Optical thermometry based on Nd^{3+}/Yb^{3+}-doped fluorophosphate glasses

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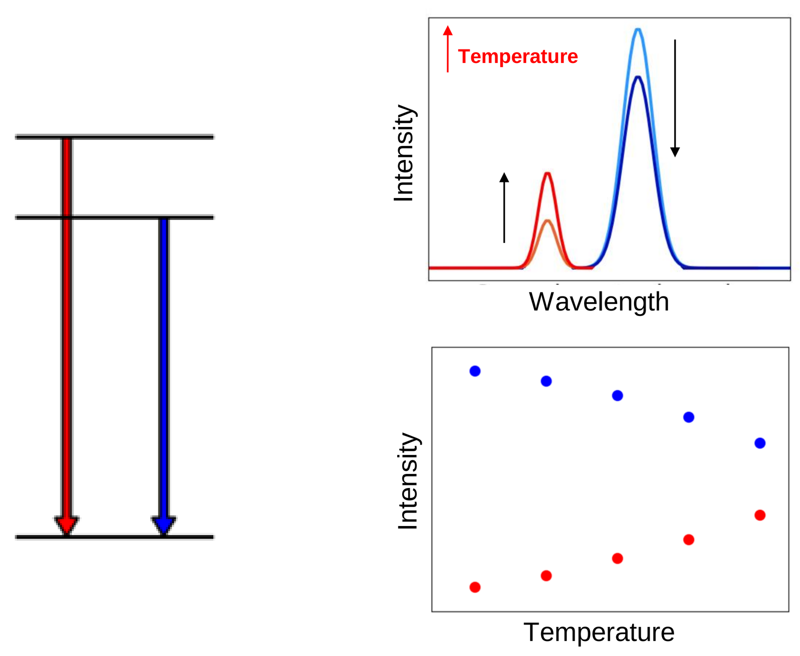
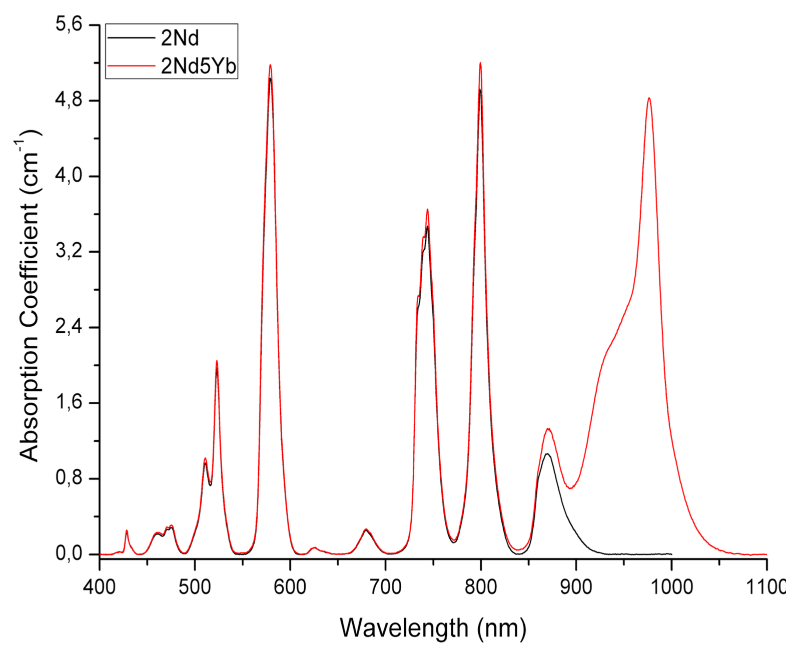
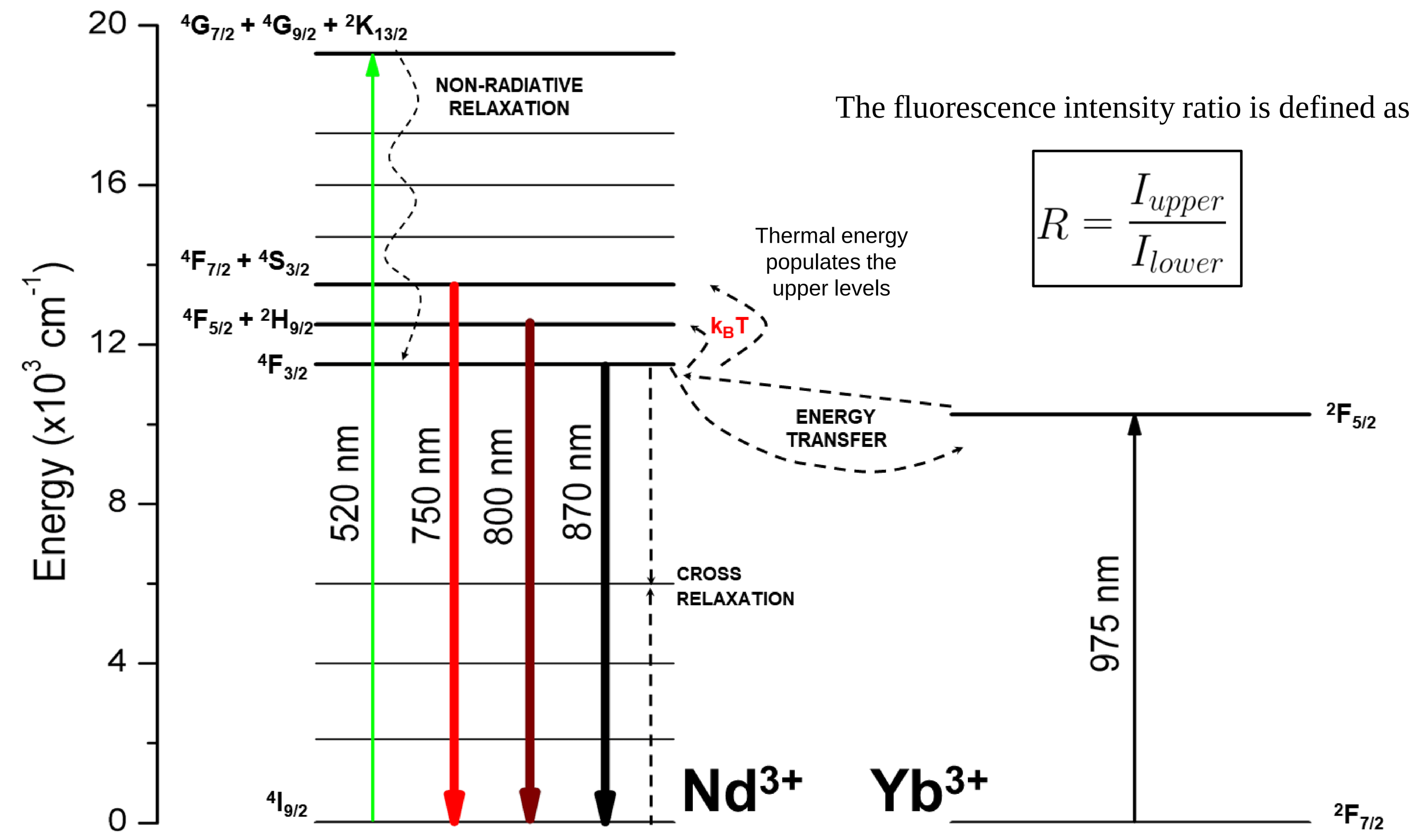
The fluorescence intensity ratio (FIR) technique [1] is one the most successful methods used in optical temperature sensing. FIR compares the emissions from two thermally coupled electronic levels of the material's emitting center, usually some trivalent lanthanide ion. Neodymium (Nd^{3+}) is of special interest since its emission bands: i) don't show great overlap; ii) lie in the near-infrared optical biological window. Nd^{3+}-doped and Nd^{3+}/Yb^{3+}-codoped fluorophosphate glasses [2] with composition $25BaF_2$-$25SrF_2$-$10Al(PO_3)_3$-$20AlF_3$-$(20\text{-}x\text{-}z)YF_3$:$xNdF_3$-$zYbF_3$, with x = 0.25, 1, 2 or 3 and z = 0, 1, 3 or 5 mol%, are employed as the temperature sensing material.



