JOURNAL OF APPLIED PHYSICS VOLUME 91, NUMBER 11 1 JUNE 2002

Temperature dependent structural and transport properties of the type II clathrates $A_8Na_{16}E_{136}$ (A=Cs or Rb and E=Ge or Si)

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(Received 1 February 2002; accepted for publication27 February 2002)

Variable temperature single-crystal structure analyses for $Cs_8Na_{16}Si_{136}$, $Rb_8Na_{16}Si_{136}$, $Cs_8Na_{16}Ge_{136}$, and $Rb_8Na_{16}Ge_{136}$ are reported along with electrical and thermal transport measurements on two polycrystalline specimens. The strong temperature dependence of the atomic displacement parameters for the alkali-metal atoms is indicative of significant disorder associated with the ‘‘rattling’’ alkali-metal atoms inside the two different polyhedra (sixteen dodecahedra and eight hexakaidecahedra per cubic unit cell) that makeup the type II clathrate hydrate framework. This disorder can lead to low lattice thermal conductivities. Transport measurements show these compounds to be metallic. The potential of type II clathrates for thermoelectric applications is discussed. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1471370]

I. INTRODUCTION

In the 1960’s, Cros and co-workers[1] reported the existence of two silicon clathrate phases, Na_8Si_{46} and Na_xSi_{136}, that are isomorphic with the type I and II clathrate hydrates, respectively.[2] Since then, there have been several compounds synthesized with these structure types. Silicon, germanium, and tin form clathrate compounds with alkali-metal, alkaline earth, and lanthanide atoms occupying the cavities. These materials are of interest due to their unusual physical properties and their interesting bonding scheme.[3]

Compounds with clathrate hydrate crystal structures are formed from two types of polyhedra (dodecahedra and tetrakaidecahedra for the type I structure and dodecahedra and hexakaidecahedra for the type II materials) that are connected to each other by face sharing. Relatively large elements, such as alkali-metal or alkaline earth atoms, can be encapsulated within these polyhedra. While all of the cages typically contain a guest atom, incomplete filling can lead to nonstoichiometric materials.[4,5] Recently, the room temperature crystal structures of several silicon and germanium type II clathrates, that contain alkali-metal atoms, have been reported.[6] In addition, nuclear magnetic resonance studies of $Cs_8Na_{16}Si_{136}$ (Ref. 7) and $Rb_8Na_{16}Si_{136}$ (Ref. 8) indicate that these compounds are metallic. In this paper, we report results from variable temperature single-crystal x-ray diffraction studies of $Cs_8Na_{16}Si_{136}$, $Rb_8Na_{16}Si_{136}$, $Cs_8Na_{16}Ge_{136}$, and $Rb_8Na_{16}Ge_{136}$. The temperature dependence of the measured atomic displacement parameters (ADPs) provides a measure of the local dynamic disorder associated with the alkali-metal atoms inside their polyhedra. Transport properties on polycrystalline specimens are also reported. These results are used to evaluate the potential of type II clathrates for thermoelectric applications.

II. SYNTHESIS AND EXPERIMENTAL DETAILS

Small single-crystals (~0.2 mm^3) of the type II clathrates were synthesized by mixing high purity elements in an argon atmosphere glove box and reacting them inside a tungsten crucible that was, itself, sealed inside a stainless steel canister. The canister was evacuated and backfilled with high purity argon gas before sealing. After maintaining 650 °C for three weeks, the contents were then cooled to room temperature at a rate of 0.2 °C/min. The products consisted of small polyhedral crystals with a shinny, bluish, metallic luster. The crystals were not reactive toward air or moisture. The identity of several small single crystals was established using an Enraf–Nonius CAD-4 diffractometer. These data could be indexed to the type II clathrate structure ($Fd\text{-}3m$ crystal structure).

