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Electronic Supplementary Information

Local structural investigation of Eu^{3+}-doped $BaTiO_3$ nanocrystals

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EXPERIMENTAL

Synthesis of Eu:BaTiO$_3$ Nanocrystals. xEu:BaTiO$_3$ (x = 0, 1, 2, 3, 4, and 5 mol%) nanocrystals were synthesized via a vapor diffusion sol–gel method described elsewhere.[1, 2] Synthetic manipulations were conducted at room temperature under N_2 atmosphere using standard Schlenk techniques. Eu(acac)$_3\cdot y$H$_2$O (99.9%, Aldrich) and a solution of BaTi(OCH$_2$CH(CH$_3$)OCH$_3$)$_6$ in *n*-butanol/2-methoxypropanol (1:3 v/v) (0.5 M, Gelest Inc.) were used as precursors. In a typical synthesis, 2.0 mL (1.0 mmol) of BaTi(OCH$_2$CH(CH$_3$)OCH$_3$)$_6$ were mixed with the appropriate mass of Eu(acac)$_3\cdot y$H$_2$O (e.g., 4.5 mg (1×10^{-2} mmol) of Eu(acac)$_3\cdot y$H$_2$O were employed in the synthesis of 1% Eu:BaTiO$_3$). The resulting mixture was stirred for 20 min, after which complete dissolution of Eu(acac)$_3\cdot y$H$_2$O occurred. Diffusion of water vapor over the precursor solution was conducted at room temperature and atmospheric pressure for 48 h. The resulting gel was collected, washed with absolute ethanol (2 × 10 mL), and dried under vacuum at room temperature for 4 h, yielding a fine, off-white powder consisting of Eu:BaTiO$_3$ nanocrystals.

Synchrotron X-ray Diffraction. X-ray diffraction (XRD) patterns were collected at the 11–ID–B line of the Advanced Photon Source at Argonne National Laboratory. An incident photon energy of 90.484 keV (λ = 0.137024 Å) was employed. Samples were loaded in Kapton tubes and diffraction data were collected in transmission mode at room temperature.

Transmission Electron Microscopy. Transmission electron microscopy (TEM) images were obtained using a JEOL JEM2100F (JEOL Ltd.) electron microscope operating at 200 kV. Samples were dispersed in methanol and deposited on a 400 mesh Cu grid coated with a ultrathin carbon film mounted on a holey carbon film (Ted Pella Inc.).

Photoluminescence. Steady-state excitation and emission spectra of Eu:BaTiO$_3$ nanocrystals were collected using a Horiba Nanolog spectrofluorometer equipped with a 450 W Xe lamp as the excitation source and a photomultiplier tube as the detector. Lifetime measurements were performed on a Photon

Technology International QuantaMaster Model C-60 spectrofluorometer equipped with a Xe flash lamp as the excitation source. The time-correlated single photon counting method was employed. All spectra were collected under ambient conditions with a spectral resolution of ±1 nm.

X-ray Absorption Spectroscopy. X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectra were collected at the 20−BM−B line of the Advanced Photon Source at Argonne National Laboratory. The incident X-ray beam was monochromatized using a Si(111) double crystal. A harmonic rejection mirror was used to eliminate higher harmonics, and the beam intensity was detuned an additional 10% to further reduce any residual harmonics. Measurements at the Eu *L*3 edge (6976 eV) were performed in fluorescence mode in the case of Eu:$BaTiO_3$ nanocrystals, and in transmission mode in the case of bulk Eu_2O_3. Samples were prepared by spreading a thin, uniform layer of powder on Kapton tape. The incident X-ray beam size was 1 × 6 mm (unfocused). Spectra were collected between 6850 and 7400 eV at room temperature and under flowing helium. Each spectrum was normalized by subtracting the pre-edge and applying an edge-jump normalization using the Athena software.[3]

