Supporting Information

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

Matt Beekman[a], Emmanuel N. Nenghabi[b,%], Koushik Biswas[c], Charles W. Myles[b], Michael Baitinger[d], Yuri Grin[d], and George S. Nolas[a,*]

[a]*Department of Physics, University of South Florida, Tampa, FL 33620*
[b]*Department of Physics, Texas Tech University, Lubbock Texas 79409*
[c]*National Renewable Energy Laboratory, Golden, CO 80401*
[d]*Max-Planck-Institut für Chemische Physik fester Stoffe, 01187 Dresden, Germany*
[%]*Deceased.*

*Corresponding author: gnolas@cas.usf.edu

S1. Specimen Preparation, Experimental Methods, and Computational Details

S1.1 Synthesis

Twelve Na_xSi_{136} specimens were synthesized by thermal decomposition of crystalline Na_4Si_4. Na_4Si_4 was first prepared by reaction of elemental Na (Alfa Aesar, 99.95%) and Si (Alfa Aesar, 99.9999%) in the nominal stoichiometry Na:Si of 1.1:1. All handling was performed in a nitrogen filled glove box due to the extreme sensitivity of Na and Na_4Si_4 to air and moisture. Reactions were carried out in tungsten metal crucibles, under high purity nitrogen gas in sealed steel reaction vessels. (SAFETY NOTE: Na_4Si_4 can react explosively with water. Take extreme caution and use appropriate safety procedures.) The steel vessels were themselves sealed under nitrogen inside fused silica ampoules. The products of this reaction contain crystalline Na_4Si_4 with excess free Na metal, which was removed by evaporation under high vacuum (10^{-6} torr) at 275 ^oC. Thermal decomposition was initiated by rapidly heating the Na_4Si_4 precursor in a process similar to that reported by Gryko [S1], resulting in a specimen with x nearly 24: $34Na_4Si_4 \rightarrow Na_{24-\delta}Si_{136} + (112 + \delta)Na$ (g), where $0 < \delta < 1$. The Na content is then further adjusted by heating temperature and time, ranging from 75 minutes at 380 ^oC for $Na_{22.8}Si_{136}$ to 5 days at 420 ^oC for $Na_{1.0}Si_{136}$. The microcrystalline products were then vented to a nitrogen atmosphere without exposure to air, washed first with ethanol then distilled water, sonicated, allowed to settle, decanted, and thoroughly dried. The resulting Na_xSi_{136} crystalline powder is very stable toward air and moisture.

S1.2 Powder X-ray Diffraction Data Collection and Rietveld Refinement

Powder specimens were thoroughly ground by hand in a nitrogen glove box prior to powder diffraction data collection. The powder was loaded into a back-loading specimen holder, which insured a uniform powder specimen with a flat top surface, minimizing sample displacement effects during powder diffraction data collection. The diameter of the cylindrical opening accepting the specimen was large enough such that beam spillover (beam footprint effects) did not occur at low angles in the 2θ range of interest. Powder X-ray diffraction step scan data were collected using a Bruker D8 diffractometer in conventional Bragg-Brentano geometry. A graphite monochromator was employed, resulting in Cu $K\alpha_{1+2}$ radiation. Step scan diffraction intensity data were collected in the 2θ range from 7^o to a

maximum angle of at least 140°, with a step size of 0.02°. High angle reflections were included to maximize the precision in lattice parameter determination.

Full-profile Rietveld refinements were carried out with the aid of the GSAS [S2] and EXPGUI [S3] software. Crystal structure refinements for all specimens were carried out within the $Fd\bar{3}m$ space group. Site occupancies for each specimen were allowed to refine. If occupancies were found to be insignificantly different from zero or unity (i.e. within 2σ), they were then fixed at the respective value in further refinement cycles. Otherwise the occupancies (i.e. Na, since silicon framework sites were always found to be fully occupied) were allowed to refine. Very large atomic displacement parameters (> 0.1 Å^2) for Na@Si_{28} are obtained for all specimens, indicating substantial disorder for this site. Both on-center [10] and off-center models [S4, S5] have been proposed for the Na@Si_{28} guest. We find two models we refined against our powder diffraction data (on-center Na at the 8*b* site and off–center Na at the 32*e* site) both describe our powder diffraction data equally well [S5], and do not result in significant differences in the lattice parameters or silicon framework positions. For the off-center model, the Na occupancy in the Si_{28} cage in all cases refines to ¼ the corresponding occupancy of the on-center model, consistent with the 4-fold increase in site multiplicity. The off-center shifts (c.f. Tables S1 – S12) are typically ~ 0.4 Å and the atomic displacement parameters are significantly reduced. The off-center model also results in more chemically reasonable Na-Si distances [S5]. In addition to overall (i.e. static) displacement, the disorder is also attributed to pronounced thermal motion of Na rattling, corresponding to an Einstein-like Na vibrational mode [S6].

The Si_{20} and Si_{28} cage volumes represented in Fig. 4 were calculated using the refined Si—Si distances and the distances from the Si framework sites (i.e. the polyhedron vertices) to the 16*c* and 8*b* sites, respectively, obtained from Rietveld refinement for each composition. Based on these distances, the irregular Si_{20} dodecahedron and Si_{28} hexacaidecahedron were partitioned into appropriate irregular tetrahedrons whose volumes were determined by appropriate vector products. The volumes of these irregular tetrahedrons were then summed to determine the respective cage volume.

S1.3 Computational Details

Our calculations were performed using the first-principles local density approximation (LDA) to density functional theory and we have used the projector augmented wave method [S7] as implemented in the Vienna *ab initio* simulation package (VASP) [S8]. The Ceperley–Alder functional [S9] as parametrized by Perdew and Zunger [S10] has been used to approximate the exchange correlation energy. The Si_{136} clathrate structure was modeled using a 34-atom face centered cubic primitive unit cell. We found that a plane-wave energy cutoff of 300 eV was sufficient to calculate the structural properties with good accuracy and it was used in all the calculations. Brillouin-zone integrations were performed using a 4×4×4 Monkhorst-Pack *k*-point grid [S11]. We have optimized the geometry by relaxing the volume as well as the cell internal coordinates. All forces were converged to within 0.1 meV/Å or less.

Compared to pristine Si_{136}, our LDA calculations find that the cell volume first contracts upon Na incorporation inside the large Si_{28} cages ($x = 4$, 8 in Na_xSi_{136}). However, as the Na content is increased further, the additional Na guests must also occupy of the smaller Si_{20} cages, which leads to a monotonic increase in cell volume for $x > 8$. As the Na content x increases from $x = 0$ to $x = 8$, our calculations find that the cell volumes for the face-centered cubic unit cell decrease from 772.46 Å^3 for Si_{136} to 768.36 Å^3 for Na_8Si_{136}. Then, as the Na content is increased above $x = 8$, we find that this volume increases from 768.36 Å^3 for Na_8Si_{136} to 775.42 Å^3 for $Na_{24}Si_{136}$. The contraction of volume (and therefore shorter Si-Si bonds) upon preferential filling of the Si_{28} cages at $x = 4$ and 8 can be explained by the attractive interaction between the Na atoms and their neighboring Si. Normally, the extra $3s^1$ electron released by

a guest Na atom would occupy the antibonding levels, which also would result in an outward lattice relaxation (that is, increased volume). Clearly, this is not the case for $x = 4$ or 8 in Na_xSi_{136}. The details of the theoretical study of the changing nature of the guest-host interactions for different x will be published elsewhere.

S2. Refinement Results

Crystallographic data, including atomic positions and atomic displacement parameters, powder diffraction data, as well as refinement results for all specimens can be found in the crystallographic information file (CIF) and in Tables S1 – S12. Observed, calculated, and difference powder diffraction patterns obtained from Rietveld refinement for all specimens are given in Figures S1 – S12.

Table S1. Refined atomic positions, occupancies, and equivalent (U_{eq}) or isotropic (U_{iso}) atomic displacement parameters for $Na_{22.8}Si_{136}$. Where U_{eq} are given, anisotropic displacement parameters and estimated standard deviations can be found in the CIF.

