

PHYSICAL PROPERTIES AND CORRELATION EFFECTS OF TRANSITION METAL PEROVSKITE OXIDES



By
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**DEPARTMENT OF PHYSICS
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By

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Dr. S. Jalali Asadabadi

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AUTHORIZATION TO SUBMIT THESIS

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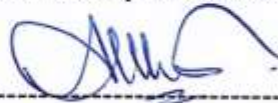
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SAIF ULLAH

Abstract

Perovskite oxides have always been attractive materials for materials scientist owing to their interesting chemical and physical properties. These properties of Perovskite oxides are directly related to their electronic behavior, which are coupled to their crystal structures. By studying and understanding the fundamental structure-property relationships present in perovskite oxides families, it is possible to engineer new compounds and functional properties.

The focus of this research is to understand and explore the physical properties of different families of perovskite oxides influenced by electronic correlation effect such as the magnetic properties, electronic band gap, ferroelectric properties and linear and nonlinear optical properties

The novel perovskite of ruthenate family, NaRuO_3 is reported. The stability tests of the novel compound confirm its existence in orthorhombic structure with Pnma (62) space group. The structural, electronic and magnetic properties of the novel material are also explored. Spin orbit coupling is used to deal with the relativistic effects of electron in the 4d state of ruthenium. Most likely this novel G-type antiferromagnetic material with weak electron correlation effects could be a potential candidate for sodium ion batteries.

The improved TB-mBj is utilized to calculate electronic band gaps and optical properties of cubic perovskites ABO_3 ($\text{A}=\text{Ca}, \text{Sr}, \text{Ba}$ and $\text{B}=\text{Ti}, \text{Zr}, \text{Hf}$). The calculated results show that covalent bond and electronegativity difference between B-cation and O atom, have considerable influence on electronic band gaps. Improved TB-mBJ treat well the electron density between them, thus result in accurate band gaps.

DFT studies are used to accurately calculate the band gap and ferroelectric polarization of the first experimentally confirmed hybrid improper ferroelectric $\text{Ca}_3\text{Ti}_2\text{O}_7$. The electronic calculation

confirm the direct wide band gap nature. The linear and nonlinear optical properties and birefringence reveals that this compound is a good for nonlinear optical applications.

The study reveals that the ground state of $\text{Li}_2\text{GeTeO}_6$ is Orthorhombic Pnn2. The electronic structure suggest wide band gap insulator with high values of polarization which confirm the experimental observation. The optical analysis show the high value of birefringence 0.08 suitable for high nonlinear optical susceptibility.

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Dedicated to my Family

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Chapter 1

Introduction

Materials science plays a significant role in the development of modern science and technology. This field is quite broad and touches almost all engineering and science disciplines. In spite of the enormous technological development in the area of electronic devices and their applications, the search for novel materials with improved properties are continuously sought to enhance quality and reduce size of the existing devices. In this regards perovskite-based compounds provide a fertile base for realization of high tech modern applications [1-4].

In the last few decades perovskite and related compounds have attracted extensive research interest because of their impressive and large variety of multifunctional properties such as optoelectronic, giant magnetoresistivity [5], high-temperature superconductivity [6], piezoelectricity [7], multiferroicity [8,9], metal–insulator transitions [9], and spintronic [10]. These properties are related to electronic and magnetic behavior arising from the interaction among spin, charge and orbital's degree of freedom as well as lattice parameters [11,12]. The applications of these compounds are not limited to sensors, substrates, catalytic electrodes, optoelectronic devices, spintronic devices, magnetic random access memory (MRAM), and hard disk read heads, electro-optic modulators and solar cells [13]. The esting physical and chemical knowledge behind the multifunctional properties of these materials are of a particular interest for both academic and technological perspectives.

Transition metal based perovskite oxides (TMPOs) having general formula ATO_3 , where A is cation, T is the first order transition metal cation and O is anion. The properties of these compounds are mostly dependent on the filling of the d state electrons of the transition metal. In 3d-TMPOs, electrons are extremely localized and feel strong Coulomb repulsion resulting narrow d-band structure and strong correlation effects, which realizes a broad range of interesting physical properties such as high-temperature superconductivity in Cuprates and Ruthenates [13-15] and unconventional charge and orbital order in manganites [16]. The 4d and 5d-TMPOs are different in several aspects from 3d-TMPOs, where the large atomic number of these compounds leads to the interesting phenomenon of strong spin orbit coupling, where as a result of this effect the electrons are more extended with a wide bandwidth and relatively weak electronic correlation effect. The interplay among electronic correlation, spin orbit coupling and crystal field splitting leads to exotic physical phenomena such as long range ferromagnetism in $SrRuO_3$ at high temperature, superconductivity in Sr_2RuO_4 [17], unconventional insulating state in $5d^4$ compounds [18], Slater-like transition in $NaOsO_3$ [19] and strongly competing ground state for 4d and 5d-TMPOs [20].

Oxide based perovskites form a large family of compounds and it is one of the most extensively investigated family in physics, chemistry, geology, materials science and engineering etc. The family of perovskite oxides with simple formula ATO_3 can accommodate approximately all the elements of the periodic table and hence make a large number of compounds with diversity in structures, physical and chemical properties. The

transition metal perovskites with strongly correlated electrons at T site have received an increasing attention due to their technologically important properties such as metal insulator transition, magnetoelectricity, ferroelectricity and nonlinear optical properties [21,22].

Perovskite has offered wide range of composition with great flexibility and they also provide base for complex structures like double and layered perovskites [23,24]. Perovskite related double perovskites can accommodate a large variety of ions of different size and variable charges in the same compounds [25]. The complex structural framework of double perovskites allows multiple tilting for subtle distortions caused by mismatch of different ions. The multiple distortion in structure altered the symmetry consideration, band energy levels, bond overlap and as a result display a useful properties of great technological interest [26,27].

A growing interest has been received by layered perovskites in the form of $A_{n+1}B_nO_{2n+1}$ ($n=0, 1, 2 \dots$) called Ruddlesden Popper perovskite [28]. The layered perovskites form artificial superlattices, which makes these type materials very important because it allows to tune important properties by keeping the original crystal structure [29]. Recently, the emergence of hybrid improper ferroelectricity (HIF) in layered perovskites has opened room for the discovery of novel multifunctional materials with both great potential and improved performance of technologically relevant applications [30,31]. In perovskite oxides, the HIF is caused by two non-polar modes, octahedral BO_6 tilting and rotation (with Glazer notations of $a^-a^-c^0$ and $a^0a^0c^+$, respectively), coupled with a

stable polar mode, which exhibits strong magnetoelectric coupling [32]. In proper ferroelectrics such as BaTiO_3 , the origin of ferroelectricity is the zone center instability caused by the displacement of second order Jahn-Teller active cation. The polarization induced by the displacement of the active cation is considered as weakly coupled to magnetism for operating in practical applications [33-35]. On the other hand, HIF is geometric improper ferroelectric where the octahedral distortion is the source of the polarization instead of typical cation-anion pairing [36]. The rotation and tilting of oxygen octahedral is known to strongly affect the electronic and magnetic properties of materials; therefore, HIF provides a strong foundation for the realization of low-power and electric field controllable high performance multifunctional devices that operate at room temperature [37-39].

With the rapid development of science and technology the demand of advance electronic devices continuously increases day by day. To meet the requirement of the consumer demand for high tech devices new materials with superior properties are continuously searched. To design and search new materials with improved properties is a great scientific challenge. To find the solution to the problem scientists have been working continuously. The traditional and standard methods are sometime very expensive, laborious and time consuming for preparation and identification of new materials and properties. In order to accelerate the process for discovering new materials, the understanding of the structural features at atomic scale and leading mechanism for the preferred properties are very important. One the most important example is the

noncentrosymmetric material, i.e. a material with lack of inversion symmetry, which is the main cause of technologically important properties such as nonlinear optical properties, ferroelectricity and piezoelectricity. It is very important to develop and use methods to distort the symmetry of crystalline solids and accurately predict the properties of the distorted materials for practical applications. The computational ab-initio (first principle) method are considered one of the most accurate, fast and versatile method for designing a new materials and also predicting the properties of the existing materials for identification of new and important properties.

The main focus of this thesis is to understand and explore the physical properties of different families of perovskite oxides influenced by electronic correlation effect such as the magnetic properties, electronic band gap, ferroelectric properties and linear and nonlinear optical properties. In this work the calculations are carried out with the density functional theory, which is based on quantum mechanics [40,41], and explored various physical properties of perovskite materials and compared our results with the available experimental and other theoretical data. Our result not only explain and support the experimental findings but also capable to design and predict new material with exciting properties.

This dissertation consists of five chapters. Chapter 1 introduces the general purpose of the study and motivation of the work. Chapter 2 includes the review of structure and some important physical properties and potential technological application of perovskite family. The methods and the background theory used in the calculations of different

properties are summarized in chapter 3. The results are presented and discussed in chapter 4. The work is summarized in the last chapter, chapter 5.

Chapter 2

Literature Review

In this section the review is carried out about the background information of perovskite oxides. Crystal structure derivatives and physical properties. In addition, the literature review for the work done in this thesis is also presented.

2.1 Perovskites Oxides

Calcium titanium oxide (CTO) CaTiO_3 was the first perovskite material discovered in 1839 by the German scientist Gustav Rose. It was named after a famous Russian scientist Count Lev Aleksevich Von Perovski in honor of his contribution in the field of mineralogy. Initially the name was specific to the CaTiO_3 , later on it was generalized to the group of compounds having similar structure to that of CTO. Perovskites are mostly ceramic materials occurring abundantly in the crust of the earth [1]. The structure of perovskite material having general formula ABX_3 include the A and B site cation and X is anion which is bonded to both the cations. Normally the A and B are in smaller size than the cation which is generally oxygen, but other large ions such as nitride, sulfide and halide are also used. The simple perovskite is composed of Octahedral BO_6 where six oxygen atoms surround the B cation and the A atom lies in space between octahedral. Perovskites oxides form a large family of compounds and it is one of the most extensively investigated family

in the field of science and technology [42,43]. The family of perovskite oxides with simple formula ABO_3 can accommodate majority of the elements of the periodic table and form a large number of compounds. The ABO_3 structure offered great flexibility and provide base for complex structures like double and layered perovskites which can accommodate a large variety of ions of different size and variable charges in the same compounds with unique and improved important properties [44]. The most important and famous families of perovskite oxides are simple perovskite, double perovskite, Ruddlesden-Popper series of perovskite and Dion-Jacobson perovskites [45-48]. Here we review the simple perovskites, double perovskites and Ruddlesden-Popper perovskites. First we discuss the crystal structure of these families.

2.2 Perovskite ABO_3

The ideal structure for perovskite materials is cubic structure with $Fm\bar{3}m$ space group. The cubic $Fm\bar{3}m$ are high symmetric structures with simple formula ABO_3 . As discussed above that normally the cation are smaller in size than the anion. The A cation is dodecahedral coordinated AO_{12} and B cation is 6 coordinated and form BO_6 octahedral as shown in the Figure 2.1. The variation of crystal structure from ideal cubic is the result of different ionic size and electronegativity, which effects the crystal symmetry of the perovskite and transforms to distorted crystal structure with different space group. At room temperature some perovskites exist in different structures transforms to cubic structures at high temperature [49]. The perovskite materials have gained a special interest and investigated

by many researchers for variety of application. Some important perovskite with applications are reviewed here. Julien et al reviewed 3d perovskites oxides LaVO_3 , CaMnO_3 , LaMnO_3 , CaFeO_3 , LaFeO_3 , YNiO_3 and discussed the band gap origin using DFT for a wide range of compounds [50-54]. The 3d compounds are considered strongly correlated and it is quite difficult to successfully describe the electronic behavior and magnetic properties. Julien group explained the causes of the problem in calculation and discussed the possible solution for predicting the accurate band gap, crystallographic and magnetic ground state, bond disproportionation, Mott-insulator transition, and magnetic moment of the strongly correlated perovskites oxides. The ruthenium based perovskite oxides are of a particular interest for their unique physical properties. Fang et al. tried to locate the magnetic monopole in the SrRuO_3 , a ferromagnetic material. They report the evidence for magnetic monopole by employing first principle calculations along with experimental proof in the momentum space of the SrRuO_3 crystal structure [55]. The correlation among the magneto transport properties and the nanoscale size of the SrRuO_3 structure for Skyrmion Devices applications are investigated by ref [56]. Shepard et al. investigated the thermodynamic properties of ARuO_3 ($\text{A}=\text{Ca}$, Sr and B) perovskites [57]. They measured the transport properties, magnetic susceptibility and specific heat of the single structure of ARuO_3 . The electronic correlation were explored in the series and it is found that the substitution of A site cation affect the correlation effect of electrons in the compound in such manner $\text{BaRuO}_3 > \text{SrRuO}_3 > \text{CaRuO}_3$. Tripathi et al. investigated the CaRuO_3 and found that ferromagnetic behavior could be obtained by the application of

tensile strain [58]. The ruthenium based perovskite oxides possess a variety of many other properties like metal to insulator transition [9,59-61], non-Fermi liquid behavior [62-64], magnetization reversal effect induced through temperature [65] and disorder induced magnetic quantum criticality [66].

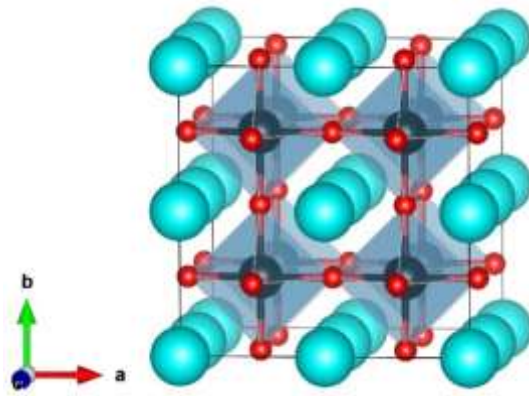


Figure 2.1: Ideal cubic perovskite CaTiO_3 $2 \times 2 \times 2$ supercell structure, cyan color is Ca, black color is Ti and red is oxygen.

2.3 Double Perovskites Oxides

The ideal cubic double perovskite is composed of A cation and two different cation at B site with twice unit cell volume. In the double perovskite the coordination number of A site cation 12 and B site cation is 6 similar to the simple perovskite as shown in Figure 2.2. The Poeppelmeier et al. explained the formation of double perovskite with respect to the arrangement of B site cation [67]. Double perovskites gained interest because it offer great flexibility with a wide range of composition that can accommodate different size ions of large variety and charges in the same compound. The different size mismatch of cations makes

complex structures with a multiple distortion in symmetry and result some useful properties such as magnetic, ferroelectric, nonlinear optics, multiferroic and pizoelectric [68-72]. Scientist intensivly investigated the double perovskites, some important double perovskites are reviewed.

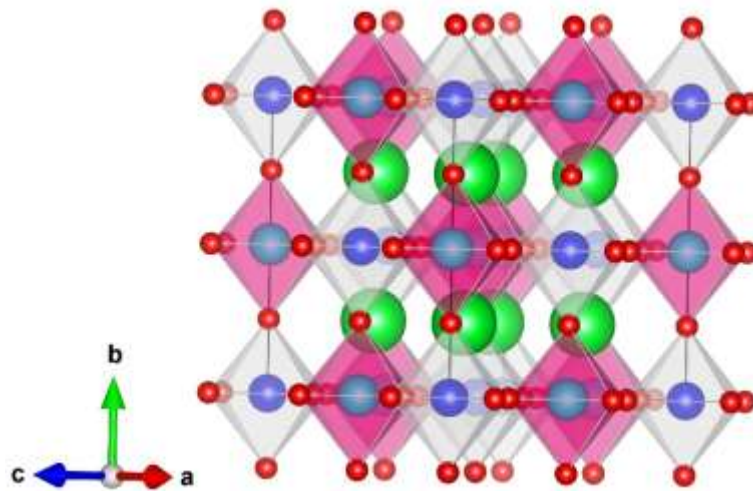


Figure 2.2: The crystal structure of cubic Double perovskite SrFeMoO_6 , where the color of the atoms are Sr-green, Fe-blue, Mo-cyan and oxygen is red.

Recently Lu et al. synthesised a double perovskite with superior nonlinear optical (NLO) properties $\text{Li}_2\text{ZrTeO}_6$ [73]. $\text{Li}_2\text{ZrTeO}_6$ was derived from a well-known NLO crystal structure LiNbO_3 commercially used in electronic engineering. The crystal structure of $\text{Li}_2\text{ZrTeO}_6$ exist in rhombohedral non-centrosymmetric space group $R\bar{3}$ and has received the similar structural behavior of its parent LiNbO_3 structure with suitable phase matching, birefringence for NLO applications. The threshold damage (1.3 GWcm^{-2}) of this compound

is almost greater than 22 times the parent structure, which makes it suitable for high energy laser application. Yin et al. reviewed the double perovskites and other derivatives for photovoltaics, photocatalysis and electrocatalysis application. They address the key issue to find a material for multifunctional environment friendly materials. It was concluded that because of the complex structural composition and low cost as well as easy syntheses makes double perovskites ideal candidates for above application [24]. A new polymorph Mg_3TeO_6 was predicted recently in double perovskite structure by Su et al [74]. First DFT was used for prediction of the exotic polymorph and it was confirmed that experimentally its excellent dielectric properties were confirmed. Zhao and coworker synthesize a new perovskite $\text{Li}_2\text{GeTeO}_6$ in non-centrosymmetric space groups in two different phases [72]. The two phases are convertible to each other by the application of temperature and pressure. It was reported that despite high polarization in $\text{Li}_2\text{GeTeO}_6$ the ferroelectric behavior is not prominent and further theoretical and experimental study was suggested.

2.4 Layered Perovskites

Perovskite oxides occur in several layered structural families but the most important and widely investigated types are Ruddlesden-Popper, Dion-Jacobson and Aurivillius phases [48]. In all these phases a 2D layer is inserted in between the perovskite ABO_3 layers. Although all the layered perovskites are very important but we are only considering the Ruddlesden-Popper series. The RP exists in many crystal structures at room temperature but at high temperature the majority of compounds crystallize in tetragonal space group. The

Ruddlesden-Popper (RP) series generally represented by $A_{n+1}B_nO_{2n+1}$ ($n=0, 1, 2, \dots \infty$) where n shows the number of perovskite sandwiched among the rock salt layer as shown in $Sr_3Ti_2O_7$ structure Figure 2.3.

A growing attention has been received by layered perovskites in the form of $A_{n+1}B_nO_{2n+1}$ ($n=0, 1, 2 \dots$). The layered perovskites form natural superlattices which makes these type material very important because it allows to tune the important properties in a single crystal structure. Some of the interesting properties possess by these type of compounds are ferroelectricity, photoluminescence, photocatalytic activity, pizoelectricity etc. Recently Benedek and Fennie proposed new type of method for inducing ferroelectricity (HIF) in bulk crystal [30]. In perovskite oxides, the HIF is caused by octahedral BO_6 tilting and rotation (with Glazer notations of $a^-a^-c^0$ and $a^0a^0c^+$, respectively), coupled with a stable polar mode, which reveled to possess strong magnetoelectric coupling. The HIF was first proposed through computational calculation and then verified experimentally by several researcher in independent investigations [75,76].

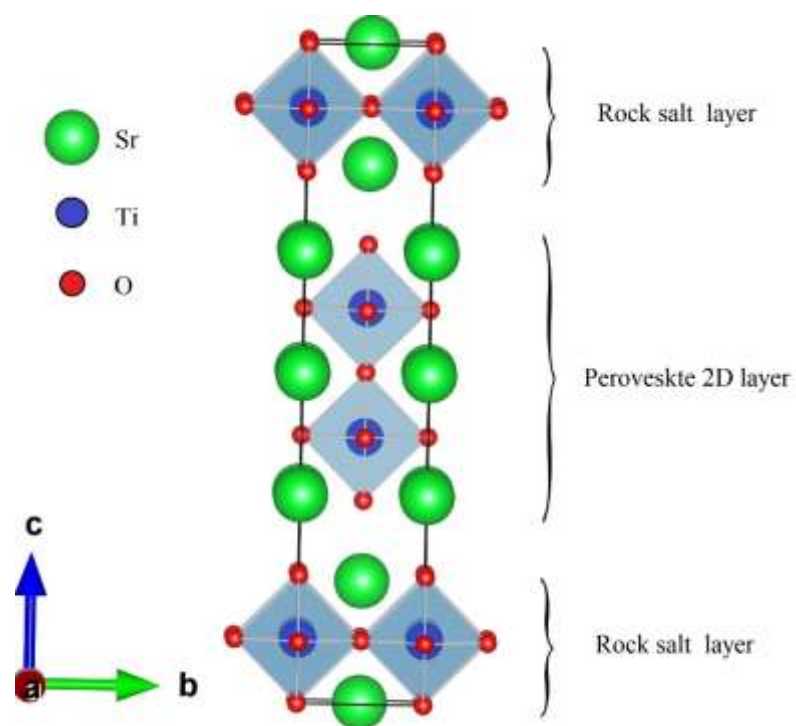


Figure 2.3: Tetragonal crystal structure of $\text{Sr}_3\text{Ti}_2\text{O}_7$

Chapter 3

Computational Method

Predicting and describing the physical properties of the material is the main goal of every ab initio method, that is, starting from scratch without using experimental parameters (or at least, using as few parameters as possible). This chapter briefly outlines the basis of the electronic structure calculation methods used in this thesis and its historical perspective. Specifically, the discussion of several approximations to make the first-principles calculations easier to deal practically with many-body system, followed by a qualitative review of these methods. Finally, I discussed the implementation of mathematical equations, a more complete review of the density functional theory (DFT) and related topics, see Refs. [77-79].

3.1 Many-body System

Theoretically, all the information (properties) about many-body (MB) system can be achieved from the solution of the Schrödinger equation i.e. by taking the corresponding expectation values. The Schrödinger equation[80], its simplest form is given as:

$$H\Psi = E\Psi, \quad (3.1)$$

which is, an appropriate Hamiltonian (H) of MB system, when operated on it many-particle wavefunction result in the ground state energy (E) of that system. Though, in actual fact, solving this equation exactly is handy for the simplest systems but impossible for complex ones. Instead of this, the solutions to this problem can be estimated using different approximations, which allow

the modeling of more interesting and complex systems like crystalline solids. The first approximation is the decomposition of Hamiltonian into a series of kinetic (T) and potential (V) energy terms of a system of nuclei (n) and interacting electrons (e), like:

$$H = H_e + H_n, \quad (3.2)$$

or
$$H = T_e + V_{ee} + T_n + V_{nn} + V_{en}, \quad (3.3)$$

where the kinetic energy terms are: for electrons

$$T_e = -\frac{\hbar^2}{2m_e} \sum_{i=1} \nabla_i^2, \quad (3.4)$$

and nuclei

$$T_n = -\frac{\hbar^2}{2m_A} \sum_{i,A=1} \nabla_i^2, \quad (3.5)$$

and the potential energy terms (describing electrostatic or Columbic interactions) are: nucleus-nucleus interaction

$$V_{nn} = \frac{e^2}{2} \sum_{A \neq B} \frac{Z_A Z_B}{r_{AB}}, \quad (3.6)$$

nuclei-electrons interaction

$$V_{en} = -e^2 \sum_{i,A=1} \frac{Z_A}{r_{iA}}, \quad (3.7)$$

electron-electron interactions

$$V_{ee} = \frac{e^2}{2} \sum_{i \neq j} \frac{1}{r_{ij}}, \quad (3.8)$$

and the kinetic energy of nuclei, T_n . In equations (3.4)-(3.8), m is the mass of an ion, Z is the charge on it, and r is the separation between two particles; A and B denote nuclei, whereas electrons are denoted by i and j .

