Transactions of the Materials Research Society of Japan 29 [8] 3651-3654 (2004)

Electronic structure, and thermoelectronic properties of the clathrates $Ba_8Ga_{16}Si_{30}$ and $Ba_8Ga_{16}Ge_{30}$

Tatsuya Kamei, Kenji Koga, Koji Akai, Kazunori Osiro, Mitsuru Matsuura
Faculty of Engineering, Yamaguchi University, 2-16-1, Tokiwa, Ube-shi, Yamaguchi, 755-8611 Japan
Fax: 81-836-85-9622, e-mail: z018fg@yamaguchi-u.ac.jp

The first principle full-potential linearlized augmented plane wave (FLAPW) method, based on the density functional theory, is used to discuss electronic and thermoelectric properties of the clathrates $Ba_8Ga_{16}Si_{30}$ and $Ba_8Ga_{16}Ge_{30}$. The lattice constants are calculated by minimizing the total energy of the system. Then the electronic structure and density of states are calculated. The clathrates $Ba_8Ga_{16}Si_{30}$ and $Ba_8Ga_{16}Ge_{30}$ are indirect semiconductors with the energy gap E_g=0.44 eV and 0.54 eV, respectively. The atomic origins of the various bands are clarified from the character of the wave function. The results are used to calculate Seebeck coefficient. Choosing the carrier density as adjustable parameters, experimental results can be reproduced very well in the wide range of temperature.
Key words: thermoelectric material, clathrate, FLAPW, Seebeck coefficient

1. INTRODUCTION

Clathrates $Ba_8Ga_{16}Si_{30}$ and $Ba_8Ga_{16}Ge_{30}$ exhibit large electrical conductivities (σ), large Seebeck coefficients (S), and small thermal conductivities (κ) [1].All of these factors combine to yield a relatively high figure of merit $ZT=S^2\sigma T/\kappa$.

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, shown in Fig. 1. The "rattling" motion of guest atoms produces low- frequency anharmonic phonon modes, which strongly scatter the heat carrying acoustic modes. This rattling scattering will significantly reduce the thermal conductivity to be a glass-like value without reducing the crystalline electrical conductivity, which is mainly determined by the framework.

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

Recently, Blake et al. determined the atomic structure by minimizing the total energy using the first principle electronic calculation. The determined atomic structure agrees well with those determined by X-ray diffraction [3]. They could also determine the Ga sitting which X-ray diffraction did not. Then, they calculated the electronic structure and study thermoelectronic properties of some clathrates $Ba_8Ga_{16}Ge_{30}$, $Sr_8Ga_{16}Ge_{30}$, $Ba_8Ga_{16}Si_{30}$, and $Ba_8In_{16}Sn_{30}$ [4].

In this work, using the first principle electronic calculation of FLAPW method we will calculate the Seebeck coefficient, whose, experiment is now available for comparison. Firstly the lattice constant determine theoretically from the minimization of the total energy. Then, by using the determined lattice parameter we calculate electronic structure. The results are used to calculate Seebeck coefficient in comparison with the experiment.

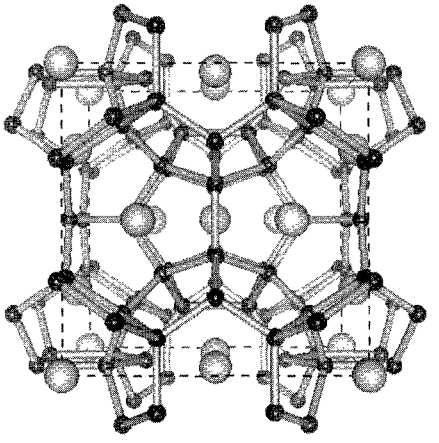

Fig. 1 Structure of clathrate $Ba_8Ga_{16}Si_{30}$ and $Ba_8Ga_{16}Ge_{30}$ consist of dodecahedral cages and tetrakeidecahedral cages of Ga and Si (Ge). Ba inside the polyhedra.

