Supporting Information
for
"A Combined First Principles and Experimental Approach to Bi$_2$WO$_6$"

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I. XRD ANALYSIS

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Crystallographic Parameters, Bond Lengths and Bond Angles

Sample/DFT	Sym.	a (Å)	b (Å)	c (Å)	α(°)	β(°)	γ(°)	V (Å³)	$d_{\text{W-O}}$ (Å)	$d_{\text{Bi-O}}$ (Å)	χ^2
SBWO	$Pca2_1$	5.433	16.415	5.454	90	90	90	486.442	1.797, 1.803, 1.859, 1.862, 2.135, 2.144	2.182, 2.242, 2.302, 2.441, 2.498, 2.500	1.75
HBWO-U	$Pca2_1$	5.449	16.348	5.450	90	90	90	485.487	1.799, 1.806, 1.853, 1.855, 2.147, 2.135	2.180, 2.241, 2.300, 2.438, 2.500, 2.502	1.45
HBWO-S	$Pca2_1$	5.452	16.340	5.440	90	90	90	484.601	1.797, 1.805, 1.852, 1.854, 2.133, 2.146	2.179, 2.240, 2.298, 2.434, 2.498, 2.502	1.27
GGA-PBE	$Pca2_1$	5.551	16.882	5.591	90	90	90	523.938	1.812, 1.819, 1.886, 1.889, 2.216, 2.204	1.791, 1.815, 1.851, 1.887, 2.142, 2.209	
GGA-PBE+U_d (2 eV)+U_p (2 eV)	$Pca2_1$	5.515	16.979	5.558	90	90	90	520.393	1.895, 1.901, 1.902, 1.903, 2.021, 2.027	1.831, 1.846, 1.893, 1.922, 1.9898, 2.160	
GGA-PBE+U_d (5 eV)+U_p (5 eV)	$Pca2_1$	5.468	17.111	5.514	90	90	90	515.931	1.895, 1.901, 1.902, 1.903, 2.021, 2.027	1.864, 1.887, 1.900, 1.926, 1.987, 2.085	
GGA-PBE+U_d (7 eV)+U_p (7 eV)	$Pca2_1$	5.438	17.206	5.488	90	90	90	513.416	1.895, 1.901, 1.902, 1.903, 2.021, 2.027	1.897, 1.899, 1.904, 1.925, 1.967, 2.028	
GGA-PBE+U_d (9 eV)+U_p (9 eV)	$Pca2_1$	5.422	17.263	5.477	90	90	90	512.634	1.895, 1.901, 1.902, 1.903, 2.021, 2.027	1.907, 1.918, 1.924, 1.937, 1.954, 1.991	
GGA-PBE+U_d (12 eV)+U_p (12 eV)	$Pca2_1$	5.408	17.340	5.478	90	90	90	513.716	1.895, 1.901, 1.902, 1.903, 2.021, 2.027	1.910, 1.923, 1.941, 1.952, 1.964, 1.974	
GGA-PBE+U_d (14 eV)+U_p (14 eV)	$Pca2_1$	5.401	17.404	5.482	90	90	90	515.284	1.895, 1.901, 1.902, 1.903, 2.021, 2.027	1.912, 1.922, 1.946, 1.954, 1.961, 1.970	

TABLE S1. Crystallographic parameters of SBWO, HBWO-U, and HBEO-S samples along with that of GGA-PBE and GGA-PBE+U_{d}+U_{p} for different values of U_{d} and U_{p}.

	Crystallographic Parameters, Bond Lengths and Bond Angles										
Sample/DFT	Sym.	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	V (Å³)	$d_{\text{W-O}}$ (Å)	$d_{\text{Bi-O}}$ (Å)	χ^2
SBWO	$Pca2_1$	5.433	16.415	5.454	90	90	90	486.442	1.797, 1.803, 1.859; 1.862, 2.135, 2.144; 1.855, 2.135, 2.147; 1.854, 2.133, 2.146	2.182, 2.242, 2.302; 2.441, 2.498, 2.500; 2.472, 2.500, 2.502; 2.462, 2.498, 2.502	1.75
HBWO-U	$Pca2_1$	5.449	16.348	5.450	90	90	90	485.487	1.799, 1.806, 1.853; 1.862, 2.135, 2.147; 1.855, 2.135, 2.147; 1.854, 2.133, 2.146	2.180, 2.241, 2.300; 2.438, 2.500, 2.502; 2.472, 2.500, 2.502; 2.462, 2.498, 2.502	1.45
HBWO-S	$Pca2_1$	5.452	16.340	5.440	90	90	90	484.601	1.797, 1.805, 1.852; 1.854, 2.133, 2.146; 1.855, 2.135, 2.158; 1.854, 2.133, 2.146	2.179, 2.240, 2.298; 2.434, 2.498, 2.502; 2.472, 2.500, 2.502; 2.462, 2.498, 2.502	1.27
GGA-PBE+vdW	$Pca2_1$	5.508	16.616	5.517	90	90	90	504.921	1.819, 1.833, 1.883; 1.835, 1.888, 1.895; 2.044, 2.114, 2.158	2.214, 2.275, 2.340; 2.469, 2.499, 2.517; 2.475, 2.485, 2.492; 2.494, 2.506, 2.508	
GGA-PBE+U_d (2 eV)+U_p (2 eV)+vdW	$Pca2_1$	5.483	16.667	5.488	90	90	90	501.493	1.835, 1.888, 1.888; 2.114	2.209, 2.275, 2.328; 2.485, 2.492, 2.506	
GGA-PBE+U_d (5 eV)+U_p (5 eV)+vdW	$Pca2_1$	5.440	16.800	5.451	90	90	90	498.105	1.869, 2.044	2.203, 2.277, 2.304; 2.475, 2.494, 2.508	
GGA-PBE+U_d (7 eV)+U_p (7 eV)+vdW	$Pca2_1$	5.416	16.868	5.432	90	90	90	496.216	1.898, 1.900, 1.900; 1.996	2.199, 2.283, 2.287; 2.484, 2.536	
GGA-PBE+U_d (9 eV)+U_p (9 eV)+vdW	$Pca2_1$	5.404	16.913	5.425	90	90	90	495.778	1.900, 1.919; 1.971	2.192, 2.274, 2.287; 2.444, 2.486, 2.551	
GGA-PBE+U_d (12 eV)+U_p (12 eV)+vdW	$Pca2_1$	5.393	16.963	5.425	90	90	90	496.259	1.902, 1.932; 1.958	2.180, 2.261, 2.285; 2.431, 2.503, 2.548	
GGA-PBE+U_d (14 eV)+U_p (14 eV)+vdW	$Pca2_1$	5.387	17.007	5.425	90	90	90	497.051	1.895, 1.935; 1.956	2.169, 2.254, 2.282; 2.424, 2.523, 2.535	

