ELECTRONIC SUPPLEMENTARY INFORMATION

Effect of local A-site strain on dipole stability in $AGaNb_9O_{30}$ (A = Ba, Sr, Ca) tetragonal tungsten bronze relaxor dielectrics

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Rietveld refinements were performed for the powder neutron diffraction data collected for $Ba_{1-x-y}Sr_xCa_yGaNb_9O_{30}$ materials using the General Structure Analysis System (GSAS) suite of programs.[1, 2] Initial refinements were performed for these materials using a non-polar *P*4/*mbm* model[3, 4] for between 55 and 65 variables (depending on the composition and the inclusion of 2nd phase models as described below) including 15 background coefficients fitted using a linear interpolation function and peak shape fitted using a Pseudo-Voigt function. Samples of composition $Ba_{6-x}Sr_xGaNb_9O_{30}$ with $0 \leq x \leq 0.5$ were refined with the inclusion of a $Ba_5Nb_4O_{15}$ 'slab-perovsite' second phase.[5] The amount of 2nd phase decreases with increasing values of x, with ~7.6 % observed in $Ba_6GaNb_9O_{30}$ and ~1.3 % in $Ba_3Sr_3GaNb_9O_{30}$. Rietveld refinement parameters and profiles for data collected using powder neutron diffraction are presented in tables S1 and S2, and figures S1 through S3 respectively.

Refinements were performed initially allowing the fractional occupancies to be refined in order to assess site preferences. As with our previous work the B-site cations remain distributed across both the B1 and B2 crystallographic sites.[3] We therefore fixed the occupancies on these sites to be Nb = 0.9 and Ga = 0.1. However, when the fractional occupancies of the A-site cations were included in the refinement, there was a clear preference for the smaller cation to occupy the smaller A1 perovskite site. For example, Ba_4Ca_2 and Ba_4Sr_2 refined such that they exhibit a nominal formula of $A1_{Ca}A2_{Ba}$ and $A1_{Sr}A2_{Ba}$ respectively. As the refinements become more complex with three A-site cations to consider it becomes difficult to assess site preference and/or occupancy. However, preliminary refinements suggested that the smallest cation preferentially occupied the smaller A1-site. In order to keep the refinements presented here comparable we have fixed the A-site cation occupancy based on cation size (*i.e.*, A2 sites are preferentially filled by Ba, then Sr and then Ca; for the A1 site, the order is reversed).

Table S1. Lattice parameters and goodness-of-fit parameters for (Ba,Sr,Ca)$GaNb_9O_{30}$ compositions at room temperature as determined from powder neutron diffraction.

Sample	*wRp (%)*	*Rp (%)*	*a (Å)*	*c (Å)*	*Cell volume (Å^3)*
$Ba_6GaNb_9O_{30}$	5.12	3.90	12.5771(1)	3.97945(5)	629.48(1)
$Ba_5SrGaNb_9O_{30}$	4.85	3.67	12.5401(2)	3.96446(6)	623.43(1)
$Ba_{4.5}Sr_{1.5}GaNb_9O_{30}$	5.59	4.29	12.5218(2)	3.95731(7)	620.48(2)
$Ba_4Sr_2GaNb_9O_{30}$	5.72	4.41	12.5078(2)	3.95019(7)	617.99(2)
$Ba_3Sr_3GaNb_9O_{30}$	6.09	4.84	12.4853(2)	3.93722(7)	613.74(2)
$Ba_2Sr_4GaNb_9O_{30}$	6.61	5.13	12.4562(2)	3.92137(8)	608.43(2)
$Ba_5CaGaNb_9O_{30}$	5.66	4.40	12.5040(2)	3.9523(1)	617.94(2)
$Ba_4Ca_2GaNb_9O_{30}$	7.92	6.26	12.4529(3)	3.9279(1)	609.11(3)
$Ba_3Ca_3GaNb_9O_{30}$	8.84	6.52	12.4386(4)	3.9139(2)	605.56(4)
$Ba_4SrCaGaNb_9O_{30}$	6.27	4.84	12.4817(2)	3.9399(1)	613.81(2)
$Ba_3Sr_2CaGaNb_9O_{30}$	6.49	5.10	12.4566(2)	3.9254(1)	609.10(2)
$Ba_2Sr_3CaGaNb_9O_{30}$	7.22	5.51	12.4287(3)	3.9088(1)	603.80(3)
$Ba_3SrCa_2GaNb_9O_{30}$	7.43	5.75	12.4380(2)	3.9167(1)	605.93(2)

Table S2. Refinement details for the room temperature powder neutron refinements performed for $Ba_{6-x-y}Sr_xCa_yGaNb_9O_{30}$ materials collected using the D2b beamline at the Institut Laue-Langevin (ILL), France at a constant wavelength, λ = 1.5943201 Å in the *P*4/*mbm* space group. Note: oxygen positions were fitted with U_{ANISO}.

