Nanoporus Silicate Frameworks

Nanoporous Copper Silicates with One-Dimensional 12-Ring Channel Systems[**]

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Crystalline materials such as zeolites, with pore arrays of nanometer sizes, are important because of their applications as catalysts and molecular sieves, and their potential use as components in advanced nanocomposites.[1–4] Nanoporous transition-metal silicates are of particular interest because they usually show good chemical and thermal stability and other physical and catalytic properties introduced by the transition-metal centers.[4,5]

We have recently developed a strategy for the synthesis of transition-metal-silicate open-framework and microporous compounds that uses a common building principle. The structures in this family of compounds are formed by linking isolated transition-metal polyhedra $MO_{4/2}X_n$ ($X = O$, F, H_2O, $n = 1,2$) with various anionic silicate building units by sharing four oxygen atoms at the corners of a square. The anionic silicate units may be simple layers of composition $\{SiO_{3/2}O_{1/1}\}$, chains of composition $\{SiO_{2/2}O_{2/1}\}$, cluster ions, or more complex units such as double layers and chains. We have reported examples that contain VO^{2+},[6–8] $NbFO^{2+}$,[9] UO_2^{2+},[10,11] and $[VO]_2^{4+}$[7] ions that link silicate units. The fluorogermanate $Ge_2ZrO_6F_2{\cdot}H_2DAB{\cdot}H_2O$ (DAB = diaminobutane) described by Li et al., which contains ZrF_2^{2+} units that link germanate chains, is closely related.[12] All of the compounds are synthesized under mild temperature and pressure conditions, similar to those used in zeolite syntheses.

Here we report the first examples of this class of compound to contain a Cu^{2+} linking group and a novel framework structure. The extension of the general building principle to copper–oxygen polyhedra is suggested by the known structures of several dense copper silicate phases that also contain copper–oxygen "squares" or tetrahedra.[13–18] The new phases have the general formula given below, and are designated CuSH-1A (A = Na, K, Rb, Cs).[19]

$$Na_4[Cu_2Si_{12}O_{27}(OH)_2][(AOH)_x(NaOH)_y(H_2O)_z];$$
$$A = Na,\ K,\ Rb,\ Cs,\ x \approx 1,\ y \approx 1,\ z \approx 6$$

These structures are unusual in several respects: They are the first examples to contain double layers of silicate tetrahedra that define straight 12-ring channels, analogous to those found in LTL-type zeolites. Unlike LTL, however,

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the framework composition $Na_4[Cu_2Si_{12}O_{27}(OH)_2]$ that defines the 12-ring channels is neutral, and as a consequence only neutral MOH and H_2O species fill these channels, presumably acting as templates during the synthesis.

Crystals of the CuSH-1A phases were synthesized as pale-blue plates with maximum dimensions of about 0.4 mm. CuSH-1Na was prepared as a single phase in high yield (greater than 80 % based on Cu). CuSH-1K and CuSH-1Rb could be synthesized only as minor phases while CuSH-1Cs is obtained as major phase (greater than 50 % based on Cu). Compositions of CuSH-1Na and CuSH-1Cs were measured by elemental analysis.[20] CuSH-1K and CuSH-1Rb were qualitatively analyzed by energy-dispersive X-ray (EDX) spectrometry using a JEOL JSM 6400 scanning electron microscope with a Link Analytical EXL spectrometer. The crystal structures were determined from single-crystal X-ray diffraction data.[21]

The CuSH-1A phases all have the same framework structure with space-group symmetry *Cmcm*. The porous framework is built from silicate double layers that are arranged perpendicular to the [100] direction, and are cross-linked by interlayer Cu–O and Na–O bonds (Figure 1). The silicate double layer contains channels defined by 12-rings of tetrahedra that run along the [001] direction and have an aperture of 7.3 × 4.4 Å, and 8-ring channels along the [011] and [01$\bar{1}$] directions, with an aperture of 3.8 × 2.5 Å. The silicate double layer that consists of two single layers related by a mirror plane is shown in Figure 2. The single layers are constructed by cross-linking single chains with a periodicity of six tetrahedra. In one period of the chain, the tetrahedron $\{Si1O_4\}$ shares corners with three tetrahedra from the same single layer and with one tetrahedron from the other single layer. The other five tetrahedra of the repeat unit are all connected to only three other SiO_4 tetrahedra, and each has a terminal oxygen atom pointing towards the space between the double layers. The double layer is an example of an unbranched vierer double layer, according to Liebau's classification, with two types of fundamental chains and a periodicity of four along the [001] direction.[22] The terminal oxygen atoms of the $\{Si2O_4\}$ and $\{Si4O_4\}$ tetrahedra are bonded to the interlayer Cu atoms, while that of the $\{Si3O_4\}$ tetrahedron is bonded to a proton to form a silanol group. Interconnection of the two single layers gives rise to the 12-ring channels. The single layer is unusual in having 5-, 6-, and 7-rings of tetrahedra in equal proportions.

