

Preparation of β -CaSiO₃ powder by water vapor-assisted solid-state reaction

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Solid-state reaction between carbonate and/or oxide precursors is a simple method to prepare ceramic powders. However, a high calcination temperature is required for this method because of limited diffusion during calcination. In this paper, we describe that the formation of β -CaSiO₃ by solid-state reaction is accelerated by water vapor. β -CaSiO₃ powders have been prepared by solid-state reaction between CaCO₃ and amorphous SiO₂ as a raw material. Single-phase β -CaSiO₃ was successfully prepared by one-step calcination at 800°C for 2 h in water vapor, while it seemed to be difficult to prepare the single-phase β -CaSiO₃ by calcination in air. Water vapor-assisted solid-state reaction is likely to be applicable to prepare other functional ceramic powders at low temperatures.

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Calcium silicate (CaSiO₃, wollastonite) has been traditionally used as a raw material for tile, pottery, and cement.^{1,2)} Recently, CaSiO₃ has been studied as bioactive materials for biomedical applications and used to improve the mechanical properties of the biopolymers because of its excellent bioactivity, biocompatibility, and biodegradability.³⁻⁵⁾ CaSiO₃ powders are conventionally prepared by solid-state reaction between CaCO₃ and SiO₂. However, this method requires a high calcination temperature for a long period of time because of the limited diffusion during calcination. Therefore, several chemical routes such as precipitation from aqueous solutions,^{6,7)} sol-gel processing,⁸⁾ and hydrothermal method⁹⁾ have been conducted to prepare CaSiO₃ powders at low temperature. Although these chemical routes are useful methods for the low temperature synthesis and morphology control of the products, the solid-state synthesis for the production of CaSiO₃ is still important method because natural minerals of CaCO₃ and SiO₂ yield abundantly.

As a way to overcome the high calcination temperatures for solid-state reaction, we have proposed the water vapor-assisted solid-state reaction.¹⁰⁻¹²⁾ Water vapor accelerates the formation of alkaline-earth titanates (MTiO₃, M = Mg, Ca, Sr and Ba)^{10,11)} and dicalcium silicate (β -Ca₂SiO₄)¹²⁾ by solid-state reactions. Therefore, water vapor should accelerate the formation of CaSiO₃. Hayashi et al.¹³⁾ have been reported the effect of water vapor on the formation of alkaline-earth silicates (MSiO₃) from various precursor powders. They indicated that the formation of CaSiO₃ from solid-mixing precursor (i.e., the mixture of CaCO₃ and SiO₂ aerogel) was promoted in humid air (H₂O partial pressure of 0.47 atm). However, the detailed information on the formation reaction of CaSiO₃ in water vapor was not provided. In this paper, we describe the formation of CaSiO₃ by solid-state reaction in water vapor at 1 atm. Water vapor effectively assists

the formation of CaSiO₃. In addition, the mechanism of accelerated reaction by water vapor is also discussed.

Commercially available CaCO₃ ($d_{\text{BET}} = 0.40 \mu\text{m}$) and amorphous SiO₂ were used as starting materials. These reagents were purchased from Wako Pure Chemical Industries, Ltd. Water content of amorphous SiO₂, which was confirmed by heating up to 1000°C, was ~2.5%. The starting mixed powder with Ca/Si molar ratio of 1 was prepared using wet mixing (in ethanol, 1 h) by planetary beads milling (Fritsch, Pulverisette 5) with zirconia pot ($V = 80 \text{ cm}^3$) and beads (1 mm ϕ). After mixing, the slurry was dried and finally sieved under 150 μm . The mixed powders were calcined at various temperatures for 2 h in air and water vapor at 1 atm by a tubular furnace. Calcinations in air were conducted in stagnant conditions. On the other hand, a water vapor atmosphere at 1 atm was produced by connecting a water evaporator to the tubular furnace. Distilled H₂O was introduced at a flow rate of 0.1–2.0 mL/min into the evaporator without a carrier gas. Flow rate of water vapor was estimated to be 0.17–3.4 L/min. Powder X-ray diffractions (XRD) were measured on a Rigaku Ultima IV diffractometer operating at 40 kV and 20 mA using Cu K α radiation. The patterns were collected in the range of 10–80° with a 0.02° step and scanning speed of 40°/min. Specific surface area (S_{BET}) was measured by the BET method using N₂ with a Yuasa-ionics NOVA-1200 instrument. The equivalent BET diameter (d_{BET}) was calculated from the following equation, $d_{\text{BET}} = 6/(\rho S_{\text{BET}})$, where ρ is the theoretical density.

