Unraveling the Thermometric Behaviour of $Tm,Yb:LiLuF_4$

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Introduction

Nanothermometry is a fast-developing field of research due to the need of precise and remote temperature readout. Commonly used is the Er,Yb upconversion (UC) two-ion ratiometric system operating in the visible range. However, for biological applications systems operating in the biological windows (BW), e.g. the BWI (650-900 nm) are best as tissue or water absorption and scattering are limited in that spectral range and autofluorescence can be minimized then. One UC system operating in the BWI is Yb,Tm in an inorganic host matrix such as $LiLuF_4$. However, the understanding of the excited state dynamics of such a system is limited.

Characterization

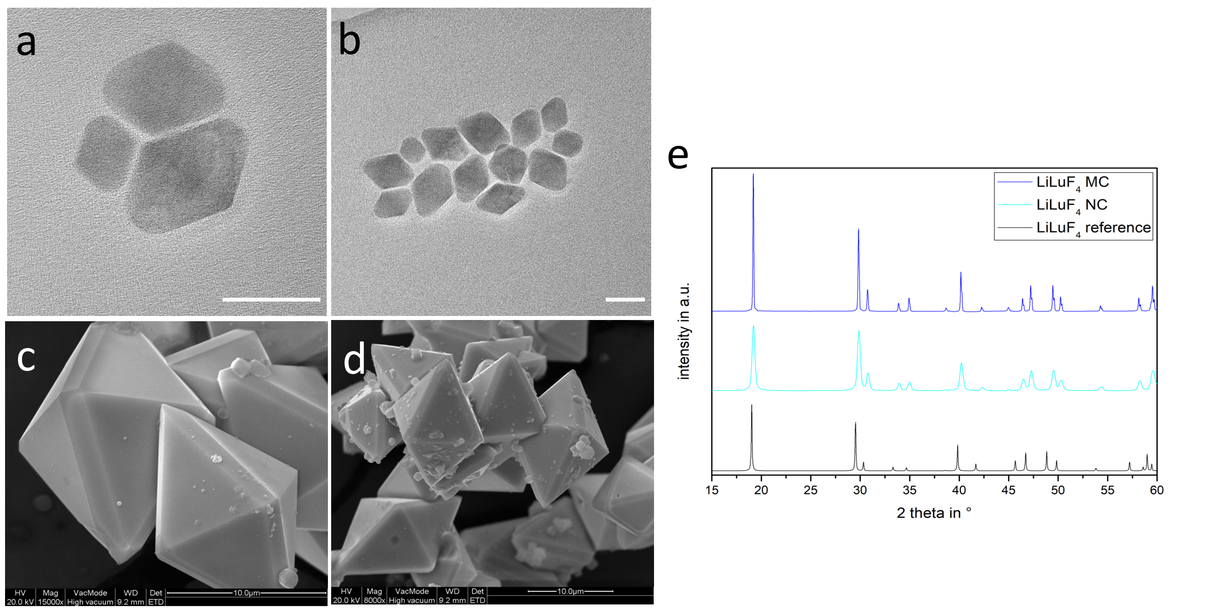

Fig. 1: (a,b) HRTEM images of $Tm,Yb:LiLuF_4$ nanocrystals from thermal decomposition route. (c,d) SEM images of the $Tm,Yb:LiLuF_4$ microcrystals. (e) PXRD patterns of the respective $Tm,Yb:LiLuF_4$ nano- and micro-crystals.

