

08.4-12 X-RAY AND NEUTRON-POWDER STUDY ON ENSTATITE. By H. Schrader, F. Frey and H. Boysen, Institut für Kristallographie und Mineralogie der Universität München, Theresienstr. 41, W-Germany.

Neutron powder diagrams of natural enstatite (MgSiO_3) from Bamble, Norway show a high diffuse background which is obviously caused by the incoherent scattering of hydrogen (talc?) and/or disorder within enstatite. The behavior of the diffuse background and the structural transformations of the (low) clino-, ortho- and protoenstatite by heat treatment was measured in the range from 300K up to 1470K and structure-refinements were carried out. X-Ray photographs of a single crystal enstatite at room temperature point out, that the material consists of ortho and clinoenstatite in a fine intergrowth with stacking faults which lead to diffuse streaks parallel to a^* . The scattered intensities of clino, ortho and proto superimpose in the powder diagram and change their contributions with various heat treatments. In any diagram only two polymorphs were simultaneously found and quantitatively separated by the Rietveld-technique: two diagrams with ortho and clino taken at room temperature from a natural crystal and from a tempered at 1470K and quenched crystal, further diagrams with ortho and proto taken at 1390K and 1470K. The relative volume ratio of the different polymorphs, the structural parameters, an analysis of the diffuse background and the time and temperature dependent transformation behavior will be given.

Work was supported by the BMFT under 03-102A04.

08.4-13 NATURAL AND SYNTHETIC OPALS : TRANSMISSION ELECTRON MICROSCOPY STRUCTURAL STUDY. By J.P. Gauthier, Laboratoire de Minéralogie, Université de Lyon I, 43 Bd du 11 Novembre 1918 - 69622 Villeurbanne Cédex, France.

Precious opal can be considered as a paracrystal when looking its regular structure, which consists in a close-packed stacking of spherulites of amorphous silica. The size of silica balls reaches several hundreds or thousands of angströms in diameter. Up to now, such ordered structures have been mainly investigated by means of reflection scanning electron microscope on fractured or polished and chemically etched surfaces or by conventional transmission on surface replicas. Here is presented a direct TEM observation achieved on ion-beam thinned opals.

Natural gem-opals show perfectly round balls with empty octahedral and tetrahedral vacancies. Some classical features of real crystals appear also in such close-packed stackings : punctual or planar defects, stacking faults, sometimes polytypism, grain boundaries, "amorphous" regions. Conversely, the silica balls of the synthetic precious opal seem slightly distorted (by compression) and the vacancies are filled with small spheres of an unidentified compound much more absorbent than the silica. Further analyses will be undertaken, allowing an open discussion on the synthesis of this opal. In addition, a piece of a common green opal has been thinned and observed in similar conditions. As seen on diffraction patterns and electron micrographs, it crystallizes into spheroids of different sizes. Some of them can be optically observed between crossed polarizers. They have a fibrous texture, radially grown from the nucleation centers.

08.4-14 SIX-COORDINATE SILICON: NEW HIGH PRESSURE SILICATES WITH THE BENITOITE AND WADEITE STRUCTURES. By B.A. Fursenko, Institute of Geology and Geophysics, USSR Academy of Sciences, Novosibirsk, 630090, USSR.

New "mixed-coordinate" compounds with silicon both in six-fold and four-fold coordinations; $\text{BaSi}[\text{Si}_3\text{O}_9]$ and $\text{Rb}_2\text{Si}[\text{Si}_3\text{O}_9]$ were synthesized at 30-40 kbar and 1000-1100°C. Two Ge-analogs of these compounds: $\text{BaGe}[\text{Si}_3\text{O}_9]$ and $\text{Rb}_2\text{Ge}[\text{Si}_3\text{O}_9]$ were synthesized at lower pressures (10 kbar at 1000°C). The powder diffraction patterns were successfully interpreted by analogy with $\text{BaTi}[\text{Si}_3\text{O}_9]$ (benitoite, sp.gr. $P6c2=D_{3h}^2$) and $\text{K}_2\text{Zr}[\text{Si}_3\text{O}_9]$ (wadeite, sp.gr. $P6_3/m=C_{6h}^2$). Rb-compounds are similar to the high pressure phases of $\text{K}_2\text{Si}[\text{Si}_3\text{O}_9]$ and $\text{K}_2\text{Ge}[\text{Si}_3\text{O}_9]$ first synthesized by N. Kinomura et al. (Mineral. Mag. (1975) 40, 40I). Six-fold coordination of silicon in benitoite structure type was not reported previously.

Lattice parameters of hexagonal HP-phases (Å)

	$\text{BaSi}[\text{Si}_3\text{O}_9]$	$\text{BaGe}[\text{Si}_3\text{O}_9]$	$\text{Rb}_2\text{Si}[\text{Si}_3\text{O}_9]$	$\text{Rb}_2\text{Ge}[\text{Si}_3\text{O}_9]$
a_0	6.4995(2)	6.5820(2)	6.7323(2)	6.7842(3)
c_0	9.3503(5)	9.5376(5)	9.5344(4)	9.6450(7)

The new synthesized compounds belong to a narrow circle of substances in which silicon adopts the six-fold coordination by oxygen at relatively low pressures (Liebau, Bull. Minéral. (1971) 94, 239). Their structure involves a peculiar framework built from corner-linked $[\text{SiO}_4]$ -tetrahedra (forming $[\text{Si}_3\text{O}_9]$ -rings) and $[\text{SiO}_6]$ -octahedra with Ba and Rb occupying the large cavities. Similarly to germano-germanates, one may regard these compounds as silico-silicates. Indeed they are closely related to corresponding Zr-, Hf-, Sn-, Ti- and Ge-silicates as it is confirmed by a regular variation of lattice constants in the series of isostructural compounds. Lattice parameters a_0 and c_0 decrease linearly with the six-coordinate cation radius (from Zr^{4+} to Si^{4+}). It can be visualized as contraction of $[\text{MO}_6]$ -octahedra, the rings of $[\text{SiO}_4]$ -tetrahedra being practically the same in dimension. Deviations from linear relationship in the case of $^{VI}\text{Si}^{4+}$ is accounted for by this cation being very small causing a drastic increase in repulsive forces between neighbour oxygen atoms in octahedron and preventing it from the further contraction.