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High thermoelectric performance of Cu substituted type-VIII clathrate $Ba_8Ga_{16-x}Cu_xSn_{30}$ single crystals

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Single crystalline samples of type-VIII clathrate $Ba_8Ga_{16-x}Cu_xSn_{30}$ ($0 \leq x \leq 0.033$) were prepared by the Sn-flux method. Upon substituting Cu for Ga, the carrier mobility at 300 K increases twice while the carrier density stays in the range $3.1 - 4.2 \times 10^{19}/\mathrm{cm}^3$. Consequently, the electrical resistivity is decreased from 5.3 mΩcm for $x = 0$ to 3.2 mΩcm for $x = 0.033$. Irrespective of x, the Seebeck coefficient is largely negative and linearly changes with temperature in the range $300 < T < 600$ K. The thermal conductivity is in the range $0.68 - 0.74$ W/Km at 300 K for all samples. The dimensionless figure of merit ZT for $x = 0.033$ reaches the maximum of 1.35 at 540 K. © *2011 American Institute of Physics*. [doi:10.1063/1.3583570]

I. INTRODUCTION

In recent years, thermoelectric (TE) materials have been explored intensively in harvesting renewable energy from waste heat and sunlight.[1] Competitive TE materials should have a high figure-of-merit ZT, defined as $ZT = \alpha^2 T/\rho\kappa$. Here, the Seebeck coefficient α, the electrical resistivity ρ, and the thermal conductivity κ, which is given by the sum of the lattice κ_L and the electronic contributions κ_e, are all dependent on the material's composition, atomic arrangement, and electronic band structure.

Since the concept of phonon-glass electron-crystal (PGEC) was proposed by Slack in 1995,[2] caged compounds such as skutterudites[3–6] and clathrates[7–9] have been extensively studied as promising thermoelectric materials. For example, type-I clathrate $Ba_8Ga_{16}Ge_{30}$ was found to possess ZT exceeding 1.0 at high temperature above 700 K.[7–11] At the moderate temperatures, Sn-based type-VIII clathrate $Ba_8Ga_{16}Sn_{30}$ was verified to be a competitive material due to the combination of large α and low κ.[12–14]

The type-VIII clathrate (space group:$I\bar{4}3m$) has the same chemical formula with type-I clathrate (space group:$pm\bar{3}n$), but the guest atoms are encapsulated in one kind of polyhedral cage which composed of 23 framework atoms of group 13 and 14 elements.[15] The cage atoms occupy four sites, 2a, 12d, 8c, and 24g. As for type-VIII clathrates, only four compounds are known so far, $Ba_8\,Ga_{16}Sn_{30}$ (Refs. 5, and 12–14), $Eu_8Ga_{16}Ge_{30}$ (Refs. 16–18), $Sr_8Ga_{16-x}Al_xGe_{30}$ ($6 \leq x \leq 10$) (Ref. 19), and $Sr_8Ga_{16-x}Al_xSi_{30}$ ($8 \leq x \leq 10$) (Ref. 20).

In type-VIII $Ba_8Ga_{16}Sn_{30}$, the atomic displacement parameter of Ba guest atom is smaller than that of Ba in the tetrakaidecahedron of the type-I compound. Nevertheless, the thermal conductivity is still as low as 1 W/Km at 300 K, which makes this compound an attractive TE material.[21] Moreover, the charge carrier type in single crystals can be turned by modifying the ratio of Ga/Sn in the flux from the stoichiometric one of 16/30. In fact, excess in Ga leads to p-type conduction while excess in Sn leads to n-type conduction.[13,14] Fine tuning of the p- and n-type carriers in $Ba_8Ga_{16}Sn_{30}$ led to ZT values of 1.0 and 0.9, respectively, in the temperature range between 450 and 500 K.[22] The band structure calculation indicated that the enhancement of ZT above 1.0 is possible for n-type samples if the carrier density is further optimized.[23] In fact, the mobility of n-type carriers has been enhanced while keeping the carrier density constant by partial substitution of Al for the framework atom Ga.[24] It was also reported that the substitution of Cu for Ga in type-I clathrate $Ba_8Cu_xGa_yGe_{46-x-y}$ enhances the carrier mobility twice.[25] In the present work, we report the synthesis and thermoelectric properties of single crystals of $Ba_8Ga_{16-x}Cu_xSn_{30}$.

