Transactions of the Materials Research Society of Japan 31[2] 311-314 (2006)

Electronic Structure and Thermoelectric Properties of Clathrate Compounds $Ba_8Al_{16}Si_{30}$ and $Ba_8Al_{16}Ge_{30}$

Takashi Uemura, Kenji Koga, Koji Akai and Mitsuru Matsuura
Faculty of Engineering, Yamaguchi University, Tokiwadai, 2-16-1, Ube 755-8611, JAPAN
Fax: 81-836-85-9622, e-mail: matsuura@yamaguchi-u.ac.jp

Electronic structure of Group IV-based Clathrate Compounds substituted by Al, *i.e.*, $Ba_8Al_{16}Si_{30}$ and $Ba_8Al_{16}Ge_{30}$, is calculated by the first principle method, *i.e.*, the Full-potential Linearlized Augmented Plane Wave (FLAPW) method, based on the density functional theory. The calculated results show that these compounds are indirect semiconductors with the band gap 0.39 eV ($Ba_8Al_{16}Si_{30}$) and 0.41 eV ($Ba_8Al_{16}Ge_{30}$). Using the calculated electronic structure, thermoelectric properties such as Seebeck coefficient, electrical conductivity, electronic thermal conductivity and the figure of merit ZT are calculated by using the constant relaxation time approximation. The calculated result reproduces the experiment reasonably well.
Key words: thermoelectric material, clathrate, FLAPW, Seebeck coefficient

1. INTRODUCTION

The thermoelectric performance of a material at a temperature T is characterized by the dimensionless figure of merit ZT, which is defined as

$$ZT = \frac{S^2 \sigma}{\kappa_e + \kappa_l} T, \qquad (1)$$

where S, σ, κ_l and κ_e are Seebeck coefficient, electrical conductivity, lattice thermal conductivity and electronic thermal conductivity of the material, respectively.

Clathrates $Ba_8Ga_{16}Si_{30}$ and $Ba_8Ga_{16}Ge_{30}$ exhibit good thermoelectric properties, *i.e.*, reasonably large electrical conductivities (σ), large Seebeck coefficients (S) and small thermal conductivities (κ) [1].

The crystal structure of these clathrate systems consists of a framework of Group-IV atoms having several polyhedral cages, each of which can incorporate relatively large guest atom, as shown in Fig. 1. The "rattling" motion of guest atoms such as Ba produces low frequency anharmonic phonon modes, which strongly scatter the heat carrying acoustic mode. This rattling scattering significantly reduces the thermal conductivity to be a glass-like value without reducing the crystalline electrical conductivity, which is mainly determined by the framework structure atoms (such as Ga, Ge, Si).

According to Slack's concept, ideal thermoelectric materials are Phonon Glass Electron Crystal (PGEC) [2]. This design concept has been achieved in the skutterudites with success. Clathrates may also have a glasslike thermal conductivity and crystal-like electrical conductivity. As a result, clathrates can also demonstrate PGEC properties.

Until now a substitution element of Group IV-based ctathrate compound was mainly Ga. There are a few studies of clathrate compounds substituted by Al.

$Ba_8Al_{16}Si_{30}$ and $Ba_8Al_{16}Ge_{30}$ are crystals with type-I structure characterized by the space group Pm-3n, which were synthesized by some authors [3]. Thermoelectric properties were studied experimentally in $Ba_8Al_{16}Si_{30}$ [4,5]. However, their electronic structures and thermoelectric properties have not been studied theoretically.

In this work, the first principle electronic structure calculation is performed by using FLAPW method based on the density functional theory. Then the results are used to calculate thermoelectric properties theoretically, which are compared with the existing experiment.

