Electronic Supplementary Material (ESI) for RSC Advances.

Theoretical Investigations of the novel zinc oxide polytypes and in-depth study of their electronic properties

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Supporting Information

Supporting Information:

The Supporting Information has been divided into three parts: Supporting Tables, Supporting Figures and Supporting References. Furthermore, Supporting Figures are presented in two individual sections: *additional E(V) curves* and *additional band structures.*

Supporting Tables

Table SI shows a summary of structural data for each calculated modification of zinc oxide found after local optimizations performed using various *ab initio* approaches.

Space group and polytype notation	**Cell parameters and fractional coordinates**		
	LDA	*B3LYP*	*HF*
P6$_3$mc (186) Wurtzite (2H) Pearson no.:hP4	a = 3.19 Å, c = 5.18 Å Zn (1/3, 2/3, 0) O (1/3, 2/3, 0.3763)	a = 3.28 Å, c = 5.29 Å Zn (1/3, 2/3, 0) O (1/3, 2/3, 0.3787)	a = 3.29 Å, c = 5.24 Å Zn (1/3, 2/3, 0) O (1/3, 2/3, 0.3843)
P6$_3$mc (186) 4H Pearson no.:hP8 Zhdanov no.: (2 2)	a = 3.19 Å, c = 10.38 Å Zn (0, 0, 0) Zn (1/3, 2/3, 0.2501) O (0, 0, 0.1876) O (1/3, 2/3, 0.4378)	a = 3.28 Å, c = 10.64 Å Zn (0, 0, 0) Zn (1/3, 2/3, 0.2504) O (0, 0, 0.1878) O (1/3, 2/3, 0.4379)	a = 3.28 Å, c = 10.60 Å Zn (0, 0, 0) Zn (1/3, 2/3, 0.2506) O (0, 0, 0.1897) O (1/3, 2/3, 0.4394)
P3m1 (156) Moissanite (5H) Pearson no.:hP10 Zhdanov no.: (4 1)	a = 3.19 Å, b = 12.95 Å Zn (0, 0, 0.9994) Zn (0, 0, 0.5998) Zn (2/3, 1/3, 0.7997) Zn (1/3, 2/3, 0.3996) Zn (2/3, 1/3, 0.1993) O (0, 0, 0.8487) O (2/3, 1/3, 0.6491) O (0, 0, 0.4489) O (1/3, 2/3, 0.2487) O (2/3, 1/3, 0.0484)	a = 3.27 Å, b = 13.29 Å Zn (0, 0, 0.9992) Zn (0, 0, 0.5999) Zn (2/3, 1/3, 0.7997) Zn (1/3, 2/3, 0.3996) Zn (2/3, 1/3, 0.1993) O (0, 0, 0.8486) O (2/3, 1/3, 0.6491) O (0, 0, 0.4490) O (1/3, 2/3, 0.2487) O (2/3, 1/3, 0.0484)	a = 3.27 Å, b = 13.25 Å Zn (0, 0, 0.9990) Zn (0, 0, 0.6007) Zn (2/3, 1/3, 0.8001) Zn (1/3, 2/3, 0.3999) Zn (2/3, 1/3, 0.1993) O (0, 0, 0.8481) O (2/3, 1/3, 0.6492) O (0, 0, 0.4491) O (1/3, 2/3, 0.2484) O (2/3, 1/3, 0.0477)
P6$_3$mc (186) 6H Pearson no.:hP12 Zhdanov no.: (3 3)	a = 3.18 Å, b = 15.57 Å Zn (0, 0, 0) Zn (1/3, 2/3, 0.1666) Zn (2/3, 1/3, 1/3) O (0, 0, 0.1248) O (1/3, 2/3, 0.2915) O (2/3, 1/3, 0.4582)	a = 3.27 Å, b = 15.97 Å Zn (0, 0, 0) Zn (1/3, 2/3, 0.1664) Zn (2/3, 1/3, 1/3) O (0, 0, 0.1249) O (1/3, 2/3, 0.2916) O (2/3, 1/3, 0.4585)	a = 3.27 Å, b = 15.92 Å Zn (0, 0, 0) Zn (1/3, 2/3, 0.1661) Zn (2/3, 1/3, 1/3) O (0, 0, 0.1254) O (1/3, 2/3, 0.2921) O (2/3, 1/3, 0.4592)
P6$_3$mc (186) 8H Pearson no.:hP16 Zhdanov no.: (4 4)	a = 3.18 Å, b = 20.78 Å Zn (0, 0, 0) Zn (1/3, 2/3, 0.1251) Zn (1/3, 2/3, 0.3752) Zn (1/3, 2/3, 0.7502) O (0, 0, 0.0937) O (1/3, 2/3, 0.2188) O (1/3, 2/3, 0.4689) O (1/3, 2/3, 0.8438)	a = 3.27 Å, b = 21.30 Å Zn (0, 0, 0) Zn (1/3, 2/3, 0.1252) Zn (1/3, 2/3, 0.3751) Zn (1/3, 2/3, 0.7502) O (0, 0, 0.0939) O (1/3, 2/3, 0.2191) O (1/3, 2/3, 0.4689) O (1/3, 2/3, 0.8439)	a = 3.27 Å, b = 21.27 Å Zn (0, 0, 0) Zn (1/3, 2/3, 0.1253) Zn (1/3, 2/3, 0.3747) Zn (1/3, 2/3, 0.7502) O (0, 0, 0.0943) O (1/3, 2/3, 0.2195) O (1/3, 2/3, 0.4690) O (1/3, 2/3, 0.8441)
R3m (160) 9R Pearson no.:hR6 Zhdanov no.: (2 1) 3	a = 3.19 Å, b = 23.42 Å Zn (0, 0, 0) Zn (0, 0, 0.4447) Zn (0, 0, 0.2211) O (0, 0, 0.0851)	a = 3.28 Å, b = 23.98 Å Zn (0, 0, 0) Zn (0, 0, 0.4447) Zn (0, 0, 0.2215) O (0, 0, 0.0855)	a = 3.28 Å, b = 23.74 Å Zn (0, 0, 0) Zn (0, 0, 0.4441) Zn (0, 0, 0.2218) O (0, 0, 0.0845)

