Supplementary information:

Structure and control of negative thermal expansion of Nd/Sm substituted $0.5PbTiO_3$-$0.5BiFeO_3$ ferroelectrics

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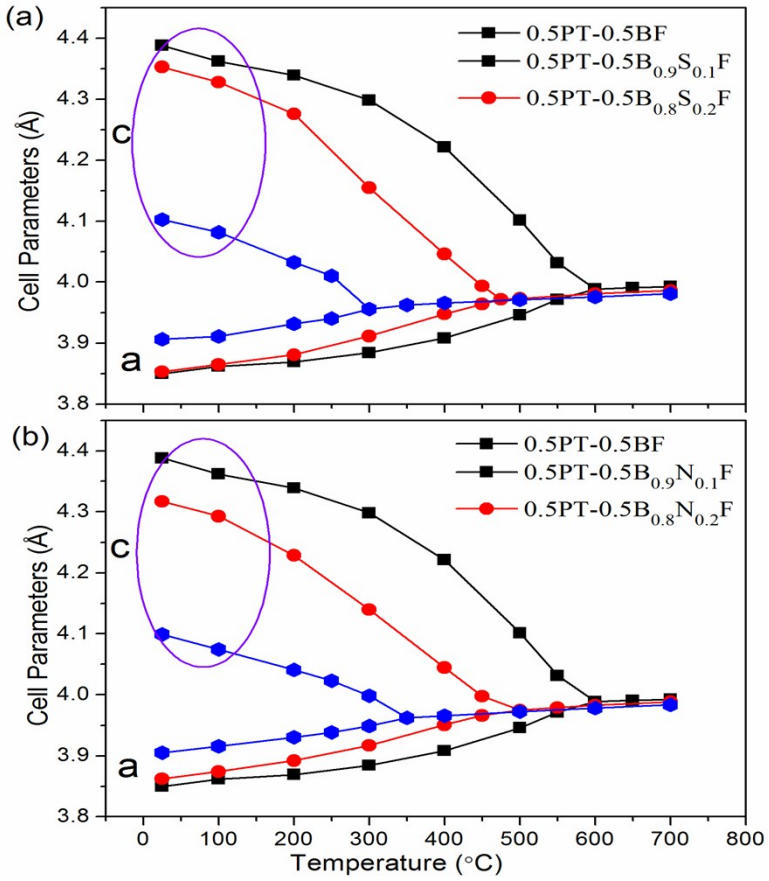

Fig. S1 Temperature dependence of lattice constant of $0.5PT\text{-}0.5B_{1-x}(N/S)_xF$, $x = 0$, 0.1, and 0.2.

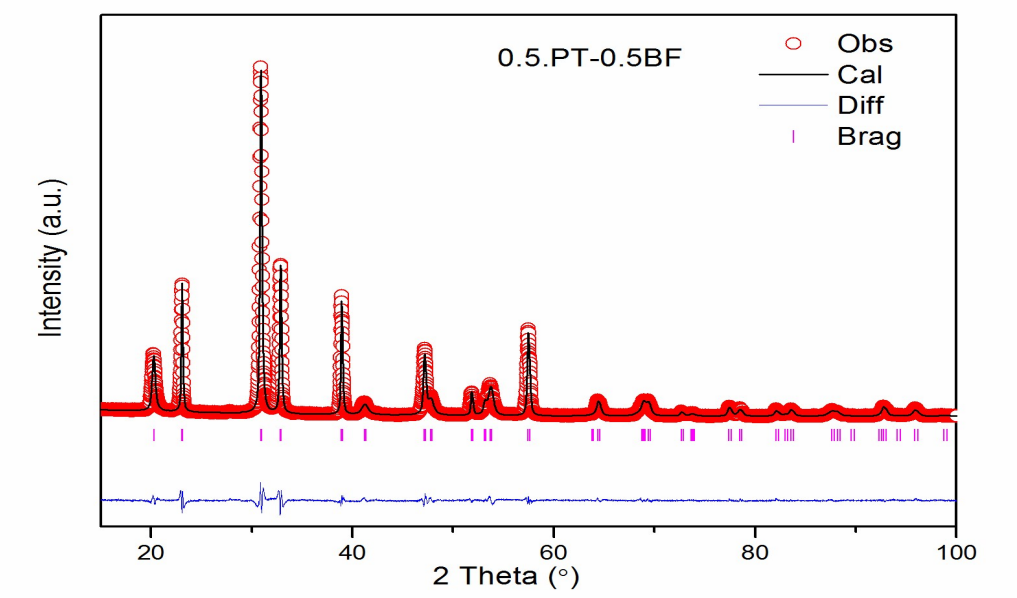

Fig. S2 Observed (point), calculated (line) and difference profiles at room temperature after Rietvrld refinement using space group *P*4*mm* for 0.5PT-0.5BF

