

The oxygen packings of low-quartz and ReO_3 under high pressure

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Abstract. Changes of structures consisting of corner-connected polyhedra under high pressure can be described by changes of the anion packing.

High-pressure structure data of the low-quartz modifications of SiO_2 and GeO_2 were used to calculate the Dirichlet domains of the oxygen anions. The results indicate that the deformation of the oxygen framework causes the changes of the quartz structure under high pressure. The framework becomes similar to the arrangement of a cubic body-centered lattice. With this model the distortion of the SiO_4 and GeO_4 tetrahedra with increasing pressure easily can be understood.

The behaviour of ReO_3 under pressure can be described by the deformation of a sphere packing which is built up by the oxygen anions.

Introduction

Hazen and Finger (1982) developed the polyhedral approach to describe the changes of crystal structures under high pressure, as well as at high temperature, and with variable composition, respectively. They generally characterize the compression or thermal expansion by means of the behaviour of the individual polyhedra. This model is very useful for qualitative prediction of the bulk modulus and thermal expansion. In the case of structures which are built up of corner-connected polyhedra, mainly polyhedral tilting should be responsible for structural changes. The volume of empty voids in the framework is reduced under pressure, and the compressibility of the crystal structure is much larger than that of a single polyhedron. A well known example for a structure consisting of corner-linked polyhedra is the quartz structure.

At room temperature and 1 bar, SiO_2 crystallizes with the low-quartz structure in the trigonal space group $P3_221$ or in the enantiomorphic space group $P3_121$. For the following investigations $P3_221$ is used with the origin of the unit cell according to the International Tables (1983). The lattice parameters are $a = 4.9134 \text{ \AA}$ and $c = 5.4052 \text{ \AA}$. The oxygen anions occupy the position 6(c) x,y,z , with $x = 0.4141(2)$, $y = 0.2681(2)$ and $z = 0.7855(1)$. The Si^{4+} cations lie on position 3(a) $x,0,2/3$ with $x = 0.46987(9)$ (Le Page and Donnay, 1976).

An isomorphous modification of GeO_2 , which is metastable at room temperature has lattice parameters of $a = 4.9845 \text{ \AA}$ and $c = 5.6477 \text{ \AA}$. The positional parameters are $x = 0.3965(3)$, $y = 0.3022(4)$ and $z = 0.7578(3)$ for the oxygen ions and $x = 0.45130(6)$ for the Ge^{4+} ions (Glinnemann et al., 1989). The oxygen ions form tetrahedra which are centered by Si^{4+} or Ge^{4+} ions.

The effect of pressure on the low-quartz structure of SiO_2 has been already studied several times. There exists one crystal structure refinement using neutron-powder diffraction data (Jorgensen, 1978) whereas three single-crystal X-ray diffraction measurements are reported (d'Amour et al., 1979; Levien et al., 1980; Glinnemann, 1987). Two high-pressure refinements of the structure of the trigonal GeO_2 modification are published. Jorgensen (1978) performed neutron-powder diffraction measurements up to 2.21 GPa and Glinnemann et al. (1989) reported single crystal investigations with X-rays up to 5.57 GPa.

It has been stated by Levien et al. (1980) that the metastable low-quartz modification of GeO_2 is a high pressure model for SiO_2 . In fact, the structure of SiO_2 at 10.2 GPa is similar to that of GeO_2 at ambient conditions. Table 1 shows the most important changes of the low-quartz structure under high pressure. With increasing pressure the c/a axial ratio increases, the SiO_4 and GeO_4 tetrahedra become more and more distorted, and the $(\text{Si,Ge})-\text{O}-(\text{Si,Ge})$ angles decrease. In addition, some inter-tetrahedral oxygen distances are shortened very clearly.

The quartz structure consists of corner-connected tetrahedra, which show cooperative rotation under pressure. The tilt angle δ which describes the tilting of the tetrahedra around the twofold axes (Grimm and Dorner, 1975) in SiO_2 goes from 16.1° at 1 bar to 26.2° at 10.2 GPa. The latter value is similar to that in GeO_2 at 1 bar with $\delta = 26.5^\circ$, which changes to 30.6° at 5.57 GPa (Glinnemann et al., 1989).

The high compressibility of quartz can be explained with the help of the model of polyhedral tilting (Hazen and Finger, 1982). However, it cannot explain the increasing distortion of the tetrahedra with increasing pressure.

The previous authors working on quartz structures (d'Amour et al., 1979; Levien et al., 1980; Glinnemann et al., 1989) suggest that there are two different mechanisms of compression. The changes of the crystal

Table 1. The characteristic changes of the low-quartz structure under high pressure.

<i>P</i> /GPa	<i>c/a</i> ratio	<(O–T*–O)		<(T*–O–T*)
		min	max	
SiO₂				
0.0001 ^a	1.1001	108.70(4)	110.39(4)	143.68(9)
2.07 ^b	1.1050	108.15(4)	110.7(1)	139.9(2)
3.76 ^b	1.1105	107.67(5)	111.3(1)	137.2(2)
4.00 ^c	1.1107	107.6(2)	111.1(2)	137.1(4)
4.86 ^b	1.1138	107.31(5)	111.6(1)	135.8(2)
5.58 ^b	1.1154	107.22(4)	111.8(1)	135.1(1)
6.14 ^b	1.1178	106.97(5)	112.2(1)	134.2(1)
7.20 ^c	1.1221	106.80(6)	112.49(6)	133.1(1)
10.20 ^c	1.1310	106.20(5)	113.72(5)	130.3(1)
GeO₂^a				
0.0001	1.1331	106.28(7)	113.24(6)	130.0(1)
1.07	1.1405	105.7(1)	113.72(9)	128.4(2)
2.18	1.1484	105.3(1)	114.5(1)	126.7(2)
3.74	1.1577	104.6(2)	115.0(1)	125.0(3)
4.53	1.1620	104.2(2)	115.4(1)	124.4(3)
5.12	1.1652	104.1(1)	116.0(1)	124.1(3)
5.57	1.1679	103.5(2)	116.2(1)	123.3(3)

* T = Si, Ge.

^a Le Page and Donnay (1976).^b Levien et al. (1980).^c Glinnemann (1987).^d Glinnemann et al. (1989)

structure of SiO₂ at lower pressures can be described in such a way that tilting of the SiO₄ tetrahedra is predominant. At higher pressures and for GeO₂ the compression is supposed to result from the distortion of the tetrahedra, while tilting is negligible.

Another example, that will be described here, is ReO₃. At ambient conditions it crystallizes in the cubic space group $Pm\bar{3}m$ with lattice constant $a = 3.7504(1)$ Å. The oxygen anions occupy the position 3(*c*) 0,1/2,1/2, the rhenium cations the position 1(*b*) 1/2,1/2,1/2 (Jørgensen et al., 1986). The structure consists of corner-linked ideal ReO₆ octahedra as in a non-distorted perovskite structure. There exist two structural investigations at high pressures. Jørgensen et al. (1986) performed neutron-powder diffraction measurements up to 2.740 GPa, and Schirber et al. (1984) determined the structure of a single crystal at 1.5 GPa. The time-of-flight Laue method was used to collect these neutron-diffraction data. A phase transition takes place at 0.52 GPa leading to space group $P4/mbm$. This structure can also be refined in space group $Im\bar{3}$ but *R*-value tests

