

Tuning Oxygen Packing in Silica by Nonhydrostatic Pressure

Yunfeng Liang,^{1,3} Caetano R. Miranda,^{2,3} and Sandro Scandolo^{2,3}

¹International School for Advanced Studies (SISSA), Trieste, Italy

²The Abdus Salam International Centre for Theoretical Physics (ICTP), Trieste, Italy

³CNR/INFN "Democritos" National Simulation Center, Trieste, Italy

(Received 5 July 2007; published 21 November 2007)

The transformation of SiO₂ from low pressure tetrahedral phases into denser octahedral phases takes place via the collapse of the oxygen sublattice into a close-packed arrangement. The transition paths and the resulting products are known to be affected by the presence of anisotropic stresses, which are difficult to control, so interpretation of the experimental results is problematic. Based on nonhydrostatic molecular dynamics simulations, we show that the collapse of the oxygen sublattice in the specific case of cristobalite is concomitant with the disappearance of tetrahedral units and that non hydrostatic stresses can be tuned to yield phases with different oxygen close-packed sublattices, including the α -PbO₂-like phase, for which we provide a microscopic formation path, and phases with a cubic close packing, like anatase, not seen in experiments yet.

DOI: [10.1103/PhysRevLett.99.215504](https://doi.org/10.1103/PhysRevLett.99.215504)

PACS numbers: 62.50.+p, 61.50.Ks, 64.70.Kb, 91.60.Gf

Understanding the structural response of silica (SiO₂) to the application of elevated pressures has wide-ranging implications in fundamental physics, earth, and material sciences. Following the discovery of stishovite [1], many other dense phases of silica have been synthesized in the laboratory [2–5], or discovered as extraterrestrial minerals [6,7]. The structural collapse of the tetrahedral network, typical of the low pressure phases, into denser lattices with silicon in octahedral (sixfold) coordination has attracted considerable interest in recent years, though its characterization has been problematic, particularly in the case of cristobalite [8–15], due to the strong dependence of the structure of the denser forms on the experimental procedures. In particular, anisotropic (nonhydrostatic) stresses have been shown to affect the experimental outcomes substantially [7,9,11,12]. Room temperature experiments on cristobalite have reported the appearance of a new phase (phase X-I) between 10 GPa and 26–30 GPa [8–14], but attempts to index the x-ray patterns have so far failed due to the poor quality of the diffraction patterns. By further compression, a number of stable or metastable octahedral phases have been reported [8–15]. Experiments at room temperature have described the direct transition of cristobalite into an α -PbO₂-like octahedral phase around 40–50 GPa [11–15]. A similar phase has been detected in the martian meteorite Shergotty, a shocked achondrite probably subjected to pressures of ~30–45 GPa [6,7]. Because experiments show that the α -PbO₂ structure becomes thermodynamically stable only above ~100 GPa [15,16], the occurrence of a transition from cristobalite to metastable α -PbO₂-like within the thermodynamical range of stability of stishovite or of the CaCl₂-like phase is consistent with the existence of a microscopic pathway connecting the two phases.

Molecular dynamics studies would in principle be ideally suited to study microscopic paths, but simulations have only obtained stishovite as the first octahedral phase

[17–19] and stishovite has never been reported so far in experiments starting from cristobalite. Moreover, simulations have never addressed so far the role of nonhydrostatic conditions, which are instead known to play a major role in the compression of cristobalite. In a recent attempt to clarify the microscopic nature of the structural collapse of cristobalite, Huang *et al.* [18], based on a combination of classical and first-principle simulations, have proposed a two-step mechanism whereby the formation of the octahedral units is preempted by a continuous transition of the oxygen sublattice, within a tetrahedral phase (named hp-cristobalite), into a (hexagonal) close-packed lattice. The concept of a two-step transition allows reconciliation of the evidence, from x-ray diffraction, of a low compressibility for phase X-I [8], with that of tetrahedral order within the same phase, as inferred from infrared and Raman spectroscopy [10,20]. However, the behavior of cristobalite would then have to be clearly distinct from that of quartz, where the oxygen sublattice approaches continuously a body-centered cubic (bcc) structure [21,22] and the collapse into a close-packed arrangement is only observed as a result of a sharp transition into post-quartz phases [18]. Moreover, hp-cristobalite is reported to transform, in the second step of the process described in Ref. [18], into stishovite, contrary to experimental findings.

