

**A FIRST PRINCIPLES INVESTIGATION OF
STRUCTURAL AND ELECTRONIC PROPERTIES
OF Cs₂XBr₆ (X=V, Ti)**

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by

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BONAFIDE CERTIFICATE

This is to certify that the project report titled **A FIRST PRINCIPLES INVESTIGATION ON THE STRUCTURAL AND ELECTRONIC PROPERTIES OF Cs_2XBr_6 ($\text{X} = \text{V}, \text{Ti}$)** is a bonafide record of the work done by **THAHA MASIH V M (RRN 230572601020)** in partial fulfillment of the requirements for the award of the degree of **Master of Science (M.Sc) in Physics** of the B.S. Abdur Rahman Crescent Institute of Science and Technology, Chennai 600 048 during the year 2023-2025.

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ABSTRACT

As the demand for the development of sustainable and non-toxic materials increases, there is an increasing search for lead-free alternatives to halide perovskites used in optoelectronic and spintronic applications. In this study, the electronic, magnetic, and structural properties of two vacancy-ordered double perovskites (VODPs) Cs_2VBr_6 and Cs_2TiBr_6 were investigated using WIEN2k framework of the first principles density functional theory (DFT) calculations. The choice of the compounds was due to the unique properties of these materials, as well as the magnetic nature introduced by V^{3+} and Ti^{4+} ions.

Structural optimizations were run for the FM, NM and AFM configurations. The AFM configuration was found energetically favorable for both compounds. The exchange correlation effects were treated with Perdew-Burke-Ernzerhof generalized gradient approximation (PBE-GGA) and the band structure was refined using the Modified Becke–Johnson potential (TB-mBJ) to predict the electronic bandgaps accurately.

Electronic structure analysis was carried out for Cs_2VBr_6 which was discovered to be half-metallic showing substantial spin polarization that make it a candidate for spintronic devices. On the contrary, Cs_2TiBr_6 has been discovered to be a narrow-gap antiferromagnetic material with an indirect energy gap. The DOS and PDOS explain that the d-orbitals of the transition metal have a huge influence towards the electronic and magnetic properties since the cations Cs and the anions Br dominate the part of the structure.

These findings show that Cs_2VBr_6 and Cs_2TiBr_6 are promising lead-free materials for various advanced electronics and optoelectronics. The authors' work fits into the context of eco-friendly material studies by providing evidence of the VODP's potential for future technologies.

Keywords: VODP's, DFT, WIEN2k, Double Perovskites

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CHAPTER 1

INTRODUCTION

The increasing global demand for energy has driven the scientific community to explore sustainable and efficient alternatives to conventional power generation. The emergence of solar cells has led to increased use of clean energy for power generation. On the other hand, thermoelectricity has become a prominent field of study for those seeking an effective nonconventional power generation mechanism. In particular, the waste heat of factories, power plants, vehicles and many others is converted into electrical power by the thermoelectric generator (TEG) technology.

Numerous research works are conducted on the improvement of thermo-electric materials of tin selenides, chalcogenides, half-Heusler alloys, Zintl phases, and perovskite based compounds, among others but despite achieving an increase in efficiency, they are cumbersome to adopt for use commercially due to their high operating temperature, cost per watt, and structural complexity.

A well-studied class of materials in optoelectronics is the A_2PbX_3 perovskite, where A represents an alkyl ammonium cation such as $CH_3NH_3^+$ or a cesium cation Cs^+ and X represents a halide anion. Despite their impressive optoelectronic properties, these materials cannot be successfully used due to their chemical and environmental instability and harmful lead content. This has prompted the search for effective lead alternatives.

Addressing the environmental and structural limitations of Pb-based materials in the development of next-generation perovskites has become a major challenge in current research. Several strategies have been proposed to address these limitations, such as using hydrophobic organic molecules, multi-cation substitutions, surface passivation, carbon coating, dimensionality reduction, or replacing lead with environmentally friendly elements. All these strategies are aimed at improving the efficiency of Pb-based perovskites in a more environmentally friendly and durable way.

Early attempts to replace Pb^{2+} ion in B site such as with Sn^{2+} , a group 14 element with a similar electronic configuration, were unsuccessful mainly because the perovskites that contain Sn were chemically unstable and they were quickly oxidized. Hence, researchers replaced Pb^{2+} ion in B site with trivalent ions Bi^{3+} and Sb^{3+} . As a result,

certain amount of B site vacancies occurred and that led to a decrease in the crystal structural dimensionality, and hence modification of the electronic band structure, generally resulting in widening of the band gap.

Upon a thorough consideration of the literature, it is apparent that there are very few possible cationic alternatives for Pb^{2+} . There is considerable interest in developing a new class of vacancy ordered, lead-free perovskite materials that can supersede the stability and toxicity concerns of lead-based halide perovskites, while preserving the optoelectronic properties associated with these materials. Discovery of these materials and ever, synthesis would be a significant scientific novelty.

Double perovskites $\text{A}_2\text{BB}'\text{X}_6$ have become a subject of high interest over the last two decades due to their high power conversion efficiencies. They were successfully applied to optoelectronic devices in 2009 and attained a power conversion efficiency of 3.8%. The efficiency rose to over 25% in 2019. The high efficiency is due to their optimal bandgap, strong light absorption, and high carrier mobility. The lead-based halide perovskites worked best for X-ray detectors, photodetectors, and light-emitting diodes (LEDs).

Vacancy ordered double perovskites (VODPs) are gaining attention in state-of-the-art research due to their new structural motifs and ability to have applied uses in catalysis, energy conversion, magnetic semiconductors, and more.

VODPs are characterized by the intentional introduction of cation vacancies to the B-site of the perovskite lattice, which is distinctly different from conventional perovskites. In some cases, vacancy ordering can even result in a doubling of the unit cell size and decrease the symmetry, which can then modify the electronic, magnetic, and optical properties of the material. The generic form for such materials is A_2BX_6 , where one of the B-sites is vacant, and X is a halide or oxide. VODPs may help stabilize otherwise unstable oxidation states, which typically also creates enhanced chemical stability and new materials properties.

Particularly anti-ferromagnetic (AFM) vacancy-ordered double perovskites are an interesting class of perovskite materials which opens exciting platforms for fundamental and applied research. The interplay between crystal symmetry, electronic structure, and magnetic ordering in these materials can result in exotic ground state and functionalities which can be very useful for spintronic and quantum information applications. In addition, the incorporation of halogens, such as bromine (Br), and large monovalent

cations, such as cesium (Cs^+), stabilizes the structure and affects the electronic band dispersion, influencing the optical absorption and transport properties.

