Influence of preparation conditions on thermoelectric properties of Ba$_8$Ga$_{16}$Si$_{30}$ clathrate by combining arc melting and spark plasma sintering methods

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Abstract. We have investigated the thermoelectric properties of clathrate samples with a nominal Ba$_8$Ga$_{16}$Si$_{30}$ composition, prepared by combining arc melting and spark plasma sintering methods under different conditions. The carrier concentration of the samples greatly decreases from the order of $10^{21}$ cm$^{-3}$ to $10^{20}$ cm$^{-3}$ due to an increase in Ga content by changing the arc melting conditions. Consequently, the Seebeck coefficient increases and the thermal conductivity decreases while the electrical conductivity decreases. The effective mass, carrier mobility and lattice thermal conductivity are determined from an analysis using a single parabolic band model with alloy disorder and phonon scattering mechanisms. The thermoelectric figure of merit $ZT$ significantly increases up to about 0.55 (900 K) for a carrier concentration of about $6 \times 10^{20}$ cm$^{-3}$ (RT). The simulation predicts that $ZT$ can reach 0.8 (900 K) at the optimum carrier concentration (about $2 \times 10^{20}$ cm$^{-3}$) in the Ba$_8$Ga$_{16}$Si$_{30}$ system.

1. Introduction

Inorganic clathrate systems, a class of semiconductors, have received much attention as high temperature thermoelectric materials based on the phonon-glass electron-crystal concept [1–5]. Among silicon clathrate systems, Ba$_{16}$Si$_{30}$ clathrate has been well characterized and demonstrated to be a potential material for high temperature applications by several researchers [6–11]. In Si clathrate systems, a deviation of the chemical composition from the Zintl condition, however, easily occurs and yields excess carriers, which degrade the thermoelectric properties due to a shift to the metallic region [12–14]. The control of the chemical composition of the Ba$_{16}$Si$_{30}$ system is one of key factors for improving the thermoelectric properties. The crystallographic properties of the Ba$_{16}$Si$_{30}$ system, including the chemical composition, defects, and homogeneity are significantly affected by the synthesis method. We have reported the thermoelectric properties of several polycrystalline Ge- and Si-based clathrates prepared by combining arc melting and spark plasma sintering (SPS) methods [15–20]. Most recently, Tsujii et al. [14] reported the synthesis of polycrystalline Ba$_{16}$Al$_{18}$Si$_{46-x}$ clathrates without a framework deficiency by a similar approach and details of their thermoelectric properties. These results support the advantage of the arc melting method for preparation of polycrystalline Si clathrates. Thus, the influence of the synthesis conditions on the chemical composition and the thermoelectric properties is one of the most important issues to...
be investigated in order to determine the ideal synthesis conditions for $\text{Ba}_8\text{Ga}_{16}\text{Si}_{30}$ clathrate. Therefore, in the present study, we prepared polycrystalline $\text{Ba}_8\text{Ga}_{16}\text{Si}_{30}$ (nominal composition) clathrate samples by combining arc melting and SPS methods under different conditions, and investigated their thermoelectric properties.

2. Experimental

Ba ingots (3N), Ga shots (5N) and Si grains (5N) were used as starting materials. $\text{Ba}_8\text{Ga}_{16}\text{Si}_{30}$ clathrate samples were first synthesized by arc melting of the constituent elements with the Ba-rich composition $\text{Ba}_{8.2}\text{Ga}_{16}\text{Si}_{30}$ at different arc melting times and arc currents of $A_1$ (short time: 4.4 min×5 times, 150 A), $A_2$ (short time: 4.6 min×5 times, 250 A), $B_1$ (long time: 16.4 min×5 times, 150 A) and $B_2$ (long time: 22.6 min×5 times, 200 A) in an argon atmosphere. Then, the arc ingots were ground to powder (< 90 $\mu$m) and the materials were sintered at 30 or 60 MPa and 1113–1273 K for 60–120 min in an argon atmosphere by using a SPS technique to obtain dense samples. Powder x-ray diffraction (XRD) measurements were performed at room temperature in the $2\theta$ range of 10–80 deg using CuKα radiation (40 kV and 40 mA) with a Rigaku Ultima-III diffractometer. The chemical compositions were determined from the polished surface of the sintered samples by field-emission scanning electron microscopy (FE-SEM, Hitachi High Technologies S-4800) combined with energy-dispersive x-ray spectroscopy (EDS, EDAX Inc).

