Supporting Information

Achieving negative thermal expansion over an extended temperature range in Rare earth-modified $PbTiO_3$-based perovskites

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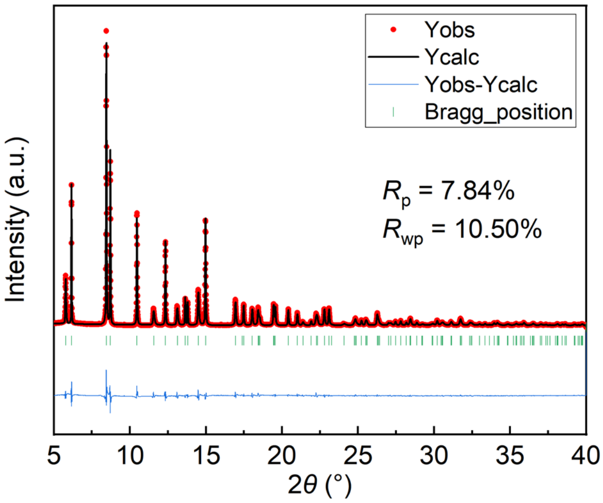

Figure S1 Rietveld full profile refinement of SXRD patterns of tetragonal 0.95PT-0.05BL at room temperature. Observed (red, solid circles), calculated (black line), and their difference profiles (bottom line) are shown. The Bragg reflection positions are indicated by the green ticks.

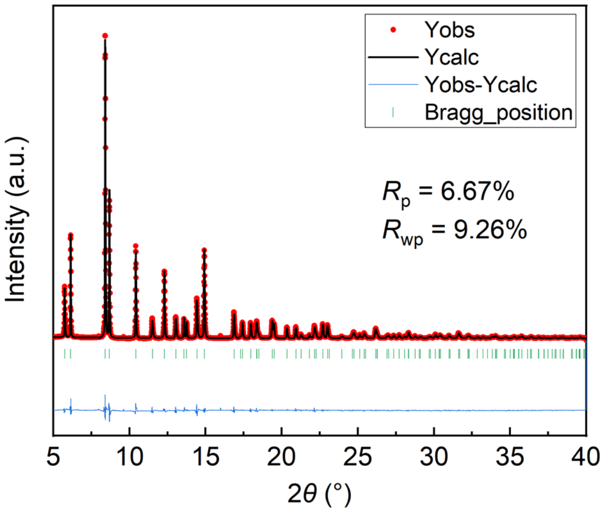

Figure S2 Rietveld full profile refinement of SXRD patterns of tetragonal 0.90PT-0.10BL at room temperature. Observed (red, solid circles), calculated (black line), and their difference profiles (bottom line) are shown. The Bragg reflection positions are indicated by the green ticks.

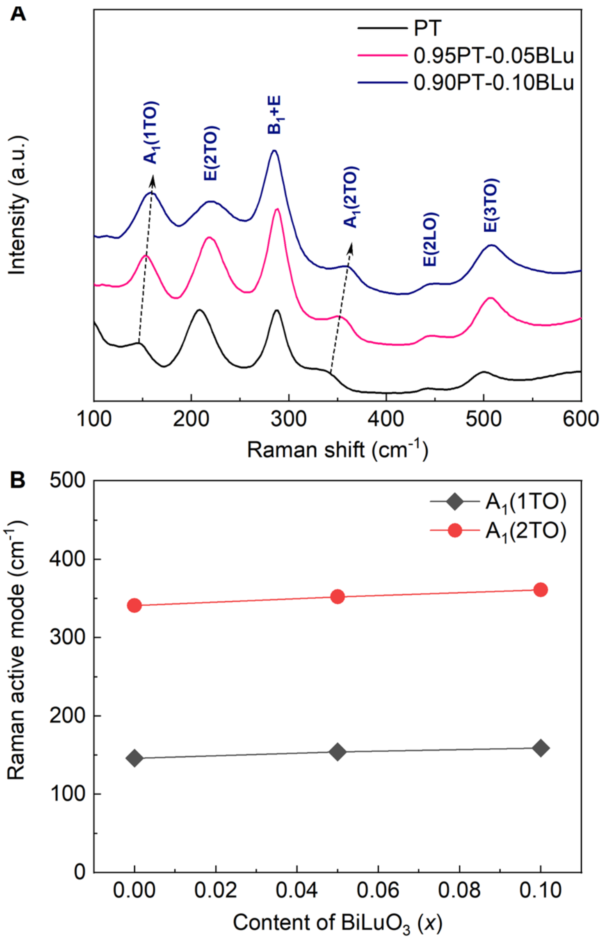

Figure S3 (A) Raman spectra and (B) Raman active soft modes of A_1(1TO) and A_1(2TO) of the (1-x)PT-xBL (x = 0.0, 0.05, and 0.10) compounds as a function of x.

