# Crystallization of Sodium Titanium Silicate with Sitinakite Topology: Evolution from the Sodium Nonatitanate Phase

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*Received March 26, 2004. Revised Manuscript Received June 23, 2004*

Titanium silicate (TS) with sitinakite topology and composition $Na_2Ti_2O_3SiO_4 \cdot 2H_2O$ has received considerable attention because of its high ion-exchange selectivity toward cesium and strontium. In this paper we report the results of the studies of the crystallization process of TS with a combination of ex and in situ experiments. The effects of various parameters, such as gel composition, time, and temperature of the synthesis, on crystallinity and composition of the final product have been investigated. In situ X-ray powder diffraction studies carried out during the synthesis of TS revealed that the process begins with the formation of layered sodium nonatitanate (SNT) with chemical composition $Na_4Ti_9O_{20} \cdot xH_2O$, which is also an excellent ion exchanger, selective for strontium and actinides. The pathway of transformation of SNT to the final product is sensitive to alkalinity of the starting gels. At high hydroxide concentration the reaction resulted in the formation of sodium titanium oxide silicate, $Na_2TiSiO_5$, which has the mineral natisite topology. This study has revealed a pathway for the synthesis of a combined SNT−TS exchanger for removal of Cs, Sr, and actinides by a single-step in-tank process.

## 1. Introduction

The Department of Energy's (DOE's) Savannah River and Hanford high-level waste (HLW) storage sites continue to search for alternative processes for efficient and cost-effective methods for cesium, strontium, and actinide removal from radioactive waste solutions. Sodium titanium silicate with mineral sitinakite topology, $Na_2Ti_2O_3SiO_4 \cdot 2H_2O$ (TS), which is usually referred to as crystalline silicotitanate (CST) in its engineered form (IONSIV IE-911, UOP, Inc., Des Plaines, IL), is considered as one of the baseline materials for cesium removal.[1−3] Besides being of great technological importance, TS is also of great academic interest because of its tunable ion-exchange properties.[4,5]

The compound possesses a tetragonal structure with $a = 7.8082(2)$ Å, $c = 11.9735(4)$ Å, and $Z = 4$. The clusters of four titanium−oxygen octahedra, located in the corners of the unit cell, are linked by silicate tetrahedra along the *a*- and *b*-axes, and by Ti−O−Ti linkages along the *c*-axis, resulting in an open-framework structure with tunnels along the *c*-axis.[6,7] Because of the richness of chemistry possible in this material, it provides an excellent platform for investigating the origin of ion-exchange selectivity in tunnel-type ion exchangers.[4,5] For instance, modification of the framework by means of heteroatom ($Nb^{5+} \leftrightarrow Ti^{4+}$) substitution does not change the compound's structure, but affects

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10.1021/cm049479a CCC: $27.50 
Published on Web 08/13/2004

its ion-exchange properties.[5] A structural study, accomplished using the Rietveld analysis of powder diffraction data, suggested different coordination environments of cesium and strontium in the two materials as the main reason for differences in the ion-exchange behavior. The change in population of water molecules and sodium ions in the channel caused by $Nb^{5+} \leftrightarrow Ti^{4+}$ substitution resulted in different hydration environments of cesium and strontium and as a result a different affinity for the ions.[5,8,9]

Investigation of the origin of ion-exchange selectivity in materials would be greatly aided if pure, highly crystalline samples, which would withstand exhaustive ion exchange without losing crystallinity, were available for the collection of accurate crystallographic data. Hydrothermal techniques reported by Dosch and Anthony[10,11] for preparation of the sodium form of CST (TAM-5) resulted in samples that were not crystalline enough for structure refinement. Synthetic procedures, reported by Poojary et al.,[7] needed to be modified to ensure higher crystallinity for the preparation of the Sr-exchanged form of these materials, that is, to prevent some loss of crystallinity during the exchange process. One way to optimize the synthesis toward producing highly crystalline materials is through the understanding of the pathway, kinetics, and mechanism of the crystallization process. Knowledge of the pathway of the crystallization process of the TS is essential because it may result in cost-cutting modification of the commercial crystallization process as well as in the identification of other phases. Several reviews have been published on the crystallization mechanisms of microporous materials, zeolites in particular.[12−14] Despite the similarities in structures and methods of synthesis between titanosilicates and zeolites, there are some differences in the chemistry of the precursors between the two. Titania species are much less soluble in the alkaline media than aluminates and silicates, and this difference may affect the nucleation mechanism significantly. Considerable information on crystallization can be obtained in ex situ experiments, by stopping the reaction at regular intervals, or by variation of synthetic parameters and collecting X-ray diffraction patterns of the samples. However, this process is generally time-consuming, provides limited information, and can be prone to misleading results if, in the process of extracting samples, the reaction is affected. Some parameters such as degree of mixing, prehydrolyzed state of the alkoxide precursor, and heating rate are difficult to control in ex situ experiments.

In situ X-ray diffraction is a convenient tool to obtain more detailed data about crystal growth of a material, which provides a continuous record of the crystallization process while leaving the reaction undisturbed. It gives easy and rapid information about any intermediate and short-lived phases formed during the hydrothermal reaction. Information about the kinetics of the reaction, which is uncertain in ex situ experiments, can be obtained from in situ experiments. These measurements also eliminate the possibility of alteration of the product by quenching, since many species may exist only at high temperatures and may change during postsynthesis treatment (filtration, drying).

