Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Materials (ESI) for the Article „Comparative density functional studies of pristine and doped bismuth ferrite polymorphs by GGA+*U* and meta-GGA SCAN+*U*"

by

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Table S1. The extended version of Table 1 from the article including uncertainties of the obtained values calculated in relation to the experimental one

	GGA	GGA+*U* (*U* = 4 eV)	HSE	SCAN	SCAN+*U* (*U* = 1 eV)	SCAN+*U* (*U* = 2 eV)	SCAN+*U* (*U* = 3 eV)	SCAN+*U* (*U* = 4 eV)	Exp.
a_{rh} [Å]	5.682 (+0.9%)	5.682 (+0.9%)	5.645 (+0.2%)	5.594 (-0.7%)	5.602 (-0.6%)	5.601 (-0.6%)	5.603 (-0.6%)	5.599 (-0.6%)	5.634
α_{rh} [°]	59.19 (-0.3%)	59.12 (-0.4%)	59.05 (-0.5%)	59.59 (+0.4%)	59.47 (+0.2%)	59.47 (+0.2%)	59.46 (+0.2%)	59.41 (+0.1%)	59.35
Bi-O [Å]	2.478 (-1.3%)	2.482 (-1.1%)	2.501 (-0.4%)	2.478 (-1.3%)	2.486 (-0.9%)	2.487 (-0.9%)	2.492 (-0.7%)	2.491 (-0.7%)	2.510
Bi-O [Å]	2.315 (+1.9%)	2.331 (+2.6%)	2.264 (-0.3%)	2.289 (+0.8%)	2.291 (+0.9%)	2.293 (+0.9%)	2.293 (+0.9%)	2.295 (+1.0%)	2.271
Fe-O [Å]	2.163 (+2.5%)	2.119 (+0.4%)	2.123 (+0.6%)	2.105 (-0.2%)	2.097 (-0.6%)	2.090 (-0.9%)	2.085 (-1.2%)	2.076 (-1.6%)	2.110
Fe-O [Å]	1.957 (-0.1%)	1.980 (+1.1%)	1.948 (-0.5%)	1.946 (-0.6%)	1.945 (-0.6%)	1.953 (-0.3%)	1.956 (-0.1%)	1.958 (0.0%)	1.958
O-Fe-O [°]	164.14 (-0.5%)	166.83 (+1.1%)	164.67 (-0.2%)	165.15 (+0.1%)	165.69 (+0.4%)	166.07 (+0.6%)	166.40 (+0.8%)	166.92 (+1.1%)	165.04
E_g [eV]	1.08 (-61.4%)	2.24 (-20.0%)	3.41 (+21.7%)	1.75 (-37.5%)	2.03 (-27.5%)	2.28 (-18.6%)	2.44 (-12.8%)	2.51 (-10.4%)	2.8
μ_{Fe} [μ_B]	3.73 (-0.5% ~ -13.9 %)	4.11 (+9.6% ~ -5.1%)	4.16 (+10.9% ~ -3.9%)	3.98 (+6.1% ~ -8.1%)	4.05 (+8.0% ~ -6.5%)	4.10 (+9.3% ~ -5.3%)	4.16 (+10.9% ~ -3.9%)	4.21 (+12.3% ~ -2.8%)	3.75-4.33

Table S2. The calculated magnitudes of the ferroelectric polarization of the investigated $BiFeO_3$ polymorphs. The components of the ferroelectric polarization of *Cm*-C and *Ima2*-G phases was also given in parentheses. The results were obtained within GGA+*U* and SCAN+*U*

