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Pressure-induced phase transition of BeO

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ABSTRACT

A constant pressure *ab initio* technique is used to study the pressure-induced phase transition in BeO. A first order phase transition from the wurtzite structure to a rocksalt structure at 700.0 GPa is successfully observed in the constant pressure simulation. The wurtzite-to-rocksalt transformation is based on two fivefold coordinated intermediate states with space groups $P6_3/mmc$ and $Cmcm$, similar to what has been observed or proposed in various wurtzite structured materials. This phase transition should occur around 70 GPa from the enthalpy calculations.

1. Introduction

Beryllium oxide (BeO), one member of the series of alkaline earth oxides, has many unique properties. It has a high thermal conductivity, a low electrical conductivity and a high melting point and hardness. It is therefore an important ceramic. BeO crystallizes under ambient conditions in the hexagonal wurtzite (WZ) structure with space group $P6_3mc$ and tetragonal coordination of the atoms. The high pressure behavior of BeO has been a subject of a few experimental and theoretical studies [1–10] but it is not yet fully understood. Raman spectra showed no evidence for a phase transition at pressures up to 55 GPa in BeO [1] and Hugoniot data did not reveal any volume change for stresses up to 100 GPa [2]. The most recent static high pressure x-ray diffraction experiment [3,4] provided first direct evidence for a phase transition from the WZ structure to a rocksalt (RS) structure in BeO at 137 GPa.

Theoretical studies based on density functional theory (DFT) reported a significant discrepancy in the magnitude of the transition pressure from WZ to RS. The calculations gave a critical pressure of about 22 GPa [1], 40 GPa [5,6], 137 GPa [7], 95 GPa [8], 147 GPa [9] and 105 GPa [10].

In the past few years, much effort has been devoted to determine the transition mechanism of the WZ-to-RS phase transition because an understanding of its mechanism is very important for technological applications and controlling transition processes. Recently, the direct observation of the transition pathway became possible experimentally using picosecond time-resolved electronic spectroscopy in shock wave experiments [11] or by monitoring the shape changes of nanocrystals [12]. So far the hexagonal and tetragonal paths have been proposed or observed for the various WZ structured materials [13–19]. In the hexagonal path the WZ structure is first compressed along the c-axis, resulting in a fivefold coordinated hexagonal intermediate state with space group $P6_3/mmc$ and then a RS phase forms through the opening of the hexagonal angle. In our preliminary work [17], we find that during the hexagonal distortion, a new intermediate phase within $Cmcm$ symmetry forms, indicating that the hexagonal path is based on two metastable phases. In the tetragonal pathway, the hexagonal angle first opens up and the atoms moves horizontally to the center of square and then a decrease of the a/c ratio results in a RS state.

Relative to the WZ structured materials studied in the previous experimental and theoretical works, BeO is a more ionic material and its Phillips' ionicity is 0.602. Therefore BeO is an ideal system to investigate the influence of ionicity on the transition mechanism of the WZ-to-RS phase transformation. In this paper, we carry out a constant pressure *ab initio* technique to study the pressure-induced phase change in BeO and find that BeO undergoes a first

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order phase transition into a RS structure. Our results show that the WZ-to-RS phase change in BeO follows the hexagonal path, similar to what has been observed or proposed for a variety of WZ structured compounds. This observation might indicate that ionicity has almost no control on the transformation mechanism for d electron free semiconducting materials.

