Electronic and Optical properties of Matlockite type LaOX(X = Cl, Br, I) compounds

Thesis submitted in partial fulfillment of the

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in

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by

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To ..

My parents

DECLARATION

I hereby declare that the work reported in this thesis has been carried out by me independently in the school of physics, University of Hyderabad, under the supervision of **Dr. G.S. Vaitheeswaran**, Advanced Centre of Research in High Energy Materials(ACRHEM). I also declare that this is my own work and effort, and it has not been submitted at any other University or Institution for any degree. Wherever contributions of others are involved, every effort is made to indicate that clearly with due reference to literature, and acknowledgement of collaborative research and discussions.

Place:

Date: **D.CHANDRA SEKHAR**

CERTIFICATE

This is to certify that the project work entitled "**Electronic and Optical properties of Matlockite type LaOX(X = Cl, Br, I) compounds**" being submitted to University of Hyderabad by **D. CHANDRA SEKHAR with Reg. No. 09PCMT16, in partial fulfillment for the award of the degree of Master of Technology in Computational Techniques, is a bonafide work carried out by him under my supervision.**

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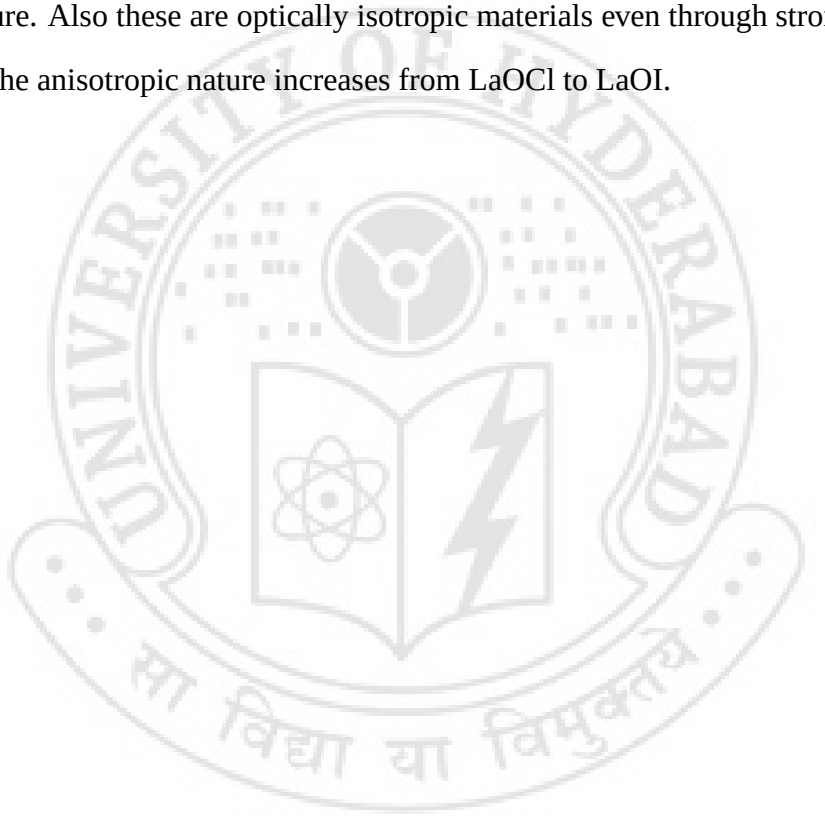
Abstract

In the present work ,we have studied the electronic and optical properties of matlockite type compounds LaOCl, LaOBr and LaOI. All the calculations were done using CASTEP based on density functional theory (DFT). It is observed that these are direct band gap($\Gamma - \Gamma$) insulators from electronic structure. Also these are optically isotropic materials even through strong anisotropy in their structure. The anisotropic nature increases from LaOCl to LaOI.



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Introduction

1.1 Introduction to the problem

Every day of our world is study the nature of matter which is determined from the fundamental particles like electrons and nucleons. The theory of electrons in matter is great challenge to theoretical physicists to develop the theoretical approaches and computational methods that can helpful to study the interacting system of many electrons and nuclei found in condensed matter and molecules. This is simply known as many body problem.

The many-body problem is general name for a vast category of physical problems pertaining to the properties of microscopic systems made of a large no of interacting particles like electrons

and nuclei in atoms or molecules. The many-body problem plays an important role in both quantum chemistry and condensed matter physics. So many approximations have done on quantum many body problem, and solve for eigen values and eigen states of Hamiltonian by using wave function methods and variational principles will be discussed briefly in next chapter. The Density functional theory(DFT) is quantum mechanical tool to solve many body problem by considering the electron density as fundamental parameter, rather than many-electron wave function. The Density functional theory was a successful approach, which has been used to study the ground state properties of solids. DFT has been very popular for calculations in solid state physics since the 1970s. However, DFT was not considered accurate enough for calculations in quantum chemistry until the 1990s, when the approximations used in the theory were greatly refined to better model the exchange and correlation interactions. In many cases the results of DFT calculations for solid-state systems agree quite satisfactorily with experimental data. Computational costs are relatively low, when compared to traditional methods, such as Hartree-Fock theory and its descendants based on the complicated many-electron wave function. Despite recent improvements, there are still difficulties in using density functional theory to properly describe intermolecular interactions, especially van der Waals forces (dispersion); charge transfer excitations, transition states, global potential energy surfaces and some other strongly correlated systems, and in calculations of the band gap in semiconductors and insulators.

Many of methods have been developed in DFT to study electronic structure at ground state level, one of the latest method is plane-wave pseudo-potential calculations. Cambridge Serial Total Energy Package(CASTEP) implements the latest total-energy plane-wave basis and pseudopotential techniques to allow the study of system of large size for first principles(ab initio) methods. Also to study the electronic structure of solids,to perform accurate theoretical calculations on wide

range of $3D$ solid state systems including metals, semiconductors,surfaces,polymers and ceramics. The local density approximation(LDA) predicts the ground state properties with greater sufficiency for total energy calculations based on DFT. The LDA deals with uniform electron gas i.e. it suits for slowly varying density systems. Generalized gradient approximation(GGA) is used to study the ground state properties of non uniform electron gas(i.e. in case of fast varying density systems.).

1.2 Matlockite type compounds

The rare–earth oxy halides REOX(RE=La,X=Cl,Br,I) belong to the class of ionic materials crystallizing in the primitive tetragonal PbFCl type structure(also matlockite)[1] with space group P4/nmm (D^7_{4th}, No 129)[2] . The structure is formed by layers parallel to (001) each occupied by a single kind of ion. The sequence of the layers is X-RE-O-O-RE-X where the X layers are doubly occupied with respect to the RE and O layers[3]. These compounds are ionic insulators with excess of three electros of RE atom being transferred to halide and oxygen anions. The bottom of the conduction bands are formed from the RE atom s and d states and the top of the valence bands arise from the halogen and oxygen p states[4]. These compounds are structurally anisotropic(tetragonal crystal structure) but surprisingly they show optically isotropic nature , which implies these compounds can be used as ceramic scintillators.

By knowing physical properties of these oxy halides, we have good estimation of its applications in many fields. When these oxy halides are doped with trivalent impurities ,like. Tb^{3+},Eu^{3+}, they exhibit luminescence properties[5]. The Ce-doped REO halides used in the scintillation process as radiation detectors[6]. Oxy halides of lanthanum terbium and optionally sensitized with

cerium are found to be some of the most efficient oxygen dominated phosphors.In the conversion of X-rays to visible light, These phosphors are superiors in their conversion efficiency.So they also known to us as X-ray phosphors and x-ray image converters[7]. So these new phosphors are useful in X-ray image intensifier tubes, in fluoroscopic screens, in radio graphic intensifier screens, in lamps, in cathode ray tubes.The triply ionized Eu^3+, and Tb^3+ offers the convenient opportunity for Crystal filed(c.f.) analysis of various host lattices[8]. The crystal filed analysis of Eu^3+ and Tb^3+ in the same host lattice should not show major differences. The c.f. effects in rare-earth oxy halides are studied[9].

The general chemical formula of rare earth lanthanum oxy halides is REOX(RE=La, x=Cl,Br,I.). These rare-earth oxy halides crystallizes in the primitive tetragonal structure with two molecular units or six atoms per unit cell. Rare-earth atoms(La) coordinated to four oxygen atoms and four halide atoms with C_{4v} point site symmetry.The tetragonal layer structure consists of two adjacent planes of halide ions perpendicular to the C-axis(i.e. 001plane).

$Atom$	$wyckoffsite$	x	y	z
O	2a	0	0	0
$X(Cl, Br, I)$	2c	0	1/2	u
$RE(La)$	2c	0	1/2	v

Table 1.1: REOX (RE = La; X = Cl, Br,I) crystal atomic positions

The atomic positions of different elements in the ternary LaOX(X=Cl,Br,I) compunds are La(0,0.5,v), O(0,0,0), and X(0,0.5,u), where v and u are internal parameters of La and X atoms respectively. In the present work, we are interested in understanding the electronic structure, density of states, bonding and optical properties of the above mentioned compounds using density

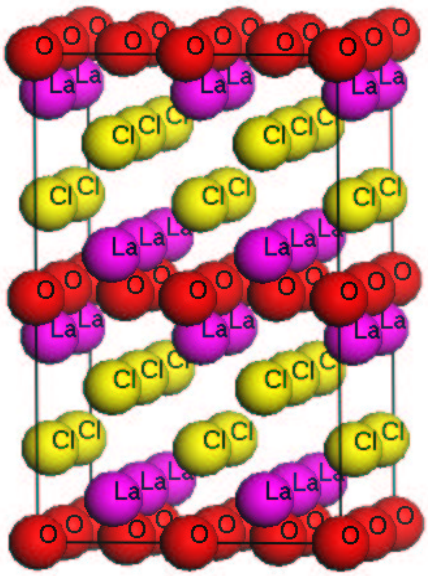

Figure 1.1: Crystal structure of matlockite type compounds

functional theory within the frame work of both local density approximation(LDA)and generalized gradient approximation(GGA). All the calculations are performed using the Cambridge Serial Total Energy Package (CASTEP) program.

