

# Low Lattice Thermal Conductivities of Sintered Type-II Clathrates $(\text{K}, \text{Ba})_{24}(\text{Ga}, \text{Sn})_{136}$ with Anharmonic and Disordered Guest Potentials Arising from Large Guest-Site Splitting and Ga–Sn Alloyed Frameworks

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## Abstract

The type-I clathrate  $\text{Ba}_8\text{Ga}_{16}\text{Sn}_{30}$  is known to exhibit very low lattice thermal conductivity due to the off-center rattling effect. The present type-II clathrates exhibited lower lattice thermal conductivities than the type-I clathrate at 400–700 K. The lowest value of  $3.3 \text{ mW cm}^{-1}\text{K}^{-1}$  at 640 K is comparable to the theoretical minimum value for Sn. We performed thermoelectric property measurements, crystal structure analyses, and electronic structure calculations for the type-II clathrates to discuss such low values. As a result, we found that the following factors contributed to the reduced thermal conductivities: the large number of atoms (160) in the unit cell, large guest-site splitting and associated off-center rattling in the large cages, and a unique guest

potential. The uniqueness of the guest potential includes the energy depth at the split sites, the anharmonic shape, and the site-to-site variation. This variation is due to the Ga-Sn alloy arrangement at the framework site. Due to their low lattice thermal conductivity, these clathrates achieved a maximum dimensionless figure of merit  $ZT$  of 1.32 at 640 K.

**Keywords:**

thermoelectric materials, clathrates, type-II clathrate, thermal conductivity, rattling, guest potential, site splitting

## Introduction

Since thermoelectric (TE) power generation converts waste heat into electricity, it is an energy-saving technology. High-performance TE materials are required for this purpose. A variety of TE materials have been investigated thus far.<sup>1,2</sup> Sn- and Ge-based clathrates, which feature cage-like structures, are promising materials.<sup>3-5</sup> Guest atoms contained in the cages of the crystal structure cause anharmonic vibrations relative to the host lattice. These vibrations scatter phonons that carry heat, resulting in low thermal conductivity. This is called the rattling effect. Clathrate compounds show several crystal structures with varying cage shapes and numbers.<sup>6</sup> Among these structures, type-I  $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$  ( $ZT = 1.2$  at 1000 K),<sup>7</sup> type-II  $(\text{K},\text{Ba})_{24}(\text{Ga},\text{Sn})_{136}$  ( $ZT = 1.19$  at 602 K),<sup>8</sup> and type-VIII  $\text{Ba}_8\text{Ga}_{16}\text{Sn}_{30}$  ( $ZT = 1.45$  at 500 K)<sup>9</sup> exhibited maximum dimensionless figures of merit,  $ZT$ , exceeding 1 at elevated temperatures. A heat-to-electricity conversion efficiency of approximately 10% can be expected. Clathrate materials are made of low-toxicity elements and exhibit both  $p$ - and  $n$ -type properties. These features are advantageous for practical applications.

The reduction in thermal conductivity due to the rattling effect has been studied both experimentally and theoretically, especially in type-I clathrates.<sup>10-22</sup> It is roughly explained as follows. In phonon dispersion, the lower optical phonon frequency of the guest atoms more



strongly suppresses the acoustic mode, which carries heat. This decreases sound velocity, leading to lower thermal conductivity.<sup>12</sup> Heavier guest atoms or smaller guest atoms, with more free space between the guest and host atoms, have lower optical phonon frequencies.<sup>11</sup> When the free space increases, the guest site splits into multiple sites (Fig. 1(a))<sup>23</sup>. This also reduces thermal conductivity through off-center rattling.<sup>13–16,18,19</sup> Since type-I  $\text{Ba}_8\text{Ga}_{16}\text{Sn}_{30}$  clathrate shows fourfold splitting of guest atoms in the 24-atom cages, it has an extremely low room-temperature (RT) lattice thermal conductivity of  $3.6 \text{ mW cm}^{-1}\text{K}^{-1}$ .<sup>24</sup> This value is the lowest among clathrates and is nearly equal to the theoretical minimum value for Sn,  $3.4 \text{ mW cm}^{-1}\text{K}^{-1}$ .<sup>25</sup>

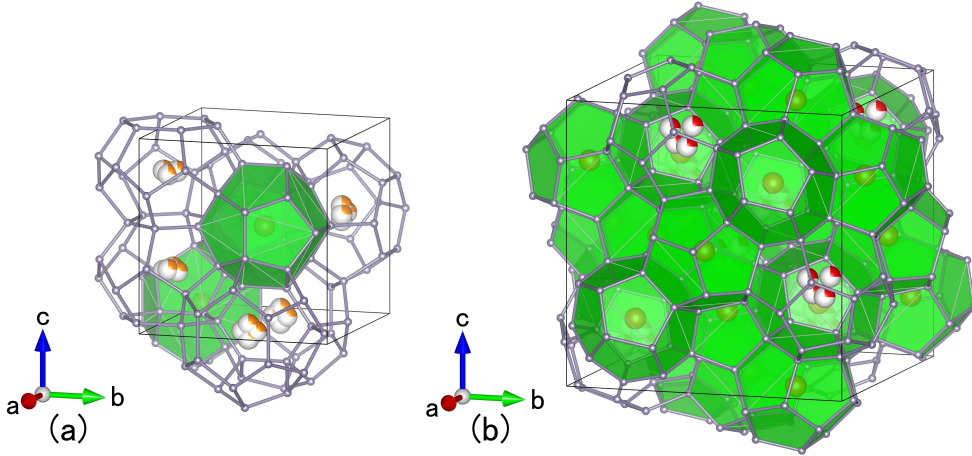


Figure 1: Crystal structures of (a) the type-I  $\text{X}_8\text{Y}_{46}$  ( $\text{X}=\text{Ba}$ ;  $\text{Y}=\text{Ga}, \text{Sn}$ ) (No. 223,  $Pm\bar{3}n$ ) and (b) the type-II  $\text{X}_{24}\text{Y}_{136}$  ( $\text{X}=\text{K}, \text{Ba}$ ;  $\text{Y}=\text{Ga}, \text{Sn}$ ) (No. 227-2,  $Fd\bar{3}m$ ) tin-based clathrates. The former unit cell has six 24-atom cages (transparent) and two 20-atom cages (green), whereas the latter unit cell has eight 28-atom cages (transparent) and sixteen 20-atom cages (green). The guest sites of the 24-atom and 28-atom cages are generally split into four positions  $(1/4 + \delta x, 1/2, \delta z)$  and  $(3/8 + \delta, 3/8 + \delta, 3/8 + \delta)$ , respectively. This figure was drawn using VESTA.<sup>23</sup>

The optical phonon frequency of guest atoms is strongly influenced by the potential energy within the cages.<sup>11,13,14,16,18</sup> Dong *et al.* calculated the guest potential for Ge-based type-I clathrates containing different guest atoms.<sup>11</sup> Figure 2 shows three typical guest potentials schematically.<sup>11</sup> As the cage size increases relative to the guest atom size, the guest potential shape changes: from a quadratic harmonic type (A) to an anharmonic quartic type (B), and

then to a quartic double-well type (C). The quartic function type is off-center<sup>18,19</sup> and can be handled by the soft-potential model (SPM).<sup>19</sup> The double-well type of the quartic function can be treated as a tunneling two-level system. However, actual Ge-based type-I clathrates do not form a double-well type. Phonon dispersion and thermal conductivity for hypothetical clathrates with enlarged cage sizes have been calculated using first-principles calculations.<sup>20</sup> When the cage size of the type-I  $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$  clathrate is virtually enlarged, the guest potential gains significant anharmonic fourth- and sixth-order components and becomes a double-well type. This lowers the optical phonon frequency and drastically reduces thermal conductivity. As a result, the predicted thermal conductivity was lower than the theoretical minimum value for Ge.<sup>25</sup>

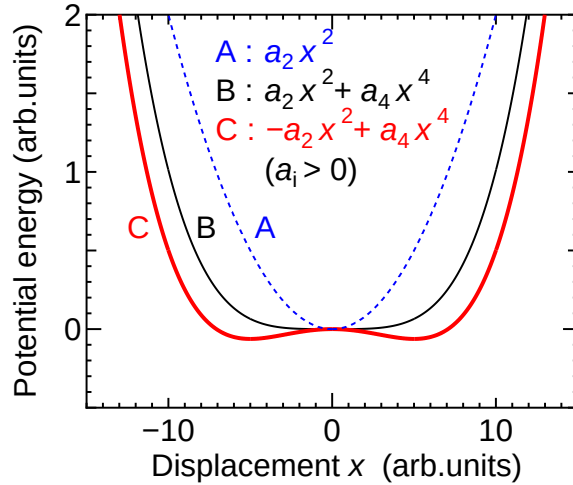


Figure 2: A schematic diagram of typical potential energy curves for guest atoms in clathrates.<sup>11</sup> The  $x$  value is the displacement from the center of the cage.

