Supporting Information

Two-dimensional Halide Perovskites: Tuning Electronic Activities of Defects

Yuanyue Liu,*1,2 Hai Xiao1 and William A. Goddard III*1

1Materials and Process Simulation Center
2the Resnick Sustainability Institute
California Institute of Technology, Pasadena, CA 91125, USA

*Correspondence to: yuanyue@caltech.edu and wag@wag.caltech.edu

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 Rb2PbI4, we use a 4x4 supercell (see the structure of the primitive cell in Fig. 1). For point defects in 2D MA2SnBr4, 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$_2$SnBr$_4$ (MA= CH$_3$NH$_3$), 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$_2$PbI$_4$. 