	O (0, 0, 0.5284) O (0, 0, 0.3077)	O (0, 0, 0.5290) O (0, 0, 0.3076)	O (0, 0, 0.5286) O (0, 0, 0.3067)
R3m (160) 12R* Pearson no.:hR8 Zhdanov no.: (3 1) 3	a = 3.19 Å, b = 31.28 Å Zn (0, 0, 0) Zn (0, 0, 0.4160) Zn (0, 0, 0.8328) Zn (0, 0, 0.5840) O (0, 0, 0.0625) O (0, 0, 0.4795) O (0, 0, 0.8974) O (0, 0, 0.6465)	a = 3.27 Å, b = 32.04 Å Zn (0, 0, 0) Zn (0, 0, 0.4163) Zn (0, 0, 0.8331) Zn (0, 0, 0.5839) O (0, 0, 0.0630) O (0, 0, 0.4799) O (0, 0, 0.8977) O (0, 0, 0.6467)	a = 3.28 Å, b = 31.75 Å Zn (0, 0, 0) Zn (0, 0, 0.4171) Zn (0, 0, 0.8339) Zn (0, 0, 0.5835) O (0, 0, 0.0633) O (0, 0, 0.4804) O (0, 0, 0.8969) O (0, 0, 0.6465)
R3m (160) 15R* Pearson no.:hR10 Zhdanov no.: (3 2) 3	a = 3.28 Å, b = 39.77 Å Zn (0, 0, 0) Zn (0, 0, 0.7335) Zn (0, 0, 0.4669) Zn (0, 0, 0.8667) Zn (0, 0, 0.2669) O (0, 0, 0.0504) O (0, 0, 0.7839) O (0, 0, 0.5171) O (0, 0, 0.9172) O (0, 0, 0.3171)	a = 3.15 Å, b = 38.32 Å Zn (0, 0, 0) Zn (0, 0, 0.7336) Zn (0, 0, 0.4660) Zn (0, 0, 0.8651) Zn (0, 0, 0.2656) O (0, 0, 0.0505) O (0, 0, 0.7834) O (0, 0, 0.5152) O (0, 0, 0.9154) O (0, 0, 0.3163)	a = 3.28 Å, b = 39.77 Å Zn (0, 0, 0) Zn (0, 0, 0.7335) Zn (0, 0, 0.4670) Zn (0, 0, 0.8668) Zn (0, 0, 0.2669) O (0, 0, 0.0504) O (0, 0, 0.7840) O (0, 0, 0.5172) O (0, 0, 0.9172) O (0, 0, 0.3171)
F-43m (216) Sphalerite (3C) Pearson no.:cF8	a = 4.49 Å Zn (0, 0, 0) O (3/4, 3/4, 3/4)	a = 4.61 Å Zn (0, 0, 0) O (3/4, 3/4, 3/4)	a = 4.62 Å Zn (0, 0, 0) O (3/4, 3/4, 3/4)

*Final optimized structure is different from the initial prototype structure

Table SI. Structure data of the energetically most favorable polytype modifications of zinc oxide found after local optimizations performed using Hartree-Fock (HF), DFT (LDA), and hybrid (B3LYP) functional.

In Table SII, the basis sets used for the *ab inito* local optimization of structures, *E(V)* and *H(p)* curves, DOS and band structure calculations are displayed.

Zn all electron basis set (AEBS)		O all electron basis set (AEBS)	
Type	Exponent and Coefficient	Type	Exponent and Coefficient
s	417016.5 0.00023 60504.2 0.00192 12907.9 0.01101 3375.74 0.04978 1018.11 0.16918 352.55 0.36771 138.19 0.40244 57.851 0.14386	s	8020.0 0.00108 1338.0 0.00804 255.4 0.05324 69.22 0.1681 23.90 0.3581 9.264 0.3855 3.851 0.1468 1.212 0.0728
sp	1079.2 -0.00620 0.00889 256.52 -0.07029 0.06384 85.999 -0.13721 0.22039 34.318 0.26987 0.40560 14.348 0.59918 0.41370 4.7769 0.32239 0.34974	sp	49.43 -0.00883 0.00958 10.47 -0.0915 0.0696 3.235 -0.0402 0.2065 1.217 0.379 0.347
sp	60.891 0.00679 -0.00895 25.082 -0.08468 -0.03333 10.620 -0.34709 0.08119 4.3076 0.40633 0.56518	sp	0.5 1.0 1.0
sp	1.6868 1.0 1.0	sp	0.191 1.0 1.0
sp	0.62679 1.0 1.0		
sp	0.15033 1.0 1.0		
d	57.345 0.02857 16.082 0.15686 5.3493 0.38663 1.7548 0.47766		
d	0.51592 1.0		

Table SII. For the local optimizations, an all electron basis set (AEBS), based on Gaussian-type orbitals (GTO), was used. In the case of Zn^{2+} a [*6s5p2d*] basis set was used as in refs. [1,2,3]. For O^{2-} a [*4s3p*] basis set was used as in refs. [3,4,5].