Type-I clathrates consist of six 24-atom cages and two 20-atom cages, whereas type-II clathrates consist of eight 28-atom cages and sixteen 20-atom cages (Fig. 1). The guest atoms in the 24-atom and 28-atom cages cause rattling motion. Type-II clathrates possess larger rattling cages. The guest sites in the type-II  $(\text{K}, \text{Ba})_{24}(\text{Ga}, \text{Sn})_{136}$  clathrate are split into four, similar to those in the previously mentioned type-I  $\text{Ba}_8\text{Ga}_{16}\text{Sn}_{30}$  (Fig. 1(b)). The off-center rattling in single crystals of type-II  $(\text{K}, \text{Ba})_{24}(\text{Ga}, \text{Sn})_{136}$  was studied by Mano *et al.*<sup>26</sup> The split distances of the guest atoms from the centers for the type-II  $(\text{K}, \text{Ba})_{24}(\text{Ga}, \text{Sn})_{136}$  and

type-I  $\text{Ba}_8\text{Ga}_{16}\text{Sn}_{30}$  clathrates were 0.067 and 0.043 nm, respectively.<sup>18</sup> In both cases, the rattler-atom motions were treated by the SPM containing a tunneling term. Their optical vibrational energies were calculated at 21 and 20 K, respectively, which were very low. Their thermal conductivities below 150 K were as low as  $10 \text{ mW cm}^{-1}\text{K}^{-1}$ . The slightly higher value for the type-II clathrate was explained by the lower density of the rattler atoms (8/24 and 6/8).

The thermal conductivity of type-I  $\text{Ba}_8\text{Ga}_{16}\text{Sn}_{30}$  increased with temperature above RT.<sup>24</sup> In contrast, that of type-II  $(\text{K},\text{Ba})_{24}(\text{Ga},\text{Sn})_{136}$  generally decreased with temperature up to about 500–600 K.<sup>27</sup> Thus, their thermal conductivities above RT show different temperature dependences. We hypothesized that the guest potential within the cage would affect the rattling effect and thermal conductivity at elevated temperatures. Mano *et al.* calculated the electrostatic potential to study the guest-atom motion in the type-II  $(\text{K},\text{Ba})_{24}(\text{Ga},\text{Sn})_{136}$  clathrate.<sup>26</sup> It was of a double-well type, although the distance from the cage center to the minimum was 0.025 nm, which was quite different from the above split distance (0.067 nm). Also, their calculation did not provide information on the well depth or on variations in the electrostatic potential in different split directions. We calculated the guest potentials in the cages for type-I  $\text{Ba}_8\text{Ga}_{16}\text{Sn}_{30}$  and type-II  $(\text{K},\text{Ba})_{24}(\text{Ga},\text{Sn})_{136}$  clathrates. As shown later, the guest potential of the type-II clathrate was of a double-well type, while that of the type-I clathrate was not. The distance from the cage center to the minimum in the type-II clathrate almost corresponded to the split distance determined by X-ray diffraction. Based on these findings, it seems likely that differences in guest potential arising from cage size cause variations in thermal conductivity at high temperatures.

In our previous studies, we investigated the TE properties at elevated temperatures for several sintered samples of the type-II  $(\text{K},\text{Ba})_{24}(\text{Ga},\text{Sn})_{136}$  clathrate with varying carrier concentrations.<sup>8,27,28</sup> The minimum RT lattice thermal conductivity in those studies was  $4.5 \text{ mW cm}^{-1}\text{K}^{-1}$ .<sup>27</sup> This value is slightly higher than  $3.6 \text{ mW cm}^{-1}\text{K}^{-1}$  for type-I  $\text{Ba}_8\text{Ga}_{16}\text{Sn}_{30}$ .<sup>24</sup> This agrees with the relative order at temperatures below 150 K reported by Mano *et al.*

We have already noted<sup>28</sup> that the thermal conductivity of the type-II clathrate was lower than that of other clathrates due to its large atomic displacement parameters (ADPs) and the large number of atoms per unit cell.<sup>29</sup> However, we did not discuss the relationship among the thermal conductivity at elevated temperatures, the split width, and the guest potential. Thus, this study aimed to investigate that relationship. To increase the variety of the sintered samples examined, two additional samples were prepared. Their preparation conditions were slightly modified from the conventional ones. Previously, after sintering, the samples were annealed at 733 K for 168 h. In this study, the samples were annealed once or twice at 773 K for 168 h. The additional samples showed larger split widths, lower thermal conductivities, and higher  $ZT$  values.

In this paper, we study why the type-II  $(\text{K,Ba})_{24}(\text{Ga,Sn})_{136}$  clathrates had low lattice thermal conductivities at elevated temperatures. For that purpose, we investigated the relationship between thermal conductivity and crystal structure for several sintered clathrates with various carrier concentrations and preparation conditions. We also calculated the guest potential using electronic structure calculations. Based on the above results, we discuss how the guest-atom split width and potential affect the reduction in thermal conductivity through the rattling effect. In addition, we measured the TE properties of additional samples to check their performance as TE materials.

## Experimental

### Sample preparation

Additional sintered type-II  $(\text{K,Ba})_{24}(\text{Ga,Sn})_{136}$  clathrate samples were prepared in a manner similar to that used previously.<sup>27,28</sup> K (98%, Sigma-Aldrich), Ba (99.9%, Furuuchi Chemical Corporation), Ga (99.9999%, Furuuchi Chemical Corporation), and Sn (99.999%, Furuuchi Chemical Corporation) were used as starting materials. They were weighed to give a nominal composition ratio of 9K·15Ba·40.5Ga·97.5Sn. The materials were placed in BN-coated Ta

crucibles, which were then sealed in stainless-steel containers under Ar. The containers were kept at 1223 K for 3 h under Ar, followed by holding at 803 K for 120 h. The melted K–Ba–Ga–Sn materials were ground into fine powders. The powders were sintered at 808–813 K for 1 h in H<sub>2</sub> at 0.5 atm under 40 MPa using graphite dies by the spark plasma sintering method (Sumitomo Coal Mining SPS-510L) to obtain disk-shaped samples (20 mm in diameter and 3 mm in thickness). The obtained samples were annealed at 733 K for 168 h in Ar, followed by one or two additional annealing treatments at 773 K for 168 h in Ar.

## Crystal structure analysis

The crystal structures of the samples were examined using a Rigaku Ultima IV X-ray diffractometer operating at 40 kV and 30 mA, with step scans performed with a step width of 0.04 ° and a fixed time of 5 s between 10 ° and 130 °. Rietveld analyses were performed using the RIETAN-FP program<sup>30</sup> to obtain the structural parameters of the samples and the weight percentages of impurity phases. The electron density distributions of the samples were calculated from their XRD data using the maximum entropy method (MEM) implemented in the program Dysnomia.<sup>31</sup> The Rietveld and MEM analyses were performed not only for the samples examined in this study but also for those from our previous studies.<sup>8,27</sup> The microstructures and chemical compositions of the samples were determined using a scanning electron microscope (SEM) (Jeol JSM-7800F) and an energy-dispersive X-ray spectrometer (EDS) (Jeol JED-2300), respectively.

