**Rationalization of hydrothermal synthesis of NaNbO3 by rapid *in situ* time resolved synchrotron X-ray diffraction**

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**Abstract**

*In situ* characterization of formation of crystalline phases during conventional hydrothermal synthesis is experimentally challenging. Here, we report an *in situ* time-resolved synchrotron X-ray diffraction study during hydrothermal synthesis of the perovskite phase NaNbO3 using a high pressure custom-made capillary cell penetrable to X-rays. The high time resolution (< 1 s) revealed a sequence of short-lived intermediate phases, including several unknown phases before the final perovskite phase NaNbO3 was formed. These new findings reveal the complexity of the hydrothermal synthesis of NaNbO3. The time resolved *in situ* characterization method presented here has a great potential for the study of fast reactions during hydrothermal synthesis.

**Introduction**

Hydrothermal synthesis is a low temperature route to well-crystalline oxide materials reducing challenges with agglomeration and coarsening taking place at higher temperatures.1 High pressure generated during the synthesis enhances the solubility of the precursors, changes the properties of the solvent and increases the reaction rate. To obtain a high pressure, stainless steel containers, microwave ovens or supercritical flow reactors are usually used. However, the reactors are non-penetrable to X-rays, thus knowledge regarding nucleation and formation mechanisms of the oxides formed under hydrothermal conditions is scarce in the literature. Several intermediate phases may be present during the reaction course, some of them short-lived and are therefore challenging or impossible to study using *ex situ* characterization techniques. However, knowledge of real-time reactions and formation scheme of the materials by using *in situ* characterization techniques will significantly enhance the understanding of the synthesis method and simplify the design of new protocols.

The perovskite NaNbO3 has attracted a lot of attention due to its ferroic properties and being the end member of the well-known piezoelectric material K0.5Na0.5NbO3 (KNN).2,3 Several intermediate phases have been reported by both *in situ* and *ex situ* methods during formation of NaNbO3 by hydrothermal synthesis using a solid niobium oxide precursor in aqueous NaOH solution.4-9 The reported formation mechanism starts with niobium oxide being transformed into HxNa8-xNb6O19 · nH2O, with the main building block being the Lindquist ion, Nb6O19.8, 9 Further, a transition to Na2Nb2O6·n H2O occurs through several intermediate phases before the perovskite NaNbO3 forms.9 The transformation between these phases has not been assessed completely although Modeshia *et al.*10 observed a new unknown short-lived intermediate phase using *in situ* energy dispersive XRD. We have recently gained preliminary information about this system in a recent *in situ* powder XRD (PXRD) study showing that several short-lived intermediate phases might be present. 9

Here we report on the investigation of the reaction course during hydrothermal synthesis of NaNbO3 by combining the use of a high pressure custom-made capillary cell penetrable to X-rays and *in situ* time-resolved synchrotron X-ray diffraction. We present the first time-resolved *in situ* PXRD study with high acquisition rate of the hydrothermal formation of NaNbO3. We show the potential of this set-up by observation of short-lived intermediate phases in the formation of NaNbO3 and its usefulness to optimize and rationalize the reaction conditions.

**Experimental**

T-Nb2O5 precursor powder was made by precipitation from (NH4)NbO(C2O4)2·5H2O (0.25 mol, Sigma-Aldrich, 99.99 %) by using NH4OH (25 wt%, Emsure) followed by calcination at 600 °C for 12 h as described by Mokkelbost *et al*.12 Highly concentrated slurries by adding T-Nb2O5 powder to solutions of 9 M and 12 M NaOH resulting in a sodium to niobium ratio of 9.5 and 13.2 were made to maximize the output XRD signal. The resulting slurry was injected into the *in situ* cell by using a plastic syringe.

