Supplementary Information

High-sensitive Eu^{3+} ratiometric thermometers based on excited state absorption with predictable calibration

Adelmo S. Souza,[a] Luiz A. O. Nunes,[b] Ivan G. N. Silva,[c] Fernando A.M. Oliveira,[b] Leonis L. da Luz,[a] Hermi F. Brito,[c] Maria C. F. C. Felinto,[d] Rute A. S. Ferreira,[e] Severino A. Júnior,[a] Luís D. Carlos,[e]* Oscar. L. Malta[a]*

[a] Departamento de Química Fundamental-CCEN-UFPE, Cidade Universitária, Recife-PE, 50670-901, Brazil

[b] Instituto de Física de São Carlos, Universidade de São Paulo - USP, CEP 13560-970, São Carlos - SP, Brazil

[c] Instituto de Química, Universidade de São Paulo, 05508-900 São Paulo - SP, Brazil

[d] Centro de Química do Meio Ambiente, Instituto de Pesquisas Energéticas e Nucleares, Av. Prof. Lineu Prestes, 2242, SP, 05508-000 São Paulo - SP, Brazil

[e] Department of Physics and CICECO Aveiro Institute of Materials, University of Aveiro, 3810–193 Aveiro, Portugal

* Correspondence to: Dr A. S. Souza, E-mail: adelmosaturnino@hotmail.com; Prof. L. D. Carlos, E-mail: lcarlos@ua.pt

Structural characterization of the Y_2O_3:Eu^{3+} (1 mol%) Nanocrystals.

The morphology and structure of the Y_2O_3:Eu^{3+} nanocrystals were characterized by transmission electron microscopy (TEM) and X-ray powder diffraction (XRPD). TEM images were recorded using a JEM 2100 ARP microscope, using an acceleration voltage of 200 kV from a LaB6 thermo-ionic filament yielding a 2.4 Å resolution. The XRPD patterns were measured by a Rigaku Miniflex II (CuKα1, 1.5406 Å) from 4 to 70° (in 2θ), as previously reported.[1]

Figure S1 shows the TEM images for selected Y_2O_3:Eu^{3+} nanocrystals prepared from the [Y(TMA):Eu^{3+}(1.0 mol%)] precursor complex, with TMA=1,3,5-benzenetricarboxylate. At lower magnification, it is possible to observe that the materials are agglomerates of individual crystallites (Figure S1a,c). Based on the TEM images crystallite size of (5 ± 1), (13 ± 3), (30 ± 7), (38 ±7), (45 ± 9) and (53 ± 11) nm were calculated for the nanocrystals annealed at 500, 600, 700, 800, 900 and 1000 °C, respectively. These results are very similar to those estimated from the Scherrer equation (6, 14, 23, 33, 40 and 52 nm, for samples annealed at 500, 600, 700, 800, 900 and 1000 °C, respectively).[1] Figures S1b,d show that at higher magnification the nanocrystals do not have defects (except in the edges), suggesting the formation of a solid solution between the Eu^{3+} ions and the Y_2O_3 host.

