High Pressure Polymorphism in Silica

David M. Teter and Russell J. Hemley
Geophysical Laboratory and Center for High Pressure Research, Carnegie Institution of Washington,
5251 Broad Branch Road NW, Washington, D.C. 20015

Georg Kresse and Jürgen Hafner
Institut für Theoretische Physik, Technische Universität Wien, A-1040 Wien, Austria
(Received 9 June 1997)

Fundamental crystal chemistry and first-principles total-energy calculations are used to examine stable and metastable high-pressure silica structures. We find that a large class of energetically competitive phases can be generated from hcp arrays of oxygen with silicon occupying one-half of the octahedral sites. Calculations for specific structures provide an explanation for a number of recent high-pressure results for crystalline silica and allow us to understand the nature of the short- and intermediate-range order in the high-pressure amorphous state. [S0031-9007(98)05385-X]

PACS numbers: 61.50.Ah, 61.50.Ks, 62.50.+p, 64.60.Cn

The nature of silica under pressure has been of long and continuing interest due to its wide ranging implications in geophysics, materials science, and fundamental physics [1]. Since the discovery of stishovite [2], a dense polymorph of silica with octahedrally coordinated silicon, there has been significant interest in the possibility of denser phases at high pressure. It has been shown that stishovite undergoes a displacive phase transformation to the $CaCl_2$ structure type at pressures above 50 GPa [3], in excellent agreement with first-principles predictions. Its behavior at higher pressures is not clear, as new phases have been observed from both static and dynamic compression of amorphous silica [4,5], α-cristobalite [6,7], and α-quartz [8,9], but the analysis of much of this data is difficult and contradictory. Several experimental studies have yielded different results at similar pressure and temperature conditions. Recently, a new post-stishovite phase designated $Pnc2$-type silica has been proposed theoretically [10] and reportedly synthesized at high pressure [5]. There is also experimental and theoretical evidence for the possibility of other post-stishovite phases including those having the Fe_2N [4], α-PbO_2 [8], $I2/a$ [11], baddelyite, fluorite, and $Pa3$ [12,13] structures. Moreover, there is considerable evidence for polymorphism in amorphous silica at high pressure [14], a phenomenon closely related to its pressure-induced amorphization [1]. Hence, it is still unclear what phases of silica are stable at high pressure, what types of metastable phases are possible, and what structural similarities may exist among them.

In this Letter, we show that the structure types of silica with octahedrally coordinated silicon can be visualized and understood in a simple manner. This allows us to methodically generate a series of previously unexamined structures. First-principles calculations of the energetics of these structures show the possibility for extensive polymorphism at high pressure with an essentially infinite number of energetically competitive structures. The results of these calculations provide an explanation for the seemingly disparate experimental results for silica and reveal the nature of the order and disorder in the dense amorphous state.

Many crystal structures can be visualized in terms of close-packed arrays of anions or cations. These arrays can be described as either hexagonal (hcp) or cubic (ccp), or mixtures of the two stacking sequences. For each ion in the array, there are two available tetrahedral interstices and one available octahedral interstice.

Stishovite, the thermodynamically stable form of silica above 7 GPa [1,2], possesses the rutile structure and can be described as a distorted hcp array of oxygen ions with one-half of the available octahedral interstices occupied by silicon ions to form straight chains of edge-sharing SiO_6 octahedra which are corner linked between $ABAB\dots$ layers to form a three dimensional network [similar to $CaCl_2$ as shown in Fig. 1(a)]. The α-PbO_2 structure is observed as a postrutile phase in a number of analogous systems, and can also be described in terms of a hcp packing of oxygen. However, in this case the silicon ions are arranged in such a way as to generate 2×2 zigzag chains of edge-sharing octahedra [Fig. 1(e)]. These structures can also be described as *deconstructions* of their MX superstructures [15], which for hcp and ccp are the NiAs and NaCl structure types. In both structures, the cations occupy all of the octahedral sites between the close-packed anion layers. The removal of one-half of the M ions from the NiAs structure can lead to the generation of the rutile and α-PbO_2 structures. Novel framework structures of MX_6 octahedra can be generated by constructing NiAs or NaCl-type supercells, or combinations of these stackings and methodically removing one-half of the metal ions according to simple rules [15].

