Electronic Supplementary Information

Lanthanide-activated scheelite nanocrystal phosphors prepared by the low-temperature vapor diffusion sol–gel method

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Experimental

General Considerations. All manipulations were conducted under a nitrogen atmosphere at ambient pressure using standard Schlenk techniques. $W(OEt)_6$ (Et = CH_2CH_3) and $Tm(acac)_3$ (acac = acetylacetonate, $C_5H_7O_2$) from Alfa Aesar, $Eu(acac)_3$ and $Tb(acac)_3$ from Sigma Aldrich, and an alcoholic solution of $Ca(OCH_2CH_2OCH_3)_2$ (20 wt% in methoxyethanol) from Gelest, Inc. were used as precursors. Methoxyethanol was purchased from Sigma Aldrich. All reagents were used as received.

Nanocrystal Synthesis. Lanthanide (Ln)-doped $CaWO_4$ nanocrystals were synthesized via a vapor diffusion sol–gel method described in detail elsewhere.[1,2] Briefly, a rotameter controls the flow of the nitrogen carrier gas through a glass bubbler filled with 0.75 M aqueous HCl, connected via Tygon tubing to a 100 mL, 3-neck round bottom flask containing the precursor solution. In a typical synthesis, 454 mg (1.0 mmol) $W(OEt)_6$ and the appropriate mass of $Ln(acac)_3$ (e.g., 4.5 mg $Eu(acac)_3$ (0.01 mmol) were employed for the synthesis of nominal $CaWO_4$:1%Eu) were added to 1.0 mL (1.0 mmol) $Ca(OCH_2CH_2OCH_3)_2$. The resulting mixture was diluted to 2.0 mL total volume with methoxyethanol and stirred at 80 °C under flowing dry

nitrogen for 2 h, after which complete dissolution of the reagents was observed. Once cooled, the solution was exposed to a controlled flow of water vapor for 48 h at room temperature and atmospheric pressure. Diffusion of water vapor into the solution resulted in the formation of a cracked gel, which was subsequently aged under a nitrogen atmosphere for 24 h at 60 °C. The resulting gel was collected, washed with absolute ethanol (3 × 10 mL), and vacuum dried at room temperature to recover an off-white fine powder consisting of $CaWO_4$:Ln nanocrystals.

Thermogravimetric Analysis (TGA). TGA analyses were performed using a thermogravimetric analyzer TA Q50 (TA Instruments) under a high-purity air flow (60 mL min^{-1}). Samples were heated from 25 to 600 °C at a linear rate of 15 °C min^{-1} and held isothermal for 15 min.

Powder X-ray Diffraction (XRD). XRD patterns were collected in the 10–80° 2θ range using a Rigaku Ultima IV diffractometer operated at 44 mA and 40 kV. Cu Kα radiation (λ = 1.5406 Å) was employed. The step size and collection time were 0.0075° and 5 s per step, respectively. All diffraction patterns were recorded under ambient conditions.

Rietveld Analysis. Rietveld structural refinements were carried out using the General Structure Analysis System (GSAS) software.[3,4] The average crystal structure of AWO_4 nanocrystals was refined with the tetragonal $I4_1/a$ (no. 88) space group. The following parameters were refined: (1) scale factor, (2) background, which was modeled using a shifted Chebyschev polynomial function, (3) peak shape, which was modeled using a modified Thomson–Cox–Hasting pseudo-Voight function,[5] (4) lattice constants (a and c), (5) fractional atomic coordinates of the oxygen atom (x_O, y_O, z_O), and (6) an isotropic thermal parameter for each chemical species (i.e., U_A, U_W, and U_O). The usual R_{wp} and χ^2 indicators were employed to assess the quality of the refined structural models.[6]

Transmission Electron Microscopy (TEM). TEM images were obtained using a JEOL JEM2100F (JEOL Ltd.) electron microscope operating at 200 kV. Samples for TEM studies were prepared by drop-casting a stable suspension of nanocrystals in ethanol on a 400 mesh Cu grid coated with a lacey carbon film (Ted Pella, Inc.).

Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP-AES). Elemental analyses were conducted at Galbraith Laboratories (Knoxville, TN).

Spectrofluorometry. Excitation and emission spectra of $CaWO_4$:Ln powders were recorded using a Horiba Nanolog spectrofluorometer equipped with a 450 W Xe lamp as the excitation source using slit widths of 4 nm and a photomultiplier tube as the detector. PL lifetime measurements were performed on a Photon Technology International QuantaMaster Model C-60 spectrofluorometer equipped with a Xe flash lamp as the excitation source. Lifetimes for the $CaWO_4$:Eu and $CaWO_4$:Tb nanocrystals were well fit with a monoexponential function and the $CaWO_4$:Tm nanocrystals were fit with a biexponential (the longer lifetime, associated with the lanthanide was reported). All spectra were collected under ambient conditions.

