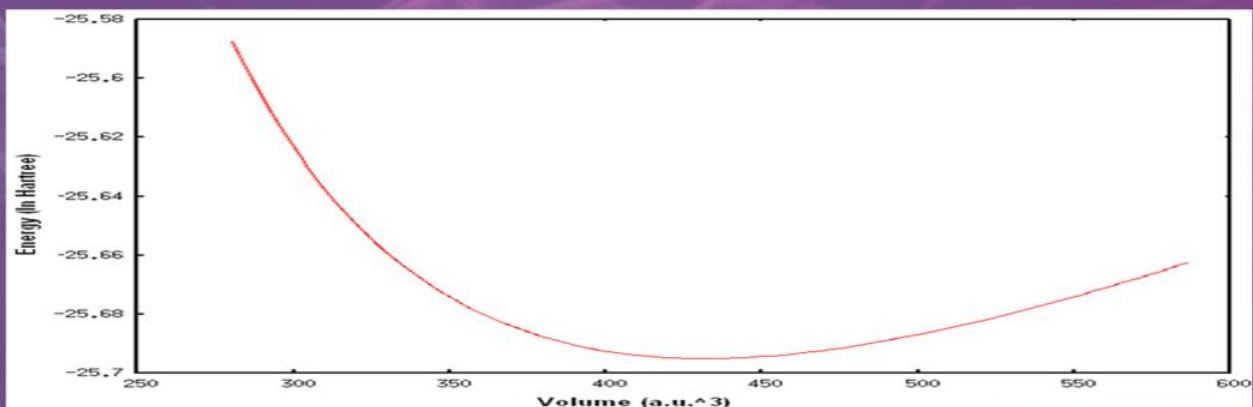
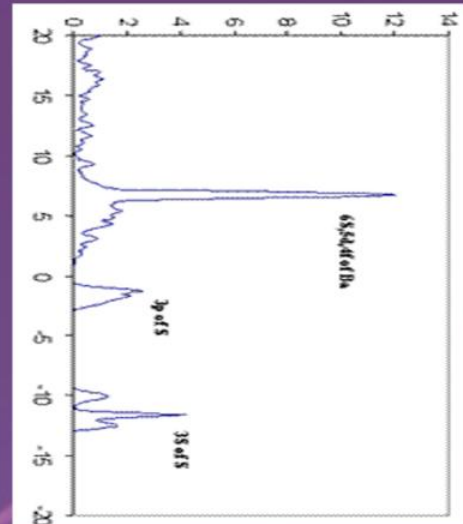
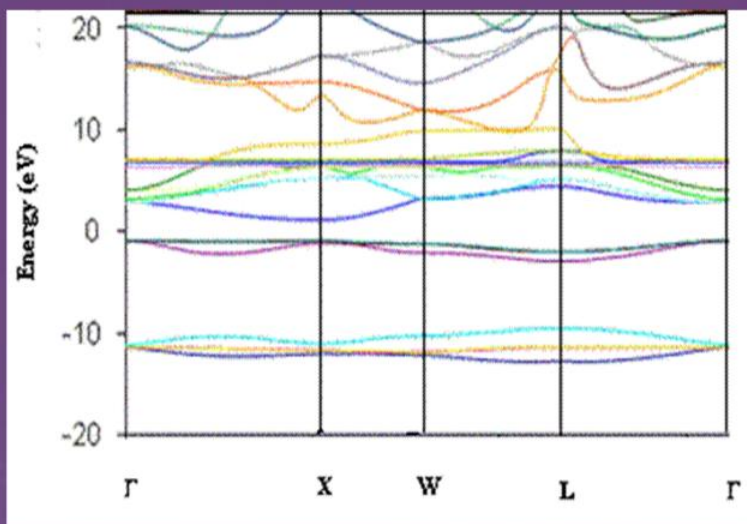


Cohesive and Electronic Properties of Barium Chalcogenide BaX (X = S, Se)



**Cohesive and Electronic Properties
Of
Barium Chalcogenides BaX (X=S,Se)**

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Preface

We have used and implemented a self-consistent density function method using standard norm-conserving pseudo-potentials and a flexible, numerical linear combination of atomic orbital's basis set, which includes multiple-zeta and polarization orbital's. Exchange and Correlation are treated with the local density approximations or generalized gradient approximations. The basis function and the electron density are projected on a real-space grid, in order to calculate the Hartree and exchange-correlation potentials and matrix element, with a number of operations that scales linearly with the size of the system. We have used a modified energy functional, whose minimization produces orthogonal wave functions, and the same energy and density as the Kohn-Sham energy functional, without the need for an explicit orthogonalization. Additionally, using localized Wannier-like electron wave functions allows the computation time and memory required to minimize the energy to also scale linearly with the size of the system. Forces and stresses are also calculated efficiently and accurately, thus allowing structure relaxation and molecular dynamics simulations.

The recent improvements in computer hardware and software allow the simulation of molecules and materials with an increasing number of atoms N , the use of so-called order- N algorithms, in which the computer time and memory scales linearly with the simulated system size, becomes increasingly important. These $O(N)$ methods were developed during the 1970s and 80s for long-rang forces and empirical interatomic potentials but only in the last 5-10 years for the much more complex quantum mechanical methods, in which atomic forces are obtained by solving the interaction of ions and electrons together. Even among quantum mechanical methods. There are very different levels of approximation: empirical or semi-empirical orthogonal tight-binding methods are the simplest ones: 'ab initio' non orthogonal tight-binding and non self-consistent Harris-functional methods are next and fully self-consistent density functional theory (DFT) methods are the most complex and reliable. The implementation of $O(N)$ methods in quantum mechanical simulations has also followed these steps, with several methods already well established within the tight-binding formalism, but much less so in self-consistent DFT. The latter also require, in addition to solving Schrodinger equation, the determination of the self-consistent Hamiltonian in $O(N)$ iterations. While this is difficult using plane waves, a localized basis set appears to be the natural choice.

