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Kinetics of the hydrothermal synthesis of nanosized KxNa1-xNbO3

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Hydrothermal synthesis is an efficient method of making nanosized functional oxide materials, and has also been used to synthesize KxNa1-xNbO3 solid solution, a promising lead-free piezoelectric material. However the control of the nucleation and growth during the synthesis to tailor the properties of the materials is challenging and this work aimed to solve the challenges reported regarding stoichiometry and size of KxNa1-xNbO3 formed by hydrothermal synthesis by *in situ* X-ray diffraction. KxNa1-xNbO3 crystallites of 18-65 nm with a controlled stoichiometry were produced by varying the Na/K ratio in the precursor solution, the solvent type and the final reaction temperature. The reaction proceeds via rapid formation of a potassium sodium hexaniobate intermediate phase during heating, which converts to KxNa1-xNbO3 at the reaction temperature. The Na occupancy in KxNa1-xNbO3 was found to correlate with the Na content in the intermediate phase and decreases with increasing temperature. We show that the *in situ* technique is powerful method to in general be able to prepare oxide nanoparticles with designed properties.

Introduction

There has been an increasing focus on harvesting the effects of nanosized piezoceramics,1 and in later years, KxNa1-xNbO3-based materials have emerged as promising lead-free piezoelectrics.2,3 Thus, synthesis routes to nanostructured KxNa1-xNbO3 with controllable stoichiometry are desired to exploit their potential as sensors and actuators in nanodevices.4 Wet chemical methods like hydrothermal synthesis provide low-temperature, water-based routes to a variety of functional oxides,5 but to control the stoichiometry and crystallite size of the product is demanding particularly in case of solid solutions such as KxNa1-xNbO3. Some studies have unveiled the challenges connected with the different solubility of Na and K niobate salts in water6,7 motivating the change to less polar solvents,8 but the actual effect on the reaction mechanism is still to be understood. Handoko *et al.* and Zhang *et al.* experienced challenges with preparing the KxNa1-xNbO3 solid solution for with hydrothermal synthesis7,9 and while others have obtained solid solutions, the crystallite sizes have been in the micrometer range.9,10 Although some studies propose a dissolution-precipitation process for the hydrothermal synthesis of KxNa1-xNbO3, similar to the mechanism observed for KNbO3,4 the majority of the literature agrees that the reaction from Nb2O5 in a solution of NaOH and KOH goes through an intermediate phase, K4+xNa4-xNb6O19 · 9 H2O (0 < x < 4).7,11–13 Sun *et al.* suggested that KxNa1-xNbO3 forms through a reaction between the K4+xNa4-xNb6O19 · 9 H2O intermediate phase and remnants of the Nb2O5 precursor 11 while López-Juãrez *et al.* suggested that K4+xNa4-xNb6O19 · 9 H2O only expels water and excess alkali to form KxNa1-xNbO3.12 These studies show that the hydrothermal synthesis is inherently challenging to study as the reaction takes place inside a closed reaction chamber,14 and the importance of *in situ* studies for further advances is evident.

Here we present here the first *in situ* time-resolved X-ray diffraction study of hydrothermal synthesis of KxNa1-xNbO3, revealing the effects of temperature, Na/K ratio in the precursor solution and type of solvent on the reaction kinetics, final stoichiometry and crystallite size of the product. We use the *in situ* data to explain why and how the crystallite size as well as the final stoichiometry can be controlled by tailoring the reaction temperature and the chemistry of the precursor solution.

Results

General reaction scheme

A similar phase evolution was revealed for all the experiments, exemplified by the reaction at 210 °C, 250 bar and *R* = 0.5 without ethanol, in Figure 1a. Figure 1b-d present single diffraction patterns of the three distinct phases, recorded at different times. The pristine slurry consisted of T-Nb2O5 and a broad feature indicating the presence of amorphous Nb-based species (Figure 1b). The broad feature is highlighted by a light blue area. The amorphous species and most of the T-Nb2O5 precursor instantaneously dissolved during heating. Simultaneously, the intermediate phase potassium sodium hexaniobate, K4+xNa4-xNb6O19 · 9 H2O (Figure 1c) appeared, a

