Electronic Supplementary Material (ESI) for RSC Advances.

First-principles study on electric structure and ferroelectricity in epitaxial $CsSnI_3$ films

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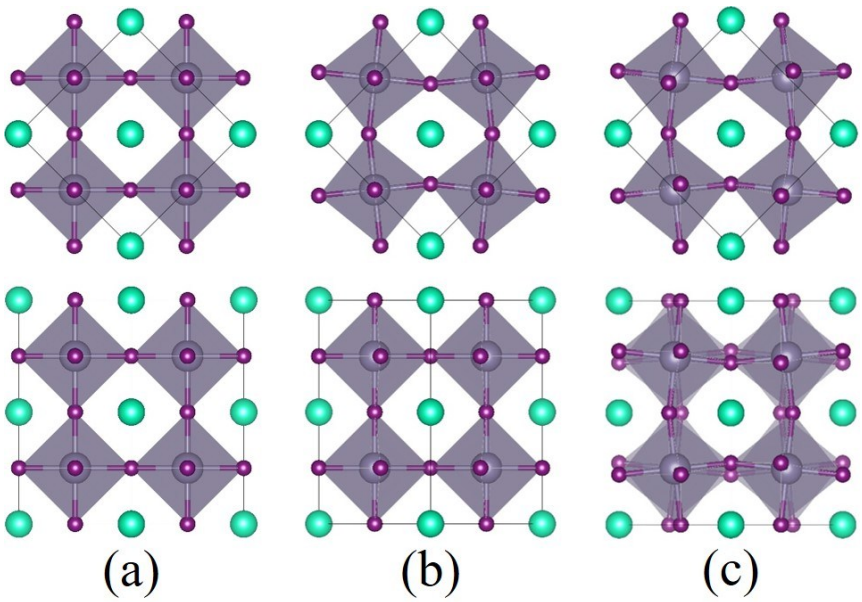

Fig. S1 The model of different experimental structures mentioned in the main text. Panel (a), (b), and (c) display the schematic description of the *P*4*/mmm*, *P*4*/mbm*, and *Pnma* phases, respectively. The first layer represents the polyhedral views of these phases from *c*-axis, while the second layer is the view from the *a* and *b*-axes. The cyan, gray, and purple balls represent the Cs, Sn and I atoms. Structural images are produced by using the software VESTA.[1]

Table S1. The calculate structure parameters of Cubic, Tetragonal, and Orthorhombic phase with PBEsol method. The experiment parameters are taken from Ref. S2.

	a (Å)	b (Å)	c (Å)
Cubic (*Pm-3m*)	6.1351	6.1351	6.1351
Exp (500 K)	6.2057	6.2057	6.2057
Tetragonal (*P4/mbm*)	8.5561	8.5561	6.2135
Exp (380 K)	8.7182	8.7182	6.1908
Orthorhombic (*Pnma*)	8.7773	8.4032	12.2544
Exp (300 K)	8.6885	8.6384	12.3775

Table S2. Biaxially strained perovskite structures computed in this work, along with their space groups (as determined using the software FINDSYM). Follow the method which has been used in Ref. S3, these calculated structures are determined from the unstable phonon modes of high symmetry *Pm-3m* structure.

Glazer notation	Space group			
		[100]	[110]	[001]
$a^0a^0a^0$	*Pm*-3*m*	*Pmm*2	*Amm*2	*P*4*mm*
$a^0a^0c^-$	*I*4/*mcm*	*Ima*2	*Fmm*2	*I*4*a*2
$a^0a^0c^+$	*P*4/*mbm*	*Pmc*2_1	*Amm*2	*P*4*bm*
$a^-a^-a^0$	*Imma*	*Ima*2	*Cm*	*Ima*2
$a^-a^-c^+$	*Pnma*	*Pmc*2_1	*Pm*	*Pna*2_1

