APPLIED PHYSICS LETTERS VOLUME 82, NUMBER 16 21 APRIL 2003

Thermoelectric properties of a clathrate compound $Ba_8Cu_{16}P_{30}$

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(Received 16 December 2002; accepted 28 February 2003)

We report the electrical resistivity (ρ), thermoelectric power (S), thermal conductivity (κ), and specific heat (C) for the clathrate compound $Ba_8Cu_{16}P_{30}$, 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 μV/K at 460 K. The analysis of $C(T)$ gives indirect evidence for low-frequency local vibrations of Ba atoms with two Einstein temperatures 120 and 90 K, respectively. These local vibrations lead to a low lattice thermal conductivity of 2.9 W/K m at 300 K. The combination of the metallic resistivity, large thermoelectric power, and low thermal conductivity, makes this compound be a prospective thermoelectric material. © *2003 American Institute of Physics.*

[DOI: 10.1063/1.1568819]

The phonon-glass and electron-crystal (PGEC) concept proposed by Slack[1] has stimulated much interest in open structure compounds to make a thermoelectric material that could conduct heat like glasses and conduct electricity like ordinary crystalline solids. The low-frequency local vibrations of guest atoms, so-called rattling, result in reduction of thermal conductivity κ. Recently, in the spirit of the PGEC concept, Nolas *et al.*[2] reported a glass-like $\kappa(T)$ for $Sr_8Ga_{16}Ge_{30}$. This compound has the cubic type I ice clathrate structure, in which the Sr atoms are encapsulated in two kinds of polyhedral cage, dodecahedron, and tetrakaidecahedron, formed by Ga and Ge atoms in disorder.[3,4] 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.[5–7] It was pointed out that additionally to the rattling of the Sr atoms, tunneling of Sr atoms among its four spilt sites plays an essential role for the glass-like temperature dependence of κ.[6,7] For the isostructural compounds $X_8Ga_{16}Ge_{30}$ (X=Ba, Sr, and Eu), the tunneling of the guest atoms gets more obvious with decreasing of their size (Ba>Sr>Eu).[7] 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. Furthermore, 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.

$Ba_8Cu_{16}P_{30}$ was first synthesized and characterized by Dünner and Mewis.[8] 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 $Ba_8Cu_{16}P_{30}$. 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 $Ba_8Cu_{16}P_{30}$ 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.[8] 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 $Ba_8Cu_{16}P_{30}$, not by $Ba_8Cu_{15.5}P_{30.5}$ 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 Θ_D can be estimated[9] using the room-temperature ADPs:

$$\Theta_D(K) = 208/[U_{\mathrm{eq}}^{\mathrm{av}}(\text{Å}^2) \times m_{\mathrm{av}}]^{1/2}, \tag{1}$$

where $U_{\mathrm{eq}}^{\mathrm{av}}$ is the weighted average of room-temperature values of U_{eq} for each atom type in the compound given in units of Å^2 (U_{eq} is defined as one-third of the trace of orthogonal-

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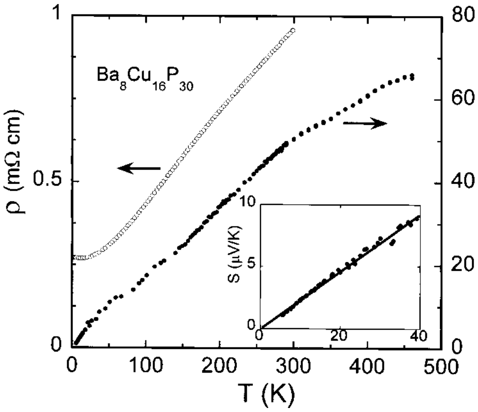

FIG. 1. Electrical resistivity ρ and thermoelectric power S of $Ba_8Cu_{16}P_{30}$ as a function of temperature T. The inset shows low-temperature data of S.

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 $Ba_8Cu_{16}P_{30}$ given in Ref. 8, we calculated Θ_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+0.07 at. % Fe. 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 μV/K with increasing temperature from 5 to 460 K. This indicates a p-type conduction in $Ba_8Cu_{16}P_{30}$. p-type conductivity in the clathrate compound is only obtained by substituting Sb for Ge in $Ba_8Ga_{16}(GaSb)_xGe_{30-2x}$ (Ref. 10). Thus, $Ba_8Cu_{16}P_{30}$ 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 $\alpha=0.23\ \mu\text{V/K}^2$. According to the free electron model, the low-temperature thermoelectric power is given by[11]

$$S(T)=\alpha T=\frac{2m\pi^2k_B^2}{3e\hbar^2(3\pi^2n)^{2/3}}T, \tag{2}$$

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 α given above leads to a carrier concentration $n=1.6\times10^{20}\ \text{cm}^{-3}$, which is comparable with the electron concentration in $Ba_8Ga_{16}Ge_{30}$, $5.2\times10^{20}\ \text{cm}^{-3}$ at 2 K.[12]

