Electronic Supplementary Information

Mixed anion control of enhanced negative thermal expansion in the oxysulfide of $PbTiO_3$

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Supplementary Figures and Tables

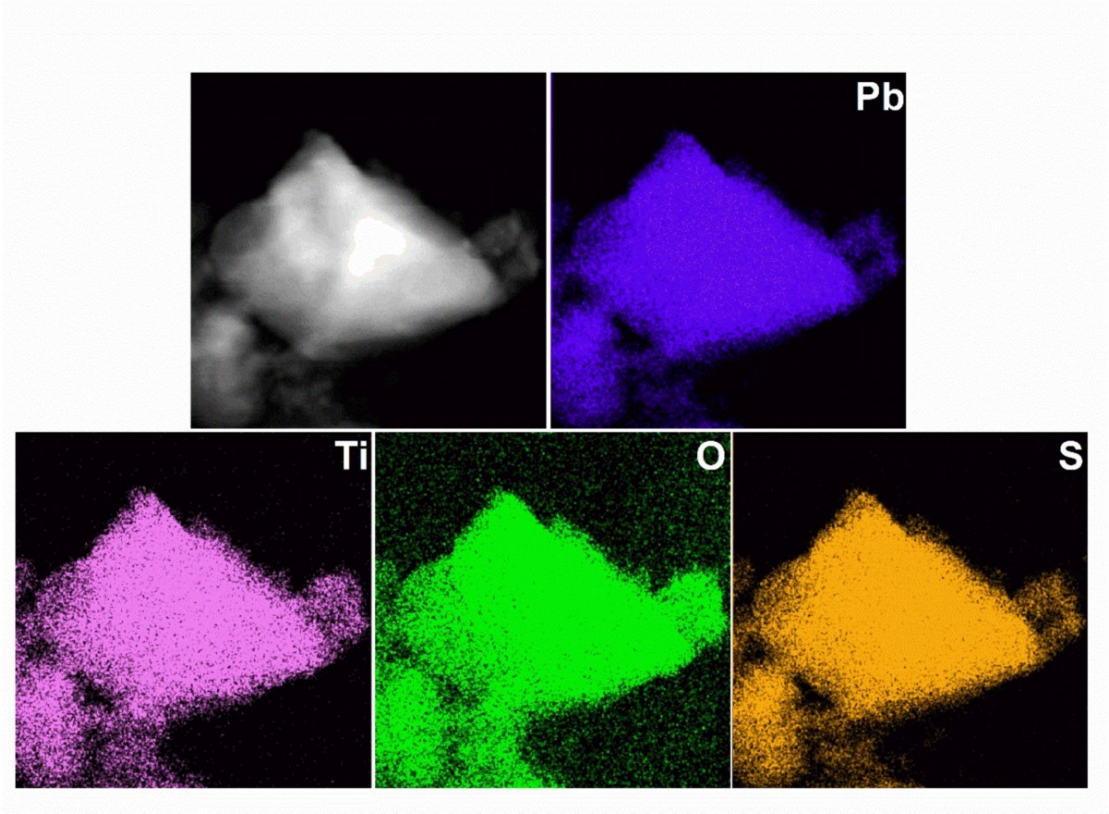

Fig. S1 Microstructural analysis. The elemental distribution of the PTOS1 sample.

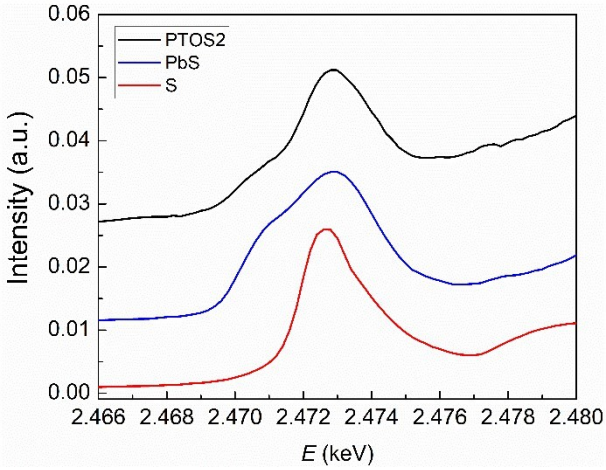

Fig. S2 XANES analysis. XANES spectra at the S-*K* edges of the PTOS2 compound. The XANES of PbS and S are shown for comparison.

