Pressure-induced phase transition and its atomistic mechanism in BeO: A theoretical calculation

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We have investigated the pressure-induced phase transition in BeO using a first-principles pseudopotential method within the generalized gradient approximation. The results show that the enthalpy of BeO with wurtzite structure is lower than that with zinc blende structure at 87 GPa and the same to rocksalt structure at 105 GPa. However, from the point of view of enthalpy barrier, the wurtzite-zinc-blende-rocksalt phase transition sequence will not happen up to 200 GPa but only the wurtzite-rocksalt transition. The phase transition mechanism can be viewed as an orthogonal strain deformation: two strain contractions in $[10\bar{1}0]$ and $[0001]$ direction and a strain expansion in $[0100]$ direction.

The properties of insulating refractory oxides at high pressure are important in both ceramics and materials science. BeO is of particular importance because of its high thermal conductivity and low electrical conductivity. As a low-Z oxide and the lightest II-VI compound, BeO is also important from a more fundamental point of view.[1] BeO crystallizes in the hexagonal wurtzite (WZ) structure with the polar space group $P6_3mc$. According to the Phillips' ionicity (f_i) argument,[2] the tetrahedral compounds with ($f_i > 0.35$) will transform into an ionic sixfold rocksalt (RS) structure under pressure. Since the Phillips' ionicity of BeO is 0.602, a phase transition from WZ to RS is expected at high pressure. During the last two decades, a few theoretical calculations and experiments have been performed to investigate the pressure-induced phase transition in BeO. However a significant discrepancy exists in the magnitude of the transition pressure. Earlier first-principles pseudopotential calculation predicted the WZ-RS transition at 22 GPa.[3] The same transition was found at 40 GPa (Ref. 1) by the potential-induced-breathing (PIB) method. Recently similar calculations predicted that the WZ first transformed into the zinc blende (ZB) and then into the RS. In the first work Van Camp and Van Doren employed soft nonlocal pseudopotentials to predict the WZ-ZB-RS transitions at 74 and 137 GPa.[4] In the second work Boettger and Wills found the corresponding transitions at 63–76 and 95 GPa, respectively by an all-electron and full-potential-electronic-structure calculation.[5] In the last work Park *et al.* obtained 91 and 147 GPa for the transient pressure using a first-principles soft nonlocal pseudopotential method within the generalized-gradient approximation.[6] In order to explore whether the phase transition sequence is WZ-ZB-RS, not only the free energy of these phases but also the transitional barriers should be investigated. A large transitional barrier might impede a transition at the equilibrium pressure, leading to a hysteresis between the forward and backward transforms even preventing a transition. For examples, GaN and SiC have high observed transformation pressures of ~50 and ~100 GPa in comparison to the calculated equilibrium transition pressures of 31 and 60 GPa, respectively.[7] Previous experiments examined the high-pressure behavior using vibrational Raman spectroscopy and

no phase transition was observed up to a pressure of 55 GPa (Ref. 1). The latest high pressure x-ray diffraction experiment was carried out by Yoshihisa Mori *et al.* This result showed no phase transition up to 126 GPa but a new phase was found at 137 GPa. With increasing pressure, the WZ phase disappeared at 175 GPa.[8]

Recently there was increasing interest to understand the mechanism of transition from a fourfold- to a sixfold-coordinated structure, for instance, the bilayer sliding mechanism in[9] SiC or the homogeneous strain deformation mechanism in GaN.[10,11] A proper understanding of the transition mechanism enables us to study the transition barrier along possible paths. The other way around we can, according to the barrier, find the most favorable transition path. For example, the study of the transition mechanism from WZ-RS in CdSe showed that there are at least three transition paths and the energy barrier is about 0.13 eV/pair.[12] For the transition mechanism, we pay more attention to the homogeneous strain deformation mechanism, because, on the one hand, BeO has the WZ type structure, and on the other hand, this mechanism is more intuitive and has been investigated in detail for ZnO (Ref. 7) and CdSe (Ref. 12).

In this paper, total energy calculations within the density functional theory (DFT) are presented to examine the phase transformation in BeO under pressure with the CASTEP code.[13] Ultrasoft pseudopotentials are expanded within a plane wave basis set with a cutoff energy of 380 eV. We use the generalized-gradient approximation (GGA) in the scheme of Perdew-Burke-Ernzerhof[14] (PBE) to describe the exchange and correlation potential, since the GGA is more accurate to predict the phase transition pressure than the local-density approximation (LDA).[15–21]

