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DIFFERENTIAL SCANNING CALORIMETRY AT HYDROTHERMAL CONDITIONS OF AMORPHOUS MATERIALS PREPARED BY DRYING SODIUM SILICATE SOLUTIONS

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Abstract

Concentrated sodium silicate solutions with a molar SiO_2:Na_2O ratio of 3.3 and a SiO_2 content of 27 mass% were dried up to 63 d at temperatures between 40 and 100°C to residual water contents between 12 and 38 mass%. The dried solid materials were investigated by differential scanning calorimetry (DSC). Pressure tight autoclave crucibles were applied to suppress evaporation and boiling of the samples during heating. Two thermal events are discussed with respect to glass transition.

Keywords: drying, glass transition, hydrothermal conditions, sodium silicate solution, thermal analysis

Introduction

Sodium silicate solutions are commonly produced by dissolving sodium silicate glasses in water at hydrothermal conditions. Commercially available solutions have compositions characterised by a molar SiO_2:Na_2O ratio of 1.8 to 3.8 (ratios of 2.0 and 3.3 are standard compositions) and a SiO_2 content of 25 to 30 mass%. The materials are used in the paper industry, for producing detergents, and as raw materials for silicate synthesis. For some applications the materials have to be dried. Spray dried powders with a water content of about 10 to 20 mass% are sold as rapidly dissolvable silicates. Compact transparent materials are used as fire protecting layers in glazings. The latter materials eventually contain minor organic additives, e.g. for enhancing long-term stability. In the following, water containing sodium silicates obtained by drying solutions are called hydrous sodium silicates.

The drying process itself and the use of dried sodium silicate materials depend on temperature. During drying the viscosity of the solution raises as a function of the water content. This was described by Vail [1], who found that viscosity raises within a narrow concentration range by a few orders of magnitude. He reports a density of

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1.46 g cm^{-3} – corresponding to a water content of about 55 mass% – for the inflection point of the viscosity curve. Glasses have a similar viscosity behaviour in the range of glass transition. But the viscosities reported by Vail – about 160 Pa s for the respective density – are not as high as those for glass melts at glass transition.

Dent Glasser and Lee [2] investigated the drying process of sodium silicate solutions with a molar SiO_2:Na_2O ratio of 3.42 and a SiO_2 content of 29 mass% by thermal analysis and leaching of the dried products. In a two-step drying process they obtained hydrous sodium silicates with water contents between 10 and 37 mass%. The materials were investigated by thermogravimetric and differential thermal analysis in separate runs. Two endothermic events were detected: the lower temperature effect was explained by the rearrangement of interstitial ions and water molecules, whereas the higher temperature effect was attributed to the evaporation of H_2O which is formed by the condensation of silanol groups. Later, the reported effects will be compared to our own results.

Another type of hydrous sodium silicates was discussed from a different point of view. It is possible to melt crystalline sodium metasilicate hydrates (e.g. $Na_2O\cdot SiO_2\cdot nH_2O$, n: 5, 6, 9) and to solidify them in the vitreous state by cooling to low temperatures [3]. There are several ways to define the glass state. Some authors (e.g. [4]) say that all solid amorphous materials are glasses, other authors (e.g. [5]) demand the demonstration of a glass transition as a necessary condition of the glass state. Background of this controversy is the question whether the glassy state can be defined independent of the liquid state or not. An overview on theories designed to explain glass transition is given by Scherer [6]. The thermal analysis of glass transition phenomena, which is the usual way to proof its existence, is described by Wunderlich [7]. He explains glass transition as that temperature point where motions with large amplitudes stop. Glass transition shows features of a second order transition, but it is not an equilibrium reaction since the exact temperature point depends on heating (or cooling) rate. The restriction of motions with large amplitudes below glass transition leads to a typical change of specific heat capacity which can be measured by differential scanning calorimetry.

