

Open-Framework Copper Titanosilicates

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ABSTRACT

Four open-framework copper titanosilicates have been synthesized by hydrothermal techniques. The crystal structure of Phase **1** determined from single crystal X-ray data is closely similar to that reported for the titanosilicate ETS-4 with ca. one third TiO_5 pyramids randomly replaced by CuO_4 squares. Phase **2** also has the ETS-4 structure but all the TiO_5 pyramids are replaced by CuO_4 squares which are not randomly disordered. Phase **3** with the composition $\text{Na}_8\text{CuTi}_3\text{Si}_{16}\text{O}_{43}$ has the same structure as the mineral narsarsukite, a titanosilicate closely related to the microporous titanosilicate ETS-10. Narsarsukite and ETS-10 have the same straight single chains of TiO_6 octahedra which are partially substituted by CuO_4 squares in **3**. Phase **4** with the composition $\text{K}_4\text{CuTiSi}_8\text{O}_{21}$ contains CuO_4 squares and TiO_5 tetragonal pyramids that crosslink a new type of silicate double layer to form an open framework.

INTRODUCTION

Microporous transition metal silicates may have important uses in diverse areas such as catalysis, ion-exchange and gas separations as recently demonstrated by the titanosilicate ETS-4. [1-3] We have been interested in metal silicate frameworks built by cross-linking 1- or 2-dimensional silicate units with transition metal coordination polyhedra. By linking various silicate layers with $[\text{VO}_5]$ pyramids we obtained a number of novel microporous frameworks. [4] Using $[\text{CuO}_4]$ squares or $[\text{UO}_6]$ distorted octahedra to replace the $[\text{VO}_5]$ pyramids led to more open-framework structures. [5,6] In all these structures, only one transition metal was incorporated in the frameworks. Adding a second transition metal to the framework provides an additional route to tune the structure and properties of the materials. Therefore, we have been investigating synthesis of silicates incorporating more than one transition metal into the framework. As first results, four new copper titanosilicates $(\text{Na}_x\text{H}_{10-x})[\text{Ti}_4(\text{TiO})_{0.7}\text{Cu}_{0.3}\text{Si}_{12}\text{O}_{38}](\text{H}_2\text{O})_y$ (**1**), $(\text{Na}_9\text{H})[\text{Ti}_4\text{CuSi}_{12}\text{O}_{38}](\text{H}_2\text{O})_6$ (**2**), $\text{Na}_8\text{CuTi}_3\text{Si}_{16}\text{O}_{43}$ (**3**), and $\text{K}_4\text{CuTiSi}_8\text{O}_{21}$ (**4**) are reported here.

EXPERIMENTAL

Synthesis

For the synthesis of **1**, 0.9 g silica gel (Sigma S-4883) was mixed with 0.6 g NaOH, 0.1 g Cu and 0.04 g Ti metal foil. The mixture was put in a Teflon tube with an open end. The tube was subsequently placed in a sealed Parr autoclave. The autoclave was filled with water to ~ 30% inner volume and the water was kept outside the Teflon tube. After sealing in air, the autoclave was heated at 245 °C for three days and then cooled to room temperature in air within four h. The product was vacuum-filtered, washed with water and dried in air. Compound **2** was synthesized in a similar way. The initial mixture consists of 0.9 g silica gel, 0.9 g NaOH, 0.1 g Cu and 0.2 g

Ti metal foil, 0.5 ml 0.8 M $\text{Ti}_2(\text{SO}_4)_3$ solution and 1 ml water. Compound **3** was similarly synthesized from a mixture of 0.9 g silica gel, 0.8 g NaOH, 0.1 g Cu and 0.2 g Ti metal foil. Compound **4** was obtained from a starting mixture of 0.9 g silica gel, 2 ml 10 M KOH solution, 0.62 ml 2.5 M $\text{Cu}(\text{NO}_3)_2$ solution, 0.2 g Ti metal foil and 0.5 ml 0.8 M $\text{Ti}_2(\text{SO}_4)_3$ solution. All products are multiphase. While phases **1** and **2** have been obtained as major phases, **3** and **4** can only be obtained as minor phases. Efforts to optimize the synthesis by changing the composition of the starting mixture were unsuccessful so far.

Characterization

The compounds were analyzed by EDX using a JEOL JSM 6400 scanning electron microscope with a Link Analytical EXL spectrometer. Manually separated samples of **2** were also characterized by IR, TGA and X-ray powder diffraction. Crystal structures of all four phases were determined from single crystal X-ray diffraction data measured on a SIEMENS/SMART platform diffractometer equipped with a 1K CCD area detector using graphite-monochromatized MoK_α radiation at room temperature. Crystallographic data are listed in Table I.

Table I Crystallographic data for compounds **1-4**.

