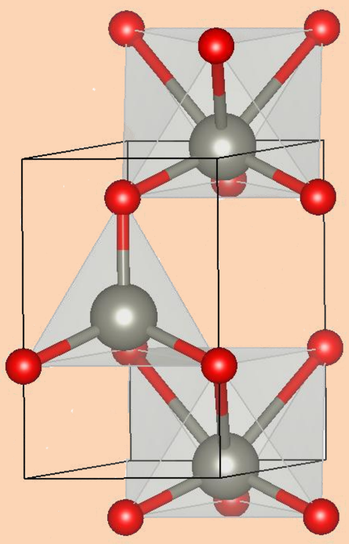
Energy landscapes of ZnO on atomic scale

Tamara Škundrić[1,2], Dejan Zagorac[1,2], Jelena Zagorac[1,2], Johann Christian Schön[3], Branko Matović[1,2]

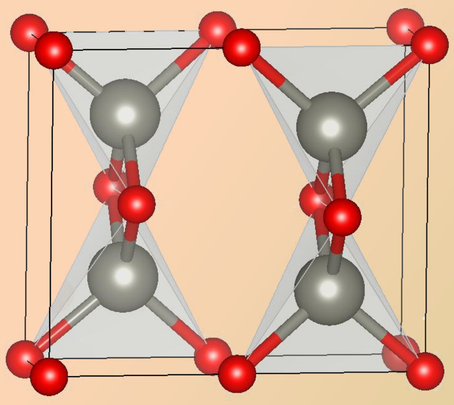
[1]Materials Science Laboratory, Institute of Nuclear Sciences "Vinča", University of Belgrade, Belgrade, Serbia
[2]Center for synthesis, processing and characterization of materials for application in the extreme conditions "CextremeLab", Belgrade, Serbia
[3]Max Planck Institute for Solid State Research, Heisenberg str. 1, D-70569, Stuttgart, Germany

In material science, ZnO is theoretically and experimentally one of the most investigated compounds. In nature, it appears only rarely, as the mineral zinzite which exibits a hexagonal crystal structure and whose colour depends on the presence of impurities such as MnO, FeO and SiO_2. There are three bulk phases experimentally known in ZnO system, a wurtzite and a sphalerite modification at ambient conditions, and a rocksalt phase at high pressures. Due to its excellent properties like good transparency, high electron mobility, strong room-temperature luminescence, it is successfully used in electronics, batteries and optical systems, but is also commonly used as an additive in various materials.

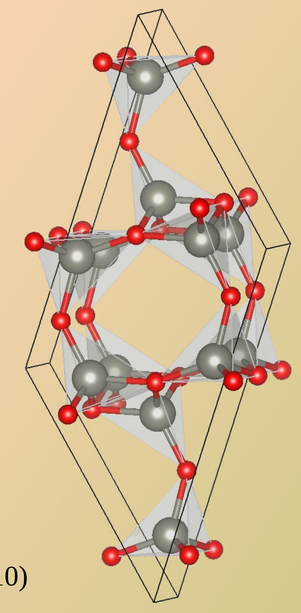
NaCl as a starting minimum



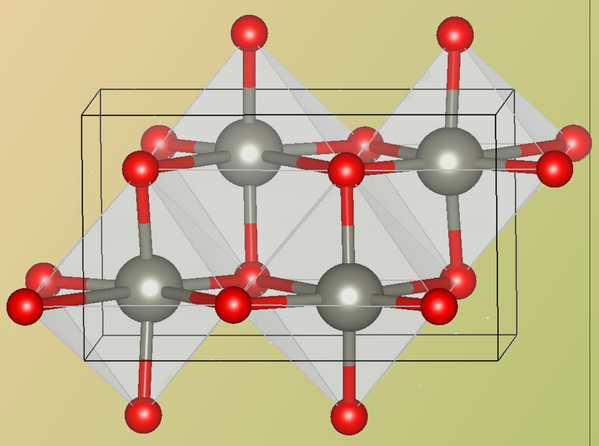
Mix NiAs-wurtzite dis.-1 (SG_no156)



