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Effect of Vapor Atmosphere on the Formation Reaction of $MSiO_3$ (M = Mg, Ca, Sr and Ba)

Shigeo Hayashi,[a] Ken-ichi Ishizu,[a] Shinya Kikuchi,[a]* Kiyoshi Okada[a†] &
Nozomu Otsuka[b]

[a]Department of Inorganic Materials, Faculty of Engineering, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152, Japan
[b]Department of Material Engineering, Faculty of Science and Technology, The Nishi Tokyo University, Uenohara, Kitatsuru, Yamanashi 409-01, Japan

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Abstract

Effect of vapor atmosphere on the formation reaction of $MSiO_3$ (M = Mg, Ca, Sr and Ba) from various precursor powders was investigated by powder X-ray diffraction. Precursors of $MgSiO_3$ and $CaSiO_3$ were prepared by the coprecipitation method by adding NH_4OH to ethanol solution dissolving a respective nitrate and tetraethyl orthosilicate (TEOS). Those of $SrSiO_3$ and $BaSiO_3$ were prepared from respective hydroxide powder and TEOS. Vapor atmosphere showed the most effective influence in the formation of $CaSiO_3$, whereas it showed the least influence in that of $MgSiO_3$ among the four kinds of $MSiO_3$ formation. The difference in effect was mainly attributed to the degree of chemical homogeneity of the precursor powder, the effect being smaller the higher the chemical homogeneity. The samples fired under a vapor atmosphere showed larger specific surface area than those under a dry atmosphere.

1 Introduction

$CaSiO_3$ (wollastonite) has been used and/or studied as a raw material of tile and pottery,[1] a filler to resin,[2] etc. Since sinterability of $CaSiO_3$, is generally not so high, fine and homogeneous powders are necessary as the raw material to prepare dense $CaSiO_3$ ceramics. A conventional synthetic method to mix and calcine raw material powders of $CaCO_3$ and SiO_2 is not appropriate to prepare fine $CaSiO_3$ powders because relatively high temperature is necessary for the formation of $CaSiO_3$ phase due to the sluggish reactivity of SiO_2 component. Several preparation methods from solution have been examined in order to prepare fine and homogeneous $CaSiO_3$ powder. We (Ref 3) reported that good $CaSiO_3$ powder could be prepared by the coprecipitation method from ethanol solution dissolving Ca nitrate and TEOS. No by-product phases were detected during the formation of $CaSiO_3$. We also clarified that fine and homogeneous $MgSiO_3$ powder could be synthesized by the same method as that of $CaSiO_3$, whereas good $SrSiO_3$[4] and $BaSiO_3$ powders could be prepared from a combination of respective hydroxide powder and TEOS.

It is well known that a vapor atmosphere has a certain effect to lower the crystallization temperature of some silicate glasses.[5,6]. Vapor is considered to react to break down Si–O–Si bonds and forms Si–OH groups, thus, weakens the glass structure. It, therefore, lowers the kinetic barrier to nucleation, and increases the mobility of atoms in the glasses.[6] Vapor atmosphere was also reported to be effective for accelerating solid state $CaSiO_3$ formation reaction.[7]

Considering these facts, formation reaction of $CaSiO_3$ and also $MSiO_3$ (M = Mg, Sr and Ba ions) were expected to be lowered by firing under a vapor atmosphere compared with firing in a normal atmosphere. In this paper, formation of $MSiO_3$ from respective precursors under a vapor and a dry air atmosphere was examined to elucidate the effect of the atmosphere on the formation of the various $MSiO_3$ phases.

2 Experimental procedures

2.1 Preparation of the starting powders

Precursor powders of $MgSiO_3$ and $CaSiO_3$ were

[†] To whom correspondence should be addressed.
[*] Nihon Cement Co., Ltd., 1-2-23, Kiyosumi, Koutou-ku, Tokyo 135, Japan

prepared using the coprecipitation method.[3] In the $MgSiO_3$ precursor powder, a starting solution was prepared by dissolving $Mg(NO_3)_2{\cdot}6H_2O$ and TEOS in ethanol. The ratio of Mg/Si in the solution was 1 and their respective concentrations were 0·2 mol/l. The same amount of 25% NH_4OH as the starting solution was added to the starting solution by stirring vigorously. The precursor powder was obtained by drying the precipitate and by calcining at 500°C for 2 h.