Parameter	$Ba_6GaNb_9O_{30}$	$Ba_5SrGaNb_9O_{30}$	$Ba_{4.5}Sr_{1.5}GaNb_9O_{30}$	$Ba_4Sr_2GaNb_9O_{30}$	$Ba_3Sr_3GaNb_9O_{30}$	$Ba_2Sr_4GaNb_9O_{30}$	$Ba_5CaGaNb_9O_{30}$
Ba1/Sr1 (0,0,0)							
Ui/Ue x 100	0.44(8)	0.5(1)	0.97(8)	1.00(8)	1.06(7)	1.25(7)	2.2(1)
Ba2/Sr2 (x,y,0)	0.1724(2) 0.6724(2)	0.1718(2) 0.6718(2)	0.1721(3) 0.6721(3)	0.1719(3) 0.6719(3)	0.1713(2) 0.6713(2)	0.1704(3) 0.6704(3)	0.1719(3) 0.6719(3)
Ui/Ue x 100	1.75(8)	2.0(1)	2.04(9)	1.8(1)	2.21(8)	3.8(1)	2.2(1)
Nb/Ga1 (0,0.5,0.5)							
Ui/Ue x 100	1.22(8)	1.16(8)	1.36(9)	1.05(9)	1.22(8)	1.48(9)	1.7(1)
Nb/Ga2 (x,y,0.5)	0.0750(2) 0.2147(2)	0.0746(2) 0.2136(1)	0.0746(2) 0.2134(2)	0.0747(2) 0.2131(2)	0.0745(2) 0.2135(2)	0.0749(2) 0.2131(2)	0.0737(2) 0.2133(2)
Ui/Ue x 100	0.83(3)	0.94(4)	1.00(4)	0.71(4)	1.05(4)	1.32(4)	1.66(5)
O1 (0,0.5,0)							
Ui/Ue x 100	1.73*	2.72*	2.98*	2.80*	3.99*	5.22*	4.11*
O2 (x,y,0.5)	0.2827(1) 0.7827(1)	0.2822(2) 0.7822(2)	0.2820(2) 0.7820(2)	0.2821(2) 0.7821(2)	0.2805(2) 0.7805(2)	0.2793(2) 0.7793(2)	0.2819(2) 0.7819(2)
Ui/Ue x 100	0.67*	0.83*	1.28*	0.90*	1.52*	2.05*	2.07*
O3 (x,y,0)	0.0765(2) 0.2080(2)	0.0759(2) 0.2063(2)	0.0759(3) 0.2051(2)	0.0756(3) 0.2046(2)	0.0760(4) 0.2038(2)	0.0775(4) 0.2029(3)	0.0754(4) 0.2046(3)
Ui/Ue x 100	0.92*	1.83*	2.43*	2.58*	3.80*	4.81*	4.28*
O4 (x,y,0.5)	0.3443(2) 0.0067(1)	0.3441(2) 0.0067(2)	0.3439(2) 0.0068(2)	0.3450(2) 0.0066(2)	0.3435(2) 0.0074(2)	0.3435(2) 0.0063(2)	0.3441(2) 0.0065(2)
Ui/Ue x 100	0.82*	1.10*	1.38*	1.19*	2.11*	2.96*	2.03*
O5 (x,y,0.5)	0.1411(2) 0.0694(2)	0.1395(2) 0.0681(2)	0.1390(2) 0.0679(2)	0.1380(2) 0.0670(2)	0.1387(2) 0.0660(2)	0.1383(2) 0.0651(2)	0.1391(2) 0.0684(2)
Ui/Ue x 100	0.55*	1.17*	1.57*	1.49*	2.45*	2.97*	3.42*
Nb/Ga1-O1	1.98972(2)	1.98223(3)	1.97865(4)	1.97504(4)	1.96861(3)	1.96069(4)	1.97614(5)
Nb/Ga1-O4	1.961(2)	1.956(2)	1.957(2)	1.947(3)	1.957(3)	1.951(3)	1.951(3)
Nb/Ga2-O2	1.984(2)	1.992(2)	1.991(2)	1.992(3)	1.995(2)	1.994(3)	1.999(3)
Nb/Ga2-O3	1.9916(2)	1.9844(2)	1.9814(2)	1.9775(2)	1.9724(3)	1.9651(3)	1.9792(3)
Nb/Ga2-O4	1.927(3)	1.929(3)	1.926(3)	1.928(3)	1.918(3)	1.9651(3)	1.919(3)
Nb/Ga2-O5	2.008(3)	1.997(3)	1.993(3)	1.993(4)	2.008(3)	2.006(3)	2.004(4)
Nb/Ga2-O5	2.038(3)	2.017(3)	2.012(3)	2.000(4)	1.987(3)	1.978(4)	1.988(3)

