Thermoelectric properties of a clathrate compound Ba$_8$Cu$_{16}$P$_{30}$

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We report the electrical resistivity ($\rho$), thermoelectric power ($S$), thermal conductivity ($\kappa$), and specific heat ($C$) for the clathrate compound Ba$_8$Cu$_{16}$P$_{30}$, in which polyhedral cages are composed of Cu and P atoms. Being in contrast to the $n$-type conduction in most of clathrate compounds, a $p$-type metallic conduction in this compound is indicated by the positive $S$, which monotonically increases up to 65 $\mu$V/K at 460 K. The analysis of $C(T)$ gives indirect evidence for low-frequency vibrations of Sr atoms among its four split sites plays an essential role for the glass-like temperature dependence of $\kappa$. It was pointed out that additionally to the rattling of the Sr atoms, tunneling of the guest atoms gets more obvious with decreasing of their size (Ba$\rightarrow$Sr$\rightarrow$Eu). The Ba atoms in the large cages are encapsulated in two kinds of polyhedral cage, dodecahedron, and tetrakaidecahedron, formed by Ga and Ge atoms in disorder. Since then, many works have been done to understand the mechanism of the glass-like $\kappa(T)$, and to explore the potential thermoelectric application of the clathrate compounds. It was pointed out that additionally to the rattling of the Sr atoms, tunneling of Sr atoms among its four split sites plays an essential role for the glass-like temperature dependence of $\kappa$. For the isostuctural compounds $X_8$Ga$_{16}$Ge$_{30}$ ($X=$ Ba, Sr, and Eu), the tunneling of the guest atoms gets more obvious with decreasing of their size (Ba$\rightarrow$Sr$\rightarrow$Eu). In order to understand the relations among the glass-like $\kappa(T)$, rattling and tunneling of the guest atoms, and atomic disorder of the cages, it is necessary to study systematically the clathrate compounds with careful selection of guest and host atoms, with and without atomic disorder. Moreover, up-to-date, $n$-type conductivity is most often obtained for the clathrate compounds. In practical thermoelectric application, thermoelements need two legs made of $n$- and $p$-type materials, respectively. It is thus urgent to search for $p$-type clathrate compounds for practical applications.

Ba$_8$Cu$_{16}$P$_{30}$ was first synthesized and characterized by Dünner and Mewis. They also reported a semiconducting behavior with an energy gap of $E_g=0.7$ eV in the electrical resistivity $\rho(T)$. It crystallizes in an orthorhombic structure (space group Pbcn), a superstructure of the type I cubic clathrate structure without atomic disorder. The Ba atoms are encapsulated in two kinds of dodecahedron (small cages) and three kinds of tetrakaidecahedron (large cages), which are formed by Cu and P atoms. The Ba atoms in the large cages have relatively large values of atomic displacement parameter (ADP). A low thermal conductivity is expected if the ADP values result from the rattling and/or tunneling of Ba atoms. Although there are many reports on Si-, Ge-, and Sn-clathrate compounds encapsulating alkaline-metal elements in the literature, it is the first clathrate compound without group 14 elements. In this letter, we report the transport and thermal properties of Ba$_8$Cu$_{16}$P$_{30}$. The experimental results indicate that it is a rare example of $p$-type clathrate compound with metallic resistivity, large thermoelectric power $S$, and low thermal conductivity, which are the ingredients for thermoelectric materials.

The sample of Ba$_8$Cu$_{16}$P$_{30}$ was synthesized by a similar method described in Ref. 8. Powder X-ray diffraction analysis revealed that the sample crystallizes in the orthorhombic structure with lattice constants, $a=14.133$, $b=10.090$, and $c=28.021$ Å, which are in good agreement with the ones reported previously. The electron-probe microanalysis (EPMA) of several samples gave the same composition, 14.8% Ba, 29.5% Cu, and 55.7% P, which is in good agreement with the ideal composition of a stoichiometric compound.

Electrical resistivity, measured by a standard four-probe method from 1.3 to 300 K, is shown in Fig. 1. In contrast to the semiconduction of $\rho(T)$ reported in Ref. 8, a metallic behavior is observed. From our EPMA results, the composition of the present sample is well described by Ba$_8$Cu$_{16}$P$_{30}$, not by Ba$_8$Cu$_{15.5}$P$_{30.5}$ suggested in Ref. 8. The metallic behavior may result from the good stoichiometry of our sample.