The precursor powder of $CaSiO_3$ was synthesized using the same method as $MgSiO_3$, using $Ca(NO_3)_2{\cdot}4H_2O$ and TEOS as the starting materials. $SrSiO_3$ and $BaSiO_3$ precursor powders were prepared using the following method:[4] hydrate powder of $Sr(OH)_2{\cdot}8H_2O$ or $Ba(OH)_2{\cdot}8H_2O$ respectively was dispersed in ethanol, and TEOS was added to this solution. They were mixed and dried on a water bath. The hydrate powder dissolved during this process and was precipitated again by condensation of the solution. The other processes were the same as in the synthesis of the $MgSiO_3$ precursor powder.

Precursor powders of $CaSiO_3$ were also prepared using the three other methods to investigate the influence of the precursors on the formation of $CaSiO_3$ in the vapor atmosphere. They were the alkoxide coprecipitation method, the two-step precipitation method and the solid mixing method. In the first method, Ca ethoxide, $Ca(OC_2H_5)_2$ was used instead of Ca nitrate in the preparation. Ca ethoxide was synthesized by reacting Ca metal powder and ethanol by refluxing in an Ar atmosphere. Then tetramethyl orthosilicate (TMOS) was added to the solution and mixed. The following processes were the same as in the coprecipitation method. The precursor powder prepared by this method was more homogeneous than the powder prepared by the coprecipitation method. In the second method, oxalic acid was added to the starting solution proceeding to the NH_4OH addition. Oxalic acid yielded precipitation of Ca oxalate and NH_4OH yielded precipitation of amorphous silica by the hydrolysis of TEOS. Formation of α-$CaSiO_3$ instead of β-$CaSiO_3$ was the characteristic result in this precursor powder. In the third method, $CaCO_3$ powder and SiO_2 aerogel powder were mixed in ethanol by ball mill for 24 h. The mixture was then dried and calcined at 500°C for 2 h. The powder prepared by this method is less homogeneous than the other ones, i.e. β-Ca_2SiO_4 was formed as the main by-product phase by firing.

2.2 Firing experiments

The precursor powders were fired at various temperatures in a vapor and a dry air atmosphere by an electric furnace. Firing experiments in the vapor atmosphere was performed by flowing a carrier gas (air), which was bubbled in a water bath. Vapor pressure of the carrier gas was controlled at 0·47 atm by adjusting the temperature of the water bath at 80°C. Firing experiments in the dry atmosphere were performed by flowing a carrier gas excluding moisture by a $CaCl_2$ drying agent.

The samples were fired at a set temperature between 400 and 1000°C for a duration of 2 h. All the experiments were performed at the flow rate of 180 ml/min.

2.3 Characterization

After the firing experiments, crystalline phases in the samples were identified by the X-ray powder diffraction method (Rigaku, Geigerflex) using monochromated CuKα radiation. The amount of crystalline phases was estimated semi-quantitatively by comparing the X-ray diffraction intensities. The reflections used were as follows; 310 in $MgSiO_3$ (clinoenstatite), 320 in β-$CaSiO_3$, 112 in α-$CaSiO_3$, 002 in β-Ca_2SiO_4, the reflection at d = 3·08 Å in $SrSiO_3$ (metastable phase), 022 in $SrSiO_3$ (stable phase) and 111 in β-$BaSiO_3$.

Specific surface area was measured by the multipoint B.E.T. method (Carlo Elba Strumentazione, Soaptomatic Series 1800) using nitrogen gas.

3 Results and Discussion

The $MgSiO_3$ precursor powder was amorphous in the as-calcined state and crystallized at around 770°C in both atmospheres. Formation curves of $MgSiO_3$ phase under both firing atmospheres are shown in Fig. 1. The amount of $MgSiO_3$ in the two curves increased very rapidly between 770 and 800°C, and saturated above this temperature. Since the two curves almost coincided with each other, it is concluded that the vapor has no effect on the $MgSiO_3$ formation reaction.