Atom	Site	*x/a*	*y/b*	*z/c*	*Occ.*	U_{eq} or U_{iso} (Å^2)
Na@Si_{28} on-center model, a = 14.7159(2) Å						
Na1	16*c*	0	0	0	0.926(4)	0.0146
Na2	8*b*	3/8	3/8	3/8	1	0.114(2)
Si1	8*a*	1/8	1/8	1/8	1	0.0055
Si2	32*e*	0.21837(6)	*x*	*x*	1	0.0080
Si3	96*g*	0.06711(4)	*x*	0.37171(6)	1	0.0073
Na@Si_{28} off-center model, a = 14.7159(2) Å						
Na1	16*c*	0	0	0	0.926(4)	0.0148
Na2	32*e*	0.386(3)	*x*	*x*	0.251(2)	0.09(2)
Si1	8*a*	1/8	1/8	1/8	1	0.0055
Si2	32*e*	0.21836(6)	*x*	*x*	1	0.0080
Si3	96*g*	0.06712(4)	*x*	0.37171(6)	1	0.0073

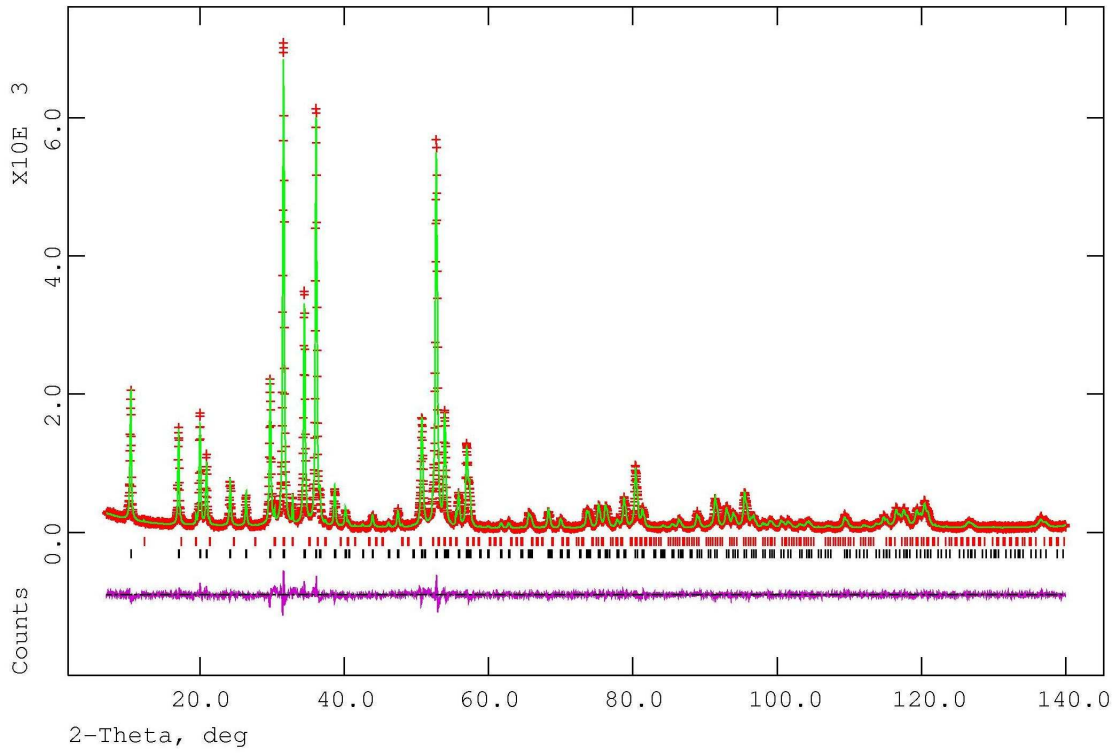

Figure S1. Observed (red crosses), calculated (green curve), and difference (purple curve) powder X-ray diffraction patterns for $Na_{22.8}Si_{136}$ (on-center model). Black tick marks (lower) indicate reflection positions for the $Na_{22.8}Si_{136}$ phase, red tick marks (upper) indicate reflection positions for the Na_8Si_{46} impurity phase (est. wt% ~ 3%). Refinement residuals: χ^2 = 1.8; wR_p = 0.088, R_p = 0.066, $R(F^2)$ = 0.027.

Table S2. Refined atomic positions, occupancies, and equivalent (U_{eq}) or isotropic (U_{iso}) atomic displacement parameters for $Na_{21.8}Si_{136}$. Where U_{eq} are given, anisotropic displacement parameters and estimated standard deviations can be found in the CIF.

Atom	Site	*x/a*	*y/b*	*z/c*	*Occ.*	U_{eq} or U_{iso} (Å^2)
Na@Si_{28} on-center model, a = 14.7097(2) Å						
Na1	16*c*	0	0	0	0.859(4)	0.0145(9)
Na2	8*b*	3/8	3/8	3/8	1	0.115(2)
Si1	8*a*	1/8	1/8	1/8	1	0.0049
Si2	32*e*	0.21829(5)	*x*	*x*	1	0.0068
Si3	96*g*	0.06715(3)	*x*	0.37168(6)	1	0.0070
Na@Si_{28} off-center model, a = 14.7098(2) Å						
Na1	16*c*	0	0	0	0.859(4)	0.0146(9)
Na2	32*e*	0.390(1)	*x*	*x*	0.250(2)	0.063(9)
Si1	8*a*	1/8	1/8	1/8	1	0.0049
Si2	32*e*	0.21829(5)	*x*	*x*	1	0.0068
Si3	96*g*	0.06716(3)	*x*	0.37167(6)	1	0.0070

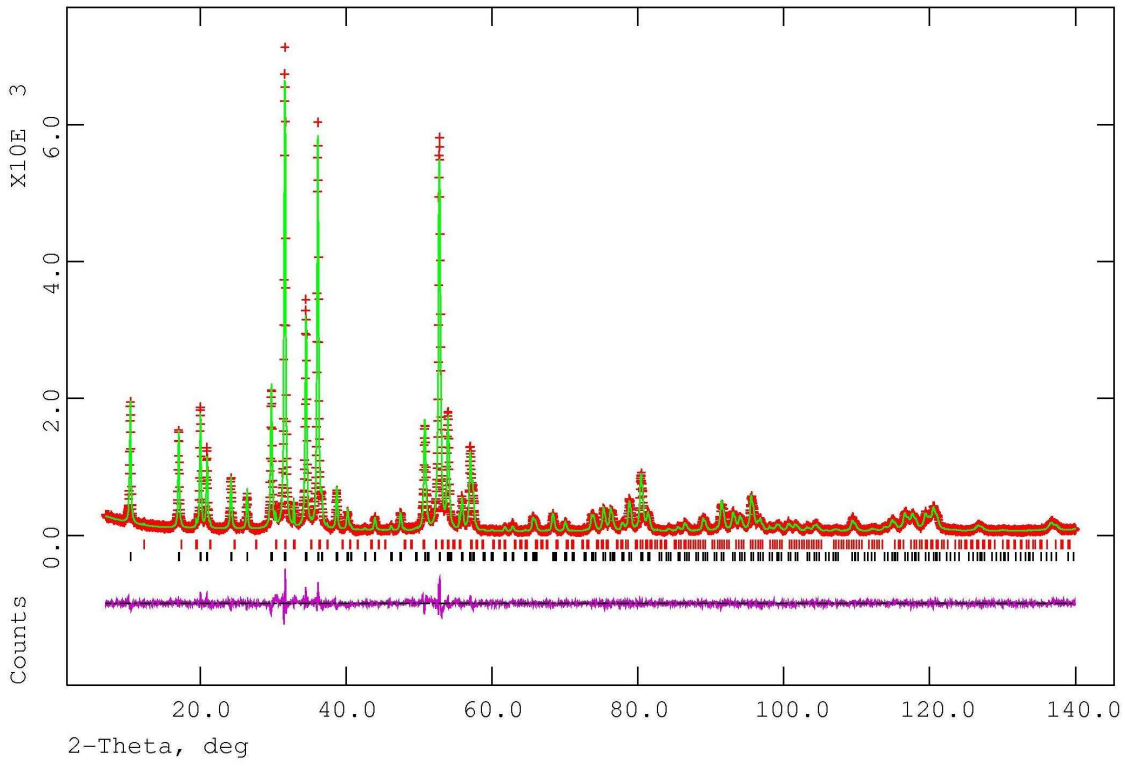

Figure S2. Observed (red crosses), calculated (green curve), and difference (purple curve) powder X-ray diffraction patterns for $Na_{21.8}Si_{136}$ (on-center model). Black tick marks (lower) indicate reflection positions for the $Na_{21.8}Si_{136}$ phase, red tick marks (upper) indicate reflection positions for the Na_8Si_{46} impurity phase (est. wt% ~ 3%). Refinement residuals: $\chi^2 = 1.7$; $wR_p = 0.087$, $R_p = 0.065$, $R(F^2) = 0.024$.

