

Supporting information:

Stoichiometric control over ferroic behavior in $\text{Ba}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_3$ nanocrystals

Julien Lombardi^{1,2,3}, Long Yang,⁴ Frederick A. Pearsall,^{1,2,3} Nasim Farahmand,^{1,2,3} Zheng Gai⁵, Simon J. L. Billinge⁴ and Stephen O'Brien^{1,2,3*}

¹The CUNY Energy Institute, City University of New York, Steinman Hall, 160 Convent Avenue, The City College of New York, New York, NY 10031, USA.

²Department of Chemistry, The City College of New York, 1024 Marshak, 160 Convent Avenue, NY 10031, USA

³ Ph.D. Program in Chemistry, The Graduate Center of the City University of New York, New York, NY 10016, USA.

⁴Department of Applied Physics and Applied Mathematics, Columbia University, 500 West 120th Street, New York, NY 10025, USA.

⁵Center for Nanophase Materials Sciences and Chemical Science Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA

*Corresponding author: sobrien@ccny.cuny.edu

EDS Figure S1.

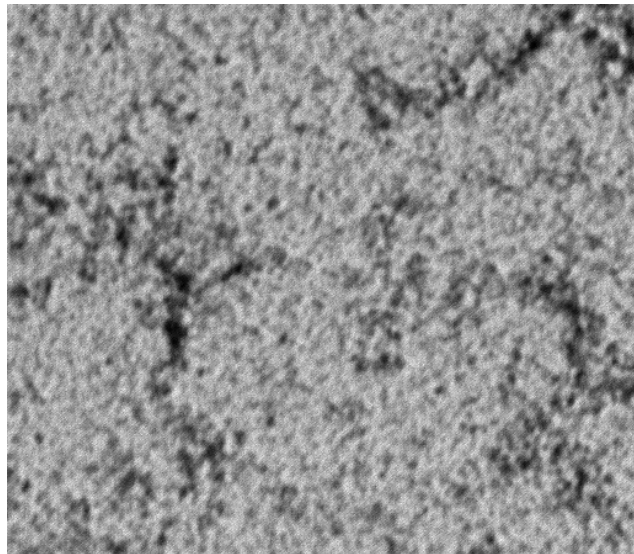


Figure S1. Image used for EDS analysis shown in Figure 4(d).

The Iron doped $\text{BaFe}_x\text{Ti}_{1-x}\text{O}_3$ ($x = 0, 0.1, 0.2, 0.3, 0.5, 0.75, 1.0$) gel-collected perovskite nanoparticles were studied using X-ray pair distribution function (PDF) analysis at room temperature.^{1,2} The sample information is listed in Table I. We sought (a) to determine whether these samples have a non-centrosymmetric structure (b) to establish that Fe was being incorporated into the structure (c) to look for any structure changes with increased Fe content.

#	Sample Name	Composition
1	BTO	BaTiO_3
2	BFT 1	$\text{BaFe}_{0.1}\text{Ti}_{0.9}\text{O}_3$
3	BFT 2	$\text{BaFe}_{0.2}\text{Ti}_{0.8}\text{O}_3$
4	BFT 3	$\text{BaFe}_{0.3}\text{Ti}_{0.7}\text{O}_3$
5	BFT 5	$\text{BaFe}_{0.5}\text{Ti}_{0.5}\text{O}_3$
6	BFT 75	$\text{BaFe}_{0.75}\text{Ti}_{0.25}\text{O}_3$
7	BFO	BaFeO_3

The PDF Method

The PDF method is a total scattering technique for determining local order in nanostructured materials.^{1,2} The technique does not require periodicity, so it is well suited for studying nanoscale features in a variety of materials.^{3,4} The experimental PDF, denoted $G(r)$, is the truncated Fourier transform of the total scattering structure function, $F(Q) = Q[S(Q) - 1]$, according to⁵:

$$(1) \quad G(r) = \frac{2}{\pi} \int_{Q_{min}}^{Q_{max}} F(Q) \sin(Qr) dQ,$$

where Q is the magnitude of the scattering momentum transfer. The structure function, $S(Q)$, is extracted from the Bragg and diffuse components of x-ray, neutron or electron powder diffraction intensity. For elastic scattering, $Q = 4\pi \sin\theta/\lambda$, where λ is the scattering wavelength and 2θ is the scattering angle. In practice, values of Q_{min} and Q_{max} are determined by the experimental setup and Q_{max} is often reduced below the experimental maximum to eliminate noisy data from the PDF since the signal to noise ratio becomes unfavorable in the high- Q region.

The PDF gives the scaled probability of finding two atoms in a material a distance r apart and is related to the density of atom pairs in the material.¹ For a macroscopic scatterer, $G(r)$ can be calculated from a known structure model according to

$$(2) \quad G(r) = 4\pi r [\rho(r) - \rho_0], \quad \rho(r) = \frac{1}{4\pi r^2 N} \sum_i \sum_{j \neq i} \frac{b_i b_j}{\langle b \rangle^2} \delta(r - r_{ij}).$$

Here, ρ_0 is the atomic number density of the material and $\rho(r)$ is the atomic pair density, which is the mean weighted density of neighbor atoms at distance r from an atom at the origin. The sums in $\rho(r)$ run

over all atoms in the sample, b_i is the scattering factor of atom i , $\langle b \rangle$ is the average scattering factor and r_{ij} is the distance between atoms i and j .

