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Thermoelectric properties of zinc based pnictide semiconductors

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We report a detailed first principles density functional calculations to understand the electronic structure and transport properties of Zn-based pnictides $ZnXPn_2$ (X: Si, Ge, and Sn; Pn: P and As) and $ZnSiSb_2$. The electronic properties calculated using Tran-Blaha modified Becke-Johnson functional reveals the semi-conducting nature, and the resulting band gaps are in good agreement with experimental and other theoretical reports. We find a mixture of heavy and light bands in the band structure which is an advantage for good thermoelectric (TE) properties. The calculated transport properties unveils the favour p-type conduction in $ZnXP_2$ (X: Si, Ge, and Sn) and n-type conduction in $ZnGeP_2$ and $ZnSiAs_2$. Comparison of transport properties of Zn-based pnictides with the prototype chalcopyrite thermoelectric materials implies that the thermopower values of the investigated compounds to be higher when compared with the prototype chalcopyrite thermoelectric materials, together with the comparable values for electrical conductivity scaled by relaxation time. In addition to this, Zn-based pnictides are found to possess higher thermopower than well known traditional TE materials at room temperature and above which motivates further research in these compounds. *© 2016 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4942011]

I. INTRODUCTION

Thermoelectric (TE) materials are considered as an alternative source of energy, which can convert waste heat into useful electricity. To meet the present energy crisis, scientific world look forward towards highly potential thermoelectric materials. For waste heat recovery, we need TE material which can perform at high temperatures, and search for potential high temperature thermoelectric material is highly demanding. The efficiency of a TE material is quantified by dimensionless figure of merit ZT. The expression of figure of merit is defined as $ZT = S^2\sigma T/\kappa$, where S, σ, κ, and T are thermopower, electrical conductivity, thermal conductivity, and the absolute temperature, respectively. κ includes both the electronic κ_e and the lattice κ_l contributions. A good thermoelectric material should have high Seebeck coefficient, high electrical conductivity, and low thermal conductivity. To attain maximum Seebeck coefficient, material with high band mass is essential, and for achieving good electrical conductivity the mobility of the material should be high, leading to lower band mass carriers, implying the need for a mixture of heavy and light bands in the band structure.[1] Parameters in the figure of merit are highly dependent on each other, which poses the challenge in thermoelectrics. Bi_2Te_3 and PbTe are traditional materials which are being used for TE applications.[2,3] Currently, thermoelectric applications are limited to small scale only because of the lesser efficiency of TE materials. A number of studies were performed, both experimentally and theoretically to identify novel thermoelectric materials and to improve the ZT value of existing TE materials, and these studies proved that one can improve the efficiency of TE materials by nano-structuring, alloying, superlattice, etc. Here, we are trying to explore potential materials for thermoelectric applications.

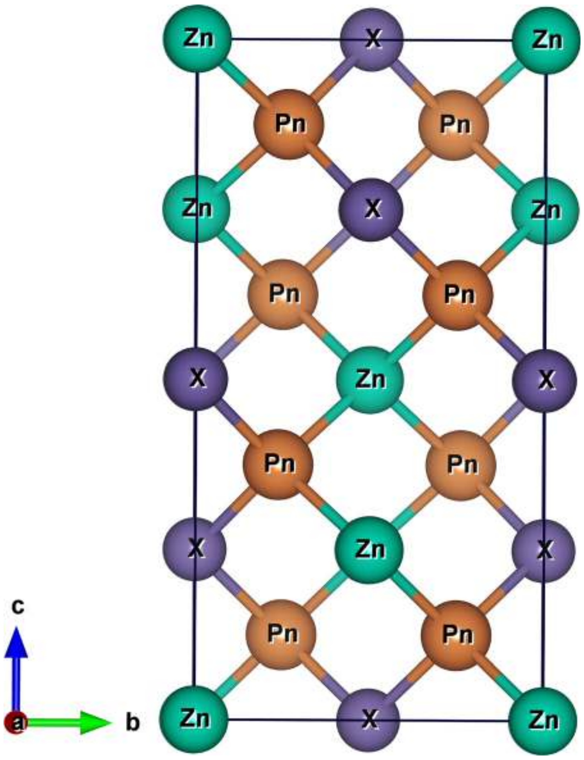

FIG. 1. Crystal structure of the investigated compound $ZnXPn_2$ (X: Si, Ge, and Sn; Pn: P and As) and $ZnSiSb_2$.

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TABLE I. Lattice parameters of $ZnXPn_2$ (X: Si, Ge, and Sn; Pn: P and As) and $ZnSiSb_2$ along with available experimental and other theoretical values.

Parameters	$ZnSiP_2$	$ZnSiAs_2$	$ZnSiSb_2$	$ZnGeP_2$	$ZnGeAs_2$	$ZnSnP_2$	$ZnSnAs_2$
a_{pre} (Å)	5.44	5.68	6.13	5.52	5.75	5.72	5.93
a_{exp} (Å)	5.4072[a]	5.60[b]	…	5.46[b]	5.672[c]	5.651[c]	5.852[c]
a_{Other} (Å)	5.398[d]	5.584[e]	6.077[f]	5.465[f]	5.663[e]	5.71[g]	5.851[h]
c_{pre} (Å)	10.56	11.07	12.08	10.88	11.35	11.48	11.95
c_{exp} (Å)	10.4539[a]	10.88[b]	…	10.71[b]	11.153[c]	11.303[c]	11.703[c]
c_{other} (Å)	10.435[d]	10.95[e]	11.68[f]	10.70[f]	11.22[e]	11.43[g]	11.702[h]
u_{pre}	0.268	0.262	0.254	0.252	0.247	0.226	0.223
u_{exp}	0.26948[a]	0.26575[b]	…	0.25816[b]	0.264[c]	0.264[c]	0.239[c]

[a] Reference 39.
[b] Reference 5.
[c] Reference 40.
[d] Reference 6.
[e] Reference 41.
[f] Reference 48.
[g] Reference 10.
[h] Reference 4.

