Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C. This journal is © The Royal Society of Chemistry 2020

Supporting Information

Upconversion-mediated Boltzmann Thermometry in Double-Layered Bi₂SiO₅:Yb³⁺,Tm³⁺@SiO₂ Hollow Nanoparticles

Elisa Casagrande,^{a,+} Michele Back,^{a,b,c,+,*} Davide Cristofori,^{a,d} Jumpei Ueda,^b Setsuhisa Tanabe,^b Stefano Palazzolo,^c Flavio Rizzolio,^{a,c} Vincenzo Canzonieri,^c Enrico Trave,^a Pietro Riello^a

^a Department of Molecular Sciences and Nanosystems, Università Ca' Foscari Venezia, Via Torino 155, 30172 Mestre-Venezia, Italy

^b Graduate School of Human and Environmental Studies, Kyoto University, Kyoto 606-8501, Japan

^c Pathology Unit, Centro di Riferimento Oncologico di Aviano (CRO) IRCCS, 33081 Aviano, Italy

^d "Giovanni Stevanato" Centre for Electron Microscopy, Università Ca' Foscari Venezia, Via Torino 155, 30172 Mestre-Venezia, Italy

* Correspondence to: michele.back@unive.it



Figure S1. (a) Diffuse reflectance spectra, of Yb,Tm co-doped Bi₂SiO₅@SiO₂ NPs, respectively, with the Kubelka–Munk function (inset) and (b) bandgap estimation as the intercept of the fitted straight line at F(R)=0 in the $(F(R)\cdot hv)^2$ versus hv plot. Capital letters represent the transitions of Tm³⁺ (A: ${}^{3}F_{4}\rightarrow {}^{1}D_{2}, {}^{3}H_{6}\rightarrow {}^{1}G_{4}, B: {}^{3}F_{4}\rightarrow {}^{1}G_{4}, C: {}^{3}H_{6}\rightarrow {}^{3}F_{2,3}, D: {}^{3}H_{6}\rightarrow {}^{3}H_{4}$).

Compound	S_r (%K ⁻¹)	S _a (K ⁻¹)	Ref.
	Tm^{3+}		
Bi ₂ SiO ₅	1.95	$1.7 \cdot 10^{-2}$	This work
Sr ₂ GdF ₇ (GC) ^a	1.45	9.7·10 ⁻⁴	[1]
YF ₃ (GC)	0.18	$2.2 \cdot 10^{-4}$	[2]
NaYF ₄	0.42	3.8·10 ⁻³	[3]
$YVO_4 ({}^3F_3 - {}^1G_4)$	0.85	$1.4 \cdot 10^{-3}$	[4]
YVO4 (³ F _{2,3} - ³ H ₄)	1.81	6.6.10-4	[4]
Y _{4.67} Si ₃ O ₁₃	2.28	4.1·10 ⁻⁵	[5]
$PbF_2(GC)$	0.26	4.6.10-5	[6]
LaPO ₄	2.86	2.1.10-5	[7]
YPO ₄	2.23	4.2·10 ⁻⁵	[7]
NaYF ₄	0.09	2.4.10-5	[8]

Table S1. Absolute and relative sensitivity (S_a and S_r) at 300 K for a series of Tm³⁺ and Nd³⁺ activated thermometers based on the Boltzmann law.

LiNbO ₃	0.054	$2.5 \cdot 10^{-6}$	[9]
Oxyfluoride GC	0.049	$7.0 \cdot 10^{-6}$	[10]
YAlO ₃ (325 K)	2.62	$2.4 \cdot 10^{-5}$	[11]
YF ₃ :Yb5,Tm	1.48	$4.2 \cdot 10^{-5}$	[12]
YF ₃ :Yb40,Tm	0.30	$4.1 \cdot 10^{-5}$	[12]
NaLuF ₄	2.65	3.6.10-5	[13]
YAlO ₃	1.875	$1.3 \cdot 10^{-4}$	[14]
$SrWO_4$ (³ F_2)	0.69	5.4.10-3	[15]
$SrWO_4$ (3F_3)	0.73	6.1·10 ⁻³	[15]
	Nd^{3+}		
Gd_2O_3	1.42	$4 \cdot 10^{-4}$	[16]
$NaYF_4 (Z)^b$	0.096	8.10-4	[17]
$LaF_{3}(Z)$	0.085	$4.6 \cdot 10^{-4}$	[18]
YAG (Z)	0.15	$1.2 \cdot 10^{-3}$	[19]
YNbO ₄ (Z)	0.28	$1.5 \cdot 10^{-3}$	[20]
LaGaO ₃	1.6	3.10-4	[21]
CaF ₂ :Y,Nd (Z)	0.13	$1.4 \cdot 10^{-3}$	[22]