The present study focuses on the compounds, Cs_2VBr_6 and Cs_2TiBr_6 , two vacancy ordered double perovskites exhibiting antiferromagnetic ordering. The choice of vanadium (V^{3+}) and titanium (Ti^{4+}) as the B-site cations is particularly interesting because of their distinct electronic configurations and tendencies toward magnetic ordering.

The theoretical investigation of the structural and electronic properties of the compounds Cs_2VBr_6 and Cs_2TiBr_6 is carried out by density functional theory (DFT). This method demands less computational power and is efficient and accurate. Universally, this method is also called as ab initio calculations.

Density functional theory is based on Kohn-Sham equations. Kohn-Sham ansatz replaces the original many body problems by an auxiliary independent single particle system (single particle orbitals). It maps the original interacting system with a real potential into an imaginary non-interacting system, where electrons move under an effective single particle potential called the Kohn-Sham potential. The complex effects of the many-body interactions are then captured approximately through the exchange-correlation functional within this effective Kohn-Sham potential.

Various approximation methods are used to construct an expression for the unknown XC functional $E_{\text{xc}}[n]$, which contains all many-body aspects of the system. Widely used are the Local Density Approximation (LDA), local Spin Density Approximation (LSDA) methods and Generalized Gradient Approximation (GGA). LDA assumes the exchange correlation energy at each point in space depends only on the local electron density whereas (GGA) incorporates the gradient of the electron density, thereby offering improved accuracy for systems where the density varies significantly. More sophisticated methods such as meta-GGA functionals, hybrid functionals also exists. Despite these advancements, the search for universally accurate and computationally efficient XC functionals remains a central challenge in modern DFT research. DFT has been a very powerful tool for predicting electronic, magnetic, mechanical, elastic, thermal properties etc. It is a useful tool which comes quite handy for the theoreticians and experimentalists to study the characteristics and properties of materials and to predict applications for them.

The findings from this study have significant implications for the development of lead-free perovskite materials. By demonstrating the viability of Cs_2VBr_6 and Cs_2TiBr_6 as candidates for spintronic and optoelectronic applications, this research contributes to the broader effort of replacing toxic lead-based materials with environmentally friendly alternatives. The insights gained from the first-principles calculations can guide experimental efforts in synthesizing and characterizing these materials, as well as in designing devices that exploit their unique properties.

Furthermore, the methodologies employed in this study can be extended to investigate other lead-free perovskite materials, facilitating the discovery of new materials with tailored properties for specific applications. The integration of theoretical and experimental approaches will be crucial in advancing the field of lead-free perovskites and realizing their potential in various technological domains.

CHAPTER 2

LITERATURE SURVEY

Zikem et al.: The present study explores the structural, optoelectronic, and thermoelectric properties of potassium tin halide vacancy-ordered double perovskites K_2SnX_6 ($X = Cl, Br, \text{ and } I$) in their stable monoclinic phase. The investigation is carried out using first-principles calculations based on density functional theory (DFT). The electronic band structures reveal direct band gaps for K_2SnCl_6 and K_2SnBr_6 , while K_2SnI_6 exhibits an indirect band gap. Theoretical computations employing the modified BeckeJohnson potential (mBJ-GGA) show that the optical band gaps decrease in the order of 2.581 eV (K_2SnCl_6), 1.707 eV (K_2SnBr_6), and 4.126 eV (K_2SnI_6), making these materials promising candidates for photovoltaic applications. Optical analyses of dielectric functions, absorption coefficients, and refractive indices further highlight their potential as efficient light absorbers. The study also evaluates the thermoelectric properties, including electronic and lattice thermal conductivities, Seebeck coefficients, and power factors, achieving maximum figures of merit (ZT) of 0.58, 0.69, and 0.50 for K_2SnCl_6 , K_2SnBr_6 , and K_2SnI_6 , respectively, at 500 K. These findings suggest that these materials have significant potential for use in solar cells and thermoelectric devices, especially at elevated temperatures.

Mohamed El Amine et al.: Our research, conducted using Density Functional Theory (DFT) within the WIEN2k framework, has revealed clear correlations between structural, electronic, mechanical, and thermoelectric properties of materials. These interrelationships provide valuable insights for designing materials with tailored functionalities and improved performance in targeted applications. By deepening our fundamental understanding of these materials, this approach not only enhances theoretical knowledge but also paves the way for technological innovations in fields such as semiconductors, thermos-electrics, and optoelectronics. In particular, we have extensively studied the vacancy-ordered double perovskite compounds Rb_2ReX_6 , concentrating on their structural, electronic, mechanical, and thermoelectric properties. We examined their formation and cohesive energies to evaluate structural stability, mechanical ductility, and electronic properties using quantum mechanical methods. Our findings show that Rb_2ReX_6 compounds are structurally stable, exhibit desirable

thermoelectric properties, and possess significant potential for spintronic, photodetector, and thermoelectric generator applications.

Huda A. Alburaih et al. (2024): Vacancy-ordered double perovskites (DPs) are emerging materials for spintronics due to their stable structures and non-toxic properties. In this study, we conducted a comprehensive investigation into the role of 4d electrons in Tc to understand their impact on the ferromagnetic properties of K_2TcZ_6 ($Z = Cl, Br$). We employed a modified Becke and Johnson potential to assess electronic and magnetic characteristics and utilized the BoltzTraP code to investigate thermoelectric effects. Experimental lattice constants confirmed the presence of stable structures, and formation energy estimates affirmed their thermodynamic stability. The Heisenberg model and density of electron states at the Fermi level provide insights into Curie temperature and spin polarization. The presence of ferromagnetism is evident in the density of states, reflecting electron spin transitions that support the exchange mechanism. The study explores how electron functionality influences ferromagnetism through exchange constants, hybridization processes, and crystal field energies. Moreover, the exploitation of magnetic moments from Tc to K and Cl/Br sites is emphasized in driving ferromagnetism. Optical absorption, dielectric constants, and refractive indices were also investigated, showing absorption across both visible and ultraviolet regions. Finally, thermoelectric properties including Seebeck coefficients, power factors, and electronic conductivity were analyzed, confirming the potential of these materials for spintronic and thermoelectric applications.

Muhammad Faizan et al.: The highly successful PBE functional and the modified Becke- Johnson exchange potential were used to calculate the structural, electronic, and optical properties of the vacancy-ordered double perovskites A_2BX_6 ($A = Rb, Cs$; $B = Sn, Pd, Pt$; $X = Cl, Br, \text{ and } I$) using density functional theory (DFT), a first-principles approach. The convex hull method was applied to verify the thermodynamic stability of these compounds. The calculated lattice constants, band gaps, and bond lengths were consistent with available experimental and theoretical data. Among the studied materials, Rb_2PdBr_6 and Cs_2PtI_6 showed band gaps within the optimal 0.9–1.6 eV range for single-junction photovoltaic applications. Photovoltaic efficiency was evaluated using the spectroscopic-limited-maximum-efficiency (SLME) metric along with optical property analysis. The ideal band gaps, high dielectric constants, and strong light absorption indicate that these perovskites are promising candidates for high-performance single and multi-junction solar cells.