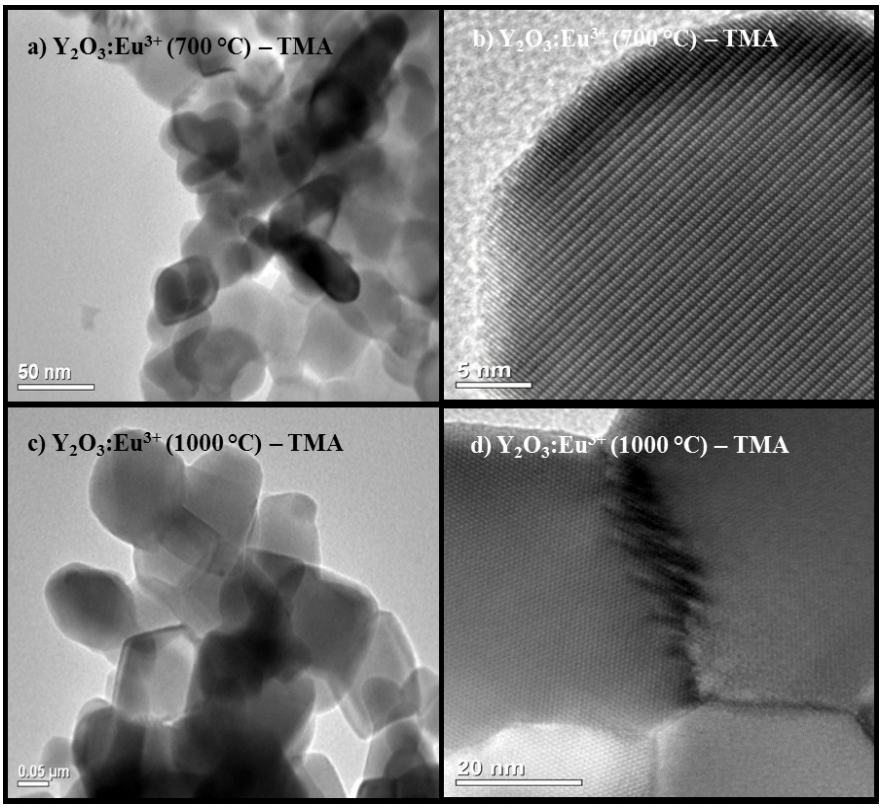

Figure S1. TEM images of Y_2O_3:Eu^{3+}(1.0 mol%) annealed at a), b) 700 and c), d) 1000 °C.

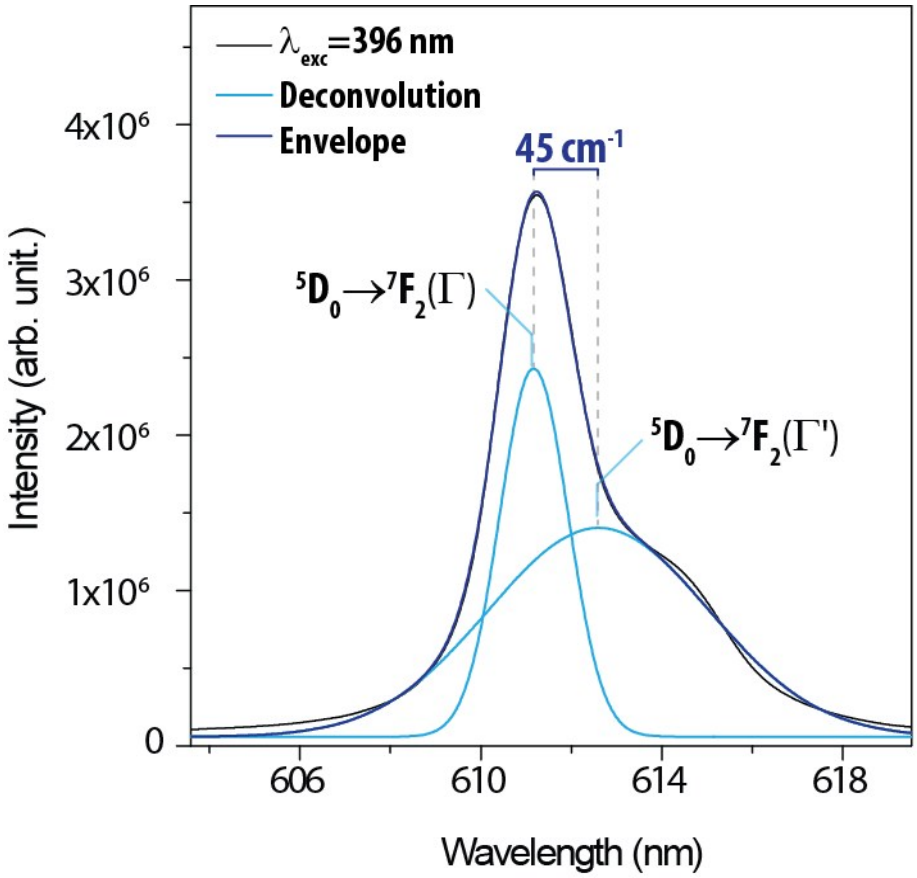

Figure S2. Emission spectra of the Y_2O_3:Eu^{3+} nanocrystals in the range 604–620 nm of the $^5D_0 \rightarrow {}^7F_2$ transition exciting at 396 nm recorded at 300 K (black line). The deconvolution is shown by the green curves.

