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Theoretical Study of the Structural and Thermodynamic Properties of Amorphous SiO_2 and Amorphous SiO_2 with an Oxygen Defect Center *

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Structural properties and thermodynamic properties of amorphous SiO_2(a-SiO_2) and amorphous SiO_2 with an oxygen defect center (a-SiO_2-ODC) are investigated by using interatomic pair potentials. Amorphous configurations of SiO_2 glass are constructed by quenching using the molecular-dynamics method and subsequent relaxation using the first-principles method. The numerical result demonstrates that the calculated short-range structural parameters coincide well with the previous experimental and theoretical results reported. The thermodynamic properties including specific heat, Debye temperature, vibrational entropy, and so on are analyzed by calculating the phonon density. Furthermore, mechanical properties of both structures are obtained.

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Silica glass has been the subject of research because of its scientific, technological, and geophysical importance.[1] The structure of a-SiO_2 has been extensively studied by using various experimental[2−4] and theoretical methods,[5−9] e.g. x-ray,[2] neutron[2,5] and NMR[3] experiments. Computer simulation[7−9] studies indicate that a-SiO_2 consists of corner-sharing $Si(O_{1/2})_4$ tetrahedral units, similar to those in crystalline silica.

Extensive experimental and theoretical studies have been devoted to structural defects in SiO_2 glass[4,9−11]Heat capacities of nanostructured SiO_2(na-SiO_2) were measured in the temperature range 9–354 K. Entropy, enthalpy, Gibbs free energy, and Debye temperature were obtained based on the low-temperature heat capacity measurement of na-SiO_2.[12] A thermodynamic model was proposed to provide a physical mechanism of the glass transition in amorphous silicates.[13] The phase relationship between neighboring atoms to distinguish between the acoustic and optical character of phonon modes was investigated in SiO_2 glass.[14]

Although numerous studies have revealed the role of thermodynamic properties and the structure of a-SiO_2 and a-SiO_2 with an oxygen defect center (a-SiO_2-ODC), the effects of the physical disorder that is intrinsic to the amorphous state on the thermodynamic properties have not been clarified. Theoretical quantum mechanical calculation has proven to be valuable for understanding the detailed electronic structure of amorphous SiO_2 and a-SiO_2 with an oxygen defect center. In this Letter, interatomic potential have been used for molecular dynamics (MD) simulation of both the structural and thermodynamic properties of silica. Here we employ it for modeling the structure and thermodynamic properties of a-SiO_2. Due to its weak Coulomb interactions, Morse-type shortrange interactions is chosen.[15−17] The interatomic potential is given as

$$U_{ij}(r) = \frac{q_i q_j}{r} + D_0\Big\{\exp\Big[\gamma\Big(1-\frac{r}{R_0}\Big)\Big] - 2\exp\Big[\frac{1}{2}\gamma\Big(1-\frac{r}{R_0}\Big)\Big]\Big\}, \quad (1)$$

where q_i and q_j denote the charges of ions i and j; for the Si atom $q_{Si} = +1.30e$ and for the O atom $q_O = 0.65e$ (e is the elementary charge unit); r represents the interatomic distance between atoms i and j; D_0, γ and R_0 are the parameters of the Morse potentials which represent the shortrange interaction in the system, D_0 is the depth of potential, γ is a parameter without units, and R_0 is the equilibrium distance. Those potentials have been used for MD simulation of both the structural and thermodynamic properties of silica,[16,17] particularly, for investigation of the structural changes in silica glass at high temperatures.[17]

A perfect model at the experimental density of 2.20 g/cm^3 was generated by quenching from the melt through the MD method and subsequent relaxation using the first-principles method with the local density approximation (LDA) as implemented in the Cambridge Sequential Total Energy Package (CASTEP) code.[18] The structural parameters were determined by using the Broyden–Fletcher–Goldfarb–Shenno (BFGS) minimization technique. All the atoms were relaxed to their equilibrium. Historically, usual DFT calculations of crystalline, amorphous, and defective SiO_2 (except cluster calculations) have used the LDA rather than the GGA, similarly to Refs. [9,19]. During the simulation, the constant-