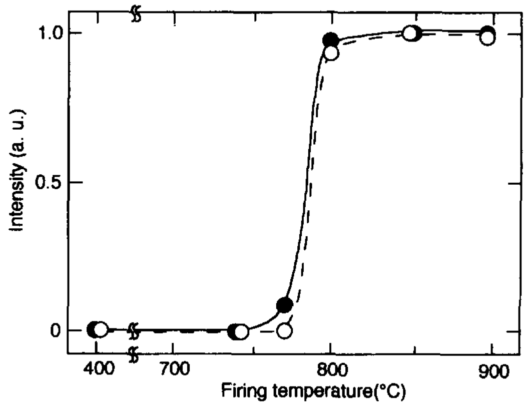

Fig. 1. Formation curves of $MgSiO_3$ by firing the precursor powder under the dry (○) and the vapor (●) atmospheres.

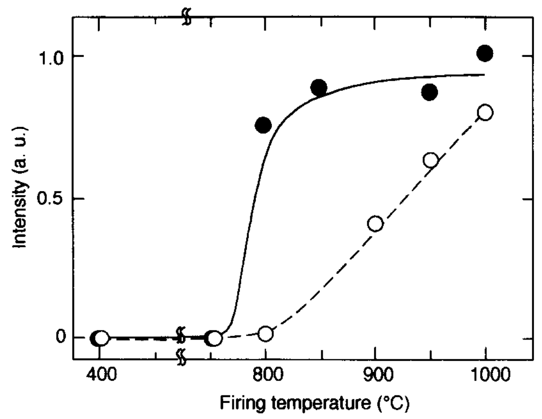

Fig. 2. Formation curves of β-$CaSiO_3$ by firing the precursor powder under the dry (○) and the vapor (●) atmospheres.

The $CaSiO_3$ precursor powder was amorphous in the as-calcined state. Fig. 2 shows the formation curves of β-$CaSiO_3$ phase after firing in the dry and the vapor atmospheres. In the dry atmosphere, crystallization occurred at 800°C and the formation amount increased gradually and linearly between 800 and 1000°C. On the other hand, β-$CaSiO_3$ started to crystallize at 750°C in the vapor atmosphere, the formation amount increased steeply up to 800°C and almost saturated over this temperature. This shows that there is a large difference in the formation of $CaSiO_3$ in the dry and the vapor atmospheres. Vapor is found to accelerate the crystallization of $CaSiO_3$ in this case.

The $SrSiO_3$ precursor powder was amorphous in the as calcined state. Crystalline $3SrO{\cdot}2SiO_2{\cdot}3H_2O$ was detected in the as-precipitated state, but it yielded an amorphous product during the calcination. Figure 3 shows the formation curves of $SrSiO_3$ phases in the two atmospheres. In these samples, the first crystalline phase appeared by firing was a metastable $SrSiO_3$ phase and it transformed to a stable $SrSiO_3$ phase by firing at higher temperature.[4] The sequence of phase changes was the same in the dry and in the vapor atmospheres but reaction temperatures were different in the two atmospheres. The reaction temperatures in the vapor atmosphere were always around 50°C lower than those in the dry atmosphere. Vapor is, therefore, fairly effective in this system.

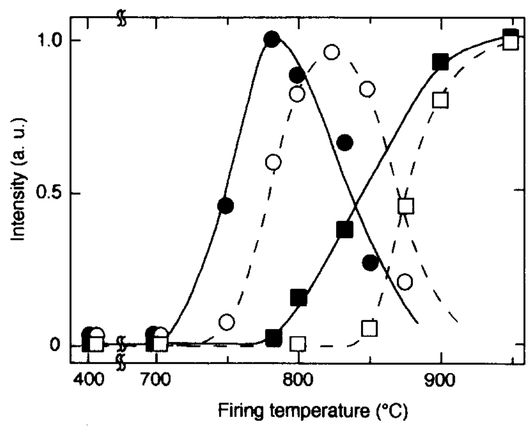

Fig. 3. Formation curves of metastable (○,●) and stable (□,■) $SrSiO_3$ by firing the precursor powder under the dry and the vapor atmospheres. Open and solid symbols correspond to the dry and vapor atmospheres, respectively.