2. Computational method

We used the first-principles pseudopotential method within DFT and the generalized gradient approximation of Perdew–Burke and Ernzerhof for the exchange–correlation energy [20]. The calculation was carried out with the *ab initio* program SIESTA [21] using a linear combination of atomic orbitals as the basis set, and norm-conservative Troullier–Martins Pseudopotentials [22]. A split-valence double-ξ plus polarized basis set was employed. A uniform mesh with a plane wave cut-off of 150 Ry was used to represent the electron density, the local part of the pseudopotentials, and the Hartree and the exchange–correlation potential. The simulation cell consists of 72 atoms with periodic boundary conditions. We used Γ-point sampling for the Brillouin zone integration, which is reasonable for a simulation cell with 72-atoms since the energy difference between the 72 atoms simulation cell with only Γ point and the 8-atoms unitcell with 256-$\mathbf{k}$ points (see below) is less than about 0.01 eV/atom. The molecular dynamics (MD) simulations were performed using the NPE (constant number of atoms, constant pressure, and constant enthalpy) ensemble. The reason for choosing this ensemble is to remove the thermal fluctuations, which facilitates easier examination of the structure during the phase transformation. Pressure was applied via the method of Parrinello and Rahman [23] and the structure is equilibrated with a period of 1000 time steps (each time step is one femto-second (fs)) at each applied pressure. We also used the power quenching technique during the MD simulations. In this technique, each velocity component is quenched individually. At each time step, if the force and velocity components have opposite sign, the velocity component is set equal to zero. All atoms or supercell velocities (for cell shape optimizations) are then allowed to accelerate at the next time step.

For the enthalpy calculations, we only considered the primitive cell for both WZ and RS structures and the Brillouin zone integration was performed with automatically generated $8 \times 8 \times 8$ k-point mesh for both phases following the convention of Monkhorst and Pack [24].

In order to determine the intermediate state during the phase transformation, we used the KPLOT program [25] that supplies detailed information about space group, cell parameters and atomic position of a given structure. For the symmetry analysis we used 0.2 Å, 4°, and 0.7 Å tolerances for bond lengths, bond angles and interplanar spacing, respectively.

3. Results

3.1. Enthalpy calculation

We first relax the unit cell of the WZ and RS structures using the variable cell optimization technique at zero pressure to obtain the equilibrium lattice constants. The calculated parameters and bulk modulus obtained from the third order Birch–Murnaghan equation of state, with available experimental and theoretical values are presented in Table 1. Overall we find a reasonable agreement of our lattice parameters and bulk properties with the experimental and theoretical data [1,4,7–9,26].

Table 1
Lattice parameters and bulk modulus B for BeO. Refs. [1,4,26] are experimental data.

Structure	Reference	a (Å)	c/a	u	B (GPa)
Wurtzide	This study	2.709	1.634	0.375	243
	[9]	2.703	1.620	0.377	203
	[9]	2.650	1.624	0.378	224
	[8]	2.668	1.633		239
	[7]	2.639	1.629	0.376	228
	[1]	2.775	1.58		186
	[26]	2.698	1.622	0.378	212
	[4]	2.693	1.623	0.378	223
Rocksalt	This study	3.629			284
	[9]	3.648			231
	[9]	3.577			264
	[8]	3.590			272
	[7]	3.571			266

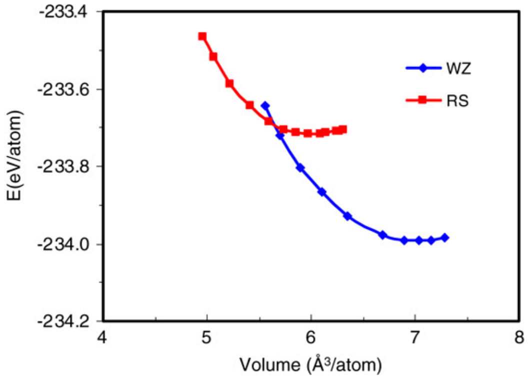

Fig. 1. The energy–volume relation for the WZ and RS structured BeO.

