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THERMAL STUDIES ON SODIUM SILICATE HYDRATES. I. TRISODIUM HYDROGENSILICATE PENTAHYDRATE, $Na_3HSiO_4 \cdot 5\ H_2O$; THERMAL STABILITY AND THERMAL DECOMPOSITION REACTIONS

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ABSTRACT

Presented in this paper is a thermoanalytical study on $Na_3HSiO_4 \cdot 5\ H_2O$ under a dry, inert nitrogen atmosphere, demonstrating the following thermal decomposition reactions and thermodynamically stable hydrate phases

$$Na_3HSiO_4 \cdot 5\ H_2O \xrightarrow[313\ K]{-3\ H_2O} Na_3HSiO_4 \cdot 2\ H_2O \xrightarrow[353-263\ K]{-H_2O} Na_3HSiO_4 \cdot H_2O \xrightarrow[413\ K]{-H_2O} Na_3HSiO_4$$

$$2\ Na_3HSiO_4 \xrightarrow[513\ K]{-H_2O} Na_6Si_2O_7$$

This reaction behaviour was reproducibly observed by means of simultaneous thermal analysis (TG, DTG, DTA), differential scanning calorimetry (DSC) and X-ray heating experiments. Annealing of $Na_3HSiO_4 \cdot 5\ H_2O$ at the above stability ranges yielded the subsequent hydrate phases as well as the dry silicate. The decomposition products were characterized by X-ray diffraction methods.

INTRODUCTION

Thermal analysis, thermogravimetry (TG), differential thermogravimetry (DTG), differential thermal analysis (DTA), differential scanning calorimetry (DSC) and X-ray diffraction heating experiments are important methods in solid state chemistry for revealing the reaction paths of crystalline inorganic compounds, especially those of hydrate phases and their decomposition reactions. Above all, it is the X-ray heating powder diffraction technique in correlation with TG, DTG and DTA experiments which provide strong and important clues pertaining to peritectic thermal decomposition reactions, in this case demonstrated using $Na_3HSiO_4 \cdot 5\ H_2O$, the phase which will be discussed in this paper.

The system Na_2O–SiO_2–H_2O has been revised repeatedly. However, data

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on the existence of hydrate phases in this system are insufficient and partly contradictory, especially for the phases of the 3 : 2 series ($Na_2O : SiO_2$ ratio), $Na_3HSiO_4 \cdot n\ H_2O$ ($n = 5, 2, 1$ or 0) [1,2]. No thermoanalytical data pertaining to this series have been published so far, whereas structural information has been given by Smolin et al. [3] for $Na_3HSiO_4 \cdot 5\ H_2O$ and by Schmid et al. [4,5] for α- and β-$Na_3HSiO_4 \cdot 2\ H_2O$.

Nevertheless, the first and so far the only thermoanalytical data on the system Na_2O–SiO_2–H_2O are those given by Gould et al. [6] upon the melting behaviour and thermodynamics of the 1 : 1 hydrate series ($Na_2O : SiO_2$ ratio), $Na_2H_2SiO_4 \cdot n\ H_2O$ ($n = 8$, 7, 5 or 4). In that paper the authors reported on DSC experiments carried out on these phases.

It is an astonishing fact that contrary to the scarcity of thermal data on the system Na_2O–SiO_2–H_2O, there exists a great deal of structural information not only upon the hydrates of the 3 : 2 series but also upon 1 : 1 series [7–10], $Na_2H_2SiO_4 \cdot n\ H_2O$ ($n = 8,7,5$ or 4).

So, to overcome this serious lack of information about the thermal and chemical properties of this interesting and technically important system, Na_2O–SiO_2–H_2O, and to correlate the data obtained with structural facts, especially hydrogen bonding, we carried out further investigations on this system. Beginning with $Na_3HSiO_4 \cdot 5\ H_2O$, the highest hydrate member of the 3 : 2 series, which should also give an insight into an understanding of the whole series, we will, in a future series of papers, describe and discuss the thermal and structural properties of all hydrate phases observed in the system Na_2O–SiO_2–H_2O.

EXPERIMENTAL

$Na_3HSiO_4 \cdot 5\ H_2O$ was prepared by isothermal crystal growth at 298 K from aqueous solutions containing 13.3% Na_2O, 4.4% SiO_2 and 82.3% H_2O (wt.%). Starting materials were NaOH, H_2O and Na_2SiO_3. As the compound is very hygroscopic and sensitive to CO_2, all our research and preparative work had to be carried out under exclusion of H_2O and CO_2 in a dry and inert atmosphere. The inert gas used was Ar in a specially designed Braun MB 80 glove-box.

