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Research Report

Smart Design of Thermoelectric Materials for a Waste Heat Regeneration System

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ABSTRACT Thermoelectric generators (TEGs) can directly convert waste heat into useful electricity. Various applications, such as utilizing waste heat generated by vehicles, radiant heat produced in the steel making process, and solar energy, have been examined in recent years. The thermoelectric conversion efficiency of TEGs is characterized by the dimensionless figure of merit (ZT) for the thermoelectric materials they are constructed from. However, because of the intrinsic trade-off between high electrical conductivity and low thermal conductivity, it is not easy to dramatically increase ZT. The strategy used in the present study is based on conceptual ideas such as co-doping with donors and acceptors, crystallographic defects, and energy filtering, which may overcome this trade-off. These concepts are implemented by atomistic modifications in conventional thermoelectric materials, designed by first-principles calculations. In the present paper, we demonstrate three thermoelectric materials systems that have been designed and synthesized using this strategy. The results show a significant improvement in thermoelectric properties, legitimating and emphasizing the importance of design concepts based on physical and chemical insights.

KEYWORDS Material Design, Thermoelectric Material, Co-doping with Donors and Acceptors, Crystallographic Defects, Energy Filtering with Nanocomposite Phases

1. Introduction

Waste heat is the unused heat inevitably generated by automobile engines or power plants. Dissipated into the atmosphere, it limits the efficiency of thermodynamic processes and contributes to global warming. A thermoelectric generator (TEG) is a promising solution to these problems since it reuses waste heat, directly converting it into useful electricity. In particular, TEGs can be installed in limited spaces, and their power density is relatively high (on the order of 1 W/cm²). Therefore, various applications of TEGs have been examined in recent years. One example is the automotive TEG. Crane et al. reported that a TEG mounted downstream of the catalytic converter on a vehicle produced 600 W of electrical power when the TEG hot side was heated by exhaust gas and its cold side was exposed to a coolant. As a result, the relative improvement in fuel efficiency exceeded 1.2% at a vehicle speed of 110 kph. Another example is a waste heat recovery system in a steel making process demonstrated by Kuroki et al. A TEG with dimensions of 2 m × 4 m produced approximately 9 kW from the radiant heat produced by casting slabs when the slab temperature and the distance between the slab and the TEG were 915°C and 2 m, respectively. Recently, we demonstrated a solar TEG with a water heating system with a high energy conversion efficiency.

The thermoelectric efficiency of TEGs is characterized by the dimensionless figure of merit (ZT) for the thermoelectric (TE) material, which is defined as

\[ ZT = \frac{\sigma S^2}{\kappa} T, \]  

where \( \sigma, S, \kappa, \) and \( T \) are the electrical conductivity, the Seebeck coefficient, the thermal conductivity, and the temperature, respectively. The average ZT (\( ZT_{ave} \)) obtained from the temperature of the cold side (\( T_c \)) and the hot side (\( T_h \)) of the TEG is required in order to estimate the TE efficiency. Here, \( ZT_{ave} \) is defined as

\[ ZT_{ave} = \frac{1}{T_c} \int_{T_c}^{T_h} ZTdT. \]
The ideal TE efficiency ($\eta_{\text{TEG}}$) is given by

$$\eta_{\text{TEG}} = \frac{T_h - T_c}{T_h} \times \frac{(1 + ZT_{\text{ave}}^{1/2} - 1}{(1 + ZT_{\text{ave}}^{1/2}) + T_c / T_h}. \quad (3)$$

Note that $ZT_{\text{ave}}$ and $\Delta T (= T_h - T_c)$ should be maximized to obtain a high $\eta_{\text{TEG}}$, but $T_h$ and $T_c$ are restricted by the TEG application. For example, for an internal combustion engine, $T_h = 600^\circ\text{C}$ for the exhaust gas and $T_c = 30^\circ\text{C}$ based on the coolant.\(^{(4,5)}\) Therefore, increasing the $ZT$ value for TE materials is a crucial topic when developing TEGs. Figure 1 shows the $T_h$ dependence of $\eta_{\text{TEG}} (T_c = 30^\circ\text{C})$. At this juncture, the practical value of $ZT_{\text{ave}}$ is approximately 1 at best for $T_h = 600^\circ\text{C}$ and $T_c = 30^\circ\text{C}$, and thus $\eta_{\text{TEG}}$ is approximately 10%.

