Lattice instability, anharmonicity and Raman spectra of BaO under high pressure: A first principles study

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Abstract

Alkaline-earth metal oxides, in particular MgO and CaO dominate Earth’s lower mantle, therefore, exploring high pressure behavior of this class of compounds is of significant geophysical research interest. Among the alkaline-earth metal oxides, BaO exhibits rich polymorphism in the pressure range of 0-1.5 Mbar. Static enthalpy calculations revealed that BaO undergoes a pressure induced structural phase transition from NaCl-type (B1) → NiAs-type (B8) → distorted CsCl-type (d-B2) → CsCl-type (B2) at 5.1, 19.5, 120 GPa respectively. B1 → B8 & B8 → d-B2 transitions are found to be first order in nature whereas d-B2→ B2 is a second order or weak first order phase transition with displacive nature. Interestingly, d-B2 phase shows stability over a wide pressure range of ∼19.5-113 GPa. Mechanical and dynamical stabilities of ambient and high pressure phases are demonstrated through the computed second order elastic constants and phonon dispersion curves, respectively. Under high pressure, significant phonon softening and soft phonon mode along M-direction are observed for B8, d-B2 and B2 phases, respectively. Pressure dependent Raman spectra suggests a phase transition from d-B2 to Raman inactive phase under high pressure. Overall, the present study provides a comprehensive understanding of lattice dynamics and underlying mechanisms behind pressure induced structural phase transitions in BaO.

Keywords:- High pressure, Phase transitions, Elastic constants, Lattice dynamics, Phonon softening, Lattice instability, Anharmonicity, Earth’s interior

Introduction

Alkaline-earth metal oxides, MO (M = Mg, Ca, Sr, Ba) have gained a considerable attention due to their technological applications in diverse fields ranging from catalysis to electrode coating and interfaces. These metal oxides are suitable candidates for CO$_2$ sorbent applications due to their high absorption capacity at moderate temperatures. Moreover, these mono-oxides are prime candidates for the Earth’s interior, especially light metal oxides
such as MgO and CaO are abundant in the Earth’s lower mantle, in which the pressure varies from 24 to 136 GPa from top of the upper mantle to the lower mantle. Therefore, exploring high pressure and/or temperature behavior of these metal oxides provides an insight on the deep interior of the Earth. These metal oxides crystallize in the rocksalt NaCl-type (B1) structure with space group $Fm\overline{3}m$ at ambient conditions. Upon compression, these metal oxides usually undergo a body centred cubic CsCl-type (B2) structure and it is well established for MgO, CaO and SrO. Amongst all these compounds, BaO has interesting structural properties and it exhibits a rich polymorphism in the pressure range of 0-1.5 Mbar over the remaining alkaline earth oxides, CaO, SrO. Therefore, understanding the high pressure structural and lattice dynamical behavior of BaO is crucial as this can be a possible candidate of the Earth’s mantle. Several high pressure X-ray diffraction (HP-XRD) measurements and theoretical studies using first principles calculations were focused on exploring the structural phase transitions, metallization, elastic properties, thermodynamic stability of MO (M = Mg, Ca, Sr, Ba) compounds under high pressure. Similarly, efforts have been put forward by the researchers to explore the phase diagram of BaO under high pressure from both experimental and theoretical perspective. A HP-XRD study revealed that BaO undergoes a structural transition from B1 to distorted B2 (d-B2) at 9.2 GPa and remains in the same structure till 29 GPa. Energy dispersive X-ray diffraction study disclosed that BaO transforms from B1 to an intermediate hexagonal NiAs-type (B8) structure at around 10 GPa, later to a tetragonal PH$_4$I-type (d-B2) structure with pseudo 8-fold coordination at around 15 GPa and this phase approaches to B2 structure with increasing pressure above 1 Mbar. First principles studies reported that BaO transforms from B1 to B8 phase at 11.3 GPa, 5 GPa, 4.3 GPa then to d-B2 from B8 at 21.5 GPa, 13 GPa, 23.2 GPa upon further compression, the d-B2 phase transforms to B2 phase at 62 GPa, 50 GPa, 108 GPa. Pandey et al and Jog et al suggested a direct B1 to B2 phase transition at 100 and 86 GPa, respectively without any intermediate high pressure phases.
On the other hand, lattice dynamics of B1 phase is well studied at ambient as well as at high pressure using first principles calculations\textsuperscript{16,51,56,57} and inelastic neutron scattering technique.\textsuperscript{58} However, very limited studies\textsuperscript{52} are available exploring lattice dynamics of high pressure phases, underlying mechanisms behind the observed structural phase transitions and spectroscopic properties under high pressure in BaO. Therefore, in the present study, we have systematically investigated the structural phase transitions, lattice dynamics of different polymorphs and Raman spectra of B8 and d-B2 phases of BaO under high pressure.