Table S3. Refined atomic positions, occupancies, and equivalent (U_{eq}) or isotropic (U_{iso}) atomic displacement parameters for $Na_{17.0}Si_{136}$. Where U_{eq} are given, anisotropic displacement parameters and estimated standard deviations can be found in the CIF.

Atom	Site	*x/a*	*y/b*	*z/c*	*Occ.*	U_{eq} or U_{iso} (Å^2)
Na@Si_{28} on-center model, a = 14.6847(2) Å						
Na1	16*c*	0	0	0	0.561(3)	0.012(1)
Na2	8*b*	3/8	3/8	3/8	1	0.117(2)
Si1	8*a*	1/8	1/8	1/8	1	0.0051(5)
Si2	32*e*	0.21791(5)	*x*	*x*	1	0.0063
Si3	96*g*	0.06715(3)	*x*	0.37147(5)	1	0.0069
Na@Si_{28} off-center model, a = 14.6848(2) Å						
Na1	16*c*	0	0	0	0.561(4)	0.012(1)
Na2	32*e*	0.3912(8)	*x*	*x*	0.250(2)	0.056(7)
Si1	8*a*	1/8	1/8	1/8	1	0.0050(5)
Si2	32*e*	0.21790(5)	*x*	*x*	1	0.0064
Si3	96*g*	0.06716(3)	*x*	0.37148(6)	1	0.0068

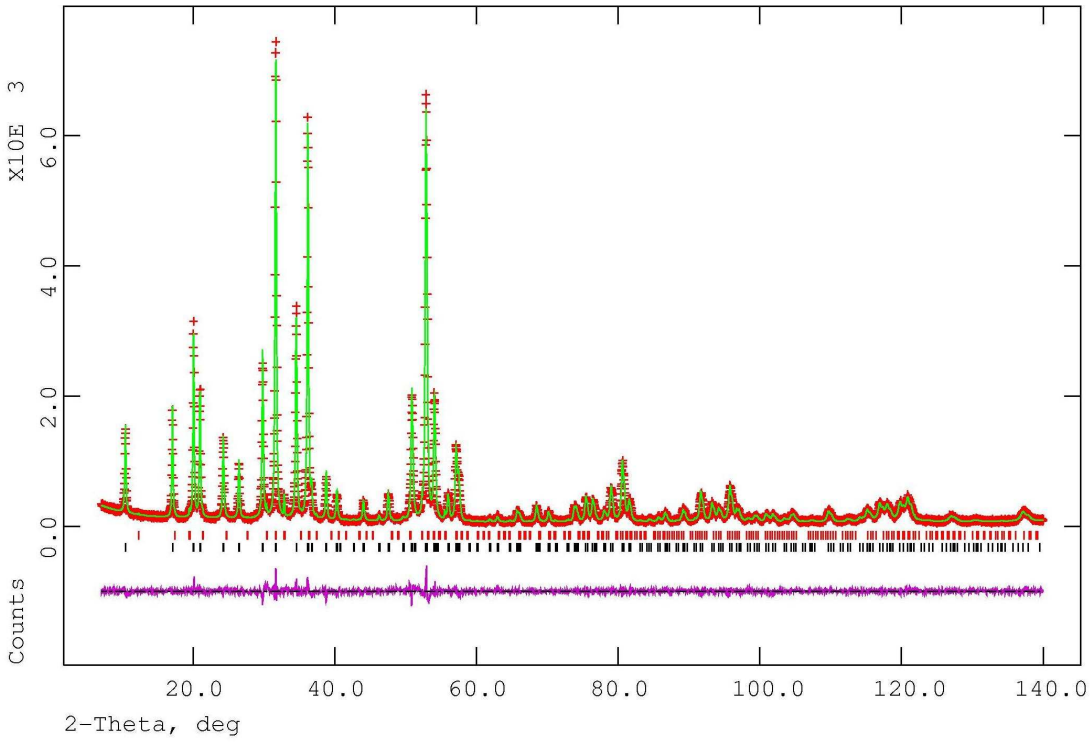

Figure S3. Observed (red crosses), calculated (green curve), and difference (purple curve) powder X-ray diffraction patterns for $Na_{17.0}Si_{136}$ (on-center model). Black tick marks (lower) indicate reflection positions for the $Na_{17.0}Si_{136}$ phase, red tick marks (upper) indicate reflection positions for the Na_8Si_{46} impurity phase (est. wt% ~ 3%). Refinement residuals: $\chi^2 = 1.6$; $wR_p = 0.081$, $R_p = 0.061$, $R(F^2) = 0.023$.

Table S4. Refined atomic positions, occupancies, and equivalent (U_{eq}) or isotropic (U_{iso}) atomic displacement parameters for $Na_{13.8}Si_{136}$. Where U_{eq} are given, anisotropic displacement parameters and estimated standard deviations can be found in the CIF.

Atom	Site	*x/a*	*y/b*	*z/c*	*Occ.*	U_{eq} or U_{iso} (Å^2)
Na@Si_{28} on-center model, a = 14.6685(2) Å						
Na1	16*c*	0	0	0	0.364(4)	0.014(2)
Na2	8*b*	3/8	3/8	3/8	1	0.122(2)
Si1	8*a*	1/8	1/8	1/8	1	0.0090(7)
Si2	32*e*	0.21768(6)	*x*	*x*	1	0.0091
Si3	96*g*	0.06708(4)	*x*	0.37128(6)	1	0.0089
Na@Si_{28} off-center model, a = 14.6685(2) Å						
Na1	16*c*	0	0	0	0.362(4)	0.0132(2)
Na2	32*e*	0.3918(8)	*x*	*x*	0.245(2)	0.050(8)
Si1	8*a*	1/8	1/8	1/8	1	0.0089(7)
Si2	32*e*	0.21768(6)	*x*	*x*	1	0.0091
Si3	96*g*	0.06709(4)	*x*	0.37130(6)	1	0.0088