TABLE S2. Crystallographic parameters of SBWO, HBWO-U, and HBWO-S samples along with that of GGA-PBE+vdW and GGA-PBE+U_d+U_p+vdW for different values of U_d and U_p. The van der Waals (vdW) interaction was included with the DFT-D3 method including Becke-Johnson (BJ) damping.

II. RAMAN ANALYSIS

TABLE S3. RT experimental Raman peaks of SBWO, HBWO-U, and HBWO-S samples along with that of DFT (GGA-PBE and GGA-PBE+U_d+U_p) simulations. ELM: External Lattice Mode, AD: Asymmetric Distortion, SBV: Symmetric Bending Vibrations, ABV: Asymmetric Bending Vibrations, TM: Translational Mode, ABrM: Asymmetric Bridging Mode, AST: Asymmetric Stretching.

Raman Peak Analysis						
SBWO	HBWO-U	HBWO-S	GGA-PBE	GGA-PBE+U_d+U_p		
(cm^{-1})	(cm^{-1})	(cm^{-1})	(cm^{-1})	(cm^{-1})	Symm.	Peak Assignment
-	129	139	129	128	E_g	ELM
153	152	152	154	158	A_{1g}	ELM
-	222	225	222	228	B_{1g}	WO$_6$ AD
242	255	260	254	260	A_{1g}	Bi-O SBV
283	282	283	274	282	E_g	WO$_6$ ABV
295	300	306	296	298	E_g	Bi^{3+} and WO$_6^{6-}$ TM
406	413	417	408	412	E_g	WO$_6$ ABV
711	716	704	713	716	B_{1g}	WO$_6$ ABrM
-	-	724	731	732	B_{1g}	O-W-O AST
800	796	796	794	804	B_{1g}	WO$_6$ ABrM
-	814	821	811	834	B_{1g}	O-W-O AST

III. FTIR ANALYSIS

TABLE S4. The SBWO, HBWO-U, and HBWO-S samples' FTIR peak designations to corresponding atomic motion along with DFT-derived peaks of phonon density of states for GGA-PBE+vdW and GGA-PBE+U_d+U_p+vdW. SV: Symmetric Vibration, AST: Asymmetric Stretching, SST: Symmetric Stretching, BV: Bending Vibration.

FTIR Peak Analysis					
SBWO	HBWO-U	HBWO-S	GGA-PBE+vdW	GGA-PBE+U_d+U_p+vdW	
(cm^{-1})	(cm^{-1})	(cm^{-1})	(cm^{-1})	(cm^{-1})	Peak Assignment
417	427	427	419	424	Bi-O SST
533	565	565	526	540	Bi-O-Bi AST
680	703	697	684	678	W-O SST
818	812	820	782	814	Bi-O SST
958	-	-	915	930	O-H BV
1056	1026	1029	-	-	W-O SST
-	1108	-	-	-	C-C SST
-	1314	1392	-	-	C=O SST
-	1636	1627	-	-	O-H SST
	3471	3469	-	-	O-H BV

IV. EDX ANALYSIS

The EDX spectra in Fig. S1 presents the characteristic peaks of X-ray radiation for Bi ($L_\alpha = 10.79$ keV, $L_\beta = 13.00$ keV, $M_\alpha = 2.42$ keV, W ($L_\alpha = 8.25$ keV, $L_\beta = 9.75$ keV, and $M_\alpha = 1.85$ keV) in all samples.

TABLE S5. Chemical species identification, atomic percentage at. (%) and weight percentage wt. (%) concentration analysis using EDX (Model: EDAX Team) of SBWO, HBWO-U, and HBWO-S.

