Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary information materials

Large polarization and dielectric response in epitaxial $SrZrO_3$ films

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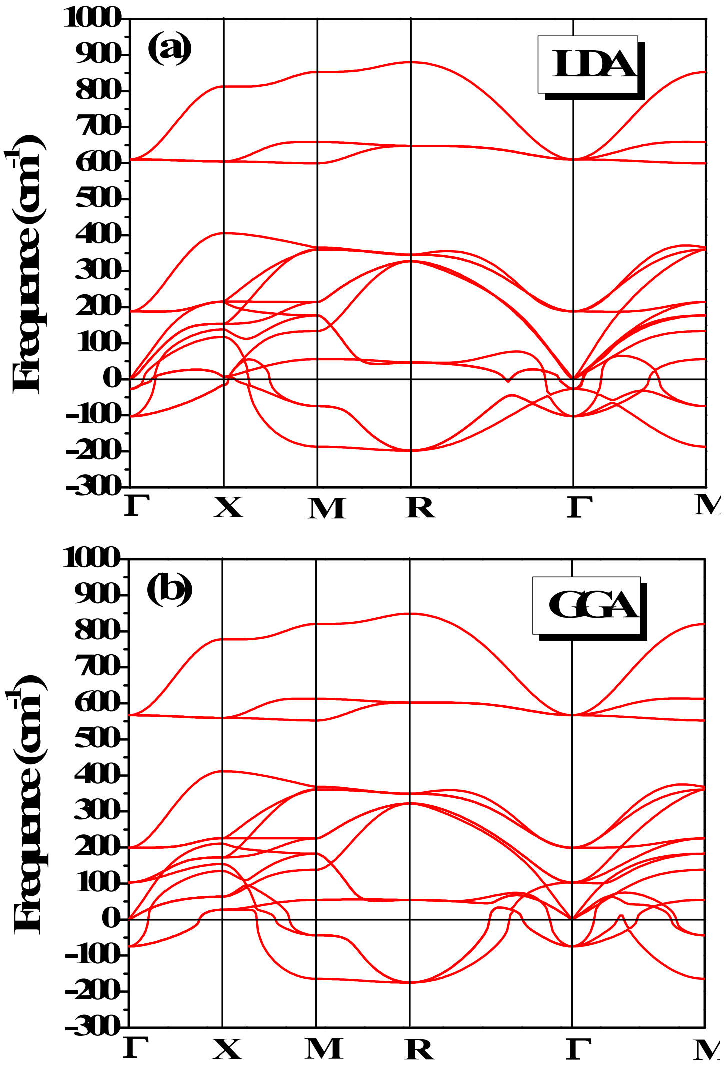

Fig .S1. Calculated phonon-dispersion curves of cubic $SrZrO_3$ (a) at LDA level and (b) at GGA level within the density functional perturbation theory (DFPT)[1] using the PHONOPY[2] code. The imaginary frequencies (unstable modes) are described as negative numbers.

Table S1. The unstable modes in cubic $SrZrO_3$.

	FE mode	AFD mode		Additional mode		
	Γ_4^-	M_3^+	R_4^+	Γ_5^-	X_5^+	M_5^-
LDA	102*i*	187*i*	198*i*	27*i*	16*i*	74*i*
GGA	74*i*	165*i*	175*i*	–	–	44*i*
GGA-WC[3]	87*i*	167*i*	179*i*	–	–	50*i*

Table S2. The optimized lattice parameters *a*, *b*, *c* and reduced atomic coordinates *x*, *y*, *z* of orthorhombic *Pbnm* phase as obtained from LDA and GGA functionals compared with the experimental measurement.

	Atoms	Wyck.	Coordinates		
			x	*y*	*z*
LDA	Sr	4c	0.009	0.537	0.25
a = 5.731 Å	Zr	4a	0	0	0
b = 5.806 Å	O1	4c	−0.083	−0.024	0.25
c = 8.132 Å	O2	8d	0.210	0.289	0.044
GGA	Sr	4c	0.007	0.533	0.25
a = 5.838 Å	Zr	4a	0	0	0
b = 5.903 Å	O1	4c	−0.077	−0.021	0.25
c = 8.285 Å	O2	8d	0.213	0.287	0.041
Expt.[4]	Sr	4c	0.004	0.524	0.25
a = 5.796 Å	Zr	4a	0	0	0
b = 5.817 Å	O1	4c	−0.687	−0.013	0.25
c = 8.205 Å	O2	8d	0.215	0.284	0.036

Table S3. The optimized lattice parameters *a*, *b*, *c* and reduced atomic coordinates *x*, *y*, *z* of the *P*4*mm*, *I*4/*mcm*, *ab-ePbnm*, *c-ePbnm*, *Ima*2, *Pmc*2_1(I) and *Pmc*2_1(II) phases in $SrZrO_3$ film for given strain. The symmetry of different equilibrium phases are determined by FINDSYM[5] code.