The rest of the thesis is organized as follows : In chapter 2, we have discussed some theoretical methods which are necessary to perform the computations. In chapter 3, the method of computational details which includes the discussion of CASTEP program to calculate and analysis the properties of these compounds are mentioned. In chapter 4, the results are presented and discussed and finally chapter 5 summarize the results with conclusions and suggestion of future work.

2

Theoretical methods

2.1 Many-body problem

A solid is collection of heavy,positively charged(nuclei) particles and lighter,negatively charged particles(electrons). If we have N nuclei, we are dealing with a problem of N+ZN electromagnetically interacting particles. This is many-body problem, and because of particles are so light at microscopic level, quantum-mechanics is indeed: a quantum system of many-body problem.

The dynamics of time-independent non-relativistic system are governed by schrödinger equation.

$$\hat{H}|\Psi\rangle = E|\Psi\rangle \tag{2.1}$$

Where Ψ is the many electron wave function, E is energy and H is Hamiltonian of the system. The exact many-particle Hamiltonian for the system is given by

$$\hat{H} = -\sum_{i=1}^{N} \frac{\hbar^2}{2M_i} \nabla^2_{\vec{R}_i} - \sum_{i=1}^{M} \frac{\hbar^2}{2m_e} \nabla^2_{\vec{r}_i} - \frac{1}{4\pi\varepsilon_0} \sum_{i,j} \frac{e^2 Z_i}{|\vec{R}_i - \vec{r_j}|} + \frac{1}{8\pi\varepsilon_0} \sum_{i \neq j} \frac{e^2}{|\vec{r_i} - \vec{r_j}|} + \frac{1}{8\pi\varepsilon_0} \sum_{i \neq j} \frac{e^2 Z_i Z_j}{|\vec{R}_i - \vec{R}_j|} \tag{2.2}$$

The mass of the nucleus at $\vec{R}_i$ is M_i, the electrons have mass m_e and are at $\vec{r_i}$. The first term is the kinetic energy operator for the nuclei, the second for the electrons. The last three terms describe the Coulomb interaction between electrons and nuclei, between electrons and other electrons, and between nuclei and other nuclei.

The above equation is simply written in the given form

$$\hat{H} = \hat{T}_n + \hat{T}_e + \hat{V}_{en} + \hat{V}_{ee} + \hat{V}_{nn} \tag{2.3}$$

The accurate wave-functions for many electron system is extremely difficult because of correlated motion of electrons and nuclei. So a number of successful hierarchy approximations have been made to compute both the ground state i.e. the corresponding to minimum energy E, and excited state energies or corresponding eigenstates. The important objective here to solve schrödinger equation for system of multiple of electrons and nuclei.

2.2 Born - Oppenheimer approximation

A fundamental approximation is Born-Oppenheimer approximation which separates the electronic and nuclear wave functions because the mass ratio of an electron to nucleus is very small.The nuclei are much heavier and therefore much slower than the electrons.In a dynamical sense, the electrons can be regarded as particles that follow the nuclear motion adiabatically, meaning that they are "dragged" along with the nuclei without requiring a finite relaxation time.So in condensed matter physics Born-Oppenheiemer approximation is also known to be Adiabatic approximation. The nuclei do not move any more, their kinetic energy is zero and the first term in Eq.2.2 disappears.The last term in Eq.2.2 reduces to a constant. We are left with the kinetic energy of the electron gas, the potential energy due to electron-electron interactions and the potential energy of the electrons in the (now external) potential of the nuclei. We write this formally as:

$$\hat{H} = -\sum_{i=1}^{M} \frac{\hbar^2}{2m} \nabla^2_{\vec{r}_i} - \frac{1}{4\pi\varepsilon_0} \sum_{i,j} \frac{e^2 Z_i}{|\vec{R}_i - \vec{r_j}|} + \frac{1}{8\pi\varepsilon_0} \sum_{i \neq j} \frac{e^2}{|\vec{r_i} - \vec{r_j}|} \tag{2.4}$$

The above equation can be written in the given form

$$\hat{H} = \hat{T}_e + \hat{V_{ext}} + \hat{V}_{ee} \tag{2.5}$$

2.3 Hartree approximation

Although the Born-Oppenheimer approximation considerably reduces the complexity of the schrödinger equation, the resulting electronic Schrödinger equation is still extremely complex, due to the electron-electron interactions. In 1928 Hartree introduced an approximation to simplify the many-electron Hamiltonian further and is called Hartree approximation. If we ignore the antisymmetry required on the wave function(violates Pauli exclusion principle)and in case of non-interacting electrons the last term in Hamiltonian (i.e.Eq. 2.5) is ignored, then the Hamiltonian could be written as sum of independent Hamiltonians and the total wave function could be written as one-electronic wave functions. Using the adiabatic approximation,the electronic part of the Hamiltonian becomes:

$$\hat{H_{el}} = -\sum_{i=1}^{M} \frac{\hbar^2}{2m_e} \nabla^2_{\vec{r}_i} - \frac{1}{4\pi\varepsilon_0} \sum_{n=1}^{M} \sum_{i=1}^{N} \frac{e^2 Z_n}{|\vec{R_n} - \vec{r_i}|} \tag{2.6}$$

Let us define a nuclear potential, V_N, which the i^{th} electron see as

$$V_N(\vec{r_i}) = -\frac{1}{4\pi\varepsilon_0} \sum_{n=1}^{N} \frac{e^2 Z_N}{|\vec{R}_n - \vec{r}_i|} \tag{2.7}$$

one can now rewrite our simplified schrödinger equation as

$$\hat{H_{el}} = -\sum_{i=1}^{M} [\frac{\hbar^2}{2m_e} \nabla^2_{\vec{r}_i} + V_{N(\vec{r}_i)}] \tag{2.8}$$

For this simple Hamiltonian,let us write the many body wave function as

$$\Psi(\vec{r}_1, \vec{r}_2, \vec{r}_3 \dots) = \phi_1(\vec{r}_1)\phi_2(\vec{r}_2)\phi_3(\vec{r}_3) \dots \tag{2.9}$$

The above equation is known as the Hartree wave function, which is the solution of eigenvalue problem. By ignoring electron-electron terms, the Hartree approximation treats the electrons moving independently in the nuclear potential. The total energy of the system is given by the sum of eigenvalues,E_i. The individual orbitals,$\phi_i(\vec{r})$,can be determined by using the minimizing the total energy with constraint that wave function is normalized.This minimization procedure results the following the Hartree equation.

$$\left(-\frac{\hbar^2}{2m}\nabla_i^2 + V_N(\vec{r}) + \sum_{\substack{i,j=1 \\ i\neq j}}^{M} \int \frac{e^2|\phi_j(\vec{r'})|^2}{|\vec{r'}-\vec{r}|} d^3r' \right) \phi_i(r) = E_i\phi_i(r) \tag{2.10}$$

The above equation is written in the following form

$$H\phi_i(\vec{r}) = E_i\phi_i(\vec{r}) \tag{2.11}$$

The Hamiltonian for each particle can be written in the form $H = -\frac{\hbar^2}{2m}\nabla_i^2 + V_N + W_H$, where W_H is Hartree potential

$$W_H = \sum_{\substack{i,j=1 \\ i\neq j}}^{M} \int \frac{e^2|\phi_j(\vec{r'})|^2}{|\vec{r'}-\vec{r}|} d^3r' \tag{2.12}$$

The self consistent filed(SCF) iteration procedure is necessary for applying Hartree approximation to the many electron system. One could be begin with some basis set of orbital, and computes iteratively new sets by solving the Eq. 2.10, using the most current set $\phi_j^{'}$s for $j \neq i$. This iteration is continued until the set of $\phi_i^{'}$ s is self-consistent.

2.4 Hartee-Fock approximation

The Hartree-Fock (HF)approximation follows directly from what was done above the Hartree approximation, only taking into account the need for antisymmetry states for fermions $i.e$ if any two fermions exchanged, the wave function must change sign. Now the wave function includes both spatial part and spin part. In the Hartree approximation, the many-electron wave function is antisymmetric and chosen to be Slater determinant of mutually orthonormal single-particle states. we use $\vec{x_i}$ to denote the complete set of coordinates associated with the i-th electron, comprised of spatial $\vec{r_i}$ and spin $\vec{s_i}$ parts. Throughout this thesis, the single particle state will be expressed as $\phi_i(x) \equiv \phi(r)\sigma(s)$. With this convention, the determinantal wave function may be written :

$$\Psi(\vec{x_1}, \vec{x_2}, ..., \vec{x_N}) = \frac{1}{\sqrt{N!}} \begin{pmatrix} \phi_1(\vec{x_1}) & \phi_1(\vec{x_2}) & . & . & . & \phi_1(\vec{x_N}) \\ \phi_2(\vec{x_1}) & \phi_2(\vec{x_2}) & . & . & . & \phi_2(\vec{x_N}) \\ . & . & . & . & . & . \\ . & . & . & . & . & . \\ \phi_N(\vec{x_1}) & \phi_N(\vec{x_2}) & . & . & . & \phi_N(\vec{x_N}) \end{pmatrix} \tag{2.13}$$

An interesting consequence of this functional form is that electrons are indistinguishable. if the two electrons are occupies same orbit at same time(i.e. x_i=x_j), then the wave function will vanishes because of two rows of determinant are identical.

