

SYNTHESIS AND CHARACTERIZATION OF NOVEL COMPLEX IRON OXIDES
WITH LAYERED AND TUNNEL STRUCTURES

By

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ABSTRACT

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Novel cathode materials for lithium ion batteries were synthesized via lithium for sodium ion exchange from the known compounds, β -NaFeO₂ and NaFeTiO₄. The resulting lithium analogs of these known sodium compounds, T-LiFeO₂ and LiFeTiO₄, contain tunnel-like structures that were characterized using Rietveld refinement of Powder X-ray diffraction, electrochemical measurements, Mössbauer spectroscopy, thermogravimetric analysis, and inductively coupled plasma spectroscopy. Similarly characterized, α - and β -NaFe₂O₃, with a double layered rock salt structure, were synthesized for the first time as a bulk powder using an oxygen pressure regulation method that provided the appropriate conditions for the two polymorphs to form.

Further, investigation into T-LiFeO₂ and NaFe₂O₃ by doping other transition metals into the iron position, to control specific properties of the two materials was performed with success. T-LiFeO₂ and the parent phase, β -NaFeO₂, were doped with up to 0.1 and 0.15 parts of cobalt per formula unit respectively. NaFe₂O₃ was successfully doped with cobalt up to 0.5 moles with pure phases of both the α -NaFe_{1.5}Co_{0.5}O₃ and β -NaFe_{1.5}Co_{0.5}O₃ forming. Manganese doping into NaFe₂O₃ also showed the formation of the α - phase.

Probing the $\text{Fe}^{3+/4+}$ redox potential of both LiFeO_2 and LiFeTiO_4 resulted in the decomposition of each. The cobalt doped LiFeO_2 though did show a greater possibility of cycling at $\text{Fe}^{3+/4+}$ redox potential, but also resulted in a reaction with the organic electrolyte. Chemical deintercalation of LiFeO_2 and LiFeTiO_4 were performed with resulting in the decomposition of LiFeTiO_4 . LiFeO_2 , indicated successful lithium deintercalation with preliminary Mössbauer results illustrating Fe^{4+} formation. Both LiFeTiO_4 and LiFeO_2 successfully cycled electrochemically at the $\text{Fe}^{2+/3+}$ redox potential, with the new calcium ferrite structure polymorph LiFeTiO_4 cycling 17 % higher capacity than the previously reported spinel and rock salt structure compounds.

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This thesis is dedicated to my family; Ashley and Ryan Bruno, Lisa and David Heagle, Barbara Skodak, Dave and Mary Sebesta, John and Betty Sebesta, Robert and Gloria Carpenter, Shane, Dane, Lindsey and Kailey.

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Chapter 1

Introduction

Synthesis and characterization of new materials have, to this point in time, paved the proverbial road to many new technologies that are used with little, if any thought, by the majority of people every day. Continued research in the synthesis of novel materials is essential to the continued growth of society. New materials have provided the world with mobile technologies that provide the use of cell phones, lap top computers, and tablets; in addition to rechargeable batteries. The hardware found within each of these devices are examples of advancements in materials research. With every advancement that occurs, new problems also arise. An example of this is storage devices; computer flash drives continue to increase in memory but are essentially the same size they were when they came out in 2000. Eventually, there will be a limit to the memory these flash drives can hold. However, continued research on semiconductors provides the ability to continue this trend of increasing the memory while maintaining small size. This is just a simple example of a material that is used to make the lives of many easier. The topics that will be discussed within will focus on the use of relatively unconventional synthetic methods to synthesize materials in bulk and new materials to be used in rechargeable lithium ion batteries.

Chapter 2 will discuss the instrumentation that was used in the characterization of the compounds within. It will include discussion on the background along with terminology that will be used throughout for each method as well as important features each method

provides to materials chemistry. Important theory will also be discussed to further understand some of the characterization methods.

Chapter 3 will describe all of the synthetic methods used within. It will include background, a detailed description, the purpose of using the selected method over alternative techniques, and how each method was performed experimentally.

Chapter 4 will explain the oxygen pressure regulation method used to prepare the divalent polymorphs α - and β - NaFe_2O_3 that were previously only prepared as single crystals. The phase diagram of their synthesis will be described in detail along with the structural and physical properties of the two polymorphs. Chemical oxidation via sodium deintercalation to synthesize $\text{Na}_{1-x}\text{Fe}_2\text{O}_3$ to alter the average oxidation state of iron in the material along with metal doping into the iron position to synthesize $\text{NaFe}_{2-x}\text{M}_x\text{O}_3$ will be discussed.

Chapter 5 will discuss the synthesis and characterization of new tunnel polymorph $\text{LiFe}_{1-x}\text{Co}_x\text{O}_2$ through the initial synthesis of β - $\text{NaFe}_{1-x}\text{Co}_x\text{O}_2$. Attempts to probe the $\text{Fe}^{4+/3+}$ redox couple through electrochemical characterization of the undoped sample along with the electrochemical characterization of the Co doped sample will be described. Electrochemical characterization of the $\text{Fe}^{3+/2+}$ redox couple will also be shown with discussion of the potential for two-electron transfer.

Chapter 6 will describe the synthesis of the new tunnel polymorph LiFeTiO_4 with the calcium ferrite structure for the purpose of a two-electron transfer rechargeable lithium ion battery. Synthesis of the precursor phase NaFeTiO_4 , ion exchange to form the new compound LiFeTiO_4 , structural and electrochemical characterization of LiFeTiO_4 , and

attempts to probe the $\text{Fe}^{4+/3+}$ redox couple will also be discussed. Further characterization of LiFeTiO_4 by chemical reduction of Fe^{3+} to Fe^{2+} using n-butyllithium was determined structurally to be $\text{Li}_2\text{FeTiO}_4$.

Chapter 2

Instrumentation

2.1 Powder X-ray Diffraction

Powder X-ray Diffraction (PXD) uses X-rays to characterize powder materials for phase identification and structural characterization. In order to acquire an accurate PXD, all possible orientations of the crystalline solid must be represented equally. This is generally achieved by grinding the sample in question in a mortar and pestle or ball mill to reduce the powder size and therefore providing an increased number of representative crystals of all orientations. The detected orientational averaging of the bulk composition projects a single dimension spectrum that, in contrast to single crystal diffraction, is a three dimensional reciprocal space projection. This will be discussed later in section 2.7. Due to the resulting spectrum being the average of the orientation of the bulk composition, it is imperative that the sample represent all possible orientations equally. If it is not representative of all orientations equally, the PXD spectrum can be altered due to what is called preferred orientation. Preferred orientation is when the distribution of the powder is non-random. This can result in PXD patterns missing peaks that would otherwise have been present, therefore leading to difficulties in the data analysis such as peak indexing. Another way to prevent preferred orientation on top of homogenous grinding is sample rotation. This provides multiple different particles in different orientations while the scan is occurring.

A powder X-ray diffractometer is composed of three basic parts: an X-ray tube, a sample holder, and an X-ray detector. X-rays are generated in a cathode ray tube by heating the

filament to produce electrons. These electrons are then accelerated toward the sample by applying a voltage. The resulting electrons that are diffracted by the material at different angles are detected producing a spectrum that corresponds to the characteristics of the sample material. X-rays produced are of a specific wavelength that is characteristic to the X-ray tube source element (Cu, Mo, Fe, Co). Herein all reported PXD patterns are the result of Cu radiation with a wavelength of 1.5418Å. X-rays with wavelengths of such magnitudes are required in PXD because they are comparable to the spacing between planes in the crystal lattice. Peaks in a PXD spectra result from constructive interference from waves, with the angle (θ) of incident radiation emerging from planes and with spacing (d) from within the crystal lattice. This is true for constructive interference when the distance is integral multiples of the wavelength λ as described by Braggs' law in Equation 2.1.

$$n\lambda=2d\sin\theta \quad \textbf{Equation 2.1}$$

Determining parameters such as d-spacing, cell parameters, or Miller indices of simple cubic structures can be relatively easy with an adequate PXD spectrum, but can become much more difficult with an increase in complexity of space groups. For instance, determining the d-spacing requires solving Braggs law Equation 2.1. Further calculations to determine a compound's cell parameters (a , b , and c) or Miller indices (h , k , and l) would require Equation 2.2.

$$\frac{1}{d_{hkl}^2}=\frac{h^2}{a^2}+\frac{k^2}{b^2}+\frac{l^2}{c^2} \quad \textbf{Equation 2.2}$$

For compounds that contain a simple cubic cell space group where $a=b=c$, Equation 2.2 can be simplified into Equation 2.3.

$$\frac{1}{d_{hkl}^2} = \frac{h^2 + k^2 + l^2}{a^2} \quad \text{Equation 2.3}$$

The solution of Equations 2.2 or 2.3 can only be determined if the unknown variables are decreased to one. This is accomplished with the knowledge of destructive interference leading to systematic absences of reflections unique to the compound's space group. Continuing with the example of a simple cubic cell, the Miller indices, M , can be determined from Equations 2.4 and 2.5.

$$M^2 = h^2 + k^2 + l^2 \quad \text{Equation 2.4}$$

$$M = \sqrt{h^2 + k^2 + l^2} \quad \text{Equation 2.5}$$

The resulting integer value of M^2 can then be compared to an appropriate table of known reflections of the compound's space group, which in turn provides three values for the sum of the h , k , and l . These indices, i.e. [220], only describe the mathematical result of M . More probable than not, this is the incorrect order of which the indexed values are for a specific peak i.e. [202] or [022]. This does though, correlate to the multiplicity, m_{hkl} , which is indicative to the number of planes that have the same d-spacing. Due to the d-spacing being inversely proportional to $h^2 + k^2 + l^2$, as seen in Equation 2.3, all combinations of h , k , and l with the same values contribute to the observed peak intensity (Equation 2.6).

$$I_{hkl} \propto m_{hkl} F_{hkl}^2 \left[\frac{1 + \cos^2 \theta}{\sin^2 \theta \cos \theta} \right]_{hkl} \quad \text{Equation 2.6}$$

Continuing this example with the hkl value of 220, because M^2 is a result of the square root of h^2 , k^2 , and l^2 (Equation 2.4), there are 12 possible ways to represent this value ([220], [202], [022], [-220], [-2-20]...), therefore 12 is the multiplicity. Though each

Miller indices contributes to each peak's intensity of which it is a subset of its multiplicity, each Miller indice can be its own peak. This becomes more complicated when the resulting M^2 value is 9, therefore the resulting h, k, and l values could be 300 or 221, again most likely not in that specific order. As seen in Equation 2.6, the peak intensity, I_{hkl} , is proportional to the structure factor, F_{hkl} , which is dependent upon how the material scatters incident radiation, calculated using Equation 2.8. In order to do so, the scattering factor, f , must first be determined using the electron density of an atom, $\rho(r)$, using Equation 2.7.

$$f = 4\pi \int_0^\infty \rho(r) \frac{\sin((4\pi/\lambda)\sin\theta)r}{(4\pi/\lambda)\sin\theta} r^2 dr \quad \text{Equation 2.7}$$

$$F_{hkl} = \sum_j f_j e^{2\pi i(hx_j + ky_j + lz_j)} \quad \text{Equation 2.8}$$

For simple cubic cells containing two, or perhaps three elements, all angles of the unit cell are 90° and all cell parameters are equal. These calculations can be easily performed using common software spreadsheets. Increasing the complexity of the space group along with increased variables, such as multiple atoms, different cell parameters, or different unit cell angles all add to the overall complexity of the calculations; therefore, requiring the use of specialized software such as TOPAS or GSAS for the compound's cell parameters, indexing, and crystal structure Rietveld refinement.

Further analysis of PXDs and the use of specialized programs allow for determination of the crystal structure using Rietveld refinements (TOPAS or GSAS), particle size determination can be performed using a program such as PM2K, or long hand calculation using the Scherrer Equation, Equation 2.9.

$$\tau = \frac{K\lambda}{\beta \cos \theta} \quad \text{Equation 2.9}$$

This equation is used, initially solving for K, the shape factor, by using a standard of which τ , the mean size of the ordered crystals is known. β , the line broadening FWHM, θ , the Bragg angle, and λ , the X-ray wavelength are known or determined values from the PXD spectra. LaB_6 powder or Al_2O_3 , corundum, with known crystallite size are common standards. The K value is then input into the Sherrer formula with the spectrum of which crystallite size is of question and τ can be solved. This formula is limited to crystallites in size up to approximately $0.1\mu\text{m}$, which are generally much smaller than compounds synthesized at high temperatures (greater than $500\text{ }^\circ\text{C}$).

Rietveld refinement method uses a least squares approach of refinement to derive a theoretical line profile calculated based on a known crystal structure model. This method is performed until the calculated line overlaps the measured reflections in a PXD spectrum. This method uses height, width, and peak positions in a spectrum to determine the structural characteristics in powder materials.

Powder samples are hand ground until homogenous and fine, poured onto a zero background silicon plate, and flattened with a glass slide. The sample is placed in the powder diffractometer and run from 10° – 65° 2θ with a step size of a 0.02° . The resulting diffraction pattern is matched to corresponding known diffraction patterns from the International Centre for Diffraction Data database. If the resulting pattern is determined to be unknown, further analysis using the Rietveld refinement programs TOPAS or General Structure Analysis System (GSAS) is performed [1].

2.2 Inductively Coupled Plasma Atomic Emission Spectroscopy

Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) furthermore referred to as ICP, is an emission spectroscopy that uses a plasma torch created by argon gas and a radio frequency output coil to determine metal concentrations within a sample. The emission spectrum is the result of the excited atoms or ions emitting electromagnetic radiation with characteristic wavelengths indicative of its corresponding element. The intensity of the emission peak in the spectra corresponds to the concentration of that element within the sample. ICP can be used for the analysis of up to 70 elements at a time while being accurate to elemental analysis in the parts per billion regimes. Limitations to ICP can include inter-elemental interfaces resulting in inaccurate data, and due to the nature of the analysis, loss of sample.

The final sample must be dissolved in a 2-5 % acidic solution, preferably a HNO_3 (Nitric Acid) solution. Therefore, depending on the sample, direct addition into concentrated HNO_3 will result in the dissolution of the metal compound. Due to the stability of some metal oxide compounds, concentrated HNO_3 will not dissolve them. Therefore, a concentrated solution of aqua regia is required. This is a mixture of concentrated HCl (hydrochloric acid) and concentrated HNO_3 (all within solutions of aqua regia are composed of a 1:1 mixture of concentrated HNO_3 : HCl). The resulting solution of dissolved metal oxides is then diluted to the 2-5 % acidic solution for ICP analysis.

Sample calibration must be performed on every element to be analyzed. This is achieved by the appropriated dilution into 2 % HNO_3 of a purchased 1000 parts per million (ppm) standards, using a micropipette to construct a calibration curve of which the analyzed sample concentrations will fall within. Qualitative ICP is performed by the analysis of the molar ratio of multiple metals within the sample, while quantitative ICP requires the accurate mass of the analyzed sample and accurate volume the dissolved sample is diluted to. Qualitative ICP is useful for analysis when determining only the metal-to-metal ratios within a sample. Quantitative ICP provides increased information due to the careful preparation of the metal oxide compound. This allows for the assumption that the remaining unobservable concentration in ppm, via ICP, are the non-metals within the compound; therefore, providing oxygen content of the material without the use of titration.

2.3 Mössbauer Spectroscopy

Mössbauer spectroscopy is used to probe the oxidation states and local environments of metals. It is most commonly used for iron in mineralogy or geophysics. It is significant in solid state chemistry for investigating the oxidation state of iron (Fe^0 , Fe^{2+} , Fe^{3+} or Fe^{4+}) and exploring the local environment of iron's coordination polyhedron (trigonal, tetrahedral, or octahedral). Mössbauer spectroscopy is an extremely useful characterization tool for explaining observed properties of different Mössbauer active compounds.

Mössbauer spectroscopy uses ^{57}Fe , the decay product of ^{57}Co , and an unstable isotope of iron, which in turn emits different types of energy including γ -rays. These energies can result in a number of different possible processes when they collide with the sample (the absorber), such as the emission of core shell electrons, which are not of interest in Mössbauer spectroscopy. If the emitted γ -rays were to collide with the nucleus of the absorber iron, and have the correct energy (14.4 keV), it would move the nucleus of iron. The nucleus must then recoil with equal and opposite energy, resulting in an emitted γ -ray with the as mentioned 14.4 keV recoil energy. This can be seen in Figure 2.1.

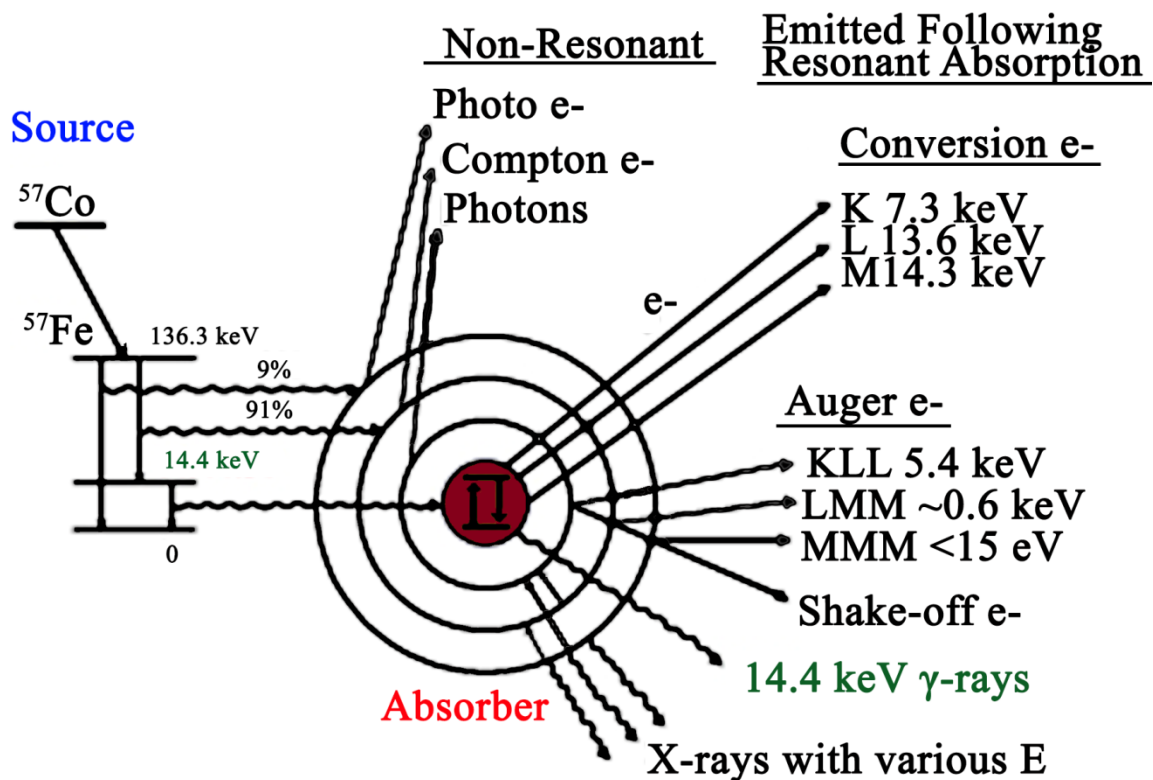


Figure 2.1 Mössbauer schematic illustrating the decomposition of ^{57}Co into ^{57}Fe resulting in the emission of energy into an absorber, in this case an iron source, at which point the absorber emits non-resonant, resonant, conversion, Auger electrons, and x-rays with other various energies.

The units of energy for Mössbauer spectroscopy are in mm/sec due to the set up of the spectrometer. The source for conventional spectrometers is mounted on a drive that oscillates the source toward and away from the absorber, therefore increasing the energy of the emitted photons. For sources such as a synchrotron, the absorber is oscillated with respect to the source.

In order to understand the resulting spectrum of Mössbauer spectroscopy, three important parameters must be discussed: the isomer shift, quadrupole splitting, and the magnetic hyperfine splitting. The combination of these three parameters is used to determine the oxidation state along with the local iron polyhedron environment. Figure 2.2 illustrates the observed results of isomer shift, quadrupole splitting, and magnetic hyperfine splitting in a Mössbauer spectrum.

Isomer shift is the comparison of two different nuclear isomeric states in two different physical or chemical environments due to the combined effect of the recoil-free transition between the two states. This difference is observed on the Mössbauer spectrum by the shift from the 0 mm/sec point. The general trend when considering two iron atoms within the same local environment is: as the isomer shift increases in positive value the oxidation state of iron is less.

Quadrupole splitting is the result of the nuclei having a non-radially-symmetric shape and is in the presences of an external electric field gradient. This results in the splitting of what would normally be a singlet peak in the Mössbauer spectrum into a doublet. The separation between the doublet peaks can be measured to provide further information on the chemical environment of the nuclei.

Magnetic hyperfine splitting (also referred to as electronic field gradient or EFG), is the result of the energy of the nuclear magnetic dipole moment of the magnetic field

generated by the electrons. This is observed in a Mössbauer spectrum by the further splitting of a singlet or doublet into a sextet from the resulting magnetic field.

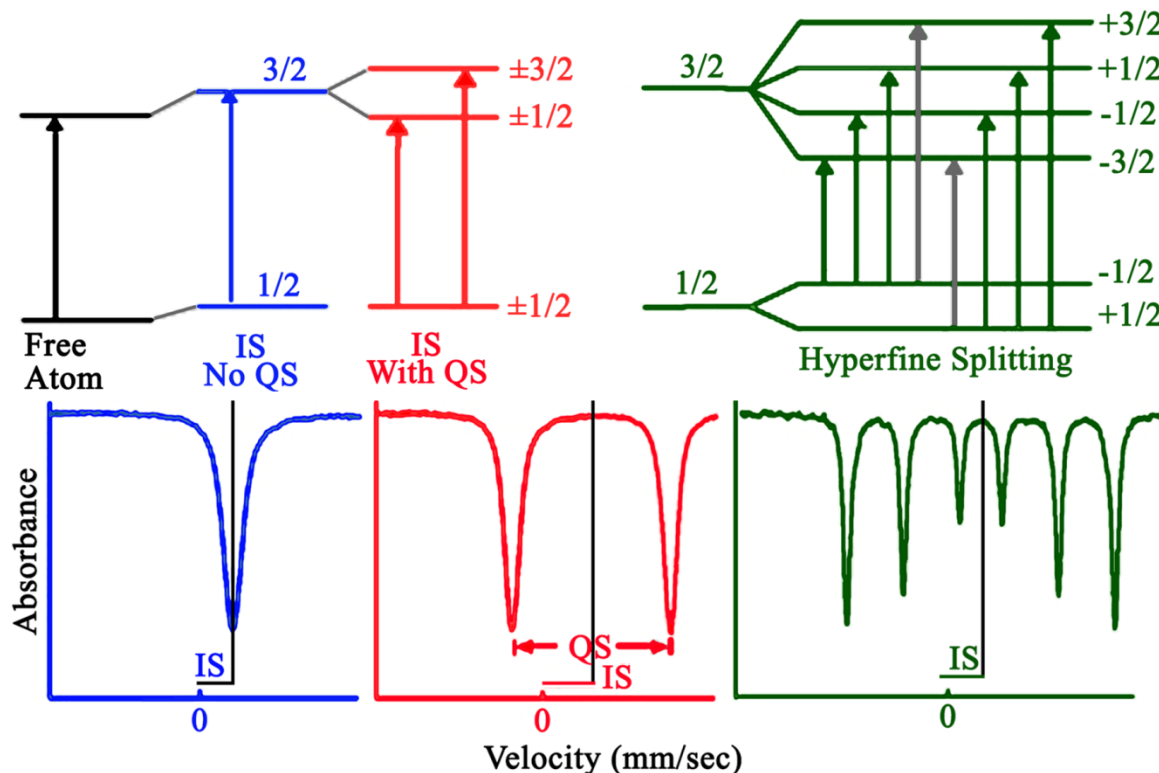


Figure 2.2 Schematic of Mössbauer isomer shift, quadrupole splitting, and hyperfine splitting illustrating the effect each has upon the Mössbauer spectrum [2,3].

The following procedure takes place inside an inert, dry nitrogen glove box to prevent any reaction that may occur between the sample and oxygen or water from air. The prepared powder sample of interest is spread in a homogenous fashion on the sticky side of a piece of Kapton tape, with a concentration of at least 10 mg of iron per square centimeter of tape. A second piece of Kapton tape is then placed sticky side to sample to "sandwich" the sample between the two pieces of tape. The now sandwiched tape sample

is cut into a square with sides of approximate length of one centimeter. Next, all sides of the square are taped to seal the edges from ambient conditions when placed in the Mössbauer spectrometer. The sample is placed inside a small vial and parafilm wrapped, then placed in a larger vial and parafilm wrapped. The large vial is finally placed inside a zip lock bag for transportation to the measuring facility.

2.4 Electrochemistry

Electrochemical characterization of potential cathode materials were performed in an argon filled glove box due to the reactivity of the anode (lithium metal) with nitrogen to form Li_3N . The cells were assembled in a split test cell. The cells used a lithium disc as an anode and counter electrode. A 1 M solution of LiPF_6 in ethylene carbonate (EC), dimethyl carbonate (DMC), and diethyl carbonate (DEC) (EC/DMC/DEC = 1:1:1 by volume) was used as the electrolyte. The anode/cathode separator was a 25 μm Microporous Monolayer Membrane. The cathode was a 19 mm disc of slurry prepared by ball milling 75% by weight active material, 10 % by weight PTFE, and 15 % by weight Super C65 carbon in 1-methyl-2-pyrrolidone. A 30 micrometers thick slurry layer was deposited on aluminum foil using a doctor-blade method. The layer was then vacuum dried and pressed for increased particle-particle connectivity. Cyclic voltammetry were initially run from 1.5 V to 5.0 V to determine the oxidation and reduction potentials of the active material. Further analysis of the active material was then performed with a narrower window and slower scan rate.

2.5 Thermogravimetric Analysis and Differential Scanning Calorimetry

Thermogravimetric analysis (TGA) is the analysis of materials in which the physical properties are measured as a function of increasing temperature at a constant rate in different gases. Differential scanning calorimetry (DSC) is the analysis for which the difference for heat required to increase the temperature of a sample function of increasing temperature at a constant rate. When coupled, TGA-DSC provides information in different gasses about mass loss or gain in oxidizing, reducing, or inert atmospheres. This information can explain exothermic or endothermic reactions, the temperature at which point a phase transition occurs, or basic information such as the temperature required to dehydrate a sample without decomposition.

2.6 Scanning Electron Microscopy

Scanning electron microscopy (SEM) uses high-speed electrons to study surface morphology and particle size in the sub micrometer regime as low as about 10 nm into the micro-regime. Morphology of the micro sized particle can provide insight into characteristics such as crystal growth along a particular axis. This may provide insight into possible observations such as preferred orientation within the PXD or intercalation or deintercalation of the electrochemical results.

Elemental analysis within both SEM and TEM is performed using energy measurements of X-rays produced by elements in the sample from the electron beam of the instrument called energy-dispersive spectroscopy (EDS). This is accomplished by evaluating the critical excitation energy difference between different elements. The differences in the critical excitation energy within the analytical spatial resolution of the whole sample are measured by the loss of energy over the distance the X-rays travel into the sample. Comparing two elements of different critical excitation energies, the greater distance the incident electron travels, the more energy is lost due to scattering. Therefore, an element with a low excitation energy would produce X-rays from a greater distance within the sample as compared to an element with a greater excitation energy. The X-rays from within the sample lead to the production of characteristic X-rays of the specific elements the sample is composed of. Each element has a fingerprint per say, a unique energy created by the filling of an inner orbital shell electron by an electron from a shell of higher energy. This specific energy difference is emitted as detectable X-rays for most elements. An element often produces many types of X-rays because multiple beam electrons are striking the sample. Each electron may differ in the interaction with the sample leading to the emission of different X-ray wavelengths produced from the relaxation of different sub-shell electrons. These different electron relaxations are named based on which shell the vacancy was created in (K, L, M, N), and the number of shells by which the electron jumped to fill the vacancy (α , β , γ ...). A downfall of EDS is the inability to detect lighter elements with lower critical excitation energies, due to the beryllium window absorbing the excitation energies of about 1 keV of energy. Peak

overlap in the spectrum is another disadvantage of EDS; therefore, analysis of compounds with multiple elements may cause peak overlap resulting in difficulties for quantitative elemental analysis. EDS has several advantages over other elemental determining methods for SEM, such as wavelength-dispersive spectroscopy (WDS). WDS does not exhibit peak overlap as does EDS, but EDS is generally the preferred elemental analysis spectroscopy in SEM and TEM due to its ability to analyze more than two elements at a time unlike WDS. Analysis software can provide relatively accurate quantitative analysis even in the instance of peak overlap in an EDS spectrum.

Backscattering electron imaging (BSE) uses a different source of excitation radiation. This radiation is created by an elastic interaction of beam electrons with the nuclei of the atom. Heavy atoms have a larger atomic number, therefore, scatter stronger than lighter elements with smaller atomic numbers. Due to this fact, backscattering images can provide an accurate elemental composition and an image illustrating the distribution of elements within the sample. This is increasingly important when determining the metal ratio and composition of new compounds or determining phase composition of impurities or element deficient compounds [4–7].

Powder samples are spread on a sticky carbon tab on an aluminum stub with the excess powder removed using compressed air. This is performed to prevent any damage or contamination by loose particles ejecting from the stub into the detectors, vacuum system, or any other parts of the SEM. Depending on the electrical conductivity of the sample, it can then be left alone or coated with carbon, gold, or osmium with appropriate

sputter coaters to increase the sample's electrical conductivity for better resolution. The sample is then inserted into the instrument for analysis.

2.7 Transmission Electron Microscopy

Transmission electron microscopy (TEM) uses high-speed electrons to study particle sizes or layer thickness of nano-materials or thin films. TEM was employed on prepared nano-crystalline samples to determine morphology, particle size, and potential core shell structures. TEM was used rather than SEM due to the magnification ability of over 500,000 times providing resolution of particles with sizes as low as 0.2 nm.

TEM is useful to determine particle size and morphology of nano-crystals, however, high resolution TEM (HRTEM) provides the ability to probe further into the crystalline nano-particles. HRTEM permits an increased accuracy in particle size measurements and greater detailed images of the sample. HRTEM also grants the ability to observe the lattice fringes of the nano-crystalline structure. The lattice fringe is the observed plane within the nano-crystal that correlates to the Miller indice observed in the PXD. Therefore measuring the distance between two lines of the observed lattice fringe provides the ability to determine which plane the nano-crystal is orientated. Furthermore, single crystal diffraction of nano-crystals is performed using Fourier transforms of HRTEM resulting in electron diffraction spots.

In order to discuss single crystal diffraction and better understand some aspects of PXD (as mentioned in 2.1), the topic of reciprocal lattices must be discussed. First, a few mathematical definitions must be defined and worked through. Initially considering planewave front vectors in terms of k , where the initial wavefront, k_I , at a specific wavelength, λ , is scattered by a plane of atoms resulting in a diffracted wavefront, k_D , that scatters at an angle of 2θ . With this, we can determine the difference in k_I and k_D as seen in Equation 2.9, where K is the change in the vector due to diffraction as illustrated in Figure 2.3.

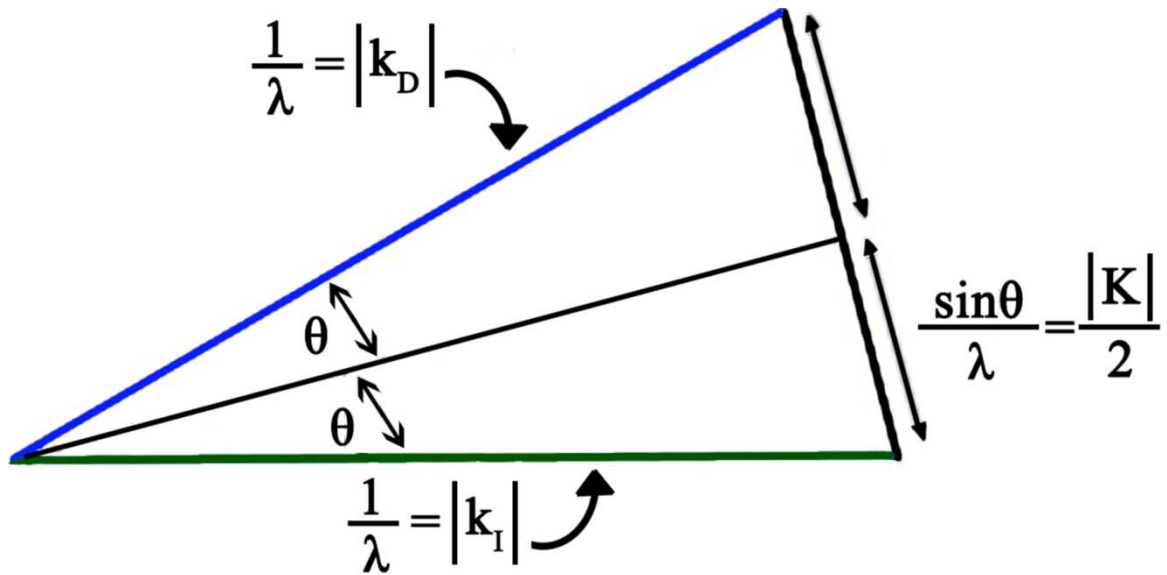


Figure 2.3 The relationship between k_I , k_D , K , θ , and λ . The initial wavefront (green), the top of the triangular shape is the point at which the wavefront is diffracted by the plane of atoms, resulting in the diffracted wavefront (blue), and the change in the vector due to diffraction (black) is K .

$$K = k_D - k_I$$

Equation 2.10

If the energy of the electron is unchanged during the diffraction, therefore is elastic so we can relate these wavefront vectors as seen in Equation 2.11.

$$|k_I|=|k_D|=\frac{1}{\lambda}=|K| \quad \text{Equation 2.11}$$

Furthermore using trigonometry to write an expression in terms of θ ,

$$\sin \theta = \frac{|K|/2}{|k_I|} \quad \text{Equation 2.12}$$

then algebraically rearranging, Equation 2.13 is observed.

$$|K| = \frac{2 \sin \theta}{\lambda} \quad \text{Equation 2.13}$$

In relating Equation 2.13 to Braggs' law, Equation 2.1, these conditions must be met: the angle θ must equal the Bragg angle and the integer value of n is one. The equations can be combined into Equation 2.14, where the vector K at the Bragg angle is K_B .

$$|K_B| = \frac{1}{d} \quad \text{Equation 2.14}$$

Under the conditions where vector K is at the Bragg angle, the magnitude of vector K has a special value, therefore is defined by g . Equation 2.15 is also very important because it represents the Laue conditions for constructive interference. The Laue diffraction will later be discussed.

$$K_B = g \quad \text{Equation 2.15}$$

Now that it has been established that K is reciprocally related to d , and K at the Bragg angle is an important value, of which further discussion will come later, it is important that real space lattice and reciprocal space lattice vectors be discussed. Here a lattice in real space, r_n , will be defined as follows;

$$r_n = n_1 a + n_2 b + n_3 c \quad \text{Equation 2.16}$$

where the vectors a , b , and c are unit-cell translations in real space and n_1 , n_2 , and n_3 are integers. Similarly the reciprocal-lattice vector, r^* , can be defined as:

$$r_n = m_1 a^* + m_2 b^* + m_3 c^* \quad \text{Equation 2.17}$$

where in this case the vectors a^* , b^* , and c^* are unit-cell translations in reciprocal space and m_1 , m_2 , and m_3 , are integers. The direction of the vectors can be seen using the dot product of the real space vectors with the reciprocal space vectors as seen in Equation 2.16, where a^* is normal to both vectors b and c .

$$a^* \cdot b = a^* \cdot c = b^* \cdot c = b^* \cdot a = c^* \cdot a = c^* \cdot b = 0 \quad \text{Equation 2.18}$$

The length of these vectors can be related as follows:

$$a^* \cdot a = 1; b^* \cdot b = 1; c^* \cdot c = 1 \quad \text{Equation 2.19}$$

Here it is seen that the dot product of the reciprocal unit-cell length on the real space unit-cell length is defined to be one, consequently, providing the scale or dimension of the reciprocal lattice. Furthermore, this relationship provides insight into the dimensionality of the reciprocal lattice, in that if a , b , and c are all large the corresponding reciprocal lattice vectors will be small.

Continuing discussion on the concept of g , the K vector at the Bragg angle, it can be established that any vector in reciprocal space can be defined as seen in Equation 2.20.

$$K = \xi a^* + \eta b^* + \zeta c^* \quad \text{Equation 2.20}$$

Here ξ , η , and ζ are three numbers, which do not have to be integers. The g_{hkl} vector, similarly written to the K vector, is an important vector in reciprocal lattice vectors because it provides the definition of h , k , and l , which are integer values that together define a plane (hkl). Due to h , k , and l being in reciprocal space, the definition of the

plane (hkl) is that it cuts the a, b, and c axes at 1/h, 1/k, and 1/l respectively. With this notation the vector BC, can also be written as c/l-b/k.

$$\mathbf{g}_{hkl} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* \quad \text{Equation 2.21}$$

Acquiring the dot product of $\mathbf{g}$ and $\mathbf{r}_n$ by using Equations 2.16 and 2.20, an integer value, N , is always achieved, therefore Equation 2.21 describes similarly, that in order to have Laue (or Bragg) diffraction, certain conditions must be satisfied. In other words, from Equation 2.20, ξ , η , and ζ must be integer values and the integer values are h , k , and l in order for Laue diffraction to occur.

$$\mathbf{K} \cdot \mathbf{r}_n = N \quad \text{Equation 2.22}$$

Setting $\mathbf{r}_n$ to three unit vectors, establishes the following relationships, which are the core principle of Laue diffraction:

$$\mathbf{K} \cdot \mathbf{a} = h \quad \text{Equation 2.23}$$

$$\mathbf{K} \cdot \mathbf{b} = k \quad \text{Equation 2.24}$$

$$\mathbf{K} \cdot \mathbf{c} = l \quad \text{Equation 2.25}$$

Knowledge of reciprocal space is required to understand Ewald's sphere, which is observed in single crystal diffraction in TEM. When the Bragg (or Laue) diffraction condition is satisfied, the scattering vector is equal to the reciprocal lattice vector, as previously described. Therefore, diffraction will occur only for the reciprocal lattice points that lie on the surface of the Ewald sphere. If the diffraction pattern is aligned perfectly, at which the Bragg condition is satisfied, where no spots will be observed, tilting of the sample will result in the appearance of diffraction spots. Continued tilting of

the sample down different planes of the sample will result in the appearance and disappearance of diffraction spots that cut through different Laue zones. [4–7]

Powder samples are dispersed in a solvent of choice in a test tube. The solvents must be completely evaporated prior to analysis in the TEM, therefore methanol or ethanol is chosen due to their volatilities. The dispersed sample is then sonicated for 15 minutes to reduce agglomerations. A drop of the resulting solution is then placed on a TEM grid and allowed to dry and be inserted into the instrument for analysis.

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Chapter 3

Synthetic Methods

3.1 Pechini (Sol-Gel)

The Pechini method, also referred to as the polymerisable complex method liquid mix technique, or sol-gel, was first proposed in the late 1960's as a technique to deposit different elements in the production of capacitors. It was later determined useful as a synthetic technique for the synthesis of multicomponent metal containing materials. The method relies on the mixing of ions in solution then controlled temperature increase to transform the solution into a gelatin-like polymer. Increasing the temperature furthermore removes the matrix resulting in homogenously mixed metal oxide precursor.

The sol-gel process involves the addition of stoichiometric ratios of metal salts or metal oxides with citric acid, ethylene glycol, nitric acid, and water. The citric acid is added to form citric complexes that upon heating to above 100 °C form the polymer citrate gel with the ethylene glycol. The addition of nitric acid is to increase the dissolution of the metal oxides within the solution. Continued heating above 400 °C removes the matrix leading to the formation of a uniform metal oxide and/or metal carbonate mixture to be further annealed under appropriate conditions to acquire the desired material.

This method has been widely used for the synthesis of materials with many different properties such as superconductivity, dielectrics, catalyst, etc. Nanocrystalline powders have also been synthesized using the Pechini method for different purposes such as dye-sensitized solar cells (DSSCs) and water splitting reactions for hydrogen production. [1–6]

3.2 Solid-state (Ceramic)

Solid-state reaction, also referred to as ceramic method, is generally the standard technique of synthesis in material sciences. Limitations are due to slow diffusion in solids as compared to liquid/liquid chemistry. High temperatures are required to increase the rate of diffusion within the reaction. The ceramic method is generally the easiest way to synthesize stable, solid-state materials directly from the metals, metal oxides, or metal oxoanion precursors. To increase the rate of diffusion, it is preferable the starting materials are homogeneously mixed prior to sintering. This provides a decreased path length of atomic diffusion for nucleation sites of the desired material to form. This type of method can result in incomplete reactions if the starting reagents are inhomogeneously mixed. After initial sintering, the material is generally reground and reannealed. This allows the nucleation sites to react with unreacted starting materials resulting in increased purity of the final product. This method has been given the nickname "the heat and beat method" because of the firing and grinding repetition that is sometimes needed to acquire a pure product. High temperature synthesis can also lead to the loss of volatile metals such as lithium or sodium; therefore, stoichiometric compensation is taken into consideration in the initial reactant addition. [7]

3.3 Reduction

Reduction of complex metal oxides, if carefully performed, can result in the formation of meta-stable complex metal oxides that may contain properties otherwise not seen in the

non-reduced phase. There are multiple reduction types in the material science synthesis like solvothermal reduction, which involves the use of metal hydrides such as sodium hydride (NaH) and a solvent inside a high-pressure autoclave with the temperature of the reaction elevated to a desired temperature. An approach resembling a solid-state synthesis reaction involves the mixing and grinding of metal hydrides with the complex metal oxide. The mixture is then heated to evolve hydrogen gas that can be involved in the reduction, or in the formation of the hydrogen gas. The resulting metal acts as a reducing agent toward the complex metal oxide. A third reduction type includes the flow of hydrogen gas at an elevated temperature to form water and the reduced complex metal oxide. All reduction of complex metal oxides discussed within will include only the third reduction process.

Reduction using 100% hydrogen gas was performed with extensive care due to the high flammability of hydrogen and the fact that hydrogen gas is the only gas that, upon expansion, is exothermic. For these reasons, all reactions with hydrogen gas were performed in a tube furnace using a fused silica tube rather than the typical alumina tube, due to the porosity of the alumina tube and the elevated temperature at which the reaction takes place. All reactions using hydrogen gas also took place inside a fume hood rather than out in the open for extra safety. The hydrogen gas was flowed at a rate of approximately 1 ml per second through the reaction tube into an oil bubbler. Final compounds of reduction are moisture sensitive; therefore, the hydrogen gas was also flowed over glass wool coated with P_2O_5 to ensure the gas was dry prior to entering the reaction tube. P_2O_5 was also placed at the end of the furnace to collect water that was

evolved from the reaction to ensure diffusion of water back into the reaction tube did not occur. The sample was placed in the tube as a non-pelleted powder and spread in an alumina boat in a thin layer to increase surface exposure to the reactive gas. Intermittent grindings inside a glove box were performed for homogenous sample exposure to the reactive gas for optimal purity of the reduced phase.

3.4 Partial Oxygen Pressure Regulation

The ceramic method provides the ability to control the atmosphere within reaction by using a reactive gas that provides different conditions to acquire desired products. Oxidizing atmospheres such as oxygen, inert atmospheres such as nitrogen or argon gas, or reducing atmospheres such as hydrogen gas, are all common gasses used in solid-state reactions providing versatility in the synthesis process of new compounds. In the synthesis of compounds, generally only one valence electronic state is available within the transition metal of the complex compound. Therefore, synthesis of bulk compounds with multiple oxidation states for the transition metals can only be achieved by increasing the temperature of the reaction; thus, decreasing the oxygen reactivity and forming oxygen deficient phases. In these circumstances, though common, the transition metal is only partially divalent due to the oxygen deficiencies within the compound only resulting in a small percentage while still maintaining the overall structure. Single crystals on the other hand, can be synthesized regularly with multiple oxidation states of the transition metal. This usually occurs within vacuum-sealed ampoules composed of different transition metals such as iron, copper, or platinum, or the ampoule can be non-metallic

such as glass or quartz. These different types of ampoules, though under vacuum, can provide different types of oxidizing environments, like the metal's reduction potentials in electrochemistry. If under the correct heating and cooling conditions, this can result in single crystal formation of compounds that can have metals with multiple oxidation states. As mentioned, synthesizing bulk materials with transition metals in multiple oxidation states of significant magnitude cannot be performed using normal reactive gasses such as oxygen or hydrogen. Therefore, the use of an oxygen buffer system to control the oxygen partial pressure within a reaction vessel to synthesize complex compounds, to this point, is the only known reaction system to be successful.

Controlled oxygen partial pressure reactions were performed using a two zone furnace; one zone to control the temperature of a metal/metal oxide buffer such as Cu/Cu₂O (copper/copper(I)oxide) or Ni/NiO (nickel/nickel(II) oxide) and the other zone to control the temperature of the sample. Nitrogen gas was flowed over glass wool covered with P₂O₅ then flowed through the reaction tube with P₂O₅ at both ends to collect any water that may have been released due to the increase in temperature during the reaction and absorbed by the powders. The temperature of the sample for all reactions is kept constant, while the temperature of the metal/metal oxide buffer is changed to appropriate temperatures for the desired partial oxygen pressure characteristic of the specific buffer. The reaction vessel is purged for at least one hour with nitrogen gas, the flow is then stopped, and valve 1 as seen in Figure 4.2, is closed. The two zones of the furnace are then initiated simultaneously with an identical ramp time, therefore, each zone reaches the desired temperatures at the same time. At the time the temperatures reach their

desired values, valve 2 is closed (Figure 4.2). The reaction is allowed to proceed for a minimum of 48 hours, but can go longer due to the equilibrium state at which the system is in. The reaction vessel is quenched to room temperature to prevent the buffer from decreasing the partial oxygen pressure in the reaction vessel for a prolonged period at an increased temperature therefore altering the final state the product. The sample is then placed in a vial and taken into an inert glove box for further analysis.

3.5 Moisture and Oxygen Sensitive Techniques

Synthesis of metal-stable, oxygen sensitive, or moisture sensitive compounds requires an increased measure of care to prevent decomposition, uncontrolled, or unknown reactions from occurring that alter the properties of the final product. Properties of moisture sensitive samples can be altered. This can be seen in the example of $\text{Na}_{0.35}\text{CoO}_2 \cdot y\text{H}_2\text{O}$, where in the case of $y=1.3$, the product is superconducting whereas the anhydrous product or the further water-intercalated products do not exhibit such properties. The discovery of the superconducting material was somewhat serendipitous due to the high relative humidity in the area where the magnetic properties were measured, which resulted in the intercalation of water molecules into the material. The original material did not contain the intercalated water; thus, the exposure to the humid atmosphere resulted in the final product's properties. Further structure refinement provided insight on the water intercalation. Without the further analysis that was performed on the material, incorrect data could have easily been presented, if the researcher assumed that, in fact, the material they sent out for measurements maintained its original composition. To

prevent any unwanted water intercalation, oxidation, or decomposition, samples can be prepared in inert nitrogen or argon glove boxes.

All samples that are prepared are initially assumed to be moisture sensitive until further analysis determines otherwise. This assumption is made for all sodium and lithium containing compounds due to the general hygroscopic nature of most compounds that contain these elements. This assumption is also made for meta-stable compounds synthesized through solid-state reduction. To determine whether the sample is in fact moisture sensitive, the sample can be washed in water then analyzed using PXD and compared with previous PXD of the non-water washed phase. Precautions for sample exposure to ambient conditions are minimized as much as possible. In the process of solid-state reduction of Perovskite structure to infinite-layer structure, the fused silica tube was made to fit within the antechamber of the nitrogen glove box, therefore, the entire reaction vessel can be inserted into the glove box without any exposure. In the case of α - and β - NaFe_2O_3 , due to the increased size of the reaction vessel to fit in a two-zone furnace, the transfer of the entire vessel cannot occur. The sample is removed from the reaction vessel, placed in a vial, immediately placed inside the glove box antechamber, and evacuated. Removing the sample from the reaction vessel is performed under a nitrogen gas flow creating an inert "blanket" over the sample when possible.

Materials that are synthesized from moisture sensitive precursors, such as NaFe_2O_3 with the moisture sensitive precursor α - NaFeO_2 , or the preparation of α - NaFeO_2 which is synthesized from the hygroscopic compound NaOH and non-hygroscopic compound

Fe₂O₃, are all prepared in a glove box. The compounds are ground, mixed, and pelleted, if required, inside the glove box then transferred to an appropriate reaction vessel.

3.6 Chemical oxidation and reduction

Studying the properties of new materials can sometimes lead to further questions, such as the effects of lithium intercalation and deintercalation on the overall structural integrity of the new material. To answer such a question, a few different processes can occur; either in situ PXD and electrochemical characterization, or oxidation via chemical lithium intercalation and reduction via chemical lithium deintercalation. In situ PXD and electrochemical characterization provides insight on the structural properties directly as the cyclic voltammogram is produced. The downfall is the expensive set up required to do such measurements. Generally, these measurements are performed at national laboratories. Oxidation and reduction via chemical lithium intercalation and deintercalation can provide the compound with deficient or inserted lithium from or into the structure respectively; therefore allowing PXD to be performed on the samples providing information on the structure and the effect of the inserted or removed lithium.

Chemical lithium intercalation was performed in a nitrogen glove box using 1 M n-butyllithium in hexanes. The ground powder sample was dispersed by stirring in pentane and the n-butyllithium solution was added drop wise until the correct volume for the required molar ratio was achieved. The mixture was stirred for at least 48 hours then

washed with pentane and filtered. The resulting powder was then stored in an inert glove box for further analysis.

Chemical lithium deintercalation was performed in a nitrogen glove bag due to the oxidizing nature of the compounds used and the metal surroundings inside a glove box. Bromine (Br_2), iodine (I_2), nitrosyl tetrafluoroborate (NOBF_4), or nitrosonium tetrafluoroborate (NO_2BF_4) are all oxidizing reagents with different reduction potentials providing the ability to deintercalate different amounts of lithium from a compound. The sample is dispersed and stirred in acetonitrile (CH_3CN) if the reaction was with NOBF_4 or NO_2BF_4 , or pentane if the reaction was with bromine or iodine. The slow addition of the dilute oxidizing agent was then performed until the required volume to reach the desired molar ratio was achieved. The mixture was then stirred for at least 48 hours or until the reaction had come to completion by visual indication. Oxidation using bromine and iodine, upon completion, would result in the color change from purple to clear indicating the bromine or iodine had reacted to produce the bromide or iodide salt. The color change provided information that the reaction has finished, which became useful for some reactions that only require as little as 10 hours to become complete. NOBF_4 and NO_2BF_4 are both colorless; therefore the reaction cannot be visibly determined to be complete, so controlled reaction times were performed. [8–12]

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Chapter 4

Synthesis of NaFe_2O_3 Using Partial Oxygen Pressure Regulation Method

4.1 Introduction

Crystal structures of a large class of transition metal oxides AMO_2 (A = alkali metal, M = 3d metal) can be described as an ordered rock-salt lattice with cubic close-packed oxygen layers where A and M occupy the octahedral sites of alternating layers. These structures contain MO_2 layers composed of face-shared MO_6 octahedra (CdI_2 -type layers) separated by A^+ ions. $\alpha\text{-NaFeO}_2$ is the prototype compound, which lends its name to the structural type.

Compounds with the $\alpha\text{-NaFeO}_2$ structure are important from both fundamental and technological points of view. NaMO_2 phases demonstrate a large variety of physical properties: frustrated magnetism in NaTiO_2 [1], two successive orbital ordering transitions in NaVO_2 [2], broad fluctuating cross-over regimes in NaCrO_2 [3, 4], strongly coupled antiferromagnetic chains in NaMnO_2 [5], two antiferromagnetic structures in $\alpha\text{-NaFeO}_2$ [6], and a nonmagnetic insulator state in NaCoO_2 [7, 8]. From the technological point of view, LiCoO_2 is an important cathode material for Li-ion batteries [9, 10] and Na_xCoO_2 is a candidate for thermoelectric applications [11-13].

Knowledge on AM_2O_3 rock-salt related compounds with layered A and M ordering is very limited. The only known example is $\beta\text{-NaFe}_2\text{O}_3$; its crystal structure consists of double rock-salt layers of octahedrally coordinated iron (Fe_2O_3 blocks) separated by Na ions (Figure 4.1) [14-17]. Generally speaking, 3d metal compounds with $\beta\text{-NaFe}_2\text{O}_3$ structures are expected to demonstrate different properties than their $\alpha\text{-NaFeO}_2$ type

counterparts due to the difference in M oxidation states as well as in the dimensionality of the 3d metal - oxygen blocks. At the same time, synthesis of the mixed valent $AM_2^{2.5+}O_3$ compounds is expected to require delicate control of the preparation conditions. In the case of β - NaFe_2O_3 , the situation is complicated by the existence of an α - NaFe_2O_3 polymorph. Similarly to the β phase, the crystal structure of α - NaFe_2O_3 contains Fe_2O_3 blocks; however, these blocks are separated by two layers of octahedrally coordinated cations with $(1/3 \text{ Fe} + 2/3 \text{ Na})$ in this shared crystallographic position (Figure 4.1).

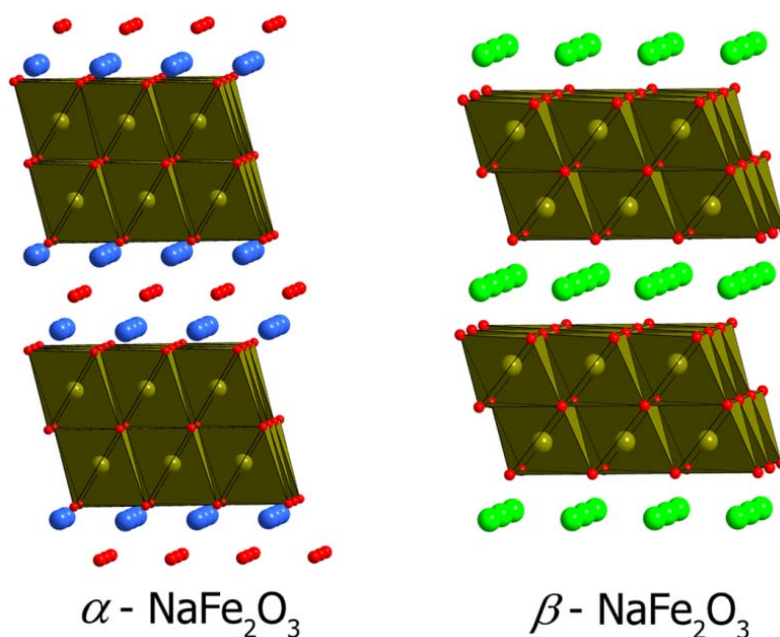


Figure 4.1 Structure models of α - and β - NaFe_2O_3 . The FeO_6 octahedra are highlighted. For α - NaFe_2O_3 , atoms in the shared Na/Fe position are shown as large blue spheres and small red balls represent O ions. For β - NaFe_2O_3 , large green spheres correspond to Na ions.

Synthesis methods and crystal structures of α - and β - NaFe_2O_3 were reported in the 1970's by El Balkhi et al. [14, 15]. For synthesis of the NaFe_2O_3 polymorphs, mixtures of NaFeO_2 , Fe_2O_3 , and Fe were sealed in ampoules and annealed at 1000 °C for 48 hours. The α and β phases were prepared in sealed steel and Cu ampoules respectively. Fe powder was also present in a separate tube inside the ampoule for the preparation of α - NaFe_2O_3 .

It needs to be emphasized that the experimental technique used relies on kinetic factors rather than on equilibrium conditions. At high temperatures, metal oxides generate some oxygen pressure. Materials of the ampoules as well as Fe powder reacted with O_2 , decreasing the partial O_2 pressure ($p\text{O}_2$), thus stabilizing NaFe_2O_3 . At the same time, Fe metal from the ampoule walls cannot be in equilibrium with a Fe^{3+} containing phase, i.e. with NaFe_2O_3 ; therefore, reactions for extended times would result in further ampoule wall oxidation to FeO as well as NaFe_2O_3 decomposition to Na doped wüstite (FeO). This consideration is in agreement with a study of the equilibrium oxygen pressure in a broad composition range in the Fe–Na–O system by measurements in electrochemical cells with an oxygen-ion-conducting solid electrolyte [18].

A synthetic approach relying on equilibrium conditions is needed for the systematic search for AM_2O_3 compounds with different 3d metals.

4.2 Synthesis of NaFe_2O_3 via controlled oxygen pressure.

The syntheses of α - and β - NaFe_2O_3 were carried out in closed silica tubes under controlled partial oxygen pressure. Stoichiometric mixtures of α - NaFeO_2 , α - Fe_2O_3 (99.5%, Alfa Aesar) and Fe metal ($\geq 99.9\%$, Sigma Aldrich) were mixed, pressed into pellets, placed in alumina boats, and closed in quartz tubes together with a second boat containing an oxygen buffer (oxygen getter) mixture. A split-open two-zone furnace was used to control the temperature of both the sample and getter mixtures independently. All samples were annealed at 850 °C for 48–72 hours. The temperature of the getter mixtures was varied between 350 °C and 900 °C in 29 different experiments, allowing for the precise control of $p\text{O}_2$ in the system. After annealing, all quartz tubes were quenched to ambient temperature in air. The syntheses of all samples and subsequent X-ray diffraction measurements were successfully reproduced. It was reported that NaFe_2O_3 slowly hydrolyzes in air [14]; therefore, all operations with initial mixtures and final compounds were performed under nitrogen.

α - NaFeO_2 was synthesized by the reaction of α - Fe_2O_3 (99.5%, Alfa Aesar) with a 20% stoichiometric excess of NaOH (98.8%, Mallinckrodt Chemicals) under O_2 flow at 500 °C for 48 hours. Excess NaOH was removed by washing with anhydrous methanol in a nitrogen-filled glove box.

The samples were characterized by Powder X-ray diffraction (PXD) on a Bruker D8 Advanced with DAVINCI design diffractometer using Cu K_α radiation. The patterns

were recorded at room temperature with a step size of 0.02° (2θ) on a zero background sample holder.

High resolution synchrotron powder X-ray diffraction data were collected using beamline 11-BM at the Advanced Photon Source, Argonne National Laboratory with an average wavelength $\lambda=0.37382$ Å. Discrete detectors covering an angular range from -6 to 16° 2θ were scanned over a 34° 2θ range, with data points collected every 0.001° 2θ and a scan speed of $0.01^\circ/\text{s}$. A three-axis translation stage holds the sample mounting and allows it to be spun, typically at ~ 5400 RPM. Rietveld refinement [19] of SPXD data was performed with the GSAS [20] program and EXPGUI [21] interface. The profile function 4, which contains pseudo-Voigt, asymmetry, and microstrain broadening components, was employed for all phases. The DRAWxtl program was employed to prepare the difference Fourier map, (Figure 4.9) [22].

Elemental composition was determined by inductively coupled plasma (ICP) spectroscopy using a Vista-MPX CCD Simultaneous ICP-OES instrument (Varian Inc.). Oxygen stoichiometry was determined using triplicate iodometric titrations. KI (ACS Grade, Jade Scientific), $\text{K}_2\text{S}_2\text{O}_3$ ($\geq 95\%$, Sigma Aldrich), KIO_3 (ACS Grade, Columbus Chemical), and Soluble Starch (ACS Grade, Columbus Chemical) were used in these titrations [23].

The initial attempt at the synthesis of NaFe_2O_3 at 850°C under N_2 flow resulted in a mixture of NaFeO_2 and Fe_3O_4 . In both compounds, the average iron oxidation state was above that in $\text{AM}_2^{2.5+}\text{O}_3$. It appears that the presence of about 2 ppm O_2 in the N_2 used

was sufficient to stabilize the Fe^{3+} compound NaFeO_2 , leading to the conclusion that the $p\text{O}_2$ of the system was too high. Synthesis in a sealed quartz ampoule resulted in the mixture of α - and β - NaFe_2O_3 polymorphs. At very low $p\text{O}_2$, Na_2O and Na doped wüstite (FeO) can be expected as equilibrium phases [18]. From this data, it becomes obvious that the synthesis of NaFe_2O_3 requires very careful control over oxygen stoichiometry. Since both the α - and β - NaFe_2O_3 polymorphs were prepared earlier at distinct, but unknown $p\text{O}_2$ [14], the dependence of phase composition vs. $p\text{O}_2$ was studied in order to prepare the pure compounds.

To control the $p\text{O}_2$ during experiments, mixtures of $\text{Cu}/\text{Cu}_2\text{O}$ or Ni/NiO were employed as oxygen buffers. Under equilibrium conditions for mixtures of metal and metal oxides, the $p\text{O}_2$ depends on both the chemical nature of the metal as well as temperature. Equilibrium $p\text{O}_2$ temperature dependences were determined experimentally for many systems [24] and [25]. In the case of Ni/NiO , the oxygen fugacity follows the Equation:

$$\log f_{\text{O}_2}(\text{atm}) = 9.36 - \frac{24930}{T} \quad (519 \text{ K} < T < 1319 \text{ K}) \quad \text{Equation 4.1}$$

where T is temperature in Kelvin. For a $\text{Cu}/\text{Cu}_2\text{O}$ mixture, the temperature dependence of the oxygen fugacity can be approximated as:

$$\log f_{\text{O}_2}(\text{atm}) = -\frac{18162.2}{T} + 12.855 - 0.6747 \times \ln(T) \quad (700 \text{ K} < T < 1338 \text{ K}) \quad \text{Equation 4.2}$$

The fugacity of a real gas is an effective pressure, which replaces the true mechanical pressure in accurate chemical equilibrium calculations. For low partial pressure

situations, as in our experiments, the fugacity is approximately equal to the partial vapor pressure; therefore, partial oxygen pressure is used throughout the text instead of the more thermodynamically strict fugacity term. This terminology is commonly accepted for solid-state synthesis [26].

It was a formidable challenge to seal quartz ampoules with two boats inside while maintaining the boat's positions without spilling the contents; therefore, a more convenient approach was developed. A simple setup consisting of a quartz tube with 24/40 standard taper joints, 2 glass stopcocks and a bubbler with mineral oil was used (Figure 4.2). Krytox high-temperature fluorinated grease was used with taper joints and all joints were held with Keck clamps. After placing the boats in the quartz tube and attaching adapters to the ends, the tube was purged with dry N₂. Afterwards, valve 1 (Figure 4.2) was closed and the furnace was heated up to desired temperatures. The increasing N₂ pressure was relieved through the bubbler. After the temperatures were reached, valve 2 was also closed. After annealing, all quartz tubes were quenched to ambient temperature in air.

