

TITANIUM NIOBIUM OXIDES

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ABSTRACT

The titanium-niobium oxide compositional system shows potential for application in a variety of technologically important material systems. However, this system is not well understood. In this study, a titanium niobium mixed-phase system was prepared via the sol gel method and characterized as a function of heat treatment temperature. Differential thermal analysis, thermogravimetric analysis and high temperature X-ray diffraction (HTXRD) were used to characterize the mixed-phase system. The purpose of the current investigation is to gain insight into the phases and their structural characteristics present in the phase-mixed system. To do so, the system was studied using three approaches. First, the influence of the titanium to niobium metal ion ratio on the phase assemblage was examined. Next, the influence of composition on crystallization temperature was determined. Finally, the influence of composition and heat treatment temperature on phase transformation temperature and assemblage was investigated. This approach suggests that the precursor materials and heat treatment regiment affects the phase assemblage.

INTRODUCTION

A. Motivation and Statement of Objectives

In engineering applications such as solar cells and fuel cells, electrodes based on single phase titanium dioxide or niobium pentoxide are used with limited success due to the high resistivity values. When niobium is added to titanium dioxide, the resistivity is reduced.^{1,2} The lowest resistivity may be reached by adjusting the ratios between titanium and niobium. Motivated by mixed phase approaches, a titanium niobium oxide system is studied here with the objective to understand the phase assemblage in such titanium niobium oxide system as a function of composition and processing temperature.

B. Material Systems of Interest

Before reviewing titanium-niobium oxide mixed-phase materials, titanium dioxides and niobium oxides will be discussed in terms of phase formation temperatures, structures, band gaps, applications and precursors.

1. Titanium Dioxides

Titanium dioxide, TiO_2 , has several phases including anatase and rutile. Both have tetragonal crystal structures. However, the space group for anatase is $I4_1/amd$ and that for rutile is $P4_2/mnm$.³ Anatase is a low temperature phase and rutile is a high temperature phase. Depending on experimental conditions, the phase transformation temperature from anatase to rutile can be between 400°C and 1200°C.⁴ In one experiment, anatase and rutile coexist at the temperature of 600°C.⁵ In another experiment, the phase transformation temperature is 1000°C.⁶ The melting temperature of rutile is approximately 1870°C.⁷ The band gap of anatase is 3.2 eV, which is slightly higher than that of rutile (3.0 eV). Doping can modify materials properties, including phase transformation temperature, and band gap.^{1,8-14}

There are many different techniques to synthesize the titanium dioxide materials such as sol-gel and co-precipitation techniques.¹⁵⁻¹⁸ The precursors for titanium oxide materials when prepared through solution-based techniques include titanium

tetraisopropoxide, titanium ethoxide, titanium tetrachloride, titanium sulfide, titanium oxide nano-powder in colloidal form, titanium oxide sulfate, titanium butoxide, and Degussa P25.¹⁹⁻²⁴ To assist the materials synthesis, additional chemicals may be used, including ethylene glycol, citric acid, ethanol, dioctyl ether, anhydrous diethyl ether, anhydrous toluene, toluene D8, 4-nitrophenol, 2-propanol, ammonia, water and/or acetic acid.^{21-23,25-30}

2. Niobium Oxides

Similar to titanium oxides, niobium oxides have a wide range of applications, including electrodes with varying electrical resistivity, optical devices and capacitors.^{10,31-36} In terms of Nb:O ratio, several phases exist including NbO₂, Nb₄O₅, Nb₁₂O₂₉ and Nb₂O₅.³⁷ For Nb₂O₅, an orthorhombic phase exists at low temperatures, and a monoclinic phase exists at high temperatures.^{31,38-40} The orthorhombic phase is formed when the niobium oxide precursor is heat treated at ~ 900°C for 1 hour; and the monoclinic phase is formed when the precursor is heat treated at ~ 1000°C for 1 hour.³⁹

Niobium oxides can be processed via sol-gel and co-precipitation synthesis techniques.^{41,42} The sol-gel precursors include niobium chloride, niobium ammonium oxalate, niobium butoxide and niobium ethoxide; and additional chemicals include butanol, acetic acid, ethylene glycol and citric acid.^{31,43,44}

3. Titanium Niobium Oxides

Similar to titanium oxides and niobium oxides, titanium niobium oxides can also be used as electrodes.^{9,45} The ionic radius of Ti⁴⁺ is slightly less than that of Nb⁵⁺.⁴⁶ As Nb⁵⁺ replaces Ti⁴⁺, the crystal structure is slightly stressed.⁹ When Nb⁵⁺ type dopants are introduced into titanium dioxide, the resistivity decreases from 10¹⁰ Ω-m to 2.3x10⁻⁶ Ω-m.^{9,45,47-52} When Ti⁴⁺ type dopants are introduced into niobium pentoxide, the resultant resistivity is lower than that of the niobium oxide.⁵³ Up-to-date, the heat treatment temperatures are usually 900°C or lower; and the Ti:Nb ratios are between 0.5:0.5 and 1:0.^{2,9,47} With Ti:Nb ratio of 0.67:0.33, multiphase titanium niobium oxide materials are formed.^{9,45-50} Thus, if the Ti:Nb ratios can vary from 1:0 to 0:1 in incremental steps, a wide range of materials properties may be achieved, resulting in more applications than

single phase metal oxides. Besides doped titanium dioxides such as $\text{Ti}_{0.84}\text{Nb}_{0.16}\text{O}_2$ and $\text{Ti}_{0.712}\text{Nb}_{0.288}\text{O}_2$, other titanium niobium oxide phases exist, including TiNb_2O_7 and $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$.⁵⁴⁻⁵⁶ Because the titanium niobium oxide system is very rich in terms of phase formation and materials properties, it is desirable to systematically study the system in terms of varying concentrations and in-situ phase formation as a function of temperature.

The TiO_2 lattice can become distorted when Nb^{5+} ions replace Ti^{4+} ions or when they occupy interstitial sites.^{9,46} Similarly when Ti^{4+} occupies interstitial sites or replaces Nb^{5+} in the Nb_2O_5 system, the unit cell may become distorted.^{57,58} If the solubility limit of the host is reached, a secondary phase may be formed. High temperature x-ray diffraction (HTXRD) could systematically study the distorted crystal structures and the mixed phase materials.⁵⁹ The phase formation temperature can be related to processing parameters such as heat treatment temperatures and holding time. For example, in $\text{TiO}_2/\text{Nb}_2\text{O}_5$ materials, the crystallization temperature and anatase to rutile phase transformation temperature can be adjusted.⁶⁰ The additional materials may alter the activation energies for the phase formations. With 3% Nb doping, the anatase to rutile phase transformation temperature is 150°C-200°C higher than that of the undoped TiO_2 material.⁹ Among all available niobium precursors, niobium chloride is relatively cheap.⁶⁰⁻⁶² For titanium niobium oxides, the sol-gel and co-precipitation techniques are similar to those for titanium oxides and/or niobium oxides. For example, titanium isopropoxide, niobium ethoxide, nitric acid, water, isopropanol and ammonium carbonate can be used to form titanium niobium oxides.⁹ Before the precursor materials can be selected, sol-gel processing techniques should be described.

C. Sol-gel Processing

1. Introduction

In a colloid mixture, the particles of suspended substance A are dispersed evenly throughout another substance B, without complete dissolution. Generally, the colloidal particle sizes are between ten and two hundred nanometers. The substance A or B can be solid, liquid or gas.^{63,64} A sol is a stable suspension of colloidal solid particles within a

liquid. A gel is a porous three dimensionally interconnected solid network that expands in a stable fashion throughout liquid medium and is only limited by the size of the container.⁶⁵ If a solid network is made of colloidal sol particles, the gel is said to be colloidal. If the solid network is made of sub-colloidal chemical units, then the gel is polymeric material.⁶⁶

A sol-gel process is illustrated in Figure 1.⁶⁴ On the left, the route is called solution route where polymer macromolecules are mixed with liquid to form a polymeric gel. On the right, the route is sol route where colloidal particles are mixed with liquid to form a colloidal gel.⁶⁴ Once the gel is obtained, different shapes can be formed during the drying process. In this work, powder materials are prepared and studied. To prepare, TiO_2 , a common alkoxide, titanium isopropoxide is used.⁶⁷ To prevent rapid alkoxide hydrolysis, chelating agents such as carboxylic acids are used, by modifying pH value of the solution.^{22,65}

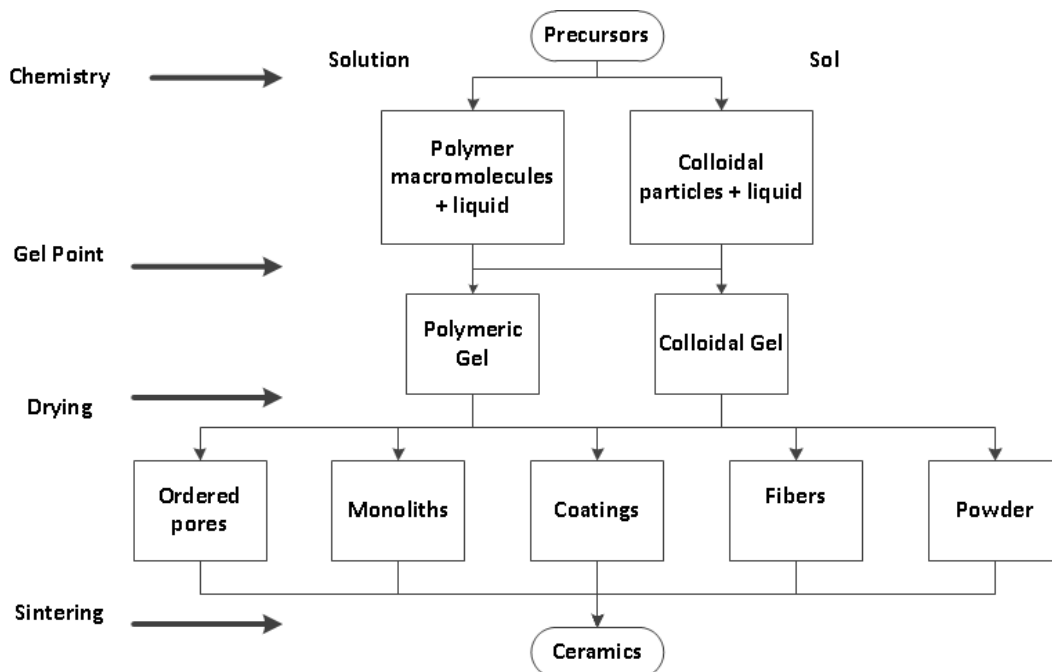


Figure 1. Illustration of sol-gel process (after Pierre, Ref # 64).

2. Advantages and Disadvantages of Sol-Gel Processing

Advantages of sol-gel processes are as follows: 1. A large amount of powder can be obtained with high chemical purity; 2. Powder can be formed at low temperatures; 3. Multi-component oxides can be obtained; and 4. Independent process control over porosity, crystal structure and grain size can be achieved due to the options available in each step outlined in Figure 1.^{68,69} The drawbacks of sol-gel processes are as follows: 1. The process may yield some solvent wastes which will need proper waste management; 2. The heat treatment may cause large volume shrinkage; 3. Some precursors may be expensive; 4. Raw materials may require special handling; and 5. Some drying requirements may lead to long fabrication times.^{70,71}

3. Oxide Systems formed by Sol-Gel Processing

A TiO₂ sol-gel process can start with the precursors such as titanium alkoxide (Ti-OR), acetic acid (AcOH) and alcohol (ROH). There are several reaction routes:

(1) $\text{Ti-OR} + \text{AcOH} \rightarrow \text{Ti-OAc} + \text{ROH}$, (2) $\text{ROH} + \text{AcOH} \rightarrow \text{ROAc} + \text{H}_2\text{O}$, (3) $\text{Ti-OAc} + \text{ROH} \rightarrow \text{ROAc} + \text{Ti-OH}$, and (4) $\text{Ti-OR} + \text{Ti-OAc} \rightarrow \text{ROAc} + \text{Ti-O-Ti}$.^{72,73} Reaction route (1) depicts the exothermic and very reactive hydrolysis reaction which may lead to large particle precipitation. Carboxylic acids such as acetic acid can control particle precipitation.⁷²⁻⁷⁵ If Ti-O-Ti is kept in suspension, gelation will take place. Titanium alkoxides include titanium ethoxide, titanium butoxide and titanium isopropoxide. The final product obtained in the last step includes Ti-O-Ti oligomers. Other titanium precursors, such as titanyl sulfate and titanium tetrachloride were considered but not used, as they would leave impurities in samples and/or require high heat treatment temperatures to decompose.⁷⁶⁻⁷⁸

Previous work used ratios of 1:10:100 for titanium isopropoxide, acetic acid and water.^{79,80} In this work, water is replaced by ethanol (EtOH). When additional alcohol is added to the precursors, water is released in reaction route (2), and an EtOH-AcOH esterification reaction occurs.^{74,75} After proper heat treatment, crystalline TiO₂ is formed.⁸¹

Niobium oxides can be prepared with niobium (V) ethoxide Nb(OC₂H₅)₅, niobium butoxide Nb(OC₄H₉)₅, niobium isopropoxide Nb(OC₃H₇)₅ or niobium chloride

NbCl₅. Since NbCl₅ is highly reactive in the atmosphere, it should be dissolved in alcohol such as butanol.^{62,82} Besides the low cost, the other advantage of NbCl₅ is its low decomposition temperature, ~ 250°C.⁸³

To solidify ceramic materials, there are two heat treatment steps, calcination and sintering. Calcination dehydrates and removes the organic materials from the sol-gel; and sintering densifies the material.⁸⁴ Depending on the precursor materials, the actual calcination temperature may vary. In general, the calcination temperature is below the melting point, and can be between 400°C and 800°C. Sintering temperature depends on several factors such as metal oxide materials, sizes of the particles and dimensions of the samples, as well as heating profiles. Usually, the sintering temperature for metal oxides may be between 800°C and 1100°C or higher.^{85,86} In this work, since most of the heat treatment occurs within the HTXRD apparatus, the sample must be preheat treated at 190°C, with the holding time of 24 hours. The main purpose of such preheat treatment is to dissociate and remove some of the organic materials to avoid volatile degassing in the HTXRD instrumentation.

Nanocomposites of TiO₂ and Nb₂O₅ phases can be formed via sol-gel processing, providing that one of the oxides has dimensions of 100 nm or less.⁸⁷ The resultant material may possess or alter mechanical, electrical, and/or optical properties of each component.^{62,87-105} The phase assemblage of nanocomposites can be analyzed by high temperature x-ray diffraction (HTXRD) and refinement techniques.

D. X-Ray Diffraction

1. Introduction

During in-situ HTXRD characterization of the nanocomposites, phase transformations and particle sizes will depend on the heating profiles.¹⁰⁶ If the heating rate is fast and/or the holding time is short, multiphase metal oxides such as titanium niobium oxides can be formed. It may be advantageous to use software packages based on Rietveld refinement algorithms to enhance HTXRD analysis for low concentrations of a particular phase in the nanocomposite, calculate crystallite sizes and lattice parameters of several phases simultaneously.

2. Principles

X-ray diffraction allows for non-destructive analysis of a sample, and is based on the scattering of an x-ray by a periodic array with long range order.¹⁰⁷ Constructive interference at a specific incident angle would yield a diffraction peak above the background. When the angle is varied, a diffraction pattern is obtained, providing the information for d-spacing and integrated intensities. Mathematically, the diffraction peak location θ_{hkl} is related to the d-spacing (d_{hkl}) between two adjacent array planes, in which (hkl) are the Miller indices. The relationship among d_{hkl} , θ_{hkl} and the wavelength of the x-ray radiation λ is expressed in Equation (3).

$$\lambda = 2d_{hkl} \times \sin \theta_{hkl} \quad (1)$$

The diffraction peak intensity I_{hkl} is proportional to a physical quantity known as structure factor F_{hkl} squared.¹⁰⁸ In Equation (4), the structure factor is given.

$$F_{hkl} = \sum_{j=1}^m N_j f_j \exp[2\pi i(hx_j + ky_j + lz_j)] \quad (2)$$

where the sum is taken over m atoms in the unit cell, N_j is the fraction of every equivalent position occupied by atom j , f_j is the scattering factor which quantifies the efficiency of x-ray scattering at any given angle by the group of electrons in each atom, and x_j , y_j and z_j are the fractional coordinates of the atom.^{107,108} Each term in Equation (4) is usually provided in a database during manual or computerized calculations. Examples of such databases include ICDD (International Centre for Diffraction Data) and ICSD (Inorganic Crystal Structure Database).¹⁰⁹

3. Applications of X-ray Diffraction

There are several applications for x-ray diffraction. First, a diffraction pattern can be used to identify a specific crystalline phase by comparing the experimental results with the standard powder diffraction files (PDFs) from the ICDD. With the diffraction data, one can obtain the lattice parameters and compare these experimental values with

the standard or nominal values. Second, if the crystalline phase diffraction pattern is superimposed on a background, the pattern can be isolated via background subtraction techniques. Third, in a mixture with two crystalline phases (α and γ), the composite diffraction pattern can be separated into individual diffraction patterns for α and γ ; and the percentage ratio between the two phases can be estimated from the individual contributions. For example, a method known as “whole pattern fitting” can be used to obtain the phase percentage distribution in the Rietveld refinement algorithm.¹⁰⁷ When an element or ion B is doped in material A below the solubility limit, the lattice distortion can be determined by comparing the peak locations. Fourth, the Scherrer equation expressed in Equation (5) can be used to determine the crystallite size L , without considering microstrain.

$$L = \frac{K\lambda}{B(2\theta) \cos \theta} \quad (3)$$

In this equation, K is known as the shape factor ($K \approx 0.9$), $B(2\theta)$ is the line broadening due to the effect of small crystallites, θ is the incident angle and λ is the wavelength.^{107,108} For Cu $K\alpha$ radiation, λ is 1.54Å. Line broadening $B(2\theta)$ is also known as FWHM_{obs} (observed full-width half-maximum). Due to the instrumentation limitation and the corresponding value $\text{FWHM}_{\text{inst}}$, any L value exceeding 5000Å is not considered in most data processing techniques. In other words, when FWHM_{obs} is the same as $\text{FWHM}_{\text{inst}}$, one cannot obtain the crystallite size.

4. Rietveld Refinement

With the Rietveld refinement technique, one should be able to determine the microstructure of a polycrystalline material. This technique uses quantitative estimations for multiphase materials. For this work, besides niobium pentoxide and titanium dioxide, there may exist titanium niobium oxide phases. In contrast to other techniques, Rietveld does not need a pure standard as a reference. Using known powder diffraction patterns, several parameters such as lattice parameters can be calculated based on experimental results. Near an experimental diffraction peak, a simulated peak can be adjusted to provide information for a simulated crystal structure. With each refinement iteration (say

step n), the parameters are corrected to the predicted values based on the previous values obtained at step n-1. With such successive refinement, the systematic errors are reduced to meet preset criteria. The iterations can also take into account the possibility for sample displacement. For example, in a thin film sample, if the film surface is not on the x-ray diffraction circle as theoretically required, the technique can adjust the sample “location” by recalculating the diffraction profiles to fit the expected result by the “least square error” approach. Specifically, the method based on “Marquardt least squares” is a procedure to minimize the differences between the observed pattern and simulated pattern. Such minimizations are carried out with a data process criterion called R-weighted pattern, R_{wp} (also known as weighted residual error).

$$R - weighted\ pattern\ (R_{wp}) = \sqrt{\frac{\sum w_m (Y_{o,m} - Y_{c,m})^2}{\sum w_m (Y_{o,m})^2}} \quad (4)$$

where $Y_{o,m}$ is the observed data at data point m, and $Y_{c,m}$ is the calculated data at data point m. In addition, w_m is weighting given to data point m. Specifically, w_m equals to $1/[\sigma(Y_{o,m})]^2$, where $\sigma(Y_{o,m})$ is the error in $Y_{o,m}$. (σ is also known as the standard deviation, and σ^2 is the variance.) Normalization $\sum w_m Y_{o,m}^2$ is the sum of the observed values squared with weight. R_{wp} indicates the closeness between the observation and calculation. The smaller the value, the better the fit. For example, if the material has a complex phase structure, such as a monoclinic structure, one usually looks for R_{wp} value around 20%.¹¹⁰ In this work, R_{wp} is used as the figure of merit.

In Rietveld numerical simulation, the key point is to see the convergence of the “total error.” If the convergence can be reached by a preset “rule” or parameter value such as $R_{wp} = 15\%$, the refinement can stop. Until such goal is reached, the computer program for the refinement will continue. Compared to other methods in FWHM determination, Rietveld refinement can be more inclusive. For example, if the FWHM is caused by lattice microstrains in addition to crystallite size, Rietveld refinement can perform multidimensional data fitting. Since the algorithm in Rietveld is relatively involved, the data fitting does take some time to complete. As a comparison, both Jade

and Rietveld provide FWHM values and crystallite sizes. With Jade, one has to manually select each “selected” diffraction peak to extrapolate the crystallite size value. Even though each calculation does not need much CPU time for Jade, the manual peak selection does take time. With Rietveld, all the peaks are simultaneously being calculated in order to fit diffraction intensities and FWHM values. Thereafter, crystallite sizes and microstrain values can be obtained for all phases. Having said that, as far as the crystallite size calculation is concerned, Jade is actually simpler and easier to use than Rietveld. In this work, Jade[®] is used as the initial screening for the Rietveld refinement performed by Topas[®], which is a software package provided by the manufacturer of HTXRD equipment, Bruker.¹¹¹ With this particular package, ICSD files can be used to input the structural information to obtain lattice parameters and associated properties such as crystallite sizes and microstrains.

5. Quantification

Qualitative analysis involves the identification of a phase or phases in a sample by comparing them to standard patterns. The standard patterns have been collected or calculated by others, usually in a collected database such as ICSD and ICDD.¹⁰⁹ With quantitative analysis, one can determine the number of different phases in a multiphase sample, and the structural characteristics of each phase and associated crystallite sizes and microstrains.

6. Limitations

As stated, XRD relies on long range order.⁹⁷ If nano-crystalline particles are embedded in an amorphous phase, XRD can only yield limited information while TEM can determine the locations and sizes of individual nanocrystals.¹¹² In a multiphase system, if one of the phases has low concentration, quantitative XRD analysis may have difficulty to determine exact phase percentage of that phase. If the number of phases is large and peaks from different phases overlap at several given 2θ angles, it will be difficult to differentiate one phase from another. For titanium niobium oxide systems, if these limitations are recognized, experimental results can be analyzed to obtain the proper phase information and related properties. Since sol-gel processing methods are

recognized as suitable processing techniques for this study, the next step is to carry out experiments to systematically synthesize the materials. With DTA/TGA (differential thermal analysis/thermogravimetric analysis) and HTXRD, these materials can be analyzed.

EXPERIMENTAL METHODS

A. Processing

The precursors used to make the initial sols were titanium (IV) isopropoxide 97% (Sigma Aldrich, 205273), niobium (V) chloride 99% (Sigma Aldrich, 215791), ethanol, butanol and/or acetic acid (Fisher Scientific). There were five different sample sets, each with different Ti:Nb ratios as tabulated in Table I.

Table I. Mole Percentage of Each Sample Set

Sample Set	Relative Mole Percent
100:0	100% Ti : 0% Nb
75:25	75% Ti : 25% Nb
50:50	50% Ti : 50% Nb
25:75	25% Ti : 75% Nb
0:100	0% Ti : 100% Nb

The mixing procedure of each sample set was shown in Figure 2. For 100:0, ethanol and acetic acid were mixed first, followed by titanium isopropoxide. For 0:100, butanol and acetic acid were mixed first, followed by niobium chloride. For the rest of the three samples (75:25, 50:50 and 25:75), ethanol, butanol and acetic acid were added sequentially, followed by niobium chloride and titanium isopropoxide. Other processing conditions did not yield the samples which were useful for this study.

In 100:0, the titanium isopropoxide: acetic acid: ethanol ratios were 1:10:100. In 75:25, 50:50 or 25:75, the titanium isopropoxide: niobium chloride: acetic acid: ethanol: butanol ratios were 1.5:0.5:18.8:150:11.8, 1:1:17.7:100:23.5 or 0.5:1.5:16.5:50:35.3, respectively. For 0:100, the niobium chloride: acetic acid: butanol ratios were 1:7.7:23.5. Once a batch of sol was prepared, it was aged in a beaker with magnetic stirring for 24 hours. Each beaker was then placed onto a hot plate at 60°C for 48 hours, and then into a ThermoScientific Lindberg Blue M (Model# 6965) at 100°C for 24 hours. The resultant powders were ground with an agate mortar and agate pestle, and sieved to a size less than 25 μm .

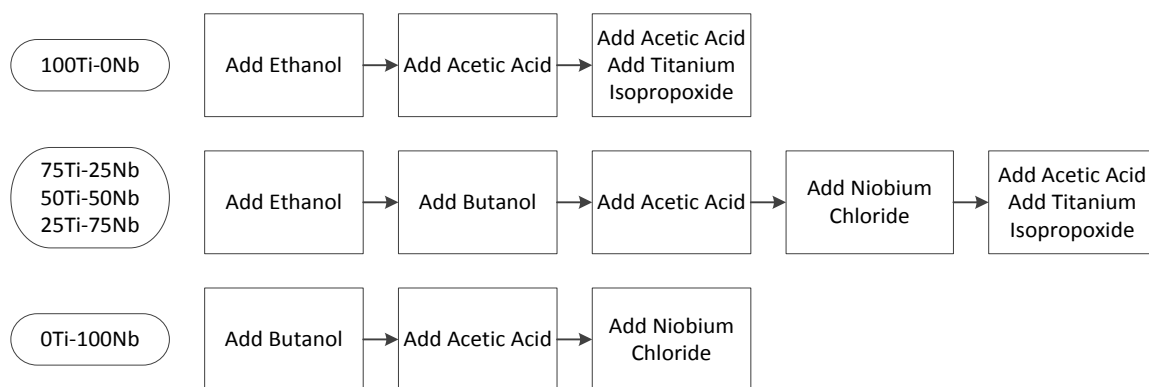


Figure 2. Sample preparations for different sample sets.

B. Sample Analysis Equipment

1. DTA/TGA

Differential thermal analysis/thermogravimetric analysis (DTA/TGA) measurements were performed using a TA Instruments SDT 2960 DTA/TGA. As stated in the previous subsection, each sample was preheat treated to 100°C before the measurements. The mass of each sample was 20-40 mg. The reference material was alumina, with similar mass. The starting temperature for both sample and reference material was approximately 25°C (room temperature), and the maximum temperature was 1500°C with a heating rate of 20°C per minute. Once the temperature reached 1500°C, the holding time was 20 minutes. Thereafter, the sample was cooled with forced air.

2. HTXRD

HTXRD was performed with a Bruker D8 Advance diffractometer equipped with an Anton Paar HTK 1200N furnace and a Kanthal APM element, and with Gobel mirrors in parallel beam orientation. Diffraction spectra were collected from 10° to 100° 2θ for 100:0, 75:25, 25:75 and 0:100 (or 140° 2θ for 50:50). The step size was 0.0313° 2θ, the count time was 200 seconds, voltage was 40 kV, and current was 40 mA, with Cu K α radiation. In a sapphire crucible, powders were heated with a ramp rate of 20°C per minute. Measurements were performed at 100°C intervals. The starting temperature was 200°C and the maximum temperature was 1100°C. A final scan was taken after the furnace was cooled to room temperature (~ 30°C), with a cooling rate of 60°C per minute.

The hold time for 100:0, 75:25, 25:75 and 0:100 was 120 seconds; and that of 50:50 was 600 seconds. The HTXRD heating profiles were somewhat different from those in DTA/TGA. Before XRD analysis, each sample was preheated a second time at 190°C for 24 hours, after the initial 100°C heat treatment. The preheat treatment might cause slight difference in a reaction temperature between DTA and HTXRD.

3. MDI Jade and Bruker Topas

To analyze the diffraction patterns, MDI Jade and Bruker Topas 4.1 software packages were used. The Jade software was used to analyze phase compositions and to determine crystallite sizes through FWHM calculations. With the Bruker Topas 4.1 software, phase compositions, crystallite sizes and microstrains were determined. In Topas, a 2nd order Chebyshev polynomial was used. Other HTXRD parameters included primary and secondary goniometer radii of 250 mm, the linear PSD 2θ angular range of 12.847°, and an LP factor of “0.” In the refinement, the specimen displacement, volume, crystallite size, strain, and lattice parameters were set on fit; and the ion site locations and occupancy were not set on fit.

RESULTS

A. 100:0

The DTA/TGA spectra of the 100:0 powdered sample is measured as a function of temperature from 25°C to 1500°C as illustrated in Figure 3. The DTA signal's units are micro-volts/mg, and the TGA weight loss is measured in percentage. In the DTA curve, endotherms are observed at approximately 110°C, 203°C, 406°C, 500°C and 684°C and exotherms are observed at approximately 172°C, 376°C, 426°C, 539°C and 833°C. TGA results show that a total weight loss is approximately 33.2% with heating. In particular, approximately 6.8% is lost between 25°C and 270°C, 22.5% is lost between 270°C and 400°C, and 3.9% is lost between 400°C and 900°C.

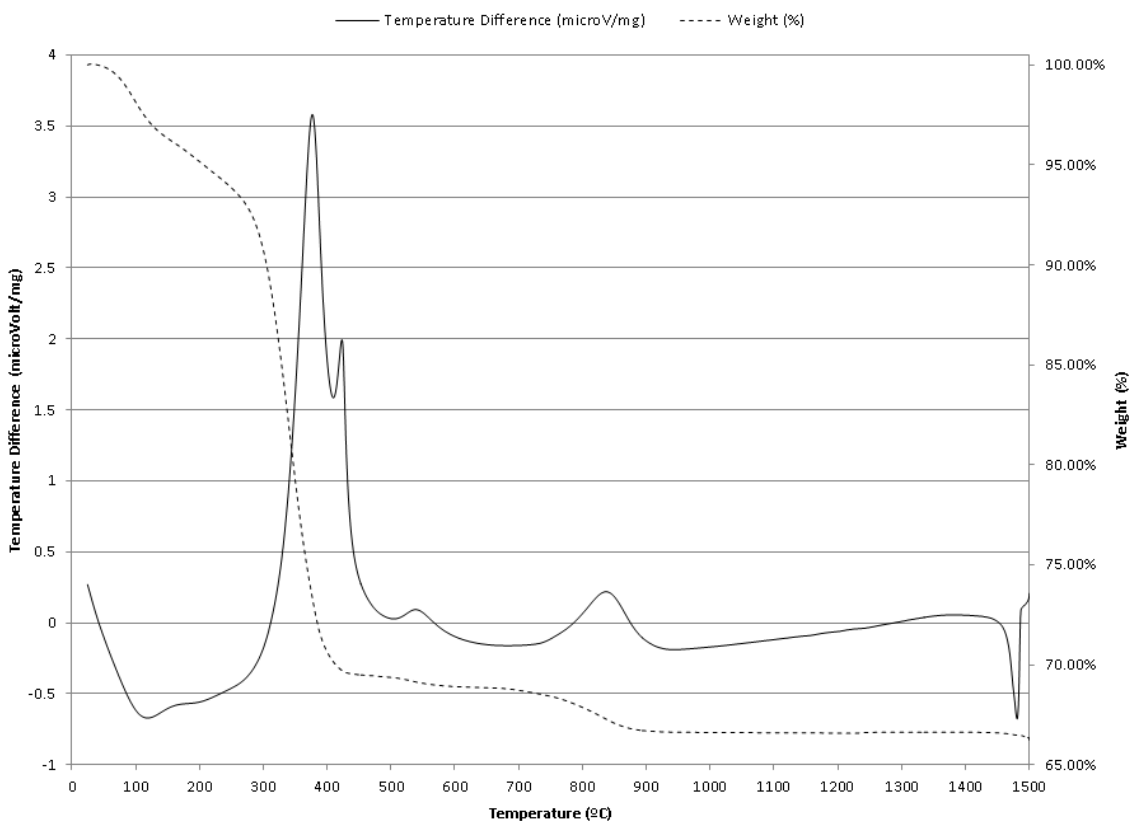


Figure 3. Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) of 100:0 sample.

The HTXRD patterns of the 100:0 powders are obtained by *in-situ* heating from 29.3°C to 1100°C; with 11 curves shown (200°C-1100°C with 100°C steps, ~30°C) are illustrated in Figure 4. Initial crystallization occurs between 400°C and 500°C and the sample remains crystalline throughout heating. A phase change occurs between 800°C and 1000°C. Peak sharpness and intensity increases with temperature.

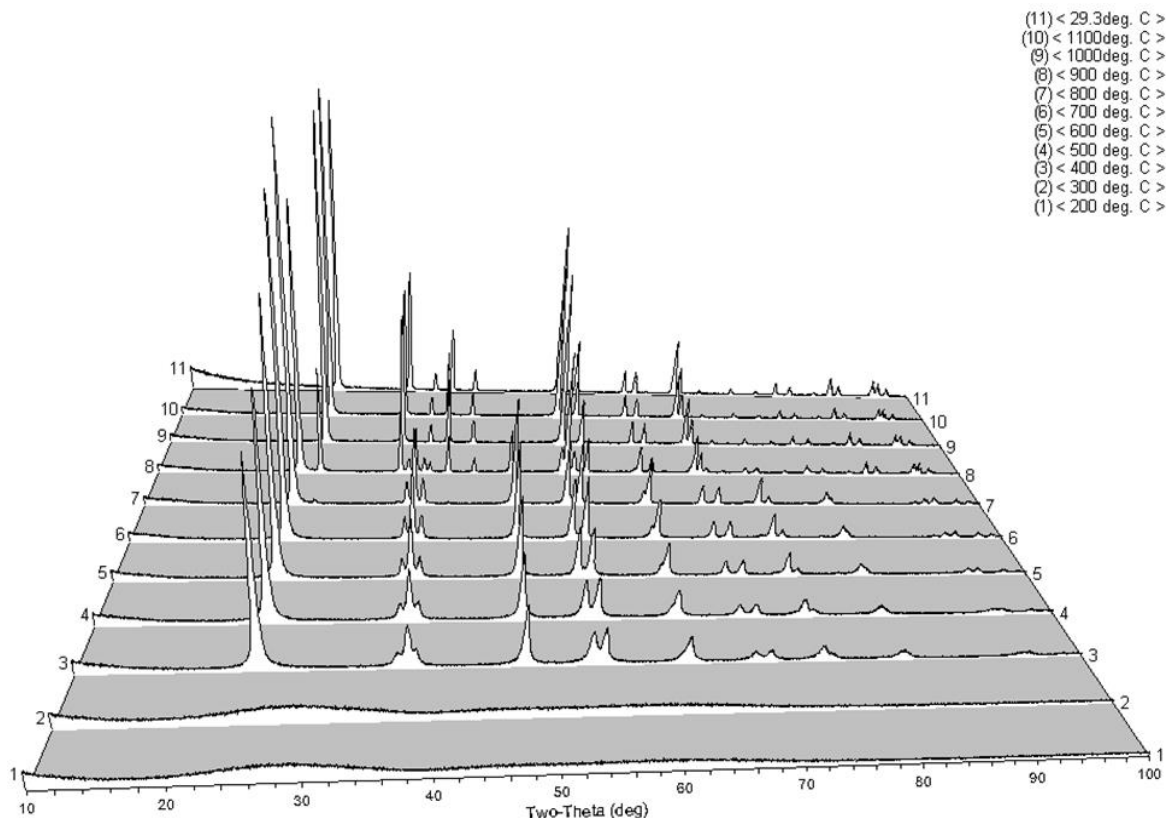


Figure 4. High temperature x-ray diffraction patterns of 100:0 powders from 200°C to 1100°C. (See Figure 5 for peak identification.)

