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Communication

Framework Contraction in Na-Stuffed Si(*cF*136)

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Systematic crystal structure refinements from powder X-ray diffraction data as well as density functional theory calculations demonstrate that the silicon clathrate II Si(*cF*136) exhibits a lattice contraction as Na is introduced solely into the Si_{28} cages. When the Si_{20} cages, in addition, begin to be filled with Na, a contrasting lattice expansion results. The nonmonotonic structural response to filling is an indication of markedly dissimilar guest−framework interactions for Na@Si_{20} and Na@Si_{28}.

When the effective guest size is comparable to or larger than the free cavity volume of the empty host, the encapsulation of atoms and molecules in the cavities of host frameworks is typically accompanied by an expansion of the latter. For clathrate hydrates,[1] the unit cell volume depends on the occupancy and interaction of the host framework with the guest species.[1,2] It has also been suggested[3] that inclusion of sufficiently small guests might induce a host compression, so that contraction of the hydrogen-bonded framework of the clathrate hydrate occurs upon filling. Despite the rather different mechanisms for guest−host interactions (van der Waals-like for hydrates and ionic character for intermetallic clathrates), phenomenologically analogous behavior was predicted[4] on the basis of density functional theory (DFT) calculations for the intermetallic clathrate II system[5] Na_xSi_{136} ($0 \leq x \leq 24$): incorporation of relatively small Na guest atoms within the expanded silicon framework Si(*cF*136) might induce a lattice contraction rather than an expansion, signifying that other guest−framework interactions dominate.
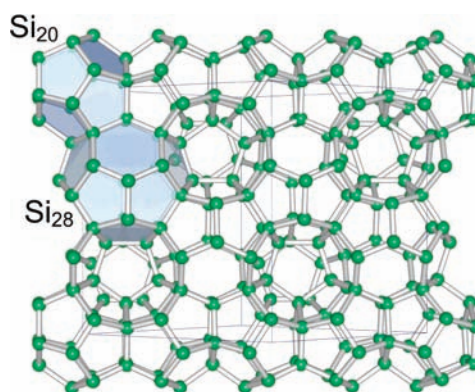

Figure 1. Cubic (space group $Fd\bar{3}m$) silicon clathrate II framework Si(*cF*136). The two silicon cages that can be occupied by Na are highlighted in the upper left.

In contrast to the clathrate hydrates, significant charge transfer from guest to host is expected to occur in intermetallic clathrates. In the course of our investigations on clathrate II Na_xSi_{136}, we have experimentally observed this intriguing lattice contraction upon filling for the first time. Supporting DFT optimizations covering the range of representative compositions are also in agreement with the experimental observation of framework contraction.

The expanded host framework of silicon ($x = 0$), corresponding to the metastable silicon allotrope Si(*cF*136),[6] is characterized by two distinct cages, Si_{20} and Si_{28} (Figure 1). These cages constitute coordination polyhedra for encapsulated guests.[7] Si(*cF*136) is a semiconductor[6] because all valence states are occupied as a result of the sp^3-like arrangement of four-bonded Si atoms. The inclusion of the Na atoms into cavities of the host framework is expected to be accompanied by occupation of the Si_{136} antibonding states depending on the degree of guest-to-host charge transfer.[4] Increasing their occupation should effectively reduce the bond order for the framework atoms, and an expansion of the lattice might

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(1) Sloan, E. D., Jr. *Clathrate Hydrates of Natural Gases*; Marcel Dekker, Inc.: New York, 1998.

(2) (a) McIntyre, J. A.; Petersen, D. R. *J. Chem. Phys.* **1967**, *47*, 3850. (b) Zele, S. R.; Lee, S.-Y.; Holder, G. D. *J. Phys. Chem. B* **1999**, *103*, 10250. (c) Ikeda-Fukazawa, T.; Yamaguchi, Y.; Nagashima, K.; Kawamura, K. *J. Chem. Phys.* **2008**, *129*, 224506.

(3) (a) Kosyakov, V. I.; Shestakov, V. A. *J. Struct. Chem.* **1998**, *39*, 786. (b) Belosludov, V. R.; Inerbaev, T. M.; Subbotin, O. S.; Belosludov, R. V.; Kudoh, J.-I.; Kawazoe, Y. *J. Supramol. Chem.* **2002**, *2*, 453.

(4) Conesa, J. C.; Tablero, C.; Wahnón, P. *J. Chem. Phys.* **2004**, *120*, 6142.

