Dissolution of Calcium Silicates in Molten CaCl₂

XIAOTIAN CHENG and XIAO YANG

Electrodeposition of silicon in molten CaCl₂ has been drawing increasing attention. Soluble silicate anions in the melt can be reduced and tailored into functional materials. To ensure a precise control of the electrochemical processes, a comprehensive knowledge on the soluble silicate anions in the melt is indispensable. Here, we clarify the formation behavior of soluble silicate anions by dissolving solid CaSiO₃ and Ca₂SiO₄ in molten CaCl₂ at temperatures from 1047 K to 1233 K (774 °C to 960 °C). It is found that Ca₂SiO₄ dissolves more and faster. The formation of Ca₂SiO₃Cl₂ or Ca₃SiO₄Cl₂ as an intermediate product is observed. Metasilicate (SiO₃²⁻) and orthosilicate (SiO₄⁴⁻) are detected as soluble anions in the melt when dissolving CaSiO₃ and Ca₂SiO₄, respectively. Mass transfer of these ions plays an important role in determining the overall dissolution rate. The polymeric chain-like structure of SiO₃²⁻ is the reason for the slower dissolution of CaSiO₃ compared with that of Ca₂SiO₄, which dissolves as SiO₄⁴⁻ with a completely isolated tetrahedral structure in the melt. Phase relationships in the CaCl₂–CaSiO₃ and CaCl₂–Ca₂SiO₄ binary systems at the CaCl₂-rich side are clarified. These results should be useful for manipulating the electrochemical reactions of Si (IV) anions on purposes.

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I. INTRODUCTION

The global photovoltaic (PV) market is growing rapidly in recent years. Despite the impact by Covid-19, approximately 175 GW of PV systems were newly installed worldwide in 2021, making the total cumulative installed capacity for PV reaching at least 942 GW at the end of 2021.¹

Silicon (Si) has been playing an important role in the PV market as the key material for PV cells. Si-based PV cells account for more than 95 pct of the global PV market.² As the second most abundant element in the crust, Si is widely distributed in rocks, gravels, dusts, and sands in the form of oxide or silicates. Generally, elemental Si is commercially prepared by carbothermic reduction of SiO₂ at temperatures higher than 1873 K (1600 °C). This reaction is strongly endothermic³,⁴ and thus the production is energy-intensive with inevitable emission of a large amount of CO₂. Si obtained by this process is called metallurgical grade Si (MG-Si), of which the purity is about 98 to 99 pct. MG-Si can be directly used to prepare various Si materials. However, in order to be used as a semiconductor for PV application, MG-Si must be purified into solar grade (SOG-Si) with a purity of at least 6N (99.9999 pct). At present, about 70 to 80 pct of SOG-Si is produced by the Siemens process based on chemical vapor deposition. Although the product is of high purity, the Siemens process is highly complex and extremely energy-intensive. Owing to these defects, development of a cost-effective technology is urgently needed for a sustainable production.

Many alternative technologies for extracting Si have been reported. Among them, molten salt electrolysis seems to be a promise one because of its advantages in cleanness and simplicity.⁵,⁶ Electrodeposition of Si from fluoride-based molten salts has been investigated since the 1960s. Monnier et al. reported the electrodeposition of Si alloys or pure Si in molten Na₃AlF₆ containing SiO₂.⁷,⁸ Cohen et al. was the first to report a successful plating of Si films onto an Ag coated Si wafer in molten LiF–KF–K₂SiF₆.⁹,¹⁰ Elwell et al. and Boen et al. also obtained compact and smooth Si films on Au or graphite substrates in molten LiF–NaF–KF–K₂SiF₆.¹¹,¹² Recently, Yasuda et al. obtained relatively high-quality Si deposits in molten KF–KCl by using K₂SiF₆ or SiCl₄ as the precursor.¹³–¹⁵ Fluoride-based molten salts are useful in depositing Si films. However, due to the corrosive and harmful nature of fluorides, impurity control in the electrodeposited Si is difficult, and waste

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fluorides may cause environmental pollution. Therefore, a fluoride-free electrolyte is desirable for the future development of this technology.