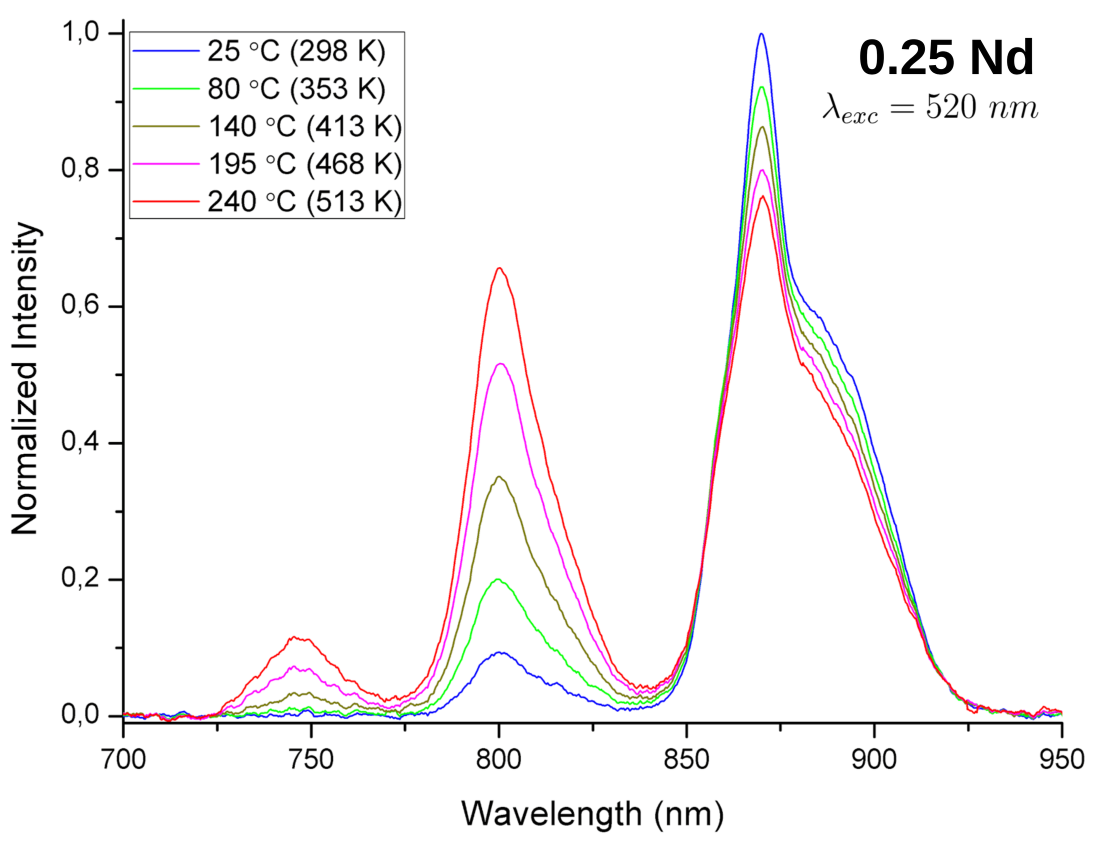


Representative absorption spectra of single doped and codoped samples.

