Crystalline Post-Quartz Phase in Silica at High Pressure

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α-quartz, which has been reported to undergo pressure-induced amorphization, was found to transform to a monoclinic, crystalline phase when compressed to 45 GPa at room temperature in a close to hydrostatic, helium pressure medium. The x-ray powder diffraction data obtained could be indexed based on a monoclinic cell, and the intensities are in agreement with a $P2_1/c$ model structure built up of 3×2 zigzag chains of SiO_6 octahedra. This new polymorph of silica, which is metastable under ambient conditions, has been isolated for the first time and is one of several possible competing dense forms containing octahedrally coordinated silicon.

The behavior of silica is of great importance for fundamental solid state physics and chemistry, Earth and materials science. The stable form of silica, α-quartz, is in many ways a model material for studies of chemical bonding, structural phase transitions, glass formation, and mineralogy. Silica exhibits a very rich polymorphism with more than 30 stable or metastable forms, some of which are abundant in nature. The majority of these polymorphs such as high and low cristobalite and quartz, the various tridymites and coesite, which are observed at ambient to moderate (<9 GPa) pressures, are built up of SiO_4 tetrahedra [1,2]. Above these pressures, dense forms [2–5] containing SiO_6 octahedra are reported such as rutile-type silica, stishovite above 9 GPa, and $CaCl_2$-type and α-PbO_2-like forms at pressures beyond 50 GPa. Because of the relatively strong Si-O bonding in silica, there are high kinetic barriers associated with the transitions to stable phases containing octahedrally coordinated silica at high pressure. This results in highly complicated metastable phenomena at high pressure and ambient temperature such as persistence of low-pressure phases and transitions to metastable crystalline and amorphous forms. Because of this great complexity and the difficulties in studying silica (slow kinetics, metastability, low x-ray scattering factors), the results of previous work on α-quartz at high pressure have left many unanswered questions concerning the behavior of this material.

The announcement of the phenomenon of pressure-induced amorphization in α-quartz [6] and α-quartz homotypes [7–9] has generated great interest. Some of the new materials formed at high pressure were found to exhibit unusual properties for amorphous solids such as elastic anisotropy [10] and memory effects [9]. The reported high-pressure behavior of α-quartz is particularly complex [11]: a transformation to a quartz II phase of unknown structure occurs at 21 GPa, and is followed by amorphization above 30 GPa. It has also been suggested that simultaneous formation of an as yet unidentified crystalline form occurs [12]. In contrast, another study claimed that amorphization occurs followed by transformation to poorly crystallized stishovite [13]. The candidate structures for these new phases have been the subject of numerous theoretical studies [14–19]. A large number of structures have been proposed, but their existence has yet to be confirmed by experiment. Poorly crystallized dense phases have recently been observed at high pressure in quartz homotypes, such as GeO_2 [20,21] and ABO_4 (A = Al, Ga, Fe; B = P, As) berlinites [22,23]. This may lead one to question the existence of pressure-induced amorphization in these materials; however, in the case of $FePO_4$, it was clearly shown that transition to the dense $CrVO_4$-type high-pressure phase and amorphization occur simultaneously [24]. In GeO_2, the degree of crystallization of the monoclinic $P2_1/c$ phase was found to be highly dependent on the hydrostatic conditions provided by the pressure-transmitting medium [20]. The present work was undertaken in order to determine whether a similar crystalline, post-quartz form occurs in silica.

Synthetic α-quartz (Prolabo No. 27.625, crystallite size <5 μm) along with a ruby crystal as a pressure calibrant [25] was loaded in a 100 μm diameter, 30 μm thick rhenium gasket between the anvils of a diamond anvil cell (DAC). The gasket hole was then filled with helium at 100 MPa. Helium was chosen as a pressure transmitting medium as our previous work [20] on GeO_2 indicated that hydrostatic conditions play an important role in the crystallization of the possible high-pressure phase. The sample was rapidly pressurized to 45 GPa in 10 s in order that no initial quartz material remained. The pressure was held at 45 GPa for 24 h, then released slowly over a period of 2 days and the material was recovered

in the gasket. The quenched sample was then studied by x-ray diffraction using 40 μm diameter monochromatic beam ($\lambda = 0.416\,93$ Å) and an imaging plate detector on the beam line ID9 at the ESRF synchrotron (Grenoble, France).

