Structural properties of BeO at high pressure

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Abstract. In the present paper, we have investigated the phase transition and elastic properties of BeO at high pressure using three-body potential model (TBPM). The present interaction potential consists of long-range coulomb and three-body interactions and short-range overlap repulsion effective up to second neighbour ions. We have studied the phase transition from wurtzite (B_4) to rock salt (B_1) for BeO. The phase transition pressure (P_t) obtained from this approach shows a respectably good agreement with experimental and other theoretical data. We have also computed the collapse of relative volume changes ($\Delta V(P_t)/V(0)$). Three-body potential model has also been used to derive the correct expressions for third-order elastic constants and pressure derivatives of second-order elastic constants for BeO.

Keywords. Phase transition pressure; three-body potential model; second-order elastic constants; third-order elastic constants.

1. Introduction

Beryllium oxide (BeO) shows interesting features because of its electrical, thermal, optical (David Groh *et al* 2009) and crystal properties (Hazen and Figer 1986; Christensen *et al* 1999). These properties show wide range of applications, from optoelectronic (Ivanov *et al* 2007) to nuclear reactor (Zeezherun *et al* 1963). BeO has the wurzite structure (B_4) under ambient condition, although the other BeX (X = S, Se and Te) crystallizes in zinc blend (B_3). In recent past, phase transition at high pressure has been a subject of great interest for experimentalists as well as theoreticians. Recently, Yashihisa Mori *et al* (2003) studied the phase transition of BeO under high pressure. They carried out powder diffraction using the synchrotron radiation source and the phase transition was found at 137 GPa. Theoretical studies have predicted the phase transition sequence to be wurtzite to zinc blend to rock salt (Lichanot *et al* 1992; van Camp and van Doren 1996; Park *et al* 1999).

In the present work, we have studied the phase transition and elastic properties of BeO, for which the experimental data are available and their theoretical model is lacking.

2. Methodology

In the present paper, we have applied the three-body interaction potential (Lowdin 1956; Lundqvist 1957; Fumi and Tosi 1962; Singh and Verma 1970, 1971; Singh

1982) to study high-pressure phase transition in BeO. This potential includes first and second terms in it are the long-range Coulomb and three-body interaction (TBI), and the remaining terms represent the short-range overlap repulsion operative up to the second neighbour ions. Accordingly, the binding energy of solid from the proposed interatomic potential can be expressed as

$$\phi = \phi_c + \phi_T + \phi_r, \quad (1)$$

$$\begin{aligned} \phi = & \sum_{ij} \frac{Z_i Z_j e^2}{r_{ij}} \left(1 + \frac{2n}{Z} f(r_{ij}) \right) \\ & + b \left[n \beta_{+-} \exp \left(\frac{r_+ + r_- + r_0}{\rho} \right) \right. \\ & \left. + \frac{n'}{2} \left\{ \beta_{++} \exp \left(\frac{2r_+ + kr_0}{\rho} \right) + \beta_{--} \exp \left(\frac{2r_- + kr_0}{\rho} \right) \right\} \right]. \end{aligned} \quad (2)$$

Here, $f(r)$, b and ρ are TBI, hardness and range (strength) parameters, respectively, and can be determined by using equilibrium condition

$$\left(\frac{d\phi}{dr} \right)_{r=r_0} = 0. \quad (3)$$

Bulk modulus, given by

$$\left(\frac{d^2\phi}{dr^2} \right)_{r=r_0} = 9K r B_T. \quad (4)$$

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with $K = V/r^3$ as the structure-dependent constant and is well known for structure.

The electron shell of adjacent ions suffers appreciable overlap during lattice vibrations and consequently gets deformed. This electron shell deformation gives rise to a transfer or exchange of charge between the overlapping ions. These transferred charges, in turn, interact with all other charges of the lattice and give rise to long-range many-body interactions, whose most significant component is the TBI. The TBI parameter $f(r)$ is dependent on the nearest neighbour distance (r) as

$$f(r) = f_0 \exp(-r/\rho). \quad (5)$$

Gibbs free energy of a system is given by

$$G = U + PV - TS, \quad (6)$$

where U is internal energy.

The Gibb's free energies $G_1(r)$ for one phase and $G_2(r)$ for second phase become equal at the phase transition pressure P and temperature 0 K, i.e. $\Delta G = G_1(r) - G_2(r)$ becomes zero.

Using the TBPM given by (2), we have derived the expressions for second-order elastic constant (SOEC), bulk modulus, shear moduli, third-order elastic constant and pressure derivative of second-order elastic constants (where a is lattice constant).