We used this method of *deconstruction* to derive new octahedral framework structures. After generating a new structure, a supercell was constructed and allowed to relax under $P1$ symmetry using an enthalpy minimization method combined with the BKS interatomic

0031-9007/98/80(10)/2145(4)$15.00

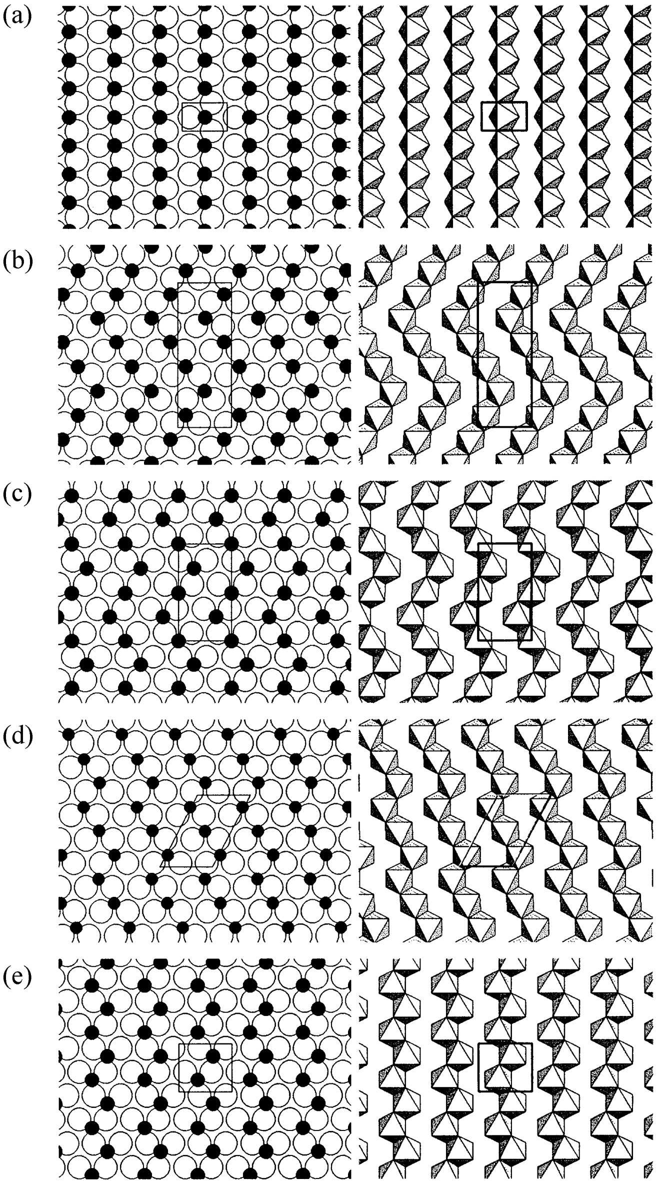

FIG. 1. Representations of the (a) $CaCl_2$, (b) 4×4-SnO_2, (c) 3×3-α-$NaTiF_4$, (d) 3×2 $P2_1/c$, and (e) α-PbO_2 structure types. The left-hand figures show one layer of the *ABAB*... stacking of hcp oxygen anions (white) with one-half of the octahedral interstices filled with silicon ions (black). The right-hand figures show how these patterns form edge-sharing octahedral chains with various degrees of kinking.

potential [16]. This potential has been shown to accurately model the equations of state of both quartz and stishovite [17]. These structures were compressed to 100 GPa and checked for both mechanical and dynamical stability. Structures with competitive enthalpies ($H = E + PV$) were optimized using first-principles calculations, and their equations of state and enthalpies were obtained.