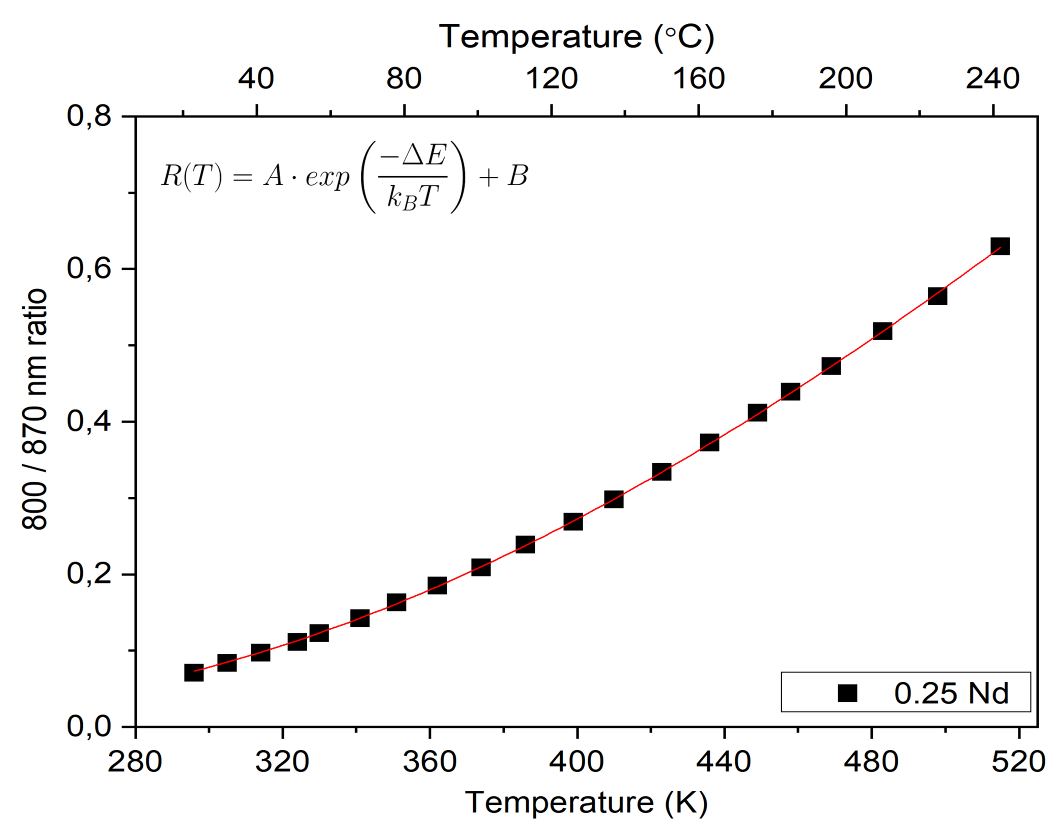


The fluorescence intensity ratio is defined as

$$R = \frac{I_{upper}}{I_{lower}}$$

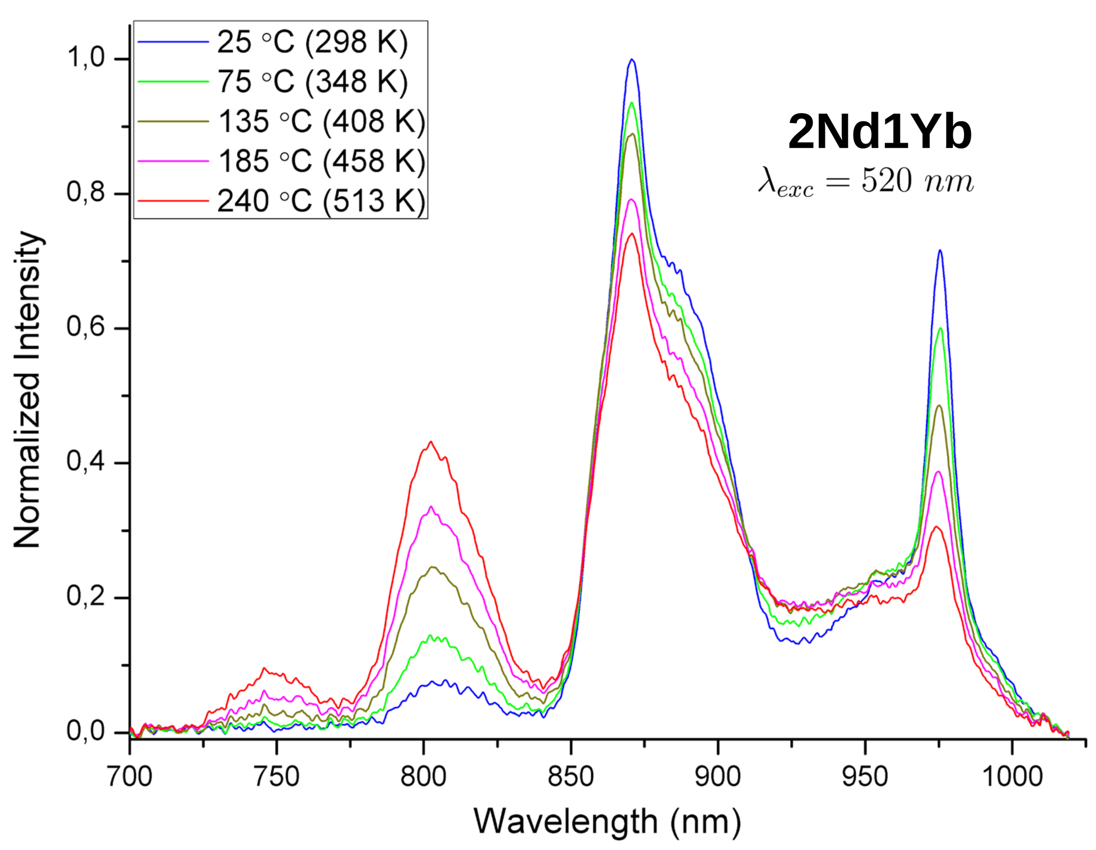


Temperature effect on the emission profile of the 0.25Nd sample after 520 nm excitation.

