$



$Pr_2(SO_4)_3$





Dieke diagram

Energy levels of lanthanides

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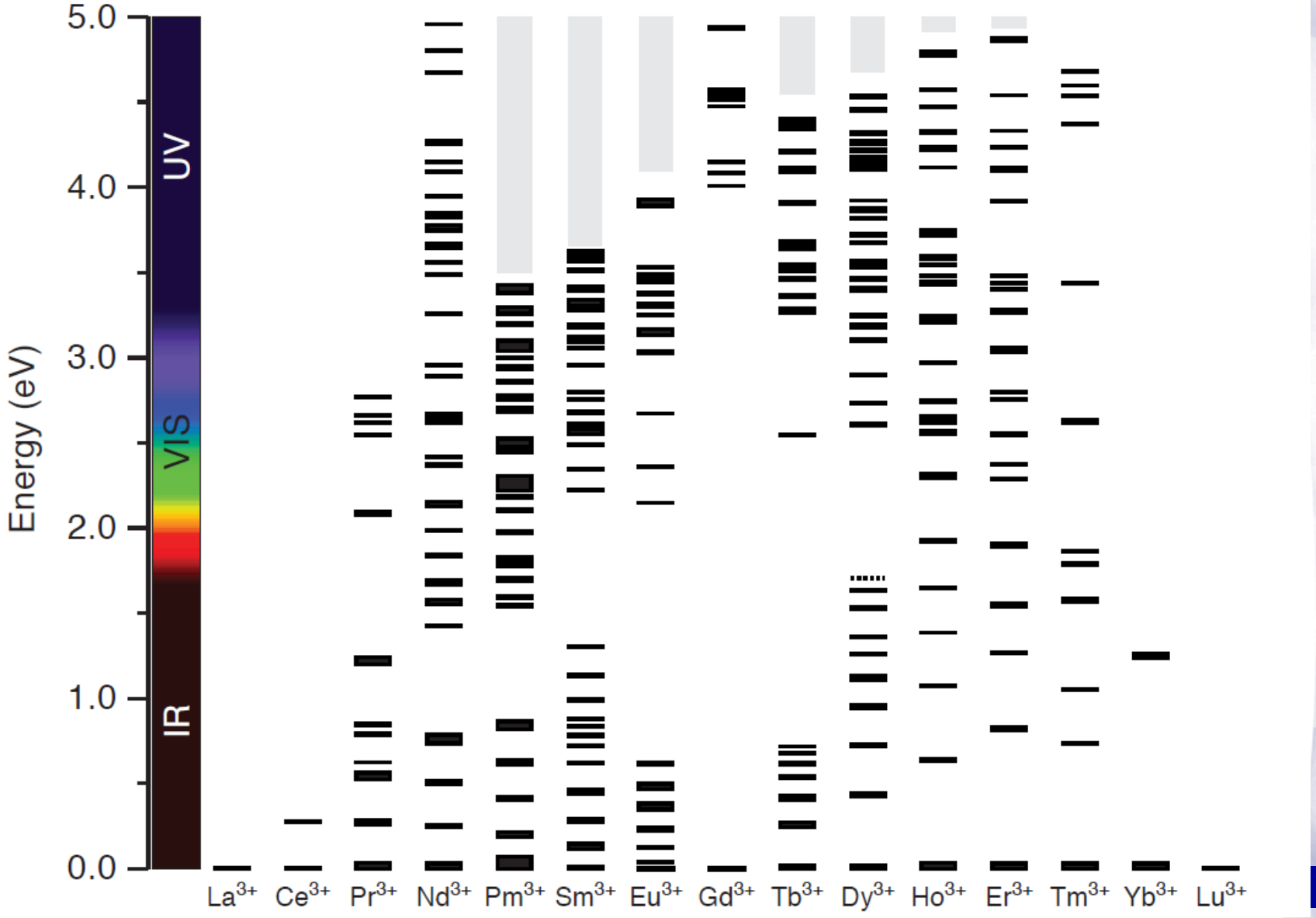
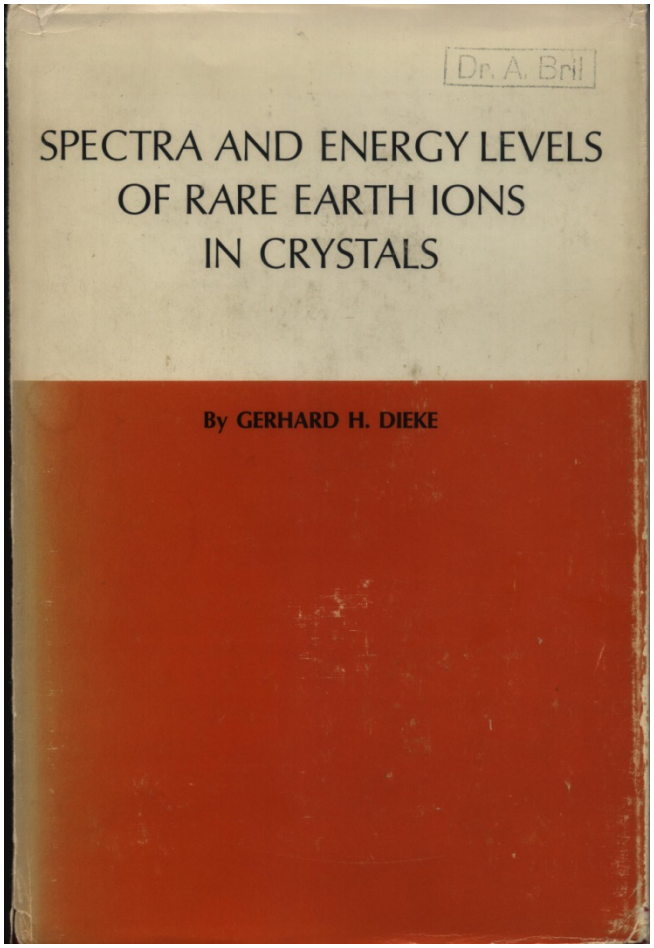
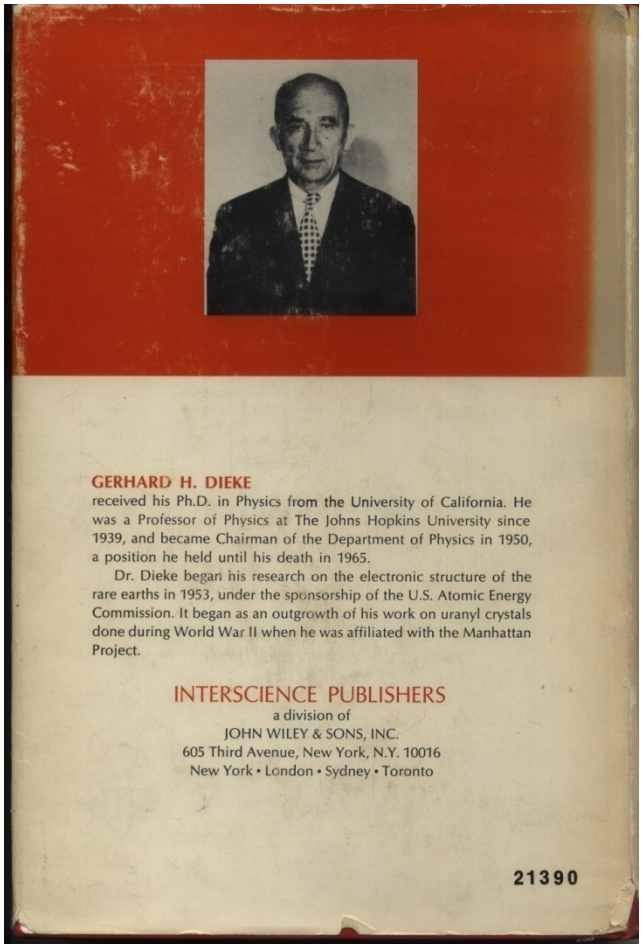
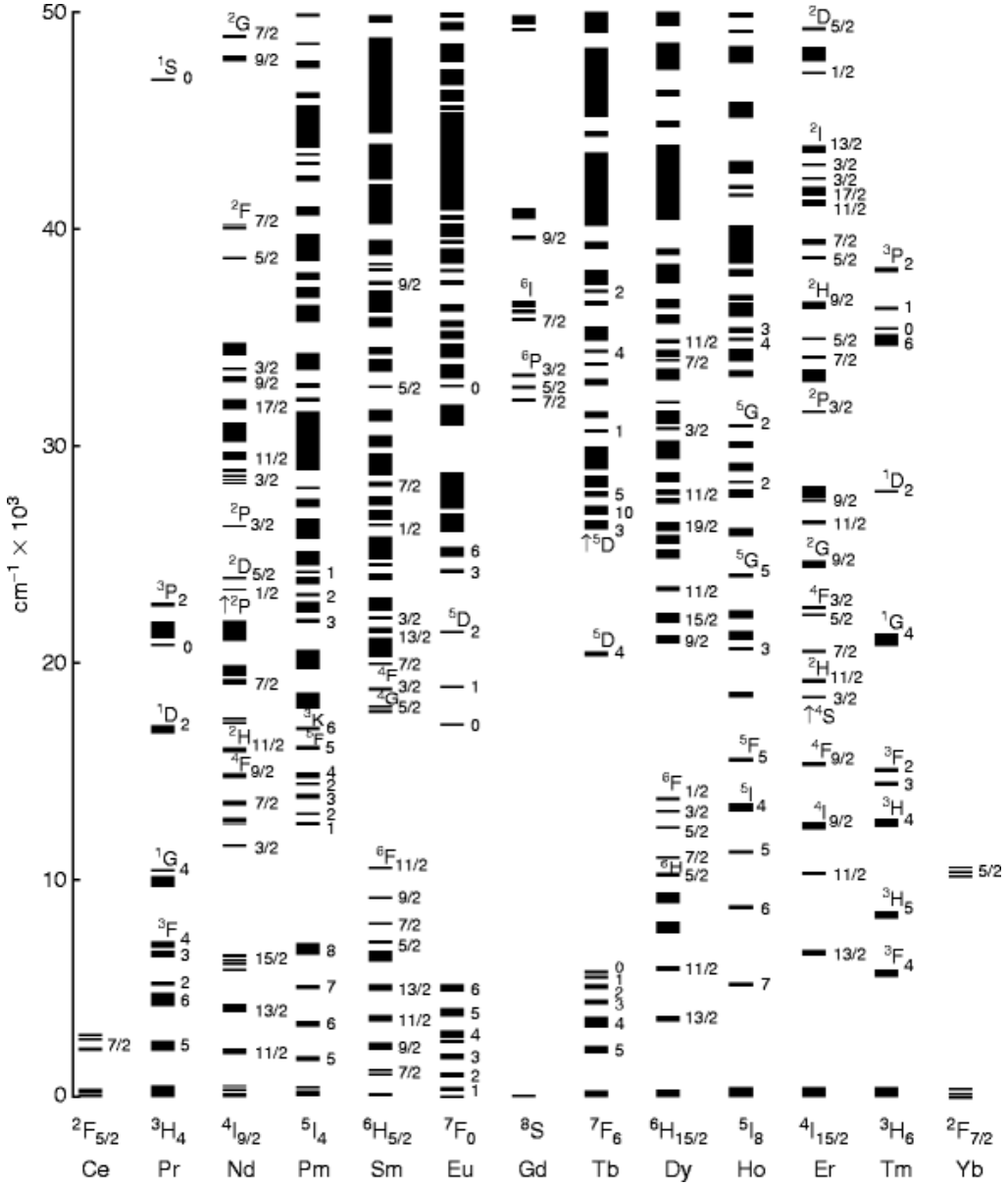


Book by Gerhard Dieke - 1968





Dieke diagram with $^{2S+1}L_J$ term symbols



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Every free ion energy level can split in (2*J*+1) or (2*J*+1)/2 crystal field components.

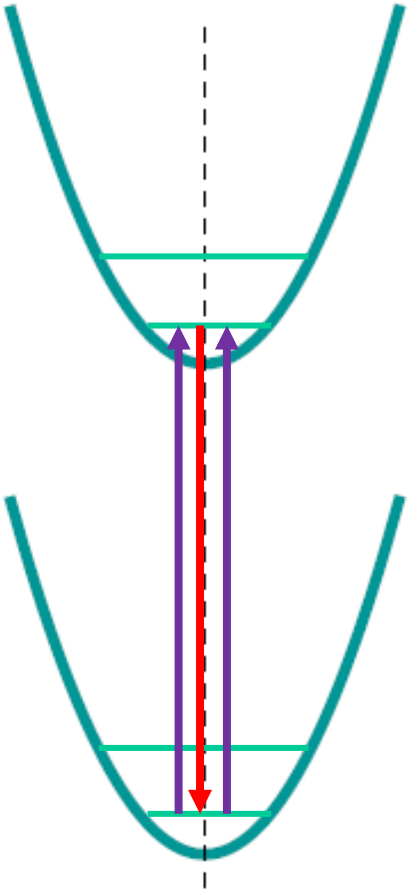
Sharp line emission from these energy levels provides a multitude of coupled levels that can serve for luminescence thermometry.

Choice in:

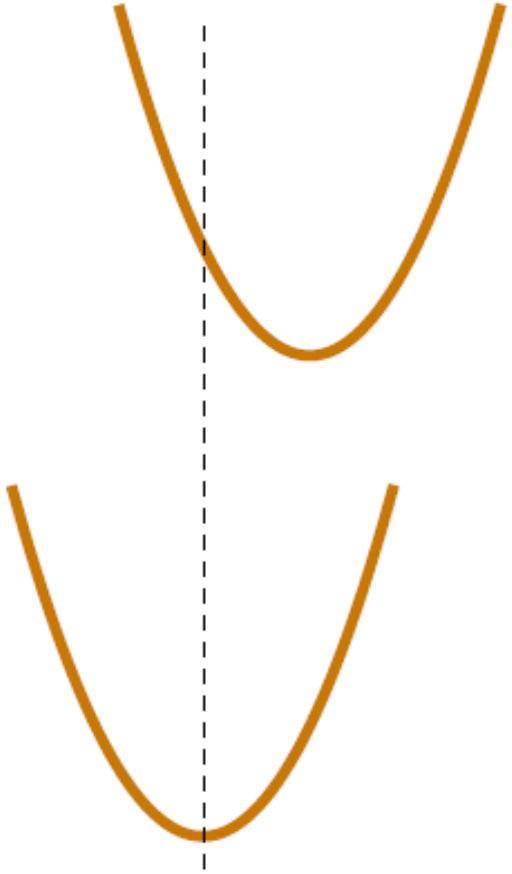
- Spectral window (UV – VIS – NIR)
- Energy separation
- Combinations of ions (for energy transfer schemes)

This is what we will work with!
Many options for thermometry

Shielding 4f-orbitals: sharp emission lines
Good for luminescence thermometry!!



vs.



$4f^n$-$4f^n$ transitions in shielded 4f inner shell → $\Delta R = 0$ – scharp zero-phonon (0-0) absorption- and emission lines for lanthanides

$\Delta R \neq 0$ – vibronic broadening of absorption and emission bands

2 – Radiative decay 4f-4f transitions

Transitions within the $4f^n$ configuration are parity forbidden – no change in dipole moment for $4f^n$-$4f^n$ transition.

So why is f-f emission observed?

1962

- Two publications: one by Judd, one by Ofelt – indepently developed theories for transitions probabilities between *J* multiplets of lanthanide ions. Driving force behind Ofelt: Wybourne
- Mechanism: forced electric dipole transitions induced by admixture of opposite parity states
- Trick: Closure approximation – assuming a single opposite parity state at a constant energy difference for all multiplets, makes it easier to calculate transition probabilities.

Sunday June 22, 2003 a historical meeting took place in Lądek Zdrój, Poland:

Brian Judd George Ofelt Brian Wybourne

Judd-Ofelt theory

Complicated mathematics – simple to use

$$S_{\mathrm{ed}} = \sum_{\lambda=2,4,6} \Omega_\lambda \left| < f^n[\gamma, S, L] J || U^{(\lambda)} || f^n[\gamma', S', L'] J' > \right|^2,$$

Calculation of transition probabilities *A:*

$$A = \frac{64\,\pi^4\,e^2\,n(n^2+2)^2\,\nu^3}{27\,h\,(2J+1)}\,S_{\mathrm{ed}},$$

Simple form:

$$A' \propto \nu^3 \sum_{\lambda=2,4,6} \Omega_\lambda \left(U^{(\lambda)} \right)^2,$$

Judd-Ofelt parameters: Ω_λ are fitting parameters that describe the admixture of the opposite parity state. The Ω_λ parameters depend on the host lattice! The Ω_λ parameters increase with higher covalency, closer position opposite parity state, larger deviations from inversion symetry…..

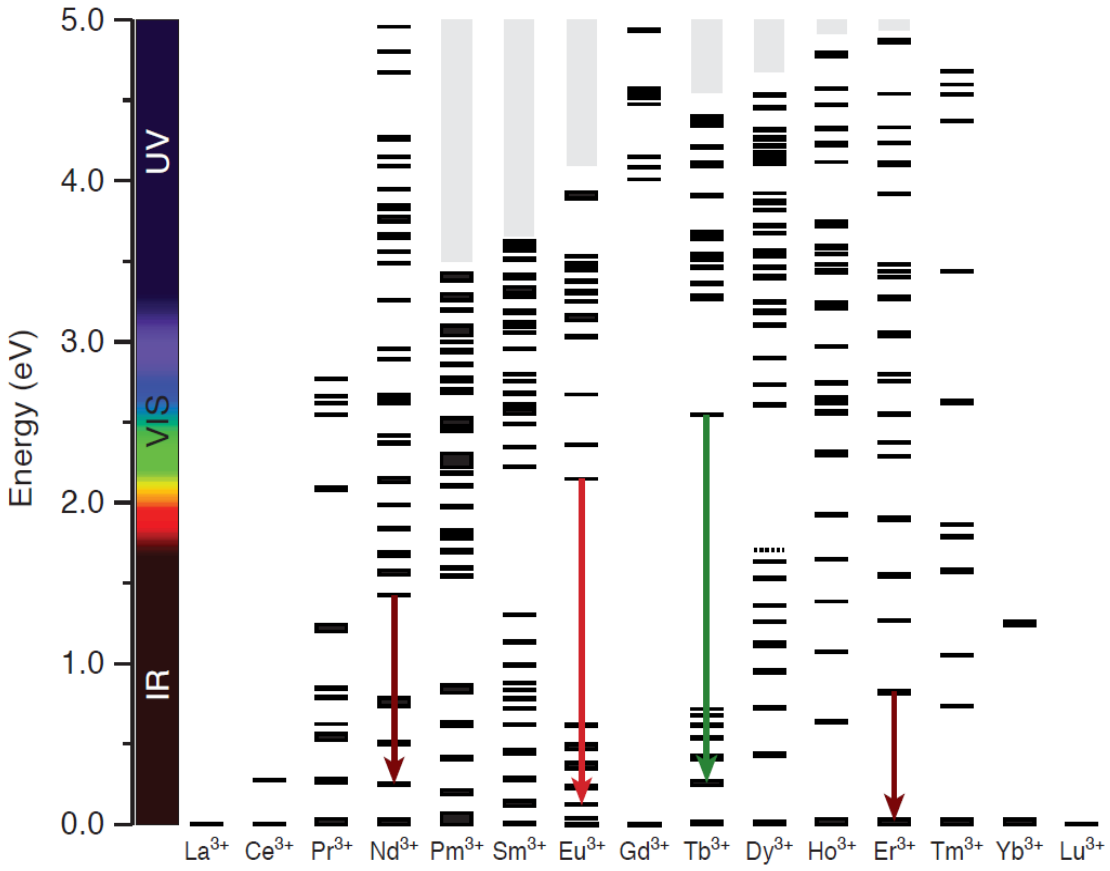
The (squared) reduced matrix elements $U^{(\lambda)}$ can be calculated for all transitions between *J*-multiplets. The reduced matrix elements are independent on the host lattice and have been tabulated for many transitions by Carnall&Crosswhite in the 1970's ('Blue Book'). Also, various websites can now be accessed for (more accurate) reduced matrix elements and Judd-Ofelt analysis.

Applications Judd-Ofelt theory

- Predict transition probabilities (absorption strengths or transition rates) by fitting Ω_λ for a number of measured lines
- Calculate optimum branching ratios for desired from calculated (and tabulated) $U^{(\lambda)}$ assuming optimum values for the Judd-Ofelt parameters
- General: stronger transitions for $\Delta J = 0, 2, 4, 6$ (not $0 \rightarrow 0$)
- Optimize thermometer performance by selecting favorable radiative decay rates/transition probabilities for emission lines in ratiometric luminescence temperature sensing.

3 – Non-Radiative decay 4f-4f transitions

Non-radiative 4f-4f decay occurs to the next lower 4f level by 'multi-phonon relaxation'. The energy gap is bridged by conversion into vibrational energy through energy transfer to a vibrational overtone of nearby vibrational system.



Rules non-radiative decay:

- **Energy gap law**:

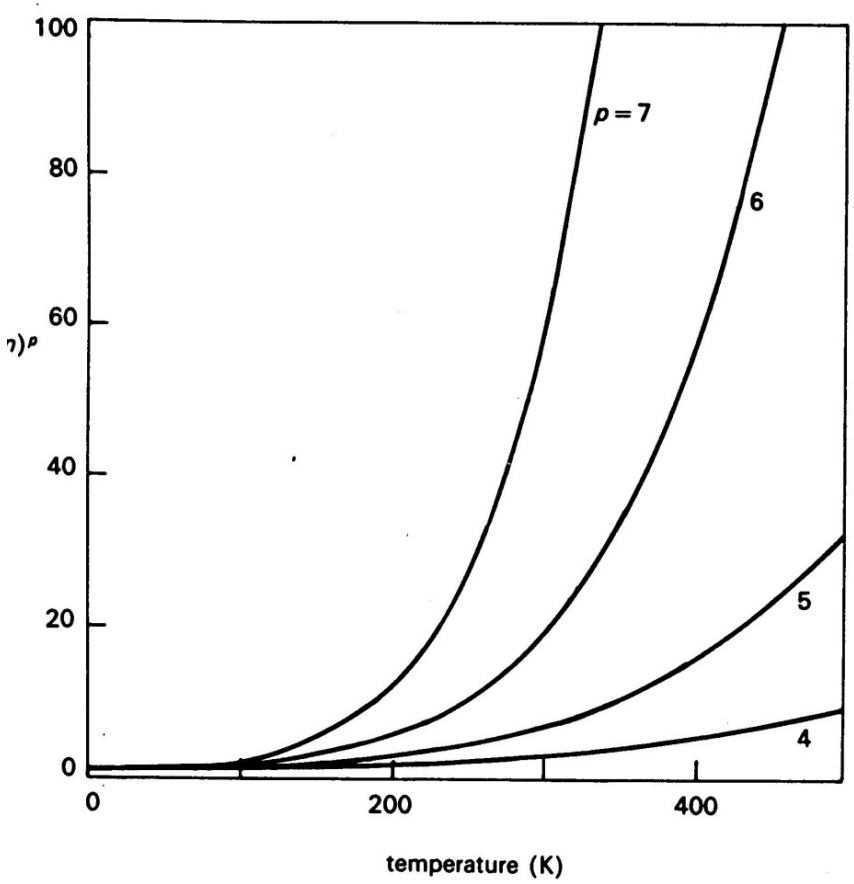
$$W_{nr} = A\exp(-\alpha\Delta E) = A\exp(-\beta p).$$

p = number of phonons needed to bridge gap

β = maximum phonon energy

- **5 phonon rule**: if ΔE larger than five times the max phonon energy, radiative decay dominates. If less than five times max phonon energy, non-radiative decay dominates → efficient emission from energy levels with large gaps (e.g. Eu^{3+} $^5D_0$ and Tb^{3+} $^5D_4$).

Temprature dependence of non-radiative relaxation rate



$W_{nr} = (1+n)^p$

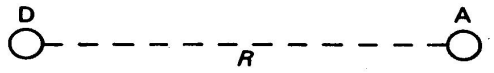
n – phonon occupation number

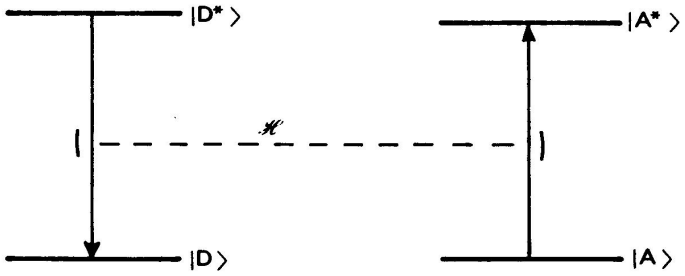
$n = 1/(e^{(E_{ph}/kT)}-1)$

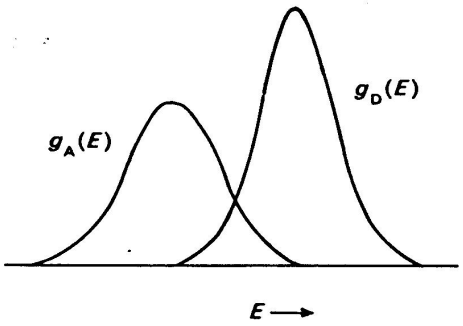
thermal effects most important for low energy phonons (bromides, chlorides, fluorides) not in borates, phosphates (at least not up to RT)!