*In situ* PXRD data were collected in transmission mode at the Swiss-Norwegian Beamline (BM01A) at the European Synchrotron Radiation Facility using a monochromatic beam with wavelength of 0.6776 Å. A custom-made *in situ* cell inspired by the previously described setup by Becker *et al.* and Jensen *et al*.13,14 was used where the reaction chamber is a single-crystal sapphire capillary with an outer diameter 1.15 ± 0.1 mm and inner diameter of 0.8 ± 0.08 mm. The capillary was connected to Swagelok® fittings with graphite ferrules which were stabilized by an adjustable steel frame. Pressure of 250 bar was provided by an HPLC pump connected to one end of the capillary, while keeping the other end closed. A volume of the sapphire capillary was heated by a hot air gun to reach sub- and supercritical conditions and the temperature was calibrated by refining the unit cell expansion of boron nitride.15 The blower was ramped up to the synthesis temperature when pointing away from the sample. Once the required pressure and temperature was reached the data acquisition was started. Only then was the blower remotely swung into position, providing quasi instant heating, allowing detection of the very first instance of the reactions. The capillary was exposed to X-rays and the diffracted signal was detected by a Pilatus 2M16 detector with acquisition times varying between 0.1 and 5 sec depending on the experiment. The as-recorded diffraction data were treated using the PILATUS@SNBL platform.17 Topas 5 (Bruker AXS, Germany), operating in launch mode, was used for the Rietveld refinements. The instrumental resolution function, wavelength calibration and detector distance corrections were performed using a NIST 660a LaB6 standard. The default approach was refining the unit cell parameters, Lorentzian isotropic size parameter, scale factors and Chebychev background parameters. The unit cell parameters were fixed for certain phases in ranges where two or more phases were overlapping and the scale factor approached the lower limit to avoid breakdown of the refinement. The change in background area was determined by describing the broad background feature with a SPVII peak while fixing the Chebychev parameters. The isotropic temperature factors and atomic positions were fixed to the literature values for each phase. The space group of the end products was determined using an averaged diffraction pattern spanning over the last 20 s of the experiment to improve the statistics.

Structural *ab initio* determination on the lattice parameters of unknown phases was accomplished using the McMaille program18 for the first 20 peaks. The choice of a good unit cell was based on a high figure of merit and that all peaks had to be identified. Finally, the more symmetric unit cell was prioritized. The chosen unit cells were used to refine the diffraction pattern with the space group with the lowest symmetry of their crystal system because they contain the least extinction condition.

**Results and discussion**

*Phase development under supercritical conditions*

**Figure 1** presents the 2D contour plot of the evolution of phases in the Na-Nb-O system in 9 M NaOH under supercritical conditions at 423 °C and 250 bar including schematics of the phase development. Diffraction lines for the unknown phases are given in Table S1. In the unheated precursor slurry, diffraction lines from T-Nb2O5 (PDF 04-007-0752)19 (PXRD of the dry precursor material is provided in Figure S1) are observed along with additional diffraction lines at low angles (Phase A). These low angle reflections are likely a result of breakup of the pristine T-Nb2O5 due to incorporation of sodium ions and/or water into the crystal structure. As the temperature is increasing, phase A disappears and T-Nb2O5 transforms rapidly (~1 s) to Na7HNb6O19·15 H2O (PDF 00-062-0888).20 Still, a complete transformation of T-Nb2O5 is not finished before new diffraction lines (most intense at 4.68°) appear after 1.4 s, belonging to a new phase B. This phase is extremely short-lived (0.4 s) and another new phase C with diffraction lines at lower angles (4.78 and 4.58º) is the only one observed after 1.8 s. Phase C was determined by ab initio refinements to belong to the monoclinic lattice system. Lattice parameters are given in Table S2. Moreover, another phase (phase D) similar to an unknown phase previously observed *ex situ* by Wu *et al*.7 appears after a total heating time of 2.9 s. This phase was determined by ab initio refinements to belong to the triclinic crystal system (Table S2). After 3.5 s, reflections due to the formation of NaNbO3 are observed and after another 1 s this is the only phase present. During this short time, the NaNbO3 crystallites grow to a size of ~225 nm (Figure 2a), and after 6 s of total heating time no further change is observed. The gradual decrease and subsequent stabilization of the background area (Figure 2b), stemming from the ionic and/or amorphous species in the solution, indicates that the formation of NaNbO3 occurs at least partially through ionic and/or amorphous species as well as the pre-existing crystalline phases. The final NaNbO3 product was refined with the space groups Pmmn (no.59, PDF 04-019-3436) and Pnma (no. 62, PDF 01-080-8672) which both describes the structure equally well (Table S2), supported by findings of Peel *et al.*21

*Phase development under subcritical conditions*

By going into subcritical conditions (215 °C and 250 bar), the rate of the reactions is lower but still a complex reaction scheme with several phases involved is observed. Contour plots for the phase development of the Na-Nb-O phases in both 9 and 12 M NaOH at this condition are presented in Figure 3 a) and b), respectively including schematics of the phase development.

