Supporting Information

Two-dimensional Halide Perovskites: Tuning Electronic Activities of Defects

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The line defects are modelled by a ribbon with width of ~3 nm (for edges) or 6 nm (for grain boundaries). For point defects in 2D Rb_2PbI_4, we use a 4x4 supercell (see the structure of the primitive cell in Fig. 1). For point defects in 2D MA_2SnBr_4, we use a 3x3 supercell to reduce the computational cost to an affordable limit.

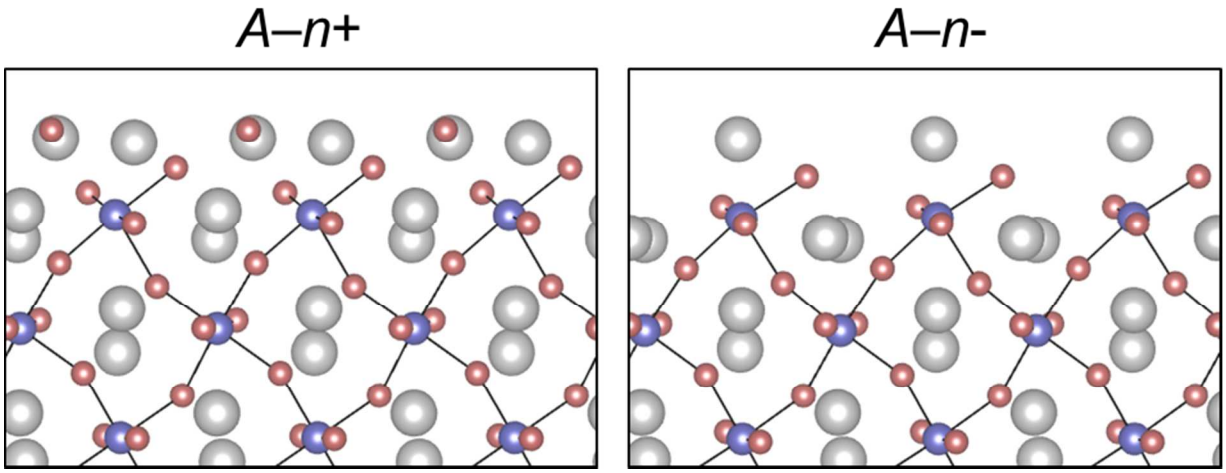

Fig. S1. Edges along *A* direction with surplus cations/deficient anions. *A*–*n*+ can be thought as adding more Rb into *A*–N+ (Fig. 2), and *A*–*n*- can be thought as removing I from *A*–N+, or adding more Rb into *A*–N- (Fig. 2).

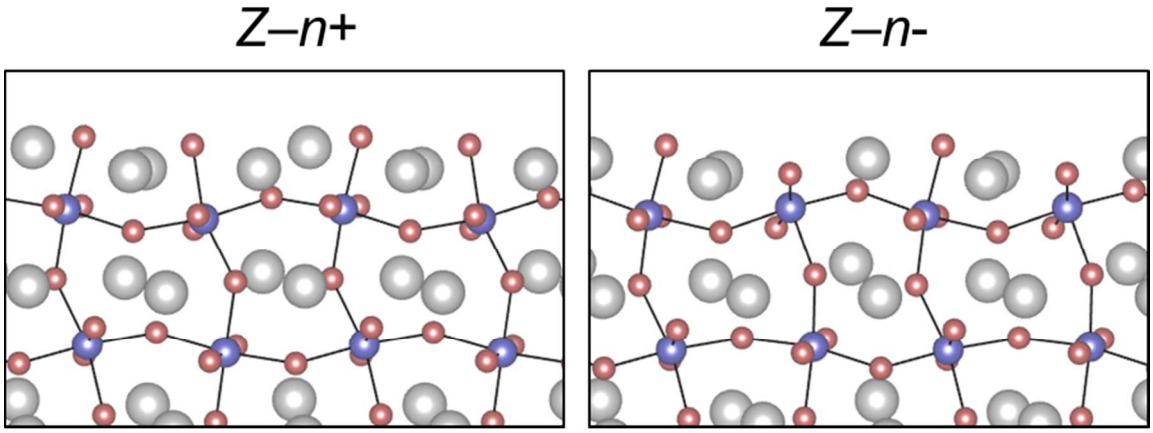

Fig. S2. Edges along *Z* direction with surplus cations/deficient anions. *Z*–*n*+ can be thought as adding more Rb into *Z*–N+ (Fig. 2), and *Z*–*n*- can be thought as removing I from *Z*–N+, or adding more Rb into *Z*–N- (Fig. 2).