Variable temperature single-crystal diffraction measurements were performed using Mo $K\alpha$ radiation and a Bruker 1 K charge coupled device (CCD) platform diffractometer equipped with a LT-2 cold stream attachment. The specimens were mounted on the end of a glass fiber using a small amount of stopcock grease. Data sets were collected in two shells. The first was collected with the detector positioned at $-28.00° \ 2\theta$ and a detector distance of 5 cm using default settings for a hemisphere (1271 frames). This gave data in the range ~3 to 57° 2θ. The detector was then repositioned so that its center was at $2\theta \sim -78.00°$ and a second shell was collected yielding data up to ~103° 2θ. The actual maximum 2θs used in the data analyses varied depending on the signal-to-noise ratio that was obtained. The temperature for each data set was determined using a calibrated copper-constantan thermocouple with 0.005 in. diameter leads

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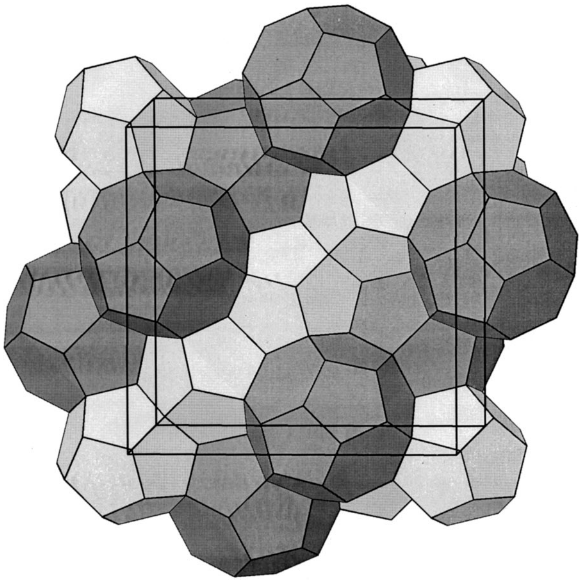

FIG. 1. Type II clathrate hydrate framework. The hexakaidecahedra are more heavily shaded.

placed at the sample position. Absorption corrections were applied using SADABS;[9] data reduction employed SAINT;[10] structure solution and refinement was performed using SHELXTL.[11] Crystallographic data can be obtained from the authors upon request.

For transport measurements $Cs_8Na_{16}Si_{136}$ and $Cs_8Na_{16}Ge_{136}$ crystals were ground to fine powders and hot pressed inside a graphite die at 650 °C and 2×10^4 lbs/in^2 for 2 h in an argon atmosphere. A cross section of each pellet was polished and analyzed using an electron-beam microprobe. They were also ground and analyzed using powder x-ray diffraction, which revealed only the type II clathrate lines with no impurities. These results were consistent with the single-crystal x-ray results and thus indicated no structural deterioration during the hot pressing. The hot pressed pellets were cut with a wire saw in the shape of a parallelpiped $2\times2\times5$ mm^3 in size. Four-probe electrical resistivity (ρ), steady-state Seebeck coefficient (S), and steady-state thermal conductivity measurements were performed in a radiation-shielded vacuum probe with the heat flow measured along the longest axis. Heat losses via conduction through the lead wires and radiation were determined in separate experiments and the data corrected accordingly. These corrections were less than 5% in the temperature range measured.

IV. RESULTS AND DISCUSSION

The type II clathate structure is made up of pentagonal dodecahedra, creating a center with $3m$ symmetry, and hexakaidecahedra formed by twelve pentagonal and four hexagonal faces creating a center with $43m$ symmetry. There are twenty four polyhedra per cubic unit cell, sixteen dodecahedra, E_{20}, and eight hexakaidecahedra, E_{28}, where $E=\mathrm{Si}$ or Ge. Figure 1 shows the clathrate framework structure. As the alkali atoms are encapsulated, these compounds are typically stable in air and moisture.

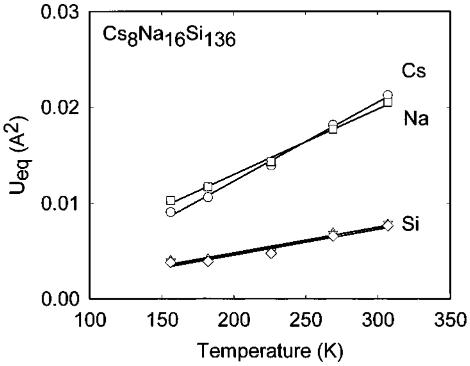

FIG. 2. Temperature dependence of ADPs for $Cs_8Na_{16}Si_{136}$.