The expressions for SOECs are

$$C_{11} = L \left[-0.2477Z(Z + 8f(r_0)) + \frac{1}{3}(A_1 + 2B_1) + \frac{1}{2}(A_2 + B_2) + 5.8243Zaf'(r_0) \right], \quad (7)$$

$$C_{12} = L \left[-2.6458Z(Z + 8f(r_0)) + \frac{1}{3}(A_1 - 4B_1) + \frac{1}{4}(A_2 - 5B_2) + 5.8243Zaf'(r_0) \right], \quad (8)$$

$$C_{44} = L \left[-0.123Z(Z + 8f(r_0)) + \frac{1}{3}(A_1 + 2B_1) + \frac{1}{4}(A_2 + 3B_2) - \frac{1}{3}\nabla(-7.53912Z(Z + 8(r)) + A_1 - B_1) \right]. \quad (9)$$

and for TOECs are

$$C_{111} = L \left[0.5184Z(Z + 8f(r_0)) + \frac{1}{9}(C_1 - 6B_1 - 3A_1) + \frac{1}{4}(C_2 - B_2 - 3A_2) - 2(B_1 + B_2) \right.$$

$$\left. -9.9326Zaf'(r_0) + 2.522Za^2f''(r_0) \right], \quad (10)$$

$$C_{112} = L \left[0.3828Z(Z + 8f(r_0)) + \frac{1}{9}(C_1 + 3B_1 - 3A_1) + \frac{1}{8}(C_2 + 3B_2 - 3A_2) - 11.64852Zaf'(r_0) + 2.522Za^2f''(r_0) \right], \quad (11)$$

$$C_{123} = L \left[6.1585Z(Z + 8f(r_0)) + \frac{1}{9}(C_1 + 3B_1 - 3A_1) - 12.5060Zaf'(r_0) + 2.522Za^2f''(r_0) \right], \quad (12)$$

$$C_{144} = L \left[6.1585Z(Z + 8f(r_0)) + \frac{1}{9}(C_1 + 3B_1 - 3A_1) - 4.1681Zaf'(r_0) + 0.8407Za^2f''(r_0) + \nabla \left[-3.3507Z(Z + 8f(r_0)) - \frac{2}{9}C_1 + 13.5486Zaf'(r_0) - 1.681Za^2f''(r_0) \right] + \nabla^2 \left[-1.5637Z(Z + 8f(r_0)) + \frac{2}{3}(A_1 - B_1) + \left(\frac{C_1}{9} \right) - 5.3138Zaf'(r_0) + 2.9350Za^2f''(r_0) \right] \right], \quad (13)$$

$$C_{166} = L \left[-2.1392Z(Z + 8f(r_0)) + \frac{1}{9}(C_1 - 6B_1 - 3A_1) - \frac{1}{8}(C_2 - 5B_2 - 3A_2) - (B_1 + B_2) - 4.1681Zaf'(r_0) + 0.8407Za^2f''(r_0) + \nabla \left[-8.3768Z(Z + 8f(r_0)) - \frac{2}{3}(A_1 - B_1) - \frac{2}{9}C_1 + 13.5486Zaf'(r_0) - 1.681Za^2f''(r_0) \right] + \nabla^2 \left[2.3527Z(Z + 8f(r_0)) + \left(\frac{C_1}{9} \right) - 5.3138Zaf'(r_0) + 2.9350Za^2f''(r_0) \right] \right], \quad (14)$$

$$C_{456} = L \left[4.897Z(Z + 8f(r_0)) + \frac{1}{9}(C_1 - 6B_1 - 3A_1) \right. \\ \left. - \frac{1}{8}(C_2 - 5B_2 - 3A_2) - B_2 \right. \\ \left. + \nabla \left[-5.0261Z(Z + 8f(r_0)) - \frac{1}{9}C_1 \right] \right. \\ \left. + \nabla^2 \left[-4.8008Z(Z + 8f(r_0)) \right. \right. \\ \left. \left. + \frac{1}{3}(A_1 - B_1) - \left(\frac{C_1}{9} \right) \right] \right]. \quad (15)$$

With $L = e^2/4a^4$ and

$$\nabla = \left[\frac{-7.53912Z(Z + 8f(r_0)) + (A_1 - B_1)}{-3.141Z(Z + 8f(r_0)) + (A_1 + 2B_1) + 21.765Zaf'(r_0)} \right]. \quad (16)$$

Expression for pressure derivatives of bulk modulus, B_T , shear moduli and elastic constant, C_{44} , using three-body potential model are given by

$$\frac{dB_T}{dP} = -(3\Omega)^{-1} [20.1788Z(Z + 8f(r_0)) \\ - 3(A_1 - A_2)4(B_1 + B_2) + (C_1 + C_2) \\ - 104.8433Zaf'(r_0) + 22.7008Za^2f''(r_0)], \quad (17)$$

$$\frac{dS}{dP} = -(2\Omega)^{-1} \left[-11.5756Z(Z + 8f(r_0)) + 2(A_1 - 2B_1) \right. \\ \left. + \frac{3}{2}A_2 - \frac{7}{2}B_2 + \frac{1}{4}C_2 + 37.5220Zaf'(r_0) \right], \quad (18)$$