	Atoms	Wyck.	Coordinates		
			x	*y*	*z*
*P*4*mm*	a = 3.770 Å, b = 3.770 Å, c = 5.123 Å				
(−7.6%)	$\alpha = 90°$, $\beta = 90°$, $\gamma = 90°$				
	Sr	1a	0	0	0.164
	Zr	1b	0.5	0.5	0.613
	O1	1b	0.5	0.5	−0.03
	O2	2c	0.5	0	0.471
*I*4/*mcm*	a = 5.536 Å, b = 5.536 Å, c = 8.460 Å				
(−4.0%)	$\alpha = 90°$, $\beta = 90°$, $\gamma = 90°$				
	Sr	4b	0	0.5	0.25
	Zr	4c	0	0	0
	O1	8h	0.675	0.175	0
	O2	4a	0	0	0.25
ab-ePbnm	a = 5.712 Å, b = 8.103 Å, c = 5.786 Å				
(−0.7%)	$\alpha = 90°$, $\beta = 90°$, $\gamma = 90°$				
	Sr1	2e	0.009	0.25	0.038
	Sr2	2e	0.491	0.25	0.538
	Zr1	2b	0.5	0	0
	Zr2	2c	0	0	0.5
	O1	2e	−0.083	0.25	0.476
	O2	2e	0.583	0.25	−0.024
	O3	4f	0.289	0.456	0.289
	O4	4f	0.789	0.544	0.211

c-ePbnm	$a = 5.798$ Å, $b = 8.101$ Å, $c = 5.798$ Å				
(+0.5%)	$\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$				
	Sr	4c	0.465	0.25	0.008
	Zr	4a	0	0	0
	O1	4c	0.023	0.25	–0.085
	O2	8d	0.786	–0.045	0.714
*Ima*2	$a = 7.885$ Å, $b = 6.028$ Å, $c = 6.028$ Å				
(+4.5%)	$\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$				
	Sr	4b	0.25	0.492	0.731
	Zr	4a	0	0	0.745
	O1	8c	0.454	0.255	0.009
	O2	4b	0.25	0.590	0.293
$Pmc2_1$(I)	$a = 7.885$ Å, $b = 6.028$ Å, $c = 6.028$ Å				
(+4.5%)	$\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$				
	Sr1	2b	0.5	0.742	0.030
	Sr2	2a	0	0.758	0.028
	Zr	4c	0.25	0.25	0.014
	O1	2b	0.5	0.840	0.466
	O2	2a	0	0.660	0.467
	O3	4c	0.704	0.494	0.251
	O4	4c	0.796	-0.004	0.749
$Pmc2_1$(II)	$a = 3.792$ Å, $b = 6.114$ Å, $c = 6.114$ Å				
(+6.0%)	$\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$				
	Sr	2b	0.5	0.179	0.058
	Zr	2a	0	0.717	0.025
	O1	2b	0.5	0.224	0.462
	O2	2a	0	–0.060	0.273
	O3	2a	0	0.567	0.692

