

FIRST PRINCIPLES STUDY OF THERMOELECTRIC PROPERTIES OF

$\text{CsPb}_{1-x}\text{Sb}_x\text{Br}_3$ ($x = 0, 0.25, 0.5, 0.75$)

Submitted in partial fulfillment of the requirements for the award of

MASTER OF SCIENCE DEGREE IN PHYSICS

By

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This is to certify that this Project Report is the bonafide work of PRIYA DHARSHNI K (40590009) who carried out the project entitled "**FIRST PRINCIPLES STUDY OF THERMOELECTRIC PROPERTIES OF $\text{CsPb}_{1-x}\text{Sb}_x\text{Br}_3$ ($x = 0, 0.25, 0.5, 0.75$)**" under my supervision from NOV 2021 to APR 2022.

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DECLARATION

I PRIYA DHARSHNI K (Reg.No: 40590009) hereby declare that the Project Report entitled **“FIRST PRINCIPLES STUDY OF THERMOELECTRIC PROPERTIES OF $\text{CsPb}_{1-x}\text{Sb}_x\text{Br}_3$ ($x=0, 0.25, 0.5, 0.75$)”** done by me under the guidance of Dr. M. MANJULA (Internal) at SATHYABAMA INSTITUTE OF SCIENCE AND TECHNOLOGY, CHENNAI is submitted in partial fulfillment of the requirements for the award of Master of Science degree in Physics.

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PRIYA DHARSHNI K

ABSTRACT

This thesis presents the effects of ternary addition of Sb in phase transition, structural, electronic and thermoelectric properties of $\text{CsPb}_{1-x}\text{Sb}_x\text{Br}_3$ ($x=0, 0.25, 0.5, 0.75$) compounds. Band structure calculations are made on cubic parent CsPbBr_3 and Sb doped CsPbBr_3 compounds.

The replacement of two, four and six Antimony atoms in parent CsPbBr_3 , leads to the phase transition of CsPbBr_3 compound. In order to analyze the structural, electronic and thermoelectric properties of $\text{CsPb}_{1-x}\text{Sb}_x\text{Br}_3$ ($x=0, 0.25, 0.5, 0.75$) compounds, the Full Potential Linearized Augmented Planewave (FP-LAPW) method is implemented in the WIEN2k code using Density functional theory.

The lattice parameters and bulk modulus of quaternary compounds are calculated and they are in good agreement with available experimental and other theoretical results. Some ground state properties like bulk modulus, equilibrium lattice parameter and total energy of ternary cubic compounds are obtained by making a super cell and by setting the volume optimization data in Birch-Murnaghan equation of states. Density functional theory calculations had been done to calculate the electronic structure and thermoelectric properties of host and Sb doped CsPbBr_3 .

All the calculations were performed by using GGA to predict the band gap and the thermoelectric behavior of the materials. From the calculations, it shows that CsPbBr_3 is direct band gap semiconductor with a band gap value of 1.33eV. The negative value of Seebeck coefficient shows that the conduction is due to electrons. The both electrical conductivity and Powerfactor (PF) increases with temperature. The thermoelectric properties of the compounds have been calculated in a temperature range of 100K–1000K.

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LIST OF SYMBOLS AND ABBREVIATIONS

$a.c$	-	lattice constant
B	-	Bulk modulus
ρ_{core}	-	core density
ρ_{val}	-	valence density
ρ_{tot}	-	total density
ϵ	-	Eigen values
E_F	-	Fermi energy
F_L	-	Fermi level
$F_{HK}[\rho]$	-	Hohenberg Kohn density functional
$N(E_F)$	-	DOS Fermi level
$n(r)$	-	electron density
V_H	-	Hartree potential
λ	-	electron-phonon coupling constant
Z_x	-	Variable positional parameter
BZ	-	Brillouine Zone
DFT	-	Density Functional Theory
DOS	-	Density of states
EFG	-	Electric Field Gradient
FP-(L)APW	-	Full Potential - (Linearized) Augmented Plane Wave
GGA	-	Generalized gradient Approximation
GUI	-	Graphical User Interface
KS	-	Kohn Sham

KKR	-	Koringa Kohn Rostoker
LDA	-	Local Density Approximation
LMTO	-	Linear Muffin Tin Orbital
LO	-	Local orbitals
LSDA	-	Local Spin Density Approximation
LCAO	-	Linear Combination of Atomic Orbitals
OPW	-	Orthogonalized Plane Wave
RMT	-	Radius of Muffin Tin spheres
EPM	-	Empirical Pseudo potential Method

Greek Letters

Ψ	wave function
σ	Electrical conductivity
τ	Relaxation time
ρ	Density
Ω	Ohm
κ	Thermal conductivity
κ_e	Electronic, thermal conductivity
κ_l	Lattice thermal conductivity

CHAPTER-1

INTRODUCTION

BRIEF HISTORY OF THERMOELECTRICS

The direct conversion of thermal to electrical energy was shown around the end of the 18th century. Luigi Aloisio Galvani (Bologna, September 9, 1737 - Bologna, December 4, 1798), an Italian physician, physicist, biologist, and philosopher, conducted studies on the impact of electricity on animals at the university of Bologna throughout those years. Alessandro Volta, an Italian physicist, correctly established in 1794 that the electromotive force was caused by the temperature differential between the junctions of two dissimilar conducting materials, a phenomenon known as the thermoelectric effect.

This occurred more than two decades before Johann Seebeck, a German physicist from a Baltic German merchant family, discovered that in a closed circuit made of two dissimilar metals, a thermocouple deflects a compass magnet positioned near the circuit, the angle of deflection depending on the temperature difference between the junctions. Seebeck, who published his findings in 1821, Mistookly assumed that the phenomena was caused by magnetism created by temperature variations, leading him to conclude that the observable Earth's magnetic field was caused by the temperature differential between the two freezing poles and the hot equator.

After Danish scientist Hans Christian oersted (Rudkbing, August 14, 1777 - Copenhagen, March 9, 1851) demonstrated in 1820 that electrical currents interact with magnetic materials, this began to happen.

Moreover, despite the fact that Ampere, Laplace, Savart, Biot, and other scientists studied the interaction of electrical currents with magnetic fields, Seebeck disputed the phenomenon's electrical basis and called the observed effect thermo-magnetism. Despite the fact that Seebeck misinterpreted the phenomenon's physical origins, he built a setup that was nearly identical to the one shown and measured the deflection angle of the magnetic compass due to the different temperature difference in series of thermocouples, but it was quickly realized that

it was induced electrical current, thus laying the groundwork for thermoelectricity's next development.

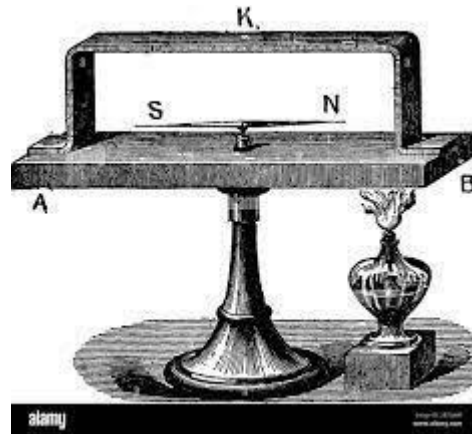


Fig.1.1. Instrument used by T.J. Seebeck during his experiment

THERMOELECTRIC MATERIAL

The world's constantly growing population, clean and renewable energy sources are increasingly important in many aspects of human existence. The need for a growing share of global primary energy supply, as well as the constraints imposed by the threat of climate change, characterize today's climate energy challenge, which is to find new, clean, and renewable energy sources.

We can use appropriate green and renewable energy sources to control the extreme changes caused by global warming and to balance the living conditions on Earth. Biomass, hydropower, wind energy, solar energy, thermoelectric energy, and other well-accepted renewable energy sources have been adequately studied and discussed in the context of energy crisis and environmental pollution in several articles [3-4], and biomass, hydropower, wind energy, solar energy, and thermoelectric energy are just a few of the well-accepted renewable energy sources. Waste heat is seen as a huge worldwide issue that has a significant impact on the global climate system. Heat wastes more than half of all energy [5-7], ranging from domestic waste to industrial waste.

Because there are no moving components, no chemical reactions, and a long life span, thermoelectric energy conversion technology has gained popularity.

Thermoelectric devices provide a way to recover energy from applications that generate a lot of waste heat. The thermoelectric generator, which plays a vital part in energy conversion, may transform heat into electricity using thermoelectric materials. Many experimentalists and theoretical physicists are looking for and inventing novel thermoelectric materials in order to provide dependable electric power without relying on nonrenewable resources.

The use of thermoelectric generators, which convert heat energy directly into electricity and offer a variety of advantages such as moderate performance, a simple system structure, and no moving components, can help enhance the long-term sustainability of power generated from waste heat. Refrigerators and thermoelectric generators are solid-state devices that convert heat energy into electricity and back. Thermoelectric generators have been employed in a number of applications, including remote power generation and electricity storage. Thermoelectric refrigerators are safe for the environment, have a long lifespan, and may replace regular refrigerators. The use of semiconducting alkaline earth metal compounds in thermoelectric device applications has sparked a lot of attention.

The dimensionless figure of merit ZT , which is defined as $ZT = \frac{S^2}{K} T$, where σ is the electrical conductivity, S is the Seebeck coefficient, K is the thermal conductivity, and T is the absolute temperature, is the parameter that evaluates the performance of thermoelectric materials. The power factor is the product of the Seebeck coefficient (S^2) and electrical conductivity (σ). Any thermoelectric generator or refrigerator's efficiency is determined by this dimensionless figure of merit ZT . The Seebeck coefficient (thermo power) of a good thermoelectric material is high, while the thermal conductivity is low.

CONSTITUENT PARAMETERS INVOLVED IN FIGURE OF MERIT

Obtaining a higher ZT value, which is regarded a stumbling barrier for the progression of thermoelectric devices to large-scale production, has been a major problem in this study field. The parameters that determine the value of ZT are intricately linked.

$ZT = S^2/k$ is the figure of merit, and for a higher ZT value, we require a greater seebeck coefficient (thermopower), a higher electrical conductivity, and a lower thermal conductivity.

This section delves into the specifics of each quantity aimed towards improving constituent factors.

(i) Seebeck coefficient (Thermopower)

The ratio of voltage difference to temperature difference is specified as the Seebeck coefficient, commonly known as thermopower. $S = \frac{\Delta V}{\Delta T}$ is the seebeck coefficient with the unit V/K, where V is the voltage difference, T is the temperature difference, and S is the seebeck coefficient. The Seebeck coefficient is equal to $S = \frac{8\pi^2 k_B^2 T}{3eh^2} m_*^2 \left(\frac{\pi}{3n}\right)^2$ of the effective mass of electrons and the concentration of charge carriers.

(ii) Thermal Conductivity

In general, electrons and phonons may conduct heat, and net thermal conductivity is equal to the sum of thermal conductivity owing to electrons and thermal conductivity due to phonons.

As a result, $k = k_L + k_E$

Where k_L is the phonon-induced heat conductivity.

k_E denotes the thermal conductivity of electrons.

Electrons cause thermal conductivity.

(iii) Electrical conductivity (σ)

The capacity of a substance to carry electric current is measured by its electrical conductivity. The counterpart of electrical conductivity is electrical resistivity(ρ). Electrical conductivity is measured in Siemens per metre ($S.m^{-1}$)

$$\sigma = \frac{1}{\rho} = ne\mu$$

Where μ is the mobility

(iv) Figure of Merit

The figure of merit is a critical metric for assessing the performance of thermoelectric materials [14]. It expresses the thermoelectric material's thermoelectric efficiency. The figure of merit is determined by $ZT = \frac{S^2 \sigma T}{k}$

Where S represents the Seebeck coefficient (V/K), σ is the electrical conductivity (S/m), k represents total thermal conductivity (W/mK), and T is the temperature (K).

The power factor is the product of the Seebeck coefficient (S^2) and electrical conductivity (S^2) (PF).

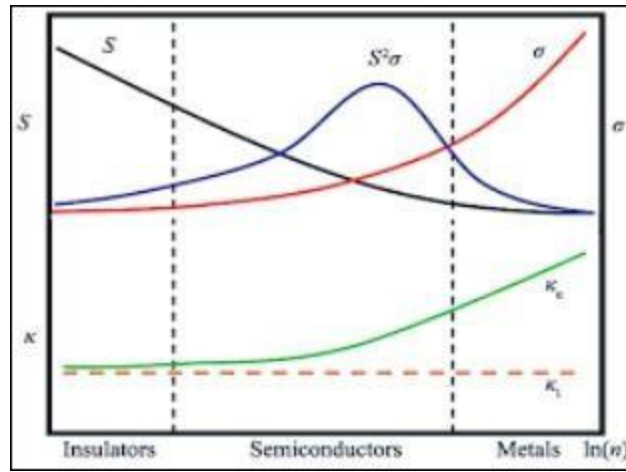


Fig. 1.2 Relationship between α , σ , k , Power Factor, zT and Carrier Concentration

To achieve a high figure of merit, a high Seebeck coefficient, low thermal conductivity, and high electrical conductivity are necessary. We can see from the graph that all of the parameters are highly connected. Because it is connected to the efficiency of the device and the single element, ZT is also known as thermoelectric efficiency. It is provided by

$$\eta = \frac{T_H - T}{T_H} \frac{\sqrt{1 + ZT} - 1}{\sqrt{1 + ZT} + \frac{T_C}{T_H}}$$

where ΔT is the temperature difference between the heated side T_H and the cold side T_C

APPLICATION OF THERMOELECTRIC MATERIALS

(i) Medical application

The thermoelectric cooler is the most popular and widely used form of cooler. These thermoelectric coolers are also known as Peltier coolers because they utilize the Peltier effect in their solid-state heat pumps. There are no leaks, and it operates quietly. The capacity to maintain temperature proportionately rather than utilizing an on-off cycle is a key characteristic of thermoelectric coolers, which is crucial for keeping biological commodities like vaccines or blood serum within a certain temperature range while in transit. Thermoelectric technology might be used to treat therapeutic hypothermia. Therapeutic hypothermia has been demonstrated to be useful in the treatment of neonatal encephalopathy (brain abnormalities) as well as in the neuroprotection of individuals who have had a cardiac arrest.



