Inorganic Chemistry

Sn$_6$SiO$_8$, a Tin(II) Silicate with a Zinc Blende Related Structure and High Thermal Stability

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ABSTRACT: The crystal structure of a novel cubic tin(II) silicate, Sn$_6$SiO$_8$ (space group F43m, a = 10.40708(2) Å, and Z = 4), synthesized by microwave-assisted hydrothermal synthesis has been solved by Rietveld refinement of the powder X-ray diffraction (PXRD) data. The structure, analogous to zinc blende, comprises a face-centered-cubic array of [Sn$_6$O$_8$]$_{4^-}$ clusters, with Si$_4^+$ occupying half of the tetrahedral holes. The tin(II) silicate has been further characterized by variable-temperature PXRD, demonstrating stability of the structure and resistance to Sn$^{II}$ oxidation up to ~600 °C, when the compound begins to thermally decompose.

In general, tin(II) compounds are relatively rare in the solid state. The only fully characterized tin(II) silicate has the chemical composition Sn$_6$SiO$_3$ and adopts a hexagonal crystal structure with space group P6$_2$mc, a = 7.3742(4) Å, and c = 11.9598(10) Å. The phase was not synthesized but rather discovered as one of several corrosion products of pewter that was believed to have spent more than a century submerged in an aqueous environment. The structure comprises [Sn$_6$O$_8$]$_{4^-}$ clusters with two different oxygen environments; four O ions are bonded solely within the cluster, whereas the other four O ions in each cluster are bonded to Si$^{IV}$ ions, forming the vertices of orthosilicate tetrahedra. The oxide ions that bond to Si$^{IV}$ are additionally bonded to three Sn$^{II}$ ions on the face of a cluster. Each Sn$^{II}$ ion is four-coordinate with two short bonds to O atoms in the cluster (2.06–2.08 Å) and two longer bonds to silicate O atoms (2.44–2.50 Å).

Another tin(II) silicate was observed previously, and it had a powder X-ray diffraction (PXRD) pattern that was indexed as cubic and can be found in the ICDD database as pattern PDF 00-020-1295. The phase, first reported in a study on SnO–SiO$_2$ glass systems, was believed to have the composition Sn$_6$SiO$_3$ based on electron microprobe analysis. Further characterization of the compound and elucidation of the crystal structure have not been reported in previous studies where the phase has been synthesized.

The only reported tin(II) oxyhydroxide, Sn$_6$O$_4$(OH)$_4$, is formed by the alkaline hydrolysis of Sn$^{II}$ salts. The structure comprises discrete Sn$_6$O$_4$(OH)$_4$ clusters with hydrogen bonding between the hydroxide and oxide ions on neighboring clusters. The six Sn$^{II}$ atoms of each cluster form an octahedral array with Sn–Sn distances between 3.52 and 3.54 Å; each oxide or hydroxide moiety is coordinated to three Sn atoms that form a face of the Sn$_6$ octahedron. The material is thermally unstable, and it dehydrates upon heating to form α-SnO at temperatures above 100 °C. Clusters containing hexanuclear octahedral arrays of Sn$^{II}$, such as those in Sn$_6$O$_4$(OH)$_4$, are also observed in organometallic tin(II) compounds with the general formula Sn$_6$O$_4$(OR)$_4$ where R corresponds to methyl, ethyl, or neopentyl moieties. Sn$_6$O$_4$(OMe)$_4$ and Sn$_6$O$_4$(OEt)$_4$ adopt monoclinic cells, whereas Sn$_6$O$_4$(ONep)$_4$ is orthorhombic. In the cases of R = Me and Et, the alkoxide and oxide ions bind to the faces of the Sn$_6$ octahedra in a μ$_3$-binding mode in the same manner as hydroxide and oxide in Sn$_6$O$_4$(OH)$_4$. In contrast, neopentoxide ions coordinate in a μ$_4$-binding mode to just two Sn atoms of each face owing to steric effects. In these compounds, the clusters are neutral and interact with one another by intermolecular forces. Sn$_6$O$_4$(OR)$_4$ clusters bearing organosilicon substituents (R = SiMe$_3$) have been synthesized in solution; however, these clusters are air-sensitive, and well-diffracting pure crystals have not been isolated. However, diffraction data from a cocrystal, 2Sn$_6$O$_4$(OSiMe$_3$)$_4$·Sn(OSiMe$_3$)$_4$·4THF, were sufficient to confirm the molecular connectivity but not any details of the molecular geometric parameters.

