

Ab initio Calculations of Electronic and Mechanical Properties of Orthorhombic Phase of BaF₂

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Electronic and mechanical properties of orthorhombic phase of BaF₂ have been calculated using *ab initio* methods. We have applied density-functional theory within generalized gradient approximation (GGA) using plane-wave pseudopotentials method and a plane-wave basis set. Our calculated lattice parameter a is 6.69 Å comparable to experimental value of 6.16 Å while the ratio of b/a in this work is 1.16 and experimental value is 1.28. Band gap is here calculated at 9 eV which is in good agreement with the experimental value. The bulk modulus derived from the elastic constant calculations of orthorhombic phase of BaF₂ is 94.5 GPa while bulk modulus from the Murnaghan methods is 108.8 GPa. The stability values in crystallographic directions are given as A_1 is 1.13, A_2 is 0.54 and A_3 is 0.86 showing that this phase is metastable.

1. Introduction

Fluorides have simple ionic structure and exhibit interesting properties with wide range of applications. CaF₂ and BaF₂ as examples of fluorides, are strongly ionic with wide band gap and are used in precision vacuum ultraviolet lithography [1]. BaF₂ is one of the fastest scintillators and is also an ideal high-density luminescent material for applications in gamma ray and elementary particle detectors [2]. In its scintillation property, BaF₂ has a fast core-valence-band transition (cross-luminescence) that represents radiative transition of electrons from valence band, which are originally from the $2p$ states of F⁻ into the upper core band of the crystal formed by the $5p$ states of Ba²⁺.

Although various experimental techniques are available for measuring electronic structure and mechanical properties of materials such as ultrasonic wave propagation, neutron scattering and Brillouin scattering, difficulties in preparing suitable specimens for many materials as well as the need to obtain accurate results fast and cheaply make theoretical calculation unavoidable. Theoretical methods are also used in temperatures that are not practical to work in or to validate the data obtained experimentally.

BaF₂ just as other alkaline earth fluorides undergo a series of pressure-induced phase transitions

to highly coordinated AX₂ structures. At ambient conditions, BaF₂ crystallizes in the cubic fluorite structure ($Fm\bar{3}m, Z = 4$) with three atoms in the primitive face-centered cubic unit cell and twelve atoms in the conventional simple-cubic cell, with cations at (0,0,0), (0,1/2,1/2), (1/2,0,1/2), and (1/2,1/2,0), and anions at $(\pm\frac{1}{4}, \pm\frac{1}{4}, \pm\frac{1}{4})$, in units of the lattice parameter.

BaF₂ undergoes phase transition to the orthorhombic cotunnite-type structure (Pnam, $Z=4$) at about 5 GPa and then to a hexagonal phase at pressures of between 10 to 15 GPa [3,4]. The orthorhombic phase has twelve atoms in the unit cell; four barium atoms and eight fluorine atoms. Our optimized values for the lattice constants a , b and c for the orthorhombic phase are 6.69 Å, 7.75 Å and 4.00 Å, respectively. The corresponding experimental values are 6.16 Å, 7.85 Å and 3.98 Å, respectively. Experimental calculations show that orthorhombic and hexagonal phases of BaF₂ are metastable at zero pressure [3] and each of these phases has a different application in industry.

While the electronic and mechanical properties of cubic phase of BaF₂ have been studied extensively [1], those of low symmetry phases such as tetragonal and hexagonal systems have received little attention. Furthermore, calculation of mechanical properties such as elastic constants of these low symmetry phases require more computations and accurate methods for determining total energies.

Elastic constants are necessary in the calculation

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of other mechanical properties such as anisotropy and bulk modulus. Reduced symmetry increases the number of independent elastic constants, creating large numbers of distortion matrices necessary for calculating these constants. In particular, the cubic phase has only three independent elastic constants; C_{11} , C_{12} and C_{44} while orthorhombic crystals have nine constants which are C_{11} , C_{22} , C_{33} , C_{44} , C_{55} , C_{66} , C_{12} , C_{13} and C_{23} .