The thermodynamic stable phase at some given pressure and temperature is the one with the lowest Gibbs free energy G, where $G = U + pV - TS$, and U is the internal energy, p is the pressure, V is the volume, T is the temperature, and S is the entropy. In general, the phase equilibrium transition pressure is determined by calculating the G-V curves of the two phases and finding the common tangent, which is difficult to calculate accurately. In fact, the variations in temperature that will normally concern us produce much smaller changes
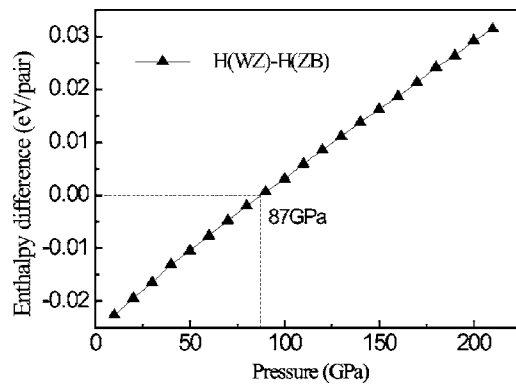
FIG. 1. The difference in enthalpy between WZ and ZB type BeO as a function of pressure.

in the relative stabilities of the different phases. Therefore we shall be mostly concerned with the Gibbs free energy at zero temperature, which is the enthalpy H given by $H = U + pV$. At zero temperature the thermodynamically stable phase at pressure p is the one with the lowest enthalpy.[22] So we have calculated the enthalpy for each phase. The transition pressure is obtained from the enthalpy curve crossings.

First we investigate the enthalpies of BeO with WZ, ZB, and RS structure. Due to the tiny difference in enthalpy between WZ and ZB structure, we have plotted the enthalpy difference as a function of pressure as shown in Fig. 1. The enthalpy difference increases from -0.026 eV to 0.029 eV/pair (per pair of BeO molecules) for increasing pressure from 0 to 200 GPa. This result is not surprising because of the high similarity between the two structures. The local environment of any atom in either zinc blende or wurtzite is exactly the same as far as the second neighbors are concerned. When the pressure is up to 87 GPa, H (WZ) is equal to H (ZB) but above 87 GPa the ZB-type BeO is more stable than the WZ-type BeO and it has a lower enthalpy. Figure 2 shows the enthalpies of the WZ and RS structure as a function of pressure. As can be seen, the enthalpies of the two structures increase almost linearly with increasing pressure. When the pressure is up to 105 GP they become equal. That means that the two phases are at thermodynamic equilibrium. With increasing pressure the RS structure becomes more stable and the enthalpy difference between them gradually increases. At 200 GPa the enthalpy
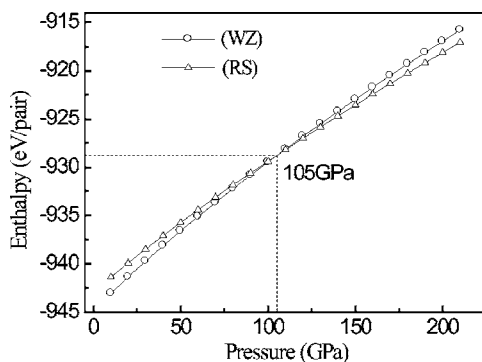

FIG. 2. The enthalpy of WZ and RS type BeO as a function of pressure.
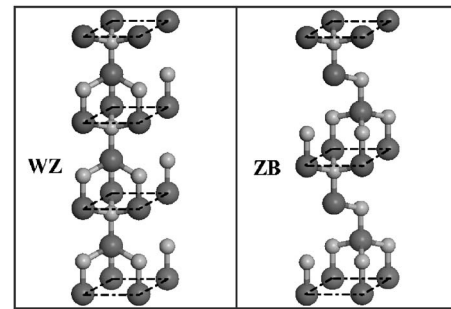

FIG. 3. BeO dimers stacking style: WZ structure *ABABABA...* and ZB structure *ABCABCA...*. Small light gray spheres denote anions and large dark gray spheres are cations.

difference is 1.173 eV per pair BeO molecules. So it is expected to undergo a phase transition from WZ to RS. In comparison with the theoretical results in Ref. 6 (91 and 147 GPa) the WZ-ZB transition pressure is almost the same whereas the WZ-RS transition pressure differs significantly from our results. This might be caused by the different methods that were used to determine the transition pressure as mentioned above. While they employed soft nonlocal pseudopotentials and found the common tangent of energy-volume curves, we used ultrasoft pseudopotentials and found the crossings of enthalpy curves.

