The Influence of bases on thermal decomposition synthesis of LaF_3

Mirijam Lederer,[a] Simona Premcheska,[a,b] , Pieter Tack,[c] Laszlo Vincze,[c] Andre Skirtach,[b] Anna M. Kaczmarek,*[a]

[a] NanoSensing Group, Department of Chemistry, Ghent University, Krijgslaan 281-S3, 9000 Ghent, Belgium
[b] Nanotechnology Laboratory, Faculty of Bioscience Engineering, Ghent University, 9000 Ghent, Belgium
[c] X-ray Microspectroscopy and Imaging (XMI), Department of Chemistry, Ghent University, Krijgslaan 281-S12, 9000, Ghent, Belgium

Contact:
Mirijam.Lederer@UGent.be
Anna.Kaczmarek@UGent.be

Introduction

Lanthanide-doped nanophosphors are popular nanoprobes to achieve high spatial resolution for remote nanothermometry as they offer sharp emission bands and low toxicity.[1,2] As host materials for such nanoparticles fluorides are known to be chemically stable and offer comparably low phonon energies. LaF_3 is a well known host material with very low vibrational energies, even compared to other fluorides. This property is linked to minimal quenching of the excited states of the Ln^{3+} ions in the NIR region.[1] However, the synthesis of well-dispersed and homogenous LaF_3 nanoparticles is rarely reported in literature and a sophisticated task.[1,2]

PXRD pattern

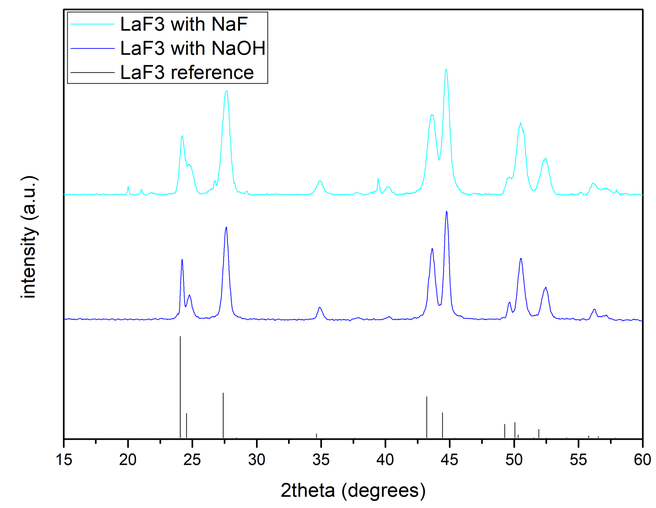

Fig. 2 PXRD patterns of 2%Er,18%Yb:LaF_3 synthesized with 2.5 mmol NaOH and 2 mmol NaF compared to the ICSD ID 23972 reference data for LaF_3[3].

