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Supporting information for article:

ZnO/ZnS (hetero)structures: *ab initio* investigations of polytypic behavior of mixed ZnO and ZnS compounds

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Supporting Information to the PCAE method

Here we show the details of the so-called Primitive Cell approach for Atom Exchange (Pcae) method. The PCAE method is simple, fast and computationally inexpensive compared to the supercell approach. The method works by first transforming the crystallographic (conventional) cell to the primitive cell, which is the minimum volume unit cell, while keeping the symmetry and multiplicity of the atom positions. The matrices describing the transformations from conventional to primitive cells of Bravais lattices are coded in e.g. the CRYSTAL code [S1,S2] or the KPLOT code [S3], and are fully consistent with the space group symmetry in the International Tables for Crystallography [S4]. Once the primitive cell of the calculated structure has been constructed, we proceed to the anion exchange. We replace the number of atoms needed to obtain a certain stoichiometry, on the symmetry related Wyckoff positions. Afterwards an *ab initio* full structure optimization without symmetry constraints is performed.

Example: Wurtzite (2H) structure. Target stoichiometry: $\text{ZnO}_{0.5}\text{S}_{0.5}$. Primitive cell: 2 anion positions.

For those structure types, where the PCAE method cannot accommodate the exact stoichiometry, a supercell approach has to be used. However, even in these cases the smallest possible supercells is chosen. Furthermore, after the first optimization cycle of the corresponding supercell, the KPLOT program, for instance, can be used to idealize the structure and determine its new symmetries, and the PCAE method is subsequently re-applied. The advantage is particularly important regarding computational times: By being able to use symmetry-adapted unit cells in the *ab initio* calculations, we have achieved up to 40 times shorter computation times compared to the standard supercell approach. In a final step, one performs a last round of local *ab initio* minimizations of the structures without any symmetry constraints, to ensure that they are kinetically stable against all perturbations.

Example: Wurtzite (2H) structure. Target stoichiometry: $\text{ZnO}_{0.75}\text{S}_{0.25}$. Supercell: 2 x 2 x 2. Primitive cell: 8 anion positions. Now, you have 8 anion positions in the primitive cell, and two of them are used for anionic exchange of O by S. If both of the sulfur atoms are placed on the symmetry related positions in the primitive cell, the number of atoms in the unit cell has been reduced and the structure becomes energetically favorable compared to random displacement of the S atoms. (see Table S1) In the case of the polytype structures, the PCAE method plays an even greater role, since with the increase of the polytype number, the size of the primitive cell also grows, implying more ways to exchange the anions. On the other hand, small distortions can have a strong influence on the calculated total energy, symmetry or even initial structure of the polytype.

type/x	0.0	0.2	0.25	1/3	0.5	0.6	2/3	0.75	1.0
2H	-1851.2631	-	-1931.7944	-1958.6318	-2012.3188	-	-2066.0095	-2092.8624	-2173.3972
4H	-1851.2630	-	-1931.7886	-	-2012.3199	-	-	-2092.8555	-2173.3970
5H	-1851.2630	-1915.6829	-	-	-	-2044.5332	-	-	-2173.3969
6H	-1851.2630	-	-	-1958.6315	-	-	-2066.0092	-	-2173.3969
8H	-1851.2630	-	-1931.7887	-	-2012.3191	-	-	-2092.8555	-2173.3969
9R	-1851.2630	-	-	-1958.6312	-	-	-2066.0093	-	-2173.3970
12R	-1851.2631	-	-1931.7883	-	-2012.3198	-	-	-2092.8555	-2173.3970
15R	-1851.2630	-1915.6833	-	-	-2012.3206	-2044.5269	-	-	-2173.3969
3C	-1851.2630	-	-1931.7883	-1958.6314	-2012.3189	-	-2066.0094	-2092.8563	-2173.3968
xE(2H,x=1) + (1-x)E(2H,x=0)	-1851.2631	-1915.6899	-1931.7966	-1958.6411	-2012.3302	-2044.5435	-2066.0192	-2092.8637	-2173.3972
Modification		Total energy (E _h)	Symmetry /Primitive Cell		Anion Positions (Final)				
Wurtzite (2H)-symmetric		-1931.7944	No.6, 4 anions		S1,O2,O3,O4				
Wurtzite (2H)-random1		-1931.7898	No. 6, 8 anions		O1,O2,O3,S4,O5,S6,O7,O8				
Wurtzite (2H)-random2		-1931.7907	No. 1, 16 anions		O1,S2,O3,O4,O5,O6,O7,S8, O9,S10,S11,O12,O13,O14,O15,O16				

Table S1. Example of the Wurtzite (2H) structure in the ZnO_{0.75}S_{0.25} compound. Calculations performed using DFT-LDA approximation in the 2 x 2 x 2 supercell. The resulting random configurations are less symmetric and energetically less favorable. Furthermore, the random1 type resulted in unrealistic Zn-Zn distances, while the random2 configuration resulted in a non-symmetric structure with a four times larger unit cell compared to the symmetric one.

Supporting tables: Overview over the LDA energies for all compositions and polytypes investigated

Table S2: Overview over all energies for all prototypes and compositions (energy: LDA), including $x^*E(2H$ at $x = 1$) and $(1-x)^*E(2H$ at $x = 0$), in units of E_h .

type/x	0.0	0.2	0.25	1/3	0.5	0.6	2/3	0.75	1.0
2H	0.0000		0.0022	0.0093	0.0114		0.0097	0.0013	0.0000
4H	0.0001		0.0080		0.0103			0.0082	0.0002
5H	0.0001	0.0070				0.0103			0.0003
6H	0.0001			0.0096			0.0100		0.0003
8H	0.0001		0.0079		0.0111			0.0082	0.0003
9R	0.0001			0.0099			0.0099		0.0002
12R	0.0000		0.0083		0.0104			0.0082	0.0002
15R	0.0001	0.0066			0.0096	0.0166			0.0003
3C	0.0001		0.0083	0.0097	0.0113		0.0098	0.0074	0.0004

Table S3: Overview over all energies (energy: LDA) for all prototypes and compositions after subtracting $x^*E(2H, x=1) + (1-x)^*E(2H, x=0)$, in units of E_h .

