Study of Zn-Substituted Germanium Clathrates as High Performance Thermoelectric Materials Assisted by First-Principles Electronic Structure Calculation

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The thermoelectric properties of the clathrate compounds Ba6ZnGe46-x, were studied theoretically and experimentally. First, a first-principles electronic structure calculation was performed. The calculated result showed that Ba6ZnGe38 is an intrinsic semiconductor with an indirect band gap, while Ba6ZnGe40 is an n-type degenerate semiconductor and Ba6ZnGe42 is a p-type degenerate semiconductor. A large x dependence for the band gap was found between x = 6 and 8, i.e., the width of band gap $E_g$ at $x = 6$, 8 and 10 were 0.83 eV, 0.40 eV, 0.35 eV, respectively. Thus, for a thermoelectric material with high performance at high temperatures, the band gap of the intrinsic semiconductor Ba6ZnGe38 is relatively small. On the other hand, it was found that the double substituted clathrate Ba6ZnGa4Ge36 is an intrinsic semiconductor with a relatively large band gap: $E_g = 0.69$ eV. Second, we synthesized Zn substituted clathrate compounds by using the mechanical alloying and spark plasma sintering method, and measured the thermoelectric properties of the synthesized samples to show the concrete advantage of the Ba-Zn-Ga-Ge system. The experimental results showed that all of the Ba6ZnGe46-x (x = 6, 8, 10, 12) samples were n-type semiconductors, and that some of the Zn clathrates (x = 6~10) had a reasonably good n-type thermoelectric ability. Moreover, it was confirmed that the band gap of Ba6ZnGa4Ge36 ($E_g = 0.9$ eV) is wider than that of Ba6ZnGe38 ($E_g = 0.4$ eV), and that Ba6ZnGa4Ge36 has better thermoelectric characteristics than Ba6ZnGe38 at high temperatures. Finally, the experimental thermoelectric properties were theoretically analyzed by using the results of the electronic structure calculation and good agreement was obtained.

[Received May 12, 2008; Accepted December 7, 2008; Published February 25, 2009]

Keywords: thermoelectric properties, clathrate compounds, Ba6ZnGe46-x, Ba6ZnGa4Ge36, the first principle electronic calculation, electronic structure, spark plasma sintering, theoretical analysis

1. Introduction

For the past decade, clathrate compounds, such as Sr4Ga46Ge30 and Ba8Ga46Ge30, have been widely investigated as high efficiency thermoelectric materials.1~6) These clathrate compounds are characterized by a caged structure of host atoms. Host atoms that are group IV elements (Si, Ge, or Sn) make a covalent bond network in the sp3 orbit with a guest atom in each cage, where the guest atom is bound loosely. The crystal structure creates various interesting properties, such as thermoelectric materials. First, these compounds have a low lattice thermal conductivity $\kappa_L$, being close to its theoretical minimum value. This is caused by the “rattling” of the guest atoms, or atomic and unharmonic vibration in the cages.7,8) Secondly, the compounds maintain a relatively high mobility $\mu$ due to carrier conduction through the sp3 network. Since the dimensionless figure of merit $ZT$ is approximately proportional to $\mu/\kappa_L$, large thermoelectric performance is thus expected from such clathrate compounds. Recently, high $ZT$ values were reported for the n-type germanium clathrate Ba8Ga46Ge30: 0.7 at 700 K for a polycrystalline sample4) and 1.35 at 900 K for a single crystalline one.5) In those clathrate compounds, the group III element Ga is substituted for Ge to compensate carriers.

