Structural and elastic properties of barium chalcogenides (BaX, X=O, Se, Te) under high pressure

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Abstract: In the present paper we have investigated the high-pressure, structural phase transition of Barium chalcogenides (BaO, BaSe and BaTe) using a three-body interaction potential (MTBIP) approach, modified by incorporating covalency effects. Phase transition pressures are associated with a sudden collapse in volume. The phase transition pressures and associated volume collapses obtained from TBIP show a reasonably good agreement with experimental data. Here, the transition pressure, NaCl-CsCl structure increases with decreasing cation-to-anion radii ratio. In addition, the elastic constants and their combinations with pressure are also reported. It is found that TBP incorporating a covalency effect may predict the phase transition pressure, the elastic constants and the pressure derivatives of other chalcogenides as well.


Keywords: structural phase transition • Gibbs free energy • volume collapse • phase transition pressure • three-body interaction

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1. Introduction

High-pressure research on structural phase transformations and the behavior of materials under compression, based on their calculations or measurements, have become quite interesting in recent years, as it provides insight into the nature of solid-state theories, and determines the values of fundamental parameters. An example can be found in the III-V semiconducting compounds, where the structural optical and electrical properties at high pressure have been extensively studied. The alkaline earth chalcogenides (AX: A=Be, Mg, Ca, Sr, Ba; X= O, S, Se, Te) form a very important closed-shell ionic system, crystallizing in an NaCl-type structure at room temperature and pressure, except for the MgTe and bergllium chalcogenides [1, 2]. These compounds are technologically important materials, having many applications ranging from catalysis to microelectronics. They also have applications in the area of luminescent devices [3]. Among these com-
pounds, barium chalcogenides (BaX, X= O, Se, Te) exhibit a structural phase transition, even with the application of moderate pressures of 85 GPa, 6 GPa, and 5 GPa respectively. These compounds share similar band structures and, in turn, have similar physical properties. In order to understand the band structure of these compounds and their rate of change with pressure, we examine barium chalcogenides under pressure from a theoretical point of view. Apart from this, these compounds exhibit interesting phenomena of metallization with the application of higher pressure. Metallization is due to band broadening with increasing pressure and subsequent overlap of the filled valence band (p-like valence band of the chalcogen atom) and the conduction band (d-like conduction band of the cation). Among these compounds, BaTe has the lowest band-overlap pressure as a result of its smaller bulk moduli and band gap. To understand some of the physical properties of these compounds, a detailed description of the electronic structure of these compounds is needed. Under normal conditions, these compounds crystallize in rock-salt structure and show a different phase at high pressure. The new phase often shows different physical and chemical properties. At elevated pressure these compounds undergo pressure-induced, structural phase transition from six-fold coordinated NaCl to a more closed eight-fold coordinated CsCl structure [4-6].

Recently, many efforts were made to interpret the experimental results by using a variety of theoretical models and Cohen mainly based on the two-body potential mainly. Froyen and Cohen [9] successfully studied phase-transition phenomena in some alkali chlorides using the pseudo-potential, total-energy (PTE) method with minor disagreements in results. They remarked that results could be improved by including the effect of non-rigidity of ions in the model. Sims et al. [5] have systematically studied the thermodynamics and mechanism of the B1-B2 transition in alkali halides and alkaline earth oxides. They found larger differences with measured values in transition pressures and activation energies. They concluded that possible reasons for disagreement include the failure of the two-body potential model.

Motivated by these results and the remarks of Sims et al. [5] and Froyen and Cohen [9] for incorporating the chargetransfer mechanism, we thought to incorporate the charge transfer through three-body interactions. It arises from the deformation of electron shells. This three-body potential model had been used earlier for the successful predictions of phase transitions and high-pressure elastic behaviour of ionic II-VI and III-V compound semiconductors [10] and divalent metal oxides [11].

We have studied phase-transition phenomena in ionic compounds using the three-body potential model (TBIP), which includes long range Coulombic, three-body interactions, and vander Waals and short-range overlap repulsive interactions. It is felt that this potential model is suitable for ionic solids but is insufficient to predict the phase transition properties of partially covalent compounds correctly. So, for partially covalent compounds, we need a potential model that also takes care of the covalent interaction. To fulfill this need, we have included the effect of covalency in the three-body potential along the lines of Motida [12] and applied it to study the phase transition and elastic properties of barium chalcogenides.

2. Potential model and method of calculations

Application of pressure directly results in compression, leading to increased charge transfer (or the three-body interaction effect [13]), due to the deformation of the overlapping electron shell of the adjacent ions (or non-rigidity of ions) in solids.

Also we have considered zero-point energy effects, which is the lowest possible energy that the compound may possess, and is the ground-state energy of the compound. The energy of the compound is \( \varepsilon = (h \nu)/\{e^{h\nu/kT} - 1\} + (h\nu/2) \), where \( \nu \), \( h \), \( t \), and \( k \) are the frequency, Planck constant, temperature and Boltzmann constant of the compound. It is clear from the above expression that even at absolute zero the energy of the compound cannot be zero but at least \( h\nu/2 \). This term shows a small effect in Gibbs free energy, but cannot be ignored completely. Hence there arises a need to include the zero-point energy term in TBIP for better agreement with experimental approaches. These effects have been incorporated in the Gibbs free energy (\( G = U + PV - TS \)) as a function of pressure and three-body interactions (TBIP) [5], which are the most dominant among the many-body interactions. Here, \( U \) is the internal energy of the system, equivalent to the lattice energy at temperature near zero, and \( S \) is the entropy. At temperature \( T = 0K \) and pressure \( P \), the Gibbs free energies for rock salt (B1, real) and CsCl (B2, hypothetical) structures are given by

\[
G_{B1}(r) = U_{B1}(r) + PV_{B1}(r),
\]

\[
G_{B2}(r') = U_{B2}(r') + PV_{B2}(r'),
\]

with \( V_{B1}(=2.00r^3) \) and \( V_{B2}(=1.54r^3) \) as unit cell volumes for \( B_1 \) and \( B_2 \) phases respectively. The first terms in (1)