Photoluminescence emission maps

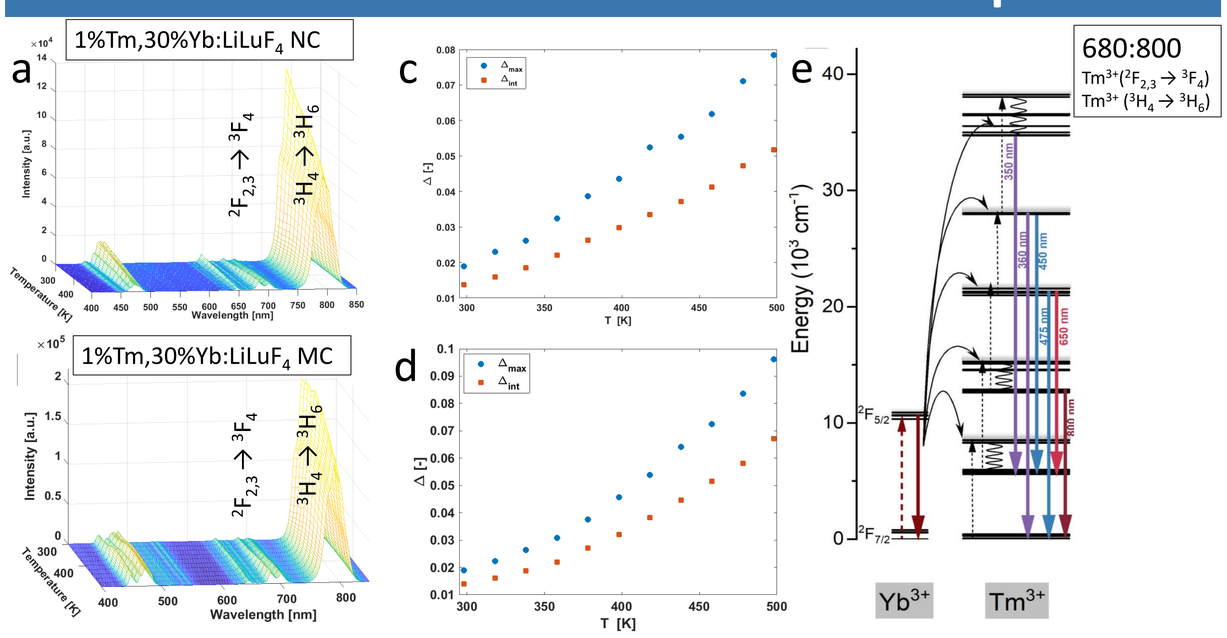

Fig. 2: Emission maps of $1\%Tm,30\%Yb:LiLuF_4$ for nano-and micro-crystals (a,b), recorded from 280 to 480 K with a step size of 20 K in solid after ligand removal. The Delta values for the 680 nm transition of Tm^{3+} ($^2F_{2,3} \rightarrow {}^3F_4$) to the 800 nm transition of Tm^{3+} ($^3H_4 \rightarrow {}^3H_6$) are also presented (c,d). E shows the the Dieke diagram for Tm^{3+} and Yb^{3+} is given with the respective electronic transitions indicated.[2]

Photoluminescence emission maps

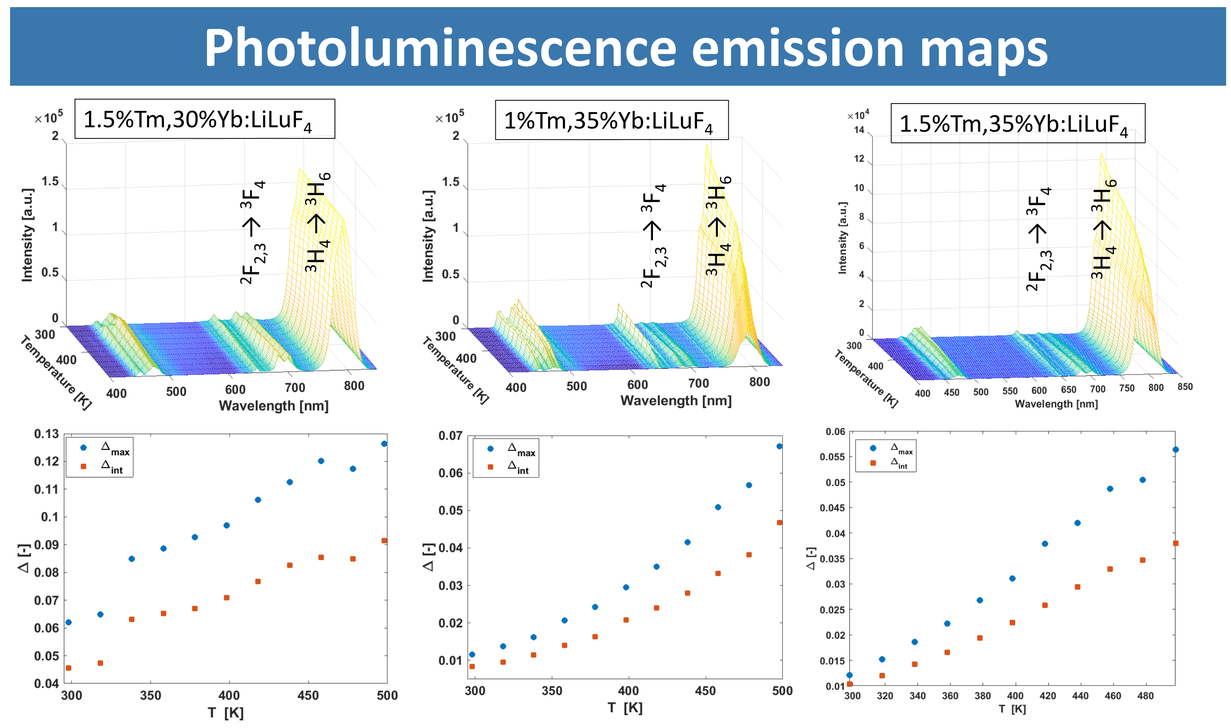

Fig. 3: Emission maps of different Tm:Yb ratios in $LiLuF_4$ nanocrystals recorded from 280 to 480 K with a step size of 20 K in solid after ligand removal. Shown below is their respective Delta values for the 680 nm transition of Tm^{3+}($^2F_{2,3} \rightarrow {}^3F_4$) to the 800 nm transition of Tm^{3+} ($^3H_4 \rightarrow {}^3H_6$).

