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Time-Resolved in Situ Neutron Diffraction under Supercritical Hydrothermal Conditions: A Study of the Synthesis of $KTiOPO_4$

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Supporting Information

ABSTRACT: In the first in situ neutron powder diffraction study of a supercritical hydrothermal synthesis, the crystallization of $KTiOPO_4$ (KTP) at 450 °C and 380 bar has been investigated. The time-resolved diffraction data suggest that the crystallization of KTP occurs by the reaction between dissolved $K^+(aq)$, $PO_4^{3-}(aq)$, and $[Ti(OH)_x]^{(4-x)+}(aq)$ species.

$KTiOPO_4$ (KTP) has been the focus of enormous attention as one of the best nonlinear optical (NLO) materials because of its large optical nonlinearity, extremely low onset power threshold, high power conversion efficiency, outstanding thermal stability, and high threshold to laser-induced damage.[1] In addition, KTP has been recognized as an extremely important material of choice for ferroelectricity and electro-optic wave guides.[2] Technologically useful large crystals of KTP are normally grown from aqueous fluxes or nonaqueous melts at high temperatures and/or pressures.[3] Laudise et al.[4] reported that good-quality crystals of KTP can be prepared in high yields in supercritical water with the use of a more basic mineralizer, K_2HPO_4. Although crystals of KTP have been prepared successfully under supercritical hydrothermal conditions, the kinetics and mechanisms of the crystallization of this material are unknown because of the extreme nature of the synthesis conditions as well as the lack of appropriate spectroscopic tools. Novel experiments that can assist in helping us to understand the mechanism of KTP synthesis are vital if we are to develop rational synthesis schemes for other superior-performing smart materials that can be prepared by the supercritical hydrothermal synthesis method. Although a few in situ powder X-ray diffraction studies have been performed under supercritical conditions,[5] we believe supercritical hydrothermal syntheses have not previously been studied using neutron powder diffraction. In fact, in contrast to these previous X-ray experiments, the use of in situ neutron diffraction studies can accurately mimic large-volume commercial laboratory autoclaves for probing crystalline phases containing light atoms and systems involving elements that strongly absorb X-rays. A number of neutron diffraction studies have been reported under subcritical hydrothermal conditions.[6] We recently developed and commissioned a large-volume (45 cm^3) hydrothermal chemical reaction cell that enables us to record in situ high-resolution neutron powder diffraction patterns of highly reactive and/or corrosive materials reacting under supercritical hydrothermal conditions.[7] Here we report the first use of the CAU-Oxford-ISIS cell to study a supercritical hydrothermal synthesis using in situ neutron powder diffraction.

The synthesis of KTP was carried out by combining TiO_2, KH_2PO_4, and D_2O in the sealed Inconel supercritical hydrothermal cell and heating to 450 °C for 250 min.[8] During data collection, the internal autogenous pressures in the cell were recorded (see the Supporting Information). At a fill volume of 50%, an internal autogenous pressure of 380 bar was generated once the cell had reached 450 °C, in good agreement with standard laboratory supercritical equipment.[9] Using the maximum power of the 450 W heating system, the cell reached supercritical temperature in 35 min at a rate of 10 °C min^{-1}. In situ neutron diffraction patterns were obtained every 5 min as the reaction vessel was heated to 450 °C.[10] After the reaction cell was cooled back to room temperature and returned to atmospheric pressure, it was opened to reveal a mass of colorless polycrystalline product in D_2O. A powder X-ray diffraction measurement on the product confirmed it to be single-phase KTP, showing a good match to the reported diffraction pattern (see the Supporting Information).

Figure 1 shows a stack plot of the neutron powder diffraction patterns recorded during the 100 min duration of the synthesis. Initially only the (200) and (101) Bragg reflections attributable to the TiO_2 starting material were observed. Interestingly, the Bragg reflections attributable to the KTP product appeared only at supercritical temperatures. Figure 2 shows the sum of the final 10 diffraction patterns (i.e., a total of 50 min of data) at 450 °C in D_2O. To evaluate the quality of this time-of-flight in situ neutron diffraction data, whole-pattern fitting was used. The refined unit-cell parameters $a = 12.880(4)$ Å, $b = 6.439(3)$ Å, and $c = 10.586(3)$ Å and a cell volume of $V = 877.9(8)$ Å^3 for KTP at 450 °C in D_2O were obtained. These measured thermally expanded unit-cell parameters are consistent with those reported for KTP at high temperatures.[11]

Since the intensities of the Bragg reflections are directly proportional to the amount of diffracting material,[12] Gaussian fitting was used to determine the integrated intensities of all of the well-resolved Bragg reflections. A typical Gaussian fit to the KTP (420) reflection at 450 °C is shown in the Supporting Information. We did not observe any significant change in the peak widths of the KTP Bragg reflections during the synthesis.

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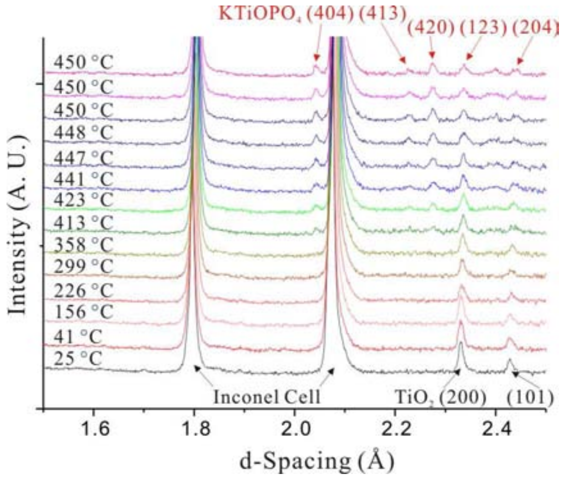

Figure 1. Neutron powder diffraction patterns measured on the POLARIS diffractometer (ISIS Facility, Didcot, U.K.). The diffractograms were measured at 5 min intervals during the crystallization of KTiOPO$_4$ in D_2O.

