ESRF	**Experiment title:** Modulated Tridymite	**Experiment number**: CH-1625
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Shifts: 3	**Local contact(s)**: Dr. Michaela Brunelli	*Received at ESRF:*

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Report:

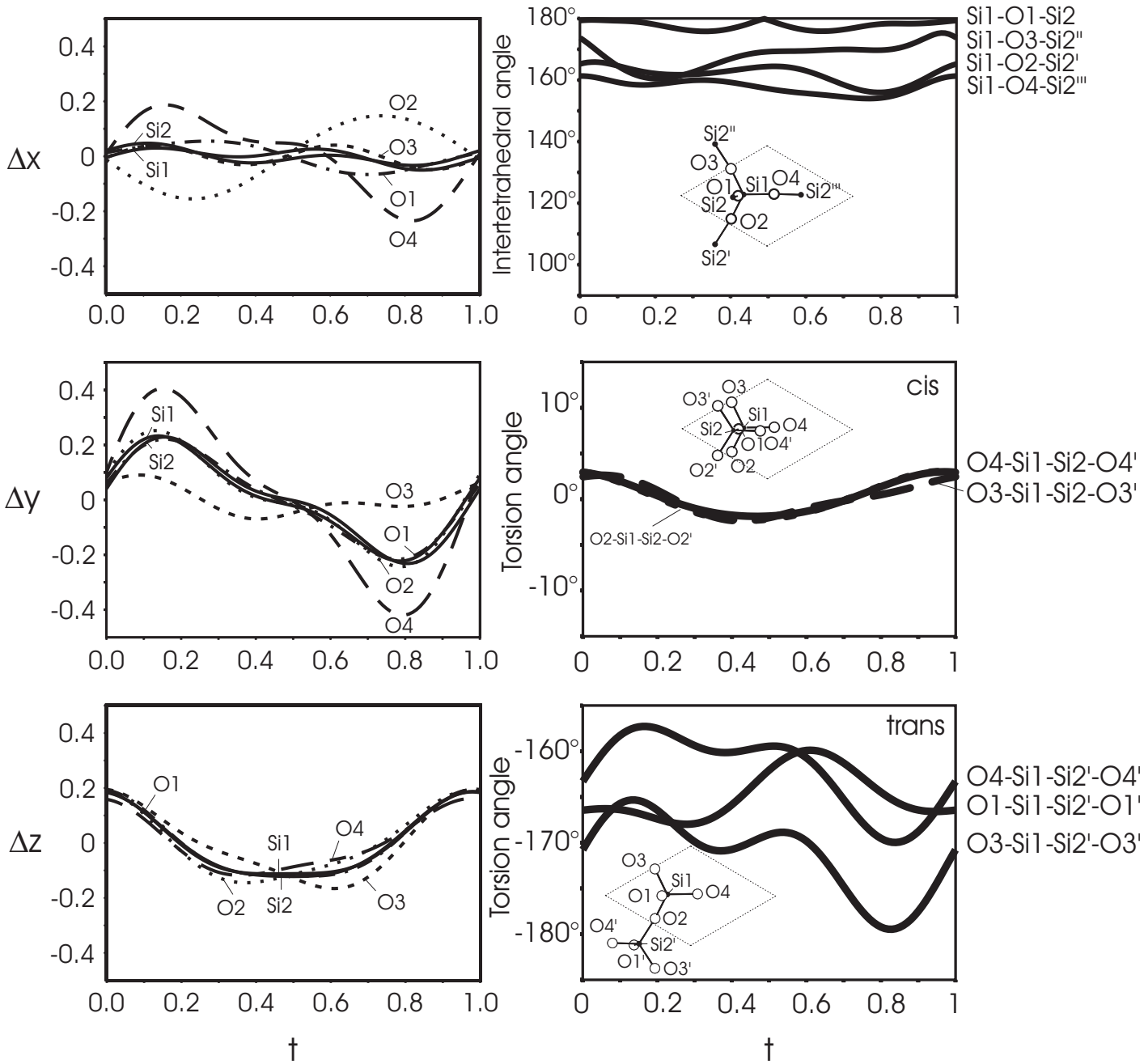
Upon heating, monoclinic SiO_2 tridymite shows a cascade of displacive phase transitions: Cc <115°C> $P2_12_12_1$ <150°C> $P112_1(\alpha\beta0)$ <200°C> $C222_1$ <400°C> $P6_3/mmc$ (Nukui, Nakazawa, Akao, 1978). Successive condensation of vibrational rigid unit modes of corner-sharing $SiO_{4/2}$ tetrahedra are assumed to be responsible for the transformation sequence (Pryde, Dove 1998). Quenching from high temperatures produces a different incommensurate tridymite modification which persists at room temperature. Heating this incommensurate tridymite leads to a variant transformation path: $Cc(\alpha0\gamma)$ <65°C> $P2_12_12_1(\alpha0\gamma)$ <110°C> $C222_1(0\beta0)$ <150°C> $P112_1(\alpha\beta0)$ <200°C> $C222_1$ <400°C> $P6_3/mmc$ with a sequence of four modulated phases below 200°C (Graetsch 1998). The incommensurate phases between 65 and 200°C are only poorly characterized and it was intended to refine the crystal structures of these phases at various temperatures.