TEM images

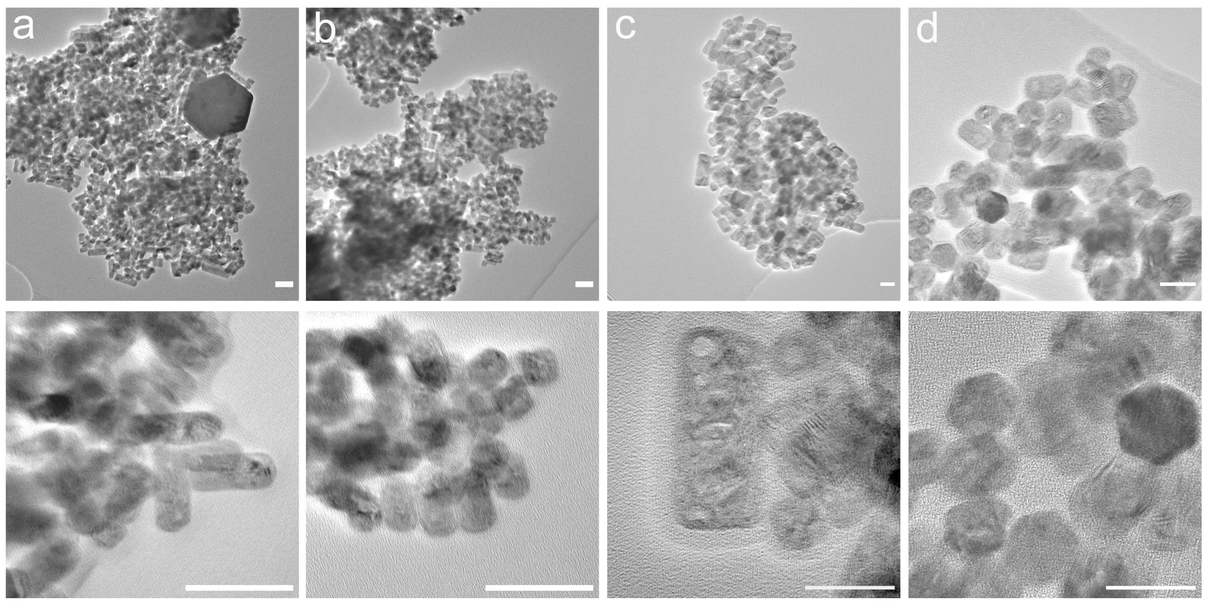

Fig. 1 TEM images of 2%Er,18%Yb:LaF_3 synthesized with 2.5 mmol NaOH (a) or 2 mmol NaF (b). (c) shows the 2%Er,18%Yb,2%Tm:LaF_3 synthesized with 2.5 mmol NaOH and (d) the respective sample synthesized with 2 mmol NaF. An overview is shown in the top row, a close-up in the bottom row. The scale bar is 50 nm for all images.

Photoluminescence emission maps

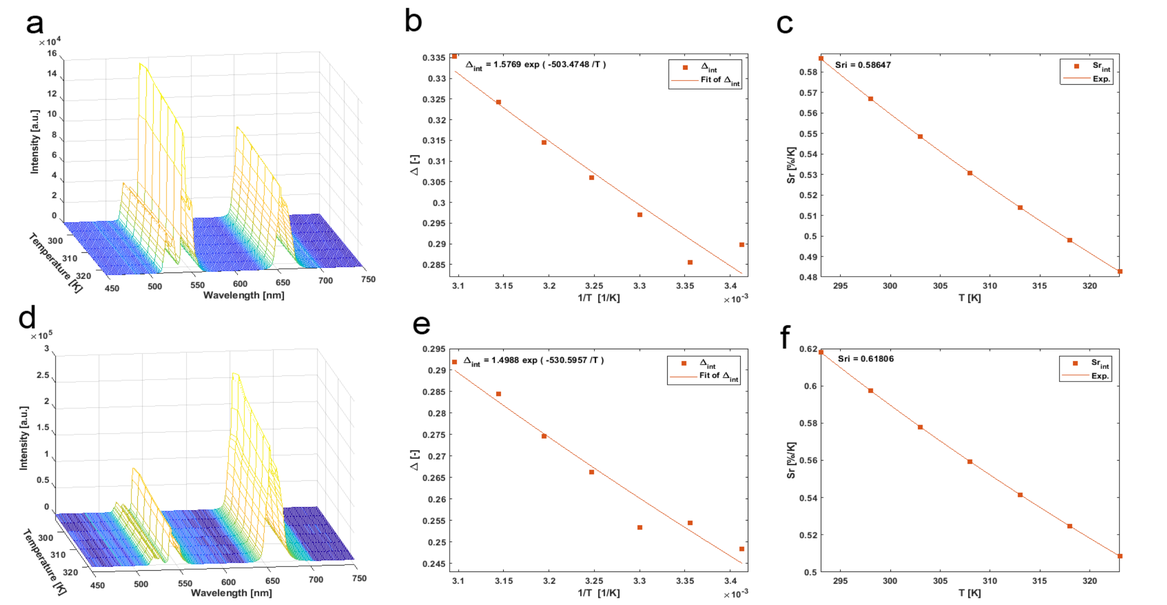

Fig. 3 Photoluminescence emission maps of 2%Er,18%Yb:LaF_3 (NaOH) (a) and 2%Er,18%Yb:LaF_3 (NaF) (d) in water for the temperature range of 20 °C to 50 °C. (b) shows the Δ_1 parameter for using NaOH as base and (d) for using NaF. The S_r is shown in (d) and (e) respectively. All fits were calculated with the integrated area under the curve for the Boltzmann distribution.