As the electrons are much lighter than nuclei, the nuclei remain frozen while the electrons can be considered is moving in an external field. Consequently, the nuclear kinetic energy (T_n) is approximately zero and its potential energy (V_{nn}) turn out to be simple classical interaction. This simplification is called the “Born-Oppenheimer” or “adiabatic” approximation [81]. Thus we are left with the so called *electronic* Hamiltonian (H_{elec}), which consists of V_{en} , V_{ee} , and T_e . The simplification made so far significantly reduces the complexity of a system, but are not adequate to permit for useful calculations of complex systems. Initially, for each of the approximately 10^{23} electrons in a real system three spatial coordinates must be specified. Additionally, the intractability in the determination of electronic correlation term (*i.e.*, V_{ee}), due to electron’s mutual interactions. Thus, we are forced to consider the formulation of DFT.

3.2 Density Functional Theory

The two theories proposed by Hohenberg and Kohn in 1964 [82], lead to the density functional theory, which was the first breakthrough after the early attempts of Thomas and Fermi. Initially, they suggested that the external potential $V(r)$ affecting the electrons, and thus the total energy, is a unique functional of the electron density $n(r)$; this further implies that all of a system’s properties can be determined from the electron density, which is a function of only the three spatial dimensions. Using variational principle (VP), one can demonstrate that the ground state energy $E[n(r)]$ is unique functional of electron density only The second theorem defined a “universal” but

unknown functional $F[n(r)]$ which contains all energy terms (i.e. T_e and V_e). Now, for a unique $V(r)$ the total energy $E[n(r)]$ is given by:

$$E[n(r)] = \int V(r)n(r)dr + F[n(r)]. \quad (3.9)$$

Notably, they then showed (from the VP) that the exact ground state is that which minimizes Equation 3.9 and thus the ground state total energy. These two theorems show very powerful understandings and allow for practical and accurate calculations, but with lack of calculation procedure for $F[n(r)]$.

Later, in the following year (1965), Kohn and Sham reported an important work presenting that it is possible to a system as of *non-interacting (N-I)* electrons, which leads to the exact same ground state density[83]. Accordingly, the different contributions to the total energy can be separated, and Equation 3.9 can be re-written as:

$$E[n(r)] = \int V(r)n(r)dr + T[n(r)] + E_H[n(r)] + E_{XC}[n(r)] \quad (3.10)$$

We now know the $F[n(r)]$, which consist of kinetic and two interaction energy terms of N-I electrons, such as kinetic energy,

$$T[n(r)] = -\frac{\hbar^2 \nabla^2}{2m}, \quad (3.11)$$

Hartree energy (E_H),

$$E_H[n(r)] = \frac{e^2}{2} \int \int \frac{n(r)n(r')}{|r-r'|} dr dr', \quad (3.12)$$

and exchange-correlation (E_{XC}) energy, $E_{XC}[n(r)]$. The E_H term describes charge density interaction with its self, whereas the $E_{XC}[n(r)]$ terms is discussed it next section.

The total energy $E[n(r)]$ have an explicit form, for which we can create a potential, known as the Kohn-Sham (KS) potential [$V_{KS}(r)$] that acts on the N-I system of electrons.

Due to same $n(r)$ must minimize electronic $E[n(r)]$ energy of both the interacting and N-I system, $V_{KS}(r)$:

$$V_{KS}(r) = V(r) + \frac{\partial E_H[n(r)]}{\partial n(r)} + \frac{\partial E_{XC}[n(r)]}{\partial n(r)}, \quad (3.13)$$

obtained via the partial derivatives of the Hartree and E_{XC} energy. From which, the related KS Hamiltonian (H_{KS}) can now be defined as:

$$H_{KS} = \frac{\hbar^2 \nabla^2}{2m} + V_{KS}(r). \quad (3.14)$$

The above Hamiltonian describes a system of N-I electrons that are affected by $V_{KS}(r)$ (the external potential) which, contains all of the information about the electron-electron interactions, as stated previously. The interacting charge density, $n(r)$, can be obtained from combination of single particle wave functions, $\Psi_i(r)$, square modulus and the Fermi-Dirac distribution f_i :

$$n(r) = \sum_i^N f_i |\Psi_i(r)|^2. \quad (3.15)$$

Using the above formalism, the Schrodinger equation (Equation 3.1) for N-I system can be written as:

$$\left[\frac{\hbar^2 \nabla^2}{2m} + V_{KS}(r) \right] \Psi_i(r) = E_i \Psi_i(r). \quad (3.16)$$

Or, in its simple form:

$$H_{KS} \Psi_i(r) = E_i \Psi_i(r). \quad (3.17)$$

For the solution of this Hamiltonian, we start with a trial electron density and single particle wavefunction, then the KS equations (Equations 3.13, 3.15, and 3.16) can be solved iteratively till self-consistency is attained; from this, the ground state $n(r)$ and total $E[n(r)]$ are obtained.

3.3 The Exchange-Correlation Energy

The DFT formalism as a result of Hohenberg, Kohn, and Sham works simplified the many body problem by using N-I electrons system instead of interaction one. Because of this the quantum mechanical calculations of real materials are practically achievable. However, the calculation issue of the exchange-correlation energy $E_{xc}[n(r)]$ is yet to solved. This term includes the many-body interaction, such as from its name, the *electron correlation* (the interaction among electrons) and the *exchange interaction* (related to the fact that wavefunctions of fermions are anti-symmetric and giving rise to the Pauli Exclusion Principle). The DFT so far is an exact theory, for its feasible application an assumption must be introduced for exchange-correlation functional and approximate its solution. The choice of such density functionals are large in number, depending the on the cost related accuracy, i.e. ranging from those using very simple approximations to those which add in additionally complex contributions [84,85]. This section about the review several of these functionals, especially those used to produce the results presented in this thesis.

The simplest possible model of interacting electrons is assumption that the electron density in real system *locally* behaves as a homogenous electron gas, which is of the first proposals up to this point, called the Local Density Approximation (or LDA)[86]. Using Hartree-Fock theory and quantum Monte Carlo methods one can easily find the exchange and correlation terms [87,88]. Then, the true $E_{xc}[n(r)]$ energy can be replaced with that of the homogenous electron gas (HEC) and be reconstructed as:

$$E_{XC}^{LDA}[n(r)] = \int n(r)E_{XC}^{LDA}[n(r)]dr. \quad (3.18)$$

Interestingly, this simple approximation is the most widely used approximate functionals and works rather well for predicting the materials properties, with some underestimates and overestimated results. For example, its underestimate the bond lengths, consequently, structural parameters like lattice parameters and cell volume. And overestimating the binding energy between atoms in a solid [89].

The introduction of semi-local functionals, like the Generalized Gradient Approximation (or GGA) [90] improves the prediction of structure parameters compared to LDA. Obviously, from its name this and similar functionals contains information of gradient of the charge density, $\nabla n(r)$; the $E_{XC}[n(r)]$ energy is given by:

$$E_{XC}^{LDA}[n(r)] = \int n(r)E_{XC}^{LDA}[n(r), \nabla n(r)]dr. \quad (3.19)$$

Another advantage GGA functional is its varieties, the most common are PBE [91] and its revised version PBEsol [92] functionals, being presented Perdew, Burke, and Ernzerhof (PBE). The inclusion of electron density gradient make GGA functionals are more computationally expensive than LDA, however, for enhanced accuracy, it is worthy. LDA and GGAs functionals offers interesting degree of accuracy and predicts very well many materials properties. However, for excited state properties like band gaps of semiconductors or insulators, they severely underestimate their band gaps, up to 50% or more [93]. Especially, in case of strongly correlated metal and oxides, and for highly localized electrons compounds containing atoms like Fe, Co, Ni, Mn, and etc. Several methods have been proposed to deal with problem. For example, DFT calculations with model Hamiltonians based on the Hubbard model [94], called DFT+U methods, i.e. the total energy of a system is given by:

$$E^{DFT+U} = E^{DFT} + E^U - E^{dc}, \quad (3.20)$$

where E^{DFT} is energy obtained with DFT, E^U the extra energy for localizing the electrons (Hubbard correction) and E^{dc} is for eliminating the interaction energy previously accounted for E^{DFT} . The U energy is only manually applied to orbital containing strongly electrons, like d states of transition metals or f states in rare earth elements. The addition of an extra parameter slightly increase the cost of calculation [95].

Another methods is to incorporate the relativist effects, such that the spin-orbit coupling (SOC)[96]. This effect is significant in heavy elements, such as W, Bi and etc. Thus for these elements one must treat the system with SOC. For GGA functional and the addition of SOC the total energy of systems can now be written as:

$$E^{DFT-SOC} = E^{DFT} + E^{SOC}, \quad (3.20)$$

where E^{SOC} represent SOC energy, depending on parameters δ , p and U_0 , denoting the Pauli spin matrices, momentum operator and Columbic potential, respectively, and is given by:

$$E^{SOC} = -\frac{\hbar}{4m_0^2} \delta \cdot p \times (\nabla \cdot U_0). \quad (3.20)$$

Alternatively, Tran and Blaha proposed semi-local functional based exchange potential called Tran and Blaha modified Becke Johnson (TB-mBJ) potential [97]. In this study, for better description of electronic band gaps of the considered compounds TB-mBJ scheme was employed to obtain TB-mBJ exchange potential, i.e., $v_x^{TB-mBJ} = \delta E_x / \delta \rho$. The TB-mBJ exchange potential [97] is defined as:

$$v_{x,\sigma}^{TB-mBJ}(\mathbf{r}) = cv_x^{BR}(\mathbf{r}) + (3c - 2) \frac{1}{\pi} \sqrt{\frac{5}{12}} \sqrt{\frac{2t_\sigma(\mathbf{r})}{\rho_\sigma(\mathbf{r})}}, \quad (3.23)$$

where v_x^{BR} is the Becke-Roussel (BR) [98] exchange potential, $\rho_\sigma(\mathbf{r})$ is the electron charge density, $t_\sigma(\mathbf{r})$ is the electron's kinetic-energy density and c is given by:

$$c = A + B\sqrt{g} , \quad (3.24)$$

And

$$g = \frac{1}{\Omega} \int_{\Omega} \frac{|\nabla \rho_\sigma(\mathbf{r}')|}{\rho_\sigma(\mathbf{r}')} d\mathbf{r}' , \quad (3.25)$$

where in Ω is the unit cell volume. It is clear from the above equations that the electronic charge density can be properly manipulated in a compound by manipulating the c -factor, which is linearly dependent on the square root of the average of $|\nabla \rho_\sigma|/\rho_\sigma$. Koller et al. [99] reparameterize Eq (2) of original TB-mBJ to set different values of c -factor for solids having large and smaller band gap semiconductors, with the aim of improving experimental band gaps. The c -factor set for smaller band gap semiconductors was adopted in the current study.

Besides these methods, there also some other methods, which computational very expensive like, hybrid functionals [100,101], GW [102], and dynamical mean field theory [103],. In this study we only implement, GGA, GGA+U and TB-mBJ functionals, comparatively less expensive then former ones.

3.4 Additional simplification for many-body problem

The consideration of N-I electrons instead of interacting ones in an effective potential have reduced the complex and unsolvable system. While, DFT offers implausible intuition but still faraway to handle in practical calculations, due to high order of electrons in a real material. Therefore, we need additional simplification to produce computationally manageable systems. The number of atoms,

consequently the electrons must be reduced to solve this problem, which can be achieved by taking the advantage of lattice periodicity of crystals.

Bloch's Theorem:

Bloch's theorem very convenient for the reduction of atoms number[104], and therefore the system's complexity. This states that in any periodic system (*i.e.*, atoms in a crystal), the single particle wavefunction Ψ is of form:

$$\Psi(r) = e^{ik \cdot r} u(r). \quad (3.26)$$

Here, $e^{ik \cdot r}$ is a plane wave *and* k is the wave vector of the crystal, while $u(r)$ is a periodic function that, importantly, matches the period of the crystal lattice. The periodic function expansion, as a three dimensional Fourier series summed over the reciprocal lattice vector G is given by:

$$u(r) = \sum_G C e^{ik \cdot r}. \quad (3.27)$$

Combing these two equation (*i.e.* Equation 3.26 and 3.27), gives:

$$u(r) = \sum_G C e^{i(k+G) \cdot r}. \quad (3.27)$$

Now with help of this theorem, *i.e.* using the plane wave expansion, the Kohn-Sham equations and the wavefunction can be easily solved. It is worthy to mention that this expansion is infinite, so we must truncate the sum at some G -vector or energy for finite expansion, such energy is called the cutoff energy (E_{cutoff}), the criterion for which is $\frac{\hbar^2}{2m} |k + G|^2 \leq E_{cutoff}$. The cutoff energy must be selected carefully to ensure calculation's convergence. The energy and charge density can now be obtained from integrals over the Brillouin zone (BZ) instead of an infinite integral over all of real space, employing the plane wave representation of the Kohan-Sham equations.

Irreducible Brillouin zone:

Applying the symmetry operation of the point group for the specific crystal phase, the size of BZ can be further reduced, such region is called the irreducible Brillouin zone. Despite this simplification of integral in a particular region of space, we must further reduce the of k -points, which is technically requires infinite number. In this thesis, we employed the Monkhorst and Pack k -point selection method, which sets up an evenly space grid throughout the BZ [105]. The number of k -points along each reciprocal space direction is typically a manually chosen input parameter, like the cutoff energy described above and again the convergence must be ensured.

3.5 Wien2k package

In this thesis all the calculation were perform with Linux environment based computational code, known as WIEN package, developed by Peter Blaha and Karlhienz Schwarz in 1980s. It is designed for periodic solids, to execute quantum mechanical calculation, written in FORTRAN computational language. In this package for KS equation solution, the full-potential (linearized) augmented plane-wave (LAPW)+local orbitals (lo) basis set are employed, and for electronic structure calculations, which is one of the best schemes. Since, its first release, the WIEN package is continuously developed to fulfil the fast advancement of computational tools. The current studies were performed with WIEN2k package, which has many interesting features including relativistic effects.

Chapter 4

Results and Discussion

4.1 Sodium Ruthenium Oxide (NaRuO₃): A Novel Perovskite with Intriguing Physical Properties

Ruthenates perovskite oxides are widely studied materials for their exceptional physical properties presented by the combination between different magnetic spin states, structure and chemical complexity. Some impressive multifunctional properties observed in these compounds are superconductivity in layered Sr₂RuO₄ [106,107], metal to insulator transition [9,59-61], non-Fermi liquid behavior [62-64], magnetization reversal effect induced through temperature [65] and disorder induced magnetic quantum criticality [66]. SrRuO₃ is the only member of the 4d perovskites family having long range ferromagnetism below 160K. This compound also provides base to the idea of magnetic monopole existence [55].

Ruthenates oxides are highly desirable for electrode materials, thin film applications [108,109], heterogeneous catalysis [110,111], spintronic devices, and electronics devices [112]. The search of new materials of this family is on peak due to their versatile physical properties for practical applications in high tech devices [113]. Sodium ruthenium oxides are of particular interest, which received a growing attention in the last decade for electrode

material in sodium ion batteries and other practical applications [114,115]. Sodium ruthenate oxides exist in different structures with interesting properties. McGuire et al. synthesize antiferromagnetic “spin-lozenge” low-dimensional magnetic material Na_3RuO_4 [13]. Allred et al. [116] reported a magnetic semiconductor $\text{Na}_{27}\text{Ru}_{14}\text{O}_{48}$ with a mixed valence sodium ruthenate in triclinic spacegroup which shows Curie-weiss behavior below 200K [16]. Na_2RuO_4 displays antiferromagnetic order while NaRuO_2 shows paramagnetic behavior [17]. Shi et al. synthesized two dimensional ruthenium oxide NaRuO_2 and oxyhydride $\text{Na}_x\text{RuO}_{2-y}\text{H}_2\text{O}$ which is used in pseudocapacitor [2].

Several structures of sodium ruthenium oxides are reported in literature, but until now no perovskite structure is reported [4]. Recently Seki et al. [117] tried to synthesize a perovskite NaRuO_3 with Ru^{+5} by doping Na in SrRuO_3 and CaRuO_3 at Sr and Ca site, but were successful upto 70% substitution. The structural phase transition was not witnessed during the substitution of Na in SrRuO_3 , which predict that NaRuO_3 will also exist in similar distorted cubic structure with orthorhombic space group Pnma (62). The only difference between SrRuO_3 and CaRuO_3 compound is the atomic radius of Sr and Ca which leads to different physical properties, while the ionic radius of Na^+ is 1.39 Å which is between 1.34 Å (Ca^{+2}) and 1.44 Å (Sr^{+2}) ionic radii of 12-fold coordinated perovskite structure [117]. The magnetic and electronic properties of these perovskites significantly changed with structural distortion either by stress or substitution at various atomic sites [118,119]. The paramagnetic, ferromagnetic and antiferromagnetic phases of Ruthenium perovskites are so close in energy which can be easily tuned for particular application [120]

. Keeping in view the exciting list of exotic phenomena of sodium ruthenates oxides, structure and atomic size resemblance of NaRuO_3 with the intensively studied alkaline earth ruthenates especially the two analogous compounds ARuO_3 ($A=\text{Ca, Sr}$) we report a new ruthenate NaRuO_3 . The physical properties of this novel material are also explored in this section for possible practical applications.

The physical properties, such as structural, electronic and magnetic, of the new member of ruthenium perovskite oxides family, NaRuO_3 are explored by utilizing one of the most accurate theoretical technique i.e. DFT with the FP-LAPW method implemented the wien2k [121]. The analytically evaluated structural parameters are used to optimize the geometry of the crystal system. We used PBEsol-GGA [92] for treating the exchange-correlation energy of electrons to calculate the ground state structural parameters. These calculated parameters are used as input for electronic and magnetic properties calculations by using GGA plus onsite Hubbard Parameter U (GGA+ U) with PBEsol parameterization of spin polarized version. To treat the 4d electrons of Ru atom we used the SIC method [122], where the Coulomb (U) and exchange parameters (J) are used for the effective value $U_{\text{eff}}=U-J$, to obtain well converged and correct result. The different values of U_{eff} for Ru are reported in the literature from 1.6 to 3eV [112,123,124]. Based on the reported value we used $U_{\text{eff}}=3\text{eV}$ to illustrate the accurate electronic and magnetic nature of the compound. To analyze the relativistic effect, spin orbit coupling (SOC) calculations GGA+ U +SO were performed using second order variational procedure by diagonalizing the Hamiltonian for SOC in the relativistic scalar Eigen-states space [125]. The valence

electrons are separated by separation energy of -7.0 Ry from the core electrons. The expansion of basis function are restricted by selecting $R_{mt}K_{max}=7$ value. A sufficient dense k-points $10\times 8\times 10$ mesh is utilized for the BZ integration. The muffin–tin radii used in this study were 2.15, 1.92 and 1.65 atomic units for Na, Ru and O, respectively.

4.1.1 Structural Properties

The crystal structure plays central role in the investigation of physical properties and practical applications of a compound. Almost all the properties of a material are related to its structural morphology, therefore the study of crystal structure is very important in solid-state science. In this article we report a novel compound NaRuO₃ based of the highly desirable ruthenium based perovskite oxide SrRuO₃. As discussed in the introduction that the high concentration doping of sodium in SrRuO₃ reveals the existence of NaRuO₃ in a similar cubic perovskite distorted structure with orthorhombic space group (Pnma). This structure consists of four formula unit (Z=4) and 20 atoms in a cell that is clear from Figure 4.1. The reported high concentration substitution of Sr⁺² by Na⁺ reveals no structural phase transition upto 70%, which leads to the motivation of investigating NaRuO₃ in the same space group Pnma (62). Recently interest has been grown to synthesize new compounds with Na⁺ and also Ru⁺⁵ ions because Na⁺ based oxides are widely used as an electrodes in sodium ion batteries and Ru⁺⁵ plays central role to greatly enhance the oxygen evolution activity [126]. To study the structural properties, we first calculate the lattice parameters analytically i.e. by increasing the Na⁺ concentration the lattice constant decreases linearly

[117]. To optimize lattice constants and atomic positions we used the calculated lattice constant and replaced Na in SrRuO_3 at Sr sites. The 3D optimization and geometry relaxation were performed to obtain optimized lattice constant and relaxed atomic positions. The computed lattice constant, bulk modulus and unit cell volume are presented in Table 4.1 and the relaxed atomic position in Table 4.2. Our calculated values for the lattice constant and unit cell volume are less than that of the 67 percent doped Na^+ in SrRuO_3 , which is in agreement with the experimental results of the variation of lattice constant and other structural parameters with the concentration of doping. Bond lengths play vital role to in the stability of a crystal and physical as well as chemical properties of a material; therefore different bond lengths of NaRuO_3 are calculated and the values are provided in Table 4.1. The calculated values for NaRuO_3 are smaller than SrRuO_3 that follows the experimentally observed behavior of bond lengths [15]. The tilting of octahedra are extremely important in describing the distortion of the oxygen network in BO_6 octahedral in cubic structure. There are two different bond length between transition atom and oxygen Ru-O1 and Ru-O2 which shows the effective role of Jahn–Teller distortion in electronic properties [127]. The tilting angle 13.38° and rotational angle 8.94° are calculated for NaRuO_3 related to Ru-O-Ru bond angle between two transition atoms and oxygen atom. The tilting angle 13.38° and rotational angle 8.94° for NaRuO_3 is greater than SrRuO_3 10.47° and 7.56° reported value [112] indicate that NaRuO_3 is more distorted than SrRuO_3 .

The bond angle between two transition atoms and oxygen atom in ruthenium perovskite is particularly important for the magnetic and other physical properties that are

dependent on the cation size of the atom. The cation size is the only difference between the two mostly studied analogous compounds SrRuO_3 and CaRuO_3 which is the main cause of diversity in the physical properties of two compounds one is ferromagnetic and the other one is paramagnetic. The optimization energies are listed in Table 4.1 of different types of antiferromagnetic and ferromagnetic calculations confirm that NaRuO_3 displays G-type antiferromagnetic behavior having bond angle of 153.229° Ru-O-Ru smaller than 161.1° [112] in SrRuO_3 and greater than 149.9° in CaRuO_3 because the ionic size of $1.39 \text{ \AA}$ (Na^+) cation is smaller from $1.44 \text{ \AA}$ (Sr^{+2}) and greater than $1.34 \text{ \AA}$ (Ca^{+2}).