Ternary chalcopyrite semiconductors and pnictide compounds of the form ABC_2 have attracted researchers because of their special physical properties like high melting point, high refractive index, high nonlinear optical susceptibility, and many more.[4–6] Because of the above mentioned diverse properties, both the chalcopyrites and pnictides are identified as promising materials for different device applications like electronic devices,[7] nonlinear optical devices,[8,9] photovoltaic cell,[10] thermoelectric applications,[11] etc. These materials crystallize in the tetragonal structure with space group $I\bar{4}2d$ and are considered as the ternary analogue of zinc blende structure. The pnictide based compounds of the type $AXPn_2$ (A: Zn and Cd; X: Si, Ge, and Sn; Pn: P, As, and Sb) possess significant importance. The compounds, $ZnGeP_2$ and $CdSiP_2$, are promising materials for nonlinear optical applications,[12,13] and $ZnSnP_2$ is identified as a good material for solar cell applications.[14] The structural, electronic, and optical properties of these compounds are widely explored by experimentalist as well as theoreticians.[5,15,16] But these compounds are not established fully in the field of thermoelectrics even though these pnictides are iso-structural to other

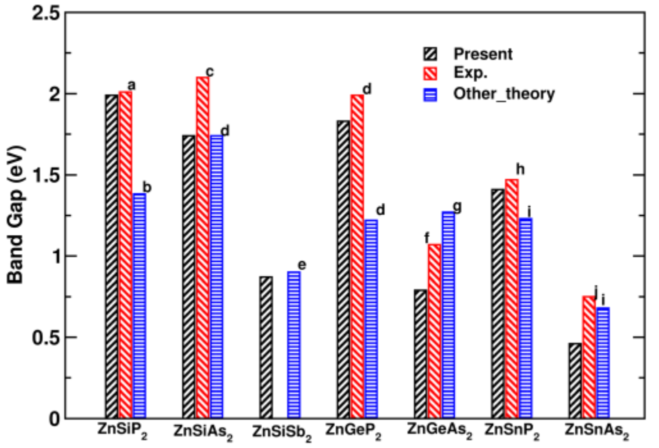
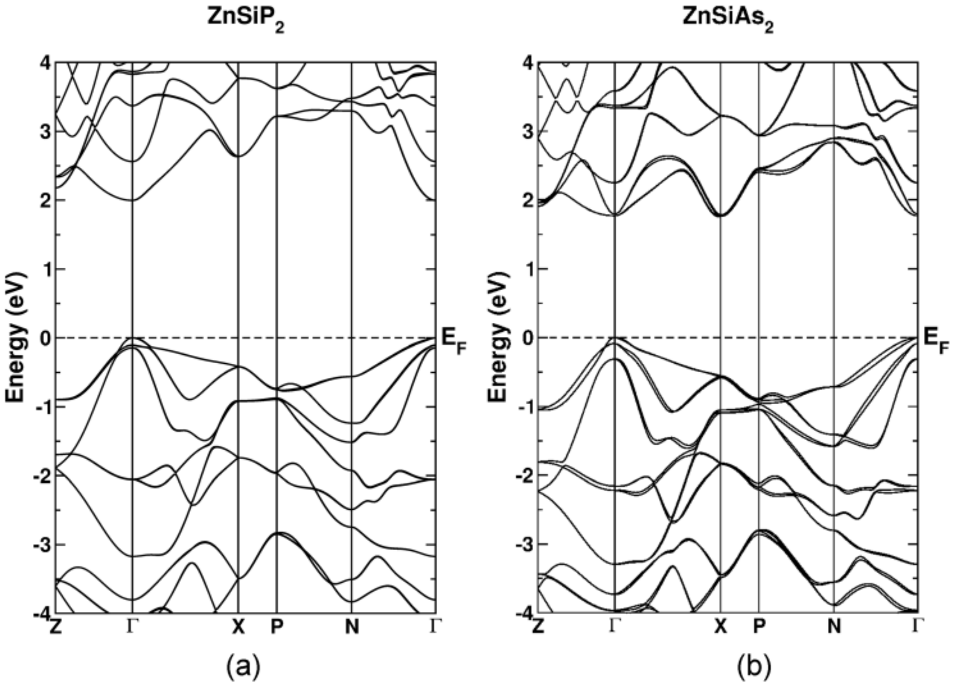


FIG. 3. Calculated band gaps for all investigated compounds along with available experimental and other theoretical reports. a: Ref. 42, b: Ref. 6, c: Ref. 40, d: Ref. 15, e: Ref. 48, f: Ref. 43, g: Ref. 44, h: Ref. 45, i: Ref. 46, and j: Ref. 47.

TABLE II. Calculated effective masses of $ZnXPn_2$ (X: Si, Ge, and Sn; Pn: P and As) and $ZnSiSb_2$ along the crystallographic directions in the unit of electron rest mass.