(5) Cros, C.; Pouchard, M.; Hagenmuller, P. *J. Solid State Chem.* **1970**, *2*, 570.

(6) (a) Adams, G. B.; O'Keefe, M.; Demkov, A. A.; Sankey, O. F.; Huang, Y.-M. *Phys. Rev. B* **1994**, *49*, 8048. (b) Gryko, J.; McMillan, P. F.; Marzke, R. F.; Ramachandran, G. K.; Patton, D.; Deb, S. K.; Sankey, O. F. *Phys. Rev. B* **2000**, *62*, R7707.

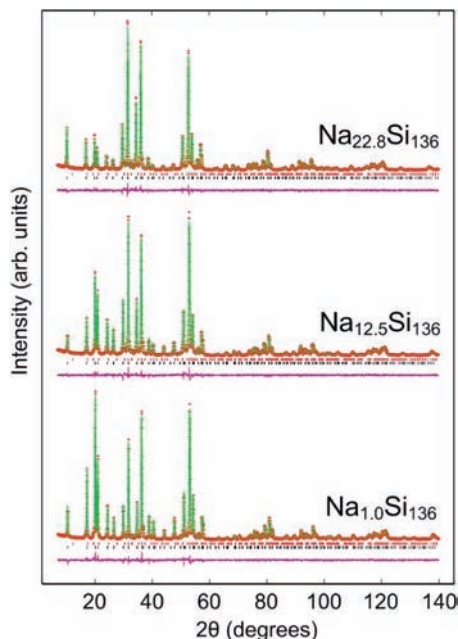(7) Beekman, M.; Nolas, G. S. *J. Mater. Chem.* **2008**, *18*, 842.

Figure 2. Rietveld refinement profiles (observed, calculated, and difference diffraction patterns) for three Na_xSi_{136} specimens (x = 1.0, 12.5, and 22.8).

also be expected in this case. Considering the effective ionic and covalent radii of Na and Si, respectively,[8] the volume contribution of the Na atoms within the oversized Si_{28} cages should be negligible. In any case, the guest−framework interaction should differ for the two distinct Na−Si environments $Na@Si_{20}$ and $Na@Si_{28}$ because of the significant differences in the cage size and coordination number.

The Na_xSi_{136} ($1 \leq x \leq 23$) specimens reported on here were synthesized via thermal decomposition of Na_4Si_4 under high vacuum, in which the Na content in the specimen is controlled by vacuum evaporation.[5] In general, specimens prepared by this method contain clathrate I Na_8Si_{46} as an impurity, the amount typically varying from a few to as much 50 wt %.[9] As estimated by multiphase Rietveld refinements, our specimens typically contain no more than 3 wt % Na_8Si_{46}.

The lattice parameter, crystal structure, and composition for each specimen were experimentally refined by the Rietveld method. Special attention was paid to specimen preparation for powder X-ray diffraction (XRD) data collection (see the Supporting Information, SI). The observation of high-angle reflections was ensured to achieve the precision needed to discern subtle changes of the unit cell parameter with the Na content. The obtained crystallographic data for all specimens can be found in the SI. Contributions of the minor impurity phase clathrate I Na_8Si_{46} to the diffraction profiles were accounted for by two-phase refinement. Representative powder XRD patterns for three specimens, $Na_{1.0}Si_{136}$, $Na_{12.5}Si_{136}$, and $Na_{22.8}Si_{136}$, are shown in Figure 2. As illustrated by these three patterns, the relative intensities of the majority of the
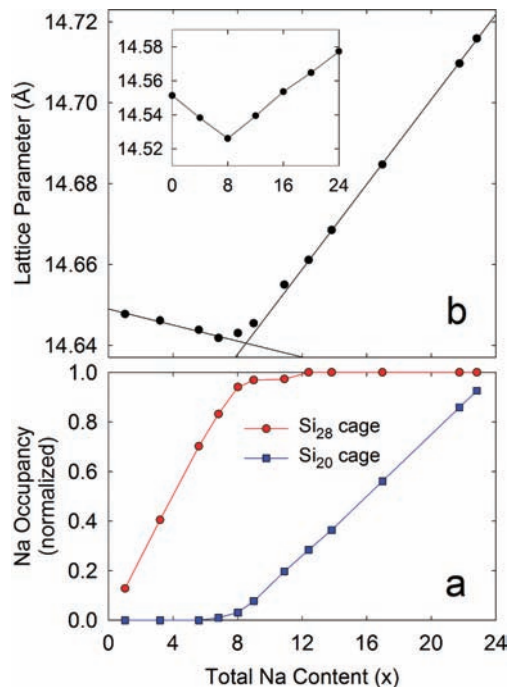

