Electronic Supplementary Information (ESI)

Band Engineering of Two-Dimensional Ruddlesden-Popper Perovskites for Solar Utilization: The Relationship between Chemical Components and Electronic Properties

An Chen,[a] Xu Zhang,[a] Zihe Zhang,[a] Sai Yao,[a] Zhen Zhou*[a,b]

[a] School of Materials Science and Engineering, National Institute for Advanced Materials, Institute of New Energy Material Chemistry, Collaborative Innovation Centre of Chemical Science and Engineering (Tianjin), Computational Centre for Molecular Science, Nankai University, Tianjin 300350, China

[b] School of Chemical Engineering and Energy, Zhengzhou University, Zhengzhou 450001, China

*Corresponding Authors. Email: zhouzhen@nankai.edu.cn (Z.Z.)

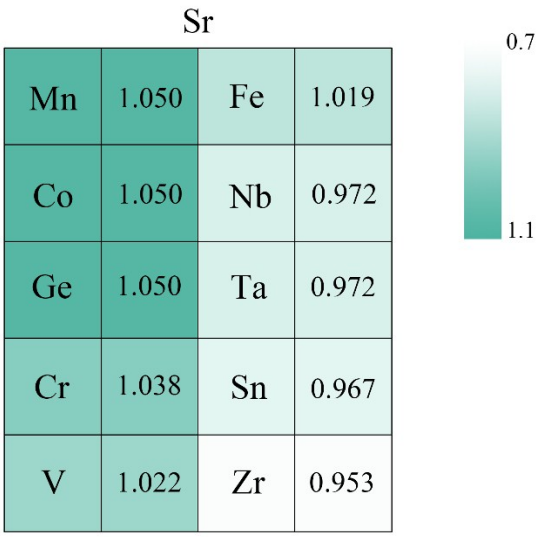

Fig. S1 The tolerance factor of the designed perovskites is presented in color map, and the arrangement of structures is shown according to the order of ionic radius.