Fig1.3 An infant being treated for hypoxic-ischemic encephalopathy (lack of oxygen at birth) with a state-of-the-art cooling blanket.

In the Fig, A newborn being treated with a cutting-edge cooling blanket for hypoxic-ischemic encephalopathy (short of oxygen after birth).

Modern polymerase chain reaction (PCR) thermal cycles for fast heating and cooling of DNA are now the most prevalent biological uses of thermoelectric devices. The DNA must be thermally treated at three different temperatures to

utilise PCR to duplicate DNA molecules: 94°C for denaturation, 54°C for annealing, and 72°C for extension. The procedure is subsequently repeated many times more, with each cycle doubling the quantity of DNA [19]. This technology might benefit from the use of solid-state thermoelectric heaters and coolers to shorten the time required for these processes' thermal cycles.

TEG modules are also used in the medical field to power a cardiac pacemaker by collecting energy from temperature variations in the human body. Pacemakers need a source of power, which is often a battery that needs to be changed every 10 years. Every operation, on the other hand, has additional hazards for the patient. A TEG power source would solve this problem because it does not need to be maintained or replaced for a long time.

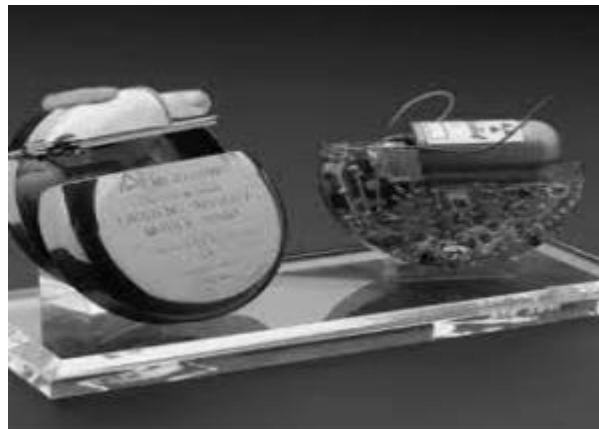


Fig.1.4 Image of implantable pacemaker with a radioisotope TEG as a power source

The radioisotope TEG is used to energise an implanted pacemaker.

(ii) Automobile application

The capacity of thermoelectric material to minimise fuel use and hence operating costs is the most tempting automobile application. By converting waste heat into electricity, ATEGs minimise fuel consumption by lowering the electrical generator load on the engine. ATEGs allow the automobile to make electricity utilising the engine's thermal energy rather than using mechanical energy to power an electric generator. The idea is that waste heat from exhaust gases may be captured by a generator mounted in the exhaust system, with the cold side cooled by ambient air or engine coolant.

The design of the module might be either cylindrical depending on how the exhaust gases are directed through it. Different driving conditions that result in a broad temperature range in exhaust gases demand either a thermoelectric material that can function at a wide temperature range or a number of TEG modules scattered throughout the exhaust system. Temperature changes may also result in mechanical stress and failure.

The automotive exhaust thermoelectric generator (AETEG) converts waste heat from exhaust gas into energy that may be stored and utilised for various electrical inputs in a vehicle, hence increasing fuel efficiency.

Agudelo et al. put a diesel passenger vehicle through its paces in a climate chamber to see if energy could be recovered from exhaust gases. They observed that potential fuel savings varied from 8% to 19%, with the silencer exhibiting the highest energy loss, necessitating the use of a TEG before it. The TEG can be fitted in one of three locations: (i) at the exhaust system's end; (ii) between the catalytic converter and the silencer, which is the best choice; or (iii) upstream of the catalytic converter and silencer, which is the best option.

Regardless of the aforementioned barriers, the ongoing desire for lower greenhouse gas emissions and better fuel efficiency has resulted in a slew of studies on the impact of thermoelectric applications in trucks and automobiles.

BMW, BSST, and Visteon worked on a project to recover waste heat from the engine radiator and exhaust gas system. The claimed reduction in fuel consumption ranged from 8% to 12.5 percent. This system uses a closed liquid loop as the main heat exchanger to carry heat from the exhaust gas to the TEG module. This strategy, as opposed to a direct attachment, aims to be more efficient. It gives you more control, which might help you avoid dangerous temperature swings.

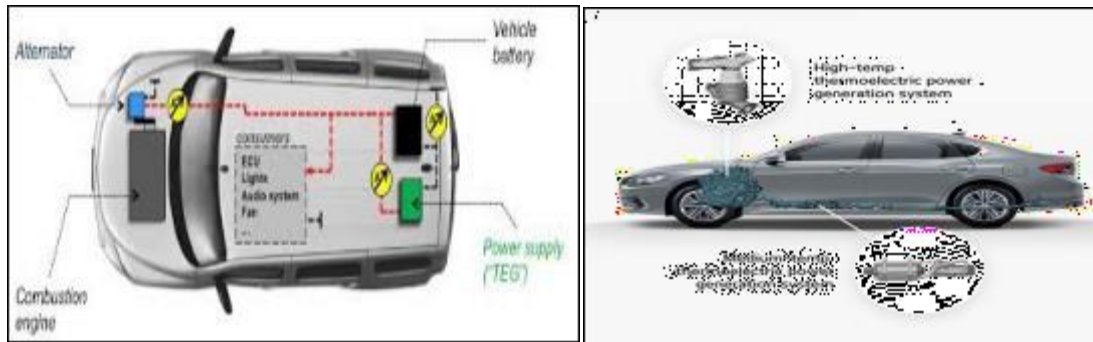


Fig.1.5 TEG integration into the exhaust line of BMW X prototype vehicle

COMPOUND SELECTION

From my literature survey in CsPbBr_3 , there are still some issues to be handled, such as lead atom toxicity and long-term durability. A perovskite is a substance with the same crystal structure as the first-discovered perovskite crystal, calcium titanium oxide. ABX_3 is the chemical formula for perovskite compounds, where 'A' and 'B' are cations and X is an anion that bonds to both cations. Because of their high efficiency, organic and inorganic halide perovskites are important for future solar cell research and commercialization. Using of Sb, reducing the toxic level.

Perovskite-phase metal oxides exhibit a variety of interesting physical properties which include ferroelectric, dielectric, pyroelectric, and piezoelectric behavior. Specifically, linear dielectric materials exhibit linear polarization behavior as a function of applied field. Ferroelectric ceramics are dielectrics with a permanent electric dipole, which can be oriented upon the application of an electric field. Pyroelectric materials yield a spontaneous polarization, but the direction of such polarization cannot be reversed upon application of an electric field. Piezoelectrics either exhibit an electrical charge when mechanically stressed or undergo mechanical deformation upon the application of an electric field. In general, these various properties arise from the crystal symmetry adopted by these materials.

CHAPTER 2

LITERATURE SURVEY

In 2022, Nazmul Hasan et al. studied structural, elastic and optoelectronic properties of inorganic cubic FrBX_3 ($\text{B} = \text{Ge}, \text{Sn}$; $\text{X} = \text{Cl}, \text{Br}, \text{I}$) perovskite: the density functional theory approach. It is determined that the material containing Ge (germanium) in the B-site has higher optical absorption and conductivity than Sn containing materials. A systematic analysis of the electronic, optical, and mechanical properties suggests that among all the perovskite materials, FrGeI_3 would be a potential candidate for optoelectronic applications.

In 2022, N. Murali et al. reported theoretical investigation of structural, electronic, dielectric and optical characteristics of cubic perovskite BaCeO_3 were calculated the real and imaginary sections of the relative permittivity, index of refraction, coefficients of absorption and reflection, energy loss function, coefficient of extinction, and optical conductivity of BaCeO_3 using FP-LAPW.

In 2021, Dan Liet al. investigated of electronic structure and optical properties of rhombohedral PbZrO_3 under pressure. Main peaks of the absorption coefficient, reflectivity, and energy-loss function shift toward to the higher energies with the increase of the pressure, and the amplitude of prominent peak in energy-loss function decreases.

In 2020, Hamid Ghaithan et al., presented the Folded and Unfolded Band Structure and Structural and Optical Properties of $\text{CsPb}(\text{I}_{1-x}\text{Br}_x)_3$ Perovskites. Observed optical property parameters, which were also investigated, demonstrated the reverse effect. The high absorption spectra in the ultraviolet–visible energy range demonstrated that $\text{CsPb}(\text{I}_{1-x}\text{Br}_x)_3$ perovskite could be used in optical and optoelectronic devices by partly replacing iodide with bromide.

In 2019, Rehan Ullah et al., analyzed the Structural, electronic and optical properties of cubic perovskite RbYbF_3 under pressure: a first principles study. The band

structure calculation shows a direct band gap of 0.80 eV that gradually decreases to 0.62 eV at 15 GPa pressure. The optical properties calculated within energy range 0-13.5 eV show that all the optical parameters shift towards higher energies under the influence of pressure. The direct band gap nature and higher absorption capability of RbYbF_3 in ultraviolet and visible range of electromagnetic spectrum indicates that they can be efficiently used in optoelectronic devices working in these range.

In 2019, R. Padmavathy et al., investigated Electronic and Optical Properties of Cubic Perovskites $\text{CsPbCl}_{3-y}\text{I}_y$ ($y = 0, 1, 2, 3$) to find that the energy gap values of these materials decrease with increase in pressure and that a semiconductor-to-metallic phase transition is observed at high pressure. The optical properties of these Pb-based compounds are analyzed. The dynamical stability of these perovskites is analyzed by their phonon dispersion curves.

In 2016, Bahaallyas and Badal H Elias., investigated the Theoretical Study of the Structural, Elastic, Electronic, Optical and Thermodynamic Properties of CsXCl_3 ($X = \text{Pb}, \text{Cd}$) under Pressure, The theoretically calculated elastic constants reveal the fact that both compounds are stable and show nature of ductility. The refractive index, extinction coefficient, complex dielectric function, energy loss function, optical conductivity, reflectivity and absorption coefficient for 0 to 25 eV incident photon energies have been predicted. The thermal effect on the heat capacities, entropy, enthalpy and Free energy were predicted using the quasi-harmonic Debye model.

In 2014, Fang Gu, et al. Predicted the First principle calculation for the structural elastic and Thermodynamic properties of cubic perovskite BaHfO_3 under pressure. It was found that the effects of pressure and temperature are inversely proportional. The obtained specific heat capacities at constant pressure, at the thermal expansion coefficient and at the thermal conductivity match well with the experimental data available in the range of 300–1300 K.

In 2011, Mohamed Amine Gheboul et al., Designed First-principles calculations on structural, elastic, electronic, optical and thermal properties of CsPbCl_3 perovskite. The thermal effect on the lattice constant, bulk modulus, Debye

temperature and heat capacity CV was predicted using the quasi-harmonic Debye model.

In 2010, G. Vaitheeswaran et al., Calculated High-pressure structural study of fluoro-perovskite CsCdF₃ up to 60 GPa: A combined experimental and theoretical study. The calculated ground-state properties—the equilibrium lattice constant, bulk modulus and elastic constants—are in good agreement with experimental results. The calculations reveal that CsCdF₃ is an indirect-gap insulator under ambient conditions, with the gap increasing under pressure.

In 2008, Chenliang Li, et al. predicted structural, elastic, electronic, and optical properties of hexagonal BiAlO₃ using First Principles Calculations.

CHAPTER 3

AIM AND SCOPE

3.1 AIM

The aim of the project is to design and develop thermoelectric materials that are potentially more efficient. It plays a critical role in energy conversion technology, and research into possible materials with good thermoelectric properties can contribute to this field.

The current thesis focuses on improving the thermoelectric properties of perovskite materials in different ways. CsPbBr₃ alkaline earth metals were discovered to have comparable transition patterns, and their thermoelectric properties were also examined.

As a result, pure CsPbBr₃ meets all of the requirements for an energy band semiconductor material. Using the pseudo potential method, we investigated the structural, electrical, and thermoelectric properties of cubic CsPbBr₃ and Sb doped CsPbBr₃ in this study. The literature lacks theoretical and experimental research of the thermoelectric characteristics of the CsPb_{1-x}Sb_xBr₃ system. CsPb_{1-x}Sb_xBr₃ compounds were explored in this work in increments of 0.25.

