Electronic Supplementary Information

Low Temperature Synthesis and Characterization of Lanthanide-Doped $BaTiO_3$ Nanocrystals

Sean P. Culver,[a] Viktor Stepanov,[a] Matthew Mecklenburg,[b] Susumu Takahashi[a] and Richard L. Brutchey*[a]

*To whom correspondence should be addressed. Email: brutchey@usc.edu.

[a]Department of Chemistry, University of Southern California, Los Angeles, California 90089, USA
[b]Center for Electron Microscopy and Microanalysis, University of Southern California, Los Angeles, California 90089, USA

Experimental

Nanocrystal Synthesis.

All manipulations were conducted under a nitrogen atmosphere at ambient pressure using standard Schlenk techniques. $Dy(acac)_3 \cdot yH_2O$ and $La(acac)_3 \cdot yH_2O$ (acac = acetylacetonate, $C_5H_7O_2$) from Sigma Aldrich and a 0.5 M solution of $BaTi(OR)_6$ (R = $CH_2CHCH_3OCH_3$) in *n*-butanol/2-methoxypropanol from Gelest, Inc. were used as precursors. All reagents were used as received. The synthetic apparatus applied herein is described in detail elsewhere.[1] In short, a rotameter controls the flow of the carrier gas (nitrogen) through a bubbler containing 0.75 M aqueous HCl, which is connected to a 100 mL, 3-neck round bottom flask containing the precursor solution. Dy:$BaTiO_3$ and La:$BaTiO_3$ (x = 0–2 mol%) nanocrystals were synthesized by first dissolving the appropriate mass of $Ln(acac)_3 \cdot yH_2O$ (Ln = lanthanide) in 4 mL (2 mmol) of $BaTi(OR)_6$ with stirring at 60 ˚C for 2 h under flowing nitrogen. For example, 4.8 mg (0.010 mmol) of $Dy(acac)_3 \cdot yH_2O$ was used for the synthesis of 0.4 mol% Dy:$BaTiO_3$ nanocrystals. After complete dissolution of the reagents, a translucent reddish-brown solution was observed. After cooling to 25 ˚C, stirring was stopped and nitrogen/HCl/H_2O vapor was allowed to flow over the reaction solution, resulting in the formation of a rigid, translucent gel within 12 h. Water vapor was allowed to flow for a total of 72 h. At this point, the flow of water vapor was stopped and the resulting gel was isolated and added to 10 mL of absolute ethanol. The mixture was sonicated for 20 min and centrifuged at 6500 rpm for 30 min to collect the solid.

For the surface treatment of undoped $BaTiO_3$ nanocrystal with Dy^{3+}, the vapor diffusion sol-gel method was performed on two 4 mL aliquots of the 0.5 M $BaTi(OR)_6$ precursor for 72 h. Following completion, the two products were sonicated in 4 mL of ethanol until dispersed. To sample 1, 1 mL of pure ethanol was added (5 mL total volume) and to sample 2, 1 mL of ethanol containing 9.6 mg of $Dy(acac)_3 \cdot yH_2O$ was added (5 mL total volume). Vapor diffusion sol-gel was then performed on the two aliquots for an additional 48 h. The products were washed with 10 mL of pure ethanol and centrifuged at 6000 rpm for 15 min. The recovered nanocrystals were dried under flowing nitrogen overnight. Dielectric characterization was then performed as described in the experimental; however, the single point measurements provided below were conducted on a GWInstek LCR-817 LCR meter at 1 kHz and 25 ˚C under nitrogen.

Material Characterization.

Thermogravimetry (TG). TG 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 100 °C, held isothermal at 100 ˚C for 15 min to remove moisture, and subsequently ramped from 100 to 800 ˚C at a linear rate of 10 ˚C min^{-1}.

Powder X-ray Diffraction (XRD). XRD patterns were collected in the 20–80° 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 0.025˚ and 1 s per step, respectively. All diffraction patterns were collected under ambient conditions.

Elemental Analysis. Elemental analyses of were performed on all samples by inductively coupled plasma optical emission spectroscopy (ICP-OES) at Galbraith Laboratories (Knoxville, TN).

Transmission Electron Microscopy (TEM). TEM images were obtained using a JEOL JEM2100F (JEOL Ltd.) transmission 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.).