Phase	1	2	3	4
Space group	<i>C2/m</i>	<i>Cccm</i>	<i>I4/m</i>	<i>Cm</i>
<i>a</i> /Å	14.352(3)	46.402(9)	10.7033(8)	8.651(1)
<i>b</i> /Å	13.954(3)	14.419(2)	10.7033(8)	12.449(2)
<i>c</i> /Å	12.173(3)	13.970(3)	7.9142(9)	9.647(1)
β /°	107.2(1)			
unique reflections	2797	5200	583	1663
variables	146	243	55	169
<i>R</i> (F)	0.066	0.073	0.030	0.036

RESULTS AND DISCUSSION

Crystals of **1** and **2** are both pale purple needles with maximum sizes of ca. 0.2 x 0.02 x 0.02 mm. The crystal structures of **1** and **2** are closely similar to that of ETS-4, the synthetic counterpart of the mineral zorite that has a complicated structure because of disorder evidenced by diffuse and weak superstructure reflections. A superposition structure model of zorite in a subcell with space group *Cmmm*, *a* = 23.24, *b* = 7.24, *c* = 6.96 Å was reported previously. [7] Similar structure models were used to refine the structure of ETS-4.[8-10] One fifth of the titanium atoms in ETS-4 are bonded to oxygen atoms to form TiO_5 tetragonal pyramids while the remaining titanium atoms form TiO_6 octahedra. The TiO_6 octahedra are connected to 1-dimensional chains that are cross-linked by SiO_4 tetrahedra into slabs of the composition $[\text{TiSi}_2\text{O}_8]$. Each TiO_5 pyramid is connected to four SiO_4 tetrahedra to form a bow-tie shaped unit of the composition $[\text{TiSi}_4\text{O}_{15}]$. The slabs are cross-linked by the bow-tie units to form a porous 3-dimensional framework. There are several possible ways to link the slabs and the bow-tie units, which leads to different ordered structures with 12-ring and 8-ring channels. [7,9] In ETS-4 the bow-tie units are disordered among the possible positions, which effectively blocks the 12-ring channel systems. The 8-ring channels of the framework are not blocked by the disorder, and are found to be responsible for interesting gas separation properties.[3] In the structure of **1**, 28(4)

percent of the TiO_5 pyramids are randomly replaced by CuO_4 squares. The corresponding bow-tie units of composition $[\text{Ti}_{0.7}\text{Cu}_{0.3}\text{Si}_4\text{O}_{14.7}]$ are found to be randomly disordered (figure 1). In **2**, all the TiO_5 pyramids are replaced by CuO_4 squares. Refinement results of the current stage show that one half of the $[\text{CuSi}_4\text{O}_{14}]$ bow-tie units are ordered while the other half are disordered, so that at least part of the 12-ring channels may not be blocked (figure 2). Simulated powder X-ray pattern from this partially ordered model agrees with the measured powder data and are similar to the pattern for the model #16 in reference [9] predicted for an ordered ETS-4. The successful substitution of CuO_4 squares for TiO_5 pyramids occurs because of their similarities in bonding to the silicate tetrahedra and in charge balance requirements.

Figure 1. The [010] projection of the structure of **1**. An ordered framework is represented by polyhedra. One $[\text{Ti}_{0.7}\text{Cu}_{0.3}\text{Si}_4\text{O}_{14.7}]$ bow-tie unit is marked by hatching.

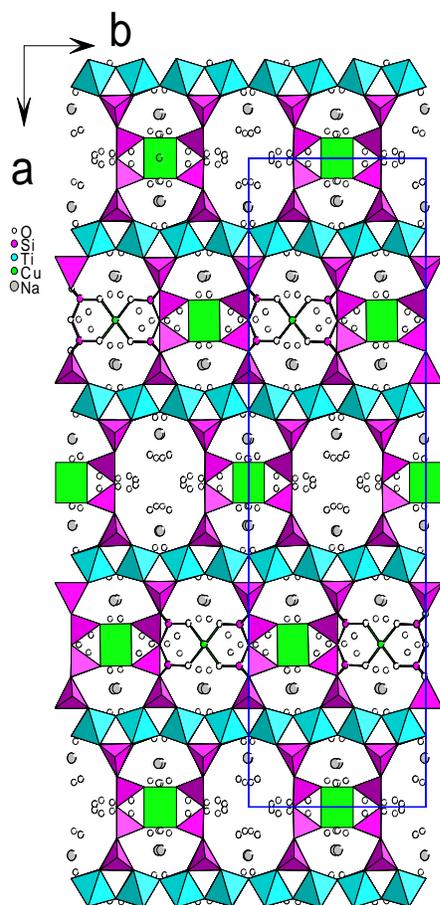


Figure 2. The [001] projection of the structure of **2**. An ordered framework is represented by polyhedra.