Subhendu Das et al.: In this work, using density functional theory (DFT) based first principles calculations, a detailed investigation on the physical properties of lead-free vacancy-ordered double perovskite In_2PdCl_6 (IPC) has been performed. The structural, electronic, elastic, mechanical, optical, and thermoelectric properties are systematically studied. The mechanical stability is confirmed by the calculated elastic constants. The electronic structure reveals an indirect bandgap, suggesting the potential of IPC in optoelectronic applications. Optical properties such as dielectric function, absorption coefficient, refractive index, and reflectivity are calculated, indicating strong absorption in the UV region. Thermoelectric properties are also discussed, showing good Seebeck coefficient and power factor values, which imply the material's application potential in thermoelectric devices. These findings highlight that IPC could be a promising candidate for environment-friendly optoelectronic and thermoelectric applications.

M. Ammar Yasir et al.: In this study, first-principles calculations based on density functional theory (DFT) are employed to explore the electronic, magnetic, and thermoelectric properties of vacancy-ordered double perovskites Na_2TaX_6 ($\text{X} = \text{Cl}, \text{Br}$). The compounds exhibit half-metallic behavior with robust ferromagnetism, suggesting their potential for spintronic applications. Mechanical stability is confirmed through elastic constants. The thermoelectric properties, including the Seebeck coefficient, power factor, and figure of merit (ZT), are evaluated and demonstrate that these materials possess favorable characteristics for thermoelectric device applications. The tunability of electronic and thermoelectric properties via chemical substitution between Cl and Br is also discussed.

M. Musa Saad H.-E. et al.: In their theoretical investigation, M. Musa Saad H.-E. and B.O. Alsobhi studied the electronic, magnetic, optical, and thermoelectric properties of vacancy-ordered rubidium double perovskites — specifically Rb_2VBr_6 , Rb_2CrBr_6 , and Rb_2MnBr_6 — using first principles calculations. Their results reveal that these materials exhibit promising characteristics suitable for spintronics, optoelectronics, and thermoelectronics applications. The study shows that Rb_2VBr_6 is a half-metallic ferromagnet, while Rb_2CrBr_6 and Rb_2MnBr_6 are indirect semiconductors with significant magnetic moments. Optical analysis indicates strong absorption in the visible range, and

thermoelectric calculations suggest reasonable efficiency, making these compounds attractive candidates for multifunctional device applications.

Sajad Ahmad Dar et al.: In this study, we have investigated the structural, electronic, magnetic, mechanical, and thermodynamic properties of the cubic double perovskite oxide $\text{Ba}_2\text{MgReO}_6$ using density functional theory (DFT) within the full potential linearized augmented plane wave (FP-LAPW) method and the quasi-harmonic Debye approximation. The structural analysis indicates ferromagnetic phase stability. The spin-polarized electronic band structure and density of states reveal a half-metallic nature, with spin-up states being metallic and spin-down states semiconducting. The total magnetic moment was found to be 1 μB , primarily contributed by Re atoms. The calculated elastic constants satisfy the mechanical stability criteria. Mechanical properties such as bulk modulus (B), shear modulus (G), Young's modulus (Y), and anisotropic factor (A) have been computed. The B/G ratio and Cauchy pressure ($C_{12}-C_{44}$) both suggest the material is ductile. Additionally, thermodynamic parameters including heat capacity, thermal expansion, Grüneisen parameter, and Debye temperature have been predicted using the Debye model.

Smahane Dahbi et al.: In this paper, the crystal structures, thermodynamic stability, electronic densities of states, band structures, and optical properties of the nontoxic Pb-free vacancy ordered double perovskites halides X_2TeY_6 ($\text{X} = \text{Cs, Rb}$; $\text{Y} = \text{I, Br, Cl}$) were investigated using first-principles calculations. It was found that at the Γ point, the conduction band splits into two bands upon inclusion of spin-orbit coupling (SOC) interaction for X_2TeY_6 compounds. Additionally, the highest occupied molecular orbital is unchanged for all studied compounds except that of X_2TeI_6 , which shifts from the W to X point. Our findings are well supported by experimental data (Annalise E. Maughan et al., J Am Chem Soc. 2016;138:8453–8464) and contrast with theoretical work by Malak Azmat Ali et al., Int. J. Energy Res. 2020;45:8448–8455. The inclusion of SOC is crucial for the correct characterization of the electronic properties of the X_2TeY_6 compounds. Without SOC, the absorption coefficients shift to the visible region upon substituting Cl with Br and I ions. Notably, Cs_2TeI_6 (62%–75%) and Rb_2TeI_6 (57%–76%) exhibit excellent absorption coefficients in the visible region, suitable forbidden bands (1.422 eV for Cs_2TeI_6 and 1.469 eV for Rb_2TeI_6), and high stabilities, making them promising candidates for single-junction solar cells.

CHAPTER 3

COMPUTATIONAL METHODOLOGY

3.1. Density Functional Theory (DFT):

DFT is a fundamental concept using electronic density to find a solution to Schrödinger equation. Thomas, Fermi, and Dirac first used the electronic density but without giving an accurate illustration of electrons in a solid (many body system). They expressed total energy as a functional of total electronic density, since then their idea supported various levels of growth and the extension brought a substantial development in the description of DFT. This revolutionary change was established by introducing two theorems by Hohenberg-Kohn and later by Kohn-Sham equations.

3.1.1. Hohenberg–Kohn (H-K) theorems:

Hohenberg and Kohn (H-K) proved two basic theorems that describe the core concept of DFT showing that the ground state electron density (ρ_e) is capable to determine the properties of interacting systems. This traditional formalism depend on two Hohenberg and Kohn theorems,

Theorem 1

“The theorem states that the electron density- ρ_e (ground state charge density) conventionally determines the external potential- V_{External} of many particle system up to a constant”.

The mapping is one-to-one between electron density- ρ_e and the external potential energy- V_{External} .

Theorem 2

“The second theorem states that the total ground state energy functional $E_{V_{\text{External}}}(\rho_e)$ attains minimum value (equal to total ground state energy) by the density- ρ_e^0 called as exact ground state density ρ_e corresponding to external potential- V_{External} ”.

