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First-principles study of pressure-induced phase transition in silicon carbide

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ABSTRACT

The phase transition of SiC from the zinc blende (ZB) structure to the rocksalt (RS) structure under pressure is investigated by the first principles plane-wave pseudopotential density functional theory method. The results obtained are in good agreement with the experimentally measured data and other theoretically calculated results. It is found that the pressures of transition of SiC from the ZB structure to the RS structure are 74.6 GPa from total energy–volume data and 75.4 GPa from the enthalpy calculations. Moreover, through the quasi-harmonic Debye model, in which the phononic effects are considered, the dependences of relative volume V/V_0 on pressure P at $T = 0$, 1400 K are successfully obtained. The calculated volume reduction at the transition is 18%. In particular, from the high-pressure elastic constants obtained, the ZB structure SiC is found unstable when the applied pressure is larger than 126.6 GPa. This value is in excellent agreement with the experimental data and the molecular dynamics (MD) simulation results.

1. Introduction

Silicon carbide (SiC) has outstanding physical properties, such as excellent chemical stability, a wide band gap, high stiffness, high hardness, high thermal conductivity and a high melting point. These properties make it useful for electronic and optical device applications. For example, microelectronic devices made of SiC can be used in high-power, high-speed, high-temperature and high-frequency applications. At ambient pressure, SiC can exist in various polytypes originating from differences in the stacking sequence of silicon–carbon bilayers along the [1 1 1] or [0 0 0 1] direction. Among about 200 known SiC polytypes, the zinc blende (ZB) structure SiC is the most commonly studied polytype [1].

It is important to study the phase stability of materials under high pressure and temperature for microscopic understanding as well as technological applications [2]. The pressure-induced phase transition of SiC [3–15] has attracted much interest from physicists.

X-ray diffraction measurements [4] have shown that the pressure of transition of SiC from the ZB structure to the rocksalt (RS) structure occurs at 100 GPa or higher, with a volume reduction of 20.3% in static diamond-anvil cell (DAC). The transition is reversible and the ZB phase is recovered below 35 GPa upon pressure release. Later, shock compression experiments on 6H SiC [5] demonstrate a first-order phase transition with a volume reduction of about 15% into a sixfold coordinated structure (most probably a RS structure) around 105 GPa. Recent shock compression studies at temperatures of 600–1500 K and at pressures 5–25 GPa show unique structural phase transitions among SiC polytypes [6]; for instance, the ZB crystal transforms to the rhombohedral phases by changing the stacking sequence of SiC atom layers.

Up to now, several research groups have theoretically investigated the pressure-induced transitions in SiC using different methods [7–12]. For example, theoretical studies based on *ab initio* density functional calculations with the local-density approximation (LDA) present the critical pressure of the ZB-to-RS phase transition to be around 60 GPa [7–10]. Miao and Lambrecht [11] found the transition pressure 63 GPa using the Perdew–Wang generalized gradient approximation (GGA) for the exchange-correlation potential and the Troullier–Martins pseudopotentials. Moreover, using the Troullier–Martins pseudopotentials and the LDA, Durandurdu [12] recently reported the phase transition pressure of 100 GPa. As pointed by the authors, this result, which might reach the limit of GGA is rather surprising because the DFT–LDA calculations tend to underestimate critical pressure for structure phase transition.

In this work, we also focus on the pressure-induced phase transition of SiC from the ZB structure to the RS structure using a different method. Allowing for the well-known overstabilization

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of high-density structures by neglecting nonlocal effects in the DFT exchange-correlation potential, we here adopt a nonlocal ultrasoft pseudopotential introduced by Vanderbilt [16] together with the Perdew–Wang 1991 (PW91) GGA for the exchange-correlation potential [17] to implement constant-pressure *ab initio* simulations. The pressures of transition of SiC from the ZB structure to the RS structure are 74.6 GPa from total energy–volume data and 75.4 GPa from equal enthalpy calculations. Moreover, through the quasi-harmonic Debye model, in which the phononic effects are considered, the dependences of relative volume V/V_0 on pressure P at $T=0$, 1400 K are successfully obtained. The calculated volume reduction at the transition is 18%. In particular, from the high-pressure elastic constants obtained, the ZB structure SiC is found unstable when the applied pressure is larger than 126.6 GPa. This value is in excellent agreement with the experimentally measured data and the molecular dynamics (MD) simulation results.

