

A Study of the Electronic Structure and Elastic Properties for m-ZrO₂ and α-Bi₂O₃ Based on First-Principles Calculations under Ambient Pressure

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Abstract. An investigation on the energy band structures, density of states, elastic coefficients and Debye temperature of monoclinic ZrO₂ and monoclinic Bi₂O₃ at ambient pressure was investigated via first-principles calculations based on density functional theory (DFT). The calculation results from the energy band structures and density of states show that both of m-ZrO₂ and α-Bi₂O₃ are separately indirect and direct band gap semiconductor materials. The band gap for m-ZrO₂ and α-Bi₂O₃ are 3.67 eV and 2.05 eV respectively. The calculated results of elastic coefficients indicate that the monoclinic structures of ZrO₂ and Bi₂O₃ are mechanically stable at ambient pressure. Moreover, the Debye temperature of m-ZrO₂ and α-Bi₂O₃ are 385 and 392K.

Introduction

Possessing excellent physico-chemical properties, Bismuth trioxide (Bi₂O₃) and ZrO₂ are interesting materials since they are potential for several promising applications. The properties make the Bi₂O₃/ZrO₂ a strong candidate for various applications like oxygen gas sensors, solid oxide fuel cells, microelectronic and glass manufacturing[1-5]. At ambient pressure, ZrO₂ has three polymorphs, cubic (c-ZrO₂), tetragonal (t-ZrO₂) and monoclinic (m-ZrO₂). ZrO₂ undergoes at least three crystal structure transitions whose stabilities depend on the pressure and temperature. Heating m-ZrO₂ results in the phase transformation between monoclinic and tetragonal phases, tetragonal and cubic phases. The most common polymorph of Bi₂O₃ found at ambient conditions is the mineral bismite (α-Bi₂O₃), which crystallizes in the monoclinic [6]. New phases of Bi₂O₃ have been recently found on increasing pressure and temperature. Such as A-type structure, HP-Bi₂O₃ and R-Bi₂O₃. That is to say, the monoclinic structure in both ZrO₂ and Bi₂O₃ is stable under ambient conditions. However, with improving external conditions, the structure of ZrO₂ and Bi₂O₃ are different. In this paper, in terms of first-principles density functional theory calculations, cell structures, electronic properties, elastic properties including elastic constants, bulk, shear and Young's modules were predicted for m-ZrO₂ and α-Bi₂O₃.

Theoretical Methods

It is known that gradient-corrected approximation(GGA) are successful in calculating materials' properties, such as structural parameters, elastic constants, energy, density of state and thermodynamic properties. Furthermore, GGA can produce more accurate formation energies, as was shown for zirconia polymorphs [7]. So the exchange correlation functional theory is adopted in GGA in this paper, which is the most advanced approximation currently available in DFT. The GGA for exchange correlation functional in the scheme of Perdew–Burke–Ernzerhof (PBE), is used to represent the exchange correlation functional in the DFT formalism. Ultrasoft pseudopotential was used in this study. The lattice constants of m-ZrO₂ is a=5.15, b=5.21, c=5.31, and the space group is P21/C. Pseudo-atom calculations were performed for Zr(4s24p64d25s2) and O (2s22p4). The lattice constants of α-Bi₂O₃ is a=5.85, b=8.16, c=7.50 and belongs to the space group symmetry P21/C. Pseudo atomic calculation performed for Bi 6s2 6p3 and O (2s22p4). The planewave cutoff energy

is 380 eV and the Brillouin-zone integration is performed over the $5 \times 5 \times 5$ grid sizes using the Monkhorst-Pack method for rutile structure optimization.

Results and Discussion

The Geometrical Properties of m-ZrO₂ and a-Bi₂O₃. At ambient conditions, the lattice constants of m-ZrO₂ and a-Bi₂O₃ are listed in table 1. The results are slightly larger than the experimental value[8,9], which are due to the systemic error in GGA.