	GGA+*U*		SCAN+*U*	
R3c-G				
pristine	90.7		90.9	
Al	89.8		91.0	
Ga	91.0		91.5	
In	93.9		93.6	
Sc	93.0		94.2	
$Pna2_1$-G				
pristine	48.6		63.5	
Al	47.9		64.0	
Ga	51.2		65.0	
In	55.1		65.2	
Sc	53.4		65.2	
P4mm-C				
pristine	142.8		138.2	
Al	139.1		134.7	
Ga	141.1		137.1	
In	144.6		139.0	
Sc	143.4		138.9	
Cm-C				
pristine	143.5	(43.4; 0.0; 137.8)	141.2	(53.2; 0.0; 131.8)
Al	143.0	(50.9; 0.0; 134.8)	136.4	(52.0; 0.0; 127.0)
Ga	144.8	(51.4; 0.0; 136.5)	139.4	(52.7; 0.0; 131.8)
In	143.4	(54.2; 0.0; 133.9)	138.3	(55.9; 0.0; 127.5)
Sc	146.5	(55.0; 0.0; 137.1)	139.7	(57.2; 0.0; 128.6)
Ima2-G				
pristine	89.2	(63.2; 62.9; 0.0)	87.7	(62.2; 61.7; 0.0)
Al	84.6	(58.5; 61.2; 0.0)	86.1	(59.8; 61.9; 0.0)
Ga	86.4	(60.3; 61.9; 0.0)	86.6	(60.8; 61.8; 0.0)
In	83.6	(58.4; 59.7; 0.0)	86.8	(61.1; 61.6; 0.0)
Sc	86.5	(60.4; 61.9; 0.0)	87.8	(61.6; 62.6; 0.0)

Table S3. The optimized pseudocubic lattice parameter for selected $BiFeO_3$ polymorphs without and with dopants calculated within GGA+*U* and SCAN+*U* with the optimal values of the Hubbard *U* parameter

	a [Å]	b [Å]	c [Å]	α	β	γ
***R3c*-G**						
SCAN+*U*						
pristine	7.879	7.879	7.879	89.56	89.56	89.56
Al	7.853	7.853	7.853	89.52	89.52	89.52
Ga	7.880	7.880	7.880	89.49	89.49	89.49
In	7.945	7.945	7.945	89.47	89.47	89.47
Sc	7.929	7.929	7.929	89.38	89.38	89.38
GGA+*U*						
pristine	7.985	7.985	7.985	89.21	89.21	89.21
Al	7.952	7.952	7.952	89.26	89.26	89.26
Ga	7.984	7.984	7.984	89.23	89.23	89.23
In	8.054	8.054	8.054	89.10	89.10	89.10
Sc	8.019	8.019	8.019	89.14	89.14	89.14
***P4mm*-C**						
SCAN+*U*						
pristine	7.438	7.438	9.435	90.0	90.0	90.0
Al	7.417	7.417	9.377	90.0	90.0	90.0
Ga	7.429	7.429	9.452	90.0	90.0	90.0
In	7.463	7.463	9.577	90.0	90.0	90.0
Sc	7.470	7.470	9.491	90.0	90.0	90.0
GGA+*U*						
pristine	7.494	7.494	9.706	90.0	90.0	90.0
Al	7.468	7.468	9.642	90.0	90.0	90.0
Ga	7.487	7.487	9.712	90.0	90.0	90.0
In	7.521	7.521	9.863	90.0	90.0	90.0
Sc	7.522	7.522	9.770	90.0	90.0	90.0
***Cm*-C**						
SCAN+*U*						
pristine	7.511	7.511	9.440	87.83	87.83	89.71
Al	7.488	7.488	9.354	87.95	87.95	89.69
Ga	7.499	7.499	9.445	87.86	87.86	89.71
In	7.562	7.562	9.535	87.80	87.80	89.66
Sc	7.568	7.568	9.440	87.81	87.81	89.69
GGA+*U*						
pristine	7.573	7.573	9.775	87.39	87.39	89.69
Al	7.549	7.549	9.701	87.47	87.47	89.62
Ga	7.569	7.569	9.780	87.39	87.39	89.61
In	7.635	7.635	9.905	87.14	87.14	89.54
Sc	7.621	7.621	9.814	87.19	87.19	89.59