## TE property measurement

The rectangular bar-shaped (approximately 2 × 2 × 15 mm<sup>3</sup>) and smaller disk-shaped (approximately  $\phi 10 \times 2$  mm<sup>3</sup>) specimens were cut from the above disk-shaped samples to measure the TE properties. For the former specimens, the electrical conductivities  $\sigma$  were measured using the four-probe method, and the Seebeck coefficients  $S$  were measured by the steady-state method with a home-made apparatus, with the  $\sigma$  and  $S$  values obtained at elevated

temperatures under vacuum.<sup>8,32</sup> For the latter specimens, the Hall coefficients  $R_H$  were measured at RT using a TOYO ResiTest8340 instrument. The carrier concentrations  $n$  and Hall mobilities  $\mu_H$  were calculated as  $|1/(eR_H)|$  and  $|R_H\sigma|$ , respectively, where  $e$  is the elementary charge. The thermal conductivities  $\kappa$  at elevated temperatures were obtained using the relationship  $\kappa = \alpha C\rho$ , where the thermal diffusivities  $\alpha$  were measured using the laser flash method (Shinku-Riko TC-7000 instrument), the specific heats  $C$  were calculated using the Dulong–Petit law, and the sample densities  $\rho$  were determined using the Archimedes method.  $ZT$  was given by  $S^2\sigma T/\kappa$ , where  $T$  is the temperature. The experimental uncertainties in the measurements of  $\sigma$ ,  $S$ , and  $\kappa$  were less than 5 %, 5 %, and 10 %, respectively.

The effective masses  $m^*$ , or the density-of-states effective masses, were obtained using the equations  $S = -(k/e)\{2F_1(\eta^*)/F_0(\eta^*) - \eta^*\}$  and  $n = 4\pi(2m^*kT/h^2)^{3/2}F_{1/2}(\eta^*)$ , where  $k$  is the Boltzmann constant,  $\eta^*$  is the reduced Fermi energy,  $F_t(\eta^*) = \int_0^\infty \frac{x^t dx}{1+\exp(x-\eta^*)}$  is a Fermi integral of order  $t$ , and  $h$  is Planck’s constant.<sup>33</sup> The lattice thermal conductivities  $\kappa_L$  were estimated as  $\kappa_L = \kappa - L\sigma T$ , where the Lorenz number  $L$  is given by  $(k/e)^2\{3F_2(\eta^*)/F_0(\eta^*) - 4F_1^2(\eta^*)/F_0^2(\eta^*)\}$ .

## Guest potential energy calculation

We calculated the total energies of type-II  $K_8Ba_{16}Ga_{40}Sn_{96}$  clathrates using a full-potential augmented-plane-wave method with the generalized gradient approximation.<sup>34,35</sup> We placed the K and Ba atoms in the 28- and 20-atom cages, respectively. The number of Ga atoms in the Ga–Sn framework was set to 2, 2, and 36 at the  $8a$ ,  $32e$ , and  $96g$  sites, respectively, based on the Rietveld analysis results in this study. The muffin-tin radii  $R_{mt}$  for K, Ba, Ga, and Sn atoms were 2.6, 2.6, 2.4, and 2.5 a.u., respectively, and the plane-wave cutoff energy was 138 eV. In the self-consistent calculation,  $8k$ -point sampling was used throughout the cell.

To obtain the guest-potential energy, we first calculated the total energy of the clathrate structure with eight K atoms positioned at the centers of the 28-atom cages. We next calcu-

lated the total energies of the clathrate structures with two of the eight K atoms displaced from the centers. Then, we determined half of the energy difference between each displaced structure and the centered structure as the guest-potential energy.

## Results and discussion

### Crystal structure and electron density distribution

During the preparation of the type-II  $(\text{K,Ba})_{24}(\text{Ga,Sn})_{136}$  clathrate samples, we annealed the sintered samples to reduce grain-boundary defect density, leading to an increase in sample mobility.<sup>27</sup> In previous studies, the annealing temperature and time were 733 K and 168 h, respectively. The melting point of the type-II  $(\text{K,Ba})_{24}(\text{Ga,Sn})_{136}$  clathrate is 820 K.<sup>28</sup> In this study, the additional annealing temperature was increased to 773 K. The Rietveld analysis results for the sample subjected to two additional annealing treatments (AA3S) are shown in Fig. 3 and Table 1. The SEM image and EDS mapping are shown in Fig. 4. The twice-annealed (AA3S) and once-annealed (A4S) samples exhibit a nearly single-phase type-II clathrate structure, like the previous samples. The guest site in the 28-atom cages was split into four positions, with a split width of 0.091 nm. Its ADP value is approximately one order of magnitude larger than those of other atoms.

Table 1: Structural parameters of the type-II clathrate  $(\text{K,Ba})_{24}(\text{Ga,Sn})_{136}$  sample (AA3S) in this study (No. 227-2,  $Fd\bar{3}m$ ,  $a = 1.70211(6)$  nm), refined by the Rietveld method using powder X-ray diffraction under the following conditions: (1) no vacancies existed; and (2) the chemical composition was equal to the value determined by energy dispersive X-ray spectrometry. The sample included 0.5 and 0.4 wt% impurity phases,  $\beta$ -Sn and the type-I clathrate, respectively. Goodness of fit:  $s = 1.54$ ;  $R_{\text{wp}} = 10.19\%$  and  $R_{\text{p}} = 7.95\%$ .

| Atom        | Site | Occupancy      | $x$        | $y$ | $z$       | $U_{\text{eq}} (10^2 \text{ pm}^2)$ |
|-------------|------|----------------|------------|-----|-----------|-------------------------------------|
| K(1)/Ba(1)  | 32e  | 0.21/0.04      | 0.344(1)   | $x$ | $x$       | 17(3)                               |
| K(2)/Ba(2)  | 16c  | 0.03/0.97(1)   | 0          | 0   | 0         | 2.6(1)                              |
| Ga(1)/Sn(1) | 8a   | 0.23/0.77      | 1/8        | 1/8 | 1/8       | 1.9(2)                              |
| Ga(2)/Sn(2) | 32e  | 0.07(1)/0.93   | 0.2180(1)  | $x$ | $x$       | 1.1(1)                              |
| Ga(3)/Sn(3) | 96g  | 0.378(4)/0.622 | 0.06790(8) | $x$ | 0.3730(1) | 0.83(5)                             |

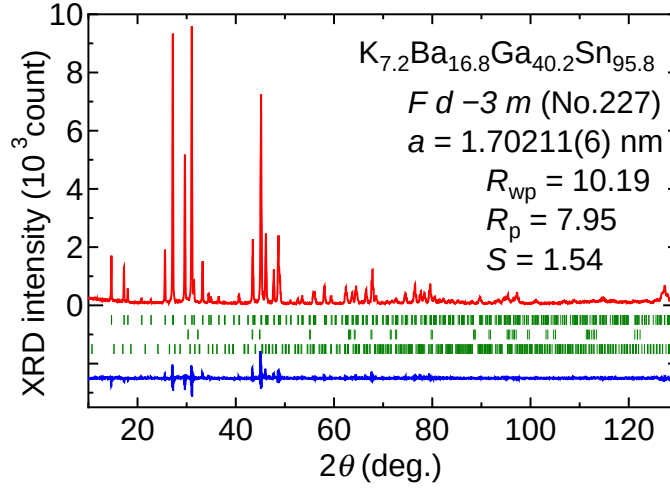


Figure 3: Powder X-ray diffraction pattern of the type-II clathrate  $(\text{K,Ba})_{24}(\text{Ga,Sn})_{136}$  sample (AA3S) refined by Rietveld analysis. The lower pattern (blue) shows the difference profile, and the upper, middle, and lower ticks (green) indicate the positions of the calculated Bragg reflections for the type-II clathrate,  $\beta$ -Sn, and the type-I clathrate, respectively.

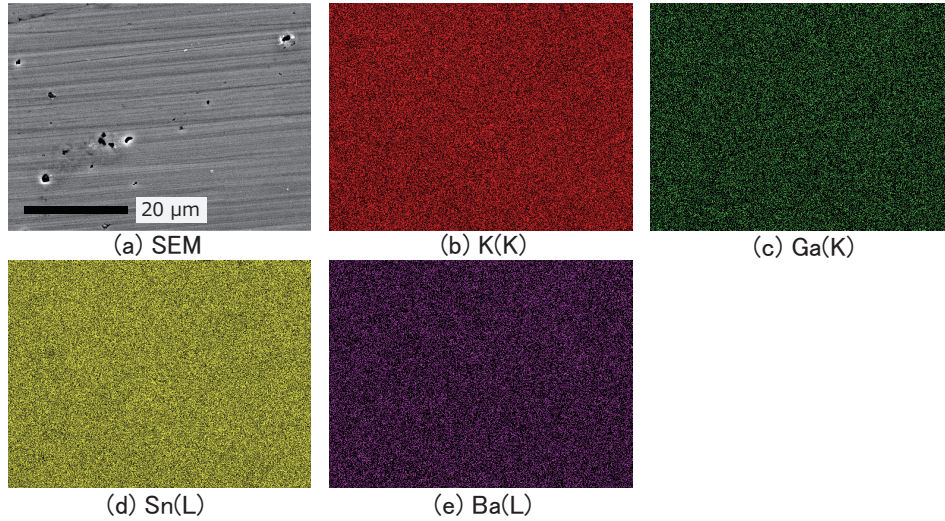


Figure 4: (a) Scanning electron microscopy image and (b)-(e) energy dispersive X-ray spectroscopy mapping for the surface of the type-II clathrate  $(\text{K,Ba})_{24}(\text{Ga,Sn})_{136}$  sample (AA3S).