**Computational details**

All the first principles calculations were carried out using projected augmented wave (PAW) method as implemented in Vienna ab-initio simulation package (VASP).\textsuperscript{59} Electron-electron interactions are treated within generalized gradient approximation (GGA) with Perdew–Burke-Ernzerhof (PBE) functional while PAW pseudopotentials are used to capture the electron-ion interactions. The plane wave basis orbitals 5s\textsuperscript{2}5p\textsuperscript{6}6s\textsuperscript{2} for Ba (Ba\textsubscript{sv,GW}) and 2s\textsuperscript{2}2p\textsuperscript{4} for O (O\textsubscript{GW}) are used as valence electrons. Plane wave cutoff energy and k-spacing are tested against the total energy to ensure the convergence. The plane wave cutoff energy was set to 600 eV and a k-spacing of 2\pi \times 0.024 \text{\AA}\textsuperscript{-1} with \Gamma\textsuperscript{-}centered Monkhorst-Pack scheme to compute structural and mechanical properties at ambient as well as at high pressure. To compute phonon dispersion curves, forces are calculated using finite displacement method for ambient and high pressure phases and then force constants are extracted and then post-processed by using phonopy package.\textsuperscript{60} Pressure dependent Raman spectra is calculated using norm conserving pseudo potentials within linear response approach as implemented in CASTEP package.\textsuperscript{61} Crystal structures are visualized and analyzed using the VESTA software.\textsuperscript{62} To include anharmonic effects, we also have calculated the finite temperature lattice dynamics for B2 phase of BaO using ab-initio molecular dynamics (AIMD) simulations and then post-processed using temperature dependent effective potential method (TDEP).\textsuperscript{63}
Results and Discussion

