Support Information for: Long range and local structure of $Sr_xBa_{1-x}Nb_2O_6$ (x = 0.33 and 0.67), across the ferroelectric-relaxor

transition

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Table S1. Quantities used during synthesis

Sample name	$Nb_2O_5(g)$	SrCO ₃ (g)	BaCO ₃ (g)
SBN33	5.2801	0.9651	2.6264
SBN67	5.5114	2.0453	1.3503



Figure S1. Rietveld refinement of the SBN33 sample at 720 K, 300 K above the paraelectric phase transition. Inset shows the zoom out high q region, highlighting the contribution from diffuse scattering which is indicative of short-range order.

To describe the peak profile, a convolution of GSAS type back-to-back exponential function, and a *d*-dependent pseudo-Voigt function (similar to that used in GSAS II for T.O.F. neutron) was used. The instrument parameters were obtained by refining a Si (NIST 640e) pattern gathered in the same configuration. Rietveld analysis reveals diffuse scattering background from up to 720 K, indicative of short range order.



Figure S2. ADP of cations sites for SBN33 and SBN67 from 300 K to 720 K.

While both A sites show linear increase of ADP over temperature, the Nb1 sites displays a significant jump of U_{33} passing the T_c , followed by continuous decrease on further increasing temperature. Note the ADP of Nb sites are highly anisotropic: displacement along the polarization c axis is much larger than that along the ab plane.



Figure S3. ADP of various oxygen sites for both SBN33 and SBN67.

All the oxygen sites display anisotropic ADP although their behaviors are quite different: the equatorial oxygen O1, O2 and O3 have larger displacement along *c* direction, whereas the apical O4 and O5 has huge displacement in the *ab* plane. Over the temperature range, a gradual decrease of oxygen ADP with increasing temperature was observed, indicating static disorder in the oxygen sublattice.



Figure S4. First two peaks in the PDF data.

The first peak centered at 1.94 Å in the PDF data represents the Nb-O pair. For both compositions, this peak becomes sharpest at T_c (500 K for SBN33 and 400 K for SBN67), as the change in point symmetry leads to equal apical Nb2-O bond length. Further increasing the temperature sees the broadening of the peak. The peak centered at 2.80(1) Å, which corresponds to the A-O bonds, continues to broaden with increasing temperature.



Figure S5. Medium range local structure of SBN67 sample, at 300K, fitted with *P4bm* space group with different sizes: $1 \times 1 \times 2$ and $1 \times 1 \times 4$. Comparing with SBN33, larger supercell seems necessary, indicating greater degree of distortion in the RE SBN67 compound.

The small box fit was conducted using TOPAS 6 Academic version with data generated from the standard data reduction at the POWGEN instrument. The peak broadening description follows that in PDFgui user guide¹, with the Q_{broad} parameter obtained by refining a Si reference pattern, and additional delta1 term refined to describe the 1/r dependent peak broadening. Additional Q_{damp} term, also obtained from the Si standard, was included to describe exponential dampening of the PDF peaks due to the Q resolution.

Due to the polar nature of the space groups, one has to select an atomic site to have a fix z position otherwise the whole structure could shift and produces unstable refinement. During the data analysis, the Sr2 displacement along z is fixed, as little displacement is expected based on the Rietveld analysis results (Figure S2). The sites in the supercell that have the same origin in the parent *P4bm* structure are set to have the same isotropic displacement parameters. Occupancy of the Sr/Ba sites were fixed based on the Rietveld results.



Figure S6. RMC real space PDF and S(Q) fitting of the SBN33 composition, from top to bottom, at 300 K, 400 K, 500 K, 600 K and 720 K respectively. Here, $G^{RMC}(r)$ is used to refer to the G(r) PDF format used in RMCProfile fitting. Refer to Ref. [1] by D. Keen about the various formats of PDF used by different software. $G^{RMC}(r)$ and G(r) in current report corresponds to G(r) and $G^{PDF}(r)$, respectively, in D. Keen's.



Figure S7. RMC real space PDF and S(Q) fitting of the SBN67 composition, from top to bottom, at 300 K, 400 K, 500 K, 600 K and 720 K respectively.



Figure S8. A comparison of Nb polarization at 300 K and 720 for the two compositions. The plot contains the same data as Figure 12, however it highlights the difference between the two composition: the average polarization for the FE composition shifts towards zero, whereas for the RE composition, wider dispersion of Nb displacement was observed.





Figure S9. Local environment of SBN33 and SBN67 at 300 K, from PDF fitting using a $1 \times 1 \times 4$ supercell with the *P4bm* space group. Larger displacement of the A1 cations was observed in the relaxor composition. A preferred local cation configuration is identified for SBN67 using BVS (c) schematics showing the bond length in the refined SBN67.

