Thermoelectric Properties of KZnX (X: P, As, Sb): A First Principles Study

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Indian Institute of Technology Hyderabad

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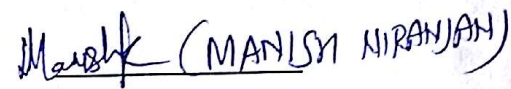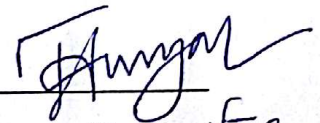
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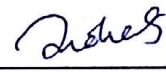
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Abstract

Electronic and transport properties of KZnX (X:P,As,Sb) are studied using calculations within the Density Functional Theory and solving the Boltzmann transport equation within the constant relaxation time approximation (CSTA) and rigid band approximation (RBA). The electronic band structures are calculated by means of the full-potential linear augmented plane wave method (FP-LAPW), using the Tran-Blaha modified Becke-Johnson potential (TB-mBJ). The calculated structural properties of lattice parameters are in excellent agreement with the existing experimental data. The calculated and analyzed electronic structure concludes that the investigated compounds will be coming under direct band gap semiconductors. The TE properties were also calculated for the currently evaluated compounds for both carrier concentrations and the variation is studied as a function of temperature. We found that under ambient conditions the thermopower is almost same for both 'n' type doping and 'p' type doping for all the investigated compounds. We have studied the variation in electronic and TE properties of the investigated compounds under varying pressure up to 10 GPa. It seems that for KZnAs and KZnSb the 'n' type doping is more favorable under higher pressure. Which enabled us to predict that 'n' type KZnAs and 'n' type KZnSb have better applications as an excellent t hermoelectric material under high pressure.

Contents

Chapter 1

Introduction

Thermoelectric energy conversion has attracted the scientific world because of several advantages, such as no moving part, less maintenance, and found application in various fields like automobiles, space technology [1]. Research claims that in our world most of the energy gets wasted in the form of heat, and here comes the role of thermoelectric materials. Thermoelectric materials on lead, tellurium, selenium, and antimony has already discovered [2]. These materials are more popular because of great figure of merit since they are toxic in nature it is not safe to handle. It is difficult to search new thermoelectric materials that are nontoxic, and nature friendly. Semiconducting alkaline earth materials is found to be more suitable for thermoelectric applications [3]. Zinc based ternary semiconductors are excellent material as a thermoelectric device because of their thermal stability, relative abundance, low density and inexpensive production. The capability of thermoelectric material is quantified by a dimensionless quantity called figure of merit ZT, and this is proportional to the efficiency of thermoelectric generator. The equation of figure of merit is given as ZT = $S^2\sigma T/\kappa$, where S, κ, σ and T are thermopower, thermal conductivity, electrical conductivity and the absolute temperature respectively. κ includes both the electronic κ_e and the lattice κ_l contributions. $\kappa = \kappa_e + \kappa_l$. It is pretty clear that the value of figure of merit (ZT) can be improved by increasing the values of thermopower as well as the electrical conductivity and keeping the low thermal conductivity low. However, from other laws of physics it is impossible. The Wiedemanne Franz law shows that the electronic part of thermal conductivity (κ) is proportional to the electrical conductivity (σ). The parameters in ZT are coupled in highly contradicting way, and getting a proper value of ZT is a challenging task.

The product between Seebeck coefficient and electrical conductivity is known as power factor ($S^2\sigma$). The relationship between efficiency η and thermoelectric figure of merit (ZT) of any thermoelectric generator is given by the equation

$$\frac{T_H - T_C\sqrt{1 + ZT} - 1}{T_H\sqrt{1 + ZT} + \dfrac{T_H}{T_C}}$$

Where T_C and T_H refer to the temperature of the cold and hot part of the material. Efficient thermoelectric materials have high thermopower and low thermal conductivity. High performance thermoelectric materials have ZT equal to or greater than one. In general semiconductors are considered to be promising candidates for thermoelectric applications. Enormous studies are available exploring novel thermoelectric materials and also aiming at improvement of existing thermoelectric materials [4,5]. Zinc based ternary

semiconductors gathered attraction due to several applications such as photovoltaic, thermoelectric and solar cells, etc... [6-10]. Here we have chosen a series of zinc based narrow band semiconductors in the form KZnX (X: P,As and Sb). We have investigated both electronic and thermoelectric properties of the above compounds at ambient and at various pressures up to 10GPa.

Here the entire thesis is divided into five chapters. The introduction which comes under the first chapter as written above clearly states the importance of thermoelectric materials. The theoretical part which comes under chapter two mainly gives an overall idea about the need and importance of density functional theory in solving many body problems and also introduces to various approximations implemented in density functional theory. The chapter three clearly introduces about the methodology implemented for the entire calculations done throughout for the thesis. The calculated results and the proper analysis have been written under results and discussions part which is chapter four. The overall conclusion obtained through the analysis and calculations has been provided under conclusion section which is chapter five.

Chapter 2

Theoretical Background

The properties of a system can be obtained by solving the quantum mechanical wave equation which governs the system dynamics. Which is the Schrödinger equation for non-relativistic systems. In principle, the quantum mechanical wave function contains all the data of a provided system. In a simple 2 dimensional potential or in case of hydrogen atom we are able to solve Schrödinger equation to get the wave function of the system. After that we are able to obtain the energy states of the system. But for an N-body system it is very hard to solve the Schrödinger equation. The main goal of most approaches in physics is to solve the non-relativistic, time-independent Schrödinger equation.

$$\hat{H}\Psi_i\left(\vec{x}_1,\vec{x}_2\ldots,\vec{x}_N,\vec{R}_1,\vec{R}_2\ldots,\vec{R}_M\right) = E_i\Psi_i\left(\vec{x}_1,\vec{x}_2\ldots,\vec{x}_N,\vec{R}_1,\vec{R}_2\ldots,\vec{R}_M\right) \quad (2.1)$$

Here H is the Hamiltonian for a system consisting of N electrons and M nuclei.

$$\hat{H} = -\frac{1}{2}\sum_{i=1}^{N}\nabla_i^2 - \frac{1}{2}\sum_{A=1}^{M}\frac{1}{M_A}\nabla_A^2 - \sum_{i=1}^{N}\sum_{A=1}^{M}\frac{Z_A}{r_{iA}} + \sum_{i=1}^{N}\sum_{j>i}^{N}\frac{1}{r_{ij}} + \sum_{A=1}^{M}\sum_{B>A}^{M}\frac{Z_A Z_B}{R_{AB}} \quad (2.2)$$

In the equation (2.2) the first and second term represent the kinetic energy of electron and nuclei. The third term represents the electrostatic interaction between electron and nuclei. Fourth and fifth term represents the repulsive potential between electron-electron and nucleus-nucleus interactions. (In terms of atomic units)

2.1 Approximation to solve Many-Body Problem

2.1.1 Born-Oppenheimer Approximation

The ions are more massive when compared to electrons, hence the kinetic energy of ions is very much smaller than electrons. This is the main idea behind Born-Oppenheimer approximation. The electrons respond instantly to the motion of the ions. We assume that electrons move in an electrostatic field generated by the nuclei. Since the nuclei is considered to be at rest thus, the electronic Hamiltonian reduces to

$$\hat{H} = -\frac{1}{2}\sum_{i=1}^{N}\nabla_i^2 - \sum_{i=1}^{N}\sum_{A=1}^{M}\frac{Z_A}{r_{iA}} + \sum_{i=1}^{N}\sum_{j>i}^{N}\frac{1}{r_{ij}} = \hat{T} + \hat{V}_{Ne} + \hat{V}_{ee}$$

$$(2.3)$$

The solution of Schrödinger equation with the Hamiltonian $\hat{H}_{ele}$ is electronic energy E_{elec} and electronic wave function Ψ_{elec}. The total energy E_{tot} is the sum of E_{elec} and E_{nuc}.

$$\hat{H}_{elec}\Psi_{elec} = E_{elec}\Psi_{elec} \qquad (2.4)$$

$$E_{tot} = E_{elec} + E_{nuc} \quad where \; E_{nuc} = \sum_{A=1}^{M}\sum_{B>A}^{M}\frac{Z_A Z_B}{R_{AB}} \qquad (2.5)$$

Further approximations are needed to solve the above Hamiltonian as the quantum many body problem obtained after this is also difficult to solve.

2.1.2 The Hartree approximation

Interactions between electrons in the given system is approximated by the Coulomb potential originating from a system of steady electrons. We can say that individual electron moves independently of each other, only experiencing the total average of electrostatic field due to all the other electrons and also the field produced due to the atoms. Hartree considered that each system will obey the Schrödinger equation and thus can write the equation for the N particle system as

$$\Psi(\vec{r_i}) = C_N \prod_i^n \Phi_i(\vec{r_i}) \qquad (2.6)$$

The limitation to this approximation is that it neglects exchange and correlation effects.

2.1.3 Hartree-Fock Method

The Hartree-Fock method involves the Hartree potential and implies the exchange interactions by forcing the antisymmetric nature of the electron wavefunction. This will lower the total binding energy of atoms by keeping the parallel spin electrons staying apart. One must include the antisymmetry as well in order to describe a wave function. The slater determinant takes care of the spin. Interchanging the position of two electrons is equivalent to interchanging the corresponding column. If two electrons at the same spin interchange positions, Ψ^D must change sign. This is known as exchange property and is the manipulation of Pauli principle.

$$\Psi^D(\vec{r}) = \frac{1}{\sqrt{N!}} \begin{bmatrix} x_1(\vec{r}_1) & \cdots & x_n(\vec{r}_1) \\ \vdots & \ddots & \vdots \\ x_1(\vec{r}_n) & \cdots & x_n(\vec{r}_n) \end{bmatrix} \tag{2.6}$$

$$H = -\sum_i \frac{1}{2}\nabla_i^2 + V_{ext}(\vec{r}_i) + \frac{1}{2}\sum_{\substack{i,j \\ i \neq j}} \frac{1}{|\vec{r}_i - \vec{r}_j|} \tag{2.7}$$

Solving the Schrödinger equation with the slater determinant as the wave function we will arrive at the Hartree-Fock equation. The problem of this theory is that it does not contain the correlations in the movement between electrons with anti-parallel spins. Adopting further approximations were needed to minimise the problem were the Density Functional Theory comes into picture.