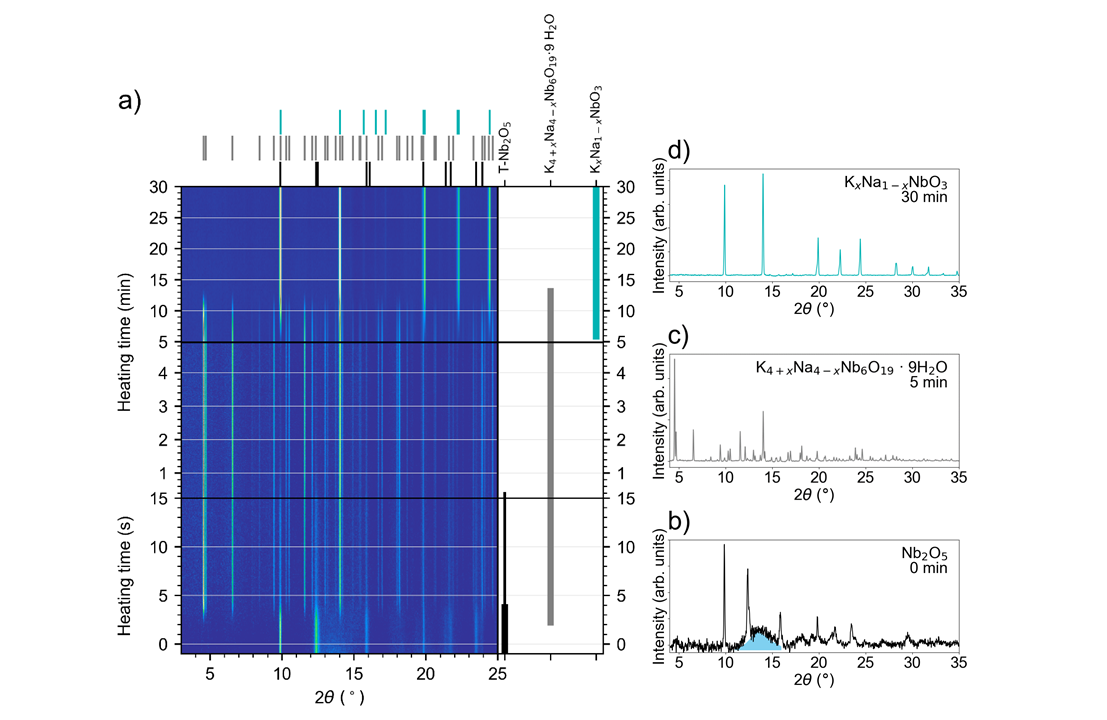


Figure 1 a) Phase evolution during hydrothermal synthesis of KxNa1-xNbO3 at 210 °C for *R* = 0.5. Horizontal dividers indicate a change in time-resolution. Figures b-d are single diffractograms of the three distinct phases observed, in addition to a broad feature represented as a light blue area in Figure d. The constant background signal from the capillary and solvent has been subtracted for clarification. The wavelength used was 0.6776 Å.

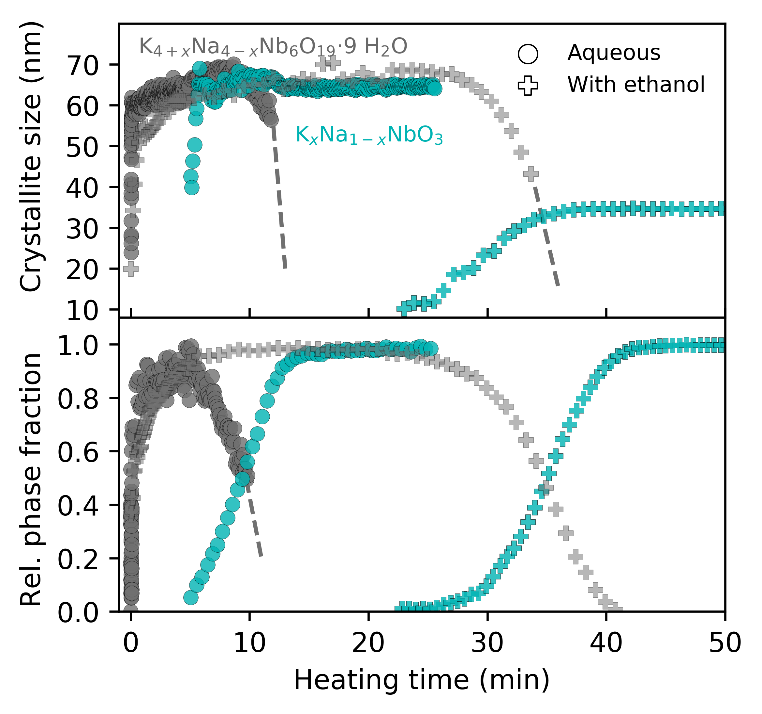
phase first reported by Kennedy.15 After approximately 0.5 min the T-Nb2O5 precursor was completely dissolved. The KxNa1-xNbO3 perovskite phase started to form after about 5 min. The intermediate phase slowly disappeared as the amount of KxNa1- xNbO3 evolved, resulting in KxNa1-xNbO3 as the final phase (Figure 1d). Figure 2 shows the time-resolved crystallite sizes and relative phase fractions during the nucleation and growth of the intermediate phase and KxNa1-xNbO3 inaqueous solution and in water/ethanol mixture. The crystallite size and relative phase fractions of the intermediate phase increased rapidly during the first seconds before stabilizing for a few minutes. The crystallite size and relative phase fraction of the intermediate phase continued to be constant for a few minutes after the nucleation of KxNa1-xNbO3 had started. In the aqueous solution, the crystallite size and relative phase fraction of the intermediate phase decreased after ~8 min, and within the next 6 min the phase completely disappeared, at which point the amount of KxNa1-xNbO3 formed ceased. For the syntheses in water/ethanol mixture, the reaction scheme was similar as in aqueous solution, but the intermediate phase was stable for a longer time delaying the onset of nucleation of KxNa1-xNbO3 by ~25 min.

