

Probing Molten Salt Flux Reactions Using Time-Resolved in Situ High-Temperature Powder X-ray Diffraction: A New Synthesis Route to the Mixed-Valence NaTi_2O_4

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A new molten salt synthesis route to the mixed-valence sodium titanate NaTi_2O_4 has been discovered. Reduction of $\text{Na}_8\text{Ti}_5\text{O}_{14}$ by Ti metal powder in a 3:1 molar mixture of NaCl:KCl at 770 °C produced crystals of NaTi_2O_4 . Use of the molten salt flux lowered the synthesis temperature of this compound by over 400 °C. Time-resolved in situ high-temperature X-ray powder diffraction was used to probe the kinetics and mechanism of the reaction. Energy-dispersive X-ray diffraction (EDXRD) data revealed that the reaction is rapid; the phase begins to form in 30 min at 770 °C, and product formation is essentially complete within 2 h. Crystalline solids are present in the molten salt flux at all times during the course of the reaction, indicating that the mechanism most likely involves reactions occurring at the surfaces of the solid particles, mediated by the molten salt flux. Possible key intermediates identified through EDXRD and quenching studies are Ti_3O , $\text{Na}_2\text{Ti}_6\text{O}_{13}$, and $\text{Na}_{0.54}\text{TiO}_2$. This new molten salt synthesis route offers a facile way to reproducibly prepare large samples of this mixed-valence compound for further study.

Introduction

Reduced alkali metal titanates exhibit a variety of interesting electronic and magnetic properties,¹ most notably superconductivity. The superconducting mixed-valence spinel, $\text{Li}_{1+x}\text{Ti}_{2-x}\text{O}_4$, is still the record holder for the highest T_c (~13 K) for an early transition metal oxide superconductor.² A number of new phases in the mixed-valence sodium titanate family have been prepared and structurally characterized in recent years.³ The properties of these compounds, however, are largely unknown. In 1989, Akimoto and Takei reported the synthesis and crystal structure of the new mixed-valence titanate, NaTi_2O_4 .⁴ Although the chemical composition is closely related to that of the superconducting spinel LiTi_2O_4 , the larger size of the sodium

cation relative to lithium results in a different structure. In NaTi_2O_4 , which crystallizes in a calcium ferrite-type structure, double rutile-type chains condense through corner-sharing to form one-dimensional tunnels in which the sodium ions are located. According to an analysis of bond distances, the two types of titanium sites in the structure appear to be randomly occupied by Ti^{3+} and Ti^{4+} ions. The chemical similarity to LiTi_2O_4 and the one-dimensional structure suggest that a study of the properties of NaTi_2O_4 might yield valuable insight into structure–property relationships in mixed-valence titanates. Toward that end, we have sought a new synthesis route to this material.

In the original report by Akimoto and Takei, black needle-shaped crystals were grown by heating a mixture of unspecified stoichiometry containing TiO, Ti_2O_3 , and Na_2O in a sealed iron vessel under Ar flow at 1200 °C.⁴ Two goals that we set for a new synthesis route included lowering the reaction temperature and eliminating the use of air-sensitive Na_2O as a reagent. Several years ago, we reported a new molten salt synthesis to CaTi_2O_4 , a reduced titanate with a related structure.⁵ Our success with the crystal growth of this compound by reduction of CaTiO_3 with Ti metal powder in a molten CaCl_2 flux led us to investigate the reduction chemistry of sodium titanates in molten chloride fluxes. We report here the

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discovery of a new synthesis route to NaTi_2O_4 via the reduction of $\text{Na}_8\text{Ti}_5\text{O}_{14}$ with Ti metal in a mixed NaCl/KCl flux at 770 °C. To further elucidate the kinetics and mechanism of this molten salt flux reaction, we have followed the reaction at three temperatures using time-resolved in situ energy-dispersive X-ray diffraction (EDXRD). Results of these EDXRD studies together with insight gained through laboratory quenching studies suggest the formation of several crystalline intermediate phases as the reactants are converted to NaTi_2O_4 in the flux. This new synthesis route provides, for the first time, a facile way to prepare large samples of the mixed-valence NaTi_2O_4 suitable for further study.

Experimental Section

Synthesis of NaTi_2O_4 . Titanium metal powder (Cerac, -325 mesh, 99.5%), TiO_2 powder (Aldrich, <5 μm , predominantly rutile, 99.9+%), and anhydrous Na_2CO_3 (Chempure, ACS reagent grade) were used as received without further purification. A salt mixture containing a 3:1 molar ratio of NaCl:KCl (ACS reagent grade) was prepared by grinding together 20.000 g (0.342 mol) of NaCl and 8.506 g (0.114 mol) of KCl. This mixture was stored in a drying oven at 120 °C prior to use and will hereby be referred to as 3:1 NaCl:KCl. The starting material, $\text{Na}_8\text{Ti}_5\text{O}_{14}$, was prepared by grinding together stoichiometric amounts of Na_2CO_3 and TiO_2 , pressing the mixture into a 1-in. diameter pellet, and firing at 900 °C for 24 h. Repeating this cycle at least once improved the purity of the product, although $\text{Na}_2\text{Ti}_3\text{O}_7$ was always identified as a residual impurity phase in the X-ray diffraction patterns of $\text{Na}_8\text{Ti}_5\text{O}_{14}$. The presence of this impurity, however, did not appear to adversely affect the subsequent synthesis of NaTi_2O_4 .

