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Crystallization of δ-$Na_2Si_2O_5$-rich layered silicates from sodium silicate solutions: seeding and temperature programmed δ-phase embryo creation

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Abstract

The effect of seed composition on the crystalline layered sodium disilicate phase development using a sodium silicate solution (SiO_2/Na_2O molar ratio = 2.1) has been investigated. To obtain δ phase-rich products, it is necessary that the α phase content in the seed be as low as possible. High temperatures (700 °C) and absence of any α phase in the initial seed substantially promote the amorphous phase→δ phase transformation reaction even if the seed contains up to 15.0 wt.% β phase. It has been shown that pretreatment in the temperature range 150–200 °C promotes significantly δ phase nucleation. Low temperature nucleation has been observed for the sodium silicate solution modulus in the range of 1.5–2.1. This finding might be implemented to solve reproducibility problems in the industrial scale production of layered disilicates from water glass. To obtain a minimum calcium binding capacity of 120.0 mg CaO/g , an α phase content of up to 20.0 wt.% is tolerable.

Keywords: Chemical properties; Layered sodium disilicates; $Na_2Si_2O_5$; Powders–solid state reaction; Seeding; X-ray methods

1. Introduction

Crystalline layered disilicates are gaining increasing importance as substitutes for pentasodium phosphate and 4A zeolite in laundry detergents. They do not induce any eutrophication activity and eventually dissolve in sewage treatment plants at dilution levels of about 100:1. Zeolite 4A as a detergent ingredient suffers from non-self dispersion. The outer surface charge of zeolite 4A particles is not enough to help them remain as a stable emulsion in water.This implies the use of additives like polycaboxylates. Instead, crystalline layered sodium silicates are self-dispersing.

Crystalline layered sodium disilicates comprehend several type of phases, namely α, β, γ, δ and their subgroups like α(I), α(II), α(III), etc.[1] It has been discovered that certain phases or combination of phases fulfill the basic requirements for a multifunctional builder.[2] δ-$Na_2Si_2O_5$ shows superior calcium and magnesium binding capacity.[3] On the other hand, an existing commercial layered silicate, i.e. SKS-6 (Hoechst AG), is a mixture of the three phases α, β and δ in the approximate weight percentages of 10, 10 and 80, respectively.[2] From an industrial point of view, it is extremely difficult to produce pure δ-phase in a reproducible fashion. Surmounting the latter problem has been the subject of several patents issued in within the past 15 years.[4–6]

Generally, the industrial process for the manufacture of crystalline layered sodium disilicates consists of the following steps: Spray drying a sodium silicate solution up to a certain final ignition loss level, grinding and high temperature heat treating in rotary kilns. The raw material may be hydrothermally produced water glass from sand or tank furnace water prepared by melting sand and soda at high temperatures followed by dissolution in hot water. The industrial processes make indispensable use of seeds to ascertain proper phase development and shortening of reaction time. However, no systematic study on the seed composition effect on the layered sodium disilicate phase developments has been published. Rieck[4] introduced the use of seeds in 1986.

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The first part of the present work studies the isothermal phase development of crystalline layered sodium disilicates using seeds of different phase compositions. A novel method for enhancing δ-phase formation, excluding seeding and introducing embryo formation via initial heat treatment, is then introduced. Holz et al.[6] preheated (50–140 °C) water glass without dehydration to enhance δ-phase formation. This requires the heating of a large amount of solution and use of large pressure vessels for temperatures exceeding 100 °C. This study optimises the heat pretreatment of the dehydrated water glass for δ-phase embryo from experimental results. It is shown that this method is effective for all the three modulus values investigated (1.5, 1.75 and 2.1).

2. Experimental

An Iranian water glass solution (Behdad Chemical Company) with the following specification was used: SiO_2/Na_2O molar ratios(moduli) 1.5, 1.75 and 2.1, 39.42 wt.% solid content, 1.2 ppm Al and less than 1 ppm Fe impurity.

For each synthesis, 10 g water glass solution unseeded or with 0.5 g seed were introduced into 250 cm^3 nickel crucibles pre-cleaned with boiling dilute sodium hydroxide aqueous solution (10^{-5} mol l^{-1}). The latter was placed into a Nabertherm furnace to be heated to the crystallization temperatures 605 and 700 °C in less than 5 min time. These values were chosen according to the conventional ones implemented in the patent literature. As the initial solution is heated, it undergoes a dehydration process. Therefore the end product of each experiment is in the form of a silicate foam which is ground before subjecting it to further analysis. In the case of initial heat treatment, the liquid samples (with or without seed) underwent 1 h isothermal heating at the predetermined temperatures (100, 150, 175 and 200 °C) before being heated up to the crystallization temperature.

The final samples were subjected to XRD (D-500, Siemens) analysis. In reporting the phase development of different phases, the intensity of the following planes have been considered: (1 4 0) for α phase, (4 0 0) for β phase and the sum of (2 2 0), (3 2 0), (4 1 0) and (3 2 1) planes for δ phase. Identification of α and β phases was performed according to the available JCPDS diffraction data files (22–1397 and 29–1261 for the α and β phases, respectively). Assignment of the δ phase peaks has been made from a recent Rietveld refinement.[9] For calcium binding capacity (CBC) analysis, samples were ground to less than 200 ìm particle size. Some 1 g of the latter was added to 500 cm^3 of a 0.005 M $CaNO_3$ solution and vigorously mixed for 15 min at room temperature. After separation of the solid phase, the filtrate was titrated with 0.01 M EDTA solution at a buffered pH of 9.8. The amount of $CaNO_3$ in the filtrate was accordingly related to the CBC of the original sample.

3. Results and discussion

The following parameters have been investigated: Reaction temperature, seeding and initial heat treatment.

