Supporting Information for

Large Negative Thermal Expansion Induced by Synergistic Effects of Ferroelectrostriction and Spin Crossover in $PbTiO_3$-Based Perovskites

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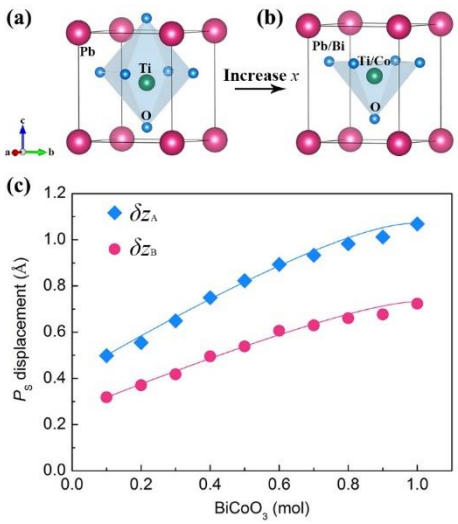

Figure S1. Crystal structure in ABO_3 perovskite-type ferroelectric of (1-x)PT-xBC at RT. The normal (a) BO_6 octahedron is transformed to (b) BO_5 pyramidal coordination with the increase in x. (c) P_S displacement of δz_A and δz_B of (1-x)PT-xBC as a function of x. The error bars are smaller than the symbols.

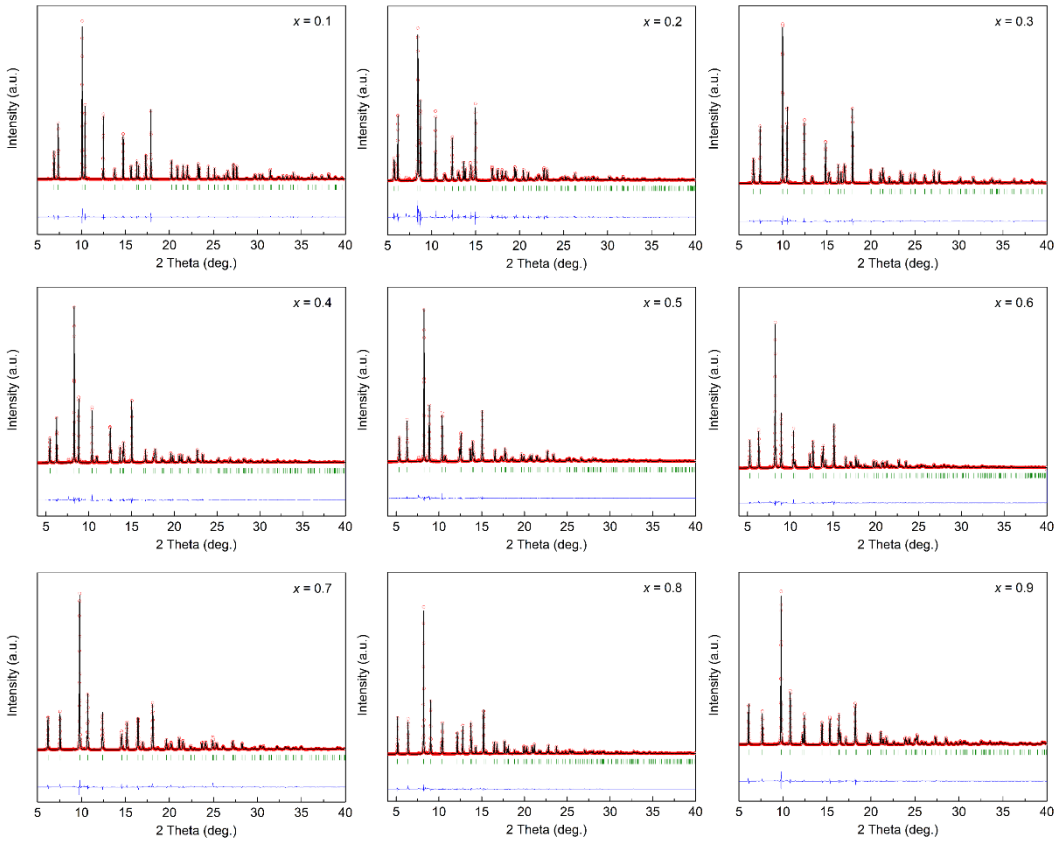

Figure S2. Rietveld refinement of SXRD patterns of tetragonal (1-x)PT-xBC (x = 0.1- 0.9) at room temperature. Observed (red circles), calculated (black line), and their difference profiles (bottom line) are shown. The Bragg reflection positions are indicated by the green ticks. The related wavelength (λ) is 0.419552 Å for x = 0.2, 0.4, 0.5, 0.6, 0.8, and 0.500000 Å for x = 0.1, 0.3, 0.7, and 0.9, respectively.