***Pna2$_1$*-G**						
SCAN+*U*						
pristine	7.791	7.791	8.017	90.0	90.0	88.36
Al	7.756	7.761	8.003	89.97	89.80	88.56
Ga	7.780	7.781	8.039	90.0	89.95	88.44
In	7.846	7.840	8.093	90.0	90.26	88.22
Sc	7.828	7.827	8.064	89.99	90.15	88.26
GGA+*U*						
pristine	7.905	7.905	7.979	90.0	90.0	88.07
Al	7.878	7.889	7.927	90.0	89.87	88.04
Ga	7.906	7.906	7.968	90.0	89.97	87.98
In	7.975	7.964	8.046	89.94	90.30	87.80
Sc	7.936	7.937	7.999	89.95	90.12	87.85
***Ima2*-G**						
SCAN+*U*						
pristine	7.973	7.973	7.744	90.0	90.0	89.43
Al	7.944	7.944	7.708	90.06	90.06	89.47
Ga	7.969	7.969	7.737	90.02	90.02	89.46
In	8.041	8.041	7.802	89.75	89.75	89.43
Sc	8.019	8.019	7.784	89.91	89.91	89.43
GGA+*U*						
pristine	8.079	8.079	7.825	90.0	90.0	89.06
Al	8.033	8.033	7.805	90.04	90.04	89.25
Ga	8.065	8.065	7.830	90.01	90.01	89.27
In	8.112	8.112	7.925	89.76	89.76	89.09
Sc	8.102	8.102	7.884	89.91	89.91	89.18
***Pnma*-G**						
SCAN+*U*						
pristine	7.805	7.805	7.768	90.0	90.0	87.81
Al	7.775	7.777	7.744	90.0	89.96	88.03
Ga	7.800	7.802	7.765	90.02	89.96	87.85
In	7.861	7.862	7.816	89.98	90.07	87.44
Sc	7.838	7.844	7.805	89.96	90.06	87.62
GGA+*U*						
pristine	7.904	7.904	7.844	90.0	90.0	87.59
Al	7.877	7.878	7.817	90.02	89.94	87.77
Ga	7.904	7.905	7.839	90.03	89.95	87.63
In	7.964	7.964	7.894	89.93	90.11	87.31
Sc	7.932	7.934	7.875	89.91	90.07	87.46

Table S4. The values of the Fe-O-Fe bond angles for the doped rhombohedral *R3c*-G, orthorhombic *Pna2₁*-G, and monoclinic *Cm*-C $BiFeO_3$ polymorphs optimized within GGA+*U* and SCAN+*U*. The numbers at the Fe atoms refer to the Figure 8 in the article.

R3c-G									
	Fe1-O-Fe2; Fe1-O-Fe3; Fe1-O-Fe5			Fe2-O-Fe4; Fe3-O-Fe7; Fe5-O-Fe6			Fe5-O-Fe7; Fe3-O-Fe4		
GGA+*U*									
BAFO	153.49			154.41			153.76		
BGFO	153.69			153.90			153.46		
BSFO	153.59			152.93			152.89		
BIFO	155.21			154.00			150.97		
SCAN+*U*									
BAFO	154.61			155.62			155.36		
BGFO	155.21			155.60			154.82		
BSFO	155.78			155.04			154.23		
BIFO	156.95			155.77			152.03		
Pna2₁-G									
	Fe1-O-Fe2	Fe2-O-Fe3	Fe3-O-Fe4	Fe4-O-Fe1	Fe5-O-Fe6	Fe5-O-Fe7	Fe2-O-Fe7	Fe3-O-Fe5	Fe4-O-Fe6
GGA+*U*									
BAFO	151.94	149.72	149.51	150.98	150.78	150.79	152.75	152.23	152.96
BGFO	150.88	149.51	149.86	150.35	150.53	150.75	153.01	153.07	152.79
BSFO	149.27	149.43	150.17	150.01	149.93	149.52	152.72	153.16	151.74
BIFO	148.66	149.37	151.52	149.83	149.75	148.98	153.08	154.04	150.94
SCAN+*U*									
BAFO	155.38	150.40	150.23	154.65	154.48	155.30	156.54	155.75	156.93
BGFO	154.34	150.17	150.66	154.12	154.17	154.15	156.45	156.78	156.30
BSFO	152.49	150.58	150.90	153.51	152.82	152.20	155.92	156.28	154.97
BIFO	152.00	150.43	151.94	153.52	152.58	151.29	156.23	156.96	154.34
Cm-C									
	Fe1-O-Fe3	Fe3-O-Fe2	Fe4-O-Fe5	Fe4-O-Fe6	Fe5-O-Fe7	Fe6-O-Fe7			
GGA+*U*									
BAFO	141.50	141.89	140.61	141.39	141.48	142.39			
BGFO	141.34	141.40	141.26	141.39	141.37	141.39			
BSFO	142.15	141.60	143.40	142.32	142.31	142.33			
BIFO	140.12	143.41	142.52	144.59	143.27	139.52			
SCAN+*U*									
BAFO	144.51	142.85	143.33	142.02	142.96	145.88			
BGFO	143.01	143.22	142.97	143.24	143.07	143.30			
BSFO	144.02	144.58	145.45	145.44	145.33	144.09			
BIFO	141.64	146.20	144.00	147.54	145.86	140.71			