Table S3. Refinement details for the room temperature powder neutron refinements performed for $Ba_{6-x-y}Sr_xCa_yGaNb_9O_{30}$ materials collected using the D2b beamline at the Institut Laue-Langevin (ILL), France at a constant wavelength, λ = 1.5943201 Å in the *P*4/*mbm* space group. Note: oxygen positions were fitted with U_{ANISO}.

Parameter	$Ba_4Ca_2GaNb_9O_{30}$	$Ba_3Ca_3GaNb_9O_{30}$	$Ba_4SrCaGaNb_9O_{30}$	$Ba_3Sr_2CaGaNb_9O_{30}$	$Ba_2Sr_3CaGaNb_9O_{30}$	$Ba_3SrCa_2GaNb_9O_{30}$
Ba1/Sr1 (0,0,0)						
Ui/Ue x 100	2.2(5)	1.92(22)	1.7(1)	1.42(10)	1.0(1)	1.2(1)
Ba2/Sr2 (x,y,0)	0.1714(3) 0.6714(3)	0.1716(5) 0.6716(5)	0.1717(3) 0.6717(3)	0.1712(3) 0.6712(3)	0.1708(4) 0.6708(4)	0.1712(3) 0.6712(3)
Ui/Ue x 100	1.6(1)	1.6(2)	1.7(1)	2.7(1)	3.2(1)	2.0(1)
Nb/Ga1 (0,0.5,0.5)						
Ui/Ue x 100	1.6(1)	1.7(2)	1.5(1)	1.4(1)	1.1(1)	1.3(1)
Nb/Ga2 (x,y,0.5)	0.0726(3) 0.2126(2)	0.0751(3) 0.2115(3)	0.0733(2) 0.2128(2)	0.0734(2) 0.2127(2)	0.0739(2) 0.2125(2)	0.0740(2) 0.2128(2)
Ui/Ue x 100	1.44(6)	1.06(8)	1.25(5)	1.27(5)	1.16(6)	0.84(6)
O1 (0,0.5,0)						
Ui/Ue x 100	4.67*	6.21*	4.05*	5.14*	6.31*	4.63*
O2 (x,y,0.5)	0.2819(3) 0.7819(3)	0.2843(4) 0.7843(4)	0.2820(2) 0.7820(2)	0.2807(3) 0.7807(3)	0.2798(3) 0.7798(3)	0.2811(3) 0.7811(3)
Ui/Ue x 100	2.42*	2.11*	1.68*	2.16*	2.27*	2.19*
O3 (x,y,0)	0.0750(6) 0.2008(4)	0.0733(9) 0.2014(6)	0.0747(4) 0.2025(3)	0.0762(5) 0.2018(3)	0.0758(6) 0.2002(4)	0.0737(6) 0.2002(4)
Ui/Ue x 100	6.59*	6.73*	4.97*	5.26*	5.57*	6.63*
O4 (x,y,0.5)	0.3440(3) 0.0068(3)	0.3434(4) 0.0073(4)	0.3442(2) 0.0067(2)	0.3437(2) 0.0068(2)	0.3430(3) 0.0068(3)	0.3434(3) 0.0071(3)
Ui/Ue x 100	2.41*	1.99*	2.14*	2.51*	3.21*	2.24*
O5 (x,y,0.5)	0.1348(4) 0.0662(4)	0.1350(5) 0.0629(5)	0.1374(3) 0.0665(3)	0.1372(3) 0.0654(3)	0.1377(4) 0.0645(3)	0.1363(4) 0.0649(3)
Ui/Ue x 100	6.07*	5.96*	3.78*	3.96*	4.22*	5.23*
Nb/Ga1-O1	1.96393(6)	1.95699(8)	1.96993(5)	1.96271(5)	1.95438(6)	1.95836(5)
Nb/Ga1-O4	1.945(4)	1.950(5)	1.947(3)	1.949(3)	1.954(4)	1.950(4)
Nb/Ga2-O2	2.007(4)	1.970(4)	2.002(3)	2.004(3)	2.001(3)	1.992(3)
Nb/Ga2-O3	1.9696(5)	1.9611(5)	1.9742(3)	1.9677(4)	1.9604(5)	1.9645(5)
Nb/Ga2-O4	1.912(4)	1.935(6)	1.920(3)	1.913(4)	1.907(4)	1.913(4)
Nb/Ga2-O5	1.980(5)	1.993(7)	1.994(4)	1.999(4)	2.003(5)	1.996(5)
Nb/Ga2-O5	1.982(5)	1.962(8)	1.982(4)	1.969(4)	1.956(5)	1.972(5)

