

## A new high-pressure silica phase obtained by molecular dynamics

ANATOLY B. BELONOSHKO, LEONID S. DUBROVINSKY, AND NATALYA A. DUBROVINSKY

Theoretical Geochemistry Program, Institute of Earth Sciences, Uppsala University, S-752 36 Uppsala, Sweden

### ABSTRACT

A molecular dynamics study with analytical and ab initio interatomic potentials revealed the possibility of a new silica phase with *Pnc2* structure, which is more stable than stishovite and its  $\text{CaCl}_2$ -like modification at pressures above approximately 120 GPa over a wide range of temperature. Our analysis of simulated X-ray diffraction patterns of various hypothetical post-stishovite phases shows that this new phase should be considered in the treatment of high-pressure experiments involving silica. The new phase might be responsible for the seismic discontinuity at 2728 km depth and should be treated as potentially stable at the pressures and temperatures of the lowermost mantle.

### INTRODUCTION

Silica is one of the most studied materials. It attracts special attention in earth science because in the chondritic model  $\text{SiO}_2$  accounts for about 50% of the composition of the Earth. Since the discovery of stishovite in 1962 by Stishov and Popova, various experimental and theoretical studies have suggested the possible existence of another, so-called “post-stishovite” phase.

Possible post-stishovite phases can be separated into two groups. Experimentally observed crystal-chemical analogs of  $\text{AX}_2$ -type oxides such as  $\alpha$ - $\text{PbO}_2$ , fluorite ( $\text{CaF}_2$ ), cottunite ( $\alpha$ - $\text{PbCl}_2$ ), and baddeleyite ( $\text{ZrO}_2$ ) (Ming and Manghnani 1982; Sato et al. 1991; Tang and Endo 1993) belong to the first group, and the phases proposed for explaining the results of high-pressure experiments on  $\text{SiO}_2$ ,  $\alpha$ - $\text{PbO}_2$ ,  $\text{Fe}_2\text{N}$ , disordered nyceline  $\text{NiAs}$ , and  $\text{CaCl}_2$  structures (Altshuler and Podurec 1973; Hemley 1987; Liu 1982; Simakov 1973; Sekine et al. 1987; Tsuchida and Yagi 1989) belong to the second group. However, the reliability of the interpretations of experimental data is questionable (Lacks and Gordon 1993; Tse et al. 1992). Despite several attempts, and with the exception of the transition to  $\text{CaCl}_2$ -like structure, which is likely a second-order transition, none of the other possible post-stishovite phases with energy lower than that of stishovite was simulated at pressures up to 150 GPa.

We investigated all the suggested post-stishovite phases up to 150 GPa on a systematic basis using molecular dynamics (MD) and lattice dynamics simulation methods with our new analytical (Belonoshko and Dubrovinsky 1995) and previously developed ab initio (TTAM, Tsuneyuki et al. 1988) interatomic potentials (IP), starting from various reasonable post-stishovite structural types. The selection of structural types for our calculations required systematization of data on high-pressure  $\text{SiO}_2$  phases. On the basis of our analysis of possible structures, we restricted starting structures to fluorite,  $\alpha$ - $\text{PbO}_2$ , modified  $\alpha$ - $\text{PbO}_2$  (with space group *I2/a*),  $\alpha$ - $\text{PbCl}_2$ , and baddeleyite  $\text{ZrO}_2$  structural types.

