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The Stable or Metastable Phases in Compressed Zn-O Systems *

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Variable-composition evolutionary structure searches are used to explore stable stoichiometries for the Zn-O system below 300 GPa. Our results confirm the previous structural phase transition sequence of pressurised ZnO. ZnO is thermodynamically stable up to 300 GPa and zinc peroxide (ZnO_2, space group $Pa\bar{3}$) is metastable under lower pressure. Insulating $I4/mcm$-ZnO_2 is thermodynamically stable between 128.3–300 GPa. Insulated metastable $P3_121$-ZnO_2, controlling the pressure range of 51.5–128.3 GPa, has a wide band gap compared to the $Pa\bar{3}$-ZnO_2 and $I4/mcm$-ZnO_2. Phonon and elastic constant calculations conclude the dynamical and mechanical stability for the explored thermodynamically stable or metastable structures.

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Under ambient conditions, zinc oxide (ZnO), as a wide band gap semiconductor, is a low-cost-effective functional material with wide practical industrial applications in chemical sensors, catalysts, solar cells, and light-emitting devices.[1−6] At high pressure, the properties of the elements would change with increasing the pressure. Thus novel exotic materials may be found at high pressure. The high-pressure behavior of ZnO has been extensively studied experimentally[7−10] and theoretically.[11−16] As a typical solid in the ⅡB–ⅥA binary system, ZnO crystallizes in hexagonal wurtzite B4 ($Z = 2$, $P6_3mc$) at normal pressure. The metastable cubic zinc-blende structure B3 ($Z = 1$, $F\bar{4}3m$) has been reported only in films grown on the cubic structure substrates.[17,18] Numbers of experiments confirmed B4 phase transforms into six-fold-coordinated B1 ($Z = 1$, $Fm\bar{3}m$) at ∼10 GPa,[8,9,19,20] which was first reported by Bates *et al.*[7] Li *et al.* suggested an intermediate phase with tetragonal PbO-type ($Z = 2$, $P4/nmm$) symmetry between B1 and hypothetical B2.[21]

Recently, great efforts have been made to find novel compounds in the binary system under ambient conditions or high pressure. The actually unexpected stable stoichiometries in Na-Cl,[22] Ca-C,[23] and Mg-O[24] systems were theoretically uncovered at high pressures and have partly been successfully synthesized via experiment. Studies revealed that nano-structured ZnO_2 can be synthesized in experiment.[25−27] Most recently, a new stable $I4/mcm$ structure of ZnO_2 was predicted above 120 GPa but with a lack of discussion on phonon and metastable phase.[28] Here the structural phase transition sequence of ZnO_2 and ZnO via evolutionary algorithm (EA)[29,30] were obtained. Our calculations on ZnO solid confirmed previous results. On the other hand, two new phases (space group, $P3_121$, $I4/mcm$) of ZnO_2 solid were found in addition to the cubic-ZnO_2 ($Z = 4$, $Pa\bar{3}$).

The EA USPEX code,[29,30] which allows for performing the variable-composition structure prediction, was coupled with PBE-DFT calculations carried out with the VASP code[31,32] to search for the thermodynamically stable Zn-O stoichiometries. In our calculations, the total number of atoms in the unit cell is less than 16 atoms. The projector augmented wave potentials[33] (the hard pseudopotential chosen for O atom) and plane-wave basis functions up to a kinetic energy cutoff of 950 eV were employed. Valence electron configurations used in our work are $3d^{10}4s^2$ for Zn, $2s^22p^4$ for O. The phonon spectrum was finished by using the Phonopy code[34] together with the VASP code to identify the obtained structures' dynamical stability.

