Supporting information for:

UV-Vis-NIR absorption spectra of lanthanide oxides and fluorides

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Experimental procedure

Deionized water (Milli-Q® purity) was used for all experiments. The lanthanide fluorides were obtained according to our previously reported synthesis protocols.[1–5] In order to prepare lanthanide fluorides (LaF_3, PrF_3, NdF_3, SmF_3, EuF_3, GdF_3, TbF_3, DyF_3, HoF_3, ErF_3, TmF_3, YbF_3), the corresponding commercially available lanthanide oxides (La_2O_3, Pr_6O_{11}, Nd_2O_3, Sm_2O_3, Eu_2O_3, Gd_2O_3, Tb_4O_7, Dy_2O_3, Ho_2O_3, Er_2O_3, Tm_2O_3, Yb_2O_3) were separately dissolved in concentrated HCl (37%, Sigma-Aldrich) to obtain water-soluble lanthanide chlorides, $LnCl_3$ (Ln = La^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Eu^{3+}, Gd^{3+}, Tb^{3+}, Dy^{3+}, Ho^{3+}, Er^{3+}, Tm^{3+}, Yb^{3+}), and then evaporated to remove the excess of acid. CeF_3 was synthesized using commercially available $CeCl_3$ (99.99%; Sigma Aldrich). Synthesis of all LnF_3 was performed for 0.5 g of final products. The appropriate amount of the $LnCl_3$ was mixed with water/ethanol 25/25 mL solvent system. The as-prepared solution was added dropwise to the solution of NH_4F (50% molar excess) previously dissolved in the analogues solvent system (second vessel). When the process was completed, the obtained white precipitate was purified by centrifugation with water 4-times. Afterwards, the precipitate was dispersed in water and transferred to a Teflon-lined vessel, placed in an autoclave and hydrothermally treated at 180°C, for 20 h. The final products were dried overnight in an oven at 80°C, and then ground in an agate mortar for further measurements.

Using the above mentioned method, all lanthanide fluorides (except of YbF_3) were successfully obtained (see Table S1 and Fig. S1). In order to obtain YbF_3 (0.5 g), the appropriate amount of the $YbCl_3$ was mixed with the previously prepared aqueous solution of $NaBF_4$ (50% molar excess). The mixture was stirred for a few minutes. Subsequently, the solution was diluted with water up to 75 mL. Then, HCl solution was added dropwise to adjust the pH of the system to ≈ 1. The as-prepared solution was transferred to a Teflon-lined vessel, placed in an autoclave and hydrothermally treated at 180°C for 20 h. The final product was dried overnight in an oven at 80°C, and then ground in an agate mortar for further measurements.

In order to obtain CeO_2, the chloride precursor - $CeCl_3 * 7H_2O$ (1 g) was placed in a crucible, then transferred into a muffle furnace, and calcined at 500°C for 5 h. After this time, the crucible was removed from the furnace and allowed to cool down. The product was ground in an agate mortar for further measurements.

Table S1 Structural information for the synthesized materials

compound name	crystal system	space group	pattern number - ICDD
LaF_3	hexagonal	P-3c1	01-070-3182
CeF_3	hexagonal	P63/mcm	01-089-1933
PrF_3	hexagonal	P6322	01-072-1437
NdF_3	hexagonal	P-3c1	01-078-1859
SmF_3	hexagonal	P6322	01-072-1439
	*orthorhombic	Pnma	01-074-2176
EuF_3	orthorhombic	Pnma	00-033-0542
GdF_3	orthorhombic	Pnma	00-049-1804
TbF_3	orthorhombic	Pnma	00-037-1487
DyF_3	orthorhombic	Pnma	00-032-0352
HoF_3	orthorhombic	Pnma	01-084-0178
ErF_3	orthorhombic	Pnma	00-032-0361
TmF_3	orthorhombic	Pnma	00-032-1352
YbF_3	orthorhombic	Pnma	00-034-0102
CeO_2	cubic	Fm-3m	00-043-1002

