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Evidence for the existence of β-Na_3AlH_6: Monitoring the phase transformation from α-Na_3AlH_6 by in situ methods

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Abstract

The phase transformation of α-Na_3AlH_6 to β-Na_3AlH_6 was characterized by in situ DSC and high-temperature X-ray diffraction methods. The detection of the phase transformation from the α- to the β-polymorph requires rapid heating rates and a very fast data acquisition. The influence of the preparation method on the stability of both polymorphic forms most probably originates from different particle sizes of the parent samples.

Keywords: Sodium hexahydroaluminate; Hydrogen storage materials; Phase transformation; Thermal analysis; X-ray diffraction

1. Introduction

Catalyst-doped metal hydrides are very promising materials for both, on-board and stationary hydrogen storage systems. In particular, Ti-doped $NaAlH_4$ recently became subject of various publications since Bogdanović and Schwickardi showed that reversible hydrogen storage systems can be formed by doping $NaAlH_4$ with titanium [1]. Hydrogen is released in two steps, where first the sodium hexahydroaluminate and then, NaH and Al are formed (Eq. (1)):

$$NaAlH_4 \rightleftarrows \tfrac{1}{3}Na_3AlH_6 + \tfrac{2}{3}Al + H_2 \rightleftarrows NaH + Al + \tfrac{3}{2}H_2 \quad (1)$$

From thermal analysis of the decomposition behavior of $NaAlH_4$, the formation of a high-temperature stable polymorph of sodium hexahydroaluminate Na_3AlH_6 at 222 °C was assumed [2]. Bastide et al. [3] were the first to report the existence of a cubic β-Na_3AlH_6 phase resulting from a polymorphic transition of the monoclinic α-Na_3AlH_6 at 252 °C, as observed by X-ray diffraction. The authors also reported on the formation of β-Na_3AlH_6 under high pressure (35 kbar) and high temperatures (900 °C). The structure of the high-temperature polymorph was proposed to be isomorphous to the crystal structure of cryolite.

For the mineral cryolite (Na_3AlF_6), the existence of low- and high-temperature polymorphs is well known. The structure of the monoclinic low-temperature form was described by Naray-Szabo and Sasvari [4]. Steward and Rooksby [5] performed in situ high-temperature X-ray powder investigations of cryolite, which revealed a transformation at about 550 °C into a cubic structure with the lattice parameter $a = 7.95$ Å and the space group $Fm3m$. The structure is reported to be isomorphous with $(NH_4)_3AlF_6$ [6]. Yang et al. [7] studied the phase transition in cryolite in the temperature range of 22–627 °C by single crystal X-ray diffraction studies. At 612 °C, a fluctuation-induced first-order phase transition from monoclinic to orthorhombic symmetry was reported. The space group for the orthorhombic phase is $Immm$ with the lattice parameters $a = 5.632(4)$, $b = 5.627(3)$ and $c = 7.958(4)$ Å. Recently, Zhou and Kennedy [8] published high-temperature powder synchrotron diffraction studies of synthetic Na_3AlF_6. The results are in good agreement with the work of Steward and Rooksby [5] but are in contrast to the orthorhombic structure proposed by Yang et al. Zhou

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and Kennedy confirm a first-order transformation into a cubic high-temperature phase at about 567 °C. This structure is characterized by static displacive disorder of the F^- anions. The effect of disorder is necessary to stabilize the cubic structure.

For the cryolite-like β-Na_3AlH_6, Bastide et al. report a cubic structure in *Fm*3*m* with $a = 7.755$ Å [3]. The authors show line diagrams of both the α- and the β-form extracted from Debye–Scherrer measurements. Even though the existence of β-Na_3AlH_6 is widely accepted, no detailed investigations on this phase transformation were performed by now.

The aim of the present work was to investigate the appearance of the high-temperature polymorph and to provide information about the kinetics of the phase transformation and the stability of the high-temperature form. Since the kinetics for doped samples is very fast, undoped samples, which exhibit a slower kinetics, were analyzed.

2. Experimental conditions

2.1. Starting materials

Na_3AlH_6 prepared by the wet-chemical method (Na_3AlH_6(w)) was synthesized according to Bogdanović and Schwickardi [1]. 1.463 g (27.09 mmol) of $NaAlH_4$ and 1.306 g (52.79 mmol) of NaH (97%) were suspended in 30 ml heptane. The suspension was stirred and kept at 162 °C for 72 h under 140 bar hydrogen pressure. For the ball-milled Na_3AlH_6 sample (Na_3AlH_6(b)), 0.54 g $NaAlH_4$ (10 mmol) and 0.50 g NaH (97%, 20 mmol) were ball-milled in a Fritsch mill (P7) at 800 rpm for 3 h.