2.2 Density Functional Theory

As a function of a function. In Density functional theory the functional is electron density electron density is considered as a function of space and time. Electron density is considered in DFT as a fundamental property .Which is different in case of Hartree-Fock theory which deals with many body wavefunction. Using electron density in DFT significantly speeds the computation. The many-body electronic wavefunction is a function of three N variables .The electron density is only a function of three variables (x,y,z). Hohenburg and Kohn who discovered the theorem gives the idea that the electron density is highly useful. The Hohenburg-Kohn theorem confirms that density of a system determines the ground-state properties of it so, if we know the electron density, we will be able to know the total energy of our system.

It is possible to derive an effective one-electron-type Schrödinger equation by focusing on the electron density the density of electron is given as

$$\rho(r) = N \int d^3r_2 d^3 \dots d^3r_N \Psi(r_1, r_2 \dots r_N) \Psi^*(r_1, r_2 \dots r_N) \qquad (2.8)$$

2.2.1 Thomas-Fermi Equation

The indication that the density can be used as a fundamental parameter as the wavefunction is originated from Thomas-Fermi equation .Based on the uniform electron gas, Thomas and Fermi proposed the following functional for the kinetic energy

$$T_{TF}[\rho(\vec{r})] = \frac{3}{10}(3\pi^2)^{\frac{2}{3}} \int \rho^{\frac{5}{3}}(\vec{r}) d\vec{r}. \qquad (2.9)$$

Energy of the atom is obtained using the expression for the electron-electron potential and the nuclear potential.

$$E_{TF}[\rho(\vec{r})] = \frac{3}{10}(3\pi^2)^{\frac{2}{3}} \int \rho^{\frac{5}{3}}(\vec{r}) d\vec{r} - Z \int \frac{\rho(\vec{r})}{r} d\vec{r} + \frac{1}{2} \int \int \frac{\rho(\vec{r_1})\rho(\vec{r_2})}{r_{12}} d\vec{r_1}\vec{r_2} \quad (2.10)$$

2.2.3 Khon-Sham Method

The total energy of an inhomogeneous electron gas, in the influence of an external potential is a functional of the electron density ρ which defines the total energy of the system, which is a function of density i.e E[ρ].

$$E = T_o[\rho] + \int V_{ext}\rho(\vec{r})d\vec{r} + \frac{1}{2}\int \frac{\rho(\vec{r})\rho(\vec{r'})d\vec{r}d\vec{r'}}{|r'-\vec{r}|} + E_{xc}[\rho] \qquad (2.11)$$

The first four terms represents the kinetic energy (of electrons), the nuclear-electronic interaction energy, Coulomb energy and the exchange correlation energy, which has all quantum mechanical contributions. The theorem is exact. As a numerical point of view one can stress the fact that the first 3 terms are huge numbers while the last is considerable but small and hence can be approximated. In a practical point it was necessary to formulate the density functional theory in such that it could be used. From the vibrational principle a set of one-particle Schrödinger equations, the Kohn-Sham (KS) equations must be solved as given in the Figure. In this approach Density functional theory is a universal and general way to approach to the quantum mechanical many-body problem, where the system of electrons is pointed in a unique way onto an effective non-interacting system that has same

density. The non-interacting particles of this system move in an effective local one-particle potential, which contains an exchange-correlation part and a classical mean-field (Hartree) part. In principle, it incorporates all correlation effects. A typical computational way implied is illustrated in Figure below.
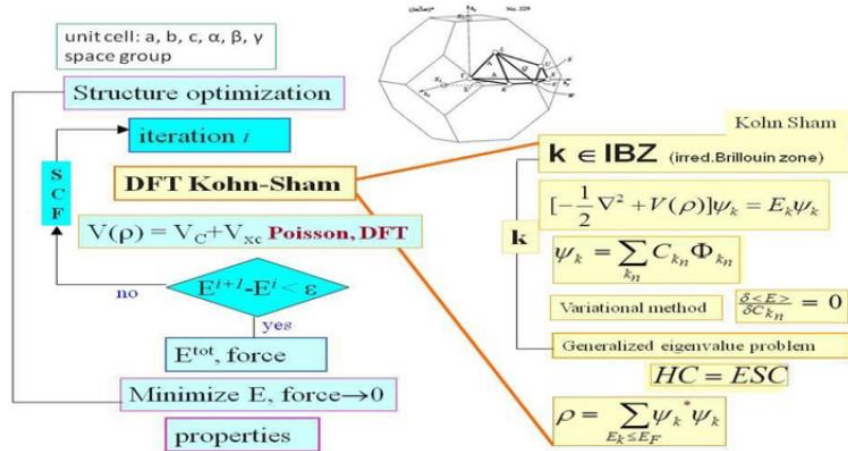

Figure: a

2.2.4 Local Density Approximation (LDA)

The main idea of local density approximation is the assumption that we will be able to write Exc in the following form. Where Exc, is the exchange-correlation energy.

$$E_{XC}^{LDA}[\rho] = \int \rho(\vec{r}) \in_{XC} (\rho(\vec{r})) d\vec{r} \qquad (2.12)$$

$\in_{xc}(\rho(\vec{r}))$ is the exchange-correlation energy per particle of a homogenous electron gas having density $\rho(\vec{r})$. The energy per particle is weighted with a probability $\rho(\vec{r})$ such that there is an electron at this position. The quantity $\in_{xc}(\rho(\vec{r}))$ can be further divided into correlation and exchange contributions.

$$\in_{XC} (\rho(\vec{r})) = \in_X (\rho(\vec{r})) + \in_C (\rho(\vec{r})) \qquad (2.13)$$

2.2.5 Generalised Gradient Approximation (GGA)

The GGA approach takes into account variations in the density by including the gradient of the density in the functional. One commonly used GGA functional is that of Becke

$$V_{xc}^{B} = -\beta \rho^{\frac{1}{3}} \frac{x^2}{(1 + 6\beta x \sinh^{-1} x)} \quad . \quad x = \frac{\nabla \rho}{\rho^{\frac{4}{3}}}$$

This functional has only one adjustable parameter, β. The value of $\beta = 0.0042$ was determined based on the best fit to the energies of six noble gas atoms using the sum of the LDA and GGA exchange terms.

2.2.6 Tran-Blaha modified Becke-Johnson potential (TB-mBJ)

The semi-local Becke-Johnson (BJ) exchange-correlation potential and its modified form proposed by Tran and Blaha (TB-mBJ) have attracted a lot of interest recently because of the surprisingly accurate band gaps they can deliver for many semiconductors and insulators. Even though traditional functions like LDA and GGA produce reasonably good results, they underestimate the band gaps of many semiconductors and insulators. Tran-Blaha modified Becke-Johnson potential (TB-mBJ) can be one of the solutions to this problem since this exchange correlation function can capture the exact band gap. This is used in the present thesis in order to accurately determine the band gaps of the investigated compounds

2.3 Introduction to Thermoelectric Materials

Thermoelectric materials attracted the attentions for decades, because it enables the direct conversion of thermal energy to electrical energy, thus having a different way for power production. Thermoelectric device is an environment-friendly power conversion technology with the merits of high reliability, little size and durability in a wide range of temperature. However, the efficiency of thermoelectric devices is not great enough compared to the solar energy making devices. There are mainly three classification in thermoelectric effect that are the Seebeck effect, Peltier effect and Thomson effect which is mentioned below

Seebeck effect

A phenomenon in which the temperature difference between dissimilar electrical conductors or semiconductors generates a potential difference. The potential difference produced by this effect are small, usually few microvolts per kelvin of temperature difference at the junction. If temperature difference is high, we may expect some devices

to produce a few millivolts. Numerous such devices can be interconnected in series to increase the total output voltage or can be interconnected in parallel to improve the maximum current. Large arrays of Seebeck setup can generate useful, small-scale electrical power if a high temperature gradient is maintained across the junctions. The Seebeck effect is responsible for the effect behind thermocouples, which are used to measure temperature variations or to make electronic switches.

Peltier Effect

It is the reverse of the Seebeck effect. Where a current through two junctions can produce a temperature variation. This method was discovered by Peltier, and thus called the Peltier effect. It may similar to Joule heating, but it is not. In Joule heating the current is only increasing the temperature. In Peltier effect a temperature difference is created and one junction becomes hotter and other junction becomes colder. Although Peltier coolers are not as efficient, they are accurate, easy to control. Peltier effect devices are used as coolers for microelectronic devices and computer CPUs.

Thomson Effect

The emission or absorption of heat when a current is passed through a circuit composed of a single material that has temperature variation along its length is called Thomson effect. The transfer of heat is superimposed on the common production of heat associated with the electrical resistance to currents in conductors. If a copper wire carrying a steady electric current is exposed to external heating at a short section while the rest remains cooler, heat is absorbed from copper as the electric current approaches the hotter part, and heat is transferred to copper just beyond the hotter point.

Chapter 3

Methodology

We have used experimental parameters as input and performed complete geometry optimization using VASP[11]. For further calculations we have used our optimized lattice parameters. Electronic structure properties are performed using full potential linearized augmented plane wave method as implemented in WIEN2k package [12]. Since the traditional functionals such as of local density approximation and generalized gradient approximation methods were underestimating the band gap, we have adopted Tran Blaha modified BeckeJohnson potential (TB-mBJ)[13] on top of GGA calculations to attain proper band gap for the investigated compounds. Spin orbit interactions were considered in every calculation. For electronic structure calculations we have used a k- mesh of 11 x 11 x 3 and for transport we have increased to denser k-mesh. All the calculations were performed using the optimized lattice parameters with an energy convergence criterion of 10^{-6} Ry per formula unit .Thermoelectric properties were calculated using Boltztrap[14] code with well-converged parameters using the self-consistent calculation within the rigid band approximation (RBA)[15][16] and the constant scattering time (τ) approximation (CSTA)[17][18]. The RBA is a good approximation to calculate the transport properties for doped semiconductors when the doping level is not very high[19][20]. It is evident that CSTA has been quite successful in predicting the thermoelectric properties of many materials. we have calculated the thermopower and electrical conductivity/scattering time (σ/τ) as a function of carrier concentration and temperature using the Boltzmann transport equation approach as implemented in the Boltztrap code

Chapter 4

Results and Discussions

4.1 Structural and Electronic properties

All the investigated compounds crystallize in hexagonal symmetry with space group P63/mmc. The schematic of the crystal structure is given in Figure(1), and the structure is found to possess a layered pattern along 'c' axis, in such a way that 'K' atoms are sandwiched between 'Zn' and 'X'(X: P, As, Sb) atoms. The optimized parameters along with available experimental and other theoretical reports are presented in Table(1). From the Table(1) it is evident that our optimized values are highly comparable with all the reported values. We know that all the physical properties are directly connected with the crystal structure, and to dig more about the same we have analysed in-plane and out of plane 'K' atom bond length and represented the same in Table(2). Both in-plane and out of plane 'K' atom distances are found to be increased from KZnP to KZnSb. In similar line we have analysed the valence electron charge density, and the charge density plot of KZnP along (100) plane is represented in Figure(2). Lines and colour in the charge density plot represent the strength of charge flow, and from the Figure(2) it is clear that the in-plane charge flow is higher compared to the out of plane charge flow. The bond length difference and charge flow difference might provide anisotropy in the physical property in this compound.