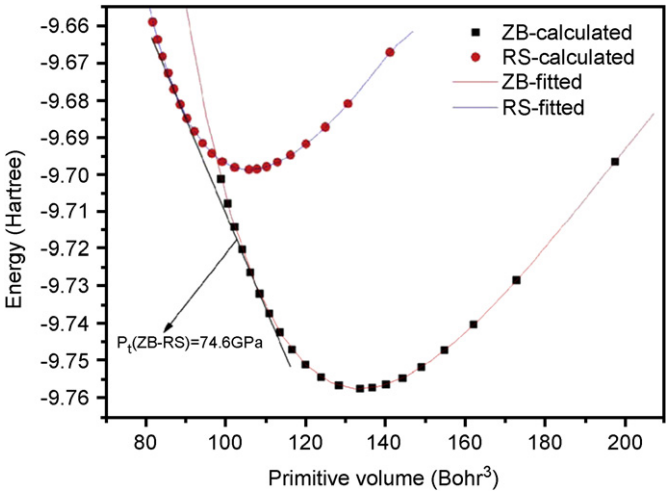

Fig. 1. Energy as a function of primitive cell volume for SiC.

2. Theoretical method

The phase transition of SiC from the ZB structure to the RS structure under pressure is investigated by the first principles plane-wave pseudopotential density functional theory (DFT) method. The nonlocal ultrasoft pseudopotential introduced by Vanderbilt [16] together with the Perdew–Wang 1991 (PW91) GGA for the exchange-correlation potential [17] is used to implement constant-pressure *ab initio* simulations. Because it is important to ensure that the ground state energy is converged within a specified tolerance in terms of the iterations for self-consistency, the convergence tests are first made carefully to determine the needed minimums of *k*-points for the Brillouin zone sampling and cut-off energy for the used plane-wave basis set in the DFT calculations. According to the result tested, the wave functions of the valence electron are expanded by plane-wave basis set with an energy cut-off of 550 eV. Pseudo-atom calculations are performed for Si $3s^2\ 3p^2$ and C $2s^2\ 2p^2$. As for the the Brillouin-zone *k*-point sampling, we use the $12\times12\times12$ Monkhorst–Pack scheme [18]. With these choices of parameter, the self-consistent convergence of the total energy is at 10^{-6} eV/atom. For each value of the applied pressures, the lattice vectors are optimized until the stress tolerance is smaller than 0.05 GPa and the maximum atomic force is smaller than 0.03 eV/Å. All the total energy electric structure calculations are performed with CASTEP code [19] based on the DFT.

3. Results and discussion

For both the ZB structure and the RS structure of SiC, we take a series of constant-pressure *ab initio* simulations to obtain the total energy E and the corresponding primitive cell volume V, which are illustrated in Fig. 1. The calculated equilibrium lattice constants a, zero-pressure bulk modulus B_0 and its pressure derivation B'_0 from the Birch–Murnaghan equation of state (EOS) [20] are listed in Table 1, together with the experimental data and other theoretical results. The agreement among them is good.

Table 1
The lattice constants (Å), bulk modulus (GPa) and its pressure derivation, elastic constants (GPa) of the ZB and RS structures of SiC at $P=0$ and $T=0$

	This work	Other theoretical calculations	Experiments
ZB structure			
a	4.30	4.37[a], 4.36[b], 4.315[c], 4.34[d],	4.36[e]
B_0	227.1	200[a], 212[b], 223[c], 223.6[d]	224[f], 225[g], 227[h]
B'_0	3.79	7.3[a], 3.7[b], 3.8[c], 3.77[d]	3.57[h]
C_{11}	415.1	420[c]	390[i]
C_{12}	131.9	126[c]	142[i]
C_{44}	265.4	287[c]	256[i]
RS structure			
a	3.97	4.04[d]	
B_0	266.6	252.3[d], 278.4[j]	
B'_0	4.64	4.26[d], 2.61[j]	
C_{11}	484.8		
C_{12}	174.7		
C_{44}	383.4		

[a] From Ref. [21] (Epw = 29.7 Ry for SiC).
[b] From Ref. [7] (Epw = 60 Ry for SiC).
[c] From Ref. [24] (from FP–LMTO method).
[d] From Ref. [8].
[e] From Ref. [22].
[f] From Ref. [23].
[g] From Ref. [25].
[h] From Ref. [27].
[i] From Ref. [26] (from sound velocities and bulk modulus).
[j] From Ref. [12].