Supplementary Information

A-site size effect in a family of unfilled ferroelectric tetragonal tungsten bronzes: $Ba_4R_{0.67}Nb_{10}O_{30}$ (R = La, Nd, Sm, Gd, Dy and Y).

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Table 1 – Pellet densities under varied sintering conditions for $Ba_4R_{0.67}\square_{1.33}Nb_{10}O_{30}$

R	2nd step sintering time (hours)	Theoretical Densities (g cm^{-3})	Pellet density (% theoretical)		
			1350 °C	1375 °C	1400 °C
La	6	5.51	94.9	96.5	95.8
Nd	6	5.54	97.2	97.3	95.3
Sm	6	5.55	94.7	96.7	96.4
Gd	6	5.57	96.5	95.9	96.0
Dy	6	5.58	95.8	95.5	95.7
Y	12	5.46	94.5	96.3	84.4

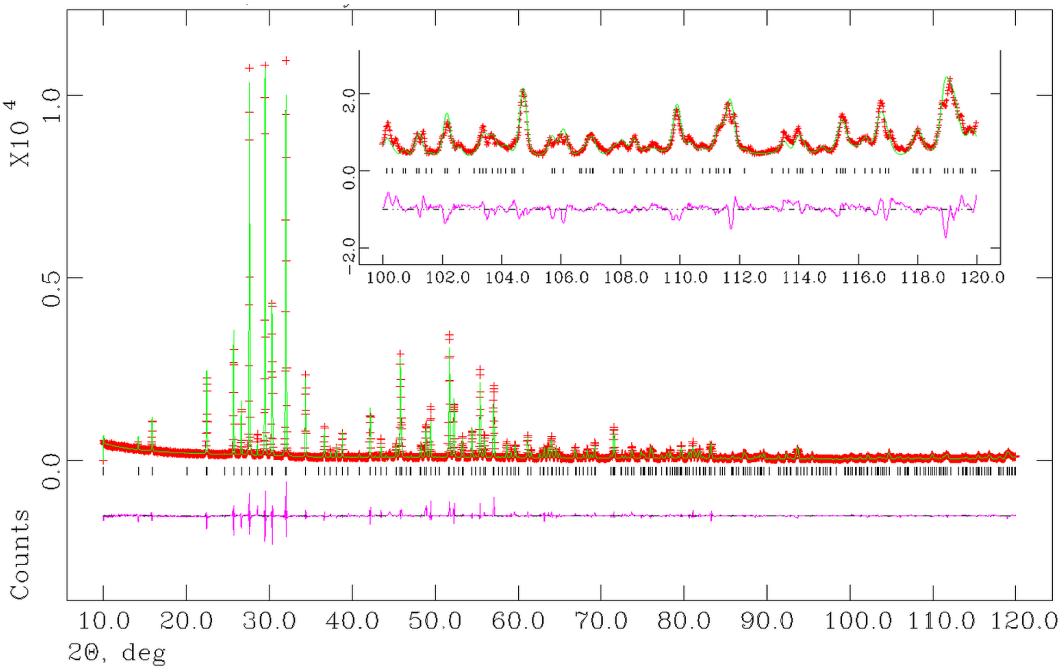

Figure S1: Rietveld refinement of PXRD data at ambient temperature for $Ba_4La_{0.67}\square_{1.33}Nb_{10}O_{30}$, with observed data (red crosses), calculated (green line), reflection positions (black tickmarks) and difference plot (pink line, bottom).