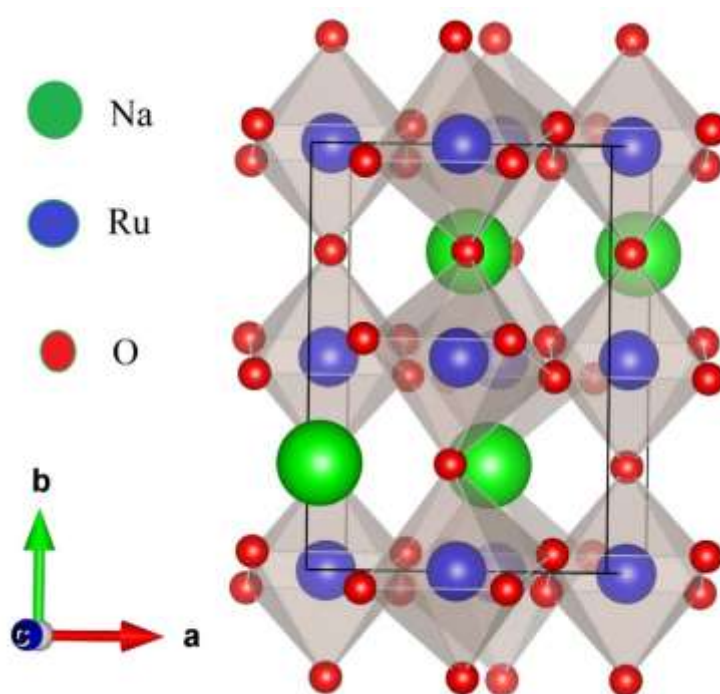


Figure 4. 1 Crystal Structure of NaRuO₃

Table 4. 1 Optimized lattice parameters and relative different magnetic configuration energies

Lattice Constant (Å)	Bond length (Ru-O, Å)	Angle (Ru-O-Ru)	Volume (V, Å ³)	Energy difference		
				AFM	FM/NM	
A	5.368	x ₁ 1.96	NaRuO ₃ 153.23°	G 0	FM	62
B	7.574	x ₂ 1.94	^a SrRuO ₃ 161.1°	C 13	N M	73
C	5.333	x ₃ 1.94	^a CaRuO ₃ 149.2°	A 27		

^a[112]
]

Table 4. 2 NaRuO₃ atomic position of the relaxed structure

Atoms	X	Y	z
Na	0.03752	0.2499	0.9922
Ru	0.0000	0.0000	0.5000
O1	0.2922	0.0412	0.7065
O2	0.4873	0.2499	0.0806

4.1.2 Stability of NaRuO₃

The stability of a crystal structure is a key factor for predicting and evaluating new crystalline materials. The concept of Goldschmidt's tolerance factor (TF) is used for predicting new perovskite structure from several decades [128-130]. The tolerance factor is the geometry parameter and it describes A and B site ions mismatch in a compound. TF is a well-known decisive factor to describe the stability of perovskite compound and effectively used by many researcher for discussing the stability of different types of perovskite families such as oxides [131,132], chlorides, fluorides, hybrid perovskite [22] and perovskite type eleminites [19]. To discuss the stability of NaRuO₃ we have calculated the tolerance factor using Shannon's ionic radii method by employing [133]:

$$t = \frac{(r_A + r_o)}{\sqrt{2}(r_B + r_o)}, \quad 4.1$$

where the ionic radii of Na, Ru and O are represented by r_A , r_B and r_O . The deviation from $t=1$ shows the distortion in the cubic structure which mainly caused by the tilting of BO₆ octahedra. The calculated tolerance factor for NaRuO₃ is 0.89 comparable to that of 0.908 (SrRuO₃). Our calculated value of tolerance factor $t=0.89$ shows that NaRuO₃ is a distorted cubic structure in orthorhombic space group like SrRuO₃. The tolerance factor is a necessary condition for the formation of perovskite compounds but not sufficient to discuss the stability of a compound. Therefore we use another necessary condition for the stability of NaRuO₃ based on electronegativity. The difference of electronegativity in ABO₃ type

perovskite shows the strength of binding energy between B and A cations [134-136]. Larger electronegativity difference reveals larger binding energy and hence higher stability of the compound. The electronegativity difference of NaRuO₃ and other stable ABO₃ type perovskites in orthorhombic space group Pnma (62) like ARuO₃ (A=Pb, Sr, Ca), SeMnO₃, SeNiO₃ and NaOsO₃ are calculated. The calculated average electronegativity difference of A and B cations with anion oxygen for NaRuO₃, CaRuO₃, SrRuO₃, PbRuO₃, NaOsO₃, SeMnO₃, SeNiO₃, and are 1.87, 1.84, 1.865, 1.175, 1.87, 1.39, 1.215, and respectively. These values show that NaRuO₃ has almost the same electronegativity difference as NaOsO₃ and greater than the other compounds, which shows that NaRuO₃ is more stable than other perovskite compounds in orthorhombic Pnma space group.

4.1.3 Electronic Properties

To explore the electronic nature of NaRuO₃, electronic structure calculations are performed using GGA-PBEsol. For the study of Coulomb interaction, which is the main cause of crystal field splitting and orbital order, we used Hubbard parameter for onsite Coulomb interaction along with GGA. The relativistic effect of electrons is also included using spin orbit coupling (SOC) calculation. The total and partial density of states are plotted in order to study the detailed behavior of electronic structure. Here we present the plots for spin-

polarized density of states in ferromagnetic and antiferromagnetic phases in order to compare it with the other family of ruthenium compounds. The total density of states in Figure. 4.3(a) and (b) for simple GGA calculations show that the material is metal as the valance band crosses the Fermi level in spin up as well as spin down states. The results for density of states of NaRuO_3 are similar to the ferromagnetic compound SrRuO_3 [124] and also with the Slater insulator NaOsO_3 [19] belongs to the same space group Pnma (62). The relative optimization energies in Table 1 confirm the G-type antiferromagnetic nature of the compound. NaRuO_3 displays similar behavior in electronic properties like similar d^3 configuration 5d compound NaOsO_3 [19]. The metallic nature decreases with the Coulomb interaction addition of $U_{\text{eff}}=3\text{eV}$, almost turns from metal to insulator as shown in Figure 4.2(c) The increase in coulomb potential U upto 6eV has no profound effect on the band gap opening shows the Slater type metal to insulator transition behavior unlike Mott- insulator. Spin orbit coupling (SOC) increases the width of DOS and reduces the effect of U and decreases the splitting between valance and conduction band and increases the metal behavior. Electronic band structure reveals that NaRuO_3 is on the verge of metal to insulator transition. It is clear from Figure 4.3(a,b) that the electronic band structures display almost semiconductor nature with addition of U and spin orbit interaction enhances

the contribution of electrons at the Fermi level (FL) and increase in metallicity. Atomic dependent density of states Figure 4.2(e) and Figure 4.2(f) show that at FL the Ru-4d and O-2p orbitals have major contribution in the total DOS. A strong hybridization occurs between O-2p and Ru-4d at the Fermi level and below the Fermi level. Na has a very minor role in the valence and the conduction states of the compound. In NaRuO₃ the transition element ruthenium exists in Ru⁺⁵, a high spin state of d³ (*t_{2g}*³) configuration with S=3/2 and d³ electrons.

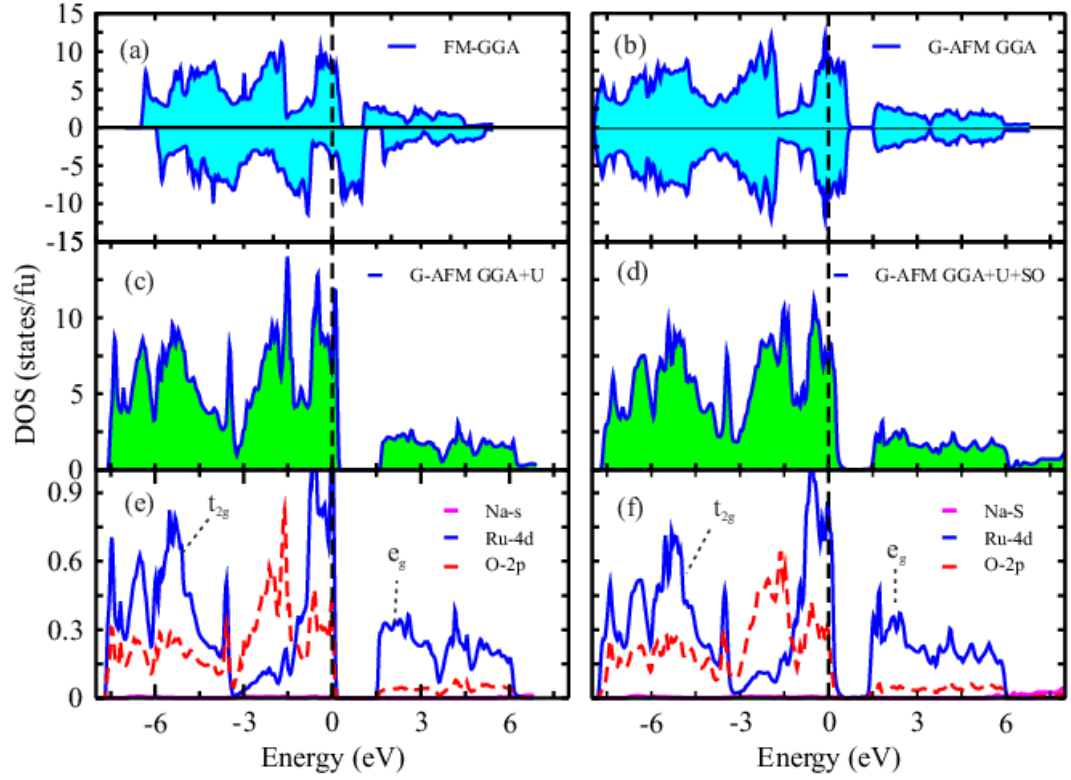


Figure 4. 2 Electronic density of states (a) FM configuration (b) G-AFM (c) Total DOS with $U=3\text{eV}$ (d) Total DOS with $U=3\text{eV}$ (e) Partial DOS by GGA+U (f) Partial DOS by GGA+U+SO.

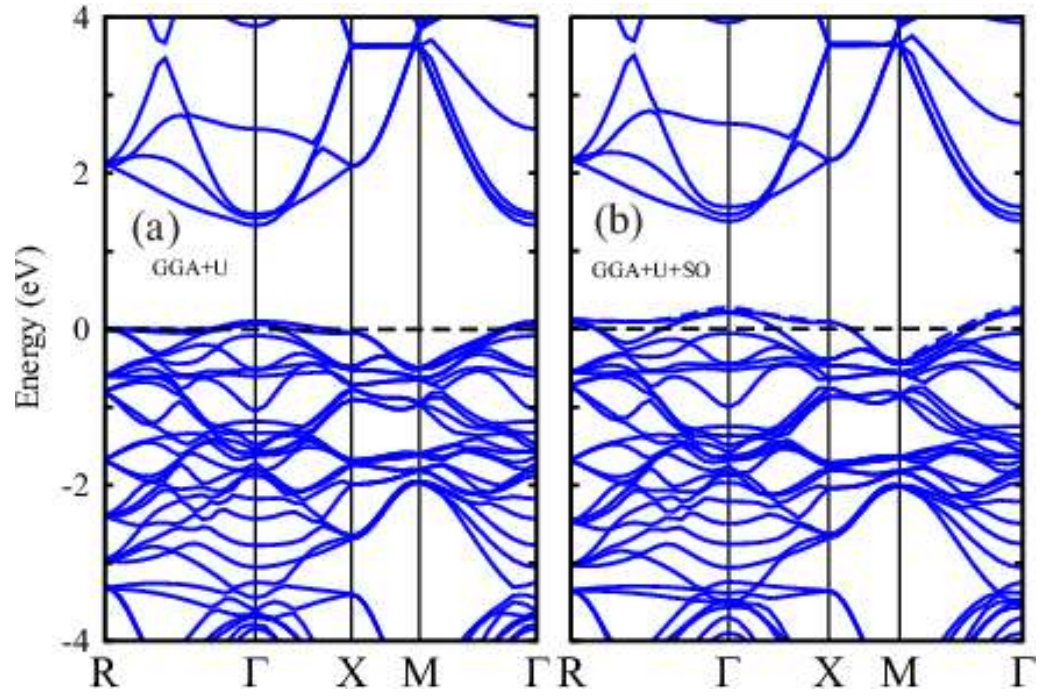


Figure 4. 3 Electronic band structure of NaRuO₃ by (a) GGA+U (b) GGA+U+SO.

Crystal field splits the $4d^3$ orbital of the Ru element into lower energy three fold degenerate states t_{2g} and two fold degenerate states e_g at higher energy. The results presented in Figure 4.2.(e) shows that the exchange splitting between t_{2g} and e_g are 1.53 eV in antiferromagnetic state. The highest peak of t_{2g} lies at 1eV below the FL and e_g 1.9eV above the FL. Spin orbit coupling (SOC) increases the width of DOS and reduces the exchange splitting of t_{2g} and e_g and shifts t_{2g} 0.5 eV towards high energy level as shown in Figure 4.2(f) . The SOC effect breaks the degeneracy of t_{2g} , reduces the peaks height and splits the peaks into several peaks as shown in Figure 4.2(f). To elaborate further the contribution of orbitals of Ru and O in crystal field splitting we plot the partial DOS for G-type AFM, shown in Figure 4.4(a) and (b). Crystal field causes splitting of Ru-d state into t_{2g} and e_g states which further split into d_{xy} , d_{yz} , d_{zx} , $d_{x^2-y^2}$ and d_{z^2} sub orbitals. Under octahedral field symmetry Ru^{+5} ions fill the lower energy state t_{2g} and the higher energy state e_g remains empty. In the DOS d_{xy} , d_{yz} and d_{xz} have major contribution because they are half filled orbitals and d_{z^2} , $d_{x^2-y^2}$ are empty having minor role shown in Figure 4.4. The figure also shows that spin orbit interaction splits the degeneracy of orbitals and splits peaks into several and move the sub orbitals toward the high energy region which reduces

the energy gap between t_{2g} orbital and e_g . The oxygen P_x , P_y and P_z orbitals strongly hybridize with the Ru. d_{xy} , d_{yz} , d_{zx} , $d_{x^2-y^2}$ and d_{z^2} . Na s orbital has minor role in the DOS.

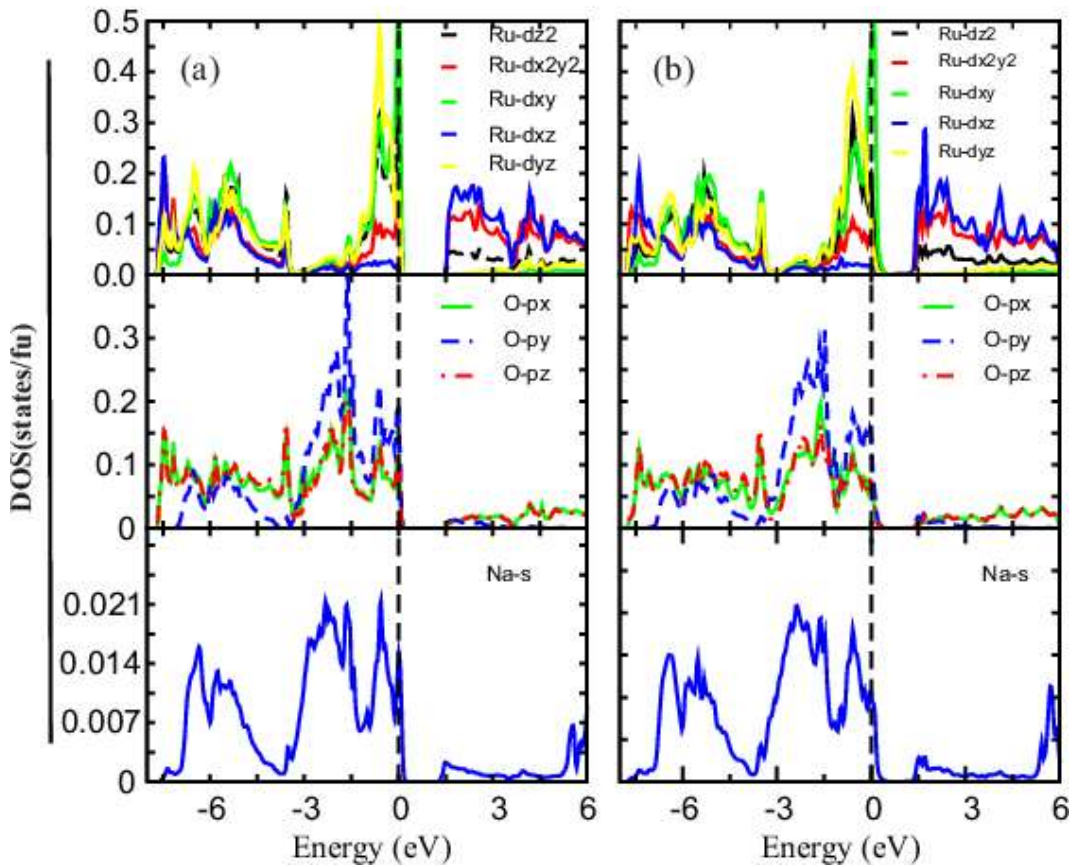


Figure 4. 3 Partial DOS for sub atomic orbitals (a) GGA+U (b) GGA+U+SO .

4.1.4 Correlation Effect

To investigate the correlation effect in NaRuO_3 the Hubbard model is used which relates the onsite coulomb potential U and the onsite hopping energy directly related to the bandwidth W of valance band DOS. This model is a commonly established criterion for the degree of correlation used by many researchers [137,138]. The strength of electronic correlation effect can be described by single parameter U/W . Generally $U/W < 1$ shows metallic behavior and weak correlation effect while $U/W > 1$ represents strong correlation effect and insulator nature. The correlation effect decreases as we move from 3d to 5d. The orbitals of 4d perovskite materials are further extended and hence it is expected that the correlation effects are weaker than 3d compounds. The electronic correlation effect in ruthenates based perovskite oxides is controversial and still under debate [137,139]. To study the nature of 4d orbital of Ru we have used different values of Coulomb potential from 1 eV to 6 eV and compared the magnetic moment and DOS of the Ru to probe a suitable Coulomb parameter U_{eff} . Magnetic properties are more sensitive to the Coulomb parameter U . The magnetic moment of Ru for $U_{\text{eff}}=3\text{eV}$ is $1.54 \mu_B$ which is comparable to the experimentally reported value $0.9\text{-}1.6\mu_B$ (ARuO_3 $A=\text{Sr, Ca}$) perovskite. Therefore in the present work $U_{\text{eff}}=3\text{eV}$ is used for U/W which is also used in literature [123,124,140] for the study of Ru in SrRuO_3 . From Figure 4.2(e) the width of the Ru-d state is 7.9 eV and we have used the $U_{\text{eff}}=3\text{eV}$ so $U/W=0.37$. The calculated $U/W=0.379$ value is less than 1 shows weak correlation weak correlation effect. The correlation effect is comparable to the other members of ruthenium perovskite family (ARuO_3 $A=\text{Sr, Ca}$).

4.1.5 Magnetic Properties

The ground state stable phase of NaRuO_3 is explored and the overall magnetic nature of the compound is investigated. First of all, the unit cell of the compound for different magnetic configurations i.e. ferromagnetic, nonmagnetic as well as A, C and G-type antiferromagnetic is optimized. The optimized energies of various magnetic phases are tabulated in Table 1 the results presented in the table shows G-type antiferromagnetic has the lowest energy and represent the stable phase of the compound, which confirms the experimental observation that higher concentration doping of Na in SrRuO_3 leads towards G-type AFM from ferromagnetic phase. The small difference of energy among the different magnetic states like other ruthenates based perovskites makes NaRuO_3 a potential material for practical applications [58,141].

The magnetic moment of the double cell calculations for G-type AFM structure is zero and the DOS for both the spins is symmetric as shown in the Figure 4.2(b). To study the effect of SOC and correlation effect on the magnetic properties we used several values of U from 1eV to 6eV. Figure 4.5 reveals that with the increase of U value the magnetic moment increases substantially while the SOC decreases it by small amount. It reveals that magnetic properties are strongly dependent on Coulomb correlation and weakly affected by SOC. The magnetic moment of different atoms and the unit cell are provided in Table 4.3. The magnetic moment of different atoms is $0.002 \mu_B$ (Na), $0.354 \mu_B$ (Ru), $0.033 \mu_B$ (O), interstitial $0.26 \mu_B$ and $2.25 \mu_B$ for the total. With the application of $U_{\text{eff}}=3\text{eV}$ the magnetic moment of all the atoms increases to $0.006\mu_B$ (Na), $1.10\mu_B$ (Ru), $0.144\mu_B$ (O),

interstitial $1.214\mu_B$ and $7.366\mu_B$. The spin orbit coupling has minor affect on the magnetic behavior and it reduces the effect of U and decreases magnetic moment. The $U_{\text{eff}}=3\text{eV}$ is applied only to transition element Ru in the compound NaRuO_3 which not only affect the magnetic behavior of transition element but also considerably affect the magnetic moment of other atoms in the compound. Two types interaction describes the nature of magnetic materials, one is double exchange interaction and the other one is super exchange interaction between the transition element via the non-magnetic element. These interactions are accountable for the magnetic nature of perovskites. Super exchange interaction causes antiferromagnetism. The exchange interaction depends on the distance between Ru-Ru and the tilting angle. As the tilting angle increases the Ru-Ru distance decreases. The tilting angle for NaRuO_3 is 13.38° is greater than the tilting angle 10.47° of SrRuO_3 and favors antiferromagnetism.

Table 4. 3 Magnetic moment of different atoms in the unit cell

	Method	Config-	μ_{Na}	μ_{Ru}	μ_{O}	μ_{Interst}	μ_{cell}
NaRuO₃	GGA		0.002	0.354	0.033	0.260	2.253
	GGA+U	G-AFM	0.006	1.100	0.144	1.214	7.366
	GGA+U+SO		0.004	0.990	0.120	1.018	6.434

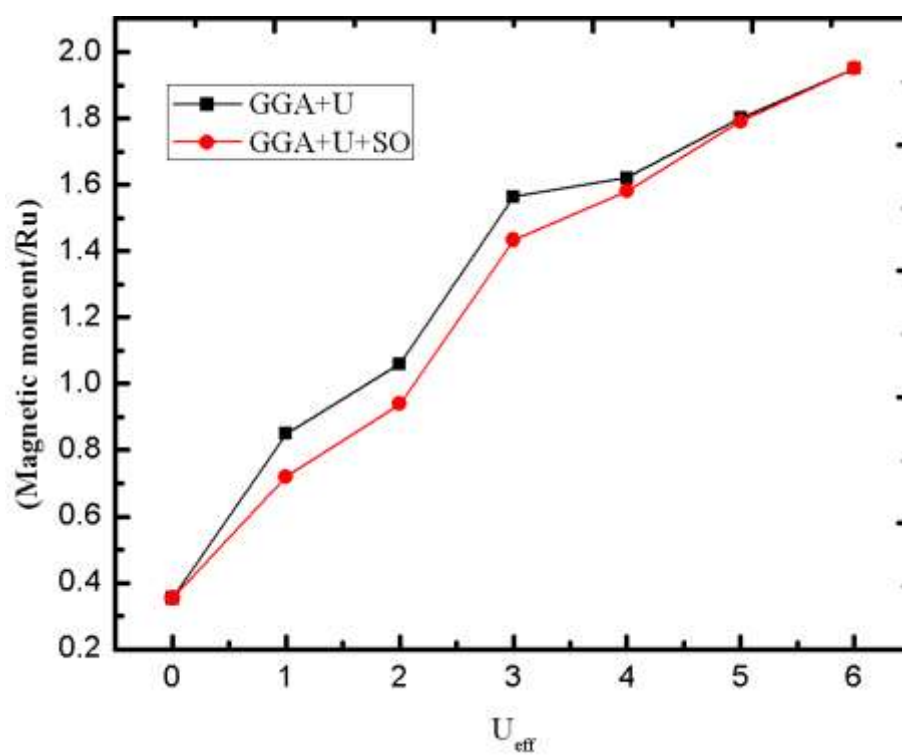


Figure 4. 4 Magnetic moment variation with Coulomb interaction parameter U_{eff} and along with SOC.

4.2 Improved TB-mBJ Study of the Electronic and Optical Properties of Group IIA-IVB Cubic Perovskite Oxides

Perovskite oxides have always been attractive materials for materials scientist owing to their interesting chemical and physical properties [142-145]. These properties of the oxides are directly connected to the electronic nature of the materials, which are also coupled to their crystal structures. As perovskite oxides exist in high symmetric crystal phase as well in low, i.e. from cubic to triclinic crystal structures. Thus, exhibit diverse electronic/physical properties, which make them extensively applicable for numerous scientific, engineering and industrial applications such as magnetic memory devices, sensors, substrates, ferroelectricity, piezoelectricity, superconductivity, magnetoresistivity, thermoelectricity, optoelectronics, spintronics and catalytic electrodes in fuel cells. Due to intriguing electronic behaviour, Perovskite oxides are highly desirable for their scientific understanding and technological applications. Therefore, such properties important to be determined correctly both, theoretically and experimentally. The dependence of the bonding nature, electronic charge density, electronegativity and size of cations (A-cation and B-cation), and other physical properties on the electronic band structure of ABO_3 type cubic perovskite oxides are required to be explored.