Reactions to prepare NaTi_2O_4 were carried out either in a Lindberg tube furnace equipped for flow of a reducing atmosphere (5% H_2 in N_2), described previously,⁵ or in evacuated, sealed fused silica ampules (10 × 12 mm, i.d. × o.d.). In a typical synthesis, 0.500 g (0.777 mmol) of $\text{Na}_8\text{Ti}_5\text{O}_{14}$, 0.110 g (2.34 mmol) of Ti metal powder, and 4.855 g (77.7 mmol) of 3:1 NaCl:KCl were loaded into a fused silica tube, and the tube was evacuated and sealed at 2×10^{-5} Torr. After sealing, the tube was shaken for several minutes to thoroughly mix the reactants. The reaction tube was heated in a furnace to 770 °C over the course of an hour, held at 770 °C for 10 h, and then the furnace was turned off and allowed to cool to room temperature at the maximum rate (about 5 °C/min). Some tube attack was evident due to the presence of a brown discoloration and crackly appearance on the inside of the tube. The product was isolated by dissolving the salt flux in deionized water and filtering to recover the insoluble solids. In a typical preparation, about 0.5 g of product was isolated. The identity of the black product as NaTi_2O_4 was confirmed by X-ray powder diffraction on a Scintag XDS-2000 diffractometer using $\text{Cu K}\alpha$ radiation. Scanning electron micrographs were obtained using an Amray 1810 scanning electron microscope operating at 30 kV.

Preparations of NaTi_2O_4 under flowing hydrogen gas were carried out in an alumina combustion boat ($l \times w \times h$: 94 × 19 × 12 mm). Several modifications to the standard sealed tube reaction conditions were found to improve the purity of the product obtained under flowing hydrogen. The starting $\text{Na}_8\text{Ti}_5\text{O}_{14}$:Ti molar ratio was increased from 1:3 to 1:4. These reactants were then mixed with about half of the 3:1 NaCl:KCl flux and the remaining flux was added on top to act as a barrier layer, preventing the surface reaction of the titanium metal powder with N_2 gas at high temperatures.

In Situ EDXRD Experiments. In situ EDXRD experiments were performed on Station 16.4 of the Synchrotron Radiation Facility (SRS), Daresbury Laboratory, U.K. This second-generation synchrotron source operates with an average stored current of 200 mA and a typical beam energy of 2 GeV. Station 16.4 is illuminated with radiation from a 6 T

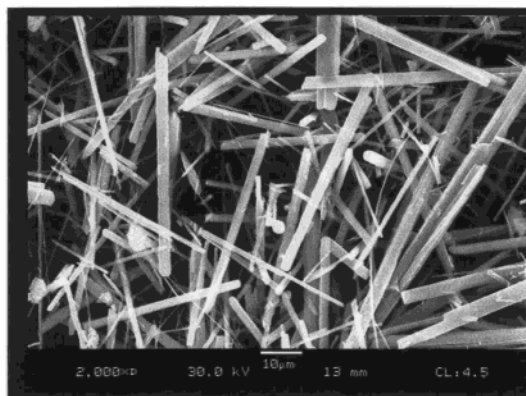


Figure 1. Scanning electron micrograph showing crystalline needles of NaTi_2O_4 . Typical crystallite size is $1\text{--}2 \times 50 \mu\text{m}$.

superconducting wiggler and receives X-rays over an energy range of 5–120 keV with a maximum X-ray flux of 3×10^{10} photons/s at around 13 keV. The position of this energy maximum is shifted by the absorption of lower energy photons by the sample containers so that, in practice, X-rays with energies above ~30 keV are useful. Data were measured from reactions taking place in flat-bottomed, sealed evacuated fused silica tubes, prepared as described above and held in a vertical tube furnace, the design, construction, and calibration of which we have previously described in detail.⁶ The EDXRD method allows rapid data collection since the incident X-ray flux is high, and all diffraction data are measured simultaneously by a fixed-angle, solid-state detector. In the EDXRD experiment, Bragg reflections with an interplanar spacing [d (Å)] are characterized by an energy [E (keV)], given by

$$E = 6.19926/(d \sin \theta) \quad (1)$$

where 2θ is the angle of the detector relative to the incident beam.⁷ Station 16.4 is equipped with a novel three-element detector,⁸ and this allows three regions of diffraction data to be recorded, the large extent of data facilitating identification of crystalline phases.⁹ Bragg reflections of crystalline standard materials were used to determine accurately the angle of each detector element (silicon for the higher angle detectors and zeolite A for the low-angle detector); the top detector was set at $2\theta = 7.47^\circ$, the middle at $2\theta = 4.63^\circ$, and the bottom at $2\theta = 1.83^\circ$. Data were collected in periods of either 60 or 120 s from the reaction carried out at 770, 820, and 870 °C. After completion of in situ studies, all reaction products were analyzed by powder X-ray diffraction collected at room temperature on a laboratory diffractometer to check sample purity. EDXRD data analysis was performed using the freely available programs DLConvert and XFIT;¹⁰ this allowed conversion of the data into ASCII format, plotting of data from individual runs, and the determination of peak areas.

