Supplementary materials for

Sliding Ferroelectricity of Multilayer h-BN

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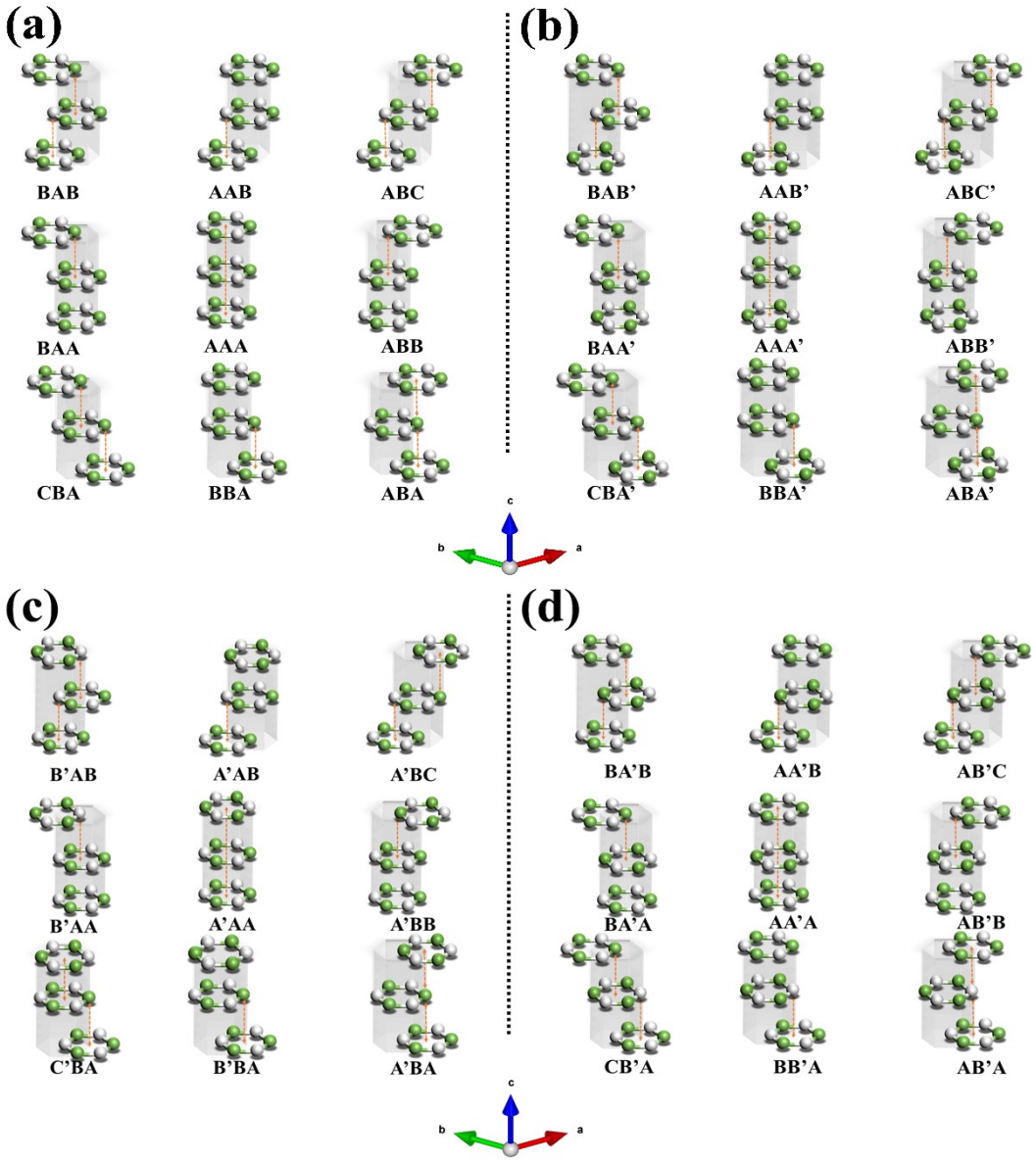

Figure S1. Structural illustration of 36 configurations of the three-layer h-BN.

Table S1. Parameters of different structures of trilayer h-BN. Interlayer spacing I (Å) and interlayer spacing II (Å) are the vertical distance between the top layer and the middle layer, and the vertical distance between the middle layer and the bottom layer.