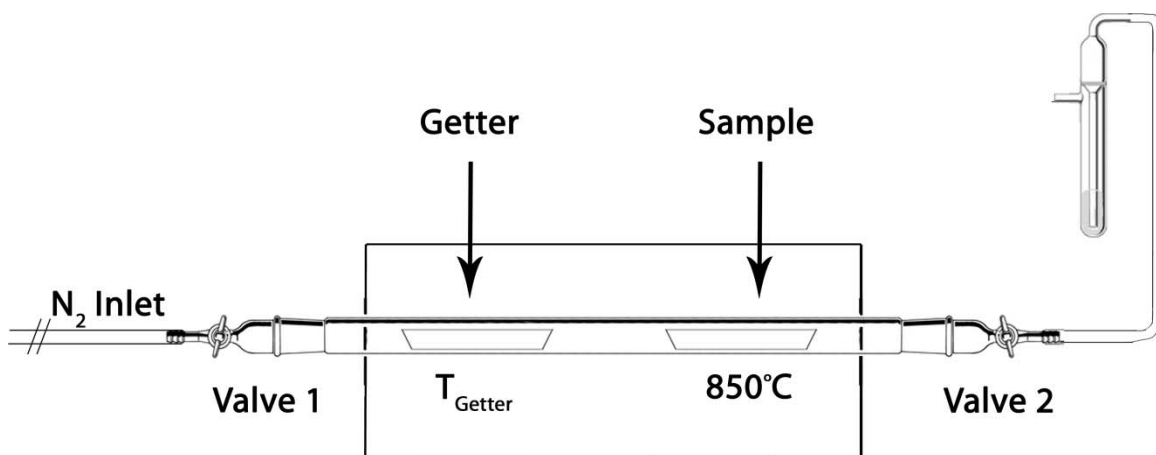


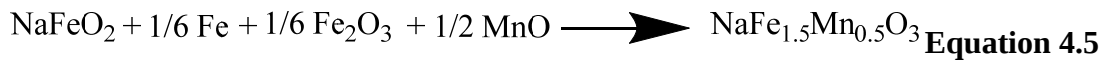
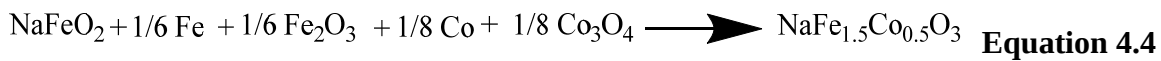
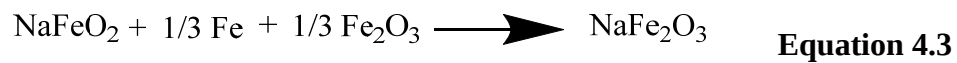
Figure 4.2 Experimental setup for the synthesis of α - and β - NaFe_2O_3 under controlled partial O_2 pressure.

4.3 Oxidation via sodium deintercalation

Oxidation via sodium deintercalation was performed using bromine as an oxidizing agent, resulting in the formation of NaBr and the sodium deficient $\text{Na}_x\text{Fe}_2\text{O}_3$. Bromine was added to acetonitrile and then added with a micropipette, in the amount of the desired stoichiometric ratio, into a vial of acetonitrile with β - NaFe_2O_3 . This was all performed in a nitrogen glove bag. The vial was sealed then stirred until the light to dark purple colored solutions became clear. This color change is indicative that all of the Br_2 reacted to form NaBr . The resulting mixture of NaBr and $\text{Na}_x\text{Fe}_2\text{O}_3$ was then washed with anhydrous ethanol to remove NaBr .

4.4 Transition Metal Doping

Due to the interesting properties that many different compounds with the rock-salt layered α -NaFeO₂ structure type contain [1-13], further investigation into the double-layered NaFe₂O₃ by doping into the iron site with similar transition metals was performed.



When mixing of a non-oxidized transition metal with its oxidized form stoichiometrically, such as iron (Fe) and iron (III) oxide, as seen in Equation 4.3, it can be considered the addition of FeO. This results in the exact stoichiometry for all metals and oxygen in the product. Due to this, similar compounds were reacted when attempting to substitute iron with other transition metals, as seen in Equation 4.4. Manganese has an oxide that exists with a stable 2+ oxidation state therefore direct substitution can be performed as seen in Equation 4.5.

4.5 Results and Discussion

A series of tests were performed to ensure that low O_2 pressures can be reached and reliably maintained in a tube with standard taper joints. For example, Ni powder was annealed in a tube at 850 °C for 20 days. The small amount of NiO formed can be related to an O_2 admixture in the N_2 purge gas. During experiments on complex bismuth oxides in the presence of oxygen buffers in an identical setup, the formation of metallic Bi from Bi_2O_3 at low pO_2 was observed [27]. This serves as additional proof of the method validity. It appears that even if a small amount of O_2 diffuses into the closed quartz tube, the equilibrium pO_2 is efficiently maintained by the buffer mixtures. The temperature of the buffer mixture was never lower than 350 °C for all experiments in order to provide high kinetic activity. PXD measurements were used after all experiments to confirm the presence of both metal and metal oxides in the buffer mixtures.

Annealing of the nominal $NaFe_2O_3$ composition at $\sim 2 \times 10^{-6}$ atm pO_2 resulted in the mixture of γ - $NaFeO_2$ and Fe_3O_4 (Figure 4.3). The γ - $NaFeO_2$ polymorph was reported to be stable in air above 1010 °C and to transform into β form at lower temperatures [28]. It appears that at lower pO_2 , the γ - $NaFeO_2$ region of stability extends to lower temperatures. Synthesis at $\sim 2.7 \times 10^{-10}$ atm pO_2 led to the formation of β - $NaFe_2O_3$ with γ - $NaFeO_2$ and Fe_3O_4 as secondary phases (Figure 4.4). Even lower pO_2 was required to prepare pure β - $NaFe_2O_3$ (Figure 4.5) while α - $NaFe_2O_3$ forms at pO_2 below $\sim 3.0 \times 10^{-19}$ atm (Figure 4.6). The experimental results of $NaFe_2O_3$ synthesis under controlled pO_2 are summarized as a schematic section of phase composition vs. pO_2 diagram at 850 °C (Figure 4.7). Buffer

mixtures used and corresponding pO_2 , as well as phase compositions are given in Table 4.1.

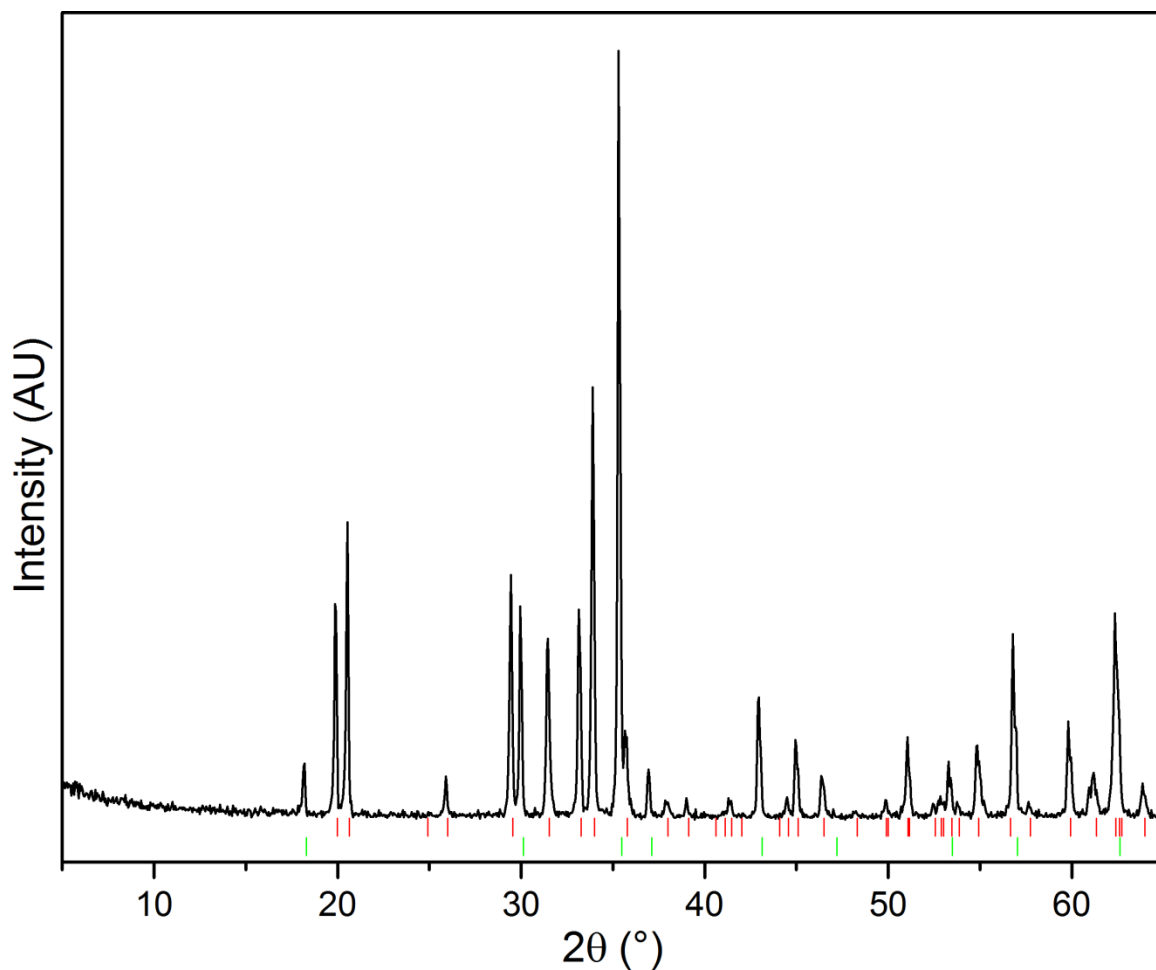


Figure 4.3 PXD of the resulting product of γ - $NaFeO_2$ (red ticks) and Fe_3O_4 (green ticks) after annealing the mixture of α - $NaFeO_2$, Fe powder and Fe_2O_3 under flowing house nitrogen at 850 °C.

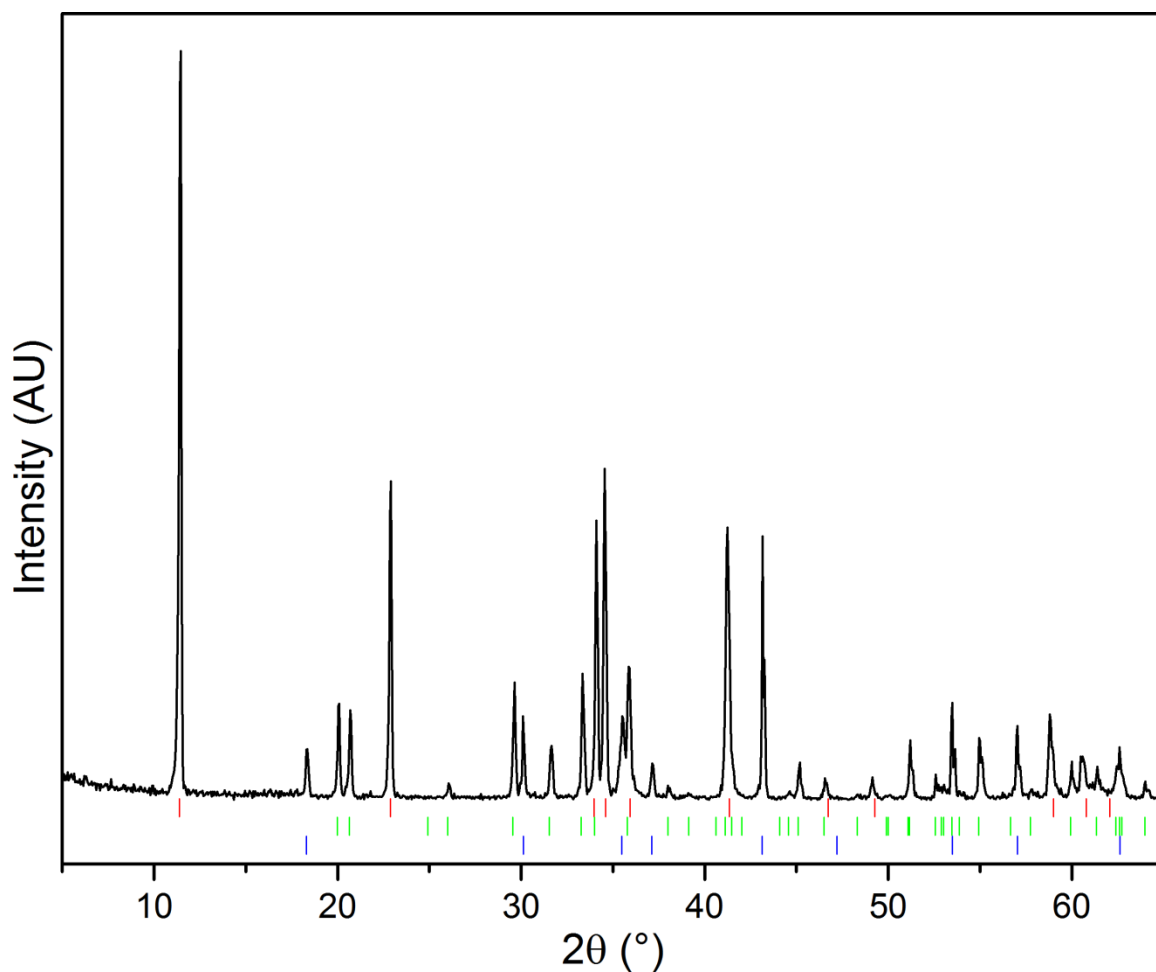


Figure 4.4 PXD of the resulting product of β - NaFe_2O_3 (red ticks), γ - NaFeO_2 (green ticks), and Fe_3O_4 (blue ticks) after annealing the mixture of α - NaFeO_2 , Fe powder and Fe_2O_3 at a $p\text{O}_2$ below $\sim 1.0 \times 10^{-10}$ atm at 850 °C.

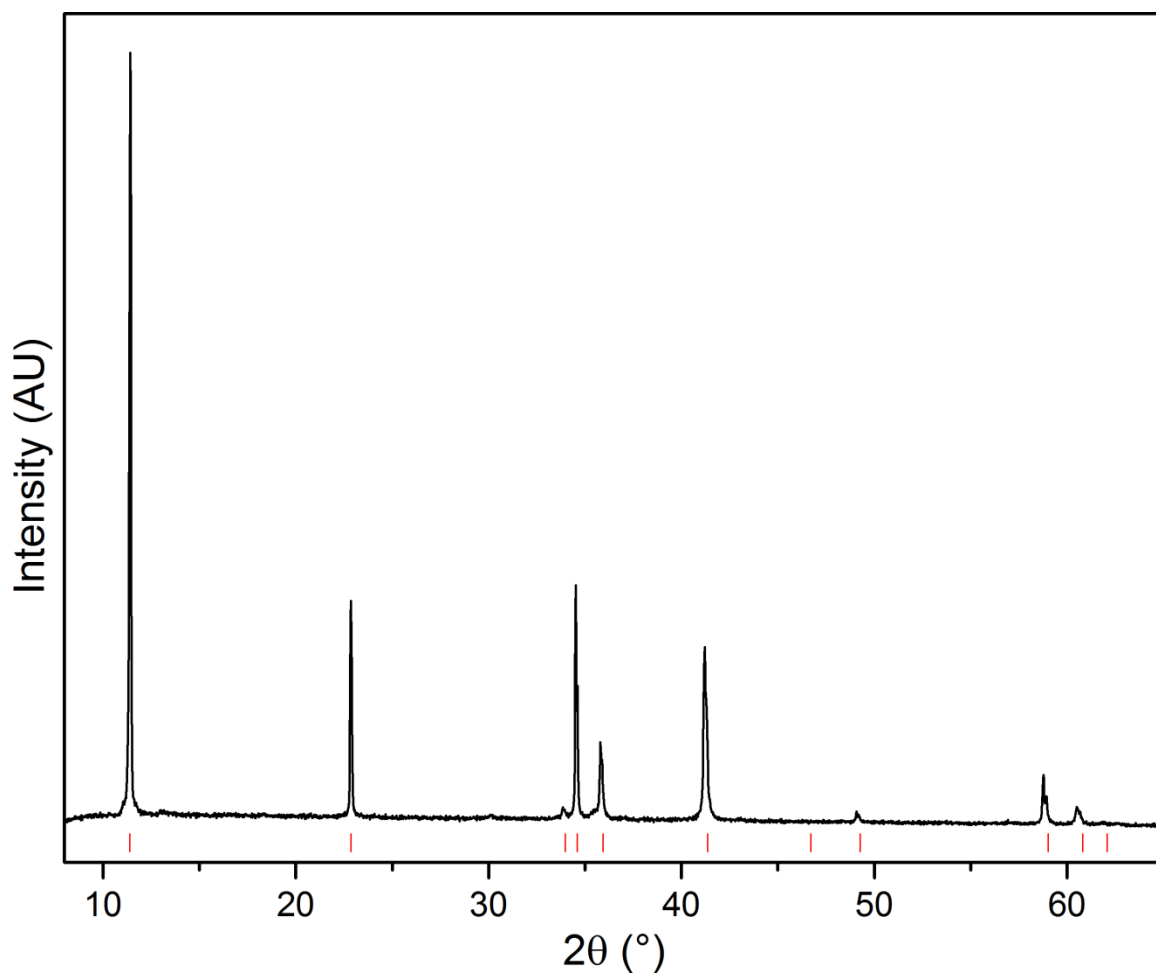


Figure 4.5 PXD of the resulting product of $\beta\text{-NaFe}_2\text{O}_3$ (red ticks) after annealing the mixture of $\alpha\text{-NaFeO}_2$, Fe powder, and Fe_2O_3 between the $p\text{O}_2$ of $\sim 1.0 \times 10^{-10}$ and $\sim 1.0 \times 10^{-19}$ atm at 850 °C.

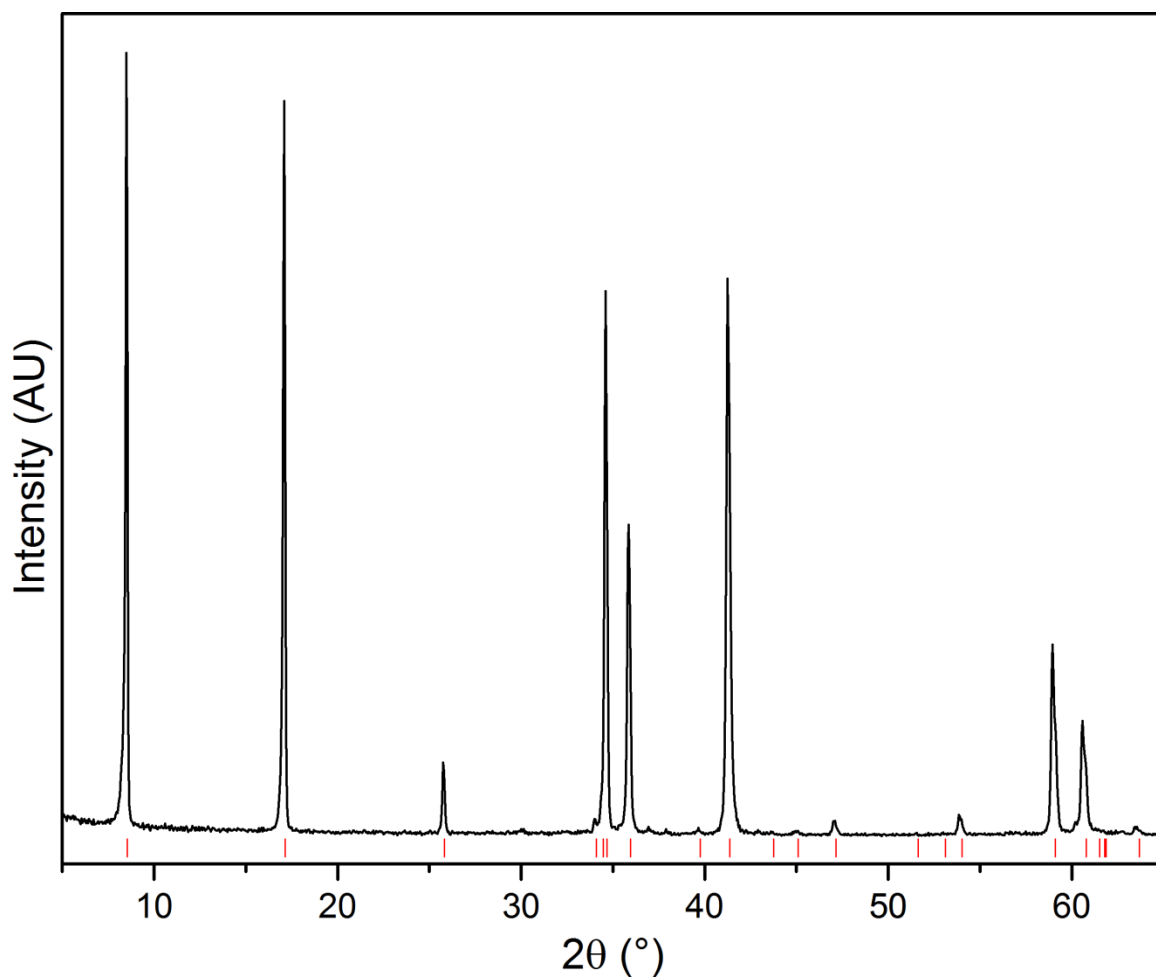


Figure 4.6 PXD of the resulting product of $\alpha\text{-NaFe}_2\text{O}_3$ (red ticks) after annealing the mixture of $\alpha\text{-NaFeO}_2$, Fe powder, and Fe_2O_3 below $p\text{O}_2 \sim 1.0 \times 10^{-19}$ atm at 850 °C.

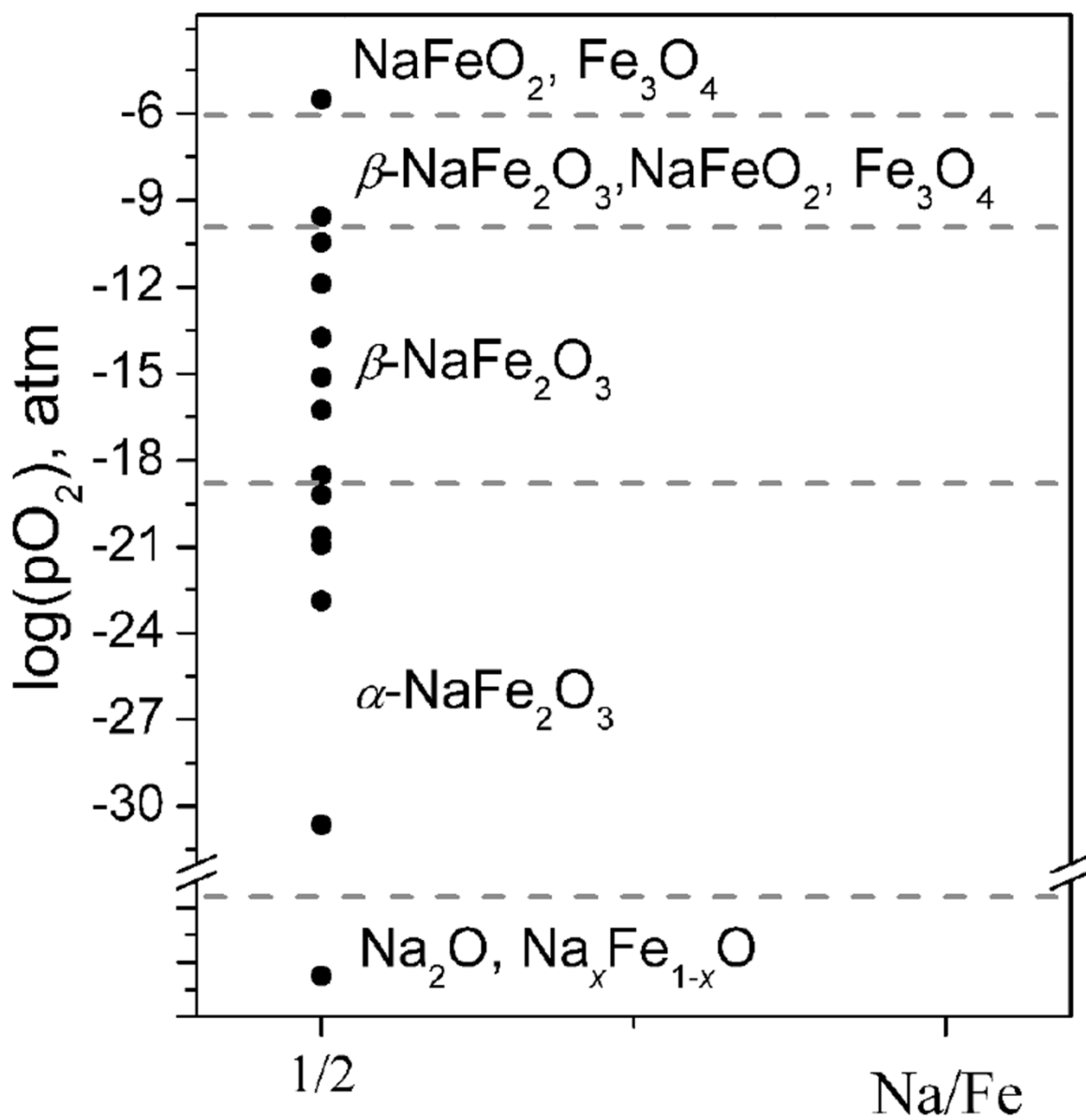


Figure 4.7 Schematic section of phase composition vs. partial O_2 pressure diagram at 850 °C for Na/Fe=1/2.

The most important result of this study is that the bulk preparation conditions for pure α - and β - NaFe_2O_3 were determined. The synthetic procedure is highly reproducible; it does not require any special equipment and can be easily implemented in virtually any chemistry laboratory.

Mixtures of α - and β - NaFe_2O_3 polymorphs were obtained when furnace cooling was used in initial attempts instead of sample quenching. At the same time, there are no α - and β - NaFe_2O_3 two-phase regions on the diagram at 850 °C. On cooling, the equilibrium $p\text{O}_2$ controlled by the buffer mixtures decreased drastically, allowing for rapid β - NaFe_2O_3 to α - NaFe_2O_3 transformation. This observation shows that phase relationships are very sensitive to both $p\text{O}_2$ and temperature, further emphasizing importance of controlled $p\text{O}_2$ method for the preparation of pure α - and β - NaFe_2O_3 .

Importantly, the 3-phase refinement, (Figure 4.8), led to insight into the chemistry of the system. Smaller cell parameters of the β - $\text{Na}_x\text{Fe}_2\text{O}_3$ phases can be related to a higher Fe oxidation state accompanied by Na deficiency. The high volatility of sodium oxide at the experimental temperature (850 °C) is the most probable reason for Na deficiency in the sample. The devitrification (crystallization) of fused silica tubes was apparent near the sample boats. The quartz devitrification process was accelerated in the presence of the reaction product of Na_2O with SiO_2 , which acts as crystallization seeds.

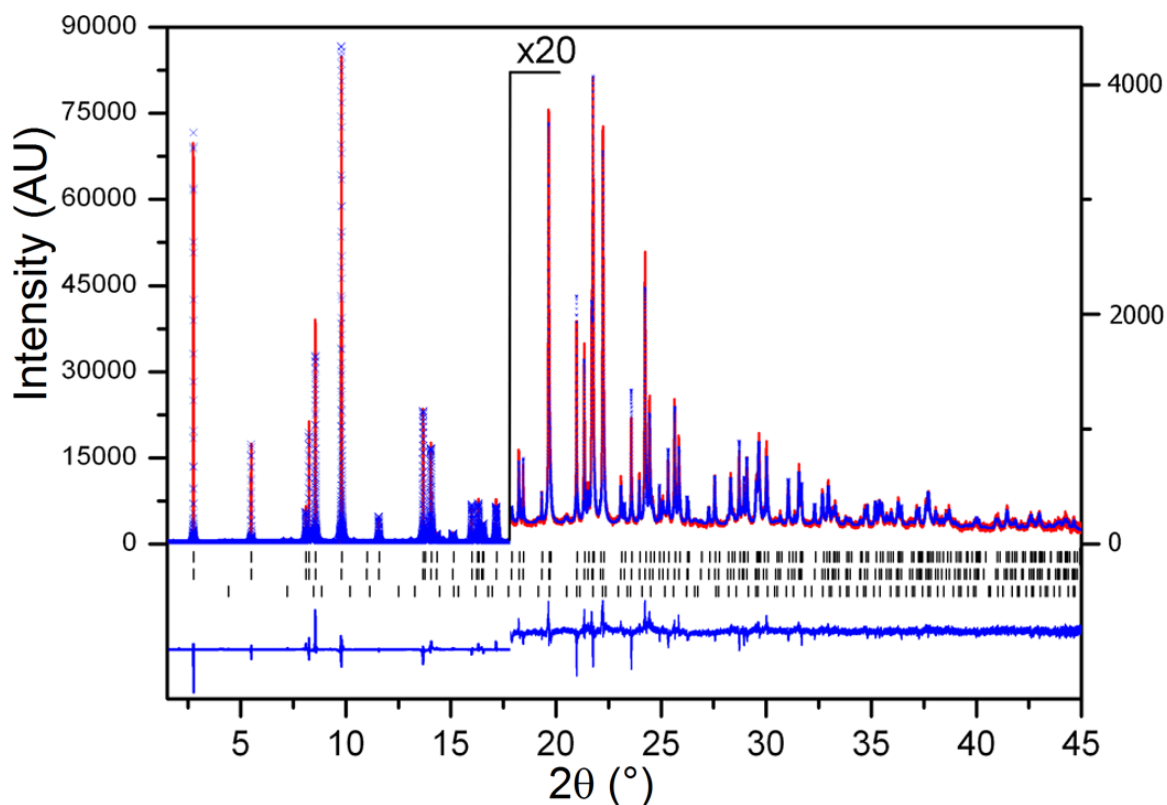


Figure 4.8 Observed (crosses), calculated (solid line), difference (bottom solid line) profiles and Bragg reflections (tick marks) for the final Rietveld refinement of β -NaFe₂O₃ and β -Na_xFe₂O₃, from SXPd data. The tick marks correspond to the positions (from top down) of β -Na_xFe₂O₃, β -NaFe₂O₃, and Fe₃O₄. The section at higher angles ($>16^\circ$ 2θ) is enlarged by a factor of 20 for clarity.

Table 4.1 Crystallographic Data for the Rietveld Refinement of β -NaFe₂O₃ and β -Na_{0.78}Fe₂O₃ from SXPD data. (Goodness of Fit Parameters: $\chi^2 = 5.87$, Rwp = 10.6%).

Crystallographic Data for β -Na₁Fe₂O₃.^a

Atom	Wyckoff position	x	y	z	10 ² Uiso (Å ²)	Occ.
Na	1b	0	0	0.5	1.06(3)	1
Fe	2d	1/3	2/3	0.1675(1)	0.64(1)	1
O1	1a	0	0	0	2.26(7)	1
O2	2d	1/3	2/3	0.7040(2)	1.03(3)	1

^aSpace group $P\bar{3}m1$ (No. 164). a = 3.05795(1) Å, c = 7.79807(2) Å; weight fraction 73%.

Crystallographic Data for β -Na_{0.78}Fe₂O₃.^b

Atom	Wyckoff position	x	y	z	10 ² Uiso (Å ²)	Occ.
Na	1b	0	0	0.5	1.06(2)	0.78(1)
Fe	2d	1/3	2/3	0.1705(2)	0.77(2)	1
O1	1a	0	0	0	2.28(9)	1
O2	2d	1/3	2/3	0.6416(6)	2.28(9)	1

^bSpace group $P\bar{3}m1$ (No. 164). a = 3.05106(4) Å, c = 7.7898(2) Å; weight fraction 21%.

Table 4.2 Phase composition of nominal “NaFe₂O₃” stoichiometry at different partial O₂ pressures at 850 °C.

Phase composition	Equilibrium partial O ₂ pressure, atm [19, 20]	Oxygen buffer (getter) mixture	Temperature of the oxygen buffer mixture, °C	Chemical analysis results
γ -NaFeO ₂ , Fe ₃ O ₄	$\sim 2 \times 10^{-6}$	- (N ₂ flow)	-	
β -NaFe ₂ O ₃ , γ -NaFeO ₂ , Fe ₃ O ₄	2.7×10^{-10}	Cu/Cu ₂ O	750	
β -NaFe ₂ O ₃	3.5×10^{-11}	Cu/Cu ₂ O	700	Na _{0.88(2)} Fe _{0.93} ²⁺ Fe _{1.07} ³⁺ O _{2.98(2)}
	1.8×10^{-14}	Cu/Cu ₂ O	550	Na _{0.80(2)} Fe _{0.89} ²⁺ Fe _{1.11} ³⁺ O _{2.96(2)}
	7.5×10^{-16}	Cu/Cu ₂ O	500	Na _{0.88(2)} Fe _{0.9} ²⁺ Fe _{1.1} ³⁺ O _{2.99(2)}
	5.5×10^{-17}	Ni/NiO	700	Na _{0.82(2)} Fe _{0.89} ²⁺ Fe _{1.11} ³⁺ O _{2.97(2)}
α -NaFe ₂ O ₃	3.0×10^{-19}	Cu/Cu ₂ O	400	Na _{0.76(2)} Fe _{1.00} ²⁺ Fe _{1.00} ³⁺ O _{2.88(2)}
	6.4×10^{-20}	Ni/NiO	600	
	1.2×10^{-21}	Ni/NiO	550	Na _{0.92(2)} Fe _{1.09} ²⁺ Fe _{0.91} ³⁺ O _{2.91(2)}
	1.3×10^{-23}	Ni/NiO	500	Na _{0.74(2)} Fe _{0.98} ²⁺ Fe _{1.02} ³⁺ O _{2.88(2)}
	2.3×10^{-31}	Ni/NiO	350	

ICP analysis confirmed Na loss via volatilization, giving an average composition of β - $\text{Na}_{0.88(2)}\text{Fe}_{2.00}\text{O}_3$ for the sample. Knowing the sample composition and fraction of each phase present, one can calculate Na content (x) for β - $\text{Na}_x\text{Fe}_2\text{O}_3$. β - NaFe_2O_3 , β - $\text{Na}_x\text{Fe}_2\text{O}_3$, and Fe_3O_4 weight fractions were calculated during the Rietveld refinement and were equal to 0.73, 0.21, and 0.06, respectively, giving a derived composition of β - $\text{Na}_{0.76}\text{Fe}_2\text{O}_3$. The Na content in β - $\text{Na}_x\text{Fe}_2\text{O}_3$ refined from SPXD data was equal to 0.78, in good agreement with the chemical analysis results.

According to the SPXD data, α - NaFe_2O_3 was essentially a pure phase. According to ICP analysis, a compositional formula of $\text{Na}_{0.98(2)}\text{Fe}_{2.00}\text{O}_3$ was obtained. Peaks related to the β - $\text{Na}_x\text{Fe}_2\text{O}_3$ polymorph were absent in the SPXD pattern while the strongest peak of the Fe_3O_4 admixture was at ~ 0.1 % of relative intensity level. Attempts to perform a Rietveld refinement using the literature structural model [14] were unsuccessful ($\chi^2 \approx 22$). While peak positions and peak profile could be fitted adequately, there were substantial differences in peak intensities, which did not change systematically with peak indices, indicating a problem with the structural model rather than preferred orientation. Attempts to include preferred orientation in the refinement were unsuccessful. Difference Fourier maps were calculated to determine the cause of said discrepancies. The difference Fourier map indicated regions of significant electron density around the shared Na/Fe and adjacent O3 positions (Figure 4.9). The extra electron density has a spherical shape near the O3 position, suggesting splitting of the position. The donut-like shape of the extra electron density around the shared Na/Fe position can be related to a Na/Fe shift from the average position. Attempts to split O3 and the shared Na/Fe positions to account for the

observed differences did not result in an improvement to the refinement; therefore, the crystal structure published by El Balkhi et al. [14] describes the average structure well, while the real structure is more complex with substantial disorder in the shared Na/Fe and O3 positions. Pair distribution function (PDF) analysis is needed to study the structure of α -NaFe₂O₃ in further detail.

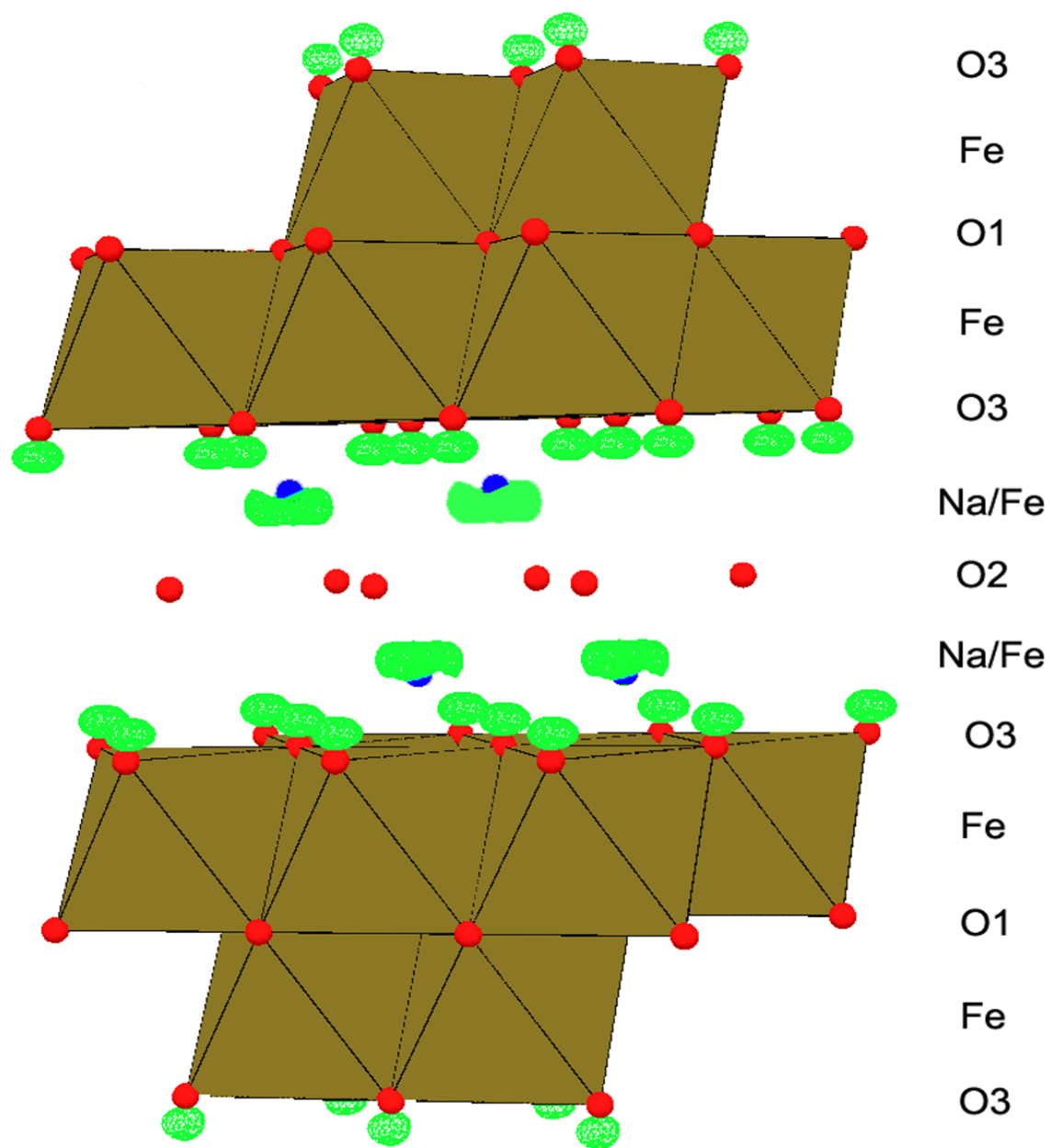


Figure 4.9 Difference Fourier map for α - NaFe_2O_3 indicating large residual electron density (green) around the Na/Fe and O3 positions. Atomic positions are denoted for this layered structure and Fe–O octahedra are highlighted. Blue and red spheres represent atoms in the Na/Fe and O positions, respectively.

A nominal NaFe_2O_3 composition of both α - and β - NaFe_2O_3 polymorphs implies the same formal Fe oxidation state in both compounds. It is not clear why α - NaFe_2O_3 begins to form at a $p\text{O}_2$ eight orders of magnitude lower than β - NaFe_2O_3 . To clarify the origin of such a drastic difference in the stability conditions, stoichiometry of representative samples were determined by a combination of ICP analysis and iodometric titration. In spite of slight differences in Na content, oxygen stoichiometry of β - NaFe_2O_3 samples prepared in a wide range of $p\text{O}_2$ (3.5×10^{-11} – 5.5×10^{-17}) were very close to ideal with a negligible amount of oxygen vacancies (Table 4.1). The $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio calculated from the sample's stoichiometry and charge balance requirements resulted in a 0.9:1.1 ratio (within error) for all β - NaFe_2O_3 samples. Contrary to our expectations, oxygen nonstoichiometry in α - NaFe_2O_3 was minimal, with 0.1 oxygen vacancies per formula unit (Table 4.1). The $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio was between 1.0/1.0 and 1.1/0.9 for α - NaFe_2O_3 samples prepared under different experimental conditions.

It has been shown that order in layered structures is favored by a large difference in the ionic radii (R) of A and M. An ionic radii ratio $R_M/R_A < 0.86$ is typical for ordered phases [30], which coincides well with the empirical rule requiring less than a 15% ionic radii difference between two elements for substitution to occur. Theoretical investigation identified that the elastic energy associated with ions of different size stabilizes the ordering of M and A into alternate layers [31]. In high spin configurations with coordination number 6, the Shannon ionic radii values for Fe^{2+} and Fe^{3+} ions are equal to 0.920 and 0.785 Å, respectively [32]. The formal Fe ionic radii for α - and β - NaFe_2O_3 are very close: 0.859 and 0.846 Å, respectively. Taking the large ionic radius of Na^+ (1.16 Å)

into consideration, one can see that $R_{\text{Fe}}/R_{\text{Na}} \approx 0.74$, which is well below the 0.86 value required for ordering. According to previous reports in the literature, structural strain has been shown to facilitate structural transformations [33]. The global instability index (GII) is often utilized as a metric of structural stress due to deviation of the bond valence sums of ions from ideal values [34]. The GII calculated for $\beta\text{-Na}_1\text{Fe}_2\text{O}_3$ using structural data from Table 4.2 was 0.14. While the GII indicates presence of structural strain, values above 0.2 generally correspond to unstable structures; thus, the simple radii ratio picture cannot unveil a reason for the β - to α - NaFe_2O_3 transformation at low $p\text{O}_2$.

A correlation between Na content and α - or β - NaFe_2O_3 polymorph formation (Table 4.2) was not established. Differences in Na content seem to be related to minute details of individual sample preparation, which indicates that further optimization of the synthetic conditions, is needed. Rietveld refinement of SPXD data for $\beta\text{-NaFe}_2\text{O}_3$ points to the presence of two phases with different Na compositions. It is probable that multiple α - or β - NaFe_2O_3 type line phases with well defined Na stoichiometry exist, as shown previously in Na_xCoO_2 [35]. Importantly, the existence of $\beta\text{-Na}_x\text{Fe}_2\text{O}_3$ indicates that partial deintercalation of Na should be possible by soft chemistry methods at room temperature, allowing for the fine tuning of the properties of the compounds by controlling the oxidation state of Fe. In the case of Na_xCoO_2 , such fine tuning results in a complex Na-content vs. physical properties diagram [36]. It would be intriguing to explore the properties of $\beta\text{-Na}_x\text{Fe}_2\text{O}_3$ with different Na compositions.

Oxygen stoichiometry of α - and β - NaFe_2O_3 differs by ~ 0.1 per formula unit. Values very close to full oxygen stoichiometry were consistently observed for β - NaFe_2O_3 while the α - NaFe_2O_3 phase compositions were systematically close to the 2.9 oxygen stoichiometry (Table 4.1). Based on the above consideration, it seems reasonable to assume that a higher stability of α - NaFe_2O_3 at low $p\text{O}_2$ is related to its ability to accommodate a greater amount of oxygen vacancies than that for β - NaFe_2O_3 .

The sodium volatility during the reaction led to further investigation of controlled sodium deintercalation using bromine. The bromine oxidation potential to deintercalate sodium against iron in the 3+ oxidation states is minimal; therefore, the oxidation of Fe^{2+} to Fe^{3+} in NaFe_2O_3 will occur and form the stable salt NaBr , as seen in Figure 4.10.

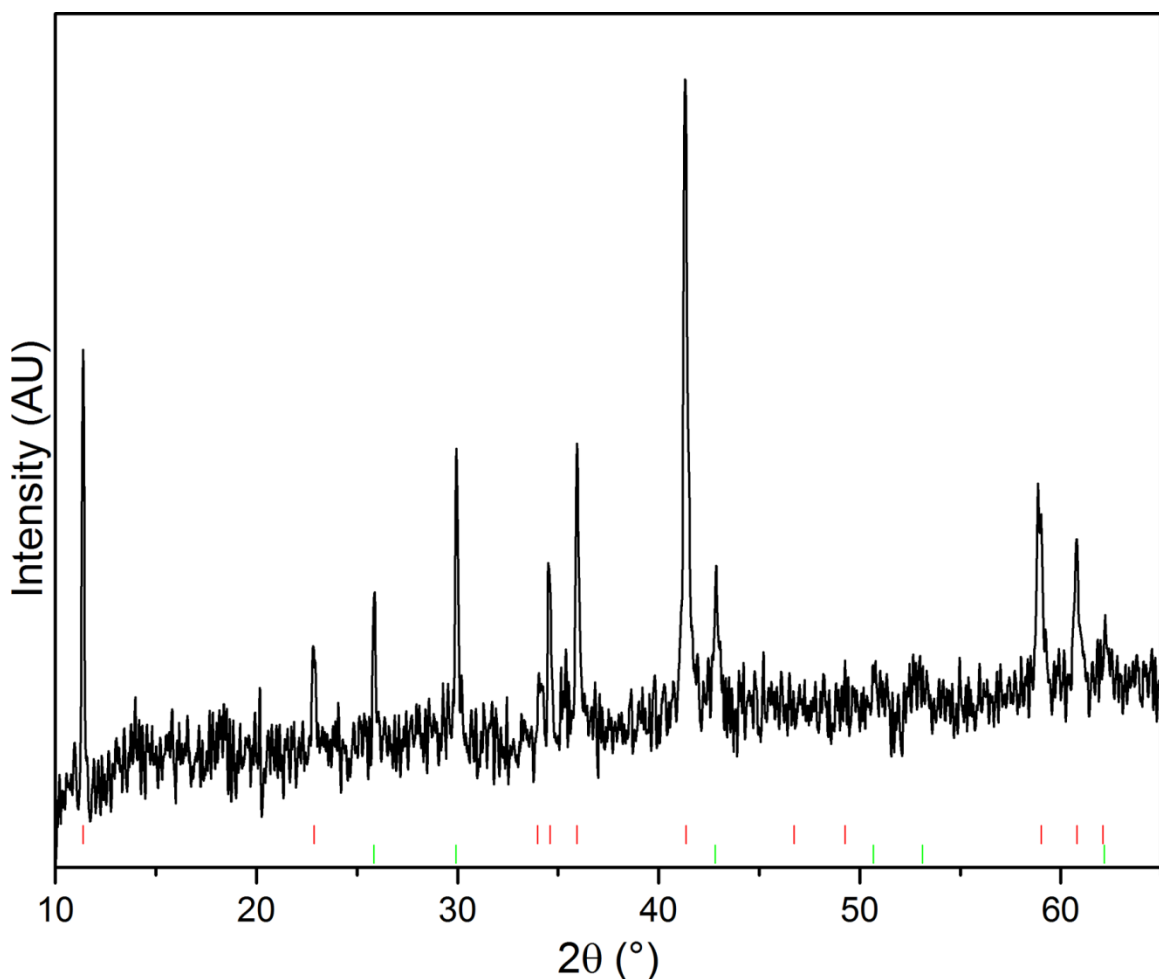


Figure 4.10 PXD of unwashed sodium deintercalated β - $\text{Na}_x\text{Fe}_2\text{O}_3$ (red ticks) with the byproduct NaBr (green ticks).

Similar to the results seen in Table 4.1, the result of the controlled removal of sodium from the initial compound will lead to the formation of an increased amount of Fe^{3+} . Chemical sodium deintercalation was performed in increasing increments of five mole percent of bromine starting at 0% and ending at 50%. This would result in a phase diagram of the sodium deficient $\text{Na}_x\text{Fe}_2\text{O}_3$ from the initial sodium deficient NaFe_2O_3 from the initial synthetic reaction, to approximately 0.5 parts per formula unit of sodium removed, or approximately $\text{Na}_{0.5}\text{Fe}_2\text{O}_3$. The samples were prepared starting with the

initial compound $\beta\text{-Na}_{0.96}\text{Fe}_2\text{O}_3$, determined from ICP, and reacted as previously described. The resulting powders were washed and analyzed for purity using a powder x-ray diffractometer. After the samples were deemed pure, further analysis using ICP to determine the actual stoichiometry of the sodium deficient phase was performed. Le Bail fit, to acquire cell parameters, was then performed on the pure phases and the cell parameters were plotted against the sodium content as seen in Figures 4.11-4.13.

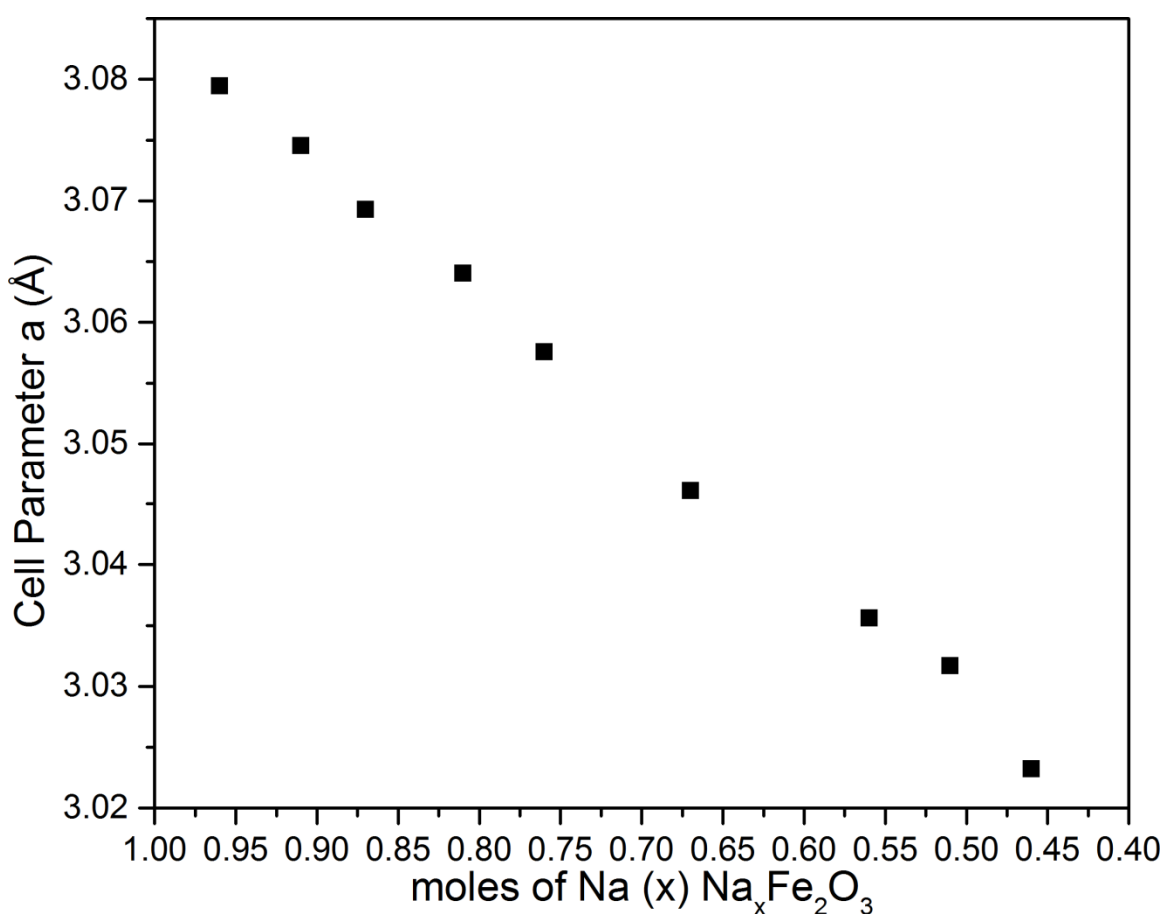


Figure 4.11 Cell parameter a as a function of parts per formula unit of sodium in $\text{Na}_x\text{Fe}_2\text{O}_3$ Le Bail fit from PXD.

According to Vegard's law, the cell parameters are expected to continue linearly as a function of sodium content in a crystal structure. This trend is seen in both the a and c parameters along with the volume, which is expected due the relationship of volume to the a and c parameters of a trigonal space group.

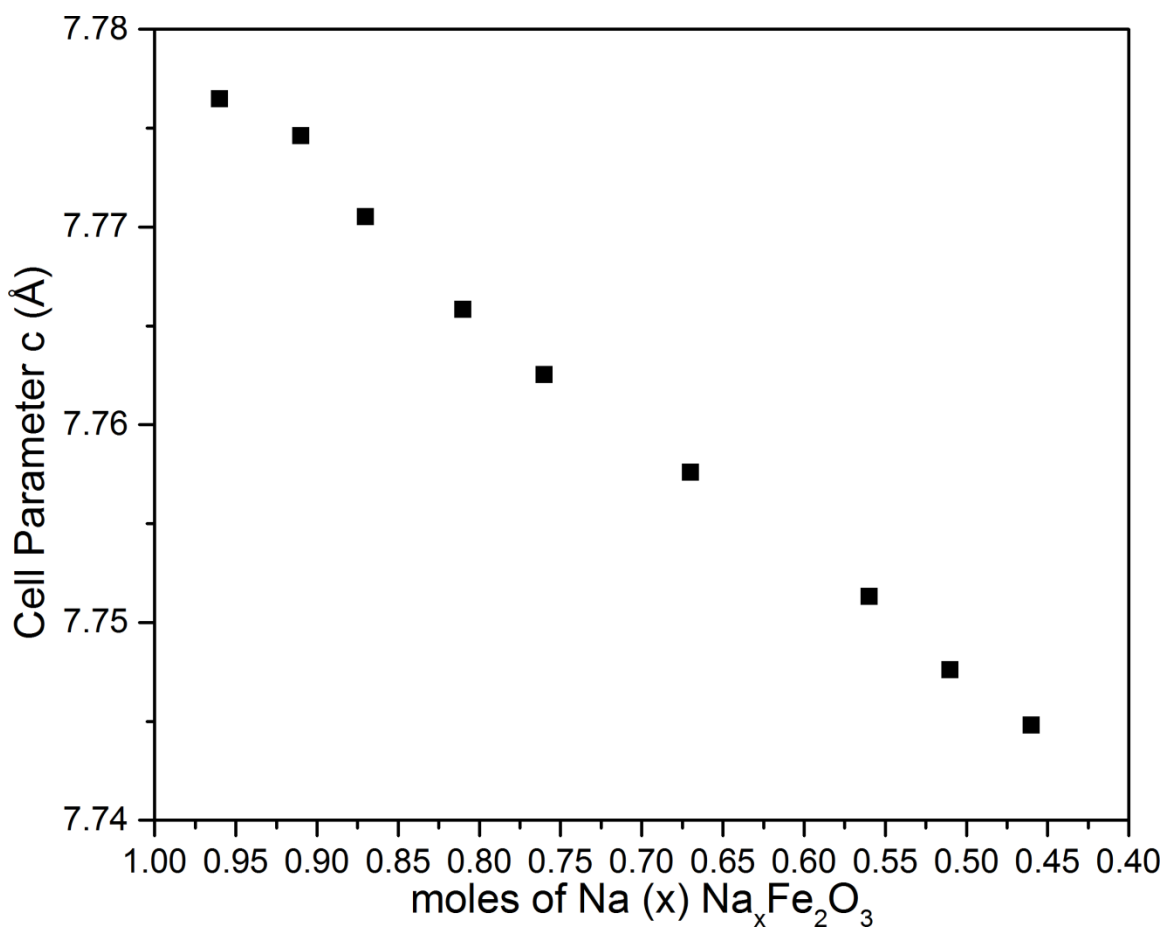


Figure 4.12 Cell parameter c as a function of parts per formula unit of sodium in $\text{Na}_x\text{Fe}_2\text{O}_3$ Le Bail fit from PXD.

As it can be seen in the Figures 4.11-4.13, there is an absence of the stable phases with the approximate formulas of $\text{Na}_{0.75}\text{Fe}_2\text{O}_3$ and $\text{Na}_{0.65}\text{Fe}_2\text{O}_3$. Multiple attempts were made to synthesize these two compounds to no avail. Therefore, it can be determined that these two sodium deficient phases are not kinetically stable. Coupled with the Rietveld refined compound in Table 4.1, $\text{Na}_{0.78}\text{Fe}_2\text{O}_3$, it can be then said that the stability of the structure within this range only varies by a few mole percent of sodium.

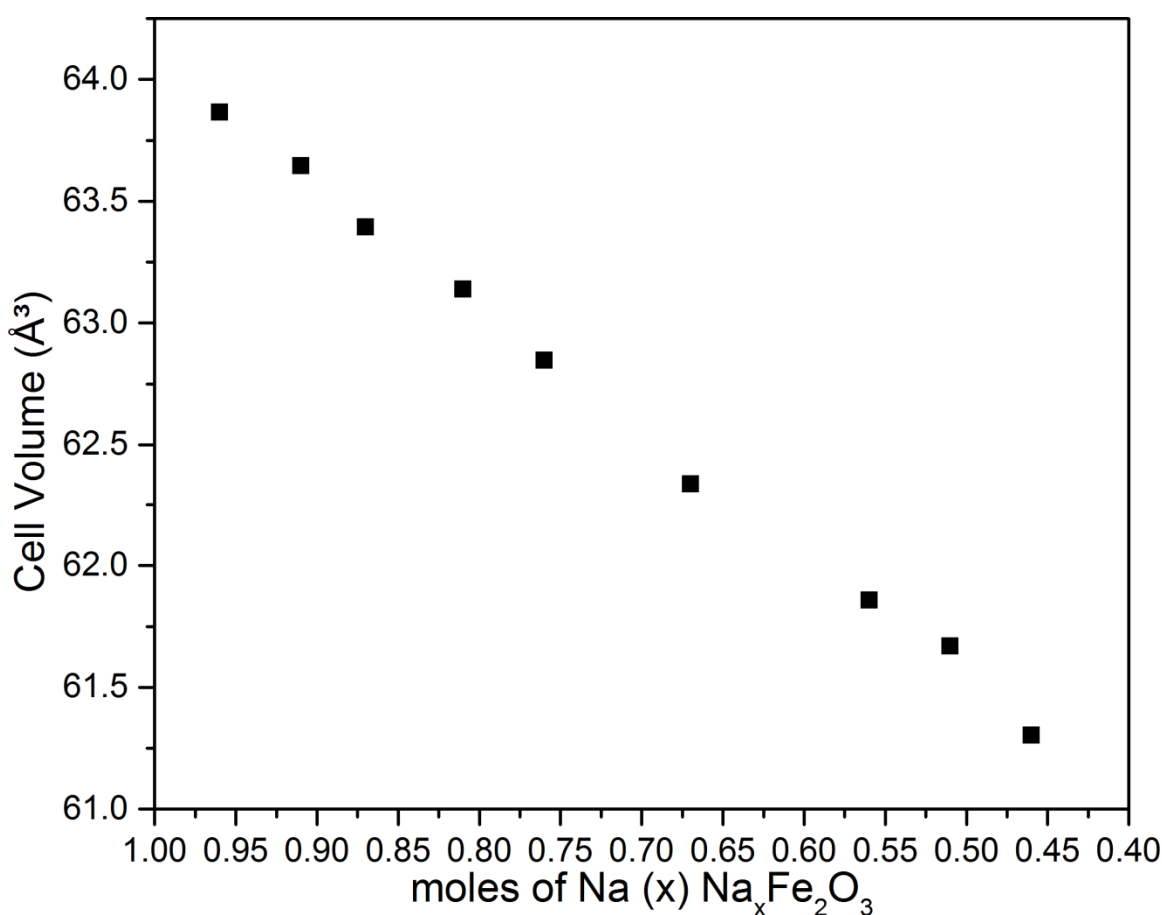


Figure 4.13 Volume as a function of parts per formula unit of sodium in $\text{Na}_x\text{Fe}_2\text{O}_3$ Le Bail fit from PXD.

Figures 4.11-4.13 are summarized in table 4.3 with the determined Le Bail fit values from laboratory PXD.

Table 4.3 $\text{Na}_x\text{Fe}_2\text{O}_3$ Cell parameters a , c and volume determined from Le Bail fit from PXD.

(x) in $\text{Na}_x\text{Fe}_2\text{O}_3$	Cell Parameter a	Cell Parameter c	Cell Volume
0.96	3.0792	7.7765	63.865
0.91	3.0746	7.7746	63.646
0.87	3.0693	7.7705	63.394
0.81	3.0640	7.7658	63.140
0.76	3.0576	7.7625	62.848
0.67	3.0461	7.7576	62.336
0.56	3.0356	7.7513	61.858
0.51	3.0317	7.7476	61.669
0.46	3.0232	7.7448	61.303

Synthesis of transition metal doped $\text{NaFe}_{2-x}\text{M}_x\text{O}_3$ was performed using manganese, cobalt, nickel, and copper. These transition metals were chosen due to their ability to form stable 2+ oxidation states along with having relatively similar ionic radii to iron. These two requirements are essential for the doping to be successful. Initial attempts were performed at a $p\text{O}_2$ of about 10^{-23} atm. This $p\text{O}_2$ is in the stability zone of $\alpha\text{-NaFe}_2\text{O}_3$, but due to the substituted transition metals' oxidation potentials different from that of iron, it can be expected that the reactivity of the doped $\text{NaFe}_{2-x}\text{M}_x\text{O}_3$ will differ from the

undoped NaFe_2O_3 . With that said, the $\alpha\text{-NaFe}_2\text{O}_3$ zone of stability was chosen to be on the cautious side. In the case that the reactivity of the doped transition metals required less oxidizing conditions to form, the formation of the β - structure would, at the very least, appear in a mixture of phases in a PXD. This was observed with the cobalt-doped compounds $\text{NaFe}_{1.75}\text{Co}_{0.25}\text{O}_3$ and $\text{NaFe}_{1.85}\text{Co}_{0.15}\text{O}_3$. As seen in Figure 4.14 at a $p\text{O}_2$ of about 10^{-23} atm, with $\text{NaFe}_{0.5}\text{Co}_{0.5}\text{O}_3$, the $\alpha\text{-NaFe}_2\text{O}_3$ structure formed.

