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Phase transition and elastic properties of BeO under pressure from first-principles calculations

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ABSTRACT

We have performed first-principles calculations to investigate the phase transition and elastic properties of Beryllium oxide (BeO) within the framework of density functional theory. The elastic constants, shear modulus, bulk modulus and its pressure derivative are all calculated for three polymorphs of BeO: wurtzite (WZ), zincblende (ZB) and rocksalt (RS). These properties at equilibrium phase agree well with the available theoretical and experimental values. Based on the enthalpy criterion, we have found that the WZ to RS structural phase transition occurs at 106 GPa, and there is no phase transition between the WZ and the ZB phases with the pressure up to 200 GPa. Especially, we studied the pressure dependence of elastic properties of these three phases for the first time. It was shown that, for the WZ structure, C_{11}, C_{12}, C_{13}, and C_{33} were sensitive to pressure in the range of 0–200 GPa, while C_{44} remains almost invariant. The similar phenomenon of C_{11}, C_{12} and C_{44} for the ZB structure was found. Differing from the WZ and ZB structures, the elastic constant C_{12} and C_{44} as a function of pressure had a crossover point at 138 GPa for the RS structure. The band structure is also investigated at 0 and 106 GPa for WZ structure. Under the influence of pressure, we have found that the WZ–BeO has transformed to indirect gap semiconductor.

1. Introduction

The earth alkali oxides play an important role as supports in catalysis [1–3]. Beryllium oxide (BeO) is special in this class of materials. It crystallizes in the wurtzite (WZ) structure while the other earth alkali oxides in the cubic structure. Furthermore, not only is BeO harder than the other alkaline-earth oxides but also it is known among the other types of hardest materials [4]. BeO is of technological importance, e.g., as catalyst, for semiconductor devices and as moderator in nuclear reactors [5].

During the last two decades, several experiments [6–9] and theoretical studies [7,10–15] have been carried out to investigate the pressure-induced phase transition in BeO. However, a significant discrepancy exits in the magnitude of the transition pressure [9–15]. The transition pressures reported are variable from 22 to 147 GPa, and the transition sequence is different from each other. In experiments, few phase transitions has been observed [6–8] except Mori et al. [9] found that the WZ to RS (rocksalt) transition of BeO occured at 137 GPa by carrying out an X-ray study. Previous first-pinciples pseudopotential calculations showed that the WZ to RS phase transition occurred at 22 GPa [10] in contrast to 40 GPa obtained by using the potential-induced-breathing (PIB) method [7]. Additionally, subsequent calculations [11–13] showed that the WZ structure transforms to the ZB (zincblende) structure, and then to the RS structure. Van Camp and Van Doren [11] found the WZ→ZB→RS phase transitions at 74 and 137 GPa, respectively by employing the soft nonlocal pseudopotentials. The same transition sequence was reported at 63–76 and 95 GPa by an all-electron and full potential-electronic-structure calculation [12], while first-principle soft nonlocal pseudopotential investigation within the generalized-gradient approximation obtained the transient pressures, 91 and 147 GPa, respectively [13]. More recently, Cai et al. [14] showed that only the WZ→RS phase transition occurred up to 200 GPa by systematically calculating the enthalpy barrier of the phase transition. Based on the full-potential linearlized-augmented-plane-wave (FP-LAPW) method, Amrani et al. [15] predicted that the WZ phase transformed to the RS phase at 107 GPa, while the ZB–RS phase transition occurred at 110 GPa. Both Cai and Amrani's results showed that there was no phase transformation from the WZ structure to the ZB structure.

The mechanical properties of material change with occurrence of the phase transition. The determination of its elastic constants

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can assess the mechanical properties. Especially, the elastic constants of materials under pressures are essential to predict and understand material response, strength, mechanical stability, and phase transition [16]. The elastic coefficients of the WZ–BeO were first reported by Bentle [17], who used the pulse-echo method to determine the five independent elastic coefficients. Subsequently, by using ultrasonic technique, Cline et al. [18] determined C_{12} and C_{13} stiffness that differed by 30–35% from those of Bentle [17]. Cline et al. [18] thought that the value $C_{66}/C_{44}=1.00$ of Bentle [17] is not reasonable for a hexagonal crystal. The results by Sirota et al. [19] showed a good agreement with those by Cline et al. [18], but it is difficult to estimate the accuracy of the data obtained with the number of approximations [19]. More recently, several different theoretical methods [20–22] have been applied to investigate the elastic constants of BeO.

However, to the best of our knowledge, there is no investigation of the elastic properties of BeO under pressure both in theoretical and experimental work. Therefore, the main aim of this work is to give a comprehensive and complementary study of behavior of phase transition and mechanical properties of BeO by using the plane-wave pseudopotential density functional theory (DFT) method through the Cambridge serial total energy package (CASTEP) [23], together with the local density approximation (LDA), by which, we have investigated the elastic properties of the WZ-type aluminum nitride [24] and diamond [25] under high pressure.

This paper is structured as follows. In Section 2, we make a brief review of the theoretical method. The results and some discussion are presented in Section 3, and the summary is given in Section 4.