In the $BaSiO_3$ samples, crystalline $BaSiO_3{\cdot}H_2O$ was formed in the as calcined state and was converted to crystalline $BaSiO_3$ during the calcination. This was the characteristic point of this sample because all the other samples were amorphous in the as calcined state. A considerable amount of $BaSiO_3$ was already formed in the samples fired at 400°C. However, crystallization to $BaSiO_3$ was not accomplished around that temperature. It means that the as-precipitated sample contains amorphous as well as $BaSiO_3{\cdot}H_2O$. Figure 4 shows the formation curves of $BaSiO_3$. The amount of $BaSiO_3$ started to increase from around 600°C and almost saturated at 800°C. Since the formation curve in the dry atmosphere differed only a little from that in the vapor atmosphere, the effect of vapor is very small in the $BaSiO_3$ samples.

In this way, the effect of vapor on the formation of crystalline $MSiO_3$ phases differed considerably largely among the samples. No significant effect was detected in the $MgSiO_3$ and $BaSiO_3$ samples whereas $MSiO_3$ crystallization was apparently accelerated in the $CaSiO_3$ and $SrSiO_3$ samples. Two different reasons were considered to yield these results. One reason can be attributed to the difference of the character of the M–O bond in the $MSiO_3$ samples. The second reason considered was the influence of the structural state of the precursor powders, i.e. the degree of homogeneity in the mixing state of the two components, and the degree of polymerization state of the silica component. Since the effect of vapor for the respective $MSiO_3$ formation showed no correlation with the order of periodic table of the alkaline earth metal ions, the second reason was considered to be

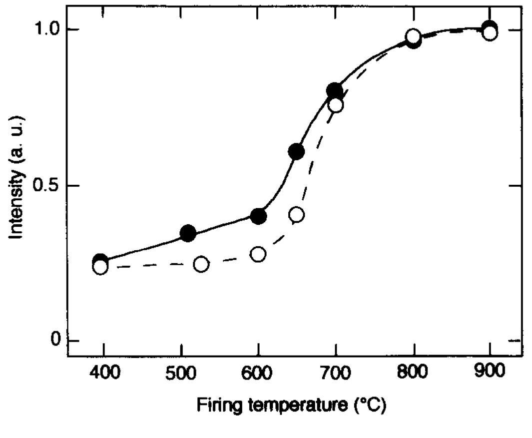

Fig. 4. Formation curves of $BaSiO_3$ by firing the precursor powder under the dry (○) and the vapor (●) atmospheres.

important. Although the precursors of $MgSiO_3$ and $CaSiO_3$ were prepared by the same method, we[8] found by an analytical transmission electron microscopy that the $MgSiO_3$ precursor powder was more homogeneous than the $CaSiO_3$ precursor powder. On the other hand, the precursors of $SrSiO_3$ and $BaSiO_3$ were prepared by the same method and crystalline phase was formed in the as-precipitated state. They were $3SrO{\cdot}2SiO_2{\cdot}3H_2O$ and $BaSiO_3{\cdot}H_2O$, respectively. Since the M/Si ratio of crystalline phase formed in the as-precipitated state was same with that of the objective crystalline phase $MSiO_3$ in the $BaSiO_3$ sample but was different in the $SrSiO_3$ sample, the $BaSiO_3$ sample was more homogeneous than the $SrSiO_3$ sample. In this way, the effect of vapor atmosphere for the crystallization was considered to change by the structural state of the as-precipitated precursor powders. Four kinds of $CaSiO_3$ precursor powders with different structural state were, therefore, prepared to examine the relationship between the effect of vapor and their degree of homogeneity. The $CaSiO_3$ formation curves in the solid mixing method, the two-step precipitation method, the coprecipitation method, and the alkoxide precipitation method are shown in Figs 5, 6, 2 and 7, respectively.

