

## DETERMINING SEEBECK COEFFICIENT OF ZnSb BY MOLECULAR ORBITAL METHOD

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### ABSTRACT

In this work we calculated the electronic structure and Seebeck coefficient of ZnSb by Molecular Orbital (MO) Method. The MO method was calculated using the Hartree-Fock-Slater (HFS) approximation, the linear combination of atomic orbital (LCAO) method and self-consistent charge (SCC). The calculation used space group symbol *Pbca* (No. 61), lattice parameter  $a = 0.6218$  nm  $b = 0.7741$  nm and  $c = 0.8115$  nm, atomic position of Sb: 0.461, 0.103, 0.878 (8c) and Zn: 0.142, 0.081, 0.111 (8c) for designing ZnSb cluster model. The results show Zn<sub>26</sub>Sb<sub>28</sub> cluster model, bond length, energy level, density of state (DOS), energy gap and Seebeck coefficient vs temperature. The energy gap has to be interesting value of 0.44 eV effective to Seebeck coefficient as it closely matches experimental reference. Also, it indicates p-type thermoelectric material.

KEYWORDS: Energy level, Fermi-Dirac distribution, P-type thermoelectric material, Hartree-Fock-Slater approximation, Density of state

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### INTRODUCTION

Zinc antimony (ZnSb) is a thermoelectric material which can convert heat energy directly to electrical energy [1-5]. The efficiency of thermoelectric materials can be determined from the dimensionless figure of merit  $ZT = S^2\sigma T/\kappa$  where  $S$  is Seebeck coefficient,  $\sigma$  is electrical conductivity,  $T$  is absolute temperature and  $\kappa$  is thermal conductivity. Thermoelectric properties of ZnSb at room temperature have electrical conductivity 528 S/m, Seebeck coefficient 300 - 500  $\mu\text{V/K}$  and thermal conductivity 1.41 W/m.K [1]. ZnSb has  $ZT$  0.6 - 0.8 at 573 K [1]. In addition, composition elements of ZnSb are low cost and non-toxic [6]. Hence, ZnSb is a good thermoelectric material because of its high performance in temperature range 450 - 650 K [1]. The band gap energy of ZnSb has 0.5 eV [1, 7-8]. ZnSb base on structure type CdSb (orthorhombic) has space group symbol and number: *Pbca* and 61, lattice parameter  $a = 0.6218$  nm  $b = 0.7741$  nm and  $c = 0.8115$  nm [9]. Recently, the electronic structure and thermoelectric properties of

Sb<sub>2</sub>Te<sub>3</sub> were calculated by Molecular Orbital (MO). These results compose of radial function, energy level, MO eigenvalues, partials density of state, bond overlap, contour map and Seebeck coefficient [10]. In this work, we calculated the electronic structure of ZnSb thermoelectric material by MO method to predict Seebeck coefficient.

### MATERIALS AND METHODS

#### Computational Method

##### 2.1 MO method

The MO method is calculated using the Hartree-Fock-Slater (HFS) approximation, the linear combination of atomic orbital (LCAO) method, and self-consistent charge (SCC) [11-13]. The Schrödinger equation is given by;

$$\left\{ -\frac{\hbar^2}{2m} \nabla^2 + V_{\text{eff}}(r) \right\} \Psi_i(r) = E_i \Psi_i(r) \quad (1)$$

where  $\Psi$  is molecular wave function,  $E$  is energy,  $m$  is electron mass,  $\hbar = h / 2\pi = 1.054571726(47) \times 10^{-34}$  J.s,  $V_{eff}(r)$  is effective potential of the position  $r$  can follow by;

$$V_{eff}(r) = V_{ion}(r) + V_H(r) + V_{XC}(r) \quad (2)$$

where  $V_{ion}(r)$  is ion Coulomb potential,  $V_H(r)$  is the Hartree potential,  $V_{XC}(r)$  is the exchange-correlation potential term and is given by the statistical local expression;

$$V_{XC}(r) = -3\alpha[3/8\pi\rho(r)]^{1/3} \quad (3)$$

where  $\alpha$  is the only parameter used in this model, the calculation is performed for  $\alpha = 0.7$  by the SCC procedure described below [11].  $\rho(r)$  is the molecular electronic density at the position  $r$ , and it can be evaluated from;

$$\rho(r) = \sum (\lambda, i, j) f_\lambda C_{i\lambda}^* C_{j\lambda}^* \chi_i^*(r) \chi_j(r) \quad (4)$$

where  $f_\lambda$  is the occupation number in the  $\lambda^{th}$  molecular orbital. The  $\lambda^{th}$  molecular wave function can be written as;