Selected XRD at three different temperatures are illustrated in Figure 5. An amorphous phase is observed at 300°C, an anatase phase (A) is observed at 600°C; and a rutile phase (R) is observed at 1100°C. For the phase pure anatase or rutile diffraction pattern, most diffraction peaks are assigned letter A or R, respectively. The major anatase peak locations are near 25.26°, 37.81° and 47.93° 2 θ , respectively. The maximum anatase peak location near 25.26° 2 θ is used later. The major rutile peak locations are

near 27.38° , 36.08° and 54.26° 2θ , respectively. The maximum rutile peak locations near 27.38° are used later.

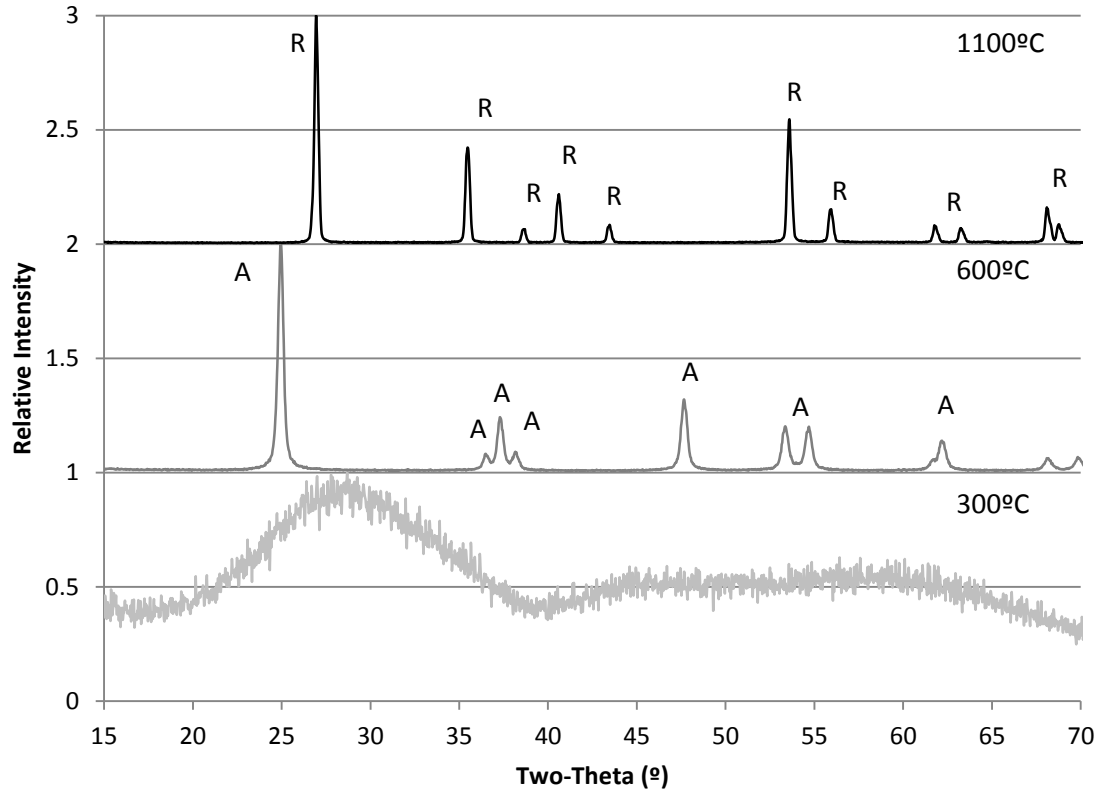


Figure 5. High temperature x-ray diffraction patterns of 100:0 powders at 300°C, 600°C and 1100°C (A: TiO₂ Anatase, R: TiO₂ Rutile).

Using PDF-matching, Table II summarizes the phase identification of 100:0 sample as a function of heat treatment temperature. The anatase and rutile TiO₂ phases are identified as PDF#04-014-0490 and PDF#01-072-4812, respectively.

Table II. Phase Identification of 100:0 as a Function of Temperature

Temperature (°C)	Phase Identification
200-300	Amorphous
400-700	TiO ₂ -Anatase #04-014-0490
800-900	TiO ₂ -Anatase #04-014-0490, TiO ₂ -Rutile #01-072-4812
1000-1100	TiO ₂ -Rutile #01-072-4812

Rietveld refinement was performed to determine crystallite size and relative phase percentages for 100:0 as a function of temperature. The figure of merit (R_{wp}) as well as some measured, calculated, and difference spectra are illustrated in Appendix A. Furthermore, unit cell lattice parameters, volumes and microstrains were calculated as a function of temperature and shown in Appendix B; however, these results are beyond the scope of this discussion and will not be presented here.

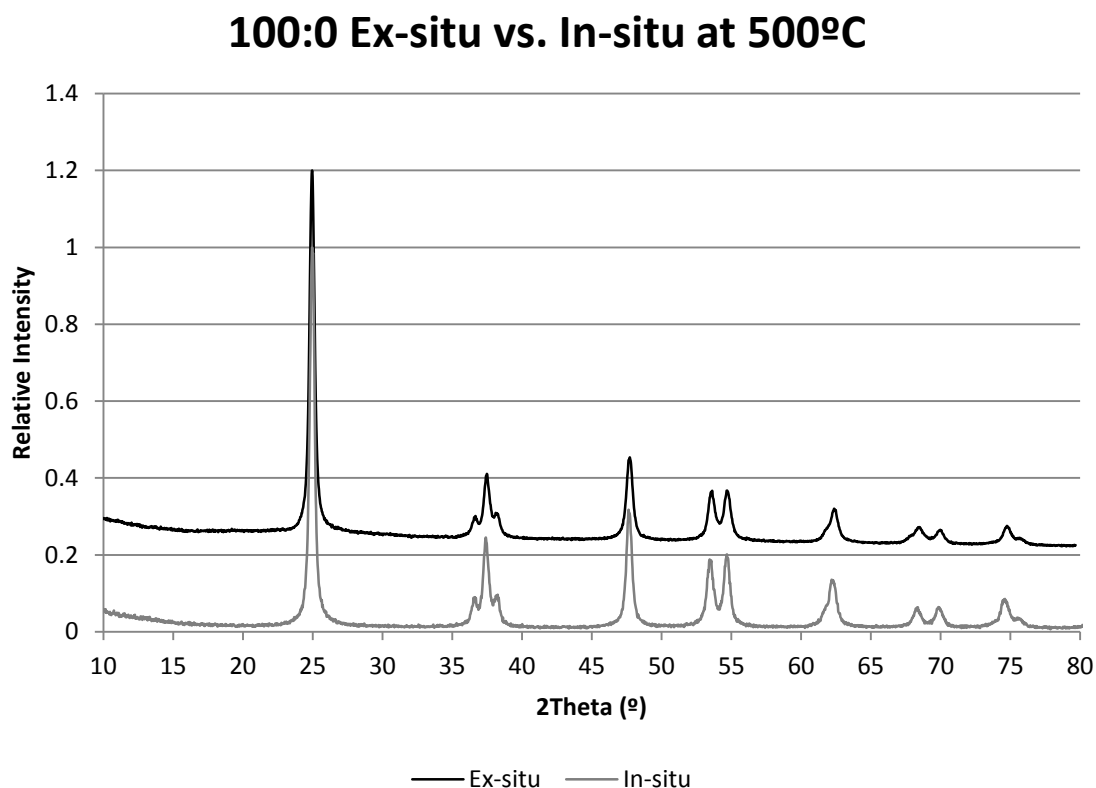


Figure 6. Comparison of 100:0 ex-situ (top) vs. in-situ (bottom) XRD patterns.

In Figure 6, a comparison is made between XRD patterns obtained via in-situ and ex-situ diffraction techniques; where diffraction peak width near a given 2θ angle such as 25° is similar between two measurements.

The crystallite sizes as a function of temperature for each of the phases present in 100:0 is illustrated in Figure 7. To clearly illustrate the changes in crystallite sizes, the

vertical axis was in logarithm scale. At 800°C or lower, the sizes are approximately 100 nm or less. Anatase crystallite size increases from approximately 38 to 109 nm between 400°C and 800°C and rutile crystallite size increased from approximately 47 to 247 nm from 800°C to 1100°C. In general, the experimental error for this sample set is between 5-10%.

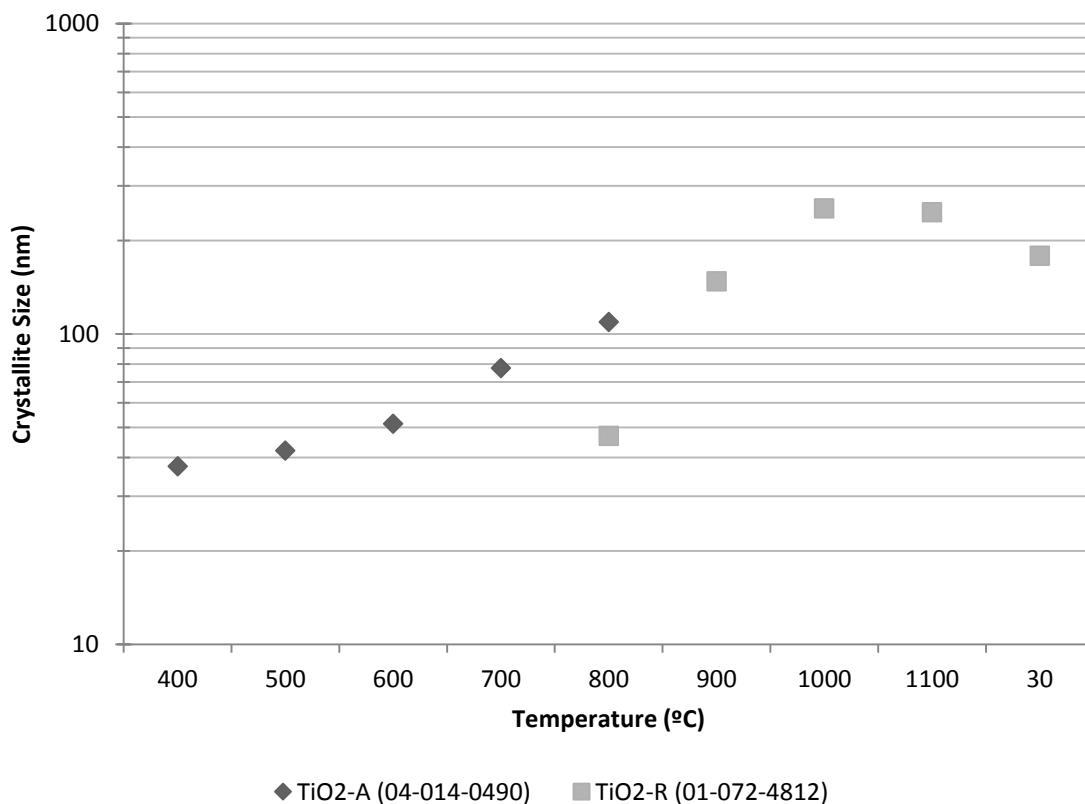


Figure 7. Crystallite size as a function of temperature for 100:0.

The relative phase percentage observed for 100:0 as a function of temperature was illustrated in Figure 8. The phase percentage is 100% anatase between 400°C and 700°C, and 100% rutile between 1000°C and 1100°C, respectively. At 800°C, the sample contains approximately 98% anatase and 2% rutile. At 900°C, the sample contains approximately 51% rutile and 49% anatase. The anatase to rutile phase transformation temperature is between 700°C and 1000°C.

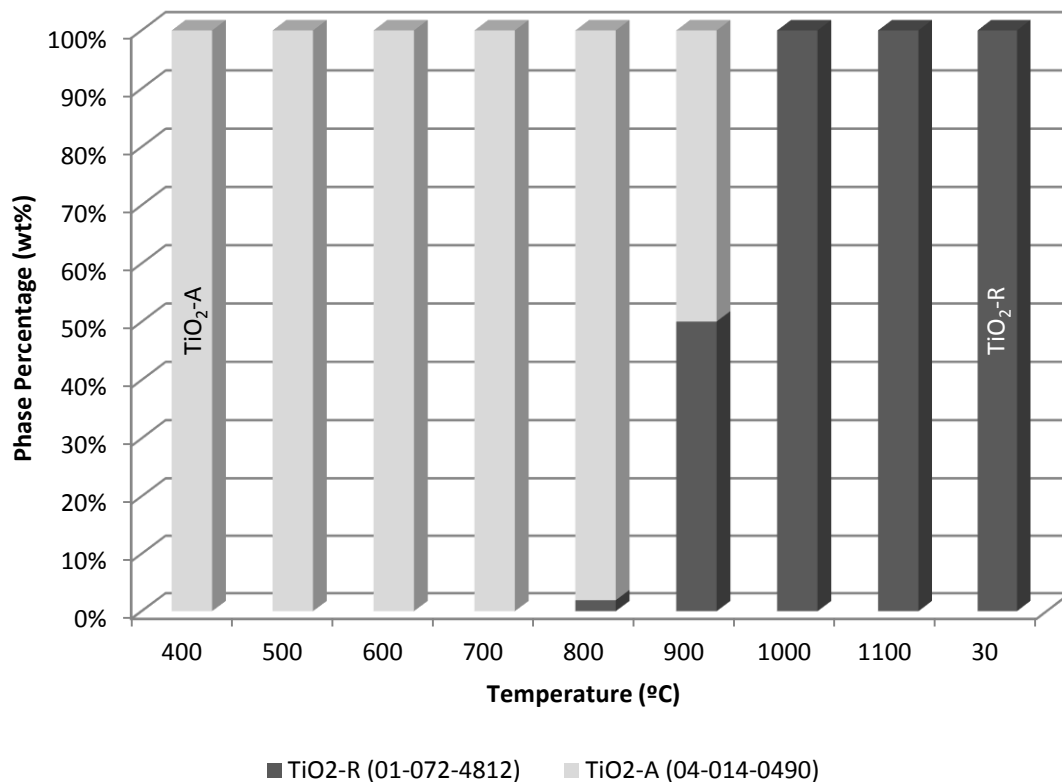


Figure 8. Relative phase percentage (wt%) as a function of temperature for 100:0.

B. 75:25

The DTA/TGA spectra of the 75:25 powdered sample is measured as a function of temperature from 25°C to 1500°C as illustrated in Figure 9. In the DTA curve, endotherms are observed at approximately 110°C, 210°C, 440°C and 600°C and exotherms are observed at approximately 240°C, 420°C, 490°C, 560°C and 690°C. TGA results show a total weight loss of approximately 25.5% with heating. In particular, approximately 2.9% is lost between 25°C and 170°C, 11.9% is lost between 170°C and 385°C, and 10.7% is lost between 385°C and 710°C.

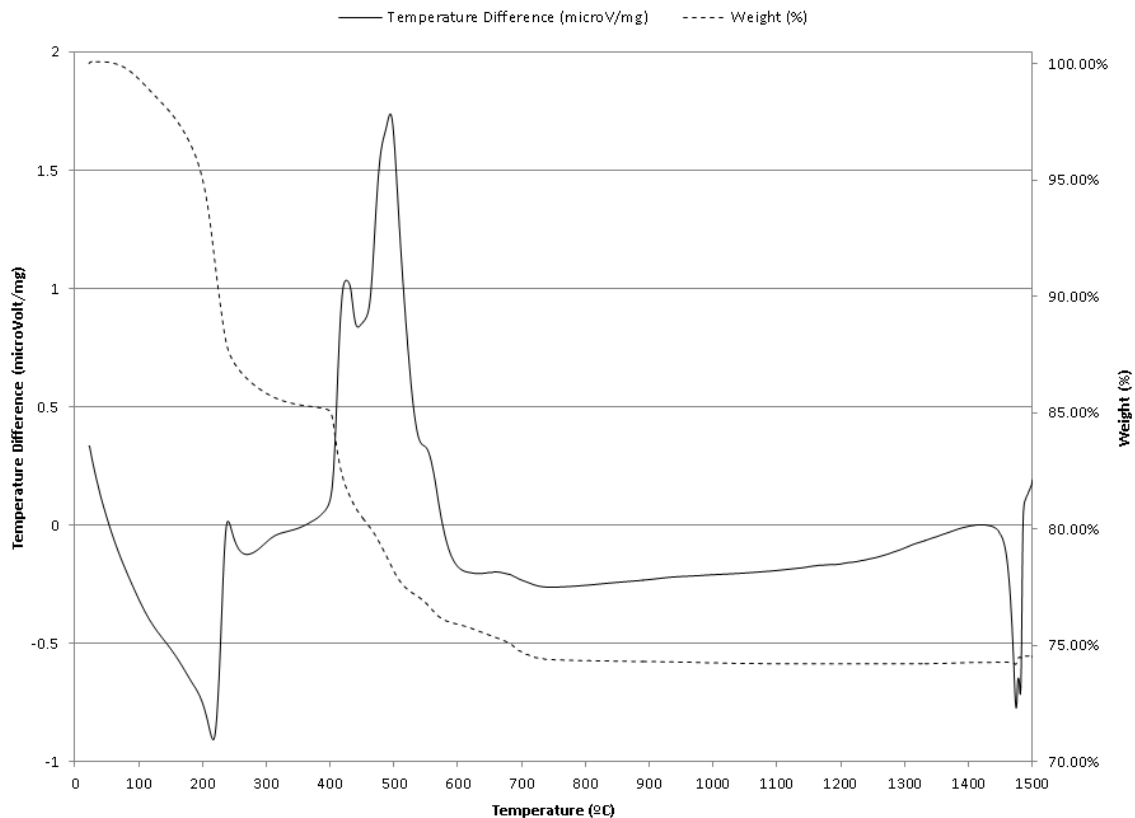


Figure 9. Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) of 75:25 sample.

The HTXRD patterns of 75:25 powders are obtained by *in-situ* heating from 29.5°C to 1100°C as illustrated in Figure 10. Initial crystallization occurs between 200°C and 300°C and the sample continues to be crystallized at higher temperatures. Peak sharpness and intensity increases with temperature.

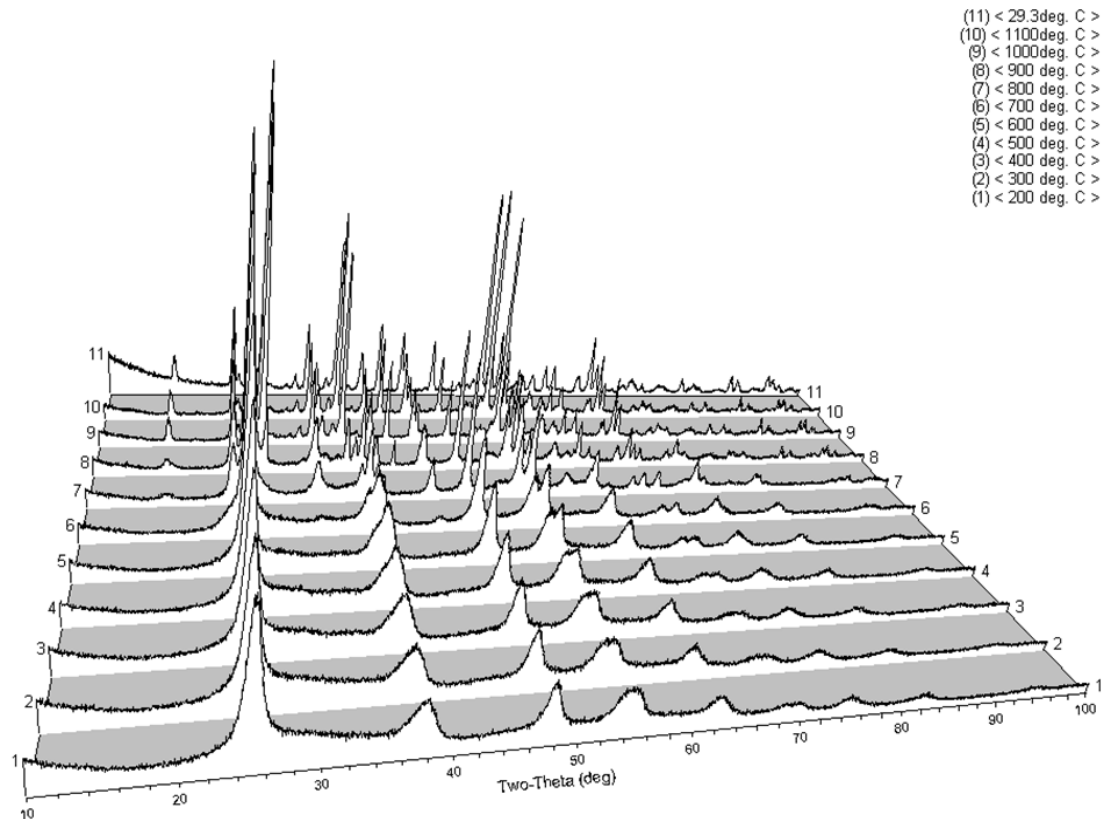


Figure 10. High temperature x-ray diffraction patterns of 75:25 powders from 200°C to 1100°C. (See Figure 11 for phase identification.)

Figure 11 shows three HTXRD patterns: 700°C (bottom), 900°C (middle) and 1100°C (top), respectively. There are two phases at 700°C: TiO_2 anatase (A) and $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ (◆). At 900°C, TiO_2 anatase, TiO_2 rutile (R) and TiNb_2O_7 (▲) coexist. At 1100°C, TiO_2 rutile and TiNb_2O_7 coexist. For $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$, the major peak locations are near 26.74°, 32.17° and 52.93° 2 θ , respectively. For TiNb_2O_7 , the major peak locations are near 23.87°, 26.22°, 35.63° and 47.70° 2 θ , respectively.

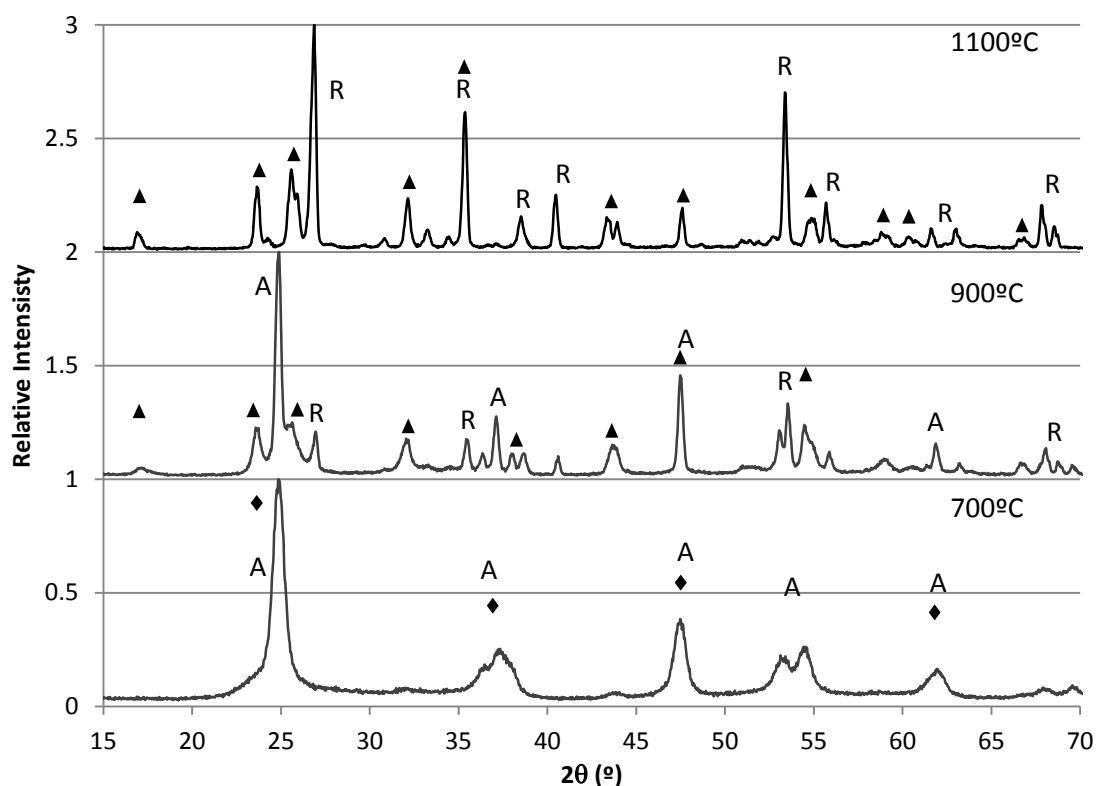


Figure 11. High temperature x-ray diffraction patterns of as prepared 75:25 powders at 700°C, 900°C and 1100°C (A: TiO₂ Anatase, R: TiO₂ Rutile, ♦: Ti₂Nb₁₀O₂₉, ▲: TiNb₂O₇).

Using PDF-matching, Table III summarizes the phase identification of 75:25 sample as a function of temperature. The anatase and rutile TiO₂ phases in 100:0 are also identified in 75:25. The Ti₂Nb₁₀O₂₉ and TiNb₂O₇ phases are identified as PDF#04-007-0496 and PDF#04-007-5182, respectively.

Table III. Phase Identification of 75:25 as a Function of Temperature

Temperature (°C)	Phase Identification
200-800	TiO ₂ -Anatase #04-014-0490, Ti ₂ Nb ₁₀ O ₂₉ # 04-007-0496
900	TiO ₂ -Anatase #04-014-0490, TiO ₂ -Rutile #01-072-4812, TiNb ₂ O ₇ #04-007-5182
1000-1100	TiO ₂ -Rutile #01-072-4812, TiNb ₂ O ₇ #04-007-5182

Rietveld refinement was performed to determine crystallite size and relative phase percentages for 75:25 as a function of temperature. The figure of merit (R_{wp}) as well as all measured, calculated, and difference spectra are shown in Appendix C. Furthermore, unit cell volumes and microstrains are calculated as a function of temperature and shown in Appendix D; however, these results are beyond the scope of this discussion and will not be presented here.

The crystallite size as a function of temperature for each of the phases present in 75:25 is shown in Figure 12. As the temperature increases from 200°C to 1100°C, the size generally increases. For example, the size of $TiNb_2O_7$ increases from approximately 17 to 95 nm when the temperature varied from 900°C to 1100°C. The anatase crystallite size increases from approximately 29 to 49 nm between 200°C and 800°C, and rutile size increases from approximately 98 to 256 nm between 900°C and 1100°C. The crystallite size for $Ti_2Nb_{10}O_{29}$ is 10 nm or less, with some scattering. The error for this sample set is between 5-10%.

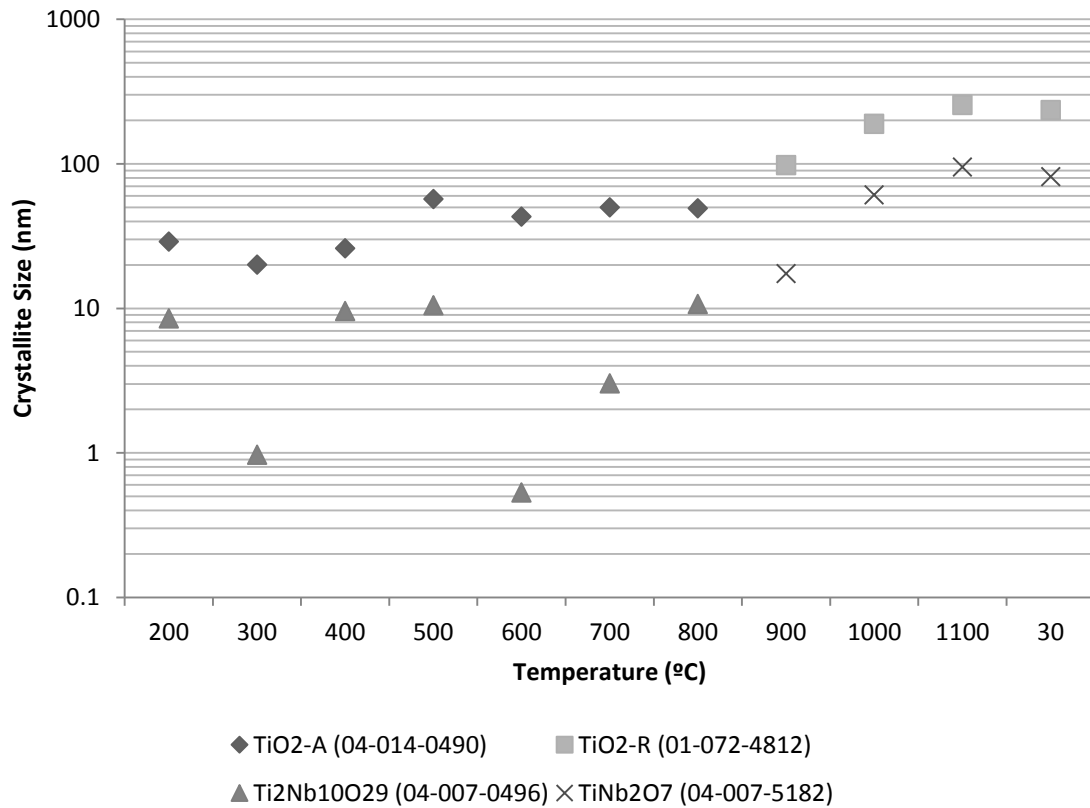


Figure 12. Crystallite size as a function of temperature for 75:25.

The relative phase percentage as a function of temperature is illustrated in Figure 13. For example, at 800°C, relative phase percentages of anatase TiO_2 and $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ are 65% and 35%, respectively. At 900°C, relative percentages of anatase TiO_2 , rutile TiO_2 and TiNb_2O_7 are 47%, 17% and 36%, respectively. At 1100°C, relative percentages of rutile TiO_2 and TiNb_2O_7 are 64% and 36%, respectively. For TiO_2 , the anatase to rutile phase transformation temperature is between 800°C and 1000°C; which is slightly different from that of 100:0 as far as lower transformation temperature is concerned.

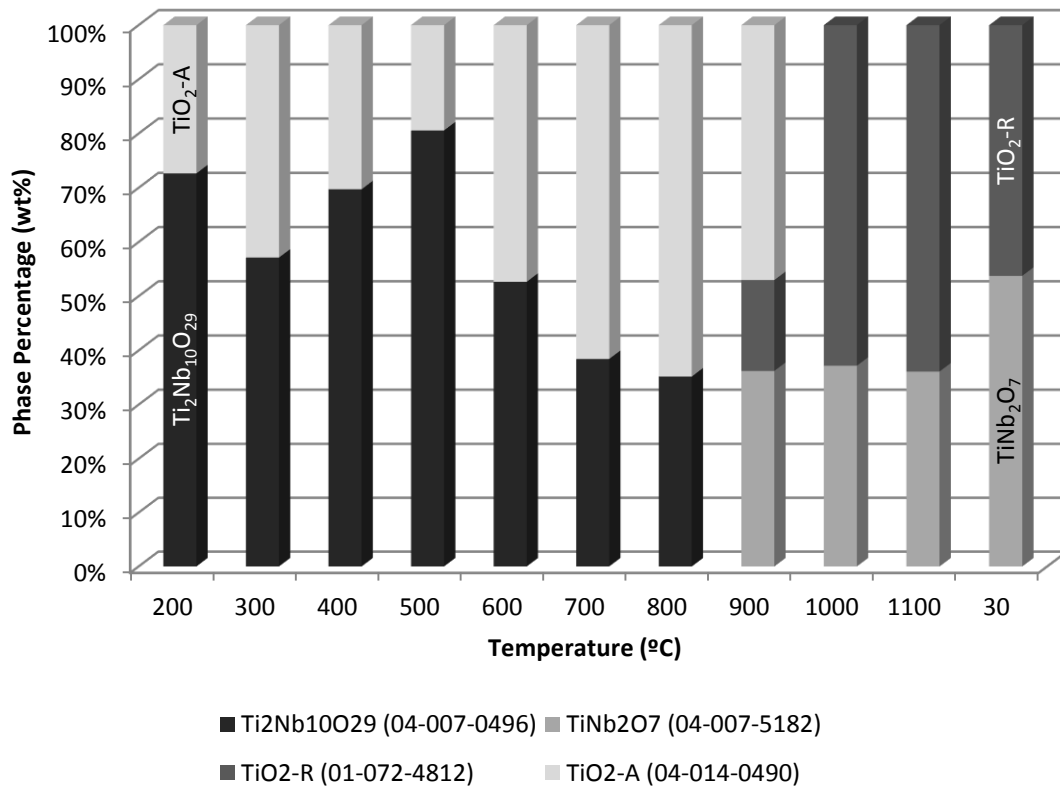


Figure 13. Relative phase percentage (wt%) as a function of temperature for 75:25.

C. 50:50

The DTA/TGA spectra of the 50:50 powdered sample is measured as a function of temperature from 25°C to 1500°C as illustrated in Figure 14. In the DTA curve, endotherms are observed at approximately 100°C, 205°C, 350°C and 940°C and exotherms are observed at approximately 232°C, 389°C, 415°C and 501°C. TGA results

showed that a total weight loss is approximately 20.9% with heating. In particular, approximately 4.1% is lost between 25°C and 185°C, 10.2% is lost between 185°C and 370°C, and 6.6% is lost between 370°C and 600°C.