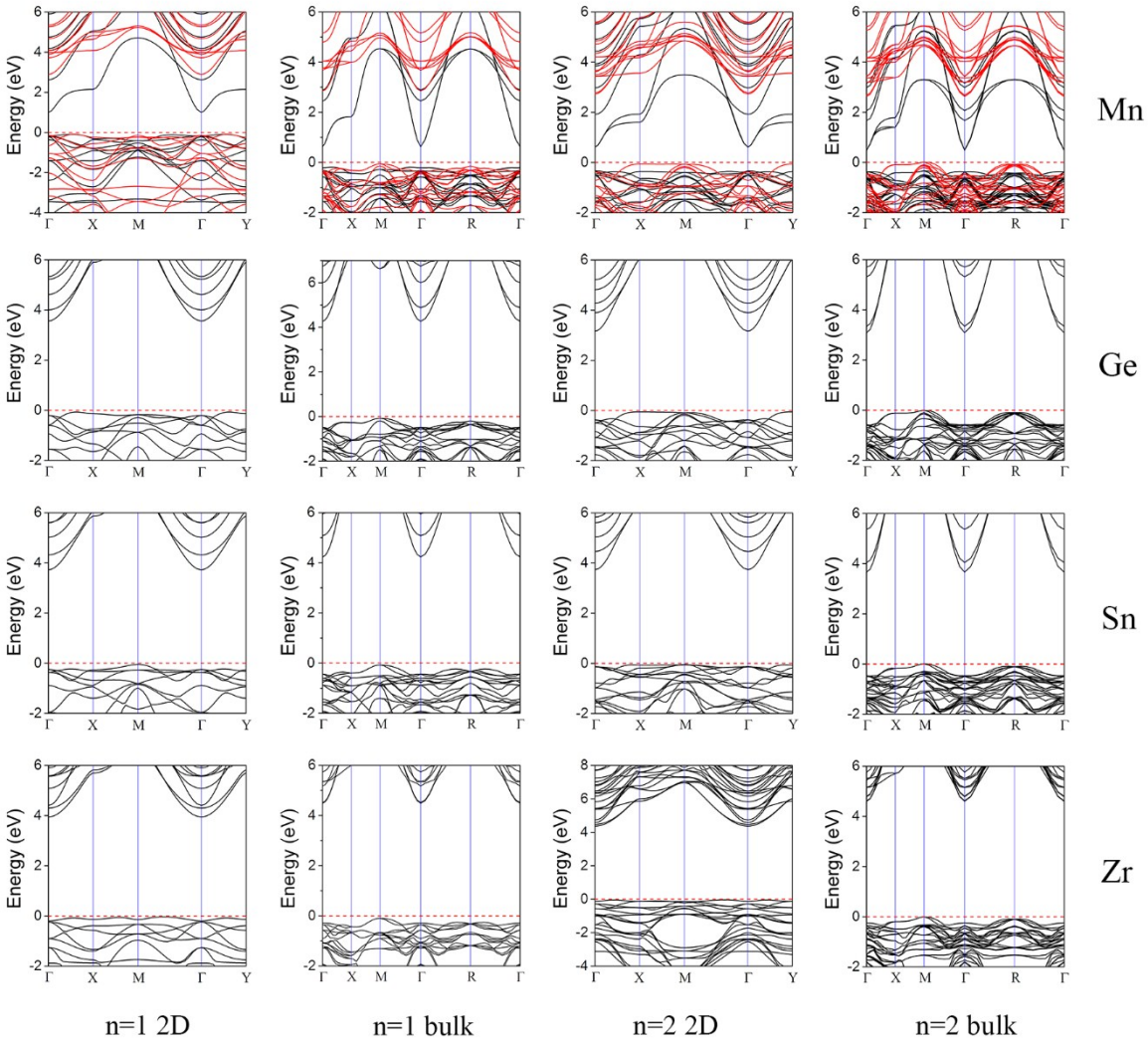

Fig. S2 Computed HSE06 band structures of $Sr_{n+1}B_nO_{3n+1}$ (B = Ge, Mn, Sn, Zr, n = 1, 2). The red dash lines show the Fermi level which is set to zero.

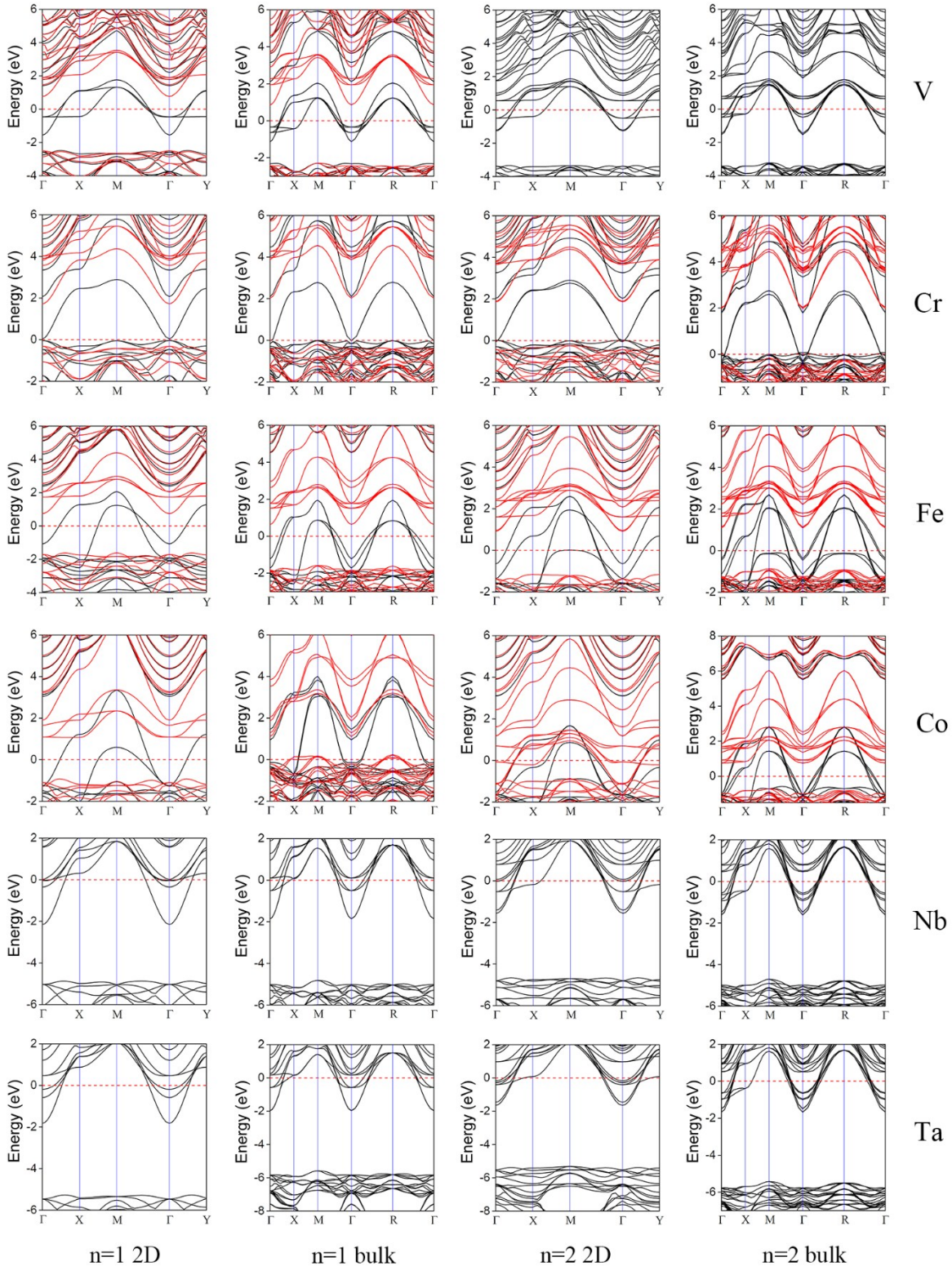

Fig. S3 Computed HSE06 band structures of $Sr_{n+1}B_nO_{3n+1}$ (B = V, Cr, Fe, Co, Sn, Ta, n = 1, 2). The red dash lines show the Fermi level which is set to zero.

