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THERMAL ANALYSIS IN THE SYNTHESIS AND CRYSTAL FORMATION OF OXIDES

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Vapour phase treatment at elevated temperatures with an activating agent is an effective method of synthesis and purposeful modification of amorphous and fine-grained crystalline substances. In the systems amorphous silica-quartz and amorphous $Al(OH)_3$ -crystalline -Al_2O_3 different forms of bound water are of prime importance. DTA, TG, DSC, NMR ^1H, ^{29}Si, ^{27}Al, IR spectroscopy, electron- and optical microscopy methods have been used. The interaction of water molecules with the base skeleton and with hydroxide groups on the surface and in the bulk of the silica is of primary significance for modification of the silica structure. The proportion of different forms of the bound water determines the integral evaporation enthalpy of water. Various properties of silica are determined by weak bound water in the surface layer of the material. In the sequence $Al(OH)_3$ – α-Al_2O_3 the structure transformation is observed according to the following scheme: γ-$Al(OH)_3$ – γ-$AlOOH$ – α-Al_2O_3, which takes place during the vapour phase treatment with activator.

Keywords: amorphous $Al(OH)_3$ -crystalline–Al_2O_3, amorphous silica-quartz, crystal formation,

Introduction

The majority of oxides are often obtained in a form which is not favourable for practical application, for example, in amorphous state or in a form of fine-grained crystalline substances with different sizes in a form of defect crystals. In these cases it becomes necessary to use technological methods to obtain perfect crystalline substances from amorphous or defect crystalline phases. In a series of investigations heat treatment has been used for this purpose. The main aim of this report is to show the advantage of an alternative method of the synthesis and modification of fine-grained crystalline monodispersed substances and materials namely the thermosteam treatment at elevated temperatures in autoclaves. The intervals of temperatures and pressures in this method are rather soft and do not exceed the critical points of water. Water steam is an extremely active agent and affects the relaxation

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of the structure of substance in the direction of the formation of thermodynamically stable phases. To control the process it was necessary to use an activating agent for purposeful action on the structure of the initial substances. This has been gained in the following way. The samples were preliminary immersed into the activating agent solution. The activator effected the chemical bonds of the central atom with oxygen to destabilize the structure, to moderate chemical bonds in the places of maximal stress or to split the bonds. Method of thermosteam treatment in an autoclave is actually the result of two actions: the influence of water at elevated temperatures and pressures and influence of activating agent to destabilize the metal-oxygen skeleton. In this method there is a possibility to control the process of the structure ordering. In the case of amorphous silica this ordering means the increase of the volume of the silica gel globules according to the mechanism of coalescence and flocculation which accompanies the formation of the secondary supermolecular aggregates, then ordering of the structure of the floccules and formation of glassy material, then crystallization of crystobalite and finally the formation of fine-grained crystalline quartz $-SiO_2$ which is the thermodynamically stable phase. For aluminium hydroxide the following scheme has been observed: $Al(OH)_3$ – amorphous hydroxide – γ–$Al(OH)_3$ gibbsite-hydrargilite – γ-AlOOH – bohmite – α-Al_2O_3 corund. Both the fine grained quartz α-SiO_2 and corund α-Al_2O_3 are valuable materials particularly for manufacturing quartz glass, abrasives and ceramics. Silica is used in fibers for telecommunication, in lenses and other optical elements.

Synthesis and modification of silica

The investigations of the interaction of water molecules with the skeleton and with hydroxide groups on the surface and in the bulk of silica and alumina respectively are of primary significance for modification of structure of these materials.

The methods of DTA, TG, DSC, NMR ^1H, ^{29}Si, ^{27}Al, IR spectroscopy (Fourier spectroscopy including), mass-spectrometry, electron and optical microscopy have been used simultaneously to study the hydroxide covering the different forms of water in silica gel and alumina gel prepared under different conditions. The thermogravimetric studies were carried out with a Hungarian-made MOM derivatograph. The thermal effects of dehydration were measured with Rigaku 8150 instrument (Japan). DSC measurements were carried out with SETARAM 111 apparatus (France). A Bruker WP–80 pulse spectrometer with Fourier transformer was used to obtain the ^1H NMR (80.13 MHz) spectra at ambient temperature. The ^{29}Si NMR (59.63 MHz) spectra with ^{29}Si–^{1}H cross polarization, proton supression and rotation of a specimen at magic angle were obtained using a Bruker MSL–300 spectrometer.

