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Chemical Preparation and Phase Stability of Ca_2SiO_4 and Sr_2SiO_4 Powders

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Abstract

A process has been developed to produce high surface area Ca_2SiO_4 and Sr_2SiO_4 powders using colloidal silica for the silicon precursor. This method was relatively straightforward and avoided the use of precipitation techniques and unstable alkoxides. Calcium carbonate and strontium carbonate were identified as intermediate compounds, and the silicates appeared to form by a low-temperature solid-state reaction. The effect of resin content and calcination conditions on the phase distribution and physical properties of the powders was examined. Finally, the sodium content of the colloidal silica was found to have a significant effect on the phase stability of β-Ca_2SiO_4 after calcination at 1400°C.

Es wurde ein Verfahren zur Herstellung von Ca_2SiO_4- und Sr_2SiO_4-Pulvern mit großer freier Oberfläche entwickelt. Als Silizium-haltiger Prekursor wurde Siliziumdioxid verwendet. Diese verhältnismäßig direkte Methode erspart die Anwendung von Ausscheidungstechniken und nicht stabiler Alkoxide. Kalziumkarbonat und Strontiumkarbonat konnten als intermediäre Verbindungen identifiziert werden. Die entsprechenden Silikate scheinen sich durch eine Festphasenreaktion bei tiefen Temperaturen zu bilden. Die Auswirkungen des Anteils an Binderharz und der Kalzinierungsbedingungen auf die Phasenverteilung und die physikalischen Eigenschaften der Pulver wurden genauer untersucht. Schließlich konnte gezeigt werden, daß der Natrium-Gehalt des kolloiden Siliziumdioxids einen beträchtlichen Einfluß auf die Stabilität der β-Ca_2SiO_4-Phase nach der Kalzinierung bei 1400°C ausübt.

Un procédé a été développé pour synthétiser des poudres de Ca_2SiO_4 et Sr_2SiO_4 présentant une surface spécifique élevée, avec de la silice colloïdale comme précurseur du silicium. Cette méthode est relativement directe et évite les techniques de précipitation et l'usage d'alcoolates instables. Les carbonates de calcium et de strontium ont été détectés en tant que composés transitoires et les silicates paraissent se former par réaction à l'état solide à basse température. Les auteurs rapportent l'influence de la teneur en résine et des conditions de calcination sur la distribution de phase et les propriétés physiques des poudres. Les résultats démontrent, enfin, que la stabilité de la phase β-Ca_2SiO_4 après calcination à 1400°C est influencée de façon significative par la teneur en sodium de la silice colloïdale.

1 Introduction

The polymorphism of dicalcium silicate (Ca_2SiO_4) has been well studied[1,2] because of the considerable importance of this compound in the cement and refractories industries. The currently accepted sequence of phase transformations is illustrated in Fig. 1. In most cases work on the material has been directed at avoiding the disruptive 12 vol.% expansion associated with the $\beta \rightarrow \gamma$ transformation, commonly referred to as 'dusting'. The α'_L- and β-phases are also important hydraulic phases in Portland cement, but the γ-phase is undesirable because it does not hydrate.

Dicalcium silicate powders have usually been fabricated by a high-temperature solid-state reaction between CaO and SiO_2. The kinetics of this reaction are slow, and temperatures of 1450°C and above are commonly used to drive the reaction to completion. The resulting powder is predominantly γ-phase after cooling to room temperature. Retention of the high-temperature polymorphs is achieved by the addition of stabilizing additives or impurities.[3]

The β-phase of Ca_2SiO_4 can also be retained after

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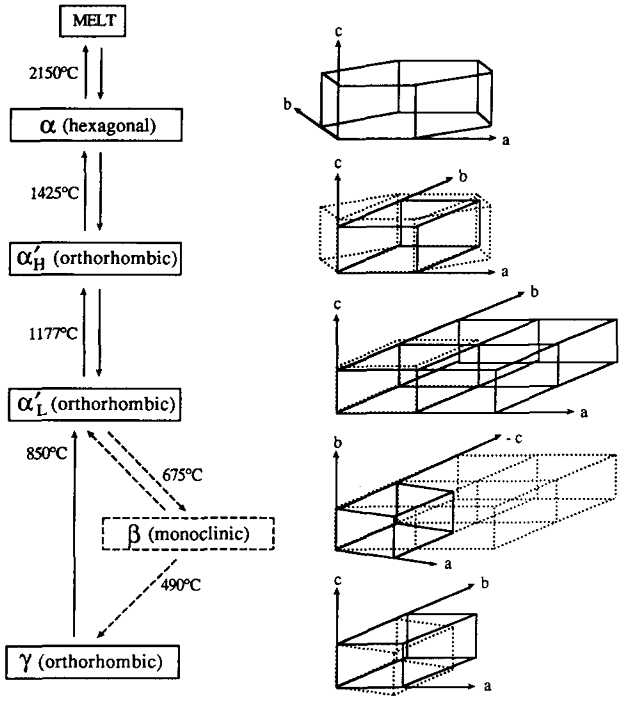

Fig. 1. The polymorphism of Ca_2SiO_4.

low-temperature heat treatment of γ-powders,[4] or by chemical preparation.[5] Both studies have linked the retention of the β-phase to a particle size effect on the $\beta \rightarrow \gamma$ transformation.

