08.2-09 CRYSTAL STRUCTURE OF PRECURSOR TO FLUORIDE-SILICALITE. By J. J. Pluth, G. D. Price and J. V. Smith, Dept. Of The Geophysical Sciences, University of Chicago, Chicago, IL 60637, USA and J. M. Bennett, Union Carbide Corporation, Terrytown, New York, NY 10598, 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=13.39Å) 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 6000 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 1.65Å was found with topology like that reported for silicalite (Flanigen et al., Nature 221, 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 next 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-HASE. By P. Korzh, D.P. Thompson and R.E. Jack, Wolfson Institute for High-Strength Materials, Crystallography Laboratory, University of Newcastle upon Tyne, England.

X-phase is a silicon aluminum oxynitride of approximate composition Si3Al08N16, which occurs in two crystalline forms, high and low. "High-X is triclinic with a=9.69 b=8.96 c=11.21Å; α=90.00°, β=124.46°, γ=106.47°. The low-X phase is monoclinic with pseudo space-group Pnma. The crystal structure of low-X consists of Si-Al-O-N sheets alternate with columns of Na+.

The oxygen atom of each Na+ 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 Na+ complex. The next fit between the silica framework and the Na+ complex is consistent with a template mechanism for crystallization.

The silicon and oxygen atoms have been found to be planar, and the nitrogen atoms are not planar as reported by Flanigen et al. (Nature 221, 512-516, 1978). The intensities of 6000 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 1.65Å was found with topology like that reported for silicalite (Flanigen et al., Nature 221, 512-516, 1978) and characterized by intersecting channels defined by ten-rings.

The nitrogen atom of each Na+ 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 Na+ complex. The next fit between the silica framework and the Na+ complex is consistent with a template mechanism for crystallization.

08.2-11 RE-INVESTIGATION OF THE STRUCTURE OF Si12O35(CH3)6 AT -165°C. By K. W. Smith, J. J. Pluth 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 Si12O35(CH3)6 has been determined 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 Rnm and the cell parameters from diffraction data are a=4.445 and c=10.74Å. The intensity data were measured on a manual single-crystal diffractometer using MoKα radiation and a low-temperature attachment. The initial parameters for the refinement were those reported by Flanigen et al. (Nature 231, 490, 1977; 402, 1953; 78, 1954). The final R index is 0.10.

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

The explicit compounds were synthesized by high pressure - high temperature treatment of KVO3 and RbVO3 in a modified belt-type apparatus. They crystallize monoclinic space group I12/m with lattice constants a=10.979(3)Å, b=9.385(3)Å, c=2.902(2)Å, α=92.26°, β=92.26°, γ=92.26° (A=K, x=1.22); a=10.979(3)Å, b=9.383(3)Å, c=2.909(2)Å, α=99.0° (A=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 A2-xV03-x, (Range et al., Acta Chem. Scand. 31, 13-14, 1977) the large alkali ions alternate randomly with V-O-V groups in the "tunnel" sites, building additional V-O octahedra and completing a nearly closepacked oxygen lattice (layer sequence ABAC...). An ordered variant of A3V03S3V6O15 was synthesized from KVO3 at 3 kbars and 900°C in a gold capsule. The unit cell is monoclinic, space-group B112/m, with a=21.96(2)Å, b=9.383(3)Å, c=5.935(2)Å, α=99.0°, and contains 4 (K,0.9V0.17,0.71,1). The crystal structure (1249 unique reflections, R=0.065) shows a pronounced separation of K+ and V-O-V groups in different tunnels. A geometrical analysis of the V3+/V4+ distribution, based on the different distortions of the VO4 octahedra, is given.

08.2-12 HIGH PRESSURE SYNTHESIS AND CRYSTAL STRUCTURES OF MODIFIED VANADIN HOLLANDITES A2-xV03-x, (Range et al., Mat. Res. Bull. 13, 13-14, 1977) the large alkali ions alternate randomly with V-O-V groups in the "tunnel" sites, building additional V-O octahedra and completing a nearly close-packed oxygen lattice (layer sequence ABAC...). An ordered variant of A3V03S3V6O15 was synthesized from KVO3 at 3 kbars and 900°C in a gold capsule. The unit cell is monoclinic, space-group B112/m, with a=21.96(2)Å, b=9.383(3)Å, c=5.935(2)Å, α=99.0°, and contains 4 (K,0.9V0.17,0.71,1). The crystal structure (1249 unique reflections, R=0.065) shows a pronounced separation of K+ and V-O-V groups in different tunnels. A geometrical analysis of the V3+/V4+ distribution, based on the different distortions of the VO4 octahedra, is given.