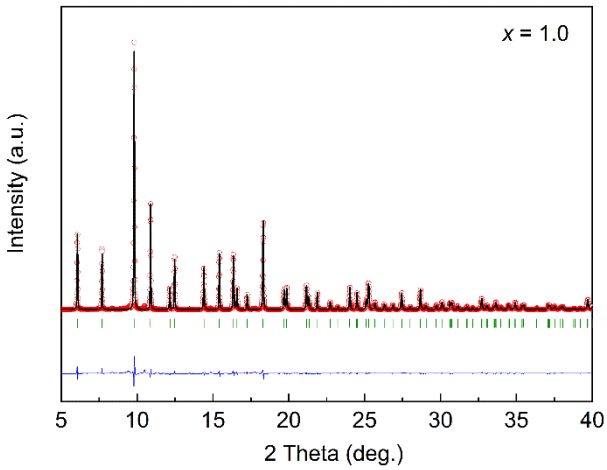

Figure S3. Rietveld refinement of SXRD patterns of tetragonal $BiCoO_3$ (x = 1.0 for (1-x)PT-xBC) at room temperature. Observed (red circles), calculated (black line), and their difference profiles (bottom line) are shown. The Bragg reflection positions are indicated by the green ticks. The related wavelength (λ) is 0.500000 Å

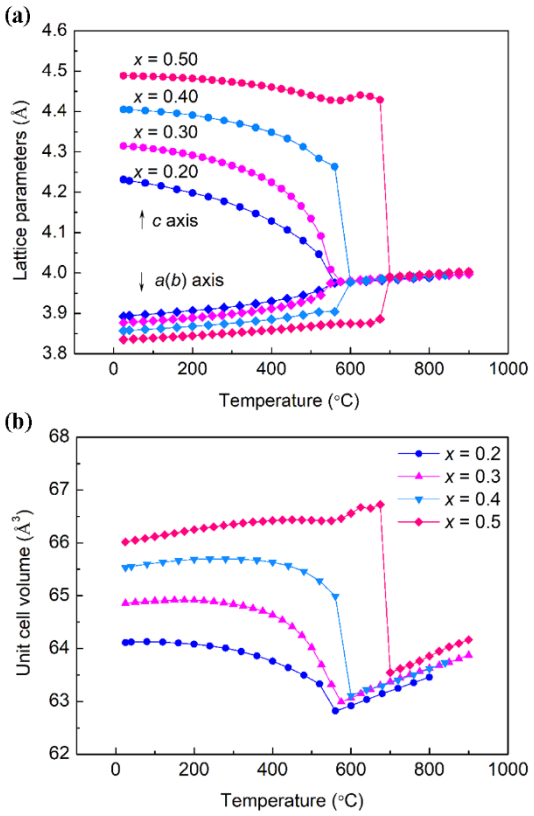

Figure S4. Structural parameters of (a) $a(b)$, c, and (b) unit cell volume as a function of temperature for (1-x)PT-xBC (x = 0.2, 0.3, 0.4, and 0.5). The error bars are smaller than the symbols.

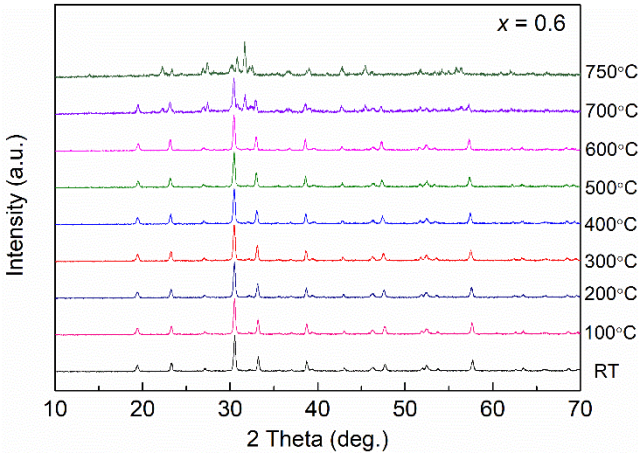

Figure S5. Temperature dependence of X-ray diffraction patterns of $0.4PbTiO_3$-$0.6BiCoO_3$.