Figure 3. (a) Experimental normalized cage occupancies for $Na@Si_{20}$ and $Na@Si_{28}$ and (b) experimental cubic unit cell parameters, both as a function of the total Na content. Inset (same units as the main figure): Theoretical lattice parameters obtained from DFT calculations.

most intense reflections display marked dependence upon the Na content or, more precisely, the particular occupation of the two different silicon cages.[9]

Our crystal structure refinements indicate full occupancy of the silicon framework sites (i.e., no silicon vacancies) for all compositions, in agreement with previous work.[9] The refined cubic unit cell parameters of the Na_xSi_{136} specimens are presented in Figure 3b. The lattice parameter of Na_xSi_{136} decreases atypically with increasing x for $x < 8$; only for $x > 8$ is a lattice expansion observed. The occupancies of $Na@Si_{20}$ and $Na@Si_{28}$ are plotted in Figure 3a, as a function of the total Na content x. For all of our specimens, a strong preferred occupation by Na of the oversized Si_{28} cages is observed, as opposed to the Si_{20} cages. Not until the Si_{28} cages are nearly completely filled (when $x \cong 8$) do the smaller Si_{20} cages begin to be occupied. These observations are in general agreement with most[4,5,9,10] but not all[12] prior reports. Preferential occupation of the 28-vertex cage in clathrate II hydrates has also been observed.[1] The preferred occupation can be directly correlated with the nonmonotonic structural response to filling the polyhedral cages of the host framework Si_{136} with Na atoms (Figure 3b) in that the minimum in the lattice parameter versus Na content occurs at the point at which the Si_{20} cages begin to show significant occupation, near $x \cong 8$.

Structure optimizations within DFT and the local density approximation (LDA)[11] for seven Na_xSi_{136} ($0 \leq x \leq 24$)

(8) (a) Shannon, R. D. *Acta Crystallogr., Sect. A* **1976**, *32*, 751. (b) Goryunova, N. A. *The Chemistry of Diamond-like Semiconductors*; Chapman Hall: London, 1965.
(9) (a) Ramachandran, G. K.; Dong, J. J.; Diefenbacher, J.; Gryko, J.; Marzke, R. F.; Sankey, O. F.; McMillan, P. F. *J. Solid State Chem.* **1999**, *145*, 716. (b) Reny, E.; Gravereau, P.; Cros, C.; Pouchard, M. *J. Mater. Chem.* **1998**, *8*, 2839. (c) Horie, H.; Kikudome, T.; Teramura, K.; Yamanaka, S. *J. Solid State Chem.* **2009**, *182*, 129.

(10) Roy, S. B.; Sim, K. E.; Caplin, A. D. *Philos. Mag. B* **1992**, *65*, 1445.
(11) Our calculations are based on the first-principles LDA and were performed using the Vienna ab initio simulation package (VASP). This method has been used in many previous studies of clathrate materials, and the calculated structural, electronic, and vibrational properties were found to be in good agreement with experimental data. See, for example: Kresse, G.; Furthmüller, J. *Comput. Mater. Sci.* **1996**, *6*, 15. Kresse, G.; Joubert, D. *Phys. Rev. B* **1999**, *59*, 1758. Also see the SI for further details.
(12) He, J.; Klug, D. D.; Uehara, K.; Preston, K. F.; Ratcliffe, C. I.; Tse, J. S. *J. Phys. Chem.* **2001**, *105*, 3475.

compositions (for details, see the SI) were performed. Guided by the experimental observations, a model was chosen in which Na exclusively fills the Si_{28} cages first as the total Na content is increased. The DFT-determined lattice parameters are shown in the inset to Figure 3b. In agreement with our experimental observations and in support of the conclusions from the four compositions studied in ref 4, our DFT calculations clearly predict that incorporation of the small Na guests in the larger Si_{28} cage induces a contraction of the unit cell volume. This contraction of the cell volume is apparent from the calculated average Si−Si bond lengths, which are shorter for Na_4Si_{136} and Na_8Si_{136} than those in pristine Si_{136}. Upon further Na incorporation ($x = 12, 16, 20$, and 24), the average Si−Si bond lengths increase with a corresponding increase in the volume.