2.2. In situ X-ray powder diffraction

The in situ high-temperature X-ray diffraction data were collected on a Stoe STADI P transmission diffractometer in Debye–Scherrer geometry (Cu Kα_1: 1.54060 Å) with a primary monochromator (curved germanium (1 1 1)) and a 40° position-sensitive detector. The samples were filled into quartz-glass capillaries (ϕ 0.5 mm) and inserted into a capillary furnace attached to the diffractometer. During the experiment, the sample was held under argon. Data were collected in the range between 22 and 65° 2θ with a step width of 0.03° 2θ. The patterns shown in Fig. 1 were collected at room temperature on a Stoe STADI P transmission diffractometer in Debye Scherrer geometry (Cu Kα_1: 1.54060 Å) equipped with a linear position sensitive detector.

2.3. Differential scanning calorimetry (DSC)

The DSC experiments were performed on a Mettler 27HP in argon flow. The DSC (see Fig. 6 in Section 3.1) were measured on a Netzsch STA 449C with a heating rate of 20 °C/min from room temperature to 450 °C in an argon flow of 100 ml/min.

3. Results and discussion

The X-ray powder patterns of both products are shown in Fig. 1a. The ball-milled sample contains still a small amount of NaH used as starting material. The different resolution and full-widths at half maximum (FWHM) of the reflections originates from different particle sizes for the samples Na_3AlH_6(b) and Na_3AlH_6(w). The formation of smaller crystals with sizes of about 40 nm for sample Na_3AlH_6(b) is a consequence of the ball-milling, whereas the sample Na_3AlH_6(w) obtained by wet-chemical synthesis consists of larger crystals (>100 nm). This becomes apparent, especially for the main reflections in the range between 32 and 33.5° 2θ for the ball-milled sample Na_3AlH_6(b) where the single

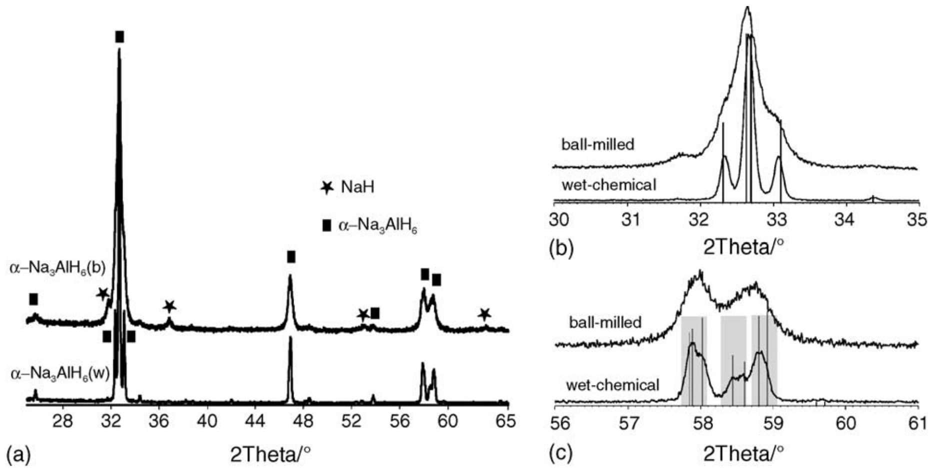

Fig. 1. (a) Powder patterns of the starting materials Na_3AlH_6(b) (top) and Na_3AlH_6(w) (bottom) measured at room temperature. (b) Comparison of the different FWHM for the sample prepared by ball-milling (top) and prepared by wet-chemical synthesis (bottom). The theoretical reflection positions calculated from the structure data are marked by the vertical lines. (c) The resolution of the reflections in the range between 57 and 60° 2θ is different for both materials according to the different preparation methods.

reflections cannot be resolved. Fig. 1b shows an enlargement of this range for both samples together with the reflection positions (vertical lines) for α-Na_3AlH_6, calculated from the structure data given by Rönnebro et al. [9]. For the ball-milled sample the reflections are very broad and overlap, while for the sample prepared wet-chemically the single reflections are well resolved. The four reflections seem to be reduced to a single one in the former sample, which can be misinterpreted as a structural change to higher symmetry. The use of the reflection group in the range between 57 and 60° 2θ is better suited to identify changes in symmetry since the separation of the reflections is much easier to observe (Fig. 1c). Due to the different FWHM, the reflections form three groups for Na_3AlH_6(w) and two groups for Na_3AlH_6(b).

