Understanding the Hydrothermal Formation of NaNbO₃: Its Full Reaction Scheme and Kinetics

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ABSTRACT: Sodium niobate (NaNbO₃) attracts attention for its great potential in a variety of applications, for instance, due to its unique optical properties. Still, optimization of its synthetic procedures is hard due to the lack of understanding of the formation mechanism under hydrothermal conditions. Through in situ X-ray diffraction, hydrothermal synthesis of NaNbO₃ was observed in real time, enabling the investigation of the reaction kinetics and mechanisms with respect to temperature and NaOH concentration and the resulting effect on the product crystallite size and structure. Several intermediate phases were observed, and the relationship between them, depending on temperature, time, and NaOH concentration, was established. The reaction mechanism involved a gradual change of the local structure of the solid Nb₂O₅ precursor upon suspending it in NaOH solutions. Heating gave a full transformation of the precursor to HNa₇Nb₆O₁₉·15H₂O, which destabilized before new polyoxoniobates appeared, whose structure depended on the NaOH concentration. Following these polyoxoniobates, Na₂Nb₂O₆·H₂O formed, which dehydrated at temperatures ≥285 °C, before converting to the final phase, NaNbO₃. The total reaction rate increased with decreasing NaOH concentration and increasing temperature. Two distinctly different growth regimes for NaNbO₃ were observed, depending on the observed phase evolution, for temperatures below and above ≈285 °C. Below this temperature, the growth of NaNbO₃ was independent of the reaction temperature and the NaOH concentration, while for temperatures ≥285 °C, the temperature-dependent crystallite size showed the characteristics of a typical dissolution−precipitation mechanism.

INTRODUCTION

Hydrothermal synthesis is a low-temperature environmentally friendly route to a variety of functional oxides reducing challenges with evaporation, agglomeration, and coarsening, which often takes place at higher temperatures.¹−⁶ Still, the development of the method has been mostly achieved through a trial-and-error approach as the conventional autoclave design, not easily penetrable by X-rays, makes it inherently challenging to study the synthesis in real time. Thus, the nature of the reactions taking place inside the reaction vessel is not completely understood.

NaNbO₃ has gained attention due to its many potential applications in high-density optical storage, enhancing nonlinear optical properties, as hologram recording materials, etc.⁷,⁸ It is also an end-member of the KₓNa₁₋ₓNbO₃ solid solution, a promising lead-free replacement for lead zirconate titanate (PZT).⁹,¹⁰ Moreover, NaNbO₃ nanowires formed by hydrothermal synthesis and subsequent calcination have proven useful in lead-free piezoelectric nanogenerator applications.¹¹ Ex situ studies of the hydrothermal synthesis of NaNbO₃ have shown that the reaction starts with the transformation of the T-Nb₂O₅ (orthorhombic structure) precursor into sodium hexaniobate (HNa₇Nb₆O₁₉·15H₂O), with the main building block consisting of the Lindqvist ion, [Nb₆O₁₉]⁸−.¹⁸ The sodium hexaniobate then transforms into Na₂Nb₂O₆·H₂O, which in turn transforms into perovskite NaNbO₃, displaying a wide range of morphologies including cubes and various agglomerated structures.¹⁹−²¹ The crystal structures of these phases are significantly different from each other, as seen in Figure S1 in the Supporting Information, and it is not clear how the structures evolve from one phase to the next or how they affect the growth mechanism of NaNbO₃.

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in situ studies have shown the presence of several more intermediate phases than previously reported.\textsuperscript{24,25} The proposed growth mechanisms may not give a full depiction of the resulting effects on the NaNbO\textsubscript{3} growth. More work is therefore needed to understand how these reaction schemes depend on temperature and mineralizer concentration and how the product is consequently affected.