Selected Area Electron Diffraction (SAED). SAED patterns were obtained using a JEOL JEM2100F (JEOL Ltd.) electron microscope operating at 200 kV. Samples for SAED studies were prepared by drop-casting a stable suspension of nanocrystals in ethanol on a 400 mesh Cu grid coated with an ultrathin lacey carbon film (Ted Pella, Inc.). Grids were previously cleaned via ozone treatment for 60 min prior to sample deposition.

Dielectric Characterization. Pellets for dielectric studies were prepared by grinding ~200 mg of Dy:BaTiO$_3$ or La:BaTiO$_3$ nanocrystals with 1 mL of a 1 mg mL^{-1} aqueous solution of polyvinyl alcohol (PVA, 10 kDa). The resulting slurry was allowed to dry for 12 h under a flowing nitrogen atmosphere. The dry powder was pressed into a 13 mm diameter pellet by applying ~5 metric tons of pressure for 3 min *in vacuo*. Then, the pressed pellet was thermally treated at 150 ˚C for 2.5 h under flowing nitrogen. The resulting pellet had a thickness of ~0.50 mm. Colloidal silver paint (Electron Microscopy Sciences) was applied to both sides of the pellet to form a simple cylindrical capacitor. Finally, the pellet was thermally treated at 100 ˚C for 2 h under flowing nitrogen and subsequently stored under a nitrogen atmosphere. Capacitance and loss tangents were measured using an Agilent 4294A Impedance Analyzer in a frequency range of 1 kHz to 2 MHz; all measurements were carried out at 25 ˚C under a nitrogen atmosphere.

Electron Paramagnetic Resonance Spectroscopy (EPR). EPR spectra were collected at 78 K on a Bruker ELEXSYS E580 X-band spectrometer equipped with an MS3 resonator. Measurements were performed on ~40 mg of powder in a frequency range of 9.6–9.7 GHz and at a constant microwave power of 0.6 mW.

References

1. F. A. Rabuffetti and R. L. Brutchey, *Chem. Mater.*, 2011, **23**, 4063.

Figures and Tables

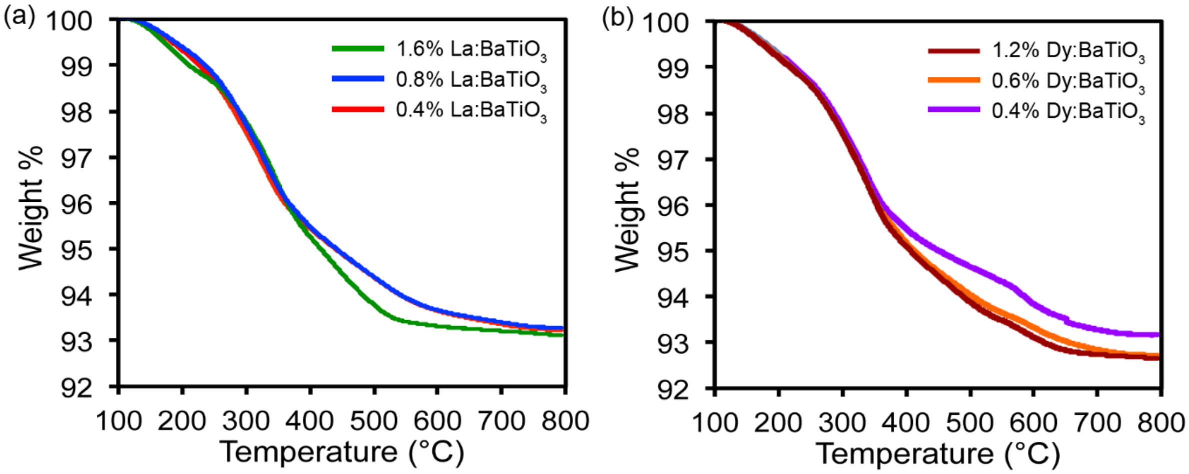

Fig. S1 TG thermograms for (a) La:BaTiO$_3$ and (b) Dy:BaTiO$_3$ nanocrystals.