To summarize, while the dominant role of the oxygen sublattice and of nonhydrostatic stresses have been recognized as central in driving the transformation of cristobalite into denser phases, the two aspects have been so far treated independently, and no attempt has been made to rationalize the diversity of the experimental outcomes.

Here we present the results of simulations of the pressure-induced collapse of cristobalite done for different combinations of non hydrostatic stress. The simulations were carried out using an interatomic force field optimized by best fit on first-principles (density-functional theory) calculations [23]. The force field describes the structural

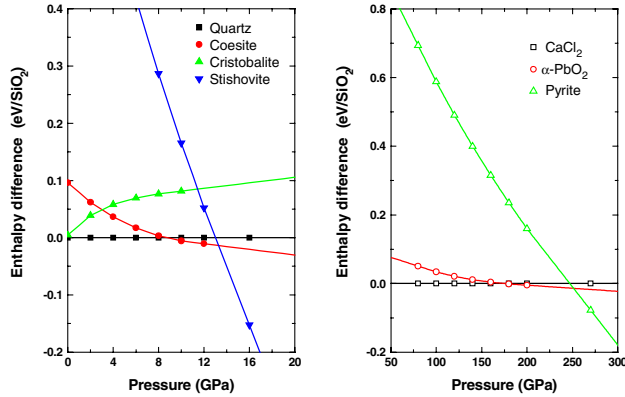


FIG. 1 (color online). Enthalpies versus pressure for a set of SiO_2 polymorphs, calculated with our force field.

and vibrational properties of most SiO_2 crystalline polymorphs, liquid and glass [23–26] better than all the available force fields to which it has been compared so far. In particular, it describes the thermodynamic stability of the crystalline polymorphs of silica (Fig. 1), at the same level of *ab initio* simulations [27], including the pressure dependence of the lattice constant and the phonon softening across the rutile-to- CaCl_2 transition [24,26].

We started our molecular dynamics (MD) simulations from a α -cristobalite cell consisting of 256 SiO_2 formula units ($4 \times 4 \times 4$ unit cells). The MD time step was set to 0.72 fs (30 a.u.). We then applied a stepwise hydrostatic compression at 300 K, with pressure increments of 2 GPa, followed, at each pressure, by an equilibration time of 20 ps. A sharp volume collapse (18%) can be identified in the equation of state, at a pressure of about 25 GPa, with a negligible dependence on the compression rate. Before the collapse, the phase is tetrahedral, shows tetragonal symmetry ($P4_12_12$) and parameters at 24 GPa ($a = 4.28$, $c = 6.10$, $u = 0.36$, $x = 0.23$, $y = 0.22$, $z = 0.22$), in reasonable agreement with the d -spacings obtained by X-ray diffraction at 3.46, 2.94, 2.67, 2.49 and 2.14 Å at the same pressure [8,9,12,13]. Infrared spectra calculated [24] at 0 GPa and 18 GPa are in very good agreement with experiments [20], both in terms of peak position and intensity (Fig. 2). Structural parameters agree with those of hp-cristobalite [18]. However, we disagree on the structure of the oxygen sublattice before the collapse, a crucial point in the analysis of Ref. [18]. To distinguish between bcc and close-packed local coordination we carried out a detailed pair analysis [28,29]. The analysis shows (Fig. 3) that the oxygen sublattice before the volume collapse is still bcc-like, and transforms to close packed only after the collapse, concomitantly with the transition of silicon to octahedral coordination. This is confirmed also by the integral of the O-O pair distribution function (PDF), which reaches a plateau value of 14, typical of bcc local coordination, in correspondence to the first minimum of the PDF, before the transition. Thus, we conclude that the behavior of the oxygen packing in cristobalite is similar to that reported for quartz [18].