Here, we present an in situ X-ray diffraction (XRD) study of hydrothermal synthesis of NaNbO\textsubscript{3}, shedding light on the entire reaction scheme for a wide range of synthesis temperatures and NaOH concentrations, commonly seen in the literature.\textsuperscript{14,20–22,26} We determine how the reaction scheme is affected by reaction temperature and NaOH concentration. Knowledge about the kinetics during formation of NaNbO\textsubscript{3}, which is affected by the reaction mechanism, is obtained and useful for the optimization of reaction rate and resulting crystallite size. Further, as most literature on hydrothermal synthesis of NaNbO\textsubscript{3} presents data at temperatures below 250 °C, we investigate the reaction at higher temperatures. In combination, the acquired knowledge provides the ability to speed up the reaction while still being able to achieve the desired reaction product, valuable for production at industrial scales.

**EXPERIMENTAL SECTION**

Orthorhombic T-Nb\textsubscript{2}O\textsubscript{5} powder\textsuperscript{27} was synthesized by precipitation from (NH\textsubscript{4})NbO(C\textsubscript{2}O\textsubscript{4})\textsubscript{2}·5H\textsubscript{2}O (Sigma-Aldrich, 99.99%) dissolved in water by adding aqueous ammonia solution (25 wt %, Emsure) before drying and then calcining at 600 °C for 12 h, as described by Makkelbo et al.\textsuperscript{17,20,26} Highly concentrated suspensions were made by mixing T-Nb\textsubscript{2}O\textsubscript{5} powder with 9 or 12 M NaOH aqueous solutions, giving a Na/Nb ratio of 9.5 or 13.2. The suspensions were stored in PET bottles and injected with a plastic syringe into a custom-made graphite ferrules and Swagelok capillary with inner and outer diameters of 0.8 and 1.15 mm,respectively, which was fixed to an adjustable aluminum frame by graphite ferrules and Swagelok fittings. A High Pressure Liquid Chromatography (HPLC) pump connected to the dead-ended cell provided a stable pressure. The mid 1/3 of the capillary’s length was heated by a hot-air blower, and the temperature was calibrated by refining the unit cell expansion of boron nitride.\textsuperscript{29} The blower was ramped up to reaction temperature while being directed away from the capillary and was remotely swung into position only after the desired pressure was achieved and data acquisition had been initiated, providing quasi-instant heating (see temperature programming). The as-recorded data were treated using the Nika Igor Pro analysis software package.\textsuperscript{41} The data were plotted and analyzed in Jupyter Lab\textsuperscript{52} with the Scipy tool packages Numpy, Matplotlib, and Pandas.\textsuperscript{53} The suspensions made for this purpose had 50 wt % of T-Nb\textsubscript{2}O\textsubscript{5} compared to the in situ PXRD experiments performed at the ESRF (as described above) to enhance the X-ray transmission. The same in situ cell as described above was used, but with a splash protection cage of aluminum bars and Kapton films around it.

Total scattering measurements on unheated suspensions of T-Nb\textsubscript{2}O\textsubscript{5} powder in NaOH solutions at ambient pressure were performed at beamline BL08W at SPring-8/JASRI in Hyogo, Japan, using an a-Si flat panel area detector.\textsuperscript{53} The wavelength (0.1077 Å) and instrumental parameters were calibrated with an NIST 660a CeO\textsubscript{2} standard. Similar suspensions to those for the in situ PXRD experiments, with 9 and 12 M NaOH solutions, fresh and aged for 1, 10, and 24 h were injected into 0.5 mm Kapton capillaries. The transmission signal was detected with 1 s acquisition time, collecting a total of 10 images per sample. The data were background-subtracted and converted to reduced structure functions, F(Q), and then Fourier-transformed to pair-distribution functions (PDF), G(r),\textsuperscript{44} using xPDFsuite\textsuperscript{45} and analyzed using the Diffpy-CMI software using a Q\textsubscript{min} of 16.5 Å\textsuperscript{−1} and a Q\textsubscript{max} of 1.2 Å\textsuperscript{−1}.\textsuperscript{56}

**RESULTS AND DISCUSSION**

All of the experiments were performed using the same T-Nb\textsubscript{2}O\textsubscript{5} solid precursor suspended in 9 and 12 M NaOH aqueous solutions. All of the suspensions were hydrothermally treated at 250 bar in the temperature range 160–285 °C. An additional reaction with 9 M NaOH was monitored under supercritical conditions (250 bar, 420 °C). The effects of NaOH concentration and reaction temperature on the phase evolution, crystallite size, unit cell volume, and reaction kinetics are discerned in the following sections. Note that the datasets for 9 and 12 M NaOH at 215 °C and 9 M NaOH at 420 °C have been published previously.\textsuperscript{25}

