Electronic Supplementary Material (ESI) for Materials Advances.

Electronic Supplementary Information

Prediction of New Phase 2D C_{2h} Group III Monochalcogenides with Direct Bandgaps and Highly Anisotropic Carrier Mobilities

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I. First-principles Structural Search via the Particle Swarm Optimization Algorithm.

In our study, computational structural search for possible polymorphs of group III monochalcogenide monolayers is based on the Particle Swarm Optimization (PSO) method as implemented in the CALYPSO (Crystal structure AnaLYsis by Particle Swarm Optimization)[1] code. The search does not need any preliminary structural information except for the chemical compositions (in this case, 1:1). The approach was initialized based on a number of randomly generated structures with certain symmetries, and the atomic coordinates are generated based on the crystallographic symmetry operations. It is followed by local optimizations through the VASP code. 60% of the structures with lower energies from the first generation are selected to construct the structures for the next generation by the PSO algorithm, and the other 40% of the structures are again randomly generated. During the process, identical structures are forbidden using the technique of bond characterization matrix. The effectiveness and validity in structural searches for 2D layered materials were evaluated in 2012[1]. In our study, 3600 structures are sampled from the free energy landscape.

II. Additional Computational Results

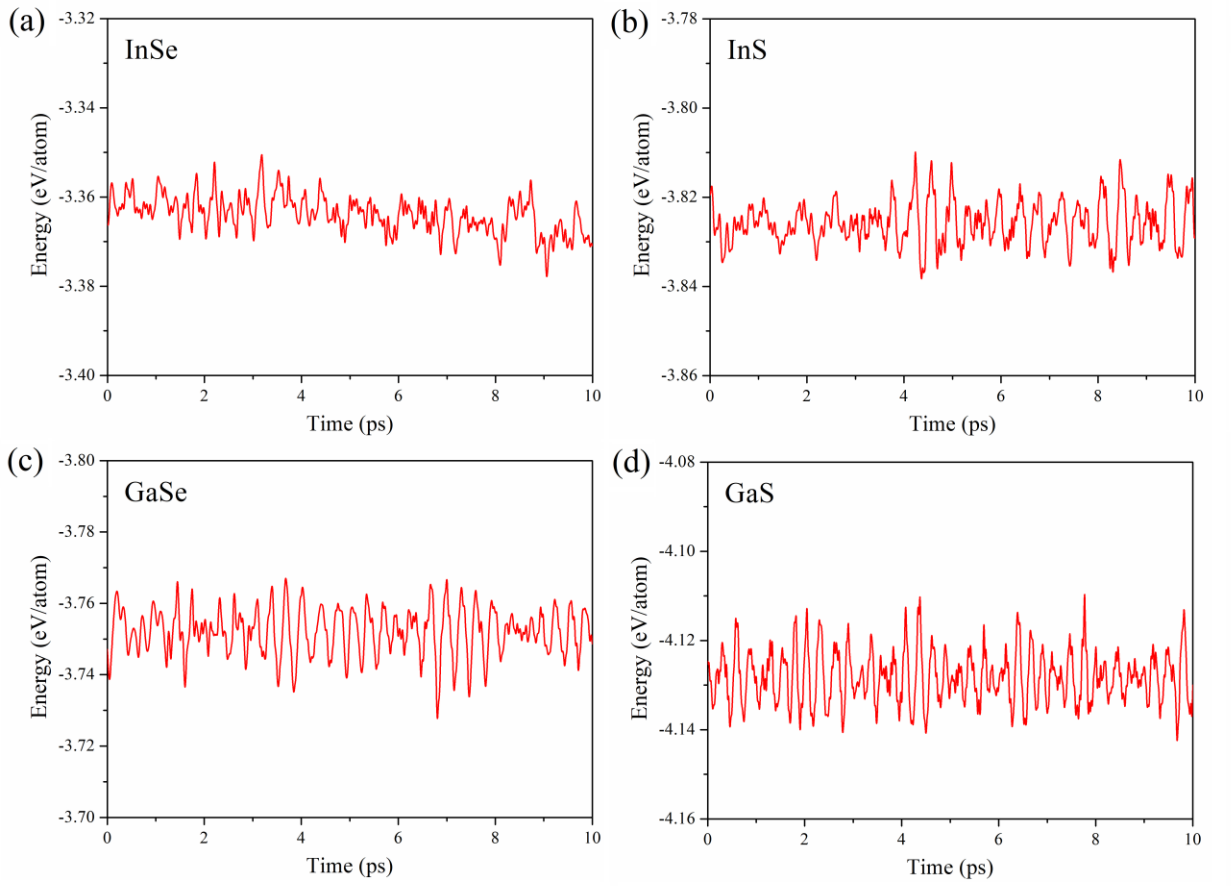

Fig. S1 Fluctuations of the potential energies of monolayer D_{3h} (a) InSe, (b) InS, (c) GaSe, and (d) GaS during the process of molecular dynamics under a temperature of 300 K.