First-principles pseudopotential plane-wave total-energy calculations within the local density approximation (LDA) to electronic exchange and correlation were performed on the model structures [18,19]. This method accurately reproduces many of the physical properties of silica [1,11,20]. Vanderbilt ultrasoft pseudopotentials [21] were generated for silicon and oxygen. The electronic degrees of freedom were minimized using a preconditioned conjugate-gradient method, and both the ionic positions and the cell parameters were fully optimized at all volumes. Because of extremely small energy differences between structures, a convergence of 0.005 eV/SiO_2 unit was employed for energy differences with respect to kinetic energy cutoff and for the total energy with respect to Brillouin zone integration. A plane-wave cutoff of 400 eV was found to sufficiently converge the structures and their energy differences. The Monkhorst-Pack special k-point grids for the Brillouin-zone integration are given in Table I. In addition, we calculated the equations of state of stishovite and $CaCl_2$-type silica using the generalized gradient approximation (GGA) proposed by Perdew *et al.* [22]. We find the

TABLE I. Calculated structural parameters at 120 GPa, space groups, formula units/cell, and Monkhorst-Pack grids for the structures described in the text.

Structure	Atom	x	y	z
$CaCl_2$-type	Si(1)	0	0	0
$Pnnm$ [58] $Z = 2$	O(1)	0.2967	0.3041	0
$a = 3.807$ Å, $b = 3.816$ Å,				
$c = 2.489$ Å				
MP grid = [446]				
4×4 SnO_2-type	Si(1)	0	0.0659	$\frac{1}{4}$
$Pbcn$ [60] $Z = 12$	Si(2)	0.9990	0.3580	0.4164
$a = 3.700$ Å, $b = 4.652$ Å,	O(1)	0.2638	0.1185	0.0274
$c = 12.551$ Å	O(2)	0.7632	0.0980	0.1395
MP grid = [442]	O(3)	0.2422	0.3393	0.1939
3×3 $NaTiF_4$-type	Si(1)	0	0.7921	$\frac{1}{4}$
$Pbcn$ [60] $Z = 8$	Si(2)	0	$\frac{1}{2}$	0
$a = 3.702$ Å, $b = 4.652$ Å,	O(1)	0.7420	0.0286	0.1656
$c = 8.352$ Å	O(2)	0.7621	0.7593	0.4156
MP grid = [442]				
3×2 $P2_1/c$-type	Si(1)	$\frac{1}{2}$	0	0
$P2_1/c$ [14] $Z = 6$	Si(2)	0.1660	0.5009	0.9688
$a = 7.088$ Å, $b = 3.705$ Å,	O(1)	0.0535	0.2429	0.6511
$c = 4.652$ Å	O(2)	0.7208	0.2418	0.1864
$\beta = 118.05°$	O(3)	0.3873	0.2373	0.6597
MP grid = [244]				
2×2 α-PbO_2-type	Si(1)	0	0.1502	$\frac{1}{4}$
$Pbcn$ [60] $Z = 4$	O(1)	0.2576	0.3870	0.4201
$a = 3.711$ Å, $b = 4.651$ Å,				
$c = 4.159$ Å				
MP grid = [444]				
2×2 $Pnc2$-type	Si(1)	0	0	0.1366
$Pnc2$ [30] $Z = 4$	Si(2)	$\frac{1}{2}$	0	0.8362
$a = 4.159$ Å, $b = 3.711$ Å,	O(2)	0.3299	0.2424	0.0995
$c = 4.651$ Å	O(2)	0.1701	0.7424	0.3734
MP grid = [444]				

LDA provides a significantly better prediction of the experimental equations of state [1].

In contrast to previous work on dense silica in which only a few specific structures were examined [1,10,11,20], we generated several thousand structures during the course of this study. We find the most favorable are constructed of edge-sharing octahedral chains with varying degrees of kinking. The density of these structures correlates with the number of kinks along the chains. Among these, stishovite (straight chains) is the least dense, while α-PbO_2 type (the most possible kinks in its 2×2 zigzag chains) is the densest, with an essentially infinite number of intermediate structures. As archetypes, we discuss the results for structures with 4×4, 3×3, and 3×2 kinked octahedral chains in ($ABAB\ldots$) stacking, and compare them to previously examined structures and experimental diffraction data.

