

Comparative study of thermoelectric properties of Co based filled antimonide skutterudites with and without SOC effect



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ABSTRACT

In this article we communicate the spin-orbit interaction effects on the thermoelectric properties of alkaline-earth (A = Ca, Sr and Ba) based fully filled skutterudites $\text{ACo}_4\text{Sb}_{12}$. From the electronic structure calculations for $\text{ACo}_4\text{Sb}_{12}$ (A = Ca, Sr and Ba) it is understood that spin-orbit coupling take part in splitting of the states of the materials, however in case of $\text{BaCo}_4\text{Sb}_{12}$, with splitting, the maximum peak around the Fermi level also becomes sharper. This in turn affects the thermal performance of this material. Maximum peak value of Seebeck coefficient is significantly reduced for $\text{CaCo}_4\text{Sb}_{12}$ and $\text{SrCo}_4\text{Sb}_{12}$, however in case of $\text{BaCo}_4\text{Sb}_{12}$ Seebeck coefficient is increased significantly in the lower chemical potential region for n-type doping when spin-orbit coupling is added to the calculations. Furthermore there is also reduction in the electrical and electronic thermal conductivities for all compounds $\text{CaCo}_4\text{Sb}_{12}$, $\text{SrCo}_4\text{Sb}_{12}$ and $\text{BaCo}_4\text{Sb}_{12}$, due to spin-orbit interaction. Maximum zT 's values obtained without spin-orbit interaction for $\text{CaCo}_4\text{Sb}_{12}$, $\text{SrCo}_4\text{Sb}_{12}$ and $\text{BaCo}_4\text{Sb}_{12}$ are 0.97, 0.95 and 0.64 whereas with the spin-orbit interaction maximum zT 's values are 0.64, 0.59 and 0.69 respectively.

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1. Introduction

Spin orbit coupling (SOC) unites the velocity of a particle to the spin associated and therefore is very important for the variety of the physical properties in the condensed matter. In solid materials, spin orbit coupling effect originates when an electron or electrons move in the field inside in a crystal, and therefore bring the quantum mechanics to the forefront to calculate the exact nature of a given material [1]. SOC usually splits the energy scale of the electronic states at which quantum effects are extremely significant. By this way the practical utilization of a material is defined and it is understood that its nature can be affected by the energy or temperature range at which that behavior is present, so temperature dependent properties of a material with spin-orbit coupling are of unique importance [2,3].

Thermoelectric (TE) materials are very important to take heat from the waste heat source and convert it useful energy. In this Skutterudites thermoelectric compounds are very effective due to

heavy fermionic conductivity and large Seebeck coefficient. Binary skutterudites, based on the mineral CoAs_3 possessing the general formula MX_3 (M = Cobalt, Rhodium, or Iridium and X = Phosphorous, Arsenics, or Antimony). These compounds have cage like crystal structure and their crystal structure is brought about by corner sharing of MX_6 octahedra [4–6].

These compounds crystallize in cubic shape having space group $\text{Im}\bar{3}$ (Space Group No. 204). The primitive unit cells of these compounds contain four formula units having a total of sixteen numbers of atoms. The transition metal occupy 8c of the Wyckoff position while the pnictogen elements resides in 24g of the crystal structure. In these compounds the pnictogen network so arrange their selves to form cages around the 2a crystallographic position and an external element or filler can have occupancy at that position. As the electronegativity differences among constituent atoms of skutterudites are small therefore bonding nature is almost covalent. These crystals structures are chemically stable, because the filling doesn't affect the chemical nature and a filling on the sites of crystal substantial degrees of freedom to obtain an optimized composition of the material for the desired purposes. Among skutterudites family, CoS_3 is found to be more attractive due to its small band gap, high carrier mobility and large Seebeck coefficient

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value which are very important parameters for thermoelectric material for good efficiency [6].

The thermal conductance of the binary CoSb₃ is of high value, which lowers the zT 's value and thus it becomes a poor converter for TE applications [4–6]. A new concept of filling in cage like structure was introduced to lower the thermal conductivity and to increase the thermoelectric efficiency of a material. Different types of atoms can be filled into cages of skutterudites, which can be rare-earth [7–11] alkaline-earth [12–14], alkali metals [15,16], and other [17–20] ions and then these crystals become the filled skutterudites.