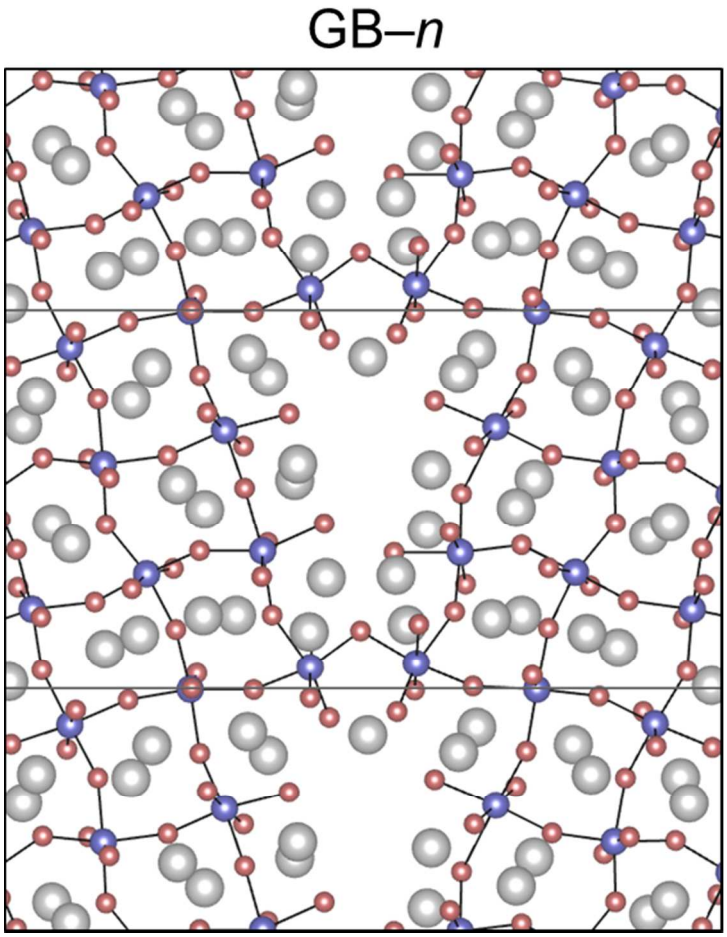

Fig. S3. Structure of grain boundary with surplus cations. This can be thought as adding more Rb into GB–N (Fig. 3).

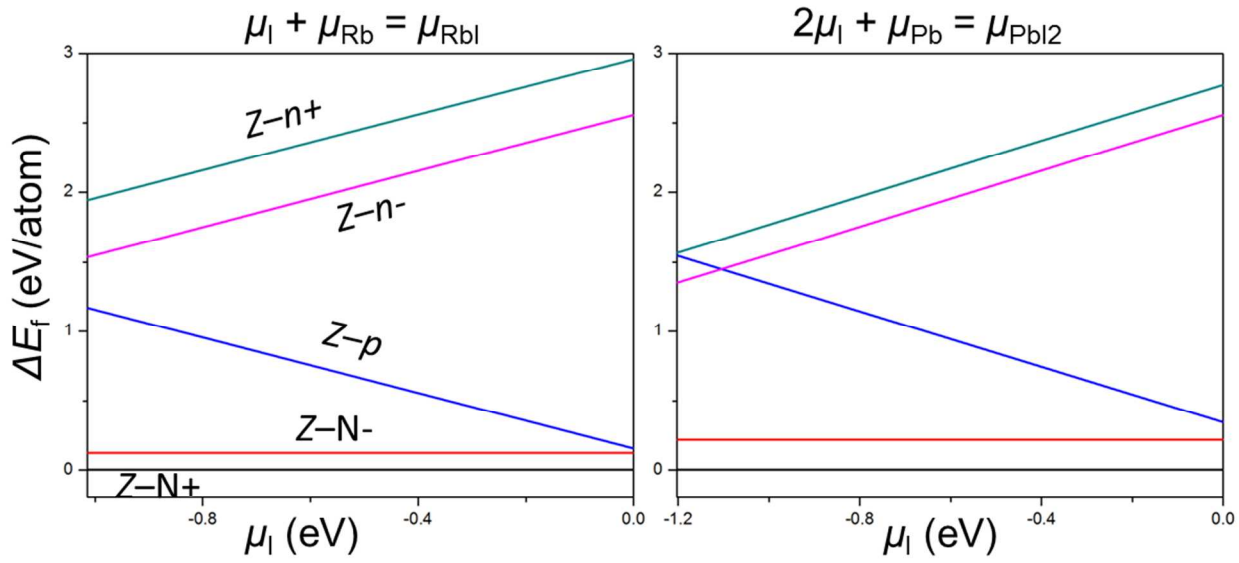

Fig. S4. Energies of various edges along *Z* direction, with respect to that of Z–N+, as a function of I chemical potential (with respect to that of I2 molecule) along phase boundaries.