The glass transition of the above mentioned hydrous metasilicate glasses was investigated by unconventional methods. Scholze and Gliemeroth [8] dried the melts to n-values between 2.6 and 4. They measured the vapour pressure above the dried materials in the temperature range of glass transition. An unsteadiness of $\partial p(H_2O)/\partial T$ was attributed to the glass transition. Koller *et al.* [9] determined the glass transition of materials with n-values between 4 and 9 via the peak shapes in ^{29}Si MAS NMR spectra (MAS: magic angle spinning; NMR: nuclear magnetic resonance). Glass transition temperatures of 256 K [8] and 262 K [9], respectively, were determined for the hydrous silicate $Na_2O\cdot SiO_2\cdot 4H_2O$, which is a good agreement for two different methods.

The glass transition temperatures of $Na_2O\cdot SiO_2\cdot nH_2O$ materials discussed above are below 100°C. The same is valid for salt solutions, as was reported by Widmann and Riesen [10]. Therefore, it is possible to investigate the glass transition of these materials with thermoanalytical methods which are easier to attain as a vapour pressure measurement.

Sodium silicate solutions with compositions in the technical range have interesting thermal effects at temperatures above 100°C. In this temperature range water vapour pressure induces the following reactions:

- evaporation,
- boiling, and
- foaming.

These reactions are accompanied by mass loss and interfere with conventional methods to demonstrate a glass transition. Therefore, pressure tight crucibles were applied, which allow caloric measurements under hydrothermal conditions. Thus, at least some of the interfering reactions should be suppressed.

Experimental

Technical grade sodium silicate solutions (Roth, Karlsruhe, Germany) were used as raw materials. The composition of the starting materials was chemically analysed: 8.6 mass% Na_2O and 27.3 mass% SiO_2 (SiO_2:Na_2O mole ratio of 3.27). The solutions (5 to 15 g) were dried in open polypropylene beakers with a volume of 120 ml. The beakers were placed in closed drying ovens above a desiccant. After drying, the beakers were closed with a lid and stored for further 24 h at the drying temperature in order to minimise concentration gradients due to the diffusion of water. The mass loss of the sodium silicate solutions was measured regularly and was used to calculate the residual water content. In most cases the samples were dried at 40°C, some additional samples were dried at temperatures up to 100°C. The drying time was extended up to 63 d.

The dried materials were examined by light microscopy and X-ray diffraction in order to identify and eliminate crystallised or cracked samples. Between the investigations the samples were stored in a desiccator. The samples investigated here are listed in Table 1.

Thermal analysis was performed with a Simultaneous Thermal Analyser Netzsch STA 409 C. The dried hydrous silicates were crushed to a particle size of about 100 μm. The samples were heated in a DSC – furnace up to 350°C with a heating rate of 10 K min^{-1}.

A closed crucible (autoclave crucible) with 27 μl volume was used. The crucible (Netzsch) consisted of stainless steel coated with gold inside. The mass of the crucible (with lid) is about 900 mg. The crucibles were filled with 12 to 20 mg of the crushed samples.

The density of the starting materials was 1.36 g cm^{-3}. After drying the density reached values up to 2.1 g cm^{-3}, e.g. 2.09 g cm^{-3} for Sample 81-3 (Table 1). That means that a residual gas volume of 14 to 20 μl was left in the crucibles.

The application range of the crucibles is limited to 500°C and 100 bar. Pure water reaches a vapour pressure of 100 bar at about 310°C. Therefore, the measurements were usually restricted to 300°C. In some cases the measurement range was extended to 350°. Only in a few runs the crucibles were not tight. This was first controlled by weighing the crucibles after the run. In the following runs the gravimetric data were recorded simultaneously, in order to have an on-line proof of tightness.