Supporting Figures

Additional E(V) curves

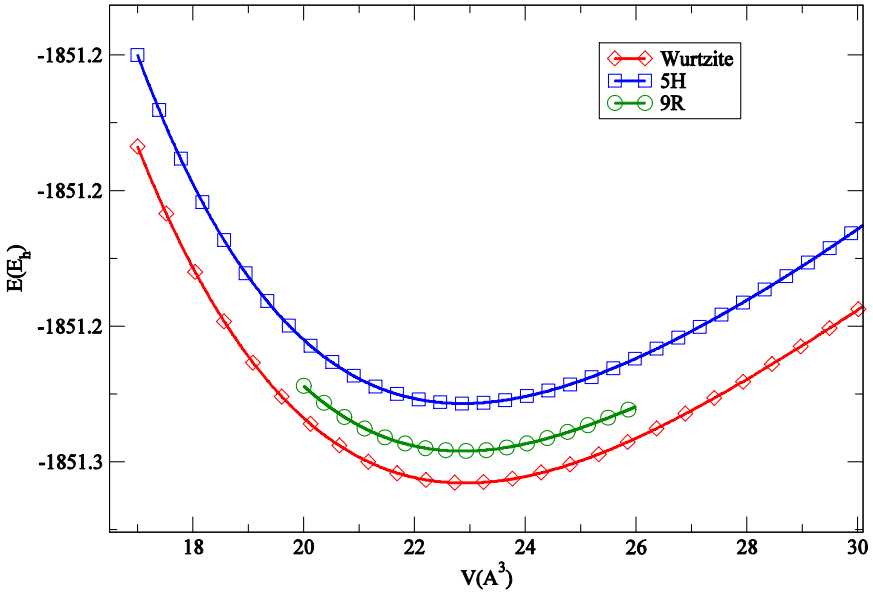

Figure S1. *E(V)* curves for the new stacking variants of ZnO calculated using DFT-LDA functional. Energies per formula unit are given in hartrees (E_h). Again, the curves for the 4H, 5H, 6H, 8H and 12R polytypes as well as the sphalerite modification exhibit essentially the same energy as the wurtzite modification, and are thus not displayed separated.

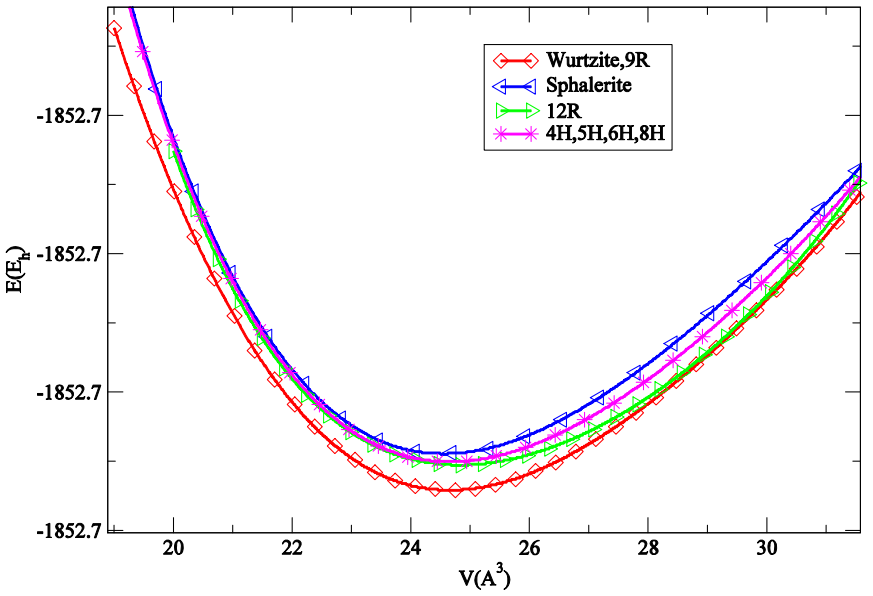

Figure S2. *E(V)* curves for the new stacking variants of ZnO at Hartree-Fock level of approximation. Energies per formula unit are given in hartrees (E_h).

