Molecular Dynamics Simulation of the Thermodynamic and Structural Properties for the CaO–SiO₂ System

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The thermodynamic, structural and transport properties for the CaO–SiO₂ system were calculated by molecular dynamics (MD) simulation using the pairwise potential model with partial ionic charges. The interatomic potential parameters were determined by fitting the physicochemical properties of calcium oxide and calcium silicates with experimentally measured results. The calculated structural properties such as the pair distribution functions and the fractions of bonding types (bridging, non-bridging and free oxygen) of oxygen with silicon atoms in CaO–SiO₂ melts were in good agreement with observed results, and also the self-diffusion coefficients of calcium, silicon and oxygen ions have been calculated at 1873 K. The ΔH⁰, ΔS⁰ and ΔG⁰ for the CaO–SiO₂ system were calculated based on the thermodynamic and structural parameters obtained from MD simulation. The phase diagram for the CaO–SiO₂ system estimated by calculated Gibbs energy of mixing shows good agreement with observed result in the range above 50 mol% CaO and the liquid–liquid immiscibility region in the CaO–SiO₂ system have also been assessed by MD calculation.

KEY WORDS: molecular dynamics; simulation; calcium silicates; thermodynamics; molten silicate structure; phase diagram.

1. Introduction

Molecular dynamics (MD) simulation has been widely employed as the very useful method for the calculation of thermodynamic, structural and transport properties for the molten slags and fluxes at high temperatures. MD simulation is applied to calculate the various physicochemical properties based on the dynamic quantities of individual particles in the solid and fluid simulation cells with pertinent potential models. Therefore, the thermodynamic, structural and transport properties of high melting temperature and high vapor pressure materials which are difficult to measure by experimental methods can be effectively estimated.

MD calculations of the crystal, glass and liquid phases for the silica and silicate systems have been performed by several researchers using various potential models for the estimation of realistic structural and thermodynamic properties at high temperatures and pressures. The interatomic potential models reported by Tsuneyuki et al.¹¹ and Beest et al.¹² were in good agreement with the experimentally measured structural properties of various silica polymorphs and molten silica. The structural properties for the potassium disilicate and sodium silicate glasses and melts calculated by Balasubramanian et al.¹³ and Horbach et al.,¹⁴ which were simulated based on the potential models reported by Tsuneyuki et al. and Beest et al. reproduced well the network structural properties in the alkali metal silicate systems. Belonoshko et al.⁵,6 have also successfully assessed the thermodynamic and structural properties for the silica and magnesium silicates at various temperatures and pressures by using the transferable pairwise interatomic potential model. Takei et al.⁷ have calculated the metastable immiscibility region in the Al₂O₃–SiO₂ system from the thermodynamic and structural data obtained by MD simulation.

In the present study, we determined the effective potential model for the CaO–SiO₂ system with optimized potential parameters. The thermodynamic, structural and transport properties for the CaO, Ca₂SiO₄, CaSiO₃ and CaO–SiO₂ melts were calculated by optimized potential model, which were compared with observed results. The phase diagram for the CaO–SiO₂ system, especially the liquid–liquid immiscibility region in the SiO₂-rich region was estimated by the thermodynamic and structural data obtained from MD calculation.

2. Molecular Dynamics Calculation

2.1. Interatomic Potential

Since the application of MD simulation for vitreous and molten silica by Woodcock et al.⁸ using simple pairwise potential model, various interatomic potential models such as two-body potential models (Born–Mayer–Huggins and Morse type)¹⁰,¹¹ and three-body potentials models (Stringer–Weber type) with the formal charges or partial charges have been proposed for the more realistic simulation of the crystal, glass and liquid phases for the silica and silicate systems based on the covalent tetrahedral network struc-
ture. The ionicity of Si–O bond of silica is about 50% according to Pauling’s electronegativity rule.