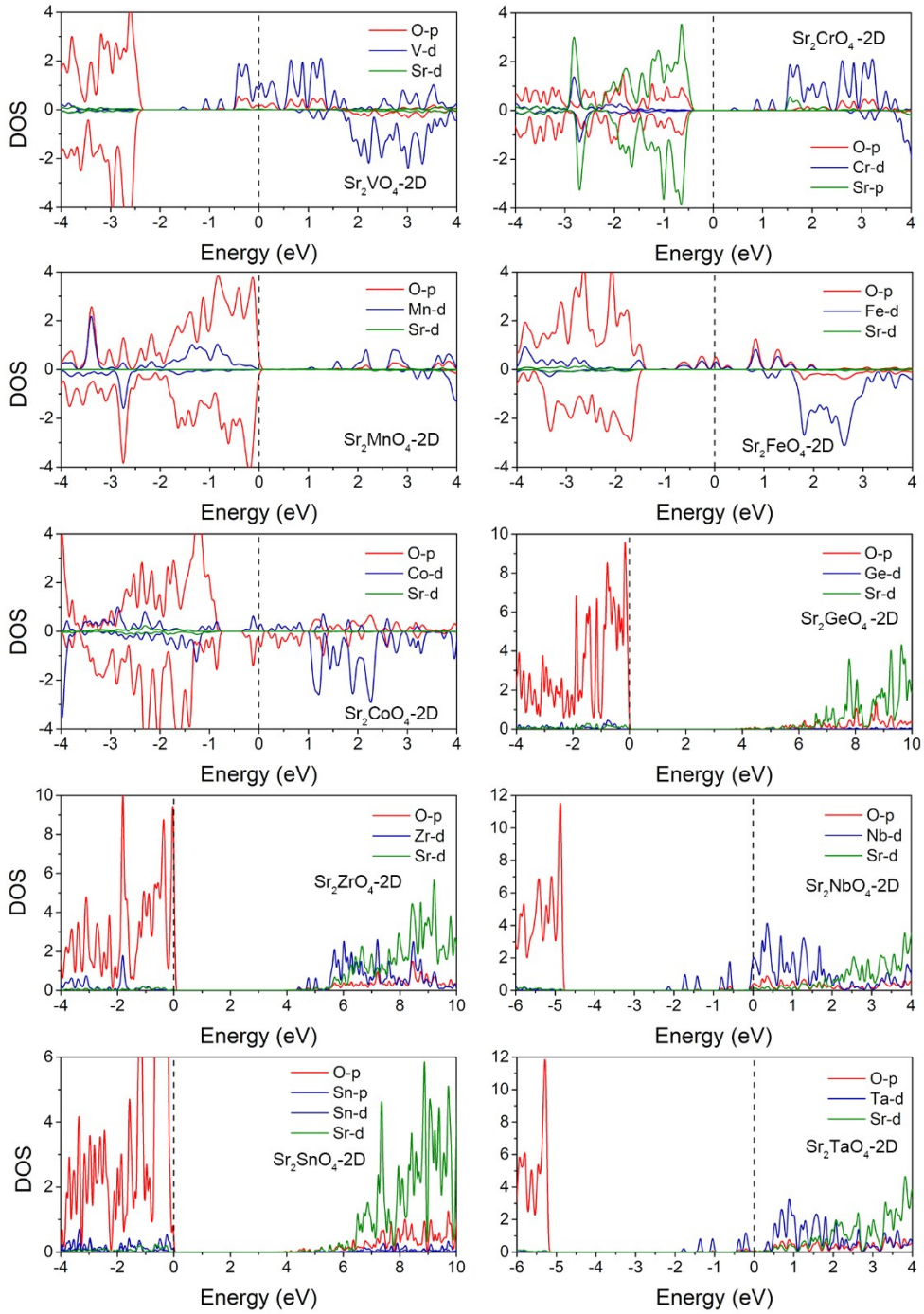

Fig. S4 PDOS of single layered Sr_2BO_4 (B = V, Cr, Mn, Fe, Co, Ge, Zr, Nb, Sn, Ta). The red lines, olive green lines and royal blue lines indicate the *p* orbital of oxygen atoms, *p*/*d* orbital of B atoms, and *p*/*d* orbital of Sr atoms, respectively. The black dash lines denote the Fermi level.