Following the above (H-K) theorems, the energy could be reported as,

$$E[\rho_e] = F[\rho_e] + \int \rho_e V_{\text{External}} dr_o \quad (1)$$

The $F[\rho_e]$ – functional takes the form

$$F[\rho_e] = T_e[\rho_e] + h[\rho_e] + E_{\text{NCL}}[\rho_e] \quad (2)$$

Where,

$T_e[\rho_e]$: Kinetic energy of the interacting system,

$h[\rho_e]$: Coulomb interaction between electrons (Hartree term)

$E_{\text{NCL}}[\rho_e]$: Self-interactions, exchange, and Correlation effect of electrons (Non-classical electrostatic contributions).

Since the equation is independent of external potential term, so, [H-K] density functional is universal could be used for any system (atom, molecule, solid). If $F[\rho_e]$, its exact form is known, the determination of ground state energy and density is easily possible by minimizing the functional in an external potential. But, finding the accurate form of functional- $F[\rho_e]$, remain a problem. The [H-K] theorems do not bring a solution to find out the exact form.

3.1.2. Kohn-Sham [K-S] Equations:

As per [H-K] theorem, the ground state density is used to determine the physical properties of many body system, but it has not given any technique to obtain the unknown density functional. To overcome this complexity, Kohn-Sham equations provided a practical technique to find unknown density functional. The central idea of [K-S] equations is that the kinetic energy of original interacting many particles systems - T_O was replaced with the kinetic energy of auxiliary non-interacting many particles system- T_N .

The energy functional could be written as,

$$E[\rho_e] = T_N[\rho_e] + V_h[\rho_e] + V_{\text{XC}}[\rho_e] + V_{\text{External}}[\rho_e] \quad (3)$$

The Kohn-Sham [K-H] Hamiltonian for equation is given as,

$$H_{K-S} = T_N + V_h + V_{\text{XC}} + V_{\text{External}} \quad (4)$$

Functional derivative of the exact ground state density defines the V_{XC} - exchange-correlation potential as,

$$V_{\text{XC}} = \frac{\delta E_{\text{XC}}[\rho_e]}{\delta(\rho_e)} \quad (5)$$

The [K-S] equations could be given as

$$H_{K-S}\varphi_i = \varepsilon_i\varphi_i \quad (6)$$

Where,

φ_i : Wave function of a single-particle.

The Kohn-Sham [K-S] method is an accurate formulation to illustrate the ground state properties of many-body systems. However, the functional (exchange-correlation) is still unknown and needs further estimation and study.

3.1.3. Exchange-Correlation approximation:

The [K-S] formalism is exact to solve the many-body system. But, the definite form of exchange-correlation functional is unfortunately unknown and approximations have to be introduced. So, the quality of density functional theory (DFT) calculations is resolved by how close the approximation (exchange-correlation) comes to the accurate value. The two approximations were constructed which are widely used for determining the ground state properties. The approximations are local density approximation-[LDA] and generalized gradient approximation-[GGA].

3.3.4. Local Density Approximation-[LDA]

The approximation used universally to the functional (exchange-correlation) is so-called local density approximation-[LDA], which considers that the energy functional (exchange-correlation) is approximate to the homogeneous electron gas posse's almost same electron density. By this statement the form of functional (exchange-correlation) in LDA with electron density- $N(\rho_e)$ can be given as,

$$E_{XC}^{LDA}[\rho_e] = \int (\rho_e) \mathcal{E}_{XC}^{Homo}[\rho_e] d\rho_e \quad (7)$$

Where,

$\mathcal{E}_{XC}^{Homo}[\rho_e]$: denotes exchange-correlation (XC) energy density of homogeneous electron gas.

The limitations of LDA exchange-correlation are (a) over binding (b) underestimation of lattice parameters (c) phase stability incorrect order (d) energetics of magnetic materials in error. To overcome such issues many approximations have been introduced. GGA is one of the most commonly used approximations to modify the LDA issues.

3.3.5. Generalized Gradient Approximation-[GGA]

In this [GGA] exchange-correlation, some modifications were developed to control the limitations of Local density approximation. The exchange-correlation (XC) density is the function of both electron density- $\rho_e(r_o)$ and the gradients of electron density- $\nabla\rho_e(r_o)$. The modification in LDA-exchange correlation density provides a new exchange-correlation known as generalized gradient approximation and could be written as:

$$E_{XC}^{GGA}[\rho_e(r_o)] = \int \rho_e(r_o) \mathcal{E}_{XC}(\rho_e(r_o), \nabla\rho_e(r_o)) d^3(r_o) \quad (8)$$

Generalized gradient approximation-GGA method, improves the structural optimization, binding energy, phase transitions, total energies, cohesive energy, etc. parameters. Despite both approximations (LDA and GGA) are fruitful in describing certain material properties, both approximations underestimate the band gap in certain systems (semiconductors and insulators).

3.2. WIEN2k:

In the present study, electronic, structural and magnetic calculation were performed using the WIEN2k software package, an advanced and widely used implementation of the full potential (linearized) augmented plane wave plus local orbitals (FP-LAPW+lo) method within the framework of density functional theory (DFT). WIEN2k has been developed primarily for accurate and efficient first-principles calculations of crystalline solids, enabling the detailed investigation of various physical and chemical properties at the atomic scale.

The WIEN2k code operates without invoking shape approximations for the potential or charge density (i.e., beyond the muffin-tin approximation), making it particularly suitable for studying complex materials, surfaces, and systems with low symmetry. The unit cell is divided into non-overlapping atomic spheres and an interstitial region, with

distinct basis functions applied to each. Inside the atomic spheres, solutions to the radial Schrödinger (or Dirac) equation are employed, while plane waves are utilized in the interstitial region.

The calculations are based on the Kohn–Sham formulation of DFT, solving the associated equations self-consistently. Exchange-correlation effects were treated using either the Local Density Approximation (LDA) or the Generalized Gradient Approximation (GGA), depending on the nature of the material system studied. For systems containing heavy elements, relativistic effects were incorporated through a scalar relativistic treatment of valence states and a fully relativistic treatment of core states using the radial Dirac equation.

The basis set quality is primarily controlled by the RK_{max} parameter, which is the product of the smallest atomic sphere radius and the maximum reciprocal lattice vector considered in the plane wave expansion. Typically, a sufficiently large RK_{max} value ensures convergence of total energies and derived properties. Brillouin zone integrations were performed using a Monkhorst–Pack k-point mesh to achieve appropriate sampling for metallic, semiconducting, or insulating materials.

In WIEN2k, additional flexibility is achieved through the use of local orbitals (LOs), which effectively handle semi-core and high-lying valence states simultaneously, improving the description of systems with closely lying energy levels, such as transition metal compounds. Furthermore, in cases requiring higher computational efficiency, the APW+lo scheme was adopted, where local orbitals are used to complement the APW basis functions, thereby achieving faster convergence without compromising the accuracy.

WIEN2k enables highly accurate and efficient predictions of structural, electronic, magnetic, and optical properties, making it an indispensable tool for modern computational materials science.