The spin of orbitals can be derived from Hartree-Fock equations which are the approximate solution for ground state many-electron wave function. The HF energy which one does'nt include correlation contributions. So define the correlation energy as the difference between exact total energy and HF energy of many-electon system as: $E_{corr} = E_{exact} - E_{HF}$.

There is one argument, The wave function based methods are not much satisfactory for many atoms to study electronic structure calculations. Computationally these are very expensive. There is an alternative other approach which is based on Density functional theory.

2.5 Density functional theory

Density Functional Theory (DFT) is a ground-state theory in which the emphasis is on the charge density as the relevant physical quantity. DFT has proved to be highly successful in describing structural and electronic properties in a vast class of materials, ranging from atoms and molecules to simple crystals to complex extended systems (including glasses and liquids). Furthermore DFT is computationally very simple. For these reasons DFT has become a powerful tool in first-principles calculations aimed at describing or even predicting properties of molecular and condensed matter systems. Hohenberg-Kohn developed density functional theory formulation introducing The electron density as fundamental parameter , which is given by

$$n(\vec{r}) = N \int \dots \int |\Psi(\vec{r}_1, \vec{r}_2, \vec{r}_3 \dots \vec{r}_N)|^2 d\vec{r}_1, d\vec{r}_2, d\vec{r}_3 \dots d\vec{r}_N \tag{2.14}$$

2.5.1 Thomas Fermi model

Thomas (1927), and independently Fermi (1928), gave a prescription for calculating the energy of an electronic system exclusively in terms of electronic density $n(\vec{r})$.Dirac improved on the theory

by including a term describing the exchange energy[10] . The total energy of the system is written

$$E_{TF} = C_1 \int n(\mathbf{r})^{5/3} d^3r + \int V_{ext}(\mathbf{r}) n(\mathbf{r}) d^3r + C_2 \int n(\mathbf{r})^{4/3} d^3r + \frac{1}{2} \int \frac{n(\mathbf{r}) n(\mathbf{r}')}{\mathbf{r} - \mathbf{r}'} d^3r d^3r' \quad (2.15)$$

where $C_1 = (3/10)(3\pi^2)^{2/3}$ and $-(3/4)(3/\pi)^{1/3}$.

The first term describes the kinetic energy, then follows the electron-nuclei interaction, the exchange and finally the Hartree term. In the expression above, the kinetic energy and correlation terms of the many-electron system is calculated assuming a homogenous electron gas (HEG). The HEG is of fundamental importance in DFT, and thus we repeat the definition of it here and also the definition of the often used parameter r_s The density n of the homogenous electron gas is

$$n = \frac{N}{\Omega} \quad (2.16)$$

where N is the total number of electrons in the volume . The electron density is often expressed using the parameter r_s, defined as

$$r_s = (\frac{3}{4\pi n})^{1/3} \quad (2.17)$$

Here, r_s is the radius of a sphere containing exactly one electron. The larger r_s is, the lower is the electron density.The Thomas-Fermi theory failed to produce any quantitatively impressive results, but the basic idea using the electron charge density as the basic variable instead of the wave function turned out to be most fruitful. Finally, we note that in (2.15), all terms are integrals of the charge density, i.e., they are functionals of the charge density.

2.5.2 The Hohenberg-Kohn (HK)theorem

The theorems initially formulated by Hohenberg and Kohn[11] constitute the theoretical basis of DFT. Let us consider a system of N interacting electrons in a non-degenerate ground state associated with an external potential V(**r**). The hamiltonian of the system is given by

$$\hat{H} = \hat{T} + \hat{V} + \hat{W} \tag{2.18}$$

Where the $\hat{T}$ is kinetic energy operator , $\hat{W}$ represents the electron electron interaction operator and $\hat{V}$ denotes the external potential operator.

Lemma 1. *The ground state density, n(**r**), uniquely determines the potential V(**r**), within an additive constant.*

The proof of this theorem not discussed here, From the result of this theorem we can conclude that the total energy of the system is a functional of the density, and is given by

$$E[n(\mathbf{r})] =< \Psi|\hat{H}|\Psi >= F[n(\mathbf{r})] + \int V(\mathbf{r})\, n(\mathbf{r}) dr \tag{2.19}$$

Where $F[n(\mathbf{r})]$ represents $< \Psi|\hat{T} + \hat{W}|\Psi >$. The energy functional can be expressed as

$$E(n(\mathbf{r})) = F[n(\mathbf{r})] + V[n(\mathbf{r})] = T[n(\mathbf{r})] + V[n(\mathbf{r})] + W[n(\mathbf{r})]. \tag{2.20}$$

Therefore, the first theorem can be summarized by saying that energy is as functional of density. The second theorem establishes the variational principle:

Lemma 2. *The ground state energy can be obtained from variational principle : The density minimizes the total energy is the exact ground state density.*

According to theorem 1, a system with ground state density n_0(**r**) determines the uniquely its own external potential V(**r**) and the ground state function Ψ_0

$$E[n_0(\mathbf{r})] =< \Psi_0|\hat{H}|\Psi_0 >= F[n_0(\mathbf{r})] + \int V(\mathbf{r})n_0(\mathbf{r})dr \tag{2.21}$$

Thus the energy given in eq 2.21 in terms of HK functional evaluated for the correct ground state density n_0(**r**).

The second theorem summarizes , if the functional F[n(**r**)] was known, then by minimizing the total energy of the system, with respect to variations in the density function n_0(**r**),one would find the exact ground state density and energy. Note that the functional only determines the ground state properties; it does not provide any guidance concerning excited states.

2.5.3 Kohn-Sham equations

The Hohenberg-Kohn theorem offers no practical guide to the explicit construction of the F[n(**r**)] universal functional. For this purpose one still has to face the full intricacies of the many-body problem. Although there are some energy functionals for Coulomb systems derived with the theory of the homogeneous electron gas or in other more elaborated approaches, the situation cannot be considered satisfactory. Only with the approach introduced by Kohn and Sham[12] has been able to calculate (not only) ground state properties of many-particle Coulomb systems with great accuracy.

From the eq.2.14 , the energy functional contains three terms: the kinetic energy T[n(**r**)] , the external potential V[n(**r**)] and the electron-electron interaction W[n(**r**)]. The kinetic and electron-electron functional are unknown. Kohn and Sham introduced a fictitious system of N noninteracting electrons to be described by the single-particle orbitals ϕ_i that appear in the Slater determinant. In this system the one-particle density known from orbitals:

$$n(\mathbf{r}) = \sum_i |\phi_i(\mathbf{r})|^2 \tag{2.22}$$

The energy functional can be taken following form

$$E[n(\mathbf{r})] = T^S[n(\mathbf{r})] + \frac{e^2}{2}\int\int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}drdr' + \int V(\mathbf{r})\, n(\mathbf{r})dr + E^{XC}[n(\mathbf{r})] \tag{2.23}$$

In this expression, the first term represents the kinetic energy in the Slater determinant(i.e. this is not the true kinetic energy but is that of a system of noninteracting electrons, and hence the superscipt S). Since the fictitious particles are non-interacting, the kinetic energy can be known exactly, and take the following form

$$T^S[n(\mathbf{r})] = \sum_i < \phi_i| -\frac{\hbar^2}{2m}\nabla_r^2|\phi_i > \tag{2.24}$$

The second term $V_H[n(\mathbf{r})]$ in Eqs. 2.23 is the bare Coulomb interaction(this term is separated out from the electron-electron interaction term $V_{ee}[n(\mathbf{r})]$. The last term in Eqs. 2.24 denotes the exchange-correlation term, which is simply the sum of the error made in using a non-interacting kinetic energy and the error made in treating the electron-electron interaction classically, and is expressed as

$$E^{XC}[n(\mathbf{r})] = (T[n(\mathbf{r})] - T^S[n(\mathbf{r})]) + (V_{ee}[n(\mathbf{r})] - V_H[n(\mathbf{r})]) \tag{2.25}$$

Applying variational principle to Eqn.2.23 , we will arrive the single particle equation is also famous known to as Kohn-Sham equation following form through variational argument,

$$\left(-\frac{\hbar^2}{2m}\nabla_r^2 + V(\mathbf{r}) + e^2\int\frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}dr' + V_{XC}(n(\mathbf{r})\right)\phi_i(r) = E_i\phi_i(r) \tag{2.26}$$

Here, a local multiplicative potential is introduced,which is the functional derivative of the exchange correlation energy with charge density

$$V_{XC}[n(\mathbf{r})] = \frac{\delta E^{XC}[n(\mathbf{r})]}{\delta n(\mathbf{r})} \tag{2.27}$$

The single particle Eqs. 2.26 is the well known Kohn-Sham equation with the resulting density n(**r**) and total energy E given by Eqs. 2.20 and Eqs. 2.23. The single particle orbitals ϕ_i that are their solutions are called Kohn-Sham orbitals. Kohn-Sham equation describes the behavior of non-interacting "electrons" in an effective local potential, which can be expressed as

$$V^{eff}[\mathbf{r}, n(\mathbf{r})] = V(\mathbf{r}) + e^2\int\frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}dr' + V_{XC}(n(\mathbf{r})) \tag{2.28}$$

The effective potential is a function of the density, and hence depends on all the single-particle states. KS results from the Hohenberg-Kohn theorems that the ground state density uniquely determines the potential at the minimum(except for a trivial constant), so that there is a unique KS potential V^{eff}(**r**)at min = V_{KS}(**r**) associated with any given interacting electron system. We will need to solve these equations by iteration until we reach self-consistency, but this is not a significant problem. For the iteration, an initial charge density is needed. To obtain the charge density, an initial guess to the Kohn-Sham orbitals is needed. This initial guess can be obtained from a set of basis functions whereby the coefficients of expansion of the basis functions can be optimized.