The chemical preparation route[5] involved either spray reacting or direct gelling of colloidal silica in the presence of $Ca(NO_3)_2$. This was an extension of the method used for the preparation of other silicates, as reviewed by Luth & Ingamells.[6] These chemical methods allowed preparation of β-Ca_2SiO_4 powders at temperatures as low as 750°C.[5] Powders of β-Ca_2SiO_4 have also been prepared by solid-state reaction of CaC_2O_4 and amorphous SiO_2 at 950°C in a CO_2 atmosphere.[7] The advantage of the latter method is that no corrosive salts, which produce acidic fumes on calcination, are used in the powder production. All the low-temperature methods already mentioned produced powders with higher surface areas than those produced by high-temperature calcination. Another advantage of the low-temperature routes is that the β-phase is retained and hence the powders are reactive in terms of their hydration behavior. Unfortunately, the nature of the chemical reactions that formed Ca_2SiO_4 has not been studied in detail and the physical properties, including the particle size, have not been fully reported, even though they are important to the hydration behavior.

Dicalcium silicate has recently been considered as a candidate for a possible alternative transformation toughener to zirconia.[8] This was based on the large volume change (12 vol.%) associated with the $\beta \rightarrow \gamma$ transformation. The desire to fabricate dense, polycrystalline Ca_2SiO_4 in order to study the transformation has also stimulated research into the preparation of high surface area Ca_2SiO_4 powders.

In comparison, Sr_2SiO_4 has been less well studied. The $\alpha' \rightarrow \beta$ transformation in this compound is structurally analogous to the $\alpha'_L \rightarrow \beta$ transformation in Ca_2SiO_4, but the transformation occurs at 90°C compared to 675°C for pure Ca_2SiO_4. This makes it easier to study the ferroelastic $\alpha' \rightarrow \beta$ type transformation in Sr_2SiO_4.[9,10] Consequently, fine Sr_2SiO_4 powders are required to process dense polycrystalline Sr_2SiO_4.

In this study a quick and comparatively easy method is reported for the chemical preparation of Ca_2SiO_4 and Sr_2SiO_4 powders. The method has previously been used to prepare Ca_2SiO_4 powders for incorporation into a calcium zirconate ($CaZrO_3$) matrix.[11] It involves a 'Pechini-type' process in which one of the constituents is colloidal. The effect of resin content and calcination conditions on the physical properties of the powder and the phase distribution are presented. The effect of the sodium content of the colloidal silica on the phase distribution of the Ca_2SiO_4 is also studied.

2 Experimental Procedures

A flow diagram detailing the preparation method is shown in Fig. 2. The resin content of the resulting gel is defined as follows:

$$\% \text{ resin content} = 100\ W_{\text{resin}}/(W_{\text{oxide}} + W_{\text{resin}})$$

where W_{oxide} is the weight of the oxide after calcination, calculated from the known weights of the precursors, and W_{resin} is the weight of resin added. In all cases the resin was composed of 60 wt% citric acid monohydrate and 40 wt% ethylene glycol.

Firstly, the calcium and strontium precursors, which were $Ca(NO_3)_2 . 4H_2O$ and $Sr(NO_3)_2$ respectively, were assayed and stored in desiccators. The

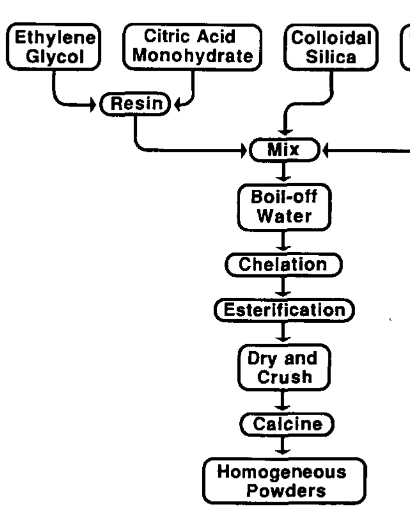

Fig. 2. Flow diagram showing the processing route for both Ca_2SiO_4 and Sr_2SiO_4 powders.