In the present investigation we utilized a combination of ex and in situ experiments to study the crystal growth of TS. The parameters that influenced the product composition the most were first detailed via ex situ synthesis studies. The crystallization of the TS was then carried out in situ using the synchrotron radiation facility at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory (BNL), Upton, NY, for collecting dynamic X-ray powder diffraction data. On the basis of the results of these studies, a pathway for TS crystallization has been proposed.

## 2. Experimental Section

**2.1. Preparation of Gels**. Two groups of gels were used in these studies. In the first group (group I), starting gels were prepared so that the titanium-to-silicon ratio (Ti/Si) was greater than 1.0, while in the second group (group II) Ti/Si = 0.5.

*2.1.1. Preparation of Group I Gels.* Several precursors with general composition $1.0TiO_2$:$x$$SiO_2$:$y$$Na_2O$:$146.0H_2O$ were prepared by variation of one of the parameters and then treated hydrothermally for time $\tau$ at temperature $T$. The ranges of variation of $x$, $y$, $T$, and $\tau$ were as follows: $1.01 \le x \le 1.6$, $3.64 \le y \le 5.67$, 110 °C $\le T \le$ 210 °C, 2 days $\le \tau \le$ 15 days.

Generally, synthetic parameters were varied one at a time. The gels were prepared by mixing titanium isopropoxide ($Ti(OC_3H_7)_4$, 97%, Alfa Aesar) with tetraethyl orthosilicate ($Si(OC_2H_5)_4$, Aldrich) in a plastic beaker. Sodium hydroxide was added to the mixture in the form of a 6.32 M solution under constant stirring, followed by addition of 15 mL of doubly deionized (ddi) water. After vigorous agitation the mixture was sealed in a 100 mL Teflon-lined pressure vessel and kept in the oven. In the experiments involving variation in the composition of the gel, hydrothermal reaction was carried out for 3.5 days at 170 °C.

After heating, the final products in all reactions were treated in the following fashion: pressure vessels were left at room temperature to cool, the solid was separated by filtration, rinsed with ddi water and ethanol, and dried at 60 °C. X-ray powder patterns of the solids were routinely recorded on a Rigaku computer-automated diffractometer with a rotating anode, operated at 50 kV and 100 mA, with a copper target. Data were collected from $2\theta = 5°$ to $2\theta = 60°$ with a step size of 0.04° and exposure time of 1 s/step.

*2.1.2. Preparation of Group II Gels.* A second group of precursors was prepared using a different source of silica. The general composition of these gels was $1.0TiO_2$:$1.98SiO_2$:$y$$Na_2O$:$218H_2O$. A total of 3.5 mL of titanium isopropoxide (Alfa Aesar), 20 mL of ddi $H_2O$, and 7 mL of 10 M NaOH were mixed in a plastic beaker. To this mixture was added 1.469 g of silicic acid (Fisher), dissolved in a NaOH solution. The amount of added NaOH was varied according to the desired gel compositions specified below. After agitation, the mixture was sealed in a Teflon-lined pressure vessel and heated in the oven at the conditions outlined below (see Sections 2.2 and 3.2). The X-ray powder patterns of the solids were recorded on a Bruker-AXS D8 powder high-resolution parallel-beam X-ray diffractometer, operating at 40 kV and 40 mA. Data were collected from $2\theta = 5°$ to $2\theta = 60°$ with a step size of 0.04° and exposure time of 1 s/step.

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**2.2. Studies of Pathways of Crystallization**. In the present investigation the process of crystallization was studied using ex situ batch experiments as well as in situ diffraction techniques.

*2.2.1. Batch-Type ex Situ Experiments.* The gel of desired composition was divided into several 20 mL pressure vessels (12 mL of gel in each liner), which were sealed, and heated in an oven at a certain temperature for different periods of time. The powder pattern of each product was collected and plotted against time.

*2.2.2. In Situ Experiments.* In situ synthesis experiments were carried out at the X7B beamline of the NSLS at BNL.

A gel of composition $1.0TiO_2$:$1.98SiO_2$:$6.77Na_2O$:$218H_2O$ was prepared by mixing of 3.5 mL of titanium isopropoxide in 20 mL of ddi $H_2O$ and 8.5 mL of 10 M NaOH with 27 mL of 0.86 M silica solution in 2.6 M NaOH. A single-crystal sapphire capillary supplied by Saphikon (0.45 mm i.d. and 0.75 mm o.d.) closed at one end with a Swagelock fitting was filled with the gel and mounted on a goniometer head with a Swagelock tee using a Vespel ferrule. An external nitrogen pressure of 250 psi was applied through the connected tubing, and a hot air stream was used to slowly heat the capillary to 220 °C at a constant rate for 2 h, followed by a 14 h synthesis at this temperature. The hydrothermal conditions were achieved in the heated part of the capillary.[15,16]

Diffracted X-ray ($\lambda$ = 0.9223 Å) data were collected on a MAR 345 imaging plate (IP) detector with a built-in scanner for online reading. Erasing, exposing, and reading the IP limit the time resolution to about 2.5 min. Data were acquired for 60 s exposures. A large dynamic range can be obtained with IPs, which in turn allows intensity data to be extracted from the image for Rietveld refinement of in situ powder diffraction data. The wavelength, sample detector distance, zero point, and imaging plate tilt were determined using a $LaB_6$ standard.[15,16]

The crystallization progress was determined from IP images using integrated intensities of the diffraction lines. After data collection, IP data were integrated using the program Fit2D.[17,18] These files were saved as a CHI file ($2\theta$ vs intensity file), and then converted to DiffracPlus and CPI format by the program ConvX.[19] These formats were used in the programs EVA[20] (data plotting), CRYSFIRE[21] (automated indexing), XFIT[22] (peak profiling), and EXPGUI[23] (Retvield refinement) as a graphical interface for GSAS[24] for the processing of data for structure refinement.