The chemical and physical properties of insulators and semiconductors are related to electronic band structures, directly or indirectly. Theoretical researcher have employed different computational approaches to accurately calculate the electronic band structures of cubic Perovskite oxides, e.g. $CaTiO_3$ [146], $SrTiO_3$ [147-149], $BaTiO_3$ [145,150,151],

BaZrO₃ [144], SrZrO₃ [152], PbZrO₃ [153], KTaO₃ [154], SrHfO₃ [155,156], BaSnO₃ [142], BaPrO₃ [143] and LaAlO₃ [157,158], but none of those methods could produce the correct electronic band structure for these compounds, while those method which are consistent with experimental results are obtained with high computational cost (e.g. hybrid functionals). The root cause of the ineffectiveness of those earlier theoretical methods, i.e., LDA [82,83] and GGA [159], etc., for the determination of the correct electronic band structures for these compounds is their inadequacy of electron density behavior in the interstitial region between the covalent bond of B-cation and oxygen (O) atom of the ABO₃ type cubic perovskite oxides.

The theoretical electronic band structure issues of these compound is resolved in this section, using improved Tran and Blaha modified Becke-Johnson exchange potential [97], known as improved TB-mBJ [99]. It has been determined that what physical factors, i.e., bonding nature, ionic size, electronegativity etc., are affecting the electronic properties of these technologically important materials. Additionally, the optical co-efficient were also determined to understand their optical response with improved TB-mBJ.

All the calculations are performed with DFT [82,83] approach, employing the APW+lo scheme [160,161], as embedded in the WIEN2k [121]. The PBEsol GGA [92] calculations are performed to generate an initial exchange-correlation energy. Correct electronic bandgaps of the compounds under consideration are computed through improved TB-mBJ scheme in such a manner to employ TB-mBJ exchange potential, i.e.,

$v_x^{TB-mBJ} = \delta E_x / \delta \rho$. The TB-mBJ exchange potential [97] is defined as:

$$v_{x,\sigma}^{TB-mBJ}(\mathbf{r}) = cv_x^{BR}(\mathbf{r}) + (3c - 2) \frac{1}{\pi} \sqrt{\frac{5}{12}} \sqrt{\frac{2t_\sigma(\mathbf{r})}{\rho_\sigma(\mathbf{r})}}, \quad (1)$$

where $\rho_\sigma(\mathbf{r})$ is the electron charge density, v_x^{BR} is the Becke-Roussel (BR) [98] exchange potential, $t_\sigma(\mathbf{r})$ is the electron's KE density and c is:

$$c = A + B\sqrt{g}, \quad (2)$$

$$\text{and} \quad g = \frac{1}{\Omega} \int_{\Omega} \frac{|\nabla \rho_\sigma(\mathbf{r}')|}{\rho_\sigma(\mathbf{r}')} d\mathbf{r}', \quad (3)$$

where Ω is the unit cell volume. In the above equations the electronic charge density can be properly manipulated in a compound by manipulating the c , which is directly dependent on the square root of the average of $|\nabla \rho_\sigma|/\rho_\sigma$. Koller et al. [99] reparameterized Eq (2) of original TB-mBJ to set different values of c -factor for solids having large and smaller band gap semiconductors, with the aim of improving experimental band gaps. The c -factor set for smaller band gap semiconductors was adopted in the current study.

In the full potential scheme, crystal cell is distributed into two parts, muffin-tin spheres and interstitial region for the non-overlapping spheres and remaining space of the unit cell, respectively. Charge densities and potential are expanded by plane waves basis set (for interstitial region) and spherical harmonics (for muffin-tin spheres). Inside the muffin-tin spheres, the value of l is confined to $l_{max} = 10$ for wave expansion and a specific radius was selected to avoid charge leakage for the muffin-tin region in to order to converged total

energy. Whereas in the interstitial region, the plane wave cut-off $K_{max}=7/R_{MT}$ is used and the charge density $G_{max}=12$ Ry value is selected for the Fourier expansion. A cut-off energy of -6.0 Ryd was set to separate the valence states from core ones. At the start, cubic structures were optimized using a k-mesh of $10 \times 10 \times 10$ in the first Brillouin zone that generates 56 k-point. Whereas for the electronic and optical properties, the k-mesh was increased to $10 \times 10 \times 10$. For all the calculations the convergence was ensured for less than 0.001 Ry/a.u on the exerted forces. The optical parameters of these compounds such as $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ i.e., real and imaginary parts of frequency dependent dielectric constant, were calculated through the procedure reported in Ref. [162].

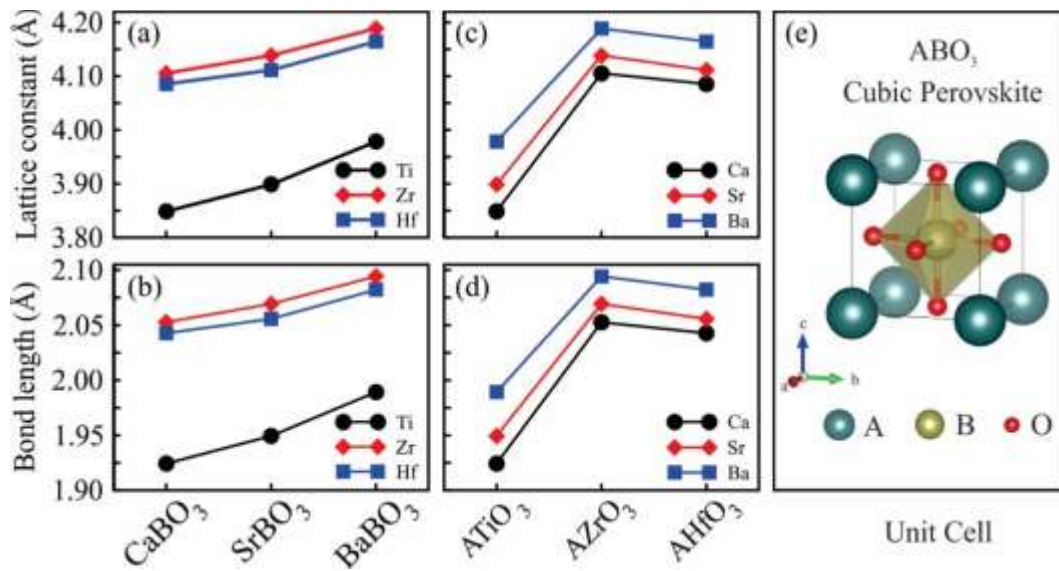


Figure 4.5 Bond length and lattice constant variation w.r.t cation substitution, **(a, b)** plots are for B-cation replacement and **(c, d)** are for A-cation; and **(e)** represent the unit cell of cubic perovskite oxides ABO_3 (A = Ca, Sr, Ba and B = Ti, Zr, Hf) .

4.2.1 Structural Properties

The physical properties of perovskite oxides compound are varied with cations having different oxidation number elements. In addition, this family of perovskite crystalizes in enormous crystal structures (e.g. cubic, tetragonal, orthorhombic, hexagonal and etc.), Hence, offering their application for various electronic and optoelectronic devices. Figure 4.6 shows an example of the cubic unit cell of ABO_3 perovskite, whereby A and B are the two cations, occupy corners and center of the unit cell, respectively, and the oxygen (O) elements are on the faces make BO_6 octahedral arrangement. In this study, we only considered the cubic oxides perovskite with Fm3m space group consisting of element of group IIA and IVB (Ca, Sr, Ba & Ti, Zr, Hf) for electronic and optical properties with improved TB-mBJ potential.

All the consider perovskite were relaxed to obtained optimum structure with minimum energy using PBEsol exchange-correlation functions. The optimized data was then fitted to Birch-Muragan equation of state to calculate the lattice parameters. The total energy as function of unit cell volume variation is illustrated in Figure 4.7, where we can see that the considered structures relaxed volume and the ground state energy of each compound increases with the increase in constituent atomic radii (volume). The lattice parameters obtained through PBEsol (e.g. equilibrium lattice constant, bond lengths and angle, and bulk modulus etc) are compared the other theoretical and experimental results in Table 4.4. It is evident from the table that the present calculated lattice constants not only agree well with the theoretical reported results using different exchange-correlation

functional, but also are consistent with the experimental results. Similarly, the Bulk moduli of these cubic perovskites are consistent with both experimental and other theoretical results. The Ba based compound's bulk modulus are overestimated to some extent than theoretical results, which is due to different exchange-correlation functional employed in this study, whereas its pressure derivative in agreement with the reported results, lie in the range 4-5 (see, Table 4.4).

Furthermore, it is evident from Table 4.4 and Figure 4.5 (a, b) that with the increase of atomic volumes of cations (A and B), the lattice constants increases, consequently increase the bond lengths. Whereas for a fixed A-cation with different B-cation the lattice constants and bond length first increase from Ti to Zr then decreases from Zr to Hf. This decrease is due to electronegativity difference between Zr and Hf atoms despite of almost similar atomic radii, the latter atom is more electronegative than the former one. As a result the bond between A-cation and Hf-cation is stronger than Zr. The same conclusion can be drawn for the B, first increased from Ti to Zr and then decrease Zr to Hf. The chemical bonding of these system are discussed in the latter section of electronic properties.

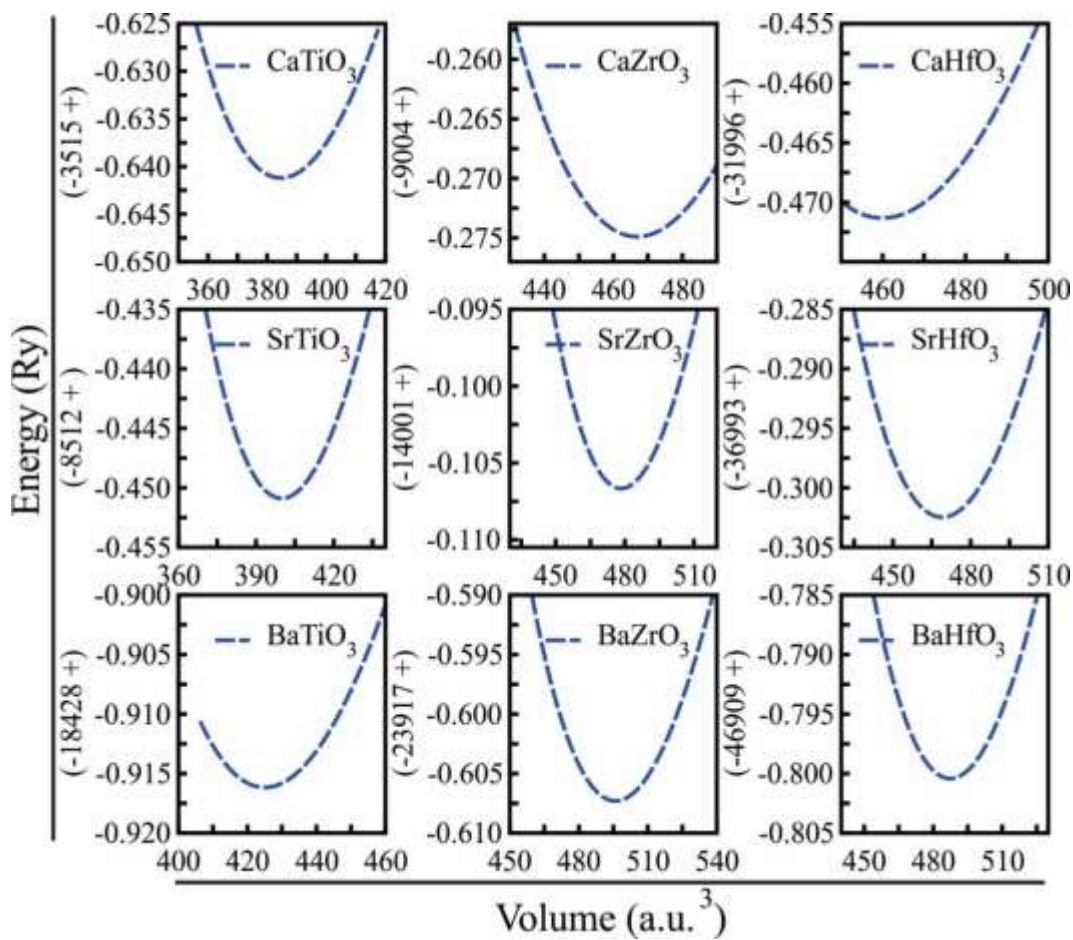


Figure 4. 6 Calculated total energies as a function of the cell volumes for cubic perovskite oxides; CaTiO₃, CaZrO₃, CaHfO₃, SrTiO₃, SrZrO₃, SrHfO₃, BaTiO₃, BaZrO₃ and BaHfO₃ using PBEsol exchange-correlational functions.

Table 4. 4 Calculated lattice parameter obtained with PBEsol functional (Present) for cubic perovskite oxides along with the experimental (Exp.) data and other theoretical results (Other). Percentage error is with respect to experimental data

Compounds	CaTiO ₃	CaZrO ₃	CaHfO ₃
Lattice Constant (a₀, Å)			
Present	3.8486	4.1053	4.0854
Error %	1.0643	0.7902	-2.3910
Exp.	3.8900 ^q	4.1380 ^r	3.9900 ^s
Other	3.8067 ^a	4.064 ^b , 4.135 ^b	4.1900 ^c
Bond Length (B—O, Å)			
Present	1.9243	2.0527	2.0427
Bulk Modulus (GPa)			
Present	191.1594	168.2056	185.1084
Other	192.400 ^u 173.000 ^q	165.300 ^u 178.085 ^p , 154.981 ^p	168.200 ^u 189.203 ^p , 167.173 ^p
Exp.	175.000 ^u	--	191.600 ^u
Derivative of Bulk Modulus (B')			
Present	4.7797	4.4039	5.0000
Compounds	SrTiO ₃	SrZrO ₃	SrHfO ₃
Lattice Constant (a₀, Å)			
Present	3.8987	4.1385	4.1114
Error %	0.1613	-0.7179	-1.0420
Exp.	3.9050 ^a	4.1090 ^e	4.0690 ^t
Other	3.8564 ^a , 3.904 ^d , 3.878 ^e , 3.8898 ^f	4.076 ^g , 4.095 ^e	4.016 ^h , 4.054 ^h , 4.0557 ⁱ , 4.069 ^j
Bond Length (B—O, Å)			
Present	1.9494	2.0693	2.0557
Bulk Modulus (GPa)			
Present	187.3924	166.0982	177.2254
Other	171.000 ^e , 181.000 ^u	191.000 ^e , 152.400 ^u	184.000 ⁱ , 157.400 ^u
Exp.	183.000 ^e , 179.000 ^u	151.0000, 150.000 ^e	--
Derivative of Bulk Modulus (B')			
Present	4.4344	4.4949	5.0757
Compounds	BaTiO ₃	BaZrO ₃	BaHfO ₃
Lattice Constant (a₀, Å)			
Present	3.9785	4.1886	4.1645
Error %	0.5375	0.0334	0.1558
Exp.	4.000 ^{k,l}	4.1900 ^l	4.1710 ^o
Other	4.000 ^k , 3.935 ^l , 3.9293 ^a	4.234 ^m , 4.148 ^l , 4.193 ^j , 4.181 ⁿ	4.171 ^j , 4.2858 ^o , 4.310 ^o , 4.2499 ^o
Bond Length (B—O, Å)			
Present	1.9893	2.0943	2.0823
Bulk Modulus (GPa)			
Present	181.6456	164.7281	175.5992
Other	172.000 ^k , 194.200 ^l , 165.00 ^u	174.700 ^l , 141.000 ^u	146.720 ^o , 144.000 ^u

Exp.	162.000 ^u	127.000 ^u	--
Derivative of Bulk Modulus (B')			
Present	4.5933	4.7719	4.4225

^aRef. [163]

^bRef. [164]

^cRef. [165]

^dRef. [166]

^eRef. [152]

^fRef. [167]

^gRef. [168]

^hRef. [155]

ⁱRef. [169]

^jRef. [170]

^kRef. [171]

^lRef. [151]

^mRef. [172]

ⁿRef. [173]

^oRef. [174]

^pRef. [175]

^qRef. [146]

^rRef. [176]

^sRef. [177]

^tRef. [178]

^uRef. [179]

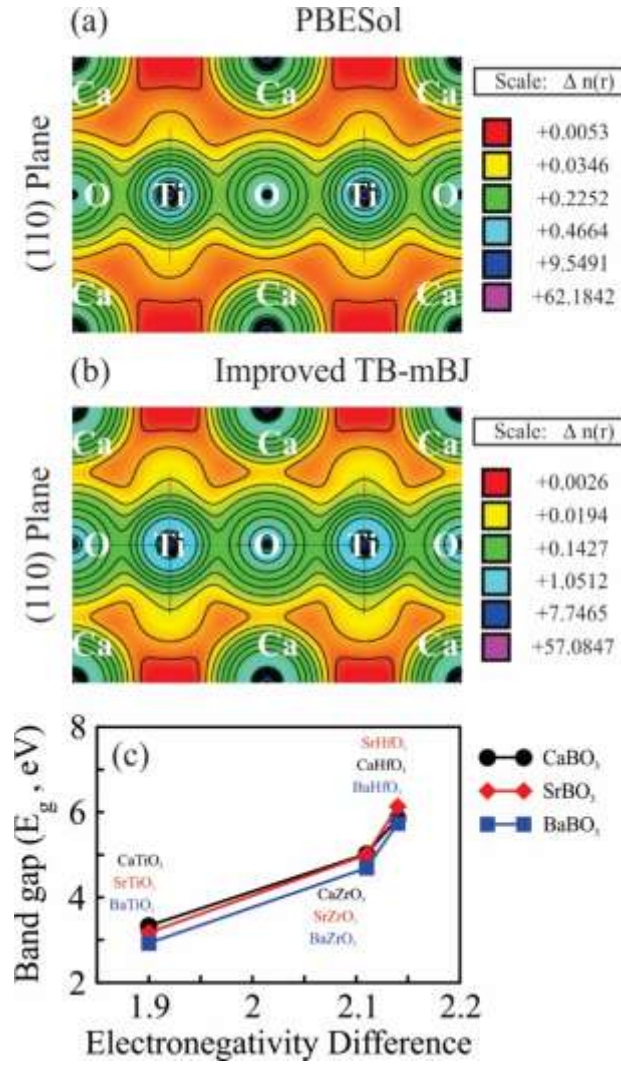


Figure 4. 7 The contour plot of electron charge density of CaTiO₃ in the (110) crystallographic plane calculated with PBEsol and improved TB-mBJ functionals. (c) Electronic band gap obtained with improved TB-mBJ versus the electronegativity difference between O and B-cations (B = Ti, Zr, Hf) of the cubic perovskites.

4.2.2 Chemical Bonding

The electronic properties of a compound are strongly dependent upon its electron charge density, where the electron charge density is related to the bonding nature and crystal structure. The bonding nature of the nine cubic perovskite oxides, such as CaTiO_3 , CaZrO_3 , CaHfO_3 , SrTiO_3 , SrZrO_3 , SrHfO_3 , BaTiO_3 , BaZrO_3 , and BaHfO_3 can be inferred from Figure 4.7 (a). The contour plot of CaTiO_3 in the (110) plane reveals the mixed covalent and ionic bonding nature (from the electron charge density difference). It clearly demonstrates predominant covalent bond between Ti and O atoms, and ionic bond in case of Ca and O atoms. Additionally, the figure also shows that for the covalent bonds, electron density substantial part lie in the interstitial region, which cannot be treated shows the electron charge density for by the computational methods like LDA and GGA functionals. Consequently such functionals result in severe underestimation of electronic band gaps, in comparison to the experimental results [142].

Table 4. 5 Fundamental indirect electronic band gaps (E_g , eV), experimental (Exp.) and theoretical results for cubic perovskite oxides obtained by different techniques; superscript ‘*’ represents calculated results and hybrid functional is denoted by HF. (The calculated results are rounded to three figures, and I-TB-mBJ represent improved TB-mBJ)

Compounds	LDA	GGA	HF	PBEsol*	TB-mBJ*	I-TB-mBJ*	Exp.
CaTiO ₃	1.97 ^a	2.45 ^h	4.20 ^p	2.02	2.95	3.33	3.50 ^a
CaZrO ₃	3.28 ^b	3.30 ⁱ	5.4 ^q	3.42	4.60	5.02	--
CaHfO ₃	3.61 ^b	3.63 ^j	--	3.78	5.29	5.86	6.2 ^u
SrTiO ₃	1.92 ^c	1.99 ^k	3.63 ^k	1.98	2.85	3.18	3.25 ^k
SrZrO ₃	3.62 ^c	3.42 ^l	4.89 ^r	3.43	4.63	5.00	--
SrHfO ₃	3.61 ^d	3.79 ^d	6.4 ^s	3.86	5.57	6.13	6.10 ^v
BaTiO ₃	1.20 ^e	2.26 ^m	3.42 ^t	1.93	2.69	2.92	3.20 ^e
BaZrO ₃	3.20 ^f	3.20 ⁿ	5.4 ^s	3.30	4.41	4.69	5.00 ⁿ
BaHfO ₃	3.53 ^g	3.61 ^o	5.8 ^s	3.72	5.31	5.73	6.0 ^w

^aRef. [146],

^bRef. [175],

^cRef. [152],

^dRef. [155],

^eRef. [150],

^fRef. [180]

^gRef. [181],

^hRef. [182],

ⁱRef. [176],

^jRef. [183],

^kRef. [148],

^lRef. [184],

^mRef. [151],

ⁿRef. [144],

^oRef. [185],

^pRef. [186],

^qRef. [187],

^rRef. [188],

^sRef. [189],

^tRef. [148],

^uRef. [190] considered from Tauc treatment of the diffuse-reflectance spectra of CaHfO₃ and SrHfO₃,

^vRef. [156],

^wRef. [191] experimental band gap is predicted from SrHfO₃.

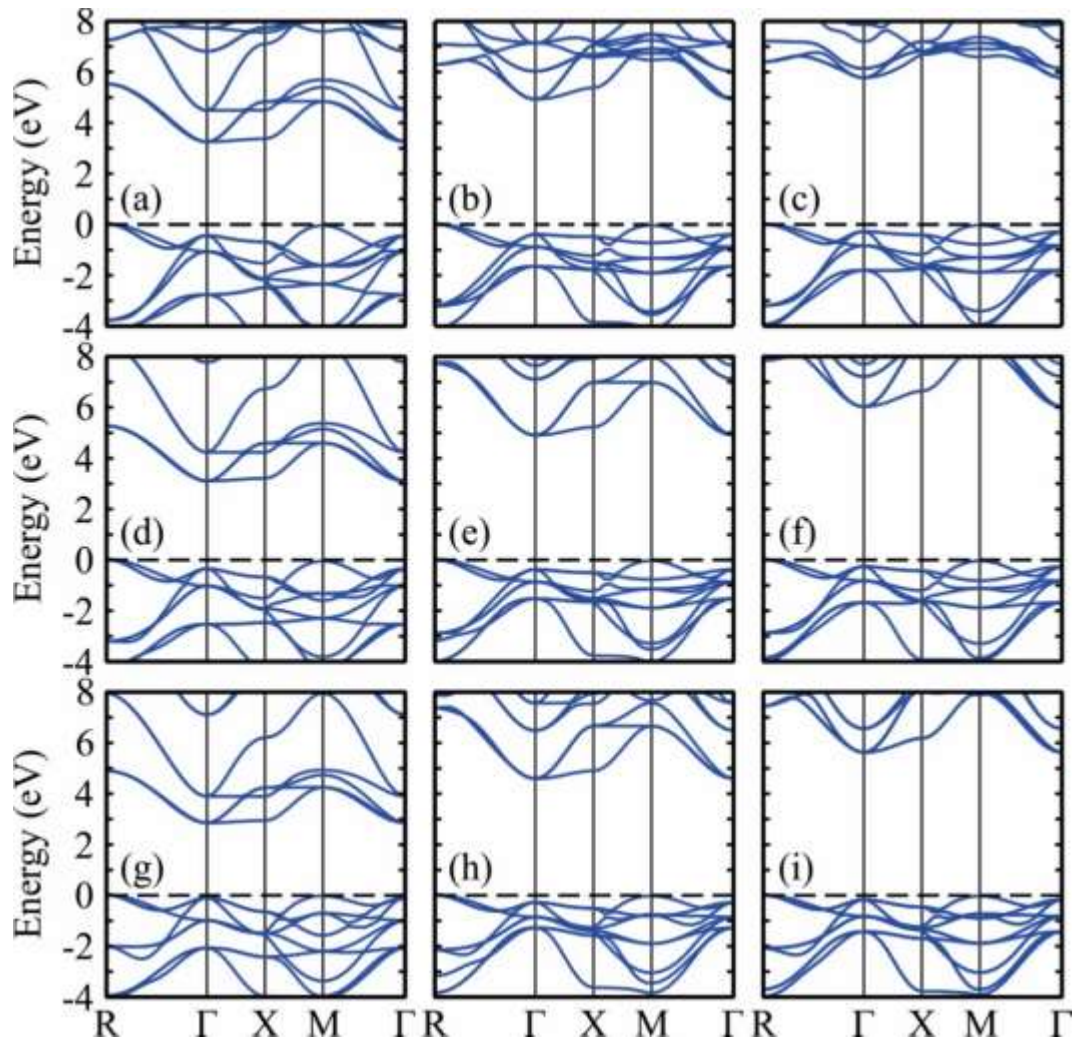


Figure 4. 8 Bandstructure of ABO_3 cubic perovskite obtained with improved TB-mBJ; **(a)** $CaTiO_3$, **(b)** $CaZrO_3$, **(c)** $CaHfO_3$, **(d)** $SrTiO_3$, **(e)** $SrZrO_3$, **(f)** $SrHfO_3$, **(g)** $BaTiO_3$, **(h)** $BaZrO_3$ and **(i)** $BaHfO_3$.