The results and discussion parts deal with the energetics of crystal structures and a full examination of electronic and thermoelectric properties using Boltzmann equations, followed by the overview of the approach used for the thermoelectric property calculation.

3.1 SCOPE

The generation of power was a significant concern in our civilization. Waste heat conversion is also a significant topic.

The most recent thermoelectric use is cookware, which produces enough electricity to charge a smartphone while trekking or camping. The temperature differential was created by burning wood on one side of the thermoelectrics while boiling water on the other. Thermoelectrics can also benefit from a solar heat recovery system. The sun's heat is concentrated on the hot side of the thermoelectric modules, while ambient air cools the cold side. This results in a high delta temperature across the thermoelectric device, which improves the device's energy conversion efficiency.

For thermoelectric medical applications, the Seebeck effect is used. The heat from the body is transformed into electricity, which is then used to power gadgets. There are two primary areas of thermoelectric material research. There are two types of medical gadgets that require power: implantable and wearable. The medical uses of thermoelectric in the realm of power generation from thermoelectric generators will be discussed next. These applications are currently being studied. Thermoelectric materials have their roots in the aerospace and astronautics industries, with the renowned radioisotope example in astronautics being the Mars rover "Curiosity," which used TEG to power all of its activities.

Medicine, physics, industry, and aerospace, astronomy applications, defence, and commercial purposes all require more and more worldly intelligent use of exact equipment. In this light, the creation of novel materials, as well as the improvement of current ones, is essential. In a follow-up effort, thermoelectric generators based on the prototypes are optimizing the process. This project's team includes BMW and Ford, as well as Tenneco and Gentherm as the programme leader.

Perovskite Solar Cells (PSCs) have a variety of intriguing features that have piqued the curiosity of researchers and developers in recent years. Perovskites are the most extensively used materials in solar cells, and their rapid growth in efficiency has made them the photovoltaic world's rising stars. Because of their

low processing costs, high conversion efficiency, and ability to be printed or sprayed, they are considered the next generation of solar technology. Furthermore, PSCs have the intriguing benefit of being simple to manufacture in a variety of ways, including solution processing and vapour decomposition processes. Perovskites are also expected to play a role in next-generation electric vehicles, sensors, lasers, and other devices. PSCs, on the other hand, are still unstable in specific conditions such as air (oxygen and moisture), UV light, and higher temperatures. The poor stability of perovskites causes solar cells and other forms of electrical devices made with these materials to have a short operating life, which is currently the principal impediment to their practical deployment. To improve the stability of PSCs, inorganic materials can be used to replace labile organic components.

Based on the above, our studied new materials namely $\text{CsPb}_{0.75}\text{Sb}_{0.25}\text{Br}_3$, $\text{CsPb}_{0.5}\text{Sb}_{0.5}\text{Br}_3$ and $\text{CsPb}_{0.25}\text{Sb}_{0.75}\text{Br}_3$ will replace the conventional materials for the thermoelectric applications.

CHAPTER 4

COMPUTATIONAL DETAILS

DENSITY FUNCTIONAL THEORY

Density functional theory (DFT) is a quantum mechanical modeling method used in Physics and Chemistry to investigate the electronic structure of many-body systems, in particular atoms, molecules, and the condensed phases[31-34]. An analytical solution of the many-electron Schrödinger equation is not available, and a numerical solution, while perfectly possible in theory, is effectively impossible in practice for more than a handful of electrons due to the finite speed and memory of computers. In this section we will introduce density functional theory (DFT) as a mean of circumventing solution of the many-electron Schrödinger equation, since the properties of a many-electron system can be determined by using just functional of the electronic density.

Density functional theory Ground state properties of metals, semiconductors, and insulators have been successfully described by DFT. DFT has been not only applied for standard bulk materials, it has been quite 74 successful for complex materials such as proteins and carbon nanotubes. The main idea of DFT is to describe a many body problem of interacting system of electrons and nuclei by mapping on to a one electron reference system that leads to same density as real system.

According to Hohenberg and Kohn theorem all observable quantities can be retrieved in a unique way from the density alone and can be written as a functional of density. Therefore, the basic variable of a system depends only on three (spatial coordinates x , y , and z) rather than $3N$ degrees of freedom. Spin densities $\rho\sigma(r)$ are the key quantities here and total energy can be written as

$$E_{\text{tot}}(\rho\uparrow, \rho\downarrow) = T_s(\rho\uparrow, \rho\downarrow) + E_{\text{ee}}(\rho\uparrow, \rho\downarrow) + E_{\text{Ne}}(\rho\uparrow, \rho\downarrow) + E_{\text{xc}}(\rho\uparrow, \rho\downarrow) + E_{\text{NN}}$$

Where T_s , E_{ee} , E_{Ne} , E_{xc} , E_{NN} are the kinetic energies of the non-interacting particles, electron-electron repulsion, nuclear-electron attraction, exchange-

correlation and repulsive Coulomb energy of fixed nuclei respectively. Out of infinite number of possible densities the one which minimizes energy is the ground state density. The problem therefore is to solve the Kohn-Sham (KS) equation.

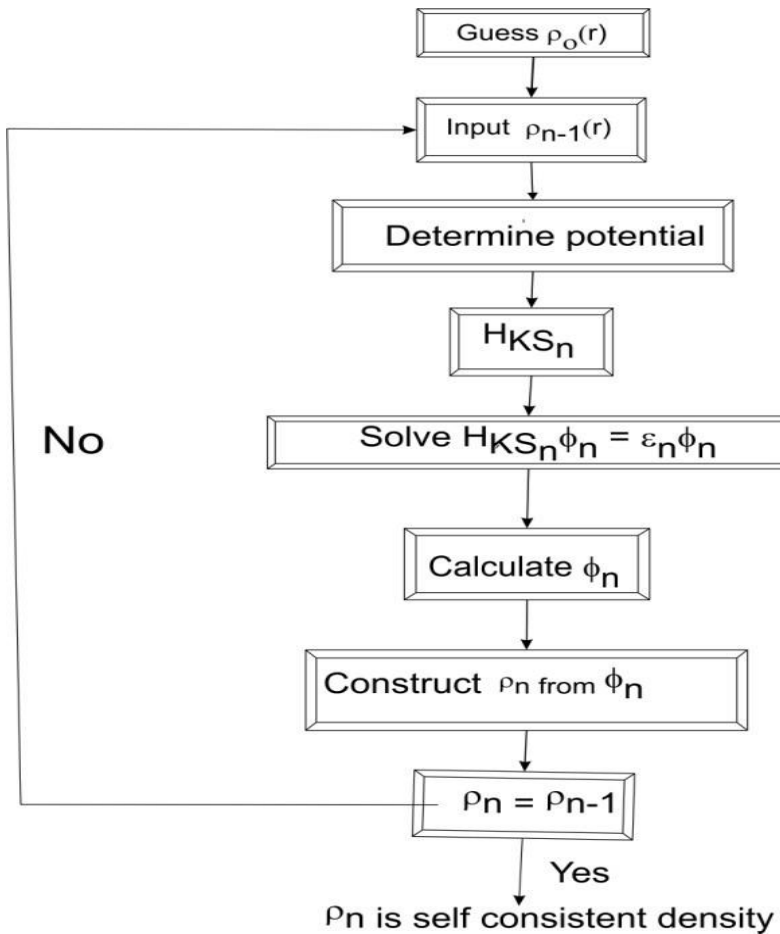


Fig.4.1. Flow chart to solve the Kohn-Sham equation

The spin densities can be written by summing over the orbitals as (3.10) are the occupation numbers such that, where is the symmetry-required weight of point k . Orbitals are wave functions of single particle (quasiparticle) but not the wave function of electrons. Overall density of these quasiparticles is equal to true electron density.

Kohn-Sham equation must be solved self-consistently in an iterative process as finding ρ_n , the orbitals require knowledge of the potentials which themselves depend on density and thus on the orbitals again. The flow chart to solve the KS equation is shown below. Fig.4.1. Flow chart to solve the Kohn-Sham

equation. Practical applications of DFT are based on approximations and one must choose the functional that is used to represent exchange and correlation (xc) effects. But after this approximation one can solve the effective Hamiltonian with high precision. A common approximation is the so called local density approximation (LDA).

MANY BODY SYSTEMS

From the microscopic point of view, a solid can be seen as a collection of heavy, positively charged nuclei (n) and lighter, negatively charged electrons (e). The nuclei and electrons are treated as electromagnetically interacting point charges and the exact non relativistic many-body Hamiltonian for this system becomes:

$$\hat{H} = -\frac{\hbar^2}{2} \sum_i \frac{\nabla_{\vec{R}_i}^2}{M_i} - \frac{\hbar^2}{2} \sum_i \frac{\nabla_{\vec{r}_i}^2}{m_e} - \frac{1}{4\pi\epsilon_0} \sum_{i,j} \frac{e^2 Z_i Z_j}{|\vec{R}_i - \vec{R}_j|} + \frac{1}{8\pi\epsilon_0} \sum_{i \neq j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} + \frac{1}{8\pi\epsilon_0} \sum_{i \neq j} \frac{e^2 Z_i Z_j}{|\vec{R}_i - \vec{r}_j|} \quad (4.1)$$

M_i is the mass of the nucleus at $\vec{R}_i$ and m_e is the mass of the electron at $\vec{r}_i$. The first and second term correspond to the kinetic energy operator of the nuclei and of the electrons respectively. The remaining terms describe the Coulomb interaction between electrons and nuclei respectively. Unfortunately, due to the high degree of complexity it is impossible to solve this equation without introducing some approximations.

THE BORN-OPPENHEIMER APPROXIMATION

Mass of the electrons is much smaller than the nuclei while the electromagnetic forces acting on them are of comparable magnitude. Consequently, the electronic motion is considerably faster than the nuclear motion. Since the nuclei move so slowly on the scale of velocities of relevance to the electrons, it is justified to assume that at any moment, the electrons will be in their ground state with respect to the instantaneous nuclear configuration. The assumption of instantaneous electronic equilibrium for every nuclear configuration

implies that the electron wave function is a solution of the Schrodinger equation for Hamiltonian (4.1) with fixed nuclear positions:

$$\hat{H} = -\frac{\hbar^2}{2m} \sum_i \nabla_i^2 - \frac{1}{4\pi\epsilon_0} \sum_{i,j} \frac{e^2 Z_i}{|\mathbf{R}_i - \mathbf{r}_j|} + \frac{1}{8\pi\epsilon_0} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} + \frac{1}{8\pi\epsilon_0} \sum_{i \neq j} \frac{e^2 Z_i Z_j}{|\mathbf{R}_i - \mathbf{R}_j|} \quad (4.2)$$

$$\hat{V}_{NN} \hat{V}_{ext}$$

This Hamiltonian corresponds to the electronic motion in the external potential produced by the nuclei. Where, $\hat{T}$ represents the kinetic energy of the electrons, $\hat{V}$ is the electronic repulsion and $\hat{V}_{ext}$ is the electron-nucleus interaction. Important to note here is that the nuclear repulsion ($\hat{V}_{NN}$) contributes to the total energy by augmenting it with a constant. As a consequence, removing this term from the Hamiltonian will not affect the corresponding wave function.

The resulting Hamiltonian can be written as:

$$\hat{H} = \hat{T} + \hat{V}_{NN} \quad (4.3)$$

This decoupling of the electronic and nuclear motion is known as the Born-Oppenheimer or adiabatic approximation.

HOHENBERG AND KOHN THEOREM

According to Hohenberg and Kohn theorem [35], all observable quantities can be retrieved in a unique way from the density alone and can be written as a functional of density. In 1964, Hohenberg and Kohn stated two theorems on which DFT has been built.

First theorem: There is a one-to-one correspondence between the ground state density $\rho(r)$ of a many-electron system and the external potential V_{ext} . An immediate consequence is that the ground state expectation value of any observable $\hat{O}$ is a unique functional of the exact ground state electron density:

$$\langle \Psi | \hat{O} | \Psi \rangle = \hat{O}[\rho(r)] \quad (4.4)$$

Second theorem: For $\hat{O}$ being a Hamiltonian $\hat{H}$, the ground state total energy functional,

$H[\rho] \equiv E_{\text{ext}}$ is of the form,

$$\begin{aligned} E_{\text{ext}}[\rho] &= \langle \Psi | \hat{T} + \hat{V} | \Psi \rangle + \langle \Psi | \hat{V}_{\text{ext}} | \Psi \rangle \\ &= F_{\text{HK}}[\rho] + \int \rho(\mathbf{r}) V_{\text{ext}}(\mathbf{r}) d\mathbf{r} \end{aligned} \quad (4.5)$$

Where the Hohenberg-Kohn density functional $F_{\text{HK}}[\rho]$ is universal for any many-electron system. $E_{\text{ext}}[\rho]$ reaches its minimal for the ground state density corresponding to $\hat{V}_{\text{ext}}$. The one-to-one correspondence between the ground state density and the external potential has some important implications. It is obvious that, with the given external potential of the system, it is possible to find a unique ground state density for the system.

Solving the Schrodinger equation yields the ground state wave function out of which the ground state density can be calculated. Intuitively, the ground state density seems to contain less information than the ground state wave function. If this were true, the inverse correspondence from ground state density to external potential would not hold.

