Electronic Supplementary Information

Temperature-dependent behavior in the local structure of $BaTiO_3$ nanocrystals

Patrick Cottingham[a] and Richard L. Brutchey[a,*]

[a]Department of Chemistry, University of Southern California, Los Angeles, CA 90089, United States

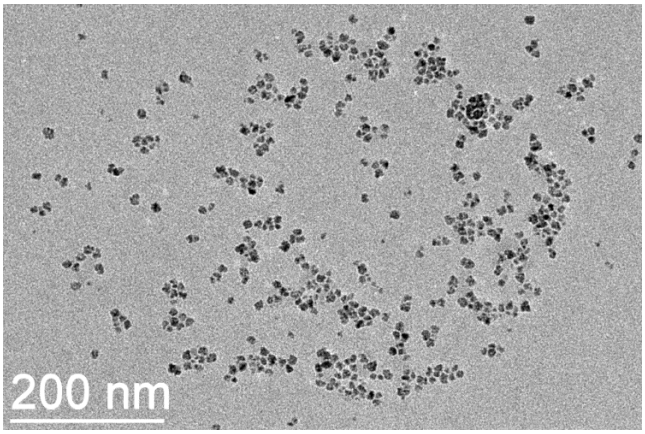

Fig. S1 TEM micrograph of *ca.* 12 nm $BaTiO_3$ nanocrystals.

Table S1. Parameters from Rietveld refinements of the $Pm\bar{3}m$ cubic structure of $BaTiO_3$ to synchrotron X-ray diffraction data collected on 12 nm $BaTiO_3$ nanocrystals at T = 253 K and T = 413 K.

T = 253 K; Rw = 3.97%				
a = 4.03646(22) Å; V = 65.766(11) Å^3				
atom	x	y	z	U_{iso}
Ba	0.0	0.0	0.0	0.00996(27)
Ti	0.5	0.5	0.5	0.0156(5)
O	0.5	0.5	0.0	0.0023(7)
T = 413 K; Rw = 3.93%				
a = 4.04086(24) Å; V = 65.981(12) Å^3				
atom	x	y	z	U_{iso}
Ba	0.0	0.0	0.0	0.01255(30)
Ti	0.5	0.5	0.5	0.0166(5)
O	0.5	0.5	0.0	0.0040(8)

Table S2. Parameters from fits of the $Pm\bar{3}m$ cubic, *P*4*mm* tetragonal, and *Amm*2 orthorhombic structures of $BaTiO_3$ to PDFs from synchrotron X-ray total scattering data collected on 12 nm $BaTiO_3$ nanocrystals at T = 253 K and T = 413 K.

$Pm\bar{3}m$ cubic $BaTiO_3$; T = 253 K; Rw = 14.9%				
a = 4.029 Å; V = 65.421 Å^3				
atom	x	y	z	U_{iso}
Ba	0.000	0.000	0.000	0.006
Ti	0.500	0.500	0.500	0.017
O	0.500	0.500	0.000	0.027
*P*4*mm* tetragonal $BaTiO_3$; T = 253 K; Rw = 13.4%				
a = 4.007 Å; c = 4.077 Å; V = 65.469 Å^3				
Atom	x	y	z	U_{iso}
Ba	0.000	0.000	0.000	0.005
Ti	0.500	0.500	0.523	0.012
O	0.500	0.500	0.000	0.025
*Amm*2 orthorhombic $BaTiO_3$; T = 253 K; Rw = 13.9%				
a = 3.994 Å; b = 5.689 Å; c = 5.763 Å; V = 130.951 Å^3				
Atom	x	y	z	U_{iso}
Ba	0.000	0.000	0.000	0.005
Ti	0.500	0.000	0.519	0.011
O	0.000	0.000	0.500	0.025
$Pm\bar{3}m$ cubic $BaTiO_3$; T = 413 K; Rw = 14.6%				
a = 4.035 Å; V = 65.718 Å^3				
Atom	x	y	z	U_{iso}
Ba	0.000	0.000	0.000	0.008
Ti	0.500	0.500	0.500	0.019

O	0.500	0.500	0.000	0.030
*P*4*mm* tetragonal $BaTiO_3$; *T* = 413 K; *R*w = 13.3%				
a = 4.012 Å; *c* = 4.086 Å; *V* = 65.771 $Å^3$				
Atom	x	y	z	U_{iso}
Ba	0.000	0.000	0.000	0.007
Ti	0.500	0.500	0.525	0.013
O	0.500	0.500	0.000	0.028
*Amm*2 orthorhombic $BaTiO_3$; *T* = 413 K; *R*w = 13.1%				
a = 3.998 Å; *b* = 5.692 Å; *c* = 5.783 Å; *V* = 131.604 $Å^3$				
atom	x	y	z	U_{iso}
Ba	0.000	0.000	0.000	0.007
Ti	0.500	0.000	0.521	0.012
O	0.000	0.000	0.500	0.028

