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Thermoelectric characterization of ZnSb by first-principles method

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ABSTRACT
The thermoelectric properties of semiconducting compound ZnSb are studied using crystalline orbitals program based on the periodic linear combination of atomic orbitals method. The calculations are done under the framework of density functional theory. We calculate the electronic band structure and the density of states. The $k$-space eigenvalues are coupled with Boltzmann transport equations to calculate transport coefficients such as the Seebeck coefficient, power factor and electronic thermal conductivity under the constant relaxation time and the rigid band approximations. Effect of the scissor correction on the transport coefficients is examined. We have found that ZnSb behaves as n-type thermoelectric. A comparison with available measurements is done and a good agreement is found. The thermoelectric performance is compared with other materials by means of the electronic fitness function which suggests ZnSb to be a good thermoelectric material.

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I. INTRODUCTION
The thermoelectric (TE) materials convert heat into electricity. Development of efficient TE materials has drawn much attention due to thrust on clean energy. Three TE quantities i.e. Seebeck coefficient ($S$), electrical conductivity ($\sigma$) and, thermal conductivity ($\kappa$) containing both lattice and electronic parts, contribute to the performance of a TE material. This is described by the figure of merit ($zT$). For a TE material with high $zT$, we have to simultaneously optimize $S$, $\sigma$ and $\kappa$. These together can be manipulated to tune the power factor ($PF=S^2\sigma$). To enhance the efficiency of a TE material, it is necessary to maximize the PF and minimize the $\kappa$. Outstanding TE properties have been reported for the Zn-Sb alloys and the Zn$_4$Sb$_3$ has received major attention of the materials science community specifically due to high thermoelectric figure of merit at relatively moderate temperatures. To see possibility of the formation of other Zn-Sb materials the challenging phase diagram of Zn-Sb alloys is reexamined computationally. It is found that the TE properties depend strongly on the specific phase and stoichiometry. ZnSb is one of the most widely studied compound of the Zn-Sb system for TE applications. It is tried as an alternative of Bi$_2$Te$_3$ and PbTe to operate in the intermediate temperature range because it is economic, non-toxic and abundant. It has high $zT$ in 450–700K range of temperature. Many experimental and theoretical studies are reported on ZnSb. Earlier studies do not arrive on a consensus on the polarity of polycrystalline ZnSb. A few experimental and theoretical studies on doped and undoped ZnSb show p-type majority carriers whereas others found n-type majority carriers whereas others found n-type majority carriers.

In this work we compute the transport coefficients namely; $S$, $\sigma$, PF and the figure of merit ($zT$). This is achieved by coupling the Boltzmann transport equations embodied in the BoltzTraP with the crystalline orbital program based on the periodic linear combination of atomic orbitals (LCAO) method by means of an interface. The TE properties are calculated by getting the $E$-$k$ spectrum which carries the fingerprint of electronic bands in terms of multi-valley structures essentially around the Fermi energy. These are coupled with the Boltzmann transport equations modeled in BoltzTraP. The scissor correction is applied to see the effect of band gap on the TE properties. The performance is examined computing the electronic fitness function (EFF) suggested recently.
II. COMPUTATIONAL DETAIL

