DFT STUDIES OF CARBON AND NITROGEN BASED CUBIC ANTIPEROVSKITE MATERIALS

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This thesis of Mr. Muhammad Bilal, submitted for the Degree of Doctor of Philosophy in Physics under title “DFT studies of carbon and nitrogen based cubic antiperovskite materials” has been reviewed in the final form. Permission, as indicated by the signatures given below, is now granted to submit the copies to the University of Malakand for the Ph.D. degree.

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Abstract

In this thesis, we present theoretical studies of antiperovskites ANCa$_3$ (A=Ge, Sn, Pb), BCFe$_3$ (B=Al, Zn, Ga), SnCD$_3$ (D=Co and Fe) and MXY$_3$ (M=Al, Ga, Ir, Mg, Pd, Pt, Rh; X=C, N; Y=Mn, Ni, Sc, Ti, Cr, Fe) as well as SbNCa$_3$, BiNCa$_3$, SbNSr$_3$ and BiNSr$_3$. The calculations are carried out with the full-potential linearized augmented plane waves plus local orbital (FP-LAPW+lo) method within the framework of density functional theory (DFT) as well as Boltzmann’s theory. The exchange–correlation effects are treated by the local density approximation (LDA), generalized gradient approximation (GGA-PBEsol) and Engel and Vosko GGA (EV-GGA). Furthermore, the modified Becke and Johnson (mBJ) as well as improved mBJ potentials are used for the exact band gaps of the semiconductors. The relativistic effects in some of the compounds under study are explored by spin-orbit coupling.

The consistency of the calculated results of the thermoelectric properties of SnCCo$_3$ and SnCFe$_3$ with the experimental results confirms the reliability of our theoretical calculations for the other investigated metallic antiperovskites, ANCa$_3$ (A=Ge, Sn, Pb), BCFe$_3$ (B=Al, Zn, Ga), SnCD$_3$ (D=Co and Fe) and MXY$_3$ (M=Al, Ga, Ir, Mg, Pd, Pt, Rh; X=C, N; Y=Mn, Ni, Sc, Ti, Cr, Fe). Our results for ANCa$_3$ (A=Ge, Sn, Pb), BCFe$_3$ (B=Al, Zn, Ga) and SnCD$_3$ (D=Co, Fe) indicate that the thermopower of these materials can be enhanced by changing the chemical potential. The dimensionless figure of merit for the three nitrides approaches to 0.96 at room temperature, which predicts the usefulness of these materials in thermoelectric devices. Furthermore, the thermal conductivity of these compounds is minimum at room temperature for chemical potential of -0.25 eV to 0.25 eV, with maximum values of dimensionless figure of merit in this range. The striking feature of these studies is identifying a metallic compound, SnNCa$_3$, with the highest value of Seebeck coefficient at room temperature out of all metals.
Furthermore, electronic and thermoelectric properties of carbon and nitrogen based twenty metallic antiperovskites $\text{MXY}_3$ ($\text{M}=\text{Al}, \text{Ga}, \text{Ir}, \text{Mg}, \text{Pd}, \text{Pt}, \text{Rh}; \text{X}=\text{C}, \text{N}; \text{Y}=\text{Mn}, \text{Ni}, \text{Sc}, \text{Ti}, \text{Cr}, \text{Fe}$) are investigated. We find high values of Seebeck coefficient and small values of electronic thermal conductivity for $\text{AlCTi}_3$, $\text{AlNSc}_3$, $\text{AlCNi}_3$, $\text{AlNTi}_3$, $\text{GaCCr}_3$ and $\text{MgCNi}_3$ between -0.25 and 0.25 eV chemical potential. These results show high dimensionless figure of merit in metallic materials and therefore, we predict these materials can be potential candidates for low temperature thermoelectric applications. Figure of merit for $\text{AlNTi}_3$, $\text{GaCCr}_3$, $\text{AlCNi}_3$, $\text{AlNSc}_3$, $\text{MgCNi}_3$ and $\text{AlCTi}_3$ materials reaches to 0.32, 0.25, 0.19, 0.19, 0.2 and 0.25 respectively, and hence are predicted to be low temperature thermoelectric materials.

The structural, electronic and optical properties of antiperovskite semiconductors, $\text{SbNCa}_3$, $\text{BiNCa}_3$, $\text{SbNSr}_3$ and $\text{BiNSr}_3$ are also studied. The calculated lattice constants for these compounds are found consistent with the available experimentally measured values and other theoretical results. The band profiles show that all of these materials are direct band gap semiconductors with the band gap values of 1.1 eV, 1.09 eV, 0.92 eV and 0.81 eV for $\text{SbNCa}_3$, $\text{BiNCa}_3$, $\text{SbNSr}_3$ and $\text{BiNSr}_3$ respectively. The direct band gap nature reveals that they may be effective in optical devices and therefore the optical properties of these compounds like the real and imaginary parts of dielectric function, refractive index and absorption coefficient are calculated and discussed. Furthermore, the thermoelectric properties of these semiconductors are also calculated. Our results show high values of Seebeck coefficient for these materials between -0.25 eV and 0.25 eV chemical potential values.
Dedicated
To
My Parents
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Chapter 1
Introduction

Materials science deals with the physical and chemical properties of compounds for their efficient use in the various fields of science and technology. Various experimental and theoretical techniques are used to design/model different materials like metals, semimetals, half metals, semiconductors, insulators and superconductors for their possible applications in the high-tech devices. These materials have enormous impact on the present day human civilization and still search is on peak for materials with better performance and small size for example smart materials are needed for the new generation phones, computers and solar cells, while lighter but strong materials are required to make automobiles and airplanes. Therefore, materials scientists are searching for compounds with unique physical properties for advanced technological applications with huge economic impact [1].

A vast number of materials in the earth crust adopt perovskite like structure with general formula $ABX_3$, where A and B are cations and X is anion. Different structures, like cubic [2], orthorhombic [3], tetragonal [4], rhombohedral [5], and hexagonal [6] are found in perovskites. Antiperovskite materials are inorganic compounds, having perovskite like structure with the positions of anions and cations interchanged [7]. These antiperovskites have attracted significant attention of the researchers in the past decade due to their industrial applications [8]. Some of these compounds have wide range of band gaps, which is one of the important reasons for the industrial use of these compounds [9, 10]. The interesting physical properties like giant magnetoresistance (GMR) [11], nearly zero temperature coefficients of resistivity [12], and magnetostriction [13] make some other members of antiperovskites family quite attractive. These
properties make them very useful in industrial applications as GMR, used in magnetic field sensors, which are used to read data in hard disk drives, biosensors, microelectromechanical systems (MEMS), and other devices. Similarly, zero temperature coefficient of resistivity makes them suitable materials for all weathers. Along with these applications, antiperovskites also show excellent mechanical properties [14–16], which make them useful in automobiles and space technology, as these technologies need materials with light weight and large mechanical strength.

In 2001, first antiperovskite material MgCNi$_3$ was reported to have superconductivity below 8K temperature [17]. This finding opened new avenues in research, regarding antiperovskites family. Literature reveals that other materials like CdCNi$_3$ and ZnNNi$_3$ also show superconductivity [18]. These compounds have immense potential to solve energy crisis as these materials have good thermoelectric (TE) properties [19]. The family of antiperovskite materials has all kind of compounds including metals, semiconductors, insulators, and superconductors, which make them applicable in various technologies. In batteries, solids having super ionic conductance are considered better than the organic liquid electrolytes [20] and hence lithium-based antiperovskites can be used as solid electrolytes in batteries [21]. The presence of wide range of band gaps in many antiperovskites make them good candidates for optical devices and researchers around the globe are taking keen interest in the optical properties of antiperovskites [10, 22, 23].

Density functional theory (DFT) has made its place in the world of physics and chemistry soon after its discovery. During the last three decades, DFT has been proved to be the most efficient theoretical tool in physics and chemistry because of its diverse applications [24]. Research opportunities are vast in computational methods and researchers can apply new ideas easily as compared to the experimental techniques. The existing knowledge about the materials is
used to determine unknown properties which helps in predicting the possible utility of the materials in industry. Computational methods only require the composition of materials like lattice constant, atomic positions and space group to calculate various physical properties [25]. Different physical properties of the modeled materials can be predicted even if the experimental parameters are not known, which means materials engineers can design new materials before they are synthesized through experimental techniques. This gives the advantage of predicting the properties of new materials, and thus provides a defined direction for the experimentalists. On the other hand, in computational methods researchers have full control over all input parameters and can study the effects of slight change in temperature, pressure, lattice parameters and any other change in the system. This makes computational methods far more interesting than experimental techniques. DFT is a quantum mechanical approach in which many body problem is solved easily. In 1960's Hohenberg and Kohn [26] introduced DFT and in acknowledgment of this achievement Walter Kohn and John A. Pople were awarded Nobel Prize [27] in chemistry in 1998. Different physical properties like structural, electronic, optical, elastic and thermoelectric properties are investigated using DFT and on comparing to experimental results, it has been proved very successful.

Density functional theory is used to investigate structural, electronic, optical and thermoelectric properties of antiperovskites. The structural, electronic and optical properties are calculated by using the full potential linearized augmented plane wave (FP-LAPW) method within the sphere of the density functional theory (DFT) [28,29] as implemented in the WIEN2k package [30], whereas the thermoelectric properties are calculated by using the BoltzTraP code [31]. In addition to local density approximation (LDA) and generalized gradient approximation (GGA) we also used modified Becke Johnson (mBJ) and improved mBJ exchange potentials
[32-34] along with GGA to handle the exchange-correlation for achieving better band gaps for the semiconductors. Furthermore, spin-orbit coupling is applied to some of these compounds to explore the relativistic effects in these compounds. The electronic properties are explained by using the plots of the electronic band structures and density of states. In thermoelectric properties, we calculated Seebeck coefficient, electronic thermal conductivity and electrical conductivity of materials. Figure of merit for thermoelectric properties show interesting results. This work will provide a deep insight to the possible utility of antiperovskites materials in industrial applications.

The thesis is comprised of five chapters. In first chapter, we present a brief introduction to the problem. The literature of antiperovskites is reviewed in chapter 2. Third chapter contains the details of research methodology used to solve the problem. Results are discussed in chapter 4 and the work is concluded in chapter 5.
Chapter 2
Literature Review

Antiperovskite type crystal structure has general formula \( AXB_3 \), where A and X are anions while B is cation. The B atoms make twelve fold symmetry being at the center of the edges of the unit cell, A atom at the center and X atoms at the corners of the unit cell. Generally, B atoms make octahedral coordination being at the face centers of the unit cell, A atom at the corners and X atom at the center [35] as presented in Fig. 2.1.

The first perovskite material \( \text{CaTiO}_3 \) was discovered by Gustav Rose [36] and he named it after a Russian mineralogist Lev Perovski. Perovskites have different types like simple perovskites (\( \text{KMnF}_3 \) [37] and \( \text{SrTiO}_3 \) [38]), antiperovskites (\( \text{SbNCa}_3 \) and \( \text{BiNCa}_3 \) [35]), inverse perovskites ((\( \text{Eu}_3\text{O})\text{In} \) and (\( \text{Eu}_3\text{O})\text{Sn} \) [39]), double perovskites (\( \text{SrLaVMoO}_6 \) [40]), and double antiperovskites (\( \text{Na}_6\text{FCl(SO}_4)_2 \) [41]) depending on the composition and chemistry of the constituent elements of the material. Most of the antiperovskite materials usually crystallize in cubic \( \text{Pm3m} \) (221) where A atom is located at \((0, 0, 0)\), X atom at \((0.5, 0.5, 0.5)\) and B atoms at \((0, 0.5, 0.5), (0.5, 0, 0.5) \) and \((0.5, 0.5, 0)\) [42]. Figure 2.1 represents cubic antiperovskite unit cell with green spheres as A atoms, brown sphere represents X atom and grey spheres represent B atoms.

The electronic properties of antiperovskites can be divided into two groups; Group II-A based antiperovskites materials which are semiconductors and transition metals based antiperovskites materials which are metals. In the preceding sections we will discuss about Group II-A based antiperovskites and transition metals based antiperovskites as well as thermoelectric properties of antiperovskites.
Figure 2.1: Crystal structure of cubic antiperovskite (AXB$_3$) with octahedral coordination, where green spheres represent A atoms, brown sphere represents X atom and grey spheres represent B atoms.
2.1 Group IIA based antiperovskites materials

Group IIA elements are very important due to their diverse applications in electronics [43], mechanical engineering [44] and military [45]. These elements have two electrons in their outer most shell and can easily loose them to make ionic bonds in general. There are many antiperovskite materials which have a group II-A element at face center of the unit cell making octahedral coordination. Chern et al. [35] synthesized calcium based antiperovskite material BiNCa$_3$, by mixing and pressing powders of Ca$_3$N$_2$ and Bi into a pellet and afterwards heating the pellet at 1000°C in flowing, dry N$_2$ gas. They substituted Bi with other trivalent elements; P, As, Sb, Ge, Sn, and Pb, and found the same result as expected. They reported that all these materials occur in cubic structure except PNCa$_3$ and AsNCa$_3$ which have distorted orthorhombic structure due to small P$^{3-}$ and As$^{3-}$ atomic size. The resistivity measurements show that PbNCa$_3$, SnNCa$_3$, and GeNCa$_3$ materials are metallic in nature, BiNCa$_3$, and SbNCa$_3$ are semiconductors with small band gaps while AsNCa$_3$ and PNCa$_3$ show insulating behavior with structural phase transitions.