Provided that static disorder can be neglected in a compound, the Debye temperature $\Theta_D$ can be estimated using the room-temperature ADPs:

$$\Theta_D(K) = 208/\left[ U_{eq}^{av}(\hat{A})^2 \times m_av \right]^{1/2},$$

where $U_{eq}^{av}$ is the weighted average of room-temperature values of $U_{eq}^i$ for each atom type in the compound given in units of $\hat{A}^2$ ($U_{eq}^i$ is defined as one-third of the trace of orthogonal-
ized $U_{ij}$ tensor), and $m_{av}$, is the average mass of an atom in the compound given in amu. Using the room-temperature ADP values for $\text{Ba}_8\text{Cu}_{16}\text{P}_{30}$ given in Ref. 8, we calculated $\Theta_D$ to be 311 K. With this value, the experimental data of $\rho(T)$ can be described by the Bloch–Grüneisen expression very well.

Thermoelectric power was measured from 5 to 300 K with a slowly varying $T$-gradient technique by the use of a thermocouple of chromel/Au. From 80 to 460 K, the measurement of $S$ was made by the use of the MMR Seebeck effect measurement system with $T$ gradient of 2–5 K. As shown in Fig. 1, the positive $S$ increases monotonically up to 65 $\mu$V/K with increasing temperature from 5 to 460 K. This indicates a $p$-type conduction in $\text{Ba}_8\text{Cu}_{16}\text{P}_{30}$. $p$-type conductivity in the clathrate compound is only obtained by substituting Sb for Ge in $\text{Ba}_8\text{Ga}_{16}(\text{GaSb})_{30-2x}$ (Ref. 10). Thus, $\text{Ba}_8\text{Cu}_{16}\text{P}_{30}$ could be the first $p$-type stoichiometric clathrate compound. The measurements of the Hall coefficient need to confirm the carrier type and to get the information of carrier concentration. Here, we estimate the carrier concentration by using the $S(T)$ data at low temperatures. As shown by the solid line in the inset of Fig. 1, the data below 40 K can be described by $S(T) = \alpha T$, with $\alpha = 0.23 \mu$V/K$^2$. According to the free electron model, the low-temperature thermoelectric power is given by

$$S(T) = \alpha T = \frac{2m_e^2k_B^2}{3e\hbar^2(3\pi^2n)^{2/3}}T,$$  \hspace{1cm} (2)

where $m$ and $e$ are the mass and charge of free carrier (positive for the present case), respectively, $n$ is the density of carrier, $k_B$ and $\hbar$ have their usual meaning. The value of $\alpha$ given above leads to a carrier concentration $n = 1.6 \times 10^{20}$ cm$^{-3}$, which is comparable with the electron concentration in $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$, 5.2 $\times 10^{20}$ cm$^{-3}$ at 2 K.\cite{12}

Figure 2 displays the thermal conductivity $\kappa(T)$ of $\text{Ba}_8\text{Cu}_{16}\text{P}_{30}$ measured with a steady-state technique from 5 to 300 K. The increase of $\kappa(T)$ above about 200 K is possibly due to radiation loss, which was not corrected in our measurements. Assuming the validity of Wiedemann–Franz law, charged carrier contribution to the thermal conductivity $\kappa_e(T)$ was estimated by the use of the data of $\rho(T)$ in Fig. 1. The $\kappa_e(T)$ and phonon contribution $\kappa_{\Phi} (T)$, obtained by subtracting $\kappa_e(T)$ from the total thermal conductivity $\kappa(T)$, are plotted in Fig. 2. The $\kappa_{\Phi}(T)$ is much larger than $\kappa_e(T)$, indicating that phonons carry the heat flow mainly. The $\kappa_{\Phi}(T)$ exhibits a pronounced maximum around 25 K, being typical of normal crystalline solids. Such a behavior in $\kappa(T)$ is at variance with the glass-like $\kappa(T)$ due to tunneling state of Ba atoms. However, the room-temperature value is only 2.9 W/K m. The reduced value of $\kappa_{\Phi}$ and its temperature dependence are similar to those of $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$ (Ref. 13). As in $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$, the low thermal conductivity of $\text{Ba}_8\text{Cu}_{16}\text{P}_{30}$ can be attributed to the scattering of acoustic phonons by the low-frequency local vibrations of Ba atoms encapsulated in the polyhedra.