The fillers have uniform arrangement inside the crystal and therefore Co-Sb skutterudite host framework is not affected. It has been realized that by adjusting the value of the filling atoms having different charge states, the material reaches to the optimum state of carrier density and ultimately the lattice vibrations are also significantly reduced. Further it is found that the fillers are bound very loosely to the Antimony host atoms in the available intrinsic cages of the crystal unit cell, which leads to Einstein like vibrational modes. And these modes are very important to strongly scatter phonons and hence there is high value reduction in the lattice thermal conductivity [21,22]. This effect produces significant increase and leads the zT 's value from 0.5 to 0.8 in doped CoSb₃ [7–16]. Skutterudite CoSb₃ with number of fillers for example Ba, La and Yb have been studied and a high value of thermoelectric figure of merit with the value $zT=1.7$ have been obtained at 850 K. This indicates that skutterudites which are partially filled having multiple fillers of different chemistry are very important for the optimization electronic and thermal transport properties resulting increase in zT value with filling from single to multiple at the voids in the skutterudite structure [23]. The same effect was also investigated through DFT that different filling atoms in cage like structure of skutterudites which scatter vibrational the frequencies of the CoSb₃. However this effect was found to be different for different chemical groups of the periodic table depending on their chemical nature [24]. It was also concluded that lattice phonons having the frequencies near the vibrational frequency of fillers can be strongly affected through phonon resonant scattering.

Spin is a major contributor to a variety of phenomenon in quantum materials, like quantum magnetism and the phenomenon related to the topological insulators. Therefore spin-orbit interaction in the present days is extensively used to extract and understand the nature of a material and significant work is also underway to include the spin-orbit effect in theoretical calculations. In this paper, a different approach is used to treat the system under consideration and at first we treated filling as an external perturbation applied to the system of CoSb₃ and then attempted to develop an insight of filling by extracting various thermoelectric aspects with and without spin-orbit coupling.

2. Calculations methodology

In this article the methodology applied for the investigation of the electronic structure is based on Full-Potential Linearized Augmented Plane Waves (FLAPW) method with and without spin-orbit coupling. In this scheme basis functions, are linear combinations of an APW plus the Local Orbital [25]. For the exchange-correlation potential, the PBE-sol08 GGA is used in the Self-Consistent Field calculations [26]. During the calculations, space of the unit cell of the crystals under investigations is divided into two main parts, interstitial regions while and non overlapping muffin-tin spherical domains. However muffin-tin have localization at the atomic sites. At the interstitial regions, the basis sets are made of plane waves. While dealing with the muffin-tin spheres, the basis set is obtained by the radial solutions of the

Schrodinger equation and their energy derivatives multiplied by spherical harmonics. All these assumptions and related parameterization is fixed in the Wien2k code [27], this code uses the inclusion of local orbital in the basis sets, hence linearization is improved improving and therefore consistency is achieved of semi-core and valence states in the same energy windows, leading to proper orthogonality. In the present case, 1000 k points is used for electronic structure calculations. The value for the cutoff used is $R_{mt} \times K_x = 7.0$, where K_{max} represents maximal value of the reciprocal lattice vector for the plane wave expansion, and R_{mt} is the value of the radius of smallest atom in unit cell of crystal structure.

From the calculated electronic structures, the thermoelectric transport parameters are evaluated through Boltzmann transport theory [28]. Boltzmann's transport theory calculates the thermoelectric transport parameters as implemented in the BoltzTraP code [29,30]. Using this approach, electrical and thermal conductivity relative to constant relaxation time τ are investigated. We have calculated the electronic transport coefficients by ensuring the rigid band approximation (RBA) [31,32]. This approximation is extensively applied in theoretical calculations for the transport properties of doped semiconductors and results obtained are reasonably good when the doping level of the system is not very large, so this approximation is best fitted for the present situation of filled skutterudites [31–35]. Also it is assumed that the relaxation time (τ) to be energy independent. Applying this limit, the Seebeck coefficient is independent of the relaxation time. Thus the T dependence approach of the Seebeck coefficient as discussed in this article is reasonably correct. However for the investigation of the electrical conductivity and the electronic thermal conductivity, the estimations of the different mechanisms such as electron phonon and electron-impurity scattering related to τ is important for a specified temperature [33,36]. The Seebeck coefficient, electrical conductivity and electronic thermal conductivity tensors are expressed as

$$S = ek_B\sigma^{-1} \sum k \left(-\frac{df_0}{d\varepsilon} \right) v_k^2 \tau_k \frac{k_B - \mu}{k_B T} \quad (i)$$

$$\sigma = e^2 \sum k \left(-\frac{df_0}{d\varepsilon} \right) v_k^2 \tau_k \quad (ii)$$

$$k_e = ek_B\sigma^{-1} \sum k \left(-\frac{df_0}{d\varepsilon} \right) v_k^2 \tau_k \left(\frac{k_B - \mu}{k_B T} \right)^2 - T\sigma S^2 \quad (iii)$$

where f_0 is the Fermi function, V_k is for the group velocity, τ_k represents the relaxation time, and μ denotes the chemical potential. By using Eqs. (i)–(iii), we can find the transport coefficients and hence thereby obtaining the zT of compounds. The thermoelectric calculations require a dense k -mesh for the convergence of the thermoelectric parameters therefore we used 12,000 k points which is a reasonable choice because thermoelectric k point selection must be more than five times as for electronic structure calculations [29]. To obtain p and n-type material, the doping levels is evaluated by changing the Fermi level.

