

Pressure-induced amorphization of β -cristobalite

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A constant-pressure molecular-dynamics (MD) study using a three-body potential is employed to study the pressure-induced structural change in β -cristobalite in the pressure range of 0–23 GPa. Our MD results demonstrate that β -cristobalite gradually transforms from a crystalline phase to an amorphous phase in the range 11–15 GPa, and abruptly changes to a sixfold-coordinated amorphous silicon structure at 13.5 GPa. Upon release of pressure, the material does not transform back into β -cristobalite but remains in the amorphous phase with a silicon coordination of nearly six. The behavior of the pressure amorphization of β -cristobalite is found to be similar to that of pressure amorphization of α -quartz. This similarity implies that they may have a similar order-disorder transition mechanism.

I. INTRODUCTION

Normally, amorphous materials are produced by rapidly quenching a liquid to prevent crystallization. It has been reported^{1,2} that some ionic amorphous materials can also be produced by applying high pressure. This direct crystalline-to-amorphous transition has resulted in considerable interest because of its technological potential in the production of bulk amorphous materials.

Among the most studied of these solids is α -quartz, which is one of many crystalline polymorphs of silica. At room temperature α -quartz was found to gradually transform from crystalline form to an amorphous form in the pressure range of 25–35 GPa.³ When the pressure was released, the silica remained amorphous, but the material was elastically anisotropic and retained the same quartz crystallographic orientation.⁴ Molecular-dynamics (MD) simulations based on pair potential were used to investigate the effect of pressure on α -quartz^{5,6} and the simulated transition occurred near the experimental amorphization pressure. Tsuneyuki *et al.*⁵ observed a transition from a fourfold-coordinated Si crystalline structure to a sixfold-coordinated Si crystalline structure, and in some of the simulation runs, to mixed fourfold-sixfold coordinated Si crystalline structures. Tse and Klug⁶ proposed a mechanism for the transformation as a mechanical instability arising from a distortion of the tetrahedral silicate units with an abrupt decrease in the elastic modulus. A recent theoretical study of α -quartz under pressure^{7,8} suggested that the amorphization of α -quartz observed experimentally originated in a lattice shear instability.

It is of great importance to explore whether the pressure-induced structural change of other silica polymorphs is similar to that of α -quartz. The basic areas of investigation are: (1) whether other polymorphs achieve pressure-induced amorphization; (2) whether the solid-state amorphization process is reversible; (3) the structural relationship between melt-quenched amorphous state and the high-pressure amorphous state; and (4) the mechanism for solid-state amorphization. Some simulation and experimental results have been reported on α -

cristobalite. MD results showed a structural transition to a novel polymorph with a space group $Cmcm$ at 16.5 GPa⁵ and to stishovite at 23 GPa. When the pressure was released, the $Cmcm$ returned to α -cristobalite, but stishovite remained stable against decompression. The experimental results⁹ showed that at 10 GPa, α -cristobalite transformed into a new crystalline phase and it transformed back into α -cristobalite on decompression. The diffraction pattern of this new high-pressure phase was different from that expected from the simulated $Cmcm$ phase. Above 30 GPa, a second new crystalline phase was formed. It was therefore concluded that α -cristobalite did not show pressure-induced amorphization.⁹ However, a report on shock amorphization of α -cristobalite has been made recently.¹⁰ The amorphization was completed by 28 GPa with a relatively sharp phase transition.

Although it has been reported that no amorphous phase is found in β -cristobalite in the pressure range 0–8 GPa,¹¹ there is still insufficient research on pressure-induced structural changes of β -cristobalite. In this work, we use MD simulation to address some of the areas of investigation mentioned earlier on the pressure-induced structural changes of β -cristobalite in the pressure range of 0–23 GPa.