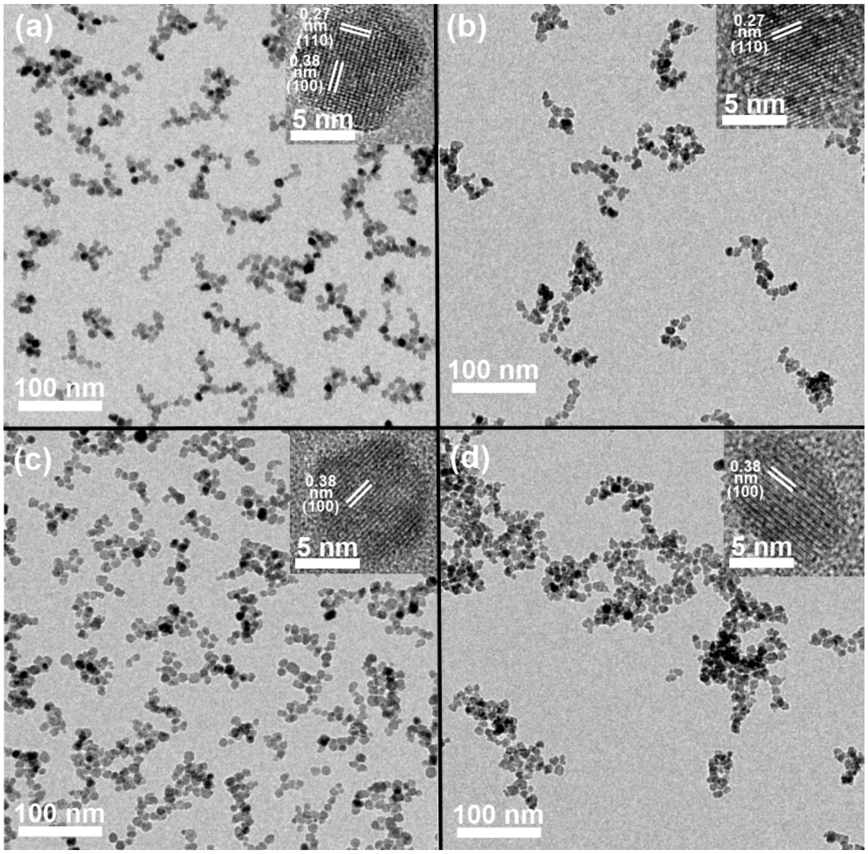

Fig. S2 TEM images of (a) 0.4 and (b) 1.2 mol% Dy:$BaTiO_3$ and (c) 0.4 and (d) 1.6 mol% La:$BaTiO_3$ nanocrystals. High-resolution TEM images are provided in the insets; the corresponding lattice fringe *d*-spacing and lattice planes are indicated.