We have used a fully self-consistent DFT, based on a flexible linear combination of atomic orbital's (LCAO) basis set, with essentially perfect $O(N)$ scaling. It allows extremely fast simulation using minimal basis sets and very accurate calculations with complete multiple-zeta and polarized bases, depending on the required accuracy and available computational power. The SIESTA (Spanish Initiative for Electronic Simulations with Thousands of Atoms) code has used for the present study.

Apart from that of Born and Oppenheimer, the most basic approximations concern the treatment of Exchange and Correlation (XC), and the use of pseudo-potentials. Exchange and correlation are treated within Kohn-Sham DFT. We allow for both the local density approximation (LDA/LSD) and the generalized gradient approximation (GGA). We use standard norm-conserving pseudo-potentials in their fully nonlocal form. We also include scalar-relativistic effects and the nonlinear partial-core correction to treat XC in the core region.

The SIESTA code has been already tested and applied to a variety of system and a variety of properties. Therefore, we shall just illustrate here the convergence of a few characteristic magnitudes of silicon, the archetypical system of the field, with respect to the main precision parameter that characterize our method: basis size (number of atomic basis orbitals); basis range (radius of the basis orbitals); fineness of the real-space integration grid and confinement radius of the Wannier-like electron states, Other parameters, such as the k-points sampling integration grid, are common to all similar methods and we shall not discuss their convergence here.

We have used SIESTA code for computation of Cohesive and Electronic properties of BaS and BaSe in NaCl phase. The dissertation is divided in to three chapters. In first chapter we have given the details the introduction of the problem along with some review on earlier work. It is accompanied by the importance of the present study. In second chapter, we have discussed the theory based on DFT in detail. The result obtained from the present theory is reported in third chapter along with the necessary discussion and conclusion on present materials in same chapter.

1. Introduction

Alkaline chalcogenide compounds are currently under intense investigations driven by their potential application in light-emitting diodes (LEDs) and laser diodes (LDs). It is expected that these compounds may provide new II-VI candidates for the fabrication of various electrical and optical devices [1]. Among the wide band gap II-VI semiconductors, the Barium chalcogenide BaX (X = S, Se, Te) and their alloys, are interesting in connection with optoelectronic application in the blue-light wavelength region, and have the understanding of their interaction mechanism and electronic and optical properties are important. These may be tuned by means of diverse bond characteristics [2-5] and by means of built-in strains produced by epitaxial growth of heterostructures under controlled conditions. Prediction and analysis of such effects require basic knowledge of the elastic constants and relevant deformation potential of the constituents. Under pressure BaS, BaSe and BaTe compounds undergo structural phase transition from the six-fold coordinated NaCl (B1) structure to the eight-fold coordinated CsCl (B2) structure at the respective pressures of 6.5, 6.0 and 4.8 GPa, as it has been found by high pressure X-ray diffraction experiments [6-9].

From a theoretical point of view, several first-principle calculations were made for these compounds by a variety of methods [5, 10-16]. Wei and Krakauer [10] have used the linearized augmented plane wave (LAPW) method to study both structural and metallization transition of BaSe and BaTe. The augmented-spherical wave method within the local-density approximation (LDA-ASW) has been used by Carlsson and Wilkins [11] to discuss the metallization transition volume of BaS, BaSe and BaTe. Kalpana and co-workers [12] have studied the electronic structure and structural phase stability of these compounds by means of the tight-binding linear muffin-orbital (TB-LMTO) method. The high pressure structure phase transition of BaSe and BaTe has also been investigated by Jha, et al. [13] by using the classical theory based on three body potential approach. Syassen and co-workers [14] have used the linear muffin-tin-orbital (LMTO) method, while Akbarzadeh, et al. [15] used the full-potential linear augmented plane wave (FP-LAPW) and the pseudo-potential plane wave (PP-PW) method to compute band structure of BaTe compound. More recent study Lin and co-workers have used the pseudo-potential plane wave to study the relationship between electronic properties and chemical bonds in BaX compounds. Khenata, et al. [16] and Pouraghazi, et al. [17]. These have also reported band structure results of these compounds.

Motivated from these, I have used the Pseudo-potential method as implemented in SIESTA code to study the electronic property of Ba-Chalcogenides.

Barium sulfide is the chemical compound with the formula BaS. This material was once known as "Bologna Stone", the first synthetic phosphor. Currently, the chalcogenides of the alkaline-earth metals are intensely studied as candidates for short wavelength emitters for electronic displays [18]. BaS is considered to be the most important synthetic material of Barium, being the precursor to BaCO₃ and the pigment lithopone, ZnS/BaSO₄ [19].

The high-pressure phase was studied utilizing a Ruoff-Baublity-type gasketed opposed diamond anvil cell described elsewhere [20]. A fine ground powder of BaSe as well as a 4:1 methanol-ethanol mixture and a small ruby chip were loaded into the 150- μ m gasket hole and pressure was obtained from the shift of the ruby fluorescence lines [21], while a hydrostatic environment is obtained by the use of the methanol-ethanol mixture [22].

The BaSe compound was obtained from CERAC Inc. [23] and was of purity greater than 99.5%. The as-received BaSe powder (-20 mesh) is deep red in color and converted to a light yellow color upon heating to 600⁰C in hydrogen gas for 36 hours. X-ray diffractometer measurements taken on the hydrogen-treated BaSe powder revealed its NaCl crystal structure with lattice constant of 6.593 \pm 0.016 Å, consistent with its American Society for Testing and Materials card designation [7].

2. Theoretical Aspects

2.1 *ab-initio* calculation

The Latin term *ab-initio* means from the beginning. A calculation is said to be "*ab-initio*" (or "from first principal") if it relies on basic and established laws of nature without additional assumption or special models. For example, an *ab-initio* calculation of the properties of liquid water might start with the properties of the constituent hydrogen and oxygen atom and the laws of electrodynamics. From these basics, the properties of isolated individual water molecules would be derived, followed by computations of the interactions of larger and larger group of water molecules, until the bulk properties of water had been determined.