3.1. Reaction temperature

Phase evolution at 605 °C is shown in Figs. 1–3. It is observed that at this temperature no alpha phase is produced for reaction times up to 90 min. Instead, the β and δ phases begin to form after an induction period of about 30 min. The β phase content approaches its maximum value after 60 min and, subsequently decreases by transformation into α phase. Willgallis and

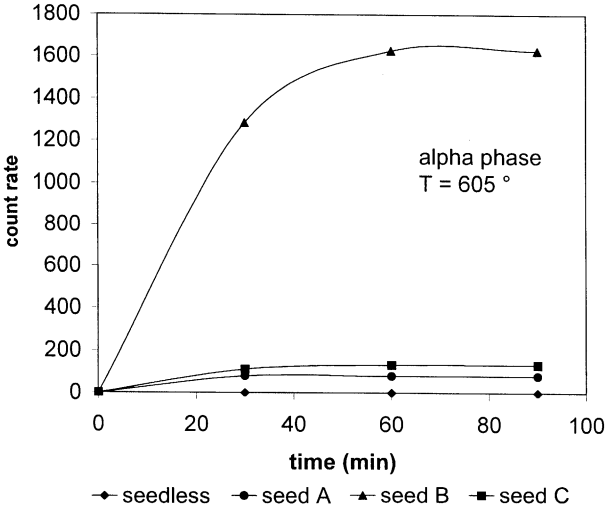

Fig. 1. Phase development of α phase for the seeded and unseeded experiments at 605 °C (modulus = 2.1).

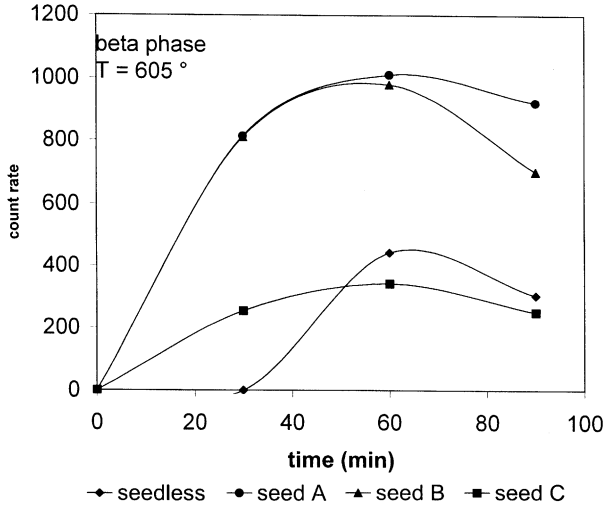

Fig. 2. Phase development of β phase for the seeded and unseeded experiments at 605 °C (modulus = 2.1).

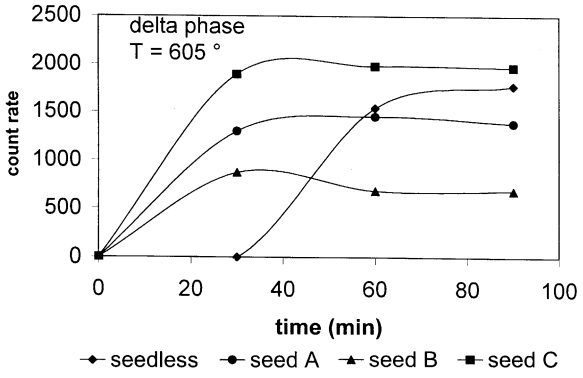

Fig. 3. Phase development of δ phase for the seeded and unseeded experiments at 605 °C (modulus = 2.1).

Range[1] have reported the following thermal phase transformation sequence: S→γ→β→α, where S stands for the amorphous dehydrated glass phase. Williamson and Glasser[8] indicate that the γ and δ phases have the highest free energy with respect to the other phases. Based on the XRD patterns obtained, no γ phase could be detected in the final products of this series of experiments. It is therefore reasonable to consider the following evolution sequence to hold: S→δ→β→α. The XRD pattern of a sample heated for 90 min is shown in Fig. 4.

A low impurity phase, identified as SiO_2 (29-85, JCPDS-card), is observed. The crystallization of the latter is attributed to the existence of excess dissolved SiO_2 in the initial sodium silicate solution (modulus > 2). In other words, if the modulus had been exactly 2, all the Na_2O and SiO_2 in the initial solution might have stoichiometrically reacted and formed crystalline $Na_2Si_2O_5$.

According to Figs. 5–7, at 700 °C there is a slight increasing tendency for α phase formation. Referring to these figures, the α phase content is relatively very low with respect to the other phases. The β phase evolution curve attains a maximum , as for the reaction temperature 605 °C, but after 25 min. The same is true for the δ phase evolution, although its maximum level occurs after 50 min. It is probable that the phase is formed at the expense of β phase extinction. The XRD pattern of a sample reacted for 75 min is shown in Fig. 4; SiO_2 impurity phase is also present. The maximum relative δ phase content obtained in this series of experiments is 85.4 wt.% (605 °C, 90 min). The weight percent of phase *i* (*i* = α, β and δ) is defined as (mass of phase *i*)/(total mass of phases α, β and δ)×100. Weight percentages of various phases of each sample were evaluated using a relation obtained between the relative intensities of the α, β and δ phase peaks of a known sample (SKS-6, Hoechst AG).