Results and Discussion

Laboratory Studies. The mixed-valence titanate, NaTi_2O_4 , can be easily prepared from the reaction of a 1:3 molar ratio of $\text{Na}_8\text{Ti}_5\text{O}_{14}$:Ti in a molten flux of 3:1 NaCl:KCl at 770 °C. The product grows as black crystalline needles, typically $1\text{--}2 \mu\text{m}$ in width and ~50- μm long as shown in Figure 1. Figure 2 shows the X-ray

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(10) Software available from <http://www.ccp14.ac.uk>.

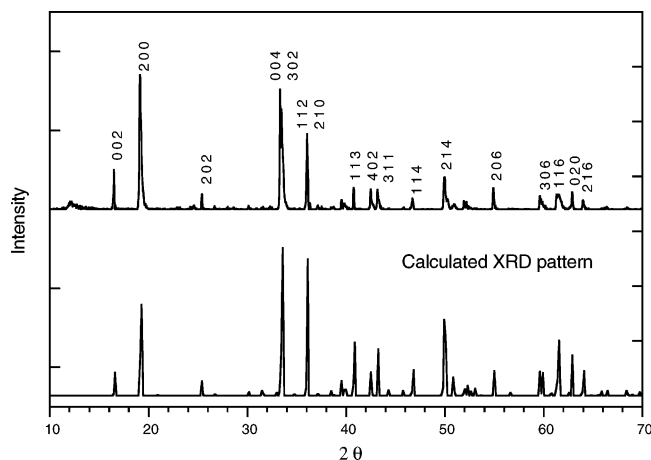


Figure 2. X-ray powder diffraction pattern of NaTi_2O_4 product (top) compared to the pattern calculated from the single-crystal structure (bottom). Peaks are labeled with hkl indices for an orthorhombic cell ($a = 9.258(2)$ Å, $b = 2.9519(7)$ Å, and $c = 10.743(2)$ Å).

powder diffraction pattern of the product compared to the powder pattern calculated from the single-crystal structure of NaTi_2O_4 .⁴ The close agreement of the two patterns confirms that the product of this molten salt flux reaction is NaTi_2O_4 . The lattice parameters refined from these data ($a = 9.258(2)$ Å, $b = 2.9519(7)$ Å, and $c = 10.743(2)$ Å) agree well with those reported from the single-crystal structure. The discovery of this new synthetic route to NaTi_2O_4 is significant because it offers several advantages over the previously reported synthetic method. First of all, the reaction temperature in the molten salt flux has been lowered by over 400 °C as compared to the original preparation at 1200 °C. Second, the molten salt flux reaction can provide relatively pure samples of NaTi_2O_4 , whereas the reaction conducted by Akimoto and Takei also produced crystals of $\text{Na}_8\text{Ti}_5\text{O}_{14}$. Furthermore, Akimoto and Takei provided few experimental details in their paper; for example, the stoichiometry of the reagents was not specified, making their route difficult to replicate. In contrast, this new molten salt synthetic route to NaTi_2O_4 provides an easy way to reproducibly make large samples of this mixed-valence titanate for further study. We have measured the magnetic susceptibility and resistivity of NaTi_2O_4 as a function of temperature as well as XANES data to probe the mixed valency in NaTi_2O_4 . These results will be reported elsewhere and compared to the results for the related Ti(III) material, CaTi_2O_4 . The remainder of this paper will focus on probing the kinetics and mechanism of the molten salt flux reaction.

In an effort to understand the role of the different reagents in this new synthetic route, several control studies were carried out in the laboratory. First of all, to test the importance of the molten salt flux, a 1:3 molar ratio of $\text{Na}_8\text{Ti}_5\text{O}_{14}:\text{Ti}$ was heated in an evacuated, sealed fused silica tube at 770 °C for 10 h. X-ray diffraction of the product identified unreacted $\text{Na}_8\text{Ti}_5\text{O}_{14}$, a small amount of $\text{Na}_2\text{Ti}_3\text{O}_7$ (residual impurity in the $\text{Na}_8\text{Ti}_5\text{O}_{14}$ starting material), and Ti_3O . Although the titanium metal has been slightly oxygenated, no further reaction was observed in the absence of the molten salt. Clearly, the molten 3:1 NaCl:KCl flux is the key to the success of this reaction. To learn the fate of the $\text{Na}_8\text{Ti}_5\text{O}_{14}$ and Ti reagents in the molten salt, each

of these was heated alone in the molten 3:1 NaCl:KCl flux at 770 °C in evacuated, sealed tubes. Titanium metal powder was recovered unchanged after heating in the flux for 10 h. $\text{Na}_8\text{Ti}_5\text{O}_{14}$ decomposed when heated alone in the flux, forming mostly $\text{Na}_2\text{Ti}_3\text{O}_7$ and some $\text{Na}_2\text{Ti}_6\text{O}_{13}$. The other product of the decomposition reaction is presumably Na_2O , which was not isolated due to the workup in water. However, the silicate $\text{Na}_2\text{-TiSiO}_5$ was also identified in the X-ray powder pattern of this product, presumably the result of chemical attack of the silica tube by the Na_2O .