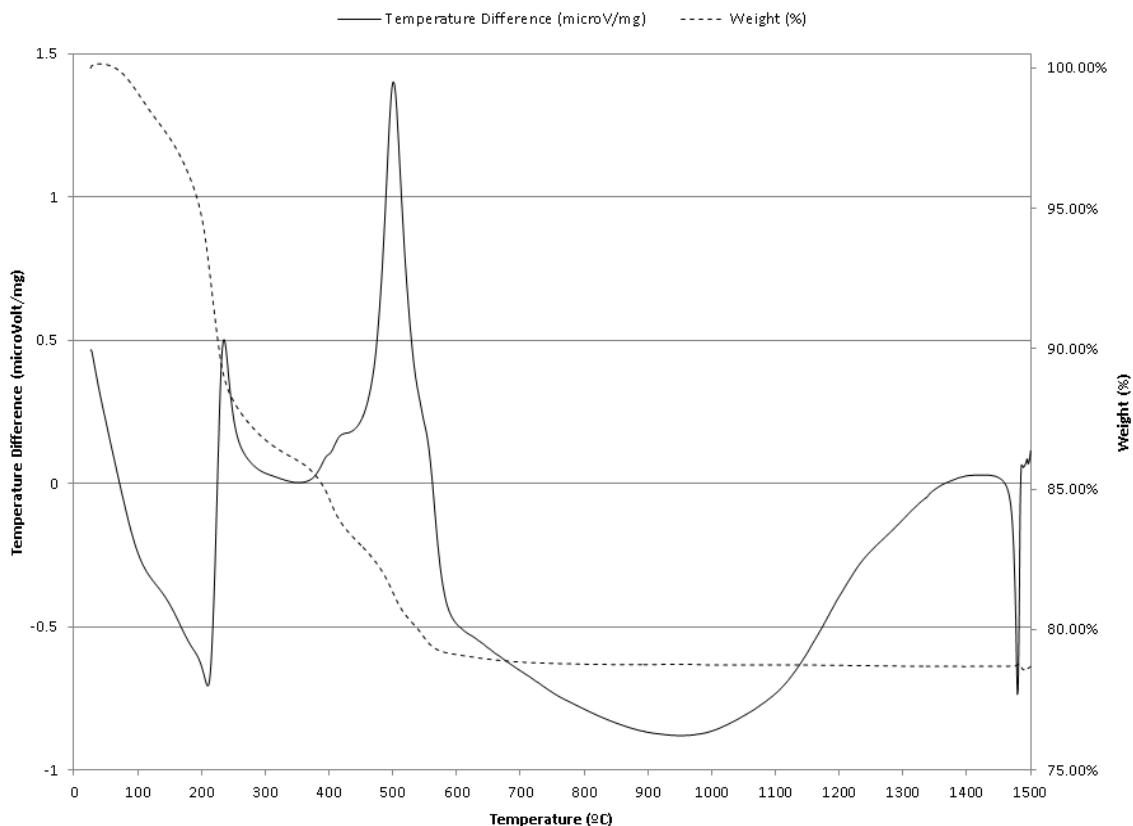


Figure 14. Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) of 50:50 sample.

HTXRD patterns of 50:50 powders are obtained as illustrated in Figure 15. Initial crystallization occurs between 600°C and 700°C and the sample remained crystalline throughout heating. Peak sharpness and intensity increases with temperature.

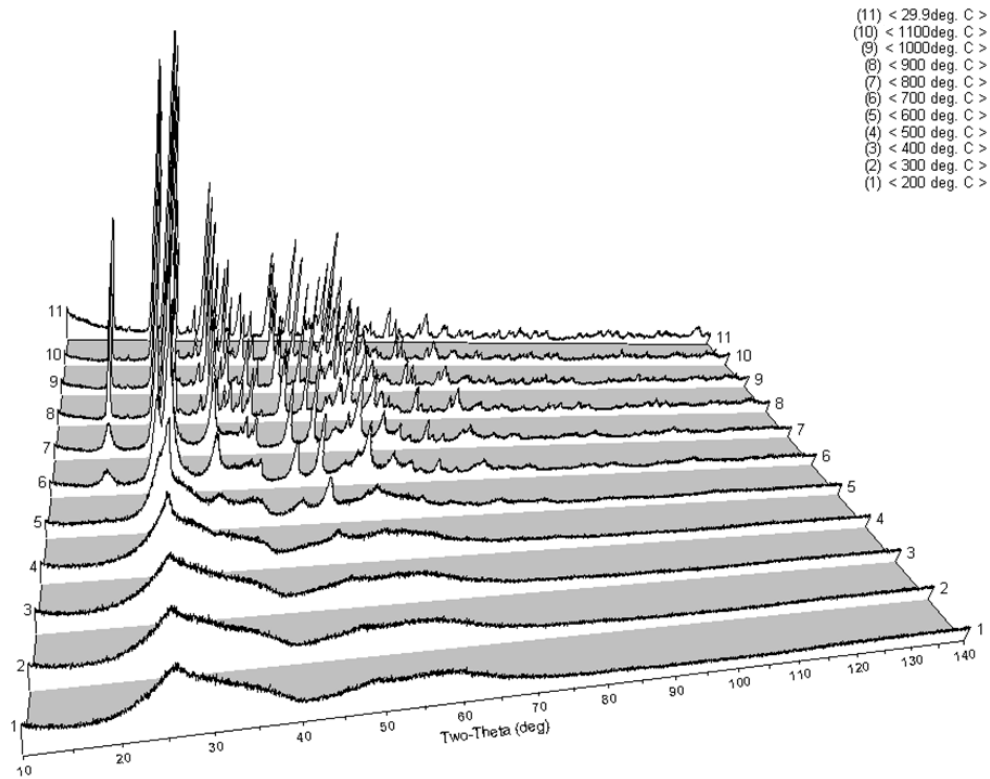


Figure 15. High temperature x-ray diffraction patterns of 50:50 powders from 200°C to 1100°C. (See Figure 16 for phase identification..)

Figure 16 illustrates three HTXRD patterns: 200°C (bottom), 800°C (middle) and 1100°C (top), respectively. An amorphous phase exists at 200°C; TiO_2 anatase (A) and TiNb_2O_7 (▲) exists at 800°C; and TiO_2 rutile (R) and TiNb_2O_7 exists at 1100°C.

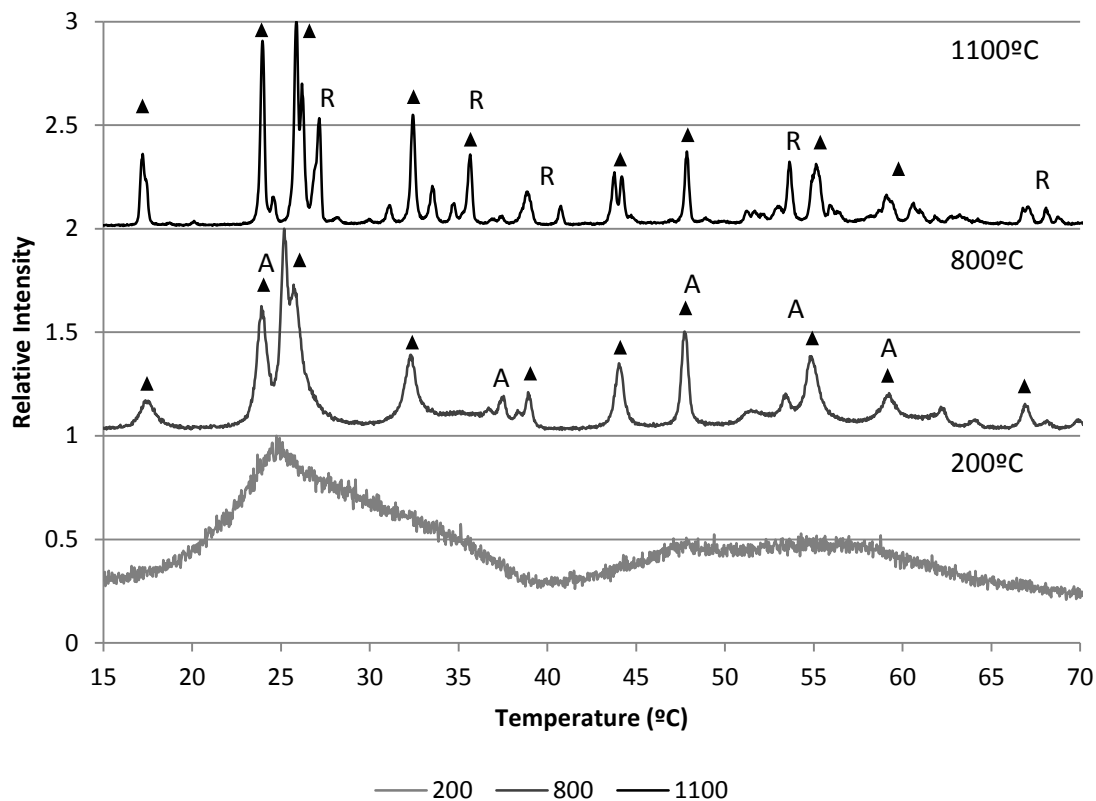


Figure 16. High temperature x-ray diffraction patterns of 50:50 powders at 200°C, 800°C and 1100°C (A: TiO₂ Anatase, R: TiO₂ Rutile, ▲: TiNb₂O₇).

Using PDF-matching, Table IV summarizes the phase identification of 50:50 sample as a function of heat treatment temperature. There are four phases identified in 50:50 sample. The anatase and rutile TiO₂ were previously identified in 100:0 sample; and both titanium niobium oxides were previously identified in 75:25 sample. The error for this sample set is between 5-10%.

Table IV. Phase Identification of 50:50 as a Function of Temperature

Temperature (°C)	Phase Identification
200-500	Amorphous
600-700	TiO ₂ -Anatase #04-014-0490, Ti ₂ Nb ₁₀ O ₂₉ # 04-007-0496 & TiNb ₂ O ₇ #04-007-5182
800-900	TiO ₂ -Anatase #04-014-0490 & TiNb ₂ O ₇ #04-007-5182
1000-1100	TiO ₂ -Rutile #01-072-4812 & TiNb ₂ O ₇ #04-007-5182

Rietveld refinement was performed to determine crystallite size and relative phase percentages for 50:50 as a function of temperature. The figure of merit (R_{wp}) as well as all measured, calculated, and difference spectra are shown in Appendix E. Furthermore unit cell volumes and microstrains are calculated as a function of temperature and shown in Appendix F; however, these results are beyond the scope of this discussion and will not be presented here.

The crystallite size for each phase is plotted as a function of temperature in Figure 17. As the temperature increases, the crystallite size generally increases. The size of anatase increases from approximately 10 to 130 nm between 600°C and 900°C; that of $Ti_2Nb_{10}O_{29}$ increases from 0.3 nm to 4 nm between 600°C and 700°C; and that of $TiNb_2O_7$ increases from 2 nm to 244 nm between 600°C and 1100°C. For rutile TiO_2 , the sizes are between 145 nm and 370 nm at 1000°C-1100°C. The error for this sample set is between 5-10%.

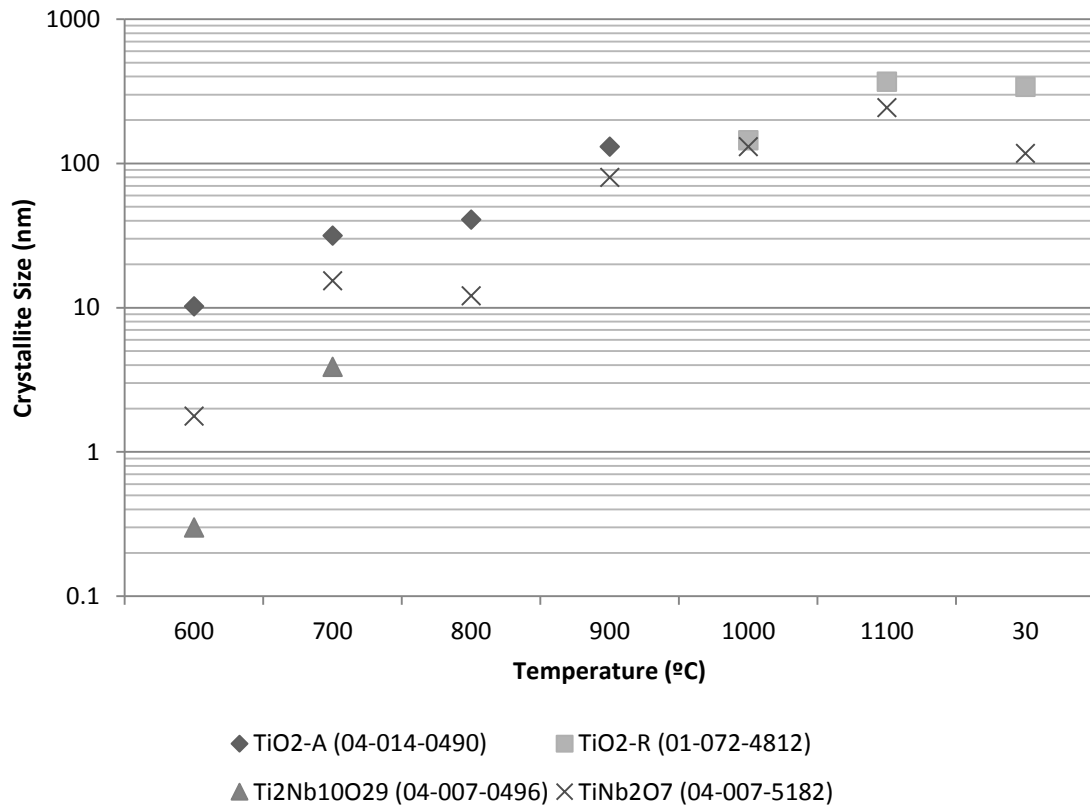


Figure 17. Crystallite size as a function of temperature for 50:50.

The relative phase percentage as a function of temperature is illustrated in Figure 18. For example, at 900°C, the relative phase percentages of anatase TiO_2 and $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ are 21% and 79%, respectively. At 1100°C, the relative percentages of rutile TiO_2 and TiNb_2O_7 are 25% and 75%, respectively, which is different from that of sample 75:25 where the percentages are approximately 64% and 36%. Such change in phase distribution is related to the addition of Nb. The TiO_2 anatase to rutile phase transformation temperature is between 900°C and 1000°C; which is slightly different from that of 75:25 as far as lower transformation temperature is concerned. In fact, as the Ti:Nb ratio varies from 100:0 to 50:50, the lower transition temperature increases from 700°C to 900°C.

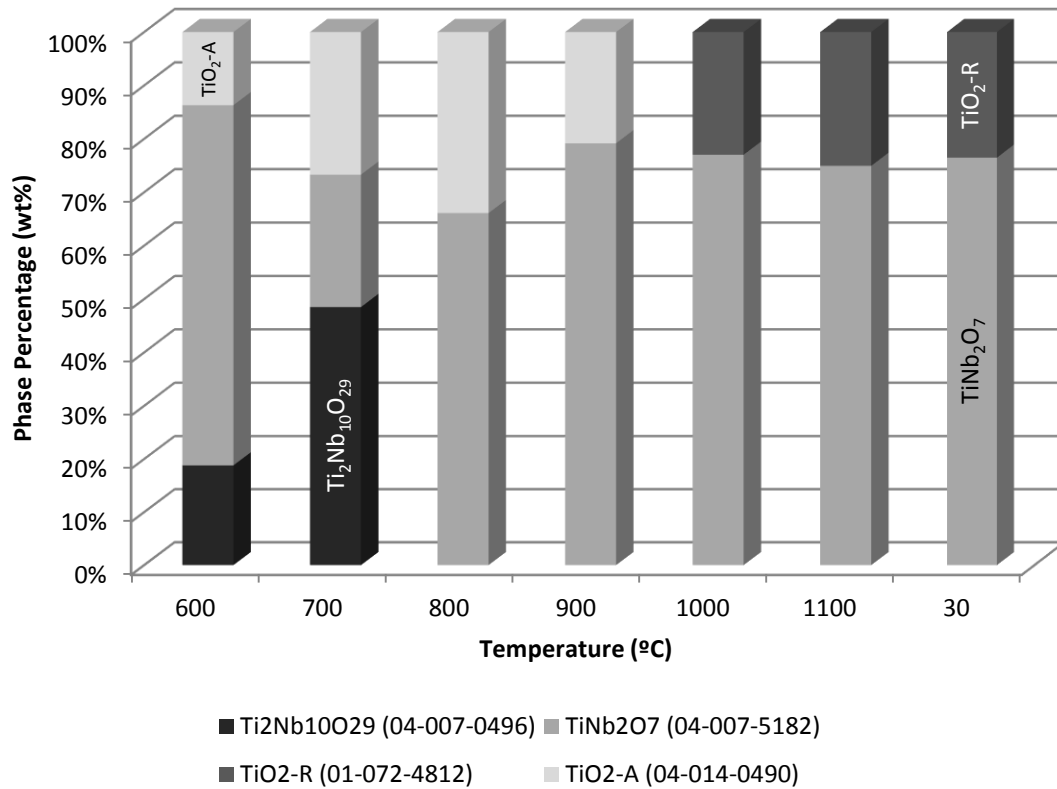


Figure 18. Relative phase percentage (wt%) as a function of temperature for 50:50.

D. 25:75

The DTA/TGA spectra of the 25:75 powdered sample was measured as a function of temperature from 25°C to 1500°C as illustrated in Figure 19. In the DTA curve, endotherms are observed at approximately 120°C, 220°C, 320°C and 570°C and exotherms are observed at approximately 250°C and 389°C. TGA results show that a total weight loss is approximately 16.8% with heating. In particular, approximately 3.8% is lost between 25°C and 190 °C, 6.4% is lost between 190°C and 250 °C, and 6.6% is lost between 250°C and 600°C.

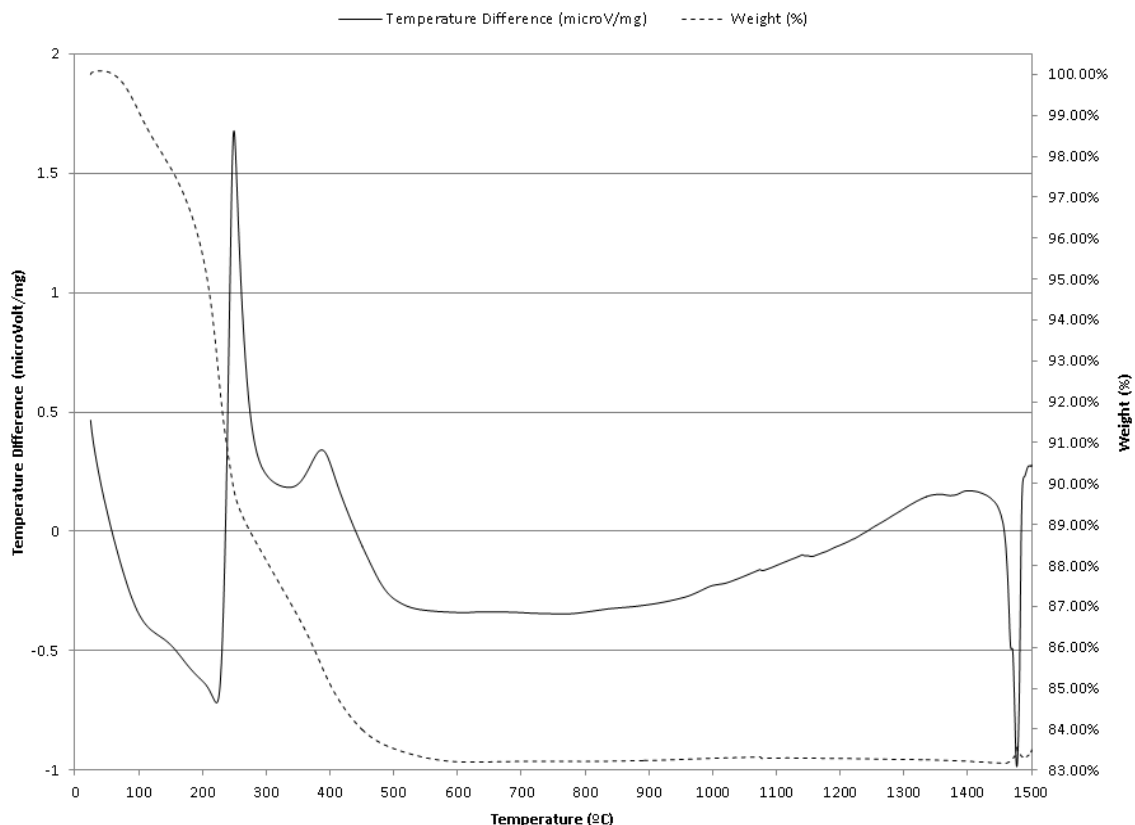


Figure 19. Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) of 25:75 sample.

Figure 20 shows the HTXRD patterns of 25:75 powders heated *in-situ* from 29.5°C to 1100°C. Initial crystallization occurs between 500°C and 600°C, and the sample remains crystalline throughout heating. Peak sharpness and intensity increase with temperature.

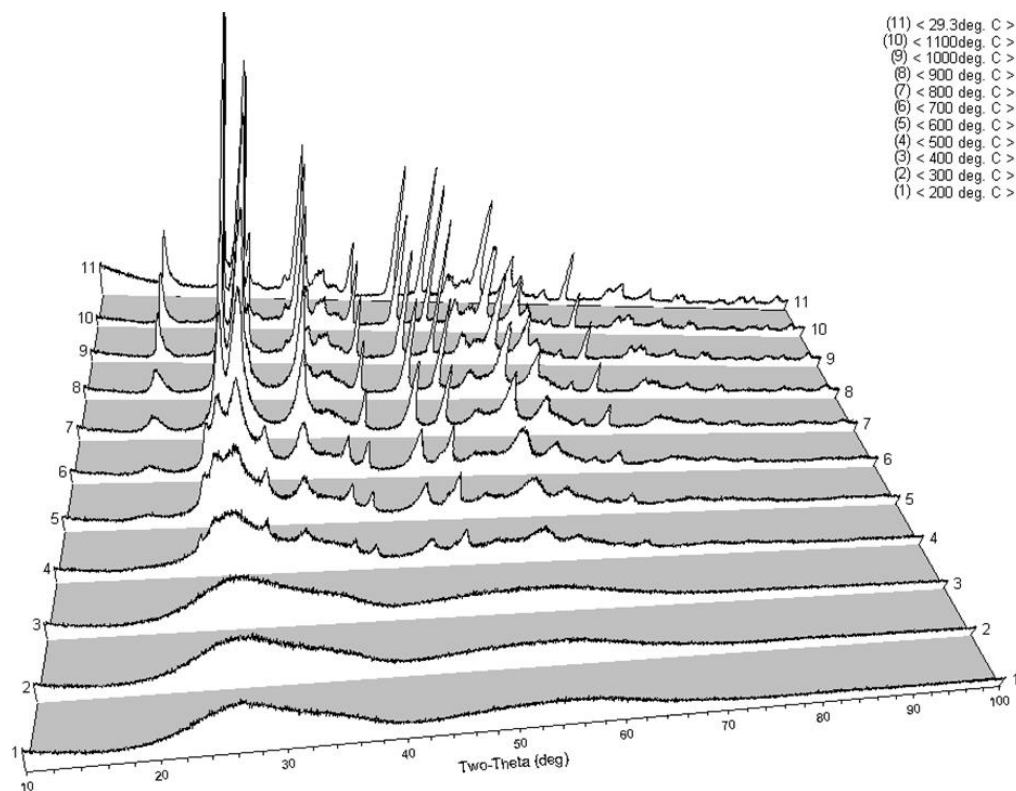


Figure 20. High temperature x-ray diffraction patterns of 25:75 powders from 200°C to 1100 °C. (See Figure 21 for phase identification.)

Figure 21 shows three HTXRD patterns: 400°C (bottom), 700°C (middle) and 1100°C (top), respectively. An amorphous phase is observed at 400°C. At 700°C, Nb_2O_5 orthorhombic (■), $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ (◆) and TiNb_2O_7 (▲) are observed. At 1100°C, Nb_2O_5 monoclinic (●) and TiNb_2O_7 are observed. The major peak locations of monoclinic Nb_2O_5 are at 23.736° and 25.509° 2θ , respectively. The major peak locations of orthorhombic Nb_2O_5 are at 22.606° , 28.399° and 36.599° 2θ , respectively.

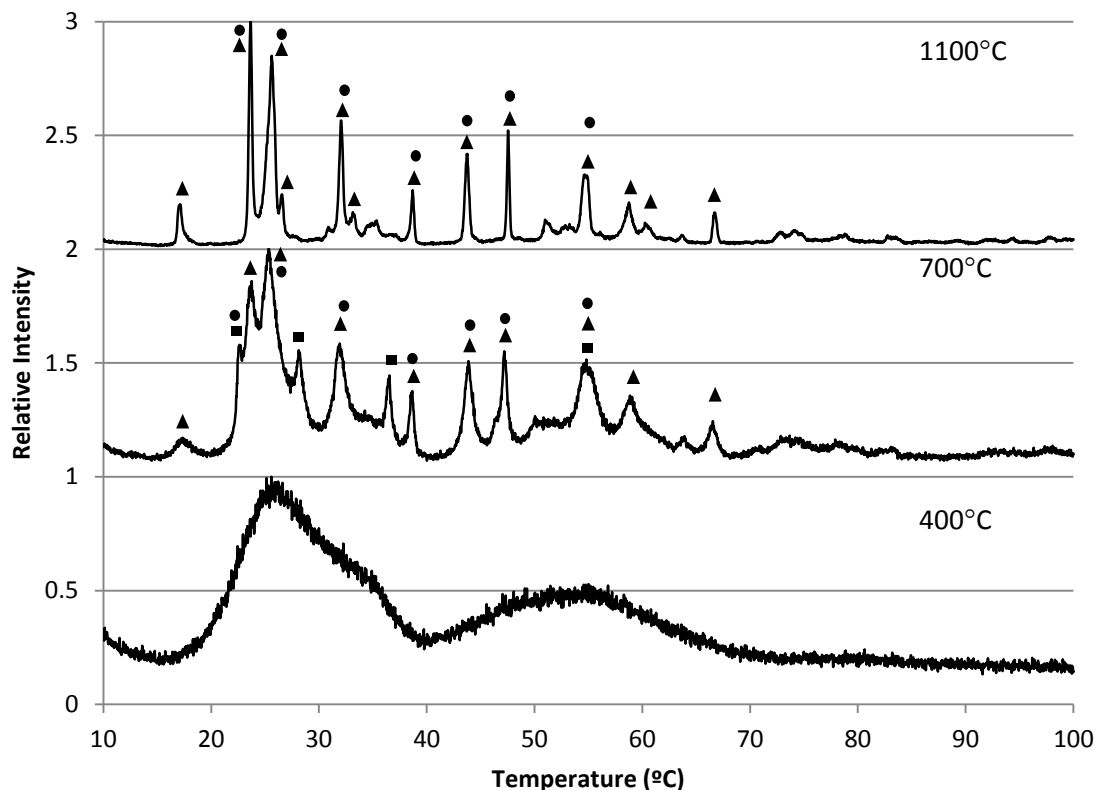


Figure 21. High temperature x-ray diffraction patterns of 25:75 powders at 400°C, 800°C and 1100°C (●: Nb₂O₅ monoclinic, ■: Nb₂O₅ orthorhombic, ▲: TiNb₂O₇).

Using PDF-matching, Table V summarizes the phase identification of 25:75 sample as a function of heat treatment temperature. Both previously identified titanium niobium oxides, Ti₂Nb₁₀O₂₉ and TiNb₂O₇, were also identified in 25:75. The orthorhombic Nb₂O₅ and monoclinic Nb₂O₅ were identified as PDF#04-007-0752 and PDF#00-037-1468, respectively.

Table V. Phase Identification of 25:75 as a Function of Temperature.

Temperature (°C)	Phase Identification
200-400	Amorphous
500-600	Orthorhombic Nb ₂ O ₅ #04-007-0752, Ti ₂ Nb ₁₀ O ₂₉ # 04-007-0496
700	Orthorhombic Nb ₂ O ₅ #04-007-0752, Monoclinic Nb ₂ O ₅ #00-037-1468, TiNb ₂ O ₇ #04-007-5182
1000-1100	Monoclinic Nb ₂ O ₅ #00-037-1468, TiNb ₂ O ₇ #04-007-5182

Rietveld refinement was performed to determine crystallite size and relative phase percentages as a function of temperature. The figure of merit (R_{wp}) as well as all measured, calculated, and difference spectra are shown in Appendix G. Furthermore unit cell volumes and microstrains are calculated as a function of temperature and shown in Appendix H; however, these results are beyond the scope of this discussion and will not be presented here.

The crystallite size for each phase is plotted as a function of temperature in Figure 24. As the temperature increases, the crystallite size generally increases. Between 500°C and 600°C, the size of $Ti_2Nb_{10}O_{29}$ increases from 5.8 to 7.2 nm. For orthorhombic Nb_2O_5 , the size increases from 1.2 to 14.5 nm between 500°C and 700°C. For $TiNb_2O_7$, the size increases from 11 nm to 194 nm between 700°C and 1100°C. For monoclinic Nb_2O_5 , the size increases from 10 nm to 160 nm when the temperature increases from 700°C to 1000°C. The error for this sample set is between 5-10%.

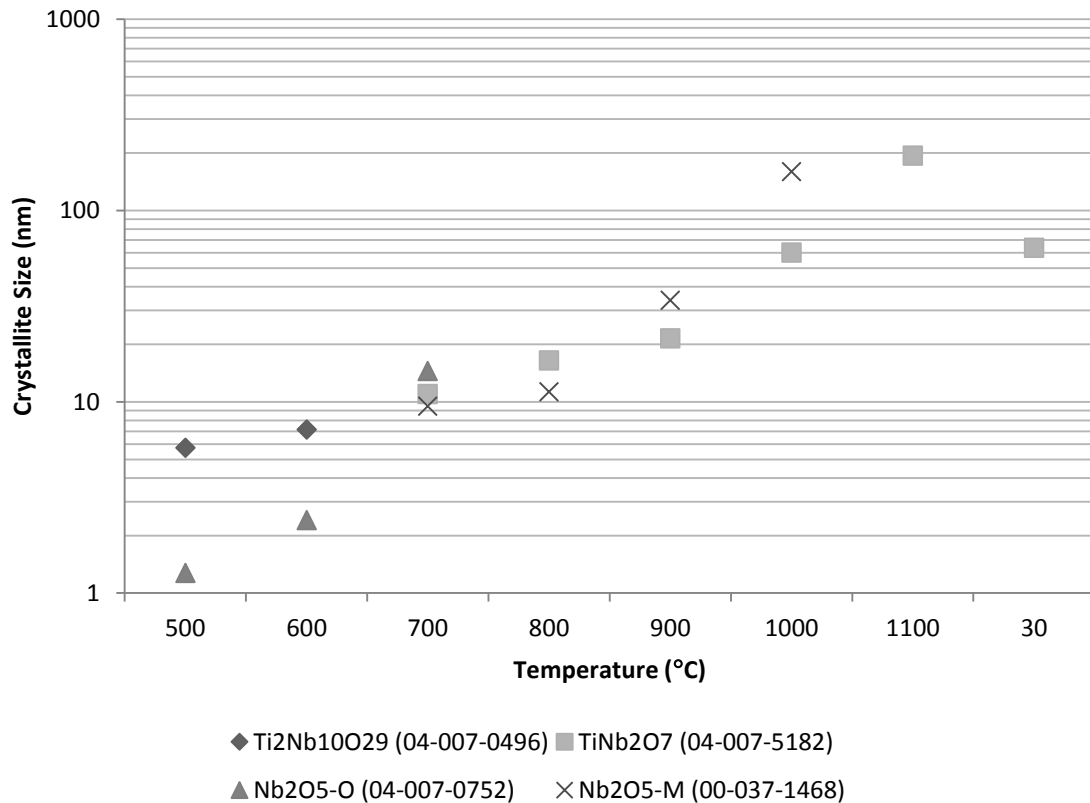


Figure 22. Crystallite size as a function of temperature for 25:75.

The relative phase percentage as a function of temperature is shown in Figure 23. At 600°C, relative phase percentages of $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ and orthorhombic Nb_2O_5 are 35% and 65%, respectively. At 700°C, relative phase percentages of TiNb_2O_7 , monoclinic Nb_2O_5 and orthorhombic Nb_2O_5 are 24%, 59% and 17%, respectively. At 1100°C, relative percentages of TiNb_2O_7 and monoclinic Nb_2O_5 are 51% and 49%, respectively; reflecting the presence of both Ti and Nb. For Nb_2O_5 , the orthorhombic to monoclinic phase transformation temperature is between 600°C and 800°C.

