

Crystal Engineering

Hydrothermal Formation of Calcium Copper Tetrasilicate

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Chem. Eur. J. 2015, 21, 17560-17564

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17560

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CHEMISTRY A European Journal Communication

Abstract: We describe the first hydrothermal synthesis of CaCuSi₄O₁₀ as micron-scale clusters of thin platelets, distinct from morphologies generated under salt-flux or solid-state conditions. The hydrothermal reaction conditions are surprisingly specific: too cold, and instead of Ca-CuSi₄O₁₀, a porous calcium copper silicate forms; too hot, and calcium silicate (CaSiO₃) forms. The precursors also strongly impact the course of the reaction, with the most common side product being sodium copper silicate (Na₂CuSi₄O₁₀). Optimized conditions for hydrothermal Ca-CuSi₄O₁₀ formation from calcium chloride, copper(II) nitrate, sodium silicate, and ammonium hydroxide are 350 °C at 3000 psi for 72 h; at longer reaction times, competitive delamination and exfoliation causes crystal fragmentation. These results illustrate that $CaCuSi_4O_{10}$ is an even more unique material than previously appreciated.

Calcium copper tetrasilicate (CaCuSi₄O₁₀) holds a special place in the history of chemistry as the first synthetic inorganic material produced on large scale.^[1,2] During the past five millennia, it has been used extensively as a blue pigment (Egyptian blue), and recent research has focused on its remarkable near infrared luminescence properties.^[3] In addition to archaeological imaging,^[4] these investigations have included using Yb³⁺ doping to increase near infrared emission,^[5] evaluating CaCu-Si₄O₁₀ as the active material in optical sensors,^[6] measuring the effects of temperature on photoluminescence,^[7] detailing the electronic structure of the blue chromophore,^[8] and utilizing the upconversion capability of CaCuSi₄O₁₀ under laser excitation to produce bright broadband light.^[9]

Traditionally CaCuSi₄O₁₀ has been prepared by salt-flux routes,^[10] the necessary reaction temperature (ca. 875 °C) was accessible even in antiquity using wood-fired ovens.^[11] Solid-state synthesis also can be used to produce CaCuSi₄O₁₀ but requires higher temperatures (> 1000 °C).^[12] Neither method provides control over product morphology or size, however, which is an important consideration for modern applications like imaging and sensing technologies. We are interested in synthesizing CaCuSi₄O₁₀ using a hydrothermal process because this method typically has the advantages of producing homogeneous and well-crystallized materials under relatively mild temperatures and pressures.^[13]

Notably, CaCuSi₄O₁₀ occurs as a rare mineral, cuprorivaite, at locations in Italy (Mount Vesuvius), Germany (the Sattelberg volcanic cone, Eifel region), South Africa (Messina copper mines), and the United States (Klamath County, Oregon).^[14] The

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[b] Dr. S. Comer, Prof. J. W. Kolis Department of Chemistry, Clemson University 219 Hunter Laboratories, Clemson, SC 29634 (USA) geology of these sites suggests that cuprorivaite forms in a hydrothermal environment. Indeed, the heavier congeners of Ca-CuSi₄O₁₀, namely SrCuSi₄O₁₀ and BaCuSi₄O₁₀, can be synthesized from the alkali earth chlorides, copper(II) oxide, and sodium silicate in basic, aqueous conditions at a modest temperature (250 °C).^[15] The hydrothermal synthesis of CaCuSi₄O₁₀ has remained elusive, however. As stated by Warner in his monograph on important inorganic materials, "Success in this area would break the historic dependency on the use of a salt flux, and may provide an insight to the conditions under which cuprorivaite forms in nature."^[2]

We now report the conditions required for CaCuSi₄O₁₀ formation in a hydrothermal environment. The key to success is threefold: the copper source must be specifically copper(II) nitrate, the mineralizer is optimally ammonium hydroxide, and the reaction temperature/pressure should be about 350 °C/ 3000 psi. In the optimized procedure, an aqueous mixture of CaCl₂·2 H₂O, Cu(NO₃)₂·2.5 H₂O, and [Na₂O(SiO₂)_x(H₂O)_x] in a 1:2:4 molar ratio is adjusted to pH 12 with NH₄OH. The resulting gelatinous material is heated at 350 °C for 3 days. These conditions result in complete conversion to highly crystalline CaCu-Si₄O₁₀. The blue product (Figure 1 b) consists of 40–60 µm crystal clusters with a uniform flowerlike morphology (see Figure S1 in the Supporting Information for additional images and a distribution analysis).

