Semiconducting Ge clathrates: Promising candidates for thermoelectric applications

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Transport properties of polycrystalline Ge clathrates with general composition $Sr_8Ga_{16}Ge_{30}$ are reported in the temperature range 5 K $\leq T \leq$ 300 K. These compounds exhibit *N*-type semiconducting behavior with relatively high Seebeck coefficients and electrical conductivity, and room temperature carrier concentrations in the range of 10^{17}–10^{18} cm^{-3}. The thermal conductivity is more than an order of magnitude smaller than that of crystalline germanium and has a glasslike temperature dependence. The resulting thermoelectric figure of merit, ZT, at room temperature for the present samples is $\frac{1}{4}$ that of Bi_2Te_3 alloys currently used in devices for thermoelectric cooling. Extrapolating our measurements to above room temperature, we estimate that $ZT > 1$ at $T > 700$ K, thus exceeding that of most known materials. © *1998 American Institute of Physics.* [S0003-6951(98)02128-7]

As evidenced by intense research presently under way in several laboratories,[1] there is a renewed interest in the field of thermoelectrics. From the mid-1950's to the present the major design concepts for bulk thermoelectrics were those used by Ioffe.[2] These were to select semiconducting compounds of heavy elements from the lower right part of the periodic table and then to reduce the lattice thermal conductivity by forming mixed crystals. This approach led to the thermoelectrics based on Bi, PbTe, and Bi_2Te_3.[3] In this letter we report on the transport properties of a semiconducting Ge clathrate with the type I clathrate-hydrate structure in which the voids are filled with Sr. The concept of a ''phonon glass and an electron crystal'' (PGEC)[4] is at the heart of this investigation. PGEC materials would possess electronic properties normally associated with good semiconductor single crystals but a thermal conductivity normally associated with amorphous materials. We believe the introduction of this concept to thermoelectrics is one of the most significant innovations in the last 30 years.

The importance of this approach emerges very clearly from the definition of the figure of merit, *Z*. The definition of a ''good thermoelectric'' lies in the magnitude of the material's Z,[3] where $Z = S^2\sigma/\kappa$. In this equation S is the Seebeck coefficient, σ the electrical conductivity, and κ the total thermal conductivity. Since the dimensions of Z are inverse temperature, a more convenient quantity is the dimensionless figure of merit ZT, where T is the absolute temperature.

The existence of crystalline materials that possess very low κ, similar to that of amorphous solids in a large temperature range, has been known for some time. Cahill, Watson, and Pohl[5] and Slack[6] have enumerated a number of mixed crystal systems that possess glasslike κ. These crystalline systems have a number of properties in common, as outlined in a recent review.[4] The relationship between glasslike κ and the theoretical minimum thermal conductivity, κ_{min}, was first pointed out by Slack.[7] One particular crystalline system which possesses low glasslike κ values most relevant in this study is that of the clathrate hydrates, or ice clathrates.

Ice clathrates have been observed with a variety of different structures. One of these is the type I hydrate structure $X_8(H_2O)_{46}$, where X represents a ''guest'' molecule or atom trapped in the cages formed by the H_2O molecules. The κ for these ice clathrates is much lower than that of $1h$ ice,[4] and decreases as the size (mass) of the ''guest'' molecules or atoms decreases (increases). Nolas *et al.*[8] have shown that a similar effect on the lattice thermal conductivity, κ_g, for skutterudite compounds occurs when trivalent lanthanide ions are present in the voids of that structure. For both classes of materials the reduction in κ_g is believed to be due to resonant scattering of phonons via localized low-frequency vibrations of the ''guests.'' This can be thought of as the ''rattling'' of the trapped atoms in their oversize cages. These observations motivated the present study and our hypothesis that the PGEC concept could be realized in Ge calthrates.

