Effect of oxygen vacancies on the elastic properties of zinc oxide: A first-principles investigation

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ABSTRACT

The effect of oxygen vacancies on the elastic properties of zinc oxide (ZnO) is examined using first-principles calculations based on density functional theory. Formation energies of vacancies in different types of oxygen deficient structures were analyzed to ascertain their stability. This analysis reveals that the doubly-charged oxygen vacancy under zinc-rich growth conditions is the most stable. Results show considerable degradation of some of the elastic moduli due to the presence of oxygen vacancies, which is in agreement with recent experiments. The decrease observed in elastic constants is more pronounced with increase in vacancy concentration. Further, the charge state of the defect structure was found to influence the shear elastic constants. Evaluation of elastic anisotropy of stoichiometric and oxygen deficient ZnO indicates the significant anisotropy in elastic properties and stiff *c*-axis orientation.

1. Introduction

The physical and mechanical properties of crystalline materials are affected markedly by the concentration and dynamics of lattice defects in them. While the presence of vacancies may not dramatically alter the elastic properties of metals and alloys, they can certainly do so in ceramic compounds such as oxides and nitrides, as was shown by many experimental and theoretical studies [1–11]. For example, the elastic moduli of group IVb nitrides such as TiN, ZrN and HfN are found to reduce with increase in the concentration of anion vacancies [3,6–9]. Similarly, carbon vacancies can result in a decrease in the elastic modulus of titanium carbide [4,5]. In the context of oxides, calcium vacancies in hydroxyapatite can lead to a striking 80% drop in the elastic modulus and hardness [1,10], and oxygen vacancies in cerium oxide and yttria stabilized zirconia also exert a similar influence [2,11].

Amongst the oxides, zinc oxide (ZnO) is one of the most important ones due to its characteristic features, such as semiconducting direct wide band gap (3.37 eV), large exciton binding energy (60 meV), piezoelectricity, and biocompatibility. Consequently, it is widely used in micro-electro-mechanical and optoelectronic devices, gas sensors and biomedical applications. ZnO is known to exhibit nonstoichiometry under equilibrium growth conditions, for which oxygen vacancies are primarily responsible [12–15]. Consequently, many theoretical studies on the nature of native defects in ZnO [14,16–24] are available in literature and the results show that the most abundant native defects are Zn and O vacancies, and the defect concentration depends on the experimental growth conditions and partial pressures. Lany and Zunger [13] developed a predictive model for defects in ZnO from first-principles calculations, and showed that the nonstoichiometry up to 1% is due to abundant O vacancies, and not due to cation interstitials. Their calculations revealed O vacancies with an equilibrium concentration of up to 10^{20} cm^{-3}, while that of Zn interstitials staying below 10^{14} cm^{-3}. Numerous experimental and theoretical studies have been carried out to understand the formation energy and electronic properties of O-deficient ZnO. However, studies on the effect of such vacancies on the elastic properties of bulk ZnO or O-deficient ZnO have not yet been reported in the literature. While Lucas et al. [25] investigated mechanical properties of individual ZnO nanobelts using modulated nanoindentation and showed an order of magnitude decrease in the elastic modulus of the nanobelts due to the presence of oxygen vacancies, theoretical understanding of the effects of oxygen vacancies on mechanical behavior of ZnO, which is essential for designing the efficient devices with high reliability, has not been achieved yet.

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As discussed above, the presence of oxygen vacancies in ZnO greatly influence its elastic properties. Here, we investigate this using first-principles calculations based on the density functional theory (DFT). Objectives of the present study are to evaluate effects on the elastic properties of ZnO arising from (i) oxygen vacancies (ii) charged defect and (iii) determine their dependence on the oxygen vacancy concentration, by considering three types of O-deficient ZnO defect structures. Formation energies for these structures are estimated and compared with the earlier reports. Elastic moduli of single crystal and polycrystalline forms are estimated for stoichiometric ZnO (S-ZnO hereafter) and O-deficient ZnO structures, and elastic anisotropic behavior is analyzed.

2. Computational details

First-principles calculations have been performed using Quantum Espresso code [26] based on plane wave basis and pseudopotential implementation of the density functional theory (DFT). Exchange correlation energy of electrons is approximated with the generalized gradient approximation (GGA) of the Perdew–Burke–Ernzerhof parameterized functional form [27], and the interaction between ionic cores and valence electrons is represented using ultrasoft pseudopotentials [28], where the Zn 3d states are explicitly treated in the valence. We have also carried out calculation with local density approximation (LDA) of Perdew–Zunger parameterized functional form of the exchange correlation energy [29] for comparison. Energy cutoff of 30 Ry is used for the plane wave expansion of the Kohn–Sham wave functions, and of 180 Ry for that of the charge density. 72-atom periodic $3 \times 3 \times 2$ supercells containing oxygen vacancies are used to simulate defects. Uniform mesh of $9 \times 9 \times 6$ k-points is used in Brillouin zone sampling during calculations with single unit cell and mesh of $3 \times 3 \times 3$ k-points during calculations with supercells. Unit cell and supercell structures are optimized by relaxing positions of all the atoms to a minimum energy structure, until the atomic forces are less than 0.001 Ry/Bohr. Note that we have not included spin–orbit coupling (SOC) in our calculations. Though, the electronic structure of defect structures are affected by SOC effects, it has insignificant effect on defect formation energy, since the difference in the calculated total energies by including the SOC effects can be separated into purely atomic contributions.