Huot et al. [10] claim the formation of β-Na_3AlH_6 by ball-milling, which can be maintained even after the processing. The X-ray powder pattern shown by the authors is interpreted as a mixture of α- and β-Na_3AlH_6. A closer check of the reflections in the range between 57 and 60° 2θ and a comparison with the theoretical pattern seemed to be advisable to distinguish unambiguously between the two polymorphs. Even though no crystal structure refinement for β-Na_3AlH_6 has been published up to now, we assumed that β-Na_3AlH_6 is isostructural to the cubic high-temperature cryolite structure. Based on that assumption, we calculated a pattern for the proposed β-Na_3AlH_6 structure using the atomic coordinates for the HT cryolite, whereas the fluorine positions were substituted by hydrogen atoms. The lattice parameter of 7.75 Å given by Bastide et al. [3] for β-Na_3AlH_6 was used for the simulation. The simulated patterns for both phases together with the theoretical reflection positions are plotted in Fig. 2. From the comparison of the two patterns, it becomes apparent that both polymorphs can be distinguished unambiguously. The symmetry change from monoclinic α-Na_3AlH_6 to cubic β-Na_3AlH_6 is associated with a reduction of seven reflections to one reflection for the cubic form in the range of 57–60° 2θ. The diagram published by Huot et al. [10] exhibits two broad reflections in the range of 57–60° 2θ instead of a single reflections as expected for cubic β-Na_3AlH_6. This makes it very improbable that the sample obtained by these authors really consisted of a mixture of both polymorphs.

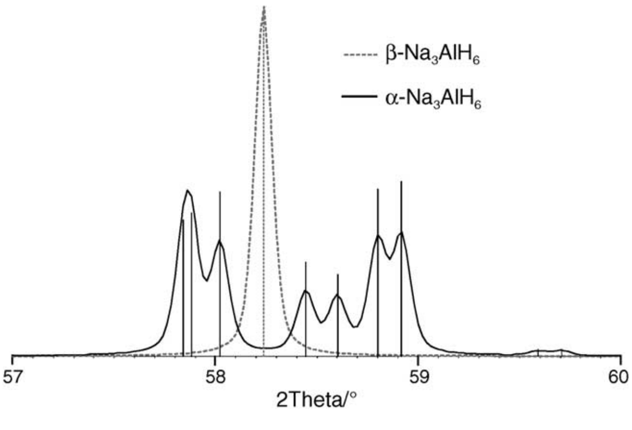

Fig. 2. Simulation of the powder patterns of both Na_3AlH_6 polymorphs in the range between 57 and 60° 2θ.

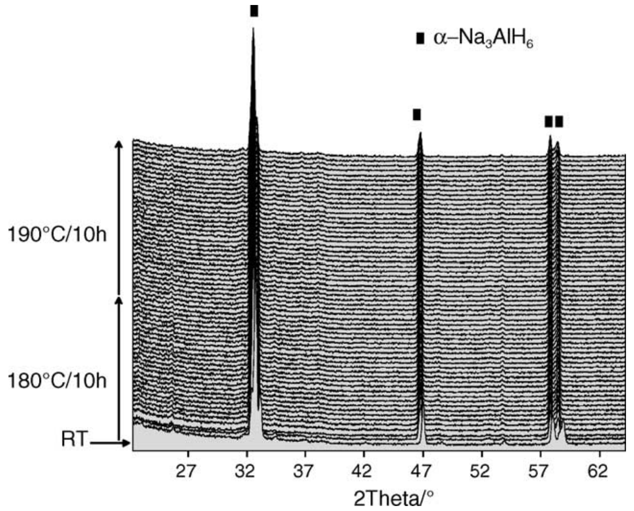

Fig. 3. In situ powder patterns of Na_3AlH_6(w) collected at 180 °C every 20 min for 10 h, and after this for 10 h at 190 °C.

3.1. Analyses of the sample prepared by the wet-chemical method

Thus, up to now no experimental data are available showing the formation and stability of β-Na_3AlH_6. In this work, in situ high-temperature X-ray diffraction studies and DSC were chosen as tools to investigate potential phase-transformation processes from α-Na_3AlH_6 to β-Na_3AlH_6. As a first test, the thermodynamic stability of the material below the decomposition temperature was analyzed. Monoclinic α-Na_3AlH_6(w) was heated to 180 °C with a heating rate of 1 K/min. The sample was kept for 10 h at 180 °C meanwhile 30 in situ X-ray diffraction measurements were performed. After that time, the sample was heated to 190 °C and again XRD patterns were recorded for 10 h (Fig. 3). The refinement of the lattice parameters at 190 °C shows an increase of *a*- and *b*-lattice parameters (Table 1) in comparison to the unit cell parameters determined at room temperature. However, the structure is stable and no decomposition is observed. During a temperature treatment for 12 h at 210 °C the decomposition of α-Na_3AlH_6 starts after about 60 min (Fig. 4), whereas heating to 250 °C leads to an immediate decomposition of the sample (Fig. 5). In both cases α-Na_3AlH_6 decomposes to NaH and Al without a detectable formation of β-Na_3AlH_6. The in

Table 1
Refined lattice parameters for α-Na_3AlH_6 analyzed at different temperatures