Supporting tables: Summary of structural data for each calculated modification of the ZnO/ZnS compounds found after local optimizations performed using LDA and HSE functionals

Structure type and space group	LDA	HSE	Experiment
Wurtzite (2H) <i>P6₃mc</i> (no. 186)	$a = 3.77, c = 6.15$ Zn 1/3 2/3 0 S 1/3 2/3 0.3792	$a = 3.86, c = 6.29$ Zn 1/3 2/3 0 S 1/3 2/3 0.3794	^a $a = 3.82, c = 6.26$ Zn 1/3 2/3 0 S 1/3 2/3 0.3748
	$a = 3.77, c = 12.30$ Zn 0 0 0.9999 Zn 1/3 2/3 0.2498 S 0 0 0.1876 S 1/3 2/3 0.4377	$a = 3.86, c = 12.59$ Zn 0 0 0.9998 Zn 1/3 2/3 0.2498 S 0 0 0.1877 S 1/3 2/3 0.4377	^b $a = 3.82, c = 12.52$ Zn 0 0 0 Zn 1/3 2/3 0.25 S 0 0 0.1875 S 1/3 2/3 0.4375
	$a = 3.77, c = 15.37$ Zn 0 0 0.9993	$a = 3.85, c = 15.71$ Zn 0 0 0.9992	not yet synthesized

P3m1 (no. 156) 6H <i>P6₃mc (no. 186)</i>	Zn 0 0 0.5993 Zn 2/3 1/3 0.7994 Zn 1/3 2/3 0.3992 Zn 2/3 1/3 0.1992 S 0 0 0.8490 S 2/3 1/3 0.6490 S 0 0 0.4491 S 1/3 2/3 0.2491 S 2/3 1/3 0.0491	Zn 0 0 0.5995 Zn 2/3 1/3 0.7995 Zn 1/3 2/3 0.3993 Zn 2/3 1/3 0.1992 S 0 0 0.8489 S 2/3 1/3 0.6490 S 0 0 0.4491 S 1/3 2/3 0.2490 S 2/3 1/3 0.0490	
	<i>a</i> = 3.77, <i>c</i> = 18.44 Zn 0 0 0.9999 Zn 1/3 2/3 0.1666 Zn 2/3 1/3 1/3 S 0 0 0.1252 S 1/3 2/3 0.2918 S 2/3 1/3 0.4584	<i>a</i> = 3.86, <i>c</i> = 18.88 Zn 0 0 0.9999 Zn 1/3 2/3 0.1665 Zn 2/3 1/3 1/3 S 0 0 0.1251 S 1/3 2/3 0.2917 S 2/3 1/3 0.4584	^c <i>a</i> = 3.82, <i>c</i> = 18.74 Zn 0 0 0.9999 Zn 1/3 2/3 0.1667 Zn 2/3 1/3 1/3 S 0 0 1/4 S 1/3 2/3 0.2917 S 2/3 1/3 0.4583
	<i>a</i> = 3.77, <i>c</i> = 24.59 Zn 0 0 0 Zn 1/3 2/3 1/4 Zn 1/3 2/3 0.3749 Zn 1/3 2/3 0.7499 S 0 0 0.0938 S 1/3 2/3 0.2188 S 1/3 2/3 0.4688 S 1/3 2/3 0.8439	<i>a</i> = 3.86, <i>c</i> = 25.18 Zn 0 0 0 Zn 1/3 2/3 1/4 Zn 1/3 2/3 0.3749 Zn 1/3 2/3 0.7500 S 0 0 0.0938 S 1/3 2/3 0.2188 S 1/3 2/3 0.4688 S 1/3 2/3 0.8439	^d <i>a</i> = 3.82, <i>c</i> = 24.96 Zn 0 0 0 Zn 1/3 2/3 1/4 Zn 1/3 2/3 3/8 Zn 1/3 2/3 3/4 S 0 0 0.0938 S 1/3 2/3 0.2188 S 1/3 2/3 0.4688 S 1/3 2/3 0.8438
	<i>a</i> = 3.77, <i>c</i> = 27.68 Zn 0 0 0 Zn 0 0 0.4444 Zn 0 0 0.2222 S 0 0 0.0834 S 0 0 0.5278 S 0 0 0.3056	<i>a</i> = 3.86, <i>c</i> = 28.32 Zn 0 0 0 Zn 0 0 0.4443 Zn 0 0 0.2221 S 0 0 0.0834 S 0 0 0.5279 S 0 0 0.3056	^e <i>a</i> = 3.82, <i>c</i> = 28.08 Zn 0 0 0 Zn 1/3 2/3 0.1111 Zn 0 0 0.2222 S 0 0 0.0833 S 1/3 2/3 0.1944 S 0 0 0.3056
	<i>a</i> = 3.77, <i>c</i> = 36.90 Zn 0 0 0 Zn 0 0 0.4167 Zn 0 0 0.8333 Zn 0 0 0.5833 S 0 0 0.0625 S 0 0 0.4792 S 0 0 0.8959 S 0 0 0.6459	<i>a</i> = 3.86, <i>c</i> = 37.76 Zn 0 0 0 Zn 0 0 0.4167 Zn 0 0 0.8333 Zn 0 0 0.5833 S 0 0 0.0625 S 0 0 0.4792 S 0 0 0.8959 S 0 0 0.6459	^e <i>a</i> = 3.82, <i>c</i> = 37.44 Zn 0 0 0 Zn 1/3 2/3 0.8333 Zn 2/3 1/3 0.1666 Zn 1/3 2/3 1/4 S 0 0 0.0625 S 1/3 2/3 0.1458 S 2/3 1/3 0.2292 S 1/3 2/3 0.3126
	<i>a</i> = 3.76, <i>c</i> = 46.28 Zn 0 0 0.9998 Zn 0 0 0.7330 Zn 0 0 0.4669 Zn 0 0 0.8667 Zn 0 0 0.2666 S 0 0 0.0498 S 0 0 0.7837 S 0 0 0.5169	<i>a</i> = 3.86, <i>c</i> = 47.40 Zn 0 0 0.9999 Zn 0 0 0.7327 Zn 0 0 0.669 Zn 0 0 0.8664 Zn 0 0 0.2667 S 0 0 0.0498 S 0 0 0.7838 S 0 0 0.5169	^e <i>a</i> = 3.82, <i>c</i> = 46.80 Zn 0 0 0 Zn 2/3 1/3 0.0667 Zn 1/3 2/3 0.1333 Zn 2/3 1/3 0.2 Zn 0 0 0.2667 S 0 0 0.05 S 2/3 1/3 0.1167 S 1/3 2/3 0.1833

	S 0 0 0.9168 S 0 0 0.3165	S 0 0 0.9170 S 0 0 0.3166	S 2/3 1/3 0.25 S 0 0 0.3167
Sphalerite (3C) <i>F-43m</i> (no. 216)	$a = 5.33$ Zn 0 0 0 S 3/4 3/4 3/4	$a = 5.46$ Zn 0 0 0 S 3/4 3/4 3/4	$^f a = 5.40$ Zn 0 0 0 S 1/4 1/4 1/4

^a Ref [S5]; ^b Ref [S6]; ^c Ref [S7]; ^d Ref [S8]; ^e Ref [S9]; ^f Ref [S10,11];

Table S4. Structural information of the calculated ZnS polytypes and experimental results. Unit cell parameters are given in Angstrom (\AA). Local optimizations were performed within the DFT (LDA), and hybrid functional (HSE) approximations.