II. COMPUTATIONAL METHODS

We have used the standard microcanonical ensemble MD, employing periodic boundary conditions and an Ewald treatment of the summation of long-range Coulomb terms. We used a cubic simulation box measuring 21.48 Å on each side and containing 648 ions. Newton's equations of motion were integrated using Beeman's algorithm.¹² The potentials of Vessal, Leslie, and Catlow,¹³ which included O-Si-O three-body interactions, were used in this work. This potential yielded a structure of β -cristobalite which agreed with experimental data¹⁴ except for the larger Si-O-Si angle of 176° compared to the experimental data of 144°. We performed a constant-pressure MD simulation at 300 K using a

timestep of 1.0×10^{-15} s. The velocities were rescaled during the first 6000 timesteps at each pressure to allow the system to reach the target pressure, and then followed by a 6000-time step production run. The radial distribution function (RDF) was calculated after running for 6000 time steps at each pressure and were accumulated for 900 time steps. The bond-angle distribution (BAD) was calculated from the coordinates, which were stored every 30 time steps, and were accumulated for 100 configurations.

We noted that β -cristobalite forms at about 500 K. The reasons we used the simulating temperature of 300 K in this work are as follows: (1) The potential we used are empirical fitted potential which is fitted at temperature 0 K, i.e., the simulated structure of β -cristobalite at 0 K is equivalent to the structure of cristobalite at about 500 K; (2) We have studied pressure-induced structural transition of silica glass¹⁵ at temperature of 300 K. (The simulated silica glass was prepared by the melt quenching of β -cristobalite using the same potentials as we used in this work.) In order to compare these two high-pressure silica structures (one is melt-quenched silica under pressure and the other is pressure-induced silica) we used the same simulation temperature of 300 K.

III. RESULTS

The changes in Si-O partial radial distribution function (RDF) with pressure are shown in Fig. 1. There are nearly no changes in Si-O RDF in the pressure range of 0–8 GPa except that all the peaks show a slight shift to smaller Si-O distance. At 11 GPa, except for the first Si-O

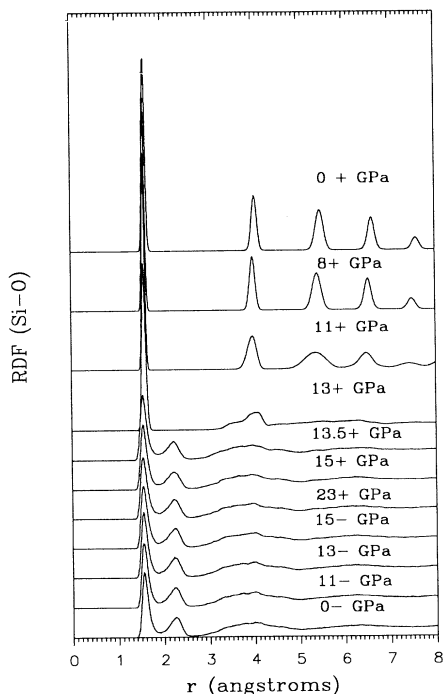


FIG. 1. Variation of Si-O partial RDF with pressure for β -cristobalite (+ indicates in compression process and - indicates in decompression process).

peaks, the breadth and the intensity of all the other peaks decrease. The Si-O RDF shows a significant change at 13 GPa. Only two peaks are observed, one at 1.58 Å and the other at 4.06 Å. The medium range order seems to no longer exist at 13 GPa. The RDF changes completely at 13.5 GPa. The intensity of the first Si-O peak drops considerably and a new peak at 2.25 Å emerges. At this pressure, the peak at 4.06 Å is not apparent, indicating that the material becomes amorphous. When pressure is continuously increased, almost no changes are observed in RDF in the pressure range 13.5–23 GPa. The pressure is released at 23 GPa and nearly no changes are observed in Si-O RDF's, indicating that the silica remains amorphous as α -quartz does.^{3,4}

