

Theoretical Analysis of the Structural Phase Transition in Alkaline Earth Oxides

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Abstract: We report a phenomenological model based calculation of pressure-induced structural phase transition and elastic properties of CaO, SrO and BaO alkaline earth oxides. Gibb's free energy is obtained as a function of pressure by applying an effective interionic interaction potential, which includes the long range Coulomb, van der Waals (vdW) interaction and the short-range repulsive interaction upto second-neighbor ions within the Hafemeister and Flygare approach. From the present study, we predict a structural phase transition from NaCl structure (B1) to the CsCl structure (B2).

INTRODUCTION

Group II-VI compound materials have attracted significant attention recently, and have been studied both experimentally and theoretically because of their potential uses for a number of well-established technologies, as well as new classes of electronic and optoelectronic devices, operating in the blue to ultraviolet spectral region [1–9]. The relative stability of different crystallographic phases and possible high pressure phase transformations among them have been of long standing interest in alkaline earth oxides CaO, SrO and BaO. These alkaline earth oxides have been considered as a typical case for understanding bonding in ionic oxides and are also one of most fundamental materials for industrial sciences. This is because of their wide range of applications ranging from catalysis to microelectronics. For example, their catalytic properties are important for chemical engineering [10].

The alkaline earth oxides form a very important closed-shell ionic system crystallizing in NaCl-type structure at room conditions [11, 12]. With the application of pressure, the NaCl-type (B1) structure of the alkaline-earth oxides undergoes structural phase transition to a CsCl-type (B2) structure with eight-fold coordination. CaO is known to have the B1–B2 transition at 61 GPa [13] and the B2 phase is stable to at least 135GPa [14,15]. Diamond anvil cell and shockwave measurements [13, 14] show that CaO trans - forms from B1 to B2 phase over a pressure range of 60–70GPa. Kalpana et al. [16] have also calculated this transition for CaO.

SrO has been studied in many experimental and theoretical works. Sato and Jeanloz [17] measured the B1–B2 phase transition. Taurian et al. [18] studied the electronic structure of the B1 phase with the linearized-muffin-tin orbital (LMTO) method. Pandey et al. [19] calculated the electronic structure following the Adams–Gilbert–Kunz (AGK) localized-orbital Hartree–Fock method. Zhang and Bokowski [20] calculated the B1–B2 transition pressure using a modified-electron gaz model. Kalpana et al. [16] calculated this transition pressure and related properties using the LMTO method in its tight-binding representation. In addition, there are few studies of high-pressure elasticity of SrO and BaO.

Among the lattice models, which have been invoked so far, to discuss the mechanical properties of several solids and alloys, charge transfer approach [26], following Hafemeister and Flygare [27] type overlap repulsion extended up to second neighbor ions besides short-range interactions. We refer to the pioneering work of Tosi [28], who properly incorporated van der Waals interaction along with dipole-dipole ($d-d$) and dipole-quadrupole ($d-q$)

interactions to reveal the cohesion in several ionic solids. In trying to understand the structural aspects, we admit that the vdW attractions are the corner stone of lattice phenomenological models that is ignored in the first principle microscopic calculations. Motivated from the remarks on band structure studies [13 - 20] and the charge transfer effect approach [26] for the successful description of the phase transition and high pressure behavior of binary compounds, we have chosen two-body interaction potential because it includes vdW attractions, which are not well described by the standard methods currently used in first principle microscopic calculations. Therefore, it is necessary to study fundamental properties, such as, structural stability of alkaline earth oxides compounds.

THEORY AND METHOD OF COMPUTATION

The understanding of thermodynamical properties for alkaline earth oxides compounds needs the formulation of an effective interionic potential. The effective interionic potential between pair of ions (i and j^{th}) is expressed as

$$U(r) = \sum_{ij} \frac{Z_m e^2}{r_{ij}} + \sum_{ij} b \beta_{ij} \exp\left(\frac{r_i + r_j - r_{ij}}{\rho}\right) + \sum_{ij} c_{ij} r_{ij}^{-6} + \sum_{ij} d_{ij} r_{ij}^{-8}. \quad (1)$$

Here, long-range Coulomb is represented by first term, second term correspond to Hafemeister and Flygare form of short-range repulsive energies [17] and van der Waals multipole are represented by third and fourth terms, respectively. The Pauling coefficients β_{ij} are defined as: $\beta_{ij} = [1 + (z_i/n_i)/(z_j/n_j)]$ with z_i (z_j) and n_i (n_j) as the valency and number of outermost electrons in the anions (cations), respectively. The symbols: c_{ij} and d_{ij} are representing the dipole-dipole ($d-d$) and dipole-quadrupole ($d-q$) van der Waals coefficients. $Z_m e$ is the modified ionic charge and parametrically includes the effect of Coulomb screening effects. b (hardness) and ρ (range) are short-range parameters. Thus, the effective interionic potential contains only three free parameters (Z_m , b and ρ) which can be determined from the crystal properties [29].