In agreement with previous work [3,20] these calculations find stishovite to be the most stable phase to 55 GPa, whereupon it undergoes a displacive phase transition to the $CaCl_2$ structure type. The layers of oxygen anions adopt what appears to be a closer packing than is allowed by the rutile structure. The concept of eutaxy [23] states that structures adopt these packings not because ions behave as "hard spheres," but because these arrays offer effective geometric solutions to maximize the anion-anion and cation-cation separations while maintaining near ideal cation-anion bond lengths. The favorability of these structures at high pressure is determined by a delicate balance between maximizing cation-anion attractions, minimizing anion-anion and cation-cation repulsions, while simultaneously maximizing the density.

Our theoretically predicted sequence of high-pressure structures is as follows (see Fig. 2). At 85 GPa, the α-PbO_2-type becomes the stable phase. It is denser than the $CaCl_2$-type and allows greater oxygen-oxygen separation. The $I2/a$-type [11], is not favored at high pressure due to its low density relative to stishovite. We also find that silica in the baddelyite structure is not energetically competitive with the structures discussed here, and it is mechanically unstable below 100 GPa. Above 95 GPa, the kinked phases presented here are all preferred relative to the $CaCl_2$-type structure. The 4×4 structure type [Fig. 1(b)] has been reported for an epitaxially modified form of SnO_2 [24]. The 3×3 structure type [Fig. 1(c)] is adopted by α-$NaTiF_4$ [25]. The 3×2 structure type [Fig. 1(d)] is previously unreported and found to be only slightly higher in enthalpy than the 2×2 α-PbO_2 type. Finally, at pressures above 205 GPa the $Pa3$-type structure becomes the stable phase. As the intermediate kinked phases are both structurally similar to and enthalpically competitive with the $CaCl_2$ and α-PbO_2 structures, there is considerable possibility that they may exist as metastable phases at high pressure. We now show that these predictions can be used to reinterpret recent experimental high-pressure results for SiO_2.

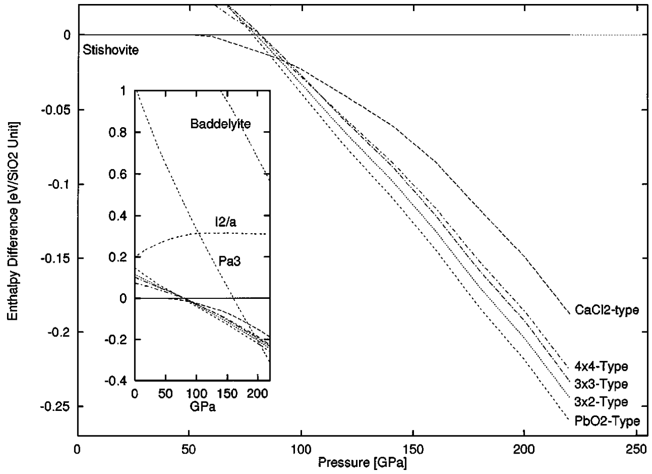

FIG. 2. Enthalpies of silica structures relative to the enthalpy of stishovite as a function of pressure. The inset considers a wider enthalpy range.

Recently, Dubrovinsky *et al.* [5] reported the synthesis of $Pnc2$-type silica through the laser heating of amorphous silica at high pressure. When the $Pnc2$-type structure is examined using first-principles methods, it adopts the higher symmetry $Pbcn$ space group. At any given pressure, the optimized $Pnc2$ and α-PbO_2 structures have the same total energies and simulated diffraction patterns. A simple cell transformation [26] confirms that the two optimized structures (Table I) are identical. It is likely that Dubrovinsky *et al.* synthesized the α-PbO_2 phase based upon the good agreement between experimental and theoretical diffraction patterns. German *et al.* [8] have claimed synthesis of α-PbO_2-type silica from the dynamic compression of quartz, but we find poor agreement between their reported and our theoretical diffraction patterns. Based upon the similarities between the experimental diffraction pattern and those reported for the kinked phases, we believe this experiment resulted in the synthesis of a similar metastable phase, as yet unidentified.