**Effects of Reaction Conditions on the Phase Evolution.** Figure 1 shows the diffraction patterns of all of the phases observed during the performed experiments, numbered 1–10, for different heating time and/or temperature, leading to the formation of NaNbO\textsubscript{3} at 160–420 °C.
The main structural elements of the previously known phases\(^{27,34-36}\) are shown on the top of the figure, and their full structures are shown in Figure S1 in the Supporting Information. The patterns in the gray areas are pH variants at equivalent times in the reaction.

The diffraction lines of T-Nb\(_2\)O\(_5\) (no. 1 in Figure 1) are seen in the diffraction pattern of the unheated precursor suspension with the addition of three diffraction lines at very low Q (0.65, 0.71, 0.76 Å\(^{-1}\)). The presence of these lines seemed to be dependent on the time since the suspensions were made, which will be investigated, along with their origin, in later paragraphs. All of the diffraction patterns except for the product, NaNbO\(_3\) (nos. 9 and 10 in Figure 1), had diffraction lines at similarly low Q-values, demonstrating the large unit cells of phases present.

In agreement with our previously reported paper,\(^{25}\) the T-Nb\(_2\)O\(_5\) precursor (no. 1 in Figure 1) is transformed into HNa\(_7\)Nb\(_6\)O\(_{19}\)·15H\(_2\)O (no. 2 in Figure 1), before several intermediate phases form (nos. 3–5 in Figure 1), ending with the formation of Na\(_3\)Nb\(_2\)O\(_5\)·H\(_2\)O (no. 6 in Figure 1) and NaNbO\(_3\) (nos. 9 and 10 in Figure 1). In this work, the temperature dependency of this phase evolution has been identified and is presented in Figure 2, where the data for an expanded temperature region (160–420 °C) for suspensions with 9 M NaOH are shown (the equivalent data for 12 M NaOH at 160–285 °C are presented in Figure S3 in the Supporting Information). Contour plots for the end temperatures are shown at each side. The colored region in the middle section of the figure shows bar plots representing the recorded phase evolution at certain temperatures, with logarithmic interpolations between them. The reaction scheme appearing in the 9 and 12 M NaOH solutions are quite similar at similar temperatures, and the reaction rate increases in a comparable manner for increasing temperature for both concentrations. All of the reactions finished with a full conversion to NaNbO\(_3\), except in 12 M NaOH at 160 °C, where the experiment was prematurely stopped after an almost complete conversion to NaNbO\(_3\) (contour plots of both experiments at 160 °C are also shown with a linear y-axis in Figure S4 in the Supporting Information). A full conversion to NaNbO\(_3\) would probably have occurred given enough time, as others have succeeded in producing phase-pure NaNbO\(_3\) under similar conditions after a longer time.\(^{26}\) Despite many similarities between the reaction schemes in the two NaOH concentrations, a few differences are still observed; first, the stability of HNa\(_7\)Nb\(_6\)O\(_{19}\)·15H\(_2\)O is higher in the 9 M solution at all temperatures, which is consistent with the literature,\(^{14}\) as the transformation from T-Nb\(_2\)O\(_5\) takes place earlier and the lifetime of the phase increases. Second, the opposite trend

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**Figure 1.** X-ray diffraction patterns for all appearing phases, with the main structural element for the previously known phases\(^{27,34-36}\) shown on the top. Gray areas indicate phases appearing at the same step in the reaction, but for different NaOH concentrations. Each diffraction pattern was taken from the slowest proceeding reaction (i.e., lowest temperature) and lowest possible NaOH concentration, where the phase was present, to optimize statistics.

**Figure 2.** Qualitative time-resolved phase evolution during hydrothermal synthesis of NaNbO\(_3\) in 9 M NaOH aqueous solutions as a function of reaction temperature. Vertical bars represent real measured data, while the colored areas between them are logarithmic interpolations. The areas are transparent to make overlapping phases visible. Complete contour plots at the temperature limits are shown at each side. Contour plot for 9 M NaOH at 420 °C has been adapted with permission from ref 25 (Copyright © 2018 American Chemical Society).
seems apparent for the following phases forming, resulting in a later onset of NaNB3O9 formation in 12 M NaOH, especially at lower temperatures.