The first theorem of Hohenberg and Kohn, however, states that this correspondence holds as well. In other words: the density contains as much information as the wave function. As a consequence of the second theorem, it is understood that the ground state density minimizes ground state total energy functional ($E_{\text{ext}}[\rho]$). The Rayleigh-Ritz Variational method can be used to obtain the ground state density. It is important to note that $E_{\text{ext}}[\rho]$ evaluated for the ground state density corresponding to external potential ($\hat{V}_{\text{ext}}$), equals the ground state energy. Only this value of $E_{\text{ext}}[\rho]$ has a physical meaning. Also in the second theorem, the Hohenberg-Kohn-functional (F_{HK}) contains no information on the nuclei and the nuclear positions. Consequently, the functional is the same for all many-electron systems. Moreover the expressions for the kinetic energy and exchange-correlation functional are unknown. Hence density-functional theory in the Hohenberg-Kohn form is found to be impractical for most of the time.

KOHN-SHAM EQUATIONS

In 1965, Kohn and Sham [36] showed that it is possible to reduce the many-body quantum mechanical problem to an exactly equivalent set of one-electron equations, solved self-consistently. Inspired by the idea of the Hohenberg-Kohn theorems, Kohn-Sham derived total energy functional including kinetic, Hartree, exchange-correlation energy, for a set of doubly occupied orbitals ψ_i and is rewritten as

$$E[\psi_i] = 2 \left[\frac{\hbar^2}{2m} \right] \sum_i |\psi_i \nabla^2 \psi_i| dr + E_H[n] + E_{xc}[n] + \int V_{ext} n(r) dr \quad (4.6)$$

where the kinetic energy functional has been replaced by its exact analytical expression acting on the set of orbitals ψ_i . The electron density $n(r)$ is then given as

$$n(r) = 2 \sum_i |\psi_i(r)|^2 \quad (4.7)$$

In the case of a crystalline solid, the external potential is simply equal to the ionic interaction between the nuclei and the electrons,

$$V_{ext} \equiv V_{ion}$$

Then according to Kohn-Sham energy functional, in order to determine the ground state total energy of the electronic system, one has to determine the set of orbitals $\psi_i(r)$ that minimizes it. This is done by self-consistently solving the Kohn-Sham equations:

$$\left[-\frac{\hbar^2}{2m_e} \nabla^2 + V_{ion}(r) + V_H(r) + V_{xc}(r) \right] \psi_i(r) = \epsilon_i \psi_i(r) \quad (4.8)$$

where ϵ_i is the Kohn-Sham Eigen value associated with electronic state i , V_H is the Hartree potential given by

$$V_H(r) = e^2 \int \frac{\rho(r')}{|r - r'|} d^3r' \quad (4.9)$$

V_{ion} is the ionic potential describing the attractive interaction between electrons and nuclei and V_{xc} is the exchange-correlation potential given by the functional derivative

$$V_{xc}(r) = \delta E_{xc}[n(r)] / \delta n(r) \quad (4.10)$$

The Kohn-Sham equations are in fact a reformulation of the Hohenberg-Kohn problem.

THEFULLPOTENTIALAPWMETHODS

The development of the Augmented Plane Wave (APW) method from Slater's APW (1937), to Linearized Augmented Plane Wave (LAPW) and the new APW+ local orbital (LO) was described by Schwarz et al., (2002).

The LAPW Method

The linearized augmented plane wave (LAPW) method is one among the most accurate methods available for performing electronic structure calculations of crystals. It is based on the density functional theory for the treatment of exchange and correlation and uses the local spin density approximation (LSDA). Several forms of LSDA potentials exist in the literature, but recent improvements were made by using the generalized gradient approximation (GGA). The LAPW method is a procedure for solving the Kohn-Sham equations for the ground state density of a many-electron system by introducing a basis set which is especially adapted to the problem. This adaptation is achieved by dividing the unit cell into (I) non-overlapping atomic spheres (centred at the atomic sites) and (II) an interstitial region. In the two types of regions different basis sets are used.

The solutions to the Kohn-Sham equations are expanded in this combined basis set of LAPW's according to the linear variation method

$$\psi_k = \sum_{k_n} C_{k_n} \phi_{k_n} \quad (4.14)$$

and the coefficients are determined by the Rayleigh-Ritz variational principle. ϕ_{kn} is the radial basis function. The convergence of this basis set is controlled by a cut off parameter $R_{mt}K_{max} = 6 - 9$, where R_{mt} is the smallest atomic sphere radius in the unit cell and K_{max} is the magnitude of the largest $\vec{K}$ vector in equation (4.14).

Singh (1994) described that in order to improve upon the linearization and to make possible a consistent treatment of semi core and valence states in one energy window, additional basis functions can be added. They are called “local orbitals (LO)” and consist of a linear combination of two radial functions at two different energies and one energy derivative (at one of these energies):

$$Y_{lm}\hat{r} \quad (4.15) \quad A_{lm}u_l(r, E_{1,l}) + B_{lm}\dot{u}_l(r, E_{1,l}) + C_{lm}u_l(r, E_{2,l})$$

The coefficients A_{lm} , B_{lm} and C_{lm} are determined by matching the value and derivative on the sphere boundary to the plane waves as usual.

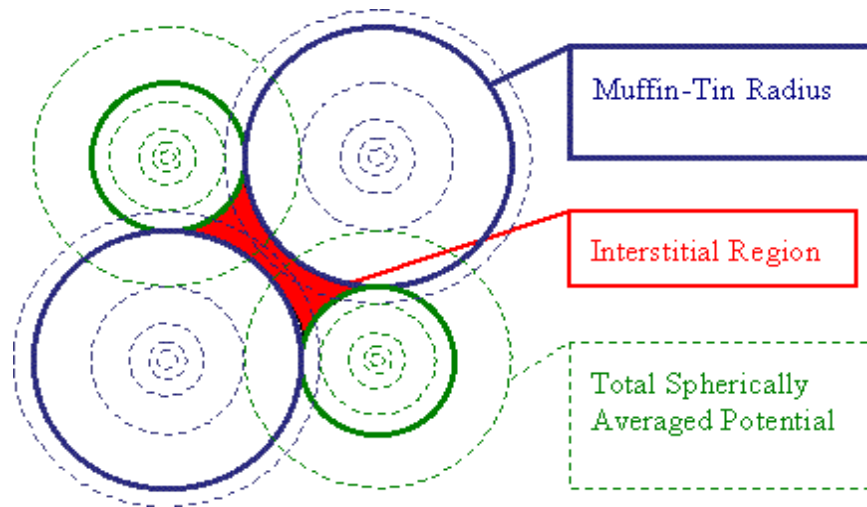


Fig.4.2. The unit cell divided into muffin-tin region and interstitial region

The APW+LO Method

The standard LAPW method with the additional constraint on the plane waves of matching in value and slope to the solution inside the sphere is not the most

efficient way to linearize Slater's APW method (SjÅostedt et al., 2000). It can be made much more efficient when one uses the standard APW basis, but of course with $u_l(r, E_l)$ at a fixed energy E_l in order to keep the linear eigen value problem. One then adds a new local orbital to have enough variational flexibility in the radial basis functions.

The new basis-functions, here after referred to as APW+LO, will differ in some important aspects from the LAPW basis functions inside the MT-region. Most important is that APW+LO set uses both in its original APW form and in a linear combination with $u(r, E_l)$.

$$\phi_{k_n} = \sum_{lm} [A_{lm, k_n} u_l(r, E_l)] Y_{lm} \hat{r} \quad (2.16)$$

$$\phi_{lm}^{LO} = [A_{lm} u(r, E_{1,l}) + B_{lm} u(r, E_{1,l}) Y_{1m} \hat{r}] \quad (2.17)$$

This new 'LO' looks almost like the old "LAPW" basis set, but here the A_{lm} and B_{lm} do not depend on k_n and are determined by the requirement that 'LO' should be zero at the sphere boundary and normalized. In this new scheme corresponding computational time is drastically reduced. i.e. the APW+LO basis functions have no restriction on their derivatives at the MT-boundaries as in LAPW. Once the standard local orbitals scheme is implemented into a LAPW code, the changes for adding the APW+LO [41] basis is straightforward. All the computations within the LAPW code, work equally well for APW+LO, with the exception that the kinetic energy needs to be treated differently. Hence, basis functions that have "kinks" at the sphere boundary are constructed which makes it necessary to include surface terms in the kinetic energy part of the Hamiltonian. However, the total wave function is of course smooth and differentiable.

WIEN2k CODE

WIEN2k is one of the fastest and reliable simulation codes among computational methods. All the computational work presented on lanthanide intermetallic compounds has been performed by using this code [42]. WIEN2k is a full-potential all-electron code developed by *Blaha* et al., at the Institute for Materialchemie, Technical University at Wien, Austria. WIEN2k consists of many independent F90 programs, which are linked together via C-shell scripts. The code is based on the Kohn-sham formalism of DFT.

In the previous chapter, we have described how to reduce the complex problem of many interacting particles to a Schrodinger wave equation. In order to solve these equations, we have to construct the effective Hamiltonian operator which depends on the electron density of the electronic system. The manner through which the Schrodinger wave equation solved within Code WIEN2k is represented by the flow chart.

Properties of WIEN2K:

Following are the considerations which are essential for a modern computer code and were made in the development of new Wien2k package.

a) Accuracy

It is achieved by well-balanced basis set, which contains numerical radial functions that are calculated in each iteration cycle. Thus, these functions adapt to effects due to charge transfer or hybridization, are accurate near the nucleus. It is a full-potential and all electron method. Relativistic effects (including spin orbit coupling) can be treated with a quality comparable to solving Dirac's equation. All atoms in the periodic table can be handled.

B) Efficiency and Good Performance

The new mixed basis APW+lo/LAPW optimally satisfies this criterion. Smaller matrix size helps to save computer time and thus larger systems can be studied.

c) Parallelization

The program can run in parallel, either in a coarse grain version where each k-point is computed on a single processor or in a fine grain scheme if the memory requirement is larger than that available on a single CPU.

d) Architecture

Depending on the given architecture, optimized algorithms and libraries are used during installation of the program package.

e) Portability

It requires the use of standards as far as possible, such as FORTRAN90, MPI, BLAS, SCALAPACK, etc.

f) User friendliness

It is achieved by a web based graphical user interface (GUI), called w2web. The program package provides an automatic choice of default options and it is also complemented by an extensive User's Guide.

APPLICATIONS OF WIEN2K

The problems considered so far in QM calculations using the LAPW method (employed in various versions of the Wien code) have covered a wide spectrum, including in particular insulators, semiconductors, (transition) metals up to f - electron systems or intermetallic compounds. A variety of applications are briefly introduced below

i) Band structure and density of states (DOS) calculations

The energy band structure and corresponding density of states are prominent quantities that determine the electronic structure of a system. Their inspection provides information about the electric property (metal, insulator or semiconductor) and gives insight into the chemical bonding.

By looking at site decomposed partial densities of states one can find a hint for the strength of interactions between the orbitals of the constituting atoms. The band structure is also useful in connection with photoelectron spectra.

ii) Electron densities

The electron density is the key quantity in DFT. By taking its Fourier transform the static structure factors can be determined easily, and it can be compared with the experimental X-ray diffraction data.

iii) Electric field gradients (EFG)

Since the EFG is uniquely defined by charge distribution and thus electron density, it can be calculated from first principles. The EFG is sensitive to anisotropy of charge density distribution close to the nucleus which can be determined by the nuclear quadrupole interaction (NQR) and can be measured by nuclear magnetic resonance (NMR), nuclear quadrupole resonance (NQR), Mossbauer or by perturbed angular correlation (PAC) measurements.

iv) Total energy and phase transitions

With the knowledge of total energy, the relative stability of different phases can be computed by keeping as many parameters constant as possible in order to have a cancellation of systematic errors.

v) Forces and structural optimization

In cases where the atoms occupy general positions that are not fixed by the crystal symmetry, the knowledge of the forces acting on atoms helps to optimize the structure parameters. Forces can be computed in Wien2k and are crucial for such optimizations.

vi) Spectra

The photoelectron spectra, X-ray emission and absorption spectra can be calculated using partial densities of states and the transition probabilities between

a valence and a core state. Such spectra provide useful information on local binding situation of the atom, whose core state is involved. Optical spectra and related quantities e.g. energy dependence of real and imaginary parts of the dielectric constant can be calculated from electronic response which is further used to determine absorption coefficient, refractive index, electron energy loss spectrum and reflectivity by using the Kramers-Kroening relation.

vii) Others:

Many properties using WIEN2k have been investigated for a large variety of structures, such as chemical bonding, structural stability, high-pressure phases, Jahn–Teller distortions, charge disproportionate, phase transitions, ferroelectric, ferroelectric or elastic properties etc. The roles of spin and orbital magnetic moments, magnetic ordering (ferro-, ferri-, antiferro-magnetic) or meta-magnetism were investigated in magnetic solids (including intermetallic compounds). LAPW calculations have helped to understand optical, core-level, photoelectron, Mossbauer, NMR spectra.

It also provides information on hyperfine or crystal fields, the magneto-optical Kerr effect or electric field gradients. It is possible to represent defects, e.g., an impurity, by studying a super-cell 2x2x2 (or larger), i.e., doubling the original unit cell in all the three dimensions. When one atom in this large unit cell is replaced by an impurity atom, the neighboring atoms can relax to new equilibrium positions.