Monitoring this reaction from 12 to 96 h by powder X-ray diffraction (PXRD) (Figure 1a) shows that some CaCuSi₄O₁₀ forms early in the reaction, but SiO₂ and calcium silicates like Ca₂(SiO₃OH)OH and CaSi₂O₇ also are present. Scanning electron microscopy (SEM) illustrates a progression from heterogeneous morphologies at 12 and 24 h (Figures 1 c and 1 d, respectively) to distinct 25 μm CaCuSi_4O_{10} platelets after 48 h (Figure 1 e). At 72 h, the product is pure $CaCuSi_4O_{10}$ in the form of well-developed clusters of square-shaped crystals (Figure 1f). At 96 h and beyond, however, crystal delamination and fragmentation become noticeable: the clusters are smaller, exhibit frayed edges, and are covered in debris (Figure 1g). The previously reported exfoliation of layered CaCuSi₄O₁₀ in 80 °C water is the likely fragmentation mechanism here.^[16] For this reason, 72 h is the ideal length of reaction time for hydrothermal CaCuSi₄O₁₀ crystal growth.

Varying the calcium and copper sources, as well as the mineralizer, has significant effects on the products of the reaction. Table 1 summarizes the results of using CaCl₂·2H₂O versus Ca(NO₃)₂·4H₂O and CuCl₂·4H₂O versus Cu(NO₃)₂·2.5H₂O with either NH₄OH or NaOH. First, these experiments show that NaOH is a problematic mineralizer in this system because the high concentration of Na⁺ leads to preferential formation of Na₂CuSi₄O₁₀, a known tubular silicate.^[17] The use of NH₄OH instead of NaOH mitigates this reaction pathway to a large extent, though [Na₂O(SiO₂)_x(H₂O)_x] is another Na⁺ source present in the system. We do not detect other previously reported sodium copper silicates, such as Na₄Cu₂Si₁₂O₂₇(OH)₂·2H₂O or Na₂Cu₂Si₄O₁₁·2H₂O.^[18]

Second, the reaction is relatively insensitive to the calcium source but sensitive to the copper source: the use of $CuCl_2$ ·4H₂O is consistently ineffective in producing CaCuSi₄O₁₀

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201503364.





Figure 1. Hydrothermal formation of CaCuSi₄O₁₀ at 350 °C: a) PXRD patterns of products from 12-96 h reactions, b) optical microscopy image of phase pure CaCuSi₄O₁₀ produced with 72 h reaction time, and SEM images of products corresponding to c) 12, d) 24, e) 48, f) 72, and g) 96 h reaction times.

compared to Cu(NO₃)₂·2.5 H₂O. This observation is surprising because both CuCl₂·4 H₂O and Cu(NO₃)₂·2.5 H₂O should convert to Cu(OH)₂, [Cu(NH₃)₄]²⁺, and mixed ligand species in the presence of excess NH₄OH. In fact, prior studies have shown that both CuCl₂ and Cu(NO₃)₂ produce nanostructured CuO via putative Cu(OH)₂ when treated with NH₄OH under hydrothermal conditions.^[19] Based on established hydrothermal chemistry, we speculate that strong Cu–Cl bonding persists at 350 °C, which influences the formation of reactive intermediates.^[20]

Although we observe the most phase pure $CaCuSi_4O_{10}$ product from $CaCl_2 \cdot 2H_2O$ and $Cu(NO_3)_2 \cdot 2.5H_2O$ starting materials, CaCuSi₄O₁₀ also forms from Ca(NO₃)₂·4H₂O + Cu(NO₃)₂·2.5H₂O. One expects little difference in chemistry between CaCl₂ and Ca(NO₃)₂ here, with both converting to Ca(OH)₂ under these conditions.^[21] Curiously, a small amount of CaCuSi₄O₁₀ also is generated from Ca(NO₃)₂·4H₂O + Cu(NO₃)₂·2.5H₂O in the presence of NaOH, despite Na₂CuSi₄O₁₀ formation, which may reflect subtle effects related to the solubility and reactivity of calcium and copper hydroxides when approaching the supercritical point of water.^[22]