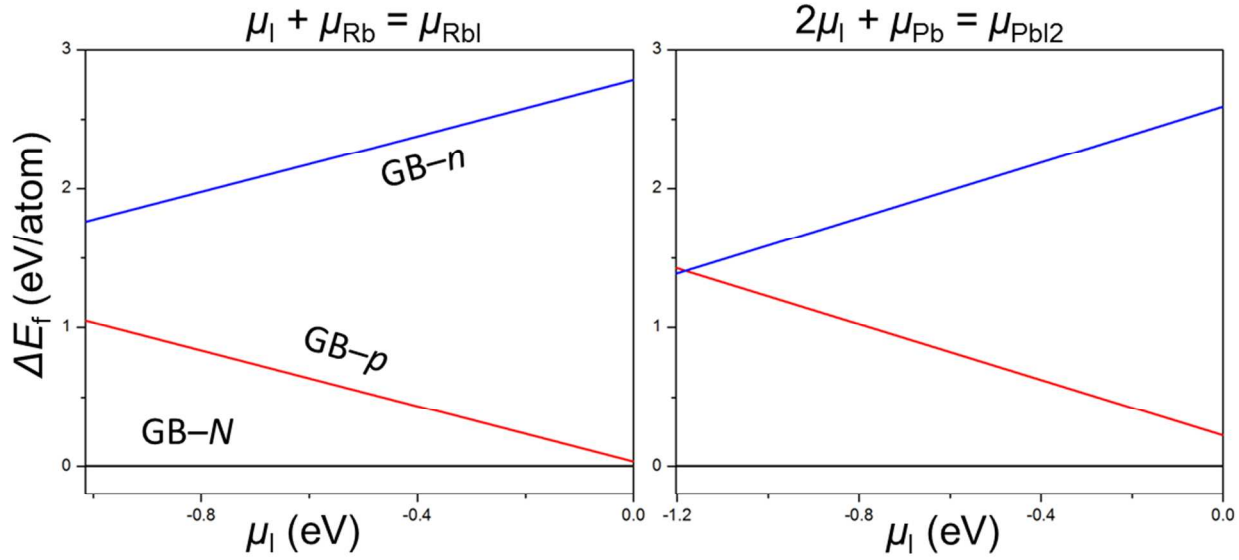

Fig. S5. Energies of various grain boundaries, with respect to that of GB–N, as a function of I chemical potential (with respect to that of I2 molecule) along phase boundaries.

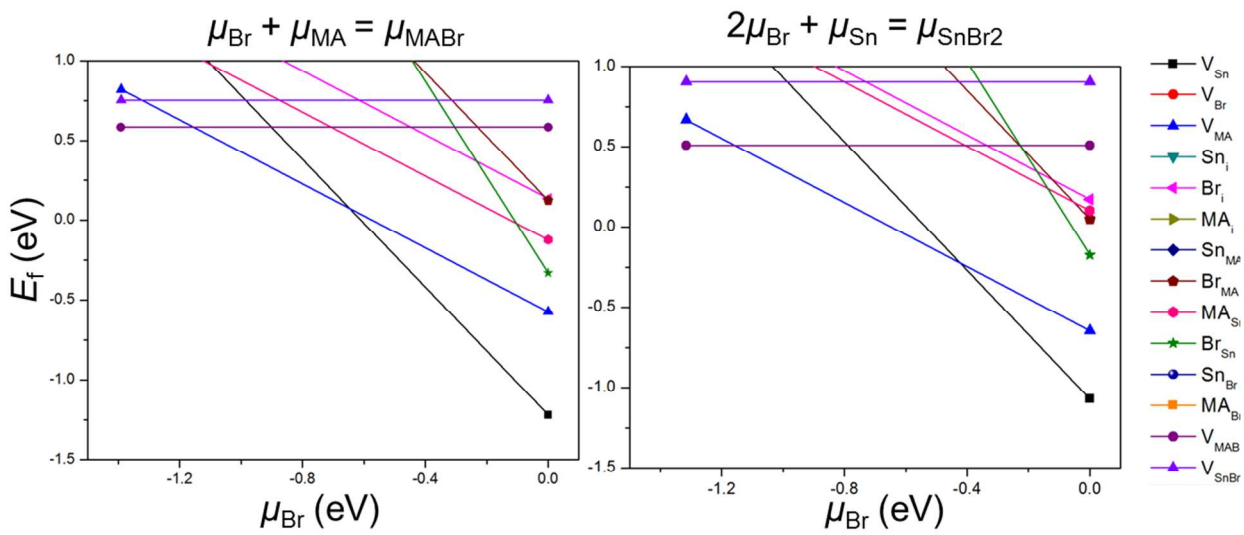

Fig. S6. Energies of various point defects in 2D MA_2SnBr_4 (MA= CH_3NH_3), as a function of Br chemical potential (with respect to that of Br_2 molecule) along phase boundaries. These suggest that the formation of harmful defects can be suppressed by decreasing the chemical potential of Br, in consistence with Rb_2PbI_4.