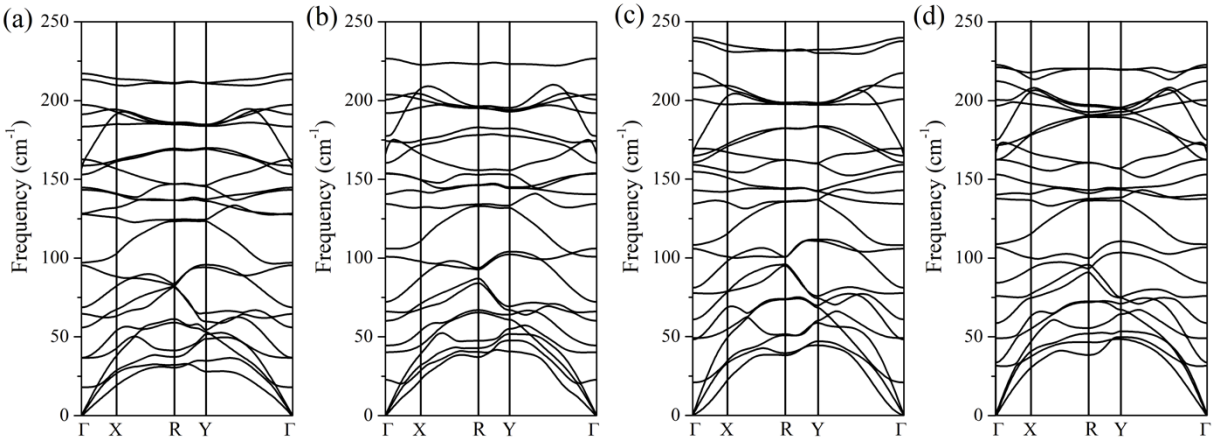

Fig. S2 Phonon spectra of monolayer C_{2h} (a) InSe, (b) InS, (c) GaSe, and (d) GaS.

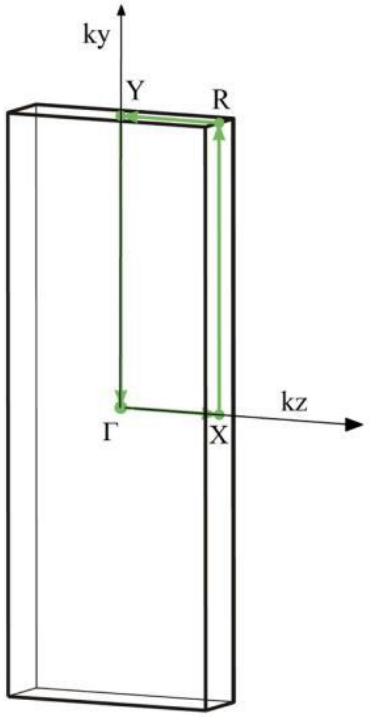

Fig. S3 High-symmetry path in the Brillouin zone of monoclinic C_{2h} monolayers for phonon spectra and band structure plots[2].

