RULE OF MIXTURE FOR COMPOSITE THERMOELECTRICS

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1 Introduction

Generally, thermoelectric performance is evaluated by the figure of merit $Z$ ($= S^2 \rho / \kappa^2$) or the dimensionless figure of merit, $ZT$, where $S$ is the Seebeck coefficient, $\rho$ is the electrical resistivity, $\kappa$ is the thermal conductivity and $T$ is the absolute temperature. For convenience, the power factor $P$ ($= S^2 \rho / \kappa$) is also used as a criterion to evaluate thermoelectric performance. Thus, to improve thermoelectric performance, the Seebeck coefficient $S$ should be increased, meanwhile, the electrical resistivity $\rho$ and the thermal conductivity $\kappa$ should be decreased. In recent years, the composite method has been frequently used to enhance the performance of thermoelectrics and thermoelectric devices. The improvement of thermoelectric performance by adding metal powder, such as Au and Ag to oxide thermoelectrics, has been tried [1-5]. In these works, the electrical resistivity was decreased by adding metal powder. Indeed, the Seebeck coefficient showed an increase trend in some works [1,2,4]. It therefore led to enhance the power factor. In our previous work, it was revealed that the power factor had the biggest value when the amount of adding Cu into Cu/TiO$_2$ composite was 12%, at which the transition from semiconductor to metal appeared [6]. On the other hand, the rule of mixture (ROMs) and effective medium theory (GET) have been commonly used to evaluate and discuss the electrical conductivity/resistivity and the thermal conductivity of laminated/sandwich-structured composites and particle composites [7-10]. Also, the effectiveness and usefulness of these theories have been confirmed by a tremendous amount of investigation. Therefore, the ROMs have been applied to the electrical conductivity/resistivity and the thermal conductivity of sandwich-structured composite thermoelectrics [11-14]. We have used the GEM to evaluate the electrical resistivity and the thermal conductivity of Cu/TiO$_2$ particle composites [6].

Further, the ROMs for the Seebeck coefficient of the sandwich-structured metal/semiconductor/metal composites were proposed [12-15]. In those studies, it was revealed that the power factor can be enhanced by sandwich structures, a series structure of metal/semiconductor/metal. The ROMs are simple and practicable to explain thermoelectric properties of the series composite thermoelectrics. However, the ROMs were only given as a function of the thickness of the sandwich-structured composites. Besides, no general ROMs for the Seebeck coefficient of the laminated/sandwich and the particle composite thermoelectrics have been given.

In the present work, the ROMs and GET were applied to the electrical resistivity and thermal conductivity of composite thermoelectrics with the series/parallel and powder-distributed structures respectively. The general ROMs for the Seebeck coefficient of the series and parallel composite models were deduced. We also tried to apply the GET to discuss the Seebeck coefficient of the particle composite thermoelectrics with random distribution.

2 ROMs for laminated composites

2.1 ROMs for the electrical resistivity and thermal conductivity

The series and parallel models for laminated composites are shown in Fig.1. It was assumed that the scattering of the carriers and phonons, and reactions never occur at the boundaries between
material A and B. In Fig.1,  \( \sigma = 1/\rho \, [\Omega \cdot m^{-1}] \), \( \kappa \, [W/(m \cdot K)] \) and \( S \, [V/(K \cdot m)] \) denote the electrical conductivity, the thermal conductivity and the Seebeck coefficient, respectively. Subscript A, B, E correspond to the material A, B and the composite, respectively. If electrical current \( J \) occurs along axis \( x \) in the models, the ROMs for the electrical conductivity of the series and parallel models can be presented as follows [7-10].

**Series model:**
\[
\sigma_E = \frac{1 - \phi_B}{\sigma_A} + \frac{\phi_B}{\sigma_B}
\]  

**Parallel model:**
\[
\sigma_E = (1 - \phi_B)\sigma_A + \phi_B\sigma_B
\]

where \( \phi_B \) denotes volume fraction of material B. If heat flow \( Q \) occurs along axis \( x \) in the models, the ROMs of the thermal conductivity for the series and parallel models can be given by replacing \( \kappa \) with \( \sigma \) in Eqs. 1 and 2, respectively.

### 2.2 ROMs for thermoelectric force

Schematic diagrams of thermoelectric force and their equivalent circuits of the series and parallel models are shown in Fig.2. \( \Delta H \), \( \Delta L \), \( \Delta T \) and \( \Delta V \) express width, length, temperature difference and thermoelectric force, respectively. For convenience, the thicknesses of the models was set to 1.