Structure type and space group	LDA	HSE
Wurtzite (2H) <i>Pm</i> (no. 6)	$a = 5.77, b = 3.32, c = 5.42,$ $\beta = 90.73$ Zn 0.1676 1/2 0.9503 Zn 0.6715 0 0.0169 Zn 0.7981 1/2 0.5207 Zn 0.3658 0 0.5235 S 0.1571 1/2 0.3695 O 0.6697 0 0.3819 O 0.8230 1/2 0.8840 O 0.3474 0 0.8812	$a = 5.91, b = 3.40, c = 5.49,$ $\beta = 90.71$ Zn 0.8293 1/2 0.9828 Zn 0.3326 1/2 0.9828 Zn 0.1333 1/2 0.4775 Zn 0.7015 1/2 0.4775 S 0.3415 1/2 0.6151 O 0.8310 1/2 0.6151 O 0.1529 1/2 0.1198 O 0.6779 1/2 0.1198
4H <i>P3m1</i> (no. 156)	$a = 3.31, c = 10.94$ Zn 0 0 0.9696 Zn 0 0 0.5110 Zn 1/3 2/3 0.2818 Zn 2/3 1/3 0.7396 S 0 0 0.1804 O 0 0 0.6899 O 1/3 2/3 0.4589 O 2/3 1/3 0.9188	$a = 3.39, c = 11.10$ Zn 0 0 0.9705 Zn 0 0 0.5100 Zn 1/3 2/3 0.2805 Zn 2/3 1/3 0.7402 S 0 0 0.1823 O 0 0 0.6891 O 1/3 2/3 0.4591 O 2/3 1/3 0.9185
8H <i>P6₃mc</i> (no. 186)	$a = 3.31, c = 21.91$ Zn 0 0 0.9852 Zn 1/3 2/3 0.1410 Zn 1/3 2/3 0.3699 Zn 1/3 2/3 0.7553 S 0 0 0.0904 O 1/3 2/3 0.2294 O 1/3 2/3 0.4596	$a = 3.39, c = 22.22$ Zn 0 0 0.9858 Zn 1/3 2/3 0.1405 Zn 1/3 2/3 0.3695 Zn 1/3 2/3 0.7551 S 0 0 0.0914 O 1/3 2/3 0.2297 O 1/3 2/3 0.4591

	O 1/3 2/3 0.8444	O 1/3 2/3 0.8441
12R <i>R3mH</i> (no. 160)	$a = 3.32, c = 32.69$ Zn 0 0 0.9899 Zn 0 0 0.4270 Zn 0 0 0.8367 Zn 0 0 0.5797 S 0 0 0.0604 O 0 0 0.4867 O 0 0 0.8966 O 0 0 0.6397	$a = 3.40, c = 33.11$ Zn 0 0 0.9898 Zn 0 0 0.4268 Zn 0 0 0.8367 Zn 0 0 0.5796 S 0 0 0.0610 O 0 0 0.4869 O 0 0 0.8966 O 0 0 0.6395
Sphalerite (3C) <i>Amm2</i> (no. 38)	$a = 3.35, b = 6.71, c = 9.29$ Zn 0 0.7277 0.9886 Zn 1/2 0 0.7501 Zn 1/2 1/2 0.7746 S 0 0 0.1221 O 1/2 0.7462 0.3754 O 0 1/2 0.1251	$a = 3.41, b = 6.84, c = 9.50$ Zn 0 0.7278 0.9889 Zn 1/2 0 0.7505 Zn 1/2 1/2 0.7737 S 0 0 0.1224 O 1/2 0.7486 0.3756 O 0 1/2 0.1243

Table S5. Structural information of the predicted polytypes in the $\text{ZnO}_{0.75}\text{S}_{0.25}$ system. Unit cell parameters are given in Angstrom (\AA). Local optimizations were performed within the DFT (LDA), and hybrid functional (HSE) approximations.

Structure type and space group	LDA	HSE
Wurtzite (2H) <i>P3m1</i> (no. 156)	$a = 3.37, c = 16.60$ Zn 1/3 2/3 0.9743 Zn 1/3 2/3 0.3272 Zn 1/3 2/3 0.6767 Zn 2/3 1/3 0.8246 Zn 2/3 1/3 0.1767 Zn 2/3 1/3 0.5284 S 1/3 2/3 0.1135 S 1/3 2/3 0.4655 O 1/3 2/3 0.7945 O 2/3 1/3 0.9426	$a = 3.45, c = 16.86$ Zn 1/3 2/3 0.9743 Zn 1/3 2/3 0.3265 Zn 1/3 2/3 0.6771 Zn 2/3 1/3 0.8249 Zn 2/3 1/3 0.1762 Zn 2/3 1/3 0.5284 S 1/3 2/3 0.1142 S 1/3 2/3 0.4663 O 1/3 2/3 0.7942 O 2/3 1/3 0.9421

	O 2/3 1/3 0.2940 O 2/3 1/3 0.6460	O 2/3 1/3 0.2939 O 2/3 1/3 0.6460
6H <i>P6₃mc (no. 186)</i>	$a = 3.35, c = 16.73$ Zn 0 0 0.9837 Zn 1/3 2/3 0.1851 Zn 2/3 1/3 0.3337 S 0 0 0.1211 O 1/3 2/3 0.3010 O 2/3 1/3 0.4505	$a = 3.43, c = 17.04$ Zn 0 0 0.9845 Zn 1/3 2/3 0.1846 Zn 2/3 1/3 0.3336 S 0 0 0.1219 O 1/3 2/3 0.3005 O 2/3 1/3 0.4499
9R <i>R3mH (no. 160)</i>	$a = 3.35, c = 25.15$ Zn 0 0 0.9890 Zn 0 0 0.4568 Zn 0 0 0.2225 S 0 0 0.0807 O 0 0 0.5340 O 0 0 0.3003	$a = 3.43, c = 25.53$ Zn 0 0 0.9895 Zn 0 0 0.4565 Zn 0 0 0.2223 S 0 0 0.0814 O 0 0 0.5338 O 0 0 0.2999
Sphalerite (3C) <i>P3m1 (no. 156)</i>	$a = 3.36, c = 8.35$ Zn 0 0 0.9679 Zn 1/3 2/3 0.6669 Zn 2/3 1/3 0.3691 S 0 0 0.2426 O 1/3 2/3 0.9012 O 2/3 1/3 0.6021	$a = 3.43, c = 8.52$ Zn 0 0 0.9690 Zn 1/3 2/3 0.6673 Zn 2/3 1/3 0.3688 S 0 0 0.2439 O 1/3 2/3 0.9000 O 2/3 1/3 0.6009

Table S6. Structural information of the predicted polytypes in the ZnO_{2/3}S_{1/3} system. Unit cell parameters are given in Angstrom (Å). Local optimizations were performed within the DFT (LDA), and hybrid functional (HSE) approximations.