Additional band structures

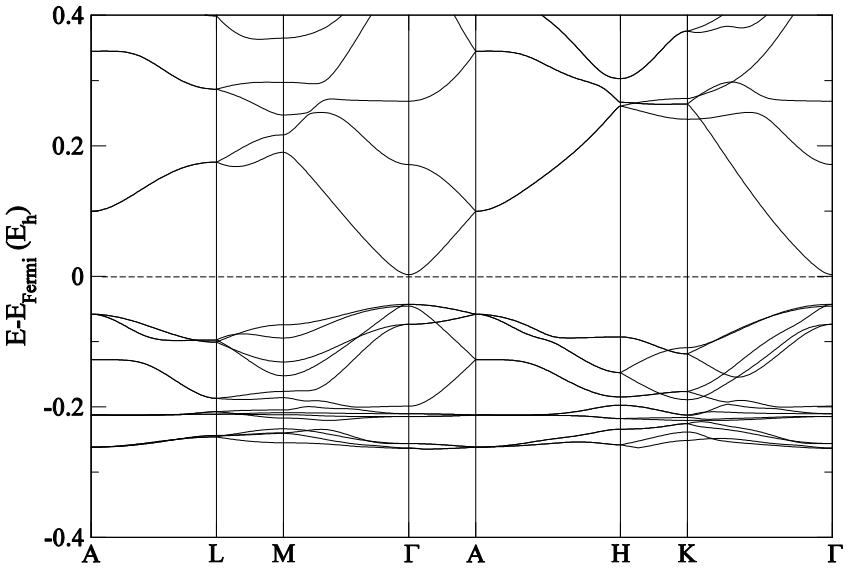

Figure. S3. Band structure calculation using the DFT-LDA functional for the wurtzite type modification in zinc oxide. Note that the labels of the special points of the Brillouin zones correspond to those of a hexagonal lattice.

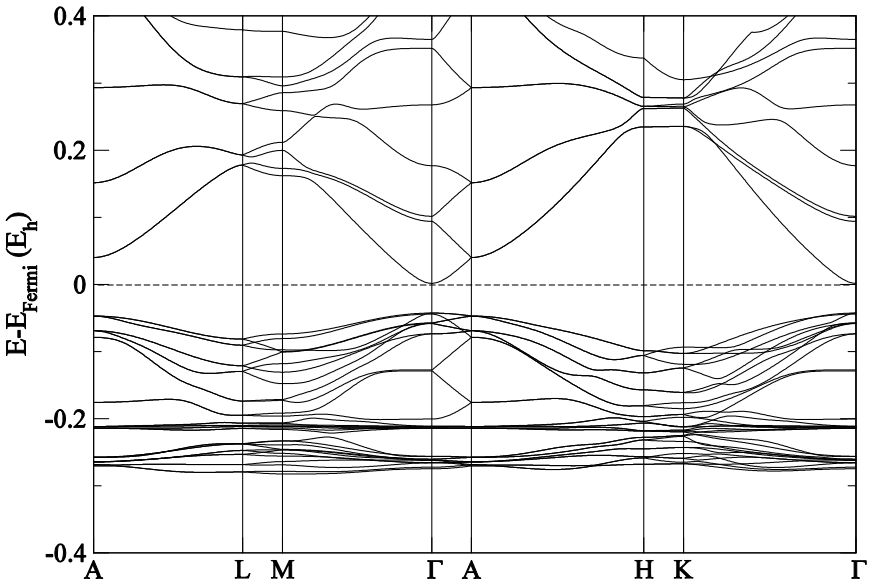

Figure. S4. Band structure calculation using the DFT-LDA functional for the 4H polytype of zinc oxide. Note that the labels of the special points of the Brillouin zones correspond to those of a hexagonal lattice.

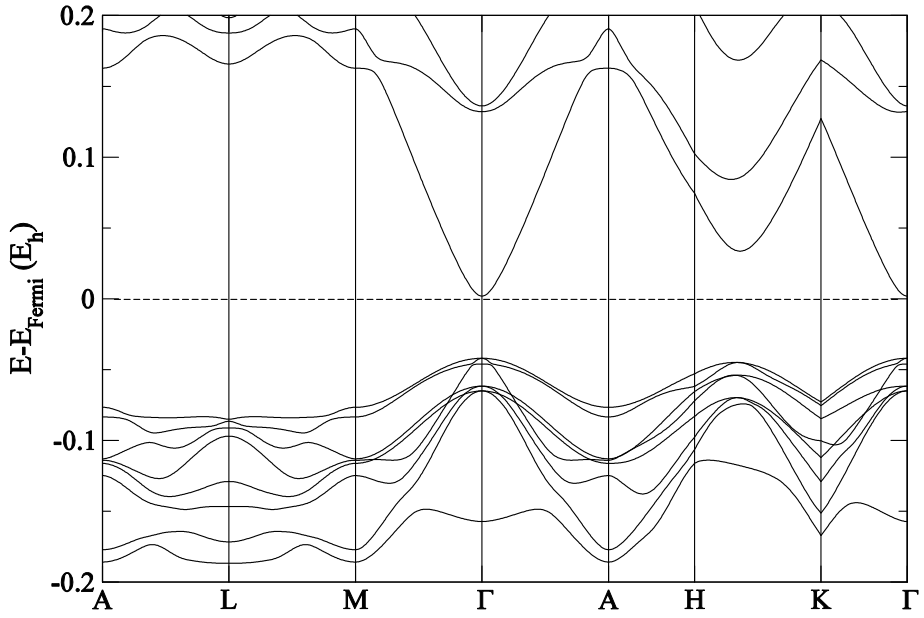

Figure. S5. Band structure calculation using the DFT-LDA functional for the 9R polytype of zinc oxide. Note that the labels of the special points of the Brillouin zones correspond to those of a hexagonal lattice.