The single-crystal x-ray diffraction data show that the E—E—E bond angles range from 105° to 120°. The Si—Si bond lengths in $Cs_8Na_{16}Si_{136}$ and $Rb_8Na_{16}Si_{136}$ are slightly larger than that of diamond structure Si. The Ge—Ge bond lengths in $Cs_8Na_{16}Ge_{136}$ and $Rb_8Na_{16}Ge_{136}$ are also slightly larger than that of diamond structure Ge. These results are in agreement with the room temperature measurements of Slavi and Sevov.[6] On cooling, there are no unusual changes in the framework bond lengths.

The nature of the framework and the ADPs of the extraframework atoms play important roles in the properties of group IV clathrates. In particular, dynamic disorder associated with the alkali-metal atoms inside their polyhedra can lead to low thermal conductivities. Figures 2–5 show the temperature dependence of the ADPs that were obtained from single-crystal diffraction measurements on $Cs_8Na_{16}Si_{136}$, $Rb_8Na_{16}Si_{136}$, $Cs_8Na_{16}Ge_{136}$, and $Rb_8Na_{16}Ge_{136}$, respectively. All the extraframework atoms reside on well defined crystallographic sites. The Na atoms are centered inside the dodecahedra (16*c* crystallographic site) while the Cs or Rb atoms are centered within the larger hexakaidecahedra (8*b* crystallographic site).

The ADPs (Figs. 2–5) for the Si and Ge framework sites display a weak temperature dependence, indicating that the framework is relatively stiff. However, the ADPs for the alkali-metal atoms show a strong temperature dependence with ordinate intercept typically slightly less than zero when extrapolated to 0 K. The temperature dependence of the ADPs can be viewed as an indication of the degree of dynamic (or "rattling") disorder amongst the alkali-metal ions.

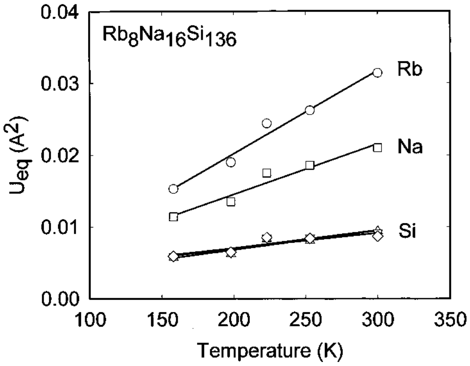

FIG. 3. Temperature dependence of ADPs for $Rb_8Na_{16}Si_{136}$.

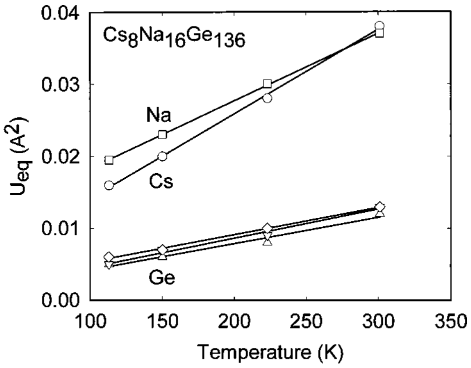

FIG. 4. Temperature dependence of ADPs for $Cs_8Na_{16}Ge_{136}$.

Very large ADPs for Sr or Eu atoms in tetrakaidecahedra for the type I clathrate compounds $Sr_8Ga_{16}Ge_{30}$ and $Eu_8Ga_{16}Ge_{30}$ are due to a combination of dynamic disorder and static disorder associated with the presence of four potential minima within the polyhedron.[12–14] In contrast, the alkali-metal atoms in type II clathrates display only localized dynamic disorder about the center of the polyhedra. While both the Cs and Na atoms have large ADPs in $Cs_8Na_{16}Si_{136}$ and $Cs_8Na_{16}Ge_{136}$, in the corresponding Rb/Na compounds the Rb has even larger ADPs than those seen for Cs. This indicates that as the alkali atom becomes smaller relative to the size of the hexakaidecahedra, the amplitude of the atom's rattling motion increases. This type of disorder strongly influences the lattice thermal conductivity, as has been shown in type I clathrates[12–16] and skutterudites.[15,17]