Si coordination is an important concept in structural descriptions of silica glass. We show the variation of Si coordination with distance in Fig. 2. In the pressure range of 0–13 GPa the Si coordination remains at 4. At 13.5 GPa a dramatic change in Si coordination is observed. Two shoulders appear in the Si coordination curves which indicate the existence of two different O sites: one of which corresponds to the Si-O separation of 1.55 Å while the other corresponds to the Si-O separation of 2.25 Å. When we use the Si coordination cutoff of 2.6 Å, we find that the Si coordination is 5.71 at 13.5 GPa. Si coordination increases to 5.87 at 15 GPa and it reaches 6 at 23 GPa. We plot the variation of Si coordination with pressure in Fig. 3. During the compression process, there is an abrupt Si coordination increase from 4 to 5.71 at 13.5 GPa. Si coordination continues to increase in the range of 13.5–23 GPa and it reaches 6 at 23 GPa. During the decompression process, no abrupt changes in Si coordination are observed. The Si coordination decreases slowly and it has a value of 5.82 at 0 GPa.

Figures 4 and 5 show the changes in O-O and Si-Si partial RDF's with pressure, respectively. In the pressure range 0–8 GPa. We observe almost no changes in O-O and Si-Si RDF's except that all the peaks shift slightly

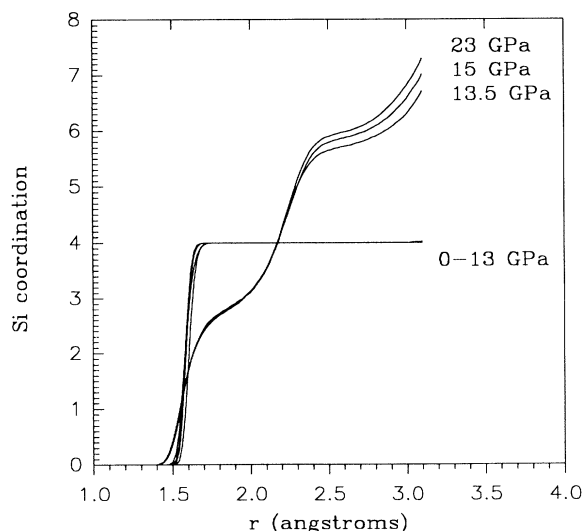


FIG. 2. Variation of Si coordination with distance for β -cristobalite.

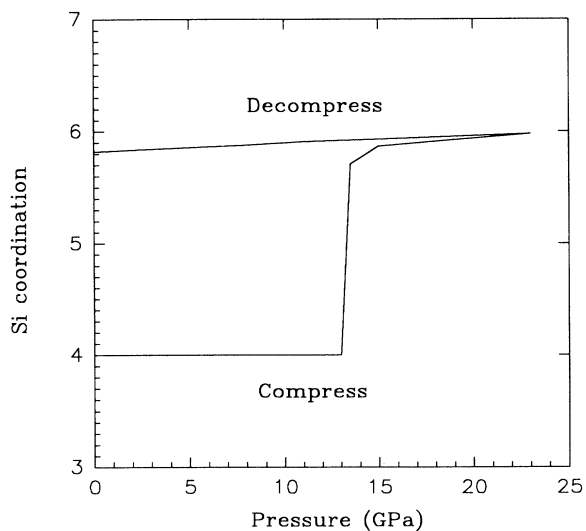


FIG. 3. Variation of Si coordination with pressure for β -cristobalite.

over small distance. At 11 GPa, the O-O and Si-Si RDF's peaks corresponding to the range 4–8 Å broaden, but the first O-O and the first Si-Si peaks remain almost unchanged. At 13 GPa both O-O and Si-Si RDF's show considerable changes: the intensity of the first O-O and the first Si-Si peaks drop and the peaks corresponding to the range 4–8 Å become difficult to distinguish. Similar

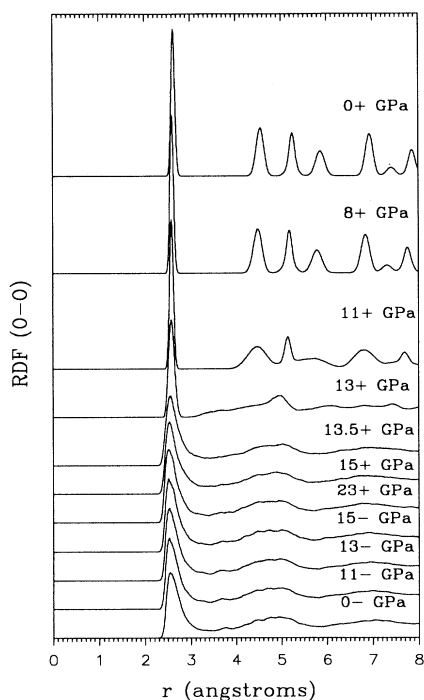


FIG. 4. Variation of O-O partial RDF with pressure for β -cristobalite (+ indicates in compression process and - indicates in decompression process).