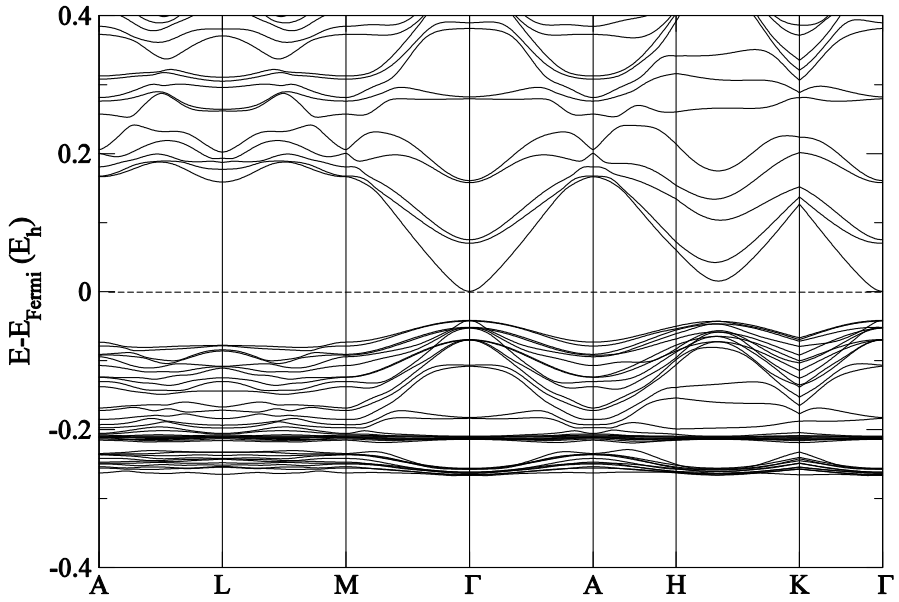

Figure. S6. Band structure calculation using the DFT-LDA functional for the 15R polytype of zinc oxide. Note that the labels of the special points of the Brillouin zones correspond to those of a hexagonal lattice.

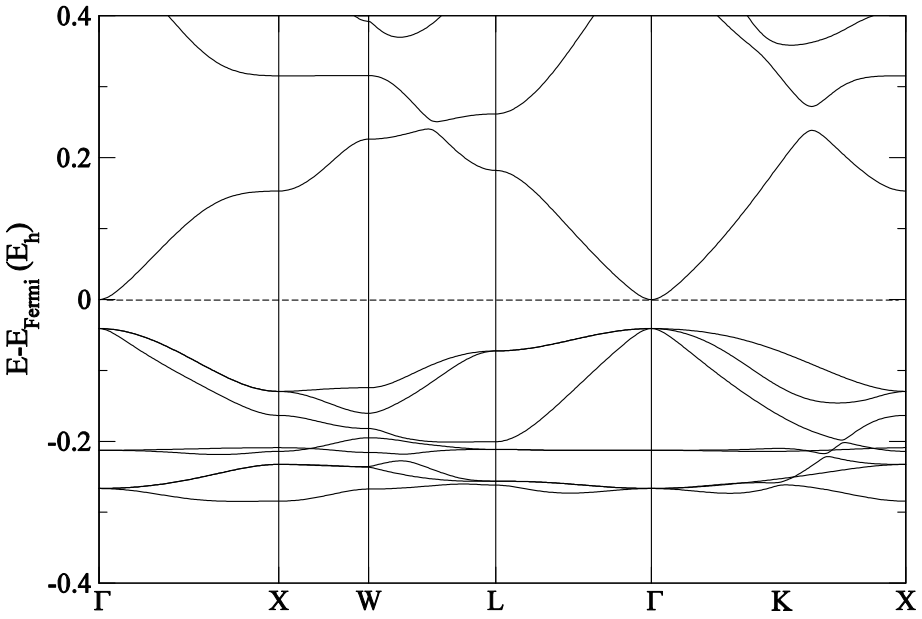

Figure. S7. Band structure calculation using the DFT-LDA functional for the sphalerite type modification in zinc oxide. Note that the labels of the special points of the Brillouin zones correspond to those of a *fcc* lattice.

