

Low-density framework form of crystalline silicon with a wide optical band gap

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Synthesis of a guest-free clathrate form of crystalline silicon was achieved by successive vacuum treatment and density separation of $\text{Na}_x\text{Si}_{136}$ -based materials. The new allotrope of silicon has an open framework structure based upon slightly distorted tetrahedral atoms bound into five- and six-membered ring structures, and corresponds to a fully saturated and condensed fullerene-type solid. Theoretical calculations indicate that the new form of silicon should be a wide bandgap semiconductor. This prediction is borne out by experiment: electrical conductivity and optical absorption measurements yield a band gap of 1.9 eV, approximately twice the value of “normal” semiconducting silicon.

The important semiconductor silicon shares the same dense tetrahedral structure with diamond, and has an indirect bandgap of 1.12 eV. Upon high pressure treatment, silicon transforms into the metallic β -Sn structure, which is octahedrally coordinated. Diamond itself is a high pressure form of carbon, and has a very large band gap (5.5 eV). At ambient pressure, low-density carbon exists as semimetallic graphite, with a planar sheet structure. Pure silicon has not yet been observed to take such an sp^2 -bonded structure. However, low-density silicon frameworks have been reported to form as clathrates, in which networks of slightly distorted silicon tetrahedra encapsulate alkali or alkaline earth metal atoms, that are thought to act as “templates” in their synthesis. These materials are structurally analogous to the ice clathrate hydrates (structures I and II). The structure II silicon clathrate structure has the formula $\text{M}_x\text{Si}_{136}$ ($x \leq 24$; M is usually an alkali metal), and contains fused fullerene-like cages: eight hexakaidecahedral (Si_{28}) structural elements are linked by sharing hexagonal faces, and also by 16 dodecahedral (Si_{20}) units. First-principles calculations carried out on the Na-free end member, that corresponds to a new expanded form of crystalline silicon, suggest that the band gap should be wide (≈ 1.9 eV) and indirect.¹ Here we report synthesis and basic electric and optical properties of this material.

Silicon clathrates were first obtained² as metastable intermediate phases during thermal decomposition of the alkali metal silicides (e.g., NaSi). Extensive initial studies by Cros *et al.*² permitted the identification of two types of clathrate structure, $\text{Na}_x\text{Si}_{136}$ ($x \leq 24$) and $\text{Na}_x\text{Si}_{46}$ ($x = 8$) (structure I). It was demonstrated that the alkali content in the structure II clathrate could be reduced by prolonged heating in vacuum,^{2,3} and that clathrate fractions with different alkali metal content could be isolated and purified by density separation in organic liquids.³ Using a combination of successive vacuum “degassing” of Na, followed by density separation and centrifugation, we have now succeeded in purifying ~ 100 mg quantities of essentially Na-free material (atomic absorption analysis yields residual Na contents < 600 ppm by weight; less than 1 Na per ~ 1400 Si atoms in the struc-

ture). Compositions down to $\text{Na}_1\text{Si}_{136}$ have been reported previously. From x-ray diffraction, the volume per Si atom of this “open framework” form is 23.01 \AA^3 , 16% greater than that of “normal” silicon ($19.90 \text{ \AA}^3/\text{atom}$).

The clathrate Si_{136} is prepared from the ionic Zintl phase sodium silicide (NaSi), which contains isolated $[\text{Si}_4]^{4-}$ tetrahedral clusters. On heating to $350\text{--}375^\circ\text{C}$, this compound transforms to an $\text{Na}_x\text{Si}_{136}$ clathrate, with a high ($x > 10$) sodium content. Such samples are semimetallic,^{4,5} and have large observed Knight shifts in ^{23}Na and ^{29}Si NMR spectra.^{6,7} Prolonged heating in vacuum causes Na atoms to be lost from the clathrate structure, and the samples become semiconducting.⁴ $\text{Na}_x\text{Si}_{136}$ samples, free of $\text{Na}_8\text{Si}_{46}$, with low sodium concentrations ($x \leq 4$), were washed in concentrated hydrochloric acid, dried and degassed at 430°C under a vacuum of 10^{-5} Torr over a period of several days. Subsequently, the resulting samples contained lower sodium fractions. This process of washing with HCl and heating under vacuum was cycled several times. Finally, the fraction with sodium content < 600 ppm was isolated by centrifuging in a dibromomethane-methanol solution.