Kingma *et al.* [9] recently reported the synthesis of a dense phase from nonhydrostatic compression of polycrystalline quartz to 213 GPa at room temperature. We find that compression of an 18-atom orthorhombic cell of α-quartz above 25 GPa using an enthalpy minimization scheme with the BKS interatomic potential [16] results in a diffusionless transformation to the 3×2-kinked $P2_1/c$ phase. We generated simulated powder diffraction patterns from LDA-derived $P2_1/c$ unit cells as a function of pressure and found a close correspondence between the experimental and theoretical d spacings (Table II). This good agreement, along with the low enthalpy of the $P2_1/c$ structure, suggests that it may have been synthesized as a metastable phase. Moreover, Liu *et al.* [4] reported synthesis of the defect-niccolite (Fe_2N) structure from laser-heating silica at high pressure. This corresponds to a dense ordered hcp array of oxygen ions with silicon disordered over the octahedral sites. This is consistent with

TABLE II. Comparison of Kingma *et al.* diffraction data to the theoretical diffraction record of the $P2_1/c$-type at a pressure of 173 GPa.

(hkl)	Experimental	$P2_1/c$-type
$(\overline{11}1)$	···	2.82
(011)	2.68	2.69
$(\bar{2}11)$	2.46	2.45
(111)	2.30	2.23
(300)	2.04	2.05
(310)	1.79	1.76
$(\overline{32}2)$	1.36	1.34
(411)	1.19	1.17
	$a = 6.9(2)$ Å,	$a = 6.96$ Å,
	$b = 3.7(2)$ Å,	$b = 3.62$ Å,
	$c = 4.7(3)$ Å	$c = 4.57$ Å
	$\beta = 118.3(2)°$	$\beta = 118.2°$

our finding that there is an essentially infinite number of energetically competitive structures based on dense ordered arrays of oxygen with silicon filling one-half of the octahedral sites. Very recently, another metastable phase that fits this framework has been synthesized from cristobalite [7].

This also explains the nature of short- and intermediate-range structure in high-pressure amorphous silica. The nature of the changes in bonding topology from a tetrahedral random network to denser forms at high pressure has remained elusive [1,14]. Our calculations indicate that the high-density amorphous form (e.g., produced on static compression of silica glass [14]) can be described as a dense array of oxygen ions with silicons disordered over the octahedral sites. Hence, the dense amorphous form may contain significant short- and intermediate-range order, as suggested by Primak [27,28].

In summary, we show there is the possibility for extensive polymorphism in silica at high pressure, with an essentially infinite number of structures that can be described as eutactic hcp arrays of oxygen with one-half of the octahedral interstices occupied by silicon. We find the sequence of stable phases with pressure to be stishovite ⇒ $CaCl_2$-type ⇒ α-PbO_2-type ⇒ $Pa3$-type, but with the possibility for distinct but closely related metastable phases. The results further lead to the view that the high-pressure amorphous state can be described as essentially ordered eutactic arrays of oxygen with the silicon disordered over the octahedral sites.

We thank G. V. Gibbs, L. Stixrude, R. E. Cohen, C. T. Prewitt, and M. P. Teter for helpful discussions. This work is supported by the Center for High-Pressure Research and by the NSF.

---

[1] R. J. Hemley, C. T. Prewitt, and K. J. Kingma, *Silica: Physical Behavior, Geochemistry, and Materials Applications,* Reviews in Mineralogy Vol. 29 (MSA, Washington, DC, 1994).

