Supplementary Information

New multiferroic BiFeO$_3$ with large polarization

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AFFILIATIONS

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Table S1 Energy (eV/atom) of different crystal structures and magnetic configurations calculated by HSE06 and PBE functional.

configuration	HSE06	PBE
$P6_3$-G-AFM	-8.7512488	-6.5477720
$P6_3$22-G-AFM	-8.7512600	-6.5480297
$R3c$-G-AFM	-8.8657991	-6.6139328
$R3c$-A-AFM	-8.86564431	-6.6021649
$R3c$-C-AFM	-8.86576768	-6.6022187
$R3c$-FM	-8.82985245	-6.5691301
$R3c$-N-FM	-8.70652646	-6.4855000

**Table S2** The first and second nearest neighbor exchange constants (meV) of $P6_3$-BiFeO$_3$ and $P6_3$22-BiFeO$_3$。

Structure	J_{1x}	J_{1y}	J_{1z}	J_{2x}	J_{2y}	J_{2z}
$P6_3$	22.56	22.61	22.69	2.91	3.68	3.38
$P6_3$22	25.89	25.90	25.88	4.42	4.33	4.37

Table S3 The elastic stiffness coefficient of $P6_3$-BiFeO$_3$ and $P6_3$22-BiFeO$_3$, the unit of C_{ij} is GPa

structure	C_{11}	C_{12}	C_{13}	C_{33}	C_{44}	C_{66}
$P6_3$	168.2	150.1	82.8	229	55.6	9.1
$P6_3$22	169.7	150.4	83.4	229.3	56.1	9.7

Table S4 Bond lengths (Å) of $R3c$, $P6_3$ and $P6_3$22.