In this study, the interatomic potential energy was calculated by the summation of pairwise interactions between ions \( i \) and \( j \) that was the Busing approximation of Born–Mayer–Huggins form of Eq. (1).

\[
\phi_{ij}(r) = \frac{q_i q_j e^2}{r_{ij}} + f_0(b_i + b_j) \left( \frac{\sigma_i + \sigma_j - r_{ij}}{b_i + b_j} \right) - \frac{c_i c_j}{r_{ij}^6}
\]

...........................................(1)

where \( r_{ij} \) is the interatomic distance between ions \( i \) and \( j \), \( q_i \) is the valence of the ion \( i \), \( e \) is the electron charge, \( f_0 \) is the standard force of 4.184 kJ Å\(^{-1}\) mol\(^{-1}\), \( \sigma_i \) and \( b_i \) are repulsive radius and softness parameter of the ion \( i \), \( c_i \) is the van der Waals interaction parameter of the ion \( i \), respectively. The interatomic potential terms of Eq. (1) represent the Coulomb, short-range repulsion and van der Waals interaction parameter of the ion \( i \), respectively. The interatomic potential parameters used in this study are listed in Table 1.

| element | \( q_i \) | \( \sigma_i \) (Å) | \( b_i \) (Å) | \( c_i \) (kJ Å\(^{-1}\) mol\(^{-1}\)) |
|---------|---------|-----------------|-------------|-----------------|
| Ca      | 1.4     | 1.1500          | 0.05600     | 0               |
| Si      | 2.4     | 0.8688          | 0.03285     | 47.41           |
| O       | \(-n \cdot q_{Ca} + m \cdot q_{Si}\) / \((n + 2m)\) | 2.0474       | 0.17566     | 143.94          |

The potential model reported by Tsuneyuki et al.\(^{1}\) that have been derived by the \textit{ab initio} Hertree–Fock self-consistent-field calculations for model clusters of silica. The effective charges for the Si and O ions have been represented 2.4 and −1.2, respectively. The potential model reported by Tsuneyuki et al.\(^{1}\) has successfully reproduced the structural and dynamical properties for various silica polymorphs, glasses and molten SiO\(_2\)\(^{12-17}\) and the thermodynamic properties such as phase transition of Quartz.\(^{18}\) The interatomic potential parameters for Ca–Ca and Ca–O ion pairs in the CaO–SiO\(_2\) system were calculated by fitting the experimentally measured structural, transport and thermodynamic properties of CaO, Ca\(_2\)SiO\(_4\), CaSiO\(_3\), CaO–SiO\(_2\), SiO\(_2\), CaO, and CaO–SiO\(_2\) melts by fixing the interatomic potential parameters of O–O ion pairs for SiO\(_2\) by Tsuneyuki et al.\(^{1}\) The effective charges of Ca and O ions for CaO were determined to be 1.4 and −1.4, respectively. The effective charges for the nCaO–mSiO\(_2\) system were determined to vary only the O ion charge by fixing the Ca and Si ion charges in order to maintain electroneutrality in the system. The charge of O ion for the nCaO–mSiO\(_2\) system was assigned from Eq. (2).

\[
q_{ca} = 1.4, \quad q_{si} = 2.4 \quad \text{and} \quad q_{o} = \frac{n \cdot q_{ca} + m \cdot q_{si}}{n + 2m} \quad ...(2)
\]

The interatomic potential parameters used in this study are listed in Table 1.

2.2. Methods for Calculation

The MD simulations were carried out using the isobaric and isothermal (\(N-p-T\)) ensemble. Temperature is controlled by velocity scaling method. Pressure is controlled by Parrinello and Rahman method at atmospheric pressure. The atomic configurations of initial cells for solid phases were taken from the respective unit cell structures. The CaO crystal structure was composed of 1 000 (Ca 500 and O 500) atoms according to an array of 5 \times 5 \times 5 unit cells of rocksalt structure (cubic, Fm\(_3\)m).\(^{19}\) The \(\gamma\)-Ca\(_2\)SiO\(_4\) and \(\beta\)-Ca\(_2\)SiO\(_4\) crystal structures were composed of 672 (Ca 192, Si 96 and O 384) atoms according to an array of 4 \times 2 \times 3 and 4 \times 3 \times 2 unit cells of \(\gamma\)-Ca\(_2\)SiO\(_4\) (orthorhombic, \text{Pbnm})\(^{20}\) and \(\beta\)-Ca\(_2\)SiO\(_4\) (monoclinic, \text{P2}_1)\(^{21}\) structure, respectively. The wollastonite and pseudowollastonite crystal structures were composed of 810 (Ca 162, Si 162 and O 486) and 720 (Ca 144, Si 144 and O 432) atoms according to an array of 3 \times 3 \times 3 and 3 \times 2 \times 1 unit cells of wollastonite (triclinic, \text{P}\(^{22}\)) and pseudowollastonite (monoclinic, \text{C2/c})\(^{23}\) structure, respectively. The initial atomic configurations for liquid phases were set to be random in the cubic cell. The total number of atoms was taken to be from 1 000 to 1 500. The densities of initial liquid cells were adopted to be 2 200–3 340 kg/m\(^3\) based on the density of solid CaO and silica glass at room temperature. All simulations have been verified using the system of about 3 000 atoms and there have not been relevant differences.