Na_3AlH_6(w)	RT	180 °C	210 °C
a (Å)	5.4073 (7)	5.4489 (7)	5.4455 (7)
b (Å)	5.5276 (7)	5.5384 (6)	5.5250 (7)
c (Å)	7.748 (1)	7.792 (1)	7.780 (1)
β (°)	89.69 (1)	89.86 (1)	89.63 (2)
V ($Å^3$)	231.6	235.0	233.9
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$

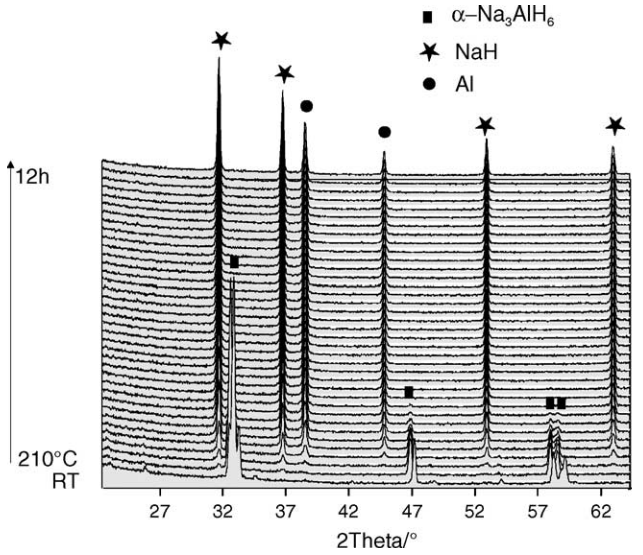

Fig. 4. In situ powder patterns of Na_3AlH_6(w) collected at room temperature (bottom diagram) and after heating to 210 °C every 20 min for 12 h.

situ X-ray investigations were confirmed by DSC analyses. In addition, a different decomposition behavior is observed depending on the heating rate. Two exothermic signals at about 228 and 327 °C at a heating rate of 1 K/min are shifted to higher temperatures when a higher heating rate is applied (Fig. 6). The signal at 228 °C is attributed to the decomposition of Na_3AlH_6 to NaH, Al and H_2 according to Eq. (1). The subsequent decomposition of NaH is represented by the second signal. Heating the sample with a heating rate of 10 K/min leads to the formation of a shoulder at the low-temperature side of the DSC signal indicating that another reaction takes place before the decomposition of the hexahydroaluminate. This thermal effect is even more pronounced when the heating rate is increased to 20 K/min.

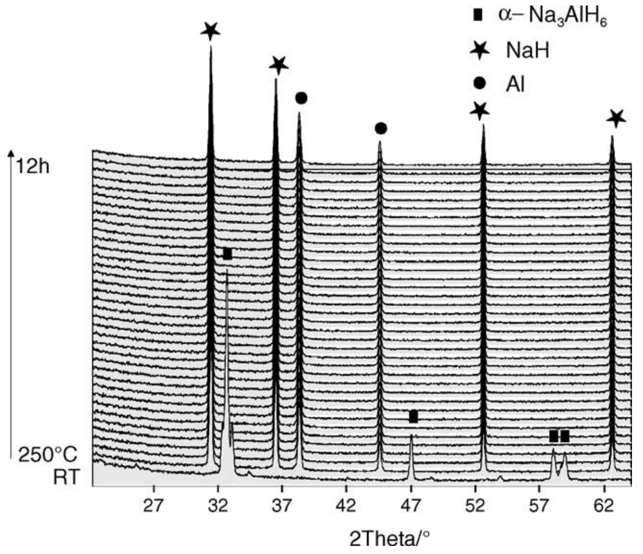

Fig. 5. In situ powder patterns of Na_3AlH_6(w) collected at room temperature (bottom diagram) and after heating to 250 °C every 20 min for 12 h.