Directions	$ZnSiP_2$	$ZnSiAs_2$	$ZnSiSb_2$	$ZnGeP_2$	$ZnGeAs_2$	$ZnSnP_2$	$ZnSnAs_2$
				VB (valence band)			
Γ-N	2.89	2.01	3.07	1.54	1.0	1.91	1.03
Γ-Z	2.20	1.59	0.92	0.70	0.71	0.97	0.90
				CB (conduction band)			
Γ-N	0.38	0.54	0.16	0.18	0.21	2.02	1.04
Γ-Z	1.17	1.43	0.68	0.19	0.16	0.82	0.71



(a) (b)

FIG. 2. Calculated band structures using TB-mBJ functional with optimized lattice parameters. (a) $ZnSiP_2$ and (b) $ZnSiAs_2$.

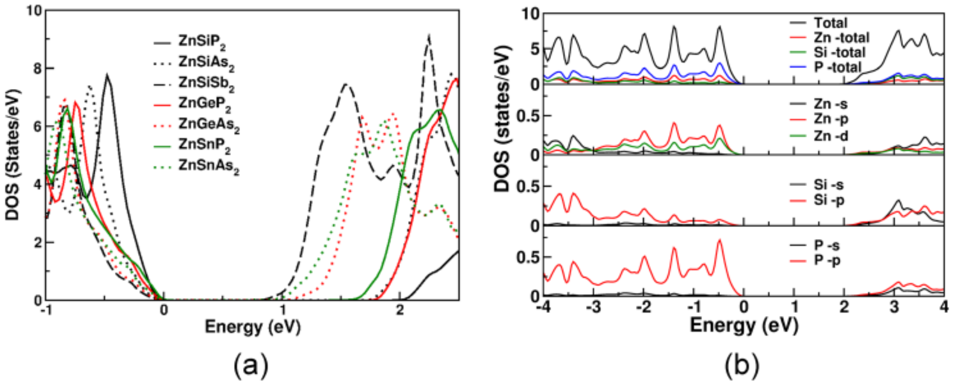


FIG. 4. (a) Calculated density of states for all the investigated compounds. (b) Total and partial density of states for $ZnSiP_2$.

chalcopyrites which show good thermoelectric properties.[17–19] The bulk Cu-based chalcopyrite $CuGaTe_2$ showed a dimensionless figure of merit around 1.4 from experiment,[20] and theoretical studies on this material also confirmed the same.[18] An iso-structural compound $AgGaTe_2$ also showed good thermoelectric properties.[17] The importance of the investigated Zn-based pnictides are based on the earth abundance and the stability at high temperatures up to around 1000 K. The band structure calculations of these series is quite appreciable with its remarkable combination of heavy and light bands that can help for TE properties.[17] We would like to investigate the TE properties of Zn-based pnictides, $ZnXPn_2$ (X: Si, Ge, and Sn; Pn: P and As) and $ZnSiSb_2$.