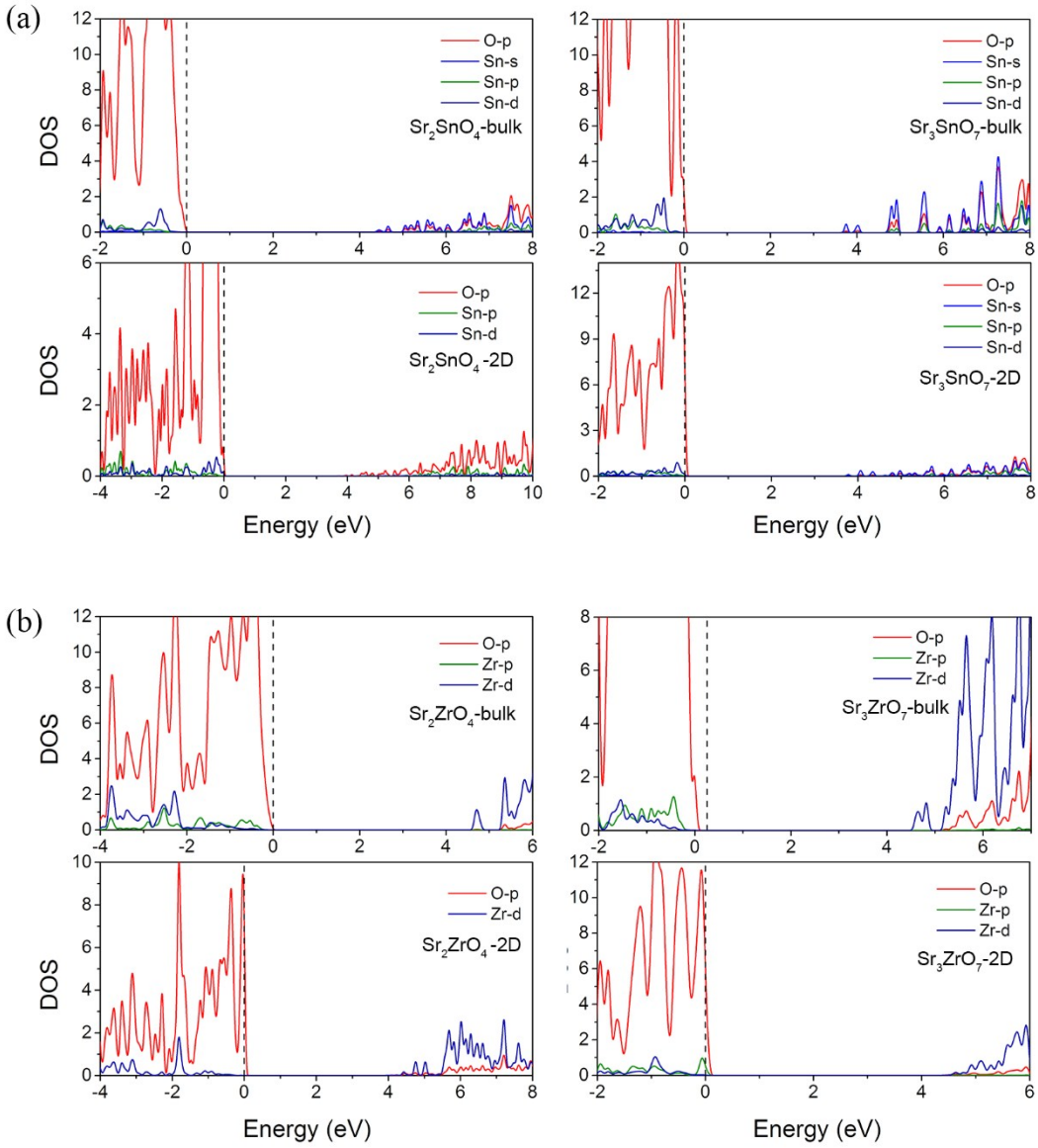

Fig. S5 PDOS of structures of $Sr_{n+1}B_nO_{3n+1}$ (B = Sn, Zr). The red lines indicate the *p* orbital of oxygen atoms, and lines with other colors indicate the orbitals of B atoms. The black dash lines denote the Fermi energy level.

Table S1 The tolerance factor *t* and computed electronic properties of 2D phase $A_{n+1}B_nO_{3n+1}$.

n = 1 2D	*t*	Band gap (eV)	Band edge positon (eV vs. Vacuum) (CBM/VBM)		n = 1 2D	*t*	Band gap (eV)	Band edge positon (eV vs. Vacuum) (CBM/VBM)	
Mg_2MnO_4	0.843	1.85	-4.57	-6.42	Mg_2GeO_4	0.843	3.91	-2.75	-6.65
Ca_2MnO_4	1.012	1.73	-3.10	-4.83	Ca_2GeO_4	1.012	4.28	-1.07	-5.35
Sr_2MnO_4	1.050	1.10	-3.51	-4.61	Sr_2GeO_4	1.050	3.64	-0.91	-4.56
Ba_2MnO_4	1.113	0.26	-3.45	-3.71	Ba_2GeO_4	1.113	2.96	-0.70	-3.66
Mg_2ZrO_4	0.765	1.81	-4.71	-6.52	Mg_2SnO_4	0.777	2.34	-4.30	-6.65
Ca_2ZrO_4	0.919	4.04	-1.47	-5.51	Ca_2SnO_4	0.933	3.95	-1.57	-5.52
Sr_2ZrO_4	0.953	3.99	-1.01	-5.00	Sr_2SnO_4	0.967	3.77	-1.20	-4.97
Ba_2ZrO_4	1.011	3.72	-0.72	-4.44	Ba_2SnO_4	1.026	3.41	-0.90	-4.30