In order to determine the most stable structure at finite pressure and temperature, the free energy $G = E_{\text{tot}} + PV - TS$ should be used. For the experimental data considered here the contribution of the last term is small and is therefore neglected in the rest of the calculation. We thus work with the enthalpy $H = E_{\text{tot}} + PV$. In order to obtain the enthalpies, we first study the total energy of the WZ and RS structures as a function of volume and fit their energy–volume relation to the third order Birch–Murnaghan equation of state. The computed total energies per atom as a function of volume are given in Fig. 1. Using the energy–volume data, we calculate the static lattice enthalpies and plot them in Fig. 2 as a function of pressure. Since at the phase transition, the two phases have the same enthalpy, the transition pressure can be easily determined by equating the enthalpy of the two phases. We obtain a transition pressure of about 70.0 GPa, which is indeed quite less than the experimental result of 137 GPa. Comparison of our result with the earlier DFT calculations is difficult because they reported a significant discrepancy in the magnitude of the transition pressure, ranching from 22 GPa to 147 GPa. We should note here that experiments show that the WZ-to-RS phase transition begins at 137 GPa and completes at 175 GPa [3,4], indicating slow kinetics. Indeed the theoretical calculations suggest that the activation barrier for this phase transition is about 0.65 eV per pair of BeO molecules [10]. Therefore, we expect that the equilibrium phase transition pressure calculated should less than the actual experimental transition pressure because of the high activation barrier.

3.2. Parrinello–Rahman simulation

Fig. 3 shows the pressure–volume relation of BeO obtained through the dynamical simulation. As can be seen from the figure, the volume changes gradually and at a pressure of 700 GPa it shows a noticeable decrease, which is typical for a first order phase transition. The structural analysis reveals that BeO adapts a RS structure, in excellent agreement with experiments. The transition pressure obtained in constant pressure simulation is,

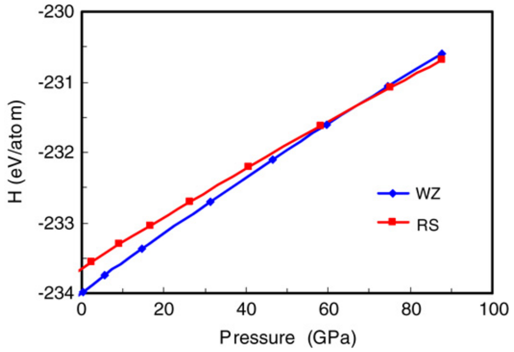

Fig. 2. The computed enthalpy curve of the WZ and RS structures. The curves cross around 70 GPa, indicating a phase transition from the WZ-to-RS structure.

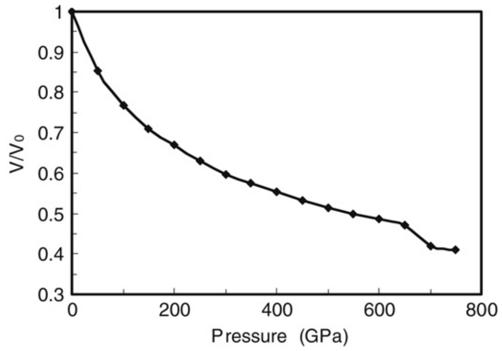

Fig. 3. The pressure–volume curve of BeO from the Parrinelo–Rahman simulation.

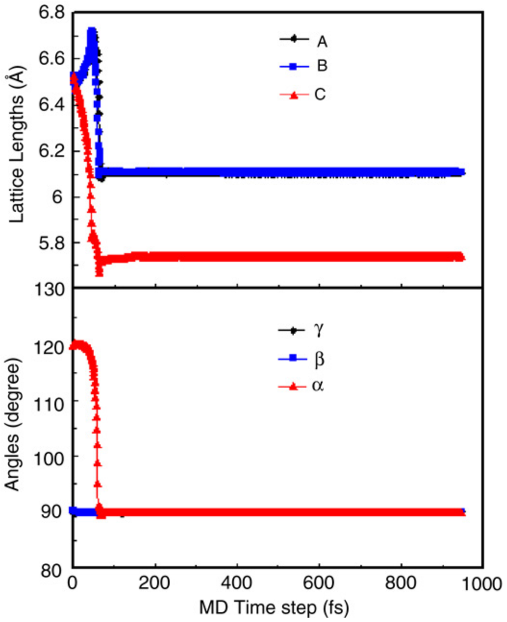

Fig. 4. Change the simulation cell lengths and angles as a function of MD time step at 700 GPa.

on the other hand, considerably larger than the experimental result of 137 GPa [10]. This tendency is indeed anticipated when some conditions in simulations are considered. Namely, the use of ideal structure with finite size and periodic boundary conditions favors homogenous phase transformations, in contrast to heterogeneous nucleation and growth seen in experiments. Consequently, simulated systems have to cross a significant energy barrier to transform from one phase to another one. The high energy barrier can be only cross when the simulation box is overpressurized [27]. This behavior is analogous to superheating MD simulations.