2. CALCULATION OF THE ELECTRONIC STRUCTURE

2.1 Volume optimization

The ab initio calculation has been performed using the full potential linearlized augmented plane wave (FLAPW) method based on density-functional theory [5]. The clathrate structures $Ba_8Ga_{16}Si_{30}$ and $Ba_8Ga_{16}Ge_{30}$ have the simple cubic lattice and space group $Pm\bar{3}n$ (No 223). The Ba atom and Ga, Si atoms occupy at 2a

(0, 0, 0), 6d (0.25, 0.5, 0) and 6c (0.25, 0, 0.5) 16i (x, x, x) 24k (0, y, z) of $Pm\bar{3}n$ Wycoff positions, respectively. Blake et al. calculated theoretically Ga sitting from the minimization of the total energy. Thus, on the Ga sitting we have used their result, i.e., 1 in 6c sites, 3 in 16i sites and 12 in 24k sites. Three position parameters x=0.1854, y=0.3062, z=0.1193 have been determined experimentally from X-ray diffraction [3].

In the calculation, we has used the following set of APW parameters: R_{mt} (Ba)=3.0 a.u., R_{mt} (Ga)=2.2 a.u., R_{mt} (Si)=2.2 a.u., $R_{mt}K_{max}$=7 and G_{max}=14 $Ry^{1/2}$. 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), and 129223 plane waves were used for constructing APWs. For all the calculation we have used the modified tetrahedron method for Brillouin zone integrations. All the *k*-point meshes have been checked for convergence. For the exchange-correlation potential we have used the GGA of Perdew et al [6].

Firstly we discuss the lattice constant determined by the minimization of the total energy. For the calculation of the total energy we need to calculate the electronic structure, which have been performed by the first principle FLAPW method, described above. Fig. 2 shows total energy as a function of the lattice constant. The figure shows the minimized value 10.60 (Å) for the lattice constant, which is compared with the experimental value 10.54 (Å). Both differ only by 0.5% each other. The similar calculation have been performed in $Ba_8Ga_{16}Ge_{30}$ and the result yield the lattice constant a=10.91 (Å), which is also close to the experimental value a=10.76 (Å).

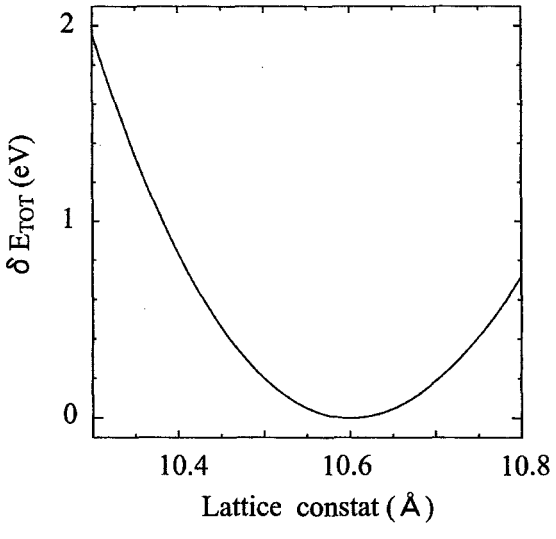

Fig. 2 The total energy as a function of the lattice constant in $Ba_8Ga_{16}Si_{30}$.

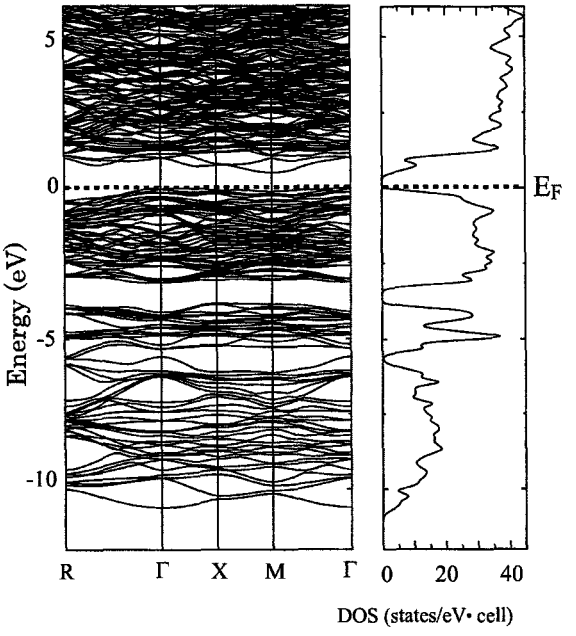

Fig. 3 The band structure and DOS for $Ba_8Ga_{16}Si_{30}$. The energy is referred to the Fermi level.