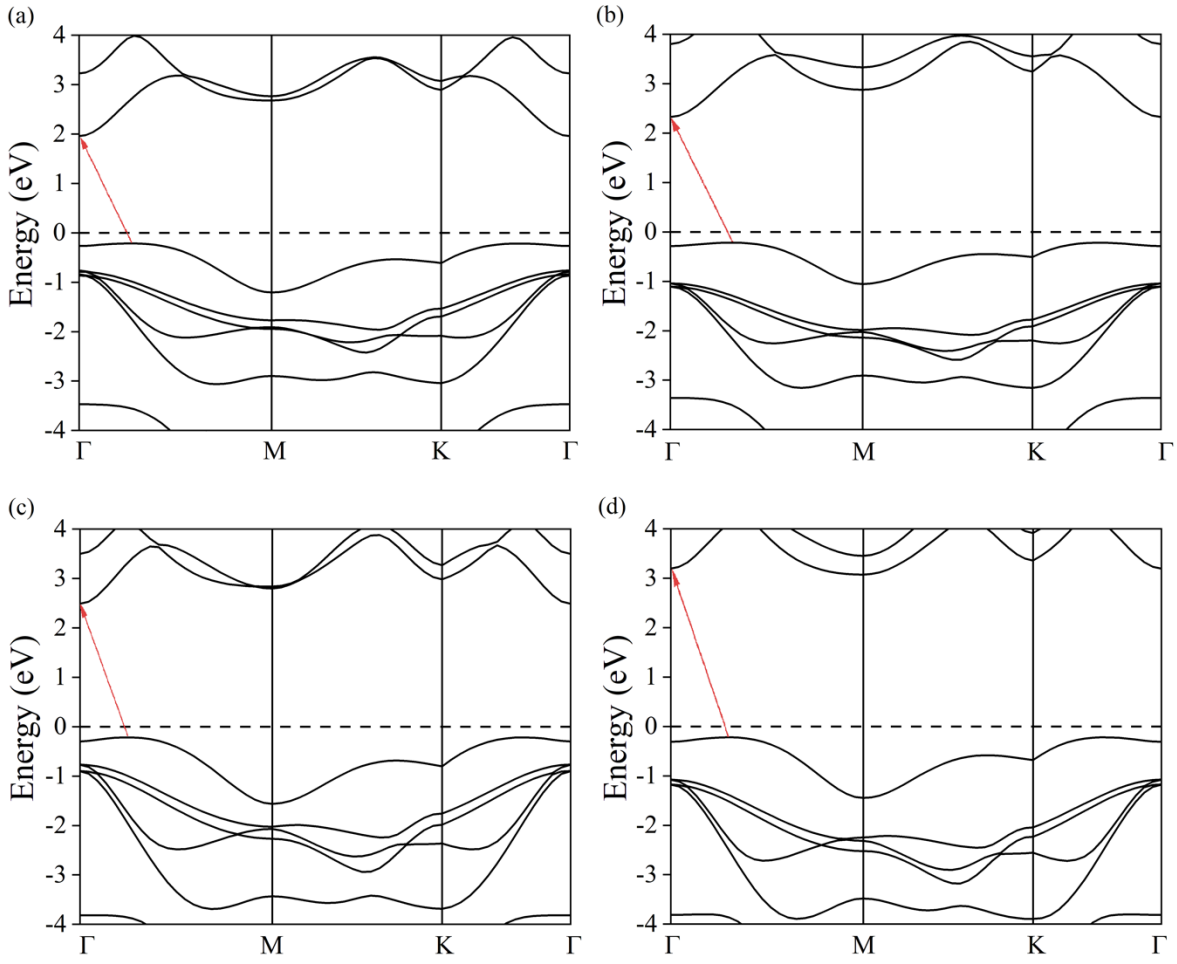

Fig. S4 Computed electronic band structures of monolayer D_{3h} (a) InSe, (b) InS, (c) GaSe, and (d) GaS at the HSE06 level. The red arrows point from VBM to CBM.