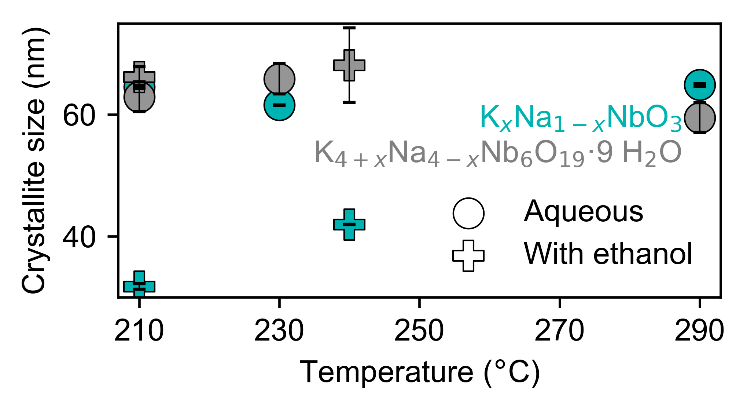
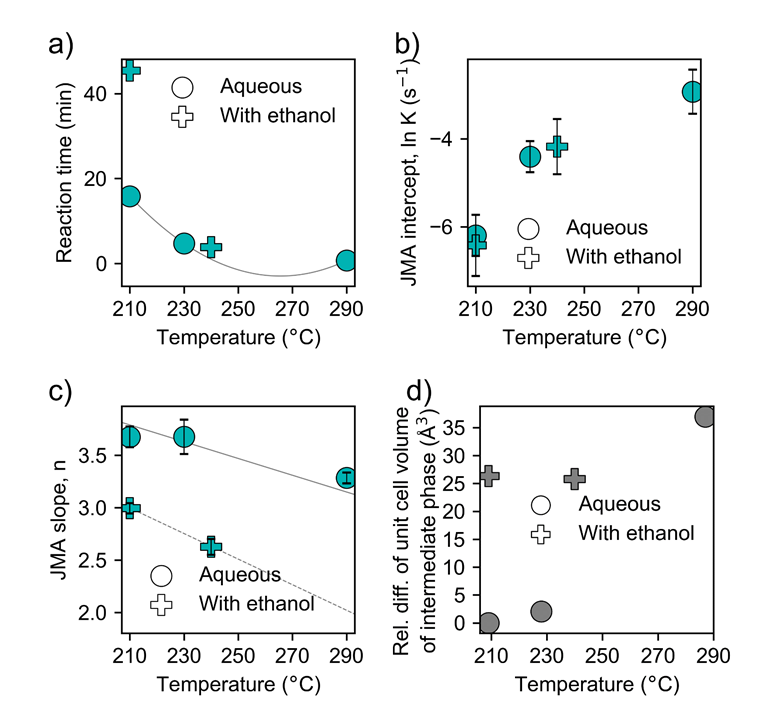
Figure 2 Crystallite size and relative phase fraction evolution of the intermediate phase and final product KxNa1-xNbO3 during hydrothermal synthesis at 210 °C for *R* = 0.5, in aqueous solution and water/ethanol mixture. Dashed lines are added for clarification where the refinements were unstable.

The indexing of the intermediate phase gave a monoclinic unit cell for all samples with varying *R*-values and temperatures (see Figure S2 for refinement visualization and the resulting unit cell parameters). Several variations of unit cell parameters gave fits with similar *Rwp*, due to the large flexibility of monoclinic Pawley fits, therefore the refinements were carefully executed so that the refinements were done in exactly the same way for all the experiments. The Rietveld refinements of KxNa1-xNbO3 resulted in a tetragonal structure (*P*4*mm*16) for *R* ≤ 0.25 and a mix with NaNbO3 (*Pbma*17) secondary phase for *R* > 0.25. The refinements of KxNa1-xNbO3 in this range were challenging due to overlapping reflections with the secondary phase NaNbO3 (up to 50 wt%) and broad reflections for *R* = 0.25-0.35. Several crystal structures (*Pm*16, *Amm*216, *I*2*mm*18*, P*2*mm*18) were tested, but they either gave a poor fit (*Amm*2, *I*2*mm*, *P*2*mm*) or similar output values as when using the *P*4*mm* phase (*Pm*). Thus the tetragonal phase was chosen for consistency.

