First-Principles Studies on Structural Properties of β-Cristobalite

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The structure of β-cristobalite has been studied through a first-principles total-energy minimization in the local-density approximation using a Car–Parrinello-type algorithm combined with the Vanderbilt ultrasoft pseudopotential scheme. It was found that the hypothetical ordered structure proposed by Wright and Leadbetter is favored and the resulting structural parameters agree very well with experiment. Also, correlated relaxation of Si and O atoms toward α-cristobalite positions in the vicinity of domain boundaries is indicated.

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SiO_2 can exist in many difference crystalline forms, such as α- and β-quartz, α- and β-cristobalite, stishovite, etc. [1,2]. Most of these structures are composed of corner-sharing tetrahedral units with a silicon atom at the center and four oxygen atoms at the corners. These structures have only subtle differences in energy since they differ from each other mainly in the way of connecting the tetrahedral units, which makes SiO_2 a very delicate system.

Although the structures of most SiO_2 polymorphs are well established, the structure of β-cristobalite is still controversial, with at least five different structural forms having been proposed [3–7]. The difficulties are partly due to the sensitivity of the structure to the sample history and the ambiguity in fitting the proposed model to the experimental data [7], especially when disorder is involved. In fact, both structures of β-cristobalite discussed in Wyckoff's widely used reference book *Crystal Structures* [1] are doubtful in light of more recent work, especially that of Wright and Leadbetter [7] who have proposed a new model incorporating disorder. On the other hand, many empirical and model theoretical calculations [8] have been carried out on the very first structure proposed by Wyckoff, mainly because of its simplicity. However, these calculations could be misleading since the results are based on an unrealistic structure.

A theoretical study of SiO_2 using the first-principles approach is difficult, in general, because of the complexity of the system and the presence of oxygen ions. Recently, Allan and Teter [9] have correctly predicted the structures of α-quartz, α-cristobalite, and stishovite based on first-principles calculations. Also, the structural change of α-quartz under pressure was investigated by Chelikowsky *et al.* [10] using a similar approach. The success is partly due to recent advances in fast algorithms for solving the one-electron Schrödinger equation and separable nonlocal pseudopotentials. However, the use of conventional norm-conserving pseudopotentials in the above schemes imposes a limit on the size of the system which can be studied since a large plane-wave cutoff is required for treating the oxygen ions. As a result, calculations on β-cristobalite would be rather expensive in view of the fact that one of the candidate structures ($P2_13$; see below) has a large primitive cubic cell containing eight SiO_2 units. The largest cell that has previously been studied contains six units [9].

A more efficient approach has recently been developed with the implementation of the Vanderbilt ultrasoft pseudopotential scheme [11] in the Car-Parrinello (CP) algorithm [12]. The validity and efficiency of this new approach has already been demonstrated in studies of ice phase transitions under high pressure [13], liquid copper [14], and ferroelectricity in barium titanate [15]. In this Letter, we report an application of this method to investigate the structural properties of β-cristobalite. Both total-energy and lattice-dynamics studies confirm the structure proposed by Wright and Leadbetter [7], thereby invalidating much of the previous theoretical work on this system which was carried out on the other alternate structures. Also, a correlated relaxation of Si and O atoms toward α-cristobalite positions is suggested to be likely to occur in the vicinity of domain boundaries.

The first structure of β-cristobalite deduced by Wyckoff [3] is now often referred to as "ideal" β-cristobalite since it has a high symmetry with a primitive cell containing two SiO_2 units or a conventional cubic cell of space group $Fd3m$ in which eight Si atoms form a diamond sublattice with sixteen O atoms at the midpoints of Si-Si separation. The obvious flaw with this structure is that the Si-O-Si angle at 180° is too large and the Si-O bond length of 1.54 Å is too small to compare to all other forms of silica, in which these values are consistently around 145°–150° and 1.61 Å. Noting these difficulties, Barth [4] suggested a different structure of space-group symmetry $P2_13$ (simple cubic with eight SiO_2 units per cell) in which Si and O atoms are displaced from $Fd3m$ positions to adjust the Si-O-Si angle and Si-O distance into the right range. However, doubts have been raised as to the quality of the sample in his experiments [7]. A disorder model for β-cristobalite was first proposed by Nieuwenkamp [5]. He presented a structure with overall average symmetry of $Fd3m$ but placed oxygen atoms ei-