The periodic boundary conditions were employed for each simulation system. The long-range Coulomb interactions have been summed by Ewald method. The equations of motion were integrated by fifth-order Gear’s predictor-corrector algorithm using a time step \(\Delta t = 1 \times 10^{-15}\) s. The run durations of all simulations were carried out for 30 000 time steps. In the critical points such as solid–solid and solid–liquid phase transition temperatures, the simulations were carried out using long runs up to 200 000 time steps. The simulations for solid phases were started at the room temperature structures of each solid crystal and then heated to the required temperatures. The liquid phases were heated to the initial temperature of 4 000 K and thermalized during the 30 000 time steps in order to stabilize the highly energetic atomic configurations of initial cells, and then were cooled stepwise from 4 000 to 1 600 K. In this study, the effect of cooling rate on the MD calculation results of all simulation systems has been verified using cooling rate of 0.1 K per step and relevant differences were not observed. Therefore, in this study, the effect of cooling rate was to be negligible. The various properties for the CaO–SiO\(_2\) system were calculated by statistical analyses of velocities and positions data after reaching the thermal equilibrium of each simulation system. All MD calculations were carried out using WinMASPHYC program (Fujitsu).
3. Results and Discussion

3.1. Structural and Thermodynamic Properties for the Calcium Oxide and Calcium Silicates

The potential model used in this study was assessed by calculation of structural and thermodynamic properties for the calcium oxide and calcium silicates with no symmetry constraint of initial cell. The structural parameters such as lattice constants, molar volumes and nearest-neighbor cation–oxygen distances of CaO, Ca$_2$SiO$_4$ ($\gamma$-Ca$_2$SiO$_4$ and $\beta$-Ca$_2$SiO$_4$) and CaSiO$_3$ (wollastonite and pseudowollastonite) are calculated by MD simulation at 300 K. The calculated structural parameters of CaO, Ca$_2$SiO$_4$ and CaSiO$_3$ successfully reproduced the measured results$^{19-23}$ in Tables 2, 3 and 4.

The enthalpies for solid and liquid phases of CaO were calculated as a function of temperature. The enthalpy of simulated system can be directly calculated from the internal energy, pressure and volume values obtained by MD simulation. The calculated enthalpies are compared with observed values at the sufficiently high reference temperature above the Debye temperature to neglect the quantum correction terms in this study. The Debye temperature for oxides and silicates is typically from 800 to 1 200 K. Figure 1 shows the calculated enthalpies of CaO with observed values$^{24}$ at reference temperature of 1 500 K. The calculated melting temperature and enthalpy of fusion of CaO are $3 210 \pm 10$ K and 74.5 kJ/mol that show good agreement with observed results of 3 200 $\pm$ 50 K and 79.5 kJ/mol.