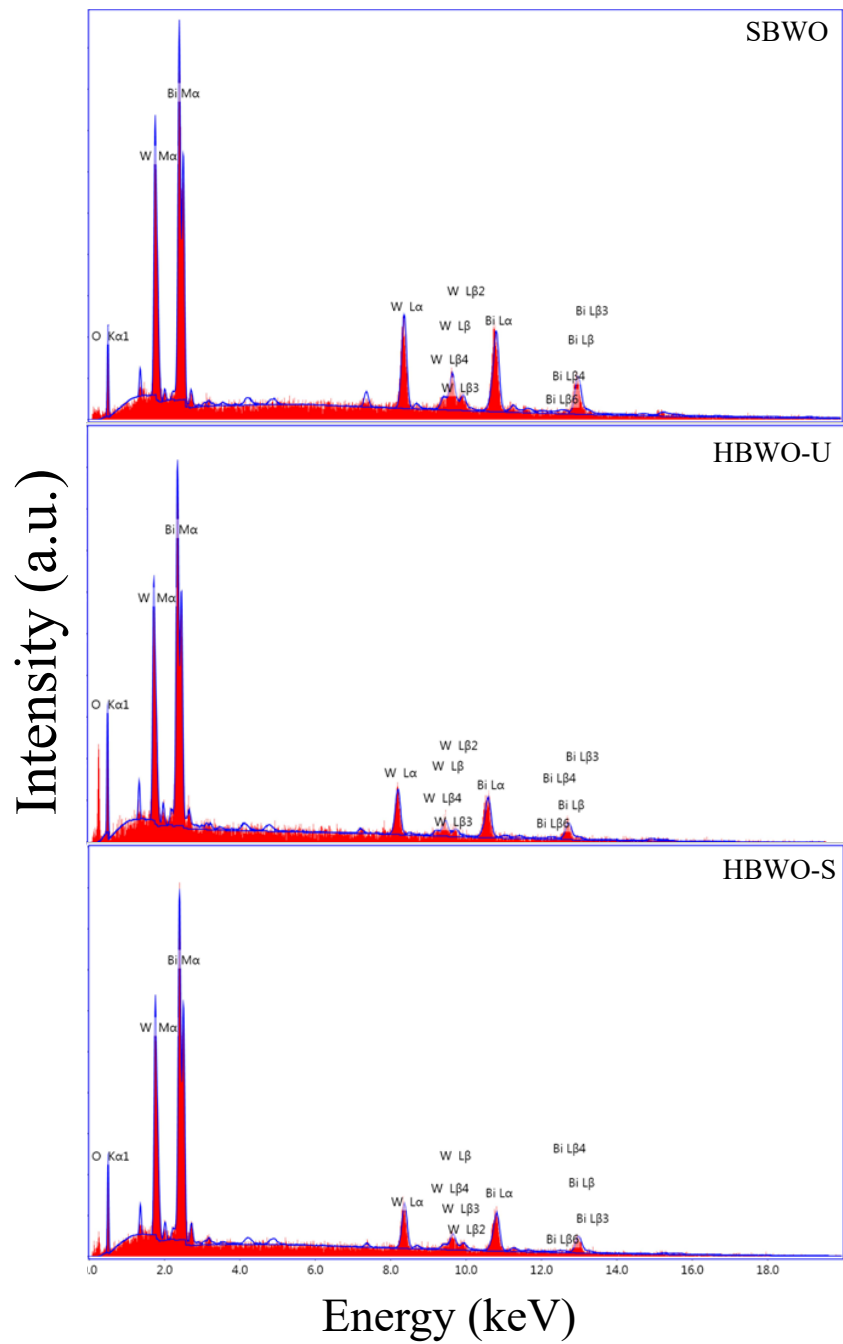| | | EDX Analysis | | | |
| | | at. (%) (Theory) | at. (%) (Exp.) | wt. (%) (Theory) | wt. (%) (Exp.) |
Sample	Element				
SBWO	Bi	22.22	22.8	59.89	59
	W	11.11	10.79	26.35	27.31
	O	66.67	66.41	13.76	13.69
HBWO-U	Bi	22.22	22.39	59.89	59.89
	W	11.11	11.12	26.35	26.66
	O	66.67	66.49	13.76	13.45
HBWO-S	Bi	22.22	22.16	59.89	59.9
	W	11.11	11.37	26.35	26.38
	O	66.67	66.47	13.76	13.72

FIG. S1. EDX spectra of (a) SBWO, (b) SBWO-U, and (c) SBWO-S measured by EDX Model: EDAX Team machine.

