Two-dimensional alkaline-earth metal monohalides in unusually low oxidation states with high performance for ion batteries and electrochemical water splitting

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Computational details

The particle swarm optimization (PSO) method within the evolutionary algorithm as implemented in the Crystal structure AnaLYsis by Particle Swarm Optimization (CALYPSO)[1] code was employed to find the lowest energy structures of MX (M=Be, Mg, Ca, Sr, Ba; X= F, Cl, Br, I) monolayers[2]. Unit cells containing 1, 2, and 4 formula units were considered. In the first step, random structures with certain symmetry are constructed in which atomic coordinates are generated by the crystallographic symmetry operations. Local optimizations using the Vienna ab initio simulation package (VASP)[3] code were done with the conjugate gradients method and stopped when Gibbs free energy changes became smaller than 1×10^{-5} eV per cell. After processing the first-generation structures, 60% of them with lower Gibbs free energies are selected to construct the next generation structures by PSO. 40% of the structures in the new generation are randomly generated. A structure fingerprinting technique of bond characterization matrix is applied to the generated structures, so that identical structures are strictly forbidden. These procedures significantly enhance the diversity of the structures, which is crucial for structural global search efficiency. In most cases, structural searching simulations for each calculation were stopped after generating 1500 ~ 2000 structures (e.g., about 30 ~ 40 generations).

The structure relaxations and property calculations were carried out by using the density functional theory method[4], within the generalized gradient approximation of the Perdew−Burke−Ernzerhof (GGA-PBE) implemented in the VASP[3, 5]. A vacuum distance of ~20 Å was used to avoid interaction between adjacent layers. The plane-wave cutoff energy of 520 eV was employed. The atomic positions were fully relaxed until the maximum force on each atom was less than 10^{-3} eV/Å. van der Waals interaction was taken into account using the semiempirical DFT-D2 approach[6]. The local structural relaxations and electronic properties calculations were performed in the framework of the density functional theory (DFT) within the GGA[5] and Heyd-Scuseria-Ernzerhof (HSE06)[7]. The phonon spectra were calculated by the finite displacement method as implemented in Phonopy code[8]. A 3×3×1 supercell for Q-, O- and C-phase, 5×5×1 supercell for R- and T-phase, 4×4×1 supercell for S- and H-phase, 4×2×1 supercell for α-, β-, γ- and δ-phase is adopted to calculated the ab initio molecular dynamics (AIMD) simulations at 300 K[9]. VASP data is processed by VASPKIT code[10]. And Bader charge analysis[11] was performed to determine charge transfer between M and X atoms.

Cohesive energy is a well-accepted parameter to evaluate the feasibility for experimental synthesis of the predicted two-dimensional materials. The larger the cohesive energy, the easier is experimental synthesis. To compare the stability of MX crystals at different compositions, the formation energy (E_{form}) and cohesive energy (E_{coh}) of the predicted structure are calculated using the following formulas:

$$E_{form} = \frac{E_{M_nX_n} - nu_M - nu_X}{2n}$$

$$E_{coh} = \frac{nE_M + nE_X - E_{M_nX_n}}{2n}$$

in which E_{form} denotes the formation energy of the corresponding 2D structures and E_{coh} is the total cohesive energy of 2D MX systems; μ_M and μ_X represent the chemical potentials of M and X in bulk M and X, respectively. E_M, E_X, and E_{MnXn} are the total energies of a single M atom, a single X atom, and 2D M_nX_n crystals; n is the number of M and X atoms per unit cell.

The mechanical properties are another important parameter for the potential applications of 2D materials. Generally, the in-plane stiffness, (or in-plane Young modulus), is used to assess the mechanical stability of 2D materials. For a mechanically stable 2D sheet, the elastic constants need to satisfy $C_{11}C_{22} - C_{12}^2 > 0$ and $C_{66} > 0$. The in-plane stiffness C and Poisson's ratio v may be obtained from the following relationships:

$$C = (C_{11}^2 - C_{12}^2)/C_{11}$$
$$v = C_{12}/C_{11}$$
$$C_{66} = (C_{11}-C_{12})/2$$

the calculated elastic constants satisfy $C_{11} > |C_{12}|$, and the calculated C_{66} is positive, indicating that the 2D sheet is mechanically stable.

It can be considered as a benchmark for the feasibility of mechanical exfoliation in experiments. All the crystals show exfoliation energies computed as

$$E_{exf}(n) = \frac{E_{iso}(n) - \frac{n}{m}E_{bulk}}{A}$$

where E_{iso} (n) and E_{bulk} denote the total energies of the primitive cell of an isolated n-layer slab and a bulk system, respectively. The parameters m and A are the number of layers and the in-plane area in the bulk.

The calculations of the quasi-particle and optical absorption properties are carried out using the rigorous many-body perturbation theory implemented by the BerkeleyGW package[12]. For the calculations implemented in the Quantum Espresso code[13, 14], we used the SG15 optimized norm-conserving Vanderbilt pseudopotentials[15], and the KS states are obtained by solving the Kohn-Sham equations using PBE exchange-correlation functional. The Coulomb interaction was truncated in the out-of-plane direction. For MX supercell size of 30 Å in the out-of-plane direction. The GW approximation in conjunction with

the Bethe-Salpeter equation (BSE) was adopted to calculate the absorption coefficients. The linear optical properties of semiconductor can be obtained from the frequency-dependent complex dielectric function $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$.

where $\varepsilon_1(\omega)$ and $i\varepsilon_2(\omega)$ are the real and imaginary parts of the dielectric function, and ω is the photon frequency.

$$\varepsilon_2(\omega) = \frac{16\pi^2 e^2}{\omega^2}\sum_S |\boldsymbol{e}\cdot\langle 0|v|S\rangle|^2\delta\ (\omega - \Omega^S)$$

where $\boldsymbol{v}$ is the velocity operator and $\boldsymbol{e}$ is the polarization of the incoming light, Ω^S is the excitation energy. The absorption coefficient can be calculated by the following equation:

$$\alpha(\omega)=\sqrt{2}\omega\left[\sqrt{\varepsilon_1{}^2(\omega)+\varepsilon_2{}^2(\omega)}-\varepsilon_1(\omega)\right]^{1/2}$$

The adsorption energy of A atoms (A= Li, Na, K Mg, Ca, Al) on MX monolayers was calculated with

$$E_{ad} = (E_{Complex} - E_{MX} - nE_A)/n,$$

where E_A is the energy per atom for the bulk metal A, $E_{Complex}$ and E_{MX} are the total energies of the MX monolayers with and without A adsorption. Here, the negative adsorption energy indicates that the MX monolayers has the intrinsic ability to adsorb atoms.

For multilayer adsorption, the average adsorption energy was calculated layer by layer, as defined by

$$E_{ave} = (E_{MX+8lA} - E_{MX+8(l-1)A} - mE_A)/m,$$

where E_{MX+8lA} and $E_{MX+8(l-1)A}$ are the total energies of MX monolayers with l and (l-1) adsorbed A layers, and the number "m" in the formula represents eight adsorbed A atoms in each layer (for a 2×2×1 super-cell on both sides).

The open-circuit voltage of a certain 2D material is calculated based on the ground-state energies before and after loading A ions, which can be evaluated from the following reaction and written as

$$MX + nA^+ + ne^- \leftrightarrow MXA_n$$

$$V \approx \frac{E_{MX+n1A} - E_{MX+n2A} + (n2-n1)E_A}{(n2-n1)e},$$

where E_{MX+nA}+ and E_A are the energies of 2D material loading of n A ions and a A in its stable bulk crystal and $n1$ and $n2$ are the number A ions with n2 > n1. The A-loaded 2D materials are also carefully optimized before ground-state energy calculation.

The volume and entropy effects are usually negligible during the half-cell reaction, the average OCV[16] was estimated by

$$V_{ave} = \frac{E_{MX} + nE_A - E_{complex}}{nzF},$$

where $E_{Complex}$ and E_{MX} are the total energies of MX supercell after and before adsorption, respectively, and E_A represents the energy per atom in bulk metal; n indicates the number of A atoms; F is the Faraday constant and z is the electronic charge of M ions in the electrolyte.

The maximum specific capacity (C) of the batteries are estimated by the equation expressed as

$$C = \frac{zF}{M_{MX}}$$

Here, z and F are the number of electrons involved in the charge/discharge process and the well-known Faraday constant (26.8 A h/g), respectively. M_{MX} represents the molar mass of the MX monolayer.

The overall OER in acid media can be written:

$$2H_2O \rightarrow O_2 + 4H^- - 4e^-$$

In our model, the OER is processed via four electrons [17]:

$$* + H_2O(l) \rightarrow OH^* + H^+ + e^- \quad (a)$$

$$OH^* \rightarrow O^* + H^+ + e^- \quad (b)$$

$$O^* + H_2O(l) \rightarrow OOH^* + H^+ + e^- \quad (c)$$

$$OOH^* \rightarrow O_2(g) + H^+ + e^- \quad (d)$$

Where the * represents an active site on the surface of catalyst. (l) and (g) are used to denote the liquid and gas phases, respectively. The reaction free energy of ΔG for each step is defined by the following equation:

$$\Delta G = \Delta E + \Delta ZPE - T\Delta S + \Delta G_{pH} + \Delta G_U \quad (8)$$

ΔE, ΔZPE, and ΔS denote the different energy change, zero-point energy change, and entropy change of the reaction, respectively. The ΔE is calculated by DFT, while the ΔZPE, and ΔS are obtained from the values of Table I in ref [17]. $\triangle G_U$ = -eU with U being the electrode potential. The T is temperature. By setting the reference potential to be the standard hydrogen electrode, the free energy of $1/2H_2$ can be used to replace that of ($H^+ + e^-$). The free energy of O_2 was obtained from the

reaction $2H_2O \rightarrow O_2 + 2H_2$ for which the free energy change is 4.92 eV. The overpotential (ɳ) could then be calculated to evaluate the performance for OER by ref [17].

$$\eta = \max(\Delta Ga, \Delta Gb, \Delta Gc, \Delta Gd,)/e - 1.23$$

The adsorption energies of oxygen-containing intermediates on MX monolayers are computed by following equations

$$\Delta E_{O*} = E_{O*} - E_{*} - [E_{H2O} - E_{H2}]$$
$$\Delta E_{OH*} = E_{OH*} - E_{*} - [E_{H2O} - 1/2E_{H2}]$$
$$\Delta E_{OOH*} = E_{OOH*} - E_{*} - [2E_{H2O} - 3/2E_{H2}]$$

where *the E_*, E_{OOH*}, E_{OH*}, and E_{O*} are the total energies of catalyst substrate without and with the adsorption of OOH, OH and O, respectively. E_{H2O} and E_{H2} are total energies of free H_2O and H_2 molecules in gas phases, respectively.*

Generally, the crucial step in a HER process can be written as

$$H + * + e^- \rightarrow H*$$

where $*$ stands for the adsorption site. According to the Sabatier principle[18], the adsorption Gibbs free energy (ΔG) can be used to evaluate the catalytic HER activity, defined as

$$\Delta G = \Delta E + \Delta E_{ZPE} - T\Delta S + neU + \Delta G_{pH}$$

where ΔE is the energy change before and after adsorption; ΔE_{ZPE} and $T\Delta S$ refer to the changes of zero-point energy and entropy between the adsorbed H* and H_2 in gas phase, respectively, which are obtained from frequency calculations at T = 298.15 K; neU is the free energy contribution from the electrode potential U, and n is the number of transferred electrons. The last term can be related to the pH by

$$\Delta G_{pH} = \ln 10 \times k_B T \times pH$$

where k_B is the Boltzmann constant and the value of pH in this work is set to zero.

The Bond Valence Sum (BVS) method has been used by several research groups to estimate the oxidation states of metal ions in coordination compounds and ionic compounds. Brown and Altermatt proposed a general expression shown in

$$V_i = \Sigma S_{ij} = \Sigma \exp[(R_0 - r_{ij})/b]$$

where V_i is the oxidation state of atom i; s_{ij} and r_{ij} are the valence and the length of the bond between atoms i and j, respectively; R_0 is the empirically determined distance for a given cation-anion pair; b is the "universal parameter" and is set equal to 0.37. V is the sum of all valences s_{ij} of a coordination sphere around the metal ion, and its value is the approximation of the formal oxidation state. Crystal structure information is obtained by Diamond

2D Phases of the MX crystals

The optimized lattice constants and other structure parameters of MX monolayers are listed in the Table S1. We examined the phase stability of these MX monolayers by calculating the energy above the convex hull in the composition space (ΔE_{hull}) as in Figures S1, which is a good indication for the synthesizability of the candidate materials. For two-dimensional (2D) structures, we researched some literature data, and found 2D structures of MX_2 monolayers[19].

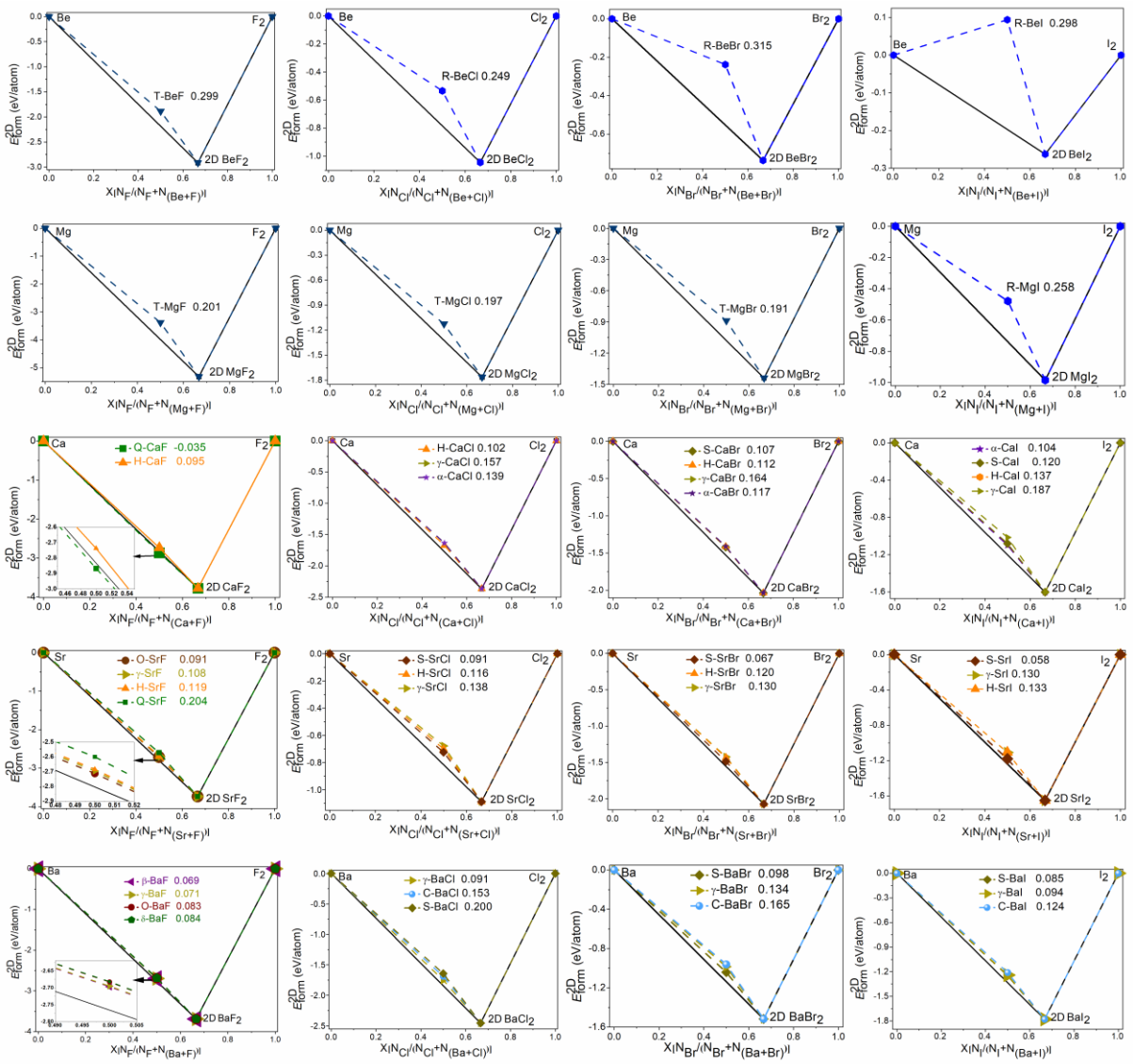
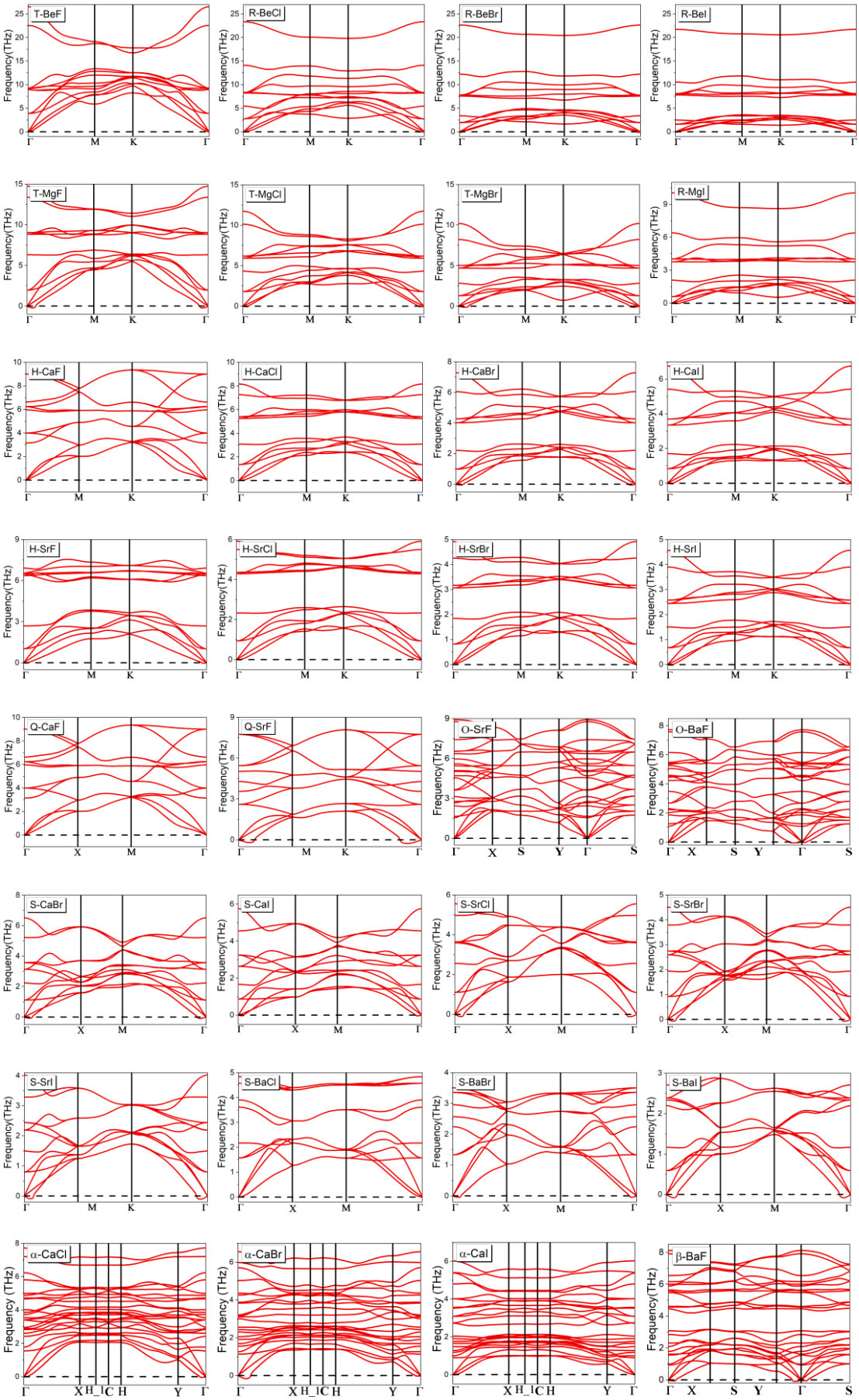


Figure S1. Stability of MX (M=Be, Mg, Ca, Sr, Ba; X=F, Cl, Br, I) monolayers: Convex hull diagrams in their isolated forms at 0 K. For MX with an X fraction of 0.5, hull distances are shown.

