

## 08.2-50 SYNTHESIS AND CRYSTAL STRUCTURES OF

$RE_3(SiO_4)_2Cl$  AND  $RE_3(SiO_4)_2OH$ . By H. Gerlach, M. Hagelestein, O. Jarchow, K.-H. Klaska, Mineralogisch-Petrographisches Institut der Universität, Grindelallee 48, 2000 Hamburg 13, West-Germany.

The crystal structures of a series of rare earth-silicates synthesized under hydrothermal conditions ( $p=1.5$  kb,  $T=800^\circ C$ ) in the  $RECl_3-SiO_4$  and  $RE_2O_3-SiO_2$  systems have been determined as a further advance in the development of crystal chemistry of RE-silicate compounds. The new compounds  $RE_3(SiO_4)_2Cl$  and  $RE_3(SiO_4)_2OH$  show isotypic structures.

Structural studies have been done for the compounds  $Sm_3(SiO_4)_2Cl$  and  $La_3(SiO_4)_2Cl$ . X-ray diffraction patterns indicated that  $Sm_3(SiO_4)_2Cl$  is orthorhombic, space group  $Pnma$ ,  $a=7.028\text{\AA}$ ,  $b=18.042\text{\AA}$ ,  $c=6.277\text{\AA}$  and  $Z=4$ . This structure is isotypic with  $Yb_3(SiO_4)_2Cl$  which has previously been described by Ayassé and Eick (Inorg. Chem. 12, (1973), 1140-1143). A single-crystal X-ray study shows a new structure type for  $La_3(SiO_4)_2Cl$ . The crystal structure was solved by direct methods and refined by least squares procedures in the space group  $C 2/c$ ,  $a=14.474\text{\AA}$ ,  $b=6.513\text{\AA}$ ,  $c=8.828\text{\AA}$ ,  $\beta=98.33^\circ$  and  $Z=4$ .

Analyses of this series of compounds revealed the dependence of the character of crystal structures on the size of the RE-ions. 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  $Sm_3(SiO_4)_2Cl$  is 8-coordinated in form of  $Sm(1)O_6Cl_2$ - and  $Sm(2)O_7Cl$ -polyhedra, while La in  $La_3(SiO_4)_2Cl$  is surrounded by eight oxygen and one chlorine atom in two different polyhedra.

08.2-51 ON THE CRYSTAL STRUCTURE OF  $NbFe_2P_{12}$ .

By U.D. Scholz and W. Jeitschko, Anorganisch-Chemisches Institut, Universität Münster, D-4400 Münster, West Germany.

Crystals of the new compound  $NbFe_2P_{12}$ , prepared by the tin flux technique, have monoclinic symmetry and the lattice constants  $a = 10.649(1)$ ,  $b = 5.706(1)$ ,  $c = 14.929(2)$  Å,  $\beta = 102.71(1)^\circ$ ,  $V = 885.0$  Å<sup>3</sup>,  $Z = 4$ . The structure was determined in space group  $I2/a$  and refined to a residual of  $R = 0.027$  for 70 variables and 2818 F values. The Nb atoms have eight P neighbors forming a slightly distorted square antiprism (Nb-P distances from 2.54 to 2.66 Å). The Fe atoms are in approximately octahedral P coordination with Fe-P distances between 2.22 and 2.26 Å. All P atoms are four-coordinated either to one metal and three P atoms or to two metal and two P atoms. If all near-neighbor interactions are rationalized by classical two-electron bonds either the Fe atoms obtain on average a  $d^{6.5}$  system with Nb being  $d^0$  or Nb has a  $d^1$  and Fe a  $d^5$  system. With other words there is one electron per formula unit which cannot fully be rationalized. Interestingly the thermal parameters of most atoms have the expected values with the most notable exception of the  $B_{33}$  values of  $1.06$  Å<sup>2</sup> of the Fe atoms. This relatively high thermal parameter is probably due to a positional disorder of the Fe atoms. Very weak superstructure reflections which violate the body centering extinction rules indicate that the Fe atoms occupy ordered positions in a cell of primitive monoclinic symmetry. This order is probably a consequence of the one electron which cannot be readily rationalized. Work on the physical properties and the ordered structure is in progress.

08.2-52 CUBIC  $[N(C_4H_9)_4]H$ ,  $[Si_8O_{20}] \cdot 5.33 H_2O$  - A DOUBLE RING SILICATE WITH A ZEOLITE LIKE STRUCTURE AND  $(H_2O)_6$  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  $Fm\bar{3}c$ ,  $a = 28.61(1)$  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  $[Si_8O_{20}]$  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  $[N(C_4H_9)_4]^+$  such that the N 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 about 2.8 Å. In addition eight oxygen atoms from  $H_2O$  are located near the centres of the "hexagons" of the truncated octahedra on the threefold axes. They are hydrogen bonded to three of the six terminal oxygen atoms which belong to three different  $[Si_8O_{20}]$  groups (0...0 distance ca. 2.8 Å) and to the inner water cube with (0...0 ca. 2.8 Å). The resulting  $(H_2O)_{16}$  group seems to be the largest 0-dimensional water cluster reported in crystalline state.

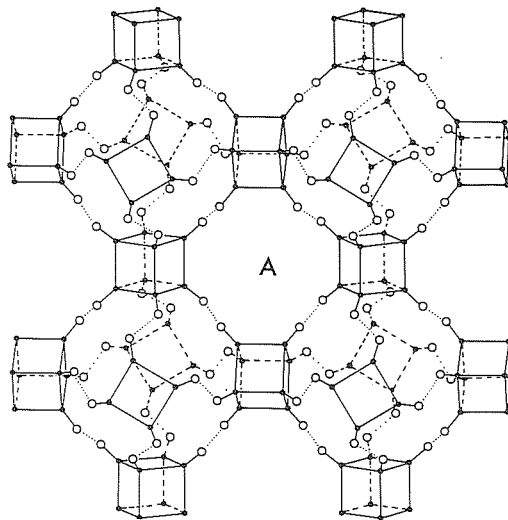


Fig. 1. Arrangement of Si atoms ( $\bullet$ ) and terminal oxygen atoms ( $\circ$ ). One half of the unit cell  $0 \leq z \leq 1/2$  is shown. A indicates the centre of one face common to two large cages and is the position of the nitrogen atom of the  $[N(C_4H_9)_4]^+$  ion.