3. Results and discussion

3.1. S-ZnO

Our estimates of lattice constants and bulk modulus (B) of S-ZnO in wurtzite structure calculated using GGA and LDA, together with experimental data from literature, are listed in Table 1. As is typical for the functionals, GGA based estimates of lattice constant a is larger by $\sim 1\%$ and B is smaller by $\sim 9\%$ than the experimental value, whereas a is underestimated by $\sim 1\%$ and B is over estimated by $\sim 10\%$ in our calculations based on LDA. This discrepancy between the calculated and the experimental values are well within the typical GGA and LDA errors. In addition, these estimates are in good agreement with earlier theoretical results [19,20,30]. As GGA results are closer to experimental values, we use GGA based calculations in further analysis.

Crystals with hexagonal symmetry have five independent elastic constants (C_{ij}'s) C_{11}, C_{12}, C_{13}, C_{33}, $C_{44} = C_{55}$, and an additional dependent constant $C_{66} = (C_{11} - C_{12})/2$ [32]. The C_{ij}'s of S-ZnO are estimated using energy-strain approach, which is described in Ref. [1]. Table 2 lists all C_{ij}'s together with earlier experimental and theoretical estimates. Our estimates of C_{11}, C_{12}, C_{13} and C_{33} are in excellent agreement with the experimental data of Azuhata et al. [33], whereas C_{44} and C_{66} are slightly overestimated. We note however that C_{44} and C_{66} are in good agreement with the experimental results of Bateman [34] and Kobiakiv [35]. Overall, calculated C_{ij}'s for S-ZnO are in acceptable agreement with the experimental and theoretical [30,33–36] results reported earlier.

3.2. O-deficient ZnO

Our goal here is to consider an isolated point defect, i.e. oxygen vacancy in an infinite crystal, though the presence of defect complexes is important. The infinite limit is approximated here by creating an oxygen vacancy in a large, periodic supercell. The dimensions of the supercell should be such that the interaction between the defects in neighboring supercells is not significant. An ideal choice of the supercell is the one for which increasing its size would not change the formation energies more than an allowed error. Kohan et al. [20] investigated the supercell size convergence using pair-potential approach, and reported that $3 \times 3 \times 2$ supercell as the optimum supercell size. In the present study, a $3 \times 3 \times 2$ supercell with 72 atoms is used, wherein periodic images of oxygen vacancies have a minimum separation of 9.8 Å. We consider three types of defect structures: (i) one oxygen atom is taken out from the supercell while maintaining the charge neutrality. Vacancy concentration is given by the number of oxygen atoms removed per unit cell volume. In this case it is calculated to be 1.1×10^{21} cm^{-3}. This will be referred to as V_O^0-1 hereafter, (ii) One oxygen ion from the supercell is taken out to form the defect structure with +2 charge and will be referred to as V_O^{+2}-1 hereafter, (iii) Two oxygen atoms from the supercell are taken out to form the defect structure, with charge neutrality. In this case, the vacancy concentration is 2.3×10^{21} cm^{-3}, and will be referred to as V_O^0-2 hereafter. We considered only the neutral and the doubly charged oxygen vacancy since it has been con-

Table 1
Calculated cell constants (in Å), volume V (in Å³/f.u.), bulk modulus B (in GPa) of the unit cell for S-ZnO wurtzite structure, determined within GGA and LDA, along with experimental values.

	Present calculations		Experimental result[a]
	GGA	LDA	
a	3.28	3.21	3.25
c	5.32	5.08	5.21
c/a	1.622	1.583	1.602
V	24.8	22.7	23.81
B	128.8	157.7	142.6

[a] Ref [31].

Table 2
Elastic constants C_{ij}'s (in GPa) of S-ZnO with experimental and theoretical results of others.

	Present work	Others	
		Experiments	Theory
C_{11}	189.8	190[a], 209.7[b], 207[c]	209[d], 230[e], 220.8[f], 187[g]
C_{12}	102.2	110[a], 121.1[b], 117.7[c]	85[d], 82[e], 139.7[f], 111.7[g]
C_{13}	93.7	90[a], 105.1[b], 106.1[c]	95[d], 64[e], 124.4[f], 95.0[g]
C_{33}	199.1	196[a], 210.9[b], 209.5[c]	270[d], 247[e], 236.7[f], 203.1[g]
C_{44}	45.2	39[a], 42.5[b], 44.8[c]	46[d], 75[e], 37.5[f], 36.7[g]
C_{66}	43.8	40[a], 44.3[b], 44.6[c]	40.6[f], 37.6[g]

[a] Polarized Brillouin scattering measurements on ZnO single crystal, Ref [33].
[b] Ultrasonic pulse technique on ZnO single crystal, Ref [34].
[c] Ultrasonic resonance technique on ZnO single crystal, Ref [35].
[d] LDA calculation Ref [30].
[e] GGA calculation Ref [30].
[f] LDA calculation Ref [36].
[g] GGA calculation Ref [36].