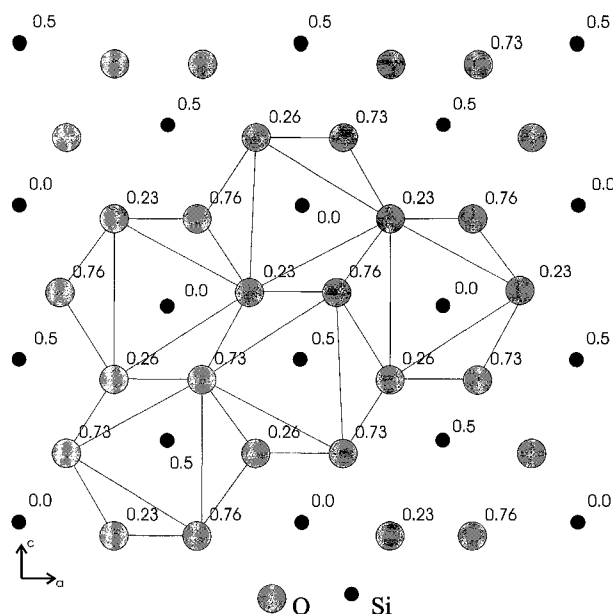
### METHOD AND RESULTS

We used the Parrinello-Rahman (Parrinello and Rahman 1981) modification of the MD method, which allows simulations at constant pressure and the possibility to change the shape and size of the computational cell, an important consideration in the simulation of phase transitions. Coulombic interaction was calculated using the Ewald method. Because there are no a priori good or bad methods, we thoroughly checked the method used in this study against well-established experimental data. We succeeded in reproducing thermoelastic properties of the  $\alpha$ -quartz, coesite, and stishovite as well as the quartz-coesite, coesite-stishovite, and stishovite-melt phase transitions in close agreement with experiment (Belonoshko and Dubrovinsky 1995; Dubrovinsky et al. 1996). This provided us with confidence in the method.

We obtained the following results starting from all the structural types described above and considered to be reasonable high-pressure modifications of  $\text{SiO}_2$ .

First, fluorite, modified fluorite (with space group *Pa3*),  $\alpha$ - $\text{PbO}_2$ , modified  $\alpha$ - $\text{PbO}_2$  (space group *I2/a*), and  $\alpha$ - $\text{PbCl}_2$ -like phases of  $\text{SiO}_2$  are unstable with respect to stishovite at pressures up to 150 GPa and 300 K. This is in agreement with theoretical (Bukowinski and Wolf 1986; Sherman 1993) and experimental (Hemley et al. 1995) studies. The phase closest to stishovite in stability is modified  $\alpha$ - $\text{PbO}_2$  (space group *I2/a*). Stishovite and  $\alpha$ - $\text{PbO}_2$  energies at 300 K and 150 GPa are  $-4352$  and  $-4332$  kJ/mol, respectively. This result is in perfect agreement with that obtained by Tse et al. (1992).

Second, at pressures near 100 GPa, orthorhombic distortion of the stishovite unit cell gradually increases and may be interpreted as a transition from stishovite to a  $\text{CaCl}_2$ -like structure. The value of the distortion increases smoothly with pressure. This possible phase transition, stishovite-to- $\text{CaCl}_2$ -like modification of  $\text{SiO}_2$ , is probably second order. Calculation of elastic constants shows that  $c_{11} - c_{12} = 0$  at 83 GPa and 300 K and indicates that at this pressure stishovite becomes unstable. The transi-



**FIGURE 1.** Projection along the  $b$  axis of the new  $\text{SiO}_2$  structure (space group  $C_{2v}^2 - Pnc2$ ) simulated with MD at 100 GPa and 300 K [ $a = 4.2275$ ,  $b = 3.8900$ ,  $c = 4.7225$  Å,  $Z = 4$ , Si1 (0.0, 0.0, 0.1450), Si2 (0.5, 0.0, 0.8271), O1 (0.8322, 0.2636, 0.3680), O2 (0.6672, 0.7586, 0.1050)]. The numbers indicate the positions of atoms along the vertical axis. This structure (which we call "SBAD") can be considered as intermediate between  $\alpha\text{-PbO}_2$  ( $Pbcn$ ) and baddeleyite ( $P2_1/c$ ). Thin lines show octahedra with an arrangement similar to the  $\alpha\text{-PbO}_2$  structure.

tion to  $\text{CaCl}_2$ -like structure is subtle, and changes of  $a/b$  ratio indicating the transition is observable in MD simulations occur above 90 GPa ( $a/b = 1.053$  at 100 GPa).