Since binary clathrate compounds, such as Ba4Ge36, are metallic due to excess electrons of the guest atoms, their Seebeck coefficients are too small for high performance thermoelectric materials. Thus carrier compensation is a significant concept for obtaining a higher ZT value. Usually, ZT is optimized by the carrier concentration of intrinsic semiconductors. Since a guest atom provides two excess electrons and a substituting group III atom provide a hole, the number of group III atoms is twice the number of guest atoms and it reaches 1/3 of the number of all host atoms. Therefore host structure designs, i.e., the selection of substituting elements, the number of substituted atoms, its atomic configuration, etc are important to an investigation of the thermoelectric performance of semiconducting clathrates. Recently, Christensen et al. investigated Ba8Al16Ge30 to improve its thermoelectric performance based on the concept of host structure engineering.9) Okamoto et al. also investigated the effects of In substitution on the thermoelectric properties of the type-I clathrate compound Ba8Ge46Ge30.10) We have been interested in Zn substitution for group IV atoms in semiconducting clathrates from the viewpoint of the number of substituted atoms. Since a Zn atom provides two holes in crystals, the number of substituted atoms for carrier compensation is less than that for Ga-substituted clathrate.11) Less substitution at the host site may yield lower alloy scattering effects for the carrier, but the Zn substitution may also yield larger ionized scattering effects. Therefore, the effect on the carrier relaxation time from the Zn substitution is not trivial. This question was one of our motivations for
the present work. Moreover Zn substitution influences not only the carrier scattering but also the electronics structure of the conduction and valence bands, which especially affects the Seebeck coefficients.

Figure 1 shows the crystal structure of Ba$_8$Zn$_6$Ge$_{38}$. There are three kinds of host sites in this structure: 6c, 16i and 24k by the Wyckoff indexes. The Zn atoms in the semiconducting clathrate Ba$_8$Zn$_6$Ge$_{38}$ are not distributed uniformly in crystals. The Zn atoms prefer to occupy the 6c site. Such a preference might also influence carrier scattering in the clathrate, which would change its thermoelectric properties. Some of the properties of Zn-substituted germanium clathrates have been investigated very recently. Deng et al. reported the thermoelectric properties of Zn-doped Ba$_8$Ga$_{16}$Ge$_{30}$ clathrates, which become p-type semiconductors due to hole doping by Zn. Melnychenko-Koblyuk et al. studied the crystal structure and some physical properties of Ba$_8$Zn$_6$Ge ternary clathrates at and below room temperature. Christensen et al. also studied the host-guest coupling in Ba$_8$Zn$_8$Ge$_{38}$ by using synthesized single crystalline samples.

In this paper, we report on a study of the thermoelectric properties of Zn-substituted semiconducting clathrates above room temperature. In particular, we discuss the ability of the materials in high-temperature regions to act as high-performance thermoelectric materials. In addition to this point, we are attracted to material design assisted by a method the first principles electronic structure calculation. Therefore, we demonstrate the ability of using this method to investigate thermoelectric materials. In the present study, we first report of a theoretical study of the electronic structure calculations for Ba$_8$Zn$_6$Ge$_{36-x}$ and the double substituted clathrate Ba$_8$Zn$_6$Ga$_2$Ge$_{36}$ to predict high performance thermoelectric materials. Second, we discuss an experimental study of the preparation and thermoelectric properties of these predicted compounds. Finally, a theoretical analysis of the experimental results is performed by using the calculated electronic structure.

2. Computational Details

2.1 Computational method

The full potential linearized augmented plane wave (FLAPW) method based on the density-functional theory was used to perform the electronic structure calculations. Then the WIEN2k code was used. For the exchange-correlation potential we used two kinds of generalized gradient approximation (GGA): (1) the Perdew-Bruke-Ernzerhof (PBE) formula and (2) the Engel-Vosko (EV) formula. These different GGAs produced different calculated results. The PBE-GGA works well in the calculation of lattice parameters, such as the lattice constant, but in many cases yields a gap energy that is smaller than the experimental value. On the other hand, the EV-GGA does not give accurate lattice parameters, but gives a larger band gap energy than the PBE-GGA. Thus the EV-GGA is better for the calculation of thermoelectric properties, especially the Seebeck coefficient, since the band gap energy is very important for analyzing them at high temperatures.

We used the following values for the muffin-tin radius $R_{mt}$: $R_{mt}$(Ba) = 2.5 a.u., $R_{mt}$(Zn) = 2.2 a.u., $R_{mt}$(Ga) = 2.2 a.u., $R_{mt}$(Ge) = 2.0 a.u. The cutoff energy of the LAPW basis was 138 eV.