An isolated phase is stable only when its free energy is minimum for the specified thermodynamic conditions. As the temperature or pressure or any other variable acting on the systems is altered, the free energy changes smoothly and continuously. A phase transition is said to occur when the changes in structural details of the phase are caused by such variations of free energy. The test materials transform from their initial $B1$ to $B2$ structure under pressure. The structural stability of a particular structure is decided by the minima of Gibbs free energy. Since these theoretical calculations are performed at $T = 0$ K, Gibbs free energy became equal to the enthalpy, $H = U + PV$. For a given pressure, a stable structure is one for which thermodynamic potential (G or H) has its lowest value.

We have estimated the Gibbs free energy for both the $B1$ and $B2$ phases. The Gibbs free energies $G_{B1}(r) = U_{B1}(r) + 2Pr^3$ for NaCl ($B1$) [real] phase and $G_{B2}(r') = U_{B2}(r') + [8/3\sqrt{3}]Pr^3$ for CsCl ($B2$) [hypothetical] phase become equal at the phase-transition pressure P and at zero temperature *i. e.*, $\Delta G (= G_{B1} - G_{B2})$. Here, U_{B2} and U_{B1} represent cohesive energies for $B1$ and $B2$ phases, and are

$$U_{B1}(r) = -1.7475 \frac{e^2 Z_m^2}{r} + 6V_{ij}(r) + 6V_{ii}(r) + 6V_{jj}(r), \quad (2)$$

and

$$U_{B2}(r') = -1.7627 \frac{e^2 Z_m^2}{r'} + 8V_{ij}(r') + 3V_{ii}(r') + 3V_{jj}(r'). \quad (3)$$

Here r and r' are nearest-neighbor (nn) separations corresponding to NaCl and CsCl phases, respectively. The short-range potentials (V_{ij}) (in equations 2 and 3) for both the phases between the ions follow

$$V_{ij}(r) = b \beta_{ij} \exp\left(\frac{r_i + r_j - r_{ij}}{\rho}\right) - c_{ij} r_{ij}^{-6} - d_{ij} r_{ij}^{-8}; \quad i, j = 1, 2. \quad (4)$$

b and ρ being the short-range parameters. The effective interionic interaction potential can then have three material parameters: modified ionic charge (Z_m), range (b) and hardness parameters (ρ), which can be determined from the known crystal properties.

RESULT AND DISCUSSION

The effective interionic potential is constructed in a hierarchical and easy generalizable manner. We have undertaken such structural and elastic properties in an ordered way. For such purposes we have then three free

parameters, namely, modified ionic charge, range and hardness parameters (Z_m , ρ and b). To estimate the free parameters, we first deduce the vdW coefficients from the Slater-Kirkwood variational method [31] and are listed in table 1. We consider that the alkaline earth oxides compounds to be partially ionic.

Table 1: The values of van der Waals coefficients c_{ij} ($i, j = 1, 2$) [in units of 10^{-60} erg cm⁶], d_{ij} ($i, j = 1, 2$) [in units of 10^{-76} erg cm⁸] for alkaline earth oxides compounds

Compound	vdW coefficients					
	c_{11}	c_{12}	c_{22}	d_{11}	d_{12}	d_{22}
CaO	128.3	2.65	1.4	14.3	3.15	0.5
SrO	96.8	1.53	1.4	150.7	2.76	0.5
BaO	168.5	1.27	1.4	251.4	1.94	0.5

Table 2: Crystal data and model parameters for alkaline earth oxides compounds

	Material Parameters			Model Parameters			
	r_i (Å)	r_j (Å)	a (Å)	B_T (GPa)	Z_m^2	ρ (10^{-1} Å)	b (10^{12} erg)
CaO	1.57	0.66	4.811 [21]	114 [21]	1.78	1.25	2.96
SrO	1.49	0.64	5.159 [21]	88 [21]	1.70	1.36	3.74
BaO	1.42	0.63	5.536 [21]	61 [21]	1.67	1.49	3.87

Table 3: Calculated (reported) transition pressure and volume collapse in alkaline earth oxides compounds

Compound	Transition pressure P_t (GPa)	Volume collapses (%)
CaO	57 (61 ^a , 60-70 ^b , 65.2 ^c , 56 ^d , 53-70 ^{a,e,f})	16.6
SrO	34 (37 ^c , 32-40 ^{a,e,f})	15.5
BaO	93 (100 ^e)	13.8

