

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

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We report on transport properties of polycrystalline $\text{Na}_8\text{Si}_{46}$ 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.

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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,¹ superconductivity,² and “glasslike” thermal transport.³⁻⁵ 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.⁶ Much of the experimental work on the transport properties of these compounds has only recently been undertaken, motivated by their potential as thermoelectric materials.

$\text{Na}_8\text{Si}_{46}$ is perhaps the most studied of all the type I clathrate compounds.⁶⁻¹⁰ 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.^{10,11} Herein we present electrical resistivity (ρ), Seebeck coefficient (S), and thermal conductivity (κ) measurements on polycrystalline $\text{Na}_8\text{Si}_{46}$ from 10 to 300 K, and compare these results to those for semiconducting type I clathrates.

The $\text{Na}_8\text{Si}_{46}$ 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 (≈ 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 $\text{Na}_8\text{Si}_{46}$ with a small amount of $\text{Na}_x\text{Si}_{136}$ clathrate. Pure $\text{Na}_8\text{Si}_{46}$ was isolated by careful density separation using a $\text{CH}_2\text{Br}_2 + \text{CCl}_4$ mixture. The x-ray diffractogram confirms a cubic unit cell with $Pm\bar{3}n$ 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 $\text{Na}_8\text{Si}_{46}$ 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 6.1×10^8 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 $2 \times 2 \times 5$ mm³ in size. Four-probe electrical measurements, and steady-state thermal conductivity (κ) 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 ρ results for measurements of polycrystalline $\text{Na}_8\text{Si}_{46}$. The temperature dependence of ρ

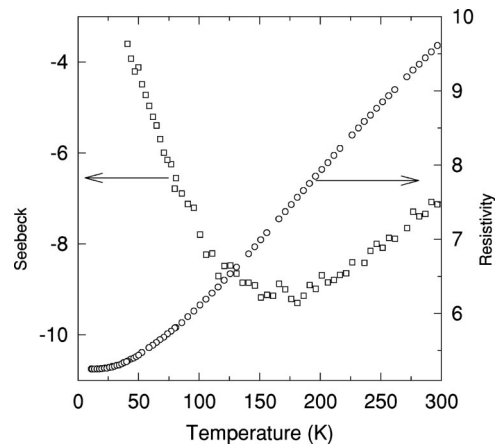


FIG. 1. Resistivity (circles) and Seebeck coefficient (squares) of polycrystalline $\text{Na}_8\text{Si}_{46}$ from 10 to 300 K.

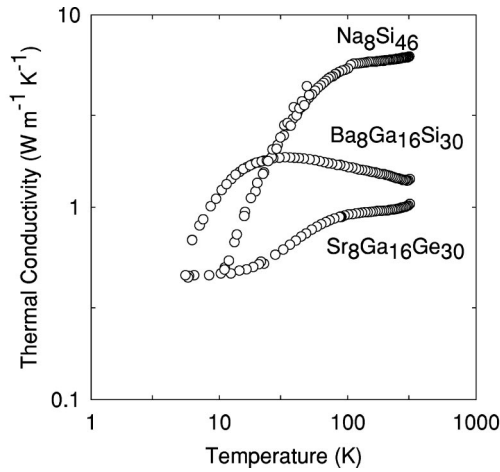


FIG. 2. Thermal conductivity versus temperature of polycrystalline $\text{Na}_8\text{Si}_{46}$. Also shown are the lattice thermal conductivities of $\text{Sr}_8\text{Ga}_{16}\text{Ge}_{30}$ and $\text{Ba}_8\text{Ga}_{16}\text{Si}_{30}$.

and the very small values of S indicate metallic behavior, as previously indicated by electronic band structure calculations^{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 ρ are relatively high. This was also the case on measurements of a second polycrystalline specimen prepared by hot pressing of powdered $\text{Na}_8\text{Si}_{46}$. 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 between the grains of our specimens. As described in Mott,¹¹ even trace amounts of such impurities will result in a large residual resistivity. For the specimens we measured, the temperature dependence of ρ is indicative of metalliclike behavior.