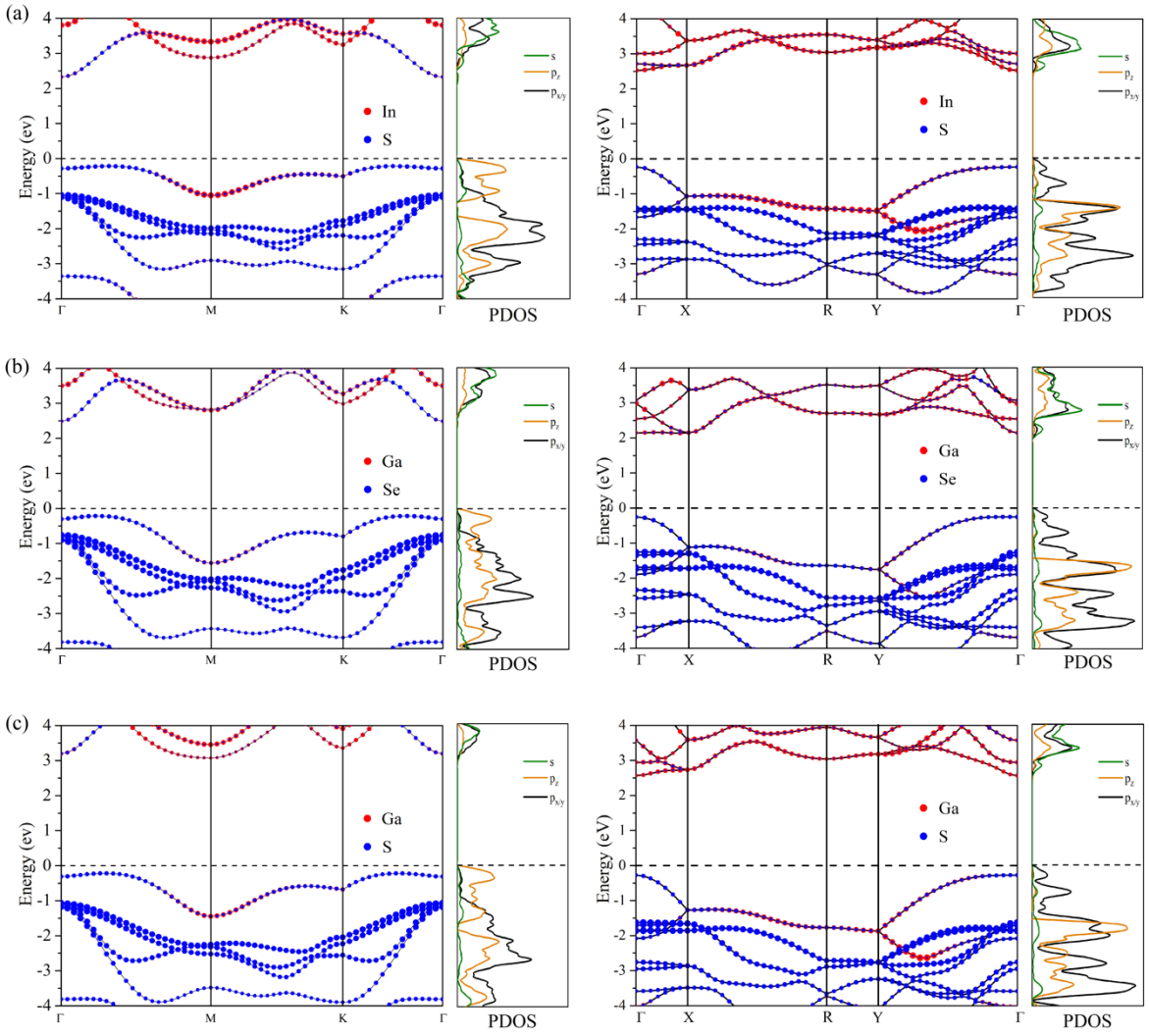

Fig. S5 Projected band structures and projected density of states (PDOS) (computed at the HSE06 level) of monolayer (a) InS, (b) GaSe, and (c) GaS with D_{3h} phase on the left and C_{2h} phase on the right. In the projected band structures, the red and blue color represents In/Ga and Se/S respectively. Decompositions into atomic-orbital contribution are also shown in the PDOS diagrams, with the green color representing the s orbital, orange representing the p_z orbital, and black representing the $p_{x/y}$ orbital. All these orbitals are from both In and Se atoms.