Different researchers have theoretically investigated the electronic properties like band structures and density of states of these materials for the deep understanding of their relevant behavior in other physical properties. Papaconstantopoulos et al. [46] studied the electronic properties of BiNCa$_3$ and PbNCa$_3$ using local density approximation (LDA) which generally underestimates band gaps. The authors show that BiNCa$_3$ is a narrow band gap semiconductor and PbNCa$_3$ is a metallic material confirming the experimental results. Pb has one electron less than Bi and BiNCa$_3$ has a very small band gap, therefore PbNCa$_3$ was expected to be a metal. The valences of the constituent elements in BiNCa$_3$ gives an ionic picture of the compound
however, authors argue that at the same time strong covalent mixing is present due to p-states of Bi and N.

Vansant et al. [47, 48] studied pressure dependent structural and electronic properties of PNCa$_3$, AsNCa$_3$ and BiNCa$_3$ using LDA. They verified that at ambient temperature and pressures AsNCa$_3$ and PNCa$_3$ adopt orthorhombic structure with Pbnm space group while BiNCa$_3$ is a simple cubic with Pm3m space group [47]. It is also worth noting that the orthorhombic AsNCa$_3$ structure turns out to be more stable than the cubic SC5 structure with increasing pressure whereas band gap decreases with pressure for this material. At 59 GPa pressure, AsNCa$_3$ shows a phase transition to cubic SC15 with 15 atoms per unit cell.

Moakafi et al. [22] studied elastic, electronic and optical properties of cubic antiperovskites SbNCa$_3$ and BiNCa$_3$. The authors used three different potentials i.e. LDA, generalized gradient approximation (GGA) and Engel Vosko (EV-GGA) to investigate the electronic properties of these materials and obtained band gaps of 0.65 and 0.36 eV for SbNCa$_3$ and BiNCa$_3$, respectively. Their work shows that EV-GGA is a better technique than LDA and GGA for the calculation of the band structures of these materials. However, the authors got wider band gaps using EV-GGA but the valance bands crossing the Fermi level shows metallic behavior of these materials which is in contradiction to the experimental results.

Chi et al. [49] synthesized magnesium-based antiperovskites, AsNMg$_3$ and SbNMg$_3$, by the reaction of pnictogen with Mg$_3$N$_2$ at 800°C and investigated structural, transport and magnetic properties of these materials. The authors report cubic structures for both materials with no distortion. Both materials show ionic bonding with negative 3 valence of As, Sb and N. The authors classified both materials as semiconductors based on their resistivity data. Paramagnetic behavior is observed according to low-field magnetization data obtained at 50 G.
Shein and Ivanovski [50] studied the electronic band structure and chemical bonding in AsNMg\textsubscript{3} and SbNMg\textsubscript{3} antiperovskite materials using GGA. Both materials show narrow band gap ionic semiconducting behavior. AsNMg\textsubscript{3} has direct band gap while SbNMg\textsubscript{3} shows indirect band gap nature.

Okoye [10] discussed structural, electronic and optical properties of AsNMg\textsubscript{3} and SbNMg\textsubscript{3} using the full potential augmented plane waves plus local-orbital (APW+ lo) method. The GGA scheme was used for the electronic and optical properties of these materials. This was the first study on the optical properties of these materials. In this work, the author verified the previous results [10], and confirmed that both materials have narrow band gaps with AsNMg\textsubscript{3} possessing direct band gap whereas SbNMg\textsubscript{3} reveals indirect band gap nature. The author argues that as DFT usually underestimates band gaps therefore the calculated positions of the optical spectrum may be smaller than the experimental values. The imaginary part of dielectric function, presented in their work, also confirms the semiconducting behavior of the materials.

Bouhemadou and co-authors [9, 51] investigated the structural, electronic, elastic and optical properties of AsNMg\textsubscript{3} and SbNMg\textsubscript{3} materials using pseudo-potential plane wave method (PP-PW) within the generalized gradient approximation (GGA). For AsNMg\textsubscript{3} the fundamental direct band gap initially increases up to 4 GPa and then decreases as a function of pressure, concurrently retaining its direct band gap nature in the entire pressure range, while SbNMg\textsubscript{3} shows transition from fundamental indirect band gap to direct band gap nature as pressure reaches to 6.85 GPa. These were the first theoretical studies on elastic properties of these materials. Later on, Belaroussi et al. [52] studied the structural and elastic properties of SbNMg\textsubscript{3} theoretically and compared their studies with this work.
Amara et al. [53] investigated the structural, elastic and electronic properties of PNMg₃, AsNMg₃, SbNMg₃ and BiNMg₃ using the full-potential augmented plane wave plus local orbital (FP-LAPW+lo) method within the DFT, while treated the exchange and correlation effects by the mBJ-GGA for the band structures, density of states and charge densities. This was the first study on PNMg₃ and BiNMg₃ antiperovskite materials. All materials show semiconducting behavior where PNMg₃ and AsNMg₃ are direct band gap materials while SbNMg₃ and BiNMg₃ are indirect band gap materials. The authors achieved largest values of band gaps as compared to previous studies due to the use of mBJ potential. The elastic properties show that PNMg₃ is the hardest while BiNMg₃ is the softest material out of all. Increase in the covalent nature is observed in these materials in moving from BiNMg₃ to PNMg₃.

Beznosikov [54] worked on nitrides with antiperovskite structure and analytically calculated lattice parameters of AsNSr₃, SbNSr₃ and BiNSr₃ materials. Gäbler et al. [55] synthesized SbNX₃ and BiNX₃ (X=Sr and Ba) antiperovskite materials in 2004 for the first time. The compositions were derived from chemical analyses and supported by Rietveld refinements based on powder X-ray diffraction patterns. SbNSr₃ and BiNSr₃ are found in cubic (Pm3m) while SbNBA₃ and BiNBA₃ are found in hexagonal (P63/mmc) structure. The authors reported magnetic, electronic, optical and bonding properties of these materials. The electrical resistivity studies show that these materials are semiconductors. The optical band gaps of 1.15 eV for SbNSr₃ and 0.89 eV for BiNSr₃ are measured by diffuse reflectivity method. The authors also calculated the electronic band gaps by DFT employing LDA and received small values arguing that LDA severely underestimates band gaps of crystalline materials. The susceptibility measurements show that the materials are diamagnetic.
Haddadi et al. [56] worked on the structural, elastic and electronic properties of ANSr$_3$ (A = As, Sb and Bi) materials in 2009 using CASTEP code, in which the plane-wave pseudo-potential total energy method is employed. The authors used theoretical lattice parameters from Ref. [54] instead of using experimental lattice parameters from Ref. [55] for optimization. Surprisingly, the lattice parameters achieved by the authors exactly matched with the experimental data. The band gap values of 0.49, 0.31 and 0.26 eV, are calculated for AsNSr$_3$, SbNSr$_3$, and BiNSr$_3$ materials, respectively which are underestimated from their experimental optical band gaps [55] (see table 1).

Hichour et al. [23] in 2010, studied pressure dependent elastic, electronic and optical properties of ANSr$_3$ (A=As, Sb and Bi) antiperovskites materials. The authors used EV-GGA potential to improve the band gaps of these materials and achieved 0.84, 0.55 and 0.36 eV for AsNSr$_3$, SbNSr$_3$ and BiNSr$_3$, respectively. The band gap values decrease for all materials as pressure increases. The charge density plots show that these materials have mixed covalent and ionic bonding nature. The semiconducting behavior for SbNSr$_3$ is also evident from the imaginary part of the dielectric function as presented in their work.

Haddadi et al. [57] investigated structural, elastic and electronic properties of the hexagonal antiperovskites SbNBa$_3$ and BiNBa$_3$ using Wu-Cohen generalized-gradient approximation (GGA-WC). The authors achieved the band gap of 0.529 eV for both of these materials which is consistent with the previous theoretical work [55]. Both materials show direct band gap semiconducting nature on ambient pressure. The band gap decreases with pressure and pressure-induced metallization is predicted at 7.95 and 8.02 GPa pressure for SbNBa$_3$ and BiNBa$_3$, respectively.
Hichour et al. [58] studied the structural and elastic properties of cubic SbNBA$_3$ and BiNBA$_3$ materials comparing structural results with theoretical data from Ref. [54]. Jha and Gupta [59] also worked on the lattice dynamic study of antiperovskite compounds AsNBA$_3$ and SbNBA$_3$ in cubic structure. The authors presented metallic band structures of these materials which are in contradiction with the experimental work [55].
Table 1. Experimental and theoretical band gap values (in eV) of semiconductor antiperovskite materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>Experimental band gap</th>
<th>LDA</th>
<th>GGA</th>
<th>EVGGA</th>
<th>mBJ</th>
</tr>
</thead>
<tbody>
<tr>
<td>SbNCa₃</td>
<td>Semiconductor[^35]</td>
<td>0.13[^22],</td>
<td>0.33[^22],</td>
<td>0.65[^22]</td>
<td></td>
</tr>
<tr>
<td>BiNCa₃</td>
<td>Semiconductor[^35]</td>
<td>0.1[^46],</td>
<td>0.08[^22],</td>
<td>0.36[^22]</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>.28[^46],</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.11[^22]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AsNCa₃</td>
<td>Insulator[^35]</td>
<td>0.87[^46]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PNCa₃</td>
<td>Insulator[^35]</td>
<td>1.1[^46]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AsNMg₃</td>
<td>Semiconductor[^49]</td>
<td>1.332[^50,10],</td>
<td>2.41[^53],</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.455[^51],</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SbNMg₃</td>
<td>Semiconductor[^49]</td>
<td>0.623[^50],0.866[^9],</td>
<td>1.48[^53],</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.726[^10],</td>
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</tr>
<tr>
<td>PNMg₃</td>
<td></td>
<td></td>
<td></td>
<td>2.6[^53],</td>
<td></td>
</tr>
<tr>
<td>BiNMg₃</td>
<td></td>
<td></td>
<td></td>
<td>1.42[^53],</td>
<td></td>
</tr>
<tr>
<td>SbNSr₃</td>
<td>Semiconductor</td>
<td>0.31[^56],</td>
<td>0.55[^23]</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.15[^55]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BiNSr₃</td>
<td>Semiconductor</td>
<td>0.26[^56],</td>
<td>0.36[^23]</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.89[^55]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AsNSr₃</td>
<td></td>
<td>0.49[^56],</td>
<td>0.84[^23]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SbNBA₃</td>
<td>Semiconductor[^55]</td>
<td>0.529[^57],</td>
<td></td>
<td>metallic[^59]</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>metallic[^59]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BiNBA₃</td>
<td>Semiconductor[^55]</td>
<td>0.529[^57],</td>
<td></td>
<td>metallic[^59]</td>
<td></td>
</tr>
</tbody>
</table>
2.2 Transition metals based antiperovskites materials

Since 1960s, extensive research has been carried out on the different physical properties of manganese based antiperovskites materials with general formula AXMn$_3$ (A is a metal or semiconducting elements, X is C or N) [60]. Mn based antiperovskites gained huge attention of the researchers as different properties like giant magnetoresistance (GMR) and magnetocaloric effect of GaCMn$_3$ [11,61], negative or zero thermal expansion (NTE or ZTE) of Cu(Ge)NMn$_3$ [62], nearly zero temperature coefficient of resistance (TCR) of Ag$_{1-x}$Cu$_x$NMn$_3$ [63] and giant magnetostriction (GMS) of CuNMn$_3$ [13] are reported. These materials show metallic behavior. The 3d orbitals of Mn have high density of states at Fermi level ($E_F$) while hybridization between X-p states and Mn-d states is the main cause of wide conduction band crossing over the Fermi level [64]. Sun et al. [8] reported unusual phase separation and irregularity in the electronic transport properties of ZnNMn$_3$. The authors further presented [65] the thermodynamic, electromagnetic, and structural properties of antiperovskite SbNMn$_3$. The authors found that at room temperature the materials exist in tetragonal structure with lattice parameters $a=b=4.17994\text{Å}$ and $c = 4.27718\text{Å}$. Wang et al. [66] studied the structural, magnetic, electrical transport properties, and reversible room-temperature magnetocaloric effect in antiperovskite compound AlCMn$_3$. The material shows good metallic behavior with ferromagnetic-paramagnetic phase transition at $T_C=287\text{ K}$. GaCMn$_3$ is a widely studied antiperovskites material [11,67,68]. It is a metallic material with paramagnetic behavior at ambient temperature. GaCMn$_3$ shows transition and becomes ferromagnet (FM) at 163.9 K and paramagnet (PM) at 245.8 K [11]. Shim et al. [64] studied the electronic properties of GaCMn$_3$, ZnCMn$_3$, SnCMn$_3$ and ZnNMn$_3$ using linearized muffin-tin orbital (LMTO) method in the local spin density approximation (LSDA). The electronic properties are calculated in paramagnetic state for these
materials. The density of states for GaCMn$_3$ show strong hybridization between Mn-3d and C-2p states which increases bonding states between -3eV and -7eV whereas the nonbonding states Mn-3d are at the Fermi level.

After the discovery of superconductivity in MgC Ni$_3$ [17], Ni based isostructural antiperovskites materials have gained enormous attention among the researchers [18]. Uehara et al. [69,70] reported superconductivity in CdC Ni$_3$ and ZnNNi$_3$ antiperovskites with transition temperatures of 3.2 and 3 K, respectively. Shim et al. [71] studied the electronic properties of MgXNi$_3$ (X=B, C and N). Ni-3d and C-2p states form the antibonding sub-band near Fermi level in MgC Ni$_3$ with Ni-3d dominant character. The DOS’s for MgXNi$_3$ reveals that changing X, changes the density of states near the Fermi level with B-2p state in MgBNi$_3$ is located higher in energy than the C-2p state of MgC Ni$_3$, and so the hybridization with Ni-3d is stronger.