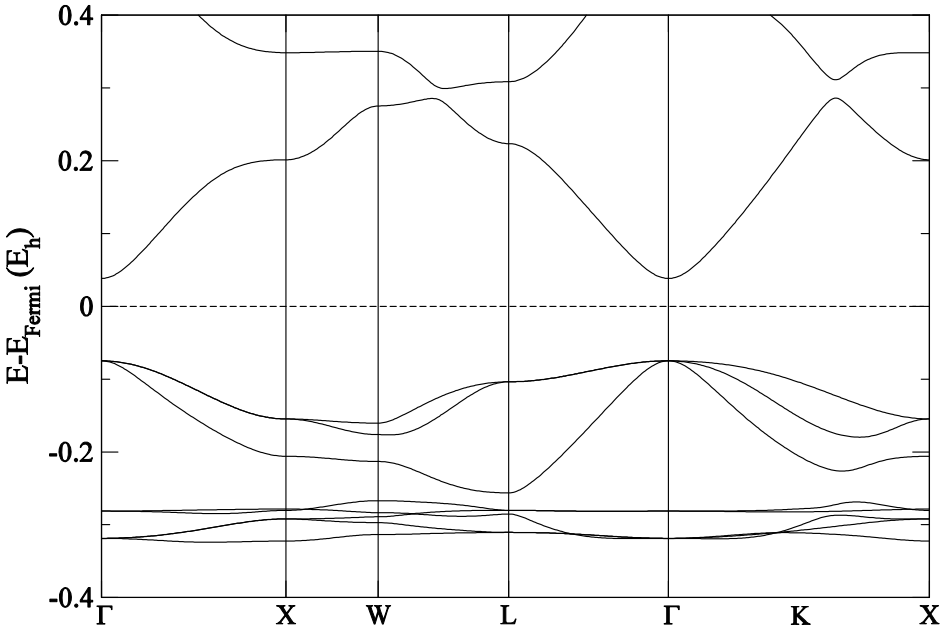

Figure. S8. Band structure calculation using the hybrid B3LYP functional for the sphalerite type modification in zinc oxide [3]. Note that the labels of the special points of the Brillouin zones correspond to those of a *fcc* lattice.

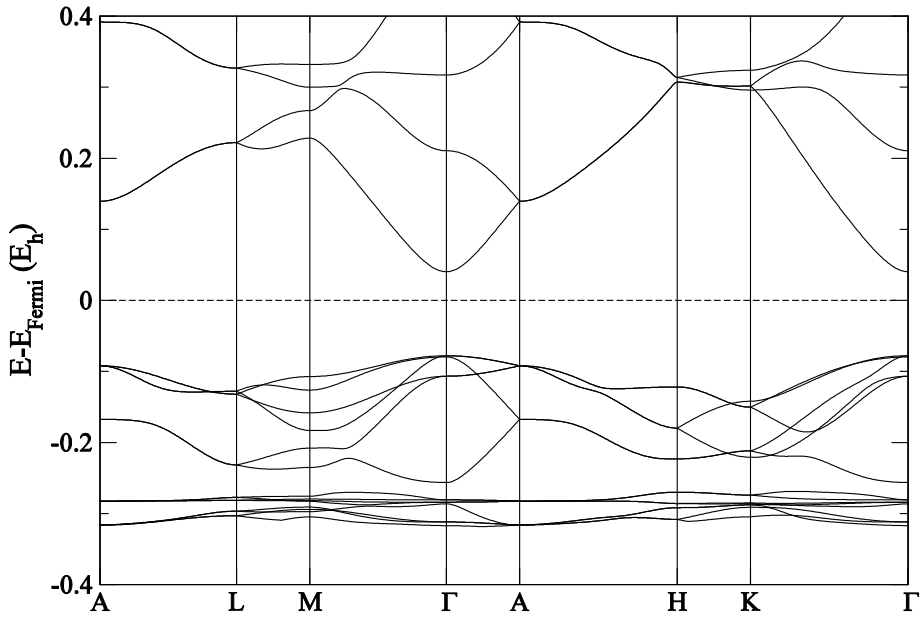

Figure. S9. Band structure calculation using the hybrid B3LYP functional for the wurtzite type modification in zinc oxide [3]. Note that the labels of the special points of the Brillouin zones correspond to those of a hexagonal lattice.

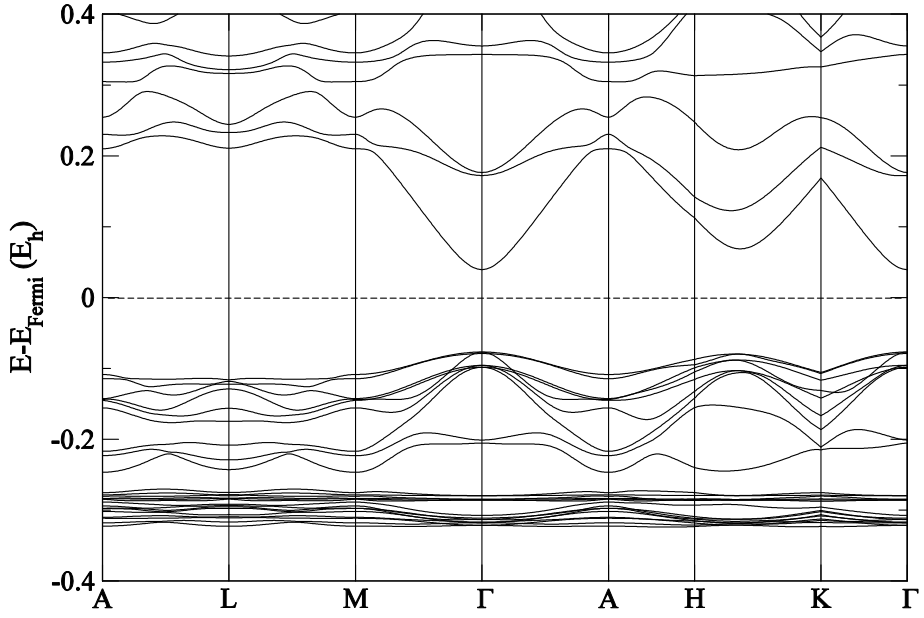

Figure. S10. Band structure calculation using the B3LYP functional for the 9R polytype of zinc oxide. Note that the labels of the special points of the Brillouin zones correspond to those of a hexagonal lattice. Also note that 4H and 15R polytype band structures calculated using B3LYP functional are included in the main text of the manuscript.

