Supporting information for: First Principles Study of Ferroelastic Twins in Halide Perovskites

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Domain Wall Energy

We define the wall formation energy, E_{W} as

$$E_{\mathrm{W}} = \frac{1}{2}\frac{E_{\mathrm{Wall}} - E_{\mathrm{Domain}}}{S}, \tag{S1}$$

where E_{Wall} and E_{Domain} are the energies of the wall and bulk domain supercells respectively (each cell contains 200 atoms) and S is the wall area contained in the supercell. The factor of 1/2 accounts for the two walls in the supercell.

Born Effective Charge Polarisation

Method

We calculated the layer by layer polarisation $\mathbf{P}$ with Born Effective Charges such that

$$\mathbf{P} = \frac{1}{\Omega}\sum_i w_i \mathbf{Z}_i \mathbf{u}_i, \tag{S2}$$

where $\mathbf{Z}_i$ and $\mathbf{u}_i$ denote the Born Effective Charge and displacement from a reference high symmetry position of the ith ion. Weights w_i scale the contributions of ions shared with neighbouring cells that lie on the edges or vertices of the volume Ω (*e.g.* an ion lying on a face–center is shared between two cells and hence $w_i = 1/2$). The sum runs over all atoms contained in the volume in which the polarisation is computed.

Axial Strain

Axial $\hat{\mathbf{s}}$ strain was estimated by the expansion/compression of perpendicular distances between Cs–Pb–I planes relative to such a distance in the wall super cell where the bulk properties were recovered. Layer widths were calculated from taking distances between av-

erage positions of Cs and Pb cations in a given plane; these approximately correspond to the width of the dotted blue box along $\hat{\mathbf{s}}$ in Fig. 2a).

Data

The input files and data required to reproduce our results are on Zenodo at `https://doi.org/10.5281/zenodo.2546900`. Included are the following files:

- HT and HH twin input and structure files relaxed to forces smaller than 10 meV/Å.
- Relaxed *I4/mcm* conventional 20 atom wall cell, relaxed to forces smaller than 10 meV/Å.
- 200 atom bulk domain structure adapted to the geometry of the wall supercells for calculating wall formation energy.
- Cubic $Pm\bar{3}m$ structure relaxed to 10^{-8} eV and associated Born Effective Charges.

As stated in the manuscript, all calculations were performed with VASP 5.4.4[1–4] using the PBEsol exchange-correlation functional.[5] Valence electron configurations $6s^1$, $6s^26p^2$ and $5s^25p^5$ were employed for Cs, Pb and I respectively with the supplied Projector-Augmented-Wave pseudopotentials generated in 2002.[1,3,6,7] We used an energy cut–off of 500 eV for the plane-wave basis set and, for the wall supercells, a $4 \times 5 \times 1$ Monkhorst-Pack grid.[8] The grid was scaled appropriately for the cubic and tetragonal structures.

References

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