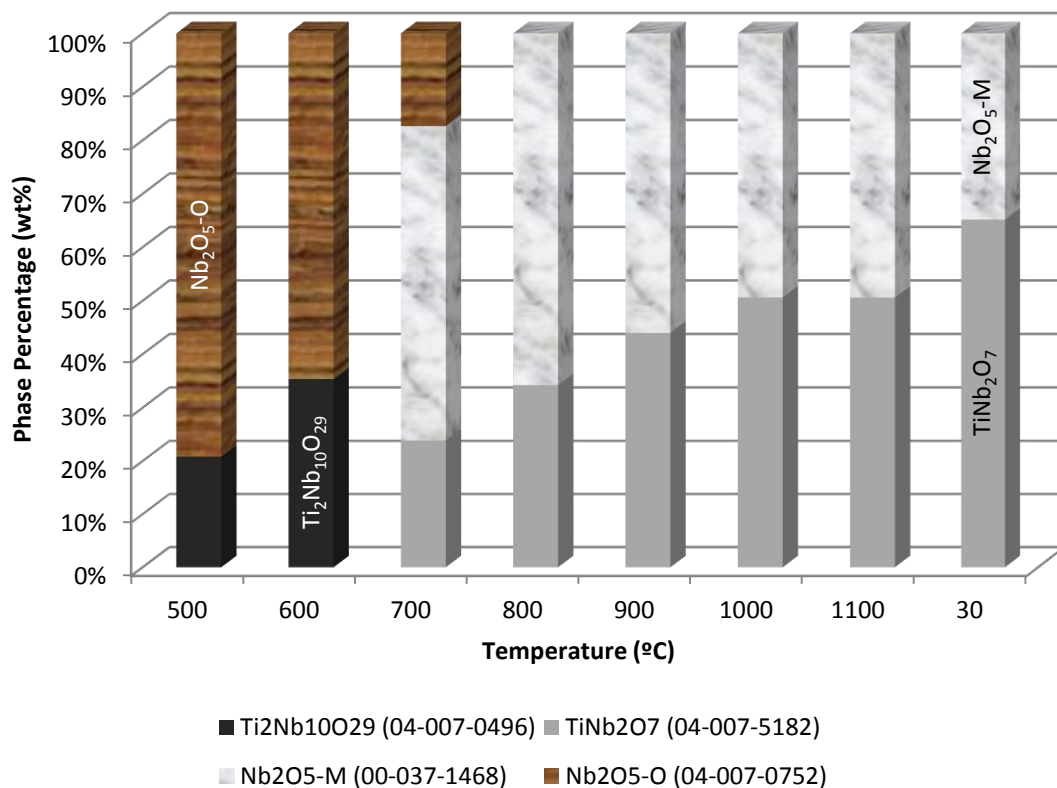


Figure 23. Relative phase percentage (wt%) as a function of temperature for 25:75.

E. 0:100

The DTA/TGA spectra of the 0:100 powdered sample were measured as a function of temperature from 25°C to 1500°C as illustrated in Figure 24. In the DTA curve, endotherms are observed at approximately 110°C, 214°C, 255°C, 530°C, 610°C and 1268°C and exotherms are observed at approximately 235°C, 305°C, 426°C, 447°C,

504°C, 550°C and 1117°C. TGA results show that a total approximately 25.7% of the sample weight is lost with heating. In particular, approximately 3.4% is lost between 25°C and 185°C, 12.6% is lost between 185°C and 385°C, 7.2% is lost between 385°C and 520°C, and 2.5% is lost between 520°C and 600°C.



Figure 24. Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) of 0:100 sample.

Figure 25 shows the HTXRD patterns of 0:100 powders heated *in-situ* from 29.5°C to 1100°C. The sample remains x-ray amorphous up to 400°C. Initial crystallization occurs between 500°C and 600°C, and the sample remains crystalline throughout heating. Peak sharpness and intensity increases with temperature.

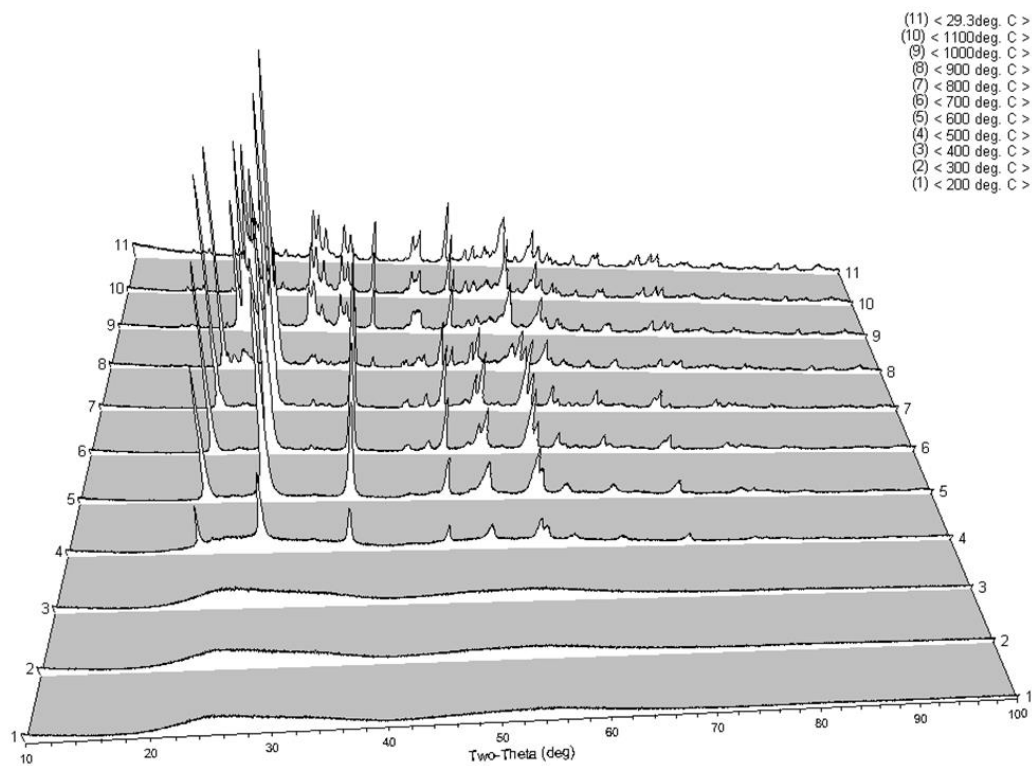


Figure 25. High temperature x-ray diffraction patterns of 0:100 powders from 200°C to 1100°C. (See Figure 26 for phase identification.)

Figure 26 shows three HTXRD patterns: 400°C (bottom), 700°C (middle) and 1100°C (top), respectively. An amorphous phase is observed at 400°C; Nb_2O_5 orthorhombic (■) is observed at 500°C; and Nb_2O_5 monoclinic (●) is observed at 900°C.

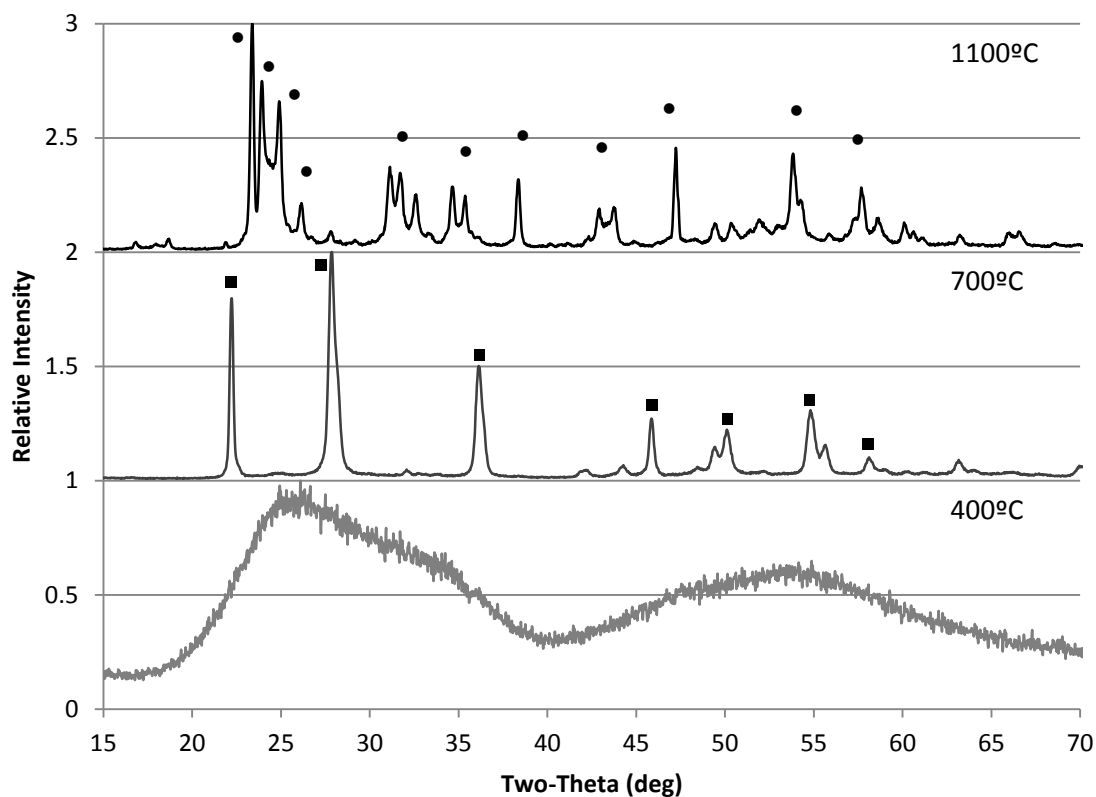


Figure 26. High temperature x-ray diffraction patterns of 0:100 powders from 400°C, 700°C and 1100 °C (•: Nb₂O₅ monoclinic, ■: Nb₂O₅ orthorhombic).

Using PDF-matching, Table VI summarizes the phase identification of 0:100 sample as a function of heat treatment temperature. The Nb₂O₅ orthorhombic and monoclinic phases identified previously in the 25:75 sample were also identified in 0:100.

Table VI. Phase Identification of 0:100 as a Function of Temperature

Temperature (°C)	Phase Identification
200-400	Amorphous
500-900	Orthorhombic Nb ₂ O ₅ #04-007-0752
1000-1100	Monoclinic Nb ₂ O ₅ #04-037-1468

Rietveld refinement was performed to determine crystallite size and relative phase percentages as a function of temperature. The figure of merit (R_{wp}) as well as all

measured, calculated, and difference spectra are shown in Appendix I. Furthermore unit cell volumes and microstrain is calculated as a function of temperature and shown in Appendix J; however, these results are beyond the scope of this discussion and will not be presented here.

The crystallite size for each phase is plotted as a function of temperature in Figure 27. As the temperature increases, the crystallite size generally increases. For monoclinic Nb_2O_5 , the crystallite size increases from 20 nm to 34 nm as the temperature increases from 1000°C to 1100°C. For orthorhombic Nb_2O_5 , the crystallite size generally increases from 2.4 nm to 440 nm when the temperature increases from 500°C to 800°C. The error for this sample set is between 5-10%.

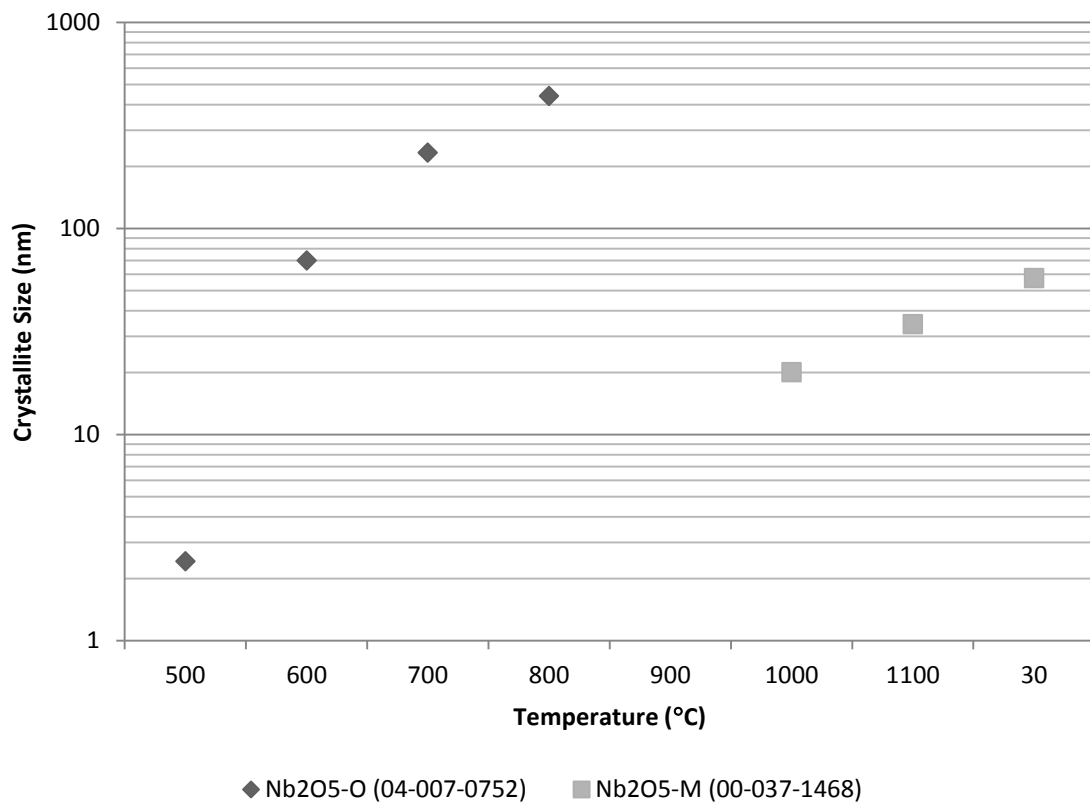


Figure 27. Crystallite size as a function of temperature for 0:100.

The relative phase percentage observed for 0:100 as a function of temperature is illustrated in Figure 28. At 500°C-900°C, the only phase present is orthorhombic Nb_2O_5 . At 1000°C-1100°C, the phase present is monoclinic Nb_2O_5 . For Nb_2O_5 , the orthorhombic

to monoclinic phase transformation temperature range is 900°C - 1000°C; which is higher than 600°C - 800°C for 25:75.

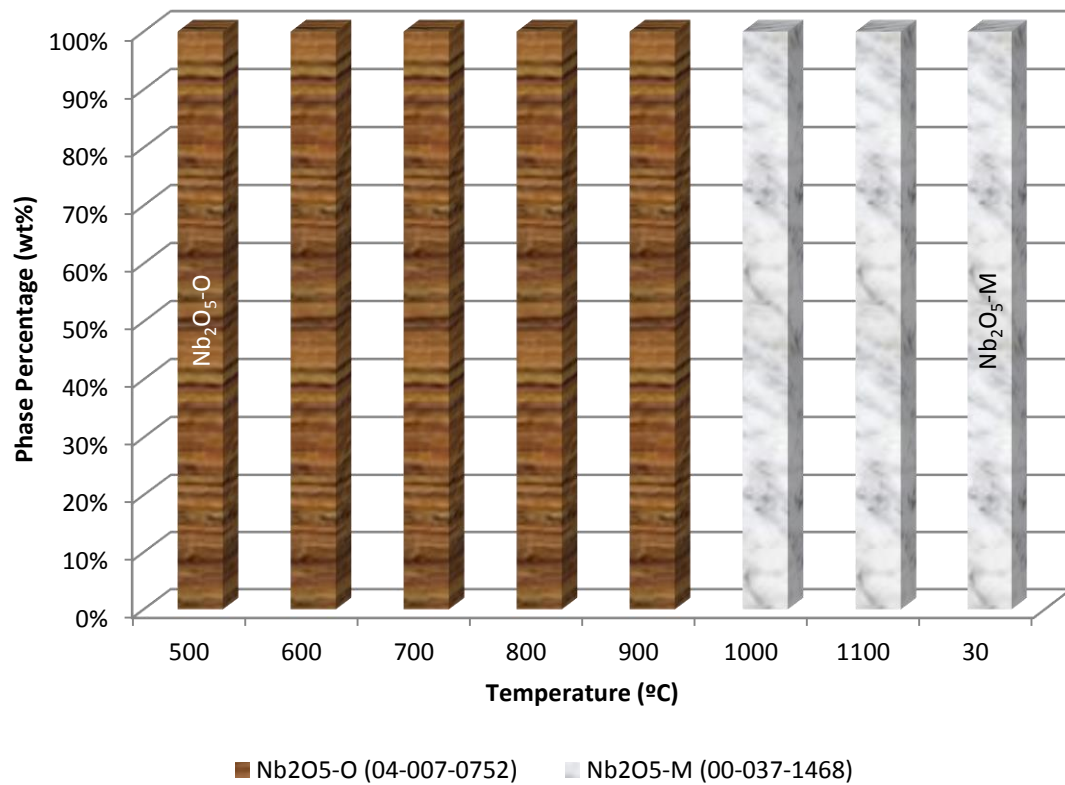


Figure 28. Relative phase percentage (wt%) as a function of temperature for 0:100.

DISCUSSION

A. Thermal Analysis

1. 100:0

From DTA and TGA results, thermal reactions and weight losses could be related to each other. The first endothermic peak at 110°C in the DTA, and the corresponding ~ 2.5% weight loss in temperature region 70°C-120°C in TGA, could be assigned to the removal of water.^{113,114} The second endothermic peak at 203°C in the DTA, and the ~ 4.3% weight loss in temperature region 128°C-210°C in TGA, could be assigned to the removal of organics such as ethanol.¹¹⁵⁻¹¹⁸ The exothermic peak at 376°C in the DTA, and the ~ 22.5% weight loss in the temperature range 275°C-400°C in TGA, could be assigned to the decomposition of organics such as acetic acid, removal of hydrolyzed isopropoxide ligands bonded in the titanium precursors and oxidation.^{19,113,114,119-121} The 426°C exothermic peak indicated the anatase crystallization temperature being between 400°C and 500°C.^{19,119,120,122-124} The exothermic peak at 539°C in the DTA, and the ~ 0.5% weight loss in the temperature range 500°C-600°C in TGA, could be assigned to the removal of hydroxyl groups.^{113,115,116,125} The exothermic peak at 833°C could be assigned to the anatase to rutile phase transformation between 650°C and 1000°C.^{122-124,126-129} The feature near 1480°C was due to the instrumentation limitation when the heating rate suddenly changed from 20°C/min to 0.1°C/min.¹³⁰

In thermal measurements, the heating rate affected the exothermic peak location; e.g., if the rate differed by 10°C/min, the peak location shifted more than 10°C.¹²³ The reaction temperature such as anatase formation temperature determined from the DTA curve was not exactly the same as that determined by XRD measurement.^{125,127,131}

When the sample temperature increased from 400°C to 900°C, the maximum anatase peak location is reduced by 0.094° 2 θ .¹³¹ Such reduction in peak location could be attributed to the anatase unit cell size expansion.^{108,132} Based on Bragg's equation, a similar 2 θ shift could be obtained via a calculation described in Appendix C.¹³³ When the temperature increased from 900°C to 1100°C, the maximum rutile peak location was reduced by 0.063° 2 θ ; which was consistent with an ex-situ XRD result in literature.¹³⁴

For anatase, the 400°C crystallite size was 38 nm, the growth rate between 400°C and 900°C could be broadly approximated as 0.5% per 1°C, and the anatase size was larger than rutile size at 800°C; which were consistent with literature.^{116,126,127,135-138} For rutile, the 800°C size was 47 nm, and the growth rate between 800°C and 1100°C could be broadly approximated as 1.4% per 1°C; which were also consistent with literature.^{135,137}

2. 75:25

From DTA and TGA, thermal reactions and weight losses could be related to each other. The first endothermic peak at 100°C in the DTA, and the ~ 1% weight loss in temperature region 70°C-120°C, could be assigned to the removal of water.^{113,114} The second endothermic peak at 210°C in the DTA, and the ~ 8% weight loss in temperature region 150°C-230°C, could be assigned to the removal of organic such as ethanol and butanol.^{55,115,116,139} The exothermic peak at 240°C in the DTA, and the ~ 4% weight loss in temperature region 230°C-300°C in TGA, could be assigned to the decomposition of organics such as acetic acid, removal of hydrolyzed isopropoxide ligands bonded in the titanium precursors and initial metal oxide crystallizations.^{9,19,31,39,55,119} The exothermic peaks between 420°C and 490°C in the DTA, and the ~ 9% weight loss in the temperature region 400°C-550°C in TGA, could be assigned to the further crystallization of metal oxides.^{113,115,120,125} The feature near 1480°C was due to the instrumentation limitation when the heating rate suddenly changed from 20°C/min to 0.1°C/min.¹³⁰

For anatase, the crystallite size was 29 nm at 200°C and the growth rate between 200°C and 800°C could be broadly approximated as 0.1% per 1°C. For rutile, the crystallite size was 98 nm at 900°C and the growth rate between 900°C and 1100°C could be approximated as 0.8% per 1°C. For TiNb_2O_7 , the crystallite size at 900°C was 17 nm and the growth rate between 900°C and 1100°C could be broadly approximated as 2% per 1°C. The ranges of crystallite sizes were similar to that in literature.^{39,55,135,137,139,140}

3. 50:50

From DTA and TGA, thermal reactions and weight losses could be related to each other. The first endothermic peak at 100°C in the DTA, and the ~ 1% weight loss in

temperature region 70°C-120°C in TGA, could be assigned to the removal of water.^{113,114} The second endothermic peak at 205°C in the DTA, and the ~ 5% weight loss in temperature region 150°C-220°C in TGA, could be assigned to the removal of organics such as ethanol and butanol.^{115,116,141} The exothermic peak at 232°C in the DTA, and the ~ 3% weight loss in the temperature region 220°C-300°C in TGA, could be assigned to the decomposition of organics such as acetic acid, removal of hydrolyzed isopropoxide ligands bonded in the titanium precursors and oxidation.^{19,39,55,58,119,139} The exothermic peak at 501°C in the DTA, and the ~ 6.6% weight loss in the temperature region 370°C-600°C in TGA, could be assigned to the crystallization of metal oxides.^{113,115,120,125} The feature near 1480°C was due to the instrumentation limitation when the heating rate suddenly changed from 20°C/min to 0.1°C/min.¹³⁰

For anatase, the crystallite size is 10 nm at 600°C and the growth rate between 600°C and 900°C could be broadly approximated as 4% per 1°C. For rutile, the crystallite size was 145 nm at 1000°C and the growth rate between 1000°C and 1100°C could be broadly approximated as 2% per 1°C. For $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$, the crystallite size at 600°C was 0.3 nm and the growth rate between 600°C and 700°C could be broadly approximated as 12% per 1°C. For TiNb_2O_7 , the crystallite size at 600°C is 2 nm and the growth rate between 600°C and 1100°C could be broadly approximated as 24% per 1°C. The ranges of crystallite sizes were similar to that in literature.^{39,94,135,137,140,141}

4. 25:75

From DTA and TGA, thermal reactions and weight losses could be related to each other. The first endothermic peak at 120°C in the DTA, and the ~ 1% weight loss in temperature region 80°C-140°C, could be assigned to the removal of water.^{113,114} The second exothermic peak at 220°C in the DTA, and the ~ 4% weight loss in temperature region 160°C-230°C, could be assigned to the removal of organic such as ethanol and butanol.^{115,116,141} The exothermic peak at 250°C in the DTA, and the ~ 3% weight loss in temperature region 235°C-300°C in TGA, could be assigned to the removal of organics such as acetic acid, removal of hydrolyzed isopropoxide ligands bonded in the titanium precursors and oxidation.^{19,39,55,58,119,139} The exothermic peak at 389°C in the DTA, and the ~ 3% weight loss in the temperature region 350°C-450°C in TGA, could be assigned

to the crystallization of metal oxides.^{113,115,120,125} The feature near 1480°C was due to the instrumentation limitation when the heating rate suddenly changed from 20°C/min to 0.1°C/min.¹³⁰

For $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$, the crystallite size at 500°C is 5.8 nm and the growth rate between 500°C and 600°C could be broadly approximated as 0.2% per 1°C. For TiNb_2O_7 , the crystallite size at 700°C was 11 nm and the growth rate between 700°C and 1100°C could be broadly approximated as 4% per 1°C. For Nb_2O_5 orthorhombic, the crystallite size was 1.2 nm at 500°C and the growth rate between 500°C and 600°C could be broadly approximated as 6% per 1°C. For Nb_2O_5 monoclinic, the crystallite size was 10 nm at 700°C and the growth rate between 700°C and 1000°C could be broadly approximated as 5% per 1°C. The ranges of crystallite sizes were similar to that in literature.^{39,94,135,137,140,141}

5. 0:100

From DTA and TGA results, thermal reactions and weight losses could be related to each other. The first endothermic peak at 110°C, and the ~ 1% weight loss in temperature region 70°C-130°C in TGA, could be assigned to the removal of water.^{113,114} The second endothermic peak at 214°C, and the ~ 13% weight loss in temperature region 200°C-230°C in TGA, could be assigned to the removal of organics such as butanol.^{32,39,141} The exothermic peak at 426°C, and the ~ 5% weight loss in temperature region 355°C-430°C in TGA, could be assigned to the removal of hydroxyl groups.^{34,36,147} The exothermic peaks between 447°C and 550°C could be assigned to the crystallization of niobium oxides.^{34,36,147,142} The last exothermic peak at 1117°C could be assigned to the orthorhombic to monoclinic Nb_2O_5 transformation.¹⁴³ The feature near 1480°C was due to the instrumentation limitation when the heating rate suddenly changed from 20°C/min to 0.1°C/min.¹³⁰

For Nb_2O_5 orthorhombic phase, the crystallite size was 2.4 nm at 500°C and the growth rate between 500°C and 800°C could be broadly approximated as 61% per 1°C.¹⁴⁴ For Nb_2O_5 monoclinic, the crystallite size was 20 nm at 1000°C and the growth rate between 1000°C and 1100°C could be broadly approximated as 0.7% per 1°C. The ranges of crystallite sizes were similar to that in literature.^{34,36,147}

B. Ti:Nb Metal Ion Ratio Influence on Phase Assemblage

When the Ti:Nb metal ion ratio was 100:0, the TiO_2 anatase and rutile phases exist as illustrated in Figure 10. When the ratio became 75:25 and 50:50, TiO_2 phases coexist with $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ and/or TiNb_2O_7 as illustrated in Figure 15 and 20. When the ratio became 25:75, the TiNbO phases coexist with Nb_2O_5 phases as illustrated in Figure 25. When the ratio became 0:100, Nb_2O_5 exist as illustrated in Figure 30. These observations could be compared with previous work. If Ti:Nb ratio was between 100:0 and 91:9, only TiO_2 phases existed.^{9,145} If Ti:Nb was approximately 90:10, TiO_2 , TiNb_2O_7 and/or $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ phases exist.^{145,146} If Ti:Nb was 17:83, Nb_2O_5 and TiNbO phases exist.^{58,139} If Ti:Nb was 5:95, on Nb_2O_5 exists.^{58,139}

Some of these observations could be explained by ionic states, with selected Ti and Nb ionic radii tabulated in Table VII for coordination number of 6. Nb^{5+} radius is closer to Ti^{4+} radius than that of Nb^{4+} . When the Ti:Nb ratio was between 100:0 and 91:9, TiO_2 phases existed with Ti^{4+} and O^{2-} states. For Nb ion to replace Ti ion, the preferred ionic radii difference between Nb and Ti should be less than 15%.⁸⁴ Both Nb^{4+} and Nb^{5+} ions could replace Ti^{4+} ; however, Nb^{5+} might be preferred in some cases.

Table VII. Shannon Ionic Radii for Ti^{4+} , Nb^{4+} and Nb^{5+} with Coordination Number of 6

	Ti^{4+}	Nb^{4+}	Nb^{5+}
Ionic Radii (Å)	0.605	0.680	0.640

When the larger Nb ion replaced Ti ion, the unit cell volume could increase and the corresponding characteristic peak locations were shifted to lower 2θ angles in XRD patterns. For example, at 400°C, the characteristic peak location of TiO_2 -A for 100:0 sample was near 24.99° 2θ , while that of 75:25 sample was shifted to a lower angle, 24.83° 2θ . In Lu's wet chemistry experiment, tetrabutyl titanate, niobium powder, hydrogen peroxide and ammonia were mixed, and heated at 180°C to form Nb doped anatase TiO_2 .⁵⁴ The XRD characteristic peak was shifted to lower 2θ angles as Nb concentration increased from 0% to 10%. Lu's results were consistent with the

observations here for 100:0 and 75:25 samples. Similarly, in Ghicov's electrochemical process, Nb doped anatase TiO_2 materials were fabricated at 450°C for 1 hour; where the characteristic peaks were down shifted and the volume was expanded.¹⁴⁷ Additionally, in Stengl's thermal hydrolysis process, titanium oxo-sulphate, niobium pentoxide and hydrogen peroxide were used as precursors, and Nb doped anatase was fabricated at 600°C .¹⁴⁸ Volume expansion was observed due to the Nb substitution when Ti:Nb ratio was between 96:4 and 87:13.

Comparing TiO_2 -R volume of 100:0 sample with that of 75:25 sample, there was an expansion when Nb is added. In Valigi's work, Nb was doped into TiO_2 by mixing acetone, TiO_2 and NbO_2 , heating in air at 200°C for 2 hours, 600°C for 2 hours, 800°C for 24 hours and 1000°C for 24 hours. When Ti:Nb ratio was between 100:0 and 94:6, Nb doped rutile was formed, and the lattice parameters increased as the Nb concentration increased. Additionally, in Stengl's thermal hydrolysis process, Nb doped rutile was fabricated at 1000°C , and volume expansion was observed. In Gao's work, Nb doped rutile was formed via molecular beam epitaxy and heat treated at 600°C .^{149,150} Using RHEED and LEED, it was determined that Ti^{4+} is replaced by Nb^{4+} . In Morris' work, Nb doped rutile was obtained by mixing TiO_2 with NbO_2 , heating at 650°C for 1 day, 950°C for 2 days and 1000°C for 5 days.¹⁵¹ Due to extended heat treatment, Morris suggested that the Nb^{4+} in his experiment was inevitably oxidized to $5+$, and the charge difference would possibly be compensated by creating Ti vacancies or oxygen interstitials.

Besides the substitutional possibilities, some Ti ions could reside in interstitial site locations, which could also contribute to unit cell volume expansion. Other defects could exist: Schottky and Frenkel defects. The number of anion vacancies was the same as that of cation vacancies in Schottky defects; and some interstitial sites could be occupied by dislocated ions in Frenkel defects. Based on prior work and this work, when Nb concentration was low, it could substitute Ti in TiO_2 lattice or form defects.

For the 75:25 sample, besides TiO_2 , formations of TiNb_2O_7 and $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ are illustrated in Figure 15. Such observations are consistent with previous publications.^{52,146,152,153} In Trenczek's sol-gel process, when Nb concentration was above 10%, TiNb_2O_7 and Nb doped rutile exist. In Uekawa's wet chemistry experiment,

peroxotitanium acid and peroxoniobium acid were mixed, and heat treated at different temperatures; resulting in TiNb_2O_7 and Nb doped TiO_2 (anatase at low temperatures and rutile at high temperatures). In Zakrzewska's sputtering process, when Nb was doped into TiO_2 , both TiO_2 rutile and TiNb_2O_7 existed. In Cava's solid state reaction experiment, TiO_2 and Nb_2O_5 were mixed, and both TiNb_2O_7 and $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ were formed. The $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ phase could be related to $\text{Nb}_{12}\text{O}_{29}$ which could be viewed as $\text{Nb}_{12}\text{O}_{30}$ or $6(\text{Nb}_2\text{O}_5)$ with a missing oxygen. Since the ionic states of each Nb_2O_5 were Nb^{5+} and O^{2-} , with the missing oxygen, two Nb ions' oxidation states would be changed from 5+ to 4+ to maintain charge neutrality in $\text{Nb}_{12}\text{O}_{29}$. Thus, as the Nb^{4+} and Ti^{4+} radii were close to each other, the Nb^{4+} could be readily replaced by Ti^{4+} , and $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ could be formed.^{154,155} The TiNb_2O_7 phase could be related to Me_3O_7 , where Me represents Ti and/or Nb ions with 4+ or 5+ oxidation states. Previous work in solid state reactions suggested that when TiO_2 was combined with Nb_2O_5 , TiNb_2O_7 was formed, where Ti^{4+} was from TiO_2 and Nb^{5+} was from Nb_2O_5 . However, it was not clear if the TiNb_2O_7 was formed via sol-gel route. The ionic states of Nb^{4+} and Nb^{5+} were usually influenced by atmosphere and precursors including acetic acid, isopropoxide and alcohols. Namely, the oxygen environment affected oxidation state.

Similar to 75:25 sample, the phases present in the 50:50 sample were TiO_2 , $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ and TiNb_2O_7 as illustrated in Figure 20. However, due to higher Nb concentration, the amount of TiO_2 was less than that in 75:25. Correspondingly, the amount of TiNbO phases was more than that in 75:25. In Mei's spray drying process, TiO_2 and TiNbO phases were formed.¹⁵⁶

In 25:75 sample, the phases present were TiNbO and Nb_2O_5 (orthorhombic and monoclinic) as illustrated in Figure 25. Due to high concentration of Nb, the amount of TiNbO phases was less than that in 50:50; and TiO_2 was no longer in existence. Such observation could be related to other publications. For example, in Schmitt's sol-gel process, when Ti was doped into Nb_2O_5 , TiNbO and Nb_2O_5 coexisted when the Ti:Nb is 77:23.^{58,139} In 0:100 sample, Nb_2O_5 phases formed as illustrated in Figure 30. Similar results were obtained via sol-gel processes, and solid state reactions.^{39,157,158} Besides metal concentration, another major factor affecting phase assemblage was the heat

treatment temperature. Such temperature effect was separated in two subsections below: crystallization temperature and phase transformation temperature.

C. Crystallization Temperature Influence on Phase Assemblage

As the Ti:Nb ratio varied from 100:0 to 0:100, different initial crystallization temperatures were obtained via XRD patterns illustrated in Figures 6, 12, 17, 22 and 27; and tabulated in Tables II – VI. The crystallization temperature may be related to precursors illustrated in Figure 2. The precursors for 100:0 included titanium isopropoxide, ethanol and acetic acid; that for 0:100 included niobium chloride, butanol and acetic acid; and that for 75:25 – 25:75 samples included titanium isopropoxide, niobium chloride, butanol, ethanol and acetic acid. The oxygen contained in ethanol, butanol, acetic acid and isopropoxide might promote oxide formation at low temperatures.

In the first three samples (100:0 – 50:50), the phases were TiO_2 and TiNbO . These three samples could be discussed using 100:0 sample as the base line. For 100:0 with TiO_2 , the initial crystallization temperature was approximately 400°C and the complete crystallization temperature was approximately 500°C, as illustrated in Figures 4 and 8. The XRD result could be related to DTA/TGA in Figure 3 where the majority of the weight loss happened before 400°C. Presumably, the titanium was fully oxidized by 400°C. In Parra's sol-gel work, titanium isopropoxide, isopropanol, acetic acid, and nitric acid were mixed first, desiccated at room temperature for 50 hours and heat treated at various temperatures.¹⁹ The initial crystallization temperature was near 350°C, which was comparable to this work. In Tuan's sol-gel work, titanium isopropoxide, ethanol, water and poly-ethylene glycol were mixed, and heated at various temperatures.¹⁵⁹ The initial crystallization temperature was approximately 400°C.