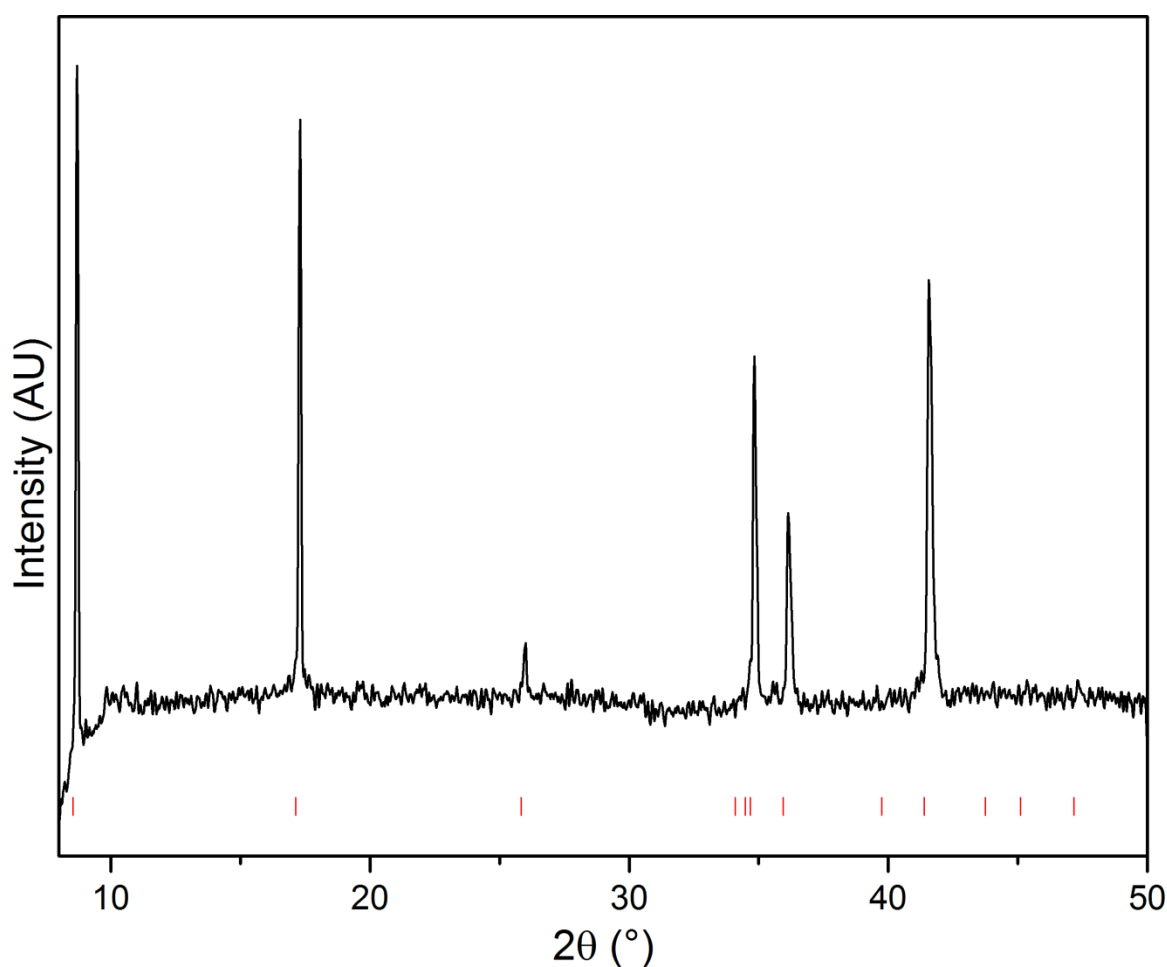


Figure 4.14 $\text{NaFe}_{1.5}\text{Co}_{0.5}\text{O}_3$ synthesized at 850 °C at a $p\text{O}_2$ of about 10^{-23} atm resulting in the formation of the $\alpha\text{-NaFe}_2\text{O}_3$ structure type (red ticks).

Similarly, at a pO_2 of about 10^{-23} atm, $NaFe_{1.75}Co_{0.25}O_3$ (Figure 4.15) and $NaFe_{1.85}Co_{0.15}$ (Figure 4.16) were synthesized resulting in mixtures of β - $NaFe_2O_3$ structure and $NaFeO_2$ for $NaFe_{1.75}Co_{0.25}O_3$, and β - $NaFe_2O_3$ mixed with $NaFeO_2$ and Fe_3O_4 for $NaFe_{1.85}Co_{0.15}$. This illustrates nicely the effect of the different doping amounts on reactivity at the same pO_2 .

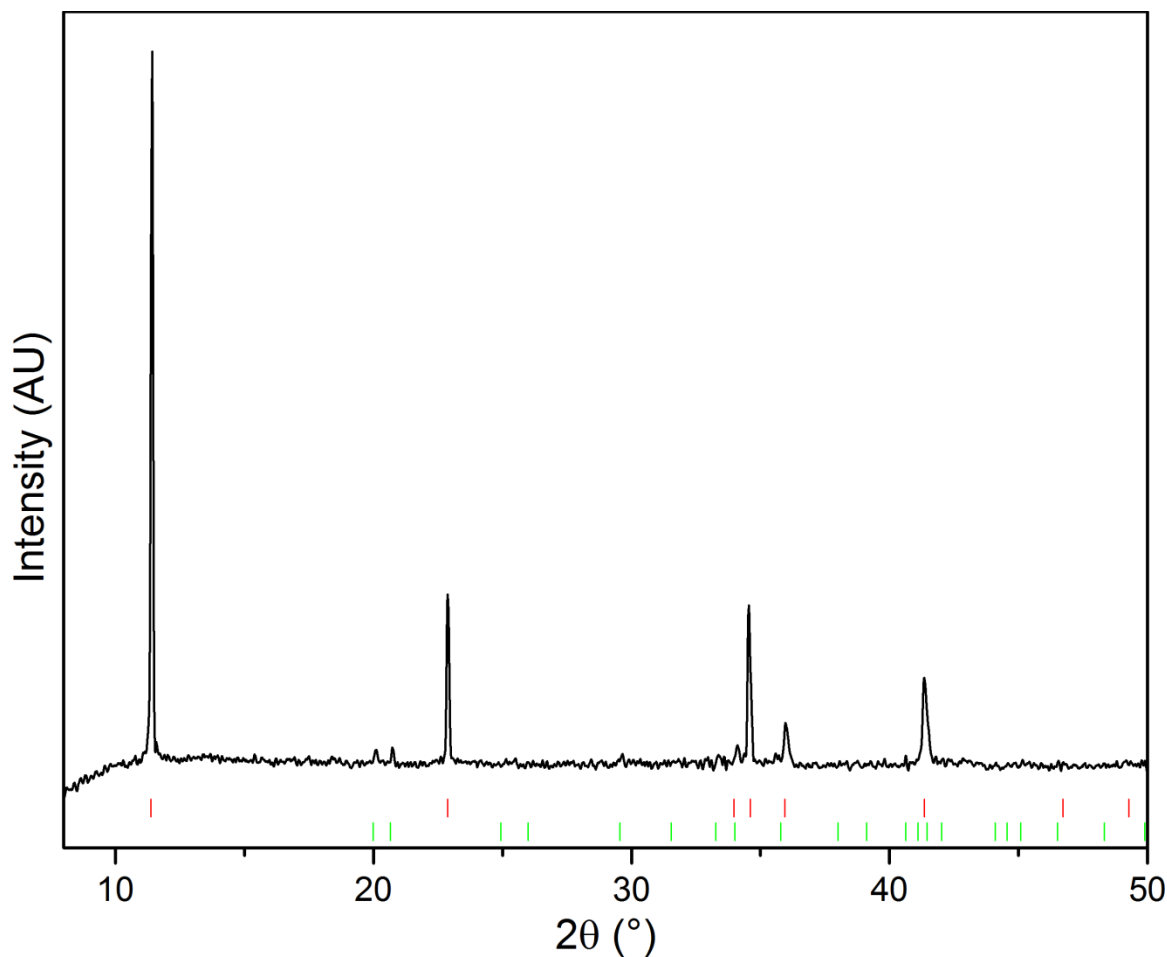


Figure 4.15 $NaFe_{1.75}Co_{0.25}O_3$ synthesized at 850 °C at a pO_2 of about 10^{-23} atm resulting in the formation of the β - $NaFe_2O_3$ structure type (red) and γ - $NaFeO_2$ (green).

Attempts to synthesize $\text{NaFe}_{1.25}\text{Co}_{0.75}\text{O}_3$ were deemed unsuccessful with the appearance of cobalt oxide. With this information, it can be said that doping of much more than 0.5 parts per formula unit of a transition metal will lead to the appearance of the respective transition metal oxide.

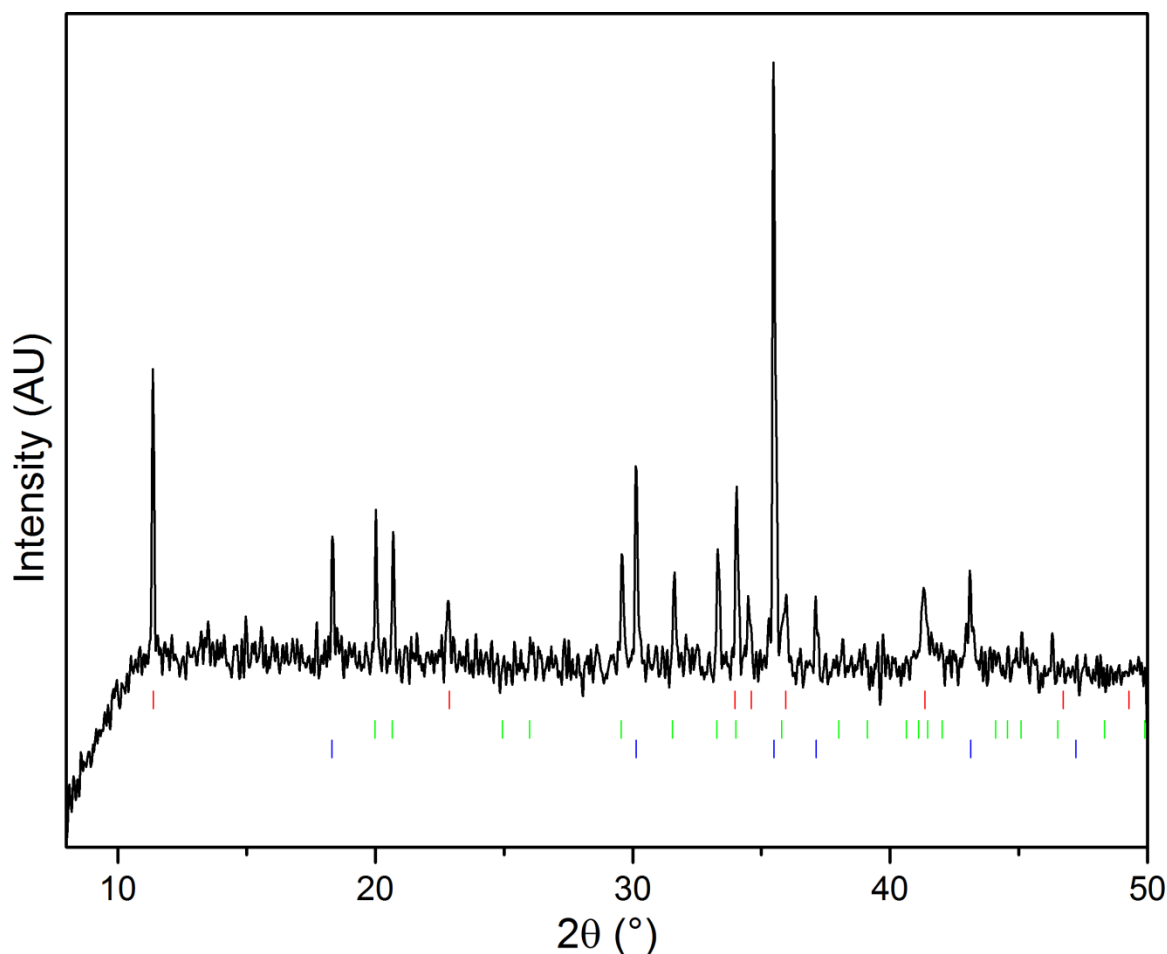


Figure 4.16 PXD of $\text{NaFe}_{1.85}\text{Co}_{0.15}\text{O}_3$ synthesized at 850 °C at a $p\text{O}_2$ of about 10^{-23} atm resulting in the formation of the $\beta\text{-NaFe}_2\text{O}_3$ structure type (red), $\gamma\text{-NaFeO}_2$ (green), and Fe_3O_4 (blue).

Doping NaFe_2O_3 with manganese was performed and the initial attempt was deemed successful. The attempt to synthesize $\text{NaFe}_{1.5}\text{Mn}_{0.5}\text{O}_3$ was performed at $850\text{ }^\circ\text{C}$ at a $p\text{O}_2$ of about 10^{-23} atm. The resulting PXD, as seen in Figure 4.17, shows the formation of the $\alpha\text{-NaFe}_2\text{O}_3$ structure, $\gamma\text{-NaFeO}_2$, and Fe_3O_4 . These results with both cobalt and manganese doping were deemed successful due to the formation of either the α - or β -phase, indicating that further attempts with different buffer conditions to form the pure phases of both α - and $\beta\text{-NaFe}_{2-x}\text{M}_x\text{O}_3$ will form the pure phases.

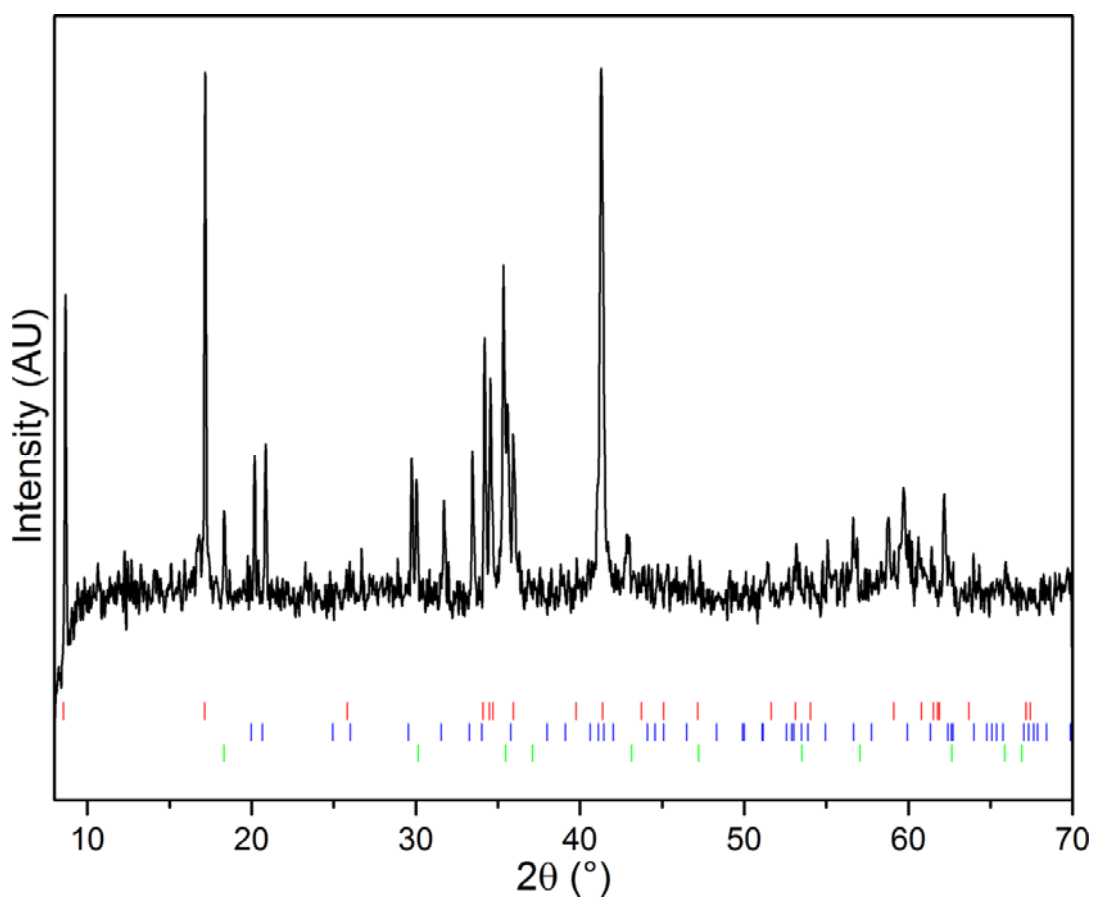


Figure 4.17 $\text{NaFe}_{1.5}\text{Mn}_{0.5}\text{O}_3$ synthesized at $850\text{ }^\circ\text{C}$ at a $p\text{O}_2$ of about 10^{-23} atm resulting in the formation of the $\alpha\text{-NaFe}_2\text{O}_3$ (red), structure type $\gamma\text{-NaFeO}_2$ (blue), and Fe_3O_4 (green).

Attempts to dope copper and nickel into NaFe_2O_3 were deemed unsuccessful. The resulting PXD of both reactions still possessed CuO and NiO indicating no reaction occurred. This result is not surprising due to the relatively high stability of the two oxides.

4.6 Conclusion

A phase composition vs. partial O_2 pressure diagram at 850 °C for $\text{Na/Fe}=1/2$ was determined which allowed for the reproducible synthesis of the divalent sodium iron oxides, α - and β - NaFe_2O_3 polymorphs. Sodium extraction from β - NaFe_2O_3 at room temperature was successfully investigated thus modifying the average Fe oxidation state. Doping cobalt and manganese into the iron position was also successfully performed and illustrates the ability to form dopant series of the compound $\text{NaFe}_{2-x}\text{M}_x\text{O}_3$ ($0 \leq x \leq 0.5$). These results lead toward the unexplored areas of possibly rich chemistry and physics of the rock-salt related homolog series $\text{AM}_n\text{O}_{n+1}$ with layered A and M ordering.

4.7 Future Direction

First, the sodium deficient compounds that have been synthesized require magnetic measurements from room temperature to 4 K at 1000 Oe and 5000 Oe respectively. This can present an interesting phase diagram of the materials due to the already measured magnetic data as seen in Figure 4.18 of β - NaFe_2O_3 . The magnetic response of the divalent sodium iron oxide indicates possible interesting properties that are possessed by

the material. Other divalent iron materials, such as Fe_3O_4 , have the spinel structure that has iron in both the tetrahedral and octahedral coordination. This is not the case for iron in NaFe_2O_3 . Different electronic ordering is expected of this material by decreasing the sodium content and altering the average oxidation state of iron.

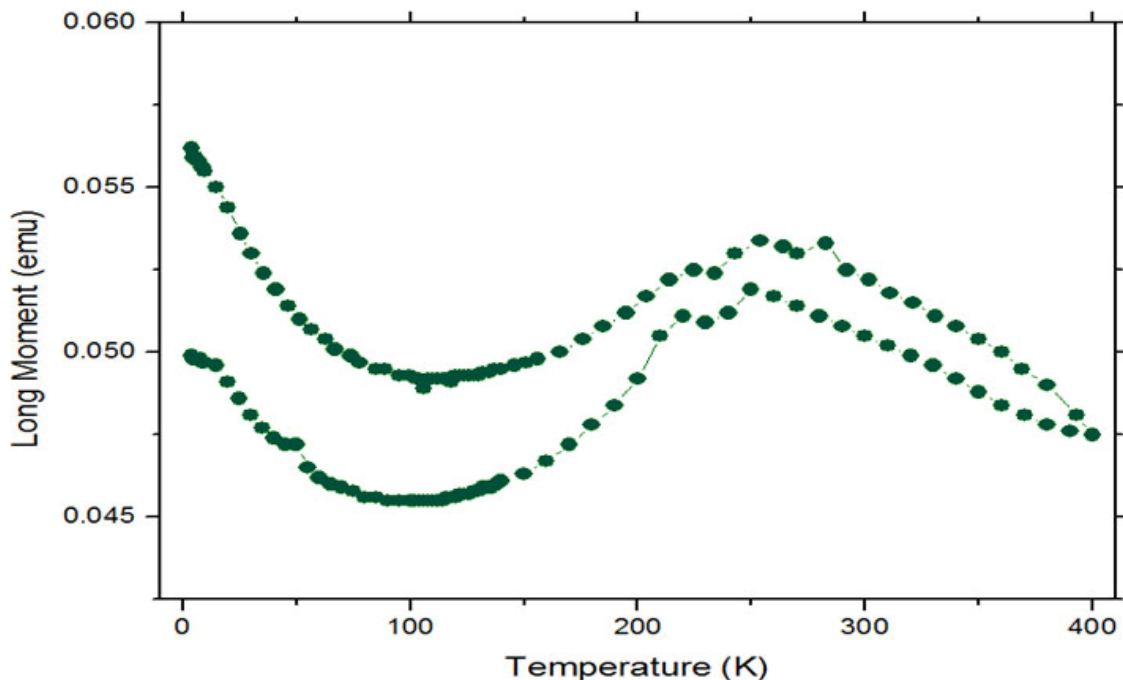


Figure 4.18 Magnetic response of NaFe_2O_3 as a function of temperature. The measurement was performed from room temperature to 4 K at 5000 Oe.

Similarly, because it was established that transition metal doping into the iron position can be attained, determining the conditions to successfully synthesize both α - and β - $\text{NaFe}_{2-x}\text{M}_x\text{O}_3$ ($\text{M} = \text{Mn}$ and Co) and ($0 \leq x \leq 0.5$) should be continued. Furthermore, after the previously mentioned materials have been synthesized, chemical oxidation via sodium deintercalation, as previously described with β - NaFe_2O_3 , could be performed and

the magnetic response of each material investigated. This would present a series of compounds with the general formula $\text{Na}_y\text{Fe}_{2-x}\text{M}_x\text{O}_3$, where $(0 \leq y \leq 0.5)$, $(\text{M} = \text{Mn and Co})$, and $(0 \leq x \leq 0.5)$.

Continuing with just the transition metal doping into NaFe_2O_3 , investigation of $\text{NaFe}_{2-x}\text{M}_x\text{O}_3$ as thermoelectric materials could also present possible interesting results. As seen in Figure 4.19, $\beta\text{-NaFe}_2\text{O}_3$ underwent transitions from being a semiconductor to insulator at about 250 K then back to electrically conducting at about 100 K. Each of the transitions correlated at the same temperatures observed the electron ordering or disordering in the magnetic response in Figure 4.18. The materials illustrated the semiconducting properties between 700 K and 250 K, at which point the material undergoes a Verway like transition into an insulator until about 100 K where the electrical conductivity begins to sharply increase.

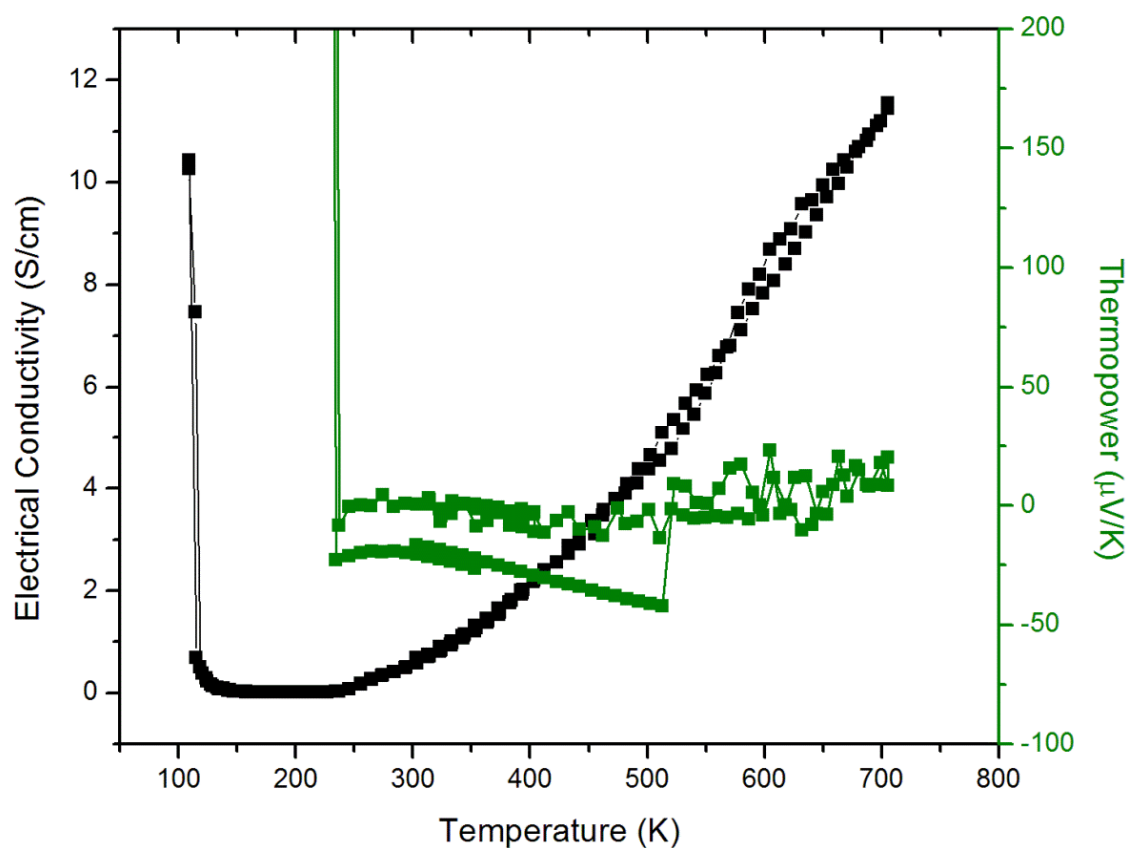


Figure 4.19 Thermopower (green) and electrical conductivity (black) measurements of β - NaFe_2O_3 with electrical conductivity showing transitions occurring at about 250 K and at about 100 K (black).

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Chapter 5

Synthesis of Tunnel Polymorph LiFeO_2 and Characterization of the Electrochemical Performance of Cobalt Doping

5.1 Introduction

Ideal cathode materials need to be both light in mass and have a high cycling voltage; therefore, the ideal lithium ion battery would be LiF . This would contain both a low mass and a high cycling voltage due to the high electrode potentials of both lithium and fluorine. However, due to safety issues, this "ideal" battery is not practical. Transition metal oxides have provided many different compounds that have high cycling voltages and relatively low masses, the properties that are ideal for good cathode materials. LiCoO_2 illustrates many properties that are promising for a cathode material. It only contains one early transition metal and only two oxygen atoms making it among the lightest of cathode materials. The cycling voltage of LiCoO_2 is at about 3.95 V, which is approaching the upper boundary of commonly used electrolytes. These two properties alone do not represent everything a good cathode material needs to contain. LiCoO_2 also has a two-dimensional diffusion pathway of the lithium between the CoO_6 octahedra and high electrical conductivity, thus requiring no special nano-particle preparation or carbon nanocoating [1–3].

Since the patent of the intercalation cathode material LiCoO_2 with the $\alpha\text{-NaFeO}_2$ structure type by Goodenough in 1980, and the intercalation patent on graphite in an organic solvent in 1981, Sony began to commercially produce lithium ion batteries in the early 1990's [3]. Because of environmental concerns of the toxicity of cobalt, developing

lithium ion batteries that reduce or eliminate the amount of cobalt used in the material has been an ever-increasing field in cathode research. This eventually led to other transition metal layered cathodes such as LiNiO_2 [4], $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ [5,6], and $\text{LiCo}_{1/3}\text{Mn}_{1/3}\text{Ni}_{1/3}\text{O}_2$ [7,8]. Spinel structure material such as LiMn_2O_4 , though lower in energy density, is commonly used due to its low cost and high abundance [9,10]. The olivine structure LiFePO_4 proposed by Goodenough in 1997, [11] increased momentum in cathode research eventually leading to an almost perfect cycling material for thousands of cycles. Originally, LiFePO_4 demonstrated poor cycle ability due to its greatest flaw of low electrical conductivity. This was eventually resolved by carbon nanocoating, leading to almost 100 % cycling capacity for over 3000 cycles as previously mentioned [12]. The structure type of LiFePO_4 , unlike the layered $\alpha\text{-NaFeO}_2$ structure type, has tunnel-like channels that the lithium ion travels out of and into during deintercalation and intercalation without any structural transformation. LiCoO_2 , in comparison, undergoes an irreversible transformation from rhombohedral crystal structure to a monoclinic crystal structure at about 50% deintercalation of lithium [13,14]. Table 5.1 shows the common transition metal oxides that are used as cathode materials in secondary lithium ion batteries.

Although LiFePO_4 does not undergo any crystal structure transformation and cycles thousands of times better than LiCoO_2 , LiCoO_2 is still the preferred material because of lower production cost, due to not having to be prepared as nano-particles or carbon nanocoated.

Table 5.1 Common transition metal oxide cathode materials.

Compound	Structure Type	Theoretical Capacity (mAh/g)	Experimental Capacity (mAh/g)	Cycle Voltage (V)	Cycle Number
LiCoO ₂ [1]	Layered α -NaFeO ₂	274	160	3.95	~300
LiFePO ₄ [11,15,16]	Olivine	170	160	3.5	>3,000
LiMn ₂ O ₄ [9]	Spinel	144	110	3.2	>1000

Due to the success of LiCoO₂ with the layered α -NaFeO₂ structure, as previously stated similar layered compounds were investigated, including LiFeO₂.

LiFeO₂ has nine known polymorphs including four ordered and disordered cubic rock-salt (NaCl) structure polymorphs. They differ depending on the order or disorder of the cations and are referred to as α -, β -, β' -, and γ -LiFeO₂ [17], the layered α -NaFeO₂ structure [18], the corrugated-layer [18], Goethite-type [2], Hollandite-type [19], and the tetrahedral LiFeO₂ (T-LiFeO₂) [20]. This compound is of particular interest due to iron's cost, abundance, and benign toxicity. The nine polymorphs can be synthesized through a variety of different methods including solid state reaction, low-temperature molten salt synthesis, hydrothermal, solvothermal, ion-exchange, and heat treatment. Table 5.2 illustrates a few synthetic procedures, the structure, and the best electrochemical performance for the different LiFeO₂ polymorphs.

Table 5.2 Polymorphs of LiFeO₂, structure, preparation, preparation procedure, and best electrochemical performance.

Type	Structure	Preparation	Preparation Procedure	Best Electrochemical Performance (mAh/g)
α -LiFeO ₂ [17,21]	Fm3m (cubic) Cations disordered	Solid State Reaction	Li ₂ CO ₃ and Fe ₂ O ₃ annealed above 700 °C	150
β -LiFeO ₂ [17,21]	Fm3m (cubic) Cations disordered	Solid State Reaction	Li ₂ CO ₃ and Fe ₂ O ₃ annealed at 400 °C	*
β' -LiFeO ₂ [17,21]	Fm3m (cubic) Cations disordered	Heat Treatment	α -LiFeO ₂ heated at 400 °C	*
γ -LiFeO ₂ [17,21]	Fm3m (cubic) Cations ordered	Solid State Reaction	Li ₂ CO ₃ and Fe ₂ O ₃ annealed above 600 °C	*
Layered-LiFeO ₂ [18,21]	R-3m (rhombohedral)	Ion-exchange	α -NaFeO ₂ and LiNO ₃ eutectic melt	115
Geothite- LiFeO ₂ [2,21]	Pbnm (orthorhombic)	Ion-exchange	α -FeOOH and C ₂ H ₅ OLi in ethanol at 170 °C	70
Hollandite- LiFeO ₂ [19,21]	I4/3 (tetragonal)	Ion-exchange	β -FeOOH and LiOH eutectic melt	150
Corrugated layer- LiFeO ₂ [2,21,22]	Pmnm (orthorhombic)	Ion-exchange	γ -FeOOH and C ₂ H ₅ OLi in ethanol at 170 °C	150
T-LiFeO ₂ [20]	Pna2 ₁ (orthorhombic)	Ion-exchange	β -NaFeO ₂ and LiNO ₃ eutectic melt	120

* Do not have electrochemical performance due to the blocked diffusion pathway by the ordering of the cations.

As seen in Table 5.2, the layered α -NaFeO₂ structure type LiFeO₂ cannot be prepared by the conventional high-temperature solid-state route, rather the precursor α -NaFeO₂ must first be prepared followed by ion exchange with a lithium salt. The direct solid-state route leads to the synthesis of different crystallographic forms of LiFeO₂ with the rock-salt structure. These ordered and disordered rock-salt structures do not show favorable intercalation and deintercalation due to their structure type, with the exception of α -LiFeO₂, of which the capacity eventually fades to less than 100 mAh/g. A nanoporous α -LiFeO₂ carbon composite was shown to have an initial capacity of 255 mAh/g, about 90 % its theoretical capacity of 282 mAh/g. This further illustrates the advancements nanoparticle preparation and carbon coating have on materials [23].

Particle size of LiFeO₂ with the layered α -NaFeO₂ structure was investigated and it was similarly determined that smaller particle size increased the discharge capacity. It was established that samples with an average particle size of 400 nm exhibited a capacity of 80 mAh/g while samples with an average particle size of 40 nm showed a higher capacity of 115 mAh/g. Each study was performed with a cycling voltage between 2.0 and 4.5 V [18].

T-LiFeO₂ is of particular interest due to its tunnel-like structure similar to that seen in LiFePO₄ [20]. This structure is also the only LiFeO₂ polymorph that contains iron-oxygen in tetrahedral coordination, whereas the other polymorphs are octahedral. T-LiFeO₂ is synthesized through ion exchange from the precursor β -NaFeO₂, which has a similar structure. The precursor was ball milled prior to ion exchange to decrease the particle size of the final compound. Electrochemical characterization of the T-LiFeO₂ polymorph

eventually stabilized with a capacity of about 100 mAh/g, but further analysis of the compounds showed a reaction with the electrolyte resulting in the formation of hydrogen, carbon monoxide, and carbon dioxide evolution. This reaction also led to the decomposition of T-LiFeO₂ to the spinel structure LiFe₅O₈.

The major flaw of LiFeO₂ in any of its polymorphs is its relatively low electrical conductivity; therefore, carbon coating or nano-particles, as previously stated, is a route commonly taken. Doping other transition metals into a structure is not only a route taken for reducing the amount of some elements as seen in LiCo_{1/3}Mn_{1/3}Ni_{1/3}O₂, but can also be performed to increase desired properties such as electrical conductivity. An example of this is cobalt doping into the α -NaFeO₂ layered structure LiFeO₂ to synthesize LiFe_{0.9}Co_{0.1}O₂ [24]. LiFe_{0.9}Co_{0.1}O₂ was synthesized simultaneously with an undoped LiFeO₂, both samples with the α -NaFeO₂ layered structure. It was reported that LiFeO₂ had an initial capacity of 205 mAh/g that eventually faded and stabilized at 140 mAh/g. Similarly, the LiFe_{0.9}Co_{0.1}O₂ had an initial capacity of 205 mAh/g, which faded and stabilized at 190 mAh/g. This finding illustrates that doping cobalt into layered LiFeO₂ produces a higher stabilized capacity than that of layered LiCoO₂ or LiFeO₂.

Further investigation into the T-LiFeO₂ polymorph with a tunnel-like structure will be discussed herein. The effects of chemical lithium intercalation and chemical lithium deintercalation on the structure were analyzed along with Mössbauer spectroscopy. Doping T-LiFeO₂ with cobalt was also investigated to determine if the electrochemical performance and structural stability could be enhanced and maintained respectively without transformation into LiFe₅O₈ and decomposition of the electrolyte.

5.2 Synthesis of β -NaFeO₂ and NaFe_{1-x}Co_xO₂

β -NaFeO₂ was synthesized through the directed ceramic method with stoichiometric amounts of Fe₂O₃ (99.5%, Alfa Aesar) and 5 % excess Na₂CO₃ (99%, Mallinckrodt Chemicals), to compensate for sodium volatility. β -NaFe_{1-x}Co_xO₂ ($0 \leq x \leq 0.15$) is synthesized similarly with the stoichiometric addition of Co₃O₄ (99.7%, Alfa Aesar) for the appropriate dopant amount. The samples were prepared by mixing the reagents and ball milling them until homogenous, at which point the samples are pressed into a 3/4 inch pellet under 6 tons of pressure. The resulting pellet was placed in a furnace programmed as follows; heat up from room temperature to 850 °C over a time of 6 hours, hold 850 °C for 12 hours, heat up to 1000 °C over 2 hours, hold at 1000 °C for 48 hours, then returned to room temperature at a natural cooling rate. The sample must be held at 850 °C to prevent the Na₂CO₃ from melting (M.P. = 851 °C), the sample was then hand ground and analyzed using PXD.

5.3 Ion exchange of NaFe_{1-x}Co_xO₂ to LiFe_{1-x}Co_xO₂ ($0 \leq x \leq 0.15$)

After β -NaFe_{1-x}Co_xO₂ was successfully synthesized, lithium for sodium ion exchange was performed using the lithium nitrate/sodium nitrate eutectic melt. Approximately two molar equivalents of lithium nitrate (LiNO₃ 99%, Alfa Aesar) were intimately mixed with β -NaFe_{1-x}Co_xO₂ in a nitrogen glove box until the mixture was homogenous. The mixture was placed in a furnace under oxygen flow and ramped to 225 °C for 48 hours. The resulting melt was washed with methanol (anhydrous 99.9%) to remove the excess LiNO₃ and NaNO₃ produced from the ion exchange. The resulting powders were

analyzed using PXD and ICP to confirm phase purity and elemental composition respectively.

5.4 Lithium intercalation and deintercalation of LiFeO_2 via chemical reduction and oxidation

Chemical lithium intercalation was performed using one molar equivalent of the as prepared T- LiFeO_2 with one, five, and ten times excess n-butyllithium (2.5M in hexanes, Sigma-Aldrich). The mixtures were stirred for 96 hours at room temperature, filtered, washed with n-pentane (anhydrous 99.8+%), then vacuum dried and stored under nitrogen in a glove box.

Chemical lithium deintercalation was performed in a nitrogen glove bag, using one molar equivalent of the as prepared T- LiFeO_2 mixed with two molar equivalents of bromine (99.5%, Jade Scientific) or iodine (99.8%, Jade Scientific) inside a round bottom flask with 100 mL of acetonitrile (99.5%, Mallinckrodt Chemicals). The solutions were stirred for 96 hours at room temperature. The compound was also mixed with 0.25, 0.5, 0.75, 1, and 2 molar equivalents of NOBF_4 (95%, Sigma-Aldrich) in acetonitrile and stirred for 48 hours. All samples were washed with acetonitrile, vacuum dried, and stored under nitrogen in a glove box.

5.5 Results and Discussion

Synthesis of $\beta\text{-NaFe}_{1-x}\text{Co}_x\text{O}_2$ was straightforward using Na_2CO_3 and Fe_2O_3 . The synthesis was successful at 770 °C in air, but required increased sintering times on the

cobalt doped samples. Increasing the temperature resulted in the formation of more crystalline PXD along with pure cobalt samples upon the initial firing as seen in Figure 5.1. Attempts to dope 0.20 parts per formula unit of cobalt into β -NaFeO₂ resulted in the formation of the NaCoO₂ with α -NaFeO₂ layered structure and an impurity peak in the PXD. This established the maximum amount of cobalt doping to be between 0.15 and 0.20 parts per formula unit. No further doping reactions were performed past 0.15 parts per formula unit of cobalt.

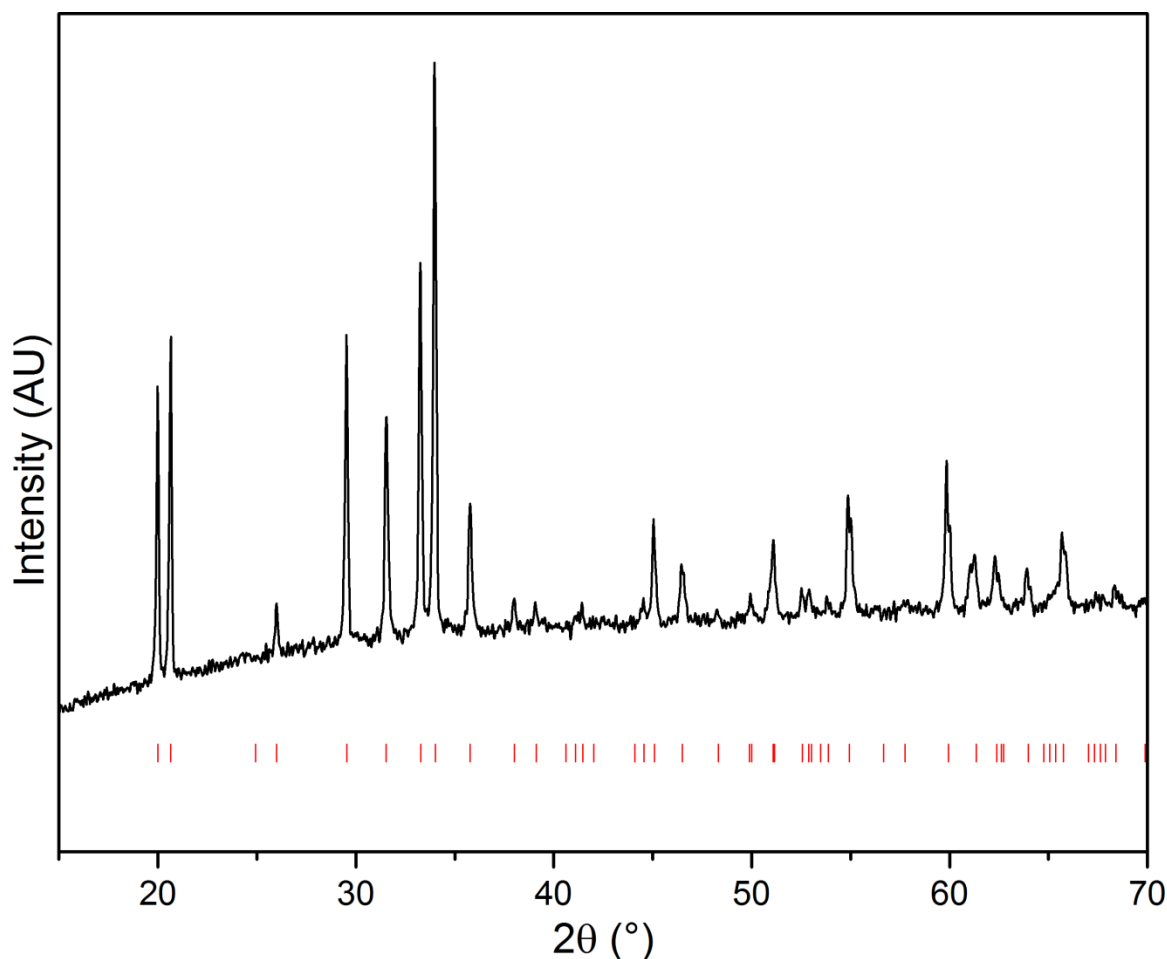


Figure 5.1 PXD of pure β -NaFeO₂ synthesized at 1000 °C in air, red ticks represent expected reflections of pure phase.

The resulting powders were analyzed using ICP to ensure the metal ratios were as expected in the initial stoichiometry and that there was no loss of sodium due to the high temperature sintering. After ICP confirmation, Le Bail fit using GSAS was performed to determine cell parameters of the cobalt doped β -NaFeO₂ compounds as seen in Figures 5.2-5.5 and Table 5.3.

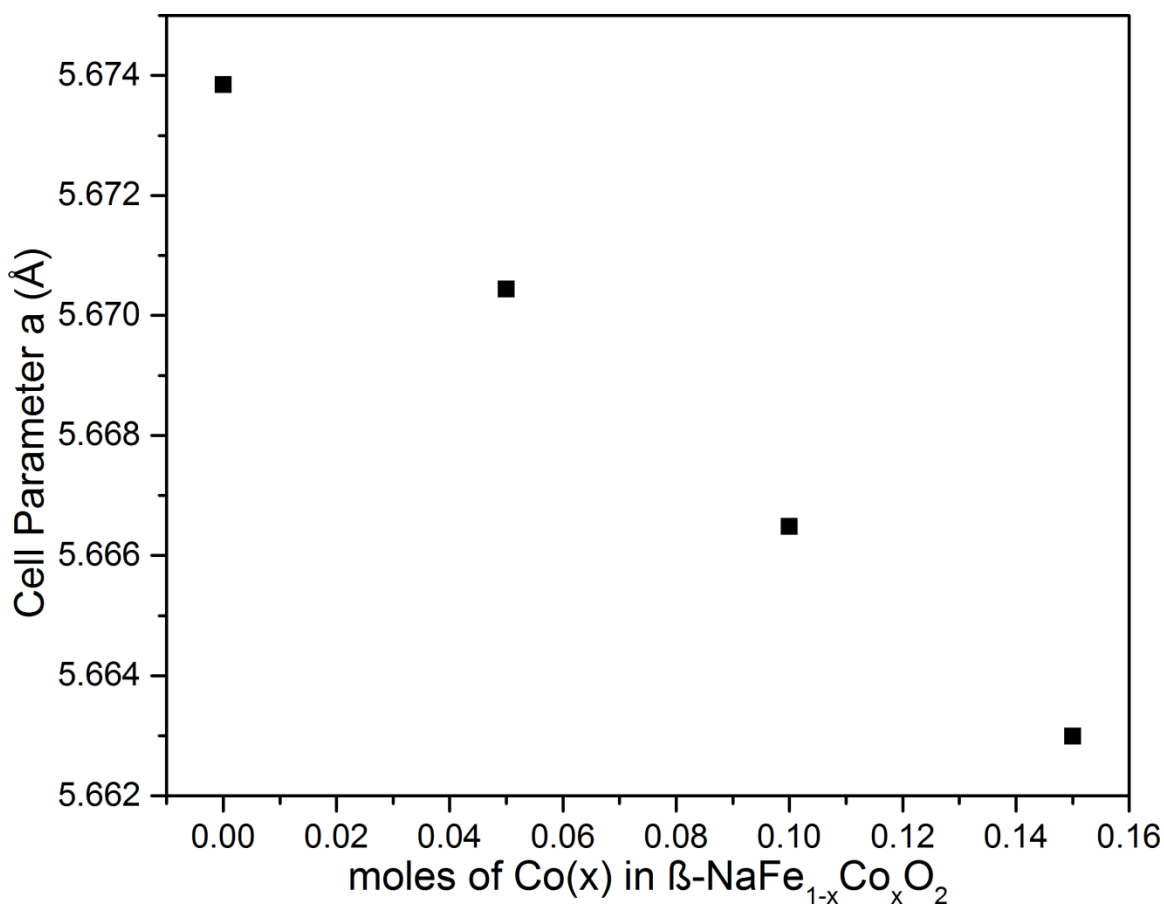


Figure 5.2 Cell parameter a of β -NaFeO₂ as a function of cobalt doping.

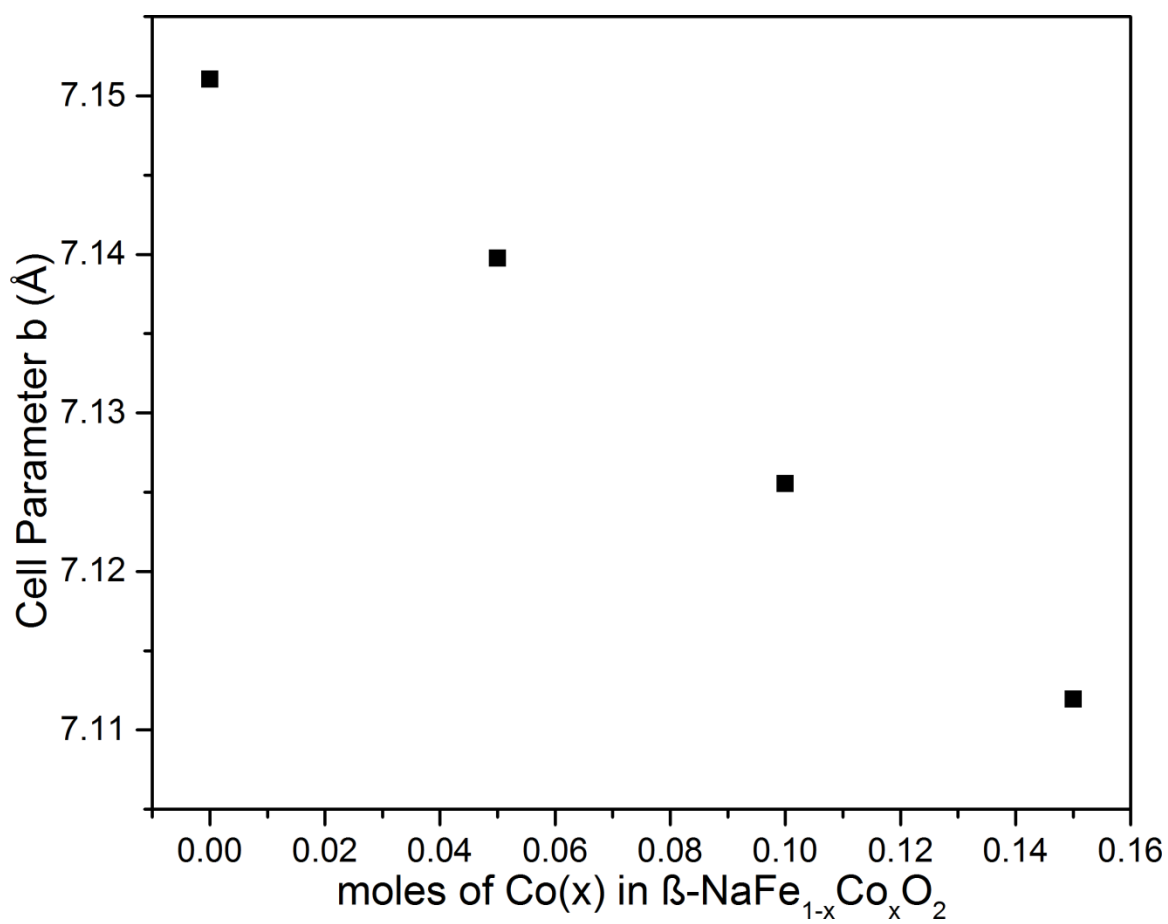


Figure 5.3 Cell parameter b of $\beta\text{-NaFeO}_2$ as a function of cobalt doping.

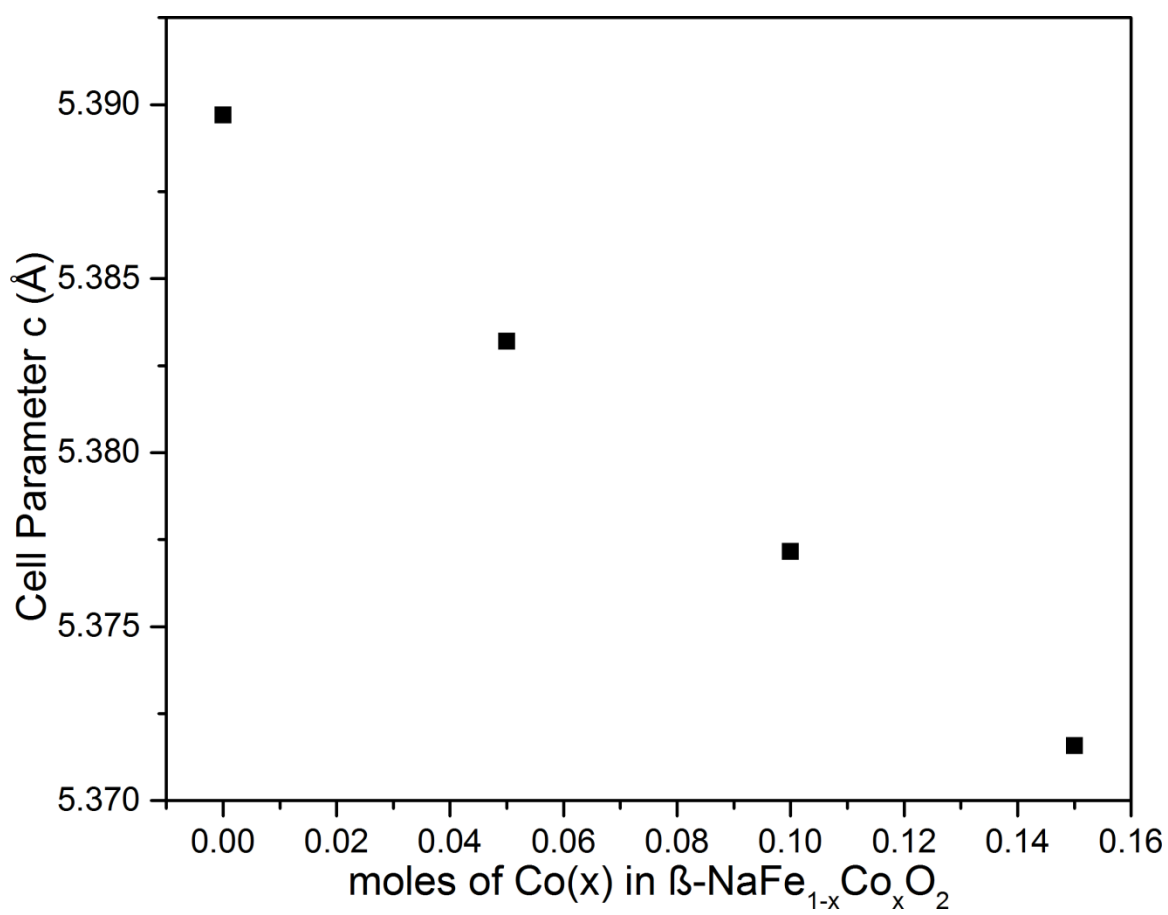


Figure 5.4 Cell parameter c of $\beta\text{-NaFeO}_2$ as a function of cobalt doping.

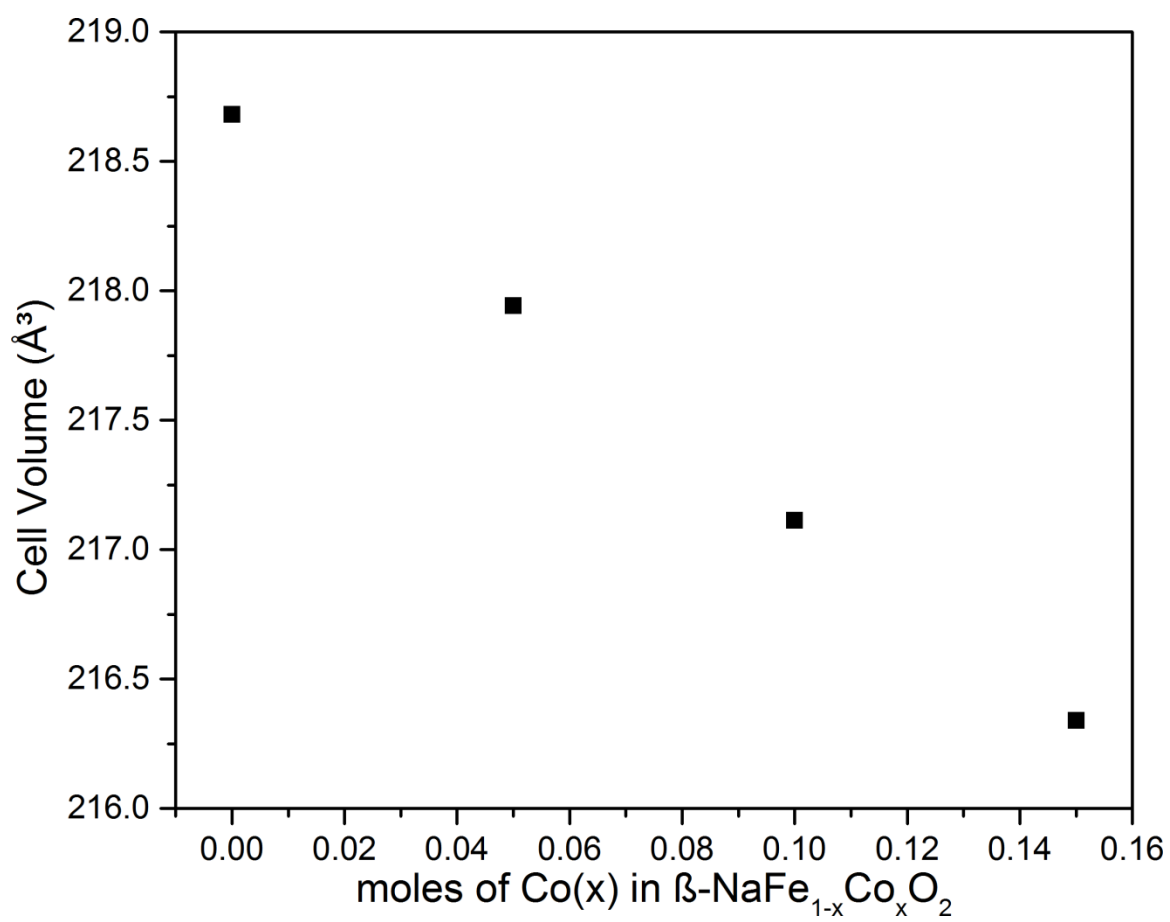


Figure 5.5 Cell volume of $\beta\text{-NaFeO}_2$ as a function of cobalt doping.

Table 5.3 Cell parameters and volume of cobalt doped β -NaFeO₂ determined from Le Bail fit.

(x) β -NaFe _{1-x} Co _x O ₂	Cell parameter a (Å)	Cell Parameter b (Å)	Cell Parameter c (Å)	Cell Volume (Å ³)
0.00	5.6739	7.1511	5.3897	218.68
0.05	5.6704	7.1398	5.3832	217.94
0.10	5.6665	7.1256	5.3772	217.11
0.15	5.6630	7.1120	5.3716	216.34

The resulting Le Bail fits of $\beta\text{-NaFe}_{1-x}\text{Co}_x\text{O}_2$ established a linear relationship between the cell parameters and the amount of cobalt doped into the $\beta\text{-NaFeO}_2$ structure. After it was determined the $\beta\text{-NaFe}_{1-x}\text{Co}_x\text{O}_2$ samples were pure, lithium for sodium ion exchange was performed. The melting points of LiNO_3 and NaNO_3 are 255°C and 308°C respectively, therefore increasing to a temperature greater than 308°C would minimize the time at which the ion exchange would occur. Because the resulting phase is not the most thermodynamically stable form of LiFeO_2 , determining the lowest temperature at which the ion exchange will occur was established using TGA-DSC as seen in Figure 5.6.

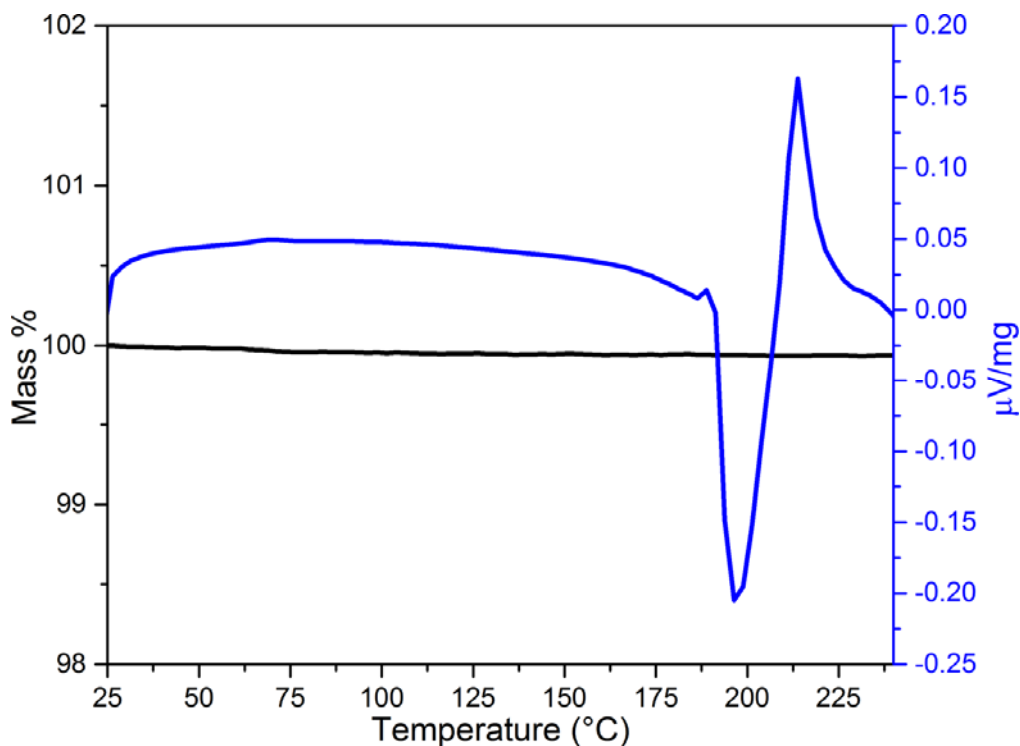


Figure 5.6 Thermogravimetric analysis (black) and differential scanning calorimetry (blue) of the lithium for sodium ion exchange. The endothermic peak begins at about 90°C and exothermic peak at about 212°C , (exothermic is positive $\mu\text{V/mg}$), are indicative of melting and ionic diffusion respectively.

The TGA-DSC indicated no change in mass between room temperature and 240 °C (Figure 5.6), but the DSC did show an endothermic peak at about 190 °C followed by an exothermic peak at about 212 °C. These peaks represent the eutectic melt (endothermic peak at about 190 °C) of LiNO₃/NaNO₃ and the lithium for sodium ion exchange occurring (exothermic peak at 212 °C). With the temperature of the ion exchange established to be about 212 °C, all of the ion exchanges performed on β-NaFe_{1-x}CoxO₂ were performed at 225 °C.

As previously mentioned, after the ion exchange, the resulting melt was washed repeatedly with methanol to remove the excess LiNO₃ and produced NaNO₃ (Equation 5.1).

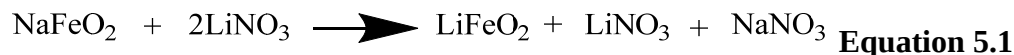


Figure 5.7 illustrates the formation of NaNO₃ from the ion exchange. The sample was briefly washed to remove the excess LiNO₃, which readily dissolved and washed away, while the NaNO₃ required multiple washings to completely remove.

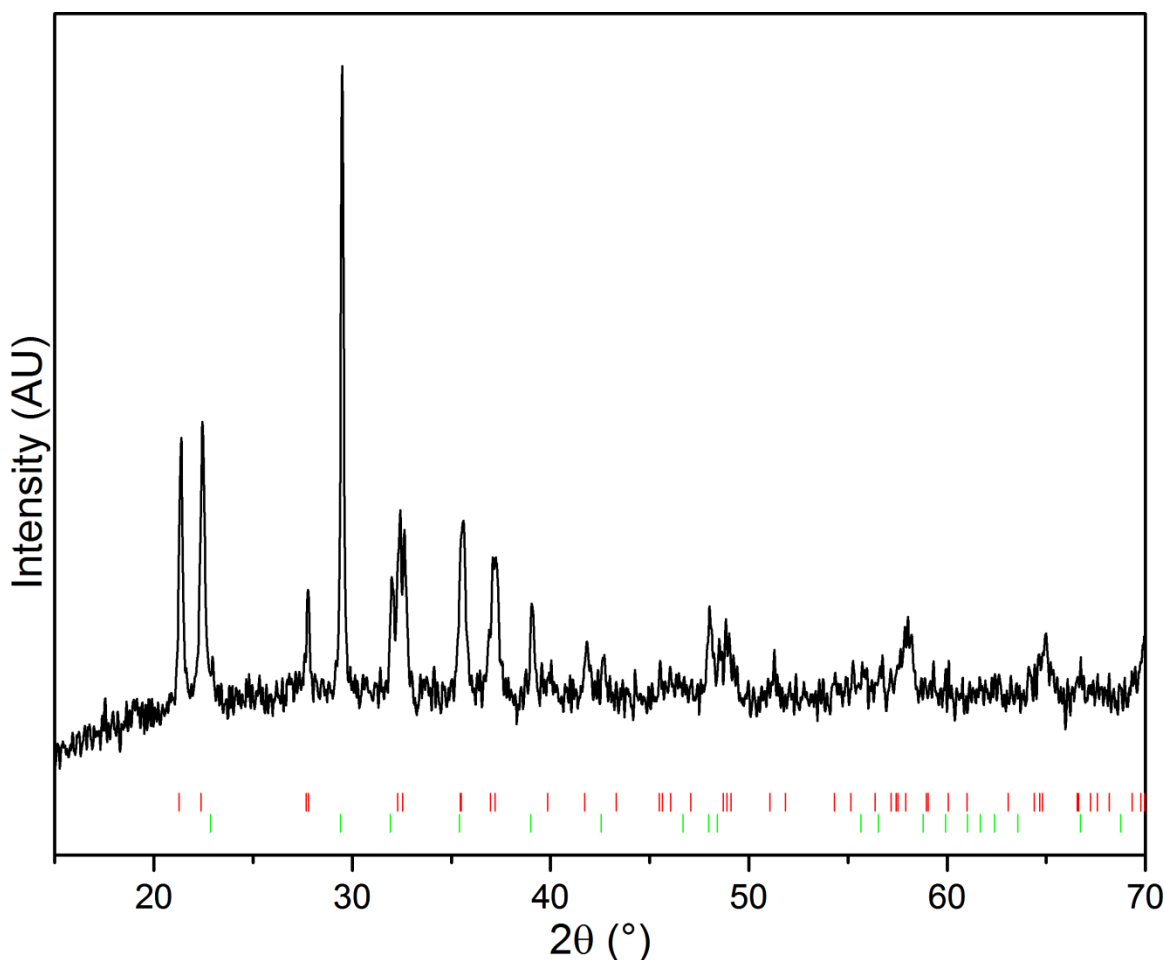


Figure 5.7 PXD of the unwashed lithium for sodium ion exchange of β -NaFeO₂ and LiNO₃ to produce LiFeO₂ (red tick marks) and NaNO₃ (green tick marks).