The diffraction pattern obtained on the imaging plate (Fig. 1) for the pressure-quenched sample clearly indicates the presence of a crystalline phase. Strong texture effects are observed, and the diffraction lines are quite broad. The pattern was integrated as a function of 2θ using the program FIT2D [26] in order to obtain a conventional, one-dimensional diffraction profile (Fig. 2). It was found that the full width at half maximum (FWHM) of the diffraction lines was typically 4 times larger than those of a silicon standard and the FWHM also varied by $\pm 10\%$ with respect to the average value of 0.24°. This was taken as an indication of internal strain in the sample arising from the crystallization process. The diffraction lines could be readily indexed using the monoclinic $P2_1/c$ model structure identified by theoretical calculations [14]. The refined unit cell constants of this recovered, monoclinic phase of SiO_2 are $a = 7.66(2)$ Å, $b = 4.10(1)$ Å, $c = 5.03(1)$ Å, and $\beta = 117.9(2)°$ (Table I). The present data are not of sufficient quality to permit the structure to be refined due to the relatively poorly crystallized nature of the sample; however, the observed diffracted intensities are in good overall agreement with those calculated (Fig. 2) using the theoretical atomic positions [14] (Table II). The diffraction data indicate that the transition to the monoclinic $P2_1/c$ phase is essentially complete. This structure type was recently found experimentally at high pressure in α-quartz-type GeO_2 [20,21]. It could potentially account for the diffraction lines observed in a quartz sample at a very high pressure of 173 GPa under nonhydrostatic conditions [12,14].
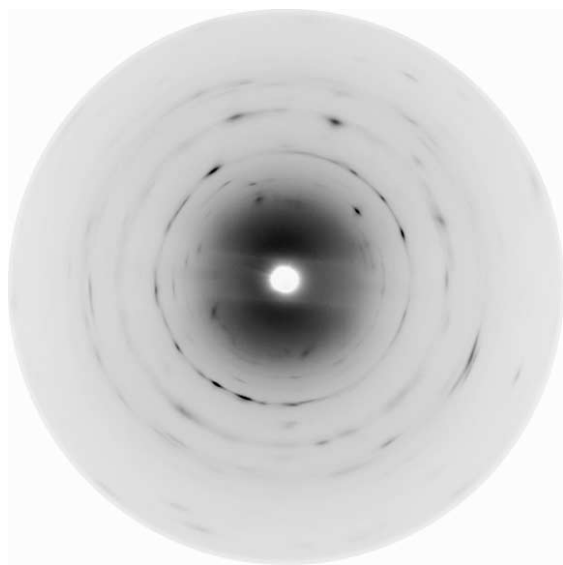
The molar volume of this new form of silica is 14.02 ± 0.12 cm³/mol, is much lower than that of α-quartz (22.70 cm³/mol), and is identical with that of the stable high-pressure form of silica, stishovite (14.03 cm³/mol), within experimental error. The structure of monoclinic $P2_1/c$ silica is built up of 3×2 kinked chains of edge-sharing SiO_6 octahedra [14]. This contrasts with the spirals of corner-sharing SiO_4 tetrahedra, which constitute the relatively open structure of α-quartz ($P3_121$, $Z = 3$). The structure of stishovite is also built up of edge-sharing SiO_6 octahedra, which in this case form straight chains. The monoclinic ($P2_1/c$, $Z = 6$) and the stishovite ($P4_2/mnm$, $Z = 2$) structures are closely related in that they can be considered as different cation-ordered superstructures of disordered Fe_2N-type silica [27] ($P6_3/mmc$, $Z = 1$). These structures are all very close in energy [14] and are consequently in competition. A transition from quartz to stishovite would be highly reconstructive, whereas theoretical calculations [14] identified a diffusionless transformation between the quartz and $P2_1/c$ structures at 25 GPa. This could explain why the former needs thermal activation, while the latter can occur at room temperature albeit with some difficulty as indicated by poorly crystallized state of the sample.

