

Electrical Transport Properties of Type-VIII Sn-Based Single-Crystalline Clathrates (Eu/Ba)₈Ga₁₆Sn₃₀ Prepared by Ga Flux Method *

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Single-crystalline samples of Eu/Ba-filled Sn-based type-VIII clathrate are prepared by the Ga flux method with different stoichiometric ratios. The electrical transport properties of the samples are optimized by Eu doping. Results indicate that Eu atoms tend to replace Ba atoms. With the increase of the Eu initial content, the carrier density increases and the carrier mobility decreases, which leads to an increase of the Seebeck coefficient. By contrast, the electrical conductivity decreases. Finally, the sample with Eu initial content of $x = 0.75$ behaves with excellent electrical properties, which shows a maximal power factor of $1.51 \text{ mW} \cdot \text{m}^{-1} \text{K}^{-2}$ at 480 K, and the highest ZT achieved is 0.87 near the temperature of 483 K.

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Thermoelectric material^[1,2] is a kind of new energy material that can convert heat into electricity. The efficiency of thermoelectric conversion η can be defined as^[3]

$$\eta = \frac{T_H - T_C}{T_H} \frac{\sqrt{1 + ZT} - 1}{\sqrt{1 + ZT} + \frac{T_C}{T_H}}, \quad (1)$$

where T_H is the hot temperature, and T_C is the cold temperature in a thermoelectric module. High efficacy requires a large temperature gradient and a high ZT . Under a stable temperature environment, the conversion efficiency is determined by ZT . Hence, ZT is expressed as^[4,5]

$$ZT = \alpha^2 \sigma T / \kappa, \quad (2)$$

where α is the Seebeck coefficient, σ is the electrical conductivity, and κ is the thermal conductivity. The efficiency can be improved by increasing the Seebeck coefficient and the electrical conductivity or by reducing the thermal conductivity.

Type-VIII clathrates^[6,7] represent a kind of material with high ZT , and these materials contain filled atoms (Ba, Sr or Eu)^[8–10] and framework atoms (composed of Ga and Si Ge Sn).^[11–13] Among them, Sn-based clathrates demonstrate excellent thermoelectric properties. For example, ZT of the n-type clathrates Ba₈Ga₁₆Sn₃₀ prepared by the Sn self-flux method has reached 0.85 at 480 K,^[14] ZT of the p-type clathrates Ba₈Ga₁₆Sn₃₀ prepared by the Ga self-flux method has reached 0.88 at 480 K,^[15] and the thermoelectric performance can also be improved by Cu, In and Sb doping.^[16–18] The superior electronic properties are derived from hybridization of sp^3 orbital of the clathrates.^[19] It is well known that the complex

structure of the material in interstitial type is beneficial to efficiently scatter phonons via the vibration of the filled atoms, and thus reduces the thermal conductivity. In addition, scattering phonons should increase with the decrease of the filled-atom radius.^[20,21]

Sr and Eu atoms are smaller than Ba atom in terms of radius, and the former atoms are perfect to be the filled atoms in theory. However, Sr₈Ga₁₆Sn₃₀ or Eu₈Ga₁₆Sn₃₀ single crystal has not yet been reported. We speculate that the complete Sr and Eu atoms are not suitable for the framework comprising Ga and Sn atoms because of their very small atomic radius. Thus many researchers intend to prepare the type-VIII Sn-based clathrates with Ba and Eu (or Sr) simultaneously filled. If the clathrates can be prepared, the much higher phonon scattering will improve the thermal properties of the materials. Doping will also influence the electrical transport properties, such as carrier density, Seebeck coefficients, and electrical conductivity, and the change of carrier density will also lead to a change in phonon scattering.^[22] To investigate the influence of Eu doping and combined with the high thermoelectric properties of the samples prepared by the Ga self-flux method, in this study, Eu/Ba-filled type-VIII Sn-based clathrates were prepared by the Ga self-flux method, and the structure and electrical properties were investigated.

In this experiment, single-crystal clathrates (Ba/Eu)₈Ga₁₆Sn₃₀ were prepared by the Ga self-flux method. High-purity elements Ba (99.9% ingot), Eu (99.99% ingot), Ga (99.99% ingot), and Sn (99.999% ingot) were weighed in accordance with their atomic ratios as follows: Ba:Eu:Ga:Sn=8: x :40:30 ($x = 0.00, 0.30, 0.50, 0.75$ and 1.00). Afterward, the mixture was transferred into a quartz glass tube, sealed in a vacuum, and heated in a rate 200 K/h ramp to 763 K, in-

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cubated at this temperature for 10 h. The mixture was cooled gradually to 663 K over 50 h. At this temperature, single crystals were separated from the molten Ga flux by centrifugation.