Molten CaCl₂ with a large solubility of O₂⁻ can be used as an alternative electrolyte to fluorides for electrodeposition of Si. [16–18] As demonstrated by Yang et al. (Figure 1), high-quality Si films can be synthesized in molten CaCl₂–CaO–SiO₂ at 1123 K by electrodeposition. [19] Dong et al. prepared Si nanowires by electrolysis of CaSiO₃ dissolved in CaCl₂-based molten salts. [20] Weng et al. also obtained Si nanowires on carbon cloth from SiO₂ dissolved in molten CaCl₂–NaCl. [21] These Si products (films or nanowires) may have applications as functional materials in many fields.

The formation of soluble Si (IV) anions in molten CaCl₂ is the prerequisite condition for electrodeposition. Xiao et al. proposed a dissolution–electrodeposition mechanism during the electrochemical reduction of solid SiO₂ in molten CaCl₂. [22,23] Ma et al. investigated the electrochemical reduction behaviors of silicates in CaCl₂-based molten salts and revealed the ionic species of silicates by Raman spectroscopy. [24–26] However, knowledge on the fundamentals of the soluble Si (IV) anions is still far from sufficient for a precise control of the electrochemical processes. This work clarifies the formation behavior of Si (IV) anions in molten CaCl₂ from solid CaSiO₃ and Ca₂SiO₄, which are considered as proper precursors due to the cost and accessibility for a commercial process in the future. Solubility and dissolution rate at different temperatures were measured. Phase relationships of the CaCl₂–CaSiO₃ and CaCl₂–Ca₂SiO₄ binary systems were clarified. Structure of soluble Si (IV) anions was characterized. These results should be useful for manipulating the electrochemical reactions of Si (IV) anions on purposes.

II. EXPERIMENTAL

A. Materials

Reagent grade CaSiO₃ (> 98 pct), CaO (> 98 pct), SiO₂ (> 98 pct), and CaCl₂ (> 97 pct) were purchased from Greagent Co., Ltd. Prior to use, CaSiO₃, CaO, and SiO₂ were calcined in a dry Ar atmosphere (200 mL/min) at 1073 K (800 °C) for 3 hours to remove residual moisture. CaCl₂ was kept in vacuum at 473 K (200 °C) for 72 hours to remove moisture. In a pre-experiment, the molar fraction of O₂⁻ in CaCl₂ was determined to be around 0.0007 by an acid–alkali titration method. [27] We considered it an acceptable low value and the effect on dissolution behaviors of silicates would not be significant. Ca₂SiO₄ (γ-type) was synthesized by heating the mixture of CaO and SiO₂ (molar ratio = 2:1) at 1673 K (1400 °C) in air for 2 hours (Figure S-1). Figure 2 shows the distribution of particle size of CaSiO₃ or Ca₂SiO₄ after calcination, measured by laser particle size analyzer (LPSA, Malvern, Mastersizer 2000/3000). 90 pct of CaSiO₃ particles were smaller than 47.7 μm, and 90 pct of Ca₂SiO₄ particles were smaller than 59.7 μm.