Table 2 lists the crystal structure parameters, RT physical properties, and the maximum dimensionless figure of merit,  $ZT_{\text{max}}$ , for additional samples and those in previous studies with high  $ZT$ .<sup>8,27</sup> The relative densities of these samples were sufficiently high, ranging from 0.975 to 0.986. It also includes literature values for single crystals.<sup>26</sup> The additional samples had slightly lower weight percentages of impurities such as Sn. In addition, the crystallographic parameters for the guest site in the 28-atom cages differed slightly from those reported for the previous samples. Specifically, the sign and value of the split parameter  $\delta$  ( $= x - 3/8$ ) differed.

Table 2: Room-temperature properties and the maximum dimensionless figure-of-merit  $ZT_{\max}$  of the sintered type-II (K,Ba)<sub>24</sub>(Ga,Sn)<sub>136</sub> clathrate samples in this and previous studies:<sup>8,27</sup>  $a$  (nm), lattice constant;  $\delta$ , split parameter of the guest atoms at the 32e site;  $g(\text{K},32e)$ , occupancy of K atoms at the 32e site;  $U_{\text{eq}}$  ( $10^2$  pm<sup>2</sup>), atomic displacement parameter of the guest atoms at the 32e site;  $W$  (wt.%), weight percentages of  $\beta$ -Sn and type-I clathrate phases;  $\kappa_{\text{L}}$  (mW cm<sup>-1</sup>K<sup>-1</sup>), lattice thermal conductivity;  $\rho$  (g cm<sup>-3</sup>), density;  $n$  ( $10^{19}$ cm<sup>-3</sup>), carrier concentration;  $\mu_{\text{H}}$  (cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>), Hall mobility; and  $m^*(m_e)$ , density-of-states effective mass, where  $m_e$  is the free electron mass. Data for a single crystal are also given.<sup>26</sup>

| Sample ID             | Ref.      | Composition                                                                     | $a$    | $\delta$             | $g(\text{K},32e)$   | $U_{\text{eq}}$ | $W$             | $\kappa_{\text{L}}$ | $\rho$ | $n$  | $\mu_{\text{H}}$ | $m^*$ | $ZT_{\max}$ |
|-----------------------|-----------|---------------------------------------------------------------------------------|--------|----------------------|---------------------|-----------------|-----------------|---------------------|--------|------|------------------|-------|-------------|
| Single crystal        | [26]      | K <sub>9.2</sub> Ba <sub>14.8</sub> Ga <sub>38.0</sub> Sn <sub>95.2</sub>       | 1.7063 | -0.023 <sup>a)</sup> | 0.229 <sup>a)</sup> | 23(1)           | -, -            | -                   | -      | 6.5  | 81               | 0.72  | -           |
| AA3S (two annealings) |           | K <sub>7</sub> Ba <sub>17</sub> Ga <sub>40</sub> Sn <sub>96</sub> <sup>b)</sup> | 1.7021 | -0.031               | 0.21                | 17(3)           | 0.5(2), 0.4(1)  | 4.3                 | 5.516  | 2.53 | 142              | 0.67  | 1.32        |
| A4S (an annealing)    |           | K <sub>7</sub> Ba <sub>17</sub> Ga <sub>42</sub> Sn <sub>94</sub> <sup>b)</sup> | 1.7018 | 0.027                | 0.18                | 33(4)           | 0.16(5), 0.3(1) | 4.6                 | 5.529  | 2.46 | 152              | 0.68  | 1.26        |
| N25                   | Ref. [27] | K <sub>7</sub> Ba <sub>17</sub> Ga <sub>41</sub> Sn <sub>95</sub> <sup>b)</sup> | 1.7040 | 0.028 <sup>c)</sup>  | 0.16                | 37(7)           | 0.55(5), 0.4(1) | 4.8                 | 5.540  | 2.47 | 145              | 0.62  | 1.19        |
| N21                   | Ref. [27] | K <sub>6</sub> Ba <sub>18</sub> Ga <sub>40</sub> Sn <sub>96</sub> <sup>b)</sup> | 1.7038 | - <sup>d)</sup>      | 0.16                | 61(24)          | 0.4(1), 0.4(1)  | 5.1                 | 5.544  | 2.12 | 164              | 0.65  | 1.15        |
| N14                   | Ref. [8]  | K <sub>8</sub> Ba <sub>16</sub> Ga <sub>39</sub> Sn <sub>97</sub> <sup>b)</sup> | 1.7021 | 0.020 <sup>c)</sup>  | 0.13                | 65(11)          | 0.45(4), 0.8(1) | 4.9                 | 5.561  | 1.43 | 161              | 0.66  | 1.19        |
| N11                   | Ref. [27] | K <sub>6</sub> Ba <sub>18</sub> Ga <sub>40</sub> Sn <sub>96</sub> <sup>b)</sup> | 1.7046 | 0.022 <sup>c)</sup>  | 0.16                | 43(10)          | 0.7(1), 0.5(1)  | 4.5                 | 5.529  | 1.08 | 130              | 0.58  | 1.17        |

<sup>a)</sup> These values were obtained at 90 K.<sup>26</sup>

<sup>b)</sup> Actual composition determined by an energy dispersive X-ray spectrometer, where the total numbers of the guest (K, Ba) and host (Ga, Sn) atoms were set to be 24 and 136, respectively.

<sup>c)</sup> Negative values may be available.

<sup>d)</sup> Not strictly determined.

Figure 5 illustrates a 28-atom cage containing a rattler atom at  $(3/8, 3/8, 3/8)$ , which is made of 12 pentagonal rings and 4 hexagonal rings.<sup>23</sup> The centers of three connected pentagonal rings correspond to the 32*e* site, whereas the remaining 24 framework positions are the 96*g* site. The split site of the guest atom with a negative split parameter  $\delta$  exists in the direction from the center of the cage to the 32*e* sites, as indicated by the red balls 1–4 in Fig. 5. The split site with a positive split parameter lies in the direction toward the centers of the hexagons, as shown by the blue balls 5–8 in Fig. 5. These two sites are in opposite directions.

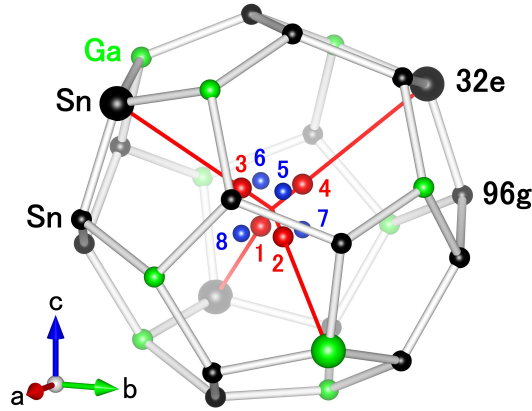


Figure 5: The 28-atom cage at the position  $(3/8, 3/8, 3/8)$  of the type-II  $\text{K}_8\text{Ba}_{16}(\text{Ga}, \text{Sn})_{136}$  clathrate structure used in the band-structure calculations. This cage is formed by 12 pentagons and 4 hexagons. The centers of the three connected pentagons are the 32*e* sites (large balls), and the other sites are the 96*g* sites (small balls). The green and black balls represent Ga and Sn atoms, respectively. The K guest site is split into four positions (red balls) toward the 32*e* sites or into the reverse four positions (blue balls) toward the centers of the hexagons. The red lines are guides to the eye. The red balls 1, 2, 3, and 4 indicate the K atom positions ‘333mmm’, ‘333ppm’, ‘333pmp’, and ‘333mpp’ in Table 3, respectively. The blue balls 5, 6, 7, and 8 indicate the opposite split site positions ‘333ppp’, ‘333mmp’, ‘333mpm’, and ‘333pmm’, respectively. This figure was drawn using VESTA.<sup>23</sup>

In this study, we performed Rietveld analyses of the data from the samples in previous studies once again.<sup>8,27</sup> As a result, we could complete the analyses using both positive and negative split parameters  $\delta$  for samples N25, N14, and N11 in Table 2. The positive split parameters gave slightly better fits. The goodness-of-fit parameters  $s$  with positive and negative split parameters were 1.1043 and 1.1025, 1.3789 and 1.3794, and 1.1720 and 1.1715,

respectively, for samples N25, N14, and N11. We therefore believe that the actual samples were a mixture of regions with positive and negative split parameters. Also, we could not strictly determine a split parameter for sample N21, whereas we fixed the split parameter for sample A4S with some ambiguity. On the other hand, we determined a negative split parameter for sample AA3S, which has the same sign as the literature value for a single crystal.