The ^{29}Si NMR spectra of samples with low sodium content ($0.5 < x < 4$) show very broad signals probably due to paramagnetic interaction between silicon and sodium nuclei.⁸ As shown in Fig. 1(a), these peaks remain very broad even at a low sodium content of $x \approx 0.5$. As the Na-free composition (600 ppm Na, or less than one sodium atom per ten unit cells) is approached, the ^{29}Si NMR spectrum becomes very sharp, with well-resolved resonances observed at 0.3, 93.0, and 50.4 ppm [Fig. 1(a)]. These values represent typical NMR shifts for nearly insulating samples with tetrahedral Si atoms.⁹ The peak intensities occur in the ratio 12:4:1, which is that expected for the three crystallographically distinct silicon sites in the Si_{136} structure (i.e., $96g$, $32e$, and $8a$, using Wyckoff’s notation). The refined crystal structure of the expanded Si_{136} phase indicates that the degree of distortion from tetrahedral symmetry of the silicon atoms is quite small [Fig. 1(b)]. The Si-Si bond lengths range from 2.336–2.381

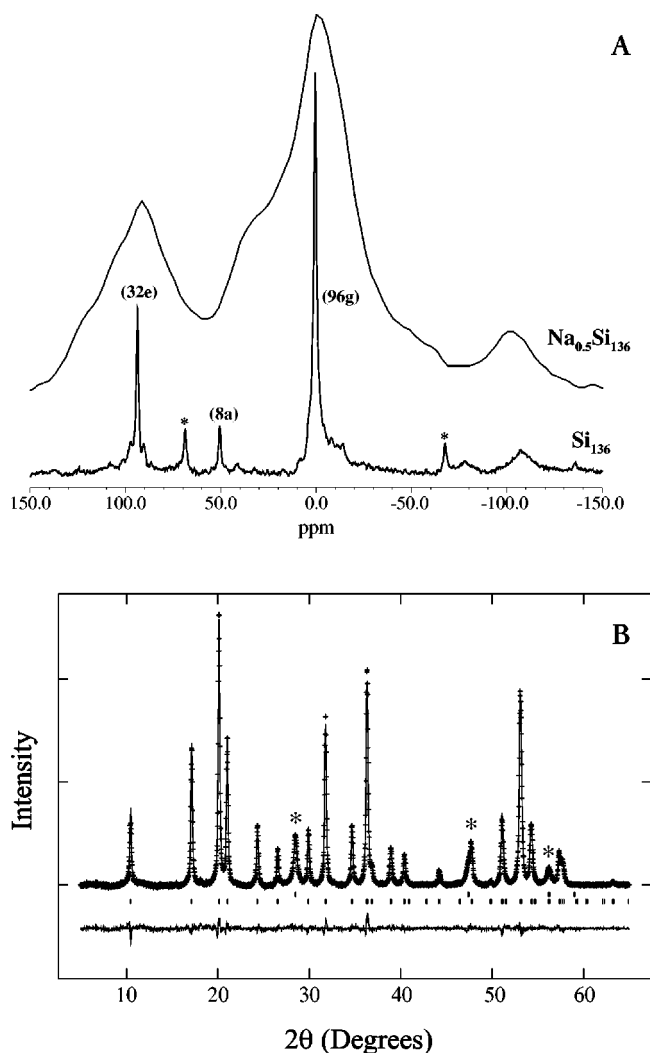


FIG. 1. (a) ^{29}Si magic angle spinning (MAS) NMR spectra for $\text{Na}_{0.5}\text{Si}_{136}$ and Si_{136} with sodium content ≈ 600 ppm. For Si_{136} the three principal resonances occur for at 0.3, 50.4, and 93.0 ppm [measured from a tetramethylsilane (TMS) standard]. Based upon their relative intensities, which stand in the ratio 12:1:4 respectively, these are unambiguously assigned to the crystallographically inequivalent 96g, 8a, and 32e sites in the material. A weak signal corresponding to a very small amount ($\approx 5\%$ by volume) of diamond structured silicon present as an impurity in the sample is observed at -79 ppm. The weak broad feature at -109 ppm is assigned to amorphous SiO_2 ,⁹ formed by some surface oxidation of the particles, as occurs for normal Si. The peaks marked with an asterisk correspond to spinning side bands of the principal resonances of Si_{136} . (b) Rietveld profile fit to powder x-ray diffraction data for Si_{136} , space group $Fd\bar{3}m$, $a = 14.62601(9)$ Å. The continuous line represents the best fit profile, and superimposed crosses are experimental data. The difference