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Supplementary Information for

La-Doped $BaSnO_3$ Electron Transport Layer for Perovskite Solar Cells

*Chang Woo Myung, Geunsik Lee, Kwang S. Kim**

Department of Chemistry, School of Natural Science, Ulsan National Institute of Science and Technology (UNIST), Ulsan 44919, Korea.

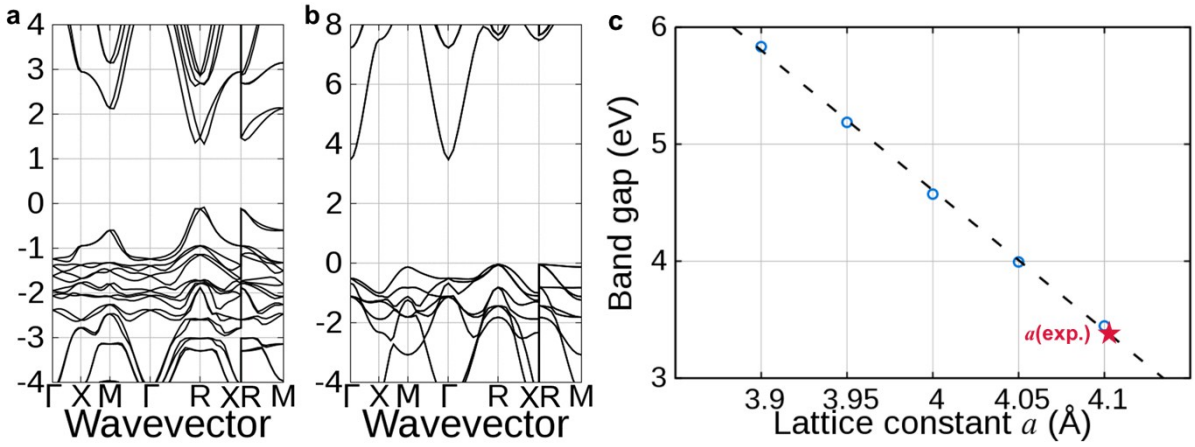
Corresponding Author

*Correspondence and requests should be addressed to K.S.K. (email: kimks@unist.ac.kr).

Supplementary Note 1 We have employed the electrostatic potential of the solid to define the common vacuum level and to relate the calculation of the PBE+SOC+D3 to that of the PBE0+SOC+D3 that includes the Hartree-Fock exchange. The reference electrostatic local potential only includes the Hartree potential so that it is independent of the exchange-correlation functionals we choose.[1,2] Then, we calculated the PBE0 correction on the PBE functional energy levels. The PBE0 correction is listed in Supporting Table 1.

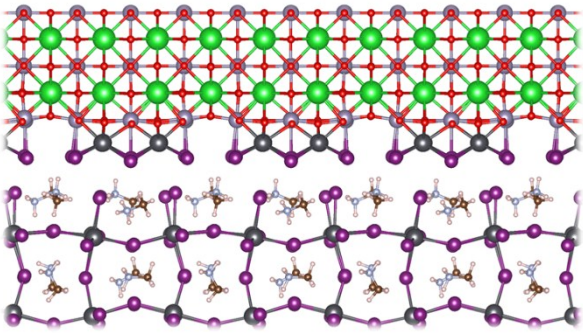
Supplementary Table 1 The PBE0 correction (in eV) on the PBE energy level for the conduction band minimum (CBM) and the valence maximum (VBM).

	$MAPbI_3$	BSO	LBSO(x=3.7 %)	LBSO(x=7.4 %)	LBSO(x=11.1 %)
CBM	0.33	0.75	0.20	0.06	-0.02
VBM	-0.61	-1.61	-1.59	-1.57	-1.55

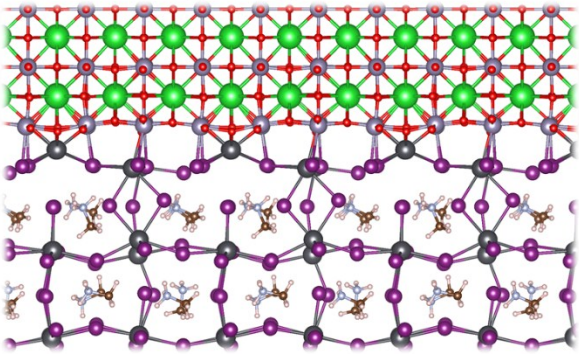


Supplementary Fig. 1 The PBE0+SOC band structure of (a) cubic $MAPbI_3$ and (b) cubic BSO along the high symmetry points, **Γ**(0.0, 0.0, 0.0), **X**(0.0, 0.5, 0.0), **M**(0.5, 0.5, 0.0), **R**(0.5, 0.5, 0.5). (c) The band gap variation of cubic $BaSnO_3$ with respect to the lattice constant *a*(BSO) at PBE0+SOC level (blue dot). The experimental lattice constant *a*(exp.) ~ 4.116 Å[3] (red star) is also highlighted. Note that for thin-film LBSO, the lattice is partially relaxed with *a*(in-plain) = 4.09 Å and *a*(out-of-plane) = 4.12 Å.[3]