In Ref. [1], properties of cubic phase of BaF_2 are extensively studied including the elastic constants, phonon and volume-pressure relations. Ref. [5] reported on the structural, electronic and optical properties of BaF_2 in the cubic, orthorhombic and hexagonal phases. Recently, the variation of the independent elastic constants C_{11} , C_{12} and C_{44} as a function of pressure has been reported [6]. Elastic constants for the cubic, orthorhombic and hexagonal phases of CaF_2 have also been reported [7]. To the best of our knowledge, the mechanical properties including elastic constants of the orthorhombic phase of BaF_2 have not been investigated. In this paper, we study the electronic and mechanical properties of orthorhombic phase of BaF_2 using plane wave pseudopotentials (PW-PP) calculations. Our results are compared with theoretical and available experimental data. The rest of this paper is organized in this order: methodology is in Sec. 2, theory is in Sec. 3, Sec. 4 discusses results while conclusions are in Sec. 5.

2. Methodology

All calculations have been performed in the framework of density functional theory by employing, for the exchange-correlation functional, the generalized gradient approximation of Perdew-Burke-Ernzerhof [8]. Pseudopotentials were taken from the Quantum-Espresso database [9]. For Ba, the pseudopotentials includes the semi-core states 5s and 5p in the valence. The total energy convergence in the iterative solution of the Kohn-Sham equations [10] was set at 2×10^{-8} Ry.

In structural optimization, we used the procedure in Jiang et al. [11] and Schmalz's work [1] and all the calculations were done at ground state conditions. Elastic constants were calculated as the second derivatives of the internal energy with respect to strain tensor (ϵ) [12]. During structural optimization, the enthalpy was minimized by varying the length of the lattice vectors, while the angles between the lattice vectors and the atomic positions in the unit cell were fixed. The applied strains were isochoric (volume-conserving), which

had several important consequences. First was the conservation of the identity of the calculated elastic constants with the strain-stress coefficients, which were appropriate for the calculation of elastic wave velocities but was not important for finite pressure. Secondly, the total energy depends on the volume much more strongly than the strain and by choosing volume conserving strains we avoided the separation of these two contributions to the total energy. Lastly, the change in the basis set associated with the applied strain was minimized and hence reducing computational errors [1].

Nine elastic constants for orthorhombic phase of BaF_2 were calculated as mentioned before. Small distortions, δ , of between -0.02 to 0.02 at the intervals of 0.002 giving a total of twenty one distortions were considered in all the three phases. Each strain was parametrized by a single variable δ , and the total energy was calculated for each distortion. The calculated total energies were fitted to a polynomial in δ and then equated to the appropriate elastic constant coefficient expression given for each matrix (Table 1).

3. Theory

3.1. Elastic constants

The face centered orthorhombic phase of BaF_2 has three lattice parameters $\vec{a}$, $\vec{b}$ and $\vec{c}$. A kinetic energy cut-off of 30 Ry and a k-point grid of $2 \times 4 \times 2$ was used in all the calculations reported here. Bravais lattice vector of the orthorhombic phase have a matrix of the form

$$\mathbf{R} = \frac{1}{2} \begin{pmatrix} 0 & 1 & c/b \\ a/b & 0 & c/b \\ a/b & 1 & 0 \end{pmatrix}. \quad (1)$$

expressed in terms of the unit vector $\mathbf{b}$. $\mathbf{R}$ can be strained according to the relation $\mathbf{R}' = \mathbf{R}\mathbf{D}$ where $\mathbf{R}'$ is the deformed matrix with distorted lattice vectors and $\mathbf{D}$ is the symmetric distortion matrix, which contains the strain components. Since we have nine independent elastic constants, we need nine different strains to determine them. The nine distortion matrices used in the present calculations are described in the distortion matrices D_1 to D_9 given in Table 1 with corresponding change in energy to volume ratio. The nature of distortions that these matrices create have been described by Ravindran et al. [5] and are given in Table 1.

TABLE I: Distortion matrices for the elastic constants for the orthorhombic phase of BaF₂ for the nine elastic constants; C₁₁, C₂₂, C₃₃, C₄₄, C₅₅, C₆₆, C₁₂, C₁₃ and C₂₃ with corresponding strain energy per unit volume.

