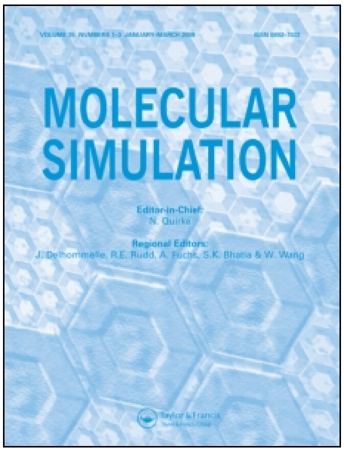

Molecular Simulation
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644482

Pressure-induced Structural Transformations in Framework Crystal Structures

Shinji Tsuneyuki[a]; Hideo Aoki[a]; Yoshito Matsui[b]
[a] Department of Physics, University of Tokyo, Tokyo, Japan [b] Institute for Study of the Earth's Interior, Okayama University, Japan

To cite this Article Tsuneyuki, Shinji , Aoki, Hideo and Matsui, Yoshito(1991) 'Pressure-induced Structural Transformations in Framework Crystal Structures', Molecular Simulation, 6: 4, 227 — 238

To link to this Article: DOI: 10.1080/08927029108022431

URL: http://dx.doi.org/10.1080/08927029108022431

Molecular Simulation, 1991, Vol. 6, pp. 227–238
Reprints available directly from the publisher
Photocopying permitted by license only

PRESSURE-INDUCED STRUCTURAL TRANSFORMATIONS IN FRAMEWORK CRYSTAL STRUCTURES: A MOLECULAR DYNAMICS STUDY OF SILICA

SHINJI TSUNEYUKI, HIDEO AOKI

Department of Physics, University of Tokyo, Hongo, Tokyo 113, Japan

and

YOSHITO MATSUI

Institute for Study of the Earth's Interior, Okayama University, Misasa, Tottori-ken 682-02, Japan

(*Received May 1990, accepted June 1990*)

Pressure-induced structural transformation of polymorphs of silica (SiO_2) at room temperature is studied with the molecular dynamics method. Novel structural transitions are predicted in which the tetrahedral coordination of silicon to oxygen collectively collapses into an octahedral coordination without breaking any Si–O bonds. The relation between such transformations and the atomic diffusion in the liquid phase is briefly discussed.

KEY WORDS: Silica, structural transformation, high-pressure, diffusion.

INTRODUCTION

Silicate minerals such as feldspars (*e.g.*, $NaAlSi_3O_8$) which abound in the crust of the Earth are known to exhibit various strange properties such as complicated phase transitions and anomalous pressure-dependence of the viscosity in the liquid phase. These properties are considered to be closely related with the fact that these materials have framework crystal structure comprising corner-shared SiO_4 tetrahedra.

Silica (SiO_2) itself, an end member of silicate compounds, has various polymorphs and shows a variety of phase transitions when temperature or pressure is changed. Some of the polymorphs are known to be stable at room temperature and ambient pressure. These polymorphs have quite wide ranges of density (2.3–4.3 g/cm^3) and bulk modulus (18–300 GPa) and this feature is a consequence of the crystal structure of silica in which the structure is purely determined by the three-dimensional network of SiO_4 units without any other ions. Silica, which is a generic material to the geophysically important minerals, is thus an ideal starting point.

We have recently shown that a first-principles many-body calculation for clusters can be used to extract effective pairwise interatomic potentials, which were then fed into a molecular dynamics (MD) study of the stability of crystalline silica [1]. Although there have been several empirical approaches to obtaining pairwise interatomic potentials for silicate [2], non-empirical determination of the potential is more preferable for the transferability, and in fact we first succeeded in simulating structural properties of framework silica within the rigid-ion approximation. Here we use this non-empirical approach to study the pressure-induced structural transformations at room temperature in various polymorphs of silica. This problem is of special interest for the following reasons:

(1) The crystal-to-amorphous transformation in the solid state is currently a subject of intense interest. Since the amorphization of H_2O ice under pressure was discovered [3], possible occurrence of such pressure-induced amorphization in other systems have been widely investigated and the mechanism of the amorphization remains a puzzle. Very recently the pressure-induced amorphization of crystalline silica at room temperature was confirmed by experiments using Raman spectroscopy[4] and X-ray diffraction [5]. We have first to characterize the resultant amorphous structure to elucidate the mechanism of amorphization. In the present paper we propose theoretically a model for the amorphization on the basis of the results for crystalline-to-crystalline transitions as discussed later.