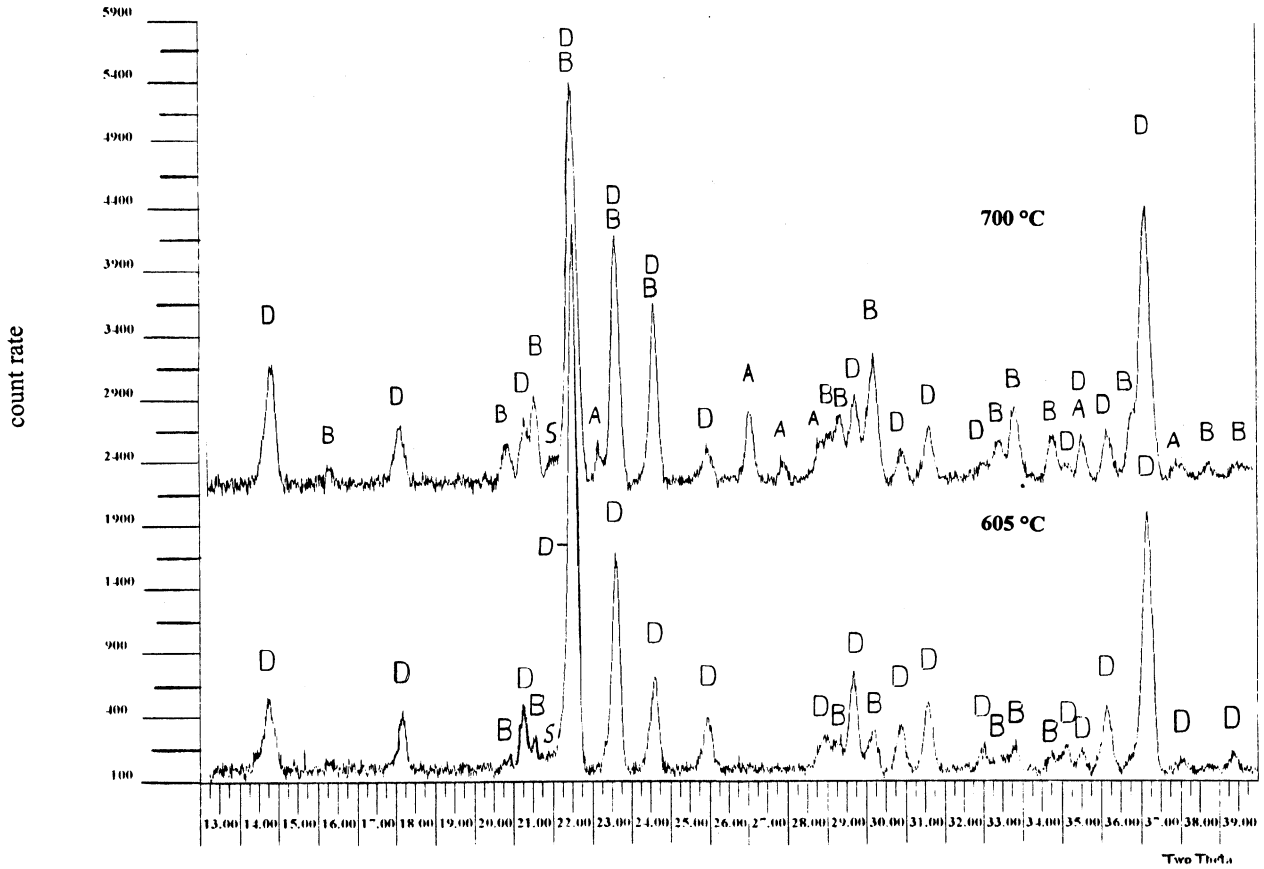

Fig. 4. XRD patterns for the experiments performed without heat treatment or seeding for the reaction temperatures of 605 and 700 °C and a respective reaction time of 90 and 75 min (modulus = 2.1).

3.2. Seeding

Three different seed phase compositions according to the following were used:

- Seed A: 14.6 wt.% β and 85.4 wt.% δ phases.
- Seed B: 11.0 wt.% α, 35.6 wt.% β and 53.4 wt.% δ phases.
- Seed C: 1.4 wt.% α and 98.6 wt.% δ phases.

The mentioned seeds had been previously produced according to the method of Riecks[4] at 700 °C. XRD analysis showed that the seeds were fully crystalline and no amorphous impurity could be detected.

3.2.1. Seed A

The phase development due to seed A at 605 °C is shown in Figs. 1–3. This seed did not contain any phase. It is observed that, with respect to the seedless experiments at the same reaction temperature, some phase is produced at early times which does not increase significantly further. The author presumes that this might be due to existing phase nuclei in the initial seed not observable by XRD.

The β phase develops to a maximum level (corresponding relative phase content of 39.2 wt.%) after 60 min and decreases slightly up to 90 min. The same behavior is observed for the δ phase, although it attains a maximum relative intensity of 59.6 wt.% at 90 min. Therefore, seeding has a marked effect on the phase development rate. The maximum β phase content obtained is more than doubled with respect to an unseeded preparation. It is clearly observed that for both seeded and seedless experiments, the rate of the β→α transformation reaction is slow. According to the XRD pattern of the sample heated for 90 min, a low content of SiO_2 impurity phase could be observed. Although seed A contained a low impurity content of SiO_2, the latter phase growth was not promoted.

For seeded experiments at 700 °C (Figs. 5–7) like 605 °C, α phase development is still scarce. On the other hand β phase formation is strongly suppressed at early times (25 min) and is reduced to zero at more than 50 min. This results in a high δ phase content. A maximum δ phase content of 98.6 wt.% could be obtained after 50 min at 700 °C.

It may be deduced that high temperatures (700 °C) and absence of any α phase in the initial seed substantially promote the S→δ phase transformation reaction even if the seed contains up to 15.0 wt.% β phase.

