Sn-based type-VIII single-crystal clathrates with a large figure of merit*

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Single-crystal samples of type-VIII $Ba_8Ga_{16-x}Cu_xSn_{30}$ ($x = 0$, 0.03, 0.06, 0.15) clathrates were prepared using the Sn-flux method. At room temperature the carrier density, n, is 3.5–5 $\times 10^{19}$ cm^{-3} for all the samples, the carrier mobility, μ_H, increases to more than twice that of $Ba_8Ga_{16}Sn_{30}$ for all the Cu doping samples, and consequently the electrical conductivity is enhanced distinctly from 1.90×10^4 S/m to 4.40×10^4 S/m, with the Cu composition increasing from $x = 0$ to $x = 0.15$. The Seebeck coefficient, α, decreases slightly with the increases in Cu composition. The κ values are about 0.72 W/mK at 300 K and are almost invariant with temperature up to 500 K for the samples with $x = 0$ and $x = 0.03$. The lattice thermal conductivity, κ_L, decreases from 0.59 W/mK for $x = 0$ to 0.50 W/mK for $x = 0.03$ at 300 K. The figure of merit for $x = 0.03$ reaches 1.35 at 540 K.

Keywords: thermoelectric material, type-VIII clathrate, thermoelectric properties

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1. Introduction

In recent years, thermoelectric materials have been studied intensively for the harvesting of renewable energy from waste heat and sunlight.[1−7] The efficiency of a given thermoelectric material is determined by the dimensionless figure of merit $ZT = \alpha^2 T\sigma/\kappa$, where α is the Seebeck coefficient, T is the temperature, σ is the electrical conductivity and κ is the thermal conductivity. The compounds with (filling) cage structures, such as skutterudite[3,4] and clathrate,[2,5−7] are considered promising materials in the moderate temperature region due to the concept of phonon-glass electron-crystal, proposed by Slack.[8] For the former research on the cage-like compounds, more attention was paid to the investigation of Ge-based clathrates, and high ZT values were obtained.[7,9−12] Among the clathrate compounds, the Sn-based type-VIII clathrate is a competitive moderate-temperature thermoelectric material due to its large Seebeck coefficient and low thermal conductivity.[13,15]

The type-VIII clathrate (space group: $I\bar{4}3m$) has the same chemical formula as that of the type-I clathrate (space group: $pm\bar{3}n$), but the guest atoms are encapsulated in only one kind of polyhedral cage composed of 23 framework atoms of group IV and III elements.[16] The cage atoms occupy four sites, which are 2a, 12d, 8c and 24g. While for the type-I clathrate, in one unit cell there are two dodecahedra and six tetrakaidecahedra formed by group IV and III elements for the guest atoms to occupy. Up to now, as for the type-VIII clathrates, only four compounds are known, $Sr_8Ga_{16-x}Al_xGe_{30}$ for $6 \le x \le 10$,[17] $Sr_8Ga_{16-x}Al_xSi_{30}$ for $8 \le x \le 10$,[18] $Ba_8Ga_{16}Sn_{30}$,[7,13−15] and $Eu_8Ga_{16}Ge_{30}$.[19−21]

In type-VIII $Ba_8Ga_{16}Sn_{30}$, the atomic displacement parameters (ADP) of the framework atoms are approximately twice as large as those of the type-I clathrate $Sr_8Ga_{16}Ge_{30}$, eight Ba atoms show relatively large ADP[15] and a small value of thermal conductivity has been reported at room temperature.[22] Moreover, for a single-crystal type-VIII $Ba_8Ga_{16}Sn_{30}$, the carrier type can be tuned by slightly deviating the ratio of Ga/Sn from the ideal value of 16/30. An excess in Ga leads to the p-type conduction, while an excess in Sn leads to the n-type conduction.[14,15] However, compared with state-of-the-art materials, the figure of merit, ZT, for the single-crystal type-VIII $Ba_8Ga_{16}Sn_{30}$ is relatively low