between experimental and fitted profiles is shown below the pattern. The bottom set of tick marks corresponds to reflections for Si_{136} . The second set correspond to diamond-structured Si, present as an impurity phase. From the refined Si site occupancies no vacancies were observed at any of the three crystallographic inequivalent sites.

Å with an average value of 2.341 Å, identical with that found in diamond structured silicon. This is a smaller value than that observed for fully occupied, metallic structure II clathrates.¹⁰ The Si-Si-Si bond angles range from 105.7°

-119.7° , compared with the ideal tetrahedral value (109.47°). The range in Si-Si bond lengths and in tetrahedral bond angles is thought to be critical in determining the wide band gap in these materials.¹ The largest deviations from the tetrahedral angle (109.47°) are encountered for the large Si-Si-Si angles (119.7°) encountered for the Si atoms involved in the shared six-membered rings, that are forced to be near planar.

It is remarkable that the expanded “empty clathrate” structure of Si is stable, in the absence of alkali atoms, even at elevated temperatures. In previous investigations of the $\text{Na}_x\text{Si}_{136}$ series,^{2,4} it had been suggested that the framework might collapse upon complete removal of the “templating” guest atoms. Our results show that this is not the case. The present observation is made even more remarkable by the likelihood that sodium loss during vacuum heating occurs via extended defects within the structure.^{11,12} Annealing of such defects apparently occurs while maintaining the clathrate structure, rather than resulting in nucleation of diamond-structured silicon, which is the thermodynamically stable phase under these conditions. Even following application of high pressure (5 kbar) at 250°C for up to 12 h, the Si_{136} clathrate was recovered untransformed. This result further demonstrates the remarkable stability of the open framework structure against collapse. Recently, Si_{136} clathrate was found to be stable up to pressures of 10 GPa at room temperature.^{13,14} Above this pressure Si_{136} transforms to a β -Sn structure, similar to diamond-structured silicon.

