

FIRST PRINCIPLE INVESTIGATION ON LEAD-FREE DOUBLE PEROVSKITE $\text{OFA}_2(\text{Ag/In})\text{BrO}_6$ (A= Ba, Sr, Ca) FOR PHOTOVOLTAIC APPLICATIONS

Submitted in partial fulfillment of the requirements for the award of
Master of Science degree in Physics

By

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DEPARTMENT OF PHYSICS
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SATHYABAMA

**INSTITUTE OF SCIENCE AND TECHNOLOGY
(DEEMED TO BE UNIVERSITY)**

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BONAFIDE CERTIFICATE

This is to certify that this Project Report is the bonafide work of V. Dharshini (41590003) who carried out the project entitled **"First Principle Investigation On Lead-Free Double Perovskite Of $A_2(\text{Ag/In})\text{BrO}_6$ (A= Ba, Sr, Ca) For Photovoltaic Applications"** under my supervision from November 2022 to May 2023.

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ABSTRACT

The first principle investigation on the structural, electronic, optical, thermal and thermoelectric properties of lead-free double perovskite **$A_2(\text{Ag/In})\text{BrO}_6$ ($A=\text{Ca, Sr, Ba}$)** in the cubic phase has been performed using the full potential linearized augmented plane wave (FP-LAPW) method in the framework of DFT (Density Functional Theory). The computational structural properties show the most stable structure in the phase group of $Fm\bar{3}m$ (225) for the proposed compound **$A_2(\text{Ag/In})\text{BrO}_6$ ($A=\text{Ca, Sr, Ba}$)**. Modified Becke-Johnson (mBJ) potential embedded in the WIEN2K code to calculate the band structure. The obtained band structure plots and density of state histogram show no band gap. Hence the proposed material is a perfect conductor. The total and partial density of states shows that the electron contribution towards the Fermi region is predominant due to O-p orbitals, Ag-d orbitals, and In-p orbitals. There is a negligible contribution arising from the alkaline earth metals namely Sr, which does not directly affect the formation of the conduction band. From the optical parameters such as refractive index, dielectric function, reflectivity, optical conductivity exhibits strong absorption of photons and great potential to conduct electrons in the UV region.

In these six compounds, $\text{Ba}_2\text{InBrO}_6$ has the preferable photovoltaic performance and conversion efficiency, making it has the potential candidate of photovoltaic application in the UV region.

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LIST OF SYMBOLS AND ABBREVIATION

DFT	DENSITY FUNCTIONAL THEORY
FP-LAPW	FULL POTENTIAL-LINEARIZED AUGMENTED PLANE WAVE
DOS	DENSITY OF STATES
NN DISTANCE	NEAREST NEIGHBOUR DISTANCE
SCF	SELF CONSISTENT CYCLE
RMT	MUFFIN TIN RADIUS SPHERE
GGA	GENERALIZED GRADIENT APPROXIMATION
EOS	EQUATION OF STATES
(E_f)	FERMI ENERGY LEVEL
$N(E_f)$	NO. OF STATES IN THE FERMI ENERGY LEVEL
γ	SPECIFIC HEAT COEFFICIENT
DPS	DOUBLE PEROVSKITES
CB	CONDUCTION BAND
VB	VALENCE BAND
CBM	CONDUCTION BAND MINIMA
VBM	VALENCE BAND MAXIMA

CHAPTER-1

1. INTRODUCTION

Understanding the nature of the material to the modern hypothetical compound is crucial to lowering the chance of error in an experiment. Computer simulation aids in the study of materials with many electrons and is a crucial step in the process of analyzing and explaining levels of complexity or in the rational planning of future experiments. Compared to the traditional trial-and-error process, where we improve material by synthesizing, characterizing, and functional assessing, the stimulation method is more effective. The features of the system, including relative stability, chemical bonding, atom relaxation, phase transitions, and electronic, mechanical, and magnetic behavior, are controlled by the electronic structure, which is governed by quantum mechanics. (Schwarz K et al 2002). Density functional theory is the widely used method for calculating the electrical characteristics of solids. (DFT). DFT is a well-known computational quantum mechanical modeling technique utilized in the study of many different body systems in the context of individual atoms, molecules, and condensed phases in physics, chemistry, and material science. It treats exchange and correlation and is based on electron density rather than wave function (Hartree Fock). Our chemicals are investigated using the WIEN2K code, which is one of many computer codes that are accessible.

The interatomic distance plays a crucial role in the majority of solid-state interactions. With no additional chemical complexity and minimal physical complexity, pressure alters the interatomic distance as well as the structure and electrical characteristics. Therefore, the study of solids' physical states, the creation of new ground states in solids, the testing of theoretical models, and the advancement of new theories have all benefited greatly from the extensive use of high-pressure techniques in recent years. For instance, more naturally non-superconducting elements than naturally existent elemental superconductors have been converted to superconductors over the past 50 years through the application of pressure. High-pressure systems can now be studied computationally as a

result. Our chemicals are investigated using the WIEN2K code, which is one of many computer codes that are accessible.

1.1 DENSITY FUNCTIONAL THEORY

Density functional theory (DFT) has emerged as the most effective and popular technique in condensed-matter physics, computational physics, and quantum chemistry for describing the properties of condensed-matter systems, which encompass complex materials like molecules, proteins, interfaces, and nanoparticles in addition to standard bulk materials. DFT's basic principle is to use a system's particle density rather than its many-body wave function to characterise a many-body interacting system. Its importance lies in its ability to use its particle density to condense the $3N$ degrees of freedom of the N -body system to only three spatial variables. The well-known Hohenberg-Kohn (HK) theorem, which states that all of a system's features can be seen as being exclusively functional of its ground state density, serves as its foundation. In addition to the Born-Oppenheimer (BO) approximation and the Kohn-Sham (KS) equation, approximations for the so-called exchange-correlation (XC) potential, which describes the effects of the Pauli principle and the Coulomb potential beyond a pure electrostatic interaction of the electrons, have made it practical and accurate DFT calculations. A common approximation is the so-called local density approximation (LDA), which locally substitutes the XC energy density of an inhomogeneous system for that of a homogeneous electron gas evaluated at the local density. This is because it is impossible to calculate the exact XC potential (by solving the many-body problem precisely). With improved XC energy function approximations during the 1990s, the results of DFT calculations for condensed-matter systems frequently corresponded pretty adequately with experimental data. Additionally, compared to earlier approaches that relied on the intricate many-electron wave function, like the Hartree-Fock theory and its offspring, the computational costs were comparatively modest. The use of DFT to accurately describe intermolecular interactions, charge transfer excitations, transition states, global potential energy surfaces, and some other strongly correlated systems, as well as in

calculations of the band gap of some semiconductors, remains challenging despite advancements in the technique. In solids where boundary conditions are used, numerous methods are used for calculating the independent particle electronic states. They are divided into three categories. (0) Plane wave codes include Quantum ABINIT, ESPRESSO, and VASP. (1) Localized atomic orbitals are CRYSTAL SIESTA (2) augmented plane wave codes are LMTO, FLEUR IENCK, and WIEN2K codes are based on estimates of the band gap of some semiconductors using the full potential (linearized) augmented plane wave (LAPW)-local orbitals (LO) approach.

1.2 FULL-POTENTIAL LINEARIZED AUGMENTED PLANE WAVE (FP-LAPW) METHOD

Utilizing the full capabilities of the LAPW technique will increase its accuracy even further. (FP). Inside the muffin-tins, the potential is set to be approximately spherically distributed and constant in the interstitial region. It is a technique based on DFT that is used to model the electrical characteristics of materials. This method, which increases the number of plane waves in the basis set and decreases the structural properties of systems accurately, has been effectively used to explore structural phase transitions of several semiconductors. High precision is used to take into account the form of the changing density. This approach divides the unit cell into two regions: the interstitial region and the entire spherically averaged potential.

The potential and charge densities are both expanded into lattice harmonics inside each atomic sphere and into a Fourier series in the interstitial region using the FP-LAPW technique. The Schrodinger equation is therefore solved by the plane wave in the interstitial region and by the sum of the radial and spherical harmonic solutions in the muffin-tin region

1.2 WIEN2K CODE

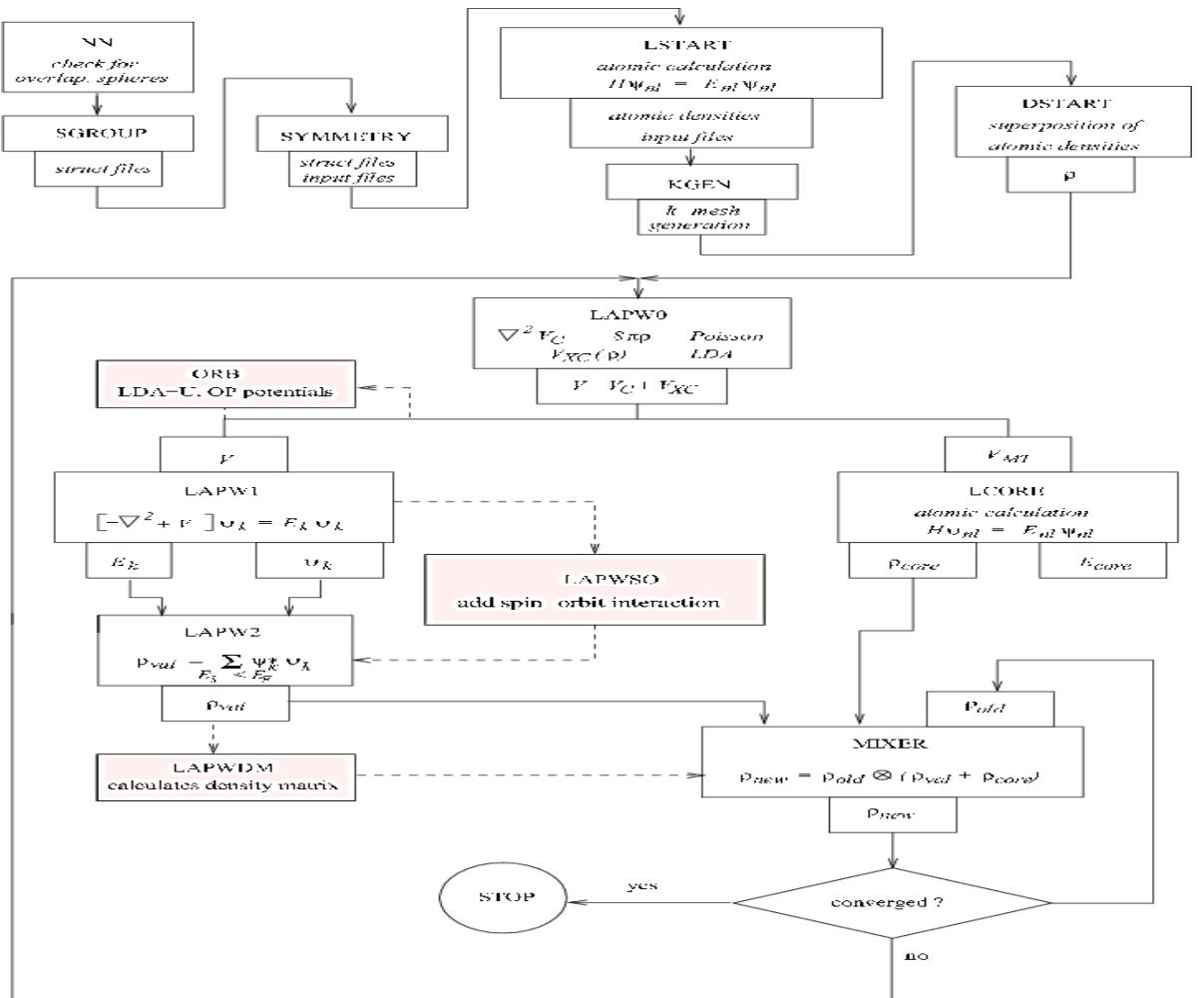
Blaha (2001) created the full-potential all-electron algorithm WIEN2K to investigate the characteristics of crystals. It is made up of numerous separate F90 programs that are knitted together using C-shell routines. The Kohn-Sham formulation of DFT is the foundation for the code. A structure generation file comprising data on the space group, lattice parameters, atomic species, atomic position, muffin tin radii, etc. serves as the code's initial starting point. The materials are initialized in a step-by-step manner based on the input numbers. In order to find the atomic sphere radii, NN distance-neighbor distances check for overlapping spheres, coordination numbers, and nearest. (i) For the specified structure, GROUP calculates the point and space groups. (ii) SYMMETRY- checks the symmetry operations and determines the point group of the individual atomic sites, (iii) LSTART- generates atomic densities for all atoms. (iv) KGEN- generates a k-mesh in the Brillouin zone. (v) DSTART generates a starting density for the SCF cycle by superposition of atomic densities.

The Schrodinger equation is chosen using the iterative self-consistent technique to produce a more precise set of orbitals, which are then used to solve the Schrodinger equation once more until the solutions converge. The SCF cycle begins with LAPW0, which adds the coulomb and exchange-correlation potentials to determine the overall potential. After setting the Hamiltonian and overlap matrix, LAPW1 then diagonalizes the Kohn-Sham equation to determine the Eigen values and Eigen vectors of the valence states. LAPW2, which produces valence charge density and calculates Fermi energy.

The overall core density is determined by separately calculating the states and energies of each core electron in a standard atomic calculation in the LCORE. Total density is the sum of the densities of the core and valence. Since the new

density frequently varies significantly from the old density, MIXER mixes them to prevent significant fluctuations between iterations that could cause divergence. When the cycle has finished, WIEN2K checks the new and new density, and if they differ from one another, a new iteration with a new density is begun. Repeat this process until the old and new densities are equal. LAPWSO computation only occurs if spin-orbit is taken into account.

connection, as displayed in fig1.1. Last but not least, additional software packages are accessible to analyze the calculated results, such as band structure, electron density plot, and density of states determination.



CHAPTER -2

2.1 AIM

we have presented systematic DFT calculations for structural, electronic, and optical properties of lead-free double perovskite $A_2(\text{Ag/In})\text{BrO}_6$ ($A=\text{Ba, Sr, Ca}$) in the cubic phase has been performed using the full potential linearized augmented plane wave (FP-LAPW) method in the framework of DFT (density functional theory). The goal of the study is to evaluate the optoelectronics applications by utilizing $A_2(\text{Ag/In})\text{BrO}_6$ ($A= \text{Ba, Sr, Ca}$).

2.2 SCOPE OF PRESENT INVESTIGATION

The study of perovskite-based solar cells has gained popularity. Their ability to convert sunlight into power has increased from a meager 5% to more than 25% in just a decade. The perovskite, which is the photoactive component in these devices, is frequently sandwiched between other layers to collect and transmit electric charge, improving performance. Double perovskites, an improved kind of single perovskites (ABO_3), have recently attracted attention due to their intriguing and physics-rich features (Maiti et al., 2019). The quaternary metal-oxides known as Double perovskites oxides have the general formula $\text{A}_2\text{BB}_2\text{O}_6$, where the A site elements are commonly alkaline earth metals like Ba, Sr, and Ca (F. Kubel et al., 2013). Because of its exceptional qualities, including superior oxidation resistance, high figure of merit, high curie temperature, significant spin polarization effect, and other fascinating features, barium-based Double perovskite is being studied in particular (Morss et al., 1982). "Saad et al." Sahnoun et al. have published another computational analysis of the barium-based Double perovskites Ba_2MWO_6 ($M = \text{Mg, Ni, Zn}$) (Sahnoun et al., 2013). The literature showed that the B and B' site cations have a significant impact on the electronic structure and other physical characteristics of Double perovskites. From (Muhammad Zafarullah Kazim et al, 2022) Ba_2XIO_6 ($X=\text{Ag,Na}$) good structural, electronic , optical and thermoelectric properties.

CHAPTER -3

3.MATERIAL AND METHODOLOGY

3.1 '2116'COMPOUNDS

In this study, first-principles computations have been used to thoroughly explore the lattice structural, electronic, optical, thermal and thermoelectric properties of the double perovskites $\text{Ba}_2\text{NaClO}_6$, $\text{Ba}_2\text{NaBrO}_6$, and Ba_2NaIO_6 . We discovered that the three compounds have direct bandgap semiconductor properties and good mechanical and dynamic stabilities. The three compounds' vast light absorption ranges, from the infrared region to the visible region and ultimately to the UV region, can be discovered by the examination of optical properties. Ba_2NaIO_6 has a cheap synthetic cost from the point of view of the synthesis pathway, but it has a great UV light absorption capability, suggesting that this material has a natural advantage in the field of energy harvesting. In the same band, $\text{Ba}_2\text{NaClO}_6$ and $\text{Ba}_2\text{NaBrO}_6$ likewise exhibit strong absorption characteristics (Hao-Jia Wu et al., 2023). Periodate double perovskites, Ba_2XIO_6 ($\text{X} = \text{Ag}, \text{Na}$), have recently piqued the interest of numerous researchers due to their inexpensive precursors and stable cubic structures at room temperature, as well as the fact that the elements that make up these double perovskites are abundant in the earth's crust (Sleight et al., 1964). Sleight and Ward performed the initial experimental investigation of the periodate compounds in 1963 and reported that the structure was cubic (with an 8.4Å and 8.3Å for Ag and Na-based systems, respectively), adopting the rock salt arrangement of the X-site cations. Ba_2XIO_6 ($\text{X} = \text{Ag}, \text{Na}$) double perovskites were made using innovative synthesis methods reported by (Volonakis et al. 2019), who also modeled the materials using the DFT-PBE functional.

The structural characterizations of several double perovskites M_2NaIO_6 ($\text{M} = \text{Pb}, \text{Ca}, \text{Ba}, \text{and Sr}$) synthesized using the solid-state reaction technique were published by Kubel et al. in 2013. Ba_2NaIO_6 adopted the undistorted Fm-3m aristo-

type crystalline structure, according to the Rietveld analysis of the XRD data. As opposed to that, The P21/c hetto-type composition along with the tilting of a rock salt-arranged B-site octahedral structure (Glazer notation: $a + bb$) was discovered to stabilize Pb_2NaIO_6 , Ca_2NaIO_6 , and Sr_2NaIO_6 . The literature discussed many synthesis techniques, but it lacked research on the compounds' optoelectronic and thermoelectric properties (F. Kubel et al., 2013). This leads us to propose the photovoltaic properties of the proposed materials, namely Ba_2AgBrO_6 , Ba_2InBrO_6 , Ba_2NaBrO_6 , Sr_2AgBrO_6 , Sr_2InBrO_6 , Ca_2AgBrO_6 , Ca_2InBrO_6 . From the thorough and reliable computational analysis in the literature the proposed materials, are not reported yet.

First principle calculations have been used in the current work to examine a number of physical features of the periodate double perovskites Ba_2AgBrO_6 , Ba_2InBrO_6 , Ba_2NaBrO_6 , Sr_2AgBrO_6 , Sr_2InBrO_6 , Ca_2AgBrO_6 , Ca_2InBrO_6 in cubic phase (Fm-3m space group). In-depth research has been done on the incident light's structural, electronic, optical, thermal, thermoelectric properties of $A_2(Ag/In)BrO_6$ ($A=Ca, Sr, Ba$).