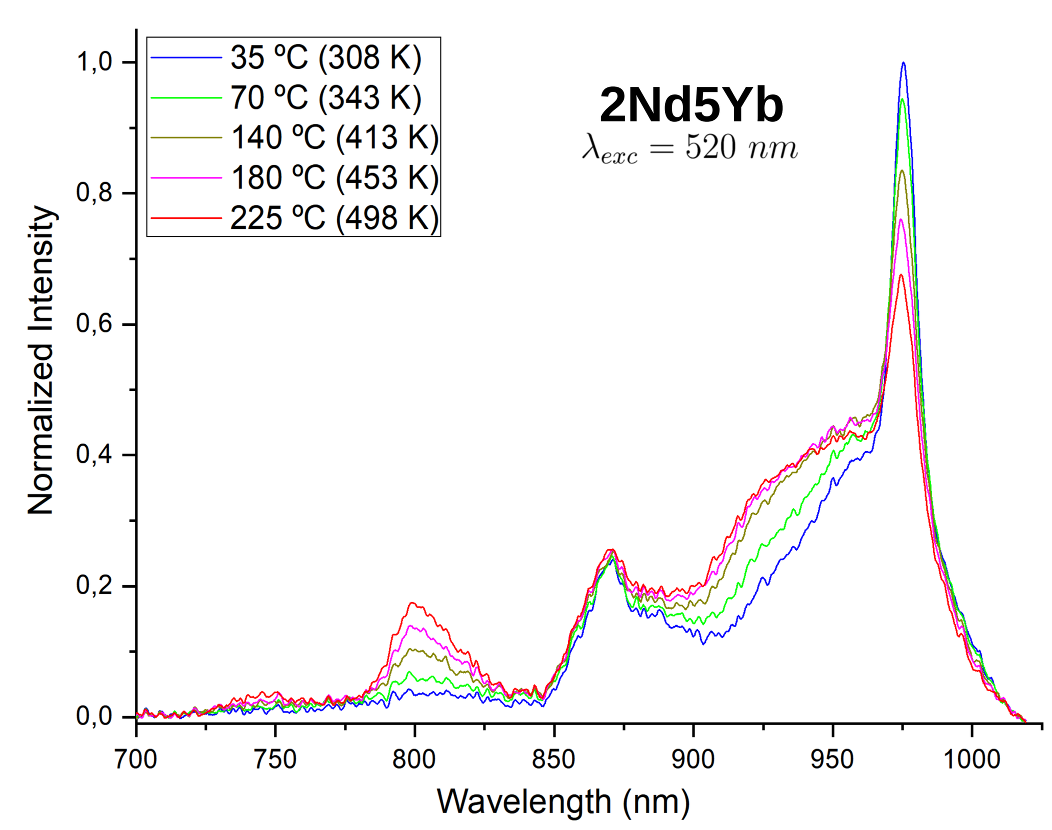


Emission ratio (squares) and calibration curve (red line)