Rietveld Analysis. Rietveld structural refinements were carried out using the GSAS software.[4] Experimental data and atomic X-ray scattering factors were corrected for sample absorption and anomalous scattering, respectively. The perovskite phase was refined in the centrosymmetric, cubic $Pm\bar{3}m$ space group, and the stoichiometry was fixed at $BaTiO_3$ (i.e., $x = 0$ Eu mol%). 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-Voigt function,[5] (4) lattice constant a, and (5) an isotropic atomic displacement parameter for each chemical species (i.e., U_{Ba}, U_{Ti}, and U_{O}). For 0 and 1 mol% Eu:$BaTiO_3$ compositions, a $BaCO_3$ phase (ICSD No. 158378, orthorhombic *Pmcn* space group) was included in the refinement. For the carbonate phase, the following parameters were refined: (1) scale factor, (2) peak shape, which was modeled using a modified Thomson−Cox−Hastings pseudo-Voigt function, (3) lattice constants *a*, *b*, and *c*, and (4) a global, isotropic atomic displacement parameter (i.e., $U = U_{\mathrm{Ba}} = U_{\mathrm{C}} = U_{\mathrm{O}}$). The R_{wp} indicator was employed to assess the quality of the refined structural models.[6]

Pair Distribution Function Analysis. The pair distribution function (PDF) $G(r)$ defined as:

$$G(r) = 4\pi r[\rho(r) - \rho_0] = (2 / \pi) \int_{Q}^{Q_{max}} Q[S(Q) - 1] \sin(Qr)\, \mathrm{d}Q$$

was employed for structural analysis. Here, r is the radial distance, $\rho(r)$ and ρ_0 are the local and average atomic number density, respectively, and Q is the magnitude of scattering vector defined as $Q = (4\pi / \lambda) \sin\theta$, where 2θ is the angle between incident and scattered X-rays. The RAD software was employed to extract $G(r)$ from the raw diffraction data.[7] These were first corrected for background, sample absorption, and Compton scattering. Then, normalized structure functions $S(Q)$ were obtained. Finally, $S(Q)$ was Fourier-transformed to yield $G(r)$. A maximum scattering vector (Q_{max}) of 25 Å^{-1} was employed in the Fourier transform. Structural refinements were carried out in the 1.5−20 Å interatomic distance range out using the PDFgui software.[8] The perovskite phase was refined in the noncentrosymmetric, tetragonal *P*4*mm* space group. The following parameters were refined: (1) scale factor, (2) lattice constants *a* and *c*, (3) *z* coordinate of the titanium atom (z_{Ti}), and (4) an isotropic atomic displacement parameter for each chemical species (i.e., U_{Ba}, U_{Ti}, and U_{O}). The stoichiometry was fixed at $\mathrm{BaTiO_3}$ (i.e., $x = 0$ Eu mol%) and the positions of the oxygen atoms were fixed at (½, 0, ½) and (½, ½, 0). The R_{w} indicator was employed to assess the quality of the refined structural models.[9, 10]

EXAFS Analysis. k^2-weighted and normalized $\chi(k)$ functions were extracted from the raw X-ray absorption data using the Atena software.[3] A first-shell, single-scattering model was employed to fit the Fourier-transform of the experimental $\chi(k)$ functions (i.e., $\chi(r)$). Fourier transforms of $\chi(k)$ were computed in the 2−8 Å^{-1} k range for 1 mol% Eu:$\mathrm{BaTiO_3}$, 2−9 Å^{-1} k range for all of the other compositions, and 2–11 Å^{-1} k range for bulk Eu_2O_3, which was employed as a standard. In all cases, a dk step of 1 Å^{-1} was used. Fits of $\chi(r)$ were carried out using the Artemis software in the 1–2.75 Å r range, with a dr step of 0.15 Å.[3] The fractional misfit R factor was employed to assess the quality of the fits.

TABLES AND FIGURES

Table S1 Structural Parameters of xEu:BaTiO$_3$ Nanocrystals Extracted From Rietveld Analysis

x (Eu mol%)	a (Å)	V (Å^3)	U_{Ba} (Å^2)^a	U_{Ti} (Å^2)^a	U_O (Å^2)^a	R_{wp} (%)
0^b	4.0357(2)	65.727(10)	0.95(6)	1.67(8)	0.00(12)	2.7
1^c	4.0335(2)	65.622(11)	1.20(5)	1.94(9)	0.22(12)	3.0
2	4.0380(3)	65.841(13)	1.25(7)	1.88(10)	0.39(15)	3.6
3	4.0400(2)	65.934(11)	1.19(6)	2.01(9)	0.50(14)	3.2
4	4.0399(2)	65.934(11)	1.23(6)	2.08(9)	0.48(14)	3.0
5	4.0402(2)	65.947(10)	1.25(5)	2.36(9)	1.06(15)	2.0

[a] Atomic displacements parameters are given as 100×U.
[b] Contains 9.10(18) wt. % of BaCO$_3$. a = 5.264(8) Å, b = 8.983(13) Å, c = 6.423(7) Å. U = 0.7(3).
[c] Contains 5.3(4) wt. % of BaCO$_3$. a = 5.272(9) Å, b = 8.943(16) Å, c = 6.424(11) Å. U = 0.4(5).

