Physica B 525 (2017) 133–136

Contents lists available at ScienceDirect

Physica B

journal homepage: www.elsevier.com/locate/physb

Mott theory predicted thermoelectric properties based on electronic structure of Bi and Sb atoms substituted PbTe material

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ARTICLE INFO

Keywords:
PbTe
Electronic structure
Thermoelectric properties
DV-Xα method

ABSTRACT

In this work, thermoelectric properties of Bi and Sb atoms substituted PbTe material were predicted by Mott theory through electronic structure calculation. This calculation has been carried by the first-principles DV-Xα molecular orbital method based on Hartree-Fock-Slater approximation. The $Pb_{14}Te_{13}$, $Pb_{13}SbTe_{13}$ and $Pb_{13}BiTe_{13}$ small clusters with a cubic rocksalt structure (*Fm*-3*m*; 225) were designed to be performed PbTe, $Pb_{0.75}Sb_{0.25}Te$ and $Pb_{0.75}Bi_{0.25}Te$ materials, respectively. The electronic structure showed that the high symmetry crystal structure, spin energy levels, partial spin density of states and electron charge density. The energy gap and Fermi level have been obtained from energy levels and density of state to be evaluated of electrical conductivity and Seebeck coefficient within Mott's theory predication.

1. Introduction

Today, thermoelectric (TE) materials are both of power generation and solid-state refrigeration via TE devices, which these represents a field of energy conversion technology under the environmentally friendly [1–3]. The efficiency of energy conversion on TE devices were depended on the Figure of merit as defined by;

$$ZT = \frac{S^2\sigma}{\kappa}T, \tag{1}$$

where S, σ, κ, and T are the Seebeck coefficient, electrical conductivity, thermal conductivity and absolute temperature, respectively [3]. Most of these compounds display semi-metallic behavior in their crystalline states, and their structural features and electronic transport mechanisms have been studied theoretically [4–7] For low band-gap semiconductors/semi-metals, minority carrier energy filtering, creating degenerate states and/or resonant energy levels close to the Fermi level, convergence of valence/conduction band valleys, and quantum confinement effects are the usual recipe for enhancement of TE performance [8]. Furthermore, the structural disorders are useful recipe to enhance the S value [9] such; metastable cubic phase of PbTe-based alloys was significantly disordered with atomic doping [10], atomic percentage of Ag in PbTe increasing has been affected to be decreased the resistivity significantly and indicate a prevalence of p-type materials. Recently, Yang et al. [11] reported Bi doped PbTe nanocubes for developing the high performance n-type PbTe-based thermoelectric materials obtain the ZT ~ 1.35 at 675 K for n-type $Pb_{0.99}Bi_{0.01}Te$. While, Sb doped PbTe showed both of p and n types thermoelectric material [12].

In this work, we designed the cluster model and calculated on the energy levels, spin orbital density of states, and charge density of $Pb_{14}Te_{13}$, $Pb_{13}SbTe_{13}$ and $Pb_{13}BiTe_{13}$ small clusters via DV-Xα molecular orbital method. The energy gap and Fermi energy of each cluster were used to be predicted on thermoelectric properties of PbTe material within Bi and Sb atoms substitution.

2. Computational details

2.1. DV-Xα theory

In this section, the DV-Xα molecular orbital method is assuming the Hartree-Fock-Slater approximation, linear combination of atomic orbital (LCAO) method and self-consistent one-electron local density theory [13–15]. The Schrödinger equation for molecular as following by

$$\left\{-\frac{\hbar^2}{2m}\nabla^2 + V_{eff}(r)\right\}\Psi_j(r) = E_j\Psi_i(r) \tag{2}$$

where $\Psi_j(r)$ is the molecular wave function at r position, E is the energy, $-\frac{\hbar^2}{2m}\nabla^2$ is the kinetic energy and $V_{eff}(r)$ is the effective potential energy at r position. The effective potential energy is

$$V_{eff}(r) = \sum -\frac{Z_N}{|r - R_N|} + \int \frac{\rho(r')}{|r - r'|}dr' + V_{XC}(r), \tag{3}$$