The crystal phases of the samples were analyzed by x-ray diffraction (XRD) with Cu K_α radiation (Ultima IV). An electron microprobe (EPMA, JXA-8230) was used to obtain the actual elemental compositions. Measurements of the electrical conductivity σ and the Seebeck coefficient α were performed in the temperature range of 300–600 K in vacuum. The electrical conductivity σ of the samples were measured by the direct current (DC) method, and the DC current is kept at 20 mA. The Seebeck coefficient was measured by a comparative method using the material of constant (Ni: 40%) as a reference sample, of which α in the measured temperature range is known. The Hall coefficient was measured by the Hall system (Nanometrics HL5500 Hall System) at room temperature (RT) in a magnetic field of 0.75 T.

Single crystalline samples with shiny metallic luster of approximately 4 mm in diameter were obtained for all samples, as an example, Fig. 1(a) displays the picture of the as-prepared single-crystalline clathrate $\text{Ba}_8\text{Ga}_{16}\text{Sn}_{30}$ (BGS), and Fig. 1(b) shows the crystal structure of the clathrates. The framework consists of Ga and Sn, and the filled atoms of Ba are located in the middle of the ‘cage’ with vibration, hence leading to the lattice thermal motion, and the Ba atoms will vibrate around the center, which will lead to the scattering of phonons, thereby decreasing the thermal conductivity.

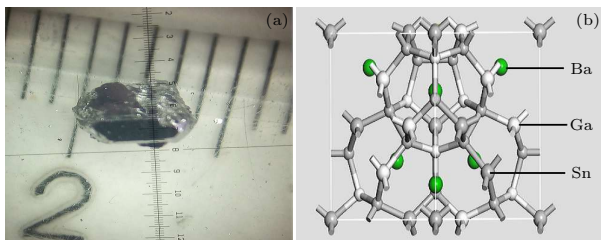


Fig. 1. (a) Photography and (b) crystal structure of the as-prepared type-VIII clathrate $\text{Ba}_8\text{Ga}_{16}\text{Sn}_{30}$.

The powder XRD patterns and local amplification for powder XRD patterns of BGS samples are shown in Figs. 2(a) and 2(b). It is clear that all the patterns are indexed by the typical type-VIII clathrate BGS with space group $I43m$ and well coincide with PDF# 217. Compared with the sample with Eu content $x = 0$, the position of the diffraction peaks slightly shifted toward a high angle with increasing x , as shown in Fig. 2(b). To further explore the reason for this finding, the lattice parameters of the samples are listed in Table 1, which indicates that the lattice parameters of the samples decrease with the increase of the Eu content. We speculate that this case is ascribed to the different ion radii, given that the radius of Eu is smaller than that of Ba, the similar result is shown in the n-type samples for the Sn flux method.^[23] In

fact, the partial substitution of Eu for Ba, in which the Eu^{3+} or Eu^{2+} replaces Ba^{2+} and the ion radius Eu (2.56 Å) is smaller than that of Ba (2.78 Å), results in the increase of lattice phonons.

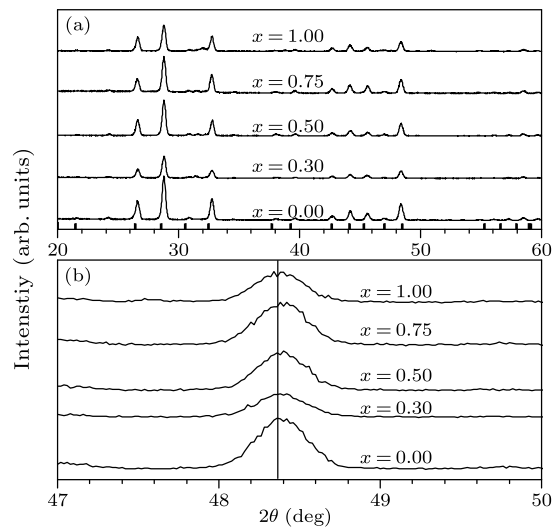


Fig. 2. (a) Powder x-ray diffraction patterns and (b) local amplification for BGS samples.