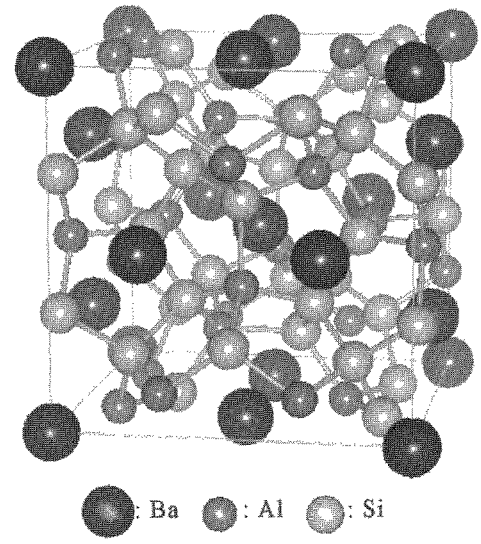

Fig. 1 Structure of clathrate $Ba_8Al_{16}Si_{30}$ and $Ba_8Al_{16}Ge_{30}$ consist of dodecahedral cages and tetrakeidecahedral cages of Al and Si (Ge). Ba is inside the polyhedra.

2. COMPUTATIONAL DETAILS

2.1 Calculational method

The ab inito calculation has been performed using the full potential linearlized augmented plane wave (FLAPW) method based on the density-functional theory [6].

In the calculation, we have used the following set of APW parameters: R_{mt} (Ba)=3.0 a.u., R_{mt} (Al)=2.2 a.u., R_{mt} (Si, Ge)=2.2 a.u., $R_{mt}K_{max}$=7 and $G_{max}(a_0/2\pi)$=14. Here, R_{mt} is the muffin-tin radius, K_{max} is the plane-wave cutoff, and G_{max} is the maximum Fourier component of the electron density. In the self-consistent calculation 23 k-sampling points have been taken in an irreducible Brillouin zone (BZ). For all the calculation we have used the modified tetrahedron method for the Brillouinzone integration. For the exchange-correlation potential we have used the GGA of Perdew *et al.* [7].

2.2 Structure

Blake *et al.* determined the atomic structure of $Ba_8Ga_{16}Ge_{30}$ and $Ba_8Ga_{16}Si_{30}$ clathrates by minimizing the total energy using the first principle electronic calculation. They found the Ga sitting with no Ga-Ga bond [8].

Here we consider Al-sitting of $Ba_8Al_{16}Si_{30}$ and $Ba_8Al_{16}Ge_{30}$ in similar way as in Blake *et al.* Three likely configurations for the substituted Al atoms in the frame structure of Si (Ge) and Al are considered (see Table 1). Total energy calculation shows the configuration with no Al-Al bond yields the lowest energy. This corresponds to Al occupation with 3 in 6c site, 1 in 16i site and 12 in 24k site.

Using this configuration, we calculate the lattice constant by the minimization of the total energy. For the calculation of the total energy we need to calculate the electronic structure, which has been performed by the first principle FLAPW method, described above. The determined lattice constants of $Ba_8Al_{16}Si_{30}$ and $Ba_8Al_{16}Ge_{30}$ are shown in Table 2. The table shows the calculated values 10.71 (Å) and 10.95 (Å) for the lattice constant in $Ba_8Al_{16}Si_{30}$ and $Ba_8Al_{16}Ge_{30}$ are close to the experimental values 10.60 (Å) and 10.83 (Å), respectively [3].

The atomic structure, determined above, is used to calculate the electronic structure and study thermoelectric properties in $Ba_8Al_{16}Si_{30}$ and $Ba_8Al_{16}Ge_{30}$ below.

Table 1 The energy of $Ba_8Al_{16}Si_{30}$ for different Al configurations

6c	16i	24k	Al-Al	ΔE (eV)
3	1	12	0	0.00
4	2	10	2	0.486
5	3	8	4	1.042

Table 2 Lattice constant

Lattice constant [Å]	Calc. (Present work)	Exp. (Eisenmann *et al.*)
$Ba_8Al_{16}Si_{30}$	10.71	10.60
$Ba_8Al_{16}Ge_{30}$	10.95	10.83