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due to its lower electrical conductivity, which results from the low carrier mobility. The results show that in $Sr_8Ga_{16-x}Al_xGe_{30}$,[17] $Sr_8Ga_{16-x}Al_xSi_{30}$,[18] and $Ba_8Ga_{16-x}Al_xSn_{30}$[23] systems, the substitution of Al with the framework atom Ga can enhance the carrier mobility without changing the carrier density. In the present work, we address the properties of single-crystal samples of $Ba_8Ga_{16-x}Cu_xSn_{30}$ (x = 0, 0.03, 0.06, 0.15) at a temperature range from 300 to 600 K. It is expected that the substitution of Cu for Ga may enhance the carrier mobility and consequently optimize the figure of merit.

2. Experiment

Single-crystal samples of $Ba_8Ga_{16-x}Cu_xSn_{30}$ (x = 0, 0.3, 0.06, 0.15) were prepared by the Sn-flux method. High purity elements were mixed in an atomic ratio of Ba:Ga:Cu:Sn = 8:16–X:X:50 (X = 0, 1 1.5, 2) in an argon atmosphere glovebox. The mixture, sealed in an evacuated quartz tube 11 mm in diameter, was heated slowly to 763 K and soaked for 10 h, and then slowly cooled to 663 K over 50 h. The constituent phase was characterized by powder X-ray diffraction (XRD, Rigaku Ultima IV), and the elemental compositions were determined by electron-probe microanalysis (EPMA, JEOL JXA-8200). The electrical resistivity and the Seebeck coefficient were measured from 300 to 600 K in the vacuum. The Hall coefficient was measured at room temperature by a direct-current method in a magnetic field of 1 T. The temperature dependent thermal conductivity, κ, was calculated via equation $\kappa = DdC_p$, where D is the thermal diffusivity measured by the laser-flash method in the vacuum, d is the density, and C_p is the heat capacity measured with a differential scanning calorimeter.

3. Results and discussion

3.1. Compositions and lattice parameters

For X = 0 and X = 1, the single-crystal samples obtained are approximately 8 mm in diameter. The as-grown crystal with X = 1 has a shiny metallic luster, as shown in Fig. 1. For X = 1.5 and X = 2, the maximum crystal size obtained is only about 3 mm in diameter, and some plate-like crystals with the $BaNiSn_3$-type structure coexist with the type-VIII clathrates.

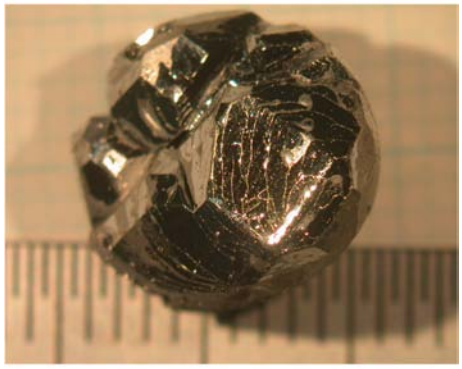


Fig. 1. (colour online) An as-grown single crystal with X = 1.

Figure 2 displays the XRD patterns for $Ba_8Ga_{16-x}Cu_xSn_{30}$. The patterns of all the samples are indexed by the type-VIII clathrate structure with the space group $I\bar{4}3m$. However, for the X = 2 sample, there are additional peaks at 2θ = 32.0° and 44.3°, which are attributed to the Sn impurity existing in the boundary of the crystal. For the samples used to measure electrical properties, the Sn impurity was excluded by choosing a homogeneous area to cut.

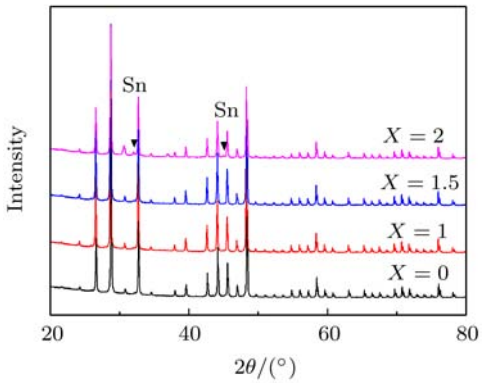


Fig. 2. (colour online) Powder XRD patterns for the prepared samples taken with Cu Kα radiation at room temperature.