use of the hydrated nitrates, which can have variable moisture contents, did not affect the phase distributions obtained in the final powder. The required amount of the nitrate precursor was dissolved in water and then added to colloidal silica. In order to prevent flocculation of the silica, the pH of the colloidal silica was adjusted to below 1·5 with nitric acid prior to the addition of the nitrates. In this study, two colloidal silicas with different sodium contents were used. The first, which was designated Silica 1 (Ludox® SM, Du Pont Chemical Company), contained more sodium than the second, which was called Silica 2 (Ludox® AS-40, Du Pont Chemical Company). Silica 1 was used for all the Sr_2SiO_4 and Silica 2 was used for most of the Ca_2SiO_4 preparations. After the nitrate solutions and colloidal silica had been mixed, the resin was added and the mixture was heated. As the water boiled off, the gel formed without flocculation of the colloidal silica, and the viscosity increased. The remaining water then evaporated, expanding the gel into a foam. Finally the foam was dried and crushed before calcination at temperatures in the range 200°C to 1400°C.

Some of the crushed Ca_2SiO_4 gel was subjected to differential thermal analysis (DTA) and thermogravimetric analysis (TGA) while heating at 5°C/min, the same heating rate used for calcination. The phase distributions in the powders were evaluated by X-ray diffraction (XRD). This was after calcination for 1 min at temperatures in the range 200°C to 800°C and also after calcination for 1 h in the temperature range 800°C and 1400°C.

The effects of resin content and calcination conditions on the specific surface area and the particle size of the powders were determined by nitrogen adsorption (BET) and sedigraph techniques respectively. Some of the powders were also examined by SEM.

Finally, chemical analysis by plasma emission spectroscopy was performed on some Ca_2SiO_4 powders to check the calcium to silicon ratio, which was found to be in the range 2 to 2·1.

3 Results and Discussion

3.1 Phase development on calcination

Figure 3(a) shows the TGA results for a Ca_2SiO_4 gel containing 85% resin. The first major weight loss took place just above 250°C and could be correlated with the first low exothermic peak in the DTA curve of the same material, shown in Fig. 3(b). This was thought to be associated with the decomposition of the gel. The other major weight loss occurred at about 450°C and corresponded to a large exothermic DTA peak in Fig. 3(b). This was the stage at which the remainder of the gel decomposed and pyrolyzed. Further weight loss at higher temperatures was attributed to the removal of carbon formed during the pyrolysis. The thermal decomposition behavior of all the Ca_2SiO_4 and Sr_2SiO_4 gels in this study had the same characteristics as already described.

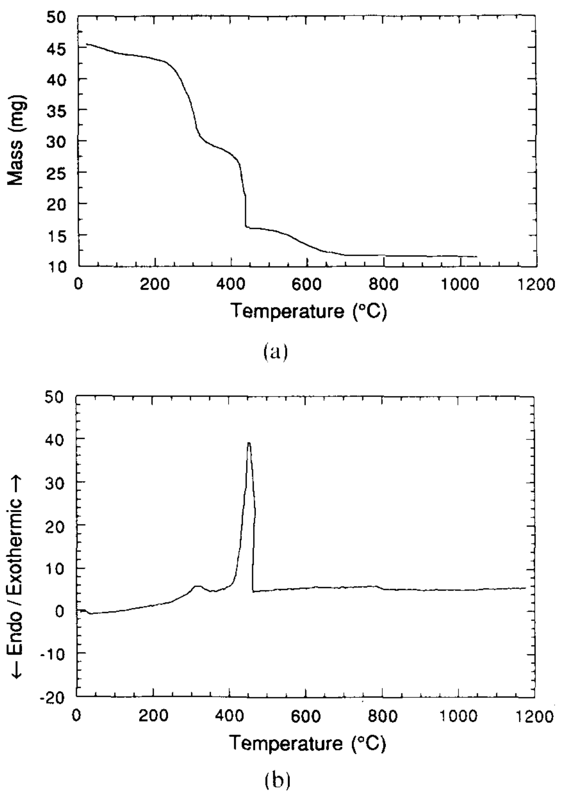

Fig. 3. (a) TGA and (b) DTA of a Ca_2SiO_4 gel containing 85% resin.

The phase distributions for the Ca_2SiO_4, gel containing 85% resin at different temperatures during the calcination are shown in Fig. 4(a). Each sample was heated at 5°C/min, held at the requisite temperature for 1 min and cooled. At temperatures below the pyrolysis stage the samples were X-ray amorphous, but after the pyrolysis at temperatures between 500°C and 650°C, the crystalline calcite phase of $CaCO_3$ could clearly be identified. As the temperature was increased, the amount of calcite appeared to diminish and the amount of Ca_2SiO_4 increased. By 700°C the sample was single phase α'_L-Ca_2SiO_4. When the calcination temperatures was increased to 800°C, the presence of β-Ca_2SiO_4 was observed. To further show that $CaCO_3$ was an intermediate compound, a sample of gel was calcined for 1 h at 600°C and then recalcined at 800°C. As can be seen in Fig. 4(b), after calcination at 600°C the only observable crystalline phase was $CaCO_3$, whereas after a second calcination at 800°C the sample was single phase β-Ca_2SiO_4. The exact nature of the reactions by which the $CaCO_3$ was removed and the Ca_2SiO_4 formed was unclear. Similar behavior was observed for the Sr_2SiO_4 gels with $SrCO_3$ being positively identified as an