^aRef. [13], ^bRef. [16], ^cRef. [22], ^dRef. [23], ^eRef. [14], ^fRef. [24], ^gRef. [25],

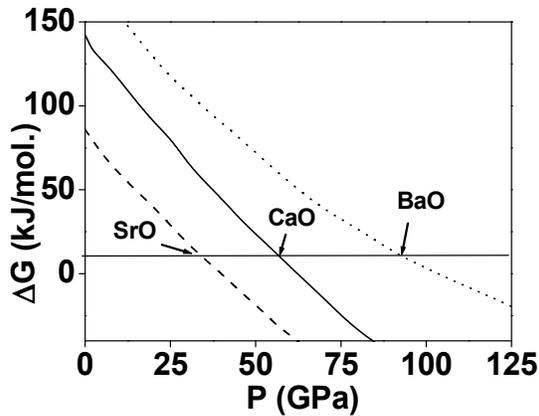


Figure 1. Variation of Gibbs free energy difference (ΔG) with pressure (P)

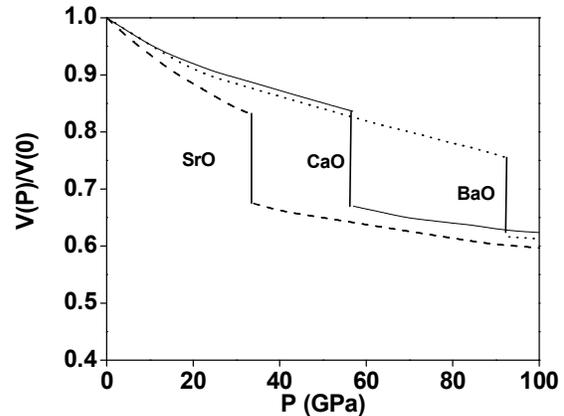


Figure 2. Variation of $V(P)/V(0)$ as a function of pressure for alkaline earth oxides compounds.

It is perhaps worth to remark that we have deduced the values free parameters modified ionic charge (Z_m), range (ρ) and hardness (b) from the knowledge of equilibrium distance and the bulk modulus following the equilibrium

conditions [30]. The input data along with their relevant references and the model parameters for MnO compounds are given in table 2.

In an attempt to reveal the structural phase transition of the test materials, we minimise the Gibbs's free energies $G_{B1}(r)$ and $G_{B2}(r')$ for the equilibrium interatomic spacing (r) and (r'). The Gibbs's free energy difference $\Delta G [= G_{B2}(r) - G_{B1}(r)]$ have been plotted as functions of pressure (P) in Fig. 1 by using the interionic potential discussed above. Let us summarize the results of the plots. The pressure corresponding to ΔG approaching to zero is the phase transition pressure (P_t) [indicated by arrows in figure]. At zero pressure, the $B1$ crystal phase is thermodynamically and mechanically stable, while the $B2$ is not. As pressure increases, beyond the phase transition pressure (P_t), the $B2$ system becomes mechanically and thermodynamically stable (its ΔG function value is negative than that of $B1$ crystal). Eventually, and at a pressure higher than the theoretical thermodynamic transition pressure, the $B1$ crystal becomes thermodynamically unstable while the $B2$ phase remains stable up to the greatest pressure studied (GPa). In alkaline earth oxides CaO, SrO and BaO a crystallographic transition from $B1$ to $B2$ occurs. These results may be successfully compared with those available reported data [13, 14, 16, 22-25] and are tabulated in Table 3.

Let us now estimate the values of relative volumes associated with various compressions following Murnaghan equation of state [32]

$$\frac{V}{V_0} = \left(1 + \frac{B'}{B_0} P\right)^{-1/B'} \quad (12)$$

V_0 being the cell volume at ambient conditions. The estimated value of pressure dependent radius for both structures, the curve of volume collapse with pressure to depict the phase diagram is illustrated in Fig. 2. It is noticed from the plot that our approach has predicted correctly the relative stability of competitive crystal structures, as the values of ΔG are positive. The magnitude of the discontinuity in volume at the transition pressure is obtained from the phase diagram and its value is tabulated in Table 3.

CONCLUSIONS

An effective interionic interaction potential is formulated in analyzing the structural as well as elastic properties in alkaline earth oxides CaO, SrO and BaO. The obtained values of free parameters allow us to predict phase transition pressure and associated volume collapse. The main result of the paper is the vast volume discontinuity in pressure volume phase diagram identifies the structural phase transition from NaCl to CsCl structure. From our calculated results it can be emphasized that the present approach reproduced the structural properties at high pressure consistently, in terms of the screening of the effective Coulomb potential through modified ionic charge (Z_m^2).

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