Table S1. Calculated values of stable, free-standing, 2D MX (M=Be, Mg, Ca, Sr, Ba; X=F, Cl, Br, I): relaxed in-plane lattice constant (a,b) (Å); formation energies and cohesive energies of MX monolayers, E_{form} (eV) and E_{coh} (eV); minimum value of the energy gap (PBE), E_g calculated (eV); Poisson ratio v, in-plane stiffness (or in-plane Young modulus): C(N/m).

	a,b	E_{form}	E_{coh}	E_g	C_{11}	C_{12}	C_{66}	v	C
T-BeF	2.58	-1.89	3.75	0.00	136.50	50.08	43.21	0.37	118.13
R-BeCl	3.24	-0.53	3.29	1.94	75.75	18.10	28.83	0.24	71.43
R-BeBr	3.51	-0.24	2.84	2.37	64.45	15.15	24.65	0.24	60.89
R-BeI	3.87	0.09	2.49	2.06	53.49	11.73	20.88	0.22	50.92
T-MgF	3.27	-2.34	3.75	0.00	81.09	24.86	28.11	0.31	73.47
T-MgCl	3.54	-1.13	2.77	0.00	46.59	18.59	14.02	0.40	39.21
T-MgBr	3.72	-0.89	2.47	0.00	40.52	21.25	9.63	0.52	29.37
R-MgI	4.24	-0.48	2.02	1.29	26.43	7.53	9.45	0.28	24.28
Q-CaF	3.90	-2.74	4.41	0.00	30.98	10.31	12.70	0.33	27.55
H-CaF	3.66	-2.87	4.47	0.35	62.99	25.03	18.98	0.40	53.04
H-CaCl	3.98	-1.67	3.52	0.32	34.77	14.27	10.25	0.41	28.91
α-CaCl	3.88,7.86	-1.64	3.35	0.00	32.83	8.54	9.04	0.26	30.64
γ-CaCl	7.83,4.05	-1.62	3.36	0.00	29.37	8.17	2.50	0.28	27.10
S-CaBr	3.75	-1.42	3.22	0.00	59.49	0.77	3.31	0.01	59.48
H-CaBr	4.07	-1.42	3.22	0.20	32.48	13.27	9.60	0.41	27.06
α-CaBr	4.00,8.16	-1.41	3.05	0.00	32.07	8.48	7.87	0.26	29.82
γ-CaBr	8.21,4.14	-1.38	3.04	0.00	26.92	8.67	-3.60	0.29	27.09
α-CaI	4.23, 8.58	-1.10	2.71	0.00	29.78	6.20	8.06	0.25	28.21
S-CaI	3.97	-1.08	2.89	0.00	53.39	1.36	3.42	0.03	53.36
H-CaI	4.23	-1.07	2.88	0.05	30.71	13.11	8.79	0.43	25.12
γ-CaI	8.51,4.30	-1.02	2.65	0.00	23.67	7.12	-3.31	0.30	21.52
O-SrF	4.24, 5.77	-2.71	4.10	0.00	59.70	16.11	20.86	0.27	55.36
γ-SrF	7.05, 4.14	-2.69	4.10	0.00	54.46	19.04	18.64	0.35	47.80
H-SrF	4.03	-2.68	4.30	0.00	60.61	21.53	19.29	0.36	52.96
Q-SrF	4.14	-2.60	4.00	0.00	37.34	7.72	8.74	0.21	35.74
γ-SrCl	8.39, 4.44	-1.65	3.26	0.00	23.53	8.55	3.79	0.36	20.42
H-SrCl	4.32	-1.67	3.42	0.28	31.53	15.61	7.96	0.50	23.80
S-SrCl	3.85	-1.70	3.44	0.00	54.42	4.57	4.58	0.08	54.04
γ-SrBr	8.79, 4.52	-1.42	2.98	0.00	25.51	8.34	2.26	0.33	22.78
H-SrBr	4.39	-1.43	3.12	0.17	24.65	10.37	6.24	0.42	20.29
S-SrBr	3.98	-1.48	3.18	0.00	47.13	0.81	5.15	0.02	47.11
S-SrI	4.16	-1.11	2.88	0.00	43.30	0.75	5.16	0.02	43.28
H-SrI	4.49	-1.11	2.62	0.02	16.51	11.54	1.54	0.70	8.45
γ-SrI	9.29, 4.63	-1.18	2.61	0.00	19.13	4.61	-0.40	0.24	18.02
β-BaF	4.45, 7.54	-2.65	4.17	0.00	43.14	18.14	12.12	0.42	35.51
O-BaF	4.57, 6.06	-2.64	4.15	0.00	41.06	11.30	13.91	0.28	37.94
γ-BaF	7.61, 4.38	-2.64	4.15	0.00	40.32	15.29	12.21	0.38	34.52
δ-BaF	7.59,4.37	-2.63	4.15	0.00	36.78	16.44	12.74	0.45	29.43

γ-BaCl	8.95, 4.75	-1.70	3.42	0.00	23.32	10.55	1.81	0.45	18.54
C-BaCl	6.46	-1.67	3.36	0.00	26.09	2.61	5.88	0.10	25.83
S-BaCl	4.46	-1.61	3.13	0.00	35.25	21.29	23.48	0.60	22.39
γ-BaBr	9.32, 4.83	-1.46	3.11	0.00	22.00	9.95	1.68	0.45	17.51
C-BaBr	6.72	-1.44	3.08	0.00	23.41	3.41	6.01	0.15	22.91
S-BaBr	4.62	-1.41	3.05	0.00	26.95	13.55	24.58	0.50	20.13
γ-BaI	10.08, 4.8	-1.98	2.54	0.00	17.00	5.58	0.46	0.33	15.17
S-BaI	4.46	-1.99	2.53	0.00	31.54	7.89	14.07	0.25	29.56
C-BaI	7.04	-1.90	2.75	0.00	20.68	4.58	5.74	0.22	19.67



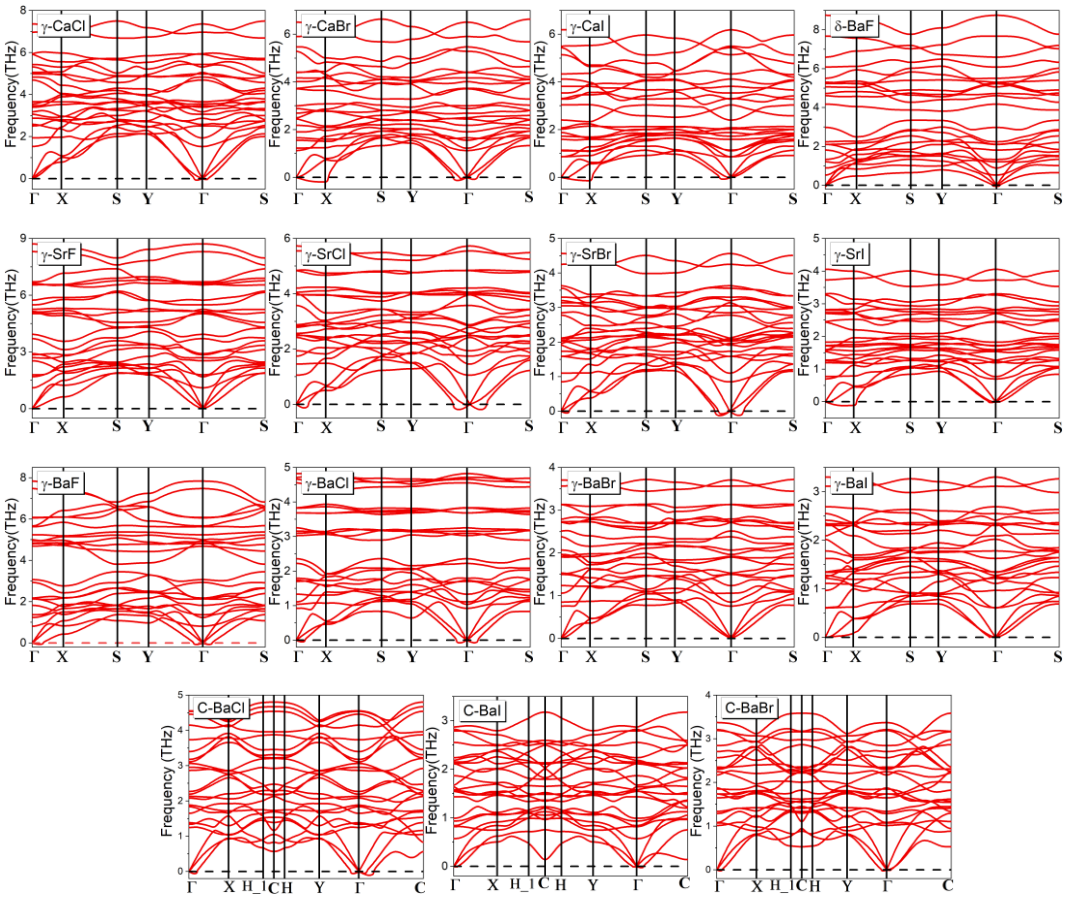
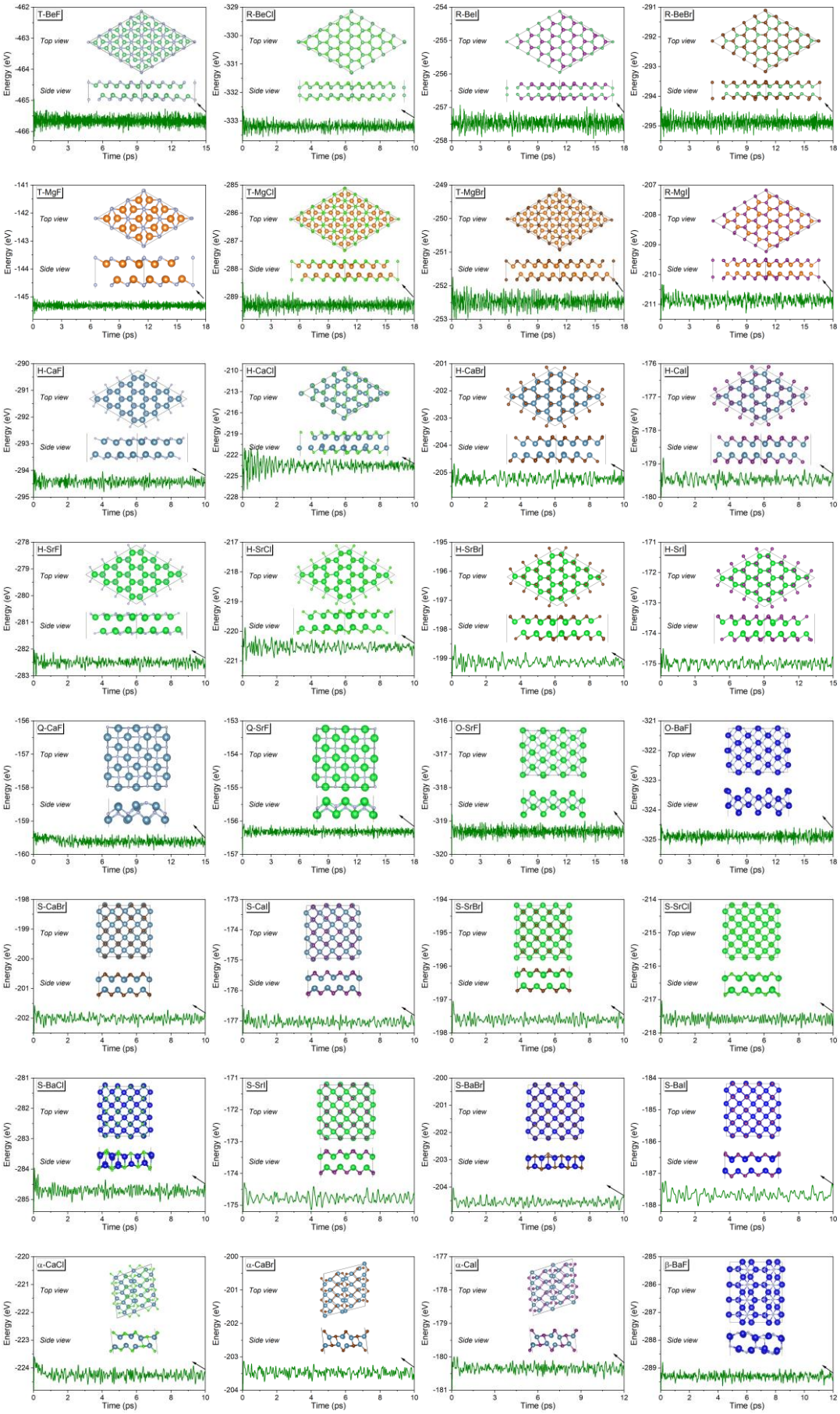


Figure S2. Phonon dispersion spectra for predicted stable MX monolayers calculated with finite displacement method.



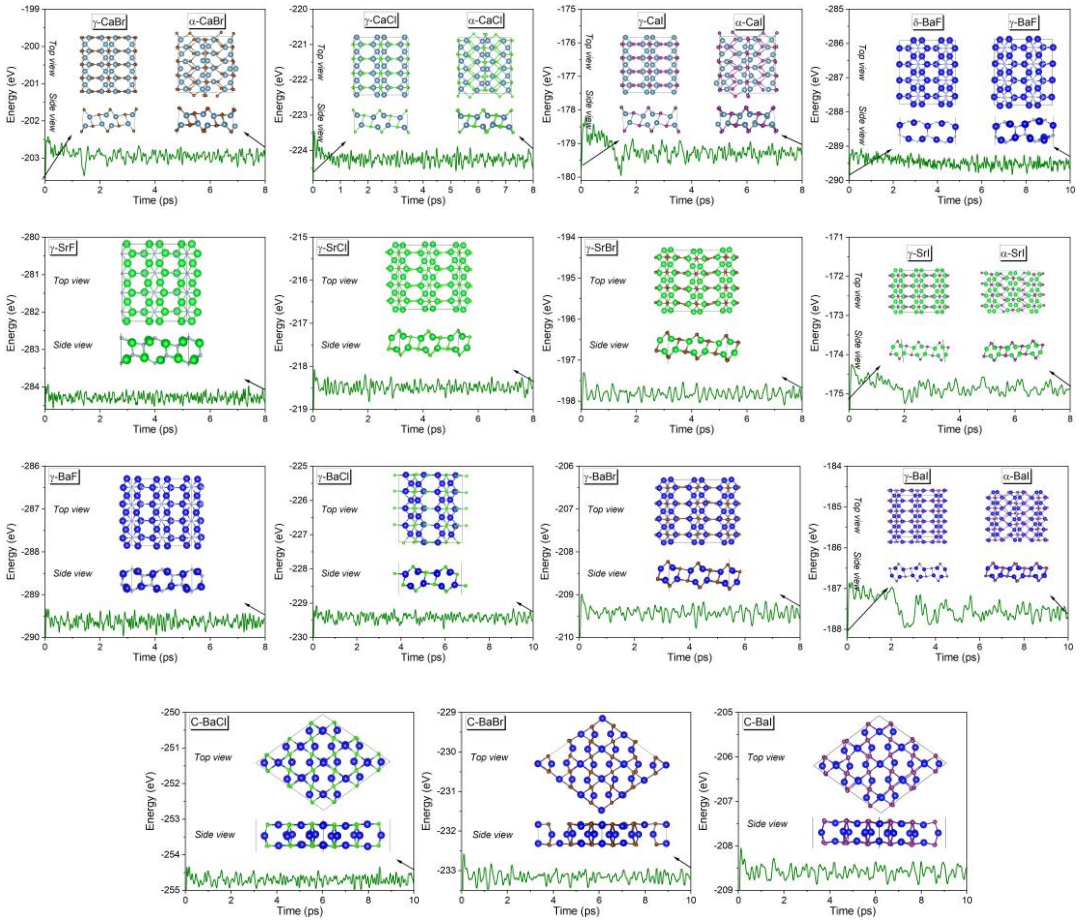
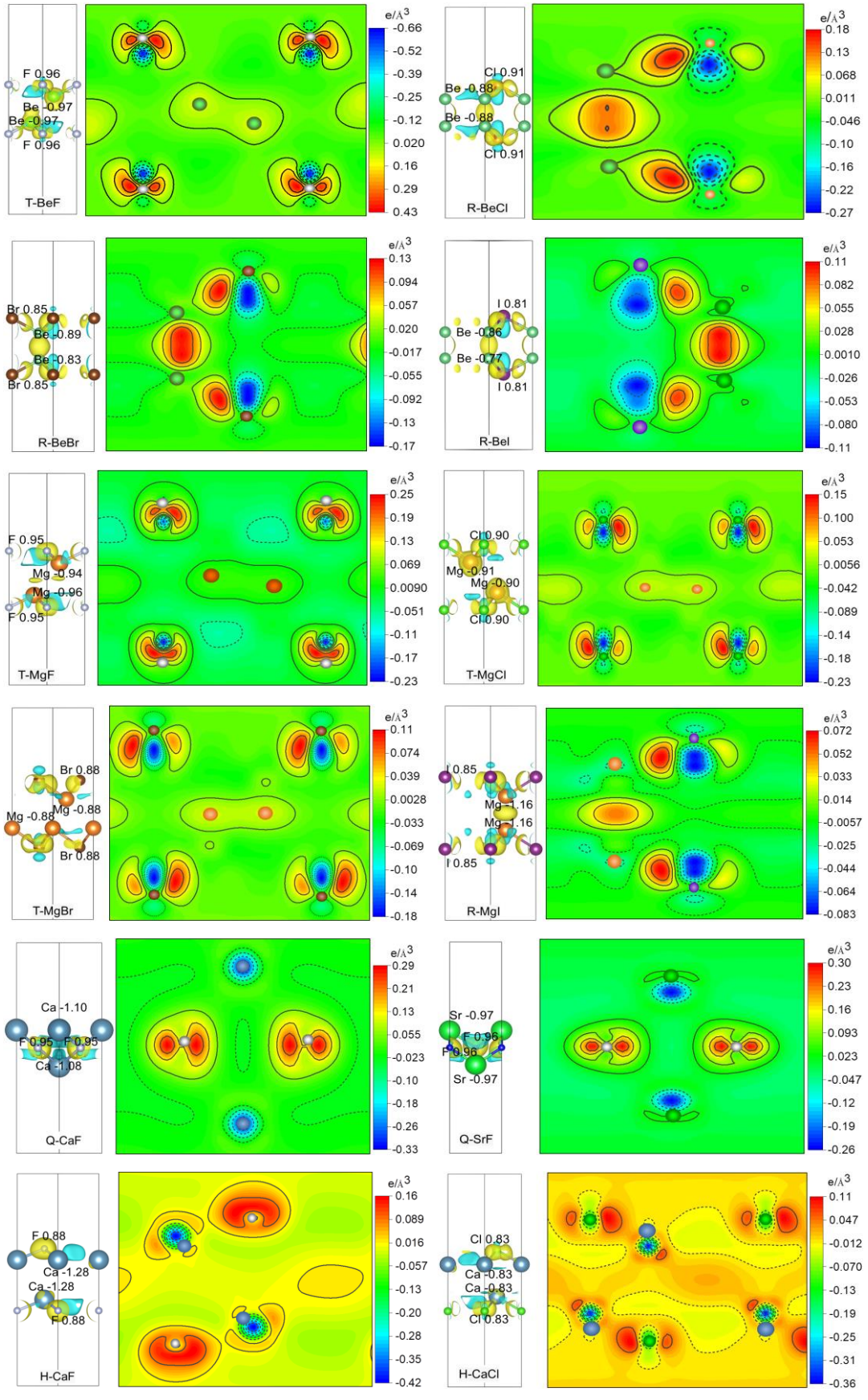
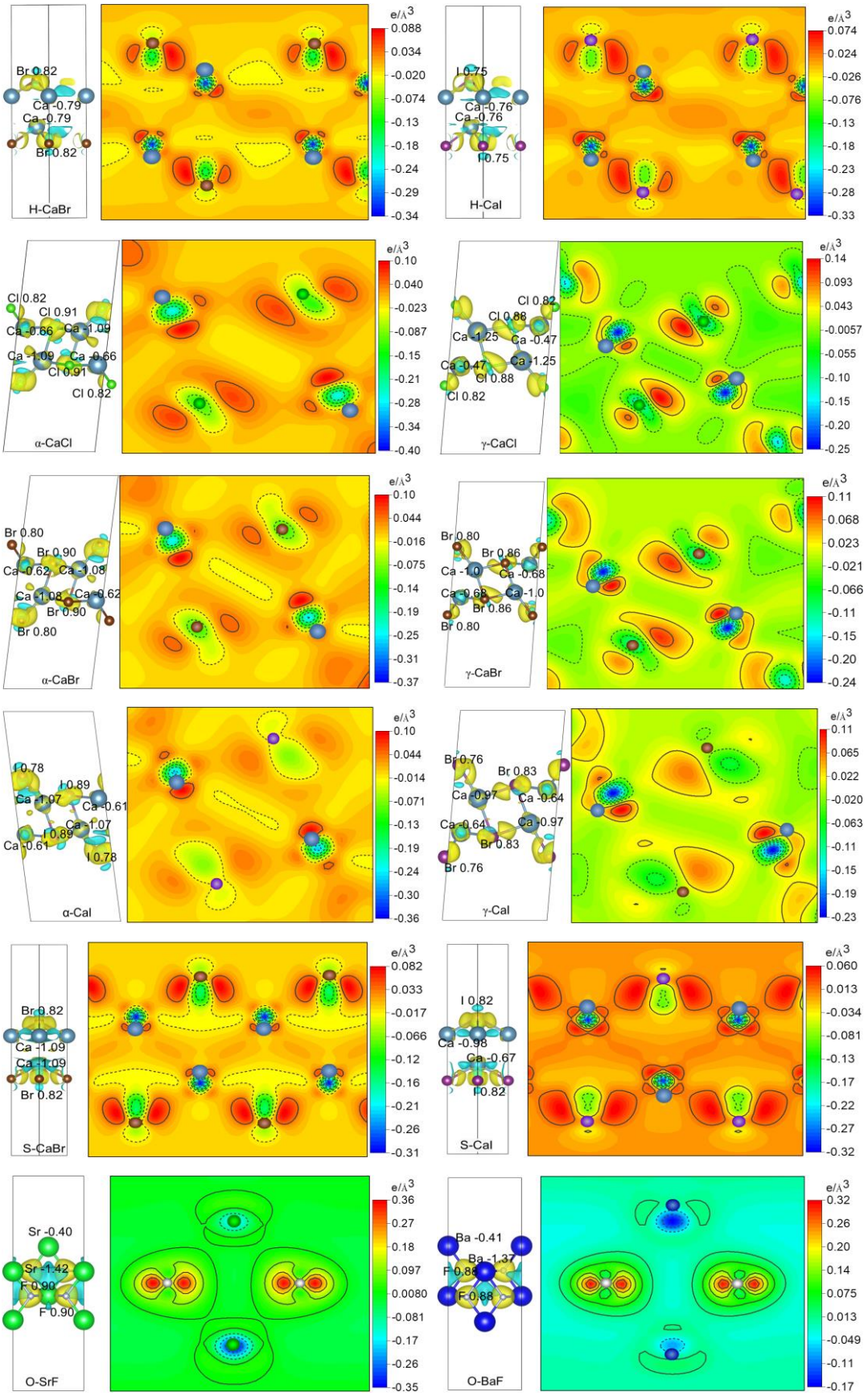
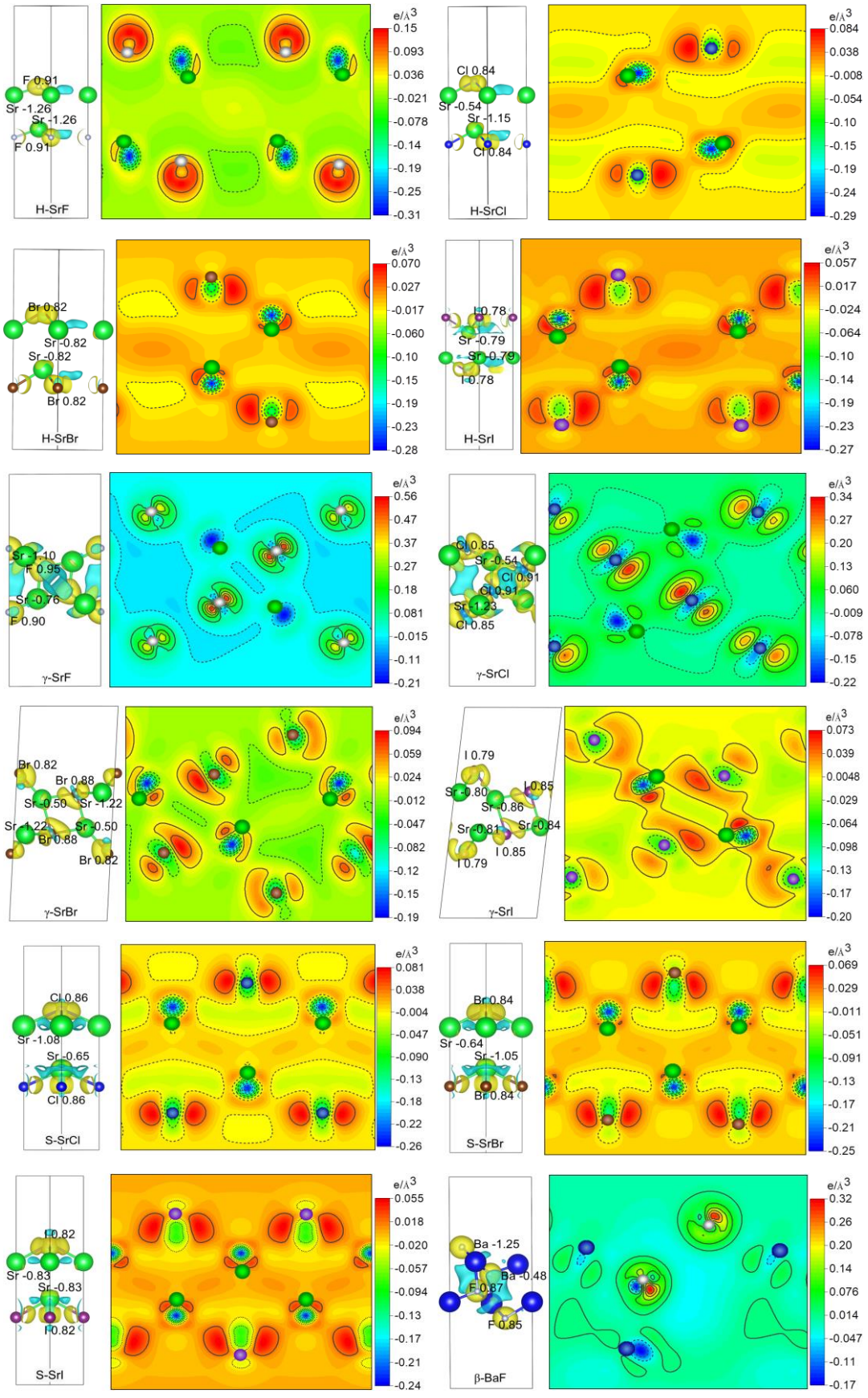