The effect of temperature and ethanol in the solvent

The effects of temperature and solvent on the reaction kinetics were investigated for *R* = 0.5. Figure 3 presents the maximum crystallite size of the intermediate phase and the final crystallite size of KxNa1-xNbO3 for different temperatures, in water and in water/ethanol mixture. For the experiments in water, the maximum size for the intermediate phase and the final size of KxNa1-xNbO3 were similar (~60-65 nm) and did not change significantly with temperature. In the water/ethanol mixture, the size of the intermediate phase was similar as in water, but the final size of KxNa1-xNbO3 became significantly smaller (~30-42 nm).

Figure 4 Reaction time for the KxNa1-xNbO3 synthesis for *R* = 0.5 in water and water/ethanol mixture and b) intercept and c) slope of the JMA equation for the growth of KxNa1-xNbO3 and d) the relative difference in unit cell volume of the intermediate phase as a function of reaction temperature. Lines are drawn as guides for the eye.

The total reaction time for the syntheses with and without ethanol in the solvent for *R* = 0.5, defined as the point where a stable crystallite size and relative phase fraction for KxNa1-xNbO3 were reached, is shown as function of temperature in Figure 4a. The reaction time was less than 1 h for all experiments, and decreased with increasing temperature. The use of water/ethanol mixture prolonged the synthesis time, especially at lower temperatures. Figure 4b and c displays the JMA intercept (*K*) and slope (*n*) from fitting the time-resolved phase fraction of KxNa1-xNbO3 to the JMA equation. All the time-resolved phase fractions could be fitted to linear Sharp-Hancock plots. The JMA intercept *K* increased with temperature but was not significantly influenced by the water content in the solvent. The JMA slope (*n*) in Figure 4c was in the range 2.5-3.7 and decreased with increasing temperature and by including ethanol in the solvent. The unit cell volume of the intermediate phase was also observed to change with the reaction conditions reflecting a difference in the alkali content in the precursor phase due to the larger size of the potassium cation relative to the sodium cation. The relative difference in the unit cell volume of the intermediate phase, shown in Figure 4d, depends on the temperature and the solvent type. The relative difference in the volume increased upon increasing the reaction temperature and by using the water/ethanol mixture.

The effect of R-value on the reaction kinetics

The effect of *R*-value on the kinetics of the formation of KxNa1-xNbO3 was investigated for *R* = 0.1-0.5 at 210 and 230 °C and is represented by JMA intercepts and slopes in Figure 5. All the time-resolved phase fractions could be fitted to linear Sharp-Hancock plots. A similar trend in JMA intercept was observed for all *R*-values at both temperatures, showing a slight decrease around *R* = 0.25-0.3. The temperature difference between the two datasets was not large enough to see any difference in the JMA slopes in Figure 5b, as expected from the values in Figure 4, but showed a consistent increase with increasing *R*-value. The values of *n* were in the range 2-3.7.

Variation in the stoichiometry of KxNa1-xNbO3 with temperature and R-value

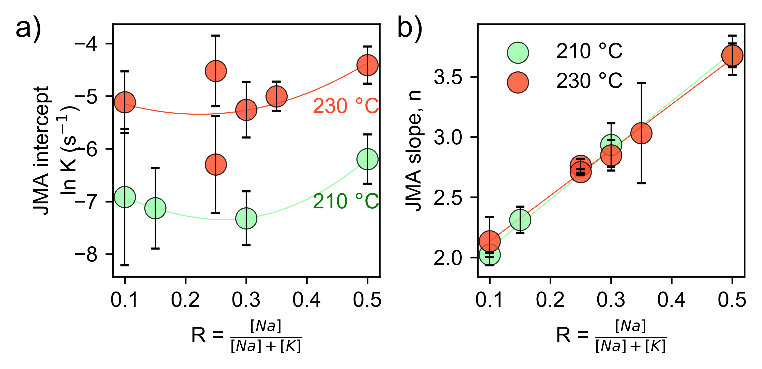
To investigate the effect of the *R*-value on the stoichiometry of KxNa1-xNbO3, solutions with *R* = 0.1-0.5 were investigated at 210 and 230 °C. Figure 6a presents the refined values of the Na occupancy of KxNa1-xNbO3. Two distinctly different regimes appeared on either side of *R* ≈ 0.25. For *R* ≤ 0.25, the structure was purely tetragonal KxNa1-xNbO3 with a Na occupancy of 1 – x < 0.65. For *R* > 0.25 the tetragonal KxNa1-xNbO3 phase was accompanied by a NaNbO3 secondary phase (up to 50 wt%), also observed *ex situ* by Handoko *et al.* at 200 °C.7 By comparing the experiments at 210 and 230 °C, complemented with the *ex situ* work of Handoko *et al*. at 200 °C, the *R*-limit for the appearance of the secondary phase increased with increasing temperature. Additionally, one experiment was done at 290 °C for *R* = 0.5, which resulted in a much lower Na occupancy compared to the experiments at lower temperatures. The Na occupancy for different reaction temperatures is also presented in Figure S3, showing that ethanol in the solvent did not have a significant effect on the final stoichiometry of KxNa1-xNbO3. Figure 6b shows the relative difference in the unit cell volume of the intermediate phase for *R* = 0.1-0.5. The volume decreased linearly with increasing amounts of Na, giving a relative difference of ~20 Å between the experiments at *R* = 0.1 and 0.5.