The pressure-composition phase diagram of the Zn-O system is displayed in Fig. 1(a) and the convex hull in Fig. 1(b). The phases whose relative enthalpy per atom (ΔH) comprise the hull are thermodynamically stable with respect to decomposition into other zinc oxides and/or solid zinc and oxygen.[23] Obviously, ZnO is a thermodynamically stable compound over the pressure range and ZnO_2 holds the thermodynamically stable pressure range from 168 GPa to 300 GPa. For ZnO, our EA searches concluded that ZnO with $P6_3mc$ symmetry is the most stable ZnO phase between 0 and 12 GPa, followed by face-centered cubic (fcc) structure, which controls a wide pressure range from 12.1 GPa to 261 GPa. Above 261 GPa, $P4/nmm$ phase was found to be a stable one. The predicted structural phase transition sequence of ZnO agrees well with the previous results.[15,21,35,36]

It should be noted that metastable phases at high temperature and high pressure conditions can be synthesized via experiment and could exist under ambient conditions. Therefore, it is instructive to explore metastable phases of ZnO_2. Two thermodynamically metastable phases of ZnO_2 were identified in our EA calculations. The cubic $Pa\bar{3}$ structure[37] is a low en-

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thalpy structure of ZnO_2 below 51.5 GPa. With increasing the pressure, it gives way to a trigonal $P3_121$ structure, followed by the body-centered tetragonal $I4/mcm$ structure at 128.3 GPa, which is still stable up to 300 GPa. The crystal structures of ZnO_2 were presented in Fig. 2. The lattice parameters and atomic fractional coordinates are listed in Table 1.

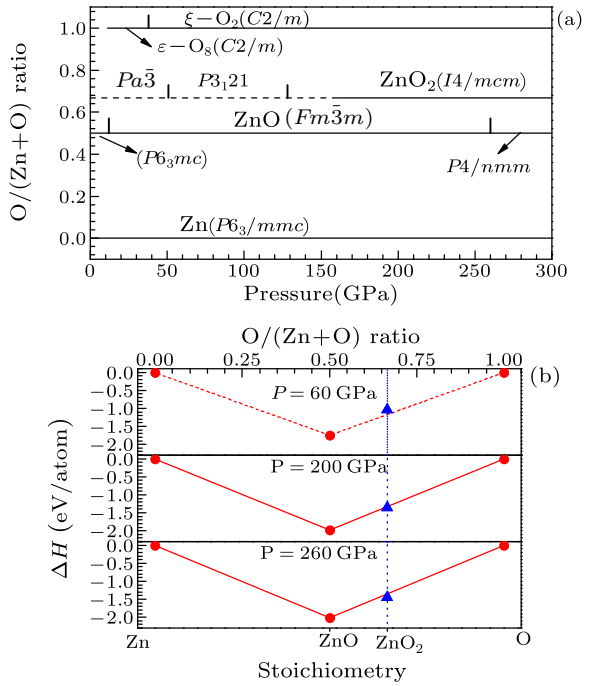

Fig. 1. Stability of new zinc oxide. (a) Pressure-composition phase diagram of the Zn-O system. Solid lines represent thermodynamically stable phases and dashed lines metastable phases. (b) Convex hull diagram for the Zn-O system at high pressures. Here ΔH denotes the enthalpy of formation per atom.

As shown in Fig. 2(a), each zinc atom is surrounded by oxygen octahedra with Zn–O bond of 2.131 Å and the O–O bond of 1.495 Å at zero pressure. For $P3_121$ structure, each zinc atom is surrounded by six O atoms, constructing a distorted oxygen octahedral with Zn–O bond lengths of about 1.997 Å and 2.026 Å at 55 GPa, while O–O bond length is 1.427 Å (see Fig. 2(b)). For the $I4/mcm$ phase, each zinc atom is surrounded by eight O atoms with the Zn–O bond length of 1.997 Å and the O–O bond length of 1.372 Å at 130 GPa (see Fig. 2(c)). Obviously, the O–O bond length in three compounds are slightly higher than that in the oxygen molecule (∼1.21 Å), indicating strong covalent bonds between oxygen atoms. The calculated density is 5.34 g/cm^3 for $Pa\bar{3}$ at 0 GPa, 7.19 g/cm^3 for $P3_121$ at 55 GPa and 8.38 g/cm^3 for $I4/mcm$ at 130 GPa. To investigate the pressure-induced structural phase transition, we have calculated the total energies of the ZnO (B4, B3, B1, B2, $P4/nmm$) and ZnO_2 ($Pa\bar{3}$, $P3_121$, $I4/mcm$) as a function of pressure.

