Phase Transitions at Elevated Temperatures of Incommensurate Low Tridymite and a New Intermediate Tridymite Phase

Graetsch, Heribert A.[1]
[1]Ruhr-Universität Bochum, Institut für Geologie, Mineralogie Geophysik

Tridymite has a very flexible framework structure. At least three different forms of SiO_2 tridymite are known to exist at room temperature. Monoclinic low tridymite L1-T_O(MC), pseudo-orthorhombic low tridymite L2-$T_D(PO_{5/10})$ and monoclinic incommensurably modulated L3-T_O(MX-1) can be distinguished by their different superstructures. L3-T_O(MX-1) can be produced from L1-T_O(MC) either by heating and subsequent quenching or by grinding (Hoffmann et al., 1983). Upon heating, L1-T_O(MC) shows a sequence of displacive phase transitions with the following changes of space group symmetries: Cc -> $P2_12_12_1$ -> *incommensurate* -> $C222_1$ -> $P6_3/mmc$ (Nukui et al., 1978). L2-$T_D(PO_{5/10})$ shows a similar behavior. Transition temperatures and temperature ranges of the phases, however, strongly depend on the degree of stacking disorder (Graetsch, Flörke, 1991). L3-T_O(MX-1) has been reported to show additional intermediate modulated phases below 100°C (Graetsch 1998) or to transform to pseudo-orthorhombic tridymite L2-$T_D(PO_{5/10})$ (Löns, Hoffmann, 1987)

With x-ray diffraction, a very slightly disordered single crystal of incommensurate L3-T_O(MX-1) was found to transform near 40°C from space group Cc(0) to F1 - a phase very similar to L2-$T_D(PO_{5/10})$ - and at about 80°C to P1. The latter represents a new intermediate form of tridymite. Upon further heating, near 100°C the usual path of phase transitions ($P2_12_12_1$ -> $P2_1(0)$ -> $C222_1$ -> $P6_3/mmc$) is followed. The phase transitions are not fully reversible. Below 200°C, the sequence of phase transitions a series of 5 different modulated structures.

The new phase existing between 80 and 100°C has a the 1 x 3 x 5 superstructure with respect to orthorhombic high temperature tridymite ($C222_1$). The superstructure can be described by two commensurate modulations: one also occurring in L2-$T_D(PO_{5/10})$ with 5 fold c-axis and another persisting above 100°C in high temperature H4-T_O(OP) with 3 fold b-axis as compared to the orthorhombic basic structure. The unit cell contains 120 formula units of SiO_2. A structure model has been developed and refined to R(obs) = 7.36 and a goodness of fit of 1.77 for 4271 reflections and 1083 variable parameters. Due to insufficient number of independent observations only two common isotropic displacement parameters for silicon and oxygen could be determined. Soft constraints were set to the Si-O bonding distance and O-Si-O tetrahedral angles. The shape of the six-membered rings of tetrahedra have both oval and ditrigonal shapes.

References

Löns, J., Hoffmann, W. (1987) Z. Kristallographie 178: 141-143
Hoffmann, W., Kockmeyer, M, Löns, J., Vach, C. (1983) Fortschr. Mineral. 61: 96-98
Nukui, A., Nakazawa, H., Akao, M. (1978) Am. Mineral. 63: 1252-1259
Graetsch, H., Flörke, O.W. (1991) Z. Kristallographie 195: 31-48
Graetsch, H. (1998) Am. Mineral. 83: 872-880

→

Abs. No. **555**
Meeting: **DMG 2008**
submitted by: **Graetsch, Heribert**
email: **heribert.graetsch@rub.de**
date: **0000-00-00**
Req. presentation: **Poster**
Req. session: **S16**