One of the recent study has confirmed the mechanical and dynamical stability of the investigated compounds [21]. Coming to the electronic structure, we have examined the same using different functionals like GGA and TB- mBJ. The obtained band gap using these functional for all the compounds are given in Table(3). As expected one can clearly see that the band gap values are improved using TB-mBJ functional. Calculated band structures using GGA functional of all the investigated compounds are presented in Figure(3). All the compounds fall into direct band gap semiconductors. Moreover, the band dispersion along different crystallographic directions are found to be different. The high symmetry direction Γ- M represents the 'a' and 'b' axes (in-plane) and Γ- A represents the 'c' axis (out of plane). In the case of KZnP and KZnAs, the band dispersion along Γ- M and Γ- A are having huge difference

and along Γ- A one can see a highly flat band in valence band. In the case of conduction band the band dispersions along in-plane and out of plane directions are almost similar. Coming to KZnSb, the scenario is little different, for both valence and conduction bands the band dispersion host a huge difference. This we have again confirmed using the effective mass calculations, and the Table(4) provides the hole and electron effective mass values in the unit of electron mass. The mixture of highly dispersed and less dispersed bands indicate the presence of heavy and light band masses, and might lead to good thermoelectric properties. In addition, the highly flat band along Γ–A might induce an anisotropy in physical properties, and then the system to quasi two dimensional one. Further to understand the contribution of each elements near the Fermi level, we have calculated total and partial density of states for all the investigated compounds and represented the same in Figure(4). It also quite evident that the contribution of K (s,p) states and Zn (s,p) states are dominating near the Fermi level.
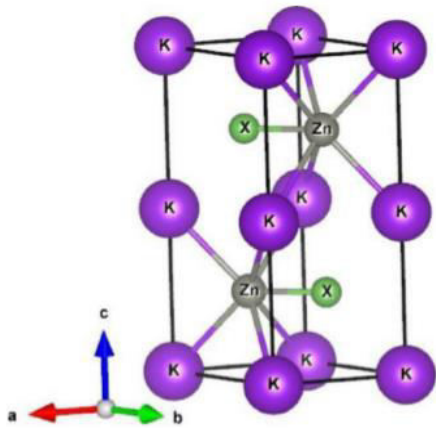
Figure.1:Crystal structure of KZnX (X=As,P,Sb).
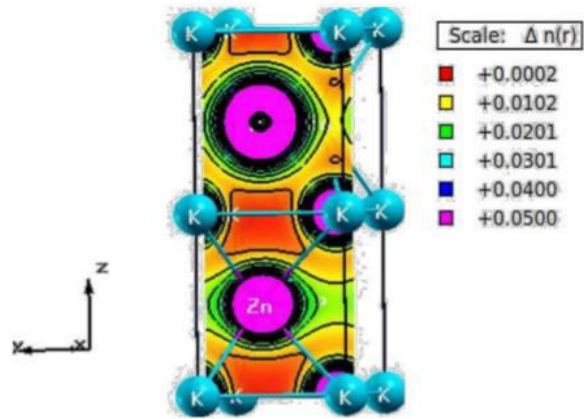
Figure.2:Calculated charge density of KZnP along (100) plane.

Cell (Å)	KZns			KZnP			KZnSb		
	Exp	Present	Other Theory [11]	E x p	Present	Other Theory [11]	E x p	Present	Other Theory [11]
a	4.23	4.26	4.327	4.09	4.10	4.103	4.54	4.57	4.59
b	4.23	4.26	4.327	4.09	4.10	4.103	4.54	4.57	4.59
c	10.23	10.40	10.35	10.14	10.28	10.207	10.50	10.71	10.658

Table.1: Ground state properties of all the investigated compounds

Compound	In-plane distance of 'K' atoms (Å)	Out of plane distance Of 'K' Atoms (Å)
KZnP	4.10	5.14
KZnAs	4.26	5.20
KZnSb	4.57	5.35

Table.2: Calculated bond lengths of all the investigated compounds

Functionals	KZnP (eV)	KZnAs (eV)	KZnSb (eV)
GGA	0.82	0.24	0.41
GGA + SO	0.81	0.16	0.21
TB-mBJ	1.96	1.30	1.13

Table.3: Calculated band gaps for all investigated compounds

Direction	KZnP		KZnAs		KZnSb	
	Holes	Electrons	Holes	Electrons	Holes	Electrons
Γ- M	0.75	0.23	0.76	0.13	0.35	0.10
Γ- A	6.12	0.44	5.18	0.71	3.83	1.38

Table .4: Calculated effective mass in the unit of electron mass for all compounds

KZnP

KZnAs

(a)

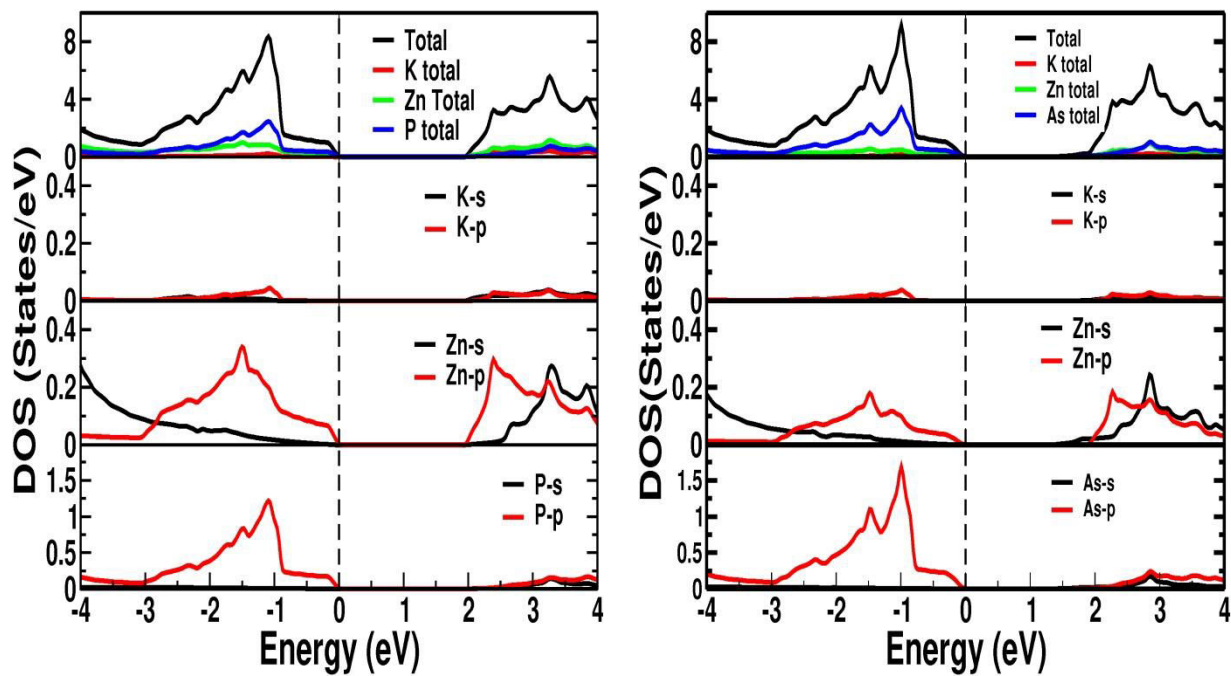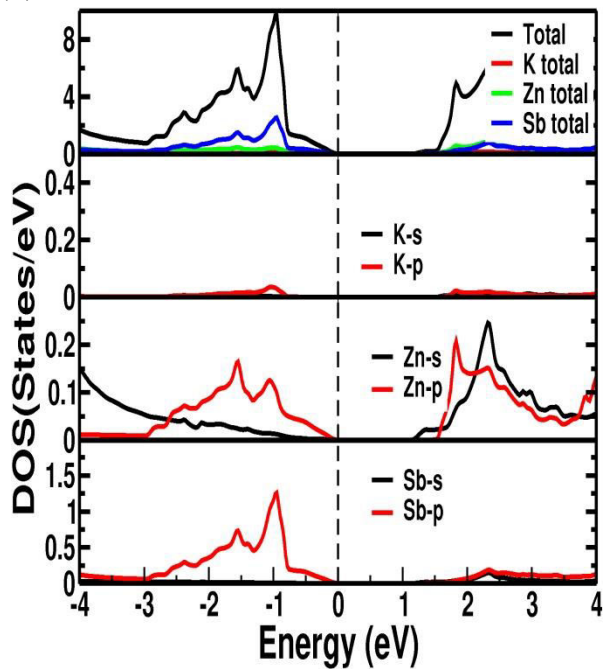**(b)**
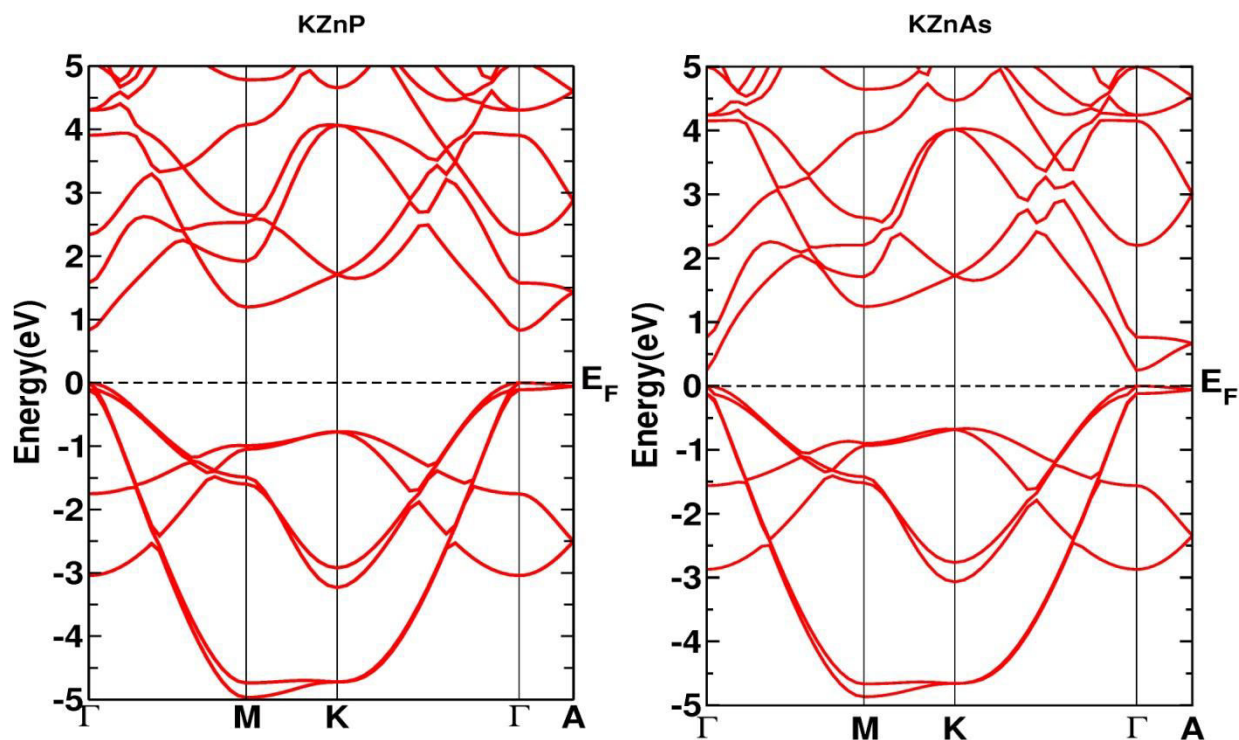
KZnSb
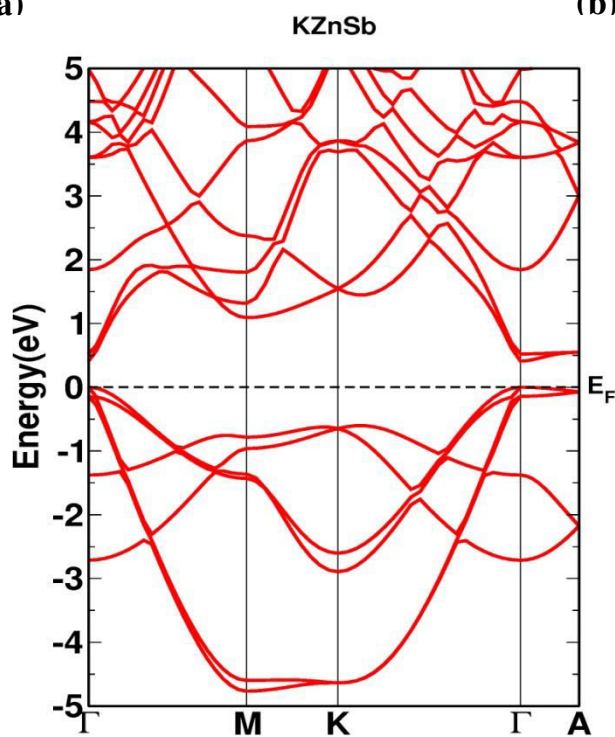
(c)