The K occupancy  $g(\text{K}, 32e)$  and ADP  $U_{\text{eq}}$  of the samples AA3S and A4S are almost the same as those of single crystals, unlike those of the previous sintered samples. The single crystals were prepared using the self-flux method, and the crystals grew during slow cooling from 823 to 723 K.<sup>26</sup> The  $g(\text{K}, 32e)$  value of the single crystal was close to the upper limit of 1/4, indicating that K atoms preferentially occupied the 32e guest sites. Since the ionic radius of  $\text{K}^+$  (0.164 nm, at a coordination number of 12) is larger than that of  $\text{Ba}^{2+}$  (0.161 nm), K atoms were likely more stable in the larger 28-atom cages. While the annealing temperature for the previous samples was 733 K, that for the additional samples was set at 773 K. Because the annealing temperature was close to the single-crystal growth temperature, the crystallographic parameters would have approached those of a single crystal.

Figure 6 shows the relationship between the absolute value of the split parameter  $\delta$  and the K occupancy  $g(\text{K}, 32e)$  at the 32e site in the 28-atom cages for the studied samples,<sup>8,26,27</sup> including sintered samples from previous studies that are not listed in Table 2. Larger  $g(\text{K}, 32e)$  values seem to correspond to larger split parameters  $\delta$ . The  $\delta$  value for the additional sample AA3S is the largest.

Regarding the split parameter  $\delta$  of the single crystal, the differential Fourier map of the guest site in the 28-atom cage was examined by Mano *et al.*<sup>26</sup> There was a toroidal charge distribution with a diameter of approximately 0.11 nm at RT, indicating the split site of the guest atom. At lower temperatures, it exhibited a quadruple-split shape. These features resemble the nuclear density obtained using MEM on neutron diffraction data for the type-I  $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$  clathrate.<sup>16</sup> Figure 7 shows the electron density distribution obtained using

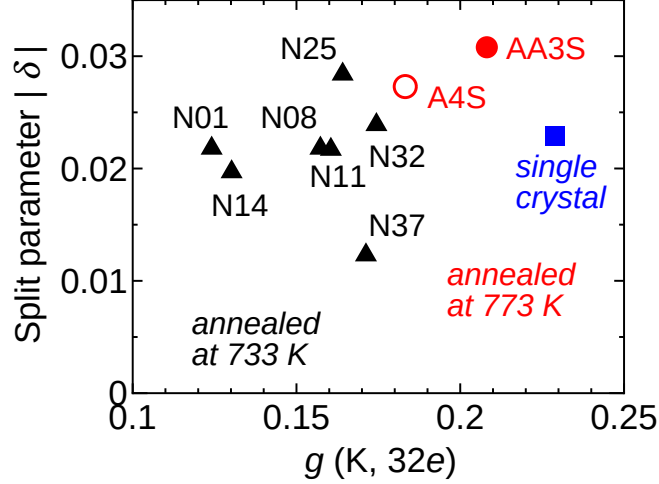


Figure 6: Absolute values of the split parameter  $\delta$  of the guest site versus K atom occupancy  $g(K, 32e)$  in the 28-atom cages for the  $(K,Ba)_{24}(Ga,Sn)_{136}$  clathrate samples from this study and previous studies.<sup>8,27</sup> The value for a single crystal is also plotted.<sup>26</sup>

MEM on X-ray diffraction (XRD) data for sample AA3S.<sup>23</sup> The displayed volume of the density distribution for the K/Ba guest atoms in the 28-atom cages is larger than those of the Ga/Sn host atoms and K/Ba guest atoms in the 20-atom cages (Fig. 7(a)). The shapes of the density distributions in the 28-atom cages, with varying isosurface levels, are shown in Fig. 7(b)-(e). They are not perfectly spherical but exhibit fourfold symmetry. Figure 8 shows the electron density distribution, with three cross-sections cut along the (100) plane shown in Fig. 7(b).<sup>23</sup> In the section cut at the center (Fig. 8(a)), a toroidal shape with a diameter of approximately 0.1 nm is observed, similar to that reported for the single crystal by Mano *et al.*<sup>26</sup> Shifting the cutting plane causes the toroidal shape to disappear, changing into a quadruple-split configuration. The split width is relatively large, approximately 0.07 nm (Fig. 8(c)).

Tabata *et al.* recently developed a direct imaging technique for atomic rattling motion in clathrate materials. They clearly visualized the directional anisotropy of the rattling motion in  $Ba_8Ga_{16}Ge_{30}$ . Their technique may be used to examine the guest atoms' motion in our type-II clathrate samples.<sup>36</sup>

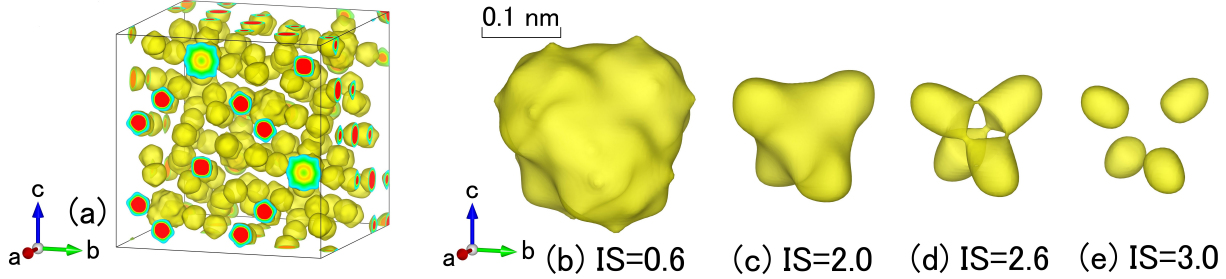


Figure 7: Electron density distributions of the type-II  $(\text{K,Ba})_{24}(\text{Ga,Sn})_{136}$  clathrate sample determined by the maximum entropy method using X-ray diffraction data: (a) the unit cell with a cutoff plane of  $(7/8, y, z)$  and (b-e) the centers of the 28-atom cage with isosurface levels of (b) 0.6, (c) 2.0, (d) 2.6, and (e)  $3.0 \times 10^3 \text{ e nm}^{-3}$ . This figure was drawn using VESTA.<sup>23</sup>

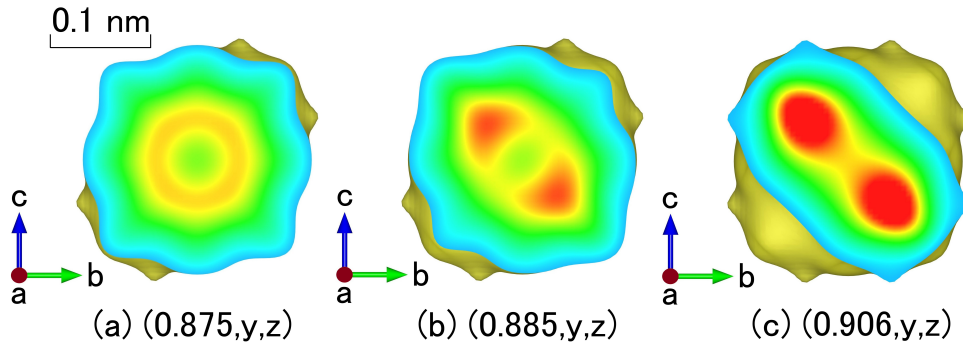


Figure 8: Electron density distributions of the guest atom in a 28-atom cage of the type-II  $(\text{K,Ba})_{24}(\text{Ga,Sn})_{136}$  clathrate sample, shown with cutoff planes of (a)  $(0.875, y, z)$ , (b)  $(0.885, y, z)$ , and (c)  $(0.906, y, z)$ . This figure was drawn using VESTA.<sup>23</sup>