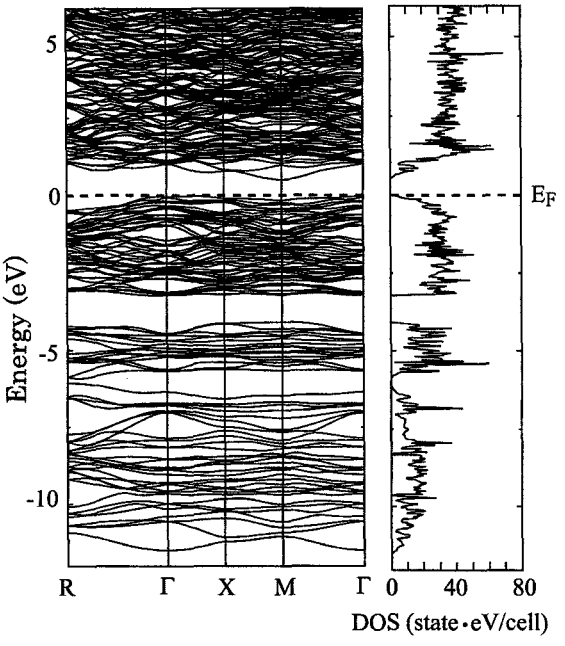

Fig. 4 The band structure and DOS for $Ba_8Ga_{16}Ge_{30}$. The energy is referred to the Fermi level.