Measurements of the electrical conductivity $\sigma$ and the Seebeck coefficient $S$ were performed in the temperature range of 300–900 K. Hall measurements were conducted at room temperature by applying an external magnetic field of 1 T using the van der Pauw method. The Hall carrier concentration $n$ was determined from the Hall coefficient $R_H$ using the relation $R_H = 1/en$, where $e$ is the electron charge. The Hall mobility $\mu$ was determined from the electrical conductivity $\sigma$ and the Hall coefficient $R_H$ using the relation $\mu = \sigma R_H$. The thermal diffusivity $\alpha$ and the specific heat $C_p$ were measured by the flash method (Xe flash analyzer, Netzsch LFA447). The thermal conductivity $\kappa$ was calculated by using the relation $\kappa = \rho \alpha C_p$, where $\rho$ is the density of the sample.

3. Results and discussion

![Figure 1. X-ray diffraction patterns for samples prepared under different conditions.](image1)

![Figure 2. SEM image and elemental mapping for selected sample (B1 condition).](image2)
Table 1. Chemical composition, lattice constant \( a \) (nm), density \( \rho \) (g/cm\(^3\)), carrier concentration \( n \) (10\(^{20}\) cm\(^{-3}\)), Seebeck coefficient \( S \) (\( \mu \)V/K), electrical conductivity \( \sigma \) (S/cm) and thermal conductivity \( \kappa \) (W m\(^{-1}\) K\(^{-1}\)) at room temperature for samples prepared under different conditions.

| Conditions | EDS composition | \( a \)   | \( \rho \) | \( n \)   | \( S \) | \( \sigma \) | \( \kappa \) |
|------------|----------------|-----------|-----------|-----------|-------|------------|-----------|
|            | Ba  | Ga  | Si  | 1.0539 | 4.287 | 13.5 | -41.6   | 1280 | 2.19     |
| A1         | 7.65| 14.42| 31.93|         |       |       |         |       |
| A2         | 7.72| 13.96| 32.32|         |       |       |         |       |
| B1         | 7.65| 14.51| 31.84| 1.0545 | 4.306 | 5.57 | -54.6   | 947  | 1.75     |
| B2         | 7.77| 14.55| 31.69| 1.0544 | 4.279 | 9.52 | -49.2   | 1090 | 1.74     |

Figure 3. Temperature dependence of Seebeck coefficient for samples prepared under different conditions.

Figure 4. Seebeck coefficient as a function of carrier concentration for samples prepared under different conditions.
Seebeck coefficient of the samples prepared under different conditions is shown in figure 4 as a function of the carrier concentration. As mentioned above, the absolute value of the Seebeck coefficient increases with decreasing carrier concentration. The dashed curves indicate the calculated Seebeck coefficient values at different effective mass $m^*$ values using the Boltzmann transport equation. The calculation of the Seebeck coefficient as well as the estimation of the effective mass will be described in detail later. The Seebeck coefficient values vary with the carrier concentration, and it seems that the effective mass $m^*$ of the samples is around $2.0m_0$ ($m_0$: the free electron mass).

Figure 5 shows a log-log plot of the temperature dependence of the electrical conductivity for samples prepared under different conditions. The temperature dependence indicates the saturation region and the electrical conductivity decreases with increasing temperature according to the scattering mechanism of carriers. We first examine the transport mechanism in the samples. In the saturation region, assuming the carrier concentration is constant, the temperature dependence of the electrical conductivity depends on the temperature dependence of the carrier mobility. The solid and dashed lines in figure 5 show the relation $\sigma \propto \mu \propto T^{-r}$ for $r = -1/2$ and $-3/2$ respectively. The temperature dependence below 700 K for all samples is very close to the relation $T^{-1/2}$ for a scattering mechanism due to alloy disorder (energy dependence $E^{-1/2}$) [21, 22]. As one possible explanation, it is likely that the disorder scattering is due to a non-uniform distribution of Ga atoms substituted for Si atoms, as is the case for Ge clathrates such as Ba$_8$Cu$_x$Ga$_{46-x}$Ge$_{4}$ [17] and Sr$_8$Ga$_{x}$Ge$_{46-x}$ [18]. On the other hand, at high temperatures above 700 K, the temperature dependence seems to come close to the relation $T^{-3/2}$ for a scattering mechanism due to acoustic phonon scattering (energy dependence $E^{-1/2}$) [22]. We thus estimated the density-of-states effective mass $m^*$ from the carrier concentration dependence of the Seebeck coefficient at room temperature by assuming a single parabolic band model with alloy disorder scattering and/or acoustic phonon scattering as the dominant scattering mechanism (energy dependence $E^{-1/2}$), as follows [23]. The Seebeck coefficient $S$ is given by