Structure type and space group	LDA	HSE
5H <i>P3m1 (no. 156)</i>	$a = 3.28, c = 13.58$ Zn 0 0 0.0250 Zn 0 0 0.5852 Zn 2/3 1/3 0.7716 Zn 1/3 2/3 0.3986 Zn 2/3 1/3 0.2124 S 0 0 0.8556 O 2/3 1/3 0.6296 O 0 0 0.4418 O 1/3 2/3 0.2543 O 2/3 1/3 0.0675	$a = 3.35, c = 13.81$ Zn 0 0 0.0233 Zn 0 0 0.5864 Zn 2/3 1/3 0.7723 Zn 1/3 2/3 0.3992 Zn 2/3 1/3 0.2119 S 0 0 0.8536 O 2/3 1/3 0.6292 O 0 0 0.4426 O 1/3 2/3 0.2553

		O 2/3 1/3 0.0679
15R	<i>R3mH</i> (no. 160)	
	$a = 3.29, c = 40.64$	$a = 3.36, c = 41.16$
	Zn 0 0 0.9909	Zn 0 0 0.9913
	Zn 0 0 0.7421	Zn 0 0 0.7418
	Zn 0 0 0.4711	Zn 0 0 0.4708
	Zn 0 0 0.8663	Zn 0 0 0.8660
	Zn 0 0 0.2622	Zn 0 0 0.2624
	S 0 0 0.0479	S 0 0 0.0485
	O 0 0 0.7905	O 0 0 0.7907
	O 0 0 0.5193	O 0 0 0.5191
	O 0 0 0.9158	O 0 0 0.9154
	O 0 0 0.3106	O 0 0 0.3106

Table S7. Structural information of the predicted polytypes in the ZnO_{0.8}S_{0.2} system. Unit cell parameters are given in Angstrom (Å). Local optimizations were performed within the DFT (LDA), and hybrid functional (HSE) approximations.

Structure type and space group	LDA	HSE
Wurtzite (2H) <i>Pm</i> (no. 6)	$a = 6.28, b = 3.60, c = 5.91, \beta = 90.28$ Zn 0.2000 1/2 0.0138 Zn 0.6344 0 0.0135 Zn 0.8434 1/2 0.5098 Zn 0.3294 0 0.4483 S 0.1776 1/2 0.6209 S 0.6512 0 0.6268 S 0.8399 1/2 0.1231 O 0.3332 0 0.1158	$a = 6.44, b = 3.69, c = 6.04, \beta = 90.19$ Zn 0.2000 1/2 0.0138 Zn 0.6344 0 0.0135 Zn 0.8434 1/2 0.5098 Zn 0.3294 0 0.4483 S 0.1776 1/2 0.6209 S 0.6512 0 0.6268 S 0.8399 1/2 0.1231 O 0.3332 0 0.1158
4H <i>P3m1</i> (no. 156)	$a = 3.63, c = 11.83$ Zn 0 0 0.9770 Zn 0 0 0.5080 Zn 1/3 2/3 0.2419 Zn 2/3 1/3 0.7745 S 0 0 0.1708 S 0 0 0.7024 S 1/3 2/3 0.4366 O 2/3 1/3 0.9389	$a = 3.72, c = 12.10$ Zn 0 0 0.9771 Zn 0 0 0.5080 Zn 1/3 2/3 0.2417 Zn 2/3 1/3 0.7751 S 0 0 0.1708 S 0 0 0.7031 S 1/3 2/3 0.4367 O 2/3 1/3 0.9375
8H <i>P6₃mc</i> (no. 186)	$a = 3.63, c = 23.67$ Zn 0 0 0.9958 Zn 1/3 2/3 0.1290	$a = 3.72, c = 24.21$ Zn 0 0 0.9958 Zn 1/3 2/3 0.1291

	Zn 1/3 2/3 0.3635 Zn 1/3 2/3 0.7625 S 0 0 0.0931 S 1/3 2/3 0.2263 S 1/3 2/3 0.4604 O 1/3 2/3 0.8446	Zn 1/3 2/3 0.3636 Zn 1/3 2/3 0.7626 S 0 0 0.0932 S 1/3 2/3 0.2265 S 1/3 2/3 0.4604 O 1/3 2/3 0.8438
12R <i>R3mH</i> (no. 160)	$a = 3.63, c = 35.53$ Zn 0 0 0.9923 Zn 0 0 0.4140 Zn 0 0 0.8360 Zn 0 0 0.5916 S 0 0 0.0569 S 0 0 0.4787 S 0 0 0.9009 O 0 0 0.6463	$a = 3.72, c = 36.33$ Zn 0 0 0.9924 Zn 0 0 0.4140 Zn 0 0 0.8361 Zn 0 0 0.5917 S 0 0 0.0569 S 0 0 0.4788 S 0 0 0.9010 O 0 0 0.6458
Sphalerite (3C) <i>Amm2</i> (no. 38)	$a = 3.62, b = 7.27, c = 10.20$ Zn 0 0.7753 0.9881 Zn 1/2 0 0.7727 Zn 1/2 0 0.2481 S 0 1/2 0.8781 S 1/2 0.7550 0.6246 O 0 0 0.8756	$a = 3.70, b = 7.43, c = 10.44$ Zn 0 0.7244 0.9883 Zn 1/2 1/2 0.7716 Zn 1/2 1/2 0.2487 S 0 0 0.8783 S 1/2 0.7461 0.6243 O 0 1/2 0.8762

Table S8. Structural information of the predicted polytypes in the $\text{ZnO}_{0.25}\text{S}_{0.75}$ system. Unit cell parameters are given in Angstrom (\AA). Local optimizations were performed within the DFT (LDA), and hybrid functional (HSE) approximations.

Structure type and space group	LDA	HSE
Wurtzite (2H) <i>P3m1</i> (no. 156)	$a = 3.57, c = 17.57$ Zn 1/3 2/3 0.0088 Zn 1/3 2/3 0.3280 Zn 1/3 2/3 0.6467 Zn 2/3 1/3 0.8275 Zn 2/3 1/3 0.1901 Zn 2/3 1/3 0.5088 S 1/3 2/3 0.1396 S 1/3 2/3 0.4587 S 1/3 2/3 0.7772 S 2/3 1/3 0.9582 O 2/3 1/3 0.3009	$a = 3.66, c = 17.96$ Zn 1/3 2/3 0.0086 Zn 1/3 2/3 0.3281 Zn 1/3 2/3 0.6467 Zn 2/3 1/3 0.8273 Zn 2/3 1/3 0.1905 Zn 2/3 1/3 0.5092 S 1/3 2/3 0.1399 S 1/3 2/3 0.4588 S 1/3 2/3 0.7774 S 2/3 1/3 0.9584 O 2/3 1/3 0.3003

	O 2/3 1/3 0.6196	O 2/3 1/3 0.6189
6H <i>P6₃mc (no. 186)</i>	$a = 3.57, c = 17.61$ Zn 0 0 0.9862 Zn 1/3 2/3 0.1675 Zn 2/3 1/3 0.3483 S 0 0 0.1167 S 1/3 2/3 0.2974 O 2/3 1/3 0.4589	$a = 3.66, c = 18.01$ Zn 0 0 0.9862 Zn 1/3 2/3 0.1674 Zn 2/3 1/3 0.3484 S 0 0 0.1168 S 1/3 2/3 0.2976 O 2/3 1/3 0.4580
9R <i>R3mH (no. 160)</i>	$a = 3.57, c = 26.44$ Zn 0 0 0.9909 Zn 0 0 0.4449 Zn 0 0 0.2323 S 0 0 0.0777 S 0 0 0.5315 O 0 0 0.3059	$a = 3.65, c = 27.03$ Zn 0 0 0.9913 Zn 0 0 0.4449 Zn 0 0 0.2323 S 0 0 0.0779 S 0 0 0.5317 O 0 0 0.3053
Sphalerite (3C) <i>P3m1 (no. 156)</i>	$a = 3.57, c = 8.82$ Zn 0 0 0.9983 Zn 2/3 1/3 0.3609 Zn 1/3 2/3 0.6360 S 0 0 0.7388 S 2/3 1/3 0.1008 O 2/3 1/3 0.4154	$a = 3.66, c = 9.01$ Zn 0 0 0.9985 Zn 2/3 1/3 0.3596 Zn 1/3 2/3 0.6364 S 0 0 0.7383 S 2/3 1/3 0.0999 O 2/3 1/3 0.4174

Table S9. Structural information of the predicted polytypes in the ZnO_{1/3}S_{2/3} system. Unit cell parameters are given in Angstrom (Å). Local optimizations were performed within the DFT (LDA), and hybrid functional (HSE) approximations.

