Supplementary Information File

Color Tunable Luminescence in ThO_2: Er^{3+}, Yb^{3+} Nanocrystals: A Promising New Platform for Upconversion

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S1. Computational Details

Density functional theory (DFT) calculations with spin polarized condition have been carried out with Vienna ab initio simulation package (VASP) with projector augmented wave (PAW) pseudo potentials.[1,2] Perdew-Burke-Ernzerhof (PBE) functional under generalized gradient approximation (GGA) has been considered during geometry optimization processes by relaxing ionic positions, cell parameter, and cell volume.[3] Electronic structure calculations were carried out with the optimized geometries. An energy cut off value of 500 eV has been chosen with self-consistent energy convergence criteria of 10^{-6}eV. Monkhorst and Pack scheme has been employed for sampling of Brillouin zone using Γ-centered k-point mesh value of 16 × 16 × 16.[4] We have employed hybrid DFT functional of the type Heyd, Scuseria, and Ernzerhof (HSE) for electronic structure calculations for more accurate calculation of the band gap,[5] and the corresponding exchange-correlation energy (E_{XC}^{HSE}) is expressed as

$$E_{XC}^{HSE} = \alpha\, E_X^{SR}(\mu) + (1-\alpha)\, E_X^{PBE,\,SR}(\mu) + E_X^{PBE,\,LR}(\mu) + E_C^{PBE} \qquad (1)$$

where, SR and LR indicate the electron-electron interaction energy at short-range and long-range, respectively. $'\alpha'$ and $'\mu'$ are the mixing coefficient (20 % of mixing exact exchange) and screening parameter (0.2 $Å^{-1}$), respectively. For phonon calculations of ThO_2, the finite displacement method was chosen as implemented in the PHONOPY program.[6] In this method, first, perturbed cells containing 96 atoms (2 × 2 × 2 supercell) were created by displacing atoms from their equilibrium positions. Then, the forces acting on the displaced atoms were calculated using a k-point mesh of 7 × 7 × 7 within GGA. The force constant matrix was generated from the obtained force set and used to calculate the phonon dispersion plot.

S2. Crystallite size from powder X-ray diffraction

From powder X-ray diffraction patterns, the crystallite sizes (d) were calculated using Debye Scherrer equation:

$$d = \frac{k\lambda}{\sqrt{(B_S{}^2 - B_M{}^2)\cos\theta}} \quad (2)$$

Here k is the Scherrer constant (0.9), λ is the wavelength of Cu-Kα line (1.5406 Å), and θ is the angle corresponding to the Bragg reflection used for calculating the FWHM. B_S and B_M are the FWHM value (in radian) of the selected diffraction peaks of sample and reference (LaB_6). The FWHM has been calculated by fitting the curve to a Gaussian function. The instrumental broadening has been considered by subtracting the contribution from the standard LaB_6.