2.2 Schrödinger Equation for Many-Body Problem

The time-independent Schrödinger equation for ions (i.e., the atomic nuclei) and electrons for a many-body wave function Ψ is given as $H\Psi = E\Psi$

$$\left(-\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 + \sum_{i,I} \frac{Z_I e^2}{|r_i - R_I|} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|r_i - r_j|} - \sum_I \frac{\hbar^2}{2M_I} \nabla_I^2 + \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J e^2}{|R_I - R_J|} - E \right) \psi = 0 \quad (1)$$

Here, lower case subscripts and nuclei (ions) with charge ZI and mass MI , respectively denote the electrons, by upper case subscripts. The 2nd, 3rd and 5th terms in the above equation denote the Coulomb interactions between electrons and ions, electron – electron and ion – ion, respectively.

According to the Copenhagen interpretation of quantum mechanics, the absolute square of the wave function is proportional to the probability density of finding a particle at each of its arguments. Particles of the same kind (e.g., electrons or identical nuclei) are indistinguishable.

When two electrons (or other fermions) are exchanged, the wave function changes its sign (anti-symmetry) whereas it is symmetric with respect to boson exchange.

Taking into account that the electrons are lighter than the nuclei by three to four orders of magnitude, we can employ the Born-Oppenheimer approximation. Assuming that the electrons adapt instantaneously to any movement of the nuclei, the motion of the electrons can be decoupled from that of the nuclei. For each atomic configuration, the electronic Schrödinger equation then reads

$$\left(-\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 + \sum_{i,I} \frac{Z_I e^2}{|r_i - R_I|} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|r_i - r_j|} - E \right) \psi = 0 \quad (2)$$

The nuclei appear here only as the point charge sources of the electrostatic potential in which the electrons move. For generality, this potential will be denoted as the external potential V_{ext} .

As, many properties depend on the electronic ground-state energetic. For this purpose, density functional theory (DFT), which builds on the ground-state electron density as the basic variable, provides an excellent choice.

2.3 Hartree and Hartree-Fock Theory

One of the earliest attempts to solve the problem was made by Hartree. He simplified the problem by making an assumption about the form of the many-electron wave function, namely that it was just the product of a set of single-electron wave functions. In a uniform system these wave functions would take the form of simple plane waves. Having made this assumption it was possible to proceed using the **variational principle**.

By using the variational method Hartree found the **Hamiltonian equation** of the many-electron system (just a fancy name for the equation of motion). In fact, for an N-electron system there are N equations; one for each of the N single-electron wave functions which made up the many-electron product wave function. These equations turned out to look very much like the time-independent Schrodinger equation, except the potential (**the Hartree potential**) was no longer coupled to the individual motions of all the other electrons, but instead depended simply upon the time-averaged electron distribution of the system. This important fact meant that it was possible to treat each electron separately as a single-particle. Consequently, the Hartree approximation allows us to calculate approximate single-particle wave functions for the electrons in crystals, and hence calculate other related properties. The Hartree product wave function is symmetric (i.e., stays precisely the same after interchange of two fermions) rather than antisymmetric, so the Hartree approach effectively ignores the Pauli's exclusion principle.

The Hartree-Fock approach is an improvement over the Hartree theory in that the many-electron wave function is specially constructed out of single-electron wave functions in such a way as to be antisymmetric. The wave function has to be much more complicated than the Hartree product wave function, but it can be written in a compact way as a so-called **Slater determinant** (for those who know what is determinant).

Starting from this assumption it is once again possible to derive the Hamiltonian equation for the system through the variational principle. Just as before, this results in a simple equation for each single-electron wave function. However, this time in addition to the Hartree potential (which described the direct Coulomb interaction between an electron and the average electron distribution) there is now a second type of potential influencing the electrons, namely the so-called **exchange potential**. The exchange potential arises as a direct consequence of including the Pauli's exclusion principle through the use of an antisymmetrised wave function.

2.4 Density Function Theory (DFT)

2.4.1 Introduction

Many-body problem has been simplified using density functional theory, in which electronic charge density is assumed as fundamental variable rather than the wave function, *i.e.*, it is assumed that for a given non-degenerate non-polarized ground state wave function, there is a unique electron density. Thus Ψ is a unique functional of the charge density, and hence the energy (E) is uniquely defined by charge density.

Hohenberg and Kohn [24] in 1964, suggested that the problem really was that the many-electron wave function was too complicated an entity to deal with as the fundamental variable in a variational approach. Firstly, it cannot adequately be described without $\sim 10^{23}$ parameters, and secondly it has the complication of possessing a phase as well as a magnitude. They choose instead to use the electron density as their fundamental variable. That is, they considered the ground state of the system to be *defined* by that electron density distribution which minimizes the total energy. Furthermore, they showed that all other ground state properties of the system (e.g., lattice constant, cohesive energy, etc.) are functionals of the ground state electron density.

2.4.2 Kohn and Sham theory

It was then Kohn and Sham who showed that it is possible to replace the many-electron problem by an exactly equivalent set of self-consistent one-electron equations. The total energy functional can be written as a sum of several terms

$$E[\rho(r)] = T_s[\rho(r)] + \frac{e^2}{2} \iint \frac{\rho(r)\rho(r')}{|r-r'|} d^3r d^3r' + E_{xc}[\rho(r)] \quad (3)$$

Where, I term represents the kinetic energy of non-interacting electrons; II term represents the electron-ion energy; III term represents the electron-electron energy (coulomb energy); IV term is the exchange-correlation energy.

2.4.3 Exchange-Correlation Energy

While DFT in principle gives a good description of ground state properties, practical applications of DFT are based on approximations for the so-called exchange-correlation potential. The exchange-correlation potential describes the effects of the Pauli's principle and the Coulomb potential beyond a pure electrostatic interaction of the electrons. Possessing the exact exchange-correlation potential means that we solved the many-body problem exactly, this is clearly not feasible in solids.