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pressure, constant-temperature ensemble (NPT) is used. For the NPT ensemble, the temperature and pressure were kept to be constant by using an extended system with a thermostat and a barostat relaxation time of 0.001 ps. Every step in the calculation corresponded to 2 fs in real time. A relaxation process of 400000 steps with a time step of 0.01 ps was calculated to obtain the 5000 K melt state under this condition.

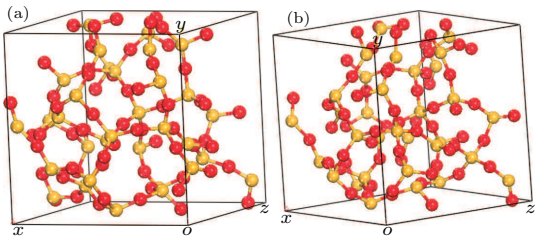


Fig. 1. Amorphous perfect (a) and defect (b) SiO_2 configurations.

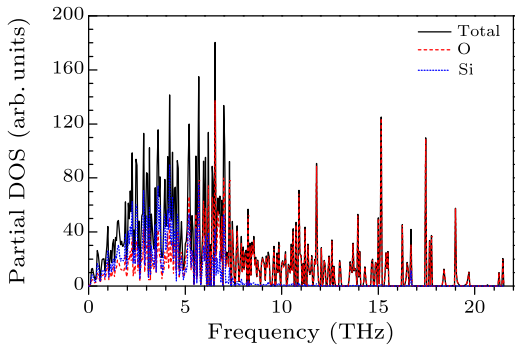


Fig. 2. Phonon densities of states of a-SiO_2.

Figure 1 shows the configuration of the perfect and defect a-SiO_2. Here a-SiO_2 with the size of 11.32 Å and containing 32 Si and 64 O atoms is configured by the first-principles calculations. It consists of a corner-sharing SiO_4 tetrahedron linked to form a continuous network with the continuous bonding of fourfold coordinated Si and twofold coordinated O. This configuration is consistent with the results of x-ray neutron[2,5] and NMR experiments[3] and with the previous theoretical studies.[8,9] The short-range structural parameters of a-SiO_2 are calculated and summarized in Table 1. The average Si–O bond length, the average Si–O–Si bond angle and the bond angle deviation are 1.63 Å, 140°, and 18°, respectively. Theses values of structural parameters are slightly larger than the values of experiments and other calculations.[11,20] By moving an O atom from the a-SiO_2 structure, the structure of a-SiO_2-ODC is constituted. Before the oxygen removal, the Si–Si distance at the removal position is near the average value in the configuration. Also, with the first-principles calculations, the relaxation is performed. The simulation results show that the relaxation does not change much of the initial structure with a basic continuous bonding network formed by the corner-sharing SiO_4 tetrahedron.

Generally, inverted interatomic pair potentials are adopted to investigate the structural properties in atomism. The phonon density of states (DOS) is a key parameter since other parameters such as Debye temperature, Einstein temperature, specific heat, and so on can be deduced from it. Starting with the effective potentials and lattice dynamic theory, we calculate the total DOS and the partial DOS of different elements for both in a cell including 96 atoms by using 936 k-points in 1/8 of the first Brillouin zone of simple cubic cell type. The cut-off distance of force constants is set at 6 Å. The calculated result for the perfect a-SiO_2 is shown in Fig. 2. The high frequency vibrations and the high frequency localized modes are mainly contributed by the O atoms. At low frequency regions, the modes are mostly excited by Si atoms. From the curve for the vibrational modes, it is found that the vibrations are composed of series of localized modes. The reason may be that the atoms in the system are amorphous and random. The calculated DOS display most of the features for the phonon spectra observed experimentally in the inelastic neutron scattering experiment.[11]