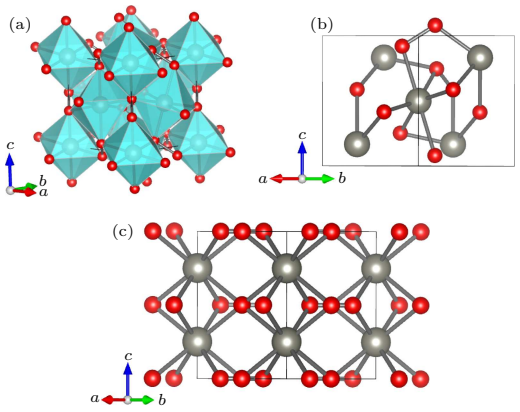

Fig. 2. Structures of ZnO_2 (a) $Pa\bar{3}$ at 0 GPa, (b) $P3_121$ at 55 GPa and (c) $I4/mcm$ at 130 GPa. Large grey and small red spheres represent Zn and O atoms, respectively.

Table 1. The equilibrium structural parameters and atomic fractional coordinates, Bader charge, and atomic volume of $Pa\bar{3}$, $P3_121$, and $I4/mcm$ phases of ZnO_2.

	Pressure (GPa)	Lattice parameters (Å)	Wyckoff position	x	y	z	Q ($\|e\|$)	V (Å^3)
$Pa\bar{3}$	0	a=4.948	Zn(4a)	0.000	0.000	0.000	1.306	9.41
			O (8c)	0.413	0.413	0.413	−0.653	10.43
$P3_121$	55	a=4.005	Zn(3b)	0.000	0.360	0.167	1.315	7.34
		c=4.751	O (6c)	0.360	0.172	0.250	−0.658	7.58
$I4/mcm$	130	a=4.046	Zn(4a)	0.000	0.000	0.250	1.328	6.26
		c=4.713	O (8h)	−0.120	0.380	0.000	−0.664	6.51

The relative enthalpies versus pressure curves of ZnO are shown in Figs. 3(a) and 3(b). Obviously, one can find that B4 transforms into B1 at ∼12.1 GPa. Between B1 and B2, there is an intermediate phase $P4/nmm$.[21] B1 phase transforms to $P4/nmm$ at about 260 GPa and subsequently $P4/nmm$ transforms to B2 at 322 GPa. The transition point is not shown in Fig. 3(b). These results about the phase transition of ZnO are consistent with Refs. [12,13,15,17]. ZnO_2 undergoes a phase transition from $Pa\bar{3}$ to $P3_121$ at ∼51.5 GPa. The phase transition from $P3_121$ to $I4/mcm$ takes place at ∼128.3 GPa (see Fig. 3(c)).

The equation of states and pressure dependence of lattice constants are shown in Fig. 4. The obvious volume change at phase transition pressure indicates that the pressure-induced structural phase transition is the first-order phase transition. There is a large volume reduction (about 6.7%) at the transition point from $Pa\bar{3}$ to $P3_121$, while volume collapse from $P3_121$ to $I4/mcm$ is only 0.4% (see Fig. 4(a)). The large change of lattice constants with increasing the pressure (see Fig. 4(b)) is attributed to strong compressibility, which in nature originates from strong ionic characteristics of the Zn–O bond.