Figure.3: Band structure obtained with GGA + SO

(a)

(b)

(c)

Figure.4: Total and partial density of states (GGA+SO) of KZnX (X = P, As, Sb)

4.2 Thermoelectric properties

We have calculated the thermopower and electrical conductivity/relaxation time (σ/τ) and power factor as a function of carrier concentration and temperature using the Boltzmann transport equation approach as implemented in the Boltztrap code. Since the square of the thermopower is directly proportional to the figure of merit ZT (ZT = $(S^2\sigma T)/\kappa$), the thermopower plays a vital role in deciding the performance of the thermoelectric material. The thermopower calculated using the electronic structure data depends on the carrier concentration and temperature. The thermopower is calculated as a function of hole and electron concentrations at different temperatures. We have investigated the transport properties for the carrier concentration between 10^{18} and 10^{21} cm^{-3} for all the investigated compounds, which is an optimum carrier concentration range for better thermoelectric performance. The investigated compounds crystallize in hexagonal structure and it is very important to observe the variation of transport properties along different crystallographic directions. We have investigated the TE properties along the crystallographic 'x' and 'z' axes. Here we have Calculated TE properties of KZnP, KZnAs and KZnSb for both electron and hole concentration at 10^{19} and 10^{20} cm^{-3} as function of temperature where temperature ranges from 100 to 900K (Figure(5), (6) and (7)). Calculated TE properties for both electron and hole temperature at 500K and 900K as function of carrier concentration were concentration ranging from 10^{18} to $10^{21} cm^{-3}$ (Figure(7)). It is observed that thermopower increases with decreasing carrier concentration for both electron and hole doping. The difference between the thermopower values between KZnP, KZnAs and KZnSb is be due to differences in effective masses of the carriers near the Fermi level of these compounds. From the Figure(7), it is found that all compounds exhibits almost same thermopower for the holes as well as electrons. The maximum thermopower is found in hole doped KZnP compared with all other compounds. It is observed that the thermopower is found to decrease from KZnP to KZnAs. The electrical conductivity scaled by relaxation time in $\Omega^{-1}m^{-1}s^{-1}$ (σ/τ) is the other important factor that influences the thermoelectric figure of merit (ZT), σ/τ is an intrinsic property of any material for all compounds as shown in Figure(6). We found that there is no significant change in σ/τ with temperature but σ/τ is found to increase with increase in concentration for all the three compounds. We obtain significant difference in thermopower as well as σ/τ along 'x' and 'z' directions which confirms the anisotropic nature in thermopower along 'x' and 'z' crystallographic directions for all the investigated compounds.
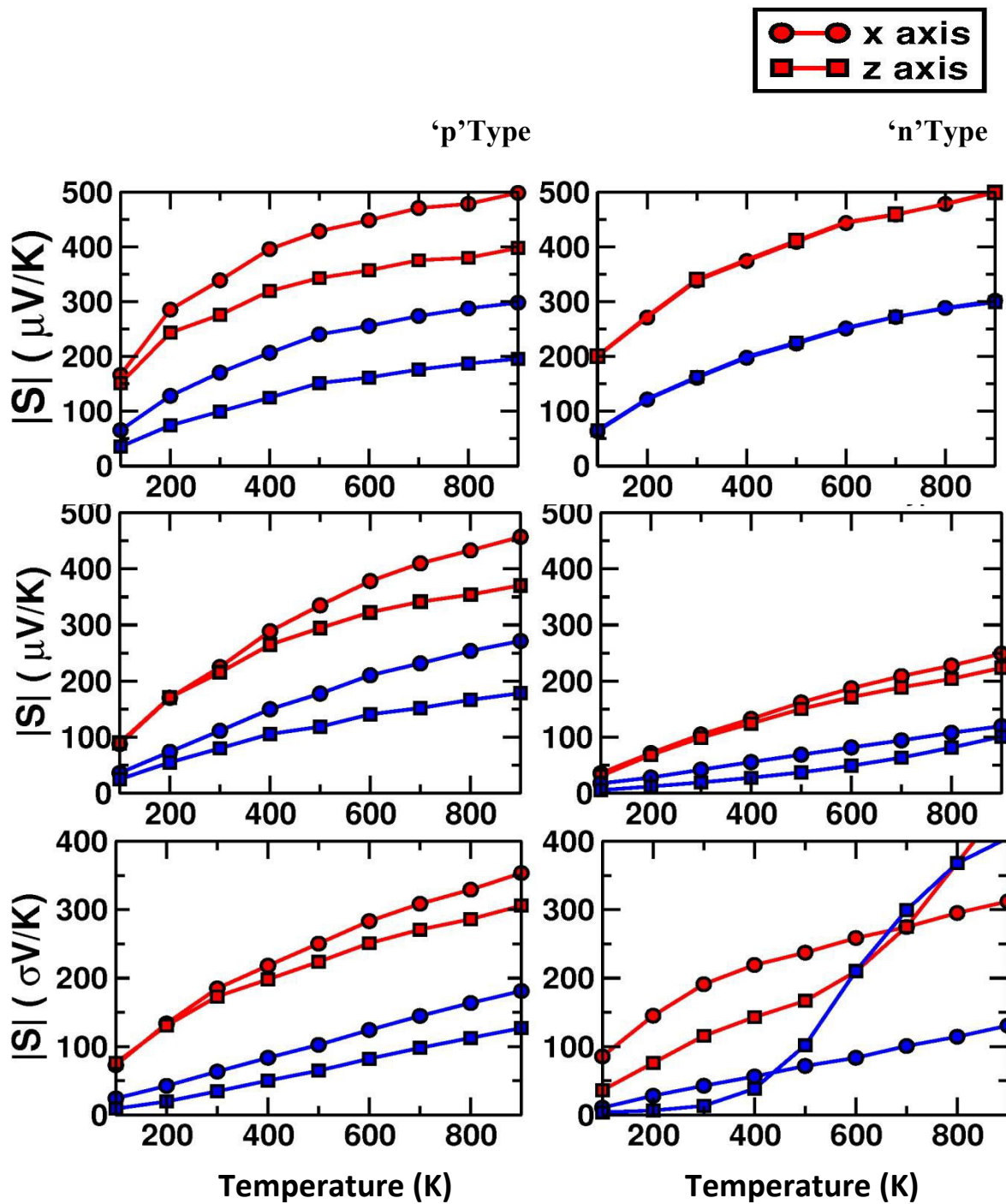
Figure.5: Thermopower is plotted against temperature of KZnP, KZnAs, KZnSb using TB-mBJ functional, along 'x' and 'z' directions for a concentration of 10^{19} cm^{-3} (red) and 10^{20} cm^{-3} (blue).
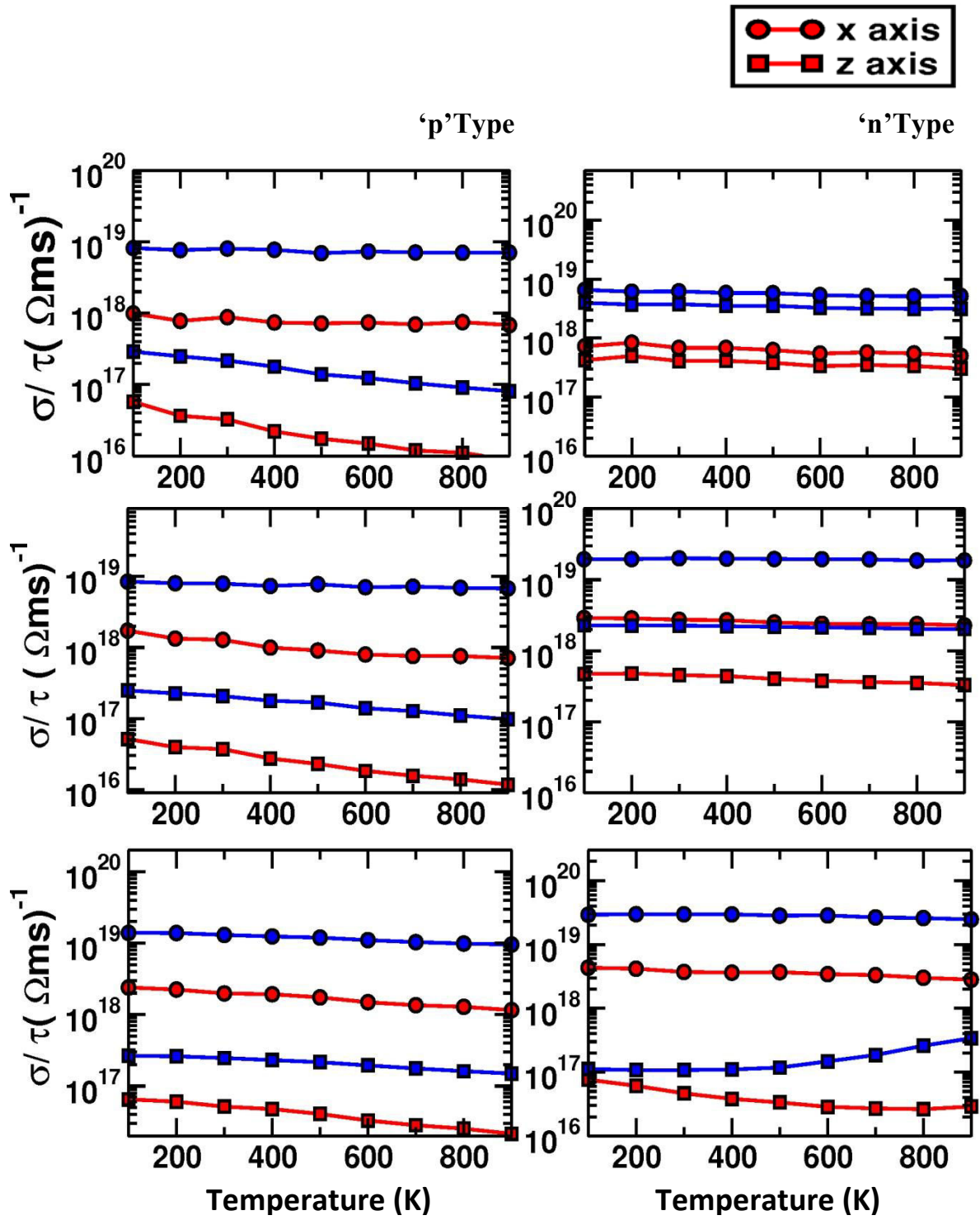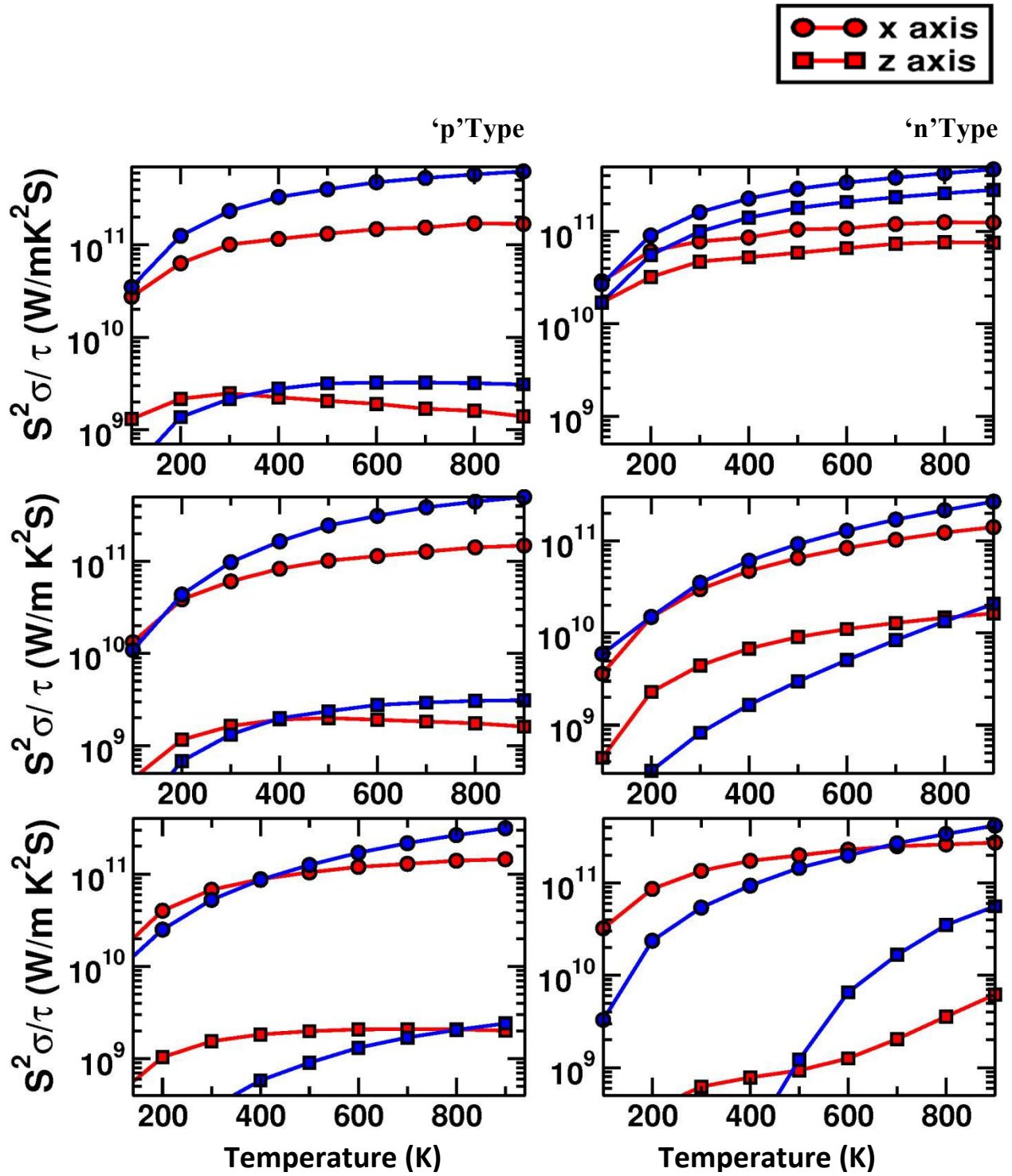
Figure.6: Electrical conductivity scaled by relaxation time is plotted against temperature of KZnP, KZnAs, KZnSb using TB-mBJ functional, along 'x' and 'z' directions for a concentration of 10^{19} cm^{-3} (red) and 10^{20} cm^{-3}(blue).