Crystal structure and pressure-induced structural phase transitions

As shown in Figure 1a, BaO crystallizes in the face centred cubic (SG: \(Fm\bar{3}m\)) rocksalt NaCl-type (B1) structure with 6-fold coordination and having \(Z = 4\) formula units (f.u.) per unit cell at ambient conditions.\(^{31}\) High pressure X-ray diffraction measurements\(^{30,31,64}\) revealed that BaO exhibits rich polymorphism under high pressure. BaO undergoes to a high pressure NiAs-type (B8) structure (SG: \(P6_3/mmc\)) from B1 phase at 9.2 GPa without changing the coordination number (CN) by having \(Z = 2\) f.u. per primitive cell. The crystal structure of B8 phase is an hexagonal analog of the B1 structure. Later, the B8 phase transforms to PH\(_4\)-type distorted CsCl-type (d-B2) at 14.0 GPa\(^{30}\) 18 GPa\(^{30}\) with pseudo 8-fold coordination (SG: \(P4/nmm\)) with \(Z = 2\) f.u. per primitive cell, and then to a 8-fold coordinated CsCl-type (B2) structure (SG: \(Pm\bar{3}m\)) with \(Z = 1\) f.u. per primitive cell upon further compression \(i.e.,\) above 1 Mbar pressure (see Figure 1 and Table I).\(^{30,31,64}\) The crystal structure of d-B2 phase is analogous to PbO-type structure without a lone-pair at Ba atom having two in-equivalent bond lengths as shown in Figure 1c. To get further insights on the observed structural phase transitions and their sequence, as a first step, we have tested with various DFT functionals such as LDA, PBE, PW91 and SCAN to reproduce the B1 to B8 transition pressure (see Figure S1). The transition pressure obtained using PBE, PW91 and SCAN functionals are consistent with each other while LDA poorly describe the phase stability between B1 and B8 phases. Later, we carried out static enthalpy calculations with PBE functional for the polymorphic phases of BaO and plotted enthalpy difference with respect to B2 phase as a function of pressure as shown in Figure 2a. The obtained phase transition sequence is B1 \(\rightarrow\) B8 \(\rightarrow\) d-B2 \(\rightarrow\) B2 and the corresponding transition pressures 5.1, 19.5, 120 GPa are in good agreement with the HP-XRD measurements\(^{30,31}\) as well as with previous first principles calculations\(^{52,53}\). Moreover, TII-type (B33) phase is found to be meta-stable for CaO\(^{65}\) and we also have included this B33 phase in the phase diagram.
of BaO to verify it’s relative phase stability w.r.t high pressure phases of BaO and then we found that the B33 phase is also meta-stable for BaO over the maximum studied pressure range (see Figure 2a). As presented in Figure 2b, the enthalpy difference between d-B2 and B2 phases is continuously decreasing with increasing pressure and they become iso-enthalpic at around 120 GPa. As shown in Figure 2c, the calculated lattice constants for the ambient and high pressure phases are monotonically decreasing with pressure. The lattice constant 'c' of d-B2 phase becomes lattice constant 'a' for B2 phase (c_{d-B2} = a_{B2}). The detailed transition mechanism for d-B2 to B2 transition is explained through elastic constants in the following section. As shown in Figure 2d, the calculated volume decreases monotonically with pressure. We observe a volume collapse during the phase transition from B1 → B8 is ∼ 3.65 % at 5.1 GPa and it is ∼ 6.4 % at 19.5 GPa for the transition B8 → d-B2. The obtained volume reduction is consistent with high pressure X-diffraction measurements and previous first principles calculations as presented in Table 2. This clearly demonstrates that B1 to B8 & B8 to d-B2 transitions are first order in nature, while d-B2 to B2 transition is a second order or weak first order in nature due to continuous change in volume during the phase transition (see Figure 2d). We then calculated the equilibrium bulk modulus (B₀) and its pressure derivative (B₀') by fitting the obtained pressure-volume (P-V) data to 3rd order Birch-Murnaghan equation of state. B₀ measures the ability of a material to resist changes in volume under hydrostatic expansion or compression. The calculated B₀ value is found to be 71.4 GPa for the ambient B1 phase, which is in good agreement with previous first principles calculations. The obtained relatively low B₀ values 68.8 GPa for B8 and 51.8 for d-B2 intermediate phases suggest the soft nature of these phases over ambient B1 (71.4 GPa) and a high B₀ value 92.4 GPa for high pressure B2 phase disclose that B2 phase is harder than B1 phase (see Table 3).

In addition, the calculated in-equivalent bond lengths are plotted as a function of pressure and the same are presented in Figure 2e. The in-equivalent bond lengths of d-B2 phase are found to converge to became a single bond length for B2 phase above 120 GPa. In addition,
in the d-B2 phase, the Ba atoms are located at (0.5, 0.0, 0.5+Δ) and (0.0, 0.5, 0.5-Δ), where
Δ is the atomic position parameter, Δ in combination axial ratio (c/a) provides a useful
information on d-B2 → B2 transition. If Δ = 0 & c/a = 1/√2 = 0.7071, then the structure
is of undistorted B2 phase.31 To confirm this, we have calculated c/a ratio and Δ as a function
of pressure for d-B2 phase. As shown in Figure 2f, both c/a ratio and Δ are decreasing with
pressure and then approaches to Δ = 0 & c/a = 0.7071 around 120 GPa. The continuous
volume change at the transition pressure, variation in the fractional coordinate of Ba atom
along c-direction (see Figure S2), c/a = 0.7071 and Δ = 0 values clearly demonstrate that
d-B2 to B2 transition to be a displacive transition under pressure. Displacive nature of z_{Ba}
with pressure suggests phonon softening in d-B2 phase as function of pressure. Further to
explore the microscopic origin of the continuous phase transition in BaO, pressure dependent
elastic constants, lattice dynamics and Raman spectra are calculated and analyzed them in
detail in the following sections.

**Elastic constants under high pressure**

To get deeper insight on the structural phase transition(s) and verify mechanical stability of
the BaO polymorphs, we have calculated second order elastic constants (C_{ij}) as a function of
pressure for all the four B1, B8, d-B2 and B2 phases. The cubic (Fm\bar{3}m, Pm\bar{3}m), hexagonal
(P6\bar{3}/mmc) and tetragonal (P4/nmm) crystal symmetries possess 3, 5 and 6 independent
elastic constants.