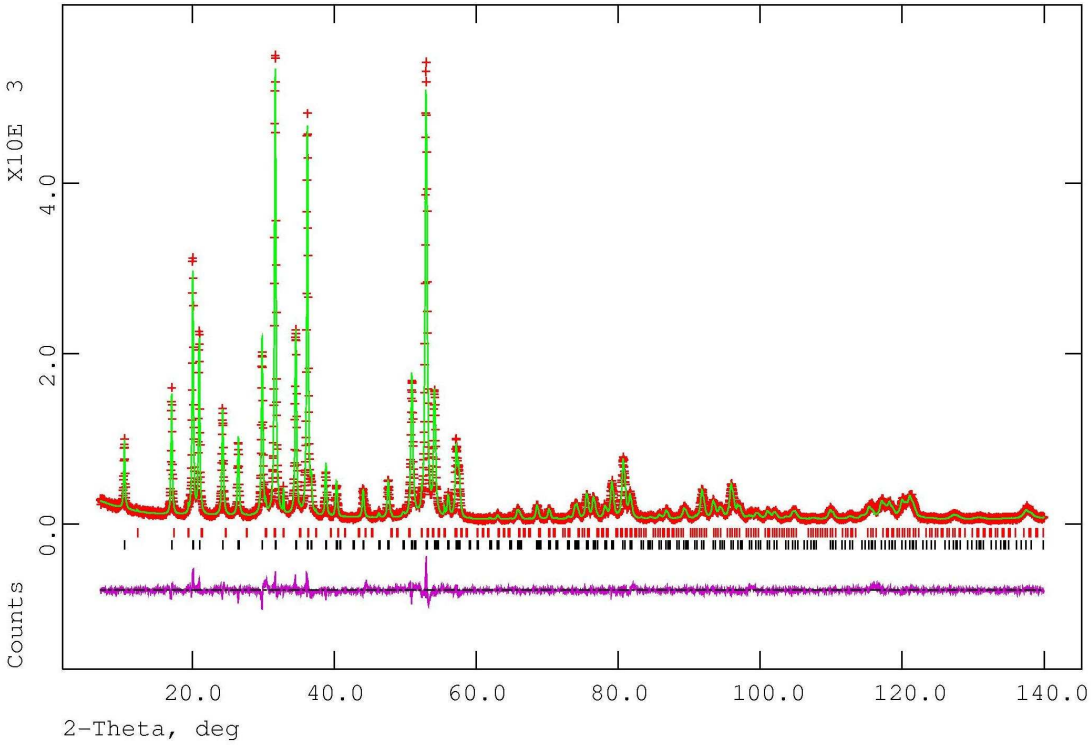

Figure S4. Observed (red crosses), calculated (green curve), and difference (purple curve) powder X-ray diffraction patterns for $Na_{13.8}Si_{136}$ (on-center model). Black tick marks (lower) indicate reflection positions for the $Na_{13.8}Si_{136}$ phase, red tick marks (upper) indicate reflection positions for the Na_8Si_{46} impurity phase (est. wt% ~ 3%). Refinement residuals: $\chi^2 = 1.9$; $wR_p = 0.095$, $R_p = 0.070$, $R(F^2) = 0.031$.

Table S5. Refined atomic positions, occupancies, and equivalent (U_{eq}) or isotropic (U_{iso}) atomic displacement parameters for $Na_{12.5}Si_{136}$. Where U_{eq} are given, anisotropic displacement parameters and estimated standard deviations can be found in the CIF file.

Atom	Site	*x/a*	*y/b*	*z/c*	*Occ.*	U_{eq} or U_{iso} (Å^2)
Na@Si_{28} on-center model, a = 14.6611(2) Å						
Na1	16*c*	0	0	0	0.284(3)	0.0104
Na2	8*b*	3/8	3/8	3/8	1	0.128(2)
Si1	8*a*	1/8	1/8	1/8	1	0.0053(5)
Si2	32*e*	0.21766(5)	*x*	*x*	1	0.0073
Si3	96*g*	0.06706(3)	*x*	0.37139(6)	1	0.0075
Na@Si_{28} off-center model, a = 14.6611(2) Å						
Na1	16*c*	0	0	0	0.282(3)	0.0095
Na2	32*e*	0.3910(9)	*x*	*x*	0.245(2)	0.063(8)
Si1	8*a*	1/8	1/8	1/8	1	0.0052(5)
Si2	32*e*	0.21766(5)	*x*	*x*	1	0.0073
Si3	96*g*	0.06707(3)	*x*	0.37141(6)	1	0.0074

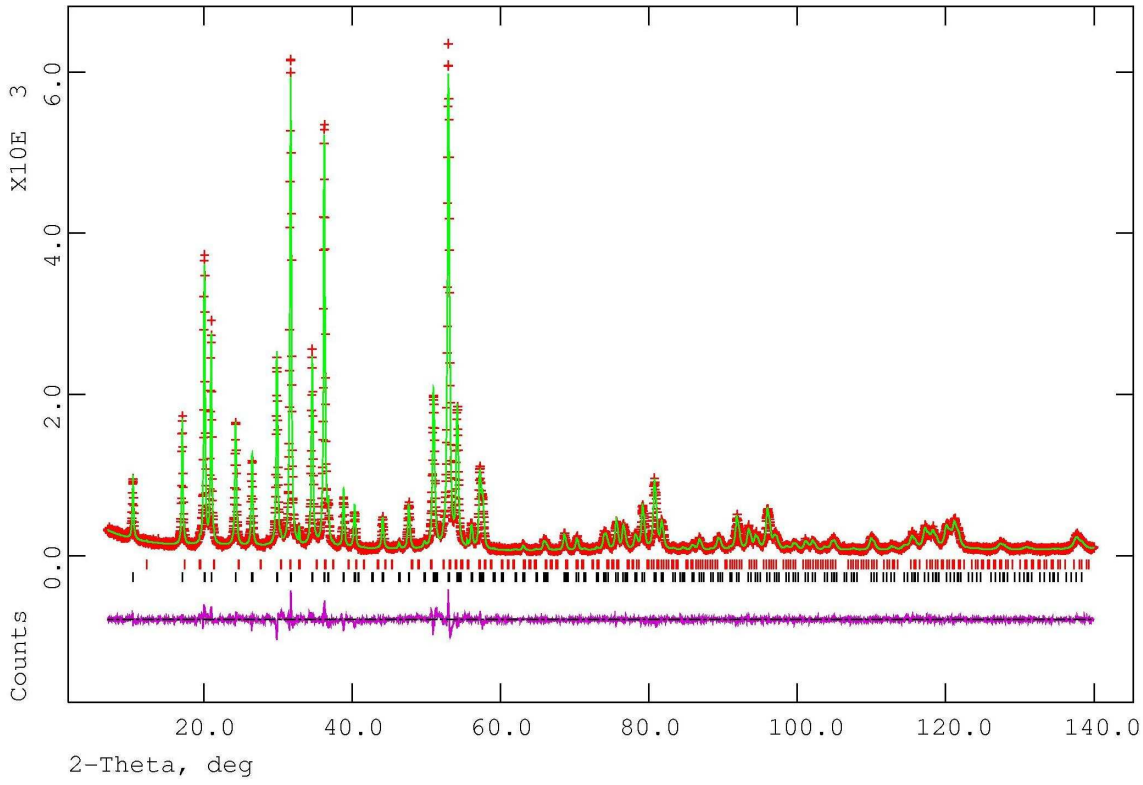

Figure S5. Observed (red crosses), calculated (green curve), and difference (purple curve) powder X-ray diffraction patterns for $Na_{12.5}Si_{136}$ (on-center model). Black tick marks (lower) indicate reflection positions for the $Na_{12.5}Si_{136}$ phase, red tick marks (upper) indicate reflection positions for the Na_8Si_{46} impurity phase (est. wt% ~ 2%). Refinement residuals: $\chi^2 = 1.6$; $wR_p = 0.081$, $R_p = 0.061$, $R(F^2) = 0.024$.

Table S6. Refined atomic positions, occupancies, and equivalent (U_{eq}) or isotropic (U_{iso}) atomic displacement parameters for $Na_{10.9}Si_{136}$. Where U_{eq} are given, anisotropic displacement parameters and estimated standard deviations can be found in the CIF file.