The exchange-correlation potential is calculated using the local density approximation (LDA) [26]. In this, the exchange-correlation energy (ECE) of an electronic system is constructed by assuming that the ECE per electron at a point r in the electron gas $e_{xc}(r)$ is equal to the ECE per electron in a homogeneous electron gas that has the same electron density at the point r . It follows that

$$E_{xc}^{LDA}[\rho(r)] = \int \varepsilon_{xc}^{hom}[\rho(r)] \rho(r) d^3x \quad (4)$$

Therefore, exchange potential in LDA

$$V^{LDA}[\rho(r)] = \frac{\delta E_{xc}^{LDA}[\rho(r)]}{\delta \rho(r)} = \frac{\delta \left[\int \rho(r) \varepsilon_{xc}^{\text{hom}} \rho(r) \right]}{\delta \rho(r)} = \varepsilon_{xc}^{\text{hom}}[\rho(r)] + \frac{\delta \varepsilon_{xc}^{\text{hom}}[\rho(r)]}{\delta \rho(r)} + \rho(r) \quad (5)$$

2.4.4 Local Density Approximation (LDA)

The simplest approximation is to assume that the density can be treated locally as an uniform electron gas; the exchange correlation energy at each point is the same as that of an uniform electron gas of the same density. This approximation was originally introduced by Kohn and Sham [26] and holds good for a slowly varying density.

2.4.5 Generalized Gradient Approximations

As the LDA approximates the energy of the true density of a local constant density, it fails in situations where the density undergoes rapid changes such as in molecules. An improvement to this can be made by considering the gradient of the electron density, the so-called Generalized Gradient Approximation (GGA). Symbolically this can be written as

$$E_{xc} = E_{xc}[\rho(r), \nabla \rho(r)] \quad (6)$$

This can lead to a large improvement over LDA results with accuracy approaching that of correlated wave function methods.

2.5 Pseudo-potentials

Pseudo-potentials assume that the localized core states do not take part in bonding, and so can be incorporated as a change in the charge state of the nucleus between the nucleus and some cut-off radius (r_c), the all-electron valence wave function can be replaced with a smoothed form; beyond this radius pseudo-wave function must be identical to the full all-electron wave function. In addition there will still be exchange interaction between core and valence electrons which must be included in the potentials. Finally, if self-consistency is easily achieved in the calculations then the potentials must have the correct atomic charge density outside the core ('norm-conserving' pseudo-potential).

2.6 SIESTA Code

SIESTA (Spanish Initiative for Electronic Simulation with Thousands of Atoms) is both a method and its computer program implementation, to perform electronic structure calculations and ab initio molecular dynamics simulation of molecules and solids. Its main characteristics are:

- It uses the standard Kohn-Sham self-consistent density functional method in the local density (LDA_LSD) or generalized gradient (GGA) approximations.
- It user norm-conserving pseudo-potentials in its fully nonlocal (Kleinman-Bylander) form.
- It uses atomic orbitals as basis set, allowing unlimited multiple-zeta and angular momenta, polarization and off-site orbital's. The radial shape of every orbital is numerical and any shape can be used and provided by the user, with the only condition that it has to be of finite support, i.e., it has to be strictly zero beyond user-provided distance from the corresponding nucleus. Finite-support basis sets are the key for calculation the Hamiltonian and overlap matrices in $O(N)$ operations.
- Projects the electron wave function and density onto a real-space grid in order to calculate the Hartree and exchange-correlation potentials and their matrix elements.
- Besides the standard Rayleigh-Ritz eigen state method, it allows the use of localized linear combinations of the occupied orbital's (valence-bond or Wannier-like functions), making the computer time and memory scale linearly with the number of atoms. Simulations with several hundred atoms are feasible with modest workstations.
- It is written in Fortran 90 and memory is allocated dynamically.

It routinely provides:

- Total and partial energies
- Atomic forces
- Stress tensor
- Electronic dipole moment
- Atomic, orbital and bond populations
- Electron density and also
- Geometry relaxation, fixed or variable cell
- Constant-temperature molecular dynamics
- Spin polarized calculations
- K-sampling of the Brillouin zone
- Local and orbital-projected density of states
- Band structure

2.7 Periodic supercells

In the preceding section it was demonstrated that certain observables of the many-body problem can be mapped into equivalent observables in an effective single-particle problem.

However, there still remains the formidable task of handling an infinite number of noninteracting electrons moving in the static potential of an infinite number of nuclei or ions. Two difficulties must be overcome: a wave function must be calculated for each of the infinite number of electrons in the system, and, since each electronic wave function extends over the entire solid, the basis set required to expand each wave function is infinite. Both problems can be surmounted by performing calculations on periodic systems and applying Bloch's theorem to the electronic wave functions.

2.7.1 Bloch's theorem

Bloch's theorem states that in a periodic solid each electronic wave function can be written as the product of a cell-periodic part and a wavelike part $\psi_i(r) = \exp[iK \cdot r] f_i(r)$ (7)

The cell-periodic part of the wave function can be expanded using a basis set consisting of a discrete set of plane waves whose wave vectors are reciprocal lattice vectors of the crystal,

$$f_i(\mathbf{r}) = \sum_{\mathbf{G}} c_{i,\mathbf{G}} \exp[i\mathbf{G} \cdot \mathbf{r}] \quad (8)$$

Where the reciprocal lattice vectors \mathbf{G} are defined by $\mathbf{G} \cdot \mathbf{l} = 2\pi m$ for all \mathbf{l} where \mathbf{l} is a lattice vector of the crystal and m is an integer. Therefore each electronic wave function can be written as a sum of plane waves, $\psi_i(r) = \sum_{\mathbf{G}} c_{i,\mathbf{K}+\mathbf{G}} \exp[i(\mathbf{K} + \mathbf{G}) \cdot \mathbf{r}]$ (9)

2.7.2 k-point sampling

Electronic states are allowed only at a set of k-points determined by the boundary conditions that apply to the bulk solid. The density of allowed k-points is proportional to the volume of the solid. The infinite number of electrons in the solid are accounted for by an infinite number of k-points, and only a finite number of electronic states are occupied at each k-point. The Bloch theorem changes the problem of calculating an infinite number of electronic wave functions to one of calculating a finite number of electronic wave functions at an infinite number of k-points. The occupied states at each k-point contribute to the electronic potential in the bulk solid so that, in principle, an infinite number of calculations are needed to compute this potential. However, the electronic wave functions at a single k-point. In this case the electronic states at only a finite number of k-points are required to calculate the electronic potential and hence determine the total energy of the solid.