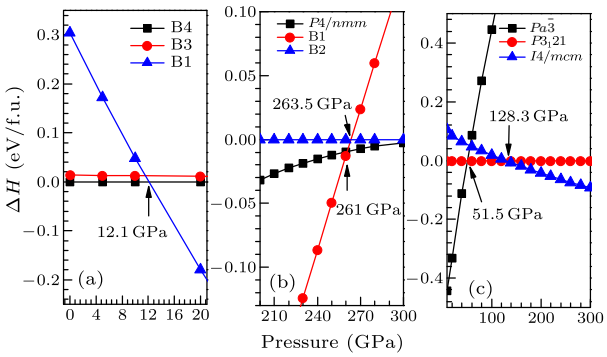

Fig. 3. Phase transition of the Zn-O compound under pressure. (a) Relative enthalpies (ΔH) per chemical formula unit (f.u.) of B1, B3, and B4 phases of ZnO, where the B4 phase is taken as the reference, (b) ΔH per f.u. of B1, B2, and B10 ($P4/nmm$) phases of ZnO with respect to the B2 phase, and (c) ΔH per f.u. of $Pa\bar{3}$, $P3_121$ and $I4/mcm$ structures of ZnO_2 with respect to $P3_121$.

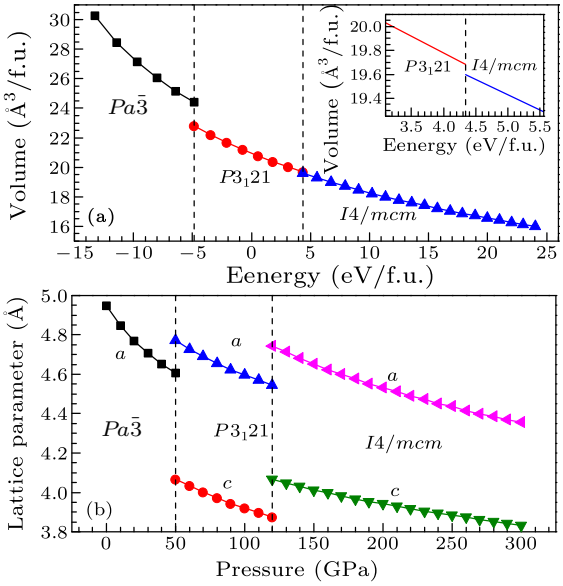

Fig. 4. (a) Total energy versus volume per chemical formula unit for $Pa\bar{3}$, $P3_121$ and $I4/mcm$ of ZnO_2. (b) Pressure dependence of lattice parameters for $Pa\bar{3}$, $P3_121$ and $I4/mcm$.

Phonon calculations for $Pa\bar{3}$, $P3_121$ and $I4/mcm$ reveal that no negative frequency exists, suggesting their dynamical stability (see Fig. 5). The width of frequency gap is 11.40 THz for $Pa\bar{3}$ at 0 GPa, 10.80 THz for $P3_121$ at 55 GPa, 11.68 THz for $I4/mcm$ at 130 GPa, which results from the strong covalent characteristic of the O–O bond.

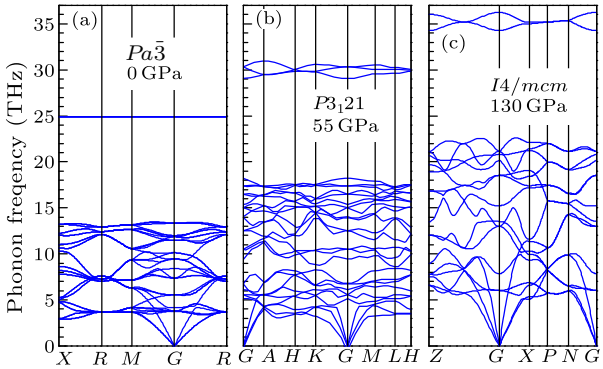

Fig. 5. Phonon dispersions of $Pa\bar{3}$ at 0 GPa, $P3_121$ at 55 GPa and $I4/mcm$ at 130 GPa.