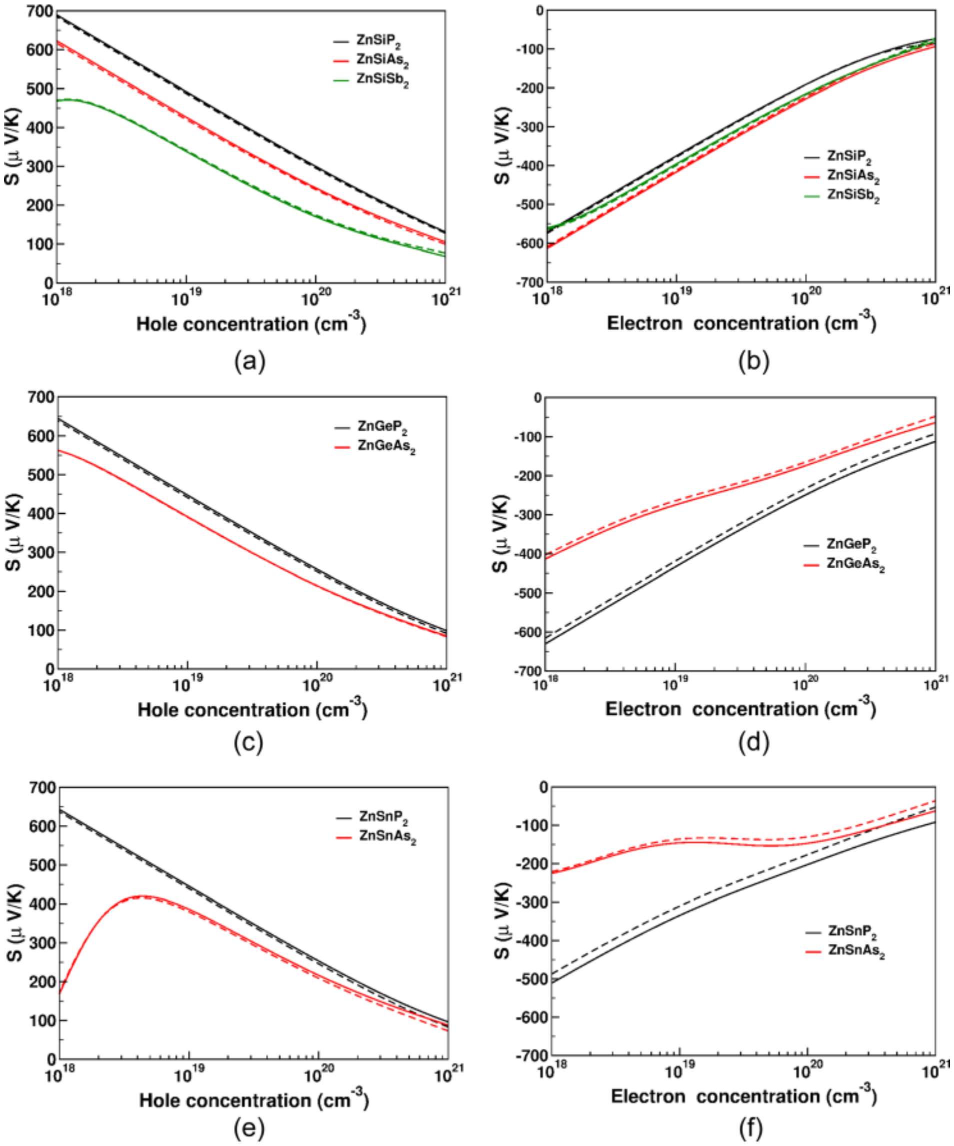


FIG. 5. Variation of thermopower as a function of both the carrier concentrations at 900 K. Solid lines represent “*a*” axis and dotted line is for “*c*” axis.

II. METHODOLOGY

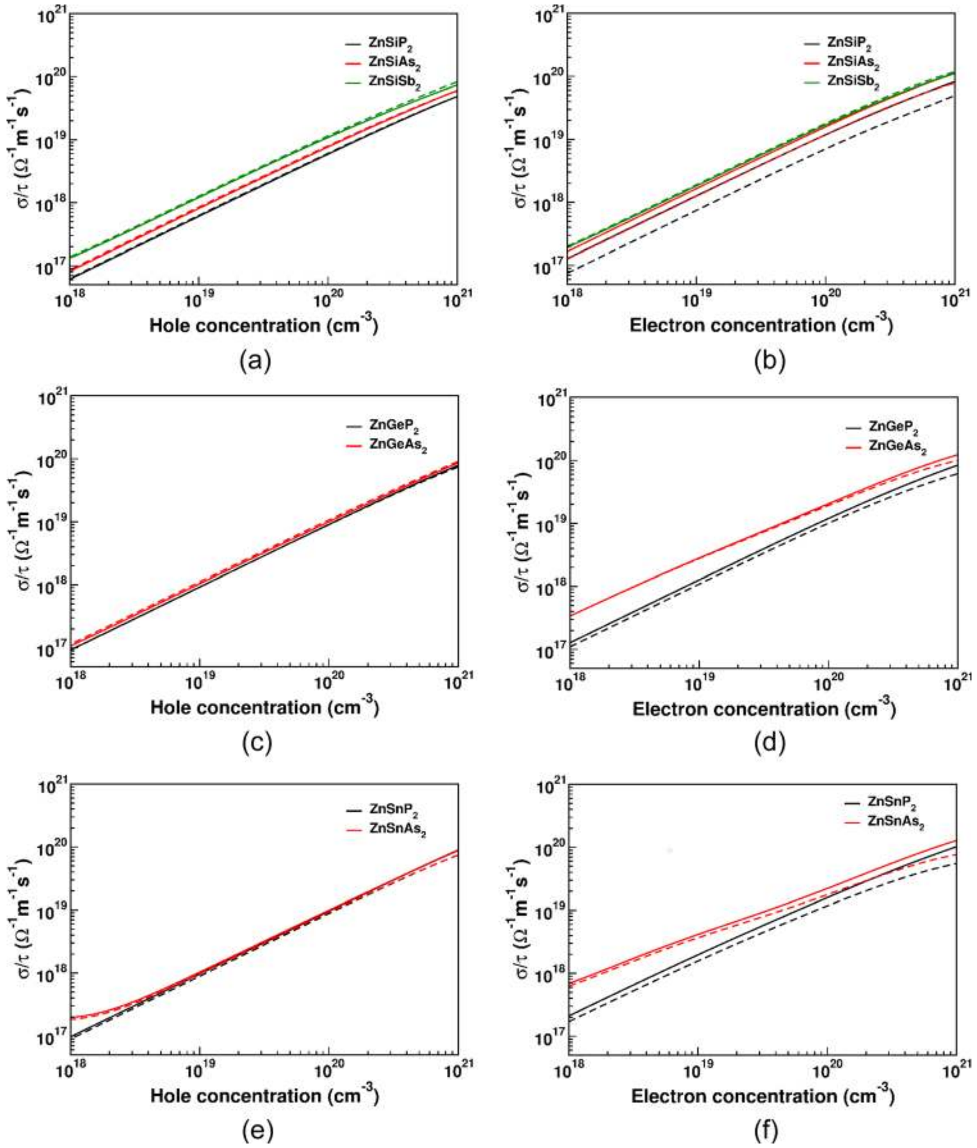
Present calculations are based on the first principles density functional theory. We have used full potential linearized augmented plane wave (FP-LAPW) method implemented in WIEN2k package.[21,22] Experimental lattice parameters are used as an input for our calculations and we have optimized the structure using generalized gradient approximation of Perdew, Burke, and Ernzerhof (GGA-PBE) functional.[23] The optimized lattice parameters are used for further calculations. It is well known that the traditional exchange functionals like local density approximation (LDA) and GGA underestimate the band gap of semiconductors and insulators, so we have used Tran-Blaha modified Becke-Johnson (TB-mBJ) functional[24,25] which is found to be quite successful in reproducing the experimental band gaps.[26,27] Due to the presence of heavy elements in the investigated compounds, we have included spin orbit coupling in our calculations. For total energy calculations, band structures, and density of states, we have used $10 \times 10 \times 10$ k-points in the full Brillouin zone. Transport coefficients such as thermopower (S in μV K^{-1}) and electrical conductivity scaled by relaxation time (σ/τ in Ω^{-1} m^{-1} s^{-1}) were calculated using BoltzTraP code[28] with a dense k-mesh of the order of $50 \times 50 \times 50$ k-points. The BoltzTraP code is based on rigid band approximation (RBA)[29–31] and the constant scattering time approximation (CSTA), and these approximations have been successfully applied for several thermoelectric materials.[32–36]

