

Supporting Information

Surface Termination and Strain-Induced Modulation of Structure and Electronic Properties in 2D Perovskites (Cs_2BCl_4 & CsB_2Cl_5 , $\text{B}=\text{Pb},\text{Sn}$): A first-principles study [†]

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Structure and Lattice dynamics

Table 1 summarizes the structural parameters for 2D perovskites calculated in the present work.

Formula unit	Lattice constant (Å)	Thickness (Å)	Rumpling (Å)	Bandgap (eV)
Cs ₂ PbCl ₄	5.65	5.77	0.40	1.72
CsPb ₂ Cl ₅	5.68	5.02	0.23	1.70
Cs ₂ SnCl ₄	5.56	5.67	0.36	1.34
CsSn ₂ Cl ₅	5.57	4.91	0.23	1.83

The cubic phase of perovskite compounds is the most commonly theoretically studied phase, and typically shows many phonon instabilities. The rich structural phases of perovskite-type compounds can trace back to the phonon instability of highly symmetric cubic structure. The phonon dispersions studied here share some of these instabilities at Γ , M and X points, which suggests a rich underlying phase diagram for these 2D systems as well. The exploration of each of the phases stemming from the instabilities, which show ferroelectric, anti-ferrodistortive instabilities.

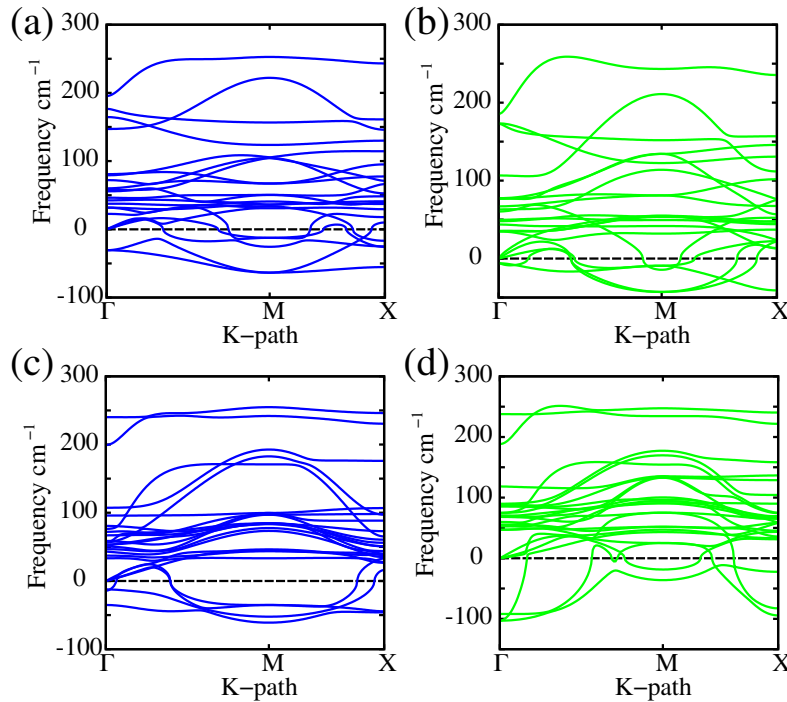


Fig. S1 Phonon dispersion along the high symmetry path $\Gamma \rightarrow M \rightarrow X$ for unstrained 2D perovskites monolayer (a) Cs₂PbCl₄ (b) Cs₂SnCl₄ (c) CsPb₂Cl₅ and (d) CsSn₂Cl₅.

Thermodynamic analysis

Surface energy, E_{surf} and Phase Diagram The relative stability of different surface terminations can be examined from their surface energies and phase diagrams considering varied chemical potential conditions. The surface energy, E_{surf} of CsCl and BCl₂ (B = Pb or Sn) terminated surfaces can be computed from their dependence on the chemical potential, μ_i of elements as:

$$E_{surf}^x = \frac{1}{2S}(E_{slab}^x - N_{Cs}\mu_{Cs} - N_B\mu_B - N_{Cl}\mu_{Cl}) \quad (1)$$

where E_{surf}^x (eV) is the total energy of slab X from the DFT calculation. N_{Cs} , N_B and N_X are the number of atoms (Cs, B, and Cl) in the slab; μ_{Cs} , μ_B and μ_{Cl} are their chemical potentials; S is the area of the symmetrical surface. The prevention conditions of bulk element (Cs, B = Pb or Sn, and Cl₂) formations on the surface corresponds to