4.2.3 Electronic Properties

The electronic properties of the group IIA and group IVB cubic ABO_3 are investigated by analyzing the DOS and band structure of the compounds. The electronic bandgaps of the materials under study from literature using LDA and GGA exchange-correlation functionals are compared with the calculated ones in this study through improved TB-mBJ approach are provided in Table 4.5. The results of the computationally expensive methods such as hybrid functional are also given in the table. As mentioned earlier, GGA and LDA functionals underestimate the experimental bandgaps, whereas the TB-mBJ improve them up to some extent. Whereas, in case of hybrid functional band gaps of perovskite oxides are better than former functionals. The electronic band structure of the considered cubic perovskite oxides obtained with improved TB-mBJ are illustrated in Figure 4.8, and their PDOS are presented in Figure 4.9. Figure 4.8 shows that the considered semiconductor compounds have indirect band gap nature, as their valence band (VB) maxima and conduction band minima are located at the R- and Γ -point of Brillouin zone, respectively. The occupied states at the top of VB in the cubic perovskite oxides are mostly as a result of the oxygen p-states, while the unoccupied states at the bottom of CB are largely populated by the d states of B-cation, see Figure 4.10. of PDOS. This reveals that the bonding type among the B-cation and oxygen atom of these cubic perovskite oxides has predominant effect on the bandgap, unlike the bonding between oxygen and A-cation. Another important character that influence the electron property is the difference in the electronegativity of B-cation and O atom. The plot between the calculated band gap with

improved TB-mBJ vs electronegativity difference between O and B-cation of the considered cubic perovskite oxides is presented in Figure 4.8 (c). The graph clearly shows that with the increase in the electronegativity difference, the band gaps are increased. On the other hand, Table 4.5 indicate a little difference in the magnitude of band gaps, e.g. BaTiO₃ and SrTiO₃, despite of high electronegativity of Sr atom than that of Ba, which confirms that the O atom and A-cation chemical bond has a minor role in the bandgap of these compounds. Though, bandgaps are reduced for A-cation replacement down the group with same electronegativity difference B-cations and O atom, which is manifested by their increasing ionic radii in these compounds. This can also be verified from their PDOS analysis, i.e. increasing states contribution in range about 3eV to Fermi level of the valence band. In short, the ionic radius size of the A-cation also affects band gap besides major influence of the difference in the electronegativity and chemical bond between O and B-cation.

After all the above discussion, we are able to settle the theoretical bandgaps issue of the oxides under investigation. We approached to the problem with the TB-mBJ method, however it is clear from Table 4.5 that this approach is also has limitation in replicating experimental band gaps for these compounds. The reason for this inconsistency compared to the experimental results in this theoretical approach is the electrons charge density inappropriate treatment. As mentioned that the electron charge density is obtained from $|\nabla\rho_\sigma|/\rho_\sigma$ (linearly dependent). This suggests that manipulating the c factor has significant role in it determination. For this reason Koller et al. [99] reparameterize Eq (2) for set to

different values of c-factor for solids having large and smaller band gap semiconductors. This approach hereafter know as improved TB-mBJ. Another way to improve the band gap of semiconductors is to optimize the c-factor with respect to exact experimental band gap [192,193]. In this study, we employed c-factor value for small semiconductors as suggested in Ref. [99] . The contour plot in Figure 4.8 clearly indicates modification in electron density calculated with improved TB-mBJ and PBEsol potentials.

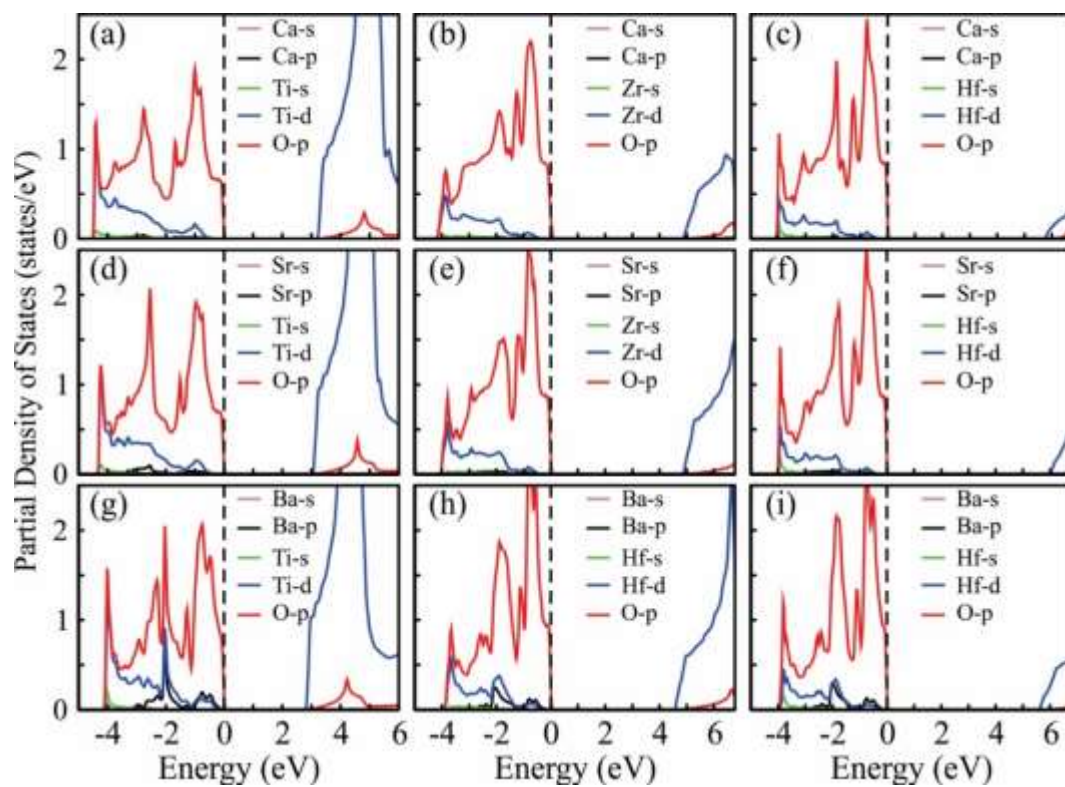


Figure 4. 9 Partial Density of states of ABO_3 cubic perovskite obtained with improved TB-mBJ; (a) $CaTiO_3$, (b) $CaZrO_3$, (c) $CaHfO_3$, (d) $SrTiO_3$, (e) $SrZrO_3$, (f) $SrHfO_3$, (g) $BaTiO_3$, (h) $BaZrO_3$ and (i) $BaHfO_3$.

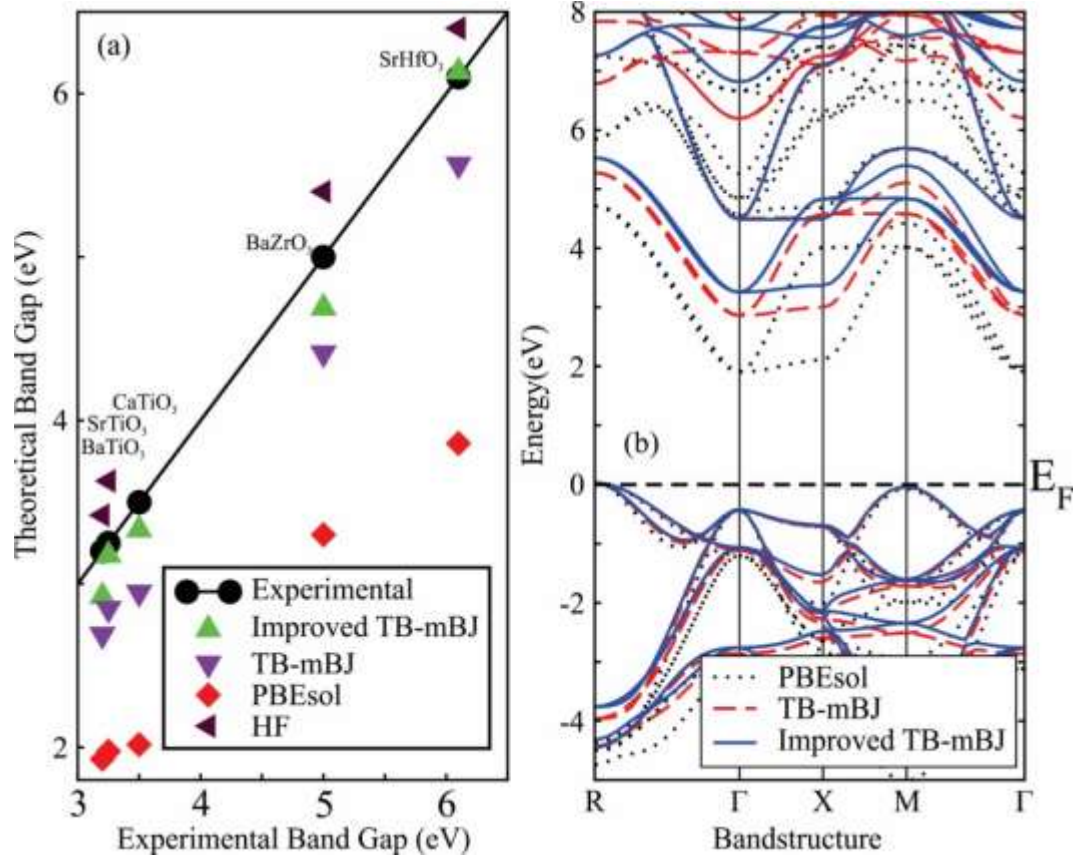


Figure 4. 10 **(a)** Experimental band gaps vs. calculated electronic band gaps plot of the perovskite CaTiO_3 , SrTiO_3 , BaTiO_3 , SrZrO_3 , BaZrO_3 , and SrHfO_3 (Hf represents hybrid functional). **(b)** Electronic band structure of the CaTiO_3 by PBEsol (dotted-line), TB-mBJ (dashed-line) and Improved-TB-mBJ (solid-line) functionals.

The calculated band gaps obtained by improved TB-mBJ approach for the considered cubic perovskite oxides CaTiO_3 , CaZrO_3 , CaHfO_3 , SrTiO_3 , $\text{SrZrO}_3\text{SrHfO}_3$, BaTiO_3 , BaZrO_3 , and BaHfO_3 are provided in Table 4.5 and the comparison with the other theoretical values and available experimental results of fundamental bandgaps is plotted in Figure 4.11 (a). The figure clearly shows that PBEsol functional severely underestimate the band gaps, whereas the results of computationally hybrid functional are agreement with the experimental but are still not accurate enough with such high cost. The plot obviously demonstrates the success of the improved TB-mBJ approach for providing comparatively correct band gaps and other electronic properties for the cubic perovskite oxides under study. However, to justify accuracy of this method must be verified that whether approach reproduces the features of the GGA scheme or not?

The answer to the above logical question is provided in Figure 4.11 (b), where the band structures of CaTiO_3 calculated with PBEsol (dotted line), TB-mBJ (dashed line) and improved TB-mBJ (solid) are illustrated. The figure shows the same feature of the bands but wider bandgas due to the additional potential. Hence, this verifies that the additions stronger repulsive TB-mBJ potential does not affect the band structure of GGA. It is evident that the conduction bands are shifted upward altogether with the application of this potential. It can be clearly seen that the unoccupied states are slightly shifted in the right ways by the TB-mBJ based method. These results suggest the recognition of improved TB-mBJ approach for cubic Perovskite oxides electronic calculations, compared to other similar methods.

4.2.3 Optical Properties

To realize the optical response of improved TB-mBJ exchange potential, the frequency dependent complex dielectric constant, $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$ is investigated, because optical properties are directly associated to the band gap of a material. The Kramers-Kronig transformations can be used to realized the real part ($\varepsilon_1(\omega)$) from imaginary parts ($\varepsilon_2(\omega)$), which shows dispersion of incident light. And the optical absorption can be revealed from $\varepsilon_2(\omega)$, demonstrate all direct transitions to conduction band from valence. Once the $\varepsilon(\omega)$ is calculate, other optical co-efficient such as refractive index $n(\omega)$, energy loss function $L(\omega)$, optical conductivity $\sigma(\omega)$ and sum rule from the $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ parts of dielectric constant using the relation reported in Ref. [162]. These optical co-efficient are illustrated in Figure 4.12. The optical band gaps of the considered compounds, realized from $\varepsilon_2(\omega)$ are consistent with their band structures direct electron transitions, from about 2.5 eV to 6.5 eV. Substituting the B-cation from Ti to Zr to Hf demonstrate blue shifts of the optical transition peaks in these system, whereas changing A-cations (Ca to Sr to Ba) shifts the peaks to lower energy regions result in red shift. These red shifts of peak are indorsed by their reduction of band gap observed earlier in the band structure. Furthermore, the wide absorption ultraviolet region beside the visible, make them favorable for the optical device fabrication in these ranges. The real part, $\varepsilon_1(\omega)$, at zero frequency decreases (increases) with the increasing (decreasing) band gap B-cation (A-

cation) replacement down the group, related with Penn's model [194]. A similar trend is observed before and after reaching the maximum value of $\varepsilon_1(\omega)$.

The refractive index $n(\omega)$ related to square root of $\varepsilon_1(\omega)$ is important for the practical application of a compound in photonic and optical devices. A variation of $n(\omega)$ is noticed with incident light in their graphs. Its trends are consistent with $\varepsilon_1(\omega)$, i.e. decreased (increased) with B-cation (A-cation) replacement, and after reaching maximum value decreases below the unity, obeying Paul Drude's Model. The influence of light on material is realized from energy loss function $L(\omega)$, observed for photo energy higher than its band gap. Noticeable peaks of $L(\omega)$ are observed in energy range about 30 eV and 45 eV generated by plasmons, which are shifted to lower energy with increasing band gap due to B-cation replacement. Finally, the sum rule (oscillator strength), plots demonstrate a rapid raise in the number of electrons involved in optical transitions at energy range from 28 eV to 38 eV and saturate after 40 eV. These optical co-efficient curves are consistent in terms of shifts energy and peak structures (positions and heights) with other theoretical results [175]. To verify the optical results, we have compared experimental data from literature of with our calculated improved TB-mBJ results. The calculated and experimental real and imaginary parts dielectric function, and optical conductivity plots are illustrated in Figure 4.13, for SrTiO₃ and SrZrO₃. Figure 4.13 shows that calculated and experimental results are in good agreement, especially, the optical bands from $\varepsilon_2(\omega)$ and $\sigma(\omega)$ for these two compounds. Thus, confirm the validity of improved TB-mBJ.

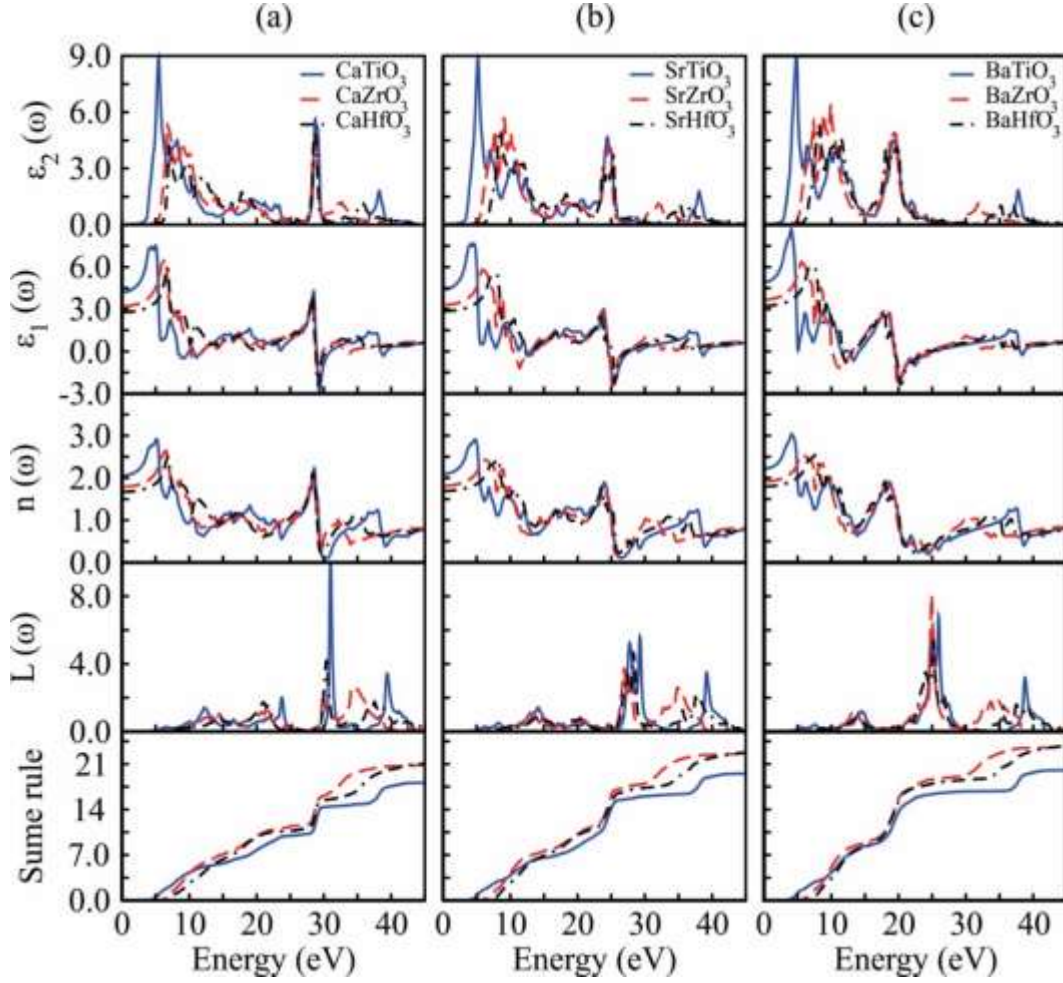


Figure 4. 11 Optical co-efficients of ABO_3 cubic perovskite obtained with improved TB-mBJ; **(a)** $CaBO_3$, **(b)** $SrBO_3$, **(c)** $BaBO_3$ ($B = Ti, Zr, Hf$), and the optical co-efficients are real $\epsilon_1(\omega)$ and imaginary $\epsilon_2(\omega)$ parts of frequency dependent dielectric constant, refractive index $n(\omega)$, energy loss function $L(\omega)$ and sum rule.

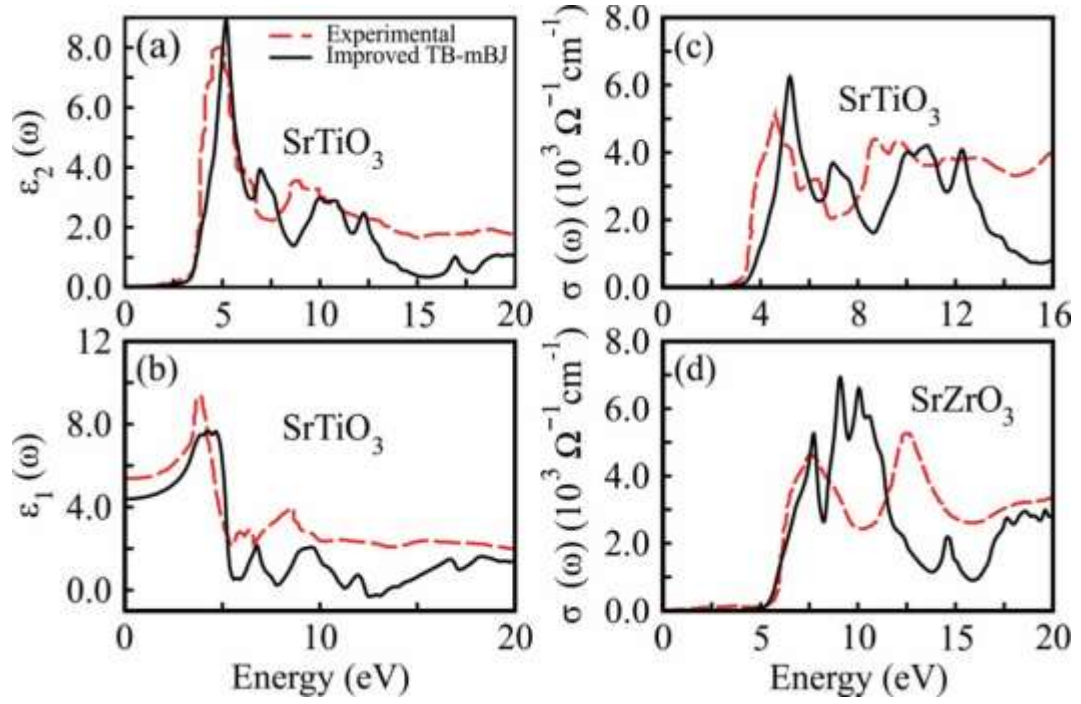


Figure 4. 12 Experimental and calculated real $\epsilon_1(\omega)$ and imaginary $\epsilon_2(\omega)$ parts dielectric function and $\sigma(\omega)$ optical conductivity spectra; (a-c) SrTiO₃ and (d) SrZrO₃. The experimental data is from Ref. [184] and Ref. [195] for $\epsilon_1(\omega)$ and $\epsilon_2(\omega)$, and $\sigma(\omega)$, respectively.