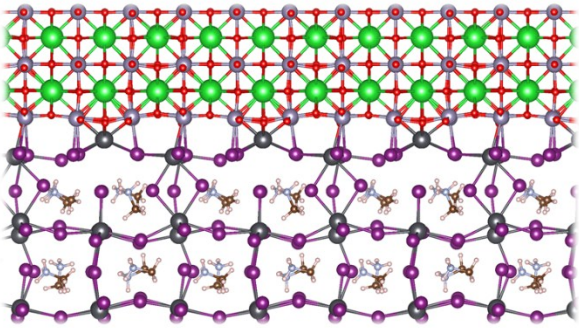
a PbI_2-SnO_2 x = 0.0 %



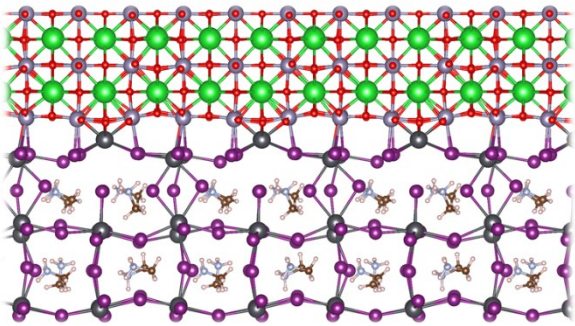
b PbI_2-SnO_2 x = 3.7 %



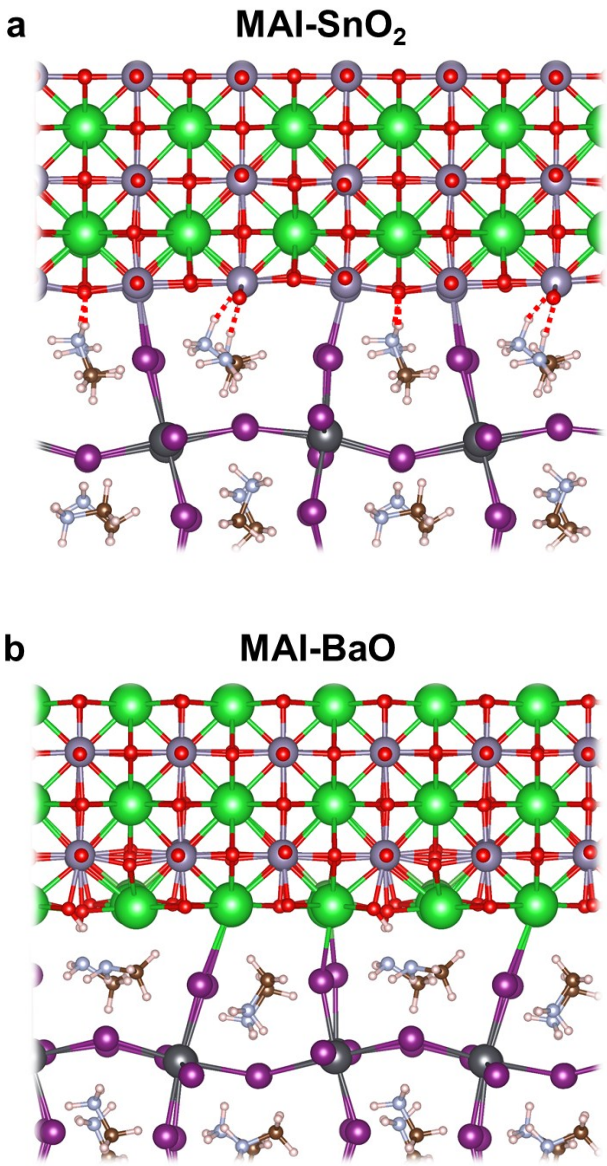
c PbI_2-SnO_2 x = 7.4 %



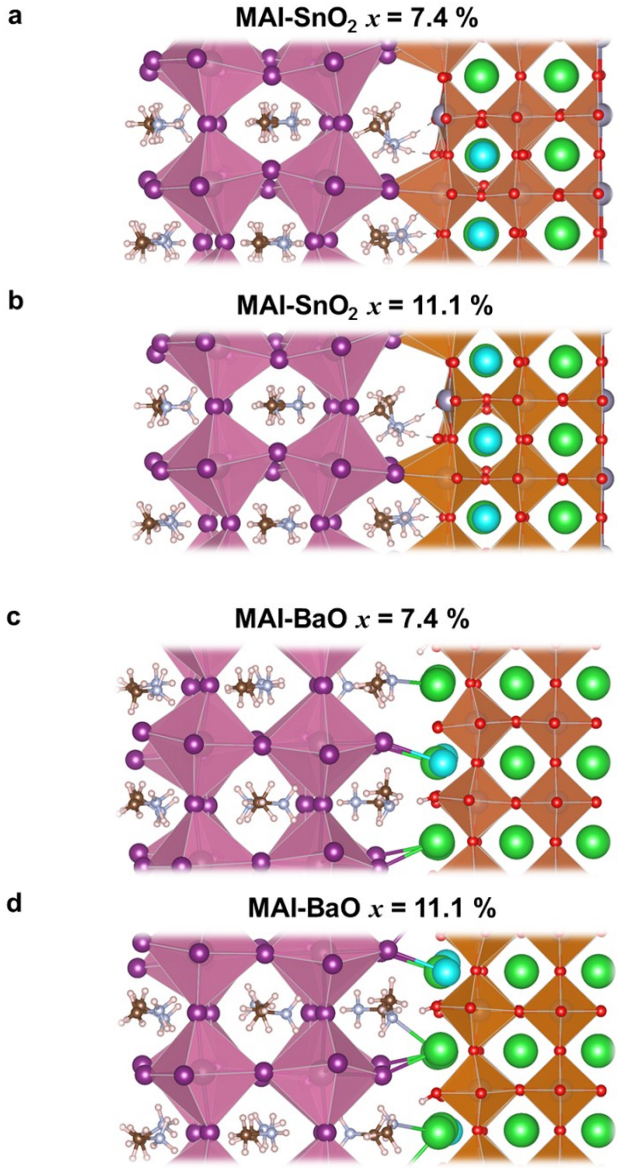
d PbI_2-SnO_2 x = 11.1 %

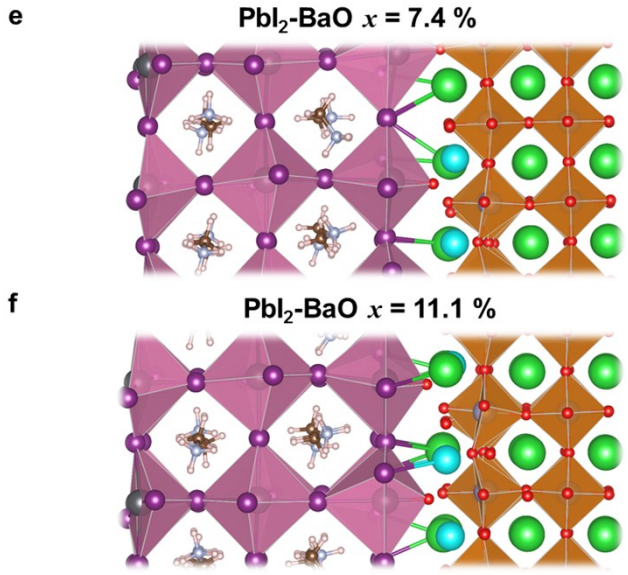


Supplementary Fig. 2 (a) Optimized geometry of the PbI_2-terminated $MAPbI_3$ and SnO_2-terminated BSO interface. Deformation of perovskite structure into plumbic-oxide-like structure. (b)-(d) This deformation is found regardless of the amount of La-doping, x = 3.7, 7.4, and 11 %.