Atom	Site	*x/a*	*y/b*	*z/c*	*Occ.*	U_{eq} or U_{iso} (Å^2)
Na@Si_{28} on-center model, a = 14.6550(2) Å						
Na1	16*c*	0	0	0	0.197(4)	0.0083
Na2	8*b*	3/8	3/8	3/8	0.973(8)	0.122(3)
Si1	8*a*	1/8	1/8	1/8	1	0.0061(6)
Si2	32*e*	0.21753(5)	*x*	*x*	1	0.0072
Si3	96*g*	0.06708(3)	*x*	0.37116(6)	1	0.0072
Na@Si_{28} off-center model, a = 14.6550(2) Å						
Na1	16*c*	0	0	0	0.196(4)	0.0081
Na2	32*e*	0.3912(9)	*x*	*x*	0.242(2)	0.060(8)
Si1	8*a*	1/8	1/8	1/8	1	0.0060(6)
Si2	32*e*	0.21752(5)	*x*	*x*	1	0.0073
Si3	96*g*	0.06709(3)	*x*	0.37117(6)	1	0.0071

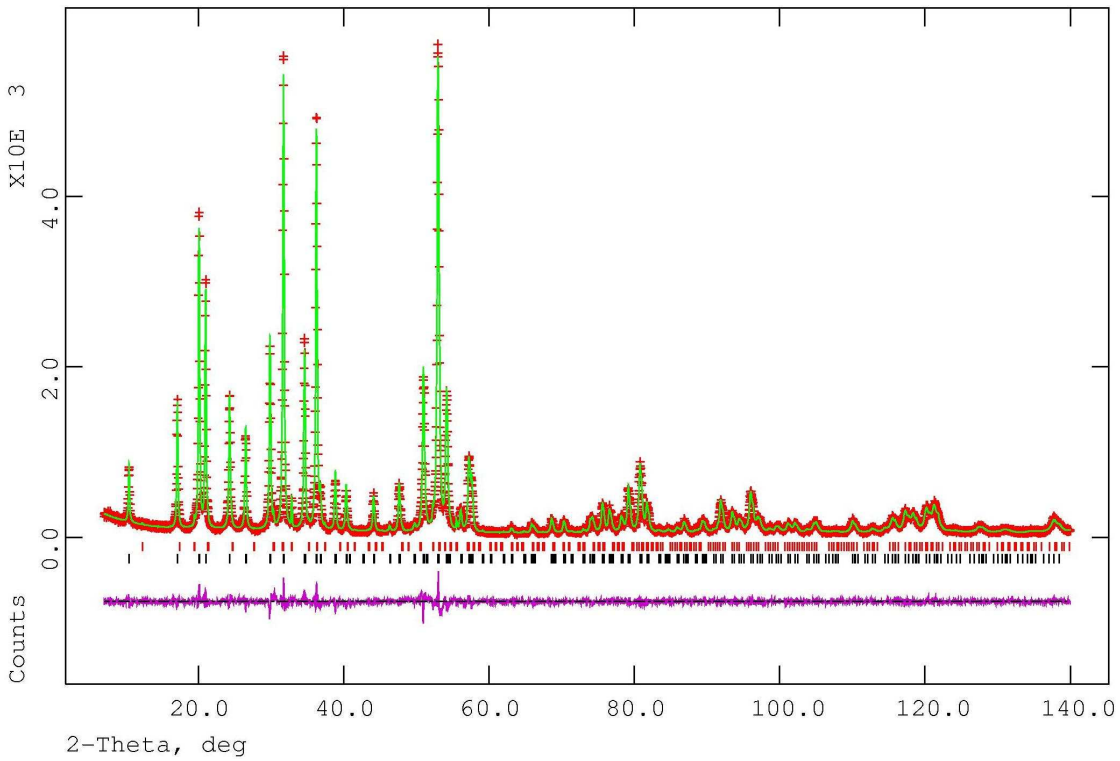

Figure S6. Observed (red crosses), calculated (green curve), and difference (purple curve) powder X-ray diffraction patterns for $Na_{10.9}Si_{136}$ (on-center model). Black tick marks (lower) indicate reflection positions for the $Na_{10.9}Si_{136}$ phase, red tick marks (upper) indicate reflection positions for the Na_8Si_{46} impurity phase (est. wt% ~ 3%). Refinement residuals: $\chi^2 = 1.7$; $wR_p = 0.086$, $R_p = 0.064$, $R(F^2) = 0.024$.

Table S7. Refined atomic positions, occupancies, and equivalent (U_{eq}) or isotropic (U_{iso}) atomic displacement parameters for $Na_{9.0}Si_{136}$. Where U_{eq} are given, anisotropic displacement parameters and estimated standard deviations can be found in the CIF file.

Atom	Site	*x/a*	*y/b*	*z/c*	*Occ.*	U_{eq} or U_{iso} (Å^2)
Na@Si_{28} on-center model, a = 14.6454(2) Å						
Na1	16*c*	0	0	0	0.077(3)	0.012
Na2	8*b*	3/8	3/8	3/8	0.969(8)	0.132(4)
Si1	8*a*	1/8	1/8	1/8	1	0.0064(6)
Si2	32*e*	0.21746(5)	*x*	*x*	1	0.0076
Si3	96*g*	0.06704(3)	*x*	0.37102(6)	1	0.0075
Na@Si_{28} off-center model, a = 14.6454(2) Å						
Na1	16*c*	0	0	0	0.076(3)	0.012
Na2	32*e*	0.3923(8)	*x*	*x*	0.240(2)	0.061(8)
Si1	8*a*	1/8	1/8	1/8	1	0.0064(6)
Si2	32*e*	0.21745(5)	*x*	*x*	1	0.0077
Si3	96*g*	0.06705(3)	*x*	0.37103(6)	1	0.0074

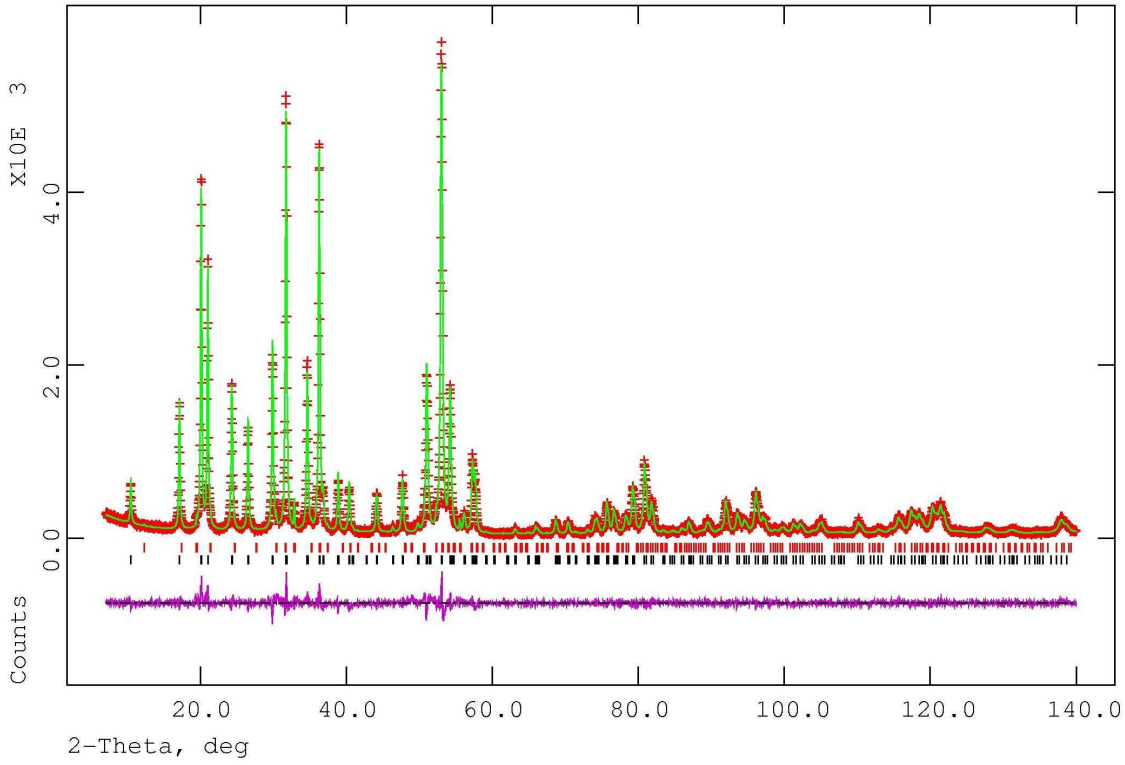

Figure S7. Observed (red crosses), calculated (green curve), and difference (purple curve) powder X-ray diffraction patterns for $Na_{9.0}Si_{136}$ (on-center model). Black tick marks (lower) indicate reflection positions for the $Na_{9.0}Si_{136}$ phase, red tick marks (upper) indicate reflection positions for the Na_8Si_{46} impurity phase (est. wt% ~ 3%). Refinement residuals: $\chi^2 = 1.8$; $wR_p = 0.089$, $R_p = 0.067$, $R(F^2) = 0.026$.