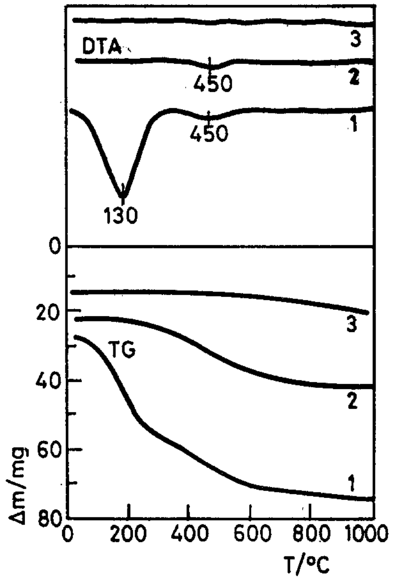

Fig. 1 DTA and TG curves of silica

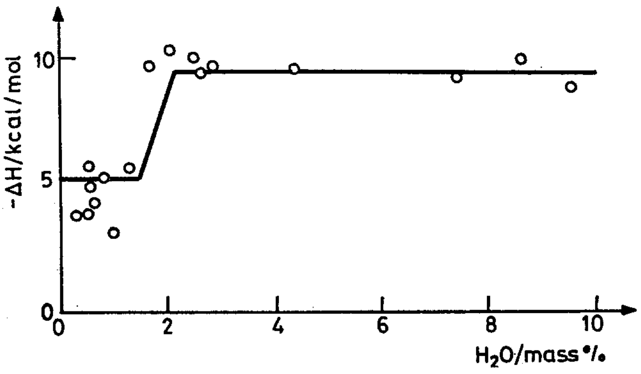

Fig. 2 Water evaporation enthalpy of silica open pores

The contents of different water forms in silica specimens were found by the DTA and thermogravimetric methods. Figure 1 shows the respective heating curves and weight loss. The initial silica specimen (curve 1) exhibits an endothermic effect at 403 K accompanies by an intensive loss of weight. At higher temperatures the weight loss is accompanied by a minor thermal effect at 723 K. The preliminary heating of the sample for 24 hours at 423 K removes water from open pores of silica (curve 2). The amount of the removed water may be found from the weight loss in the given temperature interval (TG curve 1). At higher temperatures water evaporates from the silica gel globules. The amount of the evaporated water may be found from TG curve 2 beginning from the intensive weight loss (523 K) to the point where the TG curve is practically parallel to the abscissa (1023 K). Water disappears almost completely after the sample is preliminary heated for 2 hours at 673 K (curve 3). Figure 2 represents the enthalpy of water evaporation from open pores of silica as a function of the amount of water located in open pores. For the samples containing 2.5–8 mass% of water, located in open pores i.e. on the surface of the globules, enthalpy of evaporation is about 10 kcal/mol. This value corresponds to the value of liquid water. For the samples containing less than 2 mass% of water, localized in the open pores, the evaporation enthalpy is about 5 kcal/mol. Enthalpy of evaporation for water located inside silica globules is about 4 kcal/mol. The proportion of different forms of the bonded water determines the integral evaporation enthalpy of water. Different properties of silica are determined by weakly bounded water in the surface layer of the globules. For the study of silica dehydration thermodynamics the samples were located in vacuum-tight steel ampule with a seal from nickel. Heating curves have been registered in the temperature in-