Johannes and Pickett [72] studied the electronic structure of ZnC Ni$_3$ and showed that no superconductivity is found in this material down to 2 K. According to the authors the absence of superconductivity in ZnC Ni$_3$ as compared to MgC Ni$_3$ can only be explained by assuming Mg deficient in this material. Wu et al. [73] investigated the structure, electronic and magnetic state of InC Ni$_3$ antiperovskite material using LDA and GGA. The authors reported that the material is paramagnetic with strong hybridization between Ni-3d and C-2p states. Hou [74] studied the elastic properties and electronic structures of InNC O$_3$ and InNNi$_3$ antiperovskite materials. Due to the different strength of 2p-3d hybridization for the N-Co atoms in InNC O$_3$ and the N-Ni atoms in InNNi$_3$, InNC O$_3$ is ferromagnetic while the ground state of InNNi$_3$ is non-magnetic. Li et al. [75] investigated the mechanical and electronic properties of MN Ni$_3$ (M=Zn, Mg, or Cd). The maximum states are occupied by Ni-3d and N-2p hybridization near the Fermi level while M elements have very small contribution here. However, this small contribution of M elements may
cause a small shift in the bands near the Fermi level, resulting superconductivity in ZnNNi$_3$ at $T_c \approx 3$ K while the other two compounds do not show superconductivity.

Grandjeant and Gerard [76] synthesized and studied the structural and magnetic properties of ACFe$_3$ (A=Al, Zn, Ga, Sn and Ge) antiperovskites materials. Fe based antiperovskites materials have been investigated by different researchers [109,110,77-79]. Ivanovski et al. [80-82] reported the electronic properties of these materials, while the electronic band structure of the cubic antiperovskites $M_3M'C$ ($M=Mn, Fe$; $M'=Zn, Al, Ga, Sn$) in ferromagnetic state are calculated by using LMTO-ASA nonempirical self-consistent method [80]. All materials have high density of states at Fermi level mainly due to Fe-3d states and show metallic behavior. Furthermore, the authors show that these materials are ferromagnetic in nature.

Tian et al. [83] performed transmission electron microscopy on AlCTi$_3$. Subsequently different researchers investigated the physical properties like electronic, mechanical and thermal properties of this material using different techniques [84-88]. Lie [85] studied the electronic properties of this material using GGA potential. The band structure presented by the author shows that this is a metallic material. The density of states is also discussed for the understanding of the different states at Fermi level. The strong hybridization between Ti-3d and Al-3p states and between Ti-3d and C-2p states stabilizes the structure of Ti$_3$AlC. Medkour et al. [88] studied the structural, elastic and electronic properties of ACTi$_3$ (A=Al, In and TI) antiperovskites materials using first principle calculations. All of these materials show metallic character with strong covalent bonds between Ti and C atoms, and ionic bonds along A and Ti atoms. The authors suggest that the stiffness decreases with the increase in the antibonding state between Ti and A atoms.
Brady et al. [89,90] worked on the synthesis of chromium based nitride antiperovskites PtNCr$_3$. Wiendlocha et al. [91] studied the electronic properties, superconductivity and magnetism in GaNCr$_3$ and RhNCr$_3$ materials. The band structures of these materials presented in the paper show that both materials are metallic in nature. The spin-polarized calculations show non-ferromagnetic ground state for both compounds. The authors are of the opinion that there may be superconductivity in these materials because of the high values of electronic part of electron–phonon coupling constant. Tutuncu and Srivastava [92] theoretically investigated structural, electronic, vibrational, and superconducting properties of the cubic antiperovskite RhNCr$_3$. The authors claim that this material is metallic with superconducting nature below 17 K.

Shao et al. [93] studied the structural, elastic and electronic properties of ACCr$_3$ (A = Al and Ga) antiperovskite materials using first principle methods. The analysis of formation energies shows that both materials can be synthesized at ambient pressure and are nonmagnetic in nature. The band structures show that the materials are metallic in nature. Shao et al. [94] investigated the electronic structure, magnetic properties, and lattice dynamics of the AXCr$_3$ (X=C or N, A=Zn, Al, Ga, Sn, Ag, Cd, Mg and In) using ABINIT code. The authors claim that among the nitride materials only ZnNCr$_3$, AlNCr$_3$, GaNCr$_3$, and SnNCr$_3$ can be synthesized for having negative formation energies. Furthermore, all materials show metallic nature with AlCCr$_3$, GaCCr$_3$, and ZnNCr$_3$ being the potential candidates of superconductivity.

Optical properties of antiperovskite materials are of immense importance. Table 1 shows variety of band gaps available in this family of compounds which make them suitable for investigation of optical properties. The response of a material to the incident photons is very important as it changes the internal chemistry of the material. Electrons gaining energy from the
photons change their state which results in different interesting phenomena. AsNMg₃ and PNMg₃ show the band gap values of 2.41 and 2.6 eV, respectively [53]. Literature clearly shows that these materials can be used in opto-electronic devices for industrial applications [9,10,22,23,51].

2.3 Thermoelectric Materials

The field of thermoelectrics has gained much attention of researchers in recent years [95]. Efficient thermoelectric materials can give solution to energy crisis [96-98]. Fossil fuel is the main source of generating electricity but in this conventional method, much of the heat is wasted in the environment. This causes loss of fuel at one hand and global warming at the other hand. Part of this waste heat can be converted into useful energy in TE devices, which makes them a good source of green energy [99]. Thermoelectric generators are solid-state devices with no moving parts; they are silent, reliable and scalable, making them ideal for power generation [100]. In TE devices, thermoelectric materials are used in which heat is directly converted to electrical energy [101]. Despite vast research in this field, efficiency of TE generators is still very low as compared to conventional engines and researchers are trying to find such materials which could improve the efficiency of TE generators.

The performance of a TE device is measured by a dimensionless figure of merit ZT. Materials having ZT about unity or greater than unity are considered excellent candidates for thermoelectric devices [102, 103]. Materials scientists are searching for efficient TE materials to be used in industrial applications. ZT depends on Seebeck coefficient, thermal conductivity and electrical conductivity of a material as:

\[
ZT = \frac{\alpha S^2 T}{\kappa} \quad \text{.................................................. (2.1)}
\]
where $S$ represents the Seebeck coefficient, $\sigma$ the electrical conductivity and $k$ is the thermal conductivity of a material.

In thermoelectrics, free charge carriers in metals and semiconductors are the cause of generating electric energy. Temperature gradient at the ends of a TE material causes the flow of charge carriers from hot end to the cold end. Along the charge, heat also travels with these carriers in the materials. In Seebeck effect electromotive force is generated in p-type and n-type materials connected in series and thermally in parallel as shown in figure 2.2. Seebeck observed this effect in 1823 and after twelve years, a complementary effect was discovered by Jean Charles Peltier, who observed that heat is absorbed or generated at a junction between two dissimilar conductors when a current is passed, depending on the direction of the current flow [101]. The voltage generated depends on the Seebeck coefficient $S$ and the temperature difference between the two junctions in the thermocouple, as [104].

$$V = S\Delta T \quad \cdots \quad (2.2)$$

Where $V$ is the electric voltage, $\Delta T$ is the temperature difference at the ends of the materials and $S$ is the Seebeck coefficient. The Seebeck coefficient is the entropy transported with a charge carrier divided by the charge carrier’s charge [105]. Voltage can be increased by increasing the temperature difference thus the melting point of the material limits the maximum voltage [104].
Figure 2.2: Schematic diagram of Seebeck effect.

Figure of merit of a thermoelectric material is inversely proportional to thermal conductivity $\kappa$ of a material. It is the transfer of heat from one part of a material to the other part. Thermal conductivity consists of two parts; electronic thermal conductivity $\kappa_e$ and lattice thermal conductivity $\kappa_l$ as:

$$\kappa = \kappa_e + \kappa_l \quad \text{............................................ (2.3)}$$

In metals, thermal conductivity mostly consists of electronic part only [106, 107] as there are free electrons available for conduction of heat while in semiconductors, major part of thermal conductivity consists on lattice thermal conductivity [104]. Electrical conductivity of a bulk material is directly proportional to the thermal conduction as described by the Wiedemann-Franz law [108]:

$$\kappa = \frac{3k_B^2}{2e^2} \sigma T \quad \text{............................................ (2.4)}$$
Where $\kappa$ is the total thermal conductivity, $\sigma$ is electrical conductivity, $k_B$ is the Boltzmann’s constant, $e$ is the electronic charge, and $T$ is the temperature. This makes the task of tuning efficient thermoelectric materials much difficult for the researchers as we need materials with high electrical conductivity which also increases the thermal conductivity of the material. This is the reason that despite vast research in thermoelectrics in recent years, researchers are unable to present thermoelectric generators as alternative to conventional sources of energy.

Alloys of bismuth telluride with figure of merit approaching to unity are available in industry [100]. Lin et al. [109] studied the electrical/thermal transport properties of ZnC$_x$Fe$_3$ (1.0 $\leq x \leq$ 1.5) and showed that ZnC$_{1.2}$Fe$_3$ can be a potential thermoelectric material with the dimensionless figure of merit reaching its maximum value of 0.0112 around 170 K. Maruoka and Suzuki [110] worked on phase equilibria and Seebeck coefficient of (Co,M)$_3$AlC (M=Fe or Ni) and found the maximum Seebeck coefficient of 23.3 $\mu$V/K at 873 K for Co$_3$AlC$_{0.63}$. Lin et al. [111] investigated the Seebeck coefficient and thermal conductivity of GaNCr$_3$. The author also worked on different antiperovskites materials and found SnCCo$_3$ has the largest value of figure of merit [112].

Thermoelectric properties of a material are very sensitive to the electronic structure of the material. Therefore, materials with one kind of charge carriers are desired for thermoelectric devices. In materials with large band gap values, n-type and p-type carriers can be separated, and doping can produce desired type of TE materials. Thus, good thermoelectric materials typically have band gaps large enough to have a large Seebeck coefficient, but small enough to have a sufficiently high electrical conductivity [113]. Therefore, semiconductors with narrow band gaps are considered ideal candidates for thermoelectric devices [114]. Secondly, dense electronic
states near Fermi level favor the electrical conductivity. A small change in band structure can result in huge variation in the thermoelectric properties of a material.
Chapter 3
Method of Calculations

The physical properties of a solid depend on the constituent microscopic particles i.e. electrons and nuclei. These particles collectively make a very complicated many body problem to solve. Density functional theory (DFT) proposed the solution of such problems, where in this theory electrons density is used as a fundamental variable instead of the wave function of the system. Consider M electrons with ground state wave function \( \Psi(r_1, \ldots, r_M) \), then the Schrödinger wave equation (spin effects missing) for the system is:

\[
H |\Psi\rangle = \left[ \sum_{a=1}^{M} -\frac{1}{2} \nabla_a^2 + \sum_{a \neq b} \frac{1}{|r_a - r_b|} + \sum_{a=1}^{M} V(r_a) \right] |\Psi\rangle = E |\Psi\rangle \quad \text{..........................(3.1)}
\]

Where \( H \) is Hamiltonian operator and \( E \) is total energy of the system. The first term in the above equation is the kinetic energy of electrons, the second term is the Coulombic interaction of electrons and the third term is the external potential. This is a second order differential equation for \( M \) particles with \( 3M \) degree of freedom. The solution to this equation is very complicated. In DFT, electron density \( \rho_0(r) \) is used as variable instead of wave functions of particles:

\[
\rho_0(r) = M \int d\sigma dx_2 \ldots dx_M \langle \Psi(r, \sigma, x_2, \ldots, x_M) | \Psi(r, \sigma, x_2, \ldots, x_M) \rangle \quad \text{..........................(3.2)}
\]

In equation 3.2 spin effects are also added which are represented by \( \sigma \). The electron density \( \rho_0(r) \) only depends on space with three degree of freedom, thus simplifying problem from \( 3M \) to \( 3 \) variables. The significance of this theory is revealed by the fact that DFT is the most commonly used tool for research [24].
In 1927, electron density was first time used as a basic variable replacing wave function for homogeneous electron gas, by Thomas and Fermi called Thomas-Fermi (TF) model [115, 116]. The kinetic energy of M particles according to this theory is:

\[ T_{(TF)}[\rho_0] = \frac{3}{10} (3\pi^2)^{\frac{2}{3}} \int \rho_0(r) \frac{5}{3} r^2 d^3r \] 

(3.3)

where \( \rho_0 \) is the electron density of the system. This model was not very successful because the exchange and correlation energies were not included.

Hohenberg and Kohn modified the TF model in 1964, presenting two fundamental theorems known as density functional theory [26]. The first theorem states that for any interacting system of particles in an external potential \( V(r) \) the total energy of the system is uniquely determined by its electronic density;

\[ E[\rho_0] = F_{HK}[\rho_0] + \int V(r) \rho_0(r) d^3r \] 

(3.4)

Where \( E[\rho_0] \) is the total energy and \( F_{HK}[\rho_0] \) is a universal functional independent of external potential and depends on the intrinsic properties of a materials. The second theorem states that the global minimum possible value of the functional \( F_{HK}[\rho_0] \) gives the exact ground state energy \( E_0 \) and the electronic density will be the exact ground state density [26].

\[ E_0 = \min_{\rho \rightarrow \rho_0} E[\rho] = E[\rho_0] \] 

(3.5)

The variation principle is used to determine ground state energy. This theorem shows that energy is a functional of electron density for a system and proves that the correct ground state electron density minimizes the energy functional [117].