Figure 3 Maximum crystallite size of the intermediate phase and the final crystallite size of KxNa1-xNbO3 for hydrothermal synthesis with *R* = 0.5 in water and water/ethanol mixture.

Figure 7 Morphology of the intermediate phase and K*x*Na*1-x*NbO*3* after 60 min coil synthesis of *R* = 0.23 at 220 °C. KxNa1-xNbO3 nanorods with average diameter of 100 nm are growing along the surface of large hexagonally shaped crystallites of the intermediate phase.

Figure 5 JMA equation a) intercept and b) slope for the growth of KxNa1-xNbO3 during hydrothermal synthesis for varying *R*-values at 210 and 230 °C. Lines are drawn as guides for the eye.

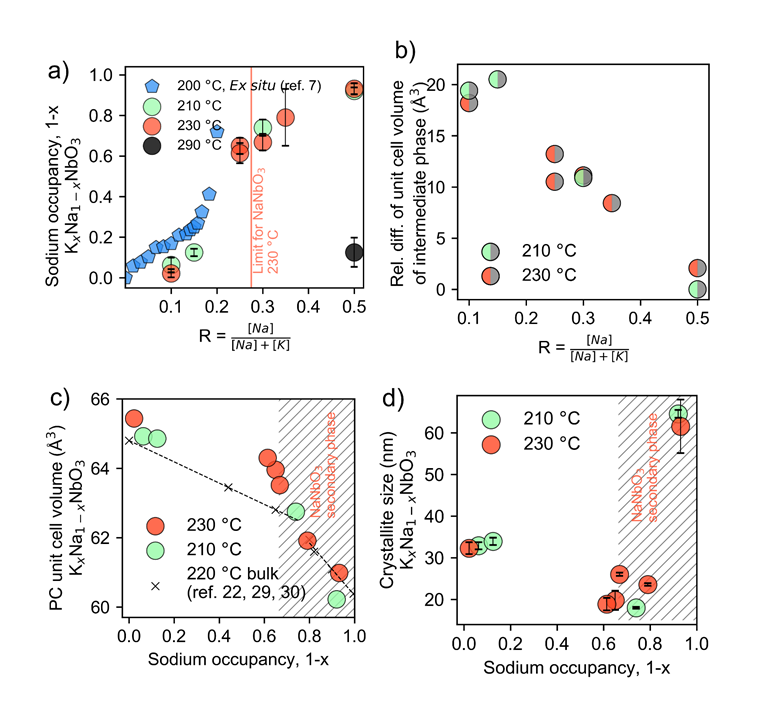
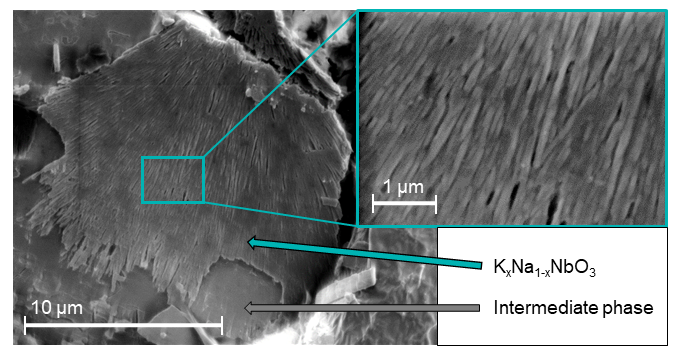


Figure 6 Sodium occupancy (1 - *x*) of KxNa1-xNbO3 as a function of the *R*-value, b) relative difference in unit cell volume for the intermediate phase, c) pseudo-cubic unit cell volume of KxNa1-xNbO3 as a function of sodium occupancy (1 - *x*) and d) crystallite size of KxNa1-xNbO3 made for varying *R*-values at 210 and 230 °C. *Ex situ* unit cell volume for bulk at 220 °C are included for comparison.