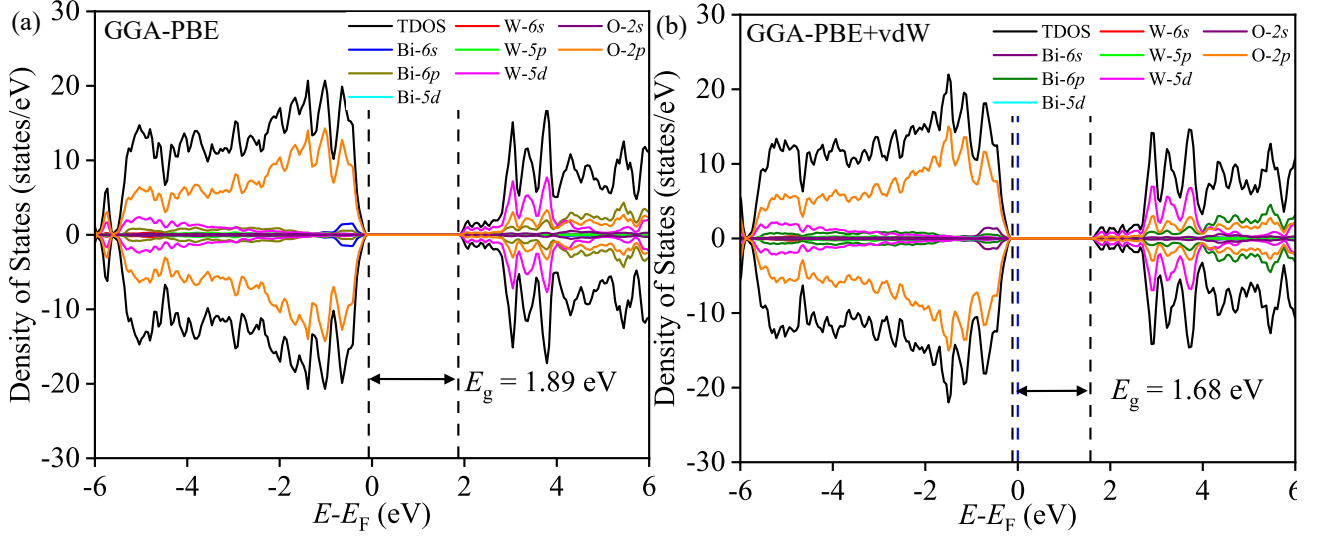# V. ELECTRONIC PROPERTIES SIMULATION

FIG. S2. TDOS and PDOS of BWO for (a) GGA-PBE and (b) GGA-PBE+vdW functionals. The inclusion of vdW force reduces the band gap E_g in DOS.
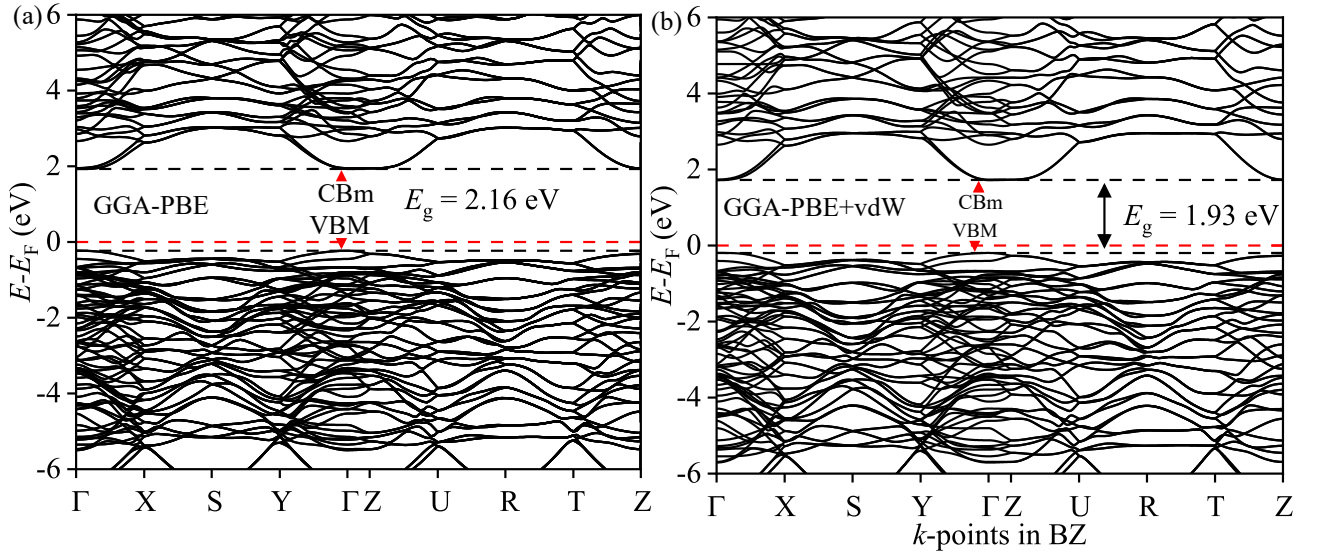
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FIG. S3. Electronic BS of BWO for (a) GGA-PBE and (b) GGA-PBE+vdW functionals. The inclusion of vdW force reduces the band gap E_g in BS. The