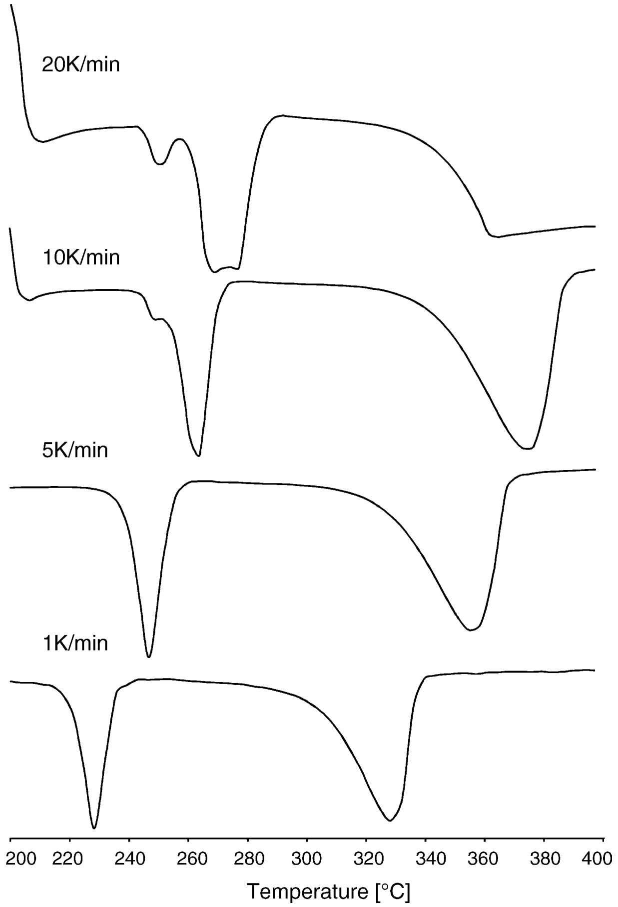

Fig. 6. DSC curves for Na_3AlH_6(w) heated with different heating rates.

As the result of these DSC experiments, the experimental conditions for a new set of in situ XRD experiments were changed. α-Na_3AlH_6 samples were heated to 250, 252, 255, 257 and 259 °C, respectively, with a heating rate of 20 K/min. After reaching the respective temperatures, X-ray powder patterns were recorded using a data acquisition time of only 60 s for each pattern. To analyze the kinetics of a possible transformation process and the decomposition of the hexahydroaluminate, the temperatures were kept constant and successive powder patterns were collected at that temperature.

After heating the sample to 250 °C, the powder pattern is not different from the pattern collected at room temperature, except for a slight 2θ-shift (Fig. 7a). The reflections mainly belong to α-Na_3AlH_6 but already after 1 min at 250 °C, small amounts of NaH appear in the powder pattern. The intensity of Na_3AlH_6 decreases while the contents of NaH and Al increase and after 13 min the decomposition of α-Na_3AlH_6 is completed. Tracing changes of the reflections between 57 and 60° 2θ show that the intensity of all reflections decreases simultaneously without any symmetry change to β-Na_3AlH_6. In another experiment, the sample was heated to 250 °C with a heating rate of 1 K/min and a data acquisition time of 60 s per pattern (data not shown here). In this case, Na_3AlH_6 is already completely decomposed after reaching 250 °C.

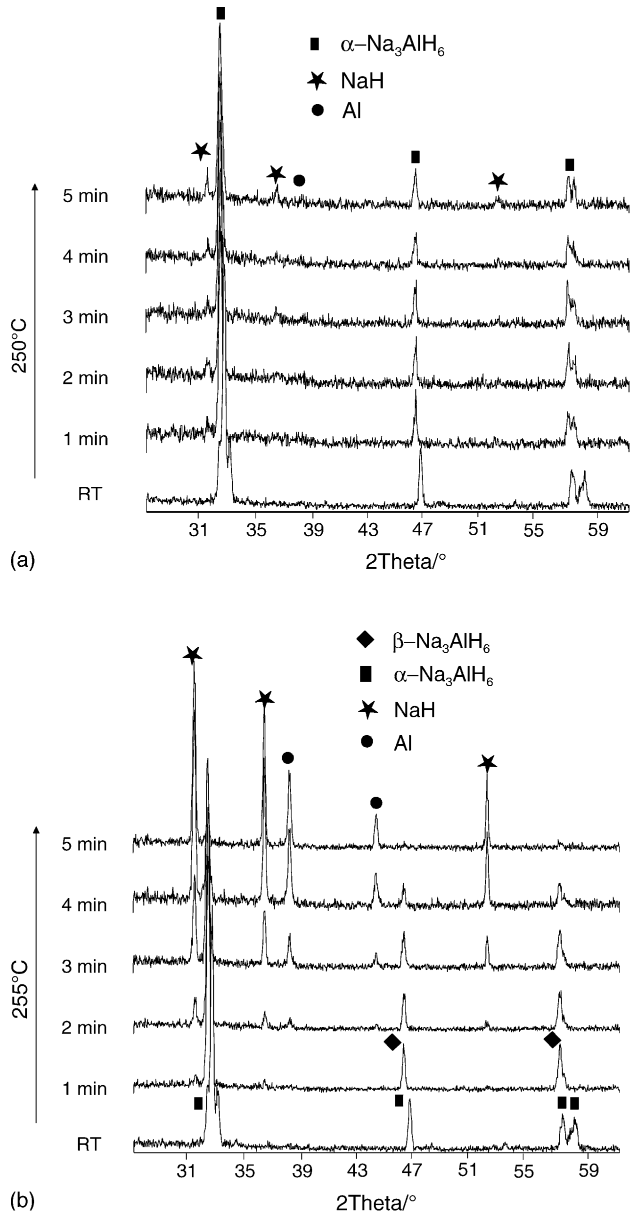

Fig. 7. (a) In situ powder patterns of Na_3AlH_6(w) heated to 250 °C and kept isothermally for 13 min. (b) In situ powder patterns of Na_3AlH_6(w) heated to 255 °C and kept isothermally for 13 min. (c) In situ powder patterns of Na_3AlH_6(w) analyzed for longer times at 250 and 255 °C.