3.2 COMPUTATIONAL DETAILS

The full-potential linearized augmented plane wave (FP-LAPW) implemented in the WIEN2k code has been used for all computing tasks (Blaha et al., 2021). The exchange-correlation energies were approximated using the non-spin polarized mBJ potential, which is well known to be more accurate than traditional GGA and LDA approximations in a number of situations (Borlido et al., 2020). For instance, in some circumstances, LDA's prediction of experimentally observed bandgaps was reportedly 40% less accurate (Perdew et al., 1985). Afterward, certain bond lengths were computed in order to fully understand the structural characteristics. Additionally, while semi local and valance states were classified as semi-relativistic, all core electrons were treated as fully relativistic. The computations used the basis sets $6s^2$ of Ba, $5s^1$ of Ag, $3s^1$ of Na, and $2p^4$ of O. For the configuration of the cells, the lattice parameters for Ba_2AgBrO_6 , Ba_2InBrO_6 , Ba_2NaBrO_6 , Sr_2AgBrO_6 , Sr_2InBrO_6 , Ca_2AgBrO_6 , Ca_2InBrO_6 , were adjusted to 8.3527Å, 8.4700Å, 8.2434Å, 8.1924Å, 8.335Å, 8.0857Å, 8.2434Å respectively. The atomic position for Ba($\frac{1}{4}$, $\frac{1}{4}$, $\frac{1}{4}$), Ag (0,0,1/2), In (0,0,1/2), Br(0,0,0),

O(0,0,0.774922). The wave function expansion inside the atomic spheres was given a maximum value of $l_{\max}$ of 12, and the value of the plane-wave cut-off ($R_{\text{MT}} \times K_{\max}$) was set at 7 with a $G_{\max}$ of 14. To solve these quantum mechanical systems, a well-converged $10 \times 10 \times 10$ k-space grid was adopted within the irreducible wedge of the Brillouin zone. For the energy convergence close to 10^{-5} Ry, self-consistency is carried out.

Additionally, the Boltz Trap code was used to compute the thermoelectric properties using an estimation of the constant relaxation time (τ) (Madsen et al., 2006).

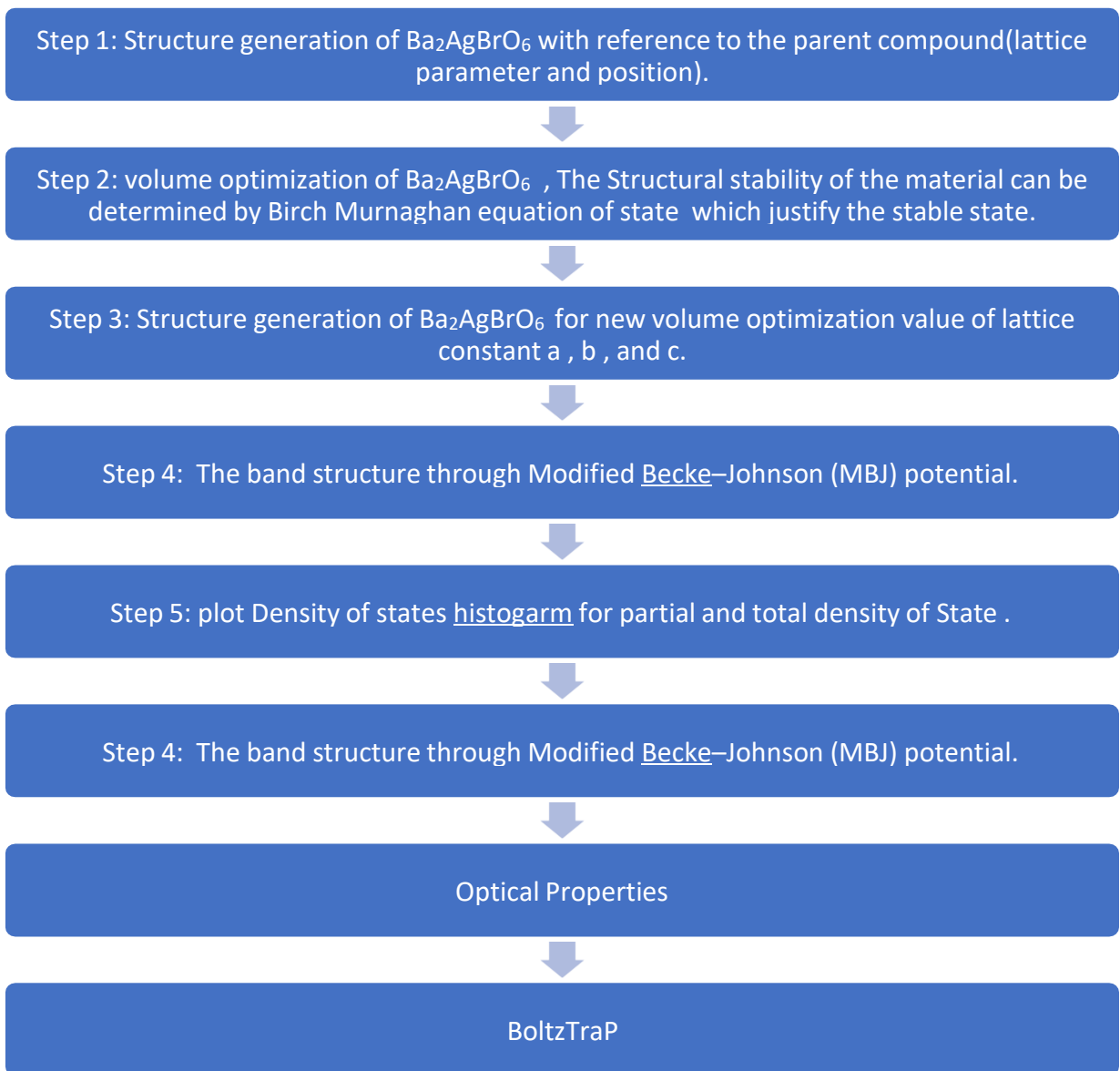


Figure 1.2 Flow Chart of Computational Work

CHAPTER -4

4. RESULT AND DISCUSSION

4.1 Structural Properties and Stability of $\text{Ba}_2\text{AgBrO}_6$ Compound

All calculations given here have been carried out using the generalized gradient approximation (GGA -mBJ), which is included in the code for the exchange-correlation potential, and the full-potential linearized augmented plane wave algorithm wien2k (Blaha, 2001). At the ground state, the lattice constants for $\text{Ba}_2\text{AgBrO}_6$ were adjusted to 8.3527Å respectively. These compounds are cubic structures with the same space group (Fm3m, #225). It is important to note that the compounds we looked at are of the A_2BCO_6 type, in which the B and C cations are organized like those in rock salt. As a result, the idealized cubic lattice (Fm3m) is twice as large as the perovskite of the ABX_3 type (F. Kubel et al., 2013). This also explains why double perovskites typically have greater lattice constants than single perovskites. The structure of $\text{Ba}_2\text{AgBrO}_6$ is shown in Fig.4.1

The optimization of cations and anions present in a compound determines how stable the crystal structures, band structures, charger carrier transport performance, and uses of Double perovskite oxides are to a considerable extent.

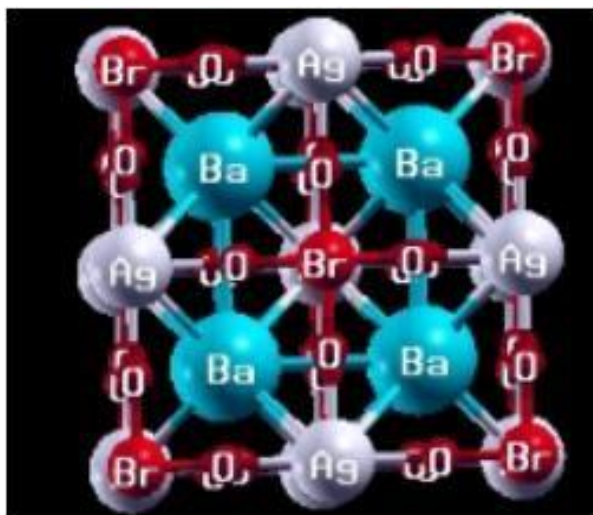


Figure 4.1 $\text{Ba}_2\text{AgBrO}_6$ Crystal structure

Table 4.1 The structural and electronic properties of Ba₂AgBrO₆ Compound

Parameters	Ba ₂ AgBrO ₆
Optimized lattice parameters	8.3527Å ⁰
Space group Name	Fm3 ⁻ m
Space group Number	225
Structural parameters	Ba 1/4 1/4 3/4 Ag 0 0 1/2 Br 0 0 0 O 0 0 0.774922
K-points	1000
Energy Convergence	0.0001 Ry
Charge Convergence	0.001 e
E _f (Ryd)	0.55890
Cv/T (J/K)	1.76
No. of Dos (states/Ryd)	10.16
d _{Ba-Br} (Bohr)	6.8348
d _{Ba-O} (Bohr)	5.5944
d _{Ag-Br} (Bohr)	7.8922
d _{Ag-O} (Bohr)	4.3395
d _{Br-O} (Bohr)	3.5527
Ba-Ag-Br (Degree)	90.529
Ba-Br-O (Degree)	70.529
Ba-Br-O (Degree)	54.736
O-Ba-Ag (Degree)	39.297
Ag-Br-O (Degree)	180.00

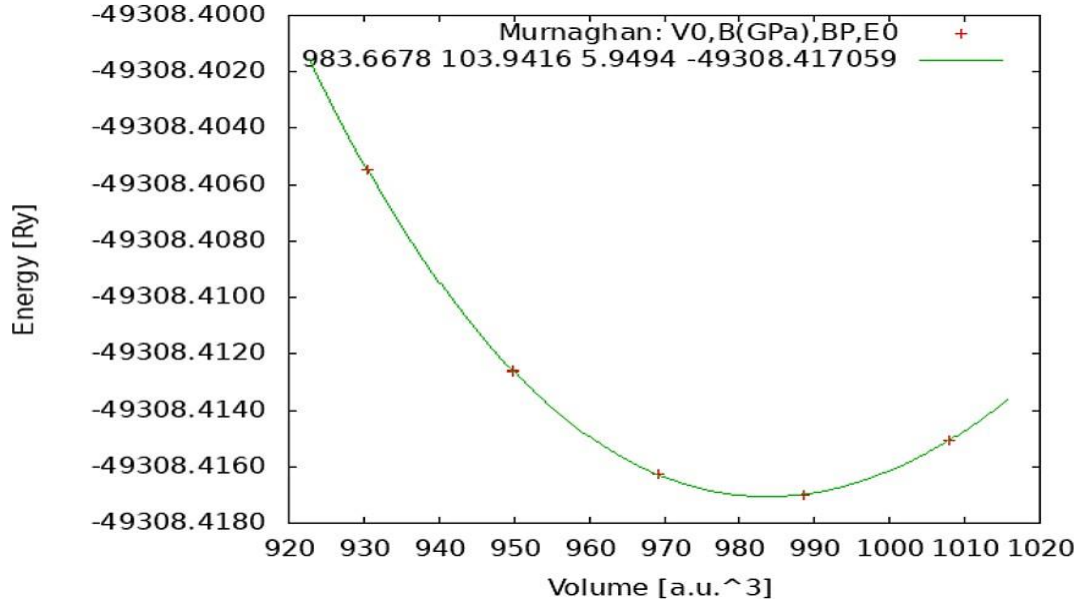


Figure 4.2 Volume optimization curve of Ba₂AgBrO₆ Compound

Fig. 4.2 shows the structural optimization curve of both titled Double perovskite in the non-magnetic phase. The cubic structures of both DPs were optimized using Murnaghan's statistical equation (provided below) (Tyuterev et al., 2006).

$$E(V) = E_0 + \frac{9V_0B_0}{16} \left\{ \left[\left(\frac{V_0}{V} \right)^{\frac{2}{3}-1} \right]^3 B'_0 + \left[\left(\frac{V_0}{V} \right)^{\frac{2}{3}-1} \right]^2 - \left[6 - 4 \left(\frac{V_0}{V} \right)^{\frac{2}{3}} \right] \right\} \quad (1)$$

Here, V_0 and V stand for equilibrium and thermodynamic volumes, respectively, whereas E_0 denotes equilibrium energy, B_0 denotes bulk modulus, and B'_0 represents the derivative's value.

Figure 4.2 depicts the volume optimization curve for each material, and using the optimized results, we were able to determine the value of each material's optimized lattice constant.

4.1.1 Electron density plot of Ba₂AgBrO₆ Compound

The electron density plot for the (100) plane of the Ba₂AgBrO₆ compound is shown in Fig 4.3. The contours around Ag and O atoms show the covalent bonding. The contour around O indicates O-O metallic bonding.

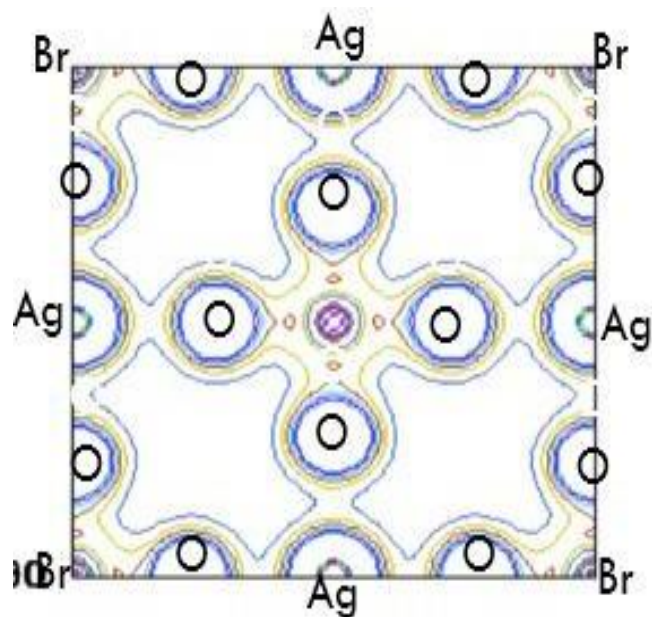


Figure 4.3 Electron density plot for Ba₂AgBrO₆ Compound

4.1.2 Electronic Band Structures of Ba₂AgBrO₆ Compound

Calculating the electronic properties of materials heavily relies on electronic ground state energies. On the basis of improved crystal structures of materials, the electrical characteristics, such as band structure (BS) and density of state (DOS), can be researched. Here, we have evaluated the electronic characteristics of titled DPs using DFT. Our findings indicate that each of the substances under study exhibits no apparent band gaps except the parent compound.

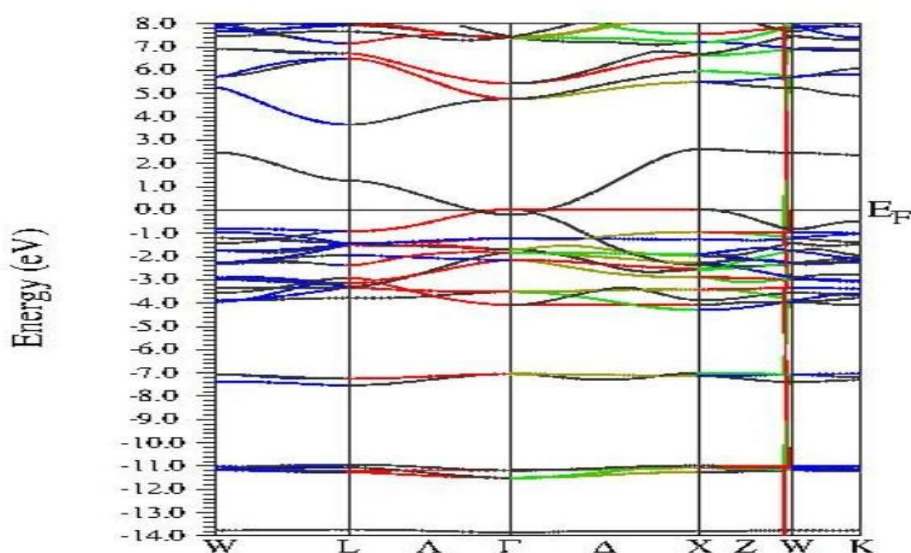


Figure 4.4 Band structure of Ba₂AgBrO₆ compound

The general forms of the Band Structure revealed that both of the named compounds' lower conduction Band (CB) and higher Valence Band (VB) are symmetrically situated at the same location factors (I-point). The overlap of the conduction band minima (CBM) and valence band maxima (VBM) of compounds having no band gap. Hence it is a conductor.

4.1.3 Electron transport properties of Ba₂AgBrO₆ compound

We must examine their electronic band structures in order to comprehend the electronic characteristics of the double perovskite Ba₂AgBrO₆. According to each compound's self-consistent computations, the Fermi levels E_f are correctly determined. Describe Ba₂AgBrO₆ partial and total densities of states (TDoS and PDoS) respectively.

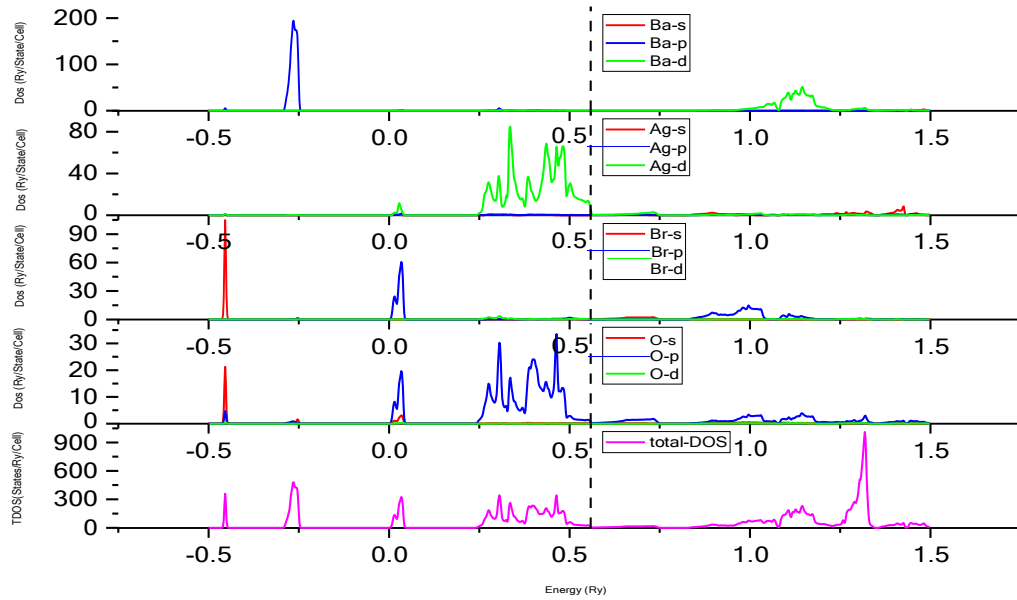


Figure 4.5 Density of states of Ba₂AgBrO₆ compound

The TDoS and PDoS are divided into two regions. At first, in the low energy region (0 Ry-0.5589Ry), we can notice that the VBM of these compounds is mainly dominated by O-p orbitals and Ag-d orbital meanwhile Ba-p orbitals also play a smaller role than the former. In addition, the Ba atom of these compounds only has electron distribution in the region greater than 0.8Ry, indicating that the Ba element does not directly affect the formation of the conduction band. It can also be seen from the PDoS that there exists an

apparent overlap between the O-p orbitals and the Br-s orbitals. This is due to hybridization of orbitals.

