

PRESSURE INDUCED PHASE TRANSFORMATIONS IN SILICA

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ABSTRACT

Silica, SiO_2 , is one of the most widely studied substance because of its complex and unusual properties. We have used a recently developed 2-body interaction force field [1] to study the structural phase transformations in silica under various pressure loading conditions. The specific transformations we studied are the α -quartz to stishovite, coesite to stishovite and fused glass to a dominantly six-coordinated dense glassy phase. Molecular dynamics simulations are performed under constant loading rates ranging from 0.1 GPa/ps to 1.0 GPa/ps, with final pressures upto 100 GPa and at temperatures of 300, 500, and 700 K. We observe the crystal to crystal transformations to occur reconstructively, whereas it occurs in a smooth and displacive manner from glass to a stishovite-like phase confirming earlier conjectures.[2] We studied the dependence of transition pressure on the loading rate and the temperature to elucidate the shock loading experiments. We also studied the unloading behavior of each transformation to assess the hysteresis effect.

INTRODUCTION

Despite its simple chemical formula, SiO_2 , silica has some of the most complex, interesting and unusual properties of any material. It is ubiquitous in the earth's crust, and silicon and oxygen are abundant elements in the solar system. The manner in which silica responds to pressure and stresses also touches many fields of study, from geology to microelectronics. Understanding the properties of silica has impact from making simple tools to glass fibers to the design, processing and manufacturing of micro- and nano-electronic devices. Due to the rich variety of its polymorphs and amorphous states, it also serves as a model system for studies of high pressure structures and structural phase transformations.

Over the last decade an increasing number of researchers from different fields of science attempted to investigate the various aspects of silica, such as structure, melting, phase behavior, and energetics using molecular mechanics, molecular dynamics and monte carlo methods. If silica is exposed to a shock wave, various low density silica polymorphs and its glass phase transform to high density stishovite along the Hugoniot isentrope. Several years ago Stolper and Ahrens[2] pointed out a difference in the α -quartz to stishovite vs. glass to stishovite transformation. "...This transformation takes place in a displacive manner rather than through reconstruction". In this study, we aim to shedding some light onto this sound conjecture by analyzing the microstructures of the model systems along the transformation path.

The representation of atomic interactions is central to all classical computational approaches. We recently developed a simple 2-body interaction potential in which the long range electrostatic interactions are handled via a variable charge model and the short range valence and van der Waals interactions are represented by a morse potential [1]. The partial charges are determined by the charge equilibration method of Rappe and Goddard.[3] We have successfully applied this potential to characterize silica polymorphs and especially the microstructure of glassy form. [4]

Our objective is to present a systematic study of crystal-crystal, glass- crystal transformations

observed in silica and to assess the role of factor, such as temperature, and pressure loading rate on the transition pressure. We also use the microscopic level information to investigate the details of transformations as it relates to the shock wave experiments at these pressures and loading rates. Furthermore, we aim to develop an understanding of the behavior of various silica polymorphs and glasses when subjected to high pressures.

In the Theory and Method section, we briefly describe the interaction potentials used in this study, and the procedures used in molecular mechanics and molecular dynamics simulations. In the Results section, we present and discuss the simulation results we obtained.

THEORY AND METHOD

Interaction Potentials for Silica

Silica can exist in several crystalline polymorphs as well as in the amorphous state. A number of interatomic potential functions have been developed which can, with reasonable accuracy, reproduce the structural characteristics of one or more of the silica polymorphs. The most widely used forms of interaction potentials have a 2-body Born-Mayer-Huggins[4-8] term along with an attractive dispersion term, *i.e.* an $exp - 6$ potential for studying silica. However, these may differ slightly in handling the electrostatic interaction, from screened coulomb (*erfc*-complementary error function) to formal charge models. Some model potentials also include a Stillinger-Weber type 3-body term. [9]

We developed the new pure 2-body interaction potential for simulation of all phases of silica, glasses and melts and extended it to alumina as well. This new MS-Q interatomic potential differs from the previous potentials by allowing the charges to adjust self-consistently to changes in the environment. These charges are determined via the Charge Equilibration (Qeq) method of Rappe and Goddard.