The ZnSb crystalizes in the orthorhombic structure belonging to the Pnma spacegroup. Both Zn and Sb occupy the 8c Wyckoff positions and there are 16 atoms in the unit cell. The crystal structure is shown in Figure 1. For current calculations the experimental lattice parameters and atomic positions reported elsewhere are taken. The periodic LCAO method is applied for the investigations. The localized Gaussian basis sets of Zn and Sb reported by earlier workers are used. The crystal Hamiltonian is generated using the Perdew-Becke-Ernzerhof (PBE) exchange and correlation functional. A grid of highly dense k-points of 46×46×46 size is considered to calculate the eigenvalues. It leads to the eigenvalues at ~14000 k-points in the irreducible Brillouin zone. These are coupled with BoltzTraP. The k-points were sufficient to ensure convergence in the Fourier transform of band energies. The transport properties are calculated in the constant relaxation time approximation assuming the rigid band model. The TE transport tensors are computed with BoltzTraP code. The efficiency of TE materials can be assessed by figure of merit defined as:  
\[ S = \frac{2k_B^2}{3e^2} m^*_{\text{DOS}} T \left( \frac{\pi}{3n} \right)^{3/2}, \]  
where \( h \) is reduced Planck constant, \( k_B \) is Boltzmann constant and \( m^*_{\text{DOS}} \) is the DOS effective mass. The effective mass can also be obtained from the multi-valley structure of the electronic bands. With high effective mass and low carrier density there is high thermopower (S) but this in turn reduce \( \sigma \). The role of inverse relationship between S, effective mass (\( m^* \)) and \( \sigma \) in ascertaining the TE properties can be guided by the EFF. It is known that a large number of eigenvalues and eigenvalues, the Kohn-Sham Hamiltonian of a crystal are needed for thermoelectric characterization of materials. We have calculated about ~14,000 eigenvalues and the corresponding eigenvalues which yield indirect band gap in ZnSb. The band structure calculation is however performed over a selective list of k-points. To find the complete band structure and hence the band gap, it is necessary to calculate bands along the paths covering each symmetry point of the irreducible Brillouin zone of a crystal. We, therefore, also include three slices in Figure 2. The large number of eigenvectors and, the band structure signify that ZnSb is a semiconductor with indirect band gap of 0.72eV. The valence band maximum is very close to the X-point and the conduction band minimum is very close to the Y-point of symmetry. There is a very small difference (0.045 eV) in the energy of the first conduction band at the Y and Z points. This is in contrast to the metallic character found by the VASP method using PBE which turns to semiconducting character on using the HSE06 exchange and correlation functional. The band structure well resembles with other calculations. The value of band gap is in agreement with the experiment and a few calculations which are summarized in Table I. Most of the theoretical values show large deviation from the experiment. Current result is in good agreement with the experiment. Though it is close to the experimental gap 0.53-0.61eV, it is albeit more than other results. The residual difference

III. RESULTS AND DISCUSSION

A. Electronic states

The electronic band structure of ZnSb is shown in Figure 2. The path of the k-points in irreducible Brillouin zone to plot the E-k curve is taken from the tools described by Setyawan and Curtarolo. It is known that a large number of eigenvectors and eigenvalues of the Kohn-Sham Hamiltonian of a crystal are needed for thermoelectric characterization of materials. We have calculated about ~14,000 eigenvalues and the corresponding eigenvalues which yield indirect band gap in ZnSb. The band structure calculation is however performed over a selective list of k-points. To find the complete band structure and hence the band gap, it is necessary to calculate bands along the paths covering each symmetry point of the irreducible Brillouin zone of a crystal. We, therefore, also include three slices in Figure 2. The large number of eigenvectors and, the band structure signify that ZnSb is a semiconductor with indirect band gap of 0.72eV. The valence band maximum is very close to the X-point and the conduction band minimum is very close to the Y-point of symmetry. There is a very small difference (0.045 eV) in the energy of the first conduction band at the Y and Z points. This is in contrast to the metallic character found by the VASP method using PBE which turns to semiconducting character on using the HSE06 exchange and correlation functional. The band structure well resembles with other calculations. The value of band gap is in agreement with the experiment and a few calculations which are summarized in Table I. Most of the theoretical values show large deviation from the experiment. Current result is in good agreement with the experiment. Though it is close to the experimental gap 0.53-0.61eV, it is albeit more than other results. The residual difference

![FIG. 1. The orthorhombic crystal structure of ZnSb.](image1)

![FIG. 2. The band structure calculated using PBE along the path of the conventional orthorhombic lattice a-b-c.](image2)
TABLE I. A comparison of the band gaps of ZnSb.

| Calculation procedure | Method | XC functional | Band gap (eV) |
|-----------------------|--------|---------------|--------------|
| CRYSAL                | PBE (This work) |               | 0.72         |
| EXPERIMENT            |        |               | 0.53, 0.50 (300K), 0.59 (77K), 0.61 (4.2K) |
| PAW                   | PBE    |               | 0.26         |
| FP-LAPW               | PBE, (EV) |               | 0.08, (0.41) |
| PAW                   | mBJ    |               | 0.60         |
| PAW                   | PBE, (HSE) |               | 0.03, (0.56) |
| LCAO                  | PBE    |               | 0.56         |

may arise from the experimental lattice constants considered by us. Since TE coefficients depend on the band gap, we also perform TE calculations taking 0.53 eV band gap applying the scissor correction.