When a finite hydrostatic pressure is applied to a crystal system, the Born stability cri-
teria\(^{68}\) at ambient conditions must be revised with modified elastic constants at a given
hydrostatic pressure conditions. According to Sinko and Smirnov the modified elastic con-
stants at a given pressure (P) are \(\widetilde{C}_{ii} = C_{ii} - P\), (for \(i = 1-6\)) and \(\widetilde{C}_{1j} = C_{1j} + P\) (for \(j = 2-3\))
for cubic and hexagonal/tetragonal systems. Therefore, the modified Born stability criteria
under hydrostatic pressure for cubic (equation 1) and hexagonal/tetragonal (equation 2) are
given as follows:

\[ C_{11} - C_{12} - 2P > 0, \quad C_{11} + 2C_{12} + P > 0, \quad C_{44} - P > 0 \]  

(1)

\[ C_{11} - C_{12} - 2P > 0, \]

\[ P^2 + P(C_{11} + C_{12} + 4C_{13}) + 2C_{13}^2 - C_{33}(C_{11} + C_{12}) > 0, \]  

(2)

\[ C_{44} - P > 0, \quad C_{66} - P > 0 \]

The calculated pressure dependent \( C_{ij} \) for B1, B8, d-B2 and B2 phases satisfy the necessary and sufficient conditions for the revised Born stability criteria under hydrostatic pressure indicating that the polymorphs are mechanically stable at the corresponding pressures. We shed more light on understanding lattice transformation from d-B2 to B2 phase through the computed pressure dependent elastic constants of d-B2 and B2 phases. The relationships between lattice constants of d-B2 and B2 phases at the phase transition are given as follows:

(a=b)\(d-B_2 = \sqrt{2}c_{d-B_2}\) and \(c_{d-B_2} = a_{B_2}\) (see Figure 3a), thus, results in merging of the following elastic constants of d-B2 to B2 phase under pressure are as depicted in Figure 3 as given below: \(C_{d-B_2}^{33} \rightarrow C_{B_2}^{11}, C_{d-B_2}^{44} \rightarrow C_{B_2}^{44}\) and \(C_{d-B_2}^{13} \rightarrow C_{B_2}^{12}\), which corroborates with pressure dependent structural and bond parameters at the d-B2 \( \rightarrow B_2 \) transition.

**Lattice dynamics and Raman spectra under high pressure**

To compliment the structural stability obtained from total energy calculations and verify dynamical stability of the ambient and high pressure phases of BaO, we calculated phonon dispersion curves including LO-TO splitting at 0 and 9 GPa for B1 phase (see Figure 4a & b) at 9 GPa and 20 GPa for B8 phase (see Figure 4c & d), at 30, 60, 90 and 120 GPa for d-B2 phase (see Figure 5) and finally at 100, 110, 120 and 140 GPa for B2 phase (see Figure 6). As shown in Figure 4a & b, B1 and B8 phases are dynamically stable at 0, 9 GPa and 9, 20 GPa
respectively. The phonon dispersion curves of B1 phase show large LO-TO splitting ($\sim 312.3$ cm$^{-1}$) along $\Gamma$-direction with two degenerate TO and one LO modes and this large LO-TO splitting causes a fall of low lying optical (LLO) phonon modes into acoustic mode region, which can increase overlap between acoustic and LLO phonon modes there by enhancing the scattering phase space and eventually this leads to lower the lattice thermal conductivity in B1 phase at ambient conditions. However, the LO-TO splitting decreases under pressure (see Figure 4a & b) for B1 phase. Moreover, the optical phonon modes are hardening with pressure while phonon softening is observed for acoustic phonon modes along X-direction in B1 phase and along M and K-$\Gamma$ directions in B8 phase. Phonon softening is observed along X-direction for B1 phase previously, which actually drives the transition from B1 $\rightarrow$ B8 phase in BaO under pressure. In addition, the B1 and B8 phases are dynamically stable above the transition pressures, which are in consistent with the first order nature of the structural phase transitions, B1 $\rightarrow$ B8 & B8 $\rightarrow$ d-B2. The d-B2 phase is found to be dynamically stable over a wide pressure range of $\sim 20$-120 GPa (see Figure 5) for BaO in contrast to the light alkaline-earth metal oxides, MgO, CaO and SrO. The calculated phonon dispersion curves show a significant phonon softening at 120 GPa along Z-$\Gamma$ and ‘A’ high symmetry directions as depicted in Figure 5d. On the other hand, the calculated phonon dispersion curves for B2 phase at 100 and 110 GPa show soft phonon mode along M high symmetry point, which clearly indicates that B2 is unstable below 110 GPa pressure. In addition, we could also observe a significant phonon softening of TO and LO modes of B2 phase at 140 GPa (see Figure 6d) compared to 120 GPa (see Figure 6b), which indicates that B2 phase becomes dynamically unstable and it may undergo a structural phase transition upon further compression above 150 GPa.

