Heat transfer studies using Ln³⁺ based nanothermometers

Carlos D. S. BRITES[a], Patrícia P. LIMA[a], Nuno J. O. SILVA[a*], Angel MILAN[b], Vitor S. AMARAL[a],
Fernando PALACIO[b] and Luís D. CARLOS[a*]

[a] *Departamento de Física & CICECO Universidade de Aveiro, Campus Santiago 3810-193, Aveiro, Portugal*

[b] *Departamento de Física de la Matéria Condensada & ICMA, Faculdad de Ciências, Universidad de Zaragoza, Calle Pedro Cerbuna, 50008, Zaragoza, Spain*

**corresponding author: carlos.brites @ua.pt*

Keywords: organic-inorganic hybrids, lanthanide ions, nanothermometry, heat transfer.

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 optofuidics, 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. The major obstacle for this has been the unavailability of a thermometer with the following requirements (that should be simultaneously satisfied): (i) high temperature resolution (<0.5 degree); (ii) ratiometric temperature output; (iii) high spatial resolution (<3 μm); (iv) functional independency of changes in pH, ionic strength and surrounding biomacromolecules; and (v) concentration-independent output. The most suitable class of thermometers to fulfil these requirements are the luminescent ones [3].

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 [2,3]. The thermometers performance can be compared using the relative sensitivity (Eq. 1) , defined as the relative change on the thermometric parameter Δ (taken as a ratio of intensities, $\Delta = I_1/I_2$ to avoid any dependences of the temperature read on local concentration, fluctuations on excitation sources, etc.):

$$S_r = \frac{\partial\Delta/\Delta T}{\Delta} \tag{1}$$

Also the spatial resolution (δx) is defined as $\delta x = \delta T \big/ \left|\vec{\nabla} T\right|_{\max}$, where δT is the temperature uncertainty and $\left|\vec{\nabla} T\right|_{\max} = \partial T/\partial x$ the largest temperature gradient that can be measured [4], and the temporal resolution defined as is defined as $\delta t = \delta T/\left(\partial T/\partial t\right)$,where $\left(\partial T/\partial t\right)$ the largest temporal temperature change measured.

In 2013 we reported the development of two luminescent ratiometric nanothermometers (**NP5-1.4**, spherical NPs, DLS diameter of 119.2 ± 11.6 nm and **NP4-1.3,** spherical NPs, DLS diameter of 40.2 ± 5.9 nm) based on a γ-Fe_2O_3 maghemite core coated with an organosilica shell co-doped with Eu^{3+} and Tb^{3+} β-diketonate chelates [2]. 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 ± 0.02 and 0.38 ± 0.04, a relative sensitivity of up to 1.5% K^{-1} (at 293 K), a spatiotemporal resolution (constrained by the experimental setup) of (64–65) μm/150 ms (to move out of the temperature uncertainty, δT, stated as 0.4 K).

The nanothermometers are easily dispersible in water forming transparent and stable nanofluids under day light illumination, making them ideal for temperature determination in micro- and nanofluidics using the temperature dependence of their emission properties. A demonstration of the use of these particles was performed by mapping the temperature of a glass tube with an inner diameter of 1 mm and a longitudinal length of 20 mm, filled with the nanothermometers nanofluids (1 g L^{-1}). A steady-state temperature gradient was induced in the nanofluids by an electrical current flowing in a coil-shaped resistance (**Fig. 1**a). The current was adjusted to produce the temperature gradient within the 293–320 K range. When illuminated with UV light, the nanofluids presented a blue-green (NP5-1.4) or a red-orange (NP4-1.3) emission (Fig. 1b and c) and an optical fiber was used to collect the emission spectra which were converted into absolute temperatures. Both nanothermometers gave analogous temperature values (temperature gradient along the capillary tube up to 3000 $K\cdot m^{-1}$), as shown in Fig. 1d. A temperature map recorded with a state-of-the-art commercial IR camera was used as a control measurement. The spatial resolutions of the nanothermometers and IR camera are 64 μm (NP4-1.3), 65 μm (NP5-1.4) and 160 μm, respectively, despite the optical fiber's inner diameter of 450 μm being ca. 1.5 times larger than the camera pixel field of view.

