Supplementary Information (SI) for Materials Horizons.
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Supplemental Material

Engineering Zero Thermal Expansion over a Wide Temperature Range in $PbTiO_3$-Based Ferroelectrics

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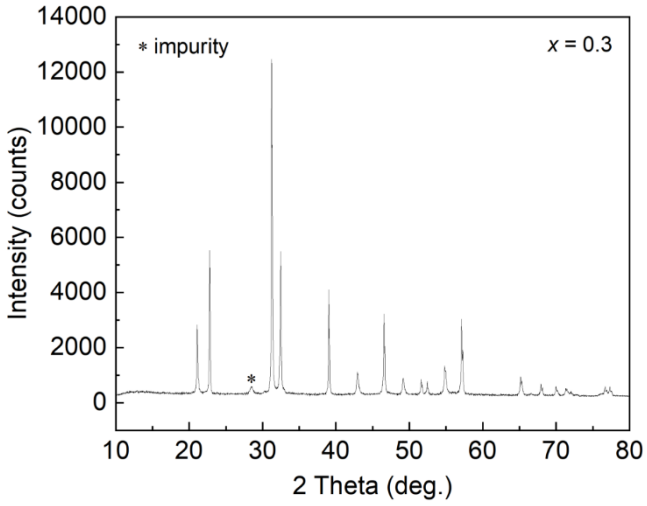


Figure S1. XRD patterns of (1-*x*)PT-*x*BCW (*x* = 0.30) measured at room temperature. Impurity peak is marked by asterisk (*).

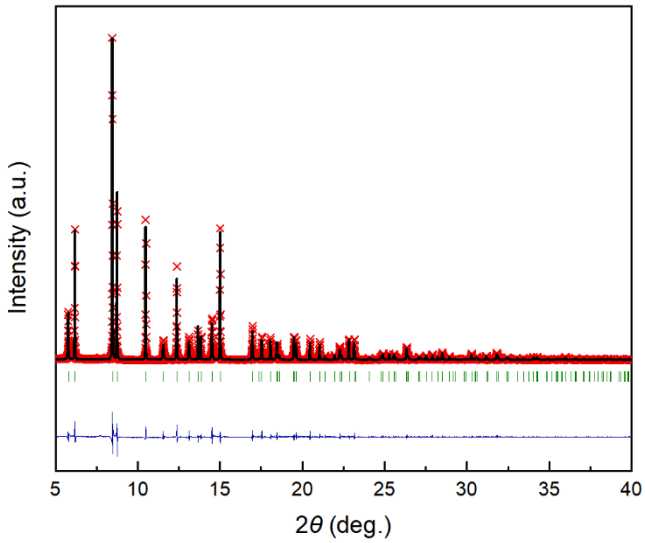


Figure S2. Rietveld full profile refinement of SXRD patterns of tetragonal 0.90PT-0.10BCW at room temperature. Observed (red, solid circles), calculated (black line), and their difference profiles (bottom line) are shown. The Bragg reflection positions are indicated by the green ticks.