For 75:25 sample, the initial crystallization temperature was approximately 200°C. In Lu's wet chemistry experiment, Nb doped TiO_2 was initially crystallized at 180°C, with Nb concentration being 2.5-10%.⁵⁴ Even though the initial crystallization temperature of 75:25 was lower than that of 100:0, the oxides were not fully crystallized until 700°C as revealed by XRD in Figure 10. As illustrated in TGA plot of Figure 9, at

200°C, the cumulative weight loss was approximately one-half of the total weight loss. The majority weight loss happened before 700°C. Between 200°C and 700°C, the metals were gradually oxidized. It is believed that the initial oxidation was caused by the oxygen in the precursors. Referring to Figure 13, the phase percentage distribution between 200°C and 700°C changed substantially. Between 700°C and 800°C, the percentage distribution did not change much, possibly indicating the fully oxidized/crystallized metal oxides (TiO_2 -A and $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$). Presumably, besides solvents in the precursor, Nb addition helped to reduce the initial crystallization temperature, and to increase the full crystallization temperature.

For 50:50 sample, the initial crystallization temperature was near 600°C and the complete crystallization temperature was 800°C. In Mei's spray drying process, the initial crystallization temperature was at approximately 600°C.¹⁵⁶ There were two differences between 50:50 and 75:25 samples in terms of the phase assemblage at 600°C. First, TiNb_2O_7 coexisted with $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ and TiO_2 in 50:50 sample, while TiNb_2O_7 phase formed at higher temperature in 75:25 sample as illustrated in Figures 13 and 18. Second, due to equal amount of Ti:Nb concentration, TiNbO phase percentage was much higher than that of TiO_2 in 50:50 sample. There were similarities between 50:50 and 75:25 samples. Anatase TiO_2 and TiNb_2O_7 coexisted at 800°C; and rutile TiO_2 and TiNb_2O_7 coexisted at 1000°C-1100°C. In this experiment, TiNb_2O_7 phase persisted at high temperatures, while $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ existed at low temperatures.

In the last two samples (25:75 – 0:100), the phases were Nb_2O_5 and TiNbO . These two samples could be discussed with the 0:100 as the base line. For 0:100, the initial crystallization temperature was near 500°C and the complete crystallization temperature was near 600°C, which could be compared with the literature. In Schmitt's sol-gel process, niobium chloride, ethanol and acetic acid were mixed, and heat treated at various temperatures.^{31,55,58,139} The initial crystallization temperature for niobium oxide was near 500°C. In Pawlicka's sol-gel process, niobium chloride, butanol and acetic acid were mixed, and heat treated at 400°C-600°C for 10 minutes.¹⁶⁰ The initial crystallization temperature of niobium oxide was approximately 500°C. In Bansal's sol-gel process, niobium ethoxide, ethanol and hydrochloric acid were mixed, and heat treated at a

temperature between 400°C and 1450°C for 1-24 hours.³⁹ The initial crystallization temperature for niobium oxide was 500°C. In Ko's sputtering work, the niobium oxide material was initially crystallized at 500°C.¹⁶¹

The initial crystallization temperature of 25:75 sample was 500°C similar to 0:100 sample; and the complete crystallization temperature was near 800°C similar to 50:50 sample. This value could be compared with the literature results. In De Costa's sol-gel process, isopropanol, titanium isopropoxide and acetic acid were mixed with Ti:Nb ratio of 25:75, and heated at 400°C-600°C for 3 hours.¹⁶² The initial crystallization temperature was near 500°C. In Schmitt's sol-gel process, titanium isopropoxide, niobium chloride, acetic acid and ethanol were mixed based on Ti:Nb ratio of 33:67 – 23:77, and heat treated at a temperature of 450°C-600°C for 30 minutes.^{55,58,139} The initial crystallization temperature was near 500°C. In 25:75 sample, the XRD peaks were relatively broad at 500°C. Such peak broadness might be attributed to the addition of the Ti ions located at the substitutional and/or interstitial sites in the orthorhombic Nb₂O₅ phase. Besides the substitutional or interstitial contributions, Ti ions might also contribute to TiNbO formation and cause peak broadening.

D. Phase Transformation Temperatures Influence on Phase Assemblage

There were two distinct phase transformations observed: TiO₂ anatase to rutile (A-R), and Nb₂O₅ orthorhombic to monoclinic (O-M). Since the phase transformation temperature might be affected by foreign ion additions (Nb in TiO₂ or Ti in Nb₂O₅), it was necessary to consider TiO₂ (or Nb₂O₅) without foreign ions. For A-R transformation, the 100:0 sample was used as the baseline for two other samples (75:25 and 50:50). For 100:0 sample illustrated in Figure 8, the TiO₂ anatase phase existed between 400°C and 700°C, the rutile phase existed between 1000°C and 1100°C, and both anatase and rutile existed at 800°C-900°C. The A-R transformation temperature range was between 700°C and 1000°C. In other words, the rutile started to form between 700°C and 800°C, and anatase was converted to rutile completely between 900°C and 1000°C. At 800°C, there was a small percentage of rutile. At 900°C, the A/(A+R) ratio was approximately 50%. In Gouma's solid state experiment, TiO₂ powder was heat treated

up to 1000°C.⁶ The A-R transformation occurred between 700°C and 1000°C. In Sotter's sol-gel experiment, titanium isopropoxide and nitric acid were mixed and heat treated.⁹ The A-R transformation occurred at 600°C - 900°C. Shannon suggested that the A-R transformation initially required activation energy to convert some anatase to rutile, i.e., the converted rutile began nucleation on the surface of anatase.⁴ Gradually, rutile growth would take place inside of the anatase. Finally, the entire anatase would be transformed into rutile. For 100:0 sample, the main factor affecting the transformation was the heat treatment conditions.

For 75:25 sample, the addition of Nb caused the A-R transformation temperature range to shift to 800°C-1000°C as illustrated in Figure 13. In comparison with 100:0 sample, the 75:25 sample had ~ 100°C shift as far as the initial crystallization temperature value was concerned. At 900°C, the A/(A+R) ratio was approximately 74%, which was larger than 50% for 100:0 sample. That is, Nb addition retarded A-R transformation. In Sotter's sol-gel experiment, two batches of samples were prepared.⁹ One batch contained titanium isopropoxide and nitric acid; and the other batch contained additional niobium ethoxide with Nb concentration around 3%. The A-R transformation temperature was increased by 150°C. In Ruiz's sol-gel experiment, two batches were prepared.¹⁶³ One batch contained titanium isopropoxide and isopropanol; and the other batch contained additional niobium ethoxide with Nb concentration around 10%. The A-R transformation temperature was increased by 200°C. In Stengl's thermal hydrolysis experiment, two batches of sample were prepared.¹⁴⁸ One batch contained titanium oxo-sulphate, potassium hydroxide, ammonium hydroxide, and hydrogen peroxide; and the other batch contained additional niobium pentoxide with Nb concentration around 13%. The A-R transformation temperature was increased by ~200°C with the addition of Nb. In Pittman's wet chemistry experiment, two batches were prepared.¹⁶⁴ One batch contained titanium isopropoxide, isopropanol, water and hexane; and the other batch contained additional niobium ethoxide with Nb concentration around 20%. The A-R transformation temperature was increased by 250°C. For the observations here, one could use literature argument provided by Shannon, Zhang, Pittman and Hishita to explain the delayed or retarded A-R transformation.^{4,164-166} Once the solubility limit of Nb⁵⁺ (3%-10%) was

surpassed in TiO_2 , the Nb^{5+} might contribute to the Ti-O-Nb bonding. Pittman suggested that the Ti-O-Nb bonding attributed to the delayed A-R transformation which inhibited the movement of the surface Ti atoms needed to start the phase transformation. When additional Nb contributed to $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ in Figure 13 at 700°C-800°C, the $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ grains might surround some anatase grains, and delay the initial A-R transformation on the anatase surface.

For 50:50 sample, further addition of Nb caused the A-R transformation to be delayed to 900°C-1000°C as illustrated in Figure 18. In comparison with 75:25 sample, 50:50 sample had $\sim 100^\circ\text{C}$ shift. For 50:50 sample at 900°C, the percentage of TiNbO exceeded that of TiO_2 . The TiNbO grains might surround the anatase grain preventing A-R transformation.

For the last two samples (25:75 and 0:100), the Nb_2O_5 O-M transformation temperature might be affected by Ti in Nb_2O_5 . It was necessary to consider Nb_2O_5 without foreign Ti ions first. For 0:100 sample illustrated in Figure 28, orthorhombic Nb_2O_5 existed between 500°C and 900°C, and monoclinic Nb_2O_5 existed between 1000°C and 1100°C. The O-M transformation temperature was between 900°C and 1000°C. In other words, the orthorhombic phase was converted to monoclinic phase completely at 1000°C. This observation was consistent with previous work. In Bansal's work, orthorhombic Nb_2O_5 existed between 500°C and 900°C, and monoclinic phase existed between 1000°C and 1450°C.³⁹ The O-M transformation temperature was between 900°C and 1000°C. In Ko's experiment, the 100% monoclinic phase was obtained at 1000°C.¹⁶¹ In Medeiros' experiment, Nb_2O_5 was fabricated by a hybrid process; solid state reaction and wet chemistry.¹⁶⁷ The orthorhombic phase existed at 600°C, and the monoclinic phase was the dominant phase at 950°C. The O-M transformation temperature was near 950°C. The transformation was believed to occur when enough energy had been provided for the niobium pentoxide phases to change.

For 25:75 sample in Figure 23, orthorhombic phases existed at 600°C, monoclinic phase existed at 800°C, and both phases existed at 700°C. The O-M transformation temperature was between 600°C and 800°C, which was lower than that in 0:100 sample. With the Ti addition, the O-M transformation in 25:75 was accelerated. Assuming that

some Ti^{4+} ions substituted Nb^{5+} in Nb_2O_5 , part of the observations could be explained by Shannon's argument: an accelerated transformation occurred when an ion with lower charge was substituted into the ionic site with higher charge.⁴

E. Phase Diagram Comparison

Based on the above three subsections, the results obtained were compared to a phase diagram illustrated in Figure 29, for temperatures at 1000°C - 1100°C.¹⁶⁸ The phase diagram was obtained by several solid state reaction results. Along the horizontal axis of the phase diagram was the mole percentage as a function of $\text{Nb}_2\text{O}_5/(\text{Nb}_2\text{O}_5 + \text{TiO}_2)$. The five sol-gel samples from this work were matched with the corresponding Ti:Nb ratio to the mole percentage. The 100:0 sample was matched with 0% Nb_2O_5 and the 0:100 sample was matched with 100% Nb_2O_5 as illustrated in Figure 29. The three middle samples (75:25, 50:50 and 25:75) were between 14% and 60% Nb_2O_5 . In Figure 29, TiO_2 rutile phase existed between 1000°C-1100°C when the Ti:Nb ratio was between 100:0 - 85:15. When the Ti:Nb ratios were 75:25 and 50:50, TiNb_2O_7 was formed. Nb_2O_5 monoclinic phase formed when the Ti:Nb ratio was 3:97 – 0:100. For the mole percentage corresponding to the Ti:Nb ratio of 25:75, $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ would form with a solid state reaction. The TiNb_2O_7 phase might be considered as a reaction between TiO_2 and Nb_2O_5 . The sol-gel process formed TiNb_2O_7 and TiO_2 rutile at 1000°C - 1100°C as illustrated a quasi phase diagram (Figure 30). The process differences might explain the phase differences seen in Figure 29 and Figure 30.¹⁶⁸ Figure 29 was generated when the thermal equilibrium states were maintained and phase pure samples were produced according to $\text{TiO}_2\text{:Nb}_2\text{O}_5$ ratios. Figure 30 was generated when dynamic or non-equilibrium states were created in HTXRD. The phase assemblage could be extended from Figure 29 to Figure 30 partially. For the first three samples (100:0, 75:25 and 50:50), TiO_2 existed, with the high temperature phase being rutile and the low temperature phase being anatase. At 1000°C - 1100°C, both 100:0 and 0:100 samples had the same phases identified between Figures 29 and 30. The sol-gel process formed TiO_2 anatase phase in addition to TiNb_2O_7 in the 75:25 and 50:50 samples. For the 25:75 sample, Nb_2O_5 monoclinic existed along with TiNb_2O_7 at 1000°C - 1100°C. For the last

sample (0:100), monoclinic Nb₂O₅ was the high temperature phase and orthorhombic was the low temperature phase.

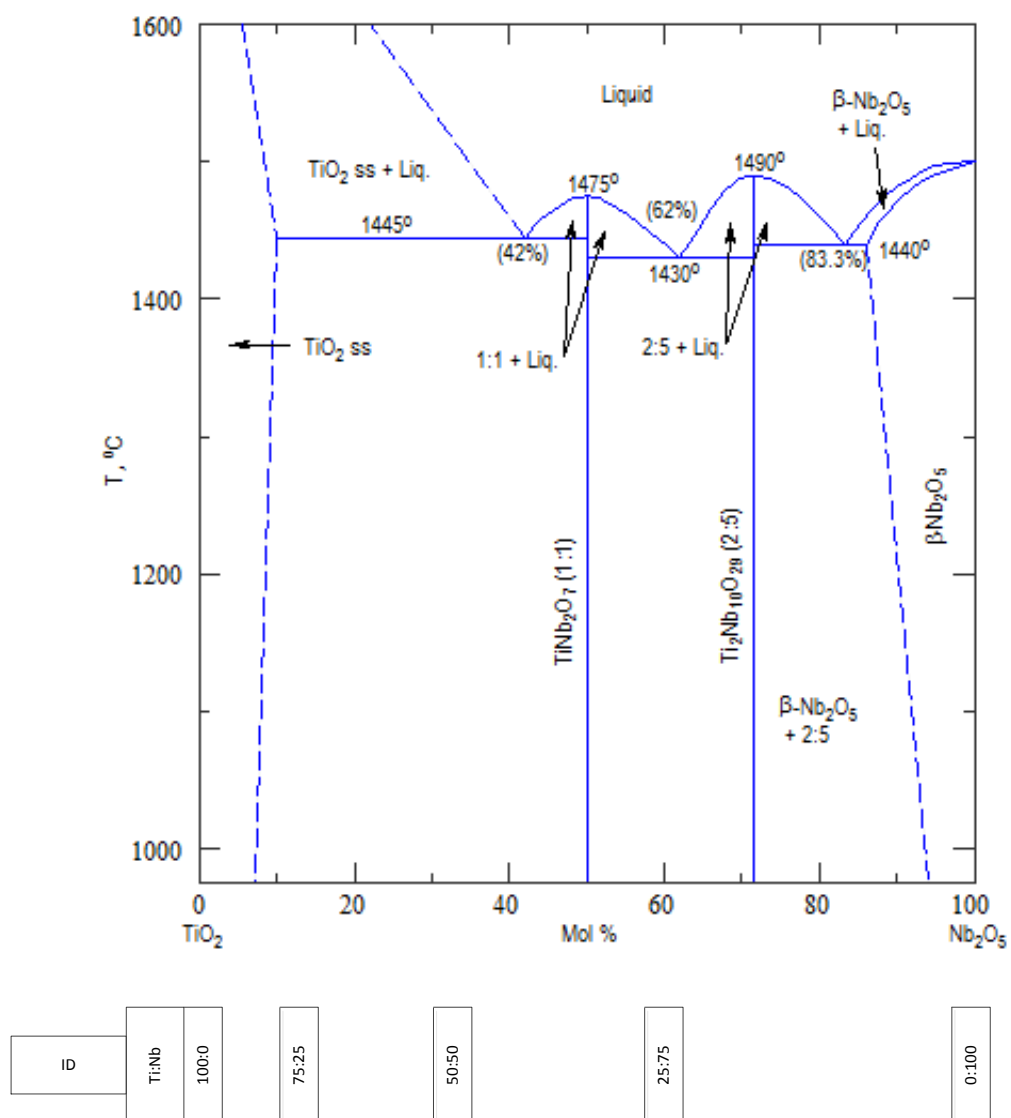


Figure 29. Phase diagram of TiO₂-Nb₂O₅.

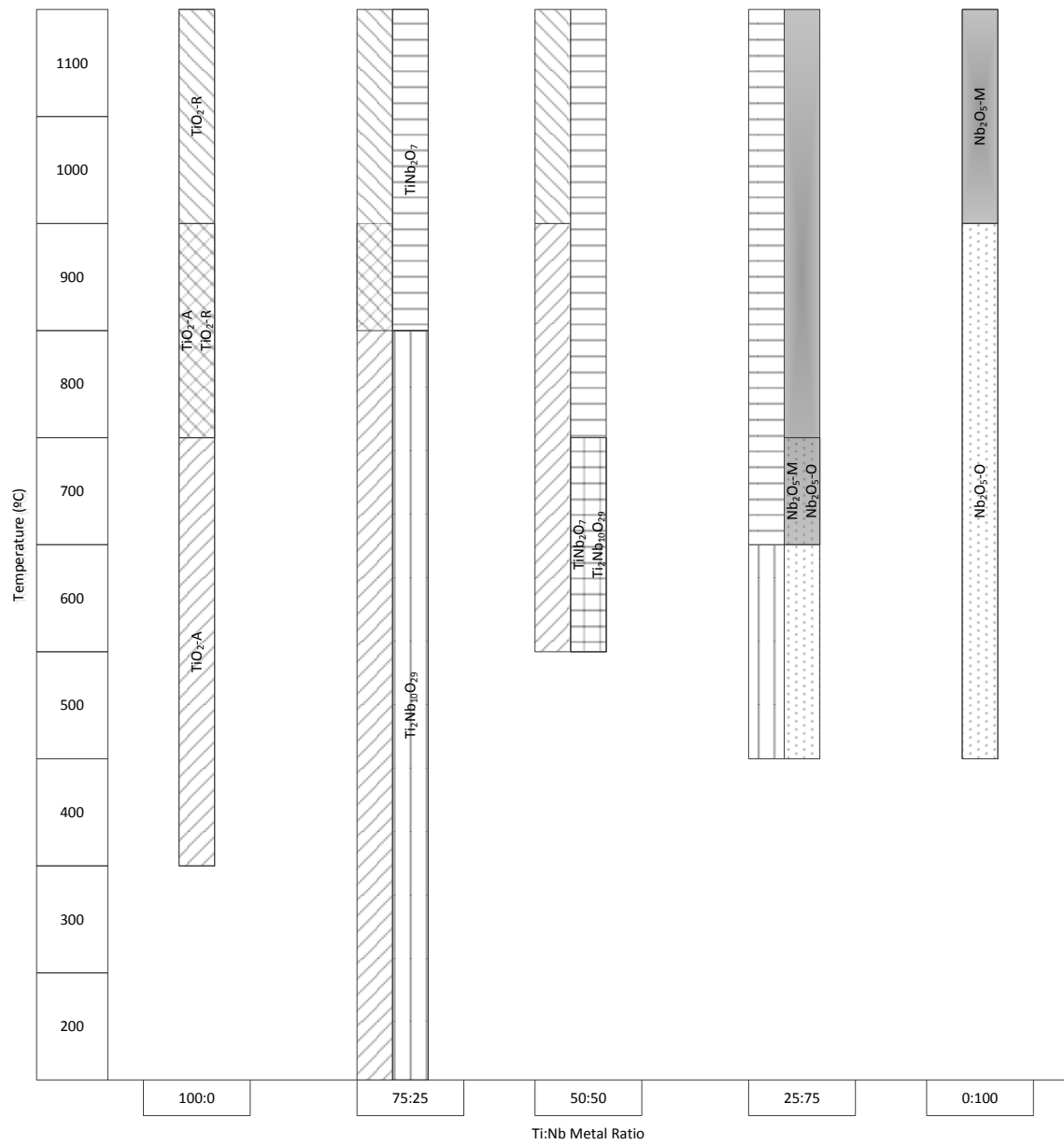


Figure 30. Phase assemblage based on Ti:Nb ratio and temperature.

CONCLUSIONS

Titanium niobium mixed-phase oxide powders were successfully prepared via sol-gel methods. The samples were analyzed via in-situ HTXRD to determine the phase assemblage and structural characteristics of each phase identified. TGA analysis showed that mixed phase oxides lost less weight percent than that of non mixed phase oxides. The majority of weight loss for the prepared powders was due to water and organic content. Analysis of the in-situ HTXRD results revealed that with increasing heat treatment temperature, the samples became more crystalline. The temperature at which the powders crystallized was affected by the initial precursor and the ratio of titanium to niobium.

Further analysis of the HTXRD results via Rietveld refinement resulted in additional understanding of the phase assemblage of the various sample systems as a function of heat treatment temperature. In the five samples, six phases were identified: anatase and rutile TiO_2 , orthorhombic and monoclinic Nb_2O_5 , TiNb_2O_7 and $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$. In the 100:0 sample, only TiO_2 was present with anatase at low temperature and rutile at high temperature. The anatase to rutile phase transformation temperature increased with increasing concentration of Nb; 700°C-1000°C for 100:0 sample, 800°C-1000°C for 75:25 sample and 900°C-1000°C for 50:50 sample. The Nb in 75:25 and 50:50 samples also contributed to two additional TiNbO phases. In the 0:100 sample, only Nb_2O_5 was present with orthorhombic at low temperature and monoclinic at high temperature. The O-M transformation temperature ranges were 900°C-1000°C for 0:100 sample and 600°C-800°C for 25:75 sample, respectively, and hence decreased with Ti addition.

FUTURE WORK

After studying titanium niobium oxide phase formation conditions, more detailed work should be carried out in the next step. First, the incremental step between each Ti:Nb sample can be less than 25. For example, the step can be 10 making eleven samples from 100:0, 90:10, ..., 10:90 and 0:100. Second, the TEM analysis should be carried out to determine the phase formation, grain sizes and distributions. Third, a sol-gel process may be developed to form TiNb_2O_7 or $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ phases at temperatures at $700^\circ\text{C} - 900^\circ\text{C}$, which are currently being considered as fuel cell and battery materials in other groups' work. Fourth, the electrical conductivity or resistivity should be measured as the function of Ti:Nb ratio, which may lead to optimized electrode designs. If the titanium niobium oxide resistivity is low enough to replace the indium tin oxide (ITO), the US DOE challenge to replace the critical indium sources may be met.¹⁶⁹ Fifth, photoelectrical conductivity can be optimized to seek applications in solar cells.

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APPENDIX

Since microstrain causes additional peak broadening, its contribution can be isolated by Williamson-Hall plot illustrated in Figure 31.¹⁷⁰ In this figure, the expression for y-axis is given as follows.

$$FWHM \times \cos(\theta) = \frac{K\lambda}{L} + Microstrain \times 4 \times \sin(\theta) \quad (5)$$

where FWHM is the difference between the observed and the instrumentation full width half maximum values, $FWHM_{obs} - FWHM_{inst}$. The x-axis is $4 \times \sin(\theta)$. For pure crystallite (grain) size effect, the y- axis value would be a constant given by Sherrer equation, shown as the intercept of y-axis and extended to a dashed horizontal line marked as grain size broadening. The slope of the plot is the microstrain value. If simulation yields the microstrain value of absolute 0%, such value is not considered.

Lastly, the x-ray diffraction can be used to estimate preferred orientation of a sample along a given axis. Since the PDF standard pattern is for a sample with random orientations, the sample with a preferred orientation would yield different peak heights at given 2θ values. In the case of a single crystal sample, many peaks in the standard powder diffraction pattern will not show. In summary, x-ray diffraction can be used to study phase formation, crystal structures and orientations, atomic arrangements in lattices, crystallite sizes and microstrain values.

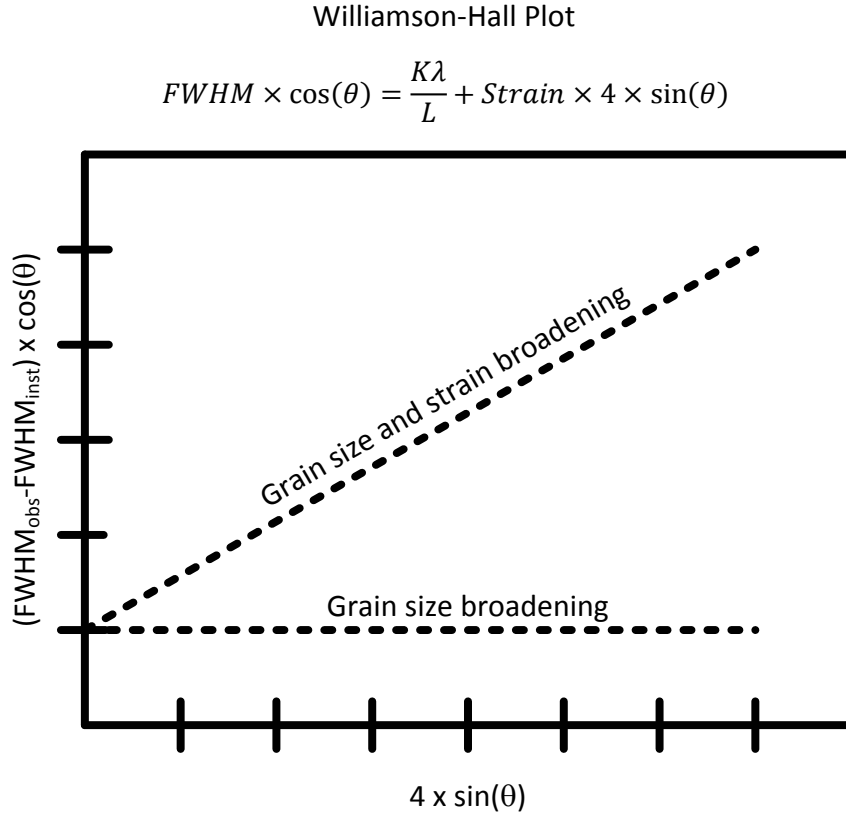


Figure 31. Microstrain via Williamson-Hall Plot.

Using a PDF in the refinement process, one can obtain the calculated profile and compare it with the measured profile. In Figure 3, several scenarios are illustrated, where the measured data points (open circles) are compared with the calculation results (solid line curve).¹¹⁰ Referring to Figure 3, the calculated and measured curves are superimposed on each other and displayed on the top portion. The bottom curve is the difference profile. In Figure 3(a), the 2θ peak location of the measurement is the same as that of the calculation, and the measured peak is lower than that of the calculation. The resultant difference profiles show a valley or dip below the horizontal zero reference line. In contrast, in scenario (b), the measured peak is taller than the calculated peak, and the resultant difference profile is a bump or peak above the horizontal zero reference line. In scenario (c), the 2θ peak location for the measured profile is at a smaller angle than that for the calculation. As a result, the difference profile shows a “symmetrical” curve about

the zero reference line, being positive first and negative next. That is, the difference profile has a peak and then a valley. On the other hand, in scenario (d), the 2θ peak location for the measurement is at a larger angle than that for the calculation. As a result, the difference profile shows an “anti-symmetrical” curve about the zero reference line, being negative first and positive next. That is, the difference profile has a valley then a peak. For both (c) and (d), there is no substantial difference between the measured and calculated peaks. In (e) and (f), both peak height and width are different between the measurement and the calculation. In (e), the measured peak height is larger than, and the width is less than that of the calculation. In (f), the measured height is less than, and the width is larger than that of the calculation.

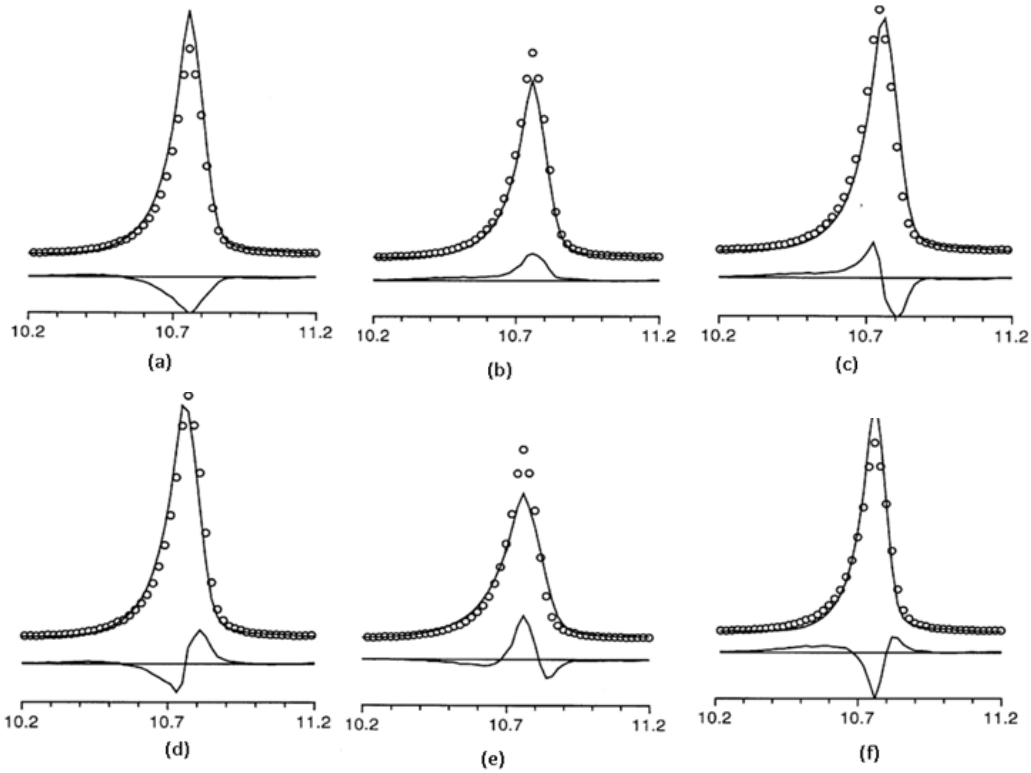
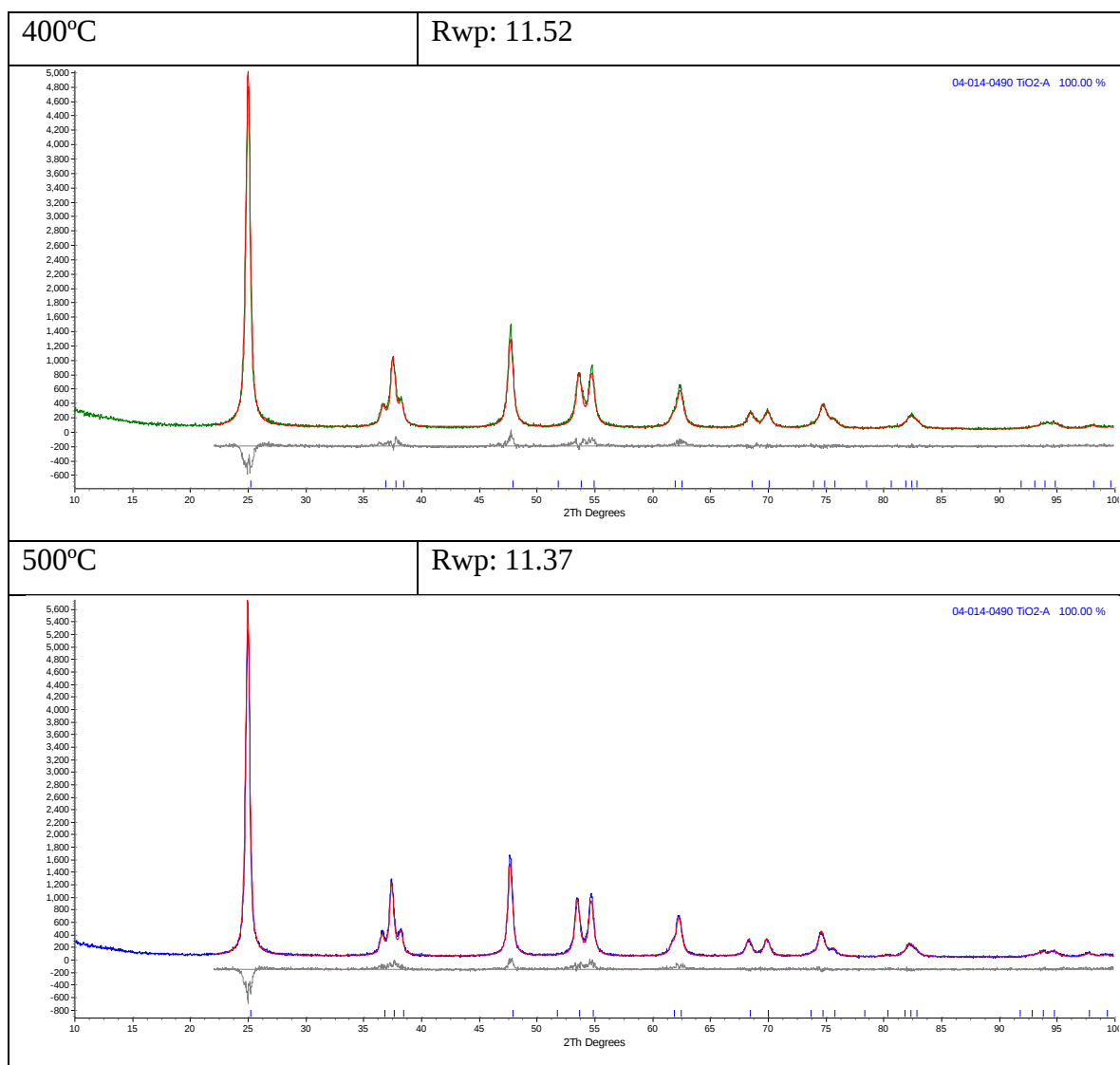