Figure 1 shows the XRD patterns of the products obtained by calcinations in different water vapor conditions at 800°C for 2 h. When the mixed powder was calcined in air, the diffraction peaks of CaSiO₃ were not observed in the product. Alternatively β -Ca₂SiO₄ was formed. On the other hand, the products obtained in water vapor (flow rate of H₂O up to 0.25 mL/min) consisted of a low crystalline phase (perhaps β -Ca₂SiO₄ phase) with a broad XRD peak ranging from 25 to 35°. When the flow rate of H₂O was over 0.5 mL/min (flow rate of water vapor, $\approx 0.85 \text{ L/min}$),

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the single-phase β -CaSiO₃ was obtained. The formation of β -CaSiO₃ by solid-state reaction between CaCO₃ and amorphous SiO₂ was accelerated by water vapor. In order to clarify the effect of water vapor, H₂O flow rate of 2.0 mL/min (flow rate of water vapor, \approx 3.4 L/min) was chosen for further calcination experiments in the water vapor atmosphere.

Figure 2 shows the XRD patterns of the products obtained by calcinations in air and water vapor at 500–850°C for 2 h. In the air atmosphere [Fig. 2(a)], CaCO₃ remained in large quantities up to 650°C. With decomposition of CaCO₃, the broad XRD peak at around $2\theta = 32^\circ$ arisen from the β -Ca₂SiO₄ was observed from

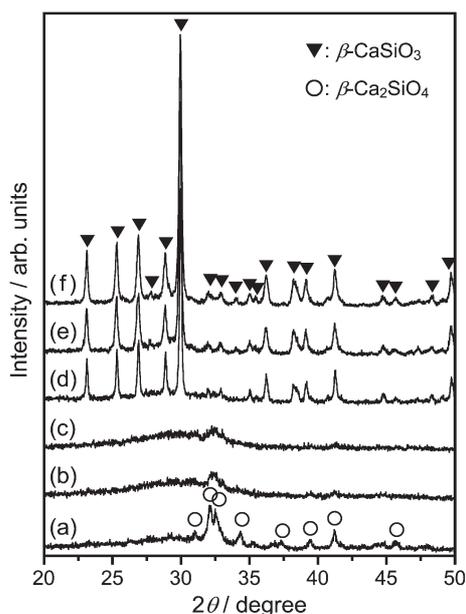


Fig. 1. XRD patterns of the products obtained by calcinations at 800°C for 2 h in (a) air and water vapor with H₂O flow rate of (b) 0.10, (c) 0.25, (d) 0.50, (e) 1.0, and (f) 2.0 mL/min.

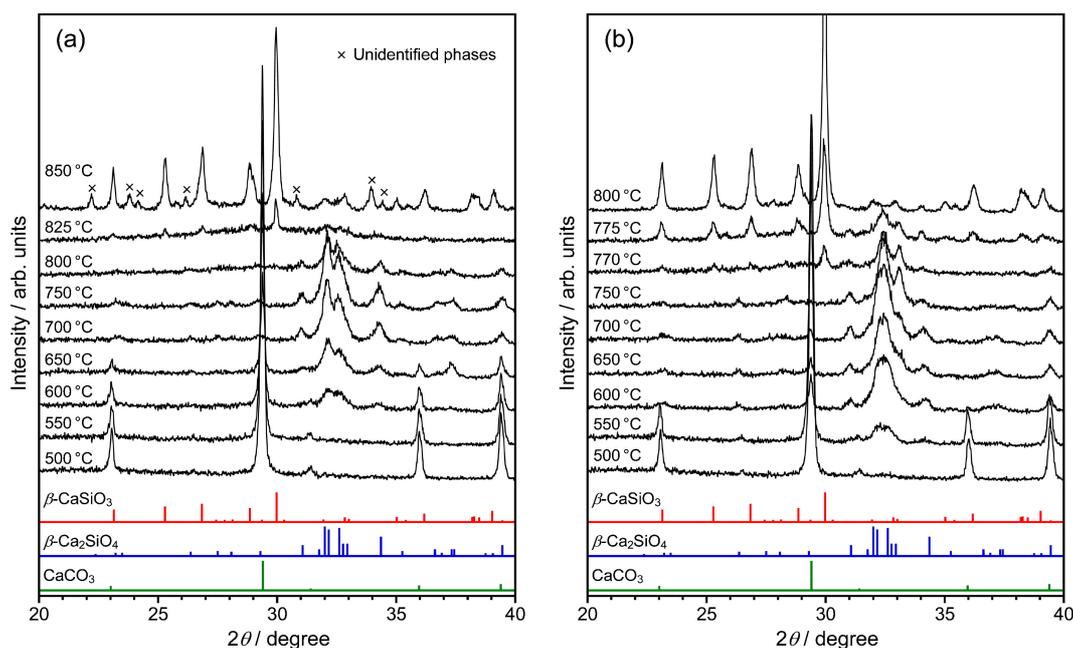
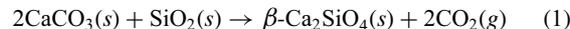


Fig. 2. (Color online) XRD patterns of the products obtained by calcinations at various temperatures for 2 h in (a) air and (b) water vapor (flow rate of H₂O, 2.0 mL/min). Standard XRD patterns of PDF No. 5-586 for CaCO₃, PDF No. 33-302 for β -Ca₂SiO₄, and PDF No. 43-1460 for β -CaSiO₃ are also shown.

