Electronic Structures and Thermoelectric Properties of Sb-Doped Type-VIII Clathrate Ba$_8$Ga$_{16}$Sn$_{30}$

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1. Introduction

Group IV-based clathrate compounds have recently attracted considerable attention as high-performance thermoelectric materials because of their "phonon glass and electron crystal" (PGEC) properties. The PGEC properties arise from the cage structure of clathrates; i.e., a guest atom is loosely bound in the host cage, causing anharmonic and localized vibration, which is referred to as rattling. This rattling mode effectively scatters thermal-conducting phonons and causes glass-like low thermal conductivity. Some researchers have reported this PGEC features lead to a high dimensionless figure of merit (ZT) in Ge clathrate compounds, with values of 1.35 (900 K, n-type Ba$_8$Ga$_{16}$Ge$_{30}$), 1.25 (940 K, n-type Ba$_2$Ga$_4$Ge$_{30}$), and 0.9 (680 K, p-type Ba$_8$Au$_{5.3}$Ge$_{40.7}$) being observed. Recently, some authors also reported high ZT values in Sn-based clathrates with type-VIII structures.

Tin-based clathrates have relatively low thermal conductivities compared with other group-IV clathrate families and crystallize to a type-I, type-III, or type-VIII structure. The type-VIII phases of Sn-based clathrates exist, whenever the Ga content and found repulsive Ga-Ga force between the nearest neighbor position. Various properties of ternary Sn-based clathrate BGS-VIII have already been investigated. For example, Kuznetsov et al. and Nolas et al. measured the thermoelectric properties of n-type polycrystalline samples. Additionally, Huo et al. prepared n-type single crystalline samples and measured their thermoelectric properties. They found that Hall mobility of the n-type BGS-VIII was 3.9 × 10$^5$ m$^2$/Vs, which is to the highest among the other clathrate structures. Avila et al. prepared p- and n-type single crystalline samples and reported that their thermoelectric properties were different. Suekuni et al. prepared p- and n-type type-I Ba$_8$Ga$_{16}$Sn$_{30}$ (BGS-I) and BGS-VIII, and studied the thermoelectric properties. Koga et al. calculated the band structure and density of states for BGS-VIII with different Ga content and found repulsive Ga-Ga force between the nearest neighbor position. This feature has been confirmed in type-I clathrates theoretically and experimentally. In our previous study, we theoretically predicted that optimized carrier densities for the ZT in both p- and n-type BGS-VIII are of the order of 10$^26$ m$^{-3}$. Saiga et al. successfully synthesized p-type BGS-VIII samples with the optimum...
carrier concentration and achieved high ZT value at approximately 1.

In addition to the study of ternary compound systems, carrier tuning was attempted by doping the fourth element. In particular, Al- and Cu-doped n-type BGS-VIII samples show high ZT values. On the other hand, Sb-doped p-type BGS-VIII has high ZT value. According to the Znln concept for the clathrate, electron carrier doping is realized by the partial substitution of Sn(5s²5p²) for the Sn(5s²5p²) site. Nevertheless, hole-carriers are introduced by the co-doping of Sb and Ga(4s²4p¹) for BGS-VIII. A single crystal of Sb-doped BGS-VIII (BGSS-VIII) has been synthesized using a self-flux method, and its crystal structure has been confirmed by powder X-ray diffraction analysis. Presence of doped Sb and high Ga content in the single crystal have been confirmed by EPMA analysis. According to the experimental results reported by Saiga et al., the maximum ZT values for both p-type BGS-VIII and BGSS-VIII are approximately 1.0 at around 450 K. The carrier concentration of p-type BGS-VIII samples is 1.4 × 10²⁶ m⁻³, but that of BGSS-VIII samples is unknown. The thermoelectric properties of a compound are strongly affected by its carrier concentration, so the effect of Sb substitution in BGS-VIII remains unclear. It is interesting to investigate whether Sb substitution improves the thermoelectric properties of BGS-VIII. In this study, we calculated the band structure (BS), density of states (DOS), and thermoelectric properties of BGSS-VIII to clarify the differences in the theoretical BS, DOS, and thermoelectric properties between BGSS-VIII and BGS-VIII.