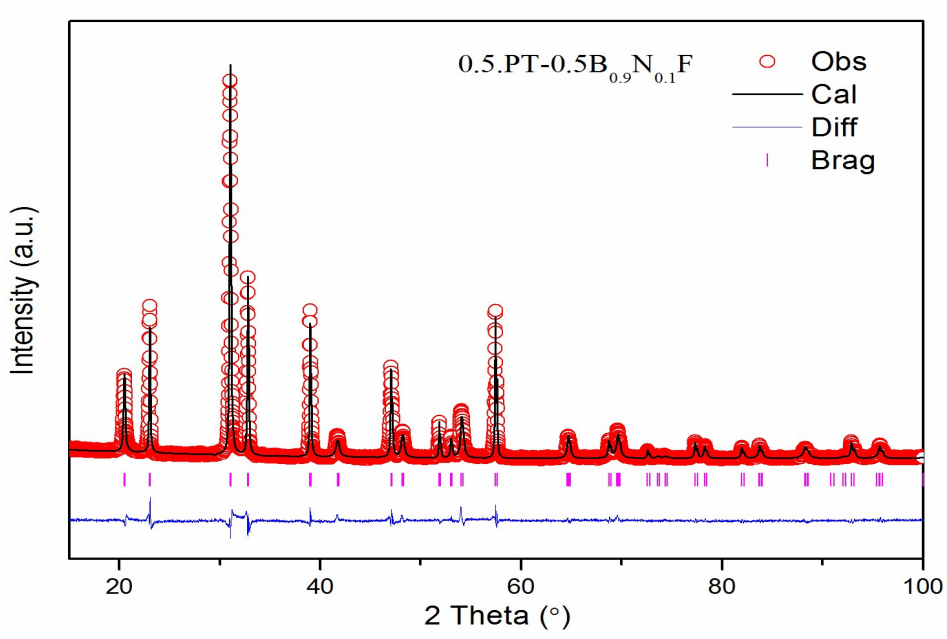

Fig. S3 Observed (point), calculated (line) and difference profiles at room temperature after Rietvrld refinement using *P*4*mm* space group for 0.5PT-0.5$B_{.0.9}N_{0.1}F$.