It has been previously shown that ADPs can be used to determine characteristic localized vibration frequencies for weakly bound atoms that "rattle" within their atomic "cages." [18] This approach, which assumes the rattling atoms act as harmonic oscillators, has been successfully applied to compounds with the skutterudite and type I clathrate crystal structures.[15,18] The localized vibration of the "rattler" atom can be described by an Einstein oscillator model such that $U=k_BT/m(2\pi v)^2$ where U is the isotropic mean-square displacement, k_B is Boltzmann's constant, m is the mass of the rattling atoms under the assumption that their cages are relatively rigid and v is the frequency of vibration. The ADP data can then be used to estimate v of the alkali-metals inside their polyhedra. In Table I, we present the frequencies calculated using this approach for the alkali-metal atoms in the four compounds that we have examined. These data and Figs. 2–5 indicate that in general the alkali-metal atoms have more room to rattle inside their polyhedra in the Ge clathrates as compared to the Si clathrates, thus leading to lower Einstein frequencies for the alkali-metal atoms in the germanium compounds. No substantial difference is observed in the computed Cs and Rb Einstein frequencies within the hexakaidecahedral cavity (see Table I). This is presumably because the expected decrease in frequency on reducing the atomic size is counterbalanced by the effect of decreasing the atomic mass. We note that our x-ray analysis did not reveal significant shrinking of the hexakaidecahedra in the Rb-containing compounds as compared to those with Cs.

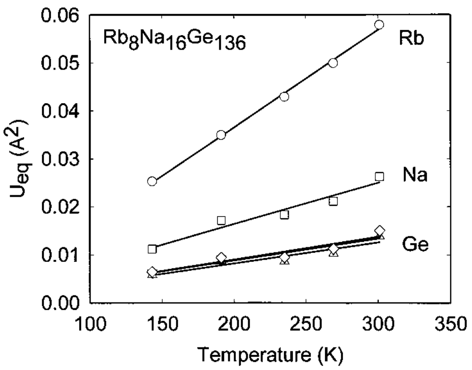

FIG. 5. Temperature dependence of ADPs for $Rb_8Na_{16}Ge_{136}$.

TABLE I. Estimate of vibrational frequencies, in cm^{-1}, for Cs and Rb inside the hexakaidecahedra and Na inside the dodecahedra of stoichiometric type II Si and Ge clathrates. The Debye temperature, (Θ_D) in K, and κ_L, in W/mK, calculated for the four compounds is also shown.

Compound	Cs or Rb	Na	Θ_D	κ
$Cs_8Na_{16}Si_{136}$	53.4	141	416	1.9
$Rb_8Na_{16}Si_{136}$	55.0	130	400	1.9
$Cs_8Na_{16}Ge_{136}$	41.8	117	230	1.0
$Rb_8Na_{16}Ge_{136}$	42.9	127	220	1.0

Previous theoretical calculations have estimated that the acoustic phonon modes of Si_{136} (Ref. 19) and Ge_{136} (Ref. 20) with the type II clathrate structure lie below 100 cm^{-1} and 60 cm^{-1}, respectively. The vibrational frequencies of the alkali atoms inside the hexakaidecahedra probably lie close to or within the acoustic phonon branch. These low-frequency rattle modes may therefore resonantly scatter acoustic phonons and lead to low lattice thermal conductivities.

It has also been shown that ADP data can be used to estimate the physical properties of a material, such as the Debye temperature, speed of sound and the lattice thermal conductivity.[15,18] Estimates of the Debye temperatures and the lattice thermal conductivity (κ_L) calculated from the diffraction data are also shown in Table I. The estimate of κ_L for each compound assumes that only the Cs or Rb atoms are involved in the scattering of the acoustic phonons, and sug-

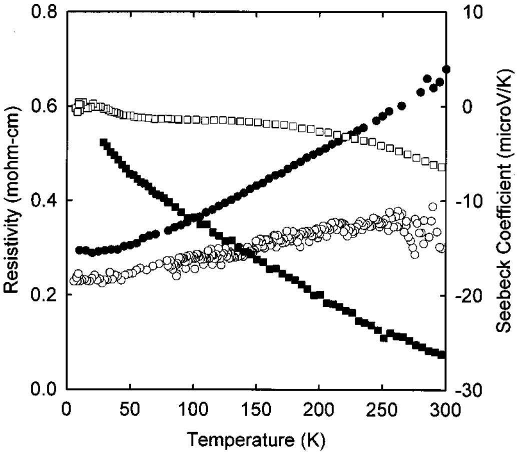

FIG. 6. Seebeck Coefficient (square symbols) and resistivity (round symbols) as a function of temperature for polycrystalline $Cs_8Na_{16}Si_{136}$ (filled symbols) and $Cs_8Na_{16}Ge_{136}$ (open symbols).