In all of the experiments, regardless of temperature and NaOH concentration, a transient phase (no. 3 in Figure 1) appears directly after the formation of HNa3Nb2O10·15H2O. This phase could not be matched with any structure file in the Inorganic Crystal Structure Database (ICSD), Crystallography Open Database (COD) or International Centre for Diffraction Data (ICDD), as specified in Table S1 in the Supporting Information. The first reflection (0.71 Å⁻¹) of the HNa3Nb2O10·15H2O phase has the index (011) and seems to remain in this transient phase, while the two next major peaks at 0.79 and 0.81 Å⁻¹, indexed (101) and (110), disappear or shift. These three Bragg reflections originate from repeating [Nb6O19]⁸⁻ units, and the difference in the diffraction patterns might therefore indicate a change in how the units are tilted and separated by water and Na⁺ in certain directions. The following transformation of this transient phase leads to two new intermediate phases (nos. 4 and 5 in Figure 1) for NaOH concentrations of 9 and 12 M, respectively. These two phases could not be well matched with any structure in the ICSD, COD, or ICDD, as specified in Table S1 in the Supporting Information. As they both form from the same starting point and also evolve into the same structure in the Supporting Information, along with the reduced structure functions, F(Q), C,12,35 possibly explaining why this phase is observed in the temperature region 285 °C.12

To shed more light on the origin of the unassigned low-Q diffraction lines in the T-Nb2O5 precursor diffraction pattern in Figure 1 and illuminate their dependence on the time since the suspensions were prepared, ex situ total scattering data were obtained for unheated suspensions of T-Nb2O5 in 9 and 12 M NaOH aqueous solutions, aged for various times. Figure 3 presents the PDFs at a local range obtained from the total scattering data of fresh and aged (1, 10, 24 h) suspensions with 12 M NaOH. Bond lengths and trends are indicated with similar colored lines and arrows for (a) a typical tetragonally distorted [NbO6]³⁻ octahedron, (b) neighboring Na—O units in the sodium hexaniobate structure, (c) a [NbO18]⁻ Lindqvist ion, and (d) a fragment of the T-Nb2O5 structure. Two similarly colored arrows pointing toward one another indicate a narrowing of a peak, while one arrow pointing upward or downward indicates growth or shrinking of peak intensity.
pentagonal bipyramid, seem to shift to higher r-values pointing to stretching of the bonds, before shrinking, further supporting the breaking up of pentagonal bipyramids. Such a breakup of the structure would require more oxygen entering the structure for the coordination around the Nb atoms to be maintained. This negative charge is likely to be neutralized by Na⁺ entering the structure, possibly explaining the increase of a peak at 2.85 Å, as this is the hydrogen-bond length expected between Na—O octahedra, presented by a gray line separating two Na—O octahedra in the inset (b) in Figure 3. When looking at the reduced structure functions, 〈F(Q)〉 in Figure S5b, the long-range order of the fresh suspensions matches well with the T-Nb2O5 structure, and there is a significant contribution from this structure even after 10 h of aging for both NaOH concentrations. Despite this, simultaneous fitting of the T-Nb2O5 and HNa7Nb6O19·15H2O to the PDFs obtained for 12 M NaOH suspensions (Figure S6 in the Supporting Information) shows that the 10 h aged suspension can be well described by the HNa7Nb6O19·15H2O structure alone. The PDFs for the 1 h aged 12 M suspension can be described well with the T-Nb2O5 structure, with only a small contribution from HNa7Nb6O19·15H2O similar to the expected PDF of a Lindqvist ion. This suggests that the HNa7Nb6O19·15H2O structure is forming through a gradual change in the local crystal structure of T-Nb2O5, which would generate a large unit cell explaining the low-Q diffraction lines appearing for this phase in Figure 1.