2.2 Structure of unit cell

We calculated the total energy of Ba$_8$Zn$_6$Ge$_{46-x}$ to determine lattice parameters theoretically. As for the Zn sitting, we used the following occupation models: 6 in the 6c site for $x = 6$, 6 in the 6c site and the rest in the 16i site for $x = 8$ and 10, taking into account the experimental results in Ref. 11. The obtained lattice constants at $x = 6$, 8, and 10 were 1.092 nm, 1.091 nm, and 1.100 nm, respectively, which agreed well with the experimental values of 1.074 nm (Ba$_8$Zn$_6$Ge$_{39}$) and 1.076 nm (Ba$_8$Zn$_8$Ge$_{38}$), respectively. The lattice models with the calculated lattice constants were used to calculate the electronic structures and thermoelectric properties of Ba$_8$Zn$_6$Ge$_{46-x}$.

In the calculation of Ba$_8$Zn$_6$Ga$_2$Ge$_{36}$ we performed two kinds of approximation to take into account the Ga substitution at the host sites, a virtual crystal approximation (VCA) and a super cell approximation (SCA). In the VCA treatment, we used an artificial atom Ga$_{1/10}$Ge$_{9/10}$ which is characterized by a non-integer atomic number: Z = 31.9, because the atomic number of Ga is 31 and that of Ge is 32. In the SCA treatment, we employed a conventional unit cell as the super cell, and then we set the Zn setting to 6 at the 6c site and the Ga setting to 4 at the 24k site. Here we avoided the Ga-Ga bond, i.e., a Ga atom did not occupy neighboring sites of other Ga atoms as in Ba$_8$Ga$_{16}$Ge$_{30}$. The lattice constant of Ba$_8$Zn$_6$Ga$_2$Ge$_{36}$ was calculated with these lattice treatments: 1.094 nm (SCA) and 1.091 nm (VCA), respectively.

2.3 Calculated results for electronic structures

First, let us consider the carrier compensation of valence electrons in a clathrate system by following the Zintl concept. The empty clathrate Ge$_{36}$ is a semiconductor with sp$^3$ bonding orbitals, in which the Ge atom has the (4s)$^2$(4p)$^2$ configuration. In Ba$_8$Zn$_6$Ge$_{38}$, 8 Ba atoms yield 16 electrons from the (6s)$^2$ configuration. These electrons are
compensated with 16 holes from the $\left(3d\right)^{10} \left(4s\right)^{2}$ configuration of 8 Zn atoms. Thus it is expected that $\text{Ba}_8\text{Zn}_x\text{Ge}_{46-x}$ is an intrinsic semiconductor at $x = 8$, and an $n$-type or $p$-type degenerate semiconductor at $x < 8$ and $x > 8$, respectively.

The electronic structures and total densities of states of $\text{Ba}_8\text{Zn}_x\text{Ge}_{46-x}$ ($x = 6, 8, 10$) were calculated, and the results are shown in Fig. 2. The dotted lines denote the highest energy of the occupied state, which corresponds to the Fermi energy of metals or degenerate semiconductors. The calculated results show that the clathrate $\text{Ba}_8\text{Zn}_8\text{Ge}_{38}$ is an intrinsic semiconductor, as expected by the Zintl concept, $\text{Ba}_8\text{Zn}_6\text{Ge}_{40}$ is an $n$-type degenerate semiconductor, and $\text{Ba}_8\text{Zn}_{10}\text{Ge}_{36}$ is a $p$-type one. The band gap results showed that the band gap strongly depends on $x$ with values of 0.83 eV ($\text{Ba}_8\text{Zn}_6\text{Ge}_{40}$), 0.40 eV ($\text{Ba}_8\text{Zn}_8\text{Ge}_{38}$) and 0.35 eV ($\text{Ba}_8\text{Zn}_{10}\text{Ge}_{36}$), respectively. The $x$ dependence of the calculated band gaps was not monotonous. We believe that the difference between them was related to the position of the Zn. Since the Zn was only sited at 6c at $x = 6$, but at $x = 8$ and $x = 10$ it was also sited at 16i in the present lattice models. The bond strength of a host Ga atom at 6c sites is weaker than that at other sites. On the other hand, the bond length between 16i-16i is the shortest and host atoms at the 16i site are tightly bonded with neighboring atoms. Therefore, it is supported that the Zn sitting at 16i strongly affects the valence band, which is composed of bonding orbits.