A Morse type function is assumed for short range bonding forces. Thus the MS-Q two body interatomic potential function has the form:

$$U(R_{ij}) = \frac{q_i q_j}{R_{ij}} + D_o \left[e^{\gamma \left(1 - \frac{R_{ij}}{R_o}\right)} - 2e^{\frac{\gamma}{2} \left(1 - \frac{R_{ij}}{R_o}\right)} \right]$$

where q_i are the charges and R_{ij} is the distance between atoms i and j . D_o , R_o and γ are adjustable parameters and their values are given in Table 1.

Table 1. MS-Q Force Field parameters for silica.

Type	R_o	D_o (kcal/mol)	γ
$O - O$	3.7910	0.53630	10.4112
$Si - Si$	3.7598	0.17733	15.3744
$Si - O$	1.6280	45.9970	8.6342

The charges for the Si atoms in the optimized silica polymorphs varied between 1.22 and 1.4. This compares with potential derived charges and Mulliken charges obtained from a Si(OH)₄

cluster ab initio Hartree Fock calculation using a 6-31G** basis set of 1.528 and 1.493 respectively. Thus, the Qeq charges appear reasonable. The Qeq charges for O vary from -0.61 to -0.70.

In our model glass simulations with this potentials, we found the pair distribution functions, $g(r)$, and angular distribution functions for $O - Si - O$ and $Si - O - Si$ to be in good agreement with experiment.[4]

Model Systems and Simulation Procedure

In our studies we employed both molecular mechanics and a variable cell Parrinello-Rahman-Nosé molecular dynamics. to optimize the structure and lattice parameters or volumes of silica polymorphs. Model systems are supercells of unit α -quartz, coesite and stishovite, and glasses which were obtained from melt through lengthy quench procedure with sizes ranging 576 atom to 640 atoms. Energy, force and stresses in the simulations which are described below all employed the Ewald summation method.

We did not impose any crystal symmetry constraints in molecular mechanics simulations. We imposed an external hydrostatic pressure on the model systems, and the pressure was incremented by 1 GPa steps up to 10 GPa, 2 GPa steps up to 30 GPa, and 5 GPa steps beyond 30 GPa. In order to explore the release "isentropé" we also re-traced the loading curve backwards for the stishovite and α -quartz case. Termination criteria for optimization was 0.1 kcal/mol/Å. The results of these are presented in the next section.

Molecular dynamics simulations are performed under constant temperature condition, in contrast to shock wave experiments. Furthermore, the imposed pressure load or profile was isotropic rather than uniaxial. In these simulations, integration step is set to be 1 femtosecond. In the course of simulations the pressure is incremented by 1 GPa at specific intervals to impose the following pressure loading rates: 0.1, 0.25, 0.5, and 1.0 GPa/ps. The configurations and velocities at the end of each pressure segment were used to start new constant pressure equilibrium molecular dynamics simulations. This additional 25 ps simulations were analyzed to study the micro structure and obtain averages of properties.

RESULTS

Molecular Mechanics simulations are used to obtain 0 K $P - \rho$ "isotherms" for α -quartz, coesite, stishovite and glass. The results are plotted in Fig. 1.a We obtained higher order mechanical properties using the second derivative matrix, *i.e.* Hessian. In these calculations we used a smaller size (maximum 2x2x2 supercell) models, We also calculated the Birch-Murnaghan equation of state parameters, (Bulk modulus, B , and its pressure derivative, B' , at zero pressure) for the crystalline phases. For α -quartz, $B = 36.4(37)GPa$, for coesite, $B = 85.3(89)GPa$ and for stishovite $B = 290.7(298)GPa$, values in parantheses are the experimental values.

The pressure-density relationships reveal sharp transitions from α -quartz to stishovite (with a number of defects) at 24 GPa, and at 20 GPa for coesite. The transition in glass however, is gradual, with the 5- 6- coordinated local structures emerging slowly as the pressure is as the pressure is increased. Even at a pressure as high as 100 GPa, the percentage of 6-coordinated atoms are less than that of structures obtained from quartz and coesite. When the loading curves for stishovite and α -quartz are retraced, the transformation to stishovite from α -quartz is found to be irreversible. Resulting structure has a density of $3.7 g/cm^3$. This is in agreement with the shock wave experiments.[10]