II. EXPERIMENTAL

Single crystalline samples of $Ba_8Ga_{16-x}Cu_xSn_{30}$ were prepared by the Sn-flux method. High purity elements were mixed in the atomic ratio of Ba: Ga: Cu: Sn = 8: 16–X: X: 50 (X = 0, 0.5, 0.75, 1.0, 1.5, 2.0) in an argon-filled glovebox. The mixture was sealed in the evacuated quartz tube, which was heated slowly to 763 K, soaked for 10 h, and then slowly cooled over 50 h to 663 K. The constituent phase was characterized by powder x-ray diffraction (XRD) using Rigaku Ultima IV, and the elemental compositions were determined by wave-length dispersive electron-probe microanalysis (EPMA) by using JEOL JXA-8200 analyzer. The electrical resistivity and Seebeck coefficient were measured from 300 to 600 K in a vacuum. The Hall coefficient was measured at room temperature by a dc method in a magnetic field of 1 T. The temperature dependent thermal conductivity κ was calculated via the equation $\kappa = DdC_p$, where D is the thermal diffusivity measured by the laser-flash method in a vacuum,

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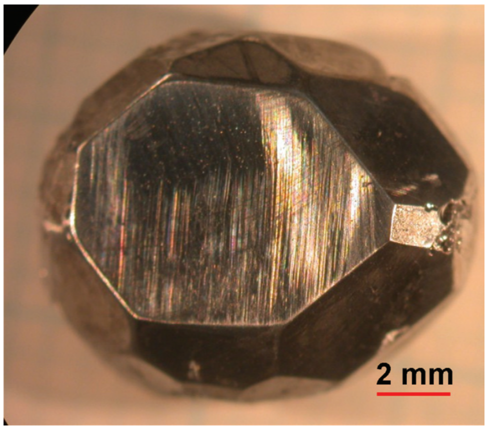

FIG. 1. (Color online) As grown single crystal of type-VIII clathrate $Ba_8Ga_{16-x}Cu_xSn_{30}$ with $x = 0.02$.

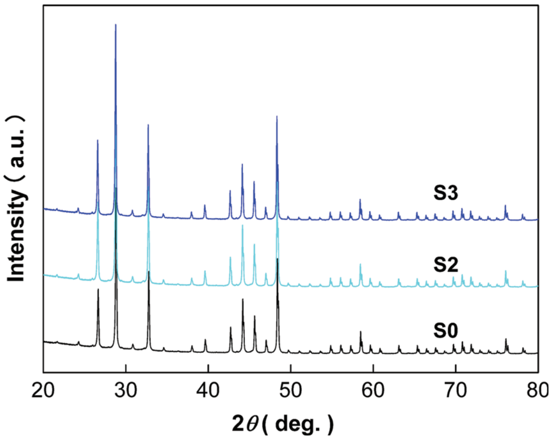

FIG. 2. (Color online) Powder x-ray diffraction patterns for samples of $Ba_8Ga_{16-x}Cu_xSn_{30}$ with $x = 0$ (S0), x = 0.020 (S2), and $x = 0.033$(S3) taken with Cu $K\alpha$ radiation at room temperature.

d is the density, and C_p is the heat capacity that was measured with a differential scanning calorimeter.