$$\Delta\mu_{Cs} < 0; \Delta\mu_B < 0; \Delta\mu_{Cl} < 0 \quad (2)$$

where, $\Delta\mu_i$ is the relative chemical potential. We define relative chemical potential $\Delta\mu_i$ as

$$\Delta\mu_i = \mu_i - E_i \quad (3)$$

where, μ_i is the elemental chemical potential and E_i (eV per atom) is the total energy of the element phase. Similarly, the condition to prevent binary compound (CsCl and BCl₂) formation corresponds to:

$$\Delta\mu_{Cs} + \Delta\mu_{Cl} < E_f(CsCl) \quad (4)$$

$$\Delta\mu_B + 2\Delta\mu_{Cl} < E_f(BCl_2) \quad (5)$$

Assuming that the surface is in equilibrium with bulk, we can write

$$\Delta\mu_{Cs} + \Delta\mu_B + 3\Delta\mu_{Cl} = E_f(CsBCl_3) \quad (6)$$

where $E_f(CsBCl_3)$ is the formation energy of bulk CsPbCl₃, i.e., $E_f(CsBCl_3) = E_{CsPbCl_3} - E_{Cs} - E_B - 3E_{Cl}$.

We defined the formation energy, E_f with respect to the elemental substances as:

$$E_f(Cs_iB_jCl_k) = E_{Cs_iB_jCl_k} - iE_{Cs} - jE_B - kE_{Cl} \quad (7)$$

where, $E_{Cs_iB_jCl_k}$ is the total energy of bulk $Cs_iB_jCl_k$ and E_{Cs} , E_B , E_{Cl} are the energies (eV per atom) of elemental substances, i.e., Cs metal, B metal and Cl₂ gas molecule. i , j and k are the number of Cs, B and Cl atoms in the bulk $Cs_iB_jCl_k$, respectively.

On using equation (3) and (6), E_{surf} can be rewritten as :

$$E_{surf}^x = \lambda^x - \frac{1}{2S}[(N_{Cs} - N_B)\Delta\mu_{Cs} + (N_{Cl} - 3N_B)\Delta\mu_{Cl}] \quad (8)$$

where, $\lambda^x = \frac{1}{2S}[E_{slab}^x - N_{Pb}E_{Bulk} - (N_{Cs} - N_B)E_{Cs} - (N_{Cl} - 3N_B)E_{Cl}]$.

On solving equation (4), (5) and (6), we obtain boundary condition for CsCl-rich and BCl₂-rich phases and equating surface energies of CsCl and BCl₂ surfaces gives the equilibrium boundary between CsCl and BCl₂ rich phase of the surface phase diagram.

We find thermodynamically stable bulk CsBCl₃ at the chemical potential region between CsCl-rich and BCl₂-rich condition: $-4.25 \leq \Delta\mu_{Cs} + \Delta\mu_{Cl} \leq -3.92$ eV for CsPbCl₃; $-4.32 \leq \Delta\mu_{Cs} + \Delta\mu_{Cl} \leq -3.92$ eV for CsSnCl₃. These conditions define the red lines in Fig. 3(a & b) of main text. Binary phase CsCl (yellow marked area) or PbCl₂/SnCl₂ (blue and green marked areas) may appear beyond these regions.

Conditions to calculate E_{surf} as a function of $\Delta\mu_{Cl}$

In order to show E_{surf} as a function of $\Delta\mu_{Cl}$, we calculate E_{surf} at specific chemical potential conditions of Cs. We assume Pb/Sn-rich condition (i.e. Pb/Sn = 0 eV) where Pb/Sn source is in equilibrium with CsPbCl₃/CsSnCl₃. Using $\Delta\mu_{Pb} = 0$ eV and $\Delta\mu_{Sn} = 0$ eV in equation (7), we obtain $\Delta\mu_{Cs} + 3\Delta\mu_{Cl} = -7.52$ eV for CsPbCl₃ ($\Delta\mu_{Cl} + 3\Delta\mu_{Cl} = -7.41$ eV for CsSnCl₃). Combining Sn-rich condition with CsCl-rich and PbCl₂/SnCl₂-rich conditions of stable CsPbCl₃/CsSnCl₃, we can obtain two typical conditions for Cs: $\Delta\mu_{Cs} = 2.12$ eV and $\Delta\mu_{Cs} = 2.61$ eV for CsPbCl₃. Similarly, $\Delta\mu_{Cs} = 2.18$ eV and $\Delta\mu_{Cs} = 2.78$ eV for CsSnCl₃. The E_{surf} as a function of $\Delta\mu_{Cl}$ are calculated at these conditions (SI Figure 2 (c,d)).