Examination of the refined atomic positions (8a, 32e, and 96g; see the SI) of the host framework silicon atoms reveals subtle but significant trends that, as with the lattice parameter, do not develop uniformly with the Na content. For the compositions having either cage less than fully filled, the local positions of the Si framework atoms for a particular composition and cage are likely to be different from cage to cage depending on whether the cage and its neighboring cages are occupied or empty. While the crystal structure refinements only provide information regarding the averaged structure, insight into the local behavior can still be gleaned by examining the evolution with the Na content. The illuminating features are summarized in Figure 4, which shows the trends in the Si_{20} cage volumes (blue square symbols) and Si_{28} cage volumes (red circular symbols) as a function of the Na content, relative to the $x = 8$ composition. These data were obtained from the calculated geometric volumes of the cages derived from the refined Si atomic positions and the refined lattice parameters (for details, see the SI). Also shown is the analogous trend in the unit cell volume (closed circles) as a function of the Na content. Because the Si($cF136$) framework is cubic, this comparison elucidates how the cage volumes individually evolve relative to the unit cell as a whole. The data in Figure 4 show that, relative to the unit cell as a whole, the Si_{28} polyhedra appear to contract more as they are filled, whereas the Si_{20} polyhedra expand significantly more as they are filled. These opposite effects, combined with the preferential occupation (Figure 3a), help to explain the minimum in the lattice parameter versus Na content near $x = 8$. We interpret these data to be an indication that the local guest−cage interaction drives the behavior of the lattice parameter shown in Figure 3b.

The observed unit cell contraction for $x < 8$ can be attributed to an attractive interaction between the Na guest and its Si_{28} cage. Prior indications of such interactions were also found in observations[4,7,13,14] that Na is shifted off-center
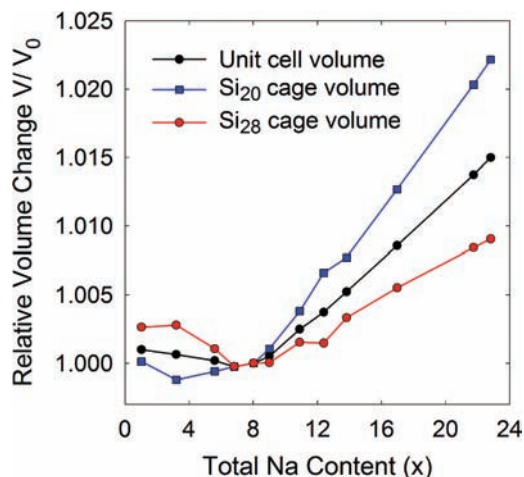

Figure 4. Trends (obtained from Rietveld refinements) in the silicon cage volumes as a function of the Na content for the Si_{28} (red filled circles) and Si_{20} (blue filled squares) cages. Also shown (closed circles) is the trend in the until cell volume as a function of the Na content. The values are given as the relative volumes compared to V_0, taken to be the corresponding volume for the $x = 8$ composition.

in the Si_{28} cage (see the SI), which significantly reduces the Na−Si distances relative to Na residing in the center of the Si_{28} cage. The extent and nature of charge transfer[15] from Na to the Si framework in the Na_xSi_{136} clathrates likely play important roles in the behavior shown in Figures 3 and 4 and are a matter of particular interest for further study.

The nonmonotonic structural evolution in the case of filling voids in the Si($cF136$) framework occurs in response to the single compositional variable, x, and in the absence of any apparent structural phase transition or induced defects. Rather, the large difference between effective guest and cage volumes for $Na@Si_{28}$ appears to be the origin of the unusual lattice response to filling. If such compositions can be prepared, the incorporation of even smaller alkali guests (e.g., $Li@Si_{28}$ or $Na@Ge_{28}$) in intermetallic clathrates would provide intriguing systems for the future study of such phenomena.

Supporting Information Available: Crystallographic data in tabular and CIF format; synthesis and experimental and computational methods; experimental, calculated, and difference powder XRD patterns for all specimens. This material is available free of charge via the Internet at http://pubs.acs.org.

(13) Brunet, F.; Mélinon, P.; San-Miguel, A.; Kéghélian, P.; Perez, A.; Flank, A. M.; Reny, E.; Cros, C.; Pouchard, M. *Phys. Rev. B* **2000**, *61*, 16550.

(14) Beekman, M.; Sebastian, C. P.; Grin, Yu.; Nolas, G. S. *J. Electron. Mater.* **2009**, *38*, 1136.

(15) Pouchard, M.; Cros, C.; Hagenmuller, P.; Reny, E.; Ammar, A.; Ménétrier, M.; Bassat, J.-M. *Solid State Sci.* **2002**, *4*, 723.