Figure 2 shows the calculated molar volumes of Ca$_2$SiO$_4$ as a function of temperature. Previously, the existence of five polymorphs of Ca$_2$SiO$_4$ on temperature has been reported, which are $\gamma$-phase (stable phase under the room conditions), $\beta$-phase (metastable phase under the room conditions), $\alpha'_1$- and $\alpha'_2$-phase (stable phases at higher temperature) and $\alpha$-phase (stable phases at the highest temperature). The sequence of generally accepted phase transition temperatures of Ca$_2$SiO$_4$ polymorphs is shown in Fig. 3$^{25}$. In Fig. 2, the temperature dependence of molar volume calculated from the $\gamma$-Ca$_2$SiO$_4$ shows the large volume decrease at about 1 750 K ($\gamma$–$\alpha$ phase transition) and the large volume increase at about 2 420 K (melting temperature). These results cannot reproduce the phase transitions from $\gamma$-Ca$_2$SiO$_4$ to $\alpha'_1$- and $\alpha'_2$-Ca$_2$SiO$_4$. However, the molar volume decrease according to the solid–solid phase transition calculated from $\gamma$-Ca$_2$SiO$_4$ is in good agreement with the large volume decrease caused by the phase transition from $\gamma$-Ca$_2$SiO$_4$ to $\alpha'_1$-Ca$_2$SiO$_4$ measured by Remy et al.$^{25}$ The calculations for $\beta$-Ca$_2$SiO$_4$ also show the phase transition temperatures at about 950 K ($\beta$–$\alpha'_1$), 1 400 K ($\alpha'_1$–$\alpha'_2$), 1 700 K ($\alpha'_2$–$\alpha$) and 2 420 K (melting temperature) from the abrupt increase of molar volume. These calculation re-

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Table 2. Observed and calculated structural parameters for CaO at 300 K.

| Property       | Observed$^{20}$ | Calculated |
|----------------|-----------------|------------|
| $a$ (Å)        | 4.79            | 4.81       |
| $c$ (Å)        | 4.79            | 4.81       |
| $V$ (Å$^3$/mol) | 16.74           | 16.74      |
| Ca-O (Å)       | 2.41            | 2.35       |

Table 3. Observed and calculated structural parameters for $\gamma$-Ca$_2$SiO$_4$ and $\beta$-Ca$_2$SiO$_4$ at 300 K.

| Phase         | Space Group | Observed$^{20}$ | Calculated |
|---------------|-------------|-----------------|------------|
| $\gamma$-Ca$_2$SiO$_4$ (Pbnm) | 5.08 | 5.28 | 5.50 | 5.71 |
| $\beta$-Ca$_2$SiO$_4$ (P2$_1$/n) | 11.23 | 11.36 | 6.75 | 6.90 |
| $c$ (Å)       | 6.76         | 6.78           | 9.31       | 9.43 |
| $a$ (Å)       | 90.0         | 90.0           | 90.0       | 90.0 |
| $\beta$ (°)   | 90.0         | 90.0           | 94.3       | 85.6 |
| $\gamma$ (°)  | 90.0         | 90.0           | 90.0       | 90.0 |
| $V$ (Å$^3$/mol) | 58.01 | 60.89 | 52.08 | 55.95 |
| Si-O (Å)      | 1.65         | 1.60           | 1.61       | 1.60 |
| Ca-O (Å)      | 2.37         | 2.35           | 2.53       | 2.40 |

Table 4. Observed and calculated structural parameters of wollastonite and pseudowollastonite at 300 K.

| Compound      | Space Group | Observed$^{20}$ | Calculated |
|---------------|-------------|-----------------|------------|
| Wollastonite (CaSiO$_3$) (Space group : P1) | 7.93 | 7.99 | 6.84 | 6.91 |
| Pseudowollastonite (CaSiO$_3$) (Space group : C2/c) | 7.32 | 7.45 | 11.87 | 12.04 |
| $c$ (Å)       | 7.07         | 7.21           | 19.63      | 20.57 |
| $a$ (Å)       | 90.1         | 90.1           | 90.0       | 90.0 |
| $\beta$ (°)   | 95.2         | 93.2           | 90.7       | 91.4 |
| $\gamma$ (°)  | 103.4        | 103.4          | 90.0       | 90.0 |
| $V$ (Å$^3$/mol) | 39.8 | 41.8 | 40.2 | 42.9 |
| Si-O (Å)      | 1.62         | 1.60           | 1.60       | 1.60 |
| Ca-O (Å)      | 2.39         | 2.4            | 2.50       | 2.30 |
results are in good agreement with the observed results such as the existence of five polymorphs of Ca$_2$SiO$_4$, phase transition temperatures of Ca$_2$SiO$_4$ polymorphs and the variations of molar volumes on temperature. Figure 4 shows the enthalpies calculated as a function of temperature of Ca$_2$SiO$_4$ at reference temperature of 1800 K. The calculated melting temperature and enthalpy of fusion of Ca$_2$SiO$_4$ are 2420 ± 10 K and 65 kJ/mol for Ca$_2$SiO$_4$ are in good agreement with observed results$^{26)}$ of 2403 K and 71.1 kJ/mol. However, the temperature dependence of calculated enthalpies shows good relationship with observed results. The calculated thermodynamic properties of CaO, Ca$_2$SiO$_4$ and CaSiO$_3$ are summarized in Table 5.