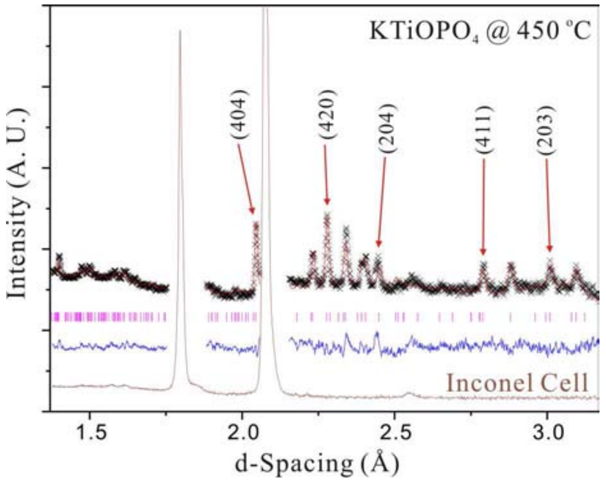

Figure 2. In situ neutron powder diffraction data measured during the supercritical hydrothermal crystallization of KTiOPO$_4$ at 450 °C and 380 bar. The observed data (×) are compared with the result of whole-pattern fitting (red solid line). The positions of the Bragg reflections and the difference between the observed and calculated profiles are indicated by the magenta vertical bars and blue solid line, respectively.

Using the normalized integrated intensities of the Bragg reflections for both TiO_2 and KTP, we were able to construct quantitative decay and growth curves for the starting material and product, respectively. Figure 3 shows the extent of reaction ($\alpha = I/I_\infty$) versus time curves for a typical reaction mixture heated to 450 °C. For the decay curve, the intensities of the (101) reflection of TiO_2 were normalized to the Bragg reflection intensity before heating, while those of the KTP Bragg reflections were normalized to the average intensity of the reflections after 1 h.

It is apparent that the source of potassium and phosphate, KH_2PO_4, rapidly dissolved before any other chemical reactions took place. It is not surprising that all of the KH_2PO_4 dissolved easily under hydrothermal conditions in view of its high solubility in water.[13] The titanium source, TiO_2, dissolved rapidly with increased temperature. As shown in Figures 1 and 3, the Bragg peak intensity for TiO_2 continuously decreased upon heating, and a significant amount (~40%) of the crystalline TiO_2 was consumed prior to the observation of any crystalline KTP. We believe the most likely mechanism is dissolution−precipitation. In other words, crystalline KTP is formed by the reaction between dissolved K^+(aq), PO_4^{3-}(aq), and $[Ti(OH)_x]^{(4-x)+}$(aq) species.

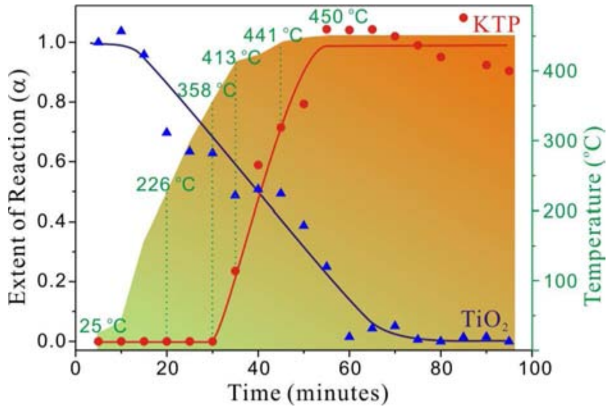

Figure 3. Changes in integrated Bragg peak intensities for the TiO_2 (101) and KTiOPO$_4$ (420) reflections obtained during the hydrothermal crystallization at 450 °C. Lines are drawn to guide the eye and are not fits to the data.

To extract quantitative rate information for the KTP crystallization, the crystallization curves were analyzed using the Avrami−Erofe'ev expression.[14] We found that the power dependence (n) of the rate expression is 0.56 ± 0.03 for the KTP (420) reflection. An n value of ~0.5 suggests that the crystallization mechanism for the specific diffraction is closely related to a diffusion-limited rate.[15] In other words, diffusion of reactive species such as K^+, PO_4^{3-}, and $[Ti(OH)_x]^{(4-x)+}$ is the rate-determining step.

In summary, we have successfully demonstrated that real-time neutron powder diffraction can be used to study crystallization processes in supercritical water. High-quality in situ time-of-flight neutron diffraction data were recorded during the synthesis of KTP. The data allowed us to determine the unit-cell parameters of KTP under these extreme conditions. We were able to observe directly the consumption and growth of reactants and the product, respectively, and on the basis of the results, a dissolution−precipitation mechanism can be proposed for the crystallization. We believe that this groundbreaking experiment can be used systematically to study syntheses of other sparingly soluble extended solids.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

$P-T$ diagram (50% fill) measured from the Inconel cell, typical Gaussian fit to the KTP (420) reflection, calculated and observed X-ray diffraction patterns, and a scanning electron microscopy image of KTP obtained from the supercritical hydrothermal reaction at 450 °C. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(8) The supercritical hydrothermal cell was loaded with TiO_2 (7.06 g), KH_2PO_4 (10.88 g), and D_2O (20 g) and rapidly heated to 450 °C under autogenous pressure.

(9) In situ neutron diffraction data were collected in the backscattering detector bank of the POLARIS diffractometer at the U.K. pulsed spallation neutron source ISIS, Rutherford Appleton Laboratory.

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