(2) In pressure-induced transformations of silica, the amorphous phases are experimentally shown to be appreciably denser than the crystalline counterparts, presumably due to the framework structure of the material just as in the case of water. Such a pressure-density relation of minerals is significant in discussing the convection of materials deep inside the earth.

(3) The application of high pressure at low (room) temperature can provide new reaction paths towards new polymorphs as is shown in the present computer simulation. Some of the high-pressure phases thus obtained could never be synthesized by high pressures at high temperatures since the latter condition tends to select only the phases thermodynamically most stable.

As for the mechanism of compression of crystal structures it is widely believed that the compression of amorphous silicate at low pressures occurs due to increased packing ratio of corner-shared SiO_4 tetrahedra with decreased Si–O–Si bridging angles. At high pressures, on the other hand, it is reported from infrared measurements that the fraction of octahedrally coordinated silicon atoms increases continuously and reversibly with increasing pressure [6]. Stolper and Ahrens [7] have proposed a mechanism for such pressure-induced coordination changes in silicate melts and glasses: according to their model, a continuous distortion of silicon atoms in the SiO_4 chain results in a closely packed arrangement of oxygen octahedra. It is an interesting problem to ask whether such structural transformations can occur in crystalline phases (of silica).

In the present paper we describe the MD study on these problems [8] in detail. Novel structural transitions for low-quartz, low-cristobalite and coesite are predicted. Some of the new phases, which appear without diffusion processes, comprise mixed array of four-fold and six-fold Si–O coordinations. Stishovite, the densest polymorph of silica ever known, is shown to hold its identity up to 250 GPa with deformation towards the $CaCl_2$ structure. Finally we briefly discuss the atomic diffusion in the liquid phase in which we relate the elementary diffusion process with the structural transformations.

INTERATOMIC POTENTIALS

Before turning to the MD study, we first examine the interatomic potential of silica

Table 1 Potential parameters.

	Q/e	a(Å)	b(Å)		C(kcalÅ^{6}mol^{-1})
O	−1.2	2.05	0.176	O–O	4956
Si	+2.4	0.86	0.033	O–Si	1633
				Si–Si	0

(f_0 = 1 kcalÅ^{-1}mol^{-1})

in applying to phase transitions accompanied by coordination changes. The effective pairwise interatomic potential extracted from the first-principles cluster calculation [1] has been fitted to a functional form,

$$U_{ij}(r) = Q_iQ_j/r + f_0(b_i + b_j)\exp[(a_i + a_j - r)/(b_i + b_j)] - C_{ij}/r^6,$$

where r is the distance between the ith and the jth atoms and $f_0 = 1$ kcalÅ^{-1}mol^{-1}. The structures and the bulk moduli of polymorphs of silica are successfully reproduced by the MD simulations.

The pairwise interatomic potential has the virtue that they can reproduce both tetrahedrally (four-fold) coordinated systems (low-quartz, low-cristobalite and coesite) and octahedrally (six-fold) coordinated systems (stishovite) in contrast to covalent potentials [9], [10] which are applicable only to tetrahedrally coordinated systems. It can also be used in the MD simulation much more easily than many-body potentials like the shell model [11]. However, as mentioned in the previous paper [1], a flaw in the cluster approach for obtaining pairwise potentials is that, since the approach concentrates on the curvature of potential surfaces, the cluster method does not necessarily reproduce the exact enthalpy difference of various phases. For example, the enthalpy of formation of the six-fold coordinated stishovite [12] is about 10 kcal/mol higher than that (−217.8 kcal/mol) of the four-fold coordinated low-quartz experimentally [13] while the calculated difference is about 1 kcal/mol in the cluster

Table 2 Physical properties of silica at room temperature and ambient pressure obtained by MD simulations using modified potential parameters in this paper.

	low-quartz		*low-cristobalite*	
	Obs.[a]	*MD*	*Obs.*[b]	*MD*
Density (g/cm^3)	2.65	2.50	2.32	2.38
K_0 (GPa)	38(3)	38.1(2)	18	15.3(2)
K_0'	6.0(2)	4.7(1)	-	12.7(4)
Energy (kcal/mol)		−1249.6		−1245.3

	coesite		*stishovite*	
	Obs.[c]	*MD*	*Obs.*[d]	*MD*
Density (g/cm^3)	2.92	2.80	4.29	4.03
K_0 (GPa)	96(3)	98.8(3.3)	296(5)	296(1)
K_0'	8.4(1.9)	5.8(1.2)	4.0(1.4)	6.0(4)
Energy (kcal/mol)		−1254.0		−1238.4