Third, starting from the baddeleyite structure, we obtained a structure with the  $Pnc2$  space group (Fig. 1). This structure (which we term "SBAD") can be considered as intermediate between  $\alpha\text{-PbO}_2$  ( $Pbcn$ ) and baddeleyite ( $P2_1/c$ ). Indeed, the octahedra of this structure are gradually distorted and transformed to seven-apex polyhedra (characteristic of baddeleyite) during pressure decrease to 10 GPa. Figure 2 shows that at pressures higher than 70 GPa, the density of SBAD becomes greater than that of stishovite and that at 150 GPa and 300 K the difference is 0.8%. At 300 K and 100 GPa, the total energies of SBAD and stishovite are  $-4437.88$  and  $-4446.35$  kJ/mol, respectively, and at 150 GPa the corresponding energies are  $-4344.69$  and  $-4352.19$  kJ/mol. Taking into account the  $P\Delta V$  term and additional simulations with a pressure step of 10 GPa, we found that at pressures of about 120 GPa and higher, stishovite (or rather  $\text{CaCl}_2$ -like silica) becomes less stable than the SBAD phase. In summary, at 300 K and from ambient pressure up to 150 GPa the sequence of change of  $\text{SiO}_2$  phases is as follows:  $\alpha$ -quartz, coesite, stishovite,  $\text{CaCl}_2$ -type  $\text{SiO}_2$ , SBAD. The transition to the SBAD structure does not depend on temperature within the precision of our pressure step, as

shown by the simulations at 3000 K. Therefore, we conclude that the SBAD phase is the best candidate structure to represent the silica phase in the Earth's mantle close to the core-mantle boundary.

Fourth, Table 1 shows X-ray diffraction patterns (Mo $K\alpha_1$  radiation) of some  $\text{SiO}_2$  phases (including the new phase SBAD, Fig. 1) obtained in this study at 100 GPa and 300 K. Table 1 shows that the shift (or even splitting) of reflections with respect to the stishovite pattern can be easily interpreted as transformation of stishovite to any post-stishovite  $\text{SiO}_2$  phase, including the  $\text{CaCl}_2$ -like modification, as noted by Tsuchida and Yagi (1989). Tse et al. (1992) also noted that the four diffraction peaks observed by Tsuchida and Yagi (1989) and attributed to the  $\text{CaCl}_2$ -like structure are in common with the ideal and modified  $\alpha\text{-PbO}_2$  structures.

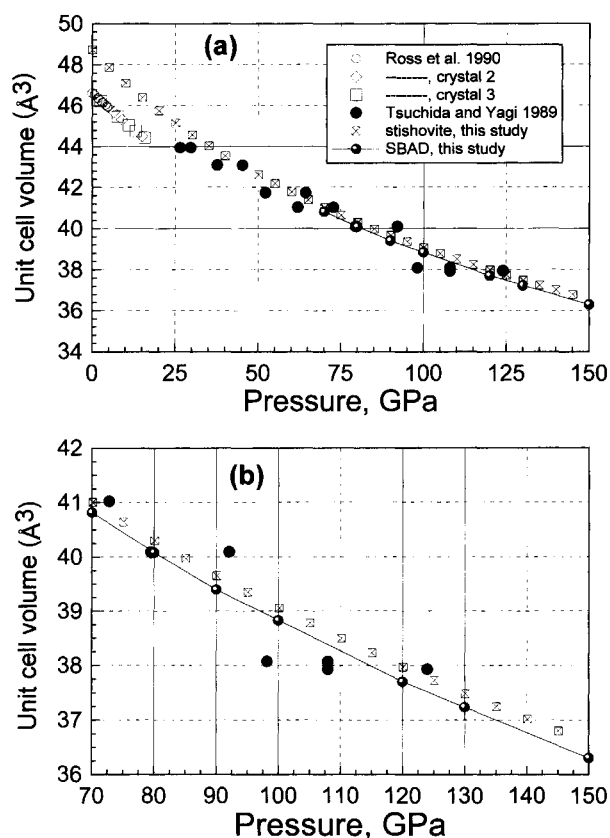
Fifth, the calculations were repeated using the ab initio TTAM potential, and a semiquantitative agreement with the results computed using our potential was obtained. This is especially compelling because these two potentials are derived from completely different methods. This proves that the simulated phase does not depend on a particular potential. Therefore, we suggest that it is necessary to consider the SBAD phase for the reliable interpretation of high-pressure experimental data on phase transformations of  $\text{SiO}_2$ .

