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Thermoelectric properties of clathrate compounds $Ba_8Cu_{16}P_{30}$ and $Ba_8Ga_{16}Sn_{30}$

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Clathrate compounds are characterized by an extended three-dimensional framework providing huge voids which are filled by large electropositive elements, as like in filled skutterudite compounds. Physical and chemical properties of Si- and Ge-clathrates have been extensively studied because of the unique superconducting and thermoelectric behaviors [1]. However, much less are known for P- and Sn-clathrares. $Ba_8Cu_{16}P_{30}$ and $Ba_8Ga_{16}Sn_{30}$ crystallize into the quasi-type I orthorhombic and type-VIII cubic structures, respectively [2,3]. In the former, Ba atoms are encapsulated in five different polyhedra formed by Cu and P atoms which are chemically ordered [2]. In the latter, Ba atoms occupy only one site in a distorted polyhedron formed by 23 atoms of Ga and Sn which are chemically disordered [3]. In both compounds, the atomic displacement parameters of Ba atoms at room temperature are rather large, 0.017 and 0.043 Å^2, respectively [2,3]. This may allow the so-called rattling motion of Ba ions which scatters the acoustic phonons propagating the heat, as was first pointed out for the filled skutterudite antimonide [4]. Keeping this in mind, we have studied the thermoelectric properties of the two clathrate compounds. Our preliminary work on $Ba_8Cu_{16}P_{30}$ has been reported in Ref. 5.

We have prepared single-crystal samples by using a self-flux method, as shown in Fig. 1. The compositions determined by electron-probe microanalysis are in good agreement with the ideal stoichiometry. Crystallographic analysis of $Ba_8Ga_{16}Sn_{30}$ indicated that the atomic displacement parameter of Ba ions decreases from 0.048 to 0.023 Å^2 on cooling from 390 K to 90 K. The physical properties have been studied by the measurements of electrical resistivity ρ, thermopower S, thermal conductivity κ, Hall coefficient R_H, and specific heat C. The weak temperature dependence of ρ with a positive slope is that of a bad metal. The values at 300 K are 1 and 4 mΩcm for $Ba_8Cu_{16}P_{30}$ and $Ba_8Ga_{16}Sn_{30}$, respectively. A p-type conduction in $Ba_8Cu_{16}P_{30}$ was indicated by the positive S, which monotonically increases up to 65 μV/K at 460 K. For $Ba_8Ga_{16}Sn_{30}$, on the other hand, the S is negative and reaches a large value of -250 μV/K at 550 K. The negative sign of S is consistent with the negative R_H, which gives an estimation of electron carriers of 3.7×10^{19}/cm^3. This carrier density is close to the optimum value at which the thermoelectric power factor S^2/ρ is maximized for a simple semiconductor with one type carrier [6].

In addition to the large S, another requirement for thermoelectric material is the low κ to enhance the figure of merit $Z = S^2/\kappa\rho$. The values of κ for $Ba_8Cu_{16}P_{30}$ and $Ba_8Ga_{16}Sn_{30}$ are 3.7 and 2.2 W/Km at 300 K, respectively, which are comparable with that of a type-I clathrate $Ba_8Ga_{16}Ge_{30}$, where the rattling of Ba ions was found [7]. The lattice contribution κ_L is dominant over the electronic one at whole temperatures as is shown in Fig. 2. With decreasing temperature, $\kappa_L(T)$ for $Ba_8Cu_{16}P_{30}$ exhibits a pronounced peak at 30 K, being typical of crystal solids. By contrast, such a peak in $\kappa_L(T)$ is absent for $Ba_8Ga_{16}Sn_{30}$. This absence may be a result of the chemical disorder in the cage formed by Ga and Sn atoms. The glass-like behavior of $\kappa_L(T)$ without a peak found for $Sr_8Ga_{16}Ge_{30}$ was attributed to the tunneling state of Sr ions in the large cage [7]. In order to confirm the tunneling of Ba ions in $Ba_8Ga_{16}Sn_{30}$, a study by ultrasonic measurements is in progress.

The presence of low-frequency local vibrations of Ba ions has been confirmed by the analysis of specific heat. It was assumed that Ba ions are Einstein oscillators and the framework is a Debye solid. Thus obtained Einstein temperatures are 120 and 90 K, respectively, for Ba ions in the small and large cages of $Ba_8Cu_{16}P_{30}$. Still lower value of 55 K for $Ba_8Ga_{16}Sn_{30}$ is consistent with the larger atomic displacement parameter, as noted above. From the knowledge of the data of S, ρ and κ, we have estimated Z. The dimensionless figure of merit ZT is 0.02 and 0.22 at 300 K for $Ba_8Cu_{16}P_{30}$ and $Ba_8Ga_{16}Sn_{30}$, respectively. The latter value would be further increased if the Ba ions could be substituted by Sr ions with smaller ionic radius.