The effect R-value on the unit cell volume and crystallite size of KxNa1-xNbO3

The pseudo-cubic unit cell volume of KxNa1-xNbO3 in Figure 6c showed a steady decrease, consistent with reported values for bulk,18–20 but were slightly higher, which has been explained in the literature by the incorporation of hydroxyl ions or water in the lattice.21 The refined crystallite size is presented in Figure 6d and shows a significant decrease for 1 - *x* = 0.6 - 0.8. Around the limit between the two observed regimes at 1 - *x* = 0.65, the relative difference in the unit cell volume relative to bulk were more pronounced, and in relation to the refined crystallite size of KxNa1-xNbO3 in Figure 6d, this can be ascribed to a finite-size effect, frequently observed in ferroelectric oxides.22 The small crystallite sizes of ~20 nm achieved for 1 - *x* = 0.6-0.8 is worth noticing as they are, to the best of the author’s knowledge, the smallest yet to be reported in the literature for hydrothermal synthesis of KxNa1-xNbO3.

*Ex situ* characterization of the morphology

Figure 7 shows the resulting morphology of the intermediate phase and KxNa1-xNbO3 after 60 min coil synthesis of a slurry with R = 0.23 at 220 °C. The large crystallites with a distinct hexagonal shape was the dominating morphology. On the surface of some of these hexagons, the growth of nanorods was observed, growing in the direction parallell to the surface and forming what appeared to be a thin layer of nanorods, limited in length by the size of the intermediate phase crystallite.

Discussion

In the following sections, we discuss the connections between the present findings and their implications on the growth mechanism and stoichiometry of KxNa1-xNbO3 as well as reaction kinetics.

Growth mechanism of KxNa1-xNbO3

The reaction temperature did not seem to affect the final crystallite size of KxNa1-xNbO3 (Figure 2), and crystallite size was in the same range as the crystallite size of the intermediate phase. If the growth of KxNa1-xNbO3 had occurred through a dissolution-precipitation mechanism, one would have expected the crystallite size to be strongly dependent on temperature, but this is not observed. *Ex situ* imaging of particles made with the coil synthesis in Figure 7, confirms that KxNa1-xNbO3 grows directly onto the surface of the intermediate phase, which has also been reported before ,12 and as will be discussed in later sections, the reaction kinetics strongly indicate heterogeneous nucleation of KxNa1-xNbO3. The crystal structure of the intermediate phase is not known in detail, but if the transformation is occurring mostly through removal of excess alkali and water from the crystal structure, the crystallite size of the intermediate phase limits or control the crystallite size of KxNa1-xNbO3. This could explain the apparent limitation of the extent of the KxNa1-xNbO3 nanorods in Figure 7, as the nanorods only grow where they are directly in contact with the surface of the intermediate phase. Heterogeneous nucleation is a prerequisite for such a mechanism as there must be direct contact between the two phases.

Following the above discussion, it is important to understand what determines the crystallite size of the intermediate phase. The relative phase fraction and crystallite size of the intermediate phase, shown in Figure 2, displays a rapid formation of the intermediate phase during the first few seconds (<10 s) of heating. The conditions were transient in this time range, as 90 % of final reaction temperature was reached after ~10 s for all the experiments (see temperature profiles in Figure S1). Such a rapid formation before reaching the final reaction temperature would imply a high nucleation rate, which would result in small crystallite size and thus the kinetics and resulting size of the crystallites would be similar for all the experiments regardless of the final reaction temperature.

The effect of temperature and R-value on the sodium occupancy in KxNa1-xNbO3

A noticeable decrease in the Na occupancy was observed when increasing the synthesis temperature, see Figure 6a. Three explanations for this are envisaged, one being that the difference in solubility of sodium and potassium niobates phases6,7 can change with temperature. Another explanation is that the relatively larger potassium ions can enter the crystal structure more easily at higher temperature due to thermal expansion. The thermally induced phase transition from orthorhombic to tetragonal at ~210 °C for bulk material16 also gives a volume expansion, adding to this possible effect. The ability to incorporate K into the crystal structure is probably directly correlated with the appearance of the NaNbO3 secondary phase, explaining why NaNbO3 was observed already at *R* = 0.21 for Handoko *et al*. at 200 °C.7 Thermodynamics provide the third explanation, as the driving force for the nucleation of KxNa1-xNbO3 depends on the Gibbs energy of formation of the phase from the solution, which depends on *x*. This will also change with the composition of the precursor solution as well as the final product. A higher reaction temperature will favor thermodynamic equilibrium and since KNbO3 has a larger thermodynamic stability than NaNbO3,23 a higher K-content with increasing temperature is anticipated. This underlines the importance of using a high enough synthesis temperature during the hydrothermal synthesis of KxNa1-xNbO3 as long as the goal is to produce single-phase KxNa1-xNbO3 with a stoichiometry of 1 - *x* ≥ 0.5.