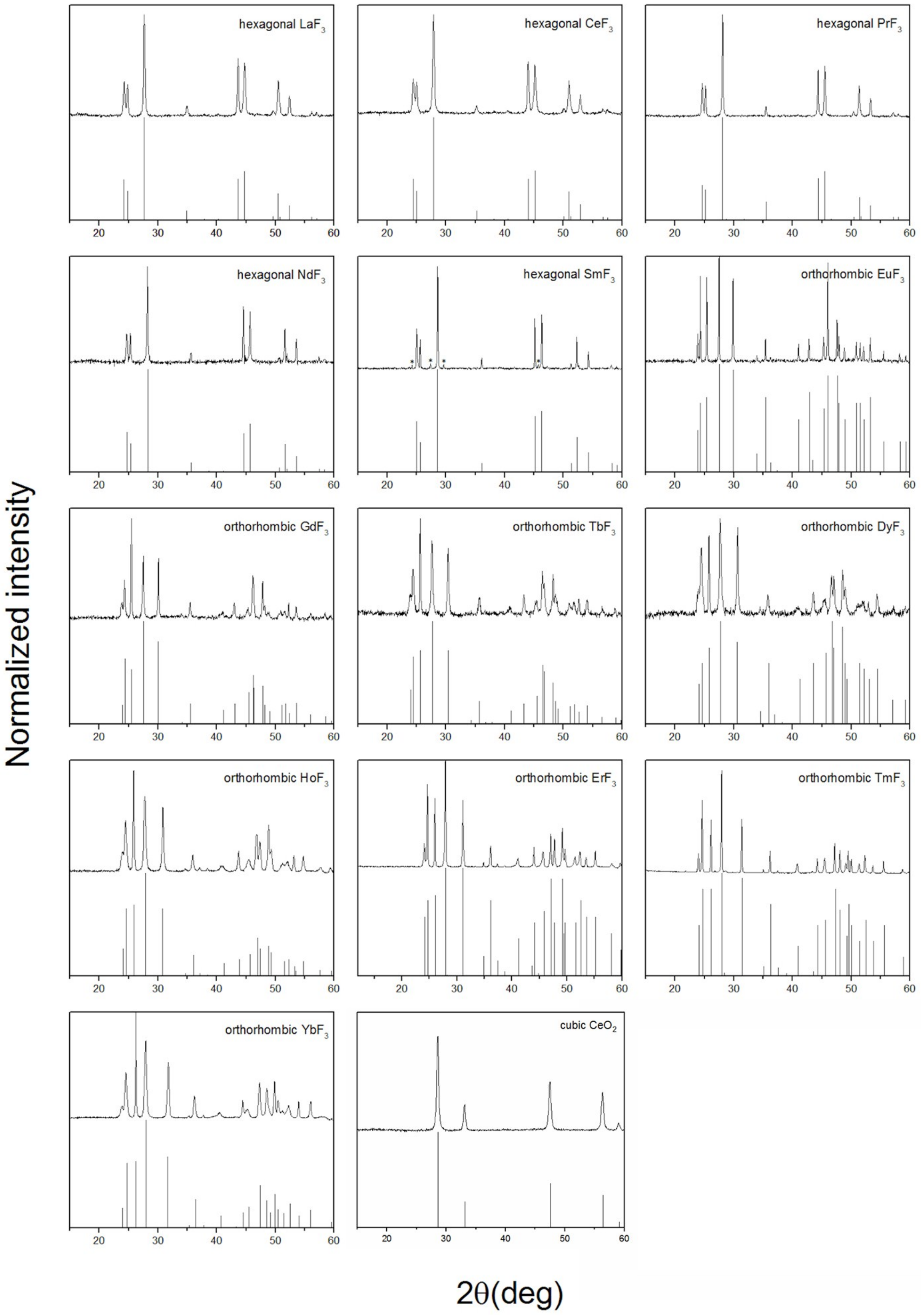

Fig. S1 Powder XRD patterns of the synthesized materials.