2.3 Thermoelectric properties

By using the linerlized Boltzmann equation with the relaxation time approximation, the Seebeck coefficient S_i, the electric conductivity σ_i and the electronic thermal conductivity κ_{ei} for the i-th band are given as

$$S_i = \frac{e}{3T\sigma_i}\int d\varepsilon\left(-\frac{\partial f(\varepsilon)}{\partial\varepsilon}\right)\rho_i(\varepsilon)v_i(\varepsilon)^2(\varepsilon-\mu)\tau_i(\varepsilon), \quad (2)$$

$$\sigma_i = \frac{e^2}{3}\int d\varepsilon\left(-\frac{\partial f(\varepsilon)}{\partial\varepsilon}\right)\rho_i(\varepsilon)v_i(\varepsilon)^2\tau_i(\varepsilon), \quad (3)$$

and

$$\kappa_{ei} = \frac{1}{3T}\int d\varepsilon\left(-\frac{\partial f(\varepsilon)}{\partial\varepsilon}\right)\rho_i(\varepsilon)v_i(\varepsilon)^2(\varepsilon-\mu)^2\tau_i(\varepsilon), \quad (4)$$

where $\rho_i(\varepsilon)$, $\tau_i(\varepsilon)$ and $v_i(\varepsilon)$ are the density of state, the relaxation time and the velocity for the i-th band. $f(\varepsilon)$ is the Fermi distribution function, and μ is the chemical potential, *i.e.*, Fermi energy. Using the above formulae thermoelectric properties are calculated.

3. RESULTS AND DISCUSSIONS

3.1 The electronic structure

Calculated band structure and the density of states (DOS) in $Ba_8Al_{16}Si_{30}$ and $Ba_8Al_{16}Ge_{30}$ are shown in Fig. 2 and 3, respectively. Dotted lines denote the Fermi level, *i.e.*, the top of the valence band. The both clathrates $Ba_8Al_{16}Si_{30}$ and $Ba_8Al_{16}Ge_{30}$ are indirect semiconductors with the energy gap Eg=0.39 eV and Eg=0.41 eV, respectively. The top of valence band is relatively flat (near Γ). The bottom of conduction band is positioned at the M point and has a parabolic nature. Fig. 4 shows partial density of states of $Ba_8Al_{16}Si_{30}$. The following points are seen: the region from –3 to 0 in the valence band mainly consists of s-electrons of Al, Si atoms and a small number of d-electrons of Ba atoms are involved. The conduction band region is mainly occupied by s- and p-electrons of Al, Si atoms, and d-electrons of Ba atoms. Thus, d-electrons of Ba flow in the s, p electron framework of Si and Al atoms, whose

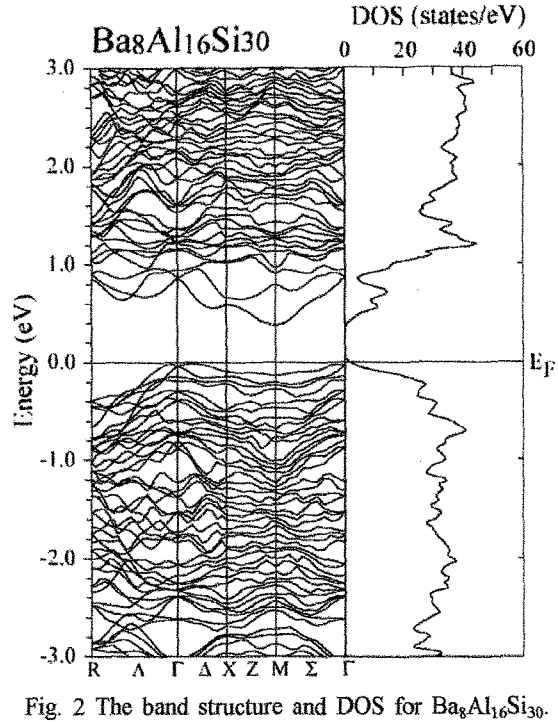

Fig. 2 The band structure and DOS for $Ba_8Al_{16}Si_{30}$. The energy is referred to the Fermi level.

mobility may be large. The calthrates $Ba_8Al_{16}Si_{30}$ and $Ba_8Al_{16}Ge_{30}$ may have a reasonably large electrical conductivity.