Most reactions including the in situ experiments were carried out in a 3:1 molar mixture of NaCl and KCl at 770 °C. Subsequent studies showed that the flux composition could be varied somewhat at 770 °C, provided that the melting point of the flux remained below the reaction temperature. The 3:1 NaCl:KCl composition melts at ~725 °C, and the equimolar eutectic 1:1 NaCl:KCl melts at 645 °C.¹¹ The pure salts, however, melt just above the typical reaction temperature (NaCl, mp = 805 °C; KCl, mp = 774 °C). Raising the temperature significantly altered the products of this reaction. For example, in the 3:1 NaCl:KCl flux, increasing the reaction temperature to 820 °C was acceptable, but at 870 °C, a considerable amount of Ti_2O_3 was formed together with NaTi_2O_4 . At even higher temperatures (950–970 °C), the sodium titanium bronze, $\text{Na}_{0.25}\text{TiO}_2$, was isolated.¹² In fluxes containing more potassium, this reaction at higher temperatures (>900 °C) often led to the hollandite phase, $\text{K}_x\text{Ti}_8\text{O}_{16}$.¹³ Finally, a note should be made of the need to over-reduce the reaction with titanium metal. Reaction mixtures containing less titanium (1:2 or 1:1 molar ratio $\text{Na}_8\text{Ti}_5\text{O}_{14}:\text{Ti}$) produced gray multiphase products, whereas the 1:3 $\text{Na}_8\text{Ti}_5\text{O}_{14}:\text{Ti}$ molar ratio consistently produced black samples of NaTi_2O_4 . At shorter reaction times, some Ti_3O was identified in the diffraction patterns; however, whether this was due to incomplete reaction or the fate of the excess titanium is difficult to determine. As seen in Figure 2, even under the optimal reaction conditions, this synthetic route never resulted in single-phase NaTi_2O_4 ; the cause of a number of weak, unassigned diffraction peaks could not be identified. However, visual inspection of the product under both an optical microscope and a scanning electron microscope suggested the total amount of impurity phases was quite small (<5%).

Our laboratory studies enabled us to optimize the reaction conditions for the synthesis of NaTi_2O_4 through a process of trial and error. However, we had little understanding of the mechanism of this reaction or the exact role of the molten salt flux. The recent development of in situ powder diffraction techniques has allowed researchers to watch solids crystallize in real time and has begun to shed some light on the formation reactions of inorganic solid-state materials.¹⁴ We recently described the construction of a large-volume furnace, from which energy-dispersive X-ray diffraction

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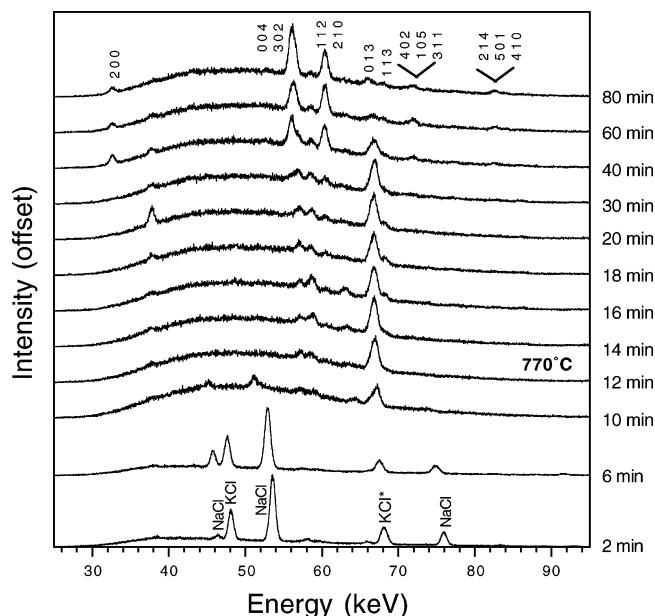


Figure 3. In situ EDXRD data at selected times from the middle detector ($2\theta = 4.63^\circ$) during the synthesis of NaTi_2O_4 in a molten 3:1 NaCl:KCl flux. The furnace is heated from room temperature and reaches 770°C within 12 min as evidenced by the disappearance of peaks for crystalline NaCl and KCl. The peak at 68 keV labeled with an asterisk (*) is due to overlapping reflections for KCl and the starting materials $\text{Na}_8\text{Ti}_5\text{O}_{14}$ and Ti. Peaks for the NaTi_2O_4 product are labeled with hkl Miller indices based on an orthorhombic unit cell.

(EDXRD) data can be measured during reactions at high temperatures,⁶ and the use of this apparatus to study, for the first time, the formation of a solid material in a molten salt flux.¹⁵ The synthesis of NaTi_2O_4 is another molten salt flux reaction that is ideally suited for in situ EDXRD studies.