3.3. Methodology:

The structural optimization was carried out for spin-polarized ferromagnetic (FM), non-spin polarized (non-magnetic) and anti-ferromagnetic (AFM) configurations of the studied compounds. I also did force minimization for the stable magnetic configuration

of the compound to get the absolute ground state of the system. The force convergence criteria was set as 0.1 mRy / a.u.

The exchange correlation potential used in this study is Perdew-Burke-Ernzerhof Generalized Gradient Approximation (PBE-GGA) because this approximation estimates the properties in ground state with great precision except the bandgap which is underestimated. This underestimation was addressed by incorporating the modified Becke and Johnson Potential of Tran and Blaha (TB-mBJ). The TB-mBJ accurately calculate the band gap of the materials.

Self-consistent field calculation was carried out with a denser k-mesh of mesh points with total k-points 4000 and the maximum value of the angular momentum (L_{\max}) was adjusted to 7 such that the product of $RMT \times K_{\max}$ becomes 8 where K_{\max} and RMT are the cutoff wave vectors and radius of muffin-tin sphere. The maximum Fourier transformation vector G_{\max} was set as 12 as well. The minimum energy convergence and charge convergence criteria in self-consistent field (SCF) were set to 0.00001 Ry (10^{-5} Ry) and 0.0001 Ry (10^{-4} Ry). All these calculations are run in parallel mode. Space group for the vacancy ordered double perovskite is assumed to be 225_Fm_3m and the atomic positions of each atom is (0.25, 0.25, 0.25), (0, 0, 0) and (0.25, 0, 0) respectively.

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1. Structural properties:

To determine the most stable magnetic phase of the compound, structural optimization was performed within the Generalized Gradient Approximation (GGA) framework for ferromagnetic (FM), non-magnetic (NM), and antiferromagnetic (AFM) configurations. The equilibrium structural parameters were then derived by fitting the total energy as a function of volume using the Vinet-Rose equation of state. Figure 1 presents the total energy versus volume curves for each magnetic configuration of Cs_2VBr_6 and Figure 2 presents each magnetic configuration of Cs_2TiBr_6 . The results indicate that the antiferromagnetic configuration for both the compounds possesses the lowest total energy, implying it is the most favorable state. Key equilibrium parameters - including the lattice constant (a), bulk modulus (B), its pressure derivative (B'), and the total energy difference between FM and AFM states ($\Delta E = E_{\text{FM}} - E_{\text{AFM}}$) - were computed for the compounds Cs_2XBr_6 ($X = \text{V}, \text{Ti}$) (Table 1).

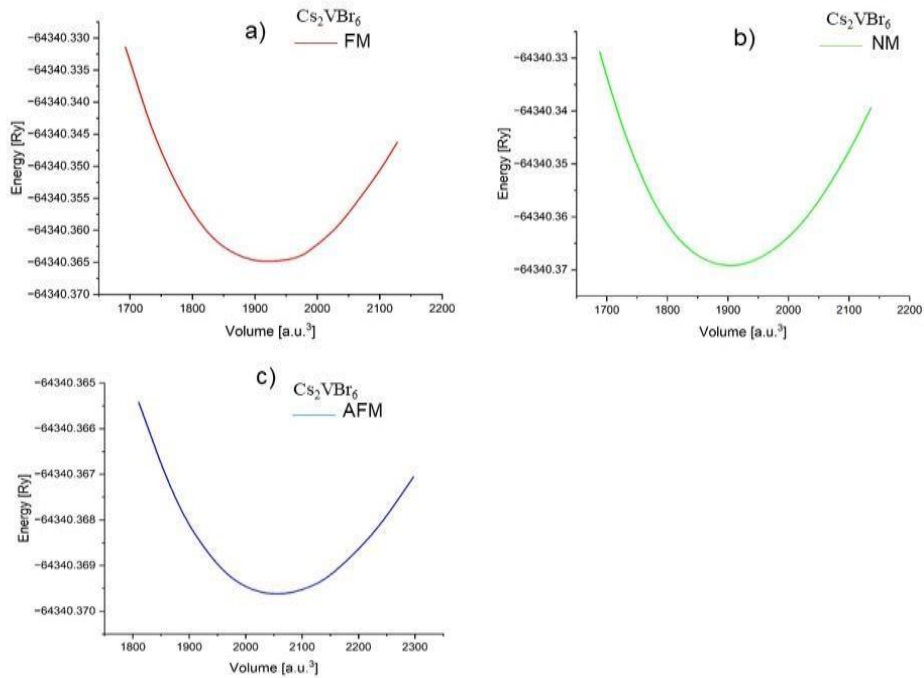


Figure 1. Variation in total energy per unit cell as a function of cell volume for a) ferromagnetic (FM), b) non-magnetic (NM) and c) anti-ferromagnetic (AFM) phases for Cs_2VBr_6 vacancy ordered double perovskites, using the GGA-PBE approximation.

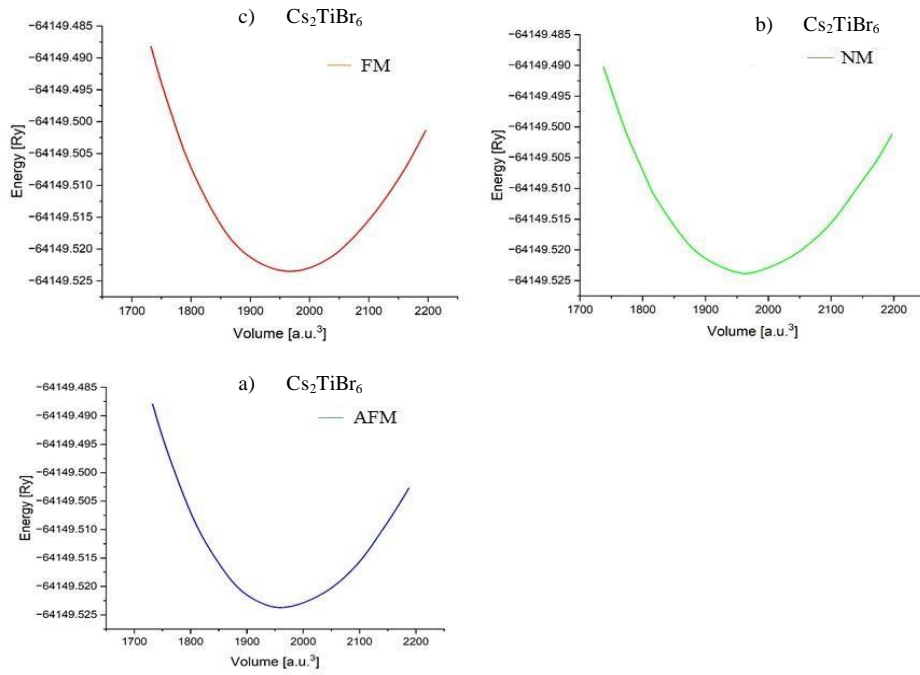


Figure 2: Variation in total energy per unit cell as a function of cell volume for a) ferromagnetic (FM), b) non-magnetic (NM) and c) anti-ferromagnetic (AFM) phases for Cs_2TiBr_6 vacancy ordered double perovskites, using the GGA-PBE approximation.