III. RESULTS AND DISCUSSION

A. Structural and electronic properties

1. Structural properties

The investigated compounds ZnXPn$_2$ (X: Si, Ge, and Sn; Pn: P and As) and ZnSiSb$_2$ crystallize in tetragonal chalcopyrite type structure with space group $I\bar{4}2d$, and the crystal structure is given in Fig. 1. Chalcopyrite crystal structure can be considered as the ternary analogue of zinc blende



(a) (b) (c) (d) (e) (f)

FIG. 6. Variation of electrical conductivity scaled by relaxation time as a function of both carrier concentrations at 900 K. Solid lines for "*a*" axis and dotted line is for "*c*" axis.

structure with slight tetragonal distortion. For all the investigated compounds, each anion Pn (Pn: P, As, and Sb) is coordinated by two Zn-type cations and two X-type (X: Si, Ge, and Sn) cations and each cation (Zn, Si, Ge, and Sn) is tetrahedrally co-ordinated by four *Pn* anions (Pn: P, As, and Sb). The optimized lattice parameters of $ZnXPn_2$ (X: Si, Ge, and Sn; Pn: P and As) and $ZnSiSb_2$ along with the available experimental and other theoretical values are reported in Table I. It is quite evident that the calculated lattice parameters are in good agreement with the experimental and other theoretical reports.

2. Electronic properties

The electronic structure of $ZnXPn_2$ (X: Si, Ge, and Sn; Pn: P and As) and $ZnSiSb_2$ compounds were calculated using TB-mBJ functional with optimized lattice parameters. The overall band profile of all the investigated compounds are almost similar, and the band structure along the high symmetry direction of $ZnSiP_2$ and $ZnSiAs_2$ are presented in Fig. 2. Calculated band gaps of all the investigated compounds along with experimental and other reported values are given in Fig. 3. From this figure, it is quite clear that our values are in good agreement with the experimental and other theoretical reports. Among the investigated compounds, $ZnSiAs_2$, $ZnSiSb_2$, and $ZnGeP_2$ show an indirect band gap, and other compounds are direct gap semiconductors. Earlier theoretical study predicted an indirect band gap in $ZnGeP_2$ by comparing it with its binary analogue GaP.[37] The present study confirm the indirect band gap nature of $ZnGeP_2$ using TB-mBJ functional along Γ-X direction. In the case of $ZnSiP_2$, Kumar and Tripathy reported the pseudo-direct band gap nature using LDA,[6] whereas the present calculations using TB-mBJ functional reveals the direct band gap nature of $ZnSiP_2$, which might be due the improved band gap obtained using TB-mBJ functional over LDA functional.

In the case of Si compounds, $ZnSiP_2$, $ZnSiAs_2$, and $ZnSiSb_2$, the band gap is found to decrease from $ZnSiP_2$ to $ZnSiSb_2$. A similar reduction in band gap is found in the case of “Ge” and “Sn” compound from “P” to “As.”. The observed decrease in band gaps as we move down the column in periodic table might be due to the increase in size of the atom. Dispersion of bands along Γ-Z direction (along c axis) is little higher than the dispersion of bands along Γ-N direction (planar direction) in valence band, whereas in conduction band dispersion of band along Γ-N direction is more than Γ-Z direction, which is confirmed through effective mass calculations as given in Table II. For all the investigated compounds, the contribution to VBM (valence band maximum) is a mixture of Zn and Pn states, whereas in CBM (conduction band minimum) it is the mixture of X and Pn states.

The total DOS of all the compounds and partial DOS for $ZnSiP_2$ are reported in Figs. 4(a) and 4(b). In the case of $ZnXPn_2$ (X: Si, Ge, and Sn; Pn: P and As), near the Fermi level (E_F) in valence band, the main contribution stems from the Pn-*p* state, Zn-*p* and *d* states, whereas in conduction band X-*s*, *p* and Pn-*s*, *p* states are contributing more. For $ZnSiSb_2$, Sb-*p* states and Zn-*p*, Zn-*d* are dominating in valence band edge, whereas in conduction band Si and Sb, *p* and *s* states play a major role. Compared with the valence band, the extent of hybridization between X and Pn states is more in the conduction band for all the investigated compounds (see Fig. 3(b)). This indicate that the electrical conductivity in the case of electron doping may dominate a little than hole doping for all the investigated compounds. We observed a sharp