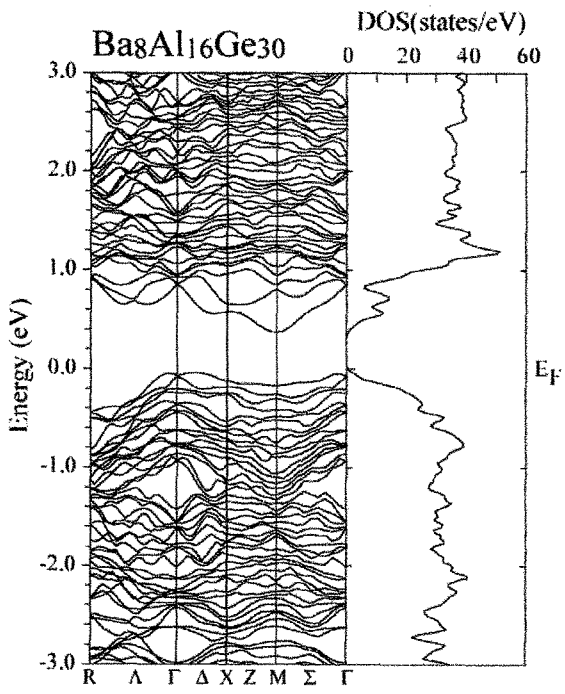

Fig. 3 The band structure and DOS for $Ba_8Al_{16}Ge_{30}$. The energy is referred to the Fermi level.

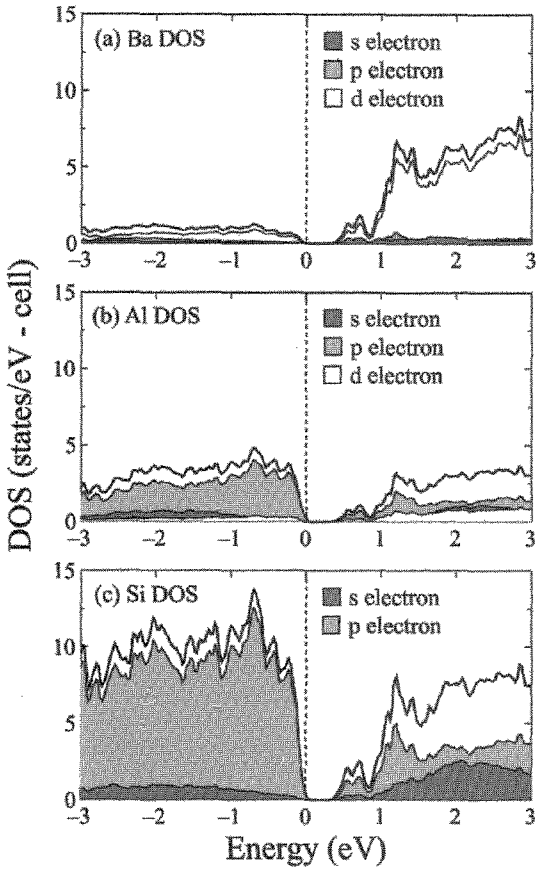

Fig. 4 Partial DOS for (a) Ba, (b) Al and (c) Si in the $Ba_8Al_{16}Si_{30}$.

3.2 Thermoelectric properties

Now we calculate thermoelectric properties in $Ba_8Al_{16}Si_{30}$ for which Koyanagi group has performed the experiment [5]. Experimental Seebeck coefficient in $Ba_8Al_{16}Si_{30}$ shows the n-type *i.e.*, the existence of the finite electron density, which is assumed in the present calculation together with the rigid band approximation, which assumes the band structure dose not change in spite of the electron doping.

Then, from Eq. (2) and (3), we calculate the Seebeck coefficient and electrical conductivity by choosing the electron concentration n_e and the relaxation time τ as parameters. Here, we have assumed the relaxation time τ to be constant, *i.e.*, the energy- and temperature-independent τ. Both parameters are determined by the following way. Firstly we notice that (i) Seebeck coefficient does not depend much on τ and is sensitive to n_e and (ii) electrical conductivity σ is very sensitive to τ. Thus we determine n_e from the best fitting of S. Next using the determined n_e, the value of τ can be fixed by the best overcall fitting in σ. Fig. 5 and 6 show the calculated and experimental Seebeck coefficients and electric conductivities of $Ba_8Al_{16}Si_{30}$ as a function of temperature, respectively. The closed triangles are the experimental results by Koyanagi group [5]. Solid lines denote the calculated result corresponding to the electron concentration n_e=3.29×10^{20} cm^{-3} and relaxation time τ =1.99×10^{-16} s^{-1}. It is seen that the calculated curve agrees well with the experiment in the wide range of temperature.