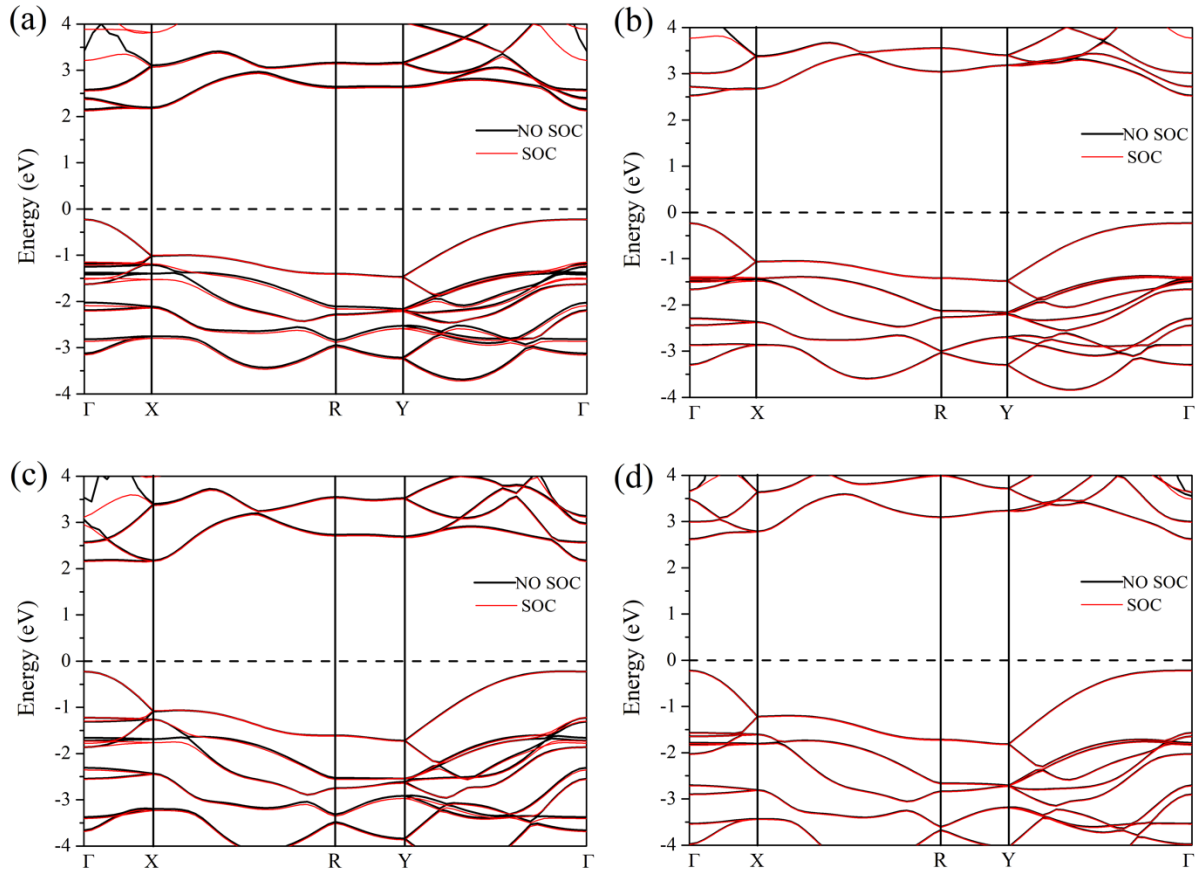

Fig. S6 Comparison between the calculated band structures of monolayer C_{2h} (a) InSe, (b) InS, (c) GaSe, and (d) GaS at the HSE06 level with and without SOC (red curves represent bands with SOC and black curves represent bands without SOC). The influence of SOC on the band structures are negligible especially near the conduction and valence band edges.

Table S1. Calculated band gaps of both monolayer D_{3h} and C_{2h} *MX*s at the level of HSE06.

	InSe	InS	GaSe	GaS
D_{3h}	2.17 eV	2.54 eV	2.70 eV	3.29 eV
C_{2h}	2.38 eV	2.76 eV	2.39 eV	2.84 eV

Table S2. Percentage contribution of In and Se to the conduction and valence band-edge states (CBM and VBM respectively) in D_{3h} and C_{2h} *MX*s.

		InSe		InS		GaSe		GaS	
		D_{3h}	C_{2h}	D_{3h}	C_{2h}	D_{3h}	C_{2h}	D_{3h}	C_{2h}
CBM	In/Ga	51.8%	71.0%	54.8%	81.8%	53.0%	65.1%	54.8%	78.2%
	Se/S	48.2%	29.0%	45.2%	18.2%	47.0%	34.9%	45.2%	21.8%
VBM	In/Ga	42.1%	47.0%	42.5%	50.5%	41.3%	42.9%	42.6%	46.9%
	Se/S	57.9%	53.0%	57.2%	49.5%	58.7%	57.1%	57.4%	53.1%

Table S3. Calculated carrier effective masses (m^*_e for electrons and m^*_h for holes) along *x*- and *y*-direction of both D_{3h} and C_{2h} single-layer *MX*s at 300 K. The data are demonstrated as a ratio of effective mass (m^*) to the rest mass of an electron (m_0).