Figure S3. Energy as a function of AIMD simulation time at the temperature of 300 K for the MX monolayers. Insets show the configurations of MX monolayers at the end of the AIMD simulations. The energies reach equilibrium speedily and fluctuate with no structural reconstructions.

Oxidation States and Chemical Bonding







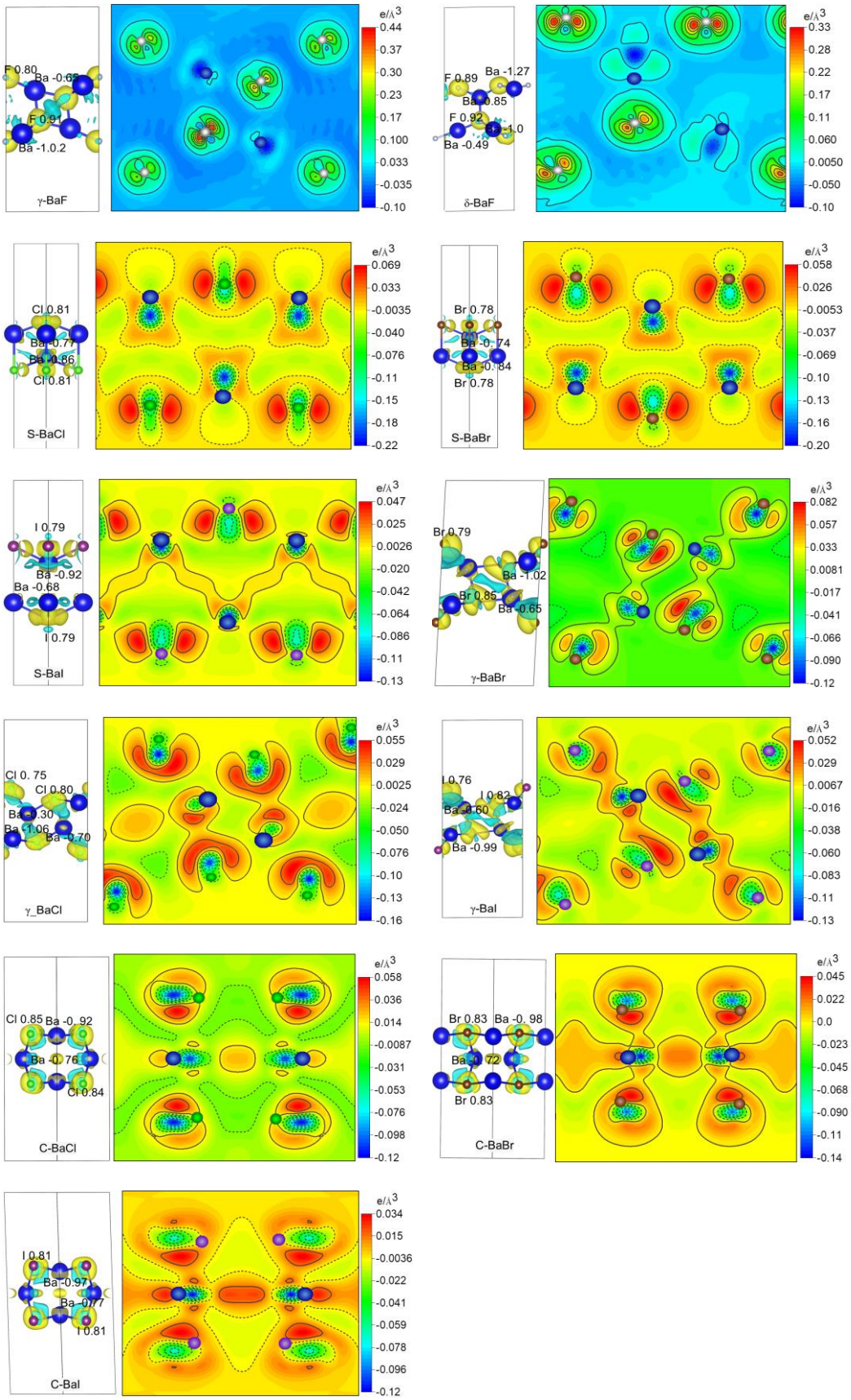


Figure S4. 3D plots and 2D plots of charge density difference of MX monolayers with different structural prototypes combining the Bader charge analysis. A positive value (yellow) indicates electron accumulation, whereas a negative value (blue) denotes electron depletion. The isosurface value is 0.003 e/Å^3. The two-dimensional plots on the right are along the (101) plane for the α-, β-, γ-, and δ-phases and the (111) plane for the other phases. The right labels of the 2D plots show the contour value of charge density difference. A positive value (solid contour line) indicates an increase in electron density and a negative value (dashed contour line) means an electron density loss with respect to the superposition of the atomic electron density.

Table S2 Bond valence sum for the M ions in MX monolayers.

	Bond number	Atom #1	Atom symmetry	Atom #2	Atom symmetry	Bond length (Å)	Valence
T-BeF	1	Be1	x, y, z	F2	1+x, y, z	1.73	0.30
	2	Be1	x, y, z	F2	1+x, 1+y, z	1.73	0.30
	3	Be1	x, y, z	F2	x, y, z	1.73	0.30
	Sum						0.90
	4	Be2	x, y, z	F1	x, 1+y, z	1.73	0.30
	5	Be2	x, y, z	F1	1+x, 1+y, z	1.73	0.30
	6	Be2	x, y, z	F1	x, y, z	1.73	0.30
	Sum						0.90

	Bond number	Atom #1	Atom symmetry	Atom #2	Atom symmetry	Bond length (Å)	Valence
T-MgF	1	Mg1	x, y, z	F1	x, 1+y, z	2.05	0.28
	2	Mg1	x, y, z	F1	1+x, 1+y, z	2.05	0.28
	3	Mg1	x, y, z	F1	x, y, z	2.05	0.28
	Sum						0.84
	4	Mg2	x, y, z	F2	1+x, y, z	2.05	0.28
	5	Mg2	x, y, z	F2	1+x, 1+y, z	2.05	0.28
	6	Mg2	x, y, z	F2	x, y, z	2.05	0.28
	Sum						0.84

	Bond number	Atom #1	Atom symmetry	Atom #2	Atom symmetry	Bond length (Å)	Valence
T-MgCl	1	Mg1	x, y, z	Cl1	x, 1+y, z	2.5	0.32
	2	Mg1	x, y, z	Cl1	1+x, 1+y, z	2.5	0.32
	3	Mg1	x, y, z	Cl1	x, y, z	2.5	0.32
	Sum						0.96
	4	Mg2	x, y, z	Cl2	1+x, y, z	2.5	0.32
	5	Mg2	x, y, z	Cl2	1+x, 1+y, z	2.5	0.32
	6	Mg2	x, y, z	Cl2	x, y, z	2.5	0.32
	Sum						0.96

	Bond number	Atom #1	Atom symmetry	Atom #2	Atom symmetry	Bond length (Å)	Valence
T-MgBr	1	Mg1	x, y, z	Br2	1+x, y, z	2.67	0.35
	2	Mg1	x, y, z	Br2	1+x, 1+y, z	2.67	0.35
	3	Mg1	x, y, z	Br2	x, y, z	2.67	0.35
	Sum						1.05
	4	Mg2	x, y, z	Br1	x, 1+y, z	2.67	0.35
	5	Mg2	x, y, z	Br1	1+x, 1+y, z	2.67	0.35
	6	Mg2	x, y, z	Br1	x, y, z	2.67	0.35
	Sum						1.05

	Bond number	Atom #1	Atom symmetry	Atom #2	Atom symmetry	Bond length (Å)	Valence
R-BeCl	1	Be1	x, y, z	Cl2	x, -1+y, z	2.05	0.46
	2	Be1	x, y, z	Cl2	x, y, z	2.05	0.46
	3	Be1	x, y, z	Cl2	-1+x,-1+y,z	2.05	0.46
	Sum						1.38
	4	Be2	x, y, z	Cl1	x, -1+y, z	2.05	0.46
	5	Be2	x, y, z	Cl1	x, y, z	2.05	0.46
	6	Be2	x, y, z	Cl1	-1+x,-1+y,z	2.05	0.46
	Sum						1.38

	Bond number	Atom #1	Atom symmetry	Atom #2	Atom symmetry	Bond length (Å)	Valence
R-BeBr	1	Be1	x, y, z	Br1	1+x, y, z	2.34	0.31
	2	Be1	x, y, z	Br1	1+x, 1+y, z	2.34	0.31
	3	Be1	x, y, z	Br1	x, y, z	2.34	0.31
	Sum						0.93
	4	Be2	x, y, z	Br2	1+x, y, z	2.34	0.31
	5	Be2	x, y, z	Br2	1+x, 1+y, z	2.34	0.31
	6	Be2	x, y, z	Br2	x, y, z	2.34	0.31
	Sum						0.93

	Bond number	Atom #1	Atom symmetry	Atom #2	Atom symmetry	Bond length (Å)	Valence
R-BeI	1	Be1	x, y, z	I2	-1+x,-1+y,z	2.56	0.29
	2	Be1	x, y, z	I2	-1+x,-1+y,z	2.56	0.29
	3	Be1	x, y, z	I2	x, y, z	2.56	0.29
	Sum						0.87
	4	I1	x, y, z	Be2	x, y, z	2.56	0.29
	5	I1	x, y, z	Be2	1+x, y, z	2.56	0.29
	6	I1	x, y, z	Be2	1+x, 1+y, z	2.56	0.29
	Sum						0.87

	Bond number	Atom #1	Atom symmetry	Atom #2	Atom symmetry	Bond length (Å)	Valence
R-MgI	1	Mg1	x, y, z	I2	1+x, y, z	2.94	0.27
	2	Mg1	x, y, z	I2	1+x, 1+y, z	2.94	0.27
	3	Mg1	x, y, z	I2	x, y, z	2.94	0.27
	Sum						0.81
	4	Mg2	x, y, z	I1	1+x, y, z	2.94	0.27
	5	Mg2	x, y, z	I1	1+x, 1+y, z	2.94	0.27
	6	Mg2	x, y, z	I1	x, y, z	2.94	0.27
	Sum						0.81

	Bond number	Atom #1	Atom symmetry	Atom #2	Atom symmetry	Bond length (Å)	Valence
H-CaF	1	Ca1	x, y, z	F1	x, y, z	2.3	0.29
	2	Ca1	x, y, z	F1	x, 1+y, z	2.3	0.29
	3	Ca1	x, y, z	F1	-1+x, y, z	2.3	0.29
	Sum						0.87
	4	Ca2	x, y, z	F2	x, y, z	2.3	0.29
	5	Ca2	x, y, z	F2	1+x, y, z	2.3	0.29
	6	Ca2	x, y, z	F2	x, -1+y, z	2.3	0.29
	Sum						0.87

	Bond number	Atom #1	Atom symmetry	Atom #2	Atom symmetry	Bond length (Å)	Valence
H-CaCl	1	Ca1	x, y, z	Cl1	-1+x, y, z	2.77	0.34
	2	Ca1	x, y, z	Cl1	x, y, z	2.77	0.34
	3	Ca1	x, y, z	Cl1	-1+x,-1+y,z	2.77	0.34
	Sum						1.02
	4	Ca2	x, y, z	F2	x, y, z	2.77	0.29
	5	Ca2	x, y, z	F2	1+x, y, z	2.77	0.29
	6	Ca2	x, y, z	F2	x, -1+y, z	2.77	0.29
	Sum						1.02

	Bond number	Atom #1	Atom symmetry	Atom #2	Atom symmetry	Bond length (Å)	Valence
H-CaBr	1	Ca1	x, y, z	Br1	x, y, z	2.9	0.33
	2	Ca1	x, y, z	Br1	1+x, y, z	2.9	0.33
	3	Ca1	x, y, z	Br1	x, -1+y, z	2.9	0.33
	Sum						0.99
	4	Ca2	x, y, z	Br2	x, y, z	2.9	0.33
	5	Ca2	x, y, z	Br2	x, 1+y, z	2.9	0.33
	6	Ca2	x, y, z	Br2	-1+x, y, z	2.9	0.33
	Sum						0.99

	Bond number	Atom #1	Atom symmetry	Atom #2	Atom symmetry	Bond length (Å)	Valence
H-CaI	1	Ca1	x, y, z	I1	-1+x, y, z	3.13	0.33
	2	Ca1	x, y, z	I1	x, y, z	3.13	0.33
	3	Ca1	x, y, z	I1	-1+x,-1+y,z	3.13	0.33
	Sum						0.99
	4	Ca2	x, y, z	I2	1+x, y, z	3.13	0.33
	5	Ca2	x, y, z	I2	1+x, 1+y, z	3.13	0.33
	6	Ca2	x, y, z	I2	x, y, z	3.13	0.33
	Sum						0.99

	Bond number	Atom #1	Atom symmetry	Atom #2	Atom symmetry	Bond length (Å)	Valence
H-SrF	1	Sr1	x, y, z	F1	x, y, z	2.46	0.30
	2	Sr1	x, y, z	F1	x, 1+y, z	2.46	0.30
	3	Sr1	x, y, z	F1	-1+x, y, z	2.46	0.30
	Sum						0.90
	4	Sr2	x, y, z	F2	x, y, z	2.46	0.30
	5	Sr2	x, y, z	F2	1+x, y, z	2.46	0.30
	6	Sr2	x, y, z	F2	x, -1+y, z	2.46	0.30
	Sum						0.90

	Bond number	Atom #1	Atom symmetry	Atom #2	Atom symmetry	Bond length (Å)	Valence
H-SrCl	1	Sr1	x, y, z	Cl1	x, y, z	2.92	0.33
	2	Sr1	x, y, z	Cl1	1+x, y, z	2.92	0.33
	3	Sr1	x, y, z	Cl1	x, -1+y, z	2.92	0.33
	Sum						0.99
	4	Sr2	x, y, z	Cl2	x, y, z	2.92	0.33
	5	Sr2	x, y, z	Cl2	x, 1+y, z	2.92	0.33
	6	Sr2	x, y, z	Cl2	#NAME?	2.92	0.33
	Sum						0.99

	Bond number	Atom #1	Atom symmetry	Atom #2	Atom symmetry	Bond length (Å)	Valence
H-SrBr	1	Sr1	x, y, z	Br1	x, y, z	3.07	0.35
	2	Sr1	x, y, z	Br1	x, 1+y, z	3.07	0.35
	3	Sr1	x, y, z	Br1	-1+x, y, z	3.07	0.35
	Sum						0.99
	4	Sr2	x, y, z	Br2	x, y, z	3.07	0.35
	5	Sr2	x, y, z	Br2	1+x, y, z	3.07	0.35
	6	Sr2	x, y, z	Br2	x, -1+y, z	3.07	0.35
	Sum						0.99

	Bond number	Atom #1	Atom symmetry	Atom #2	Atom symmetry	Bond length (Å)	Valence
H-SrI	1	Sr1	x, y, z	I1	x, y, z	3.30	0.32
	2	Sr1	x, y, z	I1	1+x, y, z	3.30	0.32
	3	Sr1	x, y, z	I1	x, -1+y, z	3.30	0.32
	Sum						0.96
	4	Sr2	x, y, z	I2	x, y, z	3.30	0.32
	5	Sr2	x, y, z	I2	x, 1+y, z	3.30	0.32
	6	Sr2	x, y, z	I2	-1+x, y, z	3.30	0.32
	Sum						0.96

	Bond number	Atom #1	Atom symmetry	Atom #2	Atom symmetry	Bond length (Å)	Valence
S-CaBr	1	Ca1	x, y, z	Br1	x, y, z	3.06	0.21
	2	Ca1	x, y, z	Br1	-1+x,1+y, z	3.06	0.21
	3	Ca1	x, y, z	Br1	x, 1+y, z	3.06	0.21
	4	Ca1	x, y, z	Br1	-1+x, y, z	3.06	0.21
	Sum						0.84
	5	Ca2	x, y, z	Br2	1+x, -1+y,z	3.06	0.21
	6	Ca2	x, y, z	Br2	x, y, z	3.06	0.21
	7	Ca2	x, y, z	Br2	1+x, y, z	3.06	0.21
	8	Ca2	x, y, z	Br2	x, -1+y, z	3.06	0.21
	Sum						0.84

	Bond number	Atom #1	Atom symmetry	Atom #2	Atom symmetry	Bond length (Å)	Valence
S-CaI	1	Ca1	x, y, z	I1	x, y, z	3.30	0.21
	2	Ca1	x, y, z	I1	-1+x, 1+y,z	3.30	0.21
	3	Ca1	x, y, z	I1	x, 1+y, z	3.30	0.21
	4	Ca1	x, y, z	I1	-1+x, y, z	3.30	0.21
	Sum						0.84
	5	Ca2	x, y, z	I2	1+x, -1+y,z	3.30	0.21
	6	Ca2	x, y, z	I2	x, y, z	3.30	0.21
	7	Ca2	x, y, z	I2	1+x, y, z	3.30	0.21
	8	Ca2	x, y, z	I2	x, -1+y, z	3.30	0.21
	Sum						0.84