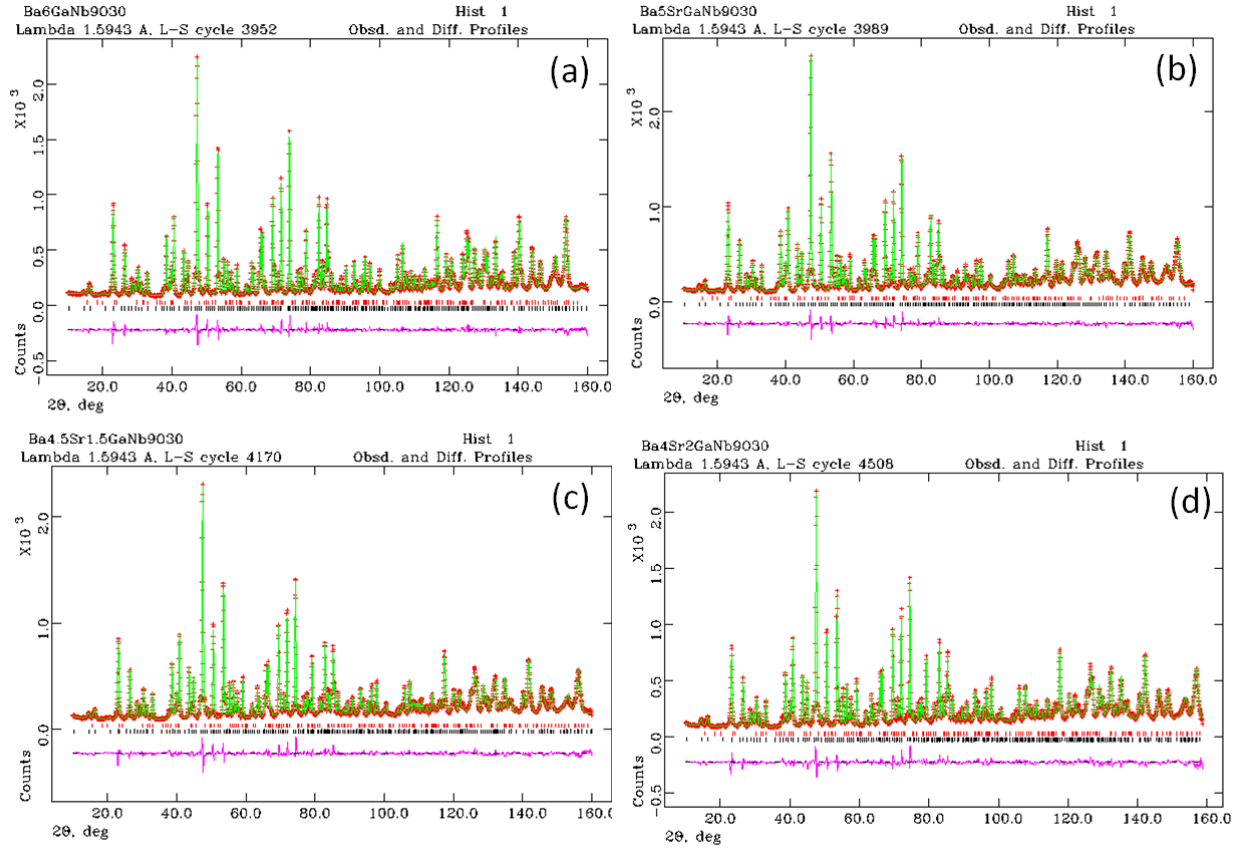

Figure S1. Rietveld refinement profiles for room temperature powder neutron diffraction data collected for (a) $Ba_6GaNb_9O_{30}$, (b) $Ba_sSrGaNb_9O_{30}$, (c) $Ba_{4.5}Sr_{1.5}GaNb_9O_{30}$ and (d) $Ba_4Sr_2GaNb_9O_{30}$ refined in the non-polar *P*4/*mbm* space group. The red circles are the collected data, the green line represents the calculated model and the pink line the difference between the two.