To get a clearer view on how the different intermediate phases nucleate and grow into particles, simultaneous in situ SAXS/WAXS measurements were obtained. Figure 4 presents the in situ SAXS data for the hydrothermal synthesis of NaNbO3 at 220 °C in a 9 M NaOH solution. The wide-angle X-ray scattering (WAXS) data (presented in Figure S7 in the Supporting Information) were used to determine the phases present during the reaction, and these phases are specified in the right panel of Figure 4. The plot in the inset shows the slope of the curves in the low Q-range (0.0045—0.0055 Å⁻¹), extracted by a fitting straight line to the double-logarithmic measured data in this low Q-range, for 4—16 min of heating. The SAXS data from the unheated precursor contains a broad distinct feature, which is assumed to originate from the T-Nb2O5 precursor particles or an amorphous phase. This feature disappears quickly upon heating and directly after its disappearance, a weak sign of another feature at approximately 0.01—0.03 Å⁻¹ appears. This second feature is interpreted as the transient presence of a new set of particles, but the crystal structure(s) cannot be unequivocally identified from the WAXS data in Figure S7 due to the low time-resolution and limited Q-range. Even so, several reflections are appearing at similar Q-values (1.68, 2.05, 2.35, 2.40, 2.70, 2.80 Å⁻¹) as for the two intermediate polyoxoniobates in Figure 1. The next phase identified with WAXS is Na2Nb2O6·H2O, and it can be seen that the SAXS slope at low Q increases steadily during the growth of this phase, before stabilizing at the same time (13 min) as the transformation from Na2NbO5·H2O to NaNbO3 completes.

To summarize, several intermediate phases are observed during the hydrothermal synthesis of NaNbO3. To understand the structural evolution from one phase to the next, one approach is to visualize the NbO6 units of each phase, as seen in the proposed reaction scheme in Figure 5. The precursor T-Nb2O5 consists mostly of octahedra [NbO6]7⁻ and pentagonal bipyramids [NbO7]9⁻ with occasional tetrahedra [NbO4]3⁻. As the PDFs of the unheated T-Nb2O5 suspensions in Figure 3 shows, [NbO19]⁸⁻ units form at local scales rather quickly upon submerging the solid T-Nb2O5 in concentrated NaOH solutions, resulting in more [NbO6]⁷⁻ at the expense of [NbO7]⁹⁻ units, as soon as Na⁺ (along with charge-balancing oxygen atoms) and water enter the structure. Na⁺ and water could, for instance, enter the cavities of the T-Nb2O5 structure, resulting in the stretching and breaking of bonds between corner-sharing pentagonal bipyramids. This gradual change in the local environment is the foundation for forming HNa7Nb6O19·15H2O, with a Na/Nb ratio of 7/6. The Na/Nb ratio in Na2NbO5·H2O is 1, and thus the intermediate phases appearing between these two phases should have a ratio between 1 and 7/6 as a gradual expulsion could be expected. The water/Nb ratio should decrease successively from 15/6 in HNa7Nb6O19·15H2O to 7/6 in Na2NbO5·H2O, which could be the reason for the consistent shift to the right for the diffraction lines at low Q-values (except for the polyoxoniobate in 12 M NaOH). Previous literature predicts fragmentation and reorganization of [NbO19]⁸⁻ units to be the main event in highly alkaline solutions. Thus, a mechanism involving the building of the Na2Nb2O6·H2O staircase-like chains from [NbO19]⁸⁻ fragments is not unlikely. The other intermediate phases appearing between HNa7Nb6O19·15H2O and Na2NbO5·H2O could thus also consist of similar fragments. The transformation of Na2NbO5·xH2O (x < 1) to NaNbO3 expels the final water in the structure, causing the octahedra to become corner-sharing instead of edge-sharing for the charge to be distributed more evenly through the structure when water is not screening the charges any longer.

**Effects of Reaction Conditions on Crystallite Size and Unit Cell Volume.** Figure 6a shows the refined crystallite size of the final NaNbO3 product at various temperatures in 9 and 12 NaOH aqueous solutions. The refinements showed that the space group Pbcn gave a good fit for NaNbO3 formed below 340 °C, while for 340 °C and above, Pnma gave a better fit.