GGA-PBE predicts the erroneous direct nature of the band gap regardless of the vdW force.
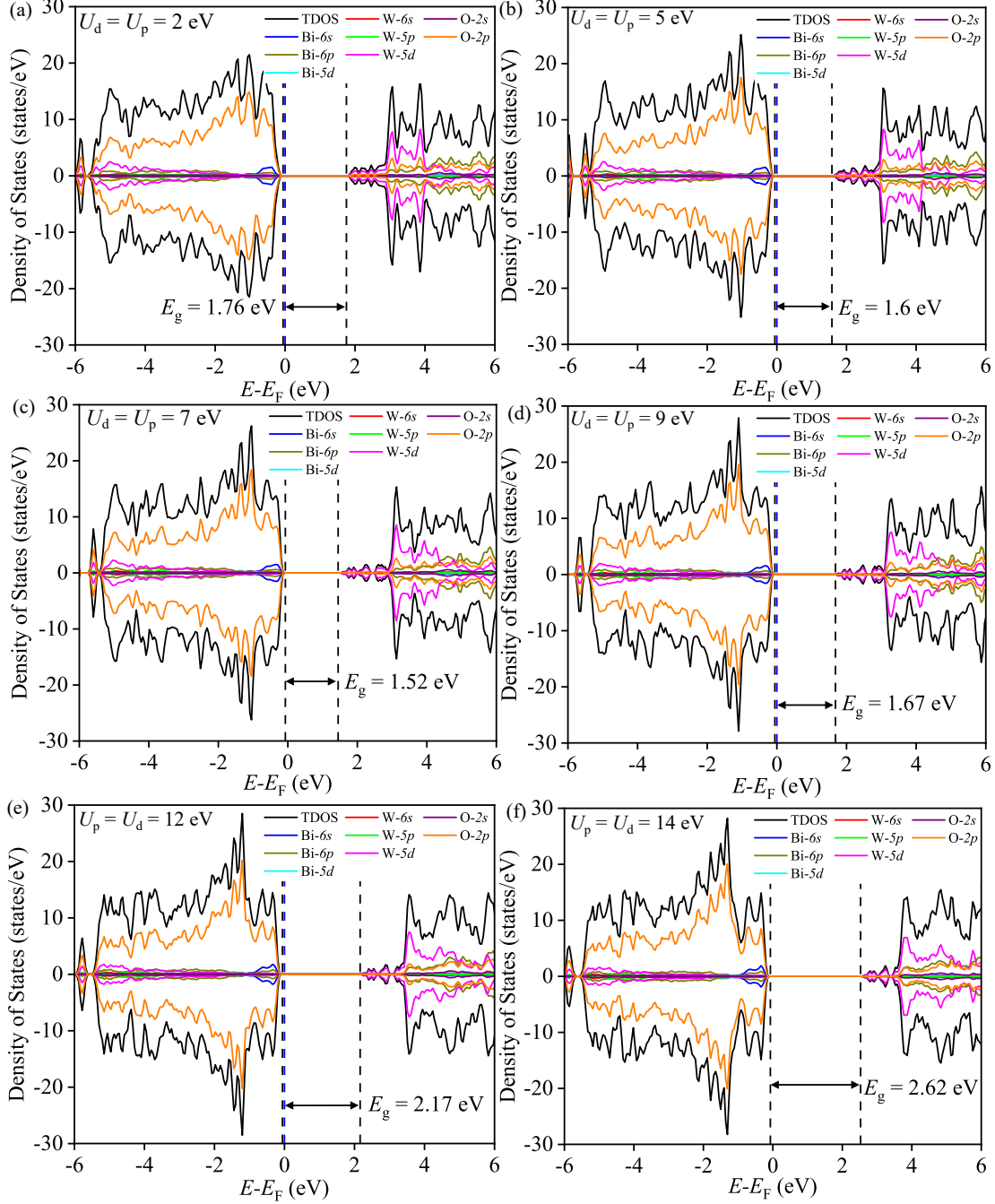
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FIG. S4. TDOS and PDOS of BWO for GGA-PBE+U_d+U_p with (a) $U_d = U_p = 2$ eV, (b) $U_d = U_p = 5$ eV, (c) $U_d = U_p = 7$ eV, (d) $U_d = U_p = 9$ eV, (e) $U_d = U_p = 12$ eV and (f) $U_d = U_p = 14$ eV. The band gap E_g varies with different values of U_d and U_p.