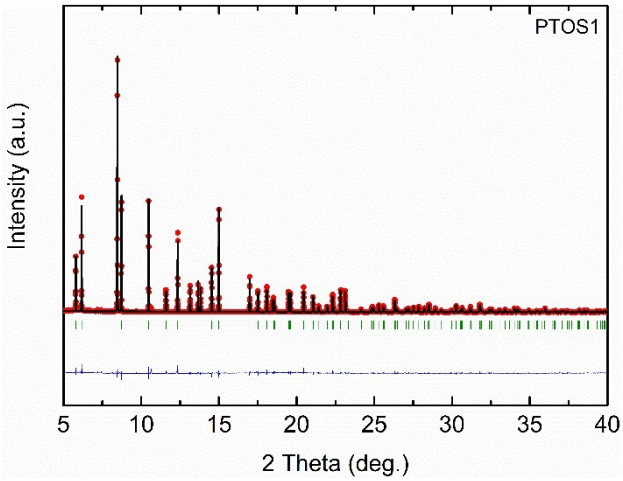

Fig. S3 Synchrotron X-ray diffraction refinement. Rietveld refinement of the SXRD pattern of tetragonal PTOS1 at room temperature. Observed (red, solid circles), calculated (black line), and their difference profiles (bottom line) are shown. The Bragg reflection positions are indicated by the green ticks (λ = 0.42 Å).

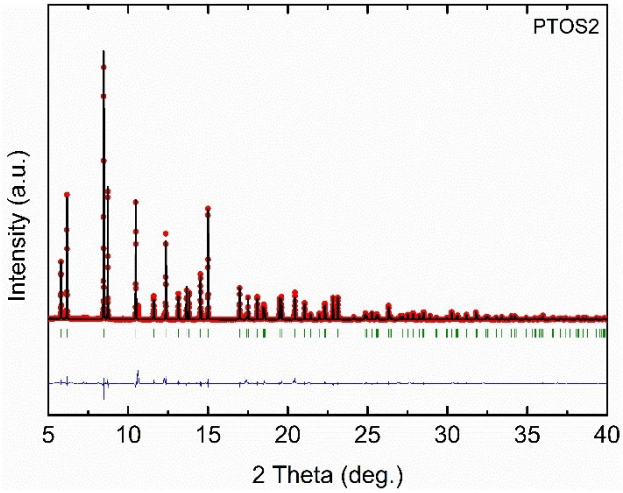

Fig. S4 Synchrotron X-ray diffraction refinement. Rietveld refinement of the SXRD pattern of tetragonal PTOS2 at room temperature. Observed (red, solid circles), calculated (black line), and their difference profiles (bottom line) are shown. The Bragg reflection positions are indicated by the green ticks (λ = 0.42 Å).

