THERMAL STUDIES ON SODIUM SILICATE HYDRATES. III. TRISODIUM HYDROGENSILICATE DIHYDRATE, $Na_3HSiO_4 \cdot 2 H_2O$: THERMAL STABILITY, THERMAL DECOMPOSITION REACTIONS AND DIMORPHISM

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ABSTRACT

$Na_3HSiO_4 \cdot 2 H_2O$ is dimorphic, the reversible transition point being found to be at 275 K with a very low heat of transition, $\Delta H_t = 0.52$ kJ mol^{-1}. Both phases of $Na_3HSiO_4 \cdot 2 H_2O$, the low-temperature or β-phase and the high-temperature or α-phase were successfully isolated and characterized by thermal and X-ray single crystal structure analysis. Both crystal structures being closely related and built of chains of $[HSiO_4]^{3-}$ tetrahedra linked by Si–O–H $\cdots$ O–Si– hydrogen bonds. Significant differences, however, appear in the H_2O-surroundings, therefore giving rise to characteristic differences in their thermal behaviour.

INTRODUCTION

The system Na_2O–SiO_2–H_2O which is of great scientific and technological interest has been revised repeatedly. However, data pertaining to phases and their thermal behaviour are insufficient so far and partly contradictory [1,2], especially in the series of the 3:2-sodium silicate hydrates ($Na_2O:SiO_2$ ratio), $Na_3HSiO_4 \cdot n\ H_2O$ ($n = 5, 2, 1, 0$). On the other hand, some thermal information exists pertaining to the crystalline hydrate phases in the series of the 1:1-sodium silicate hydrates, $Na_2H_2SiO_4 \cdot n\ H_2O$, $n = 8, 7, 5, 4$ [3]. Gould et al. [3] give a lot of information on the melting behaviour (melting points and thermodynamics) of these phases.

Although thermoanalytical data including thermogravimetry (TG), differential thermogravimetry (DTG), difference thermal analysis (DTA) and differential scanning calorimetry (DSC) correlated with single crystal structure analysis, i.e., by means of X-ray and, eventually, neutron diffraction, are the key to a correct understanding of the physico-chemical properties of hydrate phases, thermal data are scarce with respect to sodium silicate hydrates. This is astonishing, especially as a lot of information is available on the crystal structures of these hydrate phases for $Na_3HSiO_4 \cdot 5 H_2O$ [4], α- and β-$Na_3HSiO_4 \cdot 2 H_2O$ [5,6], $Na_2H_2SiO_4 \cdot n\ H_2O$ ($n = 8, 7, 5$) [7,8,9]

and $Na_2H_2SiO_4 \cdot 4\ H_2O$ [10]. To overcome this serious lack of information pertaining to the correlation between structure and reactivity was an additional aspect of our revision work on hydrate phases in this special system $Na_2O-SiO_2-H_2O$.

Hence, in a general approach to clarify the contradictions still existing in the system $Na_2O-SiO_2-H_2O$ we decided to revise the system with modern methods, e.g., DSC, TG and X-ray structure analysis including the synthesis and isolation of the possible phases. These phases were to be synthesized in the form of single crystals as only good and pure crystals allow proper and unambiguous examination of the material and a corresponding interpretation and discussion of the results.

In this paper the dimorphism of $Na_3HSiO_4 \cdot 2\ H_2O$, the reversible $\alpha \leftrightarrow \beta$ phase transition and the reactivity and thermal behaviour of both polymorphic forms of $Na_3HSiO_4 \cdot 2\ H_2O$ are reported and discussed with the aid of structural data.

EXPERIMENTAL

Single crystals of both polymorphic forms of $Na_3HSiO_4 \cdot 2\ H_2O$ were obtained from aqueous solutions containing 10–17% Na_2O, 2–4% SiO_2 and 79–88% H_2O (wt%) at 298 K (β-$Na_3HSiO_4 \cdot 2\ H_2O$) and at 300–302 K (α-$Na_3HSiO_4 \cdot 2\ H_2O$). Well-shaped single crystals were synthesized under closed system conditions (H_2O content at about 79%) and under open system conditions from solutions higher in H_2O content, when H_2O was allowed to evaporate. Both polymorphic forms were found to transform into each other reversibly at 299 K in the mother solutions.