By periodical repetition of such a super-cell an isolated impurity can be represented approximately. Super-cells can also be used to simulate surfaces and their interaction with atoms or molecules. Hypothetical or artificial structures can be considered and their properties can be calculated, irrespective of whether they can be made in reality or not. Such calculations can predict the property of a system (e.g., insulator or metal) or find its magnetic structure.

The changes in a system with deformations, under pressure or substitutions can be simulated. In the present work density of states (DOS), partial density of states (PDOS) of constituent atoms, electronic band structure and frequency

dependence of linear optical properties viz. real and imaginary part of dielectric constant, refractive index, reflectivity, electron energy loss spectra (EELS) etc. have been calculated for PbMoO_4 , BaWO_4 and $\text{NaBi}(\text{WO}_4)_2$ using WIEN2k program.

FLOW OF COMPUTATIONAL WORK

In the present work, the Full Potential Linearized Augmented Plane Wave method as implemented in the WIEN2k code is employed for calculating electronic structure of solids. The exchange and correlation energy is determined by using generalized gradient approximation (GGA) and by local density approximation (LDA). The integration in the Brillion zone was done by using Monkhorst Pack $10 \times 10 \times 10$ k-points. In order to achieve convergence, the basis function it expanded up to $R_{\text{MT}} \times K_{\text{max}} = 7$. The maximum value for partial waves inside the atomic sphere is $l_{\text{max}} = 10$ while the charge density is Fourier expanded upto $G_{\text{max}} = 12$. The self-consistent calculations are carried out to an accuracy of 0.0001 eV energy and 0.001 mRy charge. Computations are performed to find the total energy of given system and obtained total energies are then fitted into Birch–Murnaghan equation of state proposed by Birch (1947) to get the ground state properties.

Structure file generation, initialization and self-consistent field cycle performance will be carried using calculated lattice parameter. In order to do the band structure calculations for ternary cubic compounds, initially a structure file is generated using its optimized lattice constant. Then, $2 \times 2 \times 2$ supercell is created and the ternary addition is made with parent binary compound. Now the flow of calculations is carried for ternary compound as depicted in flowchart as shown in Figure 4.3.

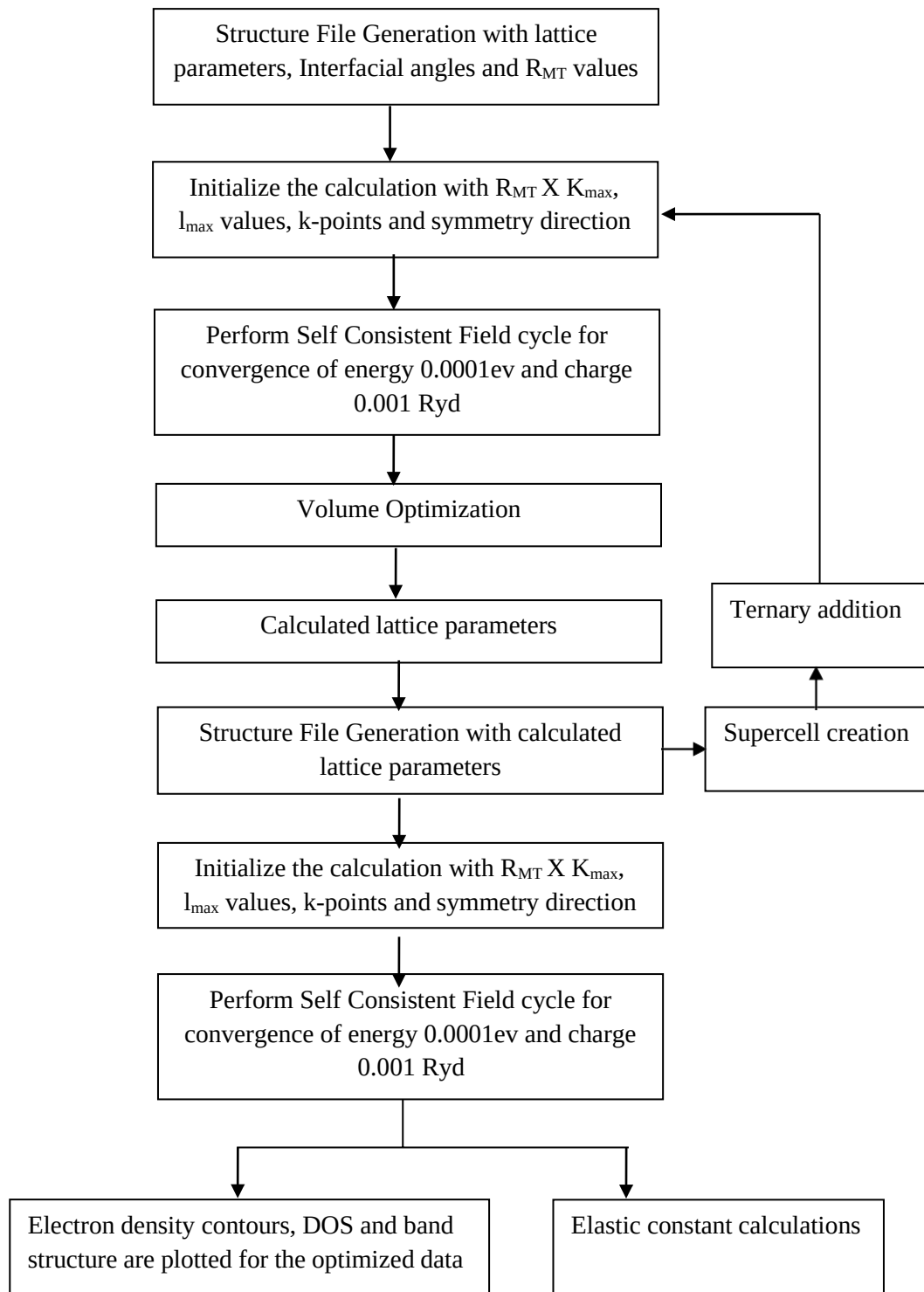


Fig.4.3.Flowchart of computational work to perform the band structure study

CHAPTER 5

RESULT AND DISCUSSION

STRUCTURAL PROPERTIES

The structural optimization is the initial stage in DFT computations. The original structure can be deduced from experimental data in the vast majority of cases. For good results, the DFT energy E_{TOT} can be estimated. Understanding the forces acting on atoms at general positions that are not controlled by crystal symmetry aids in the optimization of structural parameters. WIEN2k has the ability to calculate forces, which are crucial in such optimizations. As a function of cell volume energy, the atoms' muffin tin radius (RMT) is also tuned.

The convergence of this basis set is controlled by a cutoff parameter $R_{\text{MT}} \times K_{\text{max}} = 7$, where RMT is the smallest atomic sphere radius in a unit cell and K_{max} is the magnitude of the biggest K vector. As the smallest muffin tin radius is expanded, the closest point a plane wave will reach near a nucleus goes further away.

➤ RMT values:

Cs - a.u

Pb -a.u

Br - a.u

Sb -

➤ Convergence parameters:

Energy - below 0.0001Ry

Charge - below 0.001Ev

➤ K-Points-1000 ($10 \times 10 \times 10$)

Table 5.1 Alloy combinations

Materials	No. of atoms replaced out of 8 parent atoms	Lattice type	Space group	Space group no
CsPbBr_3	0 atom	Cubic	Pm-3m	221
$\text{CsPb}_{0.75}\text{Sb}_{0.25}\text{Br}_3$	2 atoms	Cubic	Im-3m	229
$\text{CsPb}_{0.5}\text{Sb}_{0.5}\text{Br}_3$	6 atoms	Tetragonal	P4/mmm	123
$\text{CsPb}_{0.25}\text{Sb}_{0.75}\text{Br}_3$	8 atoms	Cubic	Im-3m	229

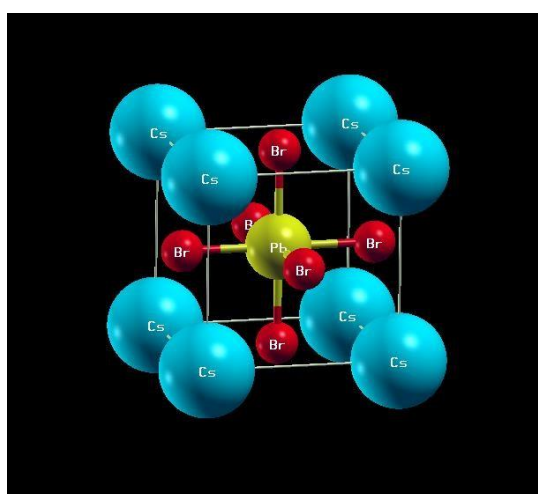


Fig.5.1. Cubic structure of CsPbBr_3

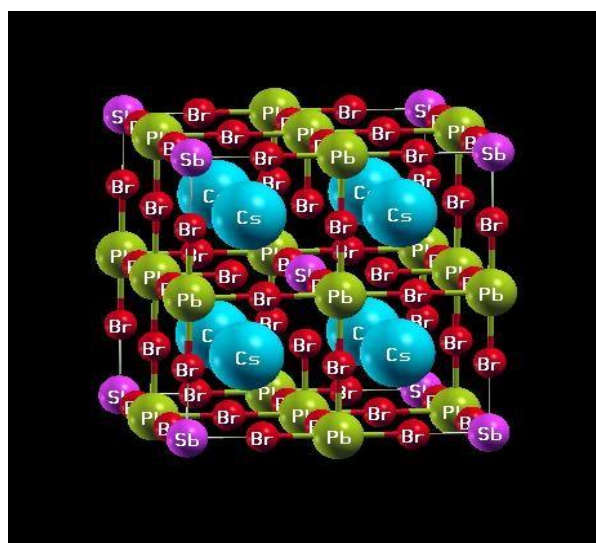


Fig.5.2. Cubic structure of $\text{CsPb}_{0.75}\text{Sb}_{0.25}\text{Br}_3$

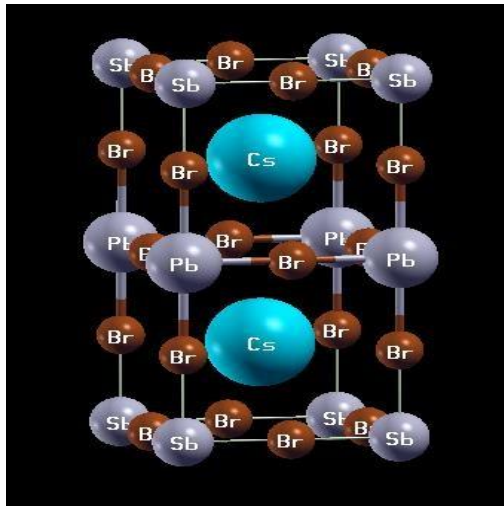


Fig.5.3. Tetragonal structure of $\text{CsPb}_{0.5}\text{Sb}_{0.5}\text{Br}_3$

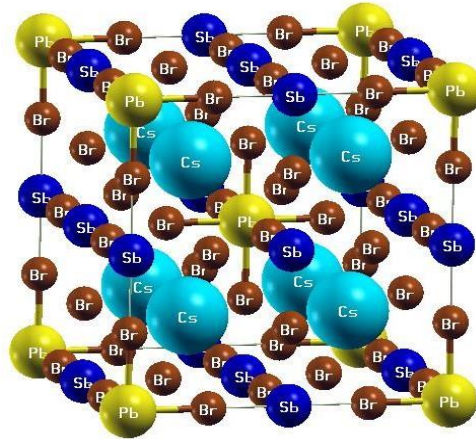


Fig.5.4. Cubic structure of $\text{CsPb}_{0.25}\text{Sb}_{0.75}\text{Br}_3$

K-POINTS

The performance of a SCF is the physically relevant Hamiltonian operator as specified by the SCF charge density. Using the Hamiltonian operator, we can extract the one particle energies and wave functions for any set of k-points. The first BZ's k-point set is made up of points along paths between high symmetry points. The k-point meshes for Brillouin zone sampling were created using the Monkhorst-Pack technique. The number of k-points is changed in relation to overall electronic capacity to ensure k-point convergence. The number of k-points is determined by the system's size and the Fermi level band structure's

complexity. For **CsPbBr₃** and **CsPb_{1-x}Sb_xBr₃** (x=0.25, 0.5, 0.75) the number of k-points reported is k-point =1000.

VOLUME OPTIMIZATION AND BULK MODULUS

By using a self-consistent run, the total energy (E) can be measured and represented as the sum of electron kinetic energy, Hartree energy, XC energy, ion-electron energy, and ion-ion energy. The size of the conventional unit cell length at equilibrium volume corresponds to the lattice constant of a solid, which is obtained computationally by minimizing total energy as a function of cell volume.

We have performed several calculations of the total energy for various lattice constants to obtain the value of lattice constant for which the total energy becomes minimal. The results thus obtained have been fitted to Murnaghan's equation of state [44]. The structural parameters have been calculated for CsPbBr₃ and CsPb_{1-x}Sb_xBr₃ (x=0.25, 0.5, 0.75) and volume optimization curve have been shown.