**2.3. Recording of the NMR Spectra**. $^{29}$Si NMR spectra of several gel filtrates and filtrates from the final products were recorded on a Varian Inova 400 NMR spectrometer equipped with a 5 mm multinuclear probe head. Gels for NMR experiments were prepared using $D_2O$ as a solvent. Chemical shifts were recorded with respect to $Si(CH_3)_4$ in $CDCl_3$ locked at $CDCl_3$. A 2 s acquisition time, 20 s relaxation delay, and 45° pulse were used to obtain the spectra. During the acquisition the field was locked at $D_2O$. A 2.620 ppm standard shift from zero was added to the chemical shifts of the peaks, and peak assignment was done on the basis of corrected values.

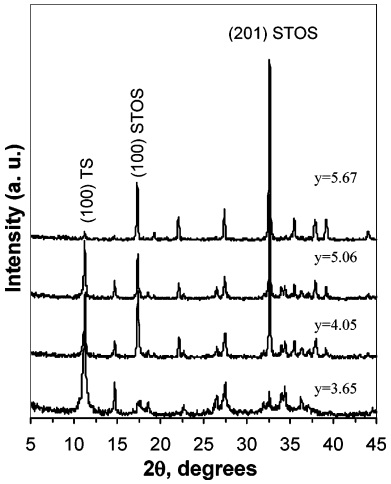


**Figure 1.** XRD powder patterns of solids obtained from the gel of composition $1.0TiO_2$:$1.01SiO_2$:$yNa_2O$:$146.0H_2O$, reaction time 84 h, temperature 170 °C.

## 3. Results

As a first step the effect of various parameters as described below on the yield and crystallinity of the final products was examined. The group I gels were prepared for this purpose. Gels with other compositions (group II) were studied subsequently.

**3.1. Experiments with Group I Gels.** *3.1.1. Effect of the Amount of $Na_2O$.* Initial attempts to synthesize TS from the gel with composition $1.0TiO_2$:$1.01SiO_2$:$5.26Na_2O$:$146.0H_2O$ resulted in crystallization of two phases: the TS phase and sodium titanium oxide silicate phase, $Na_2TiSiO_5$ (STOS), a synthetic analogue of the naturally occurring mineral natisite, whose crystal structure and chemical formula were reported previously.[25,26] The structure of STOS is built up of titanium−oxygen square pyramids that share corners with silicon tetrahedra, forming layers that are separated by sodium ions.[27] The sodium ions are trapped between the layers formed by two $TiO_5$ square pyramids and silicon tetrahedra and are not exchangeable. Figure 1 shows the XRD patterns of various phases obtained from the above gel under different conditions. In particular, the initial amount of $Na_2O$ in the gel was varied from 3.6 to 5.6 mol/mol of $TiO_2$. These syntheses resulted in a mixture of STOS and TS phases when the variable $y$ (see the preparation of gels with Ti/Si = 1) was set above 3.65.

To quantify the relative amount of each phase in a mixture of products, we compared the ratio of the intensity of the (100) reflection in the TS phase ($d$ = 7.808 Å, $I$ = 100%) to that of the (201) reflection of the STOS phase ($d$ = 2.709 Å, $I$ = 100%) for each value of $y$ (amount of $Na_2O$). The results are plotted against $y$ and NaOH concentration (calculated as the number of moles of NaOH per volume of solution; liquid Ti and Si sources are excluded from the total volume calculation) in Figure 2. As can be seen from the plot, the yield of the STOS phase increases with the alkalinity of the starting gel, resulting in the pure STOS phase when

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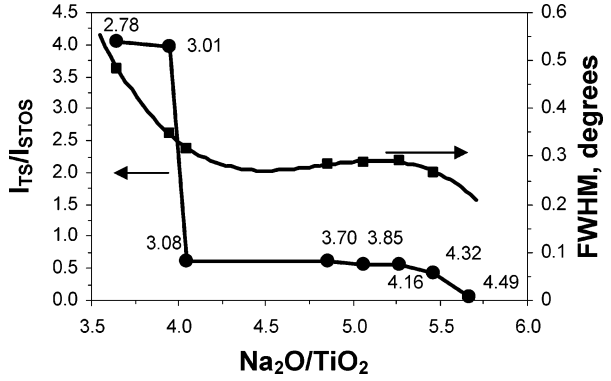


**Figure 2.** Crystallinity (fwhm) and the ratio of the most intense reflections (I TS/I STOS) for the gel of composition $1.0TiO_2$:$1.01SiO_2$:$yNa_2O$:$146.0H_2O$, temperature 170 °C, time 3.5 days for $3.0 < y < 6.0$. The labels next to the data points indicate the initial NaOH concentration in the gels.