## DISCUSSION

Several high-pressure silica phases have been suggested, and many of them are predicted over a broad pressure range. For example, Cohen (1992) and Park et al. (1988) predicted  $Pa3$  phase stability above 150 and 60 GPa, respectively, using the same LAPW method; recent experimental studies (Hemley et al. 1995) have ruled out the existence of this phase up to at least 2 Mbar. Therefore, we did not analyze available theoretical predictions of high-pressure silica phases. Such detailed analysis would go far beyond the scope of this paper.

Two experimental studies have predicted stishovite- $\text{CaCl}_2$ -like phase transition at 100 GPa (Tsuchida and Yagi 1989) and 45 GPa (Kingma et al. 1995). The interpretation provided by Tsuchida and Yagi (1989) is not the only one possible (Tse et al. 1992; see also Table 1). Kingma et al. (1995) experimented in quasi-hydrostatic conditions; in other words, the pressure was not absolutely hydrostatic. Because the pressure at which structural changes were observed depends on the rheology of the pressurizing medium (Kingma et al. 1995; H.-K. Mao, personal communication) and is subject to large hysteresis (40–58 GPa, Hemley et al. 1995), we do not know whether the observed change of Raman spectra (Kingma et al. 1995) is an indication of a phase transition or the activation of inactive modes owing to distortion of stishovite caused by stress. Therefore, the experimental studies do not contradict our prediction of a new phase.

As one can see in Figure 2a, the volume of stishovite at ambient conditions is overestimated by 4%. The volume effect of the suggested transition is about 0.8%.



**FIGURE 2.** Comparison of experimental (Ross et al. 1990; Tsuchida and Yagi 1989) and calculated (present study) volumes of stishovite and SBAD phases. Experimental data of Tsuchida and Yagi (1989) before and after heating are shown. Experimental data of Ross et al. (1990) are shown for three crystals. In **a**, calculated values of volume are shown to be in good agreement with experimental data, though at low pressures the calculated values are slightly higher [note that the potential by Tsuneyuki et al. (1988) produces higher values]. An enlargement of a portion of **a** is shown in **b**, which demonstrates that the SBAD phase is more dense than stishovite (or rather the  $\text{CaCl}_2$ -like modification). The calculated volumes are in reasonable agreement with experimental data (Ross et al. 1990).

However, although the volume of stishovite is not reproduced exactly, the calculated coesite-stishovite phase transition is in reasonable agreement with experiment (Dubrovinsky et al. 1996). This is because the absolute value of the volume is not important; what is important is correct pressure-volume dependence [the dependence is in agreement with experiment (Fig. 2); see also Belonoshko and Dubrovinsky 1995] and correct reproduction of the discontinuity of the volume at the phase transition. It is also clear that 4% volume change at 1 bar and 0.8% volume change at 1 Mbar are quite different with regard to required energy. The ability of the method to reproduce well-established phase equilibria in close agreement with experiment suggests that the value of the transition pressure is not subject to significant errors. Because the

**TABLE 1.** Calculated X-ray patterns ( $\text{MoK}\alpha_1$  radiation) of different crystal structures of  $\text{SiO}_2$  obtained by MD simulations at 100 GPa and 300 K

Stishovite		$\text{CaCl}_2$		$\alpha\text{-PbO}_2$		SBAD	
$d$ (Å)	$I$ (%)	$d$ (Å)	$I$ (%)	$d$ (Å)	$I$ (%)	$d$ (Å)	$I$ (%)
				3.8260	59		
				2.9560	57	3.0025	49
2.7595	100	2.7591	100	2.8226	49		
				2.4137	62	2.4479	100
2.1446	29	2.1401	18	2.0905	8	2.1137	5
		2.1349	12	2.0340	16	2.0615	6
				1.9888	17		
1.8795	44	1.8747	44	1.8345	54	1.8573	27
1.7453	16	1.7493	5	1.7959	100	1.8215	51
		1.7407	11	1.7068	21	1.7284	15
						1.5749	4
						1.5013	4
1.4433	72	1.4434	41	1.4409	12	1.4592	18
				1.4382	6	1.4313	33
1.3797	22	1.4386	33	1.4113	46	1.4147	54
		1.3795	24	1.3935	88		
				1.3600	10		
				1.3095	4	1.2737	17
		1.2775	14	1.2753	2		
1.2835	14			1.2606	8	1.2504	2
1.2341	8	1.2380	10	1.2300	4	1.2204	3
				1.2198	4		
		1.2299	2			1.2101	27
		1.2139	16	1.1958	42		

SBAD phase also appears to be stable according to ab initio TTAM IP, we are confident that this discovery is not potential-specific. Because the character of the chemical bonding does not change up to at least 110 GPa (Sherman 1993), it is possible that the IP correctly describes interaction in the range of pressures of SBAD stability.