Structure type and space group	LDA	HSE
5H <i>P3m1 (no. 156)</i>	$a = 3.53, c = 14.51$ Zn 0 0 0.0306 Zn 0 0 0.5871	$a = 3.61, c = 14.86$ Zn 0 0 0.0301 Zn 0 0 0.5872

15R <i>R3mH</i> (no. 160)	Zn 2/3 1/3 0.8090 Zn 1/3 2/3 0.3658 Zn 2/3 1/3 0.1987 S 0 0 0.8726 S 2/3 1/3 0.6515 S 0 0 0.4298 O 1/3 2/3 0.2317 O 2/3 1/3 0.0650	Zn 2/3 1/3 0.8089 Zn 1/3 2/3 0.3656 Zn 2/3 1/3 0.1981 S 0 0 0.8724 S 2/3 1/3 0.6512 S 0 0 0.4296 O 1/3 2/3 0.2317 O 2/3 1/3 0.0659
	$a = 3.54, c = 43.12$ Zn 0 0 0.9882 Zn 0 0 0.7295 Zn 0 0 0.4707 Zn 0 0 0.8783 Zn 0 0 0.2667 S 0 0 0.0417 S 0 0 0.7827 S 0 0 0.5238 O 0 0 0.9236 O 0 0 0.3115	$a = 3.63, c = 44.11$ Zn 0 0 0.9885 Zn 0 0 0.7294 Zn 0 0 0.4705 Zn 0 0 0.8782 Zn 0 0 0.2671 S 0 0 0.0419 S 0 0 0.7828 S 0 0 0.5238 O 0 0 0.9231 O 0 0 0.3112

Table S10. Structural information of the predicted polytypes in the $\text{ZnO}_{0.4}\text{S}_{0.6}$ system. Unit cell parameters are given in Angstrom (\AA). Local optimizations were performed within the DFT (LDA), and hybrid functional (HSE) approximations.

Structure type and space group	<i>LDA</i>	<i>HSE</i>
Wurtzite (2H) <i>P3m1</i> (no. 156)	$a = 3.46, c = 5.73$ Zn 1/3 2/3 0.0414 Zn 2/3 1/3 0.4701 O 1/3 2/3 0.3812 S 2/3 1/3 0.8713	$a = 3.55, c = 5.85$ Zn 1/3 2/3 0.0415 Zn 2/3 1/3 0.4708 O 1/3 2/3 0.3793 S 2/3 1/3 0.8724
4H <i>P3m1</i> (no. 156)	$a = 3.47, c = 11.36$ Zn 0 0 0.0374 Zn 0 0 0.4629 Zn 1/3 2/3 0.2499 Zn 2/3 1/3 0.7513 O 0 0 0.2902	$a = 3.56, c = 11.57$ Zn 0 0 0.0371 Zn 0 0 0.4632 Zn 1/3 2/3 0.2510 Zn 2/3 1/3 0.7503 O 0 0 0.2086 S 0 0 0.6666 O 1/3 2/3 0.4200 S 2/3 1/3 0.9532

	S 0 0 0.6661 O 1/3 2/3 0.4209 S 2/3 1/3 0.9522	
8H <i>P6₃mc</i> (no. 186)	$a = 3.46, c = 22.89$ Zn 0 0 0.9825 Zn 1/3 2/3 0.1259 Zn 1/3 2/3 0.3755 Zn 1/3 2/3 0.7686 S 0 0 0.0831 S 1/3 2/3 0.2254 O 1/3 2/3 0.4607 O 1/3 2/3 0.8535	$a = 3.55, c = 23.34$ Zn 0 0 0.9832 Zn 1/3 2/3 0.1258 Zn 1/3 2/3 0.3753 Zn 1/3 2/3 0.7685 S 0 0 0.0836 S 1/3 2/3 0.2260 O 1/3 2/3 0.4599 O 1/3 2/3 0.8530
12R <i>R3mH</i> (no. 160)	$a = 3.49, c = 33.88$ Zn 0 0 0.9875 Zn 0 0 0.4166 Zn 0 0 0.8457 Zn 0 0 0.5832 S 0 0 0.0556 S 0 0 0.4844 O 0 0 0.9034 O 0 0 0.6404	$a = 3.57, c = 34.57$ Zn 0 0 0.9873 Zn 0 0 0.4165 Zn 0 0 0.8459 Zn 0 0 0.5835 S 0 0 0.0556 S 0 0 0.4847 O 0 0 0.9032 O 0 0 0.6401
15R <i>Cm</i> (no. 8)	$a = 28.36, b = 3.49, c = 6.02, \beta = 94.09$ Zn 0.0164 0 0.0072 Zn 0.5187 0 0.5079 Zn 0.9043 0 0.6312 Zn 0.4007 0 0.1388 Zn 0.2945 0 0.7588 Zn 0.7814 0 0.2576 Zn 0.1908 0 0.0925 Zn 0.6866 0 0.5310 Zn 0.6045 0 0.8731 Zn 0.1017 0 0.3683 S 0.9346 0 0.9814 S 0.4378 0 0.4778 S 0.8240 0 0.5910 S 0.3192 0 0.1146 S 0.2141 0 0.7364 O 0.7117 0 0.2351 O 0.1214 0 0.0494 O 0.6175 0 0.5364 O 0.5356 0 0.8492 O 0.0337 0 0.3444	$a = 28.96, b = 3.56, c = 6.16, \beta = 94.04$ Zn 0.0165 0 0.0078 Zn 0.5187 0 0.5077 Zn 0.9044 0 0.6321 Zn 0.4009 0 0.1398 Zn 0.2944 0 0.7601 Zn 0.7813 0 0.2592 Zn 0.1908 0 0.0914 Zn 0.6865 0 0.5293 Zn 0.6040 0 0.8719 Zn 0.1012 0 0.3665 S 0.9347 0 0.9817 S 0.4377 0 0.4785 S 0.8237 0 0.5926 S 0.3189 0 0.1151 S 0.2139 0 0.7357 O 0.7118 0 0.2360 O 0.1219 0 0.0495 O 0.6180 0 0.5340 O 0.5359 0 0.8491 O 0.0340 0 0.3445

Sphalerite (3C) <i>R3mH (no. 160)</i>	$a = 3.46, c = 17.20$ Zn 0 0 0.9891 Zn 0 0 0.5126 S 0 0 0.1225 O 0 0 0.6258	$a = 3.54, c = 17.58$ Zn 0 0 0.9897 Zn 0 0 0.5126 S 0 0 0.1227 O 0 0 0.6250
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Table S11. Structural information of the predicted polytypes in the $\text{ZnO}_{0.5}\text{S}_{0.5}$ system. Unit cell parameters are given in Angstrom (\AA). Local optimizations were performed within the DFT (LDA), and hybrid functional (HSE) approximations.