## Guest potential energy

We performed band structure calculations with the configuration in which Ba and K guest atoms were placed in the 20- and 28-atom cages, respectively, and Ga and Sn host atoms were placed on the framework sites. Since  $P\bar{1}$  symmetry was used, the positions of the K atoms in the 28-atom cages were  $(3/8, 3/8, 3/8)$ ,  $(7/8, 7/8, 3/8)$ ,  $(7/8, 3/8, 7/8)$ , and  $(3/8, 7/8, 7/8)$ . We calculated the guest potential energy  $\Delta E_t$  by shifting one of these positions by a split width  $\Delta$  of 0.03. The split directions comprised eight cases, as mentioned above (Fig. 5). The results are shown in Table 3. The minimum value is  $-53$  meV, and the maximum is  $23$  meV. Most  $\Delta E_t$  values are negative, and their average is negative as well. The overall average is  $-17$  meV.  $N_{\text{Ga}/28}$ ,  $N_{\text{Ga}/10}$ , and  $N_{\text{Ga}/6}$  are the numbers of Ga atoms in the 28-atom cage, in the nearest three-connected pentagons, and in the nearest hexagon, respectively. The  $\Delta E_t$  value generally decreases as the number of nearest-neighbor Ga atoms increases. Therefore, bonding between the guest atom and neighboring Ga atoms would lower the total energy. The arrangement of Ga atoms on the framework and the number of neighboring Ga atoms exhibit some variability both in the calculations and in actual samples. This variability leads to fluctuations in  $\Delta E_t$  values.

Since the presence of Ga–Ga bonds increases the total energy,<sup>37</sup> we prepared atomic configurations with no Ga–Ga bonds, and we reduced the number of Ga–Sn–Ga bonds to minimize Ga atom clustering. In this calculation, the Ga arrangement in the Ga–Sn alloyed framework was randomly distributed. Accordingly, the  $\Delta E_t$  values show no overall site-dependent bias within the unit cell. In addition, there is no significant difference between the 32e-site direction and the hexagonal-ring-center direction. Thus, guest-site splitting could occur in either direction. This may happen in the samples N25, N14, and N11 mentioned above. On the other hand, samples such as AA3S exhibit strong splitting toward the 32e site, as suggested by XRD and MEM analyses. These samples may have a larger number of Ga atoms near the 32e site in the Ga–Sn framework configuration. In other words,  $N_{\text{Ga}/10}$  might be greater than its average value of 3.5. However, we did not perform band structure

Table 3: Guest potential energies  $\Delta E_t$  at the split sites for  $\Delta = 0.03$ , where  $N_{\text{Ga}/28}$ ,  $N_{\text{Ga}/10}$ , and  $N_{\text{Ga}/6}$  are the numbers of Ga atoms in the 28-atom cage, in the nearest three-connected pentagons, and in the nearest hexagon, respectively.  $\Delta E_{\text{tav}}$  is the average value.

| ID                | $(x, y, z)$   | Guest atom's position                  | $N_{\text{Ga}/28}$ | $N_{\text{Ga}/10}$<br>or $N_{\text{Ga}/6}^{\text{a)}$ | $\Delta E_t$<br>(meV) | $\Delta E_{\text{tav}}$<br>(meV) |
|-------------------|---------------|----------------------------------------|--------------------|-------------------------------------------------------|-----------------------|----------------------------------|
| NS                |               | No shift                               | 9.25               |                                                       | 0                     | 0                                |
| 333mmm            | (3/8,3/8,3/8) | $(x - \Delta, y - \Delta, z - \Delta)$ | 10                 | 4                                                     | -42                   | -20                              |
| 333ppm            |               | $(x + \Delta, y + \Delta, z - \Delta)$ |                    | 4                                                     | -41                   |                                  |
| 333pmp            |               | $(x + \Delta, y - \Delta, z + \Delta)$ |                    | 3                                                     | 18                    |                                  |
| 333mpp            |               | $(x - \Delta, y + \Delta, z + \Delta)$ |                    | 3                                                     | -14                   |                                  |
| Reverse direction |               |                                        |                    |                                                       |                       |                                  |
| 333ppp            |               | $(x + \Delta, y + \Delta, z + \Delta)$ |                    | 2                                                     | -7                    | -19                              |
| 333mmp            |               | $(x - \Delta, y - \Delta, z + \Delta)$ |                    | 3                                                     | -18                   |                                  |
| 333mpm            |               | $(x - \Delta, y + \Delta, z - \Delta)$ |                    | 2                                                     | -47                   |                                  |
| 333pmm            |               | $(x + \Delta, y - \Delta, z - \Delta)$ |                    | 2                                                     | -3                    |                                  |
| 773mmm            | (7/8,7/8,3/8) | $(x - \Delta, y - \Delta, z - \Delta)$ | 9                  | 4                                                     | -17                   | -12                              |
| 773ppm            |               | $(x + \Delta, y + \Delta, z - \Delta)$ |                    | 3                                                     | -16                   |                                  |
| 773pmp            |               | $(x + \Delta, y - \Delta, z + \Delta)$ |                    | 4                                                     | -30                   |                                  |
| 773mpp            |               | $(x - \Delta, y + \Delta, z + \Delta)$ |                    | 4                                                     | 13                    |                                  |
| Reverse direction |               |                                        |                    |                                                       |                       |                                  |
| 773ppp            |               | $(x + \Delta, y + \Delta, z + \Delta)$ |                    | 2                                                     | -14                   | -20                              |
| 773mmp            |               | $(x - \Delta, y - \Delta, z + \Delta)$ |                    | 3                                                     | -36                   |                                  |
| 773mpm            |               | $(x - \Delta, y + \Delta, z - \Delta)$ |                    | 2                                                     | 2                     |                                  |
| 773pmm            |               | $(x + \Delta, y - \Delta, z - \Delta)$ |                    | 2                                                     | -34                   |                                  |
| 737mmm            | (7/8,3/8,7/8) | $(x - \Delta, y - \Delta, z - \Delta)$ | 9                  | 3                                                     | 3                     | -12                              |
| 737ppm            |               | $(x + \Delta, y + \Delta, z - \Delta)$ |                    | 3                                                     | 6                     |                                  |
| 737pmp            |               | $(x + \Delta, y - \Delta, z + \Delta)$ |                    | 4                                                     | -23                   |                                  |
| 737mpp            |               | $(x - \Delta, y + \Delta, z + \Delta)$ |                    | 4                                                     | -35                   |                                  |
| Reverse direction |               |                                        |                    |                                                       |                       |                                  |
| 737ppp            |               | $(x + \Delta, y + \Delta, z + \Delta)$ |                    | 2                                                     | -3                    | -19                              |
| 737mmp            |               | $(x - \Delta, y - \Delta, z + \Delta)$ |                    | 3                                                     | -53                   |                                  |
| 737mpm            |               | $(x - \Delta, y + \Delta, z - \Delta)$ |                    | 2                                                     | -12                   |                                  |
| 737pmm            |               | $(x + \Delta, y - \Delta, z - \Delta)$ |                    | 2                                                     | -7                    |                                  |
| 377mmm            | (3/8,7/8,7/8) | $(x - \Delta, y - \Delta, z - \Delta)$ | 9                  | 3                                                     | -11                   | -15                              |
| 377ppm            |               | $(x + \Delta, y + \Delta, z - \Delta)$ |                    | 3                                                     | 23                    |                                  |
| 377pmp            |               | $(x + \Delta, y - \Delta, z + \Delta)$ |                    | 3                                                     | -35                   |                                  |
| 377mpp            |               | $(x - \Delta, y + \Delta, z + \Delta)$ |                    | 3                                                     | -36                   |                                  |
| Reverse direction |               |                                        |                    |                                                       |                       |                                  |
| 377ppp            |               | $(x + \Delta, y + \Delta, z + \Delta)$ |                    | 2                                                     | -28                   | -17                              |
| 377mmp            |               | $(x - \Delta, y - \Delta, z + \Delta)$ |                    | 3                                                     | -50                   |                                  |
| 377mpm            |               | $(x - \Delta, y + \Delta, z - \Delta)$ |                    | 2                                                     | 10                    |                                  |
| 377pmm            |               | $(x + \Delta, y - \Delta, z - \Delta)$ |                    | 2                                                     | 1                     |                                  |

a) This is for the reverse direction.



calculations to confirm this because of the high computational cost.

