First-principles simulation on thermoelectric properties in Bi-Sb System

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Abstract. Thermoelectric properties of bismuth-antimony (Bi-Sb) alloy system were simulated on the basis of first-principles calculation, to discuss the potential for thermoelectric devices. Atomistic model structures of Bi-Sb alloy system were devised in the forms of single-crystal bulk and one-dimensional nanowire under the periodic boundary condition. The cell parameters of the bulk model were simulated with respect to temperature by the quasi-harmonic approximation through phonon calculation, and dependences of the Seebeck coefficient on composition, surface condition, and temperature have been demonstrated by using our original methodology in terms of the electronic state of Bi-Sb alloy system. For the single-crystal bulk Bi-Sb models, a meaningful effect of the composition on the Seebeck coefficient has not been observed, whereas a clear difference in phonon dispersion was confirmed between pure Bi and Sb-substituted Bi, leading to the significant difference in thermal conductivity. We clarified that the surface condition is a key point to control the Seebeck coefficient for the nanowire form.

1. Introduction

Application of thermoelectric devices is spreading over a variety of special environments and conditions in power generation and refrigeration. For the low-temperature environment, bismuth-antimony (Bi-Sb) alloy is one of the most promising thermoelectric materials with highly efficient energy conversion in the temperature range less than 200 K [1-7]. Generally, the thermoelectric performance of materials is evaluated by the dimensionless figure of merit, $ZT = (S^2 σ/k)T$, where $S$ is the Seebeck coefficient, $σ$ is the electric conductivity, and $k$ is the thermal conductivity [8]. Even at low temperature $T$, the dimensionless $ZT$ for some appropriate Bi-Sb alloy systems comes up to an efficient value; for example, $ZT = 0.6$ has been reported for the single-crystal Bi$_{x}$Sb$_{1-x}$ alloy with the compositions of Bi$_{0.85}$Sb$_{0.15}$ and Bi$_{0.91}$Sb$_{0.09}$ [1]. In addition, the development of Bi-Sb alloy-based composite materials have been an important target to add a merit of mechanical point to the unique thermoelectric performance at low temperature. We have succeeded in fabricating a novel composite material based on Bi$_{0.85}$Sb$_{0.15}$ and graphene with good thermoelectric performance [2].

To enhance energy conversion efficiency, it is well known that the miniaturization of thermoelectric materials to low dimension at nanoscale is effective technique [3,9-13]. Rabina et al. has simulated $ZT$ of Bi$_{x}$Sb$_{1-x}$ nanowire numerically based on the conventional procedures [3]. We have
already developed the *ab initio* procedure without any experimental information to evaluate the Seebeck coefficient on the basis of first-principle electronic band structure [9,10,14]. In this study, thermoelectric properties of single-crystal bulk Bi, Sb alloy and Bi, Sb nanowire with small $x$ were simulated by using our original methodology, to discuss the potential for thermoelectric devices.

2. Simulation method

2.1. First-principles calculation

The electronic band structures of the periodic boundary models for bulk and nanowire were calculated using the VASP program package [15,16] based on the density functional theory (DFT) [17]. For the DFT exchange-correlation interaction, the generalized-gradient approximation method was used with the Perdew-Wang (PW91) functional [18,19]. The three-dimensional supercell approximation technique was adopted with ultrasoft pseudopotentials [20]. The cutoff energy for wave functions of electrons with plane-wave expansion was set at 40 Ry (544 eV) for bulk models and 30 Ry (408 eV) for nanowire models.

To investigate the free energy for the geometry optimization of bulk models under the condition of finite temperature, the Helmholtz free energy $F(V,T)$ with phonon free energy at temperature $T$ was derived from the quasi-harmonic approximation (QHA) [21,22]:

$$F(V,T) = E(V,0) + F_p(V,T),$$

where $E(V,0)$ is a total energy of the model structure with the geometry $V$ at 0 K, and

$$F_p(V,T) = k_B T \sum_q \sum_j \ln \left( 2 \sinh \frac{\hbar \omega_j(q)}{2 k_B T} \right).$$

In (2), $k_B$ is the Boltzmann constant, $\hbar$ is equal to Planck’s constant divided by $2\pi$, and $\omega_j(q)$ is a frequency of $j$th phonon band at $q$ point. The first-principles phonon frequencies were calculated by diagonalization of the dynamical matrix with numerical force constants from the $2 \times 2 \times 2$ supercell. The results due to the QHA have been known as to be in good agreement with experimental behaviors for thermal expansion and contraction [23-28].