A more pressing issue is the exact form of E_{XC}[n(**r**)] . In the following section I will discuss the exchange correlation functionals.

2.5.4 Exchange correlation functionals

The Kohn-Sham scheme described above was exact: apart from the preceding Born-Oppenheimer approximation, no other approximations were made. But we neglected so far the fact that we do not know the exchange-correlation functional. It is here that approximations enter our theory. A widely used approximation called the Local Density Approximation (LDA) is to postulate that the exchange-correlation functional has the following form:

$$E_{xc}^{LDA} = \int n(\vec{r})\ \epsilon_{xc}[n(\vec{r})]\ d\vec{r} \tag{2.29}$$

Exchange energy for the homogeneous electron gas can be separated into exchange and correlational contributions:

$$\epsilon_{xc}[n(\vec{r})] = \epsilon_X[n(\vec{r})] + \epsilon_c[n(\vec{r})] \tag{2.30}$$

While $\epsilon_x[n(\vec{r})]$ is analytic function of $n(\vec{r})$

$$\epsilon_x[n(\vec{r})] = -\frac{3}{4}e^2(\frac{3}{\pi}n(\vec{r}))^{\frac{1}{3}} \tag{2.31}$$

The functional form for the correlation energy density $\epsilon_c[n(\vec{r})]$ is unknown and has been simulated for the homogeneous electron gas in numerical quantum Monte Carlo calculations which yield essentially exact results (Ceperley and Alder, 1980)[13]. Various approaches, using different analytic forms for $\epsilon_c[n(\vec{r})]$, have generated several LDAs for the correlation functional, including:

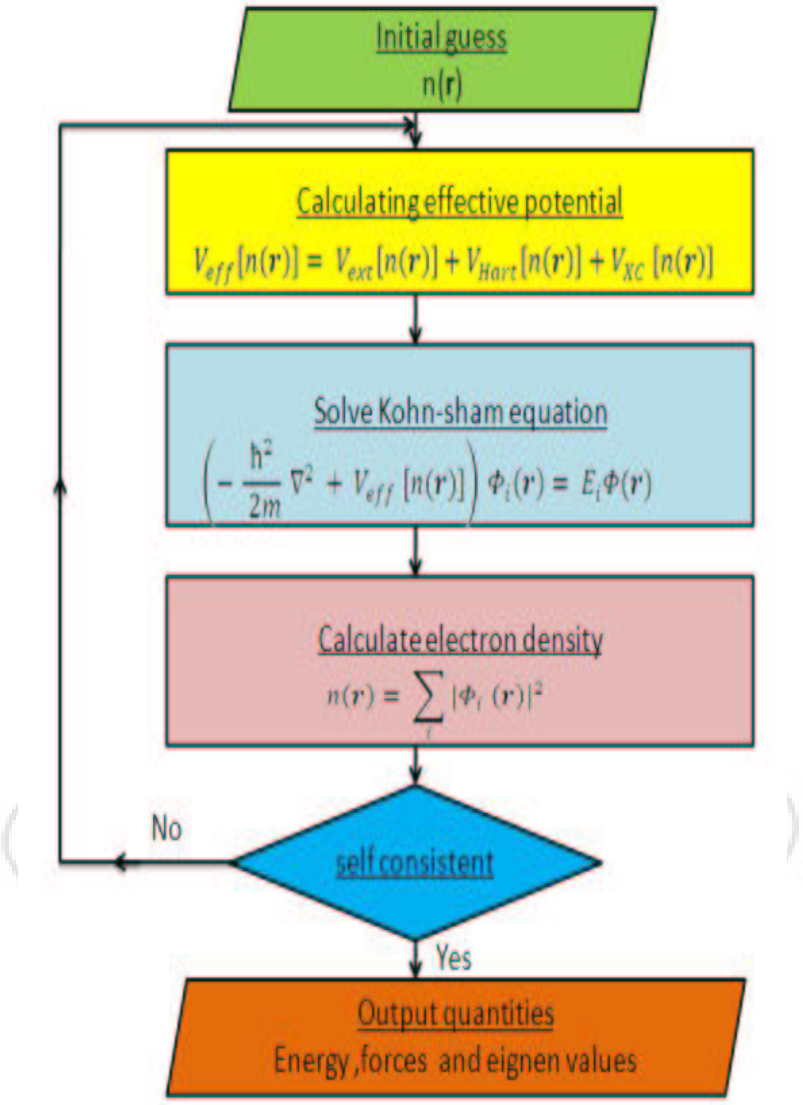

Figure 2.1: DFT algorithm

Vosko-Wilk-Nusair (VWN)[14], Perdew-Zunger (PZ81)[15], Cole-Perdew (CP)[16] and Perdew-Wang (PW92)[17]. All of these yield similar results in practice and are collectively referred to as LDA functionals. The LDA has proven to be a remarkably fruitful approximation. Properties such as structure, vibrational frequencies, elastic moduli and phase stability (of similar structures) are described reliably for many systems.

The exchange correlational energy $E_{xc}[n(\vec{r})]$ depends on $n(\vec{r})$ in locally but not like non-locally fashion. The improved functionals have been introduced recently over LDA which depends not only on density $n(\vec{r})$, but also on its gradients[18, 19]. These expansions tend to work better for some cases, but still represent a local approximation to the exchange-correlation functional. The simple General gradient approximation is postulated better exchange correlational functional over LDA in case of fast varying density $n(\vec{r})$ and the functional form is given

$$E_{xc}[n(\vec{r})] = E_{xc}[n(\vec{r}), \nabla n(\vec{r})] \tag{2.32}$$

Some of the functionals are semi-empirical, where the atomic energies(from experimental data) are used in their derivation. The most widely used functional is The Perdew-Wang (PW91) functional from first principles.

3

Computational Details

In the present work, we have used Cambridge Series of Total Energy Package(CASTEP), which is originally developed by Payne and co-workers in the late 1980s and early 1990s. The CASTEP programme[20] is a first principles quantum mechanical code for performing electronic structure calculations, within the density functional formalism based on plane-wave pseudo potential method, it can be used to simulate a wide range of materials including crystalline solids, surfaces, molecules, liquids and amorphous materials; the properties of any material that can be thought of as an assembly of nuclei and electrons can be calculated with the only limitation being the finite speed and memory of the computers being used. This approach to simulation is extremely ambitious, given that the aim is to use no experimental (empirical) data, but to rely purely on quantum mechanics. This code quickly became a hinderance to research therefore from 1999 CASTEP has been completely redesigned and a new modular Fortran 90 code written. Due to the new code

design, new methods and technologies are quickly and easily added to CASTEP, allowing users to rapidly take advantage of such developments. In addition, the new CASTEP code has been designed for parallel computers from the very beginning, allowing much larger problems to be tackled.

3.1 Planewave pseudopotential(PWPP) method

Plane wave pseudo-potential methods have been widely used for electronic structure calculations[21] Pseudopotential theory allows one to focus on the chemically active valence electrons by replacing the strong ionic potential $v_{ion}(\mathbf{r}) = z/\mathbf{r}$ by a weak pseudopotential $v_{pseudo}(\mathbf{r})$ which effectively reproduces the effects of the core electrons on the valence states. This approximation significantly reduces the number of eigen pairs to be handled, especially for heavier elements and approximation is well understood and gives a number of computational advantages:

- The pseudopotential is much weaker in the core region than the true Coulomb potential of the nucleus, and it does not have a singularity at the position of the nucleus.
- The resulting pseudo wave functions $\psi_{pseudo}(\mathbf{r})$ are smooth and node less in the core region.
- Both pseudopotentials and pseudowave functions can be efficiently represented using a plane-wave basis set
- Relativistic effects, which are mainly due to core electrons, can be included in the pseudo potential.