When $T_h$ is below 300°C, Bi$_2$Te$_3$-based materials are commonly used for TEGs because no materials with higher a $ZT$ value have yet been found. Recently, the maximum $ZT$ value for such materials has been increasing, e.g., 1.1 at 100°C (n-type)\(^{(6)}\) and 1.86 at 47°C (p-type).\(^{(7)}\) When $T_h$ is approximately 600°C, CoSb$_3$-based materials have been found to exhibit $ZT$ values of up to 1.7 at 577°C (n-type)\(^{(8)}\) and 1.06 at 427°C (p-type).\(^{(9)}\) Generally, a TEG consists of n- and p-type TE materials, which are electrically connected in series, as shown in Fig. 2. A high-efficiency TEG is therefore realized when both the n-type and p-type TE materials have a high $ZT$ value. The efficiencies of TEGs using Bi$_2$Te$_3$- and CoSb$_3$-based materials were reported to be 7.2% at $T_h = 280^\circ\text{C}\(^{(10)}\) and 8.4% at $T_h = 600^\circ\text{C}\(^{(9)}\)$ respectively. A segmented TEG consisting of Bi$_2$Te$_3$- and CoSb$_3$-based materials exhibited a higher efficiency of up to 12% at $T_h = 576^\circ\text{C}\(^{(10)}\) New TE materials are also under development, and have been found to exhibit a maximum $ZT$ of 2.3 at 650°C (p-type PbTe-based material),\(^{(11)}\) 2.1 at 727°C (p-type Cu$_2$S-based material),\(^{(12)}\) and 2.0 at 500°C (p-type SnSe-based material).\(^{(13)}\) However, toxicity, low oxidation resistance, and poor stability, which are inherent in TE materials, often hinder the practical application of such TEGs.

Because of the intrinsic trade-off between the need for a high electrical conductivity and a low thermal conductivity, it is not easy to increase $ZT$ dramatically. In the present paper, we introduce three conceptual ideas, i.e., co-doping with donors and acceptors,\(^{(14)}\) crystallographic defects,\(^{(15)}\) and energy filtering with nanocomposite phases,\(^{(16)}\) as shown in Fig. 2. Crystallographic defects and nanocomposites act as phonon scattering centers and reduce $\kappa$ drastically in some cases. Co-doping with donors and acceptors leads to the formation of local dipoles which can also give rise to a significant reduction in $\kappa$ without reducing the carrier mobility. We have previously calculated the local dipole effect of co-doping for PbTe-based materials.\(^{(17)}\) It was found that co-doping with donors and acceptors changed the band structure around the Fermi energy without changing the carrier concentration. Thus, it is possible to increase the power factor ($PF = \sigma S^2$). The nanocomposites of energy filter phases are also possible to increase $PF$ due to the restriction of low energy carrier by those potential heights. These concepts are implemented by atomistic modifications in conventional TE materials, namely TiNiSn and Bi$_2$Te$_3$ compounds, which are designed by first-principles calculations. In the present paper, we demonstrate three TE materials that are designed and synthesized using this strategy in order to determine whether an improvement in TE properties can be realized.

2. Calculations and Experiments

We used the plane-wave projector augmented-wave (PAW) method\(^{(18,19)}\) implemented in the Vienna ab initio...
simulation package (VASP) code for first-principles calculations. The generalized gradient approximation (GGA) was used for the exchange and correlation potential. A stable state for each model was determined by minimizing the total energy while relaxing the atomic positions and lattice constants using a reciprocal-space k-mesh with a spacing of less than 0.2 Å⁻¹ in each direction, and an energy convergence below 1 × 10⁻⁷ eV.