the $y$ value is above 5.7 ($[OH^-] = 4.3$ M). Unlike the STOS phase, the conditions for TS phase formation are favorable at lower $Na_2O$ content. The pure TS phase can be synthesized at $y$ values below 3.5 ($[OH^-] = 2.76$ M), but the crystallinity of the product deteriorates. Figure 2 shows the effect of the initial NaOH concentration on the crystallinity of the TS phase expressed as the value of the full width at half-maximium (fwhm) of the most intense TS peak ($d = 7.808$ Å, $I = 100\%$, $hkl = 100$). As the concentration drops below 3.7 M NaOH the fwhm value starts increasing and reaches half of a degree in $2\theta$. Transition from the pure TS phase to the pure STOS phase is not gradual, and in this region two phases coexist. The yield of STOS slightly increases as the alkalinity of the precursor increases.

*3.1.2. Variation of the Ti/Si Ratio.* In the chemical formula of TS the ratio Ti/Si = 2.[6] Synthesis attempted from gels with such a ratio resulted in formation of mixtures of several phases including layered sodium nonatitanate $Na_4Ti_9O_{20}{\cdot}xH_2O$ (SNT) and STOS.[28,29] X-ray powder diffraction patterns of the phases crystallized from the gels $1.0TiO_2$:$xSiO_2$:$5.26Na_2O$:$146.0H_2O$ for $x = 1.1$, 1.2, and 1.6 are plotted in Figure 3. The intensity of all reflections decreases almost 2 times as the value of $x$ increases from 1.1 to 1.2. The increase in the amount of silicon over titanium reduces the alkalinity of the gel as NaOH is consumed in the formation of sodium silicate. As a result the yield of the TS phase increases with the amount of Si in the starting gel. Similar to the effect of decreasing $Na_2O$, the crystallinity of the product deteriorates as the Si loading becomes higher, which can be seen from the powder pattern corresponding to $x = 1.6$ (Figure 3).

*3.1.3. Temperature Variation.* The temperature of hydrothermal reaction is one of the key parameters controlling synthesis.[12,13] Open-framework compounds typically crystallize under hydrothermal conditions with temperatures up to 250 °C.[30−32] In the present study it

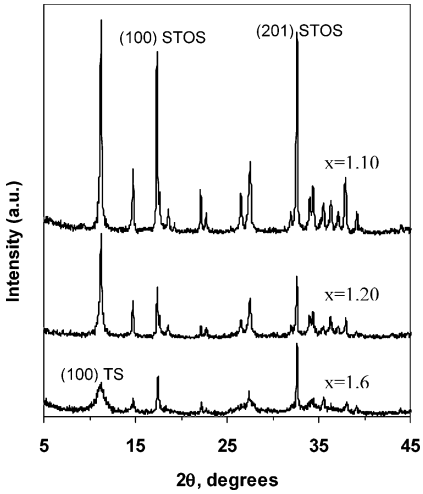


**Figure 3.** XRD powder patterns of phases obtained from the gel $1.0TiO_2$:$xSiO_2$:$5.62Na_2O$:$146.0H_2O$ for $1.1 \le x \le 1.6$, reaction time 84 h, temperature 170 °C.

**Table 1. Phases Obtained from the Gel of Composition $1.0TiO_2$:$1.01SiO_2$:$5.26Na_2O$:$146.0H_2O$ at Different Temperatures and fwhm Values of their 100% Reflections[a]**

| temp, °C | phases | fwhm, deg | | |
|---|---|---|---|---|
| | | SNT | STOS | TS |
| 110 | SNT | 0.4160 | | |
| 145 | SNT | 0.4680 | | |
| 160 | TS, STOS | | 0.1960 | 0.2080 |
| 170 | TS, STOS | | 0.1920 | 0.1240 |
| 210 | SNT, STOS | 0.1520 | 0.1400 | |

[a] All reactions were carried out for 84 h.

was found that SNT is formed both at low (110 and 145 °C) and at high (210 °C) temperatures. At temperatures above 160 °C mixtures of STOS and TS phases are formed. The yield of the TS phase decreased as the temperature was increased, resulting in almost negligible amounts at 210 °C. The phases and fwhm values of their 100% reflection (TS, $d = 7.808$ Å, $hkl = 100$; STOS, $d = 2.709$ Å, $hkl = 201$; SNT, $d = 9.5-10.0$ Å, $hkl = 001$) are summarized in Table 1. As can be seen from the values of fwhm shown in Table 1, the crystallinity of the products increases with the temperature. There is an almost 50% decrease in the fwhm value of the (100) reflection in TS as the temperature increases by 10 °C from 160 °C. The fwhm of the (001) reflection in SNT at 110 °C is 3 times larger than that at 210 °C.