Supporting figures: E(V) curves and visualizations of polytypes

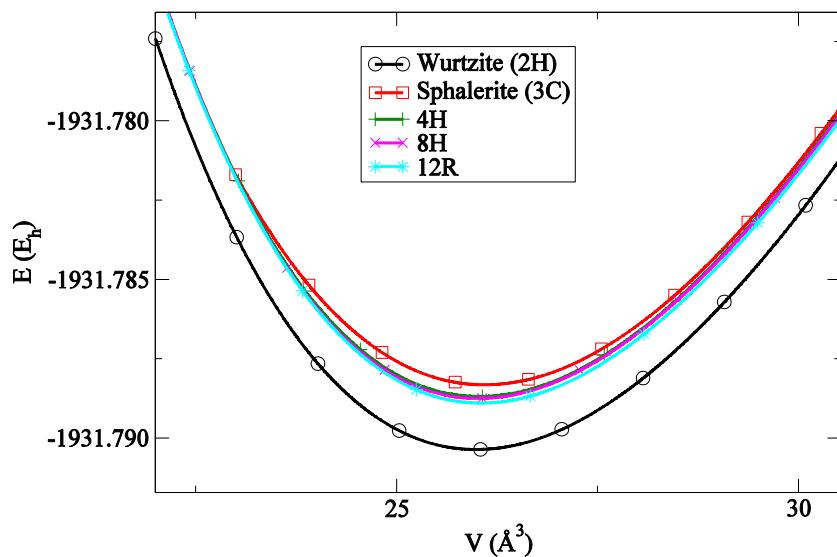


Figure S1. Calculated $E(V)$ curves for the new stacking variants of the $\text{ZnO}_{0.75}\text{S}_{0.25}$ compound at LDA level. Energies per formula unit are given in hartrees (E_h).

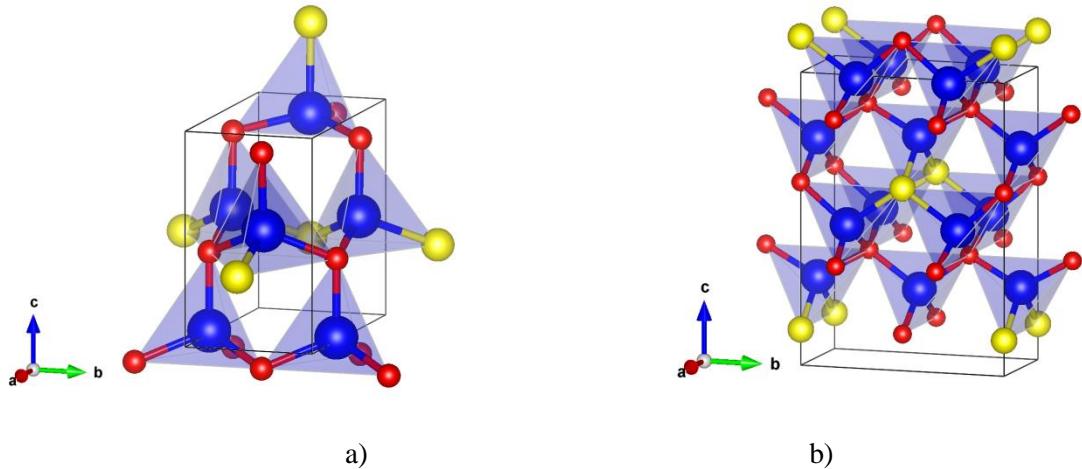


Figure S2. Visualization of predicted modifications in the $\text{ZnO}_{0.75}\text{S}_{0.25}$ compound: a) wurtzite (2H) type; b) sphalerite (3C) type. Blue, red, and yellow spheres correspond to Zn, O and S atoms, respectively.

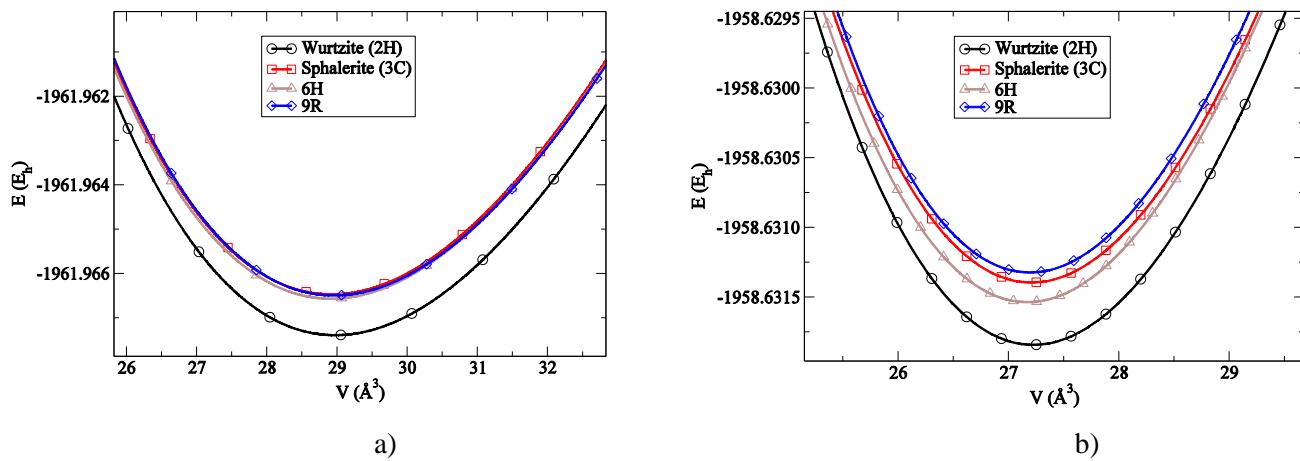


Figure S3. Calculated E(V) curves for the new stacking variants of the $\text{ZnO}_{2/3}\text{S}_{1/3}$ compound at: a) HSE; b) LDA level. Energies per formula unit are given in hartrees (E_h).