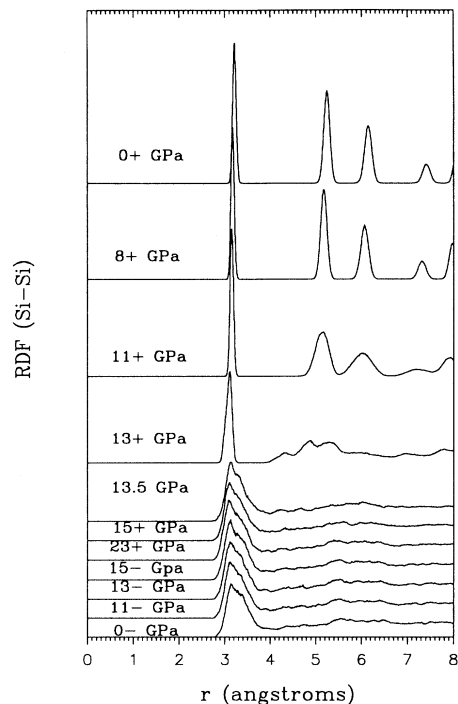


FIG. 5. Variation of Si-Si partial RDF with pressure for β -cristobalite (+ indicates in compression process and - indicates in decompression process).

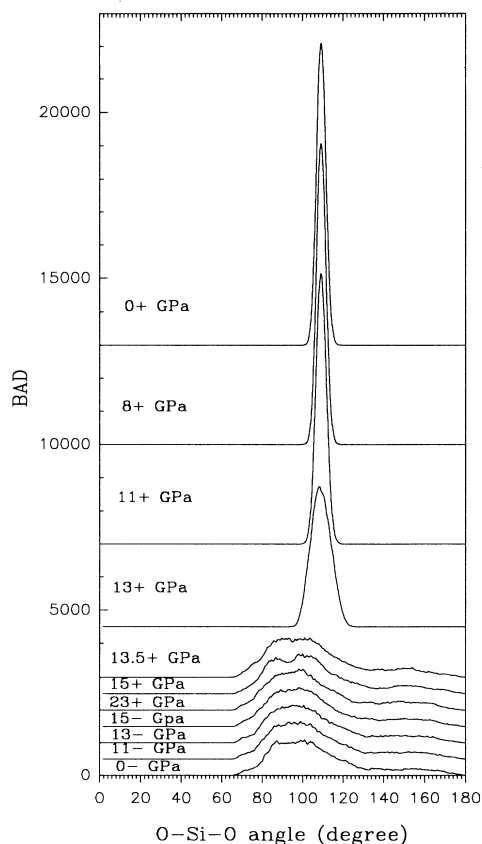


FIG. 6. Variation of O-Si-O BAD with pressure for β -cristobalite (+ indicates in compression process and - indicates in decompression process).

to the Si-O RDF, the O-O and Si-Si RDF's change completely at 13.5 GPa. Both the first O-O and first Si-Si peaks broaden and the intensity of two peaks drop as well. The peaks corresponding to the range 4–8 Å are no longer distinct. These changes indicate that the material became amorphous. In the 13.5–23 GPa range the O-O and Si-Si RDF's show only slight changes. When we release the pressure at 23 GPa, we observe almost no changes in O-O and Si-Si RDF's as we observed in the Si-O RDF.