The group IV elements also form clathrates[9] of the type X_8E_{46} where E represents a group IV element and X represents an atom in the voids, or cages, formed by E. The cubic crystal lattice has space group $Pm3n(O_h^3)$ and consists of tetrahedral networks with periodic voids (cages) of 20 and 24 coordinated E polyhedra in a 3:1 concentration ratio. The X atoms do not enter the lattice substitutionally but are interstitial, residing inside the oversize cage. The polyhedra are covalently bonded to each other by shared faces. The electronic structure of similar compounds has been investigated theoretically,[10] but few experimental transport studies have

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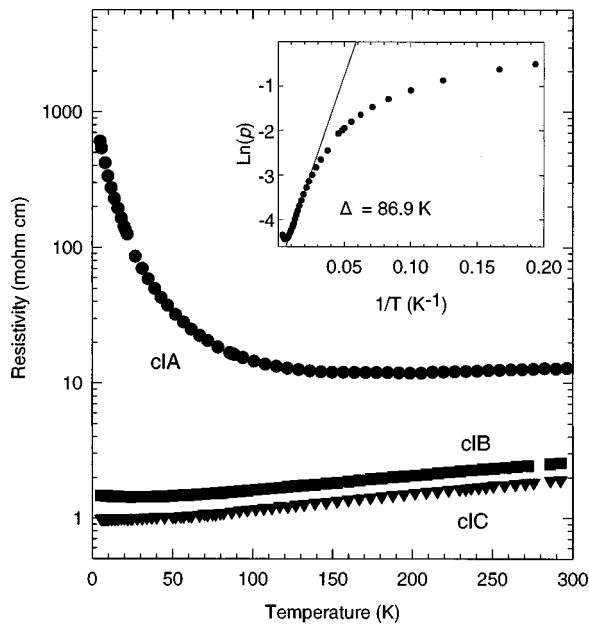FIG. 1. Resistivity vs temperature from 5 to 300 K for the three Ge-clathrate samples. The inset shows $\ln(\rho)$ vs $1/T$ for sample clA with ρ in Ω cm. The straight-line fit to the equation $\rho = \rho_0 \exp(\Delta/T)$ gives $\Delta = 86.9$ K.

FIG. 2. Seebeck coefficient vs temperature from 5 to 300 K for the three Ge-clathrate samples.

been reported.[11] No thermal conductivity measurements have been reported.

In this letter we report on the measured transport properties of three N-type polycrystalline samples of Ge clathrates with the voids filled with Sr. These Ge-clathrate samples, all with similar compositions, were readily reproducible, as indicated from structural analysis and transport properties measurements. These three samples are representative of several different Ge clathrates investigated by the present authors. The synthesis and crystal structure analysis of alkaline-earth filled Ge clathrates have been previously reported.[12] The Ge clathrates used in this report were prepared in a similar manner; the exact details will be reported elsewhere. The x-ray diffraction (XRD) patterns were analyzed on the basis of the clathrate structure by the Rietveld method, and the results were similar to that previously reported.[12] The samples were powdered and densified in a graphite die in a hot press at 2.6×10^4 lbs/in.^{2} and 650 °C. Electron-beam microprobe (XMP) analysis of a polished surface of each sample confirmed the XRD results and revealed that the samples were single phase with the exact stoichiometries as listed in Table I. Also listed in the table are other relevant physical properties of the three samples presented in this report. As seen in Table I, we were able to vary the electronic properties of these N-type samples by varying the Ga-to-Ge ratio. The Ga appears to randomly substitute for Ge in the structure and is used to produce charge compensation for the divalent alkaline-earth ion Sr^{2+}. This means that two Ga atoms act as ''acceptors'' for the two ''donated'' electrons from each Sr^{2+} ion.

Hall coefficient measurements using the van der Pauw technique were conducted at room temperature. Four-probe electrical resistivity (ρ), steady-state Seebeck coefficient (S), and steady-state thermal conductivity measurements were performed in a radiation-shielded vacuum probe.[13] Heat losses via conduction through lead wires and radiation were
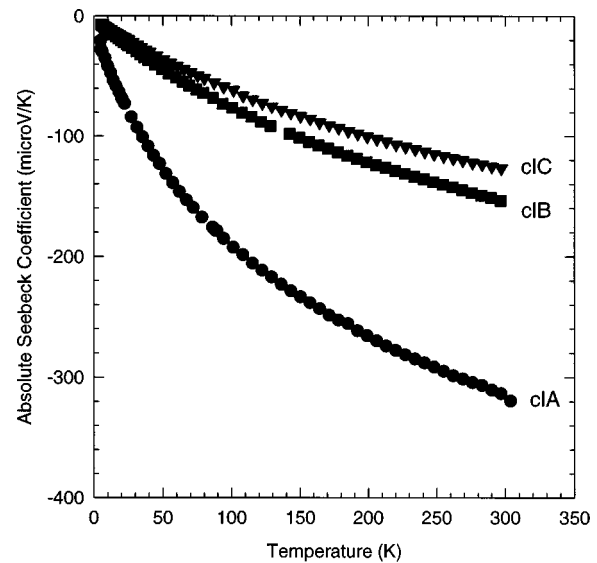
determined in separate experiments and the data corrected accordingly. These corrections were 15%–20% near room temperature and <5% at $T < 120$ K.