References

1. F. A. Rabuffetti and R. L. Brutchey, *Chem. Mater.*, 2011, **23**, 4063.
2. S. P. Culver, F. A. Rabuffetti, S. Zhou, M. Mecklenburg, Y. Song, B. C. Melot and R. L. Brutchey, *Chem. Mater.*, 2013, **25**, 4129.
3. A. C. Larson and R. B. Von Dreele, *General Structure Analysis System (GSAS)*, Los Alamos National Laboratory: Los Alamos, NM, 2000.
4. B. H. Toby, *J. Appl. Crystallogr.*, 2011, **34**, 210.
5. P. Thompson, D. E. Cox and J. M. Hastings, *J. Appl. Crystallogr.*, 1987, **20**, 79.
6. R. A. Young, *The Rietveld Method*, Oxford University Press: New York, 1993.

Figures and Tables

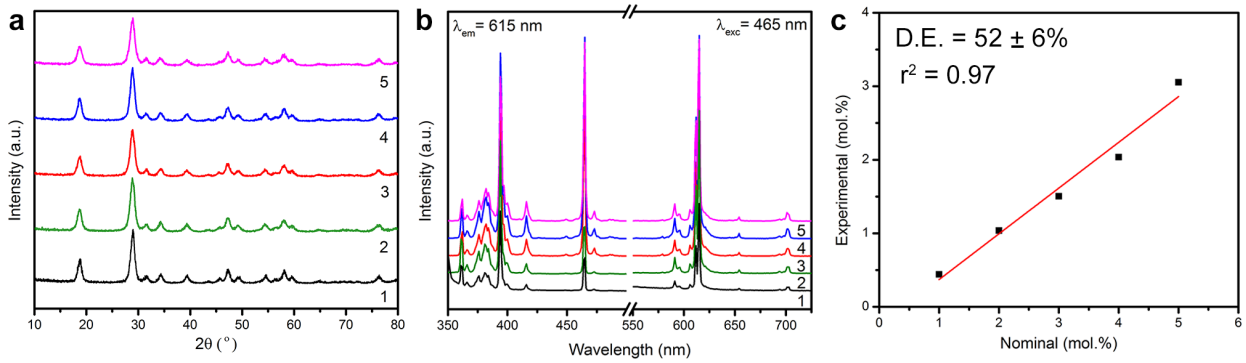

Fig. S1 (a) XRD, (b) PL, and (c) ICP results for 1–5 mol.% $CaWO_4$:Ln nanocrystals.

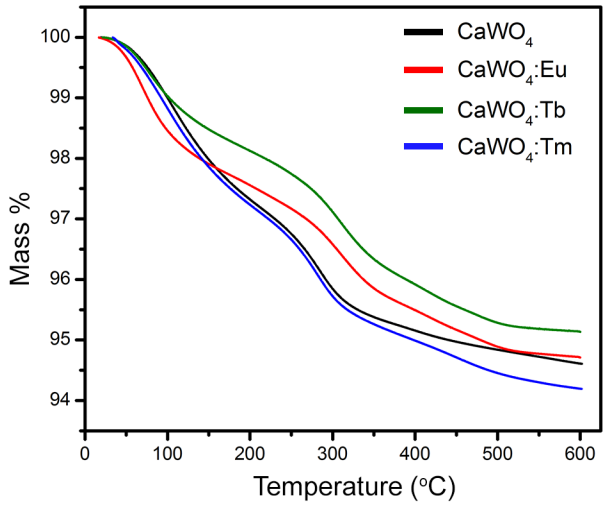

Fig. S2 TGA thermograms for undoped and $CaWO_4$:Ln nanocrystals.