Table 1 shows the crystal compositions, lattice parameter a, electrical conductivity σ, Hall coefficient R_H, carrier density n and carrier mobility μ_H at room temperature for the $Ba_8Ga_{16-x}Cu_xSn_{30}$ samples. The compositions of Ba:Ga:Cu:Sn are roughly in agreement with the ratios of 8:16–x:x:30, and the Cu composition in the crystal is relatively lower compared with the starting composition. The total compositions of the framework element are about 46 for all samples, and that of Sn is a little more than its ideal composition of 30. The lattice parameter for X = 0 is 11.602 Å, and it almost keeps invariable for the other samples.

Table 1. Crystal compositions, lattice parameters, a, electrical conductivity, σ, Hall coefficient, $R_{\rm H}$, carrier density, n, and carrier mobility, $\mu_{\rm H}$, at room temperature for the $Ba_8Ga_{16-x}Cu_xSn_{30}$ samples.

Crystal composition				a	σ	n	$R_{\rm H}$	$\mu_{\rm H}$
Ba	Ga	Cu(x)	Sn	/Å	$/10^4{\rm S\cdot m^{-1}}$	$/10^{19}{\rm cm^3}$	$/{\rm cm^3\cdot C^{-1}}$	$/{\rm cm^2\cdot V^{-1}\cdot s^{-1}}$
7.96	15.90	0	30.10	11.603	1.90	4.2	–0.146	27.8
7.99	15.80	0.03	30.17	11.588	3.08	3.5	–0.178	57.2
7.98	15.81	0.06	30.18	11.598	3.58	3.9	–0.158	57.4
7.98	15.64	0.15	30.24	11.601	4.40	4.5	–0.137	60.4

3.2. Electrical transport properties

Figure 3 shows the temperature dependence of electrical conductivity σ for $Ba_8Ga_{16-x}Cu_xSn_{30}$. For all samples, σ decreases monotonically as the temperature is increased from 300 to 600 K, and σ increases distinctly with the increase in the Cu composition.

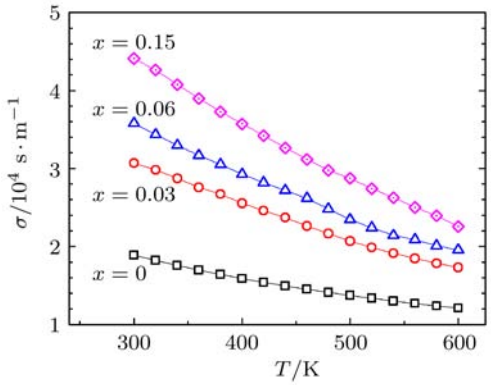


Fig. 3. (colour online) The temperature dependence of electrical conductivity, σ, for the $Ba_8Ga_{16-x}Cu_xSn_{30}$ clathrates.

To understand the composition dependence of σ, the Hall coefficients are measured at room temperature. As shown in Table 1, all samples have negative Hall coefficients. The n-type nature of the dominant carriers is related to the composition ratio of (Ga+Cu)/Sn that is smaller than the ideal value of 16/30. The carrier density is essentially a constant at 3.5–$5\times10^{19}/{\rm cm^3}$ for all samples, indicating that the conduction band structure is kept intact during the substitution.

Using the values of σ and $R_{\rm H}$ at 300 K, carrier mobility is calculated by $\mu_{\rm H} = |\alpha|\,\sigma$. The carrier mobility increases more than two times for all Cu doping samples compared with that of the type-VIII $Ba_8Ga_{16}Sn_{30}$ clathrate obtained in this and other works.[14]

Figure 4 shows the Seebeck coefficient α of $Ba_8Ga_{16-x}Cu_xSn_{30}$ as a function of temperature over the range 300 to 600 K. For all samples, α is negative, which is consistent with the negative sign of $R_{\rm H}$. At the measured temperature range, $|\alpha|$ decreases with the increase in Cu composition. The decrease in $|\alpha|$ with the increasing Cu composition can be attributed to the reduction in the carrier effective mass, which is consistent with the higher mobility of the carriers in all Cu doping samples.