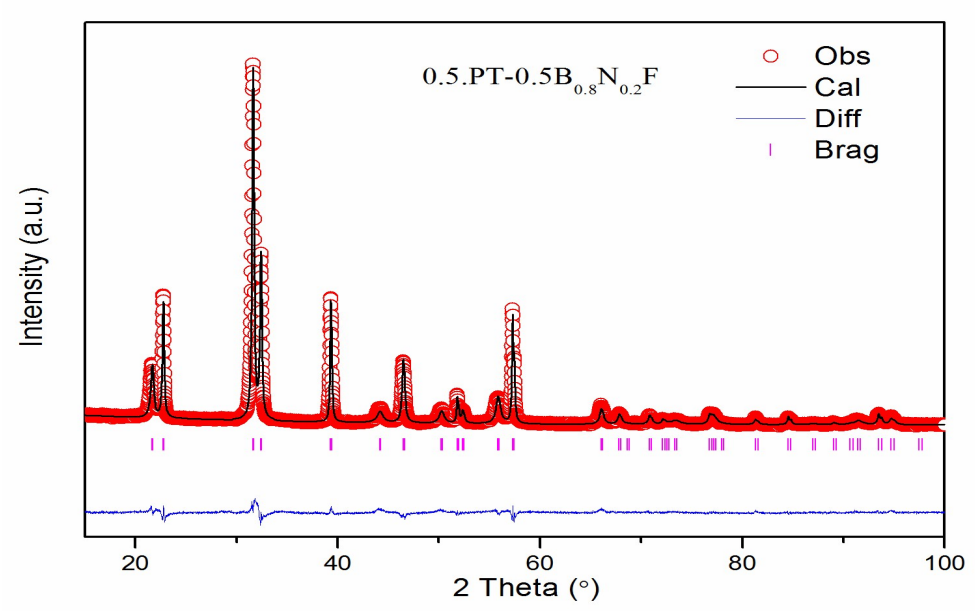

Fig. S4 Observed (point), calculated (line) and difference profiles at room temperature after Rietvrld refinement using *P*4*mm* space group for 0.5PT-0.5$B_{0.8}N_{0.2}F$.

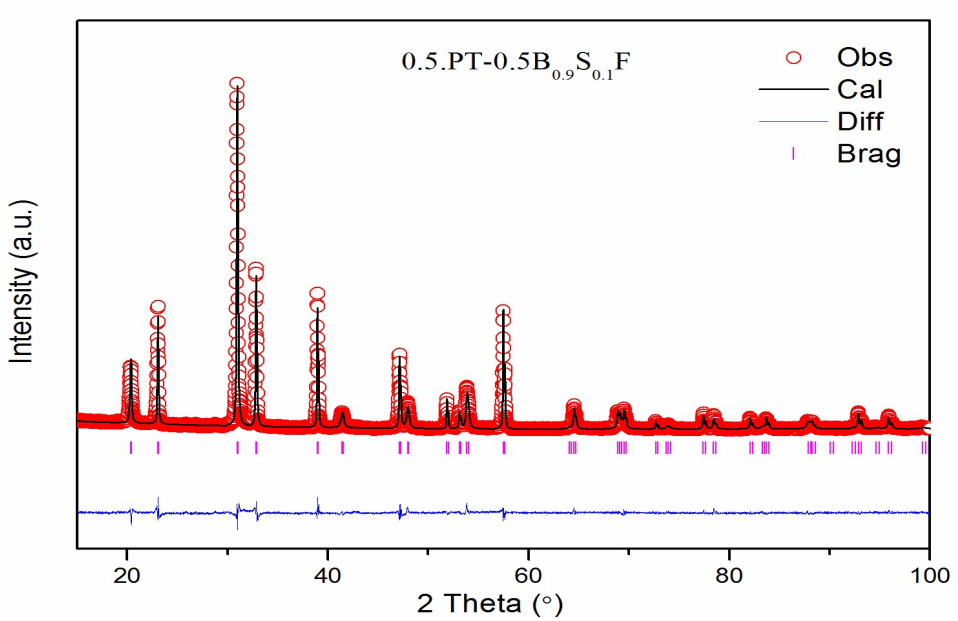

Fig. S5 Observed (point), calculated (line) and difference profiles at room temperature after Rietvrld refinement using *P*4*mm* space group for 0.5PT-0.5$B_{0.9}S_{0.1}F$.