Figure.7: Power-factor is plotted against temperature of KZnP ,KZnAs ,KZnSb using TB-mBJ functional, along 'x' and 'z's directions for a concentration of 10^{19} cm^{-3} (red) and 10^{20} cm^{-3} (blue).
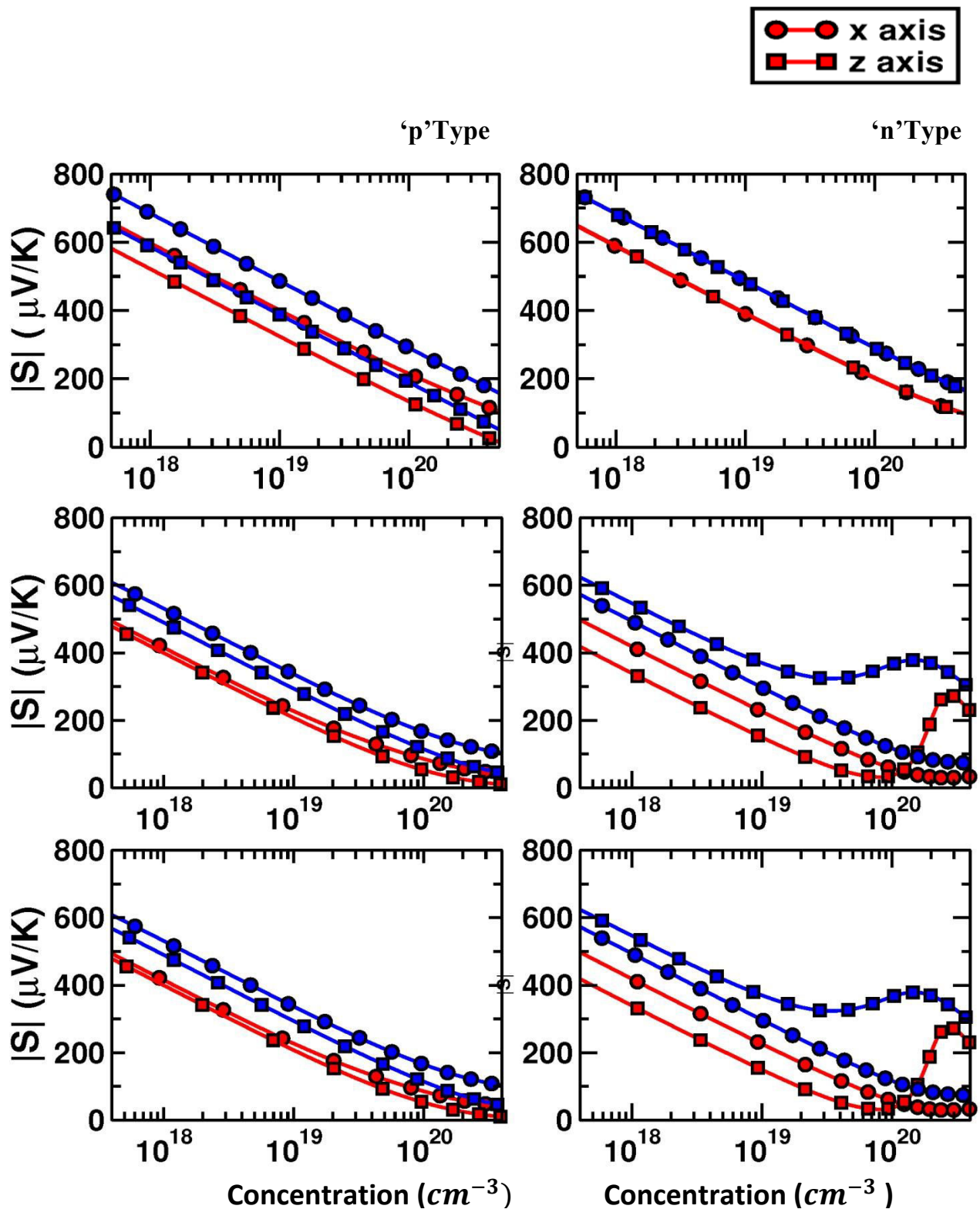
Figure.8: Thermopower is plotted against carrier concentration of KZnP, KZnAs, KZnSb using TB-mBJs functional, along 'x' and 'z' directions for a temperature of 500K(red) and 900K(blue).

The power factor is plotted as a function of temperature for carrier concentrations ranging from $10^{19} \ cm^{-3}$ and $10^{20} \ cm^{-3}$ respectively. From Figure(7) it seems that power-factor for both hole doping as well as electron doping is same for all the investigated compounds. This may be due to the similar values of S and σ / τ in case of holes as well as electron for all the investigated compounds. Due to the higher value of σ / τ along 'x' direction, power-factor will be higher along 'x' axis provided the relaxation time for electrons and holes remains the same. It is found that in the case of hole doping, the power-factor values are anisotropic along different 'x' and 'z' crystallographic direction. This eventually confirms the high anisotropic behavior of all investigated compounds. Overall we can say that the hole doping as well as electron doping is favorable for TE properties for all the investigated compounds.

4.3 Effect of pressure on electronic and thermoelectric properties of KZnX (X = P, As, Sb)