Distortion Constant	Distortion matrix	Ratio of energy change to volume
D_1	$\begin{pmatrix} 1+\delta & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	$\frac{\Delta E}{V} = (\tau_1 \delta + \frac{C_{11}}{2} \delta^2)$
D_2	$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1+\delta & 0 \\ 0 & 0 & 1 \end{pmatrix}$	$\frac{\Delta E}{V} = (\tau_2 \delta + \frac{C_{22}}{2} \delta^2)$
D_3	$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1+\delta \end{pmatrix}$	$\frac{\Delta E}{V} = (\tau_3 \delta + \frac{C_{33}}{2} \delta^2)$
D_4	$\begin{pmatrix} \frac{1}{(1-\delta^2)^{1/3}} & 0 & 0 \\ 0 & \frac{1}{(1-\delta^2)^{1/3}} & \frac{\delta}{(1-\delta^2)^{1/3}} \\ 0 & \frac{\delta}{(1-\delta^2)^{1/3}} & \frac{1}{(1-\delta^2)^{1/3}} \end{pmatrix}$	$\frac{\Delta E}{V} = 2(\tau_4 \delta + C_{44} \delta^2)$
D_5	$\begin{pmatrix} \frac{1}{(1-\delta^2)^{1/3}} & 0 & \frac{1}{(1-\delta^2)^{1/3}} \\ 0 & \frac{1}{(1-\delta^2)^{1/3}} & 0 \\ \frac{\delta}{(1-\delta^2)^{1/3}} & 0 & \frac{1}{(1-\delta^2)^{1/3}} \end{pmatrix}$	$\frac{\Delta E}{V} = 2(\tau_5 \delta + C_{55} \delta^2)$
D_6	$\begin{pmatrix} \frac{1}{(1-\delta^2)^{1/3}} & \frac{1}{(1-\delta^2)^{1/3}} & 0 \\ \frac{\delta}{(1-\delta^2)^{1/3}} & \frac{1}{(1-\delta^2)^{1/3}} & 0 \\ 0 & 0 & \frac{1}{(1-\delta^2)^{1/3}} \end{pmatrix}$	$\frac{\Delta E}{V} = 2(\tau_6 \delta + C_{66} \delta^2)$
D_7	$\begin{pmatrix} \frac{1+\delta}{(1-\delta^2)^{1/3}} & 0 & 0 \\ 0 & \frac{1-\delta}{(1-\delta^2)^{1/3}} & 0 \\ 0 & 0 & \frac{1}{(1-\delta^2)^{1/3}} \end{pmatrix}$	$\frac{\Delta E}{V} = (\tau_1 - \tau_2) \delta + \frac{1}{2} (C_{11} + C_{22} - 2C_{12}) \delta^2$
D_8	$\begin{pmatrix} \frac{1+\delta}{(1-\delta^2)^{1/3}} & 0 & 0 \\ 0 & \frac{1}{(1-\delta^2)^{1/3}} & 0 \\ 0 & 0 & \frac{1-\delta}{(1-\delta^2)^{1/3}} \end{pmatrix}$	$\frac{\Delta E}{V} = (\tau_1 - \tau_3) \delta + \frac{1}{2} (C_{11} + C_{33} - 2C_{13}) \delta^2$
D_9	$\begin{pmatrix} \frac{1}{(1-\delta^2)^{1/3}} & 0 & 0 \\ 0 & \frac{1+\delta}{(1+\delta^2)^{1/3}} & 0 \\ 0 & 0 & \frac{1-\delta}{(1-\delta^2)^{1/3}} \end{pmatrix}$	$\frac{\Delta E}{V} = (\tau_2 - \tau_3) \delta + \frac{1}{2} (C_{22} + C_{33} - 2C_{23}) \delta^2$

3.2. Stability of the Orthorhombic BaF₂

The degree of anisotropy is indicated by Zener anisotropy A . This value can be compared to those of isotropic material [13]. The Zener anisotropy factors in the orthorhombic phase are three. Firstly, A_1 , which is the shear anisotropic factor for the {100} shear planes between the $\langle 011 \rangle$ and $\langle 010 \rangle$ directions. Secondly, A_2 , which is the shear factor in the {010} shear planes between $\langle 101 \rangle$ and $\langle 001 \rangle$ directions. Lastly, for the {001} direction the shear plane between $\langle 110 \rangle$ and $\langle 010 \rangle$, is given as A_3 [5]. The formulae used in the present work to calculate these stability constants are as per the scheme of Ravindran et al. [5].