Thermoanalytical experiments were carried out on a Netzsch STA 429 thermoanalyzer (TG, DTA, DTG) and on a Perkin–Elmer DSC-2 calorimeter (DSC). For the accompanying X-ray experiments a Guinier heating camera suitable for measurements in the temperature range 298–1098 K ($\lambda = CuK_{\alpha 1}$) and a Guinier camera (System 621, Huber, Rimsting, $\lambda = CuK_{\alpha 1}$) were used. $Na_3HSiO_4 \cdot 5\ H_2O$ was not ground for the thermoanalytical studies referred to in this paper as it is partly affected by tribochemical decomposition. For this reason it was analyzed in single crystalline form.

RESULTS AND DISCUSSION

The results of the simultaneous TG, DTG and DTA thermal decomposition reactions of $Na_3HSiO_4 \cdot 5\ H_2O$, as well as the corresponding X-ray heating experiments, are shown in Figs. 1 and 2, respectively. Both figures indicate the same reaction scheme for $Na_3HSiO_4 \cdot 5\ H_2O$ down to $Na_6Si_2O_7$

$$Na_3HSiO_4 \cdot 5\ H_2O \xrightarrow[313\ K]{-3H_2O} Na_3HSiO_4 \cdot 2\ H_2O \xrightarrow[353\text{–}263\ K]{-H_2O} Na_3HSiO_4 \cdot H_2O$$

$$\xrightarrow[413\ K]{-H_2O} Na_3HSiO_4\ 2\ Na_3HSiO_4 \xrightarrow[513\ K]{-H_2O} Na_6Si_2O_7$$

All of these decomposition products could be subsequently synthesized and characterized by X-ray and TG, DTG and DTA experiments.

As can be seen in Fig. 1, $Na_3HSiO_4 \cdot 2\ H_2O$ does not show up clearly in the course of the decomposition reaction, as $Na_3HSiO_4 \cdot H_2O$ forms nearly simultaneously on the thermogram on Fig. 1, whereas on the X-ray heating photograph in Fig. 2, the dihydrate shows up more clearly. This depends on

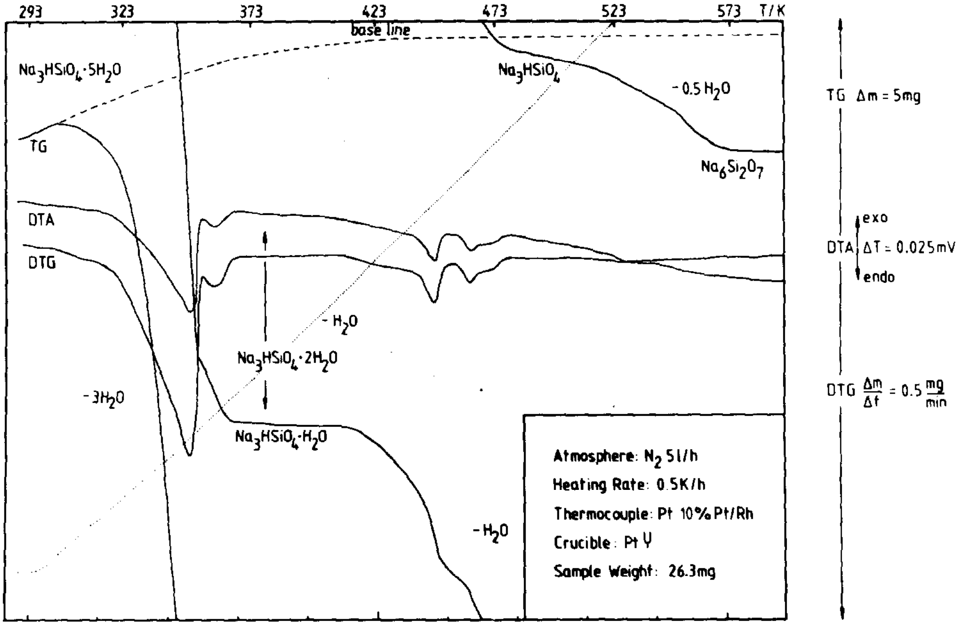

Fig. 1. Thermogram of the thermal decomposition reaction of $Na_3HSiO_4 \cdot 5\ H_2O$ under non-isothermal conditions. Decomposition is of single crystals to avoid tribochemical destruction of $Na_3HSiO_4 \cdot 5\ H_2O$. The figure shows the step-wise dehydratation scheme to three subsequent and thermodynamically stable hydrate phases and one dry silicate, $Na_6Si_2O_7$, and their ranges of stability. Due to diffusion kinetics and the dimorphism of $Na_3HSiO_4 \cdot 2\ H_2O$, this phase does not show up fully but is clearly indicated by the DTA and DTG curves and partially by the TG curve. The dotted line represents the T curve.