4.2 Structural Properties and Stability of $\text{Ba}_2\text{InBrO}_6$ Compound

The generalized gradient approximation (GGA), which is part of the code for the exchange-correlation potential, and the full-potential linearized augmented plane wave method wien2k (Blaha, 2001) were used for all computations shown here. The lattice constants for $\text{Ba}_2\text{InBrO}_6$ were modified to 8.4700 Å at the ground state. The cubic structures in these compounds belong to the same space group (Fm3m, #225). The compounds that we examined are of the A_2BCO_6 type, meaning that the B and C cations are arranged similarly to how they are in rock salt. The idealized cubic lattice (Fm3m) is therefore twice as big as the ABX_3 -type perovskite (F. Kubel et al., 2013). The structure of $\text{Ba}_2\text{InBrO}_6$ is shown in Fig.4.6 The optimization of cations and anions present in a compound determines how stable the crystal structures, band structures, charger carrier transport performance, and uses of Double perovskite oxides are to a considerable extent.

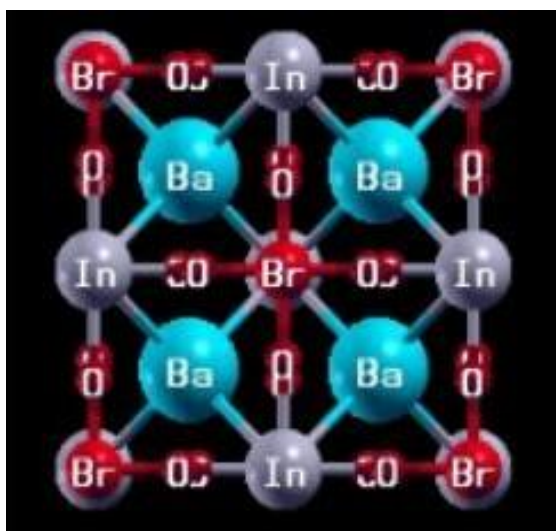


Figure 4.6 $\text{Ba}_2\text{InBrO}_6$ Crystal structure

Table 4.2 The structural and electronic properties of Ba₂InBrO₆ Compound

Parameters	Ba ₂ InBrO ₆
Optimized lattice parameters	8.4700 Å ⁰
Space group Name	Fm $\bar{3}$ m
Space group Number	225
Structural parameters	Ba 1/4 1/4 3/4 In 0 0 1/2 Br 0 0 0 O 0 0 0.774922
K-points	1000
Energy Convergence	0.0001 Ry
Charge Convergence	0.001 e
E _f (Ryd)	0.51895
Cv/T (J/K)	4.05
No. of Dos (states/Ryd)	23.40
d _{Ba-Br} (Bohr)	6.9308
d _{Ba-O} (Bohr)	6.9308
d _{In-Br} (Bohr)	5.6730
d _{In-O} (Bohr)	8.0030
d _{Br-O} (Bohr)	4.4004
Ba-In-Br (Degree)	70.529
Ba-Br-O (Degree)	31.232
Ba-In-O (Degree)	39.297
O-Ba-In (Degree)	87.673

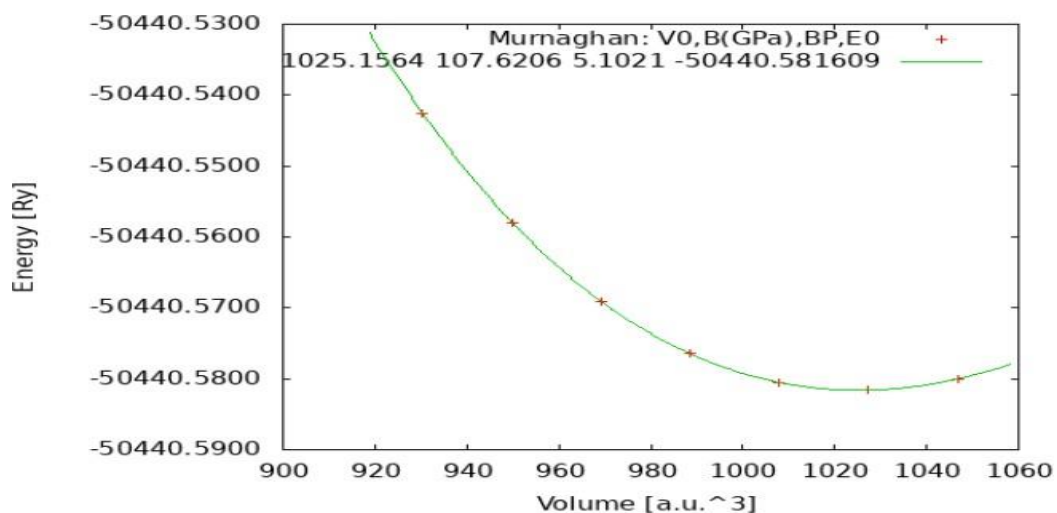


Figure 4.7 Volume optimization curve of Ba₂InBrO₆ Compound

Figure 4.7 depicts the volume optimization curve for each material, and using the optimized results, we were able to determine the value of each material's optimized lattice constant.

4.2.1 Electron density plot of Ba₂InBrO₆ Compound

The electron density plot for the (100) plane of the Ba₂InBrO₆ compound is shown in Fig4.8. The contours around In and O atoms show the covalent bonding. The contour around O indicates O-O metallic bonding.

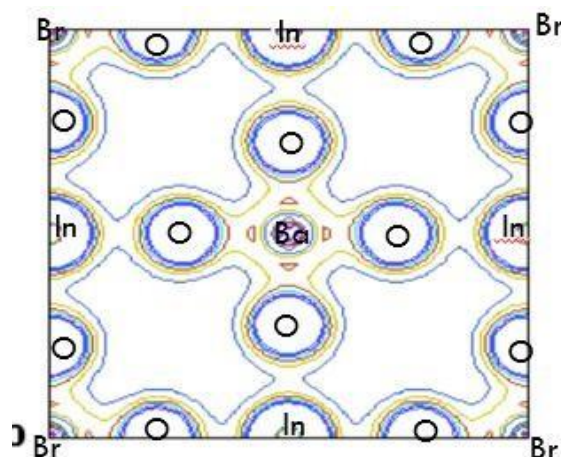


Figure 4.8 Electron density plot for Ba₂InBrO₆ Compound

4.2.2 Electronic Band Structures of Ba₂InBrO₆ Compound

Calculating the electronic properties of materials heavily relies on electronic ground state energies. On the basis of improved crystal structures of materials, the electrical characteristics, such as band structure (BS) and density of state (DOS), can be researched. Here, we have evaluated the electronic characteristics of titled DPs using DFT. Our findings indicate that each of the substances under study exhibits no apparent band gaps except the parent compound.

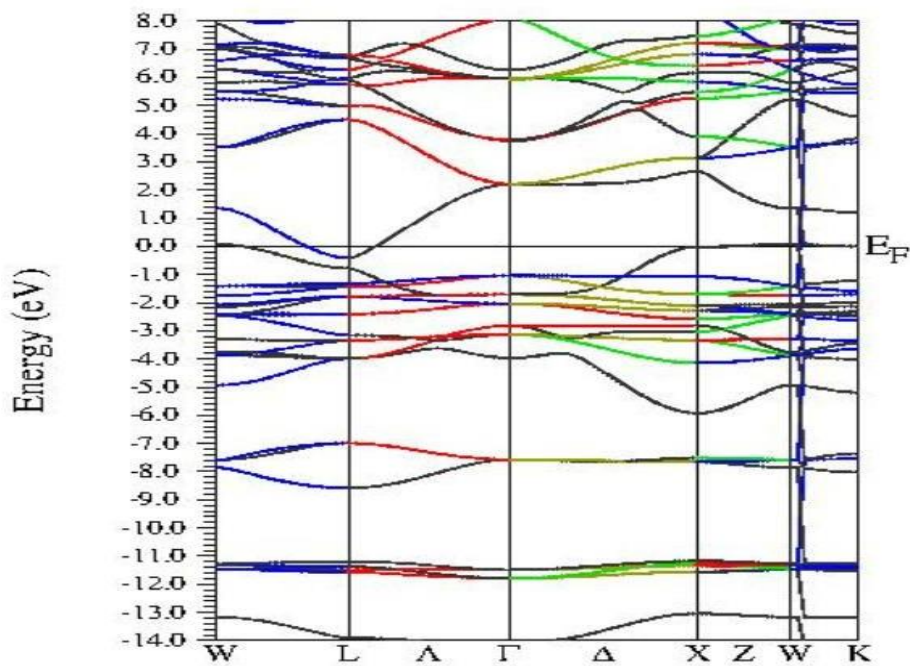


Figure 4.9 Band structure of Ba₂InBrO₆ compound

The general forms of the Band Structure revealed that both of the named compounds' lower CB and higher VB are symmetrically situated at the same location factors (I-point). The overlap of the conduction band minima (CBM) and valence band maxima (VBM) of compounds having no band gap. Hence it is a conductor.

4.2.3 Electron transport properties of Ba₂InBrO₆ compound

We must examine their electronic band structures in order to comprehend the electronic characteristics of the double perovskite Ba₂InBrO₆. According to each compound's self-consistent computations, the Fermi levels E_f are correctly determined. Describe Ba₂InBrO₆ partial and total densities of states (TDoS and PDoS) respectively.

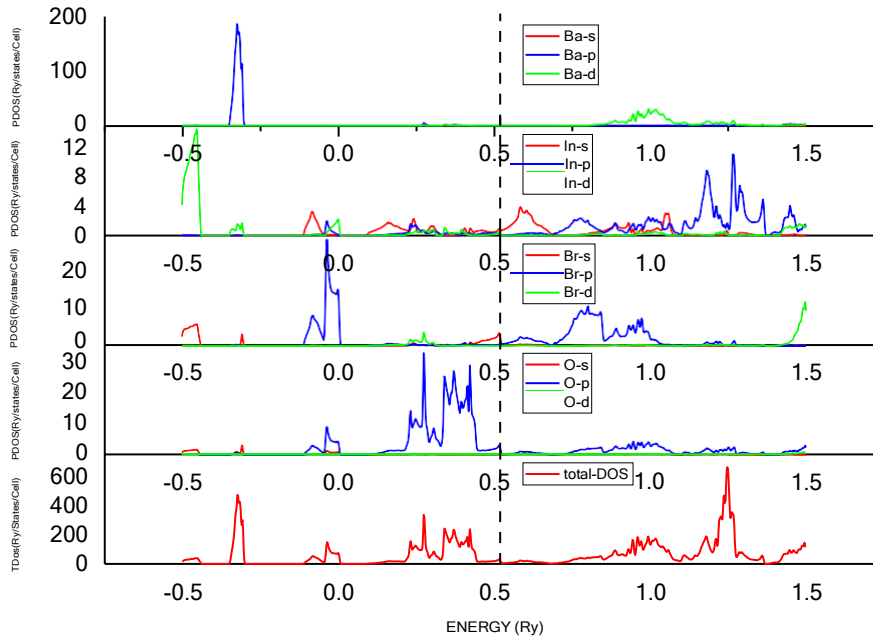


Figure 4.10 Density of states of Ba₂InBrO₆ compound

From the fig 4.10, The TDoS and PDOS are divided into two regions. At first, in the low energy region (0 Ry-0.5189Ry), we can notice that the VBM of these compounds is mainly dominated by O-p orbitals and In-d orbital meanwhile Ba-p orbitals also play a smaller role than the former. In addition, the Ba atom of these compounds only has electron distribution in the region greater than 0.8 Ry, indicating that the Ba element does not directly affect the formation of the conduction band. It can also be seen from the PDoS that there exists an apparent overlap between the O-p orbitals and the Br-s orbitals. This is due to hybridization of orbitals.

4.3 Structural Properties and Stability of Ba₂NaBrO₆ Compound

The generalized gradient approximation (GGA), which is part of the code for the exchange-correlation potential, and the full-potential linearized augmented plane wave method wien2k (Blaha, 2001) were used for all computations shown here. The lattice constants for Ba₂NaBrO₆

were modified to 8.2434 Å at the ground state. The cubic structures in these compounds belong to the same space group (Fm3m, #225). The compounds that we examined are of the A₂BCO₆ type, meaning that the B and C cations are arranged similarly to how they are in rock salt. The idealized cubic lattice (Fm3m) is therefore twice as big as the ABX₃-type perovskite (F. Kubel et al., 2013). The structure of Ba₂NaBrO₆ is shown in Fig.4.11 The optimization of cations and anions present in a compound determines how stable the crystal structures, band structures, charger carrier transport performance, and uses of Double perovskite oxides are to a considerable extent.

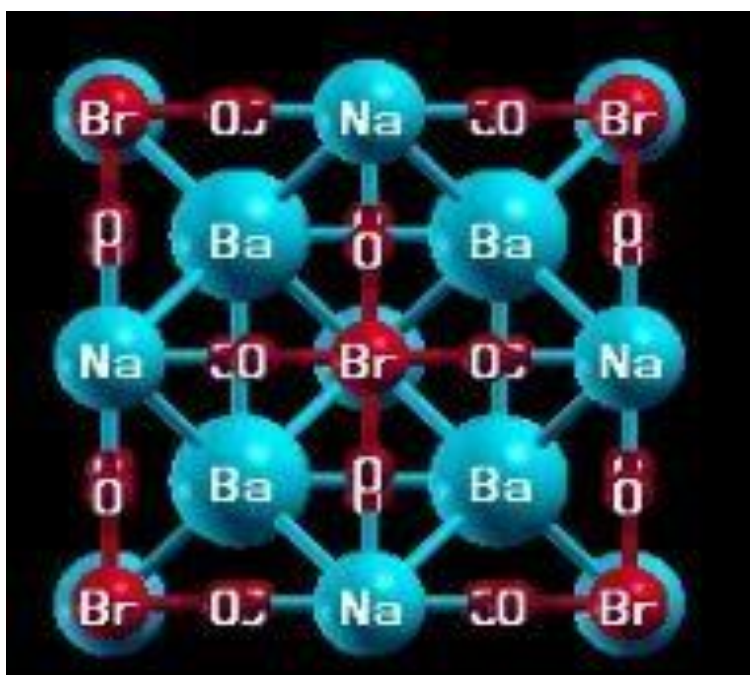


Figure 4.11 Ba₂NaBrO₆ Crystal structure

Table 4.3 The structural and electronic properties of Ba₂NaBrO₆ Compound

Parameters	Ba ₂ NaBrO ₆
Experimental Lattice parameter[A]	a=b=c=8.313 Å ⁰
Optimized lattice parameters	a=b=c=8.2434 Å ⁰
Structural parameters[A]	Ba 1/4 1/4 3/4 Na 0 0 1/2 Br 0 0 0 O 0 0 0.774922
Space group Name	Fm $\bar{3}$ m
Space group Number	225
K-points	1000
Energy Convergence	0.0001 Ry
Charge Convergence	0.001 e
E _f (Ryd)	0.42414
Cv/T (J/K)	0.14
No. of Dos (states/Ryd)	0.81
d _{Ba-Br} (Bohr)	6.7454 Bohr
d _{Ba-O} (Bohr)	6.7454 Bohr
d _{Na-Br} (Bohr)	5.5212 Bohr
d _{Na-O} (Bohr)	7.7889 Bohr
d _{Br-O} (Bohr)	4.2827 Bohr
Ba-Na-Br (Degree)	70.529
Ba-Br-O (Degree)	54.736
Ba-Na-O (Degree)	54.736
O-Ba-Na (Degree)	39.297
Na-Br-O (Degree)	180.00

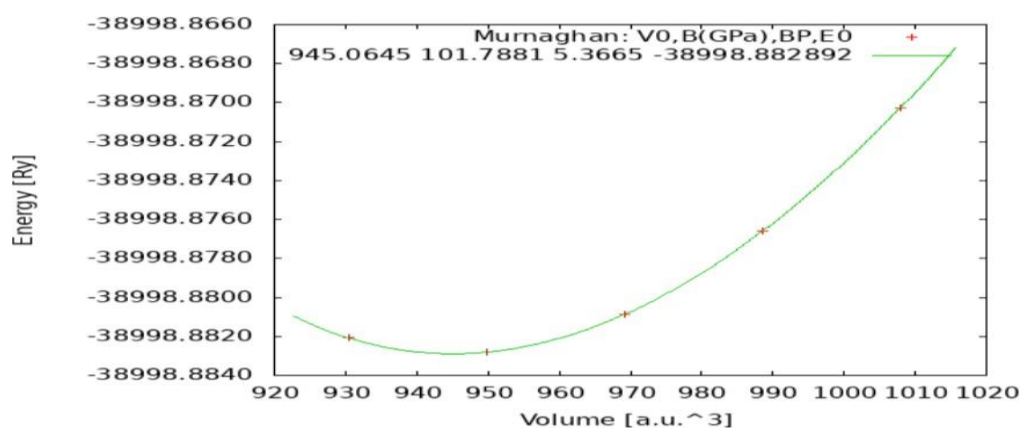


Figure 4.12 Volume optimization curve of Ba₂NaBrO₆ Compound

Figure 4.12 depicts the volume optimization curve for each material, and using the optimized results, we were able to determine the value of each material's optimized lattice constant.

4.3.1 Electron density plot of Ba₂NaBrO₆ Compound

The electron density plot for the (100) plane of the Ba₂NaBrO₆ compound is shown in Fig4.4 The contours around Na and O atoms show the ionic bonding. The contour around O indicates O-O metallic bonding.

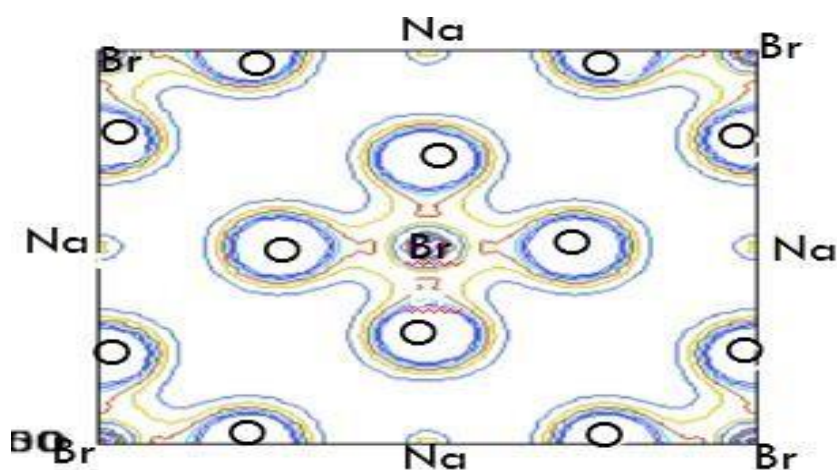


Figure 4.13 Electron density plot for Ba₂NaBrO₆ Compound

4.3.2 Electronic Band Structures of Ba₂NaBrO₆ Compound

Calculating the electronic properties of materials heavily relies on electronic ground state energies. On the basis of improved crystal structures of materials, the electrical characteristics, such as band structure (BS) and density of state (DOS), can be researched. Here, we have evaluated the electronic characteristics of titled DPs using DFT. Our findings indicate that each of the substances under study exhibits apparent band gaps and a nonmagnetic characteristic.