The formation energy (FE) for substituting an element C for an element B in a compound AB is defined as

\[ \text{FE}_{(AB \rightarrow AC)} = [E(AC) + \mu(B)] - [E(AB) + \mu(C)], \]

where \( E \) and \( \mu \) are the total energy of the compound and the chemical potential of the element in metallic state, respectively. A more negative FE means that AC is more stable than AB.

The band structure for each model was calculated by the full-potential linearized augmented plane-wave (FLAPW) method. The electrical conductivity (\( \sigma \)) and the Seebeck coefficient (\( S \)) were calculated using the band structure with the Bloch-Boltzmann equations as

\[
\sigma_e(e, T) = e^2N(e) \bar{v}(\varepsilon) \tau(e, T),
\]

\[
\sigma(T) = \int \sigma_e(e, T) \left[-\frac{\partial f(\varepsilon)}{\partial\varepsilon}\right] de,
\]

\[
S(T) = \frac{1}{eT\sigma(T)} \int (e - \mu) \sigma_e(e, T) \left[-\frac{\partial f(\varepsilon)}{\partial\varepsilon}\right] de,
\]

where \( e, N, v, \tau, f, \) and \( \mu \) are the elementary charge, the density of states, the group velocity, the relaxation time, the Fermi function, and the chemical potential, respectively.

We synthesized TiNiSn- and Bi₂Te₃-based TE materials. The TiNiSn-based materials described in Secs. 3. 1 and 3. 2 were prepared in a radiofrequency (RF) furnace under an Ar atmosphere by first melting a mixture of Ti (Kojundo Chemical Laboratory Co., Ltd., purity 99.9%), Ni (99.9%), Sn (99.99%), Hf (98%), Zr (98%), Y (99.9%), Sb (99.99%), Co (99.99%), and Sc (Shin-Etsu Chemical Co., Ltd., 99.9%) grains in appropriate molar ratios. The obtained ingots were melted again in an RF furnace and were rapidly liquid-quenched. The quenched samples were ground into powder and sintered at 1100°C for 15 min under a pressure of 50 MPa in a vacuum by employing the spark plasma sintering (SPS) technique. On the other hand, Bi₂Te₃-based materials, as described in Sec. 3. 3, were prepared as rectangular pellets pressed in a die after first mixing Bi (Kojundo Chemical Laboratory Co., Ltd., purity 99.999%) powder, Te (99.999%) powder, and Ga (99.99%) grains in appropriate molar ratios. The pellets were sealed in a vacuum quartz ampoule in order to prevent volatilization of the raw materials, and then melted for 4 h in a muffe furnace at 700°C. The obtained ingots were melted again and were rapidly liquid-quenched. The quenched samples were ground into powder and sintered at 450°C for 5 min under a pressure of 50 MPa in a vacuum by SPS. The sintered samples were sealed again in a vacuumed quartz ampoule and then heated at 400°C for 24 h in a muffle furnace. Based on the eutectic phase behavior of Ga₂Te₅–Bi₂Te₃, we employed quenching and post-annealing processing to control the size and homogeneity of the nanosized precipitations of the Ga₂Te₅ filter phases.

In order to measure the transport properties, synthesized samples were cut into bars with dimensions of 2-3 mm × 2-3 mm × 10 mm using a diamond wheel saw. The electrical conductivity, Seebeck coefficient and thermal conductivity below room temperature.

Fig. 2 Schematic diagram of a common TEG consisting of n- and p-type thermoelectric materials and the items to be studied for increasing ZT in the present paper.
were measured using a physical property measurement system (PPMS, Quantum Design, Inc.).

3. Results and Discussion

3.1 Improvement of Power Factor Due to Co-doping with Donors and Acceptors

TiNiSn-based TE materials are attracting a great deal of interest because they contain no toxic elements and have a high ZT\(^{(14)}\) value of around 600°C, which is similar to the temperature of automotive exhaust gas. Therefore, automotive TEGs using these materials have been investigated.\(^{(4,5)}\) In this section, we introduce the co-doping effect of TiNiSn-based materials\(^{(14)}\) as a case study.