		m^*_e/m_0		m^*_h/m_0	
		x	y	x	y
InSe	D_{3h}	0.190	0.190	1.142	1.142
	C_{2h}	0.743	0.216	0.304	4.020
InS	D_{3h}	0.245	0.245	1.385	1.385
	C_{2h}	0.486	0.303	0.257	5.154
GaSe	D_{3h}	0.161	0.161	0.611	0.611
	C_{2h}	1.484	0.158	0.453	6.481
GaS	D_{3h}	0.218	0.218	1.064	1.064
	C_{2h}	0.490	0.228	0.343	30.66

III. POSCAR Files of C_{2h} Structures

InSe:

InSe

1.000

11.2250446083451951 0.0000000000000000 -0.1210210517727577

0.0000000000000000 4.1032547315178496 0.0000000000000000

-0.5341247050601100 0.0000000000000000 28.9889384127153740

In Se

4 4

Direct

0.9501884683147355 0.0000000003814264 0.3398188270133299

0.1912385476610227 0.9999999984596641 0.3174743988198147

0.4501884572401523 0.5000000003938823 0.3398188272450930

0.6912385513619341 0.4999999984637853 0.3174743983721725

0.8592782672018444 0.5000000136272007 0.3875576975139247

0.2822047474439132 0.4999999875235801 0.2697402313766207

0.3592782495405587 0.0000000136226674 0.7302597686233793

0.7822047642358571 0.9999999875277865 0.2697402322090696

InS:

InS

1.000

11.0788019857266722 0.0000000000000000 -0.1517440683223216

0.0000000000000000 3.9676737382682337 0.0000000000000000

-1.0001455100055492 0.0000000000000000 32.9729129921839217

In S

4 4

Direct

0.9495912346765821 0.0000000003851426 0.2079711351067395

0.1918732693034784 0.9999999984559764 0.1882300536613529

0.4495912236019990 0.5000000003975984 0.2079711352464403

0.6918732730043901 0.4999999984600976 0.1882300533915257

0.8608195648405327 0.5000000136417952 0.2459254046153947

0.2806259618009150 0.4999999875089500 0.1502770758920362

0.3608195471792470 0.0000000136372620 0.8497229241079638

0.7806259785928590 0.9999999875131564 0.1502770763938153

GaSe:

GaSe

1.000

9.9698239809349740 0.0000000000000000 0.0000000000000000

0.0000000000000000 3.8183160487268148 0.0000000000000000

0.0000000000000000 0.0000000000000000 23.2392309794416150

Ga Se

4 4

Direct

0.9510015703815994 0.0000000020373108 0.5126927807166536

0.1904108338710984 0.9999999966312741 0.4872902275606944

0.4510015673776948 0.5000000033434375 0.5126927802680817

0.6904108353785574 0.4999999959031740 0.4872902286133284

0.8584900272283703 0.5000000355984824 0.5697018985188972

0.2830075962816352 0.4999999649777394 0.4302981014811028

0.3584900189683466 0.0000000322808802 0.5697018985123049

0.7830076035127148 0.9999999692277085 0.4302981023168826

GaS:

GaS

1.000

9.8114269559567813 0.0000000000000000 0.0000000000000000

0.0000000000000000 3.6527631618665031 0.0000000000000000

-0.4532474522176225 0.0000000000000000 33.6617098347353689

Ga S

4 4

Direct

0.9497949632774265 0.0000000003832596 0.2117547658235674

0.1916819741199376 0.9999999984575964 0.1942156800423733

0.4497949522028434 0.5000000003957155 0.2117547659667030

0.6916819778208492 0.4999999984617176 0.1942156797659118

0.8592483263200351 0.5000000136229303 0.2474686086314967

0.2821847669041161 0.4999999875280849 0.1584751536344658

0.3592483086587491 0.0000000136183971 0.8415248463655343

0.7821847836960599 0.9999999875322912 0.1584751541485820

IV. References

1. Wang, Y.; Lv, J.; Zhu, L.; Ma, Y. CALYPSO: A Method for Crystal Structure Prediction. *Comput. Phys. Commun.* **2012**, *183*, 2063-2070.
2. Hinuma, Y.; Pizzi, G.; Kumagai, Y.; Oba, F.; Tanaka, I. Band Structure Diagram Paths Based on Crystallography. *Computational Materials Science* **2017**, *128*, 140-184.