The cubic ambient B1 and high pressure B2 phases of BaO are Raman inactive, and they have only one IR active ($T_{1u}$) mode. However, the intermediate high pressure B8 and d-B2 phases are Raman active, and are thoroughly analyzed (see Figure 7). This result is in very good agreement with the Raman spectroscopic measurements, which show that BaO
is Raman inactive until 10 GPa (B1 phase) and above 11 GPa it becomes Raman active (B8), where one Raman active $E_{2g}$ mode is observed and this Raman mode shows blue-shift with increasing pressure. Later, significant changes are observed in the Raman spectra at around 14 GPa and it indicates a transition from B8 to d-B2 phase. The similar trends are observed in the present work with deviations in the transition pressures which might be due to Raman measurements were carried out at 300 K, while the calculations are performed at 0 K. Since, B8 and d-B2 phases crystallize in $P6_3/mmc$ and $P4/nnm$ space groups, respectively and they consist of four atoms per primitive cell, the symmetry decomposition of group theory predicts 12 vibrational modes along $\Gamma$ for both of these phases, which are given as follows:

$$\Gamma_{B8}^{12} = 2E_{2g} \oplus B_{2g} \oplus 4E_{1u} \oplus 2E_{2u} \oplus 2A_{2u} \oplus B_{1u}$$

Among the 12 vibrational modes of B8 phase, only $E_{2g}$ is Raman active mode which is consistent with high pressure Raman measurements, \cite{70} $E_{1u}$, $E_{2u}$, $A_{2u}$ and $B_{1u}$ are IR active modes but $B_{2g}$ is neither Raman nor IR active (silent) mode; where $E_{1u}$, $E_{2u}$ and $E_{2g}$ are doubly degenerate modes. Variation of $E_{2g}$ mode as a function of pressure is shown in Figure 7a, which is mainly due to in-plane vibrational motion of Ba atom and its intensity decreases with pressure.

$$\Gamma_{d-B2}^{12} = 4E_g \oplus B_{2g} \oplus A_{1g} \oplus 4E_u \oplus 2A_{2u}$$

On the other hand, for Litharge PbO-type d-B2 phase, the zone-center Raman active modes $B_{2g}$, $A_{1g}$ and $E_g$ are polarized along c- and a/b-axis, respectively. $E_u$ and $A_{2u}$ are IR active modes; where $E_u$ and $E_g$ modes are doubly degenerate. Pressure dependence of vibrational frequency modes are presented in Figure 7d. For each vibrational mode, frequency increases with pressure except for $A_{1g}$ mode. When the pressure is applied, the interatomic distance becomes smaller and hence interaction between neighboring atoms becomes stronger. Therefore, usually, the vibrational modes increase with pressure as shown in Figure 7b & d except for $A_{1g}$ mode. As $E_g$ mode is in plane vibrational mode, the vibrational fre-
frequency/wavenumber increases as the interaction of atoms becomes stronger. As shown in Figure 2; c/a ratio decreases with increasing pressure. Due to the out-of-plane vibrations of heavier Ba atoms in A1g mode (Figure 7c), the decrease in the wavenumber of Raman-shift is observed with pressure. The red-shift of the A1g mode with pressure shows a negative pressure coefficient and it might be responsible for introducing dynamical instability at higher pressure in the d-B2 phase. In contrast, this mode was tentatively assigned as Eg mode due to in-plane vibration of Ba atoms in the HP-Raman study. However, we thoroughly analyzed and assigned it as A1g mode rather than Eg mode, which actually shows phonon softening with pressure which is associated with displacive nature of Ba atoms along c-axis. The Intensity of four Raman active modes (Eg, B2g and A1g) are gradually diminishing with pressure (Figure 7b) for d-B2 phase, this strongly suggests that high pressure phase might be Raman inactive. Finally, the high pressure B2 phase can be stabilized above 113 GPa (see Figure 7d) which is consistent with the observations from the HP-XRD measurements.