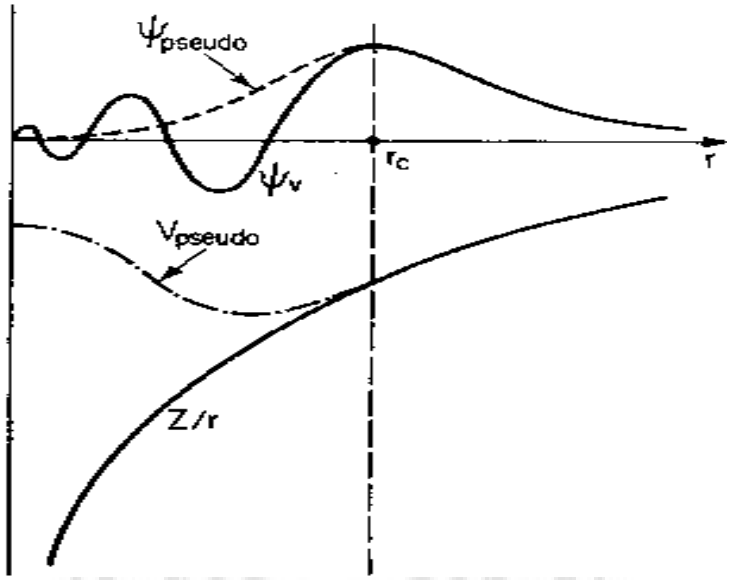

Figure 3.1: Schematic diagram for pseudo potential

The all-electron wave functions $\psi_v(r)$ are identical outside a chosen cutoff radius r_c and so exhibit the same scattering properties, but the pseudo wave functions $\psi_{pseudo}(r)$ does not possess the nodal structure that cause the oscillations inside r_c which means they can now be described with a reasonable number of planewaves. A schematic illustration of the pseudopotential concept is shown in Fig.3.1

Also, plane waves have both physical and computational drawbacks. In a plane wave representation the boundary conditions must be periodic. If one wants to study a non periodic system such as a molecule or a cluster, nontrivial precautions must be taken to reproduce the vacuum accurately, since spurious interactions between replicated images of the system must be avoided. During the last decade there has been increasing interest in developing real-space pseudopotential methods. There is no need to introduce artificial periodicity in dealing with non periodic systems and these real-space methods are inherently local, which facilitates implementation on parallel computers.

In short, real-space methods not only share the main advantages of plane wave representations, but they can also have improved scaling and they can be easily parallelized, which makes them highly attractive for computation of the electronic ground states of large, complex systems. Actually we represent the pseudo potential in reciprocal space during calculations. But CASTEP has both real and reciprocal space representation.

Considerable effort has gone into improving the pseudo potentials used. One drawback of pseudo potentials is that the ionic potential is angular momentum dependent or nonlocal, and it is computationally expensive to determine the angular momentum components of each electronic wave function around every atom. Techniques have been developed to optimize pseudo potentials[22, 23] to reduce the size of the plane-wave basis set. The Kleinman Bylander scheme[24]uses a separable form of the potential to reduce the number of nonlocal projections that have to be performed. By performing these projections in real space and exploiting the finite range of the non locality around every atom, the computational cost associated with the use of nonlocal pseudo potentials has been further reduced [25].

3.1.1 Norm-conserving and Ultra-soft pseudopotentials

Norm-conserving pseudopotentials were first introduced and used by Hamann, Schl*ü*ter, and Chiang.[26] In their scheme, inside some core radius, the all-electron (AE) wave function is replaced by a soft nodeless pseudo- (PS) wave function, with the crucial restriction that the PS wave function must have the same norm as the all-electron wave function within the chosen core radius; outside the core radius the PS and AE wave function are identical. It is now well established that good transferability requires a core radius around the outermost maximum of the AE wave func-

tion, because only then the charge distribution and moments of the AE wave functions are well reproduced by the PS wave functions[27] . Therefore, for elements with strongly localized orbitals (like first-row, 3d, and rare-earth elements) the resulting pseudopotentials require a large plane-wave basis set. To work around this, compromises are often made by increasing the core radius significantly beyond the outermost maximum in the AE wave function. But this is usually not a satisfactory solution because the transferability is always adversely affected when the core radius is increased, and for any new chemical environment, additional tests are required to establish the reliability of such soft PP's.

An elegant solution to this problem was proposed by Vanderbilt.[28] In his method, the norm-conservation constraint is relaxed and to make up for the resulting charge deficit, localized atom-centered augmentation charges are introduced. These augmentation charges are defined as the charge density difference between the AE and the PS wave function, but for convenience they are pseudized to allow an efficient treatment of the augmentation charges on a regular grid. The core radius of the pseudopotential can now be chosen around half the nearest-neighbor distance independent of the position of the maximum of the AE wave function . Only for the augmentation charges a small cutoff radius must be used to restore the moments and the charge distribution of the AE wave function accurately [29]). The pseudized augmentation charges are usually treated on a regular grid in real space, which is not necessarily the same as the one used for the representation of the wave functions.

The accurate Norm conserving pseudopotentials are extremely hard to solve the potentials for transition metals and row elements(C,O,N etc.). Norm conserving potentials in CASTEP are generated using the kinetic energy optimization scheme developed by Lin and Lee. Ultrasoft pseudopotentials as put forward by Vanderbilt is that the relaxation of the norm-conserving condition

can be used to generate much softer potentials, i.e., the basis set size can be made substantially smaller. In this scheme the pseudo-wave functions can be made softer within the core region, so that the cutoff energy can be reduced dramatically. The pseudopatriotic transferability is maintained by introducing a generalized orthonormality condition.

Here we are using plane-wave pseudo-potential which is implemented in CASTEP program to study electronic structure and ground state properties, because of plane waves which are easy to express in mathematical form in reciprocal space and plane waves do not depend on atomic positions.

The physical properties of materials that can be studied and calculated using CASTEP which includes calculation total energy , forces and stresses. And also calculate electronic charge densities, orbitals , electrostatic potentials, band structure, total and partial electronic density of states, Mulliken population analysis, and optical properties (such as reflectivity, absorption, refractive index, dielectric function), subject to the usual DFT band gap considerations.

The well known LDA and GGA exchange correlational functionals are included (such as the PW91, PBE and RPBE functionals).

4

Results and discussion

The rare-earth oxy halides REOX crystalize in the primitive tetragonal structure with two molecules or six atoms per unit cell. The O atoms occupy Wyckoff position 2a and the RE and X atoms are at the position 2c, which depends on the internal parameters v and u. These two parameters are obtained by relaxing the atomic positions in the force of direction and subsequently by lattice optimization. The Broyden-Flecter-Goldgarb-Shanno (BFGS) minimization scheme was used in geometry optimization. The exchange correlation potential were treated within both the LDA and GGA (PBE) developed by Ceperley and Alder, parameterized by Perdew and Zunger[31, 30] and Perdew , Burke and Ernzerhof [32] respectively. For each of these compounds the following plane wave basis orbitals were used La: $5s^2$, $5p^6$, $5d^1$,$6s^2$; O : $2s^2$, $2p^4$; Cl : $3s^2$, $3p^5$ Br : $4s^2$, $4p^5$ I : $5s^2$, $5p^5$. To confirm the convergence of the calculations for the Brillouin-zone sampling, we tested the dependence of the total energy on the plane wave cut-off energy and the

k-mesh according to the Monkhorst-Pack grid scheme[33]. It is found that the cutoff energy for LaOX(X = Cl, Br, I) is 740 eV and k-mesh are 10x10x8, 11x11x8, and 11x11x8 respectively. The change in total energy is minimum, so we finally choose these cut-off energy and k-mesh for the further calculations. The self consistent convergence of the total energy is $5x10^{-7}$eV/atom and the maximum force on the atom is found to be 0.01 eV/Å. The calculated total energies are fitted to Birch-murnaghan equation of state[34] to obtain bulk modulus and its pressure derivative. In the present work, we perform structural optimization for unit cell, atomic positions of the matlockite type compounds LaOCl, LaOBr and LaOI based on the density functional theory using CASTEP program. The calculated lattice parameters and internal parameters is good agreement with experimental results. The calculated ground state properties for both LDA and GGA are tabulated in table 1.

Generally LDA underestimates the volume where as GGA overestimates the same. we also found the similar behavior in our calculations. The volume of given compounds increases from oxychloride to oxyiodide in both cases LDA and GGA, because of increasing in atomic size of halogen atom. Since the bulk modulus is inversely proportional to the volume, Indeed the bulk modulus and pressure derivative for given compounds is decreases while going from oxychloride to oxyiodide.

Here, we calculated band structure, density of states, bonding and optical properties of following rare-earth oxy halides. Since we have now all compounds are iso structural, so we can expect all the properties mentioned earlier for these oxyhalides are similar.

Table 4.1: The calculated lattice constants(a, c in $\mathring{A}$),Volume(V, in $\mathring{A}^3$) fractional coordinates(u, v), Bulk modulus (B, in GPa) and its pressure derivative ($B_0^{'}$), Band gap (E_g, in eV) of LaOX(X = Cl, Br, I) compounds along with the calculated and experimental results.