Figures 1 and 2 show ρ and absolute S as functions of temperature from 300 to 5 K. The absolute S decreases with decreasing temperature, as expected in heavily doped semiconductors with negligible phonon drag. In the inset of Fig. 1 we show a plot of $\ln(\rho)$ versus $1/T$ for sample clA. This sample had the lowest electron concentration and clearly showed a semiconductor temperature dependence of ρ vs T. The straight line is a fit to the equation $\rho = \rho_0 \exp(\Delta/T)$ where the activation energy for the donors is $E_a = 2\Delta$. From this fit we obtain $E_a = 15$ meV. This value is to be compared to 14.17 meV for shallow donors such as As in Ge. The carrier mobility values in Table I are similar to those for single crystal N-type Ge at room temperature at the same carrier concentration.[14] The Sr^{2+} ions apparently do not cause serious Coulomb scattering of the carriers. Employing Fig. 2 and the carrier concentration values in Table I an estimate of the electron effective mass, m^*, can be made in a straightforward fashion using Fermi statistics and assuming acoustic phonon scattering in a single-band model, following Slack and Hussain.[14] The m^* values thus calculated are 0.1 m_0 for these compounds, where m_0 is the electron effective mass. The effective mass value for N-type Ge at a similar carrier concentration is 0.75 m_0.[15]

The most interesting aspect of our investigation is the magnitude and temperature dependence of κ for these Ge-

TABLE I. Three Ge-clathrate samples indicating the atomic percentages from XMP analysis, the lattice parameter in angstrons, a_0, the measured percent of theoretical density, average grain size in microns, the measured carrier concentration in cm^{-3}, n_0, and mobility in cm^2/V s, μ, at room temperature. The theoretical atomic percentages in the stoichiometric compound are 14.81% Sr, 2963% Ga, and 55.456% Ge.

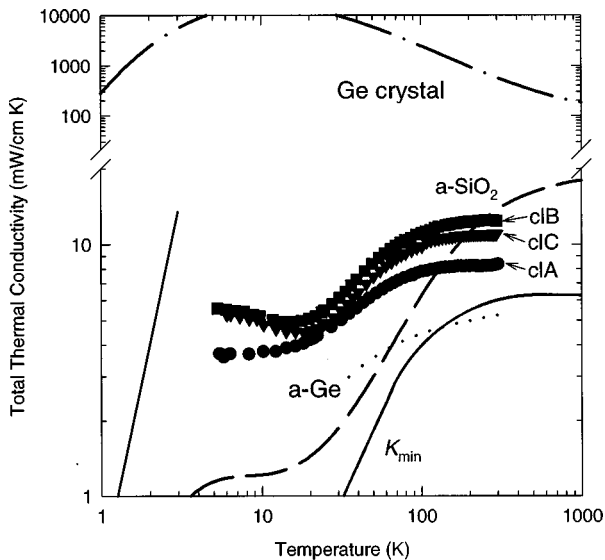| Comp	at. %: Sr, Ga, Ge	a_0	D	Grain size	n_0	μ
clA	14.5, 30.2, 55.3	10.731±0.011	87	9.6	1×10^{17}	2200
clB	14.7, 29.8, 55.5	10.732±0.006	96	17.4	9×10^{17}	1900
clC	14.6, 28.5, 56.9	10.739±0.005	93	10.7	3×10^{18}	730