Methods have been devised for obtaining very accurate approximations to the electronic potential and the contribution to the total energy from a filled electronic band by calculating

the electronic states at special sets of k-points in the Brillouin zone given by Chadi and Cohen [35], Joannopoulos and Cohen, Monkhorst and Pack [36] using these methods, one can obtain an accurate approximation for the electronic potential and the total energy of an insulator or a semiconductor by calculating the electronic states at a very small number of k-points. The electronic potential and total energy are more difficult to calculate if the system is metallic because a dense set of k-points is required to define the Fermi surface precisely.

The magnitude of any error in the total energy due to inadequacy of the k-point sampling can always be reduced by using a denser set of k-points. The computed total energy will converge as the density of k-points increases, and the error due to the k-point sampling then approaches zero. In principle, a converged electronic potential and total energy can always be obtained provided that the computational time is available to calculate the electronic wave function at a sufficiently dense set of k-points. The computational cost of performing a very dense sampling of k space can be significantly reduced by using the total-energy method given by Robertson and Payne [37].

2.7.3 Plane-wave basis sets

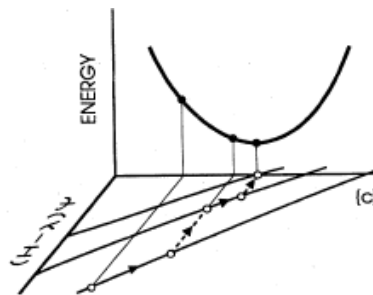
Bloch's theorem states that the electronic wave functions at each k-point can be expanded in terms of a discrete plane-wave basis set. In principle, an infinite plane-wave basis set is required to expand the electronic wave functions. However, the coefficients $c_{i,K+G}$ for the plane waves with small kinetic energy $\left(\frac{\hbar^2}{2m}\right)|K+G|^2$ are typically more important than those with large kinetic energy. Thus the plane-wave basis set can be truncated to include only plane waves that have kinetic energies less than some particular cut-off energy. If a continuum of plane-wave basis states were required to expand each electronic wave function, the basis set would be infinitely large no matter how small the cut-off energy. Application of the Bloch theorem allows the electronic wave function to be expanded in terms of a discrete set of plane waves. Introduction of an energy cutoff to the discrete plane-wave basis set produces a finite basis set.

The truncation of the plane-wave basis set at finite cut-off energy will lead to an error in the computed total energy. However, it is possible to reduce the magnitude of the error by increasing the value of the cutoff energy. In principle, the cut-off energy should be increased until the calculated total energy has converged, but it will be shown later that it is possible to perform calculations at lower cut-off energies.

One of the difficulties associated with the use of plane wave basis sets is that the number of basis states changes discontinuously with cutoff energy. In general these discontinuities will occur at different k -points in the k -point set. (In addition, at a fixed-energy cut-off, a change in the size or shape of the unit cell will cause discontinuation in the plane-wave basis set). This problem can be reduced. However, the problem is still present even with quite dense k -point samplings. It can be handled by applying a correction factor which accounts approximately for the difference between the number of states in a basis set with infinitely large number of k -points and the number of basis states actually used in the calculation by Francis and Payne [38].

2.8 Self-consistency

The acceleration of the wave function in the molecular-dynamics equations of motion are governed by the Kohn-Sham Hamiltonian. The Hartree potential and the exchange-correlation potential contribute to the Kohn-Sham Hamiltonian and depend on the charge density generated by the electronic wave function. As the wave function evolve under the molecular-dynamics equation of motion, these potentials vary. The potentials are recalculated at the end of each time step (when a new set of wave function has been generated) and lead to a new Kohn-Sham Hamiltonian. Thus the evolution of the coefficients to their stationary values is accompanied by an evolution of the Kohn-Sham Hamiltonian to self-consistency. This is illustrated in fig. each of the solid-lines shown passing through the open circles corresponds to a static Kohn-Sham Hamiltonian with a fixed charge density. During a molecular-dynamics time step, the coefficient (c) move along a trajectory that lies between two open circles. At the end of each time step, the Kohn-Sham Hamiltonian is updated with the new charge density, and the trajectory shifts to a new solid line. This shift is indicated by the dotted-line trajectory. The final time step leads to a self-consistent solution of the Kohn-Sham Hamiltonian and the determination of the minimum in the total energy.



Solid-line trajectories between open circles correspond to H with a fixed charge density. The final time step leads to a self-consistent solution of H and a simultaneous determination of the

minimum total energy. Note that, if a trajectory along a solid line were followed all the way to the (c) axis, this would correspond to conventional matrix diagonalization of H with a fixed charge density.

2.9 Norm conservation

In total-energy calculations, the exchange-correlation energy of the electronic system is a function of the electron density. If the exchange-correlation energy is to be desired accurately, it is necessary that outside the core regions the pseudo wave functions and real wave function be identical, not just in their spatial dependences but also in their absolute magnitudes, so that two wave function generate identical charge densities. Adjustment of the pseudo-potential to ensure that the integrals of the squared amplitudes of the real and the pseudo wave functions inside the core regions are identical guarantees the equality of the wave function and pseudo wave function outside the core region. One of the first attempts to construct pseudo-potentials of this type was by Starkloff and Joannopoulos [39]. They introduced a class of local pseudo-potentials that described the valence energies and wave functions of many heavy atoms accurately.