As $Na_3HSiO_4 \cdot 2\ H_2O$ is extremely hygroscopic and sensitive to CO_2, it had to be handled and synthesized in a Braun MB 80 glove-box under a dry and CO_2-free atmosphere. The open-system crystal growth was also carried out in the glove-box as it allowed continuous drying and cleaning of the atmosphere.

The thermoanalytical measurements were carried out on a Netzsch STA 429 thermoanalyzer (TG, DTG, DTA) and on a Perkin-Elmer DSC-2 (DSC).

For the X-ray powder diffraction experiments a Guinier-Lenne heating camera adapted for closed system measurements (vacuum as well as inert gas atmosphere) suitable for heating and cooling (Enraf-Nonius, Delft, $\lambda = Cu\,K_\alpha$) was used. High resolution powder measurements were carried out using a Guinier camera (System 621, Huber, Rimsting, $\lambda = Cu\,K_{\alpha_1}$).

RESULTS AND DISCUSSION

The results of the simultaneous TG, DTG and DTA thermal decomposition experiments are shown in Fig. 1a for α-$Na_3HSiO_4 \cdot 2\ H_2O$ and b for

β-Na$_3$HSiO$_4 \cdot$ 2 H$_2$O. Figure 2 shows the reversible and first order $\alpha \leftrightarrow \beta$ phase transition of Na$_3$HSiO$_4 \cdot$ 2 H$_2$O. In that context it is worth while mentioning that Na$_3$HSiO$_4 \cdot$ 2 H$_2$O undergoes an additional phase transition at 215 K which is not yet fully understood, but may be an order–disorder phenomenon within the compounds hydrogen-bonding system. Nevertheless, that phase transition will not be discussed within this paper as it is still a subject of present research work.
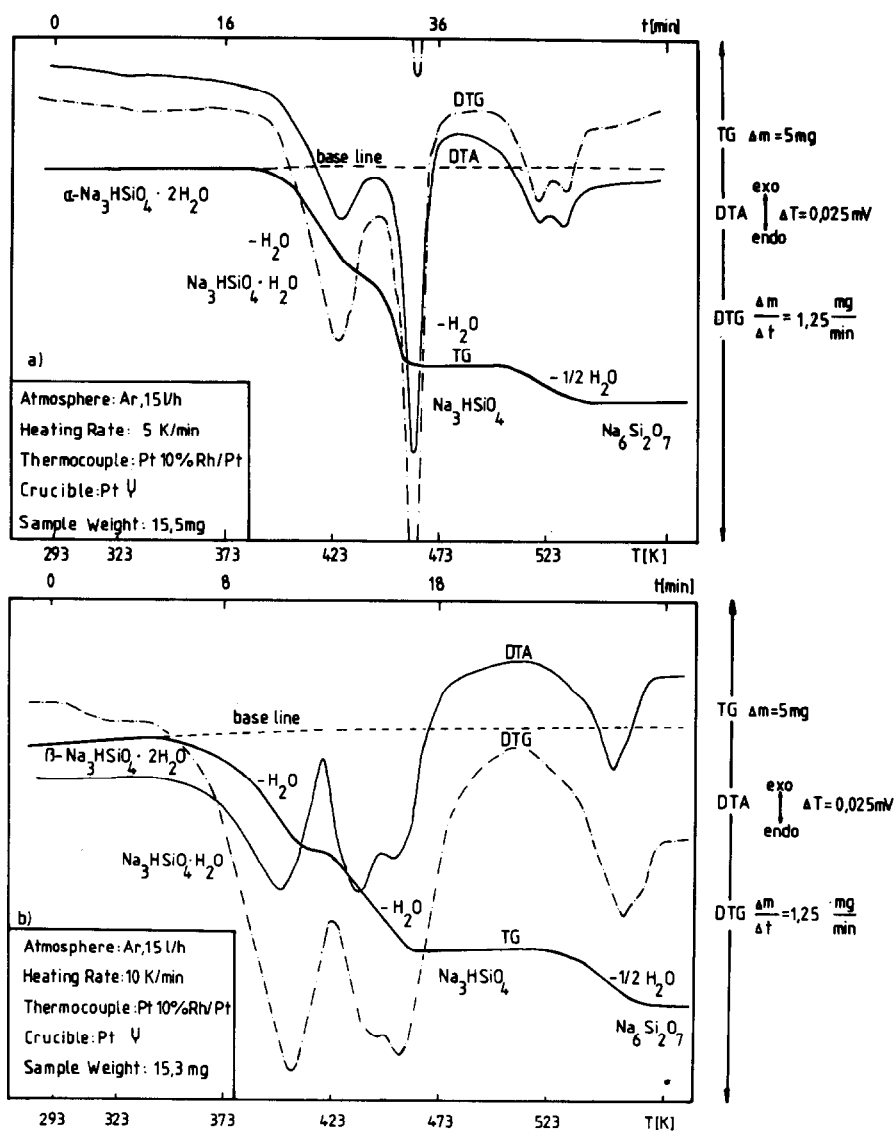

