Carbon substitution for oxygen in \(\alpha\)-cristobalite

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We investigated the carbon solubility into silica under high temperature condition. Mixtures of amorphous silica and graphite powder sealed in silica glass tubes were heated at 1300 °C. The \(a\) lattice parameter and unit cell volume of \(\alpha\)-cristobalite obtained are slightly increased compared with that heated without graphite. The \(c\) lattice parameter, on the other hand, almost unchanged. There is no clear dependency of the lattice parameter variations on carbon content mixed as the starting material. After re-heating the samples under atmospheric oxygen, the \(a\) lattice parameter and unit cell volume were reduced from the previous values. These changes indicate the possibility that carbon certainly incorporated into the \(\alpha\)-cristobalite was oxidized with the atmospheric oxygen. The ab-initio calculation of disiloxane molecule showed that with carbon substitution for the bridging oxygen the Si–C bond distance increases whereas the Si–C–Si bond angle decreases compared with the Si–O bond distance and Si–O–Si bond angle. Consequently, the distance between Si atoms increases with the carbon substitution for the bridging oxygen. Since the expansion of Si–Si distance contributes twice as much to the \(a\) and \(b\)–axes than the \(c\)–axis in the unit cell of \(\alpha\)-cristobalite, the ab-initio simulation result supports the observation that \(a\) lattice parameter increases with the carbon substitution relative to the \(c\) lattice parameter. The study strongly suggests that under reduced and high temperature conditions carbon is substituted not for silicon but for oxygen in \(\alpha\)-cristobalite structure.

Keywords: \(\alpha\)-cristobalite, Carbon substitution, X-ray diffraction, Ab-initio calculation

INTRODUCTION

Carbon is one of the most important elements in the Earth system. The exchange of carbon among atmosphere, biosphere, and oceans primarily controls the near surface carbon cycle on short timescales (Crowley, 2000; Falkowski et al., 2000). The mass of carbon stored in the mantle, however, far exceeds that in all carbon reservoirs at the Earth’s surface (Sleep and Zahnle, 2001). Emissions of CO\(_2\) from the mantle through the volcanic activity have therefore a critical influence on the Earth’s climate for long timescales of tens to hundreds of millions of years (Dasgupta and Hirschmann, 2006; Walter et al., 2011). In the Earth’s crust and upper mantle under typical redox conditions, the majority of carbon is stored as a carbon dioxide (CO\(_2\)). The carbon dissolved in silicate melt coexisting with a fluid is predominantly in the form of either molecular CO\(_2\) or carbonate group (CO\(_3^{2-}\)) depending on temperature, pressure, and melt composition (Ni and Keppler, 2013). Under more reduced conditions, the carbon is present as a methane (CH\(_4\)) together with some H\(_2\) in C–H–O fluids (Ballhaus, 1995; Manning et al., 2013). An early observation of microbubbles on dislocations in minerals from mantle xenoliths suggested that carbon may be soluble in silicates at high pressure (Green and Radcliffe, 1975). Even when a carbon solubility in olivine is of the order of a few hundred ppm by weight, it would be sufficient to incorporate all carbon in the upper mantle into olivine. Numerous attempts have been therefore made to determine the carbon solubility in olivine since the early 1980s (Freund et al., 1980; Tsong et al., 1985; Mathez et al., 1987; Tingle et al., 1988; Keppler et al., 2003). Shcheka et al. (2006) described that the carbon solubility in olivine increases exponentially by two orders of magnitude as a function of pressure. They reported that it reaches a maximum of 12 ppm by weight at 11 GPa and 1200 °C and suggested that carbon dissolved as C\(^{4+}\) must be directly substituted for Si\(^{4+}\) at the tetrahedral site (Shcheka et al., 2006). Recent study of a laser-heated diamond anvil cell showed a more explicit evidence that SiO\(_2\) with the \(\alpha\)-cristobalite-type structure

doi:10.2465/jmps.161020

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can form a solid solution with CO$_2$ under much higher $P$–$T$ conditions ($P = 16$–$22$ GPa, $T > 4000$ K) (Santoro et al., 2014). Some recent studies as to SiOC ceramics, on the other hand, have suggested another possibility that in the crust and mantle under moderately reduced conditions carbon is substituted not for silicon but for oxygen in silicate minerals (Sen et al., 2013; Mera et al., 2013; Tavakoli et al., 2015). Sen et al. (2013) mentioned that significant substitution of carbon for oxygen could occur in silicate melts in contact with graphite at moderate pressure and temperature, which may be thermodynamically far more accessible than carbon substitution for silicon. To date, however, little research has addressed a question of how carbon can be dissolved into silicate minerals under high temperature conditions.