4 – Energy transfer

Single step energy transfer







General equation donor-acceptor energy transfer rate:

$$W_{DA} = \frac{2\pi}{\hbar} |\langle D, A^* | \mathcal{H}' | D^*, A \rangle|^2 \int g_D(E) g_A(E) dE$$

Transfer rate = interaction D-A x spectral overlap integral

Critical distance for energy transfer R_0:

Distance at which transfer rate from donor to acceptor is equal to the (radiative) decay rate of the donor.

Dipole-dipole interaction (Förster ET)

$$W_{DA}^{dd} = \left(\frac{1}{4\pi\varepsilon_0}\right)^2 \frac{3\pi\hbar e^4}{n^4 m^2 \omega^2} \frac{1}{R^6} f_D(\mathrm{ED}) f_A(\mathrm{ED}) \int g_D(E) g_A(E) \mathrm{d}E$$

Energy transfer through dipole-dipole interaction:

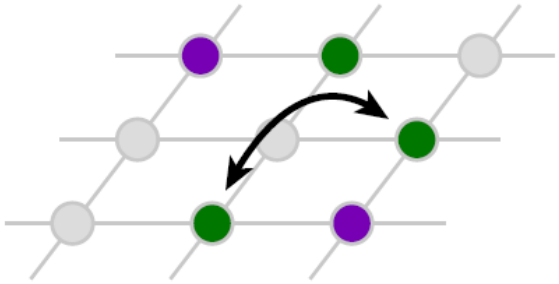
-Transfer rate proportional to oscillator strength donor and acceptor

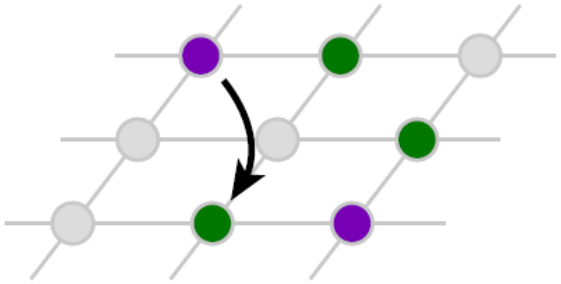
-Transfer rate decreases with 6th power of donor-acceptor distance (R^{-6})

-Transfer rate proportional to spectral overlap integral

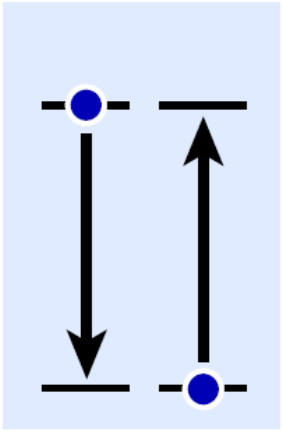
The rest are boring constants……

Different types of energy transfer

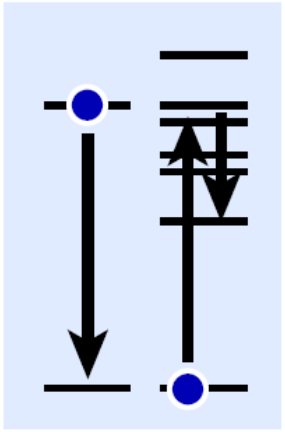




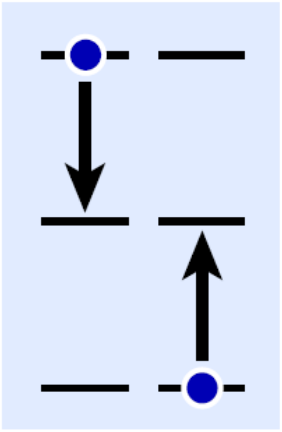
Energy migration
(back and forth)



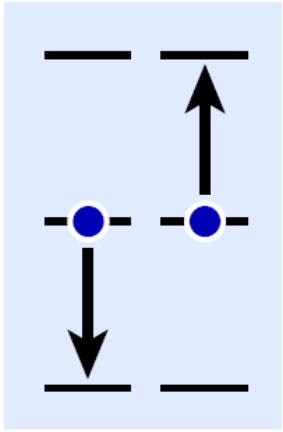
Sensitization
(one-way)



Cross-relaxation
(distribution)



Upconversion
(combination)



Modelling energy transfer:

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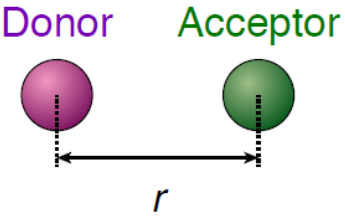
Historically Inokuti-Hirayama (single step) and Yokota-Tanimoto (energy migration) are used but do not take into account the crystal structure and actual distribution of donor-acceptor distances.

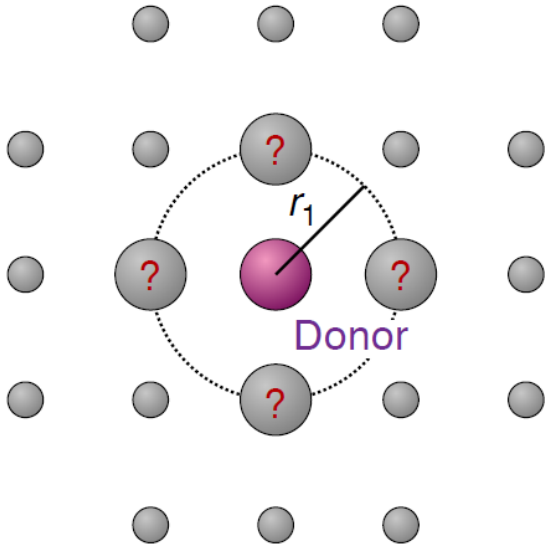
Better: Shell model to fit luminescence decay curves

Shells of neighbors surrounding each donor center

Single donor–acceptor pair



$\Gamma = \gamma_{rad} + C_{ET} r^{-6}$



Example:
20% acceptor concentration

Assume random distribution

41%: $\Gamma = \gamma_{rad}$

41%: $\Gamma = \gamma_{rad} + C_{ET} r_1^{-6}$

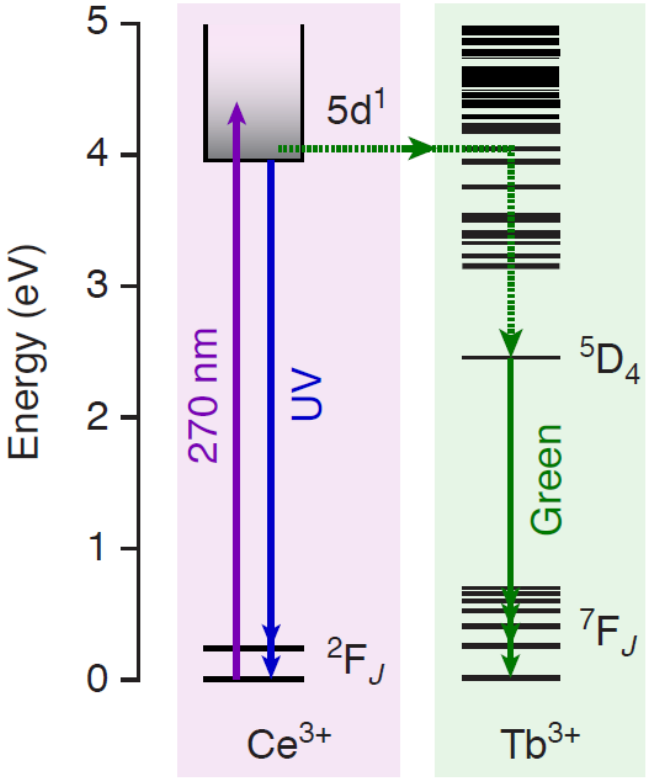
15%: $\Gamma = \gamma_{rad} + 2C_{ET} r_1^{-6}$

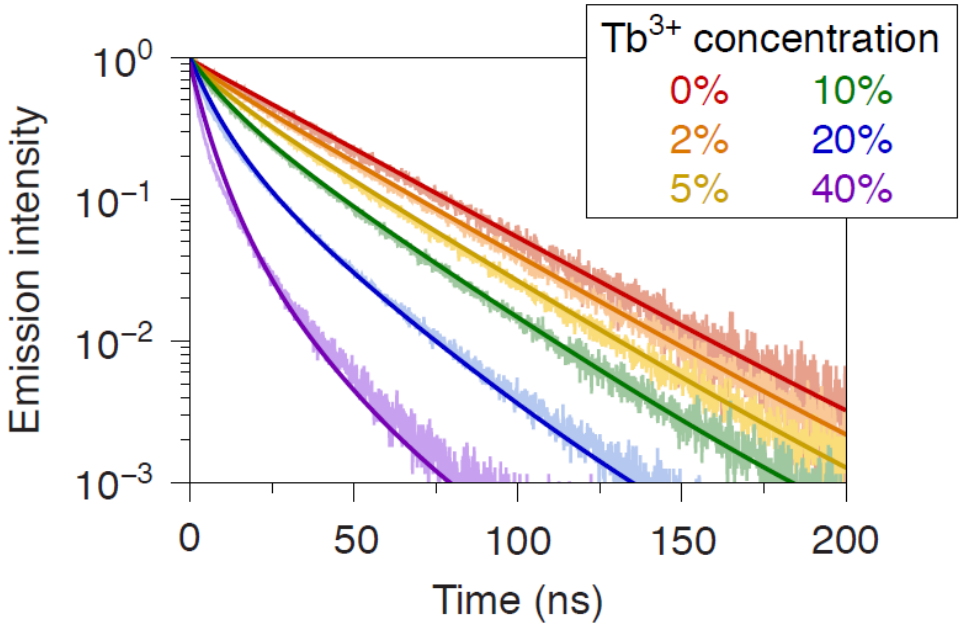
3%: $\Gamma = \gamma_{rad} + 3C_{ET} r_1^{-6}$

0.2%: $\Gamma = \gamma_{rad} + 4C_{ET} r_1^{-6}$

$$I(t) \propto e^{-\gamma_{rad} t} (1 - x + x e^{-C_{ET} r_1^{-6} t})^n \qquad n = 4,\ x = 0.2$$

One interaction parameter *C* for D-A transfer to fit luminescence decay curves of donor emission for ALL acceptor concentrations!





$C_{ET} r_1^{-6} = 10\text{–}1000\ \gamma_{rad}$
for a lanthanide acceptor

For nearest neighbors energy transfer dominates!

F. T. Rabouw, S. A. den Hartog, T. Senden and A. Meijerink *Nature Communications* **5**, 3610 (2014)

D. C. Yu, F. T. Rabouw, W. Q. Boon, T. Kieboom, S. Ye, Q. Y. Zhang and A. Meijerink, *Physical Review B* **90**, 165126 (2014)

Luminescence Thermometry

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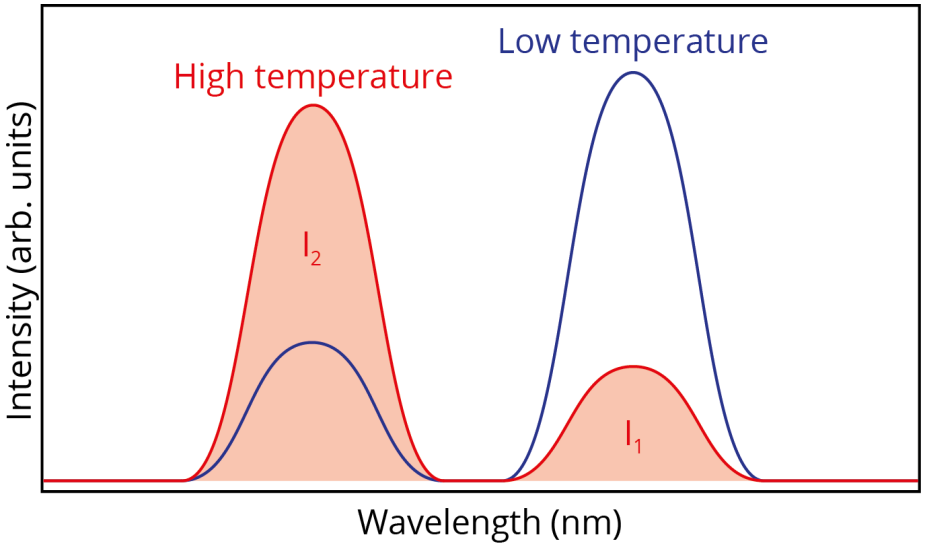
Conventional Thermometers:

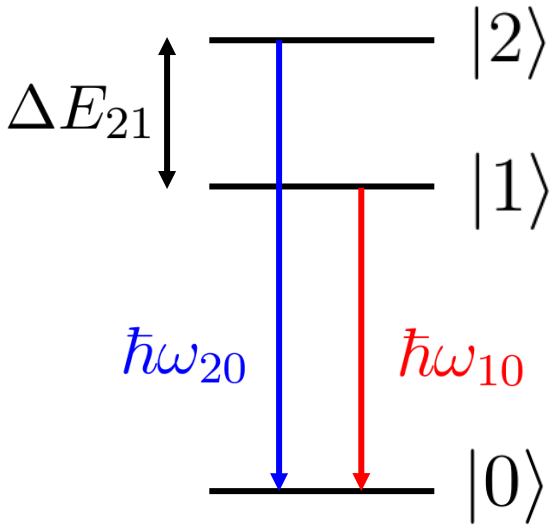
a

b

c

Luminescence thermometry:





Measure emission spectra from luminescent (nano)probe. Relative intensity of emission from higher energy level will increase with temperature.

Workhorse: Er^{3+}

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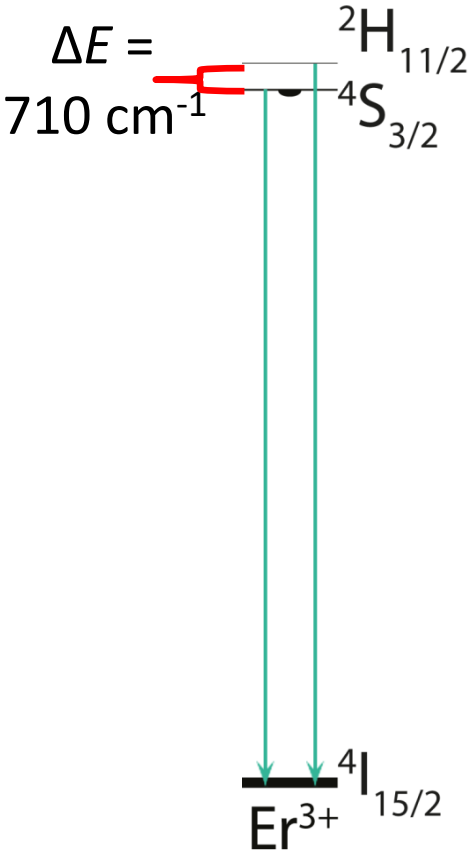
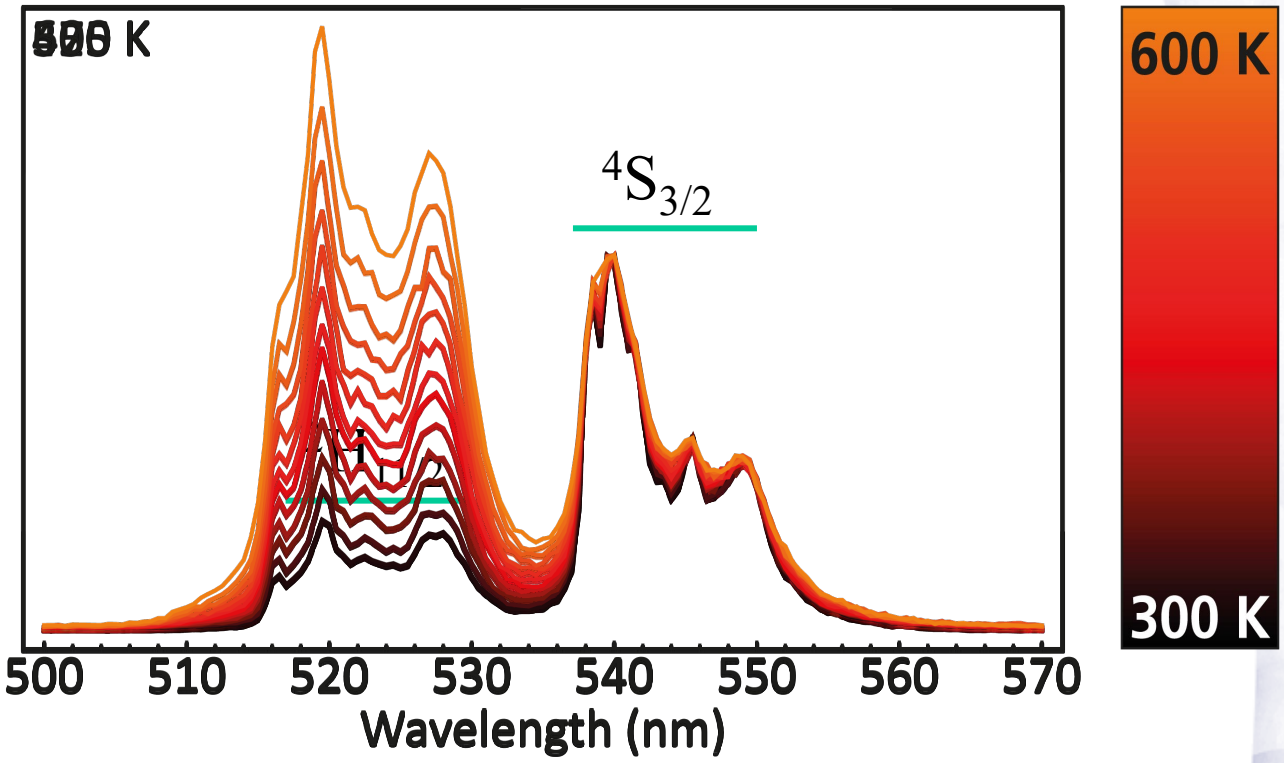
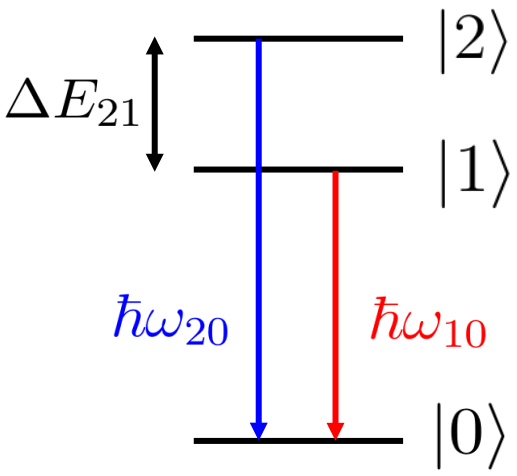
Temperature-dependent luminescence $NaYF_4$:Yb18%,Er2%





Note: sharp line emission helps - easy to quantify ratio $^2H_{11/2}$ and $^4S_{3/2}$ emission

Analysis assuming Boltzmann equilibrium:

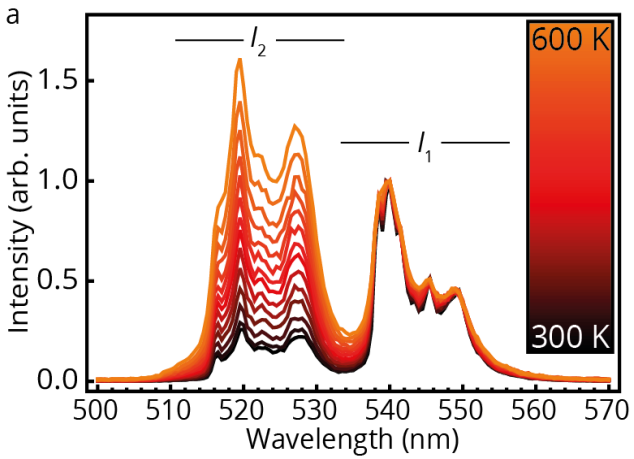


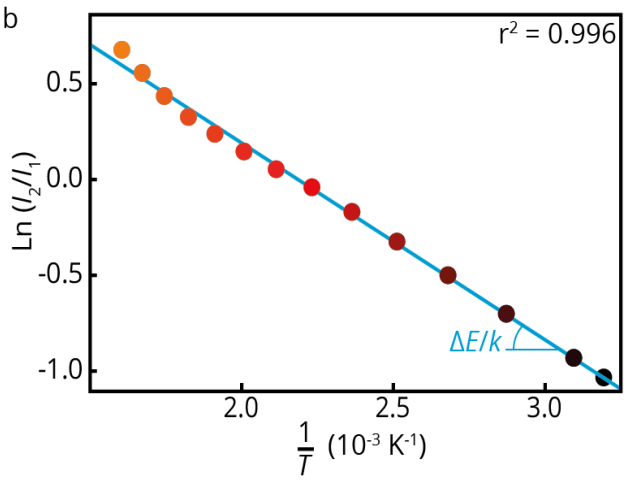
$$\frac{N_2}{N_1} = \frac{g_2}{g_1} e^{-\frac{\Delta E}{kT}}.$$

$$R(T) = \frac{I_{20}}{I_{10}} = C\frac{g_2}{g_1}\exp\left(-\frac{\Delta E_{12}}{k_B T}\right)$$

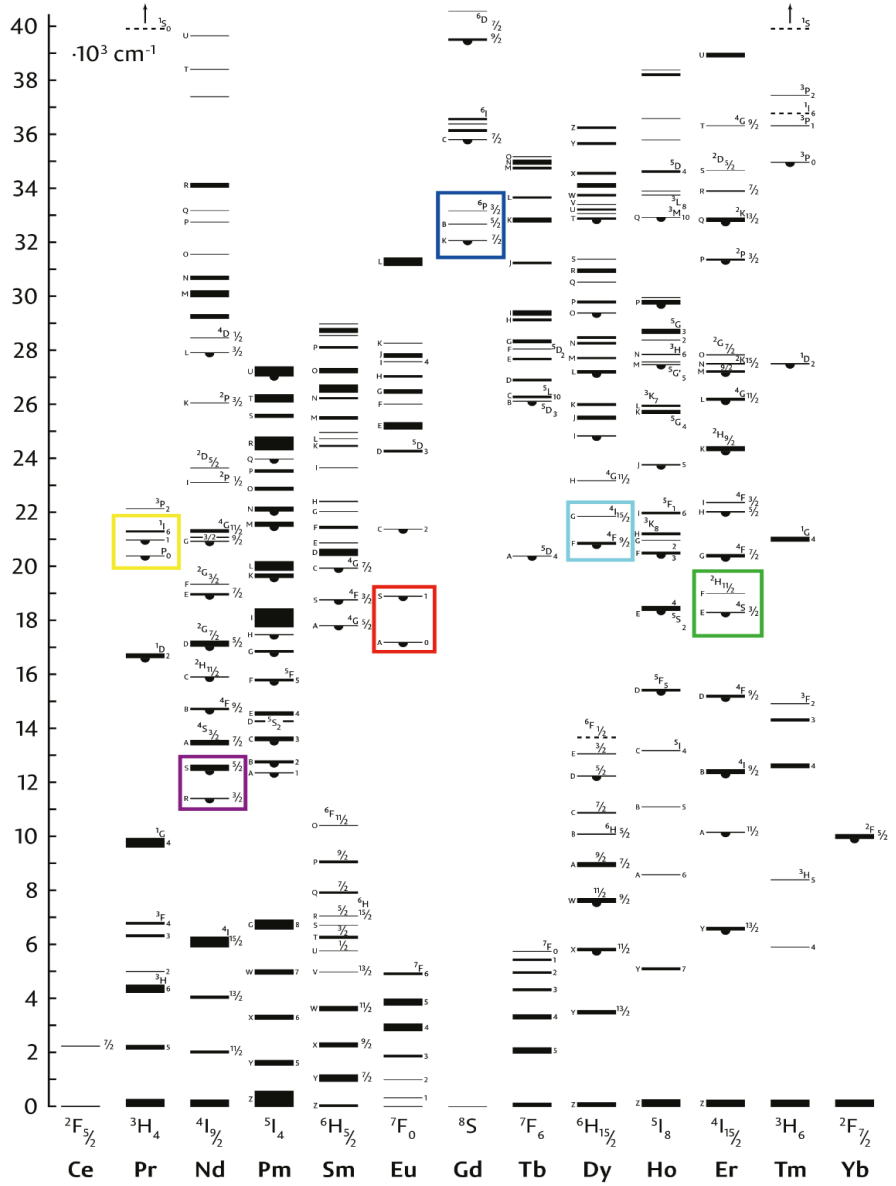
Contains Judd-Ofelt transition probabilities!