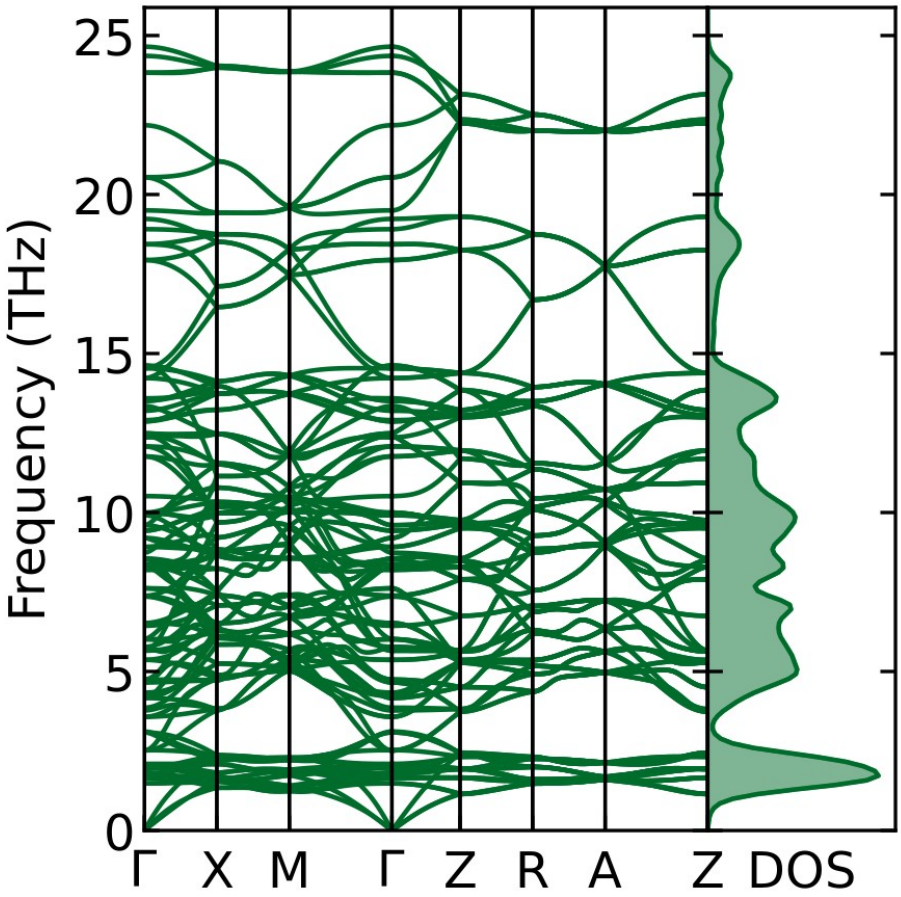

Fig. S5 The phonon dispersions and phonon density of states of the 40-atom PT supercell, indicating the dynamical stability.