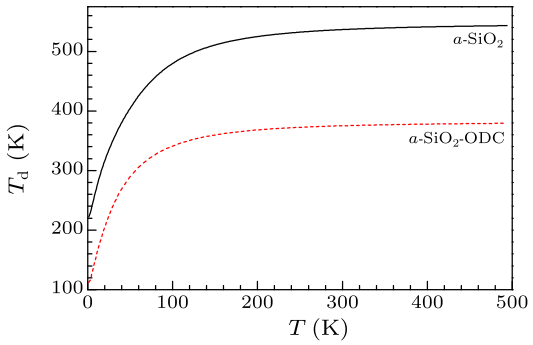


Fig. 3. Debye temperature T_d of a-SiO_2 and a-SiO_2-ODC versus temperature.

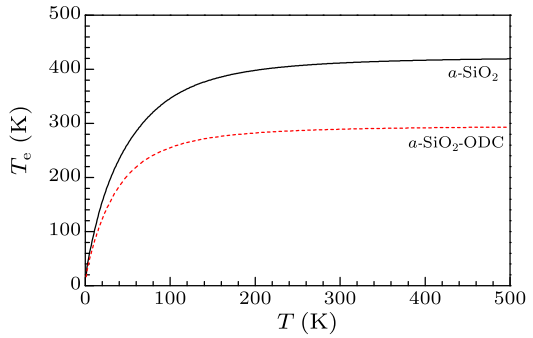


Fig. 4. Einstein temperature T_e of a-SiO_2 and a-SiO_2-ODC versus temperature.

Figures 3 and 4 show the Debye temperature and Einstein temperature of a-SiO_2 deduced by the calculated phonon DOS, respectively. In fact, the Debye model was initially proposed for approximating the

low temperature properties of materials to describe phenomena of solid-state physics that are associated with lattice vibrations, which is suitable for modeling acoustic branch.[20] However, the Einstein temperature is good at characterizing the optic branch for higher temperature. In this study, the Debye temperature and Einstein temperature are employed to characterize the vibration acoustic branches and optical branches. The calculated result implies that the Debye temperature is higher than the Einstein temperature for a-SiO_2 and a-SiO_2-ODC. Their Debye temperatures are 220 and 112 K nearly at 0 K, respectively. This value for a-SiO_2 is slightly higher than the experimental data of 198 K for coarse-grained amorphous SiO_2 (ca-SiO_2).[12]

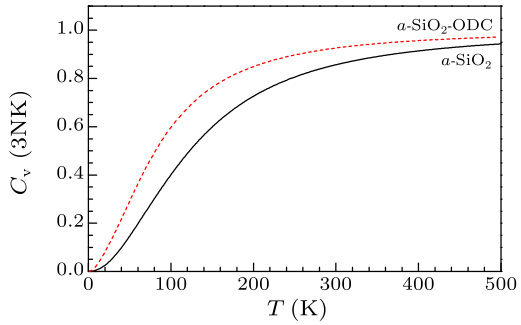


Fig. 5. Specific heat C_v of a-SiO_2 and a-SiO_2-ODC versus temperature.

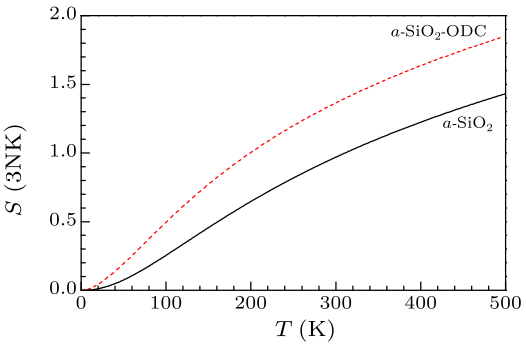


Fig. 6. Vibrational entropy S of a-SiO_2 and a-SiO_2-ODC versus temperature.