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http://dx.doi.org/10.1016/j.physb.2017.09.012
Received 5 July 2017; Accepted 5 September 2017
Available online 06 September 2017
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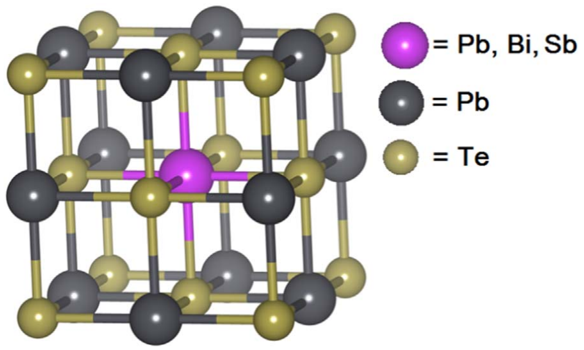

Fig. 1. (a) Small cluster (1 unit cell) model for PbTe with Bi and Sb atoms substitution in unit cell for Pb$_{0.75}$Bi$_{0.25}$Te and Pb$_{0.75}$Sb$_{0.25}$Te, respectively.

where Z_N is atomic number, r is electron position, r' is other electrons position, R_N is nucleus position, $\rho(r')$ is the electronic density at r' position and $V_{XC}(r)$ is exchange-correlation potential at r position [16]. The exchange-correlation potential for Slater's Xα potential [14,15] is given by

$$V_{XC}(r) = -3\alpha\left[\frac{3}{4\pi}\rho_{\uparrow\downarrow}(r)\right]^{1/3} \tag{4}$$

where $\rho_{\uparrow\downarrow}(r)$ is the molecular electronic density of spin up (↑) and down (↓) at r position and α fixed at 0.7. The molecular electronic density is given by

$$\rho_{\uparrow\downarrow}(r) = \sum(j)\rho_j(r) = \sum(j) f_j\,|\Psi_j(r)|^2 \tag{5}$$

where f_j is the occupation number in molecular orbital of the j th. The solution of Schrödinger Eq. (2) is given by

$$\Psi_j(r) = \sum(i) C_{ij}\chi_i(r), \tag{6}$$

where C_{ij} is weighting coefficient and $\chi_i(r)$ is symmetrized LCAO at position r written by

$$\chi_i(r) = \sum(v,\ l,\ m)\, W^{il}_{vm}\phi^{v}_{nlm}(r_v), \tag{7}$$

where v is atom, l is orbital quantum number, m is magnetic quantum number, r_v is coordinate referred to the atom v, W^{il}_{vm} is the symmetrization coefficient and φ^{v}_{nlm} is orbital functions of atom v, which can be written as

$$\varphi^{v}_{nlm}(r) = R^{v}_{nl}(r)Y_{lm}(r), \tag{8}$$

where $Y_{lm}(r)$ is taken to be real spherical harmonics and $R^{v}_{nl}(r)$ is radial part of the atomic orbital generated by numerical computation of atomic problem [14].

2.2. *DV-Xα calculation method*

The unit cell cluster model was designed based on one unit cell cluster model of PbTe. The Cubic structure of PbTe with the space group number (symbol) of 225 (*Fm*-3*m*) had lattice parameters; a = 6.462 Å [17]. and then substituted Sb and Bi atoms in Pb atomic center of unit cell to be performed Pb$_{0.75}$Sb$_{0.25}$Te and Pb$_{0.75}$B$_{i0.25}$Te. After that, the atoms were randomly generated to be stuffed atoms into unit cell. Atomic orbitals were generated by numerical computation within the symmetry of cluster through the Symorb code [18] to be obtained Sb, Te [Kr] 4d, 5s and 5p, and Pb, Bi [Xe] 5d, 6s and 6p atomic orbitals. The DV-X*α* molecular orbital method carried out using a personal computer of Intel CoreTM2 Quad of 2.83 GHz and DDR2-Ram of 4.00 GB and step calculation has been extended in previous work [19,20].