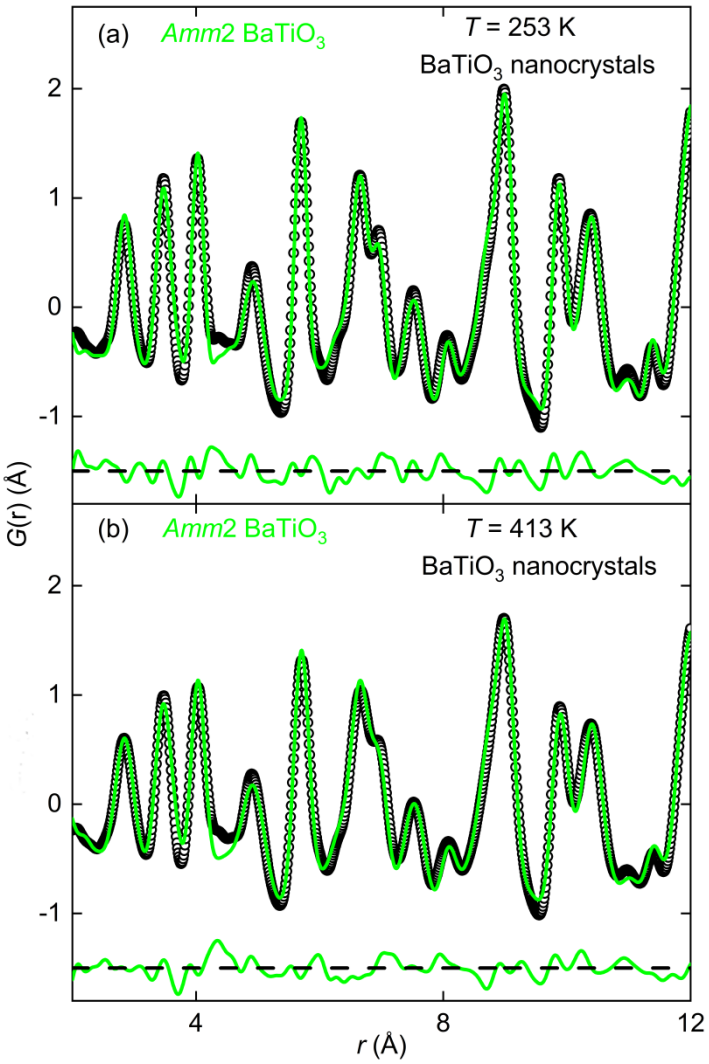

Fig. S2 Orthorhombic fits to PDFs of X-ray total scattering data collected on $BaTiO_3$ nanocrystals collected at (a) T = 253 K and (b) T = 413 K. Upper green lines represent the fit to the data. Lower green lines represent the difference between the fit and the data, with a dashed line to indicate a reference for no difference.

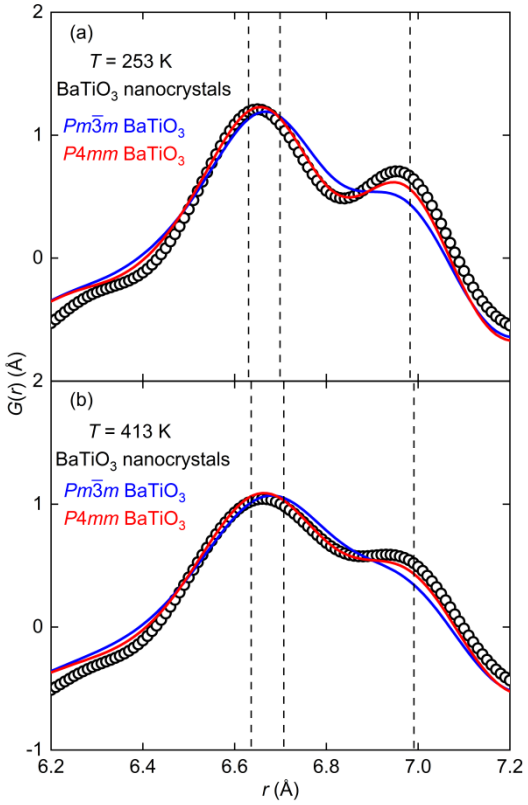

Fig. S3 Zoom-in on features of the PDFs shown in Fig. 3. The feature in the PDF centered at $r \approx 6.8$ Å contains contributions from three atomic pairs in the tetragonal model of $BaTiO_3$; that is, two Ba-Ti pairs and one Ba-Ba pair. The dashed vertical lines indicate the radii of those pairs, with $r_{Ba\text{-}Ti} = 6.63$, 6.67 and $r_{Ba\text{-}Ba} = 6.98$ Å at $T = 253$ K and $r_{Ba\text{-}Ti} = 6.63$, 6.70 and $r_{Ba\text{-}Ba} = 6.99$ Å at $T = 413$ K. The tetragonal *P*4*mm* model provides better resolution of these peaks at both temperatures.