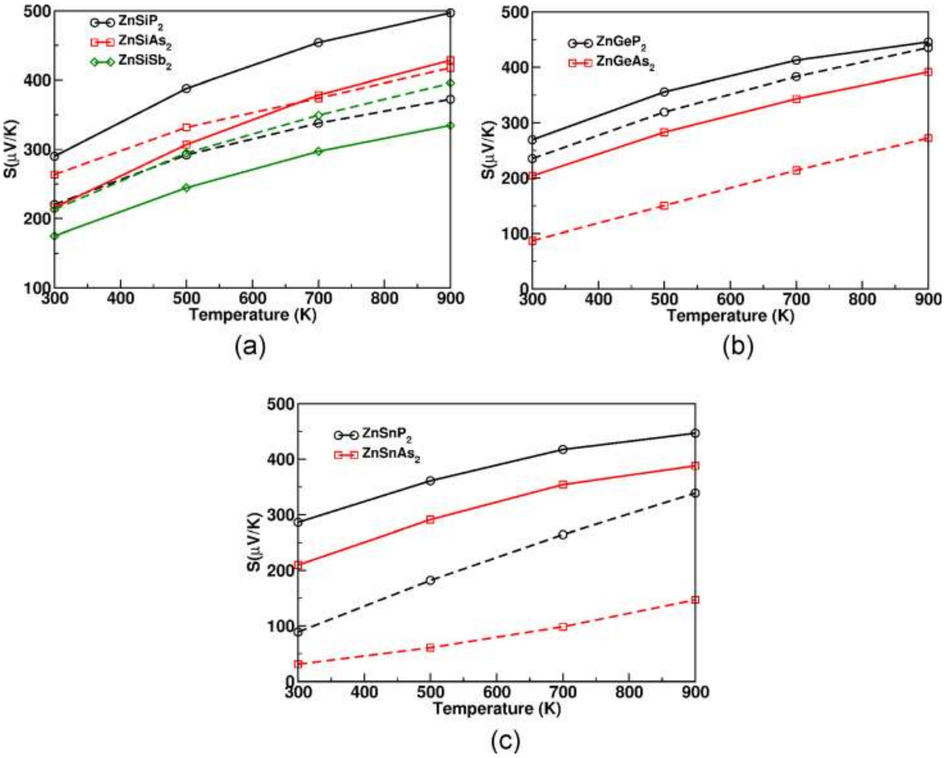


FIG. 7. Variation of thermopower as a function of temperature at carrier concentration $1 \times 10^{19}(cm^{-3})$. Solid lines are for holes and dotted line represent electrons. (a) $ZnSiX_2$ (X: P, As, Sb), (b) $ZnGeX_2$ (X: P, As), and (c) $ZnSnX_2$ (X: P, As).

increase in density of states near valence band edge for all the studied compounds, and this trend is more pronounced in $ZnXP_2$ compounds compared with As compounds. From this, we infer that hole doped $ZnXP_2$ compounds might show higher value of thermopower than As compounds. For Si compounds in conduction band, we observed the Si-*s* state to shift towards the Fermi level when the anion "P" is replaced with "As" and "Sb," causing a reduction of band gap from "P" to "Sb." The same scenario is observed in other "Ge" and "Sn" compounds when "P" is replaced with "As." Almost similar increase in DOS at both valence band and conduction band indicates good thermoelectric properties for both the carriers, in all the investigated compounds, which are explained in Sec. III B.

B. Thermoelectric properties

1. Thermoelectric properties of $ZnXPn_2$ (X: Si, Ge, and Sn; Pn: P and As) and $ZnSiSb_2$

Thermoelectric properties of investigated compounds were calculated for temperature between 300 K and 900 K. The thermopower (in $\mu V\ K^{-1}$) and electrical conductivity scaled by relaxation time (in $\Omega^{-1}\ m^{-1}\ s^{-1}$) are calculated as functions of both carrier concentration and temperature. We have investigated the transport properties for the concentration between 1×10^{18} and $1 \times 10^{21}\ cm^{-3}$ for all the investigated compounds, which is an optimum carrier concentration range for better thermoelectric performance. As mentioned earlier, the investigated compounds crystallize in tetragonal structure, and it is very important to observe the variation of transport properties along different crystallographic directions. For this purpose, we have investigated the thermoelectric properties along the crystallographic "*a*" and "*c*" axes.

We have plotted the variation of thermopower as a function of hole and electron concentrations at 900 K along the "*a*" and "*c*" axes of all the compounds and are presented in Fig. 5. For all these cases except $ZnSnAs_2$, the magnitude of thermopower is decreasing with increasing concentrations for both the carriers, which is a regular trend in TE materials. From the analysis of thermopower plots at 900 K, we found all the compounds to possess high thermopower for the holes compared with the electrons. This might be due to the bands being less dispersive in the case of valence band maximum compared with the conduction band minimum. For all the