3. Results and discussions

3.1. Electronic structure

Crystalline solids are characterized by their electronic structures. In order to calculate the electronic structure at first the unit cell of each compound is relaxed in terms of lattice constant and atomic positions with the force on each atom in the unit cell reduction to 1 Ry/atom. Based on the relaxed structure of the unit cell electronic structures of ACo₄Sb₁₂ (A = Ca, Sr and Ba) are

calculated. It is well established that in comparison to other states, on the core the effect of spin orbit interaction is small, however it has a relatively more prominent effect if we look into bands close to the Fermi level, therefore the physical properties are affected more with spin orbit coupling. The spin orbit interaction for example splits bands and without spin orbit coupling the states are degenerated. However band splitting depends on the particular system which is taken under consideration. We now discuss the electronic structure of $\text{AlCo}_4\text{Sb}_{12}$ is as given in Fig. 1, where the electronic structures of $\text{CaCo}_4\text{Sb}_{12}$, $\text{SrCo}_4\text{Sb}_{12}$ and $\text{BaCo}_4\text{Sb}_{12}$ are shown without spin-orbit and with spin-orbit effect and similar results without spin-orbit coupling for $\text{CaCo}_4\text{Sb}_{12}$ in Ref. [37] and for $\text{BaCo}_4\text{Sb}_{12}$ in Ref. [38,39] can be found. From the plot it is well clarified that spin-orbit coupling affects the electronic structure of the compounds as by the filling from Ca to Sr and then to Ba. It can be easily understood from the plot that in case of $\text{CaCo}_4\text{Sb}_{12}$ and $\text{SrCo}_4\text{Sb}_{12}$ the states splits due to spin-orbit coupling and a reduction in the peaks of these compounds occur. However in case $\text{BaCo}_4\text{Sb}_{12}$ with the splitting of states peaks around the Fermi level the maximum peak becomes sharper and at that point density of states increase which ultimately increases the thermoelectric performance of the material due to spin-orbit coupling effect. It is clear from Fig. 1 that without spin-orbit coupling the density of maximum peak is 22.7 states/eV for $\text{CaCo}_4\text{Sb}_{12}$ and $\text{SrCo}_4\text{Sb}_{12}$ which splits the electronic structure due to spin-orbit interaction become 17.5 states/eV for the same compounds. In case of $\text{BaCo}_4\text{Sb}_{12}$ the maximum peak of density of states has value of 18 states /eV which after application of spin-orbit effect becomes 22.7 states/eV, so in case of $\text{BaCo}_4\text{Sb}_{12}$ density of states maximum peak increases the electron so the thermoelectric efficiency of that material increases. It can be seen from the plots in Fig. 1, that insulating behavior is present for the compounds due to the bandgap availability in the valence band however when the spin-orbit coupling effect is included then the states are more close than the states without spin-orbit coupling, and the bandgap is decreased with the spin-orbit coupling.