3.2. Structural and Transport Properties for the CaO–SiO$_2$ Melts

Figure 6 shows the pair distribution functions of the Si–Si, Si–O, Ca–O and O–O in the 50mol%CaO–50mol% SiO$_2$ melt at 1873 K. The pair distribution functions, $g_{ij}(r)$ for the simulated system can be calculated by Eq. (3).

\[
g_{ij}(r) = \frac{V}{N_i N_j} \sum_{j} \frac{n_j (r - \Delta r/2, r + \Delta r/2)}{4\pi r^2 \Delta r} \quad \text{(3)}
\]

where $\langle n_j (r - \Delta r/2, r + \Delta r/2) \rangle$ is the average number of ion $j$ surrounding ion $i$ in a spherical shell within $r \pm \Delta r/2$, $N_i$ and $N_j$ are the total number of ions $i$ and $j$ and $V$ is the volume of the simulation cell. The positions of first peak of calculated pair distribution functions are $r_{Si-Si} = 3.15 \text{ Å}$, $r_{Ca-O} = $...
2.30 Å, \( r_{\text{Si-O}} = 1.60 \) Å and \( r_{\text{O-O}} = 2.65 \) Å, that show good agreements with the nearest-neighbor distances of ion pairs measured by Waseda et al. \(^{27}\)

The self-diffusion coefficients of Ca, Si and O ions in CaO–SiO\(_2\) melts can be estimated by the slopes of mean square displacements of ions calculated as a function of time. The mean square displacements (MSD) of ions on the time and the self-diffusion coefficients of ions can be calculated by Eqs. (4) and (5), respectively.

\[
\text{MSD} = \langle (r(t) - r(0))^2 \rangle \quad \text{............... (4)}
\]

\[
D = \frac{1}{6t} \langle (r(t) - r(0))^2 \rangle \quad \text{............... (5)}
\]

where \( r(t) \) and \( r(0) \) are the position of the ions at time \( t \) and initial position of the ions at zero time, respectively, \( \langle \cdot \rangle \) is the ensemble average and \( D \) is the self-diffusion coefficient.

Figure 7 shows the mean square displacements of Ca, Si and O ions calculated as a function of time in the 50 mol% CaO–50 mol% SiO\(_2\) melt at 1873 K. These results show that the Ca ions diffuses more rapidly than Si and O ions.

Figure 8 shows the calculated self-diffusion coefficients of Ca, Si and O ions in CaO–SiO\(_2\) melts at 1873 K with observed results. \(^{28-30}\) The calculated self-diffusion coefficients of each ion show the relationship \( D_{\text{Ca}} > D_{\text{Si}} > D_{\text{O}} \) and decrease with increasing SiO\(_2\) content in CaO–SiO\(_2\) melts. These results represent reasonably well the structural properties of CaO–SiO\(_2\) melts, which were restricted to the diffusion of Si and O ions by the formation of silica network structure in the melts. The calculated self-diffusion coefficients of Ca, Si and O ions are in good agreement with measured values by Keller et al. \(^{28-30}\)

For the calculation of the degree of polymerization in CaO–SiO\(_2\) melts, the fractions of oxygen species such as bridging (\( O^0 \)), non-bridging (\( O^- \)) and free (\( O^{2-} \)) oxygen were calculated as a function of composition. The cut-off distance between Si and O ions for the calculation of oxygen species was determined by minimum position of first peak in silicon-oxygen pair distribution function, \( g_{\text{Si-O}}(r) \).

Figure 9 shows the calculated silicon–oxygen pair distribution functions as a function of composition at 2000 and 3000 K. These results represent that the silicon–oxygen pair distribution functions do not have special composition.
and temperature dependence in CaO–SiO$_2$ melts. Therefore, in this study, the cut-off distance between Si and O ions was determined to be 2.35 Å.