The TE properties depend significantly on the density of states (DOS) particularly around the Fermi energy. The DOS calculated from the BoltzTraP is shown in Figure 3. The contribution of Sb bands is larger than the Zn from 0 to -3eV. In the -3 to -4.5eV range both Zn and Sb contribute equally. Thereafter the Zn dominates up to -6eV. Both Zn and Sb have equal contributions to form the unoccupied states up to 4eV. The broad as well as salient features very well reconcile with the DOS structure from the Bjerk et al. and Zhao et al. The multi-valley structures of the bands around top valence band and the bottom conduction band are believed to give rise to the increased PF.

B. Transport coefficients

The dependence of Seebeck coefficient $S_{xx}$, $S_{yy}$ and $S_{zz}$ on chemical potential ($\mu$) at 300K is shown in Figure 4. Anisotropy in the components is clearly visible around the Fermi energy. It can be seen that $S_{zz}>S_{xx}>S_{yy}$ and beyond $|0.1| eV$ anisotropy disappears.

In Figure 5, PFs arising from the three components of the S and $\sigma$ at 100 and 300K are plotted. The average PF is also shown. Let us focus on the anisotropic behavior of PF at 100K shown in Figure 5(a). The total PF clearly shows that electrons are the majority carriers in ZnSb. The PF$_{yy}$ has the maxima of nearly equal magnitude on both sides of the chemical potential. However, the maxima in the PF$_{xx}$ and PF$_{zz}$ are clearly high for the positive sign of the chemical potential. This clearly exhibits highly anisotropic behavior. In the $y$ direction, the effective thermal current will be very small due to both types of carriers. Increase in temperature worsens the transport because the magnitude of PF$_{yy}$ is nearly same on both sides of the chemical potential at 300K as visually obvious from Figure 5(b). At both temperatures, the average PF clearly shows that ZnSb has n-type majority carriers. Increase in PF with temperature is well in agreement with experiment. However, the average value is less by an order. As we observed, the Bottger et al have found in the experimental study that above 600K bipolar conduction sets on. Notably, n-type conductivity at 2.03 at.% and 1.06 at.% Te-doped ZnSb is found while at 3.02 at.% Te-doping ZnSb exhibits p-type conductivity. Moreover, Niedziółka and Jund reported -114 $\mu$V/K Seebeck coefficient (n-type behavior) using PBE in the Projector Augmented Wave (PAW) method which rises to -950 $\mu$V/K on adopting band gap correction using the Fermi level and rigid band shift. Following the same approach for ZnSb supercell with Zn vacancy, +11 $\mu$V/K Seebeck coefficient (p-type behavior) is found.
which rises to +81 μV/K on adopting band gap correction considering the Fermi level and rigid band shift. They attributed the p-type conductivity to Zn vacancies. None of these studies have found the directional components of the transport coefficients. Very recently, however, effective mass calculations are performed and anisotropy is seen. Our study (Figures 4,5) clearly indicates anisotropic behaviour. The measurements of the anisotropic transport coefficients shall be fruitful to examine the nature of majority carriers and anisotropies in ZnSb.

In current calculation procedure, the transport coefficient tensors give $\sigma/\tau$ and $\kappa_e/\tau$. To get accurate electrical and electronic thermal conductivities, the relaxation time is required. It can be obtained from the electrical conductivity measurements varying temperature as well as concentrations. So to get the value of $\sigma$ and $\kappa_e$ we use $\tau=10^{-14}$ s reported in earlier calculation. The resulting TE properties of ZnSb are summarized in Table II. A few experimental results are also included.