Based on the concept that local dipoles formed by co-doping with donors and acceptors can reduce \(\kappa\) drastically while maintaining a high carrier mobility, we first narrowed down the co-doping candidates by performing calculations. We evaluated the FE value in order to clarify how easily co-doping can be achieved in TiNiSn. Figure 3 shows the calculated FE value for different doped system in the Ti\(_4\)Ni\(_4\)Sn\(_4\) supercell. The dopants were selected so that the charge neutrality of the material was maintained. Since YSb (simultaneous substitution of Y at Ti sites as an acceptor and Sb at Sn sites as a donor), ScSb, and CoSb co-dopants in TiNiSn have negative FE values, they may be stable, and their solubility limit may be high. In addition, we confirmed for ScSb (YSb) co-doping that the nearest neighbor configuration of Sc (Y) and Sb in the crystal shows the lowest FE by the calculations in the case of ScSb (YSb) doping. This means that forming local dipoles of Sc (Y) and Sb is more stable than separated monopoles of Sc (Y) or Sb.

In order to determine how the local dipoles produced by co-doping affects the TE properties due to a change in the band structure, we calculated PF using the Ti\(_{32}\)Ni\(_{32}\)Sn\(_{32}\) supercell for the co-doping models. Table 1 shows the calculated \(PF/PF_0\) at 600 K for different 1% co-doped states in TiNiSn in the case of forming local dipoles.\(^{(14)}\) The PF was evaluated from the calculated \(\sigma\) and \(S\) under the assumption that the relaxation time \((\tau)\) for each model is the same as that for TiNiSn. The PF for non-doped TiNiSn \((PF_0)\) was used as the standard value for comparison. The YSb or ScSb co-doping is predicted to increase PF in comparison with non-doped TiNiSn.

We applied these co-dopants to a TiNiSn-based material, Ti\(_{0.5}\)Zr\(_{0.25}\)Hf\(_{0.25}\)NiSn, the \(ZT\) value for which is higher than that for TiNiSn due to the \(\kappa\) reduction by partial isovalent substitutions of Zr and Hf for Ti. The experimental results at 600 K, which were measured by RZ2001i of Ozawa Science Co. Ltd., are listed in Table 1. It was found that YSb or ScSb co-doping increased PF and CoSb co-doping lowered PF, which is consistent with the calculated results. Figure 4 shows the temperature dependence of ZT for the non-doped, the 0.3% Sb-doped, and the 1% YSb co-doped Ti\(_{0.5}\)Zr\(_{0.25}\)Hf\(_{0.25}\)NiSn.\(^{(14)}\) The doping concentrations for Sb and YSb in Fig. 4 were optimized so as to maximize ZT. Sb doping at Sn sites increased the \(ZT\) value due to the improvement of PF by optimization of the carrier concentration \((n)\). When \(n\) is increased by introducing donors or acceptors into a TE material, e.g., substitution of Sb at Sn sites in TiNiSn, the electrical conductivity is increased, whereas

**Table 1** Calculated and experimental \(PF/PF_0\) at 600 K for different 1% co-doped states in TiNiSn.\(^{(14)}\)

<table>
<thead>
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<th>Calculation (PF/PF_0)</th>
<th>Experiment (PF/PF_0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-doped</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>1%CoSb</td>
<td>0.76</td>
<td>0.76</td>
</tr>
<tr>
<td>1%ScSb</td>
<td>1.12</td>
<td>1.44</td>
</tr>
<tr>
<td>1%YSb</td>
<td>1.15</td>
<td>1.74</td>
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</table>
the absolute value of the Seebeck coefficient (|S|) is generally inversely proportion to the natural logarithm of the electrical conductivity (In n) as observed in the Jonker plot. Therefore, the PF improvement due to single-element doping is limited by the relation between |S| and In n. Co-doping of YSb, however, realized a further improvement of PF, and thus, surprisingly, ZT was even better than the theoretical prediction. This discrepancy may result from a change in the relaxation time induced by co-doping, which was not considered by the present calculations. These observations lead to the conclusion that appropriate co-doping is an effective method for increasing ZT, apart from optimizing the carrier concentration.