The O-Si-O BAD is shown in Fig. 6. At 0 GPa, most O-Si-O angles in β -cristobalite have a value of 109.5° which is in agreement with experiment.¹³ In the pressure range of 0–8 GPa there are nearly no changes in O-Si-O BAD. At 11 GPa the intensity of O-Si-O BAD peak decreases but most O-Si-O angles still have a value of 109° . The O-Si-O BAD changes significantly at 13 GPa. The peak broadens, the intensity of the peak decreases, and the peak shifts of 107.5° . The O-Si-O BAD shows a dramatic change at 13.5 GPa. The peak broadens considerably and most O-Si-O angles have a value between 86° – 104° , which is not the O-Si-O value for the SiO_4 tetrahedral. When pressure is continuously increased until 23 GPa, there are only small changes in O-Si-O BAD. On release of pressure the O-Si-O BAD shows slight changes and it does not transform back to the shape of

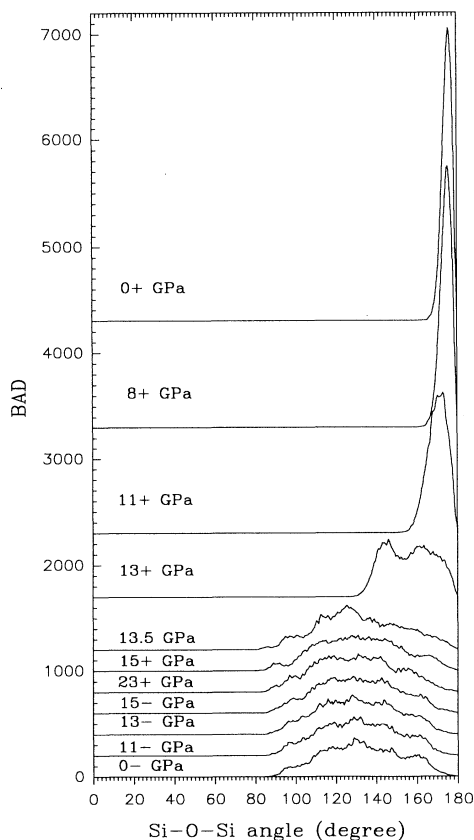


FIG. 7. Variation of Si-O-Si BAD with pressure for β -cristobalite (+ indicates in compression process and – indicates in decompression process).

the β -cristobalite at ambient pressure.

The changes of Si-O-Si BAD with pressure are shown in Fig. 7. Similarly no changes in the O-Si-O BAD are observed in the pressure range 0–8 GPa. At 11 GPa the Si-O-Si peak shifts from 176° to 171.5° and the intensity of the peak also drops. The Si-O-Si BAD changes considerably at 13 GPa. Two peaks appear: one at 144° and the other at 163.5° . When the materials become amorphous at 13.5 GPa, the Si-O-Si BAD changes completely. The possible Si-O-Si angles cover a very wide range from 90° to 175° with a peak at about 125° . At 15 GPa the Si-O-Si BAD appears as a very wide and flat band in the range 100° – 150° . In the pressure range 15–23 GPa there is almost no change in Si-O-Si BAD. When pressure is released, little change is observed in the Si-O-Si BAD, but a prominent peak appears at about 130° .

IV. DISCUSSION

We have found that β -cristobalite gradually transforms to an amorphous phase in the 11–15 GPa range and changes abruptly to an amorphous with a Si coordination of about 6 at 13.5 GPa. This behavior is very similar to that of α -quartz.^{3,7} In the range 0–13 GPa the SiO_4 tetrahedral in β -cristobalite remains basically unchanged. At 13 GPa the SiO_4 still has tetrahedral form as shown in Fig. 8(a). The abrupt change occurs at 13.5 GPa. Within a sphere of 2.6 Å in radius we found six, rather than four oxygens. Among them three have the Si-O distance of about 1.5–1.6 Å and the others have a Si-O distance of about 2.2–2.3 Å (see Fig. 2). At 13.5 GPa the Si coordination changes from 4 to about 6 (there are still some SiO_4 tetrahedral) and the Si and O cluster has a SiO_6 configuration shown in Fig. 8(b). The formation of this SiO_6 configuration is due to the displacement of both Si and O ions, rather than the displacement of Si ion only in the case of α -quartz.⁷ In Fig. 8(b) we see one of the oxygen ions (indicated in shaded circle) separate from the Si ion (indicated in open circle) with a Si-O distance of 2.48 Å. If we regard Si and O as being bonded when separated by a distance < 2.16 Å, which is a chemically acceptable bond length,⁵ this oxygen can be regarded as a non-bonded oxygen. This result is in agreement with the finding that there is bond breaking accompanying relatively small atomic displacement processes in the phase