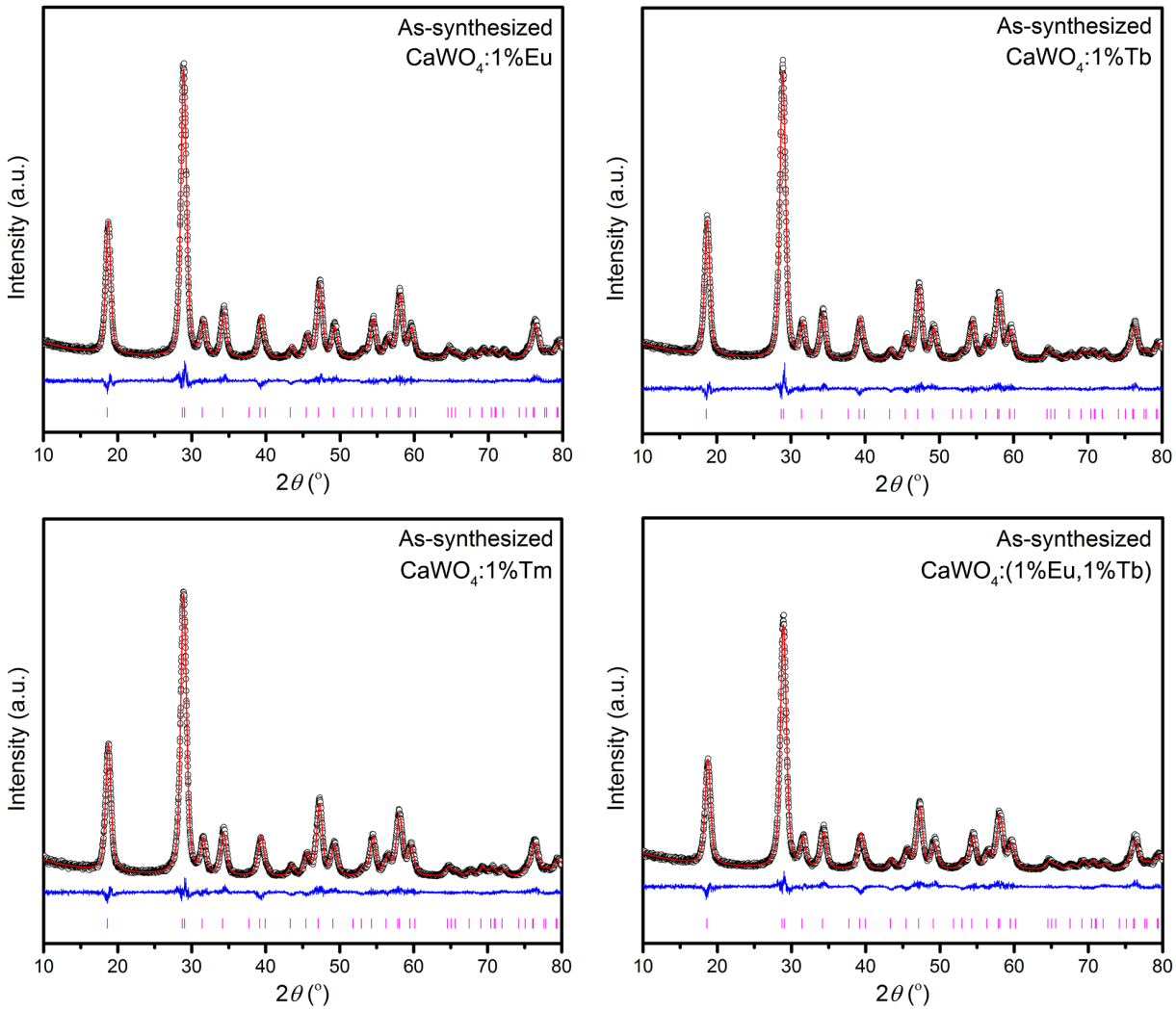

Fig. S3 Rietveld analysis of powder XRD patterns for the as-synthesized $CaWO_4$:Ln nanocrystals. Experimental (○) and calculated (—) patterns are shown, along with the difference curve (—). Tickmarks (|) corresponding to the phase refined are provided.