The band structures of $Pa\bar{3}$, $P3_121$ and $I4/mcm$ of ZnO_2 at given pressures are shown in Fig. 6. From Fig. 6(a), one can see that the valence band maximum and the conduction band minimum are located at different points in the Brillouin zone, indicating an indirect band gap. The bandgap value is about 2.17 eV at 0 GPa, which is lower than the experimentally established band gap[38] due to the well-known limitation of PBE-DFT. The calculated band gap is 3.17 eV for $P3_121$ at 55 GPa (see Fig. 6(b)) and the band gap of $I4/mcm$ 3.44 eV at 130 GPa. The wide gap implies that ZnO_2 has potential applications as an optoelectronic device. According to the projected density of states (see Fig. 6), three compounds have the similarity in electron distribution. The Zn-3d electrons mainly contribute to the covalence bands below −4 eV, while O-2p electrons mostly dominate the bottom of conduction bands and the top of covalence bands. For ZnO_2, Zn–O bonds show ionic characteristic due to obvious charge transfer between Zn and O, which are clarified by the obtained Bader charge (see Table 1).

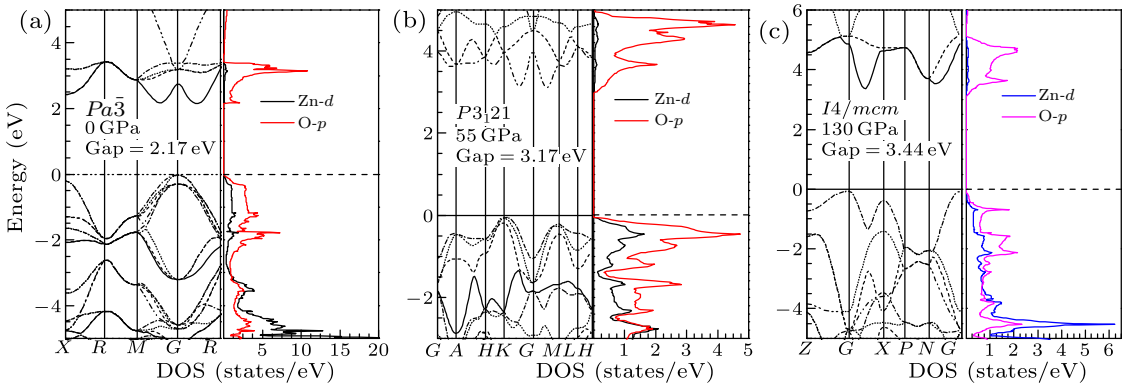

Fig. 6. Band structures and projected density of states (DOS) for $Pa\bar{3}$ (0 GPa) $P3_121$ (55 GPa) and $I4/mcm$ (130 GPa).

Generally, when discussing the stability of a given crystal, it is vital to check mechanical stability via elastic constants. To be mechanically stable, the elastic constants of a given crystal should satisfy the generalized elastic stability criteria.[39–41] All the calculated values are listed in Table 2. The calculated elastic constants of $Pa\bar{3}$, $P3_121$ and $I4/mcm$ phases of ZnO_2 satisfy the above stability criteria, indicating their mechanical stability.

Table 2. The calculated elastic constants c_{ij} of ZnO_2 with $Pa\bar{3}$, $P3_121$ and $I4/mcm$ structures at different pressures, all in units of GPa.

	Pressure (GPa)	c_{11}	c_{12}	c_{13}	c_{33}	c_{14}	c_{44}	c_{66}
$Pa\bar{3}$	0	220	106					69
$P3_121$	55	466	241	277	411	579	162	112
$I4/mcm$	130	781	531	348	780		155	372

In conclusion, the thermodynamically stable or metastable phases of the Zn-O system have been discussed by using EA together with first-principles calculations. It is confirmed that there are two thermodynamically stable compounds (ZnO and ZnO_2) below 300 GPa. The structural phase transition sequence of ZnO is readdressed and the transition points of ZnO agree well with the previous theoretical calculations. A new metastable phase (space group, $P3_121$) of ZnO_2 is obtained. For ZnO_2, the phase consecutive transition among $Pa\bar{3}$, $P3_121$ and $I4/mcm$ occurs at about 51.5 GPa and 128.3 GPa, respectively. The electronic structure calculations indicate that all three phases of ZnO_2 have an indirect bandgap. Furthermore, the calculated phonon spectra and elastic constants conclude the dynamical and mechanical stability of ZnO_2. The predicted new phases $P3_121$ and $I4/mcm$ may have potential importance for understanding the interior of planets.

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