III. RESULTS AND DISCUSSION

A. Compositions and lattice parameters

Single crystalline samples of approximately 10 mm in diameter were obtained for $X = 0$, 0.5, 0.75, and 1.0, which samples are denoted by S0, S1, S2, and S3, respectively. Figure 1 shows the picture of the as grown crystal of S3 which has a shiny metallic luster. However, the crystals grown from the mixture with $X = 1.5$ were smaller than 3mm in diameter. For $X = 2.0$, the majority of the obtained sample was composed of platelike crystals, whose crystal structure was found to be the $BaNiSn_3$-type structure.

The elemental compositions of the crystals are listed in Table I. The compositions of Ba: Ga: Cu: Sn roughly agree with the ratio 8: 16-*x*: *x*: 30. The total compositions of framework elements are closed to 46 for all samples, and that of Sn is a little larger than the ideal value 30. It is noteworthy that the Cu composition *x* in the crystal is much lower than the starting composition *X*. For example, *x* of the sample S3 with $X = 1.0$ is only 0.033.

Figure 2 displays the powder XRD patterns for selected samples of $Ba_8Ga_{16\text{-}x}Cu_xSn_{30}$ ($x = 0$, 0.020, and $x = 0.033$). The patterns are well indexed by the type-VIII clathrate structure with the space group $I\bar{4}3m$. The lattice parameters are 11.602 Å, 11.598 Å, and 11.586 Å for S1, S2, and S3, respectively. The lattice parameter slightly decreases with *x*, which is consistent with the smaller atomic radius of Cu than that of Ga. We tried to analyze the preferential site for Cu atoms among the four sites of the cage atoms by the Rietveld refinement. However, we could not specify the preferential site because the Cu composition of 0.033 is too small compared with the total cage atom number of 46.

B. Electrical transport properties

Table I summarizes the room temperature values of electrical resistivity ρ, Hall coefficient R_H, carrier density *n*, carrier mobility μ_H, and effective mass m^*/m_0 for $Ba_8Ga_{16-x}Cu_xSn_{30}$ samples. The temperature dependence of ρ is shown in Fig. 3. For all samples, ρ (*T*) increases monotonically as the temperature *T* is increased from 300 to 600 K. With *x* increasing from 0 to 0.033, the value of ρ ($T = 300$ K) decreases by 39% from 5.28 to 3.24 mΩcm. To understand the reason for the decrease in ρ with *x*, we measured the Hall coefficient R_H at room temperature. As shown in Table I, R_H is negative for all samples and does not change systematically with *x*. The *n*-type character should be maintained by the fact that the Sn composition is larger than the ideal value of 30. The carrier density is essentially unchanged to be $3.1 - 4.2 \times 10^{19}/\text{cm}^3$. The invariable carrier density implies that Cu substation for Ga does not produce extra holes to the system although the number of valence electrons for Cu atom is two less than that of Ga

TABLE I. Crystal compositions, electrical resistivity ρ, Hall coefficient R_H, carrier density *n*, carrier mobility μ_H, and effective mass m^*/m_0 at room temperature for type-VIII clathrate $Ba_8Ga_{16-x}Cu_xSn_{30}$ samples. Starting compositions of Ba: Ga: Cu: Sn are 8: (16-*X*): *X*: 50. The samples S0, S1, S2, and S3 are obtained from the mixtures with $X = 0$, 0.5, 0.75, and 1, respectively.

Sample	Crystal composition				Electrical resistivity ρ (mΩcm)	Hall coefficient R_H (cm^3/C)	Carrier density *n* (10^{19}/cm^3)	Carrier mobility μ_H (cm^2/Vs)	Effective mass m^*/m_0
	Ba	Ga	Cu	Sn					
S0	7.96	15.9	0	30.1	5.28	− 0.146	4.2	27.8	0.38
S1	7.98	15.8	0.018	30.2	4.38	− 0.197	3.1	45.2	0.23
S2	8.00	15.8	0.020	30.1	3.71	− 0.190	3.3	51.2	0.25
S3	7.99	15.8	0.033	30.2	3.24	− 0.178	3.5	57.2	0.24