2.2. Bulk and nanowire models for Bi-Sb systems

Bi and Sb belong to the same group in the periodic table, Group 15, and it is well known that the most stable crystal structure of Bi and Sb is a trigonal structure [4]. We have devised the single-crystal bulk Bi model with the primitive unit cell including two Bi atoms (Bi) and its extended-cell model including eight Bi atoms (Bi). By replacing some Bi atom(s) of the Bi model with Sb, the Bi,Sb model and three kinds of Bi,Sb models were prepared as the compositions of $x = 0.125$ and $x = 0.25$ for Bi, Sb alloy, respectively, as shown in figure 1.

![Figure 1](image)

Figure 1. The 8-atom extended cell of bulk Bi-Sb system: Bi, model where all atoms are Bi, Bi,Sb model where atom A is Sb, Bi,Sb-a model where A and B are Sb, Bi,Sb-b model where A and C are Sb, and Bi,Sb-c model where A and D are Sb. Dashed lines are the unit cell of the 8-atom extended cell, and blue solid lines are the primitive unit cell in the case of pure bulk Bi.
Bi nanowire models were devised by cutting out a fragment with one-dimensional periodic boundary condition from the optimized trigonal bulk Bi. In this paper, the direction of the fragment with the one-dimensional periodic boundary is set to the three-fold rotation axis of trigonal bulk Bi and can be defined as the longitudinal direction of Bi nanowire, as shown in figure 2. Wire diameters of nanowire models, $2R$, were set to about 2 nm, and a periodic boundary condition along the transverse or perpendicular direction to the nanowire in the three-dimensional hexagonal supercell was given by inserting sufficient space between nanowires with a large cell parameter $L_\parallel$, as listed in figure 2. Similarly as bulk models, Bi$_{1-x}$Sb$_x$ nanowire models can be introduced by replacing some Bi atoms with Sb, as explained in detail later. On the condition that sufficient space in the Bi$_{1-x}$Sb$_x$ nanowire model disturbs the interaction between nanowires, the electronic band structure of the Bi$_{1-x}$Sb$_x$ nanowire model can be reduced to be one dimensional, which is dependent on only one reciprocal coordinate, $k$.

2.3. Evaluation of Seebeck coefficient

The Seebeck coefficient $S$ is given by the ratio of electromotive force $\hat{E}$ to temperature gradient $\hat{V}_T$ incorporated implicitly in the Boltzmann transport equation [29,30]. In the stationary state, velocity distribution function of carriers $f$ in semiconductor should be derived from the Boltzmann transport equation by use of relaxation time $\tau$ as

$$f(\epsilon) - f_0(\epsilon) = \tau(\epsilon)\bar{v}(\epsilon)(df_0/d\epsilon)\cdot \left\{ e\hat{E} + [(\epsilon - \epsilon_F)/T]\hat{V}_T \right\},$$

where $e$ is the elementary charge, $\bar{v}$ is carrier velocity, $f_0$ is the Fermi-Dirac distribution, and $\epsilon_F$ is the Fermi energy. Then, $S$ can be evaluated from the information from band structure of the material in terms of integrals including carrier DOS, $g(\epsilon)$, with respect to energy $\epsilon$ by
\[ S = -\left(1/\varepsilon T\right) \left\{ \int g(\varepsilon)\tau(\varepsilon)\omega^2(\varepsilon)(df_0/\varepsilon)d\varepsilon / \int g(\varepsilon)\tau(\varepsilon)v^2(\varepsilon)(df_0/\varepsilon)d\varepsilon \right\} - \varepsilon \varepsilon \right\}, \] (4)

where the interval of the integrals corresponds to the region of carrier occupation [11]. All physical properties in the above equation except for the relaxation time can be easily determined from the first-principles electronic state [9,10,14]. In this paper, \( v(\varepsilon) \) was evaluated from