Kohn-Sham (KS) in 1965 formulated DFT as an actual technique for many body electron system including the strong electronic correlation, representing them in terms of non-interacting electrons system, obtained exactly the ground state density \( \rho_0 \) and ground state energy (\( E_0 \)) [29].
The kinetic energy of the system can be calculated for a non-interacting system of electrons, using single particle wave function ($\phi_i$):

$$ T_s = \sum_{a=1}^{M} \langle \phi_a | -\frac{1}{2} \nabla^2 | \phi_a \rangle $$

Where $T_s$ is KS functional kinetic energy of the system while total energy can be expressed as:

$$ E[\rho_0] = T_s[\rho_0] + U[\rho_0] + E_{xc}[\rho_0] + \int V(r)\rho_0(r)d^3r $$

Here $U[\rho_0]$ is electrostatic (Hartree) energy of the particles, $E_{xc}[\rho_0]$ is exchange-correlation energy (consists of unknown spin-dependent terms) and $V(r)$ represents external potential. The exchange-correlation functional $E_{xc}[\rho_0]$ has no exact solution but can only be approximated. Different approximations like local density approximation (LDA), generalized gradient approximation (GGA) as well as further modification of the existing approximations are available for the solution of the problem. LDA, proposed by Kohn and Sham for homogeneous electron system, is the most common technique used in DFT. As it is approximated only for homogeneous systems, therefore it is valid for systems with small varying electronic density. The following equation shows this approximation:

$$ E_{xc}^{LDA}[\rho_0] = \int \rho_0(r)e_{xc}^{LDA}(\rho_0(r))d^3r $$

Here the exchange part of $e_{xc}^{LDA}(\rho_0(r))$ was derived by Dirac [118] while the exact solution of correlation term is still unknown and different values are taken from Vosko et al. [119]. Quantum Monte Carlo (QMC) method was used by Ceperley and Alder [120] to determine the total ground state energy for a homogenous electron gas and solved the correlation energy. The deficiencies of LDA are considered in the generalized gradient approximations (GGA) which solves the gradient of electron density. As GGA takes gradient of density, therefore it is better approach for inhomogeneous systems.
This is the GGA equation, where $\nabla \rho_0(r)$ is the density gradient. Different GGA flavors like B88 [121], PBE96 [122], LYP88 [123], PW86 [124, 125], PW91 [126], EV [127] and Wu-C [128] are used in DFT. Spin-orbit coupling (SOC) is of great significance to treat relativistic effects in systems having d-states or f-states elements [129]. Spin and orbital interactions of electrons are treated by the generalized gradient approximations spin-orbit coupling (GGA-SOC). SOC affects the electronic density at the Fermi level that consequently changes different physical properties of a material. GGA-SOC is expressed by the following equation:

$$E_{\text{GGA-SOC}}^{\text{GGA}} = E_{\text{GGA}} + E_{\text{SOC}} \ldots \ldots \ldots \ldots \ldots \ldots (3.10)$$

Where

$$E_{\text{SOC}} = -\frac{\hbar}{4m_0^2c^2} \delta \cdot p \times (\nabla \cdot V_0) \ldots \ldots \ldots (3.11)$$

In equation 3.11, $\delta$ is Pauli spin matrices, $p$ is the momentum operator and $V_0$ represents Coulomb potential of the atomic core.

Though, LDA and GGA successfully calculate different physical properties but they underestimate band gaps of materials in the strongly correlated electrons system. Modified Beck-Johnson (mBJ) [32] exchange potential significantly solved this problem. mBJ potential is expressed as:

$$v_{x}^{\text{TB-mBJ}}(r) = cv_{x}^{\text{BR}}(r) + (3c - 2) \frac{\hbar}{\Pi \sqrt{12}} \frac{2\rho(r)}{\rho(r)} \ldots \ldots \ldots (3.12)$$

Where $v_{x}^{\text{BR}}(r)$ is the Becke-Roussel potential, $\rho(r)$ is the kinetic energy density and $\rho(r)$ is the electron density. The constant $c$ is introduced by Tran and Blaha [32] depending upon the electron density. For $c = 1$, Eq. 3.12 reduces to Beck-Johnson potential (BJ) [33].
where \( c \) is defined as:

\[
c = X + Y \sqrt{g} \quad \ldots \ldots \ldots \ldots \ldots \ldots (3.13)
\]

and

\[
\bar{g} = \frac{1}{v_{\text{cell}}} \int \frac{1}{2} \left[ \frac{\nabla \rho^+(r)}{\rho^+(r)} + \frac{\nabla \rho^-(r)}{\rho^-(r)} \right] d^3r \quad \ldots \ldots \ldots \ldots \ldots \ldots (3.14)
\]

where \( \bar{g} \) is the average of \( g = \nabla \rho / \rho \) and \( \rho \) is the electronic density. In the mBJ potential [32] the values of \( X \) and \( Y \) in equation (3.13) are taken -0.012 and 1.023 (Bohr)\(^{1/2}\), respectively. By minimizing the mean-absolute relative error (MARE) of few solids, Koller et al. [34] improved mBJ potential and introduced new values of \( X=0.488 \) and \( Y=0.500 \) (Bohr)\(^{1/2}\) for large band gap materials and \( X=0.267 \) and \( Y=0.656 \) (Bohr)\(^{1/2}\) for small band gap materials. Hence, the modified equation (3.13) is:

\[
c = X + Y \bar{g} e \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (3.15)
\]

where \( e=1 \) for simplicity.

In the present work all the calculations are carried out using the full potential linearized augmented plane wave plus local orbital (FP-LAPW+lo) method under the domain of density functional theory (DFT) [28, 29] as implemented in the wien2k package [30]. This is very effective method for the calculation of the electronic properties of materials [130, 131]. LAPW+lo method is based on the augmented plane wave (APW) method with larger basis set size. APW technique was developed in 1937 by Slater [132]. The space around the nucleus is divided into two regions on the basis of potential i.e., non overlapping muffin-tin regions with varying potential and interstitial regions with constant potential. Both core and valence electrons are treated relativistically and semi relativistically, respectively. To ensure the treatment of all electrons of the system, semi core states are described with local orbitals. The electronic
structures are calculated with GGA, GGA-mBJ and GGA-SOC. The SOC is used to explore the relativistic effects.

The basic software wien2k [133] used in the present calculations is written in Fortran 90 and supported by linux operating system. Since first package in 1990 [25], several versions of this software like Wien95, Wien97 and Wien2k are developed. Wien2k code is successfully used for approximately all types of materials and can calculate different physical properties of condensed matter.

The thermoelectric properties of the compounds under study like Seebeck coefficients, electronic thermal conductivities and electrical conductivities are calculated by using the BoltzTraP code [31]. The following equations explain the transport coefficients based on the rigid band approach to conductivity:

$$\sigma_{\alpha\beta}(\epsilon) = \frac{1}{M} \sum_{\alpha,\beta} \sigma_{\alpha\beta}(a, l) \frac{\delta(\epsilon - \epsilon_{\alpha\beta})}{\delta(\epsilon)}$$ ...........................................(3.16)

$$\sigma_{\alpha\beta}(\alpha, \beta) = e^2 \tau_{\alpha\beta} v_{\alpha}(\alpha, \beta) v_{\beta}(\alpha, \beta)$$ ...........................................(3.17)

where, $M$ is the number of k-points. Equation 3.17 explains k-dependent transport tensors, where $\tau$ is the relaxation time, and $v_{\alpha}(\alpha, \beta)$ is a component of group velocities. The Transport coefficients, which are function of temperature (T) and chemical potential ($\mu$), i.e. electrical conductivity and Seebeck coefficient tensors, can be found by integrating the transport distribution [31,134]:

$$\sigma_{\alpha\beta}(T, \mu) = \frac{1}{\Omega} \int \sigma_{\alpha\beta}(\epsilon) \left[ - \frac{\partial f_0(T, \epsilon, \mu)}{\partial \epsilon} \right] d\epsilon$$ ....................................................(3.18)

$$S_{\alpha\beta}(T, \mu) = \frac{1}{eT\Omega \sigma_{\alpha\beta}(T, \mu)} \int \sigma_{\alpha\beta}(\epsilon)(\epsilon - \mu) \left[ - \frac{\partial f_0(T, \epsilon, \mu)}{\partial \epsilon} \right] d\epsilon$$ ....(3.19)
where, $\alpha$ and $\beta$ are the tensor indices, $e$ is the electron charge, $\Omega$ is the volume of the unit cell, $\mu$ is the carrier concentration and $f_0$ is the Fermi-Dirac distribution function. The relaxation time, $\tau$, is taken constant in this study. Seebeck coefficient is calculated by the band structure calculations as it does not depend on relaxation time (under the assumption that relaxation time is constant) but electrical conductivity needs to be calculated with respect to the relaxation time.
Chapter 4
Results and Discussions

In this chapter, different physical properties like structural, electronic, optical and thermoelectric properties of various antiperovskite materials are calculated by using the DFT based theoretical tools. The exchange correlation potentials are treated with the LDA, GGA, GGA-SOC, mBJ-GGA and improved mBJ-GGA.

4.1 Electronic and Thermoelectric Properties of Metallic Antiperovskites AXD$_3$ (A=Ge, Sn, Pb, Al, Zn, Ga; X=N, C; D=Ca, Fe, Co)

4.1.1 Introduction

The search for efficient energy resources has been raised in the recent years because of the population growth and industrial development. Over the past decade, there has been a keen interest in exploring efficient thermoelectric (TE) materials for power generation [19]. A sufficiently big quantity of heat is converted into useful energy in TE devices, which makes them a good source of green energy [99]. A key material parameter, related to efficiency is the dimensionless figure of merit, $ZT = \frac{\sigma S^2 T}{k}$, where $\sigma$ is the electrical conductivity, $S$ is the Seebeck coefficient, and $k = k_e + k_l$ is the thermal conductivity, composed of electronic and lattice parts [135-137].

Different research groups have investigated thermoelectric properties of various crystal structures like skutterudites [138], clathrates [139], half-heusler alloys [140], chalcogenides [141], complex oxide [142,143] and perovskites [144,145]. A variety of physical properties of antiperovskite structural compounds have been studied after the discovery of the first antiperovskite superconductor MgCNi$_3$ in 2001 [11,13,17,63,66,68,77,79,146,147,148,149].
However, there are very few reports available [109-111,150,151] on the TE properties of antiperovskites. Very recently, Lin et al. [112] investigated TE properties of Cobalt based antiperovskites. The authors claim that the metallic antiperovskite SnCCo$_3$ has the largest Seebeck coefficient of about 50 $\mu$V/K at room temperature in the antiperovskite family. High values of figure of merit are achieved in materials having large Seebeck coefficient.

Literature clearly shows that there is a vast room for exploring TE properties of metallic antiperovskites. In this section we discuss the density of states of SnCCo$_3$, ANCa$_3$ (A=Ge, Sn and Pb) and BCFe$_3$ (B=Al, Zn, Ga and Sn) antiperovskite materials. The effects of spin-orbit coupling (SOC) on the density of states are also explored. Using these results, we calculate the TE properties of these materials and discuss the effects of SOC on the TE properties. The calculated Seebeck coefficient of SnCX$_3$ (X=Co and Fe) match well with the experimental data [112]. There is no other experimental evidence available on the TE properties of these materials to the best of our knowledge. We predict high values of ZT for these materials. The TE properties of ANCa$_3$ (A=Ge, Sn and Pb) is enhanced due to SOC effects with highest absolute Seebeck coefficient of 730 $\mu$V/K for SnNCa$_3$ at room temperature whereas the TE properties diminish in SnCCo$_3$ and BCFe$_3$ (B=Al, Zn, Sn and Ga) with the SOC. Until now, the metallic material CePd$_3$ has had the highest experimentally reported Seebeck coefficient of 125 $\mu$V/K among metals, [152,153] at 140 K. Therefore, we predict and report a new class of metals which show high Seebeck coefficient. Our results show that figure of merit of these materials can be enhanced at room temperature by changing chemical potential.
4.1.2 Electronic properties

The total density of states of these materials in spin-up states, with the effect of spin orbit coupling (SOC) and without SOC are presented in Fig. 4.1. For the deep understanding of the effects of SOC on the different states of these materials, the partial density of states (PDOS) for PbNCA$_3$ and AlCFe$_3$ are presented in Figs. 4.2 and 4.3, respectively. The PDOS of GeNCA$_3$ and SnNCA$_3$ are similar to the PDOS of PbNCA$_3$ while the PDOS of ZnCFe$_3$, SnCCo$_3$, SnCFe$_3$ and GaCFe$_3$ are similar to AlCFe$_3$ and are not presented to avoid repetition. It is evident from Fig. 4.2 that the SOC effect splits the Pb-p state into Pb-pz and Pbpx+py states in PbNCA$_3$. After splitting, the combined effect of Pb-pz and Pb-px+py states increases the density of Pb-p states at the Fermi level. A very small increase in the width of Pb-p states is also observed due to SOC effects. Similarly, SOC effect splits N-p states into N-pz and N-px+py states whereas a small increase in the width of N-p states is also observed. In case of calcium, Ca-dxz+dyz states are split into Ca-dxz and Ca-dyz states at the Fermi level due to SOC effect. The Ca-dyz states shift towards the Fermi level which increases the density of states at the Fermi level. Therefore, the effect of SOC increases the density of states at the Fermi level in PbNCA$_3$, which logically enhances the thermoelectric properties of the material.

Figure 4.3 shows the PDOS for AlCFe$_3$. Though the Al-p state and C-p states split due to SOC effect, the splitting does not increase the density of states at the Fermi level. Secondly, the contribution of these states at the Fermi level is very small for these elements. Fe-d states are dominant as compared to Al and C states where Fe-dxz+dyz states split into Fe-dxz and Fe-dyz states due to SOC effect. In contrast to Ca-dyz states in PbNCA$_3$, Fe-dyz states in AlCFe$_3$ shift away from the Fermi level, hence decreasing the density of states at the Fermi level which eventually diminishes the TE properties of this material.
Figure 4.1: (color online) Total density of states, in spin up state, for (a) AlCFe₃(b) GaCFe₃ (c) GeNCa₃ (d) PbNCA₃ (e) SnCCo₃ (f) SnCFe₃ (g) SnNCa₃ and (h) ZnCFe₃. Black lines represent density of states without SOC while red lines represents density of states with SOC.
Figure 4.2: (color online) Total and partial density of states, in spin up state, for PbNCa$_3$ (a) without SOC effects and (b) with SOC.
Figure 4.3: (color online) Total and partial density of states, in spin up state, for AlICFe$_3$ (a) without SOC effects and (b) with SOC.