Reaction temperature/pressure is another key parameter in this system. In general, a higher reaction temperature of 450 °C and corresponding pressure of 15000 psi disfavors CaCuSi₄O₁₀ formation (Table S1 in the Supporting Information). When using NH₄OH as the mineralizer, the dominant product at 450 °C is CaSiO₃ with minor amounts of CuSiO₃. In close similarity to 350 °C reactions, Ca(NO₃)₂·2 H₂O + CuCl₂·2.5 H₂O + NH₄OH yields Na₂CuSi₄O₁₀, as do all reactions utilizing NaOH. Again, some CaCuSi₄O₁₀ is generated when both nitrate salts are used in the presence of NaOH at 450 °C as at 350 °C (Figure S7 in the Supporting Information).



Figure 2. Micro-dumbbells formed at 250 °C: a) Optical microscopy image, b) SEM image, c) PXRD pattern, and d) experimental ²⁹Si NMR spectrum (black curve) with peak fitting (dashed curves).

Of the eight reactions listed in Table 1, only one provides an isolable product at 250 °C with an autogenous pressure of about 1800 psi: $Ca(NO_3)_2 \cdot 4H_2O + Cu(NO_3)_2 \cdot 2.5H_2O +$ $[Na_2O(SiO_2)_x(H_2O)_x] + NH_4OH$. As illustrated in Figure 2, the interesting product consists of 0.1-0.2 mm bright blue crystals with a dumbbell morphology. Their color is, in fact, a more pure blue than CaCuSi₄O₁₀ (Figure S8 in the Supporting Information), but this material does not luminesce in the infrared range of 700-1400 nm (Figure S9 in the Supporting Information). Elemental analysis (Table S2 in the Supporting Information) provides an approximate stoichiometry of Ca₂CuSi₈O₁₆. Although several crystalline calcium copper silicate compositions are known, including kinoite (Ca₂Cu₂Si₃O₁₀·2H₂O),^[23] stringhamite (CaCuSiO₄·H₂O),^[24] and recently discovered diegogattaite



Table 1. Hydrothermal experiments at 350 °C and 3000 psi.				
Reactants Calcium source Copper source		Mineralizer	Results (PXRD analysis)	
$\begin{array}{c} CaCl_{2}{\cdot}2H_{2}O\\ Ca(NO_{3})_{2}{\cdot}4H_{2}O\\ CaCl_{2}{\cdot}2H_{2}O\\ Ca(NO_{3})_{2}{\cdot}4H_{2}O\\ Ca(Cl_{2}{\cdot}2H_{2}O\\ Ca(NO_{3})_{2}{\cdot}4H_{2}O\\ Ca(NO_{3})_{2}{\cdot}4H_{2}O\\ CaCl_{2}{\cdot}2H_{2}O\\ Ca(NO_{3})_{2}{\cdot}4H_{2}O\\ \end{array}$	Cu(NO ₃) ₂ ·2.5 H ₂ O Cu(NO ₃) ₂ ·2.5 H ₂ O CuCl ₂ ·4 H ₂ O CuCl ₂ ·4 H ₂ O Cu(NO ₃) ₂ ·2.5 H ₂ O Cu(NO ₃) ₂ ·2.5 H ₂ O Cu(NO ₃) ₂ ·2.5 H ₂ O CuCl ₂ ·4 H ₂ O CuCl ₂ ·4 H ₂ O	NH₄OH NH₄OH NH₄OH NH₄OH NaOH NaOH NaOH NaOH	bright blue crystals (CaCuSi ₄ O ₁₀) major: bright blue crystals (CaCuSi ₄ O ₁₀); minor: larger clear crystals (SiO ₂) pale blue fibrous network [Na ₂ CuSi ₄ O ₁₀ , SiO ₂ , and Na(Si ₂ O ₄ (OH))H ₂ O] pale blue fibrous network (Na ₂ CuSi ₄ O ₁₀ and SiO ₂) pale blue fibrous network (Na ₂ CuSi ₄ O ₁₀) major: pale blue fibrous network (Na ₂ CuSi ₄ O ₁₀); minor: bright blue crystals (CaCuSi ₄ O ₁₀) pale blue fibrous network (Na ₂ CuSi ₄ O ₁₀); minor: bright blue crystals (CaCuSi ₄ O ₁₀) pale blue fibrous network (Na ₂ CuSi ₄ O ₁₀ , quartz, and SiO ₂) pale blue fibrous network (Na ₂ CuSi ₄ O ₁₀ , and quartz)	