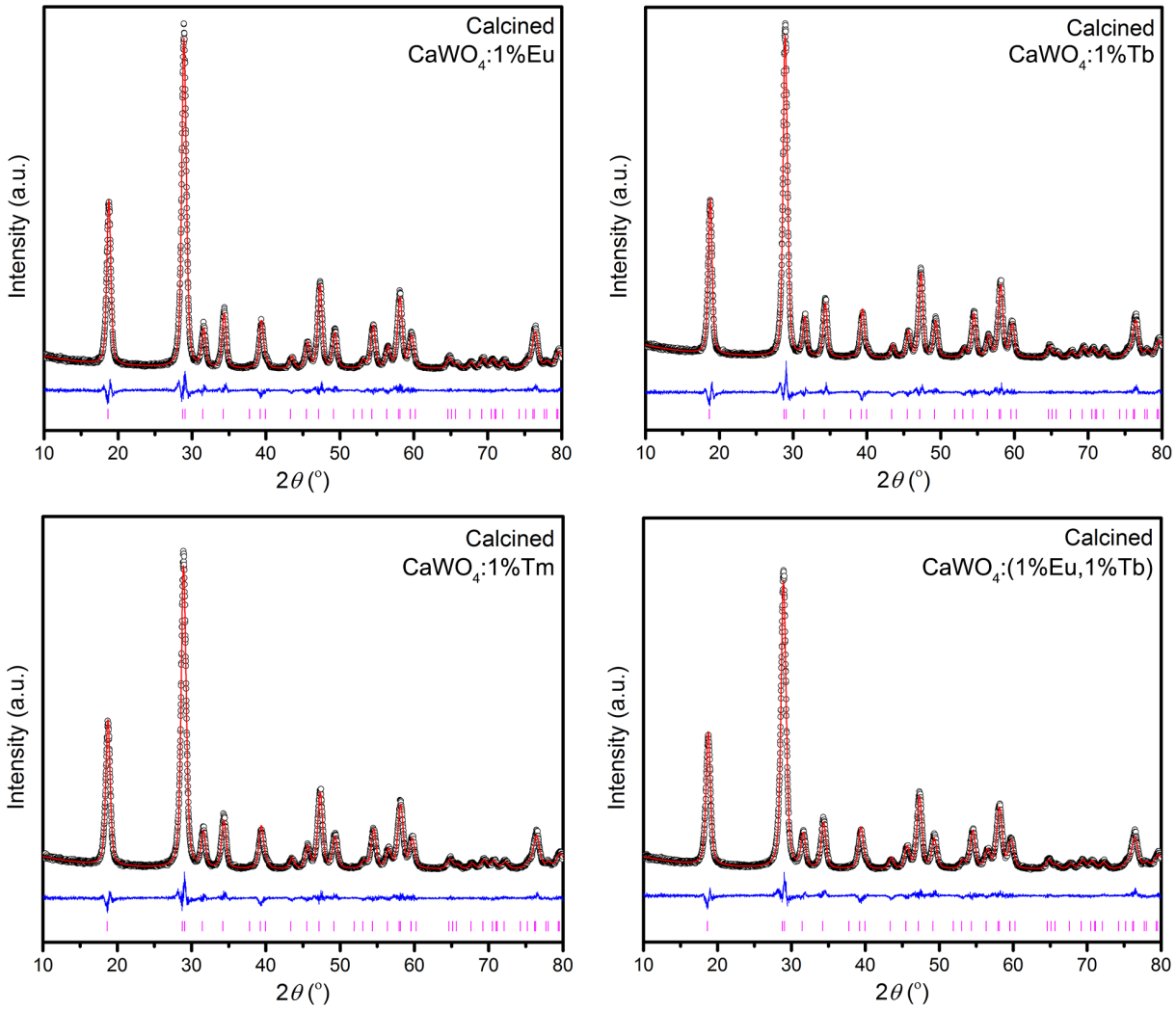

Fig. S4 Rietveld analysis of powder XRD patterns for the calcined $CaWO_4$:Ln nanocrystals. Experimental (○) and calculated (—) patterns are shown, along with the difference curve (—). Tickmarks (|) corresponding to the phase refined are provided.

Table S1 Structural Parameters of As-synthesized Ln-Doped $CaWO_4$ Nanocrystals

	$CaWO_4$	$CaWO_4$:1%Eu	$CaWO_4$:1%Tb	$CaWO_4$:1%Tm	$CaWO_4$:(1%Eu,1%Tb)
a (Å)	5.248(1)	5.245(1)	5.246(1)	5.246(1)	5.244(2)
c (Å)	11.390(3)	11.381(3)	11.384(3)	11.378(3)	11.378(4)
V (Å^3)	313.6(2)	313.1(2)	313.3(2)	313.1(2)	312.9(3)
x_O	0.6543(8)	0.6567(9)	0.6554(9)	0.6604(10)	0.6608(11)
y_O	0.4969(7)	0.4906(7)	0.4948(7)	0.4908(7)	0.4816(8)
z_O	0.2097(3)	0.2109(4)	0.2103(4)	0.2110(4)	0.2116(4)
U_{Ca} (Å^2)[a]	0.46	0.97	0.86	1.30	1.53
U_W (Å^2)	1.51	0.96	1.05	0.89	0.74
U_O (Å^2)	0.99	1.17	0.89	1.40	1.59
A–O (1) (Å)	2.425(4)	2.399(4)	2.414(4)	2.392(5)	2.369(6)
A–O (2) (Å)	2.429(4)	2.406(5)	2.421(5)	2.406(5)	2.375(5)
W–O (Å)	1.830(3)	1.866(4)	1.844(4)	1.875(4)	1.914(4)
V_{AO_8} (Å^3)	25.39	24.60	25.08	24.43	23.58
V_{WoO_4} (Å^3)	3.11	3.29	3.18	3.33	3.54
R_{wp}	7.09	7.65	7.49	7.65	8.42
χ^2	1.42	1.48	1.43	1.51	1.68

[a] Atomic displacements parameters are given as $100\times U^{ij}$.