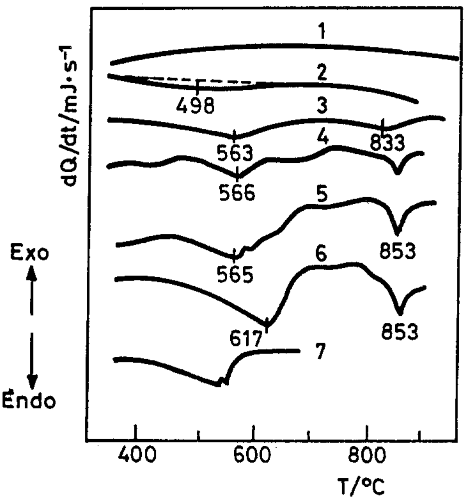

Fig. 3 DSC heating curves for the SiO_2+H_2O samples. 1) empty cell, 2) without activator, 3–6) with activator, 7) pure water

terval 300–1000 K with velocity of scanning 10 deg/min. Figure 3 presents the respective results of DSC investigations. For all samples diffused endothermic effect was observed in the interval 300–650 K which corresponded to the combined effect of dehydration of silica and evaporation of water in the volume of the ampule. For samples of silica, which are not subjected preliminary to the treatment by the solution of activating agent, only one effect was observed on the heating curve with a minimum at 498 K (curve 2). For samples subjected to treatment by solution of activator (curves 3–6) several effects were observed: endothermal dehydration of silica with a minimum at 563 K, exothermal effect in interval 700–820 K crystallization of amorphous silica, and endothermal effect of phase transition quartz at 853 K. Dehydration enthalpy depended on condition of preliminary treatment of silica samples and varied in the interval 2.2–6 kcal/mol. Enthalpy of quartz-crystobalite transformation is equal to 0.4 kcal/mol. These results confirm conclusion that integral effect of silica dehydration is determined by evaporation of different forms of water. Kinetic characteristics of water evaporation in various temperature intervals have been obtained by mass-spectroscopic method (apparatus MI–1311). Variation of flux intensity corresponding to mass number 18 has been fixed at constant temperature. Energy of the activation of water evaporation has been calculated by Arrhenius equation. Enthalpy and energy of activation of water evaporation from amorphous silica in various temperature intervals are represented in Table 1:

Table 1

Temperature interval / K	Activation energy / $kcal \cdot mol^{-1}$	Dehydration enthalpy / $kcal \cdot mol^{-1}$
423–623	10.1±0.7	8
623–673	12.0±0.4	5
723–873	25 ±0.5	1

Figure 4 presents the dependence of the adsorption line half width in the ^1H NMR spectrum on the water content on globules surface (in open pores) in the silicic acid samples heated at 383 and 423 K for different time. At these temperatures the amount of intraglobular water remains constant, while the amount of water on the globules surface decreases as a result of heating for 3 hours from 12 to 1.5 mass% at 383 K and from 12 to 0.5 mass% at 423 K. From Fig. 4 it is seen that the heating of the initial sample (1) for 3 hours results in an increase of the ^1H linewidth, $\Delta\nu$, from 370 to 2900 Hz at 383 and (2) from 370 to 3500 Hz at 423 K. Figure 5 presents IR spectroscopy inves-

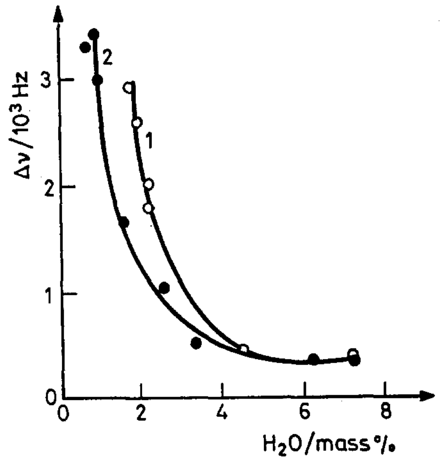

Fig. 4 Half width of ^{1}H NMR line as a function of SiO_2z surface water content

tigation of silicic acid at different temperatures. After heating at 283 and 333 K (curves 1, 2) the IR spectra exhibit intensive bands at 1640 cm^{-1}, corresponding to bending vibrations of water molecules and broad intensive bands peaking at 3450 K in the interval of stretching vibrations of hydroxide groups, thereby indicating the presence of a great amount of molecular water. The heating for 2 hours at 673 K and 1273 K (curves 3, 4) splits up the broad band in the region of the stretching vibrations of hydroxide groups into a broad band peaking at 3400 cm^{-1} and a narrow band at 3680 cm^{-1}. The