3. Results and discussion

3.1. *Electronic structure*

The atomic distribution in unit cell is displayed in Fig. 1 and composed of Pb$_{14}$Te$_{13}$, Pb$_{13}$SbTe$_{13}$ and Pb$_{13}$BiTe$_{13}$ small clusters. The cluster model of Pb$_{14}$Te$_{13}$, Pb$_{13}$SbTe$_{13}$ and Pb$_{13}$BiTe$_{13}$ one unit cell corresponded to Pb:Te; 1:1, Pb:Bi:Te; 0.75:0.25:1 and Pb:Sb:Te; 0.75:0.25:1 ratios. Total energy level and charge density of PbTe, Pb$_{0.75}$Sb$_{0.25}$Te and Pb$_{0.75}$Bi$_{0.25}$Te are plotted for one unit cell cluster model as shown in Fig. 2. Fig. 2(a) are total energy level of Pb$_{14}$Te$_{13}$, Pb$_{13}$SbTe$_{13}$ and Pb$_{13}$BiTe$_{13}$ cluster models, the solid lines are highest occupied molecular orbital (HOMO) and dot lines are lowest unoccupied molecular orbital (LUMO). The difference in energy between HOMO and LUMO can be used to predict the band gap energy [21]. Electron charge density as distributed of in unit cell was illustrated the Fermi surface at HOMO and LUMO values or frontier orbitals in frontier molecular orbital within the wave numbers; HOMO: W46, LUMO: W836, W886 and W936 for PbTe, HOMO: W622, W703 and W784, LUMO: W836, W886 and W936 for Pb$_{0.75}$Bi$_{0.25}$Te and HOMO: W109 and W161, LUMO: W613, W692 and W771 for Pb$_{0.75}$Sb$_{0.25}$Te. This approximation is valid for spherical Fermi surface that is independent of temperature, as in the free-electron model.

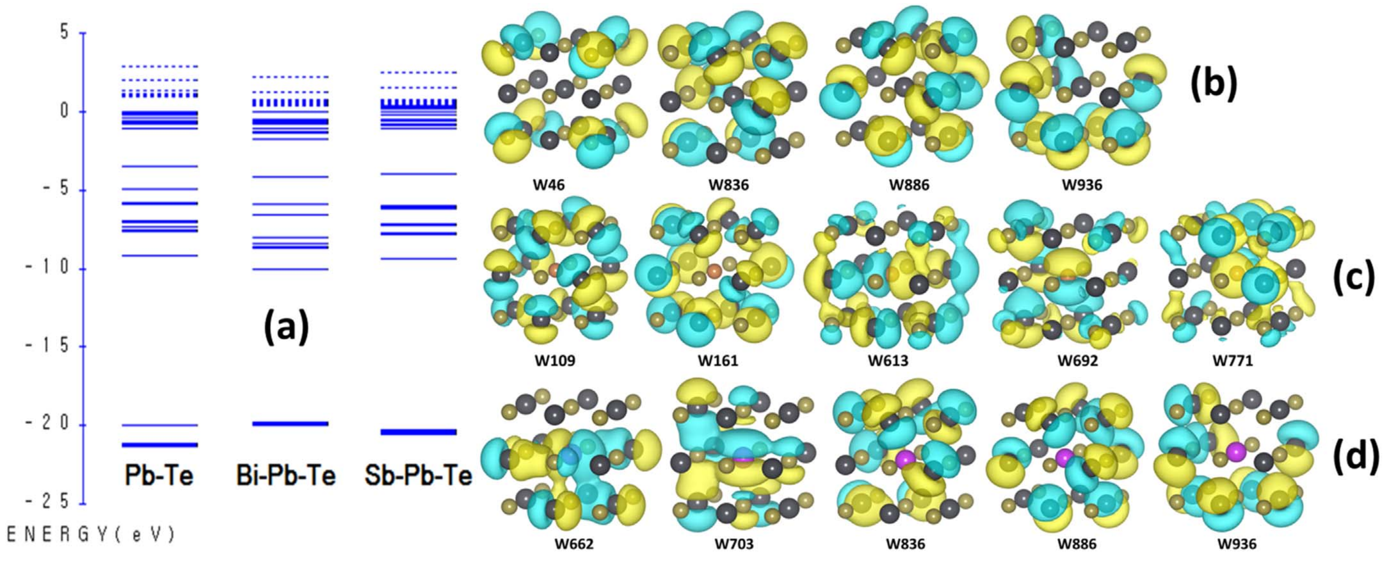

Fig. 2. (a) Total energy level performed for PbTe, Pb$_{0.75}$Bi$_{0.25}$Te and Pb$_{0.75}$Sb$_{0.25}$Te and electron charge density distribution of atomics in unit cell of (b) PbTe, (c) Pb$_{0.75}$Bi$_{0.25}$Te and (d) Pb$_{0.75}$Sb$_{0.25}$Te.

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