We calculated the dependence of the split distance on the guest potential energy for five sites: ‘333mmm’, ‘333pmp’, ‘737mmm’, ‘737pmp’, and ‘737mmp’ (Table 3). The results are shown in Fig. 9. The dependences of the four sites except ‘333pmp’ resemble curve C in Fig. 2, indicating a double-well structure. The positions of the well bottoms are around  $r = 0.09$  nm. This is consistent with the crystal structure analysis results mentioned above. The curves in the figure represent fits of the form  $a_2r^2 + a_4r^4$  ( $a_2, a_4$ : constants), which is an anharmonic quartic function, not a harmonic quadratic function. Such an anharmonic shape of the guest potential is expected to affect guest vibrations and reduce thermal conductivity.

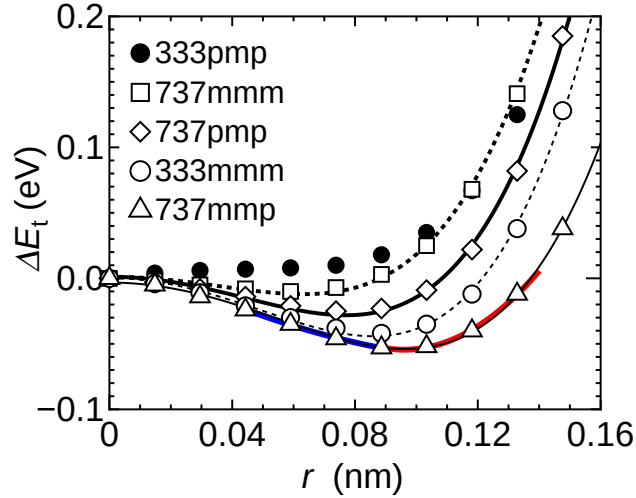


Figure 9: Guest-potential-energy curves as a function of the distance  $r$  from the guest position to the cage center. The black solid curves are fits to the equation  $a_2r^2 + a_4r^4$  ( $a_2, a_4$ : constant). The blue and red curves are quadratic fits to the data on the left and right sides of the potential energy minimum for the ‘737mmp’ data, respectively.

According to the method of Dong *et al.*, we estimated the spring constants of the guest potential by fitting quadratic functions to data from the inner and outer regions of the well bottom.<sup>11</sup> For the ‘737mmp’ direction, the spring constants  $K$  were 5.4 and 88 eV nm<sup>-2</sup>, respectively. The vibrational energies of the guest atom were calculated to be 14 and 55 K, respectively. Mano *et al.* analyzed the measured low-temperature specific heat using the SPM and derived a remarkably low mean vibrational energy of 21 K.<sup>26</sup> Considering guest potentials except that of the 737mmp direction, the vibrational frequencies of the

rattler atoms in our samples, attributed to the shapes of the guest potentials between the cage center and the well bottom, are roughly similar to the value reported by Mano *et al.* However, the vibrational energy values would change depending on the guest site. Wu *et al.* used the exponential law derived from the revised Morse potential model to treat the guest potential for the type-I clathrate  $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$ . Consequently, they estimated the vibrational energy or the Einstein temperature.<sup>38</sup>

The type-I  $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$  clathrate with a stretched virtual lattice constant of 6% has a guest potential of a double-well type, with a depth of approximately  $-30$  meV.<sup>20</sup> The type-II clathrate studied here has a deeper well of approximately  $-50$  meV. For such a deep well, the rattler atoms are expected to reside at its bottom and remain off-center at elevated temperatures. Conversely, for the shallow well, they are expected to be on-center. Overall, highly complex thermal vibrations would occur. Additionally, the disparate shapes and depths of the guest potentials at each guest site within the unit cell, arising from the Ga–Sn alloyed atomic arrangement on the framework, would lead to phonon scattering. In addition, Roy *et al.* recently demonstrated experimentally and theoretically that Ga–Ge disorder in the framework of the type-I  $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$  clathrate strongly reduces phonon group velocities, leading to a decrease in thermal conductivity.<sup>39</sup>

## Lattice thermal conductivity

Figure 10 plots the relationship between the split parameter and the RT lattice thermal conductivity for the type-II  $(\text{K},\text{Ba})_{24}(\text{Ga},\text{Sn})_{136}$  clathrate samples.<sup>8,27</sup> Data for single crystals are unavailable.<sup>26</sup> Larger split parameter  $\delta$  values tend to correspond to lower lattice thermal conductivities. This is likely due to a strong rattling effect. The minimum value approached the theoretical minimum for Sn,  $\kappa_{\min} = 3.4 \text{ mW cm}^{-1}\text{K}^{-1}$ .<sup>25</sup>

Figure 11 plots the temperature dependence of the lattice thermal conductivity of the samples,<sup>8,27</sup> with the data for the type-I  $\text{Ba}_8\text{Ga}_{16}\text{Sn}_{30}$  clathrate<sup>24</sup> and the theoretical minimum value  $\kappa_{\min}$  for Sn also shown.<sup>25</sup> The value of the type-I sample increases above RT.

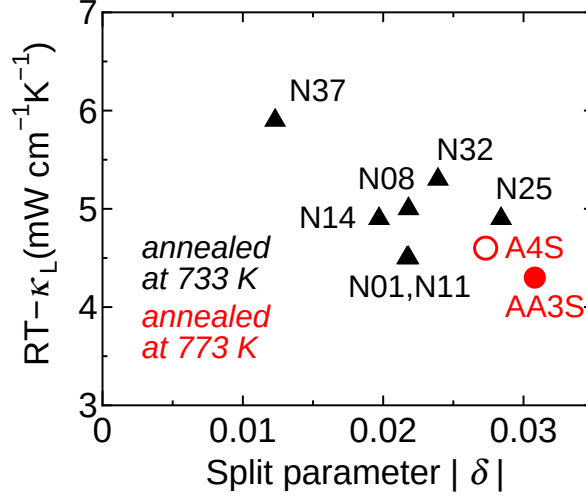


Figure 10: Relationship between room-temperature lattice thermal conductivity  $\kappa_L$  and the split parameter  $\delta$  of the guest site in the 28-atom cages for the  $(K,Ba)_{24}(Ga,Sn)_{136}$  clathrate samples from this study and previous studies.<sup>8,27</sup>

The temperature dependence has been theoretically reproduced by Ohnishi *et al.* using a first-principles-based self-consistent phonon theory.<sup>40</sup> In contrast, the values of the type-II samples decrease with increasing temperature up to around 600 K. In particular, the values of the samples with large split parameters approach the theoretical minimum for Sn at around 600 K. As discussed above, the guest potential depth is as large as  $-50$  meV, suggesting that the guest atom would remain in an off-center state even at elevated temperatures. Since the occupation of the split site may be random, phonon scattering increases due to the crystal's complex structure, leading to a decrease in thermal conductivity. At higher temperatures, contributions from phonon transport for which off-center effects become negligible are also included. However, primarily due to the increase in bipolar thermal conductivity, these effects are relatively small,<sup>28</sup> and the thermal conductivity values increase.

To summarize the discussion so far, the reasons why the type-II  $(K,Ba)_{24}(Ga,Sn)_{136}$  clathrates exhibit low lattice thermal conductivity at elevated temperatures are as follows: (1) a large number of atoms contained in the unit cell; (2) rattling with a large ADP; (3) off-center rattling; (4) weak bipolar heat conduction; (5) a double-well and anharmonic guest potential; (6) a deep-well guest potential; and (7) variations in the position and depth of the

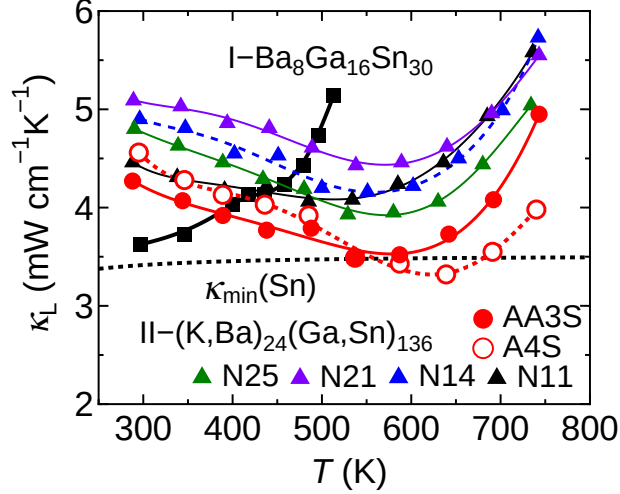


Figure 11: Temperature dependence of the lattice thermal conductivity  $\kappa_L$  for the type-II  $(K,Ba)_{24}(Ga,Sn)_{136}$  clathrates.<sup>8,27</sup> The data for the type-I  $Ba_8Ga_{16}Sn_{30}$  clathrate are also plotted.<sup>24</sup> The thick dotted curve indicates the theoretical minimum value  $\kappa_{min}$  for Sn.<sup>25</sup> The other curves are guides to the eye.

guest potential.