Because measurements of specific-heat $C$ provide information on the low-frequency local vibrations of guest atoms in open structure compounds,\cite{12–14} we measured the specific heat of $\text{Ba}_8\text{Cu}_{16}\text{P}_{30}$ from 2 to 300 K using 2 $\tau$-relaxation method with a commercial physical property measurement system (Quantum Design). Figure 3 shows the experimental result together with several contributions obtained by the analysis described later. At temperatures below 5 K, $C(T)$ can be described by $C(T) = \gamma T + \beta T^3$ with $\gamma = 26.3$ mJ/mol K$^2$ and $\beta = 2.1$ mJ/mol K$^3$. This value of $\beta$ leads to $\Theta_D = 371$ K.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig1.pdf}
\caption{Electrical resistivity $\rho$ and thermoelectric power $S$ of $\text{Ba}_8\text{Cu}_{16}\text{P}_{30}$ as a function of temperature $T$. The inset shows low-temperature data of $S$.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig2.pdf}
\caption{Thermal conductivity $\kappa$ of $\text{Ba}_8\text{Cu}_{16}\text{P}_{30}$ as a function of temperature $T$.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig3.pdf}
\caption{Specific-heat $C$ of $\text{Ba}_8\text{Cu}_{16}\text{P}_{30}$ as a function of temperature $T$. $C_{\text{total}}$ is the sum of one Debye term $C_D$, two Einstein terms $C_{E1}$ and $C_{E2}$, and the electronic term $C_{el}$.}
\end{figure}
As first approximation, we take the guest Ba atoms (8 atoms per formula of Ba₈Cu₁₆P₃₀) as Einstein oscillators and the framework (16 Cu and 30 P atoms per formula) as a Debye solid. If we use the ADPs of the framework atoms only in the Eq. (1), then the Debye temperature of 375 K is obtained. It is very close to the value yielded above from the low-temperature data of C(T). Thus, we adopt Θ_D = 371 K to calculate the Debye contribution C_D(T), and describe the lattice specific heat with C_L(T) = 8C_E(T) + 46C_D(T), where C_E(T) is the Einstein contribution. The specific heat was fitted to the sum C_total of several contributions; one Debye term C_D, two Einstein terms, C_E₁ and C_E₂, and the electronic term γT. If we neglect both the difference between the two kinds of small cage and the difference between the three kinds of large cage, the fit parameters are just two Einstein temperatures Θ_E₁ and Θ_E₂ for the oscillators in the small cages and in the large cages, respectively. With keeping in mind that the ratio of the numbers of the small cages and large cages is 1:3, the two Einstein temperatures Θ_E₁ and Θ_E₂ were obtained from fitting the low-temperature data below 50 K. The obtained values 120 and 90 K, respectively, are close to the values, 123 and 88 K, estimated by using the room-temperature ADP values given in Ref. 8 with a modified formula of Eq. (1). From the crystallographic data given in Ref. 8, the average distances d between the Ba atoms and their 20 near-neighbor framework atoms for the two kinds of small cage are 3.292 and 3.251 Å, respectively, and those for the three kinds of large cages are 3.594, 3.586, and 3.588 Å, respectively. The two sets of values are significantly smaller than those in Ba₈Ga₁₆Ge₃₀, 3.541 and 3.874 Å, respectively. It should be recalled that the d values in Ba₈Ga₁₆Ge₃₀ are smallest among the type I clathrate compounds X₈Ga₁₆Ge₃₀ (X = Ba, Sr, and Eu). For this series, the Einstein temperature of the guest atoms in the large cages increases with the decrease of the relative size of the cage from 30 K (Eu), 53 K (Sr) to 60 K (Ba). Therefore, Θ_E₂ = 90 K for Ba₈Cu₁₆P₃₀ with still smaller cages is reasonable. However, making a clear-cut distinction between the guest atoms as Einstein oscillators and the framework atoms as a Debye solid is oversimplified as pointed out by Paschen et al. The discrepancy in C(T) above 100 K between the calculation and the measurement possibly results from our simplistic model.

In summary, we reported the electrical resistivity, thermoelectric power, thermal conductivity, and specific heat of Ba₈Cu₁₆P₃₀. It is found that this compound is a p-type clathrate compound with a thermal conductivity of 3.7 W/Km and thermoelectric power of 50 μV/K at 300 K, leading to the dimensionless figure of merit ZT = 0.02. In general, compounds formed with heavier/larger framework atoms possess lower κ_ph. For example, at room temperature, κ_ph of CeFe₄Sb₁₂ is one-tenth of that of CeFe₄P₁₂ (Ref. 15). Considering the amenability of framework of the clathrate compounds, a much reduced κ_ph could be obtained if the framework of Ba₈Cu₁₆P₃₀ could be modified with As and/or Sb atoms. It is worthwhile to investigate the semiconducting variant of this compound for good thermoelectric properties.

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