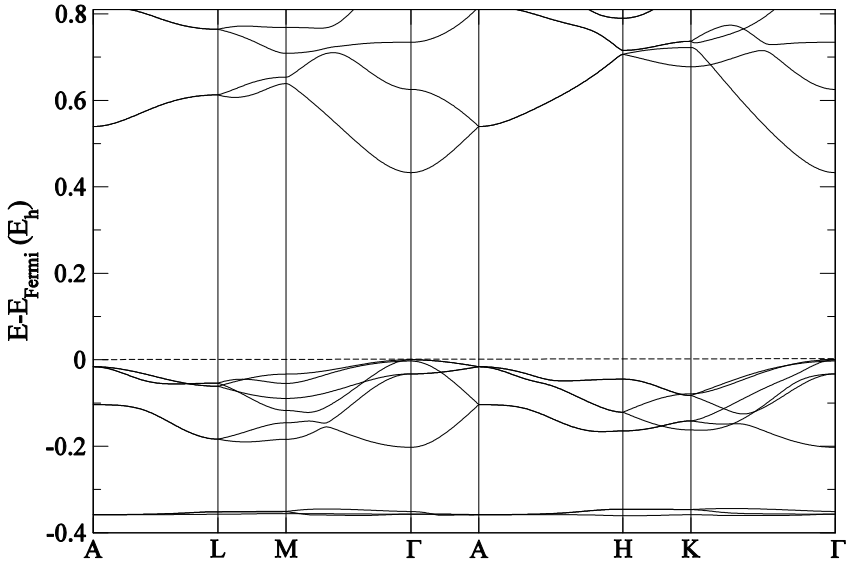

Figure. S11. Band structure calculation using the Hartree-Fock approximation for the wurtzite type modification in zinc oxide. Note that the labels of the special points of the Brillouin zones correspond to those of a hexagonal lattice.

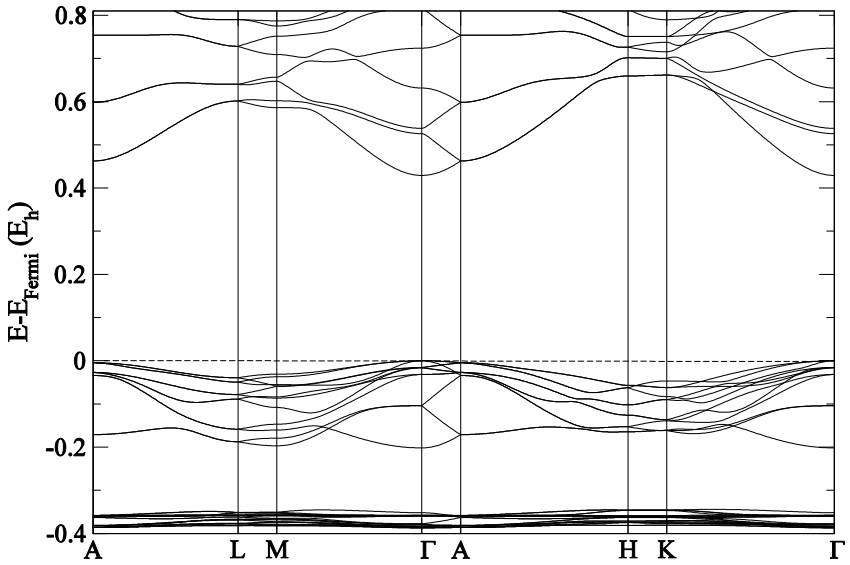

Figure. S12. Band structure calculation using the Hartree-Fock approximation for the 4H polytype of zinc oxide. Note that the labels of the special points of the Brillouin zones correspond to those of a hexagonal lattice.

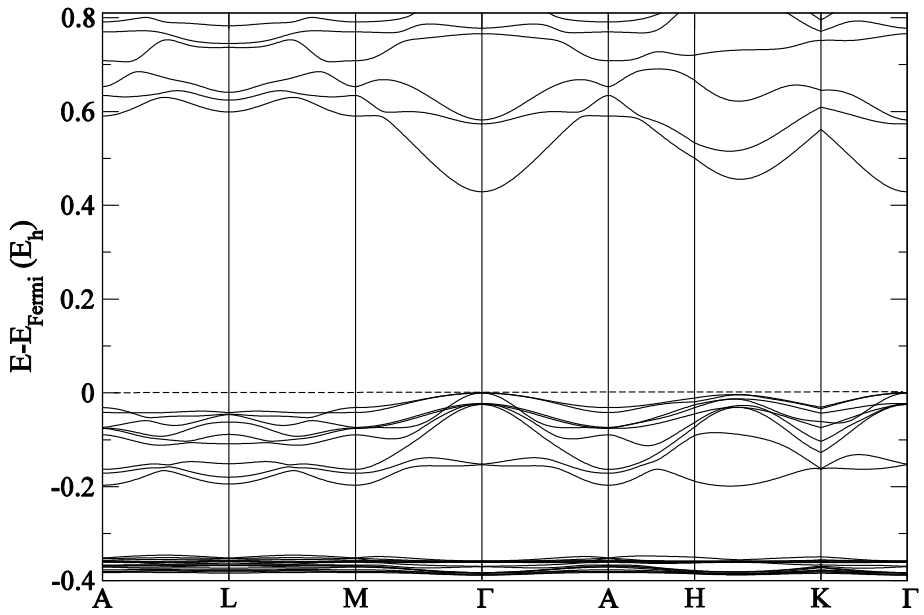

Figure. S13. Band structure calculation using the Hartree-Fock approximation for the 9R polytype of zinc oxide. Note that the labels of the special points of the Brillouin zones correspond to those of a hexagonal lattice.

