Low-temperature transport properties of polycrystalline $Ba_8Ga_{16}Sn_{30}$

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Low-temperature resistivity, Seebeck coefficient, thermal conductivity, and heat-capacity measurements were performed on $Ba_8Ga_{16}Sn_{30}$. This compound crystallizes in a cubic type-VIII clathrate phase, space group $I\bar{4}3m$, with the Ba atoms residing inside voids created by a tetrahedrally bonded network of Ga and Sn atoms. $Ba_8Ga_{16}Sn_{30}$ exhibits semiconducting behavior above 150 K with a low thermal conductivity and thus may hold potential for thermoelectric applications.

I. INTRODUCTION

Semiconducting group-IV clathrates have recently been identified as showing potential for thermoelectric applications.[1,2] Most of the work to date investigating the transport properties of clathrate compounds has focused on clathrates with the type I clathrate crystal structure (space group $Pm\bar{3}n$). These compounds have the general formula $A_8B_yC_{46-y}$, where atoms B (Al, Zn, Cd, Ga, In) and C (Si, Ge, Sn) are tetrahedrally bonded to make a framework that forms cages in which the guest atoms A (Na, K, Rb, Cs, Sr, Ba, Eu) reside. The encapsulated atoms are said to "rattle" inside their atomic-sized cages, thus creating strong phonon-scattering centers. The localized vibrations of these atoms are believed to cause a dramatic lowering in the lattice thermal conductivity. Provided the electrical conduction takes place mostly through the frame, the rattling guest atoms will not greatly diminish the electrical conductivity. Indeed, semiconducting Ge-based clathrates exhibit lattice thermal conductivities typical of amorphous materials while maintaining good electronic properties.[3,4] Materials of this type were described by Slack[1] as being "phonon-glass and electron-crystal" (PGEC) materials and meet one of the main criteria for finding new thermoelectric materials.

As part of a comprehensive study to assess the low-temperature transport properties of different clathrate compounds and their potential for thermoelectric applications, we have synthesized $Ba_8Ga_{16}Sn_{30}$, a cubic material with the same general formula as that of type I clathrates but with a different crystal structure.[5] In this report, we present low-temperature electrical and thermal transport measurements on $Ba_8Ga_{16}Sn_{30}$ and evaluate its potential for thermoelectric applications.

II. SAMPLE PREPARATION

Sample preparation consisted of mixing and reacting high-purity elements inside a pyrolitic boron nitride crucible, itself sealed inside a quartz ampoule, above the melting point of the constituents. The product was annealed for five days at 380 °C before removing from the furnace. The structural properties were analyzed by powder x-ray diffraction. The structure was identified as $I\bar{4}3m$ with a lattice constant of 11.600 Å. In this structure, the Ba atoms occupy cage voids created by the sp^3 hybridized network of Ga and Sn atoms. These cage voids can be thought of as distorted polyhedra connected by the (Ga,Sn) framework.[5] Powder x-ray diffraction indicated trace amount of elemental Sn as a secondary phase. We note that our specimen had the type VIII crystal structure with no evidence of the type I clathrate crystal structure, as has been reported in the literature.[6]

The $Ba_8Ga_{16}Sn_{30}$ powders were ground to fine grains inside a glove box and hot pressed inside a graphite die at 380 °C and 2×10^4 lbs/in^2 for 2.5 h in an argon atmosphere. The resulting pellet had a density greater than 93% of the x-ray density. Optical metallographic

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and electron-beam microprobe (XMP) analyses were performed on polished surfaces of the hot-pressed pellets. The average grain size was estimated to be 5.7 μm.[7] A thorough wavelength dispersive analysis indicated very small isolated grains of unreacted Sn among the $Ba_8Ga_{16}Sn_{30}$ grains. In some locations, unreacted Sn was also located between the $Ba_8Ga_{16}Sn_{30}$ grains. This trace amount of Sn was not observed throughout the pellet but only in some locations. The XMP analysis indicated the exact stoichiometry $Ba_8Ga_{15.8}Sn_{29.0}$, assuming the Ba sites are fully occupied. We note that this indicates vacancies on the (Ga,Sn) framework sites. Attempts to synthesize this compound with a varying Ga-to-Sn ratio, to vary the electronic properties as reported for type I Ge-clathrates,[3,8] were not successful. The resulting compositions were basically $Ba_8Ga_{15.8}Sn_{29.0}$, as indicated by careful XMP analysis, while the transport properties of those specimens had values and temperature dependencies similar to those we present below.

III. RESULTS AND DISCUSSION

The hot-pressed pellets were cut with a wire saw in the shape of a parallelepiped 2 × 2 × 5 mm^3 in size for transport measurements. Four-probe electrical resistivity (ρ), steady-state Seebeck coefficient (S), and steady-state thermal conductivity (κ) measurements were performed in a radiation-shielded vacuum probe. Heat losses via conduction through the lead wires and radiation were determined in separate experiments and the data corrected accordingly. Heat-capacity measurements were performed in the Quantum Design Physical Properties Measurement System (San Diego, CA) using the standard relaxation technique over the range of 2.2–350 K. The thermal coupling of the sample to the measurement stage was accomplished with a small amount of Apiezon N grease, and its contribution to the specific heat was measured in a separate experiment and subtracted from the final result.