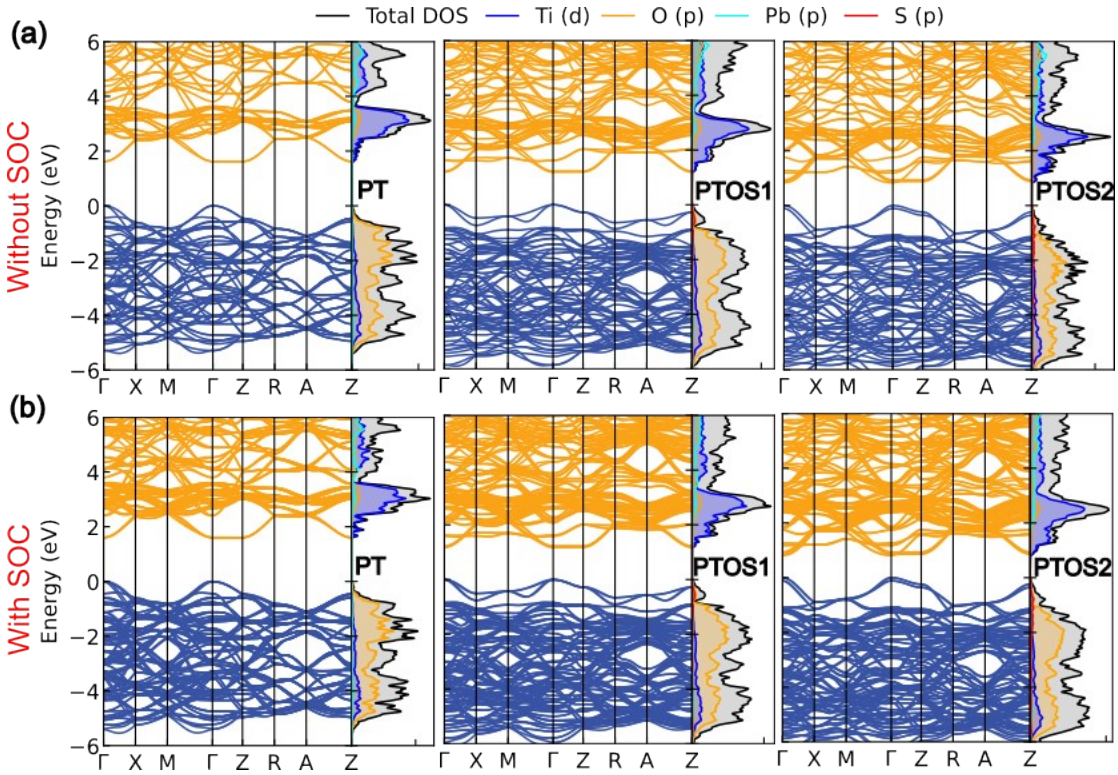

Fig. S6 Band structure and density of states. (a) Electronic structure of PT, PTOS1 and PTOS2 without spin-orbit coupling (SOC). (b) Electronic structure of PT, PTOS1 and PTOS2 with SOC. The Fermi energy is set to zero. The legend is applicable to the density of states only.

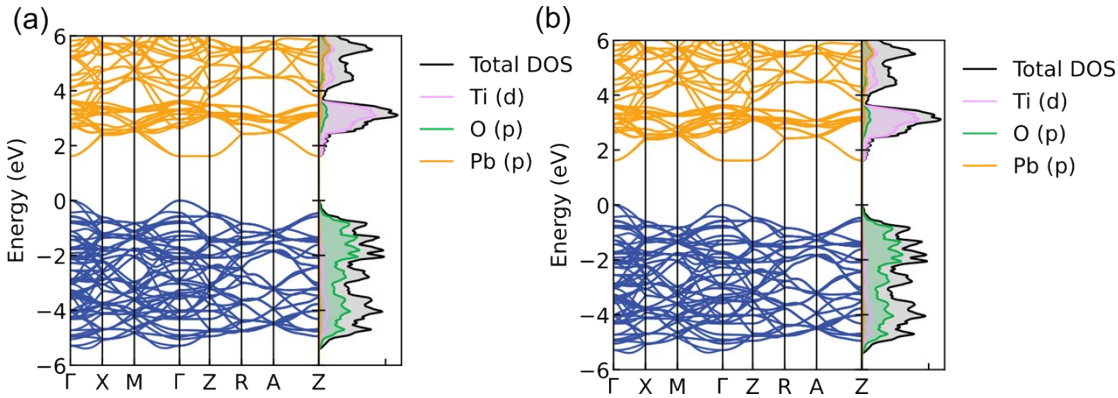

Fig. S7 Comparison between GGA and LDA results. (a) GGA calculated band structure and density of states. (b) LDA calculated band structure and density of states. The Fermi energy is set to zero. The legend is applicable to the density of states only.

Table S1 The refined structural parameters for the PTOS1 and PTOS2 compounds at room temperature.

Composition	Space group	Atom	Site	g	*x*	*y*	*z*	$100U_{iso}$(Å^2)
PTOS1[a)]	*P4mm*	Pb	1a	1.000	0.000	0.000	0.000	0.900
		Ti	1b	1.000	0.500	0.500	0.539(5)	0.600
		O1	1b	0.997	0.500	0.500	0.098(10)	1.000
		S1	1b	0.003	0.500	0.500	0.098(10)	1.000
		O2	2c	0.997	0.500	0.000	0.624(9)	1.000
		S2	2c	0.003	0.500	0.000	0.624(9)	1.000
PTOS2[b)]	*P4mm*	Pb	1a	1.000	0.000	0.000	0.000	0.900
		Ti	1b	1.000	0.500	0.500	0.538(9)	0.700
		O1	1b	0.993	0.500	0.500	0.085(10)	1.000
		S1	1b	0.007	0.500	0.500	0.085(10)	1.000
		O2	2c	0.993	0.500	0.000	0.622(8)	1.000
		S2	2c	0.007	0.500	0.000	0.622(8)	1.000

[a)]Space group *P*4*mm*, Z =1, $a = b$ = 3.9011(7) Å, c = 4.1553(2) Å, V = 63.2403(5) Å^3, R-factor (%): R_{wp} = 7.94, R_p = 6.51;

[b)]Space group *P*4*mm*, Z =1, $a = b$ = 3.9012(1) Å, c = 4.1554(6) Å, V = 63.2437(7) Å^3, R-factor (%): R_{wp} = 9.25, R_p = 7.90.