Figure 2 shows κ of polycrystalline $\text{Na}_8\text{Si}_{46}$. The data are very different than that from measurements of thermal diffusivity of a powdered sample of $\text{Na}_8\text{Si}_{46}$ in Fig. 1 of Ref. 10. In light of this work those data were revisited by the authors of Ref. 10 and are now in general agreement¹⁰ with that shown in Fig. 2. Although κ of $\text{Na}_8\text{Si}_{46}$ is much lower than that of diamond-structure Si ($156 \text{ W m}^{-1} \text{ K}^{-1}$),¹⁵ it is relatively high in comparison with the lattice thermal conductivity, κ_g , of two other type I semiconductor clathrates, $\text{Sr}_8\text{Ga}_{16}\text{Ge}_{30}$ and $\text{Ba}_8\text{Ga}_{16}\text{Si}_{30}$,^{1,4} also shown in Fig. 2, presumably because of the contribution from electronic thermal conduction in metallic $\text{Na}_8\text{Si}_{46}$ (*vide infra*). In particular, the magnitude of κ for $\text{Na}_8\text{Si}_{46}$ is very different from that of $\text{Sr}_8\text{Ga}_{16}\text{Ge}_{30}$, a crystalline semiconductor with a “glasslike” temperature dependence. The thermal transport in $\text{Sr}_8\text{Ga}_{16}\text{Ge}_{30}$ is directly related to the resonant scattering of the host acoustic phonons by the localized Sr optical vibration modes.^{1,4,5,16–19} From previous studies^{4–6,19,20} it has been found that the decrease in κ_g is proportional to the polyhedra-to-interstitial atom size ratio, and the mass of the interstitial atom. That is, the smaller and more massive the

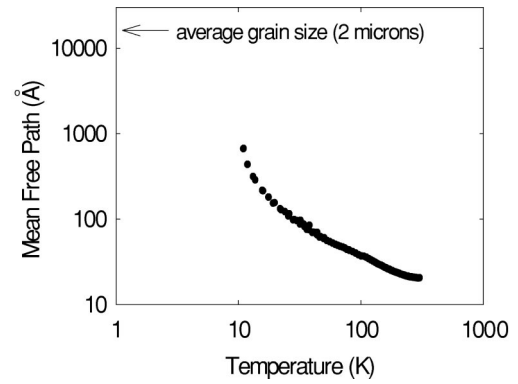


FIG. 3. Temperature dependence of the mean free path in $\text{Na}_8\text{Si}_{46}$.

interstitial atom, the lower the κ . What is the effect of the “rattling” Na in $\text{Na}_8\text{Si}_{46}$?

We take two approaches to understand how the Na vibrational modes in $\text{Na}_8\text{Si}_{46}$ 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.^{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, Θ_E , and Debye temperature, Θ_D , respectively.²² Using this approach and the room temperature ADP’s,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 $\Theta_D=570 \text{ K}$. These estimated Einstein modes (at 74 and 93 cm^{-1}) are in agreement with that assigned using neutron scattering measurements²³ at 83 cm^{-1} , and with those calculated from lattice dynamics using density functional theory²⁴ (at 72 cm^{-1} and 121 cm^{-1}). (We also note that the upper band of the acoustic modes of Si_{46} has been calculated²⁵ to be at 100 cm^{-1} .) The value calculated for Θ_D is very near the value of 590 K based on analysis of the total heat capacity,²⁴ $C_V=1160 \text{ J K}^{-1} \text{ mol}^{-1}$, and $540 \pm 25 \text{ K}$ based on theoretically determined elastic constants.²⁵ Using these results and taking the mean free path as the distance between Na atoms inside the tetrakaidekahedra, 5.10 \AA , we estimate the room temperature resonance-coupled κ_g of $\text{Na}_8\text{Si}_{46}$ to be $2.1 \text{ W m}^{-1} \text{ K}^{-1}$. The Na optic “rattle” modes then presumably do resonantly scatter the higher frequency acoustic phonon modes resulting in a much lower κ_g than that of diamond Si, but not as low as that found in other type I clathrates. Given that $\text{Na}_8\text{Si}_{46}$ is metallic, most of the heat conduction likely is due to electronic contributions. The estimated κ_g also suggests a relatively large electronic component of the thermal conductivity, $\approx 4.0 \text{ W m}^{-1} \text{ K}^{-1}$. This estimate 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 κ values shown in Fig. 2, the heat capacity of $\text{Na}_8\text{Si}_{46}$ (Refs. 24 and 26) and the velocity of sound calculated from theoretically determined elastic constants.²⁵ 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 μm, at extremely low temperatures. (Indeed, the small grain size may contribute to the low κ 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 $\text{Sr}_8\text{Ga}_{16}\text{Ge}_{30}$.

In summary, we report on the transport properties of $\text{Na}_8\text{Si}_{46}$. 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 $\text{Na}_8\text{Si}_{46}$, it is not as strong a phonon scattering mechanism as in other type I clathrates.

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