Table S8. Refined atomic positions, occupancies, and equivalent (U_{eq}) or isotropic (U_{iso}) atomic displacement parameters for $Na_{8.0}Si_{136}$. Where U_{eq} are given, anisotropic displacement parameters and estimated standard deviations can be found in the CIF file.

Atom	Site	*x/a*	*y/b*	*z/c*	*Occ.*	U_{eq} or U_{iso} (Å^2)
Na@Si_{28} on-center model, a = 14.6429(2) Å						
Na1	16*c*	0	0	0	0.031(3)	0.012
Na2	8*b*	3/8	3/8	3/8	0.941(8)	0.137(4)
Si1	8*a*	1/8	1/8	1/8	1	0.0083
Si2	32*e*	0.21743(5)	*x*	*x*	1	0.0085
Si3	96*g*	0.06705(3)	*x*	0.37092(6)	1	0.0083
Na@Si_{28} off-center model, a = 14.6429(2) Å						
Na1	16*c*	0	0	0	0.030(3)	0.012
Na2	32*e*	0.3926(8)	*x*	*x*	0.233(2)	0.062(8)
Si1	8*a*	1/8	1/8	1/8	1	0.0083
Si2	32*e*	0.21742(5)	*x*	*x*	1	0.0086
Si3	96*g*	0.06707(3)	*x*	0.37093(6)	1	0.0081

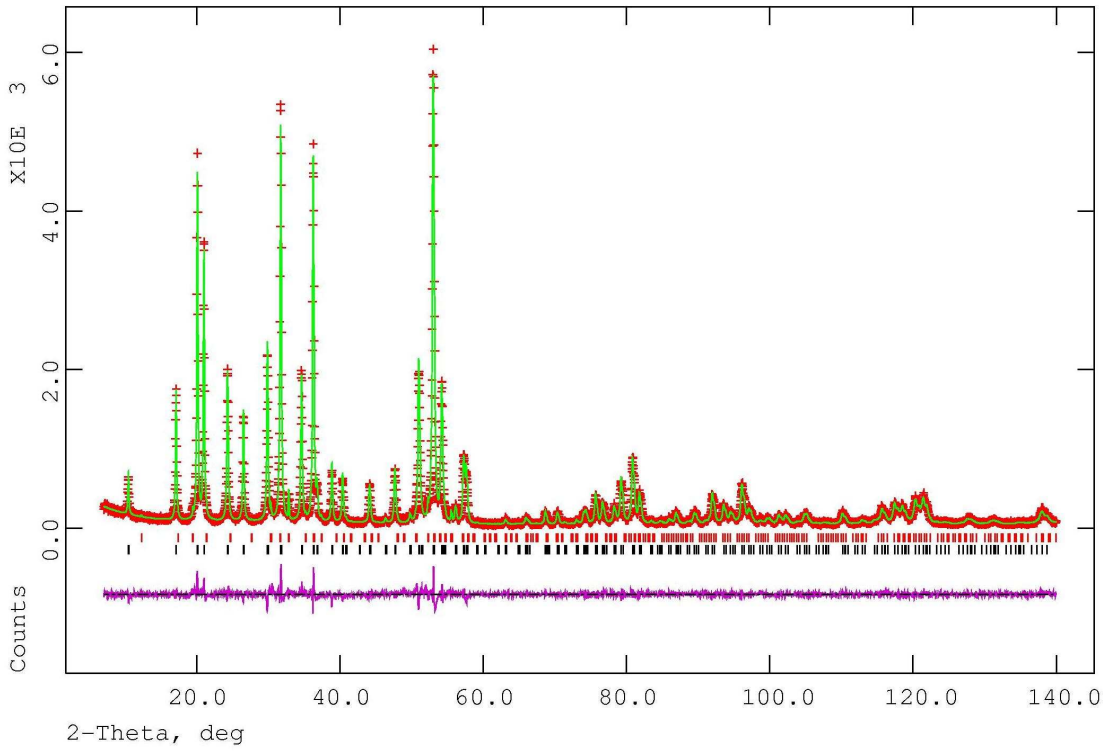

Figure S8. Observed (red crosses), calculated (green curve), and difference (purple curve) powder X-ray diffraction patterns for $Na_{8.0}Si_{136}$ (on-center model). Black tick marks (lower) indicate reflection positions for the $Na_{8.0}Si_{136}$ phase, red tick marks (upper) indicate reflection positions for the Na_8Si_{46} impurity phase (est. wt% ~ 3%). Refinement residuals: χ^2 = 1.8; wR_p = 0.089, R_p = 0.067, $R(F^2)$ = 0.026.

Table S9. Refined atomic positions, occupancies, and equivalent (U_{eq}) or isotropic (U_{iso}) atomic displacement parameters for $Na_{6.8}Si_{136}$. Where U_{eq} are given, anisotropic displacement parameters and estimated standard deviations can be found in the CIF file.

Atom	Site	*x/a*	*y/b*	*z/c*	*Occ.*	U_{eq} or U_{iso} (Å^2)
Na@Si_{28} on-center model, a = 14.6418(2) Å						
Na1	16*c*	0	0	0	0.010(3)	0.012
Na2	8*b*	3/8	3/8	3/8	0.832(8)	0.143(4)
Si1	8*a*	1/8	1/8	1/8	1	0.0063(6)
Si2	32*e*	0.21738(5)	*x*	*x*	1	0.0076
Si3	96*g*	0.06703(3)	*x*	0.37102(6)	1	0.0078
Na@Si_{28} off-center model, a = 14.6418(2) Å						
Na1	16*c*	0	0	0	0.009(3)	0.012
Na2	32*e*	0.3929(9)	*x*	*x*	0.206(2)	0.066(9)
Si1	8*a*	1/8	1/8	1/8	1	0.0062(6)
Si2	32*e*	0.21737(5)	*x*	*x*	1	0.0077
Si3	96*g*	0.06705(3)	*x*	0.37103(6)	1	0.0077

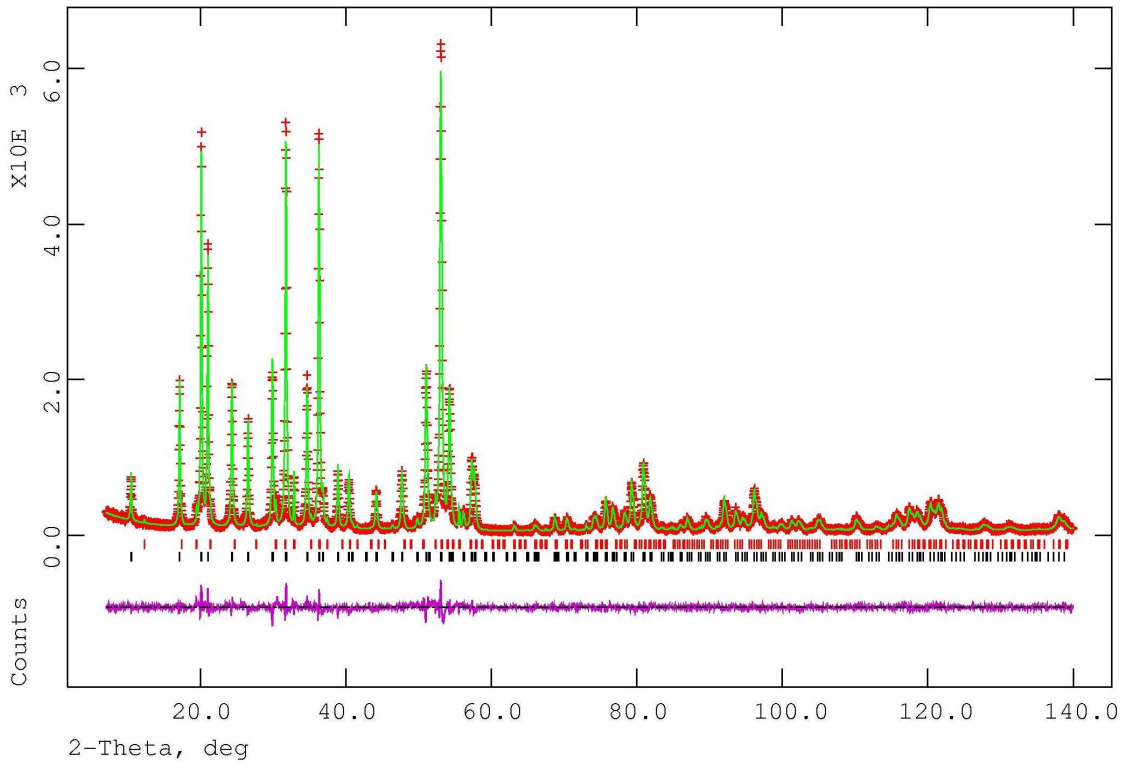

Figure S9. Observed (red crosses), calculated (green curve), and difference (purple curve) powder X-ray diffraction patterns for $Na_{6.8}Si_{136}$ (on-center model). Black tick marks (lower) indicate reflection positions for the $Na_{6.8}Si_{136}$ phase, red tick marks (upper) indicate reflection positions for the Na_8Si_{46} impurity phase (est. wt% ~ 4%). Refinement residuals: $\chi^2 = 1.9$; $wR_p = 0.089$, $R_p = 0.067$, $R(F^2) = 0.027$.