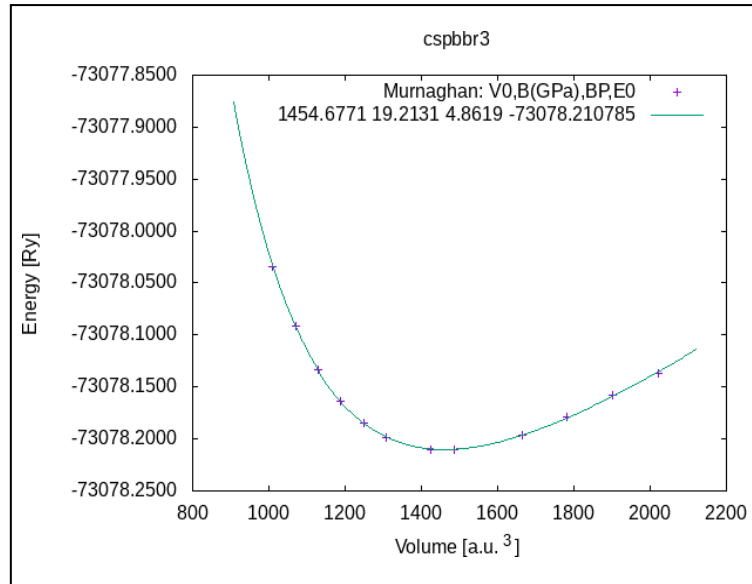


Fig.5.5. Volume optimization curve of CsPbBr₃

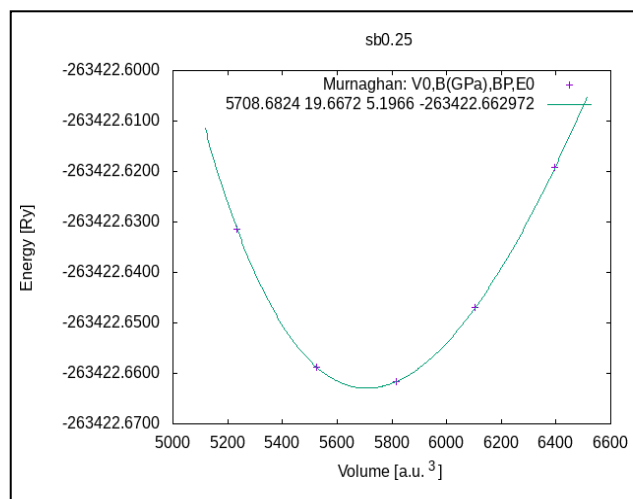


Fig.5.6. Volume optimization curve of $\text{CsPb}_{0.75}\text{Sb}_{0.25}\text{Br}_3$

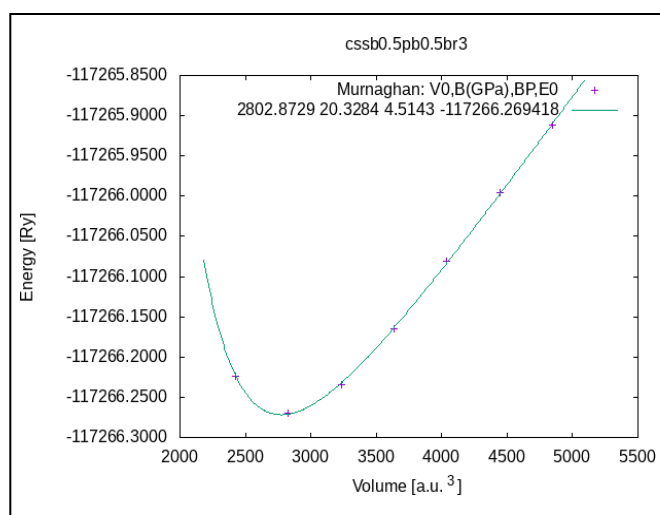


Fig.5.7. Volume optimization curve of $\text{CsPb}_{0.5}\text{Sb}_{0.5}\text{Br}_3$

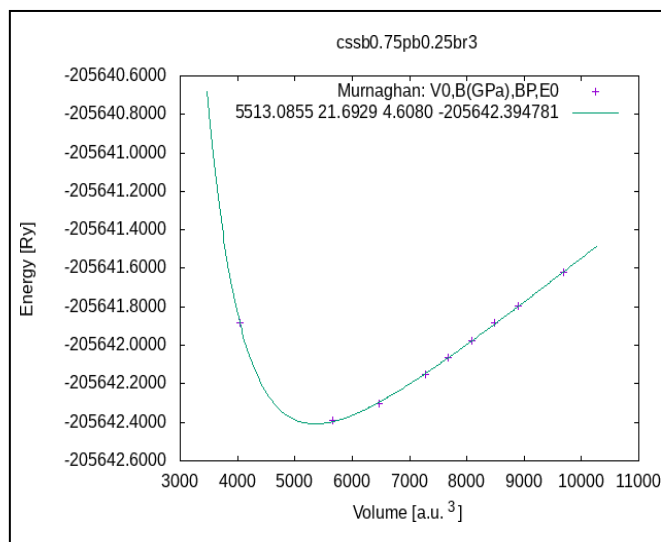


Fig.5.8. Volume optimization curve of $\text{CsPb}_{0.25}\text{Sb}_{0.75}\text{Br}_3$

Table 5.2 shows the computed lattice parameter, bulk modulus, total energy, Fermi energy, and bandgap value for CsPbBr_3 , $\text{CsPb}_{0.75}\text{Sb}_{0.25}\text{Br}_3$, $\text{CsPb}_{0.5}\text{Sb}_{0.5}\text{Br}_3$, $\text{CsPb}_{0.25}\text{Sb}_{0.75}\text{Br}_3$. From the calculations, it can be observed that no band gap values in all the studied materials. But there is a small overlap from valence band to conduction band indicating that these materials are known as semimetals. From the literature review we identified that the semimetals are more suitable materials and have better thermoelectric efficiency for thermoelectric applications.

Table 5.2: Calculated and experimental lattice parameters, bulk modulus (B) and its derivative (B') of CsPbBr_3 , $\text{CsPb}_{0.75}\text{Sb}_{0.25}\text{Br}_3$, $\text{CsPb}_{0.5}\text{Sb}_{0.5}\text{Br}_3$, $\text{CsPb}_{0.25}\text{Sb}_{0.75}\text{Br}_3$.

Parameters/ Alloys	CsPbBr_3	$\text{CsPb}_{0.75}\text{Sb}_{0.25}\text{Br}_3$	$\text{CsPb}_{0.5}\text{Sb}_{0.5}\text{Br}_3$	$\text{CsPb}_{0.25}\text{Sb}_{0.75}\text{Br}_3$
Present study				
a (Å)	5.9983	11.9157	5.9082	11.7552
b (Å)	5.9983	11.9157	5.9082	11.7552
c (Å)	5.9983	11.9157	11.164934	11.7552
$\alpha = \beta = \gamma$ (°)	90	90	90	90
V_0 (bohr ³)	1456.4014	5708.5367	2797.4692	5481.0142
B(GPa)	18.7699	19.6303	20.7570	21.7188
Bp	4.7673	5.2254	4.9331	4.9452

Table 5.3: Calculated total energy (Ry), band gap (eV) and Fermi energy (eV) of CsPbBr_3 , $\text{CsPb}_{0.75}\text{Sb}_{0.25}\text{Br}_3$, $\text{CsPb}_{0.5}\text{Sb}_{0.5}\text{Br}_3$, $\text{CsPb}_{0.25}\text{Sb}_{0.75}\text{Br}_3$ compounds.

Parameters/Alloys	Total Energy E_0 (Ry)	Fermi Energy (eV)	Band Gap (eV)
CsPbBr_3	-73078.210544	-0.1250996692	No gap
$\text{CsPb}_{0.75}\text{Sb}_{0.25}\text{Br}_3$	-263422.662964	0.1769	No gap
$\text{CsPb}_{0.5}\text{Sb}_{0.5}\text{Br}_3$	-117266.269977	0.2027580910	No gap

CsPb_{0.25}Sb_{0.75}Br₃	-205642.397440	0.2116794235	No gap
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ELECTRONIC PROPERTIES

DENSITY OF STATES (DOS)

a) CsPbBr₃

The total and partial density of states (DOS) of cubic **CsPbBr₃** is shown in Fig.5.9. In total DOS (Fig 5.9), below the Fermi level is mainly contributed by Cs atoms and there is less contribution from Br and Pb atoms.

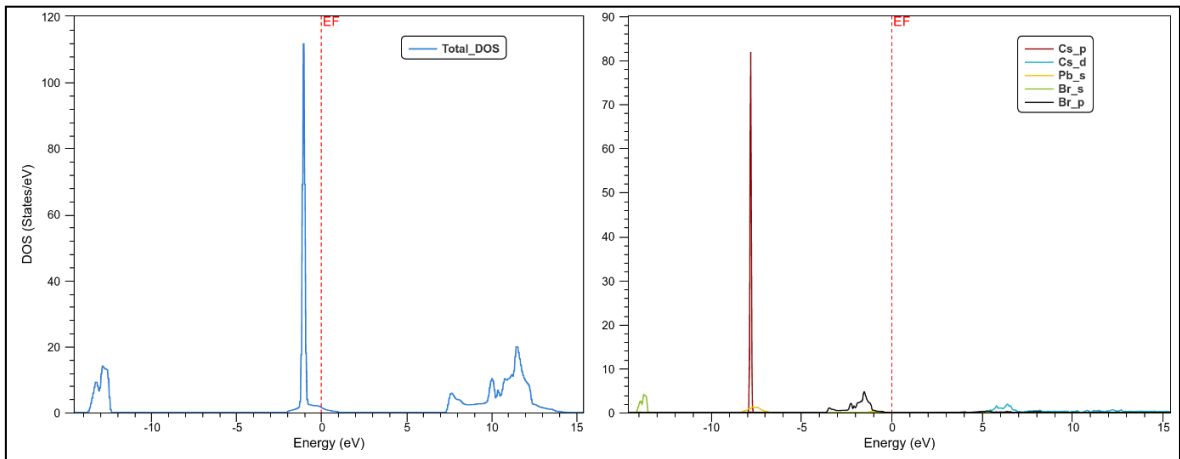


Fig.5.9. Density of States of CsPbBr₃

From the partial density of states histogram (Fig.5.9), it is observed that below the Fermi level is mainly contributed by Cs-p state and Br-p state and there is a less contribution of Pb-s state. Above the Fermi level is mainly due to Cs-d state more compare others. The peak observed in the graph is below the Fermi level. There is no band gap between valence and conduction band. There is a small overlap from valence to conduction band.

With the optimized structure, we calculated the band structure of cubic **CsPbBr₃**. The band structure of **CsPbBr₃** is shown in the Fig.5.10. Since the conduction band minimum and valance band maximum lies on the same line, so band structure of **CsPbBr₃** show the direct band gap.

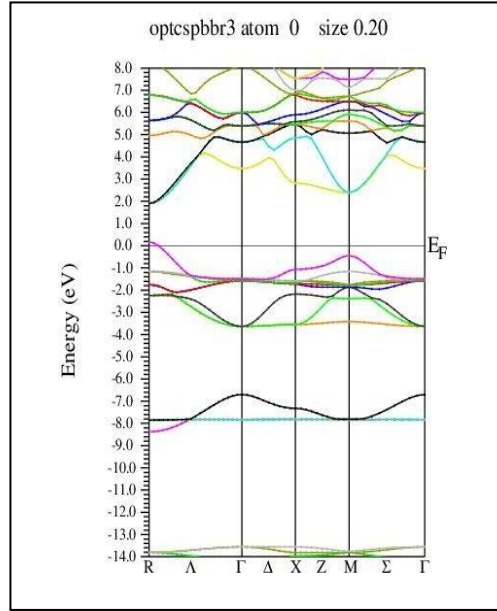


Fig.5.10. Band structure of CsPbBr_3

b) $\text{CsPb}_{0.75}\text{Sb}_{0.25}\text{Br}_3$

The total density of states (DOS) of cubic $\text{CsPb}_{0.75}\text{Sb}_{0.25}\text{Br}_3$ is shown in Fig.5.11. below the Fermi level is mainly contributed by Br and less contribution of Cs, Pb and Sb. After the Fermi level there is less contribution of Sb and Pb.

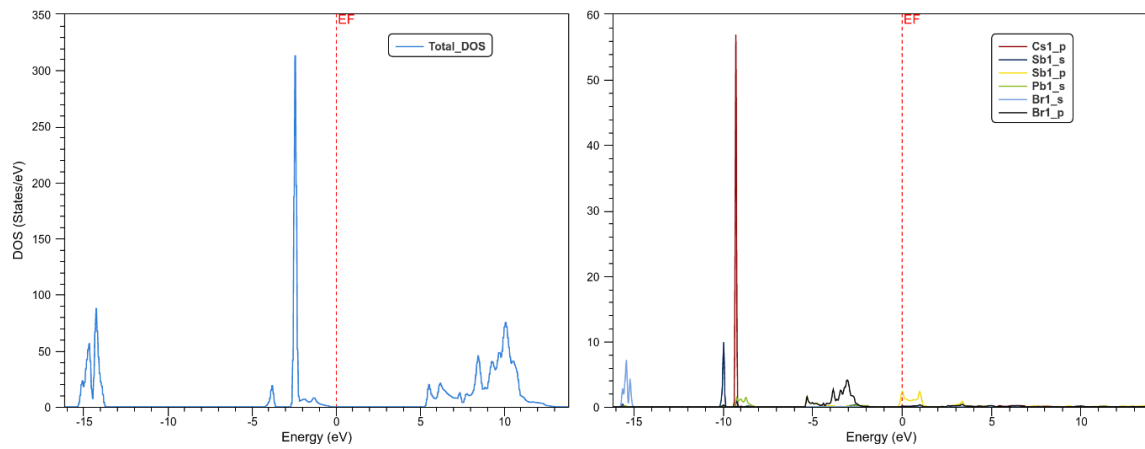


Fig.5.11. Density of States of $\text{CsPb}_{0.75}\text{Sb}_{0.25}\text{Br}_3$

In the partial density of states Fig.5.11 below the Fermi level contribution of Cs-p state is more and there is a less contribution of Sb-p&Cl-s state. After the Fermi level there is less contribution of Sb-p&Br-P.

