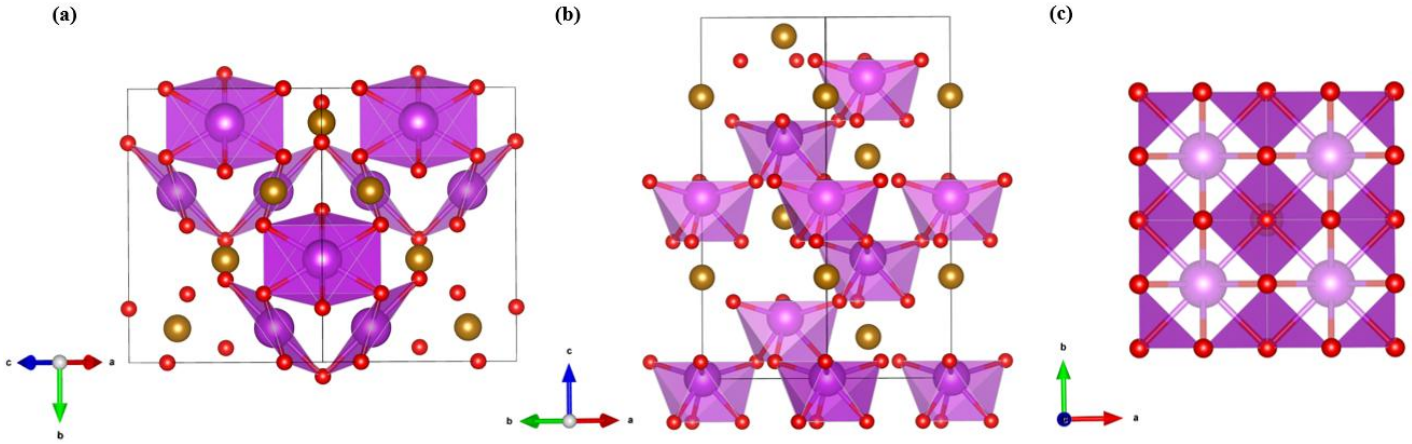

Fig. S1 Bi-O octahedrons of $Fd\bar{3}m$-$BiFeO_3$ (a), $R3c$-$BiFeO_3$ (b) and $Pm\bar{3}m$-$BiFeO_3$ (c). The purple, yellow and red spheres represent the Bi, Fe, and O atoms, respectively.

The local coordination spheres of Fe:

Firstly, the O_1-Fe-O_6 angle of $R3c$ is 167.1° (Fig. S3b), while the O_1-Fe-O_4 angles of $Fd\bar{3}m$ and $Pm\bar{3}m$ are 180° (Fig. S2a and S2c). Secondly, the Fe-O octahedron of $Pm\bar{3}m$ is a standard cubic perovskite structure (centrosymmetric). The O_1-Fe-O_2 angle of $Fd\bar{3}m$ is 86.1°, which is slightly twisted from $Pm\bar{3}m$. Thirdly, there are two types of Fe-O bond lengths in $R3c$, i.e., 2.119 Å (Fe-O_1, Fe-O_2, Fe-O_3) and 1.994 Å (Fe-O_4, Fe-O_5, Fe-O_6), while all the Fe-O bond lengths in $Fd\bar{3}m$ and $Pm\bar{3}m$ are 1.895 Å and 1.930 Å, respectively. (Table SI) The Fe-O bond lengths in $Fd\bar{3}m$ is the shortest one in the $BiFeO_3$ system, which makes its structure most compact and has superior elastic properties.

The local coordination spheres of Bi:

Firstly, the O_1-Bi-O_4 angle of $Fd\bar{3}m$ is 62.7° (Fig. S2d), while the O_1-Bi-O_2 angles of $R3c$ is 113.6° (Fig.S2e). Secondly, there are two types of Bi-O bond lengths in $R3c$, i.e., 2.480 Å (Bi-O_1, Bi-O_2, Bi-O_3) and 2.335 Å (Bi-O_4, Bi-O_5, Bi-O_6), while all the Bi-O bond lengths in $Fd\bar{3}m$ and $Pm\bar{3}m$ are 2.485 Å and 2.729 Å, respectively. (Table SI). Thirdly, $Pm\bar{3}m$ is a standard cubic perovskite structure and the local coordination number of Bi atom is 12, thus it forms the BO_{12} octahedron (Fig.S2f).