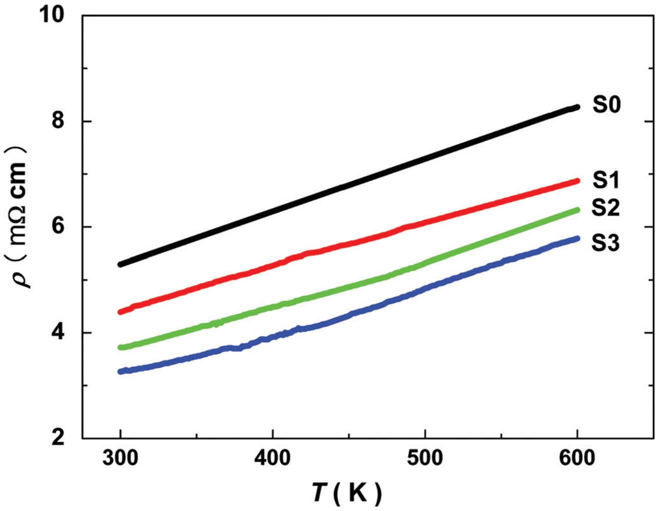

FIG. 3. (Color online) Temperature dependence of electrical resistivity ρ for type-VIII clathrate $Ba_8Ga_{16-x}Cu_xSn_{30}$.

atom. The carrier mobility was calculated by $\mu_H = |\alpha|/\rho$ using the measured values of ρ and R_H at 300 K. As shown in Table I, μ_H ($T = 300$ K) for Cu substituted samples increases twice as large as that for the sample with $x = 0$. The reason for this change will be discussed later.

Figure 4 shows the variations of $\alpha(T)$ of $Ba_8Ga_{16-x}Cu_xSn_{30}$ as a function of temperature from 300 to 600 K. For all samples, α is largely negative, in accordance with the negative sign of R_H. The systematic decrease in $|\alpha|$ with the increase of x can be attributed to the reduction of carrier effective mass. This idea is derived from the higher carrier mobility in samples with $x \neq 0$ than that in the sample with $x = 0$. It is noteworthy that the dispersion of the data becomes smaller as temperature is raised. To understand the effect of Cu substitution on the band structure, we estimate the effective mass m^* by the relationship between α and n. Assuming a single parabolic band for the conduction band, α can be expressed as

$$\alpha = \frac{2m^*\pi^2 k_B{}^2 T\left(r+\frac{3}{2}\right)}{3e\hbar^2(3\pi^2 n)^{3/2}} \qquad (1)$$

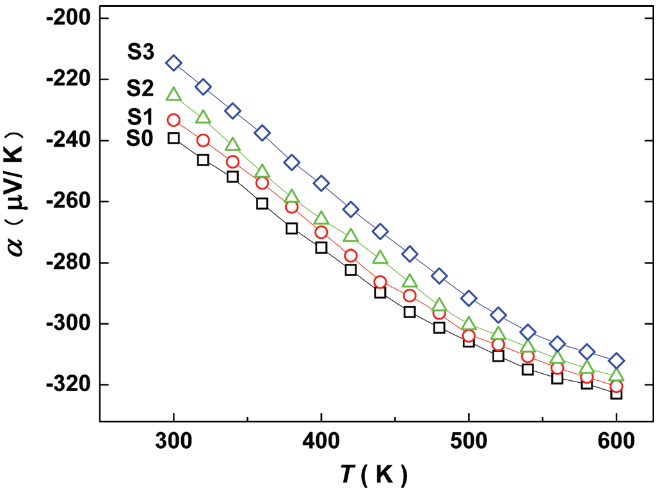

FIG. 4. (Color online) Temperature dependence of Seebeck coefficient α for type-VIII clathrate $Ba_8Ga_{16-x}Cu_xSn_{30}$.