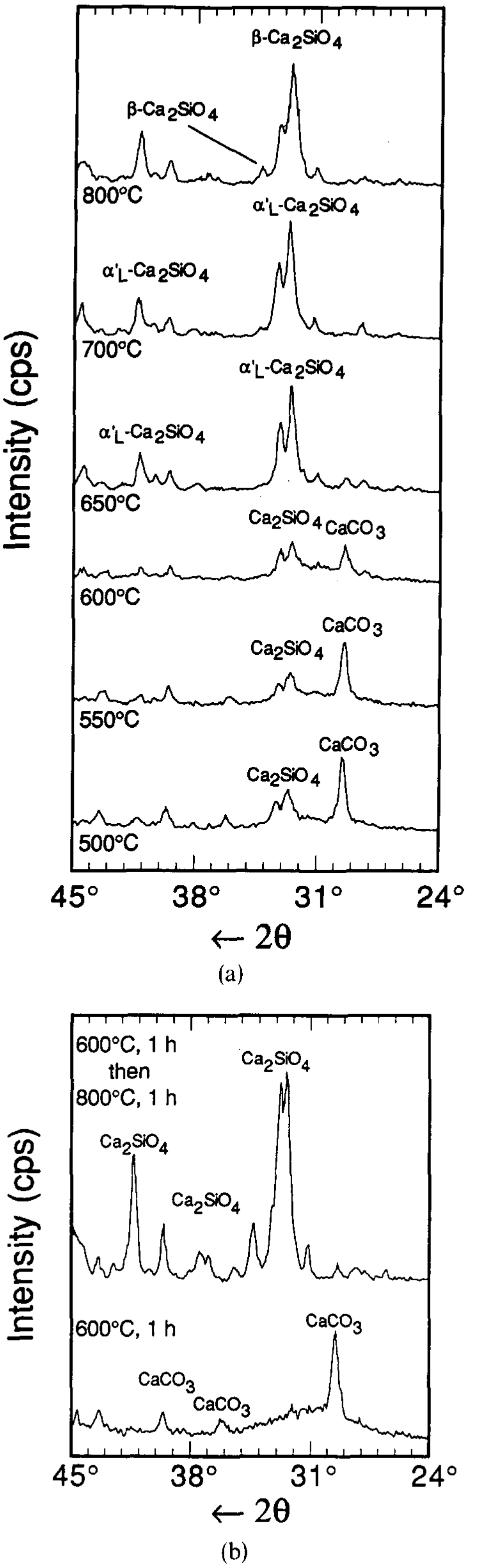

Fig. 4. (a) X-Ray diffraction traces showing the phase distribution in a Ca_2SiO_4 gel containing 85% resin, at different temperatures after the pyrolysis. Each sample was heated to temperature at 5°C/min and held at temperature for 1 min. (b) A comparison of X-ray diffraction traces of a Ca_2SiO_4 gel containing 85% resin, after calcination at 600°C for 1 h, and then after further calcination at 800°C for 1 h.

intermediate phase. Carbonates, specifically $BaCO_3$, have been identified during calcination of chemically derived powders in other studies.[12,13] They were intermediates in the formation of $BaTiO_3$, for example.

The phase distributions of Ca_2SiO_4 prepared with Silica 2 and calcined at high temperature are shown in Fig. 5(a). From 800°C to 1200°C the powders remained single phase β-Ca_2SiO_4, but the sample calcined at 1400°C showed single phase γ-Ca_2SiO_4. This could be attributed to enhanced grain growth at higher temperatures which decreased the stability of the β-phase. A particle size effect for this transformation in powders has been reported previously.[4,14-18]