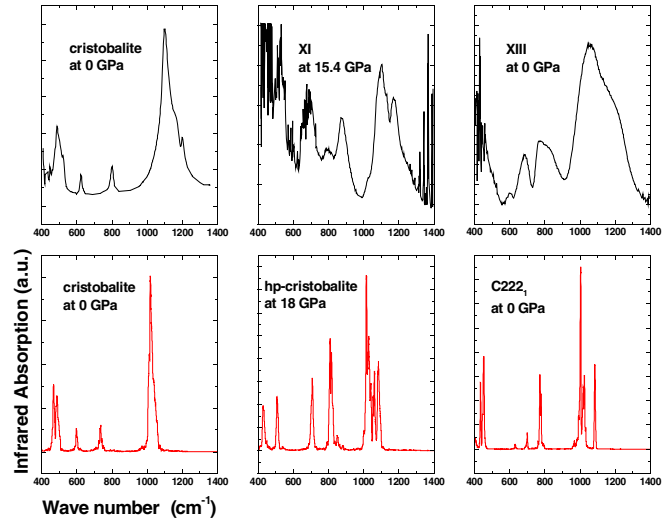


FIG. 2 (color online). Calculated IR spectra (lower panels) compared with experimental data [20] (upper panels) at different pressures. Phase $C222_1$ was recovered from phase $P2_1$ at 44 GPa (see text).

As already mentioned, further compression leads to volume collapse and to the transition to structures with silicon in higher coordination than four.

At variance with the results of Ref. [18], changes in silicon coordination and oxygen close packing take place in a single step. Central to the scope of this work is the finding that the structure resulting from the collapse depends strongly on the stress conditions. In Table I we report the results of compression of cristobalite at zero temperature by subjecting the sample to anisotropic stresses along different directions. Simulations were performed with 32 SiO_2 formula units. Tests with larger (up to 576 SiO_2 f.u.)

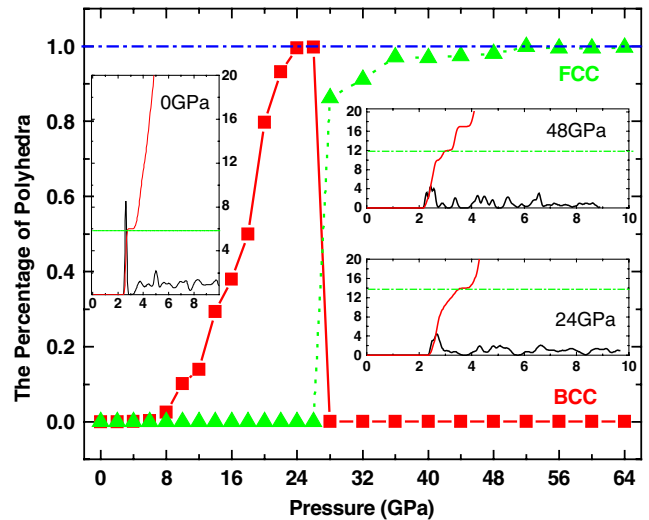


FIG. 3 (color online). Calculated polyhedral changes for hydrostatically compressed cristobalite. Insets show pair distribution functions and average coordination numbers at selected pressures. The y axis in the insets refers to coordination numbers.

TABLE I. Dependence of the resulting structures and oxygen packing geometry on the differential stresses (expressed in percentage of the average of the diagonal values of the stress tensor). Cr. and Stish stand for cristobalite and stishovite, respectively. P_{tr} refers to transition pressure. CP stands for close packing, different from hcp and fcc.