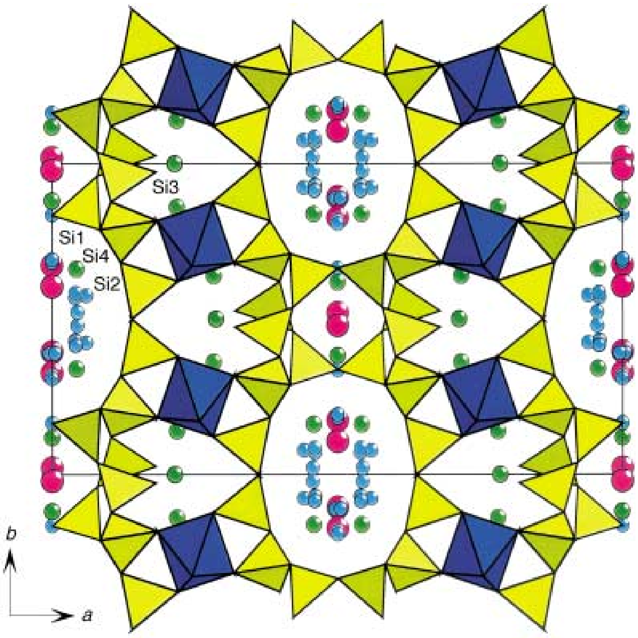

Figure 1. The structure of CuSH-1Cs viewed along the [100] direction showing the 12-ring channels. Copper–oxygen and silicon–oxygen polyhedra are dark blue and yellow, respectively. Purple, green, and cyan circles represent cesium and sodium atoms, and water molecules, respectively.

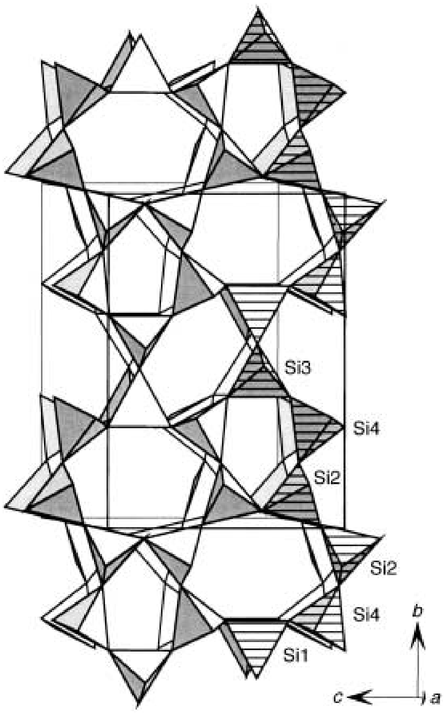

Figure 2. The silicate double layer in the CuSH-1A structures. A single chain is marked by the hatched segments and the silicon atoms in the repeat unit along the chain are labeled.

Neighboring silicate double layers are interconnected by $\{CuO_4\}$ squares that share corners with the $\{Si2O_4\}$ and $\{Si4O_4\}$ tetrahedra with Cu–O bond lengths of 1.95 Å (Figure 3). The copper-ion coordination is completed by interlayer water molecules to form single chains of $\{CuO_4(H_2O)_2\}$ elongated octahedra with Cu–OH_2 bond lengths of 2.70 Å. The interlayer water molecule is coordinated to two Cu atoms and one Na atom and forms a relatively strong hydrogen bond to the OH group ($H_2O\cdots HO$ 2.686 Å). The two independent interlayer Na sites, which both have distorted octahedral coordination and Na–O bond lengths in the range 2.33–2.64 Å, are essential structural components. The interlayer $\{CuO_4(H_2O)_2\}$ and $\{Na(O,OH,H_2O)_6\}$ octahedra form a sheet sandwiched between neighboring silicate double