In general, the scattering from the ion core is best described by a different potential for each angular momentum component of the wave function. Various groups [27, 28] have now introduced nonlocal pseudo-potentials of this type that work extremely well. Moreover, as pointed out by Hamann, Schluter, and Chiang [27] a match of the pseudo and real wave function outside the core region also assures that the first-order energy dependence of the scattering from the ion-core is correct, so that the scattering has recently been introduced by Shirley, et al. [39]. Local and nonlocal pseudo-potentials of these types are currently termed *ab-initio* or norm conserving and are capable of describing the scattering due to the ion in a variety of atomic environments, a property referred to as transferability.

3 Cohesive and Electronic Property of BaS and BaSe

3.1 Method of Calculation

3.1.1 Introduction

The material BaX (X = S, Se) belongs to the II-IV group with binary octets of $A^N B^{8-N}$ type and has certain electronic properties.

The electronic and structural properties of these compounds of the rock-salt structure have been investigated using *ab-initio* Pseudo-potential approach within the framework of density

function theory [24]. We have used the local density approximation based on exchange-correlation energy optimization for calculation of the total energy.

The aim of the present computation is to be perform a comparative study of the structure phase stability and electronic structure of Ba-Chalcogenides by using SIESTA code based on density function theory (DFT) [24] by the *ab-initio* pseudo-potential method.

3.1.2 Determination of total Energy and lattice constant

The band structure for both BaS and BaSe for NaCl structure were obtained by SIESTA, the pseudo-potential within the local-density approximation (LDA) is calculated using the scheme of Troullier-Martins [40]. Most important relativistic corrections included, while the spin-orbit coupling term is neglected.

The metal and non-metal atoms occupy the position (0, 0, 0) and (0.5, 0.5, 0.5). To optimize the calculations, sphere radii were chosen for both metal and non-metal Atoms in the case of both BaS and BaSe compound. The following basis orbitals were used, namely, in the case of BaS and BaSe, Ba: 6s,5p,5d; S: 3s,3p,3d; and Se: 4s,4p,4d.

The total energy (E) is calculated by a self-consistent run and can be expressed as the sum of the kinetic energy of electrons, self-energy, Hartree energy, electrostatic energy, local Pseudo-energy, non-local energy, exchange-correlation energy, exchange-correlation potential energy and screening energy.

The lattice constant of a solid corresponds to the size of the conventional unit cell length at the equilibrium volume and is obtained computationally by minimizing the total energy as a function of cell volume. We have performed several calculation of the total energy for various lattice constants and obtained the value of lattice constant for which the total energy becomes minimum. The calculation of lattice constant is straightforward for cubic system. It is performed at several different volumes using the same energy cut-off and k-point sampling. The results are fitted to the Murnaghan's equation of state [29]

$$PV = \frac{B_0}{B_0'} \left[\left(\frac{V_0}{V} \right)^{B_0'} - 1 \right] \quad (10)$$

Here, B_0 is the equilibrium bulk modulus and B_0' its first pressure derivative. Here the pressure (P) is the negative derivative of the total energy

$$P = -\frac{\partial E}{\partial V} \quad (11)$$

Therefore, B_0 effectively measures the curvature of the energy versus volume curve at the relaxed volume (V_0).

$$B_0 = -V \left(\frac{\partial P}{\partial V} \right)_T \quad \text{and} \quad B_0' = \left(\frac{\partial B_0}{\partial P} \right)_T \quad (12)$$

Norm-conserving non-local pseudo-potential were constructed for $Ba(2^+)$ and $X(6^+)$ ($X = S, Se$) ions using the method of Troullier-Martins [40]. Include scalar relativistic effects. A mesh of $5 \times 5 \times 5$ special k-points is taken in the whole Brillouin zone for NaCl phase and cut-off energy of 70 Ry for BaS and 80 Ry for BaSe.

3.2 Result and Discussion

3.2.1 Cohesive Properties

We have used present theory to compute the total energy at room temperature for these compounds. For any system to be stable, the free energy or interaction energy, i.e., the cohesive energy at ambient conditions must be minimum.

For computing the total energy of the system, we have used the iterative method minimization technique. The values of computed energies are obtained depicted in figure1 as a function of volume for BaS and BaSe, respectively. It is clear from these figures that the minimization of energy occurs at 431.64 (a.u.³) and 483.93 (a.u.³) for BaS and BaSe, respectively. The values of energies at various volumes were fitted to Murnaghan's equations of state [29] to obtain the optimum values of Lattice Constant, Bulk Modulus B_0 and its first-order pressure derivative B_0' for present set of materials.

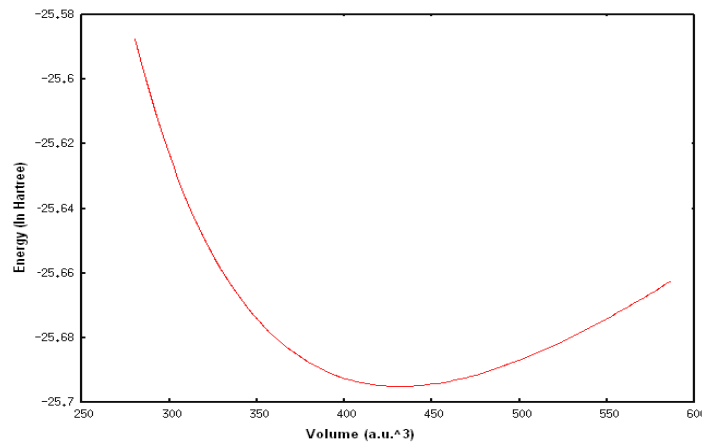


Figure-1(a): Variation of Total energy as a function of Volume of unit cell for BaS in Parent Phase at room temperature.