Figure 10 shows the fractions of oxygen species calculated as a function of composition in CaO–SiO$_2$ melts at 1 873 and 2 000 K with experimentally measured values and thermodynamic modeling result. The calculated fractions of bridging oxygen and free oxygen show the increase and decrease with the SiO$_2$ content, and the fractions of non-bridging oxygen represent the maximum value at about 33 mol% SiO$_2$. These results are in good agreement with measured values and thermodynamic modeling result. However, the degree of polymerization of the CaO–SiO$_2$ system calculated by MD method shows appreciably higher than the measured values and thermodynamic modeling result in the range from about 20 to 50 mol% SiO$_2$. The difference between these results can be considered due to the kinetic effect by the high cooling rate, which causes the increase of the fraction of free oxygen by inadequate restructuring of silica network structure with CaO and overestimation of bonding energy between ions Si and O in the melts, the finite simulation cell size with periodic boundary condition and so on. However, it is not clear yet. Nevertheless, MD simulation has successfully represented the variation of oxygen species on the composition in CaO–SiO$_2$ melts.

Figure 11 shows the fractions of bridging oxygen with the SiO$_4^{4-}$ tetrahedron calculated as a function of composition in CaO–SiO$_2$ melts at 2 000 K. In Fig. 11(a), the fractions of bridging oxygen with SiO$_4^{4-}$ tetrahedron were expressed by $Q_n$ ($n=0$ to 4, $n$ is the number of bridging oxygen bonded with silicon ion). In order to calculate the $Q_n$ fractions for only SiO$_4^{4-}$ tetrahedron, in this study, the under- and over-coordinate species such as Si–O$_3$ and Si–O$_5$ are neglected. The calculated $Q_n$ fractions show that the $Q_0$ and $Q_1$ are the gradually decrease with SiO$_2$ content and $Q_3$ and $Q_4$ are the gradually increase up to 45 mol% of system. The calculated fractions of bridging oxygen and free oxygen show the increase and decrease with the SiO$_2$ content, and the fractions of non-bridging oxygen represent the maximum value at about 33 mol% SiO$_2$. These results are in good agreement with measured values and thermodynamic modeling result. However, the degree of polymerization of the CaO–SiO$_2$ system calculated by MD method shows appreciably higher than the measured values and thermodynamic modeling result in the range from about 20 to 50 mol% SiO$_2$. The difference between these results can be considered due to the kinetic effect by the high cooling rate, which causes the increase of the fraction of free oxygen by inadequate restructuring of silica network structure with CaO and overestimation of bonding energy between ions Si and O in the melts, the finite simulation cell size with periodic boundary condition and so on. However, it is not clear yet. Nevertheless, MD simulation has successfully represented the variation of oxygen species on the composition in CaO–SiO$_2$ melts.

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SiO₂ and then drastically increase with SiO₂ content. The fractions of Q₂ show maximum value at about 45 mol% SiO₂. These calculated Q₁ fractions are in good agreement with Raman spectroscopy analysis results by Tsunawaki et al. at 2000 K in Fig. 11(b). They have not assessed the fraction of Q₃. The variations of Q₀, Q₁ and Q₃ fractions with SiO₂ content and the Q₂ fractions with maximum value at 47 mol% SiO₂ show good relationship with MD calculation results.

3.3. Thermodynamic Properties for the CaO–SiO₂ System

3.3.1. Enthalpy of Mixing

The enthalpy of mixing for the CaO–SiO₂ system can be directly calculated by MD simulation at various compositions and temperatures. Figure 12 shows the enthalpy of mixing for the CaO–SiO₂ system calculated as functions of compositions at various temperatures. The calculated enthalpy of mixing shows the exothermic behavior in a whole composition, and the calculated enthalpies of mixing at 1873 K are in good agreement with the thermodynamic modeling result calculated by Lin et al. Especially, the enthalpy of mixing calculated by MD simulation shows an abrupt positive variation in the silica-rich region at about 2150 to 2450 K.