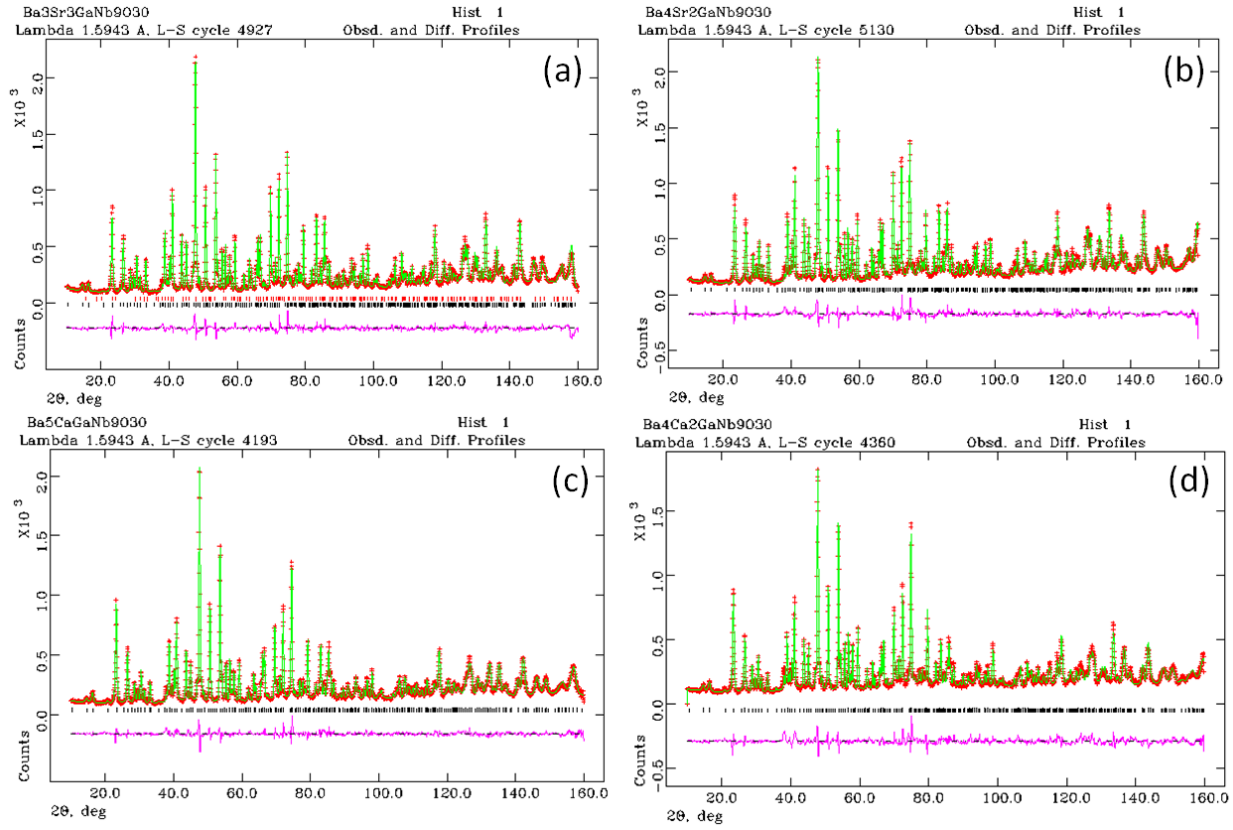

Figure S2. Rietveld refinement profiles for room temperature powder neutron diffraction data collected for (a) $Ba_3Sr_3GaNb_9O_{30}$, (b) $Ba_2Sr_4GaNb_9O_{30}$, (c) $Ba_5CaGaNb_9O_{30}$ and (d) $Ba_4Ca_2GaNb_9O_{30}$ refined in the non-polar *P*4/*mbm* space group. The red circles are the collected data, the green line represents the calculated model and the pink line the difference between the two.