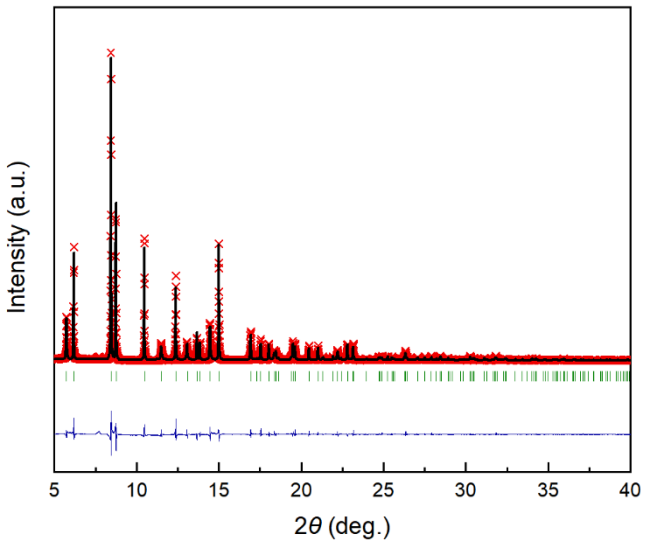


Figure S3. Rietveld full profile refinement of SXRD patterns of tetragonal 0.80PT-0.20BCW at room temperature. Observed (red, solid circles), calculated (black line), and their difference profiles (bottom line) are shown. The Bragg reflection positions are indicated by the green ticks.

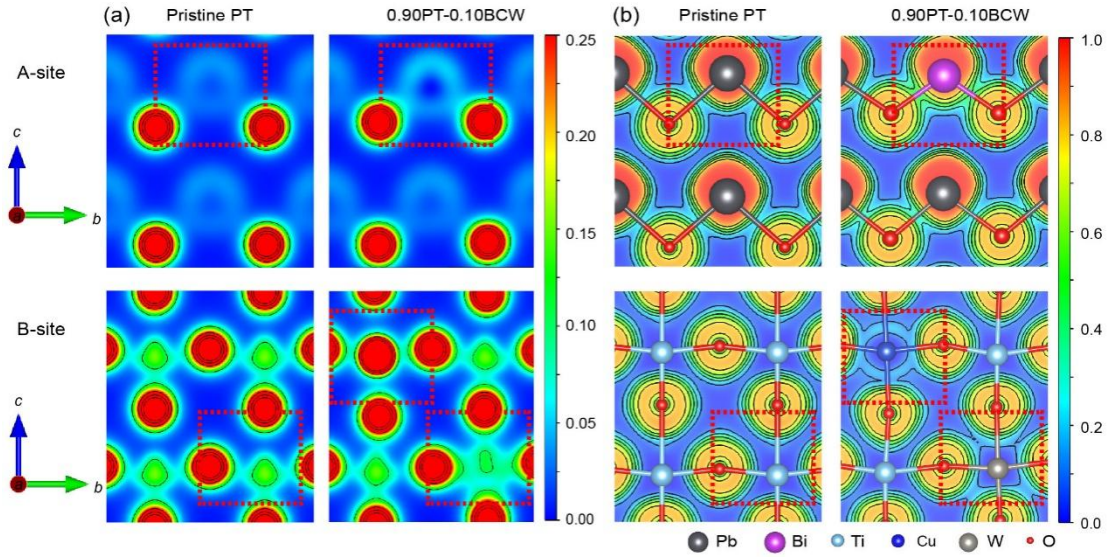


Figure S4. Calculated charge density (a) and electron localization function (ELF) (b) for the optimized structures of pristine PT and 0.90PT-0.10BCW, showing the regions around the A- and B-sites in the bc plane. In panel (a), the color bar ranges from blue(0.00) to red(0.25), representing the charge density around atoms. In panel (b), ELF isosurfaces are color-mapped on a 0-1 scale from blue to green to red, as indicated by a scale bar on the right panel. An ELF value of 0.5 corresponds to a homogeneous electron gas. A-site atoms (Pb and Bi), B-site atoms (Ti, Cu and W) and O atoms are represented by dark gray, purple, cyan, blue and light gray, as well as red spheres, respectively.