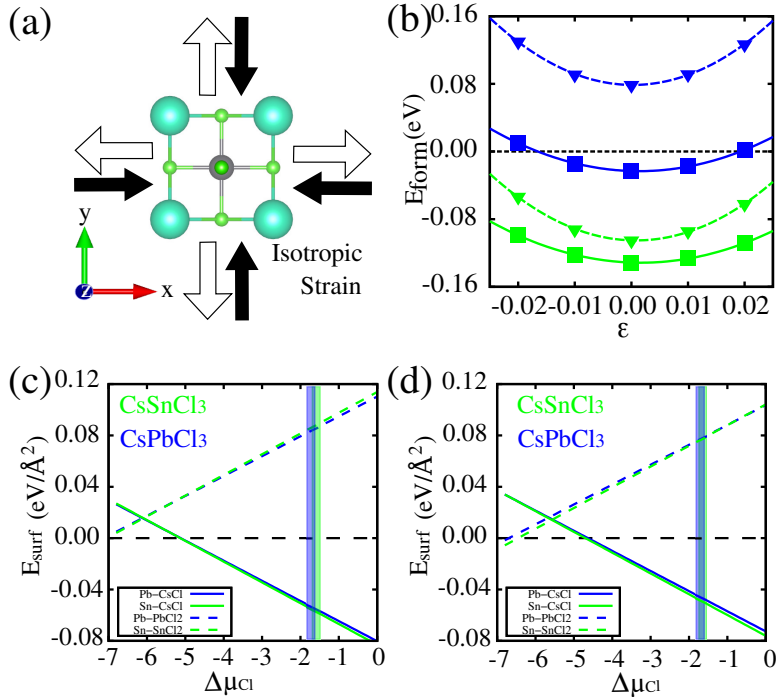


Fig. S2 (a) Schematic showing the direction of tensile (hollow arrows) and compression (filled arrows) strains on the 2D perovskites. (b) Formation energy, E_{form} computed from binary phase energies. Blue squares represent Cs₂PbCl₄, green squares represent Cs₂SnCl₄, blue triangles represent CsPb₂Cl₅, and green triangles represent CsSn₂Cl₅. (c,d) Surface energies (E_{surf}) of Cs₂BCl₄ (solid lines) and CsB₂Cl₅ (dotted lines) (B=Pb, Sn) surfaces as a function of $\Delta\mu_{Cl}$. The conditions of stable CsPbCl₃ and CsSnCl₃ are marked by blue and green areas.

Formation energy using binary compounds

We further calculate formation energies E_{form} of Cs_2BCl_4 and CsB_2Cl_5 monolayer unit cell with respect to their binaries (see Fig. S2(b)) as:

$$E_{form}(Cs_2BCl_4) = E(Cs_2BCl_4) - 2E(CsCl) - E(BCl_2) \quad (9)$$

$$E_{form}(CsB_2Cl_5) = E(CsB_2Cl_5) - E(CsCl) - 2E(BCl_2) \quad (10)$$

where E_{CsCl} , E_{BCl_2} are the total energies of CsCl, BCl₂ binary compounds atoms. According to this definition of formation energy, negative values of E_{form} indicates the energetically stable system.

Cleavage energy

The cleavage energy (E_{cl}) describing the energy cost of cleaving a bulk into two surfaces can be calculated from the total energies of complementary symmetric unrelaxed slabs as:

$$E_{cl} = \frac{1}{2S}(E_{slab}^{CsCl} + E_{slab}^{BCl_2} - N_{bulk}E_{bulk}) \quad (11)$$

where N_{bulk} is the total number of unit cells of $CsBCl_3$ in the CsCl and BCl₂ terminated slabs.