With the optimized structure, we calculated the band structure of cubic **CsPb_{0.75}Sb_{0.25}Br₃**. The band structure of **CsPb_{0.75}Sb_{0.25}Br₃** is shown in the Fig.5.12. Since the conduction band minimum and valance band maximum lie in same line, so band structure of **CsPb_{0.75}Sb_{0.25}Br₃** show the direct band gap. While doping **Sb_{0.25}** in **CsPb_{0.75}Sb_{0.25}Br₃** also direct bandgap.

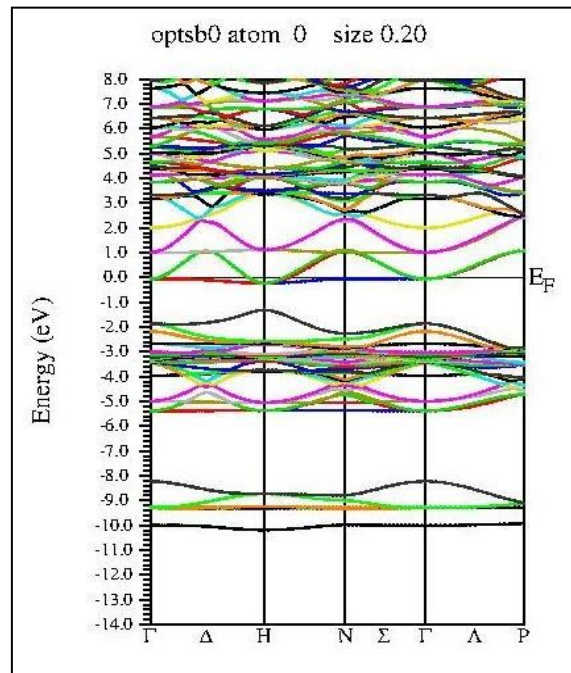


Fig.5.12. Band structure of $\text{CsPb}_{0.75}\text{Sb}_{0.25}\text{Br}_3$

c) **CsPb_{0.5}Sb_{0.5}Br₃**

The total and partial density of states (DOS) of Tetragonal **CsPb_{0.5}Sb_{0.5}Br₃** is shown in Fig.5.13. In total DOS in Fig 5.13, below the Fermi level is mainly contributed by Br atoms and less contribution of Pb atoms. Above the Fermi level there is less contribution of Pb&Cs.

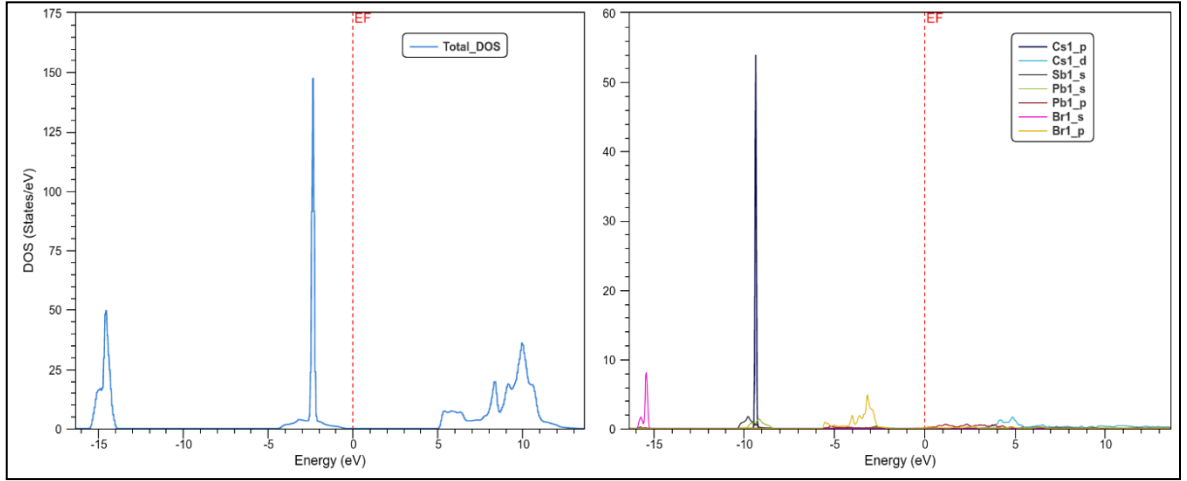


Fig.5.13. Density of States of $\text{CsPb}_{0.5}\text{Sb}_{0.5}\text{Br}_3$

In the partial density of states Fig.5.13, below the Fermi level the contribution is because of Cs-d&Pb-pstates. Above the Fermi level the contribution of Cs-d,Br-s&Br-p states are maximum.

With the optimized structure, we calculated the band structure of Tetragonal $\text{CsPb}_{0.5}\text{Sb}_{0.5}\text{Br}_3$. The band structure of $\text{CsPb}_{0.5}\text{Sb}_{0.5}\text{Br}_3$ is shown in the Fig.5.1. Since conduction band minimum and valance band maximum lie in same line, so band structure of $\text{CsPb}_{0.5}\text{Sb}_{0.5}\text{Br}_3$ show the direct band gap. While doping $\text{Sb}_{0.5}$ in $\text{CsPb}_{0.5}\text{Sb}_{0.5}\text{Br}_3$ direct bandgap no changes.

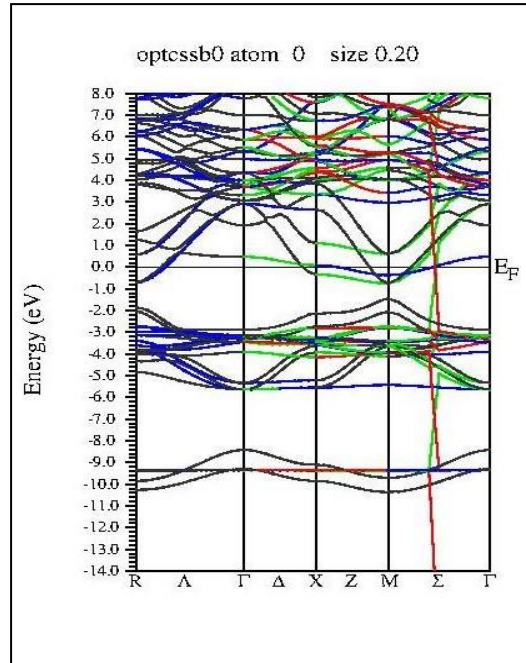


Fig.5.14. Band structure of $\text{CsPb}_{0.5}\text{Sb}_{0.5}\text{Br}_3$

d) $\text{CsPb}_{0.25}\text{Sb}_{0.75}\text{Br}_3$

The total and partial density of states (DOS) of cubic **$\text{CsPb}_{0.25}\text{Sb}_{0.75}\text{Br}_3$** is shown in Fig.5.15. In total DOS in Fig 5.15. below the Fermi level is mainly contributed by Sb-s. After the Fermi level there is less contribution of Pb, Cs & Br.

In the partial density of states Fig.5.15 below the Fermi level contribution of Br-s & Cs-s is more. Above the Fermi level contribution of Cs-d, Pb-p & Sb-p contribution is more.

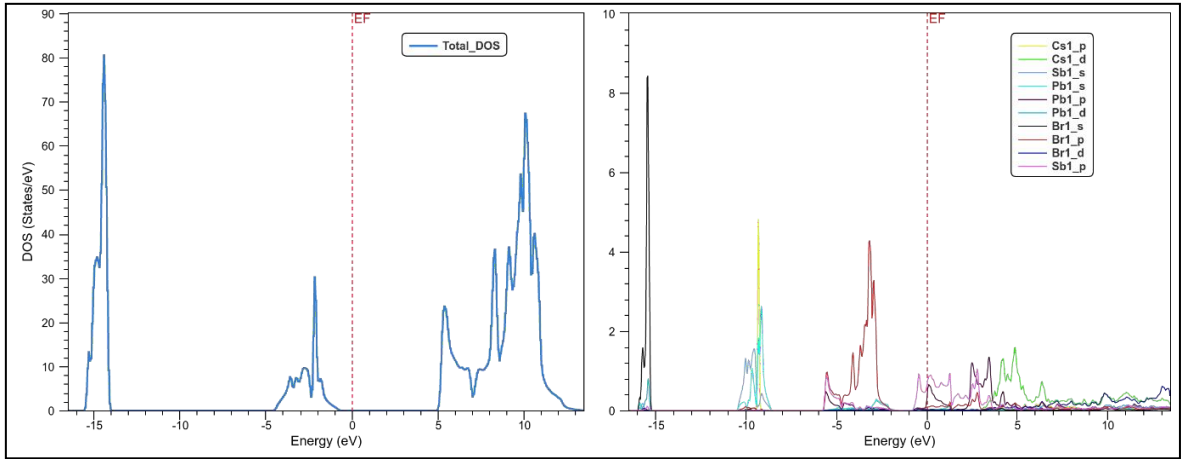


Fig.5.15. Density of States of $\text{CsPb}_{0.25}\text{Sb}_{0.75}\text{Br}_3$

With the optimized structure, we calculated the band structure of cubic **$\text{CsPb}_{0.25}\text{Sb}_{0.75}\text{Br}_3$** . The band structure of **$\text{CsPb}_{0.25}\text{Sb}_{0.75}\text{Br}_3$** is shown in the Fig.5.16. Since the conduction band minimum and valance band maximum lie in same line, so band structure of **$\text{CsPb}_{0.25}\text{Sb}_{0.75}\text{Br}_3$** show the direct band gap. While doping Sb_{0.5} in **$\text{CsPb}_{0.25}\text{Sb}_{0.75}\text{Br}_3$** direct bandgap.

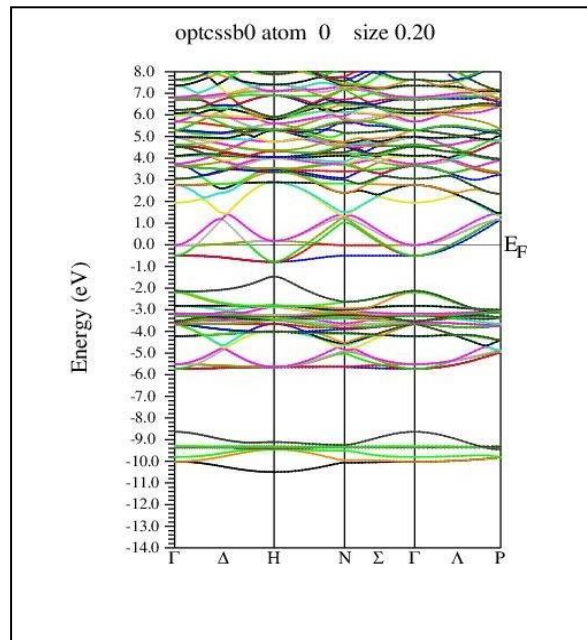


Fig.5.16. Band structure of $\text{CsPb}_{0.25}\text{Sb}_{0.75}\text{Br}_3$

THERMOELECTRIC PROPERTIES

Thermoelectric properties of CsPbBr_3 and $\text{CsSb}_x\text{Pb}_{x-1}\text{Br}_3$ ($x=0.25, 0.5, 0.75$) were calculated. The Seebeck coefficient (thermopower), electrical conductivity and power factor have been calculated for all the studied materials. All the calculation is carried out in room temperature 300K, and the results are tabulated.

Power Factor is given by $\text{PF} = S^2\sigma$

Where S – Seebeck coefficient

σ – Electrical conductivity

Increasing power factor enhance the efficiency of the thermoelectric material.