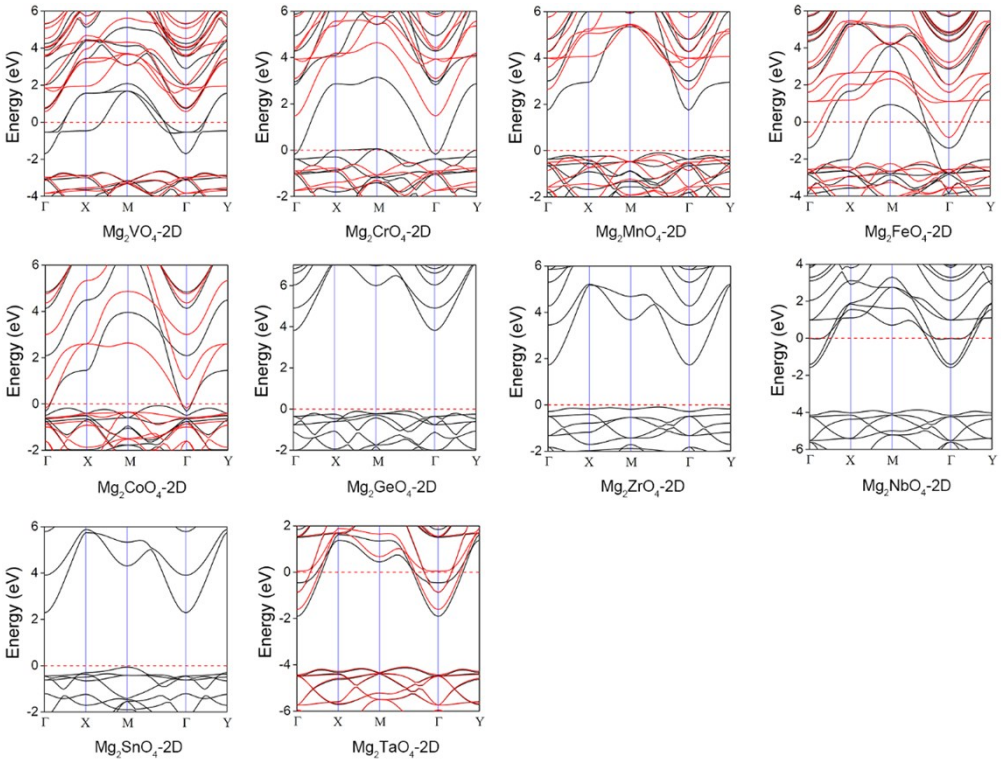

Fig. S6 Band structures of Mg_2BO_4 (B = V, Cr, Mn, Fe, Co, Ge, Zr, Nb, Sn, Ta). The red dash lines denote the Fermi level which is set to zero.

