In order to investigate the crystal chemistry of copper silicates and germanates, natural crystals as well as synthetic samples from multicomponent systems are studied, using crystallographic and thermoanalytical methods.

Dioptase (Structure after Ribbe et al., Am. Min. 62, 807, 1977) can be dehydrated continuously and completely according to the solid solution formula $Cu_6[Si_6O_{18}]·(H_2O)_{6-x}·xH_2O$ with $6 \geq x > 0$. During the dehydration the two long-distance neighbours OH of the Jahn-Teller octahedron $CuO_4·(OH)_2$ are removed, resulting in a $CuO_4$ square coordination. A colour change green/blue/grey is observed during this process. The structure persists, with lattice parameters $a=14.57\text{Å}$, $c=7.78\text{Å}$ for $x=0$ and $a=14.42\text{Å}$, $c=7.74\text{Å}$ for $x=6$. In agreement with other observations (Heide et al., Acta Cryst. B, 425, 1955) hydrothermal rehydration was not possible.

"Dry" dioptase, however, could be re-crystallized hydrothermally to microcrystalline rhombohedra of water-containing dioptase at 250°C and 2kb within 3 weeks. Above 750°C $Cu_6[Si_6O_{18}]$ decomposes into $CuO$ and a still unknown copper silicate, above 850°C into $CuO + SiO_2$, and above 1060°C into $CuO + SiO_2$.

Among chain-structure silicates and germanates, CuGeO$_3$ is the only compound with Biner-Binetke (Völlenkle et al., Min. Chem. 28, 1352, 1967). This chain type is very unstable because of repulsion forces between the small Ge$^{4+}$ and the even smaller Si$^{4+}$ ions, respectively. By hydrothermal synthesis at 800°C and 1 kb a solid solution series Cu(Ge$_{1-z}$Si$_z$)O$_3$ with up to 40% Ge, Si substitution was synthesized. Lattice parameters are $a=4.802\text{Å}$, $b=8.671\text{Å}$, $c=2.943\text{Å}$ for $z=0$ and $a=4.765\text{Å}$, $b=8.520\text{Å}$, $c=2.915\text{Å}$ for $z=0.4$. The chain direction is $\gamma$. As to be expected, the $a$ and $c$ axes and the cell volume shrink with increasing Ge, Si substitution. The surprising enlargement of the $b$ axis is interpreted as a rotation of the CuO$_6$ polyhedra around [001].

Figure: Optic angle $2V_\gamma$ as a function of annealing time $t$. Each curve refers to successive annealing of the same sample at the temperatures indicated. For example: Sample S1A, 800h at 750°C, followed by 200 h at 850°C, and 200h at 950°C, finally by 600h at 1050°C.