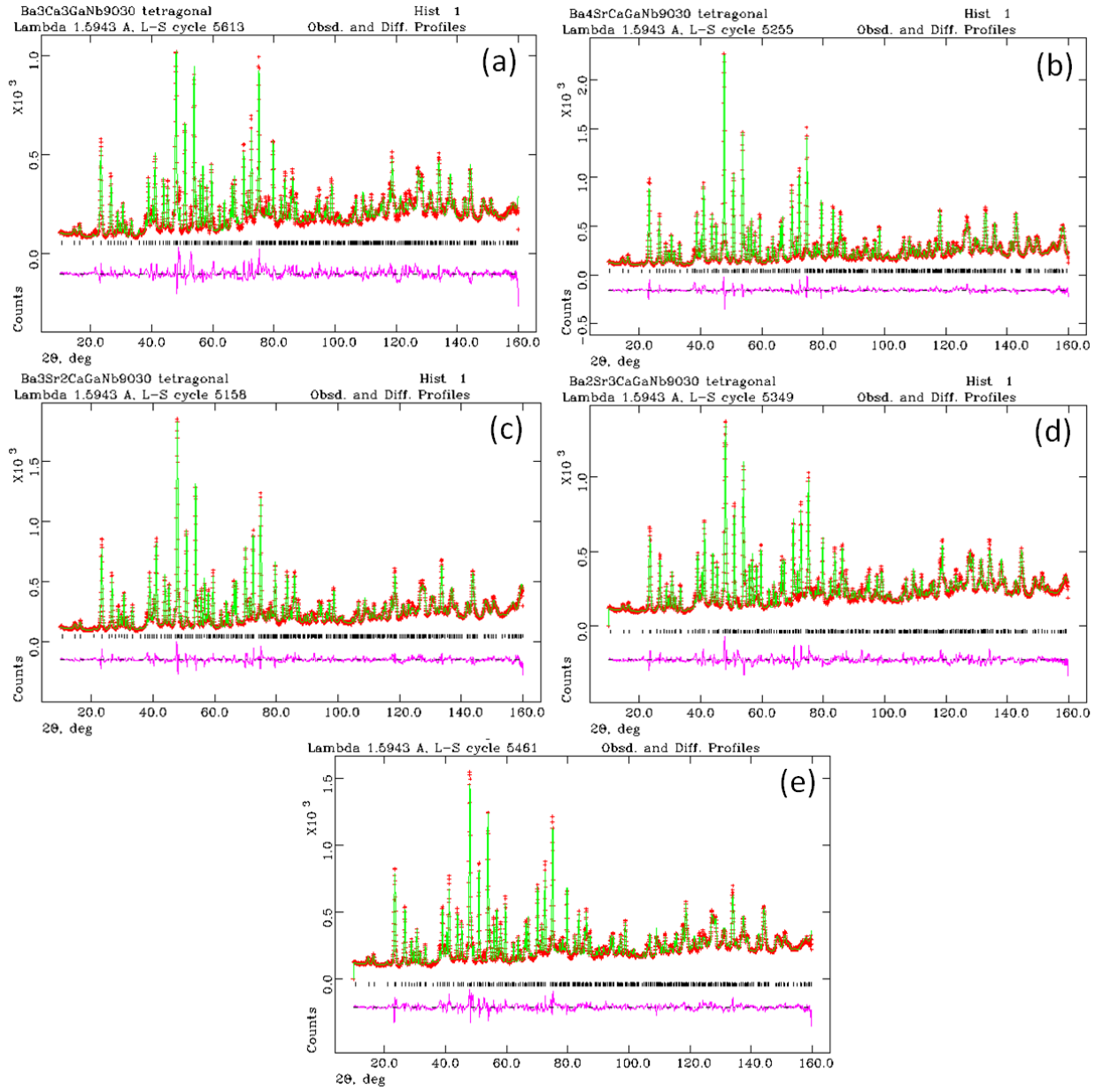

Figure S3. Rietveld refinement profiles for room temperature powder neutron diffraction data collected for (a) $Ba_3Ca_3GaNb_9O_{30}$, (b) $Ba_4SrCaGaNb_9O_{30}$, (c) $Ba_3Sr_2CaGaNb_9O_{30}$, (d) $Ba_2Sr_3CaGaNb_9O_{30}$ and (e) $Ba_3SrCa_2GaNb_9O_{30}$ refined in the non-polar *P*4/*mbm* space group. The red circles are the collected data, the green line represents the calculated model and the pink line the difference between the two.