After the produced NaNO₃ and excess LiNO₃ were completely removed, PXD and ICP were performed to establish phase purity and elemental analysis respectively. It was immediately apparent that the resulting compound T-LiFe_{0.85}Co_{0.15}O₂ was impure by PXD due to the appearance of peak reflections from LiCoO₂ with the α -NaFeO₂ layered structure type. Le Bail fits were then performed to determine the cell parameters of the cobalt doped T-LiFeO₂ compound as seen in Figure 5.8-5.11 and Table 5.4.

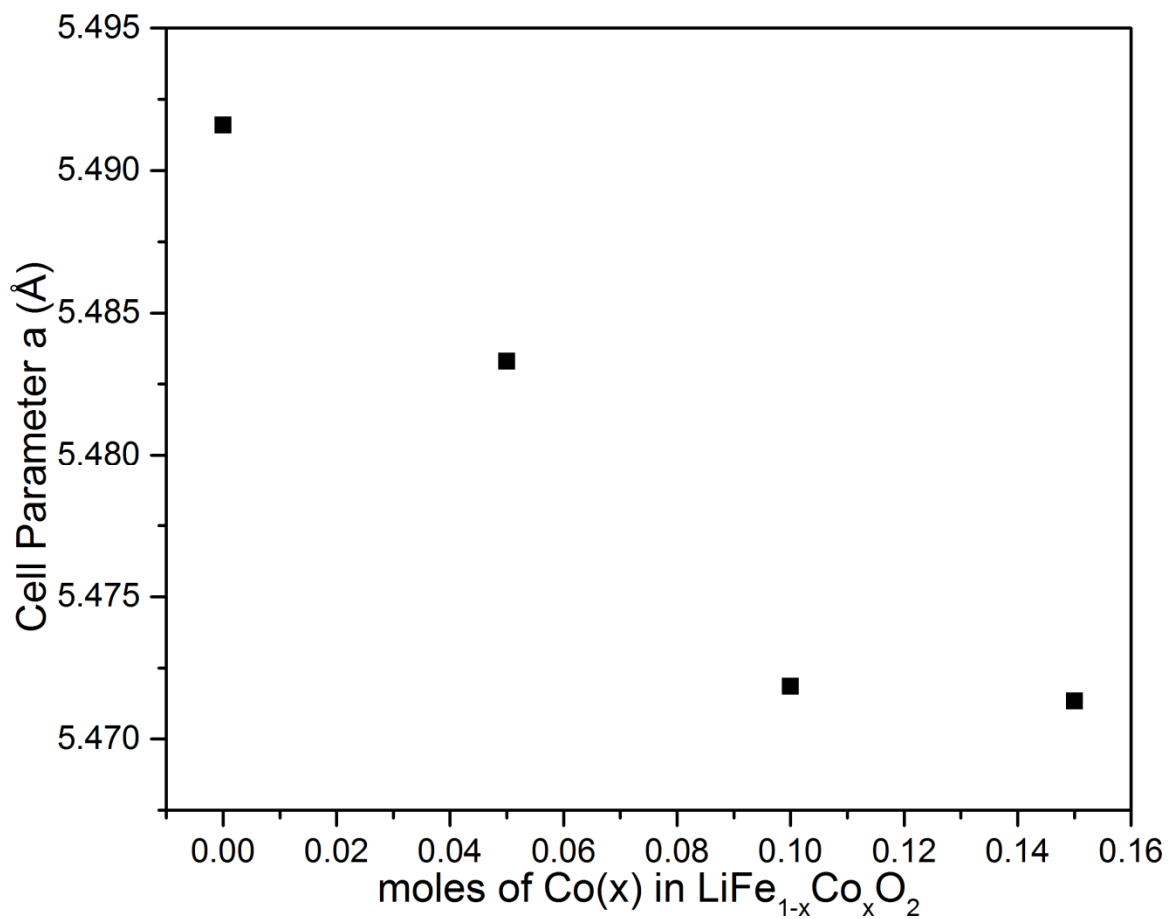


Figure 5.8 Cell parameter a of T-LiFeO₂ as a function of cobalt doping.

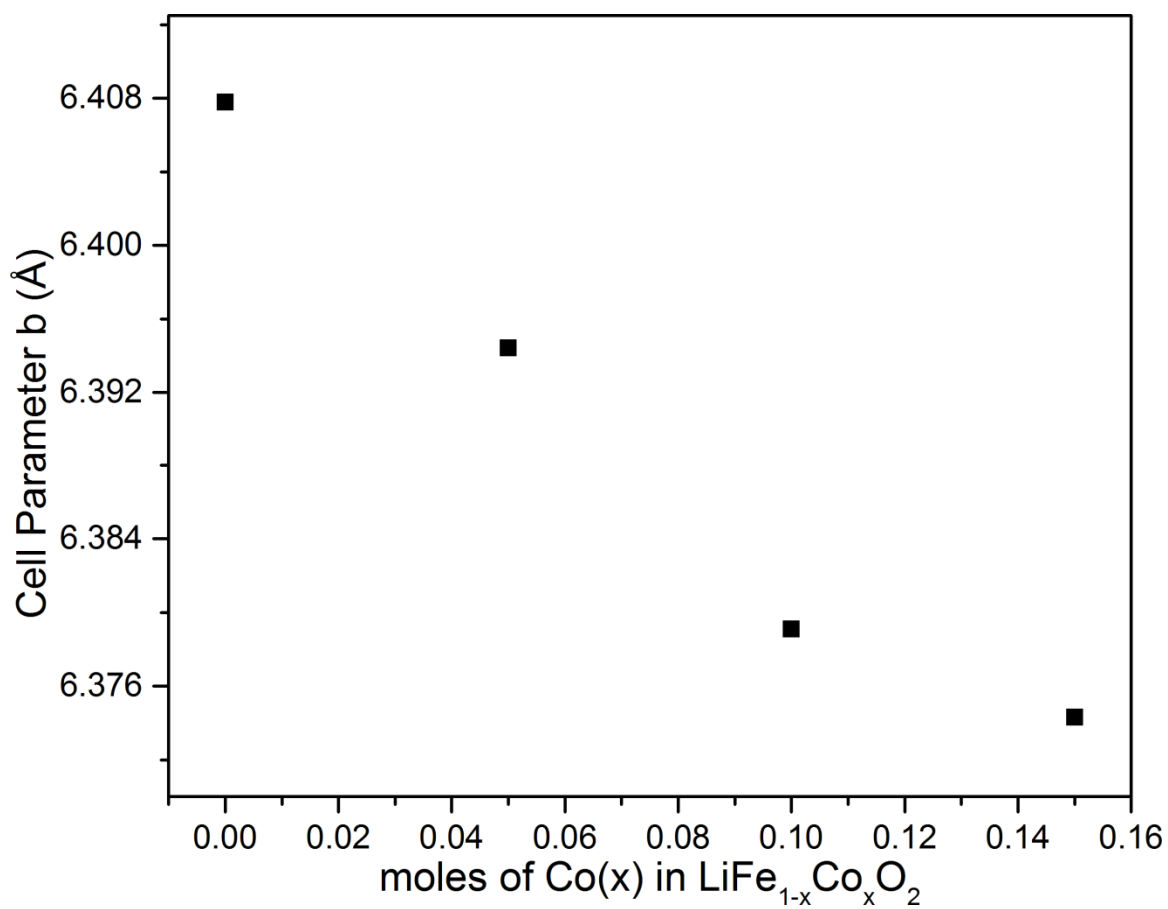


Figure 5.9 Cell parameter b of T- LiFeO_2 as a function of cobalt doping.

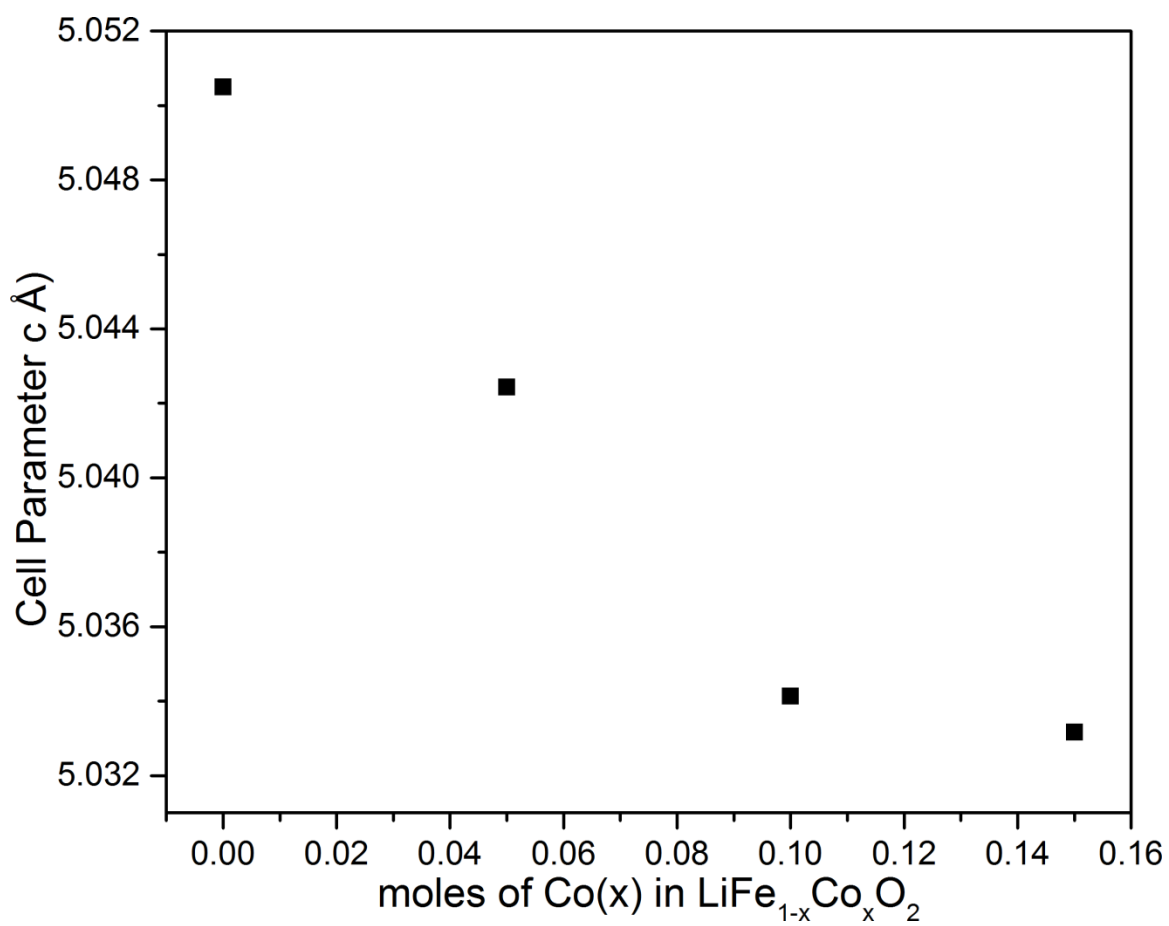


Figure 5.10 Cell parameter c of T-LiFeO₂ as a function of cobalt doping.

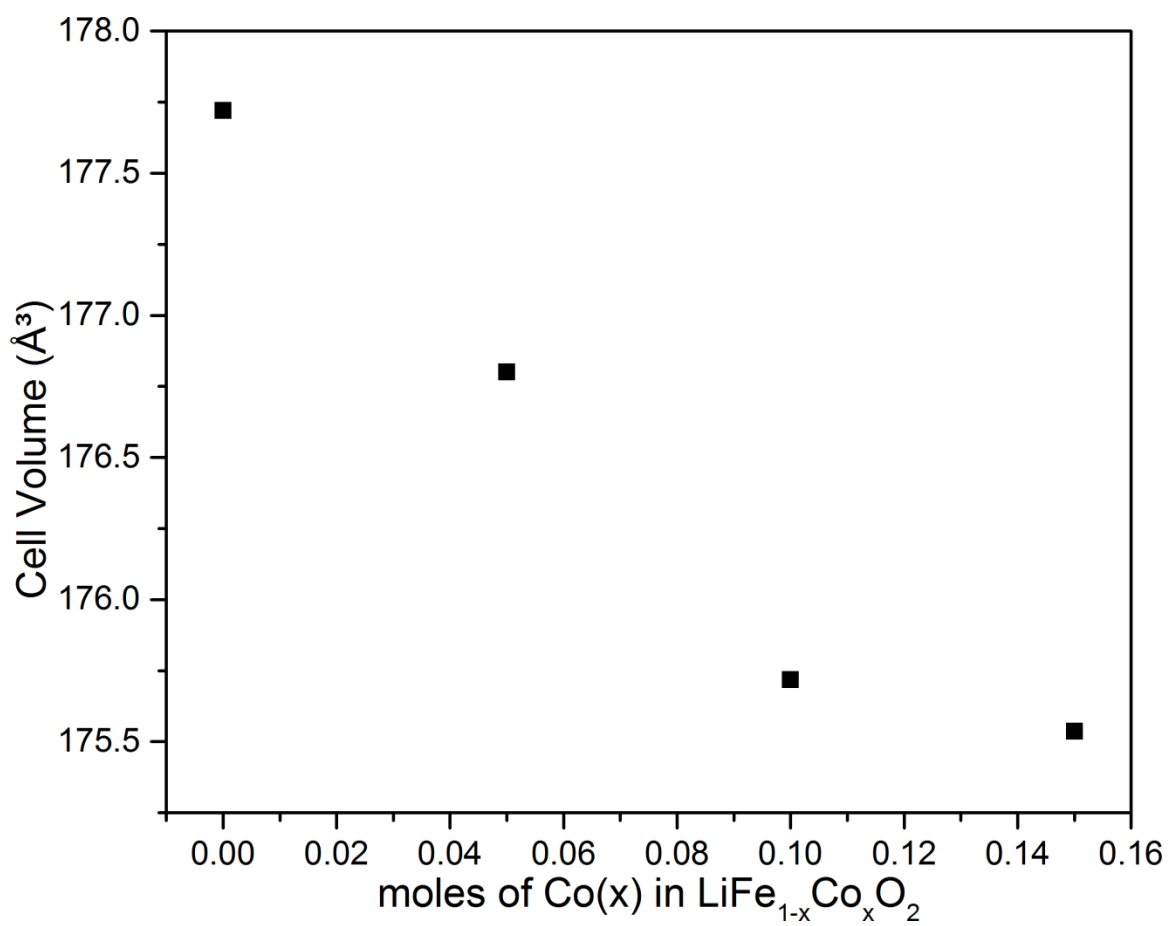


Figure 5.11 Cell volume of T-LiFeO₂ as a function of cobalt doping.

Table 5.4 Cell parameters and volume of cobalt doped T-LiFeO₂ determined from Le Bail fit.

(x) T-Li _{1-x} Co _x O ₂	Cell parameter <i>a</i> (Å)	Cell Parameter <i>b</i> (Å)	Cell Parameter <i>c</i> (Å)	Cell Volume (Å ³)
0.00	5.4916	6.4078	5.0505	177.72
0.05	5.4833	6.3944	5.0424	176.80
0.10	5.4719	6.3791	5.0341	175.72
0.15	5.4713	6.3743	5.0332	175.54

The resulting Le Bail fits of $\text{T-LiFe}_{1-x}\text{Co}_x\text{O}_2$ established a linear relationship between the cell parameters and the amount of cobalt doped into the T-LiFeO_2 structure. This linear trend was true through 0.10 parts per formula unit of cobalt, at which point the trend subsided. This is due to the maximum cobalt concentration in the solid solution; therefore, leading to an impurity, which as previously stated, was determined by PXD to be LiCoO_2 with the $\alpha\text{-NaFeO}_2$ layered structure type.

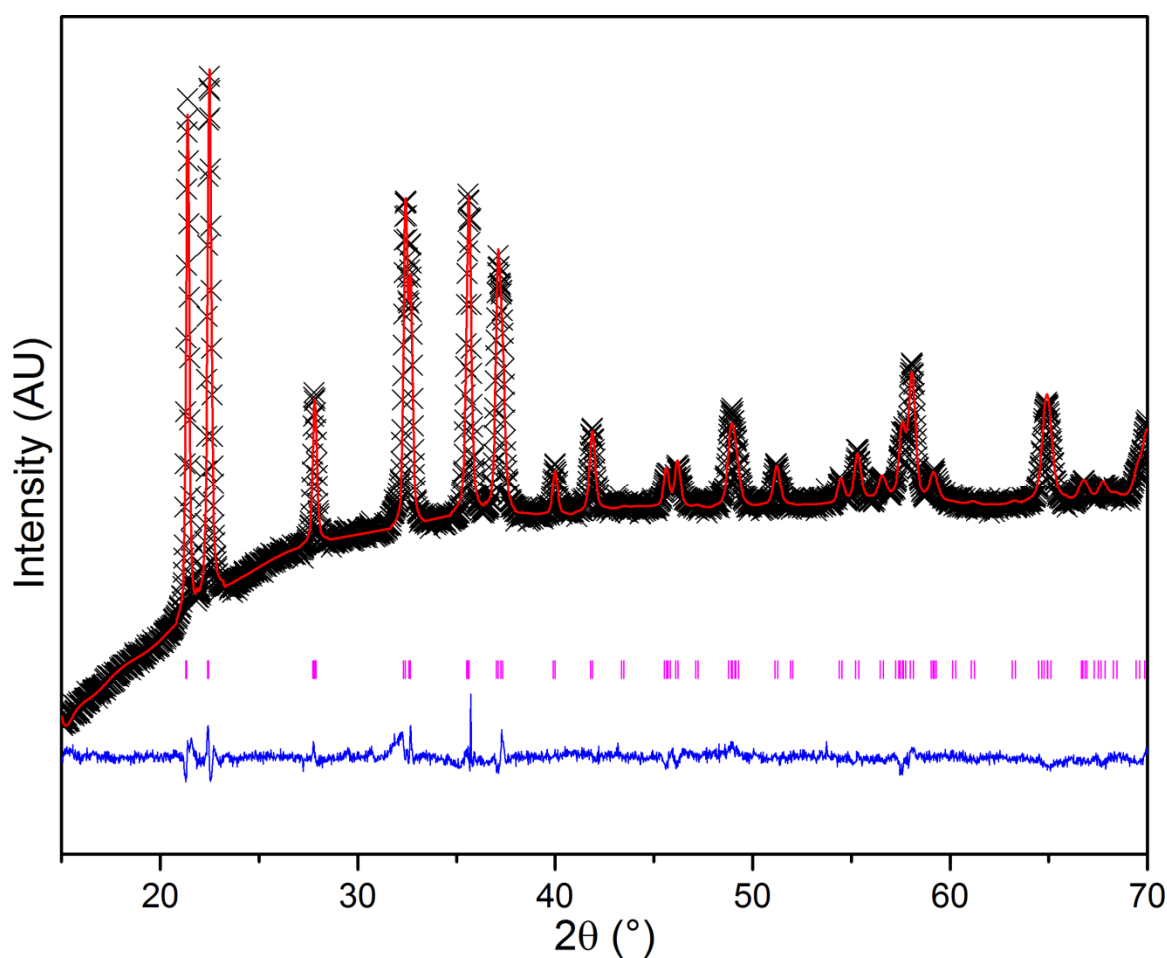


Figure 5.12 PXD and Rietveld refinement of LiFeO_2 $R_{wp}=1.49$. Observed (black crosses), calculated (solid red line), difference (solid blue line) profiles, and Bragg reflections (tick marks) for the final.

T-LiFeO₂ was previously reported [20] through back-to-back ion exchanges using ten equivalents of LiCl with β -NaFeO₂ at 160 °C. The resulting structure was determined from synchrotron data. Ion exchange performed within, though at a higher temperature than previously reported, only required one exchange.

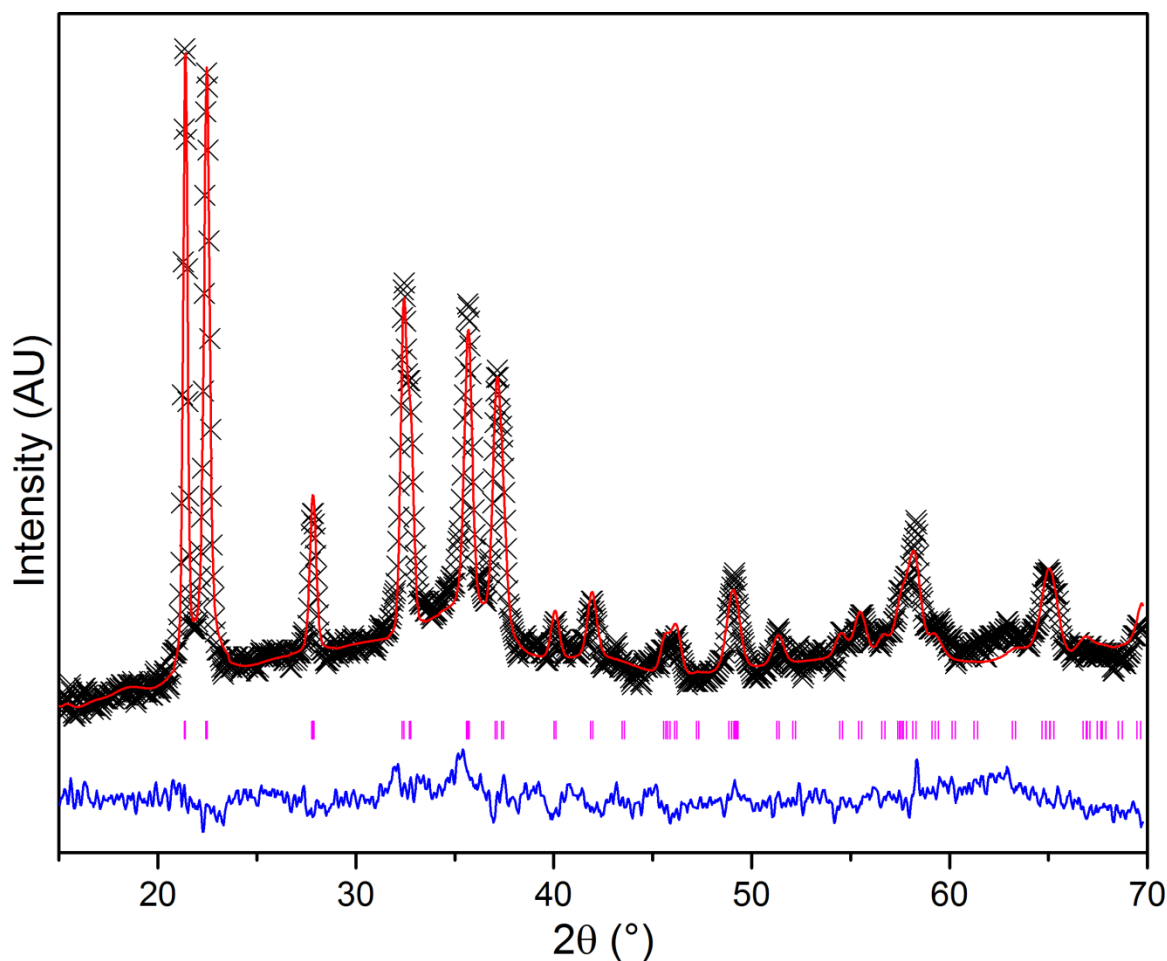


Figure 5.13 Rietveld Refinement of PXD Li_{0.57}FeO₂ Rwp=3.90. Observed (black crosses), calculated (solid red line), difference (solid blue line) profiles, and Bragg reflections (tick marks) for the final Rietveld refinement.

The resulting powder of T-LiFeO₂ was Rietveld refined from laboratory PXD spectra (Figure 5.12). The established cell parameters from the Rietveld refinement of T-LiFeO₂ were determined to be $a=5.4916\text{\AA}$, $b=6.4078\text{\AA}$, and $c=5.0505\text{\AA}$, which was in good agreement with the previously reported data of $a=5.5160\text{\AA}$, $b=6.4139\text{\AA}$, and $c=5.0789\text{\AA}$.

After T-LiFeO₂ was deemed pure by PXD and ICP, chemical lithium intercalation and deintercalation were performed to determine if the structural integrity of the tunnel compound would be maintained through the insertion and removal of a lithium ion. Initial attempts to remove lithium using bromine and iodine in pentane were performed with the resulting powders analyzed by PXD and ICP. ICP indicated only 0.12 and 0.03 parts per formula unit of lithium were removed using bromine and iodine respectively. These results were not surprising because of the relatively low oxidation potentials of bromine and iodine of 4.1 V and 3.5 V respectively. Due to the relatively high oxidation potential of Fe^{3+/4+} with respect to a lithium anode, the oxidizing agent NOBF₄, which has an oxidative potential of 4.7 V with respect to a lithium anode [25], was used. The as prepared sample of T-LiFeO₂ was stoichiometrically added to one-half, one, two, five, and ten times molar equivalents of NOBF₄, dissolved in anhydrous acetonitrile, and stirred for 48 hours at room temperature. The resulting powders were analyzed using PXD and ICP to determine phase purity and elemental analysis. The maximum amount of lithium that was removed from T-LiFeO₂ was determined to be 0.58 parts per formula unit, resulting in the compound Li_{0.42}FeO₂. Rietveld refinement of a sample that was determined to have had 0.43 parts per formula unit removed was performed (Figure

5.13). The established cell parameters from the Rietveld refinement of T-Li_{0.57}FeO₂ were determined to be $a=5.4721\text{\AA}$, $b=6.4073\text{\AA}$, and $c=5.0405\text{\AA}$.

Similarly, sodium deintercalation was performed on β -NaFeO₂ using NOBF₄ to evaluate this tunnel structure for use as a sodium ion battery. PXD, ICP, and TGA were used to determine the structural integrity of β -NaFeO₂ and β -Na_{1-x}FeO₂.

Chemical lithium intercalation was performed with concentrated n-butyllithium as previously described. Surprisingly, the color of the solution of n-butyllithium mixed with T-LiFeO₂ did not instantly change as seen with LiFeTiO₄ [26,27], another iron 3+ compound that instantly changed from a salmon color to black. Nevertheless, the n-butyllithium and T-LiFeO₂ solutions were stirred at room temperature for four days. Daily observations of the mixtures were taken. The mixtures slowly changed from the initial salmon color to black after about 60 hours. The solutions were allowed to continue to stir for another 36 hours to ensure completion.

The resulting samples were analyzed using PXD and ICP to determine phase purity and elemental analysis. There were no observable peaks of impurities and it was determined by ICP that each sample, the one, five, and ten molar equivalents n-butyllithium, contained the same stoichiometric ratio of lithium to iron of 1.57:1. Synchrotron data was Rietveld refined (Figure 5.14) with the established cell parameters determined to be $a=5.4991\text{\AA}$, $b=6.4090\text{\AA}$, and $c=5.0540\text{\AA}$. The slight decrease in cell parameters when lithium was removed and increase in cell parameters when lithium was inserted correlate well with the expected structure changes as a function of lithium content.

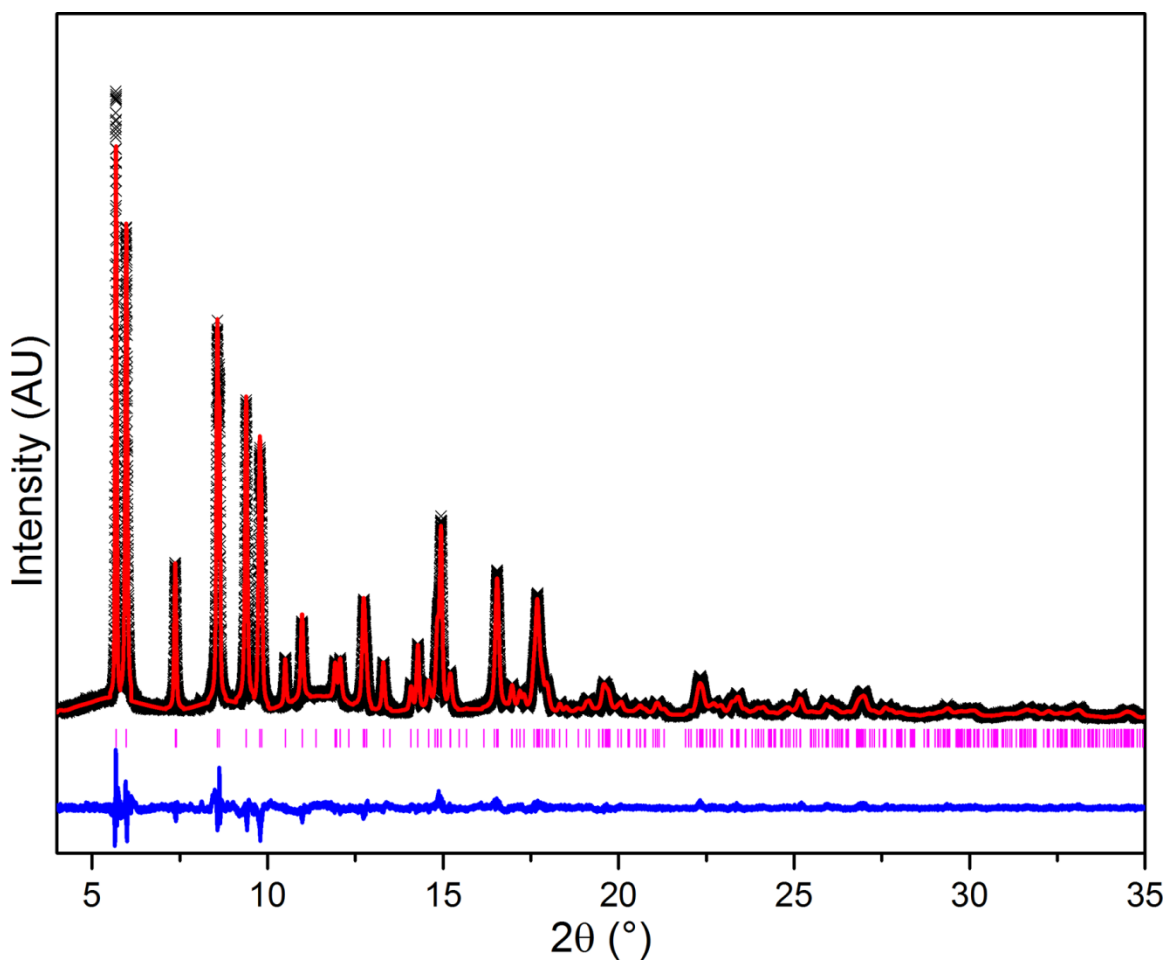


Figure 5.14 Synchrotron diffraction of $\text{Li}_{1.57}\text{FeO}_2$ $R_{\text{wp}}=5.73$ and $\chi^2=1.969$. Observed (black crosses), calculated (solid red line), difference (solid blue line) profiles, and Bragg reflections (tick marks) for the final Rietveld refinement.

After the $\beta\text{-NaFe}_{1-x}\text{Co}_x\text{O}_2$ and $\text{T-Li}_x\text{FeO}_2$ compounds were determined to be monophasic further analysis using TGA was performed.

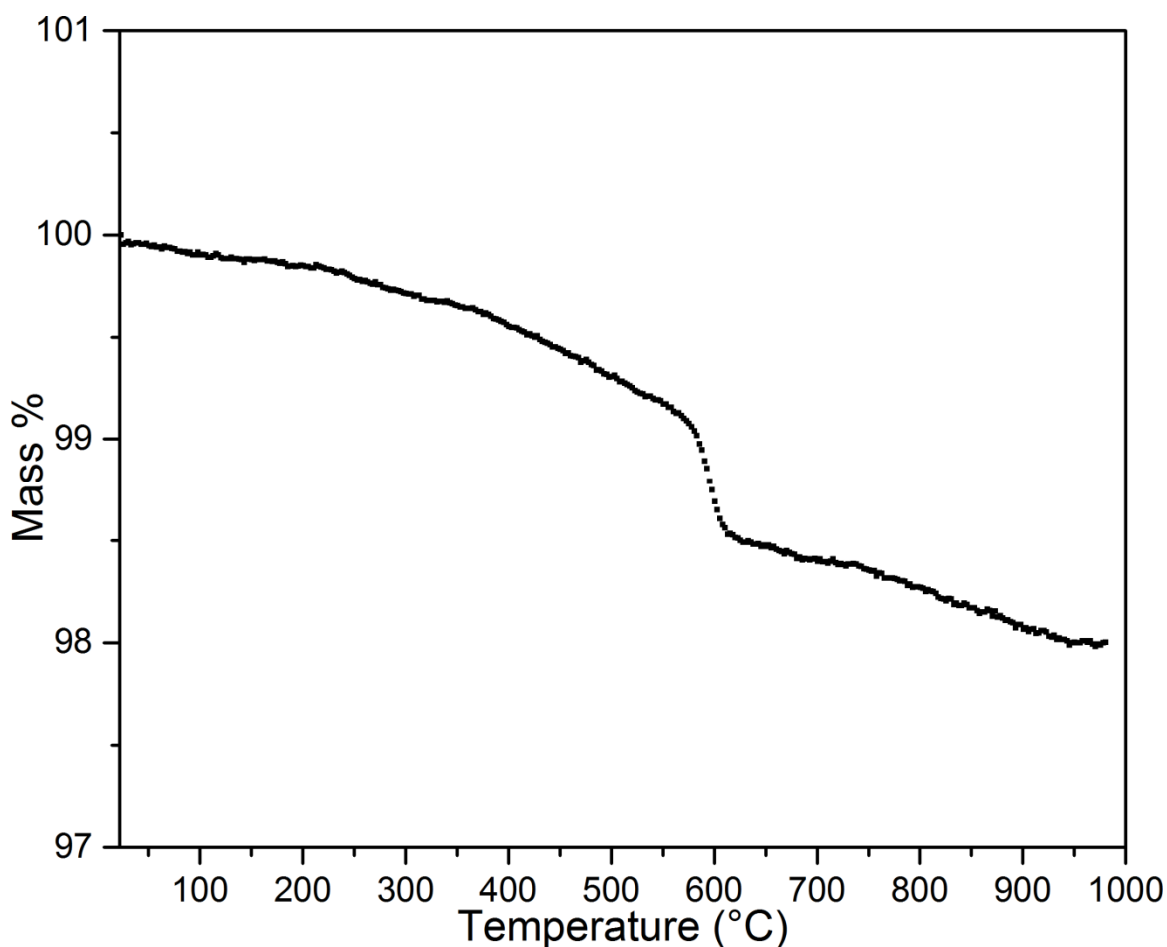


Figure 5.15 Thermogravimetric analysis of T-LiFeO₂ in oxygen up to a final temperature of 1000 °C.

Thermogravimetric analysis of T-LiFeO₂ was performed up to a final temperature of 1000 °C in oxygen. The TGA exhibited a steady mass loss until about 600 °C, where a drop of about 0.75% was observed (Figure 5.15). The mass then continued to decrease slowly until it began to plateau at about 950 °C and the final mass loss was 2 % of the initial mass. The sudden mass loss at 600 °C is due to lithium volatility and oxygen loss

during the reorganization of the elements because of the transformation of T-LiFeO₂ to the thermodynamically stable α -LiFeO₂.

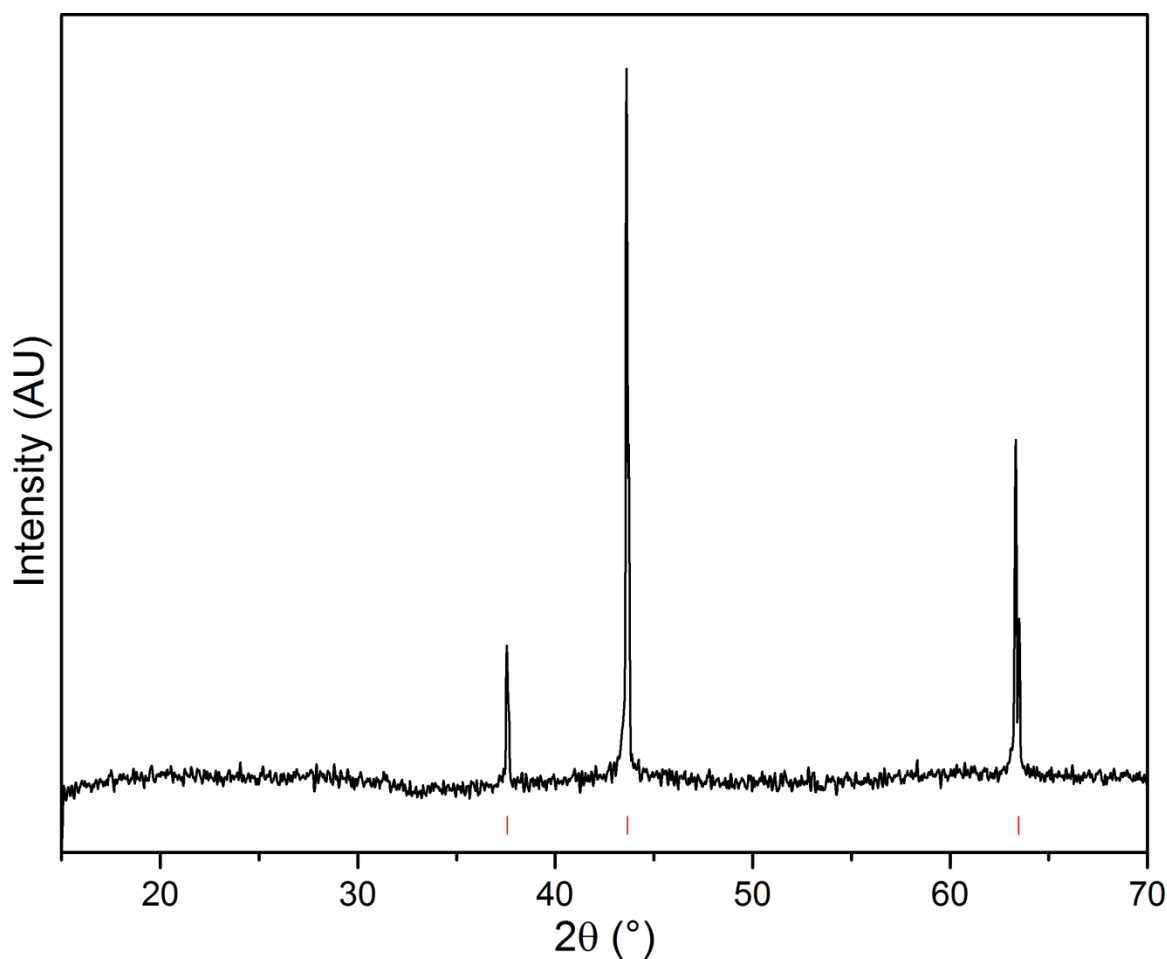


Figure 5.16 PXD of the resulting powder from the oxygen TGA of T-LiFeO₂ red ticks, are indicative α -LiFeO₂ with the rock-salt structure.

The resulting PXD from the oxygen TGA to 1000 °C, (Figure 5.16), illustrates the product α -LiFeO₂ transformation from the kinetically stable T-LiFeO₂.

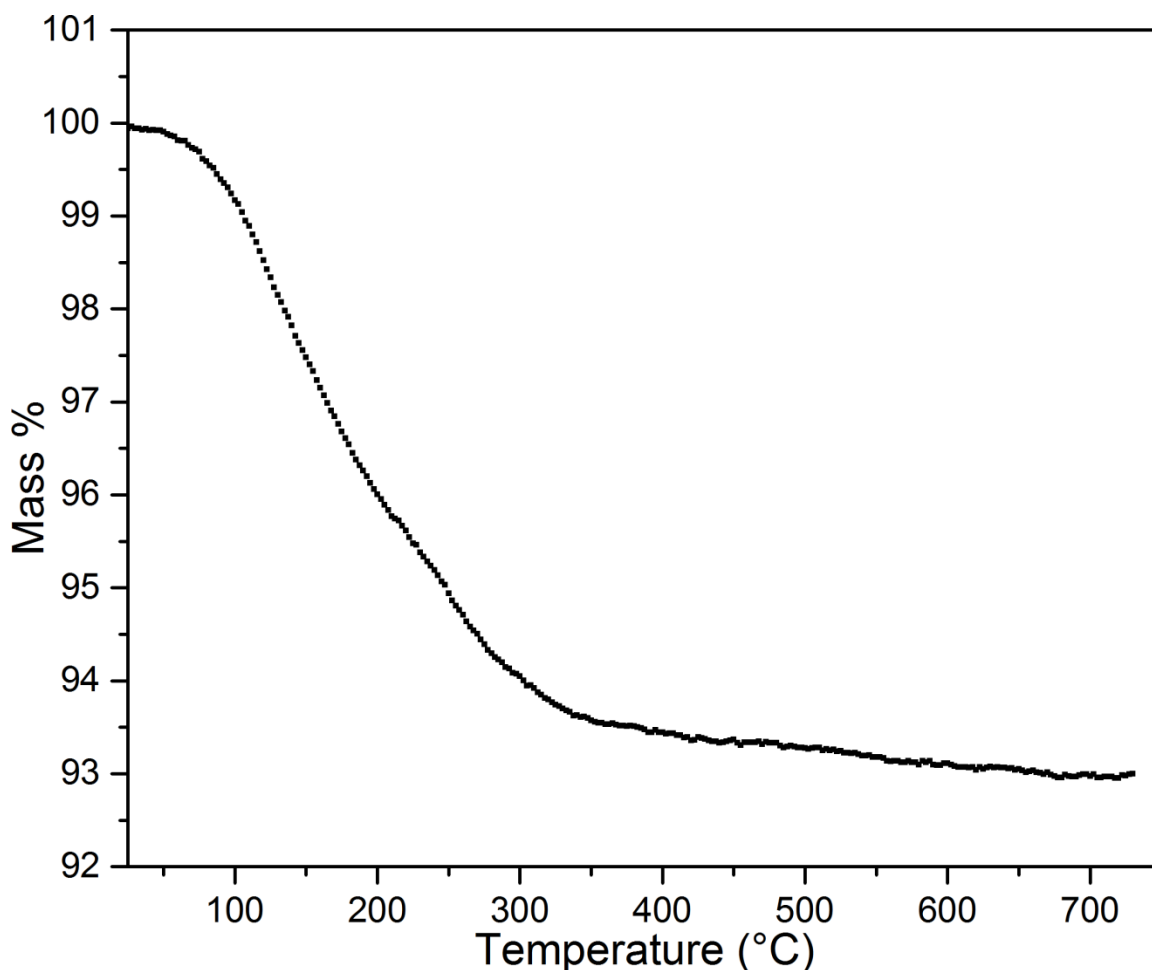


Figure 5.17 Thermogravimetric analysis of $\text{Li}_{0.42}\text{FeO}_2$ in oxygen up to a final temperature of 725 °C.

The thermogravimetric analysis of $\text{Li}_{0.42}\text{FeO}_2$ in oxygen resulted in stability up to about 75 °C (Figure 5.17), at which point the compound began to decompose until about 350 °C where the mass loss essentially plateaued after 400 °C. The powder was then analyzed by PXD (Figure 5.18), and determined to have transformed into $\text{Fe}_{0.873}(\text{Li}_{0.365}\text{Fe}_{1.2915})\text{O}_4$. $\text{Fe}_{0.873}(\text{Li}_{0.365}\text{Fe}_{1.2915})\text{O}_4$ is a spinel structure compound similar to LiMn_2O_4 . These results illustrate nicely that the lithium deficient compound that resulted from the oxygen TGA

is different from the non-lithium deficient starting phase T-LiFeO₂, (Figures 5.16 and 5.18), further confirming the success of the lithium removal using NOBF₄.

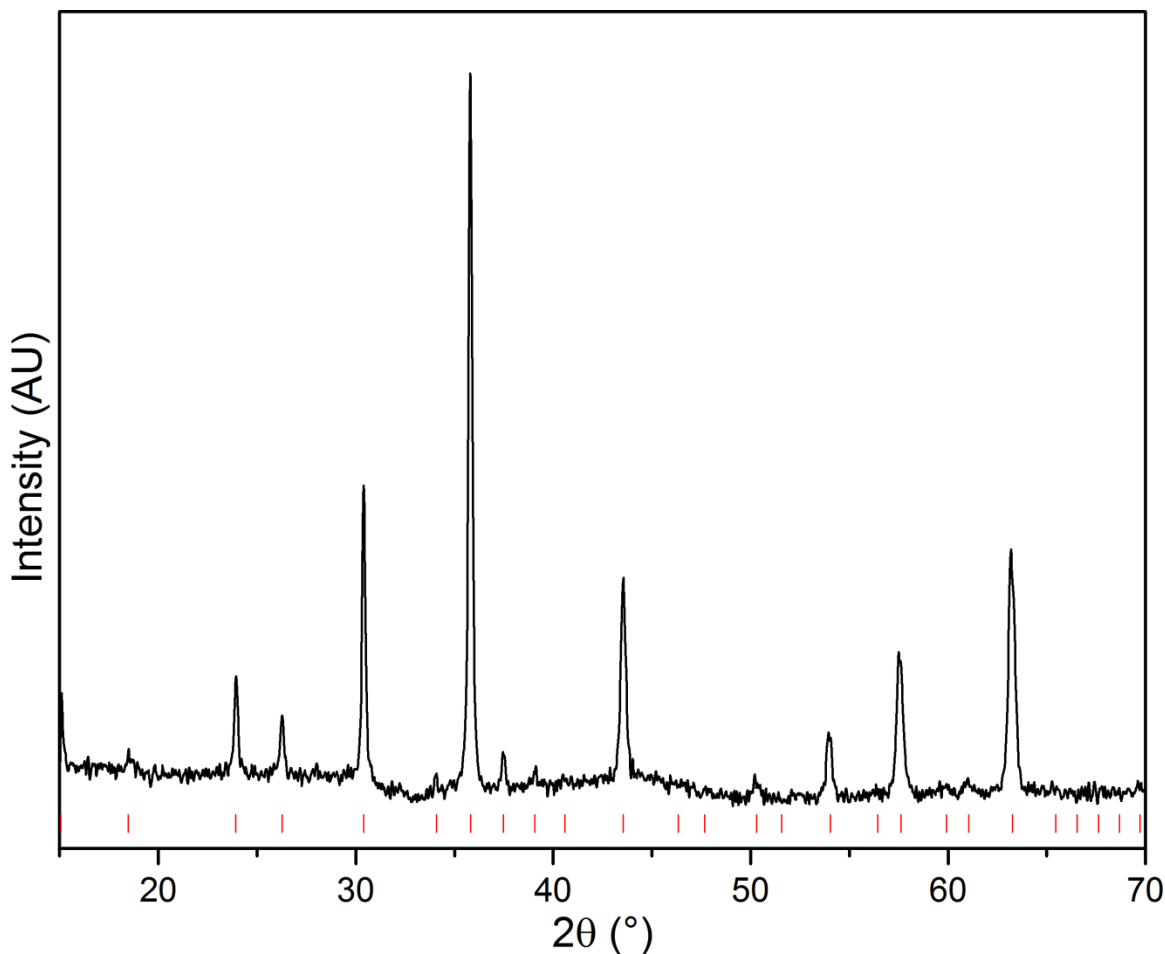


Figure 5.18 PXD of the resulting powder from of Li_{0.42}FeO₂ after TGA in oxygen, red ticks are indicative of the compound Fe_{0.873}(Li_{0.365}Fe_{1.2915})O₄.

Nitrogen TGA of T-LiFeO₂ up to 1000 °C (Figure 5.19), showed results similar to the oxygen TGA with a 2 % mass loss. The resulting PXD (Figure 5.20) was unlike the PXD that resulted from the oxygen TGA experiment. The resulting PXD from the nitrogen TGA was indicative of a structure that is likely to be lithium doped Fe₃O₄.

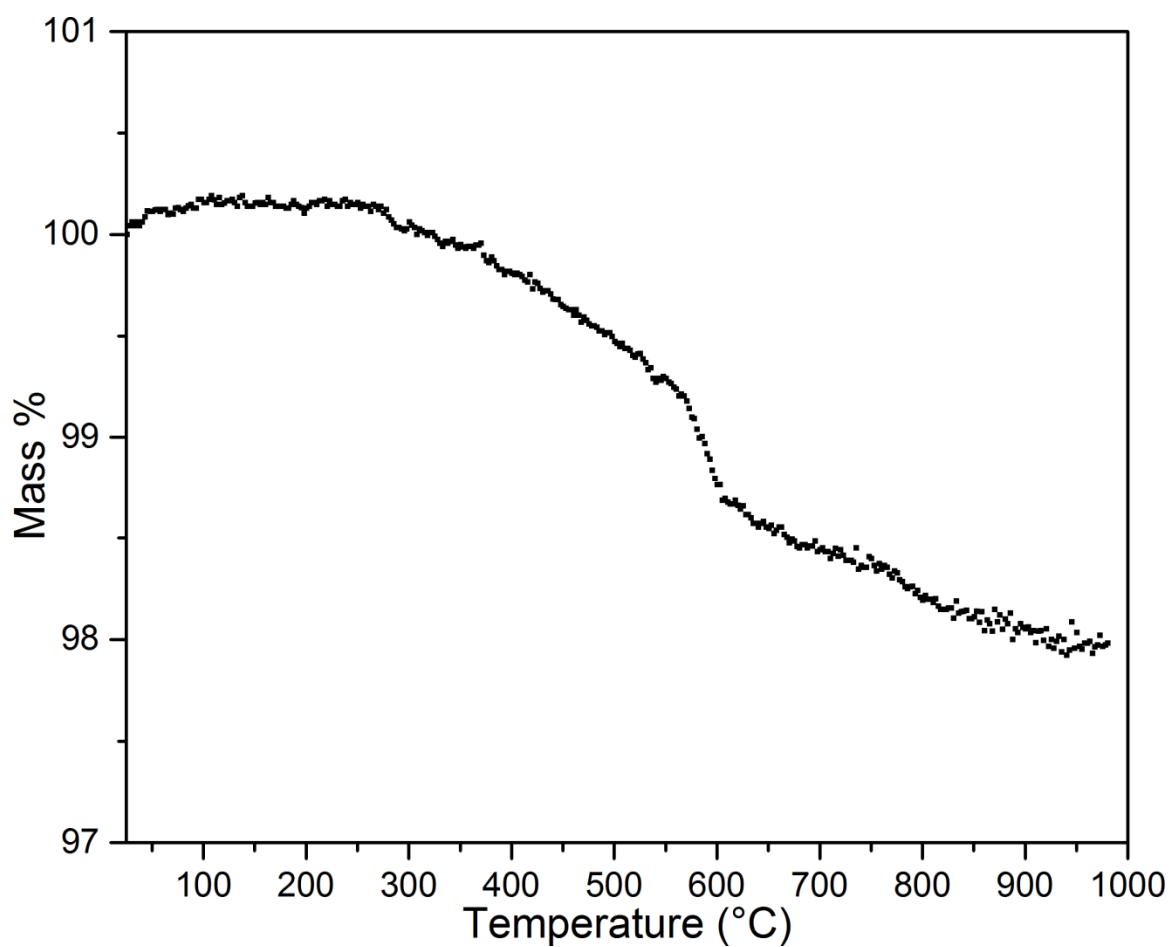


Figure 5.19 Thermogravimetric analysis of T-LiFeO₂ in nitrogen up to a final temperature of 1000 °C with a final mass loss of about 2 %.

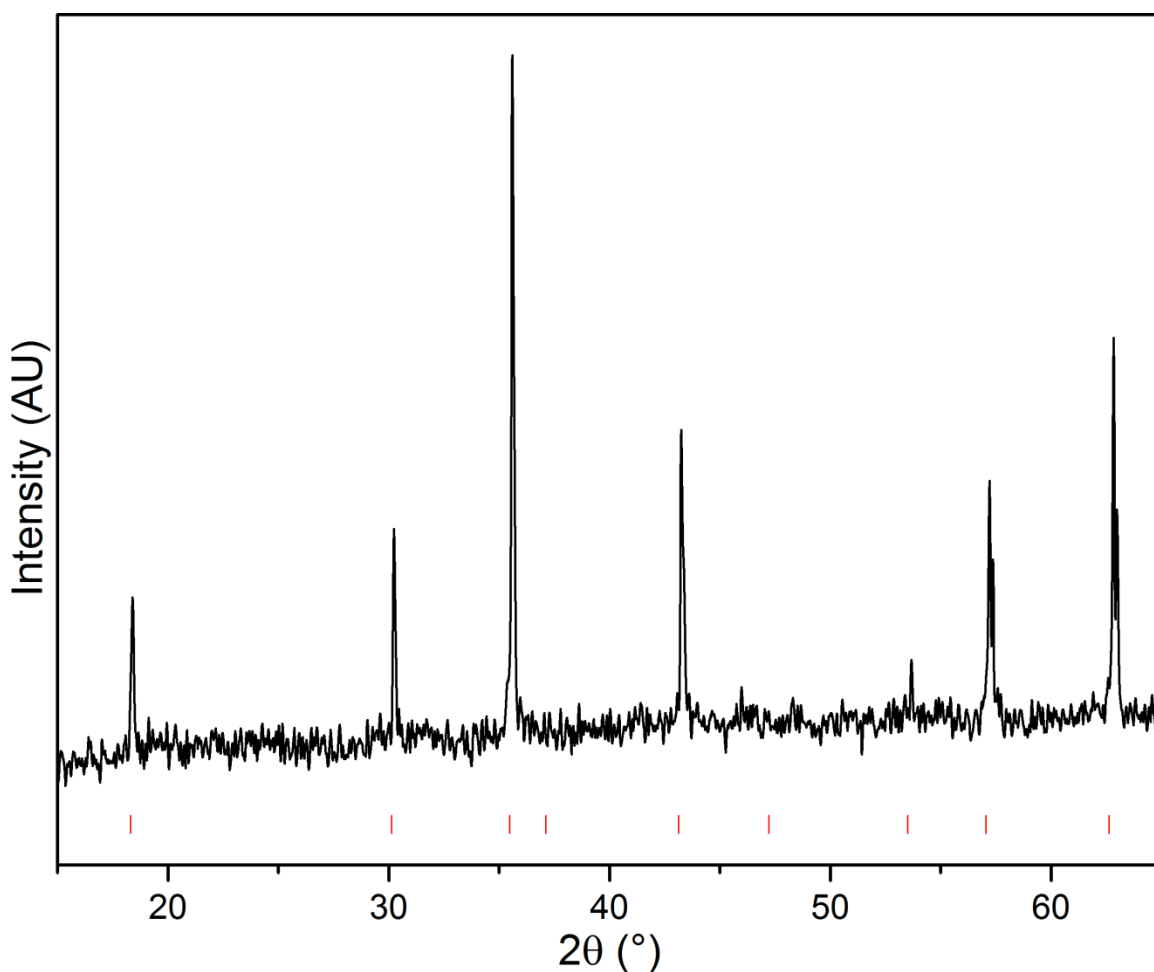


Figure 5.20 PXD of the resulting powder from the nitrogen TGA of T-LiFeO₂, red ticks are indicative Fe₃O₄, but is likely to be lithium doped Fe₃O₄.

Evaluating β -NaFeO₂ for the purpose of determining whether the compound might decompose at elevated temperatures during cycling was then performed by ICP and PXD. β -NaFeO₂ was synthesized at 1000 °C as previously mentioned, therefore its thermodynamic and structural stability are known to be stable. The issue at hand was whether or not β -Na_{1-x}FeO₂ was also stable at elevated temperatures. Electrochemical cycling at elevated temperatures generally means 50 °C and 100 °C, therefore analysis of

the resulting compounds after heating were evaluated. Figure 5.21 is the thermogravimetric analysis of β -NaFeO₂ under nitrogen flow up to 250 °C illustrating the relatively stable mass.

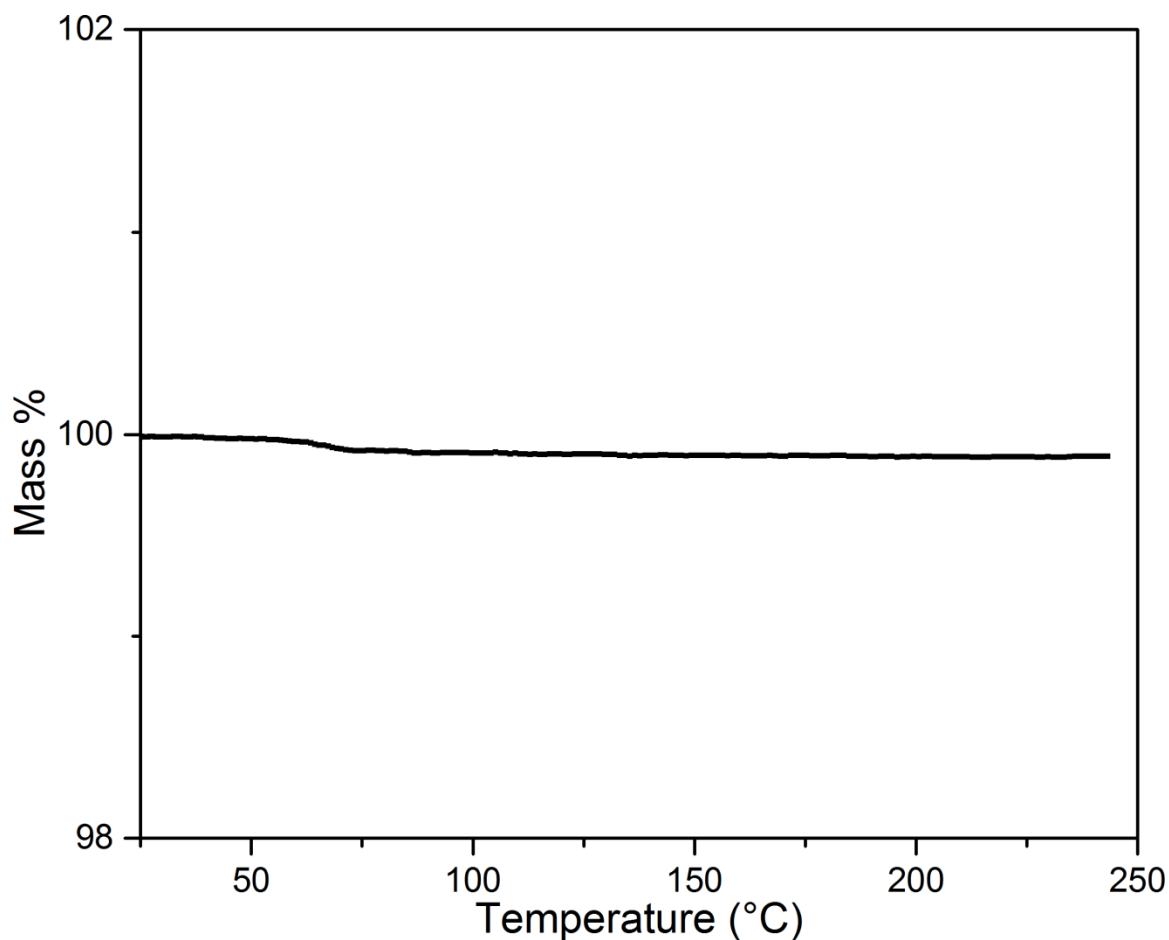


Figure 5.21 Thermogravimetric analysis of β -NaFeO₂ in nitrogen to a final temperature of 250 °C for analysis to determine structural stability for high temperature electrochemical cycling.

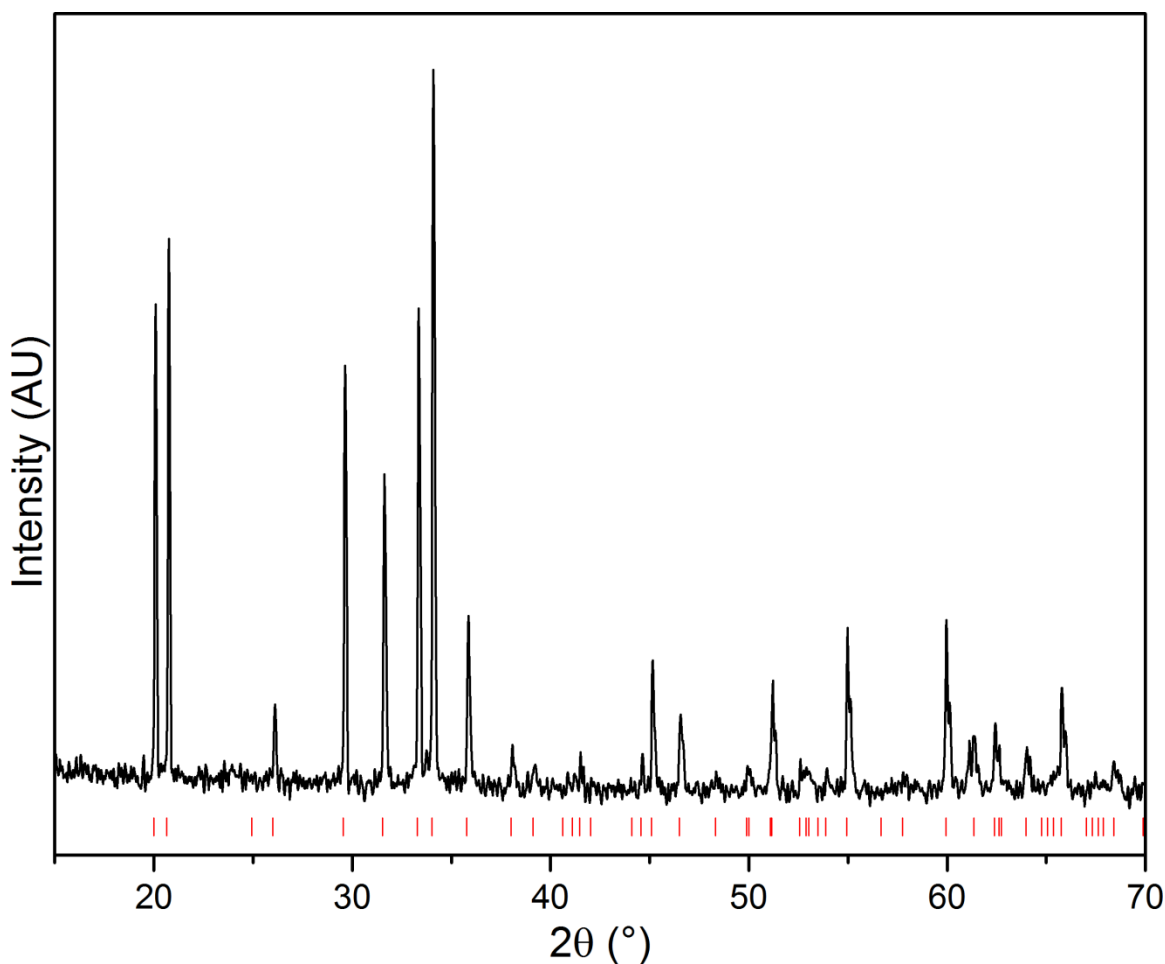


Figure 5.22 PXD of the resulting powder from the nitrogen TGA of β -NaFeO₂, red ticks are indicative β -NaFeO₂.