B. Procedure

Intermediate product of reaction between CaCl₂ and CaSiO₃ or Ca₂SiO₄ was first investigated. Mixture of powdery CaCl₂ and CaSiO₃ or Ca₂SiO₄ (molar ratio = 1.5:1) placed in an alumina crucible (o.d. 30 mm, i.d. 26 mm, height 28 mm, 99.9 pct) was heated at temperatures from 873 K to 1047 K (600 °C to 774 °C) in Ar. Postreaction samples were rinsed with distilled water, followed by filtration to recover solid residues for analysis.
Figure 3 shows the apparatus for dissolution experiment. A graphite crucible (o.d. 72 mm, i.d. 68 mm, height 23 mm, 99.9 pct) containing approximately 25 g of CaSiO₃ (or 45 g of Ca₂SiO₄) powder was set in a larger graphite crucible (o.d. 90 mm, i.d. 80 mm, height 120 mm, 99.9 pct) containing 250 g of CaCl₂. Both CaSiO₃ and Ca₂SiO₄ were excessively used. The larger graphite crucible was placed in a SiO₂ vessel (o.d. 120 mm, i.d. 112 mm, height 580 mm) with flowing Ar (200 mL/min) in a vertical furnace. Temperature was raised to setting values [1047 K to 1233 K (774 °C to 960 °C)] from room temperature at a rate of 7 K min⁻¹. After melting CaCl₂, silicates powder in the small crucible would gradually dissolve and diffuse into CaCl₂ until saturation. In some cases, flowing Ar (100 mL/min) was introduced into the molten bath through an Al₂O₃ tube (o.d. 6 mm, i.d. 4 mm, height 700 mm) immersed in the bath. The melt outside the small crucible was sampled for chemical analysis after different reaction time by dipping an alumina rod (dia. 6 mm). After experiment, undissolved residues in the small crucible were also collected for analysis.

Cooling curves of homogeneous CaCl₂–CaSiO₃ or CaCl₂–Ca₂SiO₄ melt were measured by a K-type thermocouple equipped with a temperature data logger. After melting 100 g of mixture of CaCl₂ and silicates and confirming complete dissolution of silicates, thermocouple wrapped by an Al₂O₃ tube was immersed in the bath. By cooling the furnace at a rate of 5 K min⁻¹, variation of the temperature with time was measured by the thermocouple and recorded by a data logger at an interval of 2 seconds. Thermocouple was calibrated by measuring the cooling curves of pure chlorides (MgCl₂, CaCl₂, NaCl, and CsCl₂) beforehand (result shown in Figure S-2).

C. Analysis and Characterization

Solidified melt sample attached to the alumina rod was digested by an alkali fusion method to prepare solution for analysis. A mixture of Na₂CO₃ (Sinopharm Chemical Reagent, > 99.8 pct) and H₃BO₃ (Sinopharm Chemical Reagent, > 99.8 pct) with a mass ratio of 3:1 was used as an alkali flux. Melt sample (about 0.15 g) and alkali flux (about 0.30 g) were mixed evenly in a Pt crucible, which was heated to 1273 K (1000 °C) at a rate of 4 K min⁻¹ and kept for up to 40 minutes in air before cooling to room temperature at a rate of 5 K min⁻¹. Afterward, the Pt crucible was set in a polytetrafluoroethylene (PTFE) beaker containing 100 mL of 5 pct HNO₃ at 373 K (100 °C) for 2 hours to completely dissolve the substances inside. Si concentration was measured by inductively coupled plasma mass spectrometer (ICP-MS, ThermoFisher, iCAP RQ).

In some cases, solidified melt sample was rinsed by distilled water, followed by filtration to recover insoluble residues. These residues after drying at 353 K (80 °C) for 24 hours were characterized by Powder X-ray diffractometer (PXRD, CuKα, Bruker, D8 Advance). In-situ Raman spectroscopy to evaluate the structure of Si(IV) anions was conducted by a spectrometer (WITec, Alpha300R) with a high-temperature stage (Linkam, TS1500) heated in a flowing Ar atmosphere.
III. RESULTS AND DISCUSSION

A. Formation of Intermediate Products

Figure 4 shows the XRD patterns of the water-rinsed residues after reacting CaCl₂ with CaSiO₃ or Ca₂SiO₄ at different temperatures. In the case of reacting CaSiO₃ [Figure 4(a)], new phase was rarely found when the temperature was lower than 1045 K (772 °C, melting point of CaCl₂), indicating that solid CaSiO₃ does not react with solid CaCl₂. However, when raising the temperature to 1047 K (774 °C), a new phase Ca₂SiO₃Cl₂ was detected in the residue after reaction for 20 hours, suggesting the following solid–liquid reaction

$$\text{CaSiO}_3(s) + \text{CaCl}_2(l) \rightarrow \text{Ca}_2\text{SiO}_3\text{Cl}_2(s or l).$$  \[1\]