Table S10. Refined atomic positions, occupancies, and equivalent (U_{eq}) or isotropic (U_{iso}) atomic displacement parameters for $Na_{5.6}Si_{136}$. Where U_{eq} are given, anisotropic displacement parameters and estimated standard deviations can be found in the CIF file.

Atom	Site	*x/a*	*y/b*	*z/c*	*Occ.*	U_{eq} or U_{iso} (Å^2)
Na@Si_{28} on-center model, a = 14.6438(2) Å						
Na1	16*c*	0	0	0	0	n/a
Na2	8*b*	3/8	3/8	3/8	0.702(8)	0.141(5)
Si1	8*a*	1/8	1/8	1/8	1	0.0078(6)
Si2	32*e*	0.21731(5)	*x*	*x*	1	0.0087
Si3	96*g*	0.06710(3)	*x*	0.37088(6)	1	0.0081
Na@Si_{28} off-center model, a = 14.6438(2) Å						
Na1	16*c*	0	0	0	0	n/a
Na2	32*e*	0.3936(8)	*x*	*x*	0.174(2)	0.057(9)
Si1	8*a*	1/8	1/8	1/8	1	0.0078(6)
Si2	32*e*	0.21730(5)	*x*	*x*	1	0.0088
Si3	96*g*	0.06711(3)	*x*	0.37089(6)	1	0.0080

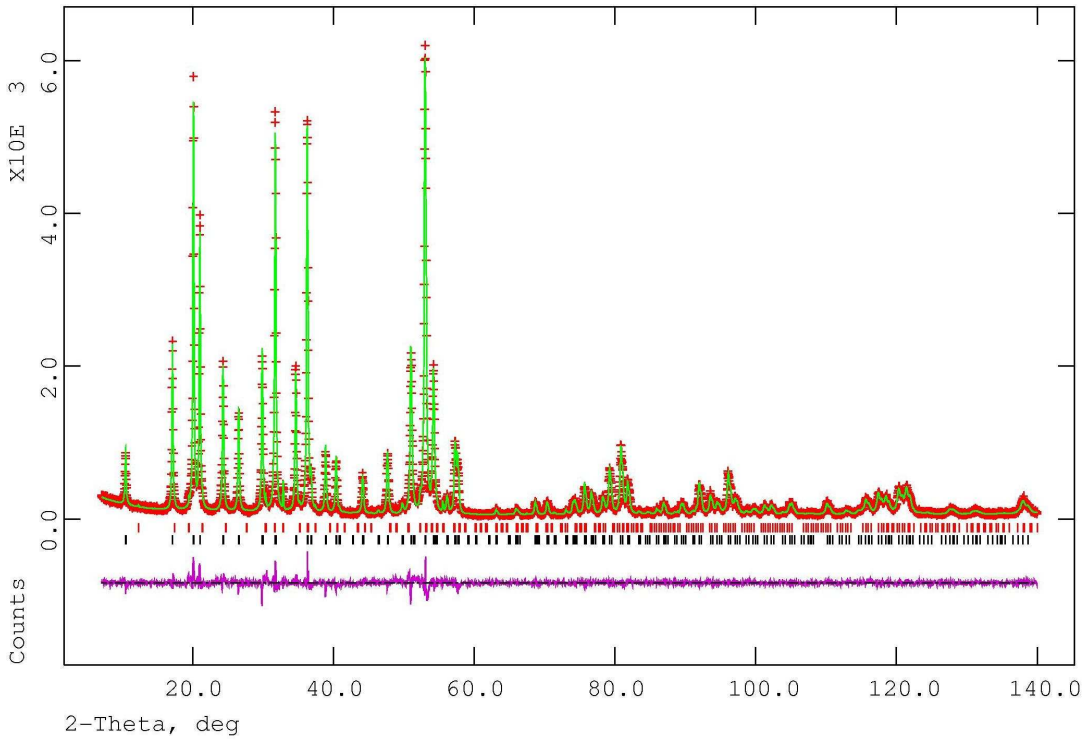

Figure S10. Observed (red crosses), calculated (green curve), and difference (purple curve) powder X-ray diffraction patterns for $Na_{5.6}Si_{136}$ (on-center model). Black tick marks (lower) indicate reflection positions for the $Na_{5.6}Si_{136}$ phase, red tick marks (upper) indicate reflection positions for the Na_8Si_{46} impurity phase (est. wt% ~ 3%). Refinement residuals: $\chi^2 = 1.9$; $wR_p = 0.090$, $R_p = 0.066$, $R(F^2) = 0.026$.

Table S11. Refined atomic positions, occupancies, and equivalent (U_{eq}) or isotropic (U_{iso}) atomic displacement parameters for $Na_{3.2}Si_{136}$. Where U_{eq} are given, anisotropic displacement parameters and estimated standard deviations can be found in the CIF file.

Atom	Site	*x/a*	*y/b*	*z/c*	*Occ.*	U_{eq} or U_{iso} (Å^2)
Na@Si_{28} on-center model, a = 14.6461(3) Å						
Na1	16*c*	0	0	0	0	n/a
Na2	8*b*	3/8	3/8	3/8	0.405(9)	0.119(9)
Si1	8*a*	1/8	1/8	1/8	1	0.0052(7)
Si2	32*e*	0.21723(6)	*x*	*x*	1	0.0074
Si3	96*g*	0.06720(4)	*x*	0.37074(7)	1	0.0076
Na@Si_{28} off-center model, a = 14.6461(3) Å						
Na1	16*c*	0	0	0	0	n/a
Na2	32*e*	0.395(1)	*x*	*x*	0.102(2)	0.026(1)
Si1	8*a*	1/8	1/8	1/8	1	0.0051(7)
Si2	32*e*	0.21722(6)	*x*	*x*	1	0.0075
Si3	96*g*	0.06721(4)	*x*	0.37074(7)	1	0.0075