Nice calibration line:





Many two-level systems possible for Ln^{3+} :

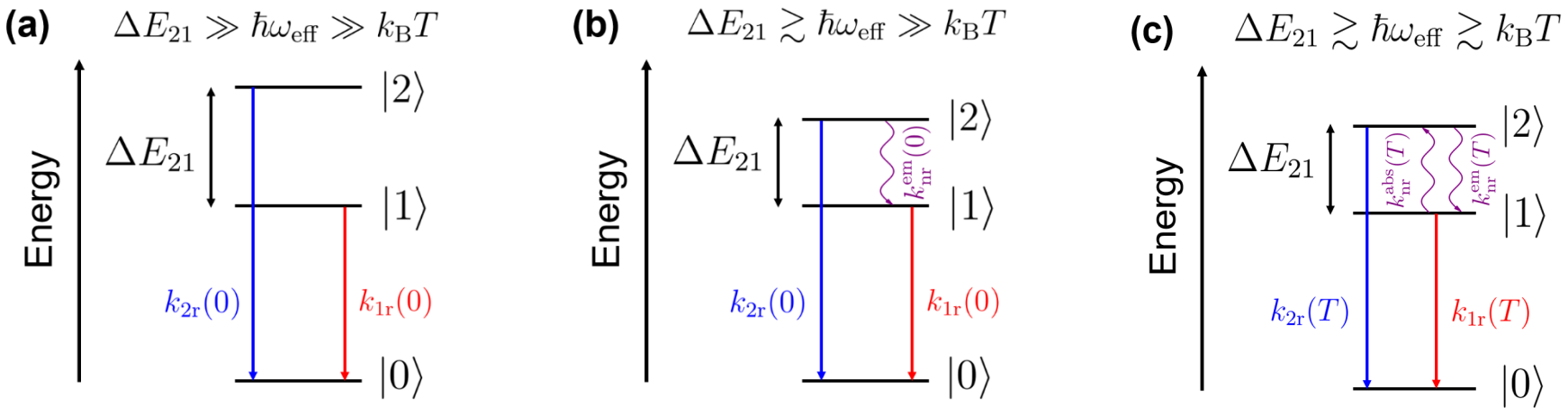


Variation possible in energy separation and spectral window. Perfect for temperature sensing for a wide variety of applications for single ion, two-level systems.

Two '**buts**' – 'pitfalls':

- Boltzmann equilibrium not always realized - be careful!
- Only good sensitivity in limited temperature range, determined by ΔE

Boltzmann problems: the non-radiative decay rates that couple the two emitting levels are not (much) faster than the depopulation rates



Non-Boltzmann (at RT)

Boltzmann!!

Example: Eu^{3+}

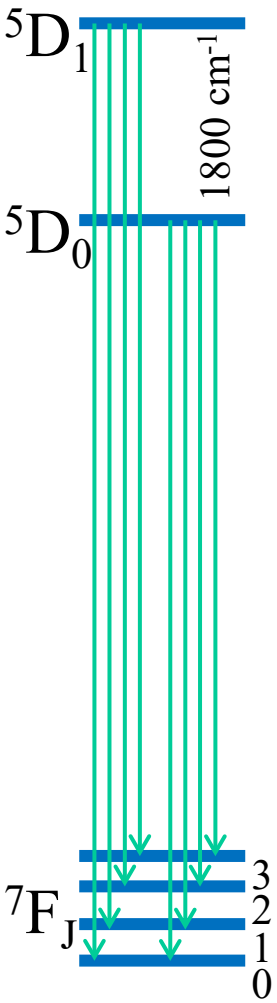
Example: Nd^{3+}

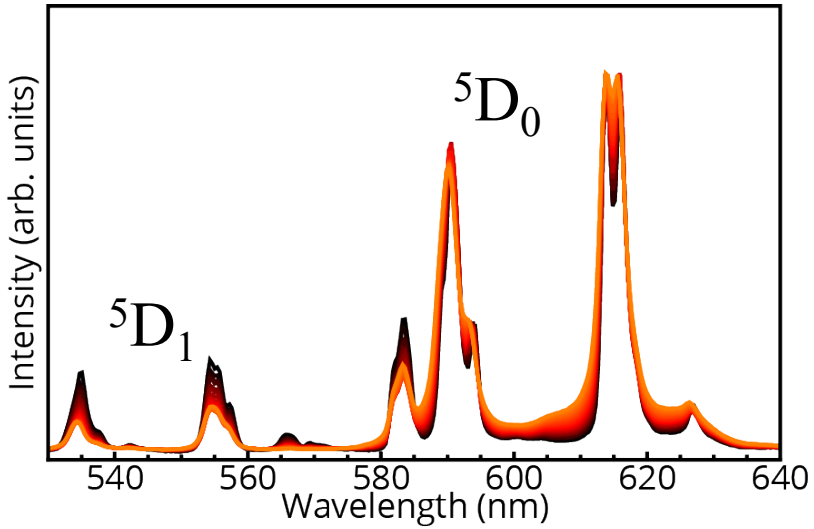
$$k_{\rm nr}^{\rm em}(T) = g_1 k_{\rm nr}(0)(1 + \langle n_{\rm eff}\rangle)^p$$

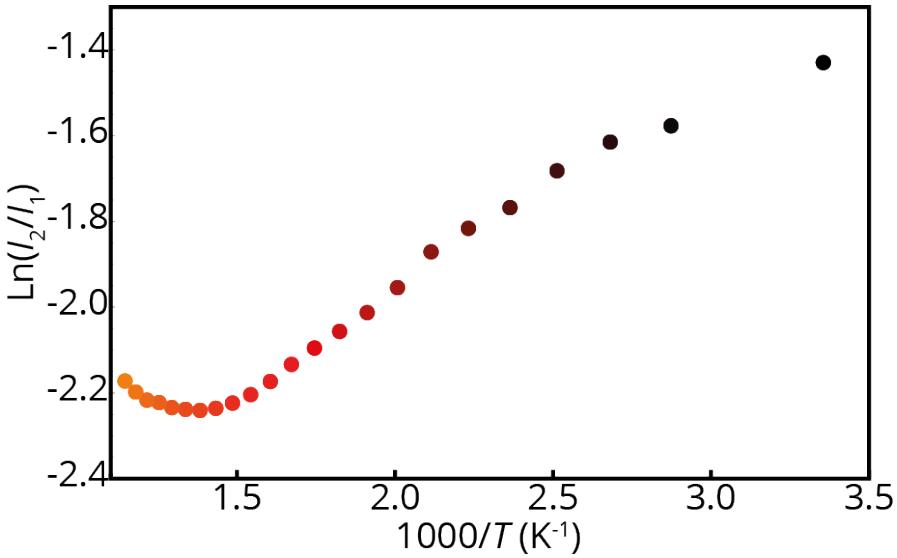
$$k_{\rm nr}^{\rm abs}(T) = g_2 k_{\rm nr}(0)\langle n_{\rm eff}\rangle^p$$

Boltzmann problem (a):

Unusual T-dependent luminescence of $NaYF_4:Eu^{3+}$



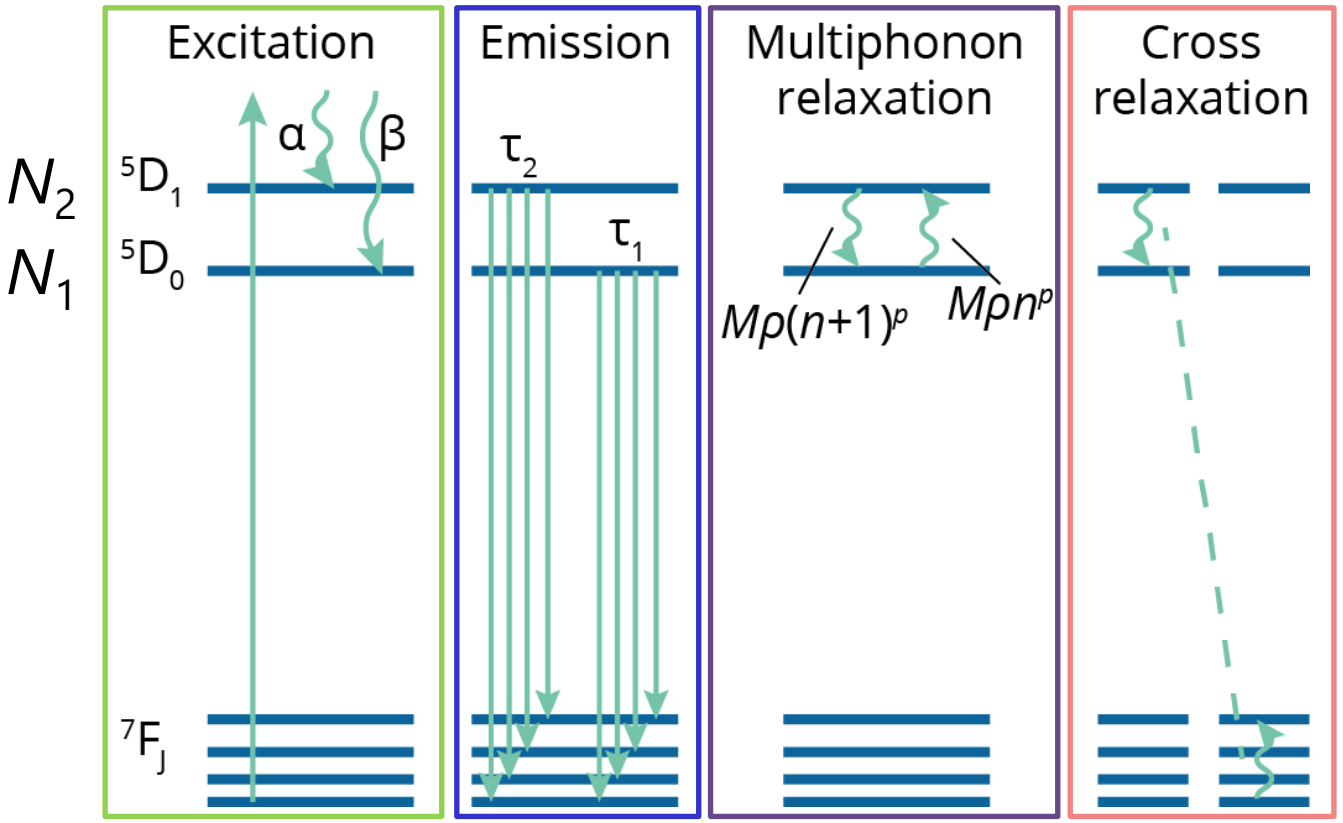




Large $^5D_1$-$^5D_0$ energy gap – with increasing temperature the relative emission intensity from the lower energy $^5D_0$ level increases with temperature – opposite to what is expected for Boltzmann behavior

R. G. Geitenbeek, H. W. de Wijn, A. Meijerink, *Phys. Rev. Applied* **2018**, *10*, 64006

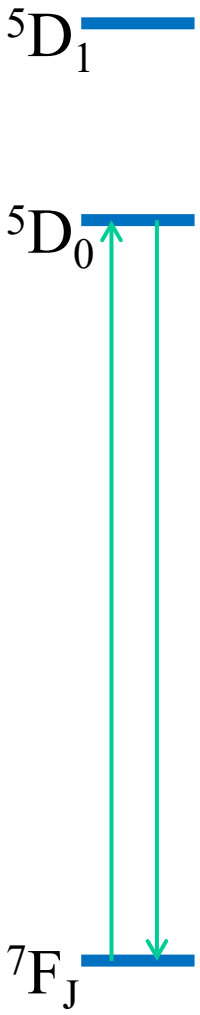
Possible processes in Eu^{3+}

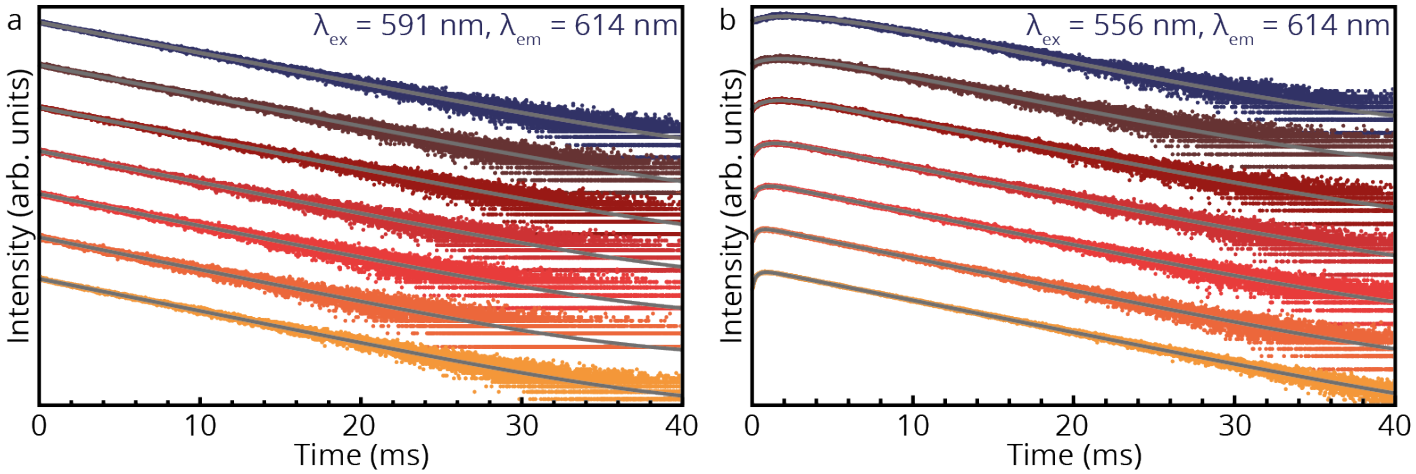


- $\frac{dN_1}{dt} = \beta - \frac{N_1}{\tau_1} + \mathrm{CR}_1 N_2 - \mathrm{CR}_2 N_1 + M\rho[(1+n)^p m_1 N_2 - n^p m_2 N_1]$ $\quad n = 1/\left[\exp\left(\frac{\Delta E}{pkT}\right) - 1\right]$
- $\frac{dN_2}{dt} = \alpha - \frac{N_2}{\tau_2} - \mathrm{CR}_1 N_2 + \mathrm{CR}_2 N_1 - M\rho[(1+n)^p m_1 N_2 - n^p m_2 N_1]$

Layne, Lowdermilk, Weber, *Phys. Rev. B*, **1977**, 16, 1611-1616
Riseberg, Moos, *Phys. Rev.*, **1968**, 174, 429-438

Time-resolved measurements: 0.4% Eu^{3+}





Time-resolved measurements: 0.4% Eu^{3+}

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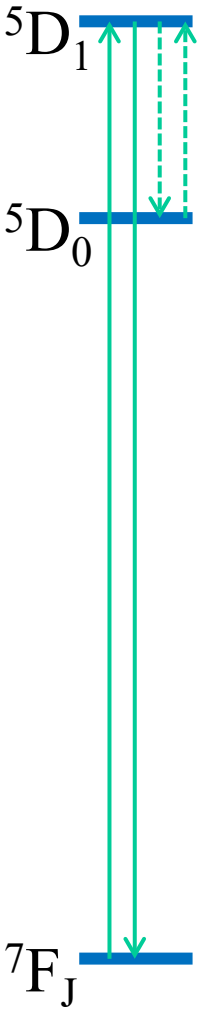
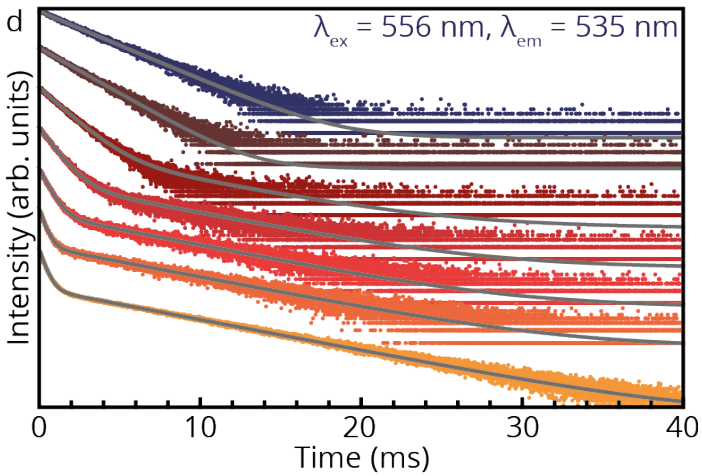
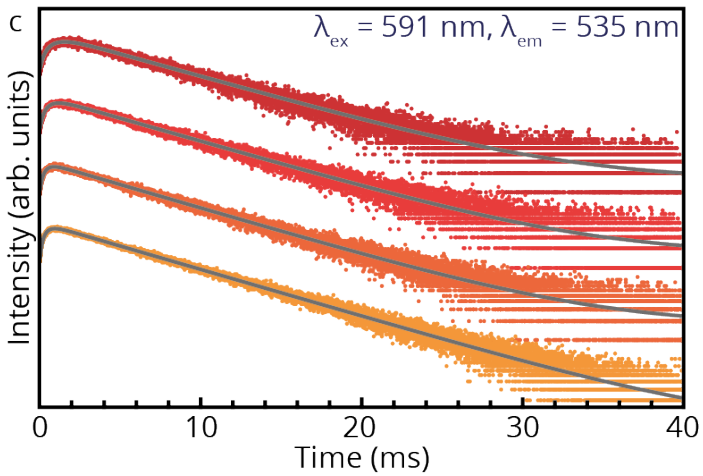




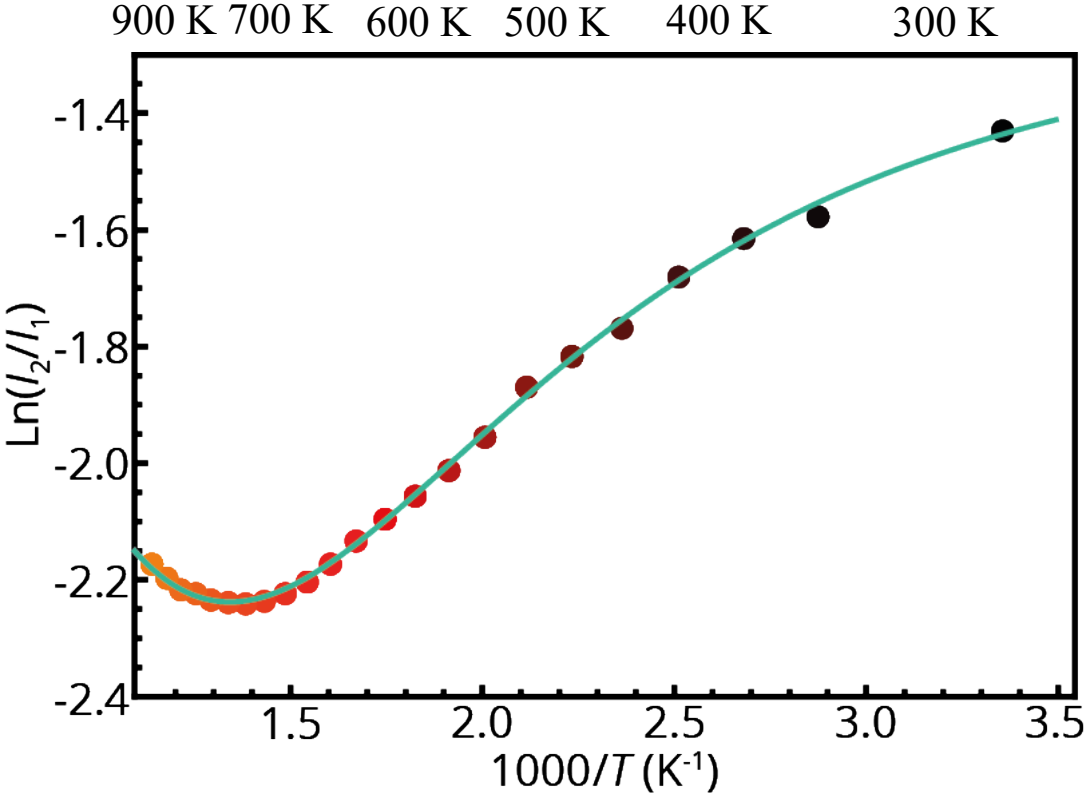


Steady state measurements: 0.4% Eu^{3+}

$$\frac{dN_1}{dt} = \beta - \frac{N_1}{\tau_1} + M\rho[N_2(1+n)^p m_1 N_1 - n^p m_2 N_1]$$

$$\frac{dN_2}{dt} = \alpha - \frac{N_2}{\tau_2} - M\rho[N_2(1+n)^p m_1 N_1 - n^p m_2 N_1]$$

$$\frac{N_2}{N_1} \propto \frac{I_2}{I_1}$$



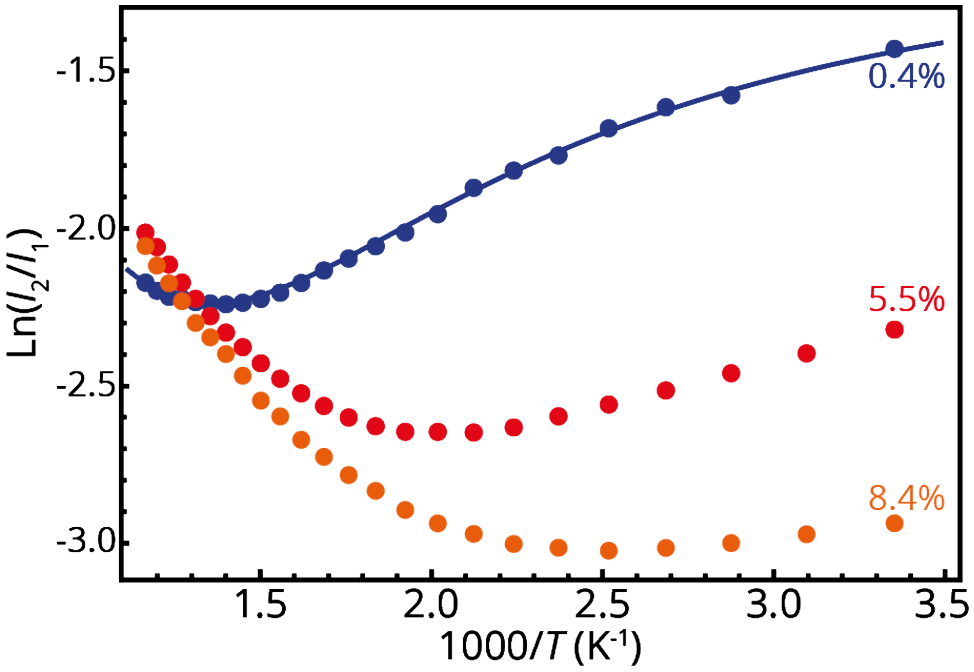
$$\frac{I_2}{I_1} = C * \frac{\frac{\alpha}{\tau} + M\rho m_2 n^p}{\frac{\beta}{\tau} + M\rho m_1 (1+n)^p}$$

Fitting parameters
C = 0.52, ***α*** = 0.85, ***β*** = 0.27
Mρ = 0.19 ms^{-1} **and** ***p*** = 3.60