3.3.2. Entropy of Mixing

The entropy of mixing for the CaO–SiO₂ system has been calculated from the enthalpy and entropy of mixing obtained by MD simulation.

\[
\Delta S^f = k \ln(\Omega_1, \Omega_2)
\]

\[
= -\left[ X_{\text{SiO}_2} \ln \frac{X_{\text{SiO}_2}}{X_{\text{SiO}_2} + N_{\text{O}^-}} + N_{\text{O}^-} \ln \frac{N_{\text{O}^-}}{X_{\text{SiO}_2} + N_{\text{O}^-}} + N_{\text{O}^-} \ln \left( \frac{N_{\text{O}^-}}{N_{\text{Si-Si}}} + (N_{\text{Si-Si}} - N_{\text{O}^-}) \ln \left( \frac{N_{\text{Si-Si}} - N_{\text{O}^-}}{N_{\text{Si-Si}}} \right) \right) \right]
\]

where \( N^0 \) is Avogadro’s number, \( X_A \) is the mole fraction of component A in the A–B binary system and \( N_{\text{O}^-} \) and \( N_{\text{O}^-} \) are the number of moles of free oxygen and bridging oxygen per mole of solution. Eq. (10) assumed that the each Si atom is associated with four oxygen, and Si and O ions in melts are randomly distributed in the tetrahedral quasi-lattice site. These assumptions are in good agreement with structural results in CaO–SiO₂ melts calculated by MD simulation.

Figure 13 shows the entropy of mixing for the CaO–SiO₂ system at 1873 K calculated based on the fractions of oxygen species on the composition obtained by MD simulation with the result calculated by equilibrium constant \( k_{1873K} = 0.0017 \) of oxygen equilibrium reaction in CaO–SiO₂ melts reported by Toop et al. The calculated entropy of mixing shows the difference with the result assessed by thermodynamic modeling about 20 mol% SiO₂ to 50 mol% SiO₂. This difference was due to the incompletely bridge broken of silica network structure in the CaO–SiO₂ system according to the degree of polymerization higher than result calculated by thermodynamic modeling. However, the entropy of mixing for the CaO–SiO₂ system has been successfully assessed by the fractions of oxygen species obtained from MD simulation.

3.3.3. Gibbs Energy of Mixing

The Gibbs energy of mixing for the CaO–SiO₂ system was calculated from the enthalpy and entropy of mixing ob-
Obtained by MD calculation. Figure 14 shows the calculated Gibbs energy of mixing as functions of compositions at various temperatures for the CaO–SiO$_2$ system. The calculated Gibbs energy of mixing shows an apparent double minimum at the silica-rich region about 2150 to 2450 K due to the effect of inflection points of enthalpy of mixing calculated by MD simulation. It represents the possibility of existence of liquid–liquid immiscibility region in CaO–SiO$_2$ melts.

3.3.4. Calculation of Phase Diagram for the CaO–SiO$_2$ System

The phase diagram for the CaO–SiO$_2$ system is estimated by Gibbs energy of mixing calculated as functions of compositions at various temperatures. For the calculation of phase diagram, the melting temperature of CaSiO$_3$ was assumed to be 1817 K, because of the difference about 450 K between MD calculation and observed result as shown in Fig. 5. The Gibbs energy of fusion of the pure CaO is calculated from the heat capacity at constant pressure on the temperature dependence of enthalpies calculated by MD simulation. The standard Gibbs energies of formation of solid Ca$_2$SiO$_4$ and CaSiO$_3$ from liquid CaO and SiO$_2$, Eqs. (11) and (13), and the enthalpies as a function of temperature of CaO, SiO$_2$, CaSiO$_4$ and Ca$_2$SiO$_4$ obtained by MD calculation.

\[
\frac{2}{3} \text{CaO}(l) + \frac{1}{3} \text{SiO}_2(l) = \frac{1}{3} \text{Ca}_2\text{SiO}_4(s) \\
\Delta G_{2420K} = -46.33 \text{kJ/mol} \quad \ldots \quad (11)
\]

\[
\frac{2}{3} \text{CaO}(l) + \frac{1}{3} \text{SiO}_2(l) = \frac{1}{3} \text{Ca}_2\text{SiO}_4(s) \\
\Delta G^o = -55 000 + 3.457 T \text{J/mol} \quad \ldots \quad (12)
\]

\[
\frac{1}{2} \text{CaO}(l) + \frac{1}{2} \text{SiO}_2(l) = \frac{1}{2} \text{CaSiO}_3(s) \\
\Delta G_{1817K} = -46.25 \text{kJ/mol} \quad \ldots \quad (13)
\]

Figure 15 shows the calculated and observed standard Gibbs energies of formation of solid Ca$_2$SiO$_4$ and CaSiO$_3$ from liquid CaO and SiO$_2$, Eqs. (12) and (14), as a function of temperature.