4.3 Structural, Electronic, Ferroelectric, Linear and Nonlinear

Optical Properties of $\text{Ca}_3\text{Ti}_2\text{O}_7$

4.3.1 Structural Properties

$\text{Ca}_3\text{Ti}_2\text{O}_7$ compounds belongs to a famous perovskite structure known as Ruddlesden-Popper (RP) series with $n=2$, generally represented by $\text{A}_{n+1}\text{B}_n\text{O}_{2n+1}$ ($n=0, 1, 2, \dots \infty$). The crystal structure of $\text{Ca}_3\text{Ti}_2\text{O}_7$ composed of layers $\text{CaO}(\text{CaTiO}_3)_2$ alternating each other in such manner that each perovskite double layer CaTiO_3 sandwich among rock salt CaO structures as shown in Figure 4.14 The crystal structure of $\text{Ca}_3\text{Ti}_2\text{O}_7$ consists of four formula unit ($Z=4$) with an orthorhombic space group $\text{Cmc}2_1$ (36) [196]. The space group $\text{Cmc}2_1$ (36) is a noncentrosymmetric means lacking the inversion symmetry which is considered the main cause of technologically important properties such as nonlinear optical properties, ferroelectricity and piezoelectricity [197-199]. The physical properties strongly dependent on the crystal structure of crystalline material, therefore the study of crystal structure of a compound is very important. To obtained best results for optimized lattice constant, other lattice parameters and relaxed atomic positions geometry relaxation and lattice optimization were performed using different exchange correlation potentials. For the geometry relaxation the experimental lattice parameters are used [196]. The optimized data was then fitted to equation of state of Birch-Murangan to calculate the structural parameters. The calculated lattice parameters, volume, bulk modulus etc. are provided in Table 4.6 using different exchange correlation potential along with experimental values.

The Figure 4.15 shows the relation among volume and the total energy of the compound. It is clear that by increasing the volume the total energy decreases up to some point where minimum energy limit is achieved reveals the ground state of the compound, but with further increase in volume the total energy increase.

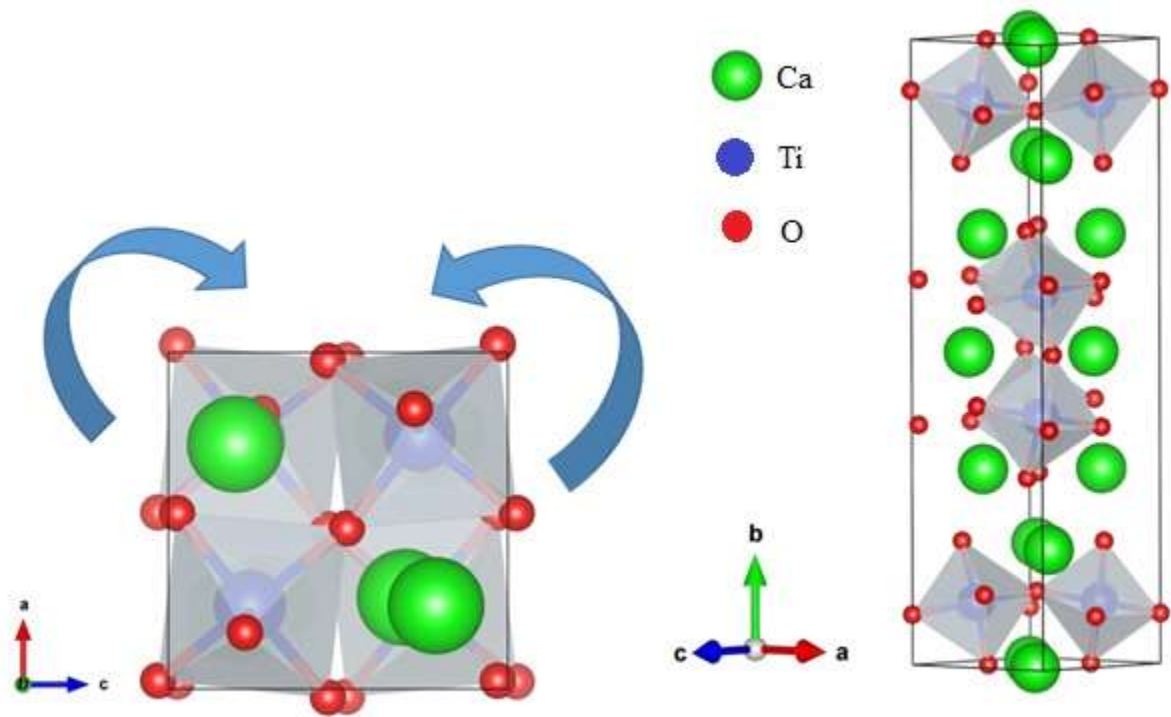


Figure 4. 13 $\text{Ca}_3\text{Ti}_2\text{O}_7$ Crystal Structure at different orientation.

Table 4. 6 The calculated structural parameters of $\text{Ca}_3\text{Ti}_2\text{O}_7$ by different potential along with experimental

Structure parameter	LDA	GGA-PBE	GGA2006	GGA-PBEsol	Experiment
a (Å)	5.357	5.464	5.409	5.411	5.4172 ^a
b (Å)	19.310	19.681	19.490	19.492	19.5169
c (Å)	5.326	5.461	5.394	5.395	5.4234
V(Å) ³	551.54	580.644	570.393	570.552	573.4
B(GPa)	194.25	163.92	178.02	177.92	

[5]^a

The listed value of structural parameter in Table 4.6 shows that the calculated lattice constant value by LDA is more underestimated as compared to GGA2006 and GGA-PBEsol, while GGA-PBE overestimate the experimental values. LDA generally underestimates and GGA-PBE overestimates the experimental parameters. Among the calculated values the of structural parameters by GGA-PBEsol are agree well with the experimental value as compared to the other potentials and therefore we used the GGA-PBEsol calculated parameters for further calculations. The bond lengths play vital role to study the stability of a crystal as well as its related physical properties, therefore we calculated different bond lengths of $\text{Ca}_3\text{Ti}_2\text{O}_7$ listed in Table 4.7. There different bond length in Table 4.7 between transition atom and oxygen Ti—O and Ca—O indicate the effective role of Jahn–Teller distortion in electronic properties. There are three different polyhedral are present in this crystal structure for Ca^{1+2} , Ti^{2+4} and Ca^{2+2} cations. The Ti—O bond length ranges from 1.94—1.96 in the plane different from the apical bond length ranges from 1.97—1.99 and the average bond length is 1.97. Similarly the bond length of Ca—O is also different in plane and apical direction as listed in Table 4.7. The tilting of octahedra are extremely important in describing the distortion of the oxygen network in BO_6 octahedral. The bond angle between the oxygen and the two transition atoms is very important for the predicting the non-centrosymmetric nature and physical properties like ferroelectricity, pezzoelectricity and nonlinear optical properties. The bond angles in Table 4.7 show variation among different transition atoms and oxygen. The variation in bonds length and bond angles

reveals the distorted nature of the compound making it suitable for the study of ferroelectricity and nonlinear optical properties.

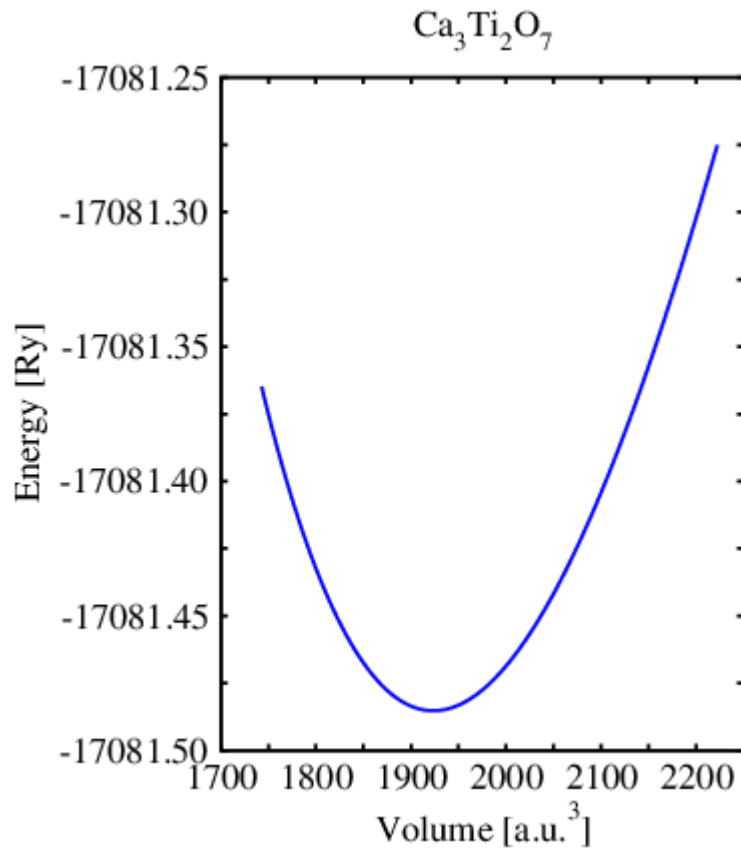


Figure 4. 14 The optimization plot shows the relation Volume vs total energy of the $\text{Ca}_3\text{Ti}_2\text{O}_7$ compound.

Table 4. 7 Selected angles and bond length of $\text{Ca}_3\text{Ti}_2\text{O}_7$

Ti1-O10-Ti4	155.3232°
Ti3-O12-Ti2	155.3233°
Ti2-O14-Ti4	154.5308°
Ti3-O13-Ti1	154.5308°
Ti2-O8-Ti3	158.1606°
Ti4-O6-Ti1	158.1607°
Ti1-O7	1.94590 Å
Ti1-O7	1.99272 Å
Ti1-O7	1.97726 Å
Ti1-O7	1.9911 Å
Ti1-O7	1.94392 Å
Ti1-O7	1.96621 Å
Ca1-O9	2.48228 Å
Ca1-O9	2.76497 Å
Ca1-O9	2.54208 Å

Table 4. 8 Calculated band gap and polarization of $\text{Ca}_3\text{Ti}_2\text{O}_7$ by various potential and experimental values

Potential used	Band gap (eV)	Polarization ($\mu\text{C}/\text{cm}^2$)
LDA	2.45	15.71
GGA-PBE	2.51	15.70
GGA2006	2.49	15.72
GGA-PBEsol	2.53	15.76
Experiment	3.94 ^b 3.6 ^c	8.0 ^f
GGA+mBj	3.74	11.41
Other reported	2.38 ^b 3.3 ^d	10 ^d , 20 ^e , 15 ^b
[200] ^b , [47] ^c , [201] ^d , [30] ^e , [202] ^f		

4.3.2 Electronic Properties

The band structure as well as total and partial DOS of layer perovskite $\text{Ca}_3\text{Ti}_2\text{O}_7$ is explored to investigate the electronic nature of the compound and compare it with the member of the same family of the bulk structure of CaTiO_3 . In order to achieve accurate results compared to experimental, we used different potentials to calculate electronic band structure. The calculated band gap by various potential is tabulated in Table 4.8 along with experimental bandgap value and other theoretical data from literature. The band gap results presented in Table 4.8 show that LDA and GGA severely underestimate the experimental band gap although the TB-mBJ improves them to great extent. Our LDA and GGA result are comparable with the other theoretical results. The calculated TB-mBJ result is in good agreement with the experimental bandgap available in literature. The bandgap of TB-mBJ 3.74 eV is little smaller than widely reported experimental value 3.94 eV and greater than 3.6 eV but is reasonably in agreement with both the experimental results. To clearly understand the electronic nature of the compound, its electronic band structure, total and partial DOS per formula unit of $\text{Ca}_3\text{Ti}_2\text{O}_7$ are illustrated in Figure 4.16. This figure reveals that the compound is wide band gap semiconductor having direct band gap nature, as its valence band (VB) maxima and conduction band minima are located at the same Γ -point of Brillouin zone. The calculated bandgap nature is in agreement with the experimental and other theoretically reported results. The right side of Figure 4.16 presents total and partial DOS, which shows the same bandgap value as that of the band structure. The partial DOS reveals that the occupied states at the top of the VB are mostly due to the oxygen p-

states and the unoccupied states at the bottom of CB are largely populated by the Ti-d states. The Ca has a very minor role in the valence and the conduction bands; its contribution mainly lies in core state. The Ti-d state is empty, therefore it has little contribution in the valence state and major contribution in the conduction band. In the conduction process electrons will be transferred from the O-p to the Ti-d state. In order to check the reliability of TB-mBJ and compare the results of layer perovskite with their bulk perovskite of the same family we have also calculated the DOS and band structure of CaTiO_3 . The total and partial DOS and band structure of CaTiO_3 are provided in Figure 4.17. This figure demonstrates that CaTiO_3 shows similar trend RP phase. The VB is predominantly populated by the O-p state and the lower of the CB is predominantly populated by the empty Ti-d state of the transition atom. A significant hybridization among the d-state of Ti and p-state of oxygen is observed, while calcium has only minor role around the Fermi level. Although the symmetry environments for the ions are different for both the compounds produces almost similar band structure with wide insulating band structure. The calculated band structure successfully reproduced the experimental trends of band gap for both the compounds. The band gap of the RP phase $\text{Ca}_3\text{Ti}_2\text{O}_7$ (3.74eV) is little greater than the bulk CaTiO_3 (3.56eV), while the experimental value for $\text{Ca}_3\text{Ti}_2\text{O}_7$ is 3.94eV and for CaTiO_3 is 3.5eV. Both of the calculated values are closer to the experimental results demonstrate the accuracy and reliability of the improved TB-mBJ exchange potential for band gap prediction of newly designed materials and existing

compounds. The accurate band gap calculation is very important for devices application because almost all the optical devices are band gap dependent.

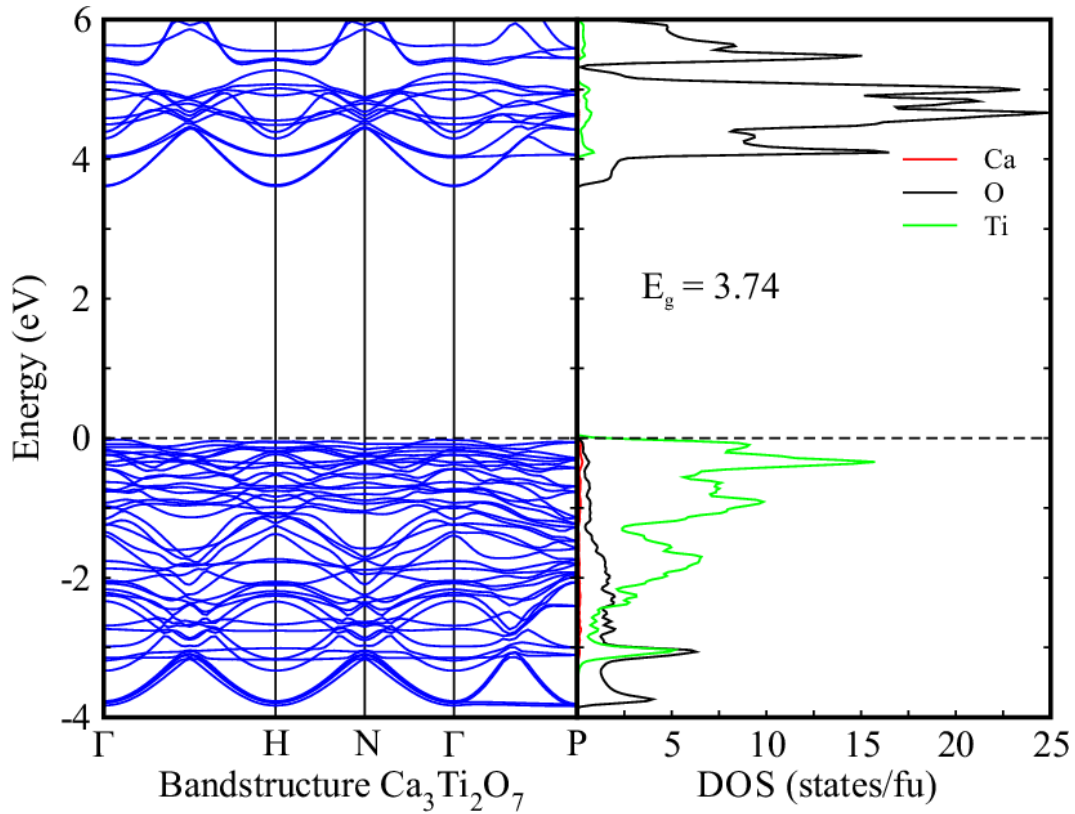


Figure 4. 15 The band structure and total and partial density of state/formula unit of $\text{Ca}_3\text{Ti}_2\text{O}_7$

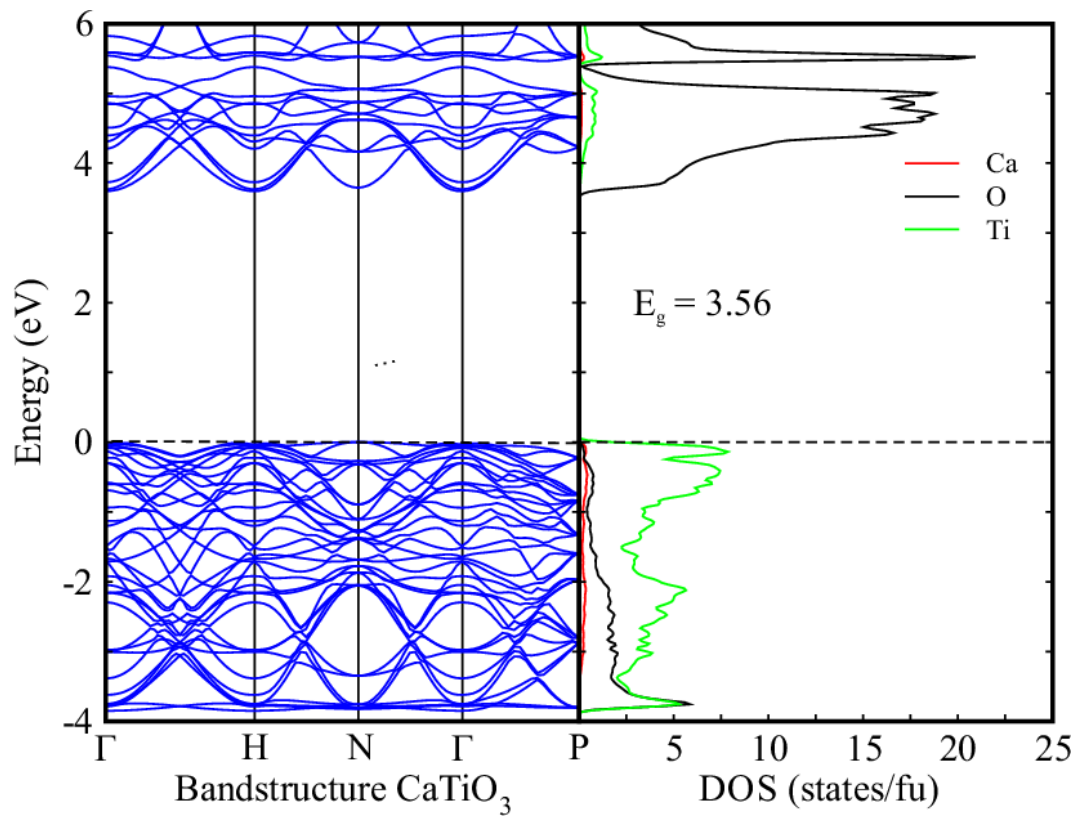


Figure 4. 16 The band structure and total and partial density of state of CaTiO_3

4.3.3 Ferroelectricity (Spontaneous Polarization)

The ferroelectric material bears spontaneous polarization that is switchable through electric field in two or more ways. The capability of switching polarization by electric field makes ferroelectric novel materials for advanced technological applications such as non-volatile memory devices, sensor, transducers, actuators and solar cells [203] . Recently, the phenomenon of hybrid improper ferroelectricity (HIF) has been proposed computationally by Benedek et al. [199], and laterally experimentally verified by several researchers [204,205]. Several compounds are identified as HIF materials [36]. Among the known HIF compounds, $\text{Ca}_3\text{Ti}_2\text{O}_7$ possesses the highest ferroelectric polarization in broad range of temperature 0K-1150K. The crystal structure of $\text{Ca}_3\text{Ti}_2\text{O}_7$ composed of layers $\text{CaO}(\text{CaTiO}_3)_2$ alternate each other in such a manner that each perovskite double layer (P) CaTiO_3 sandwich among rock salt (R) CaO structures. The perovskite layer composed of corner sharing octahedral TiO_6 , and the Ca lies in the body center of P block. The net spontaneous polarization arises from the combination of octahedral rotation represented by $a^0a^0c^+$ (Glazer notation) around [001] axes in the (001) plane. The tilting of octahedral TiO_6 represented by $a^-a^-c^0$ occurred at around the [100] axis, as a result the off-center displacement of the apical oxygen ions occurs. The simultaneous octahedral rotation and tilting accompanied by the displacement of A-site cation ions and also net electric polarization along [100] direction. The spontaneous ferroelectric polarization in $\text{Ca}_3\text{Ti}_2\text{O}_7$ is caused by two non-polar modes, octahedral BO_6 tilting and rotation (with Glazer notations of $a^-a^-c^0$ and $a^0a^0c^+$, respectively), coupled with a stable polar mode. The net

polarization in these compounds is caused by the combination of hybrid distortion mode; therefore they are termed hybrid improper ferroelectric. The ferroelectric polarization of $\text{Ca}_3\text{Ti}_2\text{O}_7$ compound are measured by several people experimentally and theoretically listed in Table 4.8. There is a prominent gap between the experimental and theoretical results. The polarization value is very sensitive therefore it is highly desirable to calculate the accurate value. Li et al. [201] tried to calculate the accurate polarization value by introducing the Hubbard parameter $U=3\text{eV}$ along with GGA and succeeded upto some extent, but with the introduction of Hubbard potential of 3eV the bandgap energy of the compound was significantly underestimated. They have also used high value of $U=4\text{eV}$ and got better results for band gap but the polarization becomes highly underestimated. This means polarization is very sensitive to the Hubbard parameter U . To obtain the correct result and solve the problem we have used several flavor of GGA and improved TB-mBJ along with Berry phase approach [206] for polarization. Our calculated result of value $11\text{ }\mu\text{C}/\text{cm}^2$ through improved TB-mBJ as shown in Table 4.8 is in good agreement with the experimental value $8\text{ }\mu\text{C}/\text{cm}^2$ and the theoretical result of Li et al. $10\text{ }\mu\text{C}/\text{cm}^2$. Although the Li et al. calculated result is close to the experimental result than our result for polarization but their band gap is highly underestimated and the calculations is based on the narrower bandgap. Our polarization value is a bit different than their value but it is based on the calculated bandgap consistent to the experimental one. Hence, our both results i.e. polarization as well as bandgap are altogether better than Li et al. results and closer to the experimental values.