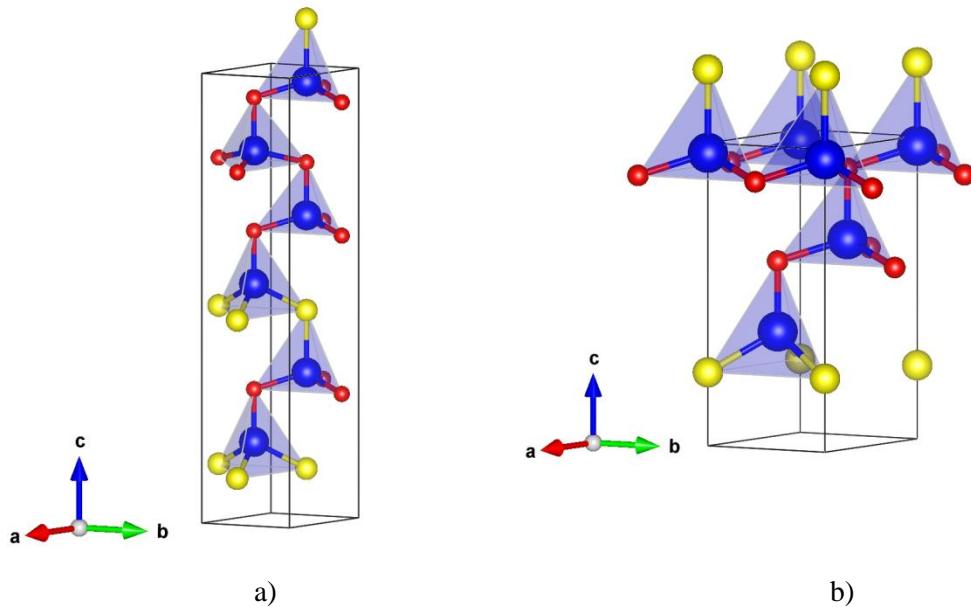


Figure S4. Visualization of predicted modifications in the $\text{ZnO}_{2/3}\text{S}_{1/3}$ compound: a) wurtzite (2H) type; b) sphalerite (3C) type. Blue, red, and yellow spheres correspond to Zn, O and S atoms, respectively.

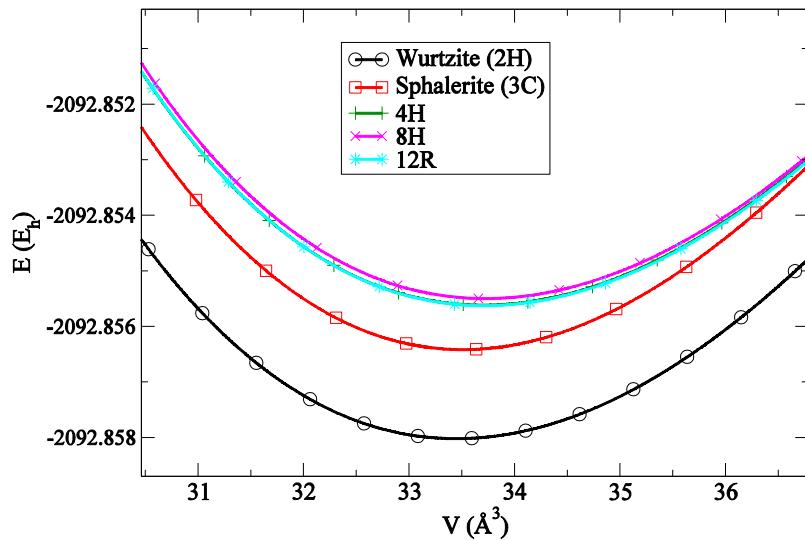


Figure S5. Calculated E(V) curves for the new stacking variants of the $\text{ZnO}_{0.25}\text{S}_{0.75}$ compound at LDA level. Energies per formula unit are given in hartrees (E_h).

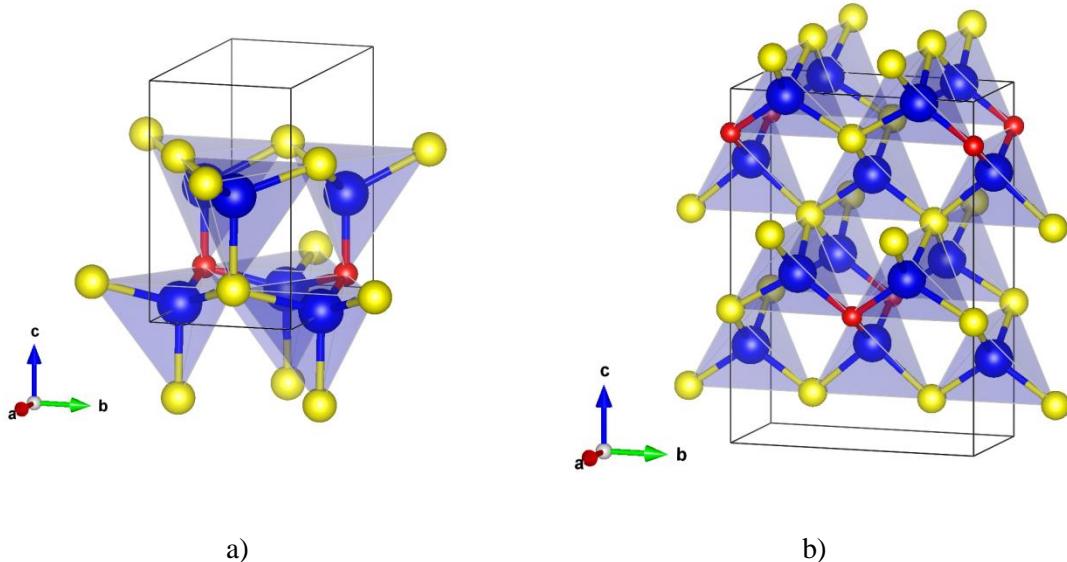


Figure S6. Visualization of predicted modifications in the $\text{ZnO}_{0.25}\text{S}_{0.75}$ compound: a) wurtzite (2H) type; b) sphalerite (3C) type. Blue, red, and yellow spheres correspond to Zn, O and S atoms, respectively.

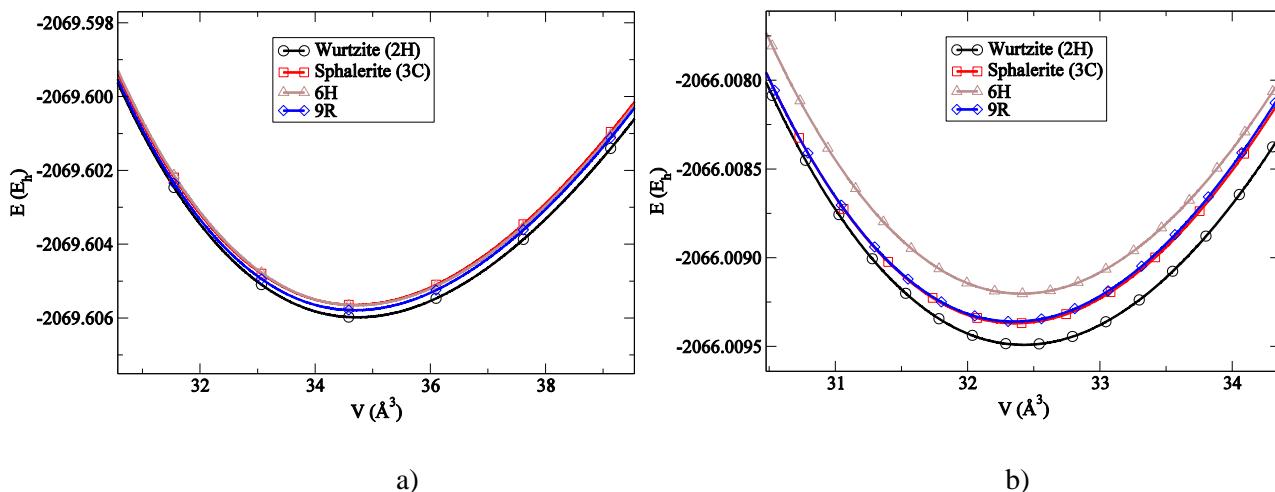


Figure S7. Calculated E(V) curves for the new stacking variants of the $\text{ZnO}_{1/3}\text{S}_{2/3}$ compound at: a) HSE; b) LDA level. Energies per formula unit are given in hartrees (E_h).