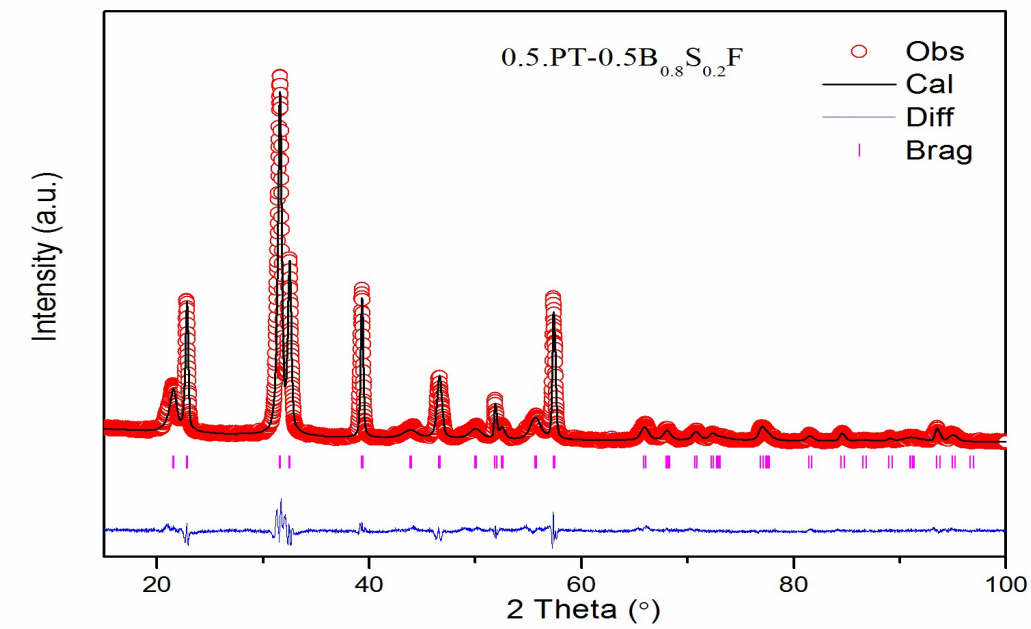

Fig. S6 Observed (point), calculated (line) and difference profiles at room temperature after Rietvrld refinement using *P*4*mm* space group for 0.5PT-0.5$B_{.0.8}S_{0.2}F$.

Table. S1 Crystal structure at room temperature, *T*c, P_S, CTE and ω_s of 0.5PT-0.5$B_{1-x}(N/S)_xF$, x = 0, 0.1, and 0.2.

	0.5PT-0.5BF	**0.5PT-0.5$B_{0.9}N_{0.1}F$**	**0.5PT-0.5$B_{0.8}N_{0.2}F$**	**0.5PT-0.5$B_{0.9}S_{.1}F$**	**0.5PT-0.5$B_{0.8}S_{0.2}F$**
***a*/Å**	3.84974	3.86227	3.90529	3.85307	3.90627
***c*/Å**	4.38816	4.31711	4.09903	4.35266	4.10256
c*/*a	1.14	1.12	1.05	1.13	1.05
V/Å^3	65.027	64.400	62.516	64.620	62.60
δz_A/Å	0.690	0.659	0.520	0.643	0.515
δz_B/Å	0.531	0.466	0.366	0.434	0.352
P_S/μC(cm)$^{-2}$	88.2	81.4	66.0	77.5	64.4
***Tc*/°C**	600	500	350	475	300
CTE/°C^{-1}	-4.18 × 10^{-5}	-5.11 × 10^{-5}	-1.23 × 10^{-5}	-6.42 × 10^{-5}	-2.08 × 10^{-5}
ω_s/%	4.84	4.52	1.91	4.38	1.82

Table. S2 Refined structure parameters of 0.5PT-0.5B_{1-x}(N/S)$_x$F, x = 0, 0.1, and 0.2.

	0.5PT-0.5BF	**0.5PT-0.5$B_{0.9}N_{0.1}$F**	**0.5PT-0.5$B_{0.8}N_{0.2}$F**	**0.5PT-0.5$B_{0.9}S_{.1}$F**	**0.5PT-0.5$B_{0.8}S_{0.2}$F**
$Z_{Pb/Bi/(Nd/Sm)}$	0	0	0	0	0
$Z_{Ti/Fe}$	0.5364	0.5447	0.5375	0.5479	0.5398
$Z_{O(I)}$	0.1469	0.1482	0.1208	0.1418	0.1196
$Z_{O(II)}$	0.6625	0.6548	0.6298	0.6508	0.6285
R_p	3.61	4.08	3.67	3.71	3.55
R_{wp}	4.98	5.52	4.75	4.87	4.72
Chi^2	5.03	4.47	4.15	3.25	4.43

Table. S3. Fitting results of A_1(1TO), A_1(2TO), and A_1(3TO) peaks. For comparison, P_S was listed in the last column.

	A_1(1TO) (cm^{-1})	A_1(2TO) (cm^{-1})	A_1(3TO) (cm^{-1})	P_S/μC(cm)$^{-2}$
0.5PT-0.5BF	201.0	359.9	690.1	88.2
0.5PT-0.5$B_{0.9}S_{0.1}$F	199.2	359.3	687.4	77.5
0.5PT-0.5$B_{0.8}S_{0.2}$F	190.4	355.4	674.3	64.4
0.5PT-0.5$B_{0.9}N_{0.1}$F	198.3	359.2	687.4	81.4
0.5PT-0.5$B_{0.8}N_{0.2}$F	189.4	355.6	678.9	66.0