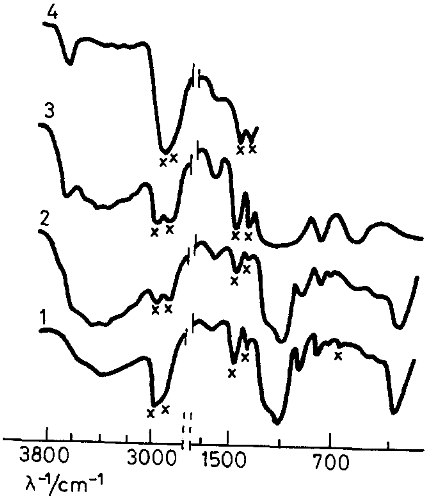

Fig. 5 IR spectra of silica heated to: 1) 383 K, 2) 423 K, 3) 673 K, 4) 1273 K

1640 cm^{-1} band does not disappear though at a much lower intensity level. After heating at 1473 K this band disappeared, only a narrow line at 3750 cm^{-1}remaining. Heating of the system silica-water at temperatures below 423 K reduced the contents of water on the surface layer of silica gel. Heating at 673 K and higher also reduces the amount of intraglobular water [1, 2].

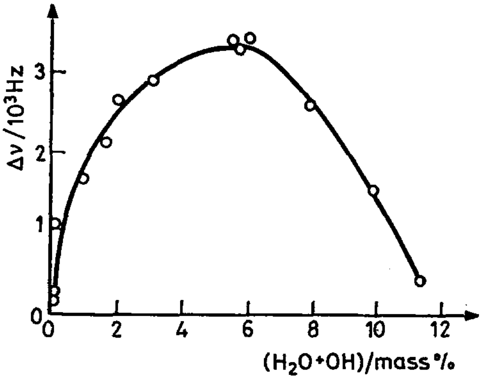

Fig. 6 Half width of ^1H NMR line as a function of the total (H_2O + OH) water content in silica

Whereas heating at temperature below 423 K reduces only the water content on silica gel surface heating at higher temperatures also reduces the amount of intraglobular water, in which case the specimens get dehydroxylated on their surfaces and in bulk. The combination of dehydrating and dehydroxylating processes defines the dependence of the absorption line half width of proton signal on the total content of H_2O and OH groups in the studies silica gel (Fig. 6). In the case of an initial specimen with water content of about 12 mass%, the ^1H NMR spectrum exhibits a relatively narrow band ($\Delta\nu \sim 370$ Hz) due to 'liquid' mobile water in the open pores of silica gel. A broad line ($\Delta\nu \sim 3000$ Hz) characterizing the less mobile intraglobular water has been observed in the specimens with water contents of 5–6.5 mass%. With further decreasing of the total contents of the OH_n groups the value of $\Delta\nu$ (^1H) gets dependent on the ratio of the concentration of intraglobular water and surface volume hydroxide groups ($\Delta\nu \sim 3000$Hz). In the presence of less than 0.5 mass% hydroxide groups the ^1H NMR spectrum exhibits only narrow line ($\Delta\nu \sim 100$–300 Hz). For example $\Delta\nu = 170$ Hz in the case of synthesized crystobalite with a 0.0035 mass% content of hydroxide groups. Figure 7 shows the ^{29}Si NMR spectra cross polarization, rotation of sample at magic angle, and proton suppression for the initial silicic acid (1), for silicic acid after hydrothermal treatment for 4 hours at 423 K (2) and (3) for silicic acid