### 3.2 Reduction of Thermal Conductivity Due to Crystallographic Defects

One of the problems of TiNiSn-based materials is the inclusion of the expensive elements Hf and Zr, which are known to decrease the thermal conductivity. In this section, we introduce an alternative low-cost method to lower the thermal conductivity, i.e., crystallographic defects in the TiNiSn crystal. Defects can lower κ drastically because they become phonon scattering centers. Several types of defects can be introduced into the crystal, e.g., vacancies, interstitials, and antisites, depending on the composition and synthesis process. We evaluated the FE value for several types of defects in TiNiSn crystals by modeling using the Ti_{32}Ni_{32}Sn_{32} supercell. Table 2 shows the calculated FE in the case of excess Ni in TiNiSn. V@Sn and V@Ti represent Sn and Ti vacancies, respectively. In addition, Ni@Ti and Ni@Sn represent substitutions of Ni for Ti and Ni for Sn, respectively. Interstitial Ni is an excess Ni atom at one of the vacancies in the TiNiSn crystal structure, as shown in Fig. 5. The FE value for the interstitial Ni defect is quite low, even though it is positive. The calculation results indicate that excess Ni atoms are preferentially located at interstitial vacancy sites, forming a weak bond with the TiNiSn crystal. This situation is similar to that for filled skutterudite materials, where the crystal structure has vacancy sites that are large enough to introduce different atoms that are weakly bonded to the original crystal framework. These foreign atoms scatter phonons and thereby reduce the thermal conductivity significantly while maintaining a high electron mobility by the rattling effect. We thus expect a similar effect in TiNiSn with excess Ni.

We synthesized TiNiSn containing excess Ni in order to introduce interstitial Ni defects, and evaluated

<table>
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<tr>
<th>Model</th>
<th>FE (eV)</th>
<th>Δa/a (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>V@Sn</td>
<td>4.71</td>
<td>−0.09</td>
</tr>
<tr>
<td>V@Ti</td>
<td>3.97</td>
<td>−0.11</td>
</tr>
<tr>
<td>Ni@Ti</td>
<td>3.35</td>
<td>−0.16</td>
</tr>
<tr>
<td>Ni@Sn</td>
<td>3.02</td>
<td>−0.14</td>
</tr>
<tr>
<td>Interstitial Ni</td>
<td>0.19</td>
<td>0.11</td>
</tr>
</tbody>
</table>

Table 2 Calculated formation energy (FE) and expansion ratio for the lattice constant (a) for different defect models in comparison with TiNiSn.
3. Improvement of Power Factor by Energy Filtering Effect of Nanocomposites

Nanocomposites are also known to improve the $ZT$ value for TE materials. In most cases, this increase is caused by phonon scattering, which reduces the $\kappa$ value more than the $PF$ value. Recently, modulation doping, i.e., the formation of nonuniform nanocomposites, is a popular method by which to increase the $PF$ value due to increasing the carrier mobility.(24) In this section, we introduce nanocomposites of energy filtering phases in n-type $\text{Bi}_2\text{Te}_3$-based materials.(16)

Figure 8 shows a schematic diagram of the band offset between the filter phase and the TE material. In the resulting TE properties. If the excess Ni occupies vacancy sites in TiNiSn, as shown in Fig. 5, the lattice constant ($a$) should increase, as predicted in Table 2. Figure 6 shows the dependence of $a$ and $\kappa$ at 300 K on the Ni content ($x$), where $0.480 \leq x \leq 0.568$. Here, $a$ was determined by powder X-ray diffraction (XRD) patterns measured by a Rigaku RAD-2X using CuKα radiation, and $x$ is the ratio of the amount of Ni to the total amount of Ti and Sn in the samples and was determined by inductively coupled plasma (ICP) spectrometry. Since $a$ becomes larger as $x$ increases, following Vegard’s law, we found that excess Ni occupies vacancy sites in the TiNiSn crystal in the range of $0.480 \leq x \leq 0.540$. These interstitial Ni defects reduce $\kappa$, as shown in Fig. 6. In the case of the $x = 0.568$ sample, $a$ is approximately the same as that for $x = 0.540$. This suggests that the solubility limit for Ni is around $x = 0.540$. Above this solubility limit, at $x = 0.568$, XRD patterns indicated the presence of TiNi$_2$Sn precipitates, and the $\kappa$ value was higher.