We note that calculated electronic part of the thermal conductivity is 4.5% of the total $\kappa$. The absolute value of calculated $S$ is ~16% larger than the experiment. The value of PF differs by ~10¹ with the experimental report of Ueda et al. The deviation may probably be due to the different carrier concentration. The experimental result has not specified the carrier concentration whereas our optimum PF occurs at $10^{19}$ cm⁻³. This may also lead to deviation in other TE coefficients when calculations are compared with measurements. Scissor correction rectifies the TE coefficients resulting from the difference between calculated and experimental band gap. The SC corrected TE properties are also given in Table II. Scissor correction does not alter the coefficients significantly. The figure of merit $zT$ is 0.24 which is well within the range proposed by temperature dependent measurement reported by Xiong et al.

There are provisions to assess performance of a thermoelectric material. The dimensionless material parameter B, proposed first by Chasmar and Strattton, has been used by earlier workers. It is based on a single parabolic band model in the nondegenerate limit. Larger value of B usually corresponds to a high $zT$ at the optimum values of the transport coefficients. The parameter guides to identify better thermoelectric materials instead of checking all the transport coefficients $S$, $\sigma$, and $\kappa$. The material parameter B takes care of the effect of alloying scattering into account, as well as additional electron (hole) bands. Despite these notions it continuously increases with the temperature. However, the $zT$ of a material drops at high temperatures due to the bipolar effect. To take into account the bipolar effect, it is necessary to go beyond a single parabolic band model.

Alternatively, the EFF takes care of the curvature of the prominent valence and conduction bands around the Fermi energy. The EFF is shown in Figure 6. It describes the TE performance and helpful in filtering the materials that give better TE performance, where materials overcome the inverse relationship between $\sigma$ and $S$. It is checked by the salient features of the complex band structure.

In Figure 6, the EFF calculated using PBE-GGA at different temperatures is shown. The function rises in the beginning and gradually decreases after achieving a maximum value. The deviation may probably be due to the different carrier concentration. The experimental result has not specified the carrier concentration whereas our optimum PF occurs at $10^{19}$ cm⁻³. This may also lead to deviation in other TE coefficients when calculations are compared with measurements. Scissor correction rectifies the TE coefficients resulting from the difference between calculated and experimental band gap.

### Table II. Calculated and experimental TE properties of ZnSb at 300K.

| TE Properties | This Work | Others |
|---------------|-----------|--------|
| S [μV/K]      | 353       | 305, 27, 28, 205-364, 29, 500, 26, 375, 8 |
| $S^2\sigma$ [W/mK²] | 2.81×10⁻³ | 2×10⁻⁴, 1.15×10⁻⁴ |
| $\kappa_e$ (κ) [W/mK] | 0.0519 | 0.02922, $\kappa_e=0.16$, (3.53)³, $\kappa=1.8$³ |
| $zT$          | 0.239    | 0.2-0.6, 0.12² |

[FIG. 5. Anisotropic components of the PF of ZnSb at (a) 100K and (b) 300K.]
is pronounced at higher temperature. The EFF becomes negligible beyond $10^{12}$ cm$^{-3}$. Two horizontal lines are shown in the Figure 6. A material having the EFF value above these horizontal lines represents a good TE material at 300 and 800K. The EFF of ZnSb points a good thermoelectric behavior at both the temperatures. According to screening criteria, the n-type materials having EFF more than that of Fe$_2$VAI ($0.79 \times 10^{-12}$ W m$^{-2}$ K$^{-1}$) at 300K and NiZrSn$_2$ ($2.01 \times 10^{-12}$ W m$^{-2}$ K$^{-1}$) are the useful thermoelectric.

IV. CONCLUSIONS

Band energies, DOS and PF of the orthorhombic ZnSb are calculated coupling band energies from the first-principles periodic LCAO method with the Boltzmann transport equation. The computed DOS and the band gap are in good agreement with earlier findings. The current results show anisotropy in TE coefficients. Quantitatively, our results are well comparable with other calculations and experimental data. The EFF exhibits that it is good TE material. The anisotropic measurements of the transport coefficients on a high purity ZnSb are required for the further rigorous study.

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FIG. 6. Dependence of the EFF (or the t-function) of ZnSb on n-type carrier concentration. The horizontal lines mark the EFF of n-type Fe$_2$VAI at 300 and NiZrSn at 800K.