The transition from T-Nb2O5 to Na7HNb6O19·15 H2O happens over a period of 7 s at pH 9 (Figure 2a) after heating is initiated. Phases B and C are observed after 6 and 8 s and these phases have longer lifetimes compared to at supercritical conditions. The hydrated phase Na2Nb2O6·H2O (PDF 04-014-2939),22 which was not observed at 423 ºC, appears after 1.9 min without the transformation through phase D. The initial formation of the product NaNbO3 occurs almost simultaneously with Na2Nb2O6·H2O after 2.9 min and the diffraction lines of both phases grow quickly (Figure 4a). After 4 min of heating, the scale factor (Figure 4b) of Na2Nb2O6·H2O reaches a maximum while the size stabilizes. The scale factor then decreases continuously while the size remains stable for approximately 7 more min and then quickly plummets as NaNbO3 reaches the end of its growth at 83 nm. This suggests that NaNbO3 grows mainly on the expense of Na2Nb2O6·H2O through a solid-solid reconstructive phase transition, where the water is expelled from the hydrated structure over time. A complete conversion to NaNbO3 happened after a significantly longer total heating time (16 min) compared to supercritical conditions. Also, the background area in the data was stable throughout the experiment except for a small decrease during the first few seconds as seen in for 2θ=12-15° in Figure 3a. This confirms the subcritical conditions ability to form crystalline phases from the ionic or amorphous species in the solution.

*Phase development at more alkaline conditions*

By increasing the pH to 12 at subcritical conditions (Figure *3*b), no traces of phase A are observed in the unheated precursor, but rather a higher amount of Na7HNb6O19·15H2O. The Na7HNb6O19·15H2O phase is still present also when the very short-lived phase B and the new unknown phase E appears. A*b initio* refinements determined that the phase belongs to the monoclinic crystal system (Table S2). Attempts of fitting he diffraction lines (Table S1) of phase E shows that phase E might have similar characteristics to an oxyhydroxide phase (NaNb2O5(OH)·3H2O, space group P21/c23, ICSD 193826, Figure S2) but several unidentified peaks are undermining the certainty of this result. The presence of a similar phase should still be considered, though, as its building blocks are similar to the pre-existing Na7HNb6O19·15H2O phase as well as the next phase to be formed, Na2Nb2O6·H2O, with edge- and corner-sharing octahedral networks with sodium ions and water in-between (Figure S3). Further, a gradual transformation from Na2Nb2O6·H2O to NaNbO3 over 10 min is observed (Figure 5). The NaNbO3 crystallites grow to a size of approximately 69 nm in a matter of 12 min total reaction time, following a similar reaction course as in 9 M NaOH. A small but significant difference of the conversion rate is observed in the favor of the higher reaction rate at higher pH. A comparison of the diffractograms of the products at their respective synthesis temperatures (Figure 6a) shows evidence of a finite size effect since the unit cell expands (Figure 6b) as the crystallites get smaller. The crystallites grows more at increasing temperature.

*Potential of the in situ method*

The general scheme for the phase evolution independent of the reaction conditions is the dissolution of the niobate precursor forming the hexaniobate Na7HNb6O19·15H2O phase. This phase is followed by formation of a very short-lived phase B surveyed by the appearance of most probably an oxyhydroxyniobate phase. At lower temperatures the hydrated Na2Nb2O6·H2O phase forms before the target NaNbO3 phase while the hydrated phase is not formed at supercritical conditions. Instead, several unknown phases occur in addition to a significant amount of ionic/amorphous species still being in the solution. This confirms that the supercritical conditions enhances the reaction kinetics. The crystallite size of NaNbO3 increases with increasing reaction temperature showing a faster growth rate at higher temperature but is decreasing with increasing pH at subcritical conditions as illustrated in Figure 7. The different phase developments during the early stages of the synthesis might also give a different nucleation rate, in turn being responsible for the different crystallite sizes. Included in Figure 7 is also the time for NaNbO3 to nucleate and the reaction time for complete conversion into the NaNbO3 end product.

The fast *in situ* XRD experimental method presented allows thus in general to investigate quantitatively the reaction product (*i.e.* phase purity, crystallite size and shape, activation energy and crystallinity) as a function of three experimental variables, pressure, temperature and pH. Furthermore, understanding is gained on the reaction pathways (i.e. intermediate phases). The experimental method presented here is also well suited for Design of experiments (DOE) by scanning over a wider range of reaction parameters in a short amount of time. Further studies will provide a detailed analysis. The understanding of the complex phase development in this Na-Nb-O system is important for the preparation of the more complex KNN-based materials by hydrothermal synthesis.

**Conclusion**

A robust and flexible method for the study of fast reactions and hence short-lived intermediate phases during hydrothermal synthesis has been developed by combining time-resolved *in situ* synchrotron X-ray diffraction and a high pressure custom-made capillary cell. The technique is used to reveal the fast reactions in the Na-Nb-O system going through a rapid sequence of short-lived intermediate phases (< 1 sec) to form NaNbO3. The *in situ* characterization method has a great potential for the study of fast reactions during hydrothermal synthesis and thereby gaining important information about the nucleation and formation of the oxide materials. The method allows the study of three experimental variables, pressure, temperature and pH and quantitatively assesses the influences this has on the reaction product allowing to rationalize the choice of optimal reaction conditions.