In the series model (Fig.2(a) and (b)), the total thermoelectric force of the composite (\( \Delta V_E = \Delta V_A + \Delta V_B \), i.e. \( S_B \Delta T_E = S_A \Delta T_A + S_B \Delta T_B \)) can be given as follows.

\[
S_E = S_A \frac{\Delta T_A}{\Delta T_A + \Delta T_B} + S_B \frac{\Delta T_B}{\Delta T_A + \Delta T_B}
\]

(3)

It is assumed that the heat flow \( Q \) along axis \( x \) is static, the temperature difference is estimated as \( \Delta T = Q \Delta H/\kappa, \Delta T_A/(\Delta T_A + \Delta T_B) \) and \( \Delta T_B/(\Delta T_A + \Delta T_B) \) in Eq.3 can be expressed as follows.

\[
\frac{\Delta T_A}{\Delta T_A + \Delta T_B} = \frac{\kappa_B}{\kappa_B + \frac{\kappa_A}{\kappa_A} + \frac{\kappa_A}{\kappa_B}} = \frac{\kappa_B}{\kappa_B + \frac{\kappa_A}{\kappa_A} + \frac{\kappa_A}{\kappa_B}}
\]

(4)

\[
\frac{\Delta T_B}{\Delta T_A + \Delta T_B} = \frac{\kappa_A}{\kappa_A + \frac{\kappa_B}{\kappa_B} + \frac{\kappa_A}{\kappa_B}} = \frac{\kappa_A}{\kappa_A + \frac{\kappa_B}{\kappa_B} + \frac{\kappa_A}{\kappa_B}}
\]

(5)

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**Fig.1** Models for laminated composite thermoelectrics.

**Fig.2** Schematic diagrams of generation of thermoelectric force in laminated composite thermoelectrics.
according to \( \Delta H_A / \Delta H_B = (1-\phi_B) / \phi_B \), the ROM equation for the total thermoelectric force of the series model by substituting Eqs. 4, 5 into Eq. 3 is expressed as

\[
S_E = \frac{k_B}{k_B + \left(\frac{\phi_B}{\rho_B}\right)k_A} S_A + \frac{k_A}{k_A + \left(\frac{\phi_A}{\rho_A}\right)k_B} S_B \quad (6)
\]

The ROM of Eq.6 is more general comparing the equations in references [11-14], also the results are consist with references [11-14] as mentioned later. On the other hand, in the parallel model (Fig.2(c) and (d)), assumed that \( \Delta T_E = \Delta T_A = \Delta T_B \) and \( \Delta V_A > \Delta V_B \) (i.e. \( S_A > S_B \)), a circulation current \( I_a \) will form between material A and B due to the difference of thermoelectric force, and \( I_a = (\Delta V_A - \Delta V_B) / (R_A + R_B) \), where \( R_A \) and \( R_B \) are the electrical resistance of the two materials along x axis respectively. The total thermoelectric force of the parallel model can be given as follows.

\[
\Delta V_E = \Delta V_A - I_a R_A = \Delta V_A - R_A \frac{\Delta V_A - \Delta V_B}{R_A + R_B} \quad (7)
\]

then

\[
S_E \Delta T_E = S_A \Delta T_A - \frac{\rho_A}{R_A + R_B} (S_A \Delta T_A - S_B \Delta T_B) \quad (8)
\]

according to \( \Delta T_B = \Delta T_A = \Delta T_B \), Eq.8 can be rewritten as

\[
S_E = S_A - \frac{R_A}{R_A + R_B} (S_A - S_B) \quad (9)
\]

then

\[
\frac{R_A}{R_A + R_B} = \frac{\rho_A \rho_B}{\rho_A \rho_B + \rho_B \rho_B} = \frac{\rho_A}{\rho_A + \rho_B} \left(\frac{1}{\phi_B} - 1\right) \rho_B \quad (10)
\]

by substituting Eq.10 into 9, the ROM for the total thermoelectric force of the parallel model is given as

\[
S_E = \frac{\left(\frac{1}{\phi_B} - 1\right) \rho_B}{\rho_A + \left(\frac{1}{\phi_B} - 1\right) \rho_B} S_A + \frac{\rho_A}{\rho_A + \left(\frac{1}{\phi_B} - 1\right) \rho_B} S_B \quad (11)
\]

Effective medium theory has been used to calculate the electrical and thermal conductivities for particle composites with random distribution as shown in Fig.3 and consists with the experimental results [7-10]. Especially, the general effective medium equation (GEM) is used to apply to the electrical and thermal conductivities of particle composites as Eq.12. In our previous work, the GEM was used to discuss the electrical resistivity and the thermal conductivity of Cu/TiO\(_2\) composite thermoelectrics, and the results from GEM are consist with those from the experiment and the analysis by FEM [6, 11]. The GEM of the thermal conductivity can be obtained by replacing \( \kappa \) with \( \rho^{-1} \) in Eq. 12.