Table 1 Lattice constants and band gaps of m-ZrO₂ and a-Bi₂O₃ at ambient pressure

material	lattice parameter/nm			Band /eV	Band type
	a	b	c		
m-ZrO ₂	5.197	5.243	5.389	3.67	indirect
a-Bi ₂ O ₃	6.073	8.187	7.444	2.05	direct

Electronic Structure. The overall band structure of m-ZrO₂ and a-Bi₂O₃ are consistent with previous works[10,11] and the semiconducting nature of these materials were found. Due to the well-known underestimation of conduction band state energies in ab initio calculations which are performed with GGA, the obtained band gaps in both m-ZrO₂ and a-Bi₂O₃ are much smaller than the experimental results. The band structure of m-ZrO₂ is shown in fig.1(a). The calculated band structure shows that m-ZrO₂ has indirect band gap because the top valence is observed at G point and the bottom conduction is found at B point. The band gap is calculated to be 3.67 eV, which is consistent with the calculated works, whereas much smaller than experiment data of 5.0V[12]. Though the electron energy-loss spectroscopy experiment revealed a low energy gap of zirconia of 3.8 that was attributed to defect states[13].

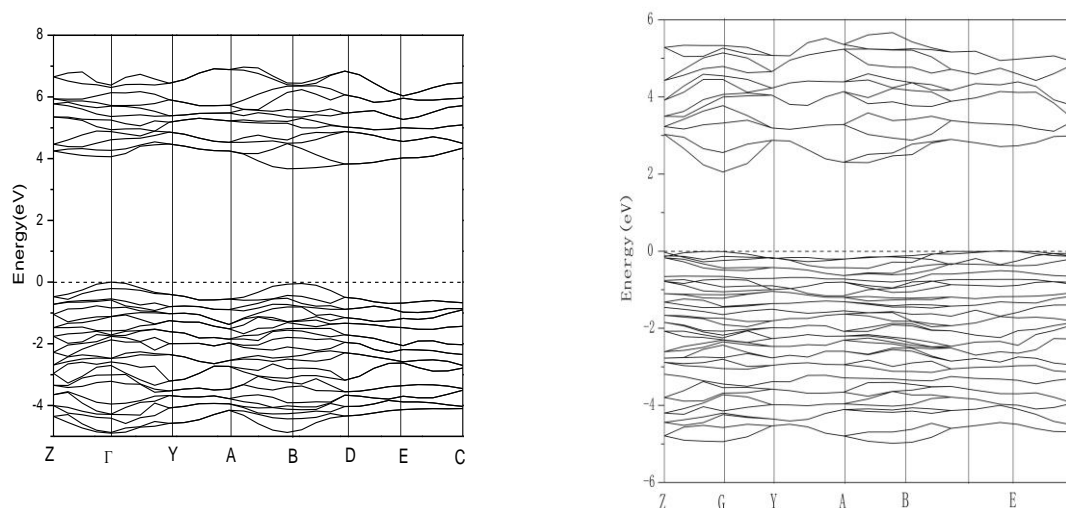


Figure 1. Energy band structures at ambient pressure (a) m-ZrO₂, (b)a-Bi₂O₃

The band structure of a-Bi₂O₃ is shown in fig1(b). The a-Bi₂O₃ has direct band gap because the top valence and the bottom conduction are all found at G point. The band gap is calculated to be 2.05 eV, which is smaller than experiment data of 2.8eV[13]. The smaller band gap of Bi₂O₃ than m-ZrO₂ means that the bismuth oxide can generate electron-hole pairs more efficiently under visible light's excitation beneath the sunlight shiny.

The total and the partial density of states of rutile m-ZrO₂ are presented in Fig.2(a). There are five distinct structures in the density of electronic states separated from each other by gaps. The lower valence narrow band between -15and -20 eV below the valence band maximum comprised mainly of O-2s states. The upper valence bands are composed predominantly of O 2p and Zr-4d which are lying

at about -6~0eV. The conduction band is composed of mainly Zr-4d with some admixture of O-2p states which are lying at about 3.5~7eV.