[a]Reference [14] [b]Reference [15][16] [c]Reference [17] [d]Reference [18][19]

method. Since we are interested in pressure-induced structural transformations, which involve change of the Si–O coordination number, we slightly modify the potential parameters to reproduce the enthalpy difference of stishovite and low-quartz. Only a reduction of the atomic radius a_{Si} by 1% (0.01 Å) is sufficient to accomplish this. The final potential parameters used here are tabulated in Table 1. Table 2 lists the densities, bulk moduli and cohesive energies of various polymorphs at normal temperature/pressure obtained by the MD calculation with these potential parameters. The structural properties of all the polymorphs known to be stable are reproduced. The agreement with the experimental results is in fact better for the modified potential than the result in the previous paper [1] especially for low-quartz. It would be desirable if we could incorporate the accuracy of the total enthalpy in the best-fit procedure for optimizing the pair potential. Such a procedure would require the first-principles bulk calculations as well as the cluster calculations.

Usually the total energy (cohesive energy) of a crystal structure is very sensitive to the potential parameters. Here we note specifically that the ratio a_{Si}/a_O is crucial for the energy difference between four-fold and six-fold Si–O coordinated structures. This result is consistent with the calssical principle by Pauling on the coordination number of anions around cations [20]: smaller a_{Si}/a_O ratio makes four-fold systems more stable. Relative stability within the tetrahedrally coordinated polymorphs is rather insensitive to the a_{Si}/a_O ratio, and the result for coesite with the modified parameters is still too stable by about 5 kcal/mol as compared with experimental results [12].

It should also be noted that the relative stability of the phases is also sensitive to the functional form of the interatomic potentials even within the pair-potential approximation. For instance, we have tested the traditional Morse potentials between Si and O in the fitting procedure only to find that the octahedrally coordinated stishovite is much more stable than the other polymorphs. When applied to the MD simulation of vitreous or liquid silica, such potentials give rise to collapsed six-fold glasses.

MOLECULAR DYNAMICS RESULTS

We apply hydrostatic pressure to each polymorph of silica in the MD study with the constant-pressure algorithm due to Parrinello and Rahman [21] while the temperature is also specified by the constant-temperature algorithm due to Nosé [22]. The number of atoms in the system is 576 (containing 48 unit cells), 576(64), 768(16) and 576(96) for low-cristobalite, low-quartz, coesite, and stishovite, respectively, with periodic boundary conditions. The pressure is increased slowly (by 1–5 GPa each time the equilibrium is attained)

The obtained equations of state for SiO_2 in various polymorphs at room temperature [8] are shown in Figure 1 along with the equations of state by *real* experiments [5]. The results for low-quartz, coesite and stishovite, before they undergo structural transitions, are in good agreement with the experimental results.

The most interesting point is the stability of each polymorph. Low-cristobalite shows a structural transition with discontinuous volume reduction at 16.5 GPa into a novel polymorph having a space group *Cmcm* (Table 3). The space group of low-cristobalite, $P4_12_12$, has an orthorhombic subgroup $C222_1$, of which *Cmcm* is another supergroup. Corresponding to the two possibilities in constructing the orthorhombic unit cell of $C222_1$ from the tetragonal unit cell of $P4_12_12$, the direction

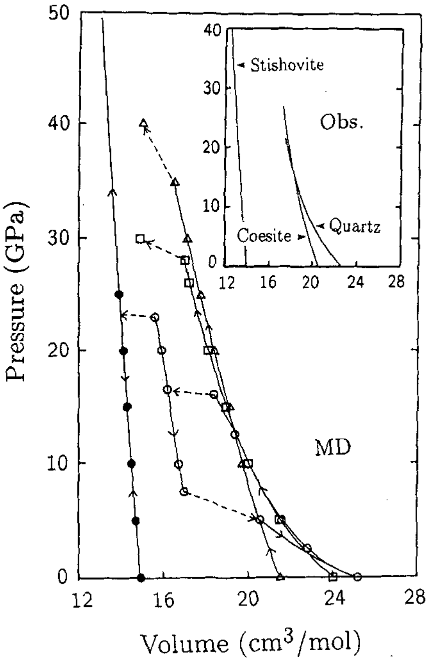

Figure 1 Pressure-volume relation for low-quartz (□), coesite (△), stishovite (●) and low-cristobalite (○) obtained by MD. Solid lines represent continuous change and broken lines discontinuous change of volume due to pressure-induced structural transition. Hysteresis is indicated by arrows. Pressure-volume relation obtained by experiments is shown in the inset (from Hemley *et al.*[5]).