3.2. Seebeck coefficient

Electrical nature of a material at the first depends on its capability to produce a potential difference across its ends. In thermoelectric phenomenon Seebeck coefficient defines the capability of developing a potential difference to the applied gradient of temperature. Mathematically Seebeck coefficient is given as $S = \Delta V / \Delta T$, where S Seebeck coefficient ΔV is the voltage produced and ΔT is absolute temperature difference across the end of the thermoelectric material. Chemical potential dependent Seebeck coefficient for $\text{CaCo}_4\text{Sb}_{12}$, $\text{SrCo}_4\text{Sb}_{12}$ and $\text{BaCo}_4\text{Sb}_{12}$ is presented in Fig. 2. It is clear from Fig. 2 that spin-orbit interaction strongly affects the Seebeck coefficient value in the lower chemical potential region from -0.4 to 0.4 eV for $\text{CaCo}_4\text{Sb}_{12}$ where Seebeck coefficient value is significantly reduced, and Seebeck coefficient maximum value without spin-orbit coupling is $500.77 \mu\text{V/K}$ for the p-type region which becomes $189.12 \mu\text{V/K}$. For the n-type region the maximum value of Seebeck coefficient without spin-orbit interaction is $-816.38 \mu\text{V/K}$ and with spin-orbit coupling is $-237.78 \mu\text{V/K}$. The similar behavior exists for $\text{SrCo}_4\text{Sb}_{12}$ and the maximum value Seebeck coefficient for the p-type region without spin-orbit coupling is $444.07 \mu\text{V/K}$, however this value reduces to $136.10 \mu\text{V/K}$ with spin-orbit coupling effect and for the n-type region Seebeck coefficient without spin-orbit coupling is $-750.71 \mu\text{V/K}$ and with spin-orbit coupling is $-199.46 \mu\text{V/K}$, but reduction in Seebeck coefficient compared to $\text{CaCo}_4\text{Sb}_{12}$ is less, which indicates that moving from 4s state to 5s state in alkaline filled $\text{Co}_4\text{Sb}_{12}$ reduces the Seebeck coefficient which is accordance with effectiveness of spin-orbit interaction. Moreover for the compound $\text{BaCo}_4\text{Sb}_{12}$ spin-orbit effect is not very prominent for the p-type region and the maximum Seebeck coefficient values are $148.91 \mu\text{V/K}$ and $154.74 \mu\text{V/K}$ for without and with spin-orbit coupling respectively, however for n-type region in the lower chemical potential region spin-orbit coupling produce a prominent increase in the Seebeck coefficient where peak of Seebeck coefficient increases from $-250 \mu\text{V/K}$ to $-440 \mu\text{V/K}$ with the spin-orbit coupling.

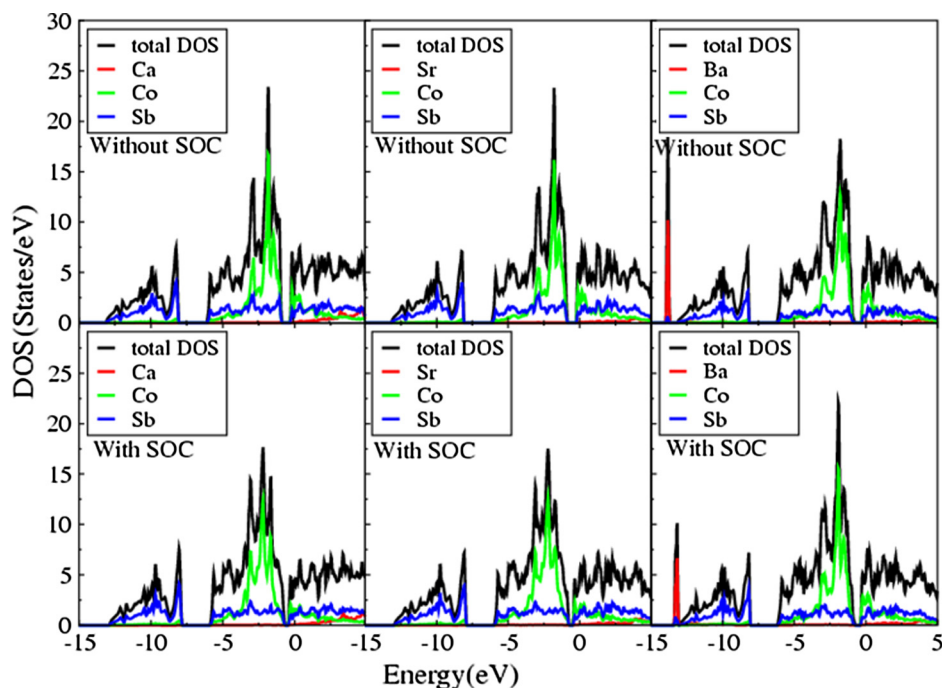


Fig. 1. Electronic structure of $\text{AlCo}_4\text{Sb}_{12}$ using PBEsol08-GGA without and with spin-orbit coupling.