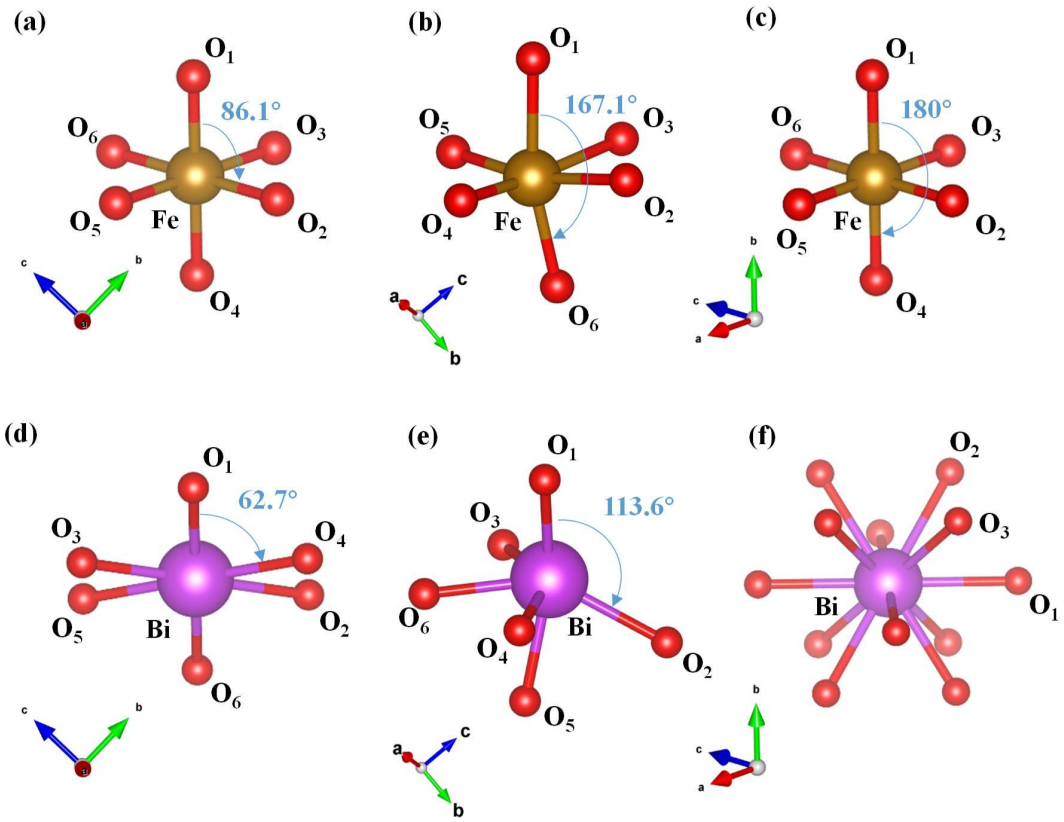

Fig. S2 The atomic coordination situation of Fe in *Fd*$\bar{3}$*m* (a), *R*3*c* (b) and *Pm*$\bar{3}$*m* (c). The atomic coordination situation of Bi in *Fd*$\bar{3}$*m* (d), *R*3*c* (e) and *Pm*$\bar{3}$*m* (f).

Table SI Bond lengths (Å) of *Fd*$\bar{3}$*m*, *R*3*c* and *Pm*$\bar{3}$*m*.

Bond	*Fd*$\bar{3}$*m*	*R*3*c*	*Pm*$\bar{3}$*m*
Fe-O_1	1.8950	2.1185	1.9297
Fe-O_2	1.8950	2.1185	1.9297
Fe-O_3	1.8950	2.1185	1.9297
Fe-O_4	1.8950	1.9942	1.9297
Fe-O_5	1.8950	1.9942	1.9297
Fe-O_6	1.8950	1.9942	1.9297
Bi-O_1	2.4851	2.4802	2.7288
Bi-O_2	2.4851	2.4802	2.7288
Bi-O_3	2.4851	2.4802	2.7288
Bi-O_4	2.4851	2.3345	2.7288
Bi-O_5	2.4851	2.3345	2.7288
Bi-O_6	2.4851	2.3345	2.7288

Table SII Lattice parameters and Wyckoff position of *Fd*$\bar{3}$*m*-$BiFeO_3$, *R*3*c*-$BiFeO_3$ and *Pm*$\bar{3}$*m*-$BiFeO_3$.