The semiconducting nature of Si_{136} is confirmed by electrical resistance (R) measurements on cold-pressed discs of the sample. Arrhenius plots of $\ln 1/R$ vs $1/T$ show some curvature, with well defined linear regions at high and low temperature (Fig. 2). The high temperature regime is due to intrinsic semiconduction consistent with a band gap (E_{int}) of ≈ 2.0 eV, which is remarkably large for a variety of elemental silicon. The Arrhenius slope of the resistance is smaller at low temperature, indicating a transition to an extrinsic regime associated with the presence of the residual Na atoms in the framework, which behave as n -type dopants in the lattice. Similar behavior was observed by Cros *et al.*² in their original work on $\text{Na}_x\text{Si}_{136}$ clathrates, for samples with $3 < x < 11$ and also for lightly n -doped silicon. Their resistivity measurements showed a low temperature regime with an extrinsic activation energy ($\delta E_D = E_{\text{ext}}/2$) that changed from $\delta E_D = 0.013$ eV for $x = 11$, to 0.04 eV for $x = 3$, from dopant levels within the gap.^{2,4} The low temperature slope for our material would correspond to $\delta E_D \approx 0.6$ eV, consistent with the trend of Cros *et al.*² for $x \leq 1$. A value of 0.04–0.1 eV was estimated for the activation energy estimated for promoting conduction electrons from localized states within the gap in $\text{Na}_x\text{Si}_{136}$ materials, from variable temperature ^{23}Na NMR studies.¹⁵ In the work of Cros *et al.*,² the value of the high temperature limiting slope decreased with lowered sodium content, to approach the gap energy of lightly n -doped silicon ($E_{\text{int}} \approx 1.2$ eV). Our sodium-free Si_{136} has a much steeper limiting slope, and a value of the intrinsic semiconducting gap that is nearly twice as large, corresponding to a gap energy ($E_g \approx 2.0$ eV) that would lie within the visible region of the spectrum ($\lambda \approx 620$ nm)

Our electrical resistance measurements of the intrinsic semiconducting gap are supported by visible spectroscopy

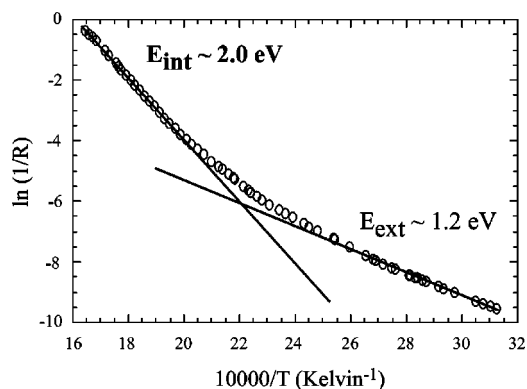


FIG. 2. Electrical resistance vs temperature measurement on cold pressed discs of Si_{136} (pressed at 15–20 kbar to $\approx 80\%$ density) obtained using a four-point probe arrangement. The samples formed circular discs 0.8–1.2 cm in diameter and 0.1–0.3 cm thick, and were held in place by four spring-loaded stainless steel electrodes. The assembly was placed inside a quartz tube within a high temperature furnace. The results were reproduced on three different aliquots of material, from different synthesis batches, and the experimental setup was tested by conductivity measurements on various samples of n -doped silicon. These always showed the expected high temperature intrinsic $\ln 1/R$ vs $1/T$ slope consistent with the well-known band gap (1.12 eV), and also showed the lower temperature extrinsic regime.

and optical examination of the samples of Si_{136} . Visible microscopy in reflectance mode indicates reflectance colors varying from silvery blue to golden yellow, depending upon the sample orientation. A reflectivity spectrum measured with the microscope coupled to an optical spectrometer indicates an initial step followed by a steep rise in reflectivity at wavelengths shorter than 675 nm (Fig. 3). Examining the sample in transmission shows that most of the grains are opaque, mainly due to scattering by the aggregates of particles of high refractive index with small size ($\approx 1\text{--}5\ \mu\text{m}$, close to the diffraction limit for optical wavelengths). However, a few grains were larger than this, and these transmitted light with a reddish hue, as expected for the wide band gap Si_{136} material. Transmission spectra taken through such samples showed onset of absorption at approximately 650 nm, consistent with an optical band edge near 1.9 eV at room temperature (Fig. 3). The resistivity and optical measurements indicate that the “expanded” Si_{136} phase of silicon has a band gap of 1.9–2.0 eV, approximately twice the value for “normal” diamond-structured silicon. Such wide band gap materials based on silicon could be developed for designing optoelectronic materials compatible with existing silicon technology.^{1,16,17} The present synthesis method is too unwieldy for obtaining precise control over form and stoichiometry, in a useful form such as a thin film intimately bonded to the substrate and associated layers within the device. However, such wide band gap “expanded silicon” crystal structures might be made by thin film deposition methods. A recent report has described a “fullerenelike” structure of silicon obtained by evaporation of solid Si in a