Table S2 Structural Parameters of Calcined Ln-Doped $CaWO_4$ Nanocrystals

	$CaWO_4$	$CaWO_4$:1%Eu	$CaWO_4$:1%Tb	$CaWO_4$:1%Tm	$CaWO_4$:(1%Eu,1%Tb)
a (Å)	5.240(1)	5.240(1)	5.239(1)	5.238(1)	5.239(1)
c (Å)	11.378(2)	11.373(2)	11.370(2)	11.368(2)	11.367(3)
V (Å^3)	312.5(2)	312.2(2)	312.0(2)	311.8(2)	312.0(2)
x_O	0.6531(9)	0.6518(9)	0.6556(9)	0.6525(8)	0.6541(9)
y_O	0.5028(8)	0.4998(7)	0.4957(8)	0.4944(7)	0.4890(7)
z_O	0.2108(4)	0.2108(4)	0.2105(4)	0.2106(3)	0.2115(4)
U_{Ca} (Å^2)[a]	0.33	0.92	0.83	0.61	0.95
U_W (Å^2)	0.92	1.21	0.90	1.27	1.13
U_O (Å^2)	0.96	0.67	1.36	0.33	1.19
A–O (1) (Å)	2.427(4)	2.415(4)	2.413(4)	2.401(4)	2.382(4)
A–O (2) (Å)	2.452(5)	2.448(4)	2.420(5)	2.429(4)	2.412(5)
W–O (Å)	1.810(4)	1.818(4)	1.839(4)	1.838(3)	1.867(4)
V_{AO_8} (Å^3)	25.77	25.55	25.03	25.04	24.45
V_{WoO_4} (Å^3)	3.02	3.06	3.16	3.15	3.30
R_{wp}	8.25	8.10	8.73	7.83	8.07
χ^2	1.55	1.75	1.99	1.66	1.75

[a] Atomic displacements parameters are given as $100\times U^{ij}$.

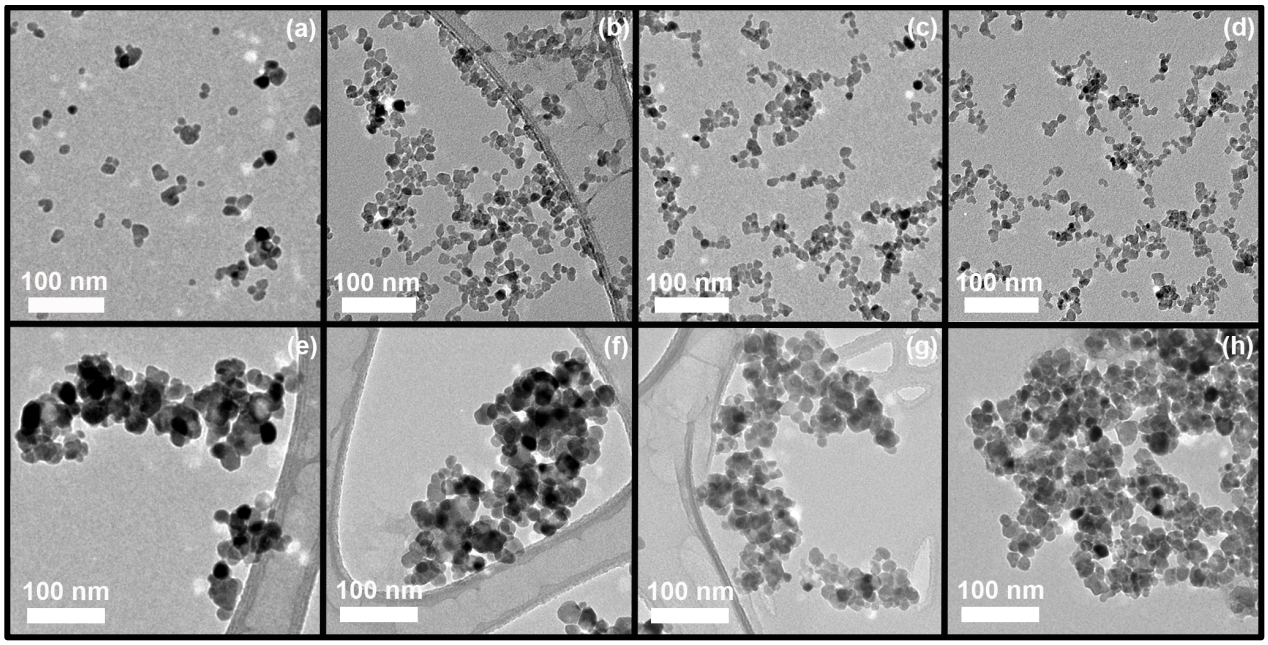

Fig. S5 TEM images of the as-synthesized (a) $CaWO_4$, (b) $CaWO_4$:1%Tb, (c) $CaWO_4$:1%Tm, and (d) $CaWO_4$:(1%Eu,1%Tb) and calcined (d) $CaWO_4$, (e) $CaWO_4$:1%Tb, (f) $CaWO_4$:1%Tm, and (g) $CaWO_4$:(1%Eu,1%Tb) nanocrystals.