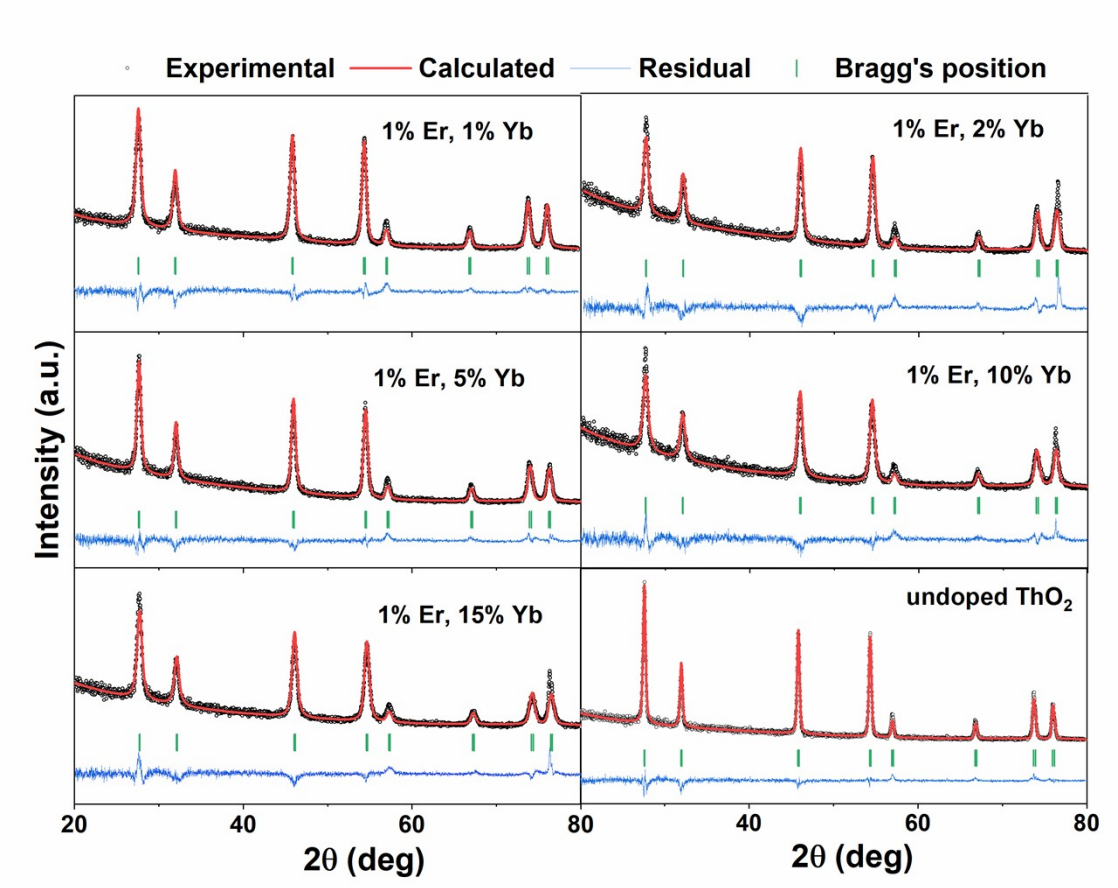

Figure S1. Rietveld refinement of the XRD spectra of ThO_2:1%Er^{3+},x%Yb^{3+} Nanophopshor (x=1, 2, 5, 10 and 15)

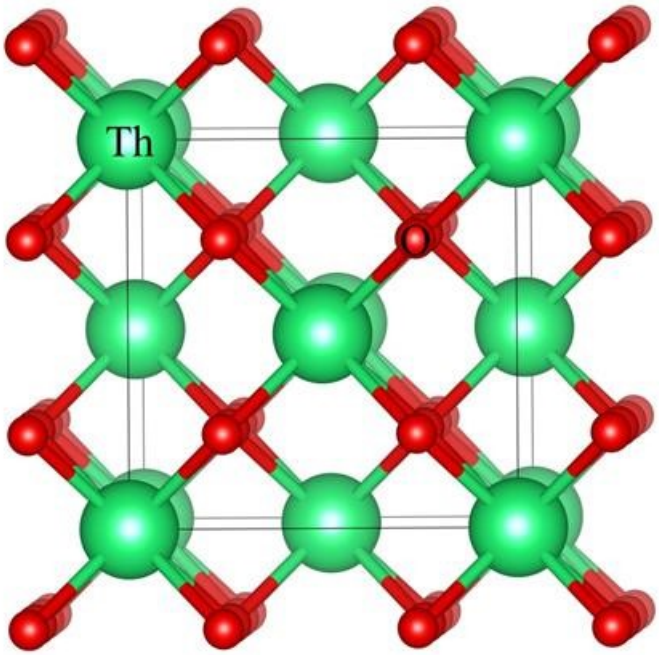

Figure S2. Crystal structure of ThO_2.