4.4.4 Linear Optical Properties

The understanding of optical nature of a material is extremely important for its application in optical devices. The RP phase's perovskite oxides have attracted greater attention for their functional optical behavior, such as luminescence [207], photochromisms, photoluminescence and mechanoluminescence. Improved TB-mBJ exchange potential is utilized to calculate frequency dependent complex dielectric constants, $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$, to explore the linear and nonlinear optical properties of the material under study. The optical properties of a material are directly related its bandgaps. As we that complex dielectric function is composed of two arts i.e. $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$. The Kramers-Kronig transformations can be used to calculate the real part ($\varepsilon_1(\omega)$) from imaginary parts ($\varepsilon_2(\omega)$), which shows dispersion of incident light. The crystal structure of considered compound is orthorhombic and noncentrocymetric (means lacking the inversion symmetry), therefore to know the exact optical nature of the compound, it is necessary to calculate the complex dielectric constant in different directions parallel and perpendicular to b-axes. The parallel component of the imaginary part is presented by ($\varepsilon_2^{\parallel}(\omega)$), and perpendicular by ($\varepsilon_2^{\perp}(\omega)$) and similarly for the real part as shown in the Figure 4.18. The difference between the parallel ($\varepsilon_2^{\parallel}(\omega)$) and the perpendicular ($\varepsilon_2^{\perp}(\omega)$) components of imaginary and real parts are presented in the figure reveals the considerably high anisotropy in the optical properties. Optical absorption can be probed from the imaginary part ($\varepsilon_2(\omega)$), which reveals that all transitions are direct, i.e. to conduction from

valence band. The calculated optical bandgap measured from the imaginary part ($\varepsilon_2(\omega)$) is in good agreement with their band structure direct electron transitions, from about 3.7 eV to 12.5 eV. Figure 4.18(b) shows that the absorptive or imaginary dielectric function contains several peaks representing the transition of electrons between the VB and the CB. The main peak is located around 4.9 eV, other major peaks lie at 5.5eV, 7eV and 10eV while several small peaks are also present. The first two peaks reveal the transition of electrons from O-p state to the Ti-d state while the peaks represent the transition from the core state. The dispersive or real part perpendicular ($\varepsilon_1^\perp(\omega)$) and parallel component ($\varepsilon_1^\parallel(\omega)$) of dielectric constant are displayed in Figure 4.18(a), where the major peaks are present at 3.7eV, 6.5eV and 8.7eV points. The refractive index $n(\omega)$ of a material is related to the square root of $\varepsilon_1(\omega)$ and is important for its application in photonic and optical devices. In Figure 4.18 (d) we have plotted $\Delta n(\omega)$ birefringence, the figure reveals the strong polarization and an anisotropy among the parallel and perpendicular component of the refractive index of materials. The birefringence $\Delta n(\omega)$ is obtained from the formula $\Delta n(\omega) = n^\perp(\omega) - n^\parallel(\omega)$. The static value of $\Delta n(\omega)$ is 0.06 and fluctuates with the increase in frequency. The calculated values for birefringence at different frequencies are listed Table 5.3. Figure 4.18 (c) clearly shows that our calculated absorption coefficient is consistent with the experimental result [18]. The fundamental optical bandgap edge 3.7eV agrees well with the calculated band structure. Total absorption occurs below 3.7eV and

increases significantly after the optical absorption edge and reaches to maximum value between 5 - 6eV.

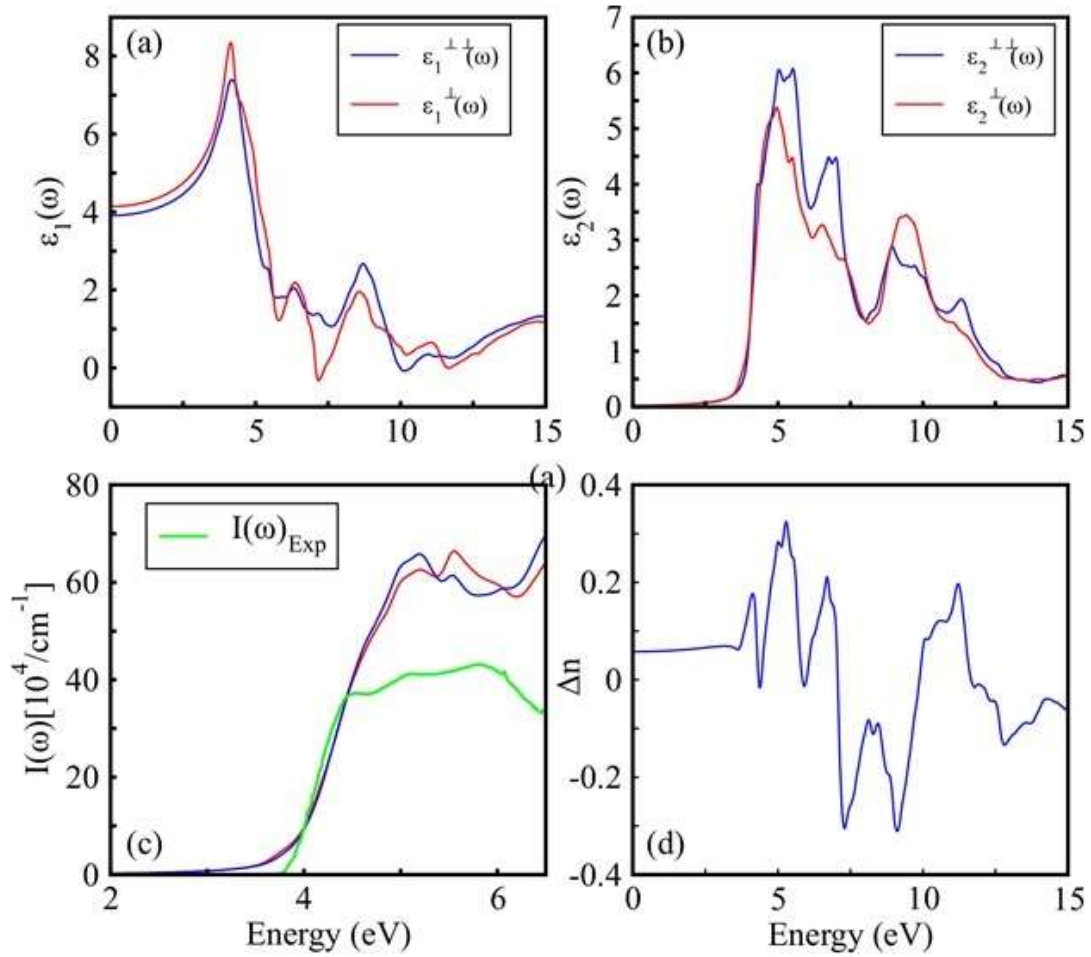


Figure 4. 17 The optical parameters for $\text{Ca}_3\text{Ti}_2\text{O}_7$ **(a)** real part of dielectric **(b)** imaginary part of dielectric **(c)** absorption coefficient **(d)** birefringence

4.4.5 Nonlinear Optical (NLO) Properties

In nonlinear optical phenomena light interacts with a material in a nonlinear manner and as a result a number of unusual phenomena arises, such as the optical frequencies generation that were absent initially. The NLO phenomenon is normally used in the production of laser generation at wavelength of light, whereas it is impossible to obtain it from traditional methods. In this work we investigate 2nd order NLO generally known as second harmonic generation (SHG). In this process, high energetic light is produced whose frequency is double as that of the input light. The primary condition for SHG is the lack of inversion symmetry in the crystalline materials, and necessary birefringence is required in the range 0.04 - 0.1eV for phase matching. In our calculations, the birefringence values at various wavelengths (frequencies) are 0.6 at static, 0.54 at 1064nm and 0.07 at 314nm listed in Table 5.4. These values are considered good for phase matching for high NLO susceptibility. The nonlinear optical properties are strongly dependent on the energy band gap of the compound. NLO is inversely proportional to the square of the band gap; therefore the accurate band gap is crucial for the correct prediction of nonlinear optical behavior of a material. We have calculated the nonlinear optical properties by using the full potential NLO code [17-19] working with the same method as Wien2k code [20]. To obtain accurate band gap we have utilized the improved TB-mBJ, one of the most precise and widely used method for the broad range of materials [21-23]. According to Kleinman symmetry there are generally total 18 non-zero components of the SHG susceptibility. In case of orthorhombic crystal symmetry there are seven non-zero components. The major

component in our case is $\chi_{333}^{(2)}(2w, w, w)$, the other non-zero components are very small and therefore neglected in this work. The NLO second-order coefficients are related to SHG susceptibility by the equation $d_{333}=0.5 \chi_{333}^{(2)}(2w,w,w)$. The calculated SHG susceptibility and second order NLO coefficient at different wavelengths at static limit, 1064nm and 314nm are presented in Table 4.9. The static coefficient is important parameter for the selection of nonlinear optical material for SHG susceptibility. The values in Table 4.9 show that the value of $\chi_{333}^{(2)}(w)$ and d_{333} increase with the decrease in wavelength and increase in the birefringence $\Delta n(w)$. Our calculated values of $\chi_{333}^{(2)}(w)$ and d_{333} at $\lambda=1064\text{nm}$ are 3.2 pm/V and 1.6 pm/V, respectively is almost 4 times of the KDP single crystal $d_{336}=0.39\text{pm/V}$ commercially used in the industry. The $d_{333}=18.1\text{pm/V}$ at low wavelength $\lambda=314\text{nm}$ is very high, which demonstrates that $\text{Ca}_3\text{Ti}_2\text{O}_7$ is a good material for NLO application in ultraviolet frequency range with high threshold damage. The real and imaginary parts of the SHG susceptibility are plotted in the Figure 4.19 (a) and (b) shows that the imaginary part is zero at 1.95eV, after it increases and starts oscillation due to $2w$ term half of the original band gap where the w term starts oscillation.

Table 4. 9 The complex optical susceptibility and second order nonlinear coefficient for $\text{Ca}_3\text{Ti}_2\text{O}_7$

Tensor component	$\chi_{ijk}^{(2)}(0)$	$d_{ijk=0.5}\chi_{ijk}^{(2)}(0)$	$\chi_{ijk}^{(2)}(\omega)$	$d_{ijk=0.5}\chi_{ijk}^{(2)}(\omega)$	$\chi_{ijk}^{(2)}(\omega)$	$d_{ijk=0.5}\chi_{ijk}^{(2)}(\omega)$
	static limit		at $\lambda=1064\text{nm}$	$\lambda=1064\text{nm}$	at $\lambda=314\text{nm}$	$\lambda=314\text{nm}$
$\chi_{333}^{(2)}(\omega)$ pm/V	2.1	1.05	3.2	1.6	36.2	18.1
$\Delta n(\omega)$	0.06		0.064		0.07	

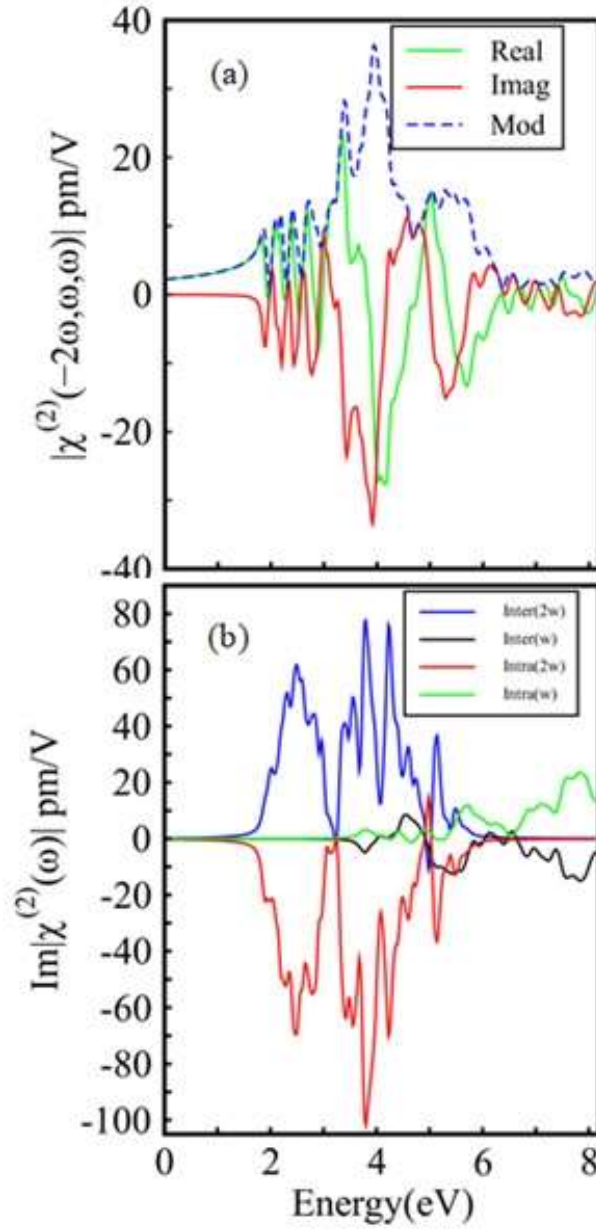


Figure 4. 18 **(a)** shows the real and imaginary part and their modulus **(b)** shows the interband and intraband contribution in imaginary part.

4.4 Structural, Electronic, Ferroelectric and Dielectric Properties of $\text{Li}_2\text{GeTeO}_6$

4.4.1 Structural Properties

The Crystal structure of $\text{Li}_2\text{GeTeO}_6$ is recently synthesised in two phases i.e., at different conditions of temperature and pressure [208]. At ambient pressure (AP) the crystal structure exists in rhombohedral R3 space group (146) like order ilmenite structure (OIL). After heating, at 1073 K temperature and applying pressure the crystal structure start distortion and at 4 GPa converts to double perovskite like structure with orthorhombic space group Pnn2 (34). Further increase of pressure have no pronounced effect on the crystal structure. After annealing temperature the crystal structure with space group Pnn2 transforms back to rhombohedral R3 spacegroup. The high pressure synthesis is used to stablize the highly desirable perovskite structure over competition to other phases like bixbyite [209] and corundum derivative [210]. We investigate the strucural properties to find the ground state stable phase of the compound for its potential practical applications. The crystal structure exist in two space group rhombohedral R3 (146) with three formula units $Z=3$ and in orthorhombic Pnn2 (34) with two formula units $Z=2$ as shown in Figure 4.20. To find relaxed atomic position and optimal lattice structural parameters we performed calculations for geometry relaxation and lattice optimization for both structures using GGA-PBEsol potential for sampling exchange correlation energy. The optimized data was then fitted in the Birch-Murangan equation of state to find the structural

parameters and plotted in Figure 4.21. This figure shows the variation of the total energy vs volume for both the structures for single formula unit. It is revealed from the optimization plot that the orthorhombic Pnn2 is the ground state stable phase. The calculated ground state energy, volume, bulk modulus, pressure derivative of bulk modulus and lattice parameters are presented in Table 4.10. The calculated values for both the structures are consistent with the available experimental values. The bulk modulus for the orthorhombic structure is greater than the rhombohedral structure reveals that orthorhombic structure is more incompressible than the rhombohedral one.

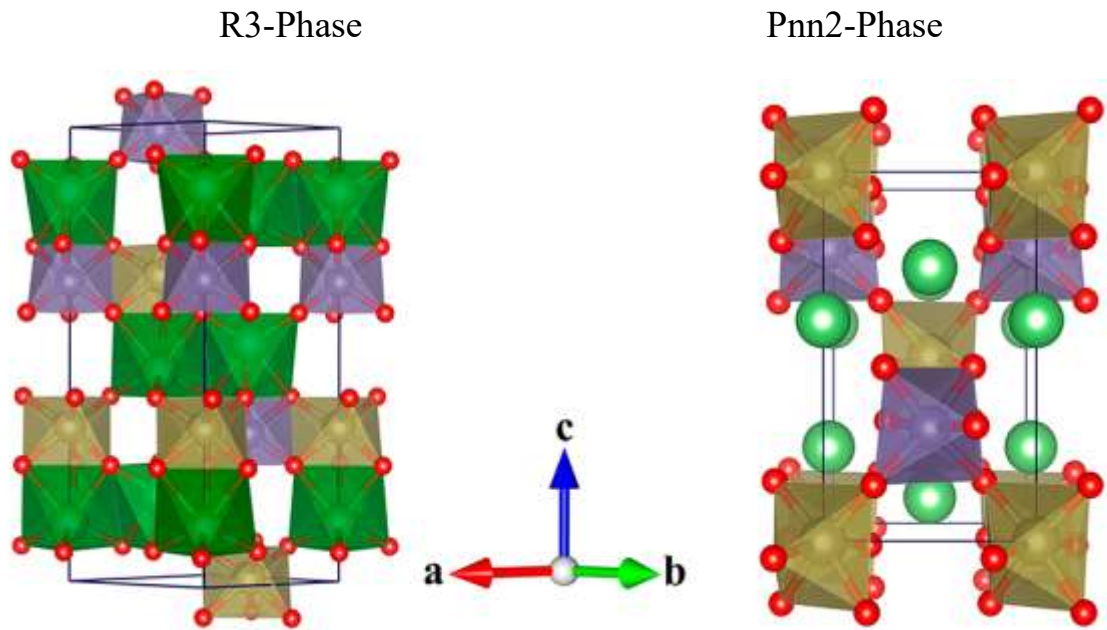


Figure 4. 19 The image of the crystal structure for rhombohedral and orthorhombic structure

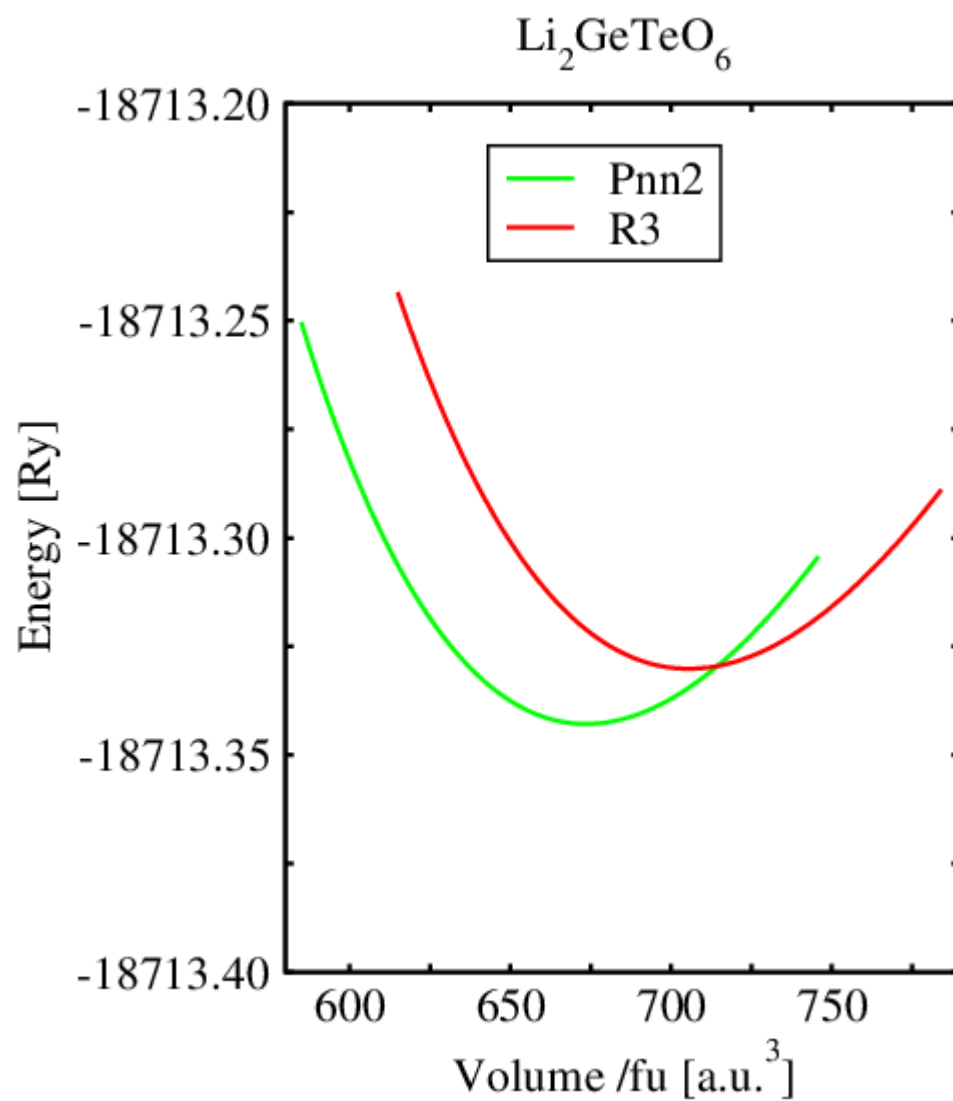


Figure 4. 20 The relative optimization plot for both the structures of $\text{Li}_2\text{GeTeO}_6$.

Table 4. 10 Structural data of Li₃GeTeO₆ for both the structures.

Space group	a	b	c	V	B(GPa)	BP	E0
Pnn2	4.9940	4.8064	8.2077	197.011	198.333	4.8	-37426.82
R3	5.0021	5.0021	14.317	310.658	196.22	4.9	-37426.75
Pnn2 (exp.)	4.996	4.9014	8.2411	199.52			
R3 (exp.)	5.00380	5.00380	14.327	315.658			

4.4.2 Electronic Properties

The physical properties of $\text{Li}_2\text{GeTeO}_6$ can be explored by knowing the electronic nature of the material. To realize the electronic behavior we investigate band structures and DOS by employing the GGA-PBEsol and improved TB-mBJ (used for wide bandgap semiconductors). The results of GGA are quite reasonable for the structural properties but it is notorious for the underestimation of bandgaps and therefore we used the improved TB-mBJ along with GGA for the reasonable bandgap calculations. The only report on the nature of bandgap in literature is that this material is a wide bandgap insulator. The calculated band structures are presented in Figure 4.22 and Figure 4.23 for rhombohedral and orthorhombic structures by GGA and TB-mBJ, respectively. The band structure graph for rhombohedral (R3) structure reveals the wide indirect band gap nature for both the potentials, 3.2eV by GGA and 5.2 eV by TB-mBJ listed in Table 4.10. Figure 4.23 displays the band structure of the orthorhombic (Pnn2) phase shows the direct bandgap nature at high symmetry Γ (Gamma) point. The band structures show the same pattern for GGA and TB-mBJ, the only difference is the width of the band gap 2.5 eV by GGA and 4.2 eV by TB-mBJ. The Band gap of the orthorhombic phase is listed in Table 4.10. The total and partial DOS for both the structure R3 and Pnn2 are plotted in order to understand the detailed behavior of the electronic structure of these compounds, Figure 4.24 and Figure. 4.25. The total DOS support the band gap structure for the value of band gap of rhombohedral phase. The analysis of the partial DOS reveals the major role of O-p state in the top of the valance and the bottom of the conduction bands, Ge-s and Te-p state also

have a significant contribution, while Li-s state have minor contribution. There is considerable hybridization among the O-p, Ge-s and Te-p state in valance band. The orthorhombic phase total and partial DOS presented in Figure 4.25 reveals the wide band insulator behavior. The major contribution comes from O-p state, while Ge-s and Te-p states also have valuable contribution. The band structures and DOS clearly demonstrate that $\text{Li}_2\text{GeTeO}_6$ is a wide band gap material.