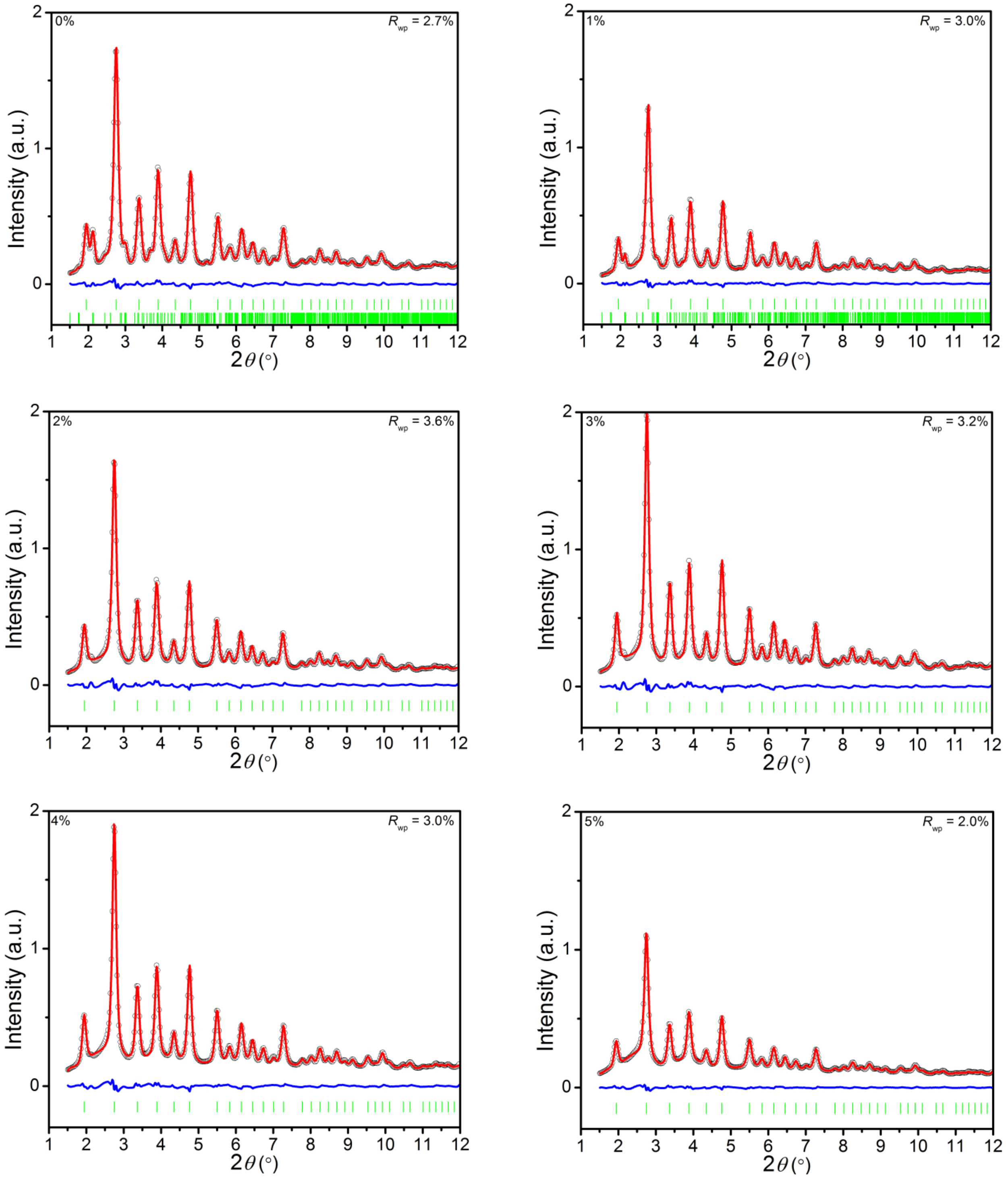

Fig. S1. Rietveld analysis of XRD patterns of Eu:BaTiO_3 nanocrystals. Experimental (○) and calculated (—) patterns are shown for each sample along with the difference curve (—) and tickmarks (|) corresponding to the phase(s) refined. Upper and lower tickmarks correspond to the perovskite and

$BaCO_3$ phases, respectively. Nominal europium concentrations (mol%) and R_{wp} residuals are shown on the top left and right corners, respectively.