In Situ EDXRD Data. Figure 3 shows selected EDXRD data measured by the middle detector during the synthesis of NaTi_2O_4 as the furnace is heated from room temperature to 770°C . Initially, at 2 min, peaks due to crystalline NaCl and KCl are apparent in the reaction mixture. The peak at 68.5 keV (2.24 Å) is due to overlapping reflections of KCl, $\text{Na}_8\text{Ti}_5\text{O}_{14}$, and Ti metal. As the temperature rises, the NaCl and KCl peaks shift to lower energies (larger d spacings), consistent with thermal expansion, and decrease in intensity as the salt mixture begins to melt. By 12 min, the furnace temperature has reached 770°C , the salt peaks have all disappeared, and the remaining peaks can be assigned to $\text{Na}_8\text{Ti}_5\text{O}_{14}$ and Ti. Although peak intensities are not measured accurately, and sample movement could conceivably cause preferred orientation effects during certain spectra, inspection of the relative peak intensities over time does allow us to gain additional information. For example, as the reaction progresses, the starting material peaks gradually decrease in intensity and reflections for the NaTi_2O_4 product grow in. These are labeled in Figure 3 with the Miller indices for an orthorhombic unit cell. The peak at 38.1 keV (4.02 Å), due to the starting material $\text{Na}_8\text{Ti}_5\text{O}_{14}$, appears to have an anomalously high intensity at 20 min; the peak

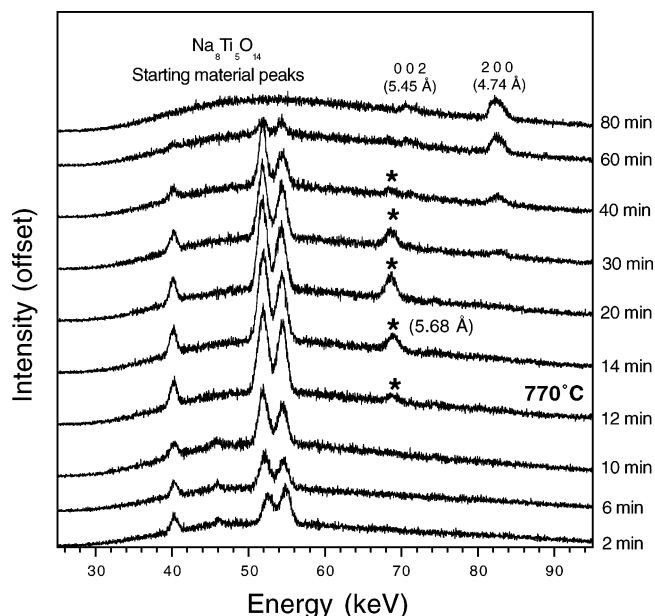


Figure 4. In situ EDXRD data at selected times from the bottom detector ($2\theta = 1.83^\circ$) during the synthesis of NaTi_2O_4 in a molten 3:1 NaCl:KCl flux. Peaks due to the $\text{Na}_8\text{Ti}_5\text{O}_{14}$ starting material are observed below 60 keV. An intermediate peak is marked with an asterisk (*). Two peaks for the NaTi_2O_4 product are labeled with hkl Miller indices based on an orthorhombic unit cell.

height is considerably less at 18 min and at 22 min. While this anomaly could be due to fluctuations in the amount of crystalline material in the X-ray beam, one would expect the intensities of all the peaks due to this phase to react similarly. It could also be due to preferred orientation effects, but pending further experiments, we have no definitive explanation at this time for the anomalous intensity of the 4.02-Å peak at 20 min.

EDXRD data from the bottom detector complement the information obtained from the middle detector. Selected plots from the bottom detector are shown in Figure 4; these are at the same time intervals as those in Figure 3. Since the fixed angle of the bottom detector is smaller than that of the middle detector, larger d spacings are observed. Consequently, no reflections from crystalline NaCl or KCl are observed with this detector. Rather, at 2 min, three strong peaks are observed (40.3 keV, 9.68 Å; 52.5 keV, 7.43 Å; and 54.8 keV, 7.11 Å) that can be assigned to the starting material $\text{Na}_8\text{Ti}_5\text{O}_{14}$. A weaker peak at 46.2 keV (8.45 Å) is due to the small amount of $\text{Na}_2\text{Ti}_3\text{O}_7$ impurity present in the $\text{Na}_8\text{Ti}_5\text{O}_{14}$. By 12 min, when the furnace temperature has reached 770°C , several changes in the diffraction pattern can be noted. First, the $\text{Na}_8\text{Ti}_5\text{O}_{14}$ peaks are considerably more intense. A plausible explanation for this is that as the salt mixture melts, more crystalline solids from higher up in the reaction tube settle down into the X-ray beam. Second, the $\text{Na}_2\text{Ti}_3\text{O}_7$ impurity peak has disappeared, perhaps due to the reaction or decomposition of this phase. Finally, a new peak at 68.7 keV (5.68 Å) has appeared that cannot be assigned to either starting materials or product. This peak continues to grow in intensity until 24 min, at which point it begins to decrease until it ultimately disappears. This is classic behavior for a transient intermediate phase. During repeated experimental runs of the NaTi_2O_4 reaction, the appearance and disappearance of this transient inter-