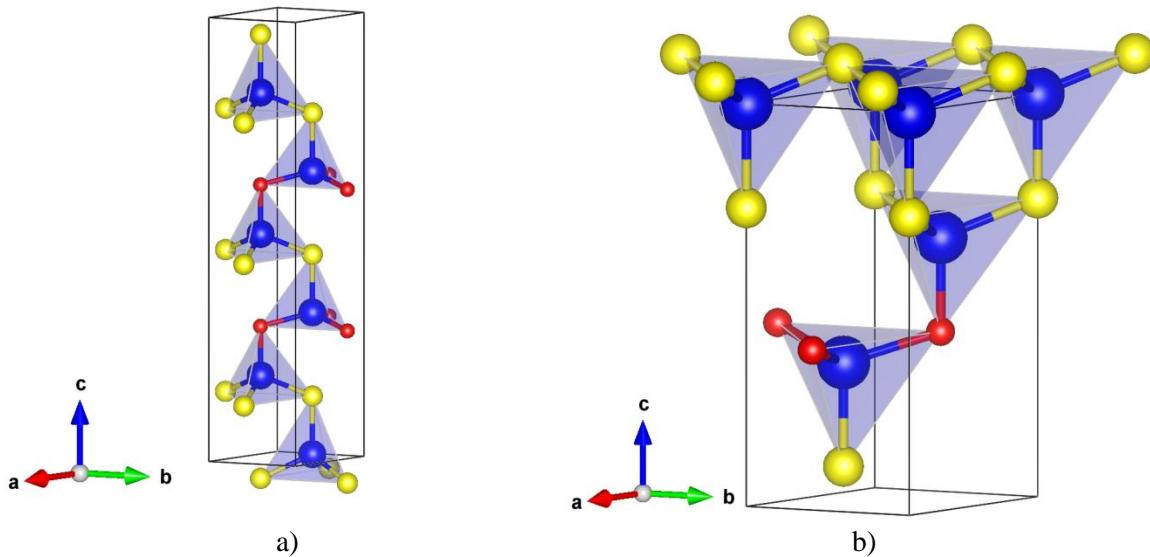


Figure S8. Visualization of predicted modifications in the $\text{ZnO}_{1/3}\text{S}_{2/3}$ compound: a) wurtzite (2H) type; b) sphalerite (3C) type. Blue, red, and yellow spheres correspond to Zn, O and S atoms, respectively.

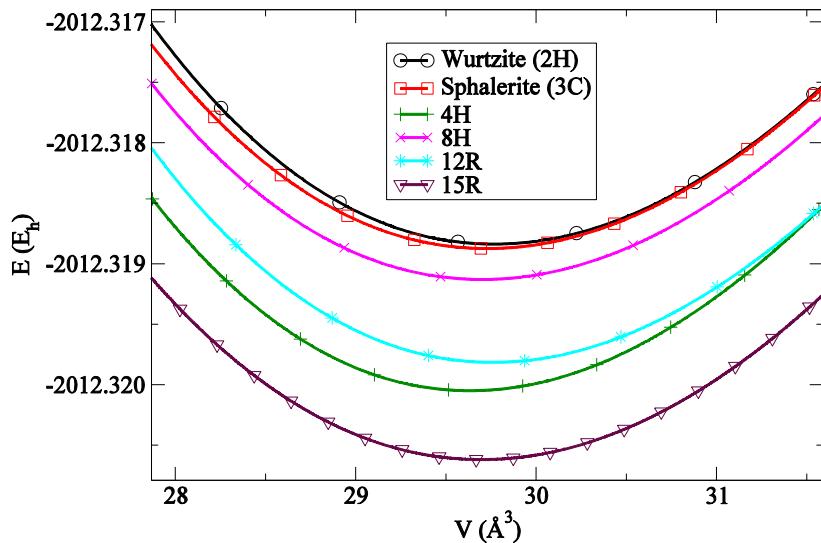


Figure S9. Calculated E(V) curves for the new stacking variants of $\text{ZnO}_{0.5}\text{S}_{0.5}$ compound at LDA level. Energies per formula unit are given in hartrees (E_h).

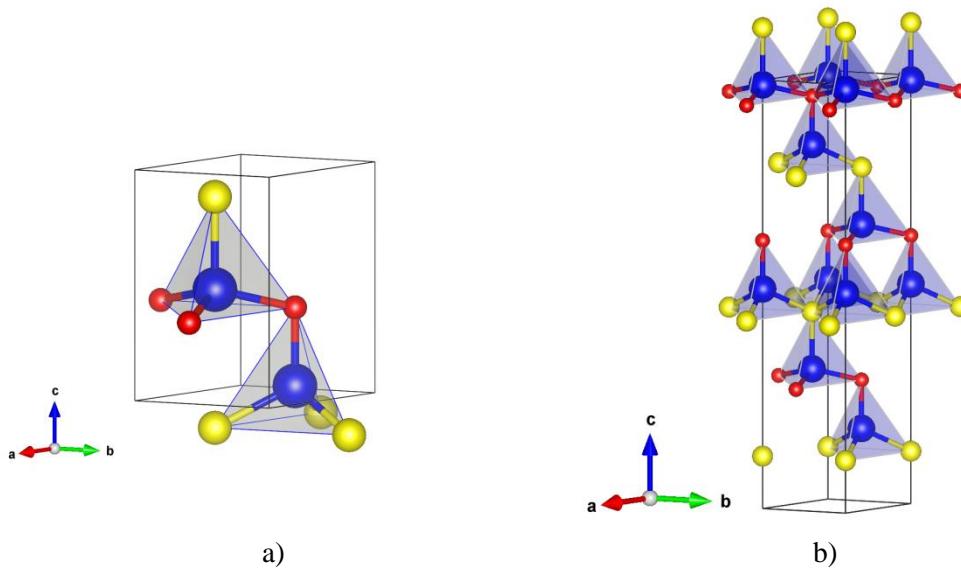


Figure S10. Visualization of the predicted modifications in the $\text{ZnO}_{0.5}\text{S}_{0.5}$ compound: a) wurtzite (2H) type; b) sphalerite (3C) type. Blue, red, and yellow spheres correspond to Zn, O and S atoms, respectively.

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