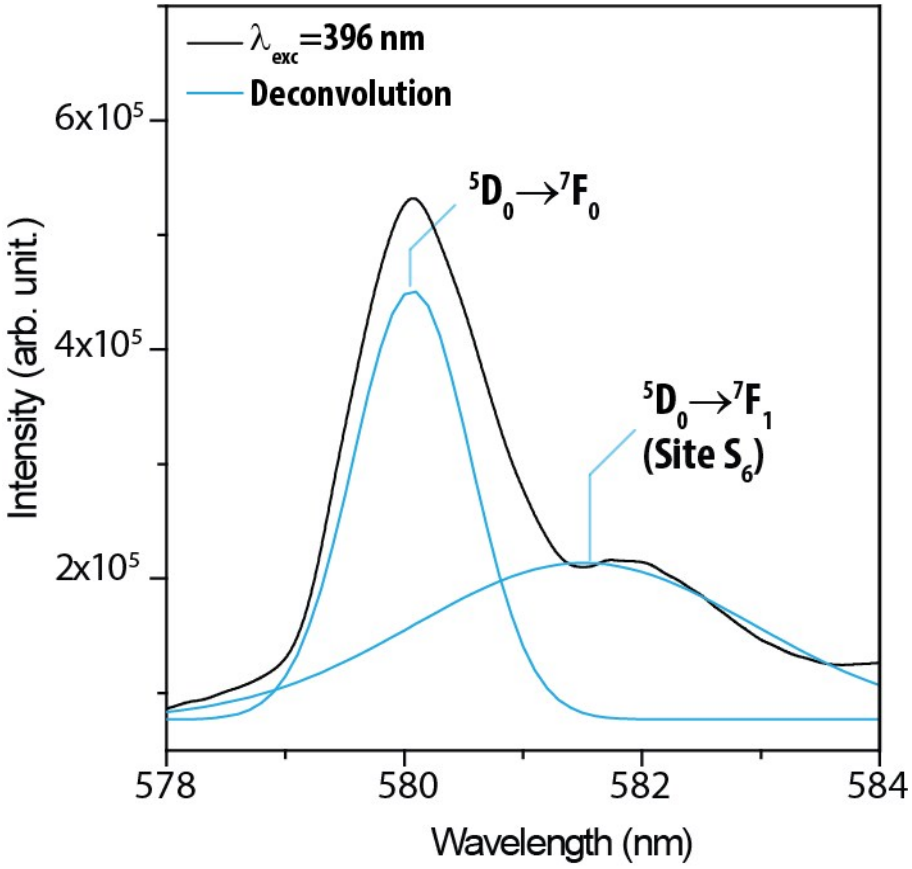

Figure S3. The same as in Fig. S1 in the range 578–584 nm of the $^5D_0 \rightarrow {}^7F_0$ transition.

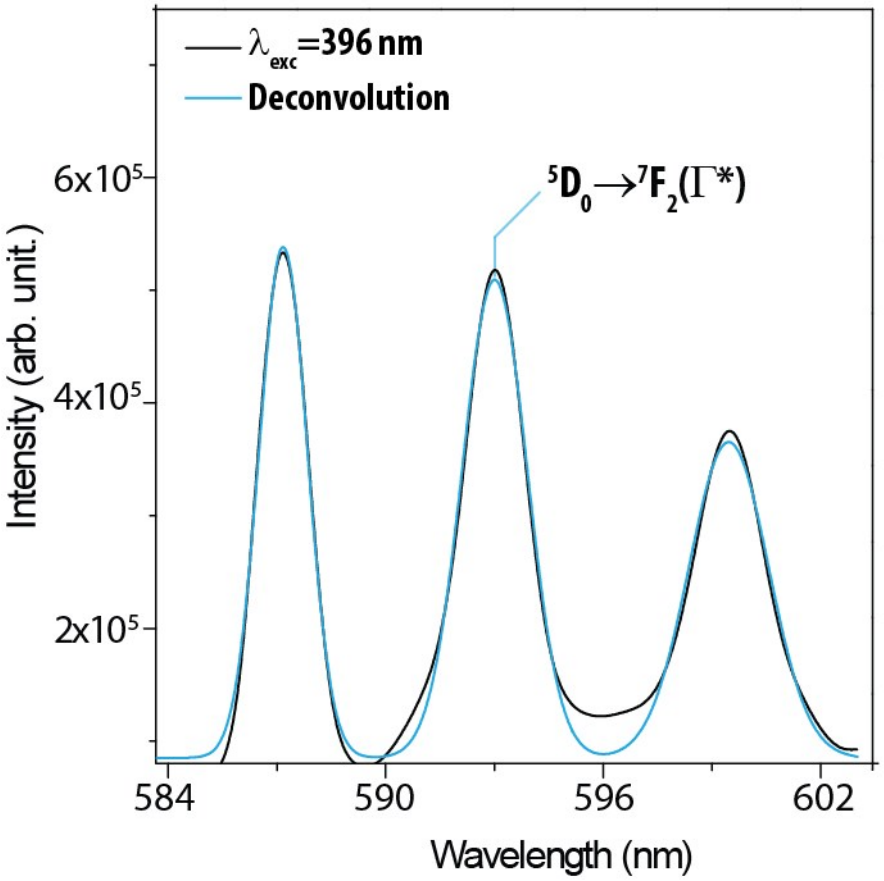

Figure S4. The same as in Fig. S1 in the range 584–602 nm of the $^5D_0 \rightarrow {}^7F_1$ transition.