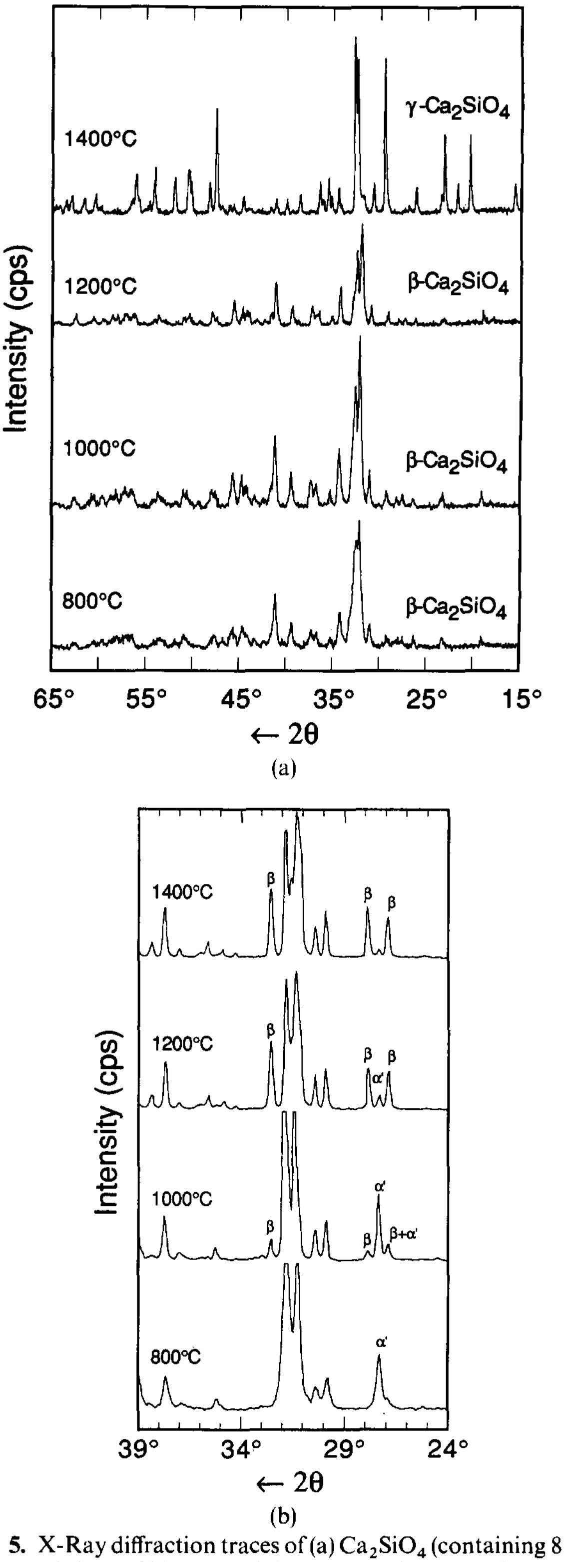

Fig. 5. X-Ray diffraction traces of (a) Ca_2SiO_4 (containing 85% resin) and (b) Sr_2SiO_4 (containing 90% resin) gels calcined for 1 h at temperatures in the range 800°C to 1400°C.

Figure 5(b) shows the development of the phase distribution for Sr_2SiO_4 prepared with Silica 1 and fired in the temperature range 800°C to 1400°C. The resin content was 90%. At 800°C the powder was single phase α' but as the temperature was increased β-phase was detected. The amount of β-phase increased with temperature until after 1400°C the sample was almost entirely β-phase.

The morphology of Sr_2SiO_4 powder calcined at 800°C for 1 h is shown in Fig. 6(a). The agglomerates were highly porous and comprised crystallites approximately 80 nm in size. Calcination at higher temperatures caused the agglomerates to densify and the crystallites to grow. Figure 6(b) shows powder calcined at 1400°C in which the agglomerates were dense and the grains were substantially larger than 1 μm. The SEM and X-ray diffraction results indicate a particle size dependence for the $\alpha' \rightarrow \beta$ transformation in Sr_2SiO_4.

3.2 Effect of resin content

It is well known that the resin content can have an effect on the physical characteristics of powders produced by the Pechini process.[19] Hence the effect of resin content on the powders was investigated in this study. Resin contents from 50% to 93% were investigated and found to have no effect on the phase distribution in Ca_2SiO_4 for a specific calcination condition. In contrast, the resin content did affect the phase distributions in the Sr_2SiO_4 powders. Lower resin contents (50% and 70%) produced significant amounts of $SrCO_3$ or SrO along with $SrSiO_3$ after calcination at 800°C and 1000°C. This was attributed to strontium nitrate observed in the dried gels by X-ray analysis.

The presence of $Sr(NO_3)_2$ in the dried gels was attributed to incomplete chelation of the strontium ions during heating of the mixture and consequent precipitation of the nitrate. However, at the high resin contents required to obtain high surface area, this behavior was not observed.

Figure 7 shows DTA traces for Sr_2SiO_4 gels with different resin contents. It can be seen that those gels which contained crystalline $Sr(NO_3)_2$ (50% and 70% resin) clearly exhibited a broad endotherm at approximately 650°C, which could be linked to the melting and decomposition of $Sr(NO_3)_2$. Such segregation would be a source of chemical inhomo-