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![Figure 4](https://doi.org/10.1021/acs.inorgchem.0c02763)
This temperature is slightly lower than previously published bulk values for this phase transition, which predicts a transition upon heating around 370–400 °C. This suppression of the phase-transition temperature can be explained as a finite-size effect, often observed for ferroelectric oxides. Two different regimes are apparent for temperatures above and below ≈285 °C. Below this temperature, the crystallite size appears fairly temperature-independent with values of 35–50 nm, being slightly smaller for the experiments in 12 M NaOH solutions. Above ≈285 °C, the crystallite size is larger and seems to decrease with increasing temperature. The refined crystallite size of Na2Nb2O6·H2O in Figure 6b shows an increasing trend with increasing temperature and NaOH concentration, and the pseudo-cubic unit cell volume in Figure 6c increases with temperature and is affected by the NaOH concentration. The increase in the unit cell volume for higher temperatures is probably due to the elevated temperatures at which the measurements were performed. It is not likely to originate from a finite-size effect, as such an effect has previously shown to give an opposite trend for this materials class (i.e., smaller crystallites gives a larger unit cell).

The difference in temperature effect on the crystallite size of NaNbO3 for reaction temperatures below and above ≈285 °C in Figure 6 shows that there is a difference in the growth mechanism for the two regimes. The features in the in situ SAXS signal in Figure 4 suggests that only one set of particles forms during the hydrothermal synthesis of NaNbO3 at 220 °C, as there is only one new feature to appear in the higher Q-range. This suggests that the particles formed in the beginning of the synthesis are converted directly into the next phases and not through a dissolution−precipitation mechanism at this temperature. The consistently larger crystallite size of Na2Nb2O6·H2O compared to NaNbO3, could thus be explained through a gradual conversion of the Na2Nb2O6·H2O particles to NaNbO3, by the expulsion of water from the structure.

**Figure 6.** Crystallite size of (a) NaNbO3 and (b) Na2Nb2O6·H2O and (c) pseudo-cubic unit cell volume of NaNbO3 as a function of temperature prepared by hydrothermal synthesis in 9 and 12 M NaOH aqueous solutions. The gray line indicates the border between two regimes showing different behaviors. Marker types indicate different space groups of the NaNbO3 product.

**Effects of Reaction Conditions on the NaNbO3 Reaction Kinetics.** The effects on the kinetics involved in the final step in the reaction scheme as well as the nucleation and growth of NaNbO3 are presented in Figure 7. The kinetics were quantified using the Johnson−Mehl−Avrami (JMA) equation \( \alpha = 1 - e^{-Kt^n} \), where \( \alpha \) is the phase fraction, \( K \) is a rate constant, and \( n \) depends on the transformation mechanism. The JMA slope \( n \) and intercept \( K \) were calculated by transforming the phase fraction with the Sharp−Hancock method.
The JMA slopes \((n)\) in Figure 7a are in the range of 2−4, with a clear difference between the reactions at temperatures above and below \(\approx 285 ^\circ C\). Below \(\approx 285 ^\circ C\), the \(n\) values are strongly dependent on the NaOH concentration, having larger values for 12 M solutions. Such a difference in the \(n\) value could imply that there is a more restricted nucleation and/or growth of NaNbO3 in 9 M compared to 12 M suspensions. Above \(\approx 285 ^\circ C\), the difference between the two NaOH concentrations appears to decrease, although this should be confirmed with more experiments. The JMA intercepts \((\ln K)\) are presented in an Arrhenius plot in Figure 7b and seem to be independent of NaOH concentration. Again, a clear difference is seen between the two regimes below and above \(\approx 285 ^\circ C\), with significantly different Arrhenius slopes, from which the activation energy can be calculated. A significantly lower activation energy can be seen above \(\approx 285 ^\circ C\) (23.4 kJ/mol), compared to below \(\approx 285 ^\circ C\) (146.7 kJ/mol). This could be related to the less crystalline preexisting phase in the high-temperature region, giving a larger surface area and less rigid species for nucleation and growth.