The tin(II) silicate prepared in this work, cubic Sn$_6$SiO$_8$, was prepared by dissolving NaOH (10 mmol) in 30 mL of deionized water, followed by the addition of fumed SiO$_2$ (1.67 mmol). Sn$_2$(C$_2$O$_4$)$_2$ (10 mmol) was added to the silicate solution with stirring, and the resulting off-white gel was homogenized for 30 min at room temperature before transfer to a Teflon-lined CEM EasyPrep vessel and heating in a CEM Mars 6 microwave oven at 160 °C for 30 min (not including 20 min of ramping time) at a microwave power of 600 W. The orange product (0.6 g) was recovered by vacuum filtration, washed with deionized water, and dried for 24 h at 60 °C. It has the same PXRD pattern as that of the material previously prepared in this work, whereas Sn$_6$O$_4$(OH)$_4$ has a monoclinic cell, whereas Sn$_6$O$_4$(ONep)$_4$ is orthorhombic. In the cases of R = Me and Et, the alkoxide and oxide ions bind to the faces of the Sn$_6$ octahedra in a μ$_3$-binding mode in the same manner as hydroxide and oxide in Sn$_6$O$_4$(OH)$_4$. In contrast, neopentoxide ions coordinate in a μ$_4$-binding mode to just two Sn atoms of each face owing to steric effects. In these compounds, the clusters are neutral and interact with one another by intermolecular forces. Sn$_6$O$_4$(OR)$_4$ clusters bearing organosilicon substituents (R = SiMe$_3$) have been synthesized in solution; however, these clusters are air-sensitive, and well-diffracting pure crystals have not been isolated. However, diffraction data from a cocrystal, 2Sn$_6$O$_4$(OSiMe$_3$)$_4$·Sn(OSiMe$_3$)$_4$·4THF, were sufficient to confirm the molecular connectivity but not any details of the molecular geometric parameters.

The structure of α-Sn$_6$SiO$_8$ has been solved by Rietveld refinement of PXRD data collected on the 111 beamline at the Diamond Light Source. The Rietveld refinement, depicted in Figure 1, was performed for 198 reflections over the 2θ range.
6–90° with the GSAS-EXPGUI software using a shifted Chebyshev background function and a pseudo-Voigt profile function with a Finger−Cox−Jephcoat asymmetry correction. The crystallographic data are presented in Table 1 and bond lengths and bond angles in Table 2.

Table 1. Crystallographic Data for α-Sn6SiO8

| property | value |
|----------|-------|
| source   | Synchrotron |
| chemical formula | Sn6SiO8 |
| fw (g mol⁻¹) | 868.218 |
| temperature | ambient |
| λ (Å) | 0.82628 |
| crys syst | cubic |
| space group | F̅43m (No. 216) |
| a (Å) | 10.40709(2) |
| V (Å³) | 1127.17(1) |
| Z | 4 |
| χ² | 3.12 |
| R_p | 0.0691 |
| R_wp | 0.0886 |

Table 2. Bond Lengths and Bond Angles in α-Sn6SiO8

| bond | distance (Å) | bond | angle (deg) |
|------|--------------|------|-------------|
| Si−O1 | 1.648(4) | O1−Sn−O1 | 141.1(2) |
| Sn−O1 | 2.475(2) | O1−Sn−O2 | 78.30(5) |
| Sn−O2 | 2.115(1) | O2−Sn−O2 | 104.9(2) |
|       |             | O1−Sn−O1 | 109.47(1) |

Systematic absences in the indexed PXRD pattern indicate that the space group belongs to the F̅43m− extinction group. The candidate space groups were further reduced by the criteria that a Wyckoff position with a multiplicity of 4 must be present, given the stoichiometry and multiplicity of the compound, leaving only two space groups, F4̅3m and F23. An initial model for Rietveld refinement was produced by placing atoms on the appropriate Wyckoff positions of the F4̅3m space group. Reasonable values for variable fractional coordinates in the Wyckoff positions were deduced by considering the stoichiometry of the compound, geometry, and expected bond lengths and interatomic distances in the related compounds β-Sn5SiO8 and Sn6O4(OH)4.

The structure of α-Sn6SiO8, depicted in Figure 2, is analogous to zinc blende, comprising a face-centered-cubic array of [Sn6O4(OH)4]4− anions, with Sn⁴⁺ occupying half of the tetrahedral holes. There are two different oxygen environments in the structure: O1 is coordinated to one Si atom and three Sn atoms, whereas each O2 is coordinated to only three Sn atoms. O1 atoms on alternating faces of the Sn6 octahedron form the vertices of discrete orthosilicate groups. Each O atom within a [SiO4] group is part of a different [Sn6O8] cluster, giving rise to a three-dimensional network of [Sn6O8] clusters connected by bonding to Si centers.

The six Sn atoms of each cluster trace a perfect octahedron. The Sn−Sn distance between each Sn atom and the nearest four Sn atoms within the cluster is 3.500(1) Å. A distorted disphenoidal coordination geometry is adopted about each Sn atom, with two shorter equatorial bonds, Sn−O2, to cluster O

Figure 1. Rietveld refinement plot of α-Sn6SiO8. The observed data points are shown as crosses, the calculated pattern is shown as a solid red line, the difference curve below these is shown as a blue line, and the allowed peak positions are shown as vertical tick marks.