Several conclusions can be drawn from the experiments regarding optimization of the conditions for TS synthesis. First, out of two impurity phases that are formed along with the TS phase, the SNT phase ($Na_4Ti_9O_{20}{\cdot}xH_2O$) does not contain any silicon, while the STOS phase ($Na_2TiSiO_5$) has 50 mol % more Si and sodium per titanium compared to the TS phase. Modifying the synthesis conditions changes the relative amount of each phase. Second, we believe it is the concentration of sodium hydroxide that has the major contribution to the purity of the TS product. An increase in the starting concentration of NaOH improves the crystallinity of the product, but reduces the yield of the TS phase. In fact, when the concentration of hydroxide ion is about 2.7 M, then the conditions for TS phase formation are most favorable, but the crystallinity of the product is reduced (Figure 2). To further support and generalize the above

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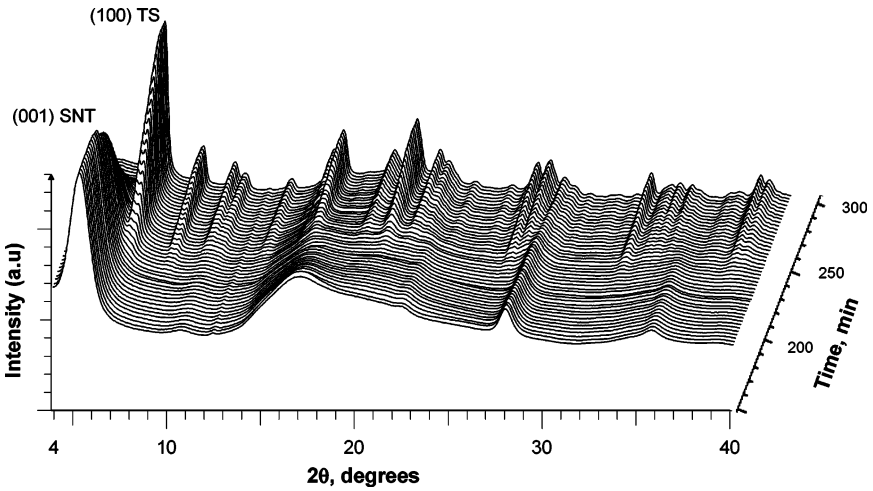


**Figure 4.** Time-resolved X-ray powder diffraction spectra of SNT−TS transformation for the gel with composition $1.0TiO_2$:$1.98SiO_2$:$6.77Na_2O$:$218\ H_2O$. Powder patterns are collected in 2.5 min intervals.

conclusions, we prepared gels with completely different compositions by increasing the amount of silica in the starting precursors, as discussed below, and changing the source of silica as well.

**3.2. Experiments with Group II Gels.** *3.2.1. Ex Situ Batch Crystallization.* Starting concentrations of titanium and silicon in the gels were decreased to 0.2 M compared to 0.8 M in the group I gels. We prepared gels with two compositions: the first (TS gel) had a composition of $1.0TiO_2$:$1.98SiO_2$:$6.77Na_2O$:$218H_2O$, while the second gel (STOS gel) had more sodium hydroxide corresponding to the composition $1.0TiO_2$:$1.98SiO_2$:$10.53Na_2O$:$218\ H_2O$. The temperature of hydrothermal reaction was set to 210 °C to ensure good crystallinity (see Table 1). The TS gel resulted in the formation of moderately and highly crystalline TS phases in 1 day and 5 days, respectively. About 2% of the STOS phase impurity was observed in the 5 day sample. The STOS gel resulted in a highly crystalline STOS phase both in 24 h and 5 days. It should be noted that in both cases $Na_2O/TiO_2$ ratios were above 5.7, which in terms of this parameter corresponds to the conditions of pure STOS phase formation (Figure 2). The concentration of NaOH, however, was set so that the conditions were favorable to formation of the TS phase in the first case (2.7 M), and the STOS phase (4.2 M) in the second case (Figure 2). When compared to the results of experiments with Ti/Si = 1 gels, the values of $Na_2O/TiO_2$ are higher for the gels with Ti/Si = 0.5, but the values of the $OH^-$ concentration are the same. This means that the initial concentration of NaOH, which accounts for the amount of solvent ($H_2O$) present in the system, should be used to predict the yield and crystallinity of the TS phase in different systems rather than the $Na_2O/TiO_2$ ratio. Being empirically obtained from the previous experiments, the values of the initial NaOH concentration, favorable for either TS or STOS formation, are the same for gels with different Ti/Si ratios.

*3.2.2. Time-Resolved in Situ Diffraction Studies.* Figure 4 shows a three-dimensional plot of the X-ray diffraction pattern as a function of time during the TS gel heating. As can be seen from the figure the process starts with formation of a phase having a broad peak at about 9.5−10 Å. This phase was identified as the SNT phase. It starts forming at an early stage of reaction, which is confirmed by collection of the X-ray powder diffraction pattern of the dried starting gel. The intensity of the (001) SNT reflection does not change as the reaction progresses until the growth of the TS phase begins. The process of transformation of the SNT phase to the TS phase started after 1 h of constant heating at 220 °C, with rapid decrease of the intensity of the SNT peaks and in growth of the TS peaks. The whole process of transformation lasted about 45 min. During the period following the transformation to TS, no significant changes occurred, except a minor increase in the TS peak intensities. No other phases were observed in this experiment.

*3.2.3. Ex Situ Studies of the Pathways of Crystallization.* Figure 5 shows the changes that occur in the powder pattern of the STOS precursor as a function of the time of hydrothermal reaction. The SNT phase remains the only product of the reaction after 9 h of heating at 200 °C. Peaks attributed to the STOS phase first appear after 12 h of heating. The intensity of the STOS peaks keeps increasing as the gels are heated further. The SNT peaks completely disappear after 17 h of heating. The reaction route is an SNT−STOS conversion, with no intermediate phases. The formation of SNT as a parent phase for STOS is also supported by the temperature variation studies undertaken with Ti/Si = 1 precursors (Table 1), where the SNT phase was obtained at 110 and 145 °C. We believe that at these temperatures Si does not react with the SNT phase.