As seen in Figure 6a, the Na occupancy in KxNa1-xNbO3 increases with *R*. Since the reaction scheme includes an intermediate phase, it is interesting to see whether a similar increase in Na content can also be observed in the intermediate phase with increasing *R*. The linearly decreasing unit cell volume of the intermediate phase with increasing *R*-value in Figure 6b implies that more Na is entering the structure, assuming that the unit cell volume is directly connected to the amount of sodium in the structure due to the smaller ionic radius of Na (1.53 Å) compared to K (1.78 Å).24 Additionally, the low Na occupancy observed for KxNa1-xNbO3 at *R* = 0.5 and 290 °C (see Figure S3 for details) corresponds well with the large increase in unit cell volume of the intermediate phase for the same temperature (Figure 4d), which can cannot be explained alone by simply an effect of thermal expansion. Therefore, we infer from the data that there is a connection between the amount of Na in the intermediate phase and in the KxNa1-xNbO3. This also supports the suggested growth mechanism in the previous section, accentuating the importance of controllingthe Na content in the intermediate phase.

The effect of R-value and ethanol on the reaction kinetics

The consistent increase of the JMA slopes with increasing temperature in Figure 5b indicates that the amount of possible nucleation sites for KxNa1-xNbO3 will increase for higher *R*-values. Generally, homogeneous nucleation with three-dimensional growth gives n = 4, so n < 4 as observed here signifies constraints for either nucleation, growth or both.25 A constant nucleation rate can be assumed since the Sharp-Hancock plots are linear (not shown). As the highest value of *n* in this paper is approaching 4, the nucleation likely occurs during the entire transformation, as instantaneous nucleation would always give *n*-values < 3. Therefore, it is suggested that the low values of *n* are due to constrained growth due to heterogeneous nucleation,26 for instance at grain corners for *R* = 0.1, while the high *n*-value for *R* = 0.5 indicates almost three-dimensional growth, with a gradual dependency between these two points. This observation is challenging to rationalize without more investigations, but if the previously proposed mechanism is assumed, one could expect that the larger ionic radius of K compared to Na limits the diffusion out of the intermediate phase.

A delayed starting point for the nucleation of KxNa1-xNbO3 was observed when using the water/ethanol mixture compared to water, seen in Figure 2, resulting in a longer total reaction time, as seen in Figure 4a. By looking at the JMA intercepts *K* for the transformation to KxNa1-xNbO3 in Figure 4b, ethanol in the solvent did not affect the rate of the transformation. Thus, the observed delay must be linked to a change in the stability of the intermediate phase when using water/ethanol mixture. All the JMA slopes (*n*) in Figure 4c were < 4 indicating heterogeneous nucleation.26

Outlook

The findings in this work accentuate the importance of understanding the entire reaction scheme for production of KxNa1-xNbO3 by hydrothermal synthesis. Since the crystallite size of the intermediate phase seems to set an upper limit for the crystallite size of KxNa1-xNbO3, a rapid heating rate is necessary when nanosized KxNa1-xNbO3 is desired. A continuous-flow setup can give much higher heating rates than the conventional autoclave setup and thus provide a great advantage for producing nanosized KxNa1-xNbO3 in industrial quantities.

Experimental

T-Nb2O5 powder27 was synthesized by precipitation from (NH4)NbO(C2O4)2·5H2O (Sigma-Aldrich, 99.99 %) dissolved in water by adding NH4OH (25 wt%, Emsure) before drying and then calcining at 600 °C for 12 h, as described by Mokkelbost *et al.*28,29 Highly concentrated slurries were made by mixing T-Nb2O5 powder with 9 M NaOH/KOH aqueous solutions of different Na/K ratios, giving an alkali/niobium ratio of 9.5. For some syntheses, 50:50 vol% of water and ethanol was used instead of pure water. The slurries were stored in PET bottles and injected with a plastic syringe into a custom-made *in situ* cell, making sure to fill the entire volume of the cell. The cell, which has been previously described,29 consisted of a sapphire capillary with an inner and outer diameter of 0.8 and 1.15 mm, respectively, which was fixed to an adjustable aluminium frame by graphite ferrules and Swagelok fittings. An 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.30 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 profiles in Figure S1). Values of R = [Na] / ([Na]+[K]) in the range 0.1-0.5 at temperatures of 210-290 °C were studied. The pressure was normally set to 250 bar, but for the syntheses with ethanol, the pressure was lowered to 100 bar to avoid supercritical conditions.

To produce powders for *ex situ* characterizationwith conditions as similar as possible to the *in situ* cell, a coil was manufactured from extra corrosion resistant stainless steel (316 L) and used as a reaction vessel. Slurries were made with *R* = 0.23 and injected into the coil before being rapidly heated to 220 °C in a fluidized sand bath. The autogenous pressure generated by heating was stabilized to 250 bar pressurized with the HPLC pump. After a total heating time of 60 min the coil was immersed in cold water. The resulting particles were washed three times with deionized water, centrifuged and dried by evaporation at room-temperature. The composition of the powders were confirmed with a Bruker D8 A25 DaVinci X-ray Diffractometer with CuKα radiation with a LynxEye™ SuperSpeed Detector before being imaged using a Hitachi SU6600 FE-SEM.