600°C. At 700°C, CaCO₃ was completely decomposed and the crystalline phase was only β -Ca₂SiO₄ as an intermediate phase. At 825°C, the XRD pattern of the product showed broadening diffraction pattern, and diffraction peaks of β -CaSiO₃ started to be observed. After calcination at 850°C, the peaks of β -CaSiO₃ rapidly increased in intensity. However, some unidentified peaks were detected. These peaks are assumed to arise from cristobalite ($2\theta = 22.2^\circ$) and silicon dioxide formed by crystallization of amorphous SiO₂. The unidentified peaks appeared even calcination at 900°C (not shown). Therefore, in the case of the calcination in air, it seems to be difficult to prepare the single-phase CaSiO₃ by one-step calcination.

On the other hand, in the case of the calcination in water vapor [Fig. 2(b)], single-phase CaSiO₃ was obtained by one-step calcination. CaCO₃ was completely decomposed at 650°C, and β -Ca₂SiO₄ was formed from 550°C. The diffraction peaks of β -CaSiO₃ were observed at 770°C and the intensity of these peaks rapidly increased at 775°C. At 800°C, single-phase β -CaSiO₃ was obtained without crystallization of amorphous SiO₂. β -CaSiO₃ was successfully prepared by solid-state reaction, and the formation temperature of single-phase β -CaSiO₃ was $>100^\circ\text{C}$ lower than in air. The specific surface area of single-phase β -CaSiO₃ was 7.1 m²/g and the equivalent BET diameter was 0.29 μm . Particle size of β -CaSiO₃ was larger than that of β -Ca₂SiO₄ even if the same raw materials were used.¹²⁾

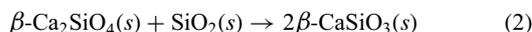
From these results, mechanisms of the formation of β -CaSiO₃ by solid-state reaction between CaCO₃ and amorphous SiO₂ and the accelerated reaction by water vapor are described below. In both atmospheres, the β -Ca₂SiO₄ as an intermediate phase was formed with decomposition of CaCO₃.



The decomposition of CaCO₃ and following formation of β -Ca₂SiO₄ were promoted by water vapor. It has been reported that the thermal decomposition of CaCO₃ is accelerated by water vapor in the atmosphere.^{14)–16)} Wang and Thomson¹⁵⁾ described

that adsorbed water vapor weakened Ca–CO₃ bond and the decomposition of CaCO₃ was accelerated by water vapor. Accelerated decomposition of CaCO₃ leads to the formation of β -Ca₂SiO₄ at lower temperatures.

The formation of β -CaSiO₃ by the reaction between β -Ca₂SiO₄ and amorphous SiO₂, occurs at higher temperatures.



For the formation of β -CaSiO₃, β -Ca₂SiO₄ as its intermediate phase is relatively stable during the calcination. The key to the phase change from β -Ca₂SiO₄ to β -CaSiO₃ stems from the structure of the two calcium silicates. β -Ca₂SiO₄ consists of isolated SiO₄ tetrahedra, while β -CaSiO₃ has a single-chain structure of SiO₄ tetrahedra, and the phase change by reaction with amorphous SiO₂ is accomplished by the rearrangement of these tetrahedra. Hayashi et al.¹³⁾ has predicted that water vapor is considered to attack surface Si–O–Si bonds in the amorphous SiO₂ and yields Si–OH bonds. The Si–O–Si bond cleavage results in increase the mobility of calcium ions. In addition, water vapor can form bridges between surface OH groups of different tetrahedra which share only one common vertex, using the two lone pairs of electrons on the oxygen. Then the formed OH groups are eliminated by the rearrangement of SiO₄ tetrahedra to the inosilicate structure of β -CaSiO₃. In this way, water vapor effectively assists the formation of β -CaSiO₃. On the other hand, in air, unreacted amorphous SiO₂ would be locally crystallized into cristobalite and silicon dioxide by heating at high temperatures.

In this paper, the formation of β -CaSiO₃ by water vapor-assisted solid-state reaction was presented. Single-phase β -CaSiO₃ was successfully prepared by one-step calcination in water vapor and obtained at lower temperatures than in air. Water vapor-assisted solid-state reaction is likely to be applicable to prepare other functional ceramic powders at low temperatures. Thus, it would be open a new field to traditional solid-state reaction.

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