Time-resolved measurements
Mρ = 0.18 ms^{-1} **and** ***p*** = 4.09

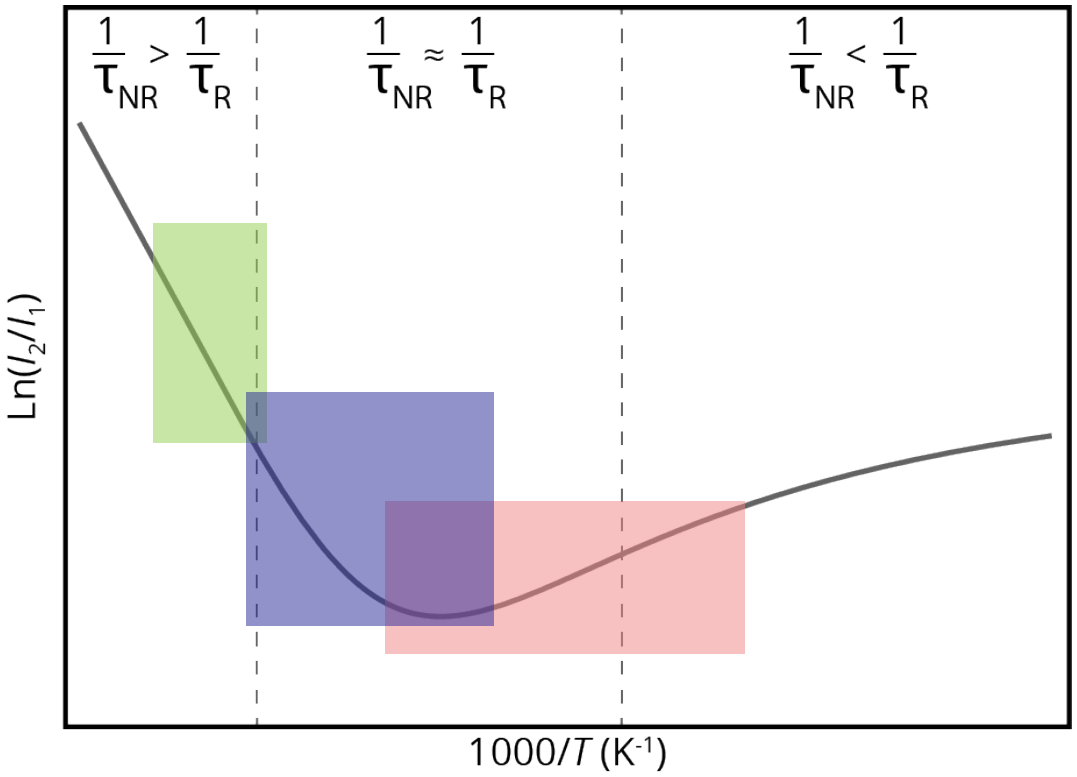
Adding cross relaxation:

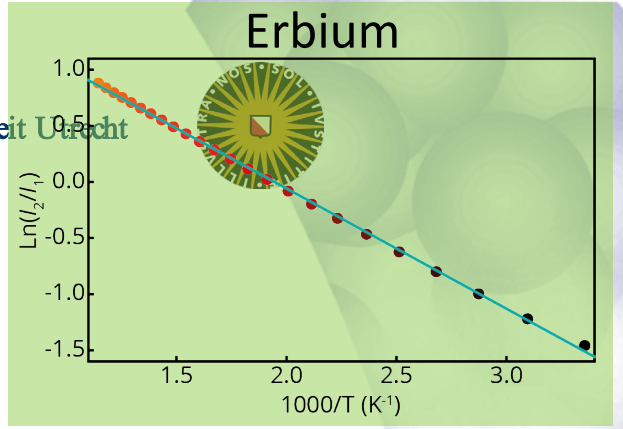
$$\frac{I_2}{I_1} = C * \frac{\frac{\alpha}{\tau} + M\rho m_2 n^p + \mathrm{CR}_1}{\frac{\beta}{\tau} + M\rho m_1 (1+n)^p + \mathrm{CR}_2}$$

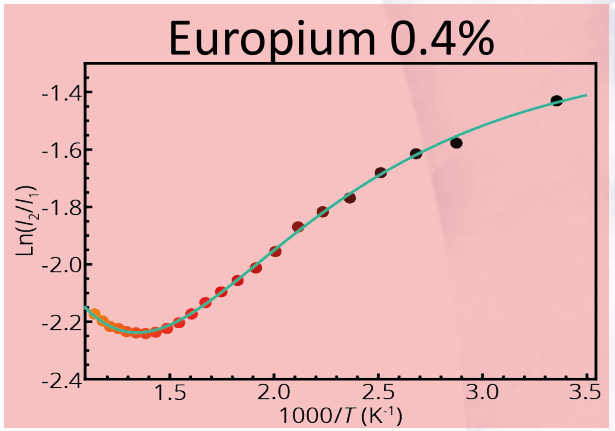


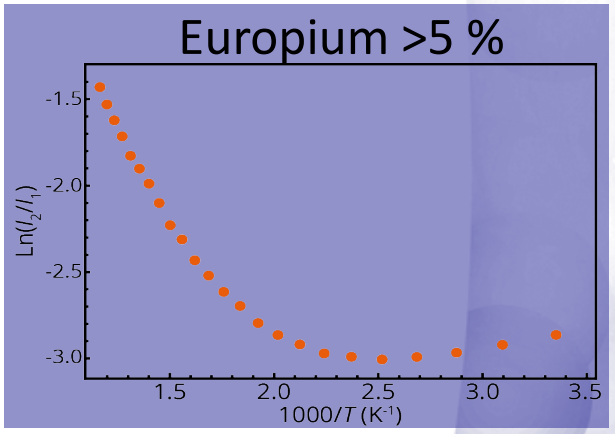
R. G. Geitenbeek, H. W. de Wijn, A. Meijerink, *Phys. Rev. Applied* **2018**, *10*, 64006

$$\frac{I_2}{I_1} = C * \frac{\frac{\alpha}{\tau} + M\rho m_2 n^p + \mathrm{CR}_1}{\frac{\beta}{\tau} + M\rho m_1 (1+n)^p + \mathrm{CR}_2}$$







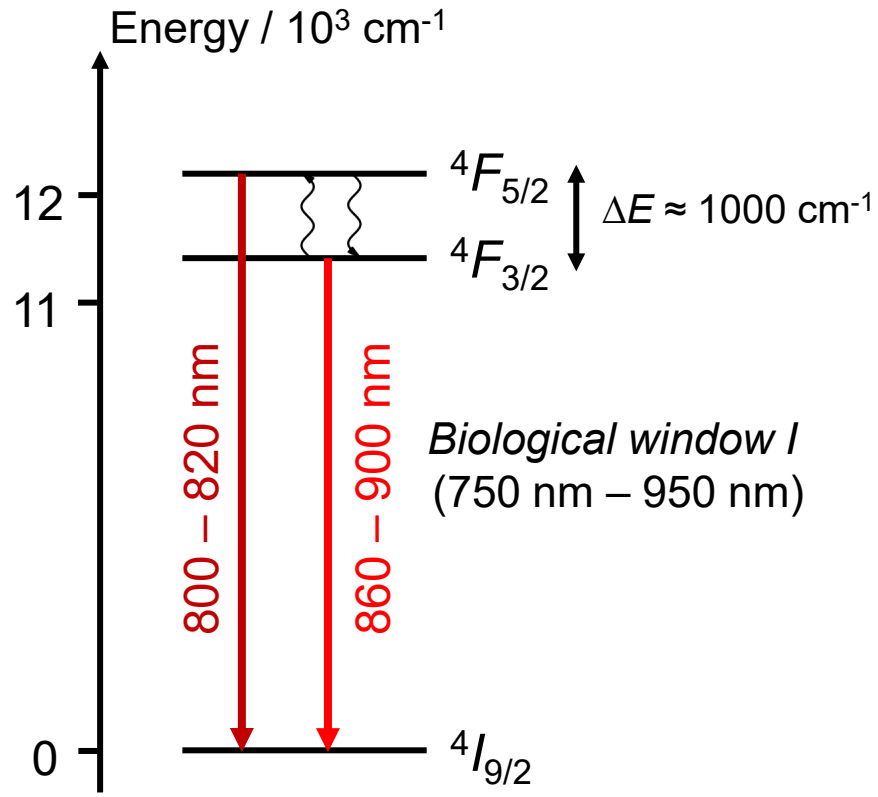


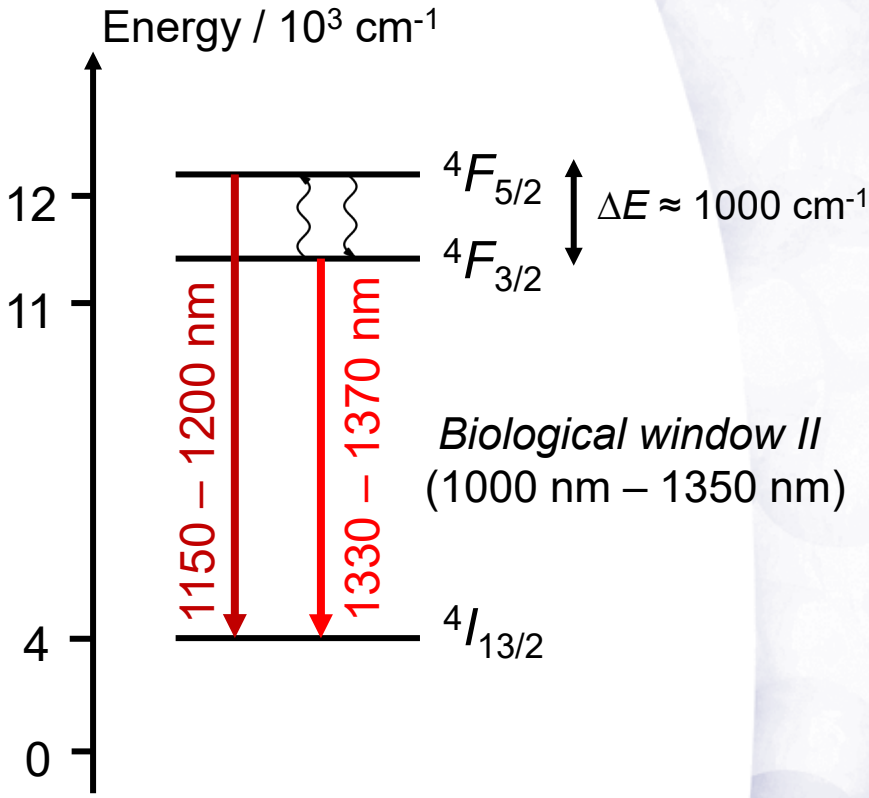
- Old theories work!
- Cross relaxation can help to realize Boltzmann
- Dopant concentrations matter!

Boltzmann problem (b):

T-dependent luminescence of Nd^{3+}

Nd^{3+} ($4f^3$): NIR emitter → promising for *in vivo* thermometry!





Low Nd^{3+} concentration:

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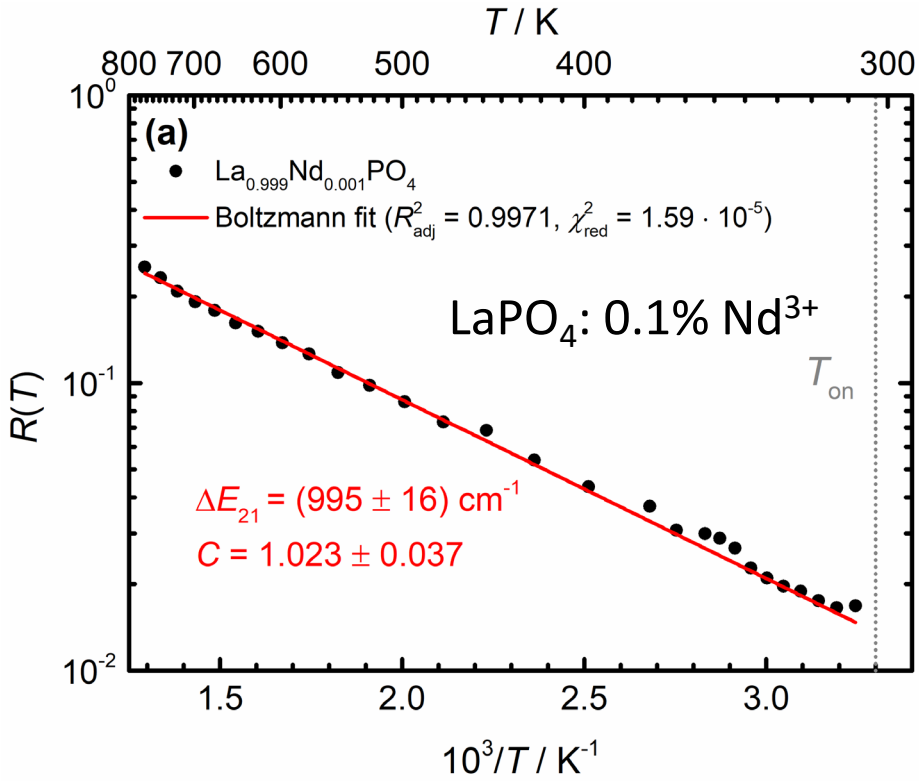
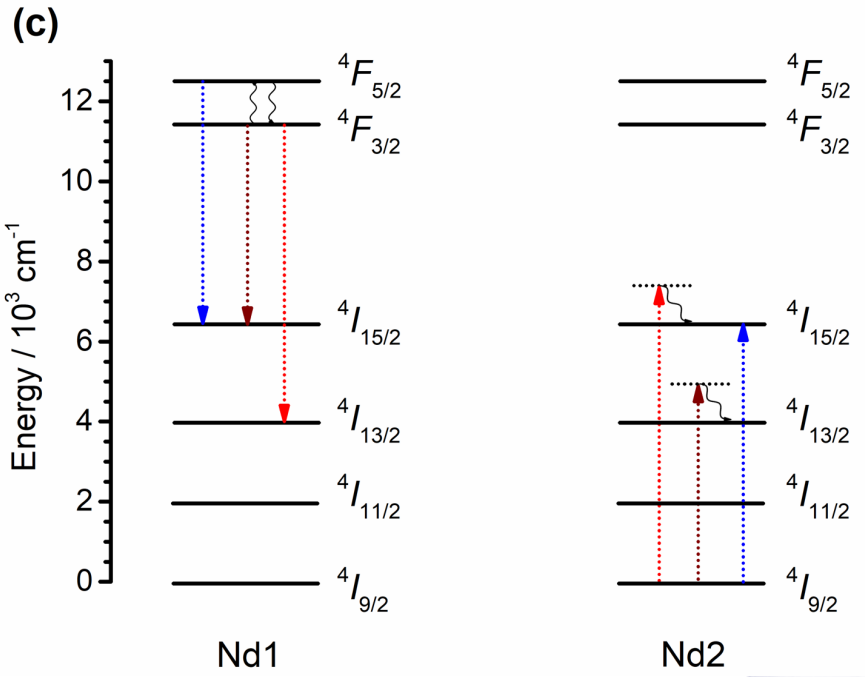
Nice Boltzmann behavior, but poor absorption → poor signal/noise

Solution: increase Nd^{3+} concentration!





M. Suta, Ž. Antić, V. Đorđević, S. Kuzman, M. D. Dramićanin, A. Meijerink, *Nanomaterials* **2020**, *10*, 543.

But: Concentration can favor cross relaxation and effectively lead to faster decay rates

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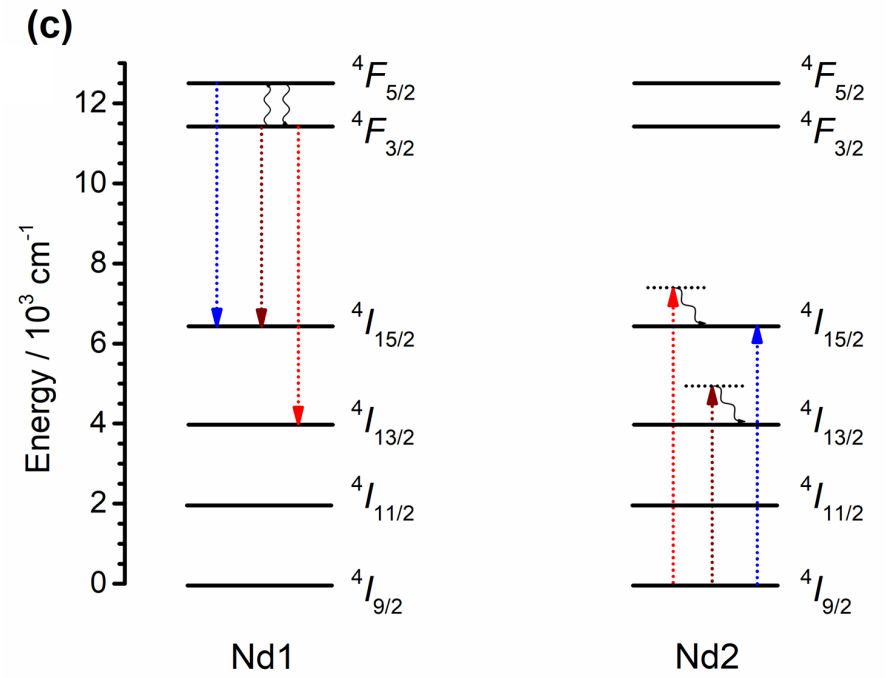
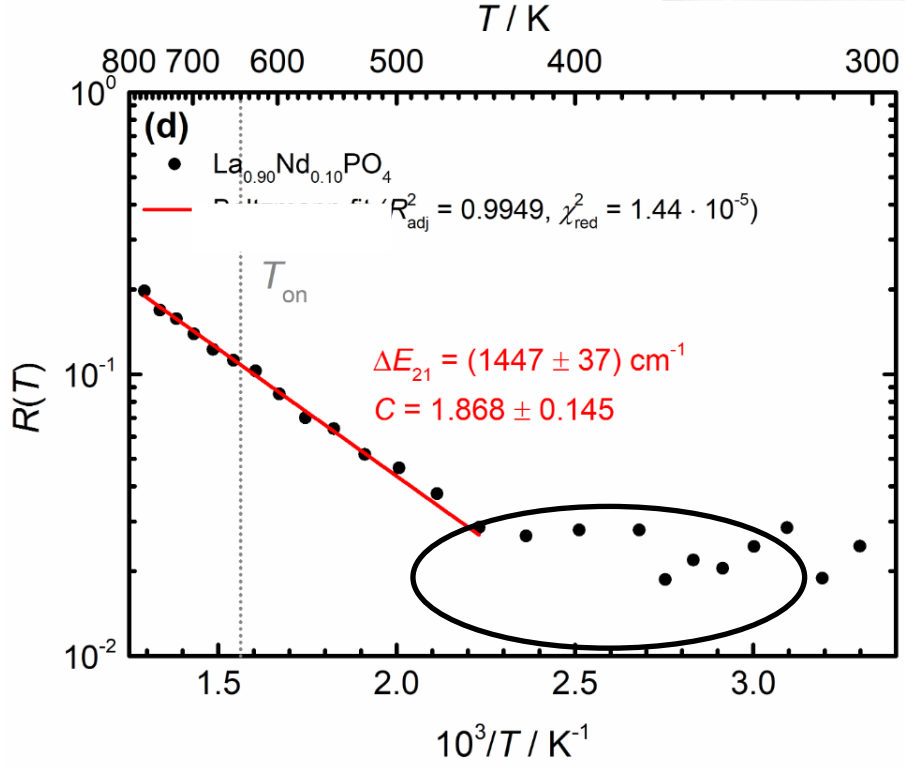
$LaPO_4$: 10% Nd^{3+}





Cross-relaxation spoils Boltzmann: faster depopulation of emitting levels makes that non-radiative rates coupling the two levels can no longer compete with population decay at RT → Boltzmann equilibrium requires higher T (> 500 K)

Performance of Thermometers

- Two figures of merit important: **Absolute sensitivity (thermal response) $S_a(T)$** and **relative sensitivity $S_r(T)$**:

$$S_a(T) = \left|\frac{dR}{dT}\right|$$

$$S_r(T) = \left|\frac{1}{R(T)}\frac{dR}{dT}\right| = \left|\frac{S_a(T)}{R(T)}\right|$$

- For applications, it is important to maximize the thermal response: **Small temperature changes** are supposed to give a **large response**!

- Boltzmann thermometer:

$$S_r(T) = \frac{\Delta E_{21}}{k_B T^2}$$

Performance two-level Boltzmann thermometer:
Trade-off between normalized thermal response $\rho(r)$ (blue) and thermal sensitivity $\sigma(r)$ (red)

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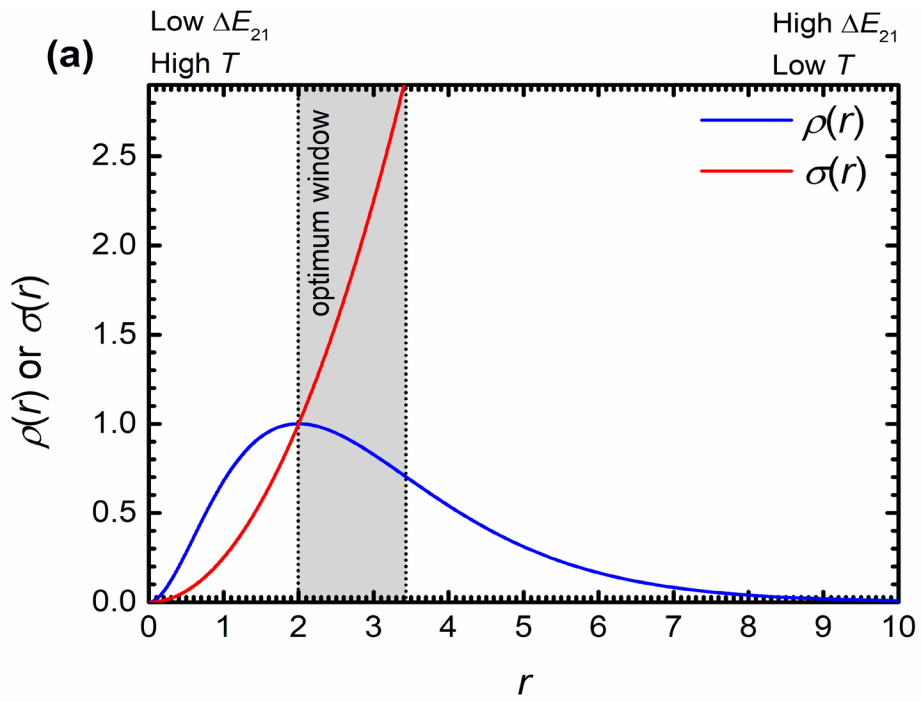
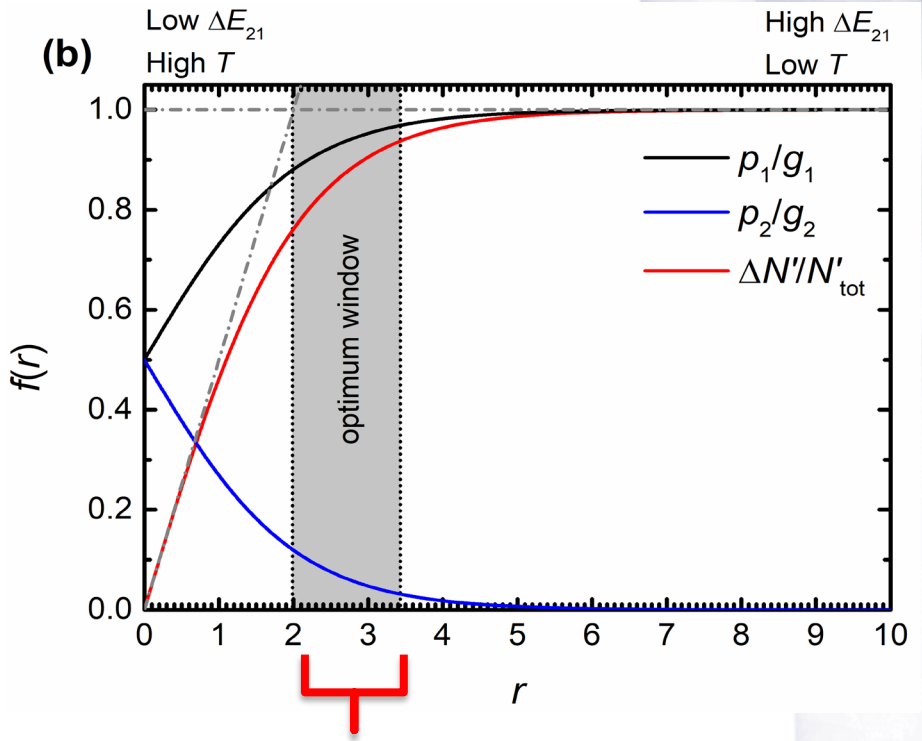




Scaling to $r = \beta\Delta E_{21} = \frac{\Delta E_{21}}{k_B T}$

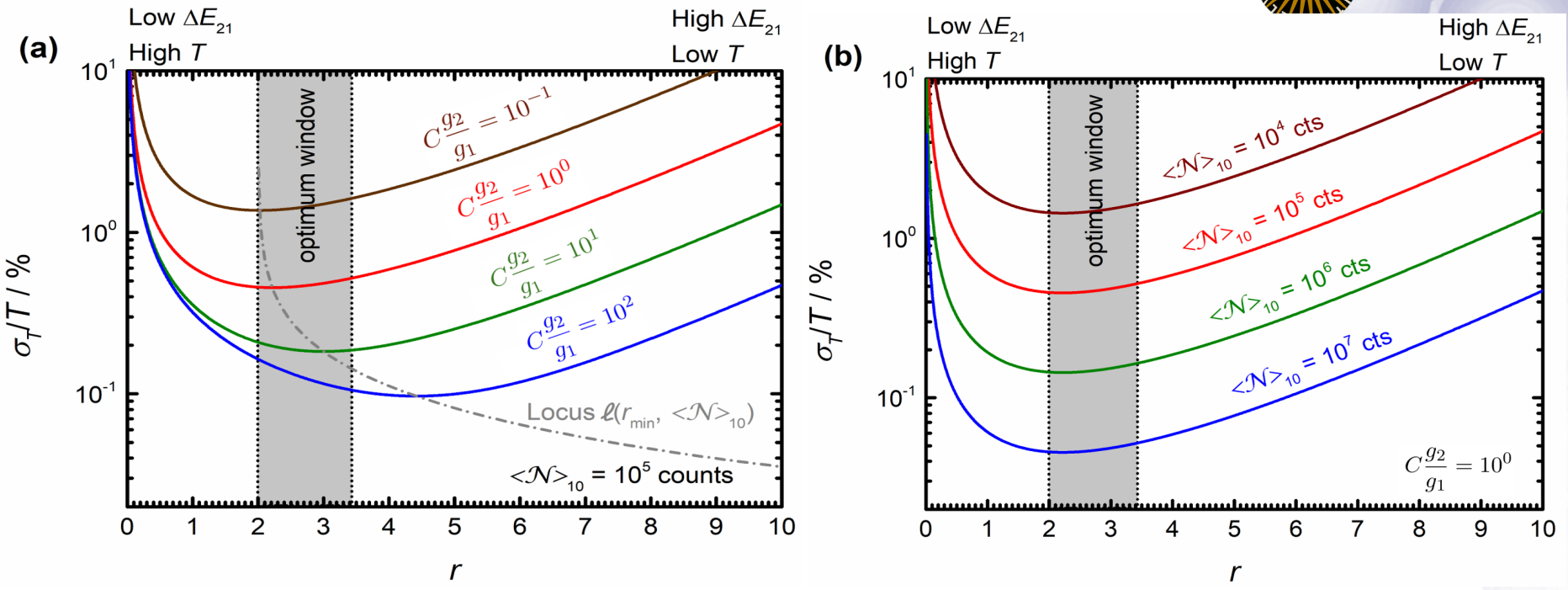
Optimum performance between:

$r = 2$ and $2 + \sqrt{2} \approx 3.41$

→ e.g. measurements between 300 and 350 K are best done with ΔE = 500 and 700 cm^{-1}

Large change in population with T, combined with significant population in 2 (p_2) to give sufficient emission from level 2 for good signal/noise ratio.