Stacking Order	BAA	AAA	ABB	BAB	AAB	ABC	CBA	BBA	ABA
Interlayer spacing I (Å)	3.324	3.606	3.327	3.326	3.601	3.327	3.328	3.609	3.326
Interlayer spacing II (Å)	3.603	3.606	3.601	3.326	3.329	3.327	3.328	3.328	3.326
Point group	3m	m2	3m	m2	3m	3m	3m	3m	m2
Energy (eV)	-53.439	-53.418	-53.439	-53.461	-53.439	-53.461	-53.461	-53.439	-53.461
Dipole (10^{-4} eÅ)	-63.8	/	59.5	/	60.6	126.5	-126.8	-61.6	/
Band Gap (eV)	4.123	3.921	4.115	4.386	4.120	4.308	4.309	4.120	4.427
Band Character	Direct	Direct	Indirect	Indirect	Direct	Indirect	Indirect	Indirect	Indirect
Stacking Order	BAA’	AAA’	ABB’	BAB’	AAB’	ABC’	CBA’	BBA’	ABA’
Interlayer spacing I (Å)	3.325	3.598	3.327	3.326	3.605	3.331	3.329	3.605	3.330
Interlayer spacing II (Å)	3.339	3.341	3.341	3.565	3.578	3.578	3.362	3.362	3.365
Point group	3m	3m	3m	3m	3m	3m	3m	3m	3m
Energy (eV)	-53.459	-53.438	-53.460	-53.434	-53.413	-53.434	-53.452	-53.430	-53.452
Dipole (10^{-4} eÅ)	-63.6	4	62.3	-63.4	1.5	60.1	-59.6	-1.4	-59.6
Band Gap (eV)	4.277	4.097	4.385	4.149	3.961	4.125	4.023	3.868	4.143
Band Character	Indirect	Indirect	Indirect	Indirect	Indirect	Indirect	Direct	Direct	Direct
Stacking Order	B’AA	A’AA	A’BB	B’AB	A’AB	A’BC	C’BA	B’BA	A’BA
Interlayer spacing I (Å)	3.574	3.349	3.358	3.360	3.338	3.359	3.357	3.338	3.361
Interlayer spacing II (Å)	3.605	3.604	3.600	3.325	3.324	3.327	3.325	3.327	3.328
Point group	3m	3m	3m	3m	3m	3m	3m	3m	3m
Energy (eV)	-53.413	-53.438	-53.431	-53.434	-53.460	-53.452	-53.434	-53.460	-53.452
Dipole (10^{-4} eÅ)	-0.3	-1.7	-0.1	62.2	63.6	61.7	62.5	64.9	60.8
Band Gap (eV)	3.959	4.103	3.862	4.154	4.277	4.020	4.121	4.385	4.140
Band Character	Indirect	Indirect	Direct	Indirect	Indirect	Direct	Indirect	Indirect	Indirect
Stacking Order	BA’A	AA’A	AB’B	BA’B	AA’B	AB’C	CB’A	BB’A	AB’A
Interlayer spacing I (Å)	3.360	3.339	3.573	3.360	3.347	3.577	3.364	3.341	3.569
Interlayer spacing II (Å)	3.342	3.340	3.341	3.360	3.361	3.362	3.573	3.574	3.569
Point group	3m	m2	3m	m2	3m	3m	3m	3m	m2
Energy (eV)	-53.433	-53.460	-53.452	-53.407	-53.388	-53.426	-53.426	-53.452	-53.444
Dipole (10^{-4} eÅ)	-1.2	/	1.8	/	1.4	0.5	-0.1	-0.4	/
Band Gap (eV)	4.120	4.351	4.135	3.964	4.109	3.952	3.948	4.131	3.911
Band Character	Direct	Indirect	Indirect	Indirect	Indirect	Direct	Direct	Indirect	Direct

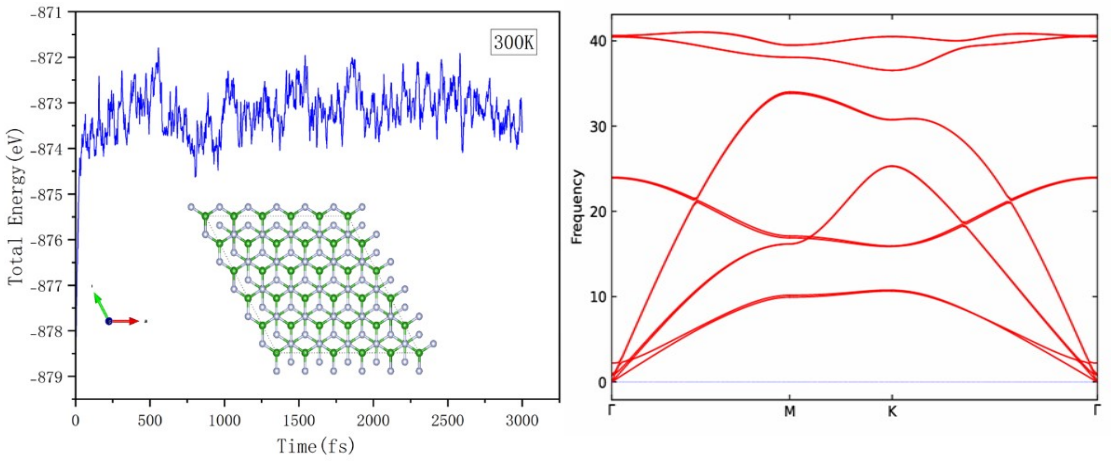

Figure S2. AIMD simulation (300K) and phonon spectrum of bilayer BA stacking h-BN.

Table S2. Lattice parameter, polarization, and energy barrier of the AB stacking order calculated by using different functionals.

Functional	Lattice parameter(Å)	Polarization (pCm^{-1})	Energy barrier (meV/unit cell)
PBE-D3	2.507	2.01	8.56
PBE	2.505	0.10	0.22
LDA	2.485	1.42	5.11
PBEsol	2.498	0.63	2.01
Experiment	2.504	2.25	