Fig. 1. TG, DTG and DTA curves for α- and β-Na$_3$HSiO$_4 \cdot$2 H$_2$O between 293 and 573 K, showing the identical decomposition steps of both phases and their significantly different thermostability. (a) Thermogram of α-Na$_3$HSiO$_4 \cdot$2 H$_2$O which is stable up to 388 K; (b) thermogram of β-Na$_3$HSiO$_4 \cdot$2 H$_2$O which is stable up to 333 K.

As indicated by Fig. 1a and b, both forms of $Na_3HSiO_4 \cdot 2\,H_2O$ differ significantly in their thermal behaviour, especially their thermal stability. β-$Na_3HSiO_4 \cdot 2\,H_2O$ is stable up to 333 K whereas α-$Na_3HSiO_4 \cdot 2\,H_2O$ is stable up to about 388 K. Nevertheless, initially, it appears to be contradictory that a compound that transforms at 275 K under non-equilibrium conditions and at about 299 K under equilibrium conditions in the mother solution should be stable up to 333 K, again under non-equilibrium conditions and in dry air! However, that can easily be explained. Both thermograms, either that of β-$Na_3HSiO_4 \cdot 2\,H_2O$ or that of the α-form, have been made with single crystals of both phases and not with ground material to avoid tribochemical effects. Taking into account both this and the fact that the β-phase transforms readily and completely into the α-form when it is ground, i.e., under a tribochemical influence, it is better to state that β-$Na_3HSiO_4 \cdot 2\,H_2O$ is metastable up to 333 K, a temperature at which it decomposes reproducibly. This mechanically-induced phase transformation could be proved X-ray powder diffraction. Grinding β-$Na_3HSiO_4 \cdot 2\,H_2O$ causes a diffuse thermal decomposition behaviour between that of crystalline α- and β-$Na_3HSiO_4 \cdot 2\,H_2O$, whereas grinding α-crystals does not affect the thermal properties of that form, i.e, its stability up to 388 K. However, it must be noted that besides the significance in the thermal stabilities of both
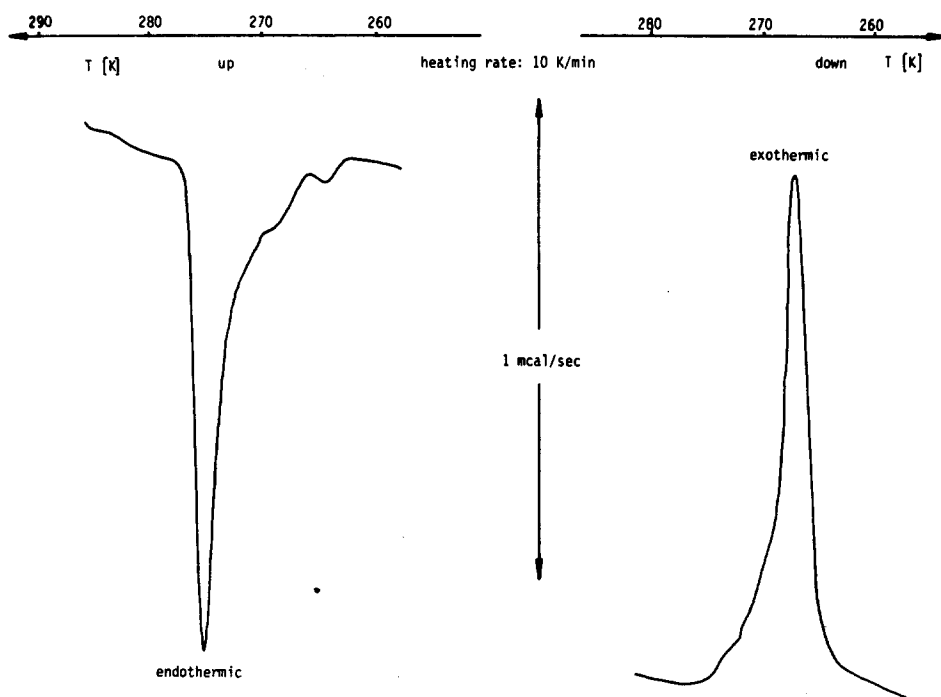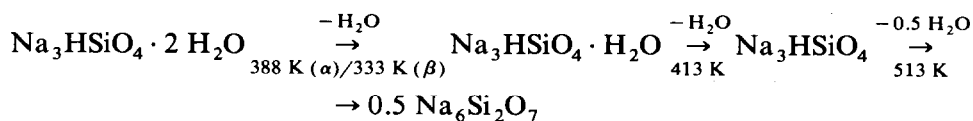