Relative temperature uncertainty



Evolution of the relative temperature uncertainty in relation to $r = \Delta E_{21}/k_B T$ with **(a)** varying pre-factor C (at a given $\langle\mathcal{N}\rangle_{10}$) or **(b)** count number of the lower energetic emission (at a given C).

Performance depends on C, on total signal but also note that performance drops off fast outside the optimum window: **single-ion two-level thermometers only work well in a limited temperature range!** (note log-scale y-axis)

Interested in more theory on single-ion two-level thermometers?

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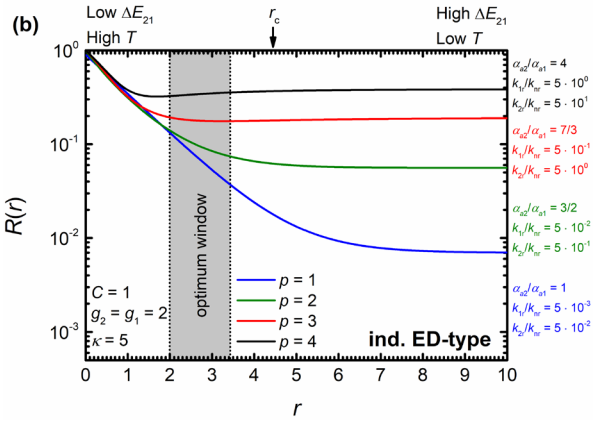
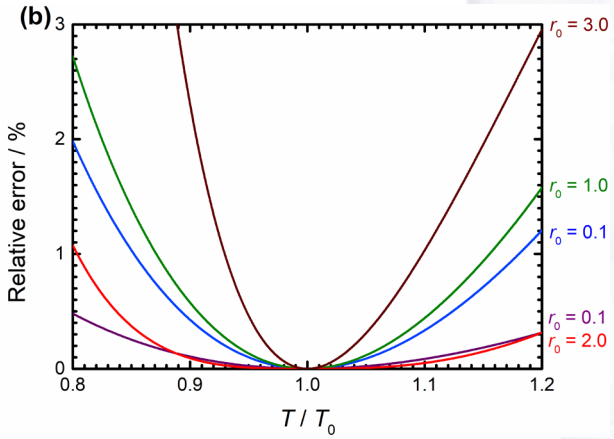
A theoretical framework for ratiometric single ion luminescent thermometers – Thermodynamic and kinetic guidelines for optimized performance

Markus Suta and Andries Meijerink,*
Advanced Theory and Simulations, almost accepted

$$R(T) = C\frac{g_2}{g_1}\frac{\alpha_{a2}}{\alpha_{a1}}\frac{\frac{\beta_{20}}{\beta_{10}C}\left(\frac{1}{\phi_1(0)}-1\right)[1+\kappa(2\langle n_{\mathrm{eff}}\rangle+1)]+\left(1+\frac{\alpha_{a1}}{\alpha_{a2}}\right)\langle n_{\mathrm{eff}}\rangle^p}{\left(\frac{1}{\phi_1(0)}-1\right)[1+\kappa(2\langle n_{\mathrm{eff}}\rangle+1)]+\left(1+\frac{\alpha_{a2}}{\alpha_{a1}}\right)(1+\langle n_{\mathrm{eff}}\rangle)^p}$$





$$\lim_{T\to 0} R(T) = \lim_{r\to\infty} R(r) = \frac{g_2\beta_{20}}{g_1\beta_{10}}\cdot\frac{\alpha_{a2}}{\alpha_{a1}}\cdot\frac{\left(\frac{1}{\phi_1(0)}-1\right)(1+\kappa)}{\left(\frac{1}{\phi_1(0)}-1\right)(1+\kappa)+\left(1+\frac{\alpha_{a2}}{\alpha_{a1}}\right)} := R(0$$

72 pages, 75 equations, 12 figures + SI

Everything you need to know about single-ion luminescence thermometry!

(+ Webinar Markus Suta later in this Webinar series)

Alternative: **Energy transfer thermometry**

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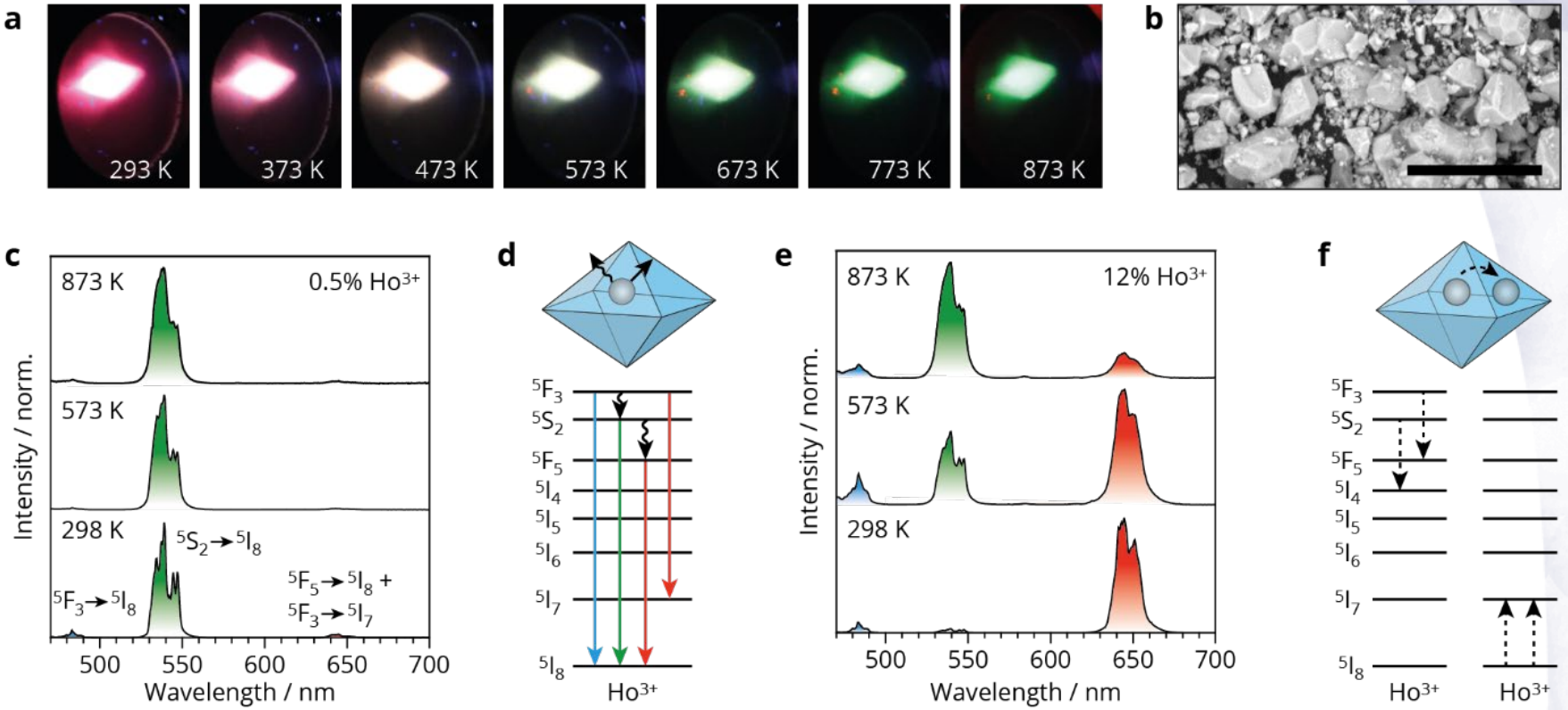
Sustain high performance over wider temperature range



$Na(Y,Gd)F_4:Ho^{3+}$ x%: Competition between cross-relaxation ET (dependent on Ho-concentration) and multi-phonon relaxation (dependent on temperature) → Optimize temperature accuracy for temperature window through concentration.

Thomas P. van Swieten, Dechao Yu, Ting Yu, Sander J.W. Vonk, Markus Suta, Qinyuan Zhang, Andries Meijerink, Freddy T. Rabouw, Adv. Opt. Mater., under review

Deep fundamental understanding by modelling

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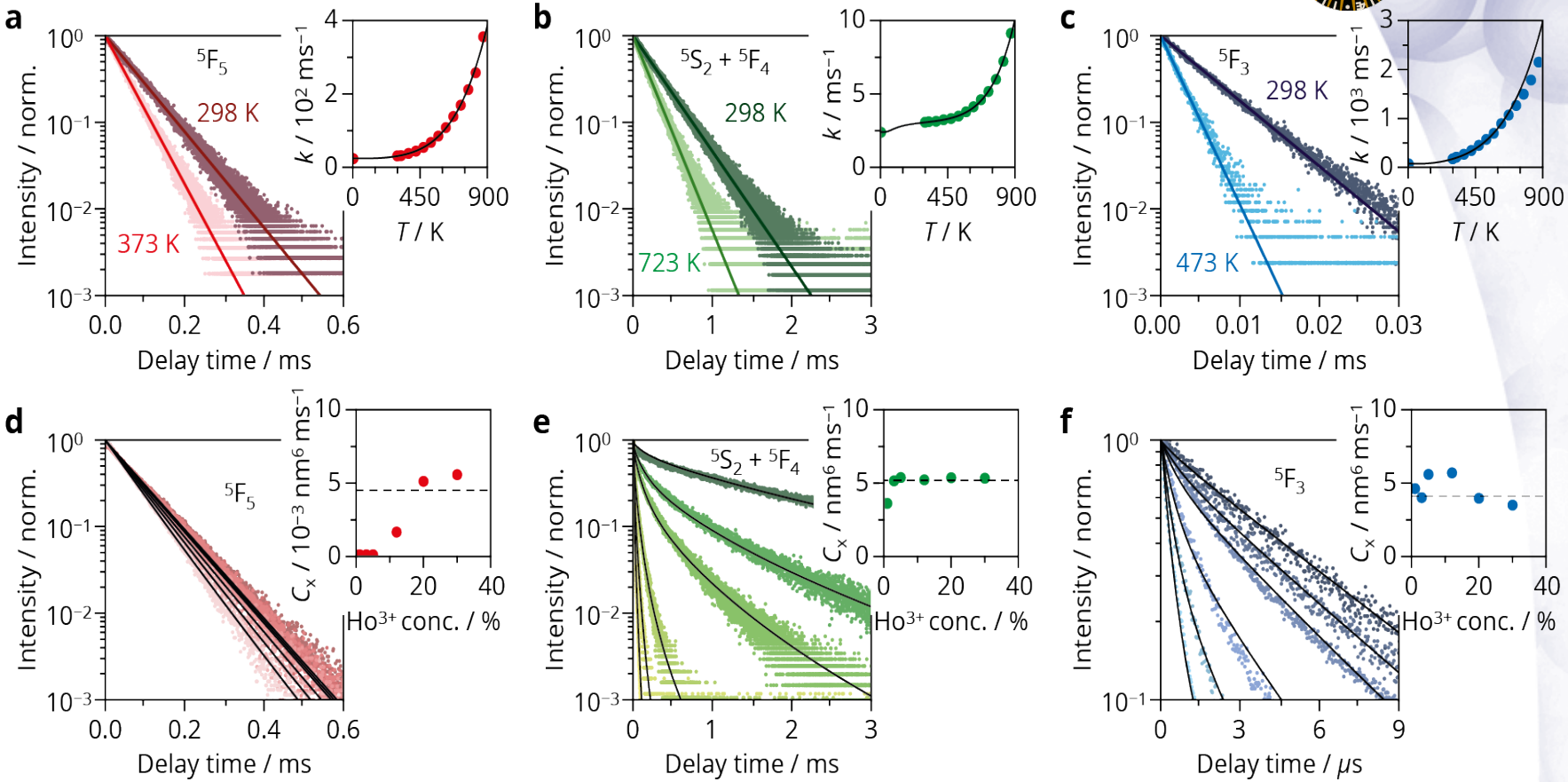
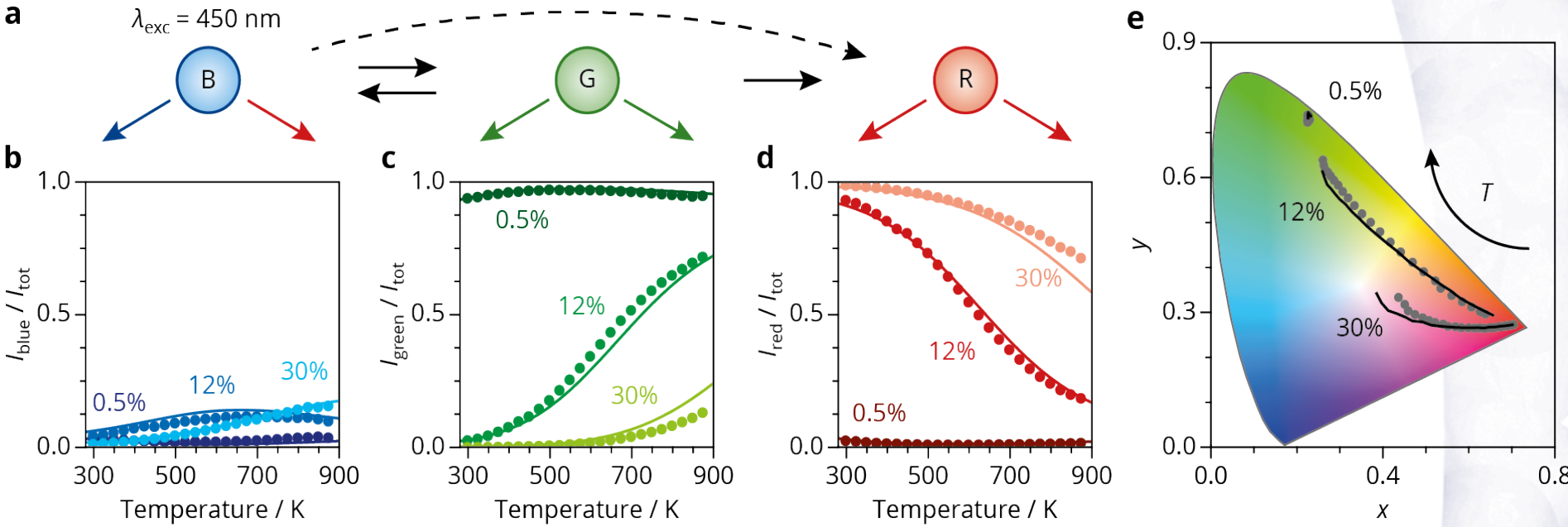


Top figures: quantitative understanding of temperature dependence multi-phonon relaxation → single fitting parameter for blue, green and red level

Bottom figures: quantitative understanding of cross-relaxation by fitting luminescence decay curves with shell-model → single CR parameter for each level

With parameters complete and accurate understanding/prediction of variation relative intensities blue, green and red emission for **all** Ho-concentrations at **all** temperatures.



Thomas P. van Swieten, Dechao Yu, Ting Yu, Sander J.W. Vonk, Markus Suta, Qinyuan Zhang, Andries Meijerink, Freddy T. Rabouw, Adv. Opt. Mater., under review

Energy transfer thermometry offers more flexibility and options to extend high performance over a wider range

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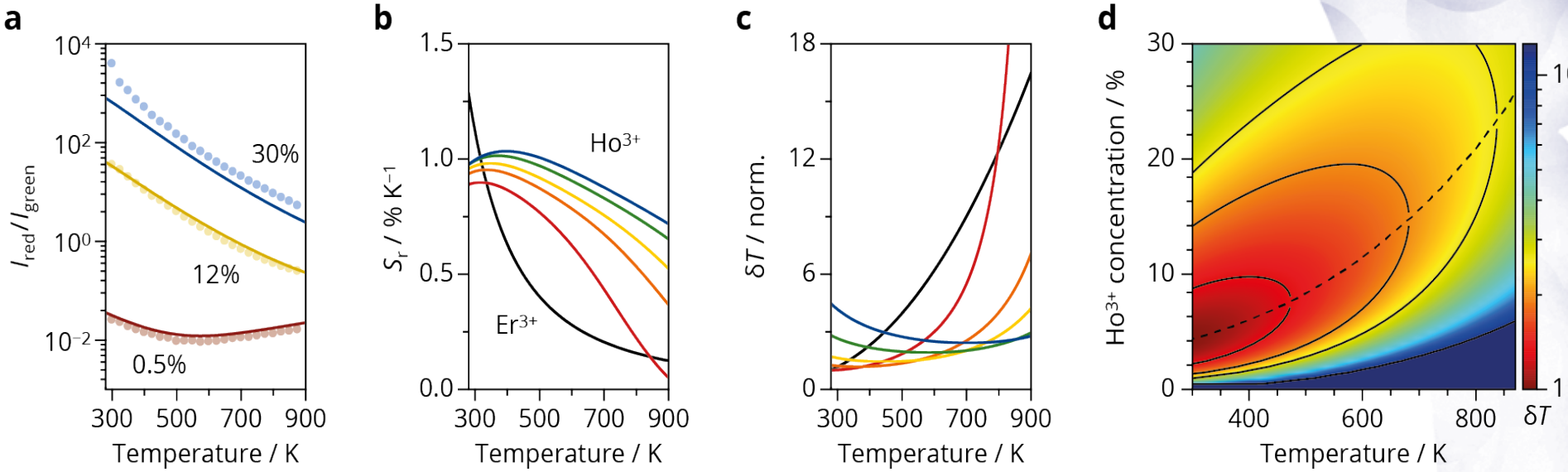


(b) Calculated relative sensitivities for a Ho^{3+} concentration of 4% (red), 8% (orange), 12% (yellow), 20% (green), and 30% (blue), as a function of temperature. The black solid line is the relative sensitivity of the $^4S_{3/2}$ and $^2H_{11/2}$ levels of Er^{3+} ions in the β-$NaYF_4$ host. (c) Calculated temperature uncertainties (δT). The same colour scheme applies as in (b).

Contents

- Introduction Lanthanides
  - Energy Levels
  - Radiative decay
  - Non-radiative decay
  - Energy transfer
- Luminescence Thermometry
  - Boltzmann – 'Single ion-Two level' systems
  - Pittfalls - non-Boltzmann, Sensitivity
  - Energy transfer thermometry
- Nano-thermometry
  - What's different? Why useful?
  - Applications/'Illustrative' examples
- Conclusions/Outlook

What's different? Why useful?

Microcrystalline	vs.	Nanocrystalline
- Easy synthesis (shake and bake) - High quantum yield (no high energy vibrations of ligands, less defects) - More reproducible, better control over lanthanide doping, easier characterization		- Complex synthesis (glove box/ Schlenk line - Lower quantum yield (high energy C-H and O-H of solvent/capping ligands quench luminescence) - Issues with reproducibility, characterization requires more advanced techniques (e.g. TEM, synchrotron)

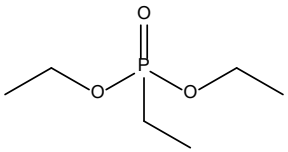
If you can do it with microcrystalline, don't bother with nano!

O. Lehmann *et al., J. Phys. Chem.*, **107**, 7449-7453 (2003);
A. Oertel *et al., Chem. Mater.*, **21**, 3883-3888 (2009)

More complex synthesis: e.g.$LaPO_4:Ce^{3+},Tb^{3+}$

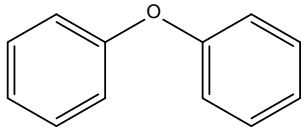
$LaCl_3 \cdot 6H_2O$
$CeCl_3$

MeOH



Vacuum

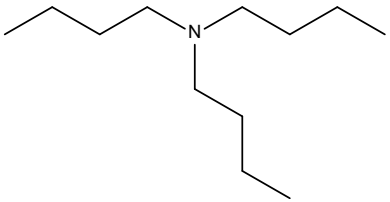
MeOH



Vacuum
25-105 °C

H_2O

1.



2. 2M H_3PO_4/ Dihexylether

200 °C / N_2
18 hours

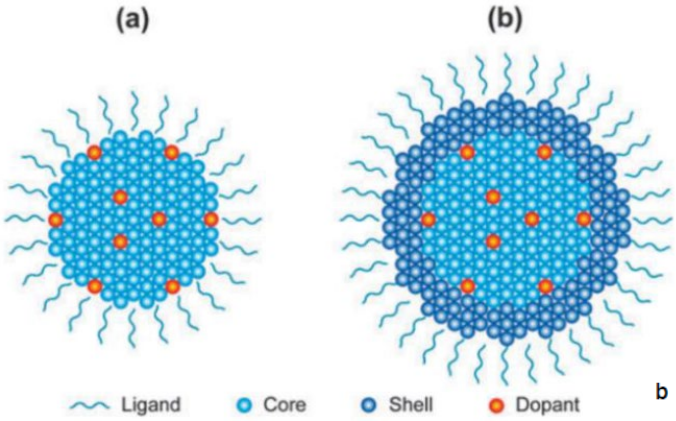
1. Centrifugation
2. Toluene + centrifugation
3. Dry under vacuum

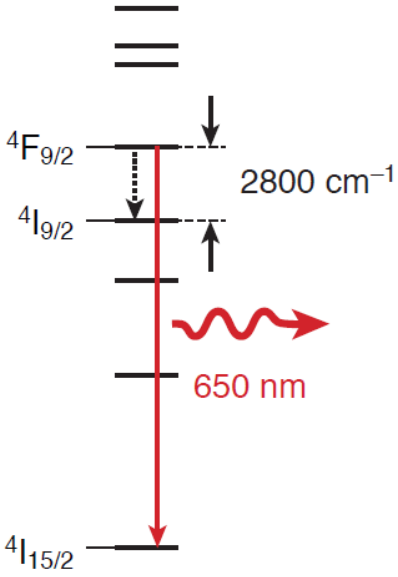
White powder

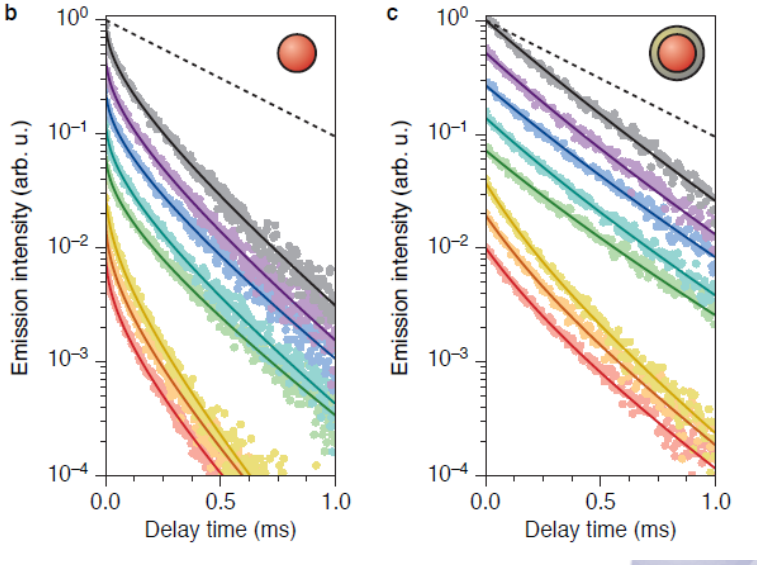
R = 2nm particles

Lower quantum yield

Quenching of emission by multi- or single-phonon relaxation from solvent vibrations and ligand vibrations







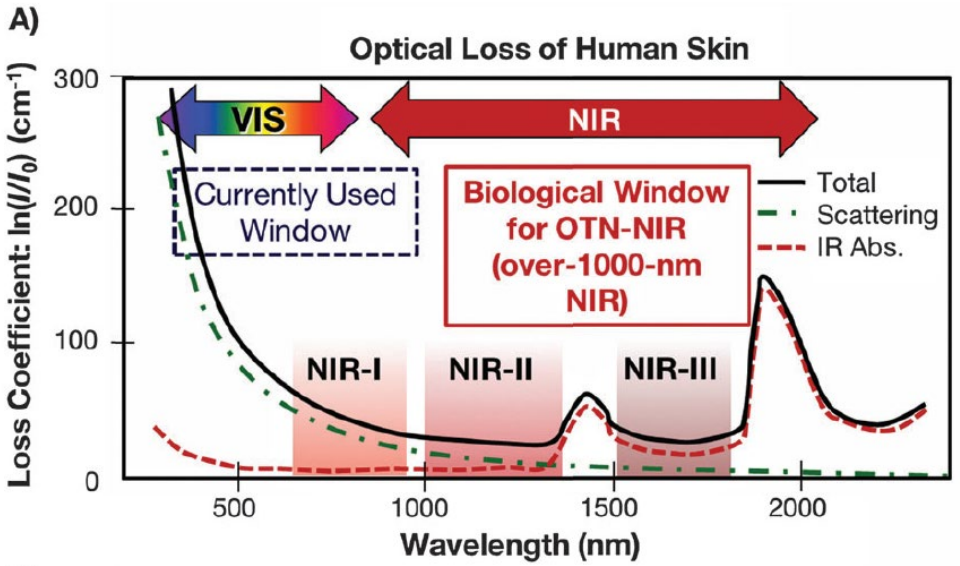
F. T. Rabouw, P. T. Prins, P. Villanueva-Delgado, M. Castelijns, R. G. Geitenbeek, A. Meijerink, *ACS Nano* **2018**, *12*, 4812.