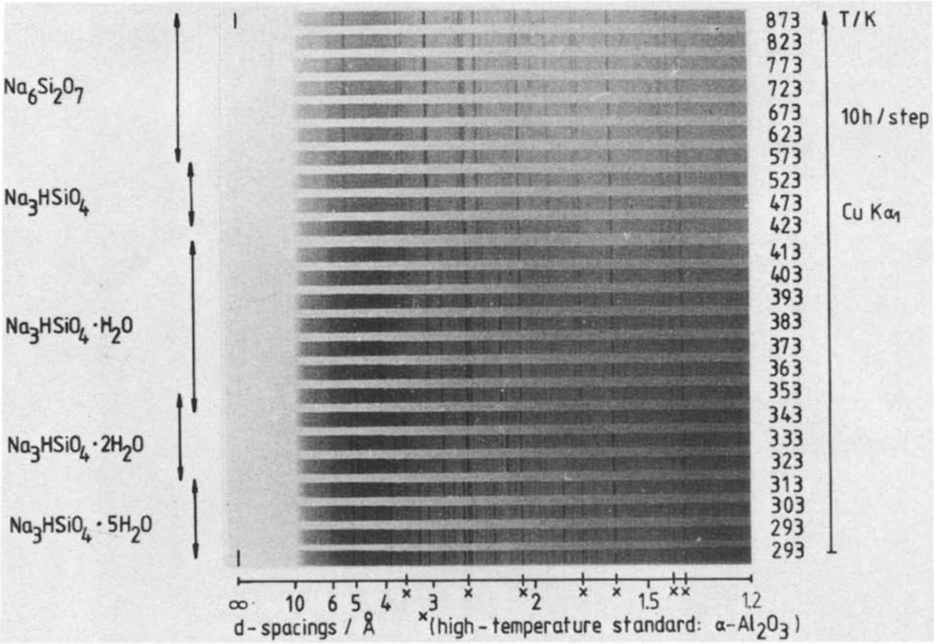

Fig. 2. Step-wise X-ray heating photograph of the thermal decomposition reaction of $Na_3HSiO_4 \cdot 5\ H_2O$ between 293 and 873 K, showing the diffraction patterns of the educt, $Na_3HSiO_4 \cdot 5\ H_2O$, and those of four subsequent dehydration products, their regions of stability and of transition. Due to a serious reduction of crystallite size in the course of the decomposition down to the dry silicate, the X-ray diffraction patterns of Na_3HSiO_4 and $Na_6Si_2O_7$ are diffuse and do not show up clearly on the photograph.

the particle size, since the $Na_3HSiO_4 \cdot 2\ H_2O$ step shows up at low heating rates and when $Na_3HSiO_4 \cdot 5\ H_2O$ is thoroughly ground, and also on the dimorphism of $Na_3HSiO_4 \cdot 2\ H_2O$. So, in Fig. 1, only a small alteration in the TG curve, as well as faint DTG and DTA peaks, indicate the existence of $Na_3HSiO_4 \cdot 2\ H_2O$ and its decomposition down to $Na_3HSiO_4 \cdot H_2O$, which has a very large range of stability. However, in the course of the X-ray heating experiment the strongest reflection of both dimorphic forms of $Na_3HSiO_4 \cdot 2\ H_2O$ is observed. $Na_3HSiO_4 \cdot 2\ H_2O$ can be easily held in the high temperature form, α-$Na_3HSiO_4 \cdot 2\ H_2O$, which is stable up to 383 K, by annealing the pentahydrate at 313 K for 24 h. This particular behaviour of $Na_3HSiO_4 \cdot 2\ H_2O$ will be published separately.

Unfortunately, there is no clear evidence, either from the X-ray structural data for $Na_3HSiO_4 \cdot 5\ H_2O$ given by Smolin et al. [3] or from the thermoanalytical data discussed in this paper, for any possibility of correlation between the thermal behaviour of $Na_3HSiO_4 \cdot 5\ H_2O$ and its crystal structure. Taking into account the structural data, there exist no striking peculiarities in the hydrogen bonding and H_2O coordination, i.e., bond lengths, angles and unusual coordination polyhedra, which could give rise to the special decomposition behaviour with a loss of three molecules of H_2O, yielding $Na_3HSiO_4 \cdot 2\ H_2O$. However, these structural data are taken from X-ray data which contain naturally incorrect H-atom positions. A fresh determination of the crystal structure of $Na_3HSiO_4 \cdot 5\ H_2O$ by means of neutron diffraction might solve this problem.