The bonding nature of Zn is shown in its partial density of states (PDOS). The PDOS of $\text{Ba}_8\text{Zn}_8\text{Ge}_{38}$ are shown in Fig. 3. The highest energy shell of a Zn atom is characterized by the $\left(3d\right)^{10} \left(4s\right)^{2} \left(4p\right)^{0}$ configuration. The $3d$ states lie deeply between $-11$ eV and $-5$ eV, and effects on the band structure by the $3d$ states are small near the band gap. The PDOS of $4s$ (Zn) is very different from that of $4s$ (Ge) in the low energy range from $-12$ eV to $-4$ eV. In Fig. 3(b), the $4s$ dominant band of Zn appears in the range from $-5$ eV to $-4$ eV, it seems that the $4s$ state of Zn is shallow in comparison with that of Ge. The $4p$ component of Zn appears conspicuously close to the band edge of the valence band in Fig. 3(b). This indicates that the $sp$ states of Zn make covalent hybridized bonds with neighboring Ge. But these states are shallow, as seen in Fig. 3(b). Thus the energy of the hybridized bond between Zn and Ge becomes higher and the band gap becomes narrow. In particular, it is thought that the narrowing effect appears in the case of the 16i setting of Zn, as the bonding between 16i sites is the strongest of the host bonds.
The band gap narrowing near $x=8$ is a significant problem from the viewpoint of thermoelectric application. Ge clathrates are expected to show high thermoelectric performance at 600–900 K, which demands a band gap magnitude of about 10k_B T $\sim$ 0.8 eV. This condition was maintained for Ba$_4$Zn$_6$Ge$_{36}$, but the band gap width for Ba$_4$Zn$_6$Ge$_{38}$, 0.40 eV, was a little small. Therefore, material design for a wider band gap is needed.

As mentioned before, the band narrowing of Zn clathrates ($x=8, 10$) was caused by the 16i setting of Zn. On the other hand, to achieve carrier compensation, 8 Zn atoms had to be substituted for Ge in a unit cell, and then two Zn atoms occupied host sites, except 6c sites, as 6 Zn atoms were sitting at 6c. In addition to this, a Zn atom avoided other Zn atoms due to the Coulomb repulsive interaction between two anions, and it was difficult to set Zn at 24k, because the 24k sites surround the 6c sites. From these results we obtained the following conditions for band gap widening: (1) Zn atoms should only occupy the 6c sites, (2) further carrier compensation should be carried out by other kinds of elements, and then the energy of the $sp$ states will be larger than that of Zn. The substitution of group III elements holds on these conditions, especially Ga. Thus we studied the ability of Ba$_4$Zn$_6$Ga$_4$Ge$_{36}$.

The band structure of Ba$_4$Zn$_6$Ga$_4$Ge$_{36}$ was calculated and the results with the SCA and the VCA treatments are shown in Fig. 4. The band shapes were similar to each other. The band gaps were $E_g = 0.54$ eV (SCA) and 0.69 eV (VCA). The band gap of Ba$_4$Zn$_6$Ga$_4$Ge$_{36}$ became wider than that of Ba$_4$Zn$_6$Ge$_{36}$, and it was expected that thermoelectric performance of Ba$_4$Zn$_6$Ga$_4$Ge$_{36}$ became larger. Those theoretical predictions were confirmed experimentally, as discussed in the following sections.

3. Experiment

3.1 Sample preparation and measurement

Polycrystalline clathrate samples of Ba$_4$Zn$_x$Ge$_{46-x}$ ($x=4, 6, 8, 10, 12, 14$) and Ba$_4$Zn$_x$Ga$_4$Ge$_{36}$ were prepared by powder metallurgy as follows: Ba (99.9%), Ge (99.999%), and/or Ga (99.999%) were melted together using an arc-melting technique. The obtained ingots were crushed into powder smaller than 106 μm. The obtained powder and Zn (99.99%) powder were placed in a stainless-steel milling vial with Si$_3$N$_4$ balls, and the vial was sealed in a glove box under a high vacuum.

The crystal structure was checked by X-ray diffraction (XRD) measurement using the Rietveld analysis program RIETAN-FP. The sample density $\rho$ was determined using the Archimedes method. The electrical conductivity $\sigma$ was measured using the four-probe method. The Seebeck coefficient $S$ was measured using the steady-state method. The electrical conductivity $\sigma$ and the Seebeck coefficient $S$ were obtained in a temperature range of 300 to 1000 K in vacuum.