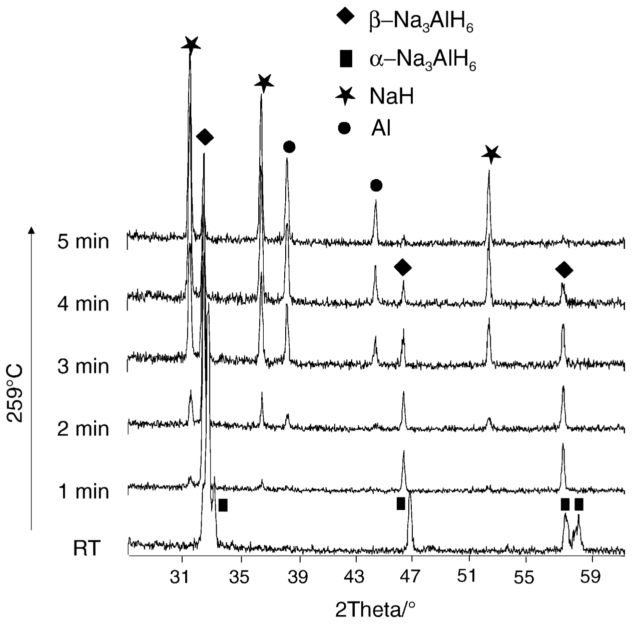

Fig. 8. In situ powder patterns of Na_3AlH_6(w) collected at 259 °C.

The analysis of the data collected at 252 °C (heating rate 20 K/min, data not shown here) exhibit the same results as observed at 250 °C, namely α-Na_3AlH_6 decomposes without any noticeable phase transformation to β-Na_3AlH_6. The powder patterns of the sample analyzed at 255 °C show that the decomposition of Na_3AlH_6 is already completed after keeping the sample for 5 min at this temperature (Fig. 7b). However, before the complete decomposition of the hexahydroaluminate is achieved, the group of reflections in the significant range between 57 and 60° 2θ exhibits a different behavior than for the sample analyzed at 250 °C (Fig. 7c). While for the sample treated isothermally at 250 °C, the reflection positions remain more or less the same and only the intensities decrease, a part of the reflections disappears almost completely for the sample treated at 255 °C. This cannot be explained only by the decomposition of the hexahydroaluminate. Obviously, a change of the crystal structure takes place, which can be explained by a phase transformation from the monoclinic to the cubic polymorph. The reflection at about 58° 2θ is very asymmetrical indicating an incomplete transformation of α-Na_3AlH_6 to β-Na_3AlH_6. However, after a further increase of the temperature to 257 °C (not shown here) and finally to 259 °C (Fig. 8), the shapes of the hexahydroaluminate reflections indicate a complete transformation into the cubic high-temperature polymorph represented by a single reflection at about 57.4° 2θ. The main reflections of the powder pattern collected after 1 min all belong to the cubic β-Na_3AlH_6. The high-temperature polymorph is stable only for a few minutes before it decomposes completely to NaH and Al. This phase transformation is reversible for a short time as shown in Fig. 9. Applying a heating and cooling rate of 20 K/min, the phase transformation can be reversibly repeated for several minutes prior to the complete decomposition of the hexahydroaluminate. Because of the symmetry change from monoclinic to cubic, the expected reduction of the number of reflections in the range 57–60° 2θ to a single peak (see also Fig. 2) is observed. The phase transformation from α-Na_3AlH_6 to β-Na_3AlH_6 is indeed a very fast process and therefore, rather difficult to trace. A rapid heating rate and fast data acquisition are mandatory requirements to show the transformation. For slow heating rates and/or long data acquisition times, the transformation of the α- to the β-form is not measurable. This can have two possible explanations. Firstly, for a slow heating rate, the α-form decomposes directly to NaH and Al before the temperatures necessary for