Table 1 Dried hydrous sodium silicate analysed in autoclave crucibles; samples 81-1, 81-2, and 81-3 were first dried 26 d at 40°C, then a second period at 60°C

Materials code	T/°C	t/d	H_2O/mass%
94-8	40	2	37.1
94-1	40	3	34.9
94-4	40	10	30.9
94-2	40	8	30.3
94-5	40	12	28.5
94-6	40	15	27.2
94-7	40	17	26.0
97-5	50	1	38.9
97-5	50	2	35.3
99-1	50	30	24.4
99-2	60	29	24.6
99-3	80	43	13.3
99-4	90	43	13.8
99-5	100	64	12.9
81-1	40/60	26/2	33.5
81-2	40/60	26/4	28.3
81-3	40/60	26/23	18.1

At first an empty crucible was used as reference, since it was supposed that filling a 900 mg autoclave crucible with 20 mg of an inert standard does not change the results significantly. The result was quite good for temperatures above 100°C. Below 100°C a steep increase of the DSC – signal made an evaluation difficult. In order to expand the measuring range toward lower temperatures, a water filled reference crucible was tried. DSC curves obtained with both types of references – other conditions were kept identical – are shown in Fig. 1. The water filled reference flattened the DSC signal in the lower temperature range, but led to a steadily rising DSC curve. In the following a water filled crucible was applied as standard reference. In the DSC runs with a water filled reference crucible an equivalent base line was recorded. It should be noted that water behaved like an inert material. This is demonstrated by a DSC measurement of water in an autoclave crucible (Fig. 2a).

For temperature calibration the melting points of benzil (diphenylglyoxal), benzoic acid, and saccharine (2-sulfobenzoic acid imide) were determined. As an example, the melting peak of benzoic acid is shown (Fig. 2b). The deviation of the measured values from the tabulated data [11] decreases from 5 to 1 K with increasing temperature.

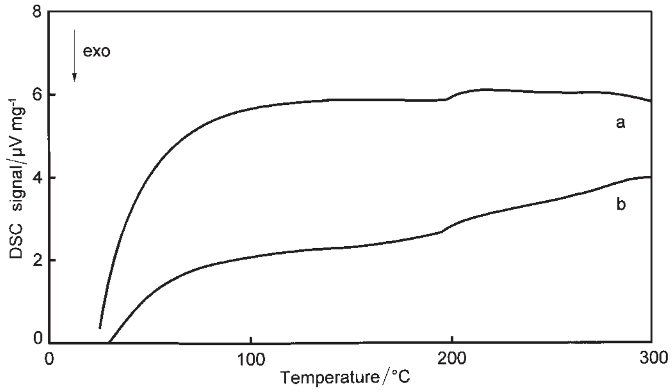

Fig. 1 DSC analysis of a hydrous sodium silicate dried 1 d at 40°C *vs.* different reference materials; heating rate 10 K min^{-1}; a – empty autoclave crucible as reference; b – H_2O filled autoclave crucible as reference

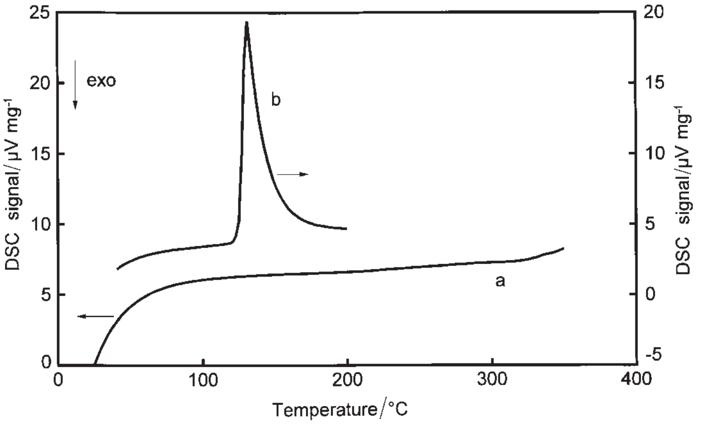

Fig. 2 DSC analysis of standard materials in an autoclave crucible; heating rate 10 K min^{-1}; a – H_2O; b – benzoic acid

Results

During drying the viscosity of the sodium silicate solution raises through stages of honeylike (water content 55 mass%; 8 h at 40 °C) and viscoplastic behaviour (water content 49 mass%; 16 h at 40°C) to the solid state. When the water content is <45 mass% the dried materials are brittle at room temperature.