$$\frac{dC_{44}}{dP} = -(\Omega)^{-1} \left[\left\{ 0.4952Z(Z + 8f(r_0)) \right. \right. \\ \left. \left. + \frac{1}{3}(A_1 - 4B_1 + C_1) + \frac{2A_2 - 6B_2 + C_2}{4} \right. \right. \\ \left. \left. + [4.9667Zaf'(r_0) + 2.522Za^2f''(r_0)] \right. \right. \\ \left. \left. + \nabla \left\{ -17.5913Z(Z + 8f(r_0)) + A_1 - B_1 \right. \right. \right. \\ \left. \left. \left. - \frac{2}{3}C_1 + 40.6461Zaf'(r_0) - 5.0440Za^2f''(r_0) \right\} \right. \right. \\ \left. \left. + \nabla^2 \left\{ 3.1416Z(Z + 8f(r_0)) + \frac{2}{3}(A_1 - B_1) \frac{C_1}{3} \right. \right. \right. \\ \left. \left. \left. - 15.9412Zaf'(r_0) + 8.8052Za^2f''(r_0) \right\} \right] \right], \quad (19)$$

with

$$\Omega = -5.0440Z(Z + 8f(r_0)) + (A_1 + A_2) \\ - 2(B_1 + B_2) + 17.4730Zaf'(r_0). \quad (20)$$

3. Results and discussion

The present interaction potential has only three parameters as given by (2). The value of these parameters has been determined with the help of (3) and (4). The input constants and calculated model parameter for BeO are given in table 1.

The cohesive energies computed for BeO are reported in table 2. With the knowledge of these cohesive energies, we have tried to predict the relative ability of competitive structure B_4 – B_1 by finding out the energy difference

Table 1. Input constant for phase transition.

Solid	Input parameters			Calculated model parameters		
	r_+ (Å)	r_- (Å)	a (Å)	ρ (Å)	b (10^{-12} ergs)	$f(r)$
BeO	1.12 (David Groh <i>et al</i> 2009)	0.66 (David Groh <i>et al</i> 2009)	2.698 (David Groh <i>et al</i> 2009)	0.12	0.28	0.133

Table 2. Phase transition properties.

Solid	Equilibrium lattice constants (Å)		Cohesive energy (kJ/mol)			Phase transition pressure (P_t) (GPa)	Relative volume change (%)
	r_1 (B_1)	r_2 (B_2)	ϕ_1 (–)	ϕ_2 (–)	$\Delta\phi$		
Present	1.59	1.63	4102.58	3506.94	595.64	133.7	35
Expt.	1.6541 (Hazen and Figer 1986)	–	–	–	–	137 (Yashihisa Mori <i>et al</i> 2003)	–
Other theory	1.65 (David Groh <i>et al</i> 2009)	–	–	–	–	105 (Yingxiang Cai <i>et al</i> 2006)	–

Figure 1. Energy vs pressure.

Figure 2. Phase diagram of BeO. Solid lines show present calculation.

Table 3. The values of SOEC and TOEC (in unit of $10^9 \text{ dyn}\cdot\text{cm}^{-2}$).

BeO	C_{11}	C_{12}	C_{44}	C_{111}	C_{112}	C_{123}	C_{166}	C_{144}	C_{456}
Present	3.87	2.61	1.22	-9.824	26.13	-25.51	-27.62	-33.38	-27.62
Other theory	4.7	1.68	1.53	—	—	—	—	—	—
	(Bai-Ru Yu <i>et al</i> 2009)	(Bai-Ru Yu <i>et al</i> 2009)	(Bai-Ru Yu <i>et al</i> 2009)						

Table 4. Value of first-order pressure derivative of second-order elastic constants (dimensionless units).

BeO	dB_T/dP	dS/dP	dC_{44}/dP
Present	4.037	-10.33	-1.106

($\Delta\phi = \phi_2 - \phi_1$). The values of these $\Delta\phi$ show that their values are always positive for the solids studied in this work. This, according to the criteria laid down by Sangster *et al* (Hazen and Figer 1986), demonstrates that our model potential and parameters are capable of predicting the relative stability of solids. We have evaluated phase transition from graphical analysis in which the differences in Gibb's free energy, $\Delta G = G_1(r) - G_2(r)$, are plotted against the pressure (P). It is seen from table 2 and figure 1 that the values of phase transition pressure obtained from the graphical analysis in the framework of the present three-body potential are in closer agreement with their experimental data available for BeO.

The phase transition predicted in figure 2 has followed a systematic trend similar to those obtained from the experimental observation. We also calculated the value of volume collapses ($\Delta V(P_t)/V_0$) at the phase transition pressure obtained from the phase diagram.

The force constants A_i , B_i and C_i ($i = 1, 2$) have been calculated from the knowledge of the model parameters. Their values have been able to compute the TOEC and the pressure derivatives of SOEC of the BeO. We have described the anharmonic properties of BeO by calculating SOEC, TOEC and pressure derivatives SOEC and bulk and shear moduli. Their calculation values are listed in tables 3 and 4 and compared with their available experimental results.

In view of the overall achievements, as discussed before, it is concluded that the present three-body potential model is capable of successfully describing the lattice mechanical and anharmonic properties of BeO.

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