Next we investigate the enthalpy barrier of the phase transition based on an atomistic mechanism of transition. The phase transition from WZ to ZB corresponds to the BeO dimers stacking style changing from *ABABABA...* to *ABCABCA...* as shown in Fig. 3. We take the two layer BeO molecules at the bottom in Fig. 3 for example. The BeO molecules stack into BA and CA respectively for WZ and ZB structure. It is not difficult to image that a potential barrier exists on the WZ-ZB transition path as shown in Fig. 4. A Be-O bond breaking and forming takes place during the *B* layer dimer sliding to the *C* layer. Although the enthalpy difference between the WZ and ZB structure is greater than zero, the potential barrier must be taken into account when we investigate the phase transition. The enthalpy difference between the WZ and the transient structure (TS), i.e., enthalpy barrier, is 0.267 eV/pair at 87 GPa. If the actual transformation process could take place, not only the enthalpy of ZB has to be lower than or equal to that of WZ but also the enthalpy difference between the two phases has to be more
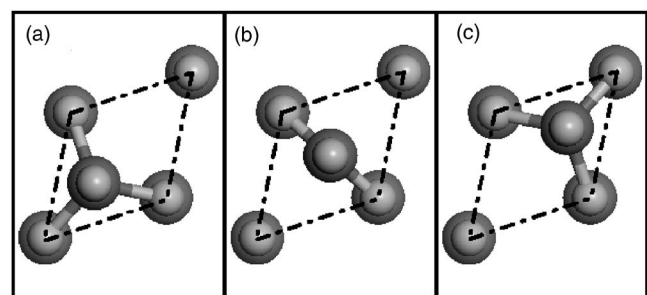

FIG. 4. Top view of relative sliding for the two layer BeO dimers at the bottom in Fig. 3. The stacking style changes from *BA* to *CA*. (a) WZ structure; (b) transient structure; (c) ZB structure.

TABLE I. Structural parameters of BeO with WZ and RS structure and phase transition pressure p_t. The values in square brackets are the parameters at p_t.

	WZ	RS
Volume (Å³/pair)	28.9 [21.5]	25.0 [19.3]
a (Å)	2.741 [2.480]	3.685 [3.377]
c/a	1.626 [1.626]	1 [1]
u	0.377 [0.377]	0.5 [0.5]
b/a	1.732 [1.732]	1 [1]
v	0.333 [0.333]	0.5 [0.5]
V_t^{RS}/V_t^{WZ}		0.898
Transition pressure p_t (GPa)		105

than the enthalpy barrier with increasing pressure. Since the maximum enthalpy difference between WZ and ZB is about 0.029 eV (far less than the enthalpy barrier) up to 200 GPa it can be predicted the WZ will not transform into ZB structure in the range of 200 GPa. At a much higher pressure, the enthalpy difference between WZ and ZB might be larger than the enthalpy barrier, however, the WZ has transformed into the much more stable RS structure as stated in the following.

For the possible WZ-RS transition, we first investigate the uniaxial strains c/a and b/a at a fixed and inner parameters u and v relaxed. We find the stains c/a and b/a to be independent which is similar to the situation in GaN (Ref. 10). It seems reasonable to assume that the WZ transforms into the RS only by two independent uniaxial strains. An important fact should not be neglected in the course of considering this kind of phase transition, namely the change of a. Table I lists the structure parameters of BeO with the WZ and RS structure and the transition pressure. It can be seen that for the ideal WZ-type BeO structure the lattice constant a is 2.480 Å but is 3.377 Å for the RS structure at the transition pressure. Hence the a axis must expand significantly during the phase transition process. From the crystallographic consideration, the main driving force of the a expansion is the increasing enthalpy caused by the shortening of Be-Be and Be-O distance. During the uniaxial strain in c direction the distance of nearest Be-Be between top and middle (or middle and bottom) layers in Fig. 5 will shorten and during the uniaxial strain in $[10\bar{1}0]$ direction as shown in Fig. 6 the distance of nearest Be-Be between left and middle (or middle and right) list of Be atoms and the Be-O bonds which
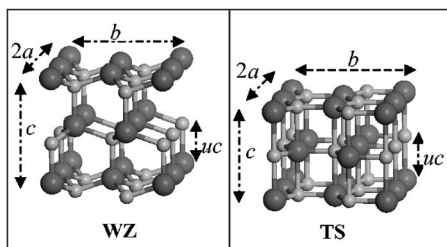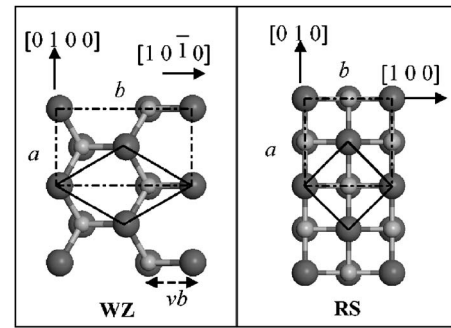

FIG. 6. Crystal structures of WZ and RS. The parameters b and v defining the structure are indicated.

projects in (0001) do not parallel the $[10\bar{1}0]$ direction, will shorten under the condition of a fixed. So the a axis should be relaxed during the calculation.