Table S1. Parameters from Rietveld refinement of the XRD patterns of ThO_2:1%Er^{3+}, x%Yb^{3+} Nanophopshor (x=1, 3, 5, 10 and 15)

Sample	Fit Parameters	Lattice Parameters (Å)	Lattice Volume ($Å^3$)
Undoped ThO_2	R_p = 4.94 ; R_{wp} = 6.14 R_{exp} = 3.98 ; χ^2 = 2.38	5.5984(1)	175.46(1)
ThO_2: 1% Er, 1% Yb	Rp = 4.75; R_{wp} = 5.89 R_{exp} = 3.68; χ^2 = 2.57	5.5990(1)	175.52(1)
ThO_2: 1% Er, 2% Yb	R_p = 5.80 ; R_{wp} = 8.76 R_{exp} = 4.09 ; χ^2 = 4.59	5.5765(6)	173.41(2)
ThO_2: 1% Er, 5% Yb	R_p = 4.49; R_{wp} = 5.70 R_{exp} = 3.89 ; χ^2 = 2.15	5.5837(1)	174.09(1)
ThO_2: 1% Er, 10% Yb	R_p = 5.53; R_{wp} = 7.22 R_{exp} = 4.72; χ^2 = 2.34	5.5824(2)	173.96(1)
ThO_2: 1% Er, 15% Yb	R_p = 5.20 ; R_{wp} = 7.28 R_{exp} = 4.08 ;χ^2 = 3.18	5.5691(2)	172.72(1)

Table S2: Color coordinates values extracted from corrected UC emission spectra of ThO_2:1%Er^{3+}, x%Yb^{3+}nanophopshor(x=1, 3,5,10 and 15).

Sample	x	y
ThO_2-1%Er, 1%Yb	0.28034	0.70107
ThO_2-1%Er, 2%Yb	0.27558	0.70495
ThO_2-1%Er, 5%Yb	0.28373	0.69228
ThO_2-1%Er, 10%Yb	0.32902	0.64789
ThO_2-1%Er, 15%Yb	0.44734	0.53602

Table S3: UCL lifetime values extracted from corrected decay curve after bi-exponential fitting of ThO_2:1%Er^{3+}, x%Yb^{3+}Nanophopshor (x=1, 3,5,10 and 15).

Sample	T_1(µs)	T_2(µs)	Population of T_1 (%)	Population of T_2 (%)
ThO_2-1Er, 1Yb	236.9	514.7	54.75	45.25
ThO_2-1Er, 2Yb	247.2	523.7	44.41	55.59
ThO_2-1Er, 5Yb	46.7	232.3	47.14	52.86
ThO_2-1Er, 10Yb	24.5	107.1	67.96	32.04
ThO_2-1Er, 15Yb	23.3	57.8	64.19	35.81

S3. References

1. Blöchl, P. E., Projector augmented-wave method. *Physical Review B* **1994,** 50, (24), 17953.
2. Kresse, G.; Joubert, D., From ultrasoft pseudopotentials to the projector augmented-wave method. *Physical Review B* **1999,** 59, (3), 1758.
3. Perdew, J. P.; Burke, K.; Ernzerhof, M., Generalized gradient approximation made simple. *Physical review letters* **1996,** 77, (18), 3865.
4. Monkhorst, H. J.; Pack, J. D., Special points for Brillouin-zone integrations. *Physical Review B* **1976,** 13, (12), 5188.
5. Paier, J.; Marsman, M.; Hummer, K.; Kresse, G.; Gerber, I. C.; Ángyán, J. G., Screened hybrid density functionals applied to solids. *The Journal of chemical physics* **2006,** 124, (15), 154709.
6. Togo, A.; Oba, F.; Tanaka, I., First-principles calculations of the ferroelastic transition between rutile-type and $CaCl_2$-type SiO_2 at high pressures. *Physical Review B* **2008,** 78, (13), 134106.