As evident from the in situ TS crystallization experiment, the strontium-selective SNT phase precedes the crystallization of the cesium-selective TS phase. The mixture of the phases can be obtained if the reaction is stopped during the transformation process, yielding the material which is selective for both Cs and Sr. To synthesize a mixture of phases, several syntheses were carried out ex situ in 100 mL pressure vessels by stopping the reaction after different periods of heating at 200 °C. The SNT phase formed after 1 h of heating, while in 10 h the TS phase started to crystallize (see Figure 6). In 24 h, the SNT phase completely converted to the TS phase. Several mixtures of phases were obtained between 9 and 11 h of heating at 200 °C, with different ratios of the two phases.

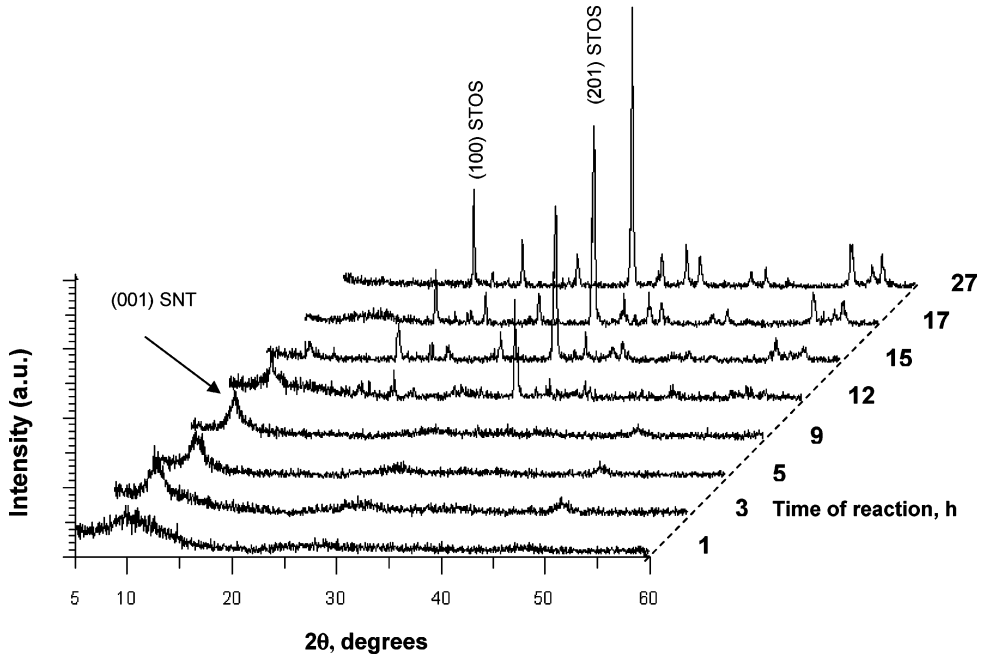


**Figure 5.** Dynamic XRD spectra of the evolution of the STOS phase obtained in ex situ experiments from the gel of composition $1.0TiO_2$:$1.98SiO_2$:$10.53Na_2O$:$218H_2O$, $T = 200$ °C.