3.2.2. Seed B

As indicated in Section 3.2, seed B includes 11.0 wt.% α phase behind the other phases. It is observed that for the reaction temperature of 605 °C, the presence of

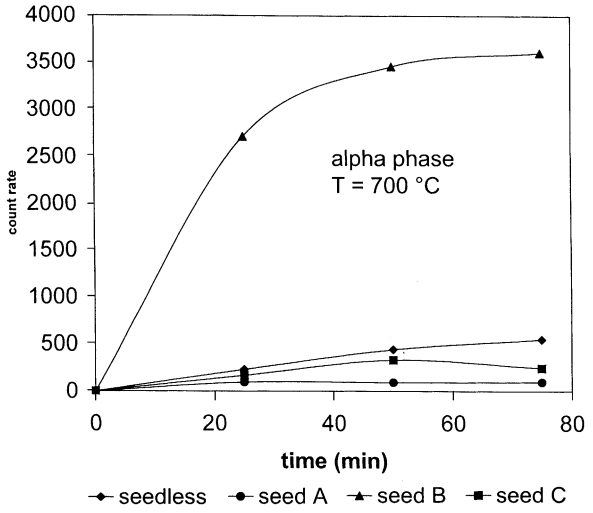

Fig. 5. Phase development of α phase for the seeded and unseeded experiments at 700 °C (modulus = 2.1).

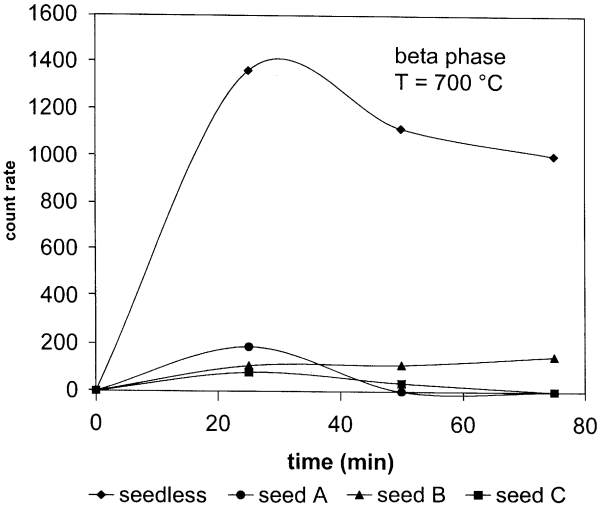

Fig. 6. Phase development of β phase for the seeded and unseeded experiments at 700 °C (modulus = 2.1).

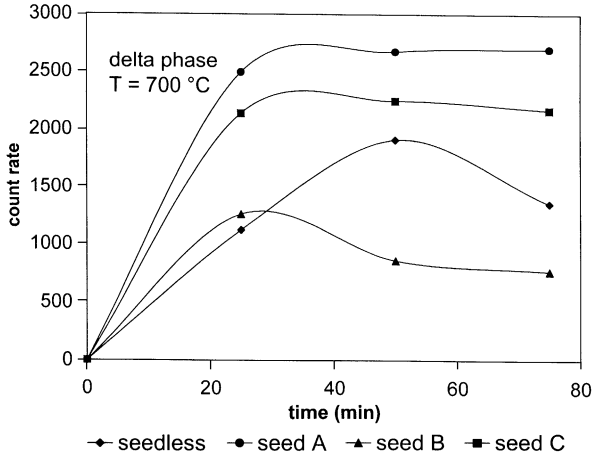

Fig. 7. Phase development of δ phase for the seeded and unseeded experiments at 700 °C (modulus = 2.1).

α phase is detrimental (Figs. 1–3). The low content of α phase particles in the seed enhance significantly α phase formation, suppressing strongly δ phase formation. Seed B contains 2.2 times more β phase than seed A. However, the maximum β phase production (after 60min) is as for seed A and it further reduces with time. This can be attributed to the enhanced β→α phase transformation due to the significantly higher active α phase particles surface present.

The XRD patterns of the samples obtained at the crystallization temperatures 605 and 700 °C for the reaction times 90 and 75 min showed SiO_2 impurity peaks. The initial silica phase in the seed has not promoted further growth. The phase development curves for the temperatures 605 and 700 °C are quite similar (Figs. 5–7). Again, α phase formation is strongly enhanced and δ phase formation suppressed. The major deduction is that α phase in the seed significantly promotes α phase nucleation and growth.

3.2.3. Seed C

This seed is high in δ phase but low in α phase (1.4 wt.%) and has no β phase. According to Fig. 1, a slight increase in α phase content is observed up to 90 min at 605 °C. The β phase content for times larger than 60 min is even lower than for the unseeded experiments (Fig. 2). The maximum yield of δ phase is larger than the corresponding value for the before mentioned seeded (A and B) and unseeded experiments (Fig. 3). The same trend is observed for the C-seeded experiments at 700 °C (Figs. 5–7). Nonetheless, the final δ phase content is less than that achieved at the same temperature in which the initial seed was lower in δ phase content without α phase (seed A). This may be attributed to the higher rate of α phase formation due to a higher temperature.

3.3. Initial heat treatment (modulus = 2.1)

Experiments have been performed only at 700 °C. The main purpose was to investigate the possibility of typical δ phase embryo production at low temperatures. Low temperature nucleation of specific phases is well known in the glass industry.

The experimental results are shown in Figs. 8–10. Surprisingly, pretreatment at 150 °C strongly suppresses α phase nucleation and growth. Quite the same trend is observed for pretreatment temperatures of 175 and 200 °C, although the maximum δ phase yield is obtained for a pretreatment temperature of 150 °C corresponding to a relative δ phase content of 92.3 wt.% after 75 min. The XRD pattern of the latter showed again the presence of SiO_2 impurit phase.