Bond	$R3c$	$P6_3$	$P6_322$
Fe-O$_1$	2.1185	2.0296	2.0415
Fe-O$_2$	2.1185	2.0297	2.0415
Fe-O$_3$	2.1185	2.0540	2.0415
Fe-O$_4$	1.9942	2.0550	2.0415
Fe-O$_5$	1.9942	2.0290	2.0415
Fe-O$_6$	1.9942	2.0547	2.0415
Bi-O$_1$	2.4802	2.3670	2.3940
Bi-O$_2$	2.4802	2.3661	2.3940
Bi-O$_3$	2.4802	2.3673	2.3940
Bi-O$_4$	2.3345	2.4252	2.3940
Bi-O$_5$	2.3345	2.4259	2.3940
Bi-O$_6$	2.3345	2.4254	2.3940
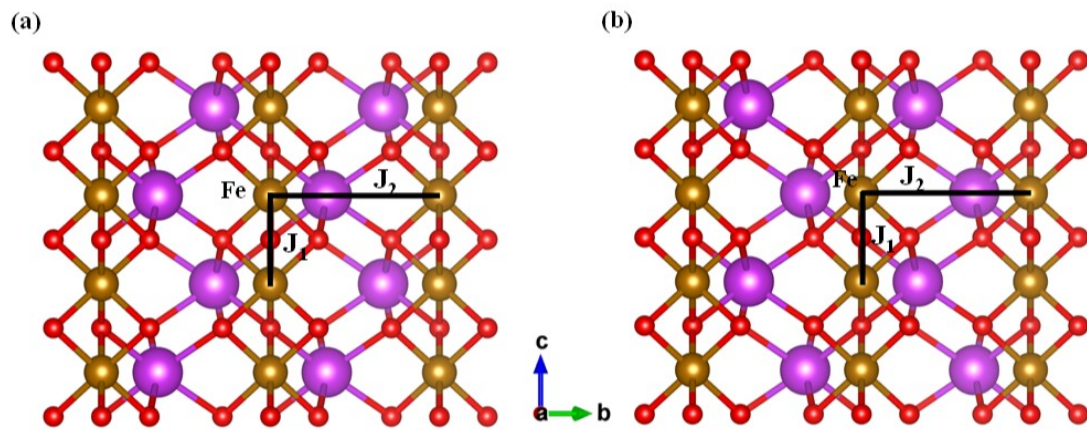
Fig. S1 Crystal structure of $P6_3$-BiFeO$_3$ (a) and $P6_322$-BiFeO$_3$ (b). The purple, yellow and red spheres represent the Bi, Fe, and O atoms, respectively. Two magnetic exchange constants are marked with J$_1$ and J$_2$.
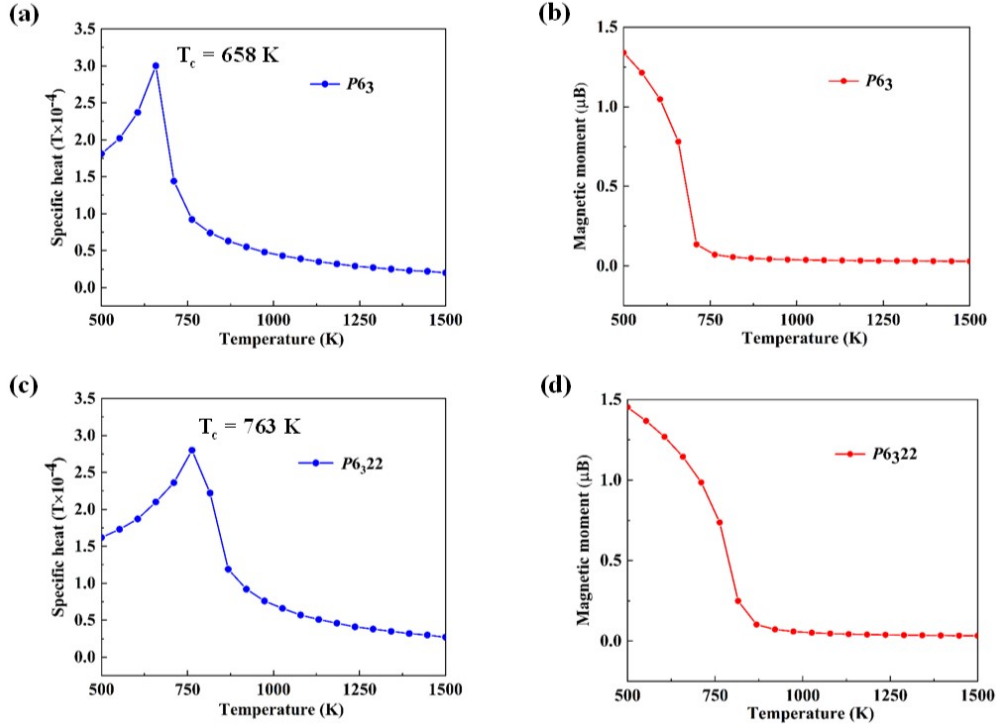
Fig. S2 Specific heat curves for $P6_3$-BiFeO$_3$ (a) and $P6_3$22-BiFeO$_3$ (c) were calculated by Monto Carlo simulations. Magnetic moment curves for $P6_3$-BiFeO$_3$ (b) and $P6_3$22-BiFeO$_3$ (d) were calculated by Monto Carlo simulations.
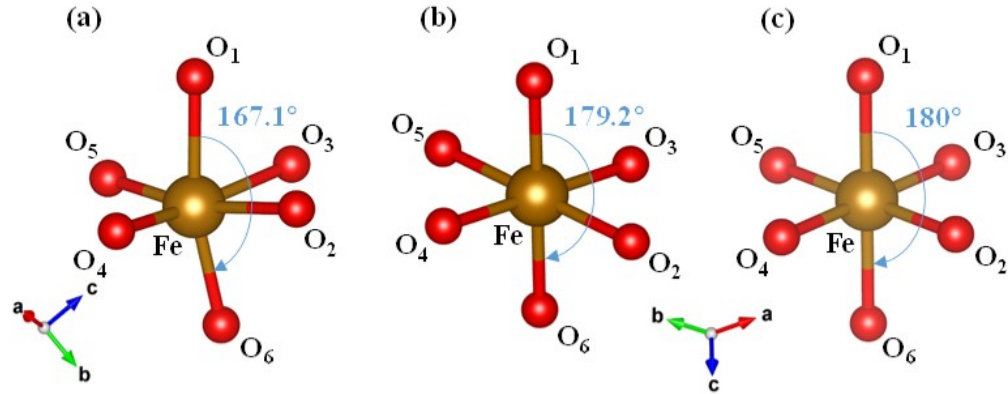
Fig. S3 The atomic coordination situation of Fe in $R3c$ (a), $P6_3$ (b) and $P6_3$22 (c).