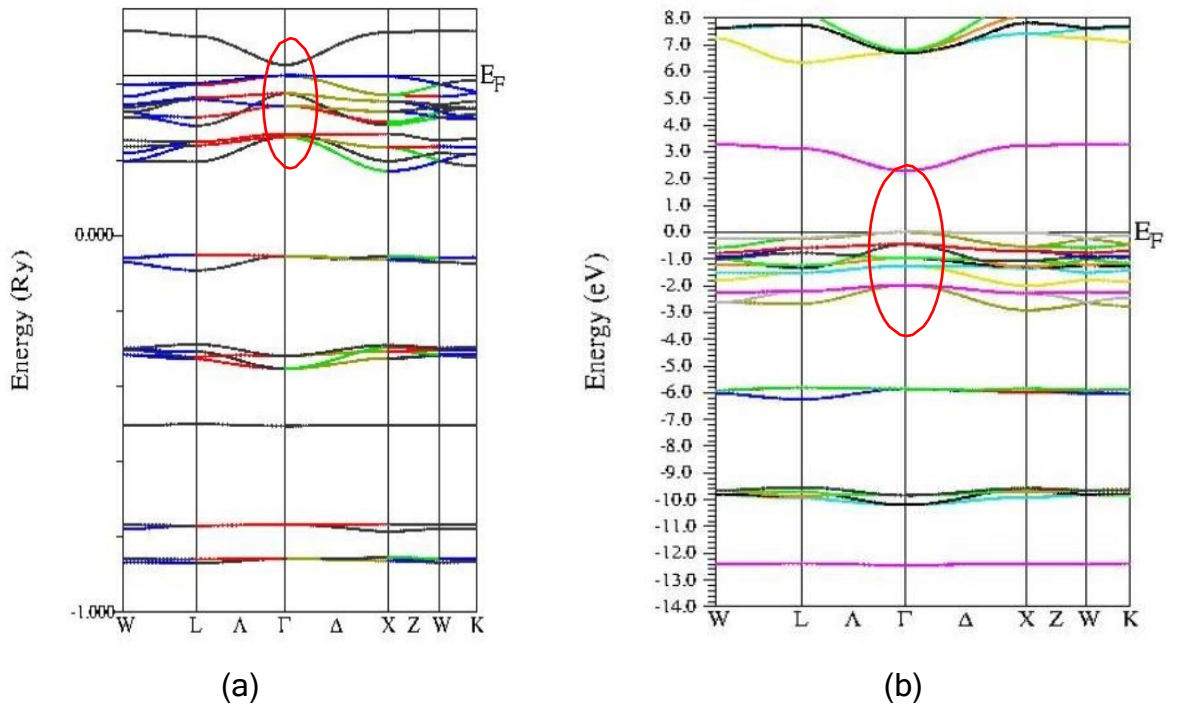


Figure 4.14: SHOWS (a) Band structure of Ba₂NaBrO₆ compound

(b) Band structure of Ba₂NaBrO₆ compound with mBJ

From the fig 4.14, we can find that the conduction band minima (CBM) and valence band maxima (VBM) of compounds are located at the same high symmetry points, which indicates their direct bandgaps. Due to mBJ calculation the band gap increases and the obtained band gap is 2.298eV (Hao -Jia et al).

4.3.3 Electron transport properties of Ba₂NaBrO₆ compound

We must examine their electronic band structures in order to comprehend the electronic characteristics of the double perovskite Ba₂NaBrO₆. According to each compound's self-consistent computations, the Fermi levels E_f are correctly determined. Describe Ba₂NaBrO₆ partial and total densities of states (TDoS and PDoS) respectively.

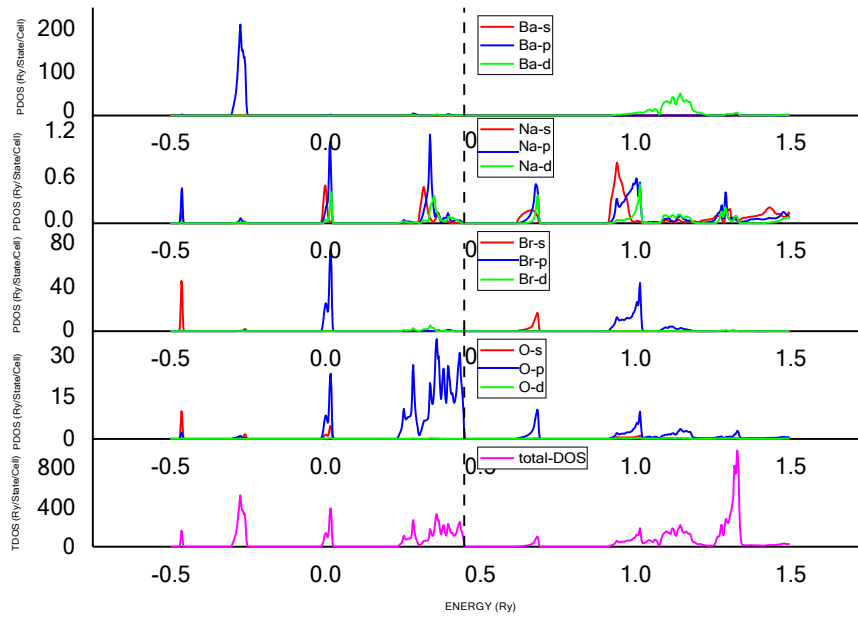


Figure 4.15 Density of states of Ba₂NaBrO₆ compound

From the fig 4.15, The TDoS and PDoS are divided into two regions. PDoS are divided into two regions. At first, in the low energy region (-0.2 4 Ry-0.4Ry), we can notice that the VBM of these compounds is mainly dominated by O-p orbitals, meanwhile Ba-p orbitals also play a smaller role than the former. there exist few electrons in the valence band coming from Na-p orbitals. In addition, the Ba atoms of these compounds only have electron distribution in the region greater than 0.8Ry, indicating that the Ba element does not directly affect the formation of the conduction band. we can note that there is no sharp peak at

the Fermi level E_f , which indicates that those compounds are not pure conductors

4.4 Structural Properties and Stability of $\text{Sr}_2\text{AgBrO}_6$ Compound

The generalized gradient approximation (GGA), which is part of the code for the exchange-correlation potential, and the full-potential linearized augmented plane wave method wien2k (Blaha, 2001) were used for all computations shown here. The lattice constants for $\text{Sr}_2\text{AgBrO}_6$ were modified to 8.1924 Å at the ground state. The cubic structures in these compounds belong to the same space group (Fm3m, #225). The compounds that we examined are of the A_2BCO_6 type, meaning that the B and C cations are arranged similarly to how they are in rock salt. The idealized cubic lattice (Fm3m) is therefore twice as big as the ABX_3 -type perovskite (F. Kubel et al., 2013). The structure of $\text{Sr}_2\text{AgBrO}_6$ is shown in Fig.4.16 The optimization of cations and anions present in a compound determines how stable the crystal structures, band structures, charger carrier transport performance, and uses of Double perovskite oxides are to a considerable extent.

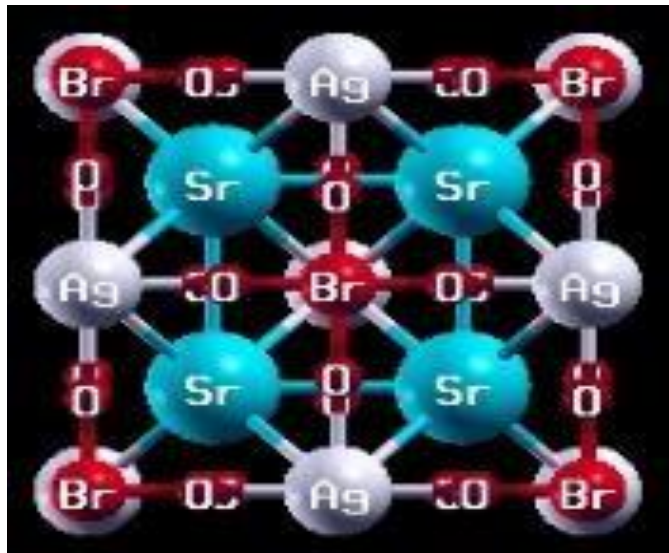


Figure 4.16 $\text{Sr}_2\text{AgBrO}_6$ Crystal structure

Table 4.4 The structural and electronic properties of Sr₂AgBrO₆ Compound

Parameters	Sr ₂ AgBrO ₆
Optimized lattice parameters	8.1924 Å
Space group Name	Fm $\bar{3}$ m
Space group Number	225
Structural parameters	Sr 1/4 1/4 3/4 Ag 0 0 1/2 Br 0 0 0 O 0 0 0.774922
K-points	1000
Energy Convergence	0.0001 Ry
Charge Convergence	0.001 e
E _f (Ryd)	0.42176
Cv/T (J/K)	4.74
No. of Dos (states/Ryd)	27.36
d _{Sr-Br} (Bohr)	6.7036
d _{Sr-O} (Bohr)	6.7036
d _{Ag-Br} (Bohr)	5.4871
d _{Ag-O} (Bohr)	7.7407
d _{Br-O} (Bohr)	4.2562
Sr-Ag-Br (Degree)	70.529
Sr-Br-O (Degree)	54.736
Sr-Ag-O (Degree)	54.736
O-Sr-Ag (Degree)	87.673
Ag-Br-O (Degree)	180.00

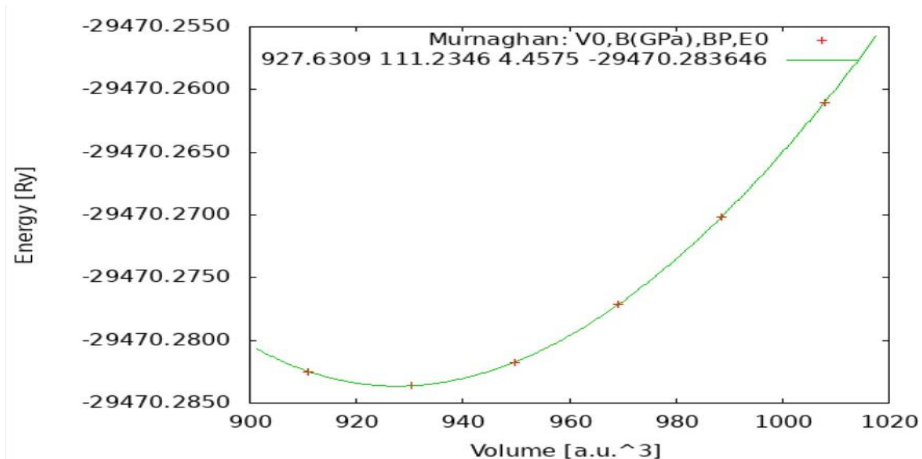


Figure 4.17 Volume optimization curve of $\text{Sr}_2\text{AgBrO}_6$ Compound

Figure 4.17 depicts the volume optimization curve for each material, and using the optimized results, we were able to determine the value of each material's optimized lattice constant.

4.4.1 Electron density plot of $\text{Sr}_2\text{AgBrO}_6$ Compound

The electron density plot for the (100) plane of the $\text{Sr}_2\text{AgBrO}_6$ compound is shown in Fig4.4. The contours around Ag and O atoms show the covalent bonding. The contour around O indicates O-O metallic bonding.

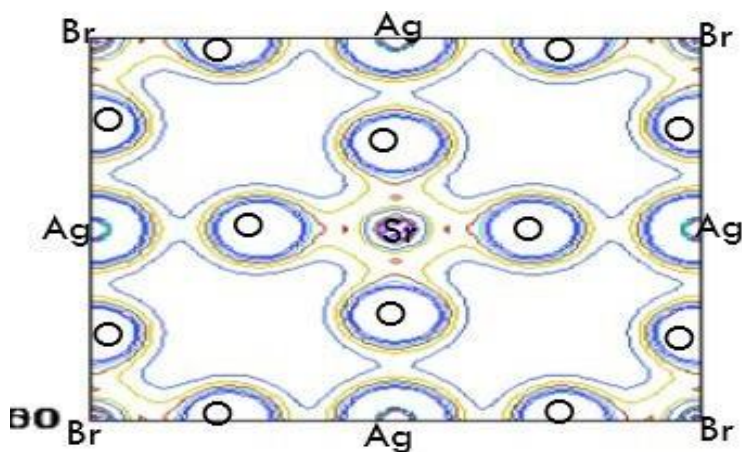


Figure 4.18 Electron density plot for $\text{Sr}_2\text{AgBrO}_6$ Compound

4.4.2 Electronic Band Structures of $\text{Sr}_2\text{AgBrO}_6$ Compound

Calculating the electronic properties of materials heavily relies on electronic ground state energies. On the basis of improved crystal structures of materials, the electrical characteristics, such as band structure (BS) and density of state (DOS), can be researched. Here, we have evaluated the electronic characteristics of titled DPs using DFT. Our findings indicate that each of the substances under study exhibits no apparent band gaps except the parent compound.

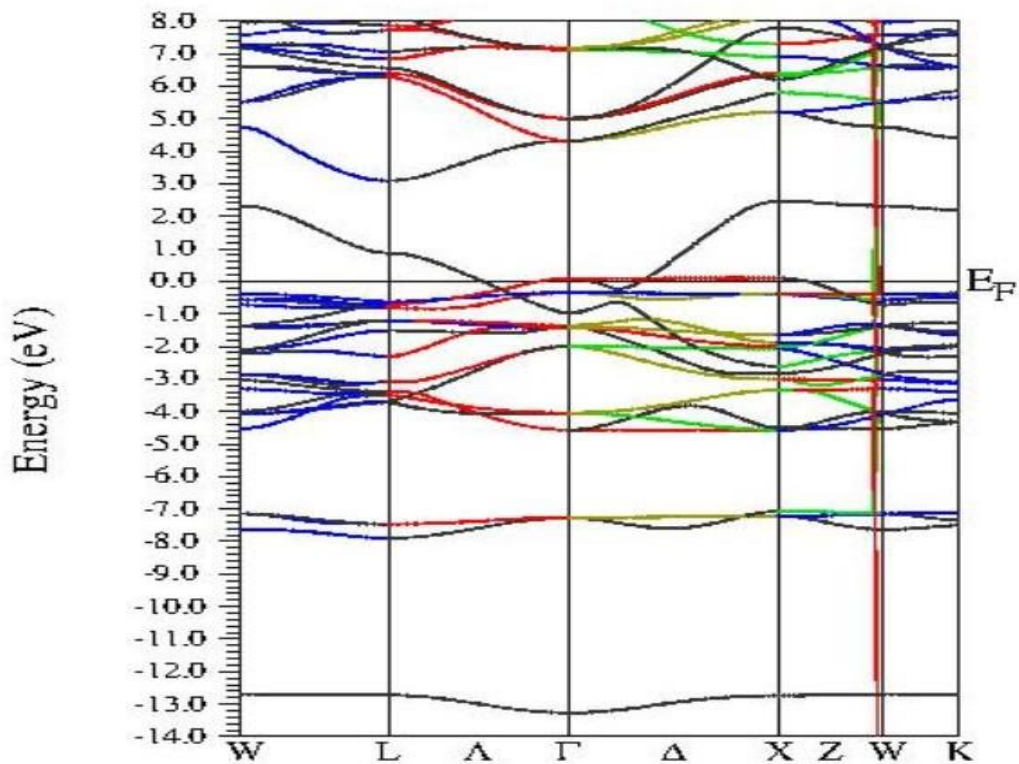


Figure 4.19 Band structure of $\text{Sr}_2\text{AgBrO}_6$ compound

From the fig 4.19, The general forms of the Band Structure revealed that both of the named compounds' lower CB and higher VB are symmetrically situated at the same location factors (l-point). The overlap of the conduction band minima (CBM) and valence band maxima (VBM) of compounds having no band gap. Hence it is a conductor.

4.4.3 Electron transport properties of $\text{Sr}_2\text{AgBrO}_6$ compound

We must examine their electronic band structures in order to comprehend the electronic characteristics of the double perovskite $\text{Sr}_2\text{AgBrO}_6$. According to each compound's self-consistent computations, the Fermi levels E_f are correctly determined. Describe $\text{Sr}_2\text{AgBrO}_6$ partial and total densities of states (TDoS and PDoS) respectively.

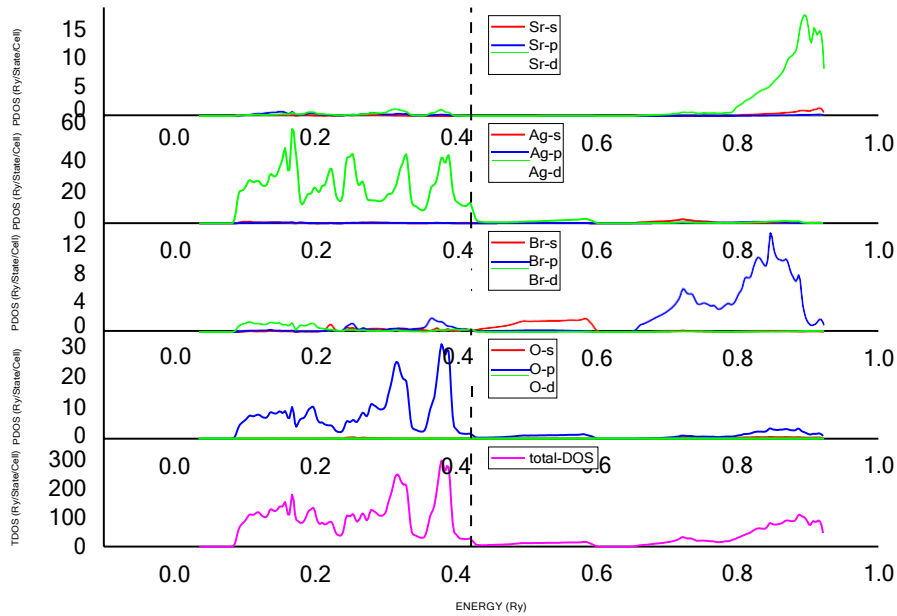


Figure 4.20 Density of states of $\text{Sr}_2\text{AgBrO}_6$ compound

From the fig 4.20, The TDoS and PDoS are divided into two regions. At first, in the low energy region (0 Ry-0.4Ry), we can notice that the VBM of these compounds is mainly dominated by O-p orbitals and Ag-d orbitals. In addition, the Sr atom of these compounds only has electron distribution in the region greater than 0.8Ry, indicating that the Sr element does not directly affect the formation of the conduction band. It can also be seen from the PDoS that there exists an apparent overlap between the O-p orbitals and the Br-s orbitals. This is due to hybridization of orbitals.

4.5 Structural Properties and Stability of $\text{Sr}_2\text{InBrO}_6$ Compound

The generalized gradient approximation (GGA), which is part of the code for the exchange-correlation potential, and the full-potential linearized augmented plane wave method wien2k (Blaha, 2001) were used for all computations shown here. The lattice constants for $\text{Sr}_2\text{InBrO}_6$ were modified to $8.335\text{\AA}$ at the ground state. The cubic structures in these compounds belong to the same space group ($\text{Fm}\bar{3}\text{m}$, #225). The compounds that we examined are of the A_2BCO_6 type, meaning that the B and C cations are arranged similarly to how they are in rock salt. The idealized cubic lattice ($\text{Fm}\bar{3}\text{m}$) is therefore twice as big as the ABX_3 -type perovskite (F. Kubel et al., 2013). The structure of $\text{Sr}_2\text{InBrO}_6$ is shown in Fig.4.21. The optimization of cations and anions present in a compound determines how stable the crystal structures, band structures, charger carrier transport performance, and uses of Double perovskite oxides are to a considerable extent.