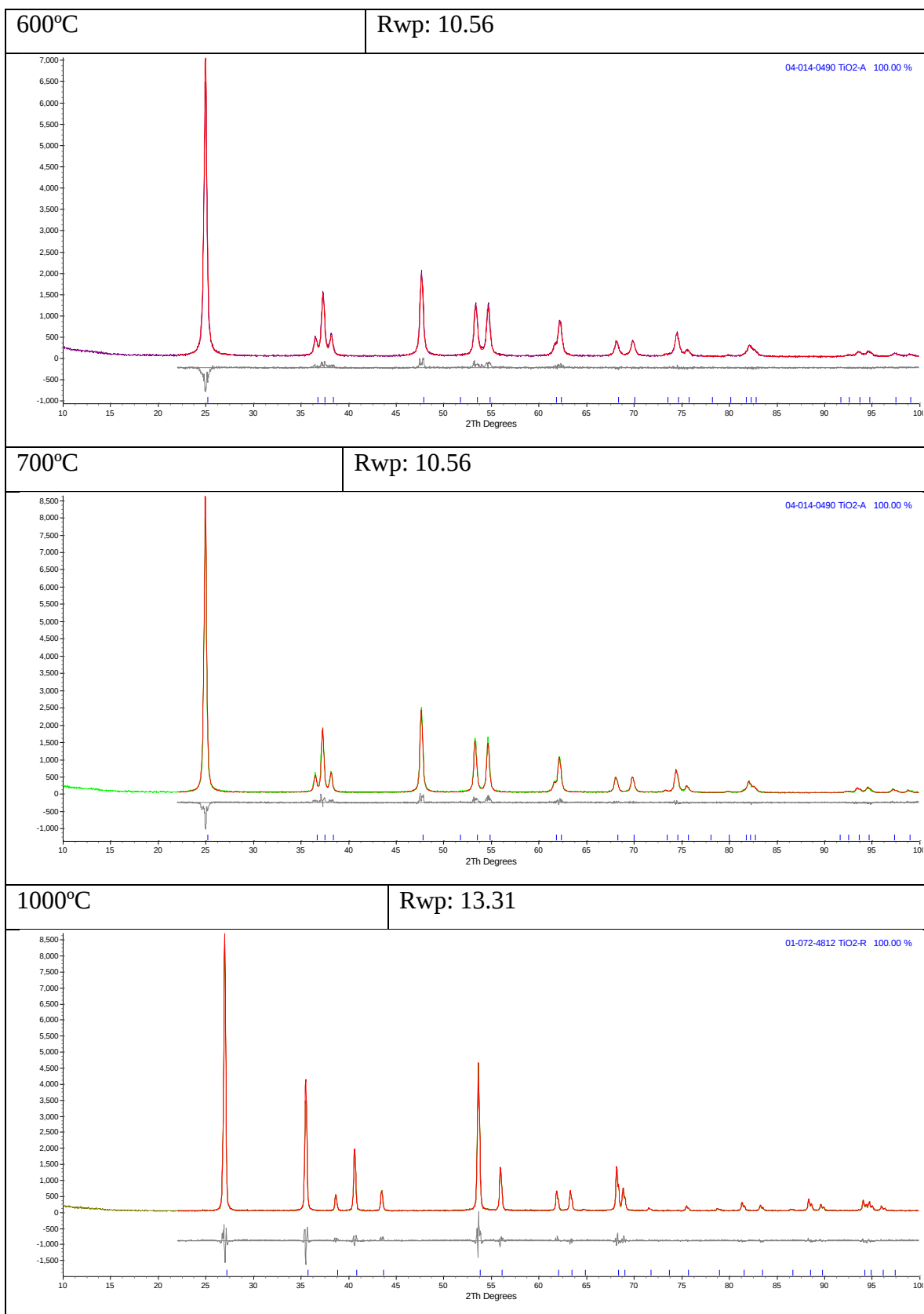
Figure 32. Measured, calculated, and difference profiles for various scenarios. (from McCusker, Ref # 110)

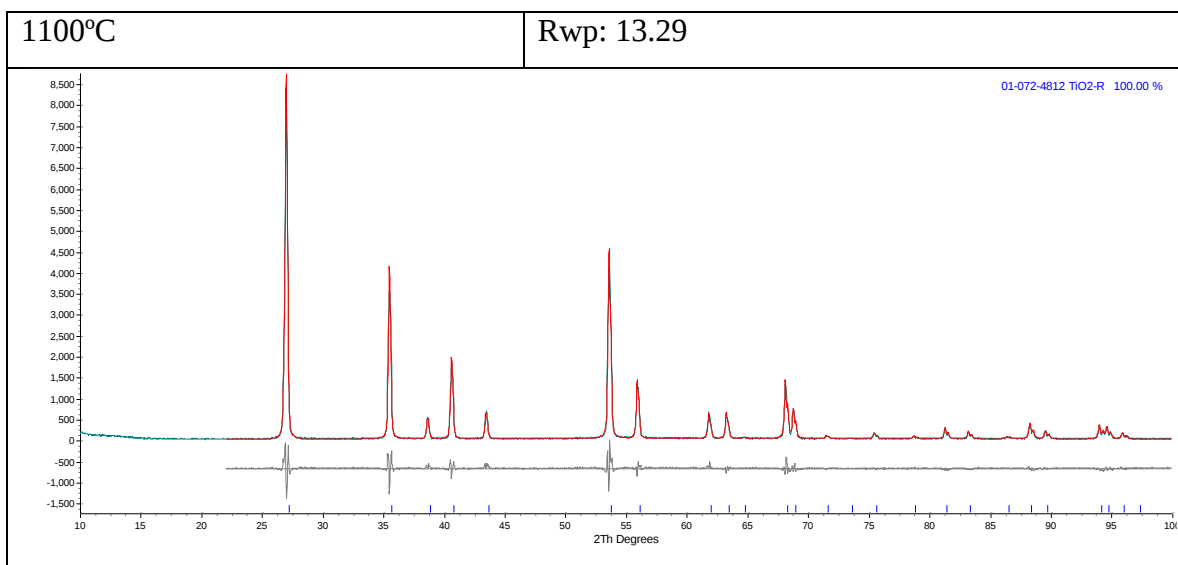
A. Appendix A: XRD Patterns from Rietveld Refinement for 100:0

In Table A-1, examples of the Rietveld refinement results are shown. In this table, there are three sets of data: the measured pattern (ranging from 10° to 100° 2 θ), the calculated pattern (red curve), and the difference profile (grey curve). The temperature is given in the table at top left corner, along with the Rwp.

Table A-1. Rwp of 100:0







Referring to Table A-1, features (a)-(f) in Figure 3 can be seen. For example, at 400°C, the dip near 25° 2 θ reflects the fact that the calculated value is greater than that of the measurement as illustrated in Figure 3(a). Near 48° 2 θ , the peak reflects the fact that the calculated value is smaller than that of the measurement as illustrated in Figure 3(b).

B. Appendix B: Numerical Values of Lattice Parameters for 100:0

Unit cell parameter changes are provided here along with volume percentage changes and strain values. In Figure B-1, the lattice parameter percentage changes for TiO₂-A are plotted as a function of temperature, using the standard lattice parameter values in PDF 04-014-0490 as references ($a = b = 3.7927 \text{ \AA}$, $c = 9.509 \text{ \AA}$). At 400°C, lattice parameter a and c values are slightly larger than that of the standard values, respectively. The lattice parameters for TiO₂-A increase monotonically as temperature increases from 400°C to 900°C.

Lattice Parameter % Changes of 100:0 TiO₂-A (04-014-0490)

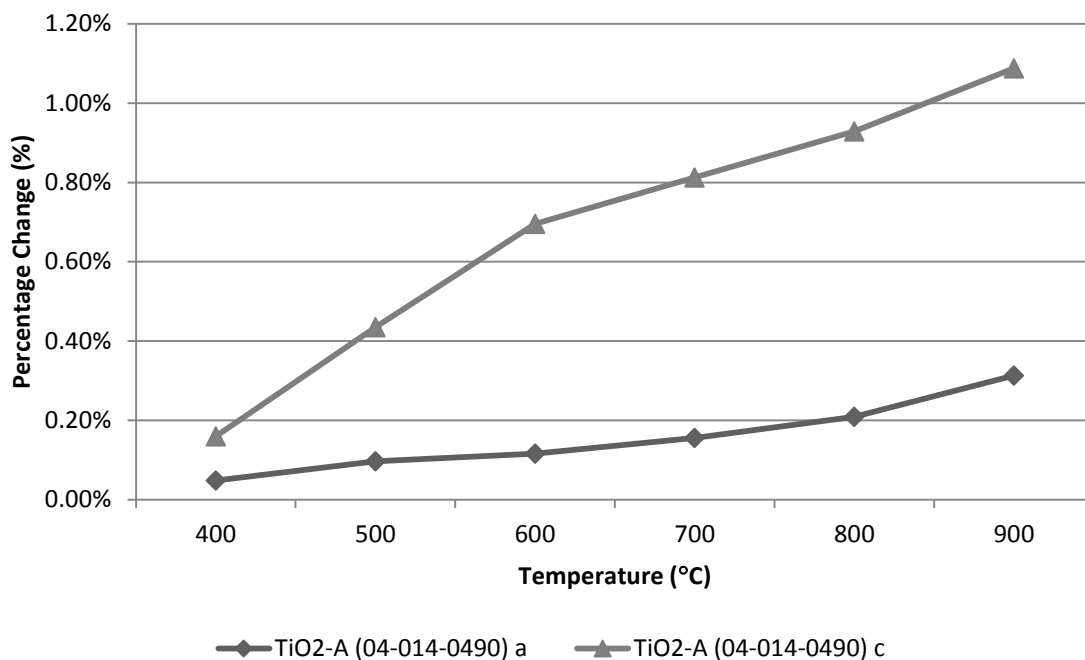


Figure B-1. Lattice parameter percentage changes versus temperature for TiO₂-A.

In Figure B-2, lattice parameter percentage changes for TiO₂-R are plotted as a function of temperature. As the temperature increases from 900°C to 1100°C, the lattice parameters increase monotonically. As the temperature decreases to 30°C, the parameters decrease to the values close to the standard values within $\pm 0.2\%$ using PDF 01-072-4812 as the reference (01-072-4812: $a = b = 4.6021 \text{ \AA}$ and $c = 2.9563 \text{ \AA}$).

Lattice Percentage % Changes of 100:0 TiO₂-R (01-072-4812)

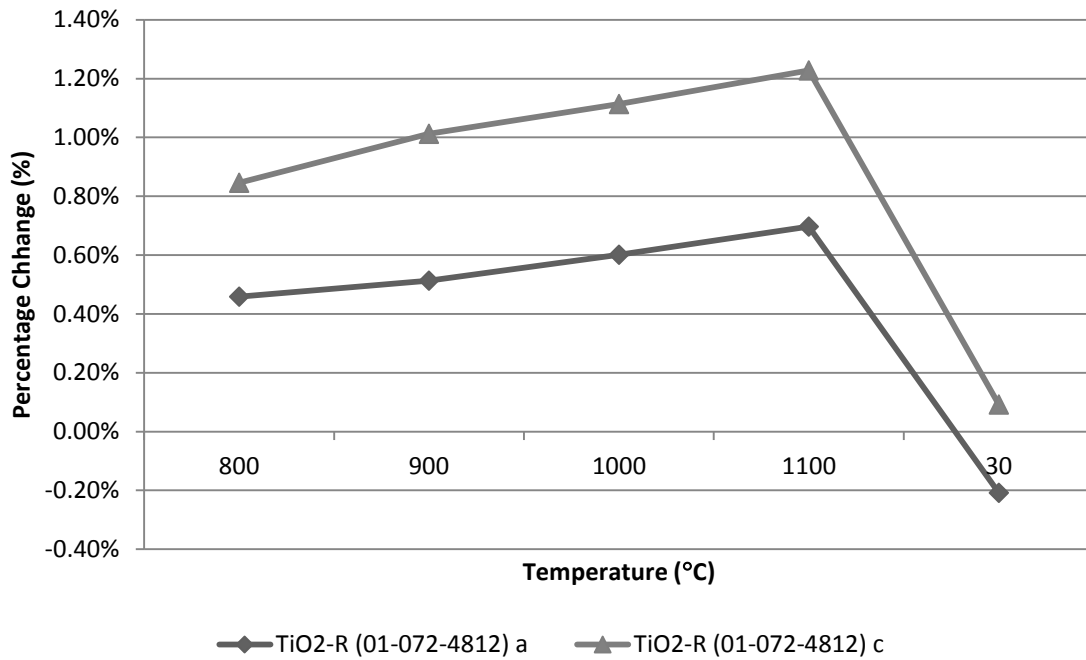


Figure B-2. Lattice parameter percentage changes versus temperature for TiO₂-R.

Anatase or rutile has a tetragonal structure, the volume is given as $c(a^2)$. In Figure B-3, TiO₂ volume percentage is given as a function of temperature. Using PDF 04-014-0490 as reference for anatase, the standard volume is 136.7829 Å³. From 400°C to 900°C, the anatase volume increases, which is due to the expansions of lattice parameters a and c in Figure B-1. For rutile, the volume in the PDF file 01-072-4812 is 62.61 Å³. From 900°C to 1100°C, the rutile volume percentage change increases slightly from 2% to 2.6%, which is due to the expansions of lattice parameters a and c in Figure B-2. When the sample cools to 30°C, the measured volume is slightly less than the standard value because of the smaller lattice parameter a in Figure B-2.

Unit Cell Volume % Changes of 100:0

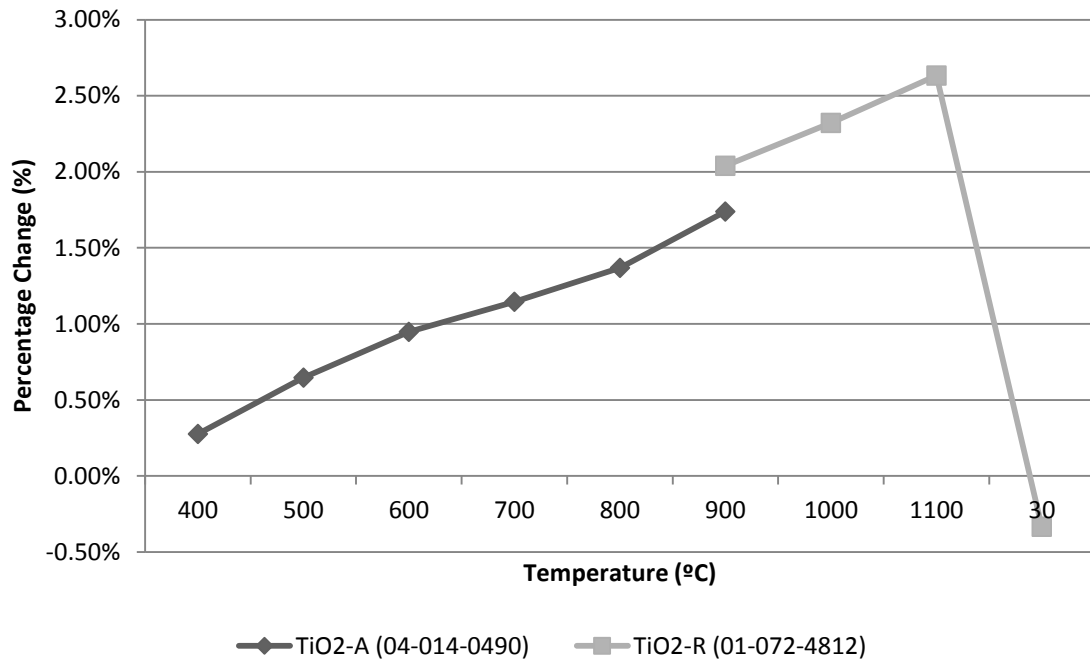


Figure B-3. Unit cell volume percentage change as a function of temperature for TiO₂.

In Figure B-4, microstrain is plotted as a function of temperature for TiO₂. For the anatase phase, the microstrain value decreases as the temperature increases from 400°C to 800°C; and increases between 800°C and 900°C. For the rutile phase, the strain value does not change between 800°C and 900°C; increases as the temperature increases from 900°C to 1000°C; does not change much between 1000°C and 1100°C; and is less than that at 1100°C when the sample is cooled down to 30°C.

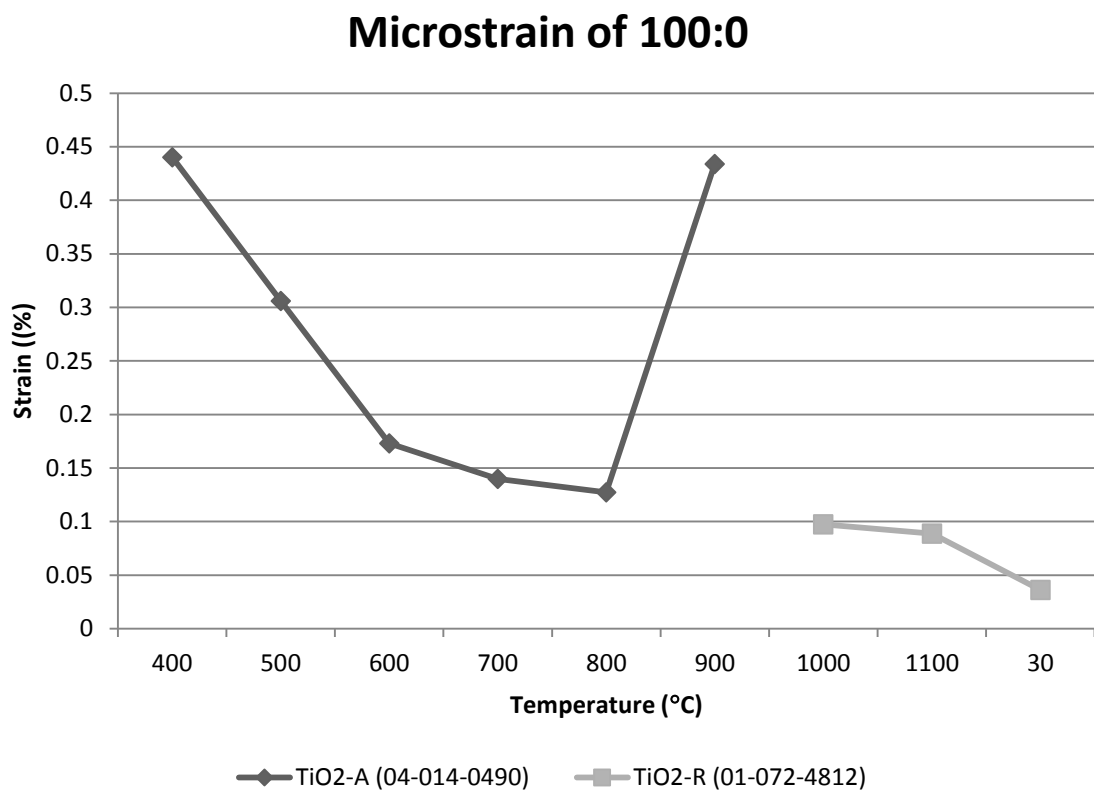
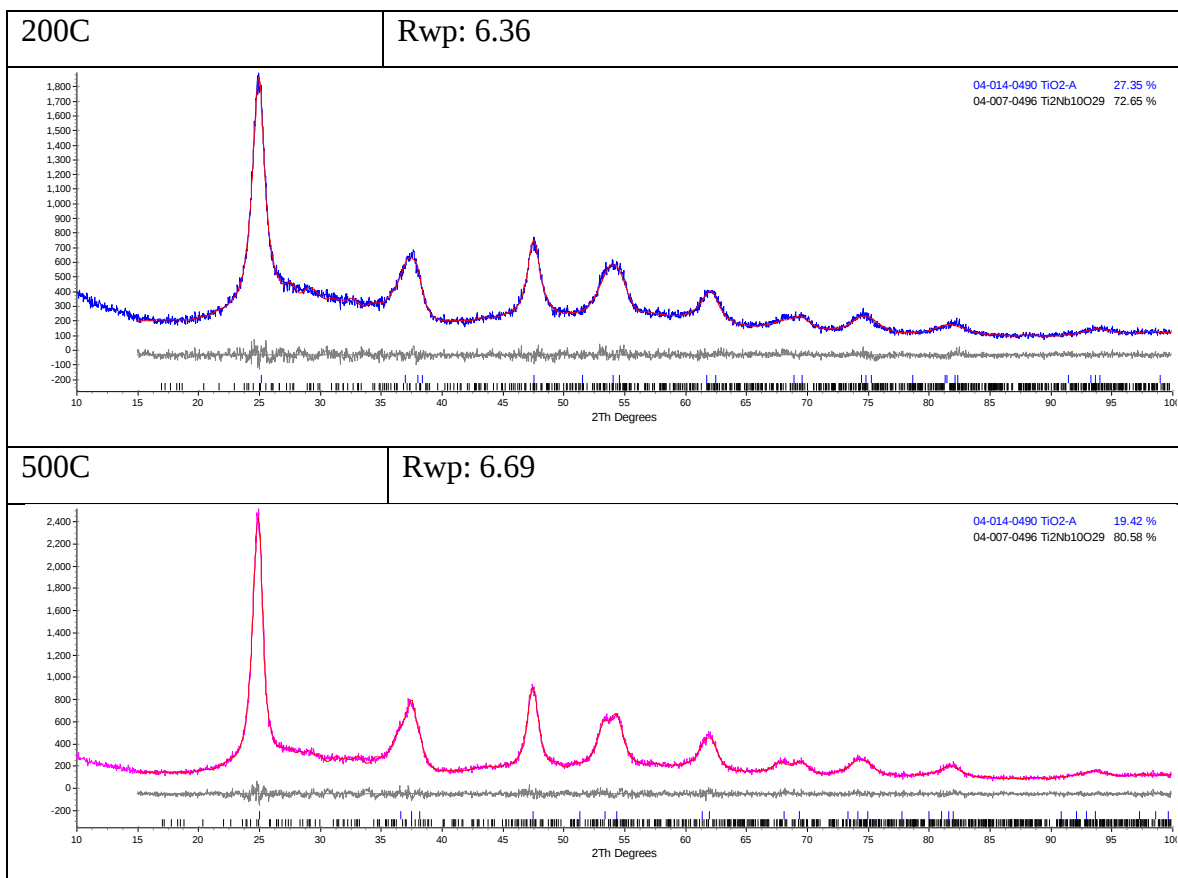


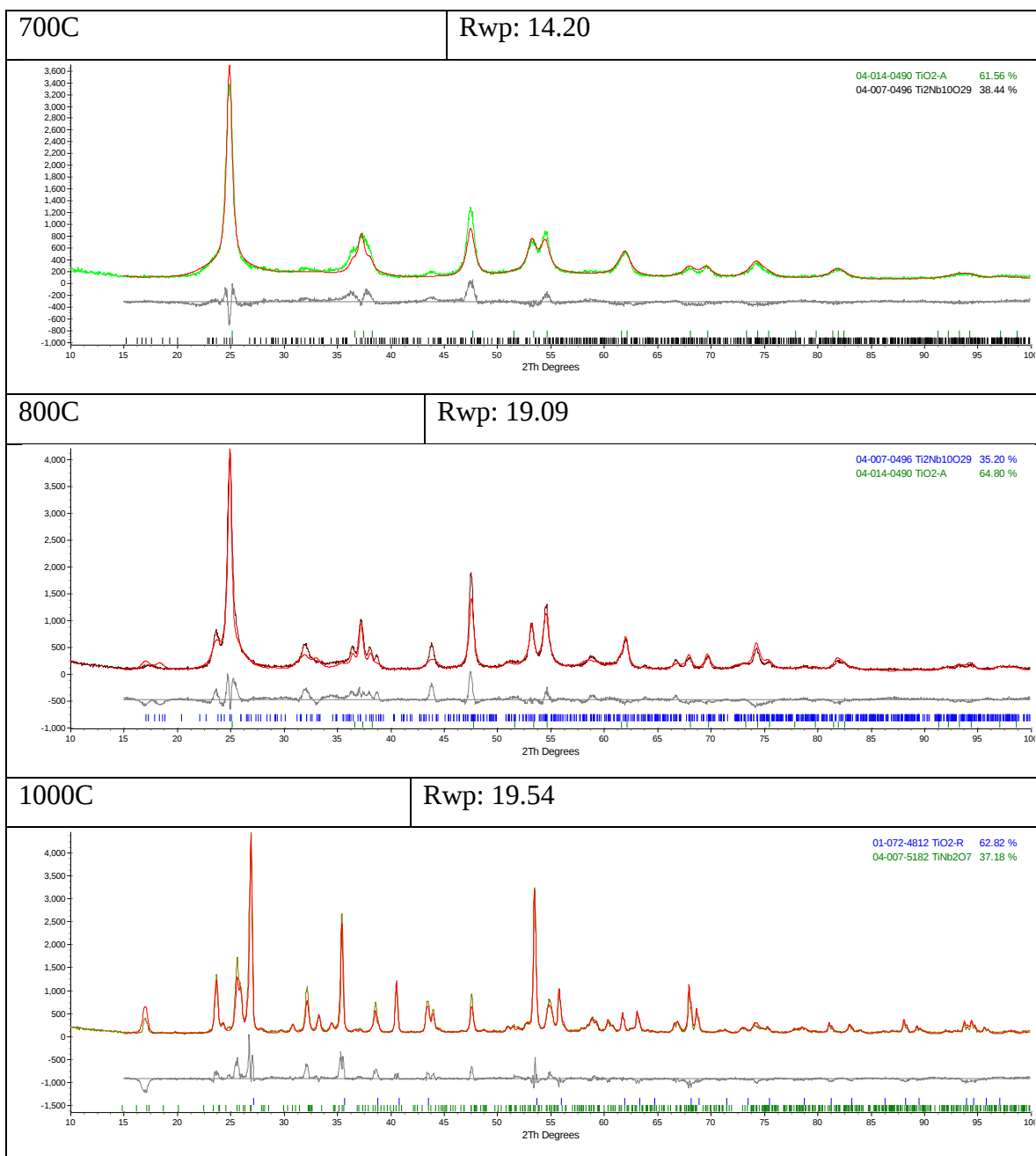
Figure B-4. Microstrain versus temperature.

C. Appendix C: XRD Patterns from Rietveld Refinement for 75:25

In Table C-1, examples of the Rietveld refinement results are shown. In this table, there are three sets of data: the measured pattern (ranging from 10° to 100° 2 θ), the calculated pattern (red curve), and the difference profile (grey curve). The temperature is given in the table at top left corner, along with the Rwp values.

Table C-1. Rwp of 75:25





In Table C-1, features (a)-(f) Figure 3 can be seen. For example, at 1000°C, the peak near 54° 2θ reflects the fact that the calculated value is smaller than that of the measurement as illustrated in Figure 3(b).

D. Appendix D: Numerical Values of Lattice Parameters for 75:25

For TiO₂ anatase phase, the lattice parameters and volumes at 500°C-900°C are tabulated Table D-1, along with the results from Stengl's work.¹⁴⁸ For this work, when Nb is added, the lattice parameters and volume increase; which is consistent with Stengl's trend.

Table D-1. Comparison of 100:0, 75:25 and Stengl's Anatase Lattice Parameters and Volumes

100:0					
	Temperature (°C)				
	500	600	700	800	900
a	3.797	3.797	3.799	3.801	3.805
c	9.550	9.575	9.586	9.597	9.612
V	137.67	138.08	138.35	138.65	139.16
75:25					
	Temperature (°C)				
	500	600	700	800	900
a	3.830	3.817	3.813	3.810	3.810
c	9.589	9.593	9.601	9.612	9.621
V	140.68	139.76	139.55	139.49	139.67
Stengl TiO ₂ Anatase with different Nb dopant mol %					
	0%	5%	10%	15%	
a	3.79656	3.79794	3.79951	3.80414	
c	9.51192	9.51724	9.52113	9.52898	
V	137.1036	137.28	137.4497	137.8985	

For rutile, the lattice parameters and volume increase as Nb is added. In Table D-2, the values are all tabulated.

Table D-2. Comparison of 100:0 and 75:25 Rutile Lattice Parameters and Volumes

100:0			
	Temperature		
	900	1000	1100
a	4.626	4.630	4.634
c	2.986	2.989	2.992
V	63.89	64.06	64.26
75:25			
	Temperature		
	900	1000	1100
a	4.636	4.643	4.650
c	2.991	2.995	3.000
V	64.28	64.57	64.85

Unit cell parameter changes are provided here along with volume percentage changes and strain values. In Figure D-1, the lattice parameter percentage changes for $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ are plotted as a function of temperature, using the standard lattice parameter values in PDF 04-007-0496 as references. At 200°C, lattice parameter values are near $\pm 2\%$ of the standard values. At 800°C, the lattice parameter values are near $\pm 0.5\%$ of the standard values.

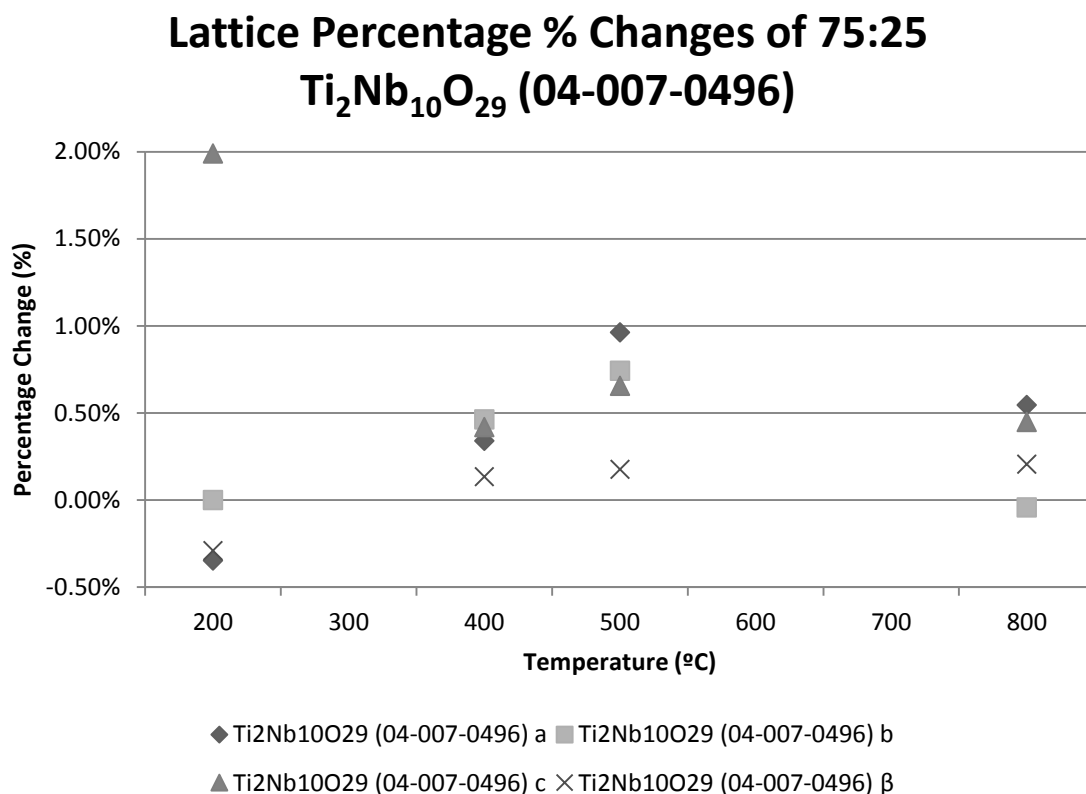


Figure D-1. Lattice parameter percentage changes versus temperature for Ti₂Nb₁₀O₂₉.

In Figure D-2, the lattice parameter percentage changes for TiNb₂O₇ are plotted as a function of temperature, using the standard lattice parameter values in PDF 04-007-5182 as references. At 900°C, lattice parameter values are near the standard values by $\pm 0.8\%$. At 1100°C, the lattice parameter values are near the standard values by $\pm 0.4\%$.

Lattice Percentage % Changes of 75:25 TiNb_2O_7 (04-007-5182)

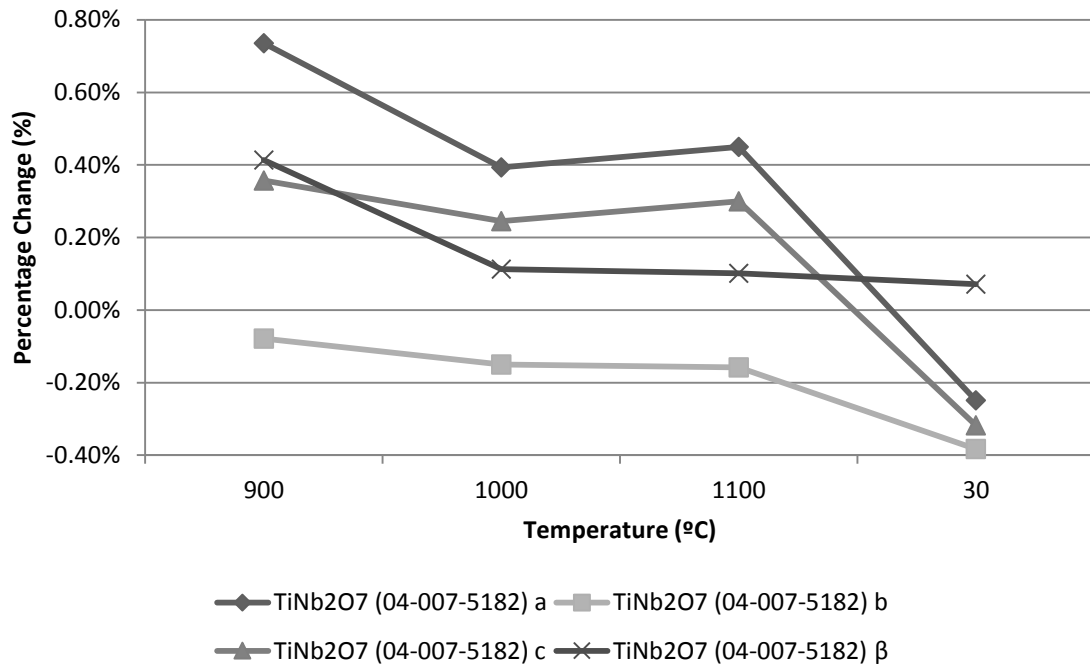


Figure D-2. Lattice parameter percentage changes versus temperature for TiNb_2O_7 .

In Figure D-3, the lattice parameter percentage changes for $\text{TiO}_2\text{-A}$ are plotted as a function of temperature, using the standard lattice parameter values in PDF 04-014-0490 as references. At 200°C, lattice parameter values are near the standard values by $\pm 0.7\%$. At 900°C, the lattice parameter values are near the standard values by 1.2%.