In practice, we use Eqs. 2 to fit the PDF generated from a structure model to a PDF determined from experiment. For this purpose, the delta functions in Eqs. 2 are Gaussian-broadened and the equation is modified to account for experimental effects. PDF modeling, where it is carried out, is performed by adjusting the parameters of the structure model, such as the lattice constants, atom positions, and isotropic atomic displacement parameters, to maximize the agreement between the theoretical and an experimental PDF. This procedure is implemented in the PDFgui program⁶. Least-squares fits were performed by minimizing the fit residual, with the goodness-of-fit R_ω , given by:

$$(3) \quad R_\omega = \sqrt{\frac{\sum_{i=1}^n [G_{obs}(r_i) - G_{calc}(r_i, P)]^2}{\sum_{i=1}^n G_{obs}(r_i)^2}},$$

where G_{obs} and G_{calc} are the experimental and calculated PDFs and P is the set of parameters refined in the model.

Sample Phase	BTO	BFT1		BFT2		BFT3	
	NT	NT-BFTO	BCO	NT-BFTO	BCO	NT-BFTO	BCO
a (Å)	4.0170	4.0232	5.2954	4.0271	5.3173	4.0270	5.3228
b (Å)	-	-	9.0207	-	9.0409	-	9.0111
c (Å)	4.0424	4.0564	6.3406	4.0683	6.3673	4.0753	6.4076
Ba z	-0.0011	-0.0081	-	-0.0077	-	-0.0068	-
Ti (Fe) z	0.5328	0.5283	-	0.5282	-	0.5282	-
O1 z	-0.0180	-0.0228	-	-0.0267	-	-0.0245	-
O2 z	0.4756	0.4867	-	0.5009	-	0.5059	-
Ba U_{iso} (Å ²)	0.0083	0.0104	0.0104	0.0117	0.0117	0.0128	0.0128
Ti (Fe) U_{iso} (Å ²)	0.0099	0.0108	-	0.0121	-	0.0124	-
O U_{iso} (Å ²)	0.0255	0.0266	0.0266	0.0249	0.0249	0.0236	0.0236
SPD (Å)	132.4	80.8	-	65.4	-	55.2	-
Mass Ratio (%)	-	96.4	3.6	96.1	3.9	95.7	4.3
δ_1 (Å)	1.57	1.59	-	1.57	-	1.55	-

R_{ω}	0.118	0.138	0.141	0.150
--------------	-------	-------	-------	-------

Table S1: Structure refinement results of NT-BFTO+BCO model fit to the low-doped $\text{BaFe}_x\text{Ti}_{1-x}\text{O}_3$ ($x = 0.1, 0.2, 0.3$) sample PDFs, i.e. BFT1 to BFT3, over a range of $1.5 < r < 50 \text{ \AA}$. The model is introduced in Section II. In NT-BFTO model, the occupancies on the Ti and Fe sites are fixed during the refinement keeping the total site occupancy as 1.0. The occupancies on the Fe site are fixed as 0.1, 0.2, and 0.3 for BFT1, BFT2, and BFT3, respectively. The ADPs of Ba and O ions are constrained to be the same in two phases. Here, R_{ω} is the goodness of fit; x, y and z are the refinable atomic positions in fractional coordinates (see Table II for details); U_{iso} , in units of (\AA^2), is the isotropic atomic displacement parameter (ADP); δ_l in units of (\AA) is a correlated motion related PDF peak sharpening coefficient; SPD, in units of (\AA), is the spherical particle diameter. The refinement result from the undoped BTO sample is listed together for easier comparison.

References

- ¹ Egami, T., Billinge, S. J. L. *Underneath the Bragg Peaks: Structural Analysis of Complex Materials*, 2nd ed.; Elsevier: Amsterdam, 2003.
- ² Billinge, S. J. L.; Levin, I. The Problem with Determining Atomic Structure at the Nanoscale. *Science* **2007**, 316, 561.
- ³ Billinge, S. J. L. Nanoscale Structural Order from the Atomic Pair Distribution Function (PDF): There's Plenty of Room in the Middle. *J. Solid State Chem.* **2008**, 181 (7), 1695–1700.
- ⁴ Billinge, S. J. L.; Kanatzidis, M. G. Beyond Crystallography: The Study of Disorder, Nanocrystallinity and Crystallographically Challenged Materials with Pair Distribution Functions. *Chem. Commun.* **2004**, 0 (7), 749–760.
- ⁵ Farrow, C. L.; Billinge, S. J. L. Relationship between the Atomic Pair Distribution Function and Small-Angle Scattering: Implications for Modeling of Nanoparticles. *Acta Cryst A* **2009**, 65 (3), 232–239.
- ⁶ Farrow, C. L.; Juhas, P.; Liu, J. W.; Bryndin, D.; Božin, E. S.; Bloch, J.; Proffen, T.; Billinge, S. J. L. PDFfit2 and PDFgui: Computer Programs for Studying Nanostructure in Crystals. *J. Phys.: Condens. Matter*, **2007**, 19, 335219.