4.3.1 Electronic Properties

Here the changes in both electronic and TE properties of KZnX (X =P, As, Sb) were investigated on the application of pressure. At various pressures (0GPa to 10GPa) the ternary compounds were optimized. The electronic properties such as density of states and bandstructure and the TE properties like Seebeck coefficient (µV/K), electrical conductivity/scattering time (Ωms^{-1}) and power factor (W/mK^{2}S) were obtained under different pressures. The bandgaps in electron volts were calculated for the optimized structures for each pressure using GGA, TB-mBJ potentials with the inclusion of spin orbit coupling which is shown in the figure(**9**) The bandgap obtained using TB-mBJ is slightly higher than that obtained using GGA. It is found that the there is no big change in the bandgap for KZnP on increasing the pressure from 0 GPa to 10 GPa. While for KZnAs the band gap increases from 0GPa to 6GPa and decreases after that. In case of KZnSb the bandgap found to increase on increasing the pressure from 0 GPa to 10 GPa. The main aim in this section is to investigate the variation in TE properties of the given ternary compounds under the application of pressure ranging from 0GPa to 10 GPa.
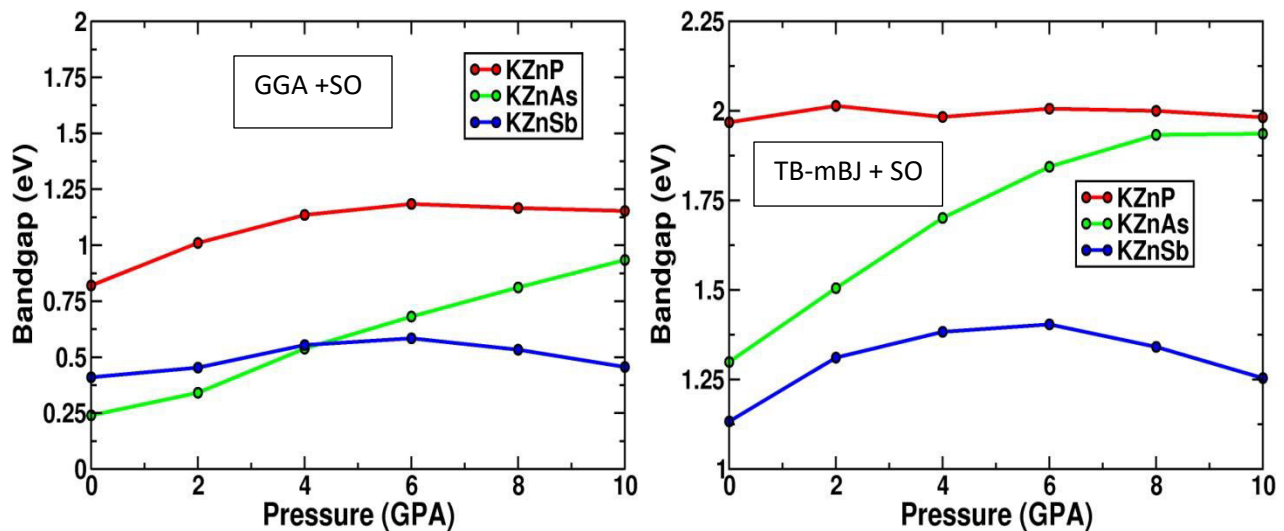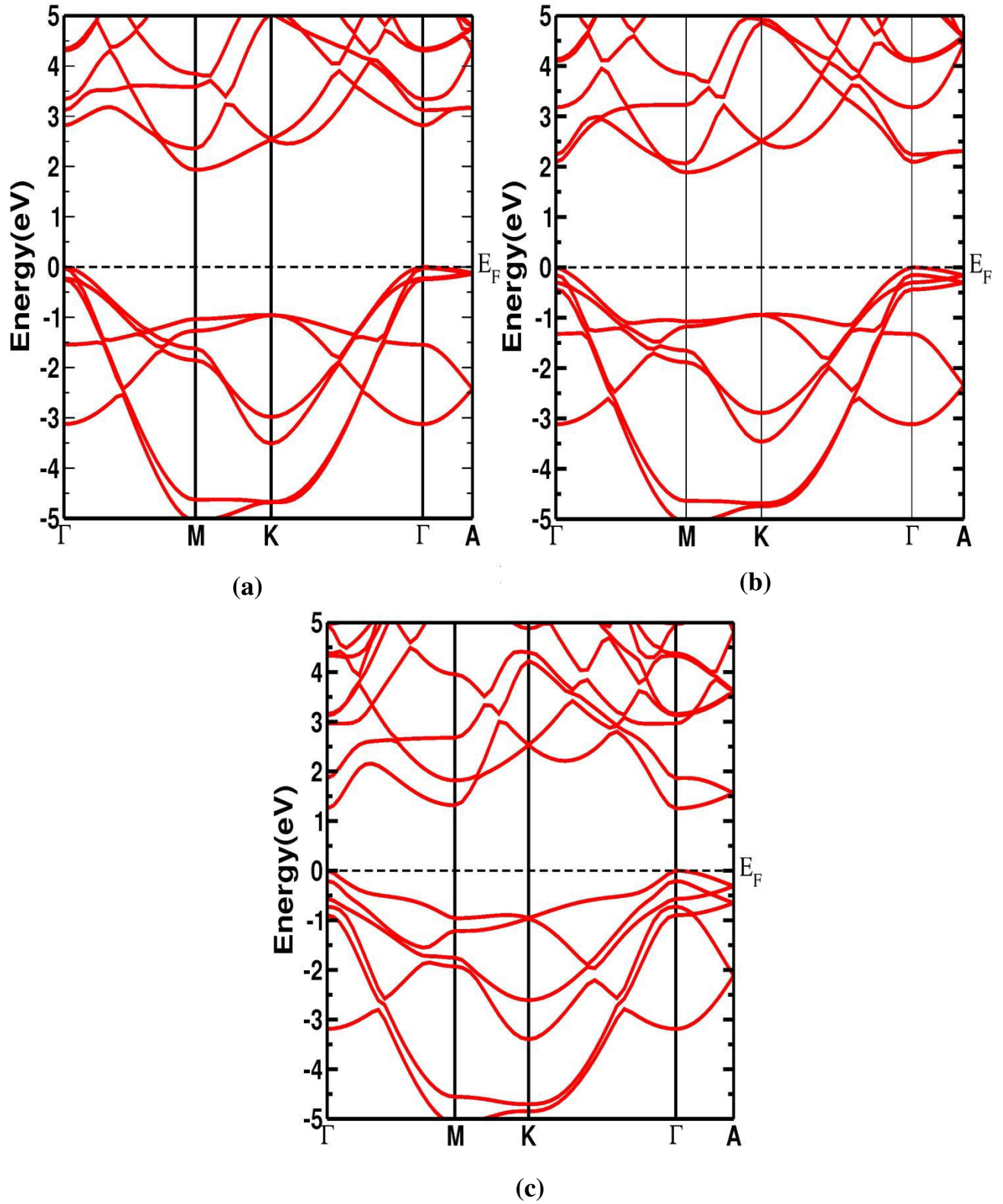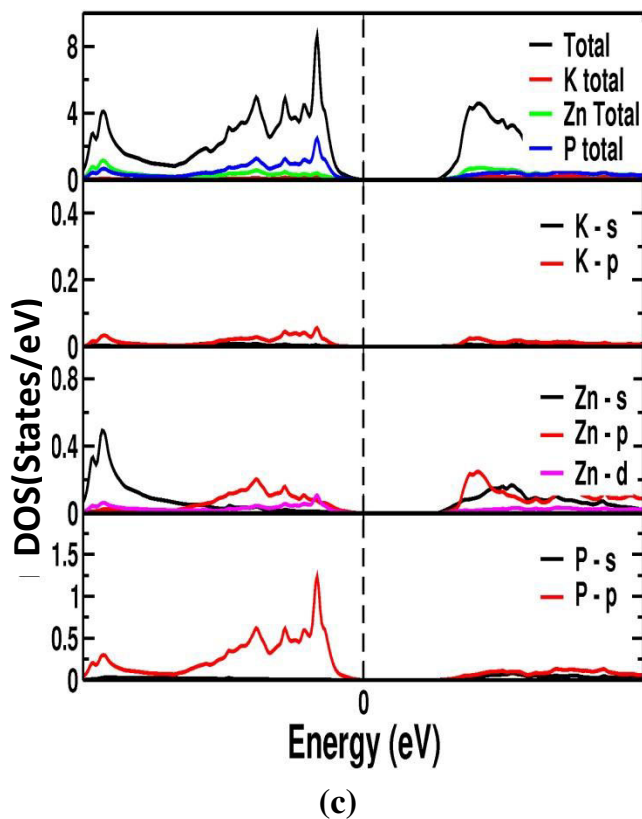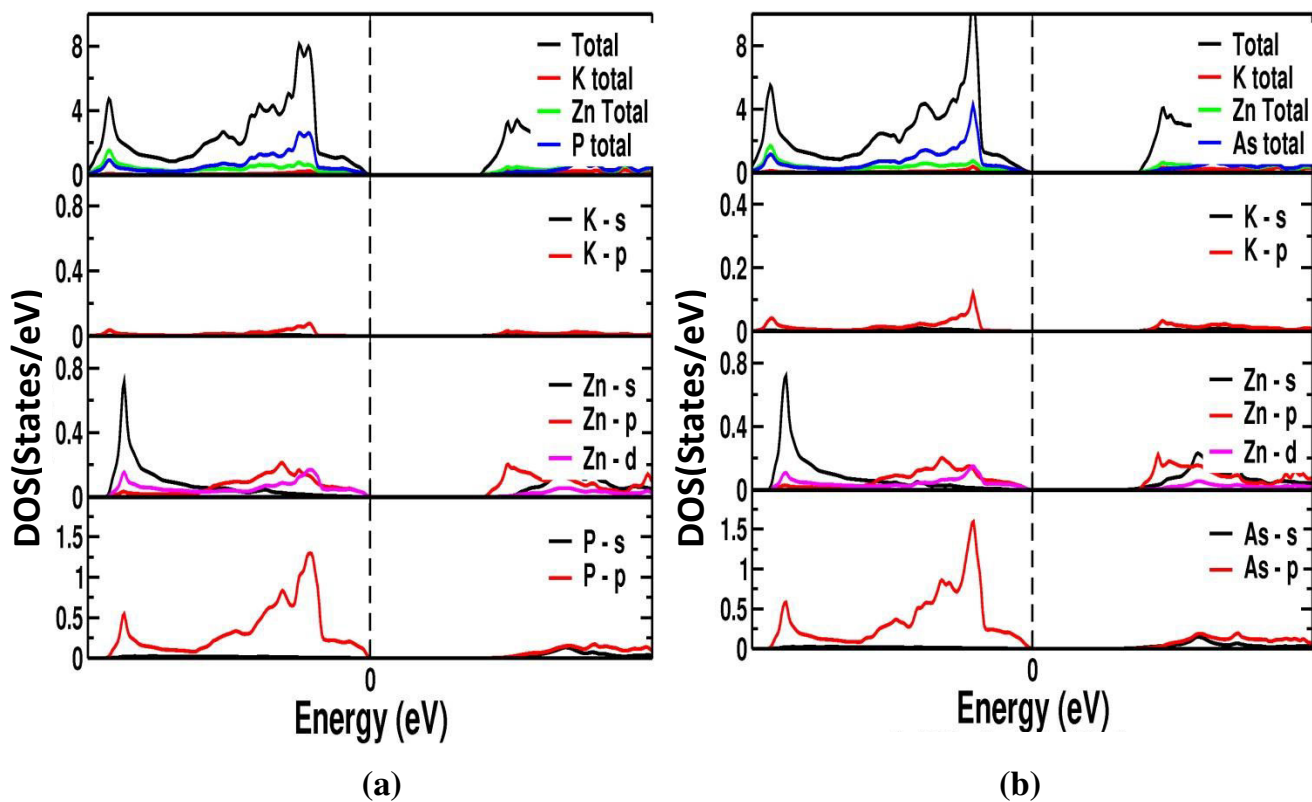