Electronic band structure and DOS/PDOS

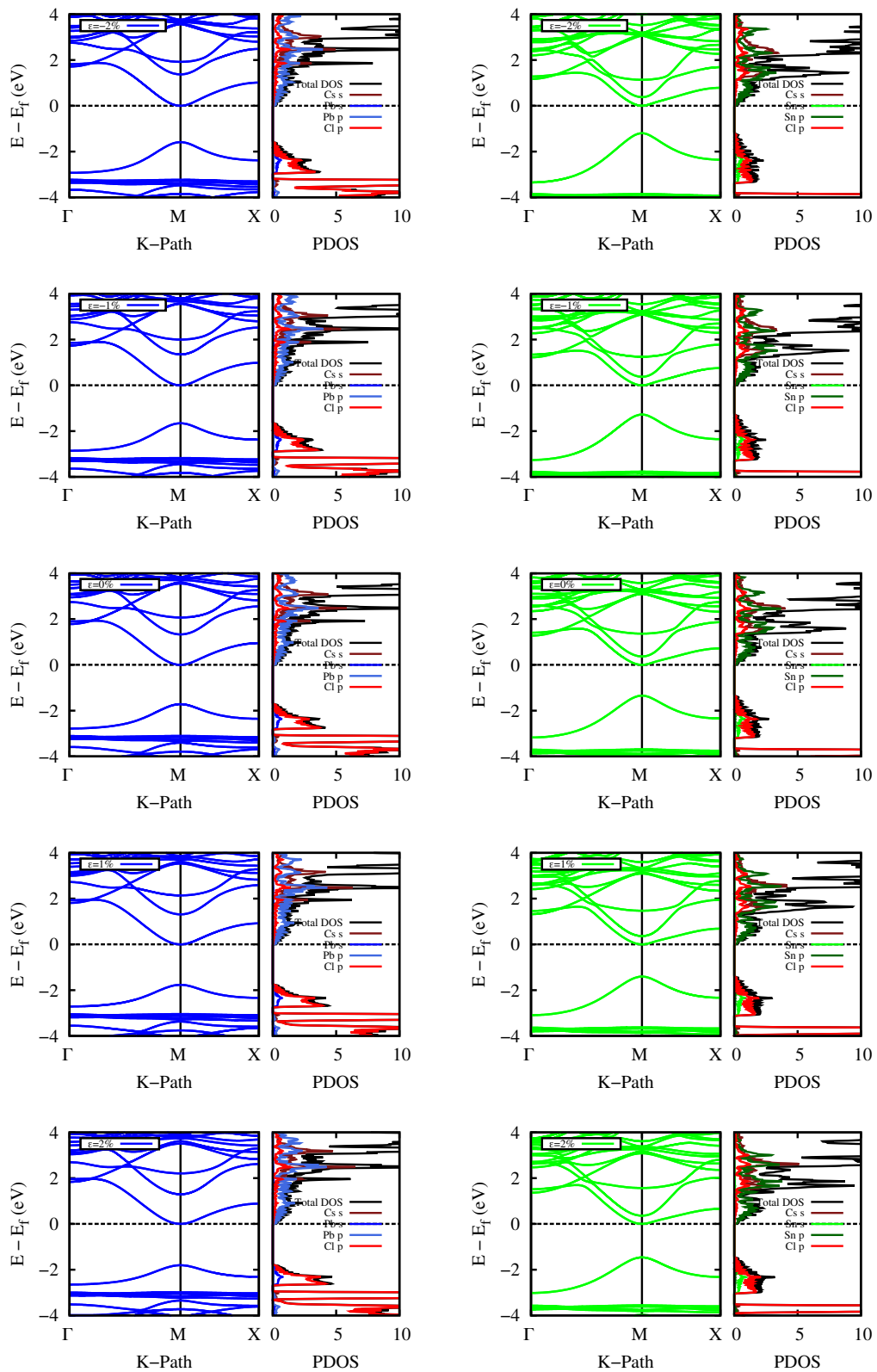


Fig. S3 Electronic band structure along the high symmetry path $\Gamma \rightarrow M \rightarrow X$ and total and orbital resolved Density of states for strained and strain-free CsCl terminated 2D perovskites, Cs₂PbCl₄ (left column) and Cs₂SnCl₄ (right column).