^a (GC): Glass Ceramic

^b (Z): Thermometer based on the ${}^{4}F_{3/2}$ Stark levels (Z₁-Z₂)

References

- [1] W. P. Chen, J. K. Cao, F. F. Hu, R. F. Wei, L. P. Chen, H. Guo. J. Alloys Compd. 2018, 735, 2544.
- [2] D. Chen, S. Liu, Z. Wan, Y. Chen. J. Alloys Compd. 2016, 672, 380.
- [3] S. Zhou, G. Jiang, X. Li, S. Jiang, X. Wei, Y. Chen, M. Yin, C. Duan. Opt. Lett. 2014, 39, 6687.

[4] P. C. de Sousa Filho, J. Alain, G. Leménager, E. Larquet, J. Fick, O. A. Serra, T. Gacoin. J. Phys. Chem. C 2019, 123, 2441.

- [5] G. Chen, J. Zhang. Opt. Mater. Express 2018, 8, 1841.
- [6] Y. Fu, L. Zhao, Y. Guo, H. Yu. New J. Chem. 2019, 43, 16664.

[7] M. Runowski, A. Shyichuk, A. Tyminski, T. Grzyb, V. Lavin, S. Lis. *ACS Appl. Mater. Interfaces* **2018**, *10*, 17269.

[8] X. Wang, J. Zheng, Y. Xuan, X. Yan. Opt. Express 2013, 21, 21596.

[9] L. Xing, Y. Xu, R. Wang, W. Xu, Z. Zhang. Opt. Lett. 2014, 39, 454.

[10] W. Xu, X. Gao, L. Zheng, Z. Zhang, W. Cao. Sens. Actuator B Chem. 2012, 173, 250.

[11] M. A. Hernandez-Rodriguez, A. D. Lozano-Gorrin, V. Lavin, U. R. Rodriguez-Mendoza, I. R. Martin. *Opt. Express* **2017**, *25*, 27845.

[12] H. Suo, F. Hu, X. Zhao, Z. Zhang, T. Li, C. Duan, M. Yin, C. Guo. J. Mater. Chem. C 2017, 5, 1501.

[13] L. Tong, X. Li, R. Hua, L. Cheng, J. Sun, J. Zhang, S. Xu, H. Zheng, Y. Zhang, B. Chen. *Curr. Appl. Phys.* **2017**, *17*, 999.

[14] L. Garcia-Rodriguez, L. de Sousa-Vieira, M. A. Hernandez-Rodriguez, A. D. Lozano-Gorrin, V. Lavin, U. R. Rodriguez-Mendoza, J. Gonzalez-Platas, S. Rios, I. R. Martin. *Opt. Mater.* 2018, 83, 187.

[15] H. Song, C. Wang, Q. Han, X. Tang, W. Yan, Y. Chen, J. Jiang, T. Liu. Sens. Actuator A Phys. **2018**, 271, 278.

[16] S. Balabhadra, M. L. Debasu, C. D. S. Brites, L. A. O. Nunes, O. L. Malta, J. Rocha, M. Bettinelli, L. D. Carlos. *Nanoscale* 2015, 7, 17261.

[17] D. Wawrzynczyk, A. Bednarkiewicz, M. Nik, W. Strek, M. Samoc. *Nanoscale* **2012**, *4*, 6959-6961.

[18] U. Rocha, C. J. da Silva, W. F. Silva, I. Guedes, A. Banayas, L. Martinez Maestro, M. A. Bovero, F. C. J. M. van Veggel, J. A. Garcia Sole, D. Jaque. *ACS Nano* **2013**, *7*, 1188.

[19] A. Benayas, B. del Rosal, A. Pérez-Delgado, K. Santacruz-Gomez, D. Jaque, G. Alonso Hirata, F. Vetrone. *Adv. Optical Mater.* **2015**, *3*, 687.

[20] Lj. Dacanin Far, S. R. Lukic-Petrovic, V. Dordevic, K. Vukovic, E. Glais, B. Viana, M. D. Dramicanin. *Sens. Actuator A Phys.* **2018**, *270*, 89.

[21] M. Back, J. Ueda, J. Xu, D. Murata, M. G. Brik, S. Tanabe, ACS Appl. Mater. Interfaces 2019, 11, 38937.

[22] P. Cortelletti, C. Facciotti, I. X. Cantarelli, P. Canton, M. Quintanilla, F. Vetrone, A. Speghini, M. Pedroni. *Opt. Mater.* **2017**, *68*, 29.