Table 1. Lattice parameter (a), Ground state volume V_0 , bulk modulus (B), derivative of bulk modulus (B'), for FM, AFM, NM states for Cs_2XBr_6 (X=V, Ti) by the GGA-PBE and the energy difference (eV) $\Delta E = E_{\text{AFM}} - E_{\text{FM}}$ between FM and AFM states.

COMPOUND	METHOD	MAGNETIC PHASE	A	v_0	B	BP	ΔE
			(Å)	a.u. ³	(GPa)		(meV)
Cs_2VBr_6	GGA-PBE	FM	10.4331	1915.9337	29.9339	5.0593	3.71×10^{-2}
		AFM	10.6783	2054.1916	27.4003	4.9246	
		NM	10.4083	1902.2729	30.9936	4.9267	
Cs_2TiBr_6	GGA-PBE	FM	10.5188	1963.5137	30.2779	4.8867	9.9×10^{-6}
		AFM	10.5187	1963.4867	30.2988	4.8939	
		NM	10.5188	1963.4994	30.2856	4.8872	

4.2. Electronic properties:

4.2.1. Band structure:

The spin-polarized band structures for Cs_2VBr_6 and Cs_2TiBr_6 compounds at the equilibrium lattice constant using Perdew-Burke-Ernzerh of generalized gradient approximation (GGA-PBE) and improved the modified Becke-Johnson TB-mBJ approximations are shown in figure 3. We can see that Cs_2VBr_6 is half-metallic in nature, as there is no energy gap between the valence and conduction bands. Near the fermi level (0 eV) the conduction bands overlap with the valence bands around the high-symmetry points Γ and X. The spin-up channel appears to exhibit indirect band gap at the Fermi level indicating semiconducting behavior whereas the spin-down channel exhibits half metallic behavior since there is no gap (Figure 3 a). From the band structure (Figure 3 b) Cs_2TiBr_6 exhibits a clear band gap between the valence band maximum (VBM) and conduction band minimum (CBM), with no bands crossing the Fermi level. The band gap appears to be indirect, as the VBM is located at a different k-point than the CBM.

Conduction bands are relatively flat, particularly at the Γ point, indicating localized Ti 3d states. This flatness typically results in a higher effective mass for electrons, which might limit carrier mobility. The valence bands show more dispersion compared to the conduction bands, suggesting that hole transport could be more efficient than electron transport in this material. It can be seen that the spin-up and spin-down bands are symmetrical, this shows Cs_2TiBr_6 is anti-ferromagnetic. It is evident from the clear band gap in both spin-up and spin-down channels that Cs_2TiBr_6 is semiconductor in nature. The band gap values for Cs_2VBr_6 and Cs_2TiBr_6 compounds are 1.62 eV, 1.54 eV in GGA-PBE and 2.32 eV, 2.20 eV in mBJ-GGA respectively.

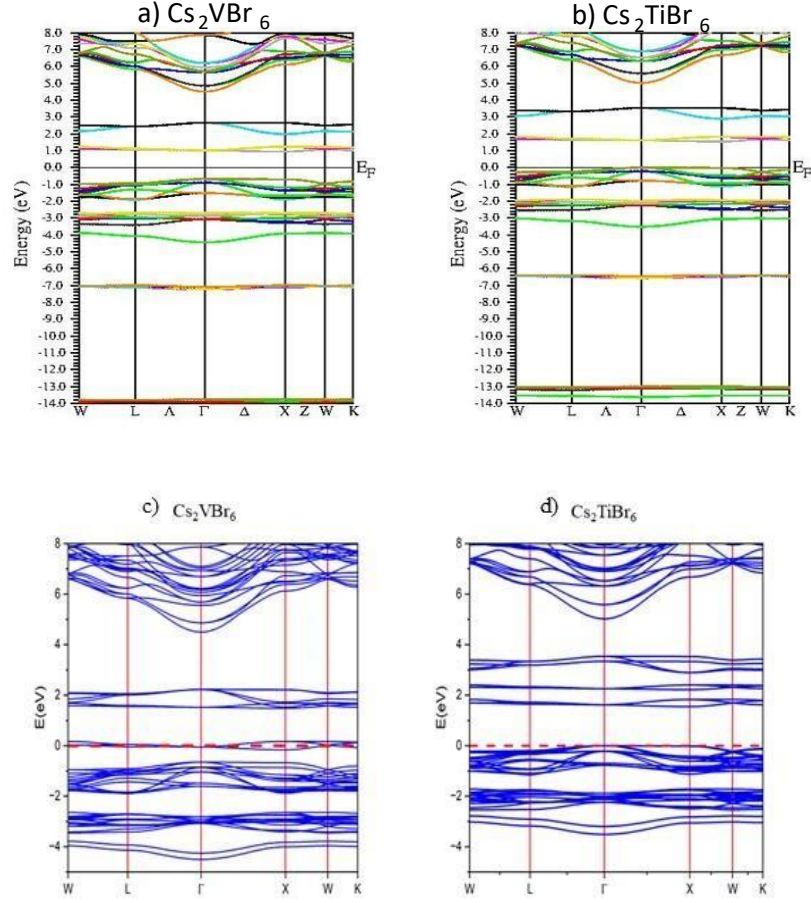


Figure 3. Comparison of GGA-PBE and mBJ-GGA-PBE spin-polarized band structures spin up, and spin down of Cs_2VBr_6 (a, c) and Cs_2TiBr_6 (b, d) calculated at the equilibrium lattice constant. The horizontal dashed line indicates the Fermi level.

4.2.2. Density of states (DOS):

COMPOUND I : Cs_2VBr_6

Total Density of States (TDOS): The spin-polarized total density of states (DOS) plot reveals significant asymmetry between the spin-up and spin-down channels, indicating a pronounced spin polarization within the system. In particular, near the Fermi level (set at 0 eV), a notable difference in DOS intensity between spin-up and spin-down states is observed, suggesting a potential half metallic or spintronic behavior. The up-spin states display a higher density of occupied states below the Fermi level, while the down-spin states are comparatively suppressed in this energy region. The presence of

finite DOS at the Fermi level for at least one spin channel confirms the half metallic character of the material.