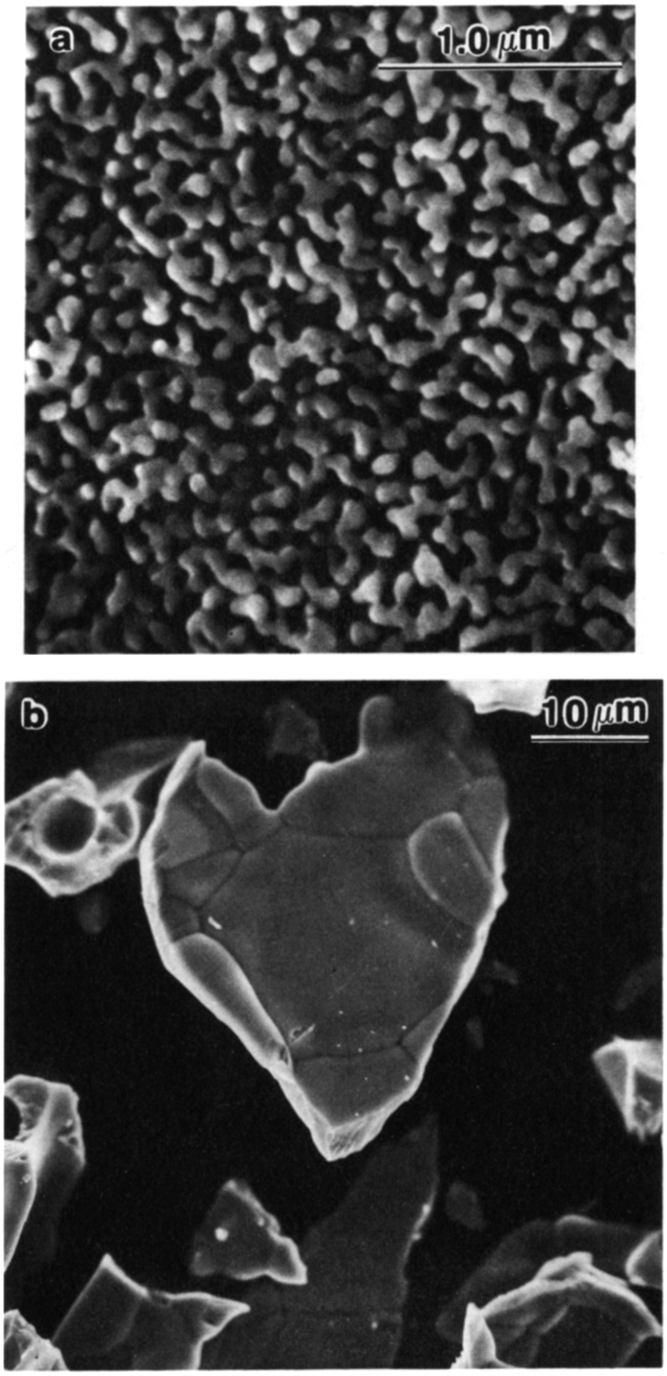

Fig. 6. SEM micrographs of Sr_2SiO_4 powder derived from a gel containing 90% resin calcined at (a) 800°C for 1 h (the individual crystallites have sintered together into highly porous agglomerates), and (b) 1400°C for 1 h (the agglomerates have fully sintered).

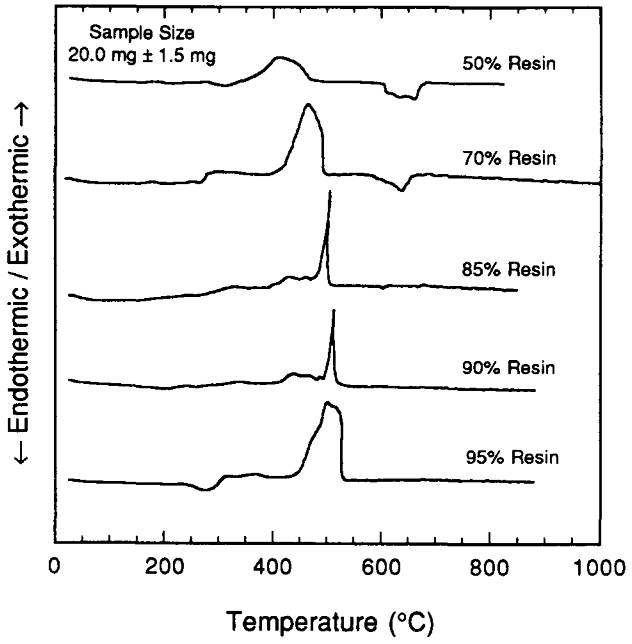

Fig. 7. DTA of Sr_2SiO_4 gels containing different resin contents.

geneity that could lead to the formation of SrO during calcination. It may also have been responsible for the retention of the $SrCO_3$ intermediate at temperatures above 700°C. In order to avoid reprecipitation of $Sr(NO_3)_2$ in the gels during drying, resin contents of 90% or above were used in the preparation of Sr_2SiO_4.