2. Theoretical method

In the structure calculation, the electronic wave functions are expanded in a plane-wave basis set with energy cut-off 380.00 eV for the three phases (WZ, RS, and ZB) of BeO. Pseudoatomic calculations are performed for Be $2s^2$ and O $2s^22p^4$. For the Brillouin-zone sampling, we use the Monkhorst–Pack mesh [26] with $11\times11\times6$ for the WZ structure and $11\times11\times11$ for both the ZB and RS structures, where the self-consistent convergence of the total energy is 5.0×10^{-7} eV/atom. For the correlation part we use the Ceperley–Alder [27] expression as parametrized by Perdew and Zunder [28]. This correlation functional is the only one consistent with the LDA as it is a fit to the Monte Carlo solution of the uniform electron gas. To ensure the convergence of our calculations, the dependences of the total energy on the cut-off energy and the *k*-point set mesh according to the Monkhorst–Pack grid are investigated carefully. We found that these parameters are sufficient in leading to well converged total energy.

Elastic constants are defined by means of a Taylor expansion of the total energy, $E(V,\delta)$, for the system with respect to a small strain δ of the lattice primitive cell volume V. The energy of a strained system is expressed as follows [29]

$$E(V,\delta)=E(V_0,0)+V_0\left[\sum_i \tau_i\xi_i\delta_i+\frac{1}{2}\sum_{ij}C_{ij}\delta_i\xi_i\delta_j\right] \tag{1}$$

where $E(V_0,0)$ is the energy of the unstrained system with equilibrium volume V_0, τ_i is an element in the stress tensor, δ_i is a small strain of the lattice, ξ_i is a factor to take care of Voigt index, and C_{ij} is the adiabatic elastic constant. Here, the elastic stiffness constants at normal and hydrostatic pressure conditions have been calculated to investigate the mechanical stability of BeO in the WZ, ZB and RS crystal structures. There are five independent elastic constants for the WZ structure, i.e. C_{11}, C_{12}, C_{13}, C_{33}, and C_{44}, while only three elastic constants are independent for the cubic phases, i.e. C_{11}, C_{12} and C_{44}.

According to the elastic constants obtained, we can calculate the zero-pressure bulk modulus B_0 in the form of

$$B_0=\frac{C_{33}(C_{11}+C_{12})-2C_{13}^2}{C_{11}+C_{12}+2C_{33}-4C_{13}} \tag{2}$$

$$B_0=\frac{1}{3}(C_{11}+2C_{12}) \tag{3}$$

for the hexagonal and cubic phases, respectively. There are two approximation methods to calculate the polycrystalline modulus, namely the Voigt method [30] and the Reuss method [31]. Shear modulus is given in the expression: $\gamma=(\gamma_V+\gamma_R)/2$. Here, γ_R is the Reuss modulus and γ_V is the Voigt modulus. The shear modulus γ_V of a hexagonal crystal is defined as

$$\gamma_V=\frac{1}{15}(2C_{11}-C_{12}+C_{33}-2C_{13}+6C_{44}+3C_{66}) \tag{4}$$

and the Reuss modulus γ_R has the following expression

$$\gamma_R=\frac{15}{8S_{11}+4S_{33}-4S_{12}-8S_{13}+6S_{44}+3S_{66}} \tag{5}$$

where S_{ij} is the elastic compliance coefficient. For a hexagonal structure, the elastic compliance coefficient S_{ij} has the following relationship with the elastic stiffness coefficient C_{ij}:

$$S_{11}=\frac{C_{33}C_{11}-C_{13}^2}{(C_{11}-C_{12})[C_{33}(C_{11}+C_{12})-2C_{13}^2]} \tag{6}$$

$$S_{12}=\frac{C_{13}^2-C_{33}C_{12}}{(C_{11}-C_{12})[C_{33}(C_{11}+C_{12})-C_{13}^2]} \tag{7}$$

$$S_{13}=-\frac{C_{13}}{C_{33}(C_{11}+C_{12})-2C_{13}^2} \tag{8}$$

$$S_{33}=\frac{C_{11}+C_{12}}{C_{33}(C_{11}+C_{12})-2C_{13}^2} \tag{9}$$

$$S_{44}=\frac{1}{C_{44}} \tag{10}$$

$$S_{66}=\frac{1}{C_{66}} \tag{11}$$

where $C_{66}=(C_{11}-C_{12})/2$. For the cubic structures, the shear modulus has the following form:

$$\gamma=\frac{1}{2}\left[\frac{C_{11}-C_{12}+C_{44}}{5}+\frac{5C_{44}(C_{11}-C_{12})}{4C_{44}+3(C_{11}-C_{12})}\right] \tag{12}$$

3. Results and discussion

We determined the most stable structure of BeO in the WZ, ZB and RS phases at $P=0$ and $T=0$ through the method described in Ref. [32]. By using a third-order Birch–Murnagham equation of state [33] to fit the total energy versus the volume, we obtained the ground state properties of BeO in the three phase, such as the equilibrium lattice parameter a, c, the bulk modulus B_0 and its pressure derivative B', which are listed in Table 1, together with other theoretical and experimental data. Our results are in agreement with these available data. The overestimate of the lattice constant a and c are 1.00% and 1.07%, respectively, for the WZ–BeO, and the value of c/a is almost equal to the experimental data. The bulk modulus we calculated is 214 GPa, closest to the experimental data except for that in Ref. [34]. From Table 1, we can see that the bulk modulus of BeO in the WZ and ZB structures