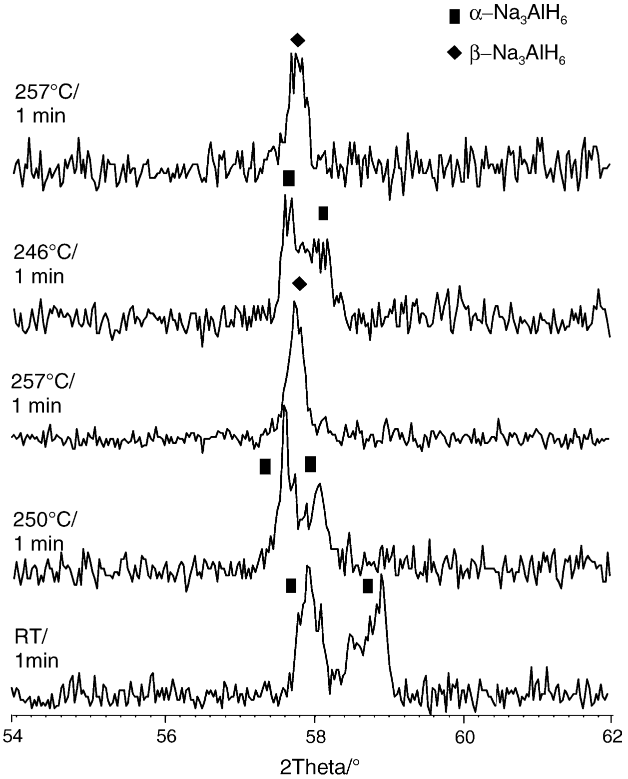

Fig. 9. In situ powder patterns of Na_3AlH_6(w) collected at different temperatures for 60 s each.

the transformation to the β-form are attained. Secondly, the transformation already has taken place but due to the slow heating, this process is already finished and the decomposition has started before it was possible to analyze the phase transformation.

The experimental results obtained for Na_3AlH_6(w) can be summarized as follows. Well below the decomposition temperature, the parent material is stable even if kept isothermally for 10 h at 190 °C. Increasing the temperature to 210 °C (heating rate 1 K/min), which is about 20 °C below the decomposition temperature of 230 °C, already decreases the stability of the material. After 60 min at 210 °C, the decomposition of Na_3AlH_6(w) to NaH and Al starts. Heating the sample to 250 °C (heating rate 1 K/min) leads to the immediate decomposition of Na_3AlH_6(w). A different picture can be drawn for the samples heated with rates of 20 K/min. Below a certain temperature, α-Na_3AlH_6(w) decomposes to NaH and Al without a detectable phase transformation to the β-form. At a specific temperature, a phase transformation from the α-form to the β-form takes place, followed by a very fast decomposition to NaH and Al. Despite the fast decomposition, we were able to record the reversibility of the phase transformation by in situ X-ray diffraction experiments. If α-Na_3AlH_6(w) decomposes directly to NaH and Al, the stability of hexahydroaluminate is higher. If prior to the decomposition β-Na_3AlH_6(w) is formed, the phase transformation runs faster.

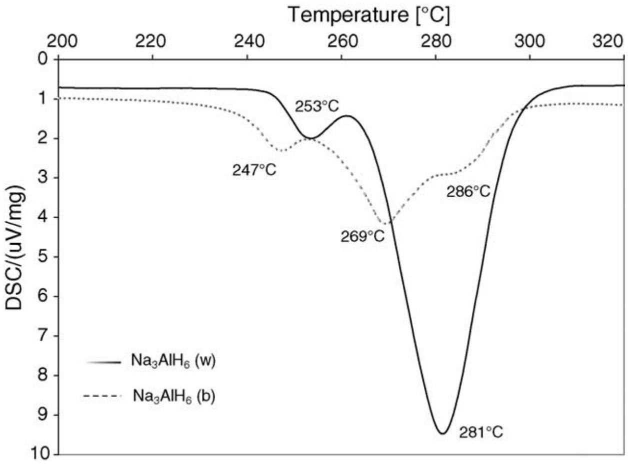

Fig. 10. DSC curves for Na_3AlH_6(w) and Na_3AlH_6(b), collected with a heating rate of 20 K/min.

3.2. Analyses of the samples prepared by ball-milling

The question arises, if and how the preparation method of the hexahydroaluminate and different particle sizes influence the formation of the high-temperature polymorph. The comparison of the DSC curve obtained for Na_3AlH_6(b) with the curve of Na_3AlH_6(w) (Fig. 10) collected with a heating rate of 20 K/min shows two different features. Firstly, the decomposition starts at lower temperatures and secondly, the decomposition signal for Na_3AlH_6(b) consist of three signals instead of two signals as observed for Na_3AlH_6(w). These observations are corroborated by in situ X-ray investigations, which show a different decomposition behavior for the two materials. The decomposition of Na_3AlH_6(b) to NaH and Al is already visible at 247 °C, but the powder patterns do not indicate a phase transformation to β-Na_3AlH_6. Already after 1 min at 250 °C, the transformation from α-Na_3AlH_6(b) to β-Na_3AlH_6(b) took place (Fig. 11a). This is different to Na_3AlH_6(w) where no phase transformation was observed at 250 °C. As indicated by Fig. 9, the equilibrium transformation from α- to β-Na_3AlH_6 lies between 250 and 257 °C for the wet-chemically synthesized sample. For the ball-milled sample, the transformation already occurs at 250 °C indicating that not only the kinetics, but also the thermodynamics is different to the wet-chemically prepared sample. The reason for this could be either changes of the surface energy of the smaller particles, or a more easy decomposition to NaH and Al in these small particles as the driving force for the transformation. The X-ray observation confirms the DSC result that the transformation for Na_3AlH_6(b) starts at lower temperatures. Another difference to Na_3AlH_6(w) is the stability of β-Na_3AlH_6 keeping the sample isothermally. Even after keeping the sample for 13 min at 257 °C, the composition to NaH is still not completed (Fig. 11b). This shows that the polymorph β-Na_3AlH_6(b) is much longer stable before it decomposes completely compared to β-Na_3AlH_6 obtained from Na_3AlH_6(w). This is also shown in the comparison of the powder patterns for both samples, Na_3AlH_6(w) and