Phases	Parameters (**Å, degree**)	Wyckoff Position				
		atom	site	x	y	z
Fd$\bar{3}$*m*	*a*=*b*=*c*=9.9189 *α*=*β*=*γ*=90	Bi	8a	0.125	0.625	0.625
		Fe	48f	0.375	0.125	0.875
		O	96g	0.5	0.803	1.000

*R*3*c*	*a*=*b*=5.6156 *c*=14.0816 *α*=*β*=90 *γ*=120	Bi	18b	0.667	0.333	0.832
		Fe	6a	0.000	0.000	0.778
		O	18b	0.085	0.768	0.877
Pm$\bar{3}$*m*	*a*=*b*=*c*=3.8591 *α*=*β*=*γ*=90	Bi	1a	0.000	0.000	0.000
		Fe	1b	0.500	0.500	0.500
		O	3c	0.500	0.000	0.500

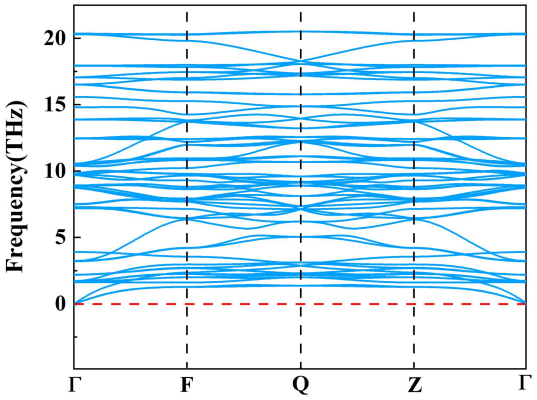

Fig. S3 The Phonon dispersion curve of *Fd*$\bar{3}$*m*-$BiFeO_3$.

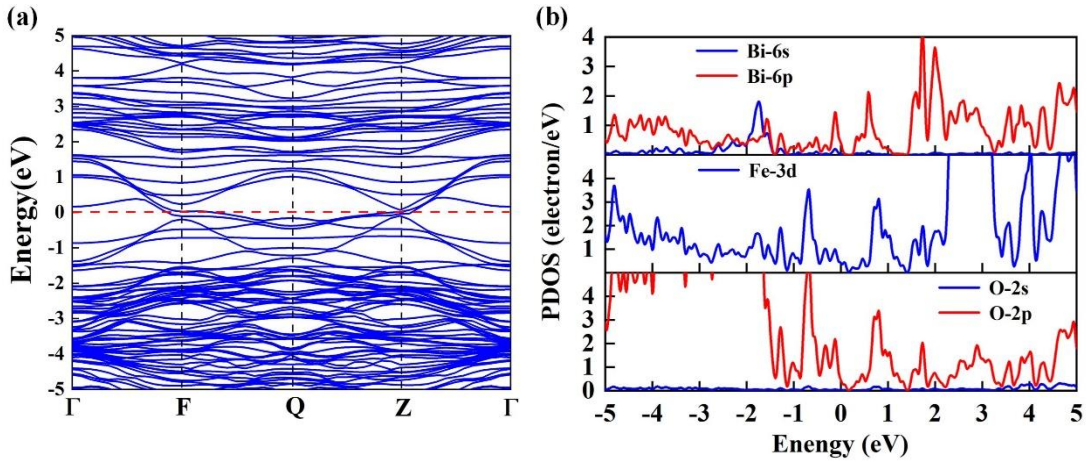

Fig. S4 The band structure (a) and PDOS (b) of *Fd*$\bar{3}$*m*-$BiFeO_3$ based on the HSE06 hybrid exchange-correlation functional.

Table SIII The elastic properties of the predicted $BiFeO_3$ structures with lower energy, including equilibrium volume V_0 (Å^3/atom), bulk modulus B_0 (GPa), and its pressure derivative B'_0 obtained by fitting calculated total energy to EoS, elastic constants c_{ij}'s (GPa) calculated from equilibrium structure, bulk modulus *B* (GPa), and shear modulus *G* (GPa), Young's modulus *E* (GPa), k = B/G ratio, Vickers hardness *Hv* (GPa), Debye temperature K (K), Poisson's ratio *v* calculated by Voight-Reuss-Hill method.