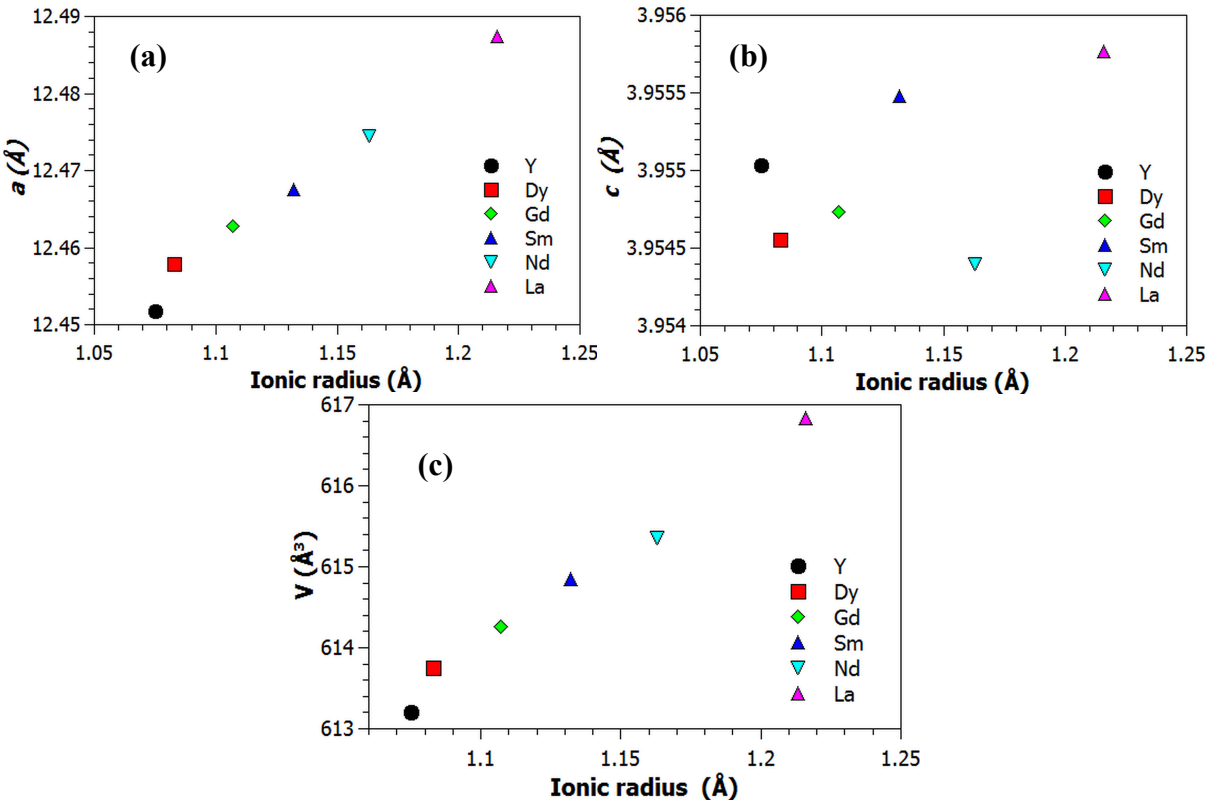

Figure S2: (a) *a* and (b) *c* lattice parameters, (c) unit cell volume as a function of R ionic radius.