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FIG. S5. The vdW force is included. TDOS and PDOS of BWO for GGA-PBE+U_d+U_p+vdW with (a) $U_d = U_p = 2$ eV, (b) $U_d = U_p = 5$ eV, (c) $U_d = U_p = 7$ eV, (d) $U_d = U_p = 9$ eV, (e) $U_d = U_p = 12$ eV and (f) $U_d = U_p = 14$ eV. The band gap E_g varies with different values of U_d and U_p.
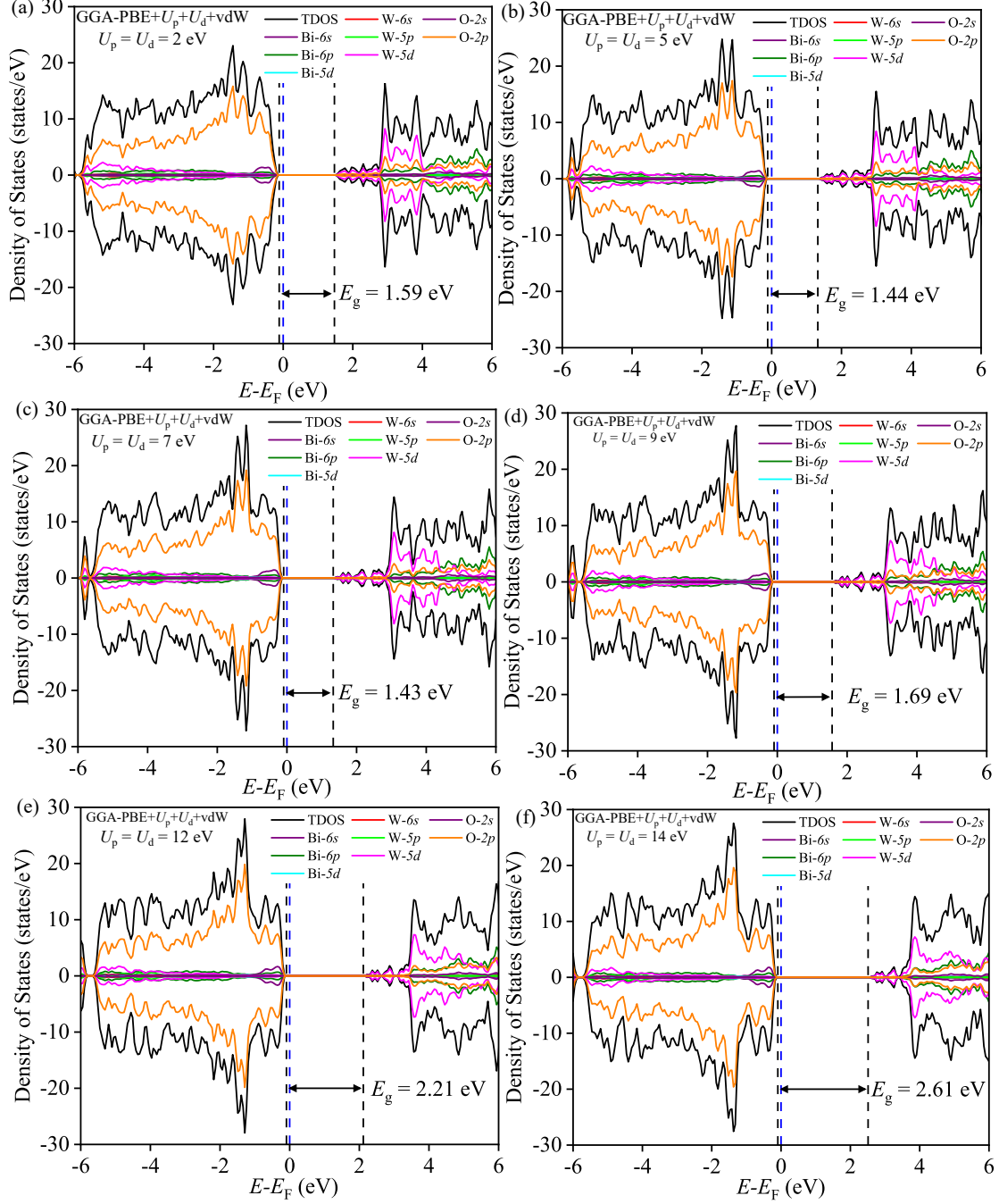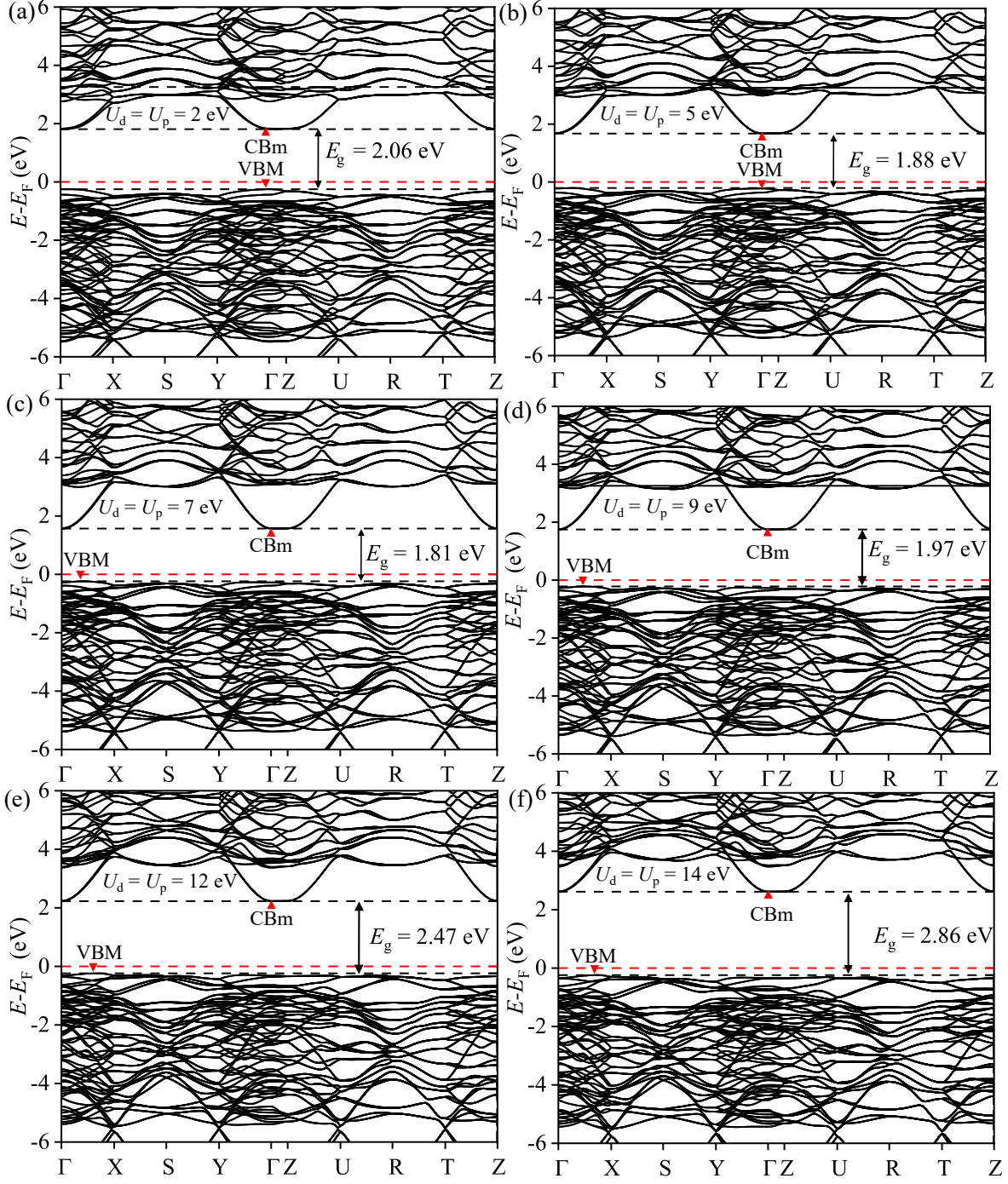
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FIG. S6. Electronic BS of BWO in the absence of vdW force for GGA-PBE+U_d+U_p with (a) U_d = U_p = 2 eV, (b) U_d = U_p = 5 eV, (c) U_d = U_p = 7 eV, (d) U_d = U_p = 9 eV, (e) U_d = U_p = 12 eV and (f) U_d = U_p = 14 eV. The band gap E_g in the BS varies with different values of U_d and U_p.