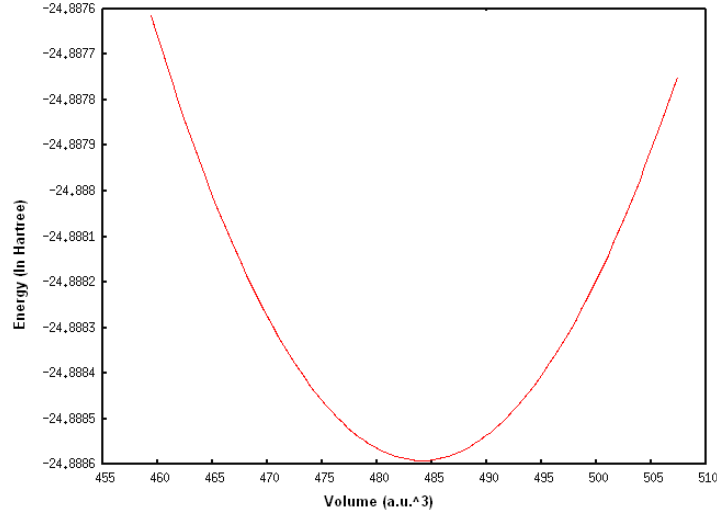


Figure-1(b): Variation of Total energy as a function of Volume of unit cell for BaSe in Parent Phase at room temperature.

These values are reported in table1 along with experimental [7-9] and other theoretical values computed by [12] using different theories. Results for the convergence of energy with respect to volume are shown in figure-1. It is found that the convergence occurs close to the experimental lattice constant. This correct description of lattice constant shows that the interaction considered in the present formulation is capable of predicting correctly the minimum free energy of BaS and BaSe in parent phase.

Table.1. Values of the calculated lattice parameter (a in Å), the bulk modulus (B_0 in GPa) and its pressure derivative (B'_0) at equilibrium volume in NaCl phase.

a	B_0	B'_0	Reference
BaS in NaCl Phase			
6.348	55.76	3.90	Present work
6.389	39.42	-	Expt. [7,9]
6.294	52.46	-	Other [12]
BaSe in NaCl Phase			
6.595	45.00	-5.87	Present work
6.593	43.40	-	Expt. [8,9]
6.508	45.41	-	Other [12]

The value of bulk modulus is found to be quite higher than the measured values but these values are close to the values obtained by others [12]. The values of the first-order pressure derivative of bulk modulus seem to be computed, theoretically for first time and hence cannot be compared with experimental as well as other theoretical results. Hence, we cannot comment on the reliability of these values but these values are of academic interest at present

and will serve as guide to design future experiments. The higher prediction of bulk-modulus may be attributed to the fact that LDA is not capable of taking care of proper interaction in between Ba and chalcogen atom. The results can be improved by considering GGA or LDA+U methods.

3.2.2 Electronic structure

Electronic structure calculation have been performed within the framework of the local density approximation (LDA) [42] has demonstrated their ability to accurately predict different physical properties.

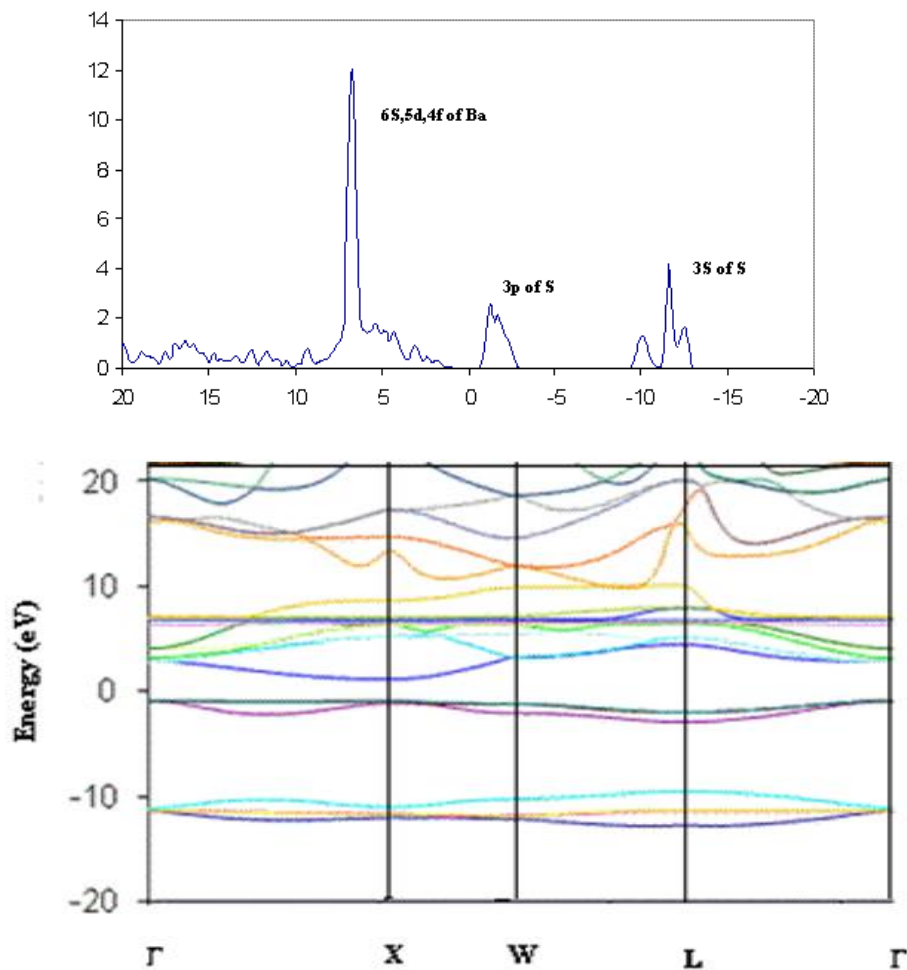


Figure-2(a) : The band structure and Density of State (DOS) for BaS in B1 phase.