A second x-ray diffraction experiment was performed on ID9 at the ESRF in order to investigate *in situ* the transformation between quartz and this new form of silica. The sample of quartz was loaded in a DAC with the 4:1 methanol:ethanol pressure-transmitting medium. The transition at 19–20 GPa was observed as in previous studies [11,12] with the appearance of new diffraction

FIG. 1. X-ray diffraction pattern of the silica phase obtained after compression of α-quartz to 45 GPa.
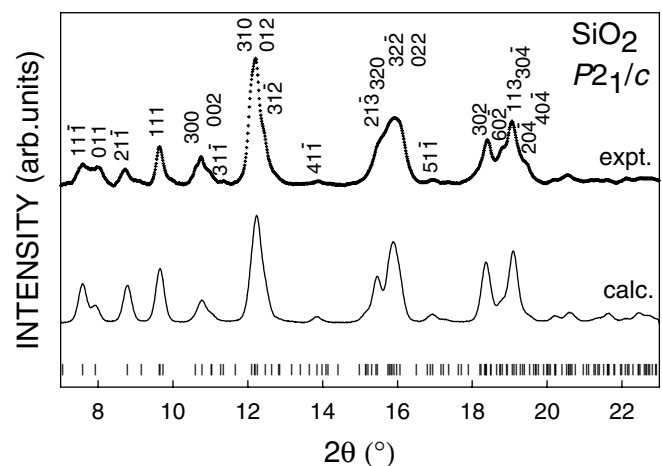

FIG. 2. Experimental and calculated diffraction profiles for the monoclinic $P2_1/c$ phase of silica. The background due to x-ray scattering from air was subtracted from the experimental profile. The calculation was performed using the program FULLPROF [28] with the refined cell constants given in the text and the atomic positions from Table II. A preferred orientation along [001] was included in the calculation in order to partially account for the observed texture in the diffraction pattern. The principal diffraction lines are indexed.

TABLE I. X-ray diffraction data and indexation for the recovered sample of monoclinic silica, space group $P2_1/c$, $Z = 6$. d values calculated using the refined cell constants: $a = 7.66(2)$ Å, $b = 4.10(1)$ Å, $c = 5.03(1)$ Å, and $\beta = 117.9(2)°$.

d_{obs} (Å)	d_{calc} (Å)	hkl
3.161	3.151	$11\bar{1}$
2.976	3.014	011
2.745	2.722	$21\bar{1}$
2.480	2.476	111
2.225	2.220	002
2.175	2.167	$31\bar{1}$
1.968	1.952	012
1.926	1.919	$31\bar{2}$
1.725	1.729	$41\bar{1}$
1.546	1.550	$21\bar{3}$
1.517	1.518	320
1.492	1.491	$32\bar{2}$
1.413	1.415	$51\bar{1}$
1.305	1.306	302
1.278	1.280	$23\bar{1}$
1.258	1.259	113
1.236	1.241	$20\bar{4}$
1.191	1.188	$10\bar{4}$
1.169	1.167	231

lines previously attributed to quartz II (Fig. 3). In addition at 21 GPa, the diffraction lines of the $P2_1/c$ phase were found to appear yielding an extremely complicated diffraction pattern corresponding to a mixture of these two high-pressure forms and some untransformed quartz. The diffraction lines of the latter slowly decreased in intensity with increasing pressure and were no longer present above 35 GPa. Quartz II appears to be an intermediate form as the quantity of this phase increases only between 19 and 26 GPa, whereas above this pressure, transformation of the remaining quartz to the $P2_1/c$ phase continued to occur. The two-phase quartz II $-P2_1/c$ mixture persisted to 40 GPa and down to below 10 GPa on decompression. The recovered sample under ambient conditions was a mixture of the $P2_1/c$ phase with a small amount of quartz with slightly larger than normal cell constants and a trace amount of quartz II. This indicates that most of the quartz II retransformed to quartz on pressure release. In addition, at the phase transition between 19 and 21 GPa, the new lines attributed to quartz II exhibit the same texture as the neighboring low-angle lines of the parent quartz phase. The observed retransformation and the similar

TABLE II. Fractional atomic coordinates [14] for monoclinic SiO_2, space group $P2_1/c$, $Z = 6$.

Atom	Site	x	y	z
Si1	$2b$	1/2	0	0
Si2	$4e$	0.1660	0.5009	0.9688
O1	$4e$	0.0535	0.2429	0.6511
O2	$4e$	0.7208	0.2418	0.1864
O3	$4e$	0.3873	0.2373	0.6597

texture indicate that the structure of this phase bears some relationship to that of quartz. Because of the complicated phase mixtures obtained, it was possible to positively identify only six diffraction lines definitely belonging to quartz II ($d = 3.603$, 2.862, 2.504, 1.962, 1.718, and 1.287 Å at 40 GPa). The three strongest lines ($d = 3.603$, 2.862, and 1.962 Å) may be indexed as the three strongest lines of quartz, 100, 101, and 102, respectively, yielding a hexagonal cell ($a = 4.165$ Å, $c = 4.679$ Å, $Z = 3$) corresponding to a "collapsed quartz" with a molar volume only 12% greater than that of stishovite at 40 GPa. All six lines can be indexed using an orthohexagonal cell with a doubled c parameter. The present diffraction data are too limited to confirm such a supercell, and the structure of quartz II still remains unknown. The pressure dependence of the d spacings for this phase is similar to those for the $P2_1/c$ phase and stishovite, indicating that the coordination number of silicon is greater than four.