Structure type	Oxygen packing	Initial structure	Differential Stresses (xx, yy, zz) [%]	P_{tr} [GPa]
hp-Cr.	bcc	α -Cr.	$xx, yy, zz = 0$	~ 10
Anatase	fcc	hp-Cr.	$xx, yy \leq 10; zz \leq 4$	28
PbCl ₂	fcc	hp-Cr.	$xx, yy > 10; zz = 0$	28
α -PbO ₂	hcp	$P2_1$	$xx, yy, zz = 0$	58
$P2_1$...	hp-Cr.	$6 < xx, yy, zz \leq 20$	36–50
$P2_1$...	hp-Cr.	$xx = 0, zz = -yy = 6$	50
Stish.	hcp	hp-Cr.	$xx, yy = -3; zz = 6$	32
Stish.	hcp	hp-Cr.	$xx, yy = -2.5; zz = 5$	34
CaCl ₂	hcp	Stish.	$xx, yy, zz = 0$	50
$P2_1/c$	CP	hp-Cr.	$xx, zz = 5, yy = -10$	48
$P2_1$...	hp-Cr.	$zz = -xx = 5, yy = 0$	52
Pyrite	...	$P2_1$	$xx = yy = -10, zz = 20$	74

and smaller (down to 16 f.u.) cells yielded identical results. Identical results were also obtained by replacing the use of the MD time evolution with a structural optimization (i.e. quenching the structures to zero temperature) at each pressure, indicating that temperature effects are negligible at least at 300 K. As shown in Table I, stishovite could be obtained by applying a small (about 5%–6%) uniaxial compressive component along the bcc [100] axis (or c axis in our setting). Of particular interest is a phase of symmetry $P2_1$ ($z = 4$) obtained for compressive uniaxial components larger than 6%. The phase has silicon in five-fold coordination, and transforms, under further hydrostatic compression to 58 GPa, into the α -PbO₂ phase. The existence of a microscopic path connecting cristobalite to α -PbO₂ explains the observation of α -PbO₂ from the compression of cristobalite at pressures much below the thermodynamic range of stability of the α -PbO₂ phase. The existence of an intermediate phase in the transformation of cristobalite to α -PbO₂ is consistent with the evidence that samples recovered from 40 GPa display an infrared spectrum which does not match neither that of cristobalite nor that of α -PbO₂ [20]. Quenching the intermediate $P2_1$ monoclinic phase to 0 GPa, we obtained a new tetrahedral phase with $C222_1$ ($z = 8$) space group, whose infrared spectrum (Fig. 2) is in very good agreement with the spectrum measured for the phase recovered from compression of cristobalite to 40 GPa [20]. On the other hand the α -PbO₂-like phase obtained at 58 GPa could be recovered to 0 GPa in our simulations, without further transitions. We therefore conclude that the transformation from cristobalite to α -PbO₂-like, proceeds through the formation of an unquenchable intermediate phase and we confirm that the phase recovered from 60–64 GPa in Ref. [13], and from 53.1 GPa in Ref. [8] is predominantly α -PbO₂-like. Finally, anisotropic compression of the $P2_1$ phase leads to the pyrite structure at 74 GPa. Pyrite-like SiO₂ has been reported to form in hydrostatic conditions at about 268 GPa [3] and becomes thermodynamically stable

with our force field at 250 GPa. Our results indicates that anisotropic compression lowers the transition pressure to pyrite considerably. A new octahedral monoclinic phase with space group $P2_1/c$ ($z = 8$) was also obtained, with a close-packed oxygen lattice that is neither hcp nor fcc.