The dried materials were usually amorphous, as was controlled by microscopy and X-ray diffraction. Crystallisation was observed in samples drying very slowly (e.g. at lower temperatures) and for very long times. At higher temperatures and in later drying stages cracks developed, which effected the transparency of the materials. Crystallised or cracked samples were not investigated here.

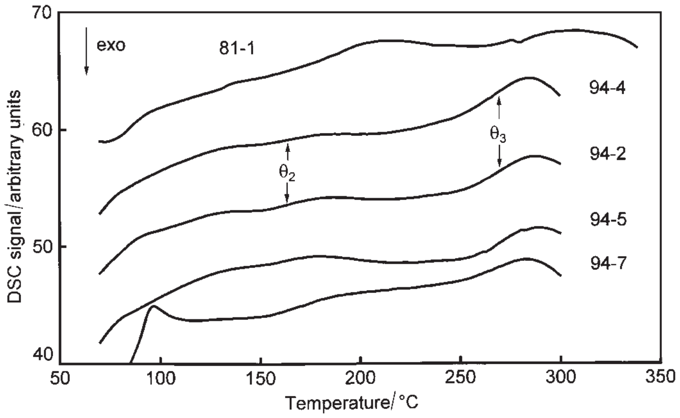

Fig. 3 DSC analysis of hydrous sodium silicates with a molar SiO_2:Na_2O ratio of 3.3 analysed with an autoclave crucible; heating rate 10 K min^{-1}

Thermal analysis was carried out up to temperatures of 350°C. Below 80°C the DSC signal was hard to evaluate (discussed above).

No indication of melting or crystallisation reactions was observed. No distinct DSC peaks were observed, unless in cases of leaky crucibles. Instead, small DSC steps with a height between 0.02 and 0.2 μV/mg could be detected. Typical DSC-graphs of hydrous sodium silicates with H_2O contents between 25 and 35 mass% are shown in Fig. 3. Some samples stored for a longer time gained some mass, as was controlled gravimetrically, and showed a peak at about 100°C. Those samples were dried additional 24 h at their original drying temperature. This treatment reduced the peak at 100°C significantly. The peak was therefore attributed to the water absorbed during storage.

The results of the DSC runs are listed in Table 2. In many DSC runs more than one DSC step was observed. The midpoints of the DSC steps are shown in Fig. 4 as a function of the water content after drying. In this plot three different types of DSC steps were identified. They were called θ_1, θ_2, and θ_3, respectively. After the DSC runs, the materials were either foamed or had a curved surface reminding the meniscus of a liquid.

This observation was further checked. The original sample 94-5 (water content 28.5 mass%) was heated with 10 K min^{-1} up to 300°C. The hydrous sodium silicate obtained by that treatment had a curved, but smooth surface (Fig. 5a). A second sample of 94-5 was heated under identical conditions to a temperature of 175°C (just above θ_2) and then cooled down. The crucible was opened and a foamed material was found, which is documented in Fig. 5b.

Table 2 Results of the DSC runs with autoclave crucibles; θ_1, θ_2, and θ_3 are the midpoints of DSC steps

Sample	H_2O/mass%	θ_1/°C	θ_2/°C	θ_3/°C
94-8	37.1			231
94-1	34.9		143	261
94-4	30.9		165	268
94-2	30.3		165	269
94-5	28.5		161	288
94-5	28.5		165	268
94-6	27.2		160	268
94-6	27.2		161	274
94-7	26.0		177	267
97-5	38.9		116	
99-2	24.6		210	
99-3	13.3	190	262	
99-4	13.8	201	274	
99-5	12.9	182	267	
81-1	33.5		134	
81-2	28.3			269
81-3	18.1		270	

Additionally, most of the other samples were submitted to a second DSC-run (without opening the crucible). In these second runs only θ_3 was observed, not θ_2.