The produced silicate foams (prior to crystallization at 700 °C) were X-ray amorphous and almost totally dehydrated.. Heating for 1 h between 150 and 200 °C results in some sort of short range order rearrangement

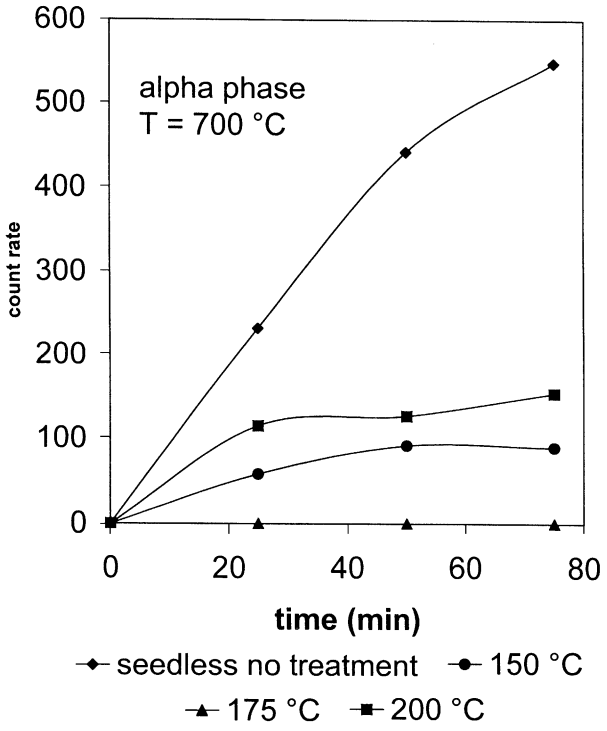

Fig. 8. Phase development of α phase for the seedless experiments at 700 °C with and without heat treatment (modulus = 2.1).

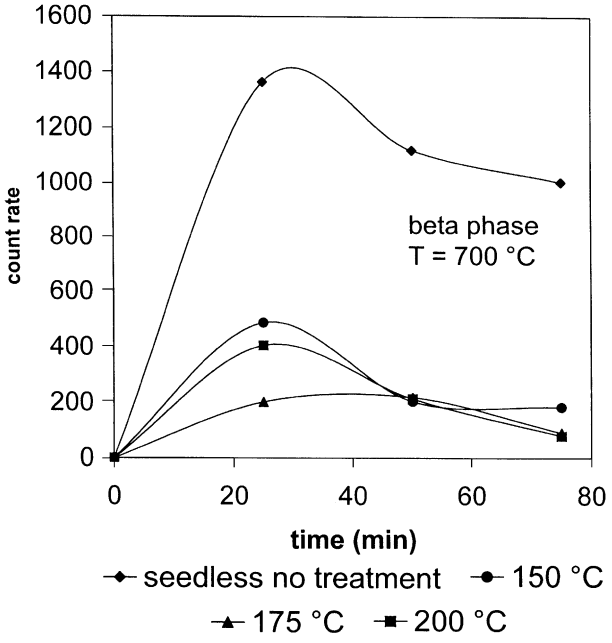

Fig. 9. Phase development of β phase for the seedless experiments at 700 °C with and without heat treatment (modulus = 2.1).

of the Si, Na and O atoms. Compared with the unseeded experiments at the same temperature, the latter treatments result in significant higher relative δ phase content at 700 °C. Therefore it might be presumed that heat treatment promotes δ phase embryo nucleation. These nuclei accelerate δ phase

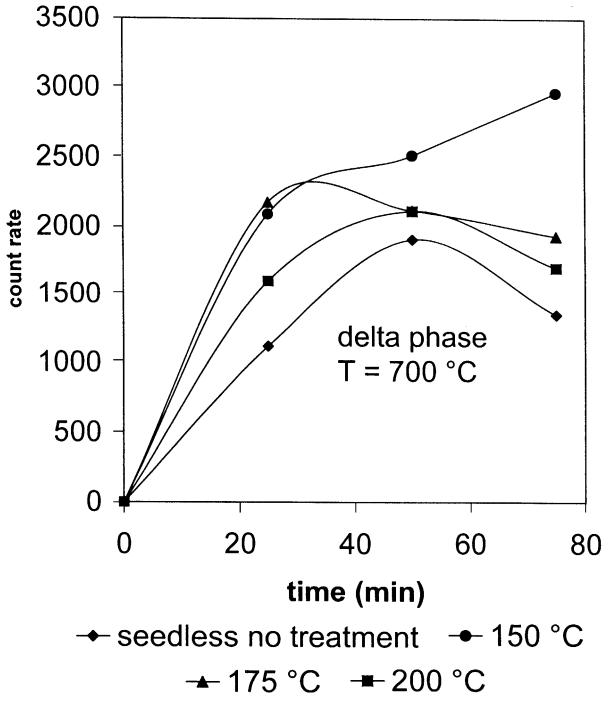

Fig. 10. Phase development of δ phase for the seedless experiments at 700 °C with and without heat treatment (modulus = 2.1).

growth at the crystallization temperature. Such a pretreatment may substitute the use of δ phase enhancing seeds in the industrial manufacturing processes.

XRD analysis for the product obtained after a reaction time of 90 min at 100 °C showed a relative δ phase content of 56.5 wt.%. Hence it can be deduced that there exists a limit for the minimum treatment temperature. The data obtained in this study are insufficient to define such an extremum.

At this stage, it is interesting to investigate the effect of the pretreatment procedure for lower initial water glass moduli. This is the subject of the following section.

3.4. Initial heat treatment (moduli 1.75 and 1.5)

Preliminary treatment consisted of 1 h isothermal heating at 150 °C followed by 700 °C. The pertaining XRD patterns for a reaction time of 75 min are shown in Fig. 11. It is clearly observed that moduli lower than 2 result in relatively high α phase contents while the β phase is suppressed. A low content impurity phase identified as $Na_2Si_4O_9$ could be detected. The effect of heat treatment on increasing δ phase content is promising. Referring to Figs. 12 and 13, it is observed that the suppression of the α phase formation occurs for both moduli 1.5 and 1.75. The latter effect is more pronounced for modulus = 1.5.