When reacting Ca₂SiO₄ with CaCl₂ [Figure 4(b)], XRD patterns of the residues after reaction change apparently. After reaction at 873 K (600 °C) for 4 hours, except for the peaks of Ca₂SiO₄, peaks of a new phase Ca₃SiO₄Cl₂ can be observed. By extending the reaction time [873 K (600 °C) for 8 hours] or raising the temperature [923 K (650 °C) for 1 hour or 973 K (700 °C) for 4 hours], peaks of Ca₃SiO₄Cl₂ were intensified and those of Ca₂SiO₄ were weakened. These results indicate that the solid-state reaction between Ca₂SiO₄ and CaCl₂ to form Ca₃SiO₄Cl₂ proceeds at temperatures above 873 K (600 °C):

$$\text{Ca}_2\text{SiO}_4(s) + \text{CaCl}_2(s) \rightarrow \text{Ca}_3\text{SiO}_4\text{Cl}_2(s).$$  \[2\]

It is known from these results that CaCl₂ reacts more readily with Ca₂SiO₄ than with CaSiO₃, which may bring different dissolution behaviors between the two silicates in molten CaCl₂.

B. Solubility of CaSiO₃ and Ca₂SiO₄ in Molten CaCl₂

Figure 5 shows the dissolution curves of solid CaSiO₃ and Ca₂SiO₄ in molten CaCl₂ at various conditions. Raw data are listed in Supplementary Tables S-1 to S-4. Dissolution of solid silicates in molten CaCl₂ leads to an increase in concentration of Si (IV) until saturation. Nonzero concentration at time \(t = 0\) in some cases was because of inevitable dissolution of a small amount of solute after the temperature exceeding the melting point of CaCl₂ [1045 K (772 °C)] during heating. Under Ar bubbling, it takes around 20 hours at most for the melt to become saturated with CaSiO₃ and about 10 hours for Ca₂SiO₄ at all temperatures [Figures 5(a) and (c)]. The results under static condition at 1095 K and 1233 K (822 °C and 960 °C) are plotted for comparison [Figures 5(b) and (d)]. As can be seen, it takes more than 30 hours for the melt to become saturated with CaSiO₃ or Ca₂SiO₄. As highlighted in Supplementary Figure S-3, Ar bubbling greatly shortens the time to reach saturation in all cases. Dissolution kinetics will be discussed in the following section. Here, solubility of CaSiO₃ and Ca₂SiO₄ in molten CaCl₂ is obtained by averaging the concentration of Si (IV) in the melt after dissolution for 15 hours with Ar bubbling. As listed in Table I, solubility increases as temperature rises, and Ca₂SiO₄ dissolves more in molten CaCl₂ than CaSiO₃ at equal conditions. It is considered that Ca₂SiO₄ is a precursor more suitable than CaSiO₃ for electrodepositing Si in molten CaCl₂, because a large solubility of soluble Si (IV) can provide a wider range to design molten salt composition. In addition, as highlighted in Supplementary Figure S-4, Ca₂SiO₄ also dissolves faster than CaSiO₃. For instance, it takes around 2 hours for the Si concentration to reach 0.94 mass pct (Table S-1) when dissolving CaSiO₃ in molten CaCl₂ at 1233 K (960 °C). In the case of dissolving Ca₂SiO₄ at the same temperature, it only takes less than 0.5 hours for the Si concentration to reach 0.94 mass pct (Table S-3).
Figure 6 shows the XRD patterns of undissolved residues in the small graphite crucible recovered after dissolution at 1047 K and 1233 K (774 °C and 960 °C) with Ar bubbling for 24 hours. In the case of dissolving CaSiO$_3$ [Figure 6(a)], peaks of Ca$_2$SiO$_3$Cl$_2$ are clearly shown, whereas those of CaSiO$_3$ are not. This observation applies to the residues recovered at other temperatures. When dissolving Ca$_2$SiO$_4$ in molten CaCl$_2$ [Figure 6(b)], Ca$_3$SiO$_4$Cl$_2$ were detected regardless of the temperature. Although not dissolved, calcium silicates transformed into something else. These results confirm the findings in the previous section that intermediate products are formed when dissolving calcium silicates in molten CaCl$_2$.