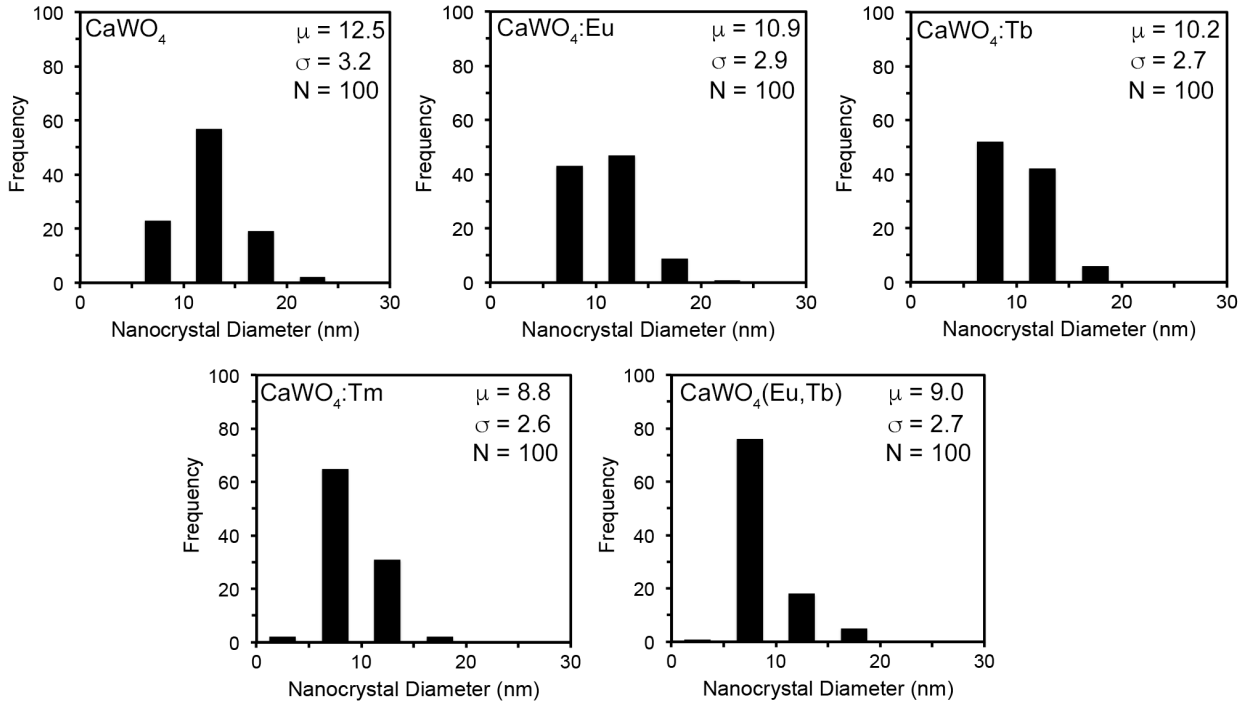

Fig. S6 Nanocrystal size distribution histograms for the as-synthesized $CaWO_4$:Ln nanocrystals. The total number of nanocrystals counted (N), mean diameter (μ) in nm, and standard deviation (σ) in nm are indicated.