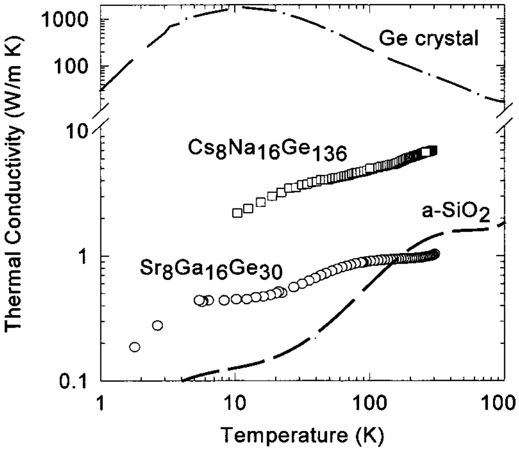

FIG. 7. Thermal conductivity of polycrystalline $Cs_8Na_{16}Ge_{136}$, polycrystalline $Sr_8Ga_{16}Ge_{30}$, single-crystal Ge and vitreous silica (a-SiO_2).

gest that these compounds should possess low lattice thermal conductivities. This is of interest for thermoelectric applications.

In Fig. 6 we show the temperature dependence of the resistivity and the Seebeck coefficient over the range 10 to 300 K for polycrystalline $Cs_8Na_{16}Si_{136}$ and $Cs_8Na_{16}Ge_{136}$. The Seebeck coefficients are small and indicate that the majority carriers are electrons, while the temperature dependence of ρ indicates metallic behavior for both specimens. The ρ values are somewhat large, particularly for $Cs_8Na_{16}Si_{136}$, and may be an indication of a high residual resistivity. This is typically caused by defects within the crystals or grains, or impurities between grains. Our single-crystal x-ray analyses did not indicate the presence of large amounts of defects, however there may be impurities at the grain boundaries of our polycrystalline specimens. Even trace amounts of such impurities will result in a large residual resistance and we speculate this is the case, particularly for our Si clathrate specimen. The thermal conductivities (κ) for these two specimens are relatively large. Figure 7 compares the measured thermal conductivity for a polycrystalline $Cs_8Na_{16}Ge_{136}$ specimen with that of diamond structured Ge and $Sr_8Ga_{16}Ge_{30}$. The κ values for $Cs_8Na_{16}Ge_{136}$ are smaller than those for diamond Ge, but much larger than those for $Sr_8Ga_{16}Ge_{30}$. This is due to the electronic contribution to κ in this metallic compound. Clearly these metallic compounds will not be good thermoelectric materials, but semiconducting type II clathrates should have much improved thermoelectric properties due to their expected lower thermal conductivity and higher Seebeck coefficients.

V. CONCLUSIONS

We report temperature dependent single-crystal x-ray diffraction data as well as electronic and thermal transport measurements on type II clathrates containing alkali metals inside the polyhedra that form the crystal structure. These compounds are metals and therefore poor thermoelectric materials. The temperature dependent structural properties indicate localized dynamic disorder due to the rattling alkali-metal atoms. As in the case of type I clathrates, this represents the potential for a strong acoustic phonon-scattering mechanism and therefore a low lattice thermal conductivity. We speculate that semiconductor variants of these compounds may have good thermoelectric properties.

ACKNOWLEDGMENTS

The authors are grateful to Timothy Weakly for room temperature single-crystal x-ray diffraction measurements. One of the authors (G.S.N.) is grateful to Brian Sales for very useful discussions and acknowledges support from the University of South Florida. Another author (A.P.W.) is grateful for support from the NSF through DMR 9623890. Part of this work was conducted at Marlow Industries, Inc., through funds from an U.S. Army Research Laboratory Contract No. DAAD 17-99-C-0006.

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