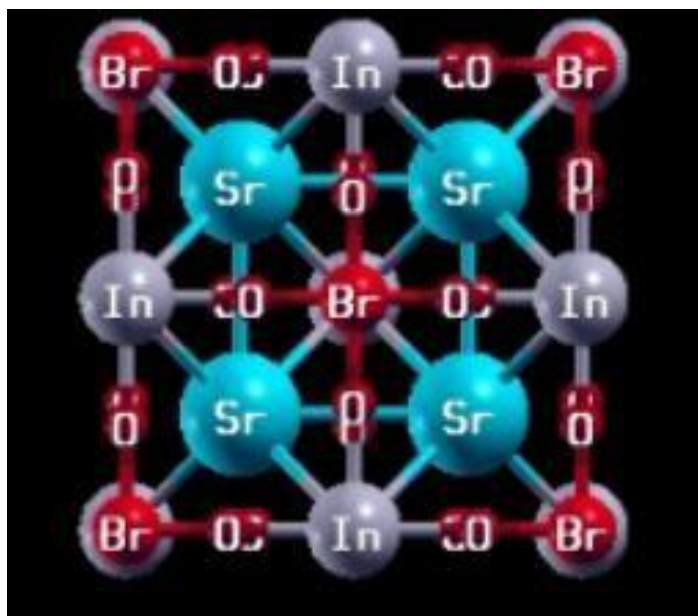


Figure 4.21 $\text{Sr}_2\text{InBrO}_6$ Crystal structure

Table 4.5 The structural and electronic properties of Sr₂InBrO₆ Compound

Parameters	Sr ₂ InBrO ₆
Optimized lattice parameters	8.335 Å ⁰
Space group Name	Fm3̄m
Space group Number	225
Structural parameters	Sr 1/4 1/4 3/4 In 0 0 1/2 Br 0 0 0 O 0 0 0.774922
K-points	1000
Energy Convergence	0.0001 Ry
Charge Convergence	0.001 e
E _f (Ryd)	0.47930
Cv/T (J/K)	2.81
No. of Dos (states/Ryd)	16.20
d _{Sr-Br} (Bohr)	6.8203
d _{Sr-O} (Bohr)	6.8203
d _{In-Br} (Bohr)	5.5826
d _{In-O} (Bohr)	7.8754
d _{Br-O} (Bohr)	4.3303
Sr-In-Br (Degree)	70.529
Sr-Br-O (Degree)	54.736
Sr-In-O (Degree)	54.736
O-Sr-In (Degree)	87.673
In-Br-O (Degree)	180.00

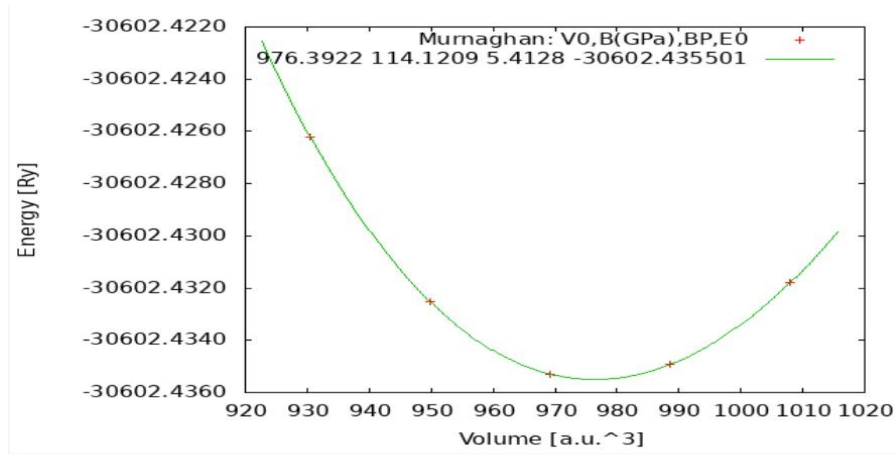


Figure 4.22 Volume optimization curve of $\text{Sr}_2\text{InBrO}_6$

Figure 4.22 depicts the volume optimization curve for each material, and using the optimized results, we were able to determine the value of each material's optimized lattice constant.

4.5.1 Electron density plot of $\text{Sr}_2\text{InBrO}_6$ Compound

The electron density plot for the (100) plane of the $\text{Ba}_2\text{InBrO}_6$ compound is shown in Fig4.4 The contours around In and O atoms show the covalent bonding. The contour around O indicates O-O metallic bonding.

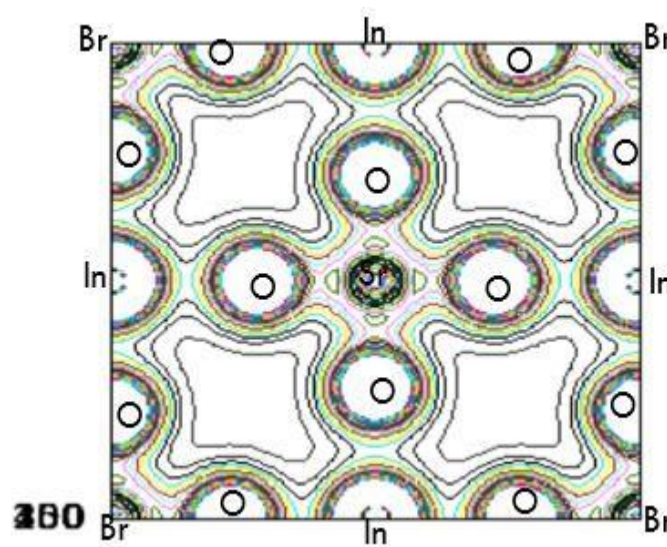


Figure 4.23 Electron density plot for $\text{Sr}_2\text{InBrO}_6$ Compound

4.5.2 Electronic Band Structures of $\text{Sr}_2\text{InBrO}_6$ Compound

Calculating the electronic properties of materials heavily relies on electronic ground state energies. On the basis of improved crystal structures of materials, the electrical characteristics, such as band structure (BS) and density of state (DOS), can be researched. Here, we have evaluated the electronic characteristics of titled DPs using DFT. Our findings indicate that each of the substances under study exhibits no apparent band gaps except the parent compound

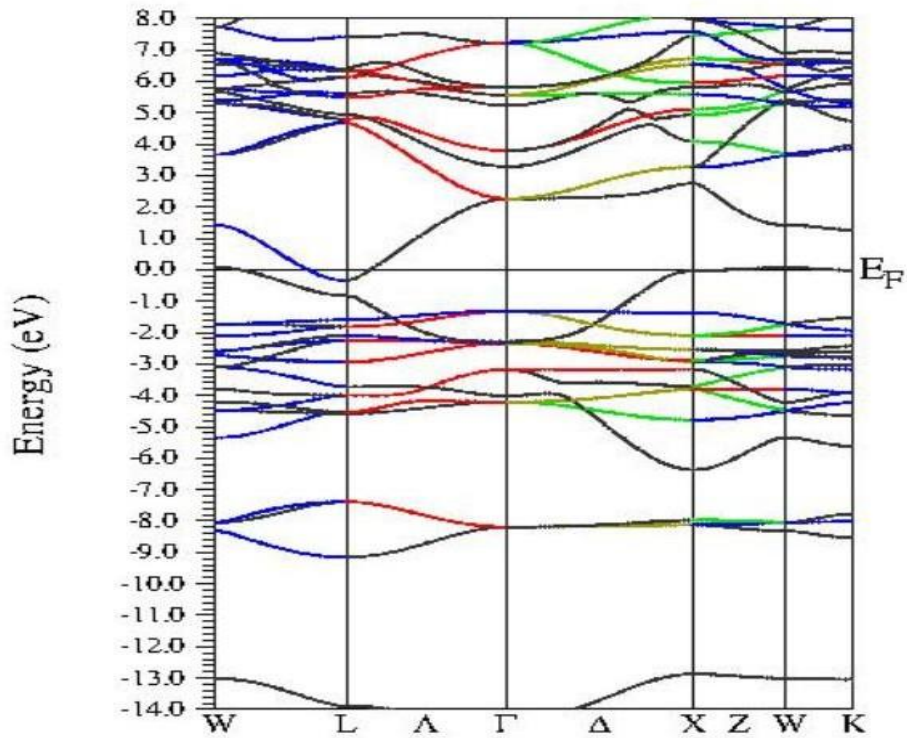


Figure 4.24 Band structure of $\text{Sr}_2\text{InBrO}_6$ compound

From the fig 4.24, The general forms of the Band Structure revealed that both of the named compounds' lower CB and higher VB are symmetrically situated at the same location factors (I-point). The overlap of the conduction band minima (CBM)

and valence band maxima (VBM) of compounds having no band gap. Hence it is a conductor.

4.5.3 Electron transport properties of $\text{Sr}_2\text{InBrO}_6$ compound

We must examine their electronic band structures in order to comprehend the electronic characteristics of the double perovskite $\text{Sr}_2\text{InBrO}_6$. According to each compound's self-consistent computations, the Fermi levels E_f are correctly determined. Describe $\text{Sr}_2\text{InBrO}_6$ partial and total densities of states (TDoS and PDoS) respectively.

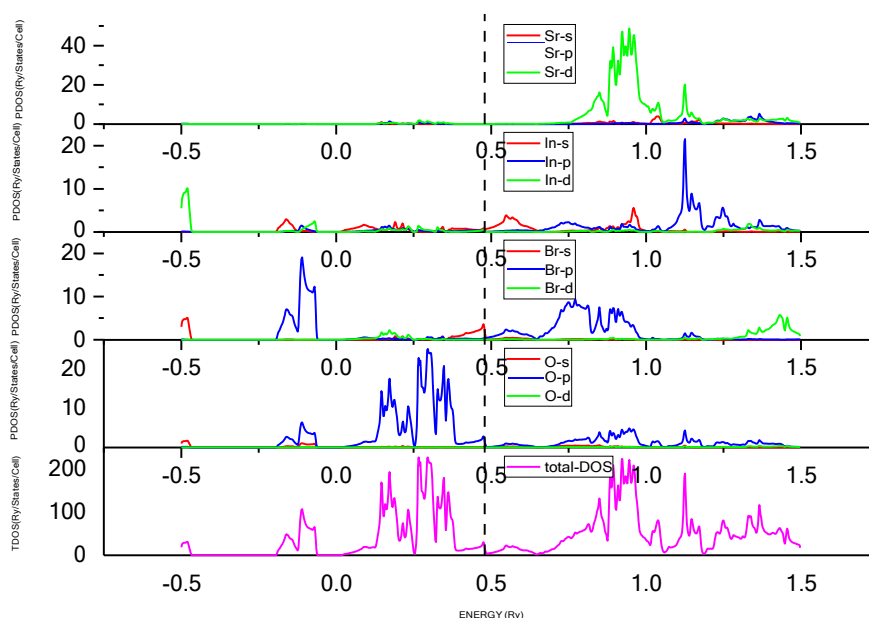


Figure 4.25 Density of states of $\text{Sr}_2\text{InBrO}_6$ compound

From the fig 4.25, The TDoS and PDoS are divided into two regions. At first, in the low energy region (0 Ry-0.47930 Ry), we can notice that the VBM of these compounds is mainly dominated by O-p orbitals and In-d orbital meanwhile Sr-p orbitals also play a smaller role than the former. In addition, the Sr atoms of these compounds only have electron distribution in the region greater than 0.8Ry, indicating that the Sr element does not directly affect the formation of the

conduction band. It can also be seen from the PDoS that there exists an obvious overlap between the O-p orbitals and the Br-s orbitals. This is due to hybridization of orbitals

4.6 Structural Properties and Stability of $\text{Ca}_2\text{AgBrO}_6$ compound

The generalized gradient approximation (GGA), which is part of the code for the exchange-correlation potential, and the full-potential linearized augmented plane wave method wien2k (Blaha, 2001) were used for all computations shown here. The lattice constants for $\text{Ca}_2\text{AgBrO}_6$ were modified to $8.0857\text{\AA}$ at the ground state. The cubic structures in these compounds belong to the same space group ($\text{Fm}\bar{3}\text{m}$, #225). The compounds that we examined are of the A_2BCO_6 type, meaning that the B and C cations are arranged similarly to how they are in rock salt. The idealized cubic lattice ($\text{Fm}\bar{3}\text{m}$) is therefore twice as big as the ABX_3 -type perovskite (F. Kubel et al., 2013).

The structure of $\text{Ca}_2\text{AgBrO}_6$ is shown in Fig.4.26 The optimization of cations and anions present in a compound determines how stable the crystal structures, band structures, charger carrier transport performance, and uses of Double perovskite oxides are to a considerable extent.

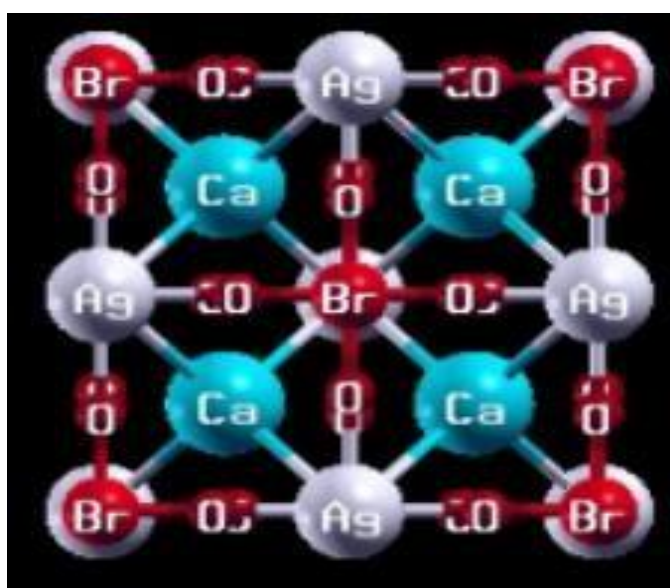


Figure 4.26 $\text{Ca}_2\text{AgBrO}_6$ Crystal structure

Table 4.6 The structural and electronic properties of Ca₂AgBrO₆ compound

Parameters	Ca ₂ AgBrO ₆
Optimized lattice parameters	a=b=c=8.0857 Å
Space group Name	Fm $\bar{3}$ m
Space group Number	225
Structural parameters	Ca 1/4 1/4 3/4 Ag 0 0 1/2 Br 0 0 0 O 0 0 0.774922
K-points	1000
Energy Convergence	0.0001 Ry
Charge Convergence	0.001 e
E _f (Ryd)	0.3911
Cv/T (J/K)	4.43
No. of Dos (states/Ryd)	25.56
d _{Ca-Ag} (Bohr)	6.6163
d _{Ca-Br} (Bohr)	6.6163
d _{Ca-O} (Bohr)	5.4156
d _{Ag-Br} (Bohr)	7.6399
d _{Ag-O} (Bohr)	4.2007
Ca-Ag-Br (Degree)	70.529
Ca-Br-O (Degree)	54.736
Ca-Ag-O (Degree)	54.736
O-Ca-Ag (Degree)	87.673
Ag-Br-O (Degree)	180.00

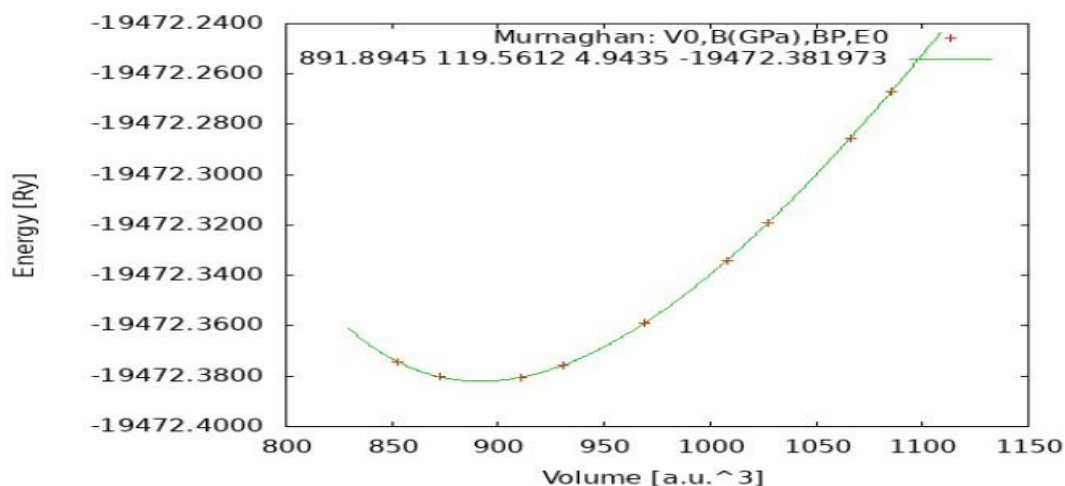


Figure 4.27 volume optimization curve of $\text{Ca}_2\text{AgBrO}_6$ Compound

Figure 4.27 depicts the volume optimization curve for each material, and using the optimized results, we were able to determine the value of each material's optimized lattice constant.

4.6.1 Electron density plot of $\text{Ca}_2\text{AgBrO}_6$ compound

The electron density plot for the (100) plane of the $\text{Ca}_2\text{AgBrO}_6$ the compound is shown in Fig4.4 The contours around Ag and O atoms show the ionic bonding. The contour around O indicates O-O metallic bonding.

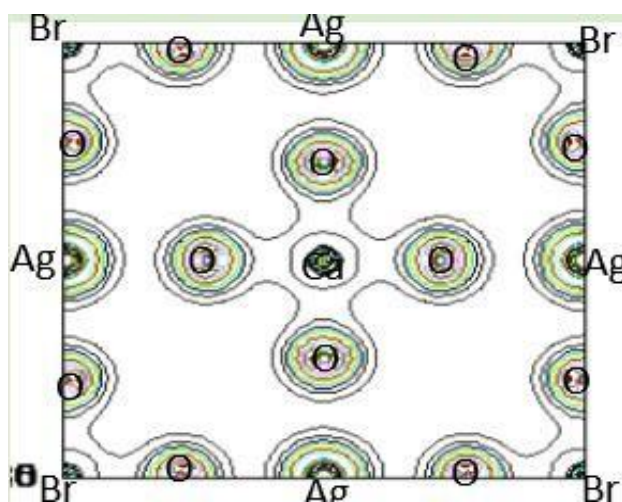


Figure 4.28 Electron density plot for $\text{Ca}_2\text{AgBrO}_6$

4.6.2 Electronic Band Structures of $\text{Ca}_2\text{AgBrO}_6$ Compound

Calculating the electronic properties of materials heavily relies on electronic ground state energies. On the basis of improved crystal structures of materials, the electrical characteristics, such as band structure (BS) and density of state (DOS), can be researched. Here, we have evaluated the electronic characteristics of titled DPs using DFT. Our findings indicate that each of the substances under study exhibits no apparent band gaps except the parent compound.