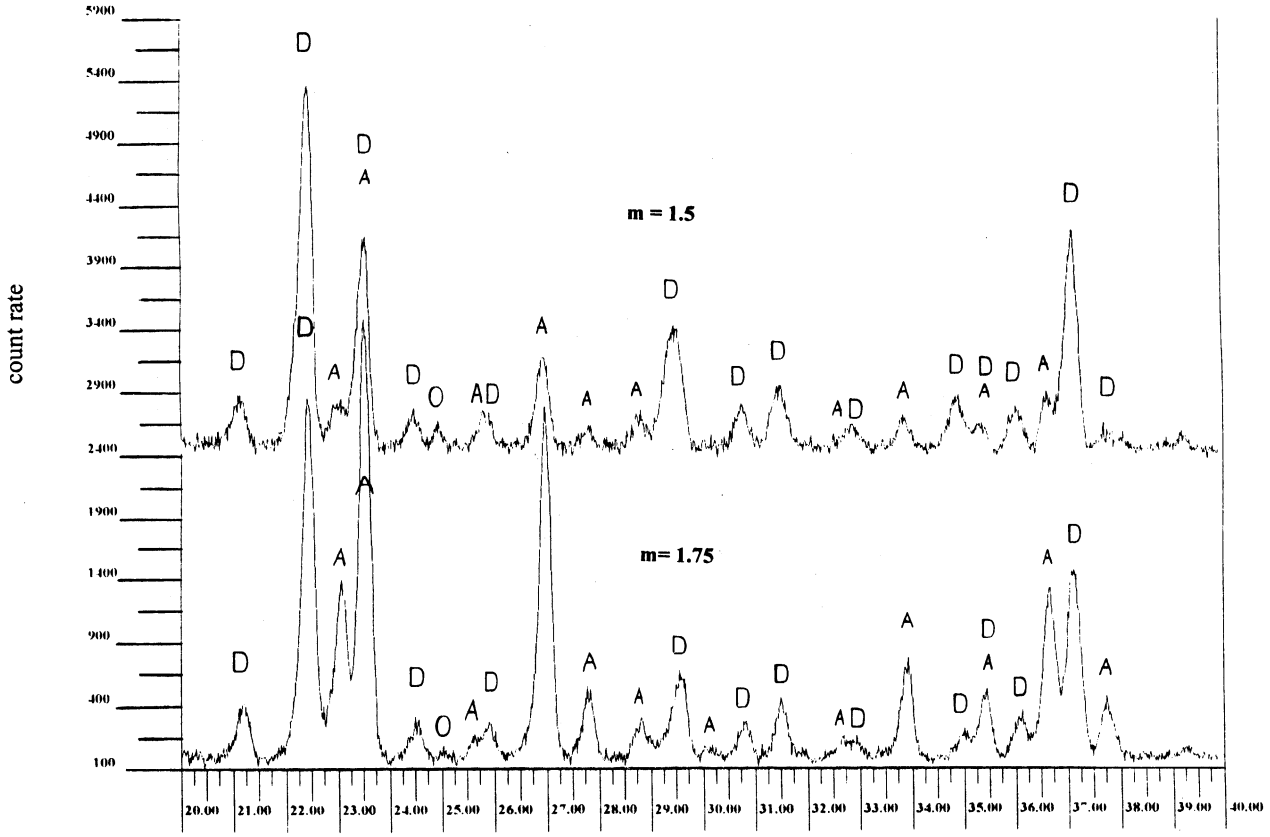

Fig. 11. XRD patterns for the seedless experiments with 1 h initial heat treatment at 150 °C , 75 min reaction time at 700 °C for the two moduli of 1.5 and 1.75.

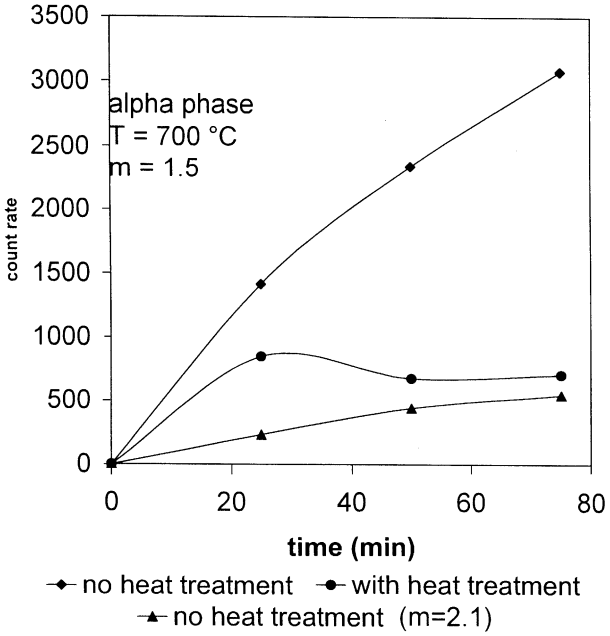

Fig. 12. Phase development of α phase for the seedless experiments at 700 °C with and without heat treatment (modulus = 1.5).

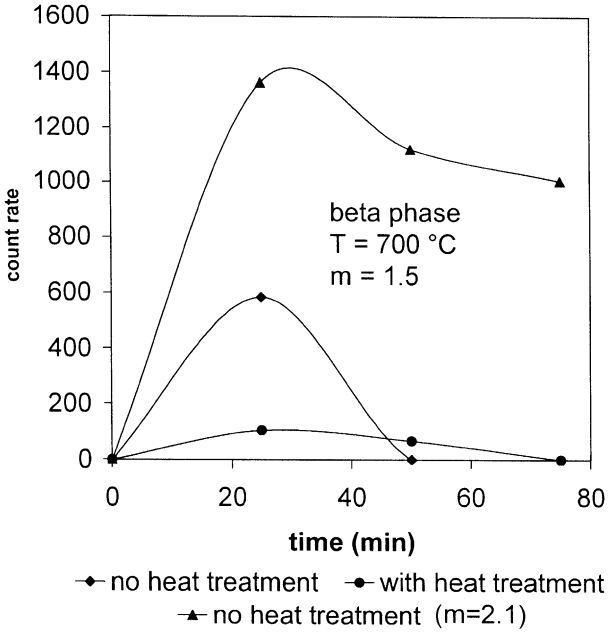

Fig. 14. Phase development of β phase for the seedless experiments at 700 °C with and without heat treatment (modulus = 1.5).