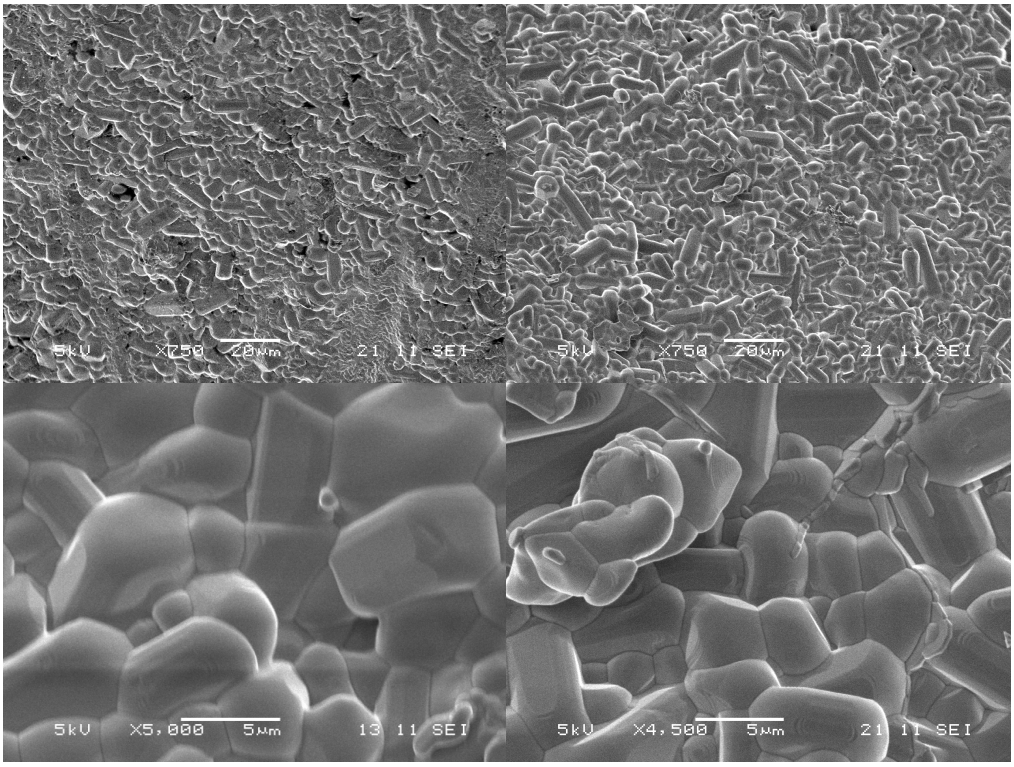

Figure S3: SEM micrographs of Gd (left) and La (right) showing uniform grain size and low porosity.

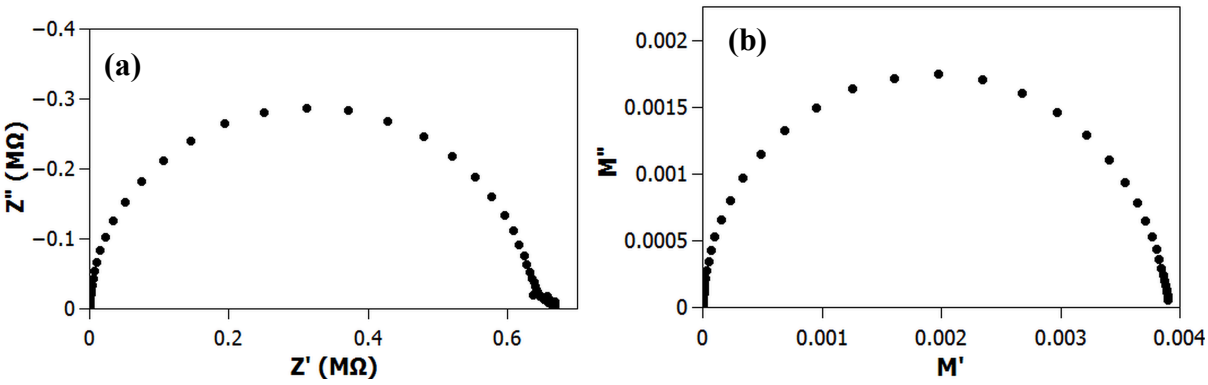

Figure S4**:** High temperature immittance spectroscopy data for $Ba_4Dy_{0.67}\square_{1.33}Nb_{10}O_{30}$ showing complex impedance, Z* (a) and modulus, M* (b) plane plots (both at 847 K).