$$\Psi_\lambda = \sum (i) C_{i\lambda} \chi_i(r) \quad (5)$$

where  $C_{i\lambda}$  is a weighting coefficient,  $\chi_i(r)$  is symmetrized LCAO at position  $r$ , and can be evaluated from;

$$\chi_i(r) = \sum (v, l, m) W_{vm}^{il} \phi_{nlm}^v(r_v) \quad (6)$$

where  $r_v$  is the coordinate referred to atom  $v$ ,  $W_{vm}^{il}$  is the symmetrization coefficients obtained from group theory and basis function  $\phi_{nlm}^v(r)$  is orbital function centred on the atomic sites, which can be written as;

$$\phi_{nlm}^v(r) = R_{nl}^v(r) Y_{lm}(\hat{r}) \quad (7)$$

where  $R_{nl}^v(r)$  is the radial part of the atomic orbital and generated by numerical computation of atomic problem. The angular part of the atomic orbital  $Y_{lm}(\hat{r})$  is taken to be real spherical harmonics.

## 2.2 Computational Details

The calculation used data of crystal structure of ZnSb such as space group symbol *Pbca* (No. 61), lattice parameters  $a = 0.6218$  nm,  $b = 0.7741$  nm and  $c = 0.8115$  nm, atomic position of Sb: 0.461, 0.103, 0.878 (8c) and Zn: 0.142, 0.081, 0.111 (8c) [9]. This present design cluster model of ZnSb was used to calculate bond length, energy level and density of state. The energy level result give the energy gap ( $E_g$ ) to predict the Seebeck coefficient. The Seebeck coefficient can be evaluated from the Fermi energy ( $E_F$ ) where  $E_F$  of a semiconductor is one half of  $E_g$ . The Seebeck coefficient can be expressed as follows from Fermi-Dirac distribution [14];

$$S(T) = \frac{k_B}{e} \ln \left[ \frac{1-f(E)}{f(E)} \right] \quad (8)$$

where  $S(T)$  is the Seebeck coefficient,  $k_B$  is Boltzmann constant =  $1.3806488(13) \times 10^{-23}$  J/K,  $e$  is electron charge =  $1.60217657 \times 10^{-19}$  C,  $f(E)$  is Fermi-Dirac distribution function which given by;

$$f(E) = \exp \left[ -(E - E_F) / k_B T \right] + 1 \quad (9)$$

where  $E$  is energy,  $E_F$  is Fermi energy. The band gap in semiconductors of the order of  $\sim 1$ eV, which is much larger than  $k_B T$ . Therefore;

$$f(E) \approx \exp \left[ -(E - E_F) / k_B T \right] \quad (10)$$

Replacing the Fermi-Dirac distribution function to obtain the Seebeck coefficient;

$$\begin{aligned} S(T) &= \frac{k_B}{e} \ln \left[ \frac{1}{e^{-(E-E_F)/k_B T} - 1} \right] \\ &= \frac{k_B}{e} \left[ \ln e^{(E-E_F)/k_B T} - \ln 1 \right] \end{aligned} \quad (11)$$

$$S(T) = \frac{k_B}{e} \left[ \frac{(E - E_F)}{k_B T} \right] \quad (12)$$

when  $(E - E_F) \approx E_F$  at T = 0 K, and  $E_F$  of a semiconductor is one half of energy gap ( $E_g$ ),  $S(T)$  is given by;

$$S(T) \approx \left[ \frac{E_g}{2eT} \right] \quad (13)$$

## RESULTS AND DISCUSSION

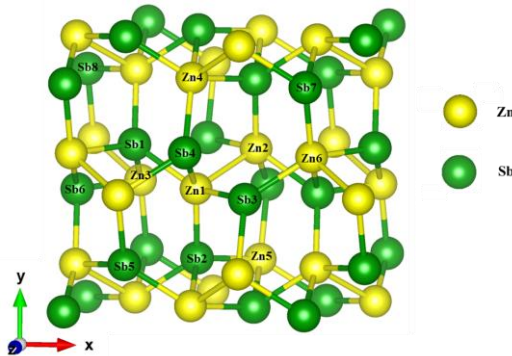


Fig. 1.  $Zn_{26}Sb_{28}$  cluster model

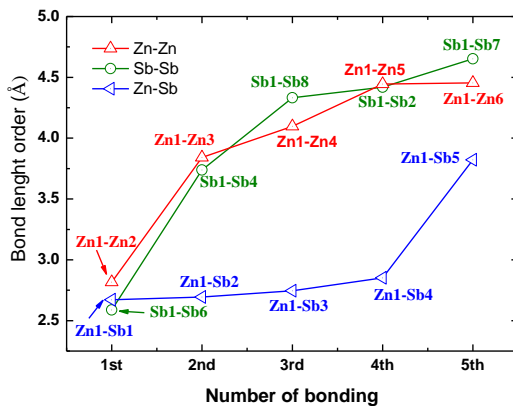


Fig. 2. bond length of Zn-Zn, Sb-Sb, and Zn-Sb in  $Zn_{26}Sb_{28}$  cluster model