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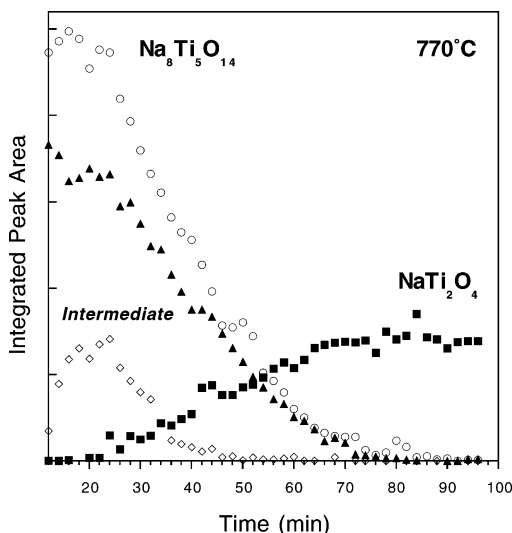


Figure 5. Integrated peak areas from the bottom detector ($2\theta = 1.83^\circ$) during the synthesis of NaTi_2O_4 at 770°C showing the decay of two $\text{Na}_8\text{Ti}_5\text{O}_{14}$ starting material reflections (open circles and closed triangles), the growth and decay of an intermediate peak (open diamonds), and the growth of an NaTi_2O_4 product peak (closed squares). The peak positions correspond to 51.8 keV, 7.52 Å (open circles) and 54.2 keV, 7.20 Å (closed triangles) for the $\text{Na}_8\text{Ti}_5\text{O}_{14}$ starting material reflections, 68.7 keV, 5.68 Å for the intermediate peak, and 82.2 keV, 4.74 Å for the NaTi_2O_4 peak.

mediate peak was reproducible. The peak did not show up in experiments on numerous other systems, however, so we are confident that it is not an artifact of the experimental setup. Efforts to identify the phase responsible for this 5.68-Å peak will be discussed below. As the reaction progresses, the three $\text{Na}_8\text{Ti}_5\text{O}_{14}$ peaks steadily decrease in intensity, while two new peaks for the NaTi_2O_4 product grow in. These changes in peak intensity over the course of the reaction are summarized in Figure 5, which shows the integrated peak areas for two $\text{Na}_8\text{Ti}_5\text{O}_{14}$ peaks (at 51.8 keV, 7.52 Å and 54.2 keV, 7.20 Å), the intermediate peak (at 68.7 keV, 5.68 Å) and one NaTi_2O_4 peak (at 82.2 keV, 4.74 Å), as a function of time. After 96 min, there were no further changes in the EDXRD data: The starting material peaks had decayed away and the NaTi_2O_4 peak intensity leveled off.

After the furnace cooled, the product of this reaction was recovered and characterized by conventional X-ray powder diffraction, revealing nearly pure NaTi_2O_4 . The product did contain a small amount of Ti_3O , identified by its most intense diffraction peak. This may suggest that the reaction had not quite reached completion, as this peak was considerably smaller in samples that had been reacted in the laboratory for 10 h at 770°C . An alternate explanation for the presence of Ti_3O in the sample is that this is the ultimate fate of the excess Ti metal needed in the optimal reaction stoichiometry.

We also investigated this reaction at higher temperatures using in situ EDXRD. At 820°C , the EDXRD data are qualitatively very similar to the data obtained at 770°C . The integrated peak areas from the bottom detector as a function of time are shown in Figure 6 for the synthesis of NaTi_2O_4 at 820°C . The anomalies in these data suggest fluctuations in the amount of solids in the X-ray beam over time. The beam was positioned approximately 2 mm from the bottom of the reaction

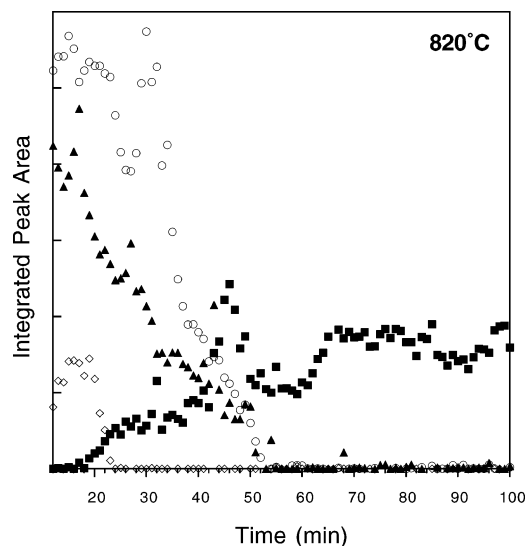


Figure 6. Integrated peak areas from the bottom detector ($2\theta = 1.83^\circ$) during the synthesis of NaTi_2O_4 at 820°C showing the decay of two $\text{Na}_8\text{Ti}_5\text{O}_{14}$ starting material reflections (open circles and closed triangles), the growth and decay of an intermediate peak (open diamonds), and the growth of an NaTi_2O_4 product peak (closed squares).