	SBI	N33 this study	y, RT	SBN33, single crystal, X-ray, RT ²			
	<i>U</i> ₁₁	U ₂₂	<i>U</i> ₃₃	U_{11}	U ₂₂	<i>U</i> ₃₃	
A2	0.0255(12)		0.0125(16)	0.0276(1)		0.0137(1)	
A1	0.0054(9)		0.0037(17)	0.0086(1)		0.0087(2)	
Nb1	0.0039(6)		0.0181(18)	0.0080(1)		0.0075(1)	
Nb2	0.0057(5)	0.0084(6)	0.0104(6)	0.0094(1)	0.0090(2)	0.0098(1)	
01	0.0071(7)		0.0250(2)	0.0105(4)		0.0202(12)	
02	0.0137(9)	0.0042(8)	0.0530(20)	0.0188(6)	0.0091(5)	0.0469(17)	
03	0.0115(9)	0.0028(7)	0.0490(17)	0.0145(6)	0.0067(5)	0.0436(14)	
04	0.062(3)		0.001(2)	0.0472(15)		0.018(2)	
05	0.071(2)	0.0269(12)	0.0115(12)	0.0735(16)	0.0319(9)	0.0067(12)	

Table S1. Comparison of U_{aniso} between current study and references

	SBN33 this study, 600 K				SBN35, 650 K, electron diffraction ³			
	<i>U</i> ₁₁	U ₂₂	U33		U_{11}	U ₂₂	<i>U</i> ₃₃	
A2	0.0355(12)		0.018(2)		0.0474(6)		0.0274(10)	
A1	0.0102(9)		0.015(2)		0.0122(9)		0.017(2)	
Nb1	0.0074(6)		0.032(5)		0.0156(6)		0.0320(15)	
Nb2	0.0098(5)	0.0103(5)	0.0198(6)		0.0165(5) 0.0148(5)		0.0222(7)	
01	0.0116(7)		0.0226(14)		0.0158(14)		0.023(3)	
02	0.0225(9)	0.0069(7)	0.0406(12)		0.0105(16)	0.0213(18)	0.044(3)	
03	0.0190(9)	0.0045(6)	0.0397(14)		0.0114(17)	0.023(2)	0.045(3)	
04	0.0534(19)		0.001(4)		0.046(3)		0.012(5)	
05	0.0477(13)	0.0315(10)	0.0073(7)		0.030(2)	0.050(3)	0.011(2)	

	SBN67 this study, RT		SBN61, single crystal, X-ray, RT ²			SBN61, poled crystal, neutron, RT ^{4,5}			
	<i>U</i> ₁₁	U ₂₂	U33	<i>U</i> ₁₁	U ₂₂	U ₃₃	<i>U</i> ₁₁	U ₂₂	U33
A2	0.0361(18)		0.017(3)	0.0329(1)		0.0162(1)	0.0400(10)		0.009(1)
A1	1 0.0071(10)		0.001(2)	0.0083(12)		0.0091(2)	0.0031(8)		0.000(1)
Nb1	0.0056(9)		0.028(4)	0.0095(1)		0.0079(1)	0.0058(5)		-0.0016(7)
Nb2	0.0082(7)	0.0082(7)	0.0196(11)	0.0104(1)	0.0094(1)	0.0122(1)	0.0065(5)	0.0053(4)	0.0043(5)
01	0.0120(11)		0.032(4)	0.0128(6)		0.0311(17)	0.0085(6)		0.0028(2)
02	0.0157(13)	0.0059(11)	0.083(4)	0.0198(8)	0.0102(7)	0.0649(19)	0.0147(8)	0.0032(6)	0.0680(30)
03	0.0182(15)	0.0019(10)	0.081(4)	0.0188(9)	0.0094(7)	0.079(2)	0.0140(7)	0.0033(6)	0.0086(3)
04	0.113(7)		0.001(5)	0.085(3)		0.0045(19)	0.086(4)		0.000(1)
05	0.1140(40)	0.0480(30)	0.0024(15)	0.124(3)	0.0391(12)	0.0030(10)	0.118(4)	0.043(2)	0.000(1)

Anisotropic displacement parameters from literature and this study are listed in Table S1. Although the temperature dependent study on SBN is quite scares, current results are nevertheless consistent

with the reported values, despite variations in the experiment conditions. The comparison reinforces the general trend in the U_{aniso} observed in Figure. S2 and S3 as summarized below:

- 1. A1 site is confined in the tetragonal channel, whereas A2 site has a less confined environment, leading to a larger U_{11}
- 2. Displacement of oxygen is highly anisotropic, O3 has large component along c axis whereas O4 and O5's ADP is restricted within the ab plane.
- 3. In general, SBN67 has larger displacement parameters comparing with SBN33