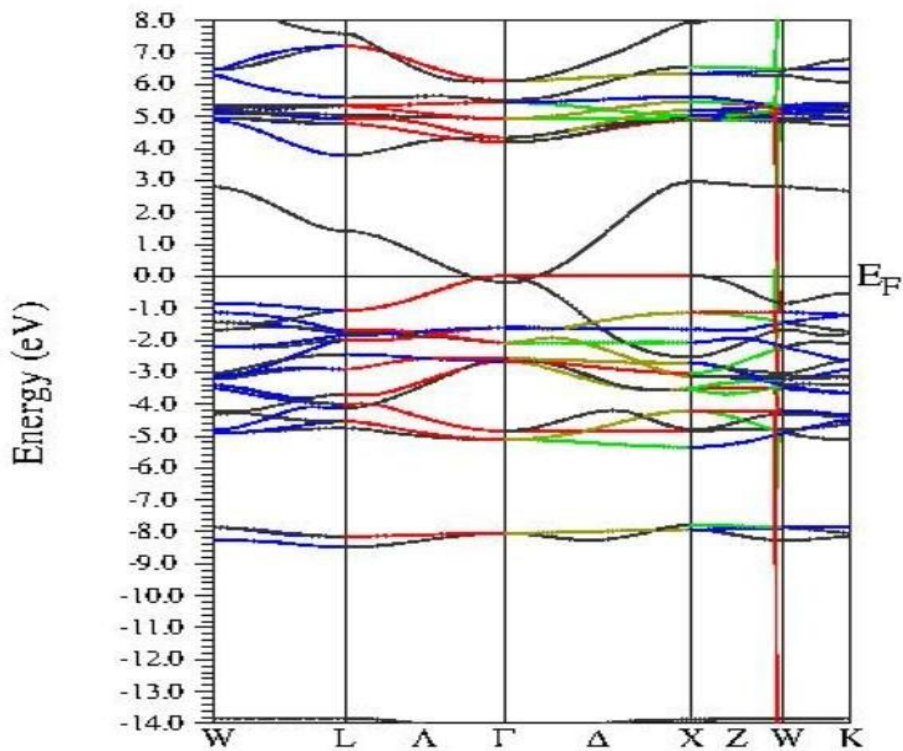


Figure 4.29 Band structure of $\text{Ca}_2\text{AgBrO}_6$ compound

From the fig 4.29, The general forms of the Band Structure revealed that both of the named compounds' lower CB and higher VB are symmetrically situated at the same location factors (I-point). The overlap of the conduction band minima (CBM) and valence band maxima (VBM) of compounds having no band gap. Hence it is a conductor.

4.6.3 Electron transport properties of $\text{Ca}_2\text{AgBrO}_6$ compound

We must examine their electronic band structures in order to comprehend the electronic characteristics of the double perovskite $\text{Ca}_2\text{AgBrO}_6$. According to each compound's self-consistent computations, the Fermi levels E_f are correctly determined. Describe $\text{Ca}_2\text{AgBrO}_6$ partial and total densities of states (TDoS and PDoS) respectively.

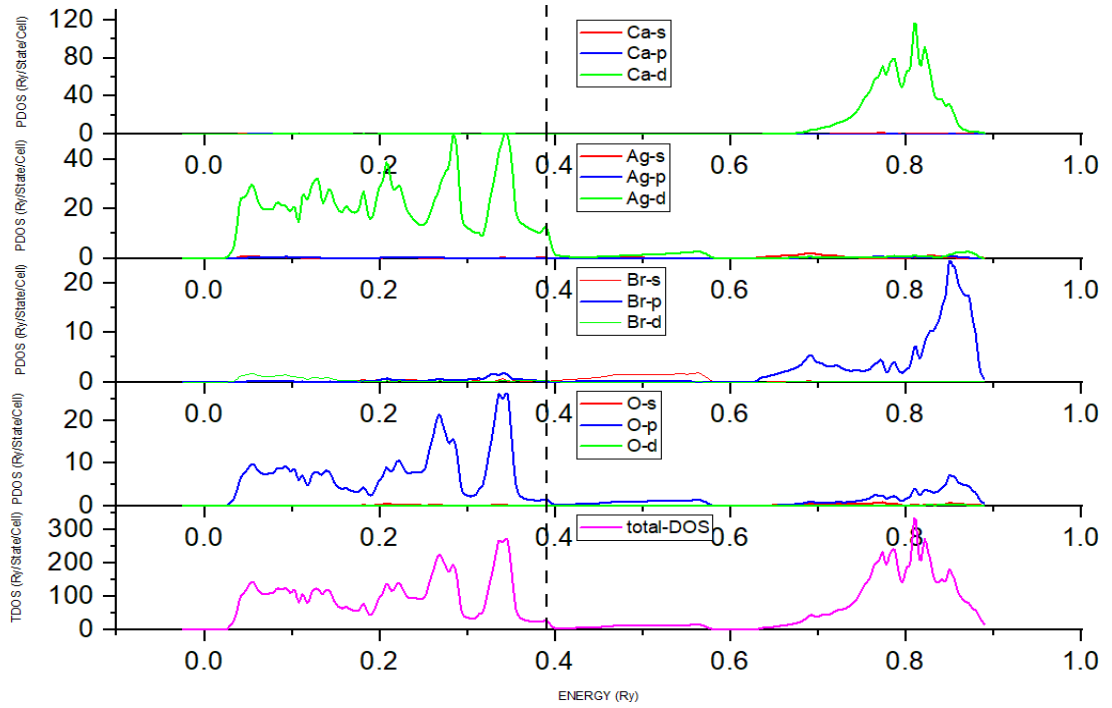


Figure 4.30 Density of states of $\text{Ca}_2\text{AgBrO}_6$ compound

From the fig 4.30, The TDoS and PDoS are divided into two regions. PDoS is divided into two regions. At first, in the low energy region (0 Ry-0.4Ry), we can notice that the VBM of these compounds is mainly dominated by O-p orbitals and Ag-d orbitals. In addition, the Ca atom of these compounds only has electron distribution in the region greater than 0.8Ry, indicating that the Ca element does not directly affect the formation of the conduction band. It can also be seen from the PDoS that there exists an apparent overlap between the O-p orbitals and the Br-s orbitals. This is due to hybridization of orbitals.

4.7 Structural Properties and Stability of $\text{Ca}_2\text{InBrO}_6$ Compound

The generalized gradient approximation (GGA), which is part of the code for the exchange-correlation potential, and the full-potential linearized augmented plane wave method wien2k (Blaha, 2001) were used for all computations shown here. The lattice constants for $\text{Ca}_2\text{InBrO}_6$ were modified to 8.2434 Å at the ground state.

The cubic structures in these compounds belong to the same space group (Fm3m, #225). The compounds that we examined are of the A_2BCO_6 type, meaning that the B and C cations are arranged similarly to how they are in rock salt. The idealized cubic lattice (Fm3m) is therefore twice as big as the ABX_3 -type perovskite (F. Kubel et al., 2013).

The structure of $\text{Ca}_2\text{InBrO}_6$ is shown in Fig.4.31 The optimization of cations and anions present in a compound determines how stable the crystal structures, band structures, charger carrier transport performance, and uses of Double perovskite oxides are to a considerable extent.

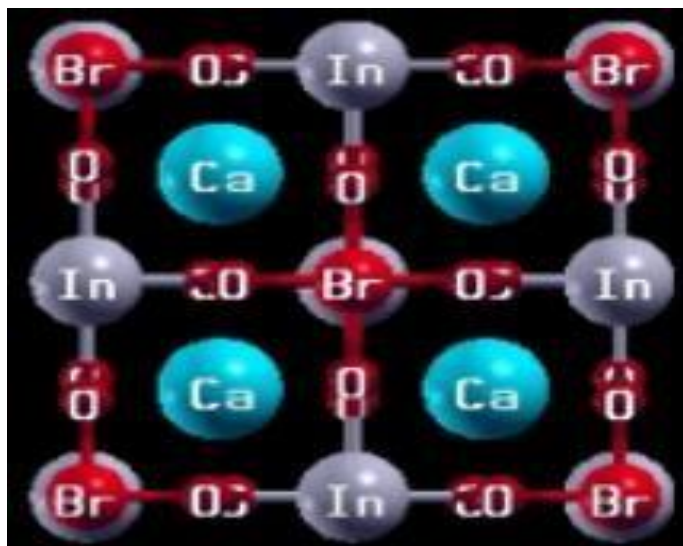


Figure 4.31 $\text{Ca}_2\text{InBrO}_6$ Crystal structure

Table 4.7 The structural and electronic properties of $\text{Ca}_2\text{InBrO}_6$ Compound

Parameters	$\text{Ca}_2\text{InBrO}_6$
Optimized lattice parameters	$a=b=c=8.2434 \text{ \AA}$
Space group Name	$\text{Fm}\bar{3}m$
Space group Number	225
Structural parameters	Ca $\frac{1}{4}$ $\frac{1}{4}$ $\frac{3}{4}$ In 0 0 $\frac{1}{2}$ Br 0 0 0 O 0 0 0.774922
K-points	1000
Energy Convergence	0.0001 Ry
Charge Convergence	0.001 e
E_f (Ryd)	0.4474
Cv/T (J/K)	2.28
No. of Dos (states/Ryd)	13.17
$d_{\text{Ca-In}}$ (Bohr)	6.7454
$d_{\text{Ca-Br}}$ (Bohr)	6.7454
$d_{\text{Ca-O}}$ (Bohr)	5.5212
$d_{\text{In-Br}}$ (Bohr)	7.7889
$d_{\text{In-O}}$ (Bohr)	4.2827
Ca-In-Br (Degree)	70.529
Ca -Br-O (Degree)	54.736
Ca-In-O (Degree)	54.736
O-Ca-In (Degree)	39.297
In-Br-O (Degree)	180.00

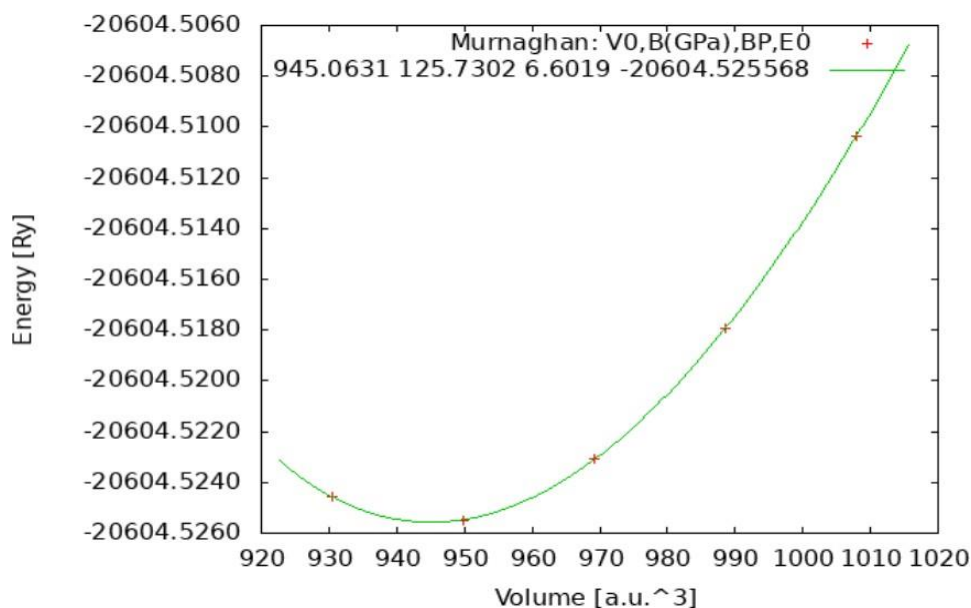


Figure 4.32 Volume optimization curve of $\text{Ca}_2\text{InBrO}_6$ Compound

Figure 4.32 depicts the volume optimization curve for each material, and using the optimized results, we were able to determine the value of each material's optimized lattice constant.

4.7.1 Electron density plot of $\text{Ca}_2\text{InBrO}_6$ Compound

The electron density plot for the (100) plane of the $\text{Ca}_2\text{InBrO}_6$ compound is shown in Fig4.33. The contours around In and O atoms show the ionic bonding. The contour around O indicates O-O metallic bonding.

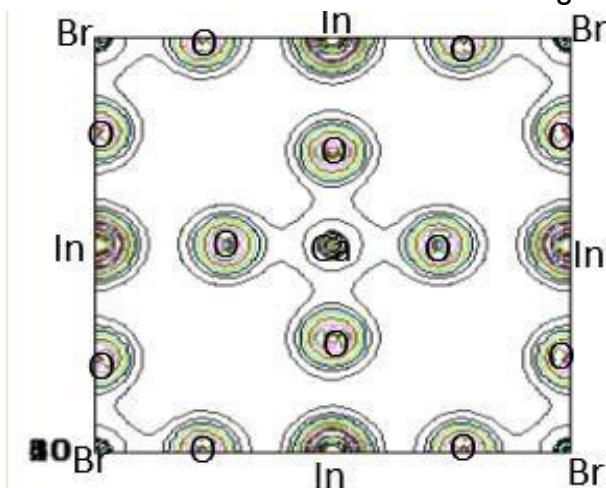


Figure 4.33 Electron density plot for $\text{Ca}_2\text{InBrO}_6$ Compound

4.7.2 Electronic Band Structures of $\text{Ca}_2\text{InBrO}_6$ Compound

Calculating the electronic properties of materials heavily relies on electronic ground state energies. On the basis of improved crystal structures of materials, the electrical characteristics, such as band structure (BS) and density of state (DOS), can be researched. Here, we have evaluated the electronic characteristics of titled DPs using DFT. Our findings indicate that each of the substances under study exhibits no apparent band gaps except the parent compound.

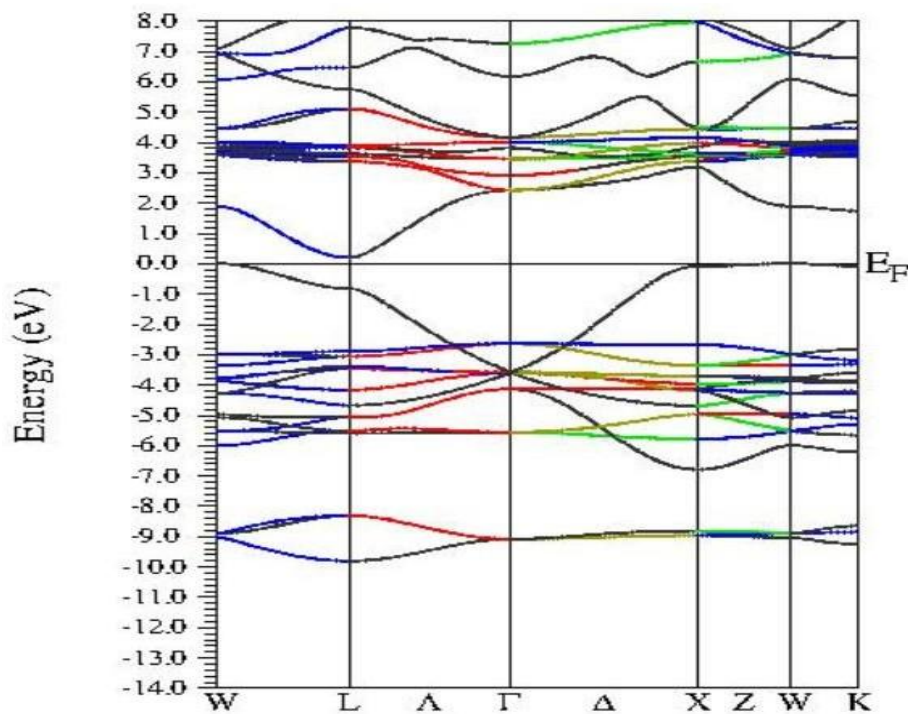


Figure 4.34 Band structure of $\text{Ca}_2\text{InBrO}_6$ compound

From the fig 4.34, The general forms of the Band Structure revealed that both of the named compounds' lower CB and higher VB are symmetrically situated at the same location factors (I-point). The overlap of the conduction band minima (CBM) and valence band maxima (VBM) of compounds having no band gap. Hence it is a conductor.

4.7.3 Electron transport properties of $\text{Ca}_2\text{InBrO}_6$ compound

We must examine their electronic band structures in order to comprehend the electronic characteristics of the double perovskite $\text{Ca}_2\text{InBrO}_6$. According to each compound's self-consistent computations, the Fermi levels E_f are correctly determined. Describe $\text{Ca}_2\text{InBrO}_6$ partial and total densities of states (TDoS and PDoS) respectively.

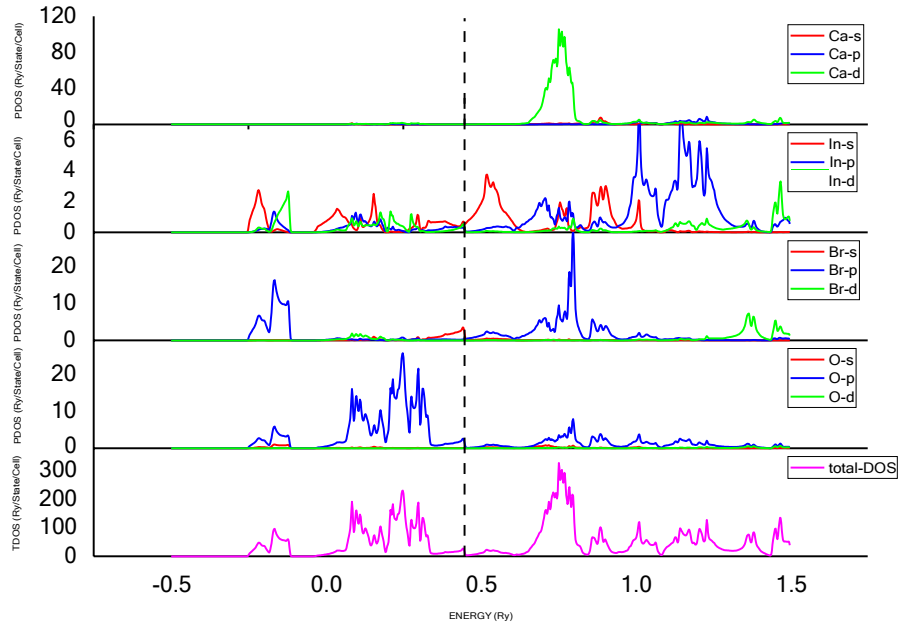


Figure 4.35 Density of states of $\text{Ca}_2\text{InBrO}_6$ compound

From the fig 4.35, The TDoS and PDoS are divided into two regions. At first, in the low energy region (0 Ry-0.4775 Ry), we can notice that the VBM of these compounds is mainly dominated by O-p orbitals and In-d orbitals meanwhile Ca-p orbitals also play a smaller role than the former. In addition, the Sr atoms of these compounds only have electron distribution in the region greater than 0.8Ry, indicating that the Ca element does not directly affect the formation of the conduction band. It can also be seen from the PDoS that there exists an obvious overlap between the O-p orbitals and the Br-s orbitals. This is due to hybridization of orbitals

4.8.1 Optical properties

For its prospective applications, the optical characteristics of the double perovskite $A_2(\text{Ag/In})\text{BrO}_6$ ($A=\text{Ca, Sr, Ba}$) must be thoroughly investigated. In the range of 0 eV-30 eV, we investigate their refractive index $n(\omega)$, energy-loss function $L(\omega)$, reflectivity $R(\omega)$, and conductivity $\sigma(\omega)$, dielectric function. Primarily, the capability of a material to interact with an electric field depends on their $\epsilon_1(\omega)$, while $\epsilon_2(\omega)$ affect the ability to absorb energy from a time-varying electric field.