Materials	$BiFeO_3$													
Groups	*Fd*$\bar{3}$*m*	*R*3*c*	*P*4*mm*	*Pm*$\bar{3}$*m*	*C*2/*m*	*P*2$_1$/*c*	*C*2/*c*	*Cc*	*P*$\bar{1}$	*P*6$_3$	*P*6$_3$22	*Pnma*	*Cmcm*	*Imma*
c_{11}	256.82	223.74	180.60	238.99	205.21	216.42	223.18	255.02	218.50	168.18	169.72	231.03	252.89	209.66
c_{12}	117.12	115.95	86.66	128.89	51.71	79.01	105.19	115.47	112.94	150.09	150.39	131.67	76.83	121.02
c_{13}	117.12	54.21	51.43	128.89	116.28	68.09	113.17	116.98	120.56	82.75	83.43	119.28	82.44	52.97
c_{14}	0	16.27	0	0	-24.51	0	0	0	16.53	0	0	0	0	-22.51
c_{33}	256.82	149.80	104.48	238.99	123.29	112.37	256.89	213.31	247.71	228.98	229.27	246.90	219.73	133.46

c_{44}	99.23	47.59	39.47	56.86	63.29	51.31	47.54	62.78	40.93	55.80	56.07	73.379	81.27	32.93
c_{66}	99.23	53.90	82.57	56.86	14.55	36.95	60.61	72.15	57.88	9.07	9.67	85.75	21.80	44.25
G_V	85.12	54.67	50.71	56.13	42.96	45.43	56.85	70.51	51.44	40.74	41.12	62.34	60.96	43.91
G_R	82.36	48.20	45.89	56.12	25.37	38.21	54.02	68.09	46.98	18.55	19.52	58.56	48.17	27.85
G_H	83.74	51.44	48.30	56.13	34.17	41.82	55.44	69.30	49.21	29.64	30.32	60.49	54.57	35.88
B_V	164.28	116.22	93.86	165.59	108.36	98.96	157.47	150.47	152.16	133	133.69	161.67	130.30	111.69
B_R	164.24	106.54	83.67	165.59	96.55	84.61	150.85	156.28	149.66	132.98	133.66	161.59	129.55	99.67
B_H	164.25	111.38	88.76	165.59	102.45	91.79	154.17	158.37	150.91	132.99	133.68	161.63	129.92	105.68
E	214.72	133.73	122.66	151.29	92.24	108.92	148.51	188.28	133.15	82.78	84.57	161.24	143.60	96.70
v	0.28	0.30	0.27	0.35	0.35	0.30	0.34	0.37	0.35	0.40	0.40	0.33	0.32	0.35
k	0.51	0.46	0.54	0.34	0.33	0.47	0.36	0.37	0.33	0.22	0.23	0.37	0.42	0.34
Hv	9.12	5.12	6.48	2.95	3.09	4.47	3.43	4.51	2.62	1.37	1.42	4.33	6.06	3.11
K	451.97	357.53	350.06	369.50	293.20	323.42	370.30	407.93	349.83	279.21	282.26	386.50	366.61	300.072

Table SIV The elastic properties of $BiFeO_3$ reported recently[1, 2], for the same space group, we select the lowest energy for calculation. Including equilibrium volume V_0 (Å^3/atom), bulk modulus B_0 (GPa), and its pressure derivative B'_0 obtained by fitting calculated total energy to EoS, elastic constants c_{ij}'s (GPa) calculated from equilibrium structure, bulk modulus B (GPa), and shear modulus G (GPa), Young's modulus E (GPa), k = B/G ratio, Vickers hardness Hv (GPa), Debye temperature K (K), Poisson's ratio v calculated by Voight-Reuss-Hill method.