For ideal hydrostatic conditions the structure resulting from the volume collapse is, in our simulation, isostructural to anatase. The phase can be recovered to ambient pressure and the analysis of the structure factor at 0 GPa shows peaks at 3.2, 2.15, 2.05, 1.74, and 1.48 Å which coincide with the peaks observed for the recovered α -PbO₂-like phase, except for an additional peak that the latter has around 2.5 Å [13]. The discrepancy between our simulations and those based on *ab initio* MD, which reported stishovite as an outcome of the collapse [17,18], can be explained by the difference in time scales in the two simulations. A simulation with our force field at a much higher compression rate, comparable to that of *ab initio* MD, yielded in fact a much higher pressure for the volume collapse (40–50 GPa), and stishovite as a product. Neither the anatase nor the stishovite structure have been seen in experiments from cristobalite yet. Whether this discrepancy is due to difficulties in reaching perfect hydrostatic conditions in experiments, or to a systematic error in the calculation of stresses in *ab initio* and classical simulations, or, finally, to kinetic arguments, remains to be seen. Interestingly however, anatase differs with respect to all octahedral forms reported so far by its cubic close-packed (fcc) arrangement for the oxygen sublattice (Fig. 3), as opposed to the hexagonal close-packed arrangement found in all other forms. Monitoring the atomic trajectories of the oxygen sublattice during the collapse to anatase shows that the transition from a bcc to a fcc arrangement follows the Bain path [30], which proceeds through the elongation of one of the bcc [100] axes (Fig. 4). Similarly, the collapse into the hcp oxygen sublattice in stishovite proceeds through the compression of the bcc [100] axis, i.e., along the so-called Burgers path [31]. The above transition path

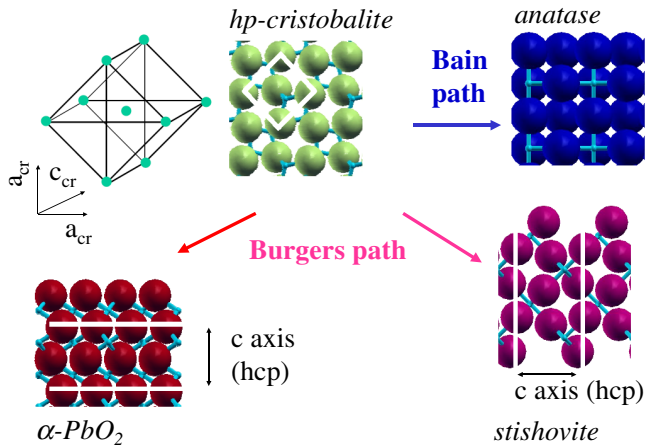


FIG. 4 (color online). Crystallographic orientations of the oxygen quasi-bcc sublattice in the initial phase (hp-cristobalite) and after transformation to octahedral phases. Axes with cr subscripts refer to the principal axes of hp-cristobalite. Notice that the hcp basal planes in α - PbO_2 and stishovite are orthogonal.

analysis and, in particular, the finding that fcc or hcp sublattice formation proceeds through opposite strains along the original bcc [100] axis (Fig. 4), explains the sensitivity of the resulting oxygen sublattice to the residual anisotropic components of the microscopic stress tensor in the sample, and may therefore explain the large diversity of results reported in the literature.

This observation also explains why the transition between CaCl_2 and α - PbO_2 -like phases is very sluggish even at very high temperature [15]. Stishovite and the α - PbO_2 -like phase share the same hcp oxygen sublattice, but the two hexagonal basal planes are orthogonal (Fig. 4), if seen from the perspective of the bcc sublattice from which they both originate; therefore, a large structural reorganization is required to transform them into one another. Different paths (besides Bain and Burgers) can also be activated through particular stress configurations, leading to more complex close packing arrangements. For example, oxygen packing in the octahedral monoclinic phase with space group $P2_1/c$ ($z = 8$) is neither hcp nor fcc. A complete exploration of the stress configurations with off-diagonal terms has not been attempted because the results obtained with diagonal stresses are already richer than expected.

To summarize, we find that the collapse of the tetrahedral network in cristobalite is concomitant with the collapse of the oxygen sublattice from a bcc-like to a close-packed arrangement, and does not take place in two steps, as recently proposed. Our analysis explains the large amount of conflicting experimental evidence regarding the dense phases of silica by invoking the important role of nonhydrostatic stresses in driving the formation of different oxygen packing arrangements, including the appearance of the α - PbO_2 -like phase which, so far, lacked a microscopic connection with the original cristobalite phase, and the suggestion that a phase with a cubic close-

packed arrangement for the oxygen sublattice may be synthesized under appropriate stress conditions. Controlling the amount and geometry of nonhydrostatic components in diamond-anvil cell experiments is challenging, but the present results suggest that efforts in that direction may prove fruitful.