Contrary to $Na_3HSiO_4 \cdot 2\ H_2O$, which shows very diffuse formation and decomposition behaviour between 353 and 363 K in Fig. 1, the subsequently formed $Na_3HSiO_4 \cdot H_2O$ shows a wide range of stability and a narrow decomposition range of about 413 K. Considering that the monohydrate is stable up to about 413 K, a very strong and rigid hydrogen bonding scheme can be expected. Unfortunately, structural data for $Na_3HSiO_4 \cdot H_2O$ are missing, as well as suitable crystal X-ray structure analysis. At about 413 K, $Na_3HSiO_4 \cdot H_2O$ decomposes, yielding Na_3HSiO_4, which is stable up to 513 K and whose crystal structure is also unknown. As Figs. 1 and 2 indicate, the final decomposition step is the condensation reaction of two $[HSiO_4]^{3-}$ anions, of which all 3:2 hydrates are constructed, to form the so-called pyrosilicate anion, $[Si_2O_7]^{6-}$. This is expected for most hydroxylic decompositions, because breaking a chemical bond, in this case a Si–OH bond, affords more energy than breaking a hydrogen bond and removing a water molecule from the solid phase into the atmosphere by means of a diffusion process. Furthermore, the decomposition of Na_3HSiO_4 is endothermic (see the DTA curve in Fig. 1), so that the gain in energy by the formation of a Si–O bond in the course of the condensation reaction, yielding an oxygen-bridged $[Si_2O_7]^{6-}$ anion, must be lower than the energy which is needed to destroy the hydrogensilicate anion. In other words, the so formed pyrosilicate anion is very unstable, as it decomposes at about 1300 K to give the SiO_3^{2-} endless chain of sodium metasilicate, Na_2SiO_3, a fact that has already been pointed out by Schmid [11]. Unfortunately, the endothermic nature of the $[HSiO_4]^{3-}$ condensation peak shows up only very faintly on the DTA curve in Fig. 1, being affected by the low heating rate of 0.5 K min^{-1}, but is clearly visible at higher rates, which would make $Na_3HSiO_4 \cdot 2\ H_2O$ nearly undetectable by thermogravimetry and under the experimental conditions.

As can be seen in Fig. 1, the decomposition reaction of $Na_3HSiO_4 \cdot H_2O$ down to Na_3HSiO_4 shows an additional step and additional DTA and DTG peaks. This feature could not be reproduced by test runs. The reason for taking this diagram, as represented in Fig. 1, was the clarity with which $Na_3HSiO_4 \cdot 2\ H_2O$ showed up.

As pointed out in the preceding paragraphs, no values pertaining to hydrogen bonding and water geometry in the crystal structure of $Na_3HSiO_4 \cdot 5\ H_2O$ could explain a loss of three molecules of H_2O yielding $Na_3HSiO_4 \cdot 2\ H_2O$. Particle size and the dimorphism of $Na_3HSiO_4 \cdot 2\ H_2O$ may explain its diffuse appearance in Figs. 1 and 2. However, the best model, which explains the competing formation of both α- and β-$Na_3HSiO_4 \cdot 2\ H_2O$ as well as that of $Na_3HSiO_4 \cdot H_2O$ at slightly elevated temperatures, is the complete breakdown of the crystal structure of $Na_3HSiO_4 \cdot 5\ H_2O$ which takes place in the solid state. $Na_3HSiO_4 \cdot 5\ H_2O$ is built up of dimeric units of $[HSiO_4]^{3-}$ anions which are hydrogen bonded, whereas both forms of $Na_3HSiO_4 \cdot 2\ H_2O$ are built up of linear, endless chains of hydrogen bonded $[HSiO_4]^{3-}$ tetrahedra. This linear arrangement of the $[HSiO_4]^{3-}$ anions is also expected for $Na_3HSiO_4 \cdot H_2O$ and Na_3HSiO_4 which was shown by Cooksley and Taylor [12] for $CaNaHSiO_4$. Nevertheless, all these arguments discussed are only models which might explain some details. However, without more accurate structural information pertaining to hydrogen bonding in $Na_3HSiO_4 \cdot 5\ H_2O$ as well as structural information on $Na_3HSiO_4 \cdot H_2O$ and Na_3HSiO_4, these models cannot be confirmed.

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