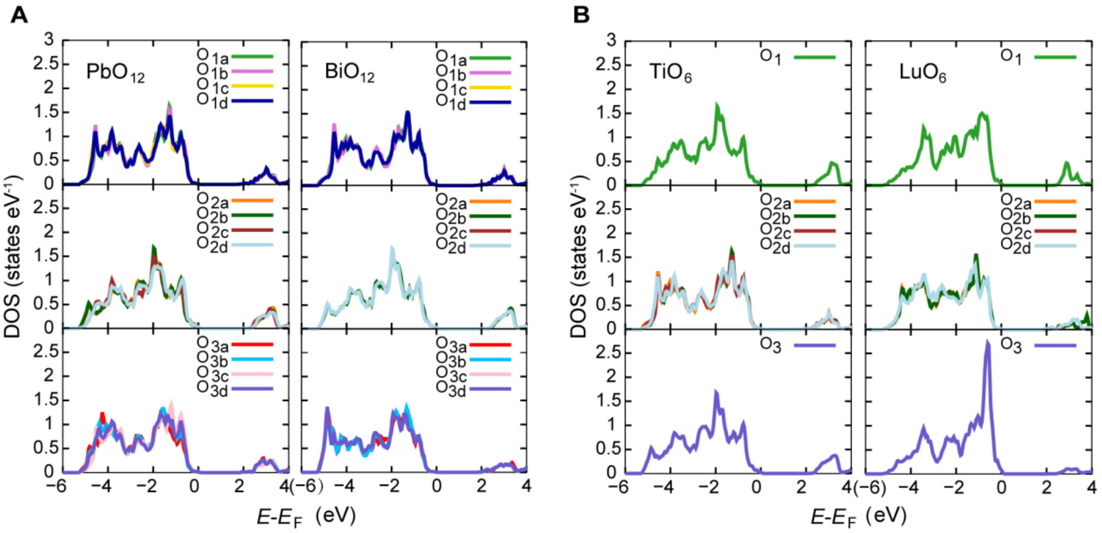

Figure S4 The calculated density of states (DOS) for the local (A) AO_{12} and (B) BO_6 environments is presented. The DOS contributions from three types of oxygen atoms, categorized by their bond lengths, are shown in the upper (l_1), middle (l_2), and lower (l_3) panels.

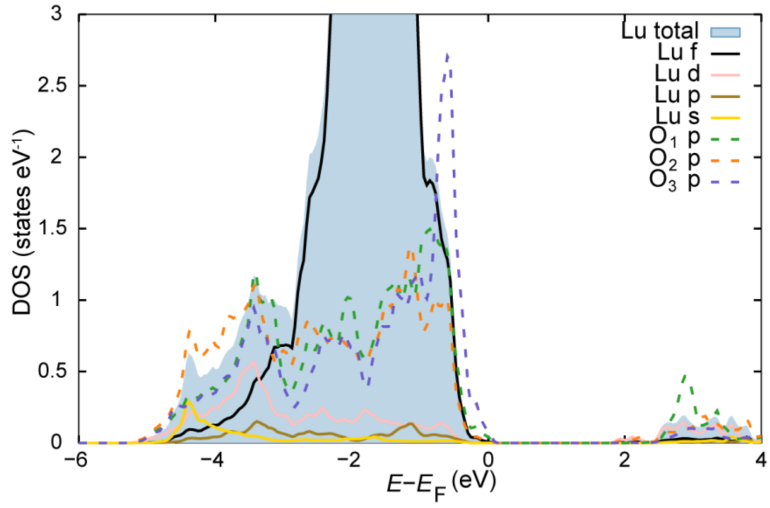

Figure S5 Partial DOS for Lu (solid line) and its nearest O atom (dashed line). In $BiLuO_3$, the ideal ionic state for Lu is 3+, which means it loses three of its outermost electrons in $4f^{14}6s^{2}5d^{1}$, with the *f*-electrons remaining non-bonding. However, due to the spontaneous B-site atom displacement in the $PbTiO_3$-based compound, Lu substitution at the B-site induces unusual orbital hybridization, leading to significant changes in the system's electronic structure. As shown below, our theoretical calculations reveal the existence of strongly localized *f* electrons just below the Fermi level, which interact intensely with the nearest O_3 electrons, leading to significant hybridization. As discussed in our manuscript, these hybridized electrons play a key role in enhancing the system's ferroelectric polarization, making Lu a crucial factor in the observed polarization improvement and thermal behavior.

Table S1 Refined structural parameters of the (1-x)PT-xBL (x = 0.05 and 0.10) compounds at room temperature.

Composition	Space group	Atom	Site	x	y	z	U	Cell (Å)	R (%)
x = 0.05	*P*4*mm*	Pb	1a	0	0	0	0.010		
		Bi	1a	0	0	0	0.010		
		Ti	1b	0.5	0.5	0.5446	0.007	a = 3.91335	R_{wp} = 10.5
		Lu	1b	0.5	0.5	0.5446	0.007	c = 4.17109	R_p = 7.84
		O1	1b	0.5	0.5	0.1114	0.013		
		O2	2c	0.5	0	0.6271	0.013		
x = 0.10	*P*4*mm*	Pb	1a	0	0	0	0.012		
		Bi	1a	0	0	0	0.012		
		Ti	1b	0.5	0.5	0.5469	0.009	a = 3.92550	R_{wp} = 9.26
		Lu	1b	0.5	0.5	0.5469	0.009	c = 4.19385	R_p = 6.67
		O1	1b	0.5	0.5	0.1187	0.015		
		O2	2c	0.5	0	0.6307	0.015		

Table S2 Averaged bond lengths in the ground state AO_{12} and BO_6 structures, unit in Å.

	AO_{12}		BO_6	
	PbO_{12}	BiO_{12}	TiO_6	YbO_6
l_1	3.21	3.39	2.36	2.37
l_2	2.79	2.78	1.98	2.14
l_3	2.54	2.30	1.80	2.09