$$ S = -\frac{k_B}{e} \left[ 2 \frac{F_\eta(n)}{F_\eta(\eta)} - \eta \right], $$

where $k_B$ is the Boltzmann constant, $\eta$ is the reduced Fermi energy and $F_\eta$ is the Fermi-Dirac integral of $n$-th order. The carrier concentration $n$ is given by

$$ n = \frac{4}{\sqrt{\pi}} \left( \frac{2\pi m^* k_B T}{h^2} \right)^{3/2} F_{3/2}(\eta), $$

$$ F_{3/2}(\eta) = \int_0^\eta \frac{e^{-x^2} dx}{\sqrt{x}}, $$

$$ F_{3/2}(\eta) = \frac{1}{2} \sqrt{\frac{\pi}{2}} \left[ 1 + \frac{1}{\sqrt{\pi}} \int_0^\eta e^{-x^2} dx \right]. $$
where \( h \) is the Planck constant. The dashed curves in figure 4 are calculated using equations (1) and (2) as a function of \( \eta \) for different effective mass values. The effective mass \( m^* \) for the samples is almost constant at about \( 2.0m_0 \). The effective mass \( m^* \) value of the samples agrees well with the value reported \( (m^* = 2.2m_0) \) by Kuznetsov et al. [7]. The effective mass \( m^* \) of the samples is larger than the reported ones for n-type Ba\(_8\)Ga\(_{46-x}\)Ge\(_{46}\)–x clathrates [16], suggesting that the optimum carrier concentration for the Ba\(_8\)Ga\(_{16}\)Si\(_{30}\) system should be higher than that for Ba\(_8\)Ga\(_{46}\)–x.

The room temperature Hall mobility of samples prepared under different conditions is plotted in figure 6 as a function of the carrier concentration. The Hall mobility increases gradually with decreasing carrier concentration. The Hall mobility for the samples is comparable to that for Ba\(_8\)Ga\(_{46}\)–x clathrate samples [16]. The Hall mobility value is about 10 cm\(^2\)V\(^{-1}\)s\(^{-1}\) in the carrier concentration range of \( 10^{20} \) cm\(^{-3}\), which corresponds to the optimum carrier concentration (about \( 2\times10^{20} \) cm\(^{-3}\)), as mentioned later. The relaxation time \( (\tau = \mu m^*/e) \) of the order of \( 10^{-14} \) s is consistent with the typical value obtained in theoretical calculations of the transport properties of some clathrates [8].

Figure 7 shows the temperature dependence of the thermal conductivity of the samples prepared under different conditions. The thermal conductivity \( \kappa \) for the B1 and B2 conditions is smaller than that for the A1 and A2 conditions. One of factors that cause the difference in the thermal conductivity is the difference in the electronic contribution \( \kappa_e \) to \( \kappa \). The electronic thermal conductivity \( \kappa_e \) was estimated by the Wiedemann-Franz relation \( \kappa_e = LT\sigma \), where \( L \) is the Lorenz number. \( L \) was calculated using the reduced Fermi energy determined from the Seebeck coefficient by the Boltzmann transport
The dimensionless thermoelectric figure of merit \( ZT \) was estimated from the temperature dependence of the Lorenz number \( L \) for samples prepared under different conditions. The Lorenz number for the B1 and B2 conditions was smaller than that for the A1 and A2 conditions due to the lower carrier concentration. The electronic thermal conductivity \( \kappa_e \) for the B1 and B2 conditions is lower than that for the A1 and A2 conditions due to the smaller \( L \) and \( \sigma \). The lattice thermal conductivity \( \kappa_L \) was thus estimated by subtracting the electronic thermal conductivity \( \kappa_e \) from \( \kappa \). Figure 9 shows the temperature dependence of the lattice thermal conductivity \( \kappa_L \) for samples prepared under different conditions. The lattice thermal conductivity \( \kappa_L \) for the B1 and B2 conditions is lower than that for the A1 and A2 conditions. The lattice thermal conductivity \( \kappa_L \) for the B1 condition is estimated to be as low as about 1.1 W m\(^{-1}\) K\(^{-1}\), which is comparable to the reported value for Ba\(_{0.16}\)Ga\(_{0.84}\)Si\(_3\) [4]. The lattice thermal conductivity \( \kappa_L \) decreases with increasing temperature. The temperature behavior is attributed to the Umklapp process as a typical scattering mechanism of phonons at high temperatures [24–27], and is fitted to the relation \( \kappa_L \propto T^{-b} \) (\( b \) is constant): 0.36 < \( b \) < 0.45, which is in good agreement with the theoretical value (\( b = 0.5 \)).