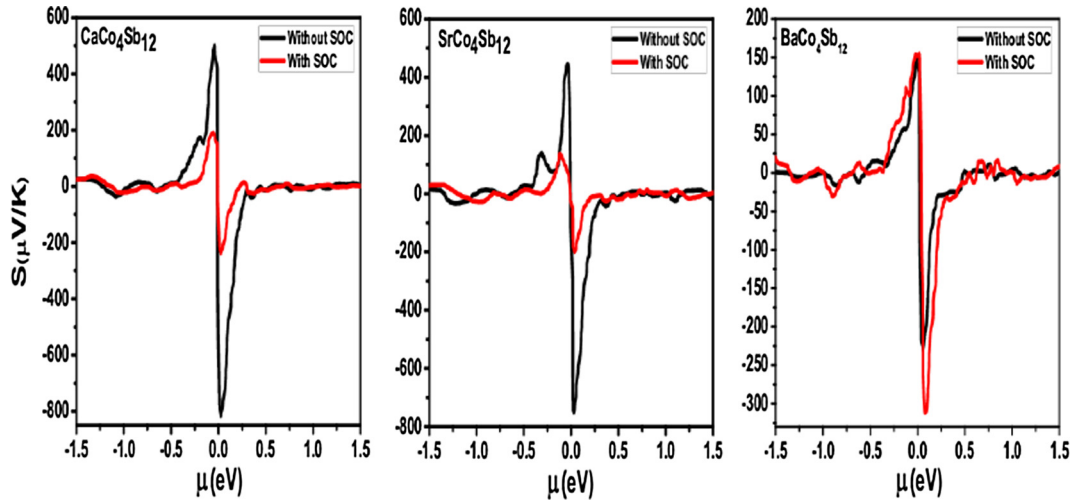


Fig. 2. Seebeck coefficient of $\text{AlCo}_4\text{Sb}_{12}$ at the temperature of 300 K against the chemical potential.

3.3. Electrical conductivity

Electrical conductivity measures the ability of a material of the flow of electric current either due to negative electrons or positive holes. From Fig. 3 spin-orbit effects can clearly observed on electrical conductivity of the materials and electrical conductivity reduces for each case of the compounds $\text{CaCo}_4\text{Sb}_{12}$, $\text{SrCo}_4\text{Sb}_{12}$ and $\text{BaCo}_4\text{Sb}_{12}$ when spin-orbit effect is included in calculations. In these calculations, electrical conductivity is given in the units of order $10^{20} \text{ 1}/\Omega \text{ m s}$. For $\text{CaCo}_4\text{Sb}_{12}$ in the p-type region at the chemical potential of 1.5 eV the electrical conductivity is $1.2 \times 10^{20} \text{ 1}/\Omega \text{ m s}$ which reduces to the value of $0.5 \times 10^{20} \text{ 1}/\Omega \text{ m s}$ with the application of spin-orbit coupling. The maximum value of electrical conductivity in the p-type region without spin-orbit coupling is at the chemical potential of -0.53 eV with the value of $1.21 \times 10^{20} \text{ 1}/\Omega \text{ m s}$ and with the application of spin-orbit coupling becomes $0.82 \times 10^{20} \text{ 1}/\Omega \text{ m s}$ at the chemical potential of -0.51 eV . In the n-type region at the 1.5 eV chemical potential, electrical conductivity value is $2.1 \times 10^{20} \text{ 1}/\Omega \text{ m s}$ without spin-orbit coupling, then decreased to $1.25 \times 10^{20} \text{ 1}/\Omega \text{ m s}$ with the application of spin-orbit coupling, however the maximum value in the n-type region

without spin-orbit coupling is $2.6 \times 10^{20} \text{ 1}/\Omega \text{ m s}$ at the chemical potential value 1.25 eV and maximum value with spin-orbit coupling is $1.36 \times 10^{20} \text{ 1}/\Omega \text{ m s}$ at the chemical potential of 1.07 eV. For $\text{SrCo}_4\text{Sb}_{12}$ in the p-type region, the electrical conductivity is $1.00 \times 10^{20} \text{ 1}/\Omega \text{ m s}$ at the chemical potential of 1.5 eV without spin-orbit coupling. However, at this chemical potential for $\text{SrCo}_4\text{Sb}_{12}$ the electrical conductivity value is $0.4 \times 10^{20} \text{ 1}/\Omega \text{ m s}$, which shows a reduction with the spin-orbit coupling. The maximal value for the p-type region in case of $\text{SrCo}_4\text{Sb}_{12}$ without and with spin-orbit coupling are $1.3 \times 10^{20} \text{ 1}/\Omega \text{ m s}$ and $0.75 \times 10^{20} \text{ 1}/\Omega \text{ m s}$ respectively. For n-type region the maximal values for $\text{SrCo}_4\text{Sb}_{12}$ without and with spin-orbit coupling are $3.0 \times 10^{20} \text{ 1}/\Omega \text{ m s}$ and $0.80 \times 10^{20} \text{ 1}/\Omega \text{ m s}$ respectively. Similarly for $\text{BaCo}_4\text{Sb}_{12}$ in the p-type region electrical conductivity at the chemical potential value of -1.5 eV without spin-orbit coupling is $0.9 \times 10^{20} \text{ 1}/\Omega \text{ m s}$ which for the spin-orbit coupling becomes $0.38 \times 10^{20} \text{ 1}/\Omega \text{ m s}$, where is the maximum value of electrical conductivity in the p-type region without spin-orbit coupling is $1.54 \times 10^{20} \text{ 1}/\Omega \text{ m s}$ at the chemical potential -0.50 eV and with spin-orbit coupling reduces with the maximum value of electrical conductivity is $0.63 \times 10^{20} \text{ 1}/\Omega \text{ m s}$ at the chemical potential of -0.72 eV . In between