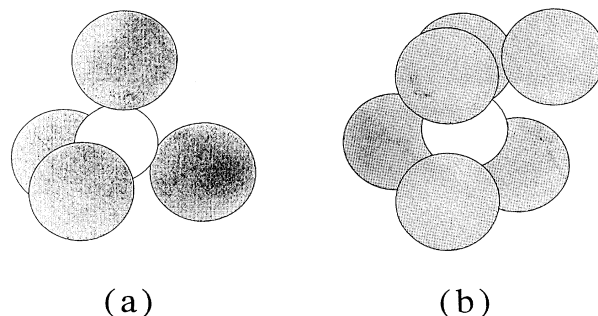


FIG. 8. The SiO_n configurations in pressure-induced silica structure. (a) the SiO_4 configuration at 13 GPa; (b) the SiO_6 configuration at 13.5 GPa.

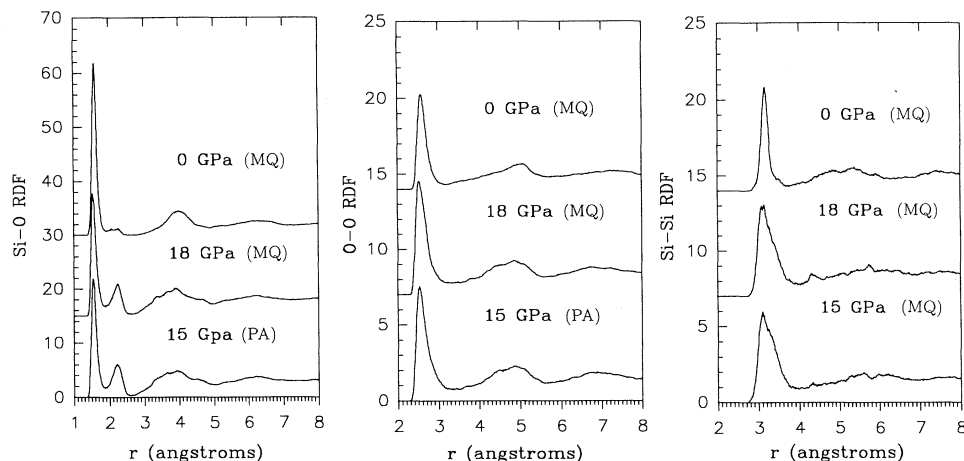


FIG. 9. Comparison of the partial RDF for melt-quenched amorphous silica (indicated by MQ) and pressure-amorphization amorphous silica (indicated by PA).

transition from a crystalline to an amorphous state for the case of pressure-induced amorphization of α -quartz.¹⁶