If there is free silica in the mantle, the transition to the denser SBAD phase should produce seismic discontinuity at depth corresponding to the pressure of the transition ( $\sim 120\text{--}130$  GPa corresponds to  $\sim 2600\text{--}2800$  km depth according to Preliminary Reference Earth Model, Dziewonski and Anderson 1981). In fact, there is a sharp increase in velocity of  $\sim 2.8\%$  at 2728 km (Weber and Davis 1990; Wright et al. 1985), which corresponds to the top of D'' layer. This suggests either that there is also free silica above 2728 km or that free silica appears as the result of the breakdown of  $\text{MgSiO}_3$ , perovskite (Hu et al. 1994), either because of the higher stability of MgO (periclase) and  $\text{SiO}_2$  (SBAD) in comparison with  $\text{MgSiO}_3$ , perovskite or because of chemical reactions at the core-mantle boundary (Goarant et al. 1992; Knittle and Jeanloz 1989).

#### ACKNOWLEDGMENTS

A.B.B. is thankful to K. Refson for providing the computer program Moldy. Discussions with J. Akella, H.-K. Mao, A. Navrotsky, G. Ottonello, S.K. Saxena, and V. Swamy are gratefully acknowledged. Comments by J. Rustad and an anonymous reviewer were helpful. Calculations were made using an IBM SP2 in the High-Performance Computing Center in Maui, Hawaii. The research was supported by the Swedish Natural Science Research Council (NFR) and Royal Swedish Academy of Sciences.