EXPERIMENTAL METHODS

Commercially available amorphous silica (Wako Pure Chemical, purity $>$99.5%) and graphite powder (Wako Pure Chemical, purity $>$98.0%) were used as starting materials. Compositions of the starting mixtures were as follows: C/SiO$_2$ molar ratio of (1) 0:1 (188 mg amorphous silica), (2) 1:1 (20 mg graphite and 100 mg amorphous silica), (3) 1.5:1 (60 mg graphite and 200 mg amorphous silica), and (4) 2:1 (40 mg graphite and 100 mg amorphous silica). First, the mixed powders were sealed in silica glass tubes under vacuum. The silica glass tubes had dimensions of 12 mm outer diameter, 6 mm inner diameter, and about 10 cm length. They were subsequently placed into an electric furnace and heated at 1300 °C for 72 h. The silica glass tubes were then removed from the furnace and air-cooled to room temperature. The mixed powders were extracted from the tubes to perform powder X-ray diffraction measurement. Next, the samples heated with graphite in the silica glass tubes were re-heated in a platinum crucible (under atmospheric oxygen) for 72 h at 1300 °C. The samples re-heated were measured by the powder X-ray diffraction to compare the previous lattice parameters.

The powder X-ray diffraction measurement was performed on Rigaku RAD A X-ray diffractometer system with monochromatic CuK$_{α1}$ radiation in the Bragg–Brentano geometry. Data were collected over a 20 range of 10–60° with a step size of 0.02° at a scanning rate of 2.0°/min. Silicon powder (NIST SRM640c) was added to the samples as an internal standard material for accurate determination of the lattice parameters. A non-linear least-squares refinement of the lattice parameters was carried out using the program UnitCell (Holland and Redfern, 1997).

Molecular orbital calculations were performed with the quantum chemical calculation software package Gaussian-09 (Frisch et al., 2009). The geometries were optimized using the second-order Møller–Plesset (MP2) perturbation theory with 6-311G++ (2d,2p) basis set. A disiloxane molecule has been generally applied for theoretical investigations of crystalline and amorphous silicates (e.g., Xiao and Lasaga, 1994; Al Derzi et al., 2008; Morrow et al., 2009; Noritake and Kawamura, 2015). In the study, therefore, the disiloxane molecule was assumed as the simplest interior structural unit of SiO$_2$. The orbital surfaces were rendered with the Gauss-View molecular visualization package (Dennington et al., 2009).

RESULTS AND DISCUSSION

Figure 1 shows the typical X-ray diffraction patterns of run products (C/SiO$_2$ = 0.0, 2.0). All of the run products were α-cristobalite. Figure 2 shows the variations of lattice parameters and unit cell volume of the α-cristobalite as a function of graphite content in the starting material. The $a$ lattice parameter and unit cell volume were apparently increased by the heating with graphite. The $c$ lattice parameter was, on the other hand, essentially unchanged within the experimental error. After the re-heating experiment, the sample’s color was changed from
The X-ray diffraction peaks derived from graphite were completely disappeared. With the re-heating treatment, the lattice parameter and unit cell volume were consequently reduced from the previous values (Fig. 2). The changes indicate that carbon in the unit cell was oxidized by the atmospheric oxygen, which supports the possibility that carbon was certainly dissolved into the α-cristobalite. According to the result of high pressure and high temperature experiment (Santoro et al., 2014), the unit cell volume of α-cristobalite decreased when carbon was substituted for silicon in a tetrahedral site because the ionic radii of C$^4+$ cation (0.15 Å) in a tetrahedral coordination was considerably smaller than that of Si$^{4+}$ cation (0.26 Å) (Shannon, 1976). Therefore, our result that the unit cell volume of α-cristobalite was expanded by the heating with graphite suggests that either carbon was substituted for oxygen or incorporated into defects in the crystal structure. When carbon atoms are incorporated into the randomly distributed point defects (vacancies) or linear defects (dislocations) in α-cristobalite structure, the unit cell must be isotropically expanded. Molecular dynamics simulations showed that the unit cell of cristobalite isotropically expands up to 2000 K through the α–β phase transition and returns to the original values of α-cristobalite at room temperature without any hysteresis (Bourova et al., 2000). In the study, only a lattice parameter became larger than that of α-cristobalite heated without graphite. That is, there is a site preferential occupation of carbon. This suggests that carbon atoms were not incorporated into defects but located at a specific crystal site. These results therefore strongly imply that carbon atoms were substituted for oxygen in the α-cristobalite structure.