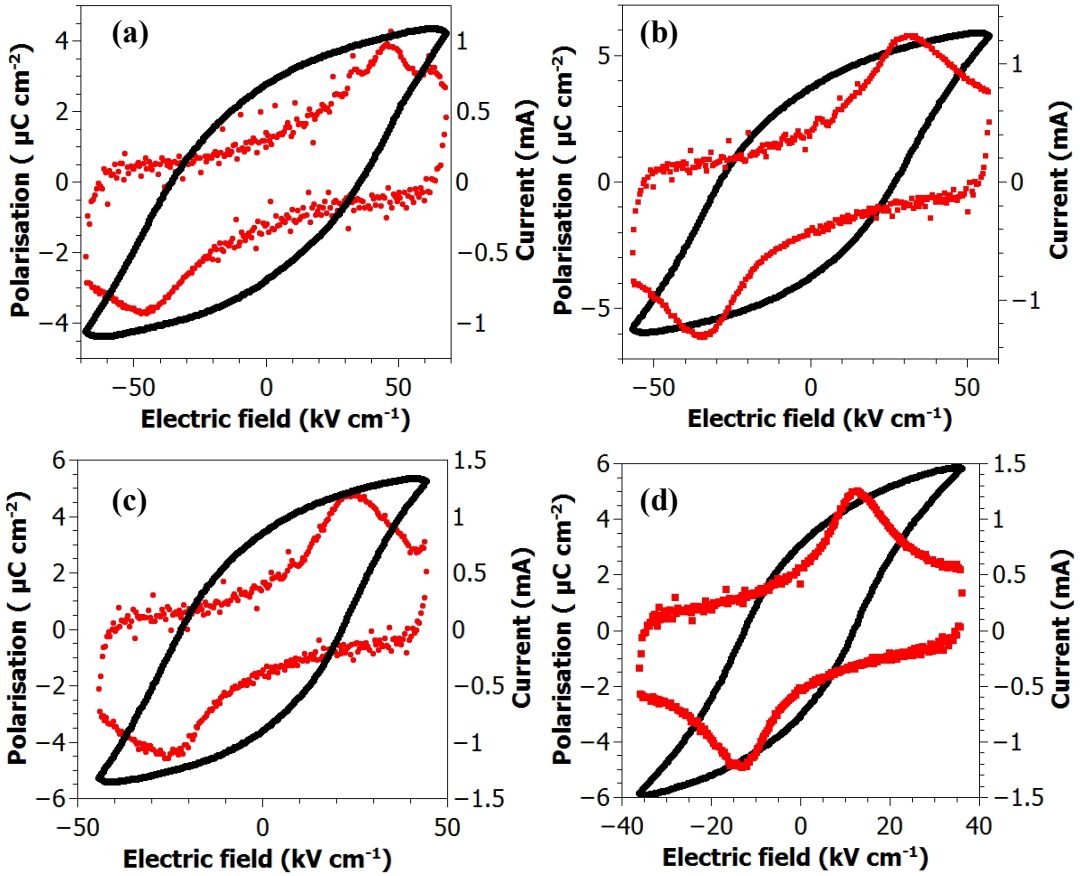

Figure S5: *P-E* hysteresis loop for $Ba_4R_{0.67}\square_{1.33}Nb_{10}O_{30}$ R = Y, Gd, Sm and Nd, (a)-(d), respectively. Data collected at 100Hz and 296 K.