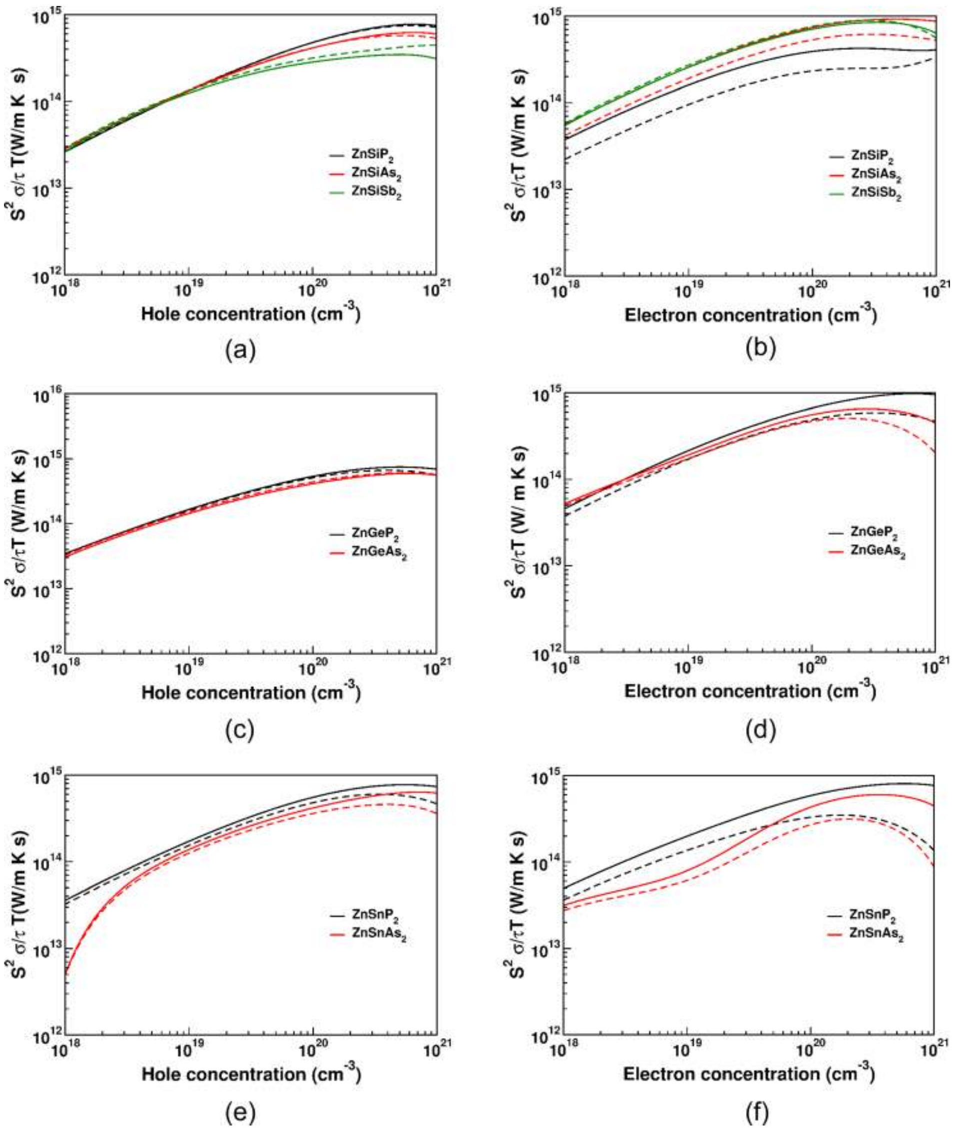


FIG. 8. Variation of power-factor times temperature as a function of both carrier concentrations at 900 K. Solid lines are for "*a*" axis and dotted lines represent "*c*" axis.

compounds, we did not observe any significant difference in thermopower along "*a*" and "*c*" directions which confirms the isotropic nature in thermopower along "*a*" and "*c*" crystallographic directions. The maximum thermopower is found in hole doped $ZnSiP_2$ compared with all other compounds. For hole doped $ZnSnAs_2$, we observed a bipolar conductivity at 900 K, which might be due to the lesser band gap of $ZnSnAs_2$ compared with other investigated compounds. Electrical conductivity scaled by relaxation time (σ/τ) as a function of both holes and electrons along different crystallographic directions at 900 K are presented in Fig. 6. For all the compounds, electrical conductivity scaled by relaxation time is increasing with increasing carrier concentration for both holes and electrons. A similar type of isotropic nature is found in electrical conductivity also, implying the investigated compounds to possess isotropic nature of TE properties.

To see the effect of temperature on thermoelectric properties of investigated compounds, we have plotted the temperature dependent thermopower for both holes and electrons at a carrier concentration of $1 \times 10^{19}\,\mathrm{cm}^{-3}$ and is shown in Fig. 7. Since there is no significant anisotropy observed in thermopower, we have represented "*a*" direction alone for thermopower. For all the investigated compounds, the magnitude of thermopower is increasing with increasing temperature. From Figs. 7(a)–7(c), it is quite evident that thermopower of all the compounds is higher for holes compared with the electrons except for $ZnSiAs_2$ and $ZnSiSb_2$. In the case of $ZnSiAs_2$, we found electron doped thermopower to be higher at low temperature and hole doped thermopower is higher at elevated temperature, whereas in the case of $ZnSiSb_2$, we observed electron doped thermopower to be dominating compared with the hole doped thermopower for all the studied temperature. Further, we found that the thermopower is found to decrease from *P* to *As* and from *Si* to *Sn* in $ZnXPn_2$ (X: Si, Ge, and Sn; Pn: P and As).

To understand the net TE properties, we have plotted the variation of power-factor times temperature as a function of carrier concentrations at 900 K, and the same given is in Fig. 8, and from the figure it is clear that the power-factor values are higher for all the investigated compounds for the range of optimum carrier concentrations. For hole doping, power-factor value is decreasing down the column, and for electron doping also a similar trend is observed except for $ZnSiPn_2$. From the analysis, we found that the magnitude of thermopower is increasing with temperature implying that the power-factor might be higher at elevated temperature, which need to be explored further experimentally.

Another vital point to be mentioned about the investigated compounds is that the reported lattice thermal conductivity is higher compared with the other TE materials.[38] If one can reduce the lattice thermal conductivity by some techniques (such as superlattice, nano-structuring, etc.), all investigated compounds would be promising materials for TE applications.