4.1.3 Thermoelectric properties

The Seebeck coefficient is an important tool, which provides a sensitive test of the electronic structures of the materials in close proximity to the Fermi energy. In Fig. 4.4 the calculated Seebeck coefficient of SnCCO$_3$ and SnCFe$_3$ against temperature are compared with the experimental results [112] presented, where Fig. 4.4 (a) shows calculated results and Fig. 4.4 (b)
shows experimental results. At room temperature, the Seebeck coefficients for SnCCo$_3$ and SnCFe$_3$ are 50 $\mu$V/K and 20 $\mu$V/K, respectively. In comparison with the available experimental results, [112] we found that our results follow the experimental curves almost in the entire temperature range. The positive values of the Seebeck coefficient show that these materials favor p-type doping. A small difference between calculated and experimental results can be attributed to the fact that DFT produces results after the materials are optimized at the ground state, while the experimental results are not obtained from the ground state. Secondly, only pseudo-eigenvalues are available in the DFT approximation [154]. Therefore, it is important to note that besides its advantages, DFT has its limitations [155,156].

We also calculated the Seebeck coefficient of these materials against chemical potential at 300, 600 and 900 K temperature for better understanding of its behavior, as presented in Figs. 4.5 (a) and (b). It is clear from the figure that the values of Seebeck coefficient can be tuned by chemical potential. At room temperature we achieve the maximum values of 82 $\mu$V/K and 78 $\mu$V/K for SnCCo$_3$ and SnCFe$_3$, respectively, at -0.1 eV chemical potential without considering the effects of SOC. Further, it is clear from the figure that high values of Seebeck are achieved between -0.25 eV and 0.25 eV while beyond these points the Seebeck coefficient decreases. Thus, it is obvious that we shall get the best TE response of these materials in this region. Figure 4.6 shows that SOC diminishes the Seebeck coefficient of these materials.

Figures 4.7 and 4.8 present Seebeck coefficients without considering the effects of SOC and with the effects of SOC respectively, for ANCa$_3$ (A=Ge, Sn, Pb) and BCFe$_3$ (B=Al, Zn, Ga), against chemical potential at 300, 600 and 900 K. All materials show high values for the Seebeck coefficient. We see approximately similar behavior of the Seebeck coefficient in both p-type and n-type regions. The Seebeck coefficients of ANCa$_3$ (A=Ge, Sn, Pb) are enhanced while they are
diminished for BCF$_3$ (B=Al, Zn, Ga) due to the SOC. The spin and orbital degrees of freedom are entangled at a local level by the SOC, where the total angular momentum provides a good description of the ordered phases and fluctuation properties of a material and can also describe the possible uses of a material in various devices with prominent functionalities [157, 158]. In 5d electrons, SOC is very strong [159] and considerably changes the 5d band dispersion [160-163]. At 0.1 eV chemical potential, considering the effects of SOC, SnNCA$_3$ shows the highest value of -730 $\mu$V/K at room temperature among all nitride and carbide antiperovskites investigated in this work. Therefore, we can predict that this material will show better TE response than the other materials.

Heat is transferred in a material through electrons and lattice vibrations. In semiconductors, lattice vibrations are mostly responsible for the conduction of heat while in metals free electrons are good sources of thermal conductivity [102]. In metals, the lattice part of the thermal conductivity is less than 2% of the total thermal conductivity and can be safely neglected [106,107]. For materials used in TE generators, thermal conductivity is desired to be small so that the temperature gradient could be maintained across the material. Figure 4.9 and 4.10 present electronic thermal conductivity, without considering the effects of SOC and with the effects of SOC respectively, for ANCA$_3$ (A=Ge, Sn, Pb) and BCF$_3$ (B=Al, Zn, Ga), against chemical potential at 300, 600 and 900 K. The same behavior is observed for all materials as thermal conductivity is minimum at zero chemical potential and increases as chemical potential is increased. As we need small values of thermal conductivity to achieve higher figure of merit, it is clear from the figure that the materials will give good TE response in the region between -0.25 and 0.25 eV chemical potential, as in this region thermal conductivities are minimum. In particular, for nitrides with SOC effects, the graph remains zero between -0.2 and 0.2 eV
chemical potential at room temperature. Further, we see that the thermal conductivity increases with temperature for all materials because by increasing temperature free electrons gain energy and result in more transfer of heat. The figure shows that nitride antiperovskites have lower values of thermal conductivity as compared to carbide antiperovskites.

Electrical conductivity is the flow of charge carriers in a material. Electrons move from the hot regions of a material to the cold regions. In TE devices current is produced as a result of this phenomena. Therefore, for good TE performance we need materials having high values of electrical conductivity. Figure 4.11 and 4.12 present electrical conductivity, without considering the effects of SOC and with the effects of SOC respectively, of ANCa₃ (A=Ge, Sn, Pb) and BCFe₃ (B=Al, Zn, Ga) against chemical potential at 300, 600 and 900 K. It is clear from the figures that electrical conductivity is minimum for all materials near zero chemical potential and increases as chemical potential is increased. This means that we can achieve desired values of electrical conductivity for these materials by changing chemical potential. Further, we see that carbide antiperovskites have higher values of electrical conductivity than nitride antiperovskites. In carbides, n-type materials show good response, with peak value of $3.5 \times 10^{20} /\Omega \text{ms}$ at 1 eV, while in nitrides, this is true for p-type materials, with peak value of $2.1 \times 10^{20} /\Omega \text{ms}$ at 0.9 eV chemical potential. Further, we see that SOC slightly decreases electrical conductivity for all materials.
Figure 4.4: (color online) Calculated (a) and experimental [112] (b) Seebeck coefficients for SnCCo$_3$ and SnCFe$_3$ as a function of temperature without SOC.

Figure 4.5: (color online) Seebeck coefficients for (a) SnCCo$_3$ and (b) SnCFe$_3$ at 300, 600 and 900 K as a function of chemical potential without SOC.
Figure 4.6: (color online) Seebeck coefficients for (a) SnCCo$_3$ and (b) SnCFe$_3$ at 300, 600 and 900 K as a function of chemical potential with SOC.
Figure 4.7: (color online) Seebeck coefficients for (a) GeNCa$_3$ (b) SnNCa$_3$ (c) PbNCa$_3$ (d) AlCFe$_3$ (e) ZnCFe$_3$ and (f) GaCFe$_3$ at 300, 600 and 900 K as a function of chemical potential without SOC.
Figure 4.8: (color online) Seebeck coefficients for (a) GeNCa$_3$ (b) SnNCa$_3$ (c) PbNCa$_3$ (d) AlCFe$_3$ (e) ZnCFe$_3$ and (f) GaCFe$_3$ at 300, 600 and 900 K as a function of chemical potential with SOC.
Figure 4.9: (color online) Thermal conductivity for (a) GeNCa$_3$ (b) SnNCa$_3$ (c) PbNCa$_3$ (d) AlCF$_3$ (e) ZnCF$_3$ and (f) GaCF$_3$ at 300, 600 and 900 K as a function of chemical potential without SOC.
Figure 4.10: (color online) Thermal conductivity for (a) GeNCa$_3$ (b) SnNCa$_3$ (c) PbNCa$_3$ (d) AlCFe$_3$ (e) ZnCFe$_3$ and (f) GaCFe$_3$ at 300, 600 and 900 K as a function of chemical potential with SOC.
Figure 4.11: (color online) Electrical conductivity for (a) GeNCa₃ (b) SnNCa₃ (c) PbNCa₃ (d) AlCFe₃ (e) ZnCFe₃ and (f) GaCFe₃ at 300, 600 and 900 K as a function of chemical potential without SOC.
Figure 4.12: (color online) Electrical conductivity for (a) GeNCa$_3$ (b) SnNCa$_3$ (c) PbNCa$_3$ (d) AlCFe$_3$ (e) ZnCFe$_3$ and (f) GaCFe$_3$ at 300, 600 and 900 K as a function of chemical potential with SOC.
4.1.4 Figure of merit

Figures 4.13 and 4.14 present dimensionless figure of merit, without considering the effects of SOC and with the effects of SOC respectively, for ANCa$_3$ (A=Ge, Sn, Pb) and BCF$_3$ (B=Al, Zn, Ga) against chemical potential at 300, 600 and 900 K. ZT is calculated from the Seebeck coefficient (S), the electrical conductivity ($\sigma/\tau$) and the electronic part of thermal conductivity ($k_e/\tau$), presented above. It is clear from the figures that the figure of merit increases due to SOC in nitride antiperovskites while it decreases in carbide antiperovskites. SnNCa$_3$ shows the highest value of figure of merit and at room temperature it reaches to 0.96 at 0.1 eV chemical potential, considering the effects of SOC. The result is understandable because this material has the highest Seebeck coefficient. As the Seebeck coefficient and electronic thermal conductivity show good response between -0.25 and 0.25 eV chemical potential, we get the peak values of figure of merit in this region. Small values of figure of merit, beyond this region, may be attributed to the large values of electrical conductivity. Furthermore, it is clear from the figure that nitride antiperovskites show good response in p-type while carbide antiperovskites show good response in n-type materials.
Figure 4.13: (color online) Dimensionless figure of merit for (a) GeNCa\textsubscript{3} (b) SnNCa\textsubscript{3} (c) PbNCa\textsubscript{3} (d) AlCFe\textsubscript{3} (e) ZnCFe\textsubscript{3} and (f) GaCFe\textsubscript{3} at 300, 600 and 900 K as a function of chemical potential without SOC.
Figure 4.14: (color online) Dimensionless figure of merit for (a) GeNCa$_3$ (b) SnNCa$_3$ (c) PbNCa$_3$ (d) AlCFe$_3$ (e) ZnCFe$_3$ and (f) GaCFe$_3$ at 300, 600 and 900 K as a function of chemical potential with SOC.
4.2 DFT and Post-DFT Studies of Metallic MXY$_3$-type Compounds for Low Temperature TE Applications

4.2.1 Introduction

High temperature thermoelectric (TE) materials with large Seebeck coefficient are attractive for power generation. Large Seebeck coefficient is commonly observed in narrow band gap semiconductors with low carrier concentration [113] and therefore, narrow band gap semiconductors are extensively studied for this purpose. On the other hand low temperature TE materials, used in cooling, are not studied with the same seriousness as compared to the high TE materials, consequently the studies of the metallic TE materials are rare [19, 152]. Lin et al. [112] reported the TE properties of metallic antiperovskites with a maximum experimental $ZT$ value of 0.035 for SnC$_x$Co$_3$ around 250 K. Recently, we worked on the TE properties of metallic antiperovskites theoretically and observed that the Seebeck coefficient of SnNCa$_3$ enhances significantly with the effects of spin orbit coupling at room temperature. The motivation of this work is to search low temperature TE materials in metallic antiperovskites, therefore we explore the TE properties of metallic compounds AlCMn$_3$, AlCNI$_3$, AlCSc$_3$, AlCTi$_3$, AlCCr$_3$, AlNCr$_3$, AlNSc$_3$, AlNTi$_3$, GaCCr$_3$, GaCNI$_3$, GaCMn$_3$, GaNCr$_3$, IrNCr$_3$, MgCNI$_3$, MgNCr$_3$, PdNCr$_3$, PtNCr$_3$, PtNFe$_3$, RhNCr$_3$ and RhNFe$_3$.

Thermoelectric properties are strongly dependent upon the thermal conductivity which consists of electronic part and phonons. In semiconductors, phonons effects are prominent and electronic part of thermal conductivity is small. In metals, unlike semiconductors, contribution of phonons in thermal conductivity is a very small fraction of the total thermal conductivity and therefore can be safely neglected. Highest value of the lattice part of thermal conductivity in metals is at intermediate temperatures, i.e., between high and low asymptotic regimes, and even these highest values are lesser than 2%, [106, 107] therefore for the metals under investigation,
our studies are focused on their electronic part of thermal conductivities. Secondly, phonon drag increases effective mass of conducting electrons and can increase the Seebeck coefficient but it is only applicable for low temperatures (T<200 K) [164].

4.2.2 Electronic properties

Total and partial densities of states of the selected materials are presented in Fig. 4.15 in spin up and spin down states. Figure presents density of states for RhNFe$_3$ and AlCMn$_3$. The values of density of states near Fermi level are small in spin down states as compared to spin up states. It is clear from the figure that the conduction band is mostly composed of p-states of nitrogen and carbon in RhNFe$_3$ and AlCMn$_3$, respectively. TE properties depend on the density of electronic states near Fermi level. We can see that top of valance band in RhNFe$_3$ is composed of Rh-d states. Similarly, in AlCMn$_3$ Mn-dz$_2$ and Mn-dxz+dyz states have peaks near Fermi level. Therefore, these states play important role in TE properties of these materials.