Even with major advances in computer technology, the magnitude of the computational effort needed to calculate crystals is still enormous, and therefore a large interest exist for improving the computational methods for the electronic structure of solids. Replacing the effect that the chemically inert core states exert on the chemically active valence states by an effective pseudo-potential, dates back to the early work of Fermi [43] and has been a sizeable

amount of interest and further developments since the seminal work of Phillips and Kleinman [44]. The physical reason behind the pseudo-potential approximation is simple as the core electrons wave functions of an atom remain essentially unchanged when placed into different chemically environments and since that the core wave functions' only major contribution to chemical bonding is to enforce the valence wave functions orthogonality to the core states, the true atomic potential can justifiably be replaced by a pseudo-potential that effectively reproduces the effects of the core electrons, with only this physical constraint, an infinite number of pseudo-potentials can be generated and it has been the objective of much active work to try to determine what auxiliary conditions are needed to produce a pseudo-potential that both adequately reproduces the all-electron behavior outside the core region when placed in different chemical environments, and is still computational efficient.

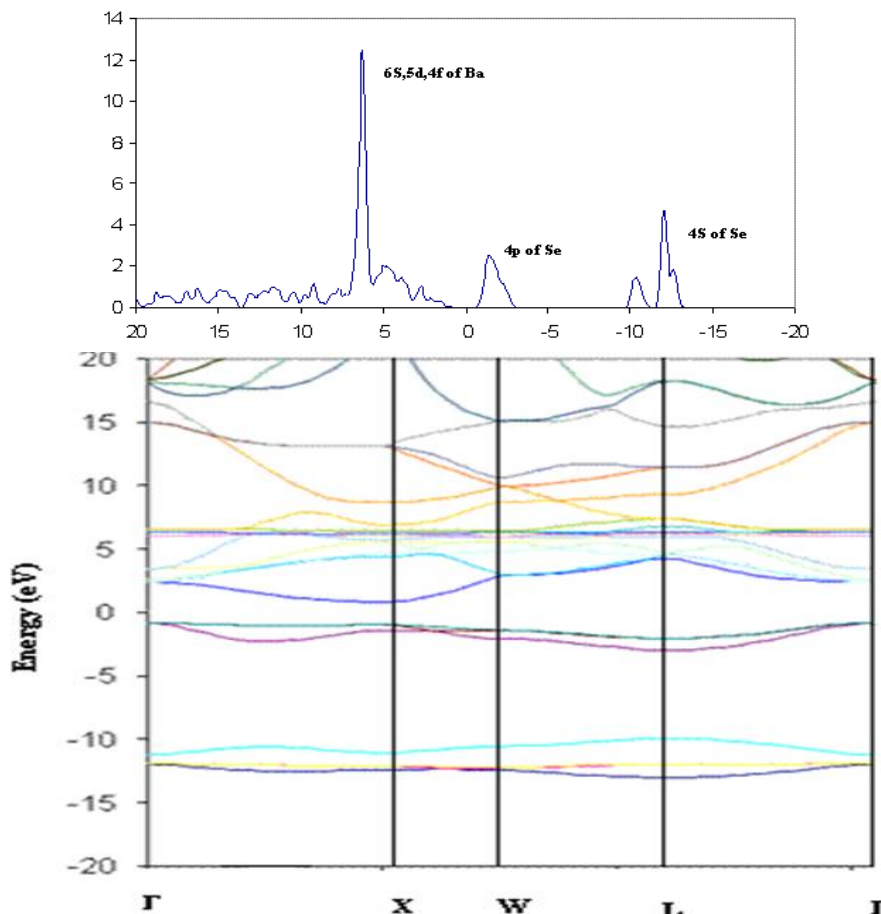


Figure-2(b) : The band structure and Density of State (DOS) for BaSe in B1 phase.

Mathematically and numerically, plane wave-basis formalism [43] is one of the simplest and most natural formalism to implement for crystals. However, expanding the core wave functions or the core oscillatory region of the valence wave function into plane waves is extremely inefficient. Therefore, plane-wave basis sets are practically always used in

conjunction with the pseudo-potential approximation. The combination of pseudo-potentials and plane waves has become one of the most popular methods for electronic structure calculations [46]. The self-consistent scalar-relativistic band structure for both the compounds was calculated in NaCl (B1) phase. The band structure in the B1 phase at ambient condition has been plotted in figure 2.

The self-Consistent relativistic band structure for both the compounds was calculated in NaCl structure. The band structure for the NaCl phase in both cases is given in figure 2. The overall band profile is found to be same with earlier works [12]. In both cases, the valence band maximum (VBM) and conduction band minimum (CBM) occurs at Γ and X points, respectively for BaS. Thus the energy gap is found to be indirect between the top of the valence band and the bottom of the conduction band. Similar type of trend has been found for BaSe which is depicted in figure 2(b). The calculated values of band gap under ambient condition are reported in table 2 and compared with the experimental [41] and others theoretical [12] values.

Table 3 : Energy band gap E_g (eV) in the NaCl structures for BaS and BaSe.

Compound	Present work	Expt. [41]	Others [12]
BaS	2.1	3.9	2.1
BaSe	1.7	3.6	1.8

3.3 Conclusions

We have studied the structural and electronic properties of BaS and BaSe compounds by employing the LDA method. A summary of our results may be seems as follows:

1. The calculated Cohesive Properties are in a good agreement with the available experimental [7,8] and theoretical values [11, 12].
2. The band gap is smaller than the experimental value [41]. Whereas, the calculated values agree with the others [11, 12] theoretical results. It is within the limits of LDA, because LDA predicts comparatively lower band gap in semiconductors.

It may be concluded that the LDA is not capable of explaining the band gap correctly for these Ba-chalcogenides, although other crystal properties were predicted correctly. For this purpose, we can use other approximation, like, GGA or LDA+U or LSDA+U for these compounds for further improved results on band gap.

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Cohesive and Electronic Properties of Barium Chalcogenide BaX (X = S, Se)



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