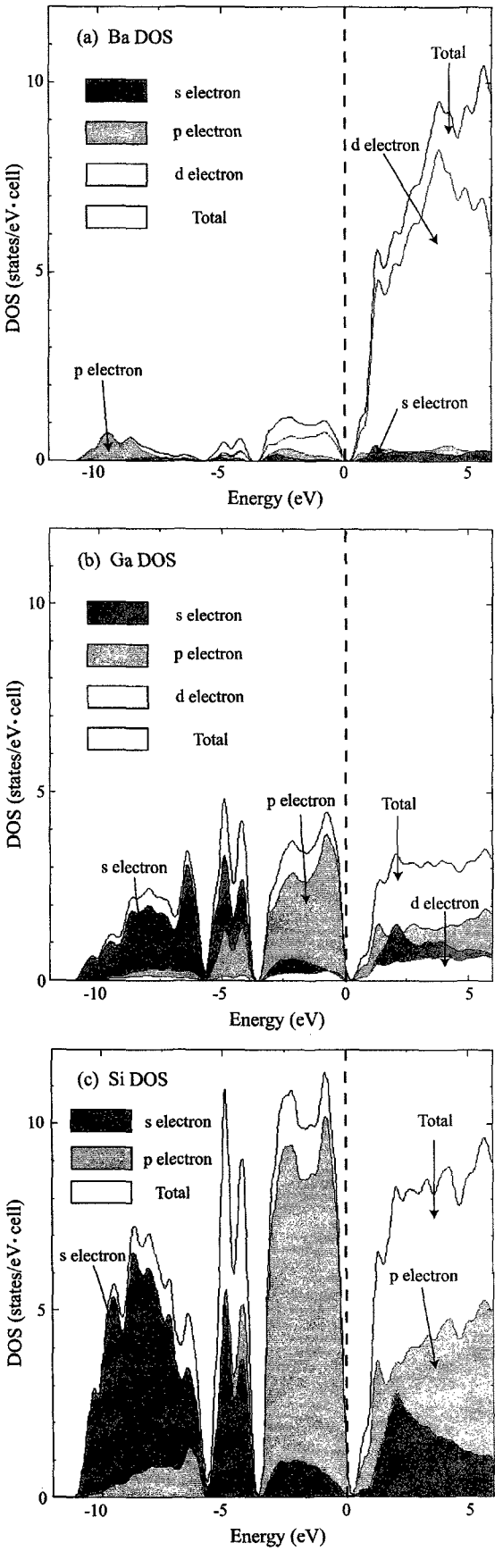

Fig. 5 Partial DOS for (a) Ba, (b) Ga and (c) Si in the $Ba_8Ga_{16}Si_{30}$

2.2 Electronic structure

Band structure and the density of states (DOS) in $Ba_8Ga_{16}Si_{30}$ and $Ba_8Ga_{16}Ge_{30}$ are shown in Fig. 3 and 4, respectively. Dotted lines denote the Fermi level, i.e., the top of the valence band: both are semiconductors. The clathrates $Ba_8Ga_{16}Si_{30}$ and $Ba_8Ga_{16}Ge_{30}$ are indirect semiconductors with the energy gap E_g=0.44 eV and E_g=0.54 eV. The top of valence band is relatively flat nature (near Γ). The bottom of conduction band is positioned at the M point and has a parabolic nature. The band gap and the overall structure in the wide energy range are in a good agreement with those of N. P. Blake et al.

Fig. 5 shows partial density of states of $Ba_8Ga_{16}Si_{30}$. The region from –4 to 0 mainly consists of s-electrons of Ga, Si atoms and a small number of d-electrons of Ba atoms are included. The conduction band region is mainly occupied s- and p-electrons of Ga, Si atoms and d-electrons of Ba atoms. This way, d-electrons of Ba flow in the framework of Si and Ga atoms whose mobility has a large value. Calthrate's $Ba_8Ga_{16}Si_{30}$ and $Ba_8Ga_{16}Ge_{30}$ may have a large electrical conductivity.

3. CALCULATION OF THE SEEBECK COFFICIENT

By using the linerlized Boltzmann equation with the relaxation time approximation, the Seebeck coefficient α and the electric conductivity σ_e are given as

$$\alpha = \frac{8\pi e}{3T\sigma_e}\int d\varepsilon\left(-\frac{\partial f}{\partial \varepsilon}\right)\rho(\varepsilon)\tau(\varepsilon)v(\varepsilon)^2(\varepsilon-\mu), \quad (1)$$

with

$$\sigma_e = \frac{8\pi e^2}{3}\int d\varepsilon\left(-\frac{\partial f}{\partial \varepsilon}\right)\rho(\varepsilon)\tau(\varepsilon)v(\varepsilon)^2, \quad (2)$$

where $\rho(\varepsilon)$, $\tau(\varepsilon)$ are the density of state and relaxation time, f(ε) is Fermi distribution function, μ is the chemical potential, i.e. Fermi energy. The velocity $v(\varepsilon)$ is given as

$$v(\varepsilon)^2 = \sum_{nk}\left|\frac{\partial \varepsilon_{nk}}{\hbar\,\partial k}\right|^2 \delta(\varepsilon-\varepsilon_{nk}). \quad (3)$$

In the present calculation the energy dependence of $\tau(\varepsilon)$ will be neglected, then $\tau(\varepsilon)=\tau$, involved in (1), cancel out. Thus, α, being independent of τ, can be calculated only by the electronic structure, assuming that the band structure is not to be changed when carrier (electron, hole) is doped.

The calculated and experimental Seebeck coefficient of n-doped $Ba_8Ga_{16}Si_{30}$ is shown in Fig. 6 as a function of temperature. By choosing the electron concentration as a parameter, Seebeck coefficient is calculated. Solid lines denote the result corresponding to three electron concentration 1×10^{18}, 1×10^{19} and 1×10^{20}. The open circles and the closed triangles are the experimental results by Koyanagi group [7] and by V. L. Kuznetsov et al. [8]. It is seen that calculation with the electron concentration of 8×10^{19} can reproduce the both experiments fairly well in the wide range of temperature.

We should pay attention the behavior of calculated the Seebeck coefficient for the various electron concentrations. For the electrons concentration of 1×10^{18} the highest Seebeck coefficient value, approximately –300 (μV/K) at 550 (K) is obtained. But Seebeck coefficient decreases rapidly in high temperature. The origin of the decrease in high temperature region is thermal excitation of electrons. As the electron concentration increase, this effect became gradually smaller.

