08. INORGANIC AND MINERALOGICAL CRYSTALLOGRAPHY

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08.2–50 SYNTHESIS AND CRYSTAL STRUCTURES OF RE$_2$(SiO$_4$)$_2$Cl AND RE$_3$(SiO$_4$)$_2$OH. BY H. Gerlach, H. Hapelsteine, O. Jarchow, K.-H. Klaska, Mineralogisch-Petrographisches Institut der Universität, Grindelallee 48, 4000 Hamburg 13, West-Germany.

The crystal structures of a series of rare earth-silicates synthesized under hydrothermal conditions (pH 5, b = 800°C) in the RE$_2$-SiO$_4$ and RE$_3$-SiO$_4$-OH systems have been determined as a further advance in the development of crystal chemistry of RE-silicate compounds. The new compounds RE$_2$(SiO$_4$)$_2$Cl and RE$_3$(SiO$_4$)$_2$OH show isotypic structures.

Structural studies have been done for the compounds Sm$_3$(SiO$_4$)$_2$Cl and La$_3$(SiO$_4$)$_2$Cl. X-ray diffraction patterns indicated that Sm$_3$(SiO$_4$)$_2$Cl is orthorhombic, space group Pnma, a = 7.028 Å, b = 18.042 Å, c = 6.777 Å, Z = 4. This structure is isotypic with Yb$_3$(SiO$_4$)$_2$Cl which has previously been synthesized on EIR (Inorg. Chem. 12, 1973, 1140–1143). A single-crystal X-ray study shows a new structure type for La$_3$(SiO$_4$)$_2$Cl. The crystal structure was solved by direct methods and refined by least squares procedures. In the space group C2/c, a = 14.470 Å, c = 6.313 Å, c = 0.826 Å, Z = 9 and Z = 2.

Analyses of this series of compounds revealed the dependence of the character of crystal structures on the size of the RE-ion. The symmetry decrease from orthorhombic to monoclinic with increasing size of the RE-ion. The reason of symmetry-change is the different coordination-behaviour of the small and the large RE-ions. Sm in Sm$_3$(SiO$_4$)$_2$Cl is 8-coordinated in form of Sm(10)Cl$_4$- and Sm(2)O$_6$Cl$_4$-polyhedra, while La in La$_3$(SiO$_4$)$_2$Cl is surrounded by eight oxygen and one chlorine atom in different polyhedra.

08.2–52 CUBIC [Ni(C$_4$H$_4$)$_2$]H$_2$[Si$_4$O$_8$] 5.33 H$_2$O – A DOUBLE RING SILICATE WITH A ZEOLITE LIKE STRUCTURE AND H$_2$O WATER CLUSTERS. BY G. Bissert and F. Liebau, Mineralogisches Institut der Universität Kiel, Germany.

Single crystals synthesized by Gerke et al. (ACS Symposium Series 194, J. S. Falcone Jr., editor, 1982, 305–318) crystallize with space group Fm3c, a = 28.61 (1) Å and Z = 24. The structure was solved by direct methods (MULTAN) and refined to R = 0.059 for 1521 independent reflections.

One tetrabutylammonium and seven H$^+$ ions per four-membered double ring [Si$_4$O$_8$] are present. The H$^+$ ions form short hydrogen bonds of 2.6 Å between terminal oxygen atoms of the double rings. The resulting structure (Fig. 1) resembles that of zeolite A with Si-O...H...O-Si bonds replacing the Si-O-Si bonds of the zeolite. The silicate "framework" contains two types of cages which resemble truncated octahedra and truncated cuboctahedra. The larger cages are occupied by the [Ni(C$_4$H$_4$)$_2$]$_2$H$_2$O$_8$ groups such that the H$_2$O atoms lie in the centres of the "cube faces" common to two large cages and the alkyl groups extend pairwise into these adjacent cages. Each large cage contains 12 butyl groups.

Each truncated octahedron houses eight water molecules with their oxygen atoms located on the threefold rotation axes. Eight such oxygen atoms are arranged as a cube with 0...0 distances of 2.8 Å. In addition eight oxygen atoms from H$_2$O$_2$ are located near the centres of the "hexagons" of the "cube faces" on the threefold axes. They are hydrogen bonded to three of the six terminal oxygen atoms which belong to three different [Si$_4$O$_8$] groups (0...0 distance ca. 2.8 Å) and to the inner water cube with 0...0 ca. 2.8 Å. The resulting (H$_2$O)$_8$ group seems to be the largest 0-dimensional water cluster reported in crystalline state.

Fig. 1. Arrangement of Si atoms (•) and terminal oxygen atoms (○). One half of the unit cell 0 ≤ z ≤ 1/2 is shown. A indicates the centre of one face common to two large cages and is the position of the nitrogen atom of the [Ni(C$_4$H$_4$)$_2$]$_2$H$_2$O$_8$ group.