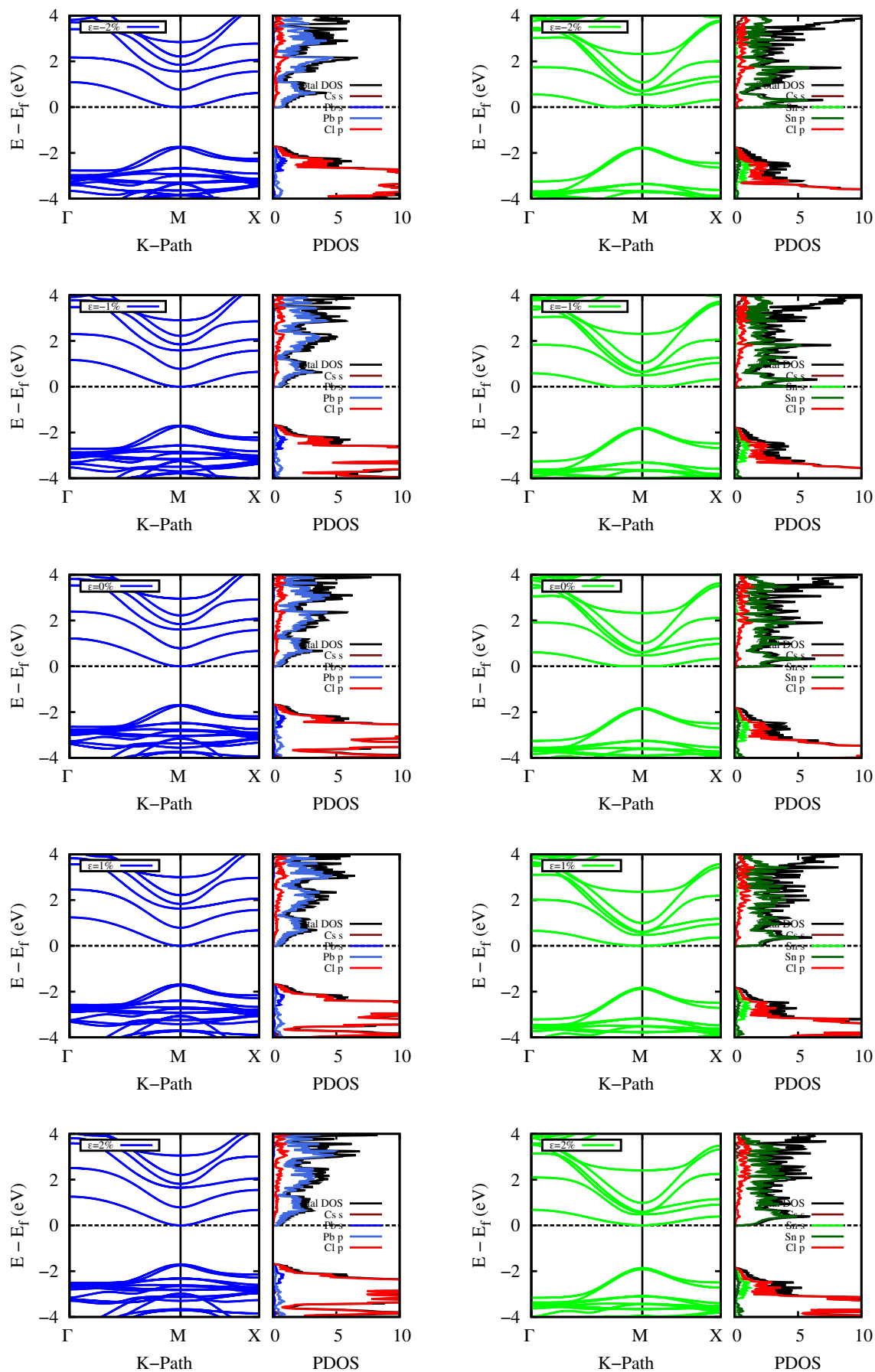


Fig. S4 Electronic band structure along the high symmetry path $\Gamma \rightarrow M \rightarrow X$ and total and orbital resolved Density of states for strained and strain-free BCl_2 ($B=\text{Pb}$ or Sn) terminated 2D perovskites, CsPb_2Cl_5 (left column) and (b) CsSn_2Cl_5 (right column).

