Thermoelectric enhanced ZT regime calculated by Fermi integral method

Hirofumi Kakemoto

1Clean Energy Research Center, University of Yamanashi, 4-3-11, Takeda, Kofu, Yamanashi 400-8511, Japan

We report about dimensionless figure of merit (ZT) calculated by using Fermi integral method (compared with Bi$_2$Te$_3$, CoSb$_3$, SrTiO$_3$) for thermoelectric (TE) material’s design and its module application. Particularly, TE properties: electrical conductivity (small polaron: $\sigma(m^*)$), Seebeck coefficient ($S$), thermal conductivity ($\kappa$), and ZT were calculated by using reduced energy ($\zeta=E/k_BT$), as the functions of $T$, and effective mass ($m^*/m$). Enhancement of ZT was investigated by the contour plots of $T$, and $m^*/m$ versus $\zeta$.

(Dated: 23 January 2018)

Keywords: thermoelectric properties, Fermi integral method, dimensionless figure of merit, effective mass

1. Introduction

Nowadays, renewed and recycled energies from sun light heat or waste heat are demanded to realize the sustainable society. Thermoelectric (TE) material is possible to generate thermal electromotive force (EMF) from several waste heats. Recently, TE material, such as metallic: Bi$_2$Te$_3$,[1] CoSb$_3$ (p-type),[2] SiGe (n-type), and oxide: Na$_2$CoO$_2$ (p-type), and SrTiO$_3$[3] (n-type) show high TE properties. Particularly, more high-performance n-type TE oxide material is demanded to develop for realizing high performance $p$-$n$ pairs of TE module use.

To design TE material, 1) Fermi integral [4-9] or Boltzmann equation by using band structure ($E_F$ and $E_F$ etc) [10], 2) Heikes formula [11], and 3) space charge [12] theories are reported. Electrical conductivity ($\sigma$), Seebeck coefficient ($S$), and thermal conductivity ($\kappa$) calculation are able to be expressed by carrier density ($N$), finally expressed by Fermi integral ($F_i$), hence design for enhancement of TE properties is not simple. Enhancement of dimensionless figure of merit (ZT) is reported about i) small polaron or ii) rattling, with increasing $S$ and decreasing $\kappa$.

Hicks and Dresselhaus presented the low dimensional density of state model and $B$-parameter for increasing ZT by using Fermi integral method. [1]

Mahan also reported about Z calculation. The highest $Z$ is calculated from near band edge, and $Z$ is close to $B$-parameter. [7,8]

In addition, small polaron conductivity ($\sigma(m^*)$) and its band structure model are reported for many TE materials. [11] Here, ZT is defined as $S^2\sigma T(\kappa/\kappa_{ph})$, and ZT can be modified as $S^2/[L+\kappa_{ph}/\sigma(m^*)T]$ by using $\sigma(m^*)$. $\sigma(m^*)$ is increased with increasing $\zeta$. Therefore, $\sigma(m^*)$ gives a direction for enhancement of ZT.

We report about enhancement of ZT about TE material calculated by using Fermi integral method as the functions of reduced energy ($\zeta$) and effective mass ($m^*$).

2. Calculation

$\sigma$, $S$ and $\kappa$ ($=L\sigma T$) were calculated using eq.(1)-(4) by using Fermi integral method. Fermi integral ($F(\zeta)$) is defined as $\int_{-\infty}^{\infty} d\zeta \zeta [\exp(-\zeta)\zeta + 1]$, where $\zeta \equiv -0.05$ for $\sigma$ and $S$, and $\tau$ are $E_F/k_BT$ ($T=300K\sim1000K$) and $\tau_{e^{-1/2}}$, respectively, and Fermi integral can be approximated as $F(\zeta) = \Gamma(r+1)e^{\zeta}\Sigma(-1)/e^{\zeta (j+1)}$, while $\zeta < -0.05$ for $\sigma$, $S$, and $n>-1$.[9]

$$N = (1/2\pi^2)(2k_BT/h^2)^3/2 m^{3/2} F_{1/2}(\zeta),$$

$$\sigma(m^*) = (1/2\pi^2)(2k_BT/h^2)^3/2 m^{3/2} F_{1/2}(\zeta) q \mu,$$

$$S = -(k_B/q) \{d(\zeta^2)\zeta - q \zeta \},$$

$$\kappa = 3F_{3/2}(\zeta)/3F_{1/2}(\zeta).$$

$$L = (2k_B^2 3q m^{1/3} \mu)(7F_{2+1/2}/2F_{1/2} - 25F_{2+1/2}/6F_{1/2}).$$

Dimensionless figure of merit (ZT) is expressed as $ZT = S^2\sigma T(\kappa/\kappa_{ph}) = S^2/[L+\kappa_{ph}/\sigma(m^*)T]$. (5)
3. Results and discussion