A closer look at the DSC steps reveals significant differences. The DSC steps called θ_2 are observed at all drying conditions. The step covers a temperature range of

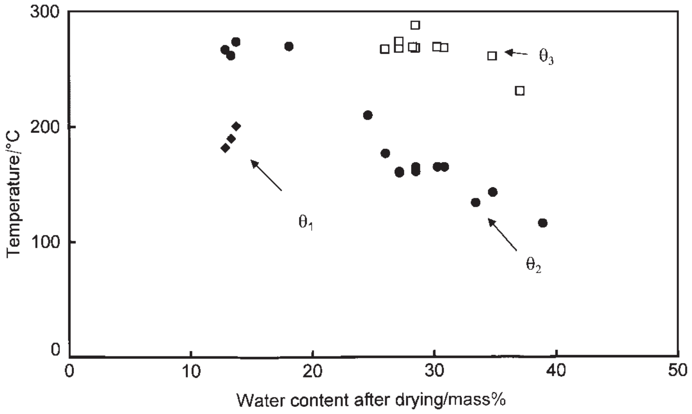

Fig. 4 Midpoints of DSC steps of dried sodium silicates with a molar SiO_2:Na_2O ratio of 3.3 analysed with autoclave crucibles as a function of the water content after drying; heating rate 10 K min^{-1}

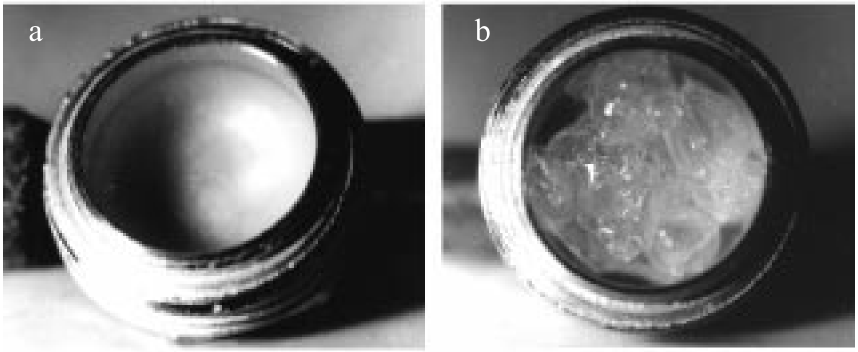

Fig. 5 Photos of hydrous sodium silicate 94-5 heated to 260 (a) or 175°C (b) in an autoclave crucible; heating rate 10 K min^{-1}

about 60 K. The θ_1 step was observed only for the samples dried at temperatures ≥80°C to low water contents (<15 mass%). The θ_1 steps are rather sharp and cover a temperature range of only 10 K. The two cases are shown in Fig 6. The θ_1 step was always followed by a θ_2 step.

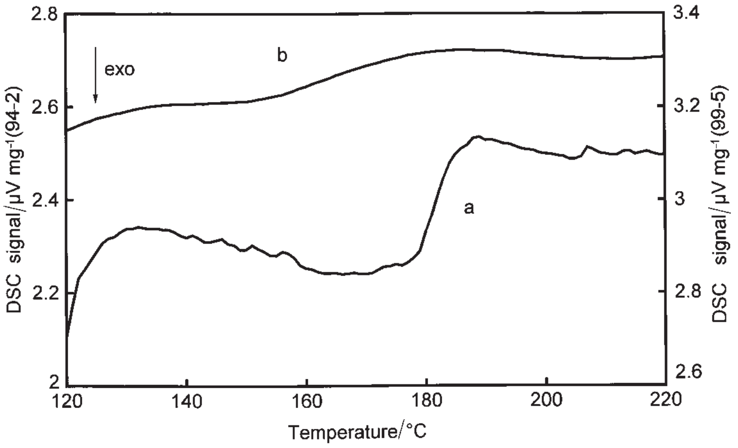

Fig. 6 Comparison of typical θ_1 and θ_2 DSC steps; heating rate 10 K min^{-1}; a – 99-5 (θ_1); b – 94-2 (θ_2)

The shape of the observed DSC steps was compared to a DTA measurement (Netzsch STA 409 C) of a sodium silicate glass with a molar SiO_2:Na_2O ratio of 3.3 which was prepared by conventional melting at 1400°C. A DTA step of 0.02 μV mg^{-1} was observed at 496°C, which is again very broad and can be compared to θ_2.