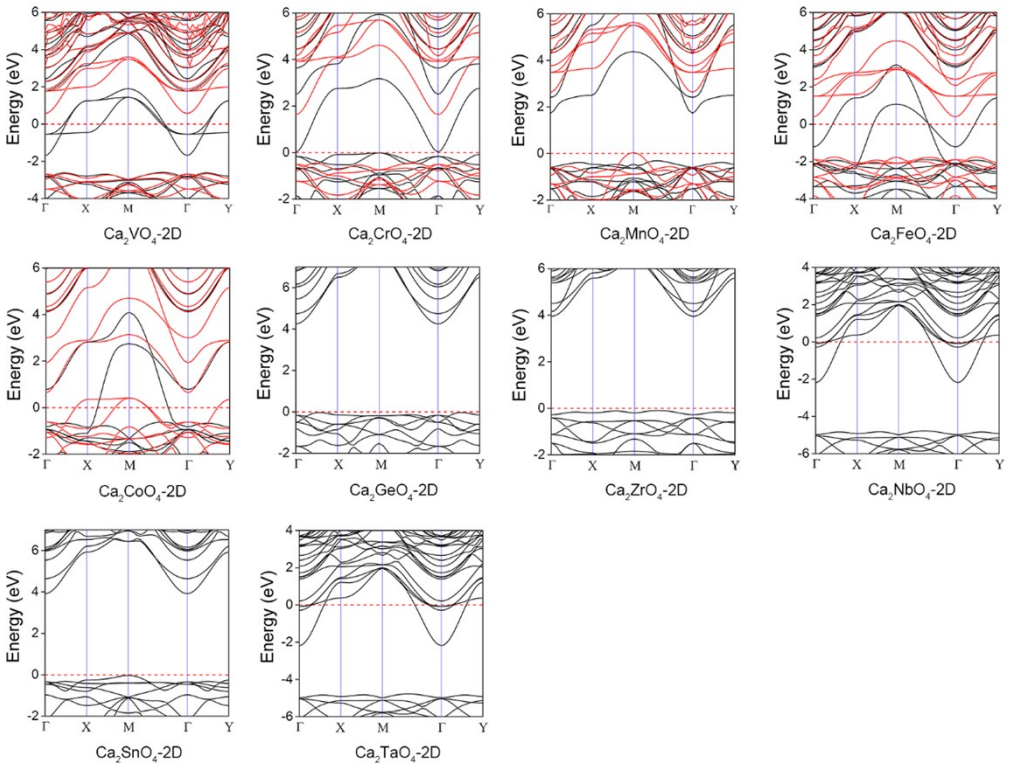

Fig. S7 Band structures of Ca_2BO_4 (B = V, Cr, Mn, Fe, Co, Ge, Zr, Nb, Sn, Ta). The red dash lines denote the Fermi level which is set to zero.

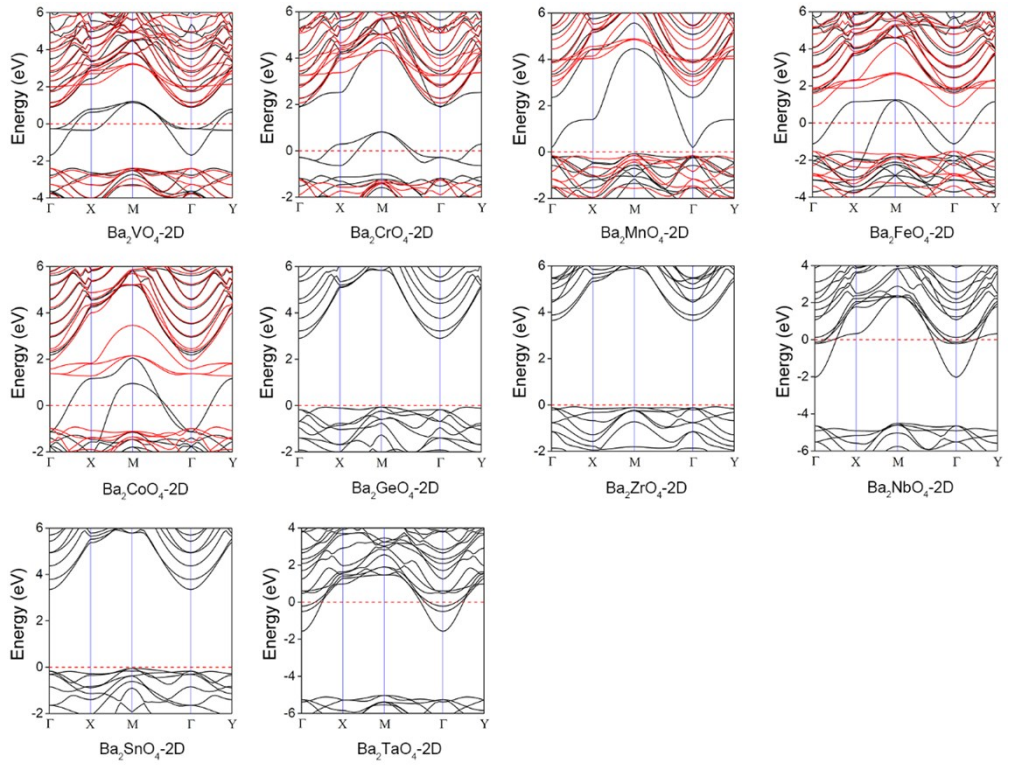

Fig. S8 Band structures of Ba_2BO_4 (B = V, Cr, Mn, Fe, Co, Ge, Zr, Nb, Sn, Ta). The red dash lines denote the Fermi level which is set to zero.