The physical characteristics of the powder were also affected by the resin content of the gel. Figure 8(a) shows the surface area of Ca_2SiO_4 powder as a function of calcination temperature for different resin contents. Above 1000°C, the resin content did not appear to have any significant effects on the surface areas of the powders. However, at lower temperatures the situation was very different. After calcination at 800°C the 85% and 93% resin contents showed the highest surface areas ($\sim 17\,m^2/g$), while the gels made without resin by direct casting of the colloidal silica in the presence of $Ca(NO_3)_2.4H_2O$ had the lowest surface area ($6\,m^2/g$). This increase in surface area with resin content was attributed to the extensive internal porosity seen in the powders made using high resin contents (Fig. 6(a)). When the calcination temperature was increased, sintering and grain growth of the powder agglomerates reduced the internal porosity (Fig. 6(b)) and led to lower specific surface areas.

Figure 8(b) displays the effect of resin content on the surface area of Sr_2SiO_4 powders. As was the case with Ca_2SiO_4, gels with higher resin contents produced powders with higher surface areas. This plot clearly showed that resin contents above 85% must be employed to produce high surface area powders.

The particle size of the powders was also affected by resin content. The results of different resin contents for Sr_2SiO_4 powders calcined at 800°C are shown in Fig. 9(a). The 50% and 70% resin contents gave powders with large median values of 20 μm and 11 μm respectively. Further increases in the resin content shifted the distributions to smaller particle sizes. The median value for 85% resin was about 6 μm and the largest particles in the distribution were approximately 20 μm. This trend to smaller sizes may have been due to the more violent pyrolysis in gels containing higher resin contents, leading to smaller, highly porous agglomerates. The highest resin contents used, including 90% and 95%, gave powders with the lowest median particle sizes. However, the largest particles in the distributions were of a similar size to the largest particles in the powders made from gels with 70% resin. Interestingly, both of the higher resin contents give bimodal distributions and 40% of the powder was submi-

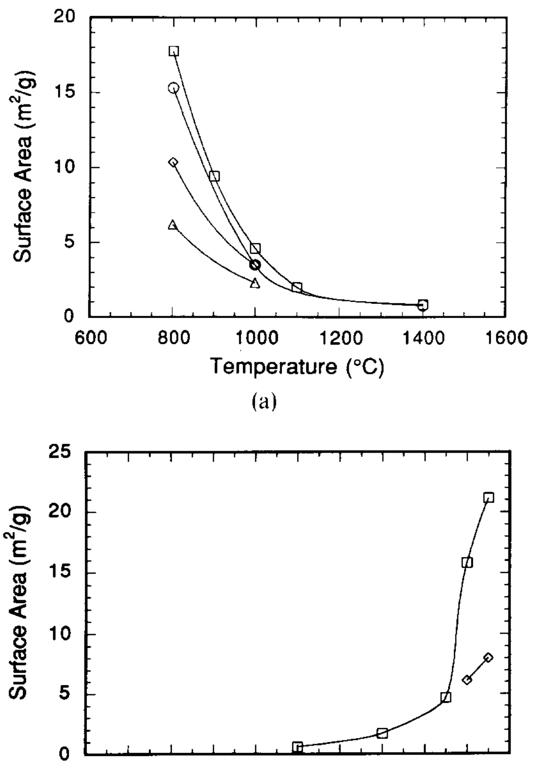

Fig. 8. (a) Surface areas of Ca_2SiO_4 powders containing different resin contents and calcined in the temperature range 800°C to 1400°C. (△) 0%, (◇) 50%, (□) 85%, and (○) 93% resin. (b) Effect of resin content on the surface area of Sr_2SiO_4 powders calcined at (□) 800°C and (◇) 1000°C for one hour.