Table S5. The elements of the Born effective charge tensors for the *Cm*-C phase

	xx	yy	zz	xy	xz	yx	yz	zx	zy
BFO									
Fe	3.271	3.285	3.877	0.000	0.366	0.000	0.000	0.649	0.000
O1	-2.592	-2.272	-3.307	0.000	-0.559	0.000	0.000	-0.716	0.000
O2	-2.891	-2.896	-2.065	0.036	-0.115	-0.001	0.311	-0.028	0.146
BAFO									
Al	3.032	3.072	3.519	0.000	0.278	0.000	0.000	0.111	0.000
O1	-2.834	-2.352	-2.524	0.000	-0.541	0.000	0.000	-0.574	0.000
O2	-2.765	-2.721	-2.152	-0.164	0.037	-0.118	0.180	0.141	-0.037
O3	-2.812	-2.777	-2.113	-0.184	-0.232	-0.246	0.376	-0.207	0.213
O4	-2.765	-2.721	-2.152	0.164	0.037	0.118	-0.180	0.141	0.037
O5	-2.812	-2.777	-2.113	0.184	-0.232	0.246	-0.376	-0.207	-0.213
BGFO									
Ga	3.185	3.202	3.607	0.000	0.268	0.000	0.000	0.098	0.000
O1	-2.826	-2.508	-2.569	0.000	-0.430	0.000	0.000	-0.590	0.000
O2	-2.809	-2.814	-2.111	-0.176	-0.025	-0.163	0.205	0.106	-0.024
O3	-2.847	-2.845	-2.158	-0.097	-0.213	-0.175	0.388	-0.145	0.222
O4	-2.809	-2.814	-2.111	0.176	-0.025	0.163	-0.205	0.106	0.024
O5	-2.847	-2.845	-2.158	0.097	-0.213	0.175	-0.388	-0.145	-0.222
BIFO									
In	3.238	3.154	3.815	0.000	0.176	0.000	0.000	0.029	0.000
O1	-2.801	-2.874	-2.547	0.000	-0.267	0.000	0.000	-0.479	0.000
O2	-2.814	-2.900	-2.020	-0.389	-0.064	-0.432	0.184	0.142	-0.041
O3	-2.808	-2.941	-2.248	-0.023	-0.210	-0.157	0.490	-0.119	0.383
O4	-2.814	-2.900	-2.020	0.389	-0.064	0.432	-0.184	0.142	0.041
O5	-2.808	-2.941	-2.248	0.023	-0.210	0.157	-0.490	-0.119	-0.383
BSFO									
Sc	3.722	3.648	4.356	0.000	0.299	-0.000	0.000	0.122	0.000
O1	-2.714	-2.426	-3.439	0.000	-0.559	-0.000	0.000	-0.615	0.000
O2	-3.023	-3.061	-2.065	0.005	-0.121	-0.041	0.326	-0.007	0.167
O3	-3.004	-3.084	-2.140	0.167	-0.073	0.094	0.379	-0.021	0.259
O4	-3.023	-3.061	-2.065	-0.005	-0.121	0.041	-0.326	-0.007	-0.167
O5	-3.004	-3.083	-2.140	-0.167	-0.073	-0.094	-0.379	-0.021	-0.259