### Table I. Solubility (Mass pct) of CaSiO$_3$ and Ca$_2$SiO$_4$ in Molten CaCl$_2$

| Temperature (K) | CaSiO$_3$ | Ca$_2$SiO$_4$ |
|-----------------|-----------|--------------|
| Si(IV) Compound | Si(IV) Compound |
| 1047            | 0.278     | 1.15         | 0.967 | 5.94 |
| 1068            | —         | —            | 1.34  | 8.22 |
| 1095            | 0.322     | 1.33         | 1.45  | 8.90 |
| 1123            | 0.433     | 1.80         | —     | —    |
| 1139            | 0.488     | 2.02         | 1.79  | 11.0 |
| 1185            | 0.609     | 2.52         | 2.13  | 13.0 |
| 1233            | 0.913     | 3.79         | 2.76  | 17.0 |

C. Thermodynamic Analysis of the Dissolution Process

The overall process of dissolving a solute A in a solution can be written as

$$A(s) \rightarrow A(a	ext{solution}, l).$$

After reaching saturation,

$$
\Delta G_{\text{soln}}^0 = \Delta H_{\text{soln}}^0 - T\Delta S_{\text{soln}}^0 = -RT\ln \frac{a_A^l}{a_A^s},
$$

where $\Delta G_{\text{soln}}^0$ is the change of standard Gibbs free energy in dissolution; $\Delta H_{\text{soln}}^0$ and $\Delta S_{\text{soln}}^0$ are standard dissolution enthalpy and entropy, respectively; $R$ is gas constant ($= 8.314$ J mol$^{-1}$ K$^{-1}$); $a_A^l$ and $a_A^s$ are the activities of A relative to pure liquid or solid,
respectively. Here, $A$ is taken as unity and $c_{l}A = x_{l}A$, where $c_{l}A$ and $x_{l}A$ are activity coefficient and saturated mole fraction of $A$ in the solution, respectively. Then, Eq. [4] can be written as

$$
\ln x_{l}A = \frac{\Delta S_{\text{soln}}}{R} - \ln c_{l}A - \frac{\Delta H_{\text{soln}}}{R}.
$$

By plotting $\ln x_{l}A$ against $1/T$ (Van’t Hoff plot), provided $\Delta H_{\text{soln}}$ and $\Delta S_{\text{soln}}$ are constant in a small temperature range, $\Delta H_{\text{soln}}$ can be obtained according to the slope $\left(-\frac{\Delta H_{\text{soln}}}{R}\right)$ of the fitted line. If assuming $c_{l}A = 1$ for an ideal case, $\Delta S_{\text{soln}}$ can also be obtained according to the intercept $\left(\frac{\Delta S_{\text{soln}}}{R}\right)$. From the solubility data in Table I, Van’t Hoff plots of dissolving solid CaSiO$_3$ and Ca$_2$SiO$_4$ at temperatures from 1045 K to 1233 K (772 °C to 960 °C) are obtained, as shown in Figure 7. Accordingly, standard dissolution enthalpy and entropy can be calculated, as listed in Table II. Dissolution of both silicates in the temperature range are endothermic. A larger dissolution enthalpy for CaSiO$_3$ indicates that dissolution of CaSiO$_3$ is more difficult and requires more energy input.

| Item | CaSiO$_3$ | Ca$_2$SiO$_4$ |
|------|-----------|---------------|
| Van’t Hoff plot | | |
| Slope | $-8576$ | $-6702$ |
| Intercept | $3.53$ | $3.27$ |
| Enthalpy (kJ mol$^{-1}$) | $71.3$ | $55.7$ |
| Entropy (J mol$^{-1}$ K$^{-1}$) | $29.3$ | $27.2$ |

Note: Enthalpy and entropy are assumed to be constant in the temperature range. Activity coefficients of solutes with reference to their pure liquid are assumed to be unity.