As shown in Figure S3 & 6, the calculated room temperature phonon dispersion curves in combination with AIMD and TDEP disclose that B2 phase is dynamically unstable at 80 GPa and 300 K whereas it becomes dynamically stable at 100 GPa and 300 K, while harmonic lattice dynamical calculations show that B2 phase is dynamically unstable below ~ 113 GPa. This clearly shows the importance of anharmonicity to determine the stability of B2 phase above 85 GPa and this is in good accord with the HP-XRD diffraction measurements.

Conclusions

To summarize, we have systematically investigated the polymorphism of BaO under hydrostatic compression using first principles calculations based on density functional theory. We found that BaO undergoes series of pressure-induced structural phase transitions from B1 → B8 → d-B2 → B2 and the corresponding transition pressures are 5.1 , 19.5, 120 GPa respectively. The obtained structural phase transition sequence and transition pressures are
consistent with HP-XRD measurements and previous first principles calculations. TII-type (B33) phase is found to be metastable for BaO over the studied pressure range. The d-B2 phase exhibits stability over a wide pressure range \( \sim 19.5-113 \text{ GPa} \) in contrast to light alkaline-earth metal oxides. The transitions from B1 \( \rightarrow \) B8 and B8 \( \rightarrow \) d-B2 are first order in nature with a volume collapse of \( \sim 3.65 \) and 6.4 \%, respectively while d-B2 \( \rightarrow \) B2 is a second order or weak first order phase transition with displacive nature. Mechanical stability has been established for ambient and high pressure phases of BaO through computed elastic constants. The pressure dependent elastic constants provide an insight on lattice transformation from d-B2 to B2 phase. The calculated phonon dispersion curves indicate the dynamical stability of BaO polymorphs and a significant phonon softening is observed for B8 and d-B2 phases at high pressures and also a soft phonon mode (along M-direction) in B2 phase explained its dynamical instability below 110 GPa. Finally, gradual diminishing of Raman active modes of d-B2 phase under pressure suggests that high pressure phase could be a Raman inactive. Overall, the present study provides an in depth understanding of structural phase transitions in BaO under high pressure and further exploration of high pressure behavior of light alkaline-earth oxides (MgO, CaO and SrO) have important implications on composition of the Earth’s lower mantle.

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Figure 1: Crystal structure of (a) ambient rocksalt NaCl-type (B1) and high pressure (b) NiAs-type (B8), (c) PH₄-type distorted CsCl-type (d-B2) and (d) CsCl-type (B2) phases of BaO. Where SG and CN denote space group and coordination number, respectively. Green and red color balls represent Ba and O atoms, respectively.
Figure 2: Calculated (a,b) relative enthalpy difference of B1, B8, B33, d-B2 phases w.r.t B2 phase, (c) lattice constants, (d) volume, (e) bond lengths for B1, B8, DB2 and B2 phases as a function of pressure and (f) variation of c/a ratio and ∆ with pressure for d-B2 phase.
Figure 3: (a) Lattice transformation from d-B2 to B2 and (b) calculated elastic constants of d-B2 and B2 phases of BaO as a function of pressure.
Figure 4: Calculated phonon dispersion curves of (a, b) B1 phase at (a) 0, (b) 9 GPa and for (c, d) B8 phase at (c) 9 GPa, (d) 20 GPa. Phonon softening is observed along X-direction for B1 phase and for B8 phase at high pressure (20 GPa) along M and K-Γ directions, which destabilize the B1 and B8 phases upon further compression.
Figure 5: Calculated phonon dispersion curves for d-B2 phase at (a) 30, (b) 60, (c) 90 and (d) 120 GPa. Optical phonon softening along Z-Γ direction and acoustic phonon softening along A-direction are observed with pressure and it is predominant above 90 GPa.
Figure 6: Calculated phonon dispersion curves for B2 phase at high pressures (a) 100 GPa, (b) 110 GPa (c) 120 GPa and (d) 140 GPa at 0K as well as at 300 K. B2 phase is dynamically stable including anharmonic effects at 100 and 110 GPa at 300 K but it is dynamically unstable within the harmonic approximation at 0 K.
Figure 7: Calculated Raman spectra of (a) B8 and (b) d-B2 phase as a function of pressure. Eigen vectors of Raman active modes are presented for (a) B8 and (c) d-B2 phases of BaO. Pressure evolution of (d) Raman and IR active modes of d-B2 phase and (e) Transverse acoustic mode of B2 phase along M-high symmetry direction without and with inclusion of anharmonic effects.
Table 1: Calculated equilibrium lattice constants (a, c in Å) of BaO at ambient and high pressure and are compared with the available X-ray diffraction data and other first principles calculations.