*In situ* powder X-ray diffraction (PXRD) data were collected at the Swiss-Norwegian Beamlines (BM01) at the European Synchrotron Radiation Facility (ESRF) using a monochromatic beam with wavelengths of 0.6776 and 0.6999 Å (two different beam times). The diffraction signal was detected by a Pilatus 2M detector31 with acquisition times of 0.1, 1 or 5 s depending on the experiment. The as-recorded data were treated with the Pilatus@SNBL platform31 and the refinements were performed using Topas 5 in launch mode using JEdit with macros for Topas.32 Batch refinements were made possible by launching Topas with Jupyter Lab/Notebook.33

The instrumental resolution function, wavelength and detector distance were found and calibrated by refining a NIST 660a LaB6 standard. The diffraction patterns of the product phases were summed (25-60 s total acquisition time) to enhance statistics and the default approach was a full Rietveld refinement, refining the unit cell parameters, the Gaussian and Lorentzian isotropic size parameters, isotropic temperature factors, scale factor, Na/K occupancy and Chebychev background parameters. The KxNa1-xNbO3 phase in all the experiments was tentatively refined with several structures (*Pm*,16 *P*4*mm*,16 *I*2*mm*,18 *Amm*218) but P4mm was chosen for all the experiments. For refinements of the formed NaNbO3 secondary phase the space group *Pbma*17 was used. Atomic positions in all the structures were fixed to literature values.16,17 The unit cell used to fit the intermediate phase was found by a grid search using the McMaille software34 on the 20 most intense peaks in summed (100 s) diffraction patterns. The choice of a proper unit cell was based on a high figure of merit, provided that all the reflections were identified. The least symmetric space group was then chosen to avoid extinction of any reflections.

For the time-resolved Rietveld refinements of KxNa1-xNbO3 the same approach as described above was used, but with additionally fixing the isotropic temperature factors and Na/K occupancy to the final refined values to avoid breakdown of the refinements. The phase fraction evolution of KxNa1-xNbO3 was assumed to correspond to the normalized time-resolved scale factor. The refinements of the intermediate phase were accomplished with the Pawley method.35 The crystallite size was refined using Gaussian and Lorentzian isotropic size parameters while the unit cell parameters were fixed to the values found for a summed pattern (100 s). The time-evolution of the phase fraction was found by summing the intensity of all the diffraction lines found for each diffraction pattern by the Pawley fit, and then normalized using the minimum and maximum value. As the Pawley method cannot provide information about the absolute amount of a phase relative to another, the time-evolution of the phase fraction of the intermediate phase can only be seen in relation to itself and not relative to the phase fraction of KxNa1-xNbO3.

Information about the growth mechanism of KxNa1-xNbO3 was extracted by fitting the refined phase fraction over time to the Johnson-Mehl-Avrami (JMA) equation ( , where *α* is the phase fraction, *K* is a rate constant and *n* depends on the transformation mechanism).36,37 The JMA slope *n* and intercept *K* were found by transforming the phase fraction with the Sharp-Hancock method.38

Conclusions

The kinetics of the formation of KxNa1-xNbO3 by hydrothermal synthesis were studied by *in situ* X-ray diffraction. A similar phase evolution was observed for all investigated temperatures and *R*-values, where the precursor T-Nb2O5 dissolved and rapidly formed a potassium hexaniobate intermediate phase which in turn transformed into nanosized KxNa1-xNbO3 (~18-65 nm) via a proposed mechanism where water and excess alkali is leaving the structure of the intermediate phase. This mechanism is supported by the observation of heterogeneous nucleation (*n* = 2-3.7) of KxNa1-xNbO3 and the non-existent temperature dependence on the final crystallite size of KxNa1-xNbO3. Using water/ethanol mixture instead of an aqueous solution prolonged the reaction time by stabilizing the intermediate phase and gave a smaller final KxNa1-xNbO3 crystallite size.

The Na occupancy in KxNa1-xNbO3 is proposed to be linked to the Na content in the intermediate phase which both increased when increasing the *R*-value. For *R* < 0.25, purely tetragonal (*P*4*mm*) KxNa1-xNbO3 was observed, whilefor *R* > 0.25 a NaNbO3 secondary phase appeared. The Na occupancy decreased and the *R*-limit for the presence of NaNbO3 secondary phase increased when increasing the synthesis temperature, accentuating the importance of using a high enough synthesis temperature when producing KxNa1-xNbO3 with hydrothermal synthesis.

Conflicts of interest

There are no conflicts to declare.

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‡ Supplementary information is available.

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