	Bond number	Atom #1	Atom symmetry	Atom #2	Atom symmetry	Bond length (Å)	Valence
S-SrCl	1	Sr1	x, y, z	Cl1	x, y, z	3.06	0.23
	2	Sr1	x, y, z	Cl1	-1+x, 1+y,z	3.06	0.23
	3	Sr1	x, y, z	Cl1	x, 1+y, z	3.06	0.23
	4	Sr1	x, y, z	Cl1	-1+x, y, z	3.06	0.23
	Sum						0.92
	5	Sr2	x, y, z	Cl2	1+x, -1+y,z	3.06	0.23
	6	Sr2	x, y, z	Cl2	x, y, z	3.06	0.23
	7	Sr2	x, y, z	Cl2	1+x, y, z	3.06	0.23
	8	Sr2	x, y, z	Cl2	x, -1+y, z	3.06	0.23
	Sum						0.92

	Bond number	Atom #1	Atom symmetry	Atom #2	Atom symmetry	Bond length (Å)	Valence
S-SrBr	1	Sr1	x, y, z	Br1	x, y, z	3.21	0.24
	2	Sr1	x, y, z	Br1	-1+x, 1+y,z	3.21	0.24
	3	Sr1	x, y, z	Br1	x, 1+y, z	3.21	0.24
	4	Sr1	x, y, z	Br1	-1+x, y, z	3.21	0.24
	Sum						0.96
	5	Sr2	x, y, z	Br2	1+x, -1+y,z	3.21	0.24
	6	Sr2	x, y, z	Br2	x, y, z	3.21	0.24
	7	Sr2	x, y, z	Br2	1+x, y, z	3.21	0.24
	8	Sr2	x, y, z	Br2	x, -1+y, z	3.21	0.24
	Sum						0.96

	Bond number	Atom #1	Atom symmetry	Atom #2	Atom symmetry	Bond length (Å)	Valence
S-SrI	1	Sr1	x, y, z	I1	x, y, z	3.44	0.22
	2	Sr1	x, y, z	I1	-1+x, 1+y,z	3.44	0.22
	3	Sr1	x, y, z	I1	x, 1+y, z	3.44	0.22
	4	Sr1	x, y, z	I1	-1+x, y, z	3.44	0.22
	Sum						0.88
	5	Sr2	x, y, z	I2	1+x, -1+y,z	3.44	0.22
	6	Sr2	x, y, z	I2	x, y, z	3.44	0.22
	7	Sr2	x, y, z	I2	1+x, y, z	3.44	0.22
	8	Sr2	x, y, z	I2	x, -1+y, z	3.44	0.22
	Sum						0.88

	Bond number	Atom #1	Atom symmetry	Atom #2	Atom symmetry	Bond length (Å)	Valence
S-BaCl	5	Ba1	x, y, z	Cl1	x, y, z	3.13	0.31
	6	Ba1	x, y, z	Cl1	-1+x, 1+y,z	3.13	0.31
	7	Ba1	x, y, z	Cl1	x, 1+y, z	3.13	0.31
	8	Ba1	x, y, z	Cl2	x, y, z	3.48	0.12
	4	Ba1	x, y, z	Cl1	-1+x, y, z	3.13	0.31
	Sum						1.36
	5	Ba2	x, y, z	Cl2	x, -1+y, z	3.13	0.31
	6	Ba2	x, y, z	Cl2	1+x, -1+y,z	3.13	0.31
	7	Ba2	x, y, z	Cl2	x, y, z	3.13	0.31
	8	Ba2	x, y, z	Cl2	1+x, y, z	3.13	0.31
	4	Ba2	x, y, z	Cl1	x, y, z	3.48	0.12
	Sum						1.36

	Bond number	Atom #1	Atom symmetry	Atom #2	Atom symmetry	Bond length (Å)	Valence
S-BaBr	**5**	Ba1	x, y, z	Br2	-1+x,-1+y,z	3.32	0.30
	6	Ba1	x, y, z	Br2	x, -1+y, z	3.32	0.30
	7	Ba1	x, y, z	Br2	-1+x, y, z	3.32	0.30
	8	Ba1	x, y, z	Br2	x, y, z	3.32	0.30
	4	Ba1	x, y, z	Br1	x, y, z	3.59	0.15
	Sum						1.35
	5	Ba2	x, y, z	Br1	1+x, y, z	3.32	0.30
	6	Ba2	x, y, z	Br1	x, 1+y, z	3.32	0.30
	7	Ba2	x, y, z	Br1	1+x, 1+y, z	3.32	0.30
	8	Ba2	x, y, z	Br2	x, y, z	3.59	0.15
	4	Ba2	x, y, z	Br1	x, y, z	3.32	0.30
	Sum						1.35

	Bond number	Atom #1	Atom symmetry	Atom #2	Atom symmetry	Bond length (Å)	Valence
S-BaI	**5**	Ba1	x, y, z	I2	-1+x, y, z	3.58	0.30
	6	Ba1	x, y, z	I2	x, y, z	3.58	0.30
	7	Ba1	x, y, z	I2	-1+x, 1+y,z	3.58	0.30
	8	Ba1	x, y, z	I2	x, 1+y, z	3.58	0.30
	4	Ba1	x, y, z	I1	x, y, z	3.78	0.17
	Sum						1.37
	5	Ba2	x, y, z	I1	1+x, -1+y,z	3.58	0.30
	6	Ba2	x, y, z	I1	x, y, z	3.58	0.30
	7	Ba2	x, y, z	I1	1+x, y, z	3.58	0.30
	8	Ba2	x, y, z	I2	x, y, z	3.78	0.17
	4	Ba2	x, y, z	I1	x, -1+y, z	3.58	0.30
	Sum						1.37

	Bond number	Atom #1	Atom symmetry	Atom #2	Atom symmetry	Bond length (Å)	Valence
Q-CaF	1	Ca1	x, y, z	F1	x, -1+y, z	2.37	0.24
	2	Ca1	x, y, z	F1	x, y, z	2.37	0.24
	3	Ca1	x, y, z	F2	x, y, z	2.37	0.24
	4	Ca1	x, y, z	F2	1+x, y, z	2.37	0.24
	Sum						0.96
	5	Ca2	x, y, z	F1	x, y, z	2.37	0.24
	6	Ca2	x, y, z	F2	x, y, z	2.37	0.24
	7	Ca2	x, y, z	F2	x, 1+y, z	2.37	0.24
	8	Ca2	x, y, z	F1	-1+x, y, z	2.37	0.24
	Sum						0.96

	Bond number	Atom #1	Atom symmetry	Atom #2	Atom symmetry	Bond length (Å)	Valence
Q-SrF	1	Sr1	x, y, z	F1	x, y, z	2.53	0.25
	2	Sr1	x, y, z	F2	x, y, z	2.53	0.25
	3	Sr1	x, y, z	F2	1+x, y, z	2.53	0.25
	4	Sr1	x, y, z	F1	x, -1+y, z	2.53	0.25
	Sum						1
	5	Sr2	x, y, z	F1	x, y, z	2.53	0.25
	6	Sr2	x, y, z	F2	x, y, z	2.53	0.25
	7	Sr2	x, y, z	F2	x, 1+y, z	2.53	0.25
	8	Sr2	x, y, z	F1	-1+x, y, z	2.53	0.25
	Sum						1

	Bond number	Atom #1	Atom symmetry	Atom #2	Atom symmetry	Bond length (Å)	Valence
O-SrF	5	Sr1	x, y, z	F2	x, y, z	2.53	0.25
	6	Sr1	x, y, z	F3	x, y, z	2.57	0.23
	7	Sr1	x, y, z	F3	1+x, y, z	2.57	0.23
	8	Sr1	x, y, z	F4	x, y, z	2.57	0.23
	9	Sr1	x, y, z	F4	1+x, y, z	2.57	0.23
	4	Sr1	x, y, z	F1	x, y, z	2.53	0.25
	Sum						1.42
	5	Sr2	x, y, z	F4	x, y, z	2.48	0.28
	6	Sr2	x, y, z	F3	x, -1+y, z	2.48	0.28
	Sum						0.56
	5	Sr3	x, y, z	F1	x, -1+y, z	2.57	0.23
	6	Sr3	x, y, z	F2	-1+x, y, z	2.57	0.23
	7	Sr3	x, y, z	F2	x, y, z	2.57	0.23
	8	Sr3	x, y, z	F3	x, -1+y, z	2.53	0.25
	9	Sr3	x, y, z	F4	x, y, z	2.53	0.25
	4	Sr3	x, y, z	F1	-1+x,-1+y,z	2.57	0.23
	Sum						1.42
	5	Sr4	x, y, z	F2	x, y, z	2.48	0.28
	4	Sr4	x, y, z	F1	x, y, z	2.48	0.28
	Sum						0.56

	Bond number	Atom #1	Atom symmetry	Atom #2	Atom symmetry	Bond length (Å)	Valence
O-BaF	5	Ba1	x, y, z	F3	x, -1+y, z	2.65	0.29
	4	Ba1	x, y, z	F1	x, y, z	2.65	0.29
	Sum						0.58
	5	Ba2	x, y, z	F4	x, y, z	2.65	0.29
	4	Ba2	x, y, z	F2	x, y, z	2.65	0.29
	Sum						0.58
	5	Ba3	x, y, z	F1	x, y, z	2.75	0.22
	6	Ba3	x, y, z	F2	x, y, z	2.70	0.25
	7	Ba3	x, y, z	F3	-1+x, y, z	2.75	0.22
	8	Ba3	x, y, z	F3	x, y, z	2.75	0.22
	9	Ba3	x, y, z	F4	x, y, z	2.70	0.25
	4	Ba3	x, y, z	F1	-1+x, y, z	2.75	0.22
	Sum						1.38
	5	Ba4	x, y, z	F2	x, y, z	2.75	0.22
	6	Ba4	x, y, z	F2	1+x, y, z	2.75	0.22
	7	Ba4	x, y, z	F3	x, -1+y, z	2.70	0.25
	8	Ba4	x, y, z	F4	x, -1+y, z	2.75	0.22
	9	Ba4	x, y, z	F4	1+x, -1+y,z	2.75	0.22
	4	Ba4	x, y, z	F1	x, y, z	2.70	0.25
	Sum						1.38

	Bond number	Atom #1	Atom symmetry	Atom #2	Atom symmetry	Bond length (Å)	Valence
α-CaCl	5	5	Ca1	x, y, z	Cl1	x, y, z	3.04
	6	6	Ca1	x, y, z	Cl4	-1+x,-1+y,z	2.80
	7	7	Ca1	x, y, z	Cl4	x, -1+y, z	2.80
	4	4	Ca1	x, y, z	Cl1	-1+x, y, z	3.03
	Sum						Sum
	5	5	Ca2	x, y, z	Cl2	1+x, y, z	3.034
	6	6	Ca2	x, y, z	Cl3	x, 1+y, z	2.796
	7	7	Ca2	x, y, z	Cl3	1+x, 1+y, z	2.798
	4	4	Ca2	x, y, z	Cl2	x, y, z	3.041
	Sum						Sum
	5	5	Ca3	x, y, z	Cl2	x, y, z	2.995
	6	6	Ca3	x, y, z	Cl2	1+x, y, z	2.979
	7	7	Ca3	x, y, z	Cl3	x, y, z	2.735
	4	4	Ca3	x, y, z	Cl1	x, y, z	2.989
	Sum						Sum
	5	5	Ca4	x, y, z	Cl1	x, y, z	2.995
	6	6	Ca4	x, y, z	Cl2	x, y, z	2.988
	7	7	Ca4	x, y, z	Cl4	x, y, z	2.736
	4	4	Ca4	x, y, z	Cl1	-1+x, y, z	2.979
	Sum						Sum

	Bond number	Atom #1	Atom symmetry	Atom #2	Atom symmetry	Bond length (Å)	Valence
α-CaBr	5	Ca1	x, y, z	Br1	x, y, z	3.21	0.14
	6	Ca1	x, y, z	Br4	-1+x,-1+y,z	2.97	0.27
	7	Ca1	x, y, z	Br4	x, -1+y, z	2.96	0.28
	4	Ca1	x, y, z	Br1	-1+x, y, z	3.19	0.15
	Sum						Sum
	5	Ca2	x, y, z	Br2	1+x, y, z	3.19	0.15
	6	Ca2	x, y, z	Br3	x, 1+y, z	2.96	0.28
	7	Ca2	x, y, z	Br3	1+x, 1+y, z	2.97	0.27
	4	Ca2	x, y, z	Br2	x, y, z	3.21	0.14
	Sum						Sum
	5	Ca3	x, y, z	Br2	x, y, z	3.14	0.17
	6	Ca3	x, y, z	Br2	1+x, y, z	3.14	0.17
	7	Ca3	x, y, z	Br3	x, y, z	2.89	0.34
	4	Ca3	x, y, z	Br1	x, y, z	3.11	0.19
	Sum						Sum
	5	Ca4	x, y, z	Br1	x, y, z	3.14	0.17
	6	Ca4	x, y, z	Br2	x, y, z	3.11	0.19
	7	Ca4	x, y, z	Br4	x, y, z	2.89	0.34
	4	Ca4	x, y, z	Br1	-1+x, y, z	3.14	0.17
	Sum						Sum

	Bond number	Atom #1	Atom symmetry	Atom #2	Atom symmetry	Bond length (Å)	Valence
α-CaI	5	Ca1	x, y, z	I1	x, y, z	3.46	0.14
	6	Ca1	x, y, z	I4	-1+x, -1+y, z	3.19	0.28
	7	Ca1	x, y, z	I4	x, -1+y, z	3.19	0.28
	4	Ca1	x, y, z	I1	-1+x, y, z	3.45	0.14
	Sum						0.84
	5	Ca2	x, y, z	I2	1+x, y, z	3.45	0.14
	6	Ca2	x, y, z	I3	x, 1+y, z	3.19	0.28
	7	Ca2	x, y, z	I3	1+x, 1+y, z	3.19	0.28
	4	Ca2	x, y, z	I2	x, y, z	3.46	0.14
	Sum						0.84
	5	Ca3	x, y, z	I2	x, y, z	3.32	0.20
	6	Ca3	x, y, z	I2	1+x, y, z	3.32	0.20
	7	Ca3	x, y, z	I3	x, y, z	3.12	0.34
	4	Ca3	x, y, z	I1	x, y, z	3.28	0.22
	Sum						0.96
	5	Ca4	x, y, z	I1	x, y, z	3.32	0.20
	6	Ca4	x, y, z	I2	x, y, z	3.28	0.22
	7	Ca4	x, y, z	I4	x, y, z	3.12	0.34
	4	Ca4	x, y, z	I1	-1+x, y, z	3.32	0.20
	Sum						0.96

	Bond number	Atom #1	Atom symmetry	Atom #2	Atom symmetry	Bond length (Å)	Valence
γ-CaCl	5	Ca1	x, y, z	Cl2	x, y, z	2.91	0.23
	6	Ca1	x, y, z	Cl3	x, y, z	2.80	0.31
	4	Ca1	x, y, z	Cl1	x, y, z	2.73	0.37
	Sum						0.91
	5	Ca2	x, y, z	Cl2	x, y, z	2.93	0.22
	6	Ca2	x, y, z	Cl4	-1+x,-1+y,z	2.81	0.30
	7	Ca2	x, y, z	Cl4	-1+x, y, z	2.81	0.30
	4	Ca2	x, y, z	Cl2	x, -1+y, z	2.93	0.22
	Sum						1.04
	5	Ca3	x, y, z	Cl1	1+x, y, z	2.81	0.30
	6	Ca3	x, y, z	Cl3	x, -1+y, z	2.93	0.22
	7	Ca3	x, y, z	Cl3	x, y, z	2.93	0.22
	4	Ca3	x, y, z	Cl1	1+x, -1+y,z	2.81	0.30
	Sum						1.04
	5	Ca4	x, y, z	Cl3	x, y, z	2.91	0.23
	6	Ca4	x, y, z	Cl4	x, y, z	2.73	0.38
	4	Ca4	x, y, z	Cl2	x, y, z	2.80	0.31
	Sum						0.92

	Bond number	Atom #1	Atom symmetry	Atom #2	Atom symmetry	Bond length (Å)	Valence
γ-CaBr	5	Ca1	x, y, z	Br2	x, y, z	3.056	0.22
	6	Ca1	x, y, z	Br3	x, y, z	2.98	0.27
	4	Ca1	x, y, z	Br1	x, y, z	2.888	0.34
	Sum						0.83
	5	Ca2	x, y, z	Br2	x, 1+y, z	3.117	0.18
	6	Ca2	x, y, z	Br4	-1+x, y, z	2.972	0.27
	7	Ca2	x, y, z	Br4	-1+x,1+y,z	2.972	0.27
	4	Ca2	x, y, z	Br2	x, y, z	3.117	0.18
	Sum						0.90
	5	Ca3	x, y, z	Br1	1+x, 1+y, z	2.976	0.27
	6	Ca3	x, y, z	Br3	x, y, z	3.123	0.18
	7	Ca3	x, y, z	Br3	x, 1+y, z	3.123	0.18
	4	Ca3	x, y, z	Br1	1+x, y, z	2.976	0.27
	Sum						0.90
	5	Ca4	x, y, z	Br3	x, y, z	3.07	0.21
	6	Ca4	x, y, z	Br4	x, y, z	2.90	0.33
	4	Ca4	x, y, z	Br2	x, y, z	2.99	0.26
	Sum						0.80

	Bond number	Atom #1	Atom symmetry	Atom #2	Atom symmetry	Bond length (Å)	Valence
γ-CaI	5	Ca1	x, y, z	I2	x, y, z	3.25	0.24
	6	Ca1	x, y, z	I3	x, y, z	3.23	0.26
	4	Ca1	x, y, z	I1	x, y, z	3.12	0.34
	Sum						0.83
	5	Ca2	x, y, z	I2	x, y, z	3.36	0.18
	6	Ca2	x, y, z	I4	-1+x,-1+y,z	3.22	0.26
	7	Ca2	x, y, z	I4	-1+x, y, z	3.22	0.26
	4	Ca2	x, y, z	I2	x, -1+y, z	3.36	0.18
	Sum						0.90
	5	Ca3	x, y, z	I1	1+x, y, z	3.22	0.26
	6	Ca3	x, y, z	I3	x, -1+y, z	3.36	0.18
	7	Ca3	x, y, z	I3	x, y, z	3.36	0.18
	4	Ca3	x, y, z	I1	1+x, -1+y,z	3.22	0.26
	Sum						0.90
	5	Ca4	x, y, z	I3	x, y, z	3.252	0.24
	6	Ca4	x, y, z	I4	x, y, z	3.115	0.34
	4	Ca4	x, y, z	I2	x, y, z	3.225	0.26
	Sum						0.80

	Bond number	Atom #1	Atom symmetry	Atom #2	Atom symmetry	Bond length (Å)	Valence
γ-SrF	5	Sr1	x, y, z	F2	x, y, z	2.54	0.24
	6	Sr1	x, y, z	F3	x, y, z	2.49	0.28
	4	Sr1	x, y, z	F1	-1+x, y, z	2.43	0.33
	Sum						0.85
	5	Sr2	x, y, z	F2	x, y, z	2.57	0.23
	6	Sr2	x, y, z	F4	x, -1+y, z	2.475	0.29
	7	Sr2	x, y, z	F4	x, y, z	2.476	0.29
	4	Sr2	x, y, z	F2	x, -1+y, z	2.57	0.23
	Sum						1.04
	5	Sr3	x, y, z	F1	x, y, z	2.476	0.29
	6	Sr3	x, y, z	F3	x, -1+y, z	2.57	0.23
	7	Sr3	x, y, z	F3	x, y, z	2.57	0.23
	4	Sr3	x, y, z	F1	x, -1+y, z	2.475	0.29
	Sum						1.04
	5	Sr4	x, y, z	F3	x, y, z	2.543	0.24
	6	Sr4	x, y, z	F4	1+x, y, z	2.432	0.33
	4	Sr4	x, y, z	F2	x, y, z	2.488	0.28
	Sum						0.85

	Bond number	Atom #1	Atom symmetry	Atom #2	Atom symmetry	Bond length (Å)	Valence
γ-SrCl	5	Sr1	x, y, z	Cl2	x, y, z	3.096	0.21
	6	Sr1	x, y, z	Cl3	x, y, z	2.937	0.32
	4	Sr1	x, y, z	Cl1	x, y, z	2.894	0.35
	Sum						0.88
	5	Sr2	x, y, z	Cl2	x, y, z	3.047	0.23
	6	Sr2	x, y, z	Cl4	x, -1+y, z	2.958	0.30
	7	Sr2	x, y, z	Cl4	x, y, z	2.958	0.30
	4	Sr2	x, y, z	Cl2	x, -1+y, z	3.047	0.23
	Sum						1.06
	5	Sr3	x, y, z	Cl1	-1+x, y, z	2.958	0.30
	6	Sr3	x, y, z	Cl3	x, -1+y, z	3.047	0.23
	7	Sr3	x, y, z	Cl3	x, y, z	3.047	0.23
	4	Sr3	x, y, z	Cl1	-1+x,-1+y,z	2.958	0.30
	Sum						1.06
	5	Sr4	x, y, z	Cl3	x, y, z	3.096	0.21
	6	Sr4	x, y, z	Cl4	-1+x, y, z	2.895	0.35
	4	Sr4	x, y, z	Cl2	x, y, z	2.935	0.32
	Sum						0.88