3.2 Experimental results and discussion

3.2.1 Crystalline features

The obtained samples were dense enough to allow an investigation of their thermoelectric properties. For example, the density of the Ba$_4$Zn$_6$Ge$_{36}$ sample was 5.78 g/cm$^3$, which is 99% of its theoretical density.

Figure 5 plots the XRD patterns of the nominal Ba$_4$Zn$_x$Ge$_{46-x}$ ($x=4, 6, 8, 10, 12, 14$) and Ba$_4$Zn$_x$Ga$_4$Ge$_{36}$ sintered samples. The nominal Ba$_4$Zn$_x$Ge$_{46-x}$ samples with $x=8, 10, 12$ and the Ba$_4$Zn$_6$Ga$_4$Ge$_{36}$ sample showed a single phase of the type-I clathrate structure (Pm-3n), while the nominal Ba$_4$Zn$_x$Ge$_{46-x}$ samples with $x=4$ and 6 and that with $x=14$ slightly contained a diamond-type of Ge and BaZn$_2$Ge$_2$, respectively, as a secondary phase. These features almost agreed with the results previously reported.$^{11,13}$ Kuhl et al.$^{11}$ and Melnychenko-Koblyuk et al.$^{13}$ prepared Ba$_4$Zn$_x$Ge$_{42-x/2}$ ($x=4, 6, 8, 10$) and Ba$_4$Zn$_x$Ge$_{46-x}$ ($x=0, 2, 4, 6, 8, 10$) clathrates, respectively. Their Ba$_4$Zn$_x$Ge$_{46-x}$ samples with $x=0$ to 8 consisted of a single phase of Ba-Zn-Ge clathrate. The Ba-Zn-Ge clathrate phase, however, contained defects in the Zn/Ge framework site; the number of defects in the unit cell decreased with the Zn...
content \( x \). Their sample with \( x = 10 \) contained a secondary phase. Our samples with \( x = 4 \) and 6 probably possessed similar defects in the Ge site, and consequently, excess Ge crystallized in the secondary phase.

A Rietveld analysis was made on the \( {\text{Ba}}_{8}{\text{Zn}}_{x}{\text{Ge}}_{46-x} \) sample. The lattice constant of 1.07670(2) nm was approximately equal to the 1.07678(2) nm value previously reported.\(^{13}\) The occupancies of Zn in the framework of the 6c, 16i, and 24k sites were 100, 2, and 7%, respectively, while the reported values were 100, 11, and 0%, respectively.\(^{13}\) Clearly, the Zn atoms preferred to exist in the 6c site of the Ba-Zn-Ge clathrate.

### 3.2.2 Thermoelectric properties

Figures 6 and 7 respectively display the temperature dependences of the electrical conductivity and the Seebeck coefficient for the \( {\text{Ba}}_{8}{\text{Zn}}_{x}{\text{Ge}}_{46-x} \) (\( x = 4, 6, 8, 10, 12, \) and 14) sintered samples. Both figures clearly indicate that the samples were degenerate semiconductors of the \( n \) type. The electrical conductivity decreased and the absolute Seebeck coefficient increased with an increase in \( x \), because the electron density increased by a decrease in the number of defects as well as an increase in the number of holes supplied by Zn atoms. The temperature dependences of the samples with \( x = 4 \) and 6 seemed to be rather metallic. The sample with \( x = 12 \) exhibited the maximum Seebeck coefficient value in our samples. However, the sample with \( x = 14 \) showed a decrease in the Seebeck coefficient, which was attributed to the presence of a secondary phase.

The dotted curves MK in Figs. 6 and 7 represent the values of the \( {\text{Ba}}_{8}{\text{Zn}}_{17}{\text{Ge}}_{38.3} \) clathrate prepared by Melnychenko-Kobylyuk \( \text{et al.} \)\(^{13}\) The nominal composition of their sample was \( {\text{Ba}}_{8}{\text{Zn}}_{9}{\text{Ge}}_{38} \). Our nominal \( {\text{Ba}}_{8}{\text{Zn}}_{8}{\text{Ge}}_{38} \) and \( {\text{Ba}}_{8}{\text{Zn}}_{10}{\text{Ge}}_{38} \) samples had the similar magnitudes for the Seebeck coefficient, as shown in Fig. 7. However, the electrical conductivities at low temperatures for our samples were somewhat lower than that of their sample. It is possible that the grain boundaries in our sintered samples reduced their conductivities.