D. Phase Relationships of the CaCl$_2$–CaSiO$_3$ and CaCl$_2$–Ca$_2$SiO$_4$ Binary Systems

It is considered that CaSiO$_3$ or Ca$_2$SiO$_4$ and CaCl$_2$ will form eutectic mixtures. Location of the liquidus lines of the CaCl$_2$–CaSiO$_3$ and CaCl$_2$–Ca$_2$SiO$_4$ binary systems on both sides of a eutectic point can be estimated by the solubility of CaSiO$_3$ or Ca$_2$SiO$_4$ in CaCl$_2$ at different temperatures and the cooling curves at different compositions. Figure 8 shows the measured cooling curves of homogeneous melts containing different amount of CaSiO$_3$ or Ca$_2$SiO$_4$. Because precipitation of solute during cooling will release heat and affect the cooling behavior, the inflection point on the cooling curve is regarded as the point on the liquidus line.
Therefore, phase relationships in the CaCl\(_2\)-CaSiO\(_3\) and CaCl\(_2\)-Ca\(_2\)SiO\(_4\) binary systems at the CaCl\(_2\)-rich side can be clarified, as shown in Figure 9. Eutectic points are determined as the intersections of the extensions of the liquidus lines determined by solubility and cooling behavior. Eutectic temperatures are around 1031 K (758 °C) for in both cases, while eutectic compositions are CaCl\(_2\)-0.9mass pctCaSiO\(_3\) and

![Diagram showing cooling curves for various compositions of CaCl\(_2\)-CaSiO\(_3\) and CaCl\(_2\)-Ca\(_2\)SiO\(_4\) systems.](image-url)

Fig. 8—Cooling curves of (a) pure CaCl\(_2\), (b) CaCl\(_2\)-0.22mass pctCaSiO\(_3\), (c) CaCl\(_2\)-0.52mass pctCaSiO\(_3\), (d) CaCl\(_2\)-0.91mass pctCaSiO\(_3\), (e) CaCl\(_2\)-1.34mass pctCa\(_2\)SiO\(_4\), (f) CaCl\(_2\)-2.65mass pctCa\(_2\)SiO\(_4\), (g) CaCl\(_2\)-3.75mass pctCa\(_2\)SiO\(_4\), (h) CaCl\(_2\)-4.94mass pctCa\(_2\)SiO\(_4\) from molten state to solid state.

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CaCl$_2$–5.5 mass pct Ca$_2$SiO$_4$. Due to the formation of intermediates, the solid phase in the two-phase region at the silicate-rich side should be Ca$_2$SiO$_3$Cl$_2$ or Ca$_3$SiO$_4$Cl$_2$.

Locations of liquidus lines in this work are at higher temperatures compared with a previous report by Stemmermann et al., who employed differential thermal analysis (DTA) to determine the phase diagram. For instance, according to the Ca$_2$SiO$_4$–CaCl$_2$ phase diagram reported by Stemmermann et al., the solubility of Ca$_2$SiO$_4$ in molten CaCl$_2$ is around 26.66 mass pct (19 mol pct) at 1079 K (822 °C). However, our work indicates that only 8.90 mass pct (5.93 mol pct) of Ca$_2$SiO$_4$ can dissolve at this temperature. We believe our results resting on chemical analysis are more accurate because the DTA method usually could not exclude the influence of solid–solid phase transitions with heat transfer.

Clarification of the liquid regions of the CaCl$_2$–CaSiO$_3$ and CaCl$_2$–Ca$_2$SiO$_4$ binary systems is necessary to design the molten salt composition for an efficient electrodeposition of Si.