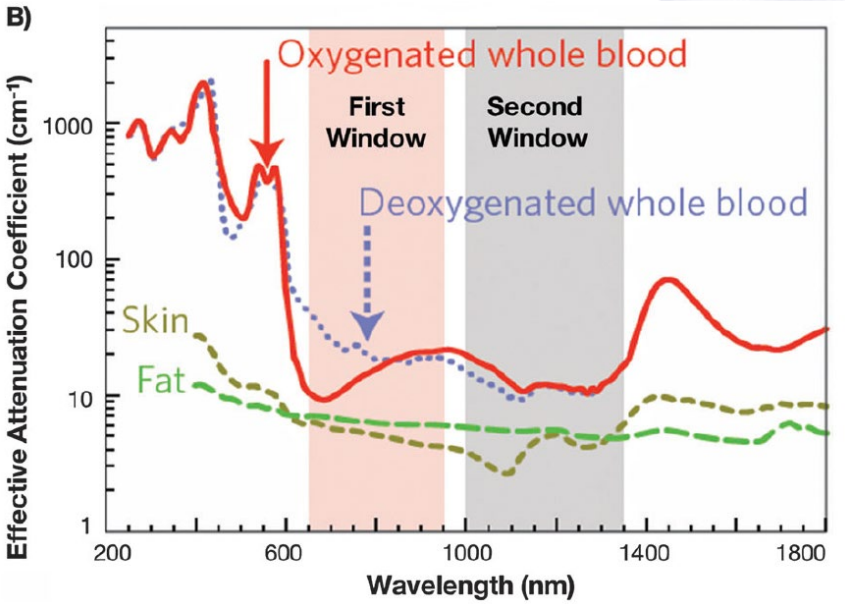
What's different? Why useful?

Microcrystalline	vs.	Nanocrystalline
- They are BIG		- They are small, similar in size to biomolecules - No light scattering - Stable colloidal solutions possible

If you need to probe processes/temperatures on the micrometer/ nanometer scale, if you need to probe inside cells, map temperature profiles with high spatial resolution, study dynamic processes in solutions: nanocrystals are your choice!

Luminescence thermometry for *in vivo* imaging





Extensive research in biological systems – Near Infrared preferred because of superior penetration depth. Biological windows NIR-I, II and III are explored for lanthanide luminescence thermometry.

A. M. Smith, M. C. Mancini, S. Nie, *Nat. Nanotechnol.* **2009**, *4*, 710 – 711.
E. Hemmer, A. Benayas, F. Légaré, F. Vetrone, *Nanoscale Horiz.* **2016**, *1*, 168 – 184.

Today three other/new examples:

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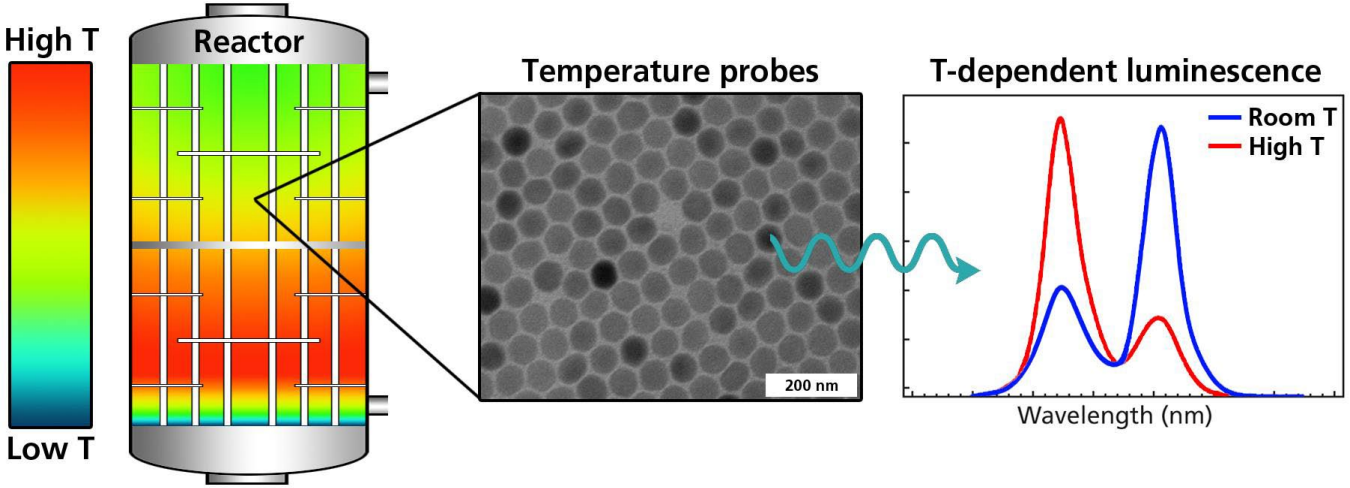
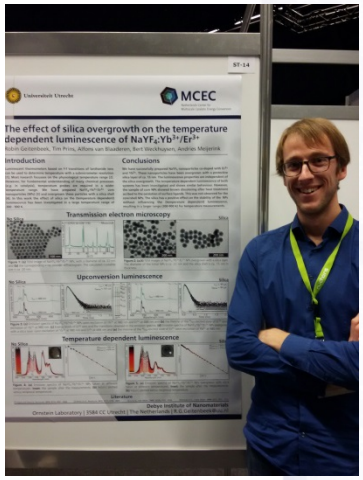
- High temperature probes for catalysis
- Measuring temperatures in microfluidic systems
- Mapping temperature distributions in micro-electronics

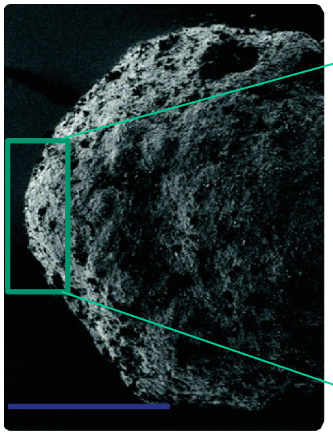


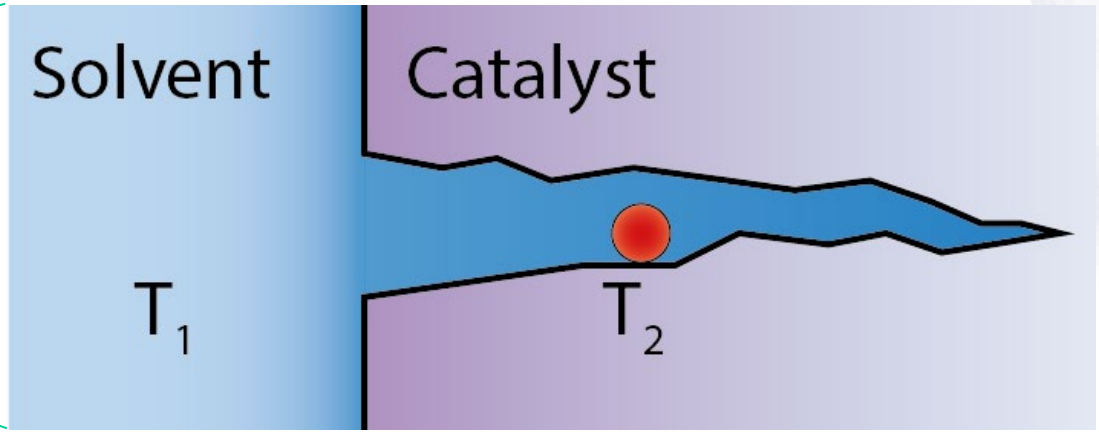


Sponsored by MCEC Gravity programme, with Robin Geitenbeek and Thomas van Swieten in cooperation with the groups of prof. Weckhuysen, prof. Van Blaaderen and prof. van de Berg)

Temperature nanoprobes for Catalysis

High T sensing, e.g. useful in catalysis to measure local temperatures at active sites and inside the reactor (instead of the reactor surface)





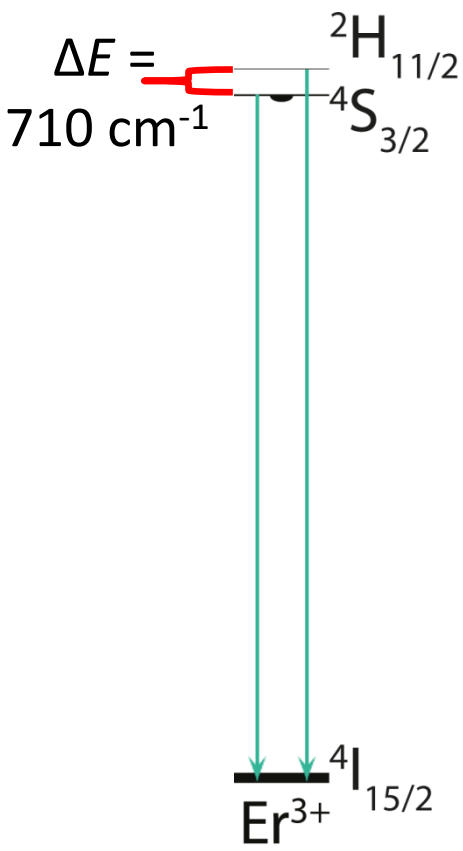
Scalebar corresponds to 40 µm

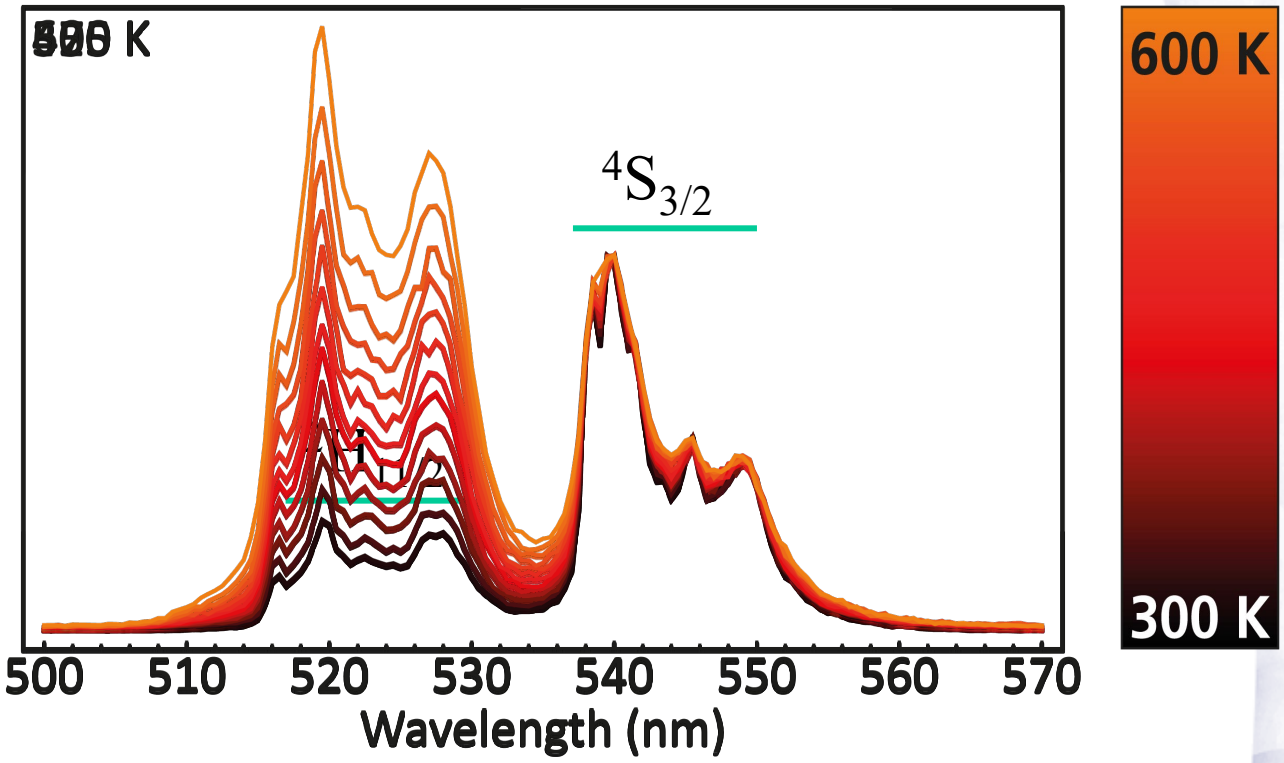
Non invasive

High resolution

Higher temperatures (400-800 °C)

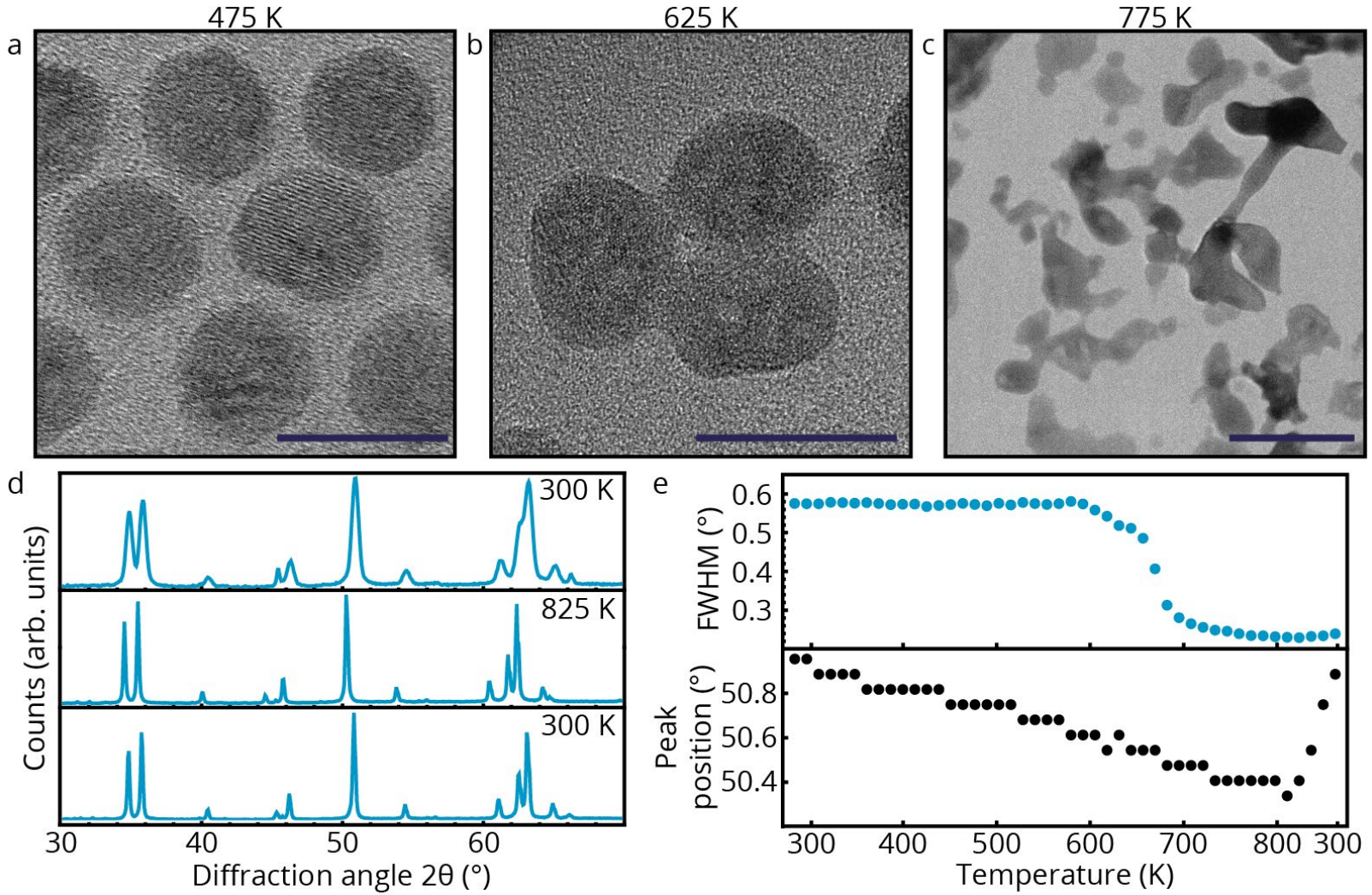
Temperature-dependent luminescence $NaYF_4$:Yb18%,Er2%





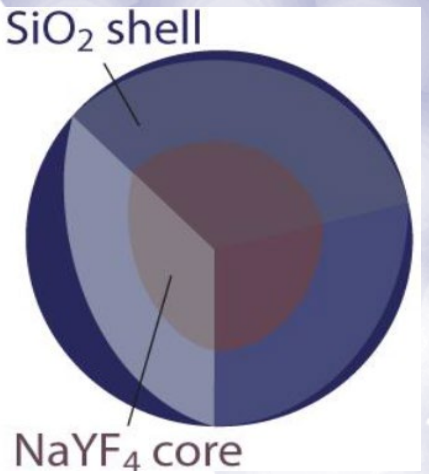
R. G. Geitenbeek, P. T. Prins, W. Albrecht, A. van Blaaderen, B. M. Weckhuysen, A. Meijerink, *J. Phys. Chem. C* **2017**, *121*, 3503.

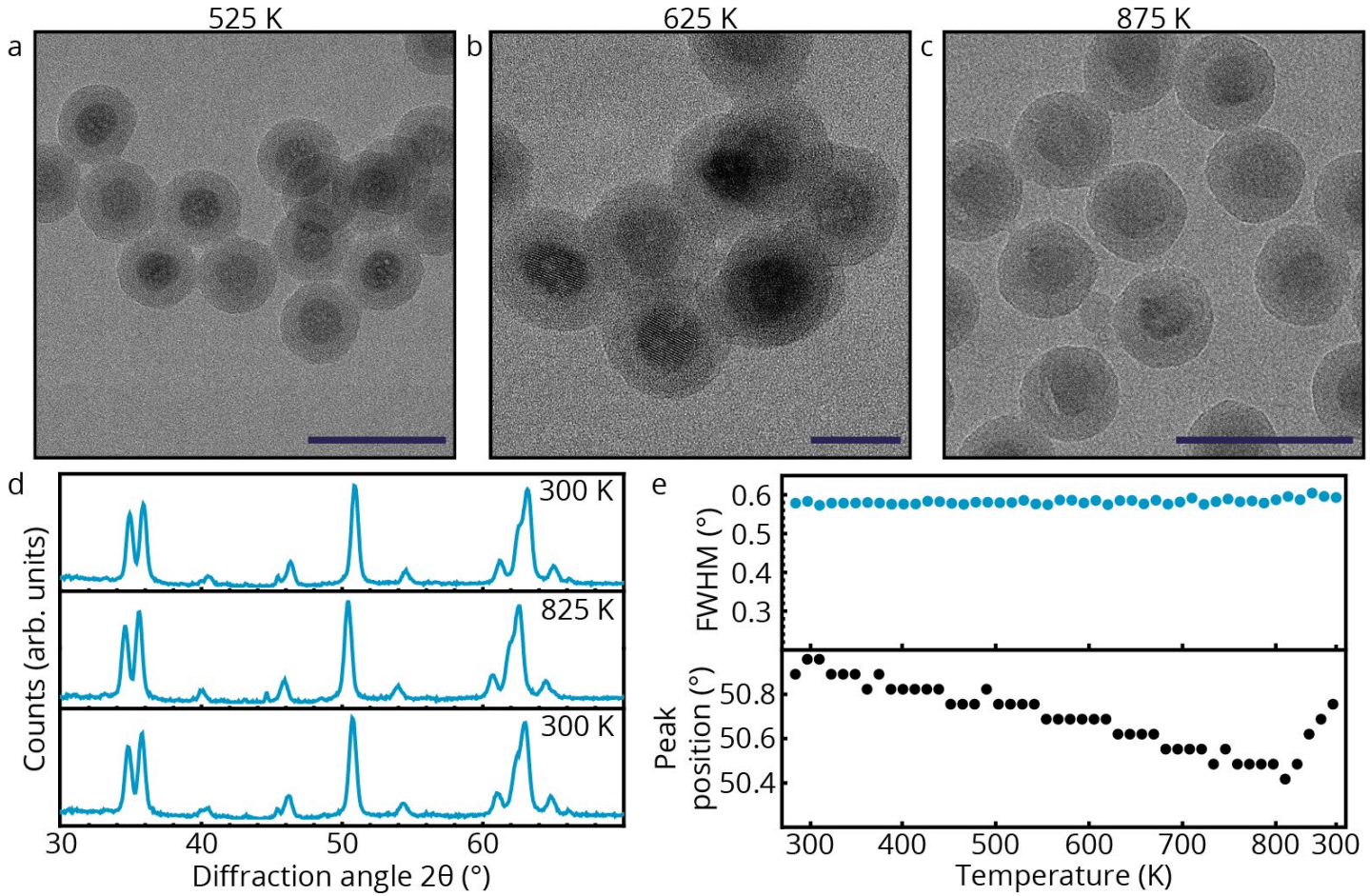
Temperature stability – not stable above 600 K



Scalebars correspond to 20 nm, 20 nm and 200 nm, respectively.