Figure 2. (a) Diagram of the crystal structure of α-Sn6SiO8. Blue tetrahedra represent [SiO4] groups, gray octahedra represent the Sn₆ array of [Sn₆O₈] clusters, red spheres correspond to O atoms, and gray spheres correspond to Sn atoms. The unit cell is traced in black. (b) Another projection of the crystal structure showing only polyhedra corresponding to [SiO4] and the Sn₆ arrays, with Sn and O atoms omitted for clarity. (c) Depiction of a [Sn₆O₈] cluster with labeled O atoms. Dashed lines trace the Sn₆ octahedron.
atoms and two longer axial bonds, Sn–O, to O atoms in the silicate groups.

The structures of polymorphs α-Sn₆SiO₈ and β-Sn₆SiO₈ share many similarities including disphenoidal tin coordination environments, the presence of four-coordinate O ions binding the clusters to Si centers, and the remaining O ions bonding in a μ₃-binding mode, solely to Sn ions in the cluster. There are also clear structural differences in the polymorphs: only one tin environment and two oxygen environments are present in α-Sn₆SiO₈ whereas in β-Sn₆SiO₈, there are two tin and four oxygen environments. Consequently, the Sn₆ array in α-Sn₆SiO₈ does not trace a perfect octahedron unlike the Sn₆ array in β-Sn₆SiO₈. As the structure of the cubic polymorph, α-Sn₆SiO₈, is analogous to zinc blende, the hexagonal polymorph, β-Sn₆SiO₈, is a structural analogue to wurtzite. The similarity to wurtzite was not realized in the initial reports.¹

A diffuse-reflectance (DR) UV-vis spectrum has been recorded for α-Sn₆SiO₈ (see the Supporting Information, SI). A Tauc plot of the Kubelka–Munk function (see the SI), derived from the DR UV-vis spectrum,¹³ indicates that the band gap of α-Sn₆SiO₈ is 2.42 eV, in agreement with the orange color of the compound.

The Raman spectrum of α-Sn₆SiO₈ (Figure 3) contains four peaks at 123, 236, 255, and 348 cm⁻¹. Similarly, the Raman spectrum of Sn₆O₄(OH)₄ contains peaks at 132, 229, and 264 cm⁻¹, all with comparable relative intensities and within 10 cm⁻¹ of corresponding peaks observed in the α-Sn₆SiO₈ spectrum.¹⁴ These peaks are likely caused by vibrational modes inherent to the [Sn₆O₈]⁴⁻ clusters common to both materials. The peak at 348 cm⁻¹ has no corresponding peak in the Sn₆O₄(OH)₄ spectrum and, therefore, likely corresponds to a vibrational mode of the orthosilicate moieties in α-Sn₆SiO₈.

Variable-temperature PXRD (Figure 4), recorded on a Bruker D8 diffractometer (reflection mode, Ni-filtered Cu Kα source), reveals that α-Sn₆SiO₈ is stable up to ca. 600 °C in air, at which point it begins to thermally decompose, giving rise to cassiterite, SnO₂, and an amorphous SiO₂ phase. A PXRD pattern recorded at 600 °C matches that recorded at 25 °C with no loss of crystallinity. The only reflection at 600 °C not attributed to α-Sn₆SiO₈ is a broad peak of low intensity at 2θ = 26.7°, corresponding to the cassiterite (110) reflection; however, no other cassiterite reflections are present. The intensities of reflections corresponding to α-Sn₆SiO₈ diminish over the range 630–670 °C, and by contrast, the intensities of cassiterite reflections grow markedly over this range. Ultimately, at 670 °C, only cassiterite is present. SnO reported thermally decomposes in the range 300–500 °C, ultimately oxidizing to SnO₂, initially via mixed-valent tin oxides.¹⁵ The enhanced thermal stability, and resilience to oxidation of Sn²⁺, at relatively high temperatures in α-Sn₆SiO₈ compared to SnO is likely a result of the enhanced stability afforded by bonding between [Sn₆O₈] clusters and a Si atom in the structure.

In summary, we report the first synthesis of tin(II) silicate, α-Sn₆SiO₈, by microwave-assisted hydrothermal synthesis, in addition to a full structural characterization for this previously unsolved structure. α-Sn₆SiO₈ demonstrates stability at higher temperatures than SnO likely because of the presence of silicate groups within the structure.

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.9b02615.

DR UV–vis spectrum, Tauc plot of the Kubelka–Munk function, Raman spectrum (100–3200 cm⁻¹), magic-angle-spinning²⁹Si NMR spectrum and discussion, X-ray fluorescence spectrum and discussion, and scanning electron micrograph (PDF)

### Accession Codes

CCDC 1943369 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.
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Author Contributions
The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes
The authors declare no competing financial interest.

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