The PXD resulting from the nitrogen TGA to 250 °C, (Figure 5.22), shows conservation of β -NaFeO₂. This indicates the initial structure will not decompose at elevated temperatures, which was initially hypothesized based on the synthetic temperatures required for pure phase.

Thermogravimetric analysis was similarly performed on β -NaFeO₂ under oxygen flow (Figure 5.23), with the same expected results as seen in the nitrogen TGA. Similar to the

nitrogen TGA, there was a slight mass loss in the initial 75 °C. This can be attributed to water absorption, which is common for lithium and sodium containing compounds because they are very hygroscopic. The powder sample, when loaded into the crucible for thermogravimetric analysis, was exposed to ambient conditions briefly, therefore providing the conditions for water absorption.

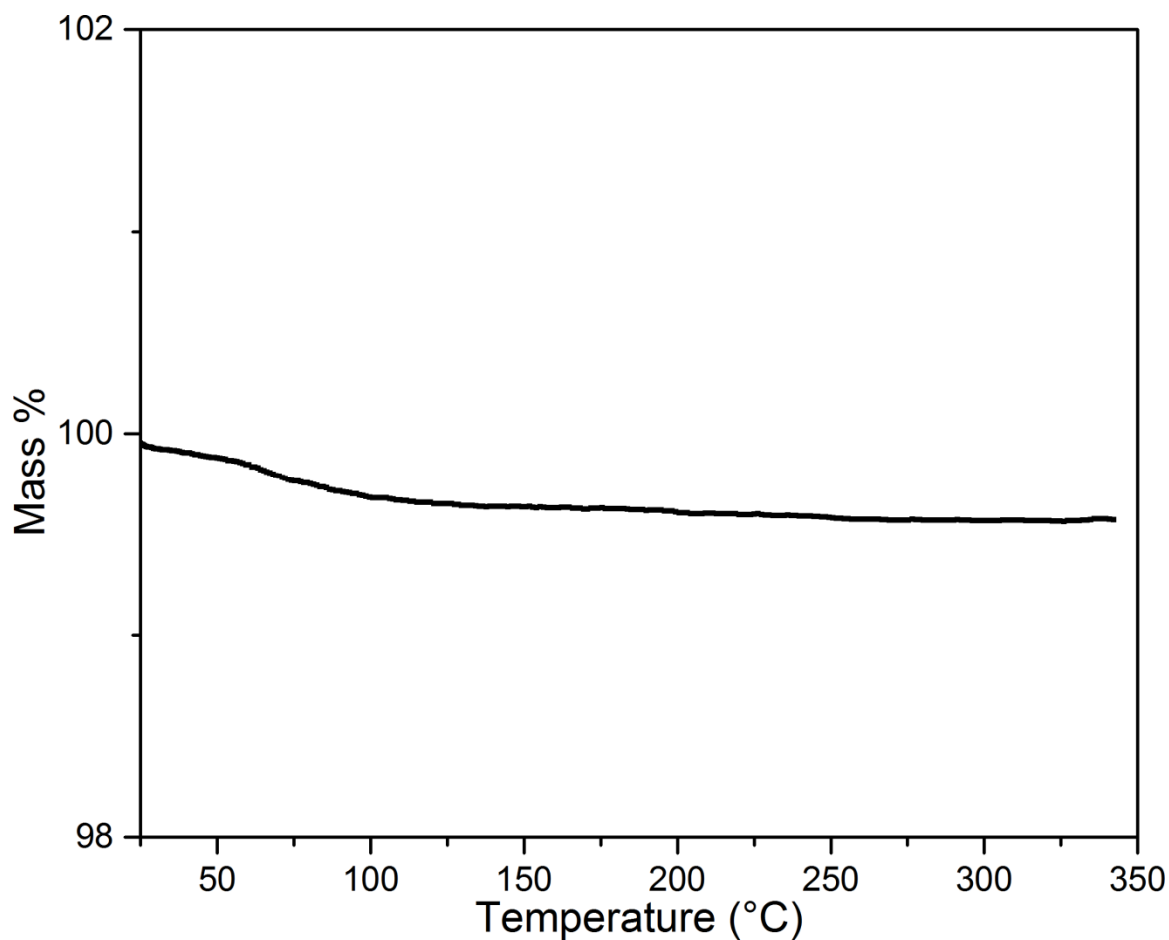


Figure 5.23 Thermogravimetric analysis of β -NaFeO₂ in oxygen to a final temperature of 350 °C for analysis to determine structural stability for high temperature electrochemical cycling.

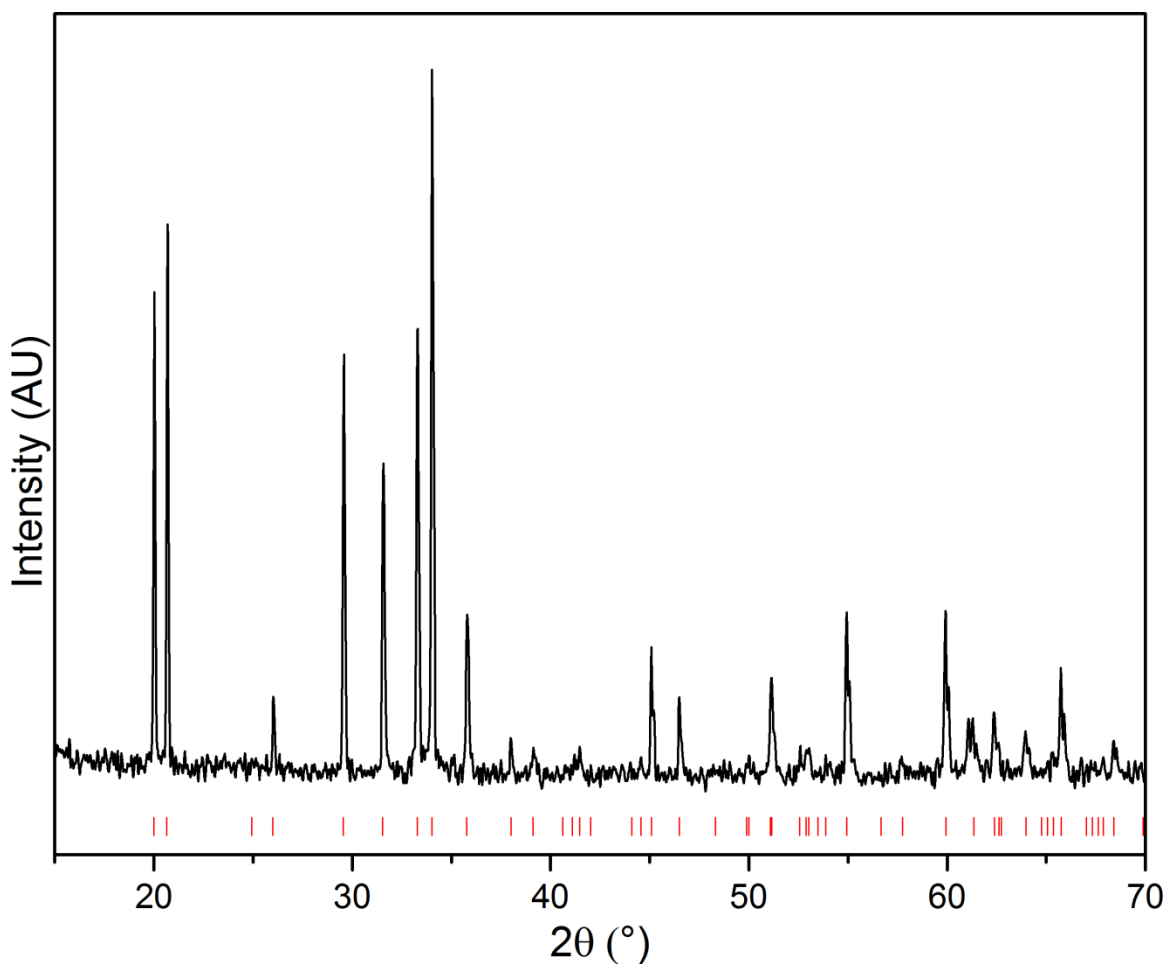


Figure 5.24 PXD of the resulting powder from the oxygen TGA of β -NaFeO₂, red ticks are indicative of β -NaFeO₂.

As previously stated, the expected results for the thermogravimetric analysis up to 350 °C in oxygen should maintain the pure compound β -NaFeO₂. This was seen in Figure 5.24. If the temperature were elevated, it would be expected that some sodium would be lost from the topmost portion of the powder sample due to sodium's volatility, resulting in a sodium deficient phase.

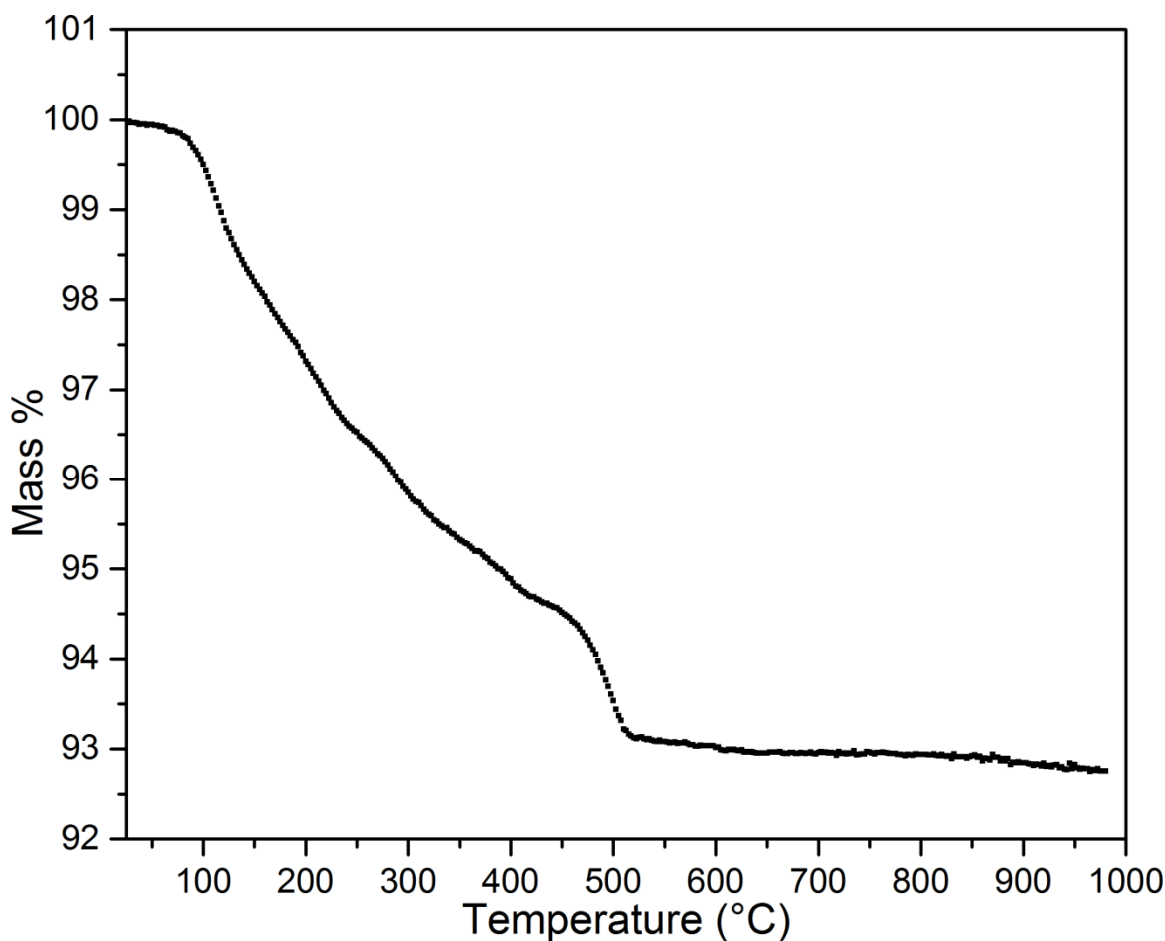


Figure 5.25 Thermogravimetric analysis of the sodium deficient $\beta\text{-Na}_{0.79}\text{FeO}_2$ in nitrogen to a final temperature of 975 °C.

As previously stated, the decomposition of $\beta\text{-NaFeO}_2$ was not expected at elevated temperatures; rather the sodium deficient phase would be more likely to decompose. Therefore, thermogravimetric analysis of the sodium deficient phase, $\beta\text{-Na}_{0.79}\text{FeO}_2$, which was synthesized by sodium deintercalation from $\beta\text{-NaFeO}_2$ using NOBF_4 , was performed. This compound was more stable to a slightly higher temperature under oxygen flow, (Figure 5.25), than was the lithium deficient T-LiFeO_2 . $\beta\text{-Na}_{0.79}\text{FeO}_2$ did

not show decomposition until almost 100 °C, which is the upper limit of elevated temperature cycling.

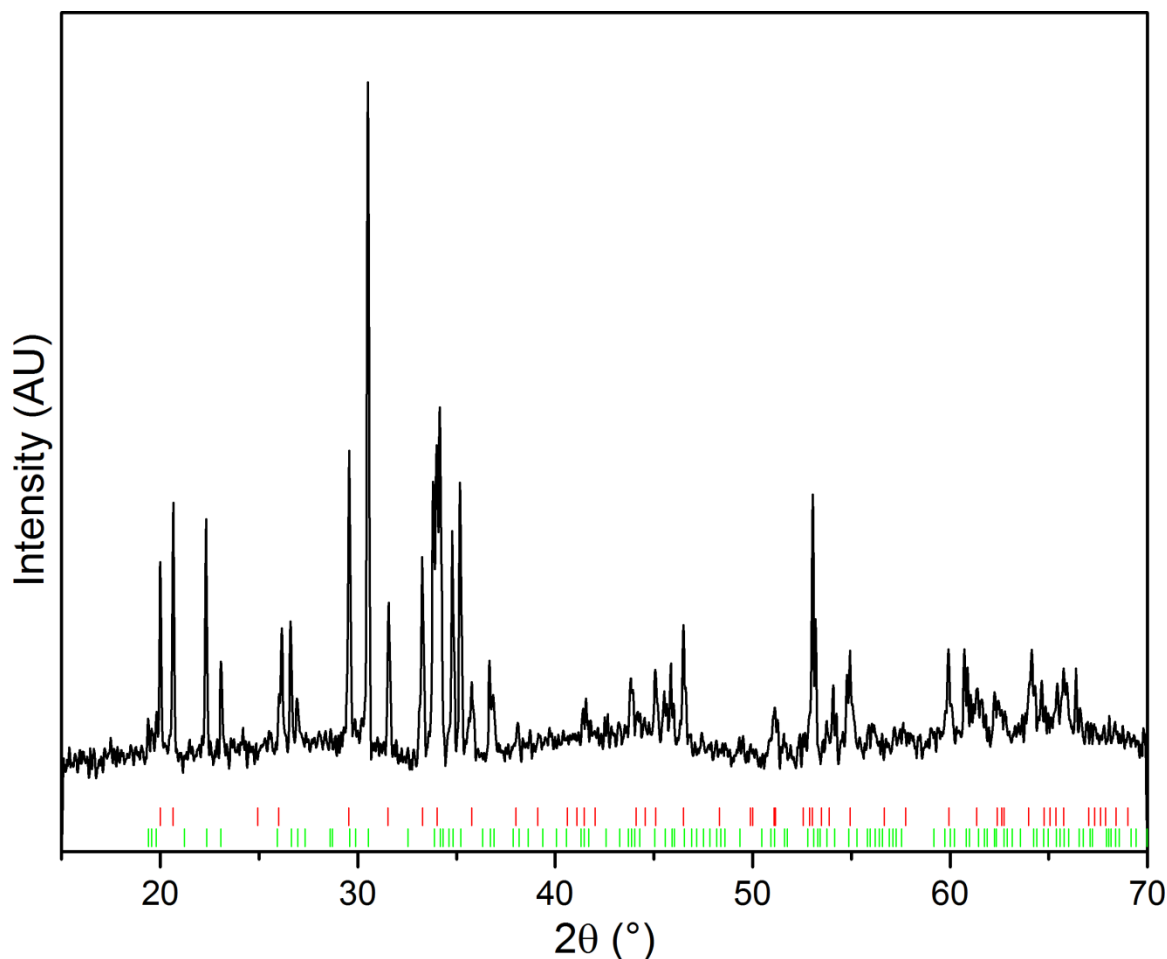


Figure 5.26 PXD of the resulting powder from the nitrogen TGA of $\beta\text{-Na}_{0.79}\text{FeO}_2$, $\beta\text{-NaFeO}_2$ (red) and $\text{Na}_3\text{Fe}_5\text{O}_9$ (green) were the resulting phases.

The PXD of $\beta\text{-Na}_{0.79}\text{FeO}_2$, run in the TGA to 1000 °C, under nitrogen flow, resulted in the formation of $\text{Na}_3\text{Fe}_5\text{O}_9$ and $\beta\text{-NaFeO}_2$, (Figure 5.26). This result is not surprising due to the relative stability of $\beta\text{-NaFeO}_2$ at high temperatures, because of the instability of the

sodium deficient β -NaFeO₂. The formation of β -NaFeO₂ resulted in even less available sodium to form another phase which in turn resulted in the formation of Na₃Fe₅O₉ (NaFe_{0.6}O₃), and the loss of some unreacted sodium during the formation at these elevated temperatures.

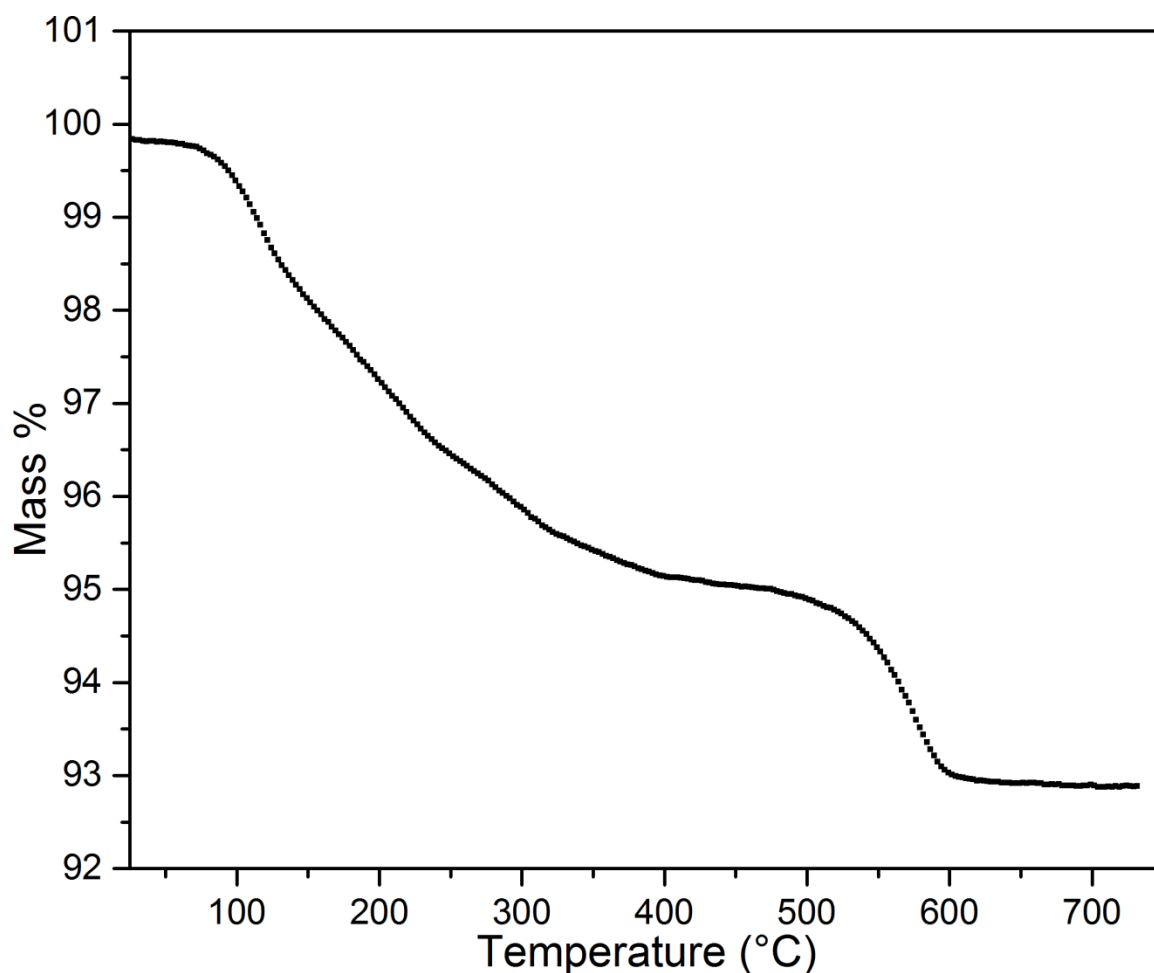


Figure 5.27 Thermogravimetric analysis of the sodium deficient β -Na_{0.79}FeO₂ in oxygen to a final temperature of 725 °C.

Similar to the results of the nitrogen TGA, β -Na_{0.79}FeO₂ run under oxygen also resulted in the decomposition at about 100 °C (Figure 5.27).

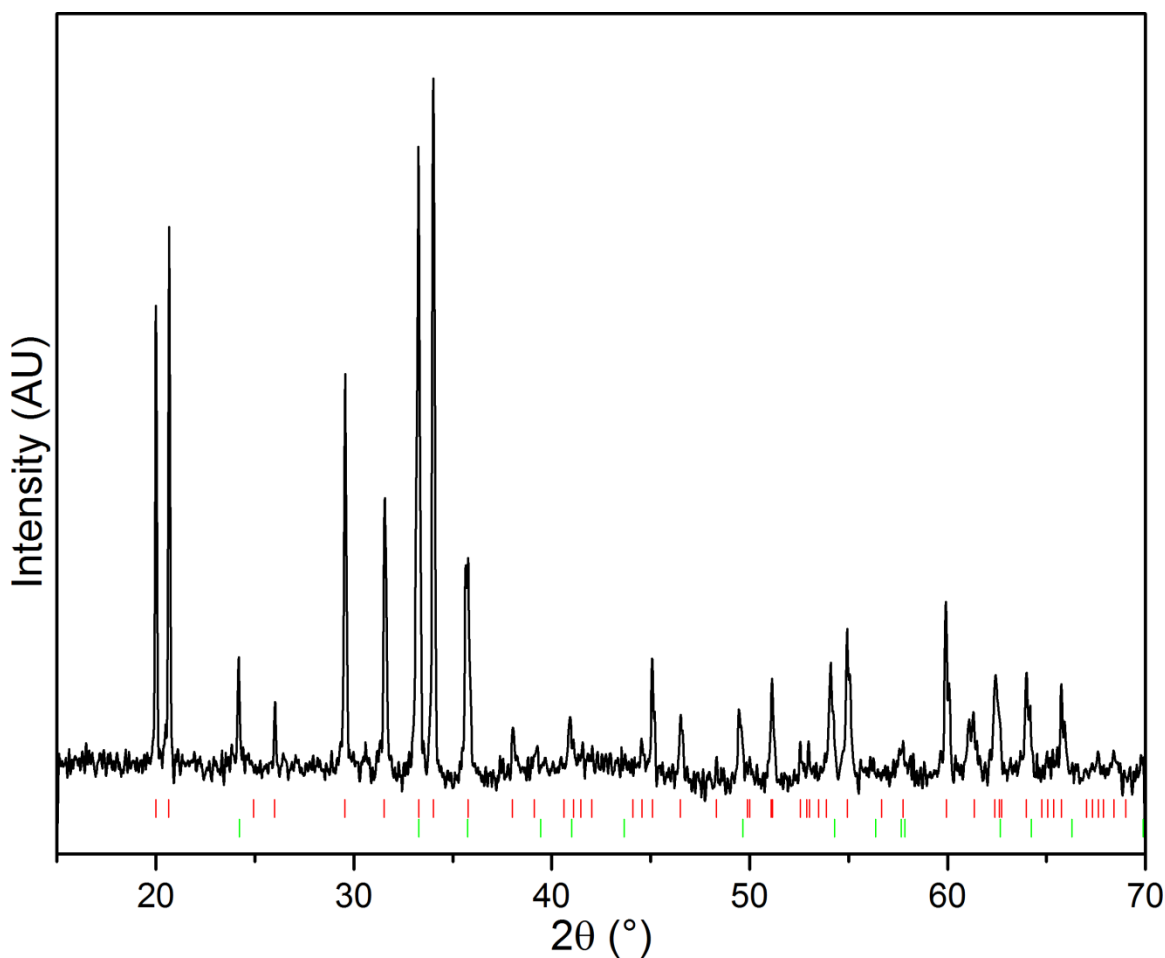


Figure 5.28 PXD of the resulting powder from the oxygen TGA of $\beta\text{-Na}_{0.79}\text{FeO}_2$, $\beta\text{-NaFeO}_2$ (red) and Fe_2O_3 (green) were the resulting phases.

The PXD of $\beta\text{-Na}_{0.79}\text{FeO}_2$ run in the TGA to 700 °C under oxygen flow resulted in the formation of $\beta\text{-NaFeO}_2$ and Fe_2O_3 as seen in Figure 5.28. This result, unlike that from $\beta\text{-Na}_{0.79}\text{FeO}_2$, which was run in the TGA under nitrogen, contained Fe_2O_3 . The Fe_2O_3 similar to the Fe_3O_4 previously discussed is most likely doped with some sodium, but in order to determine this for sure, further analysis would have to be performed and would provide no beneficial insight into the results.

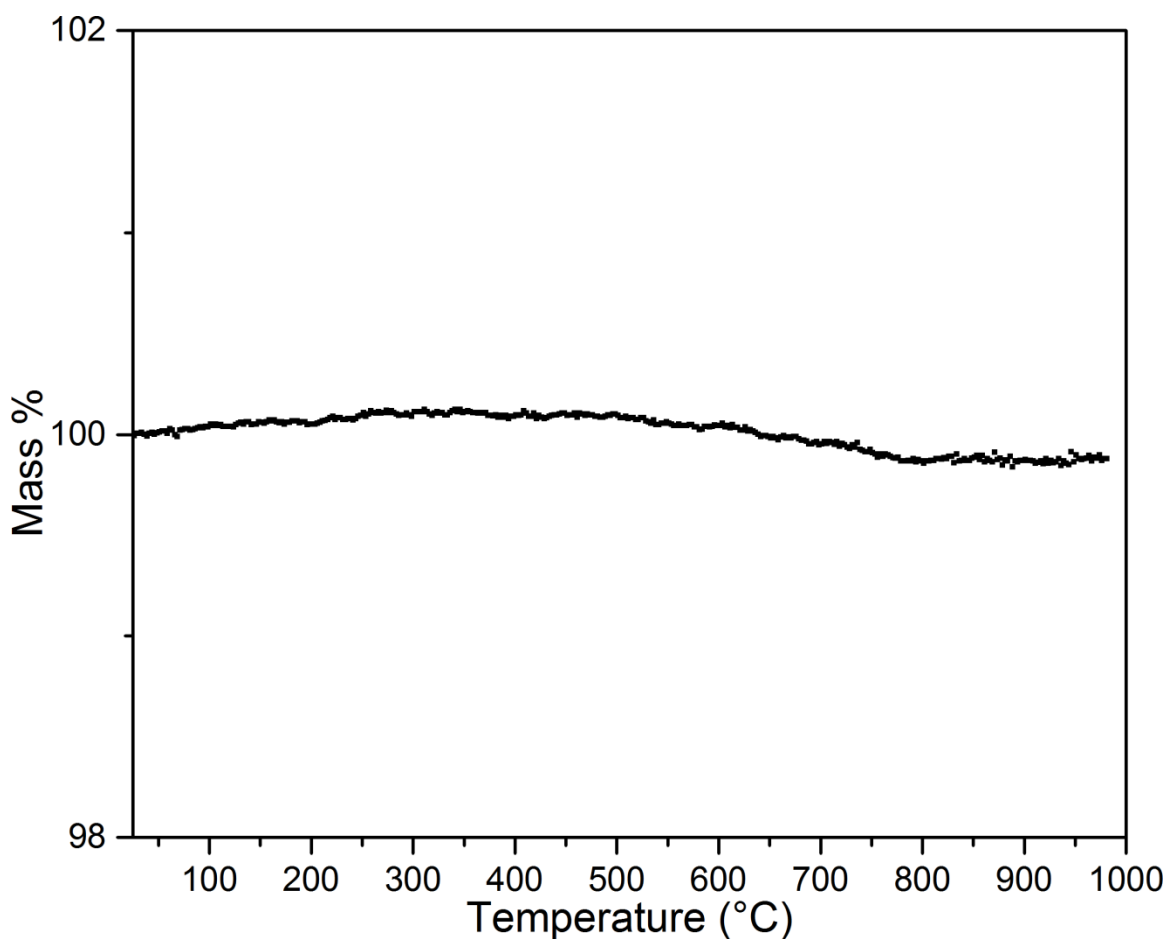


Figure 5.29 Thermogravimetric analysis of $\beta\text{-NaFe}_{0.9}\text{Co}_{0.1}\text{O}_2$ in nitrogen to a final temperature of 1000 °C.

Thermogravimetric analysis of the cobalt-doped $\beta\text{-NaFeO}_2$ was run in nitrogen and oxygen to a temperature of 1000 °C. As previously mentioned, the results were expected to be sodium deficient $\beta\text{-NaFeO}_2$ materials. Figure 5.29 illustrates the TGA of $\beta\text{-NaFe}_{0.9}\text{Co}_{0.1}\text{O}_2$ under nitrogen flow to 1000 °C with no substantial loss in mass.

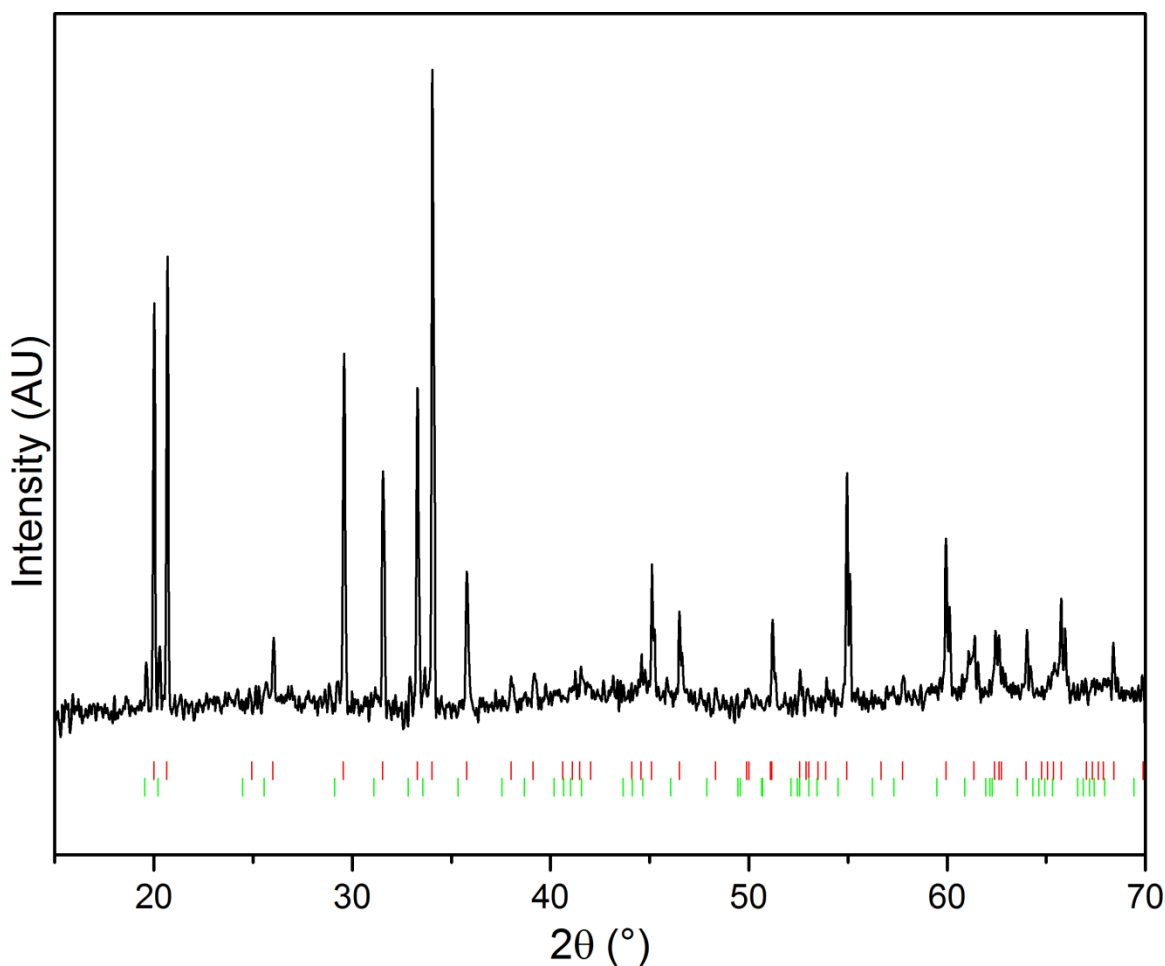


Figure 5.30 PXD of the resulting powder from the nitrogen TGA of $\beta\text{-NaFe}_{0.9}\text{Co}_{0.1}\text{O}_2$, $\beta\text{-NaFeO}_2$ (red) and $\beta\text{-Na}_{1-x}\text{FeO}_2$ (green) were the resulting phases.

The resulting PXD of $\beta\text{-NaFe}_{0.9}\text{Co}_{0.1}\text{O}_2$ run in the TGA under nitrogen flow (Figure 5.30) indicated two phases. The main phase was a compound with the same general peak reflections as $\beta\text{-NaFeO}_2$. The second phase, which was much less evident, presented peaks close in 2θ values as seen in the $\beta\text{-NaFeO}_2$ structures. Therefore, it can be said that the second phase is the initially hypothesized sodium deficient phase. Due to the increase

in relative surface area of the powder run in the TGA, sodium and lithium volatility is /much more probable.

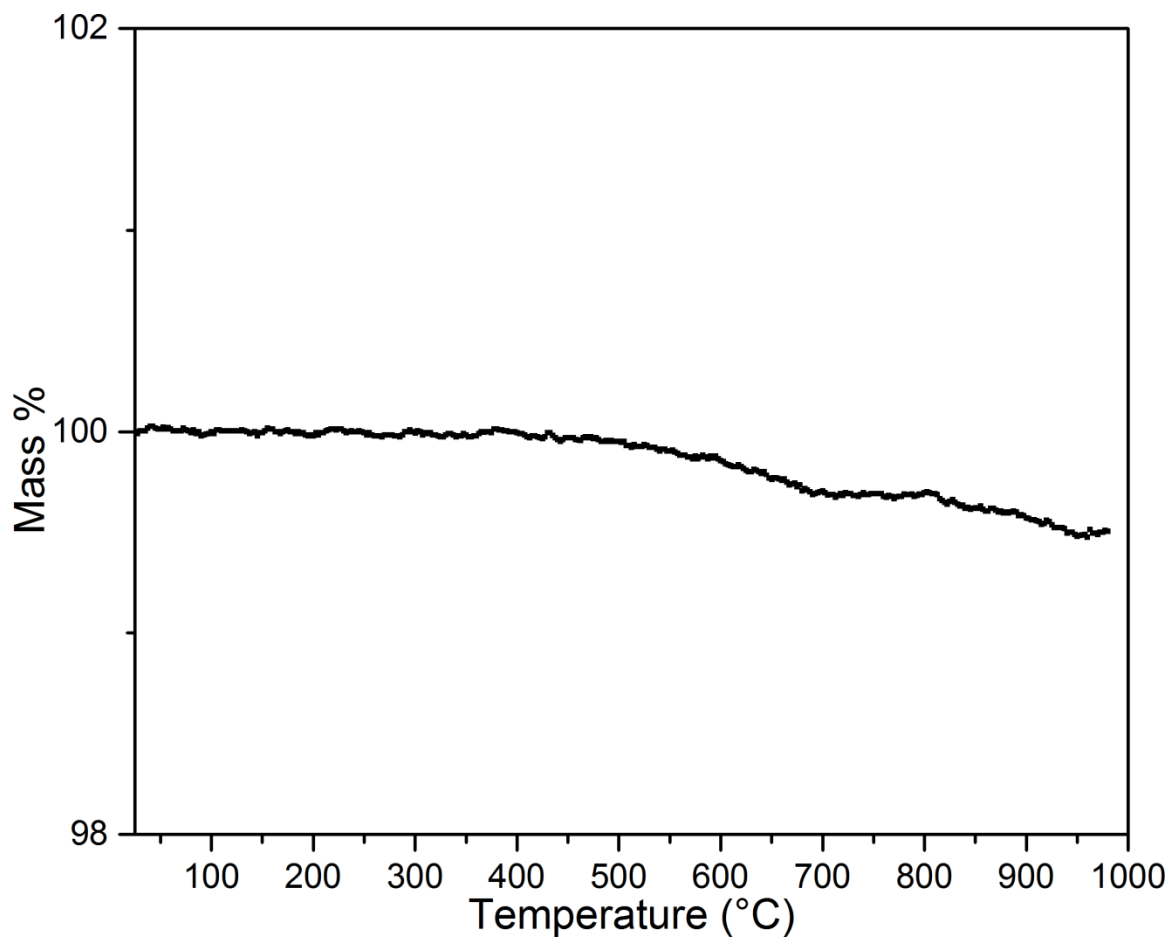


Figure 5.31 Thermogravimetric analysis of the $\beta\text{-NaFe}_{0.9}\text{Co}_{0.1}\text{O}_2$ in oxygen to a final temperature of 1000 $^{\circ}\text{C}$.

Thermogravimetric analysis was also performed on $\beta\text{-NaFe}_{0.9}\text{Co}_{0.1}\text{O}_2$ (Figure 5.31), under oxygen. The resulting mass loss was relatively low, but again, this is expected due to the stability of the initial phase and any mass loss is due to sodium loss.

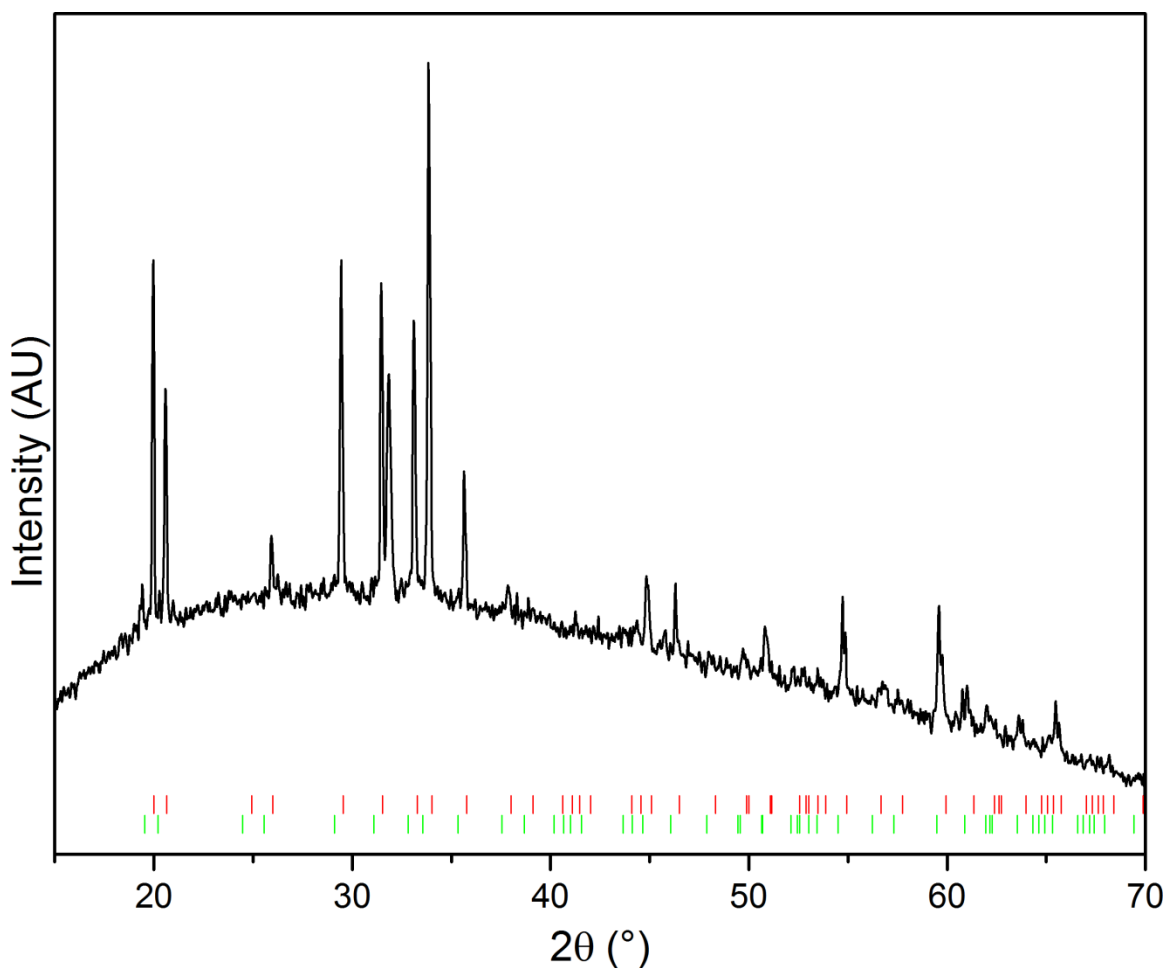


Figure 5.32 PXD of the resulting powder from the nitrogen TGA of $\beta\text{-NaFe}_{0.9}\text{Co}_{0.1}\text{O}_2$, $\beta\text{-NaFeO}_2$ (red) and $\beta\text{-Na}_{1-x}\text{FeO}_2$ (green) were the resulting phases.

Similar to the $\beta\text{-NaFe}_{0.9}\text{Co}_{0.1}\text{O}_2$ sample run under nitrogen flow (Figure 5.32), the resulting PXD from $\beta\text{-NaFe}_{0.9}\text{Co}_{0.1}\text{O}_2$ run in the TGA under oxygen presented a mixture of $\beta\text{-NaFeO}_2$ and a sodium deficient phase.

Now that the stability of the compounds has been established, electrochemical cycling of T-LiFeO₂ will be discussed. This was done by attempting to probe the $\text{Fe}^{3+/4+}$ redox couple by cycling the materials at voltages above 4 V. Figure 5.33 illustrates the initial

cycling of undoped T-LiFeO₂. As it can be seen, there is no distinct deintercalation peak that would typically be seen in the oxidation of a cathode material.

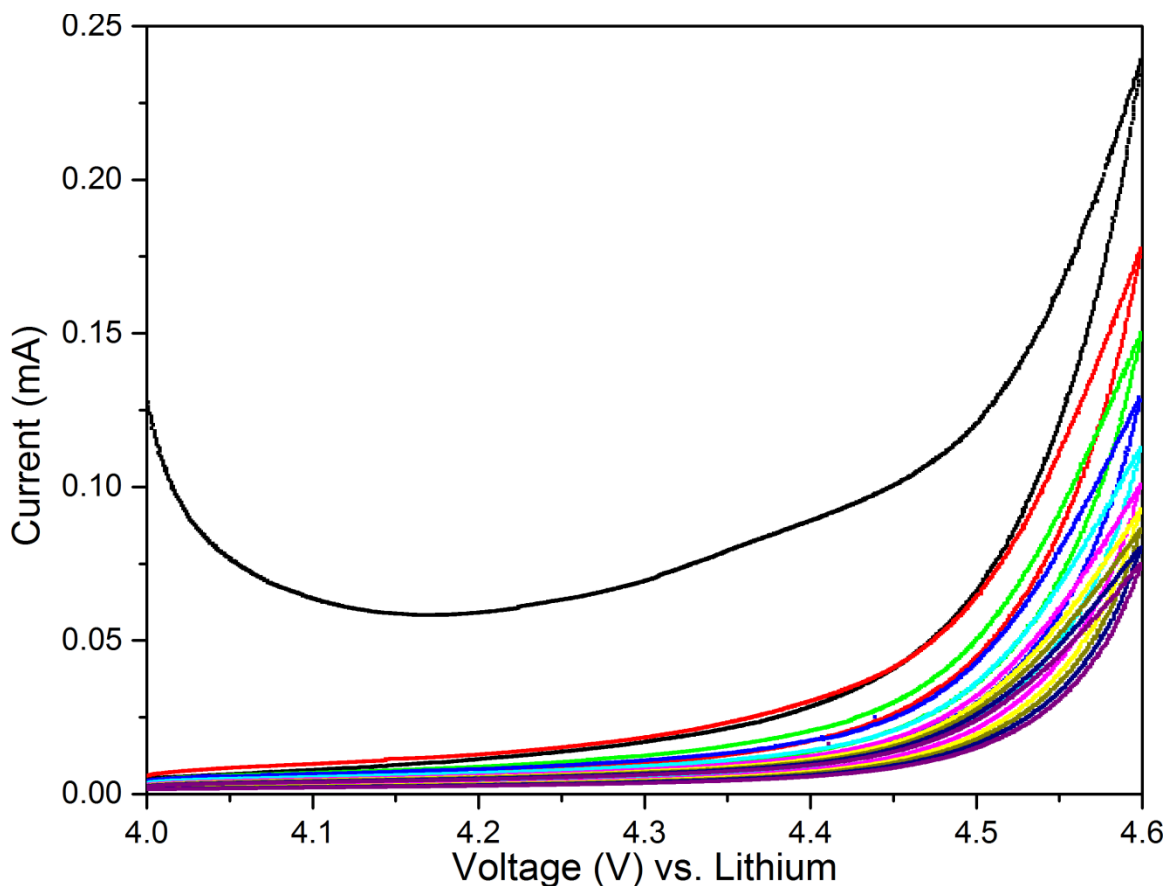


Figure 5.33 Cyclic voltammogram of T-LiFeO₂ between 4.0 and 4.6 V probing the Fe^{3+/4+} redox potential showing the reaction of T-LiFeO₂ with the electrolyte.

This material was previously reported to cycle at about 4.5 V with a capacity of 120 mAh/g, but during this cycling the compound decomposed into LiFe₅O₈ due to a reaction that occurred between the cathode material and the electrolyte at increased voltages. The initial cycling of the as prepared T-LiFeO₂ was also integrated to determine what the capacity was per cycle as seen in Figure 5.34. The initial cycle had a deintercalation

capacity of 40 mAh/g but quickly faded to 15 mAh/g then 10 mAh/g, and upon subsequent cycles after that, the capacity continued to fade.

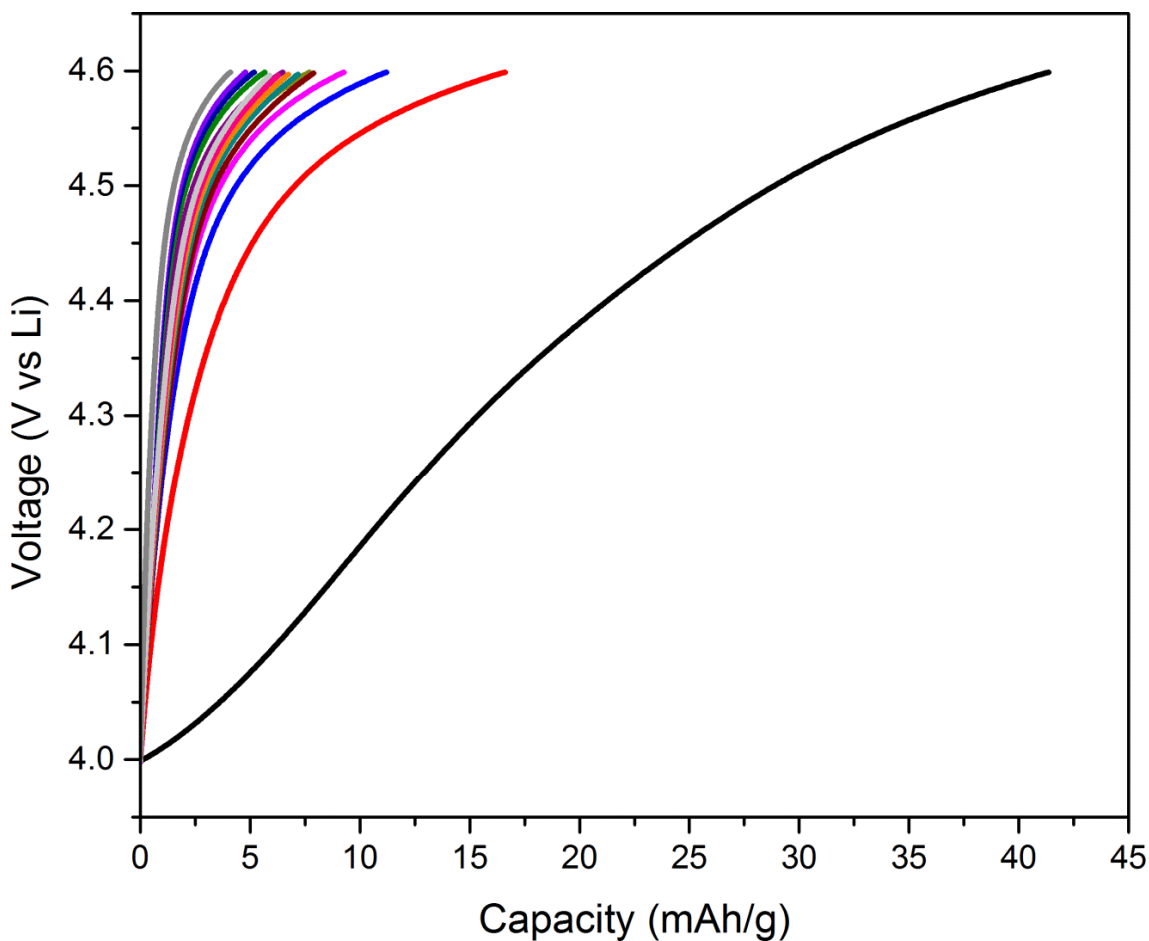


Figure 5.34 Integrated cyclic voltammogram of T-LiFeO₂ illustrating what would normally be the deintercalation of lithium, but this is the reaction of T-LiFeO₂ with the electrolyte. This is also seen by the absence of lithium intercalation.

As seen in Figure 5.34, there was no lithium intercalation into the structure, therefore resulting in an intercalation capacity of zero. This can be seen by the lack of an

intercalation curve in Figure 5.34. This response was determined to be caused by the poor electrical conductivity of the as prepared LiFeO_2 .

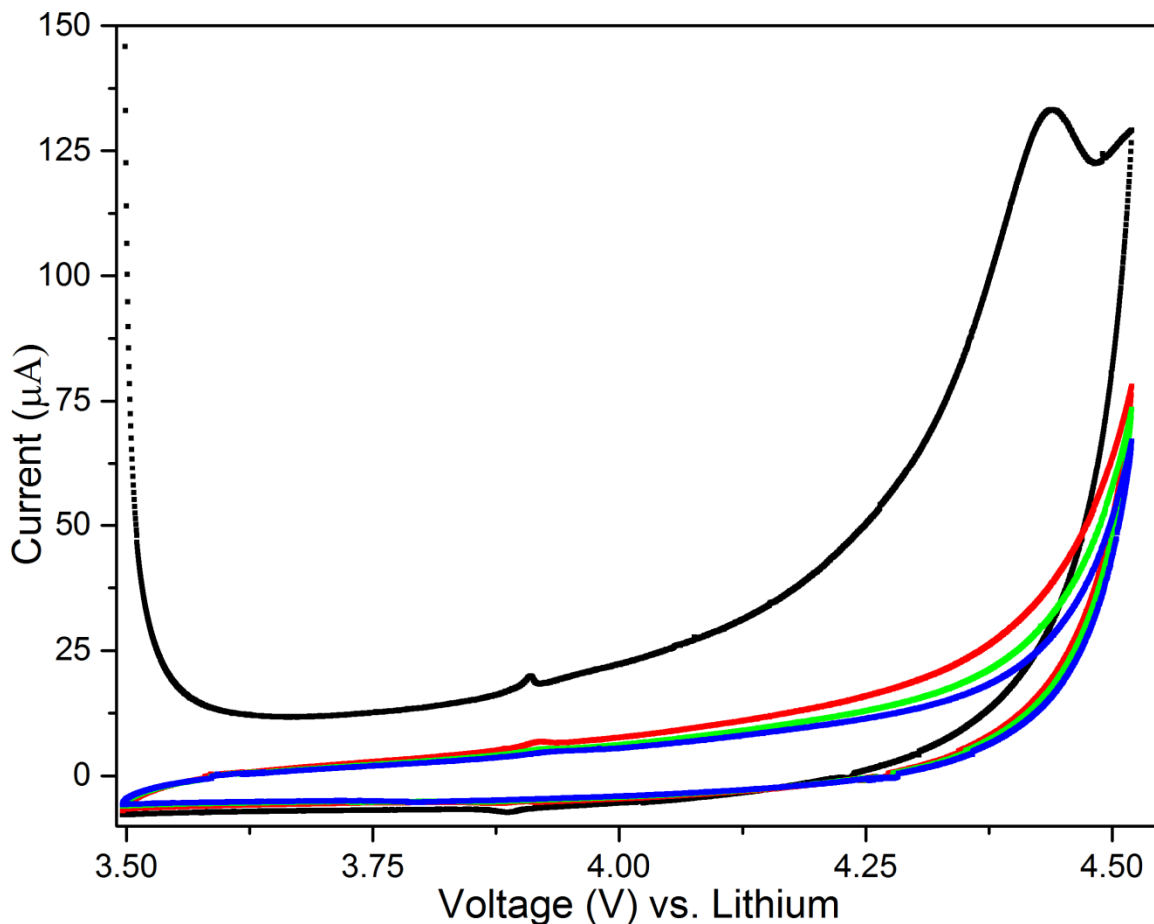


Figure 5.35 High voltage cycling of $\text{LiFe}_{0.9}\text{Co}_{0.1}\text{O}_2$ between 3.5 and 4.6 V probing the $\text{Fe}^{3+/4+}$ redox couple, the lithium deintercalation peak is present at about 4.4 V and where a distinct intercalation peak does not exist due to the compound's reaction with the electrolyte.

The $\text{LiFe}_{1-x}\text{Co}_x\text{O}_2$ was hypothesized to reduce the challenge presented by the undoped T- LiFeO_2 by increasing the electrical conductivity, which in turn should provide successful

cycling. As seen in Figure 5.35, a distinct oxidation curve was established at about 4.4 V. This did indicate that the doping was contributing to the deintercalation of lithium from $\text{LiFe}_{0.9}\text{Co}_{0.1}\text{O}_2$. However, as seen after the oxidation peak in Figure 5.35, the oxidation curve continued increasing, this again is due to the cathode material, in this case, $\text{LiFe}_{0.9}\text{Co}_{0.1}\text{O}_2$, reacting with the electrolyte, therefore decomposing.

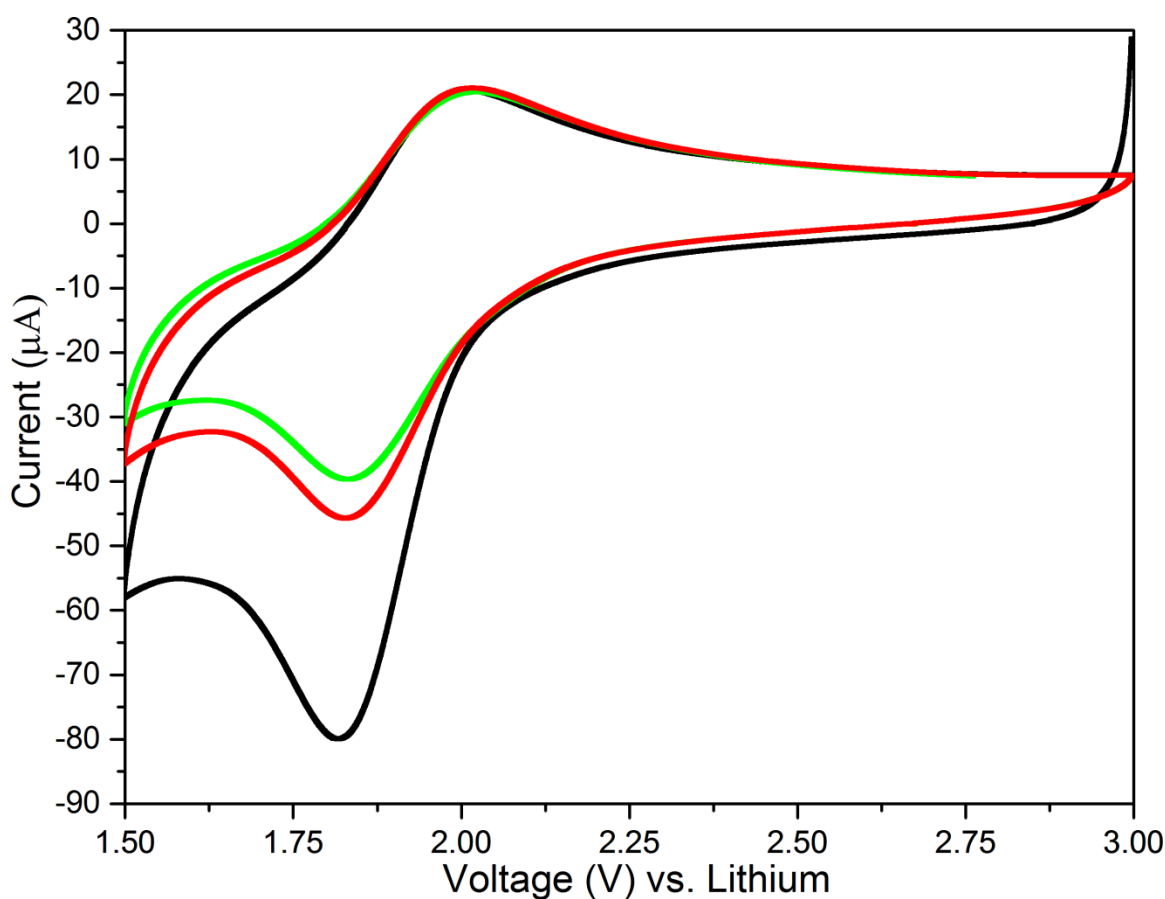


Figure 5.36 Low voltage cyclic voltammogram of $\text{LiFe}_{0.9}\text{Co}_{0.1}\text{O}_2$ probing the $\text{Fe}^{2+/3+}$ redox couple between voltages of 1.5 and 3.0 V, with lithium intercalation occurring at about 1.8 V and deintercalation occurring at about 2.0 V.

It was established that cobalt doping is essential in the successful cycling of the tunnel structure, but the reaction with the electrolyte was stopping progress in establishing successful $\text{Fe}^{3+/4+}$ cycling materials. Therefore, focus was shifted to determine if this material could accept an additional lithium ion, as it was previously determined chemically that it could receive about 0.6 lithium ions (Figure 5.14). Electrochemical characterization probing the $\text{Fe}^{2+/3+}$ redox couple was then performed by initially intercalating lithium into the material as seen in Figure 5.36. The cyclic voltammogram started at 3.0 V and ended at 1.5 V with a distinct reduction peak at about 1.8 V. Successful cycling probing this redox couple was further confirmed by the distinct oxidation peak at 1.95 V. Though it is obvious there is a dramatic capacity fade, the ability to intercalate a lithium ion was further established electrochemically.

The as prepared LiFeO_2 Mössbauer spectrum, as seen in Figure 5.38, was fit with one site that consisted of an isomer shift of 0.141 mm/sec, (Table 5.6) which is expected in an iron in 3+ oxidation state in the tetrahedral coordination.

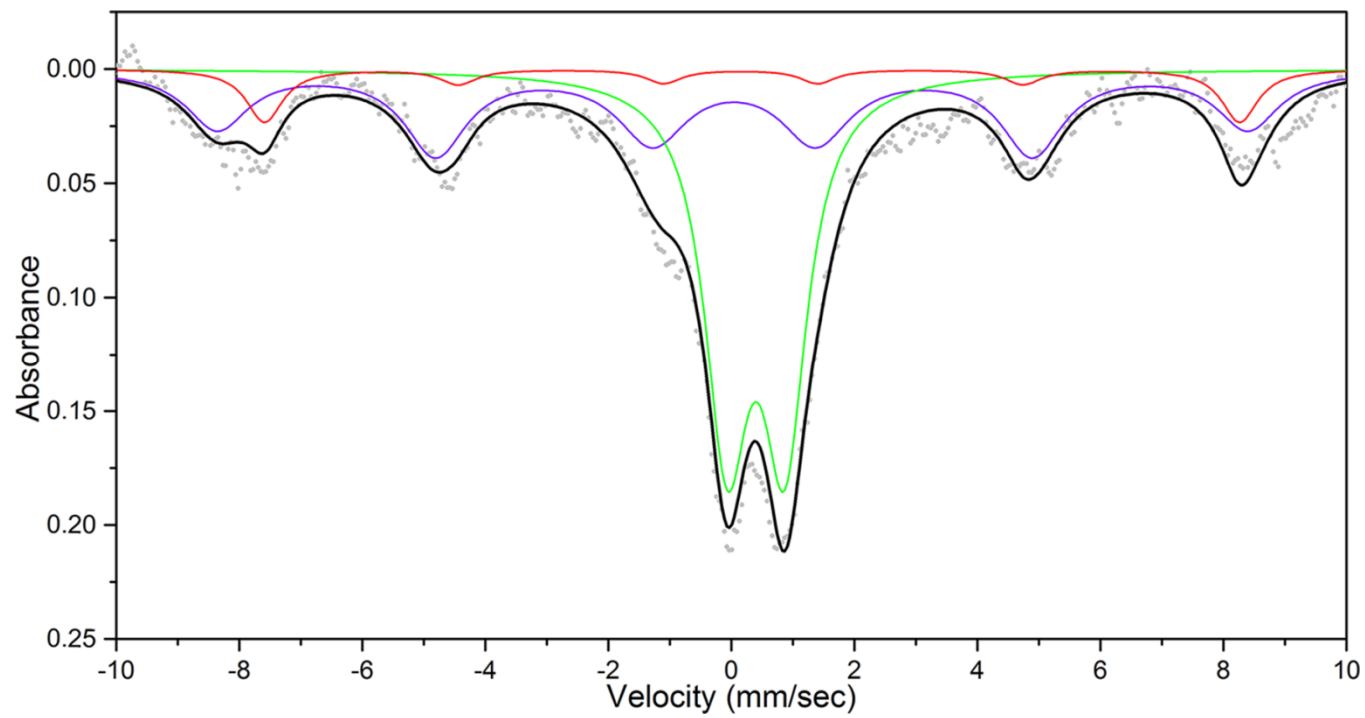


Figure 5.37 Mössbauer spectrum of $\text{Li}_{0.42}\text{FeO}_2$ after chemical lithium intercalation fit with 3 sites the total fit (black) and the three sites correlating to isomer shifts are 0.129 (red), -0.09 (blue), and 0.53 (green).