## REFERENCES CITED

- Altshuler, L.V., and Podurec, M.A. (1973) High-dense fluorite and rutile polymorphs. *Solid State Physics*, 15, 1436–1441 (in Russian).
- Belonoshko, A.B., and Dubrovinsky, L.S. (1995) Molecular dynamics of stishovite melting. *Geochimica et Cosmochimica Acta*, 59, 1883–1889.
- Bukowski, M.S.T., and Wolf, G.H. (1986) Equation of state and stability of fluorite-structured  $\text{SiO}_2$ . *Journal of Geophysical Research*, 91, 4704–4710.
- Cohen, R.E. (1992) First principles predictions of elasticity and phase transitions in high pressure  $\text{SiO}_2$  and geophysical implications. In Y. Syono and M.H. Manghnani, Eds., *High-pressure research: Application to earth and planetary sciences*, p. 425–432, Terra Scientific, Tokyo, Japan.
- Dubrovinsky, L.S., Belonoshko, A.B., Dubrovinsky, N.A., and Saxena, S.K. (1996) New high-pressure silica phases obtained by computer lattice dynamics simulation. In W. Trezciakowski, Ed., *High pressure science and technology*. World Scientific, Warsaw, Poland, in press.
- Dziewonski, A.M., and Anderson, D.L. (1981) Preliminary reference Earth model. *Physics of the Earth and Planetary Interiors*, 25, 297–356.
- Goarant, F., Guyot, F., Peyronneau, J., and Poirier, J.-P. (1992) High-pressure and high-temperature reactions between silicates and liquid iron alloys, in the diamond anvil cell, studied by analytical electron microscopy. *Journal of Geophysical Research*, 97, 4477–4488.
- Hemley, R.J. (1987) Pressure dependence of Raman spectra of  $\text{SiO}_2$  polymorphs:  $\alpha$ -quartz, coesite, and stishovite. In Y. Syono and M.H. Manghnani, Eds., *High-pressure research in mineral physics*, p. 347–359, Terra Scientific, Tokyo, Japan.
- Hemley, R.J., Kingma, K.J., Mao, H.K., Hu, J., and Shu, J. (1995) Compression of silica to multimegabar pressures. Abstracts, Joint XV AIR-APT and XXXIII EHPRG International Conference, September 11–15, Warsaw, Poland.
- Hu, J., Meade, C., and Mao, H.-K. (1994) High temperature phase transition and dissociation of  $(\text{Mg,Fe})\text{SiO}_3$  perovskite at lower mantle pressures. *Eos*, Fall Meeting abstract supplement, 605.
- Kingma, K.J., Cohen, R.E., Hemley, R.J., and Mao, H.K. (1995) Transformation of stishovite to a denser phase at lower-mantle pressures. *Nature*, 374, 243–245.
- Knittle, E., and Jeanloz, R. (1989) Simulating the core-mantle boundary: An experimental study of high-pressure reactions between silicates and liquid iron. *Geophysical Research Letters*, 16, 609–612.
- Lacks, D.J., and Gordon, R.G. (1993) Calculations of pressure-induced phase transitions in silica. *Journal of Geophysical Research*, 98, 22147–22155.
- Liu, L. (1982) High-pressure phase transformations of the dioxides: Implications for structures of high pressure. In M.H. Manghnani and S. Akimoto, Eds., *High pressure research in geophysics*, p. 329–347. Center of Academic Publications, Japan.
- Ming, L.S., and Manghnani, M.N. (1982) High-pressure phase transformations in rutile-structured dioxides. In M.H. Manghnani and S. Akimoto, Eds., *High pressure research in geophysics*, p. 348–357. Center of Academic Publications, Japan.
- Park, K.T., Terakura, K., and Matsui, Y. (1988) Theoretical evidence for a new ultra-high-pressure phase of  $\text{SiO}_2$ . *Nature*, 336, 670–672.
- Parrinello, M., and Rahman, A. (1981) Polymorphic transitions in single crystals: A new molecular dynamics method. *Journal of Applied Physics*, 52, 7182–7190.
- Ross, N.L., Shu, J.-F., Hazen, R.M., and Gasparik, T. (1990) High-pressure crystal chemistry of stishovite. *American Mineralogist*, 75, 739–747.
- Sato, H., Endo, S., Sugiyama, M., Kikegawa, T., Shimomura, O., and Kusaba, K. (1991) Baddeleyite-type high-pressure phase of  $\text{TiO}_2$ . *Science*, 251, 786–788.
- Sekine, T., Akaishi, M., and Setaka, N. (1987)  $\text{Fe}_2\text{N}$ -type  $\text{SiO}_2$  from shocked quartz. *Geochimica et Cosmochimica Acta*, 51, 379–381.
- Sherman, D.M. (1993) Equation of state and high-pressure phase transitions of stishovite ( $\text{SiO}_2$ ): Ab initio (periodic Hartree-Fock) results. *Journal of Geophysical Research*, 98, 11865–11873.
- Simakov, T. (1973) New data on compressibility of oxides and fluorides and the theory of homogeneous Earth's composition. *Transactions of USSR Academy of Sciences*, 310, 1447–1449.
- Tang, J., and Endo, S. (1993) X-ray study of the transitions among the rutile  $\alpha$ - $\text{PbO}_2$  and baddeleyite phases of  $\text{TiO}_2$  at high pressure and high temperature. In S. Schmidt, J.W. Shaner, G.A. Samara, and M. Ross, Eds., *High-pressure science and technology*, part 1, p. 367–370. Terra Scientific, Tokyo, Japan.
- Tse, J.S., Klug, D.D., and Page, Y.L. (1992) Novel high-pressure phase of silica. *Physical Review Letters*, 69, 3647–3649.
- Tsuchida, Y., and Yagi, T. (1989) A new, post-stishovite high-pressure polymorph of silica. *Nature*, 340, 217–220.
- Tsuneyuki, S., Tsukada, M., Aoki, H., and Matsui, Y. (1988) First-principles interatomic potential of silica applied to molecular dynamics. *Physical Review Letters*, 61, 869–872.
- Weber, M., and Davis, J.P. (1990) Evidence of a laterally variable lower mantle structure from P- and S-waves. *Geophysics Journal International*, 102, 231–255.
- Wright, C., Muirhead, R.J., and Dixon, A.E. (1985) The P wave velocity structure near the base of the mantle. *Journal of Geophysical Research*, 90, 623–634.

MANUSCRIPT RECEIVED OCTOBER 30, 1995

MANUSCRIPT ACCEPTED APRIL 4, 1996