On the other hand, both figures indicate that there were intrinsic regions at high temperatures where the electrical conductivity increased and the Seebeck coefficient decreased with temperature. The electrical conductivity \( \sigma \) values almost obey the relation for activation-type: \( \sigma \sim \exp (-E_a / k_B T) \), where \( E_a \) is an activation energy. Because the activation energy for the \( {\text{Ba}}_{8}{\text{Zn}}_{x}{\text{Ge}}_{46-x} \) clathrate was 0.28 eV, its band gap energy was estimated to be 0.56 eV. This value is in reasonable agreement with the theoretical prediction of the first principles calculation: 0.40 eV (\( {\text{Ba}}_{8}{\text{Zn}}_{8}{\text{Ge}}_{38} \)).

Figure 8 plots the Seebeck coefficient versus the electrical conductivity for the \( {\text{Ba}}_{8}{\text{Zn}}_{x}{\text{Ge}}_{46-x} \) (\( x = 4, 6, 8, 10, 12, \) and 14) sintered samples, where the solid curve indicates the relation of power factor \( P = S^2 \sigma \) of \( 1 \times 10^{-3} \text{ Wm}^{-1} \text{ K}^{-2} \). The solid square (MK) represents the data for the \( {\text{Ba}}_{8}{\text{Zn}}_{17}{\text{Ge}}_{38.3} \) clathrate prepared by Melnychenko-Kobylyuk \( \text{et al.} \)\(^{13}\).

In the Zn content region the power factor is smaller than \( 1 \times 10^{-3} \text{ Wm}^{-1} \text{ K}^{-2} \).
Figure 9 shows the electrical conductivity and the power factor of Ba$_8$Zn$_6$Ga$_4$Ge$_{36}$, where the values of Ba$_8$Zn$_6$Ge$_{38}$ are also shown for comparison. The room temperature electrical conductivity of Ba$_8$Zn$_6$Ga$_4$Ge$_{36}$ was larger than that of Ba$_8$Zn$_6$Ge$_{38}$; the temperature dependences near room temperature were quite different. These differences were probably caused by a difference in the carrier concentration.

On the other hand, we designed the Ba$_8$Zn$_6$Ga$_4$Ge$_{36}$ to spread the band gap of Ba$_8$Zn$_6$Ge$_{38}$ and this band gap widening was supported by the band structure calculation, as mentioned above. The band gap energy of Ba$_8$Zn$_6$Ga$_4$Ge$_{36}$ was estimated to be 0.90 eV from the electrical conductivity at high temperatures, as shown in Fig. 9(a). Thus the theoretical prediction was confirmed by the experiment.

It is noted that the calculated band gap was a little under estimate in comparison with the experimental value. As for the power factor, the experimental result of Ba$_8$Zn$_6$Ga$_4$Ge$_{36}$ showed a peak position shift toward the high temperature side, as seen in Fig. 9(b). This feature is in accordance with the band gap widening. The power factor behavior was related to not only the band gap but also the carrier concentration. Therefore, we will analyze the properties theoretically in the next section.

### 4. Theoretical Analysis

#### 4.1 Calculation of thermoelectric properties

Thermoelectric performance can be characterized by the dimensionless figure of merit $ZT$, which is defined as

$$ZT = \frac{S^2\sigma}{\kappa_e + \kappa_l},$$

where $\kappa_l$ and $\kappa_e$ are the lattice thermal conductivity and electronic thermal conductivity of a material, respectively. These thermoelectric properties are calculated from the following expression, which is derived from the linearized Boltzmann equation with the relaxation time approximation. The Seebeck coefficient and the electrical conductivity are given as

$$S = \frac{e}{3T\sigma} \int d\epsilon \left( -\frac{\partial f(\epsilon)}{\partial \epsilon} \right) \rho(\epsilon)v(\epsilon)^2(\epsilon - \mu)\tau(\epsilon),$$

$$\sigma = \frac{e^2}{3} \int d\epsilon \left( -\frac{\partial f(\epsilon)}{\partial \epsilon} \right) \rho(\epsilon)v(\epsilon)^2\tau(\epsilon),$$