Figure.9: Band gap obtained for KZnX when GGA, TB-mBJ functional were employed with inclusion of Spin orbit coupling from 0 GPa to 10 GPa

Figure.10: Calculated bandstructure using TB-mBJ functional of KZnP(a), KZnAs(b), KZnSb(c), under the pressure of 10GPa

Figure.11: Calculated density of states using TB-mBJ functional of KZnP(a), KZnAs(b), KZnSb(c), under the pressure of 10GPa

4.3.2 Thermoelectric Properties

The TE properties were calculated as a function of hole and electron concentrations at 500K. We have investigated the transport properties for the carrier concentration ranging from $10^{-19}cm^{-3}$ and $10^{-20}cm^{-3}$ along 'x' and 'z' axis of the compound. It is found that for KZnP there is no change in the thermal properties on increasing the pressure. This could be due to the negligible change in the bandgap of KZnP. For KZnP the Seebeck coeffient, electrical conductivity/relaxation time (σ/t) and power factor remains almost same under different pressures. For KZnAs it is found that the anisotropic nature slightly decreased on increasing the pressure and there is no great variations of thermoelectric properties in case of 'p' type but some variations in TE properties has been observed in case of 'n' type KZnAs . The trend in variation of TE properties in case of KZnSb is found to be almost same for that of KZnAs. It is also seen that with the increase in pressure, the Seebeck coefficient of 'n' type KZnAs increases, which is shown in figure(13). It is because with the increase in pressure results in an increased effective mass. The increase in effective mass affects the TE properties. Since the seebeck coefficient and power factor is found to be almost same under all pressures for both 'n' and 'p' type KZnP, it can be concluded that hole as well as electron doping is favorable for TE properties for KZnP compound under all pressure range from 0GPa to 10GPa. At 0GPa the TE properties is found to be same for both 'n' type and 'p' type KZnAs. But at higher pressures the enhancement of TE properties is observed for 'n' type KZnAs compared to that of 'p' type. The difference in the thermopower between electrons and holes at higher pressure in case of KZnAs is found to be the order of 150µ/K which implies that at higher pressures electron doping may be more favorable for TE properties for KZnAs. In case of