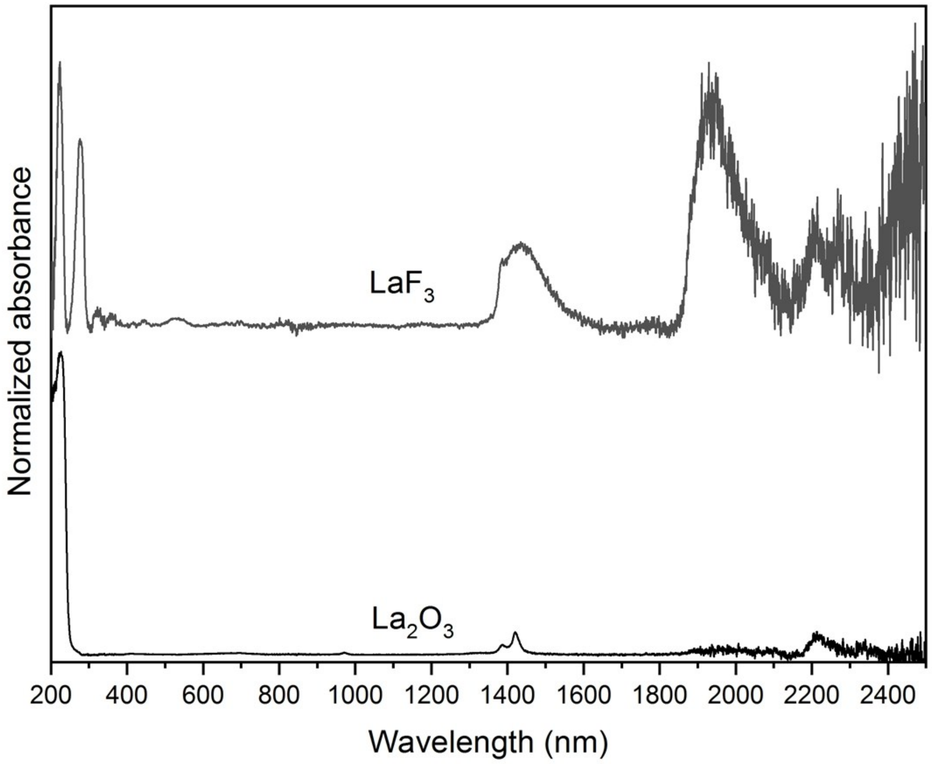

Fig. S2 Normalized absorption spectra of LaF_3 and La_2O_3.

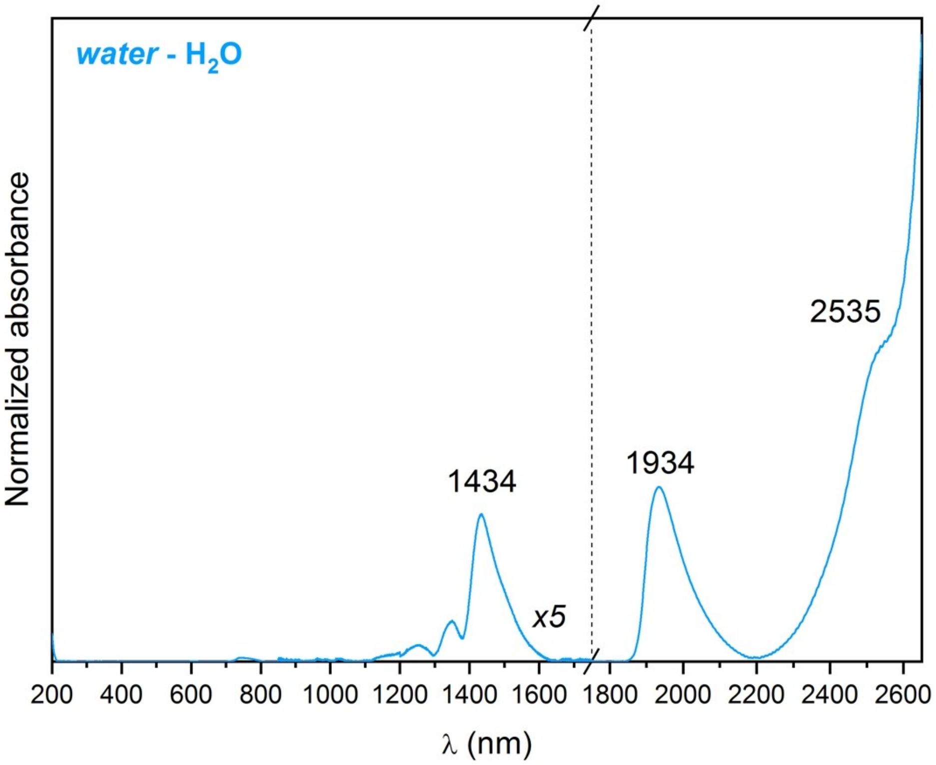

Fig. S3 Normalized absorption spectrum of water.