Table 5.5 Mössbauer parameters of the chemically deintercalated $\text{Li}_{0.42}\text{FeO}_2$ fit with three sites.

$\text{Li}_{0.42}\text{FeO}_2$	Weight of Sublattice	Weight %	Isomer Shift	Magnetic Hyperfine Field	Quadrupole splitting
Site A	0.541	25.5	0.129	50.96	-0.37
Site B	0.752	35.5	-0.09	3.63	1.07
Site C	0.827	39.0	0.53	0.64	1.17

Mössbauer spectroscopy was performed, at room temperature, on the as prepared LiFeO_2 , $\text{Li}_{1.57}\text{FeO}_2$, and $\text{Li}_{0.42}\text{FeO}_2$ to determine if the chemical oxidation and reduction could further illustrate the different oxidation states of the three compounds. Figure 5.37 and Table 5.5 depict the results of $\text{Li}_{0.42}\text{FeO}_2$ with three sites. The spectrum was fit and isomer shifts of the three sites were fit and established to be 0.129, -0.09, 0.53 mm/sec. Of these three values, 0.129 and 0.53 are indicative of iron present with a 3+ oxidation state, while the -0.09 indicates a 4+ oxidation state. The 0.53 mm/sec value is unusually high for a tetrahedrally coordinated iron, which is generally expected to be between 0.1 and 0.3 mm/sec. This could indicate that even though the overall fit matches relatively well with the observed data, there may be other factors that cannot be seen in this data that was collected at room temperature.

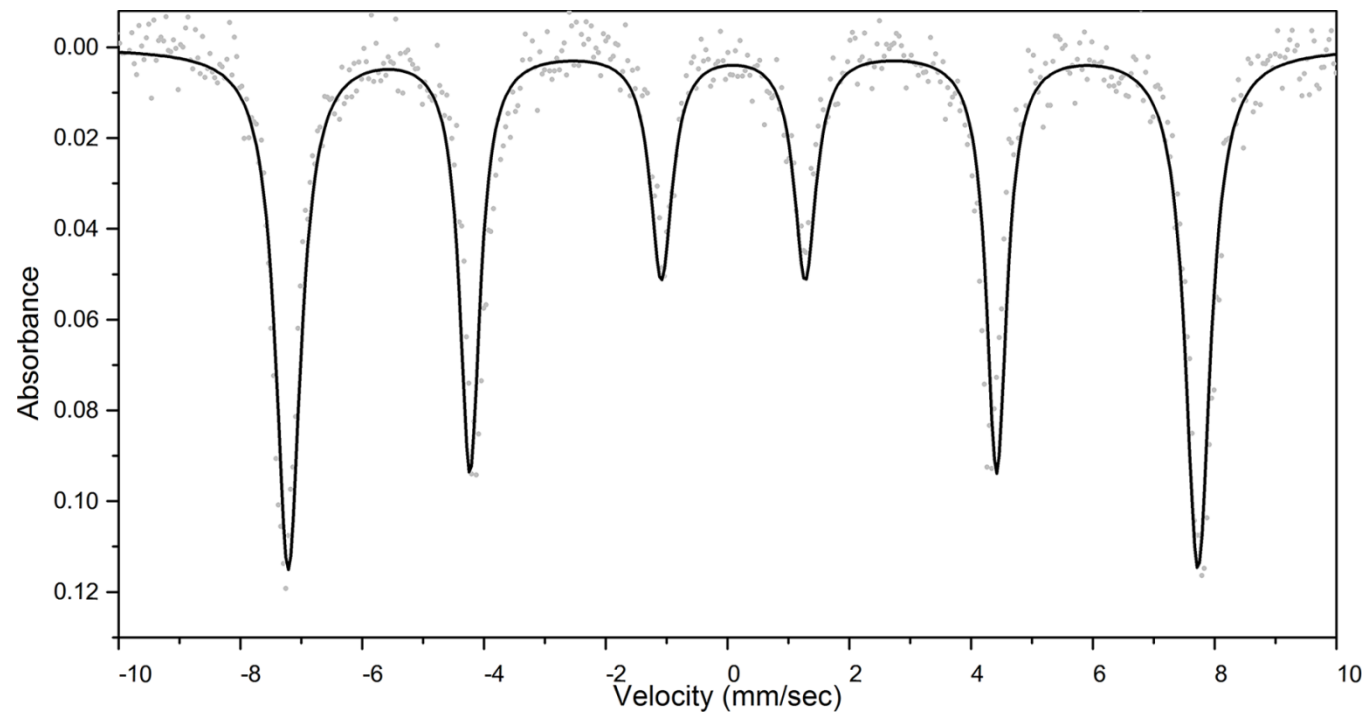


Figure 5.38 Mössbauer spectrum of the as prepared LFeO₂ with one site.

Table 5.6 Mössbauer parameters of the as prepared LiFeO_2 fit with one site.

LiFeO_2	Weight of Sublattice	Weight %	Isomer Shift	Magnetic Hyperfine Field	Quadrupole splitting
Site A	1	100	0.141	46.46	-0.319

The as prepared LiFeO_2 Mössbauer spectrum as seen in Figure 5.38 was fit with one site that consisted of an isomer shift of 0.141 mm/sec, (Table 5.6) which is expected in an iron 3+ oxidation state in the tetrahedral coordination. T- LiFeO_2 is the first seen polymorph with magnetic ordering observed at room temperature.

The chemically intercalated $\text{Li}_{1.57}\text{FeO}_2$, (Figure 5.39 and Table 5.7), was also fit with three sites with isomer shifts of 0.161, 0.438, and 0.494 mm/sec. The values of 0.438 and 0.494 mm/sec are within the expected range of a tetrahedrally coordinated iron with a 2+ oxidation state, which is what was expected from the low voltage electrochemical cycling that illustrated chemical intercalation, (Figure 5.36).

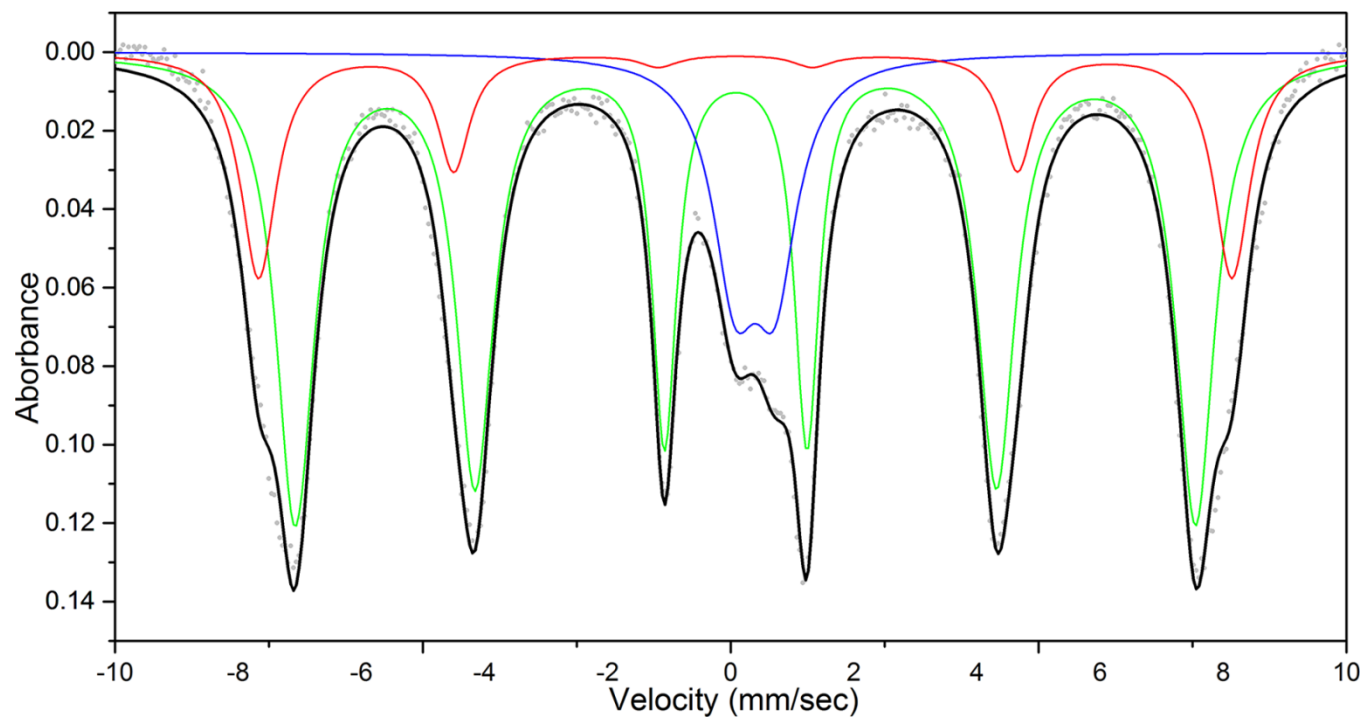


Figure 5.39 Mössbauer spectrum of $\text{Li}_{1.57}\text{FeO}_2$ after chemical lithium intercalation fit with 3 sites, the total fit (black) and the three sites correlating to isomer shifts are 0.161 (green), 0.438 (red), and 0.494 (blue).

Table 5.7 Mössbauer parameters of the chemically intercalated $\text{Li}_{1.57}\text{FeO}_2$ fit with three sites.

$\text{Li}_{1.57}\text{FeO}_2$	Weight of Sublattice	Weight %	Isomer Shift	Magnetic Hyperfine Field	Quadrupole splitting
Site A	1.04	70.8	0.161	47.68	-0.293
Site B	0.324	22.1	0.438	0	-1.038
Site C	0.105	7.1	0.494	0	-0.291

As it can be seen with the somewhat similar isomer shifts values between the $\text{Li}_{0.42}\text{FeO}_2$ (0.53 mm/sec) and $\text{LiFe}_{1.57}\text{FeO}_2$ (0.438 and 0.494), it is apparent that room temperature measurements are not enough to strongly confirm Fe^{4+} due to the unexpectedly high value of the other Fe^{3+} containing site. What can be said though, is that it is highly unlikely that this compound would contain both iron 2+ and iron 4+ sites. Mössbauer measurements at liquid helium temperature would exhibit magnetic ordering within each of the sites within the structure, therefore providing separation of the peaks and more accurate fitting.

5.6 Conclusion

The T-LiFeO₂ polymorph was successfully doped with up to the 0.10 parts per formula unit of cobalt and was prepared from ion exchange with the parent doped compound, β -NaFe_{1-x}Co_xO₂. The cobalt doped T-LiFeO₂ did show improved cycling over the undoped T-LiFeO₂ with a distinct reduction peak observed in the Fe^{3+/4+} redox couple. This was not observed in the undoped T-LiFeO₂. Similar to undoped T-LiFeO₂, the cobalt doped reacted with the electrolyte, therefore decomposing. T-LiFeO₂ was investigated to determine whether chemical lithium intercalation and deintercalation would result in structural decomposition, and was analyzed using PXD, ICP, electrochemistry, and Mössbauer spectroscopy. The resulting Mössbauer spectra were matched, with the results indicating Fe^{2+/3+}, Fe³⁺, and Fe^{3+/4+} in their respective spectra. Due to inadequate peak separation, low temperature Mössbauer spectroscopy should be employed to achieve the appropriate peak separation to be able to make an accurate conclusion on the final oxidation states of the T-Li_xFeO₂ compounds.

5.7 Future Direction

The future direction of LiFeO₂ can be separated into two-sections: continuing research of the tetrahedral iron oxide and investigation into similar tunnel-like tetrahedral compounds.

Focusing on the tetrahedral iron oxides, a collaboration to perform low temperature Mössbauer spectroscopy on the T-Li_{0.42}FeO₂ and T-Li_{1.57}FeO₂ to determine the oxidation states of the respective compounds should be conducted. After confirmation of the

oxidation states, magnetic response of these divalent materials could also be very interesting. During synthesis of the lithium deficient compound, it was observed that the compound was attracted toward a magnet. This was not seen in the initial compound.

Cycling the cobalt-doped T-LiFeO₂ against a solid electrolyte or ionic liquids should be investigated. This could provide the required conditions for two electron cycling without a reaction with the organic electrolyte, due to the formation of Fe⁴⁺, upon lithium deintercalation.

β-NaFeO₂ and β-Na_{1-x}Co_xFeO₂ should be investigated as potential cathode materials and solid electrolytes. Magnetic response and thermoelectric measurements into these compounds should also be investigated.

Materials similar to the tunnel-like compound would involve the synthesis and ion exchange of KCoO₂ [28]. This compound contains tetrahedrally coordinated cobalt similar to T-LiFeO₂. The challenge with this compound will be determining conditions to synthesize KCoO₂ in bulk, because the only reported synthesis was a single crystal. Derivatives from this compound could exhibit very interesting properties, i.e. NaCoO₂ from ion exchange with KCoO₂, (Figure 5.40), would be a polymorph to the known and highly characterized NaCoO₂ with the α-NaFeO₂ layered structure type. Sodium deficient layered Na_xCoO₂ have also been reported as thermoelectric materials and superconductors. Therefore, it would be logical to attempt similar studies with this tunnel structure.

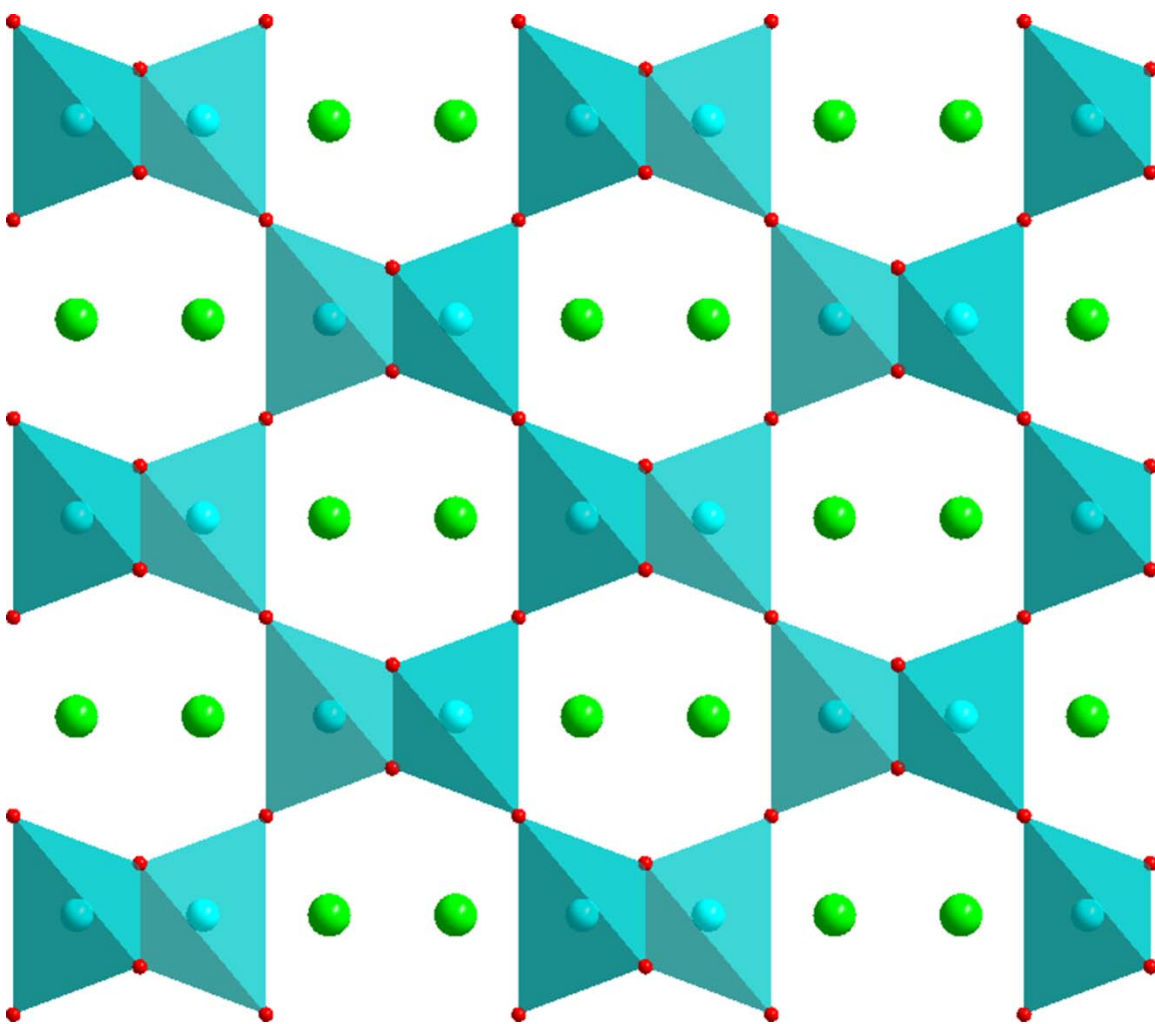


Figure 5.40 Proposed structure of tunnel NaCoO_2 resulting from the ion exchange using NaNO_3 with the known compound KCoO_2 .

Successful ion exchange of lithium for potassium in KCoO_2 would result in tunnel LiCoO_2 (Figure 5.41), which would be a polymorph to the most commonly used cathode material in lithium ion batteries.

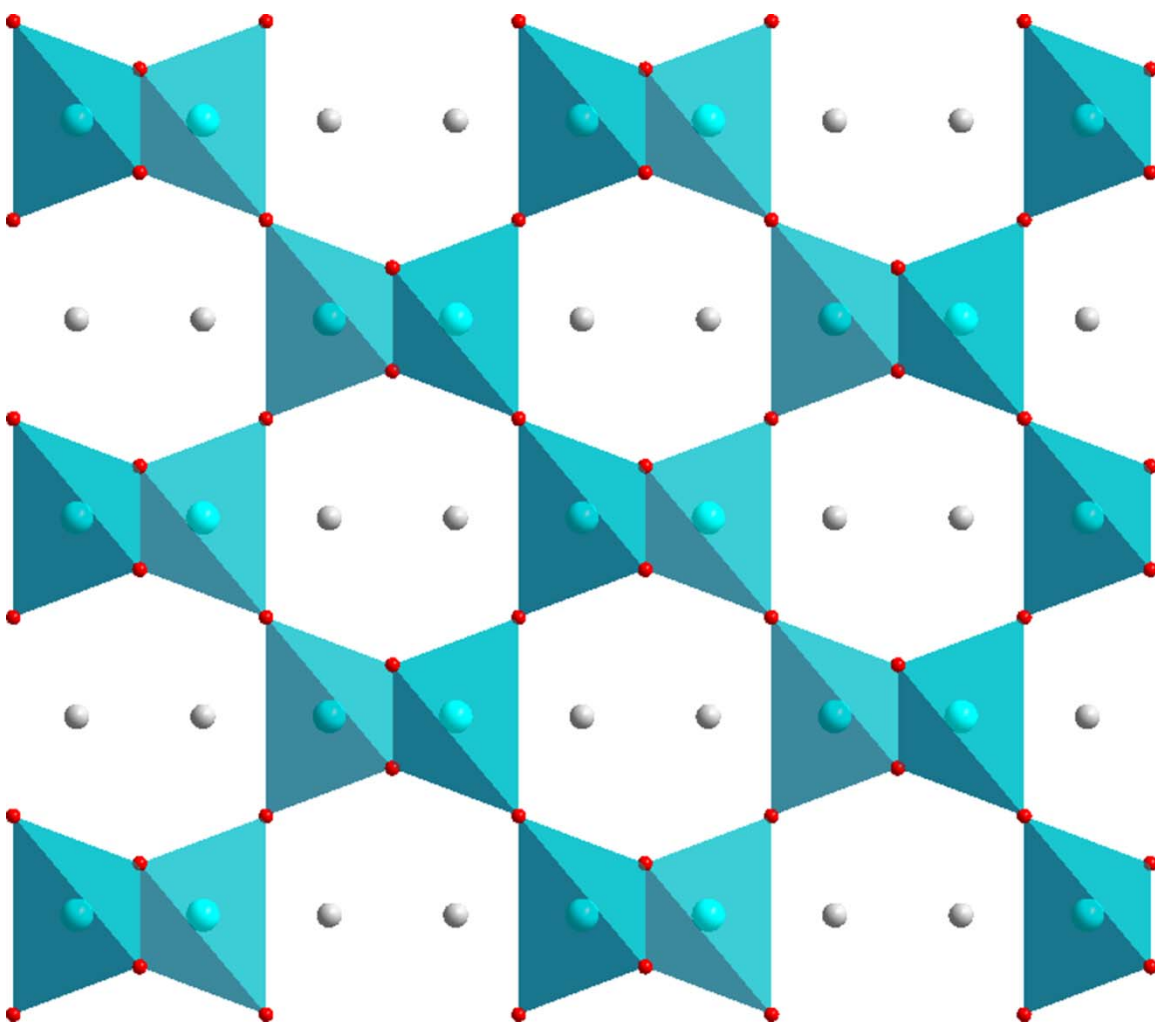


Figure 5.41 Proposed structure of tunnel LiCoO_2 resulting from the ion exchange using LiNO_3 with the known compound KCoO_2 .

Tunnel LiCoO_2 , if successfully synthesized, could result in one full electron transfer, unlike the layered structure, which can only cycle 50 % of theoretical capacity. Multiple electron transfer could be investigated with this material based on the information achieved from the similar structure T- LiFeO_2 .

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Chapter 6

Synthesis of the Novel Polymorph, LiFeTiO_4 , with Calcium Ferrite Structure

6.1 Introduction

Synthesis of novel materials to be used in rechargeable lithium ion batteries (LIBs) has played a pivotal role in the advancement of modern day technologies because it offers lighter weight and longer life cycle in portable electronics and hybrid electric vehicles. In 1997, Goodenough's group suggested the cathode material LiFePO_4 [1] which in turn resulted in an array of research into polyoxoanions as potential cathode materials. Following the synthesis and characterization of LiFePO_4 , many new compounds were achieved [2-5]. Further investigation into many of these compounds has resulted in new synthetic techniques that alter particle morphology and/or size to better engineer the compounds, therefore enhancing their electrochemical performance [6,7].

Polymorphs of known phases have also shown promise with different physical properties due to their different structure types [2-4]. Investigation into sodium analogs of successful LIBs has also shown promise for potential sodium ion batteries along with mixed stoichiometry LIBs [7]. Polymorph investigation into sodium ion batteries has also stemmed interest. Recently, $\text{Na}_2\text{MnP}_2\text{O}_7$, a $\text{Mn}^{2+/3+}$ redox potential, was electrochemically probed resulting in the highest capacity for Na-ion batteries known [8]. Lithium analogs to well characterized oxides such as NaCoO_2 have resulted in the α - NaFeO_2 structure compound LiCoO_2 , currently the most commonly used cathode material for rechargeable LIBs. Due to an increased concern over toxicity and cost of the

transition metal used, many researchers have focused on inexpensive and less toxic transition metals such as Mn, Ni, and Fe [9–12].

The lithium analog to α -NaFeO₂ was synthesized through ion exchange, then found to undergo a phase transition by attempting to probe the Fe³⁺/Fe⁴⁺ redox potential [13,14]. Investigation into another lithium analog of a sodium iron oxide was performed through the ion exchange of lithium for sodium into the β -NaFeO₂ polymorph resulting in the new compound T-LiFeO₂ [15]. It was reported that probing the Fe³⁺/Fe⁴⁺ redox potential of this tetrahedrally coordinated iron oxide resulted in the transformation of the tunnel-like structure into LiFe₅O₈ (Li_{0.2}FeO_{1.6}) through a reaction with the electrolyte leading to oxygen loss.

Investigating the synthesis of new materials via ion exchange of lithium for sodium, with known sodium metal oxides allows for the formation of compounds that would normally not form due to more thermodynamically stable polymorphs that form in one-step or one-pot synthetic reactions. Previous investigations of LiFeTiO₄ with different concentrations of transition metals in the spinel structure have been characterized as an intercalation anode to form compounds with the general formula Li_{1+x}Fe_{1-3x}Ti_{1+2x}O₄ and cycling voltages below 2 V [16]. Li₂FeTiO₄ with the disordered rock salt structure was synthesized using the carbon precursor approach and heat-treated under CO/CO₂ atmosphere at 700 °C. The resulting carbon coated material exhibited reversible cycling between about 2.3 and 2.7 V, intercalation and deintercalation respectively, with a

capacity of about 83% of its theoretical capacity, but only when particle size was between 10 nm and 25 nm [17].

Synthesis of the polymorph LiFeTiO_4 with the calcium ferrite structure was performed [18]. It was initially synthesized to probe the $\text{Fe}^{2+}/\text{Fe}^{3+}$ and the $\text{Fe}^{3+}/\text{Fe}^{4+}$ redox potentials due to its tunnel-like structural similarity to LiFePO_4 . The initial hypothesis was that the rigid structure would provide stability to intercalate and deintercalate lithium, thus leading to the first 2-electron transfer iron based cathode material. Previously, the removal of lithium was observed through chemical deintercalation of the calcium ferrite structure LiFeTiO_4 in the presence of Br_2 and I_2 [19], therefore providing preliminary evidence of Fe^{4+} . Rietveld refinement of diffraction data of LiFeTiO_4 and $\text{Li}_2\text{FeTiO}_4$ is presented. Electrochemical characterization of the as prepared LiFeTiO_4 showed reversible cycling between 2 and 2.3 V against lithium with an average particle size of 10 μm determined by SEM. Mössbauer spectroscopy was performed on the as prepared and lithium deintercalated $\text{Li}_{0.33}\text{FeTiO}_4$ and determined to only contain Fe^{3+} .

6.2 Synthesis of NaFeTiO_4

All reagents used were of ACS grade purity or higher and were used without further purification. Fe_2O_3 (99.5%), TiO_2 (rutile, 99.5%), and methanol, (anhydrous 99.9%) were obtained from Alfa Aesar. Na_2CO_3 (99%) was purchased from Mallinckrodt Chemicals. Initial attempts to synthesize NaFeTiO_4 were performed as described in [20] with stoichiometric amounts of Na_2CO_3 , Fe_2O_3 , and TiO_2 . The starting materials were mixed in an agate mortar then fired in air at 1200 °C repeatedly with intermittent grindings.

Following the procedure as described, the initial batch of NaFeTiO_4 was pelleted, placed into an alumina boat, inserted into a furnace with a heating rate of $100\text{ }^\circ\text{C}/\text{hour}$, held at $1200\text{ }^\circ\text{C}$ for 48 hours, then allowed to cool to room temperature naturally. The resulting product had formed single crystals due to the melting of the reactants at such high temperatures. Synthesis of NaFeTiO_4 was then altered, ratios of Na_2CO_3 , Fe_2O_3 , and TiO_2 , were intimately mixed stoichiometrically with 10% excess Na_2CO_3 using a mortar and pestle. Excess sodium is required due to volatility of sodium at high temperatures. Using the resulting powder, the mixture was pelleted and fired at $850\text{ }^\circ\text{C}$ for 450 hours with intermittent grindings until pure. The synthetic procedure was optimized with ratios of Na_2CO_3 , Fe_2O_3 , and TiO_2 that were intimately mixed stoichiometrically with 5% excess Na_2CO_3 using a planetary ball mill. The powders were mixed for six cycles of five minutes in steel ball mill jars at 500 RPM using four tungsten carbide balls per jar. The mixture was then pressed in a 3/4" pellet at 5 tons, placed in an alumina boat, and fired at $850\text{ }^\circ\text{C}$ for 12 hours in air. Further annealing at $975\text{ }^\circ\text{C}$ was performed for 48 hours.

6.3 Ion Exchange of NaFeTiO_4 to LiFeTiO_4

LiNO_3 (99%) and methanol (anhydrous 99.9%) were obtained from Alfa Aesar. LiFeTiO_4 was synthesized via an ion exchange of Li^+ for Na^+ in NaFeTiO_4 . Two times excess LiNO_3 was intimately mixed with one equivalent of NaFeTiO_4 then heated at $325\text{ }^\circ\text{C}$ for 48 hours under O_2 flow. The reaction product was washed with anhydrous methanol, dried under vacuum, and then stored under N_2 in a glove box.

6.4 Chemical intercalation and deintercalation

Bromine (99.5%) and iodine (99.8%) were obtained from Jade Scientific and acetonitrile (99.5%) was purchased from Mallinckrodt Chemicals. Chemical lithium deintercalation of $\text{Li}_x\text{FeTiO}_4$ ($0 \leq x < 1$) was performed using a nitrogen glove bag, with two times molar excess bromine or iodine to LiFeTiO_4 , in a round bottom flask topped with 100 mL of acetonitrile. The reaction mixtures were then stirred at room temperature for 48 hours. Next the mixture was filtered, washed with acetonitrile, vacuum dried and stored under N_2 in a glove box. The resulting compounds were analyzed using PXD and ICP [21].

n-pentane (anhydrous 99.8+ %) was obtained from Alfa Aesar and n-butyllithium (2.5M in hexanes) was purchased from Sigma-Aldrich. Lithium intercalation into LiFeTiO_4 was performed in a nitrogen glove box using an equivalent of the prepared LiFeTiO_4 and one equivalent of n-butyl lithium. The mixture was stirred at room temperature for 48 hours, filtered, washed with pentane, vacuum dried, and stored under N_2 in a glove box. The resulting compounds were then analyzed using PXD and ICP [21].

6.5 Results and Discussion

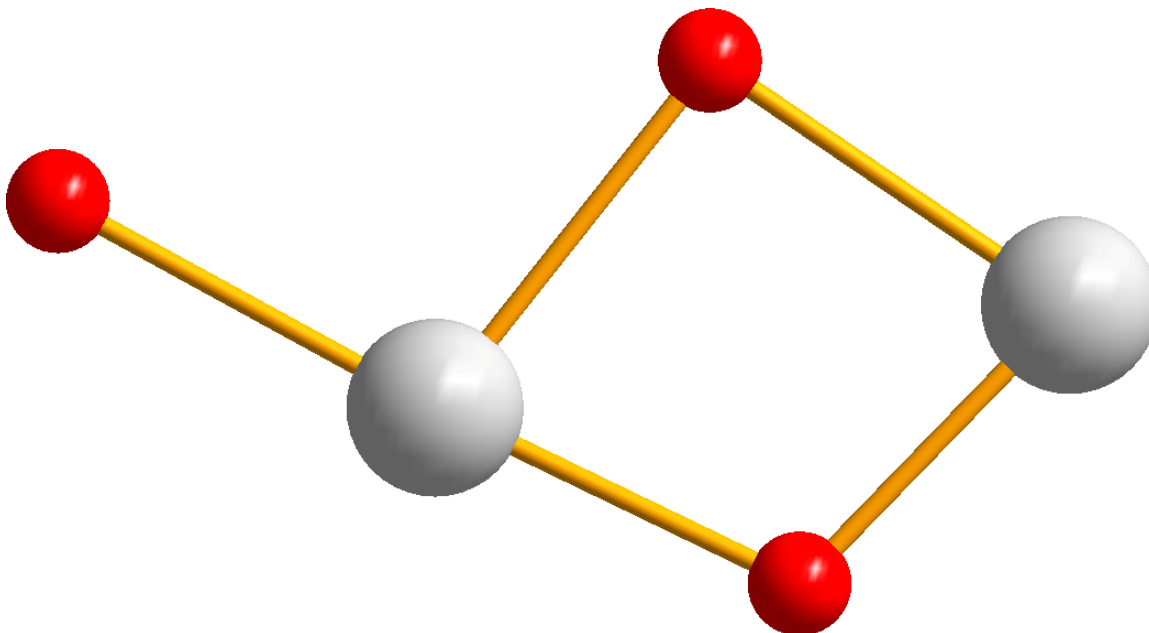


Figure 6.1 Single crystal diffraction of Anosovite, Ti_3O_5 , formed during initial attempt to synthesize NaFeTiO_4 from literature preparation. Space group Cmcm , $a=3.7097(2) \text{ \AA}$, $b=9.7308(4) \text{ \AA}$, $c=9.9716(5) \text{ \AA}$, and volume $357.96(3) \text{ \AA}^3$ from a molybdenum source single crystal diffractometer.

The literature preparation of NaFeTiO_4 , as previously mentioned, was prepared through the solid-state reaction of the mixed reagents Na_2CO_3 , Fe_2O_3 , and TiO_2 . This mixture was pelleted then fired at 1200°C for 48 hours in air. The sample was allowed to cool to room temperature at the natural cooling rate of the turned off furnace. The pelleted melted at temperatures elevated above 851°C (M.P. of Na_2CO_3) therefore, acting as a flux and forming single crystals (Figure 6.1). This was determined to be single crystals of

Anosovite, Ti_3O_5 originally discovered in 1951 and more recently reinvestigated in 1998 [22].

Further attempts to synthesize NaFeTiO_4 with altered furnace programming were then carried out as previously described using the initial reagents Na_2CO_3 , TiO_2 , and Fe_2O_3 stoichiometrically mixed with 10% excess Na_2CO_3 , to compensate for sodium volatility until homogenous. The resulting product was a mixture of NaFeTiO_4 and $\text{Na}_{0.79}\text{Fe}_{0.8}\text{Ti}_{1.2}\text{O}_4$ as seen in Figure 6.2.

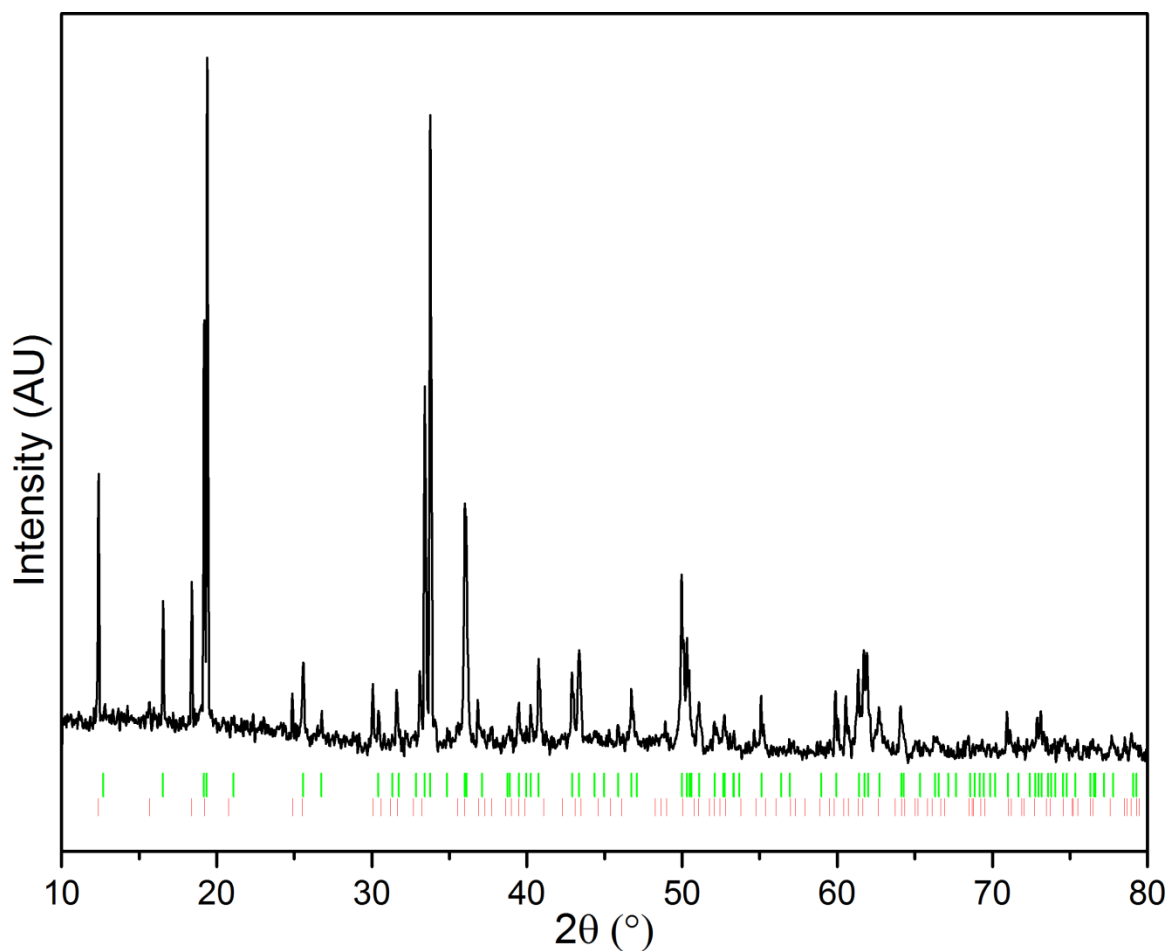


Figure 6.2 The mixture containing NaFeTiO_4 (green ticks) and $\text{Na}_{0.79}\text{Fe}_{0.8}\text{Ti}_{1.2}\text{O}_4$ (red ticks).

Further annealing at 975 °C of this sample with intermittent grindings and pelleting eventually led to the mixture of NaFeTiO_4 and the $\alpha\text{-NaFeO}_2$ structure $\text{Na}_{0.75}\text{Fe}_{0.75}\text{Ti}_{0.25}\text{O}_4$ (Figure 6.3).

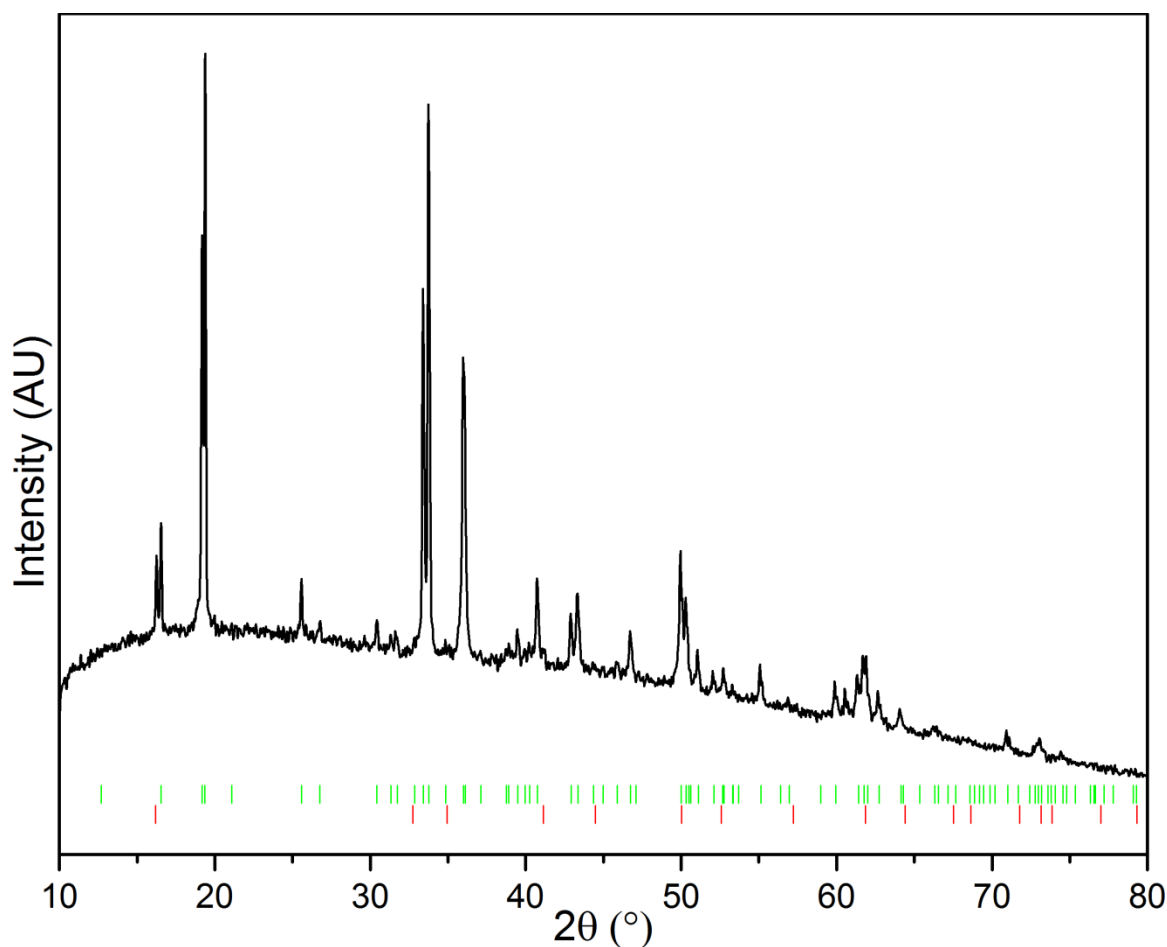


Figure 6.3 The mixture containing NaFeTiO_4 (green ticks) and $\text{Na}_{0.75}\text{Fe}_{0.75}\text{Ti}_{0.25}\text{O}_2$ with the $\alpha\text{-NaFeO}_2$ structure type (red ticks).

Continued intermittent grinding, pelleting, and firing at 975 °C for durations longer than 350 hours led to the formation of pure NaFeTiO_4 as seen in Figure 6.4. It was determined that the initial 10% excess Na_2CO_3 was too much, therefore, decreasing this excess

amount to 5 %, reduced the synthetic preparation of NaFeTiO_4 to 48 hours at 975 °C with no requirement for intermittent grinding and pelleting.

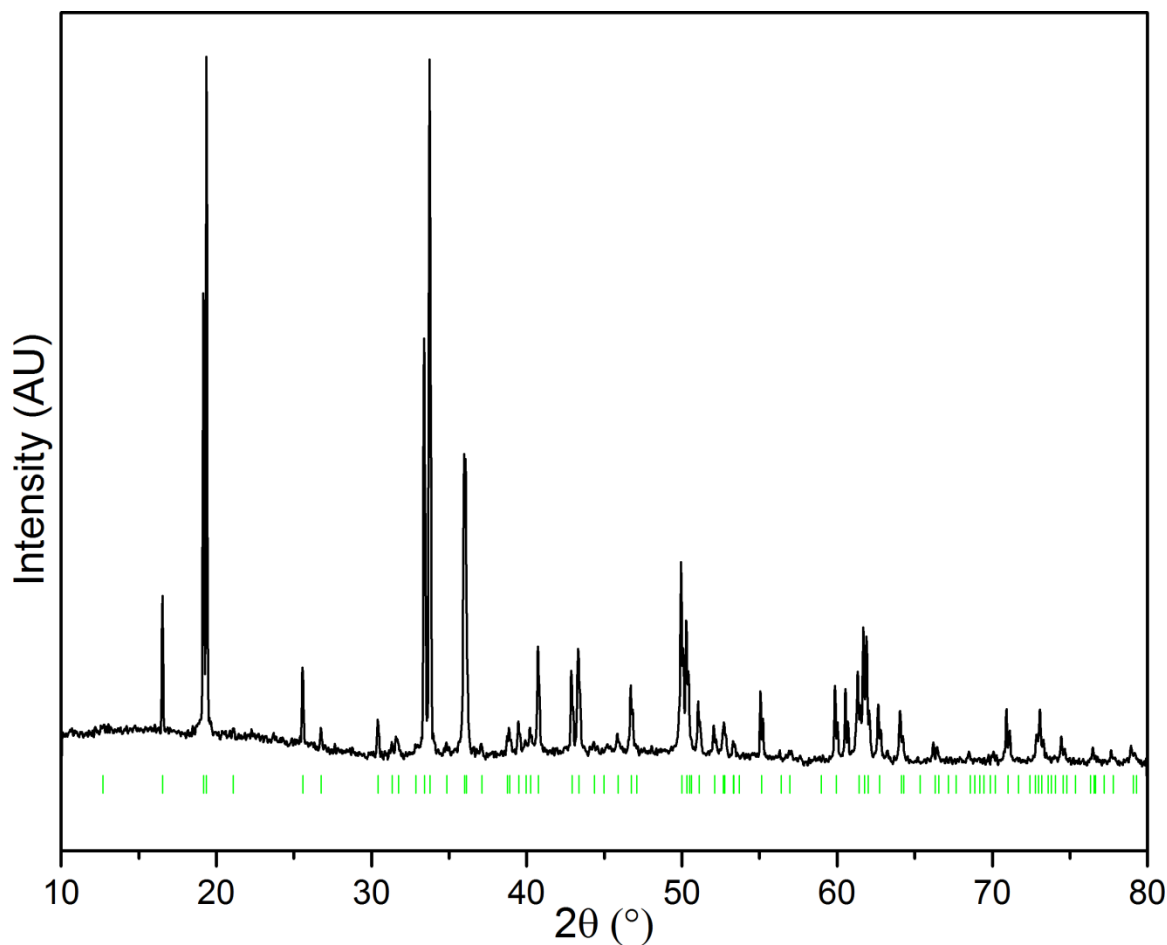


Figure 6.4 The PXD pattern of NaFeTiO_4 (green ticks) was determined to be a pure phase sample.

Initial attempts to synthesize LiFeTiO_4 through the ion exchange of Li^+ for Na^+ from NaFeTiO_4 at 250 °C under O_2 flow were unsuccessful. Upon increasing the temperature to 350 °C, successful ion exchange was observed after 48 hours. This was determined

though ICP analysis giving a Li:Fe ratio of 1:1 with no sodium detection. PXD of the exchange product at 350 °C was impure with peaks of the known LiFeTiO₄ spinel structure appearing. Further attempts at the ion exchange at 300 °C for 250 hours showed successful exchange with less intense peaks of the spinel structure. Decreasing the exchange time to 24 hours at 300 °C resulted in partial exchange, while increasing the time to 72 hours resulted in the formation of the spinel structure. Holding the exchange time to 48 hours at 300 °C allowed the ion exchange to occur with no sodium precursor phase, or spinel structure in the PXD. Longer exchange times and higher temperatures clearly led to the transformation of the calcium ferrite type LiFeTiO₄ to the spinel polymorph. The tunnel structured LiFeTiO₄ is only kinetically stable and is unstable toward the transformation to the thermodynamically preferred spinel polymorph. This observation was further confirmed by TGA experiments in both nitrogen and oxygen and their respective PXDs as seen in Figures 6.5-6.8.

Thermogravimetric analysis (TGA) of the calcium ferrite structured LiFeTiO₄ in both oxygen and nitrogen to a temperature of 1000 °C was performed. The resulting sample was removed and analyzed by PXD, whereby it was determined that the LiFeTiO₄ calcium ferrite structure transforms to the more thermodynamically stable spinel structure, ICSD 050387, under both O₂ and N₂ atmospheres. The transformation of the calcium ferrite structure to the spinel structure is thermodynamically driven. This is also seen in increased annealing times and temperatures as earlier described with the formation of the spinel phase peaks at 350 °C or exchange times of 250 hours at 300 °C.

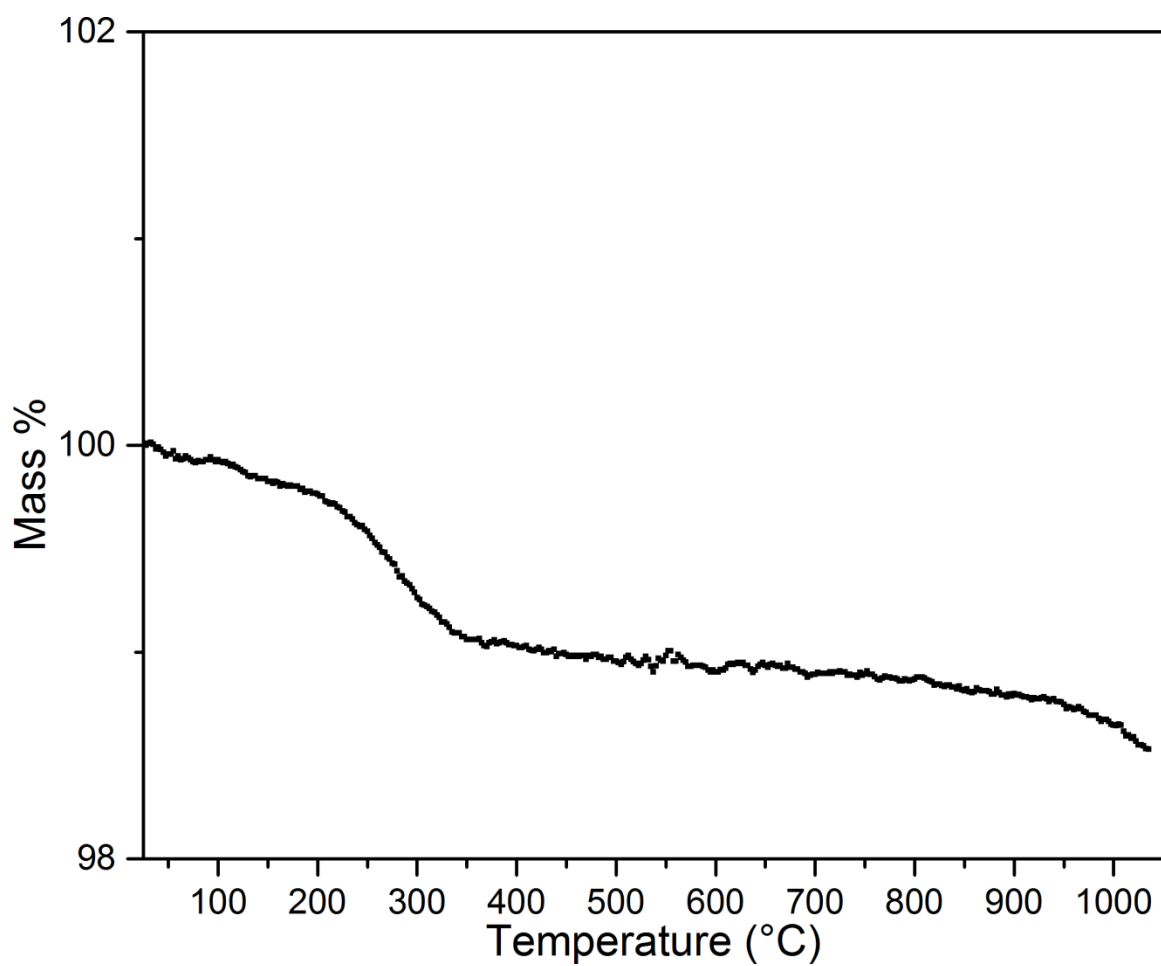


Figure 6.5 Thermogravimetric analysis of calcium ferrite polymorph LiFeTiO_4 in nitrogen to a final temperature of 1050 $^{\circ}\text{C}$.

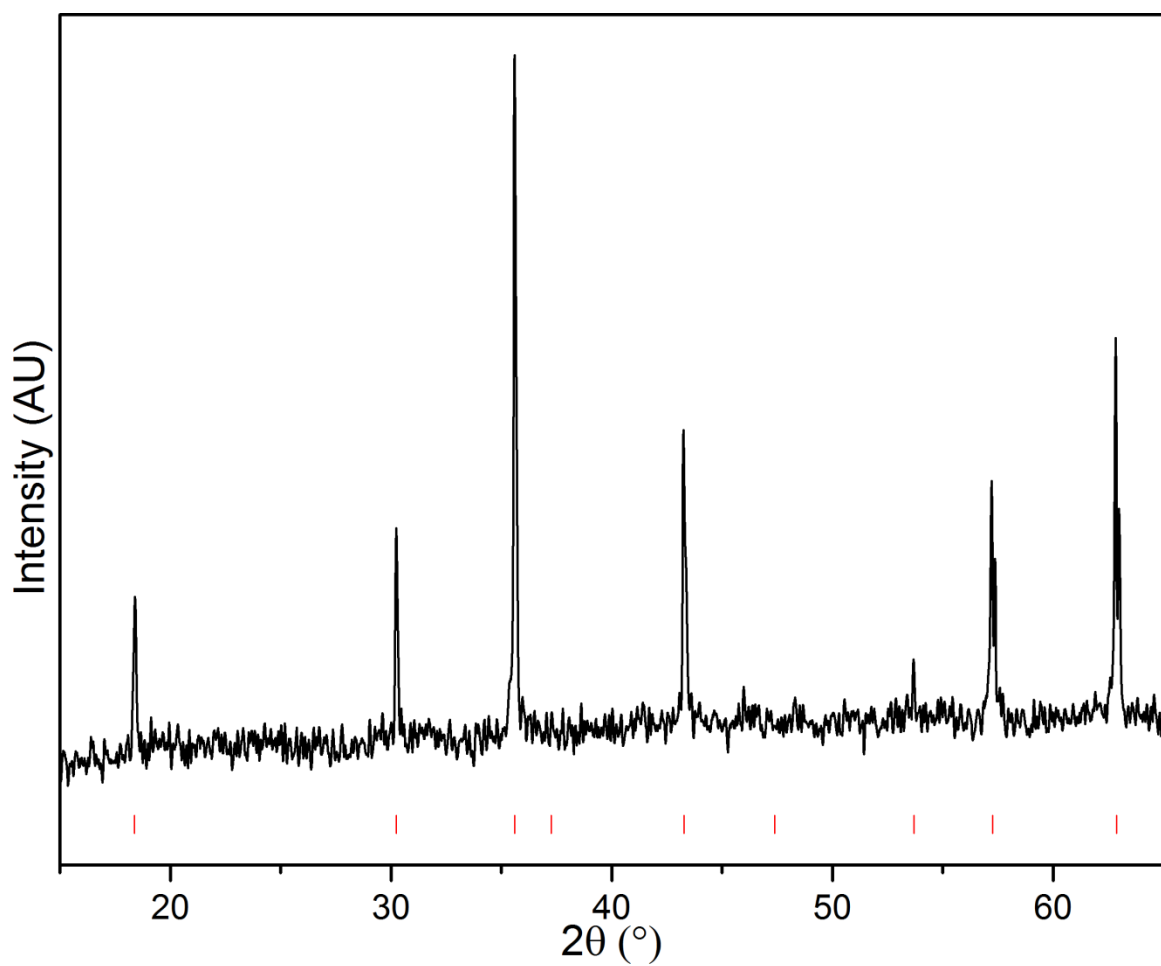


Figure 6.6 PXD of LiFeTiO_4 after TGA in nitrogen to 1050 °C. Red ticks illustrate peak reflection locations of the spinel structure LiFeTiO_4 .

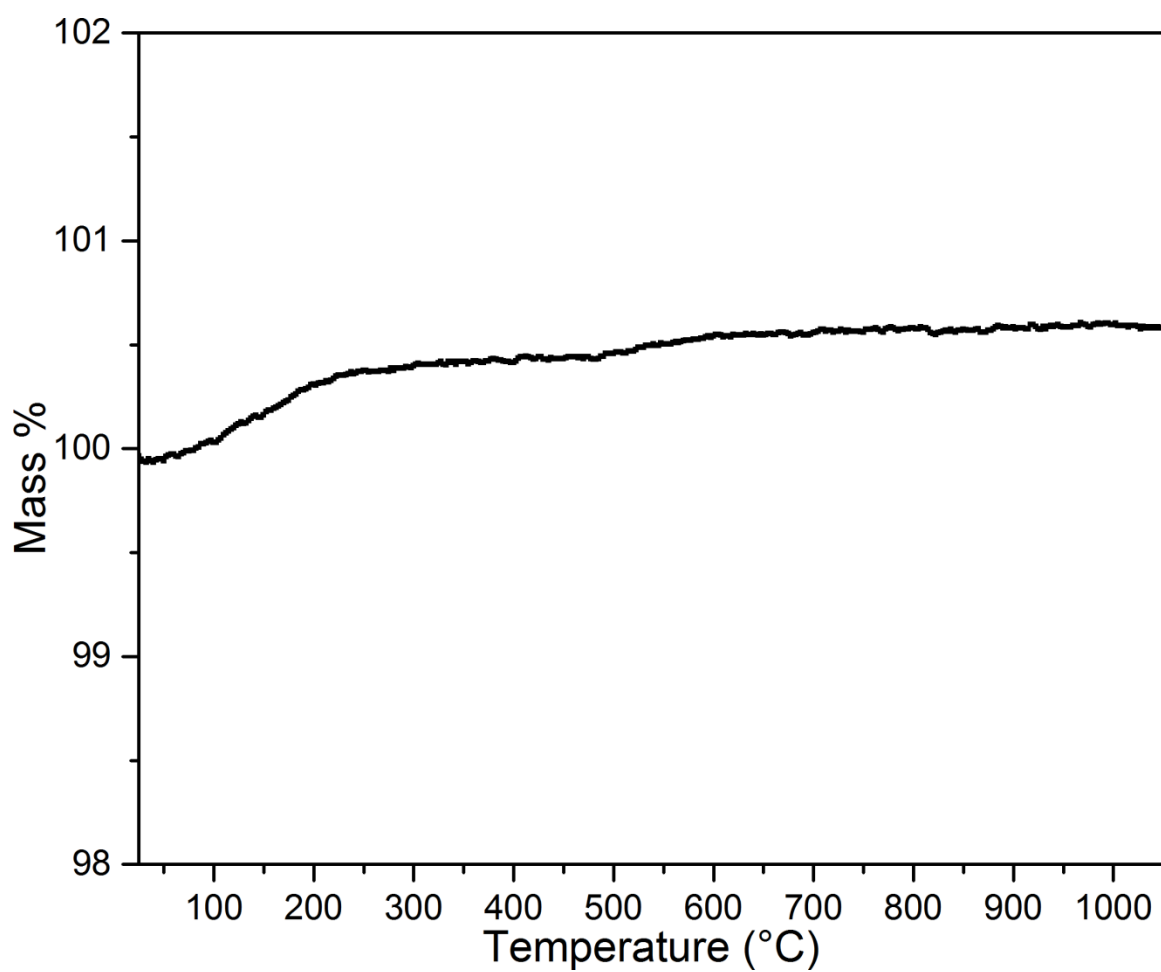


Figure 6.7 Thermogravimetric analysis of calcium ferrite polymorph LiFeTiO_4 in oxygen to a final temperature of 1050 $^{\circ}\text{C}$.

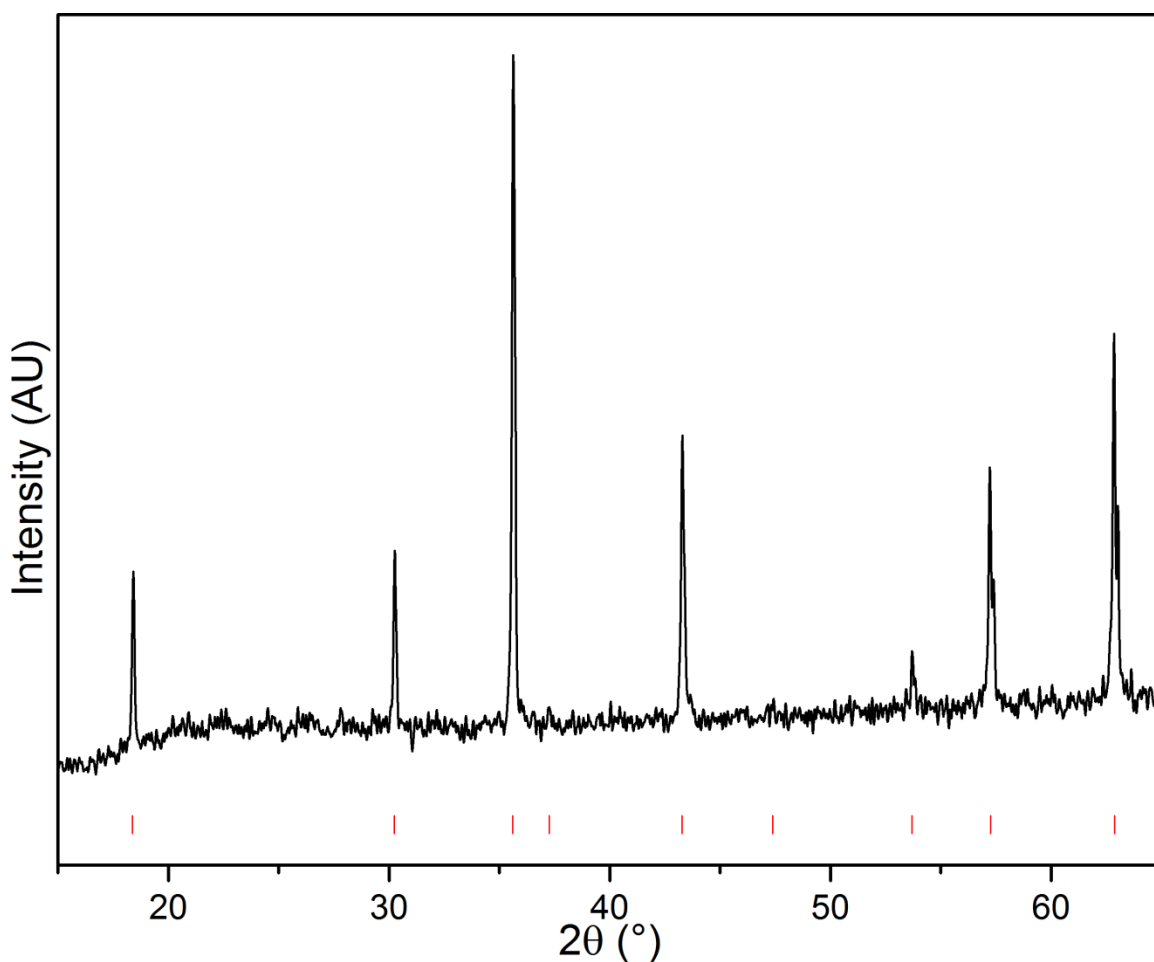


Figure 6.8 PXD of LiFeTiO_4 after TGA in oxygen to 1050 °C. Red ticks illustrate peak reflection locations of the spinel structure LiFeTiO_4 .

Scanning electron microscopy was employed to determine the morphology and particle size of the as prepared LiFeTiO_4 . The particles, as seen in Figures 6.9-6.11, were observed to have a size in the micrometer regime as expected from the synthetic procedure used. The morphology of the particles was generally rod-like. Smaller particles were observed on the surface of the LiFeTiO_4 , but due to exposure to ambient conditions

in the mounting process and the hygroscopic nature of the material, these smaller particles can be attributed to carbonate formation or the slight hydrolysis of LiFeTiO_4 .