\[ \tilde{v}_j(\varepsilon_{j,k}) = (1/\hbar) \left[ \frac{\partial \varepsilon_{j,k}}{\partial \vec{k}} \right], \] (5)

where \( \tilde{v}_j(\varepsilon_{j,k}) \) is the carrier velocity for \( j \)th subband at \( \vec{k} \) point with band energy \( \varepsilon_{j,k} \). At the case that the relaxation time is constant regardless of \( \varepsilon \), the effect of \( \tau \) on \( S \) is canceled.

Bi and Sb are typical semimetals. In practical n- or p-doped semimetals, the total number of carriers per unit cell, \( \delta = nV \), must be a few orders less than 1, where \( n \) is the carrier concentration and \( V \) is the volume of structure in the unit cell. Under the condition that a small amount of carrier occupation does not cause significant change in the band structure, \( \delta \) can be given by an appropriate shift of \( \varepsilon \) as

\[ \delta = \pm \left[ 2g(\varepsilon)f_0(\varepsilon)d\varepsilon - N \right] = \pm \left[ 2\sum_{\text{All } k} w_k f_0(\varepsilon_{j,k}) - N \right]. \] (6)

where \( N \) is the total number of valence electrons in the system, \( w_k \) is the k-point weight for \( \vec{k} \), and plus-minus sign means plus for n-doped state or minus for p-doped state [14]. In this study, the Fermi energy \( \varepsilon \) was determined according to (6) for each condition, and then the value of \( S \) was evaluated by using (4) under the condition that the relaxation time is constant. Practically, (4) can be rewritten as

\[ S = -\left(1/\varepsilon T\right) \left\{ \left[ \sum_j \sum_k w_k v(\varepsilon_{j,k})e_j \frac{df_0(\varepsilon_{j,k})}{d\varepsilon} / \left[ \sum_j \sum_k w_k v(\varepsilon_{j,k}) \frac{df_0(\varepsilon_{j,k})}{d\varepsilon} \right] - \varepsilon \right\}. \] (7)

The sampling for \( w_k \) is performed using the three-dimensional Gauss-Legendre quadrature [31] with 29 \( \times 29 \times 29 \) \( \vec{k} \) points for bulk Bi, Sb models and the Newton-Cotes formula [32] with 21 \( k \) points for Bi, Sb nanowire models.

3. Results and discussion

3.1. Optimized structure of Bi, Sb models

In the regular first-principles calculation, lattice constants of the optimized structure of Bi, model were obtained as \( a = 4.767 \) Å and \( \alpha = 57.7^\circ \), under the Monkhorst-Pack 6 \( \times 6 \times 6 \) \( \vec{k} \) point set. These values are close to the measured values, \( a = 4.746 \) Å and \( \alpha = 57.2^\circ \) [4], so we judged that our calculation level is reasonable for the simulation in this paper. Each Bi atom is bonding to six neighboring Bi atoms, and its six Bi–Bi bonds are classified into three short bonds (3.138 Å) and three long bonds (3.502 Å). By using the QHA, the lattice constant a at 100 K was obtained as 4.772 Å. The calculated linear coefficient of thermal expansion, 10.5 \( \times \) 10\(^{-6}\) K\(^{-1}\), has the same order as the measured value at room temperature, 13.4 \( \times \) 10\(^{-6}\) K\(^{-1}\) [33].

For the extended-cell models of single-crystal bulk Bi, Sb, the lattice constants of each optimized structure are tabulated in table 1. The result of optimized structure of Bi, model is not completely identical with that of Bi, model owing to difference of the calculation level such as the fast-Fourier-transform grids, but the lattice constants are also close to the measured values for bulk Bi. In the Sb-
substituted models, six Sb–Bi and Sb–Sb bonds for each Sb atom are also classified three short bonds and three long bonds as shown in table 2, and significant change of internal coordinates for Sb atoms

Table 1. Cell parameters of the 8-atom extended-cell models.