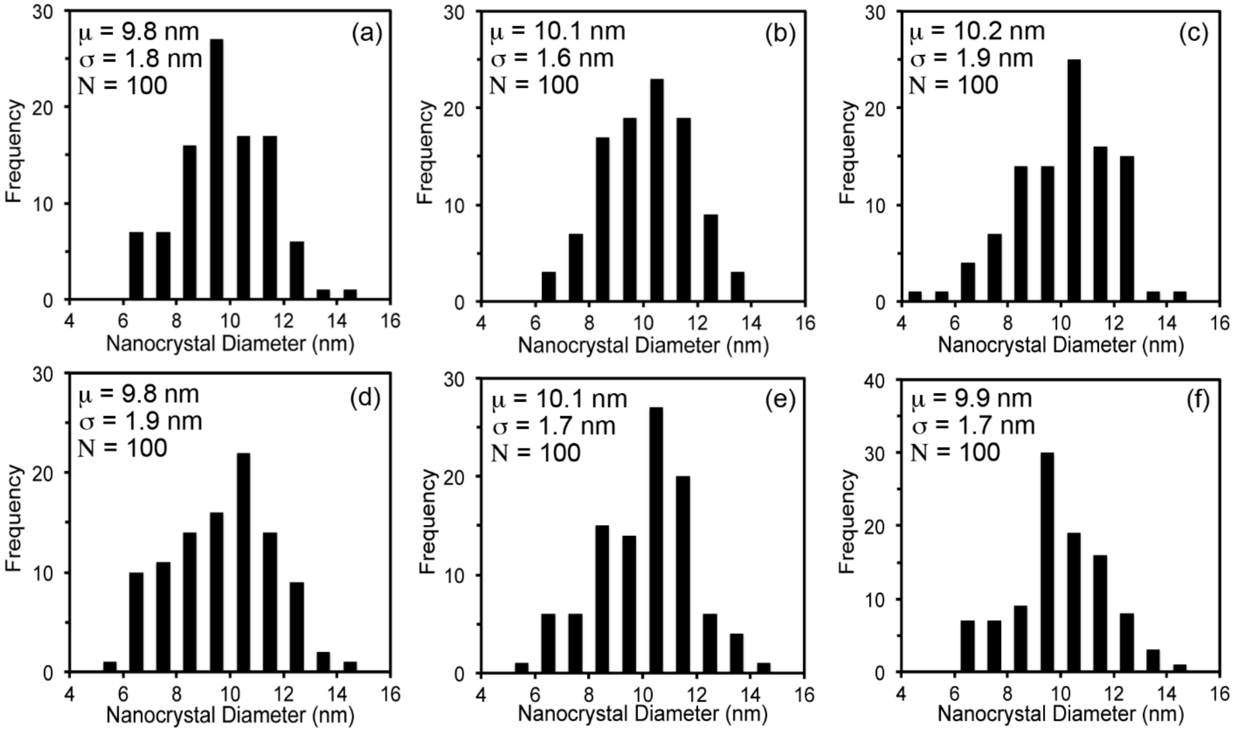

Fig. S3 Nanocrystal size distribution histograms for (a) 0.4, (b) 0.6, and (c) 1.2 mol% Dy:$BaTiO_3$ and (d) 0.4, (e) 0.8, (f) 1.6 mol% La:$BaTiO_3$ nanocrystals. The total number of nanocrystals counted (N), average diameter (μ), and standard deviation (σ) are indicated.

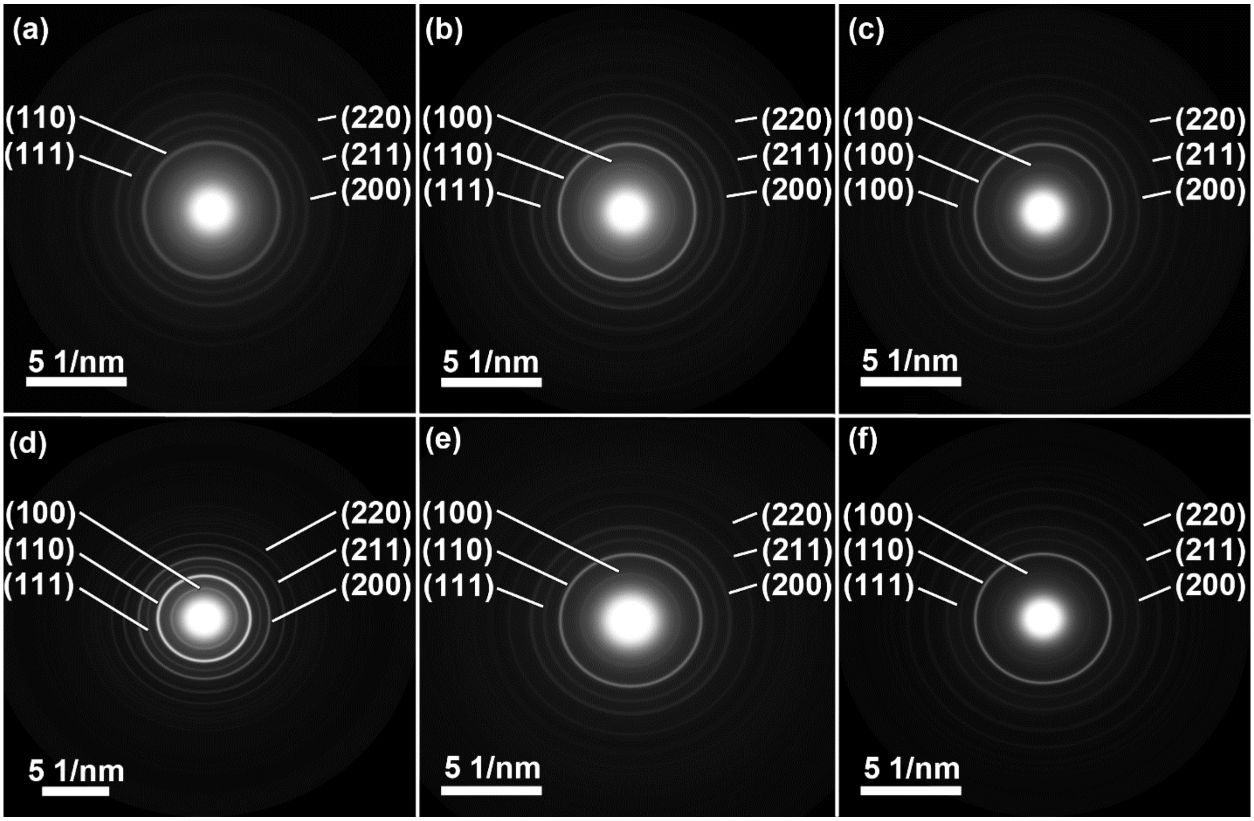

Fig. S4 SAED patterns for (a) 0.4, (b) 0.6, and (c) 1.2 mol% Dy:BaTiO$_3$ and (d) 0.4, (e) 0.8, and (f) 1.6 mol% La:BaTiO$_3$ nanocrystals with their corresponding crystal planes indexed.