In order to estimate the enthalpy barrier of WZ-RS phase transition we should map out the enthalpy difference as a function of two strain parameters b/a and c/a varied from 1.732 to 1 and 1.626 to 1, respectively, similar to the studies carried out in Refs. 7 and 10. However an important difference between our study and theirs is that the lattice parameter a besides the internal parameters u and v is allowed to relax for each b and c configuration. Hence, it will give a more reasonable enthalpy barrier by avoiding excessive constrains on the atoms. We have investigated 99 strained configurations corresponding to an interval of 0.1 Å of b (from 4.295 to 3.377 Å) and c (from 4.043 to 3.377 Å). For each pair of b and c configuration, the corresponding lattice parameter a and enthalpy are obtained from structure optimization. With the purpose of mapping out the contour of enthalpy difference in strain parameters b/a and c/a space, each pair of b and c is divided by the corresponding a and the enthalpy difference at this configuration is obtained by calculating $\Delta H = H - H_t^{RS}$, where H is the enthalpy at given configuration and H_t^{RS} is the enthalpy of RS-type BeO at the

FIG. 5. Transformation of WZ to an intermediate structure or transient structure (TS) under c/a compression.
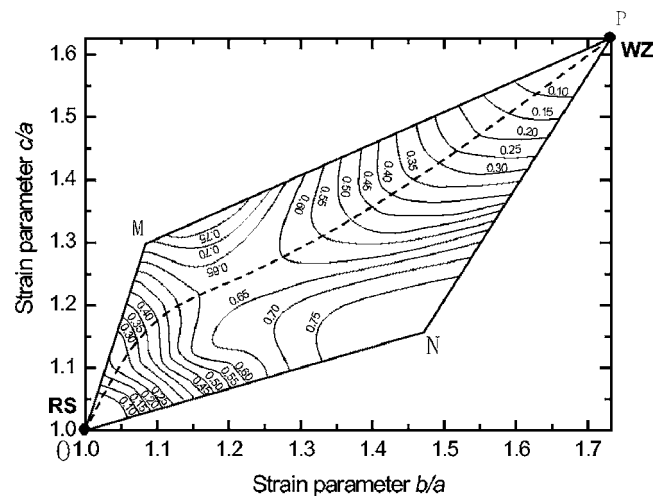

FIG. 7. Contour plot of the enthalpy difference ($H - H_t^{RS}$ or $H - H_t^{WZ}$) as a function of strain parameters b/a and c/a under the equilibrium transition pressure $p_t = 105$ GPa. The dashed line indicates a transition path with the least enthalpy barrier.

equilibrium transition pressure and equals to H_t^{WZ}. Figure 7 shows the contour of ΔH as a function of b/a and c/a. The solid lines $\overrightarrow{PMO}$ and $\overrightarrow{PNO}$ denote two special phase transition paths. The $\overrightarrow{PM}$ and $\overrightarrow{MO}$ segment correspond to b contracting from 4.295 to 3.377 Å at $c=4.043$ Å and c contracting from 4.043 to 3.377 Å at $b=3.377$ Å, respectively. That is to say, that along this path b axis first strain only, then c axis strain only. Similarly, the $\overrightarrow{PN}$ and $\overrightarrow{NO}$ segment denote c changing from 4.043 to 3.377 Å at $b=4.295$ Å and b changing from 4.295 to 3.377 Å at $c=3.377$ Å, respectively. Both paths have higher enthalpy barrier. Indeed, the phase transition path is neither $\overrightarrow{PMO}$ nor $\overrightarrow{PNO}$ but in the region enclosed by them. The dashed line is a more favorable path because the enthalpy barrier (<0.65 eV/pair) along it is the smallest. Furthermore, Fig. 4 shows that the enthalpy difference $[H(\mathrm{WZ})\text{-}H(\mathrm{RS})]$ increases to 1.173 eV with pressure up to 200 GPa. Accordingly, it can be predicted that the WZ-RS phase transition could happen in BeO. The least enthalpy path shows that the b axis is easy to strain at the beginning

and the c axis is easy at the end of the phase transition. It is expected that this path can be confirmed by experiments in the future.

In conclusion, we have studied in detail the phase transition sequence in BeO using first-principles enthalpy calculations. The results show that the ZB and WZ enthalpies become equal at 87 GPa and for the RS and WZ at 105 GPa. However, from the point of view of enthalpy barrier based on atomistic mechanisms of phase transition, the WZ-ZB-RS phase transition sequence will not occur but only the WZ-RS transition with increasing pressure. Our calculational results are consistent with the latest experimental results. At the same time, the minimum transformation enthalpy barrier is estimated to be not more than 0.65 eV per pair of BeO molecules. Although the WZ-RS phase transition is a complicated path, its mechanism is still viewed as an orthogonal strain deformation: two strain contractions in the $[10\bar{1}0]$ and $[0001]$ direction and a strain expansion in the $[0100]$ direction.

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