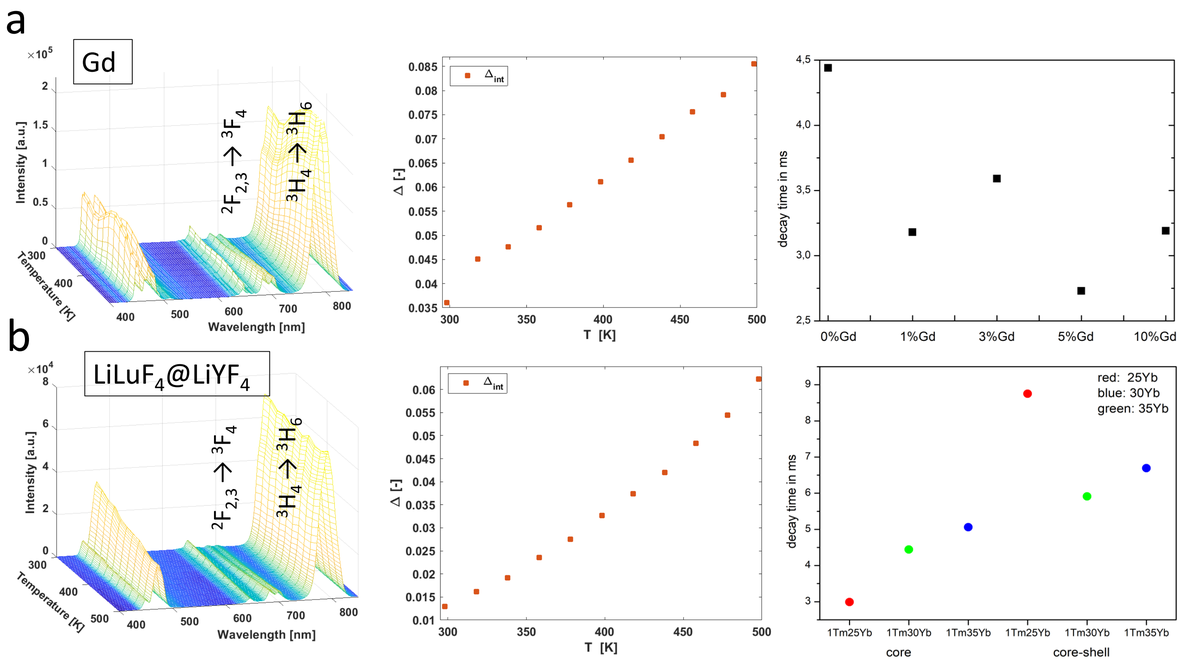

Fig. 4: (a) Emission map of $1\%Tm,30\%Yb,5\%Gd:LiLuF_4$ and (b) core-shell $1\%Tm,30\%Yb:LiLuF_4@LiYF_4$. The emission maps were recorded from 280 to 480 K with a step size of 20 K in solid after ligand removal. Shown in the middle are the respective Delta values for the 680 nm transition of Tm^{3+} ($^2F_{2,3} \rightarrow {}^3F_4$) to the 800 nm transition of Tm^{3+} ($^3H_4 \rightarrow {}^3H_6$). To the right the change in decay time is shown for Gd co-doping and core-shell nanocrystals.

Results

Here we present $Tm,Yb:LiLuF_4$ UC nanothermometers utilizing the ratio of the $^3F_{2,3} \rightarrow {}^3H_6$ electronic transition (680 nm) to the $^3H_4 \rightarrow {}^3H_6$ electronic transition (900 nm) of Tm^{3+}, operating in the BWI. All experimental results follow expected trends according to multi-phonon relaxation processes. We investigated the excited state dynamics in the various nano- and micro crystals with time-resolved and temperature-dependent luminescence. A heterogeneous $Tm,Yb:LiLuF_4@LiYF_4$ core-shell geometry was grown to investigate the influence of an inorganic protective layer. Such a matrix combination is necessary, as Li^+ containing host materials are in need of a heterogeneous core-shell structure[1]. Additionally, Gd^{3+} ions were co-doped to induce lattice distortions and therefore reduce Tm^{3+}-Tm^{3+}-cross relaxation.

Conclusions

In this work we investigated the Tm,Yb UC system in $LiLuF_4$. We were able to gain deeper understanding in the mechanisms and provide an explanation. Additionally, we were able to investigate the claim of Tm^{3+}-Tm^{3+}-cross relaxation and lessen its effect via co-doping of Gd^{3+} ions in the host matrix. Finally, a heterogeneous Tm,Yb: $LiLuF_4@LiYF_4$ core-shell geometry was grown to show the effect of an inorganic protective layer. We were able to show that the nanothermometric performance improves significantly due to the introduction of Gd^{3+} ions as well as growing a heterogeneous core-shell geometry. We investigated the nanoparticles with HRTEM imaging, PXRD, decay time measurements as well as high temperature thermometry.

Sources

[1] M. Lederer, H. Rijckaert, A.M. Kaczmarek, *ACS Appl. Nano Mater*. **6**(4) (2023) 2438-2449.
[2] M. Misiak, O. Pavlosiuk, M. Szalkowski, A. Kotulska, K. Ledwa, A. Bednarkiewicz, *Nanotechnology*. **34**(34) (2023) 345702.