After that, we calculate the thermal conductivity $\kappa = \kappa_e + \kappa_l$, where electronic thermal conductivity. κ_e is calculated from Eq. (4) by using the above determined electron concentration n_e and relaxation time τ. The lattice thermal conductivity κ_l is treated as a constant, which is chosen as a parameter to

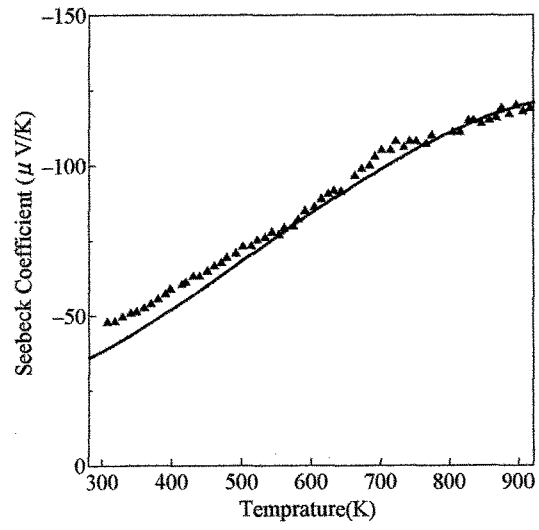

Fig.5 Temperature dependence of Seebeck coefficient for $Ba_8Al_{16}Si_{30}$.

reproduce the experimental thermal conductivity as better as we can.

Then, the calculated and experimental thermal conductivities of $Ba_8Al_{16}Si_{30}$ are shown in Fig. 7. It is seen that calculation with the lattice thermal conductivity of κ_l =0.026 W/cmK shows the good agreement with the experiment.

Finally, the Figure of merit ZT is calculated from Eq.(1), using the above calculated Seebeck coefficient S, electrical conductivity σ and thermal conductivity κ. In Fig. 8 the calculated and experimental results of ZT in $Ba_8Al_{16}Si_{30}$ are shown to be in fairly good agreement.

The constant relaxation time τ may be a crude treatment and the consideration of the microscopic scattering mechanism such as phonon scattering seems to be appropriate. Thus we have performed also the calculation by using the relaxation time τ due to the acoustic phonon scattering. It is found that the agreement of the calculation and experiment becomes worse, especially in electrical conductivity.

4. CONCLUTION

We have calculated the electronic structure of the clathrate $Ba_8Al_{16}Si_{30}$ and $Ba_8Al_{16}Ge_{30}$ by using the first principle FLAPW method with GGA. $Ba_8Al_{16}Si_{30}$ and $Ba_8Al_{16}Ge_{30}$ are found to be indirect semiconductor of energy gap E_g=0.39 (eV) and 0.41 (eV), respectively. The top of valence band is relatively flat (near Γ). The bottom of conduction band is positioned at the M point and has a parabolic nature. The conduction and valence bands consist of s-, p-electrons of Al, Si (Ge) atoms and d-electrons of Ba atoms.

The above obtained electronic structure is used to calculate thermoelectric properties, *i.e.*, Seebeck coefficient, electrical conductivity, thermal conductivity and the figure of merit ZT in $Ba_8Al_{16}Si_{30}$. Choosing the carrier density, the relaxation time and the lattice thermal conductivity as parameters, the calculation reproduces the experiment reasonably well.