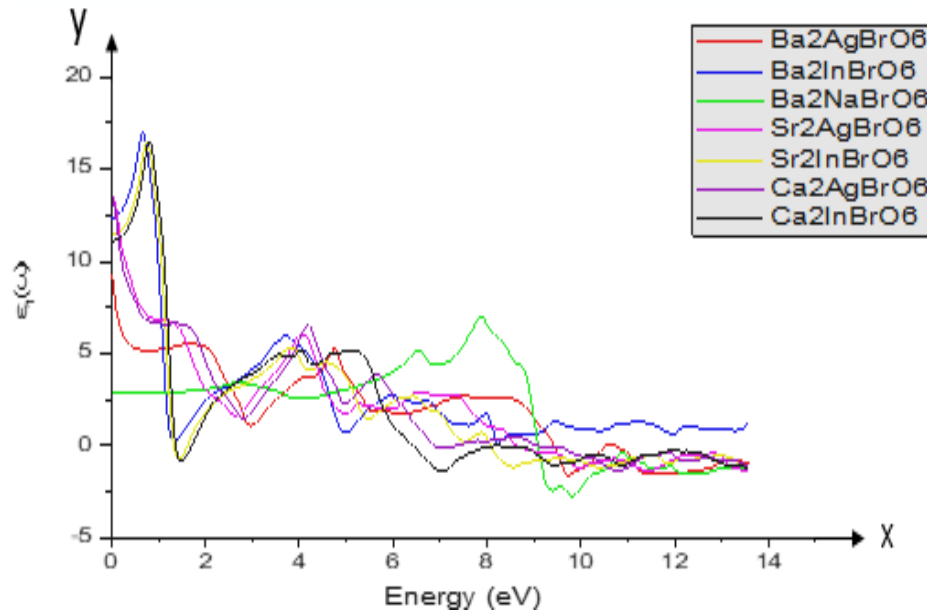


Figure 4.36 Optical properties of real dielectric function

From the fig 4.36, The dielectric function's real part describes the crystal's optical dispersion. Here the real $\epsilon_1(\omega)$ values of dielectric functions of all the materials are maximum in the IR region and decrease in the visible and UV regions. The static dielectric constants $\epsilon_1(0)$ of $\text{Ba}_2\text{AgBrO}_6$, $\text{Ba}_2\text{InBrO}_6$, $\text{Sr}_2\text{AgBrO}_6$, $\text{Sr}_2\text{InBrO}_6$, $\text{Ca}_2\text{AgBrO}_6$, $\text{Ca}_2\text{InBrO}_6$ maximum comes out to be 0.014, 0.6667, 7.8777, 0.0136, 0.74831, 0.01361, 0.80274 eV.

With the increasing phonon energy, the major peaks of $\epsilon_1(\omega)$ are found at 9.2593, 16.9697, 7.0289, 13.5432, 16.4871, and 13.4155, 16.482. The value of $\epsilon_1(\omega)$ is a negative number showing the unique metallic behavior.

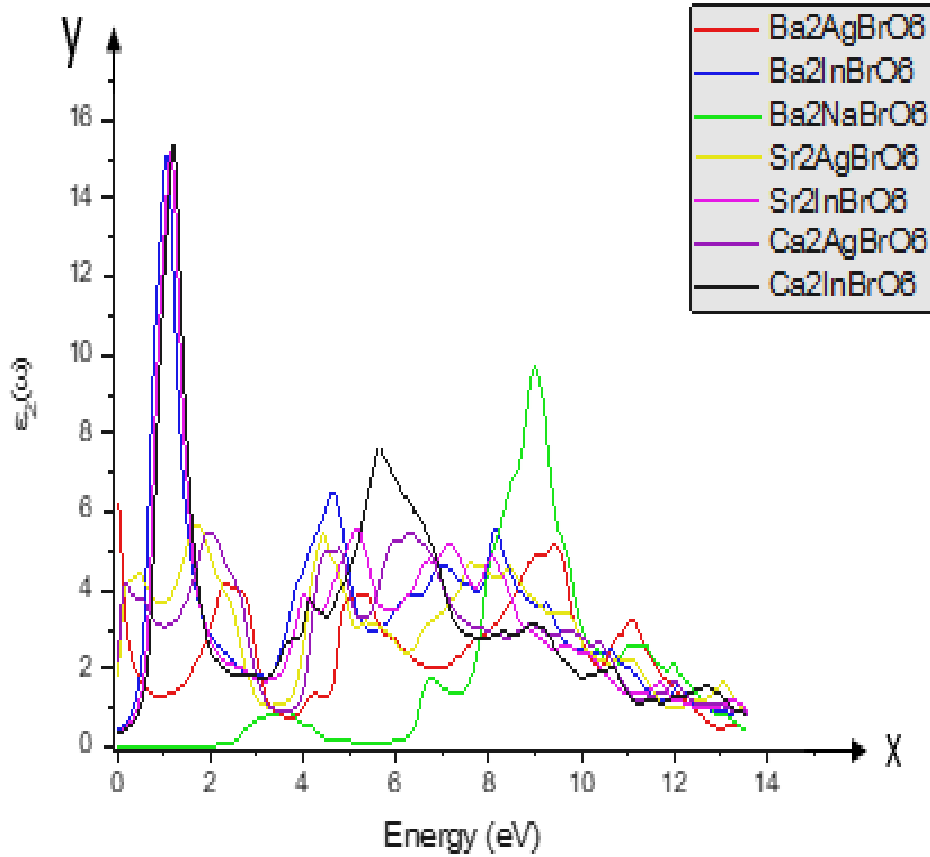


Figure 4.37 Optical properties of imaginary dielectric function

From the fig 4.37, $\epsilon_2(\omega)$ approaches almost zero at the 13.56 eV energy range representing photon absorption in the materials. The static dielectric constants $\epsilon_2(\omega)$ of $\text{Ba}_2\text{AgBrO}_6$, $\text{Ba}_2\text{InBrO}_6$, $\text{Ba}_2\text{NaBrO}_6$, $\text{Sr}_2\text{AgBrO}_6$, $\text{Sr}_2\text{InBrO}_6$, $\text{Ca}_2\text{AgBrO}_6$, $\text{Ca}_2\text{InBrO}_6$ maximum comes with 0.0136, 1.07485, 8.9933, 1.70071, 1.1564, 1.9728, 1.2109 eV the increasing phonon energy, the major peaks of $\epsilon_2(\omega)$ are found at 6.20672, 15.1145, 9.71513, 5.64981, 15.222, 5.49307, 15.3601.

Here the imaginary $\epsilon_2(\omega)$ values of dielectric functions of all the materials are maximum in the IR region and decrease in the visible and UV regions.

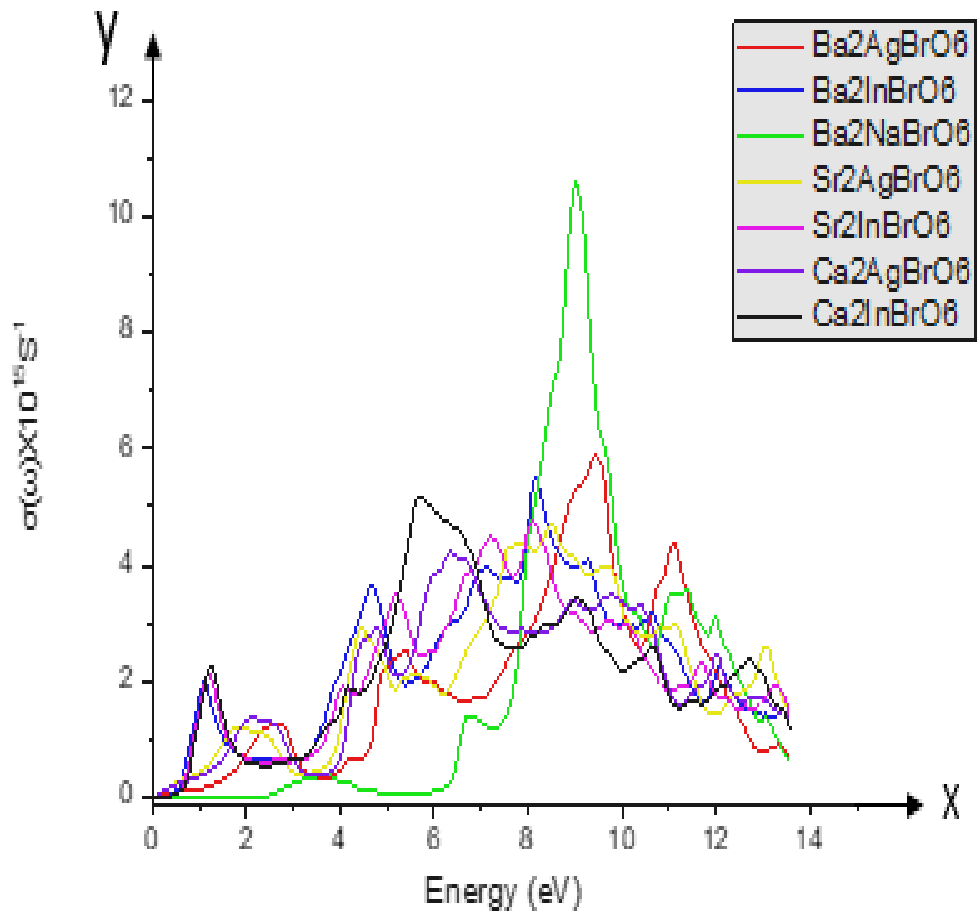


Figure 4.38 Optical properties of real optical conductivity

From the fig 4.37, maximum optical conductivity of $\text{Ba}_2\text{AgBrO}_6$, $\text{Ba}_2\text{InBrO}_6$, $\text{Ba}_2\text{NaBrO}_6$, $\text{Sr}_2\text{AgBrO}_6$, $\text{Sr}_2\text{InBrO}_6$, $\text{Ca}_2\text{AgBrO}_6$, $\text{Ca}_2\text{InBrO}_6$ occurs at the region of 9.4287, 8.1498, 9.0205, 8.4763, 8.0953, 6.3538, and 5.6735 eV increasing the phonon energy. The maximum peak occurs at the $5.865 \times 10^{16} \text{ s}^{-1}$, $5.5022 \times 10^{16} \text{ s}^{-1}$, $10.5752 \times 10^{16} \text{ s}^{-1}$, $4.762 \times 10^{16} \text{ s}^{-1}$, $4.7621 \times 10^{16} \text{ s}^{-1}$, $4.20909 \times 10^{16} \text{ s}^{-1}$, $5.5196 \times 10^{16} \text{ s}^{-1}$.

These results imply that these double perovskites have an excellent ability to conduct electrons in the UV range.

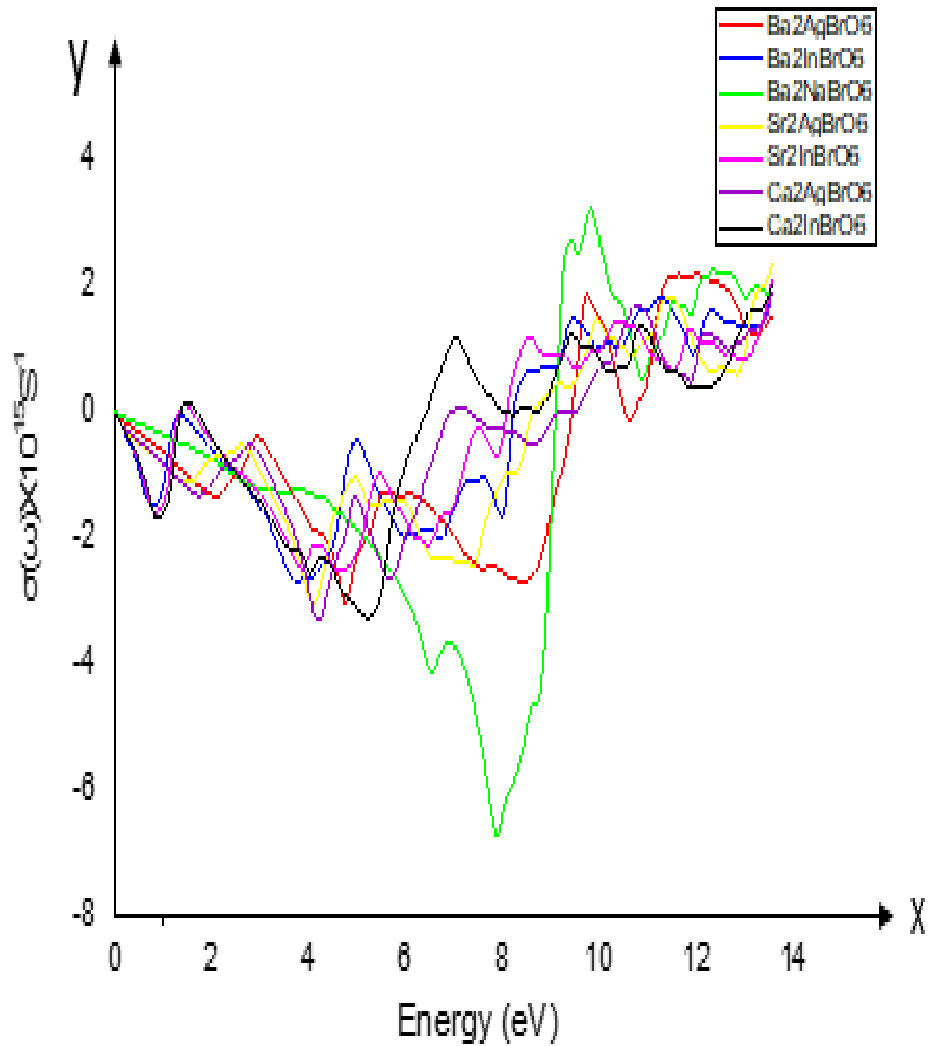


Figure 4.39 Optical properties of imaginary optical conductivity

From the fig 4.39, maximum optical conductivity of $\text{Ba}_2\text{AgBrO}_6$, $\text{Ba}_2\text{InBrO}_6$, $\text{Ba}_2\text{NaBrO}_6$, $\text{Sr}_2\text{AgBrO}_6$, $\text{Sr}_2\text{InBrO}_6$, $\text{Ca}_2\text{AgBrO}_6$, $\text{Ca}_2\text{InBrO}_6$ occurs at the region 13.5649 eV increasing the phonon energy. The maximum peak occurs at $2.1756 \times 10^{16} \text{ s}^{-1}$, $2.07384 \times 10^{16} \text{ s}^{-1}$, $3.2097 \times 10^{16} \text{ s}^{-1}$, $2.3484 \times 10^{16} \text{ s}^{-1}$, $2.1214 \times 10^{16} \text{ s}^{-1}$, $1.9158 \times 10^{16} \text{ s}^{-1}$, $2.0523 \times 10^{16} \text{ s}^{-1}$. These results imply that these double perovskites have an excellent ability to conduct electrons in the UV range

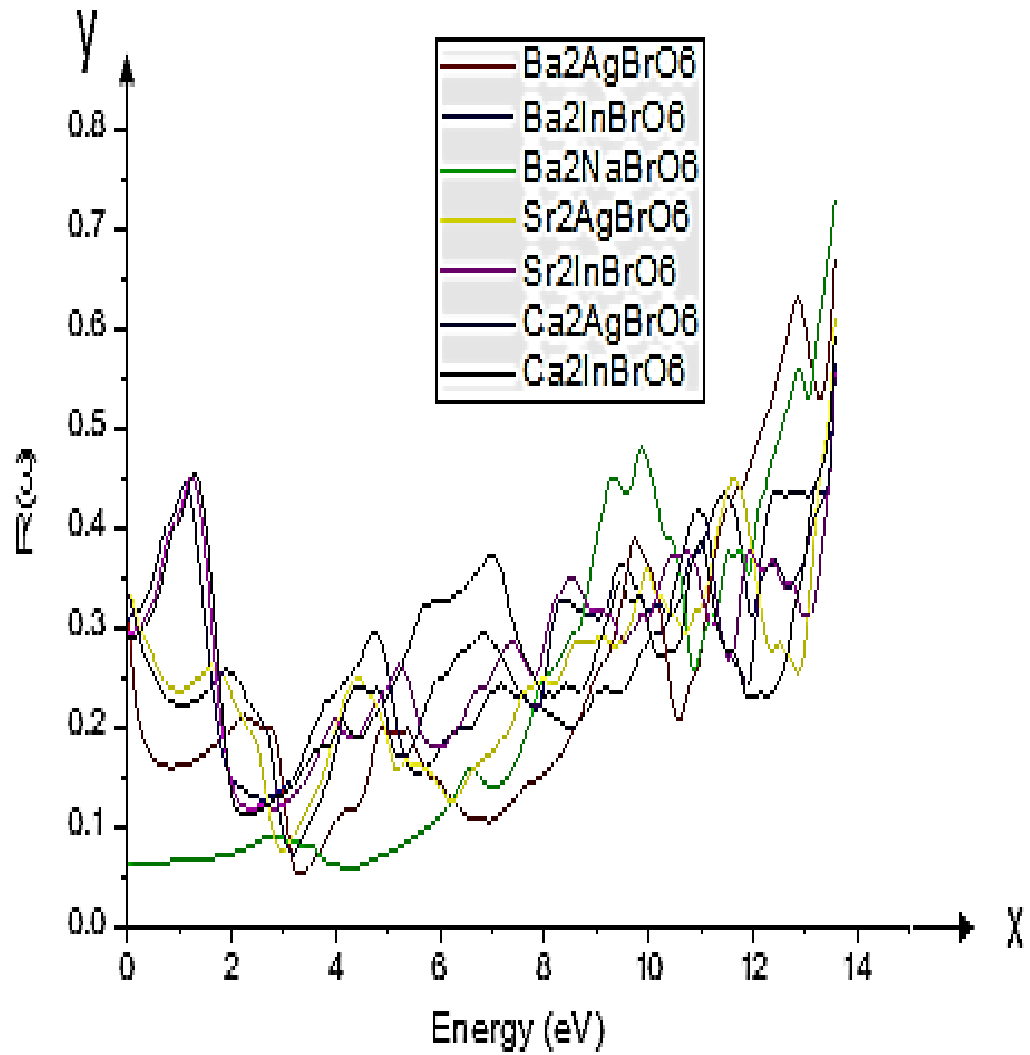


Figure 4.40 Optical properties of reflectivity

From the fig 4.40, The reflectivity maximum value of $\text{Ba}_2\text{AgBrO}_6$, $\text{Ba}_2\text{InBrO}_6$, $\text{Ba}_2\text{NaBrO}_6$, $\text{Sr}_2\text{AgBrO}_6$, $\text{Sr}_2\text{InBrO}_6$, $\text{Ca}_2\text{AgBrO}_6$, $\text{Ca}_2\text{InBrO}_6$ occur in the region of 13.5649eV. With increasing the phonon energy, the peak reaches the maximum value 0.6674,0.5620,0.7292,0.6089,0.5564,0.5528,0.59203. These results imply that these double perovskites have a maximum reflection at the uv region.