Figure 16 shows the phase diagram for the CaO–SiO$_2$ system estimated by MD simulation with observed result. In this study, the solid–liquid phase equilibrium in the SiO$_2$-rich region for the CaO–SiO$_2$ system has not clearly been calculated. The various potential models suggested for SiO$_2$ have not yet definitely assessed the thermodynamic properties such as solid phase transitions and fusion data of various silica polymorphs. Therefore, the potential model of Tsuneyuki et al. adopted for the calculation of SiO$_2$ in this study has also not exactly reproduced the thermodynamic properties such as solid phase transitions and fusion data of cristobalite with measured results.
However, the calculated phase diagram was in good agreement with observed result in the range above 50 mol% CaO and the liquid–liquid immiscibility region in the CaO–SiO$_2$ system has also been assessed by MD simulation.

These calculation results show that the MD simulation is a useful method for the calculation of thermodynamic and structural properties for the silicate systems at high temperature. Finally, MD calculation of the more realistic and exact thermodynamic and structural properties of silica and silicates can be established by the improvement of potential model with the addition of three-body potential and angle-dependence terms, application of elaborate interatomic potential based on the ab initio calculation and development of more efficient MD calculation algorithm.

4. Conclusions

The thermodynamic, structural and transport properties for the CaO–SiO$_2$ system were calculated by MD simulation using Born–Mayer–Huggins type pairwise potential model with the optimized potential parameters. The calculated thermodynamic and structural properties for the CaO, Ca$_2$SiO$_4$ (γ-Ca$_3$SiO$_4$ and β-Ca$_3$SiO$_4$), and CaSiO$_3$ (wollastonite and pseudowollastonite) have quite successfully reproduced the measured results. The calculated structural properties in CaO–SiO$_2$ melts such as the pair distribution functions and the fractions of oxygen ion species with silicon atoms were in good agreement with observed results. The self-diffusion coefficients of Ca, Si and O ions calculated at 1 873 K have also reproduced well the experimental results. The self-diffusion coefficients of Ca, Si and O ions calculated at 1 873 K have also reproduced well the experimental results. The self-diffusion coefficients of Ca, Si and O ions calculated at 1 873 K have also reproduced well the experimental results. The self-diffusion coefficients of Ca, Si and O ions calculated at 1 873 K have also reproduced well the experimental results. The self-diffusion coefficients of Ca, Si and O ions calculated at 1 873 K have also reproduced well the experimental results. The self-diffusion coefficients of Ca, Si and O ions calculated at 1 873 K have also reproduced well the experimental results. The self-diffusion coefficients of Ca, Si and O ions calculated at 1 873 K have also reproduced well the experimental results. The self-diffusion coefficients of Ca, Si and O ions calculated at 1 873 K have also reproduced well the experimental results. The self-diffusion coefficients of Ca, Si and O ions calculated at 1 873 K have also reproduced well the experimental results. The self-diffusion coefficients of Ca, Si and O ions calculated at 1 873 K have also reproduced well the experimental results. The self-diffusion coefficients of Ca, Si and O ions calculated at 1 873 K have also reproduced well the experimental results. The self-diffusion coefficients of Ca, Si and O ions calculated at 1 873 K have also reproduced well the experimental results. The self-diffusion coefficients of Ca, Si and O ions calculated at 1 873 K have also reproduced well the experimental results. The self-diffusion coefficients of Ca, Si and O ions calculated at 1 873 K have also reproduced well the experimental results. The self-diffusion coefficients of Ca, Si and O ions calculated at 1 873 K have also reproduced well the experimental results. The self-diffusion coefficients of Ca, Si and O ions calculated at 1 873 K have also reproduced well the experimental results. The self-diffusion coefficients of Ca, Si and O ions calculated at 1 873 K have also reproduced well the experimental results. The self-diffusion coefficients of Ca, Si and O ions calculated at 1 873 K have also reproduced well the experimental results.

The calculated phase diagram for the CaO–SiO$_2$ system has also been assessed by MD simulation. These results are concluded that the MD simulation with optimized potential model is a useful method for the calculation of thermodynamic and structural properties for the silicate systems at high temperature.

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