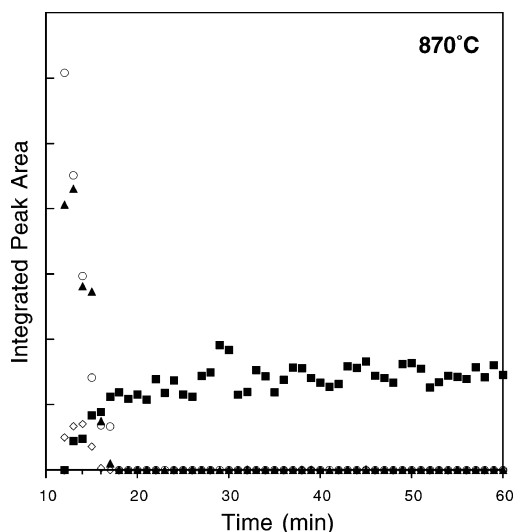


Figure 7. Integrated peak areas from the bottom detector ($2\theta = 1.83^\circ$) during the synthesis of NaTi_2O_4 at 870°C showing the decay of two $\text{Na}_8\text{Ti}_5\text{O}_{14}$ starting material reflections (open circles and closed triangles), the growth and decay of an intermediate peak (open diamonds), and the growth of an NaTi_2O_4 product peak (closed squares).

tube, and as the reaction was not stirred, thermal convection could cause solids in the liquid flux to move in and out of the beam. Nonetheless, the overall trends in the data are clear, showing that the reaction occurs more rapidly at 820°C than at 770°C . The intermediate phase has a shorter lifetime, the starting material decays more quickly, and the product peaks appear sooner in the course of the reaction. This trend in increasing reaction rate with temperature continues at 870°C ; the integrated peak areas from the bottom detector as a function of time are shown in Figure 7. At 870°C , the changes in peak intensity occur very rapidly; the reaction appears to be nearly complete by 20 min. The higher reaction temperature leads to considerable impurities in the product, however. Laboratory X-ray diffraction of the product recovered from the in situ

studies at 870 °C contained a large amount of Ti₂O₃ in addition to NaTi₂O₄. With this in mind, the EDXRD data from the middle detector were re-examined carefully for indications of the temporal evolution of the Ti₂O₃ impurity. Although there is some overlap between Ti₂O₃ and NaTi₂O₄ peaks in the EDXRD data, the first conclusive evidence of the appearance of Ti₂O₃ occurs after about 45 min. Since this appears to be well after the reaction is complete at 870 °C, it may be possible to obtain pure NaTi₂O₄ at this temperature if the reaction time is limited to 30 min.

Quenching Studies. In an effort to identify the intermediate phase with a *d* spacing of 5.68 Å observed in the bottom detector, quenching studies were carried out back in the laboratory. Sealed tubes of reactants were heated to 770 °C using a furnace with a comparable heating profile to the furnace used in the in situ experiments and then quenched to room temperature after varying amounts of time. The salt mixture was dissolved in water, and insoluble solids were isolated and characterized by X-ray diffraction. After 15 min of heating (the furnace reaches 770 °C in about 12 min), the unreacted starting materials Na₈Ti₅O₁₄ and Ti metal were recovered. Although the solids were poorly crystalline, there was no evidence for the impurity phase Na₂Ti₃O₇, consistent with the EDXRD results that suggest this phase disappears within 15 min of heating. By 20 min, the Ti metal has begun to be converted to Ti₃O. Also, the Na₈Ti₅O₁₄ has started to decompose to form Na₂Ti₆O₁₃, although only a few broad, weak peaks can be identified for each of these phases. It should be noted that the in situ EDXRD data clearly show that crystalline Na₈Ti₅O₁₄ is still present in the flux at this time. The presence of Na₂Ti₆O₁₃ in the flux is more difficult to confirm in the EDXRD data since the most intense peak of this phase overlaps with a peak for Na₈Ti₅O₁₄. However, in Figure 4, the reversal in the relative intensities of the adjacent peaks at 51.8 keV (7.52 Å) and at 54.2 keV (7.20 Å) is one indication that both phases are present in the flux since the most intense peak for Na₂Ti₆O₁₃ occurs at 7.47 Å at room temperature. The presence of Na₂Ti₆O₁₃ in the flux could be an explanation for the disappearance of the Na₂Ti₃O₇ impurity; eqs 2 and 3 show that both of these phases are related to the starting Na₈Ti₅O₁₄ through loss of Na₂O.



After 25 min, Ti₃O is clearly discernible in the quenched products, and Na₂Ti₃O₇ has reappeared, although there is no evidence for the reappearance of this phase in the in situ EDXRD data. Thus, it is not obvious whether crystalline Na₂Ti₃O₇ is present in the melt at 770 °C but is below the detection limit of the EDXRD technique or whether it crystallizes as the reaction mixture is quenched. Poorly crystalline Na₂Ti₆O₁₃ is also present in the quenched products along with the first signs of the NaTi₂O₄ product. Most significantly, in the sample quenched after 25 min, there is no evidence for the phase responsible for the 5.68-Å diffraction peak in the EDXRD data, even though this intermediate phase should be near its highest concen-

tration at this time according to the data in Figure 5. This suggests that the 5.68-Å intermediate phase is either not stable at room temperature in the absence of the molten salt or that it decomposes when the salt mixture is washed away in working up the quenched products. After 30 min, Ti₃O dominates the XRD pattern of the quenched products. Na₂Ti₆O₁₃ and the product NaTi₂O₄ are also present, although Na₂Ti₃O₇ has again disappeared. In reactions quenched after 35 min and longer, the amount of NaTi₂O₄ present in the products steadily increases, whereas the amount of Ti₃O decreases. Although there is no more evidence for crystalline sodium titanium(IV) oxides in these products, white powders and colorless needles were observed under the optical microscope in these samples. By 2 h of reaction time, the products are uniformly black in color and contain nearly pure NaTi₂O₄ with some remaining Ti₃O.

