

**08.2-09** CRYSTAL STRUCTURE OF PRECURSOR TO FLUORIDE-SILICALITE. By J. J. Pluth, G. D. Price and J. V. Smith, Dep. of The Geophysical Sciences, University of Chicago, Chicago, IL 60637, USA and J. M. Bennett, Union Carbide Corporation, Tarrytown, New York, NY 10591, USA.

The crystal structure of a tetrapropylammonium (TPA) fluoride containing precursor to fluoride silicalite, a new microporous crystalline silica polymorph (Flanigen et al. U. S. Patent NM. 4,073,865, Feb. 14, 1978) similar in some properties to silicalite, is reported.

The structure of the precursor ( $a=20.04$ ,  $b=19.92$ ,  $c=13.39\text{\AA}$ ) was determined for interpenetrant twins on (110) with optically monoclinic symmetry and pseudo space-group  $Pnma$ , first to  $R=0.10$  for the silica framework and then to  $R=0.05$  after location of the tetrapropylammonium fluoride complex. The intensities of 8000 X-ray diffractions did not deviate significantly from orthorhombic symmetry, and full account was taken in the refinement of the twinning.

A tetrahedral silica framework with Si-O distances ranging from 1.55 to 1.65\AA was found with topology like that reported for silicalite (Flanigen et al., Nature 271, 512-516, 1978) and characterized by intersecting channels defined by ten-rings.

The nitrogen atom of each TPA complex lies at the near-tetrahedral intersection of a straight and a zig-zag channel, and a propyl limb projects along each channel to approach a propyl limb from the next TPA complex. The neat fit between the silica framework and the TPA complex is consistent with a template mechanism for crystallization.

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**08.2-10** THE CRYSTAL STRUCTURE OF SIALON X-Y-PHASE.

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X-phase is a silicon aluminium oxynitride of approximate composition  $\text{Si}_3\text{Al}_6\text{O}_{12}\text{N}_2$  which occurs in two crystalline forms, high and low. High-X is triclinic with  $a$ , 9.69  $\text{\AA}$ ,  $b$ , 8.56  $\text{\AA}$ ,  $c$ , 11.21\AA;  $\alpha$ , 90.00,  $\beta$ , 124.45,  $\gamma$ , 98.47° and low-X is a superlattice of high-X with  $b_{\text{low}} = 3b_{\text{high}}$ . The crystal structure of low-X consists of mullite-type sheets of alternate chains of octahedra and tetrahedra in the (100) plane joined together either by six tetrahedra arranged in two groups of three as in  $\beta\text{-Si}_3\text{N}_4$  or by a more loosely-grouped arrangement of tetrahedra. The octahedra repeat every 2.8\AA along the y-axis but the tetrahedra are ordered with a repeat distance of  $3 \times 2.8\text{\AA}$ . Twinning occurs on (100) and stacking faults also occur when alternative vacant tetrahedral sites are occupied; this introduces disorder into the structure with high-X corresponding to the case of complete disorder.

**08.2-11** RE-INVESTIGATION OF THE STRUCTURE OF  $\text{Si}_3\text{O}_3(\text{CH}_3)_6$  AT  $-165^\circ\text{C}$ . By R. Pomés, Yu.I. Smolin and Yu.F. Shepelev, Department of X-ray, Faculty of Physics, University of Oriente, Santiago de Cuba, Cuba; and Institute of Silicate Chemistry, Academy of Sciences of the USSR, Leningrad, USSR.

The crystal structure of  $\text{Si}_3\text{O}_3(\text{CH}_3)_6$  has been redetermined and refined by least-squares calculations using X-ray counter data, and with anisotropic thermal parameters for the non-hydrogen atoms.

The space group is  $R3m$  and the cell parameters from diffractometer data are  $a = 4.445$  and  $c = 18.74\text{\AA}$ . The intensity data were measured on a manual single-crystal diffractometer using  $\text{Mo}(\text{K}\alpha)$  radiation and a low-temperature attachment. The initial parameters for the refinement were those reported by G. Peyronel (Atti. Acad. Naz. Lic. Rend. ce Sci. Fis. Mat. 15, 402 (1953); 16, 78, 231 (1954)). The final R index is 0.10.

From our results, we are able to conclude that the molecule of  $\text{Si}_3\text{O}_3(\text{CH}_3)_6$  is not planar as reported by Peyronel. The silicon and oxygen atoms have been located on different levels with a separation of 0.19 \AA between them.

Despite the utilization of low temperature, we observed very strong thermal oscillations, and it was necessary to correct the interatomic distances for thermal motion.

**08.2-12** HIGH PRESSURE SYNTHESIS AND CRYSTAL STRUCTURES OF MODIFIED VANADIUM HOLLANDITES  $\text{A}_2-x\text{V}_8+2x\text{O}_{16+x}$  ( $\text{A} = \text{K}, \text{Rb}$ ). By K.-J. Range, W. Abriel and C. Garbe, Institut für Anorganische Chemie, Universität Regensburg, Regensburg, Bundesrepublik Deutschland.

The title compounds were synthesized by high pressure - high temperature treatment of  $\text{KVO}_3$  and  $\text{RbVO}_3$  in a modified belt-type apparatus. They crystallize in monoclinic space group  $I112/m$  with lattice constants  $a = 10.979(3)\text{\AA}$ ,  $b = 9.383(3)\text{\AA}$ ,  $c = 2.922(1)\text{\AA}$ ,  $\gamma = 92.26^\circ$  ( $\text{A} = \text{K}$ ,  $x = 1.22$ );  $a = 10.979(3)\text{\AA}$ ,  $b = 9.383(3)\text{\AA}$ ,  $c = 2.902(2)\text{\AA}$ ,  $\gamma = 92.26^\circ$  ( $\text{A} = \text{K}$ ,  $x = 1.08$ );  $a = 10.895(3)\text{\AA}$ ,  $b = 9.385(3)\text{\AA}$ ,  $c = 2.909(2)\text{\AA}$ ,  $\gamma = 92.25^\circ$  ( $\text{A} = \text{Rb}$ ,  $x = 1.1$ ). The crystal structures were determined from single crystal data and refined to an R of 0.068, 0.074 and 0.061 for the three compounds. In contrast to the normal vanadium hollandites  $\text{A}_2-x\text{V}_8\text{O}_{16}$  (Range et al., Mat.Res.Bull. (1979) 14, 1463) the large alkali ions alternate randomly with V-O-V groups in the "tunnel" sites, building additional  $\text{VO}_6$  octahedra and completing a nearly close packed oxygen lattice (layer sequence ABAC...). An ordered variant of  $\text{K}_2-x\text{V}_8+2x\text{O}_{16+x}$  was synthesized from  $\text{KVO}_3$  at 3 kbars and  $900^\circ\text{C}$  in a gold capsule. The unit cell is monoclinic, space group  $B112/m$ , with  $a = 21.96(2)\text{\AA}$ ,  $b = 9.383(3)\text{\AA}$ ,  $c = 5.935(2)\text{\AA}$ ,  $\gamma = 92.26^\circ$ , and contains 4 ( $\text{K}_{0.9}\text{V}_{10.2}\text{O}_{17.1}$ ). The crystal structure (1249 unique reflections,  $R = 0.065$ ) shows a pronounced separation of  $\text{K}^+$  and V-O-V groups in different tunnels. A geometrical analysis of the  $\text{V}^{3+}/\text{V}^{4+}$  distribution, based on the different distortions of the  $\text{VO}_6$  octahedra, is given.