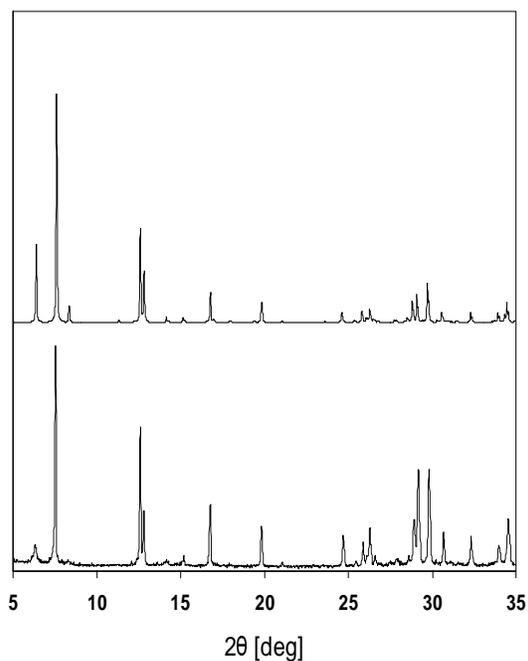
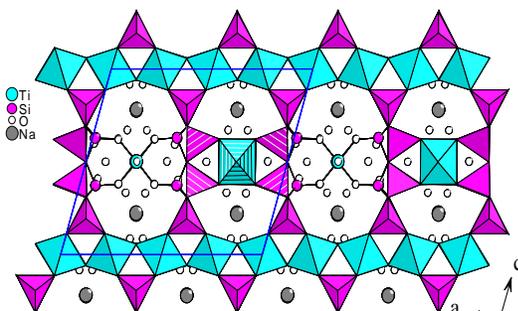


Figure 3. Measured (bottom) and simulated (top) powder X-ray patterns for the compound **2**.

The crystals of compound **2** are pale purple-blue prisms with maximum sizes of 0.1 x 0.04 x 0.04 mm. The crystal structure is closely similar to the mineral narsarsukite $\text{Na}_2\text{TiSi}_4\text{O}_{11}$. [11] In narsarsukite, TiO_6 octahedra form straight 1-dimensional chains by sharing the axial oxygen atom corners. The octahedral chains are laterally connected to tubular chains of silicate tetrahedra to form a framework with Na atoms located in the voids. The silicate tubular chain can be formed by linking 4-rings of SiO_4 tetrahedra. In the structure of **2** (figure 4), about one quarter of the TiO_6 octahedra in the narsarsukite octahedral chain are randomly substituted by CuO_4 squares. The original Ti site is found triply split. Two positions slightly shifted in opposite directions along the chain axis are occupied by Ti atoms each with occupancies of 36 % and 40 % respectively. The third position in the middle of the two Ti positions is occupied by Cu atoms with an occupancy of 24(1) %. The shifting of the Ti positions leads to distorted TiO_6 octahedra with short and long Ti-O bonds along the chain axis. The Ti atoms next to a Cu atom probably have tetragonal pyramidal coordination environments as shown in figure 5, which is supported by the refined occupancies of the axial oxygen atoms.

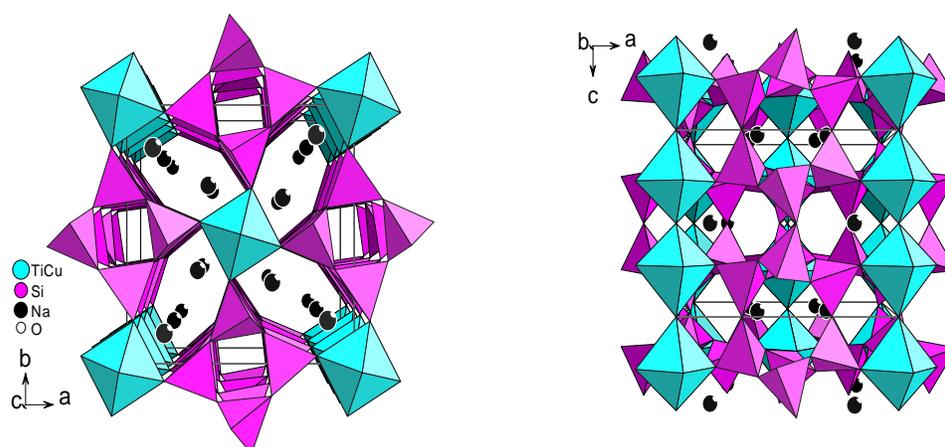


Figure 4. Two views of the crystal structure of **2**.