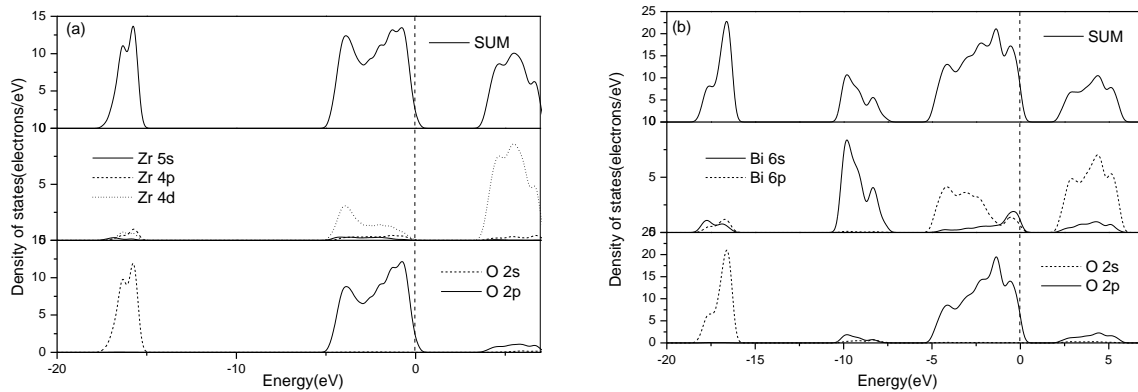


Figure 2. Density of states of m-ZrO2 and a-Bi2O3 at ambient pressure.(a) m-ZrO2; (b)a-Bi2O3

The density of states of a-Bi2O3 are presented in Fig.2(b). The lower valence band between -15 and -17eV mainly comes from the contribution of O 2s states, the upper valence bands lying at about -10~-7 and -5~0 are composed of Bi-6s and O-2p, respectively. The conduction band is composed of mainly Bi-6p with some admixture of O-2p states which are lying at about 2~6eV. However, the band gap mainly comes from the interaction of p states in both the Bi-6p states and O-2p states.

Elastic properties. The elastic constants is a significant parameter in the mechanical stabilities which provide important information concerning the nature of the forces operating in crystal. The elastic constants of m-ZrO2 and a-Bi2O3 in monoclinic phase at ambient conditions are tabulated in table 2. For Monoclinic phase, the criteria for mechanical stability are given by [14]

$$\begin{aligned}
 &C_{11} > 0, C_{22} > 0, C_{33} > 0, C_{44} > 0, C_{55} > 0, C_{66} > 0, \\
 &[C_{11} + C_{22} + C_{33} + 2(C_{12} + C_{13} + C_{23})] > 0, \\
 &(C_{33}C_{55} - C_{35}^2) > 0, (C_{44}C_{66} - C_{46}^2) > 0, (C_{22} + C_{33} - 2C_{23}) > 0, \\
 &[C_{22}(C_{33}C_{55} - C_{35}^2) + 2C_{23}C_{25}C_{35} - C_{23}^2C_{55} - C_{25}^2C_{33}] > 0, \\
 &\{2[C_{15}C_{25}(C_{33}C_{12} - C_{13}C_{23}) + C_{15}C_{35}(C_{22}C_{13} - C_{12}C_{23}) \\
 &+ C_{25}C_{35}(C_{11}C_{23} - C_{12}C_{13})] - [C_{15}^2(C_{22}C_{33} - C_{23}^2) + \\
 &C_{25}^2(C_{11}C_{33} - C_{13}^2) + C_{35}^2(C_{11}C_{22} - C_{12}^2)] + C_{55}g\} > 0
 \end{aligned} \tag{1}$$

$$g = C_{11}C_{22}C_{33} - C_{11}C_{23}^2 - C_{22}C_{13}^2 - C_{33}C_{12}^2 + 2C_{12}C_{13}C_{23} \tag{2}$$

The elastic coefficients of m-ZrO2 and a-Bi2O3 are satisfied the criteria for mechanical stability, which indicated that the m-ZrO2 and a-Bi2O3 have the stable mechanical properties.