Sphalerite-zeolithic type dis.-1 (SG_no10)



Zeolithic type-1 (SG_no12)

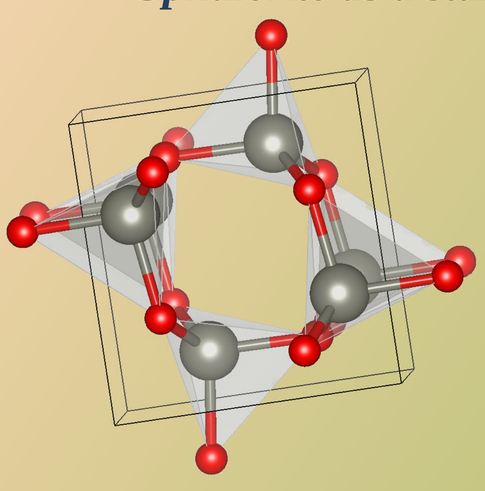


ZnO-I dis.-1 (SG_no62)

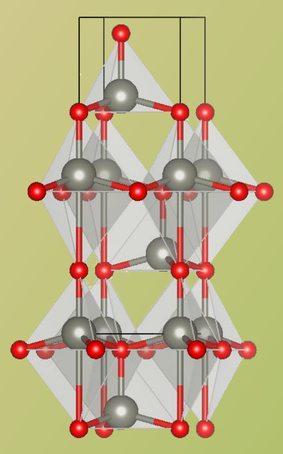
In order to investigate the energy landscape of zinc oxide, we have performed several sets of calculations using different approaches. First, we have performed several global optimizations using empirical potentials followed by local optimizations on ab initio level, using different number of atoms, temperatures and/or pressures within the calculations [1,2].

Sphalerite as a starting minimum

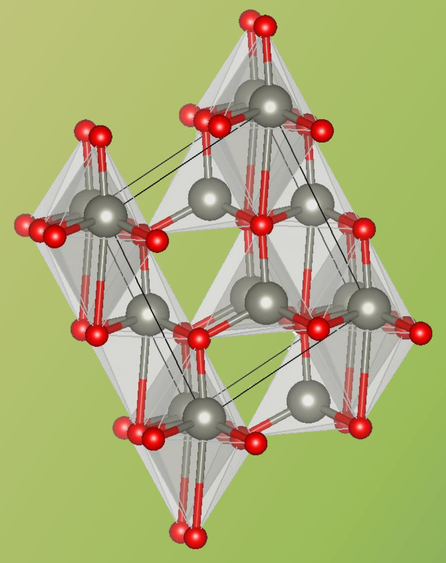
Full analysis of the landscape was performed and important minima were identified. Very important aspect beyond the identification of local minima is the analysis of the barrier structure of the landscape surrounding the minima, and of the possible transition paths connecting the major locally ergodic regions.



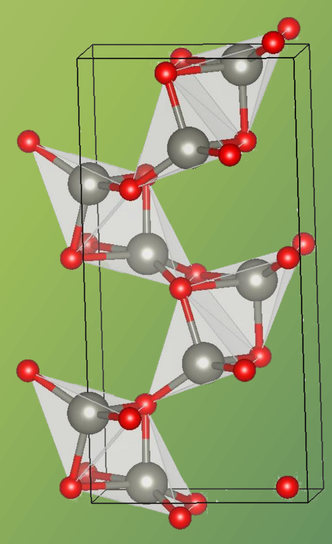
Wurtzite-zeolithic type dis.-1 (SG_no58)