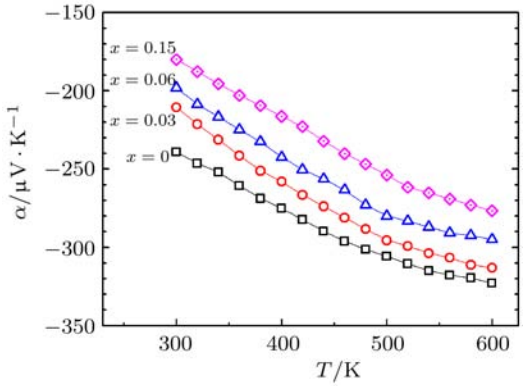


Fig. 4. (colour online) Temperature dependence of the Seebeck coefficient α for $Ba_8Ga_{16-x}Cu_xSn_{30}$ clathrates.

Figure 5 displays the power factor $P = \alpha^2\sigma$. For the sample with Cu doping, the power factor is enhanced obviously compared with that of $x = 0$ due to the increased value of σ, and the largest power factor is 1.87×10^{-3} W/mK^2 for $x = 0.15$ at 518 K, which is enhanced by 46% compared with that of the sample with $x = 0$. The studies of type-VIII $Ba_8Ga_{16}Sn_{30}$ single crystals reveal that the electrical transport properties strongly depend on the composition,[13,24] and the Sn atoms preferentially occupy the 12d and 2a sites of the cage, while the Ga atoms occupy the 8c site with relatively short bond distances to the neighbours. Both Ga and Sn occupy the 24g site randomly. It is further found that a slight change in the occupation probabilities results in a rather large change in the transport properties.[24] Therefore, the Cu substitution for Ga at a very low concentration may induce the rearrangement of Ga and Sn atoms on the cage, which results in the increase in carrier mobility and consequently in the distinct enhancement of the electrical conductivity and the relatively large power factor.

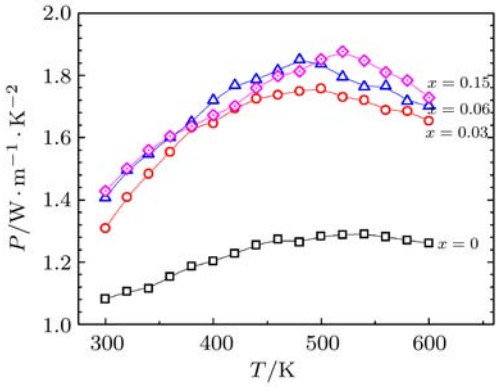


Fig. 5. (colour online) The temperature dependence of power factor P for the $Ba_8Ga_{16-x}Cu_xSn_{30}$ clathrates.

3.3. Thermal properties

The temperature dependence of thermal diffusivity for samples $x = 0$ and $x = 0.03$ was measured by the laser-flash method. The data for the other samples could not be obtained because the sizes of the single crystals were smaller than the required size of 6 mm in diameter. Figure 6 shows the data of thermal conductivity κ and lattice thermal conductivity κ_L from 300 to 600 K. The values of κ are about 0.72 W/mK at 300 K, and are almost invariant with temperature up to 500 K. The marked increase in κ at higher temperatures can be attributed to the so-called bipolar effect[25] due to the excitation of the p-type carriers coexisting with the n-type carriers.