2. Computational Details

2.1 Band structure and density of states calculation

We calculated the BS and DOS of BGSS-VIII using a periodic structure model in which Sb and Ga atoms are randomly and partially positioned at host sites in the unit cell under experimentally determined conditions. EPMA analysis indicated that the chemical composition was Ba₈₀₂₋₀·₀₂−Ga₁₆·₈₁Sn₂₈·₄₆Sb₀·₂₄. For the model calculation, we assumed a chemical formula Ba₈GaₓSn₂₈Sb₁. Based on our previous structural data obtained from the powder X-ray diffraction analysis at SPring-8, it became clear that the site occupation probability of Ga at the 2a site increases as Sb composition increases. However, doped Sb sites have not been determined. The atomic number of Sb is only one more than those of Sn; therefore, these atoms could not be easily identified by the powder X-ray diffraction analysis. To determine the Sb position, we calculated the total energy dependence of four possible Sb positions, sites 2a, 8c, 12d, and 24g (Fig. 1). For each case, we obtained an optimum crystal structure and the total crystal energy. The lattice parameters and total energies of the crystal deduced from our calculations are shown in Table 1. The lowest total energy in above four cases was realized when a Sb atom occupies 8c site. In this study, we calculated the BS and DOS of BGSS-VIII assuming that the 8c site are partly occupied by Sb and compared them with those of BGS-VIII.

The BS and DOS calculations were performed using the full potential linearized augmented plane wave (FLAPW) method based on the density-functional theory. The following radii Rₓ and the plane wave cutoff Kₓ were used for the present calculation. In the self-consistent field calculation, 64 k-point sampling points were used in the first Brillouin zone (BZ). Optimum lattice parameters and atom positions were determined. The Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation (GGA) was then used to estimate the exchange correlation energy. In the BS and the DOS calculation, 512 k-point sampling points were used in the first BZ. The exchange correlation energy of the Engel–Vosko GGA was used for calculation of BS and DOS because the band gap was underestimated for the PBE-GGA potential. We assumed an ordered arrangement of Ga, for BGS-VIII and BGSS-VIII, which gives fewer Ga-Ga nearest neighbor bonds. The ordered arrangement of Ga was chosen in the same way, Carrillo-Cabrera et al. were used.

2.2 Thermoelectric properties

We calculated transport properties using a linearized Boltzmann equation with a relaxation time approximation. We assumed naturally acceptable constant relaxation time. The Seebeck coefficient α, electrical conductivity σ, and electronic thermal conductivity κₑ are given as

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

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

$$\kappa_e = LT\sigma, \quad (3)$$

where ρ(ɛ) is the DOS, τ(ɛ) is the relaxation time, f(ε) is the Fermi distribution function, μ is the chemical potential, v(ɛ) is the carrier velocity, and L is the Lorentz number, 2.45 W/K². The carrier velocity v(ɛ) is then given as

$$\rho(\epsilon)v(\epsilon)^2 = \sum_{nk} \delta(\epsilon - E_{nk}) \left| \frac{\hat{P}}{m_0} |nk\rangle \right|^2. \quad (4)$$

Here, \( \hat{P} \) is the momentum operator, \( m_0 \) is the electron rest mass, and \( |nk\rangle \) and \( E_{nk} \) are the electronic state and energy of the n-th band at wave number k, respectively. In the present calculation, the energy dependence of \( \tau(\epsilon) \) is neglected; therefore, \( \tau(\epsilon) = \tau \). The relaxation time \( \tau \) in eq. (1) is canceled out between Σ in the denominator and the numerator. Thus, the Seebeck coefficient \( \alpha \) is independent of \( \tau \) and can be determined by the BS. We assumed a rigid band scheme, i.e., the BS does not change by the carrier doping (electrons or holes). The dimensionless ZT of thermoelectric material is given by