![Figure 4.15](image)

Figure 4.15: Total and partial densities of states for RhNFe$_3$ and AlCMn$_3$ in spin up and spin down states.
4.2.3 Thermoelectric properties

Seebeck coefficient is an important tool, which provides a sensitive test of the electronic structures of the materials in close proximity to the Fermi energy. Large values of Seebeck coefficient are desired for efficient TE devices. Figure 4.16 present Seebeck coefficients for AlCMn$_3$, AlCTi$_3$, AlNSc$_3$, MgCNi$_3$, PtNCr$_3$ and AlCNi$_3$ against chemical potential at 300, 600 and 900 K while the results for rest of the materials are presented in appendix A. The values of Seebeck coefficient lie between 25 to 100 $\mu$V/K. Seebeck coefficient of AlNTi$_3$ and AlCTi$_3$ approaches to 110 and 100 $\mu$V/K respectively, at room temperature. Lin et. al [112] experimentally investigated thermoelectric properties of antiperovskites and presented SnCCo$_3$ with the Seebeck coefficient of 53 $\mu$V/K at 278 K. This is the largest Seebeck, not only among all antiperovskites materials but also in other metals like AuCo ($\sim$42 $\mu$V/K, 300 K), CuFe ($\sim$15 $\mu$V/K, 20 K), heavy Fermi metals CeCu$_2$Si$_2$ (34 $\mu$V/K, 200 K), CeAl$_3$ (42 $\mu$V/K, 50 K), CePb$_3$ (40 $\mu$V/K, 20 K), and YbInCu$_4$ ($\sim$30 $\mu$V/K, 50 K) [152]. Literature clearly shows our results are very significant in TE applications. For AlCMn$_3$ and AlCTi$_3$ we see better values of Seebeck coefficient in p-type as compared to n-type region while for other materials we see similar behavior for both p-type and n-type regions. The results provided in this section and appendix A show that some materials have good thermoelectric properties in p-type and others in n-type region. In practice, materials have both charge carriers and the Seebeck depends on dominant carriers in the material. In purely p-type materials, Seebeck is positive and in n-type Seebeck is negative. Therefore, by Seebeck coefficient of the materials, we can predict about the dominant carrier concentration in a material and doping can enhance desired type of carriers. Thus, we can say that materials with better response in p-type region have holes while materials with better response in n-type region have electrons as the mobile carriers [113]. As AlNTi$_3$ and AlCTi$_3$
show highest thermo power therefore, we can predict that these materials will show better TE response than other materials discussed in this section.

Conducting electrons and lattice vibrations are the two sources of heat transfer across a material. In metals, thermal conduction through electrons is dominant while in semiconductors, lattice vibration is mostly responsible for the conduction of heat [102]. Materials with small thermal conductivity are required to make thermoelectric generators, as we need to maintain temperature gradient across the material. Figure 4.17 presents electronic thermal conductivity for AlCMn$_3$, AlCTi$_3$, AlNSc$_3$, MgCNi$_3$, PtNCr$_3$ and AlCNi$_3$ against chemical potential at 300, 600 and 900 K. Thermal conductivity is minimum around zero chemical potential and increases as chemical potential is increased. The materials will give high figure of merit in the region between -0.25 and 0.25 eV chemical potential as in this region thermal conductivities are minimum. Thermal conductivity increases when one moves away from $\mu = 0$. Explanation for this may be given from the basic definition of chemical potential $\mu$. When one atom is placed in an element and you want to place another, the first one will oppose the second. Similarly when a third atom is placed the first two will oppose. This opposition of the already placed atoms in an element or compound to the new incoming atoms is called chemical potential. When chemical potential increases then repulsion to the incoming atoms also increases, causing more lattice vibration. This increased lattice vibration results in high conductivity. Similarly if chemical potential is negative it means a new entering atom is welcomed by the already present atoms in the element or compound and hence attraction occurs. Because of the attraction again lattice vibration increases as there is a force involved. This causes an increase in thermal conductivity. When chemical potential is negligibly small then repulsive or attractive force is also small resulting less vibrations and hence small conductivity [151]. The figure shows that AlCNi$_3$ and
AlNSc$_3$ have the smallest electronic thermal conductivities. Further, we see an increase in thermal conductivity with temperature for all materials. Temperature increases electrons energy and as a result we get more transfer of heat.

Flow of electrons from the high temperature region to the low temperature region in material results in electric current and this phenomenon is used to produce electrical energy in TE devices. Therefore, materials with high values of electrical conductivity are required for good TE generators. Figure 4.18 presents electrical conductivity for AlCMn$_3$, AlCTi$_3$, AlNSc$_3$, MgCNi$_3$, PtNCr$_3$ and AlCNi$_3$, against chemical potential at 300, 600 and 900 K. It is clear from the figure that electrical conductivity is maximum at higher values of chemical potential. PtNCr$_3$ gives the highest values of electrical conductivity near Fermi level. Further, we see that the values of electrical conductivity can be tuned by varying chemical potential.
Figure 4.16: Seebeck coefficients for (a) AlCMn$_3$, (b) AlCTi$_3$, (c) AlNSc$_3$, (d) MgCNi$_3$, (e) PtNCr$_3$ and (f) AlCNi$_3$ at 300, 600 and 900 K as a function of chemical potential.
Figure 4.17: Electronic thermal conductivities for (a) AlCMn$_3$, (b) AlCTi$_3$, (c) AlNSc$_3$, (d) MgCNi$_3$, (e) PtNCr$_3$ and (f) AlCNi$_3$ at 300, 600 and 900 K as a function of chemical potential.
Figure 4.18: Electrical conductivities for (a) AlCMn$_3$, (b) AlCTi$_3$, (c) AlNSc$_3$, (d) MgCNi$_3$, (e) PtNCr$_3$ and (f) AlCNI$_3$ at 300, 600 and 900 K as a function of chemical potential.
4.2.4 Figure of merit

Figure of merit (ZT) is a parameter to determine the performance of a TE device, where it depends on high Seebeck coefficient, high electrical conductivity and low thermal conductivity. Materials with high value of ZT are desired for industrial applications. ZT greater than unity is considered very efficient in thermoelectric devices. Despite extensive research in thermoelectrics in recent years, scientists are still struggling to find such materials, which may replace conventional methods of energy production. Till now, SnCCo$_3$ (ZT=0.035 at 258K) and Sn$_{0.95}$Co$_{0.05}$CCo$_3$ (ZT=0.04 at 258K) have the largest figure of merits among all antiperovskites materials [112]. Table 2 presents the values of ZT at room temperature calculated in this work for AlCMn$_3$, AlCNi$_3$, AlCSc$_3$, AlCTi$_3$, AlCCr$_3$, AlNCr$_3$, AlNSc$_3$, AlNTi$_3$, GaCCr$_3$, GaCNi$_3$, GaCMn$_3$, GaNCr$_3$, IrNCr$_3$, MgCNi$_3$, MgNCr$_3$, PdNCr$_3$, PtNCr$_3$, PtNF$_3$, RhNCr$_3$ and RhNF$_3$. It is clear from the table that few materials show good thermoelectric response. The plots of figure of merit for AlCMn$_3$, AlCTi$_3$, AlNSc$_3$, MgCNi$_3$, PtNCr$_3$ and AlCNi$_3$, against chemical potential at 300, 600 and 900 K are shown in Fig. 4.19. It is clear from the figure that the peak values of ZT are found close to Fermi level. AlNTi$_3$ shows the highest value of figure of merit among these materials and it reaches to 0.32 at room temperature. This is due to the fact that this material has the highest values of the Seebeck coefficient and smallest electronic thermal conductivity. Large peaks of ZT between -0.25 and 0.25 eV chemical potential are due to the fact that Seebeck has large values while electronic thermal conductivity has small values in this region. Small values of figure of merit, beyond this region, may be attributed to the large values of electrical conductivity. The comparison with the available data clearly shows that these materials may be useful in thermoelectric devices.
Figure 4.19: Figure of merit for (a) AlCMn$_3$, (b) AlCTi$_3$, (c) AlNSc$_3$, (d) MgCNi$_3$, (e) PtNCr$_3$ and (f) AlCNi$_3$ at 300, 600 and 900 K as a function of chemical potential.
<table>
<thead>
<tr>
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<th>ZT</th>
<th>Materials</th>
<th>ZT</th>
</tr>
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<td>PtNCo₃</td>
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<td>PtNF₃</td>
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</tr>
<tr>
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<td>RhNCo₃</td>
<td>0.032</td>
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<tr>
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<td>RhNF₃</td>
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<tr>
<td>AlCCr₃</td>
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<td>GaCCr₃</td>
<td>0.25</td>
<td>MgNCo₃</td>
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</tr>
</tbody>
</table>
4.3 Antiperovskite compounds SbNSr$_3$ and BiNSr$_3$: Potential Candidates for Thermoelectric Renewable Energy generators

4.3.1 Introduction

The demand of energy is growing with the quality of life, increase in human population and depletion of fossil fuels. The solution to the problem is not possible by a single source; therefore, different means of renewable energy are investigated to resolve the energy crisis of the world. Extensive experimental and theoretical studies are in progress in fossil fuel alternatives, where one of these alternatives is thermoelectricity. Conventionally, thermoelectricity is considered as the most suitable source for waste heat recovery where, materials with high Seebeck coefficient and small thermal conductivity are commonly used in thermoelectric generators for large-scale power generation [99,165,166-170].

In this section, we explore thermoelectric (TE) properties of antipervoskites SbNSr$_3$ and BiNSr$_3$ because of their narrow bandgaps and dense electronic states near Fermi level in both valance and conduction bands. This identifies them to be potential materials for thermoelectric devices and hence good sources of green energy in thermoelectric power generators, devices which directly convert thermal energy into electrical energy. The synthesis of SbNSr$_3$ and BiNSr$_3$, is reported by Gäbler et al. [55] for the first time in literature in 2004. They investigated some of their physical properties, including band gaps using diffuse reflectivity method and obtained optical gap of 1.15 eV for SbNSr$_3$ and 0.89 eV for BiNSr$_3$. They also calculated the electronic band gaps for these materials within Local Density Approximation (LDA) and obtained very small band gap values arguing that LDA severely underestimates band gaps of crystalline materials. In another theoretical study, Haddadi et al. [56] worked on the electronic properties of these materials using the Generalized Gradient Approximation (GGA). The authors
obtained bandgap of 0.31 eV for SbNSr$_3$ and 0.26 eV for BiNSr$_3$, which were later on improved by Hichour et al. [23] using modified version of GGA, i.e. Engel and Vosko GGA (GGA-EV) and achieved band gaps of 0.55 and 0.36 eV for SbNSr$_3$ and BiNSr$_3$, respectively but still severely under estimated results.

Thermoelectric properties are highly sensitive to band gaps, and therefore accurate calculated band gaps are required in the theoretical studies of the thermoelectric materials for their logical and rational results for practical applications. Realizing this important aspect of the thermoelectric compounds, we use a recently developed DFT based theoretical technique, improved modified Becke-Johnson (I-mBJ) potential [34] for high accuracy of the band gaps, while using these electronic structures, the thermoelectric properties of the compounds are explored.

### 4.3.2 Electronic properties

Thermoelectric properties are sensitive to electronic properties and therefore accurate band gap value of a material is required for its reliable thermoelectric nature. The band structures of SbNSr$_3$ and BiNSr$_3$ are calculated by I-mBJ [34] potential and are presented in Fig. 4.20. The overall band profiles of these compounds are in good agreement with the previous theoretical works, [23,56] where the top of the valance bands and bottom of the conduction bands lie at $\Gamma$ point for both materials, resulting in direct band gap semiconductors. Unlike the other theoretical works the band gaps obtained by the I-mBJ for SbNSr$_3$ and BiNSr$_3$ are consistent with the experimental values. Table 3 clearly indicates that I-mBJ is very effective in the prediction of band gaps of these compounds and also confirms the superiority of this theoretical method over LDA, [55] GGA, [56] and EV-GGA [23]. The accurate I-mBJ electronic structures of SbNSr$_3$
and BiNSr₃, as shown in Fig. 4.20 are further used to calculate the thermoelectric properties of these compounds.

Figure 4.20: Band structures for SbNSr₃ and BiNSr₃ by improved modified Becke-Johnson potential (I-mBJ).

Table 3. Calculated band gaps (in eV) for SbNSr₃ and BiNSr₃ are compared with the experimental and other theoretical results

<table>
<thead>
<tr>
<th></th>
<th>Present work</th>
<th>Experimental Work</th>
<th>Other Work</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>I-mBJ</td>
<td>EV-GGA</td>
<td>GGA</td>
</tr>
<tr>
<td>SbNSr₃</td>
<td>0.92</td>
<td>1.15ᵃ</td>
<td>0.55ᶜ</td>
</tr>
<tr>
<td>BiNSr₃</td>
<td>0.81</td>
<td>0.89ᵃ</td>
<td>0.36ᶜ</td>
</tr>
</tbody>
</table>

ᵃExp[55],ᵇ[56],ᶜ[23]
4.3.3 Thermoelectric properties

In Seebeck effect, the temperature difference across the ends of a thermoelectric material causes potential difference, which pushes electrons from one end to the other. In Fig. 4.21 a-b, Seebeck coefficients for SbNSr$_3$ and BiNSr$_3$ are presented at different temperatures, 300, 600 and 900 K. It is clear from the plots that the response of the materials is same in both p-type and n-type regions. In the p-type region, SbNSr$_3$ shows the peak value of 1590 $\mu$V/K, while BiNSr$_3$ shows the peak value of 1540 $\mu$V/K at room temperature, which predict that these are good TE materials. Similarly, both materials show good response in n-type region too. The plots show that the Seebeck coefficient decreases exponentially with temperature. Furthermore, it is can be seen that the Seebeck coefficient exists between -0.3 eV and 0.3 eV of the chemical potential and becomes zero beyond these points. Hence, materials are strongly responsive in this region. The comprehensive study of the plots reveals that both of the materials show approximately the same behavior with small differences in details.

Fig. 4.22 a-b presents the electronic thermal conductivities for SbNSr$_3$ and BiNSr$_3$ at 300, 600 and 900 K. It is clear from the figure that thermal conductivities increase with the increase in temperature; which is obvious as the energy of free electrons increase with temperature. The figure shows that both materials have approximately same behavior. Thermal conductivities remain zero at room temperature between -0.3 eV and 0.3 eV of the chemical potential, so high figure of merit can be attained in this region. The plots reveal that the thermal conductivities are smaller in the p-type region as compared to the n-type region for both materials.