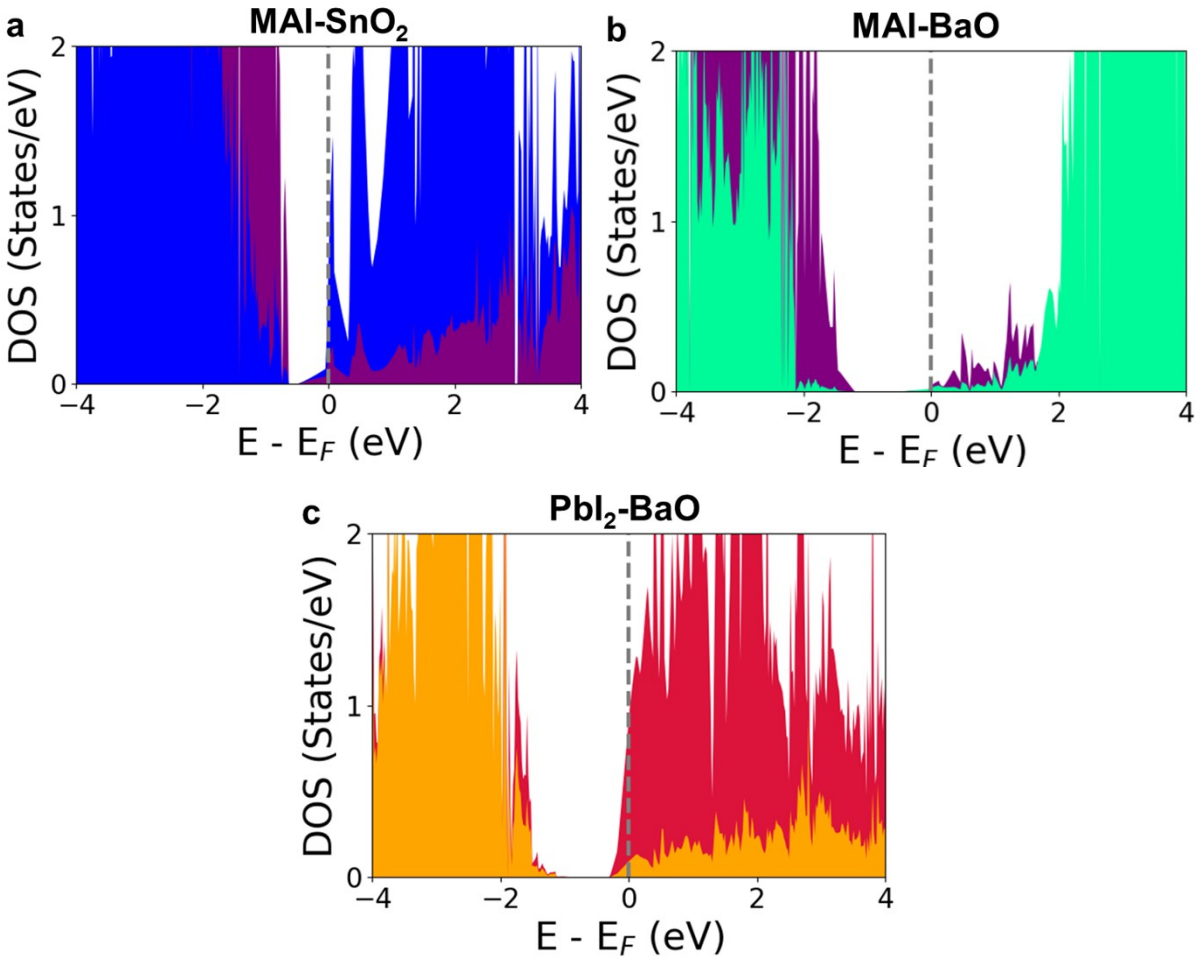


Supplementary Fig. 3 (a) Strong HB (red dashed line) between H (white) of MA^+ and O (red) of SnO_2 at MAI-SnO_2 interface of $MAPbI_3$/LBSO with La-doping x = 3.7 %. (**b**) The proton transfer of H (white) in MA^+ to O (red) of BaO at the MAI-BaO interface of $MAPbI_3$/LBSO with La-doping x = 3.7 %. We note the protons of MA^+ being transferred to O of BaO terminations.