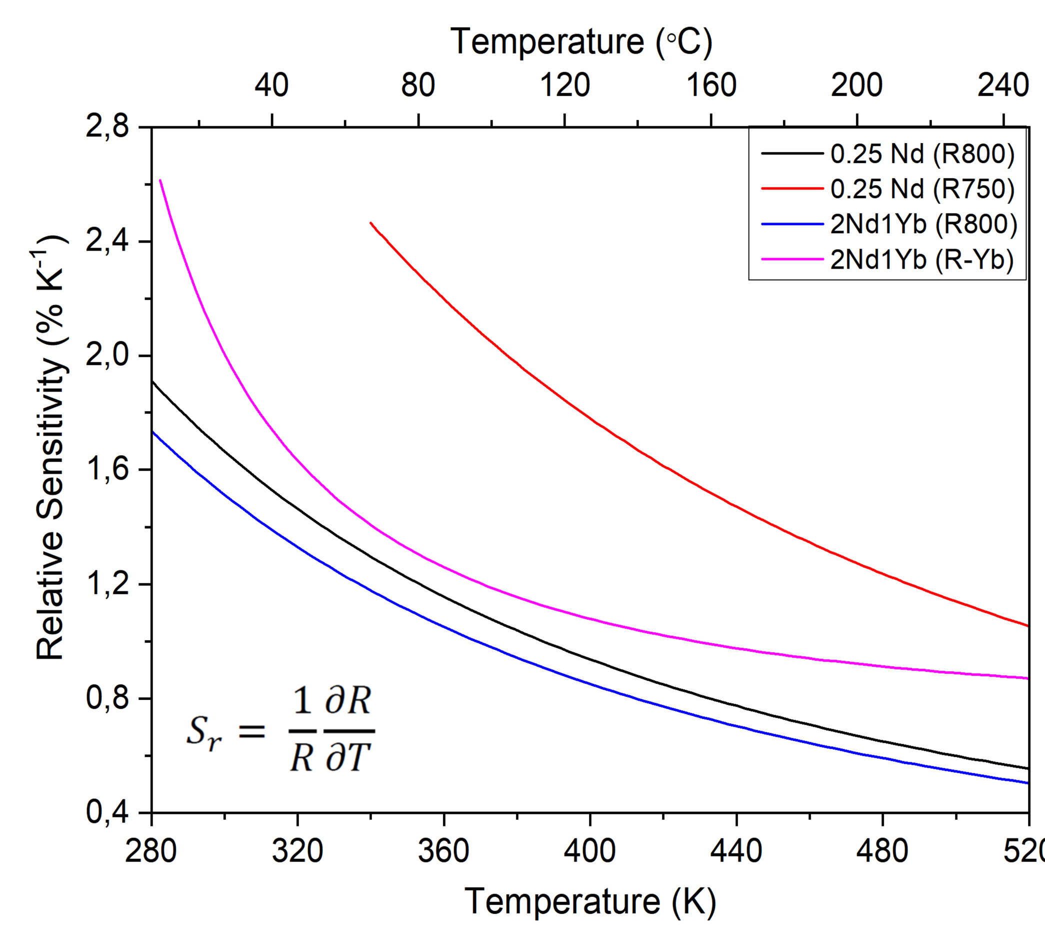
- The Nd^{3+} emission band located at 800 nm shows a constant increase in the whole 15-240 ºC range;
- The less intense band at 750 nm is only detectable for temperatures above 60 ºC but gives a greater sensitivity;
- The Nd^{3+} emission band at 870 nm is used as the reference (I_{lower}) in the above cases;
- If the offset parameter B is equal to zero the sensitivity is simply $\Delta E/k_BT^2$;
- The low energy Yb^{3+} emission (975 nm) shows a great decrease around room temperature and can also be used as I_{lower};
- More than one ratio can be monitored simultaneously.



Temperature effect on the emission profile of the 2Nd1Yb codoped sample after 520 nm excitation.



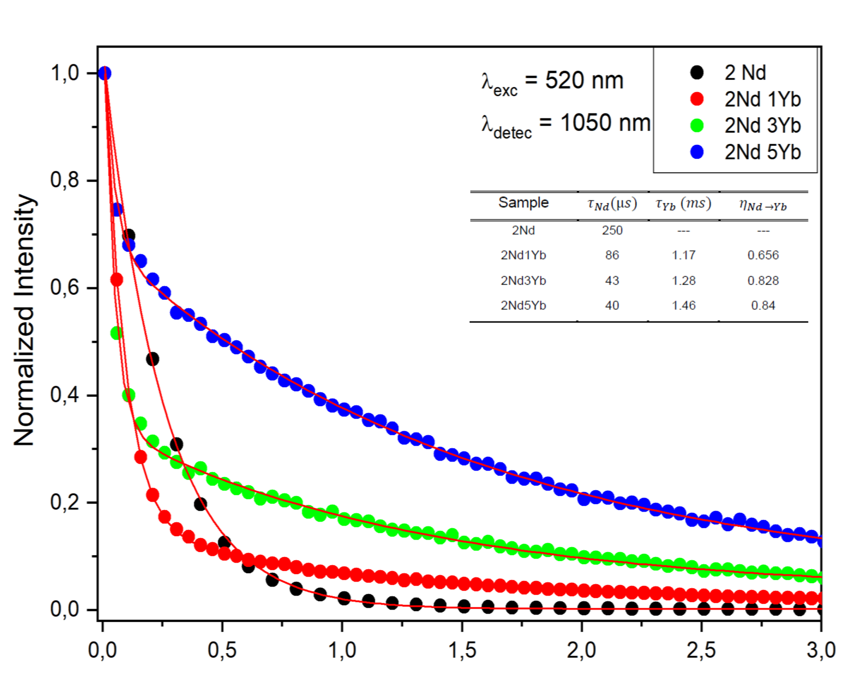
Temperature effect on the emission profile of the 2Nd5Yb codoped sample after 520 nm excitation.