2. Comparison of thermoelectric properties with other chalcopyrites

In order to understand how better are the TE properties of the investigated compounds, we have compared it with well-known chalcopyrite TE materials. The comparison between the studied compounds ($ZnSiP_2$, $ZnSiAs_2$, $ZnGeP_2$, $ZnGeAs_2$, and $ZnSnP_2$) with prototype chalcopyrite compound $CuGaTe_2$ which has a high figure of merit of 1.4 from experiment[20] and $AgGaTe_2$ are shown in Fig. 9. From this figure, it is quite evident that the investigated systems are

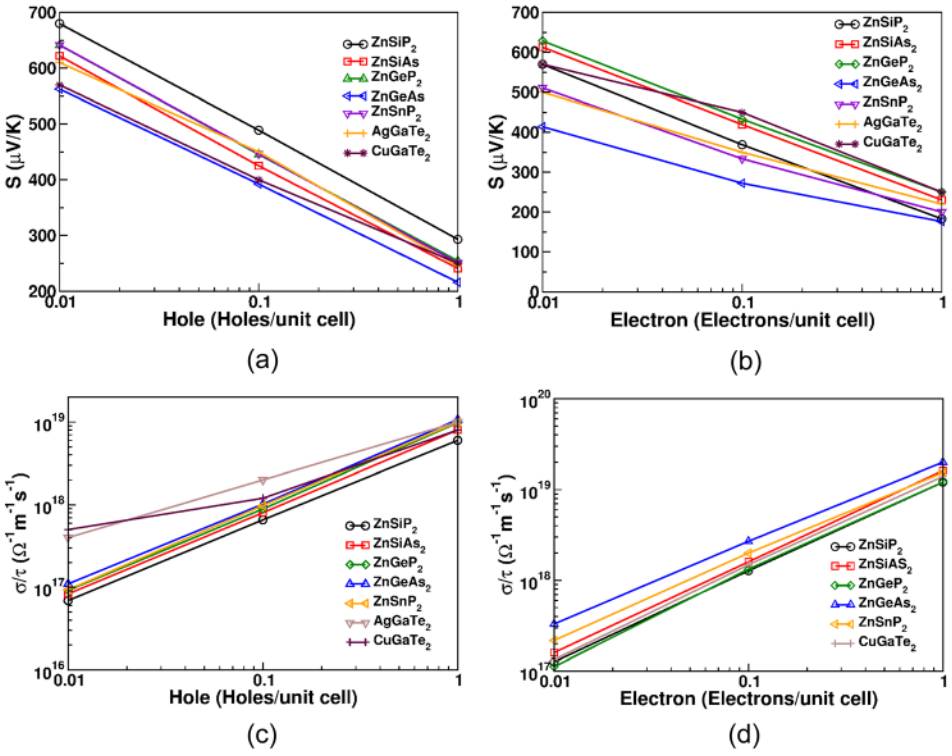


FIG. 9. Comparison of ((a) and (b)) thermopower and ((c) and (d)) electrical conductivity scaled by relaxation time with $AgGaTe_2$ and $CuGaTe_2$ along planar axis, at 900 K. One hole per unit cell is considered as $1 \times 10^{20}\,\mathrm{cm}^{-3}$.

appreciable similar to the well known TE materials $CuGaTe_2$ and $AgGaTe_2$ for both electrons and holes. At 900 K, $ZnSiP_2$ possess a higher thermopower in the case of holes, which is even higher than other hole doped $AgGaTe_2$ and $CuGaTe_2$. We also found that the electrical conductivity is also very similar with that of the compared compounds, so it is imperative that the power-factor value might be higher or comparable with other prototype compounds. This shows that the investigated pnictide compounds almost show better thermoelectric properties compared with the well known chalcopyrite materials $CuGaTe_2$ and $AgGaTe_2$.[17,18] In addition to this, we have also compared the thermopower values of the present studied systems with traditional TE material, Bi_2Te_3. At room temperature, and around a carrier concentration of $4 \times 10^{18}\,\mathrm{cm}^{-3}$, Bi_2Te_3 has a thermopower of 313 μV/K for p-type and 196 μV/K for n-type, while for our compound (we have chosen $ZnSiP_2$) at the same conditions, it is 358 μV/K for p-type and 292 μV/K for n-type.[2] This shows that the investigated compounds are found to have higher value of thermopower compared with the well known traditional TE materials, which lead us to claim that investigated compounds are potential materials for TE applications.

IV. CONCLUSION

The band structure of $ZnXPn_2$ (X: Si, Ge, and Sn; Pn: P and As) and $ZnSiSb_2$ is studied, where $ZnSiAs_2$, $ZnSiSb_2$, and $ZnGeP_2$ show indirect band gap nature and other investigated compounds are direct band gap semiconductors. From the transport properties, it is quite clear that most of the investigated compounds are favorable for TE applications in all temperature range from 300 K to 900 K. The investigated pnictide compounds show almost comparable thermoelectric properties with the well-known TE materials of chalcopyrite. Among the studied compounds, p-type $ZnSiP_2$, $ZnGeP_2$, and $ZnSnP_2$ and n-type $ZnGeP_2$ and $ZnSiAs_2$ are found to have good TE properties. This study reveals that along with the chalcopyrite materials, pnictides also emerges as good thermoelectric materials and can be best used, if one could reduce the thermal conductivity by alloying or nanostructuring.

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