

Crystal structures of the low-temperature quartz-type phases of SiO₂ and GeO₂ at elevated pressure

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Dedicated to Professor F. Liebau on the occasion of his 65th birthday

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Abstract. Lattice parameters and crystal structures of the low-temperature quartz-type ('low-quartz') forms (space group $P3_121$) of SiO₂ and GeO₂ were refined from single-crystal X-ray diffraction data under hydrostatic pressures up to 10.2 GPa for SiO₂ and 5.57 GPa for GeO₂. $R_w(F)$ values range from 2 to 5%.

Hexagonal unit-cell parameters for SiO₂: $a = 4.921(1)$, $c = 5.4163(8)$ Å at ambient conditions; $a = 4.604(1)$, $c = 5.207(1)$ Å at 10.2(1) GPa. For GeO₂: $a = 4.9844(2)$, $c = 5.6477(2)$ Å at normal pressure; $a = 4.750(1)$, $c = 5.548(5)$ Å at 5.57 GPa. Volume decrease, 16% for SiO₂ and 11% for GeO₂ is accomplished mainly by tetrahedral tilting, the rest arising from tetrahedral angle distortion.

GeO₂-quartz is an almost perfect high-pressure model for SiO₂-quartz: At 10 GPa the geometry of the SiO₂-quartz structure approaches that of GeO₂ at ambient pressure (e.g. similar values for c/a , atomic parameters, tetrahedral tilt angle, tetrahedral distortion). These values then further change for GeO₂ with increasing pressure reflecting increasing structural distortion.

The Si—O—Si angle decreases with pressure from 144.2(2) to 130.3(1)°, the Ge—O—Ge angle from 130.0(1) to 123.4(3)°. The Si...Si distance between vertex-connected tetrahedra shrinks from 3.0627(4) to 2.9152(8) Å,

the respective Ge...Ge distance from 3.1515(3) to 3.054(1) Å. Both distances, at maximum pressures, fall slightly below smallest reported values for silicates and germanates at ambient conditions. The variations in the angle T–O–T and the nonbonded distance T...T are nearly independent of changes in the T–O bond lengths.

The shortest O...O distance between unconnected tetrahedra decreases from 3.345(2) to 2.793(2) Å in SiO₂, and from 3.023(3) to 2.809(9) Å in GeO₂. For quartz this distance remains longer than the longest tetrahedral edge, which increases from 2.640(3) to 2.690(2) Å. For GeO₂ however, it shrinks to the second-shortest oxygen–oxygen distance in the structure; only two symmetry equivalent tetrahedral edges are shorter, 2.725(4) Å, at the maximum pressure. The two symmetry equivalent second-shortest inter-tetrahedral O...O distances in GeO₂ decrease from 3.192(2) to 2.926(6) Å, becoming shorter than the largest tetrahedral edge, which increases from 2.903(2) to 2.943(5) Å. Extrapolating these developments, the oxygen atoms would reach positions at the lattice points of a cubic body-centred lattice (Sowa, 1988).

Increasing tetrahedral distortion with pressure is displayed mainly by angle distortion. The quantity, DI(OTO) (Baur, 1974), increases from 0.6 to 2.6% for SiO₂ and from 2.5 to 4.2% for GeO₂. The longer Si–O bond remains constant at 1.614(2) Å, whereas the shorter one decreases from 1.605(2) to 1.599(2) Å. These values reflect the stiffness of the respective bonds. The changes in the Ge–O bond lengths are correspondingly small but are less regular with increasing pressure. The variations of bond angles O–T–O and respective tetrahedral edges are nearly independent of changes in the T–O bond lengths.

Tetrahedral distortion mechanisms are seen to differ in comparing changes in pressure or temperature.

Introduction

Quartz has been the subject of numerous studies. Among the many reasons are: its importance as a mineral, its interesting physical properties, its commercial importance as a piezoelectric material and as a component of glass, and its comparatively simple crystal structure.

For SiO₂ the low-quartz form is the stable phase at ambient conditions. At room temperature coesite becomes the stable phase above 2 GPa, and stishovite above 8 GPa (for the phase boundaries see Akaogi, Navrotsky, 1984). However, at room temperature the low-quartz form is preserved metastably to approximately 15 GPa. Above this pressure it transforms, in a not well understood manner, to an amorphous state (Hemley et al., 1988; Hazen, Finger, Hemley, Mao, 1989; Tattevin et al., 1990).