The  $Zn_{26}Sb_{28}$  cluster model as shown in Fig. 1.  $Zn_{26}Sb_{28}$  cluster model has Ci (1) symmetry and volume  $390.604 \text{ \AA}^3$ . The bond lengths of Zn-Zn, Sb-Sb, and Zn-Sb are shown in Fig. 2. The first number of bonding, Zn1-Sb1 bond length is  $2.6709 \text{ \AA}$ , Zn1-Zn2 bond length is  $2.8172 \text{ \AA}$  and Sb1-Sb6 is  $2.5882 \text{ \AA}$  in  $Zn_{26}Sb_{28}$  cluster

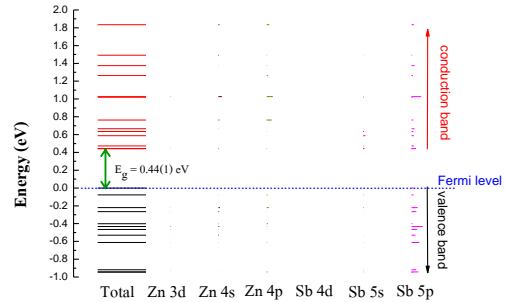


Fig. 3. Valence band and conduction band in energy level of  $Zn_{26}Sb_{28}$  cluster model

The valence band and conduction band in energy level of  $Zn_{26}Sb_{28}$  composed of the total, Zn 3d, Zn 4s, Zn 4p, Sb 4d, Sb 5s and Sb 5p as shown in Fig.3. The energy gap is determined from the difference in the valence band and conduction band. In this work an energy gap of 0.44 eV was found, which agrees with the experimental data [1]. Fig. 4 shows the density of state (DOS) of  $Zn_{26}Sb_{28}$ , where the total DOS peak is at  $-7.5 \text{ eV}$ . The total DOS of  $Zn_{26}Sb_{28}$  has negative value indicating p-type thermoelectric material agree with literature [1-5].

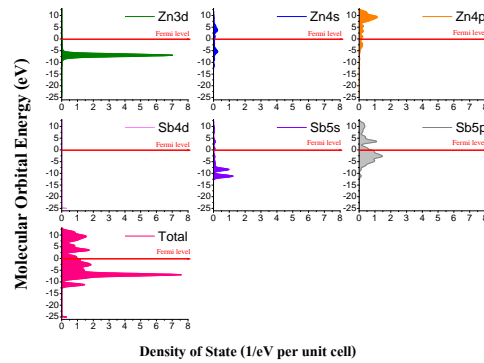


Fig. 4. Density of states for  $Zn_{26}Sb_{28}$  cluster model

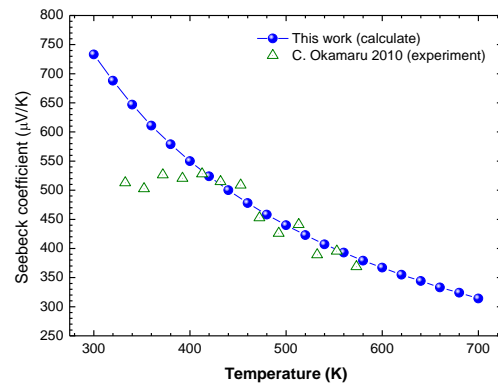


Fig. 5. Calculation of Seebeck coefficient vs temperature of ZnSb

Seebeck coefficient values of ZnSb together with C. Okamaru et al. [1] are shown in Fig. 5. This result has the Seebeck coefficient of 733  $\mu\text{V/K}$  at 300 K. The Seebeck coefficient decreased with increasing temperature and agrees with the experiment of C. Okamaru at temperature range 400 – 570 K.

## CONCLUSION

The  $\text{Zn}_{26}\text{Sb}_{28}$  cluster model shows the unit cell of ZnSb. The bond length of Zn1-Sb1 is 2.6709 Å. The energy gap of ZnSb is 0.44 eV and DOS of  $\text{Zn}_{26}\text{Sb}_{28}$  indicated p-type thermoelectric material. Calculation of Seebeck coefficient decreased with increasing temperature agrees with the literature data at temperature range 400 – 570 K. The molecular orbital (MO) method can be used to calculate the electronic structure of ZnSb thermoelectric material to predict Seebeck coefficient.

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