Furthermore, the specific heat and vibrational entropy for a-SiO_2 and a-SiO_2-ODC can also be obtained by the calculating phonon DOS as shown in Figs. 5 and 6. The curve of the specific heat C_v in Fig. 5 has very similar tendency with the experimental data of molar heat capacity C_p for na-SiO_2 over the temperature range 9–354 K.[12] The difference is that the data of molar heat capacity C_p for na-SiO_2 are about one times larger than those of C_v here. At the beginning, the specific heat is approximately linear with the variation of temperature and then has a tendency of flattening at a certain temperature threshold. This threshold temperature is 200 K for a-SiO_2 and 300 K for a-SiO_2-ODC. For the vibrational entropy in Fig. 6, there is the same tendency with the corresponding specific heat. It is known that the specific heat enhancement of the nanostructure materials is usually associated with an increase in the vibrational entropy.[12] This conclusion is also verified in our result. Numerical results demonstrate that the entropy of a-SiO_2-ODC with larger specific heat is higher than that of a-SiO_2 with smaller specific heat, but Debye temperature of the a-SiO_2-ODC system with larger specific heat is smaller than that of a-SiO_2 with smaller specific heat.

Table 1. Short-range structural parameters for SiO_2.

	Bond length (Å)			Bond angle(deg)	
	Si–O	O–O	Si–Si	O–Si–O	Si–O–Si
This work	1.63	2.69	3.20	110	140
Ref. [22]	1.62	2.68	2.98	109	136
Ref. [9]	1.62	2.64	3.06	109.5	145
Experiment	1.61[23]	2.63[23]	3.08[23]	109.7[24]	144[25]

Table 2. Poisson's ratios and Young's modulus.

Compounds	Poisson's Ratios (GPa)		Young Modulus (GPa)
a-SiO_2	E_{xy}=0.256	E_{xz}=0.360	x=21.648
	E_{yx}=0.249	E_{yz}=0.336	y=12.590
	E_{zx}=0.342	E_{zy}=0.329	z=10.688
a-SiO_2-ODC	E_{xy}=0.261	E_{xz}=0.340	x=20.890
	E_{yx}= 0.249	E_{yz}=0.357	y=10.347
	E_{zx}=0.315	E_{zy}=0.346	z=8.228

Finally, we calculate the mechanical properties of a-SiO_2 and a-SiO_2-ODC. A huge computer resource is needed to calculate them with an *ab initio* method due to their complex structure. Therefore, we choose to analyze Young's modulus and Poisson's ratios of a-SiO_2 and a-SiO_2-ODC by using pair potentials. The calculated results are summarized in Table 2. The average value of Poisson's ratios of a-SiO_2 is slightly larger than the experimental data of 0.175 for the a-SiO_2 film.[21] This can be explained by the fact that the size of the cluster is a limit factor. Due to the absence of one O atom, all the values about the mechanical properties for a-SiO_2-ODC are smaller than those for a-SiO_2.

In summary, the structural properties and thermodynamic properties of a-SiO_2 and a-SiO_2-ODC have been investigated. The configurations of a-SiO_2 have been constructed by quenching using the molecular-dynamics method and the subsequent relaxation using the first-principles method, which consists of corner-sharing SiO_4 tetrahedral link to form a continuous network. This configuration is in good agreement with the previous reports. Furthermore, the thermodynamic properties including specific heat, Debye temperature, vibrational entropy, and so on are calculated by using the calculated phonon density. Numerical results demonstrate that the entropy of a-SiO_2-ODC with larger specific heat is higher than that of a-SiO_2 with smaller specific heat, but the Debye temperature

of the a-SiO_2-ODC system with larger specific heat is smaller than that of a-SiO_2 with smaller specific heat. Due to the absence of one O atom, all the values about the mechanical properties for a-SiO_2-ODC are smaller than those for a-SiO_2.

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