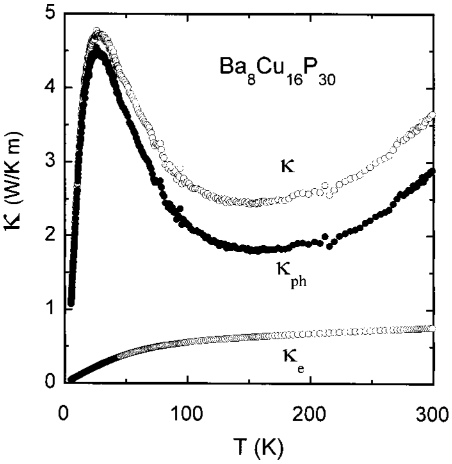

FIG. 2. Thermal conductivity κ of $Ba_8Cu_{16}P_{30}$ as a function of temperature T.

Figure 2 displays the thermal conductivity $\kappa(T)$ of $Ba_8Cu_{16}P_{30}$ 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 $\kappa_{ph}(T)$, obtained by subtracting $\kappa_e(T)$ from the total thermal conductivity $\kappa(T)$, are plotted in Fig. 2. The $\kappa_{ph}(T)$ is much larger than $\kappa_e(T)$, indicating that phonons carry the heat flow mainly. The $\kappa_{ph}(T)$ 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 κ_{ph} and its temperature dependence are similar to those of $Ba_8Ga_{16}Ge_{30}$ (Ref. 13). As in $Ba_8Ga_{16}Ge_{30}$, the low thermal conductivity of $Ba_8Cu_{16}P_{30}$ 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,[12–14] we measured the specific heat of $Ba_8Cu_{16}P_{30}$ from 2 to 300 K using 2 τ-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 $\gamma=26.3\ \text{mJ/mol K}^2$ and $\beta=2.1\ \text{mJ/mol K}^3$. This value of β leads to $\Theta_D=371$ K.

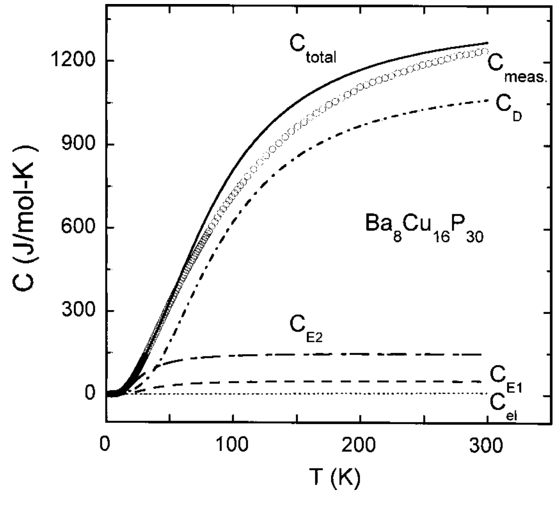

FIG. 3. Specific-heat C of $Ba_8Cu_{16}P_{30}$ as a function of temperature T. C_{total} is the sum of one Debye term C_D, two Einstein terms C_{E1} and C_{E2}, and the electronic term C_{el}.

As first approximation, we take the guest Ba atoms (8 atoms per formula of $Ba_8Cu_{16}P_{30}$) 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 $\Theta_D = 371$ 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).[9] From the crystallographic data given in Ref. 8, the average distances $\bar{d}$ 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 $Ba_8Ga_{16}Ge_{30}$, 3.541 and 3.874 Å, respectively.[7,12] It should be recalled that the $\bar{d}$ values in $Ba_8Ga_{16}Ge_{30}$ are smallest among the type I clathrate compounds $X_8Ga_{16}Ge_{30}$ (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).[7,13] Therefore, $\Theta_{E2} = 90$ K for $Ba_8Cu_{16}P_{30}$ 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.*[12] 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 $Ba_8Cu_{16}P_{30}$. It is found that this compound is a p-type clathrate compound with a thermal conductivity of 3.7 W/K m 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 $CeFe_4Sb_{12}$ is one-tenth of that of $CeFe_4P_{12}$ (Ref. 15). Considering the amenability of framework of the clathrate compounds,[16,17] a much reduced κ_{ph} could be obtained if the framework of $Ba_8Cu_{16}P_{30}$ could be modified with As and/or Sb atoms. It is worthwhile to investigate the semiconducting variant of this compound for good thermoelectric properties.

The authors would like to acknowledge S. Paschen for valuable discussion and Y. Shibata for the electron-probe microanalysis. This work was supported by a Grant-in Aid for Scientific Research (COE 13CE2002) of MEXT Japan, and a NEDO International Joint Research Grant.

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