The electrical conductivities for SbNSr$_3$ and BiNSr$_3$ at different temperatures, i.e. 300, 600 and 900 K, are presented in Fig 4.23 (a) and (b), respectively. The response of electrical conductivities for both materials is approximately same at a given temperature. The threshold
points for the electrical conductivities of these materials in p-type and n-type regions are -0.25 eV and 0.25 eV chemical potentials, respectively. Electrical conductivities remain zero between these points while beyond these points materials have good electrical conductivities and at 1.4 eV chemical potential we get the peak values of $5.7 \times 10^{20} \, \Omega^{-1} \cdot \text{m}^{-1} \cdot \text{s}^{-1}$ and $5.6 \times 10^{20} \, \Omega^{-1} \cdot \text{m}^{-1} \cdot \text{s}^{-1}$ for n-type SbNSr$_3$ and BiNSr$_3$, respectively. Chemical potential is regarded as carrier density [171] therefore, in the vicinity of zero chemical potential, carrier density will be small. Due to this small carrier density, there will be minimum conduction charges available, resulting in low values of electrical conductivities near zero chemical potential. As conduction charges are responsible for electronic thermal conductivity, the unavailability of carriers in this region is also the cause of minimum electronic thermal conductivity.
Figure 4.21: Seebeck coefficients for (a) SbNSr$_3$ and (b) BiNSr$_3$ as a function of chemical potential at 300, 600 and 900 K.
Figure 4.22: Electronic thermal conductivities for (a) SbNSr\textsubscript{3} and (b) BiNSr\textsubscript{3} as a function of chemical Potential at 300, 600 and 900 K.
Figure 4.23: Electrical conductivities for (a) SbNSr$_3$ and (b) BiNSr$_3$ as a function of chemical potential at 300, 600 and 900 K.
4.4 Detailed DFT studies of the band profiles and optical properties of antiperovskites SbN\textit{Ca}_3 and BiN\textit{Ca}_3

4.4.1 Introduction

Ternary carbides and nitrides having cubic antiperovskite structure are emerged as promising compounds in recent years [9,10,149,172]. Chern et al. [35] reported the synthesis of AN\textit{Ca}_3 (A = P, As, Sb and Bi) materials by mixing and pressing Ca$_3$N$_2$ powders and group V elements into a pellet and subsequently heating the pellets at 1000 °C in the flowing dry N$_2$ gas. They observed semiconducting nature for SbN\textit{Ca}_3 and BiN\textit{Ca}_3 compounds. In the same year, the electronic structure and bonding properties of BiN\textit{Ca}_3 and PbN\textit{Ca}_3 materials were studied by Papaconstantopoulos and Pickett [46] using the augmented plane-wave method. They are of the opinion that the bandgap of these compounds is very narrow, about 0.07 eV for BiN\textit{Ca}_3. A few years later the structural properties of AsN\textit{Ca}_3, P\textit{Ca}_3 and BiN\textit{Ca}_3 were investigated by Vansant et al. [47] using local density approximation (LDA) and are also of the opinion that BiN\textit{Ca}_3 is a narrow band gap semiconductor. In a relatively recent studies, Haddadi et al. [173] investigated the pressure dependent elastic properties of AN\textit{Ca}_3 (A = P, As, Sb and Bi) using the plane wave pseudo-potential method, while Moakafi et al. [22] explored the elastic, electronic and optical properties of SbN\textit{Ca}_3 and BiN\textit{Ca}_3 using a full relativistic version of the full-potential linearized augmented plane-wave plus local orbitals method based on the density functional theory. The results reported in Ref. [22] contradict the claim of the authors that “SbN\textit{Ca}_3 and BiN\textit{Ca}_3 are semiconductors in nature”. As the figures of the band profiles presented in the article clearly show that for both materials the top of valance band crosses the Fermi level and enters into the conduction band and hence these materials are not semiconducting, which is also in disagreement with the experimental results [35]. In this section, this anomaly is addressed with
great care using different theoretical techniques, based on the full potential linearized augmented plane waves (FP-LAPW) method, like local density approximation (LDA), generalized gradient approximation (GGA), Engel-Vosko GGA (EV-GGA) and modified Becke–Johnson (mBJ) potential. It is expected that the present work will not only rectify the errors in the existing theoretical work, but will also provide a realistic picture of the compounds which will be helpful in understanding various physical properties of these compounds and will also identify their potential applications in optical and optoelectronic devices.

4.4.2 Structural properties

To obtain the ground-state properties such as the equilibrium lattice parameter $a_o$ and bulk modulus $B_o$ for SbNCa$_3$ and BiNCa$_3$ materials, the total energy-volume curves are calculated and fitted to the Birch–Murnaghan’s equation of state [174]. We obtained lattice constants and bulk moduli for these materials using LDA, PBEGGA, PBEsol-GGA, WC and three versions of EV-GGA, see Fig. 4.24. There are three potential options for applying EV-GGA in these calculations which are called EV1, EV2, and EV3. In the first potential, EV1, Engel–Vosko 93 GGA exchange term is combined with the LSDA correlation term in the WIEN2k code, see LAPW0 which generates potential. The LAPW0 calculates the total potential by summing Coulomb and exchange-correlation potentials using the total electron (spin) density. In the second potential, EV2, a combination of Engel-Vosko 93 GGA exchange term with Perdew-Wang 91 GGA correlation term is used in the LAPW0 of WIEN2k code. In the third EV3 potential option, Engel–Vosko 93 GGA exchange term, LSDA potential correlation term, Perdew-Wang 91 GGA exchange energy, and Perdew-Wang 91 GGA correlation term are combined in the LAPW0 of the WIEN2k code. Results obtained from the different theoretical models are presented in Table 4. The calculated results are also compared with the
experimentally measured values and other theoretical data. The table clearly indicates that our results are in good agreement with the other available data. The results show that the EV1 and EV2 cannot satisfactorily predict the lattice parameters. The table also reveals that PBE-GGA, and PBEsol, as well as EV3 are more appropriate techniques than the others for the calculations of the lattice parameters of these compounds, while EV1, EV2, and LDA may not be considered as suitable approximations if we compare the results with the experimental data. The shortcoming of the EV1 and EV2 is that they improve the properties that depend on the exchange potential, such as the electronic properties, but not those depend on the exchange-correlation energy. Therefore, EV1 and EV2 yield unsatisfactory results for properties that depend on the exchange-correlation energy such as structural properties and forces. From Table 4 and Fig. 4.24, it is clear that it is the GGA-PBE and EV3 which provide better values of the lattice constants than EV1 and EV2, compared to the measured results. No experimental data about the bulk moduli of these compounds is available in literature, to the best of our knowledge, for comparison. The lattice constant of SbNCa$_3$ is smaller than the lattice constant of BiNCa$_3$, which is due to the fact that the radius of Sb (R$_{\text{Sb}} = 1.4$ Å) is smaller than the radius of Bi (R$_{\text{Bi}} = 1.56$ Å). It shows that the lattice constant increases with the increase in the atomic size of A atom. Unlikely, the bulk modulus decreases with the increase in the atomic size of the A site element which is in concurrence with the well known relationship between B and lattice constant, i.e., $B \propto V^{-1}$, where $V$ is volume of the unit cell.
Figure 4.24: Total energy in Ry as a function of volume in Bohr\(^3\) fitted by Birch–Murnaghan equation of state within a variety of exchange–correlation functionals, i.e., LDA, PBE-GGA, PBEsol-GGA, WC, and three versions of Engel–Vosko-GGA. Experimental values are indicated for comparison. Left panel shows E–V curves of BiNCa\(_3\), and right panel shows E–V curves of SbNCa\(_3\).
Table 4. Calculated equilibrium lattice constant $a$ (Å) and bulk modulus $B$ (GPa) of SbNCa$_3$ and BiNCa$_3$ compounds in comparison with experimental and other theoretical results.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>SbNCa$_3$</th>
<th>BiNCa$_3$</th>
</tr>
</thead>
<tbody>
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<td><strong>Lattice Constant a (Å)</strong></td>
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<tr>
<td>PBE-EV3</td>
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<tr>
<td>PBE-EV2</td>
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<td>PBE-EV1</td>
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<td>WC</td>
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<td>PBEsol</td>
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<td>4.7846</td>
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<td>Exp.</td>
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<td>4.888$^a$</td>
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<td>4.783$^b$, 4.85$^c$</td>
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<td><strong>Bulk modulus B (GPa)</strong></td>
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<tr>
<td>PBE-EV3</td>
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</tr>
<tr>
<td>PBE-EV2</td>
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</tr>
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<td>PBE-EV1</td>
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<td>WC</td>
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<td>65.89$^b$, 54.01$^b$</td>
</tr>
</tbody>
</table>

$^a$Exp [35], $^b$GGA [22], $^c$Analytical [54],

### 4.4.3 Electronic properties

The experimentally demonstrated semiconducting behavior of SbNCa$_3$ and BiNCa$_3$ compounds [35] has not been extensively investigated by any theoretical work, and therefore needs careful analysis to ensure the real picture of these compounds. In the present work, the electronic properties of these compounds in the cubic phase are investigated using four functionals, i.e., LDA, GGA, EV-GGA and mBJ. The calculated band structures by all the four models are illustrated in Fig. 4.25. The careful examination of the band profiles shows that for the same compound the band structures obtained by different models are similar with minor differences in details, whereas they are different for different compounds. The results obtained
by all the four functionals depicted in the figures indicate that SbNCa$_3$ and BiNCa$_3$ are direct bandgap semiconductors, which is consistent with the experimentally observed nature of these compounds [35] and contradicts with the theoretical results [22]. The calculated band gaps for these materials are presented in Table 5. It is clear from the table that LDA provides the smallest, while mBJ gives the largest band gaps for these materials. Similar to LDA, GGA also underestimates [175,176] band gaps but it provides relatively better results. This is due to the fact that LDA assumes constant electron density for a system whereas in real the charge density is not uniform. However, GGA also has its limitations, as it does not reproduce both exchange–correlation energy and its charge derivative [177]. To overcome this problem, Engel and Vosko [127] designed a new functional form of the GGA at the expense of less agreement in exchange energy. As LDA and GGA are notorious for the underestimation of band gaps and mBJ is effective in the estimation of band gaps, hence in the present study we can rely on the mBJ potential and expect that the experimental band gaps for both of these compounds will be consistent with the results obtained by mBJ, i.e., 1.1 eV (Fig. 4.25 and Table 5). Despite using small number of k-points for mBJ as compared to the other three functionals, we get the largest band gap by mBJ, which shows mBJ is the best potential for studying the electronic structure for these materials. It is well understood that mBJ works well for the band gap calculations as compared to LDA and GGA, because of the extra exchange potential, not only for transition metal compounds but also for sp-type semiconductors [32]. The clear picture of the electronic properties of SbNCa$_3$ and BiNCa$_3$ compounds can be obtained from the total and partial density of states (DOS), depicted in Fig. 4.26. It is clear from the figure that both materials have approximately same DOS curves with a small difference in details. It can be seen from the figure that the region below the Fermi level is divided into two regions; semi-core and valence states.
The semi-core states, lying between -11.5 eV and -12.8 eV for both materials, are entirely composed of nitrogen s states while semi-core states, lying between -8 eV to -8.7 eV for SbNCa$_3$ and -9.7 eV to -10.3 eV for BiNCa$_3$, are dominated by Sb/Bi-s states. In the upper valence band, states are mainly occupied by nitrogen p state, which is strongly hybridized with Sb/Bi-p states. The band gaps of 1.1 eV and 1.09 eV for SbNCa$_3$ and BiNCa$_3$ are also confirmed by the corresponding DOSs, respectively. The conduction band is dominated by Ca-d states with a mixture of Sb/Bi and N-p states showing hybridization. It is also worth noting that the amplitude of Bi-s states is higher in BiNCa$_3$ than the amplitude of Sb-s states in SbNCa$_3$ and the amplitude of N-p states is higher in BiNCa$_3$ than the amplitude of N-p states in SbNCa$_3$. 
Figure 4.25: Band structures for SbN\textsubscript{3}Ca\textsubscript{3} and BiN\textsubscript{3}Ca\textsubscript{3} by mBJ, EVGGA, GGA and LDA.
Figure 4.26: Density of states (DOS) for SbNCa$_3$ and BiNCa$_3$ by mBJ

Table 5. Band gaps (in eV) for SbNCa$_3$ and BiNCa$_3$ by mBJ, EV-GGA, GGA and LDA.