of the *Cmcm* phase assumes one of two equivalent directions depending on the MD run. The *Cmcm* phase is stable until the second phase transition into stishovite sets in at 23 GPa. The space group of stishovite, $P4_2/mnm$, is in turn a supergroup of *Cmcm* and $P4_12_12$. The actual atomic displacements along the reaction path of the transformation is illustrated in Figure 2. Remarkably the *Cmcm* structure includes equal numbers of four- and six-coordinated silicon atoms. Note that these structural phase transitions occur continuously without diffusion processes, that is, no isolated atoms nor disordered states appear around the transition point. The mechanism of the diffusionless transformation is illustrated in Figure 3. Figure 3(a) represents the framework of corner-shared SiO_4 tetrahedra in the low-cristobalite structure. When the pressure is increased the framework structure is continuously deformed into a structure shown in Figure 3(b). This structure can be regarded to comprise six-fold Si-O coordination if we examine the Si-O bond length: an SiO_6 octahedron is

Table 3 Crystallographic data of the *Cmcm* phase of silica at 15 GPa, 300 K.

Orthorhombic cell $a = 5.20$Å,	$b = 7.44$Å,	$c = 5.58$Å	$\rho = 3.70\,g/cm^3$
Si(4a)	$x = 0$	$y = 0$	$z = 0$
Si(4c)	$x = 0$	$y = 0.357$	$z = 0.25$
O(8f)	$x = 0$	$y = 0.223$	$z = 0.029$
O(8g)	$x = 0.260$	$y = 0.481$	$z = 0.25$

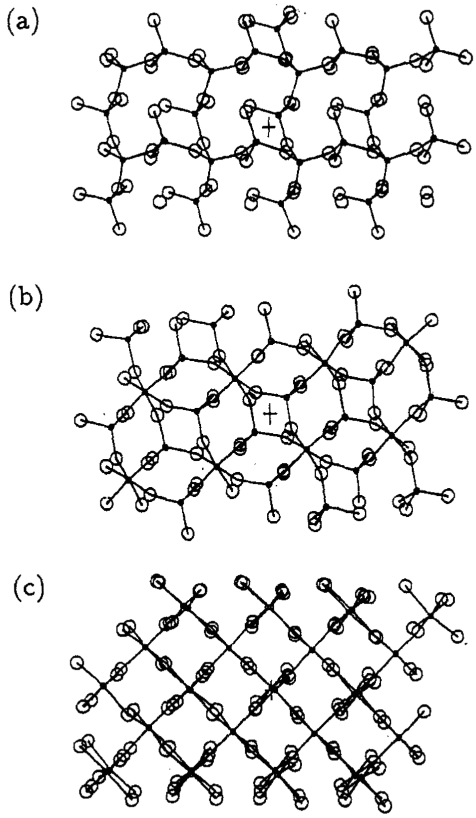

Figure 2 Continuous structural transformations induced by compression from (a) low-cristobalite (at 15 GPa) to (b) the *Cmcm* phase (at 17 GPa) to (c) stishovite (at 25 GPa). Small spheres represent silicon atoms and large spheres oxygen atoms.

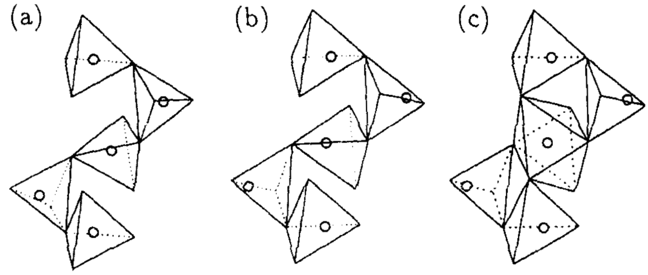

Figure 3 Mechanism of pressure-induced structural transformation. (a) The framework of corner-shared SiO_4 tetrahedra in the low-cristobalite structure, where silicon atoms are shown with circles. (b) The framework structure deformed under pressure. (c) SiO_6 octahedron explicitly shown using the same atomic configuration as that in (b).