ther moving around or being randomly distributed on a small circle normal to the Si-Si axis instead of staying at the midpoints. The overall symmetry of $Fd3m$ and the presence of disorder were later confirmed by Peacor [6] and Wright and Leadbetter [7]. Peacor modified Nieuwenkamp's model by assigning oxygen atoms to occupy randomly one of six fixed positions on the circle or to dynamically change from one fixed position to another. Wright and Leadbetter, with better sample preparation and structure refinement than all of the previous work, proposed a particular assignment of each oxygen to one of the six positions. The structure can be visualized as resulting from rotations of about $\pm 20°$ of each SiO_4 tetrahedron of the ideal structure around its $\bar{4}$ axis, with the sense of rotational axes antiparallel with each other on the neighboring tetrahedra. This gives rise to an $F\bar{4}d2$ symmetry, or more properly, a tetragonal space group of $I\bar{4}2d$ symmetry with two SiO_2 units in the primitive body-centered tetragonal (bct) cell or four units in a conventional tetragonal cell. The relationship between the new structure and the ideal one has been fully discussed by O'Keefe and Hyde [16]. Wright and Leadbetter [7] proposed that the actual structure would be composed of small domains with six possible orientations of the $I\bar{4}2d$ type, giving rise to an average structure of $Fd3m$ symmetry.

Despite many experimental investigations of β-cristobalite, there are very few theoretical studies of the structural properties [17]. To the best of our knowledge, there have been to date no *ab initio* theoretical studies of this phase. Therefore, a study based on first-principles techniques will be very useful in leading us to a better understanding of the system. We have carried out *ab initio* total-energy and force calculations using a CP-type algorithm in which the electronic solution is obtained via a preconditioned [18] steepest-descent method. The ultrasoft pseudopotential by Vanderbilt has been implemented to further improve the computational efficiency. The soft oxygen potential generated with this scheme enabled us to use a small plane-wave cutoff of 20 Ry while correctly predicting the structural parameters for five polymorphs of silica [19]; the best that has previously been done with conventional norm-conserving pseudopotentials is about 40 Ry for SiO_2. In the present study, however, we opted to work with a larger cutoff of 25 Ry to ensure the accuracy of the comparison of small energy differences between different symmetries. The Ceperley-Alder form of exchange-correlation potential was used to treat the exchange-correlation effects within the local-density approximation. The details of the pseudopotential construction and computation method will be published elsewhere [19].

We have taken a simple cubic unit cell containing eight SiO_2 units. The adiabatic potential energy surface was searched subject to the three different symmetries $P2_13$, $Fd3m$, and $F\bar{4}d2$, respectively. Although a smaller primitive cell containing two SiO_2 units could be used for the last two symmetries, we have used the larger conventional cell in order to make the parallel comparison with the $P2_13$ symmetry. All the calculations were conducted with one **k** point at (0.25,0.25,0.25). In Fig. 1 we plot the binding energies of the three structures as a function of volume. The structure of $P2_13$ symmetry can be simply ruled out since it is shown to have much too high energy. It has been pointed out that the false deduction by Barth was likely due to the impure sample used in the experiment [7]. The structure of $F\bar{4}d2$ symmetry was found to be energetically favored. The calculated lattice constant and internal oxygen coordinate (or the rotation angle of the tetrahedra) are in very good agreement with experiments. In Table I both theoretical and experimental results are listed for comparison, and the error is within a few percent. We also found that the rotation angle of the tetrahedra decreases as the volume increases, and vanishes at about 51 $Å^3$/molecule, beyond which the ideal $Fd3m$ structure appears to be stable. The energy minimum of the ideal structure is only slightly higher ($\sim$0.05 eV/molecule) than that of the favored structure, but the optimal volume is about 10% bigger. Therefore, if β-cristobalite had a true $Fd3m$ symmetry, the atomic density would be smaller than what has been observed. In fact, the optimized theoretical density gives rise to a Si-O distance of 1.6 Å, which is consistent with general