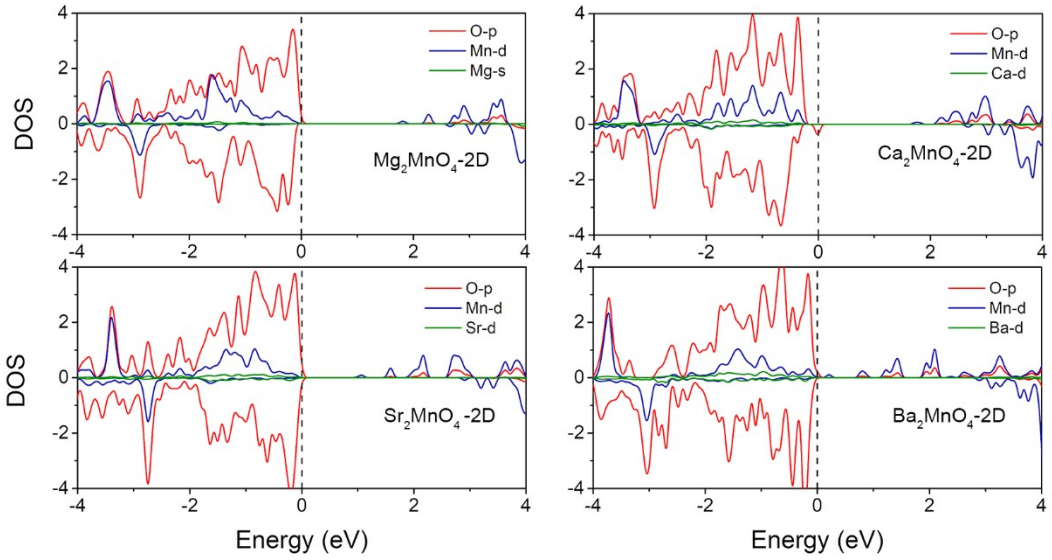

Fig. S9 PDOS of Mn-based single layer perovskites. The black dashed lines denote the Fermi level.

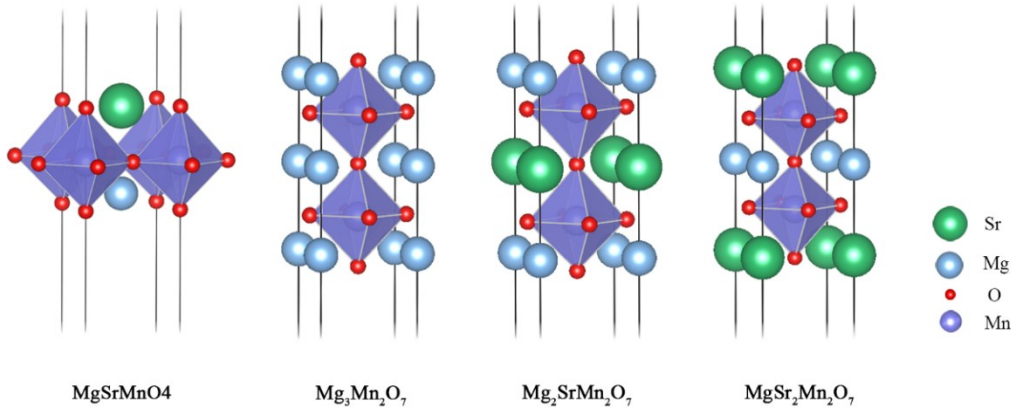

Fig. S10 The unit cells of 2D phase $Mg_3Mn_2O_7$ and three new structures, $MgSrMnO_4$, $Mg_2SrMn_2O_7$ and $MgSr_2Mn_2O_7$.

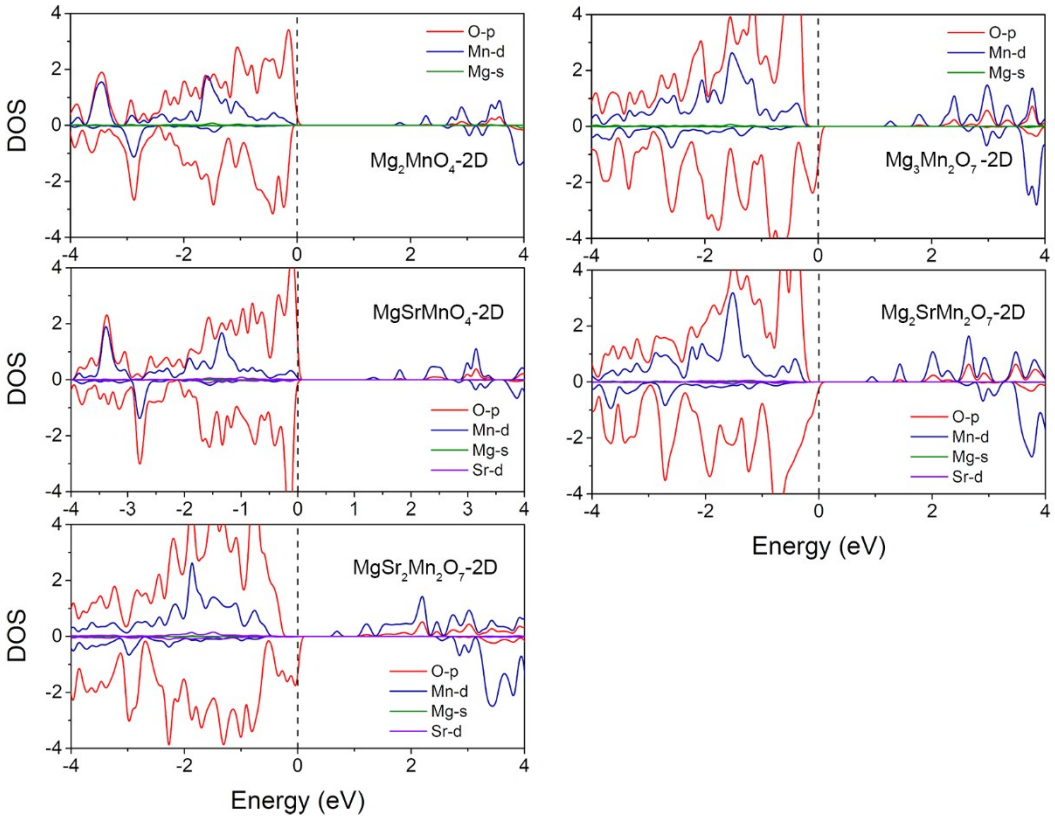

Fig. S11 Computed PDOS of layered Mg_2MnO_4, $Mg_3Mn_2O_7$ and three new designed materials. The black dashed lines denote the Fermi level.