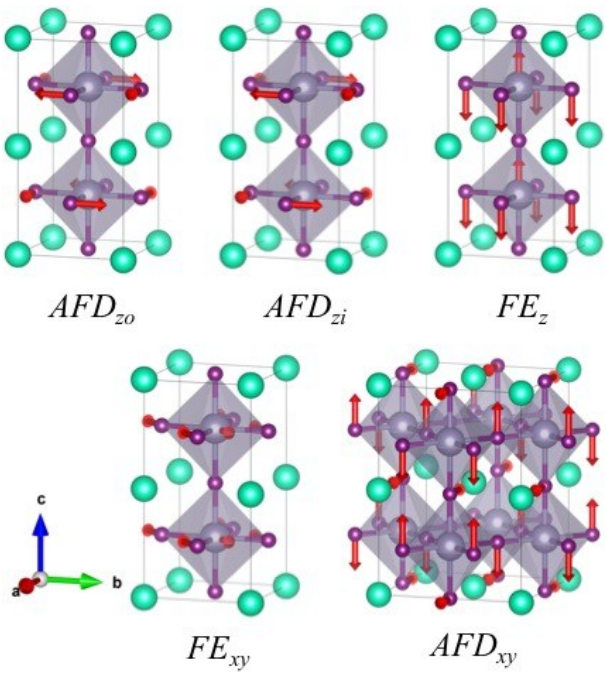

Fig. S2 Schematic view of the prototype *Pm*-3*m* atomic motions associated to different energy lowering distortions. *The* AFD_{zo} represents the SnI_6 octahedron rotates along [001] direction out-of-phase; the meanings of AFD_{zi}, FE_z, FE_{xy}, and AFD_{xy} are described in the main text.

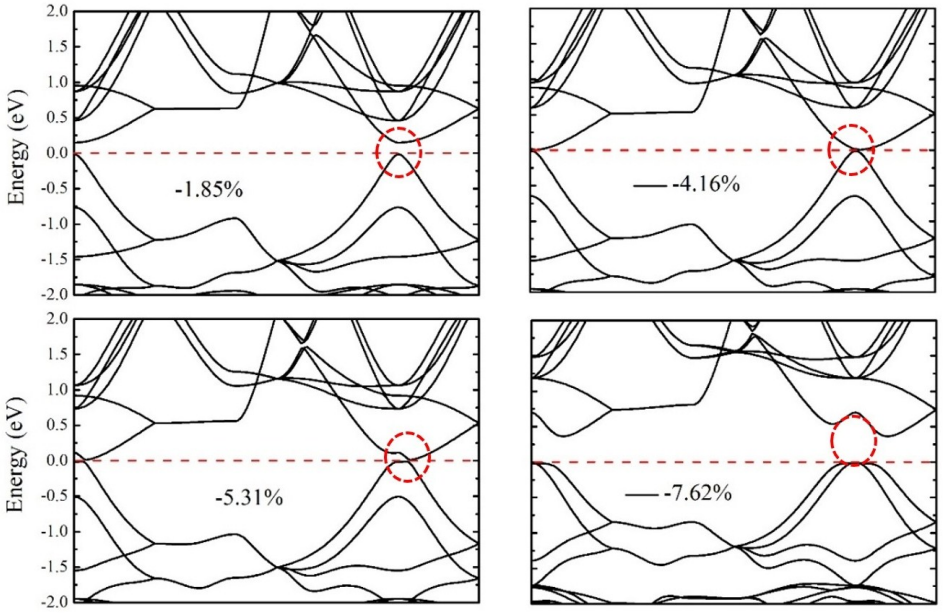

Fig. S3 PBEsol method computed electric band structure of *P*4*bm* phase, with the valence band maxima defined as zero energy. As the strain decrease, at the Γ point of the Brillouin zone (see the red dashed circle) the band gaps decrease to zero, and then reopen as the strain decrease, furthermore, become an indirect semiconductor.

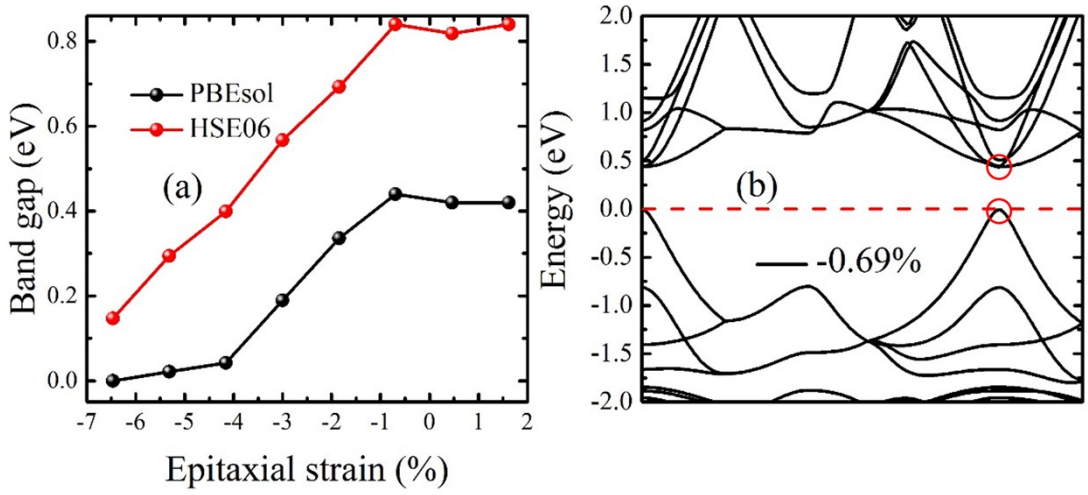

Fig. S4 PBEsol method computed electric structure of *Pnma* phase. (a) Band gaps. (b) Band structure at e = -0.69%. The valence band maxima defined as zero energy. The red cycle represents the valence band maximum and conduction band minimum. Both of the located at the Γ point of the Brillouin zone (see the red solid circle).