Lattice Percentage % Changes of 75:25 TiO₂-A (04-014-0490)

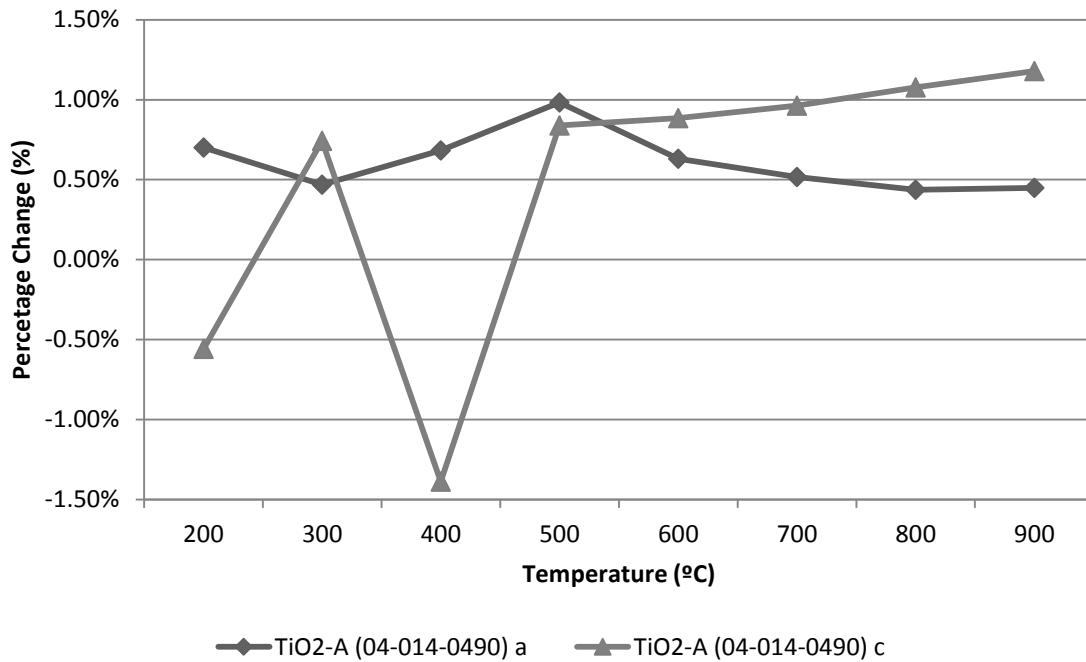


Figure D-3. Lattice parameter percentage changes versus temperature for TiO₂-A.

In Figure D-4, the lattice parameter percentage changes for TiO₂-R are plotted as a function of temperature, using the standard lattice parameter values in PDF 01-072-4812 as references. At 900°C, lattice parameter values are within 1.2% of the standard values. At 1100°C, the lattice parameter values are within 1.5% of the standard values. Specifically, the trend in Figure D-4 is similar to that in Figure B-2 for lattice parameter *a* or *c*, respectively. That is, both *a* and *c* values increase as the temperature increases. As the temperature decreases to 30°C, both values are close to the standard values within 0.2%.

Lattice Percentage % Changes of 75:25 TiO₂-R (01-072-4812)

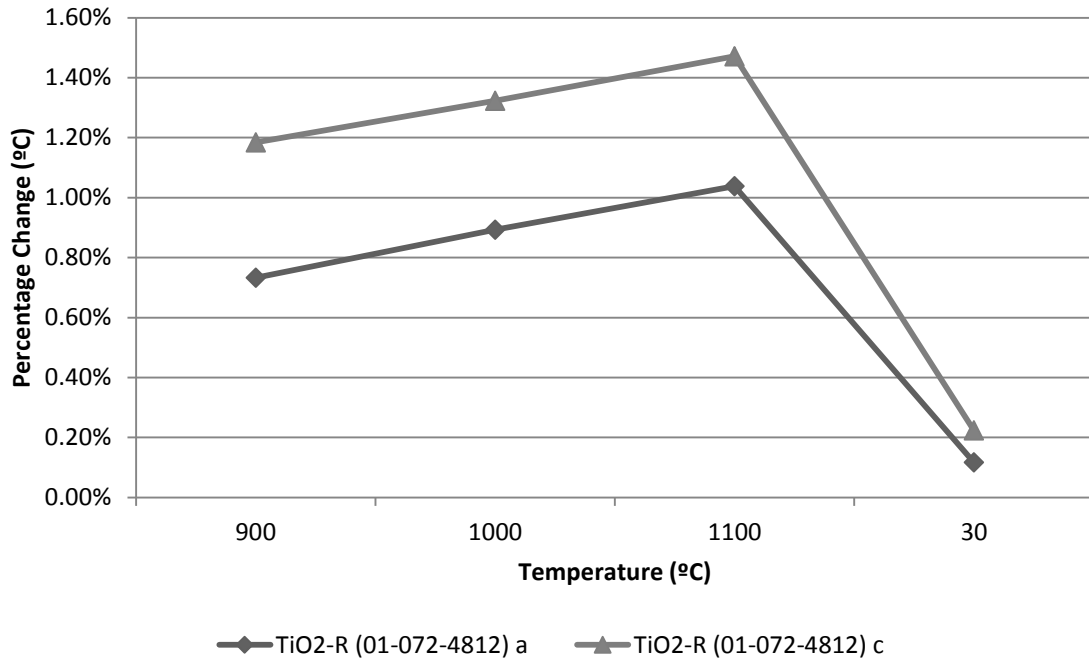


Figure D-4. Lattice parameter percentage changes versus temperature for TiO₂-R.

Anatase or rutile has a tetragonal structure, the volume is given as $c(a^2)$. Ti₂Nb₁₀O₂₉ or TiNb₂O₇ has a monoclinic structure, the volume is given as $a(b)(c)\sin(\text{beta})$. In Figure D-5, each of the four phases' volume percentage is given as a function of temperature. At 200°C, the percentage changes of volumes are within 2% of the standard values. At 1100°C, the percentage changes of volumes are within 3.5% of the standard values. When the sample cools to 30°C, the percentage changes are within $\pm 1\%$ of the standard values. Focusing on TiO₂ rutile, the general trend from 900°C to 1100°C can be compared with that in Figure B-3.

Unit Cell Volume % Changes of 75:25

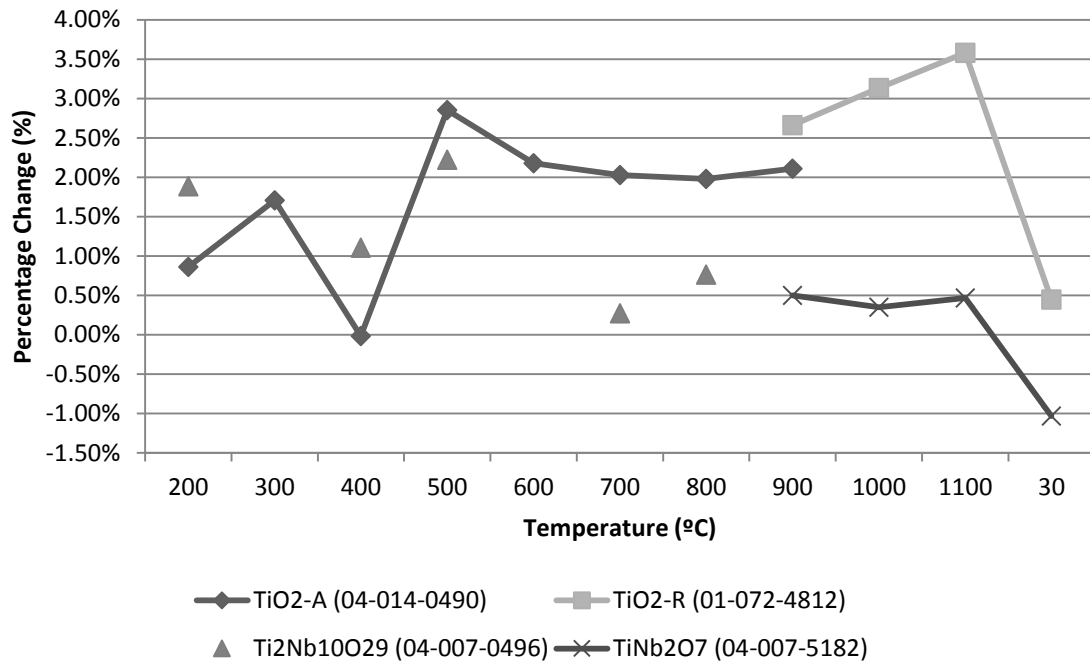


Figure D-5. Unit cell volume percentage change as a function of temperature for 75:25.

In Figure D-6, microstrain is plotted as a function of temperature for all four phases between 200°C and 1100°C. As the temperature increases from 200°C to 800°C, the microstrain value decreases. Between 900°C and 1100°C, the value does not change much for each phase. When the sample cools down to 30°C, the strain values are 0.1% larger than the standard values.

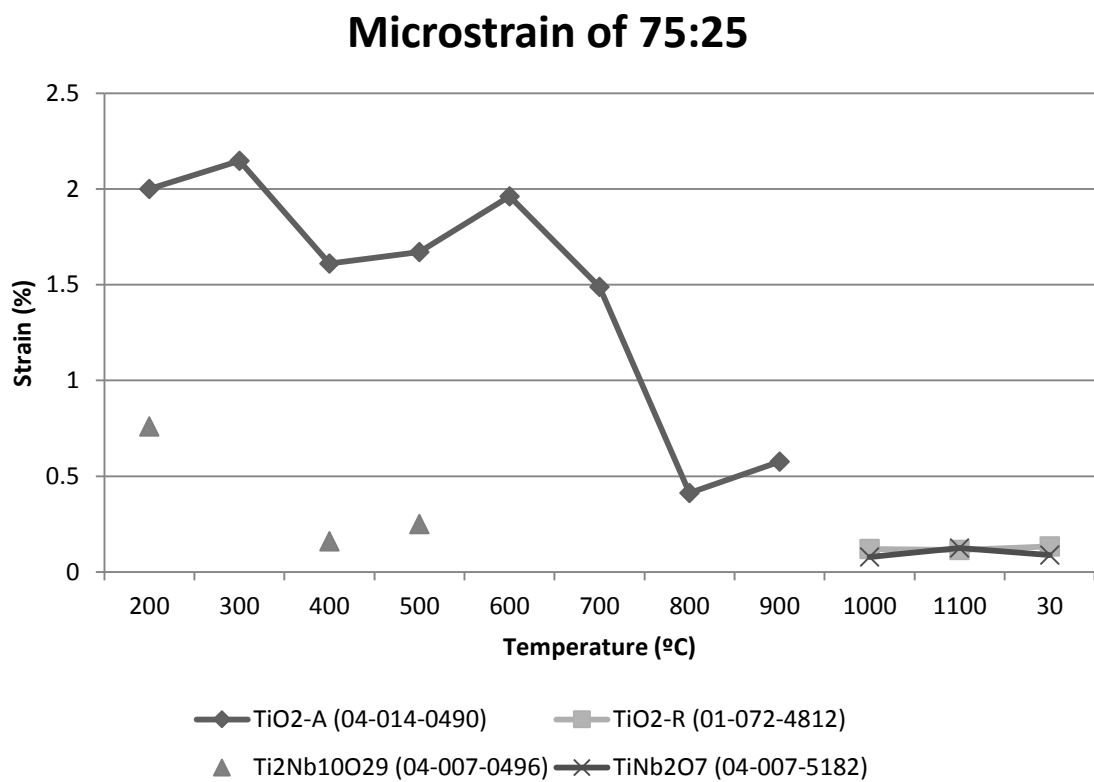
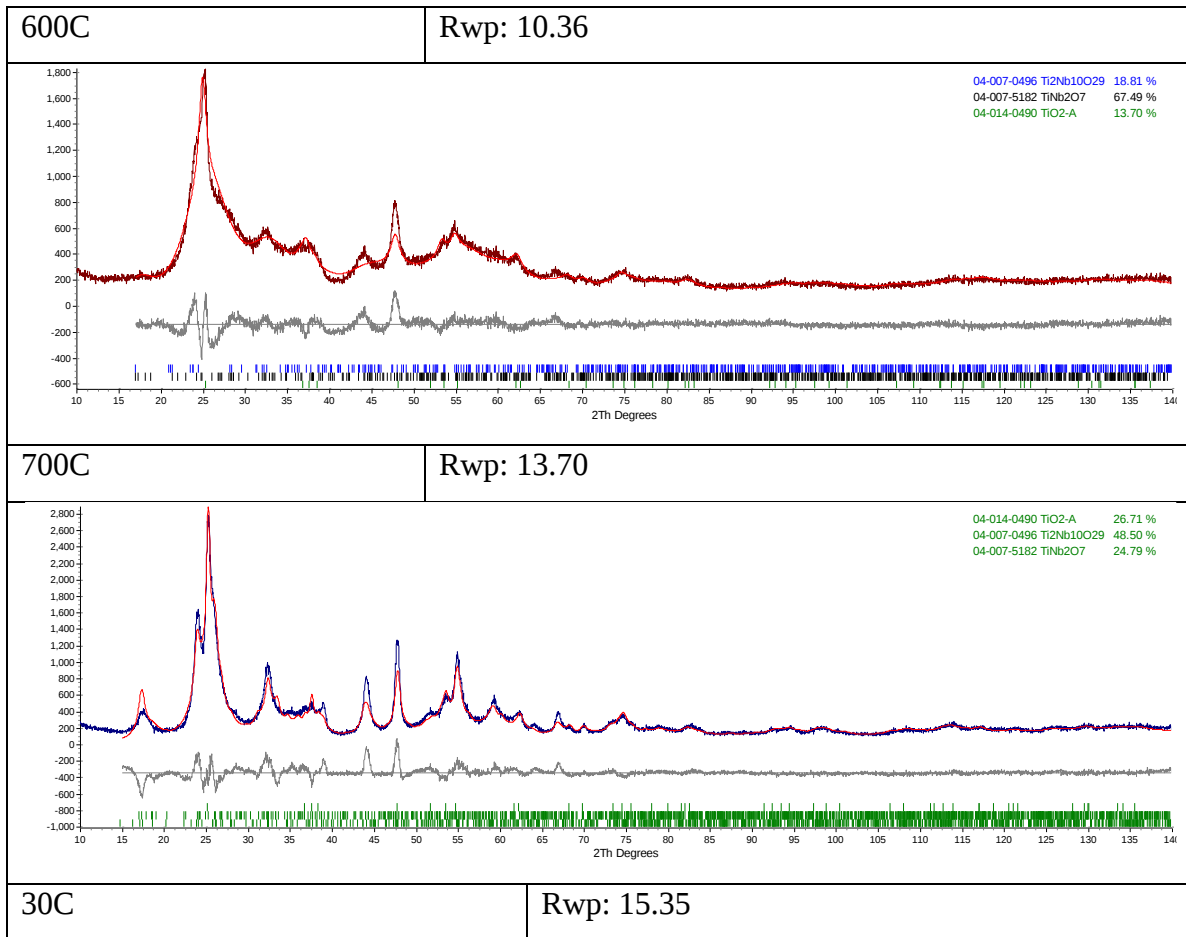


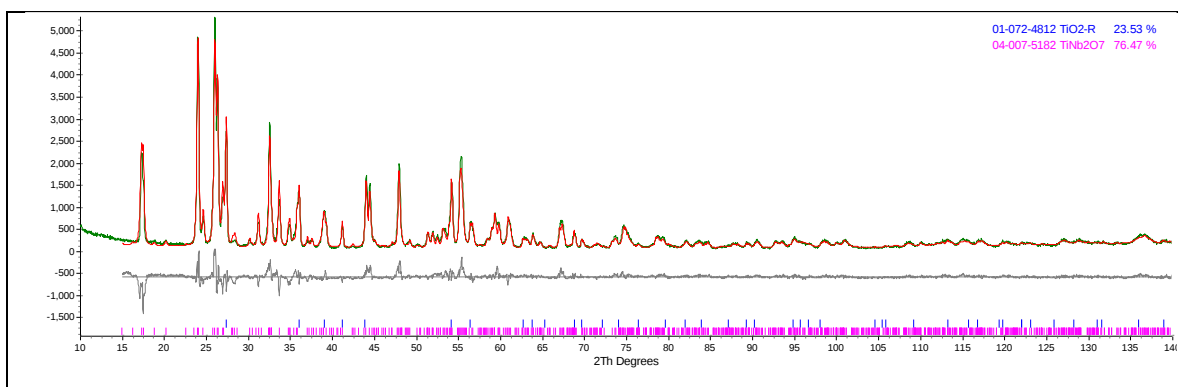
Figure D-6. Microstrain versus temperature for 75:25.

E. Appendix E: XRD Patterns from Rietveld Refinement for 50:50

In Table E-1, examples of the Rietveld refinement results are shown. In this table, there are three sets of data: the measured pattern (ranging from 10° to 100° 2θ), the calculated pattern (red curve), and the difference profile (grey curve). The temperature is given in the table at top left corner, along with the Rwp values.

Table E-1. Rwp of 50:50





In Table E-1, features (a)-(f) Figure 3 can be seen. For example, at 30°C, the peak near 17° 2θ reflects the fact that the calculation is larger than the measured values for TiNb₂O₇, as illustrated in Figure 3 (b).

F. Appendix F: Numerical Values of Lattice Parameters for 50:50

For TiO₂ anatase phase, the volumes at 600°C-900°C are tabulated Table F-1. The data from 100:0 and 75:25 samples are also included for comparison. The volume does not change when the sample changes from 75:25 to 50:50, implying substitutional ions are reaching the limit when the sample is 75:25.

Table F-1. Comparison of 100:0, 75:25 and 50:50 Volumes at 600°C

100:0					
	Temperature (°C)				
	500	600	700	800	900
V	137.67	138.08	138.35	138.65	139.16
75:25					
	Temperature (°C)				
	500	600	700	800	900
V	140.68	139.76	139.55	139.49	139.67
50:50					
	Temperature (°C)				
		600	700	800	900
V		136.80	139.11	139.51	139.64

Unit cell parameter changes are provided here along with volume percentage changes and strain values. In Figure F-1, the lattice parameter percentage changes for TiNb_2O_7 are plotted as a function of temperature, using the standard lattice parameter values in PDF 04-007-5182 as references. At 600°C, lattice parameters are near the standard values within $\pm 3\%$. As the temperature increases to 1100°C, the lattice parameters are closer to the standard values, within $\pm 0.3\%$.

Lattice Percentage % Changes of 50:50 TiNb_2O_7 (04-007-5182)

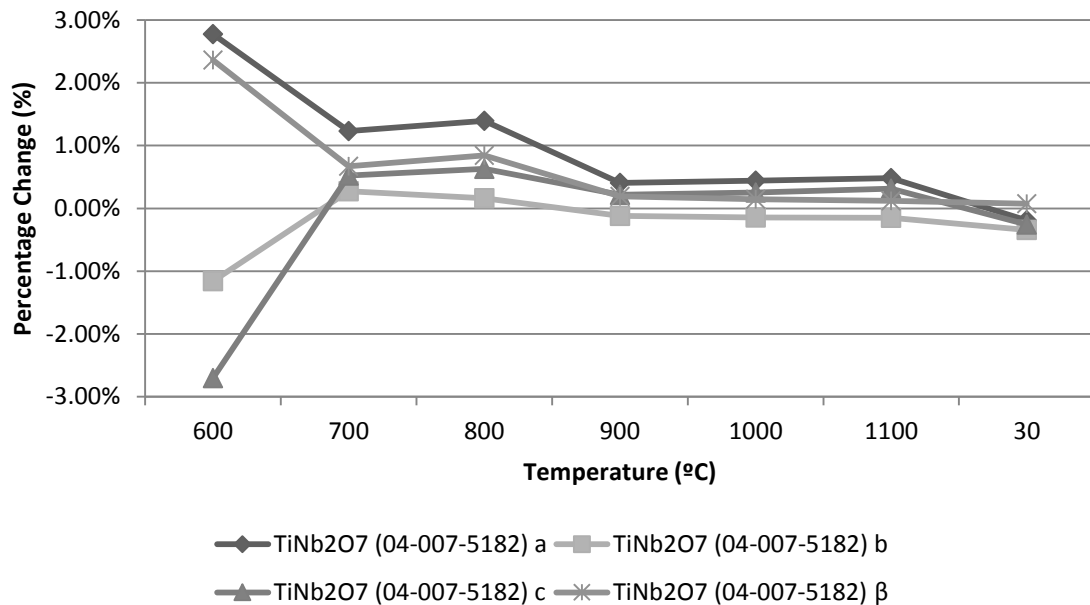


Figure F-1. Lattice parameter percentage changes versus temperature for TiNb_2O_7 .

In Figure F-2, the lattice parameter percentage changes for rutile TiO_2 are plotted as a function of temperature, using the standard lattice parameter values in PDF 01-072-4812 as references. At 1000°C, lattice parameter values are near the standard values within 1.4%. Specifically, the trend in Figure F-2 is similar to that in Figures D-4 and B-2 for lattice parameter a or c , respectively. That is, both a and c values increase as the

temperature increases. As the temperature decreases to 30°C, both values are close to the standard values within 0.2%.

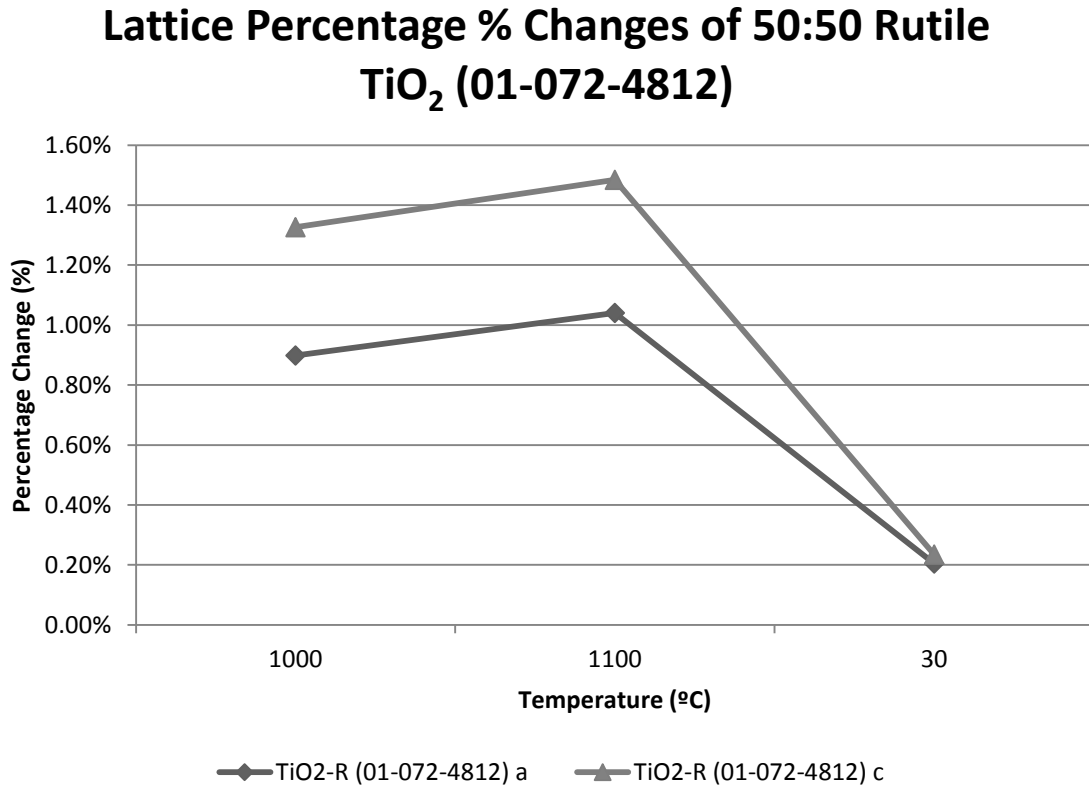


Figure F-2. Lattice parameter percentage changes versus temperature for rutile TiO₂.

In Figure F-3, the lattice parameter percentage changes for TiO₂-A are plotted as a function of temperature, using the standard lattice parameter values in PDF 04-014-0490 as references. At 600°C, lattice parameter values are near the standard values within $\pm 0.7\%$. As temperature increases to 700°C, the a value increases. Thereafter, the a value does not change much. As the temperature increases from 700°C to 900°C, the c value increases monotonically until it reaches 1.2%.

Lattice Percentage % Changes of 50:50 Anatase TiO₂ (04-014-0490)

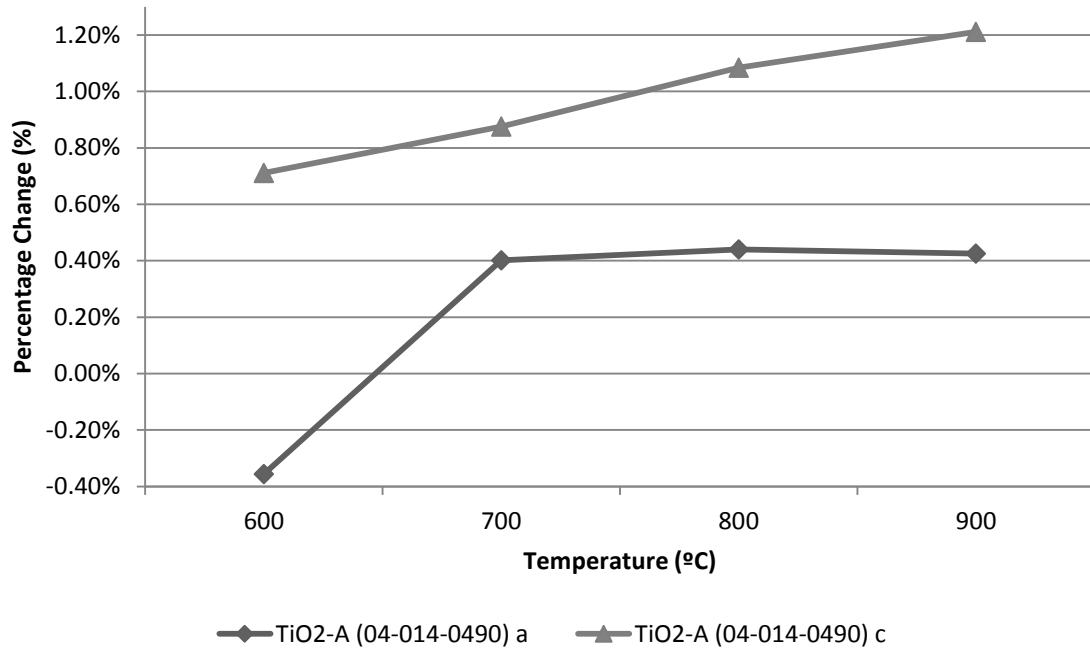


Figure F-3. Lattice parameter percentage changes versus temperature for TiO₂-A.

Anatase or rutile has a tetragonal structure, the volume is given as $c(a^2)$. TiNb₂O₇ has a monoclinic structure, the volume is given as $a(b)(c)\sin(\text{beta})$. In Figure F-4, the volume percentage change for each of the phases is given as a function of temperature. At any given temperature, the volume changes are within $\pm 4\%$ of the standard values. The anatase TiO₂ volume increases as the temperature increases from 600°C to 900°C; and the rutile volume increases from 1000°C to 1100°C and then decreases upon cooling to 30°C. This trend for TiO₂ is similar to that in Figure B-3.

Unit Cell Volume % Changes of 50:50

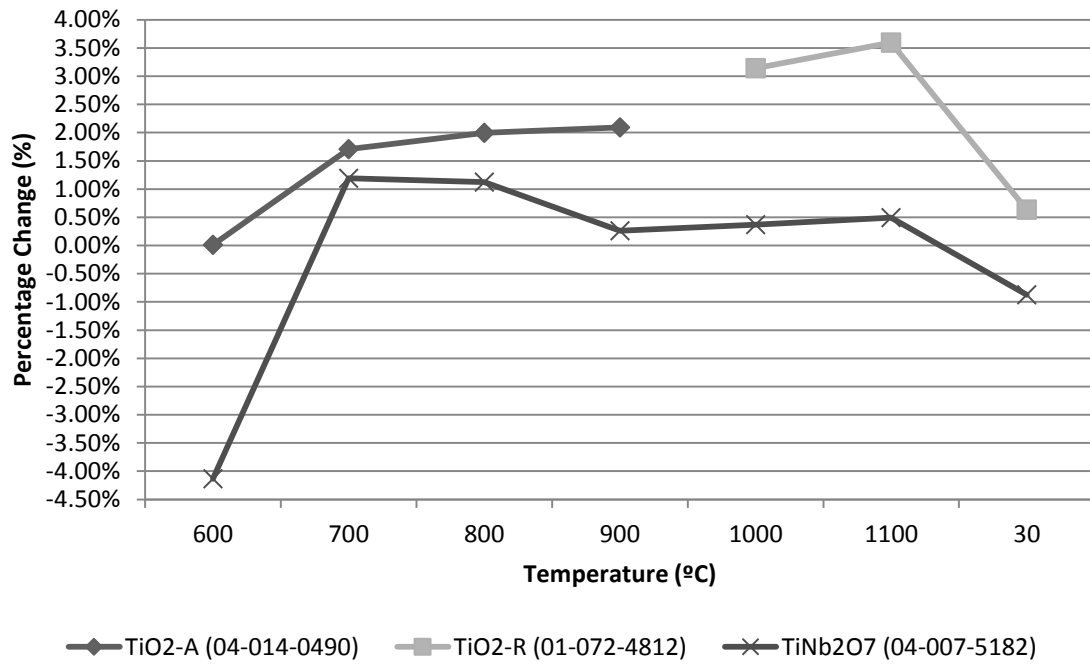


Figure F-4. Unit cell volume percentage change as a function of temperature for 50:50.

In Figure F-5, microstrain is plotted as a function of temperature for each phase. The microstrain values are approximately 0.6 or less.

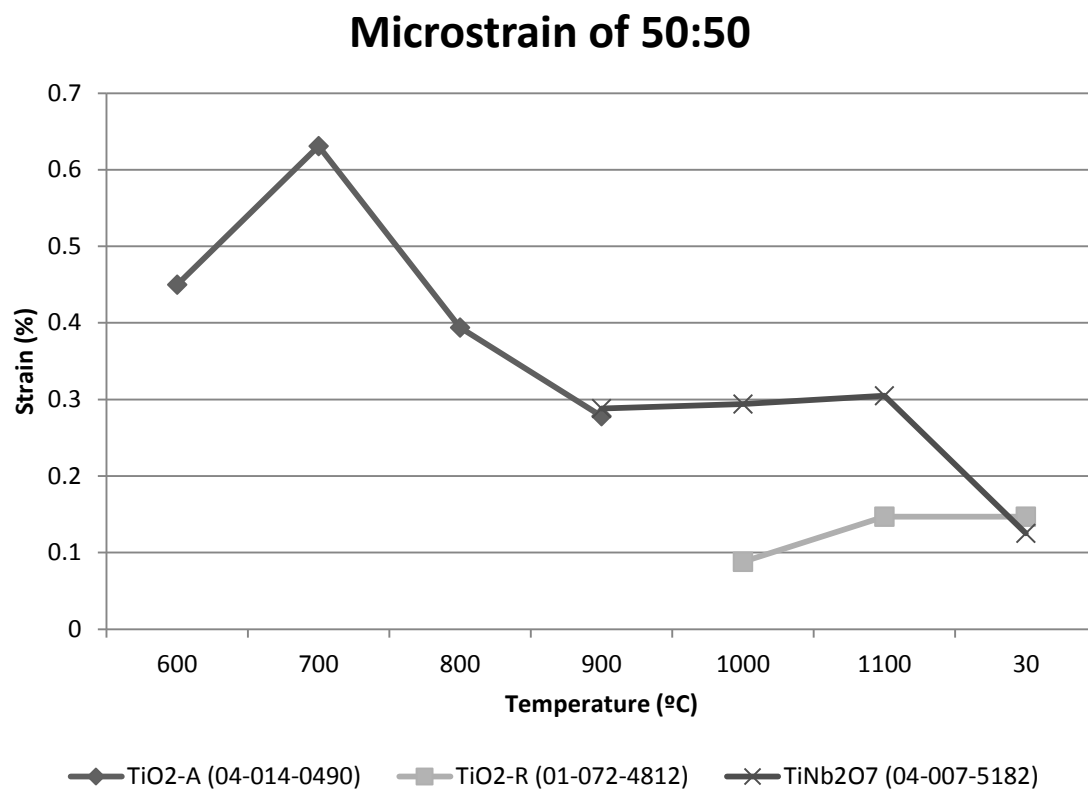


Figure F-5. Microstrain versus temperature for 50:50.

G. Appendix G: XRD Patterns from Rietveld Refinement for 25:75

In Figure G-1, the orthorhombic Nb₂O₅ volume of 0:100 is compared to 25:75. In general, the 0:100 volume is larger than that of 25:75 at any given temperature between 500°C and 700°C. The titanium ion radius is smaller than that of niobium, and possibly causes a small reduction in the unit cell volume. The titanium contribution also allows orthorhombic phase to transform to monoclinic phase after 700°C.