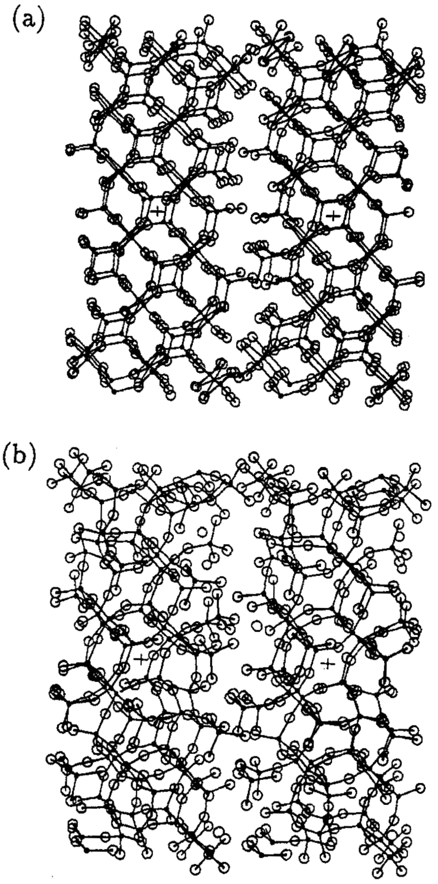

Figure 4 Structural transformation induced by decompression from (a) the *Cmcm* phase to (b) the amorphous phase which contains only tetrahedrally coordinated silicon atoms (stereoscopic view).

explicitly depicted in Figure 3(c) for the same atomic configuration as that in Figure 3(b). Thus the Si–O coordination number increases smoothly by neither breaking any Si–O bonds nor introducing global atomic diffusion. This mechanism for compression is essentially the same as that suggested by Stolper and Ahrens for amorphous silica [7].

From the mechanism above, it is naturally expected that the transformation from four-fold to six-fold Si–O coordination is reversible. Upon decreasing the pressure, the *Cmcm* phase indeed becomes unstable at about 7 GPa resulting in an amorphous phase (Figure 4), whose structure and density are similar to those of low-cristobalite.

The fact that the decompression gives rise to an amorphous rather than a crystalline phase means that the way of unfolding six-fold coordination into four-fold coordination is locally not unique. Recall that in a reverse (four- to-six) transformation from low-cristobalite to the *Cmcm* phase described above the crystal axis also has a freedom of two equivalent directions to choose from. On the other hand, once stishovite is formed above 23 GPa, it remains stable against decompression, which

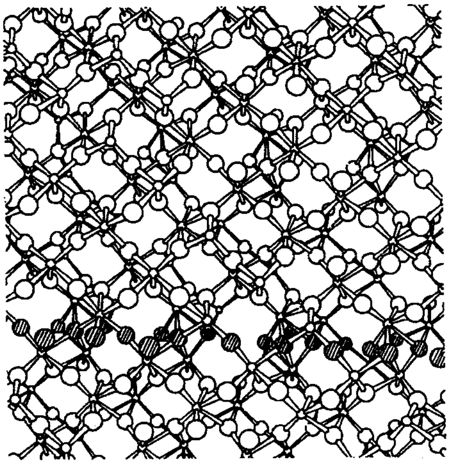

Figure 5 The α-PbO_2 phase with some defects obtained by compression of low-quartz up to 30 GPa at room temperature. Small spheres represent silicon atoms and large spheres oxygen atoms. Hatched atoms represent a basal plane of the close-packed oxygen atoms.

owes to the large activation energy needed for the six-to-four transformation in this less-strained crystal.

Low-quartz also exhibits a novel structural transition at about 28 GPa. One of the pressure-induced phases is shown in Figure 5, which is basically the α-PbO_2 structure with some defects. The perfect α-PbO_2 structure with only six-fold Si–O coordinations is slightly denser than stishovite and has been proposed, but not established, as a highpressure form of SiO_2 [23].

Interestingly, another pressure-induced phase has been obtained depending on the MD run as shown in Figure 6(a)(b) which is also crystalline but frustrated in the following sense. The phase contains both four- and six-coordinated Si atoms as in the *Cmcm* phase, while the average coordination number is not $(4 + 6)/2$ but 5.3 in this case. The three-fold screw axes of he starting low-quartz are destroyed. Conspicuous feature is that despite their ordered array the unusual configuration of the four- and six-fold sites demands considerable distortion of bond lengths and angles. This appears as a random distribution of missing bonds which exist with a finite density. Here we regard Si and O bonded when they are separated less than 2.16 Å, a chemically acceptable bound. Frustrated aspect also appears in the corrugated SiO_2 sheet (SiO bond angles $\neq 90°$) in Figure 6(b). Peaks in the radial distribution function are also shown to be broadened like in a glass. The configuration of these missing bonds fluctuates in time (of which Figure 6 is a snapshot), and the missing bonds are shown to disappear when the pressure is increased to 50 GPa. Reflecting the three equivalent directions in the quartz, the direction of the obtained crystal assumes one of the three, depending on the MD run. it is thus conceivable that compression of a macroscopic sample should produce domains of these α-PbO_2 or frustrated crystal phases, which may require a careful experimental study to distinguish from a conventional amorphous phase. The mixed coordinations predicted here could be identified by the infrared measurement. The critical pressures for structural transitions obtained here are consistent with the recent experimental results by Hemley *et al.* [5] on the amorphization of low-quartz at about 25–30 GPa.