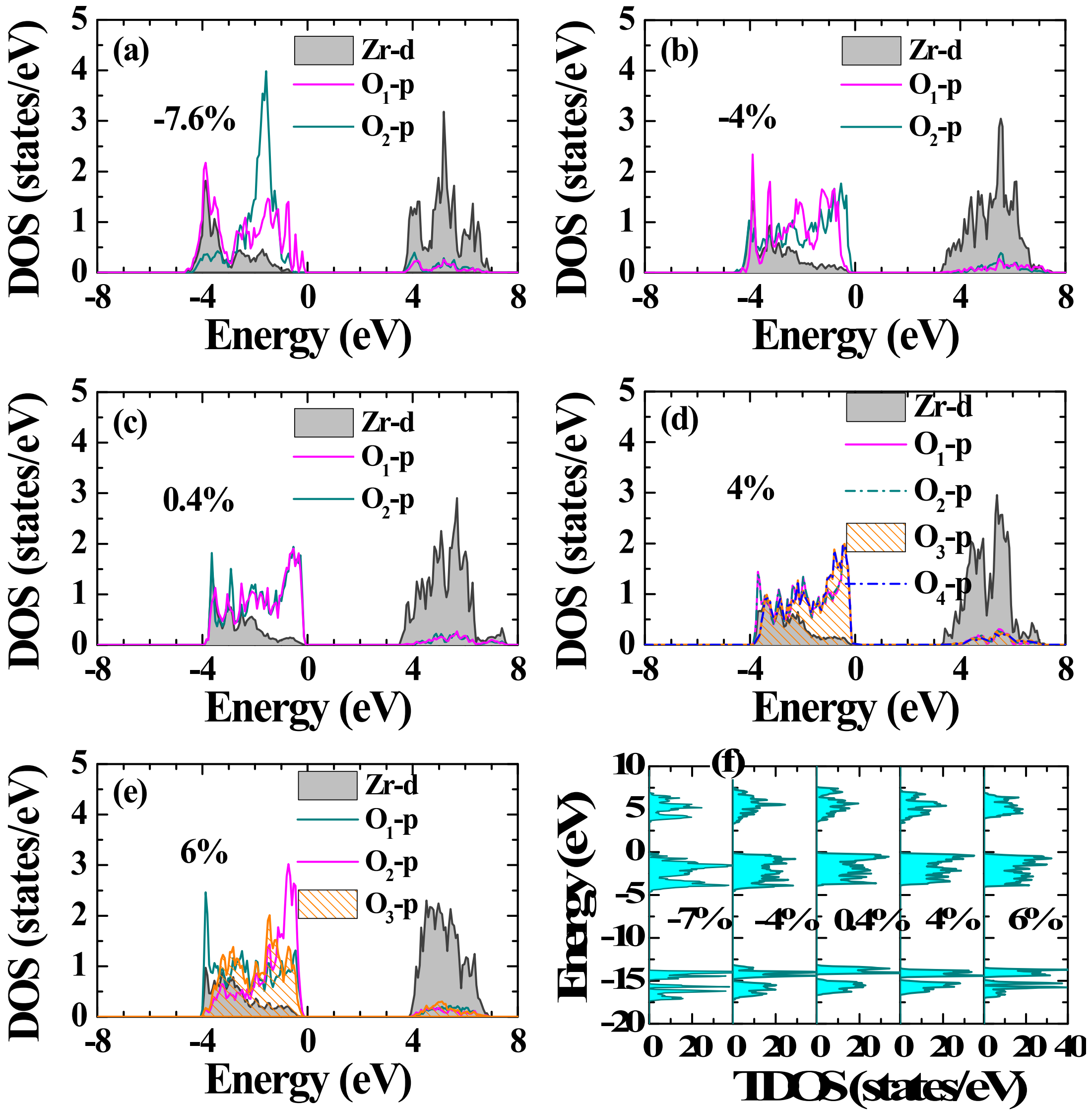

Fig .S2. The projected (a-e) and total (f) density of states for SZO films with different misfit strain.

According to Fig. 5 and Fig .S2, the total density of states (TDOS) and projected density of states (PDOS) in paraelectric phases clearly show the strong hybridization between Zr d and O p orbitals, which are mainly located from -5 eV to 0 eV (that is, the Fermi level, which is set to zero). In detail, the *c-ePbnm* and *I*4/*mcm* phases exhibit the energy overlap and hybridization peaks between Zr d and O p orbitals (not only in-plane O_1 p orbital but also out-of-plane O_2 p orbital). However, the *P*4*mm* phase possesses stronger hybridization between Zr d and in-plane O1 p orbitals (especially at -4 eV), while the orbital hybridization between Zr d and out-of-plane O_2 p is mainly shifted to about -1.5 eV, which implies highly covalent interaction between Zr d and in-plane O_1 p orbitals and corresponds to the complete vanishing oxygen octahedral tilting as well as the relative z-displacements of these two atoms. As for the tensile strain, the hybridization between Zr d and O p orbitals is also enhanced. Due to the lower symmetry induced by in-plane strain, more hybridization peaks emerge between different O p and Zr d orbitals in the distinct $Pmc2_1$ phases. According to Table 1 and Fig .S2, the stronger hybridization also corresponds to the enhanced polarization with the increase of misfit strain. Practically, the major hybridization peaks are located from -3.5 eV to -2 eV at 4.5% tensile strain, while a stronger hybridization peak emerges at -4 eV and there are relatively obvious hybridization peaks at the range between -2 eV and 0 eV at 6% tensile strain. In summary, the DOS demonstrates that the hybridization between Zr d and O p orbitals becomes stronger in the presence of strain, which corresponds to the enhanced polarization with the increase of misfit strain.

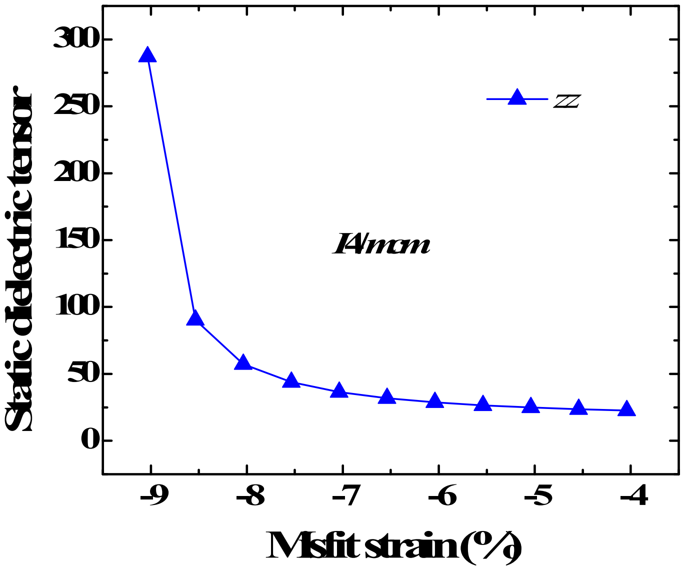

Fig .S3. Calculated out-of-plane component of static dielectric tensor ε^0_{zz} in the *I*4/*mcm* phase, as a function of compressive strain.

References

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