In this study, we are particularly interested in the transformation mechanism to see whether ionicity has any influence on it. Therefore, as a next step, we study the atomic movement during the phase transformation by analyzing the modification of the simulation cell vectors. We plot the simulation cell lengths and angles as a function of MD time step in Fig. 4. The simulation cell vectors **A**, **B**, and **C** are originally along the [100], [$\bar{1}$ 10] and [001] directions, respectively. The magnitude of these vectors is plotted in the figure. As clearly seen from the figure, the transformation mechanism from the WZ-to-RS structure in BeO is straightforward and occurs in two steps. Firstly the structure is significantly compressed along the [001]-direction while it is expanded along the other directions. Secondly a noticeable decrease in $|\mathbf{B}|$ and $|\mathbf{A}|$ and a change from 120° to 90° in the hexagonal α-angle (between **A** and **B** lattice vectors) occur simultaneously, resulting in a tetragonal modification of the simulation cell during the phase transformation. The structural analysis using the KPLOT program [25] indicates that this transformation pathway is based on two intermediate phases: at 40 MD step, when the c-axis is compressed about 30%, a fivefold coordinated hexagonal structure with the space group $P6_3/mmc$ is formed. The structure is characterized by the lattice parameters $a = b = 2.267$ Å, and $c = 2.912$ Å. This fivefold coordinated intermediate state consists of stacked flat honeycomb lattices in the c-direction. When the α-angle is about 112°, we observe the formation of another intermediate phase. This state has an orthorhombic structure within $Cmcm$ symmetry. The lattice constants of the $Cmcm$ phase are $a = 2.453$, $b = 3.641$ Å and $c = 2.094$ Å. This phase is still fivefold coordinated. When the α-angle is about 92° at the MD step 65, a distorted sixfold coordinated RS state is formed with the unit cell parameters $a = b = c = 3.26$ Å.

The previous studies have shown that the WZ-to-RS phase transformation follows two different pathways, hexagonal and tetragonal. Saitta and Decremps [18] analyze both mechanisms for some WZ-structured materials through *ab initio* calculations of the full phonon properties and suggest that the transformation pathway of the WZ crystals depends on the presence of d electrons on cation atoms. In particular they propose that the hexagonal transformation path is only possible for the semiconductors containing light (d electron free) cations such as SiC and AlN while the tetragonal phase is favorable in materials whose cations have d electrons such as GaN, CdS and ZnO. The present simulation reveals that the WZ-to-RS transformation mechanism in BeO corresponds to the hexagonal transformation path, in agreement with Saitta and Decremps' prediction [18].

The observation of the hexagonal transformation mechanism in a more ionic material BeO, compared with SiC [17] and AlN [16], is particularly important because it suggests that the hexagonal pathway might be universal for d electron free semiconducting materials.

4. Conclusions

An *ab intio* constant pressure technique is applied to study the pressure-induced phase transition in BeO. A first order phase change into a RS structure is successfully reproduced thorough the simulations. The WZ-to-RS phase transition is associated with a tetragonal adaption of the simulation cell and based on two metastable states. Compression along the c-axis flats the hexagonal basal (001) planes in the WZ structure, results in a fivefold coordinated hexagonal intermediate state with space group $P6_3/mmc$, and then the hexagonal state becomes unstable with respect to shear deformation on (001) planes and converts to first a fivefold coordinated orthorhombic intermediate state within the $Cmcm$ symmetry, and then a RS state. The WZ-to-RS transformation mechanism of BeO corresponds to a previously known hexagonal path. Our results might indicate that ionicity has no influence on the transformation mechanism for d electron free semiconducting materials.

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