The height of the DSC steps differs too. In the case of θ_1 a value of about 0.3 mV mg^{-1} was measured, whereas θ_2 reached only 0.13 mV mg^{-1}.

Discussion

Dried sodium silicates with a water content of less than 45 mass% are transparent, non-crystalline, X-ray amorphous and brittle materials. According to [4] they can be recognised as vitreous materials.

The appearance of the investigated materials after thermal treatment – especially the observations documented in Figs 5a and 5b – indicate a macroscopic solid–liquid transition in the DSC runs at temperatures $\leq\theta_2$. The dried materials as well as the thermally analysed materials are to the most part amorphous (in some cases minor amounts (<5% by volume) of crystals were detected which grew during thermal analysis).

The shape of the observed DSC steps fits to a glass transition. This was shown for the θ_2 events by comparison with a conventional sodium silicate glass having the same molar SiO_2:Na_2O ratio of 3.3. The shape of the θ_1 events can be compared to the DSC results reported for glass transitions in salt solutions [10], which are also very sharp. Only three samples with water contents <15 mass% were investigated. In each case both effects, θ_1 as well as θ_2, were observed. In DSC runs with samples having higher water contents, the θ_1 effect was not observed. This is possibly due to the steep DSC curve below 100°C (Fig. 1).

It is hard to imagine homogeneous materials with two consecutive glass transitions separated by a temperature difference of 100 K. Under the assumption that both effects are caused by a glass transition, the greater height of the DSC step θ_1 indicates that the structural units responsible for such a transition would be smaller than those responsible for θ_2. This corresponds to earlier results, where two different microstructures of amorphous hydrous sodium silicates were found [12], a homogeneous or small-scale structure at water contents below 30 mass% and a larger one in the 50 nm range at higher water contents.

Both effects might be correlated to the macroscopic solid–liquid transition. Nevertheless, the nature of both effects has to be investigated further.

The θ_3 steps were observed at rather high temperatures and are usually preceded by smaller DSC steps at lower temperatures. It was shown for sample 94-5 that the hydrous sodium silicate foams at θ_2 and forms a meniscus at θ_3. It was first supposed that a second glass transition occurs at θ_3, because hydrous sodium silicates dries during foaming and should then have higher glass transition temperature. But the amount of water which can be evaporated into the gas volume of the autoclave crucible (about 0.4 mg at 150°C and 1.2 mg at 200°C) is not high enough to explain a second glass transition at these temperatures. Also the θ_3 event occurs very near to the high end of the temperature range. Therefore, it is preferred not to discuss these events, they might be artefacts.

The presented results lead to the conclusion that hydrous sodium silicates are submitted to a glass transition when heated at hydrothermal conditions to temperatures $\leq\theta_2$. A demonstration of a heating rate dependence of the θ_1 or θ_2 events would back this conclusion and will be tried in further investigations.

A glass transition may also explain the behaviour of fire protecting glazings based on hydrous sodium silicates: The fire protecting layer foams in the case of application to a porous thermal insulation layer. Foaming occurs when the hydrous sodium silicate is liquid, that is above glass transition. In the case of fire protecting glazings the hydrous sodium silicates can expand unrestrained until the water content of the glass is so low that it solidifies again.

Comparison with literature data

The values of θ_1 and θ_2 have been compared with the data published by Dent Glasser and Lee [2]. The result is shown in Fig. 7. If one takes into account that the water contents reported in [2] are possibly overestimated – no correction of evaporation losses is reported – it is obvious that the events reported there occur below θ_2. The temperatures of the peak maxima of the upper DTA effects reported in [2] and the θ_1 midpoints coincide to a certain degree. On the other hand in the DSC runs presented here, the evaporation of water was suppressed successfully and neither endothermic nor exothermic peaks were detected.