4. Results

4.1. Structural optimization

In Fig. 1, the optimized structure of orthorhombic BaF₂ is shown. The corresponding parameters are given in Table 2.

The computed structural properties show good agreement with both theoretical and experimental calculations. The calculated cell parameters for the orthorhombic unit cell compare well with the corresponding experimental values with a deviation of about 7% for the lattice constant a . However, other values such as b/a and c/a show good agreement between theory and experiment.

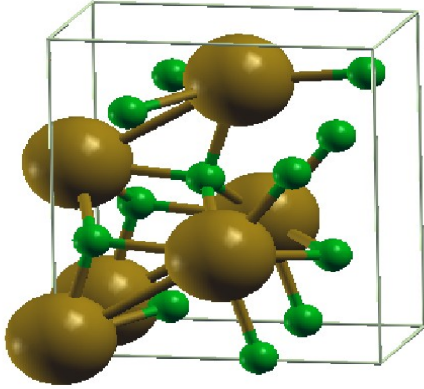


FIG. 1: Optimized orthorhombic unit cell crystal structure of BaF_2 . The unit cell contains four cations (big spheres) and eight anions (small spheres).

TABLE II: Structural optimization results of orthorhombic phase of BaF_2 at zero pressure.

Orthorhombic (C23)	a(Å)	b/a	c/a	Ref.
Quantum espresso (GGA)	6.692	1.158	0.598	Present
CRYSTAL (GGA)	6.871	1.174	0.608	Ref.[11]
Expt. (300K)	6.159	1.275	0.646	Ref.[3]

4.2. Electronic properties and band structure

The density of states (DOS) and band structure of orthorhombic phase of BaF_2 are shown in Figs. 2 and 3, respectively. The band gap is calculated at about 6.9 eV, which is decreased from the cubic value of 7.2 eV. This shows that the band gap decreases as one moves from cubic to orthorhombic phase. This phase transition can also vary with increase in pressure and this is in agreement with earlier work of Yang [6]. The same trend has also been observed in CaF_2 as reported by Shi et al. [7]. This decrease in band gap is an indication that BaF_2 , or fluorites undergo transition from wide to narrower band gap, which is expected to improve the conduction.

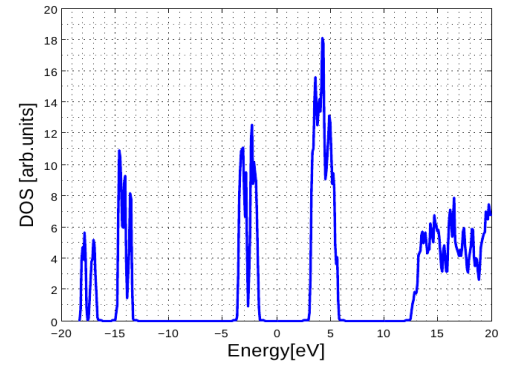


FIG. 2: Density of states of the orthorhombic phase of BaF_2 .

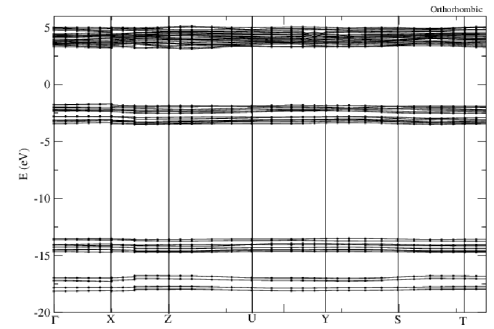


FIG. 3: Band structures of the orthorhombic phase of BaF_2 .