<table>
<thead>
<tr>
<th>Sb site</th>
<th>Lattice Parameter, a/(10^{-15})m</th>
<th>Total Energy, E/Ry</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>11.839</td>
<td>-555329.371</td>
</tr>
<tr>
<td>8c</td>
<td>11.804</td>
<td>-555329.382</td>
</tr>
<tr>
<td>12d</td>
<td>11.839</td>
<td>-555329.373</td>
</tr>
<tr>
<td>24g</td>
<td>11.805</td>
<td>-555329.372</td>
</tr>
</tbody>
</table>

*Four different calculations were performed for BGSS-VIII while assuming the Sb site to be 2a, 8c, 12d or 24g.
where $\kappa_l$ is the lattice thermal conductivity, which is constant in this study, and $\kappa_e$ is the electronic thermal conductivity. The details of the computational method are explained in Ref. 23).

3. Results and Discussion

3.1 Band structure and density of states

The BSs and DOS for BGS-VIII and BGSS-VIII are shown in Figs. 2 and 3, respectively. The results indicate that both clathrates are indirect band gap semiconductors. The calculated band gaps of BGS-VIII and BGSS-VIII are 0.35 and 0.40 eV, respectively, suggesting that the band gap of BGS-VIII becomes wider after the Sb doping. The band dispersion of the highest valence band in BGSS-VIII is slightly larger than that in BGS-VIII. For the conduction bands, the BSs near the band edge are similar. Figure 4 shows the DOS near the band edge for both the valence and conduction bands. In Fig. 4(a), the slope of the DOS curve for BGSS-VIII is smaller than that for BGS-VIII above $-0.1$ eV, except for the flat region of the DOS for BGS-VIII.

3.2 Thermoelectric properties

We calculated the Seebeck coefficients of both p- and n-type BGSS-VIII using eq. (1) at $n = 1 \times 10^{25}$, $1 \times 10^{26}$, and $1 \times 10^{27}$ m$^{-3}$ as shown in Fig. 5. The Seebeck coefficients of BGS-VIII are also plotted in Fig. 5. The absolute values of Seebeck coefficient of both p- and n-type BGSS-VIII are
similar with those of BGS-VIII because the DOS curve near the Fermi level of BGSS-VIII and BGS-VIII are similar. For both p- and n-type BGS-VIII with \( n = 1 \times 10^{25} \, \text{m}^{-3} \), the Seebeck coefficients decrease at a lower temperature than those of BGSS-VIII, since the band gap of BGS-VIII is narrower than the BGSS-VIII. Figure 6 shows experimental\(^3\) and calculated Seebeck coefficients for p-type BGSS-VIII. The carrier concentrations \( n = 3.8 \times 10^{25} \, 5.6 \times 10^{25} \), \( 7.2 \times 10^{25} \, \text{m}^{-3} \) used in this calculation have been selected to fit the experimental results of Saiga et al.\(^6\)

We also calculated the electrical conductivities for p-type BGSS-VIII using eq. (2). The calculated and experimental electrical conductivities are shown in Fig. 7. The calculated electrical conductivity is fitted with the experimental results at 300 K. The relaxation times for p-type BGSS-VIII and BGS-VIII calculated using the Saiga’s data are \( 1.56 \times 10^{-16} \) and \( 1.62 \times 10^{-15} \, \text{s} \), respectively. These relaxation times are remarkably similar, indicating that Sb substitution does not affect the relaxation time. The relaxation time of BGS-VIII obtained in the present study is three times longer than the previously calculated value (\( \tau = 5.40 \times 10^{-17} \, \text{s} \)).\(^23\) We believe that this difference is due to some difference in the crystallization process of the samples.