Materials	$BiFeO_3$															
Groups	$Fd\bar{3}m$	$R3c$	$Pnma$	$Pmc2_1$	$Cmc2_1$	$P2_1/c$	Cm	Cc	$P\bar{1}$	$P2_1/m$	$Pmn2_1$	$Ima2$	$Pbca$	$Pbam$	$P2_1$	Pm
c_{11}	256.82	223.74	231.03	142.34	146.09	216.42	255.39	255.02	218.50	214.33	143.56	153.51	226.46	229.35	222.34	254.13
c_{12}	117.12	115.95	131.67	38.65	39.54	79.01	115.95	115.47	112.94	77.42	38.93	76.37	127.61	129.38	115.36	112.54
c_{13}	117.12	54.21	119.28	80.46	82.11	68.09	117.38	116.98	120.56	65.65	81.25	36.04	113.46	119.90	122.57	116.97
c_{14}	0	16.27	0	0	0	0	0	0	16.53	0	0	0	0	0	11.65	0
c_{33}	256.82	149.80	246.90	82.65	84.02	112.37	214.96	213.31	247.71	110.26	83.76	107.45	223.35	235.56	249.56	213.45
c_{44}	99.23	47.59	73.38	35.01	35.42	51.31	63.08	62.78	40.93	50.35	35.35	25.21	71.23	72.65	45.71	61.97
c_{66}	99.23	53.90	85.75	54.98	56.13	36.95	72.85	72.15	57.88	35.68	55.67	50	84.65	84.97	58.22	71.58
G_V	85.12	54.67	62.34	36.88	37.18	45.43	70.93	70.51	51.44	44.69	37.02	44.35	61.65	61.98	52.35	70.93
G_R	82.36	48.20	58.56	34.59	21.02	38.21	68.53	68.09	46.98	37.35	35.96	39.75	60.46	61.56	48.06	67.62
G_H	83.74	51.44	60.49	35.46	29.10	41.82	69.80	69.30	49.21	41.32	36.23	42.05	60.23	61.73	50.65	68.12
B_V	164.28	116.22	161.67	78.47	79.22	98.96	150.96	150.47	152.16	98.73	79.02	73.89	159.65	160.32	153.97	150.26
B_R	164.24	106.54	161.59	75.95	76.02	84.61	156.76	156.28	149.66	83.46	75.99	67.13	159.62	160.30	150.72	155.46
B_H	164.25	111.38	161.63	76.92	77.62	91.79	158.85	158.37	150.91	90.65	77.35	70.51	159.63	160.31	151.51	157.15
E	214.72	133.73	161.24	76.52	77.60	108.92	189.04	188.28	133.15	108.26	76.92	105.23	160.32	162.97	139.54	185.16
v	0.28	0.30	0.33	0.33	0.33	0.30	0.38	0.37	0.35	0.30	0.31	0.25	0.33	0.34	0.35	0.38
k	0.51	0.46	0.37	0.37	0.38	0.47	0.38	0.37	0.33	0.46	0.36	0.60	0.39	0.36	0.33	0.37
Hv	9.12	5.12	4.33	3.57	3.81	4.47	4.67	4.51	2.62	4.30	3.69	6.68	4.19	4.29	3.75	4.51
K	451.97	357.53	386.50	266.23	268.29	323.42	408.26	407.93	349.83	321.43	267.56	318.60	385.76	385.36	350.94	405.68

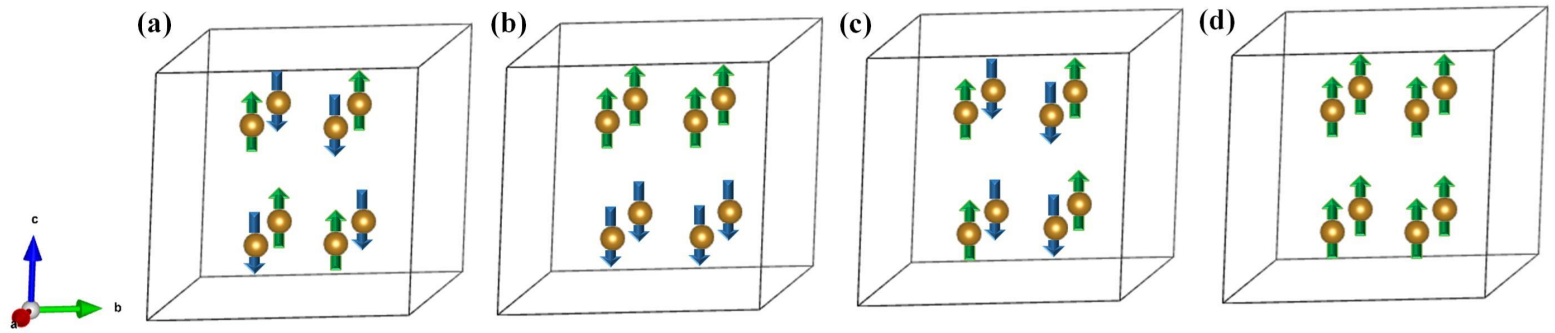

Fig. S5 Different magnetic patterns are considered for $BiFeO_3$. The green and blue arrows indicate the spin up and down of the iron atoms, respectively. For clarity, only the iron atoms are shown in the 2×2×1 cell. (a) G-AFM ordering, (b) A-AFM ordering, (c) C-AFM ordering, (d) FM ordering.