Figure 1. Molecular Mechanics simulation of Equation of State for silica polymorphs and a model silica glass: a) Pressure vs. Density for α -quartz, coesite, stishovite and glass models. b) Loading and release isotherms (at 0 K) for quartz and stishovite

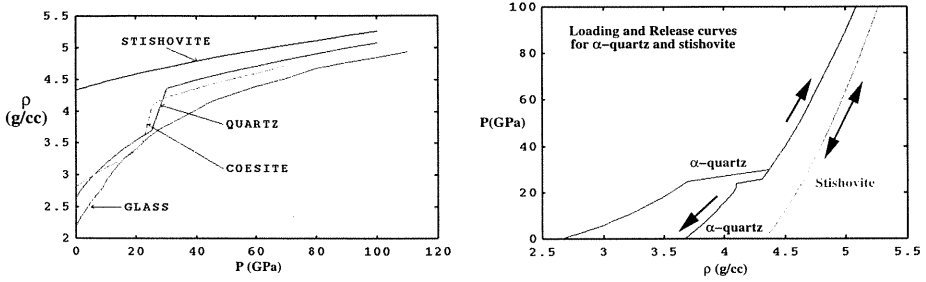
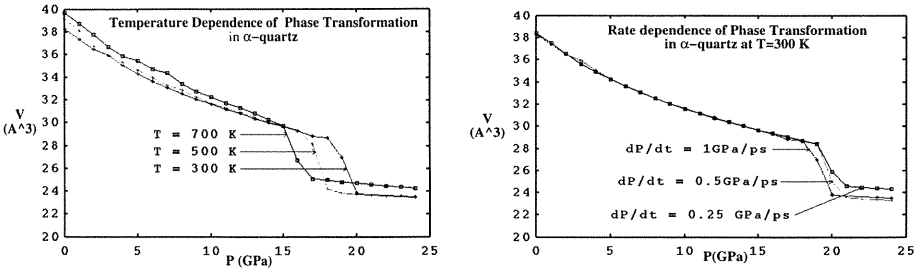


Figure 2. Temperature and pressure loading rate dependence of transformation pressure for α -quartz to stishovite; a) Temperature dependence, pressure loading rate is 1.0 GPa/ps, b) Pressure loading rate dependence, $T = 300K$



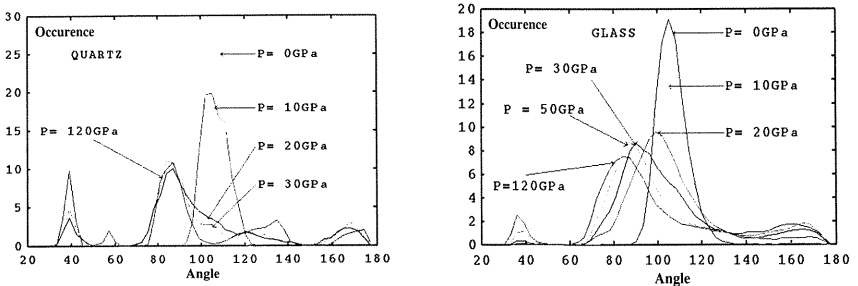
We studied the rate and temperature dependence of the phase transformation using isothermal-isostension molecular dynamics, which mimics a non-equilibrium process by subjecting the system to increasing isotropic pressure over time. The time interval between steps are varied to investigate the loading rate dependence of pressure loading. The rates were varied from 0.1 GPa to 1.0 GPa per picoseconds. The simulations for 1 GPa/ps rate were repeated at two higher temperatures, 500 and 700 K, to investigate the temperature dependence of the transition pressure in the α -quartz case. These temperatures are considerably lower than the temperatures observed in shock wave experiments. The results of pressure loading rate and temperature effects are displayed in Fig. 2.a

and 2.b respectively.

The temperature dependence of transformation pressure is stronger than the rate dependence, at least for the rates used in this study. The phase transition pressure changes by about 3 GPa for a temperature increase of 400 K. Experimental Hugoniot data shows evidence of transition starting at about 14 GPa for 500 K [10], which is in agreement with our result of 15-16 GPa at 500 K.