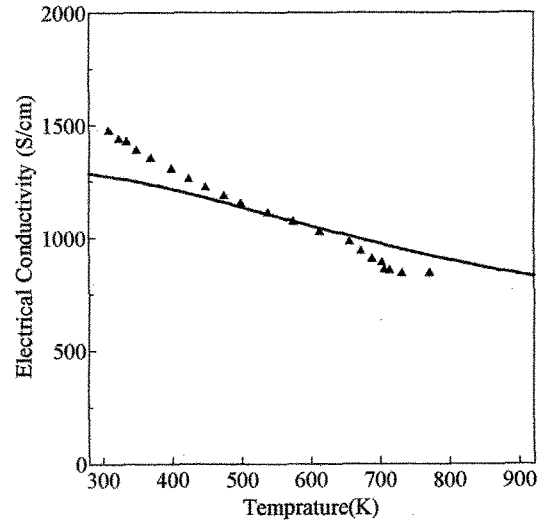

Fig.6 Temperature dependence of electrical conductivity for $Ba_8Al_{16}Si_{30}$.

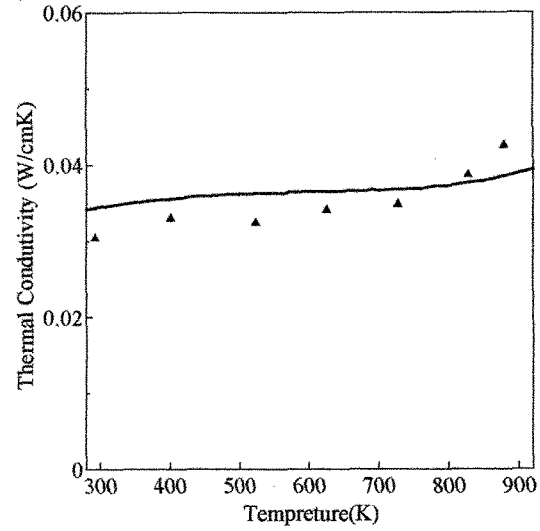

Fig.7 Temperature dependence of thermal conductivity for $Ba_8Al_{16}Si_{30}$.

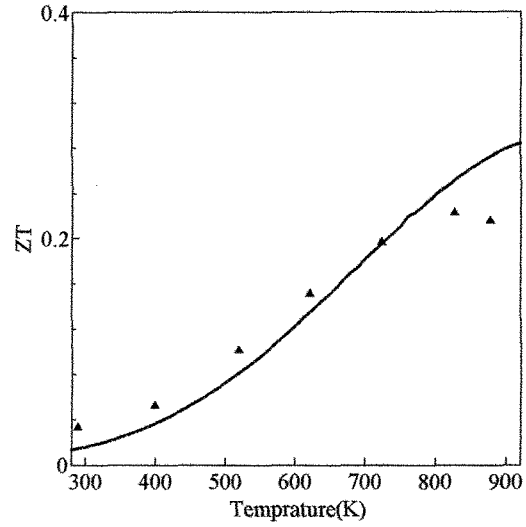

Fig.8 Temperature dependence of ZT for $Ba_8Al_{16}Si_{30}$.

References

[1] B. C. Sales, B. C. Chakoumakos, R. Jin, J. R. Thompson and D. Mandrus, Phys. Rev. B, 63, 245113 (2001).

[2] G. A. Slack, Materials Research Society, 478, 47 (1997).

[3]B. Eisenmann, H. Schäfer and R. Zagler, J. Less-common Metals, 118(1986)

[4]D. Natarj, J. Nagao, M. Ferhat, T. Ebinuma and H. Anno, Proceedings ICT'02 (2002) pp. 72-75.

[5]T. Koyanagi *et al.*, Private Communication.

[6] P. Blaha, K. Schwarz, G. Madsen, D. Kvasnicka and J. Luitz, Computer code WIEN2K, Karlheinz Schwarz, Technical Universitat, Wien, Austria, (1999).

[7] J. P. Perdew, S. Burke and M. Ernzerhof, Phys. Rev. Lett., 77, 3865 (1996).

[8] N. P. Blake, J. D. Bryan, S. latturner, L. Møllnitz, G. D. Stucky and H. Metiu, J. Chem. Phys., **114**, 10063 (2001).

[9] N. P. Blake, S. latturner, J. D. Bryan, G. D. Stucky, H. Metiu, J. Chem. Phys., **115**, 8060 (2001).

(Received January 15, 2006; Accepted March 30, 2006)