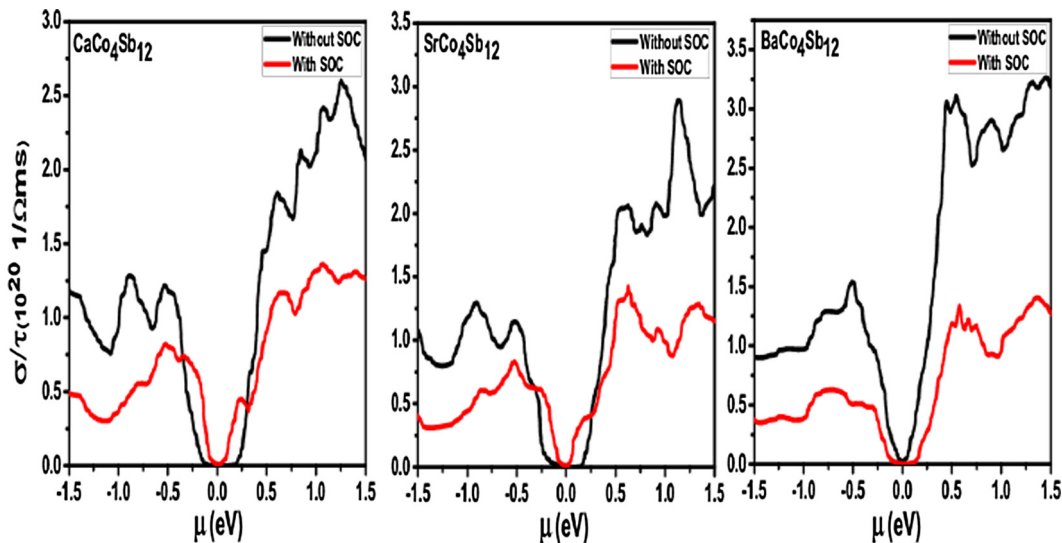


Fig. 3. Electrical conductivity of $\text{AlCo}_4\text{Sb}_{12}$ at the temperature of 300 K against the chemical potential.

the -1.5 eV and 1.5 eV chemical potential regions, reduction in the electrical prevails and spin-orbit coupling reduces the electrical conductivity for all materials $\text{CaCo}_4\text{Sb}_{12}$, $\text{SrCo}_4\text{Sb}_{12}$ and $\text{BaCo}_4\text{Sb}_{12}$.

3.4. Electronic thermal conductivity

Thermal conductivity is the measure of heat flow through a material as the temperature gradient is applied. Phonon vibrations as well free electrons are responsible for the thermal conductivity are responsible for the heat flow in a material. However in semiconductors lattice part mainly contribute to the thermal conductivity whereas in metal major contribution to the thermal conductivity is from the free electrons. BoltzTraP code has the limitation that it can calculate electronic part of thermal conductivity but can't calculate the lattice part of the thermal. In the present case electronic thermal conductivity is measured for the $\text{ACo}_4\text{Sb}_{12}$ ($A = \text{Ca}, \text{Sr}$ and Ba) as BoltzTraP code can measure the electronic part of thermal conductivity only. Electronic thermal conductivity is measured in units of 10^{14} W/m K s and is given in Fig. 4. Similar to electrical conductivity, the electronic thermal conductivity also decreases with the inclusion of spin-orbit coupling in the calculations. It is clear from Fig. 4 that in the case of $\text{CaCo}_4\text{Sb}_{12}$, the electronic thermal conductivity in the p-type region at the chemical potential of -1.5 eV without spin-orbit coupling is 8.6 W/m K s , however with the spin-orbit interaction the value of electronic thermal conductivity at the chemical potential of -1.5 eV becomes 3.10 W/m K s . For overall results of $\text{CaCo}_4\text{Sb}_{12}$ in the p-type region the maximum value of electronic thermal conductivity without spin-orbit coupling exits at -1.5 eV as discussed earlier, however with spin-orbit interaction the maximum value of electronic thermal conductivity is 5.62 W/m K s at the chemical potential of -0.52 eV. In the n-type region for $\text{CaCo}_4\text{Sb}_{12}$ the electronic thermal conductivity at 1.5 eV without spin-orbit coupling is 15.50 W/m K s and with spin-orbit coupling is 9.30 W/m K s . The maximum value of electronic thermal conductivity is found at the chemical potential of 1.17 eV with the value of 18.09 W/m K s without spin-orbit coupling and with spin-orbit coupling maximum value is 9.50 W/m K s at the chemical potential 1.2 eV. For the material $\text{SrCo}_4\text{Sb}_{12}$ the value of electronic thermal conductivity in the p-type region at chemical potential of -1.5 eV is 7.99 W/m K s and 3.03 W/m K s for without and with spin-orbit coupling respectively. However the maximum values for electronic thermal conductivity in p-type region are 8.46 W/m K s at the chemical potential -0.82 eV and 5.5 W/m K s at the chemical potential value -0.50 eV for without and with spin-orbit coupling