Firstly, two adjacent Fe-O octahedrons of $R3c$ are connected by an oxygen atom, while the two adjacent Fe-O octahedrons of $P6_3$ and $P6_3$22 are connected by three oxygen atoms (Fig. 3). Secondly, the O$_1$-Fe-O$_6$ angle of $R3c$ is 167.1°, while the O$_1$-Fe-O$_6$ angles of $P6_3$ and $P6_3$22 are 179.2° and 180° (Fig. S3). Thirdly, there are two types of Fe-O bond lengths in $R3c$, i.e., 2.1185 Å (Fe-O$_1$, Fe-O$_2$, Fe-O$_3$) and 1.9942 Å (Fe-O$_4$, Fe-O$_5$, Fe-O$_6$), while all the Fe-O bond lengths in $P6_3$22 are 2.0415 Å (Table S4). Therefore, the Fe-O octahedron is noncentrosymmetric in $R3c$, while the Fe-O octahedron is centrosymmetric in $P6_3$22 and almost centrosymmetric in $P6_3$ (Fig. S3).
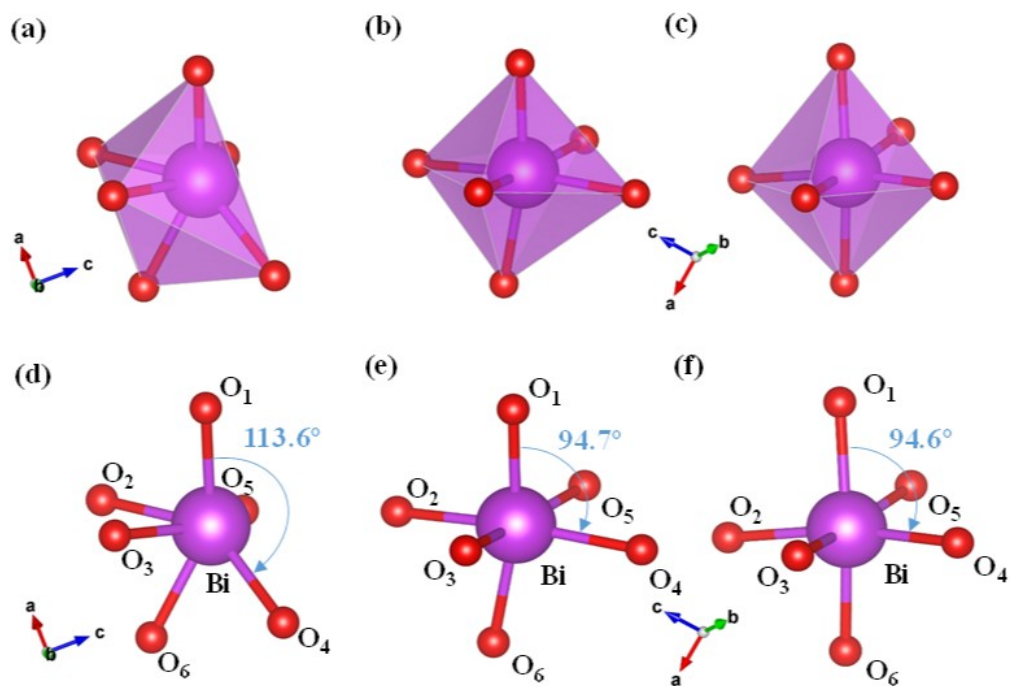
Fig. S4 The Bi-O octahedrons of $R3c$ (a), $P6_3$ (b) and $P6_322$ (c). The atomic coordination situation of Bi in $R3c$ (d), $P6_3$ (e) and $P6_322$ (f).

For the Bi-O octahedron, firstly, the distribution of Bi-O bond is nonuniform in $R3c$, while it is relatively uniform in $P6_3$ and $P6_322$ (Fig. S4). Secondly, the O_1-Bi-O_4 angle of $R3c$ is 113.6°, while the O_1-Bi-O_4 angles of $P6_3$ and $P6_322$ are 94.7° and 94.6° (Fig. S4). Thirdly, there are two types of Bi-O bond lengths in $R3c$, i.e., 2.4802 Å (Bi-O_1, Bi-O_2, Bi-O_3) and 2.3345 Å (Bi-O_4, Bi-O_5, Bi-O_6), while all the Bi-O bond lengths in $P6_322$ are 2.3940 Å (Table S4).