	Bond number	Atom #1	Atom symmetry	Atom #2	Atom symmetry	Bond length (Å)	Valence
γ-SrBr	5	Sr1	x, y, z	Br2	x, y, z	3.22	0.23
	6	Sr1	x, y, z	Br3	x, y, z	3.14	0.29
	4	Sr1	x, y, z	Br1	x, y, z	3.06	0.36
	Sum						0.88
	5	Sr2	x, y, z	Br2	x, y, z	3.24	0.22
	6	Sr2	x, y, z	Br4	-1+x,-1+y,z	3.14	0.29
	7	Sr2	x, y, z	Br4	-1+x, y, z	3.14	0.29
	4	Sr2	x, y, z	Br2	x, -1+y, z	3.24	0.22
	Sum						1.02
	5	Sr3	x, y, z	Br1	1+x, y, z	3.14	0.29
	6	Sr3	x, y, z	Br3	x, -1+y, z	3.24	0.22
	7	Sr3	x, y, z	Br3	x, y, z	3.24	0.22
	4	Sr3	x, y, z	Br1	1+x,-1+y,z	3.14	0.29
	Sum						1.02
	5	Sr4	x, y, z	Br3	x, y, z	3.20	0.23
	6	Sr4	x, y, z	Br4	x, y, z	3.06	0.36
	4	Sr4	x, y, z	Br2	x, y, z	3.14	0.29
	Sum						0.88

	Bond number	Atom #1	Atom symmetry	Atom #2	Atom symmetry	Bond length (Å)	Valence
γ-SrI	5	Sr1	x, y, z	I2	x, y, z	3.42	0.23
	6	Sr1	x, y, z	I3	x, y, z	3.38	0.26
	4	Sr1	x, y, z	I1	x, y, z	3.28	0.34
	Sum						0.83
	5	Sr2	x, y, z	I2	x, y, z	3.48	0.20
	6	Sr2	x, y, z	I4	x, -1+y, z	3.36	0.28
	7	Sr2	x, y, z	I4	x, y, z	3.36	0.28
	4	Sr2	x, y, z	I2	x, -1+y, z	3.48	0.20
	Sum						0.96
	5	Sr3	x, y, z	I1	x, y, z	3.36	0.28
	6	Sr3	x, y, z	I3	1+x, -1+y,z	3.48	0.20
	7	Sr3	x, y, z	I3	1+x, y, z	3.48	0.20
	4	Sr3	x, y, z	I1	x, -1+y, z	3.36	0.28
	Sum						0.96
	5	Sr4	x, y, z	I3	x, y, z	3.42	0.23
	6	Sr4	x, y, z	I4	-1+x, y, z	3.24	0.39
	4	Sr4	x, y, z	I2	x, y, z	3.38	0.26
	Sum						0.88

	Bond number	Atom #1	Atom symmetry	Atom #2	Atom symmetry	Bond length (Å)	Valence
γ-BaF	5	Ba1	x, y, z	F2	x, y, z	2.69	0.26
	6	Ba1	x, y, z	F3	x, y, z	2.70	0.25
	4	Ba1	x, y, z	F1	x, y, z	2.62	0.31
	Sum						0.82
	5	Ba2	x, y, z	F2	x, y, z	2.73	0.23
	6	Ba2	x, y, z	F4	x, -1+y, z	2.62	0.31
	7	Ba2	x, y, z	F4	x, y, z	2.62	0.31
	4	Ba2	x, y, z	F2	x, -1+y, z	2.73	0.23
	Sum						1.08
	5	Ba3	x, y, z	F1	1+x, y, z	2.61	0.32
	6	Ba3	x, y, z	F3	x, -1+y, z	2.73	0.23
	7	Ba3	x, y, z	F3	x, y, z	2.73	0.23
	4	Ba3	x, y, z	F1	1+x,-1+y,z	2.61	0.32
	Sum						1.10
	5	Ba4	x, y, z	F3	x, y, z	2.69	0.26
	6	Ba4	x, y, z	F4	1+x, y, z	2.63	0.30
	4	Ba4	x, y, z	F2	x, y, z	2.70	0.25
	Sum						0.81

	Bond number	Atom #1	Atom symmetry	Atom #2	Atom symmetry	Bond length (Å)	Valence
γ-BaCl	5	Ba1	x, y, z	Cl2	x, y, z	3.12	0.31
	6	Ba1	x, y, z	Cl3	x, y, z	3.24	0.23
	4	Ba1	x, y, z	Cl1	x, y, z	2.99	0.44
	Sum						0.98
	5	Ba2	x, y, z	Cl2	x, y, z	3.15	0.29
	6	Ba2	x, y, z	Cl4	-1+x,-1+y,z	3.06	0.37
	7	Ba2	x, y, z	Cl4	1+x, y, z	3.06	0.37
	4	Ba2	x, y, z	Cl2	x, -1+y, z	3.15	0.29
	Sum						1.32
	5	Ba3	x, y, z	Cl1	1+x, y, z	3.06	0.37
	6	Ba3	x, y, z	Cl3	x, -1+y, z	3.15	0.29
	7	Ba3	x, y, z	Cl3	x, y, z	3.15	0.29
	4	Ba3	x, y, z	Cl1	1+x,-1+y,z	3.06	0.37
	Sum						1.32
	5	Ba4	x, y, z	Cl3	x, y, z	3.12	0.31
	6	Ba4	x, y, z	Cl4	x, y, z	2.99	0.44
	4	Ba4	x, y, z	Cl2	x, y, z	3.24	0.23
	Sum						0.98

	Bond number	Atom #1	Atom symmetry	Atom #2	Atom symmetry	Bond length (Å)	Valence
γ-BaBr	5	Ba1	x, y, z	Br2	x, y, z	3.34	0.29
	6	Ba1	x, y, z	Br3	x, y, z	3.30	0.32
	4	Ba1	x, y, z	Br1	x, y, z	3.20	0.42
	Sum						1.03
	5	Ba2	x, y, z	Br2	x, y, z	3.38	0.26
	6	Ba2	x, y, z	Br4	-1+x,-1+y,z	3.27	0.34
	7	Ba2	x, y, z	Br4	-1+x, y, z	3.27	0.34
	4	Ba2	x, y, z	Br2	x, -1+y, z	3.38	0.26
	Sum						1.20
	5	Ba3	x, y, z	Br1	1+x, y, z	3.27	0.34
	6	Ba3	x, y, z	Br3	x, -1+y, z	3.38	0.26
	7	Ba3	x, y, z	Br3	x, y, z	3.38	0.26
	4	Ba3	x, y, z	Br1	1+x,-1+y, z	3.27	0.34
	Sum						1.20
	5	Ba4	x, y, z	Br3	x, y, z	3.34	0.29
	6	Ba4	x, y, z	Br4	x, y, z	3.20	0.42
	4	Ba4	x, y, z	Br2	x, y, z	3.30	0.32
	Sum						1.03

	Bond number	Atom #1	Atom symmetry	Atom #2	Atom symmetry	Bond length (Å)	Valence
γ-BaI	5	Ba1	x, y, z	I2	x, y, z	3.54	0.33
	6	Ba1	x, y, z	I3	x, y, z	3.54	0.33
	4	Ba1	x, y, z	I1	x, y, z	3.42	0.46
	Sum						1.12
	5	Ba2	x, y, z	I2	x, y, z	3.60	0.28
	6	Ba2	x, y, z	I4	-1+x,-1+y,z	3.51	0.35
	7	Ba2	x, y, z	I4	-1+x, y, z	3.51	0.35
	4	Ba2	x, y, z	I2	x, -1+y, z	3.60	0.28
	Sum						1.26
	5	Ba3	x, y, z	I1	1+x, y, z	3.51	0.36
	6	Ba3	x, y, z	I3	x, -1+y, z	3.60	0.28
	7	Ba3	x, y, z	I3	x, y, z	3.60	0.28
	4	Ba3	x, y, z	I1	1+x, -1+y,z	3.51	0.36
	Sum						1.28
	5	Ba4	x, y, z	I3	x, y, z	3.54	0.33
	6	Ba4	x, y, z	I4	x, y, z	3.42	0.46
	4	Ba4	x, y, z	I2	x, y, z	3.54	0.33
	Sum						1.12

	Bond number	Atom #1	Atom symmetry	Atom #2	Atom symmetry	Bond length (Å)	Valence
β-BaF	5	Ba1	x, y, z	F1	x, y, z	2.58	0.35
	6	Ba1	x, y, z	F3	x, y, z	2.54	0.39
	7	Ba1	x, y, z	F4	-1+x, y, z	2.52	0.41
	8	Ba1	x, y, z	F4	x, y, z	2.51	0.42
	4	Ba1	x, y, z	F1	-1+x, y, z	2.57	0.36
	Sum						1.93
	5	Ba2	x, y, z	F2	x, y, z	2.58	0.35
	6	Ba2	x, y, z	F3	x, y, z	2.51	0.42
	7	Ba2	x, y, z	F3	1+x, y, z	2.52	0.41
	8	Ba2	x, y, z	F4	x, y, z	2.54	0.39
	4	Ba2	x, y, z	F2	#NAME?	2.59	0.34
	Sum						1.91
	5	Ba3	x, y, z	F4	x, y, z	2.46	0.48
	4	Ba3	x, y, z	F1	x, 1+y, z	2.64	0.30
	Sum						0.78
	5	Ba4	x, y, z	F3	x, 1+y, z	2.49	0.44
	4	Ba4	x, y, z	F2	#NAME?	2.60	0.33
	Sum						0.77

	Bond number	Atom #1	Atom symmetry	Atom #2	Atom symmetry	Bond length (Å)	Valence
δ-BaF	5	Ba1	x, y, z	F2	x, y, z	2.57	0.36
	6	Ba1	x, y, z	F4	x, y, z	2.69	0.26
	4	Ba1	x, y, z	F1	1+x, y, z	2.56	0.36
	Sum						0.98
	5	Ba2	x, y, z	F3	x, y, z	2.64	0.30
	6	Ba2	x, y, z	F4	x, -1+y, z	2.73	0.23
	7	Ba2	x, y, z	F4	x, y, z	2.73	0.23
	4	Ba2	x, y, z	F3	x, -1+y, z	2.64	0.30
	Sum						1.06
	5	Ba3	x, y, z	F1	x, y, z	2.68	0.27
	6	Ba3	x, y, z	F2	x, -1+y, z	2.68	0.26
	7	Ba3	x, y, z	F2	x, y, z	2.68	0.26
	4	Ba3	x, y, z	F1	x, -1+y, z	2.68	0.27
	Sum						1.06
	5	Ba4	x, y, z	F4	-1+x, y, z	2.67	0.27
	4	Ba4	x, y, z	F3	x, y, z	2.58	0.35
	Sum						0.62

	Bond number	Atom #1	Atom symmetry	Atom #2	Atom symmetry	Bond length (Å)	Valence
C-BaCl	5	Ba1	x, y, z	Cl2	x, y, z	3.21	0.24
	6	Ba1	x, y, z	Cl3	x, 1+y, z	3.21	0.24
	7	Ba1	x, y, z	Cl4	x, y, z	3.21	0.24
	4	Ba1	x, y, z	Cl1	x, 1+y, z	3.21	0.24
	Sum						0.96
	5	Ba2	x, y, z	Cl3	x, 1+y, z	3.24	0.23
	6	Ba2	x, y, z	Cl4	x, y, z	3.24	0.23
	7	Ba2	x, y, z	Cl4	1+x, y, z	3.24	0.23
	4	Ba2	x, y, z	Cl3	x, y, z	3.24	0.23
	Sum						0.92
	5	Ba3	x, y, z	Cl1	x, 1+y, z	3.24	0.23
	6	Ba3	x, y, z	Cl2	x, y, z	3.24	0.23
	7	Ba3	x, y, z	Cl2	1+x, y, z	3.24	0.23
	4	Ba3	x, y, z	Cl1	x, y, z	3.24	0.23
	Sum						0.92
	5	Ba4	x, y, z	Cl2	1+x, y, z	3.21	0.24
	6	Ba4	x, y, z	Cl3	x, y, z	3.21	0.24
	7	Ba4	x, y, z	Cl4	1+x, y, z	3.21	0.24
	4	Ba4	x, y, z	Cl1	x, y, z	3.21	0.24
	Sum						0.96

	Bond number	Atom #1	Atom symmetry	Atom #2	Atom symmetry	Bond length (Å)	Valence
C-BaBr	5	Ba1	x, y, z	Br2	x, y, z	3.37	0.27
	6	Ba1	x, y, z	Br3	x, 1+y, z	3.37	0.27
	7	Ba1	x, y, z	Br4	x, y, z	3.37	0.27
	4	Ba1	x, y, z	Br1	x, 1+y, z	3.37	0.27
	Sum						1.08
	5	Ba2	x, y, z	Br3	x, y, z	3.38	0.26
	6	Ba2	x, y, z	Br4	x, -1+y, z	3.38	0.26
	7	Ba2	x, y, z	Br4	x, y, z	3.38	0.26
	4	Ba2	x, y, z	Br3	-1+x, y, z	3.38	0.26
	Sum						1.04
	5	Ba3	x, y, z	Br1	x, y, z	3.38	0.26
	6	Ba3	x, y, z	Br2	x, -1+y, z	3.38	0.26
	7	Ba3	x, y, z	Br2	x, y, z	3.38	0.26
	4	Ba3	x, y, z	Br1	-1+x, y, z	3.38	0.26
	Sum						1.04
	5	Ba4	x, y, z	Br2	1+x, y, z	3.37	0.27
	6	Ba4	x, y, z	Br3	x, y, z	3.37	0.27
	7	Ba4	x, y, z	Br4	1+x, y, z	3.37	0.27
	4	Ba4	x, y, z	Br1	x, y, z	3.37	0.27
	Sum						1.08

	Bond number	Atom #1	Atom symmetry	Atom #2	Atom symmetry	Bond length (Å)	Valence
C-BaI	5	Ba1	x, y, z	I2	x, y, z	3.60	0.28
	6	Ba1	x, y, z	I3	1+x, y, 1+z	3.60	0.28
	7	Ba1	x, y, z	I4	x, 1+y, 1+z	3.60	0.28
	4	Ba1	x, y, z	I1	x, y, z	3.60	0.28
	Sum						1.12
	5	Ba2	x, y, z	I3	1+x, y, z	3.57	0.30
	6	Ba2	x, y, z	I4	x, y, z	3.57	0.30
	7	Ba2	x, y, z	I4	x, 1+y, z	3.57	0.30
	4	Ba2	x, y, z	I3	x, y, z	3.57	0.30
	Sum						1.20
	5	Ba3	x, y, z	I1	x, y, z	3.57	0.30
	6	Ba3	x, y, z	I2	x, -1+y, z	3.57	0.30
	7	Ba3	x, y, z	I2	x, y, z	3.57	0.30
	4	Ba3	x, y, z	I1	#NAME?	3.57	0.30
	Sum						1.20
	5	Ba4	x, y, z	I2	x,-1+y,-1+z	3.60	0.28
	6	Ba4	x, y, z	I3	x, y, z	3.60	0.28
	7	Ba4	x, y, z	I4	x, y, z	3.60	0.28
	4	Ba4	x, y, z	I1	-1+x,y,-1+z	3.60	0.28
	Sum						1.12

The 2D Compounds containing the Al, Ga, Zn, and Cd elements in low oxidation states

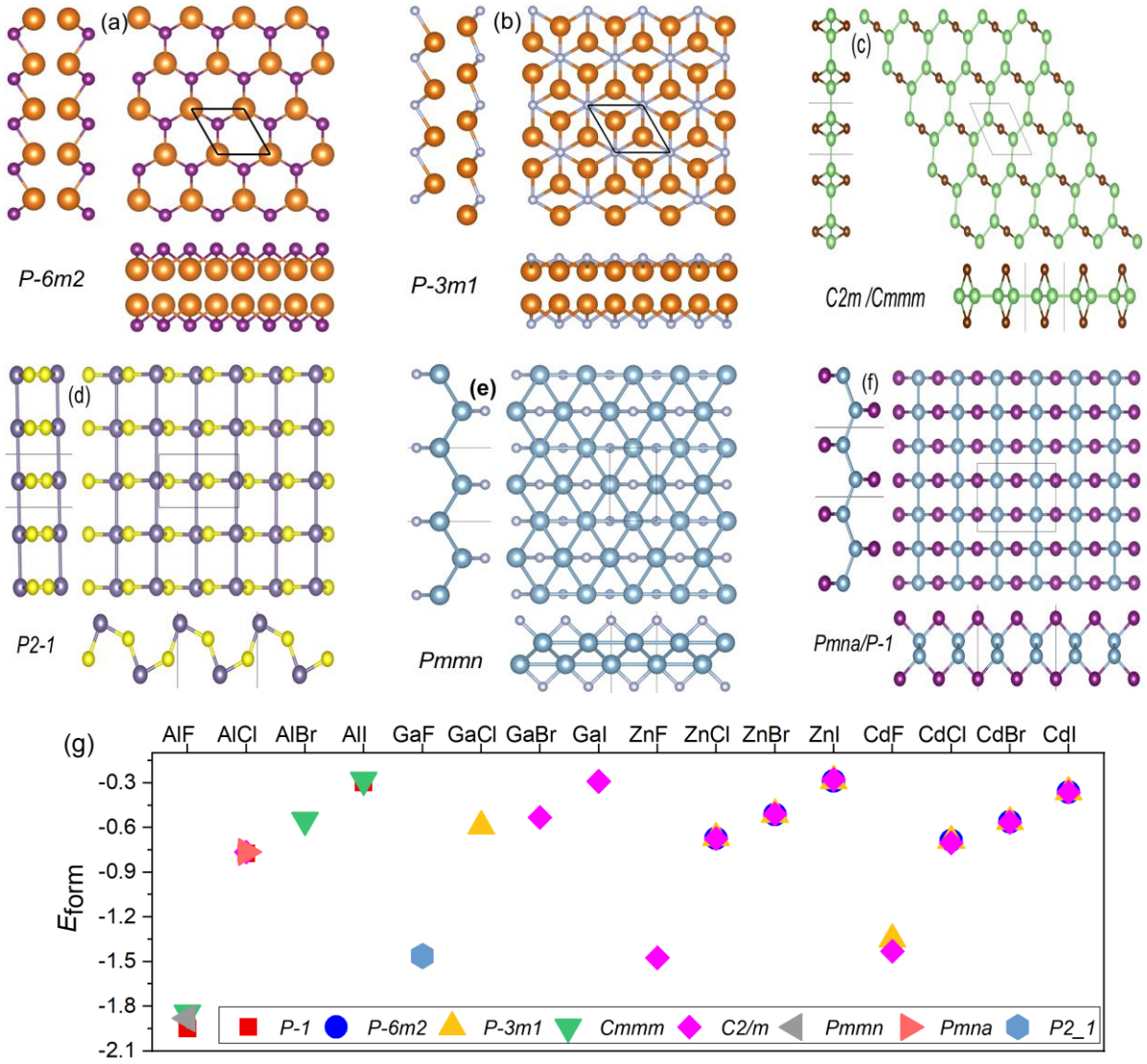


Figure S5. Atomic arrangements of IIIAX (a-f). Formation energies per atom of the AlX, GaX, ZnX, and CdX monolayers(g).