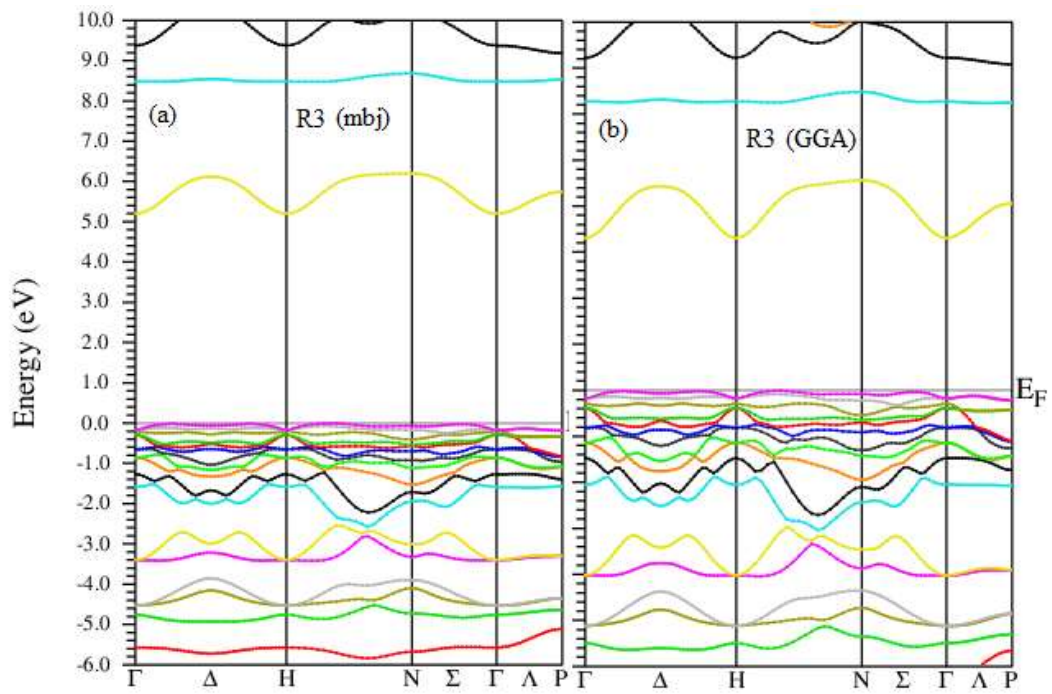


Figure 4. 21 The band structure for R3 structure by GGA and by TB-mBJ

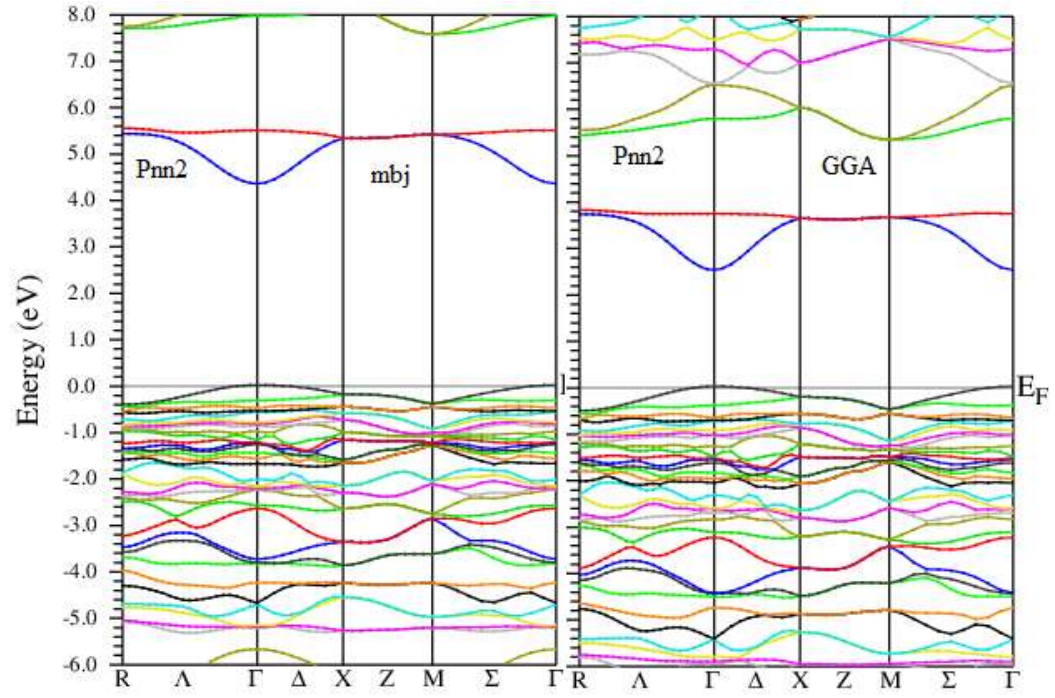


Figure 4. 22 The band structure for R3 structure by GGA and by TB-mBJ.

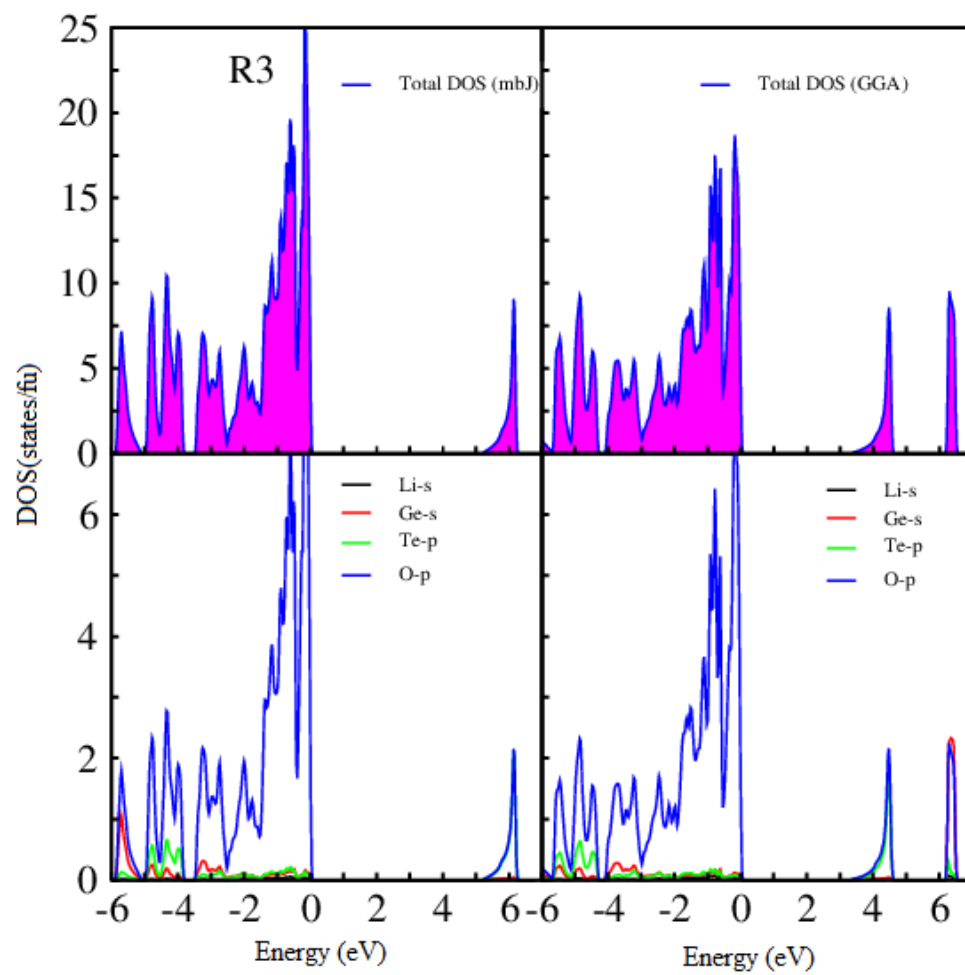


Figure 4. 23 The total and partial density of state (DOS) for R3 phase by GGA and TB-mBJ.

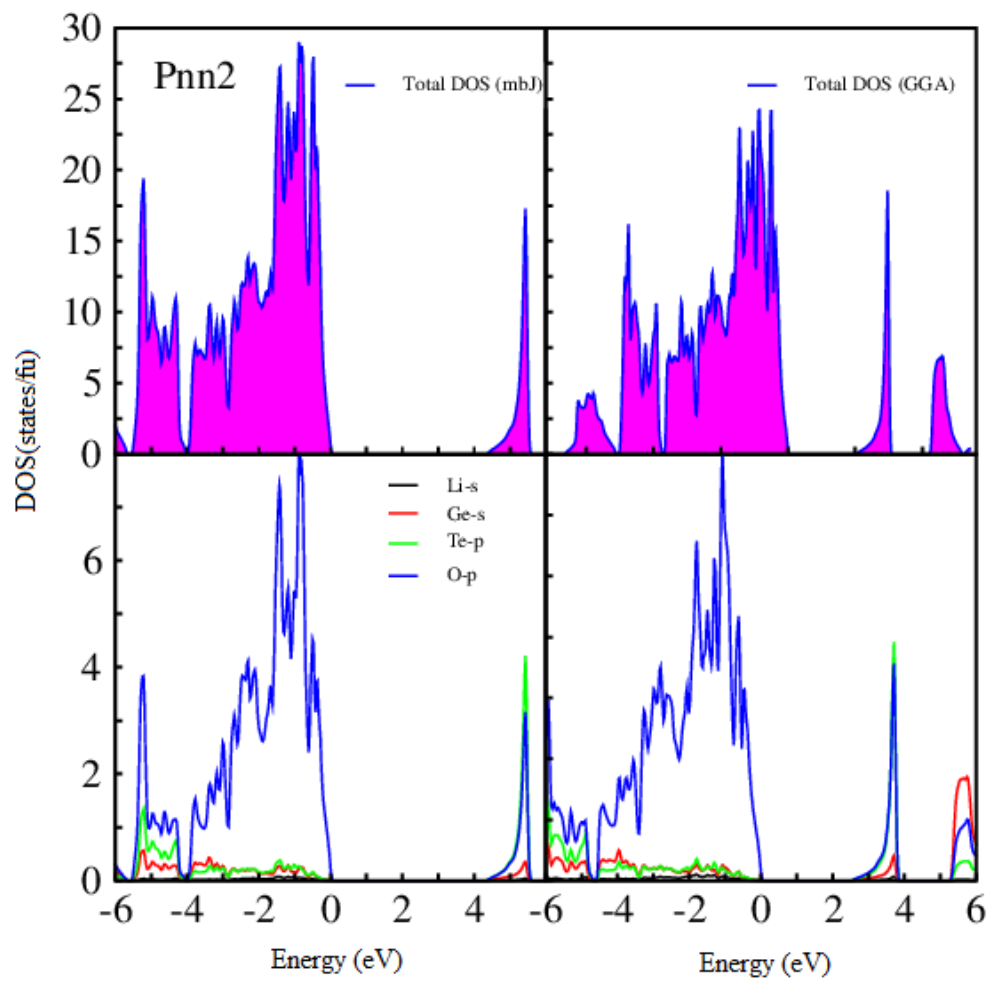


Figure 4. 24 The total and partial density of state (DOS) for Pnn2 orthorhombic phase by GGA and TB-mBJ.

4.4.4 Ferroelectric Properties

The Crystal structure of $\text{Li}_2\text{GeTeO}_6$ is recently synthesised in two phases, at ambient pressure its phase is rhombohedral (R3) and its high pressure phase is orthorhombic (Pnn2). Both of these structures are noncentrosymmetric means lacking the inversion symmetry which is the fundamental requirement for nonlinear optics, pezzoelectricity and ferroelectricity. The ferroelectric material bears spontaneous polarization that is switchable through electric field in a required direction. The property of switching of polarization by electric field makes ferroelectric appealing materials for high tech electronic devices such as non-volatile memory devices, sensor, transducers, actuators and solar cells [211-214]. To study the ferroelectric nature and origin of ferroelectricity in $\text{Li}_2\text{GeTeO}_6$ we calculate the ferroelectric polarization using Berry phase approach [18] with GGA and TB-mBJ for both structures. The calculated polarizations listed in Table 4.11 reveals that our calculated values are closer to the experimental results. The GGA values for R3 is $26 \mu\text{C}/\text{cm}^2$ and for Pnn2 is $87 \mu\text{C}/\text{cm}^2$ are comparable to the experimental results $17 \mu\text{C}/\text{cm}^2$ for R3 phase and $80 \mu\text{C}/\text{cm}^2$ for Pnn2 phase [72]. The TB-mBJ results $24 \mu\text{C}/\text{cm}^2$ for R3 phase and $83 \mu\text{C}/\text{cm}^2$ for Pnn2 Phase are closer to the experimental result as compared to the GGA. So it is concluded that TB-mBJ is not only good for electronic band structure dependent properties but also gives better results for other properties as well. For the understanding of the origin of such high polarization it we investigate the structural distortion. The crystal structure of $\text{Li}_2\text{GeTeO}_6$ in Pnn2 is more distorted than that of R3 phase. The Li—O bond length ranges 1.73 - 2.6 in Pnn2 phase and in R3 phase Li—O ranges in 2.03 - 2.41. The

greater bond variation in Pnn2 structure than the R3 structure makes it more distorted and hence shows greater polarization. The greater polarization and relative high stability makes orthorhombic Pnn2 double perovskite more desirable than the rhombohedral R3 elementite structure.

Table 4. 11 Calculated polarization and band gap in $\text{Li}_2\text{Ge}_2\text{O}_7$ in different space group

Space group	Band gap E_g (eV)		Spontaneous Polarization ($\mu\text{C}/\text{cm}^2$)		
	GGA	mBj	GGA	mBj	Experimental
R3	3.4	5.1	26	24	17
Pnn2	2.5	4.2	87	83	80

4.4.5 Optical Properties

The interaction of light with matter is the base of many optical phenomena practically used in various important fields of science and technology. For the effective use of light with matter it is necessary to the optical behavior of a compound. Here we investigate the optical response of $\text{Li}_2\text{GeTeO}_6$ in different crystal structures. Optical properties are dependent upon the bandgap nature of a material. The experimental available information suggest wide band gap for both the structures, therefore we have used GGA-TB-mBJ for the bandgap as well as optical response of the material for better results. First the complex frequency dependent dielectric coefficient is evaluated by employing the TB-mBJ along with GGA, which is composed of real and imaginary parts $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$ [8]. The parallel and perpendicular components relative to electric field ($\varepsilon_2^{\parallel}(\omega)$) and ($\varepsilon_2^{\perp}(\omega)$) are calculated to explore the optical anisotropy in the present compound. The Kramers-Kronig transformations [9] are employed for the calculation of the real parts ($\varepsilon_1^{\parallel}(\omega)$) and ($\varepsilon_1^{\perp}(\omega)$) and for imaginary parts ($\varepsilon_2^{\parallel}(\omega)$) and ($\varepsilon_2^{\perp}(\omega)$), which shows dispersion of incident light. The optical parameters are presented in Figure 4.26 for R3 phase. The real parts ($\varepsilon_1^{\parallel}(\omega)$) and ($\varepsilon_1^{\perp}(\omega)$) are inversely related to bandgap and shows the dispersion of a material. The static value of the real part is 2 and increases with frequency to 10eV and then decreases as shown in Figure 4.26 (a). The major peaks are located at 5.2 eV and 10 eV. The perpendicular ($\varepsilon_1^{\perp}(\omega)$) component is shifted towards high frequency region as compared to the parallel

component $\varepsilon_1^{\parallel}(\omega)$). The imaginary parts parallel ($\varepsilon_2^{\parallel}(\omega)$) and perpendicular ($\varepsilon_2^{\perp}(\omega)$) can be used to probe the absorption of light and explain the electronic excitation in band structure. The major peaks at 5.8eV, 7eV, 8.5eV, 10eV and 10.5eV in Figure 4.26 (b) show the successive excitation of electrons in band structure. The absorption coefficient in Figure 4.26 (c) shows similar behavior as that of imaginary part of dielectric function.

The birefringence is the difference between the Parallel and perpendicular component of refractive index relative to the electric field. The calculated birefringence for the R3 is 0.08, which is considered very high and suitable for phase matching for better nonlinear optical properties. The optical parameters of orthorhombic Pnn2 structure are displayed in Figure 4.27. The greater value of 2.4 of the real part of the dielectric function of Pnn2 (Figure 4.27(a)) than R3 structure demonstrates the relative small band gap of Pnn2 than R3 structure. The imaginary part in Figure 4.27(b) successfully estimates the electronic band structure of 4.2 eV. There are several prominent peaks at 6eV, 8.5eV, 10eV, and 11eV illustrate the successive electronic transition in the band structure between different orbitals. The absorption coefficient shows similar trend like the imaginary part of dielectric function. Figure 4.27 (d) represents the parallel and perpendicular components of refractive index having 1.59 and 1.51 values, respectively. The difference between these values gives the birefringence of 0.08, which is the most important parameter and shows strong anisotropic behavior of the crystal structure. The birefringence of 0.08 shows that this material possesses very good nonlinear optical properties.

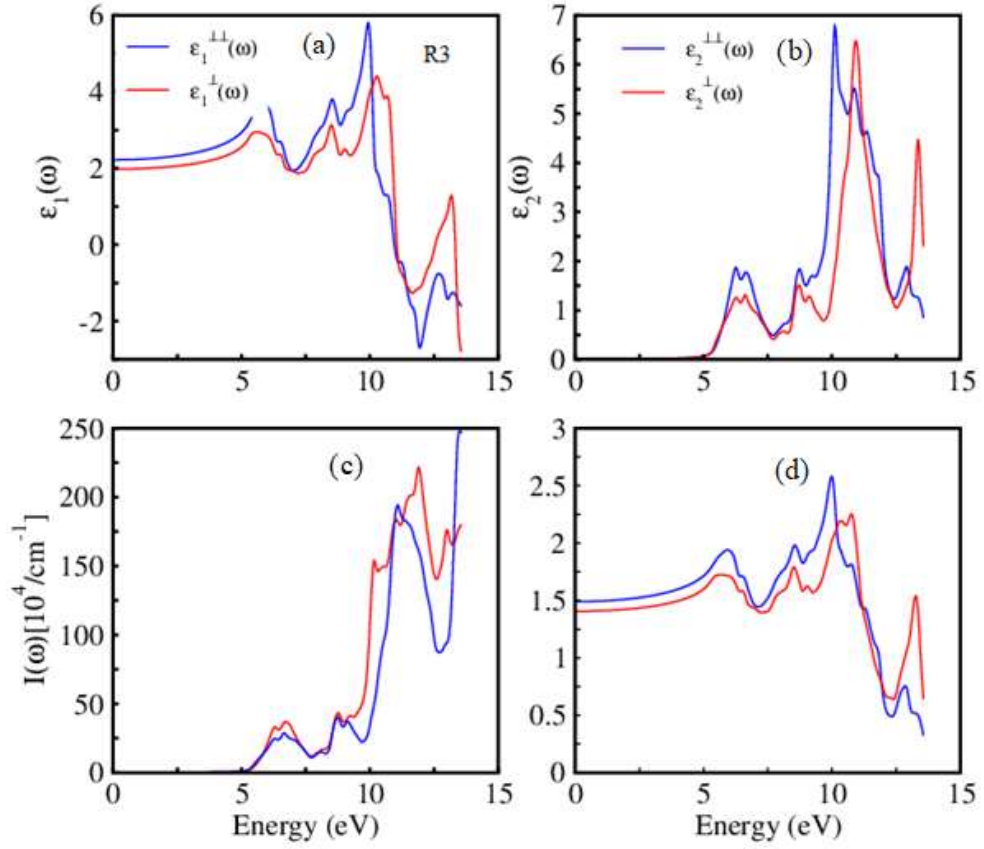


Figure 4. 25 The calculated optical parameters for R3 phase, where **(a)** real part and **(b)** imaginary part of dielectric function, **(c)** absorption coefficient and **(d)** refractive index

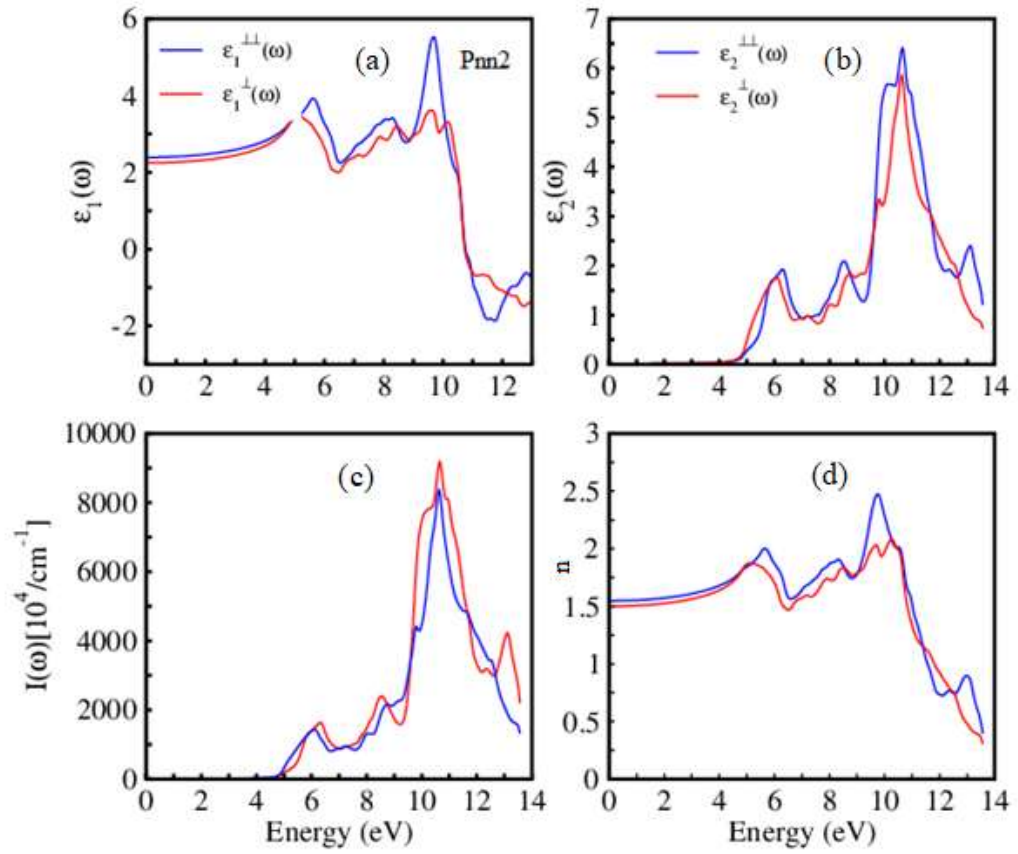


Figure 4. 26 The calculated optical parameters for Pnn2 phase, where **(a)** real part and **(b)** imaginary part of dielectric function, **(c)** absorption coefficient and **(d)** refractive index

Chapter 5

Conclusion

In summary we report a novel ruthenate perovskite, NaRuO_3 . The stability tests confirm the existence of the novel compound in orthorhombic structure with space group Pnma (62). The electronic and magnetic properties of the compound reveal G-type antiferromagnetic phase with weak electron correlation effects. Although the electron correlation effect is weak but it plays crucial role in the electronic and magnetic properties of the compound as compared to the relativistic spin orbit coupling effect. The combined effect, of Coulomb interaction (U) and the ground state G-type antiferromagnetic configuration as well as density of states and electronic band structures, illustrates that this ruthenate perovskite can be easily tuned from metal to insulator just like in NaOsO_3 . It is expected that this novel material could be ideal candidate for sodium ion batteries and hence needs further experimental and theoretical studies.

The detailed studies of the bonding nature, bonds strength, electronic charge density, electronegativity of B-site cation and the size of the A-site cation show significant effect on the electronic band structure, consequently on their optical properties of ABO_3 type cubic perovskite oxides; $A = \text{Ca, Sr, Ba}$ and $B = \text{Ti, Zr, Hf}$. The calculated results show that, the electronic band gap for these compounds is linearly dependent upon the electronegativity difference between of the covalent bond between oxygen and B-cation in

these perovskites. It is also concluded that the ionic bond strength between oxygen and A-cation has negligible effect on the band gap; however the radius of the A-cation affects the gap of perovskite oxide. Furthermore, the issue of the electronic band structures for these compounds is resolved by properly treating electron density within the improved TB-mBJ approach. Finally, optical response shows wide range of light absorption from visible to ultraviolet range in these compounds. These results suggest that improved TB-mBJ exchange potential is an appropriate scheme for electronic and optical properties of cubic perovskite oxides, for their possible applications in various optoelectronic devices.

Structure, electronic, ferroelectric and nonlinear optical properties of the first The $\text{Ca}_3\text{Ti}_2\text{O}_7$ perovskite theatrically proposed and experimentally confirmed as hybrid improper ferroelectric are studied. TB-mBJ is utilized and the results are compared with the experimental and theoretical results. It is concluded that TB-mBJ results for band gap and polarization are better than the other theoretical results including GGA+U. The moderate birefringence and high nonlinear optical susceptibility makes this material a potential candidate for nonlinear optical applications.

The structure, electronic, ferroelectric polarization and optical properties of $\text{Li}_2\text{GeTeO}_6$ in rhombohedral R3 and in orthorhombic Pnn2 phases are studied. From the ground state energy it is concluded that orthorhombic Pnn2 is the stable phase. The electronic band structure reveals the wide band gape semiconductor nature for both the structures. The calculated band profile shows the indirect band gap nature for R3 phase and direct band gap nature for Pnn2 structure. Our calculated polarization values $24 \mu\text{C}/\text{cm}^2$

for R3 and $83 \mu\text{C}/\text{cm}^2$ for Pnn2 agrees well with experimental data $17 \mu\text{C}/\text{cm}^2$ and $80 \mu\text{C}/\text{cm}^2$. Both the phase possess the greater anisotropy and birefringence of 0.08 makes these material ideal for nonlinear optical applications.

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