Figure 1 (a) shows reported $Z$ for $n$-type Bi$_2$Te$_3$, $n$-type Si$_{1-x}$Ge$_x$, $p$-type CoSb$_3$, and $n$-type SrTiO$_3$ (dots and solid lines), and $ZT$ (solid lines: 0.1, 1 and 2) as a function of $T$. Bi$_2$Te$_3$ reported up to $ZT$=1 at 400K, CoSb$_3$ takes $ZT$=0.1 at 600K, and SrTiO$_3$ shows $ZT$=1 at around 1200K, and $ZT$=0.8 at 1000K. [13]

The classical $S$, $\sigma$ versus logarithmic carrier density ($\log N$) (Ioffe phenomena) is plotted in Fig.1 (b). $\sigma$ is possible to represent the enhancement by increased $m^*$: small polaron effect, but power factor ($S^2\sigma$) term of $ZT$ cannot be increased from the simple relationship between $S$ and $\sigma(m^*)$ with $m^*/m=1$.

The mobility ($\mu$) of TE materials versus $m^*/m$ is plotted in Fig.1 (c). Small polaron is reported in $\mu$ of Bi$_2$Te$_3$: 1200 cm$^2$/Vs at 300K, CoSb$_3$: 310 cm$^2$/Vs at 600K, and SrTiO$_3$: 0.5 cm$^2$/Vs at 1000K. [3]

![Figure 1](image)

**Figure 1** (a) $Z$ of Bi$_2$Te$_3$: 1, CoSb$_3$: 2, Si$_{1-x}$Ge$_x$: 3, and SrTiO$_3$: 4 (dots and solid lines), and $ZT$ (solid lines) versus $T$, (b) $S$, $\sigma$ versus $\log N$ plot, (c) mobility ($\mu$) versus effective mass: $m^*/m$ (dots), and extrapolated line (solid and dashed lines) [14].

With comparing these experimental values, we try to reproduce theoretically these values by using Fermi integral method. The calculating conditions for $F_i$: $m^*/m$, $\xi$, and $T$ are listed in Table I. In calculation, $E_F$ was selected from $-66.4$ meV to 0.01 eV, at $T=300$K–1000K, and was input to $\xi=\epsilon_F/k_BT$ in eq.(1)–(4).

![Figure 2](image)

**Figure 2** Results of (a) $\sigma$, (b) $|S|$, and (c) $L$ for $n$-type Bi$_2$Te$_3$ (condition I), $p$-type CoSb$_3$ (condition II), and $n$-type SrTiO$_3$ (condition III) calculated by using Fermi integral method introducing $m^*$ in Table I.

From Fig.2, $ZT$ is reproduced to be 1–2, $\sim 0.1$, 0.8–1.0 using eq.(5) for Bi$_2$Te$_3$, CoSb$_3$, and SrTiO$_3$ at $\xi=0.05\sim0.2$.

The theoretical calculation for Bi$_2$Te$_3$ by using Fermi integral method was reported as $ZT=0.52$ at 300K (experimental data: $ZT=0.67$). Our result for Bi$_2$Te$_3$ in Fig.2 is close to above values.[1] The results of experimental data for CoSb$_3$ was reported as $ZT=0.1$ at 600K[2], and theoretical calculation by using Boltzmann eq. was also carried out.[10] Our result for CoSb$_3$ is consisted with above value.

The experimental study for SrTiO$_3$ was reported as $ZT=0.1$ at 1000K.[3] Our result for SrTiO$_3$ is consisted with above value.

| Material   | $E_F$, $E_C$, $E_V$, $E_E$ (eV) | type | $m^*/m$ | $\xi$ | $T$(K) | Condition | Ref. |
|------------|-------------------------------|------|---------|-------|--------|-----------|------|
| PbTe       |                               |      | 0.05    | -5–5  | 500K   | II        | [1]  |
| Bi$_2$Te$_3$ | 0.05, $-0.05$, 0.01, 0.13    | $n$  | 0.43    | $-5$  | 350–400K | I         | [1]  |
| CoSb$_3$   | 0.1, $-0.1$, ± 66.64 meV, 0.63 | $p$  | 0.15    | $-5$  | 550–600K | II        | [2]  |
| Si$_{1-x}$Ge$_x$ | $n$ | 1.06 |       |       | 1100K  |           |      |
| SrTiO$_3$  | 1.5, $-1.5$, $-0$, 3         | $n$  | 5.00    | $-5$  | 950–1000K| III       | [3]  |
In Fig.