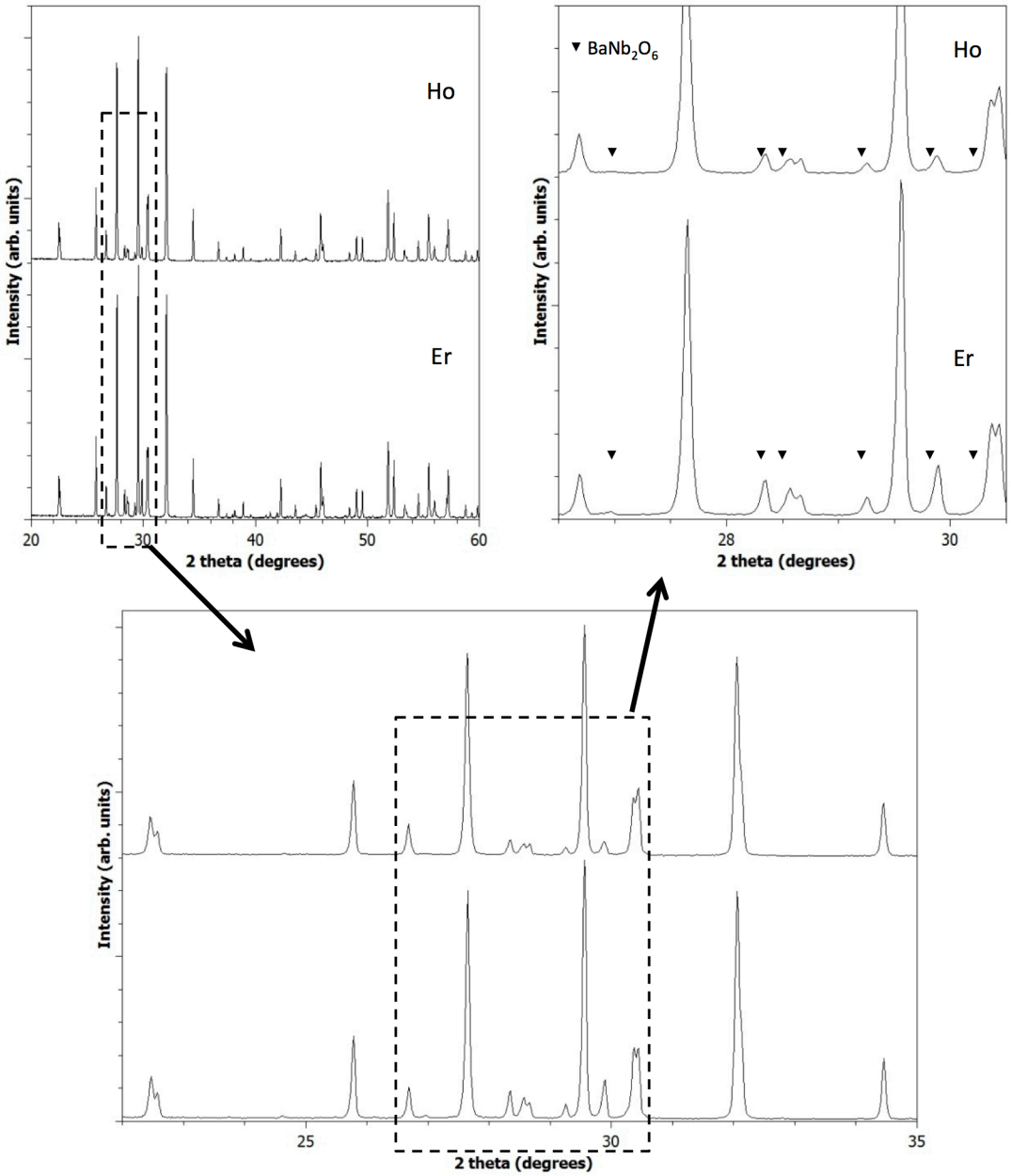

Figure S6: PXRD data for $Ba_4R_{0.67}\square_{1.33}Nb_{10}O_{30}$ R= Ho and Er with systematically expanded 2 theta scale (anti-clockwise from top) indicating the presence of significant amounts of the secondary phase $BaNb_2O_6$ (ICSD Code 39320, from V.P. Sirotinkin and S.P Sirotinkin, *Zhurnal Neorganicheskoi Khimii*, 1990, 35, 2189). The main TTB phase for each was refined in space group *P4bm* with the resulting lattice parameters: Ho sample, a = 12.453518 Å, c = 3.956334 Å; Er sample a = 12.45120 Å, c = 3.954213 Å.

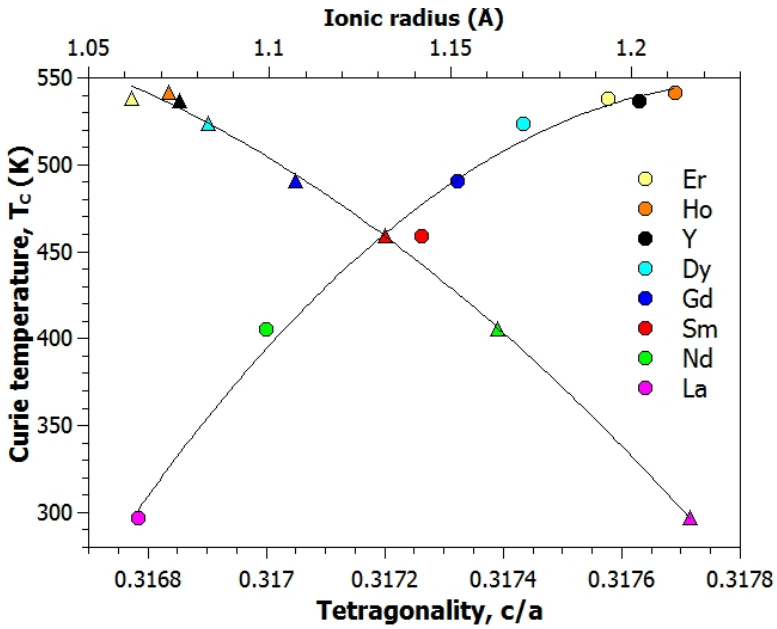

Figure S7: Correlation of Curie temperature with tetragonality and ionic radius with data for the main TTB phase of Ho and Er samples included. Note that the nominal composition of these TTB phases is not known, but is unlikely to be $Ba_4R_{0.67}\square_{1.33}Nb_{10}O_{30}$.