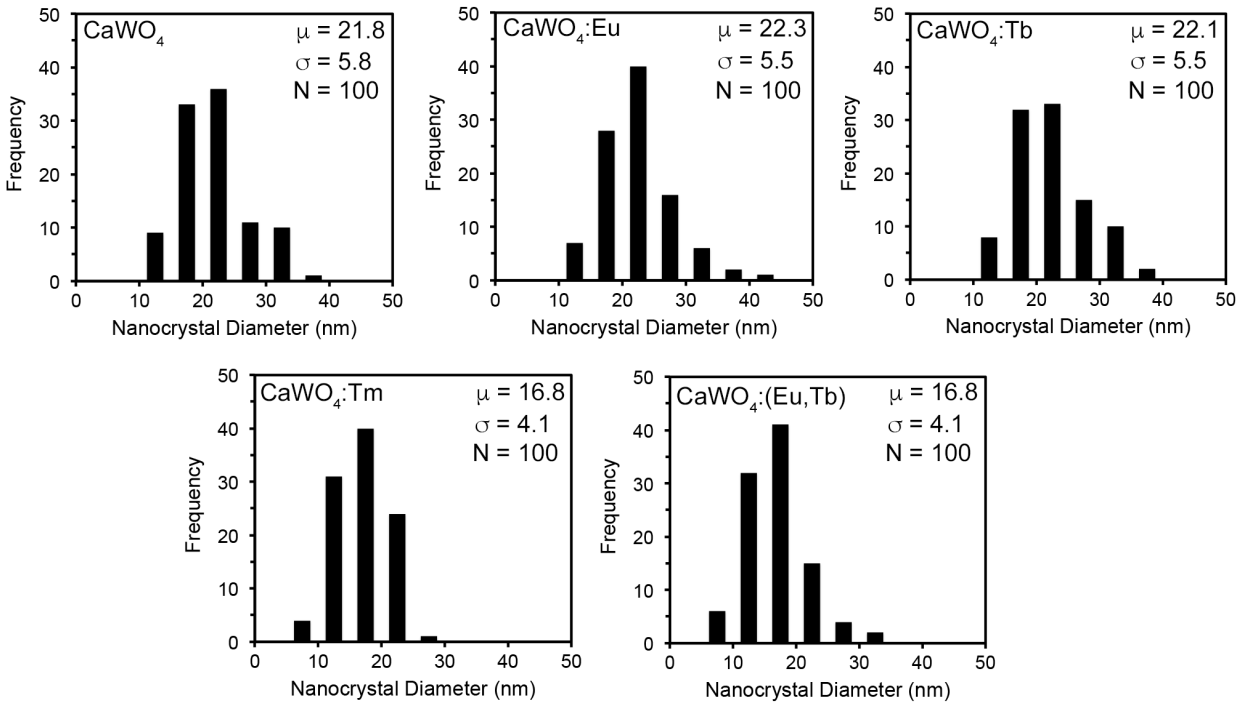

Fig. S7 Nanocrystal size distribution histograms for the calcined $CaWO_4$:Ln nanocrystals. The total number of nanocrystals counted (N), mean diameter (μ) in nm, and standard deviation (σ) in nm are indicated.

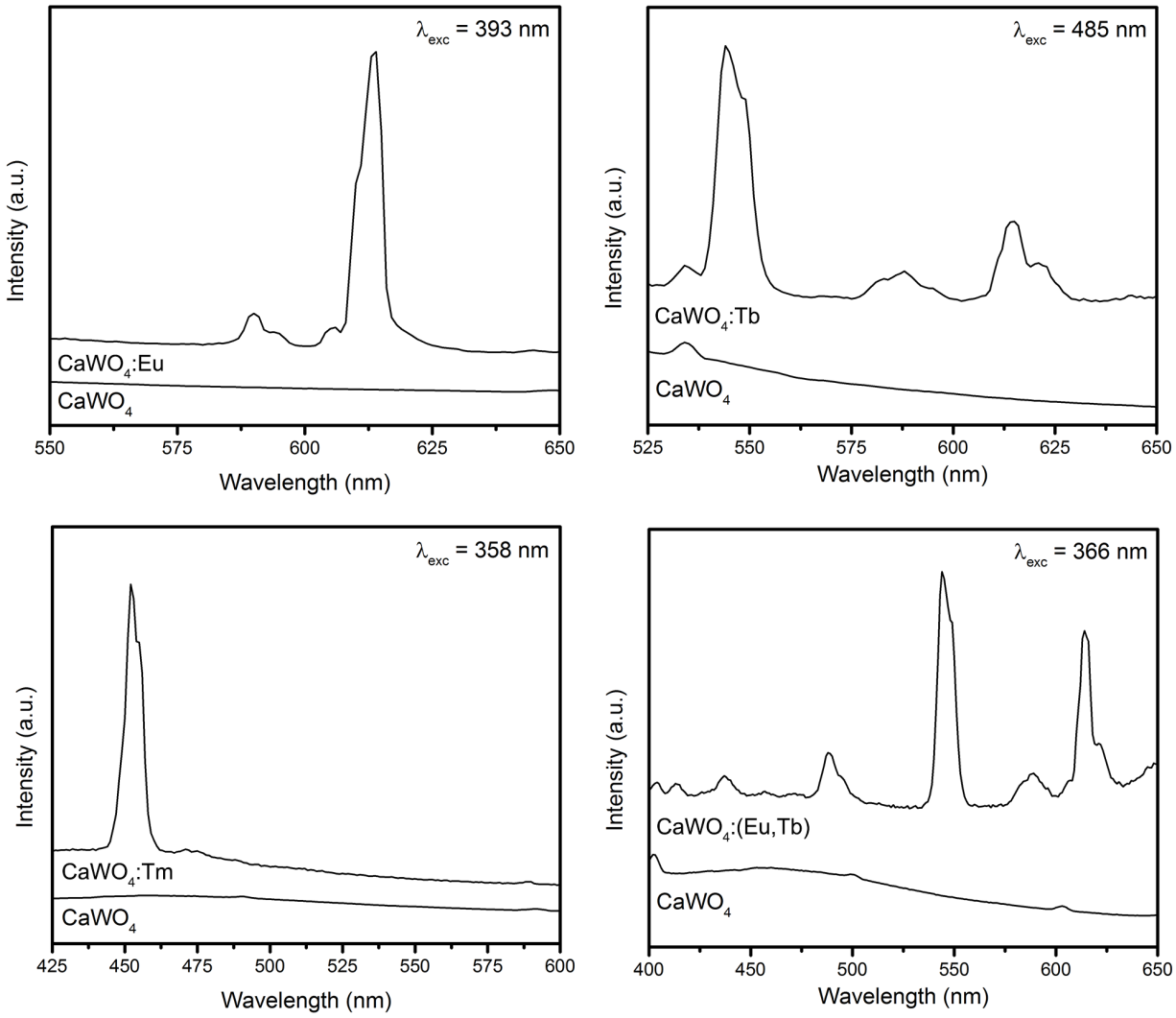

Fig. S8 Room temperature emission spectra for calcined $CaWO_4$ nanocrystals at the relevant excitation wavelengths. The room temperature emission spectra for the calcined $CaWO_4$:Ln nanocrystals are also provided.