Although the results of the quenching studies did not always concur with the in situ EDXRD results, they did provide strong evidence that one step in the mechanism of the reaction is the conversion of Ti metal to Ti₃O. This conversion is nearly impossible to detect with the EDXRD data due to the poor resolution of peaks with similar *d*-spacings. The observed EDXRD peak in question from the middle detector occurs at 2.28 Å (67.2 keV) at 770 °C. For comparison, at room temperature, the most intense diffraction peaks for Ti metal and Ti₃O occur at 2.24 and 2.26 Å, respectively. Allowing for thermal expansion in the high-temperature EDXRD data, either of these phases could be assigned to the experimental peak. Nonetheless, the unambiguous identification of Ti₃O in the quenched products argues that this is an intermediate phase produced in the course of this reaction. The quenching studies also suggest that the slow decomposition of Na₈Ti₅O₁₄ into Na₂Ti₃O₇ and Na₂Ti₆O₁₃ is likely to be involved in the mechanism of this reaction. Interestingly, however, it seems that the process of isolating and/or quenching alters the products in such a way that they are no longer true intermediates of this reaction. We found that reheating the quenched products, isolated from the reaction after 30 min, in fresh 3:1 NaCl:KCl at 770 °C did not produce any NaTi₂O₄ but rather a multiphase mixture containing Na_{0.25}TiO₂, Na₂Ti₆O₁₃, and TiO₂. This result supports the hypothesis that the 5.68-Å intermediate phase is a key component of the reaction mixture and that the decomposition of this phase upon workup of the quenched reaction prevents any subsequent conversion to the desired NaTi₂O₄.

Searching the ICDD powder diffraction file¹⁶ for phases with a strong diffraction line near 5.68 Å suggested a possible identity for this intermediate phase. Mixed-valence Na_{0.54}TiO₂, reported by Akimoto and Takei¹⁷ is characterized by a strong diffraction line at 5.64 Å (100% relative intensity) and a second reflection at 2.20 Å (53% relative intensity) at room temperature. Considering thermal expansion at high temperature, the strong line agrees with the peak observed in the bottom detector. Moreover, there is a small peak observed in the middle detector at 68.7 keV (2.23 Å) that

(16) Powder Diffraction File, PDF-2/Release 2001; International Centre for Diffraction Data, Newtown Square, PA.

(17) Akimoto, J.; Takei, H. *J. Solid State Chem.* **1990**, *85*, 31.

could account for the second reflection. Since this small peak is a shoulder on the more intense peak assigned to Ti_3O in the EDXRD data, it was difficult to obtain a temporal profile. However by visual inspection of the data, this shoulder appears most clearly at the times when the 5.68 Å peak is also most intense. According to Akimoto and Takei, $\text{Na}_{0.54}\text{TiO}_2$ was extremely air-sensitive, which could account for why we were unable to isolate this phase in the quenching studies. It is interesting to note that $\text{Na}_{0.54}\text{TiO}_2$ and NaTi_2O_4 have the same relative compositions and titanium valence. Indeed, Akimoto and Takei reported that in the synthesis of $\text{Na}_{0.54}\text{TiO}_2$, crystals of NaTi_2O_4 grew together with $\text{Na}_{0.54}\text{TiO}_2$.¹⁷ The α - NaFeO_2 -type structure of $\text{Na}_{0.54}\text{TiO}_2$ is considerably different from the structure of NaTi_2O_4 , however. So it is unclear whether $\text{Na}_{0.54}\text{TiO}_2$ should be considered a true intermediate from a mechanistic point of view or rather as a phase that crystallizes under similar conditions as NaTi_2O_4 , but over time is converted to the desired NaTi_2O_4 .

What is clear from the EDXRD data is that crystalline solids are present in the reaction mixture throughout the course of this reaction. This is not a case in which the starting materials first dissolve in the flux before the product precipitates. Although the flux is clearly

necessary, it is uncertain whether it is acting as a solvent in this reaction. In situ Raman spectroscopy might be a useful probe to detect whether there are any soluble titanium species in the melt. In the absence of this information, we conclude that reactions occurring at the surfaces of solid particles, mediated by the molten salt flux, are most likely the key steps in the mechanism of the reaction of $\text{Na}_8\text{Ti}_5\text{O}_{14}$ and Ti metal to form NaTi_2O_4 .

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Supporting Information Available: X-ray powder diffraction patterns of products isolated from the salt flux after quenching the synthesis of NaTi_2O_4 at the denoted times (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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