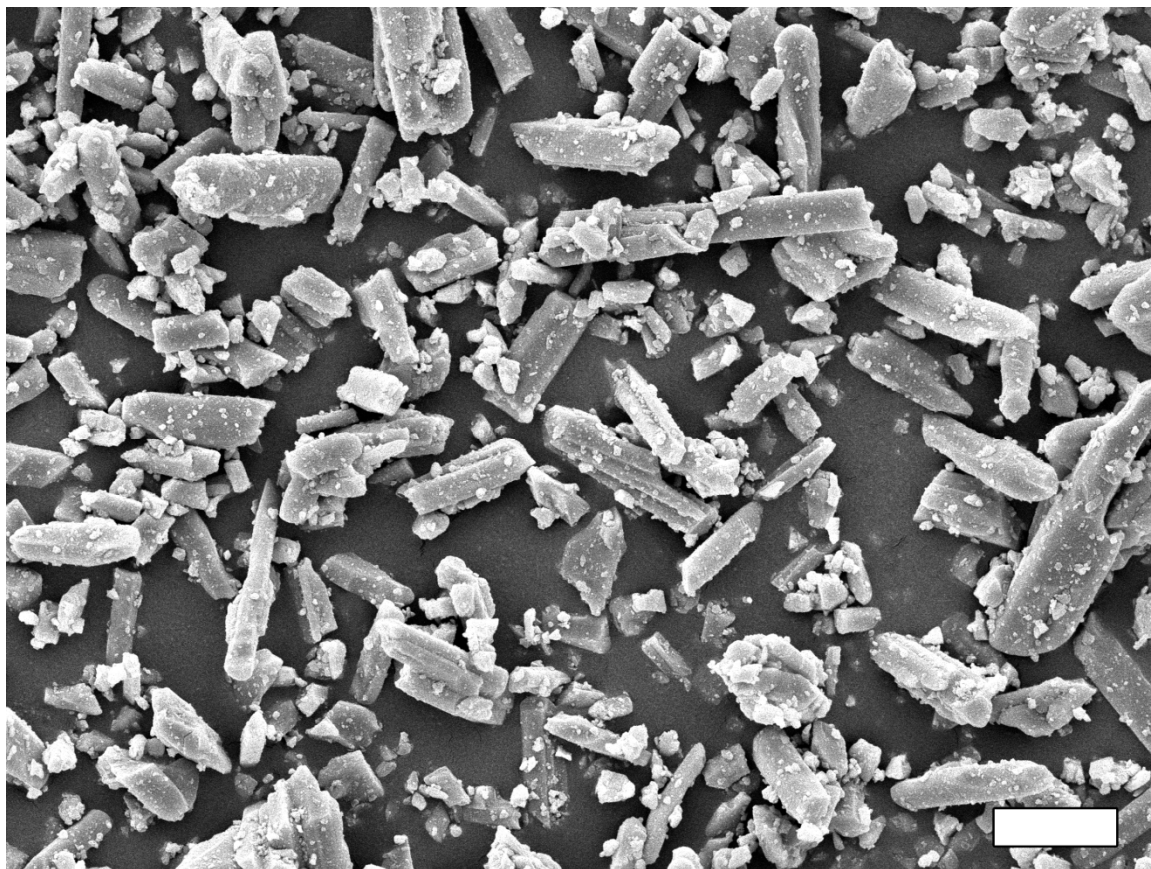


Figure 6.9 SEM images of as prepared LiFeTiO_4 illustrating the particle size of the compound in the micrometer regime, scale bar represents 5 μm .

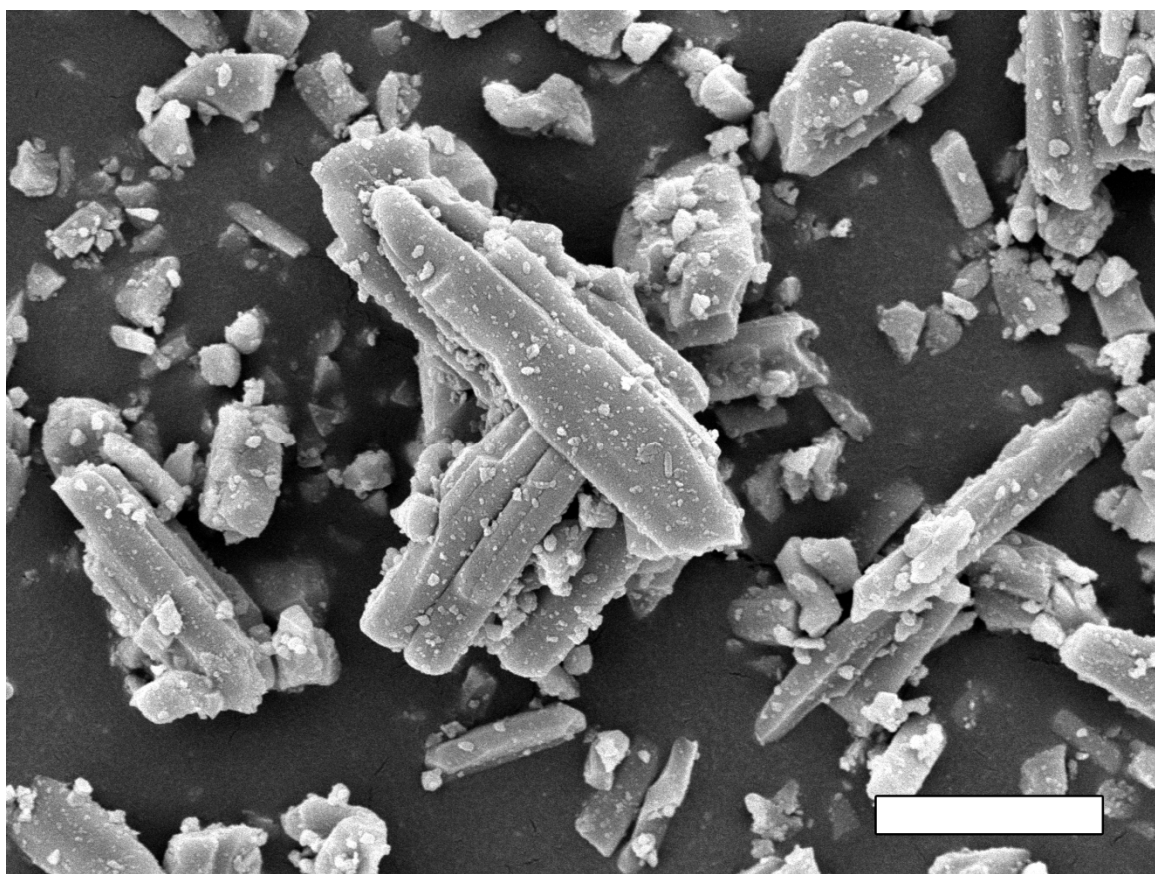


Figure 6.10 SEM images of as prepared LiFeTiO_4 illustrating the particle size of the compound in the micrometer regime, scale bar represents 5 μm .

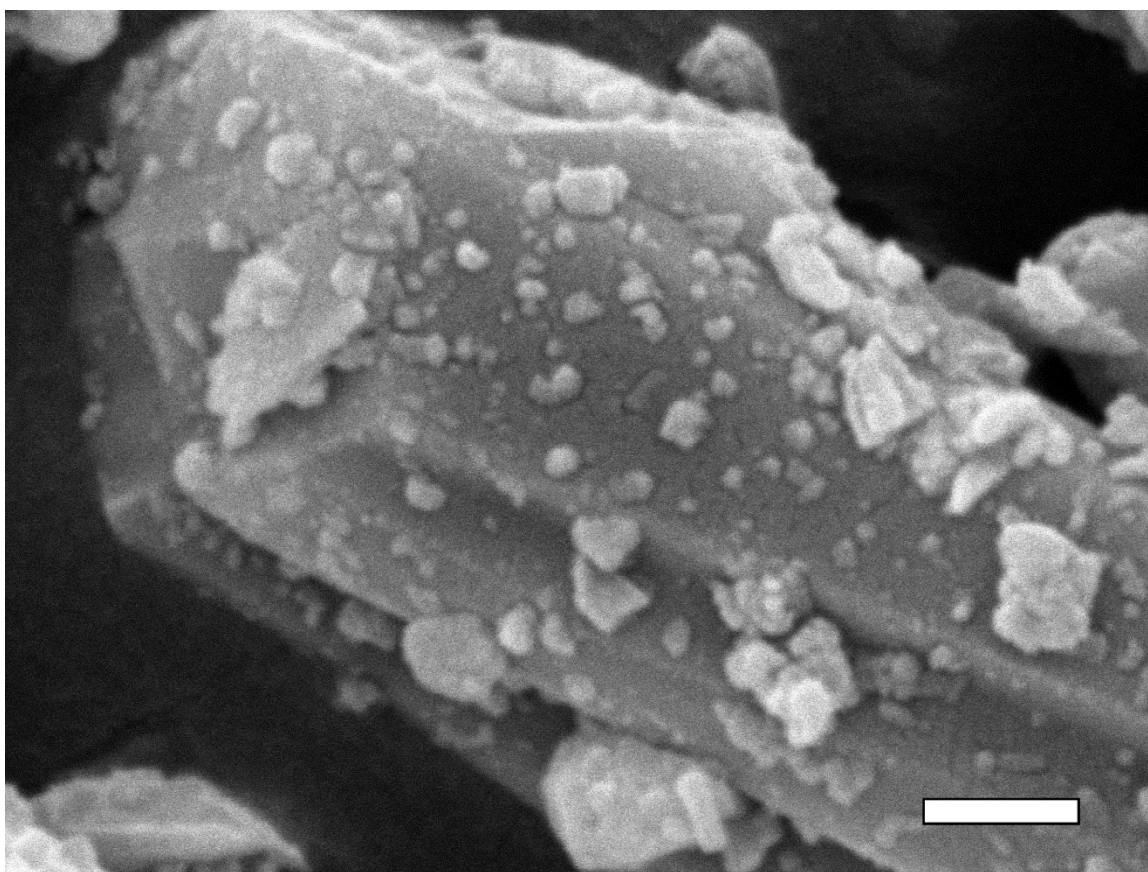


Figure 6.11 SEM images of as prepared LiFeTiO_4 illustrating the particle size of the compound in the micrometer regime, scale bar represents 500 nm.

Oxidation via chemical lithium deintercalation was attempted by the addition of bromine and iodine as described [19,21]. ICP ratios resulted in surprisingly low values of lithium to iron $\text{Li}_{0.33}\text{FeTiO}_4$ and $\text{Li}_{0.55}\text{FeTiO}_4$ for bromine and iodine respectively [19]. These values were deemed low due to the relatively low oxidizing power of bromine and iodine against iron in the 3+ oxidation state. Electrochemical characterization did indicate that oxidation of the compound, the deintercalation of lithium from LiFeTiO_4 , during the initial cycling below 4 V, corresponds to the chemical potential of iodine and bromine

[23]. Further investigation using PXD, electrochemistry and Mössbauer spectroscopy, determined that deintercalation resulted in the decomposition of the compound.

Reduction via chemical lithium intercalation was initially attempted by the addition of concentrated solutions of one, five, and ten times molar excess of n-butyl lithium to one equivalent of LiFeTiO_4 . This resulted in an instant color change for all three reactions, from the salmon colored precursor LiFeTiO_4 to a black powder. PXD of the five and ten times excess products indicated the decomposition of LiFeTiO_4 with no observable peaks and only an amorphous background [19]. The resulting PXD from the addition of an equimolar ratio of concentrated n-butyl lithium and LiFeTiO_4 had observable peaks of LiFeTiO_4 that were just over the amorphous and unusually high background. They were similar to those seen in the completely decomposed and amorphous five and ten times excess n-butyl lithium reactions. ICP of this product indicated a metal ratio of lithium:iron to be 3.5:1. These results can be explained by the large particle size of the precursor LiFeTiO_4 . The high reactivity of the n-butyl lithium over reduced the outside of the particles resulting in the decomposition and observed amorphous background while the center of the large particles were unreacted. This explains the observed peaks with decreased intensities of LiFeTiO_4 . Further attempts to intercalate lithium into the structure were successful upon the slow (1-hour) drop wise addition of diluted (0.1 molar) n-butyl lithium into a round bottom flask of 100 ml pentane and LiFeTiO_4 in a nitrogen glove box. Due to the pyrophoric nature of the resulting compound, the PXD measurements were taken on a Bruker D2 Phaser in a nitrogen filled glove box.

LiFeTiO₄ was Rietveld Refined using GSAS and determined to have an Rwp=4.42. The crystal structure of LiFeTiO₄ was refined using the NaFeTiO₄ structure as an initial model (Figure 6.12). The space group Pnma was maintained from the precursor and the cell parameters were determined to be a=8.9206(5) Å, b=2.9595(3) Å, and c=10.7103(7) Å. LiFeTiO₄ has a tunnel structure built up by (Fe/Ti)O₆ octahedra that form double edge-sharing chains. The edge-sharing Fe₂O₁₀ dioctahedra also vertex share with other Fe₂O₁₀ dioctahedra. This connectivity gives rise to the "double rutile" chain; the lithium ions are located in a single tunnel surrounded by four chains. Crystallographic data for the Rietveld refined LiFeTiO₄ can be seen in Table 6.1.

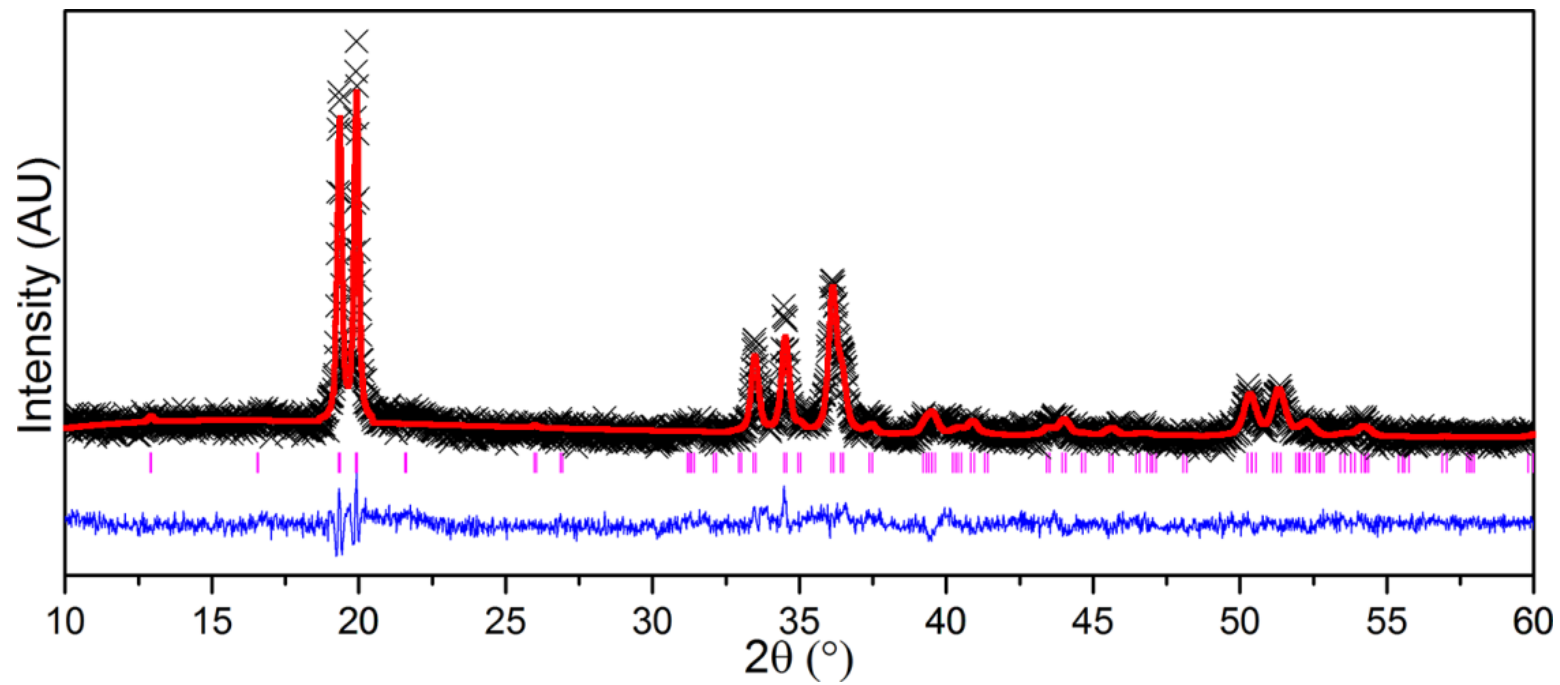


Figure 6.12 Observed (black crosses), calculated (red line), difference (blue) profiles, and Bragg reflections (tick marks) for the final Rietveld refinement of LiFeTiO_4 from PXD data, $R_{\text{wp}}=4.42$ and $\chi^2=0.260$.

Table 6.1 Crystallographic data for the Rietveld refinement of LiFeTiO_4 (space group Pnma), $a=8.9206(5)$ Å, $b=2.9595(3)$ Å, $c=10.7103(7)$ Å.

Atom	Site	x	y	z	$U_{\text{iso}}(10^3 \text{Å}^2)$	Occupancy
Li	4c	0.3409(5)	1/4	0.3498(5)	1.09(4)	1.
Fe1	4c	0.0774(3)	1/4	0.6344(5)	1.00(3)	0.5
Fe2	4c	0.0725(5)	1/4	0.1313(5)	0.99(6)	0.5
Ti1	4c	0.0774(3)	1/4	0.6344(5)	1.03(3)	0.5
Ti2	4c	0.0727(4)	1/4	0.1313(5)	0.99(5)	0.5
O1	4c	0.8945(6)	1/4	0.5201(1)	1.03(3)	1.
O2	4c	0.9996(3)	1/4	0.2875(3)	1.02(8)	1.
O3	4c	0.3079(2)	1/4	0.6299(8)	1.06(7)	1.
O4	4c	0.0676(1)	1/4	0.9434(2)	1.12(5)	1.

Following the synthesis of LiFeTiO_4 , chemical lithium intercalation was performed as previously described. PXD and ICP were used to confirm single-phase synthesis and proper metal stoichiometry. $\text{Li}_2\text{FeTiO}_4$ was Rietveld refined using GSAS and determined to have an $R_{\text{wp}}=5.50$ (Figure 6.13). The crystal structure for $\text{Li}_2\text{FeTiO}_4$ was refined using LiFeTiO_4 as an initial model. The space group Pnma was maintained from the precursor and the cell parameters were determined to be $a=9.0525(3)$ Å, $b=2.9566(2)$ Å, and $c=10.7575(5)$ Å (Table 6.2).

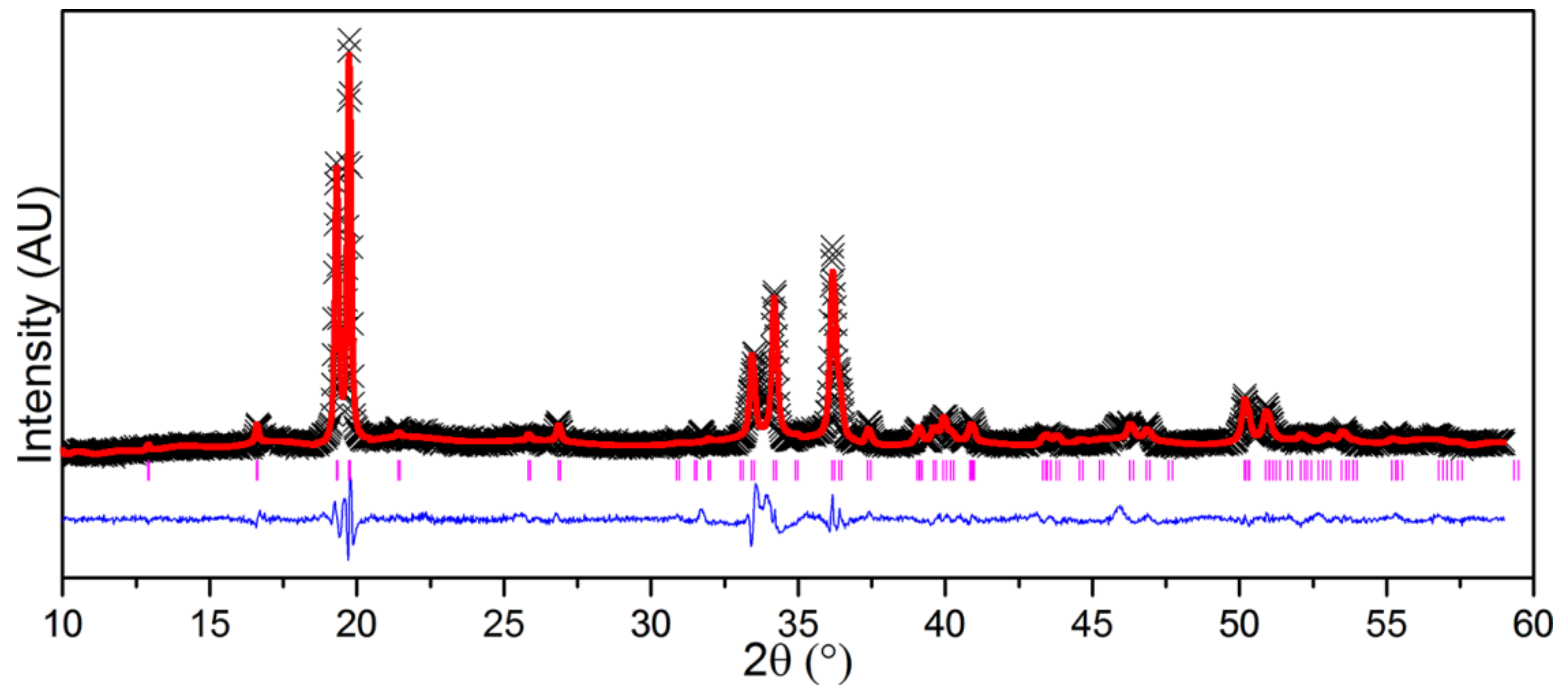


Figure 6.13 Observed (black crosses), calculated (red line), difference (blue) profiles, and Bragg reflections (tick marks) for the final Rietveld refinement of $\text{Li}_2\text{FeTiO}_4$ from PXD data, $R_{\text{wp}}=5.50$ and $\chi^2=0.183$.

Table 6.2 Crystallographic data for the Rietveld refinement of $\text{Li}_2\text{FeTiO}_4$ (space group Pnma), $a=9.0525(3)$ Å, $b=2.9566(2)$ Å, $c=10.7575(5)$ Å.

Atom	Site	x	y	z	$U_{\text{iso}}(10^2\text{\AA}^2)$	Occupancy
Li	4c	0.3733(7)	1/4	0.3540(6)	0.96(2)	1.
Li	4c	0.1146(9)	1/4	0.3124(1)	1.15(2)	1.
Fe1	4c	0.0869(3)	1/4	0.6095(3)	1.07(3)	0.5
Fe2	4c	0.0684(3)	1/4	0.1161(3)	1.00(5)	0.5
Ti1	4c	0.0869(3)	1/4	0.6095(3)	1.09(2)	0.5
Ti2	4c	0.0684(3)	1/4	0.1161(3)	1.00(6)	0.5
O1	4c	0.8982(1)	1/4	0.5221(1)	0.98(5)	1.
O2	4c	0.9528(1)	1/4	0.2728(1)	1.13(7)	1.
O3	4c	0.3216(9)	1/4	0.6590(1)	1.00(4)	1.
O4	4c	0.0830(1)	1/4	0.9215(1)	1.11(7)	1.

Electrochemical characterization was performed using LiFeTiO_4 as a cathode vs. a lithium anode. Initial cycling between 3.0 and 4.0 V results indicated the electrochemical intercalation was greater than the deintercalation on the same cycle. This trend continued for 8 cycles with no major fade in the cycling potential, indicating the structure's ability to harbor more lithium ions in the cavities as seen in Figure 6.20 [18]. Continued cycling of LiFeTiO_4 between these voltages eventually resulted in the decomposition of the compound as seen in Figures 6.14, 6.15, and 6.16. This explains the surprising ICP results observed from the bromine and iodine oxidation indicating that the LiFeTiO_4 decomposed under the mild oxidizing conditions of bromine and iodine. The PXDs

observed previously [19] can be explained due to the particle size with the outermost parts decomposing and the center remaining unreacted.

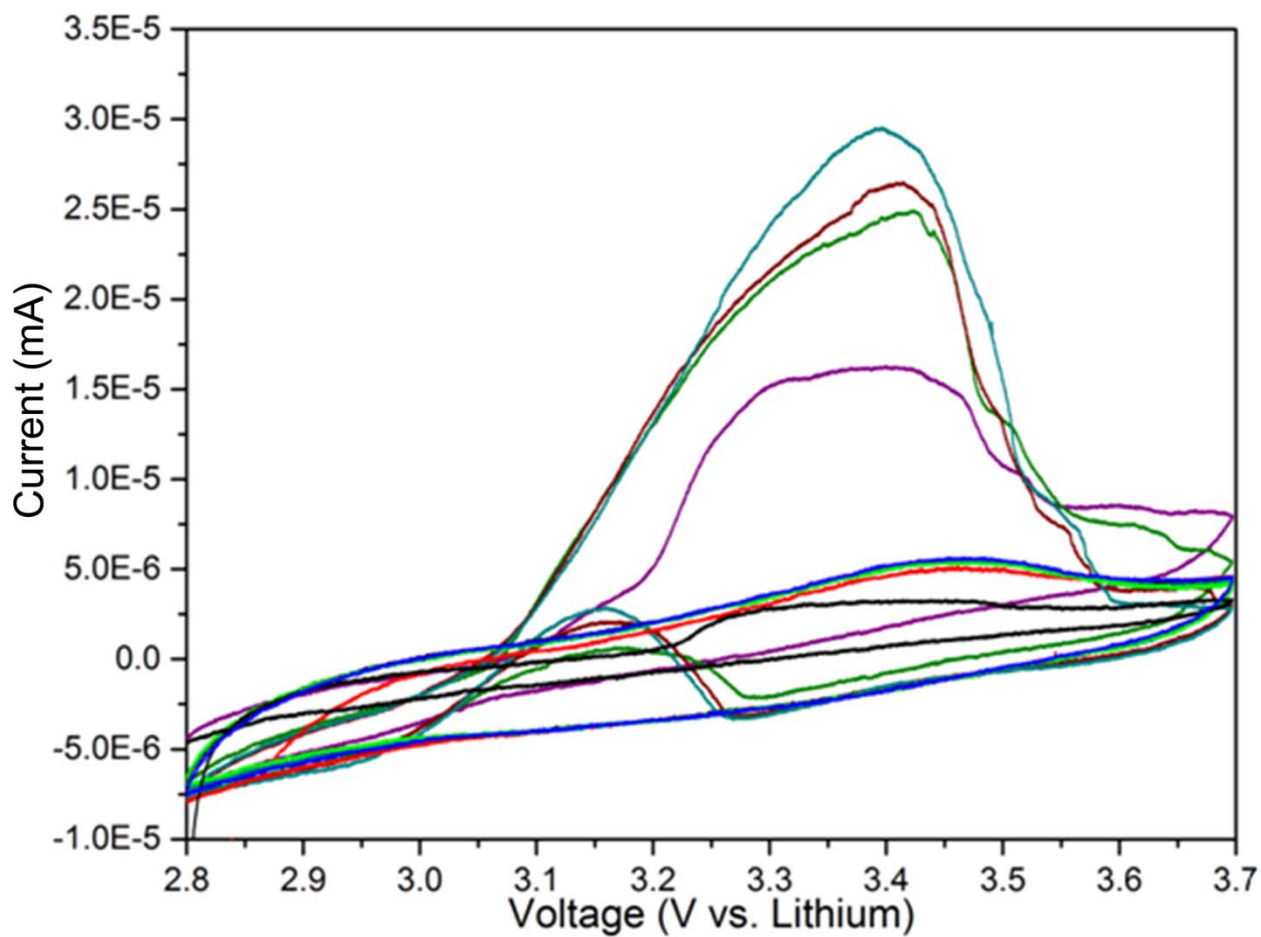


Figure 6.14 Cyclic voltammogram of LiFeTiO_4 between 2.8 and 3.7 V decomposing after the initial cycles as also illustrated by the low current.

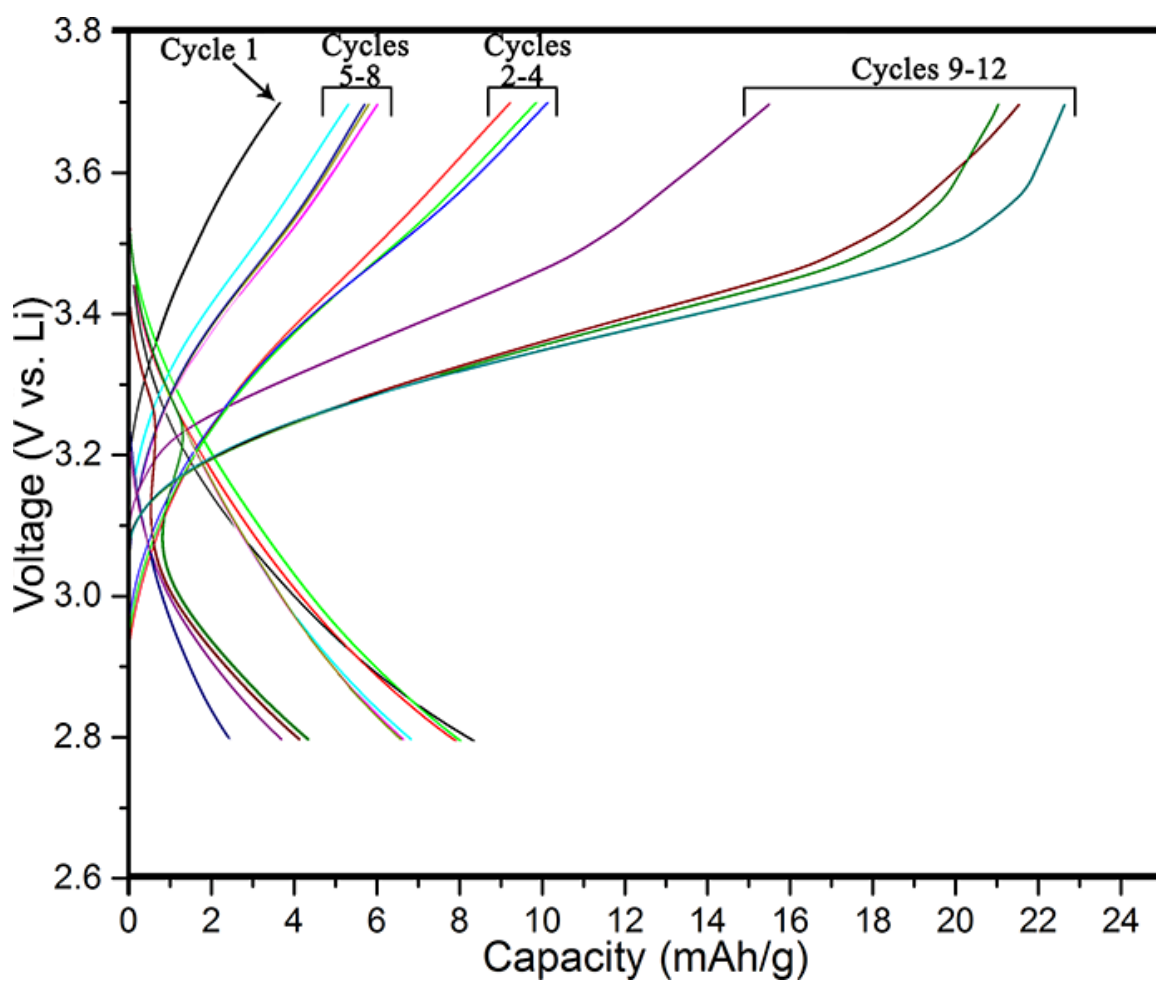


Figure 6.15 Integrated cyclic voltammogram illustrating the voltage as a function of capacity of LiFeTiO_4 in the attempt to probe the $\text{Fe}^{3+/4+}$ oxidation states resulting in the decomposition of the tunnel structure.

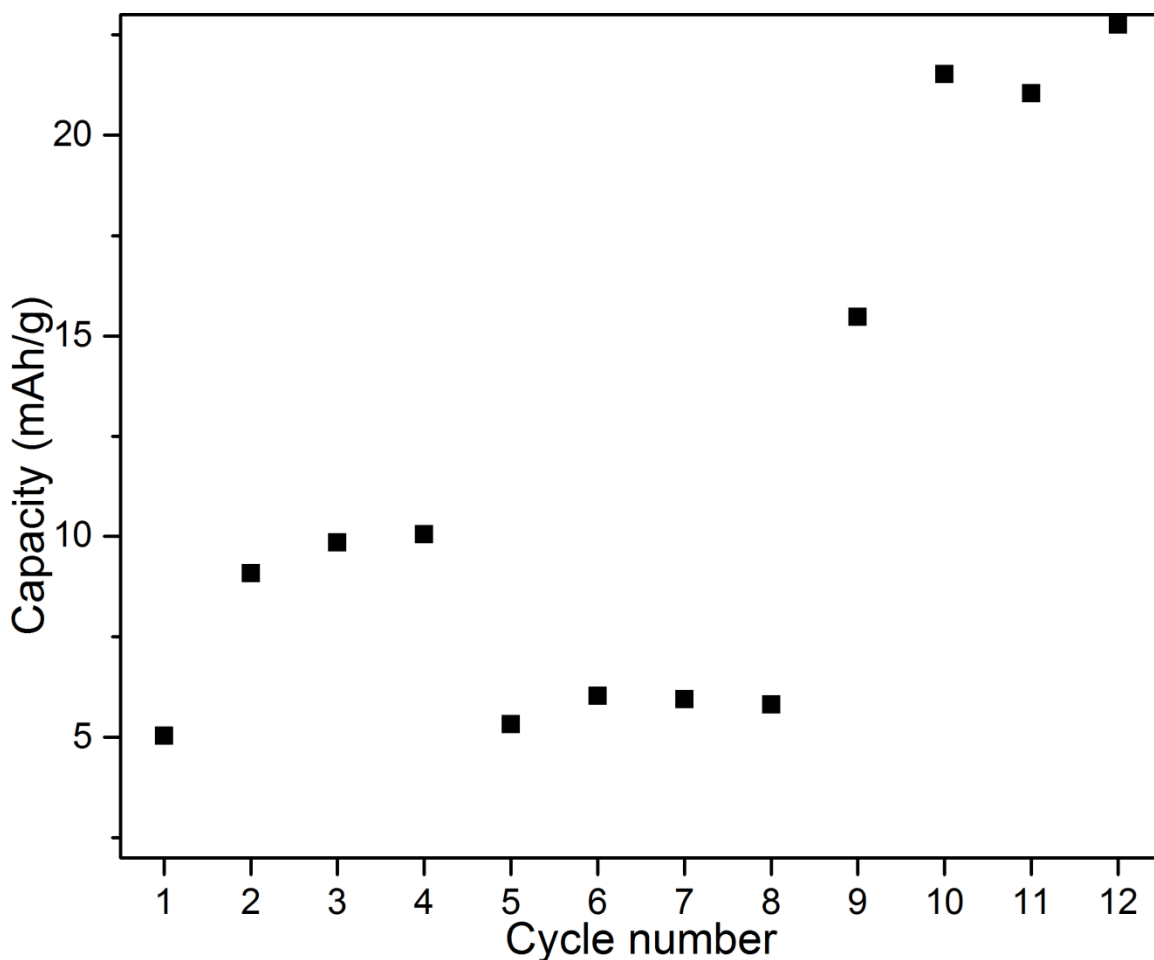


Figure 6.16 Capacity as a function of the cycle number showing the instability of the compound with no indication of a cycling trend.

Cycling the material at voltages between 1.5 and 3.0 V at a rate of C/5 showed initial intercalation at about 2.3 V (Figure 6.17), with a capacity of about 148 mAh/g (Figures 6.18 and 6.19). This correlates to the insertion of one lithium into the structure (Figure 6.20) confirming the initial hypothesis that the tunnels of this structure could harbor more lithium. Continued cycling at this rate resulted in a capacity fade of 8% over ten cycles. Increasing the rate to C/2.5 for 50 cycles had a similar fade trend with a decreased

starting capacity of about 121 mAh/g and a final capacity of 99 mAh/g and a capacity fade of 18% over the 50 cycles as seen in Figures 6.18 and 6.19. In the cycling rate of C/2.5, the initial capacity fade is about 1% of each subsequent cycle and eventually decreases to less than 0.5%.

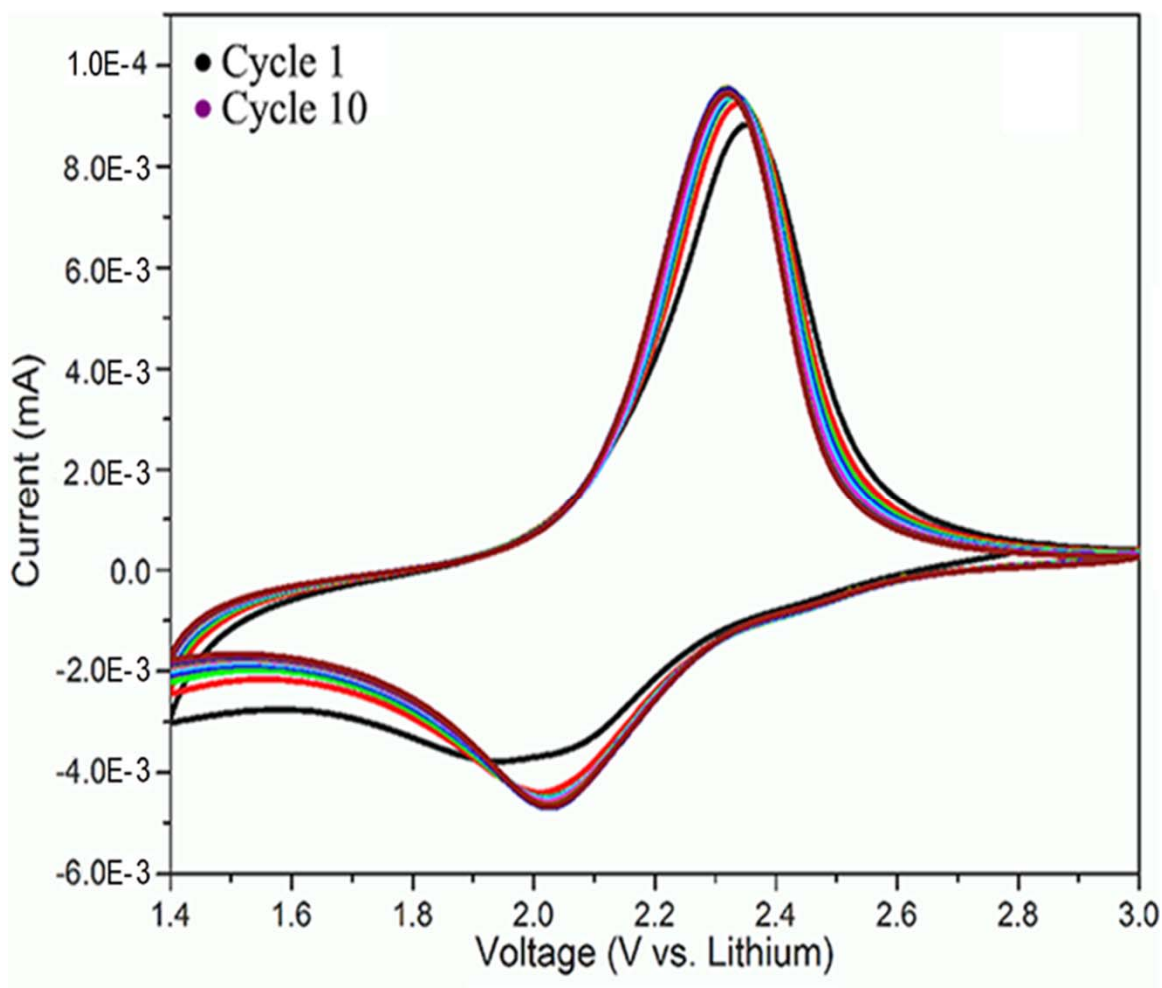


Figure 6.17 Cyclic voltammogram of LiFeTiO₄ between 1.4 and 3.0 V showing relative stable cycling intercalation and deintercalation of the Fe^{2+/3+} oxidation states.

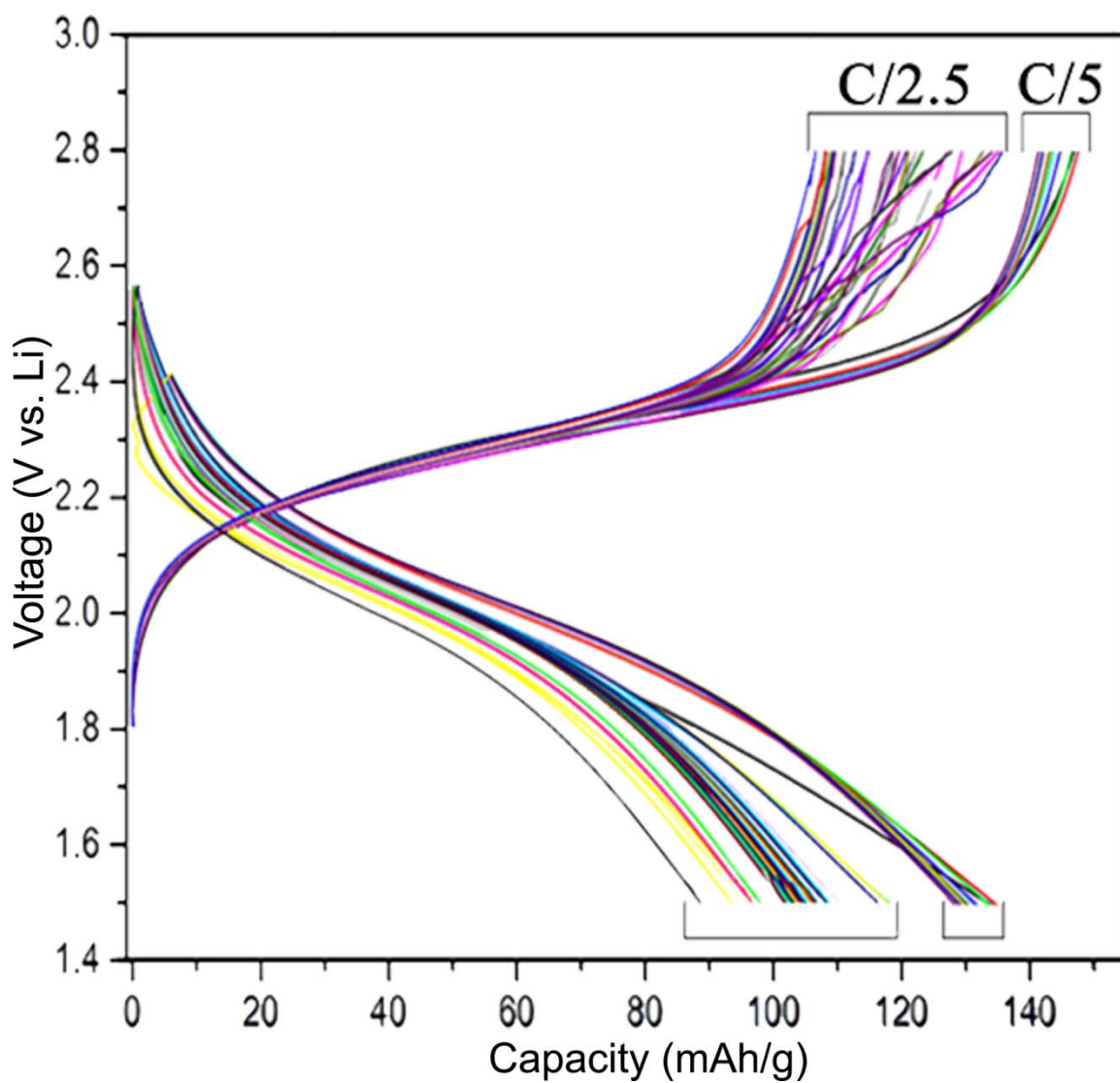


Figure 6.18 Integrated cyclic voltammogram of the voltage as a function of capacity of LiFeTiO_4 probing the $\text{Fe}^{2+/3+}$ oxidation state at the two cycling rates C/5 and C/2.5.

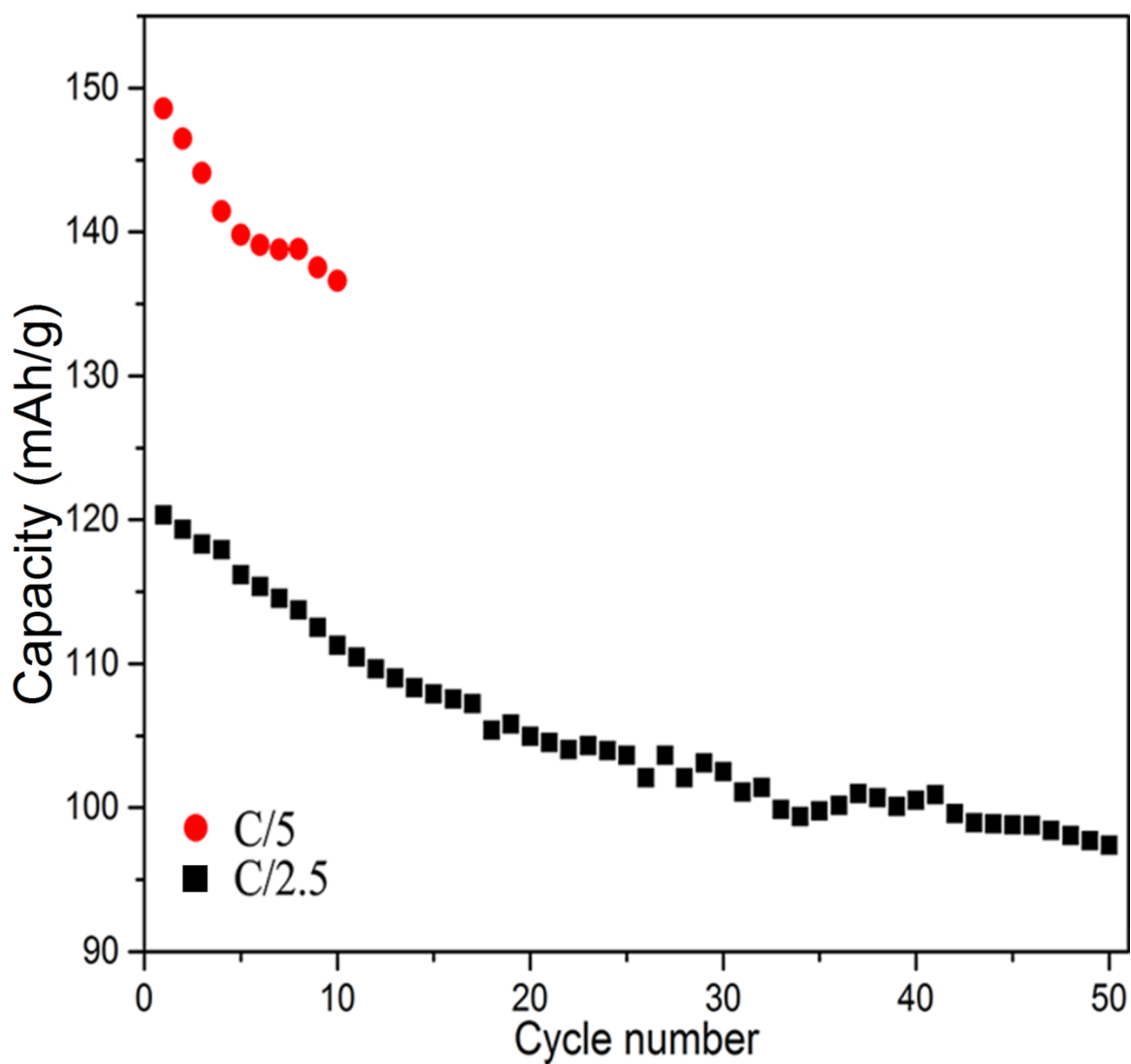


Figure 6.19 Capacity as a function of cycle number of the two cycling rates of C/5 (red) and C/2.5 (black), illustrating the cycling capacity and the capacity fade.

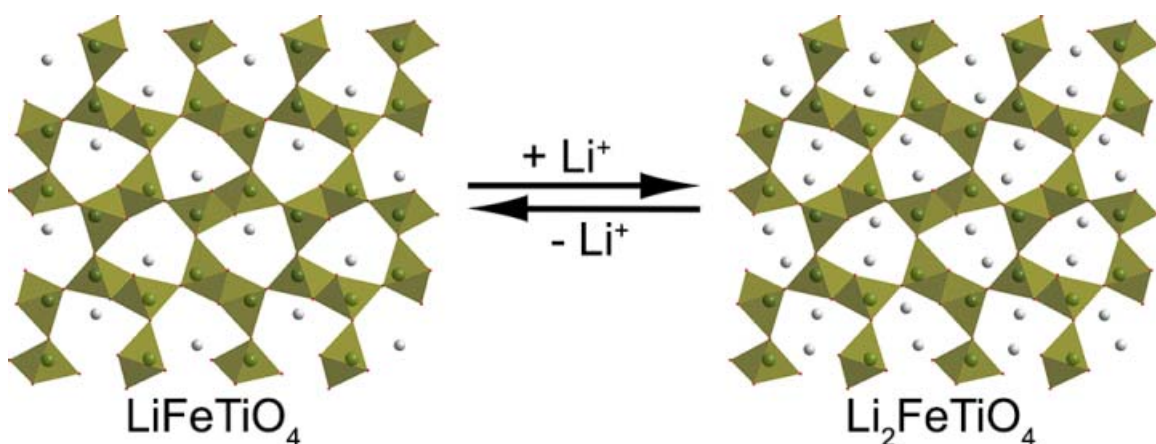


Figure 6.20 Rietveld refined structure of LiFeTiO_4 and of $\text{Li}_2\text{FeTiO}_4$ after electrochemical/chemical intercalation of a lithium ion.

Mössbauer spectroscopy was performed on the as prepared LiFeTiO_4 and lithium deintercalated $\text{Li}_{0.33}\text{FeTiO}_4$. The as prepared sample could be fit with one site as seen in Figure 6.21, indicating Fe^{3+} in an octahedral coordination as also determined by PXD. The chemically deintercalated $\text{Li}_{0.33}\text{FeTiO}_4$ was fit with two sites, (Figure 6.22), both indicating Fe^{3+} (Table 6.3), further illustrating the decomposition upon oxidation, as also seen in the cyclic voltammogram (Figure 6.14), of LiFeTiO_4 between 2.8 V and 3.7 V. The PXD of the chemically delithiated compound [19] did not show a crystalline Fe_2O_3 , but did show a dramatic increase in background. This can be attributed to an amorphous Fe_2O_3 resulting from the decomposition through the oxidation reaction.

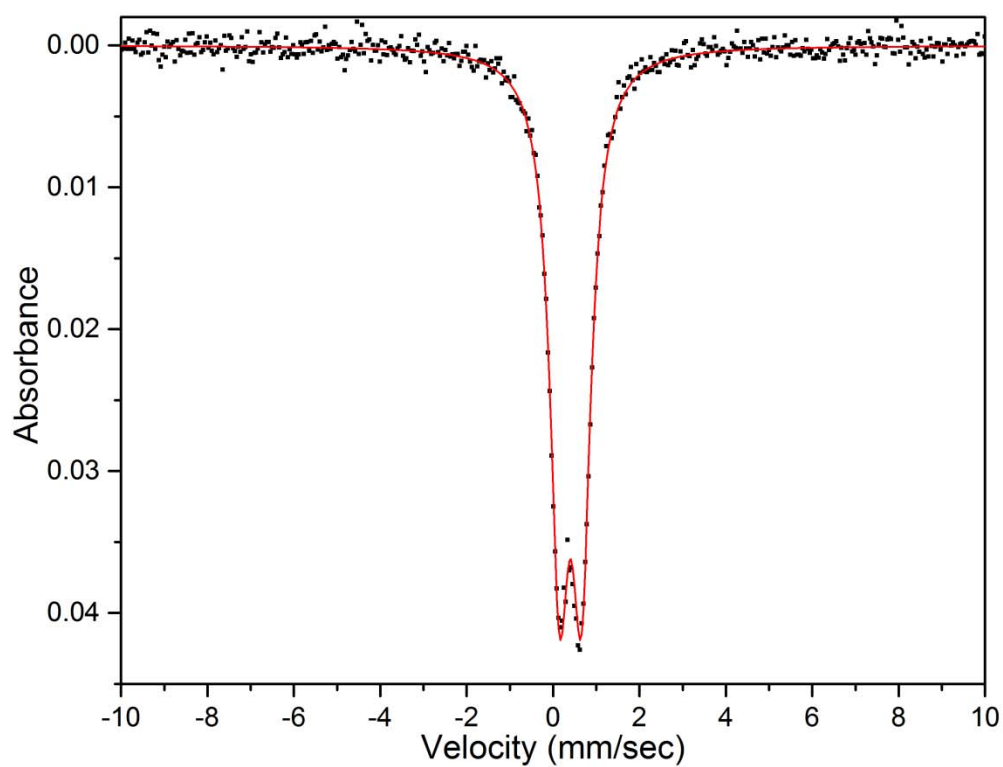


Figure 6.21 Mössbauer spectroscopy of LiFeTiO₄ fit with one Fe³⁺ site.

The Mössbauer spectroscopy of LiFeTiO₄ shows one site with a quadrupole splitting of 0.509 mm/sec and isomer shift of 0.403 mm/sec, which is indicative of Fe³⁺ in octahedral coordination. This correlates to the Rietveld refined structure with Fe/TiO₆ octahedra.

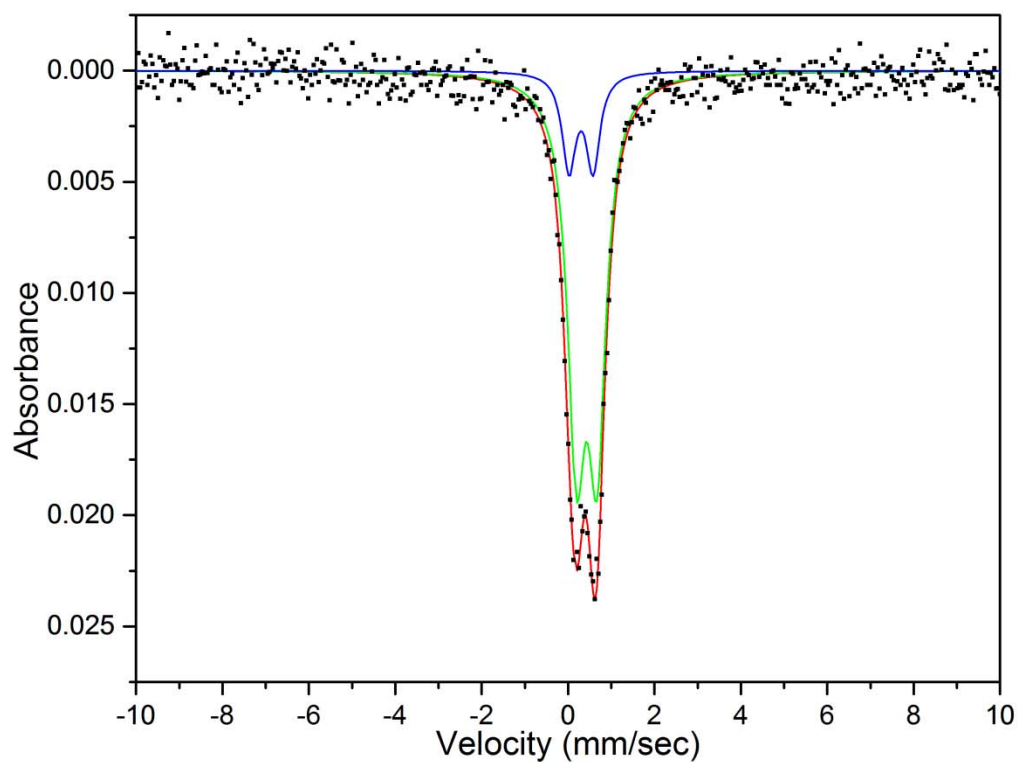


Figure 6.22 Mössbauer spectroscopy of lithium deintercalated $\text{Li}_{0.33}\text{FeTiO}_4$ with the total of the fit two sites (red), LiFeTiO_4 (green) and the amorphous iron oxide (blue).

Table 6.3 Mössbauer spectroscopy of LiFeTiO_4 and lithium deintercalated $\text{Li}_{0.33}\text{FeTiO}_4$.

Compound	Isomer Shift (mm/sec)	Hyperfine Splitting (T)	Quadrupole Splitting (mm/sec)	Area %
LiFeTiO_4	0.403	0	0.5094	100
$\text{Li}_{0.33}\text{FeTiO}_4$	0.431	0	0.4795	83.4
	0.300	0	0.5581	16.6

6.6 Conclusion

New polymorphs LiFeTiO_4 and $\text{Li}_2\text{FeTiO}_4$ both with the calcium ferrite structure were successfully synthesized, structures determined, and electrochemically characterized. Known polymorphs of both LiFeTiO_4 and $\text{Li}_2\text{FeTiO}_4$ have previously been reported with the spinel crystal structure and disordered rock salt structure respectively. Mössbauer spectroscopy of the chemically deintercalated LiFeTiO_4 was determined to only have iron with a 3+ oxidation state therefore containing amorphous iron oxide. Electrochemical characterization at room temperature showed intercalation of one lithium ion and an initial reversible capacity of about 148 mAh/g between 2 and 2.35 V with a capacity fade of 8% over 10 cycles. These results show an increased capacity of 17% over the previously reported $\text{Li}_2\text{FeTiO}_4$ rock-salt-type polymorph, which required nano preparation and special carbon coating, not required for this polymorph. LiFeTiO_4 was determined to be only kinetically stable, as it transformed into the known thermodynamically stable spinel polymorph at increased temperatures under both oxygen and nitrogen.

6.7 Future direction

LiFeTiO_4 was explored in-depth as a cathode material. The only further measurements that may be of interest would be the ionic conductivity of the as prepared sample to investigate the potential of LiFeTiO_4 as a solid electrolyte or performing magnetic measurements of the lithium-intercalated compound, $\text{Li}_{1+x}\text{FeTiO}_4$. My hypothesis would be that the as prepared LiFeTiO_4 would not function well as a solid electrolyte due to its

instability upon deintercalation of lithium along with the relatively low percentage of lithium within the structure. My hypothesis for the magnetic measurements of the lithium intercalated $\text{Li}_{1+x}\text{FeTiO}_4$ is that it could present some interesting properties within the tunnel structure. Different lithium insertion amounts would alter the overall oxidation state of iron between 2+ and 3+, which generally occurs in spinel, or reverse spinel structures containing iron in both the octahedral and tetrahedral positions.

Future direction of this project would mostly focus on the use of calcium ferrite structure due to tunnels that would grant structural stability upon oxidation or reduction via lithium deintercalation or lithium intercalation respectively. An example of this is the compound NaV_2O_4 , (Figure 6.23), which contains vanadium in the 3+ and 4+ oxidation states [24].

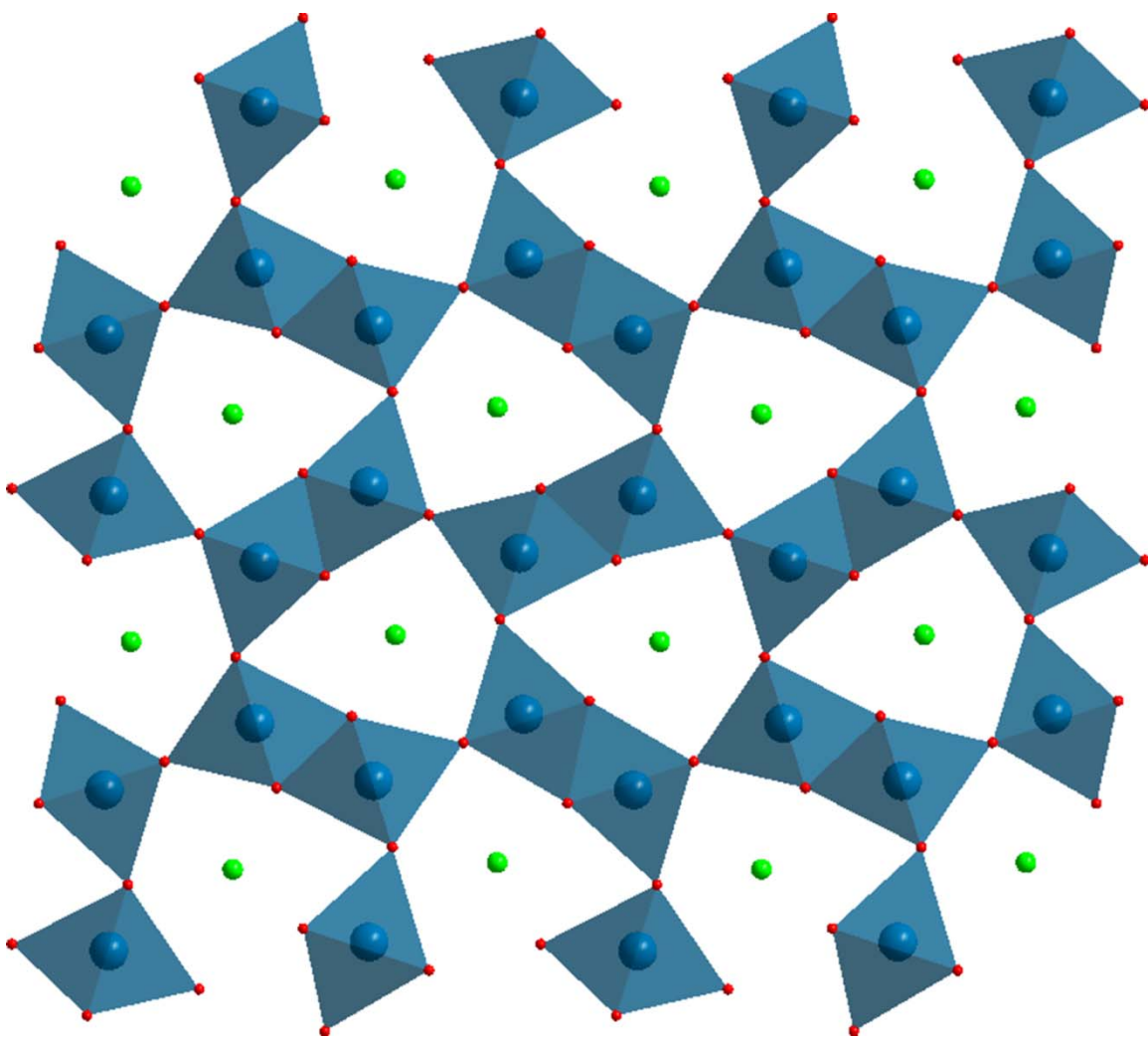


Figure 6.23 The known structure NaV_2O_4 with the calcium ferrite structure as a potential starting point for probing new cathode materials.

NaV_2O_4 with the calcium ferrite structure would be a potential starting point for lithium for sodium ion exchange. Following successful exchange, structural characterization can be carried out through chemical lithium intercalation and deintercalation. Most importantly, cyclic voltammetry probing both sodium ion and lithium ion batteries as a cathode material should be carried out. This structure is nearly identical to NaFeTiO_4 and

LiFeTiO_4 , with the benefit of vanadium, which is known for multiple stable oxidation states when cycled as a cathode material. This would give a theoretical capacity of 155 mAh/g for LiV_2O_4 (Figure 6.24) and 298 mAh/g for $\text{Li}_2\text{V}_2\text{O}_4$ (Figure 6.25).

Similar to LiFeTiO_4 representing a polymorph of the spinel structure LiFeTiO_4 , upon successful lithium for sodium ion exchange, LiV_2O_4 would also be a polymorph to a known spinel structure [25]. Therefore, the calcium ferrite structure would most probably be only kinetically stable as is the calcium ferrite structure LiFeTiO_4 . If the synthesis of the calcium ferrite structure LiV_2O_4 were to be successful, further investigation into this compound through transition metal doping would be the next appropriate step, as it has been reported by replacing a vanadium with a nickel in the spinel structure cycling voltages were observed at 4.8 V [26].