The dimensionless thermoelectric figure of merit \( ZT \) was estimated from the temperature dependence of the Seebeck coefficient \( S \), the electrical conductivity \( \sigma \) and the thermal conductivity \( \kappa \). The thermal conductivity values at 575 K were used in the estimation of \( ZT \) above 575 K. Figure 10 shows the temperature dependence of \( ZT \) for samples prepared under different conditions. As shown in Figure 10, the samples prepared by the B1 and B2 conditions show a relatively high \( ZT \) of about 0.55 at 900 K. The improvement of \( ZT \) is attributed mainly to the decrease in the carrier concentration toward the optimum value (about 2 \times 10^{20} \text{ cm}^{-3} as mentioned below) by achieving a relatively high Ga content.

Figure 11 shows the carrier concentration dependence of the dimensionless thermoelectric figure of merit \( ZT \) for samples prepared under different conditions. \( ZT \) was calculated using a modified model that was proposed originally by Slack [1] with the Boltzmann transport equation using the experimental values of the effective mass \( m^* = 2.0m_0 \), Hall mobility \( \mu_0 = 10 \text{ cm}^2\text{V}^{-1}\text{s}^{-1} \) and lattice thermal conductivity \( \kappa_{L,0} = 1.1 \text{ W m}^{-1}\text{K}^{-1} \) at room temperature. The model calculation takes into account the temperature dependence as \( \mu = \mu_0 (T/T_0)^{-1/2} \) for alloy disorder scattering and \( \kappa_L = \kappa_{L,0} (T/T_0)^{-0.41} \),

\[
L = \left( \frac{k_e}{e} \right)^2 \frac{3F_0(\eta)F_2(\eta) - 4F_1(\eta)^2}{F_0(\eta)^2}.
\]
where the $b$ value is an average value extracted from the experimental fits, assuming a constant $L = 2.44 \times 10^{-8} \ V^2/K^2$. If the Lorenz number presented in figure 8 is used, an estimation of $ZT$ is obtained that is larger than that shown in figure 11. The calculated curve agrees well with the experimental data. Further, the calculation predicts that the $ZT$ at 900 K is about 0.8 at the optimum carrier concentration of about $2 \times 10^{20} \ cm^{-3}$. Thus, it is likely that the $ZT$ value will be further improved if the carrier concentration can be reduced in the Ba$_{8}$Ga$_{16}$Si$_{30}$ system. In addition, the $ZT$ value will become higher if the carrier mobility is improved by optimization of the synthesis process such as annealing of polycrystalline samples.

4. Conclusions
Preparation conditions and the thermoelectric properties were investigated for polycrystalline samples with a nominal Ba$_{8}$Ga$_{16}$Si$_{30}$ composition by combining arc melting and SPS methods. The chemical composition of polycrystalline samples depends significantly on the synthesis conditions. The adjustment of the arc melting conditions leads to an increase in the actual Ga content in the samples. As a result, the carrier concentration of the samples decreases from the order of $10^{21} \ cm^{-3}$ to $10^{20} \ cm^{-3}$. The long arc melting time and low arc current conditions are effective to some degree but still insufficient for obtaining the Zintl condition. The thermoelectric properties of the samples vary reasonably with carrier concentration. The thermoelectric material parameters $m^*$, $\mu$ and $\kappa$ that govern the material efficiency were determined for the polycrystalline samples. The thermoelectric figure of merit $ZT$ was estimated to be about 0.55 at 900 K and a relatively high $ZT$ value of about 0.8 (900 K) is predicted from the material parameters if the carrier concentration is optimized. Further investigation into the optimization of the thermoelectric properties of the Ba$_{8}$Ga$_{16}$Si$_{30}$ system is in progress.

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