Figure 1 shows S and ρ measurements from 300 to 5 K. The negative S values indicate electrons as majority carriers. The room temperature electron concentration, determined from Hall measurements, was 2.8 × 10^{19} cm^{-3}. The magnitude of S increases with increasing temperature towards a modest value of −137 μV K^{-1} at room temperature, a behavior typical of degenerately doped semiconductors. However, ρ exhibits a non-monotonic temperature dependence: a metallic-like behavior with $d\rho/dT > 0$ at low temperatures and a semiconducting-like dependence ($d\rho/dT < 0$) for $T >$ 150 K. This latter behavior may be characterized by a simple activation-type conduction mechanism, with activation energy E_a ~18 meV. Kuznetsov et al.[9] reported a similar value of E_a (15 meV) for a specimen with similar electron concentration. The metallic-like behavior of ρ at $T <$ 150 K indicates conduction in an impurity band. We identify the activation energy of 18 meV as the energy difference between the impurity band and those in the conduction band.

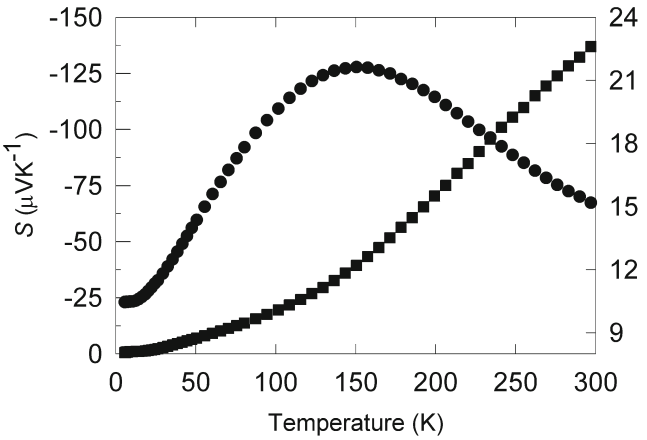

FIG. 1. Temperature dependent resistivity, in mohm-cm (circles), and Seebeck coefficient (squares) of $Ba_8Ga_{16}Sn_{30}$.

Figure 2 shows the heat capacity as a function of temperature. The heat capacity C increases smoothly with temperature and shows typical Debye behavior. The Debye temperature, estimated to be 223 K, was calculated from a fit to the data at temperatures below 10 K, as shown in the inset in Fig. 2. The fit is extended in the inset to $T = 0$ to estimate γ (= 1.26×10^{-3} $Jmol^{-1}$ K^{-2}), the electronic contribution to the heat capacity where $C/T = \gamma + \alpha T^2$.[10] Here γ and α correspond to the electronic and lattice contributions to the heat capacity, respectively.[10] The estimated value for γ is within the range of values between pure metals and metal alloys.[11,12]

Figure 3 shows the lattice thermal conductivity κ_L of $Ba_8Ga_{16}Sn_{30}$ along with a theoretical fit (solid line) to the data. The total thermal conductivity can be written as

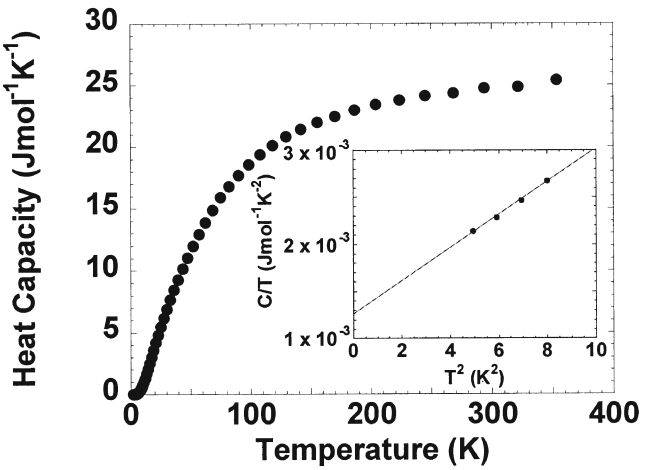

FIG. 2. Heat capacity of $Ba_8Ga_{16}Sn_{30}$ from 2.2 to 300 K. The inset shows the straight line fit of C/T versus T^2 for temperatures below 10 K used to estimate the Debye temperature.

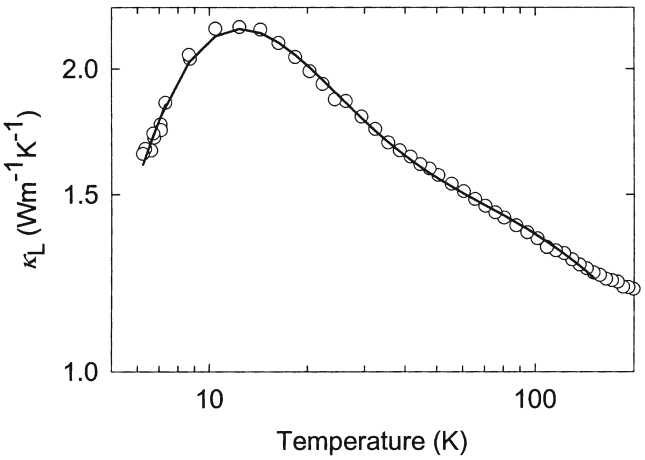

FIG. 3. Lattice thermal conductivity of $Ba_8Ga_{16}Sn_{30}$. The open circles are the experimental data and the solid line is a fit based on Eqs. (1) and (2).