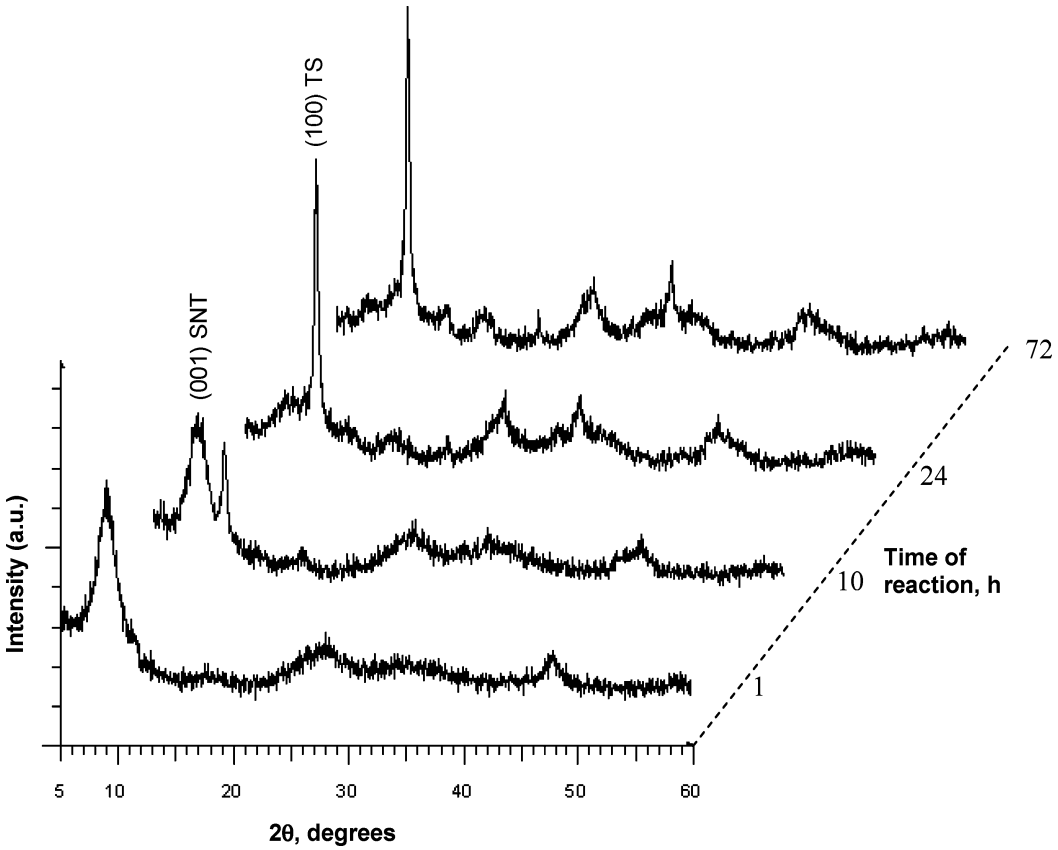


**Figure 6.** Dynamic XRD spectra of the crystallization of the TS phase obtained in ex situ experiments from the gel of composition $1.0\ TiO_2$:$1.98SiO_2$:$6.51Na_2O$:$250H_2O$, $T = 200$ °C. A mixture of phases was obtained after 10 h of heating.

*3.2.4. Silica Speciation in Solutions.* As mentioned earlier, the STOS and TS gels have different initial concentrations of NaOH. Since in both cases the alkalinity is high, both systems are likely to have the same Si species in the solution. Figure 7 shows typical $^{29}Si$ NMR spectra of the filtrates obtained from the starting gels. The spectra of the starting filtrates show that only two types of species are present in the solution in both syntheses. The narrow, low-field peak ($Q_0$) corresponds to the monomeric silicate species, while the peak denoted as $Q_1$ corresponds to end group Si atoms (i.e., those connected through oxygen to another silicon).[33] From the ratio of the peaks it is obvious that the relative

(33) Gould, R. O.; Lowe, B. M.; MacGilp, N. A. *Chem. Commun.* **1974**, 720.

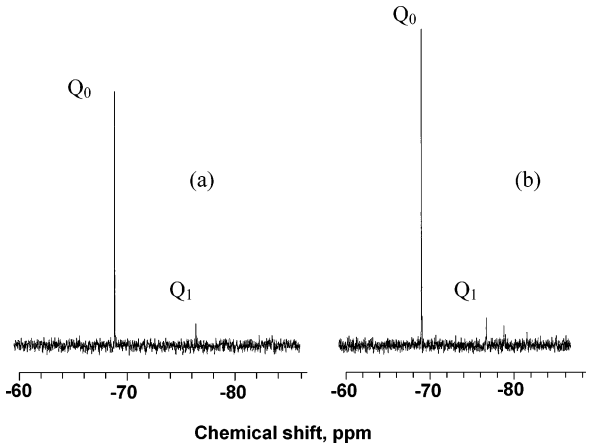


**Figure 7.** $^{29}$Si NMR spectra of STOS (a) and TS (b) gel filtrates.

amount of dimeric species is small compared to that of the monomeric species. In the spectra of the final filtrates, the $Q_1$ reflection was not observed, which indicates that only monomeric silicate species were present in the solution. The NMR studies showed that there is no detectable difference in Si speciation for these gels.

## 4. Discussion

In situ X-ray powder diffraction studies provide a unique opportunity to follow the process of crystal growth and observe the formation of phases during the synthesis without gel alteration during quenching and the ambiguity arising from utilization of several vessels to monitor crystallization. The sequence of powder patterns collected every 2.5 min leaves almost no uncertainty in the route of the reaction. Coupled with ex situ studies, it is possible to suggest with a certain degree of confidence the reaction pathways in this system. There are several steps that can be distinguished in the process of product crystallization. The first step is the formation of a layered SNT ($Na_4Ti_9O_{20}\cdot xH_2O$) phase, which can be described by the reaction shown below. This reaction starts with hydrolysis of titanium(IV) isopropoxide at the stage of admixing of reagents:

$$Ti(OR)_4 + 4H_2O \rightarrow Ti(OH)_4 + 4ROH$$

(titanium isopropoxide hydrolysis)

$$9Ti(OH)_4 + 4NaOH \rightarrow Na_4Ti_9O_{20}\cdot xH_2O + (20 - x)H_2O$$

(SNT formation)

The second step is the conversion of the SNT phase to the titanium silicate phases. We believe that the possible number of routes of the consequent reaction is limited to three, depending on the alkalinity of the gels. Route A is the transformation of the SNT phase to the STOS ($Na_2TiSiO_5$) phase, while route B is the transformation of SNT to the pure TS ($Na_2Ti_2O_3SiO_4\cdot 2H_2O$) phase. The other possibility, route C, is the transformation of the SNT phase to a mixture of TS and STOS phases. The difference between these transformations is the amount of Si and Na consumed in the reaction. The fact that in the STOS phase the stoichiometric ratio Ti/Si is 1, while in TS it is 2, implies that, in route A, twice as much Si is consumed compared to that in route B.