Compound	Method	a	c	V	u	v	B_0	B_0'	E_g
LaOCl	LDA	4.1087	6.7909	114.6400	0.6278	0.1796	105.930	4.5213	3.81
	GGA	4.1893	6.9865	122.6147	0.6276	0.1755	87.881	4.3129	4.13
	Expt.	4.1190	6.8830	116.7781	0.6350	0.1780			
LaOBr	LDA	4.1554	7.2612	125.3817	0.6316	0.1657	97.038	4.5408	3.58
	GGA	4.2208	7.5066	133.7312	0.6345	0.1622	80.773	4.3270	3.88
	Expt.	4.1590	7.3920	127.8615	0.6350	0.1640			
LaOI	LDA	4.1351	8.9078	152.3150	0.6593	0.1352	78.832	4.5508	3.06
	GGA	4.2092	9.1278	161.7205	0.6641	0.1321	65.479	4.3461	3.20
	Expt.	4.1440	9.1260	156.7184	0.6600	0.1350			

4.1 Band structure calculations of REOX

The band structure for LaOCl is shown in Fig 4.1. It is clear from the band structure LaOCl is a wide and direct band gap insulator. The contributions of which electronic states for valance band and conduction band can be known by their density of states(DOS) and partial DOS of individual atoms. The total DOS and PDOS of LaOCl shown in Fig. 4.2. We can observe from density of states of rare-earth atom states having less contribution from -3.5 eV to Fermi level, which implies the rare-earth atom shows electron-donor character in that composition. The states near the Fermi level contributed from the 2p, 3p states of oxygen and chlorine respectively. Above the Fermi level the d-states of rare-earth atom plays dominant role in contributing for conduction band and very

less contribution from s-states of O and Cl atoms.

The calculated band structure for LaOBr is shown in Fig 4.3., which is similar to LaOCl band structure. From Fig. 4.3 we can clearly observed that it is a direct band gap insulator along Γ direction. In this compound the contributions electronic states from rare earth atom is less for valance bond. The states near by the Fermi level from -3.5 eV to 0 eV are due to the 2p,4p states of oxygen and bromine atoms below the Fermi level. For the conduction band above the Fermi level the contributions from s and d-states of rare earth (La) atom. we observed the states near by Fermi level ,have small overlapping between Br and O atoms leads to existence of covalent nature.

Similarly electronic band structure of LaOI shown in Fig.4.5. Here, also we can observe the direct band gap occur at Γ point as like in LaOCl and LaOBr. We can observe from density of states of rare-earth atom states having less contribution from -3.5 eV to Fermi level and the peaks of DOS at the Fermi level coming from the p-states of halogen and oxygen. Above the Fermi level the d-states of rare-earth atom plays dominant role in contributing for conduction band and very less contribution from s-states of all atoms. The covalent nature increases here, because of the strength of overlapping between La and O atoms are more rather than LaOCl and LaOBr compounds.

The band gap value decreases from oxychloride to oxyiodide because of electro-negativity of halide which is decreases from chlorine to iodine. Since the atomic size is increase with decreasing electronegativity , also increasing ionization energy. Here we mentioned the electro negativity of elements of oxyhalide compounds in Pauling units.

La : 1.1 , O : 3.44 , Cl : 3.16 , Br : 2.96, I : 2.66 .