3 shows contour plots of ZT, T, and m*/m versus ζ in the range from −5 to 3. In Figs. 3(a, b), the results of Bi2Te3, from condition I: (by using eq. (3-5), n-type, S = −60μV/K, σ = 1.1x10⁴ S/cm, κ = 1.5 W/mK, at 0.42 < m*/m < 0.44, 350 < T < 400K, and ζ = 0.2) are estimated, and ZT is possible to be enhanced up to 1.1. In Figs. 3(c, d), the results of CoSb3, from condition II: (by using eq. (3-5), p-type, S = 192 μV/K, σ = 250 S/cm, κ = 4.8 W/mK, at 0.14 < m*/m < 0.16, 550 < T < 600K, and ζ = −0.05), ZT is also slightly enhanced up to 0.1. In Figs. 3(e, f), the results of SrTiO3, condition III: (by using eq. (3-5), S = 1243 μV/K, σ = 67 S/cm, κ = 10 W/mK, at 4.9 < m*/m < 5.1, 950 < T < 1000K, and ζ = 0.05). ZT is also estimated to be 0.9. From calculation results, ZT can be reproduced by the enhancement by small polaron conductivity (σ(m*)).

4. Conclusion

In this report, electrical conductivity affected by small polaron: σ(m*) was introduced to calculate the dimensionless figure of merit (ZT) for thermoelectric materials: n-type Bi2Te3, p-type CoSb3, and n-type SrTiO3, and Seebeck coefficient (S), thermal conductivity (κ), and ZT were carried out the calculation by using Fermi integral method.

Enhanced ZT were estimated its contour plots of T and m*/m versus reduced energy (ζ†).

In future study, the investigation of n-type Nb related TE oxide will be carried out using Fermi integral method.

Acknowledgment

This work was partly supported by Japan Society for the Promotion of Science (JSPS) KAKENHI Grant-in-Aid for Scientific Research(C) Number JP25410238.

*Present address: 1-15-11, Sakura-cho, Tsuchiura, Ibaraki, 300-0037, Japan, Techno Pro R&D company (Tsukuba branch), Techno Pro Inc.

e-mail: hakakemoto@yamanashi.ac.jp

Reference

[1] L. D. Hicks, and M. S. Dresselhaus, Phys. Rev. B 47 12727 (1993).
[2] J.W. Sharp, E.C. Jones, R.K. Williams, P.M. Martin, and B.C. Sales, J. Appl. Phys. 78 1013 (1995).
[3] S. Ohta, T. Nomura, H. Ohta, and, K. Koumoto, J. Appl. Phys. 97 034106 (2005); S. Ohta, T. Nomura, H. Ohta, M. Hirano, H. Hosono, and, K. Koumoto, Appl. Phys. Lett. 87, 092108 (2005).
[4] R. P. Chasmar and R. Stratton: J. Electron. Control 7 52. (1959).
[5] J. Callaway, Phys. Rev. 113 1046 (1959).
[6] G. Leibfried and E. Schomann: Nachr. Akad. Wiss. Gottingen Math. Physik, K1 (1954) 4, 71.
[7] G. D. Mahan, J. Appl. Phys. 65 1578 (1989).
[8] G. D. Mahan, and J.O. Sofo, Proc. Natl. Acad. Sci. USA 93 7436 (1996).
[9] L. D. Cloutman, Astrophys. J. Suppl. Ser. 71, 677 (1989).
[10] G. K. H. Madsen and D. J. Singh, arXiv:cond-mat/0602203v1 [cond-mat.mtrl-sci] 8 Feb 2006.
[11] V. E. Gasumyants et al., Physica C 248, 255 (1995); H. Kakemoto, arXiv:cond-mat/1712.09840 [cond-mat.mtrl-sci] 28 Dec 2017.
[12] Mahan, J. Electronic Materials, 44, 431, (2015).
[13] http://www.asem.kyushu-u.ac.jp/~ohtaki/archives/2003/research/te/Z_summary.GIF
[14] Theoretical μ affected by small polaron (μ = σ(m*)/Ne, solid lines) is represented as μ = (2g z/3m*)(r + 3/2)F_{r+1/2}(ζ)/F_{r+3/2}(ζ), as the functions of m* and ζ, and can be fitted as the extrapolated lines.