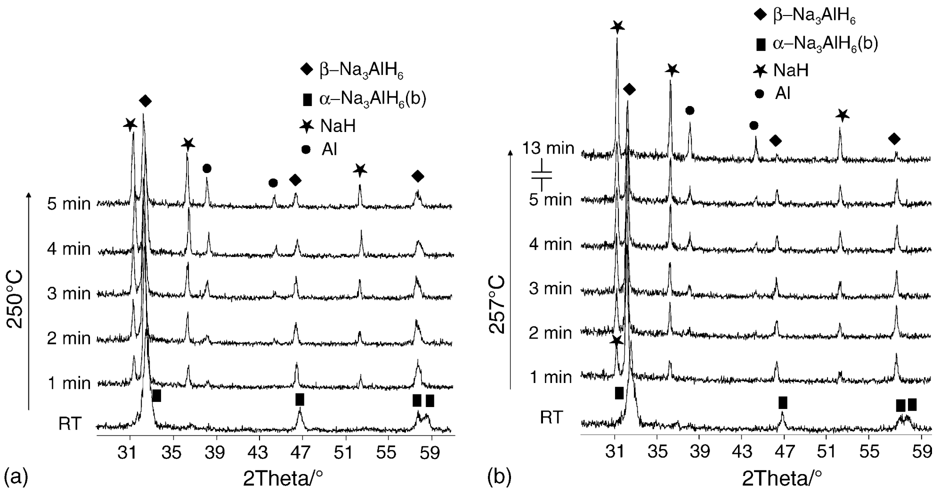

Fig. 11. In situ powder patterns of the ball-milled sample analyzed isothermally at (a) 250 and (b) 257 °C.

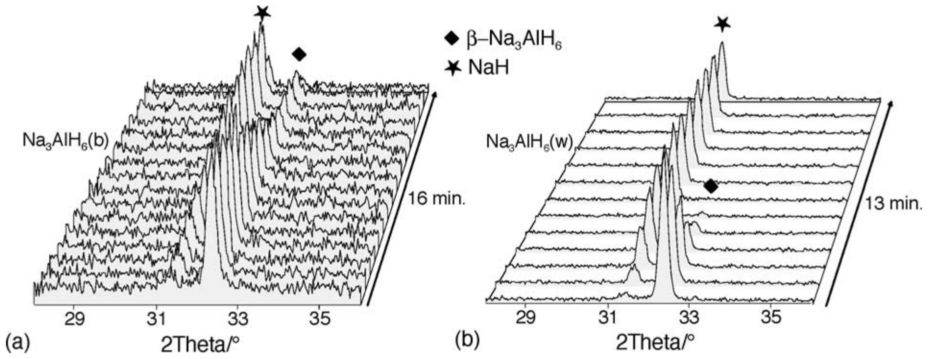

Fig. 12. Comparison of the in situ powder patterns of (a) ball-milled Na_3AlH_6 and (b) Na_3AlH_6 synthesized by wet-chemical method collected at 259 °C.

Na_3AlH_6(b), kept for a longer period isothermally at 259 °C (Fig. 12).

In conclusion, it can be stated that the preparation has some influence on the stability of both polymorphic forms, which most probably originates from different particle sizes of the parent samples. For the ball-milled Na_3AlH_6(b), the phase transformation from the α- to the β-form starts at lower temperatures. This can be expected since smaller particles and/or lower crystallinity of the structure due to the milling procedure would support an earlier and faster transformation. Even though the phase transformation happens at lower temperatures and the decomposition starts earlier, β-Na_3AlH_6(b) is longer stable than β-Na_3AlH_6(w). The heat transfer between the individual grains is reduced due to the smaller size of the particles.

4. Conclusion

For the first time, it was possible to follow the proposed phase transformation of α-Na_3AlH_6 to β-Na_3AlH_6 by in situ characterization methods. The detection of the phase transformation from the α- to the β-polymorph with analysis methods as in situ X-ray diffraction or DSC requires rapid heating rates and a very fast data acquisition. For slow heating rates and/or long data acquisition times, the transformation of the α- to the β-form is not measurable. The preparation has some influence on the stability of both polymorphic forms, which most probably originates from different particle sizes of the parent samples.

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