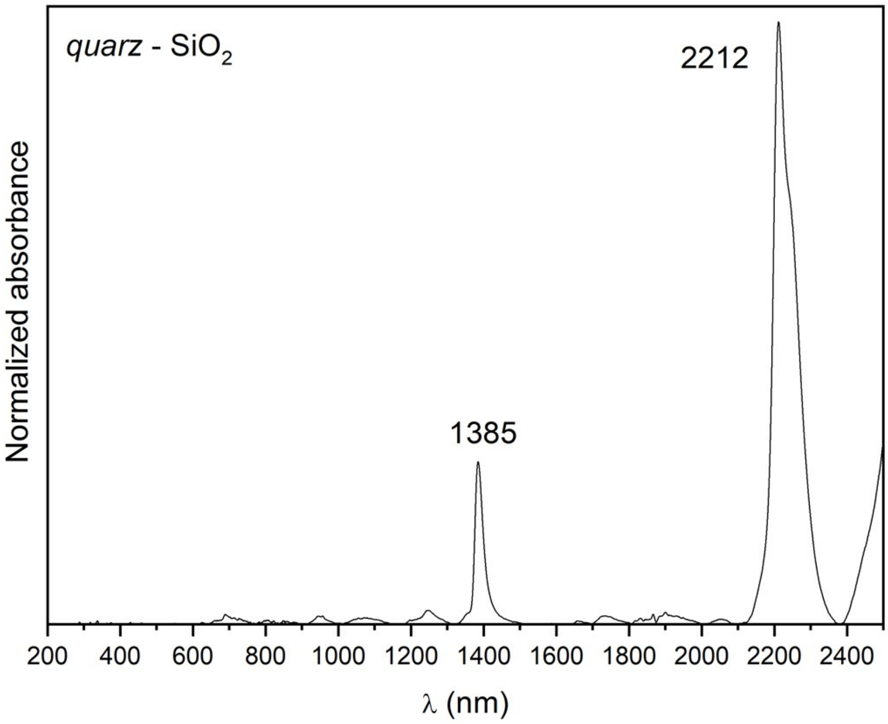

Fig. S4 Normalized absorption spectrum of quartz.

References

[1] M. Runowski, S. Lis, Synthesis of lanthanide doped CeF$_3$:Gd^{3+}, Sm^{3+} nanoparticles, exhibiting altered luminescence after hydrothermal post-treatment, J. Alloy. Compd. 661 (2016) 182–189. https://doi.org/10.1016/j.jallcom.2015.11.182.

[2] T. Grzyb, L. Mrówczyńska, A. Szczeszak, Z. Śniadecki, M. Runowski, B. Idzikowski, S. Lis, Synthesis, characterization, and cytotoxicity in human erythrocytes of multifunctional, magnetic, and luminescent nanocrystalline rare earth fluorides, J. Nanopart. Res. 17 (2015) 399–416. https://doi.org/10.1007/s11051-015-3191-2.

[3] M. Runowski, S. Lis, Preparation and photophysical properties of luminescent nanoparticles based on lanthanide doped fluorides (LaF$_3$:Ce^{3+}, Gd^{3+}, Eu^{3+}), obtained in the presence of different surfactants, J. Alloy. Compd. 597 (2014) 63–71. https://doi.org/10.1016/j.jallcom.2014.01.209.

[4] T. Grzyb, M. Runowski, S. Lis, Facile synthesis, structural and spectroscopic properties of GdF$_3$:Ce^{3+}, Ln^{3+} (Ln^{3+}=Sm^{3+}, Eu^{3+}, Tb^{3+}, Dy^{3+}) nanocrystals with bright multicolor luminescence, J. Lumin. 154 (2014) 479–486. https://doi.org/10.1016/j.jlumin.2014.05.020.

[5] T. Grzyb, M. Runowski, A. Szczeszak, S. Lis, Structural, morphological and spectroscopic properties of Eu^{3+}-doped rare earth fluorides synthesized by the hydrothermalmethod, J. Solid State Chem. 200 (2013) 76–83. https://doi.org/10.1016/j.jssc.2013.01.012.