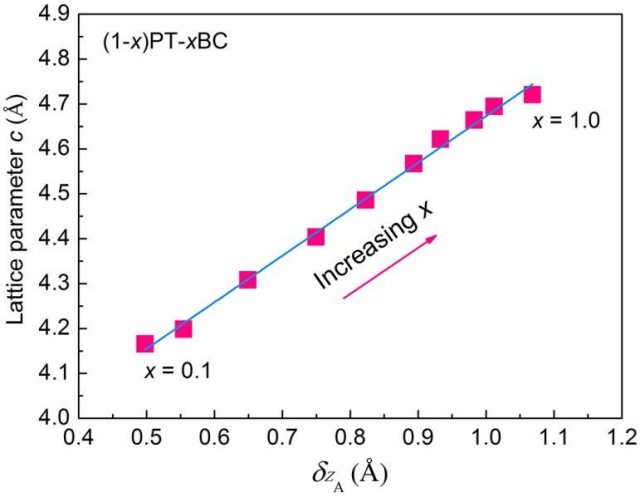

Figure S6. The coupling between the P_S displacement (δz_A) and the lattice parameter c axis of (1-x)PT-xBC (x = 0.0 ~ 1.0). The error bars are smaller than the symbols.

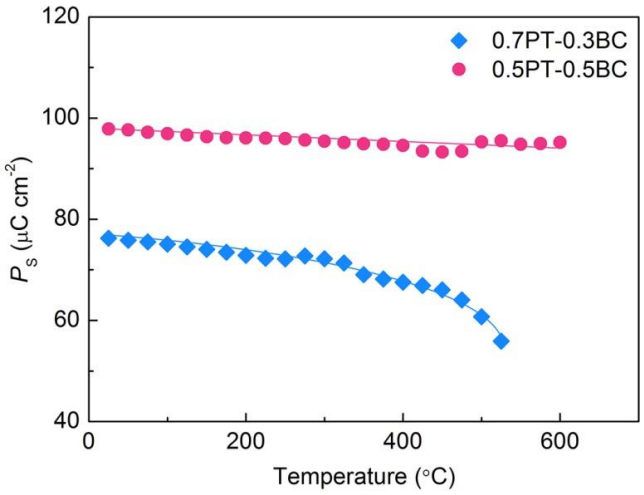

Figure S7. Temperature dependence of calculated P_S for 0.7PT-0.3BC and 0.5PT-0.5BC.

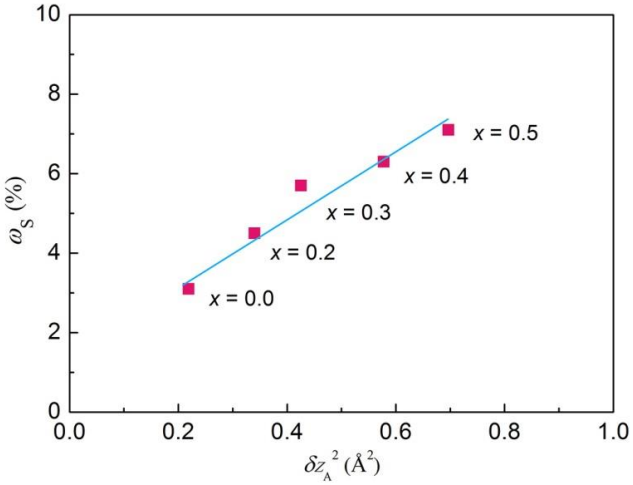

Figure S8. The correlation between the spontaneous volume ferroelectrostriction (ω_S) and P_S displacement (δz_A). There is a strong correlation of $\omega_S = \alpha \delta z_A^2$ for (1-x)PT-xBC (x = 0.0, 0.2, 0.3, 0.4, and 0.5) ferroelectrics.

