08.2-50 SYNTHESIS AND CRYSTAL STRUCTURES OF 

\( \text{RE}_3(\text{SiO}_4)_2\text{Cl} \) AND \( \text{RE}_3(\text{SiO}_4)_2\text{OH} \). By H. Gerlach, H. Hapke- 
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The crystal structures of a series of rare earth-sili-
cates synthesized under hydrothermal conditions (psi.35k, T=800'C) in the REI-, SiO1, and RE..-SiO1 systems 
have been determined as a further advance in the development of 
chemical crystallography for the RE-silicate compounds. The new 
compounds \( \text{RE}_3(\text{SiO}_4)_2\text{Cl} \) and \( \text{RE}_3(\text{SiO}_4)_2\text{OH} \) show isotopic 
structures.

Structural studies have been done for the compounds 
\( \text{Sm}_3(\text{SiO}_4)_2\text{Cl} \) and \( \text{La}_3(\text{SiO}_4)_2\text{Cl} \). X-ray diffraction pat-
terns indicated that \( \text{Sm}_3(\text{SiO}_4)_2\text{Cl} \) is orthorhombic, space 
group \( \text{Pnma} \), \( a=14.470\text{Ä}, b=6.513\text{Ä}, c=6.777\text{Ä} \) and \( Z=4 \). 
This structure is isotypic with \( \text{Yb}_3(\text{SiO}_4)_2\text{Cl} \) which has 
group \( \text{Pmna} \) and \( a=14.652\text{Ä}, b=6.572\text{Ä}, c=6.742\text{Ä} \) and \( Z=4 \). 
A single-crystal X-ray study 
shows a new structure type for \( \text{La}_3(\text{SiO}_4)_2\text{Cl} \). The crystal 
structure was solved by direct methods and refined by 
least squares techniques in the space 
group \( \text{Pbnm} \), \( a=14.470\text{Ä}, b=6.480\text{Ä}, c=6.828\text{Ä}, Z=8 \), and \( Z=2 \).

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. \( \text{Sm} \) in \( \text{Sm}_3(\text{SiO}_4)_2\text{Cl} \) is \( s \)-coordinated in form of 
\( \text{Sm}(10)\text{Cl}_4^1 \) and \( \text{Sm}(2)\text{Cl}_6 \)-polyhedra, while \( \text{La} \) in 
\( \text{La}_3(\text{SiO}_4)_2\text{Cl} \) is surrounded by eight oxygen and one 
chlorine \& Atom in two different polyhedra.

08.2-52 CUBIC \( \{\text{Ni(C,H)}_2\}_{2}\text{H}_2\text{O} \) — 
A DOUBLE RING SILICATE WITH A ZEOLITE LIKE 
STRUCTURE AND \( \text{H}_2\text{O} \) WATER CLUSTERS.

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Single crystals synthesized by Gerke et al. 
(ACS Symposium Series 194, J. S. Falcone Jr., 
editor, 1982, 305-318) crystallize with space 
group \( \text{Fm}3c \), \( a=28.61(1)\text{Ä} \) 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 \( \text{H}^+ \) ions per 
four-membered double ring \( \{\text{Si}2\text{O}12\}^\text{2-} \) are present. 
The \( \text{H}^+ \) ions form short hydrogen bonds of 2.6 \( \text{Å} \) 
to terminal oxygen atoms of the double rings. The resulting 
structure (Fig. 1) resembles that of zeolite \( \text{A} \) with \( \text{Si}-0... \text{H}^+-\text{O}-\text{Si} \) 
bonds replacing the \( \text{Si} \)–\( \text{O} \)–\( \text{Si} \) bonds of the zeo-
lite. The silicate "framework" contains two 
types of cages which resemble truncated octa-
hedra and truncated cuboctahedra.

The larger cages are occupied by the \( \{\text{Ni(C, H)}_2\}_{2}\text{H}_2\text{O} \) 
ion such that the \( \text{Ni} \) atoms lie in the centres of the 
"cube faces" common to two large cages and the 
alkyl groups extend pairwise into these adja-
cent 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 \( \text{Å} \). In addition eight oxygen 
atoms from \( \text{H}_2\text{O} \) are located near the centres of the 
"hexagons" of the silicate framework on the 
threefold axes. They are hydrogen bonded 
to three of the six terminal oxygen atoms which 
belong to three different \( \{\text{Si}2\text{O}4\}^\text{2-} \) groups 
(0...0 distance ca. 2.8 \( \text{Å} \)) and to the inner 
water cube with 0...0 ca. 2.8 \( \text{Å} \). The resulting 
\( \{\text{Ni(C, H)}_2\}_{2}\text{H}_2\text{O} \) group seems to be the largest 3-dimen-
sional water cluster reported in crystalline 
state.

Fig. 1. Arrangement of \( \text{Si} \) atoms (.) and ter-
ninal oxygen atoms (o). One half of the unit 
cell 0 \( \leq z \leq 1/2 \) is shown. A indicates the cen-
tre of one face common to two large cages and 
is the position of the nitrogen atom of the 
\( \{\text{Ni(C, H)}_2\}_{2}\text{H}_2\text{O} \) ion.