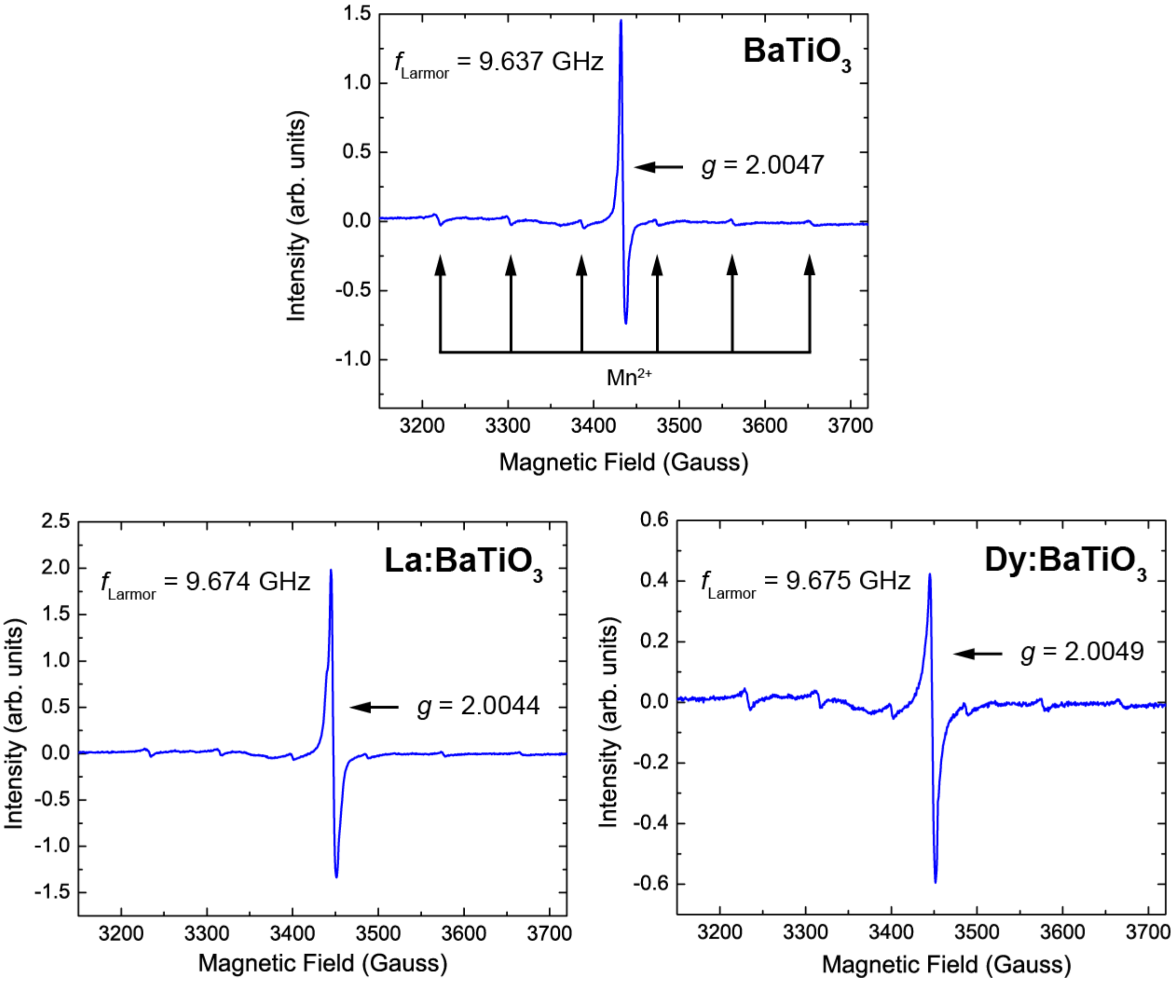

Fig. S5 EPR spectra for undoped BaTiO$_3$, 1.6 mol% La:BaTiO$_3$, and 1.2 mol% Dy:BaTiO$_3$ nanocrystal powder samples at 78 K. The observed sextet corresponds to Mn^{2+} EPR signals. The *g*-values for the signals resulting from V_{Ti} are shown.