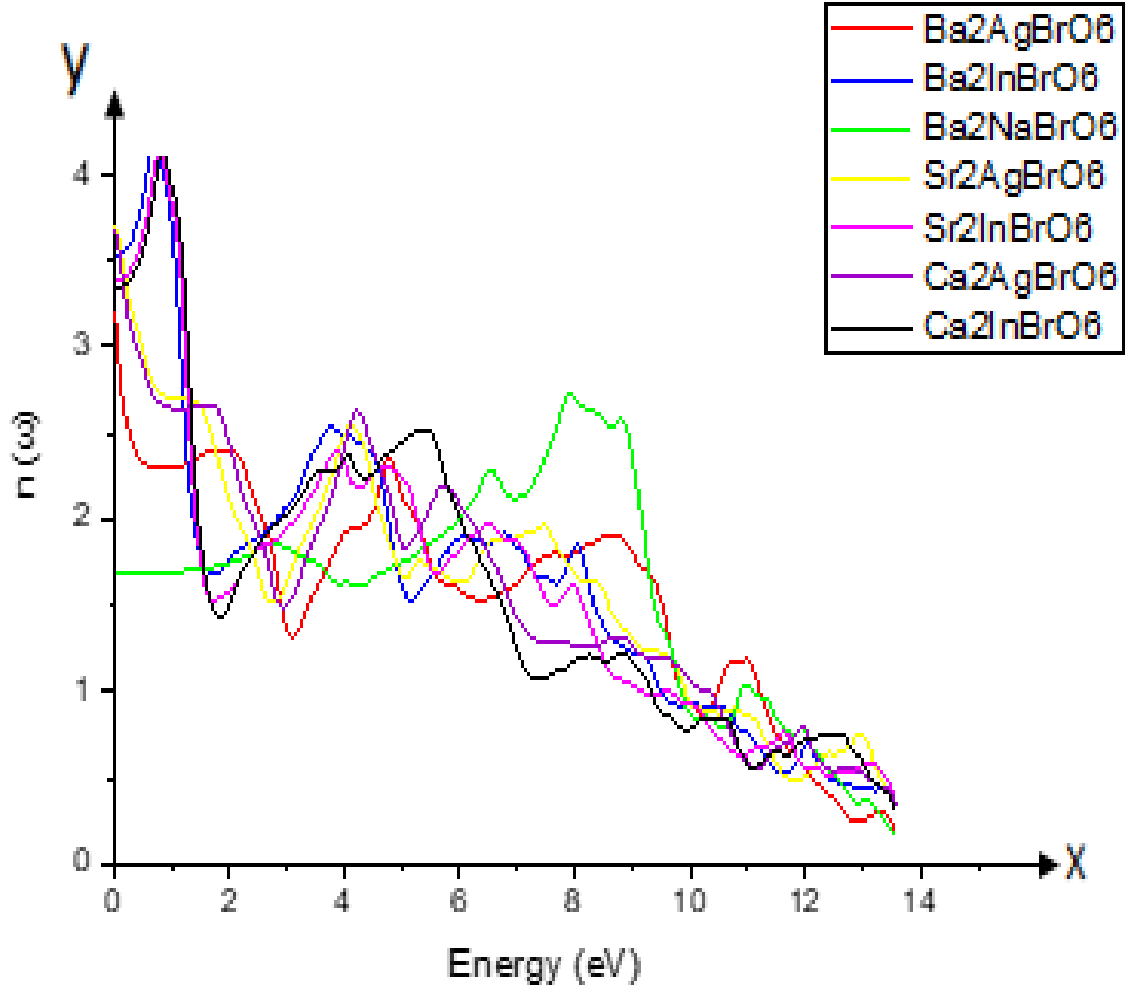


Figure 4.41 Optical properties of refraction

From the fig 4.41, In the range of 0 eV-14 eV, we investigate their refractive index $n(\omega)$ is used to measure the phase velocity in the material. The curve shapes of $n(\omega)$ and $\epsilon_1(\omega)$ are similar, the maximum values of $\text{Ba}_2\text{AgBrO}_6$, $\text{Ba}_2\text{InBrO}_6$, $\text{Ba}_2\text{NaBrO}_6$, $\text{Sr}_2\text{AgBrO}_6$, $\text{Sr}_2\text{InBrO}_6$, $\text{Ca}_2\text{AgBrO}_6$, $\text{Ca}_2\text{InBrO}_6$ occur in the region of 0.01361, 0.6938, 7.90491, 0.01361, 0.7755, 0.01361 eV. The maximum peaks at 3.1942, 4.19056, 2.7339, 3.6885, 4.14356, 3.67501. there exists a maximum value around 7.9041 eV where the value of $\text{Ba}_2\text{AgBrO}_6$, $\text{Ba}_2\text{InBrO}_6$, $\text{Sr}_2\text{AgBrO}_6$, $\text{Sr}_2\text{InBrO}_6$, $\text{Ca}_2\text{AgBrO}_6$, $\text{Ca}_2\text{InBrO}_6$ is lower than that of $\text{Ba}_2\text{NaBrO}_6$.

4.8.2 Thermal properties

We used the Gibbs program to calculate the thermodynamic characteristics of this material. In order to determine the macroscopic energy, we have used the total energy $E(V)$ for various primitive cell volumes computed in the previous section.

Using the common thermodynamic relations, determine the relationship between the thermal characteristics and temperature and pressure. The quasi-harmonic Debye model, on which the non-equilibrium Gibbs function is built, serves as the foundation for the Gibbs program. From the fig 4.42 by comparing the parent compound with the novel compound the thermodynamic stability of the material is excellent.

a)

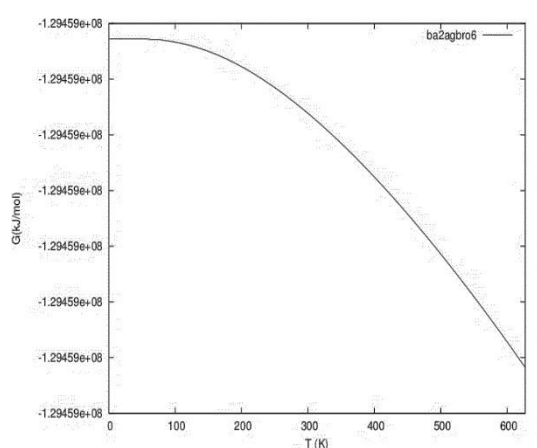


Figure 4.42 (a) Temperature Vs Gibbs free energy of $\text{Ba}_2\text{AgBrO}_6$ compound

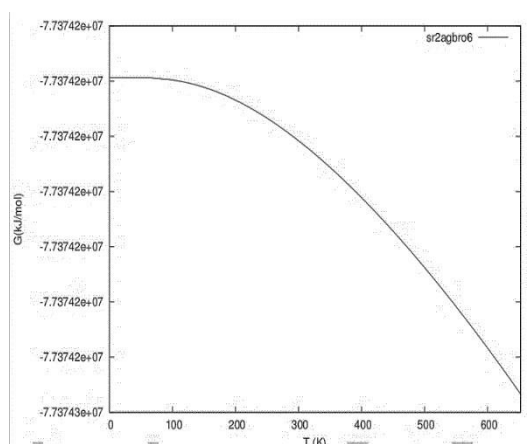


Figure 4.42 (b) Temperature Vs Gibbs free energy of $\text{Sr}_2\text{AgBrO}_6$

c)

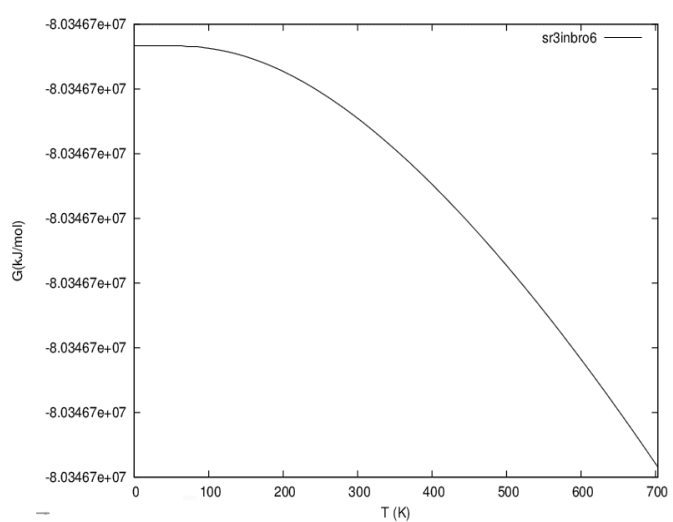


Figure 4.42 (c) Temperature Vs Gibbs free energy of $\text{Sr}_2\text{InBrO}_6$

d)

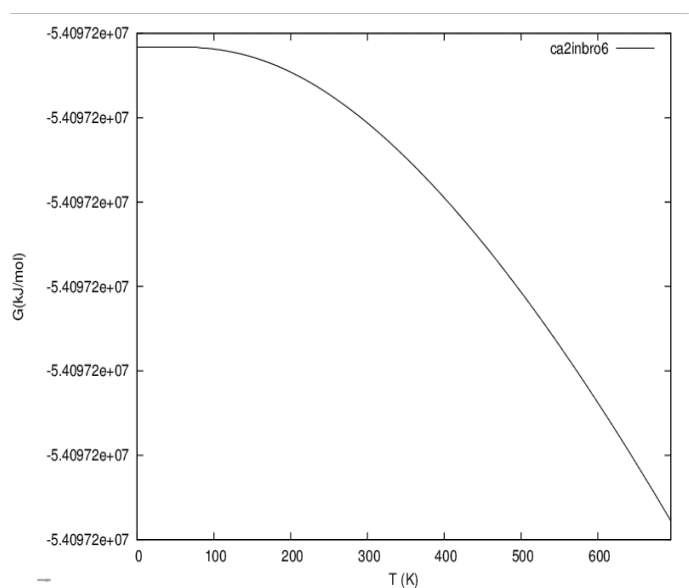


Figure 4.42 (d) Temperature Vs Gibbs free energy of $\text{Ca}_2\text{InBrO}_6$

e)

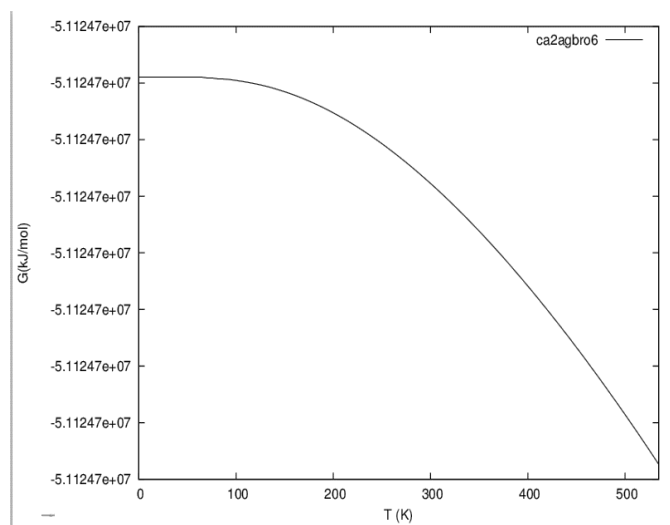


figure 4.42 (e) Temperature Vs Gibbs free energy of $\text{Ca}_2\text{AgBrO}_6$

4.8.3 Thermoelectric properties

Seebeck and Peltier phenomena are the foundation of thermoelectric materials. Thermoelectric generators are built using the Seebeck effect, and the latter is employed for cooling applications. The thermoelectric materials' figure of merit value determines how effective they are. The variables used to calculate the figure of merit are the Seebeck coefficient, electrical conductivity, and thermal conductivity. The zT value for a possible thermoelectric material will be close to or higher than one.

It is a dimensionless quantity and is calculated by the three important parameters such as Seebeck coefficient (S), electrical conductivity (σ), electronic thermal conductivity (k_e) and lattice thermal conductivity (k_l). The equation of the figure of merit becomes, $zT = S^2\sigma T / k_e + k_l$. Thermoelectric materials are also called eco-friendly green materials and studies about these materials are a recent demand crisis for many researchers. Researchers attained maximum zT using their materials both theoretically and experimentally.

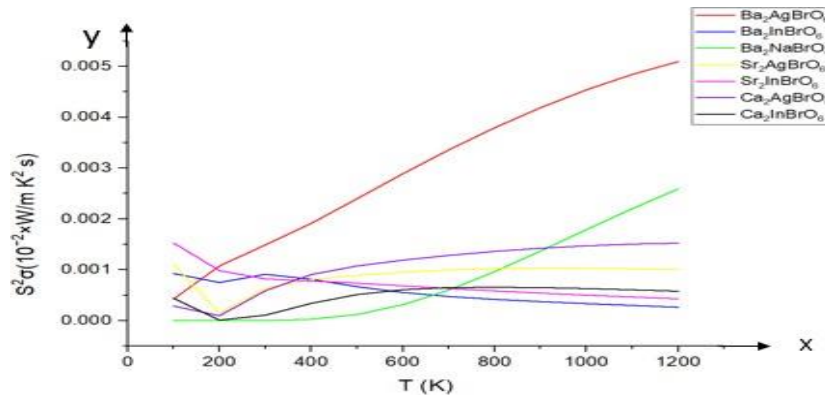


Fig 4.43 power factor of Ba_2AgBrO_6 , Ba_2InBrO_6 , Ba_2NaBrO_6 , Sr_2AgBrO_6 , Sr_2InBrO_6 , Ca_2AgBrO_6 , Ca_2InBrO_6

The power factor (σS^2) Ba_2AgBrO_6 reached the maximum value of 0.0015 at $T=1200K$.

The power factor(σS^2) $\text{Sr}_2\text{InBrO}_6$ reached the maximum value of 0.0051 at below room temperature.

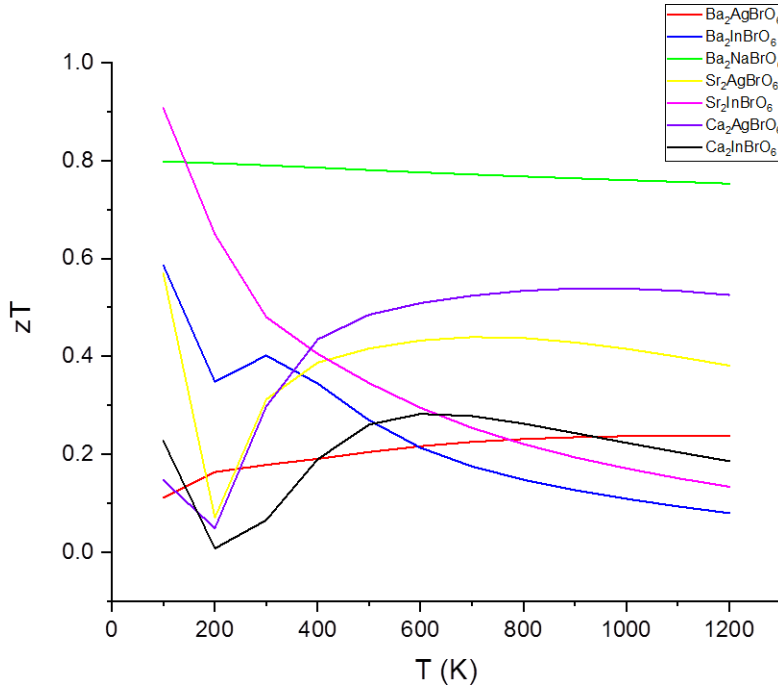


Fig 4.44 Thermoelectric properties of the figure of merit

The figure of merit (zT) is very important to find the efficiency of thermoelectric materials. The phonon contribution is so small in metal systems, we didn't use the lattice thermal conductivity (k_l), only using the electronic thermal conductivity (k_e), to calculate the figure of merit. The $\text{Ba}_2\text{NaBrO}_6$ exhibited the value of the $zT \sim 0.78$ over the Fermi level (Hao-Jia Wu et al., 2023). $\text{Ba}_2\text{NaBrO}_6$ reaches the maximum value zT value of 0.729 at 100K. $\text{Sr}_2\text{InBrO}_6$ reaches the maximum value zT value of 0.907 at 100K. $\text{Ca}_2\text{AgBrO}_6$ reaches the maximum value zT value of 0.539 at 900K. The power factor ($S^2\sigma$) $\text{Ba}_2\text{AgBrO}_6$ reached the maximum value but the zT value is decreased due to their high thermal conductivity.

CHAPTER -5

SUMMARY

The compounds namely $\text{Ba}_2\text{AgBrO}_6$, $\text{Ba}_2\text{InBrO}_6$, $\text{Ba}_2\text{NaBrO}_6$, $\text{Sr}_2\text{AgBrO}_6$, $\text{Sr}_2\text{InBrO}_6$, $\text{Ca}_2\text{AgBrO}_6$, $\text{Ca}_2\text{InBrO}_6$ which are tetragonal in structure and space group $\text{Fm}\bar{3}\text{m}$ (225) is studied under the Full Potential Linearized Augmented Plane Wave (FP-LAPW) method as implemented in the WIEN2K code. The generalized Gradient Approximation (GGA) parameterized has been applied to calculate the exchange-correlation potential. Muffin tin spheres of radius R_{MT} are chosen in such a way that there is minimal charge leakage from the core. The calculations are performed with 1000 k-points in the Brillouin zone. The plane wave expansion ($R_{\text{MT}} K_{\text{MAX}}$) is taken as 7. The atomic position for Ba ($\frac{1}{4}$, $\frac{1}{4}$, $\frac{1}{4}$), Ag (0,0, $\frac{1}{2}$), In (0,0, $\frac{1}{2}$), Br (0,0,0), O (0,0,0.774922). The wave function expansion inside the atomic spheres was given a maximum value of l_{max} of 12, and the value of the plane-wave cut-off ($R_{\text{MT}} \times K_{\text{max}}$) was set at 7 with a G_{max} of 14. To solve these quantum mechanical systems, a well-converged $10 \times 10 \times 10$ k-space grid was adopted within the irreducible wedge of the Brillouin zone. For the energy convergence close to 10^{-5} Ry, self-consistency is carried out.

Additionally, the BoltzTraP code was used to compute the thermoelectric properties using an estimation of the constant relaxation time (τ) (Madsen et al., 2006).

CONCLUSION

- we have systematically investigated the structural, electronic, optical and thermoelectric properties of $\text{Ba}_2\text{AgBrO}_6$, $\text{Ba}_2\text{InBrO}_6$, $\text{Ba}_2\text{NaBrO}_6$, $\text{Sr}_2\text{AgBrO}_6$, $\text{Sr}_2\text{InBrO}_6$, $\text{Ca}_2\text{AgBrO}_6$, $\text{Ca}_2\text{InBrO}_6$ double perovskites by first-principles calculations.

- From the electron density plot shows that compound of $\text{Ba}_2\text{AgBrO}_6$, $\text{Ba}_2\text{InBrO}_6$, $\text{Ba}_2\text{NaBrO}_6$, $\text{Sr}_2\text{AgBrO}_6$, $\text{Sr}_2\text{InBrO}_6$, $\text{Ca}_2\text{AgBrO}_6$, $\text{Ca}_2\text{InBrO}_6$ having covalent, ionic and metallic behavior. This anisotropic bonding nature of the compound shows good agreement with the existing literature.
- From the band structure parent compound $\text{Ba}_2\text{NaBrO}_6$ is a semiconductor. The proposed novel compound of $\text{Ba}_2\text{AgBrO}_6$, $\text{Ba}_2\text{InBrO}_6$, $\text{Sr}_2\text{AgBrO}_6$, $\text{Ca}_2\text{AgBrO}_6$, $\text{Ca}_2\text{InBrO}_6$, $\text{Sr}_2\text{InBrO}_6$ compounds shows no band gap. Hence it is the conductor.
- optical properties of all the materials are calculated at ambient conditions with a wide energy range of 0 eV-13.56 eV, From the predictions, $\text{Ba}_2\text{InBrO}_6$ have high reflectivity, high refractive index, high optical conductivity compare to other novel compound. From the observation $\text{Ba}_2\text{InBrO}_6$ in the IR, visible and UV energy regions, making it suitable for optoelectronic, LED's, solar cells, infrared detectors, and UV spectroscopy.
- From the thermal properties, all the materials show good thermal Stability.
- Finally, the thermoelectric properties of all materials are calculated, and $\text{Ca}_2\text{AgBrO}_6$ reaches the maximum value zT value of 0.539 at 900K $\text{Ca}_2\text{AgBrO}_6$ exhibited interesting thermoelectric behaviour and significant power factor and zT values which is important for applications in thermoelectric devices.
- Among the six compounds, after weighing their advantages and disadvantages, $\text{Ba}_2\text{InBrO}_6$ is the most likely to be applied to the field of optoelectronics in the future due to the preferable photovoltaic performance and conversion efficiency in the IR and UV region.

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