Table S6. The elements of the Born effective charge tensors for the *Pna2₁*-G phase

	xx	yy	zz	xy	xz	yx	yz	zx	zy
BFO									
Fe	3.963	3.860	3.985	0.295	0.356	0.073	0.167	0.038	0.307
O1	-2.728	-3.220	-2.869	0.032	0.664	0.320	0.466	0.554	0.264
O2	-3.345	-2.214	-3.242	0.281	-0.107	0.174	-0.118	-0.127	-0.214
O3	-2.775	-2.939	-2.981	-0.091	-0.539	-0.154	0.459	-0.409	0.436
O4	-2.728	-3.220	-2.869	-0.032	0.664	-0.320	-0.466	0.554	-0.264
O5	-3.345	-2.214	-3.242	0.281	0.107	0.174	0.118	0.127	0.214
O6	-2.775	-2.939	-2.981	-0.091	0.539	-0.154	-0.459	0.409	-0.436
BAFO									
Al	3.342	3.390	3.349	0.230	0.272	0.109	0.168	0.116	0.188
O1	-2.811	-2.893	-2.917	0.097	0.605	0.374	0.495	0.488	0.346
O2	-3.190	-2.342	-2.994	0.314	-0.375	0.174	-0.211	-0.423	-0.340
O3	-2.464	-2.994	-2.873	-0.026	-0.273	-0.196	0.479	-0.131	0.500
O4	-2.863	-2.562	-2.937	0.036	0.686	-0.223	-0.334	0.611	-0.127
O5	-3.041	-2.313	-3.111	0.126	0.439	0.068	0.088	0.449	0.180
O6	-2.671	-3.068	-2.664	-0.153	0.220	-0.206	-0.488	0.049	-0.400
BGFO									
Ga	3.606	3.644	3.595	0.215	0.261	0.113	0.184	0.144	0.149
O1	-2.796	-2.995	-2.932	0.094	0.704	0.391	0.537	0.576	0.388
O2	-3.286	-2.271	-3.065	0.337	-0.336	0.202	-0.179	-0.406	-0.316
O3	-2.474	-3.018	-2.922	-0.037	-0.342	-0.157	0.444	-0.208	0.466
O4	-2.842	-2.716	-2.948	0.056	0.730	-0.248	-0.342	0.626	-0.102
O5	-3.116	-2.262	-3.169	0.156	0.385	0.099	0.060	0.400	0.162
O6	-2.707	-3.054	-2.644	-0.111	0.307	-0.167	-0.452	0.157	-0.389
BIFO									
In	3.632	3.671	3.633	0.177	0.171	0.118	0.173	0.148	0.098
O1	-2.757	-2.940	-2.961	0.071	0.819	0.353	0.595	0.644	0.492
O2	-3.368	-2.198	-3.029	0.427	-0.361	0.287	-0.167	-0.477	-0.311
O3	-2.315	-3.111	-2.991	-0.047	-0.270	-0.104	0.363	-0.198	0.421
O4	-2.836	-2.623	-2.986	0.084	0.819	-0.229	-0.247	0.679	0.015
O5	-3.075	-2.179	-3.227	0.181	0.471	0.091	-0.085	0.479	-0.006
O6	-2.777	-3.061	-2.439	-0.049	0.338	-0.073	-0.412	0.172	-0.365
BSFO									
Sc	4.415	4.254	4.420	0.284	0.186	0.120	0.256	0.168	0.139
O1	-2.710	-3.411	-2.867	0.021	0.667	0.301	0.518	0.526	0.344
O2	-3.526	-2.219	-3.321	0.338	0.036	0.232	-0.097	-0.046	-0.161
O3	-2.820	-3.026	-3.159	-0.079	-0.570	-0.148	0.394	-0.490	0.443
O4	-2.771	-3.341	-2.940	-0.023	0.652	-0.316	-0.419	0.535	-0.198
O5	-3.429	-2.209	-3.397	0.333	0.046	0.205	0.042	0.020	0.097
O6	-2.963	-2.981	-3.055	-0.112	0.686	-0.084	-0.499	0.478	-0.372