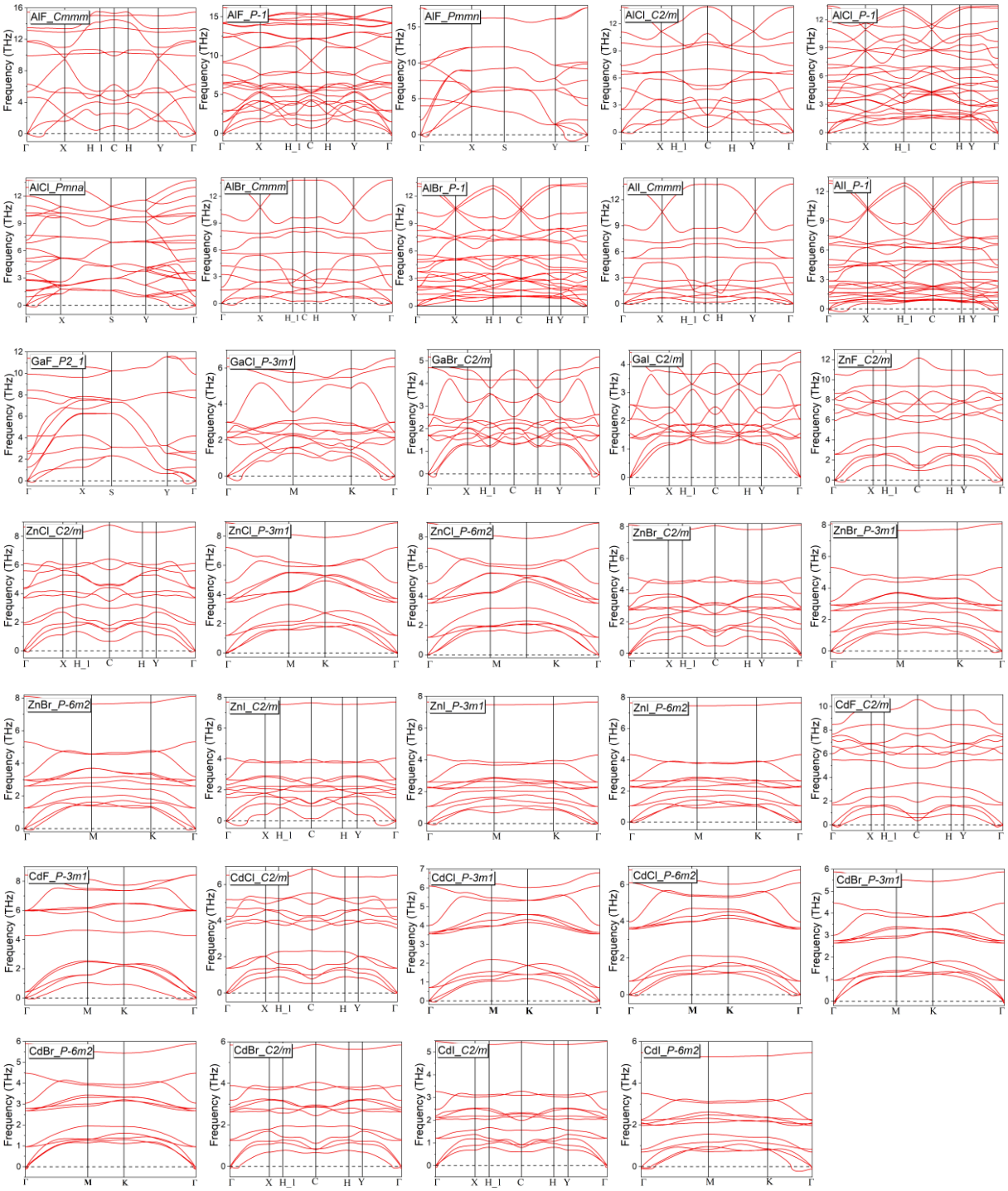


Figure S6. Phonon dispersion spectra for AlX, GaX, ZnX, and CdX monolayers calculated with finite displacement method.

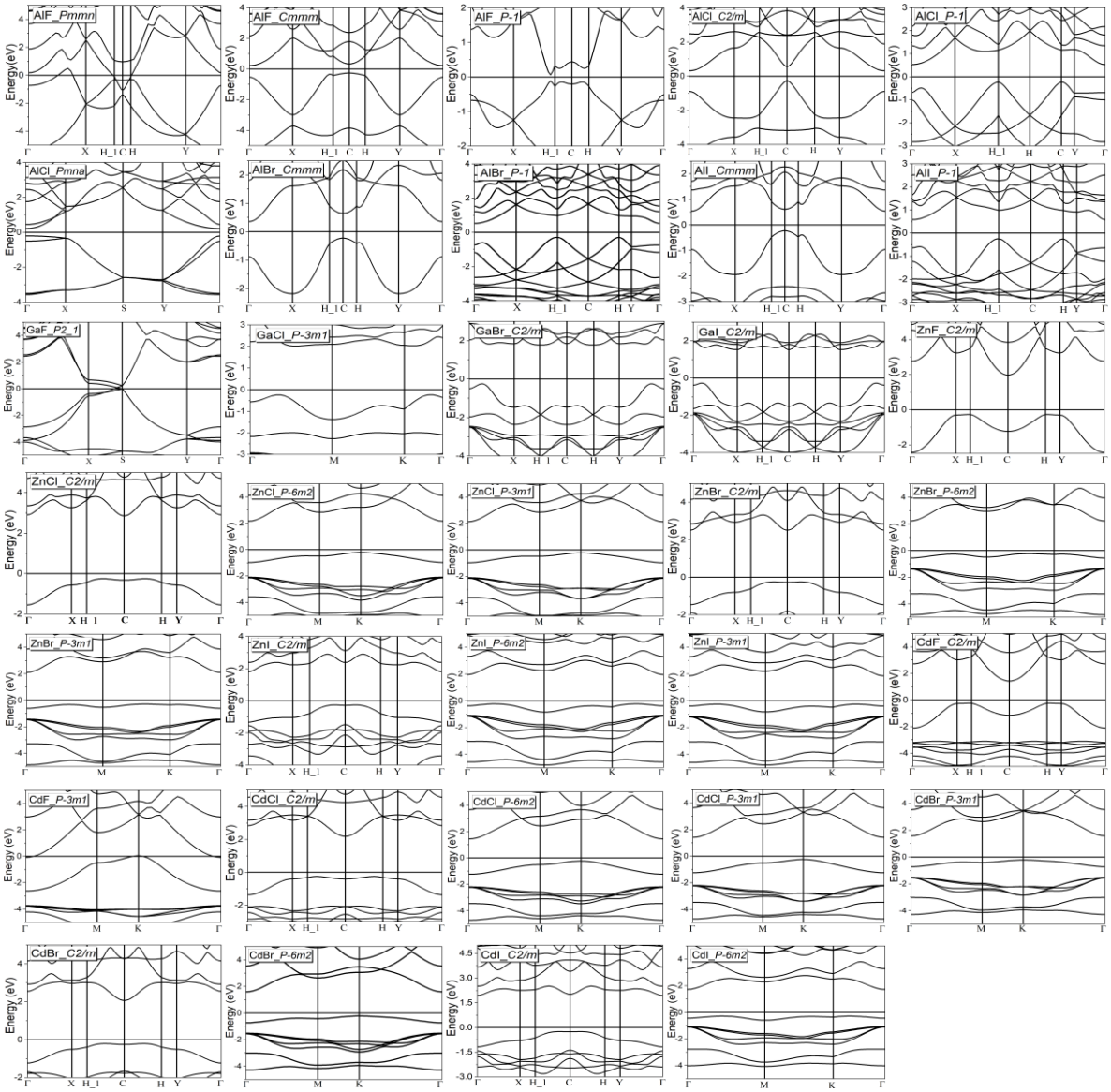
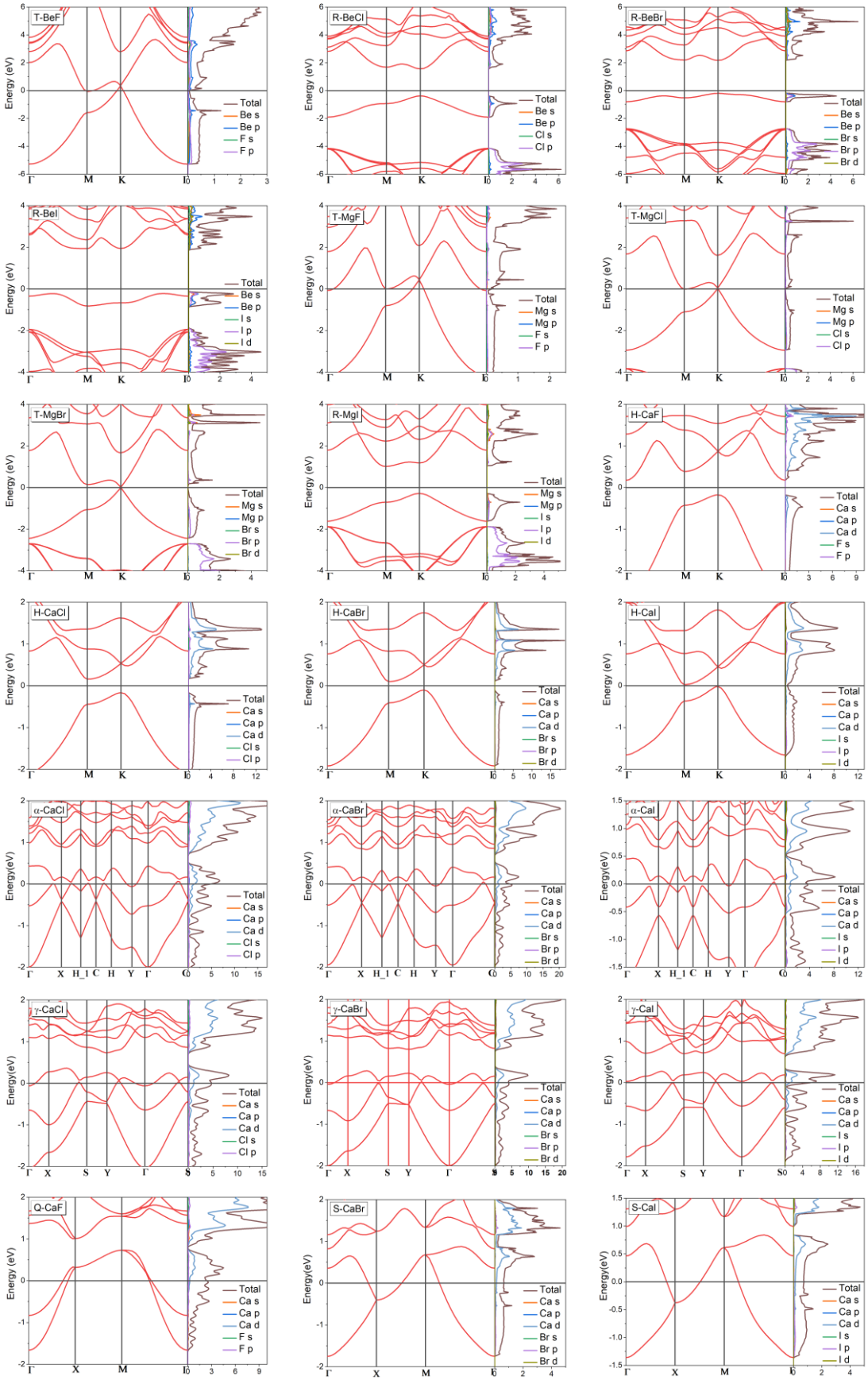
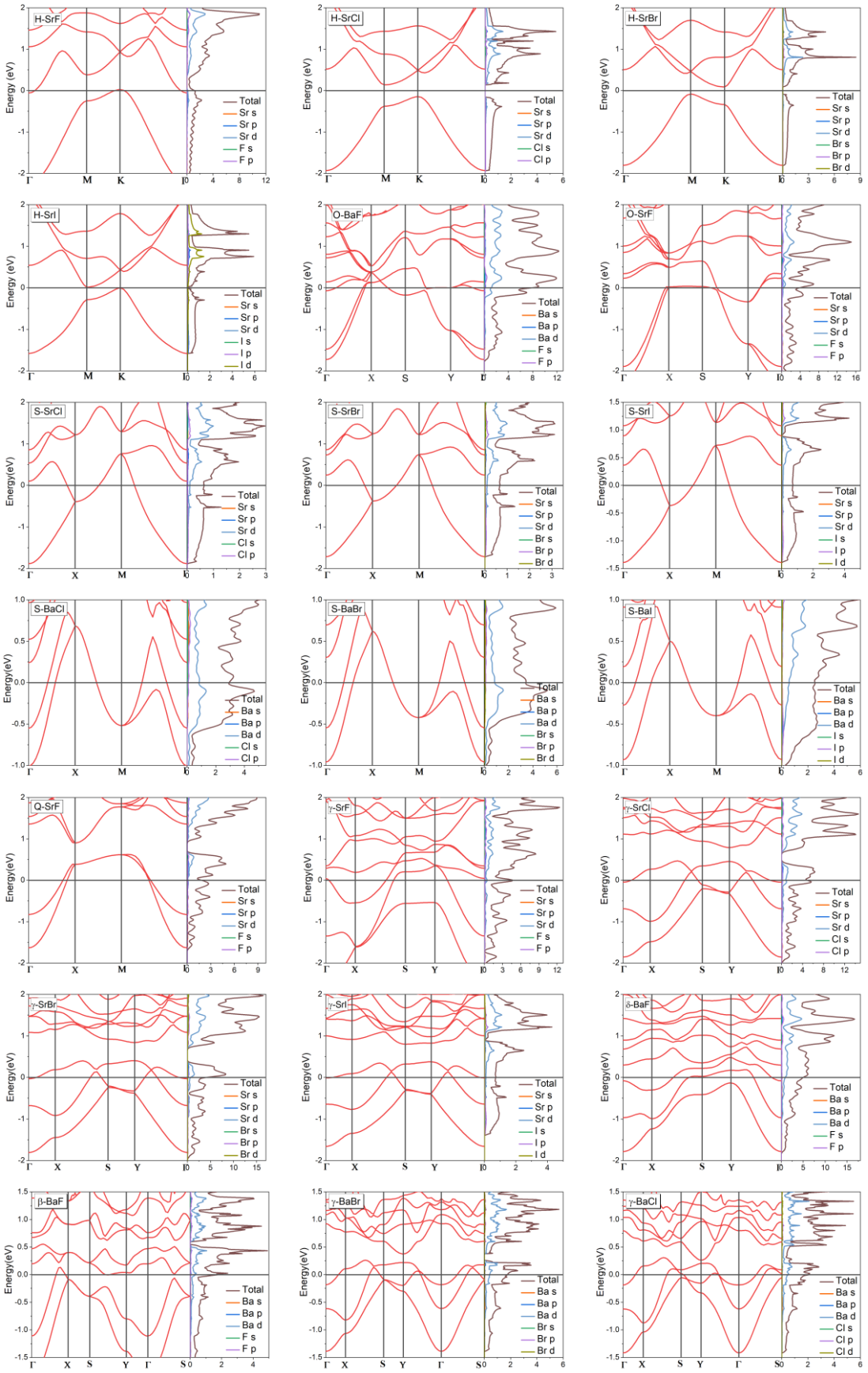


Figure S7. Band structures of AlX, GaX, ZnX, CdX monolayers employing PBE. The same band path was used as dispersion spectra in Figure S6. The Fermi level is assigned at 0 eV.

Electronic properties of MX monolayers.





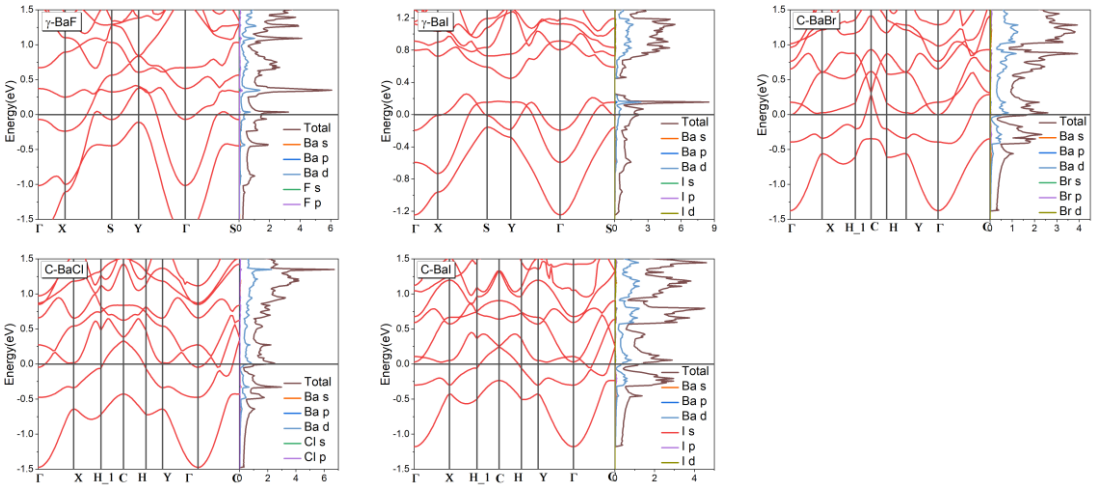


Figure S8. Band structures and DOS of MX monolayers employing PBE. Same band path was used as dispersion spectra in Figure S2. The Fermi level is assigned at 0 eV.

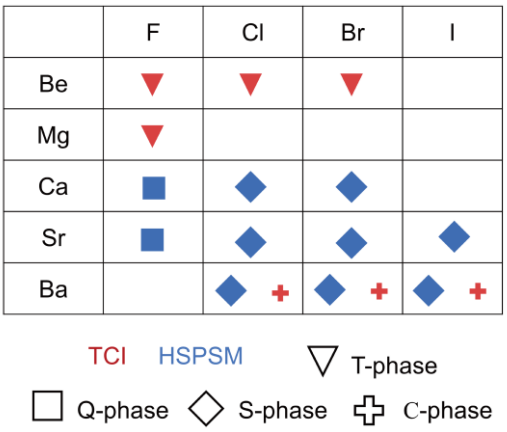


Figure S9. Topological characterization of MX monolayers using SymTopo with spin-orbit coupling.

Convergence test, band gap, the exciton binding energy, and the excitonic wave functions and absorbance spectrum of the MX monolayers.

We choose H-SrBr monolayer for the convergence test[20]. The kinetic-energy cutoff finally is set to be 60 Ry, the 2D Coulomb cutoff is set to be 16 Ry, the number of empty bands is set as 1600, and the k-point sampling is set to be 20×20×1, which ensure the band-gap convergence within 0.005 eV. A coarse k-mesh of 20×20×1 is used to perform the mean field calculations, and a fine k-mesh of 40×40×1 is used for the BSE calculation. Besides, the degeneracy-allowed the six highest valence bands and eight lowest conduction bands to be incorporated during BSE calculations.

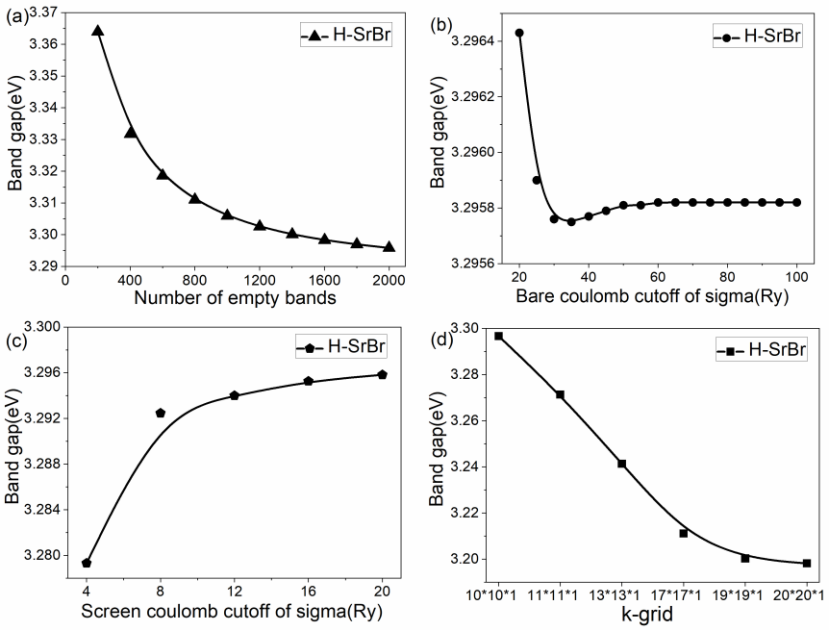


Figure S10. Convergence of band gap to the kinetic energy cutoff(a), the bare coulomb cutoff of sigma (b), the screened cutoff of sigma (c), k-point sampling (d) for H-SrBr monolayer.

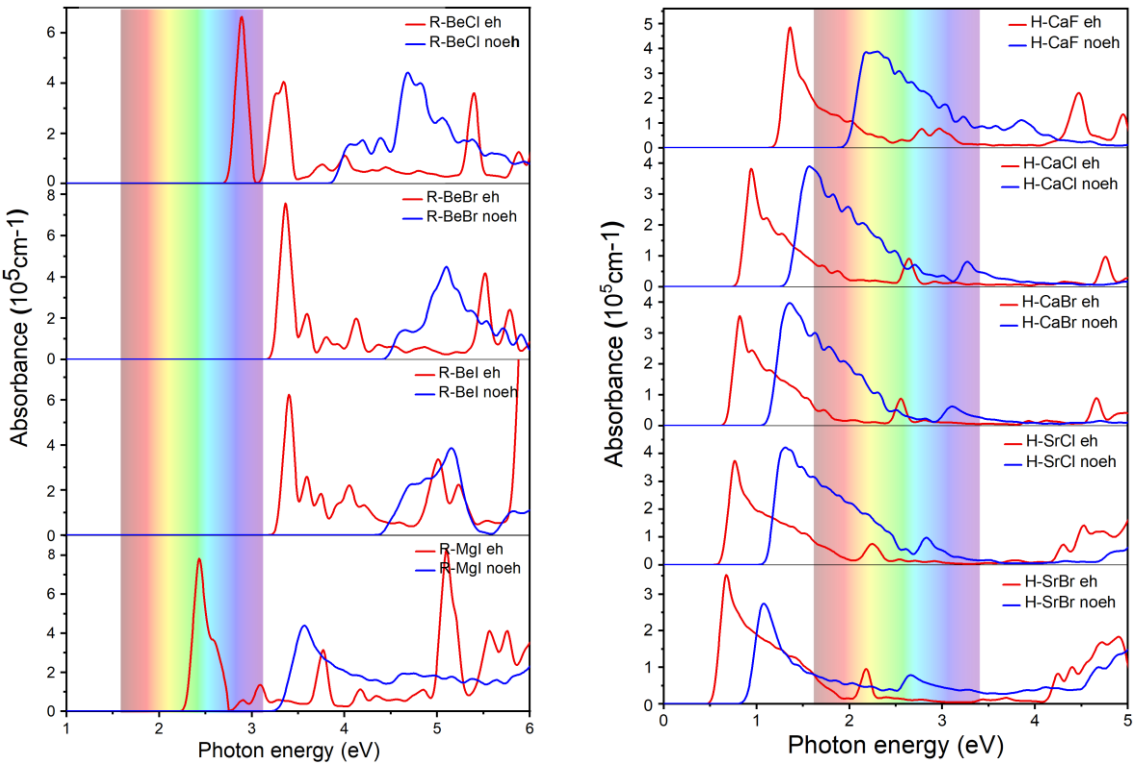


Figure S11. Absorbance spectrum of R-MX and H-MX monolayers based on GW + BSE and GW+ RPA levels. The light absorbance calculated with (without) e−h interactions are shown in red(blue).