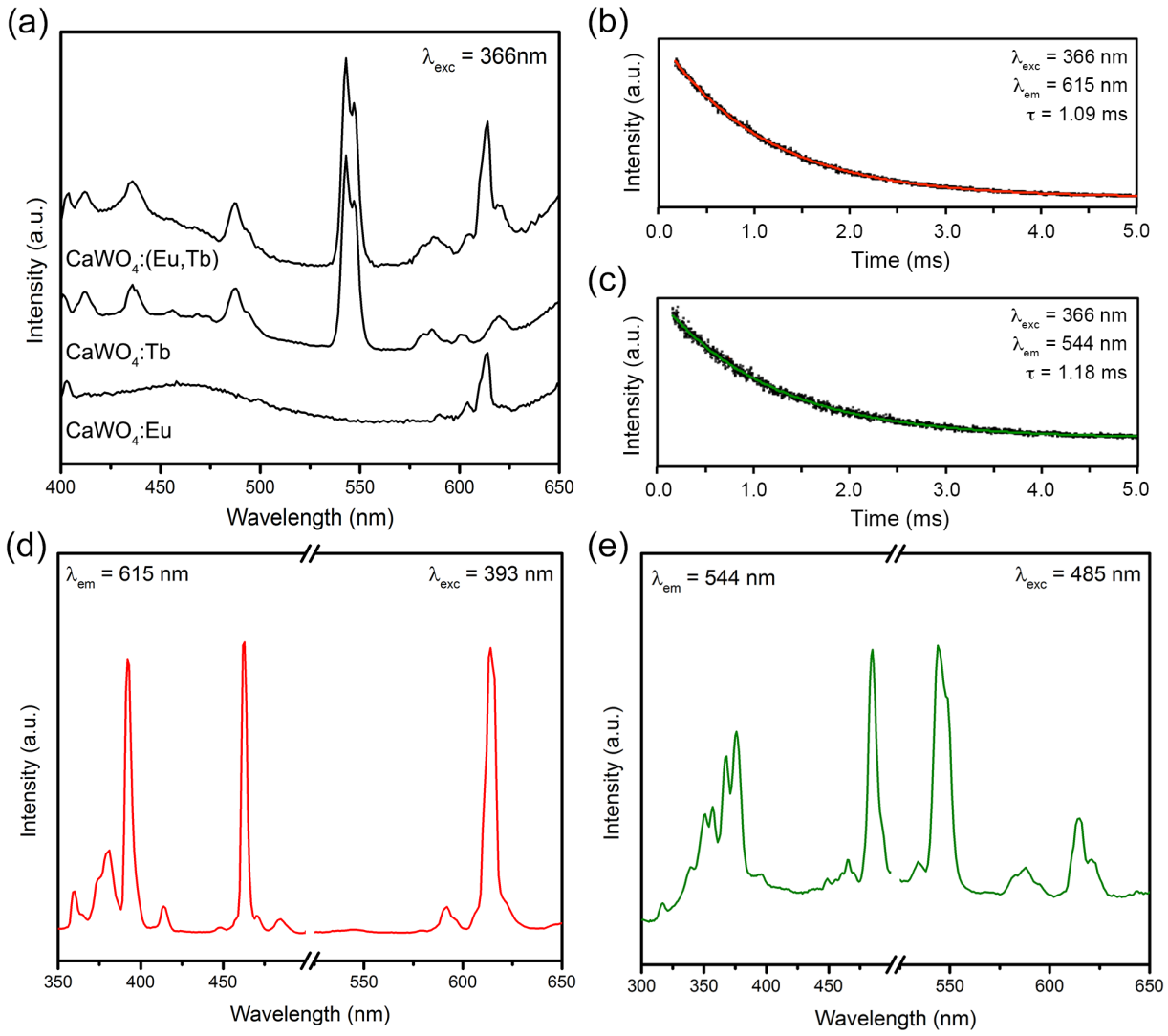

Fig. S9 (a) Room temperature emission spectra for calcined $CaWO_4$:1%Eu, $CaWO_4$:1%Tb, and $CaWO_4$:(1%Eu,1%Tb) nanocrystals upon excitation at 366 nm. Photoluminescence decay curves for $CaWO_4$:(1%Eu,1%Tb) nanocrystals monitored at (b) 615 and (c) 544 nm. The associated excitation and emission wavelengths, and lifetimes (τ) are also provided. Room temperature emission spectra for $CaWO_4$:(1%Eu,1%Tb) nanocrystals upon excitation at (d) 393 and (e) 485 nm.