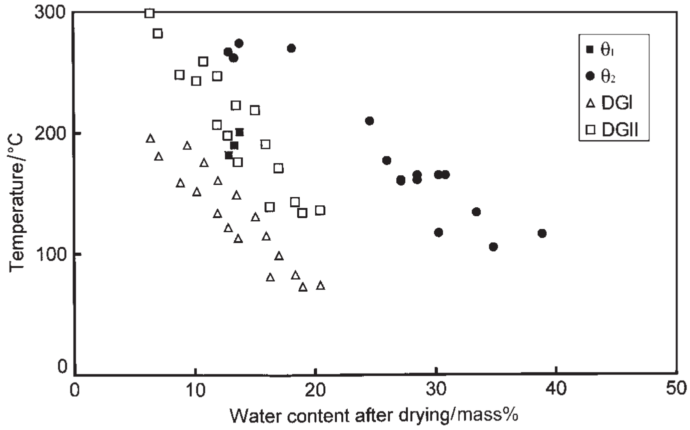

Fig. 7 Comparison of thermal events measured in this paper (θ_1 and θ_2; closed symbols) with data from [2] (DGI and DGII; open symbols) as a function of water content after drying

A comparison of the following results may be allowed, too (Fig. 8):

- The θ_2 temperatures.
- The T_g value measured for the melted glass, which has a water content below 0.1 mass%.
- The inflection point of viscosity data measured as a function of the density of drying sodium silicate solutions ([1], p. 89, Fig. 3.41). These data show that at room temperature the viscosity of dried sodium silicate solutions (SiO_2:Na_2O mole ratio of 3.27) increases several orders of magnitude when the water content is about 55 mass% H_2O. Therefore, the point at 25°C and 55 mass% water content was included in Fig. 8.
- The T_g value reported for pure water [10].

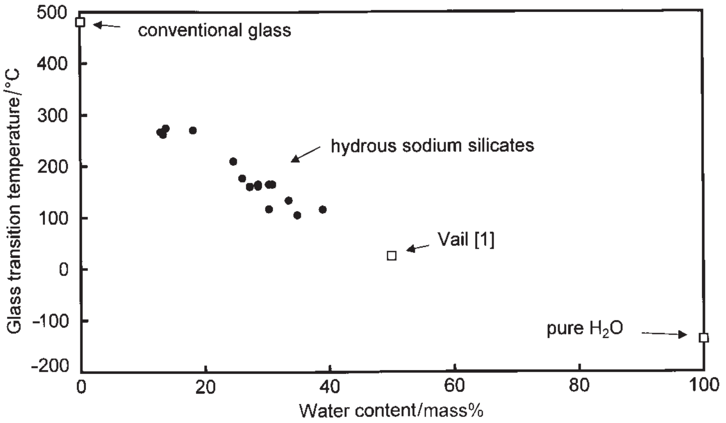

Fig. 8 Comparison of glass transition temperatures of amorphous materials of the Na_2O_3·3.3SiO_2–H_2O system as a function of water content after drying; Vail: transition point derived from viscosity data of [1]; H_2O: [10]

The comparison suggests that glass transition is a common phenomenon of hydrous sodium silicates with a molar SiO_2:Na_2O ratio of 3.3.

Summary

The application of simultaneous thermal analysis and of autoclave crucibles helps to identify thermal reactions occurring upon heating hydrous sodium silicates. There were no signs of crystallisation or melting reactions. Strong caloric effects reported in previous literature were successfully suppressed by the autoclave crucible. Thus, it was possible to detect small DSC steps. One of these steps might be attributed to a glass transition of the hydrous sodium silicates under investigation. The demonstration of a glass transition in these materials extends our knowledge of their structure and explains the behaviour of hydrous sodium silicates as fire protection materials. Drying sodium silicate solutions with a molar ratio of 3.3 was thus proofed to be an unconventional method to make glasses.

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