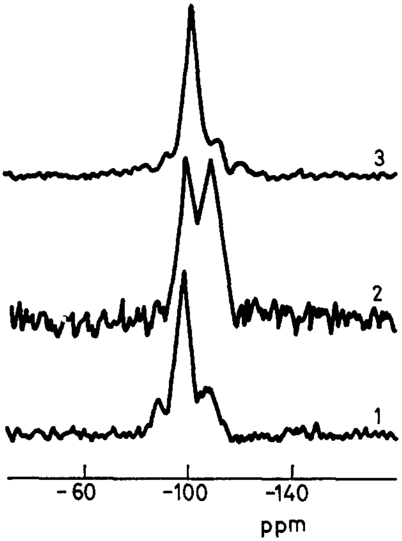

Fig. 7 ^{29}Si NMR CP MA spectra of silica

heated for 4 hours at 623 K. The lines with ^{29}Si chemical shift of −91, −100.6 and 109.2 p.p.m. relative to the signal from a tetramethyl silane are observed in the initial specimen. The three lines are respectively identified with the silicon forms Q_2 = (...Si–O)$_2$Si(OH)$_2$, Q_3 = (...Si–O)$_3$Si(OH), and Q_4 = (...Si–O)$_4$Si. The hydrothermal treatment (2) removes the line with the −91 p.p.m. chemical shift and raises the intensity of the line with the −109.2 p.p.m. chemical shift. Heating of the initial specimen at 423 K gives rise to two lines with chemical shifts of −82.0 and 120.0 p.p.m. in addition to three lines observed in the initial specimen. The occurrence of these lines may be ascribed to the forms Q_1 = (...Si–O)Si(OH)$_3$ and (...Si–O)$_3$SiOH$_2^+$ respectively [3–6].

Synthesis of crystalline alumina

The sequence of structural transformation for different initial forms of aluminium hydroxide by thermosteam treatment using activating agent has been revealed as a result of physico-chemical investigation of processes of phase formation in the system aluminium hydroxide – water at temperature 673–683 K and pressure 10–30 MPa. This can be illustrated by the following scheme:

$Al(OH)_3$ amorphous–$Al(OH)_3$ hydrargillite–AlOOH bohmite–Al_2O_3 corund

The material designed for investigation high purity Al(OH)$_3$ has been activated by water solution of KCl 3 mass% and KOH 0.05 mass%. To identify phases emerging in the process of heating and to interpret the corresponding thermal effects of transformation the heating process was simultaneously reproduced in a series of autoclave experiments identical to DSC conditions. Autoclaves were located in the heating module operating with the same heating rate (10 deg/min). The substances from autoclaves after corresponding temperature treatment have been investigated by the X-ray method. Figure 8 represents the DSC heating curve for Al(OH)$_3$ with two endothermal effects.