FIG. S7. The vdW force is included. Electronic BS of BWO for GGA-PBE+U_d+U_p+vdW with (a) $U_d = U_p = 2$ eV, (b) $U_d = U_p = 5$ eV, (c) $U_d = U_p = 7$ eV, (d) $U_d = U_p = 9$ eV, (e) $U_d = U_p = 12$ eV and (f) $U_d = U_p = 14$ eV. The band gap E_g in the BS varies with different values of U_d and U_p.
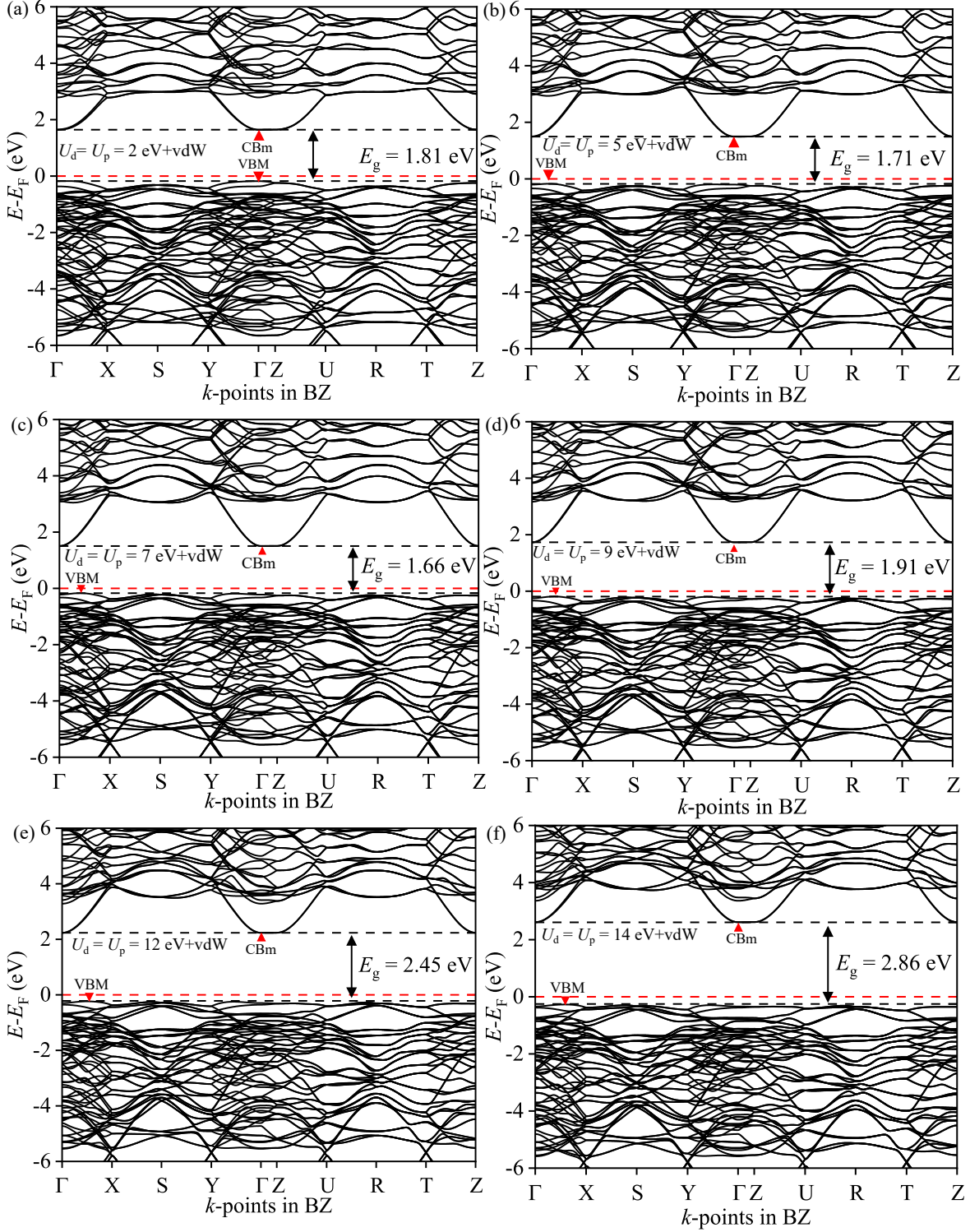
VI. ELASTIC PROPERTIES SIMULATION