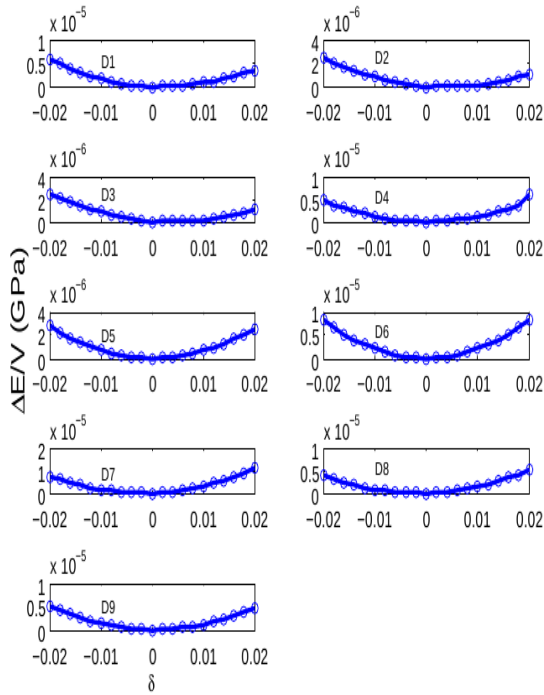
4.3. Elastic constants

Fig. 4 shows the plots used to obtain parameters needed in the computation of the elastic constants. These are associated to the distortion constants D shown in Table 1. Fig. 4 shows results of the distortions for the orthorhombic phase of BaF_2 . Each figure shows the parabolic shape.

Table 3 shows elastic constants for the orthorhombic phase of BaF_2 . It is shown that C_{22} at 346 GPa is the stiffest constant while C_{12} is the least stiff.

TABLE III: Elastic constants for the orthorhombic phase of BaF₂ in GPa.

Elastic constant	C ₁₁	C ₂₂	C ₃₃	C ₄₄	C ₅₅	C ₆₆	C ₁₂	C ₁₃	C ₂₃
Quantum espresso	275.5	346	126	91.7	47.2	147.5	32	39	60

FIG. 4: Changes in the pressure ($\Delta E/V_0$) as a function of strain δ for the orthorhombic phase of BaF₂. The dots represent the calculated values and the solid lines are the polynomial fit. The D1 to D9 correspond to the distortion matrices given in Table 1.

The bulk modulus of the orthorhombic phase is calculated from the derived values of the elastic constants as discussed in Ravindran et al. [5,14] and the results are given in Table 4. From this table, calculated value of 94.5 GPa is obtained while from the Murnaghan methods a value of 108.8 GPa was obtained. The variation can be attributed to the many estimations necessary in the estimations of the elastic constants. But this variation notwithstanding, the methods used in elastic constant appear satisfactory even though no data was available from the experiment to compare our results with.

The shear anisotropic factors for the orthorhom-

TABLE IV: Stability properties of orthorhombic phase compared to hexagonal phase of BaF₂.

Phase	A ₁	A ₂	A ₃	Bulk Modulus B (GPa)
Orthorhombic	1.13	0.54	0.86	94.5
Hexagonal	0.015	0.023	161	Present [16]

bic and hexagonal phases of BaF₂ are shown in Table 4. An isotropic material has the factors A₁, A₂ and A₃ equal to one while any other value less or greater than one indicates the degree of anisotropy. From Table 4, the orthorhombic and hexagonal phases of BaF₂ are anisotropic though the degree of anisotropy varies with the phase and the direction of study. Given that A₂ is greater than A₁ in the hexagonal phase means that contraction is easiest in any direction normal to the hexagonal axis [15]. In addition, hexagonal phase is anisotropic in all directions for BaF₂ according to values shown in Table 4.

5. Conclusion

In this work, the electronic and mechanical properties of the orthorhombic phase of BaF₂ have been studied using first-principles Plane wave pseudopotentials. Lattice parameters and band gap show a good agreement with other theoretical calculations and experimental data available. All the elastic constants of orthorhombic phase of BaF₂ have also been calculated. These values of elastic constants are used to calculate the bulk modulus of this phase and good agreement is established with other calculations showing that our theoretical approach is accurate. Stability of this phase show A₁ is the only anisotropic direction while the other two phases are isotropic.

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