 $(Na_2CaCu_2Si_8O_{20} \cdot H_2O)$,^[25] the PXRD pattern of the micro-dumbbells (Figure 2 c) does not match anything previously reported. However, the low-angle data show features similar to data from calcium silicates like gyrolite $(Ca_{16}Si_{24}O_{60}(OH)_8 \cdot (14 + x) H_2O)$ and hillebrandite $Ca_2(SiO_3)(OH)_2$.^[26] Gyrolite in particular is known to readily incorporate Cu^{2+} into its layered structure.^[27]

We further investigated the structure of the dumbbell material using solid-state ²⁹Si magic angle spinning (MAS) nuclear magnetic resonance (NMR) spectroscopy. The spectrum exhibits three overlapping peaks (Figure 2d) at -103, -109, and -117 ppm, which we assign to one Q³ species [Si(OSi)₃OH] and two distinct Q⁴ species [Si(OSi)₄]. Such a low silanol content is consistent with a porous framework silicate and is similar to data reported for Cu²⁺-doped zeolites and mesoporous silica materials.^[28] These results suggest that the dumbbells contain coordinated Cu²⁺ within pores or channels formed by the silicate structure.

The micro-dumbbells convert to CaCuSi₄O₁₀ when heated at 350 °C under hydrothermal conditions, with the cleanest reaction obtained by heating isolated dumbbells in deionized water. SEM analysis (Figure S11 in the Supporting Information) shows that the product mixture contains relatively thick CaCu-Si₄O₁₀ crystals, thin CaCuSi₄O₁₀ platelets, and needlelike and globular morphologies that may correspond to unreacted material.

In conclusion, the conditions for the hydrothermal formation of CaCuSi₄O₁₀ are surprisingly specific. Although both SrCu-Si₄O₁₀ and BaCuSi₄O₁₀ form in a range of temperatures and from variable precursors, highly crystalline and phase pure Ca-CuSi₄O₁₀ forms readily only at 350 °C using copper nitrate and ammonium hydroxide. This significant difference in chemistry explains in part why cuprorivaite is not found in the same natural mineral deposits as wesselsite (SrCuSi₄O₁₀) or effenbergerite (BaCuSi₄O₁₀).^[29] The final question is, why has it taken until now for the hydrothermal formation of CaCuSi₄O₁₀ to be reported? We suggest that the experimental challenge of conducting hydrothermal reactions at temperatures > 250 °C (beyond the capability of Teflon-lined pressure vessels) has been the main impediment to developing this chemistry.

Experimental Section

General: CaCl₂·2 H₂O (ACS reagent, \geq 99% purity), sodium silicate solution [Na₂O(SiO₂)_x(H₂O)_x] (reagent grade purity, 26.5% SiO₂),

 $\rm NH_4OH~(ACS~reagent,~28–30\%~NH_3~basis),~and~5~m~NaOH~(ACS~Reagent,~<math display="inline">\geq 97.0~\%)$ were purchased from Sigma-Aldrich. Cu(NO_3)_2.2.5 H_2O~(certified~ACS~grade)~was~purchased from Fischer Scientific. Ca(NO_3)_2.4 H_2O~(certified~ACS~crystalline~grade)~was~purchased from J. T. Baker.