After recording a diagram at room temperature, the sample was heated stepwise to 70, 90, 115, 130 and 165°C. High resolution powder diffractograms were recorded in the range from 2.5 to 60° 2 theta at a wavelength of 0.85066 Å. The capillary was rotated during the measurement and heated with a hot air blaster directed at right angle to the rotation axis.

The x-ray powder patterns obtained at room temperature and at 165°C displayed incommensurate low tridymite ($Cc(\alpha0\gamma)$ and intermediate tridymite ($P112_1(\alpha\beta0)$, respectively, as the only phase. The diffractograms recorded at 70, 90, 115 and 130°C showed the coexistence of two tridymite phases which is probably caused by a temperature gradient in the capillary.

Up to now only the crystal structure of the intermediate tridymite phase at 165°C was refined using the program Jana2000 (Petricek & Dusek 2000). The superspace group is $P112_1(\alpha\beta0)$. Soft constraints of 1.60(1) Å were set on the intratetrahedral Si-O bonding distances. The O-Si-O tetrahedral angles were restrained to 109.5(5)°. Refinement with individual anisotropic thermal displacement parameters and individual harmonic modulation functions for all 6 atoms in the asymmetric unit resulted in profile R-values of Rp = 3.34, Rwp = 5.13 (Rwp(exp) = 3.72) and gof = 1.38 for 98 parameters. Strongly anisotropic ADP's indicate the presence of residual thermal vibrations of rigid $SiO_{4/2}$ tetrahedra. The satellite reflections are due to a frozen rigid unit mode. The satellites are broader than the main reflections which can be ascribed to the temperature gradient

in the sample as the wavelength of the modulation varies much stronger with the temperature as the lattice parameters of the basic structure. The modulation consists of rotations and tilting of the tetrahedra with mainly transversal displacements of the atoms. The wave vector is r = 0.054 a* + 0.004 b* at 165°C. The largest amplitude is ca. 0.4 Å for oxygen and ca. 0.2 Å for silicon. Si-O-Si intertetrahedral and O-Si-Si-O torsion angles vary by more than 10°. The torsion rotations are larger for pairs of adjacent tetrahedra in trans configuration than for those in cis configuration. This is thought to be a consequence of different repulsive forces in both configurations acting between oxygen atoms belonging to neighboring tetrahedra. The shape of six-membered rings of tetrahedra, which make up the crystal structure, changes from almost hexagonal to ditrigonal along the modulation vector.



Incommensurate modulation of intermediate tridymite. Left side: positional displacements in Å; right side: intertetrahedral Si-O-Si angles and selected torsion angles as a function of the internal t coordinate.

References

Graetsch, H. Am. Mineral. 83 (1998) 872-880

Nukui, A., Nakazawa, H., Akao, M. Am. Mineral. 63 (1978) 1252-1259

Petricek, V., Dusek, M.: *Jana2000*. Institute of Physics, Praha, Czech Republic

Pryde, A.K.A., Dove, M.T. Phys. Chem. Minerals 26 (1998) 171-179