| Phase | Pressure | This work | Expt. | Others |
|-------|----------|-----------|-------|--------|
| B1    | 0        | a=5.533   | 5.520
g        | 5.562
d, 5.454
e, 5.614
c, 6.349
d, 5.552
e, 5.462|
| B8    | 13.9     | a= 3.612,c= 6.365 | 3.617,c= 6.349
g    | -|
| d-B2  | 60.5     | a= 4.187,c= 3.007 | 4.1,c= 2.998
g    | -|
| B2    | 130      | a=2.8     |       | -      |

*aRef.71 bRef.72 cRef.51 dRef.62 eRef.47 fRef.19 gRef.31

Table 2: Calculated phase transition pressure (P_t, in GPa) and volume collapse (VC in %) of BaO and are compared with the available experimental data and other first principles calculations.

| Parameter | Transition | This Work | Expt. | Others |
|-----------|------------|-----------|-------|--------|
| P_t       | B1 → B8   | 5.1       | 9.2
d, 10
c | 5 e,4.3
d, 5.5 |
|           | B8 → d-B2 | 19.5      | 18
d, 18.8
e | 13 c,23.2
d |
| VC        | B1 → B8   | 3.65      |       | 3.6
d, 1.5
c |
|           | B8 → d-B2 | 6.4       | 7
d | 8.7
c |

*a Ref.30 bRef.31 cRef.17 dRef.54 eRef.53 fRef.52

Table 3: Calculated equilibrium bulk modulus (B_0) and its pressure derivative (B_0') of ambient and high pressure phases of BaO and are compared with the available experimental data and previous first principles calculations.

| Phase | Pressure range | B_0 (B_0') | Expt. | Others |
|-------|----------------|-------------|-------|--------|
| B1    | 0-9            | 71.4 (4.35) | 69
d, 66.2
e, 61
c | 68.912
d (4.09
d), 73
c (4.3
c), 71.22
d (4.52
d), 75.7
c |
|       |                |             | 74.1
d, 74.06
e (5.07
c) | 62.75
d, 71.72
e, 73
c |
| B8    | 6-30           | 68.6(4.32)  |       | 68.04
d (4.19
d), 72.7
c |
| d-B2  | 20-120         | 51.3 (4.67) | 33.2
d (6.02
e), 27.13
d | 74.69
d (4.07
d), 72.57
d (3.7
d), 86
d, 59.1
d |
| B2    | 70-150         | 90.6 (4.15) |       |       |

*a Ref.30 bRef.21 cRef.22 dRef.19 eRef.47 fRef.53 gRef.54 hRef.74 iRef.75 kRef.76
Supporting Information

Lattice instability, anharmonicity and Raman spectra of BaO under high pressure: A first principles study

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Figure S1: Calculated relative enthalpy difference of B8 phase w.r.t B1 phase for BaO using various functionals such as LDA, PBE, PW91 and SCAN.
Figure S2: Displacive nature of $z_{Ba}$ as a function of pressure for d-B2 phase in the pressure range of 20-120 GPa.
Figure S3: Calculated phonon dispersion curves of B2 phase at 80 GPa and 300 K using ab-initio molecular dynamics (AIMD) and temperature dependent effective potential (TDEP).