Y.L. acknowledges useful discussions with C.S. Liu. We acknowledge partial support from CNR/INFM through the ESF program “EuroMinSci.”

-
- [1] S. M. Stishov and S. V. Popova, *Geochemistry (USSR)* **10**, 923 (1961).
 - [2] L. S. Dubrovinsky *et al.*, *Nature (London)* **388**, 362 (1997).
 - [3] Y. Kuwayama *et al.*, *Science* **309**, 923 (2005).
 - [4] K. J. Kingma *et al.*, *Nature (London)* **374**, 243 (1995).
 - [5] D. Andrault *et al.*, *Science* **282**, 720 (1998).
 - [6] T. G. Sharp *et al.*, *Science* **284**, 1511 (1999).
 - [7] P. Dera *et al.*, *Am. Mineral.* **87**, 1018 (2002).
 - [8] Y. Tsuchida and T. Yagi, *Nature (London)* **347**, 267 (1990).
 - [9] M. Yamakata and T. Yagi, *Proc. Japan Academy, Series B (Physical and Biological Sciences)* **73**, 85 (1997).
 - [10] R. J. Hemley, C. T. Prewitt, and K. J. Kingma, *Rev. Mineral.* **29**, 41 (1994).
 - [11] L. S. Dubrovinsky *et al.*, *Phys. Earth Planet. Inter.* **143**, 231 (2004).
 - [12] V. B. Prokopenko *et al.*, *J. Alloys Compd.* **327**, 87 (2001).
 - [13] L. S. Dubrovinsky *et al.*, *Chem. Phys. Lett.* **333**, 264 (2001).
 - [14] V. B. Prakapenka *et al.*, *J. Phys. Chem. Solids* **65**, 1537 (2004).
 - [15] S. R. Shieh, T. S. Duffy, and G. Shen, *Earth Planet. Sci. Lett.* **235**, 273 (2005).
 - [16] M. Murakami *et al.*, *Geophys. Res. Lett.* **30**, 1207 (2003).
 - [17] D. D. Klug *et al.*, *Phys. Rev. B* **63**, 104106 (2001).
 - [18] L. P. Huang, M. Durandurdu, and J. Kieffer, *Nat. Mater.* **5**, 977 (2006).
 - [19] S. Tsuneyuki *et al.*, *Nature (London)* **339**, 209 (1989).
 - [20] Y. Yahagi, T. Yagi, H. Yamawaki, and K. Aoki, *Solid State Commun.* **89**, 945 (1994).
 - [21] H. Sowa, *Z. Kristallogr.* **184**, 257 (1988).
 - [22] N. Binggeli and J. R. Chelikowsky, *Nature (London)* **353**, 344 (1991).
 - [23] P. Tangney and S. Scandolo, *J. Chem. Phys.* **117**, 8898 (2002).
 - [24] Y. F. Liang, C. R. Miranda, and S. Scandolo, *J. Chem. Phys.* **125**, 194524 (2006).
 - [25] Y. F. Liang, C. R. Miranda, and S. Scandolo, *Phys. Rev. B* **75**, 024205 (2007).
 - [26] D. Herzbach, K. Binder, and M. H. Muser, *J. Chem. Phys.* **123**, 124711 (2005).
 - [27] T. Demuth *et al.*, *J. Phys. Condens. Matter* **11**, 3833 (1999); B. B. Karki *et al.*, *Phys. Rev. B* **55**, 3465 (1997).
 - [28] J. D. Honeycutt and H. C. Andersen, *J. Phys. Chem.* **91**, 4950 (1987).
 - [29] G. X. Li, Y. F. Liang, Z. G. Zhu, and C. S. Liu, *J. Phys. Condens. Matter* **15**, 2259 (2003).
 - [30] E. C. Bain, *Trans. AIME* **70**, 25 (1924).
 - [31] W. G. Burgers, *Physica (Amsterdam)* **1**, 561 (1934).