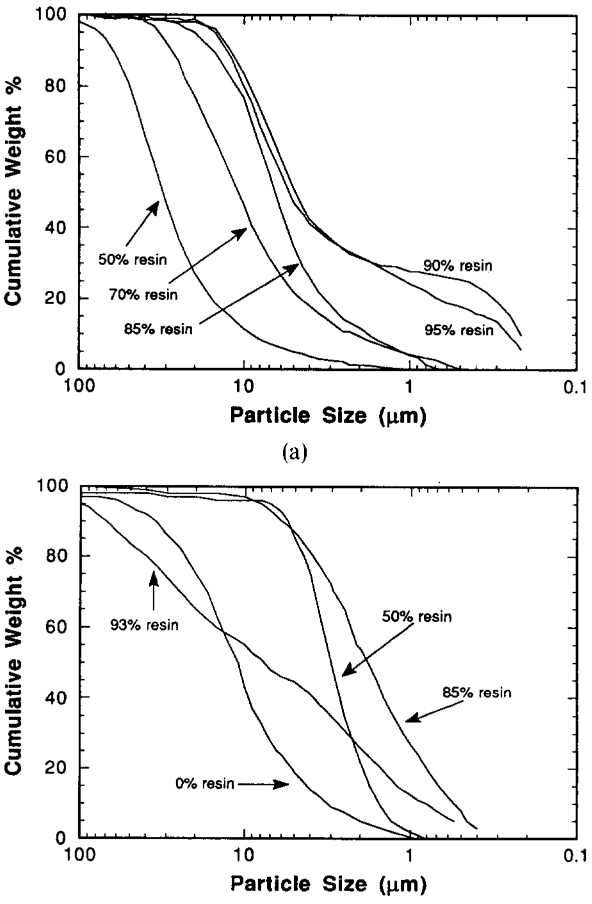

Fig. 9. Effect of resin content on particle size distribution of (a) Sr_2SiO_4 and (b) Ca_2SiO_4 powders calcined at 800°C for one hour.

cron. This biomodal characteristic was reproducible although difficult to explain.

Figure 9(b) shows the effect of resin content on the particle size of the Ca_2SiO_4 powders. The trend with resin content was not as systematic as in the Sr_2SiO_4 powders. With no resin, the distribution was wide. The 50% resin sample had a narrow distribution, between 10 μm and 1 μm with a median of approximately 2 μm. This was in contrast to the trend in Fig. 9(a), but may be explained by the fact that during calcination, the Ca_2SiO_4 gel with this resin content exploded at about 200°C. This was thought to be a consequence of the sudden and violent release of moisture, leading to smaller particles. When the resin content was increased to 85%, the particle size distribution shifted to smaller particle sizes. For this powder, the large particles were about 6 μm in size but there was also approximately 30% of submicron powder. Further increase in the resin content to 93% gave a very wide particle size distribution from submicron to 100 μm. This contrasted with the results for Sr_2SiO_4 using similar resin contents. In this case interagglomerate sintering was thought to have taken place during pyrolysis and calcination.

3.3 Effect of sodium on the phase distribution in dicalcium silicate powders

The phase distributions in Ca_2SiO_4 powders prepared with Silica 1 and Silica 2 were markedly different after calcination for 1 h at 1400°C. This was attributed to the difference in sodium content, since sodium is known to be a stabilizer for β-Ca_2SiO_4.[20] Calculation showed that Silica 2 would give Ca_2SiO_4 with 0·14 wt% Na_2O and Silica 1 would give Ca_2SiO_4 with 0·67 wt% Na_2O. Sodium was added in preparations of Ca_2SiO_4 with Silica 2 in the form of $NaNO_3$ dissolved with the $Ca(NO_3)_2 \cdot 4H_2O$. In this way, powders containing up to 1 wt% Na_2O were prepared, and calcined at temperatures ranging from 800°C to 1500°C. The results of the phase analysis are shown in Table 1. All the powders exhibited β-phase after calcination at temperatures below 1400°C. However, after calcination at 1400°C, samples containing less than 0·5 wt% Na_2O transformed to γ-phase on cooling, while the other compositions remained β-phase. Consequently, there was evidence to suggest that the difference in phase distribution for samples prepared with Silica 1 and Silica 2 was due to the sodium content of these colloidal silica precursors.

Table 1. Phase distributions of Ca_2SiO_4 powders with different sodium contents, calcined for 1 h at various temperatures

Na_2O (wt%)	*800°C*	*1000°C*	*1200°C*	*1400°C*
0·14 (Silica 2)	β	β	β	γ
0·27	β	β	β	γ
0·41	—	—	β	γ
0·54	—	—	β	β
0·67 (Silica 1)	β	β	β	β
1·0	—	β	β	β

4 Summary

A quick and relatively simple method for the preparation of both Ca_2SiO_4 and Sr_2SiO_4 powders of high surface area has been developed. The method avoided the use of unstable alkoxides and precipitation techniques. The powders so produced were very porous and friable and could easily be milled into submicron particle sizes.

The development of single phase powders at 700°C or above appeared to involve the formation of $CaCO_3$ or $SrCO_3$ as intermediate compounds. The desired silicate then developed by a low-temperature solid-state reaction between 500°C and 700°C. When the temperature was increased in this range, the silicate developed and the carbonates disappeared. The exact nature of the reaction was unknown.

Single phase powders of α'_L-, β- and γ-Ca_2SiO_4 could easily be produced by this route. The method has also been used to prepare single phase α'-powders of Sr_2SiO_4 for the first time.

The physical characteristics of the powders could be controlled by the resin content of the gel and the calcination conditions. In the case of Sr_2SiO_4, the resin content was also used to control chemical inhomogeneity caused by the reprecipitation of $Sr(NO_3)_2$ during drying of the gel. The effect of resin content on surface area was generally the same for both systems, but there were marked differences in how the resin content affected the particle size distributions.

Finally, the difference in the phase distributions observed in the Ca_2SiO_4 powders prepared with Silica 1 and Silica 2 was attributed to the difference in the sodium content of these colloidal silicas.

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