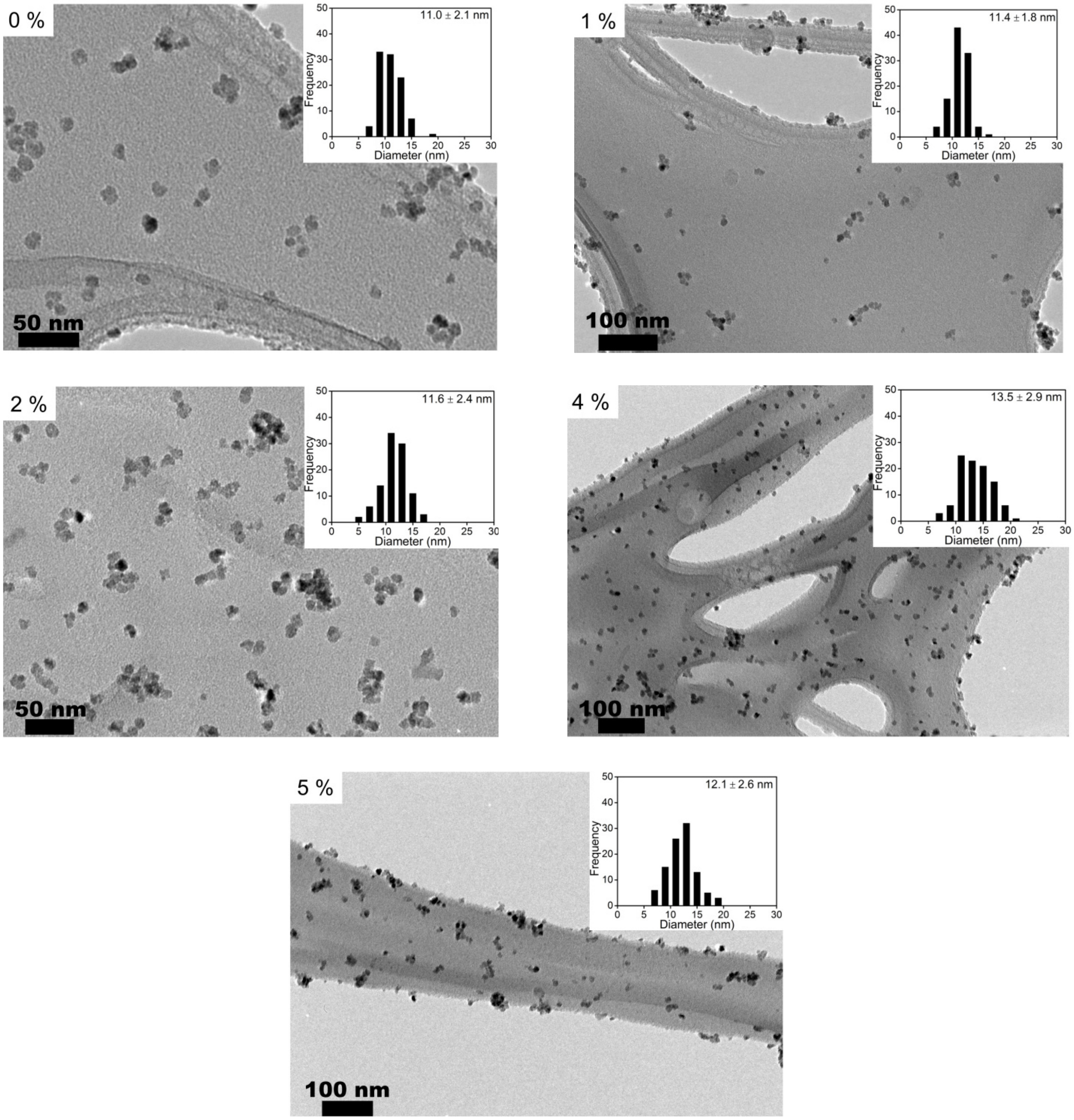

Fig. S2. TEM images of Eu:BaTiO$_3$ nanocrystals. Nominal europium concentrations (mol%) are indicated. Particle size distribution histograms are shown in the insets. Nanocrystals sit in the holey carbon support film.