<table>
<thead>
<tr>
<th>Parameters</th>
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<th>BiNCa$_3$</th>
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<td></td>
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<tr>
<td>mBJ</td>
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<td>GGA-EV3</td>
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<td>GGA</td>
<td>0.42</td>
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<tr>
<td>LDA</td>
<td>0.40</td>
<td>0.38</td>
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<tr>
<td>Other theo.</td>
<td>0.28$^a$, 0.07$^b$</td>
<td></td>
</tr>
</tbody>
</table>

$^a$LDA[47], $^b$LDA[46]
4.4.4 Optical properties

Optical properties of a material are very helpful to identify the internal character of that material. The real and imaginary parts of the dielectric function, refractive index and absorption spectrum are calculated to observe the response of SbNCa$_3$ and BiNCa$_3$ to the applied electromagnetic field. The calculated optical properties for these materials with the mBJ formalism are presented in Figs. 4.27–4.30. It is clear from the figures that both materials show approximately same behavior with small differences in details. The dielectric function $\varepsilon(\omega)$, consists of real part $\varepsilon_1(\omega)$ and an imaginary part $\varepsilon_2(\omega)$. The calculated results for $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ are presented in Figs. 4.27 and 4.28 for SbNCa$_3$ and BiNCa$_3$, respectively. The value of the static dielectric constant $\varepsilon_1(0)$ for SbNCa$_3$ is 7.8 and for BiNCa$_3$ is 8.5. The $\varepsilon_1(\omega)$ increases steadily with energy and reaches to its peak value at 2.36 eV for SbNCa$_3$ and 2.1 eV for BiNCa$_3$. Then it decreases to minimum negative value at 4.9 eV for SbNCa$_3$ and 4.6 eV for BiNCa$_3$. Collective excitations of large effective mass in the interfaces induced by electric field may be responsible [178] for the negative $\varepsilon_1(\omega)$ showing absorption in this energy range. After this point, it increases with some variations and becomes positive after 12.5 eV for both materials. The imaginary part $\varepsilon_2(\omega)$, presented in these figures clearly show the critical point ($E_0$) at 1 eV for these materials, which also confirms the band gap. After this point, we have a threshold ($E_1$) for transition from valance to conduction band. For higher energies, $\varepsilon_2(\omega)$ keeps increasing which shows steady increase in absorption up to 3.2 eV ($E_2$). In the energy range from 3.2 eV to 3.9 eV, the curve stays at the same point and shows constant absorption for SbNCa$_3$ but slowly increase for BiNCa$_3$. After this point, we see a sharp increase in the curves for both materials and receive peaks at 4.5 eV ($E_3$), where materials show maximum absorption. The absorption curves, in Fig. 4.29, also confirm this pattern as we see zero absorption up to 1 eV ($E_0$). At higher energies, we
see peaks at 4.5 eV ($E_1$) and 7.5 eV ($E_2$), hence, the materials can be used as filters in this energy range of ultraviolet spectrum. Fig. 4.30 shows refractive index $n(\omega)$ for these materials. At zero energy the value of $n(\omega)$ is 2.8 ($E_0$) and 2.92 for SbNCa$_3$ and BiNCa$_3$ respectively. $n(\omega)$ reaches to maximum value at 4.3 eV ($E_1$) for SbNCa$_3$ and 2.4 eV ($E_2$) for BiNCa$_3$.

Figure 4.27: Dielectric function $\varepsilon(\omega)$ for SbNCa$_3$ by mBJ
Figure 4.28: Dielectric function $\varepsilon(\omega)$ for BiNCa$_3$ by mBJ.

Figure 4.29: Absorption coefficient for SbNCa$_3$ and BiNCa$_3$ by mBJ.
Figure 4.30: Refractive index for SbNCa$_3$ and BiNCa$_3$ by mBJ.
4.5 Thermoelectric properties of SbNCa$_3$ and BiNCa$_3$ for thermoelectric devices and alternative energy applications

4.5.1 Introduction

TE compounds are considered as the compounds that can solve the problems of power generation and refrigeration technologies [95-98]. These compounds are also useful in smart sensors, energy harvesting, and the new concept of thermo-power wave sources [179-184]. In thermoelectric power generators, thermal energy is directly converted into electrical energy [165] and thus acts as good sources of green energy. High quality and good TE materials are used and required for power generation and other thermoelectric applications depend upon the nature of the materials [168,135].

Perovskites are also reported to be suitable TE materials and potential candidates in this field [144,145]. Weidenkaff et al. [185] experimentally studied the effects on thermoelectric properties of Ca doping in LaCoO$_3$ perovskite. Wilfried et al. [186] investigated TE properties of NaTaO$_3$ based perovskites. For Nb doped SrTiO$_3$ the confined electron gas has been successfully investigated and it is proved that their Seebeck coefficients are ten times larger than bulk materials [187-189]. Flahaut et al. [190] worked on structure and thermoelectric properties of polycrystalline samples Ca$_{1-x}$A$_x$MnO$_3$ (A=Yb, Tb, Nd and Ho). However, the TE properties of antiperovskite materials are not studied extensively. A wide variety of semiconductors show good thermoelectric properties [105,114,191] and there are many antiperovskites materials which are semiconductors in nature.

In the present work, we discuss the TE properties of two antiperovskite materials SbNCa$_3$ and BiNCa$_3$ at 300K, 600K and at 900K temperatures. Chern et. al [35] reported experimentally that these two compounds are semiconductors having lattice constants of 4.8541 Å and 4.888 Å for SbNCa$_3$ and BiNCa$_3$, respectively. In section 4.4, we calculated structural and electronic
properties of these materials and showed a band gap of approximately 1.1 eV for these materials. Our studies also show that there are dense electronic states at Fermi level in valance band and in conduction band especially. Due to the small band gap and dense electronic states at Fermi level, we consider these materials to be good candidates for TE applications. Thermoelectric results, investigated in this report, show that our predictions are correct. All thermoelectric properties like Seebeck coefficients, electrical conductivity and thermal conductivity prove that these materials are excellent candidates for TE applications.

4.5.2 Thermoelectric properties

Figure 4.31 (a) and (b) represent curves of Seebeck coefficients for SbNCa$_3$ and BiNCa$_3$ respectively at 300 K, 600 K and 900 K. We can see that the highest value of Seebeck coefficient for both the materials is achieved at room temperature. Both materials exhibit approximately same behavior. For p-type SbNCa$_3$ and BiNCa$_3$, Seebeck coefficients have the maximum values of 1740 $\mu$V/K and 1730 $\mu$V/K respectively at 300 K, which shows that these are good thermoelectric materials. It is clear from the figure that Seebeck coefficient decreases almost exponentially with temperature. Similar behavior is observed for n-type SbNCa$_3$ and BiNCa$_3$, which shows that these materials are as good in n-type as in p-type. The peaks are obtained between -0.5 eV and 0.5 eV chemical potential, while beyond these points Seebeck coefficient drops rapidly to zero which means these materials will exhibit good thermoelectric properties between these points.

Figure 4.32 (a) and (b) present thermal conductivities for SbNCa$_3$ and BiNCa$_3$ respectively at 300 K, 600 K and 900 K as a function of chemical potential. Same behavior is observed for both materials. It is clear from the figures that thermal conductivity for room temperature remains approximately zero between -0.4 eV to 0.4 eV chemical potential for both
materials. This is the region where these materials can give maximum efficiency. Further, we see that thermal conductivity has lower values in p-type materials as compared to n-type. At 300 K the peak values are $18 \times 10^{14}$ W/Kms and $16 \times 10^{14}$ W/Kms for p-type SbNCa$_3$ and BiNCa$_3$ respectively.

Free electrons, on gaining heat, gain kinetic energy and move towards the colder part of the material thus producing electric current. For a good thermoelectric device, materials should have high electrical conductivity to reduce Joule heating effect [138]. Figure 4.33 (a) and (b) represent electrical conductivities for SbNCa$_3$ and BiNCa$_3$ respectively at 300 K, 600K and 900K. Both materials show approximately same behavior at given temperatures. It is clear from the figure that -0.3 eV and 0.3 eV chemical potentials are the critical points for electrical conductivity in p-type and n-type materials respectively. It means that material will give good thermoelectric properties beyond these points. The figure shows that leaving a small range of chemical potential in the vicinity of $\mu = 0$, both materials have good electrical conductivities for all other values of chemical potential. The peak values of $5 \times 10^{20}$ /$\Omega$ms and $5.2 \times 10^{20}$ /$\Omega$ms are achieved for n-type SbNCa$_3$ and BiNCa$_3$ respectively at 1.3 eV chemical potential.
Figure 4.31: Seebeck coefficients for (a) SbNCa$_3$ and (b) BiNCa$_3$ at 300 K, 600 K and 900 K.
Figure 4.32: Thermal conductivities for (a) SbNCa$_3$ and (b) BiNCa$_3$ as a function of chemical potential.
Figure 4.33: Electrical conductivities for (a) SbNCa$_3$ and (b) BiNCa$_3$ as a function of chemical potential at 300 K, 600K and 900K.
Chapter 5
Conclusions

In this work, different physical properties like structural, electronic, optical, and thermoelectric properties of cubic antiperovskites materials are calculated by using the full potential linearized augmented plane waves (FP-LAPW) method within the frame work of density functional theory (DFT) as well as Boltzmann’s theory.

Thermoelectric properties of twenty eight metallic antiperovskites MXY$_3$ (M=Ge, Sn, Pb, Zn, Al, Ga, Ir, Mg, Pd, Pt, Rh; X=C, N; Y=Mn, Ni, Sc, Ti, Cr, Fe, Ca, Co) are calculated using first principle calculations. The effects of spin orbit coupling on electronic and thermoelectric properties is studied. The high values of Seebeck coefficients between -0.25 and 0.25 eV chemical potential and low thermal conductivities, i.e. almost zero in this region, confirm the maximum values of figure of merit in this region. Ca based antiperovskites give figures of merit of about 0.96 from which we conclude that these materials maybe useful in thermoelectric power generation. Electrical conductivity gives maximum values beyond -0.5 and 0.5 eV chemical potential in p-type and n-type regions, respectively. Out of all metals, SnNCa$_3$ shows highest value of figure of merit (0.96) at room temperature, considering SOC effects. This study reveals that antiperovskites materials have immense potential for their possible application in thermoelectric devices.

Physical properties of SbNSr$_3$ and BiNSr$_3$ are studied using improved modified Becke–Johnson potential and we got band gap values in agreement with the experimental data. Thermoelectric properties of the materials are also calculated and very attractive results are obtained for these materials at room temperature. High values of Seebeck coefficients are obtained between -0.3 and 0.3 eV chemical potential which shows these materials can be useful
in thermoelectric generators. Peak values for electrical conductivities are observed beyond -0.5 and 0.5 eV of the chemical potential in the $p$-type and $n$-type regions, respectively. The overall pattern of the thermoelectric properties shows that SbNSr$_3$ and BiNSr$_3$ are good thermoelectric materials and can be useful in thermoelectric power devices as green energy sources.

SbNCa$_3$ and BiNCa$_3$ are semiconductors and our calculated electronic structures show that these materials have band gaps of 1.1 and 1.09 eV, respectively. We used four different potentials for electronic properties i.e. LDA, GGA, EV-GGA and mBJ exchange correlation potentials and found mBJ giving the best result. Lattice constants and bulk moduli are in agreement with the experimental data. Both materials are direct band gap semiconductors. LDA underestimates band gaps in comparison to the other potentials as it treats electron density as constant. The band gaps of these materials are also confirmed by imaginary part of the dielectric function. The materials show maximum absorption at 4.5 eV. Hence, in these energy ranges of ultraviolet spectrum the materials can be used as filters. Furthermore, thermoelectric properties of these materials are also calculated. Interesting results are obtained at room temperature for these materials. High values of Seebeck coefficients and small values of thermal conductivities are obtained between -0.5 and 0.5 eV chemical potential. Electrical conductivity has maximum values between 1.2 and 2.5 eV chemical potential. High Seebeck indicates that these are good thermoelectric materials and can be used in thermoelectric devices.
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Appendix A

Thermoelectric Properties of AlCCr$_3$, AlCSc$_3$, AlNiCr$_3$, AlNiTi$_3$, GaCCr$_3$, GaCMn$_3$, GaCNi$_3$, GaNiCr$_3$, IrNiCr$_3$, MgNiCr$_3$, PdNiCr$_3$, PtNiFe$_3$, RhNiCr$_3$, and RhNiFe$_3$

![Graphs showing Seebeck coefficient, electronic thermal conductivity, electrical conductivity, and figure of merit for AlCCr$_3$ at 300 K.]

Fig. 1: (a) Seebeck coefficient (b) electronic thermal conductivity (c) electrical conductivity and (d) figure of merit for AlCCr$_3$ at 300 K.
Fig. 2: (a) Seebeck coefficient (b) electronic thermal conductivity (c) electrical conductivity and (d) figure of merit for AlCS$_3$ at 300 K.
Fig. 3: (a) Seebeck coefficient (b) electronic thermal conductivity (c) electrical conductivity and (d) figure of merit for AlNCr$_3$ at 300 K.
Fig. 4: (a) Seebeck coefficient (b) electronic thermal conductivity (c) electrical conductivity and (d) figure of merit for AlNTi₃ at 300 K.
Fig. 5: (a) Seebeck coefficient (b) electronic thermal conductivity (c) electrical conductivity and (d) figure of merit for GaCCr$_3$ at 300 K.
Fig. 6: (a) Seebeck coefficient (b) electronic thermal conductivity (c) electrical conductivity and (d) figure of merit for GaCMn$_3$ at 300 K.
Fig. 7: (a) Seebeck coefficient (b) electronic thermal conductivity (c) electrical conductivity and (d) figure of merit for GaCNi$_3$ at 300 K.
Fig. 8: (a) Seebeck coefficient (b) electronic thermal conductivity (c) electrical conductivity and (d) figure of merit for GaNCr$_3$ at 300 K.
Fig. 9: (a) Seebeck coefficient (b) electronic thermal conductivity (c) electrical conductivity and (d) figure of merit for IrNCr$_3$ at 300 K.
Fig. 10: (a) Seebeck coefficient (b) electronic thermal conductivity (c) electrical conductivity and (d) figure of merit for MgNCr$_3$ at 300 K.
Fig. 11: (a) Seebeck coefficient (b) electronic thermal conductivity (c) electrical conductivity and (d) figure of merit for PdNCr$_3$ at 300 K.
Fig. 12: (a) Seebeck coefficient (b) electronic thermal conductivity (c) electrical conductivity and (d) figure of merit for PtNiFe$_3$ at 300 K.
Fig. 13: (a) Seebeck coefficient (b) electronic thermal conductivity (c) electrical conductivity and (d) figure of merit for RhNCr$_3$ at 300 K.
Fig. 14: (a) Seebeck coefficient (b) electronic thermal conductivity (c) electrical conductivity and (d) figure of merit for RhNFe$_3$ at 300 K.