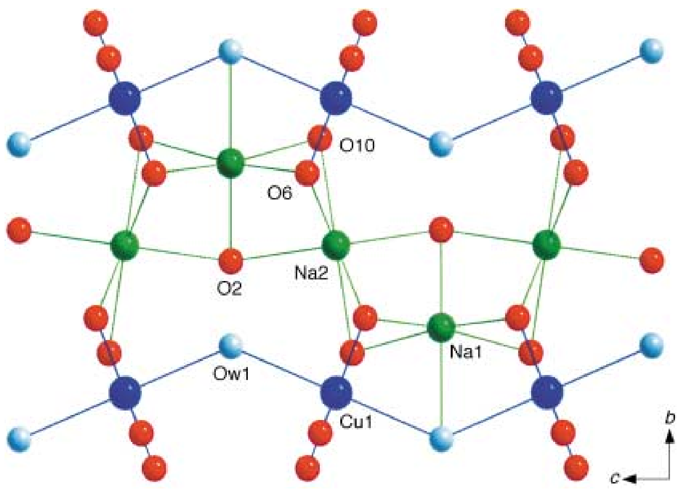

Figure 3. The copper- and sodium-ion coordination environments in the region of the CuSH-1A structure between the silicate double layers. Blue, green, red, and cyan circles represent copper, sodium, and oxygen atoms, and water molecules, respectively.

layers, which gives rise to an electroneutral framework with the composition $\{Na_4Cu_2Si_{12}O_{27}(OH)_2(H_2O)_2\}$. Bond valence sums calculated for the Cu atoms in the CuSH-1A phases are very close to 2.0 valence units, which indicates their divalent character, as expected from the bonding features.[23] The CuSH-1A structure is related to that of the known compounds $A_2Cu_2Si_8O_{19}$ (A = Rb, Cs), which also have silicate double layers cross-linked by $\{CuO_4\}$ squares.[15,16]

The 12-ring channels and the side cavities inside the silicate double-layers of the CuSH-1A structures are filled with highly disordered AOH groups, and water molecules with fractional occupancies. Elemental and thermogravimetric analyses (TGA) and structure refinements indicate that the x, y, and z values in the structural formula are approximately 1, 1, and 6, respectively, for both CuSH-1Cs and CuSH-1Na. For CuSH-1Cs, about 60% of the Cs ions were located inside the 12-ring channels and the remaining 40% were located within a cavity defined by two 8-rings and two 6-rings in the double layer (see Figure 1). Two Na sites were identified according to their separations from the framework oxygen atoms. One site is located inside the 12-ring channels and the other is near the 8-ring of the side cavity mentioned above. In CuSH-1Rb, CuSH-1K, and CuSH-1Na, the extra-framework Cs ions are replaced by smaller alkali-metal ions. As the size of the ions decreases, they shift further away from the cavity center and from the channel axis, which optimizes the bonding with the framework oxygen atoms.

TGA measurements of compound CuSH-1Na in air at a heating rate of $5\,K\,min^{-1}$ show that the sample loses water immediately upon heating, and is completely dehydrated by approximately 260 °C. X-ray data measured on powder and single-crystal samples after different thermal treatments indicate that the framework is stable to 400 °C in air. Upon complete dehydration at 300 °C, an orthorhombic superstructure is observed with doubled a and b cell dimensions ($a = 44.78$, $b = 26.006$, $c = 9.447$ Å) and an apparent contraction along the a axis. Rehydration is slow but complete after several days in air. The original crystal structure was fully recovered after rehydration, as confirmed by refinements of the single-crystal X-ray data.

A unique feature of the structure of the CuSH-1A species is that, because of the neutral framework, as-prepared samples contain neutral alkali hydroxide species in the channels. On dehydration, these alkali-metal hydroxide (or oxide) species remain and effectively block nitrogen adsorption. Treatment with water or dilute acid partially removes the alkali-metal hydroxide and increases the nitrogen adsorption capacity, but we have not yet found conditions that lead to a complete "cleaning-out" of the channels and realization of the full sorption capacity that is anticipated from the structure. Further experiments are in progress.

In conclusion, the CuSH-1A phases further demonstrate the effectiveness of our approach for building porous frameworks by cross-linking transition-metal coordination polyhedra that can share four corners in a square geometry with condensed silicate components.

