

## Heat transfer studies using Ln<sup>3+</sup> based nanothermometers

There is an increasing demand for accurate, non-invasive and self-reference temperature measurements as technology progresses into the nanoscale. This is particularly so in micro- and nanofluidics where the comprehension of heat transfer and thermal conductivity mechanisms can play a crucial role in areas as diverse as energy transfer and cell physiology [1,2].

In fact, the integration of optics and micro/nanofluidic devices to provide novel functionalities in nanosystems is stimulating a promising new area of optofluidics, for nanomedicine and energy. Despite promising progress precision control of fluid temperature by accounting for local temperature gradients, heat propagation and accurate temperature distributions have not yet been satisfactorily addressed, *e.g.*, investigating heat transfer mechanisms in nanofluids or mapping temperature distributions within living cells.

With the objective of investigate the heat transfer mechanisms in nanofluids and mapping temperature distributions we have focused in the development and characterization of nanothermometers that can be dispersed in different base fluids or incorporate organic-inorganic hybrid films. The thermometers performance can be compared using the relative sensitivity, defined as the relative change on the thermometric parameter, the spatial resolution ( $\delta x$ ) and the temporal resolution ( $\delta t$ ) the largest temporal and spatial temperature change measured.

In 2013 we reported the development of two luminescent ratiometric nanothermometers based on a  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> maghemite core coated with an organosilica shell co-doped with Eu<sup>3+</sup> and Tb<sup>3+</sup>  $\beta$ -diketonate chelates. The design of either the siloxane-based hybrid host or the chelate ligands permits the nanothermometers to be used in nanofluids (*i.e.* water suspensions of the nanothermometers) at 293–320 K with an emission quantum yield between  $0.24 \pm 0.02$  and  $0.38 \pm 0.04$ , a relative sensitivity of up to  $1.5\% \text{ K}^{-1}$  (at 293 K), a spatiotemporal resolution (constrained by the experimental setup) of (64–65)  $\mu\text{m}/150 \text{ ms}$  (to move out of the temperature uncertainty,  $\delta T$ , stated as 0.4 K).

When illuminated with UV light, the thermometric nanofluids are able to map the temperature. None of luminescent devices proposed so far can map the temperature in a micro/nanofluid in the 293–320 K range with such high emission quantum yields, relative sensitivity, temperature uncertainty, and spatio-temporal resolution values. Furthermore, a velocity in of heat traveling within the nanofluid,  $(2.2 \pm 0.1) \text{ mm s}^{-1}$ , was determined at 294 K simply using the Eu<sup>3+</sup>/Tb<sup>3+</sup> steady-state spectra of the nanothermometers.