Table 1 displays the elemental compositions and some electrical properties of the samples at room temperature. The Hall coefficient R_H was measured using the Hall system, and the carrier density n is calculated by

$$n = \frac{1}{eR_H}. \quad (3)$$

The carrier mobility μ_H is calculated by

$$\sigma = ne\mu_H, \quad (4)$$

where σ is the electrical conductivity obtained from the experiments, and e is the electron charge.

Based on the EPMA analyses of the chemical compositions of the samples, we can obtain that these samples roughly agree with the ratio of Ba:Ga:Sn=8:16:30, which is consistent with the result of the previous report.^[15,24] With the increasing Eu initial content, the proportion of Eu within the crystals increases while the amount of Ba decreases, suggesting that the Eu atoms tend to replace the Ba atoms. A similar result has been reported in Si-based clathrates.^[25] In addition, as listed in Table 1, the carrier density of the samples is between 6×10^{19} and $21 \times 10^{19} \text{ cm}^{-3}$, and being similar to the result ($11 \times 10^{19} \text{ cm}^{-3}$) reported by Saiga *et al.*^[15] It may be attributed to guest atoms Ba and Eu, which can improve thermoelectric performance significantly by scattering heat-carrying lattice phonons intensively. The values of μ_H ($T = 300 \text{ K}$) for the Ga-flux samples are in the range $1.38\text{--}13.54 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, and the larger carrier mobility may be attributed to the fewer defects in our single-crystal samples. It is indicated that the carrier density increases and the carrier mobility basically decreases

with the increase of the Eu content due to the enhancement of impurity scattering. On the other hand, the increase of the carrier density will also lead to the decrease of the carrier mobility. Hence, with the doping

of Eu atoms, the impurity energy levels are brought in the Fermi energy, and the lattice defects are also introduced because of the difference in atomic radius between Eu and Ba.

Table 1. Lattice parameter a , crystal compositions, carrier density n , carrier mobility μ_H , effective mass m^*/m_0 and Hall coefficient R_H at room temperature of single crystal clathrates.

Eu initial content	a (Å)	Crystal compositions				n (10^{19} cm^{-3})	μ_H ($\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)	R_H ($\text{cm}^3 \text{ C}^{-1}$)	m^*/m_0
		Ba	Eu	Ga	Sn				
$x = 0.00$	11.586(2)	7.83(1)	0.00(0)	15.81(3)	30.36(4)	6.31	13.54	0.099	0.851
$x = 0.30$	11.583(3)	7.83(4)	0.03(3)	15.83(0)	30.31(3)	6.57	12.73	0.095	1.039
$x = 0.50$	11.582(2)	7.81(3)	0.05(2)	15.75(2)	30.39(3)	7.15	8.05	0.087	1.319
$x = 0.75$	11.582(4)	7.77(1)	0.12(3)	15.83(1)	30.28(2)	10.02	6.41	0.062	1.939
$x = 1.00$	11.579(2)	7.58(2)	0.22(2)	15.85(4)	30.35(4)	20.19	1.38	0.031	3.120

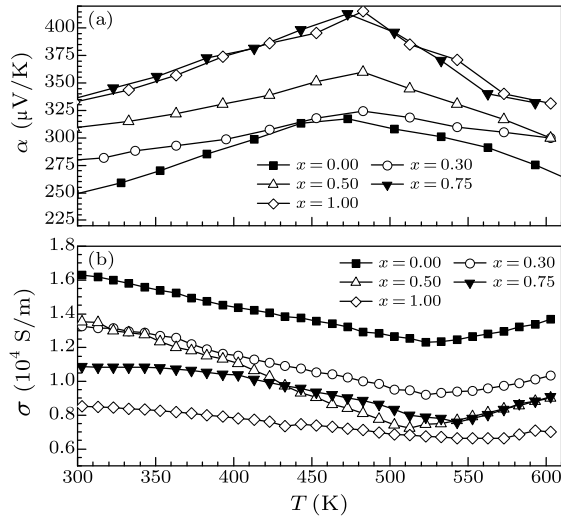


Fig. 3. Temperature dependence of (a) the Seebeck coefficient σ and (b) the electrical conductivity σ for BGS samples.