Finally, to check the conjecture of Stolper and Ahrens, we analyzed the trajectories for microstructural evolution. The α -quartz to stishovite or glass to dense stishovite-like phase transition can easily be characterized by the variation of the distribution of O-Si-O angles in the structure. This angle is 100 % tetrahedral for quartz, dominantly tetrahedral, but not all, for glass structure, however in stishovite this angle is octahedral. In Figure 3.a and 3.b, we present the variation of the O-Si-O angles for quartz and silica glass. We see an abrupt change in the distribution for quartz whereas the change in glass is continuous even at pressures up to 120 GPa. Pressure vs. density curves follow a parallel path to that of stishovite, both for the results obtained from α -quartz and glass models, implying similar bulk modulus.

Figure 3. Microscopic analysis of pressure induced transformations using O-Si-O angle distribution as a precursor: a) α -quartz, b) model silica glass



The angle distribution for dense structure obtained from the model glass has a peak almost twice broader than that of the results obtained from α -quartz at the octahedral angle value. As a note, the peaks observed at 45 and 135 degrees are due to the silicon bonds to oxygens on the bisectors of 90 degree O-Si-O angles. We conclude that the transformation from α -quartz to stishovite is reconstructive. But the transformation observed in the glass is gradual and displacive, with the peaks of the angle distributions progressively approaching to the octahedral coordination values.

CONCLUSIONS

We have used a recently developed interaction potential to study the pressure induced structural transformations in silica, by molecular mechanics and molecular dynamics techniques. The effects of hydrostatic pressure, hydrostatic pressure loading rates and the temperature are systematically investigated. We identified that the transition pressure is more strongly dependent

on the temperature at the loading rates used in our simulation. This is plausible since the crystal to crystal transformation requires an activation energy more readily available at higher temperatures. We found good agreement with the shock wave transition pressure data at 500 K. The transition pressure will be further depressed to 7-9 GPa range as in some shock experiments where measured shock temperatures are closer to 2000 K.[11] As a caution, these computational experiments based on described molecular dynamics procedures by no means mimics the conditions, and thermodynamics of a shock experiment. However, it clarifies the progression of phase transitions under hydrostatic pressure and isothermal conditions. With our simulations we confirmed the validity of the conjecture by Stolper and Ahrens for the glass to stishovite transformation by investigating the microstructure of the model systems as a function of increasing pressure load. We found that the transformations from α -quartz to stishovite are reconstructive whereas the transformation in the glass takes place in a displacive manner, with the peaks of the angle distributions progressively approaching to the 6-fold coordinated values.

ACKNOWLEDGEMENT

This research was supported by the NSF (CHE 95-22179 and ASC 92-17368). The facilities of the MSC are also supported by grants from DOE-AICD, Chevron Petroleum Technology, Asahi Chemical, Chevron Chemical Co., Owens Corning, Aramco, Seiko-Epson, Avery Dennison, Chevron Refinery Technology, and the Beckman Institute.

REFERENCES

1. E. Demiralp, T. Cagin, W.A. Goddard, III, MRS Spring 1997 Spring Meeting Proceedings, unpublished.
2. E.M. Stolper and T.J. Ahrens, *Geophys. Res. Lett.* **14**, 1231 (1987).
3. A. K. Rappe and W.A. Goddard, III, *J. Phys. Chem.* **89**, 8900 (1990).
4. E. Demiralp, T. Cagin, W.A. Goddard, III, MRS Spring 1997 Spring Meeting Proceedings, unpublished.
5. S. Tsuneyuki, M. Tsukada, H. Aoki, Y. Matsui, *Phys. Rev. Lett.* **61**, 869 (1988).
6. A.B. Belonoshko, L.S. Dubrovinsky, *Geoch. Cos. A.* **59**, 1883 (1995).
7. A. Nakano, R.K. Kalia, P. Vashishta, *Phys. Rev. Lett.* **73**, 2336 (1994).
8. B.W.H. van Beest, G.J. Kramer and R.A. van Santen *Phys. Rev. Lett.* **64**, 1955 (1990)
9. S.H. Garofalini, *J. Am. Ceram. Soc.* **67**, 133 (1984).
10. J. W. Swegle, *J. Appl. Phys.* **68**, 1563 (1990).
11. R. F. Grieve, F. Langenhorst, D. Stoffler, *Meteor. Planet. Sci.* **31**, 6 (1996).