Solution: protective SiO_2 shell





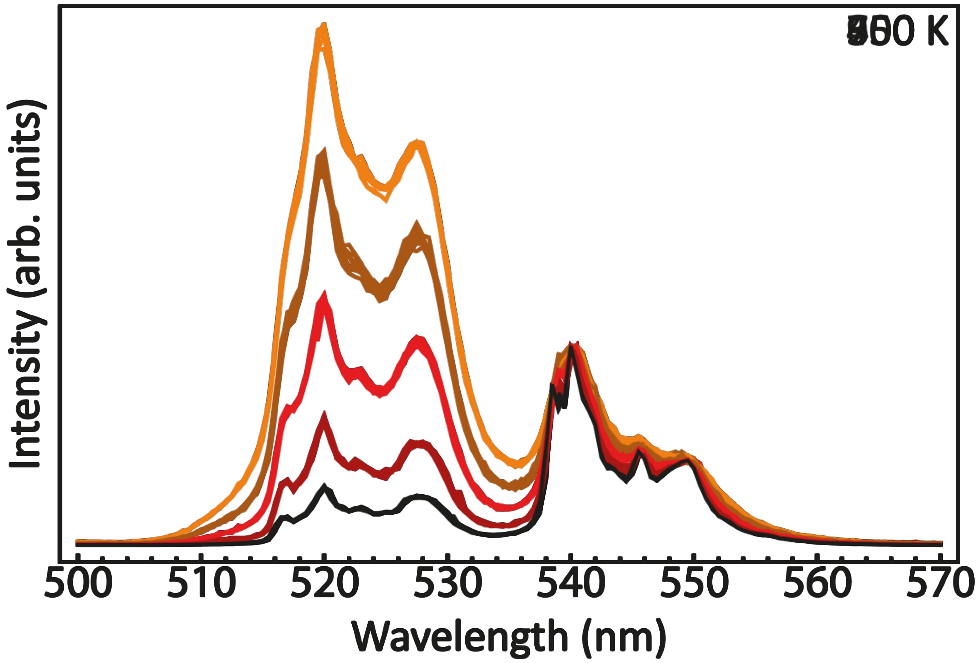
High temperature stability up to at least 900 K

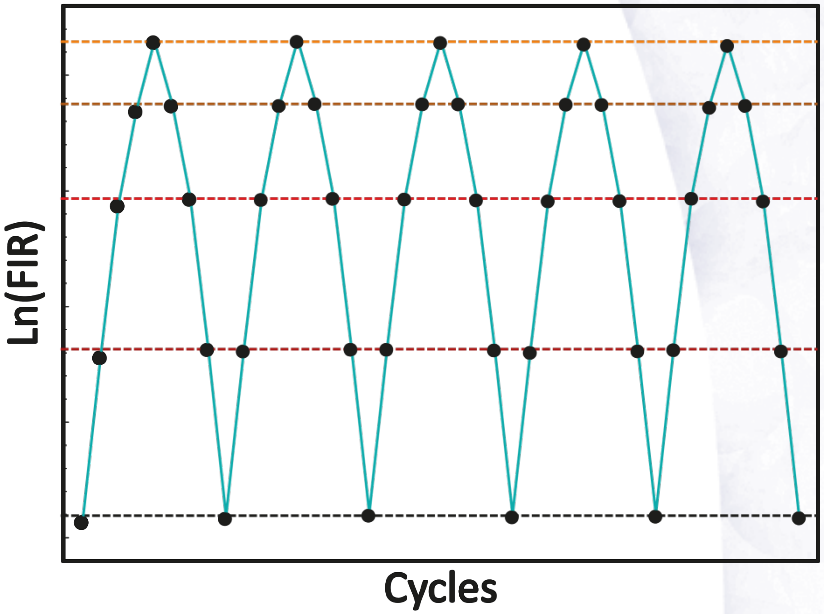
R. G. Geitenbeek, P. T. Prins, W. Albrecht, A. van Blaaderen, B. M. Weckhuysen, A. Meijerink, *J. Phys. Chem. C* **2017**, *121*, 3503.

Cycling experiments

Universiteit Utrecht

Stable and reproducible through many temperature cycles



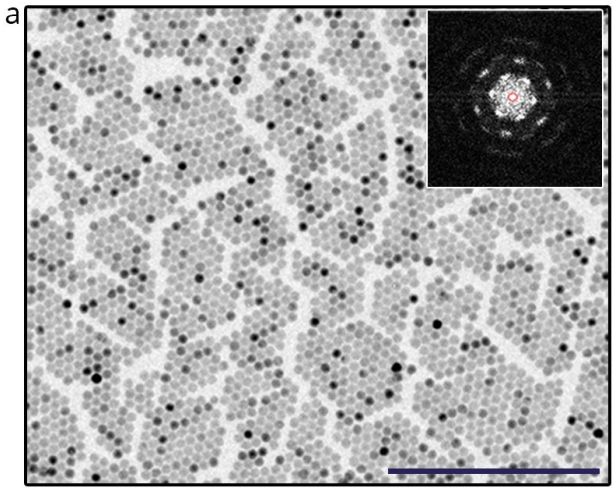


$NaYF_4$@SiO_2 form temperature stable nanoprobes to 900 K and beyond → extend temperature range of nanothermometry and other remote sensing techniques with high resolution

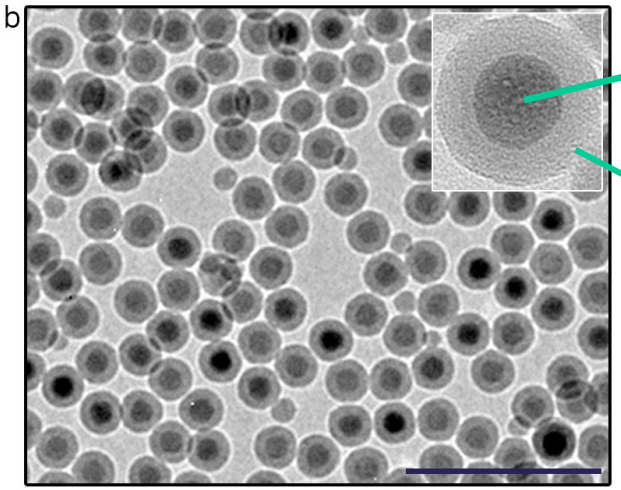
Catalytic reactions

Universiteit Utrecht

Core NPs



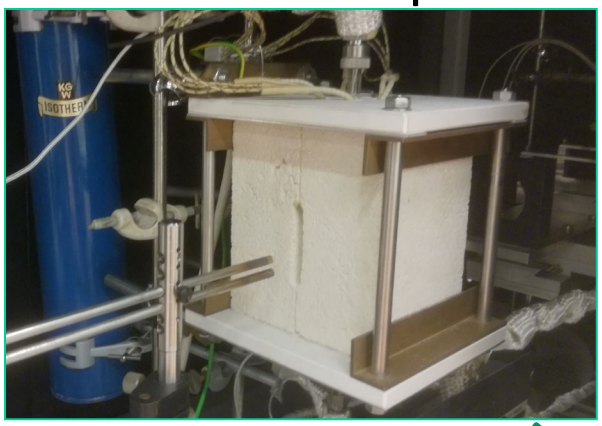
Core/Shell NPs



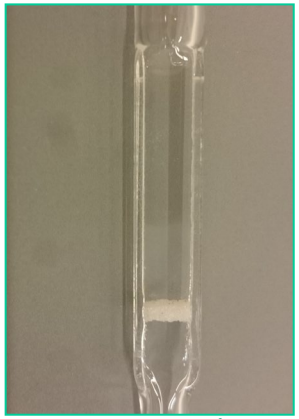
$NaYF_4:Er^{3+},Yb^3$

SiO_2

Final setup



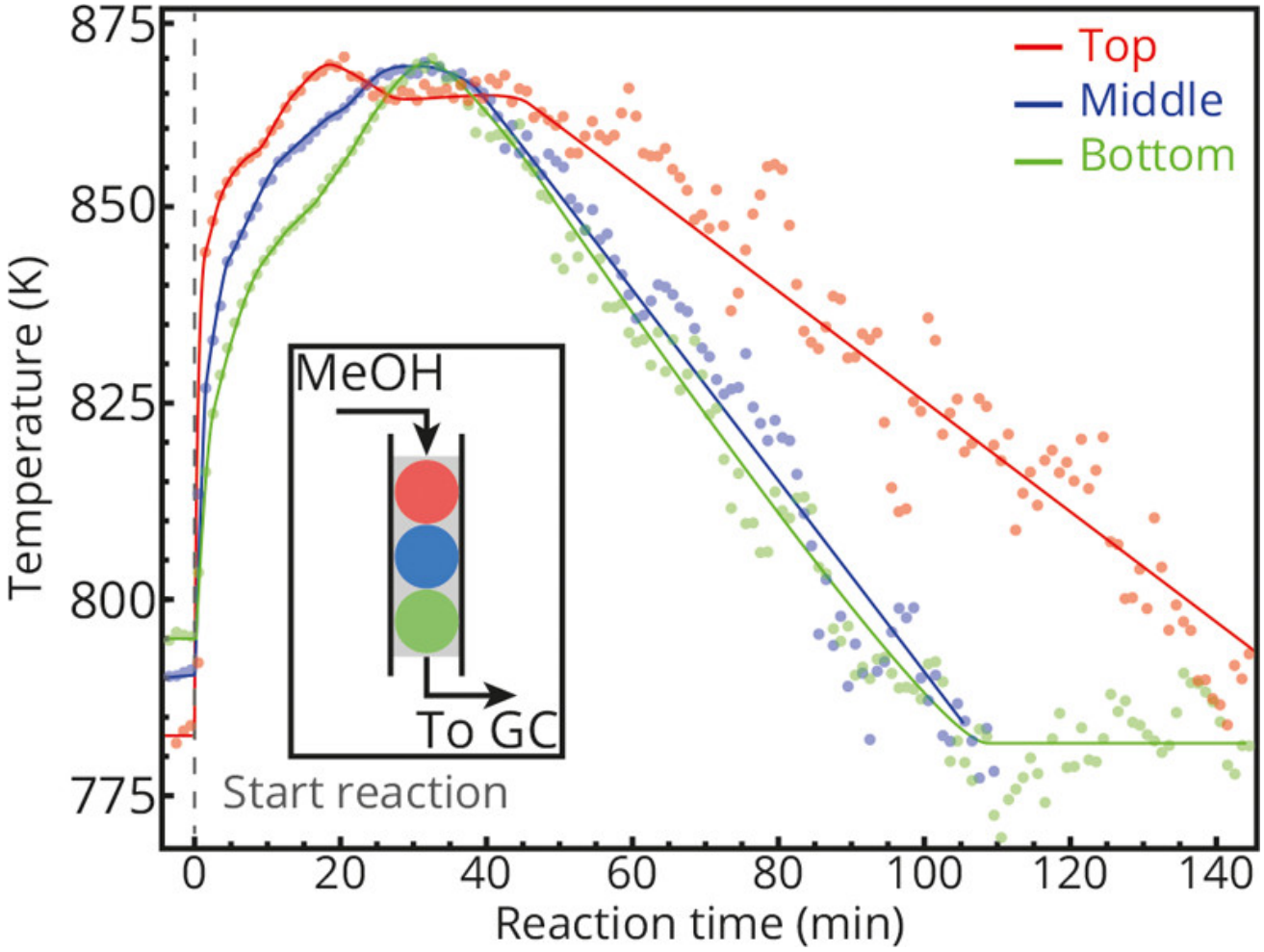
Quartz



Extrudates

Methanol to olefin reaction – follow T and reaction products as f(time)

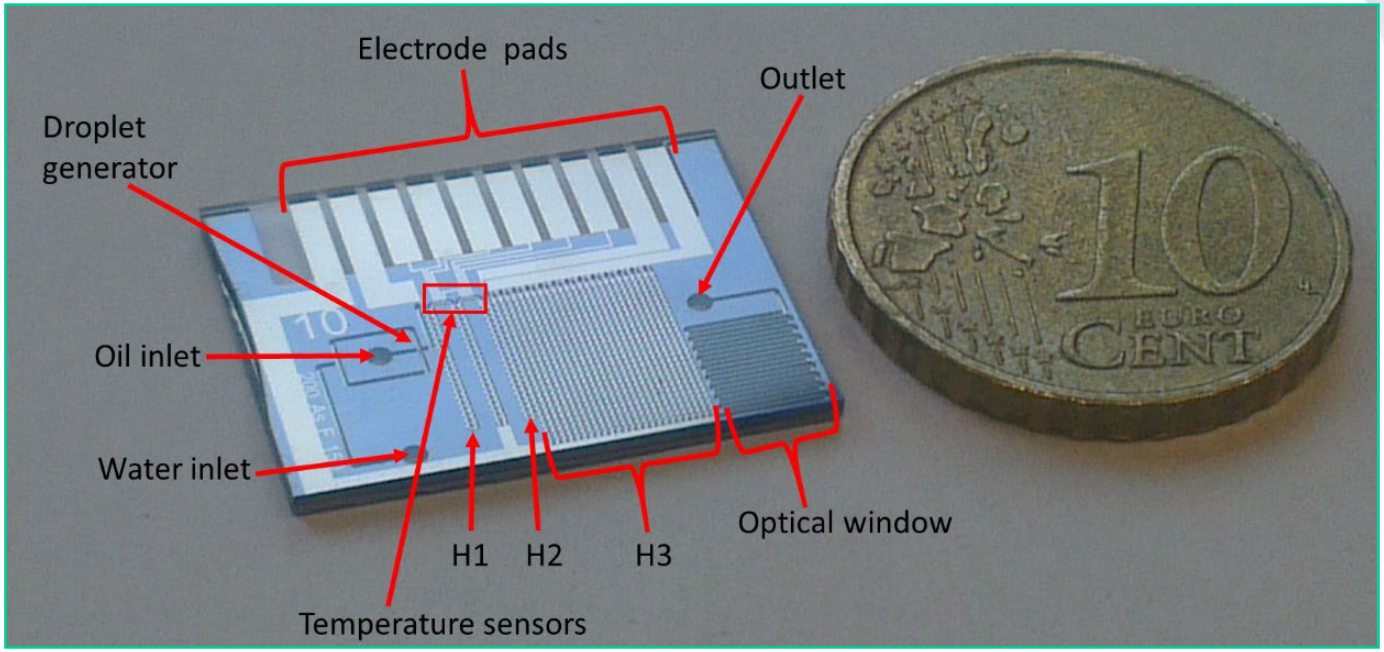
Universiteit Utrecht



R. G. Geitenbeek, B. B.V. Salzmann, A.-E. Nieuwelink, A. Meijerink, B. M. Weckhuysen, *Chem. Eng. Sci.* **2019**, *198*, 235.

R. G. Geitenbeek, A.-E. Nieuwelink, T. S. Jacobs, B. B. V. Salzmann, J. Goetze, A. Meijerink, B. M. Weckhuysen, *ACS Catal.* **2018**, *8*, 2397.

Microfluidics – high resolution T-sensing

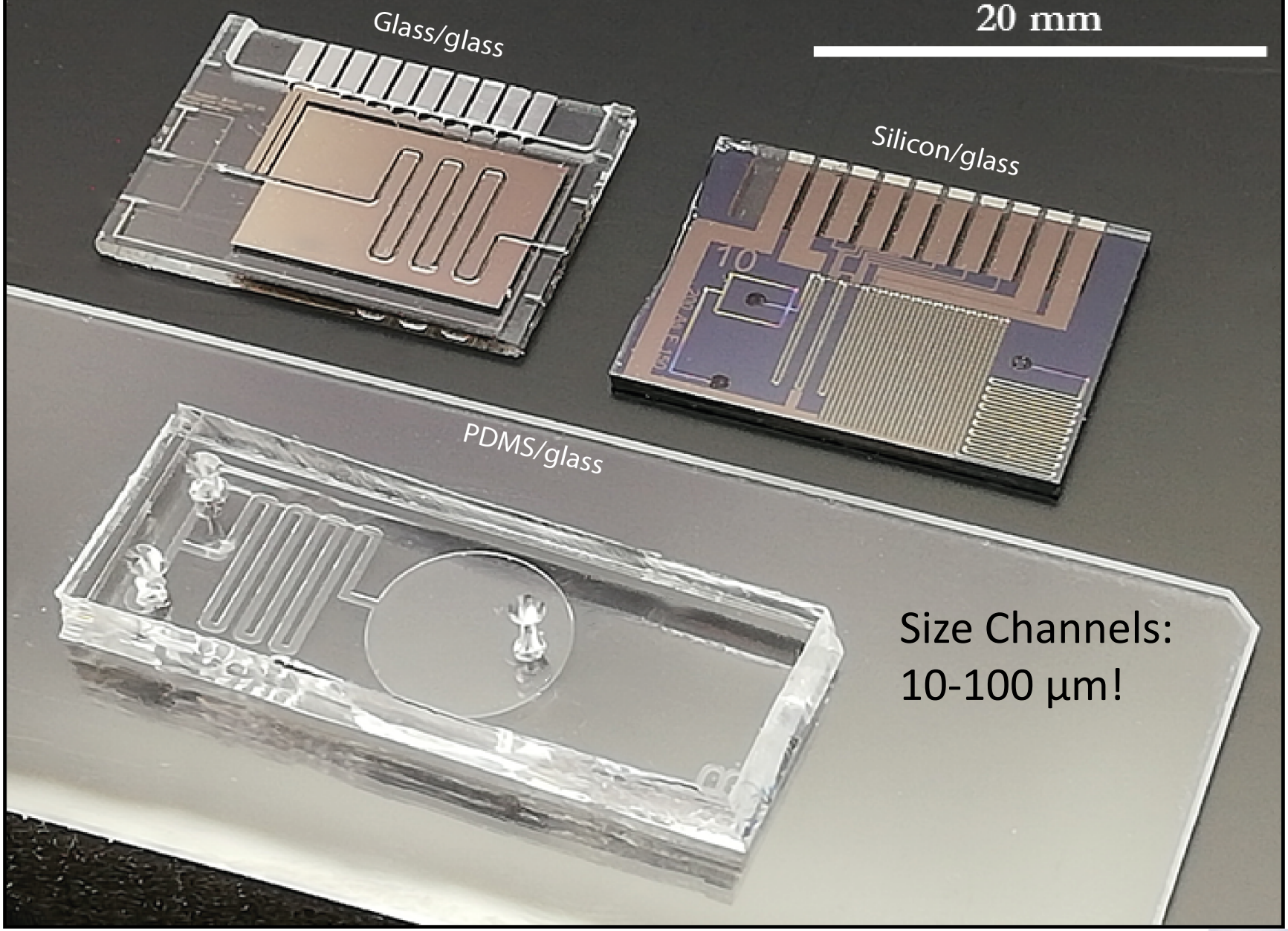


Built-in T-sensors Built-in heaters

Temperature variation in microfluidic reactor?

How to probe T inside microchannels?

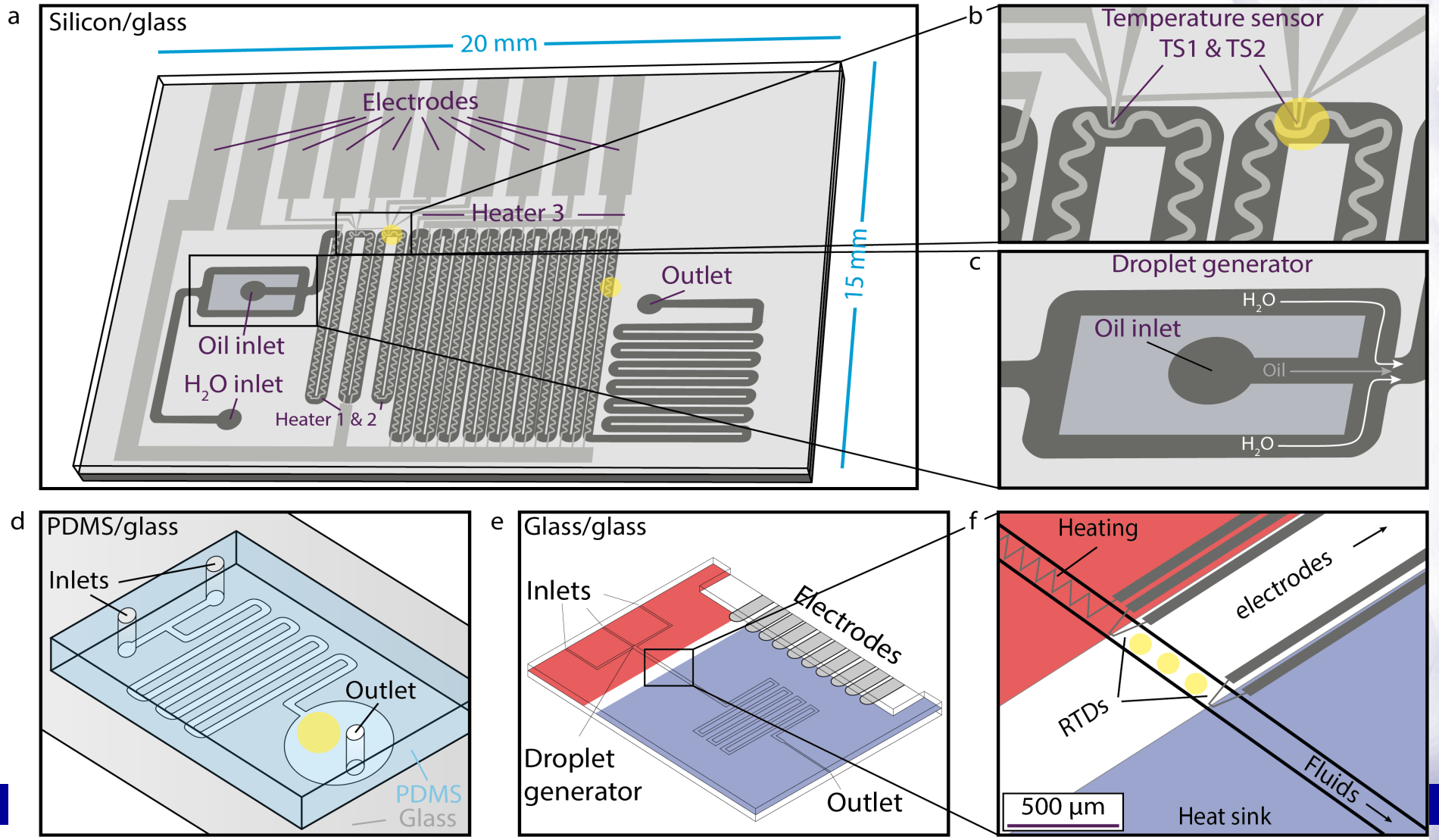
R. G. Geitenbeek, J. C. Vollenbroek, H. M. H. Weijgertze, C. B. M. Tregouet, A.-E. Nieuwelink, C. L. Kennedy, B. M. Weckhuysen, D. Lohse, A. van Blaaderen, A. van den Berg, M. Odijk, A. Meijerink, *Lab Chip* **2019**, *19*, 1236