Table5.4. Transport properties of CsPbBr_3 , $\text{CsPb}_{0.75}\text{Sb}_{0.25}\text{Br}_3$, $\text{CsPb}_{0.5}\text{Sb}_{0.5}\text{Br}_3$ and $\text{CsPb}_{0.25}\text{Sb}_{0.75}\text{Br}_3$

Parameters	S $\mu\text{V/K}$	σ/T in $\Omega^{-1}\text{m}^{-1}\text{s}^{-1}$	$S^2\sigma/\tau \times 10^{16}\mu\text{Wm}^{-1}\text{s}^{-1}\text{K}^{-2}$
CsPbBr_3	-20.7	0.527×10^{20}	2.25×10^{16}
$\text{CsPb}_{0.75}\text{Sb}_{0.25}\text{Br}_3$	-37.7	0.104×10^{21}	14.78×10^{16}
$\text{CsPb}_{0.5}\text{Sb}_{0.5}\text{Br}_3$	6.63	0.204×10^{21}	0.89×10^{16}
$\text{CsPb}_{0.25}\text{Sb}_{0.75}\text{Br}_3$	-3.36	0.194×10^{21}	0.219×10^{16}

Table5.5. Transport properties of CsPbBr_3 , $\text{CsPb}_{0.75}\text{Sb}_{0.25}\text{Br}_3$, $\text{CsPb}_{0.5}\text{Sb}_{0.5}\text{Br}_3$ and $\text{CsPb}_{0.25}\text{Sb}_{0.75}\text{Br}_3$ for Temperature 100k to 1000k

	TEMPERATURE (K)	SEEBECK COEFFICIENT (10^6)	ELECTRICAL CONDUCTIVITY (10^{20})	POWER FACTOR (10^{16})
CsPbBr_3	100	-14.4	0.481	0.99
	200	-17.1	0.498	1.45
	300	-20.7	0.527	2.25
	400	-22.8	0.548	2.84
	500	-21.7	0.562	2.64
	600	-17.6	0.573	1.77
	700	-11.2	0.584	0.73
	800	-3.46	0.597	0.07
	900	4.89	0.611	0.14
	1000	13.2	0.626	1.09
$\text{CsPb}_{0.75}\text{Sb}_{0.25}\text{Br}_3$	100	-21	0.994	4.38
	200	-24.5	1.05	6.3
	300	-37.7	1.04	14.78
	400	-49.8	1.2	29.76
	500	-60.2	1	36.24
	600	-68.9	0.985	46.76
	700	-76.2	0.973	56.49
	800	-82.3	0.964	65.29
	900	-87.5	0.951	72.81
	1000	-91.8	0.952	80.22
$\text{CsPb}_{0.5}\text{Sb}_{0.5}\text{Br}_3$	100	11.7	1.87	25.59
	200	14	2.08	40.76
	300	6.63	2.04	0.89

	400	-2.73	1.97	0.14
	500	-11.9	1.91	2.7
	600	-20.1	1.86	7.514
	700	-27	1.82	13.26
	800	-32.8	1.79	19.25
	900	-37.79	1.77	25.27
	1000	-42.4	1.76	31.64
CsPb _{0.25} Sb _{0.75} Br ₃	100	-6.16	2.01	0.76
	200	-7.84	1.99	1.22
	300	-3.36	1.94	0.21
	400	-1.29	1.93	0.03
	500	-1.58	1.92	0.04
	600	-3.27	1.93	0.2
	700	-5.71	1.94	0.63
	800	-8.56	1.95	1.42
	900	-11.7	1.96	2.68
	1000	-14.9	1.97	4.37

ELECTRICAL CONDUCTIVITY

Variation of electrical conductivity with temperature difference is shown in the Fig.5.17. At 100K we can see greater electric conductivity value for **CsPb_{0.75}Sb_{0.25}Br₃**, **CsPb_{0.5}Sb_{0.5}Br₃** and **CsPb_{0.25}Sb_{0.75}Br₃** compared with the parent compound **CsPbBr₃**. Electrical conductivity is a measure of a material's capability to move electric charge carriers throughout the material. It depends on the type of material, stress states, and the chemical composition, and it provides information about the current flow and energy required to traverse the energy gaps.

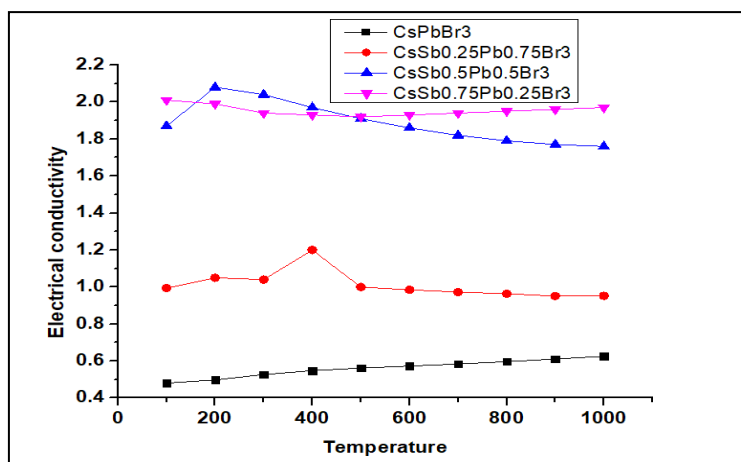


Fig. 5.17 Variation of electrical conductivity with temperature

From the Fig.5.17, it can be observed that the electrical conductivity increases with the increase of temperature except $\text{CsPb}_{0.5}\text{Sb}_{0.5}\text{Br}_3$. At higher temperature range, the electrical conductivity values for $\text{CsPb}_{0.75}\text{Sb}_{0.25}\text{Br}_3$, $\text{CsPb}_{0.25}\text{Sb}_{0.75}\text{Br}_3$ and CsPbBr_3 materials reaches saturation.

SEEBECK COEFFICIENT

In this fig.5.18. shows the variation of Seebeck coefficient(S) with temperature. The Seebeck coefficient also called as the thermoelectric power, and the convention of the Seebeck coefficient depends on the majority of charge carriers. Seebeck coefficient is considered positive for these materials represents the majority charge carriers are holes i.e., conductivity due to the holes. Seebeck coefficient increase with temperature value.

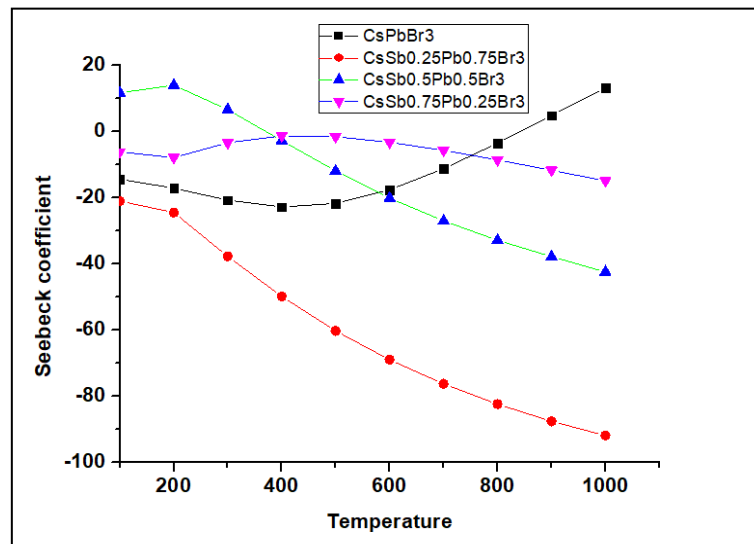


Fig. 5.18 Variation of Seebeck coefficient with temperature

From Fig.5.18, it is clear that the seebeck coefficient value of the parent CsPbBr_3 increases with temperature; whereas for $\text{CsPb}_{0.5}\text{Sb}_{0.5}\text{Br}_3$, first it increases and decreases with increasing of temperature. For $\text{CsPb}_{0.75}\text{Sb}_{0.25}\text{Br}_3$ and $\text{CsPb}_{0.25}\text{Sb}_{0.75}\text{Br}_3$ materials, there is a continuous decrease of seebeck coefficient with increasing of temperature.

POWER FACTOR

The figure of merit (ZT) is the most significant factor for investigating the quality of a material for its possible use in thermoelectric applications, and is dependent on the Seebeck coefficient, electrical conductivity, thermal conductivity and temperature. For a good thermoelectric material, the material should have a high Seebeck coefficient and electrical conductivity and low thermal.

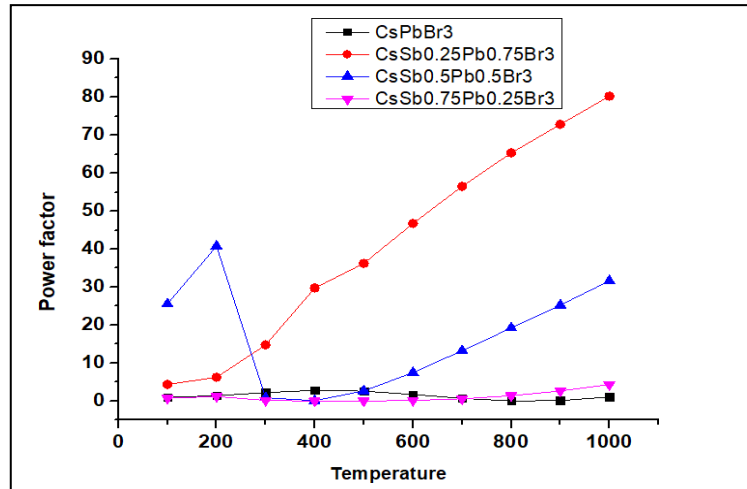


Fig. 5.19. Power factor with temperature

From the Fig. 5.19, the linear increasing of power factor is observed for CsPb_{0.25}Sb_{0.75}Br₃ combination; whereas the gradual increasing is observed in both CsPbBr₃ and CsPb_{0.75}Sb_{0.25}Br₃ materials. From the results, along with parent material the CsPb_{0.25}Sb_{0.75}Br₃ and CsPb_{0.75}Sb_{0.25}Br₃ combinations are identified as better thermoelectric materials with increasing power factor.

CHAPTER 6

CONCLUSION

In the present study, electronic, structural and thermoelectric properties of $\text{CsPb}_{1-x}\text{Sb}_x\text{Br}_3$ ($x = 0, 0.25, 0.5, 0.75$) materials have been reported. All the calculations were performed by FP-LAPW method using PBE-GGA in the framework of density function theory. The calculated lattice constant is found to be in good agreement with the experimental and theoretical results. Also, we have reported band structure, total and partial density of states for all the combinations. Here, antimony is chosen as the doping element to enhance the thermoelectric properties.

From the results of Band and DOS calculations, it can be identified that parent material and Sb doped material are in direct band gap. But there is a small overlap from valence band to conduction band indicating that these materials are known as semimetals. From the literature review we identified that the semimetals are more suitable materials and have better thermoelectric efficiency for thermoelectric applications.

The calculated results show that all the studied compounds exhibit the p-type conduction. Therefore, the conduction is due to holes. Seebeck coefficient decreases with increasing of doping combinations: whereas electrical conductivity increases initially then decreases.

Out of the four studied alloys, the $\text{CsPb}_{0.25}\text{Sb}_{0.75}\text{Br}_3$ and $\text{CsPb}_{0.75}\text{Sb}_{0.25}\text{Br}_3$ combinations are identified as better thermoelectric materials with increasing power factor, larger electrical conductivity and corresponding Seebeck coefficient. Though there is no linear variation in power factor and gradual increase is observed in $\text{CsPb}_{0.25}\text{Sb}_{0.75}\text{Br}_3$ and $\text{CsPb}_{0.75}\text{Sb}_{0.25}\text{Br}_3$. Hence, the two materials are identified as a good thermoelectric material for thermoelectric applications.

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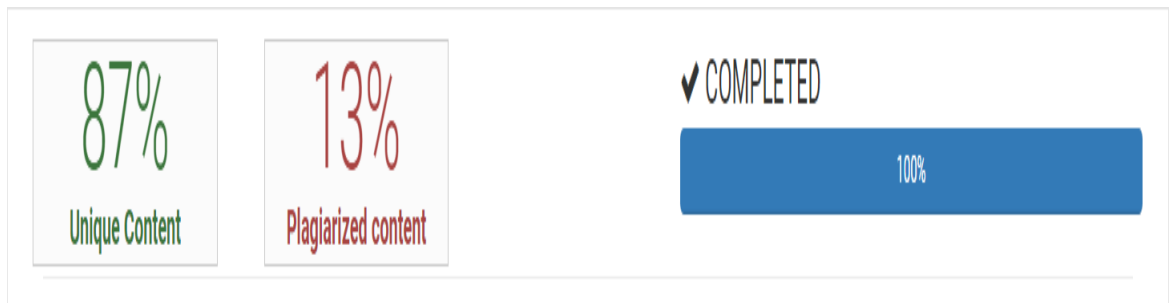
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Authors	Conferences	Date	Title	Presentation
Priya dharshni K ¹ , Prithiveraj P ² , Manjula M ^{3*} and Muthumari M ⁴	SGCA 2021	13-15 Sep 2021	First principle study of thermoelectric properties of CsPb _{1-x} Sb _x Br ₃ (x = 0, 0.25)	Oral presentation on (14-09-2021)
Priya dharshni K ¹ , Prithiveraj P ² , Manjula M ^{3*} and Muthumari M ⁴	ICFMAA 2021	29-30 Oct 2021	First principle study of thermoelectric properties of CsPb _{1-x} Sb _x Br ₃ (x = 0, 0.25)	Best oral presentation award on 30-10-2021
Priya dharshni K ¹ , Prithiveraj P ² , Manjula M ^{3*} and Muthumari M ⁴	ICAMMC 2021	2-4 Dec 2021	First principle study of thermoelectric properties of CsPb _{1-x} Sb _x Br ₃ (x = 0, 0.25, 0.5)	Poster presentation on (04-12-2021)

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(Dr. M. MANJULA)