$\kappa = \kappa_L + \kappa_e$. The electronic thermal conductivity κ_e was calculated using the Wiedemann–Franz relation ($\kappa_e = L_0 T/\rho$ with $L_0 = 2.45 \times 10^{-8}$ V^2 K^{-2}) from the measured ρ. In this approximation the dominant contribution to the thermal conduction is from lattice phonons because at all temperatures κ_e is not more than 4% κ.

The thermal conductivity is similar in magnitude to (or smaller than) that of many compounds presently under investigation for thermoelectric applications.[13] In fact, near room temperature the value ($\kappa_L = 1.1$ Wm^{-1} K^{-1}) is similar to that of vitreous silica,[14] a quintessential amorphous material. The temperature dependence of κ_L somewhat resembles that of a crystalline solid with a rising κ_L as temperature decreases leading to a peak at low temperatures. This rise in κ_L goes as $T^{-0.3}$ from approximately 25 to 15 K. This slow rise in κ_L with decreasing temperature indicates that "rattle" scattering of Ba may play a strong role on the phonon transport, along with other typical scattering mechanisms in dielectric solids. We explore the effect of the resonant "rattle" scattering contribution in theoretical modeling of the lattice thermal conductivity below.

The κ_L data were fit according to the equation[15]

$$\kappa_L(T) = \frac{k_B}{2\pi^2 \upsilon}\left(\frac{k_B T}{\hbar}\right)^3 \int_0^{\theta_{D/T}} \tau_c \frac{y^4 e^y}{(e^y - 1)^2}\, dy \quad , \qquad (1)$$

where ω is the phonon frequency, k_B is the Boltzmann constant, $\hbar$ is the reduced Planck constant, y stands for the dimensionless parameter $y = \hbar\omega/k_B T$, θ_D is the Debye temperature, υ is the velocity of sound, and τ_c is the combined phonon scattering relaxation time. This can be written as[16,17]

$$\tau_c^{-1} = \frac{\upsilon}{L} + A\omega^4 + B\omega^2 T \exp\left(-\frac{\theta_D}{3T}\right) + C\frac{\omega^2 T^2}{[\omega^2 - \omega_0^2]^2} \quad , \qquad (2)$$

where the terms represent boundary, point defect (Rayleigh), phonon–phonon (Umklapp), and resonant scattering, respectively. Experimental values for θ_D (= 223 K) and L (= 5.7×10^{-6} m) were taken from specific heat data and optical metallographic analysis, respectively, while υ, A, B, C, and ω_0 were used as fitting parameters. These values were 2984 m/s, 1.440×10^{-41} s^3, 5.448×10^{-18} s K^{-1}, 3.002×10^{32} s^{-3} K^{-2}, and 8.365×10^{11} s^{-1}, respectively. Comparing the fitting parameters for Rayleigh and Umklapp scattering to that of another material of interest for thermoelectric applications, polycrystalline $CoSb_3$,[16] A (the pre-factor for point defect scattering) is 50 times larger in the tin clathrate, while B is similar. This is reasonable, as we would expect alloy scattering due to the large number of vacancies on the framework sites suggested by our XPA analysis. The value for ω_0 is similar to that of Sr in $Sr_8Ga_{16}Ge_{30}$,[17] indicating the possibility of resonance of the Ba vibrational modes with acoustic phonons in this compound. We note that attempts to fit the low-temperature data without the resonance scattering term proved unsuccessful. Further, the fact that only one resonant frequency is needed is consistent with the type-VIII clathrate structure in which there is only one cage size, unlike in the type-I structure, e.g., $Sr_8Ga_{16}Ge_{30}$, where there are two cages sizes and thus two frequencies[17] are needed to describe the κ_L data.

IV. CONCLUSION

In summary, temperature-dependent electronic and thermal conductivity measurements on *n*-type Sn-clathrate with nominal composition $Ba_8Ga_{16}Sn_{30}$ have been reported. The κ values are low enough to make $Ba_8Ga_{16}Sn_{30}$ worthy of further investigations aimed at improving its thermoelectric performance. However, the electronic properties show a complex behavior. The ρ values are too high (by an order of magnitude) for this compound to be useful for thermoelectric applications. Thus the dimensionless figure of merit ($ZT = S^2/\rho\kappa$) at room temperature is only $ZT = 0.03$. Substitution of Zn or Cd instead of Ga and doping studies with Sb for *p*-type specimens, along with theoretical band-structure calculations, may help elucidate the electronic properties of this compound and guide their optimization for thermoelectric performance.

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