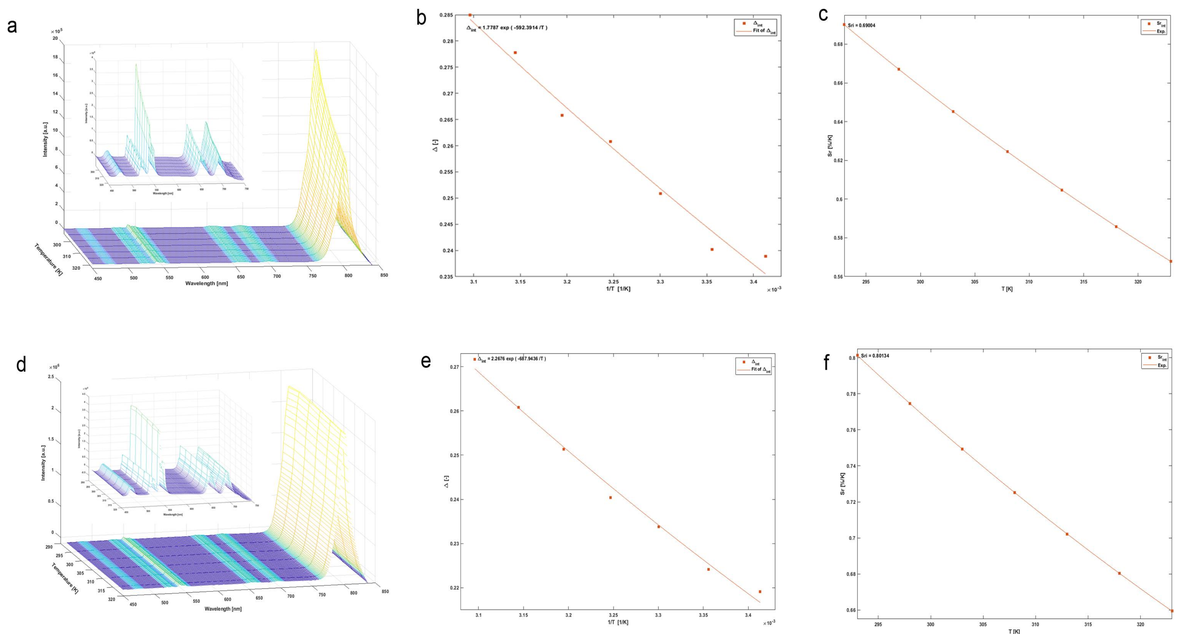

Fig. 4 Photoluminescence emission maps of 2%Er,18%Yb,2%Tm:LaF_3 (NaOH) (a) and 2%Er,18%Yb:LaF_3 (NaF) (d) in water for the temperature range of 20 °C to 50 °C. (b) shows the Δ_1 parameter for using NaOH as base and (d) for using NaF. The S_r is shown in (d) and (e) respectively. All fits were calculated with the integrated area under the curve for the Boltzmann distribution.

Results

Here we present a novel thermal decomposition synthesis route with the addition of different bases, namely LiOH, KOH, NaOH and NaF to influence the pH value. Only the addition of NaOH and NaF yielded LaF_3 nanocrystals. The obtained nanoparticles were investigated via PXRD, XRF, TEM imaging, temperature-dependent photoluminescence and cytotoxcitity test and showed promising results. The morphology is either rod-like (NaOH) or cubic (NaF) with well-dispersed and homogeneous nanoparticles. The here presented system for nanothermometry relies on a tri-doped system of Er,Yb and Tm, which is a rarely explored system for thermometry but offers increased performance.

Sources

[1] J.W. Stouwdam, F.C. van Veggel, *Nano letters*, 2002, ***2***(7), 733-737.
[2] A. M. Kaczmarek, M. K. Kaczmarek and R. Van Deun, *Nanoscale*, 2019, **11**, 833– 837.
[3] P. Debye, P. Scherrer, American Crystallographic Association 38 (1919) 445.

Conclusions

In this work we showed the successful synthesis of both 2%Er,18%Yb:LaF_3 and 2%Er,18%Yb,2%Tm:LaF_3 synthesized from NaOH and NaF as base in a novel Schlenk line synthesis. The morphology is homogeneous and the PXRD patterns confirm the correct crystal phase. The thermometric performance in water in the biological temperature region for both double-doped 2%Er,18%Yb:LaF_3 and tri-doped 2%Er,18%Yb,2%Tm:LaF_3 is promising with a S_r reaching 0.587% per K at 293 K (NaOH) and 0.618% per K at 293 K (NaF) for the double-doped and 0.706% per K at 323 K (NaOH) and 0.857% per K at 323 K (NaF) for the tri-doped system with an excellent temperature uncertainty.