respectively. For n-type region the electronic thermal conductivity at 1.5 eV is 19.24 W/m K s at the chemical potential of 1.17 eV where is maximum value of electronic thermal conductivity with spin-orbit coupling is 7.80 W/m K s at the chemical potential 0.88 eV. In case of $\text{BaCo}_4\text{Sb}_{12}$ the electronic thermal conductivity for p-type region at the -1.5 eV chemical potential is 6.74 and 3.32 W/m K s without and with spin-orbit coupling respectively. In the p-type region the maximum value of electronic thermal conductivity without spin-orbit coupling is 10.40 W/m K s at the chemical potential value -0.52 and the maximum value of electronic thermal conductivity with spin-orbit coupling is 4.37 W/m K s at the chemical potential -0.70 eV. For the n-type region the electronic thermal conductivity at the chemical potential of 1.5 eV is 22.60 and 9.48 W/m K s without and with spin-orbit coupling respectively. However in the n-type region the maximum value of electronic thermal conductivity without spin-orbit coupling is 23.76 W/m K s at the chemical potential 1.44 eV and with spin-orbit coupling the maximum value in the n-type region for $\text{BaCo}_4\text{Sb}_{12}$ is 9.82 W/m K s at the chemical potential of 1.41 eV.

3.5. Thermoelectric figure of merit

Thermoelectric figure of merit is important parameter to understand the efficiency of a compound. Mathematically it is given as $zT = S^2 \sigma T / \kappa$, where S is for Seebeck coefficient, σ represents electrical conductivity, κ is the thermal conductivity and T is the temperature at which calculations are performed for the given thermoelectric parameters. Figure of merit is shown in Fig. 5 for the $\text{ACo}_4\text{Sb}_{12}$ ($A = \text{Ca}, \text{Sr}$ and Ba). It is clear from the figure that in all cases of $\text{ACo}_4\text{Sb}_{12}$ there is significant increase in the region from -0.5 to 0.5 eV chemical potential as in this area Seebeck coefficient is highest values and zT is dependent on the square of the Seebeck coefficient. In the p-type region of $\text{CaCo}_4\text{Sb}_{12}$ the maximum value of zT for the without spin-orbit coupling is 0.85 at the chemical potential -0.063 eV and in this region with spin-orbit interaction the zT value becomes 0.53 at the chemical potential of -0.11 eV. For $\text{CaCo}_4\text{Sb}_{12}$ in the n-type region the maximum value of zT without spin-orbit interaction is 0.97 at the chemical potential of 0.07 eV and with spin-orbit coupling in the n-type region the maximum value is 0.64 at the chemical potential of 0.018 eV. In case of $\text{SrCo}_4\text{Sb}_{12}$ for the p-type region the maximum value of zT without spin-orbit coupling is 0.86 at the chemical potential of -0.054 eV and with spin-orbit coupling the maximum value of zT is 0.41 at the chemical potential value of -0.11 eV and for the n-type region without spin-orbit coupling the maximum