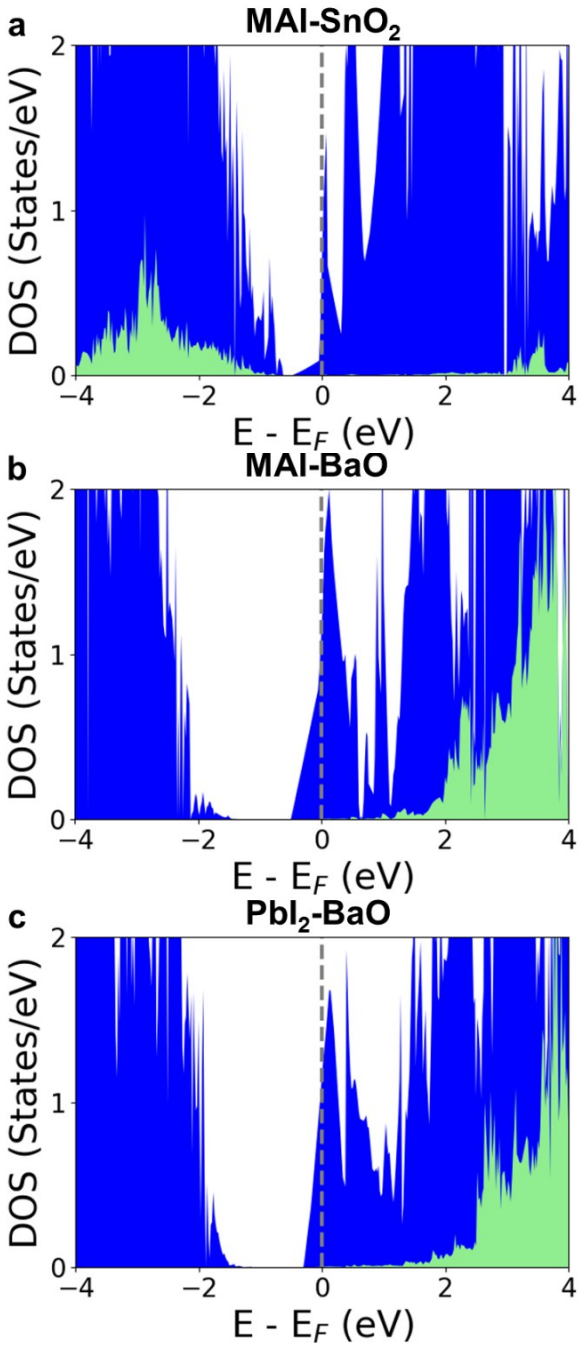

a
MAI-SnO2 x = 7.4 %
b
MAI-SnO2 x = 11.1 %
c
MAI-BaO x = 7.4 %
d
MAI-BaO x = 11.1 %



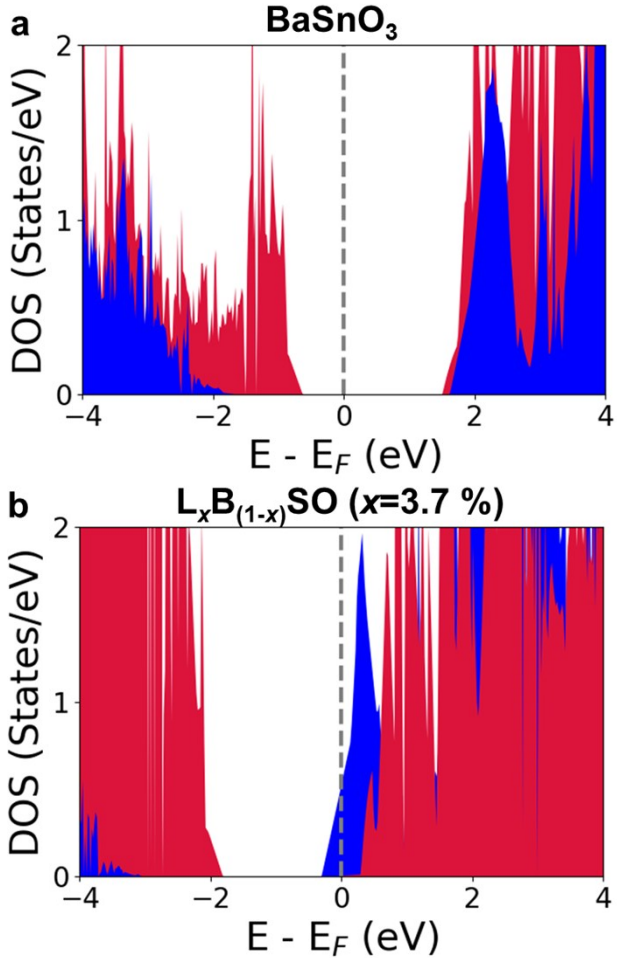
Supplementary Fig. 4 All-perovskite heterostructure of the MAI-SnO_2 terminated $MAPbI_3/L_xB_{(1-x)}SO$ for (**a**) x = 7.4 and (**b**) 11 %, the MAI-BaO terminated $MAPbI_3/L_xB_{(1-x)}SO$ for (**c**) x = 7.4 and (**d**) 11 %, and the PbI_2-BaO terminated $MAPbI_3/L_xB_{(1-x)}SO$ for (**e**) x = 7.4 and (**f**) 11 %.