Figure 3 shows the optimized structures for the disiloxane molecule and the highest occupied molecular orbital (HOMO) obtained by the ab-initio calculations. In the disiloxane molecule, the Si–O bond distance and Si–O–Si bond angle were optimized to the values of 1.6148 Å and 142.30° (Fig. 3a), which were roughly similar to the observed values of Si–O = 1.603(1) Å and Si–O–Si = 146.49(6)° in α-cristobalite (Downs and Palmer, 1994). The calculated Mulliken atomic charges in the disiloxane were +2.535 for the Si and −1.647 for the bridging oxygen. When carbon was substituted for silicon, the bond distance was drastically decreased from 1.6148 to 1.3580 Å (Fig. 3b). The bond angle of Si–O–C was also decreased from 142.30 to 127.69°. The Mulliken atomic charges of Si, O, and C were +2.412, −1.137, and +1.132, respectively. The interatomic distance between silicon and carbon was contracted from 3.0564 to 2.6896 Å. Since the carbon substitution for silicon must induce the pronounced contraction of the unit cell, the result is entirely consistent with that of high P–T experiment (Santoro et al., 2014). Next, when carbon was substituted for the oxygen shared by two tetrahedra, the bond distance was increased from 1.6148 Å to 1.8484 Å (Fig. 3c), which is almost consistent with that of moissanite SiC (1.8898 Å) (Capitani et al., 2007). The bond angle was decreased to 126.58° (Fig. 3c). It can clearly be seen that in the HOMO the lone pair $\rho$ orbital of carbon contributes the formation of $\pi$ bonding orbital, resulting in the characteristic large bending angle of Si–C–Si angle. The Mulliken atomic charges of Si and C were changed to +2.003 and −0.839, respectively. The carbon shared by two tetrahedra bore a negative charge. The most noteworthy finding

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Figure 2. Variations of lattice parameters and unit cell volume of α-cristobalite with graphite content. Open diamonds represent those of α-cristobalite heated with graphite in sealed silica glass tubes, while solid squares show those re-heated under atmospheric oxygen.
was that the interatomic distance between silicon atoms was consequently expanded from 3.0564 to 3.3024 Å with the substitution although the bond angle of Si–C–Si becomes rather smaller than that of Si–O–Si. The increase of the Si–Si distance gives a reasonable account of the anisotropic expansion of α-cristobalite structure observed in the study. The silicon atoms in α-cristobalite are located in the Wyckoff position 4a around the four-fold screw axis running along c-axis in the tetragonal system (Downs and Palmer, 1994). The vector between the Si and Si atoms is oriented to [0.5 −0.1 0.25] and [0.1 0.5 0.25] directions. That is, the expansion of Si–Si distance contributes twice as much to the a and b-axes than the c-axis. This can well explain the reason why the a lattice parameter was increased with the carbon substitution relative to the c lattice parameter.

In the study, the variations of a lattice parameters and unit cell volume were not in proportion to graphite content in the starting materials. Taking into consideration the resulting largely bended Si–C–Si angle with the carbon substitution, there would be an upper limit of carbon substitution in the α-cristobalite structure.

Conclusively, the results of this study strongly suggest that under highly reduced conditions carbon is substituted not for silicon but for oxygen in α-cristobalite. It can be considered that the carbon substitution for oxygen is more accessible than that for silicon under high temperature and low pressure conditions. This study will contribute to a fundamental understanding of direct interaction at the interface between silicates and graphite at high temperature.

ACKNOWLEDGMENTS

The work was supported by a Grant–in-Aid for Scientific Research (C) from the Japan Society for the Promotion of Science (project no. 26400511).

REFERENCES

Al Derzi, A.R., Gregusova, A., Runge, K. and Bartlett, R.J. (2008) Structure and properties of disiloxane: An ab initio and post-Hartree-Fock study. International Journal of Quantum Chemistry, 108, 2088–2096.

Ballhaus, C. (1995) Is the upper mantle metal–saturated? Earth and Planetary Science Letters, 132, 75–86.

Bourova, E., Parker, C.S. and Richet, P. (2000) Atomistic simulation of cristobalite at high temperature. Physical Review B, 62, 12052–12061.

Capitani, G.C., Di Pierro, S. and Tempesta, G. (2007) The 6H-SiC structure model: Further refinement from SCXRD data from a terrestrial moissanite. American Mineralogist, 92, 403–407.

Crowley, T.J. (2000) Causes of climate change over the past 1000 years. Science, 289, 270–277.

Dasgupta, R. and Hirschmann, M.M. (2006) Melting in the Earth’s deep upper mantle caused by carbon dioxide. Nature, 440, 659–662.

Dennington, R., Keith, T. and Millam, J. (2009) GaussView, Version 5. Semichem Inc., Shawnee Mission, KS.