| Model   | \(a' (\text{Å})\) | \(\alpha' (\text{deg})\) |
|---------|-------------------|--------------------------|
| Bi,     | 6.614 (\(a = 4.758 \text{ Å}\)) | 88.0 (\(\alpha = 57.7^{\circ}\)) |
| Bi:Sb   | 6.590             | 87.8                     |
| Bi:Sb-a | 6.548; 6.588      | 87.6; 88.1               |
| Bi:Sb-b | 6.555; 6.556      | 87.9; 87.9               |
| Bi:Sb-c | 6.565             | 87.7                     |

Table 2. Bond lengths of the 8-atom extended-cell models (Å).

| Model   | Short Bi–Bi | Long Bi–Bi | Short Sb–Bi | Long Sb–Bi | Sb–Sb |
|---------|-------------|------------|-------------|------------|-------|
| Bi,     | 3.154       | 3.475      |             |            |       |
| Bi:Sb   | 3.144–3.152 | 3.456–3.459| 3.057       | 3.553      | 2.923 |
| Bi:Sb-a | 3.129–3.150 | 3.420–3.470| 3.070       | 3.504–3.682|       |
| Bi:Sb-b | 3.145–3.151 | 3.424–3.425| 3.059–3.066 | 3.510–3.514|       |
| Bi:Sb-c | 3.147       | 3.441      | 3.051       | 3.533      |       |

owing to its smaller atomic radius makes the short Sb–Bi bonds shorter and the long Sb–Bi bonds longer than the short and long Bi–Bi bonds, respectively, in bulk Bi. Therefore, it is clearly found that the long Sb–Bi bonds in bulk Bi:Sb are effected by much weaker interaction than the long Bi–Bi bonds in bulk Bi, and the weaker interaction would affect the phonon structure in Bi:Sb alloy with small \(x\).

Figure 3 shows the phonon dispersion diagrams for the single-crystal Bi, and Bi:Sb models. The difference in frequencies between Bi, and Bi:Sb is mainly due to mass of Sb atom, but some effects by the peculiar Sb–Bi interaction should be involved in the phonon structure. The clear difference in phonon dispersion leads to the significant difference in thermal conductivity [11,29].

3.2. Seebeck coefficient of single-crystal bulk Bi:Sb models

The electronic band diagrams near the Fermi energy for the extended-cell models of single-crystal bulk Bi:Sb are shown in figure 4. For all models, carriers are mainly located in the vicinity of Z point in the Brilouin zone of the extended unit cell. The band diagrams closely resembles one another, owing to similarity of electronic state in Bi and Sb as the members of Group 15.

![Figure 3](image1)  ![Figure 3](image2)

**Figure 3.** Phonon dispersion diagrams of the Bi, and Bi:Sb models. Paths in the reciprocal lattice space are referred to figure 4.
Figure 4. Brillouin zone of the 8-atom extended cell and electronic band diagrams of the Bi$_8$, Bi$_7$Sb, and Bi$_6$Sb$_2$-c models. Zero energy is defined at the Fermi level.

Temperature and doped-state dependences of the calculated Seebeck coefficients for the extended-cell models of bulk Bi$_x$Sb$_{1-x}$ are shown in figure 5. The effect of volume expansion owing to temperature increase is quite small, so the geometries of model structures listed in tables 1 and 2 were used for the Seebeck coefficient simulation. A meaningful effect by the composition change on the Seebeck coefficient has not been observed in our simulation. As common characteristics in the Bi$_8$ and Sb-substituted models from 100 to 200 K, absolute value of the Seebeck coefficient for the intrinsic semi-metal state is small, and the Seebeck coefficients for n- and p-doped states respectively show negative and positive values, similarly as the cases for semiconducting materials [9,10,29]. Practically, the calculated Seebeck coefficients are quantitatively very sensitive to the k-point sampling, and the quantity of them is smaller than that of measurement values for bulk Bi$_x$Sb$_{1-x}$, −110 ± 10 µV K$^{-1}$, with
Figure 5. Temperature and doped-state dependences of the Seebeck coefficients for the Bi₈, Bi₇Sb, Bi₆Sb₂-a, Bi₆Sb₂-b, and Bi₆Sb₂-c models. Circle (black), square (red), and triangle (blue) plots respectively correspond to the intrinsic state, n- and p-doped state with 10² cm⁻³ carrier concentration.