Figure 8 shows the calculated thermal conductivity \( \kappa = \kappa_e + \kappa_l \) (\( \kappa_e \): electronic thermal conductivity, \( \kappa_l \): lattice thermal conductivity) of p-type BGSS-VIII with a carrier concentration of \( n = 5.6 \times 10^{25} \, \text{m}^{-3} \). The electronic thermal conductivity \( \kappa_e \) was calculated using eq. (3). The lattice thermal conductivity \( \kappa_l \) of BGSS-VIII was not measured because the sample sizes are too small to measure using the laser-flush method. Hence, we estimated the lattice thermal conductivity from BGS-VIII to be \( \kappa_l = 0.53 \, \text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1} \).\(^6\) This value was then used for the thermal conductivity calculation for p-type BGSS-VIII. The temperature dependence of the lattice thermal conductivity is assumed to be constant in this calculation.

We used eq. (5) to calculate \( ZT \) for p-type BGSS-VIII based on the calculated Seebeck coefficient, electrical conductivity, and thermal conductivity with a carrier concentration of \( n = 5.6 \times 10^{25} \, \text{m}^{-3} \). As shown in Fig. 9, the calculated \( ZT \) of BGSS-VIII reproduces the experimental result well at temperatures below 480 K. However, at temperatures above 480 K, the experimental \( ZT \) decreases much more quickly than the calculated \( ZT \). The reason for this rapid decrease in the experimental \( ZT \) above 480 K is not attribute to the rapid increase in the thermal conductivity as shown in Fig. 4 of Ref. 6). The experimental \( ZT \) values were estimated from the thermal conductivity of BGS-VIII. Saiga et al. reported that the increase in the thermal conductivity of BGS-VIII is attributable to the increase in the thermally exited carriers, i.e., electrons and holes increase by the thermal excitations. On the other hand, in BGSS-VIII, metallic electrical conductivity \( \sigma \) was concluded as exper-
imotional observation shown in Fig. 7 below 550 K. Therefore, we may indicate that in BGSS-VIII the increase of the electronic thermal conductivity \( \kappa_e \) due to electron–hole excitations thermally is negligible below that temperature, and then the \( ZT \) value of p-type BGSS-VIII becomes large as shown in Fig. 9 indicating that the \( ZT \) values exceed 1 at higher temperatures.

Figure 10 shows the calculated \( ZT \) values at 480 K for both p-type BGS-VIII and p-type BGSS-VIII as a function of carrier concentration. The estimated maximum \( ZT \) of p-type BGSS-VIII at 480 K is 1.04 with \( n = 0.8 \times 10^{26} \text{ m}^{-3} \). This maximum \( ZT \) is very similar to the experimental results obtained by Saiga et al., for which \( ZT = 0.98 \). The calculated \( ZT \) values for p-type BGS-VIII and BGSS-VIII are almost identical. This implies that Sb doping of BGS-VIII has great potential for the production of high-performance \( ZT \) materials.

4. Conclusion

We have calculated the BS, DOS, and thermoelectric properties of the Sb-doped type-VIII clathrate Ba\(_8\)Ga\(_{16}\)Sn\(_{30}\). According to the calculated BS values, both BGS-VIII and BGSS-VIII are indirect band-gap semiconductors, and the band gap for BGSS-VIII is wider than that for BGS-VIII. The energy derivative of the DOS curve, \( \frac{\partial \rho}{\partial \varepsilon} \big|_{\varepsilon_E} \), in BGSS-VIII is slightly smaller than that in BGS-VIII, but the energy dispersion of the highest valence band; i.e. the effective mass, \( m^* \), is larger than that in BGS-VIII, and the Seebeck coefficient of the p-type BGSS-VIII and BGS-VIII are similar. On the other hand, Sb-doping provides tunable hole concentration up to the optimized carrier density range. Present calculation indicates that Sb-doped Ba\(_8\)Ga\(_{16}\)Sn\(_{30}\) becomes a high-performance thermoelectric material with \( ZT > 1 \).

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REFERENCES