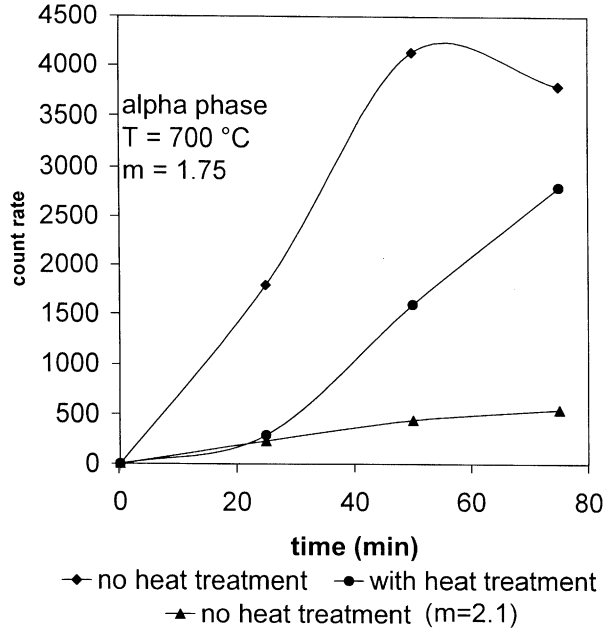

Fig. 13. Phase development of α phase for the seedless experiments at 700 °C with and without heat treatment (modulus = 1.75).

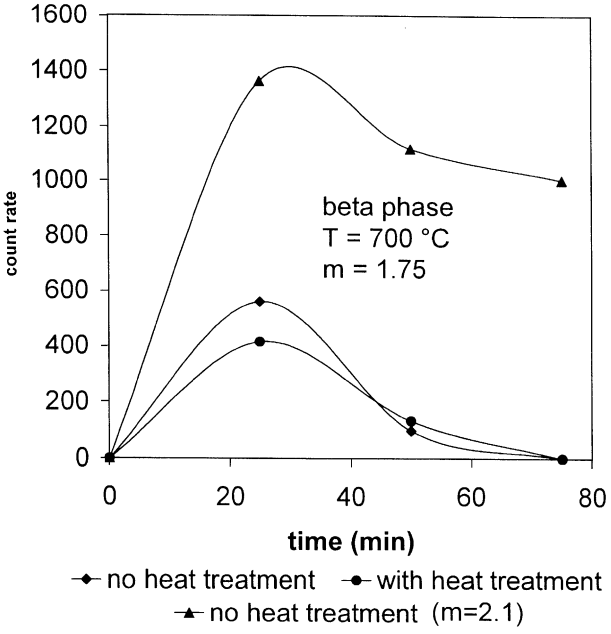

Fig. 15. Phase development of β phase for the seedless experiments at 700 °C with and without heat treatment (modulus = 1.75).

Heat treatment also results in the suppression of the β phase for both moduli employed (Figs. 14 and 15). The development of the δ phase is significantly promoted for both moduli, as seen in Figs. 16 and 17. The δ phase content after 75 min is larger for a modulus of 1.75 than modulus 1.5. This was expected, as the stoichiometry of the latter initial solution is closer to 2, the SiO_2/Na_2O molar ratio of the final disilicate.

The maxima observed for the α phase development in two of the curves shown in Figs. 12 and 13 should not be considered true extrema. The α phase is stable and its further transformation is doubtful. The "slight" maxima may be regarded as a result of measurement error considering only the (1 4 0) plane peak intensity.

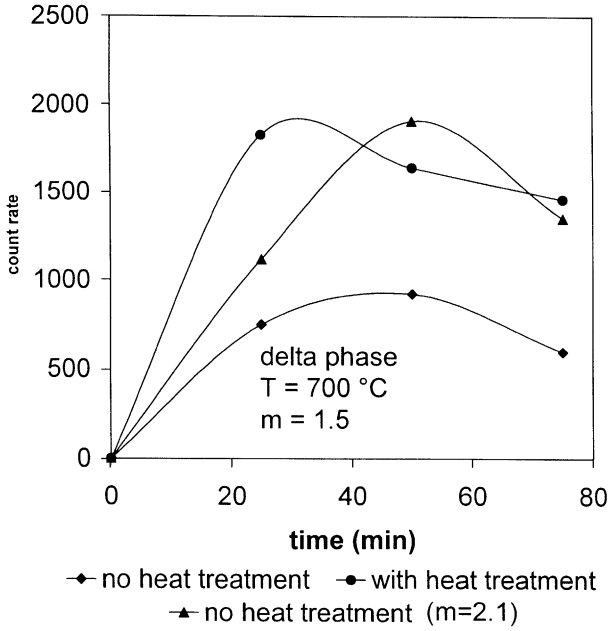

Fig. 16. Phase development of δ phase for the seedless experiments at 700 °C with and without heat treatment (modulus = 1.5).