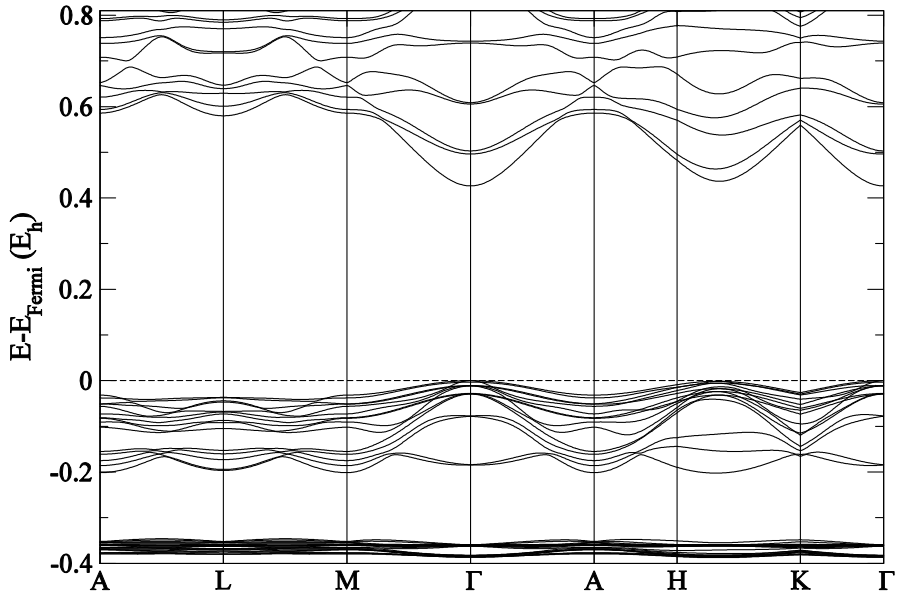

Figure. S14. Band structure calculation using the Hartree-Fock approximation for the 15R polytype of zinc oxide. Note that the labels of the special points of the Brillouin zones correspond to those of a hexagonal lattice.

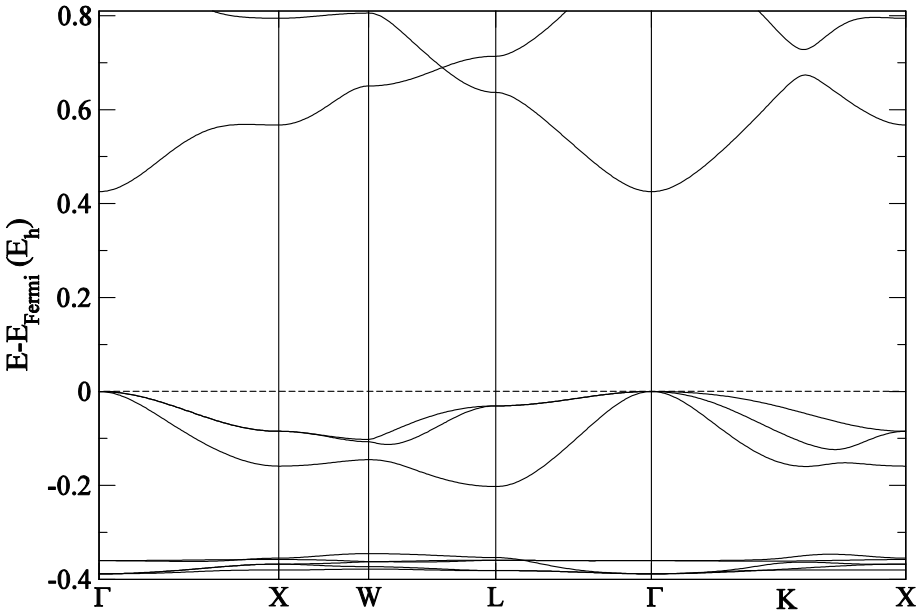

Figure. S15. Band structure calculation using the Hartree-Fock approximation for the sphalerite type modification in zinc oxide. Note that the labels of the special points of the Brillouin zones correspond to those of a *fcc* lattice.

Supporting References

1. J. E. Jaffe, and A. C.Hess, *Phys. Rev. B,* **48**, 7903, (1993).
2. T. Homann, U. Hotje, M. Binnewies, A. Borger, K. D. Becker, and T. Bredow, *Sol. Stat. Sci*., **8**, 44 (2006).
3. D. Zagorac, J. C. Schön, J. Zagorac, and M. Jansen, *Phys. Rev B*, **89**, 075201 (2014).
4. M.D. Towler, N.L. Allan, N.M. Harrison, V.R. Saunders, W.C. Mackrodt, and E. Apra., *Phys. Rev. B*, **50**, 5041 (1994).
5. A.M. Ferrari and C. Pisani, *J. Phys. Chem*., **110**, 7909 (2006).