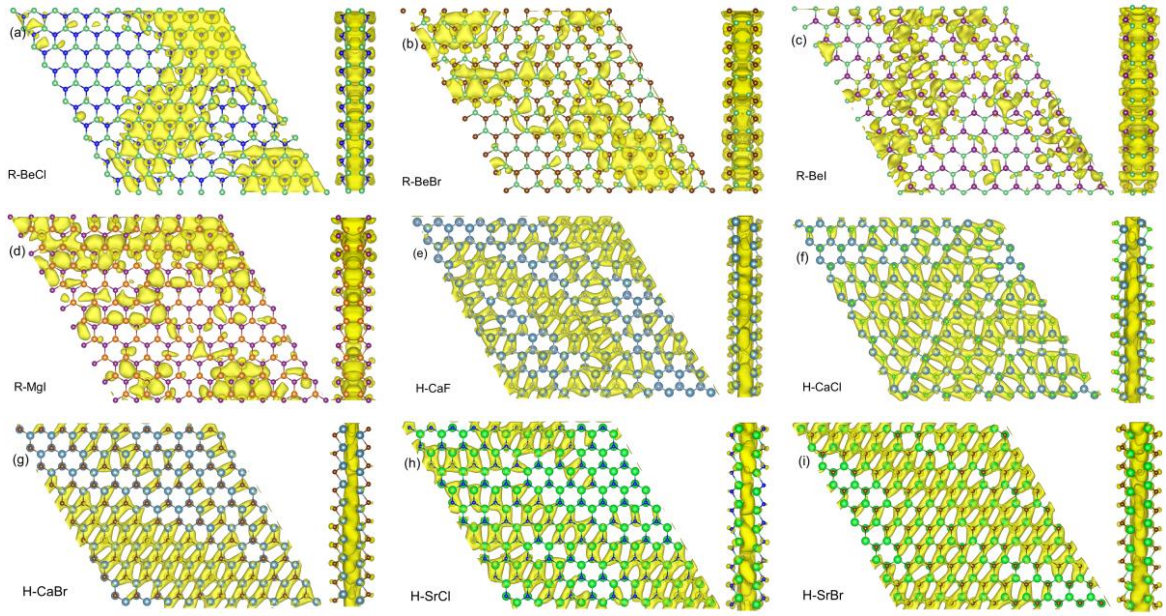


Figure S12. Top and side views of exciton wave function of BeCl(a), BeBr(b), BeI(c), MgI(d), CaF(e), CaCl(f), CaBr(g), SrCl(h), SrBr(i).

Table S3. The calculated electronic band gaps (E_g) based on PBE, HSE06 and G_0W_0 (BGW(BerkeleyGW) software and VASP software), optical band gaps (E_g^{opt}), exciton binding energy of MX monolayers. The optical band gap (E_g^{opt}), defined as the energy corresponding to the first prominent peak. The exciton binding energy (E_b) is defined as the difference between the energy of the optical band gap and the quasiparticle band gap in transition matrix. The unit is eV. D and ID stand for Direct and InDirect bandgaps.

	Type	E_g/PBE	E_g/HSE06	E_g/G_0W_0(BGW)	E_g/G_0W_0(VASP)	E_g^{opt}	E_b
R-BeCl	D	1.94	2.79	3.95	4.00	2.86	1.18
R-BeBr	D	2.37	3.29	4.52	4.19	3.34	1.19
R-BeI	ID	2.06	2.99	4.14	3.95	3.37	1.10
R-MgI	ID	1.29	1.90	3.21	2.96	2.41	2.59
H-CaF	ID	0.35	0.74	1.36	1.21	1.33	0.73
H-CaCl	ID	0.32	0.59	0.99	1.16	0.91	0.49
H-CaBr	ID	0.20	0.43	0.76	0.96	0.79	0.39
H-SrCl	ID	0.28	0.85	0.89	1.07	0.74	0.28
H-SrBr	ID	0.17	0.73	0.70	0.66	0.64	0.56

The MX monolayers with inherent metallicity for electrochemical water splitting

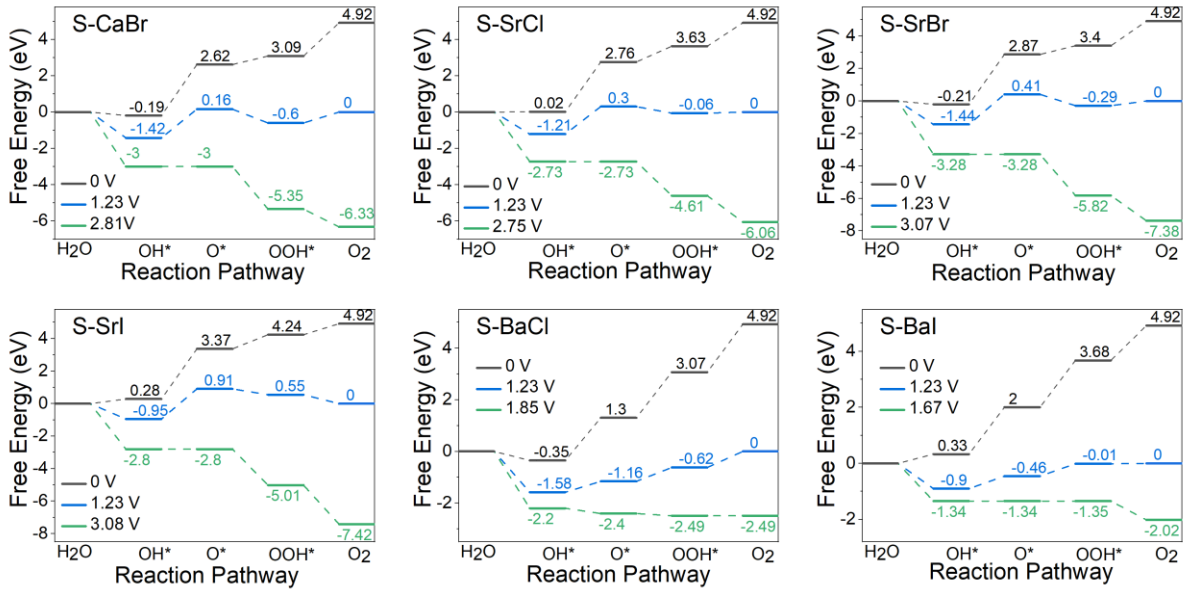


Figure S13. The free energy diagrams for water oxidation half-reactions in MX monolayer.

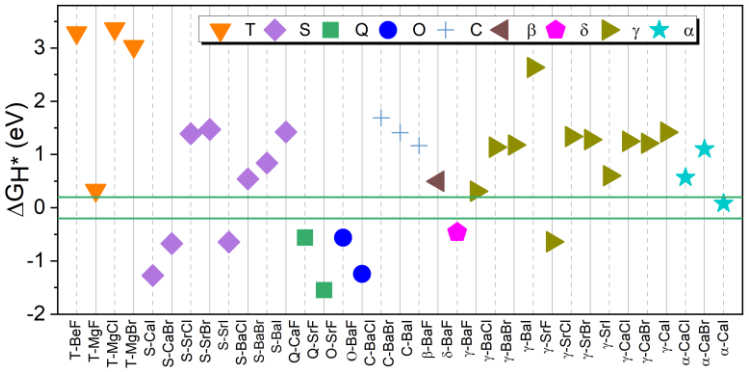


Figure S14. The adsorption free energy (ΔG_{H*}) of hydrogen on MX monolayer. Green lines represent the adsorption energy -0.2 and 0.2 eV. It is commonly accepted that a material with $|\Delta G_{H*}| < 0.2$ eV is considered an excellent HER catalyst.

The MX monolayers with inherent metallicity as an anode material for ion batteries

We first examine the most favorable adsorption sites for a single A atom on the surface of the MX monolayers. In order to avoid interactions between the adjacent metal adatoms, large enough super-cells of 2×2×1 for MX monolayers. To investigate the adsorption of higher concentrations of A atoms, we considered the adsorption on both sides and used a 2×2×1 supercell for all those predicted monolayers. To obtain further insight into the adsorption process, we investigated the charge transfer by carrying out the valence electron localization function (ELF).

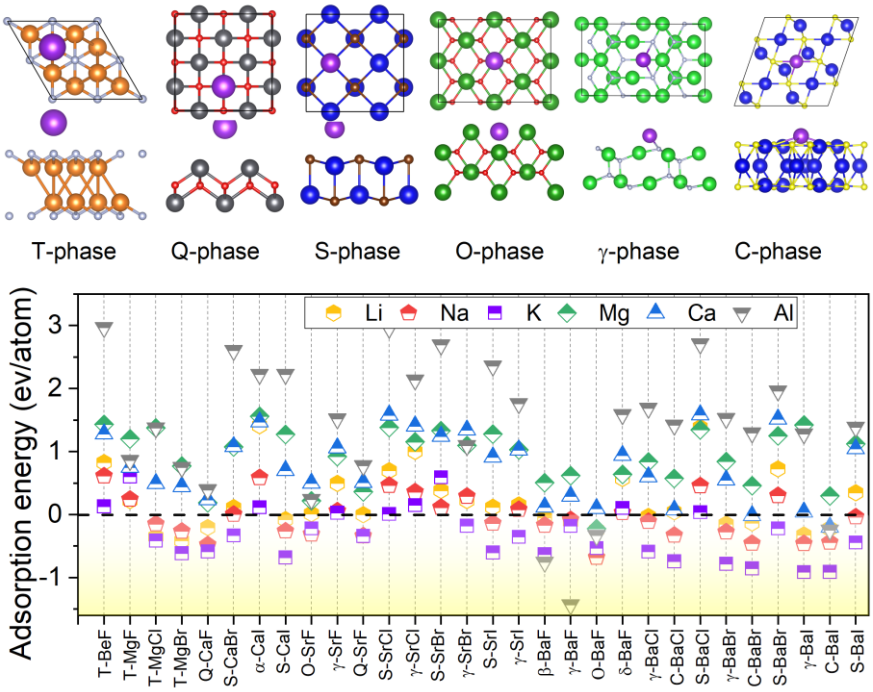


Figure S15. The side and top views of ion adsorption on MX monolayers, metal (A = Li, Na, K, Mg, Ca, Al) ions adsorption energies.

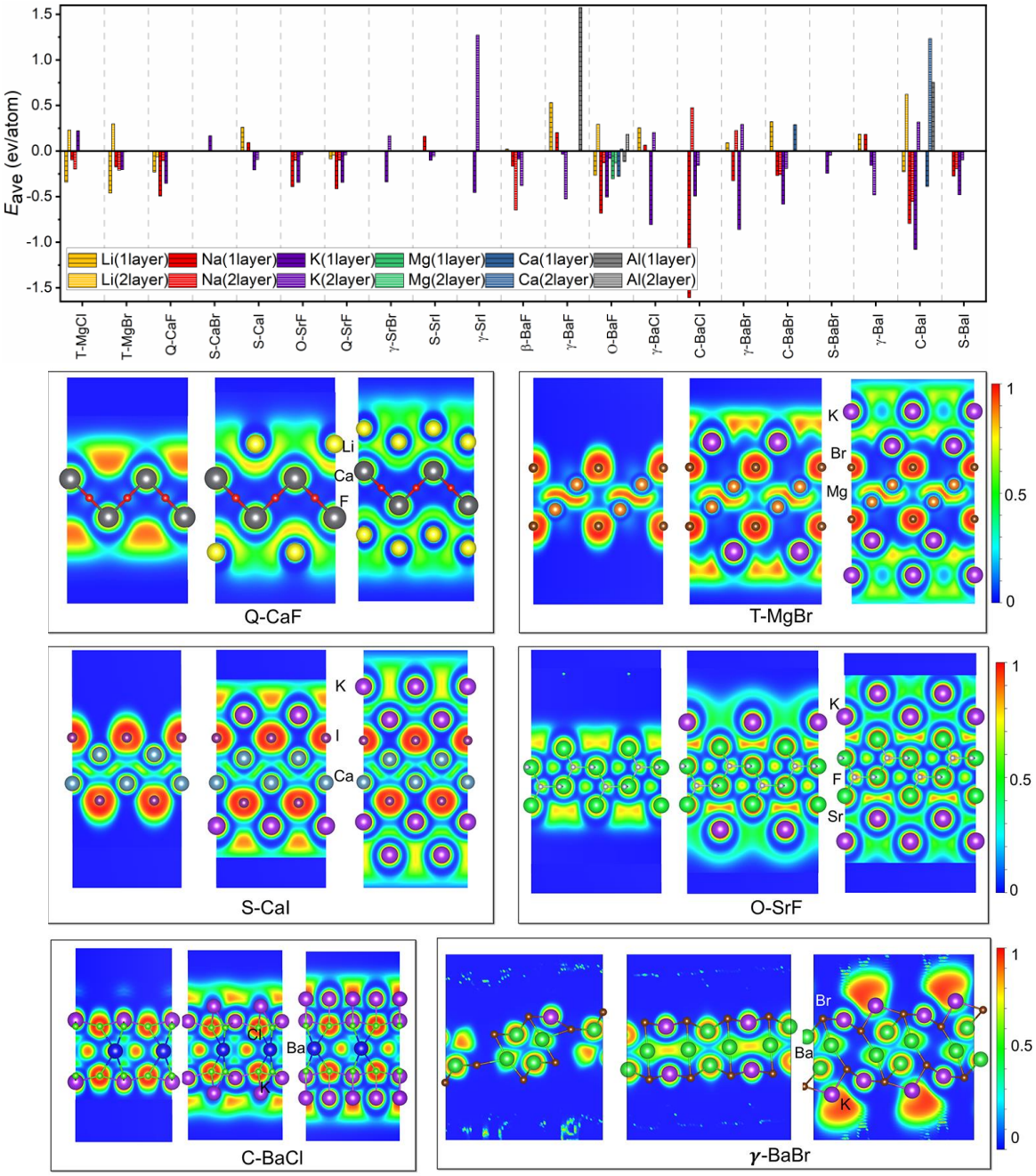
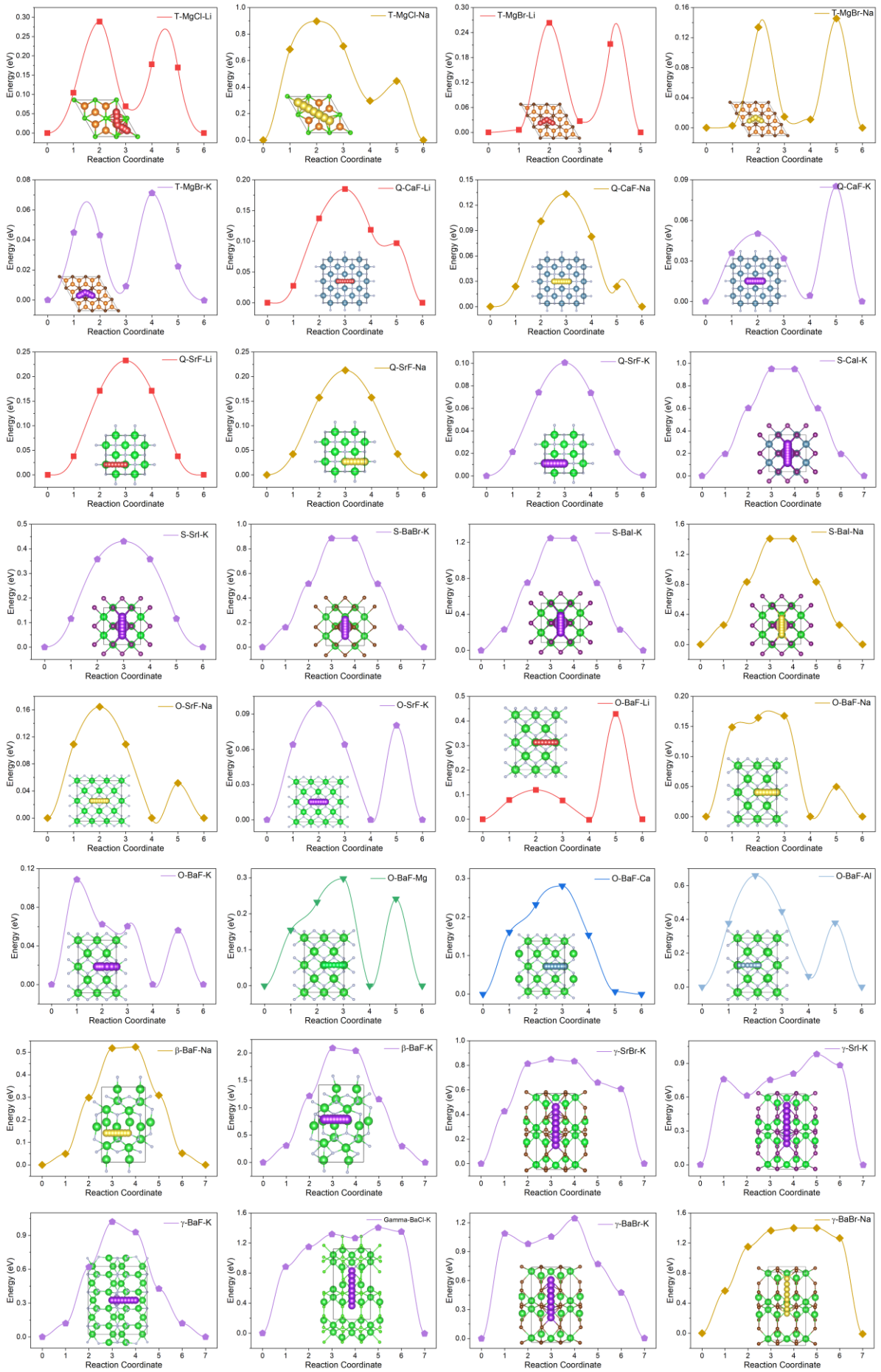


Figure S16. The average adsorption energy as a function of A concentration for MX monolayers. Electron localization functions of (111 and 011) section with one layer and two layers of A atoms. Red represents the electrons that are highly localized and blue signifies the electrons with almost no localization.