Relative sensitivities for all possible emission ratios

Energy transfer efficiency as a function of Yb3+ concentration

$$\eta = \frac{W^{transf}}{W^{rad} + W^{nrad} + W^{transf}} = 1 - \frac{\tau_{CO}}{\tau_{SINGLE}}$$

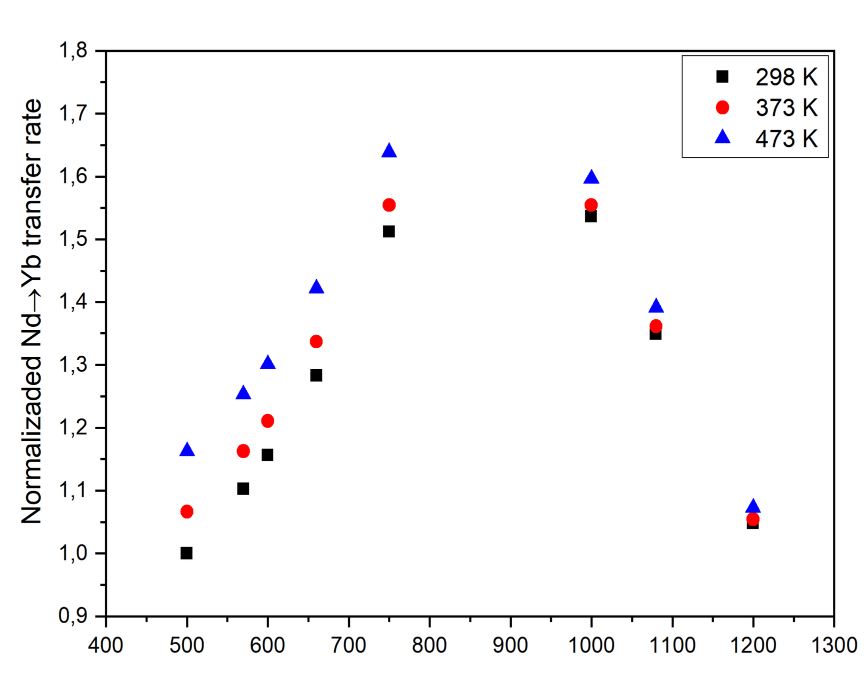


Sample	τ_{Nd} (μs)	τ_{Yb} (ms)	$\eta_{Nd\rightarrow Yb}$
2Nd	250	---	---
2Nd1Yb	86	1.17	0.656
2Nd3Yb	43	1.28	0.828
2Nd5Yb	40	1.46	0.84

Emission lifetimes at 1050 nm (both Nd3+ and Yb3+ emissions)

Phonon mediated energy transfer rate

$$W^{transf}(E_f) \propto \frac{1}{1 - e^{-E_f/k_BT}} \int \frac{I_{emis}(E - E_f)\, I_{abs}(E)\, dE}{E^2}$$



Normalized energy transfer rate

Conclusion and Perspective

Nd^{3+}-doped and Nd^{3+}/Yb^{3+}-codoped fluorophosphate glasses are characterized as temperature sensors by the means of the FIR technique. Relative sensitivities as high as 2.5% K^{-1} at 340 K (~70 ºC) are achieved for the most energetic emission band at 750 nm. The use of the Yb^{3+} emission at 975 nm is also adressed and results in high sensitivity for temperatures close to 25 ºC. The $Nd^{3+}\rightarrow Yb^{3+}$ energy transfer does not increase dramatically with Yb^{3+} concentration, so the system with less Yb^{3+} is prefered due to the smaller band overlap.

Future work may explore:

- Energy transfer rates with fixed Yb^{3+} concentration;
- Judd-Ofelt parameters calculation and prediction of the exponential pre-factor;
- Detailed analysis of the overlap region can help to predict the offset B.

References

[1] S.A. Wade, S.F. Collins and G.W. Baxter, J. Appl. Phys. 94, 4743 (2003)

[2] T.S. Gonçalves et al. , Mater. Chem. Phys. 157, 45 (2015)

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