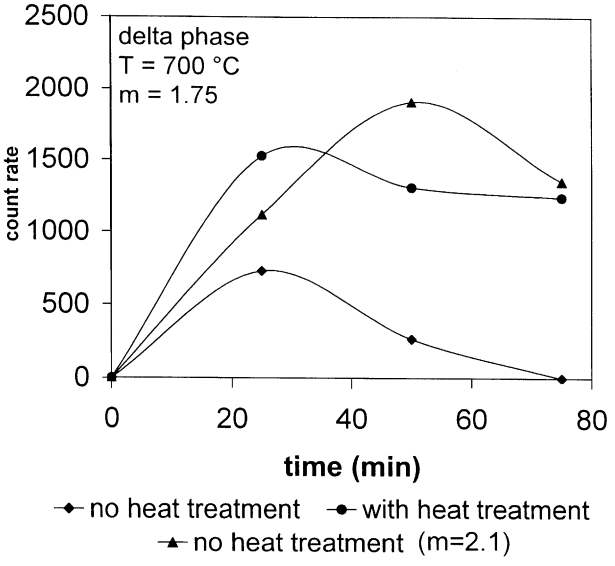

Fig. 17. Phase development of δ phase for the seedless experiments at 700 °C with and without heat treatment (modulus = 1.75).

3.5. Calcium binding capacity

The cation exchange capacity of sodium layered disilicates is due to two main processes: (a) Exchange of Ca^{++} cations of the intermediate layers and (b) dissolution of the silicate and subsequent precipitation with Ca^{++} cations. The dissolution process is a slow one, especially at room temperature. Instead, the sodium exchange is relatively fast. This is why layered sodium disilicates generally behave as finely dispersed solids of low solubility in the wash liquor. Instead, they behave as soluble builders in waste water systems and in the sewage.[2] Then, the CBC, as evaluated by the method explained in the experimental section, is mainly a property related to the ion exchange capability of the intermediate layers, i.e., the phase structure.

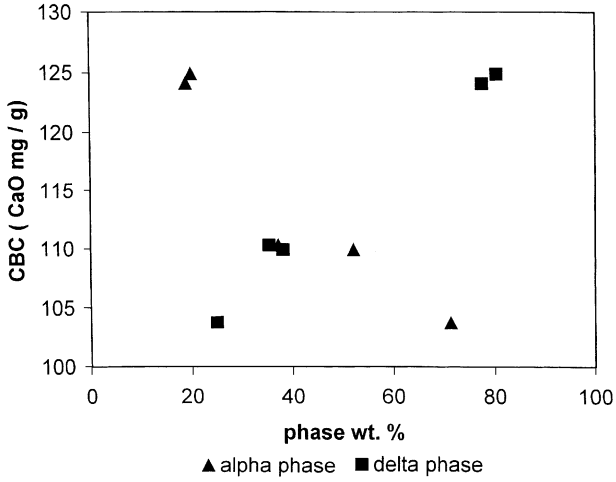

Fig. 18. CBC of the final products of the experiments performed at 700 °C, initial modulus of 1.5 and 75 min reaction time (with and without heat treatment at 150 °C).

The CBC of the final products of crystallization at 700 °C and an initial modulus of 1.5 (with and without heat treatment at 150 °C before crystallization at 700 °C) is shown in Fig. 22. These samples contained a low amount of $Na_2Si_4O_9$ crystalline phase impurity. Referring to Fig. 18, it may be concluded that the calcium binding capacity strongly depends on the relative α phase content of the samples, rather than α + β relative content. The CBC of the SKS-6 sample by the method applied in the present work was measured to be 121.0 mg CaO/g . As observed, an α phase content of up to 20 wt.% can be tolerated without having the CBC falling below 120 mg CaO/g.

4. Conclusion

The effect of seed composition on the crystalline layered sodium disilicate phase development has been studied. To obtain δ phase-rich products, it is necessary that the α phase content in the seed to be as low as possible. High temperatures (700 °C) and absence of any α phase in the initial seed substantially promote the S→δ phase transformation reaction even if the seed contains up to 15.0 wt.% β phase.

The experimental results heavily support the idea that heat pretreatment in the temperature range of 150–200 °C promotes significantly δ phase embryo nucleation. The optimum pretreatment temperature has been found to be 175 °C. This method may be used to exclude the use of δ phase rich seeds without reducing δ phase total yield. Low temperature embryo production has been observed for the sodium silicate solution modulus in the range of 1.5–2.1. This finding might be

implemented to solve reproducibility problems in the industrial scale production of layered disilcates.

The calcium binding capacity strongly depends on the relative α phase content of the samples, rather than $\alpha+\beta$ relative content.

It is speculated that non-layered crystalline phase impurities might be avoided using an initial modulus very close to 2.

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References

1. Willgallis, V. A. and Range, K. J., Zur polymorphie des $Na_2Si_2O_5$. *Glastech. Ber*., 1964, **37**, 194.
2. Wilkens, J., Structure–property relationships of sodium disilicates. *Tenside Surf. Det*., 1995, **32**(6), 476.
3. Dong, J., Jing, X. and Hong, X., Synthesis of layered sodium disilicate δ-$Na_2Si_2O_5$ with high stability in water. In *13th International Zeolite Conference, Recent Research Reports*, Groupe Francais des Zeolithes, 2001, O5-R-12.
4. Rieck, H. P., US Patent 4 585 642, 1986, pp. 1–11.
5. Holz, J., Schimmel, G., Tapper, A. and Thewes, V., US Patent 6 036 733, 2000, pp. 1–10.
6. Holz, J., Schimmel, G., Tapper, A. and Thewes, V., US Patent 6 099 595, 2000, pp. 1–11.
7. Kahlenberg, V., Wenduschuh-Josties, M., Fisher, R. X., Bauer, H., Holz, J., Schimmel, G. and Tapper, A., X-ray powder diffraction data for δ-$Na_2Si_2O_5$. *Powder Diffraction*, 2000, **15**(2), 139–141.
8. Williamson, J. and Glasser, F. P., The crystallization of $Na_2O_2SiO_2$–SiO_2 glasses. *Phys. Chem. Glasses*, 1966, **7**, 127–138.