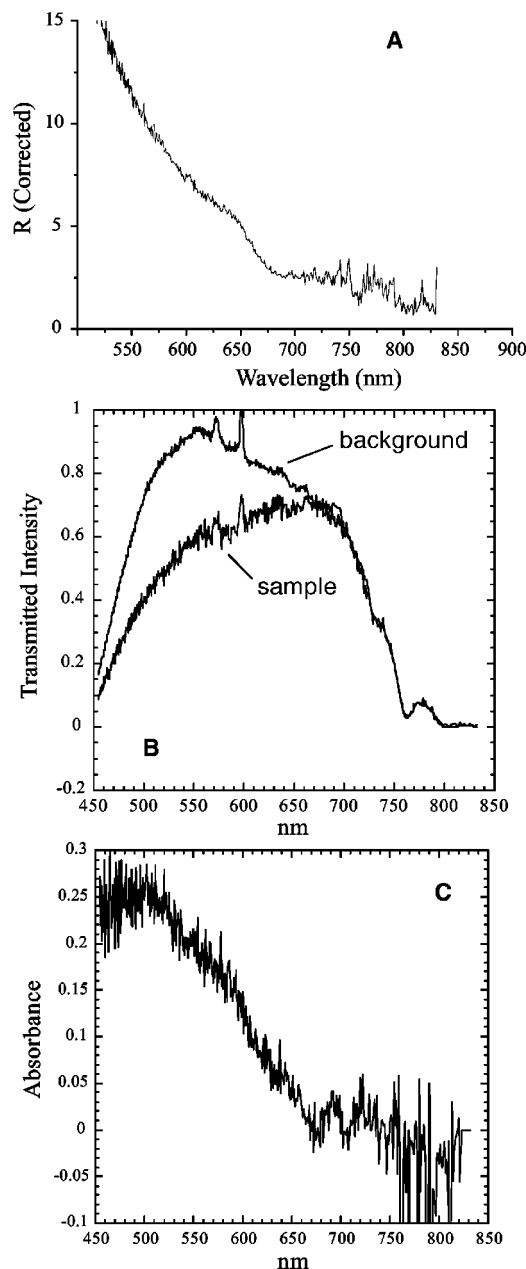


FIG. 3. Visible light spectroscopy of the Si_{136} particles, obtained with an optical microscope (quartz-halogen lamp source: $150\times$ dry Olympus objective) coupled to a visible spectrometer (ISA U-1000 micro-Raman system). Reflectance spectra (a) were referenced to the reflectivity of Al metal over the visible region. The reflectivity is computed as $R_{\text{sample}}/R_{\text{Al}}$, in reflectivity units ($R_{\text{max}}=1$). Comparable spectra were taken at several points within the sample. In (b), we show the transmission spectrum (I_{sample}) through a representative group of small ($1\text{--}10\ \mu\text{m}$) particles, relative to that through a particle-free region of the glass slide, that serves as a background (I_0). The absorption spectrum in (c) is obtained by taking $\log_{10}(I_0/I_{\text{sample}})$, after normalizing within the long wavelength region ($>750\ \text{nm}$) for attenuation due to scattering and multiple reflection within the sample.

helium environment.¹⁸ The unit cell parameter reported is in fact close to that of structure II clathrate, and it is possible that crystalline Si_{136} has in fact been formed in this experiment.¹⁹ It is also of interest that workers are obtaining

amorphous silicon films based upon “fullerene-type” structures reminiscent of the building blocks present in the clathrates, utilizing laser ablation and vapor deposition methods upon various substrates.^{20,21}

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