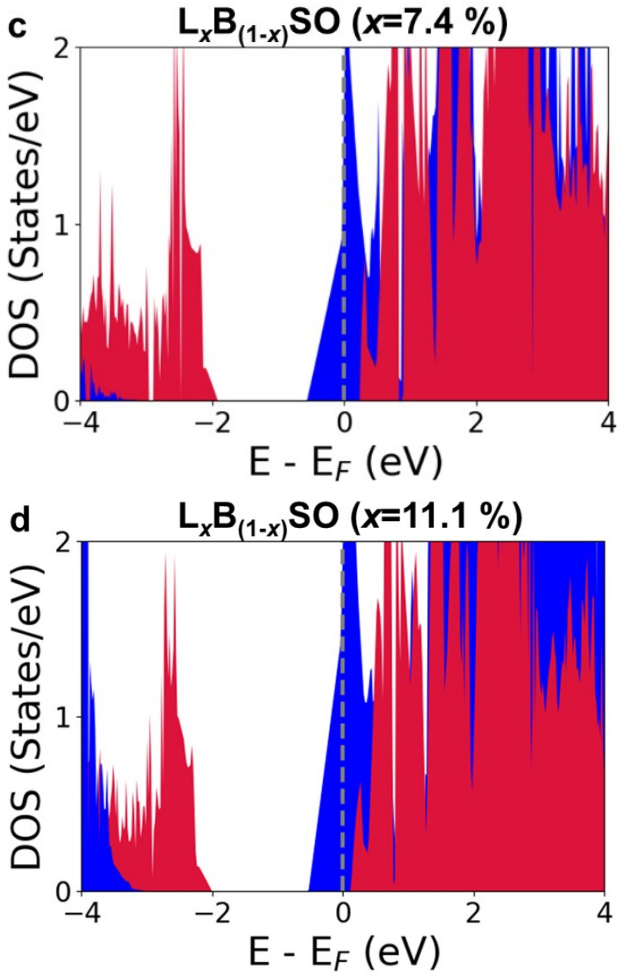


Supplementary Fig. 5 PDOS for $MAPbI_3$/LBSO (La-doping of x = 3.7 %) interface of (a) MAI-SnO_2 with the interfacial I (purple) and Sn (blue), (b) MAI-BaO with the interfacial I (purple) and Ba, La (green), and (c) PbI_2-BaO with the interfacial Pb (red) and O (orange) with PBE+SOC+D3 are plotted. At the MAI-SnO_2 interface, we observe the hybridization of interfacial I and Sn states. At the MAI-BaO, the hybridization between I, Ba, and La occurs, lowering the Ba and La levels by ~ 2 eV. At the PbI_2-BaO, we find the hybridization between Pb and O atoms which forms the ionic bonds.



Supplementary Fig. 6 PDOS of the La-*d* state and Sn-*s* state of the $MAPbI_3$/LBSO interface at the (a) MAI-SnO_2, (b) MAI-BaO and (c) PbI_2-BaO terminations. We find that the La-*d* states are 2-4 eV away from the conduction band without hybridization.


a
BaSnO3
DOS (States/eV)
E - EF (eV)
b
LxB(1-x)SO (x=3.7 %)
DOS (States/eV)
E - EF (eV)



Supplementary Fig. 7. PDOS of the MAI-BaO-terminated $MAPbI_3/La_xB_{(1-x)}SO$ with La-doping of (**a**) $x = 0.0$ %, (**b**) $x = 3.7$ %, (**c**) $x = 7.4$ %, and (**d**) $x = 11.1$ % interfaces with the PBE0+SOC+D3 corrections, where interfacial Pb *s*, *p* (red) and Sn *s*, *p* (blue) states. The Fermi level (E - E_F) is indicated as a gray dashed line.

Supplementary references

(1) C. V. De Walle, R. M. Martin, *Phys. Rev. B, 1987*, 35 (15), 8154.

(2) J. C. Conesa, *J. Phys. Chem. C, 2012*, 116 (35), 18884–18890.

(3) Z. Lebens-Higgins, D. O. Scanlon, H. Paik, S. Sallis, Y. Nie, M. Uchida, N. F. Quackenbush, M. J. Wahila, G. E. Sterbinsky, D. A. Arena, J. C. Woicik, D. G. Schlom and L. F. J. Piper, *Phys. Rev. Lett.*, *2016*, 116, 1–5.