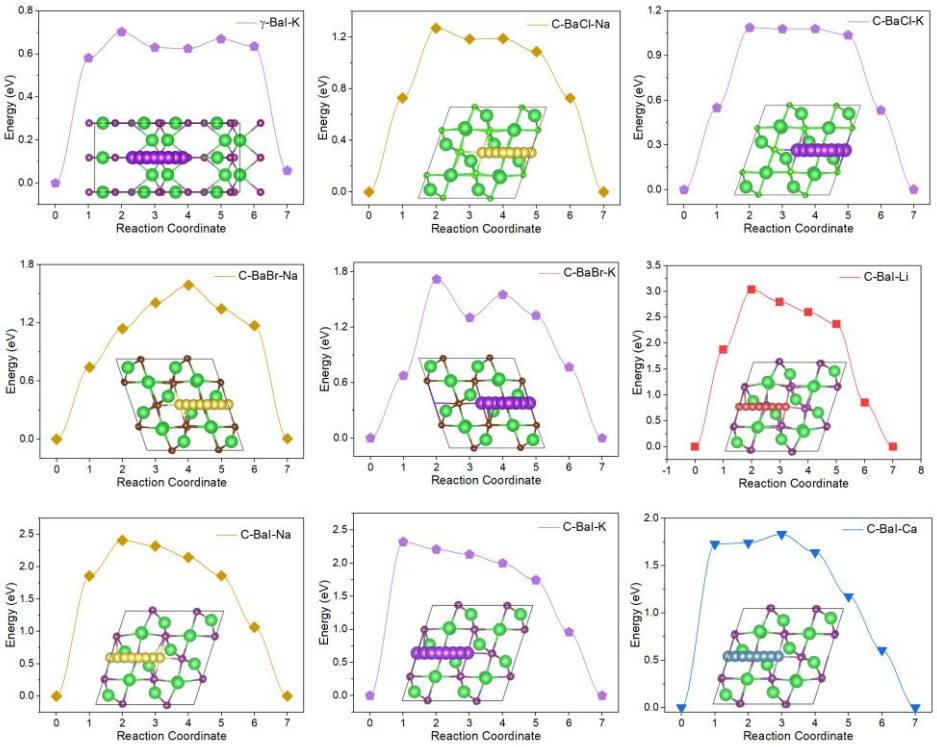
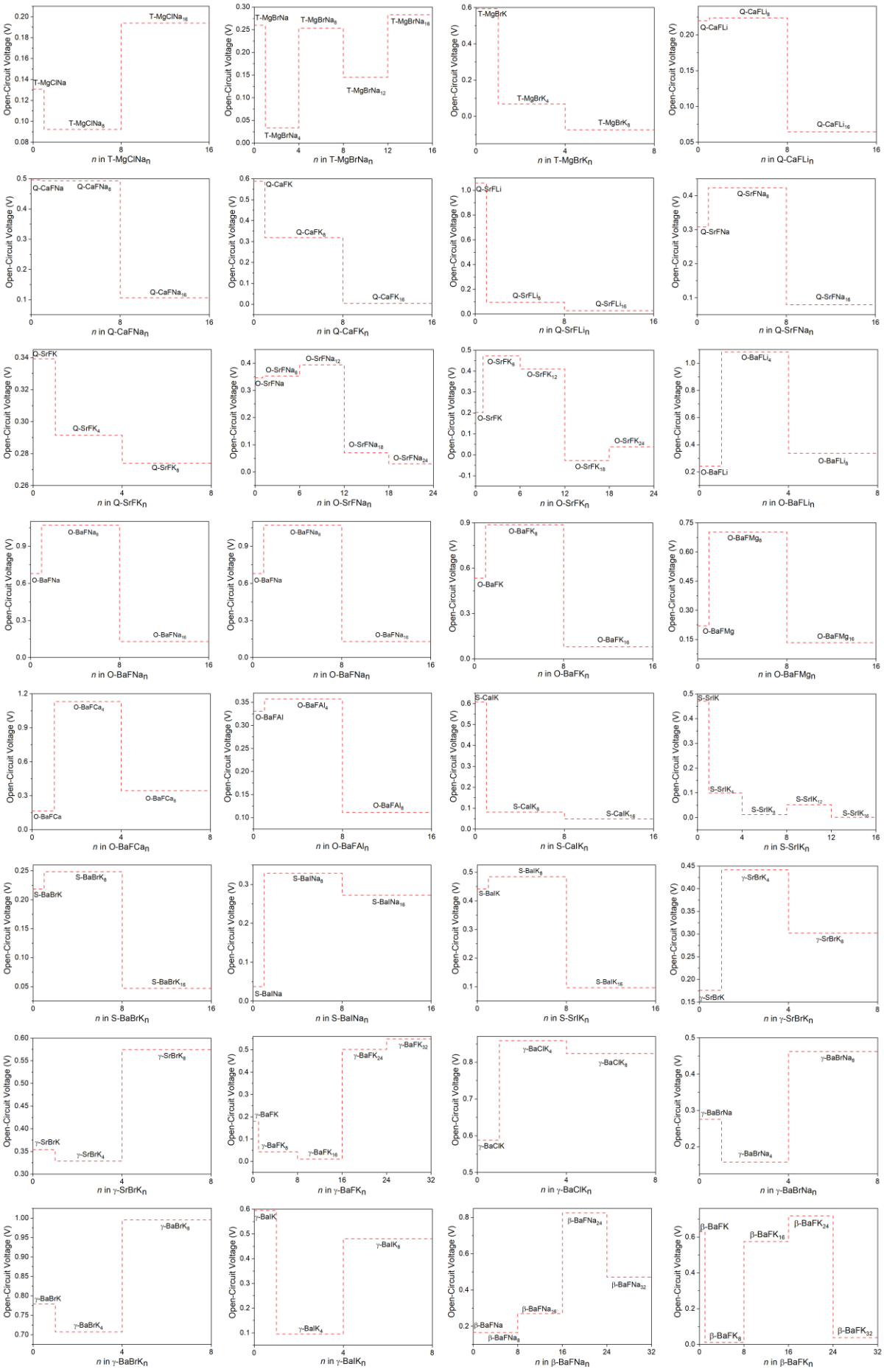


Figure S17. The calculated A-ion diffusion profiles of MX monolayers.



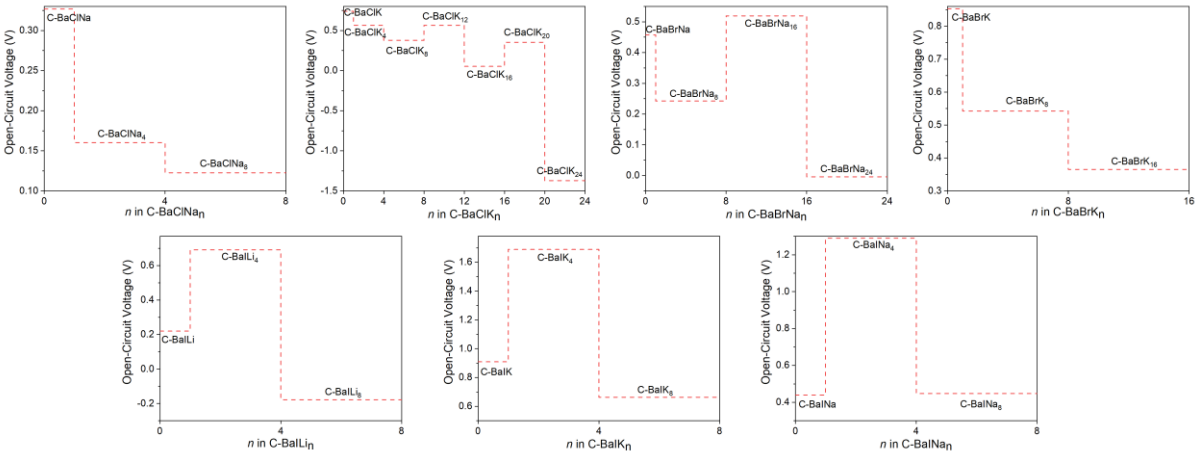


Figure S18. The OCV value as a function of the concentrations of A ions in MXAn.

Bulk phases of MX crystals

To discuss thermodynamic stability of layered bulk MX crystals, we generated convex hull diagram of layered bulk MX phase as in Figures S3. Most of the stable MX monolayers can form layered structure as shown in the Figure S6.

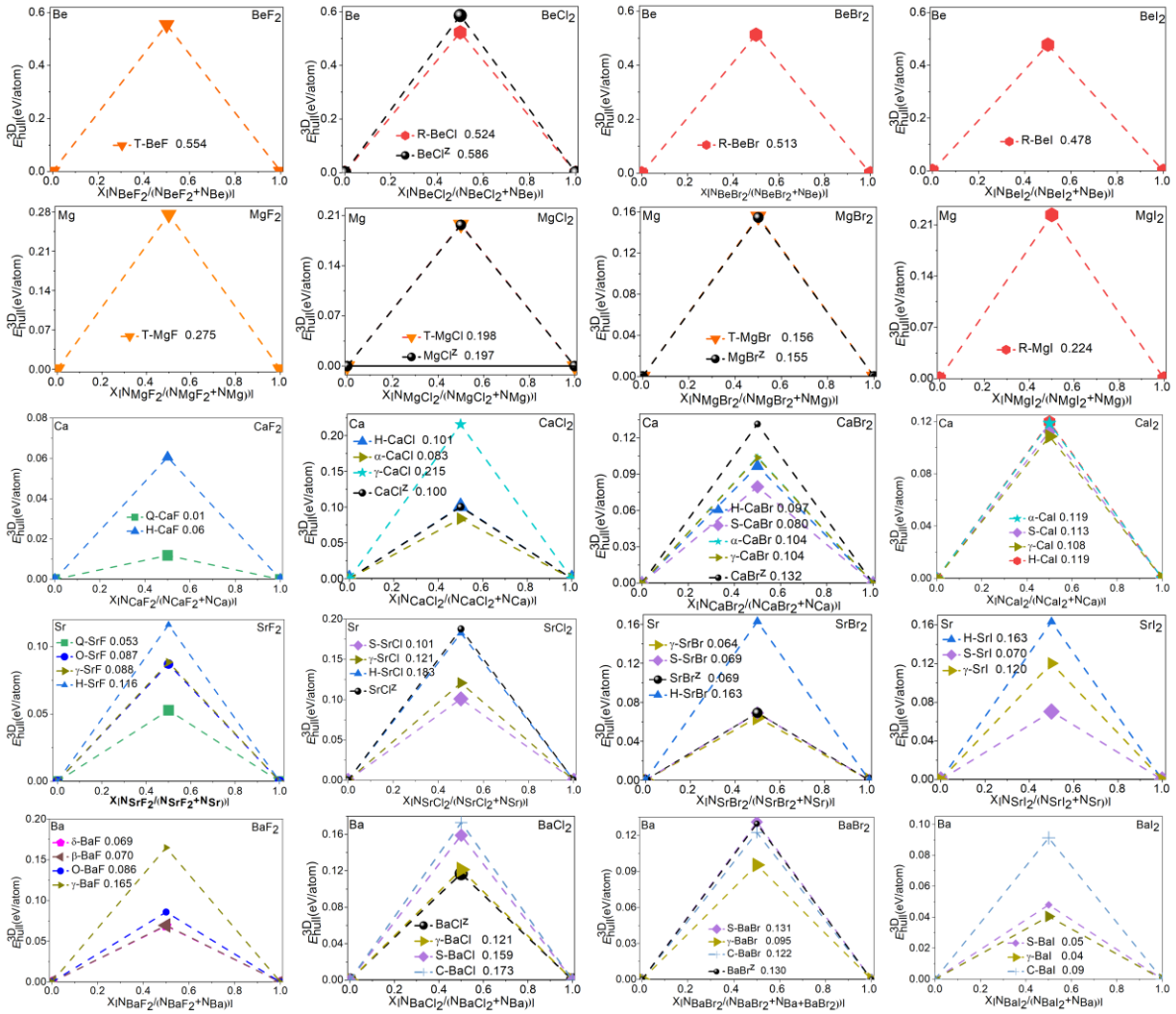
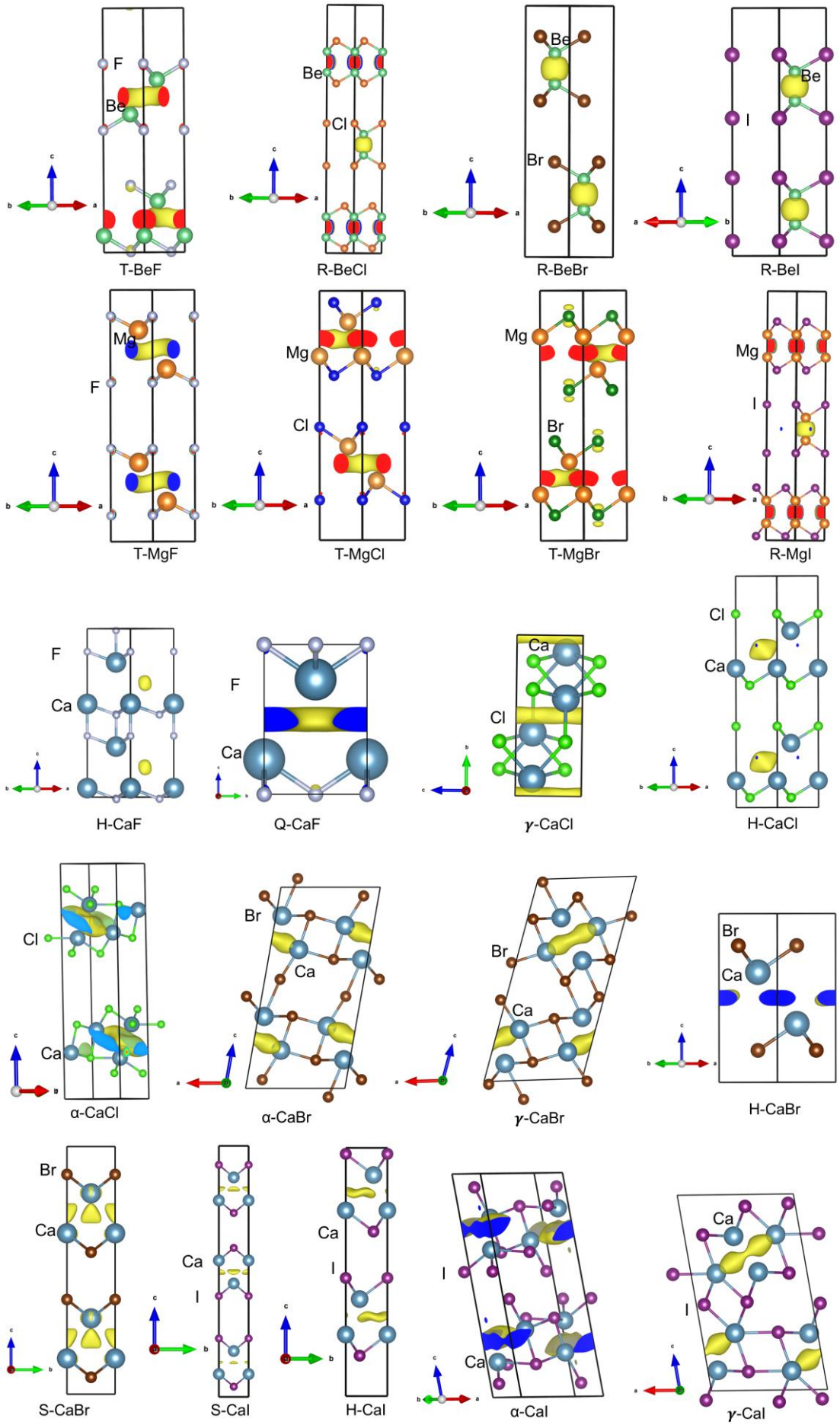
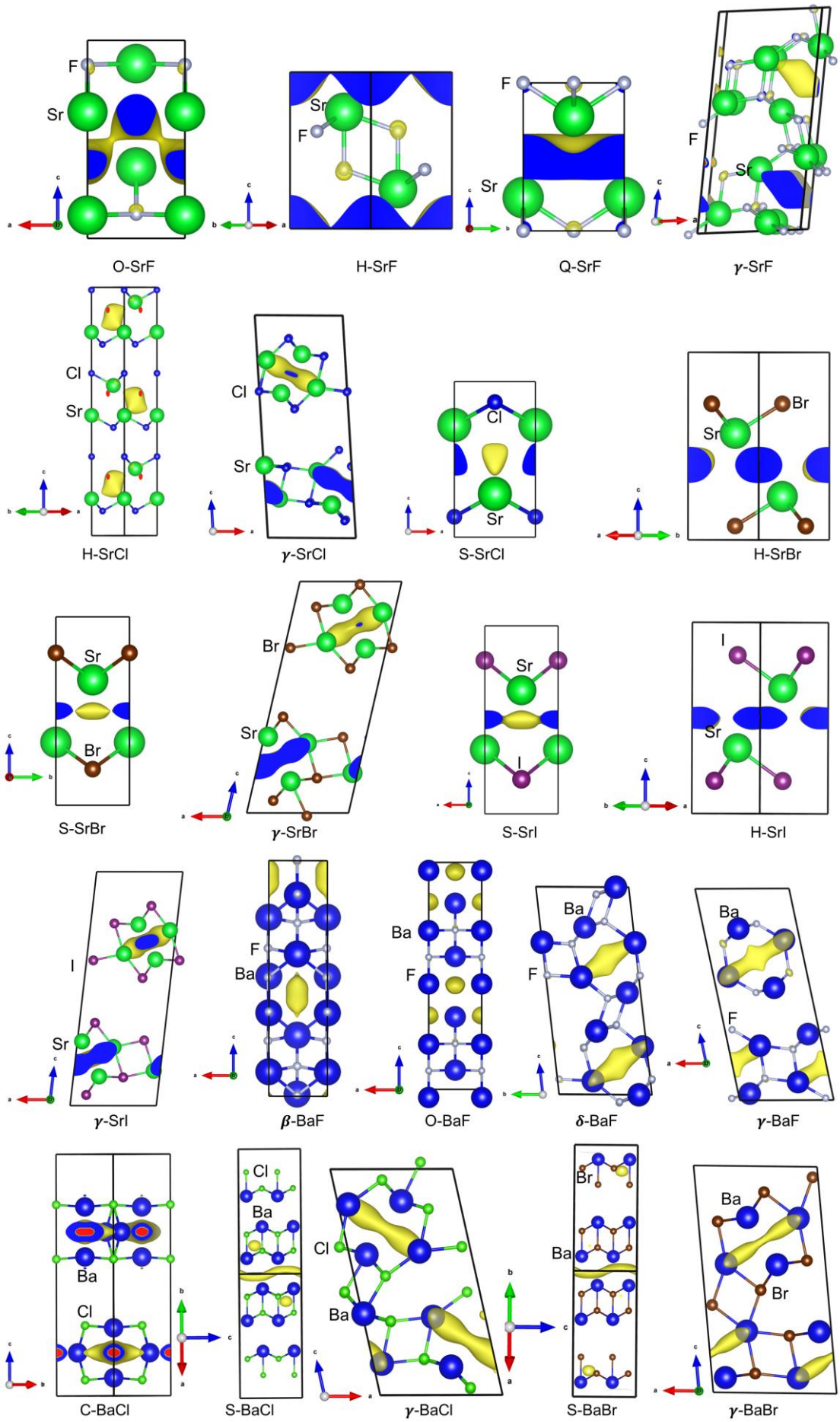


Figure S19. Stability of MX (M = Be, Mg, Ca, Sr, Ba; X = F, Cl, Br, I) monolayers: Convex hull diagrams in their isolated forms at 0 K. We also compared the structure of the same ratio in Zhang's work[21], as ref *z*.





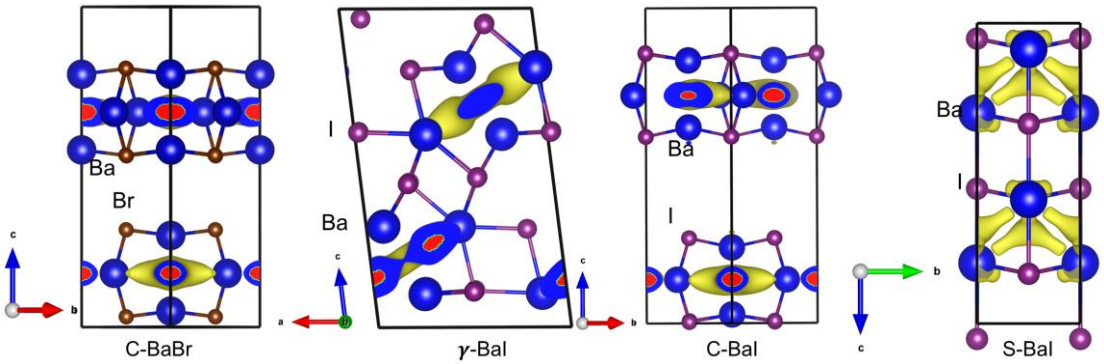


Figure S20. The partial charge density for states near the Fermi level of these MX bulk electrides.

Synthesizability of MX monolayers

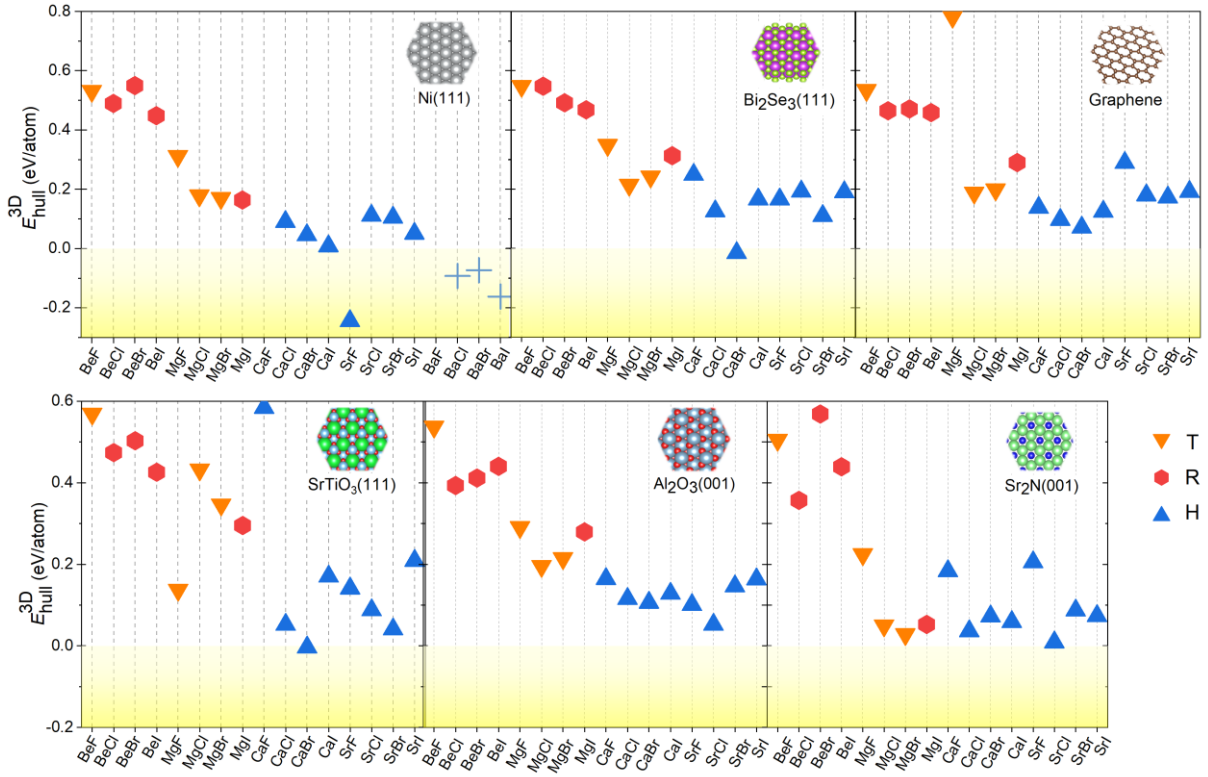


Figure S21. The synthesis of 2D MX monolayers adopts the bottom-up method. Growth of MX crystals: convex hull diagrams in MX monolayer growth on different substrates.

Rerferences

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