Experimental Section

Synthesis of CuSH-1A single crystals: A solution was prepared by dissolving fumed silica (3.7 g) in an aqueous mixture of AOH and NaOH (4.2 M, 27 mL; 1:1 A/Na molar ratio). 1.4 mL of such a solution was then mixed with $CuSO_4{\cdot}5H_2O$ (0.36 g). The mixture was sealed in air and heated at 240 °C for 2 days in a 23-mL teflon-lined autoclave. Pale-blue crystals of CuSH-1A were recovered by vacuum filtration, together with other impurity phases such as $Na_2CuSi_4O_{10}$[13] and $Na_2Cu_3Si_4O_{12}$.[14] To prepare single-phase samples of CuSH-1Na, fumed silica (0.79 g) was mixed with aqueous solutions of $Cu(NO_3)_2$ (1.25 M, 0.56 mL) and NaOH (4.24 M, 0.80 mL). The mixture was sealed, together with H_2O_2 (0.2 mL) and a saturated aqueous solution of Na_2HPO_4 (0.52 mL) in air and heated at 245 °C for 54 h. The product was vacuum-filtered and washed thoroughly with water. No phosphorus was detected in the sample by EDX analysis. IR (KBr; Galaxy FTIR 5000): $\tilde{\nu} = 457$(s), 538(m), 619(w), 677(m), 995(vs), 1115(s), 1163(s), 1655(m), 2937(w), 3527(s), 3616 cm^{-1} (s).

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[19] We use the general notation MSH-nA (Metal Silicate Houston, n is the framework type and A is the nonframework cation) to designate this series of compounds. Thus CuSH-n is used for the copper silicate family.

[20] Elemental analyses (Galbraith Lab., Knoxville, TN, USA) calcd (%) for CuSH-1Cs ($Na_4[Cu_2Si_{12}O_{27}(OH)_2][(CsOH)(NaOH)(H_2O)_6]$): Cs 10.07, Na 8.71, Cu 9.63, Si 25.53; found: Cs 10.37, Na 8.78, Cu 9.66, Si 25.62. Calcd for CuSH-1Na ($Na_4[Cu_2Si_{12}O_{27}(OH)_2]$ $[(NaOH)_2(H_2O)_6]$): H 1.32, Na 11.40, Cu 10.50, Si 27.85; found: H 1.31, Na 11.13, Cu 10.38, Si 27.46

[21] X-ray single-crystal analysis for CuSH-1Na: pale-blue plate, 0.26 × 0.08 × 0.01 mm, space group *Cmcm,* $a = 25.578(4)$, $b = 13.098(2)$, $c = 9.890(1)$ Å, $V = 3313.4(8)$ Å^3, $Z = 4$. Final R indices ($I > 2\sigma(I)$): $R1 = 0.0687$, $wR2 = 0.1678$. For CuSH-1K: pale-blue plate, 0.24 × 0.12 × 0.01 mm, space group *Cmcm,* $a = 25.474(2)$, $b = 13.1346(8)$, $c = 9.8537(6)$ Å, $V = 3297.0(3)$ Å^3, $Z = 4$. $R1 = 0.0528$, $wR2 = 0.1249$. For CuSH-1Rb: pale-blue plate, 0.30 × 0.12 × 0.01 mm, space group *Cmcm,* $a = 25.425(2)$, $b = 13.135(1)$, $c = 9.9068(7)$ Å, $V = 3308.4(4)$ Å^3, $Z = 4$. $R1 = 0.0323$, $wR2 = 0.0824$. For CuSH-1Cs: pale-blue plate, 0.29 × 0.11 × 0.01 mm, space group *Cmcm,* $a = 25.639(7)$, $b = 13.142(4)$, $c = 9.960(3)$ Å, $V = 3356(2)$ Å^3, $Z = 4$. $R1 = 0.0410$, $wR2 = 0.1059$. Intensities were measured on a SMART platform diffractometer equipped with a 1 K CCD area detector using graphite-monochromated $Mo_{K\alpha}$ radiation at 293 K for CuSH-1Na and at 243 K for the other three phases. The structures were solved by direct methods and refined using the SHELXTL program. All ordered non-hydrogen atom positions were refined anisotropically in the final refinements. The disordered water oxygen atoms were forced to have an equal but variable displacement parameter in order to refine their relative occupancies. The total amount of observed water is consistent with that measured from TGA measurements, and was fixed to the formula based on the TGA data. Further details on the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository numbers CSD-412966, -412967, -412968, -412969.

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