\[
\frac{(1-\phi_C)\left(\rho_{\kappa A}^{-1}\right)^{-1} - (\rho_{\kappa A}^{-1})^{1/2}}{(\rho_{\kappa A}^{-1})^{1/2} + \{1-\phi_C\}/\phi_C \{\rho_{\kappa A}^{-1}\}^{1/2}} + \frac{\phi_C\left(\rho_{\kappa B}^{-1}\right)^{-1} - (\rho_{\kappa B}^{-1})^{1/2}}{(\rho_{\kappa B}^{-1})^{1/2} + \{1-\phi_C\}/\phi_C \{\rho_{\kappa B}^{-1}\}^{1/2}} = 0
\]

where \( \phi_C \) is the critical volume fraction, which takes account an effective percolation threshold. The value of \( t \) determining the effective percolation slope, is usually located between 1 and 3. We know that the thermoelectric effect originates in transport events caused by thermal and electrical flows under a temperature potential. That is, the thermoelectric events are similar physical ones with the thermal or electrical transport. Therefore, we propose to apply the GEM to discuss thermoelectric

![Fig. 3 Random model for particle composite thermoelectrics.](image-url)

force by replacing \( \rho^{-1} \) in Eq.12 with the Seebeck coefficient \( S \) as follows.

3 Effective medium equation of random model for particle composites
\[
\frac{(1-\phi_c)(S_c)^{\phi_c}-(S_p)^{\phi_p}}{(S_c)^{\phi_c}+(1-\phi_c)/(\phi_d)(S_p)^{\phi_p}} + \\
\phi_d((S_p)^{\phi_d}-(S_d)^{\phi_d})/(S_d)^{\phi_d}+(1-\phi_c)/(\phi_d)(S_d)^{\phi_d} = 0
\]

Certainly, \( \phi_c \) and \( t \) should be deferent values for the thermal conductivity, electrical resistivity and the Seebeck coefficient.

Taking the account of the influence extent of the added phase in a wide range, the critical volume fraction \( \phi_c \) was set 0.3, 0.5 or 0.7 in the following calculation. Also, the value of \( t \) was given 1 or 2.

### 4 Thermoelectric properties of the composites by ROMs and GEMs

In this work, thermoelectric properties, including electrical resistivity, the thermal conductivity and the Seebeck coefficient of Cu/Bi and Ni/Bi series composites, parallel composites and particle composites, were calculated by the ROMs and GEMs as mentioned above. In the case of the series composite, the thermoelectric properties were also compared with those from reference [12]. Thermoelectric properties of the source materials for calculation are listed in Table 1.

In the case of particle composites, substituting the thermoelectric parameters of the source materials into Eqs. 12 and 13, and the thermoelectric properties of the composites were calculated by Newton-Raphson method.

<table>
<thead>
<tr>
<th>Property</th>
<th>Bi</th>
<th>Cu</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \rho ) (( \mu \Omega m ))</td>
<td>1.222</td>
<td>0.0171</td>
<td>0.0720</td>
</tr>
<tr>
<td>( S ) (( \mu \text{VK}^{-1} ))</td>
<td>-70</td>
<td>1.9</td>
<td>-15</td>
</tr>
<tr>
<td>( \kappa ) (( \text{Wm}^{-1}\text{K}^{-1} ))</td>
<td>7.9</td>
<td>401</td>
<td>91</td>
</tr>
<tr>
<td>( P ) (( \text{mWm}^{-1}\text{K}^{-1} ))</td>
<td>4.01</td>
<td>0.21</td>
<td>3.13</td>
</tr>
<tr>
<td>( ZT \times 10^3 )</td>
<td>151</td>
<td>0.157</td>
<td>10.2</td>
</tr>
</tbody>
</table>

#### 4.1 Calculations of the power factor of the composites

The electrical resistivity of Cu/Bi and Ni/Bi composite thermoelectrics by the ROMs and GEM are shown in Fig.4 and Fig.5, respectively. On the whole, the resultant electrical resistivities decrease with the volume fraction of the addition metal. In the case of the series, the resultant electrical resistivity by the ROM is consistent with those of the calculation and the experiment as well as reference [12]. In the cases of the series and parallel...
The resultant Seebeck coefficient of Cu/Bi and Ni/Bi composite thermoelectrics by the ROMs and GEM are shown in Fig.6 and Fig.7, respectively. The resultant Seebeck coefficients decrease with the volume fraction of the addition metal, and the trends are similar to those of the resultant electrical resistivity above. In the case of the series, on the whole the resultant Seebeck coefficient from the ROMs and GEM is higher than those from the ROM. It may be caused by the welding in the interfaces of Cu/Bi and Ni/Bi composite thermoelectrics [11].