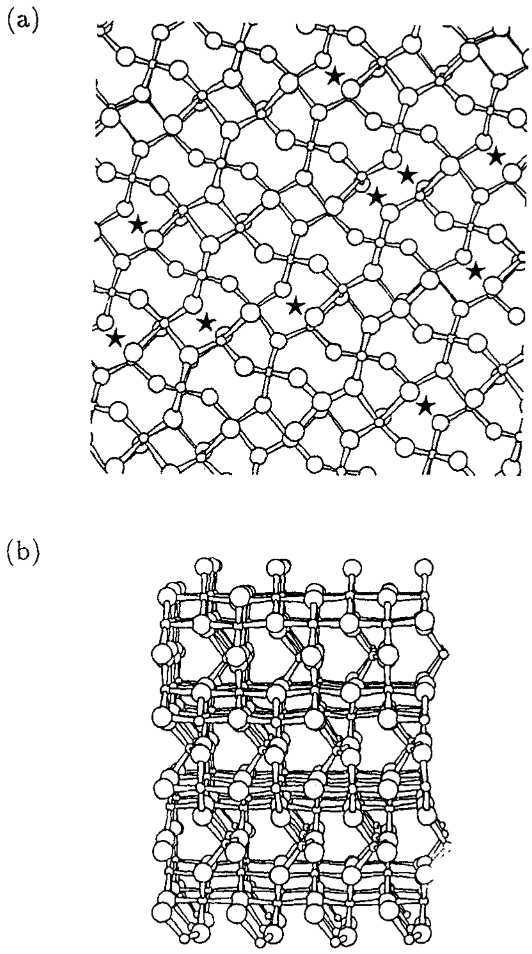

Figure 6 A frustrated crystal phase obtained by compression of low-quartz up to 30 GPa at room temperature: (a) A projection to the plane normal to the a-axis and (b) a perspective view seen from the c-axis of starting low-quartz. Small spheres represent silicon atoms and large spheres oxygen atoms. The missing bonds of the frustrated crystal phase are marked with ★ in (a).

These structural transformations of low-quartz are again diffusionless, and the six-fold Si–O coordinations almost completely return to four-fold after decompression to normal pressure. This is consistent with the infrared-spectrum result that the coordination number of amorphous SiO_2 changes reversibly with pressure even at room temperature [6].

As for the MD method we note that there are some technical details: since the constant-temperature algorithm is used here, the heat of reaction produced during the structural transition is rapidly removed in the present MD, so that metastable phases are more favoured. Also, there is a problem of the finite system-size. If we employ $3 \times 3 \times 3 = 27$ unit cells instead of $4 \times 4 \times 3 = 48$ for the basic cell of the periodic boundary condition, the *Cmcm* phase, which is made of two unit cells of low-cristobalite and is incommensurate with this boundary condition, is by-passed and low-cristobalite changes directly into stishovite above 20 GPa. Thus the detail of the new polymorph may have to be determined for larger system sizes. Yet we expect that the same kind of transition involving the mixed coordination numbers will occur in real systems.

An experimental study on the compression of low-cristobalite at room temperature was carried out by Tsuchida and Yagi very recently [16] and novel crystalline-to-crystalline transformations were discovered at ~10 GPa and ~30 GPa, although the characterization of the new phases is not finished yet.

As for the coesite, the basic cell is shown to slightly change from monoclinic to triclinic at 15–20 GPa, which may be associated with the observed change of Raman spectrum at 22–25 GPa [4]. Coesite, too, undergoes a structural transition into a six-fold rich phase at 35–40 GPa, which is consistent with the experimentally reported amorphization at 30–34 GPa [5].