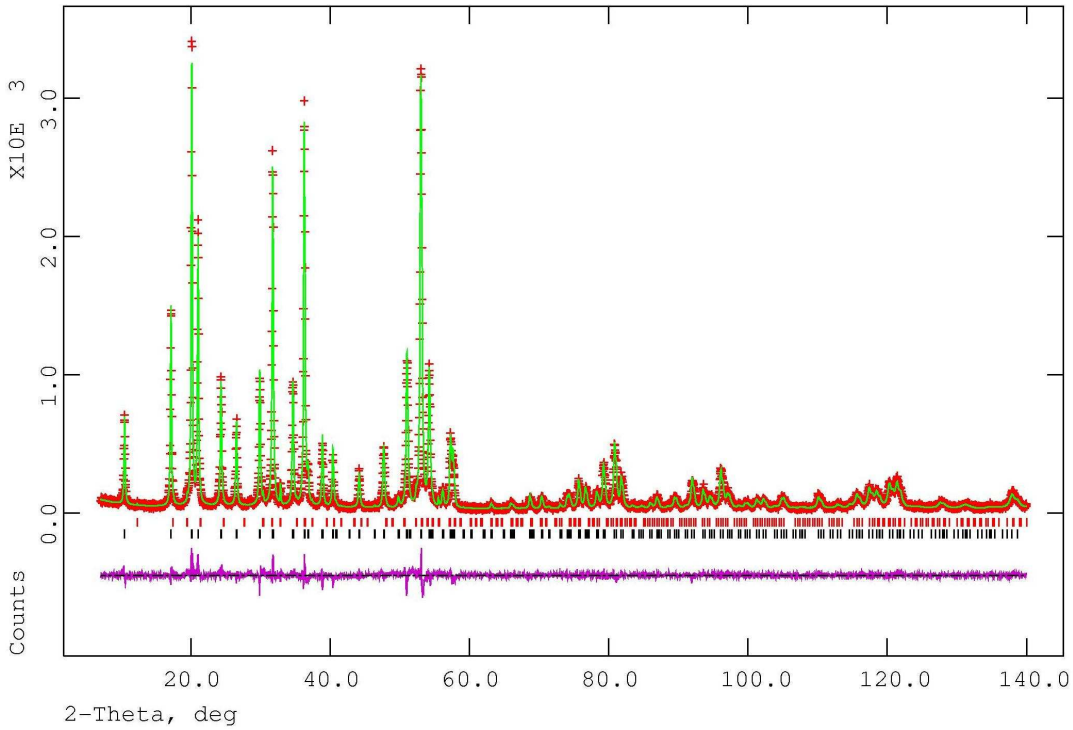

Figure S11. Observed (red crosses), calculated (green curve), and difference (purple curve) powder X-ray diffraction patterns for $Na_{3.2}Si_{136}$ (on-center model). Black tick marks (lower) indicate reflection positions for the $Na_{3.2}Si_{136}$ phase, red tick marks (upper) indicate reflection positions for the Na_8Si_{46} impurity phase (est. wt% ~ 2%). Refinement residuals: $\chi^2 = 1.5$; $wR_p = 0.107$, $R_p = 0.079$, $R(F^2) = 0.034$.

Table S12. Refined atomic positions, occupancies, and equivalent (U_{eq}) or isotropic (U_{iso}) atomic displacement parameters for $Na_{1.0}Si_{136}$. Where U_{eq} are given, anisotropic displacement parameters and estimated standard deviations can be found in the CIF file.

Atom	Site	*x/a*	*y/b*	*z/c*	*Occ.*	U_{eq} or U_{iso} (Å^2)
Na@Si_{28} on-center model, a = 14.6477(2) Å						
Na1	16*c*	0	0	0	0	n/a
Na2	8*b*	3/8	3/8	3/8	0.128(5)	0.12
Si1	8*a*	1/8	1/8	1/8	1	0.0061(6)
Si2	32*e*	0.21724(5)	*x*	*x*	1	0.0069
Si3	96*g*	0.06725(3)	*x*	0.37100(6)	1	0.0067
Na@Si_{28} off-center model, a = 14.6478(2) Å						
Na1	16*c*	0	0	0	0	n/a
Na2	32*e*	0.4059(17)	*x*	*x*	0.041(2)	0.06
Si1	8*a*	1/8	1/8	1/8	1	0.0065(6)
Si2	32*e*	0.21722(5)	*x*	*x*	1	0.0073
Si3	96*g*	0.06728(3)	*x*	0.37098(6)	1	0.0067

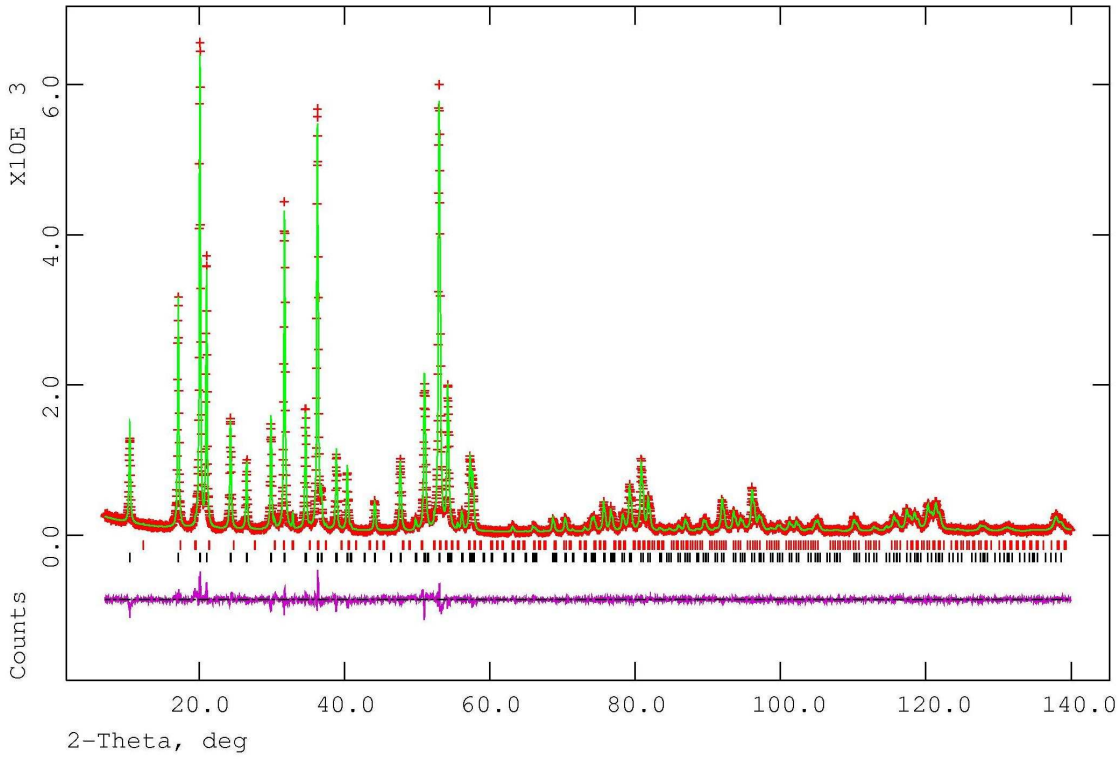

Figure S12. Observed (red crosses), calculated (green curve), and difference (purple curve) powder X-ray diffraction patterns for $Na_{1.0}Si_{136}$ (on-center model). Black tick marks (lower) indicate reflection positions for the $Na_{1.0}Si_{136}$ phase, red tick marks (upper) indicate reflection positions for the Na_8Si_{46} impurity phase (est. wt% ~ 2%). Refinement residuals: $\chi^2 = 1.9$; $wR_p = 0.093$, $R_p = 0.068$, $R(F^2) = 0.029$.

S3. Supplementary References

[S1] Gryko, J. U.S. Patent No. 6,423,286.

[S2] Larson, A.C.; Von Dreele, R.B. General Structure Analysis System (GSAS), Los Alamos National Laboratory Report LAUR 86-748, 2004.

[S3] Toby, B.H. *J. Appl. Cryst.* **2001**, *34*, 210.

[S4] 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.

[S5] Beekman, M.; Sebastian, C.P.; Grin, Yu.; Nolas, G.S. *J. Electr. Mater.* **2009**, 38, 1136.

[S6] Beekman, M.; Schnelle, W.; Borrmann, H.; Baitinger, M.; Grin, Yu.; Nolas, G.S.; *Phys. Rev. Lett.* **2010**, *104*, 018301.

[S7] Blöchl, P. E.; *Phys. Rev. B* **1994**, 50, 17953.

[S8] Kresse, G. and Furthmüller J.; *Comput. Mater. Sci*. **1996**, *6,* 15; Kresse, G. and Joubert D.; *Phys. Rev. B* **1999**, *59,* 1758.

[S9] Ceperley, D. M. and Alder, B J; *Phys. Rev. Lett.* **1980,** *45,* 566.

[S10] Perdew, J. and Zunger, A.; *Phys. Rev. B* **1981**, 23, 5048.

[S11] Monkhorst, H. J. and Pack, J. D.; *Phys. Rev. B* **1976**, 13, 5188.