The SNT phase is highly selective for strontium, and its strontium selectivity is related to its crystallinity.[28,29,34] It was determined that the amorphous phase, as depicted in the first few X-ray patterns of Figures 4 and 5, displayed the highest selectivity for $Sr^{2+}$. Treatment of these amorphous forms with more concentrated sodium hydroxide solution at higher temperatures and for longer times under hydrothermal conditions resulted in higher levels of crystallinity. However, as the crystallinity increases the affinity of the exchanger for $Sr^{2+}$ decreases. Some of the X-ray patterns of the semicrystalline materials resembled those in the series of sodium titanates[35,36] of the general formula $Na_2Ti_nO_{2n+1}$. There is another series of titanates of general composition $Na_4Ti_nO_{2n+2}$ whose formula type fits that of nonatitanate.[37] However, none of these layered titanates are selective for strontium. Thus, we suspect that the amorphous phase contains defects with small cavities or tunnels that enhanced the observed selectivity. Such a structure is certainly thermodynamically unstable and therefore susceptible to formation of lower energy phases either by continued crystal growth or in the presence of silicate ion. In the latter case we have seen that either the TS or STOS phase forms, depending upon the alkalinity of the gel.

The structure of STOS is dense compared to that of TS, and it is likely more thermodynamically stable. Thus, it forms preferentially at higher temperatures and in more concentrated base solutions. Since the open-framework TS is a kinetic phase, it can be synthesized in a limited range of concentrations and temperatures only. When the mixture of phases forms, then a combination of processes occurs. We believe that the transformation starts with formation of the STOS phase, and once enough NaOH is consumed in the formation of the STOS phase and its concentration decreases, the TS phase starts forming. However, at lower alkalinity the SNT phase converts directly to the TS phase. What is remarkable is that the SNT phase can readily transform from a layered structure where there is a high level of edge sharing to a framework phase containing $Ti_4O_4$ clusters with a cubane-like unit bridged in the *a*- and *b*-directions by silicate groups and the *c*-axis direction by oxo groups.[6,7]

The main result of this study is the discovery of the route of TS crystallization. The fact that SNT precedes the formation of the TS phase is of particular interest because SNT itself has the ability to remove strontium and actinides from highly alkaline media. In fact, the National Research Council in its report[38] referred to the utilization of SNT for strontium and actinide removal as "an appealing alternative from the standpoint of reliable sources" and stated that "... a range of possibilities can be considered—for example SNT could be used

(34) Cahill, R. Ph.D. Dissertation, Texas A&M University, College Station, TX, 1996; p 220.
(35) Marchand, R.; Brohan, L. *Mater. Res. Bull.* **1985**, *15*, 1129.
(36) Sasaki, T.; Watanabe, M.; Komatsu, Y.; Fujiki, Y. *Inorg. Chem.* **1985**, *24*, 2265.
(37) Werthmann, R.; Hoppe, R. *Z. Anorg. Allg. Chem.* **1984**, 117.
(38) *Alternatives for High-Level Waste Salt Processing at the Savannah River Site*; National Research Council: Washington, DC, 2000.

in an ion-exchange mode, either alone or in some combination with crystalline silicotitanate". Being used for cesium removal, the TS phase when utilized in combination with SNT would remove not only cesium but also strontium and actinides from liquid HLW, that is, remove all of the highly radioactive isotopes. Besides, the mixtures of SNT and TS phases in different ratios can be synthesized from one precursor by adjusting the time of the hydrothermal treatment. The synthesis of both materials from one precursor would reduce the manufacturing costs dramatically as opposed to a two-step procedure, where the $Cs^+$ is removed separately from the other isotopes.

## 5. Conclusion

Studies of the crystallization process of titanium silicate with sitinakite topology suggest the composition of the final product and its crystallinity depend on the sodium hydroxide concentration in the starting gels. The synthesis resulted in pure TS phase, pure STOS phase, or mixtures of the two depending on the hydroxide ion concentration in the starting gels. At higher concentration conditions are more conducive for the formation of the Si-rich STOS phase with a dense structure. The open-framework TS phase formed at lower concentration, and the mixtures were formed at intermediate concentration.

In situ studies revealed the route of the TS crystallization and allowed us to optimize the conditions for synthesizing mixtures of SNT and TS phases with different ratios. The SNT phase is being considered as an alternative material for strontium and actinide removal in the process of liquid HLW remediation at the Savannah River site. It also was proposed to coat the TS particles with a Sr/actinide-absorbing agent to enhance the cesium ion-exchange process.[38] We believe that the SNT−TS combination product synthesized from one precursor is a promising material for a combined actinide, strontium, and cesium removal. We are currently investigating the decontamination properties of this material.

**Acknowledgment.** We acknowledge the U.S. DOE Environmental Management and Science Program, Grant DE-FG07-01ER63300 with funds supplied through the Westinghouse Savannah River Technology Center. J.B.P. and A.J.C. acknowledge the support of CEMS, funded through Grant NSF-CHE-0221934, and support via Grant NSF-DMR-0095633. This research was carried out in part at the National Synchrotron Light Source, Brookhaven National Laboratory, which is supported by the U.S. Department of Energy, Division of Materials Sciences and Division of Chemical Sciences, through Contract No. DE-AC02-98CH10886. We also acknowledge the NMR facility of the Department of Chemistry of Texas A&M University for acquisition of $^{29}Si$ NMR spectra.

CM049479A