FIG. 3. Thermal conductivity vs temperature from 5 to 300 K for the Ge-clathrate compounds, single crystal Ge (dotted–dashed line), amorphous Ge (dotted line), amorphous SiO$_2$ (dashed line), and κ_{min} of Ge (solid line). The straight, solid line below 4 K is a calculation due to grain boundary scattering for a 10 μm grain size.

clathrate compounds. Figure 3 shows κ as a function of temperature for the three Ge-clathrate samples as well as for single crystal Ge,[16] amorphous Ge (a-Ge)[17] and amorphous SiO$_2$ (a-SiO$_2$).[5] The calculated κ_{min} for Ge is also shown in the figure. The κ_{min} curve was calculated employing Slack,[7] however we followed Cahill *et al.*[5] by taking the minimum mean free path of the acoustic phonons as one-half of their wavelength. We see that κ for these clathrates is lower than that of a-SiO$_2$, is only a factor of approximately 2 greater than that of a-Ge and exhibits a temperature dependence similar to that of amorphous materials. Using the measured values of ρ from Fig. 1 and the Wiedemann–Franz law we estimate κ_e, the electronic component of κ. For sample clA κ_e is estimated to be 6% of the total κ at room temperature and lower at lower temperatures. The other two samples had larger κ_e values, since their electrical conductivities were an order of magnitude larger than that of samples clA. The data for sample clA essentially indicate the lattice component of the total κ in this compound.

The grain size of approximately 10 μm in the present samples gives a computed κ limited by boundary scattering as shown in Fig. 3. Clearly the low thermal conductivity values measured are not produced by boundary scattering of the phonons at the grain boundaries. The results in Fig. 3 are suggestive of a "resonance dip" in the phonon scattering at about $T_r = 20$ K. If this dip is caused by phonon interaction with a "rattling" frequency of the Sr at an energy $h\nu_r$, then ν_r is approximately[18] given by $h\nu_r = 3.9kT_r$. This gives ν_r in wave numbers as $\nu_r = 55$ cm^{-1}. Similar values have been estimated for "guest" atoms in ice clathrates.[19]

Note that in the Sr$_8$Ga$_{16}$Ge$_{30}$ we have replaced the traditional alloy phonon scattering,[14] which predominantly scatters the highest frequency phonons (near 250 cm^{-1} in Ge) by a much lower frequency "rattle" scattering. The highest frequency phonons have very low or zero group velocity and contribute little to the total thermal conductivity. The low frequency phonons have the highest group velocity and con-

tribute most to κ. That is why the Sr "impurities" produce such pronounced decrease in κ.

For the three samples in this report we calculate $ZT \approx 0.25$ at 300 K. These results were confirmed by measurements on a standard Z meter used for testing thermoelectric materials. Using the estimated value of $m^* = 0.1m_0$ as calculated above and assuming a single band model with predominantly acoustic phonon scattering, we can make an estimate of the high temperature transport properties using Fermi statistics, as outlined in Ref. 3. From this we obtain $ZT \geq 1$ for temperatures of $T > 700$ K for these samples. This prediction represents a larger ZT than found for PbTe-based thermoelectric materials.[3] The ZT values could presumably be increased by optimizing the doping level.

The Sr$_8$Ga$_{16}$Ge$_{30}$ structure can be thought of as a derivative of the four coordinated diamond lattice structure of Ge. The presence of Sr induces a crystal structure change in the Ge, in this case to that of the type I clathrate hydrate crystal structure. This means that this Ge clathrate is a cryptoclathrate (or hidden clathrate) induced by the presence of Sr. The skutterudites, which have been extensively studied as potential thermoelectric materials,[1] also possess open crystal lattice structures. In the skutterudite system however the voids are present in the structure whether or not the "guest" atoms are present. The skutterudite system was therefore ideal for the study and evaluation of κ_g of a crystal lattice structure with voids either filled or unfilled.[8] The Sr$_8$Ga$_{16}$Ge$_{30}$ compound presented here is a true PGEC material system where the thermal conductivity is drastically reduced, to nearly that of the theoretical minimum, while good electronic properties are maintained. The promising properties of Sr$_8$Ga$_{16}$Ge$_{30}$ reported here suggest a new category of possible thermoelectric materials for investigation.

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