Finally, stishovite exhibits no drastic structural change up to 250 GPa, the highest pressure studied here, except that the structure eventually becomes orthorhombic (with the $CaCl_2$ structure). The result is consistent with a recent experiment [24]. The result also implies that the recently proposed $Pa\bar{3}$ phase [25], which is predicted to be denser and thermodynamically more stable than stishovite above 60 GPa, may be difficult to attain dynamically by simple compression at room temperature. This does not necessarily mean, however, that the $Pa\bar{3}$ phase is unstable. Even if the $Pa\bar{3}$ phase is more stable than stishovite, it is possible that the potential barrier in the atomic configuration space separating the two phases would be higher than k_BT at room temperature so that a diffusion process at high temperatures would be necessary for the transition to the $Pa\bar{3}$ phase.

CONCLUDING REMARKS

We have performed an MD simulation of pressure-induced structural transformations of crystalline silica. The simulated equations of state agree very well with those observed in the real experiments. Pressure-induced structural transformations of the polymorphs have also been found.

The mechanism of the pressure-induced structural transformation of tetrahedrally coordinated silica at room temperature is shown to be primarily the increase of the Si–O coordination number, which occurs locally without diffusion process. As the pressure increases, the network structure of tetrahedrally coordinated Si collectively collapses to more closed-packed structures with rich octahedrally coordinated Si, which results in a discontinuous reduction of volume. In some cases, four-fold silicon atoms partly survive the transition, resulting in mixed coordination numbers. The application of high pressure at room temperature thus provides intriguing reaction paths towards new polymorphs.

Although we have focused on the structural transformation of crystals here, the compression mechanism of silica described in the present paper is considered to be applicable to vitreous or liquid silica. In a disordered system, different local configurations are realized for different places in the system, so that a coordination change (like four-fold cristobalite into four- and six-fold *Cmcm* phase) may not occur collectively as in a crystal. This also means that different sites undergo the coordination change at different pressures. This will lead to a continuous reduction of volume. The reversibility of the process is in fact confirmed by the MD result: the α-PbO_2 phase with defects, which is obtained by the compression of quartz, returns almost completely to four-fold structure after decompression to normal pressure as described above.

Finally we comment on the atomic diffusion. We have stressed that the structural phase transitions obtained here are diffusionless. However, this is in a specified meaning of the word, in which a diffusive transition is defined as the one accompanied by an appearance of an amorphous phase or isolated atoms. The diffusionless transition modes in fact contribute to the mechanism of diffusion in the following sense. If we look at Figures 2 and 4, it is seen that, when cristobalite is compressed into the *Cmcm* phase followed by a decompression to the normal pressure, the system becomes an amorphous phase, in which the framework structures are topologically deformed from those in the starting cristobalite, although no isolated oxygens appear during the process. Thus, if we envisage a process in a disordered phase in which the compressions and decompressions are repeated, this could result in a diffusion of atoms. Since the local pressure is thought to fluctuate in a melt, we can expect such a diffusion in a liquid silica. Note that the diffusion considered here does not accompany isolated atoms but is regarded as local changes of Si–O coordination numbers, which will require much less energies than those needed for stripping an oxygen atom from a four-fold coordinated silicon atom. The study of this problem will be published elsewhere [26].

Acknowledgements

We would like to thank S. Nosé and M. Matsui for providing and helping us modify the MD programmes and M. Tsukada and K. Kawamura for useful discussions. Numerical calculations were performed at the Institute for Study of the Earth's Interior, Okayama University and the Computer Centre, the University of Tokyo. This work was supported in part by a Grant-in-Aid from the Ministry of Education, Science and Culture, Japan.

References

[1] S. Tsuneyuki, M. Tsukada, H. Aoki and Y. Matsui, "First-principles interatomic potential of silica applied to molecular dynamics", *Phys. Rev. Lett.*, **61,** 869 (1988). This approach has been extended to the α to β phase transition in quartz by S. Tsuneyuki, H. Aoki, M. Tsukada and Y. Matsui, "Molecular dynamics study of the α to β structural phase transition of quartz", *Phys. Rev. Lett.*, **64,** 776 (1990).

[2] For example, G.D. Price and S.C. Parker, "Computer simulations of the structural and physical properties of the olivine and spinel polymorphs of Mg_2SiO_4", *Phys. Chem. Minerals*, **10,** 209 (1984).

[3] O. Mishima, L.D. Calvert and E. Whalley, "'Melting ice' I at 77 K and 10 kbar: a new method of making amorphous solids", *Nature*, **310,** 393 (1984).