Figure 7 shows the temperature dependence of $ZT$ for TiNiSn compounds.(15) The $ZT$ value at $x = 0.540$ is the highest among the synthesized samples because of the reduced $\kappa$ value and the increased $PF$ value due to the presence of interstitial Ni defects. We thus confirmed the effectiveness of introducing crystallographic defects to improve $ZT$. Note that following our research, the effect of interstitial Ni defects in TiNiSn has been investigated in detail.(23) The significant reduction in $\kappa$ for TiNiSn without the need for expensive elements such as Zr and Hr is an attractive approach for practical applications.

![Fig. 6](image1.png)  
**Fig. 6** Ni content ($x$) dependence of the lattice constant ($a$) and the thermal conductivity ($\kappa$) at 300 K for TiNiSn compounds ($0.480 \leq x \leq 0.568$). (15)

![Fig. 7](image2.png)  
**Fig. 7** Temperature dependence of $ZT$ for TiNiSn compounds ($0.48 \leq x \leq 0.568$). (15)

![Fig. 8](image3.png)  
**Fig. 8** Schematic diagram of the band offset between the filter phase and the thermoelectric (TE) material.
figure, CBM and VBM indicate the conduction band minimum and valence band maximum, respectively, and $E_F$, $\Delta E$, and $W_0$ refer to the Fermi level of the TE material, the potential barrier height, and the size of the filter phase, respectively. The filtering effect originates from an asymmetry in the density of states of the filter phase, respectively. The filtering effect for the TE material, the potential barrier height, and the size of the filter phase with an appropriate value of $E_F$, i.e., such that the CBM for the filter phase is aligned and $\Delta E$ approximately coincides with that for the TE material, and $W_0$ for the filter phase in order to maximize the filtering effect. However, this is difficult to achieve with bulk materials.

In the case of n-type $\text{Bi}_2\text{Te}_3$, $E_F$ can be shifted by approximately 0.2 eV above the CBM. We therefore searched for a material with a low $\Delta E$ of approximately 0.2 eV and found that $\text{Ga}_2\text{Te}_3$ may be suitable as the filter phase. The $\Delta E$ value for $\text{Ga}_2\text{Te}_3$ with respect to the CBM of $\text{Bi}_2\text{Te}_3$ was estimated based on $E_{\text{core}}$, obtained based on the $\text{Bi}_2\text{Te}_3$ and $\text{Ga}_2\text{Te}_3$ crystal structure models, $E_\text{b}$ at the $\text{Bi}_2\text{Te}_3$/Ga$_2$Te$_3$ interface, and the experimentally determined bandgap ($E_g$) for $\text{Bi}_2\text{Te}_3$ and $\text{Ga}_2\text{Te}_3$. Here, $E_{\text{core}}$ and $E_\text{b}$ are the energy difference between the VBM and the Te 1s core level ($E_{\text{core}}$), and between the Te 1s levels for $\text{Ga}_2\text{Te}_3$ and $\text{Bi}_2\text{Te}_3$, respectively. Figure 9 shows the band offset between $\text{Ga}_2\text{Te}_3$ and $\text{Bi}_2\text{Te}_3$ obtained by the calculations. The value of $\Delta E$ was estimated to be 1.0 eV, which is larger than the expected value of 0.2 eV. However, we chose $\text{Ga}_2\text{Te}_3$ as the filter phase considering the tunneling effect and the possible reduction of the band gap of $\text{Ga}_2\text{Te}_3$ depending on the defect structure. Concerning the size of the filter phase, as $W_0$ increases, $\sigma$ will decrease due to the decreasing transmittance of low energy electrons in the filter phase, whereas a smaller $W_0$ will reduce the energy filtering effect because electrons are only somewhat restricted because of tunneling in the filter phase.