Effect of thickness on structure and electronic properties

To understand the effect of material thickness on transport properties, we model 3D bulk and 2D bilayer of these MHPs (see main text fig 5(a)). The corresponding structural and transport parameters highlighting the impact of material thickness are listed in below Table ?. We note that as the number of layers (N) increases, the lattice constant increases and electronic bandgap decreases.

Table 2 : Comparison of structural and electronic parameter evolution with thickness and strain

Material	1/N		a (Å)	Thickness (Å)	Rumpling (Å)	E_g (eV)	$\Delta\mu_h(-2\%)$	$\Delta\mu_e(-2\%)$
Bulk	0	Pb	5.738	–	–	0.98	31	29
		Sn	5.636	–	–	0.67	76	67
Bilayer	0.5	Pb	5.72	10.5488	0.4986	1.55	63	16
		Sn	5.62	10.4928	0.4341	1.18	47	17
Monolayer	1	Pb	5.648	4.9651	0.4018	1.72	79	18
		Sn	5.557	4.9622	0.3565	1.34	49	21

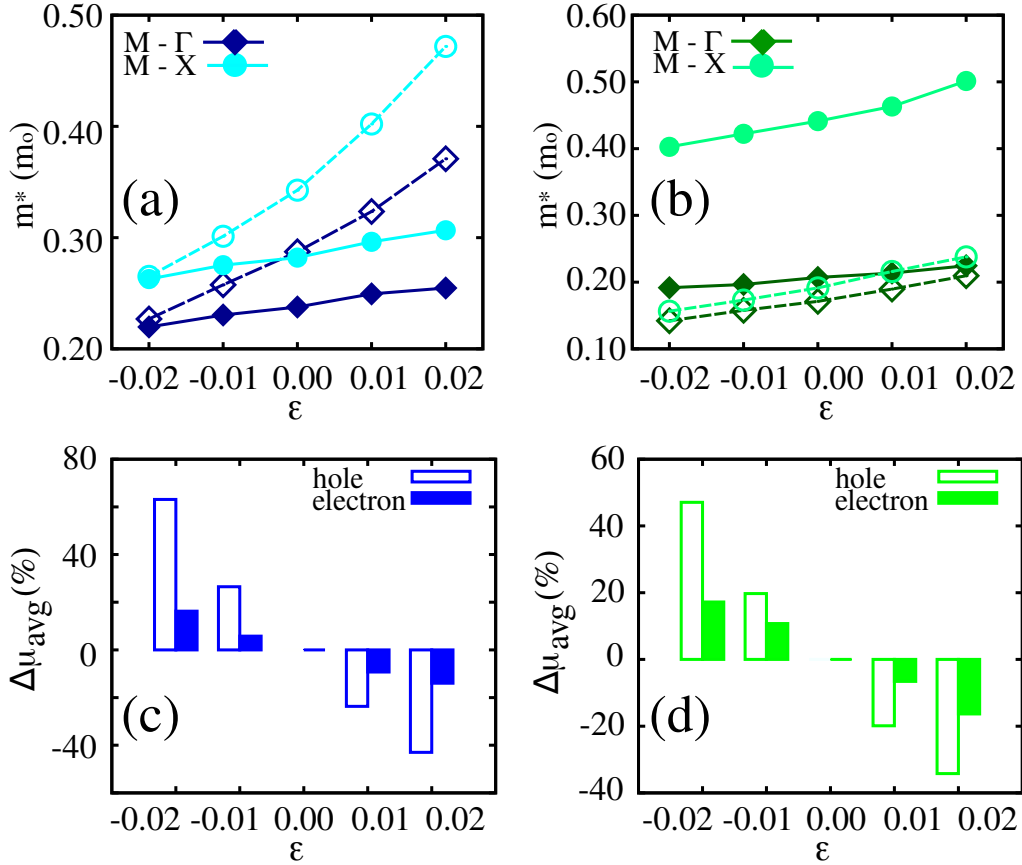


Fig. S5 Effective mass, m^* variations with strain, along $M \rightarrow \Gamma$ and $M \rightarrow X$ for bilayer (a) 2D Cs₃Pb₂Cl₇ and (b) 2D Cs₃Sn₂Cl₇. Hollow and filled markers have been used for holes and electrons, respectively. Direction average mobility variations with biaxial strain for (c) Cs₃Pb₂Cl₇ and (d) Cs₃Sn₂Cl₇.