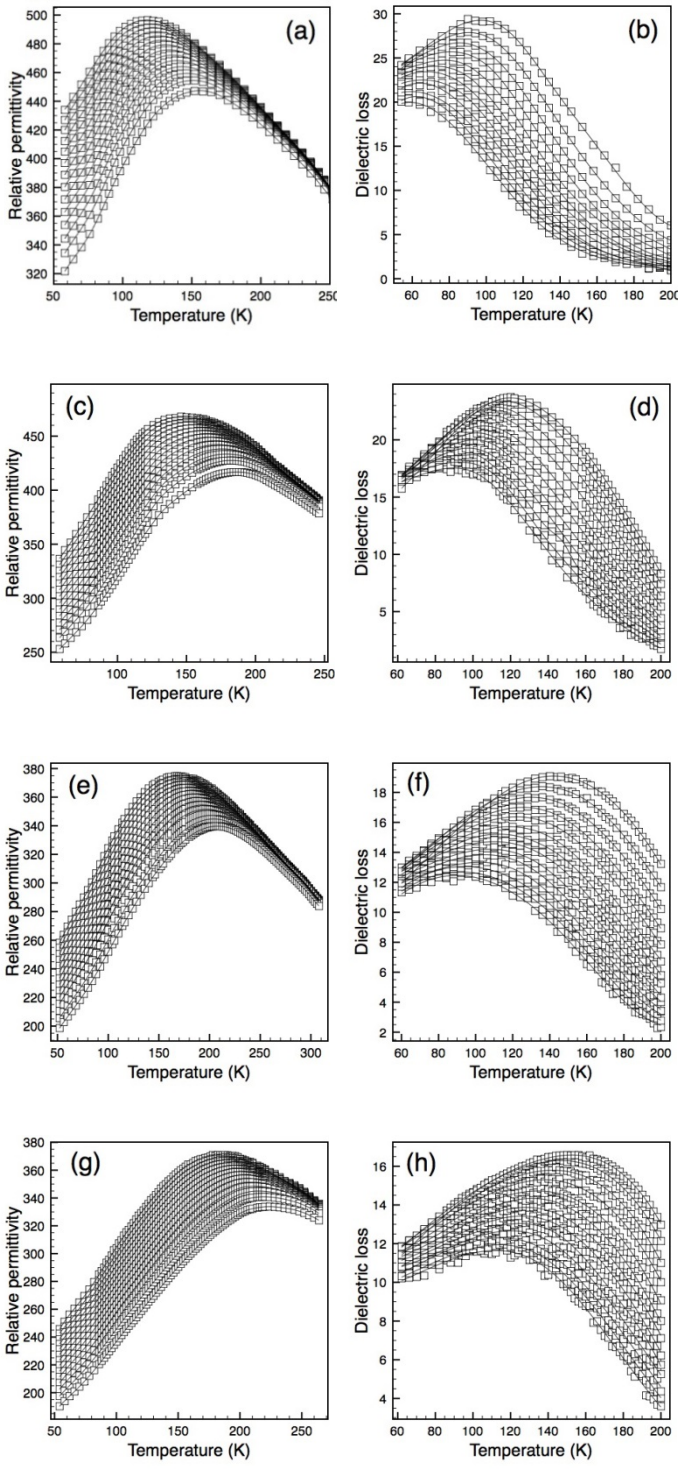

Figure S4. Dielectric data as a function of frequency and temperature showing relaxor behaviour for $Ba_4Sr_{1-z}(Ba_{0.37}Ca_{0.63})_zGaNb_9O_{30}$. Relative permittivity and dielectric loss for z = 0.5 (a,b), 1.0 (c,d), 1.5 (e,f) and 2.0 (g,h).

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