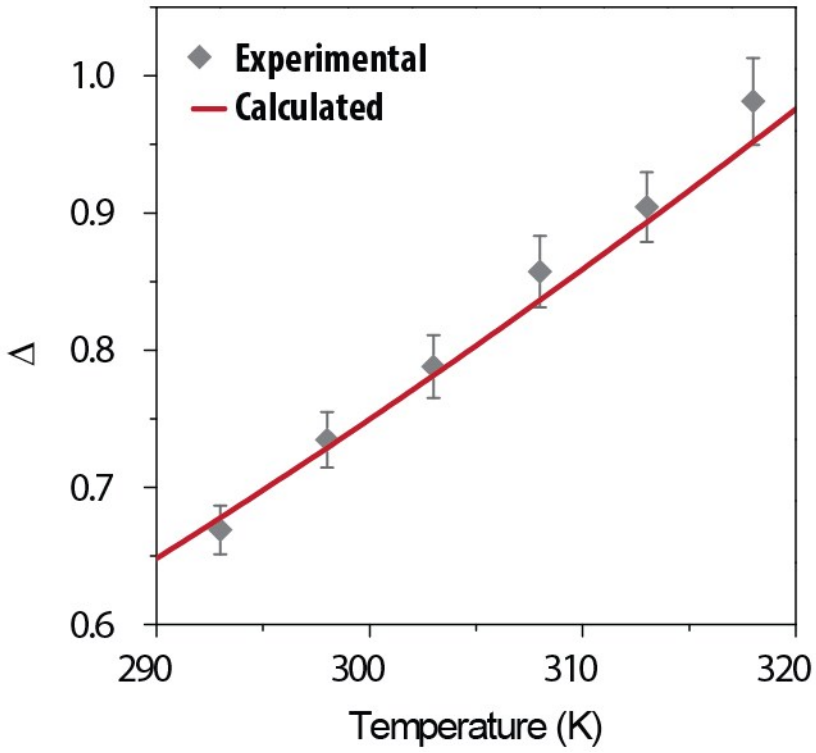

Figure S5: Thermometric parameter for the physiological range using the Y_2O_3:Eu^{3+} microcrystal (exciting at 611 nm). Points are the experimental values of the Δ parameter. The line was obtained from Eq. (12).

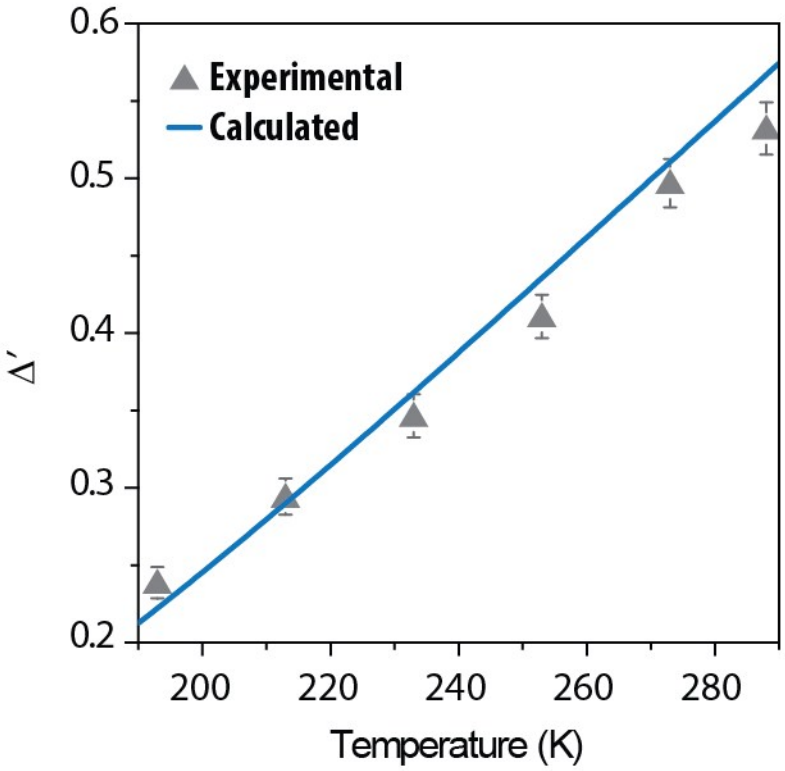

Figure S6: The same as in Fig. S4 for the lower temperature range (exciting at 593 nm, $^7F_1$ (Γ^*) level).

References

1. I. G. N. Silva, L. C. V. Rodrigues, E. R. Souza, J. Kai, M. C. F. C. Felinto, J. Holsa, H. F. Brito and O. L. Malta, *Opt. Mater.*, 2015, **40**, 41-48.