Figures 3(a) and 3(b) show the Seebeck coefficients and the electrical conductivity of the samples. The data of Seebeck coefficient for various Eu contents are presented in Fig. 3(a). The positive sign of the Seebeck coefficient of the samples agrees with the positive Hall coefficient. The Seebeck coefficient of the samples without Eu doping reached $315 \mu\text{V/K}$ at 460 K , and this finding is smaller than the result ($350 \mu\text{V/K}$ at 480 K) obtained by Saiga *et al.*^[26] and our previous result ($348 \mu\text{V/K}$ at 550 K).^[19] This difference would be related to the specific fabrication conditions. However, in the whole temperature range, with the increase of the Eu initial content, the Seebeck coefficient increases, and the Seebeck coefficient of the sample with the Eu initial content of $x = 1.00$ reaches $416 \mu\text{V/K}$ at 475 K . This finding is higher than that of the sample without Eu doping. Figure 3(b) shows the electrical conductivity between 300 K and 600 K . The electrical conductivity without Eu doping is between 1.1×10^4 and $1.7 \times 10^4 \text{ S/m}$, which agrees well with the result of Saiga *et al.*,^[15] in which the increase of the Eu initial content causes considerable decrease in the electrical conductivity. The Seebeck coefficient and the electrical conductivity are closely related to the band structure, and the high Seebeck coefficients

are associated with a high local density of states but exert a counteractive effect on the carrier mobility because of the low electronic dispersion.^[27] We speculate that with the increase of the Eu content, the density of states also increases, leading to the increase of the Seebeck coefficients and the decrease of the carrier mobility. The decreasing carrier mobility leads to the decreasing electrical conductivity, as listed in Table 1. Moreover, the lattice defect is the other reason for the decrease of the electrical conductivity. Combining with the report of Eu doping n-type BGS samples prepared by the Sn flux method,^[23] the Eu doping decreases the Seebeck coefficient and increases the electrical conductivity of the n-type samples, contrary to that of the p-type samples. So, we speculate that the different carrier types between the n-type and p-type samples lead to the various effects on the electrical properties of Eu doping samples.

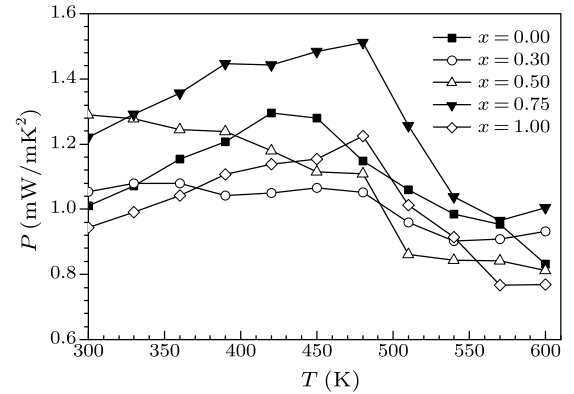


Fig. 4. Temperature dependence of the power factor for type-VIII single-crystal clathrates.

To discuss the effect of the Eu doping content on transport properties, we estimate the carrier effective mass m^* by expressing the Seebeck coefficient directly in terms of the Fermi-Dirac integrals,^[28]

$$\alpha = \pm \frac{k_B}{e} \left[\eta - \frac{[r + (5/2)]F_{r+3/2}(\eta)}{[r + (3/2)]F_{r+1/2}(\eta)} \right], \quad (5)$$

where e is the carrier charge, k_B is Boltzmann's constant, r is the exponent of the energy dependence of the carrier relaxation time, $\sigma = E_F/k_B T$ is the reduced Fermi energy, and $F(\eta)$ is the Fermi integral.

The + and − signs correspond to valence band carriers and conduction band carriers, respectively. This estimate requires the following assumptions: a single carrier type in a parabolic band, the absence of multi-band effects, and no phonon-drag effects. The carrier density is given by

$$n = N_0(T) \left(\frac{m^*}{m_0} \right)^{2/3} F_{1/2}(\eta), \quad (6)$$

where m_0 is the free electron mass, and m^* is the effective electron mass. Assuming the mixed ionized impurity and phonon scatterings ($r = 1/2$), the estimated effective mass is calculated for the present specimens and is listed in Table 1. The values of m^*/m_0 are in the range of 0.85–3.12, and are larger than 0.63 of the $\text{Ba}_8\text{Ga}_{16}\text{Sn}_{30}$ single crystal reported by Chen *et al.*^[7] As mentioned above, the samples with larger Eu composition demonstrate a larger m^*/m_0 , and it is speculated that the band structure may be affected by the increase of the Eu content.

The power factor P is calculated by the measured Seebeck coefficient and the electrical conductivity. As shown in Fig. 4, the power factor of the sample without Eu doping has reached $1.28 \text{ mW} \cdot \text{m}^{-1} \text{K}^{-2}$ at 450 K, with the increase of the Eu content, the power factor decreases slightly because of the decrease of the electrical conductivity. However, the power factor of the sample with the Eu initial content of $x = 0.75$ reaches $1.51 \text{ mW} \cdot \text{m}^{-1} \text{K}^{-2}$ at 480 K, which is higher than that of the sample without doping.