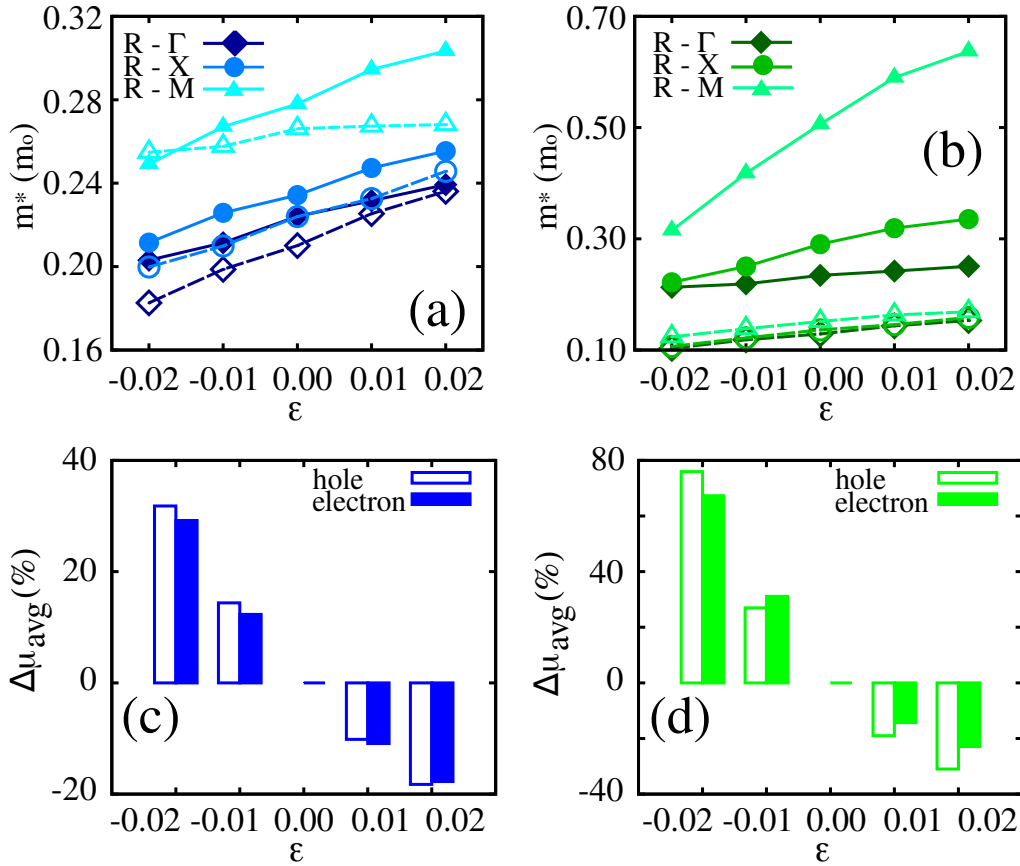


Fig. S6 Effective mass, m^* variations with strain, along $R \rightarrow \Gamma$, $R \rightarrow X$ and $R \rightarrow M$ for (a) CsPbCl₃ and (b) CsSnCl₃ Bulk. Hollow and filled markers have been used for holes and electrons, respectively. Direction average mobility variations with biaxial strain for (c) CsPbCl₃ and (d) CsSnCl₃.

Born effective charges

We estimated the Born effective charges as an indicator of ferroelectricity, and find anomalously large charges on the B atom and the Cl ion, which can further be modulated with strain. Our phonon dispersions are consistent with rich phase diagrams in the material. Born effective charges, $Z_{\alpha\beta}^*$, manifest coupling between lattice displacements and electrostatic fields. We note that Z^* is anomalously large for the parallel Cl and B atom (see fig S5. a-d). The effective charges on the B atom increase from Pb to Sn, with corresponding decrease in size of B-atom, while the effective charge on the Cl atom increases with B-atom size increase. The effective charges on the B-atom increase linearly with decrease in the lattice parameter, while the Cl-atom charge decreases. These variations could be attributed to electronegativity differences between the B atom and the Cl atom.