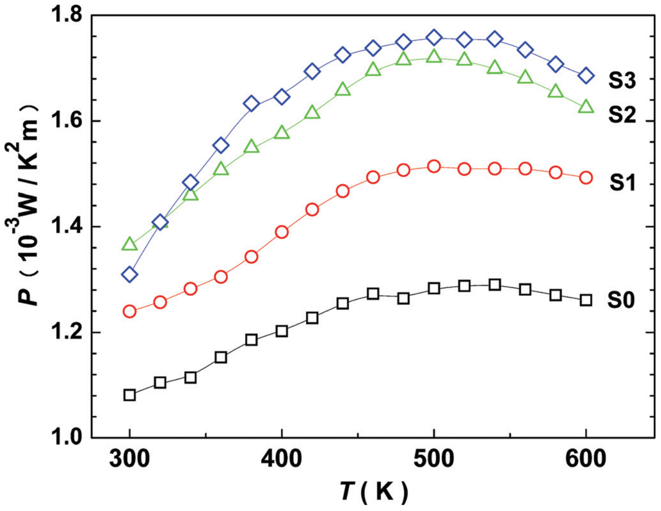

FIG. 5. (Color online) Temperature dependence of power factor P for type-VIII clathrate $Ba_8Ga_{16-x}Cu_xSn_{30}$.

where k_B is the Boltzmann's constant, $\hbar$ is the reduced Planck constant, e is the carrier charge, and r is the scattering factor.[1] By using the values of α, and n, the effective mass m^* can be estimated on the assumption that the electrons are scattered by a mixed scattering process of ion impurity and acoustic phonon ($r = 1/2$).[26] The obtained values of m^*/m_0 at 300 K are listed in Table I. We note that m^*/m_0 is decreased by Cu substitution. This trend occurs if the conduction band curvature at the bottom becomes larger by Cu substitution.

Figure 5 displays the power factor $P = \alpha^2\sigma$ as a function of temperature. With the increase of x, the power factor is enhanced dramatically, that is the consequence of the significant decrease in ρ as shown in Fig. 3. The power factor for S3 reaches 1.77×10^{-3} W/K^{2}m at 518 K. Let us consider why the carrier mobility is increased by the substitution of Cu at the very low level. Previous studies of single crystals type-VIII $Ba_8Ga_{16}Sn_{30}$ revealed that the electrical transport properties strongly depend on the composition.[12,22] The structural refinement of single crystal XRD indicated the preferential occupations of Ga and Sn in the four sites of

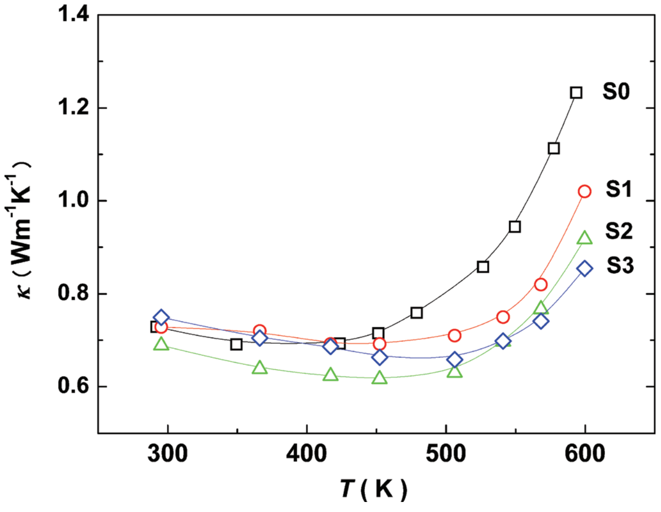

FIG. 6. (Color online) Temperature dependence of thermal conductivity κ for type-VIII clathrate $Ba_8Ga_{16-x}Cu_xSn_{30}$.