We synthesized $\text{Bi}_2\text{Te}_3$ with nanosized $\text{Ga}_2\text{Te}_3$ regions and evaluated its TE properties. Figure 10 shows a backscattered electron (BSE) image of the synthesized $\text{Bi}_{0.85}\text{Ga}_{0.15}\text{Te}_3$. The sample was confirmed to contain homogeneously dispersed nanosized $\text{Ga}_2\text{Te}_3$ precipitates in $\text{Bi}_2\text{Te}_3$, and the average $\text{Ga}_2\text{Te}_3$ grain size was approximately 100 nm. Figure 11 shows $\sigma$ versus $\ln \sigma$ for $\text{Bi}_{1-x}\text{Ga}_x\text{Te}_3$ ($0 \leq x \leq 0.25$) at 300 K. Since the relationship is linear, i.e., a Jonker plot, the maximum $PF$ ($PF_{\text{max}}$) for $\text{Bi}_2\text{Te}_3$ is evaluated to be $1.75 \times 10^{-3}$ W/mK. However, the presence of the nanosized $\text{Ga}_2\text{Te}_3$ precipitates in $\text{Bi}_2\text{Te}_3$ ($0.07 \leq x \leq 0.15$) increases the $PF_{\text{max}}$ in comparison with $\text{Bi}_2\text{Te}_3$. The predicted $PF_{\text{max}}$ is $2.80 \times 10^{-3}$ W/mK, which approximately coincides with that for $x = 0.10$. The enhanced $PF$ value is much larger than the optimum value with respect to the given carrier concentration. Therefore, we concluded that this enhancement may result from the proposed filtering effect. Here, the $\kappa$ value for the $x = 0.10$ sample is not reduced in the nanocomposite, but the $ZT$ value is higher than that for $\text{Bi}_2\text{Te}_3$ due to the high $PF$. Concerning the size of the filter phase, we found that micron-sized $\text{Ga}_2\text{Te}_3$ precipitates in $\text{Bi}_2\text{Te}_3$ do not affect $PF_{\text{max}}$. The $PF_{\text{max}}$ for the $x = 0.2$ sample was much lower than that for the samples with $0.07 \leq x \leq 0.15$ because the TE properties of $\text{Ga}_2\text{Te}_3$ could not be ignored by increasing the volume ratio of $\text{Ga}_2\text{Te}_3$ to $\text{Bi}_2\text{Te}_3$. The appropriate amount of nanocomposites with the proper $\Delta E$ and $W_0$
significantly lowered the thermal conductivity and improved the \( PF \). Finally, an energy filtering effect for Bi\(_2\)Te\(_3\)-based TE materials was implemented using a Ga\(_2\)Te\(_3\) filter phase selected by the calculations. Bi\(_2\)Te\(_3\) with homogeneously dispersed nanosized Ga\(_2\)Te\(_3\) precipitates was synthesized, and its maximum power factor was higher than that for Bi\(_2\)Te\(_3\) due to the filtering effect. In all three cases, we obtained a significant improvement in the TE properties, thereby validating the strategy and emphasizing the importance of design concepts resulting from physical and chemical insights.

As mentioned in Sec. 1, TEGs are a green technology that are expected to be used in a variety of applications. However, the present TEG technology is still not mature for practical applications. Recently, we developed a solar TEG with a water heating system for efficiently using solar energy. Here, we can consider the applicability of TE materials we have developed, such as CoSb\(_3\)-based and sulfide TE materials, as well as TiNiSn- and Bi\(_2\)Te\(_3\)-based TE materials. It is, however, necessary to ensure the performance, stability, and reliability of TEGs, especially under practical heat cycles. Thus, we need to study related technologies along with TE materials for commercial applications. In this context, extended studies are being performed, such as a search for electrodes with a low contact resistance and low thermal stress, and oxidation-resistant coating materials for TE materials.

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References


Fig. 7

Figs. 9-11

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