Appendix

Extraction ADPs from the RMC configuration

For the extraction of ADPs from RMC configuration, the first step is to collapse the supercell back into a unit cell, through which one gets a distribution of atoms surrounding each inequivalent (under P1 symmetry) positions in the unit cell. Since in the structure configuration file used by RMCProfile package there is a unique label specifying which position that a certain atom originally belongs to, it is straightforward to group all the atoms belonging to the same inequivalent atomic position (again, under P1 symmetry). Suppose there being N atoms belonging to a certain atom in the collapsed unit cell, one can first calculate the average position as follows:

$$\overline{x} = \frac{\sum_{i=1}^{N} x_{i}}{N}, \ \overline{y} = \frac{\sum_{i=1}^{N} y_{i}}{N}, \ \overline{z} = \frac{\sum_{i=1}^{N} z_{i}}{N}$$

Then the thermal parameters corresponding to this specific position can be calculated as follows:

$$U_{11} = \frac{\sum_{i=1}^{N} (x_i - \overline{x})^2}{N}, \ U_{22} = \frac{\sum_{i=1}^{N} (y_i - \overline{y})^2}{N}, \ U_{33} = \frac{\sum_{i=1}^{N} (z_i - \overline{z})^2}{N}$$
$$U_{12} = U_{21} = \frac{\sum_{i=1}^{N} (x_i - \overline{x})(y_i - \overline{y})}{N}, \ U_{13} = U_{31} = \frac{\sum_{i=1}^{N} (x_i - \overline{x})(z_i - \overline{z})}{N}, \ U_{23} = U_{32} = \frac{\sum_{i=1}^{N} (y_i - \overline{y})(z_i - \overline{z})}{N}$$

Here x, y and z are all Cartesian coordinates. Furthermore, for atomic positions that are connected under original symmetry (the starting point from which the supercell is expanded), a simple scheme is used here to take the average of the calculated thermal parameters over all equivalent positions.

Kernel density estimation (KDE)

The kernel density estimation (KDE) is a data smoothing approach that estimates the probability density of a variable, based on a finite data sample. In the current report, KDE was used to estimate the Nb displacement based on the RMC results.

Nb displacement in the 5 x 5 x 10 supercell, from a total of 2500 independent sites, were binned from -0.5 Å to 0.5 Å with 0.01 Å bin size, creating a vector space with 100 elements. Afterwards, the KDE smooth function in the following format,

$$f = \frac{1}{n} \sum_{i=1}^{n} \frac{1}{\sqrt{2\pi\omega}} e^{\frac{-(x-x_i)^2}{2\omega^2}}$$

was applied to all of the n = 100 datapoints; x_i is the current bin center for the *i*th datapoint; ω , the kernel bandwidth, estimates the optimal kernel bandwidth for the given x_i and is given as,

$$\omega = 0.9\sigma n^{-0.2}$$
$$\sigma = \min(\hat{\sigma}, IQR/1.349)$$

where $\hat{\sigma}$ is the standard deviation of x_i ; and *IQR* is the interquartile range of x_i

References

- Farrow, C. L.; Juhas, P.; Liu, J. W.; Bryndin, D.; Boin, 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* (33), 335219.
- Podlozhenov, S.; Graetsch, H. A.; Schneider, J.; Ulex, M.; Wöhlecke, M.; Betzler, K. Structure of Strontium Barium Niobate Sr_xBa_{1-x}Nb₂O₆ (SBN) in the Composition Range 0.32 ≤ x ≤ 0.82. *Acta Crystallogr. Sect. B Struct. Sci.* 2006, 62 (6), 960–965.
- Buixaderas, E.; Kempa, M.; Bovtun, V.; Kadlec, C.; Savinov, M.; Borodavka, F.; Vaněk, P.; Steciuk, G.; L. Palatinus; J. Dec Multiple Multiple polarization mechanisms across the ferroelectric phase transition of the tetragonal tungsten-bronze Sr_{0.35}Ba_{0.69}Nb₂O_{6.04} *Phys. Rev. Materials* 2018, (2), *124402*.
- (4) Schefer, J.; Schaniel, D.; Petříček, V.; Woike, T.; Cousson, A.; Wöhlecke, M. Reducing the Positional Modulation of NbO₆-octahedra in Sr_xBa_{1-x}Nb₂O₆ by Increasing the Barium Content: A Single Crystal Neutron Diffraction Study at Ambient Temperature for x = 0.61 and x = 0.34. *Zeitschrift fur Krist.* 2008, 223 (6), 399–407.
- (5) Schefer, J.; Schaniel, D.; Pomjakushin, V.; Stuhr, U.; Petříček, V.; Woike, T.; Wöhlecke, M.; Imlau, M. Structural Properties of Sr_{0.61}Ba_{0.39}Nb₂O₆ in the Temperature Range 10-500 K Investigated by High-Resolution Neutron Powder Diffraction and Specific Heat Measurements. *Phys. Rev. B Condens. Matter Mater. Phys.* 2006, 74 (13), 1–9.