E. Dissolution Kinetics of CaSiO$_3$ and Ca$_2$SiO$_4$ in Molten CaCl$_2$

As shown in Figure 5, Ar bubbling can greatly shorten the time to reach saturation when dissolving CaSiO$_3$ and Ca$_2$SiO$_4$ in molten CaCl$_2$, indicating that mass transfer in the melt plays an important role in the dissolution process. Assuming mass transfer in the melt is the rate-determining step for the whole procedure of dissolution, dissolution rate of Si (IV), $r$, can be expressed by

$$ r = V \frac{dC_t}{dt} = k(C_s - C_t), $$

where $A$ is the sectional area of the small graphite crucible containing silicates. Here, the sectional area is taken as the dissolution interfacial area, as an approximation to simplify the calculation. $k$ is the apparent mass transfer coefficient of Si (IV) in the melt (m sec$^{-1}$); $t$ is dissolution time (sec); $V$ is the volume of molten CaCl$_2$; $C_t$ represents the instant concentration (g cm$^{-3}$) of Si (IV) in the melt at time $t$; $C_s$ is the solubility (g cm$^{-3}$) of Si (IV). Integration of Eq. [6] in the time range from $t_0$ to $t$ leads to

$$ -\frac{V}{A} \ln \frac{(C_s - C_t)}{(C_s - C_0)} = k(t - t_0), $$

where $C_0$ is the concentration of Si (IV) at $t_0$. Using the data in Figure 6, plots of $-\frac{V}{A} \ln \frac{(C_s - C_t)}{(C_s - C_0)}$ against $t - t_0$ for CaSiO$_3$ and Ca$_2$SiO$_4$ are obtained, as shown in Figure S-5. Since mass transfer behavior may change dramatically when the melt is approaching saturation due to increased viscosity, only the data not exceeding 80 pct of solubility are used. It is shown that two variables are linearly related at all temperatures. The value of $k$ is represented by the slope of the fitted line.

Figure 10 shows the temperature dependence of apparent mass transfer coefficients of Si (IV) in the melt under Ar bubbling condition. In the case of dissolving CaSiO$_3$, a sharp increase of $k$ can be noticed as temperature rises from 1123 K (850 °C) to higher, whereas temperature shows little influence when
dissolving Ca$_2$SiO$_4$. The distinction in temperature dependence of mass transfer behavior is considered to be the different microstructures and the physical properties of the melts. Clarification of these issues needs more in-depth studies.

F. Characterization of Si (IV) Anions in the Melts

Some homogeneous melt samples saturated with CaSiO$_3$ or Ca$_2$SiO$_4$ were water-rinsed to remove CaCl$_2$. According to XRD characterization in Figure 11, the as-water-rinsed residues exhibited poor crystallinity. After heating at 1023 K (750 °C) in Ar for 5 hours, crystalline CaSiO$_3$ or Ca$_2$SiO$_4$ ($\beta$-type) was detected, indicating that the initial as-water-rinsed residues were amorphous CaSiO$_3$ and Ca$_2$SiO$_4$, respectively. Being amorphous is due to fast cooling of the melt samples after sampling. These results suggest that Si in the silicate-saturated melts may occur as SiO$_3^{2-}$ or SiO$_4^{4-}$, the same as it does in the crystal lattice of solid CaSiO$_3$ or Ca$_2$SiO$_4$.

Figure 12 shows the in-situ Raman spectra for pure molten CaCl$_2$ and the silicate-saturated melts at 850 °C. According to Virgo et al., Raman frequencies of the Si–O stretching vibrations in various silicate anions are in the range of 700 to 1100 cm$^{-1}$. For pure molten CaCl$_2$, no band was observed. A band near 960 cm$^{-1}$ assigned to SiO$_3^{2-}$ was clearly detected for the melt saturated with CaSiO$_3$, while a band near 830 cm$^{-1}$ close to that of SiO$_4^{4-}$ monomers was detected for the melt saturated with Ca$_2$SiO$_4$. The Raman spectrum of the melt saturated with CaSiO$_3$ largely agrees well with a previous study by Ma et al. Pure solid CaSiO$_3$ and Ca$_2$SiO$_4$ at 850 °C were also analyzed as references. Despite a few extremely weak bands assigned to other anions in the Raman spectra, SiO$_3^{2-}$ and SiO$_4^{4-}$ are believed to be the dominant in the melts after dissolving CaSiO$_3$ and Ca$_2$SiO$_4$, respectively.