where $\rho(\epsilon)$, $\tau(\epsilon)$, and $v(\epsilon)$ are the density of state and relaxation time, and the velocity of an electron, respectively. $f(\epsilon)$ is a Fermi distribution function and $\mu$ is the chemical potential. The velocity $v(\epsilon)$ is given as

$$v(\epsilon)^2\rho(\epsilon) = \sum_{nk} \left| \langle nk | P | nk \rangle \right|^2 \delta(\epsilon - \varepsilon_{nk}),$$

where $|nk\rangle$ and $\varepsilon_{nk}$ are the wave function and the energy of $n$-th band at wave number $k$, $P$ is a momentum operator of an electron, and $m_0$ is the mass of a free electron.
above formulas of eqs. (2)–(4) thermoelectric properties are obtained from the result of the calculated electronic structure. If the energy dependence of the relaxation time $\tau$ is weak and the relaxation time is considered to be constant, we can see from eqs. (2) and (3) that Seebeck coefficient is independent of $\tau$ and the electrical conductivity is proportional to $\tau$. Thus, the Seebeck coefficient and the electrical conductivity have the features of weak and strong relaxation time dependence, respectively.

We can calculate the thermoelectric properties by using the calculated band structure. From the expressions of eqs. (2) and (3), we can calculate the Seebeck coefficient and electrical conductivity by choosing the electron concentration $n_e$ and the relaxation time $\tau$ as parameters as in our previous work, the finite electron carrier concentration is assumed in this calculation. Also we have assumed that the relaxation time $\tau$ is expressed by a constant term, plus an acoustic phonon scattering (APS) term that is proportional to $1/(T\rho(\epsilon))^{1/2}$ which is valid for a parabolic band. Then the DOS is proportional to $\epsilon^{1/2}$. In the constant relaxation time approximation (CRTA) both parameters, $n_e$ and $\tau$, are determined by noticing that (i) the Seebeck coefficient does not depend much on $\tau$ and is sensitive to $n_e$ and (ii) the electrical conductivity $\sigma$ is very sensitive to $\tau$. Thus we determine $n_e$ from the best fitting of $S$. By using the determined $n_e$, the value of $\tau$ can be fixed by the best overall fitting in $\sigma$. Taking the APS effect into account, we adjust the relaxation time parameter with the APS term to fit the experimental $\sigma$ once more.

4.2 Results of analysis

We analyzed the experimental thermoelectric properties of $\text{Ba}_8\text{Zn}_8\text{Ge}_{38}$ and $\text{Ba}_8\text{Zn}_6\text{Ga}_4\text{Ge}_{36}$. Figure 10 shows the calculated results, which are compared with the experimental results: the dotted line denotes the calculated result of $\text{Ba}_8\text{Zn}_8\text{Ge}_{38}$ with the electron concentration $n_e = 5 \times 10^{25} \text{m}^{-3}$ and the relaxation time $\tau = 1.0 \times 10^{-14} \text{s}^{-1}$ in the CRTA. For $\text{Ba}_8\text{Zn}_6\text{Ga}_4\text{Ge}_{36}$, we calculated the thermoelectric properties by using two kinds of calculated band structures in the SCA and VCA treatments, respectively.
and then the electron concentrations were $1.3 \times 10^{26}$ m$^{-3}$ (SCA) and $1.4 \times 10^{26}$ m$^{-3}$ (VCA). The solid line denotes the SCA, and the broken and the dashed-and-dotted lines denote the VCA. In the SCA the relaxation time was treated by the CRTA. In the VCA we treated the relaxation time by the CRTA or the CRTA plus APS effects (CRTA+APS). The former is shown by a broken line, while the latter is shown in a dashed-and-dotted line. In the CRTA, the value of $\tau$ was $1.2 \times 10^{-14}$ s.

Blake et al. used the experimental results for $n$-type Ba$_{8}$Ga$_{16}$Ge$_{30}$ and Sr$_{3}$Ga$_{38}$Ge$_{30}$ and theoretically calculated the values of the carrier concentration and the relaxation time, namely, $n_0 = 1-10 \times 10^{26}$ m$^{-3}$ and $\tau \sim 1 \times 10^{-14}$ s, respectively. Their results for Zn-substituting clathrates were similar to those results of Blake et al. for Ga-substituting clathrates, which indicated that the values of our results were reasonable, because the thermoelectric properties of Zn-substituting clathrates are similar to that of Ga-substituting clathrates.