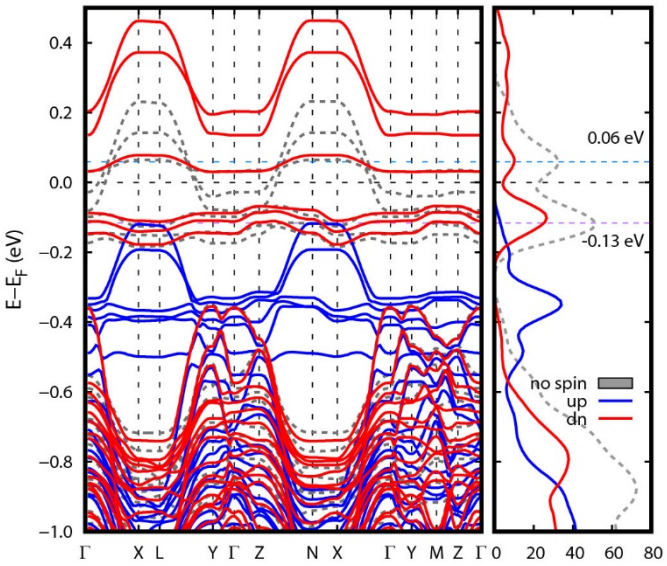


Figure S5. Calculated band structure and the corresponding DOS in PT-BCW. The black, blue and red colors represent the band of not-spin-polarized, spin-up and spin-down channel, respectively. The black, blue, and purple dashed horizontal lines indicate the Fermi level and the energies corresponding to the two DOS peaks, respectively.

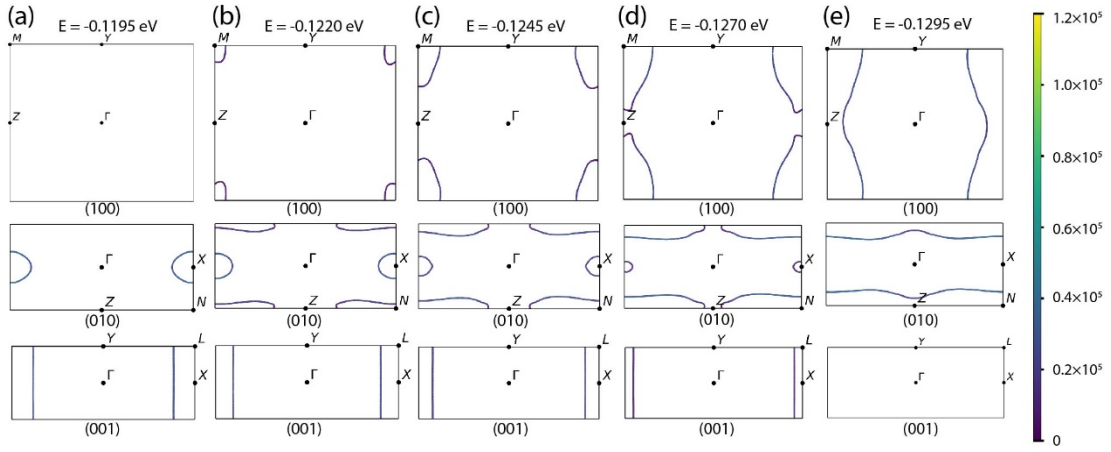


Figure S6. Formation and evolution of the von Hove pockets as the energy decreases from -0.1195 eV to -0.1295 eV.

Table S1. Refined structural parameters of the (1-*x*)PT-*x*BCW (*x* = 0.10 and 0.20) compounds at room temperature.

Composition	Space group	Atom	Site	g	*x*	*y*	*z*	*B*	Cell (Å)	*R* (%)
x = 0.10	*P*4*mm*	Pb	1a	0.9	0	0	0	1.06(4)	*a*(*b*) = 3.8986(1) *c* = 4.1717(8)	R_{wp} = 12.0 R_p = 9.07
		Bi	1a	0.1	0	0	0	1.06(4)		
		Ti	1b	0.9	0.5	0.5	0.5441(8)	0.58(2)		
		Cu	1b	0.075	0.5	0.5	0.5441(8)	0.58(2)		
		W	1b	0.025	0.5	0.5	0.5441(8)	0.58(2)		
		O1	1b	1	0.5	0.5	0.1095(0)	1.00(0)		
		O2	2c	1	0.5	0	0.6212(2)	1.00(0)		
x = 0.20	*P*4*mm*	Pb	1a	0.8	0	0	0	1.44(8)	*a*(*b*) = 3.8983(6) *c* = 4.1936(2)	R_{wp} = 12.0 R_p = 8.86
		Bi	1a	0.2	0	0	0	1.44(8)		
		Ti	1b	0.8	0.5	0.5	0.5514(4)	0.72(1)		
		Cu	1b	0.15	0.5	0.5	0.5514(4)	0.72(1)		
		W	1b	0.05	0.5	0.5	0.5514(4)	0.72(1)		
		O1	1b	1	0.5	0.5	0.1050(7)	1.00(0)		
		O2	2c	1	0.5	0	0.6257(6)	1.00(0)		