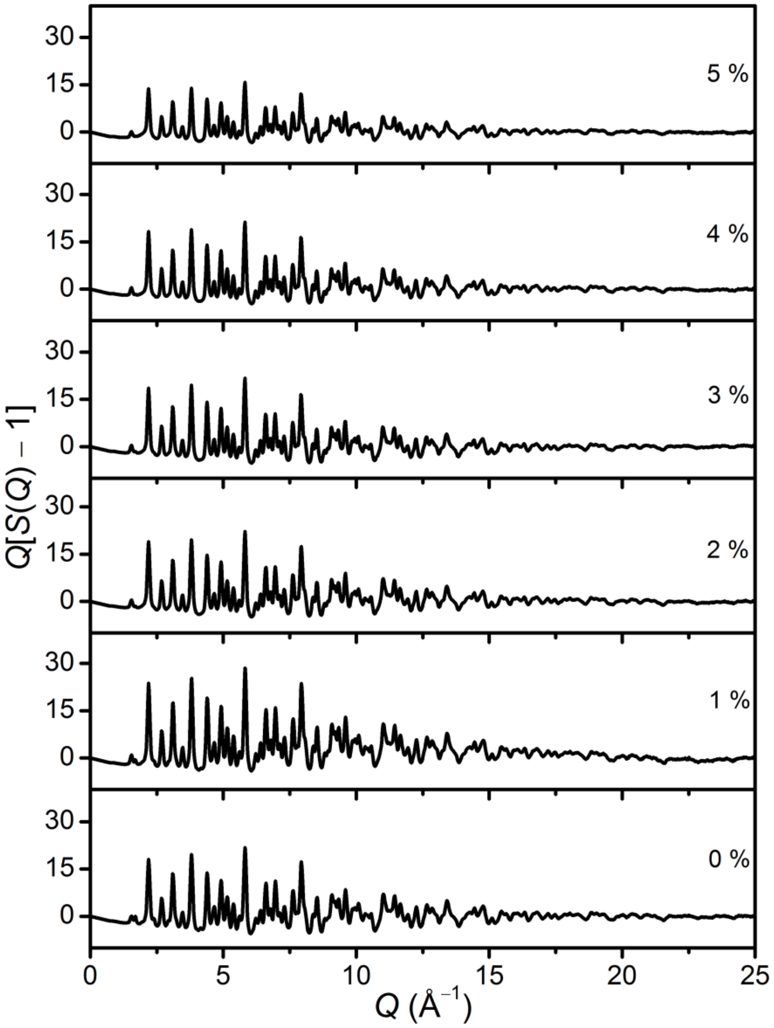

Fig. S3. Structure functions *S*(*Q*) of Eu:BaTiO$_3$ nanocrystals. Nominal europium concentrations (mol%) are indicated.