Partial Density of States (PDOS):

Cesium (Cs) Contribution: The Cs atom exhibits minor contributions to the total DOS in the vicinity of the Fermi level. The electronic states are predominantly derived from the Cs *s* and *p* orbitals at higher energies (above 5 eV), consistent with the expected behavior of alkali metals where conduction bands are formed from these orbitals. The *d* and *f* orbital contributions are negligible throughout the energy range considered, indicating that Cs primarily plays a role in charge donation rather than active participation in bonding near the Fermi level.

Vanadium (V) Contribution: Vanadium displays a more significant contribution, particularly through its *d* orbitals. Sharp peaks in the *d* orbital DOS are present close to the Fermi level, implying that the V *d*-states are actively involved in the electronic conduction and magnetic properties of the material. The strong localization and high intensity of these states highlight the crucial role of vanadium in dictating the material's metallic and magnetic characteristics.

Bromine (Br) Contribution: The Br atom's electronic structure is dominated by *p* orbitals, with distinct peaks located below the Fermi level (between approximately -4 eV to -1 eV). This behavior is typical for halogens, where the *p* orbitals are fully or partially filled and participate in covalent bonding. The absence of significant Br contributions near the Fermi level suggests that Br is more involved in structural stability and bonding rather than electronic conduction.

Overall, the total and atom-resolved DOS analyses confirm that the electronic and magnetic properties of the system are predominantly influenced by the *d* orbitals of the transition metal vanadium, while Cs and Br contribute minimally near the Fermi level. The material exhibits metallic conductivity with notable spin polarization, making it a potential candidate for spintronic applications.

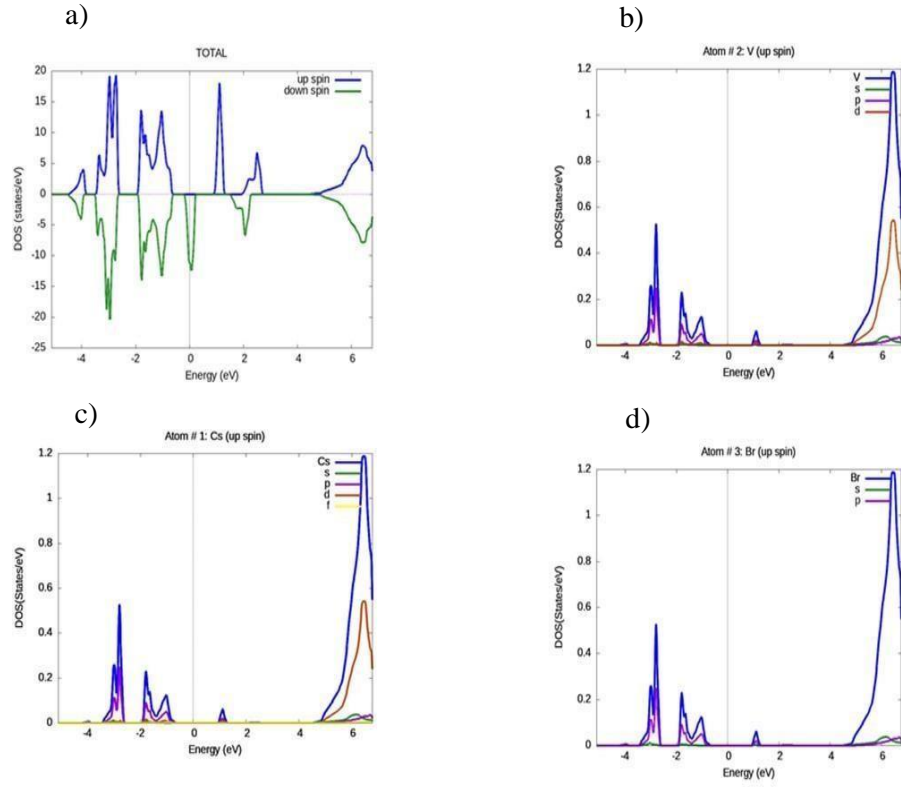


Figure 4. TDOS and PDOS for Cs_2VBr_6 are plotted for both up and down spin channels.

COMPOUND II : Cs_2TiBr_6

Total Density of States (TDOS): The total DOS plot reveals a distinct asymmetry between the up-spin and down-spin channels, indicating spin polarization and thus a potential magnetic ground state. The DOS is nearly symmetric around the Fermi level (set at 0 eV). The pronounced peaks between -6 eV and -5 eV point to deeply localized states, while the region surrounding the Fermi level shows a low but non-zero density of states. This characteristic suggests that Cs_2TiBr_6 is a narrow-gap semiconductor.

Partial Density of States (PDOS):

Cesium (Cs): The PDOS for Cs reveals sharp peaks located around -6 eV, predominantly arising from the s and p orbitals. These states are deeply embedded in the valence band and do not extend near the Fermi level. This implies that Cs atoms contribute minimally to the electronic transport and are largely electronically inert.

Titanium (Ti): Ti atoms exhibit weak DOS contributions in the deep valence band but show noticeable features near the Fermi level, primarily from d orbitals. This suggests that Ti d states play a key role in forming the conduction band, contributing to the material's semiconducting nature. The asymmetry between spin-up and spin-down states at these energies also supports the magnetic character of the compound.

Bromine (Br): Br atoms contribute significantly to the valence band, particularly through p orbitals, which dominate the peaks observed near -6 eV. Additionally, Br p states extend towards the Fermi level, indicating participation in both bonding and antibonding interactions, potentially through hybridization with Ti d orbitals.

The DOS analysis highlights the key roles of Br p and Ti d orbitals in defining the electronic and magnetic properties of Cs_2TiBr_6 . The compound is best described as a narrow-gap, spin-polarized semiconductor.

