

08.4-14 CRYSTAL CHEMISTRY OF COPPER SILICATES AND GERMANATES.

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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.

Diopase (Structure after Ribbe et al., *Am. Min.* **62**, 807, 1977) can be dehydrated continuously and completely according to the solid solution formula $\text{Cu}_6[\text{Si}_6\text{O}_{18}] \cdot (\text{H}_2\text{O})_{6-x} \square_x$ with $6 \geq x \geq 0$. During the dehydration the two long-distance neighbours OH of the Jahn-Teller octahedron $\text{CuO}_4(\text{OH})_2$ 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 $a=14.570\text{\AA}$, $c=7.780\text{\AA}$ for $x=0$ and $a=14.427\text{\AA}$, $c=7.741\text{\AA}$ for $x=6$. In agreement with other observations (Heide et al., *Acta Cryst.* **8**, 425, 1955) hydrothermal rehydration was not possible.

"Dry" diopase, however, could be re-crystallized hydrothermally to microcrystalline rhombohedra of water-containing diopase at 250°C and 2kb within 3 weeks. Above 750°C $\text{Cu}_6[\text{Si}_6\text{O}_{18}]$ decomposes into CuO and a still unknown copper silicate, above 800°C into $\text{CuO}+\text{SiO}_2$ and above 1060°C into $\text{Cu}_2\text{O}+\text{SiO}_2$.

Among chain-structure silicates and germanates, CuGeO_3 is the only compound with Einer-Einfachkette (Völlenknecht et al., *Mh. Chem.* **98**, 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 600°C and 1 kb a solid solution series $\text{Cu}(\text{Ge}_{1-z}\text{Si}_z)\text{O}_3$ with up to 40% Ge, Si substitution was synthesized. Lattice parameters are $a=4.802\text{\AA}$, $b=8.471\text{\AA}$, $c=2.943\text{\AA}$ for $z=0$ and $a=4.765\text{\AA}$, $b=8.520\text{\AA}$, $c=2.915\text{\AA}$ for $z=0.4$. The chain direction is c . 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 $[001]$.

08.4-15 THE UNUSUAL ANNEALING BEHAVIOUR OF EIFEL SANIDINE. By Chr. Zeipert and H. Wondratschek, Institut für Kristallographie der Universität (TH), Postfach 6380, D-7500 Karlsruhe; Germany, Federal Republic.

Slabs of sanidine crystals from the Eifel/West Germany, cut perpendicular to the acute bisectrix, were annealed at temperatures of 750° , 850° , 950° , and 1050°C for 5 to 1600 hours. Changes of Al, Si order were determined by measurements of the optic angle $2V_x$. The values ranged from 10° to 44° , with the optic plane always parallel to (010). The optical homogeneity of the slabs had not changed even after prolonged heating.

Two remarkable observations have been made, see Figure.

- (i) The optic angles have changed after annealing at temperatures as low as 750°C .
- (ii) Under the same heat treatment, previously untreated slabs show considerably larger changes of the optic angles than do preheated ones.

The changes of the optic angles as well as those of the lattice constants (determined by X-rays) may be explained by Al, Si order-disorder transformation. The unusual behaviour might be due to previous exposure to radiation, but in this case the source and kind of radiation are not known.

Figure: Optic angle $2V_x$ 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_{2,4} 800h at 750°C , followed by 200 h at 850°C , and 200h at 950°C , finally by 600h at 1050°C .