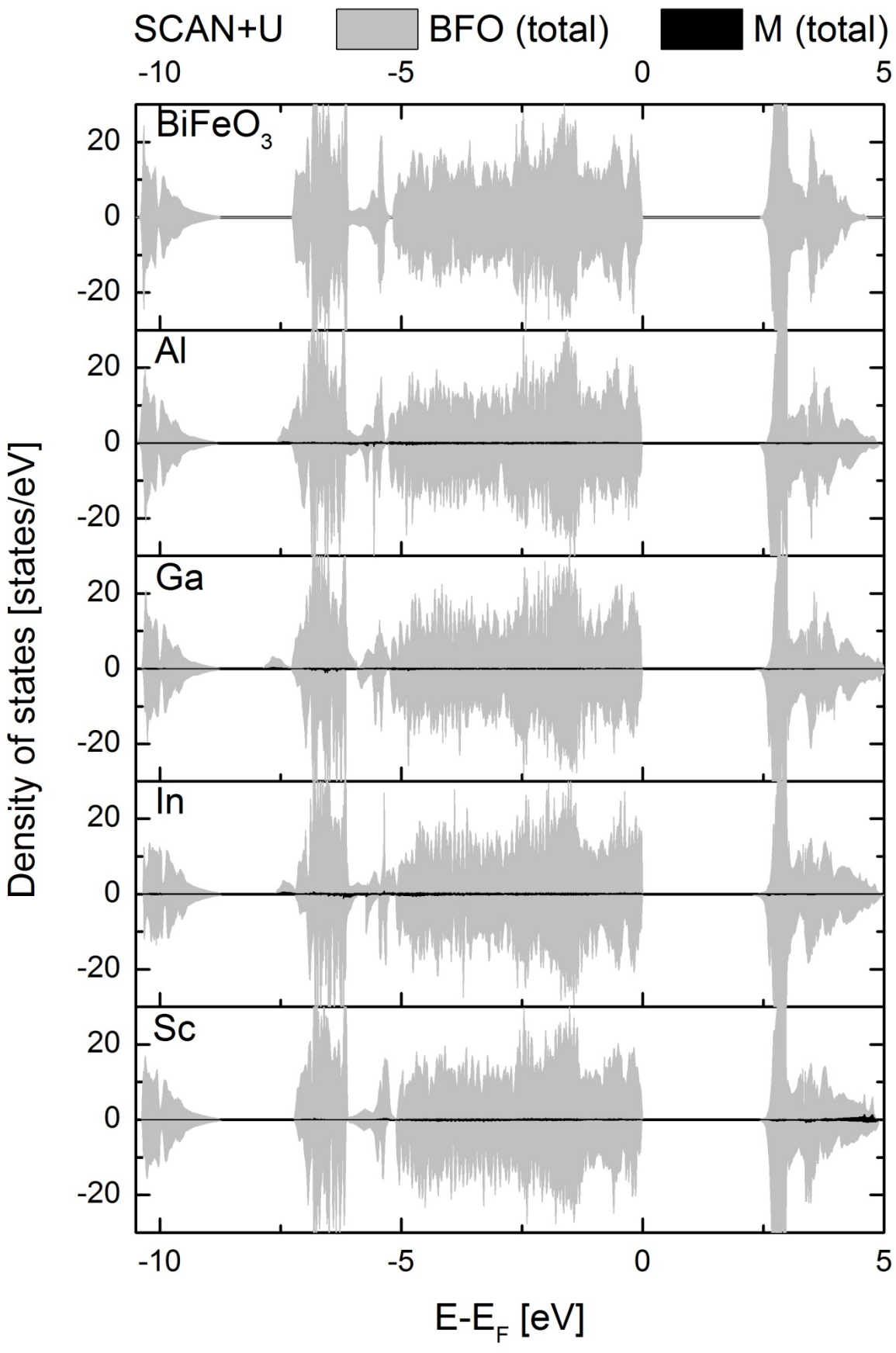

Fig. S1. The total density of states of the rhomboedral *R3c*-G phase of BFO without and with dopants