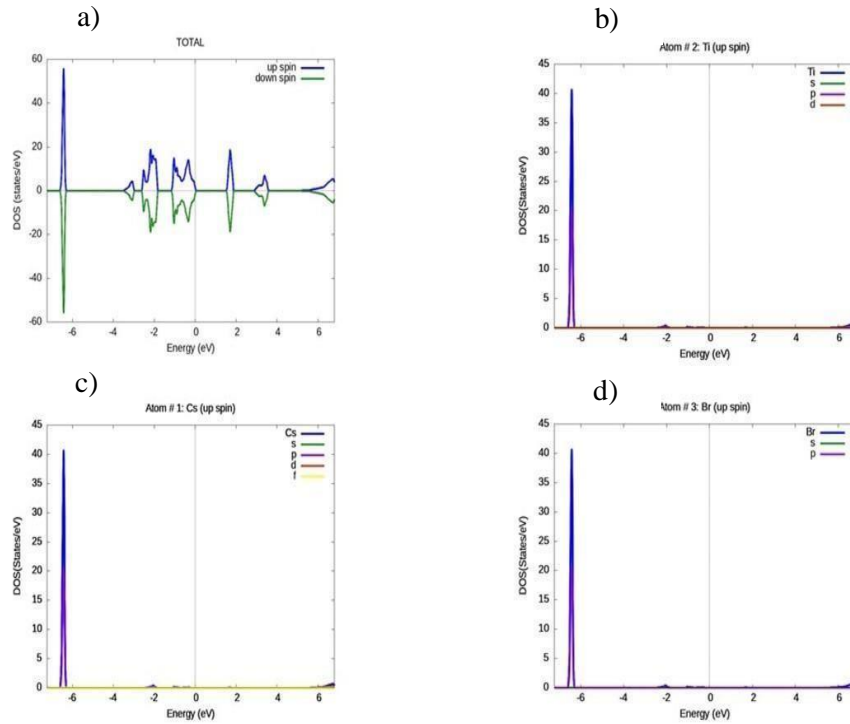


Figure 4. TDOS and PDOS for Cs_2TiBr_6 are plotted for both up and down spin channels.

4.3. Magnetic properties:

From Table 2 we can see that for compound one Cs_2VBr_6 , the vanadium atom (atom 2) contributes most of the magnetism with a strong negative moment in both GGA-PBE and mBJ-GGA, suggesting it's the magnetic center and the total spin magnetic moment is 1.00000 μB . The other atoms Cs and Br show minimal or nearly zero moments, consistent with their closed-shell nature. The "-1 μB " means that the majority of spin-down electrons outnumber the spin-up electrons by one electron overall in the unit cell suggesting the system is ferromagnetic or ferrimagnetic, or potentially anti-ferromagnetic with net imbalance. As for the compound Cs_2TiBr_6 the total magnetic moment in cell is -0.00000 μB , This suggests that the system is a non-magnetic, likely the magnetic moments of each atom cancels out each other due to symmetry as in anti-ferromagnetism.

Table 2: The total, partial magnetic moments in GGA-PBE and the type of band gap of the material.

COMPOUND	METHOD	ATOM 1	ATOM 2	ATOM 3	TOTAL	E_g	BAND GAP TYPE
		(μB)	(μB)	(μB)	(μB)	(eV)	
Cs_2VBr_6	GGA-PBE	+0.00052	-1.05722	+0.02591	-1.00000		Indirect Gap
	mBJ-GGA	+0.00126	-0.97475	+0.01288	-1.00000		
Cs_2TiBr_6	GGA-PBE	0.00000	0.00000	- 0.00000	-0.00000	1.549	
	mBJ-GGA	0.00000	-0.00000	0.00000	-0.00000	2.20	Indirect Gap

CHAPTER 5

CONCLUSION

In this study, we performed a comprehensive first-principle study of structural, electronic, and magnetic properties of lead-free vacancy-ordered double perovskite Cs_2VBr_6 and Cs_2TiBr_6 using density functional theory (DFT) implemented within the WIEN2k framework. Because of the need to replace the lead perovskites, which are hazardous and have poor structural stability, we considered the compounds incorporating environmentally friendly elements, such as vanadium and titanium.

When compared with conventional lead-based perovskites, Cs_2VBr_6 and Cs_2TiBr_6 offer a compelling set of advantages that address both environmental and functional limitations. Traditional halide perovskites such as $\text{CH}_3\text{NH}_3\text{PbI}_3$ have achieved remarkable success in photovoltaic applications due to their excellent optoelectronic properties; however, their inherent toxicity and poor long-term stability significantly hinder large-scale commercial deployment. In contrast, the lead-free perovskites studied in this work are composed of environmentally benign elements like vanadium and titanium, which not only eliminate toxicity concerns but also enhance the chemical and thermal stability of the materials.

Structural optimization was done in various magnetic configurations which include nonmagnetic (NM), ferromagnetic (FM) and antiferromagnetic (AFM) that indicated that the optimum state for both materials was AFM. This is a great discovery for the materials in terms of magnetic applications. PBE-GGA approximation was used to treat the exchange correlation energy and TB-mBJ potential was used to refine the electronic band gap to realize improved accuracy.

The electronic band structure analysis were performed for Cs_2VBr_6 and Cs_2TiBr_6 . The obtained results showed that the former material represents a half-metal with being a semiconductor (in the spin-up channel) and an ordinary metal (the spin-down channel). That is why the first substance is recommended for spintronic applications. By contrast, the compound Cs_2TiBr_6 is a narrow-gap antiferromagnetic semiconductor and might be utilized for optoelectronic devices.

Density of states (DOS) calculations illustrated that the d-orbitals of transition metals are the most influential in the vicinity of the Fermi level. They have the strongest impact

on the materials' magnetic and conduction properties. In the meantime, cesium and bromine atoms actively participated in the network without making a significant contribution to the electronic structure close to the Fermi level.

This study carries significant scientific implications by demonstrating the potential of Cs_2VBr_6 and Cs_2TiBr_6 as multifunctional, lead-free double perovskite materials suitable for advanced electronic applications. Through detailed first-principles analysis, we have shown that Cs_2VBr_6 exhibits half-metallic behavior with complete spin polarization, making it a strong candidate for spintronic devices where control over electron spin is essential for data storage and processing. Meanwhile, Cs_2TiBr_6 , as a narrow-bandgap antiferromagnetic semiconductor, offers promise in optoelectronic applications such as light-emitting diodes and photodetectors. The findings also reveal the dominant role of transition metal d-orbitals in determining electronic and magnetic behavior, highlighting opportunities for targeted material design via orbital engineering. By replacing toxic lead with earth-abundant, non-toxic elements like vanadium and titanium, this research not only addresses environmental concerns but also expands the functional diversity of perovskite-based materials. Overall, the study contributes to a deeper understanding of structure-property relationships in double perovskites and opens new avenues for their application in sustainable, next-generation electronics.

CHAPTER 6

FUTURE WORK

The structural, electronic, and magnetic properties of Cs_2VBr_6 and Cs_2TiBr_6 have been studied using first-principles DFT calculations. The optical properties of these compounds can be investigated to explore their potential in photovoltaic and photodetector applications. For example, dielectric function, absorption coefficient, and refractive index calculations can reveal the light harvesting potential of these materials. The future work can also investigate the elasticity constants of these materials using IRelast, a python that is compatible with WIEN2k. Thus, mechanical stability, anisotropy, brittle/ductility behavior, and other mechanical properties can be investigated.

Moreover, the thermoelectric properties of these compounds - such as the Seebeck coefficient, electrical and thermal conductivity, and figure of merit (ZT) - can be explored using Boltzmann transport theory. These evaluations are crucial for determining their suitability in waste heat recovery and energy conversion technologies.

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