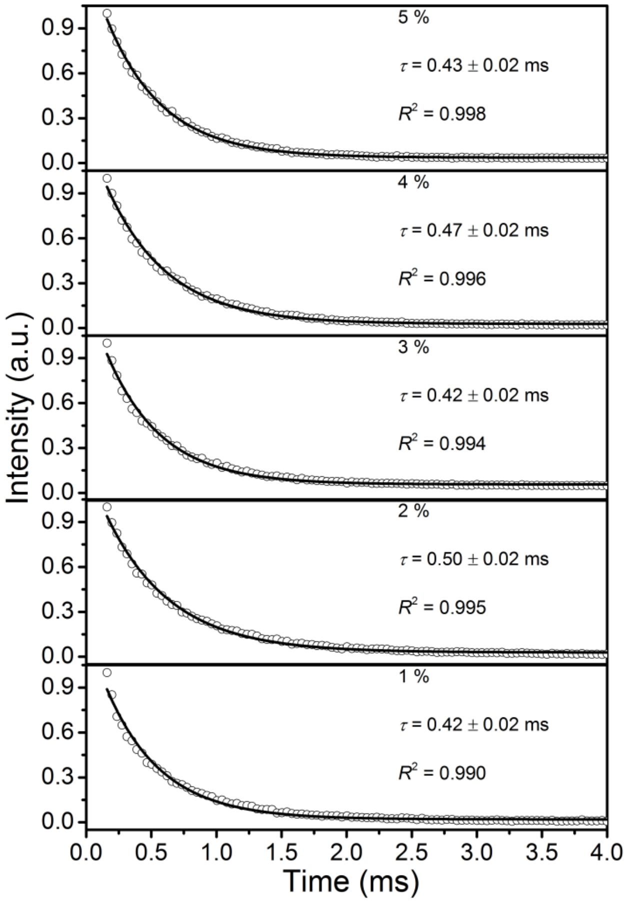

Fig. S4. Experimental (○) and calculated (—) $^5D_0\rightarrow{}^7F_2$ decay of the Eu^{3+} ions in Eu:$BaTiO_3$ nanocrystals. Nominal europium concentrations (mol%), lifetimes (τ), and fit residuals (R^2) are indicated. A single exponential of the form $I_{615}(t) = A \times \exp(-t / \tau) + B$ (A and B are constants) was employed to fit the experimental data;

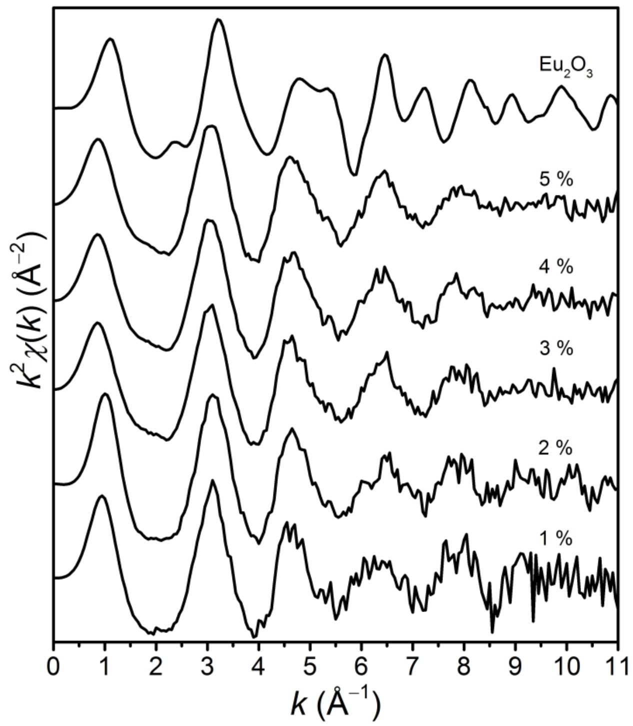

Fig. S5. k^2-weighted and normalized $\chi(k)$ spectra of Eu:$BaTiO_3$ nanocrystals. Nominal europium concentrations (mol%) are indicated.

REFERENCES

1. F. A. Rabuffetti, J. S. Lee and R. L. Brutchey, *Adv. Mater.* 2012, **24**, 1434−1438.
2. F. A. Rabuffetti, J. S. Lee and R. L. Brutchey, *Chem. Mater.* 2012, **24**, 3114−3116.
3. B. Ravel and M. Newville, *J. Synchrotron Rad.* 2005, **12**, 537−541.
4. A. C. Larson and R. B. Von Dreele, *General Structure Analysis System (GSAS)*; Los Alamos National Laboratory: 2000.
5. P. Thomson, D. E. Cox and J.M. Hasting, *J. Appl. Crystallogr.* 1987, **20**, 79−83.
6. R. A. Young, *The Rietveld Method*. Oxford University Press: New York, 1993.
7. V. Petkov, *J. Appl. Crystallogr.* 1989, **22**, 387−389.
8. C. L. Farrow, P. Juhas, J. W. Liu, D. Bryndin, E. S. Bozin, J. Bloch, Th. Proffen and S. J. L. Billinge, *J. Phys.: Condens. Matter* 2007, **19**, 335219.
9. T. Egami and S. J. L. Billinge, *Underneath The Bragg Peaks: Structural Analysis of Complex Materials*. Pergamon: 2003.
10. V. Petkov, M. Gateshki, M. Niederberger and Y. Ren, *Chem. Mater.* 2006, **18**, 814−821.