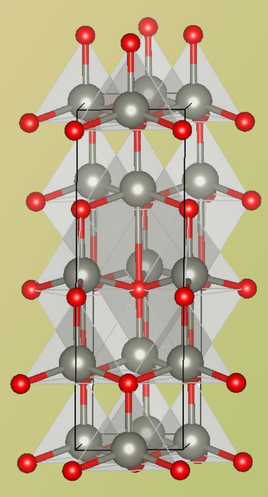
Mix wurtzite 5H-5-5 dis.-1 (SG_no186)



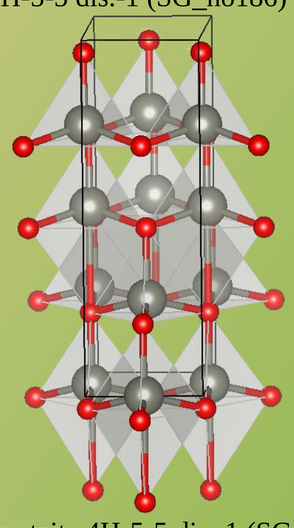
Mix NaCl-wurtzite dis.-1 (SG_no8)



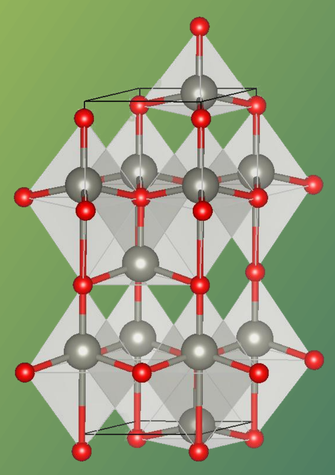
Mix wurtzite-GeP dis.-1 (SG_no9)



Mix wurtzite 5H-5-5 dis.-2 (SG_no8)



Mix wurtzite 4H-5-5 dis.-1 (SG_no36)



Mix wurtzite 4H-5-5 dis.-2 (SG_no186)

Therefore, in the next step we have performed threshold algorithm (TA) calculations for different numbers of formula units of ZnO. A particular focus is the dependence of the shape of the landscape on the number of atoms per simulation cell, and the structural equivalence of local minima due to the periodicity of the system. In the following example we have used 4 Zn and 4 O atoms per simulation cell (Z=4) using cubic sphalerite and rock-salt as a starting minimum.

Sphalerite	Restl	P1	distortion BeO	BeO	distortion wurtzite	wurtzite	wurtzite 4H	NaCl	Zeolithic type	distortion sphalerite	distortion sphalerite polytype	sphalerite	sphalerite polytype	distortion wurtzite+ sphalerite	GeP+ sphalerite
1-5 eV	27	15								11		1598			
%	1.63	0.91								0.67		96.79			
6-10 eV	43	117				279			22	20		1170			
%		7.09				16.90			1.33			70.87			
11-15 eV	118	200	77	106		533		84	21	18		442		52	
%	7.15	12.11	4.66	6.42		32.28		5.09	1.27	1.09		26.78		3.15	
16-20 eV	119	315		52		413		46	86	21		446		130	23
%	7.21	19.08		3.15		25.01		2.77	5.21			27.01		7.87	1.39
21-25 eV	159	536		25	48	193	27		161	34	22	315		132	
%	9.57	32.47		1.51	2.91	11.69	1.64		9.75	2.06	1.33	19.08		7.99	
26-28 eV	189	404	11	10	24	76			89	19		125	22	22	
%	19.07	40.77	1.11	1.01	2.42	7.67			8.98	1.92		12.61	2.22	2.22	

References

[1] D. Zagorac, J. C. Schön, J. Zagorac, and M. Jansen: Prediction of structure candidates for zinc oxide as a function of pressure and investigation of their electronic properties. Phys. Rev. B 89, 075201 (2014).

[2] D. Zagorac, J. C. Schön, J. Zagorac, and M. Jansen: Theoretical investigations of novel zinc oxide polytypes and in-depth study of their electronic properties, RSC Advances, 5, 25929 (2015).

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