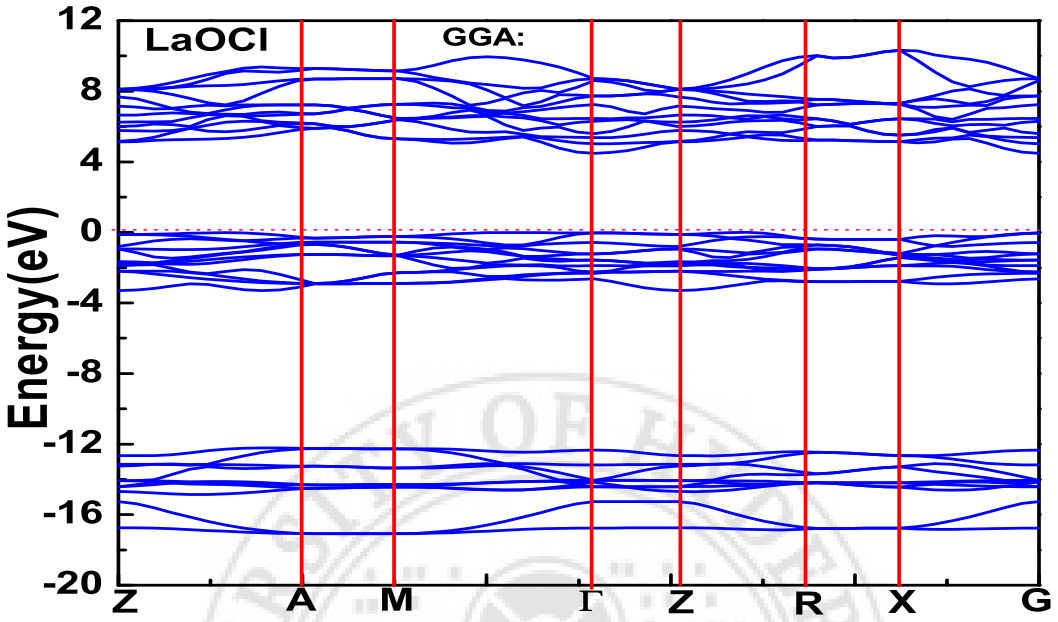

Figure 4.1: Band structure of LaOCl

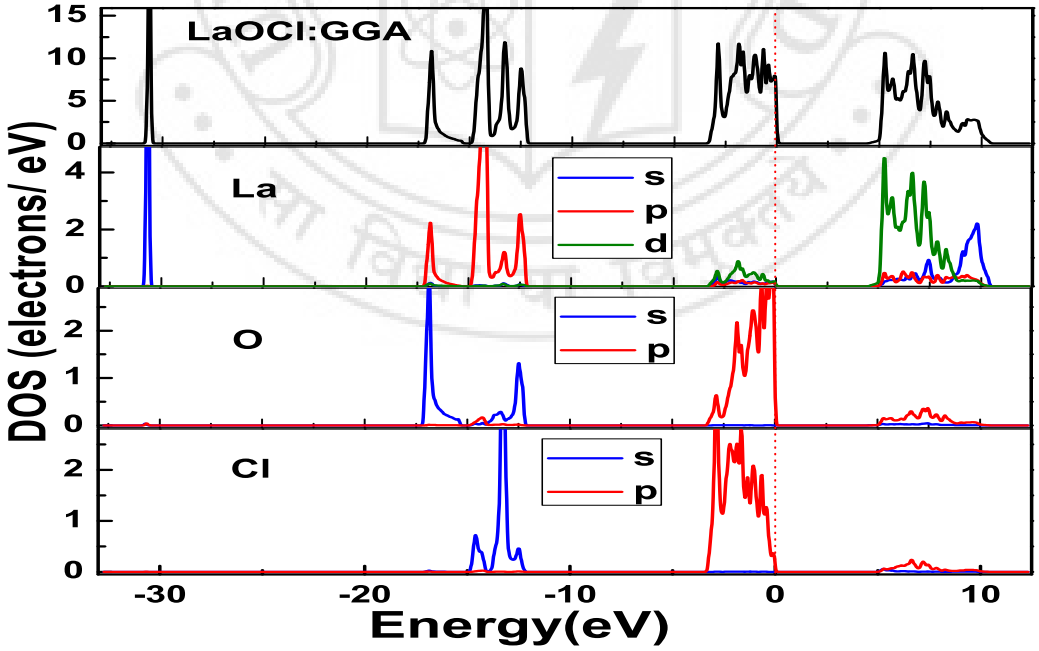

Figure 4.2: Density of states of LaOCl

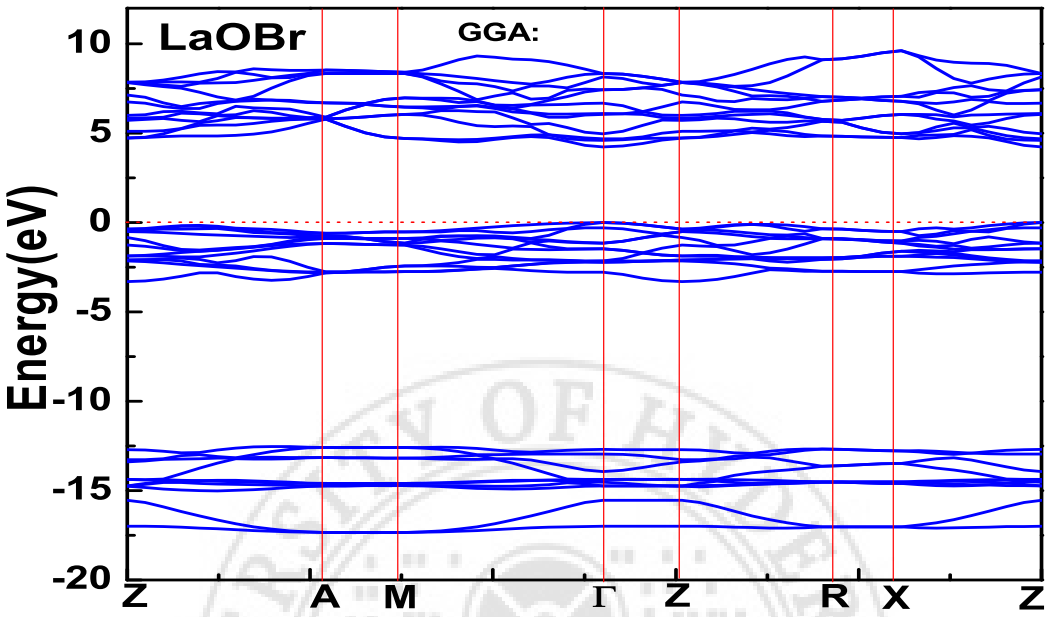

Figure 4.3: Band structure of LaOBr

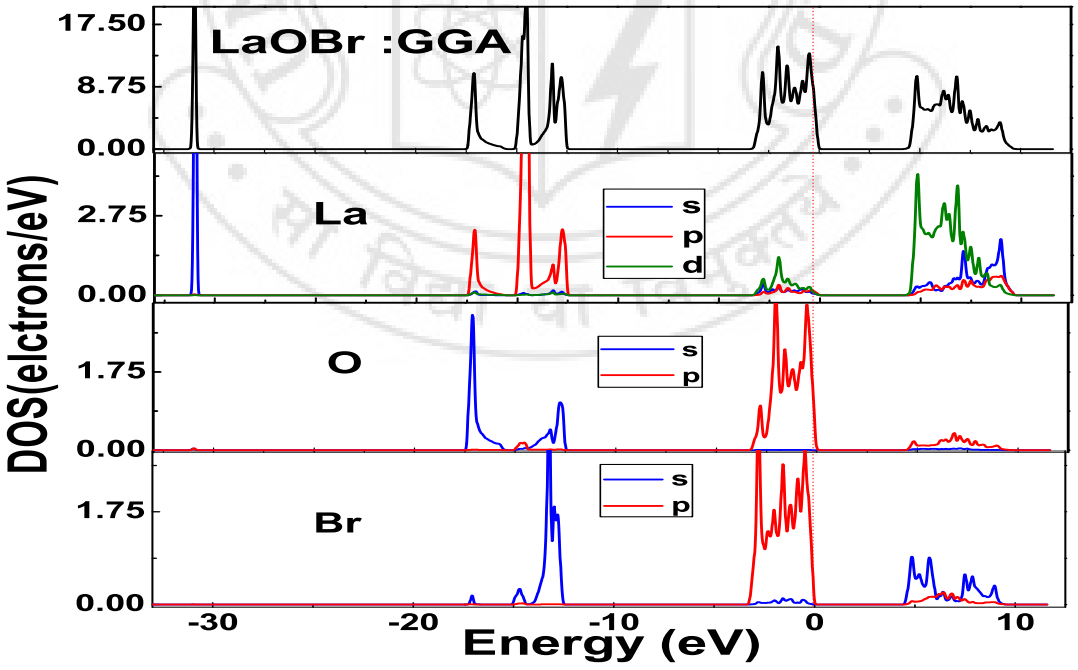

Figure 4.4: Density of states of LaOBr

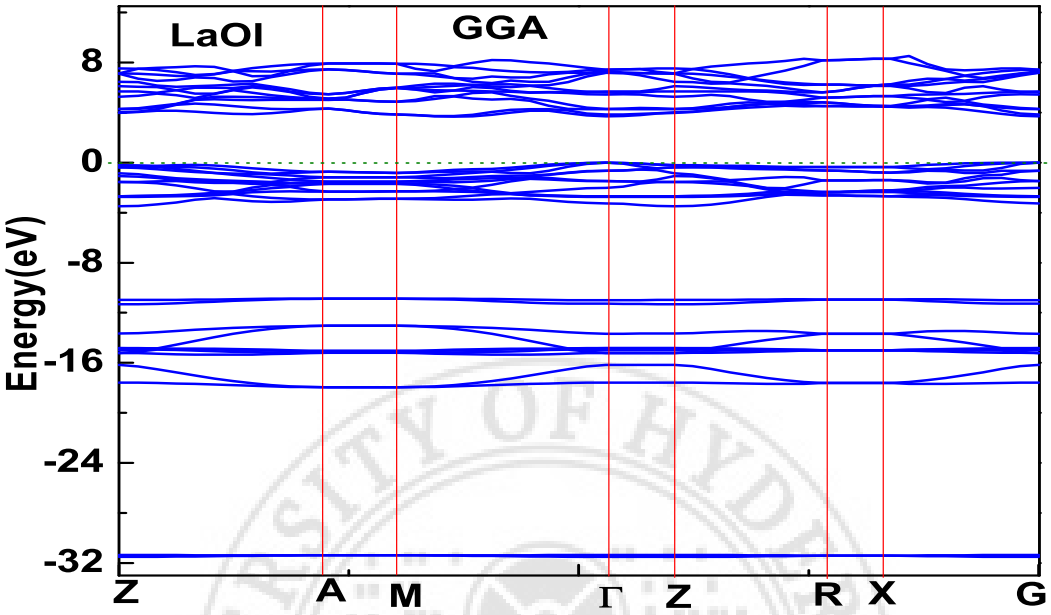

Figure 4.5: Band structure of LaOI

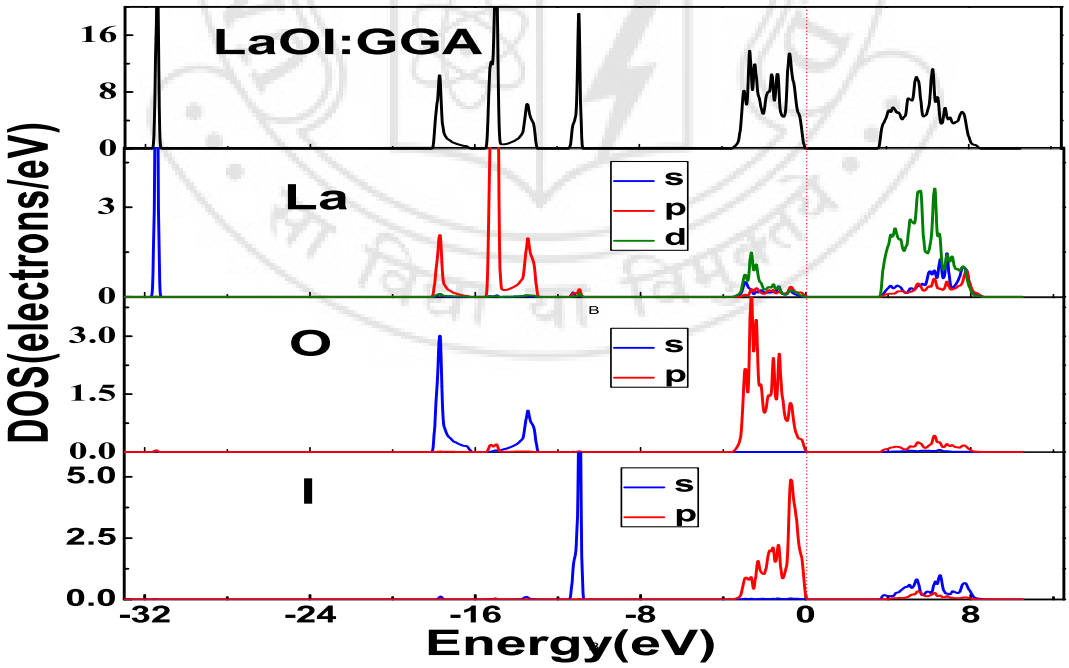

Figure 4.6: Density of states of LaOI

The softness of LaOX compounds increases from X=Cl to X=Br to X=I, due to bulk modulus of LaOX decreases from oxychloride to oxyiodide.

4.2 Optical properties

The optical properties of solids that are due to electronic transitions. In general, the difference in the propagation of an electromagnetic wave through vacuum and some other material can be described by a complex refractive index, $N = n + ik$. However, when performing calculations of optical properties it is common to evaluate the complex dielectric constant and then express other properties in terms of it. The complex dielectric constant, $\epsilon(\omega)$, is given by

$$\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega) = N^2 \tag{4.1}$$

and hence the relation between the real and imaginary parts of the refractive index and dielectric constant is $\epsilon_1 = n^2 - k^2, \epsilon_2 = 2nk$.

CASTEP calculates the imaginary part of the dielectric constant, which is given by

$$\epsilon_2\left(\mathbf{q} \to \mathbf{O}_{\hat{u},\bar{h}\omega}\right) = \frac{2e^2\pi}{\Omega\epsilon_0} \sum_{k,v,c} |\langle\psi_k^c|\hat{u}.r|\psi_k^v\rangle|^2 \delta\left(E_k^c - E_k^v - E\right) \tag{4.2}$$

where u is the vector defining the polarization of the incident electric field.
This expression is similar to Fermi's Golden rule for time dependent perturbations, and $\epsilon_2(\omega)$ can be thought of as detailing the real transitions between occupied and unoccupied electronic states. Since the dielectric constant describes a causal response, the real and imaginary parts are linked by

a Kramers-Kronig transform. This transform is used to obtain the real part of the dielectric function, $\epsilon(\omega)$. $\epsilon^{\perp}(\omega)$ and $\epsilon^{\parallel}(\omega)$ are complex functions having real and imaginary parts. We calculate the imaginary parts from the band structure. The real parts $\epsilon^{\perp}(\omega)$ and $\epsilon^{\parallel}(\omega)$ of the frequency-dependent dielectric function can be derived from the imaginary part using the KramersKronig relations[35].

The calculated optical refractive indices of the three compounds are shown in Fig.4.7 ,4.8 and 4.9. The usual trend toward higher refractive index with lower band gap is followed going from X =Cl to X=Br to X=I. The real and imaginary parts of the refractive index, n and k, for LaOX(X = Cl, Br, and I) where n starts from y-axis shown as above curve and k starts from zero energy which is shown in the bottom curve. The extinction coefficient k rises up at about 4.13 eV, 3.88 eV and 3.20 eV eV for LaOCl,LaOBr and LaOI respectively and these values are band-gap energy of LaOX(X = Cl, Br, and I). The calculated zero energy($\lambda = \infty$) direction averaged refractive indices are 1.98,2.08 and 2.155 for X = Cl, Br, and I.