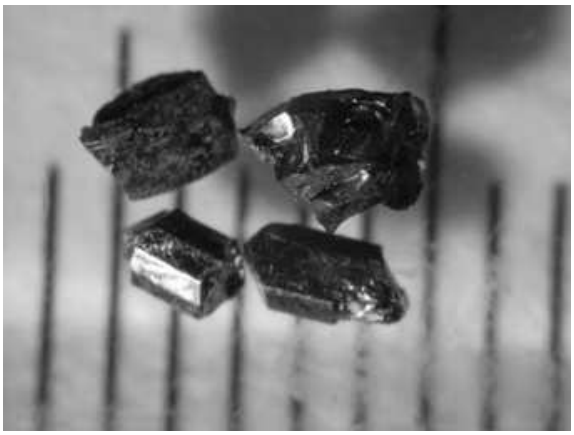

Fig. 1(a) $Ba_8Cu_{16}P_{30}$ crystals

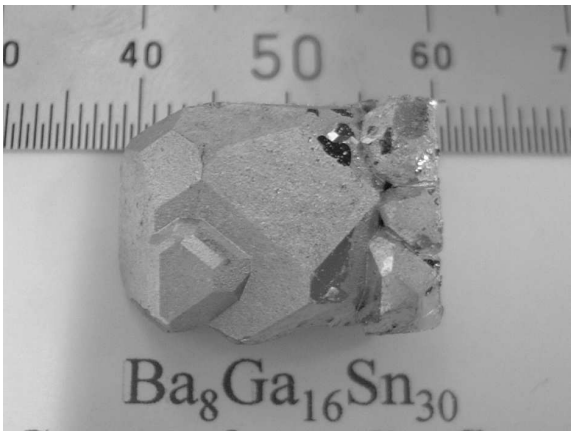

Fig. 1(b) $Ba_8Ga_{16}Sn_{30}$ crystals

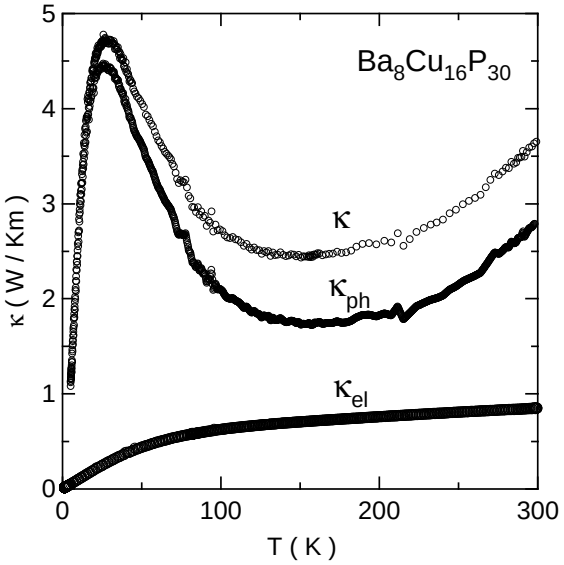

Fig. 2(a) Thermalconductivity of $Ba_8Cu_{16}P_{30}$

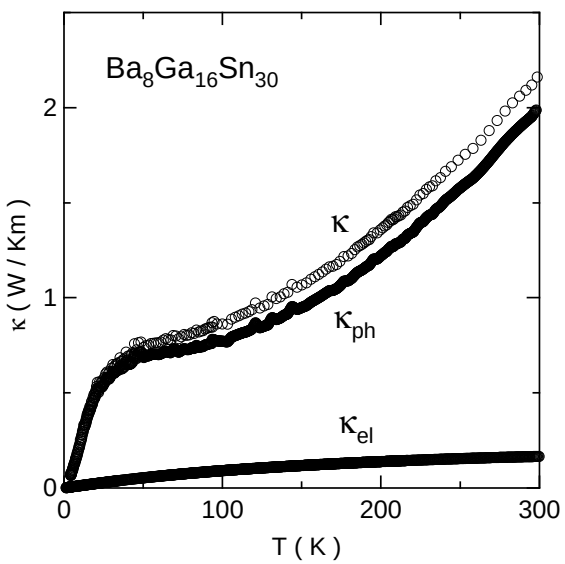

Fig. 2(b) Thermalconductivity of $Ba_8Ga_{16}Sn_{30}$

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