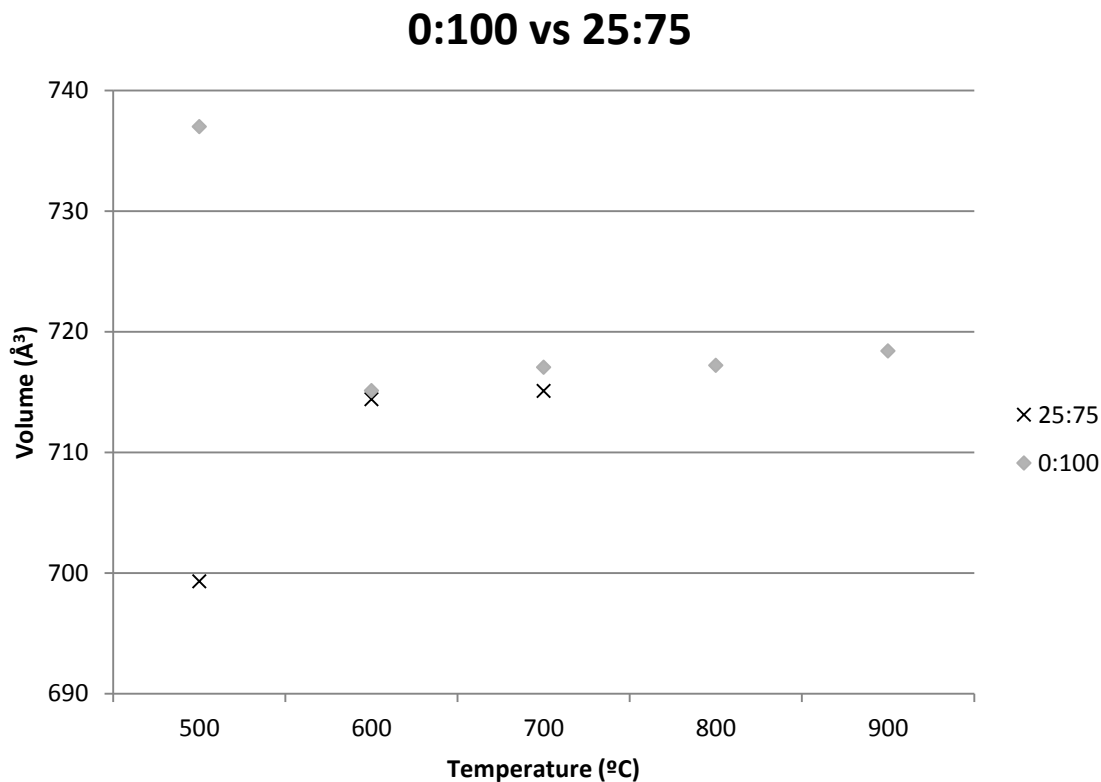
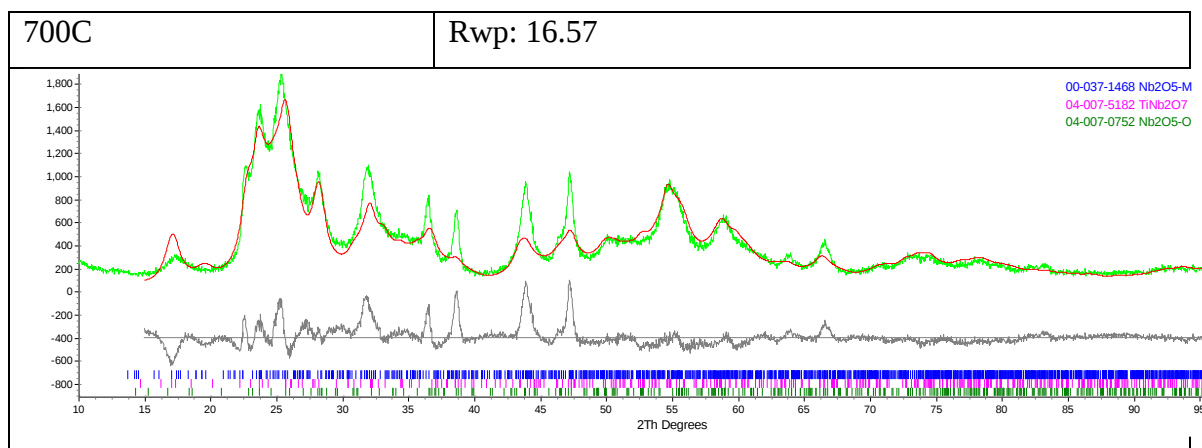


Figure G-1. Graph comparing the orthorhombic Nb₂O₅ unit cell volumes of 0:100 and 25:75.

In Table G-1, examples of the Rietveld refinement results are shown. In this table, there are three sets of data: the measured pattern (ranging from 10° to 100° 2θ), the calculated pattern (red curve), and the difference profile (grey curve). The temperature is given in the table at top left corner, along with the Rwp values. Referring to Table G-1, features in Figure 3 (a)-(f) can be seen.

Table G-1. Rwp of 25:75



H. Appendix H: Numerical Values of Lattice Parameters for 25:75

Unit cell parameter changes are provided here along with volume percentage changes and strain values. In Figure H-1, the lattice parameter percentage changes for TiNb_2O_7 are plotted as a function of temperature, using the standard lattice parameter values in PDF 04-007-5182 as references. At 700°C, lattice parameter values are within 1.8% of the standard values. As temperature increases, the values are closer to that of the standard values by 0.7%.

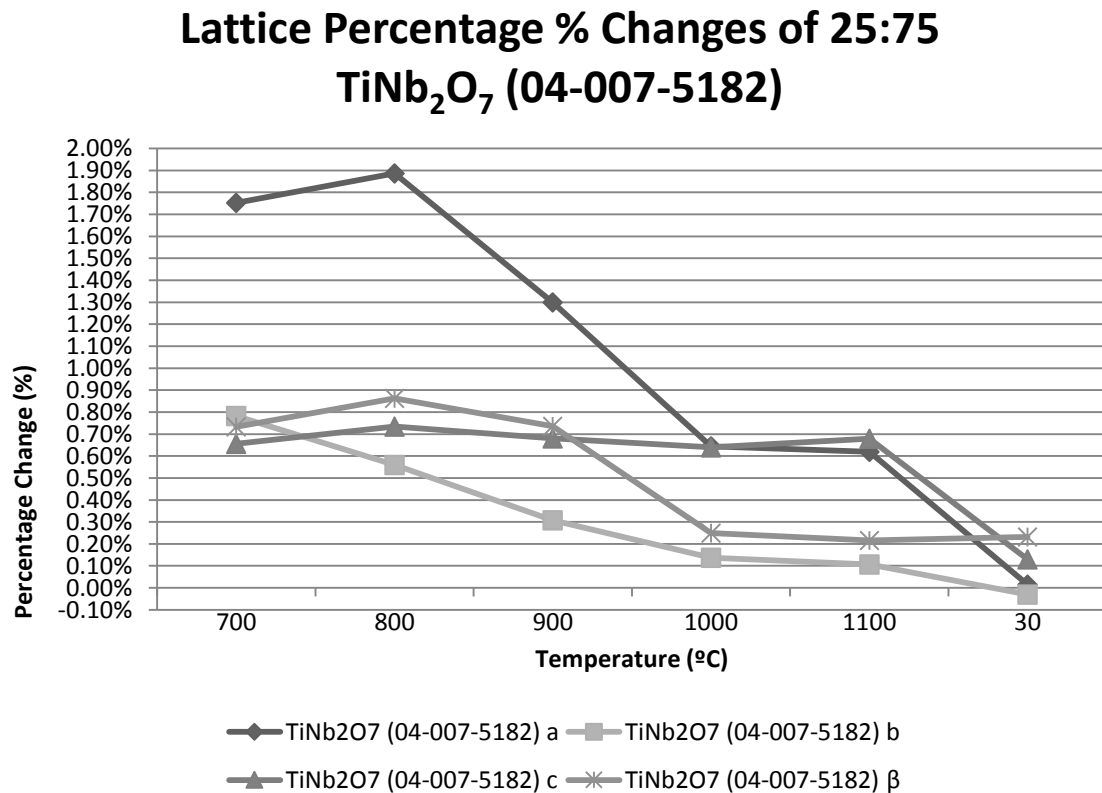


Figure H-1. Lattice parameter percentage changes versus temperature for TiNb_2O_7 .

In Figure H-2, the lattice parameter percentage changes for $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ are plotted as a function of temperature, using the standard lattice parameter values in PDF 04-007-0496 as references. At 500°C, lattice parameter values are within $\pm 1.6\%$ of the standard value. At 600°C, the values are within $\pm 0.5\%$ of the standard values.

Lattice Percentage % Changes of 25:75 $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ (04-007-0496)

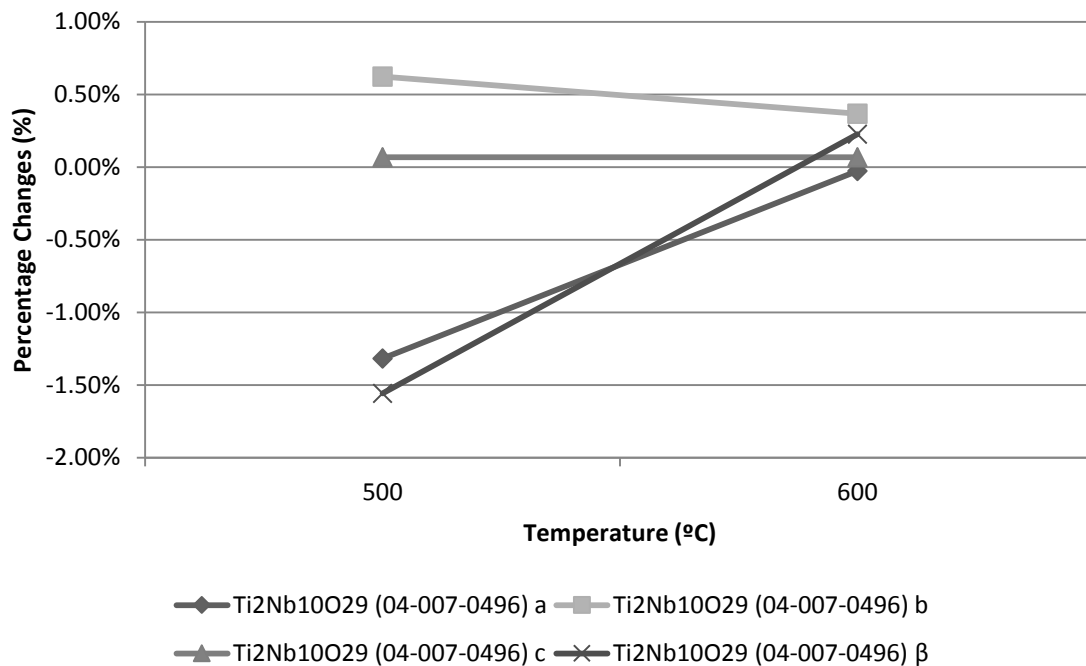


Figure H-2. Lattice parameter percentage changes versus temperature for $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$.

In Figure H-3, the lattice parameter percentage changes for $\text{Nb}_2\text{O}_5\text{-O}$ are plotted as a function of temperature, using the standard lattice parameter values in PDF 04-007-0752 as references. At 500°C, lattice parameter values are within $\pm 6\%$ of the standard values. At 700°C, the lattice parameter values are within $\pm 3\%$ of the standard values.

Lattice Percentage % Changes of 25:75 Orthorhombic Nb₂O₅ (04-007-0752)

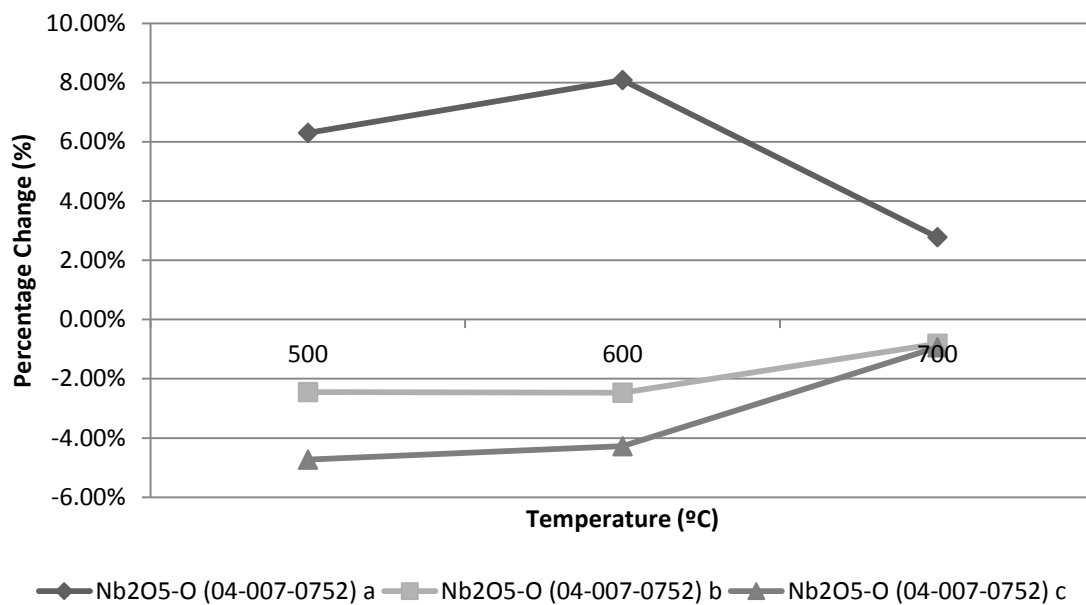


Figure H-3. Lattice parameter percentage changes versus temperature for Nb₂O₅-O.

In Figure H-4, the lattice parameter percentage changes for Nb₂O₅-M are plotted as a function of temperature, using the standard lattice parameter values in PDF 00-037-1468 as references. At 700°C, lattice parameter values are within $\pm 2.7\%$ of the standard values. At 1100°C, the lattice parameter values are within $\pm 2.1\%$ of the standard values.

Lattice Percentage % Changes of 25:75 Monoclinic Nb₂O₅ (00-037-1468)

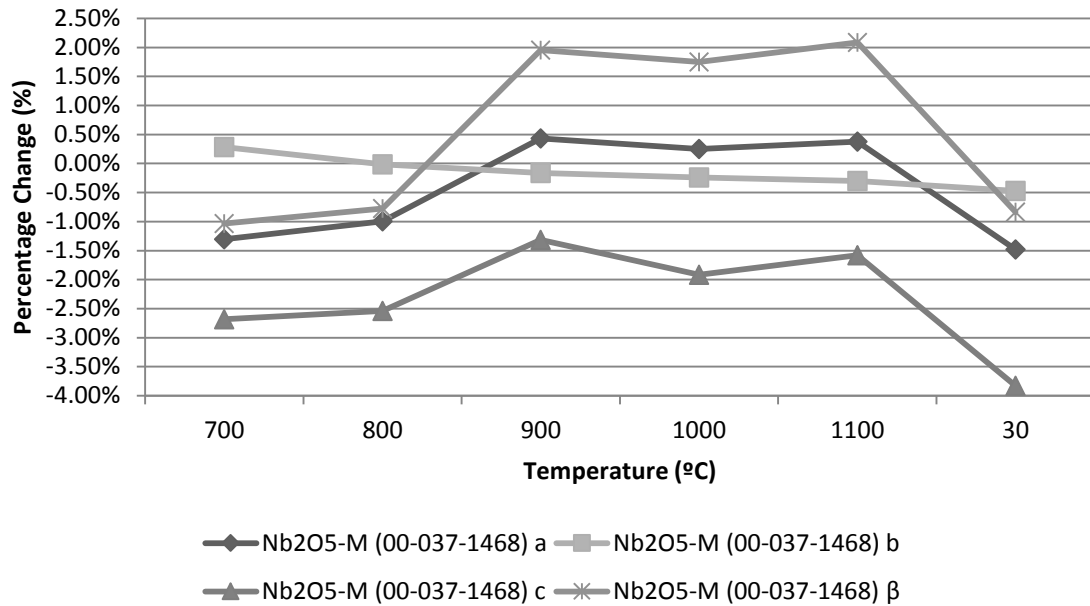


Figure H-4. Lattice parameter percentage changes versus temperature for Nb₂O₅-M.

Nb₂O₅-O has a orthorhombic structure, the volume is given as a(b)(c). Nb₂O₅-M, Ti₂Nb₁₀O₂₉ or TiNb₂O₇ has a monoclinic structure, the volume is given as a(b)(c)sin(beta). In Figure H-5, each of the four phases' volume percentage is given as a function of temperature. At 500°C, the volumes are within ±1.5% of the standard value. At 1100°C, the volumes are within ±4.5% of the standard value. When the sample cools to 30°C, the measured volumes are within ±5% of the standard value.

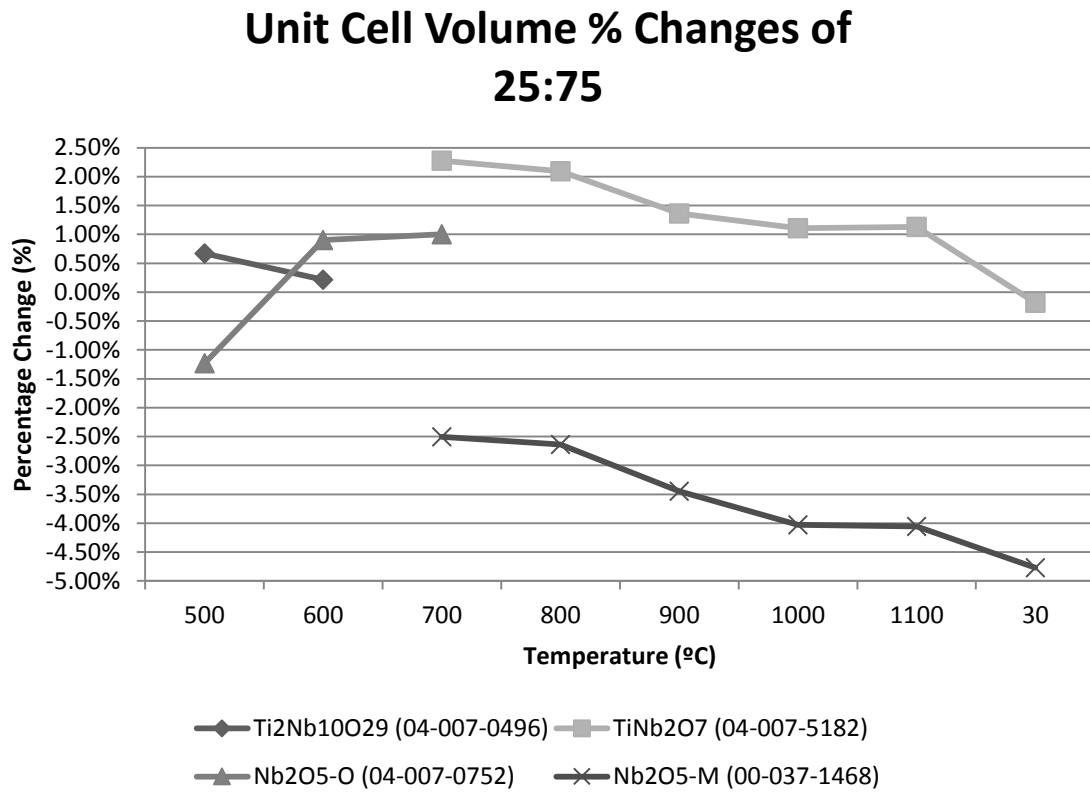


Figure H-5. Unit cell volume percentage change as a function of temperature.

In Figure H-6, microstrain is plotted as a function of temperature for each phase between 500°C and 1100°C. As the temperature increases from 600°C to 900°C, the microstrain values generally decrease.

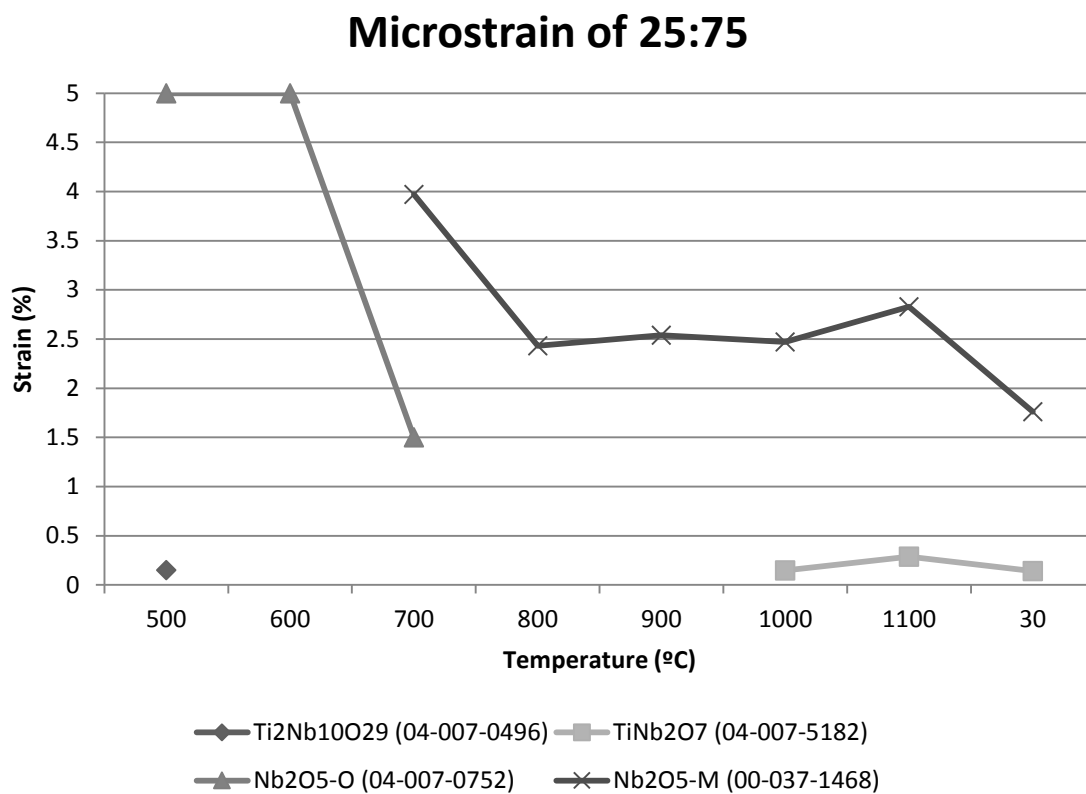
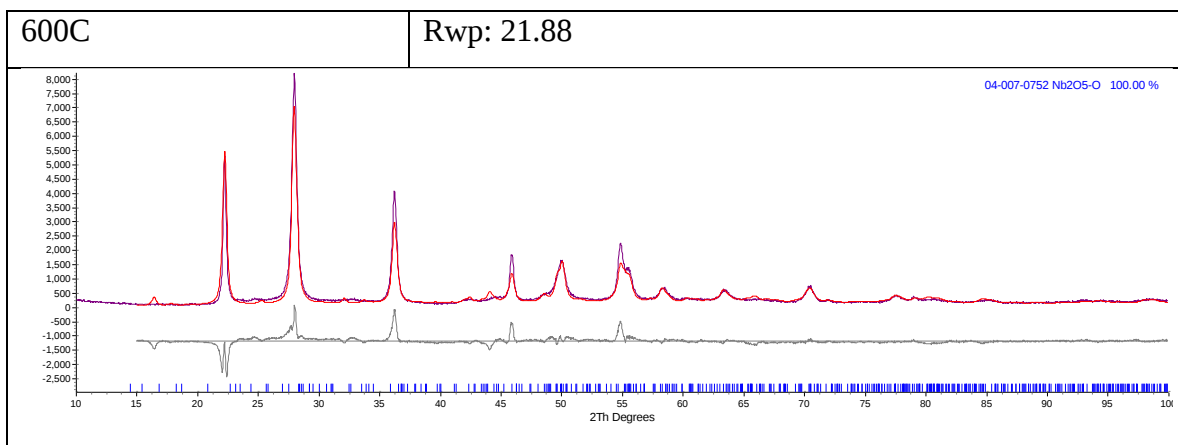


Figure H-6. Microstrain versus temperature of 25:75.

I. Appendix I: XRD Patterns from Rietveld Refinement for 0:100

In Table I-1, examples of the Rietveld refinement results are shown. In this table, there are three sets of data: the measured pattern (ranging from 10° to 100° 2 θ), the calculated pattern (red curve), and the difference profile (grey curve). The temperature is given in the table at top left corner, along with the Rwp values. Referring to Table I-1, features in Figure 3 (a)-(f) can be seen.

Table G-1. Rwp of 0:100



J. Appendix J: Numerical Values of Lattice Parameters for 0:100

Unit cell parameter changes are provided here along with volume percentage changes and strain values. In Figure I-1, the lattice parameter percentage changes for orthorhombic Nb₂O₅ are plotted as a function of temperature, using the standard lattice parameter values in PDF 04-007-0752 as references. At 500°C, lattice parameter values are within $\pm 4\%$ of the standard values. At 900°C, the lattice parameter values are within 1.5% of the standard values.

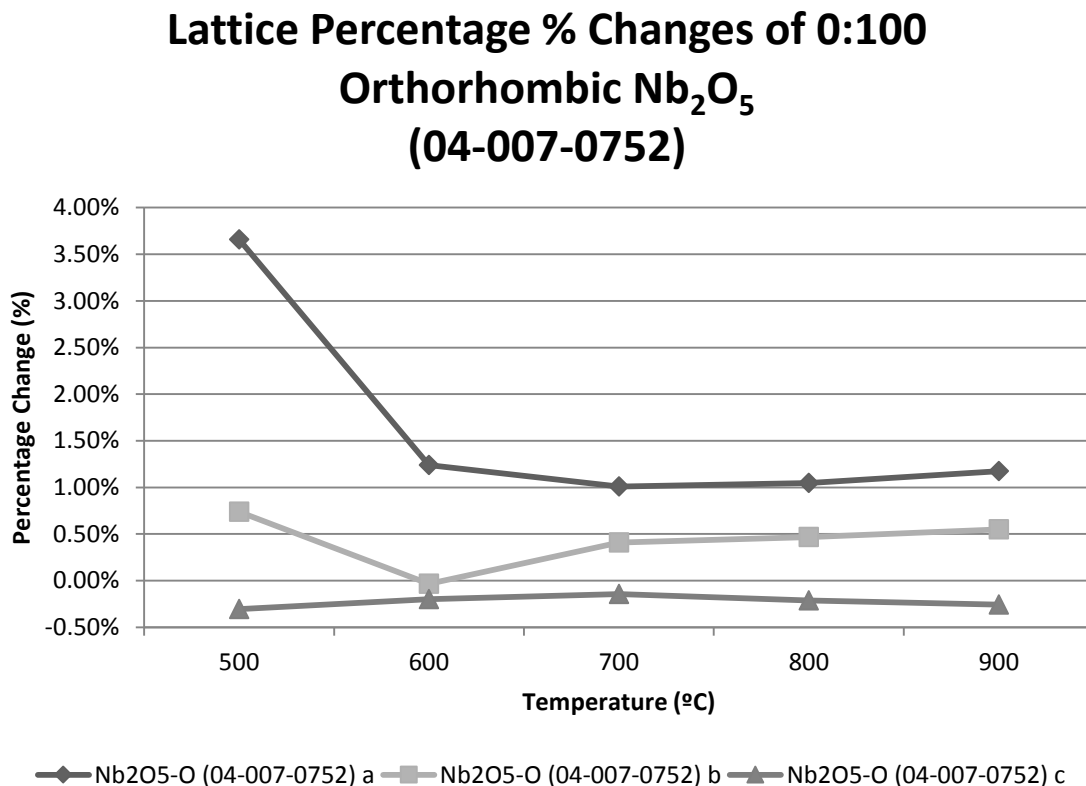


Figure I-1. Lattice parameter percentage changes versus temperature for Nb₂O₅-O.

In Figure I-2, the lattice parameter percentage changes for Nb₂O₅-M are plotted as a function of temperature, using the standard lattice parameter values in PDF 00-037-1468 as references. Between 100°C and 1100°C, the lattice parameter values are within $\pm 0.9\%$ of the standard values.

Lattice Percentage % Changes of 0:100 **Monoclinic Nb₂O₅** **(00-037-1468)**

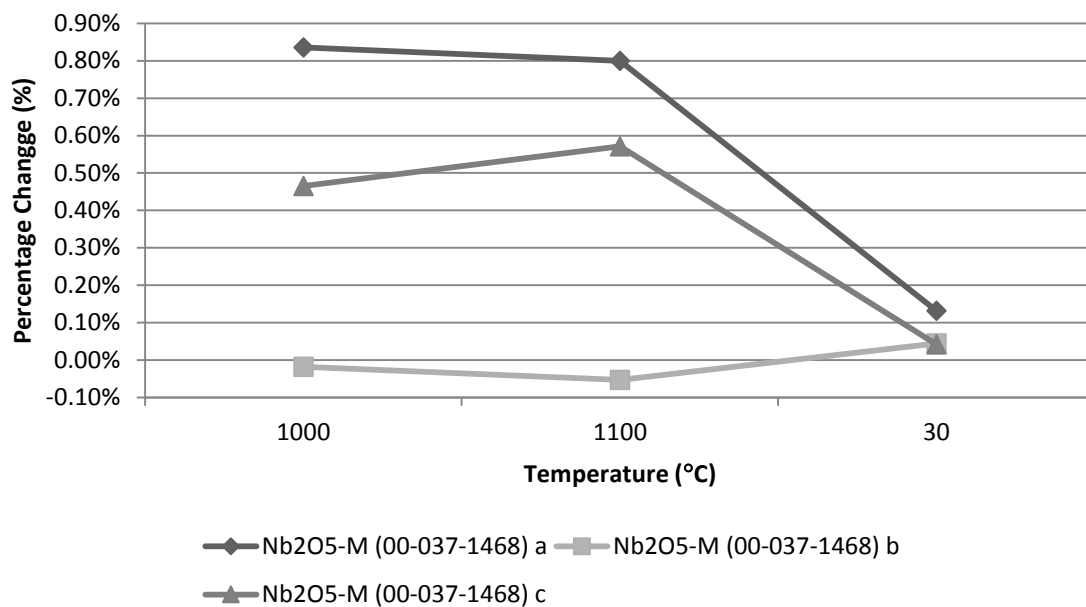


Figure I-2. Lattice parameter percentage changes versus temperature for Nb₂O₅-M.

Nb₂O₅-O has a orthorhombic structure, the volume is given as a(b)(c). Nb₂O₅-M has a monoclinic structure, the volume is given as a(b)(c)sin(beta). In Figure I-3, each of the phases' volume percentage is given as a function of temperature.

Unit Cell Volume % Changes of 0:100

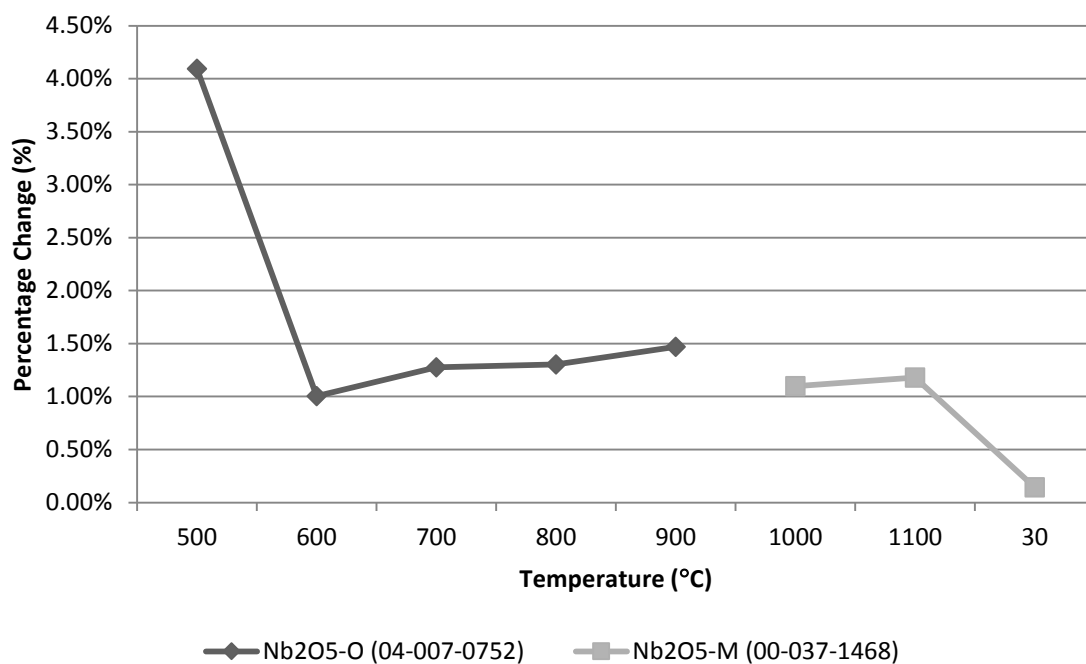


Figure I-3. Unit cell volume percentage change as a function of temperature.

In Figure I-4, microstrain is plotted as a function of temperature for each phase between 500°C and 1100°C.

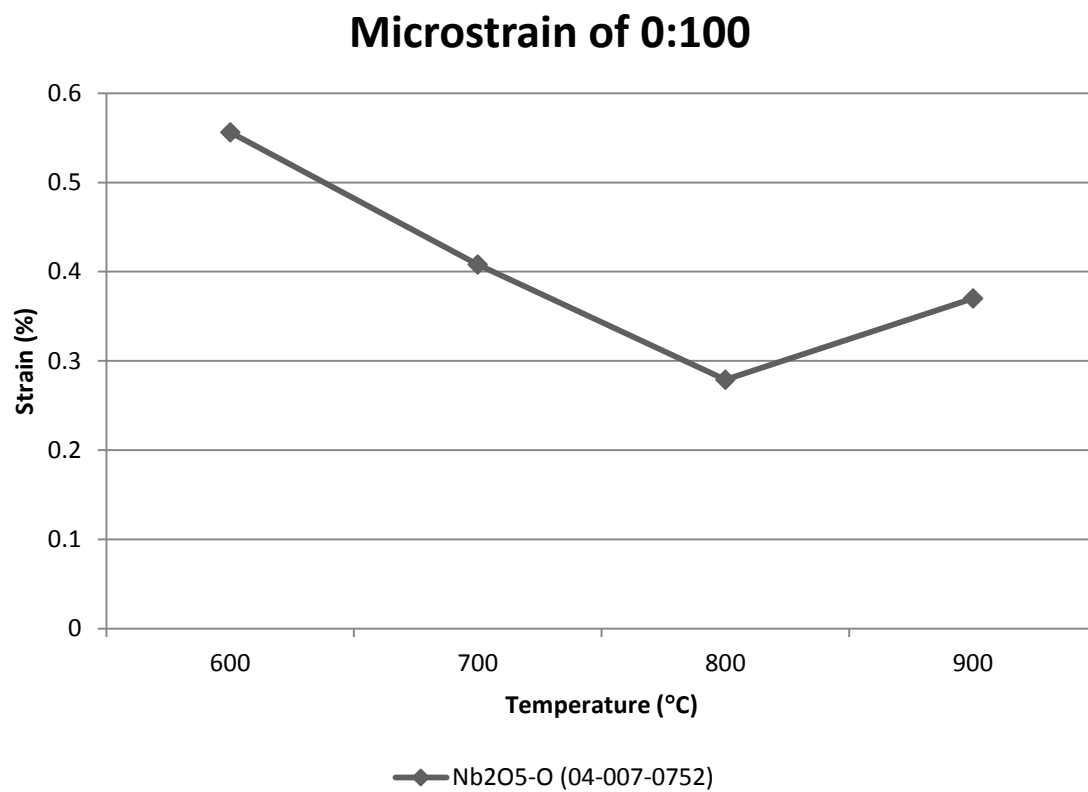


Figure I-4. Microstrain versus temperature of 0:100.