Fig. 2. DSC-curves of the reversible and first order $\alpha \leftrightarrow \beta$ phase transition up and down of $Na_3HSiO_4 \cdot 2\,H_2O$.

forms they show the same decomposition scheme down to $Na_6Si_2O_7$, the dry 3 : 2-sodium silicate:

$$Na_3HSiO_4 \cdot 2\,H_2O \underset{388\,K\,(\alpha)/333\,K\,(\beta)}{\overset{-H_2O}{\rightarrow}} Na_3HSiO_4 \cdot H_2O \underset{413\,K}{\overset{-H_2O}{\rightarrow}} Na_3HSiO_4 \underset{513\,K}{\overset{-0.5\,H_2O}{\rightarrow}}$$

$$\rightarrow 0.5\,Na_6Si_2O_7$$

On the other hand, the differences between the thermal stabilities of both polymorphic forms do not only depend on the kinetics of metastability, as might be derived from the arguments discussed within the preceding paragraph, because the β-phase decomposition point of 333 K is too fixed and does not depend on sample weights, heating rates, etc. These differences rather depend on drastic structural differences, especially in the H_2O-coordination polyhedra, and the hydrogen bonding system.

In general, both crystal structures are similar. Both are constructed of linear chains of $[HSiO_4]^{3-}$ tetrahedra which are linked by Si–O–H $\cdots$ O–Si hydrogen bonds. However, the lengths of the hydrogen bonds between two tetrahedra are 2.917 Å in the case of the β-phase and 2.693 Å in that of the α-form as shown in Fig. 3, and which is, therefore, stronger and more stable.
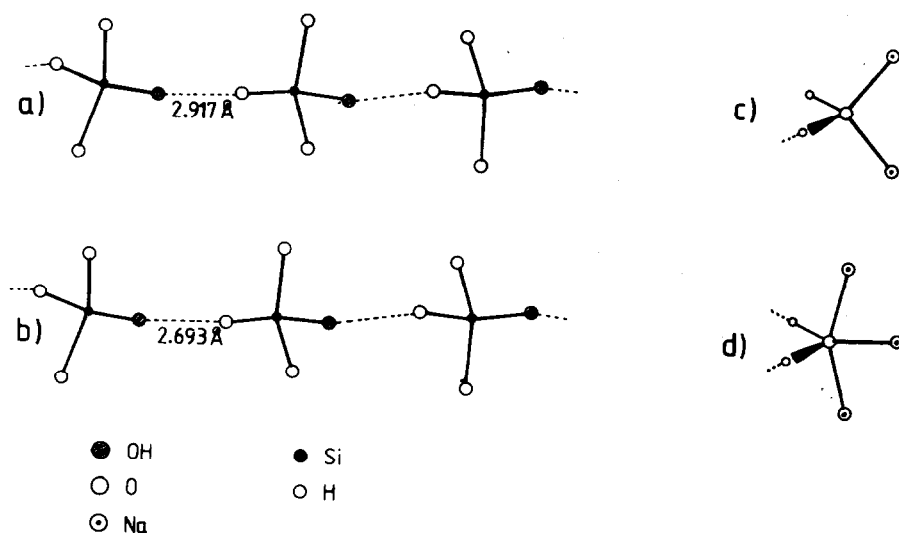