Table 2 Elastic coefficients Cij of m-ZrO2 and a-Bi2O3 at ambient pressure (GPa)

Cij	m-ZrO2	a-Bi2O3
C11	332.18715 +/- 2.303	114.40845 +/- 9.147
C22	351.31480 +/- 1.028	57.49660 +/- 7.973
C33	276.59880 +/- 6.050	124.50120 +/- 6.112
C44	77.23750 +/- 0.632	35.71610 +/- 1.572
C55	64.11540 +/- 2.188	49.24480 +/- 4.915
C66	112.37170 +/- 0.697	50.39135 +/- 2.302
C12	140.47785 +/- 1.920	21.14745 +/- 6.693
C13	89.02280 +/- 4.176	41.67165 +/- 5.611
C15	34.48895 +/- 2.055	0.20680 +/- 3.484
C23	127.45015 +/- 4.029	12.74782 +/- 2.043
C25	3.70135 +/- 1.795	-11.10043 +/- 3.990
C35	7.56172 +/- 1.700	17.26163 +/- 5.005
C46	-12.55337 +/- 0.483	4.12015 +/- 0.874

Debye temperature. The Debye temperature (θ_D) can describe maximum phonon frequencies in the lattice vibrations. The Debye temperature (θ_D) of m-ZrO₂ and a-Bi₂O₃ were estimated from the averaged sound velocity, v_m ; by the following equation [15]:

$$\theta_D = \frac{h}{k} \left[\frac{3n}{4\pi} \left(\frac{N_A \rho}{M} \right) \right]^{1/3} v_m \quad (3)$$

Where h is Planck's constant, k is Boltzmann's constant, N_A is Avogadro's number, ρ is the density, M is the molecular weight and n is the number of atoms in the molecule. The average sound velocity (v_m), the longitudinal sound velocity (v_l) and the transverse sound velocity (v_t) in the polycrystalline material are approximately given by [15]:

$$v_m = \left[\frac{1}{3} \left(\frac{2}{v_t^3} + \frac{1}{v_l^3} \right) \right]^{-1/3} \quad (4)$$

$$v_l = \sqrt{\frac{3B + 4G}{3\rho}} \quad (5)$$

$$v_t = \sqrt{\frac{G}{\rho}} \quad (6)$$

Where G is shear modulus and B is the bulk modulus. The calculated Debye as well as bulk modulus B and shear modulus G for m-ZrO₂ and a-Bi₂O₃ are given in table 3. The Debye temperature is near 400K, which means the maximum of lattice vibrate frequency is 10^{13} Hz.

Table 3 The calculated longitudinal, transverse, and average sound velocity (v_l ; v_t ; v_m in m/s) calculated from polycrystalline elastic modulus (bulk modulus B and shear modulus G), and the Debye temperatures calculated from the average sound velocity (θ_D in K)

Compound	B	G	$v_l (m \cdot s^{-1})$	$v_t (m \cdot s^{-1})$	$v_m (m \cdot s^{-1})$	θ_d / K
m-ZrO ₂	177.26706	83.84073	7407	4074	4540	385
a-Bi ₂ O ₃	41.43141	36.92767	4208	2638	8715	392

Conclusion

The first-principles calculations of the electronic structure, elastic properties and Debye temperature of m-ZrO₂ and a-Bi₂O₃ using the plane-wave ultrasoft pseudopotential technique within the generalized gradient approximation (GGA). The results indicate that the m-ZrO₂ is indirect band gap semiconductor and the energy band is mainly contribute by O 2p and Zr-4d states; the a-Bi₂O₃ is direct band gap and the energy band is dominated by Bi-6s6p and O-2p states. The elastic coefficients of m-ZrO₂ and a-Bi₂O₃ indicated that the m-ZrO₂ and a-Bi₂O₃ have the stable mechanical properties at ambient pressure. Moreover, the Debye temperature of m-ZrO₂ and a-Bi₂O₃ are 385 and 392, respectively.

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