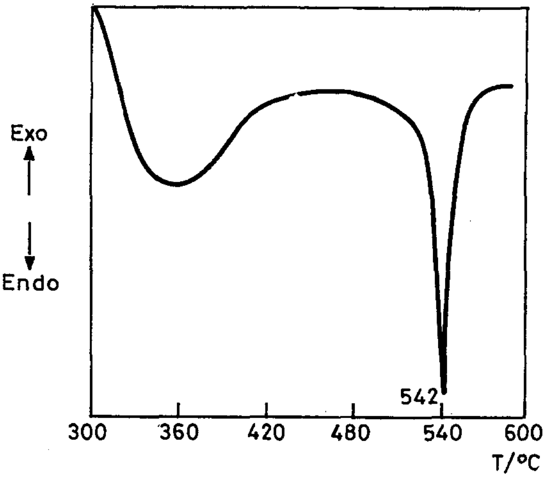

Fig. 8 DSC curve of activated -Al(OH)$_3$

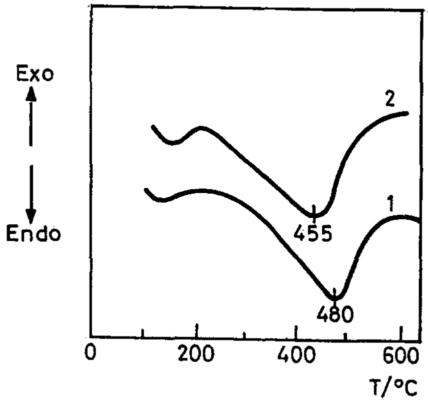

Fig. 9 DTA curves of disordered bohmite

Data of X-ray investigation of products of parallel autoclave processes carried out under identical conditions allow to interpret the endothermal effect peaking at 633 K as a thermal effect of dehydration of hydrargilite when it transforms into bohmite. The second sharp endothermal effect at 815 K corresponds to bohmite-corund transition. Hence, DSC data allowed to conclude that solid phase transition bohmite-corund takes place in an autoclave by thermosteam treatment: $2AlOOH–Al_2O_3+H_2O$. The influence of the activating agent on the character of structural transformation in the system $Al_2O_3–H_2O$ by thermosteam treatment has been investigated by DTA method. Heating DTA curves are represented in Fig. 9. In this case samples were sealed in quartz ampules with some amount of water. In both cases (without or with an activator) two endothermal effects have been observed. The first effect at 383 K corresponds to water loss from open pores of hydroxide. The second endoeffect has been interpreted on the basis of X-ray investigation as transformation of bohmite into a weakly ordered γ–oxide of aluminium. It is important to stress that for sample which has been treated by an activator the temperature of endoeffect was 753 K while for the sample subjected to the treatment of activating agent the temperature of the endoeffect was 30 K lower (723 K). DTA investigation of the same samples heated in air in the interval 293–1473 K with the heating rate 10 deg/min did not reveal any differences in the resulting curves. Hence, activator distinctly influenced the transformation process by heating hydroxide in a closed system in steam atmosphere. To investigate the mechanism of activating agent influence NMR ^{27}Al method has been used. Hydrosols $Al(OH)_3$ were obtained by neutralization of acid solution of $AlCl_3$ (pH =4.0–4.5) by 5%-solution of NH_4OH. The following samples for investigation were prepared:

1. Sol $Al(OH)_3$ pure
2. Sol with addition of 3 mass% KCl
3. Sol with addition of 0.1 mass% KOH
4. Sol with addition of 3 mass% KCl and 0.03 mass% KOH

Spectral data of NMR ^{27}Al (78.18 MHz) for samples of hydrosols aluminium hydroxide have been obtained using spectrometer Bruker MSL–300. Chemical shift has been measured respectively of signal from ion hexaaquaaluminium $Al(H_2O)_6^{3+}$ water solution $Al(NO_3)_3$. Spectral data represented in the Fig. 10. Spectra 1–3 show narrow intensive singlet corresponding to ions $Al(H_2O)_6^{3+}$ with octahedral coordination of cations Al^{3+}. The addition (spectrum 4) of mixed composition gives rise to new signal with low intensity and chemical shift in a range 62.5 p.p.m.

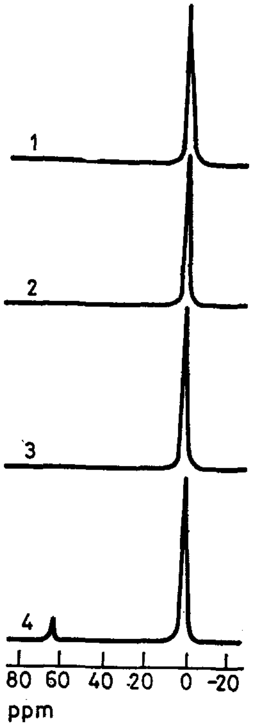

Fig. 10 NMR ^{27}Al spectra of $Al(OH)_3$ hydrosol: 1) pure, 2) KCl–3 mass%, 3) KOH–0.03 mass%, 4) KCl–3 mass% + KOH–0.03 mass%