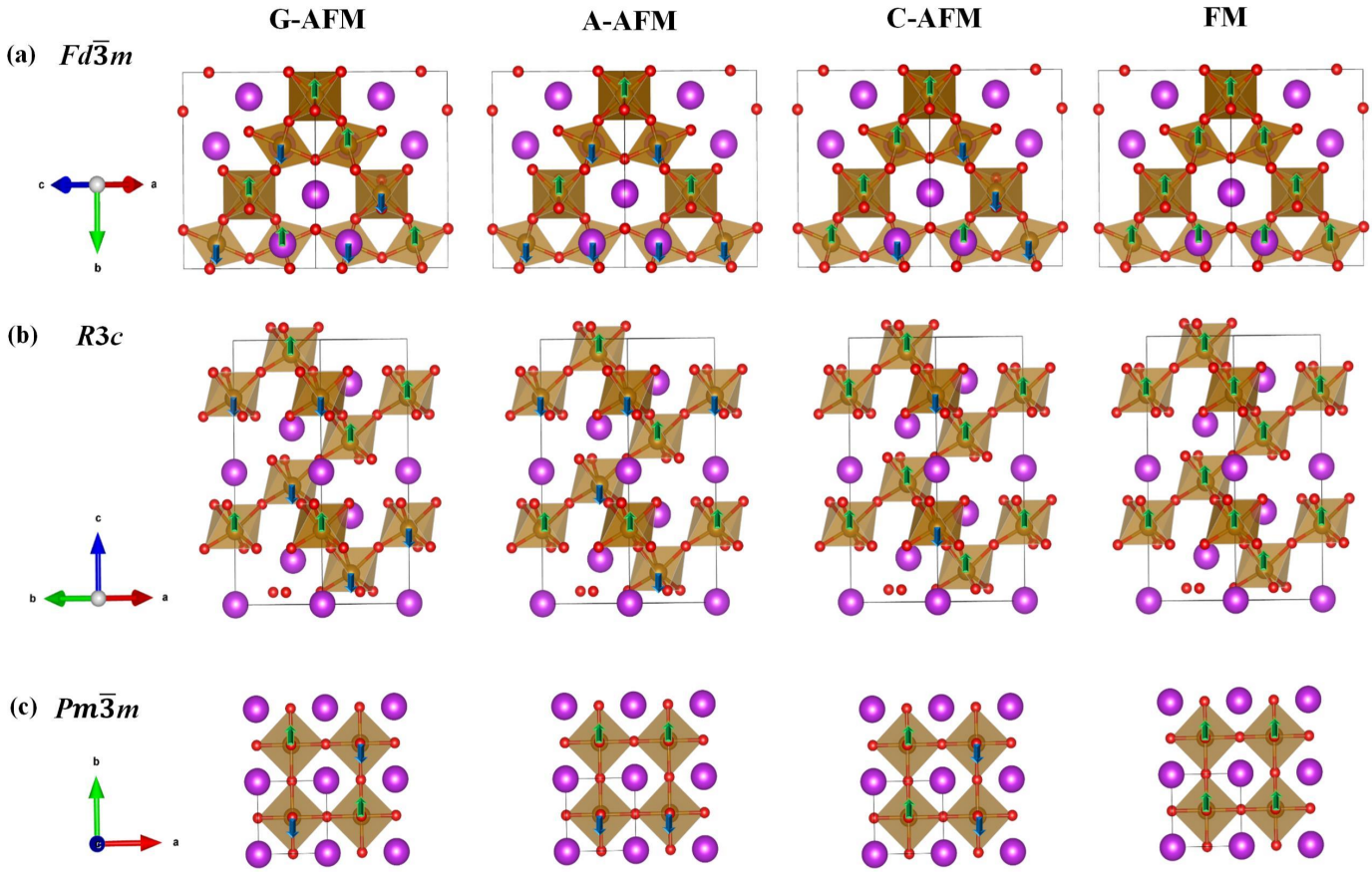

Fig. S6 Crystal structure diagrams of $Fd\bar{3}m$-$BiFeO_3$ (a), $R3c$-$BiFeO_3$ (b) and $Pm\bar{3}m$-$BiFeO_3$ (c), whose magnetic orderings consider G-AFM ordering, A-AFM ordering, C-AFM ordering, and FM ordering, , respectively. The green and blue arrows indicate the spin up and down of iron atoms, respectively.

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2. B. F. Grosso, N. A. Spaldin and A. M. Tehrani, *J. Phys. Chem. Lett.*, 2022, **13**, 7342-7349.