KZnSb the TE properties is found to be same for 'n' type and 'p' type at ambient conditions but a great increase of TE properties has been observed in 'n' type KZnSb at higher pressures. The difference in the thermopower between electrons and holes at higher pressure in case of KZnSb is found to be the order of 100-150µ/K which shows that electron doping is more favorable for KZnSb at higher pressures.
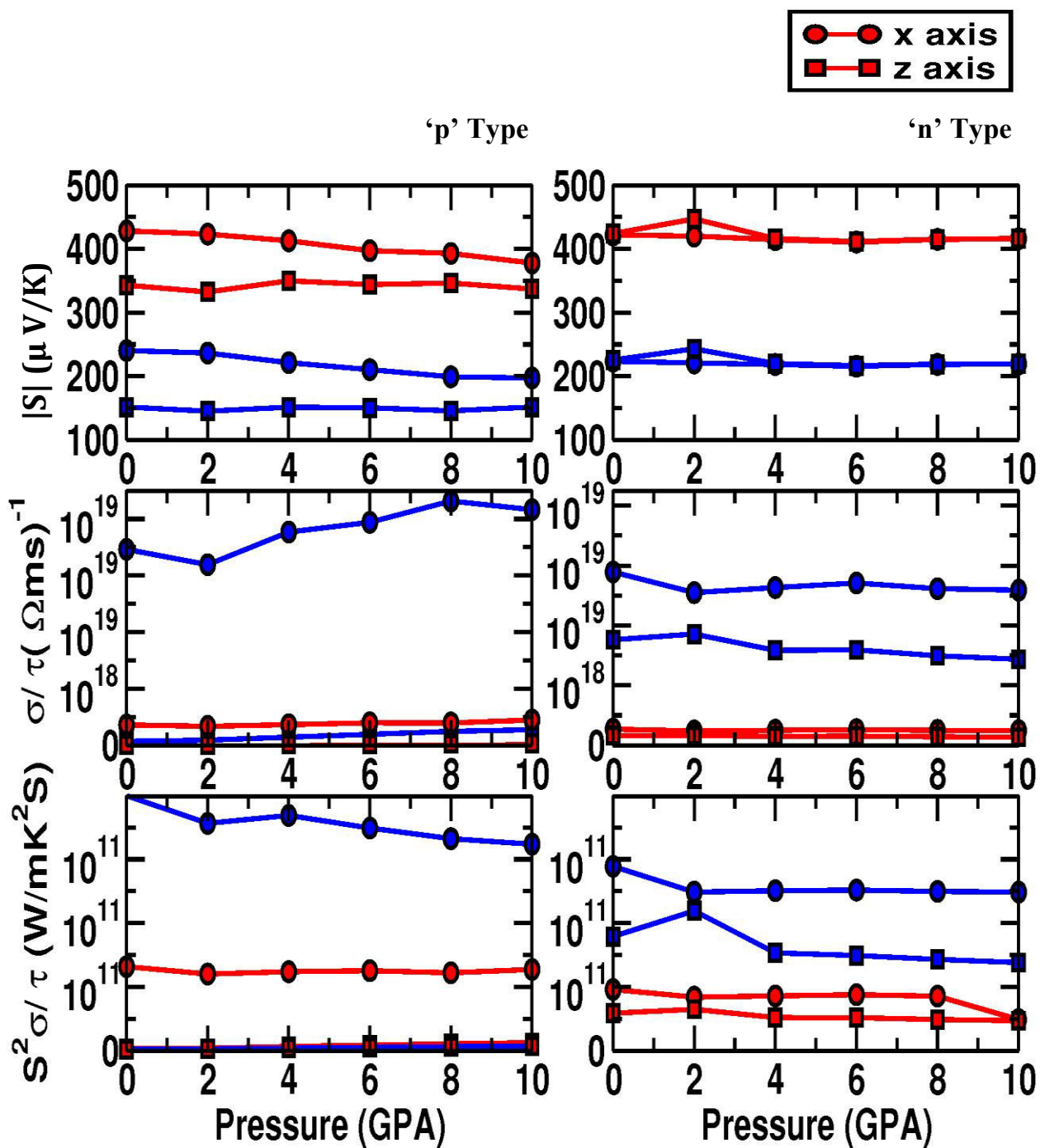
Figure.12: Variations in TE properties of KZnP using TB-mBJ functional with increasing pressure from 0GPa to 10 GPa
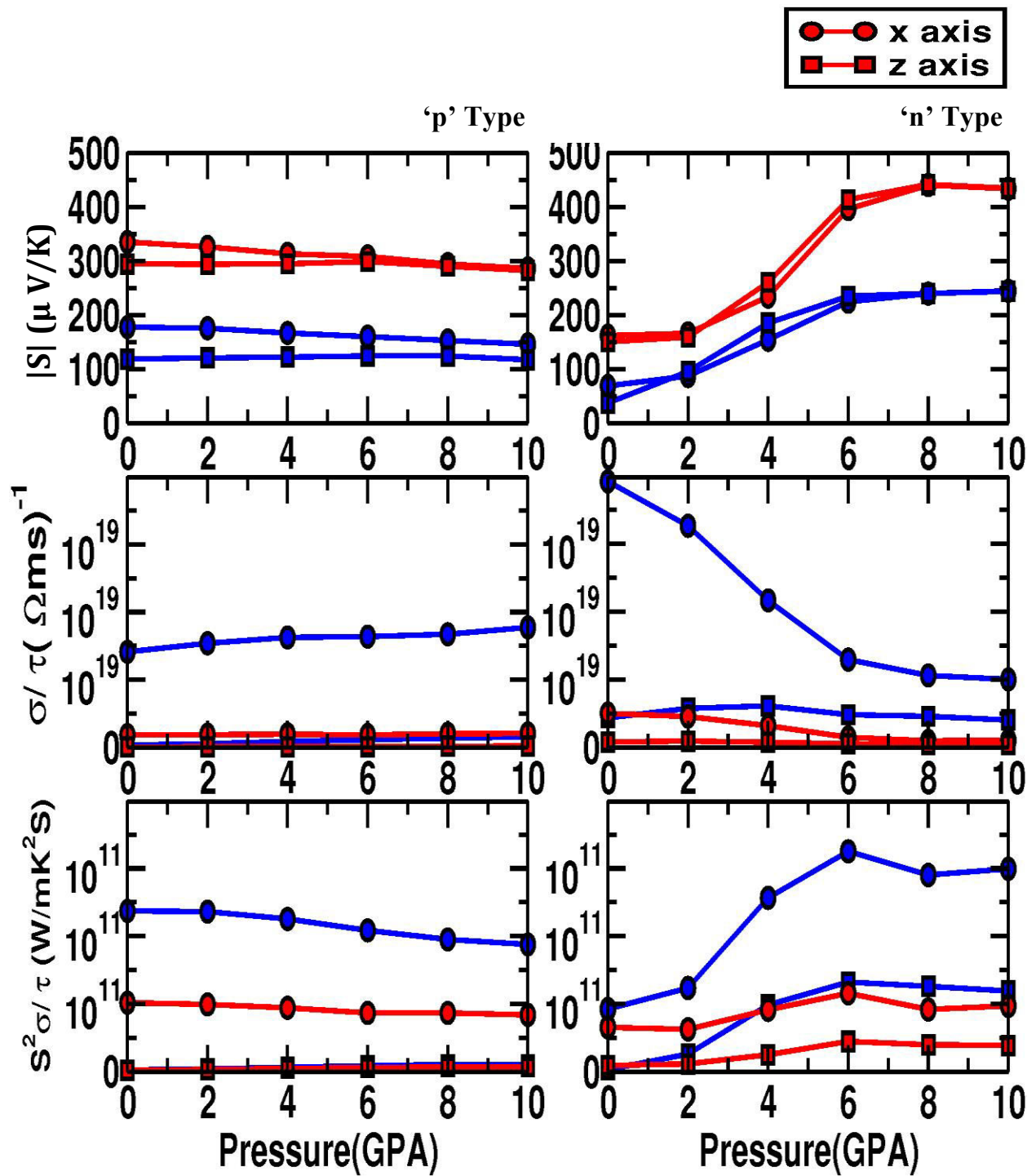
Figure.13: Variations ins TE properties of KZnAs using TB-mBJ functional with increasing pressure from 0GPa to 10 GPa
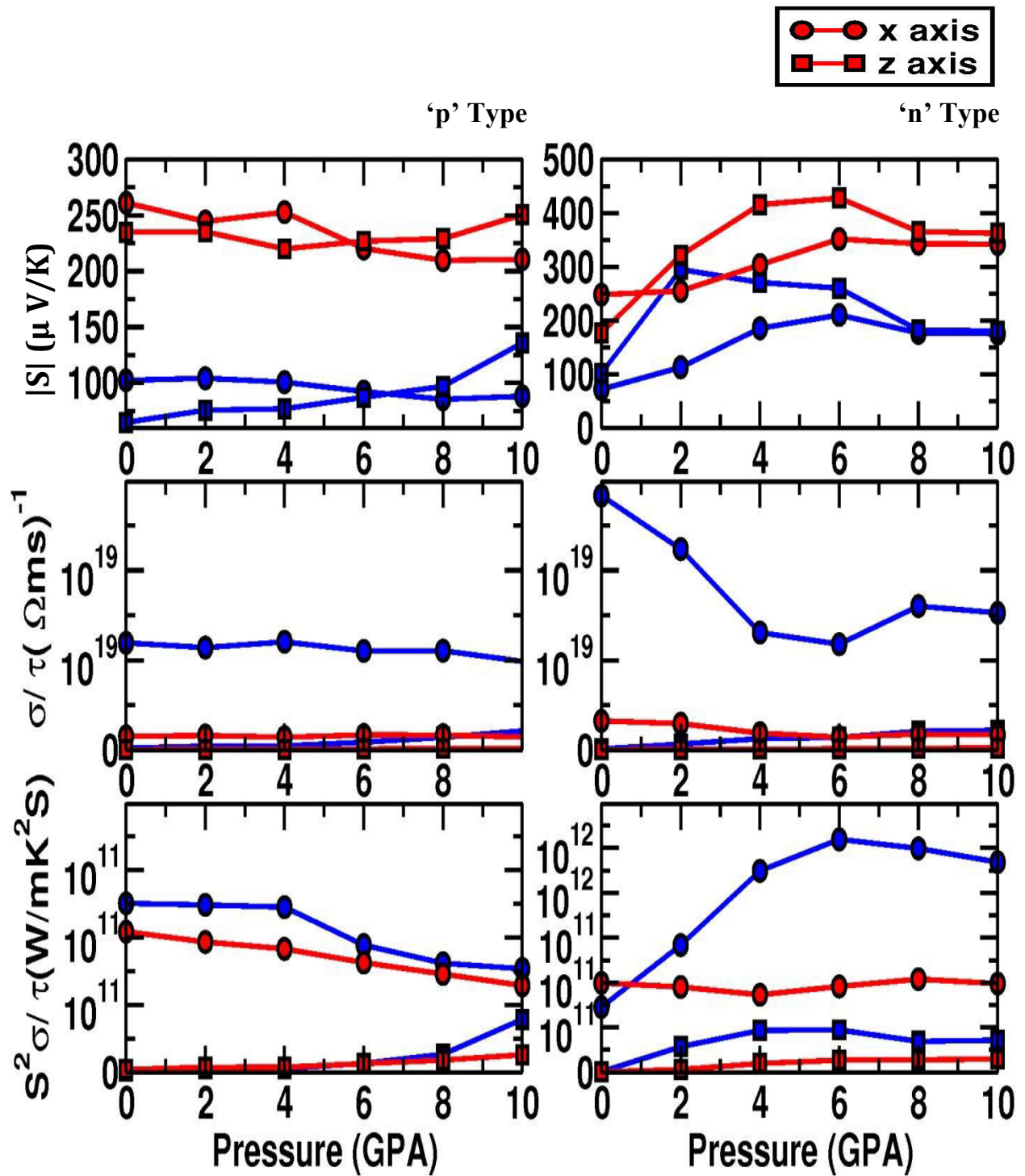
Figure.14: Variations in TE properties of KZnSb using TB-mBJ functional with increasing pressure from 0GPa to 10 GPa

Chapter 5

Conclusion

Electronic and transport properties of KZnX (X:P, As, Sb) are studied using calculations within DFT as a function of carrier concentration at various temperature and solving the Boltzmann transport equation within the constant relaxation time approximation (CSTA) and rigid band approximation (RBA). The electronic band structures are calculated by means of the full-potential linear augmented plane wave method (FP-LAPW), using the Tran-Blaha modified Becke-Johnson potential (TB-mBJ). The calculated lattice parameters are in good agreement with available experimental data. The calculated electronic structure shows the investigated compounds to be direct band gap semiconductors. The TE properties were also calculated for the currently investigated compounds for both carrier concentrations and the variation is studied as a function at various temperatures. We found that under ambient conditions the thermopower is almost same for both 'n' type doping and 'p' type doping for all the investigated compounds. We have studied the variation in electronic and TE properties of the investigated compounds under varying pressure from 0 GPa to 10 GPa. It seems that for KZnAs and KZnSb the 'n' type doping is more favorable under higher pressure, which enabled us to predict that 'n' type KZnAs and 'n' type KZnSb might have promising applications as a good thermoelectric material under high pressure.

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