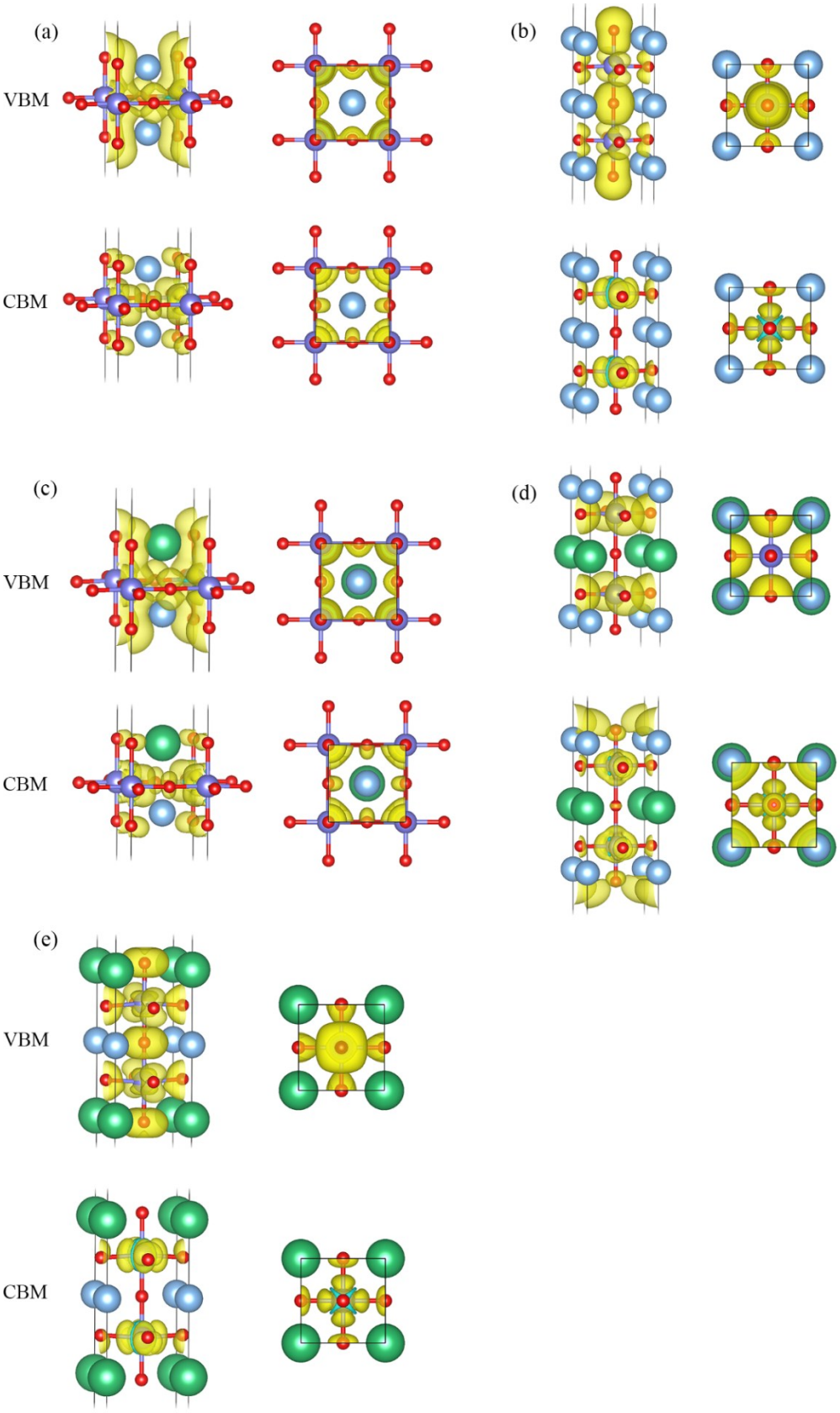

Fig. S12 The lateral and top view of charge density of (a) Mg_2MnO_4, (b) Mg_3MnO_7, (c) $MgSrMnO_4$, (d) $Mg_2SrMn_2O_7$, and (e) $MgSr_2Mn_2O_7$. The yellow surface and green surface exhibit the charge accumulation and loss; the isosurface level is set as 0.002 e/Å^3.