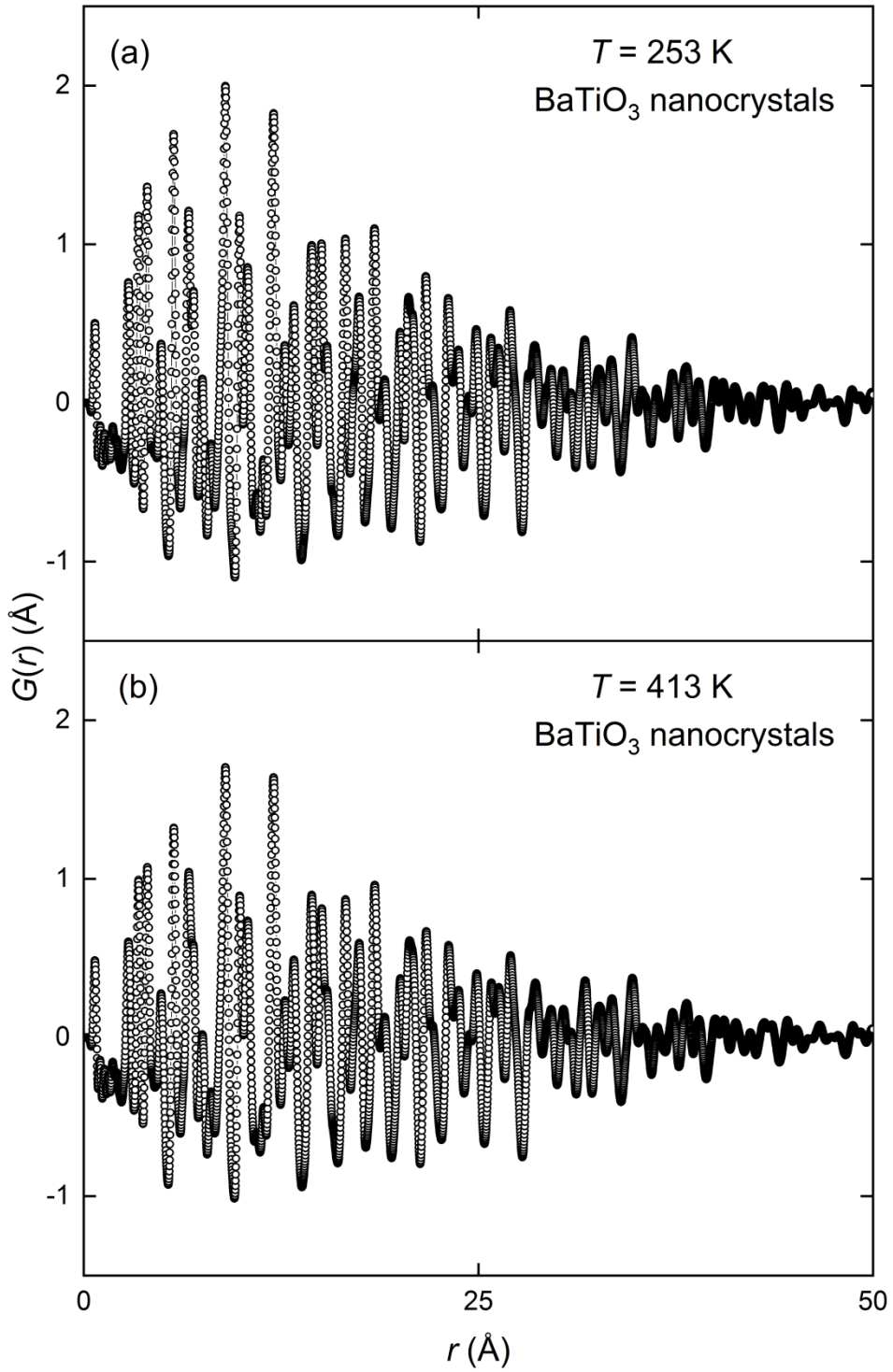

Fig. S4 PDFs, $G(r)$, of $BaTiO_3$ nanocrystals collected at (a) T = 253 K and (b) T = 413K. The rapid attenuation of $G(r)$ at higher values of r is due to the loss of coherence of the overall structure.