By comparing the phase evolution in Figure 2 with the crystallite size in Figure 6, it is interesting that the three reactions resulting in the largest crystallite size were the reactions going through the poorly crystalline dehydrated \(\text{Na}_2\text{Nb}_2\text{O}_6 \cdot x\text{H}_2\text{O}, x < 1\), phase on their way to NaNbO3. These reactions also have a lower activation energy and JMA slope compared to the reactions where the highly crystalline \(\text{Na}_2\text{Nb}_2\text{O}_6 \cdot \text{H}_2\text{O}\) phase is present. The low crystallinity of the dehydrated phase opens for a dissolution–precipitation-based transformation to NaNbO3, resulting in a decreasing crystallite size with decreasing temperature, which is what is observed.

The complex temperature-dependent reaction scheme and its effect on the kinetics and product crystallite size presented here underline the importance of in situ studies during the hydrothermal synthesis of oxides. The revealing of two distinctly different growth regimes may offer important insight when untangling the growth mechanisms, leading to the various sizes and morphologies resulting from the hydrothermal synthesis of NaNbO3.

## CONCLUSIONS

The entire reaction scheme, including several known and unknown intermediate phases, was observed during the hydrothermal synthesis of NaNbO3, and through observations over a large temperature range for two different NaOH concentrations, the relationship between them has been established. Ex situ PDF indicated that the \(\text{T-Nb}_2\text{O}_5\) precursor partially transformed into \(\text{HNa}_7\text{Nb}_6\text{O}_{19}\cdot 15\text{H}_2\text{O}\), before heating was initiated and a complete transition would occur quickly upon heating. After some time, depending on temperature and NaOH concentration, \(\text{HNa}_7\text{Nb}_6\text{O}_{19}\cdot 15\text{H}_2\text{O}\), consisting of \([\text{Nb}_6\text{O}_{19}]^{8-}\) clusters, was destabilized and fragmentized. These fragments are the most likely building blocks for the subsequent formation of polyoxoniobates, whose structure depended on the NaOH concentration. Following these polyoxoniobates was \(\text{Na}_2\text{Nb}_2\text{O}_6 \cdot \text{H}_2\text{O}\), which appeared in a dehydrated form at temperatures \(\geq 285 ^\circ C\), before converting into the final phase, NaNbO3. The total reaction rate increased with decreasing NaOH concentration and increasing temperature, due to the increased stability of the intermediate polyoxoniobate phases. The final NaNbO3 particles had an orthorhombic structure with the \(\text{Pbcm}\) space group \(<340 ^\circ C,\) and \(\text{Pnma} \geq 340 ^\circ C\), showing suppression of the phase-transition temperature due to finite-size effects. Thermal expansion of the unit cell was observed, probably due to the elevated temperatures at which the measurements were performed.

Two distinctly different growth regimes for NaNbO3 were observed, based on the observed phase evolution and the resulting growth kinetics of NaNbO3, for temperatures below and above \(\approx 285 ^\circ C\). Below this temperature, the resulting crystallite size of NaNbO3 was independent of the reaction temperature and the NaOH concentration due to NaNbO3 growing at the expense of a less crystalline intermediate phase, \(\text{Na}_2\text{Nb}_2\text{O}_6 \cdot \text{H}_2\text{O}\). A high activation energy of 146.7 kJ/mol and pH- and temperature-dependent \(n\)-values were observed. When NaNbO3 grew at the expense of a less crystalline dehydrated intermediate phase for temperatures \(\geq 285 ^\circ C\), the resulting crystallite size was larger and showed a temperature-dependent trend typical for the dissolution–precipitation mechanism. The activation energy was significantly lower in this regime (23.4 kJ/mol) with \(n\)-values of \(\approx 2.0−2.5\).

## ASSOCIATED CONTENT

* Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c02763.

VESTA visualizations of relevant structures; in situ heating profiles; phase evolution diagram with contour plots for the reactions in 12 M NaOH; contour plots of...
the two reactions at 160 °C with linear y-axis; pair-distribution functions and reduced structure functions from the in situ total scattering experiments; fits of niobate and hexaniobate structures to selected pair-distribution functions; and WAXS data recorded simultaneously with our SAXS data (PDF) NaNbO₃·28SC·12M (MP4)

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**Notes**

The authors declare no competing financial interest.

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