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**Figures**

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**Figure 1** 2D contour plot of the evolution of phases in the Na-Nb-O system during hydrothermal synthesis in 9 M NaOH at 423 °C and 250 bar including a schematic showing the phase development.



Figure 2 Crystallite size of NaNbO3 and background area originating from ionic or amorphous species in 9 M NaOH solution under supercritical conditions (423 °C and 250 bar).





Figure 3 2D contour plots of the evolution of phases in the Na-Nb-O system during hydrothermal synthesis in a) 9 M NaOH and b) 12 M NaOH at 215 °C and 250 bar including schematics showing the phase development. The horizontal lines marks change in acquisition rate.



Figure 4 a) Crystallite size and b) scale factor of Na2Nb2O6·H2O and NaNbO3 at 9 M NaOH, 215 °C and 250 bar



Figure 5 a) Crystallite size and b) scale factor of Na2Nb2O6·H2O and NaNbO3 at 12 M NaOH, 215 °C and 250 bar.



Figure 6 Comparison of a) the end products and b) the pseudocubic unit cell parameters as a function of crystallite size at their respective synthesis temperatures.

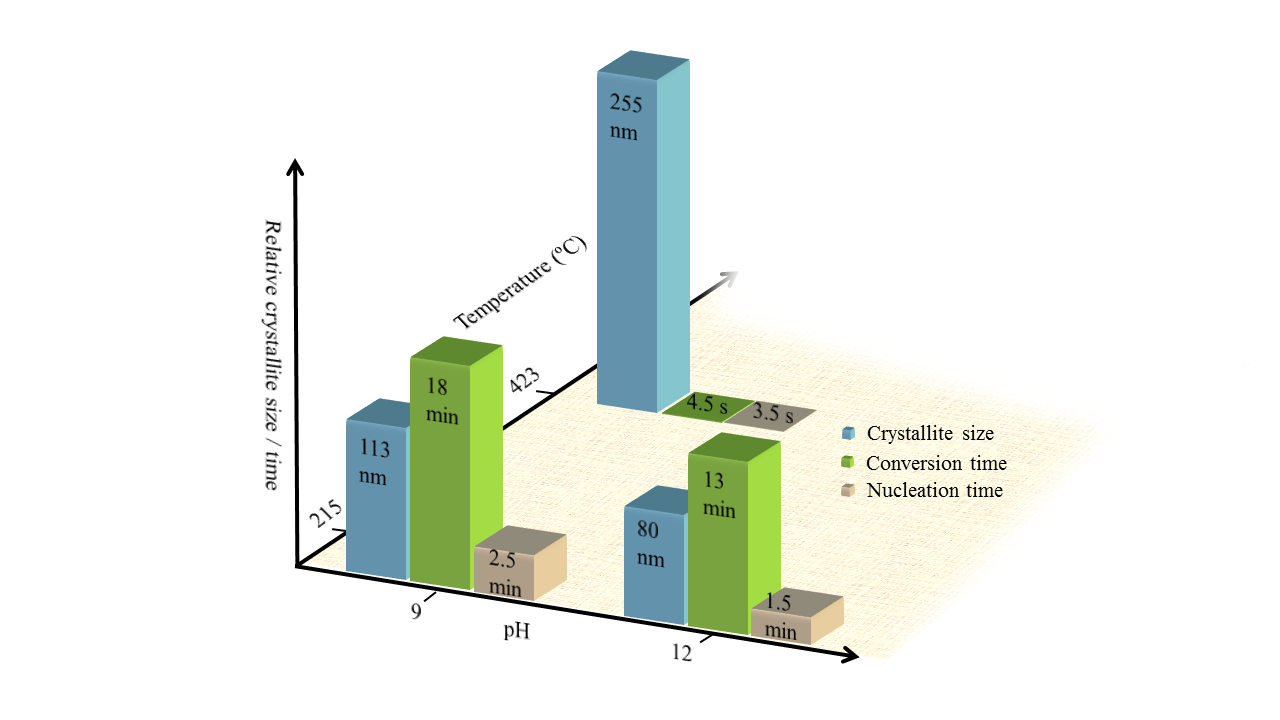


Figure 7 Schematics showing the potential of the in situ fast X-ray diffraction method illustrated here by plotting the crystallite size, nucleation time and conversion time of NaNbO3 as a function of reaction temperature and pH.