TABLE S6. Elastic constants (C_{ij}), bulk moduli (B_V, B_R and B_H), shear moduli (G_V, G_R, G_H), Young's moduli (E_V, E_R, E_H), Poisson's ratio (ν_V, ν_R, ν_H) and Pugh's ratio (k_V, k_R, k_H) in Voigt–Reuss–Hill framework for for BWO using GGA-PBE, GGA-PBE+U_d+U_p and GGA-PBE+U_d+U_p+vdW.

	Elastic Properties (E.P.) of BWO		
E.P.	GGA-PBE	GGA-PBE+U_d+U_p	GGA-PBE+U_d+U_p+vdW
C_{11} (GPa)	131.293	201.29	233.269
C_{12} (GPa)	4.028	68.734	90.058
C_{13} (GPa)	42.544	48.644	58.849
C_{22} (GPa)	103.827	190.576	215.771
C_{23} (GPa)	12.643	8.052	18.775
C_{33} (GPa)	98.635	100.703	106.653
C_{44} (GPa)	44.365	36.669	39.994
C_{55} (GPa)	60.567	70.187	80.6
C_{66} (GPa)	33.829	104.078	106.212
B_V (GPa)	50.240	82.600	99.010
B_R (GPa)	48.632	68.254	78.834
B_H (GPa)	49.438	75.428	88.920
G_V (GPa)	46.050	66.660	71.230
G_R (GPa)	43.064	56.286	60.287
G_H (GPa)	44.559	61.474	65.758
E_V (GPa)	105.830	157.590	172.350
E_R (GPa)	99.749	132.449	144.122
E_H (GPa)	102.794	145.024	158.261
ν_V	0.150	0.180	0.210
ν_R	0.158	0.177	0.195
ν_H	0.153	0.180	0.203
k_V	1.090	1.240	1.390
k_R	1.129	1.213	1.308
k_H	1.109	1.227	1.352

VII. BORN CHARGE

The Born effective charge (BEC) embodies the atomic charge dynamics. The BEC has its origin in the screening of long-range Coulomb potential of the ions whose motion forms the phonon characteristics. The simulated BEC tensor is displayed in Table S7 for both GGA-PBE+vdW and GGA-PBE+U_d+U_p+vdW.

TABLE S7.   Born effective charge tensor of BWO using GGA-PBE+vdW and GGA-PBE+U_d+U_p+vdW.

	Z_B	Position	xx	xy	xz	yx	yy	yz	zx	zy	zz
BWO	Bi	4a	4.779	−0.263	0.495	−0.201	4.793	0.010	0.907	0.536	4.453
GGA-PBE+vdW	Bi	4a	4.781	0.264	0.493	0.202	4.792	−0.011	0.907	−0.536	4.454
	W	4a	8.196	0.005	0.450	−0.003	6.820	0.001	0.411	0.000	7.989
	O1	4a	−2.207	0.042	1.306	0.301	−2.201	0.639	1.214	1.222	−4.509
	O2	4a	−3.699	−2.142	−0.434	−2.112	−3.039	−0.339	−0.404	−0.254	−1.342
	O3	4a	−3.696	2.143	−0.432	2.112	−3.042	0.340	−0.402	0.256	−1.341
	O4	4a	−2.206	0.041	1.305	0.302	−2.202	0.571	1.212	1.225	−4.509
	O5	4a	−2.974	−0.254	0.452	0.117	−2.961	0.150	0.193	0.218	−2.598
	O6	4a	−2.975	0.253	−0.452	−0.116	−2.961	0.150	−0.193	0.218	−2.598
BWO	Bi	4a	4.791	−0.272	0.620	−0.362	4.736	0.123	1.028	0.385	4.251
GGA-PBE+U_d+U_p	Bi	4a	4.791	0.272	0.620	0.362	4.735	−0.123	1.028	−0.385	4.251
+vdW	W	4a	8.357	0.002	0.502	−0.002	7.950	0.000	0.573	0.000	8.582
	O1	4a	−2.450	0.160	1.230	0.370	−2.190	0.222	1.262	0.506	−4.382
	O2	4a	−3.560	−2.058	−0.134	−2.187	−3.527	−0.099	−0.075	0.005	−1.657
	O3	4a	−3.560	2.058	−0.134	2.187	−3.528	0.173	−0.075	−0.004	−1.657
	O4	4a	−2.450	0.160	1.230	0.370	−2.190	0.223	1.262	0.506	−4.383
	O5	4a	−2.960	−0.320	0.405	0.256	−2.993	0.249	0.130	0.276	−2.502
	O6	4a	−2.959	0.320	−0.405	−0.256	−2.993	0.249	−0.130	0.276	−2.502