Hydrothermal synthesis of CaCuSi₄O₁₀: CaCl₂·2H₂O (0.196 g, 1.33 mmol) and Cu(NO₃)₂·2.5 H₂O (0.619 g, 2.66 mmol) or CuCl₂·2H₂O (0.227 g, 1.33 mmol) were dissolved in deionized water (30 mL). While monitoring the pH and stirring, sodium silicate solution $[Na_2O(SiO_2)_x(H_2O)_x]$ (1.27 mL; 5.31 mmol of SiO₂) was added drop-wise to the solution. The final pH of the solution was then adjusted to 12 using 14.6 M NH₄OH (28-30% NH₃ basis). Then a sample of the resulting gelatinous mixture (0.8 mL) was placed into a silver ampule, welded shut, placed in a high temperature autoclave (filled with deionized water to counter-pressure the ampules), and heated to 350°C for 12-96 h. Once the reaction time was complete, the vessel was cooled to room temperature, the solid product was washed with water and collected by vacuum filtration. The isolated yield of blue crystals was 0.007 g (54%). Additional experiments to examine varying reaction conditions were carried out in the same manner with Ca(NO₃)₂·4H₂O (0.314 g, 1.33 mmol), CuCl₂·2H₂O (0.227 g, 1.33 mmol), and 5 м NaOH at 350 or 450 $^{\circ}$ C.

Hydrothermal synthesis of calcium copper silicate hydrate micro-dumbbells: $Ca(NO_3)_2 \cdot 4H_2O$ (0.314 g, 1.33 mmol) and $Cu(NO_3)_2 \cdot 2.5H_2O$ (0.619 g, 2.66 mmol) were dissolved in deionized water (30 mL). While monitoring the pH and stirring, sodium silicate solution $[Na_2O(SiO_2)_x(H_2O)_x]$ (1.27 mL; 5.31 mmol of SiO_2) was added drop-wise to the solution. The final pH of the solution was then adjusted to 12 using 14.6 M NH₄OH (28–30% NH₃ basis). The resulting gelatinous mixture was placed into a 45 mL capacity Teflon-lined autoclave (Parr Instrument Co. acid digestion vessel) and heated at 250 °C for 96 h. The blue product (0.140 g) was isolated by decanting the gelatinous supernatant and washing the crystals with water. Additional experiments to examine varying reaction conditions were carried out in the same manner with CaCl₂·2 H₂O (0.196 g, 1.33 mmol), CuCl₂·2 H₂O (0.227 g, 1.33 mmol), and 5 M NaOH at 250 °C.

Characterization: Product composition was confirmed using a Bruker D8-Advance powder x-ray diffractometer ($Co_{K\alpha}$ radiation source) operated at 40 mA and 40 kV. PXRD patterns were recorded in the 2θ range of $10-70^{\circ}$ with a scanning rate of 0.5 s per step. The morphology of products was examined by FEI Inspect F field emission gun scanning electron microscope (SEM) operated at 20 keV. The samples were prepared for SEM by sprinkling the powders on carbon sticky tape and then coating with gold. EDS data were collected with an EDAX Inc. instrument. Solid-state ²⁹Si magic angle spinning (MAS) nuclear magnetic resonance (NMR) spectra



were collected using a Bruker AV3–400 solid-state NMR spectrometer with a 4 mm MAS BB HX probe. The sample was packed in a 4 mm ZrO₂ rotor with a spinning speed of 10 kHz. The experiment used direct polarization with ¹H decoupling with a repetition delay of 10 s, a pulse length of 2 μ s (ca. 35 degree pulse length) and 6136 scans collected. For electron probe micro-analysis (EPMA), the micro-dumbbells were imbedded in resin, polished, and then carbon-coated. EPMA data were collected using a JEOL JXA 8600 Superprobe operated at 10 KeV.

Acknowledgements

Work by T.T.S. and D.J.M. was supported by a U.S. Department of Energy (DOE), Office of Science, Basic Energy Sciences (BES) Early Career Research Program Award (#DE-SC0008065). J.W.K. and S.C. are indebted to the National Science Foundation #DMR-1410727. Many thanks to Dr. Chris Fleisher (UGA Geology) for his help with collecting the EPMA data, and to Dr. Johannes Leisen (Georgia Institute of Technology) for assistance with the NMR experiments.

Keywords: crystal engineering · crystal growth · hydrothermal synthesis · layered compounds · silicates

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Received: August 25, 2015 Published online on October 20, 2015