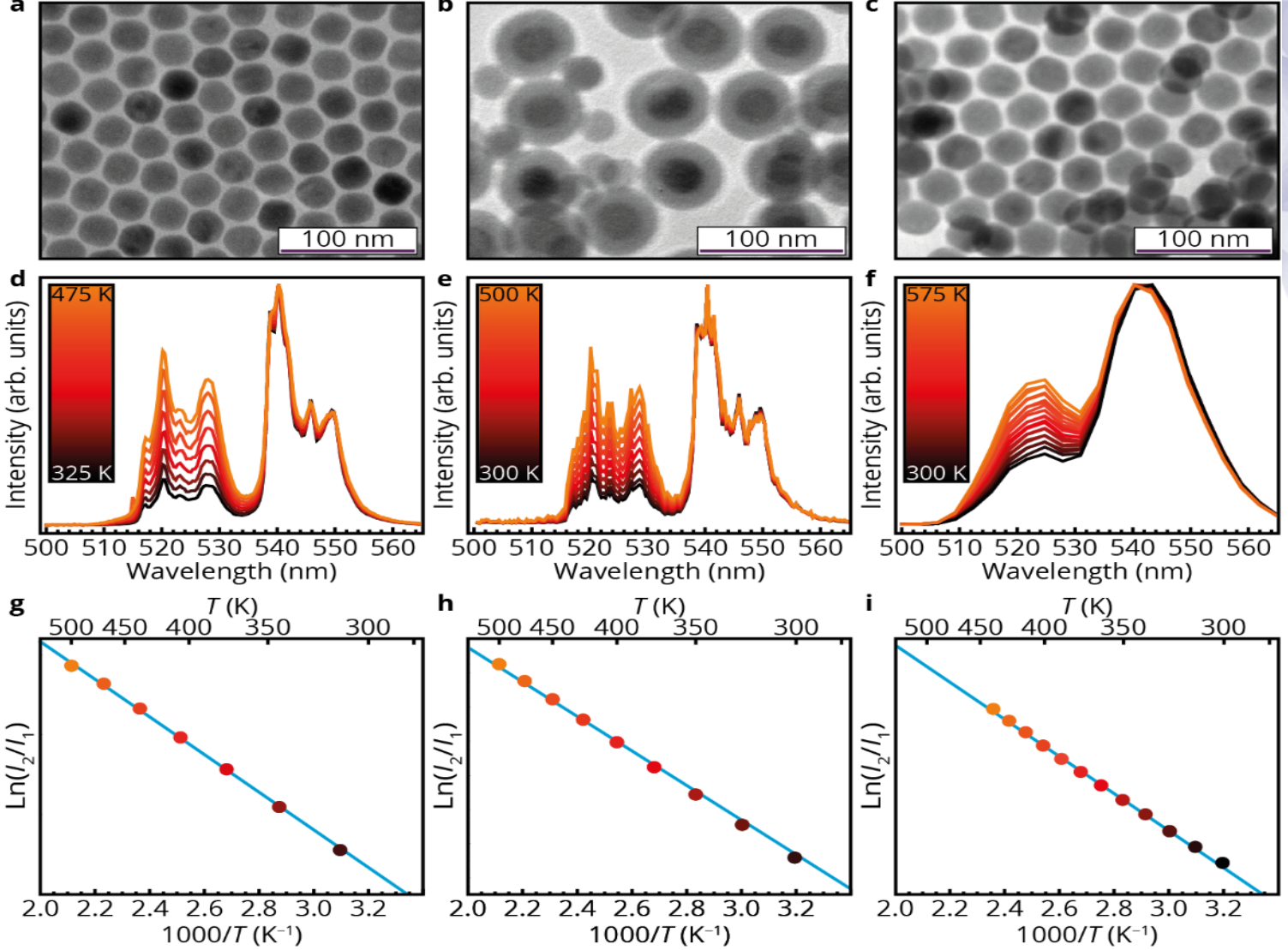


Three types of microfluidic devices to demonstrate T-sensing

Schematic T-sensing experiments in three microfluidic devices

Universiteit Utrecht



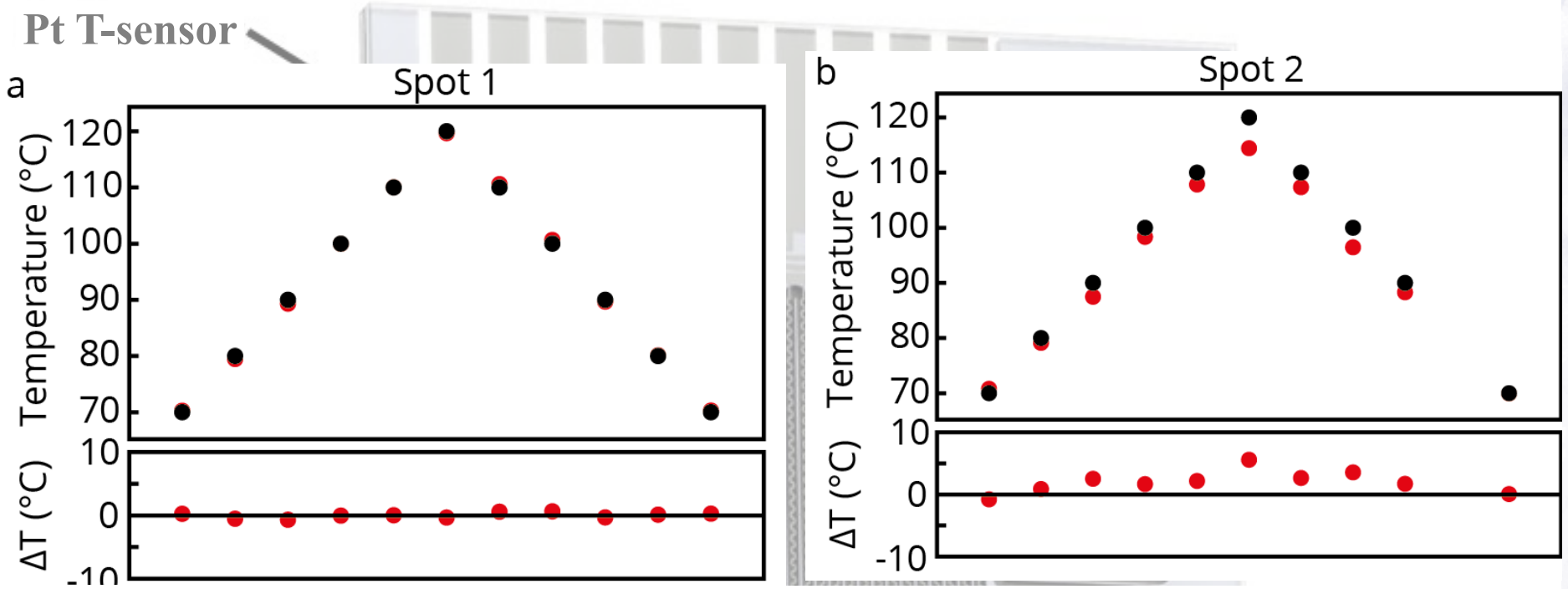


Measuring T in channel at two locations

Measuring T rise for reaction NH_3 and HCl

Measuring T-gradient with µm resolution

1. Microfluidics

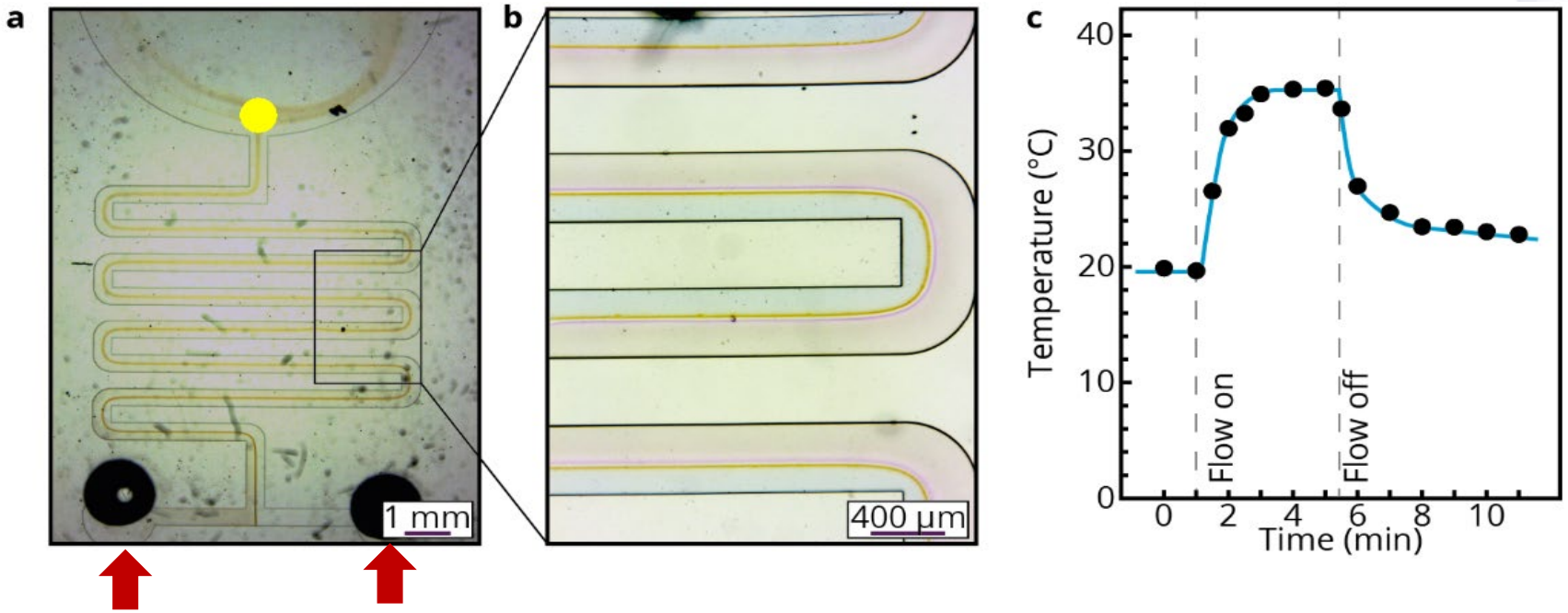


Average ΔT = 0.35 ˚C
T-sensor works fine!

Maximum ΔT = 5.6 ˚C
Insufficient at remote spots!

2. Chemical reaction

Reaction in microfluidic device between 5M NH_3 and 4 M HCl, both with $NaYF_4$:Yb,Er NCs capped with silica added:



Inlet HCl Inlet NH_3

- Rise in temperature can be measured in situ to be around 15 °C
- Exothermic reactions can cause deviation between temperature in channel and set temperature on chip.

3. Temperature gradient in microfluidic system (e.g. for polymerization reaction)

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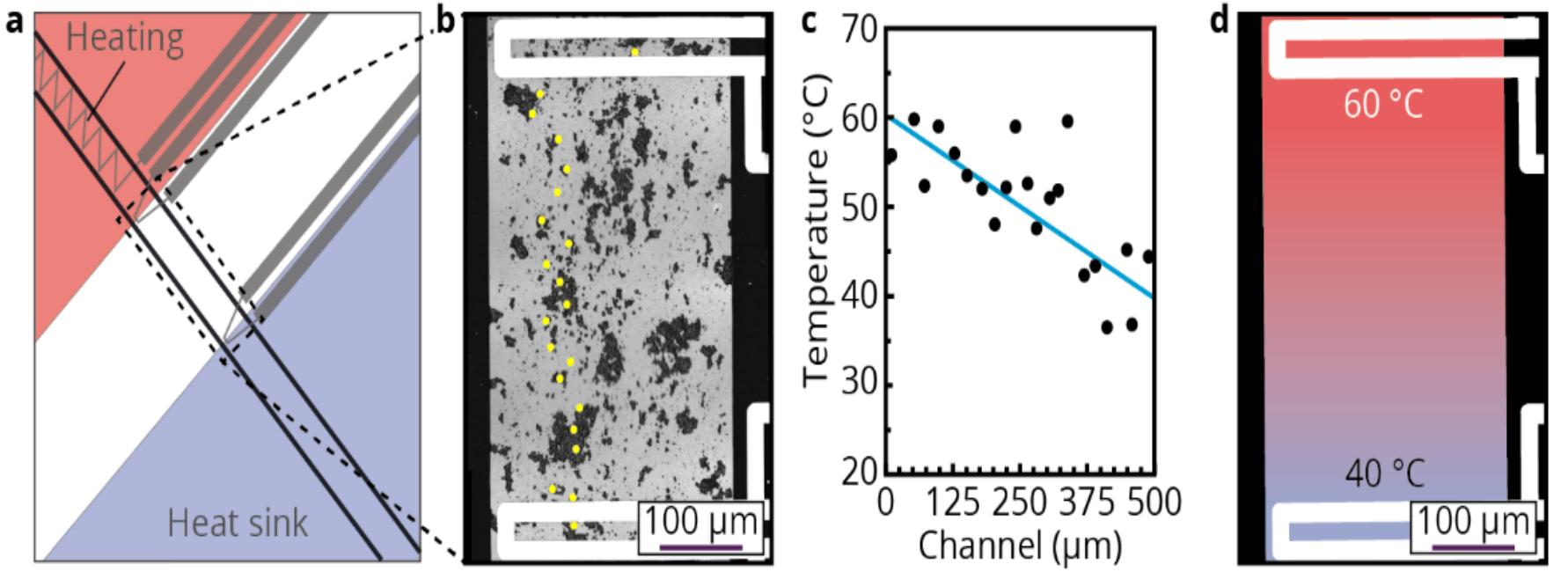

Flow of $NaYF_4$:Er,Yb NCs in hexane through microchannel over temperature gradient: high resolution mapping of T in channel, spatial resolution of 9 µm.

Outlook: brighter (larger) particles and higher detection efficiency will give **resolution below 1 µm**.

Temperature mapping in microheaters

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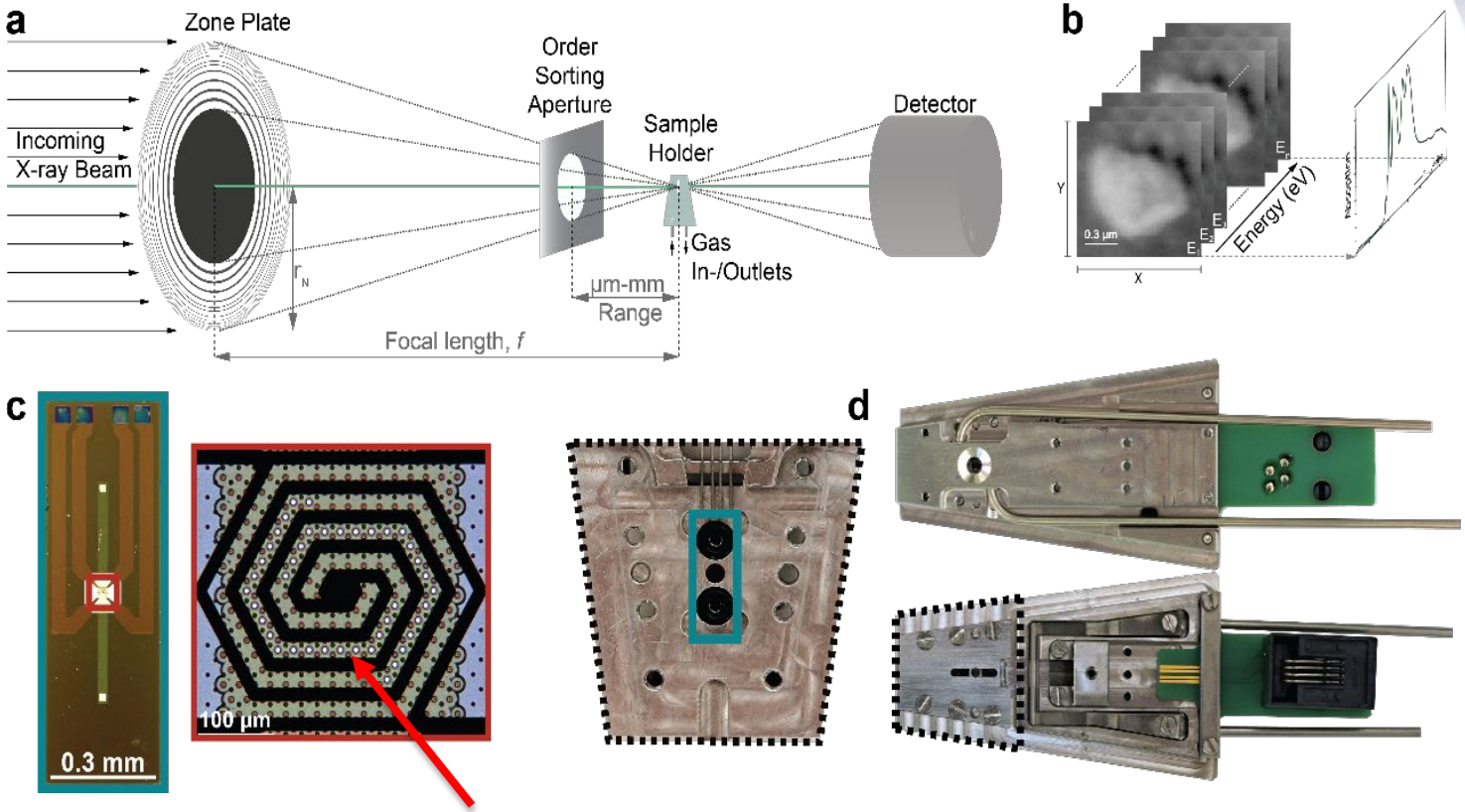
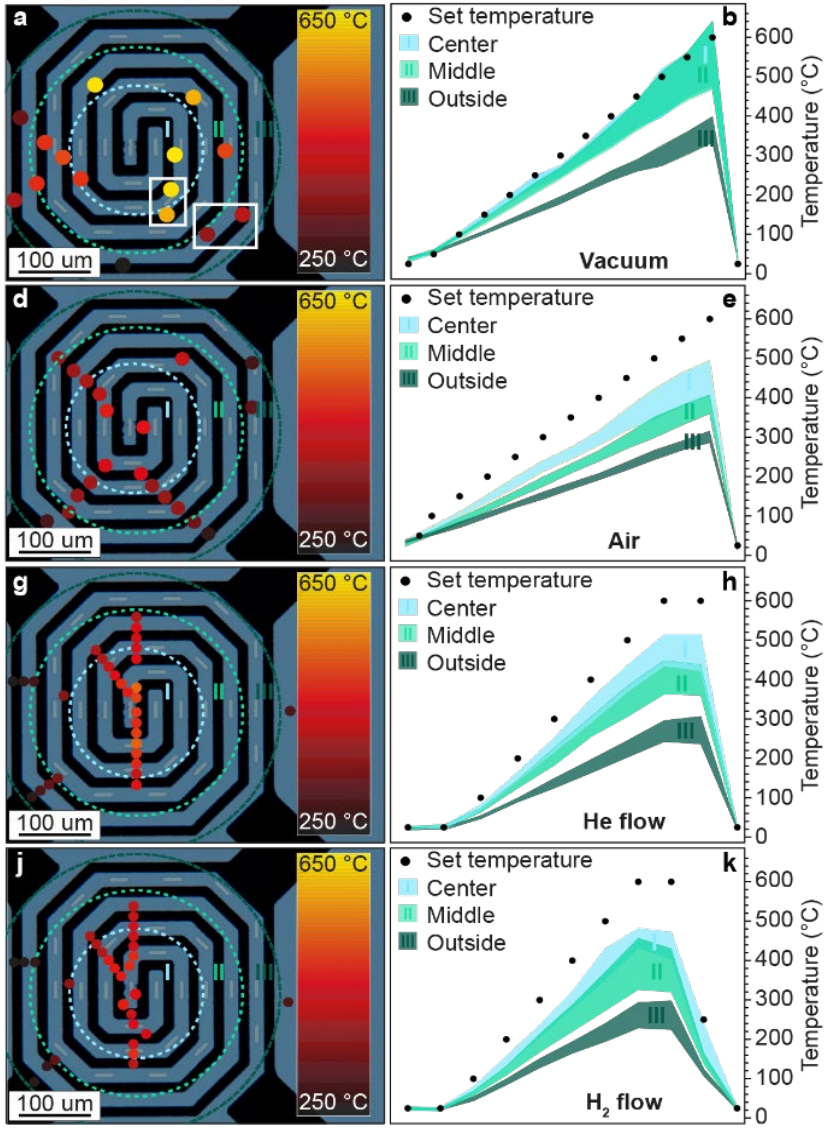
Used in electron microscopy and synchrotron for single particle measurements:



How homogeneous is the temperature? Role gases or vacuum around?

Interested manufacturer: DENS Solutions – adapt design to improve temperature homogeneity – nice cooperation with industry.

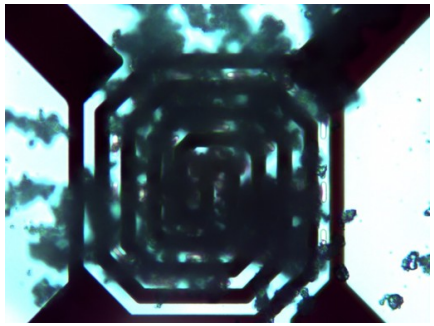


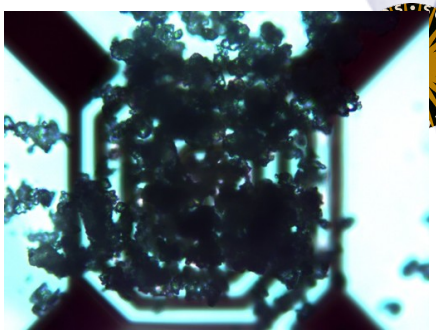
Procedure:

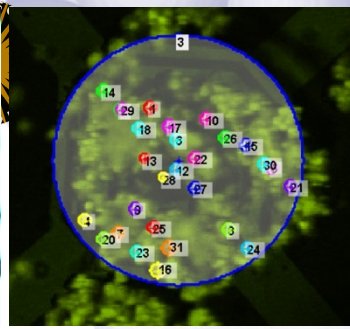
1. Deposit thin layer of NaYF4:Er,Yb NCs on microheater
2. Assemble it all to fit in a confocal microscope
3. Vary set-point and map temperature distribution by measuring Er^{3+} emission spectra

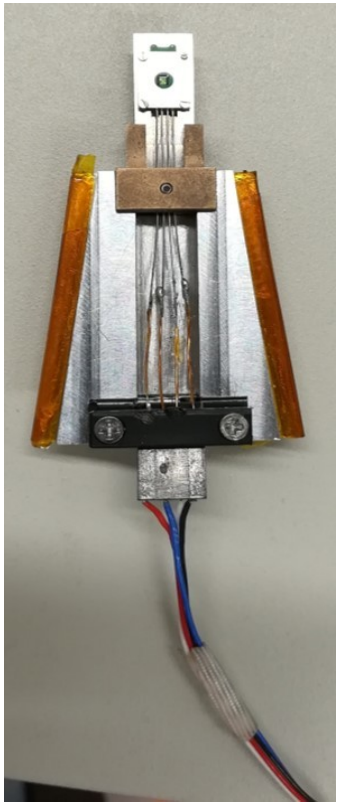
I. K. Ravenhorst, R. G. Geitenbeek, M. J. Eerden, J. van Tijn Omme, H. H. Peréz Garza, F. Meirer, A. Meijerink, B. M. Weckhuysen, *ChemCatChem* **2019**, *11*, 5505

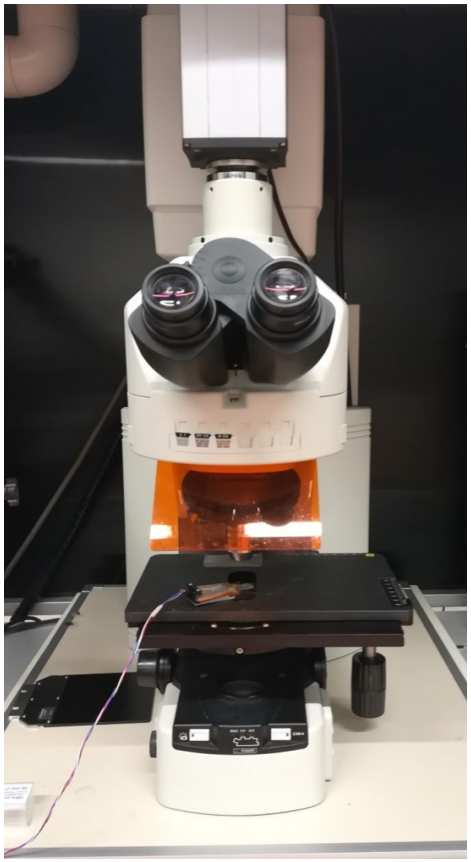
Seems simple: supporting information tells the real stories:

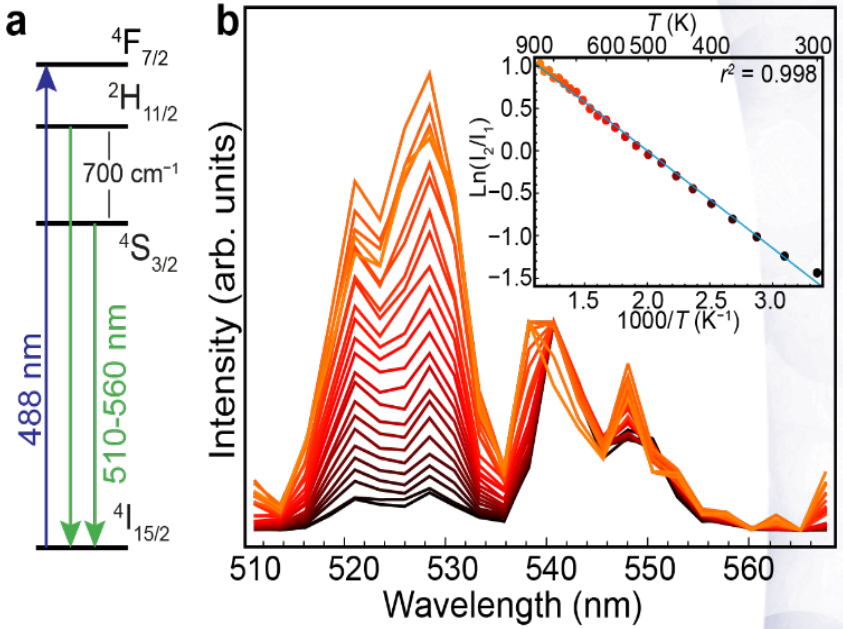












Improvements in progress!!

Conclusions

- Insight in basics of lanthanide luminescence, important for understanding and development of nano T-probes
- Lanthanides ions are versatile probes for luminescence nanothermometry, both spectral and temperature window
- Single-ion Boltzmann thermometry is robust, reliable, reproducible but has limitations and we now understand!
- Concentration matters! Even for single-ion two-level thermometry it is crucial to know/optimize/specify the dopant concentration.
- Energy transfer luminescence thermometry offers opportunities and challenges and requires more research
- New developments allow high temperature sensing and mapping and open new areas of application.

Acknowledgements

- Markus Suta
- Thomas van Swieten
- Robin G. Geitenbeek
- Dechao Yu
- Ting Yu
- Anna Kaczmarek
- Bert Weckhuysen
- Freddy T. Rabouw
- Many other PhD/MSc/BSc students

nanoTBtech consortium:

- Vinča team: Željka Antić, Vesna Đorđević, Sanja Kuzman, Miroslav D. Dramićanin
- Luís Carlos, Eliana Cavaleiro (U. Aveiro)
- Łukasz Marciniak, Artur Bednarkiewicz (Wroclaw PAS)
- Daniel Jaque, Erving Ximendes (U. Madrid)
- Bruno Viana (Chimie ParisTech)
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