Discussion

Hence the NMR ^{27}Al method makes it possible to fix the effect of introducing the activator. The addition of activator destabilizes the initial structure and promotes to the formation of polynucleous hydroxocomplexes $Al_{13}(OH)_{32}$ according to the scheme:

$$Al^{3+} - Al_2(OH)_2^{4+} - Al_{13}O_4(OH)_{24}^{7+} - Al_x(OH)_y^{3x-y}$$

The structure of $Al_{13}(OH)_{32}$ is characterized by mixed coordination of cations Al^{3+}. The central tetrahedron AlO_4 is surrounded by twelve octahedrons AlO_6 . Only central atom in the tetrahedron can be observed by NMR ^{27}Al (chemical shift 62.5 p.p.m.). The $Al_{13}(OH)_{32}$ complex structure has been investigated by X-ray method. There are six member rings $Al_6(OH)_{12}(H_2O_6)^{6+}$ motive similar to aluminium hydroxide: octahedral vacancies are occupied by ions Al^{III} in the plane (001). Hence, it is possible to suppose that formation of polynucleus aluminium hydrocomplexes in the presence of activator reduces the activation energy of phase transition by thermosteam treatment. Only in case of mixed activating agent (KCl + KOH) the additional signal of NMR ^{27}Al may be detected. It shows that effective nucleofile attack of aquacomplexes Al^{3+} by Cl^{-} ions is favourable in the presence of OH^{-} ions. Partial substitution in aquacomplexes of molecules of water by OH^{-} ions takes place by the following scheme:

$$\mathrm{Al(OH)}^{3+}_{26} + \mathrm{OH}^{-} = \mathrm{Al(OH)(OH_2)}^{2+}_{5} + \mathrm{H_2O}$$

$$\mathrm{Al(OH)(OH_2)}^{2+}_{5} + \mathrm{OH}^{-} = \mathrm{Al(OH)(OH_2)}^{+}_{4} + \mathrm{H_2O}$$

This substitution together with formation of heaxaaquahydroxyl ions accompanied by destruction of quasimonomeric octahedrons probably promotes the transport of chloride ions. The substitution plays an important role in the 6 → 4 transition.

Thus, thermosteam treatment at elevated temperatures with a properly selected activating agent is an effective method of synthesis and purposeful modification of fine-grained, monodispersed perfect crystalline materials.

References

1 G. P. Panasyuk, G. P. Budova and V. B. Lazarev,J. Thermal Anal., 16 (1979) 441.
2 V. B. Lazarev, G. P. Panasyuk, G. P. Budova and J. A. Kesler, Thermochim. Acta, 52 (1982) 41.
3 G. E. Maciel and D. W.Sindorf, J. Amer. Chem. Soc., 102 (1980) 7606.
4 D. W. Sindorf and G. E. Maciel, J. Phys. Chem., 86 (1982) 5208.
5 A. J. Vega and G. W. Scherer, J. Non-Cryst. Solids, 11 (1989) 153.
6 R. H. Glaser, G. I. Wilkes and C. E. Bronnimann, J. Non-Cryst. Solids, 113 (1989) 73.

Zusammenfassung — Eine Dampfphasenbehandlung bei höheren Temperaturen mit einem Aktivierungsmittel ist eine effektive Methode zur Synthese und zielgerichteten Modifizierung von amorphen und feinkörnigen kristallinen Substanzen. In den Systemen amorphes Siliziumdioxid–Quarz sowie amorphes Al(OH)$_3$–kristallines–Al$_2$O$_3$ hat verschiedenartig gebundenes Wasser eine primäre Bedeutung. Bei den Untersuchungen kamen DTA, TG, DSC, ^{1}H-, ^{29}Si-, ^{27}Al-NMR, IR-Spektroskopie sowie Elektronen- und optische Mikroskopie zur Anwendung. Die Wechselwirkung von Wassermolekülen mit dem Grundgerüst und mit Hydroxidgruppen an der Oberfläche und im Innern von Silika ist für die Modifizierung der Silikastruktur von primärer Bedeutung. Der Anteil der verschiedenartig gebundenen Wasserformen bestimmt die vollständige Verdampfungsenthalpie des Wassers. Die verschiedenen Eigenschaften von Silika werden durch schwach gebundenes Wasser in der Oberflächenschicht der Substanz bestimmt. Die Umwandlung Al(OH)$_3$ – α-Al$_2$O$_3$ durchläuft folgendes Schema: γ-Al(OH)$_3$ – γ-AlOOH – α-Al$_2$O$_3$, nach dem der Vorgang bei der Gasphasenbehandlung mit Aktivator abläuft.