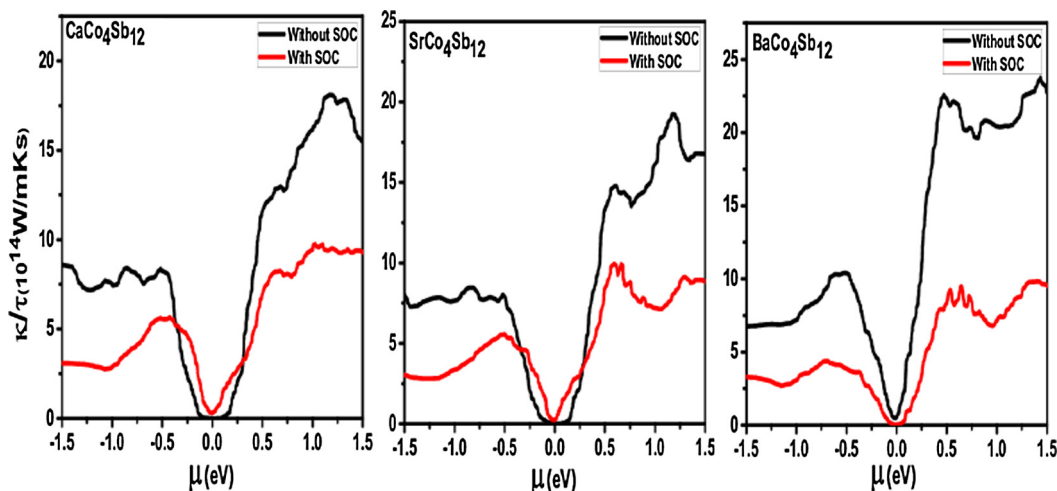


Fig. 4. Electronic thermal conductivity of $\text{ACo}_4\text{Sb}_{12}$ at the temperature of 300 K against the chemical potential.

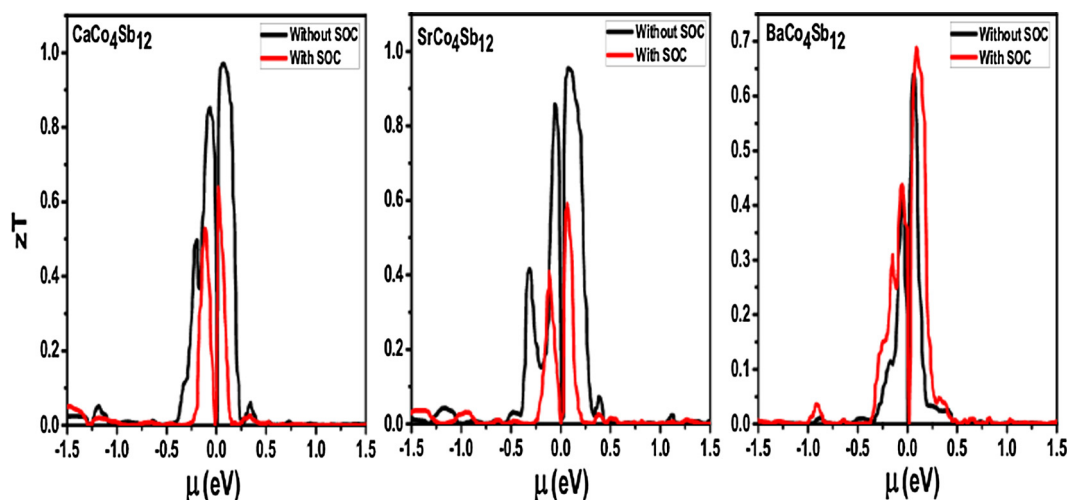


Fig. 5. Thermoelectric figure of merit of $\text{AlCo}_4\text{Sb}_{12}$ at the temperature of 300 K against the chemical potential.

value of zT is value 0.95 at the chemical potential value of 0.061 eV, however when spin-orbit coupling is applied its maximum value reduced to 0.59 at the chemical potential of 0.066 eV. The maximum zT value for $\text{BaCo}_4\text{Sb}_{12}$ in the p-type region without spin-orbit coupling is 0.41 at the chemical potential value -0.04 eV and with spin-orbit coupling the maximum value of zT in the p-type region is 0.44 at the chemical potential of -0.049 eV. Where is in the n-type region the maximum value of zT without spin-orbit coupling for $\text{BaCo}_4\text{Sb}_{12}$ is 0.64 at the chemical potential point of 0.07 eV and the application of spin-orbit coupling the value is increased to 0.69 at the chemical potential value of 0.093 eV.

4. Conclusions

Fully filled $\text{ACo}_4\text{Sb}_{12}$ ($A = \text{Ca}, \text{Sr}$ and Ba) system is studied as a test case to investigate, how the ab initio modeled electronic transport properties are affected by spin-orbit coupling at the computational level. A two-step computational procedure, band structure adopted from DFT and thermoelectric properties from Boltzmann's transport theory is tested. It is concluded that spin-orbit coupling has significant effect on the thermoelectric properties of $\text{ACo}_4\text{Sb}_{12}$ ($A = \text{Ca}, \text{Sr}$ and Ba). Spin-orbit coupling splits the electronic density of states of the materials due to which the density peaks are reduced in the core as well as at the Fermi level; this affects the thermoelectric nature of the materials under consideration. In case of $\text{CaCo}_4\text{Sb}_{12}$ and $\text{SrCo}_4\text{Sb}_{12}$ thermoelectric parameters are decreased with inclusion of spin-orbit coupling in the calculation, however in case of $\text{BaCo}_4\text{Sb}_{12}$ Seebeck coefficient due to spin-orbit coupling is increased which in turn increases the zT value for the same compound whereas electrical conductivity and electronic thermal conductivity is reduced when spin-orbit coupling is added to the systems.

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