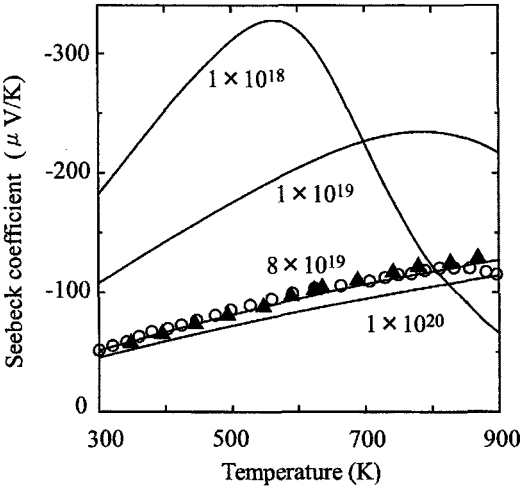

Fig. 6 The Seebeck coefficient of n-doped $Ba_8Ga_{16}Si_{30}$ as a function of temperature. Solid lines denote calculated Seebeck coefficient for three electron concentration 1×10^{18}, 1×10^{19} and 1×10^{20}. The open circles and the closed triangles are the experimental results by Koyanagi group [7] and by V. L. Kuznetsov et al. [8], respectively.

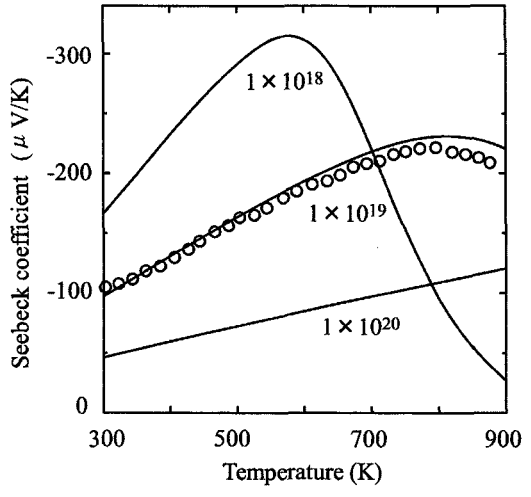

Fig. 7 The Seebeck coefficient of n-doped $Ba_8Ga_{16}Ge_{30}$ as a function of temperature. Solid lines denote calculated Seebeck coefficient for three electron concentration 1×10^{18}, 1×10^{19} and 1×10^{20}. The open circles are the experimental resultss by Koyanagi group [7].

For the electron concentration of 1×10^{19} high Seebeck coefficient of around –200 (μV/K) is realized in the wide temperature of range. For the electron concentration of 1×10^{20} the decrease of the Seebeck coefficient in high temperature does not appear in the temperature range in the present figure.

The calculated and experimental Seebeck coefficients of n-doped $Ba_8Ga_{16}Ge_{30}$ are shown in Fig. 6 as a function of temperature. By choosing the electron concentration as a parameter. Seebeck coefficient is calculated. Solid lines denote the result correspond to three electron concentration 1×10^{18}, 1×10^{19} and 1×10^{20}. The open circles are the experimental results by Koyanagi group [7]. It is found that calculation with the electron concentration of 1×10^{19} can also reproduce the experiment very well in the wide range of temperature. For the various electron concentrations, Seebeck coefficient in $Ba_8Ga_{16}Ge_{30}$ behaves similarly as in the case of $Ba_8Ga_{16}Si_{30}$.

4. CONCLUTION

We have calculated the electronic structure of the clathrate $Ba_8Ga_{16}Si_{30}$ and $Ba_8Ga_{16}Ge_{30}$ by using first principle FLAPW method with GGA. $Ba_8Ga_{16}Si_{30}$ and $Ba_8Ga_{16}Ge_{30}$ are indirect semiconductor of energy gap E_g=0.44 (eV) and 0.54 (eV), respectively. The top of valence band is relatively flat nature (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 mainly s-, p-electrons of Ga, Si (Ge) atoms and d-electrons of Ba atoms.

The results are used to calculate important thermoelectric property, i.e., Seebeck coefficient, choosing the carrier density as a parameter. For both $Ba_8Ga_{16}Si_{30}$ and $Ba_8Ga_{16}Ge_{30}$, the calculation can reproduce the experiment very well in the wide range of temperature.

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(Received October 21, 2003; Accepted June 25, 2004)