Fig. 3. Characteristic structural features in α- and β-$Na_3HSiO_4 \cdot 2\,H_2O$. Chains of $[HSiO_4]^{3-}$ tetrahedra and H_2O–Na coordination polyhedra. (a) The linear chain of hydrogen bonded $[HSiO_4]^{3-}$ tetrahedra in β-$Na_3HSiO_4 \cdot 2\,H_2O$ with an inter-tetrahedral Si–O $\cdots$ O–Si hydrogen bond; (b) the linear chain of hydrogen bonded $[HSiO_4]^{3-}$ tetrahedra in α-$Na_3HSiO_4 \cdot 2\,H_2O$ with an inter-tetrahedral Si–O $\cdots$ O–Si hydrogen bond; (c) the tetrahedral H_2O-molecule in β-$Na_3HSiO_4 \cdot 2\,H_2O$ with Na and H atoms; (d) the trigonal bipyramidal H_2O molecules in α- and β-$Na_3HSiO_4 \cdot 2\,H_2O$ with Na and H atoms. (- - - - - -) O $\cdots$ O-bonds, ($\cdots\cdots$) H $\cdots$ O-bonds (H_2O molecules c and d) in the hydrogen bonds.

TABLE 1

Thermodynamic values for the reversible $\alpha \leftrightarrow \beta$ phase transition of $Na_3HSiO_4 \cdot 2\ H_2O$

T (K)	ΔH (kJ mol^{-1})	AS (J mol^{-1} K^{-1})
275 ± 0.5	0.52 ± 0.03	1.85 ± 0.2

Nevertheless, the most significant structural difference arises from the H_2O-coordination geometry and hydrogen bonding. In α-$Na_3HSiO_4 \cdot 2\ H_2O$ both crystallographically independent H_2O- molecules show regular coordination geometry, i.e., both hydrogen atoms and one Na atom being coplanar and with two additional Na atoms perpendicular to that plane. All H atoms of the H_2O molecules in the α-phase are involved in hydrogen bonding [6]. In β-$Na_3HSiO_4 \cdot 2\ H_2O$, however, only one H_2O shows this trigonal bipyramidal coordination scheme, whereas the second one shows a tetrahedral coordination geometry consisting of two H and two Na atoms which are situated along the oxygens lone-pair orbitals [5]. Moreover, this tetrahedral H_2O molecule forms only one hydrogen bond, the second hydrogen atom being terminal and not H-bonded. The H_2O-coordination polyhedra can also be seen from Fig. 3. These structural differences between both forms of $Na_3HSiO_4 \cdot 2\ H_2O$ are so significant that they in fact define the differences in thermal stability between them.

As previously indicated β-$Na_3HSiO_4 \cdot 2\ H_2O$ does not transform if not ground but decomposes yielding $Na_3HSiO_4 \cdot H_2O$. On the other hand, the phase transition is easily performed when it is ground, i.e., when it is tribochemically induced. Doing this, i.e., grinding crystals of β-$Na_3HSiO_4 \cdot 2$ H_2O as well as those of the α-form, both forms (as educts) showed the same reversible calorimetric behaviour, as indicated in Fig. 2. Table 1 gives the thermodynamic data for the $\alpha \leftrightarrow \beta$ transition.

The transition temperature was obtained by averaging the onset-points of the transition peaks from ten runs up and down.

That heat of transition of $\Delta H = 0.52$ kJ mol^{-1} for this solid–solid phase transition is, in fact, very low. The reason for this must be that both forms show the same space group symmetry and only slightly different unit cell volumes so that changes in the course of a rearrangement, i.e., translation and rotation of the structural units, are at a minimum.

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