We can only estimate theoretically the thermal conductivity of the samples owing to the size of the samples, which do not meet the requirement of the thermal conductivity testing in this study. In thermoelectric materials, the thermal conductivity calculation is based on the carrier and photon thermal conductivity, which can be expressed by^[29]

$$\kappa = \kappa_C + \kappa_L, \quad (7)$$

where κ_C is the carrier thermal conductivity, and κ_L is the phonon thermal conductivity. Here κ_C can also be represented as $\kappa_C = L\sigma T$ according to the Wiedemann–Franz equation law, with L being the Lorentz number (as reported in previous works this is $L = 2.44 \times 10^{-8} \text{ V}^2 \text{K}^{-2}$), and σ being the electrical conductivity, which is stated above. The value of $\kappa_L(T)$ ^[16] can be obtained from the literature.

On the basis of the measured Seebeck coefficient, the electronic conductivity and the calculated thermal conductivity of the samples, ZT of the samples are obtained by Eq. (2). As shown in Fig. 5, the sample with the Eu initial content of $x = 0.75$ possessed the highest ZT curve and the highest ZT achieved are 0.87 at 483 K, and the finding is different from the sample prepared using the Sn self-flux method that the sample with the Eu initial content of $x = 0.75$ shows a lower ZT .^[23] This difference would be related to the specific fabrication conditions. Furthermore, with the

increase of the Eu initial content, ZT of the samples change in different extents because of the increasing Seebeck coefficient and the decreasing electrical conductivity, and the highest ZT of the sample without Eu doping is 0.76 in 450 K, which is lower than the previous reports^[15] (ZT is 0.88 in 480 K), which is due to the lower Seebeck coefficients.

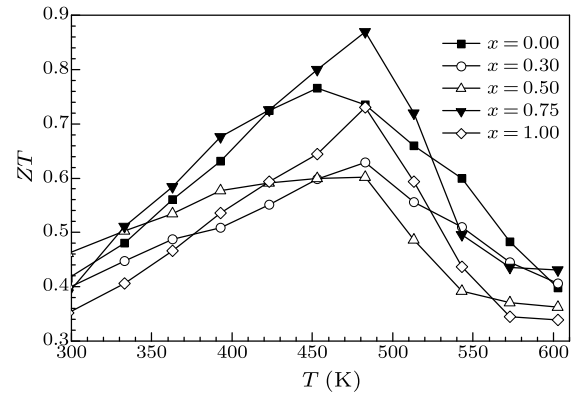


Fig. 5. Temperature dependence of ZT for type-VIII single-crystal clathrate.

In summary, we have prepared several samples of type-VIII Sn-based single-crystalline clathrates $(\text{Eu}/\text{Ba})_8\text{Ga}_{16}\text{Sn}_{30}$ to investigate their thermoelectric properties via the Ga self-flux method in accordance with the atomic ratios $\text{Ba}:\text{Eu}:\text{Ga}:\text{Sn}=8:x:40:30$ ($x = 0.00, 0.30, 0.50, 0.75$ and 1.00). The results indicate that all samples are p-type single-crystal clathrates in the $I\bar{4}3m$ space group. Eu atoms tend to replace Ba atoms. Accordingly, with the increase of the Eu initial content, the carrier density increases and the carrier mobility decreases, respectively. High local density of states increases the Seebeck coefficient, but the electrical conductivity decreases. This finding indicates that the Seebeck coefficient and the electric conductivity can be well regulated by Eu doping, contrary to the result for n-type samples. With the increase of the Seebeck coefficient and the decrease of the electric conductivity, the power factor slightly changes. Finally, the sample with the Eu initial content of $x = 0.75$ demonstrates excellent electrical properties, which shows a maximal power factor of $1.51 \text{ mW} \cdot \text{m}^{-1} \text{K}^{-2}$ at 480 K, the highest ZT achieved is 0.87 near the temperature of 483 K. The highest ZT of the sample without Eu doping is 0.76 at 450 K, which is lower than the previous reports. Therefore, suitable initial Eu content is vital for the optimization of TE performance for the single-crystalline clathrate $\text{Ba}_8\text{Ga}_{16}\text{Sn}_{30}$ prepared by the Ga-flux method.

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