Table S2. CTEs and the corresponding temperature ranges of representative ZTE materials.

sample	CTE (× 10^{-6}/K)	temperature range (K)
Invar Alloy[1]	0.07 ($\bar{\alpha}_{\square}$†)	278 ~ 303
$Fe[Co(CN)_6]$[2]	-4.41 ($\bar{\alpha}_{\square}$)	4.2 ~ 300
$Zr_{0.4}Sn_{0.6}Mo_2O_8$[3]	-0.18 ($\bar{\alpha}_{\square}$)	12 ~ 600
$Mn_3Cu_{0.5}Ga_{0.5}N$[4]	0.354 ($\bar{\alpha}_{\square}$)	12 ~ 230
$N(CH_3)CuZn(CH_3)_4$[5]	0.6 ($\bar{\alpha}_{\square}$)	200 ~ 400
$(Sc_{0.85}Ga_{0.05}Fe_{0.10})F_3$[6]	0.702 ($\bar{\alpha}_{\square}$)	300 ~ 900
$Er_{0.9}Fe_{10}V_{1.7}Mo_{0.3}$[7]	1.87 ($\bar{\alpha}_{1}$‡)	100 ~ 493
$Ho_2Fe_{16}Co$[8]	0.5 ($\bar{\alpha}_{\square}$)	3 ~ 460
0.8PT-0.2BCW	-0.46 ($\bar{\alpha}_{\square}$)	300 ~ 725

†$\bar{\alpha}_V$ denotes the average volume CTE;

‡$\bar{\alpha}_l$ indicates the average linear CTE.

Table S3. Calculated average atomic displacements along the z-direction, referenced to the ideal cubic perovskite structure. Values in parentheses are the relative displacements compared with pristine PTO. Unit in Å.

	A-site		B-site			O-site
Atom	Pb	Bi	Ti	Cu	W	O
PTO	-0.09	-	0.12	-	-	0.44
0.90PT-0.10BCW	-0.10(-0.01)	-0.19	0.19(0.07)	0.16	0.33	0.50(0.06)

Table S4. Local lattice vectors (Å) and corresponding *c*/*a* ratios for the BiO_{12} and $Cu(W)O_6$ coordination environments.

Lattice Parameter	Bi_1	Bi_2	Bi_3	Bi_4	Cu_1	Cu_2	Cu_3	W	PT-BCW	Pristine PT
a	3.80	3.82	3.83	3.81	3.95	3.99	3.93	3.79	3.90	4.15
b	3.75	3.83	3.81	3.72	3.96	3.99	3.95	3.83	3.90	3.90
c	4.19	4.07	4.11	4.08	4.64	4.75	4.60	3.95	4.17	4.15
c/*a*	1.11	1.06	1.08	1.08	1.17	1.19	1.17	1.04	1.07	1.06
Avg.	1.08				1.18			1.04	1.07	1.06

Table S5. Average bond lengths in the AO_{12} and BO_6 local environments, unit in Å.

Parameter	AO_{12}		BO_6		
	PbO_{12}	BiO_{12}	TiO_6	CuO_6	WO_6
l_1	3.28	3.44	2.40	2.54	2.15
l_2	2.79	2.78	1.97	2.00	1.91
l_3	2.54	2.30	1.79	2.12	1.80

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