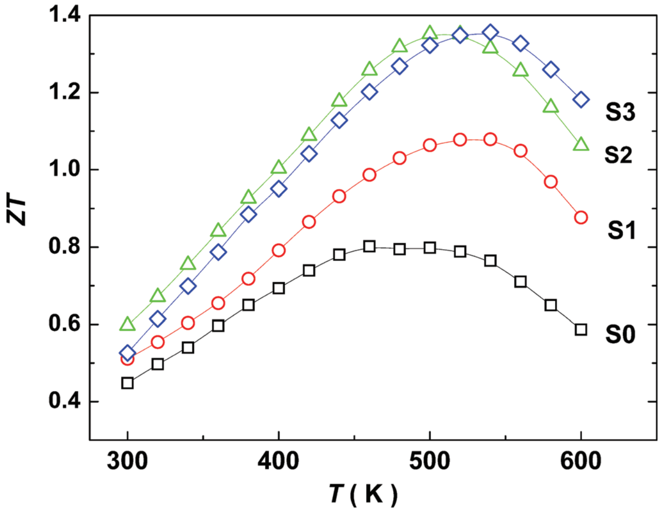

FIG. 7. (Color online) Temperature dependence of dimensionless figure of merit *ZT* for type-VIII clathrate $Ba_8Ga_{16-x}Cu_xSn_{30}$.

the cage.[12] Sn atoms preferentially occupy 12*d* and 2*a* sites of the cage, while Ga atoms occupy 8*c* site with relatively short bond distances to the neighbors. Both Ga and Sn occupy 24*g* site at random. It was further found that the salient change in the occupation probabilities results in rather large change of transport properties.[22] Therefore, we conjecture that Cu substation for Ga at a small level induces rearrangement of Ga and Sn atoms on the cage, which results in the increase of carrier mobility and thus in a better combination of σ and α as for TE material.

C. Thermal conductivity and figure of merit

Figure 6 shows the thermal conductivity κ as a function of temperature from 300 to 600 K. At 300 K, the values are in the range $0.68-0.74$ W/Km. The marked increase of κ at $T > 500$ K can be attributed to the so-called bipolar effect[27] arising from the excitation of *p*-type carriers above the bandgap. Ongoing from S0 to S3, the temperature at which the bipolar effect appears shifts to higher temperatures. In order to evaluate the lattice thermal conductivity κ_L, the carrier thermal conductivity κ_e was estimated by using the Wiedenann-Franz law $\kappa_e = LT/\rho$, where L is 2.4×10^{-8} V^2/K^2 (Ref. 7). Then, κ_L is given by $\kappa_L = \kappa - \kappa_e$. We found that κ_L ($T = 300$ K) is decreased from 0.59 W/Km for S0 to 0.50 W/Km for S3.

Using the values of α, ρ, and κ, the *ZT* was calculated and plotted in Fig. 7. The *ZT* for S3 with $x = 0.033$ reaches the maximum value of 1.35 at 540 K. This enhancement originates from the combination of the significant reduction of ρ and the little change in α in the relevant temperature range.

IV. CONCLUSIONS

Single crystalline samples of type-VIII clathrates $Ba_8Ga_{16-x}Cu_xSn_{30}$ $(0 \le x \le 0.033)$ were prepared by the Sn-flux method. Upon increasing x to 0.033, the carrier mobility at 300 K increased twice, while keeping the carrier density in the range $3.1-4.2 \times 10^{19}/cm^3$. As a result, the electrical resistivity is decreased by 39% whereas the absolute value of the Seebeck coefficient is decreased only by 10%. The thermal conductivity κ stays in the range $0.68-0.74$ W/Km at 300 K, and the bipolar effect appearing above 500 K becomes less pronounced. As a consequence, *ZT* for $x = 0.033$ reaches 1.35 at 540 K, indicating that $Ba_8Ga_{16-x}Cu_xSn_{30}$ is a competitive thermoelectric material at intermediate temperatures.

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