[2] S. M. Stishov and S. V. Popova, Geokhimiya **10**, 837 (1961).

[3] K. J. Kingma, R. E. Cohen, R. J. Hemley, and H. K. Mao, Nature (London) **374**, 243 (1995).

[4] L. G. Liu, W. A. Bassett, and J. Sharry, J. Geophys. Res. **83**, 2301 (1978).

[5] L. S. Dubrovinsky, S. K. Saxena, P. Lazor, R. Ahuja, O. Eriksson, J. M. Wills, and B. Johansson, Nature (London) **388**, 362 (1997).

[6] Y. Tsuchida and T. Yagi, Nature (London) **347**, 267 (1990).

[7] M. Yamakata and T. Yagi, Proc. Jpn. Acad. B **73**, 85 (1997).

[8] V. N. German, M. A. Podurets, and R. F. Trunin, JETP **37**, 107 (1973).

[9] K. J. Kingma, H. K. Mao, and R. J. Hemley, High Press. Res. **14**, 363 (1996).

[10] A. B. Belonoshko, L. S. Dubrovinsky, and N. A. Dubrovinsky, Am. Mineral. **81**, 785 (1996).

[11] J. S. Tse, D. D. Klug, and Y. Le Page, Phys. Rev. Lett. **69**, 3647 (1992); J. S. Tse, D. D. Klug, and D. C. Allan, Phys. Rev. B **51**, 16 392 (1995).

[12] A. Tressaud and G. Demazeau, High Temp.-High Press. **16**, 303 (1984).

[13] Y. Matsui and M. Matsui, *Advances in Physical Geochemistry*, edited by S. Ghose, E. Salje, and J. M. D. Coey (Springer, New York, 1988), Vol. 7, pp. 129–140.

[14] M. Grimsditch, Phys. Rev. Lett. **52**, 2379 (1984); R. J. Hemley, H. K. Mao, P. M. Bell, and B. O. Mysen, Phys. Rev. Lett. **57**, 747 (1986).

[15] A. F. Wells, *Structural Inorganic Chemistry* (Clarendon Press, Oxford, 1975), 4th ed.

[16] B. W. H. van Beest, G. J. Kramer, and R. A. van Santen, Phys. Rev. Lett. **64**, 1955 (1990).

[17] J. S. Tse and D. D. Klug, J. Chem. Phys. **95**, 9176 (1995).

[18] Calculations were performed using the Vienna *ab initio* simulation program (VASP) developed at the Technische Universität Wien.

[19] G. Kresse and J. Hafner, Phys. Rev. B **47**, 558 (1993); **49**, 14 251 (1994); G. Kresse and J. Furthmüller, Comput. Mater. Sci. **6**, 15 (1996); Phys. Rev. B **54**, 11 169 (1996).

[20] B. B. Karki, M. C. Warren, L. Stixrude, G. J. Ackland, and J. Crain, Phys. Rev. B **55**, 3465 (1997).

[21] D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990); G. Kresse and J. Hafner, J. Phys. Condens. Matter **6**, 8245 (1994).

[22] J. P. Perdew *et al.,* Phys. Rev. B **46**, 6671 (1992).

[23] M. O'Keeffe, Acta Crystallogr. Sec. A **33**, 924 (1977).

[24] V. E. Müller, Acta. Crystallogr. Sec. B **40**, 359 (1984).

[25] P. J. Omaly *et al.,* Acta. Crystallogr. Sec. B **32**, 2106 (1976).

[26] The transformation matrix between the $Pnc2$ (1) and the α-PbO_2 (2) is $a_1 = c_2$, $b_1 = a_2$, $c_1 = b_2$ combined with an origin shift of $[+\frac{1}{2}, +0.5136, \frac{1}{4}]$.

[27] W. Primak, *The Compacted States of Vitreous Silica* (Gordon and Breach, New York, 1975); see p. 81.

[28] These results further suggest that states of order-disorder can be achieved by heating silica under pressure, consistent with the results of Liu *et al.* [4].