In the solid mixing method, β-Ca_2SiO_4 crystallized preceding to β-$CaSiO_3$. Such a phenomenon to form an alkaline earth metal rich phase is generally known when the formation reaction proceeds mainly by the diffusion of ions and the diffusion paths are long, because the diffusion coefficient of alkaline earth metal is larger than that of silicon. Vapor atmosphere was effective in accelerating the formation of β-$CaSiO_3$ from β-Ca_2SiO_4 and amorphous silica. Vapor is considered to attack surface Si–O–Si bonds in the amorphous silica and yields Si–OH bonds. It is very effective to cause the powder active state. Therefore, formation of β-$CaSiO_3$ largely accelerated under the vapor atmosphere.

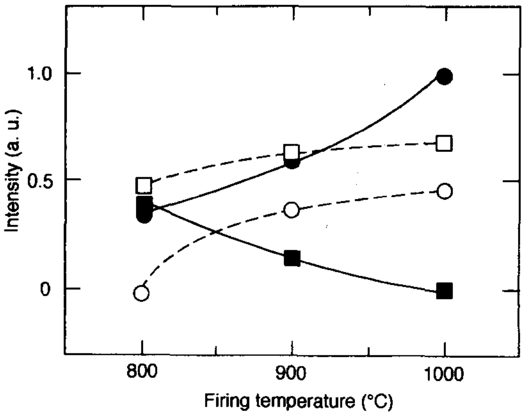

Fig. 5. Formation curves of crystalline phases by firing the solid-mixing $CaSiO_3$ precursor powder under the dry and the vapor atmospheres. Circles and squares correspond to β-$CaSiO_3$ and β-Ca_2SiO_4, and open and solid symbols correspond to the dry and the vapor atmospheres, respectively.

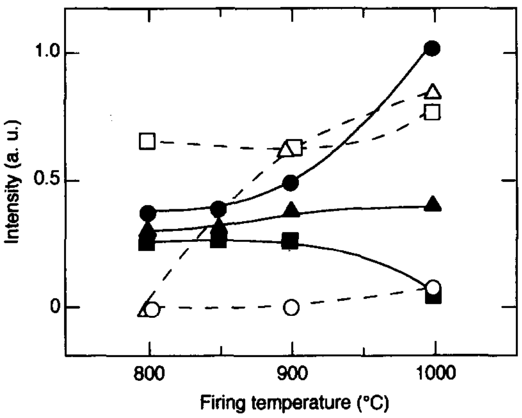

Fig. 6. Formation curves of crystalline phases by firing the two-step precipitated $CaSiO_3$ precursor powder under the dry and the vapor atmospheres. Circles, triangles and squares correspond to β-$CaSiO_3$, α-$CaSiO_3$ and β-Ca_2SiO_4, respectively. Open and solid symbols correspond to the dry and the vapor atmospheres, respectively.

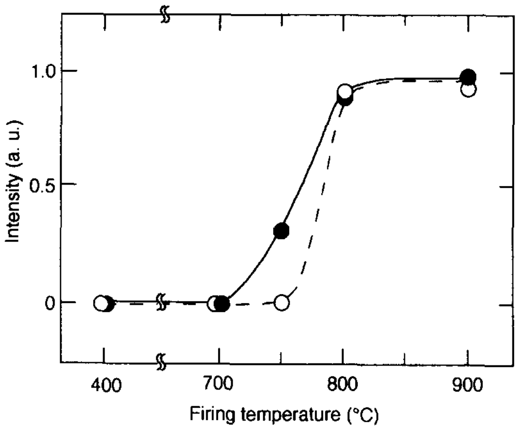

Fig. 7. Formation curves of β-$CaSiO_3$ by firing the alkoxide coprecipitated $CaSiO_3$ precursor powder under the dry (○) and the vapor (●) atmospheres.

Crystallization reaction in the two-step precipitation method was much more complicated and not only β-$CaSiO_3$ and β-Ca_2SiO_4 but also α-$CaSiO_3$ (pseudowollastonite) were formed simultaneously. Formation of α-$CaSiO_3$ was the characteristic point of this preparation method. It is the high-temperature phase of $CaSiO_3$ and is stable at the temperature range between 1125 and 1544°C.[9] The actual reason for the formation of this phase was not certain. Since β-Ca_2SiO_4 remained even after firing at 1000°C in the dry atmosphere, vapor was found to be very effective to accelerate the decomposition of β-Ca_2SiO_4 and formation of $CaSiO_3$ in this sample.