The relationship between pressure-induced amorphous solids and amorphous materials produced by the melt-quenched method is an unanswered question of great importance.¹⁷ Using the same potential used in this work, we have generated the computed amorphous silica from the β -cristobalite by use of the conventional melt-quenched method. The structure and structural changes of this melt-quenched amorphous silica under pressure are studied and the results will be reported elsewhere.¹⁵ A comparison of the structure of the pressure-amorphization amorphous silica and the melt-quenched amorphous silica is also made. Figure 9 shows the individual RDF for the pressure-amorphization amorphous silica (indicated by PA) at 15 GPa and the melt-quenched amorphous silica (indicated by MQ) at 0 and 18 GPa. We have found that the structure of the pressure-amorphization amorphous silica is different from the structure of melt-quenched amorphous silica. The pressure-amorphization amorphous silica at 15 GPa have a Si-O distance of about 2.25 Å and a Si coordination number of six, whereas the melt-quenched amorphous silica made at 0 GPa has a Si coordination of four. (There is a trace of Si-O distance of about 2.25 Å in this amorphous silica. This is due to the high density of the simulated system. It is found that if silica glass is simulated at -4 GPa, using the same potential, the trace of the 2.25 Å peak disappears completely).¹⁸ The O-O and Si-Si RDF's of the pressure-amorphization amorphous silica at 15 GPa are also different from that of the melt-quenched amorphous silica, with much broader first O-O and Si-Si peaks. The bond-angle distributions (BAD's) are also different for these two materials (see Fig. 10). The melt-quenched amorphous silica made at 0 GPa has an O-Si-O angle of 109.5° and a Si-O-Si angle of about 150°-165°, while the pressure-amorphization silica has a O-Si-O angle about 82°-108° and a Si-O-Si angle of about 110°-150°. It is not surprising that there are structural differences between the one produced at high pressure and the other at ambient pressure. It is more interesting, however, to compare the two amorphous silicas under high pressure. This comparison is shown in Figs. 9 and

10. It is found that melt-quenched amorphous silica and pressure-induced amorphous silica have very similar individual RDF's and have sixfold silicon coordination, but there is some difference in the BAD's especially in Si-O-Si BAD.

We have noted that the pressure-induced amorphization of β -cristobalite has not been previously reported. Our MD prediction of the pressure-induced amorphization of β -cristobalite need to be verified by further theoretical and experimental work. A great number of work has been done to study the mechanism of pressure-induced amorphization of α -quartz.⁶⁻⁸ Tse and Klug⁶ suggested that the opening of some O-Si-O angles allows oxygen atoms to fill the voids leading to increase of Si coordination. Binggeli and Chelikowsky^{7,8} proposed that a shear instability can be the driving force toward a metastable crystal collapse, such as the quartz amorphization. We noted that there are many similarities between the pressure-induced amorphization of α -quartz and the pressure-induced amorphization of β -cristobalite. For example, both have a gradual transition pressure range and both have sixfold silicon coordination in high-

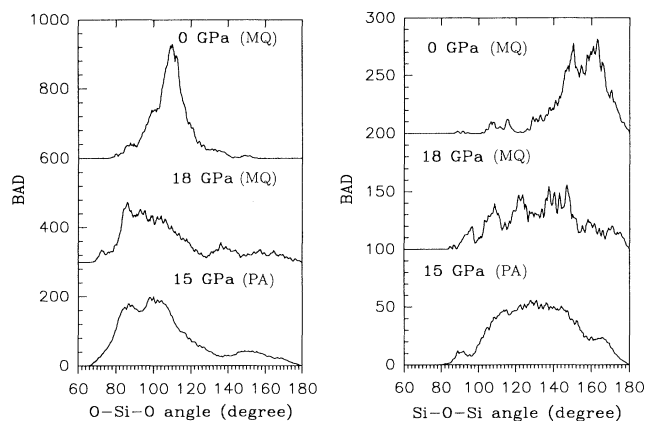


FIG. 10. Comparison of the BAD for melt-quenched amorphous silica (indicated by MQ) and pressure-amorphization amorphous silica (indicated by PA).

pressure amorphous phases. These similar features imply that they may have similar mechanism for order-disorder transition. The study of the mechanism of the pressure-induced amorphization of β -cristobalite is our future work.

V. CONCLUSION

Our MD results predict that pressure-induced amorphization of β -cristobalite occurs in the pressure range of 11–15 GPa. At 13.5 GPa the Si coordination changes abruptly from 4 to 6. In the pressure range of 13.5–23

GPa, the material shows little change. When we release the pressure, the material remains amorphous with little change in Si coordination. It has been found that the structure of the pressure-amorphization amorphous silica is different from that of melt-quenched amorphous silica, but is similar to that of melt-quenched amorphous silica under high pressure.^{15,19,20}

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