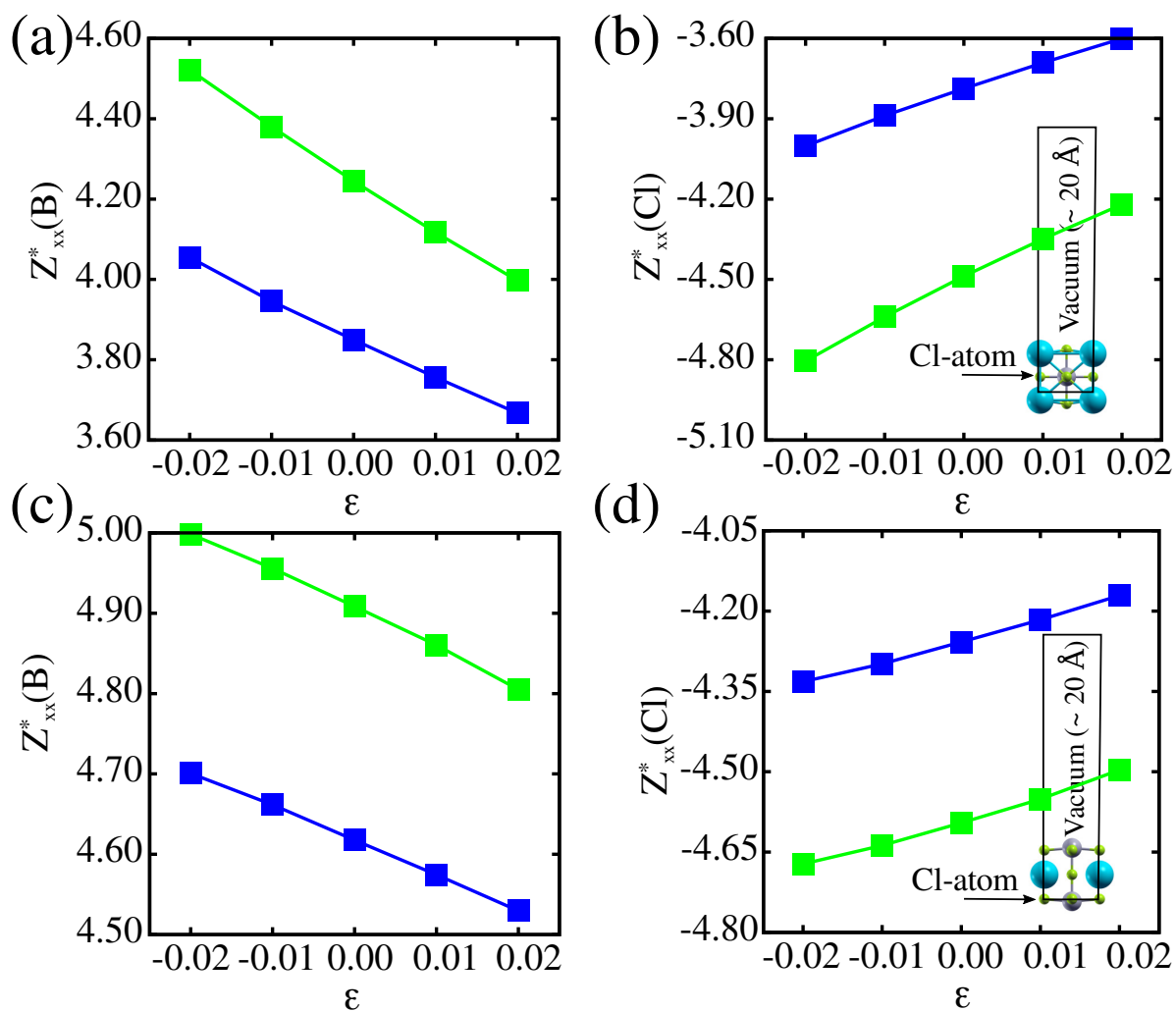


Fig. S7 Polarization given Born effective charges, Z^* variation with strain (a) B-atom (B=Pb, Sn), (b) Cl-atom of Cs_2BCl_4 , (c) B-atom (B=Pb, Sn) (d) Cl-atom of CsB_2Cl_5 . Blue, green curves correspond to Pb and Sn perovskites, respectively.