These are at the level of the computational uncertainty. In any case, as may be seen, the trend toward weak optical anisotropy in heavy halides extends to the LaOX compounds, and in particular the optical anisotropy is very weak. Therefore, in spite of the strong anisotropy of the structure, we find nearly isotropic optical properties.

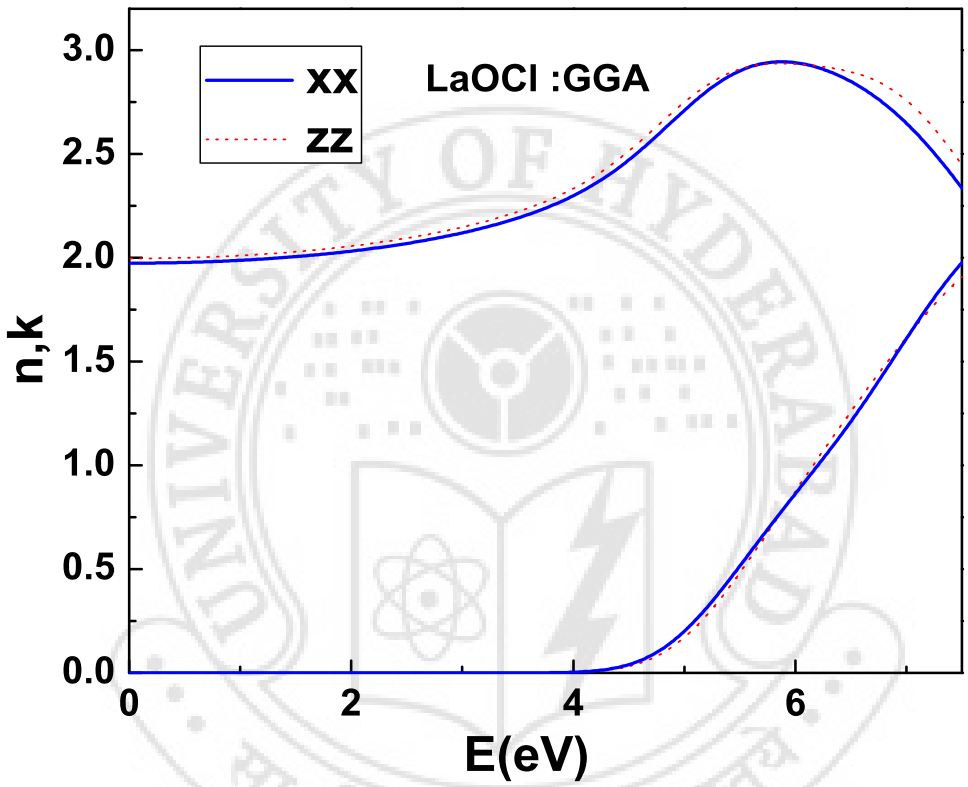

Figure 4.7: Calculated refractive index(n) and extinction coefficient(k) of LaOCl

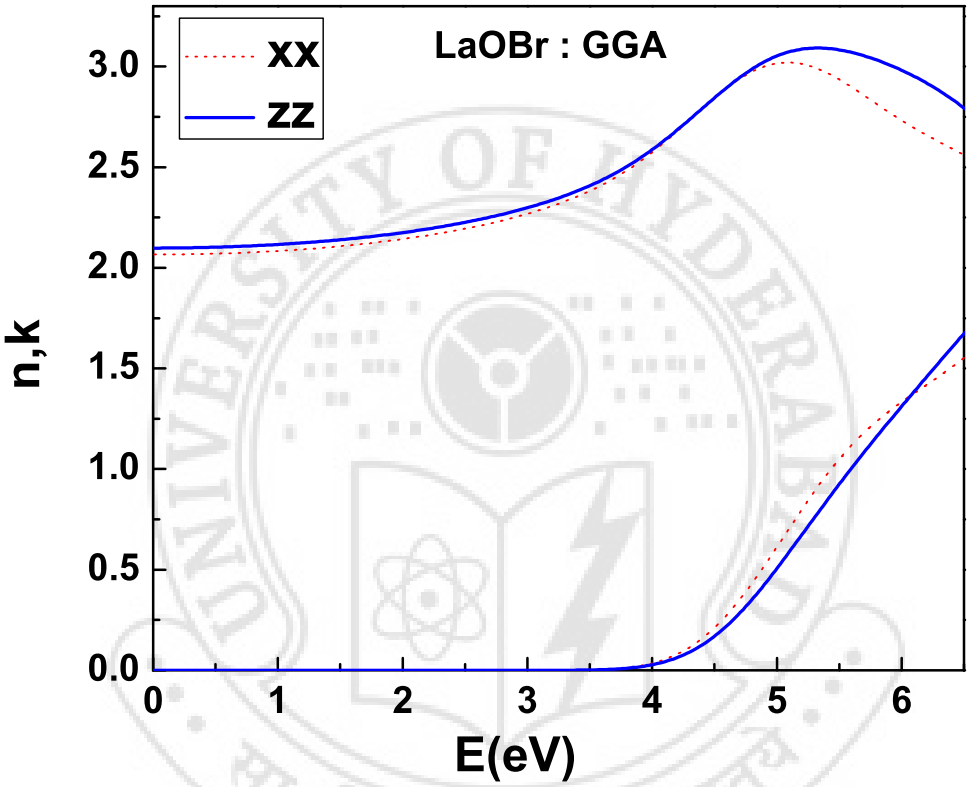

Figure 4.8: Calculated refractive index(n) and extinction coefficient(k) of LaOBr

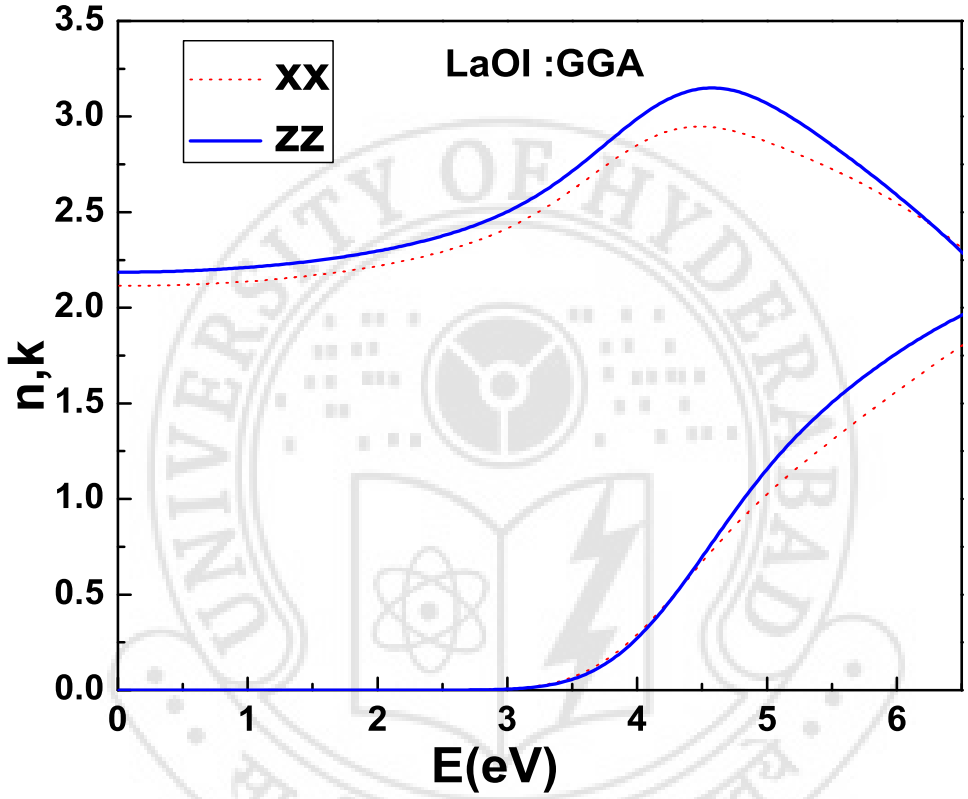

Figure 4.9: Calculated refractive index(n) and extinction coefficient(k) of LaOI

5

Conclusions

In the present work we have performed the electronic structure and frequency-dependent optical properties of the of the matlockite type (LaOX ;X= Cl, Br and I) compounds, using the Plane-wave Pseudo-potential method implemented in CASTEP program. We have done structural optimization for unit cell and the calculated lattice parameters, fractional coordinates are in good agreement with experimental results differ by 1% error in LDA and 2% error in GGA. And also calculated bulk modulus and its pressure derivative . Our calculations show that these compounds are direct band gap inslutaors. We have calculated the $(n,k)^{\perp}(\omega)$ and $(n,k)^{\parallel}(\omega)$ and it is clearly observed from the calculated refractive index, the compounds LaOCl and LaOBr show optical isotropy whereas LaOI shows optical anisotropy along XX and ZZ. Also find that the values n_{XX} and n_{ZZ} increases with decreasing energy gap. This could be explained on the basis of the Penn model. Further in future ,we are interested in calculating the elastic constants of these compounds.

6

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