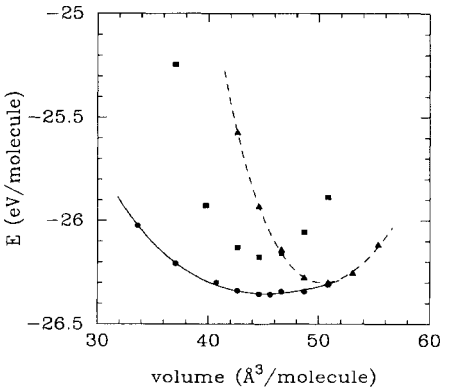

FIG. 1. Binding energy as a function of volume of three different structures of symmetry $P2_13$ (squares), $Fd3m$ (triangles), and $F\bar{4}d2$ (circles). The solid and dashed lines are Murnagham fits to the $E(V)$ data of $F\bar{4}d2$ and $Fd3m$ symmetry, respectively.

TABLE I. Structural parameters of β-cristobalite ($F\bar{4}d2$).

Parameter	Theory	Experiment[a]	Error(%)
a(Å)	7.147	7.131	0.22
Si(u)	0.125	(in $Fd3m$ position)	
O(x)	0.081	0.079	2.53

[a]Reference [7].

findings for silica. In the ideal structure both O-Si-O and Si-O-Si angles are fixed at 109.47° and 180°, respectively. The only variable to be optimized is the Si-O distance. Then we would expect this distance to be around 1.6 Å as in all other forms of silica.

Based on the total-energy calculation, we can discard structures with $P2_13$ and $Fd3m$ symmetry in favor of one with $F\bar{4}d2$ symmetry, which is derived from the rotations of SiO_4 tetrahedra in the ideal $Fd3m$ structure. Since there are six equivalent sets of rotations, it is reasonable to assume the actual structure consists of small domains of each of the possible orientations resulting in an average pseudocubic $Fd3m$ symmetry, provided that the strain on domain boundaries is small. This assumption is supported by the lattice-dynamics studies. The phonon frequency at the zone center ($q=0$) of a particular optical normal mode F_{2g} in the $Fd3m$ symmetry was calculated within the frozen phonon approximation. This mode was chosen because it is Raman active and the experimental information is available for comparison [20]. The calculation was conducted at the experimental lattice constant for both ideal and pseudocubic $Fd3m$ symmetry. In the latter case, the results were averaged over cells of lower symmetry ($F\bar{4}d2$) in six orientations. The frequencies obtained for these two structures are 25.99 and 22.98 THz, respectively, while the experimental value is 23.30 THz [20]. The agreement is evidently much better for the pseudocubic $Fd3m$ structure.

In addition to the orientational disorder, Wright and Leadbetter [7] also attributed the observed unusually large Debye-Waller factors to a static relaxation of Si and O atoms away from ideal lattice positions so as to reduce the stress on domain boundaries. O'Keefe and Hyde [16] pointed out that some boundaries can be constructed to have thin layers of α-cristobalite structure with a local symmetry of $P4_12_12$. This is not surprising if one realizes that similar to β-cristobalite, α-cristobalite can also be derived from the same parent $Fd3m$ structure by rotating the SiO_4 tetrahedra except that the rotations are slightly larger ($\sim 24°$) and the rotation axes are orthogonal rather than antiparallel with each other on the neighboring tetrahedra. Therefore, it is very possible that Si and O atoms at boundaries in β-cristobalite tend to be displaced in a correlated manner reflecting the local $P4_12_12$ symmetry of α-cristobalite. This was also suggested by Wright and Lehmann [21]. To investigate this possibility, we placed four SiO_2 units into a tetragonal unit cell of experimental lattice constant and ideal c/a ratio ($\sqrt{2}$). The possible small tetragonal strain has been neglected. We first arranged atoms into $I\bar{4}2d$ symmetry positions (β-cristobalite) and calculated the total energy as the reference. Then, we displaced oxygen atoms into $P4_12_12$ symmetry positions (α-cristobalite), mimicking the local structure that would be found at a domain boundary, and followed by moving Si and O atoms subject to $P4_12_12$ symmetry until the forces on the atoms