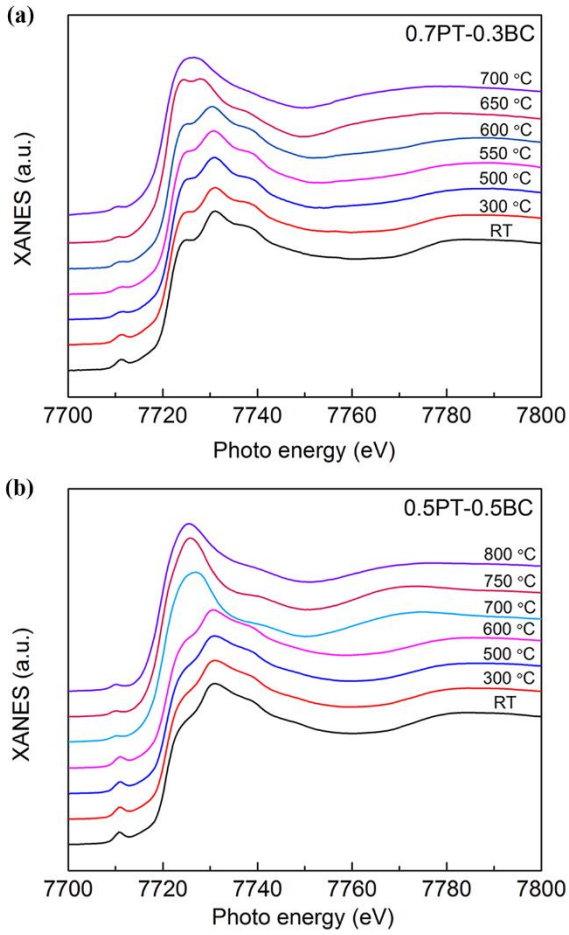

Figure S9. XANES structural analysis. Temperature dependence of Co K-edge XANES spectra for **(a)** 0.7PT-0.3BC and **(b)** 0.5PT-0.5BC.

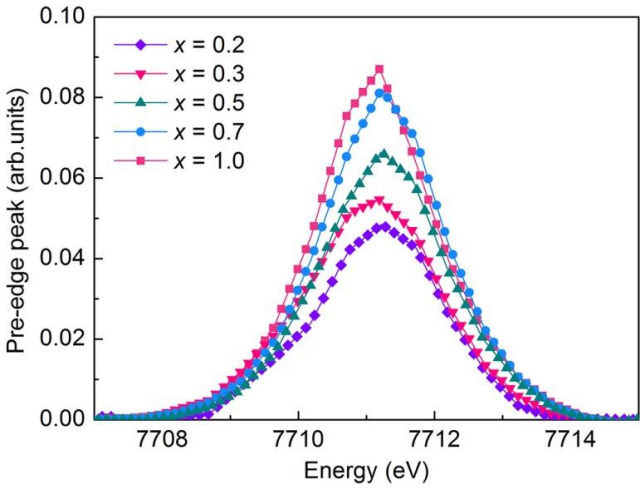

Figure S10. Composition dependence of Co *K* pre-edge peak for (1-*x*)PT-*x*BC (*x* = 0.2, 0.3, 0.5, 0.7, and 1.0) at RT.

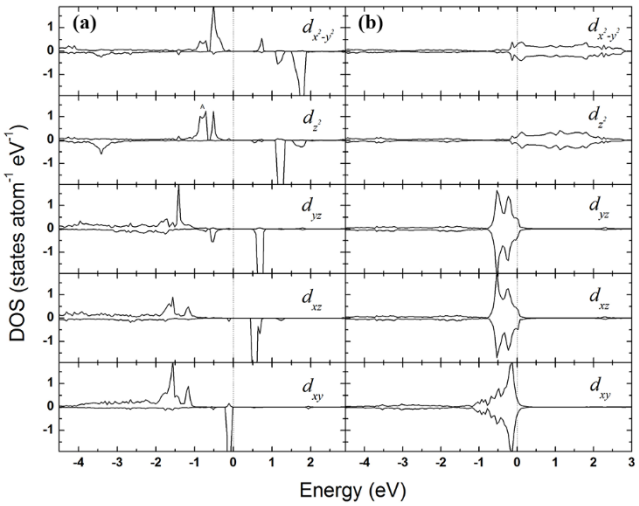

Figure S11. Calculated orbital projected DOS for 0.5PT-0.5BC in the ferroelectric (a) and the paraelectric (b) phases.

Table S1. The data of the CTE, volume contraction, and T_C of (1-*x*)PT-*x*BC.

content	$x = 0$	$x = 0.2$	$x = 0.3$	$x = 0.4$	$x = 0.5$
T_C (°C)	490	560	575	600	700
CTE ($\times 10^{-5}$/°C)	-1.99	-3.78	-5.24	——	——
ΔV	-1.29%	-2.04%	-2.97%	-3.24%	-4.76%

Table S2. Structural refinement results of NPD of 0.5PT-0.5BC at 5 K. O1 and O2 were refined by using anisotropic atomic displacement parameters (U_{11}, U_{22}, and U_{33}). Others are isotropic ones. The quality of the agreement between the observed and calculated profiles is indicated by the weighted R_{wp} and the goodness of fit χ^2.

atom	site	*x*	*y*	*z*	U_{iso}/U_{ij}
Pb/Bi	1a	0	0	0	0.02177
Co/Ti	1b	0.5	0.5	0.597305	0.02456
O1	1b	0.5	0.5	0.178456	0.03044(U_{11}) 0.03044(U_{22}) 0.01287(U_{33})
O2	2c	0.5	0	0.684938	0.01585(U_{11}) 0.00963(U_{22}) 0.02077(U_{33})

*Space group *P*4*mm*, *a*(*b*) = 3.82055(4) Å, *c* = 4.49313(2) Å, m_z (Co) = 3.24 μB, χ^2 = 1.28, R_{wp} = 6.82%.