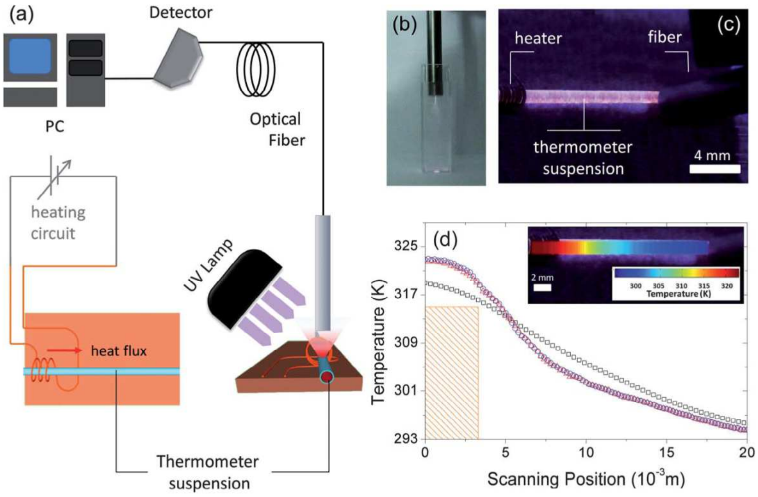

Figure 3: Temperature maping using Ln^{3+}-based nanothermometers. (a) Experimental setup used for temperature mapping in nanofluids. (b) Photograph of the NP5-1.4 suspension under UV irradiation (c) Photograph of the NP4-1.3 suspension under UV irradiation (handheld lamp). The heater, the capillary tube and the optical fibre are also visible. (d) Comparison of the temperature profile obtained with an IR camera (black squares) and with the light emission of NP4-1.3 (blue circles) and NP5-1.4 (red triangles). The shadowed area corresponds to the position of the heater. The pseudo-colour image of the NP4-1.3 suspension is represented in the inset.

None of the ratiometric luminescent and non-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 ± 0.1) mm s^{-1}, was determined at 294 K simply using the Eu^{3+}/Tb^{3+} steady-state spectra of the nanothermometers (**Fig. 2**). There is no precedent of such an experimental measurement in a thermometric nanofluid, where the same nanoparticles constituting the nanofluid are used to measure the temperature and to study the heat transfer.

In this communication we will present our most recent heat transfer studies using Ln^{3+} based nanothermometers and compare the experimental values with the ones reported in the literature.

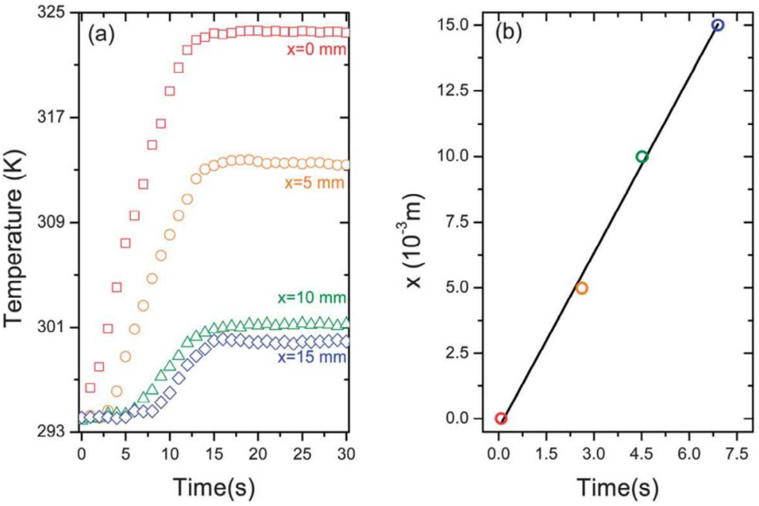

Figure 2 : Temperature dynamics on the capillary tube a) temperature dynamics monitored at different points x along the capillary tube using the NP5-1.4 thermometer . (b) linear relationship (r^2 = 0.996) between the distance x travelled by the thermal wave and the time instant t_0 for which the temperature starts to increase relative to the equilibrium value (294 K).

The work is partially supported by FCT Project RECI/CTM-CER/0336/2012 and FEDER, ref COMPETE: FCOMP-01-0124-FEDER-027465. CDSB tanks FCT (SFRH/BPD/ 89003/ 2012) for a grant.

References

[1] C.D.S. Brites, P.P. Lima, N.J.O. Silva, , A. Millan, V.S. Amaral, F. Palacio, , L.D. Carlos "Thermometry at the Nanoscale", *Nanoscale* **4**, 4799, 2012.

[2] C.D.S. Brites, P.P. Lima, N.J.O. Silva, , A. Millan, V.S. Amaral, F. Palacio, , L.D. Carlos " Ratiometric Highly Sensitive Luminescent Nanothermometers Working in the Room Temperature Range. Applications to Heat Propagation in Nanofluids", *Nanoscale* **5**, 7572, 2013.

[3] C.D.S. Brites, P.P. Lima, N.J.O. Silva, , A. Millan, V.S. Amaral, F. Palacio, , L.D. Carlos " A Luminescent Molecular Thermometer for Long-Term Absolute Temperature Measurements at the Nanoscale", *Adv. Mater.* **22**, 4499, 2010.

[4] K. Kim, W. H. Jeong, W. C. Lee and P. Reddy," Ultra-High Vacuum Scanning Thermal Microscopy for Nanometer Resolution Quantitative Thermometry" *ACS Nano*, **6**, 4248, 2012.