The results of the coprecipitation method have already been discussed. In method, only the objective crystalline phase β-$CaSiO_3$ was formed and no by-productive crystalline phase was detected. Therefore, homogeneity of the precursor powder in this method was considered to be better than those in the solid mixing and the two-step precipitation methods. The formation reaction of β-$CaSiO_3$ was apparently accelerated under the vapor atmosphere as shown in Fig. 2. It may mean that the precursor is not homogeneous in the molecular level and is examined by the ^{29}Si NMR spectra.[10]

In the alkoxide precipitation method, β-$CaSiO_3$ crystallized at the lowest temperature among the four synthetic methods. It may mean that the precursor of this method was in the most homogeneous state. The formation curve showed only a little difference in the vapor and the dry atmospheres and the effect of vapor was the smallest among the various $CaSiO_3$ samples.

Summarizing the results of the four kinds of $CaSiO_3$ precursors, we can conclude as follows:

(1) When the mixing of CaO and SiO_2 components was particle size order, i.e. submicron to micron meter, Ca-rich by-product phase crystallized preceding to the $CaSiO_3$ phase. In this case, vapor played an important role in accelerating the formation reaction of $CaSiO_3$ by attacking Si–O–Si bonds in amorphous SiO_2. The solid mixing and two-step precipitation methods belong to this category.

(2) When the mixing of two components was partly molecular level but remained partly inhomogeneous, vapor was effective in activating the reactivity of the inhomogeneous region. The coprecipitation method may belong to this category.

(3) When the mixing was more homogeneous than the other methods and was molecular level, vapor showed little influence to $CaSiO_3$ formation because no silica-like polymerized structure remained in the precursor.

Figure 8 shows the specific surface area of $CaSiO_3$ samples prepared by the coprecipitation method and fired at various temperatures under the dry and the vapor atmospheres. The surface area fired under the vapor atmosphere was always larger than that under the dry atmosphere irrespective of the firing temperature. Ito[7] reported that the $CaSiO_3$ powder synthesized by the conventional solid reaction method was very easy to grind into fine powder when it was fired under a vapor atmosphere. This is compatible with the present results. Although the formation amount of β-$CaSiO_3$ in the sample fired at 800°C under the vapor atmosphere was almost same with that in the sample fired at 1000°C under the dry atmosphere, the surface area of the former was 5 times as large as that of the latter one. This result shows that the heat treatment under a vapor atmosphere is effective to prepare fine crystalline silicate powder at lower temperatures than that in a dry atmosphere or in a normal atmosphere.

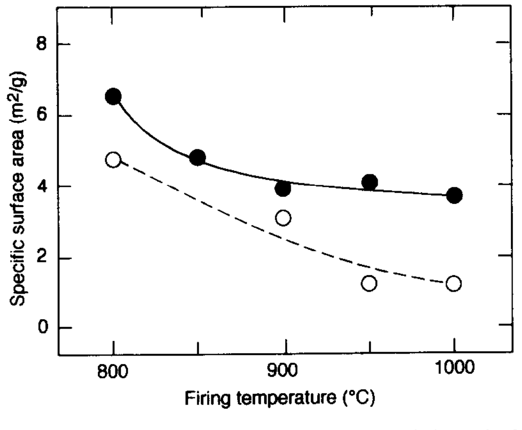

Fig. 8. Specific surface area of the coprecipitated $CaSiO_3$ precursor powder fired under the dry (○) and the vapor (●) atmospheres.

4 Summary

The effect of a vapor atmosphere on the formation of $MSiO_3$ (M = Mg, Ca, Sr and Ba) was examined using the precursor mainly prepared by the coprecipitation method. Among the four kinds of $MSiO_3$, vapor showed most effective influence in the $CaSiO_3$ sample and the least effective influence in the $MgSiO_3$ sample. The reason for these differences was mainly attributed to the chemical homogeneity of the precursor powder. It was further confirmed using the several kinds of $CaSiO_3$ precursor powders prepared by the different methods. The heat treatment of the precursor under the vapor atmosphere was effective to prepare fine crystalline powder compared with that under the dry atmosphere.

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