Transport properties of Na$_8$Si$_{46}$

G. S. Nolas*
R & D Division, Marlow Industries, Inc., 10451 Vista Park Road, Dallas, Texas 75238

J.-M. Ward and J. Gryko
Department of Physical & Earth Sciences, Jacksonville State University, Jacksonville, Alabama 36265

L. Qiu and M. A. White
Department of Chemistry, Dalhousie University, Halifax, NS B3H 4J3 Canada

(Received 13 March 2001; revised manuscript received 13 June 2001; published 18 September 2001)

We report on transport properties of polycrystalline Na$_8$Si$_{46}$ in the temperature range 10 to 300 K. The compound is a type I clathrate with Na incorporated into polyhedra formed by framework Si atoms. Seebeck coefficient and resistivity measurements indicate metallic behavior. The thermal conductivity is low in comparison with crystalline Si, but high in comparison with other type I clathrates with a large contribution due to electronic conduction. The potential for thermoelectric applications also is discussed.

DOI: 10.1103/PhysRevB.64.153201 PACS number(s): 65.40.—b, 72.20.My, 81.05.Bx

Compounds with the type I clathrate hydrate crystal structure continue to be of scientific interest due to their broad range of promising properties such as semiconducting behavior, superconductivity, and “glasslike” thermal transport. These properties are a direct result of the nature of the structure and bonding in these materials. In addition, these materials continue to be of interest for thermoelectric applications. Much of the experimental work on the transport properties of these compounds has only recently been undertaken, motivated by their potential as thermoelectric materials.

Na$_8$Si$_{46}$ is perhaps the most studied of all the type I clathrate compounds. The Si framework is comprised of two dodecahedra and six tetrakaidecahedra per cubic unit cell. The Na atoms reside inside these polyhedra. The Si-Si-Si bond angles are close to the ideal tetrahedral angle and the Si-Si bonds are similar to those of diamond structured Si. Although the crystal structure of this compound has been studied extensively, there have been few reports on the transport properties of this compound.

Herein we present electrical resistivity ($\rho$), Seebeck coefficient ($S$), and thermal conductivity ($\kappa$) measurements on polycrystalline Na$_8$Si$_{46}$ from 10 to 300 K, and compare these results to those for semiconducting type I clathrates.

The Na$_8$Si$_{46}$ prepared for this report was synthesized by slow thermal decomposition of sodium silicide, NaSi, at a temperature of 385 °C under argon at low pressure ($\approx$ 0.01 Torr). After several days of heating, undecomposed sodium silicide was washed out with oxygen-free, cold ($-15$ °C) methanol. In these conditions the main product was Na$_8$Si$_{46}$ with a small amount of Na$_8$Si$_{136}$ clathrate. Pure Na$_8$Si$_{46}$ was isolated by careful density separation using a CH$_2$Br$_2$ : CCl$_4$ mixture. The x-ray diffractogram confirms a cubic unit cell with $Pm\overline{3}n$ symmetry space group and a lattice parameter at room temperature of 10.20 Å. Rietveld analysis indicates the silicon polyhedra are fully occupied by sodium atoms, in agreement with the Na$_8$Si$_{46}$ composition; no vacancies were detected in the Si$_{46}$ silicon framework. No detectable amorphous background was present in the x-ray results, indicating that the bulk sample was not contaminated by detectable quantities of either amorphous silicon or silicon dioxide.

For transport measurements the as-synthesized powder was hot pressed in a graphite die at 400 °C and 6.1 $\times$ $10^8$ Pa for 3 h in an argon atmosphere resulting in a solid, moderately dense specimen, approximately 75% of the theoretical density, with an estimated grain size of 2 μm from standard metallographic analyses. The hot-pressed pellet was cut with a wire saw in the shape of a parallelepiped $2 \times 2 \times 5$ mm$^3$ in size. Four-probe electrical measurements, and steady-state thermal conductivity ($\kappa$) 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. These losses were less than 4% of the measured thermal conductivity at room temperature and less at lower temperatures.

Figure 1 shows the $S$ and $\rho$ results for measurements of polycrystalline Na$_8$Si$_{46}$. The temperature dependence of $\rho$
and the very small values of $S$ indicate metallic behavior, as previously indicated by electronic band structure calculations\textsuperscript{10,12–14} and from simple crystal chemistry considerations. The negative sign of $S$ indicates that the majority carriers are electrons. The observed values of $\rho$ are relatively high. This was also the case on measurements of a second polycrystalline specimen prepared by hot pressing of powdered Na$_8$Si$_{46}$. The residual resistivity of these compounds is apparently quite high. This is typically due to impurities, surrounding the grains for example, or defects incurred during the densification process. Although our x-ray analysis did not indicate any impurities or defects, we speculate that perhaps there is a trace amount of amorphous SiO$_2$ material surrounding the grains for example, or defects incurred during the densification process. Although our x-ray analysis did not indicate any impurities or defects, we speculate that perhaps there is a trace amount of amorphous SiO$_2$ material

![Figure 2](image)

**FIG. 2.** Thermal conductivity versus temperature of polycrystalline Na$_8$Si$_{46}$. Also shown are the lattice thermal conductivities of Sr$_8$Ga$_{16}$Ge$_{30}$ and Ba$_8$Ga$_{16}$Si$_{30}$.