For Ba$_{8}$Zn$_{6}$Ge$_{38}$ the CRTA could reproduce the experimental Seebeck coefficient and electrical conductivity, as shown in Fig. 10(a) and (b). But over 800 K, an overestimate is seen from the experimental results for the Seebeck coefficient and the calculated conductivity was also somewhat underestimated under 500 K. The calculated power factor is overestimated in a wide range. This deviation was caused by two different overestimates, the Seebeck coefficient at high temperature and the electrical conductivity under 500 K. For Ba$_{8}$Zn$_{6}$Ga$_{36}$ the CRTA was a little poor compared with the Ba$_{8}$Zn$_{6}$Ge$_{38}$ case. Therefore, when we take the APS effect into account in the Ba$_{8}$Zn$_{6}$Ga$_{36}$ case, it seems that the calculated curve reproduces the experiments fairly well in a wide range of temperatures, from room temperature to 900 K.

From Fig. 10 we are able to see that the calculated results with the SCA were very similar to those with the VCA. The band structure with the SCA resembles that with the VCA, but the band gap width is different, i.e., 0.69 eV (VCA) and 0.54 eV (SCA). The difference between these band gaps contributed to the thermoelectric properties slightly below 700 K, but at higher temperature the difference in the band gap width appears in the power factor as shown in Fig. 10(c).

We would like to note the treatment of the relaxation time. Relaxation times were treated by the CRTA or the CRTA+APS. The inclusion of both terms of the CRT and APS reproduces well the experimental temperature dependence of electrical conductivity. If only the CRT term is considered, the calculated electrical conductivity yields a weaker temperature dependence and the agreement with the experiment is not as good as at present, being similar to Fig. 6 in Ref. 24. Nonetheless both of the CRTA and the CRTA+APS reproduce well the experimental temperature dependence of the power factor.

5. Summary

We have studied the thermoelectric properties of the single substituted compound Ba$_{8}$Zn$_{6}$Ge$_{38}$ and the double substituted one Ba$_{8}$Ga$_{16}$Ge$_{30}$. First, we calculated those electronic structures by using the first principles method based on the density functional theory. The calculated results showed that in single substituted clathrates, Ba$_{8}$Zn$_{6}$Ge$_{38}$ is an intrinsic semiconductor at $x = 8$, an $n$-type degenerate semiconductor at $x = 6$, and a $p$-type degenerate semiconductor at $x = 10$. That is in agreement with the Zintl concept.

Also the EV-GGA treatment for the exchange-correlation potential yields a relatively larger band gap in Ba$_{8}$Zn$_{6}$Ge$_{30}$, i.e., $E_g = 0.83$ eV for $x = 6$, $E_g = 0.40$ eV for $x = 8$ and $E_g = 0.35$ eV for $x = 10$. In Ba$_{8}$Zn$_{6}$Ga$_{36}$, the calculated band structure shows that it is a semiconductor with a larger band gap, $E_g = 0.69$ eV, than that of Ba$_{8}$Zn$_{6}$Ge$_{38}$.

Second, we synthesized the single and double substituted clathrate compounds and measured their thermoelectric properties. At $x = 8$ we obtained the largest power factor for various Zn contents $x$ of Ba$_{8}$Zn$_{6}$Ge$_{38}$. Also the double substituted compound Ba$_{8}$Zn$_{6}$Ga$_{36}$ showed a larger band gap width than that of Ba$_{8}$Zn$_{6}$Ge$_{38}$ and good thermoelectric characteristics experimentally.

By using the results of the electronic structure calculation, these thermoelectric properties were analyzed by choosing the electron concentration $n_0$ and the relaxation time $\tau$ as adjustable physical parameters. The calculated results agreed with the experiment reasonably well over a wide range of temperatures.

Acknowledgements

The authors would like to acknowledge the PC cluster resources of the Media and Information Technology Center, Yamaguchi University, for the calculation of the electronic structure. This work is partially supported by a Grant-in-Aid for Scientific Research (C) (No. 20510106) from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

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Study of Zn-Substituted Germanium Clathrates as High Performance Thermoelectric Materials Assisted

216223/1–26.