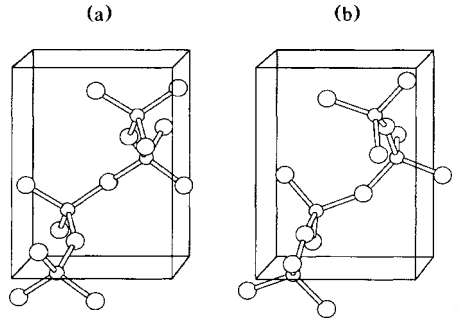

FIG. 2. Atomic configurations of space group (a) $I\bar{4}2d$ and (b) $P4_12_12$ symmetry. Small circles denote Si atoms and large circles denote O atoms.

vanished. A schematic view of the initial ($I\bar{4}2d$) and final ($P4_12_12$) atomic configurations is depicted in Figs. 2(a) and 2(b), respectively. In Fig. 3 the Born-Openheimer potential surface for the correlated motion of Si is drawn. With silicons at the high symmetrical point ($u=0.25$) the energy is lower by 0.26 eV/molecule for oxygens in $I\bar{4}2d$ positions than in $P4_12_12$ positions, which represents the order of magnitude of the domain-boundary strain energy. From the potential curve, we note that this amount of energy can be released by relaxing Si and O atoms toward the energy minimum. Thus, we find that the α-cristobalite structure can be almost degenerate in energy with β-cristobalite, even in a cubic cell with the β-cristobalite lattice constant. These results support the notion that domain boundaries will have α-cristobalite character. From the minimum of the potential well ($u=0.21$), we estimated the displacement for relaxed Si atoms to be 0.20 Å, which is again in good agreement with the experimental value [7] of 0.18 Å.

Recently, based on a Landau free energy symmetry

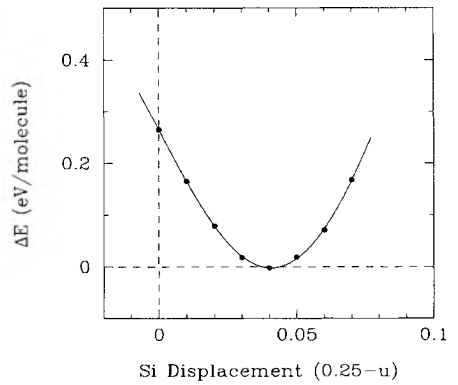

FIG. 3. Adiabatic potential energy surface for the correlated relaxation of Si with oxygen coordinates relaxed subject to $P4_12_12$ symmetry for given Si displacement. The solid line is a fit to the calculated data (circles). The energy of $I\bar{4}2d$ structure is set to zero at the origin.

analysis on the α-β transition, Hatch and Ghose [22] have proposed yet another model for β-cristobalite, in which the $Fd3m$ symmetry is a result of dynamical averaging over twelve microscopic domains of α-cristobalite, $P4_12_12$ symmetry. Our results cannot simply rule out this model; however, it is not clear how low-energy domain boundaries would arise in such a model. One of the key factors in assessing the plausibility of this model is the energy barrier between lcoal domains. Silvi *et al.* [23], using a pseudopotential periodic Hartree-Fock method, calculated the barrier for a particular path to be about 0.07 eV/molecule [23], while our calculation produced a much higher value of 0.3 eV/molecule for the same barrier. We think the small barrier obtained by Silvi *et al.* [23] is an artifact of incomplete relaxation in their calculation. The α-β cristobalite transition has also been successfully observed by Tse and Klug [24] in a recent classical molecular dynamics simulation, but the structural details of the β-phase are not given.

In conclusion, the optimal structural form of β-cristobalite has been determined based on *ab initio* total-energy and lattice-dynamics calculations. The computational efficiency is augmented by a combination of the CP-type algorithm and the Vanderbilt ultrasoft pseudopotential scheme. Our work supports the assignment of a structure which has an average pseudocubic $Fd3m$ symmetry consisting of small domains of $I\bar{4}2d$ symmetry distributed in six orientations. In addition, correlated relaxation of Si and O atoms toward α-cristobalite positions on domain boundaries is proposed. All the structural parameters obtained agree quantitatively with experimental results.

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