In both the composites of the series and parallel, the resultants Seebeck coefficients become the upper limit and the lower limit, respectively. The resultant Seebeck coefficients of the particle composites located between the upper limit and the lower limit. Interestingly, when \( t = 2 \), the Seebeck coefficients have a sudden fall and then get close to that of the addition metal phase around \( \phi_C \) (Fig.6). These events were also observed in Cu/TiO\(_{2x}\) composites [6]. As a conclusion, the ROMs and GEM for the Seebeck coefficient of the composites seem reasonable.

The resultant power factors of Cu/Bi and Ni/Bi composite thermoelectrics by the ROMs and GEM are shown in Fig.8 and Fig.9, respectively. In both of the ROMs and the experiment, the power factors of the series composites have a similar trend, and show a peak in the range over \( \phi = 0.8 \), and is higher than those of the source materials. Besides, in the cases of \( \phi_C = 0.3, t = 1 \) and \( \phi_C = 0.5, t = 2 \), the power factors of the particle composites by the GEM have a peak, and are higher than those of the source materials in a certain range. It means that the power factor can be enhanced by the series-structured composite or
Fig. 9  Power factor by the ROMs and GEM for Ni/Bi composite thermoelectrics.

particle composite. Indeed, it has been verified by experiments in the series composites [11-14] and particle composites [1-5]. However, the power factor cannot be increased by the parallel-structured composite.

4.2 Calculations of dimensionless figure-of-merit of the composites

The thermal conductivities of Cu/Bi and Ni/Bi composite thermoelectrics by the ROMs and GEM are shown in Fig.10 and Fig.11, respectively. In the cases of the series and parallel composites, the resultant thermal conductivities are inverse to those of the resultant electrical resistivities and Seebeck coefficients, became the lower limit and the upper limit, respectively. There is a steeper trend against the volume fraction in the case of a small $t$ value ($t = 1$). As attention point, it is a negative effect for thermoelectrics that the thermal conductivity is increased by metal addition in all composite structures. The dimensionless figure-of-merits of Cu/Bi and Ni/Bi composite thermoelectrics by the ROMs and GEM are shown in Fig.12 and Fig.13, respectively. In the cases of the series and parallel composites, the resultants $ZT$ became the upper limit and the lower limit respectively. Although the power factor can be increased by metal addition as discussed, there is no improvement in thermoelectric performance by metal addition due to the increase of the thermal conductivity. In this work, the deductions of the ROMs and GEM were based on the assumptions without the scattering of carriers and phonons, and no reactions at the boundaries between the source

Fig. 10  Thermal conductivity by the ROMs and GEM for Cu/Bi composite thermoelectrics.

Fig. 11  Thermal conductivity by the ROMs and GEM for Ni/Bi composite thermoelectrics.
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Fig. 12 Dimensionless figure-of-merit by the ROMs and GEM for Cu/Bi composite thermoelectrics (at 298 K).

Fig. 13 Dimensionless figure-of-merit by the ROMs and GEM for Ni/Bi composite thermoelectrics (at 298 K).

Those from the ROMs. The upper limit and lower limit of the thermal conductivity is inverse to those of the other properties. The ROMs and GEM for the Seebeck coefficient of the composites seem reasonable. Although the power factor can be enhanced by composite effect for simple composites, however, the thermal conductivity is increased. Thus, the performance improvement is difficult by only simple composite method. The thermoelectric figure of merit of $M/T/M$ ($M = \text{Cu or Ni}$ and $T = \text{Bi}_{0.85}\text{Sb}_{0.12}$) was enhanced because of the interface effect according to the reaction at the interface. In the other work, high-performance bulk thermoelectrics was attained through all-scale process including nano- and meso-scale [16]. Therefore, to improve the thermoelectric performance by composite method, the nanocomposite and reactions at the interfaces should be introduced.

Conferences

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5 Conclusions

In this work, the ROMs of the Seebeck coefficient for the series and parallel composite models were deduced. The GEM was applied to the Seebeck coefficient of particle composite model. The ROMs of the series and parallel models take values of the upper limit and lower limit of the electrical resistivity and the Seebeck coefficient, respectively. On the other hand, the GEM takes values between materials. That is, although the power factor can be enhanced for simple composites by composite effect, the improvement of the performance is difficult.