Accordingly, dissolution mechanism of solid CaSiO$_3$ and Ca$_2$SiO$_4$ in molten CaCl$_2$ can be summarized based on the above results. When solid CaSiO$_3$ (or Ca$_2$SiO$_4$) contacts molten CaCl$_2$, intermediate phase Ca$_3$SiO$_4$Cl$_2$ (or Ca$_2$SiO$_4$Cl$_2$) may form at the solid/liquid interface, followed by dissociation into soluble ions (Ca$^{2+}$, SiO$_3^{2-}$, SiO$_4^{4-}$, and Cl$^-$) and diffusion of ions from interface to the bulk melt. These processes repeat until the melt becomes saturated with the silicate. Mass transfer of Si (IV) anions in the melt might be the rate-determining step. Difference in the structure between SiO$_3^{2-}$ and SiO$_4^{4-}$ in the melts explains the different dissolution behavior between solid CaSiO$_3$ and Ca$_2$SiO$_4$ in molten CaCl$_2$. As illustrated in Figure 13(a),

![Figure 11](image1.png)
![Figure 12](image2.png)

Fig. 11—XRD patterns of solid residues recovered from the water-rinsed melt samples collected after dissolving CaSiO$_3$ (a) and Ca$_2$SiO$_4$ (b) in molten CaCl$_2$ at 1233 K (960 °C) with Ar bubbling for 24 hours.

Fig. 12—Raman spectra for pure CaCl$_2$, CaSiO$_3$, Ca$_2$SiO$_4$ and molten CaCl$_2$ saturated with CaSiO$_3$ (or Ca$_2$SiO$_4$) at 1123 K (850 °C).
SiO₃²⁻ has a polymeric chain-like structure formed by linking multiple basic units of [SiO₄]⁴⁻ tetrahedron in one direction with one bridging oxygen between two adjacent units. In comparison, SiO₄⁴⁻ occurs as an isolated unit without bridging oxygen sharing with others [Figure 13(b)]. Therefore, SiO₄⁴⁻ anion with a smaller size has more freedom in moving and filling the spaces in molten CaCl₂ than SiO₃²⁻, and thus Ca₂SiO₄ dissolves more and faster than CaSiO₃.

IV. CONCLUSION

In this contribution, dissolution behaviors of solid CaSiO₃ and Ca₂SiO₄ in molten CaCl₂ in the temperature range from 1047 K to 1233 K (774 °C to 960 °C) were revealed. Major findings can be summarized as follows:

1. During dissolution, solid CaSiO₃ and Ca₂SiO₄ react with CaCl₂ to form Ca₂SiO₃Cl₂ and Ca₃SiO₄Cl₂ as intermediate phases, respectively.
2. Solubility of CaSiO₃ and Ca₂SiO₄ in molten CaCl₂ increases as temperature rises. CaSiO₃ dissolves 1.15 mass pct and 3.79 mass pct of Si (IV) in the melt at 1047 K (774 °C) and at 1233 K (960 °C), while Ca₂SiO₄ contributes 5.94 mass pct and 16.98 mass pct of Si (IV) at 1047 K (774 °C) and at 1233 K (960 °C), respectively.
3. Phase relationships of the CaCl₂–CaSiO₃ and CaCl₂–Ca₂SiO₄ binary systems at CaCl₂-rich side were determined. Eutectic temperatures are around 1031 K (758 °C) for in both cases, while eutectic compositions are CaCl₂–0.9mass pctCaSiO₃ and CaCl₂–5.5mass pctCa₂SiO₄.
4. Metasilicate (SiO₃²⁻) and orthosilicate (SiO₄⁴⁻) are the dominant Si (IV) anions in the melts after dissolving CaSiO₃ and Ca₂SiO₄, respectively. Mass transfer of these anions plays an important role in determining the dissolution rate. The formation of SiO₃²⁻ anion with a polymeric chain-like structure from CaSiO₃ is the reason for the slower dissolution compared with that of Ca₂SiO₄, which dissolves in molten CaCl₂ as isolated units of SiO₄⁴⁻.

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CONFLICT OF INTEREST

On behalf of all authors, the corresponding author states that there is no conflict of interest.

SUPPLEMENTARY INFORMATION

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