[4] R.J. Hemley, "Pressure dependence of Raman spectra of SiO_2 polymorphs: α-quartz, coesite, and stishovite", in *High Pressure Research in Mineral Physics* eds. M.H. Manghnani and Y. Syono, Geophysical Monograph **39** (American Geophysical Union, Washington D.C., 1987) p. 347.

[5] R.J. Hemley, A.P. Jephcoat, H.K. Mao, L.C. Ming and M.H. Manghnani, "Pressure-induced amorphization of crystalline silica", *Nature*, **334,** 52 (1988).

[6] Q. Williams and R. Jeanloz, "Spectroscopic evidence for pressure-induced coordination changes in silicate glasses and melts", *Science*, **239,** 902 (1988).

[7] E.M. Stolper and T.J. Ahrens, "On the nature of pressure-induced coordination changes in silicate melts and glasses", *Geophys. Res. Lett.*, **14,** 1231 (1987).

[8] S. Tsuneyuki, Y. Matsui, H. Aoki and M. Tsukada, "New pressure-induced structural transformations in silica obtained by computer simulation", *Nature*, **339,** 209 (1989).

[9] A.C. Lasaga and G.V. Gibbs, "Applications of quantum mechanical potential surfaces to mineral physics calculations", *Phys. Chem. Minerals*, **14,** 107 (1987).

[10] L. Stixrude and M.S.T. Bukowinski, "Simple covalent potential models of tetrahedral SiO_2: applications to α-quartz and coesite at pressure", *Phys. Chem. Mineral*, **16,** 199 (1988).

[11] M.J. Sanders, M. Leslie and C.R.A. Catlow, "Interatomic potentials for SiO_2", *J. Chem. Soc., Chem. Commun.* 1271 (1984).

[12] J.L. Holm, D.J. Kleppa and E.F. Westrum Jr., "Thermodynamics of polymorphic tansformations in silica", *Geochim. Cosmochim. Acta*, **31,** 2289 (1967).

[13] S.S. Wise, J.L. Margrave, H.M. Feder and W.N. Hubbard, "The heat of formation of silica and silicon tetrafluoride", *J. Phys. Chem.*, **66,** 381 (1962).

[14] L. Levien, C.T. Prewitt and D.J. Weidner. "Structure and elastic properties of quartz at pressure", *Am Mineral.*, **65,** 920 (1980).

[15] D.R. Peacor, "High-temperature single-crystal study of the cristobalite inversion", *Z. Kristallogr.*, **138,** 274 (1973).

[16] Y. Tsuchida and T. Yagi, "New high pressure polymorphs of silica", *Technical Report of ISSP*, Ser. A, No. 2099 (1989): Y. Tsuchida and T. Yagi, submitted.

[17] L. Levien and C.T. Prewitt, "High-pressure crystal structure and compressibility of coesite", *Am. Mineral.*, **66,** 324 (1981).

[18] R.J. Hill, M.D. Newton and G.V. Gibbs, "A crystal chemical study of stishovite", *J. Solid State Chem.*, **47,** 185 (1983).

[19] Y. Sato, "Equation of state of mantle minerals determined through high-pressure X-ray study", in *High-Pressure Research, Applications in Geophysics*, M.H. Manghnani and S. Akimoto, eds, Academic Press, New York, 1977, pp. 307–323.

[20] L. Pauling, *The Nature of the Chemical Bond*, 3rd ed. (Cornell Univ. Press, Ithaca, New York, 1960).

[21] M. Parrinello and A. Rahman, "Polymorphic transition in single crystals: a new molecular dynamics method", *J. Appl. Phys.*, **52,** 7182 (1980).

[22] S. Nosé, "A univied formulation of the constant temperature molecular dynamics methods", *J. Chem. Phys.*, **81,** 511 (1984).

[23] Y. Matsui and K. Kawamura, "Computer-experimental synthesis of silica with the α-PbO_2 structure", in *High Pressure Research in Mineral Physics* (eds. M.H. Manghnani and Y. Syono), Geophysical Monograph **39** (American Geophysical Union, Washington D.C., 1987) p. 305.

[24] Y. Tsuchida and T. Yagi, "A new, post-stishovite high-pressure polymorph of silica", *Nature*, **340,** 217 (1989).

[25] K.T. Park, K. Terakura and Y. Matsui, "Theoretical evidence for a new ultra-high-pressure phase of SiO_2", *Nature*, **336,** 670 (1988).

[26] S. Tsuneyuki, H. Aoki and Y. Matsui, to be submitted.