We take two approaches to understand how the Na vibrational modes in Na$_8$Si$_{46}$ affect its thermal conduction. First, we employ the atomic displacement parameters (ADP’s) to estimate the thermodynamic properties, as has been successfully done previously for other type I clathrates.\textsuperscript{5,16,21} In such an approach the localized vibrations of the Na atoms are soft modes that can be described by an Einstein oscillator model. The Debye model is employed to correlate the motion of the framework atoms in the crystal. The ADP’s of the Na and Si framework can then be used to estimate the Einstein temperatures, $\Theta_E$, and Debye temperature, $\Theta_D$, respectively.\textsuperscript{22} Using this approach and the room temperature ADP’s,\textsuperscript{8} assuming most of the disorder is dynamic and caused by the Na “rattle” modes, we obtain $\Theta_E=107$ and 134 K for Na inside the dodecahedra and tetrakaidekahedra, respectively, and $\Theta_D=570$ K. These estimated Einstein modes (at 74 and 93 cm$^{-1}$) are in agreement with that assigned using neutron scattering measurements\textsuperscript{23} at 83 cm$^{-1}$, and with those calculated from lattice dynamics using density functional theory\textsuperscript{24} (at 72 cm$^{-1}$ and 121 cm$^{-1}$). (We also note that the upper band of the acoustic modes of Si$_{46}$ has been calculated\textsuperscript{25} to be at 100 cm$^{-1}$.) The value calculated for $\Theta_D$ is very near the value of 590 K based on analysis of the total heat capacity.\textsuperscript{24} $C_V=1160$ JK$^{-1}$mol$^{-1}$, and 540 ± 25 K based on theoretically determined elastic constants.\textsuperscript{25} Using these results and taking the mean free path as the distance between Na atoms inside the tetrakaidekahedra, 5.10 Å, we estimate the room temperature resonance-coupled $\kappa_e$ of Na$_8$Si$_{46}$ to be 2.1 W m$^{-1}$K$^{-1}$. The Na optic “rattle” modes then presumably do resonantly scatter the higher frequency acoustic phonon modes resulting in a much lower $\kappa_e$ than that of diamond Si, but not as low as that found in other type I clathrates. Given that Na$_8$Si$_{46}$ is metallic, most of the heat conduction likely is due to electronic contributions. The estimated $\kappa_e$ also suggests a relatively large electronic component of the thermal conductivity, $\approx 4.0$ Wm$^{-1}$K$^{-1}$. This estimates serves to verify that the electronic component of the thermal conductivity is the largest contribution to the thermal conduction in these compounds.
Our second approach is to analyze the mean free path of the heat carriers based on the $\kappa$ values shown in Fig. 2, the heat capacity of Na$_8$Si$_{46}$ (Refs. 24 and 26) and the velocity of sound calculated from theoretically determined elastic constants. The results are shown in Fig. 3, where the mean free path is about 20 Å at room temperature. The mean free path increases dramatically as the temperature is lowered, presumably becoming comparable with the grain size, estimated to average about 2 $\mu$m at extremely low temperatures. Indeed, the small grain size may contribute to the low $\kappa$ values at low temperatures. This may be an indication that the Na atom motions “freeze out” as the temperature is lowered. The mean free path results are consistent with room-temperature coupling of heat-carrying acoustic phonons with the “rattling” of the Na atoms in their cages, but not as efficiently as for a strong acoustic phonon scatterer such as Sr in Sr$_5$Ga$_{16}$Ge$_{30}$.

In summary, we report on the transport properties of Na$_8$Si$_{46}$. The metallic behavior of this compound precludes it from being a useful thermoelectric material, and its thermal conductivity is observed to be high in comparison with semiconducting type I clathrate compounds. While there is dynamical disorder of the interstitial atoms in Na$_8$Si$_{46}$, it is not as strong a phonon scattering mechanism as in other type I clathrates.

This work was supported in part by the U.S. Army Research Laboratory under Contract No. DAAD17-C-99-0006, and by the Natural Sciences and Engineering Research Council of Canada and the Killam Trusts. We acknowledge useful information from J. J. Dong.

9 Current address: Department of Physics, University of South Florida, Tampa, FL 33620. E-mail address: gnolas@chuma1.cas.usf.edu


10 J.S. Tse, K. Uehara, R. Rousseau, A. Ker, C.I. Ratcliffe, M.A. White, and G. MacKay, Phys. Rev. Lett. 85, 114 (2000). See also the erratum submitted with updated adjustments to Fig. 1.

11 N.F. Mott, J. Solid State Chem. 6, 348 (1973), and references therein.