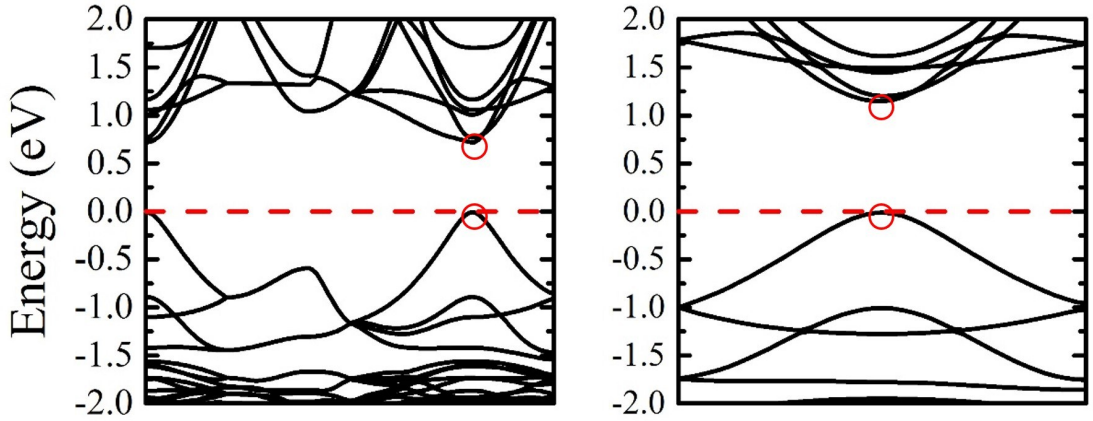

Figure S5. PBEsol method computed electric band structure of *Pmc*2_1 phase. (a) PBEsol method. (b) HSE06 method. The valence band maxima defined as zero energy. The red cycle represents the valence band maximum and conduction band minimum. Both of the located at the Γ point of the Brillouin zone (see the red solid circle).

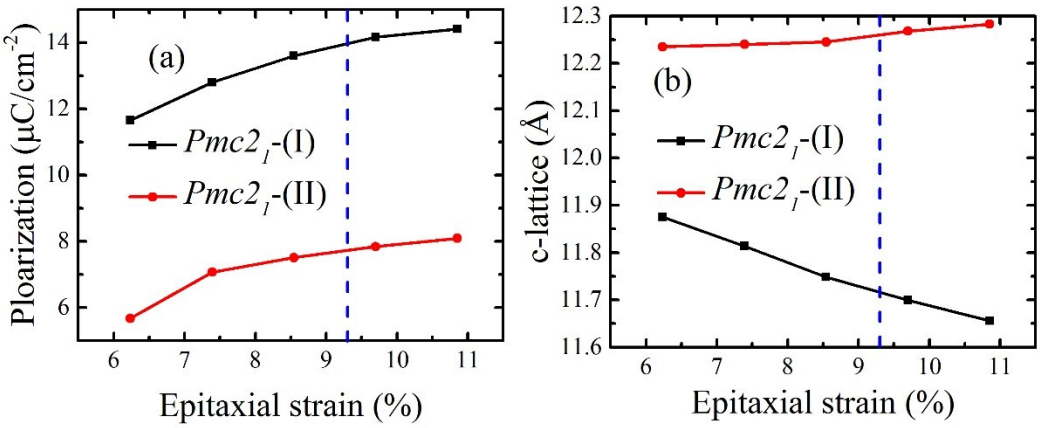

Fig. S6 PBEsol method computed the (a) electric polarization and (b) structure parameter of the *Pmc*2$_1$-(I) and *Pmc*2$_1$-(II) phases. The blue dashed line indicate the phase boundary of these two phases. In the vicinity of the phase boundary, the difference of the electric polarization is 6.09 μC/cm^2, while the *c*-lattice is 0.497 Å.

References

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2 I. Chung, J.-H. Song, J. Im, J. Androulakis, C. D. Malliakas, H. Li, A. J. Freeman, J. T. Kenney and M. G. Kanatzidis, *J. Am. Chem. Soc.*, 2012, **134**, 8579-8587.

3. E. Bousquet, M. Dawber, N. Stucki, C. Lichtensteiger, P. Hermet, S. Gariglio, J.-M. Triscone and P. Ghosez, *Nature*, 2008, **452**, 732-736.