## Other TE properties

Figure 12 plots the temperature dependences of the Seebeck coefficient  $S$ , the electrical conductivity  $\sigma$ , the power factors  $S^2\sigma$ , the thermal conductivity  $\kappa$ , and  $ZT$  for the type-II  $(K,Ba)_{24}(Ga,Sn)_{136}$  clathrates listed in Table 2.<sup>8,27</sup> The samples with larger carrier concentrations generally had lower Seebeck coefficients  $S$  and higher electrical conductivities  $\sigma$ , as expected. The  $S$  values of samples AA3S, A4S, N25, and N21 were close to the optimized value of  $-200 \mu V K^{-1}$  at 600 K (Fig. 12(a)). The optimum carrier concentration seems to be approximately  $2.5 \times 10^{19} cm^{-3}$ . The power factors  $S^2\sigma$  for samples AA3S, A4S, N25, and N21 were nearly the same at around 600 K, and were larger than those of the others (Fig. 12(c)). Due to the reduction in lattice thermal conductivity  $\kappa_L$ , samples AA3S and A4S exhibited lower thermal conductivities than samples N25 and N21 (Fig. 12(d)). As a result, samples AA3S and A4S had higher  $ZT$  values than the others (Fig. 12(e)). Since the total thermal conductivities were quite low, even a small reduction in thermal conductivity

resulted in a substantial increase in  $ZT$ . The maximum  $ZT$  value of 1.32 at 640 K and an average  $ZT$  of 1.04 between 300 and 700 K were achieved.

## Conclusions

The sintered samples of the type-II  $(\text{K,Ba})_{24}(\text{Ga,Sn})_{136}$  clathrate showed large site splitting, large ADPs of the rattler atoms, and low lattice thermal conductivities at elevated temperatures. These crystallographic parameters were due to the large cages in the type-II clathrate. The samples annealed at higher temperatures showed these properties more clearly. The minimum lattice thermal conductivity and the maximum  $ZT$  obtained in this study were  $3.3 \text{ mW cm}^{-1}\text{K}^{-1}$  and 1.32, respectively, at 640 K.

The guest potential of the rattler K atoms in the 28-atom cages was calculated to examine the mechanism underlying the low lattice thermal conductivities. The guest potential appears to be anharmonic and of a double-well type due to the large cages. In addition, its depth varied from site to site due to variations in the number of neighboring Ga atoms on the Ga–Sn alloyed framework. Its average and lowest values were  $-17$  and  $-50$  meV, respectively. For deep wells, the rattler atoms would reside at the well bottoms and remain off-center at elevated temperatures, whereas for shallow wells, they would not be in an off-center state. Overall, highly complex thermal vibrations are anticipated in this clathrate. Therefore, in the type-II  $(\text{K,Ba})_{24}(\text{Ga,Sn})_{136}$  clathrate with large rattler cages and Ga–Sn alloyed frameworks, strong phonon scattering would occur, resulting in low lattice thermal conductivity.

We discussed several factors that reduce the thermal conductivities of the type-II clathrates in this study. However, the mechanisms behind these factors have not yet been fully revealed. Further studies will be needed to clarify these mechanisms.

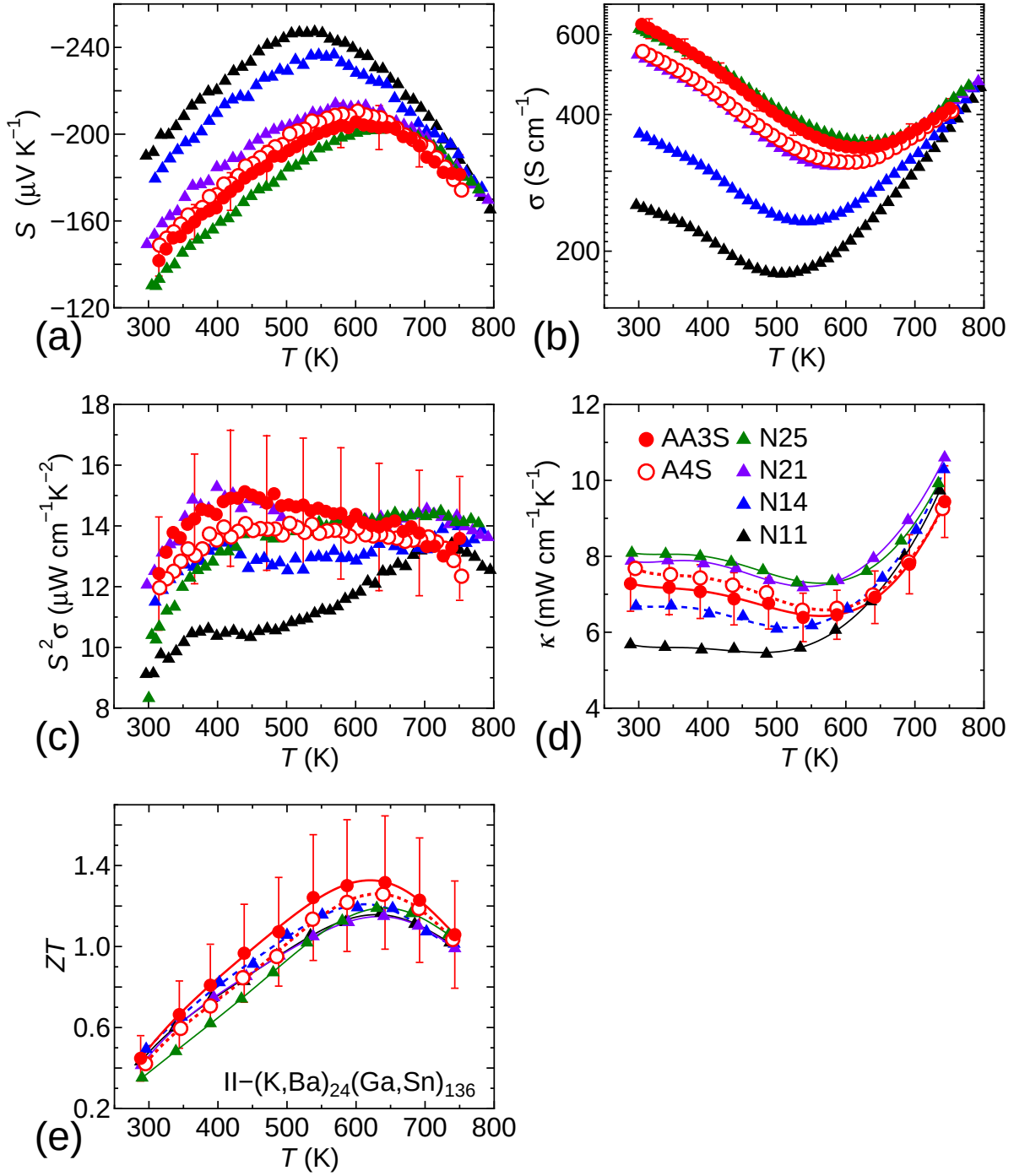


Figure 12: Temperature dependence of (a) the Seebeck coefficients  $S$ , (b) electrical conductivities  $\sigma$ , (c) power factors  $S^2\sigma$ , (d) thermal conductivities  $\kappa$ , and (e) dimensionless figure of merit  $ZT$  for the type-II  $(\text{K,Ba})_{24}(\text{Ga,Sn})_{136}$  clathrates.<sup>8,27</sup> The curves in (d) and (e) are guides to the eye.

## Acknowledgement

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## Supporting Information Available

The following file is available free of charge.

- 2K8Ba16Ga40Sn96-GA2-2-36-struct: The struct files of band-structure calculation program WIEN2k for the 333mmm atomic configuration and the configuration where no guest atoms are shifted.

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# Graphical TOC Entry