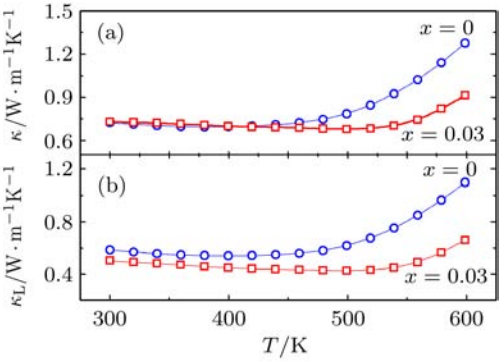


Fig. 6. (colour online) The temperature dependence of (a) thermal conductivity κ and (b) lattice thermal conductivity κ_L for the $Ba_8Ga_{16-x}Cu_xSn_{30}$ clathrates.

Lattice thermal conductivity, κ_L, can be estimated by $\kappa_L = \kappa - \kappa_e$, and carrier thermal conductivity, κ_e, can be calculated using the Wiedenann–Franz law, $\kappa_e = L\sigma T$, where L is the Lorenz number, σ is the electrical conductivity and T is the absolute temperature. L can be calculated by using the Fermi level. In this study, $L = 2.4 \times 10^{-8}\mathrm{V^2/K^2}$ is used.[7] As shown in Fig. 6, at 300 K the lattice thermal conductivity, κ_L, decreases from 0.59 W/mK for $x = 0$ to 0.50 W/mK for $x = 0.03$.

4. Figure of merit

Using the lattice thermal conductivity, κ_L of $x = 0$, the κ values of $x = 0.06$ and $x = 0.15$ are estimated, and then the ZT values are calculated using the estimated κ. As shown in Fig. 7, the maximum value of ZT for $x = 0$ reaches 1.35 at 540 K. The large ZT is attributed to the distinct enhancement of electrical conductivity, and at the same time the Seebeck coefficient does not decrease too much at the higher temperature range.

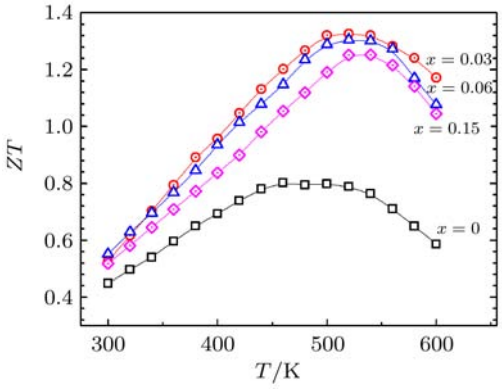


Fig. 7. (colour online) The temperature dependence of ZT for the $Ba_8Ga_{16-x}Cu_xSn_{30}$ clathrates.

5. Conclusion

Single-crystal samples of type-VIII $Ba_8Ga_{16-x}Cu_xSn_{30}$ ($x = 0$, 0.03, 0.06, 0.15) clathrates are prepared by the Sn-flux method with a starting composition of Ba:Ga:Cu:Sn = 8:16–X:X:50 ($X = 0$, 1, 1.5, 2). The patterns of all samples are indexed by the type-VIII clathrate structure with space group $I\bar{4}3m$. The lattice parameter is 11.602 Å for the sample with $x = 0$, and almost keeps invariable for the other samples. At room temperature, the carrier density is $3.5–5 \times 10^{19}/\mathrm{cm^3}$ for all samples. The carrier mobility increases obviously from 27.8 $\mathrm{cm^2/Vs}$ for $x = 0$ to 60.4 $\mathrm{cm^2/Vs}$ for $x = 0.15$. Consequently, the electrical conductivity is enhanced from 1.90×10^4 S/m to 4.40×10^4 S/m. The Seebeck coefficient α is negative from 300 to 600 K, and decreases slightly with the increase in Cu composition. The values of κ are about 0.72 W/mK at 300 K and are almost invariant with temperature up to 500 K for the samples with $x = 0$ and $x = 0.03$. The lattice thermal conductivity, κ_L, decreases from 0.59 W/mK for $x = 0$ to 0.50 W/mK

for $x = 0.03$ at 300 K. The ZT value for $x = 0.03$ reaches 1.35 at 540 K.

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