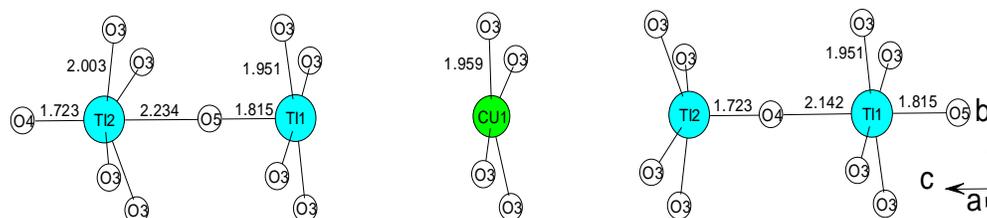


Figure 5. A probable local structure of the octahedral chains in **2**. Bond lengths are given in Å.

Compound **4** is obtained as pale blue prisms with maximum sizes of 0.1 x 0.05 x 0.03 mm. It has a novel crystal structure containing silicate double layers (figure 6). The double layer consists of two single layers related by a pseudo inversion center. The single layer is characterized by maple-leaf like ten-ring voids, and may be constructed from a fundamental single chain of tetrahedra with a periodicity of four. The double layer represents a new type of silicate layer to our knowledge. The double layers are cross-linked by TiO_5 tetragonal pyramids and CuO_4 squares to form a framework with 6- and 8-ring channels. The K atoms are located within the channels. The structure is polar because all the apical oxygen atoms of the TiO_5 tetragonal pyramids point to the same direction. The CuO_4 square is linked to the TiO_5 pyramid by a rather weak bond (3.11\AA) between the Cu atom and the apical oxygen atom of the TiO_5 pyramid to form a dimer unit. Columns of such dimers are arranged along the $[100]$ direction (figure 7).

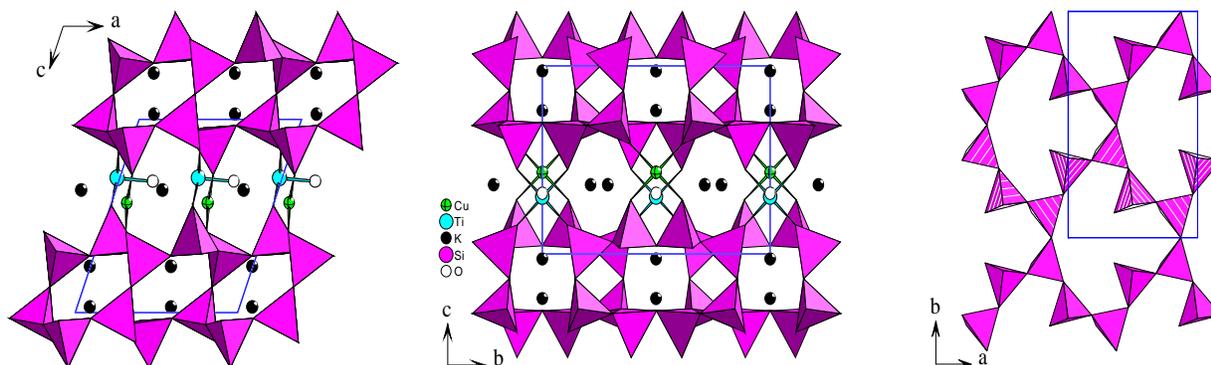


Figure 6. The structure of **4** viewed along $[010]$ (left), $[100]$ (middle) and the silicate single layer (right). A fundamental chain of the single layer is marked by hatching.

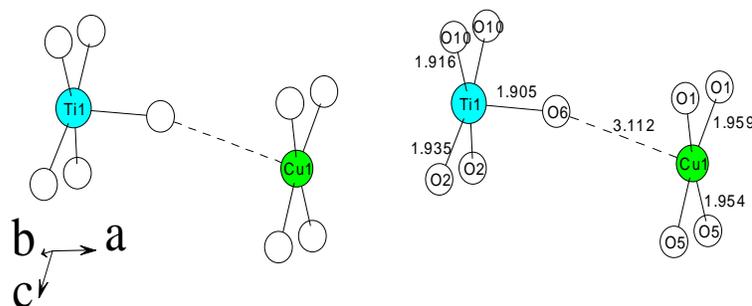


Figure 7. The $[100]$ column of dimers formed by the CuO_4 squares weakly linked to the TiO_5 pyramids.

CONCLUSIONS

The four new copper titanasilicates reported here demonstrate the feasibility of substituting Cu for Ti in silicate frameworks. The substitution can occur both in separated coordination

polyhedra and in extended 1-dimensional units, and in both disordered and ordered ways. Synthesis of Cu - substituted microporous titanosilicate ETS-10 is in progress as the structure of **2** is related to ETS-10 that has straight octahedral chains. [12,13] More copper titanosilicates are anticipated considering the large number of known titanium silicates. A similar synthesis strategy may also be extended to other metal silicates.

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