Figure 6. Temperature and doped-state dependences of the Seebeck coefficients for the Bi₁₈, Bi₁₁₀, and Bi₁₂₂ nanowire models. Circle (black), square (red), and triangle (blue) plots respectively correspond to the intrinsic state, n- and p-doped state with 10² cm⁻³ carrier concentration.
$x = 0.05 - 0.12$ [5,6]. The reason of underestimate in simulation would be due to the single-crystal geometries of the Bi and Sb-substituted models and inevitable drops in electronic band energies for subbands upper than the Fermi level in DFT calculation.

3.3. Seebeck coefficient of Bi$_{1-x}$Sb$_x$ nanowire models

Figure 6 shows temperature and doped-state dependences of the calculated Seebeck coefficients for the Bi nanowire models. In our simulation, the nanowire model with uneven surface such as Bi$_8$ has positive Seebeck coefficients. On the contrary, as the surface condition gets smooth like the Bi$_{122}$ nanowire model, the Seebeck coefficients tend to show negative values. Accordingly, the thermoelectric properties should be strongly affected by the surface condition of Bi. For the application to thermoelectric devices, the surface condition of device materials should be taken into careful consideration.

Bi$_{1-x}$Sb$_x$ alloys have negative Seebeck coefficient in the measurement [5,6] as mentioned above, so we tried to simulate the Seebeck coefficient in Bi$_{1-x}$Sb$_x$ nanowires, based on the Bi$_{122}$ model. We have introduced four models of Bi$_{104}$Sb$_{18}$ nanowire in the case of $x = 0.15$ by replacing eighteen Bi atoms with Sb, as shown in figure 7(a), with keeping the three-fold rotation symmetry. The calculated Seebeck coefficients for the Bi$_{1-x}$Sb$_x$ nanowire models are shown in figure 7(b) and (c). Similarly as the simulation in the bulk models, a meaningful effect of the atom replacement on the Seebeck coefficient has not been observed. Among these models, the Bi$_{104}$Sb$_{18}$-D model, where some surface Bi atoms have been replaced with Sb, has a relatively large quantity of negative Seebeck coefficient in the range from 100 to 200 K.

![Figure 7](image-url)

**Figure 7.** The Seebeck coefficients for the Bi$_{1-x}$Sb$_x$ nanowire models: (a) top views of the unit cell of Bi$_{104}$Sb$_{18}$-A, Bi$_{104}$Sb$_{18}$-B, Bi$_{104}$Sb$_{18}$-C, and Bi$_{104}$Sb$_{18}$-D nanowire models, where 9 yellow atoms are Sb, and other 9 Sb atoms are located point-symmetrically on the back side; (b) temperature dependence of the Seebeck coefficients for them; (c) temperature and doped-state dependences of the Seebeck coefficients for the Bi$_{104}$Sb$_{18}$-D nanowire model.
4. Summary
We simulated thermoelectric properties of Bi-Sb alloy system on the basis of first-principles calculation. Atomistic model structures of Bi-Sb alloy were devised in the forms of single-crystal bulk \((x = 0, 0.125, \text{and } 0.25)\) and one-dimensional nanowire \((x = 0 \text{ and } 0.15)\) under the periodic boundary condition. The cell parameters of the bulk model were simulated with respect to temperature by the QHA \([21,22]\) through phonon calculation, and dependences of the Seebeck coefficient on composition, surface condition, and temperature have been demonstrated by using our original methodology \([9,10,14]\) in terms of the electronic state of Bi-Sb alloy models. For the single-crystal bulk Bi-Sb models, a meaningful effect of the composition on the Seebeck coefficient has not been observed, whereas a clear difference in phonon dispersion was confirmed between pure Bi and Sb-substituted Bi, leading to the significant difference in thermal conductivity \([11,29]\). Furthermore, we clarified that the surface condition is a key point to control the Seebeck coefficient for the nanowire form. For the application to thermoelectric devices, the surface condition of device materials should be taken into careful consideration.

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