It appears that there is competition between the transitions in quartz to quartz II and to the $P2_1/c$ phase. In certain cases, in particular, in the presence of strongly,
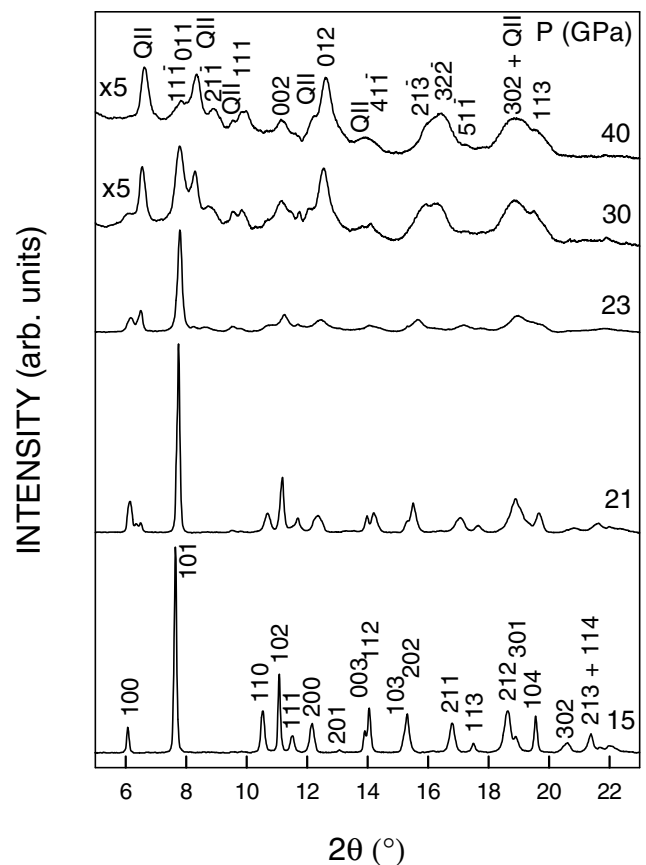

FIG. 3. X-ray diffraction data for SiO_2 as a function of pressure. The background due to the DAC has been subtracted. The intensities in the profiles at 30 and 40 GPa have been multiplied by 5 with respect to the lower pressure data. The principal diffraction lines of α-quartz and the monoclinic phase are indexed in the 15 and 40 GPa profiles, respectively. The lines of quartz II are indicated by QII.

nonhydrostatic stress, the mixture of the three phases with broadened lines may give the impression of an x-ray amorphous material. A highly disordered material may also be produced by fine intergrowth of the two high-pressure phases. Such materials should thus exhibit elastic anisotropy due to domains of the poorly crystallized quartz II and/or $P2_1/c$ phases. These phases may coexist with truly amorphous material.

The present results indicate that the high-pressure behavior of α-quartz depends strongly on the degree of hydrostatic conditions produced by the pressure-transmitting medium used. This can be readily understood as we are dealing with metastable phenomena (stishovite is the stable form of silica from 9 to 50 GPa) and nonhydrostatic stress influences the pathways followed by α-quartz outside its stability field as it transforms towards various denser phases of lower energy. The monoclinic form of silica obtained under close to hydrostatic conditions has a density equivalent to that of stishovite, but lies higher in energy [14]. At room temperature, kinetic factors and the corresponding energy barriers play an essential role in the formation of these metastable silica polymorphs.

In this study, we were able to show that pressurization of α-quartz to 45 GPa under close to hydrostatic conditions yielded a novel crystalline form of silica. This polymorph has been isolated for the first time and is one of several possible competing dense forms containing octahedrally coordinated silicon found in theoretical calculations [14]. This form is metastable under ambient conditions and may potentially occur in nature depending on the pressure-temperature path which the initial quartz material follows.

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