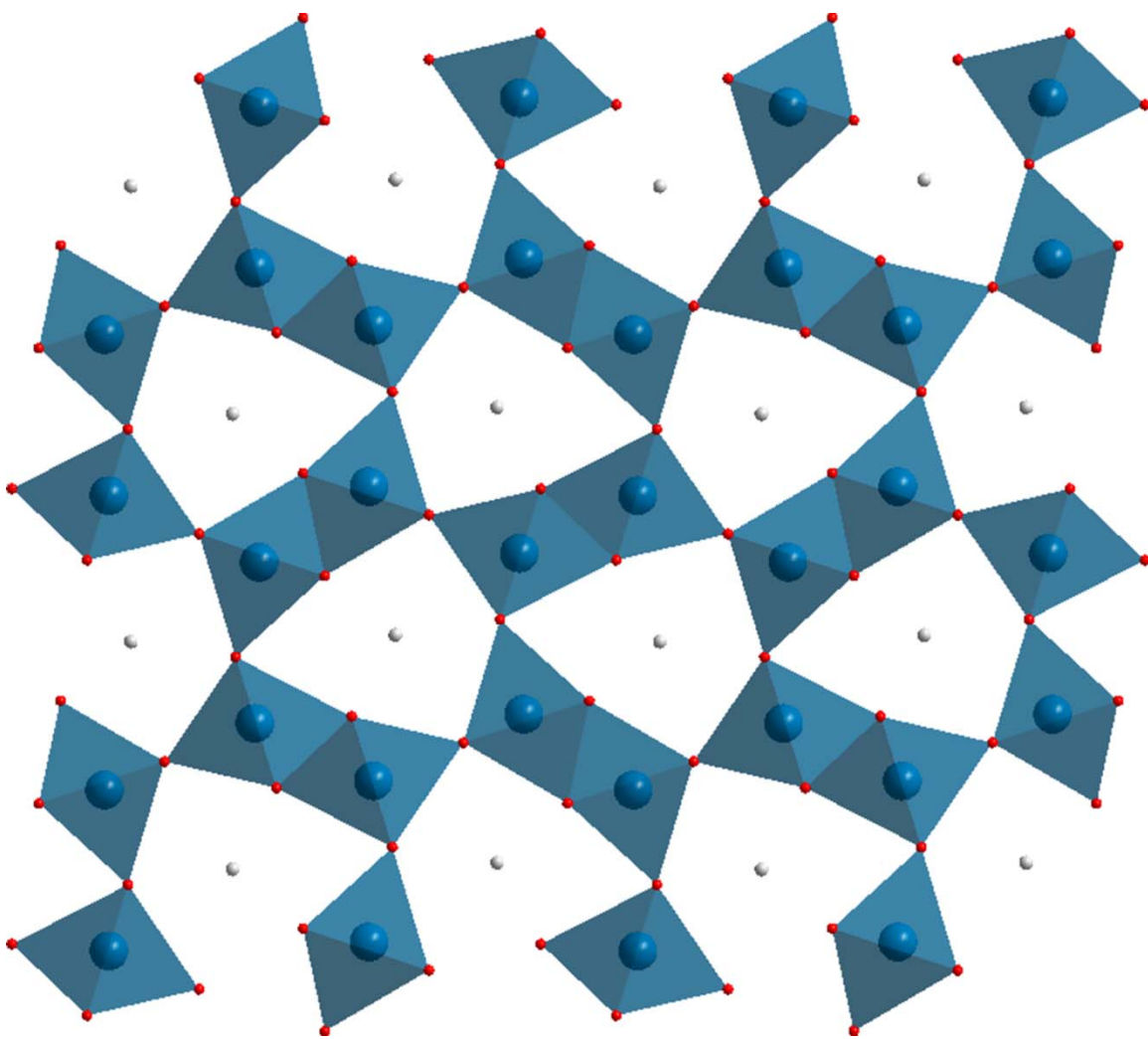


Figure 6.24 Proposed structure of LiV_2O_4 resulting from the successful lithium for sodium ion exchange of the known compound NaV_2O_4 .

After lithium for sodium ion exchange, a series of experiments could be performed on the new material including, as previously stated, chemical lithium intercalation as seen in Figure 6.25, chemical lithium deintercalation as seen in Figure 6.26, and cyclic voltammetry.

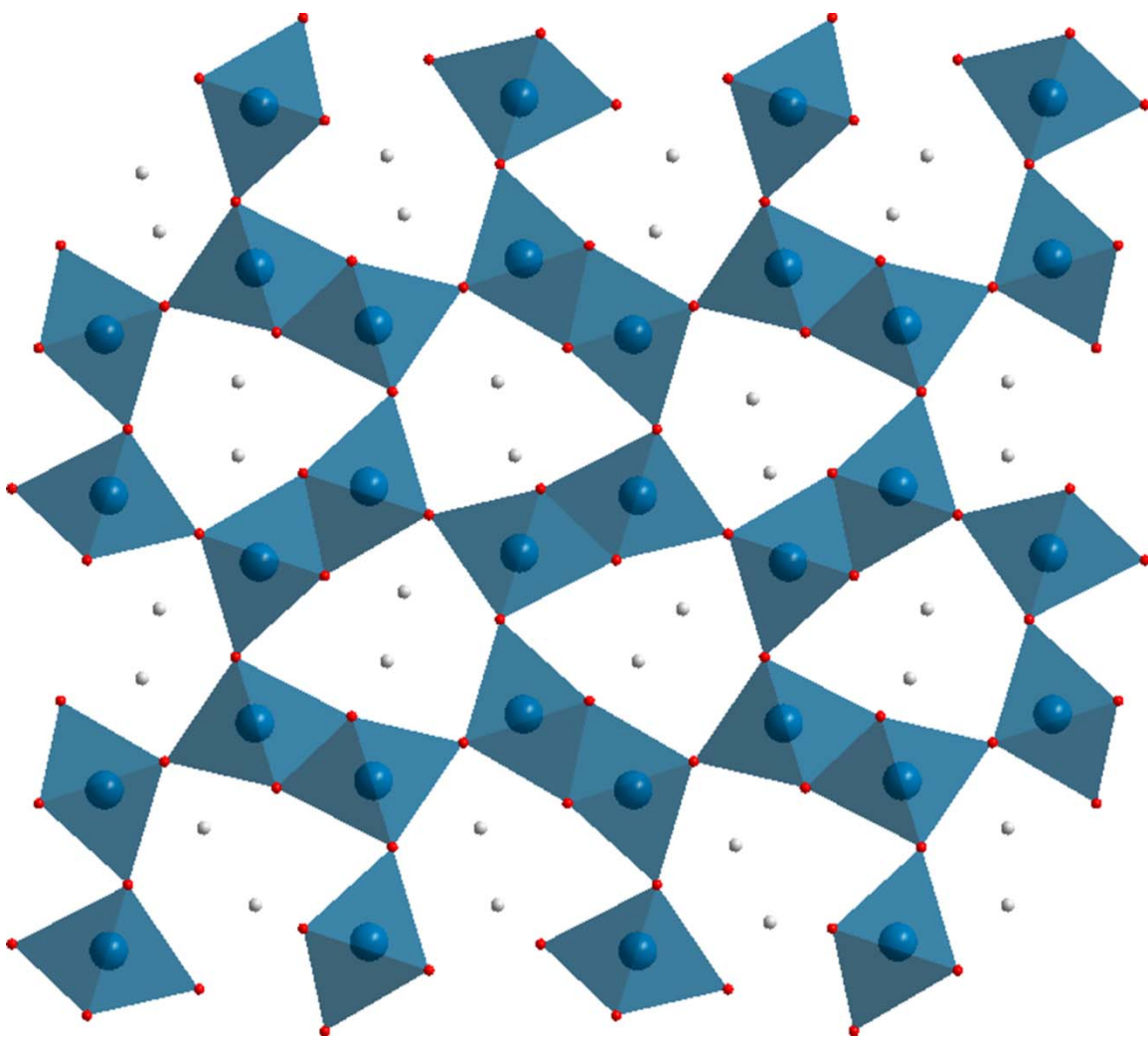


Figure 6.25 Proposed structure of $\text{Li}_2\text{V}_2\text{O}_4$ after successful chemical lithium ion intercalation or electrochemical lithium intercalation during cyclic voltammetry.

The disadvantage to this material, though it has the potential of nearly 300 mAh/g, is the lower cycling voltage which could range between 2 and 3 V [27,28], therefore decreasing the energy density of the compound when cycled as a cathode.

The challenge with this material would be similar to that seen in the synthesis of α - and β - NaFe_2O_3 . The transition metal, in this case vanadium, is divalent. This would require

the careful synthesis, most likely oxygen pressure regulation, of the starting material NaV_2O_4 .

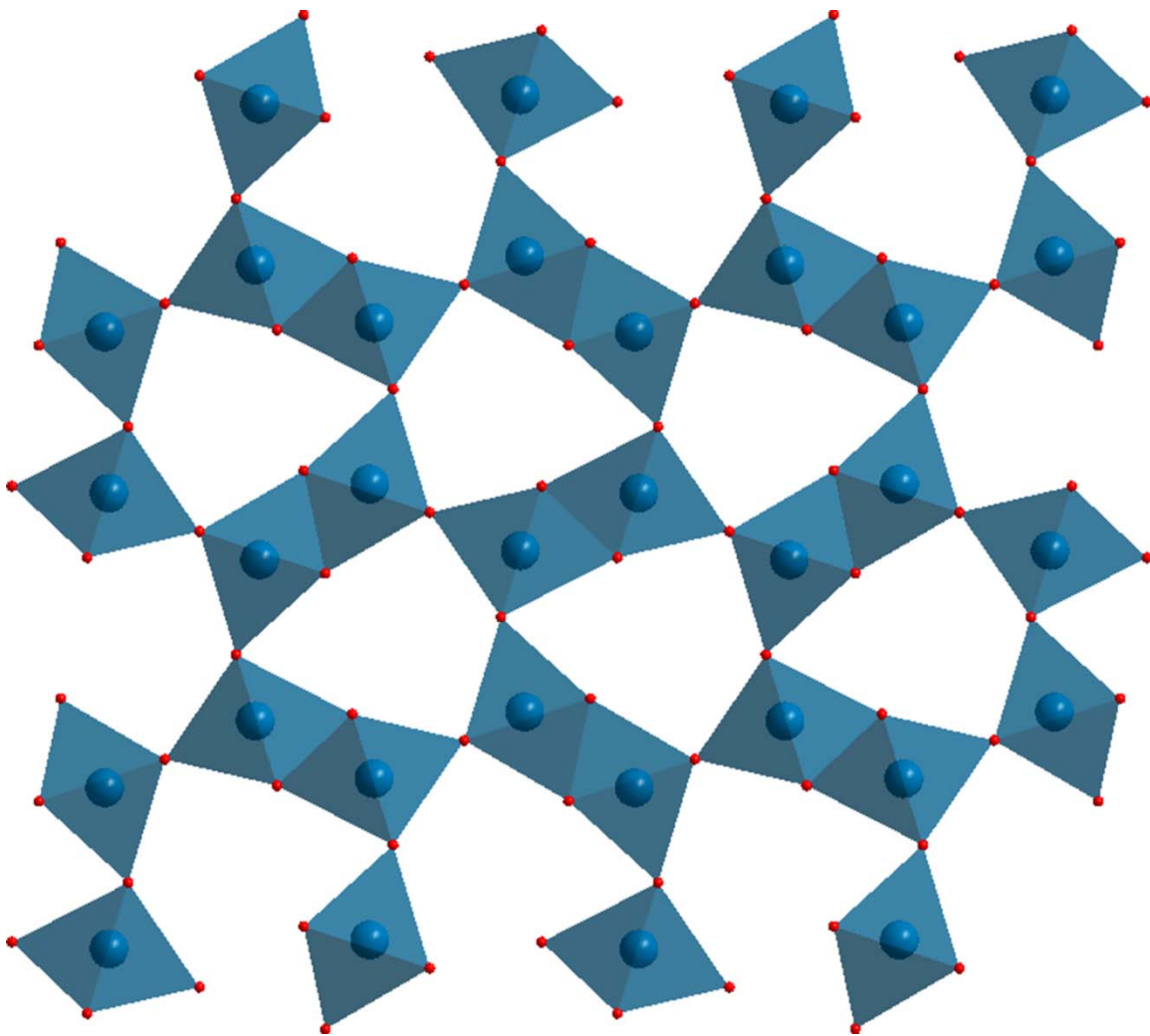


Figure 6.26 Proposed structure of V_2O_4 after successful chemical lithium ion deintercalation or electrochemical lithium deintercalation during cyclic voltammetry.

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REFERENCES

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Chapter 7

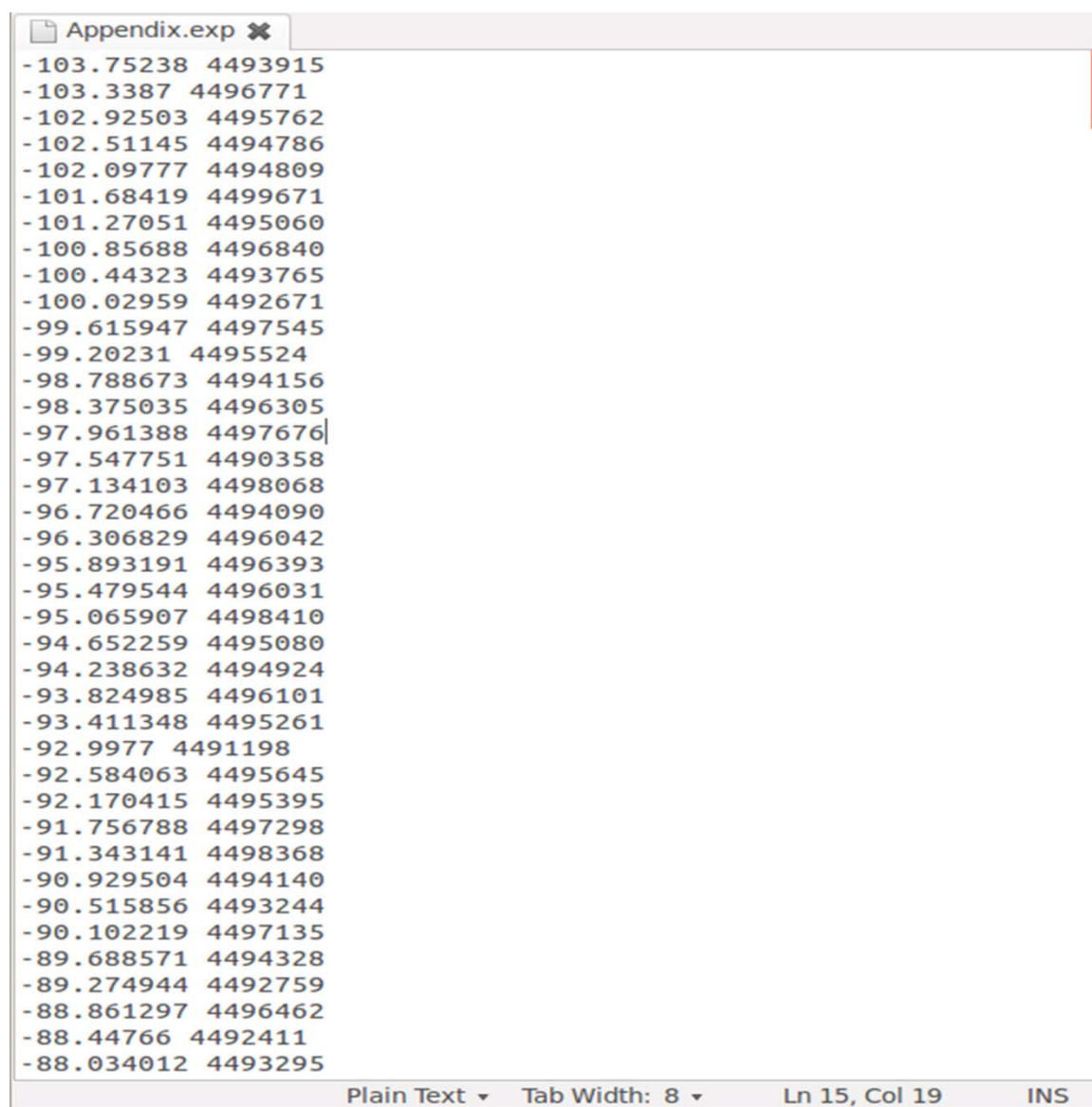
Mössbauer Data Analysis

7.1 Introduction

COherent NUclear Scattering from Single crystals (CONUSS)[1] was developed in the mid 1980's after the discovery of nuclear resonant scattering of synchrotron radiation. It has been continuously updated and improved by one of its primary creators, Wolfgang Sturhahn, who has an active relationship with Argonne National Laboratory Geophysics beamline 3-ID-B, Ercan Alp, and the Geological and Planetary Science division at California Institute of Technology. In November 2012, Argonne National Laboratory held a workshop on data evaluation using CONUSS and PHOENIX; two programs written by W. Sturhahn for the analysis of elastic and inelastic nuclear resonant scattering. The workshop was instructed by W. Sturhahn on the two programs' uses. Because no manual exists for the programs, the only way to learn how to appropriately use them requires mandatory attendance at this workshop. Therefore, the following will include a generic manual for the operation of CONUSS for future members use of the program to evaluate Mössbauer data.

7.2 Data Fitting

The received raw data with the ".exp" extension must be converted into a two-column space separated file with the extension ".exp", as seen in A1, and saved in a folder with the program files for CONUSS analysis. The folder should have 8 files in it, the provided data_graph.exp, the converted .exp, and 6 files needed in every analysis: the NAME_in, in_kctl, in_kfit, in_kmco, in_kmix, and the in_kref as seen in A2.



```
Appendix.exp
-103.75238 4493915
-103.3387 4496771
-102.92503 4495762
-102.51145 4494786
-102.09777 4494809
-101.68419 4499671
-101.27051 4495060
-100.85688 4496840
-100.44323 4493765
-100.02959 4492671
-99.615947 4497545
-99.20231 4495524
-98.788673 4494156
-98.375035 4496305
-97.961388 4497676
-97.547751 4490358
-97.134103 4498068
-96.720466 4494090
-96.306829 4496042
-95.893191 4496393
-95.479544 4496031
-95.065907 4498410
-94.652259 4495080
-94.238632 4494924
-93.824985 4496101
-93.411348 4495261
-92.9977 4491198
-92.584063 4495645
-92.170415 4495395
-91.756788 4497298
-91.343141 4498368
-90.929504 4494140
-90.515856 4493244
-90.102219 4497135
-89.688571 4494328
-89.274944 4492759
-88.861297 4496462
-88.44766 4492411
-88.034012 4493295
Plain Text ▾ Tab Width: 8 ▾ Ln 15, Col 19 INS
```

Figure 7.1 Two-column space separated raw data saved with the ".exp" extension.

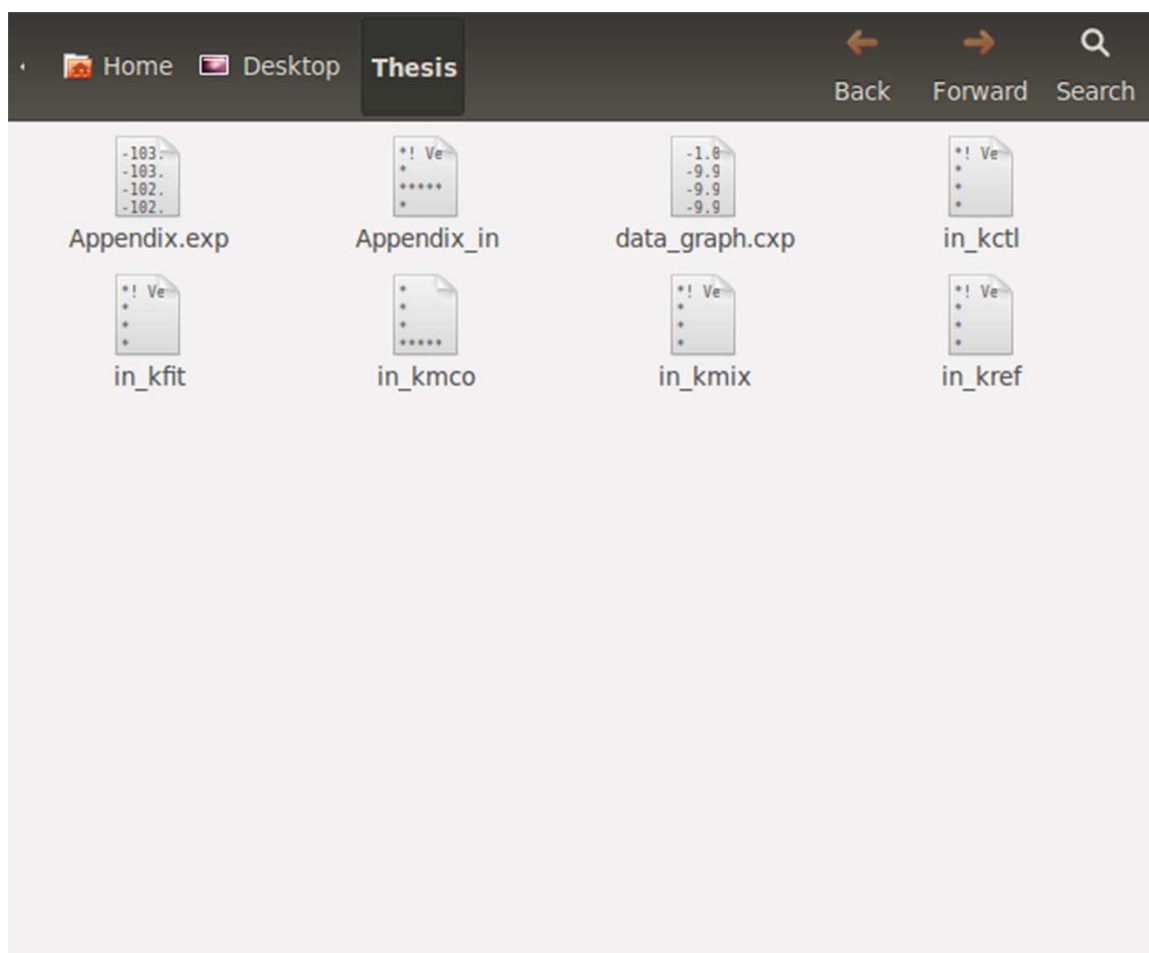


Figure 7.2 Folder containing the required program files, raw data, and converted experimental file.

Each file has a purpose in the operation of CONUSS; therefore, the lack of presence of one can result in CONUSS not working. For every experiment data set, the 6 files (NAME_in, in_kctl, in_kfit, in_kmco, in_kmix, and the in_kref) should just be copied from the original CONUSS folder, named accordingly to the current experiment, and each important parameter should be adjusted appropriately as described within. From here, a brief explanation and major functions of each file will be provided.

```

in_kctl
*! Version 1.5
*
*   Standard input file of program CONUSS module KCTL
*
*   created      :   May 12, 1996   by W.Sturhahn
*
*****
*
*   Lines which first character is an asterisk (*) are
*   supposed to be comments and can occur anywhere
*   in the input stream.
*
*   Lines which first character is the char. (@)
*   will be interpreted as commands. They must match a
*   simple pattern :
*
*       @ variable_name := string
*
*   In the following input stream @variable_name will
*   be substituted by string. variable_name may be up
*   to 8 chars long. Continuation lines are not allowed.
*
*   Every valid input line (begins not with *) looks like
*       <comment> :: <data> :: <comment>|
*   or like
*       <comment> :: <data>
*   and <data> is read by CONUSS with free format.
*
*****
*
* input and output files
* =====
*
*
*   (1) input file for module KREF   :: in_kref
*   (2) input file for module KMIX   :: in_kmix
*   (3) input file for module KFIT   :: in_kfit
*
*****
*
* file listing available hosts
* =====
*
*   (4) name of host file   ::
*
*****
*
* iteration control
* =====
*
*   (5) maximum number of iteration steps :: 40
*
*   (6) quality needed to stop the iteration :: 0.001
*
*****
*

```

Figure 7.3 The in_kctl file with highlighted input files and parameters required for CONUSS analysis.

The `in_kctl` file is a program file that directs the CONUSS program which input files to use in the analysis as seen in A3. The input files `in_kref` and `in_kfit` will be looked at individually. The `in_kmix` is used for synchrotron data, which requires enriched iron. This is beyond the scope of research in this laboratory. A3 also shows the iteration control. This provides the user with the power to dictate the maximum number of steps and the minimum iterations that will stop the program from continuing on unnecessarily after the analysis has converged.

The `in_kfit` file, as seen in A4, has four parameters of interest (2), (10), (11), and (15) which are highlighted. The experimental data file (2), instructs CONUSS which file to use and what format the file is in. This is the two-column ".exp" file that was initially prepared from the raw data provided. The background parameter (10) must be refined at the beginning of every analysis along with the scaling factor (10) and thickness (15). The background parameter (10) will also be maintained open to refinement throughout the entire process.

```

in_kfit
*
* Every valid input line (begins not with *) looks like
* <comment> :: <data> :: <comment>
* or like
* <comment> :: <data>
* and <data> is read by CONUSS with free format.
*
*****
* input and output files
* =====
*
* the intensity data input files used by KFIT
* are the intensity data output files created
* by KMIX
*
* name of the intensity data input file (IIF) or
* name of the file that contains a list of IIFs
*
* (1) input file :: data_ints_alfe
*
* name of experimental data input file
*
* (2) exp. data file :: Appendix.exp 2column
*
* name of output data file for graphical representation
*
* (3) output data file :: data_graph
*
*****
* data window
* =====
*
* fitting or representation of theory will be
* restricted to the given range ..
*
* (4) begin thickness range :: -999
* (5) end .. :: 999
*
* (6) begin energy/time range / gamma/ns :: -100
* (7) end .. :: 100
*
*****
* for the weight function the
* following selections are possible..
* g = gaussian
* l = lorentzian
* r = rectangular
* ag <R> = asymmetric gaussian with <R> giving the
* ratio of left FWHM to right FWHM
*
* (8) weight function for the thickness grid :: g
* (9) weight function for the time/energy grid :: ag 0.3
*
*****
* internal fit parameters
* =====
*
* the following parameters are internal fit parameters
* tag the parameters you want to be fitted
* by a per cent sign '%' in col. 1
*
* if you don't tag any parameter and no external
* fit parameters are defined only the theory data
* will be forwarded to the output data set
* in this case the measured data is ignored
*
* (10) background :: -1.59D+07
* (11) scaling factor :: 2.04e5
* (12) shift of the energy/time scale / gamma/ns :: 0.054
* (13) thickness distribution FWHM :: 0.001
* (14) energy/time resolution FWHM / gamma/ns :: 1.1
* (15) thickness :: 0.005
*
*****
* creating thickness curves
* =====
*
* thickness curves can be created instead of
* the normal energy/time representation
* this is supported only if no fit parameters are selected
*
* (16) do you want to create thickness curves [y/n] :: no
* (17) thickness curve distance / gamma/ns :: 10
*
*****

```

Figure 7.4 The in_kfit file with highlighted parameters for Mössbauer refinement.

```

in_kmco ✖
*   Standard input file of program CONUSS module KMCO
*
*****
*
*   Lines which first character is an asterisk (*) are
*   supposed to be comments and can occur anywhere
*   in the input stream.
*
*   Lines which first character is the char. (@)
*   will be interpreted as commands. They must match a
*   simple pattern :
*
*       @ variable_name := string
*
*   In the following input stream @variable_name will
*   be substituted by string. variable_name may be up
*   to 8 chars long. Continuation lines are not allowed.
*
*   Every valid input line (begins not with *) looks like
*   <comment> :: <data> :: <comment>
*   or like
*       <comment> :: <data>
*   and <data> is read by CONUSS with free format.
*
*****
*
*   input and output files
*   =====
*
*   (1) input file for module KREF      :: in_kref
*   (2) input file for module KMIX      :: in_kmix
*   (3) input file for module KFIT      :: in_kfit
*
*****
*
*   sampling
*   =====
*
*   (4) number of levels                :: 100
*   (5) random samples per level        :: 500
*
*   (6) search box level-reduction factor  :: 0.6
*   (7) factor for acceptable chi^2 minima :: 3
*
*****
*

```

Figure 7.5 The in_kmco file with highlighted parameter files and input files.

The in_kmco file, as seen in A5, is the file responsible for the Monte Carlo-like method that repeatedly takes random samplings in order to eventually approach the best possible

fit. The two parameters of interest here are (4) and (5) which represent the number of levels and the random samples per level. The operator can change each of these parameters to optimize the analysis.

```

in_kref ✖
* supposed to be comments and can occur anywhere
* in the input stream.
*
* Lines which first character is the char. (@)
* will be interpreted as commands. They must match a
* simple pattern :
*
*   @ variable_name := string
*
* In the following input stream @variable_name will
* be substituted by string. variable_name may be up
* to 8 chars long. Continuation lines are not allowed.
*
* Lines which first character is a percent sign (%)
* identify parameters that will be fitted on request.
*
* Every valid input line (begins not with *) looks like
*   <comment> :: <data> :: <comment>
* or like
*   <comment> :: <data>
* and <data> is read by CONUSS with free format.
*
*****
*
* input and output files
* =====
*
* (1) material data input file      :: Appendix in
*
* (2) transmission data output file :: data_trns_alfe
*
*
* (3) name of the material          :: Appendix
*
*****
*
* module run mode
* =====
*
* you may use :  r  for  reflected channel in Bragg/Laue geometry
*                t      transmitted  ..".."
*                f      forward scattering geometry
*
* (4) mode :: forward scattering
*
*****

```

Figure 7.6 The in_kref with highlighted material data input to be changed in each experiment.

```

in_kref ✕
(13) polar angle of B_ext / deg.      :: 90
*
* magnitude of the external magnetic field
*
(14) magnitude / Tesla  :: 0
*
*****
*
* energy range relative to the nuclear resonance
* =====
*
(15) begin calculation at this energy / gamma  :: -200
(16) stop ...                                :: +200
(17) nr. of steps (max. 2801)                  :: 2801
*
*****
*
* thickness of the material perpendicular to the surface
* =====
*
(18) thickness unit / micron  :: 0.005
*
*
* thickness range, give values in units defined above
*
(19) begin calculation at this thickness / units :: 1
(20) stop ...                                :: 100
(21) nr. of steps (max. 100)                  :: 100
*
*****
*
* control of the printout
* =====
*
*      description of the internal
*      variables to be printed
*
*                                          print?
S01 : Miller indices                      :: yes
S02 : direction of the incoming beam      :: yes
S03 : direction of the external magn. field :: yes
S04 : Bragg angle                         :: yes
S05 : energy grid                         :: yes
S06 : base vectors of the unit cell       :: no
S07 : normal vectors of netplanes and surface :: yes
S08 : incident beam k in                  :: no

```

Figure 7.7 Thickness unit / micron parameter highlighted also in in_kref that will need to be initially refined to optimize data analysis.

The NAME_in file will be the file that is most often used in the Mössbauer refinement. This file, as seen in A8-A13, contains the main parameters in Mössbauer. A8 illustrates the constant values that are to remain unchanged by the user. A9 highlights the number of sites of the Mössbauer atom. This parameter is to be changed if the sample has multiple Mössbauer atom sites with different coordination, oxidation states, or local environments. A10 continues to show the NAME_in file with the @ &dist1, weight of the sublattice, isomer shift, magnetic hyperfine field, and quadrupole splitting. The @ &dist1 is directly linked to A11-A13 which allows for peak fluctuations, shifts, or widening depending upon whether isomer shift, efg, or magnetic hyperfine splitting has been entered as seen in A11-A13. It should also be noted that entering magnetic hyperfine splitting as the target for a sample that does not have hyperfine splitting will not provide any benefit. The same concept goes for entering efg for a sample that does not exhibit quadrupole splitting. This is generally an issue when the sample contains multiple Mössbauer sites. The weight of the sublattice is the percentage that this particular Mössbauer site had within in the sample. Therefore, a sample with only one site would represent 100% of the data, thus it would have a value of 1. A sample that has multiple sites would have different representative values for each site. The isomer shift, magnetic hyperfine splitting, and quadrupole splitting are the common parameters in Mössbauer spectroscopy, which will be the primary focus throughout the refinement and fitting process.

```

Appendix_in ✕
*
* =====
*
* the first number gives the start value for each parameter
* the second number gives the parameter variation when
* the derivatives are calculated
*
*
* -----1-----2-----3-----4-----5-----6-----7-->
*
* MB isotope and MB transition
* =====
*
* (1) mass number      :: 57
*
* ground state
* (2) spin              :: 0.5
* (3) g-factor          :: 0.18121
* (4) quadrupole moment / barn :: 0
*
* excited state
* (5) spin              :: 1.5
* (6) g-factor          :: -0.10348
* (7) quadrupole moment / barn :: 0.187
* (8) half life time   / ns  :: 97.81
* (9) internal conversion factor :: 8.21
*
* transition
* (10) energy / keV      :: 14.41303
* (11) multipolarity     :: M1
* (12) interference coefficient :: 0
*
* ****+*****1*****+*****2*****+*****3*****+*****4*****+*****5*****+*****6*****+*****7**
*
* Lattice parameters
* =====
*
* (13) Debye temperature of the material / K :: 200
* (14) real temperature of the material / K :: 300
*
*
* size and angles of the unit cell of the material
* artificial unit cell, matches density of iron
*
* length of base vectors
* (15) length of #1 / Angstroem :: 2.277
* (16)      #2 / Angstroem :: 2.277

```

Figure 7.8 The NAME_in file illustrating the known constant values of iron for Mössbauer spectroscopy.

```

Appendix_in ✕
(15) length of #1 / Angstroem :: 2.277
(16)          #2 / Angstroem :: 2.277
(17)          #3 / Angstroem :: 2.277
*
* angles between base vectors
(18) angle between      #2,#3 / degrees  :: 90
(19)                   #3,#1 / degrees  :: 90
(20)                   #1,#2 / degrees  :: 90
*
*****1*****2*****3*****4*****5*****6*****7**
*
* defining the lattice of the MB atom
* =====
*
*
(21) name of the MB atom           :: iron
(22) abundance of the MB atom      :: 0.95
(23) atomic charge number of the MB atom :: 26
(24) number of sites of the MB atom :: 1
*
*****
*
* defining the hyperfine interactions
* =====
*
* the following modes are supported :
*
* 'poly'          averaging over all directions
*                  and polarizations of the incident photon
*                  while keeping the angles between magnetic
*                  hyperfine field (Bhf) and electric field
*                  gradient (EFG) fixed. The texture of a
*                  sample is given in input lines 26.*.1.18
*                  for each individual site. This is a good
*                  approximation for forward scattering from
*                  textured powder samples without external
*                  fields.
*
* 'random_efg<N>' averaging over all directions of
*                  the EFG while keeping the directions
*                  of Bhf and incident photon fixed.
*                  This is a good approximation for
*                  forward scattering of none texture
*                  powder samples with an external
*                  magnetic field applied.
*                  <N>*24 specifies the number of sites
Plain Text ▾ Tab Width: 8 ▾ Ln 112, Col 49  INS

```

Figure 7.9 The NAME_in file with highlighted number of sites of the Mössbauer atom.

```

Appendix_in ✕
*
(25) mode to run on hyperfine int. :: poly
*
@ &dist1 := 1
*
*****
*
*   defining MB site #1
*
(26.1.1) memo name for the site      :: iron
(26.1.2) number of MB atoms in the site :: 1
(26.1.3) ionization number          :: 0
(26.1.4) weight of the sublattice    :: 1
*
(26.1.5) isomer shift                / mm/s      :: 0.25
*
(26.1.6) magnetic hyperfine field / T          :: 0
(26.1.7) magnetic polar anisotropy             :: 0
(26.1.8) magnetic azimuthal anisotropy         :: 0
(26.1.9) magn.hyp.field dir. angle theta / deg :: 90
(26.1.10) magn.hyp.field dir. angle phi  / deg :: 0
*
(26.1.11) quadrupole splitting      / mm/s      :: 0
(26.1.12) asymmetry parameter              :: 0
(26.1.13) euler angle alpha for efg=>xtal /deg :: 0
(26.1.14) euler angle beta  for efg=>xtal /deg :: 0
(26.1.15) euler angle gamma for efg=>xtal /deg :: 0
*
(26.1.16) name of the relaxation input file  ::
(26.1.17) name of the distribution input file :: <!
Target isomer shift
Make Gaussian 80 @&dist1
!
(26.1.18) texture coefficient / %           :: 0.0
(26.1.19) reserved for later versions      ::
*
* (26.1.20 etc.) positions of the MB atoms of site #1
*
*
0 0 0
*
*****1*****2*****3*****4*****5*****6*****7**
*
*   defining the lattices of the non MB atoms
*   =====

```

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Figure 7.10 The NAME_in file with highlighted parameters that will be analyzed in Mössbauer refinement.

```

*Appendix_in ✖
*
(25) mode to run on hyperfine int. :: poly
*
@ &dist1 := 1
*
*****
*
*   defining MB site #1
*
(26.1.1) memo name for the site      :: iron
(26.1.2) number of MB atoms in the site :: 1
(26.1.3) ionization number          :: 0
(26.1.4) weight of the sublattice    :: 1
*
(26.1.5) isomer shift                / mm/s      :: 0.25
*
(26.1.6) magnetic hyperfine field / T          :: 0
(26.1.7) magnetic polar anisotropy             :: 0
(26.1.8) magnetic azimuthal anisotropy         :: 0
(26.1.9) magn.hyp.field dir. angle theta / deg :: 90
(26.1.10) magn.hyp.field dir. angle phi  / deg :: 0
*
(26.1.11) quadrupole splitting      / mm/s      :: 0
(26.1.12) asymmetry parameter       :: 0
(26.1.13) euler angle alpha for efg=>xtal /deg  :: 0
(26.1.14) euler angle beta  for efg=>xtal /deg  :: 0
(26.1.15) euler angle gamma for efg=>xtal /deg  :: 0
*
(26.1.16) name of the relaxation input file  ::
(26.1.17) name of the distribution input file :: <!
Target efg
Make Gaussian 80 @&dist1
!
(26.1.18) texture coefficient / %          :: 0.0

(26.1.19) reserved for later versions  ::
*
* (26.1.20 etc.) positions of the MB atoms of site #1
*
*
0 0 0
*
****+****1****+****2****+****3****+****4****+****5****+****6****+****7**
*
*   defining the lattices of the non MB atoms
*   =====

```

Plain Text ▾ Tab Width: 8 ▾ Ln 188, Col 14 INS

Figure 7.11 The NAME_in file illustrating electric field gradient as the target for distribution input file.

```

*Appendix_in ✕
*
(25) mode to run on hyperfine int. :: poly
*
@ &dist1 := 1
*
*****
*
*   defining MB site #1
*
(26.1.1) memo name for the site      :: iron
(26.1.2) number of MB atoms in the site :: 1
(26.1.3) ionization number          :: 0
(26.1.4) weight of the sublattice    :: 1
*
(26.1.5) isomer shift                / mm/s      :: 0.25
*
(26.1.6) magnetic hyperfine field / T          :: 0
(26.1.7) magnetic polar anisotropy             :: 0
(26.1.8) magnetic azimuthal anisotropy         :: 0
(26.1.9) magn.hyp.field dir. angle theta / deg :: 90
(26.1.10) magn.hyp.field dir. angle phi  / deg :: 0
*
(26.1.11) quadrupole splitting      / mm/s      :: 0
(26.1.12) asymmetry parameter       :: 0
(26.1.13) euler angle alpha for efg=>xtal /deg  :: 0
(26.1.14) euler angle beta  for efg=>xtal /deg  :: 0
(26.1.15) euler angle gamma for efg=>xtal /deg  :: 0
*
(26.1.16) name of the relaxation input file  ::
(26.1.17) name of the distribution input file :: <!
Target isomer shift
Make Gaussian 80 @&dist1
!
(26.1.18) texture coefficient / %          :: 0.0
(26.1.19) reserved for later versions  ::
*
* (26.1.20 etc.) positions of the MB atoms of site #1
*
*
0 0 0
*
****+****1****+****2****+****3****+****4****+****5****+****6****+****7**
*
*   defining the lattices of the non MB atoms
*   =====

```

Plain Text ▾ Tab Width: 8 ▾ Ln 188, Col 23 INS

Figure 7.12 The NAME_in file illustrating isomer shift as the target for distribution input file.

```

*Appendix_in ✕
*
(25) mode to run on hyperfine int. :: poly
*
@ &dist1 := 1
*
*****
*
*   defining MB site #1
*
(26.1.1) memo name for the site      :: iron
(26.1.2) number of MB atoms in the site :: 1
(26.1.3) ionization number           :: 0
(26.1.4) weight of the sublattice    :: 1
*
(26.1.5) isomer shift                / mm/s      :: 0.25
*
(26.1.6) magnetic hyperfine field / T           :: 0
(26.1.7) magnetic polar anisotropy              :: 0
(26.1.8) magnetic azimuthal anisotropy          :: 0
(26.1.9) magn.hyp.field dir. angle theta / deg  :: 90
(26.1.10) magn.hyp.field dir. angle phi  / deg  :: 0
*
(26.1.11) quadrupole splitting      / mm/s      :: 0
(26.1.12) asymmetry parameter              :: 0
(26.1.13) euler angle alpha for efg=>xtal /deg  :: 0
(26.1.14) euler angle beta  for efg=>xtal /deg  :: 0
(26.1.15) euler angle gamma for efg=>xtal /deg  :: 0
*
(26.1.16) name of the relaxation input file  ::
(26.1.17) name of the distribution input file :: <!
Target magnetic hyperfine field
Make Gaussian 80 @&dist1
!
(26.1.18) texture coefficient / %           :: 0.0
*
(26.1.19) reserved for later versions ::
*
* (26.1.20 etc.) positions of the MB atoms of site #1
*
*
0 0 0
*
*****1*****2*****3*****4*****5*****6*****7**
*
*   defining the lattices of the non MB atoms
*   =====

```

Figure 7.13 The NAME_in file illustrating magnetic hyperfine field as the target for distribution input file.

Prior to running CONUSS, a description of the used command must first be undertaken. The three commands that can be used with CONUSS are `krmf`, `kctl`, and `kmco`. Each one of the commands can eventually get the operator to the final result with the major difference of the three commands being the path taken by CONUSS or the user.

The command `krmf` is much more of a hands on approach by the user. It evaluates the individual input parameter without any further optimization by CONUSS, therefore; CONUSS will only evaluate the specific parameter input by the user.

The command `kctl` takes the open input parameter by the user, then optimizes it by making minor changes to the parameter while evaluating the χ^2 to determine if the change was better than the initial value. If the value meets the iterations set by the user in the `in_kctl` file (A3), the command will continue to run until it converges or meets the maximum iteration steps, set in `in_kctl`.

The command `kmco` uses the Monte Carlo approach by taking the open input parameters by the user, then optimizing the parameters through a randomized search with restrictions placed on the command by the operator. This command is generally used as a starting command for complex spectra and should be followed by the `kctl` command.

In order to run the CONUSS program to fit the acquired Mössbauer data, the background and thickness in both the `in_kfit` and the thickness in `in_kref` must be refined. This is performed by inserting a "%" symbol at the beginning of the line of the parameter of interest. In this case, as seen in A14, the background and thickness both have a "%" highlighted to illustrate what it should look like. Note there should be a space between

the "%" and the next character. This is not as applicable in the other parameters, but is essential when opening the @ &dist function, therefore, it is suggested to maintain the space when opening any parameter. It should also be noted in the case of non-Gaussian shaped peaks, the peak shapes can be changed in the in_kfit file as seen at the top of A14.

```

*in_kfit ✕
* following selections are possible..
* g      = gaussian
* l      = lorentzian
* r      = rectangular
* ag <R> = asymmetric gaussian with <R> giving the
*          ratio of left FWHM to right FWHM
*
(8) weight function for the thickness grid    :: g
(9) weight function for the time/energy grid  :: ag 0.3
*
*****
*
* internal fit parameters
* =====
*
* the following parameters are internal fit parameters
* tag the parameters you want to be fitted
* by a per cent sign '%' in col. 1
*
* if you don't tag any parameter and no external
* fit parameters are defined only the theory data
* will be forwarded to the output data set
* in this case the measured data is ignored
*
% (10) background                :: -1.59D+07
% (11) scaling factor            :: 2.04e5
% (12) shift of the energy/time scale / gamma/ns :: 0.054
% (13) thickness distribution FWHM :: 0.001
% (14) energy/time resolution FWHM / gamma/ns  :: 1.1
% (15) thickness                 :: 0.005
*
*****
*
* creating thickness curves
* =====
*
* thickness curves can be created instead of
* the normal energy/time representation
* this is supported only if no fit parameters are selected
*
(16) do you want to create thickness curves [y/n] :: no
(17) thickness curve distance / gamma/ns          :: 10
*
*****
*
* end of input file

```

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Figure 7.14 The in_kfit illustrating the input of the % symbol, this opens the parameter for spectrum fitting.

```
shaun@ubuntu: ~/Desktop/Thesis
File Edit View Search Terminal Help
shaun@ubuntu:~$ cd ~/Desktop/Thesis
shaun@ubuntu:~/Desktop/Thesis$ kctl
```

Figure 7.15 Terminal screen shot illustrating input of the kctl command.

```
shaun@ubuntu: ~/Desktop/Thesis
File Edit View Search Terminal Help

reading file : in_kmix
total number of lines : 134
      valid lines : 12

reading file : in_kfit
total number of lines : 121
      valid lines : 17

  | iteration |   Quality   |   Chi^2   |
  |-----+-----+-----|
  | start    |             | 227.957   |
  | # 1 G    | 3.391E+10   | 227.957   |
  | final    | 3.391E+10   | 227.957   |

-- CPU time : user  0.64 s system  0.03 s
-- CONUSS module KCTL finished

[2]+  Done                  xmgrace *.cxp *.fit
shaun@ubuntu:~/Desktop/Thesis$
```

Figure 7.16 Terminal screen shot illustrating the results of the kctl command after fitting background and thickness.

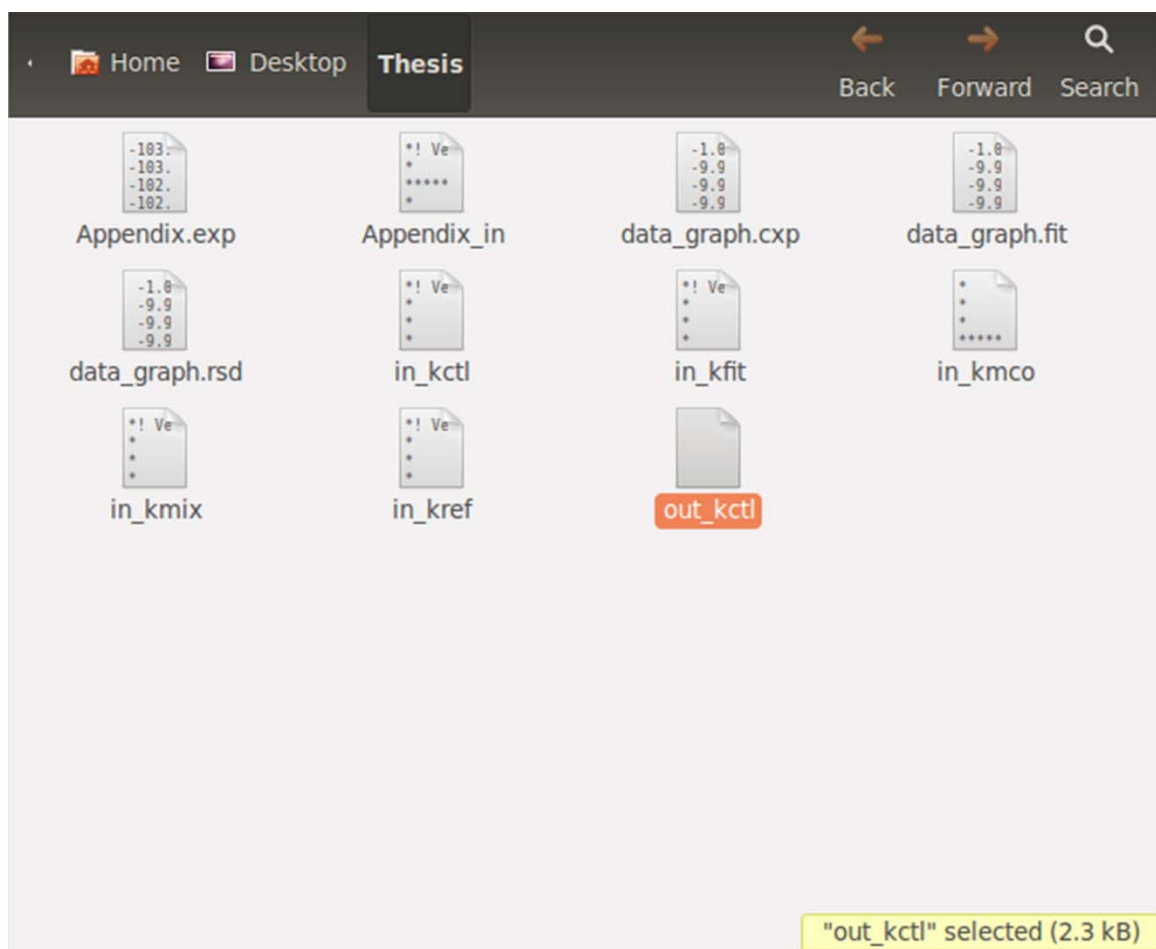


Figure 7.17 The main folder with out_kctl file highlighted.

After the specified parameters have been opened, enter the terminal, open the folder of interest, and enter the kctl command as illustrated in A15. The terminal will run the command and finish when the χ^2 converges as seen in A16. This will result in an output file that will be found in the main folder. This file will be labeled as out_kctl, as illustrated in A17. The results from the kctl command will be in this file. The final data that resulted in the best χ^2 will be at the bottom of the file as seen in A18. By inputting these values into the appropriate location, in the kref, NAME_in,, kfit files etc. will

provide better guesses for CONUSS when fitting the data in the future commands. Continued background fitting needs to be preformed next by refining the thickness in the in_kref file as seen in A19. After CONUSS has run the kctl command, at any point the operator can view the resulting spectra with the following terminal input, "xmgrace *.exp *.fit". This will open the program grace and plot the original data file (.exp) along with the resulting fit curve (.fit) from the kctl command.

```

in_kref x in_kfit x Appendix_in x out_kctl x
Fit group structure :
=====
| name of the fit group | members | modifiers |
|-----+-----+-----|
| (10) background      | 1       |           |
| (15) thickness       | 1       |           |
|-----+-----+-----|

Start values :
Chi**2 : 2.279573D+02
(10) background : -1.590000D+07
(15) thickness : 5.000000D-03 L

1. step of iteration :
Chi**2 : 2.279573D+02
Quality : 3.391069D+10
(10) background : -1.590632D+07
(15) thickness : 5.000000D-03 L

=====

Results :
=====

Chi**2 (normalized) : 227.9573 +- 0.6870

| parameter name | ## | value | +- error | % error |
|-----+-----+-----+-----+-----|
| (10) background | 1 | -1.5906D+07 +- 2.4D+03 | 0.015 |
|-----+-----+-----+-----+-----|

Error estimates are based on a 90% confidence level.

Error correlation matrix ( 0 strong correlations):

## | 1 2 ...
---+---+---
1 | 1.000

```

Figure 7.18 The out_kctl file with the resulting values providing the best χ^2 from the kctl command.

```

in_kref x in_kfit x Appendix_in x
*
* angle between the projection of k_in and the
*   projection of B_ext to the surface
*
(12) azimuthal angle of B_ext / deg.  :: 0
*
* angle between B_ext and the surface normal
*
(13) polar angle of B_ext / deg.      :: 90
*
* magnitude of the external magnetic field
*
(14) magnitude / Tesla  :: 0
*
*****
*
* energy range relative to the nuclear resonance
* =====
*
(15) begin calculation at this energy / gamma  :: -200
(16) stop ...                                :: +200
(17) nr. of steps (max. 2801)                  :: 2801
*
*****
*
* thickness of the material perpendicular to the surface
* =====
*
% (18) thickness unit / micron  :: 0.005
*
*
* thickness range, give values in units defined above
*
(19) begin calculation at this thickness / units  :: 1
(20) stop ...                                    :: 100
(21) nr. of steps (max. 100)                      :: 100
*
*****
*
* control of the printout
* =====

```

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Figure 7.19 The in_kref with thickness unit / micron highlighted to be opened for background refinement.

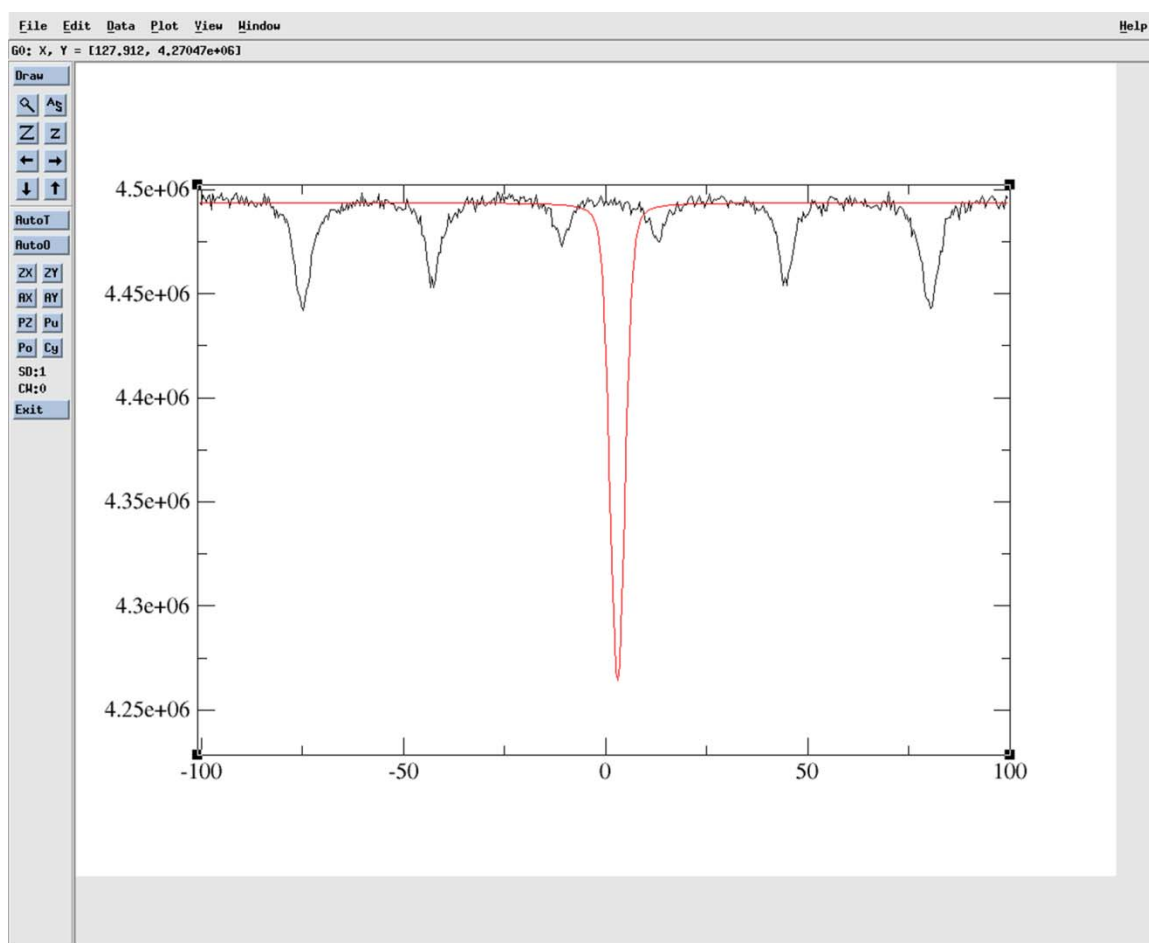


Figure 7.20 The resulting spectrum from the background refinement with unchanged parameters.

As seen in A20, the background has been established by refining the background and thickness parameters in kfit and the thickness in kref. While the remaining spectra does not match well, this is due to the initial parameters set in the NAME_in file which were 0.25, 50, and 1 for the isomer shift, magnetic hyperfine field, and quadrupole splitting respectively.

Now that the background has been established, the remaining focus can be switched into the NAME_in file. From here on, the operator will use the krmf, kctl, and kmco commands to optimize the Mössbauer fit.

```

Appendix_in ✖
(25) mode to run on hyperfine int. :: poly
*
@ &dist1 := 0.35
*
*****
*
*   defining MB site #1
*
(26.1.1) memo name for the site      :: iron
(26.1.2) number of MB atoms in the site :: 1
(26.1.3) ionization number          :: 0
(26.1.4) weight of the sublattice    :: 1
*
% (26.1.5) isomer shift / mm/s      :: 0.25
*
% (26.1.6) magnetic hyperfine field / T      :: 50
(26.1.7) magnetic polar anisotropy          :: 0
(26.1.8) magnetic azimuthal anisotropy      :: 0
(26.1.9) magn.hyp.field dir. angle theta / deg :: 90
(26.1.10) magn.hyp.field dir. angle phi / deg :: 0
*
% (26.1.11) quadrupole splitting / mm/s      :: 1
(26.1.12) asymmetry parameter                :: 0
(26.1.13) euler angle alpha for efg=>xtal /deg :: 0
(26.1.14) euler angle beta for efg=>xtal /deg :: 0
(26.1.15) euler angle gamma for efg=>xtal /deg :: 0
*
(26.1.16) name of the relaxation input file  ::
(26.1.17) name of the distribution input file :: <!
Target isomer shift
Make Gaussian 80 @&dist1
!
(26.1.18) texture coefficient / %           :: 0
*
(26.1.19) reserved for later versions      ::
*
* (26.1.20 etc.) positions of the MB atoms of site #1
*
*
0 0 0
*

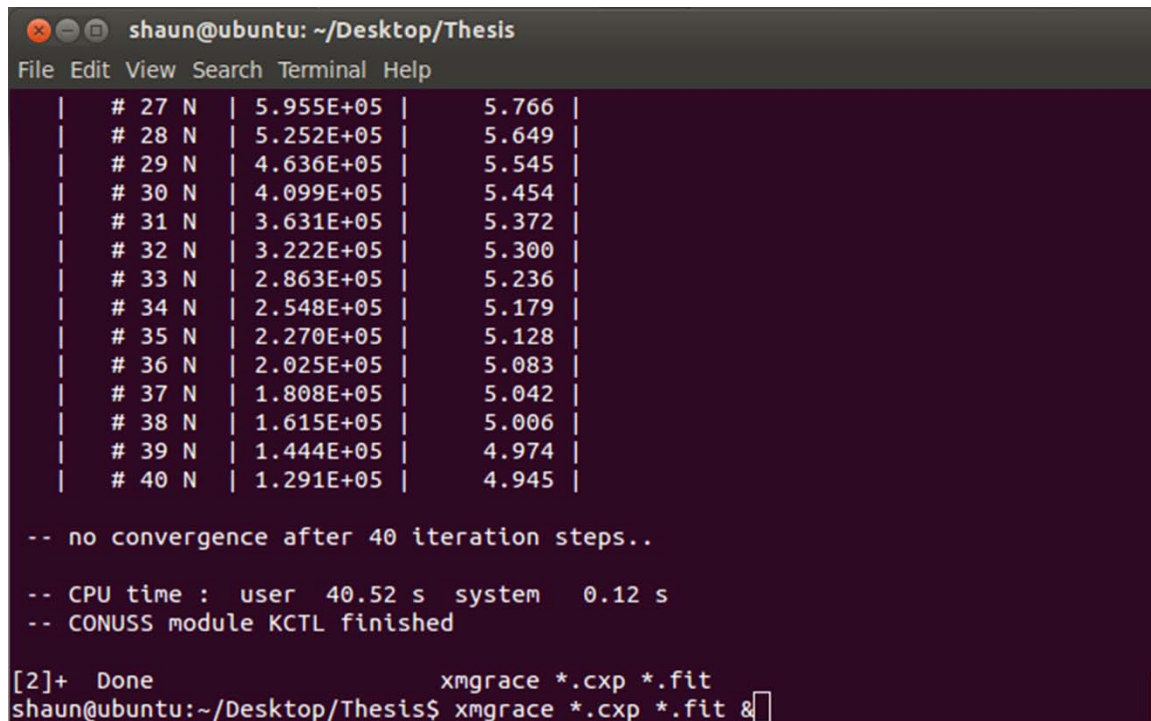
```

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Figure 7.21 The NAME_in file illustrating the isomer shift, magnetic hyperfine field, and quadrupole splitting parameters open with the "%" for fitting.

In the NAME_in file the isomer shift, magnetic hyperfine field, and quadrupole splitting parameters need to be opened as seen in A21. Depending upon the complexity of the

spectrum, where in the instance there are multiple sites, opening and fitting one parameter at a time is suggested. For this example, the sample only contains one site, therefore opening all three parameters will not cause unreasonable results.



```
shaun@ubuntu: ~/Desktop/Thesis
File Edit View Search Terminal Help

| # 27 N | 5.955E+05 | 5.766 |
| # 28 N | 5.252E+05 | 5.649 |
| # 29 N | 4.636E+05 | 5.545 |
| # 30 N | 4.099E+05 | 5.454 |
| # 31 N | 3.631E+05 | 5.372 |
| # 32 N | 3.222E+05 | 5.300 |
| # 33 N | 2.863E+05 | 5.236 |
| # 34 N | 2.548E+05 | 5.179 |
| # 35 N | 2.270E+05 | 5.128 |
| # 36 N | 2.025E+05 | 5.083 |
| # 37 N | 1.808E+05 | 5.042 |
| # 38 N | 1.615E+05 | 5.006 |
| # 39 N | 1.444E+05 | 4.974 |
| # 40 N | 1.291E+05 | 4.945 |

-- no convergence after 40 iteration steps..
-- CPU time : user 40.52 s system 0.12 s
-- CONUSS module KCTL finished

[2]+ Done xmgrace *.cxp *.fit
shaun@ubuntu:~/Desktop/Thesis$ xmgrace *.cxp *.fit &
```

Figure 7.22 Terminal illustrating kctl command with no convergence after 40 iterations.

After the desired parameters have been opened and the NAME_in file has been saved, the kctl command should be run in terminal as seen in A22. If the command does not result in a convergence, the terminal will note this. In this case, this is due to the iteration steps set in the in_kctl file only being set to 40.

```

Appendix_in ✖ out_kctl ✖ in_kfit ✖
Quality : 2.292145D+05
(26.1.5) isomer shift : 1.508098D-01
(26.1.6) magnetic hyperfine field : 4.657465D+01
(26.1.11) quadrupole splitting : 2.763912D-02 L
(10) background : -1.590628D+07

40. step of iteration :
Chi**2 : 6.764008D+00
Quality : 2.027020D+05
(26.1.5) isomer shift : 1.504358D-01
(26.1.6) magnetic hyperfine field : 4.656953D+01
(26.1.11) quadrupole splitting : 2.487521D-02 L
(10) background : -1.590628D+07

-- no convergence after 40 iteration steps..

=====

Results :
=====

Chi**2 (normalized) : 6.7640 +- 0.1187

| parameter name | ## | value | +- error | % error |
|-----|
| (26.1.5) isomer shift | 1 | 1.5009D-01 +- 8.6D-03 | 5.741 |
| (26.1.6) magnetic hyperfine fi | 2 | 4.6565D+01 +- 6.0D-02 | 0.128 |
| (26.1.11) quadrupole splitting | 3 | 2.2388D-02 +- 3.4D-02 | 153.946 |
| (10) background | 4 | -1.5906D+07 +- 4.1D+02 | 0.003 |
|-----|

Error estimates are based on a 90% confidence level.

Error correlation matrix ( 0 strong correlations):

## | 1 2 ...
|-----|
1 | 1.000 -0.002 0.286 -0.000
2 | -0.002 1.000 -0.006 -0.000
3 | 0.286 -0.006 1.000 -0.001
4 | -0.000 -0.000 -0.001 1.000

```

Figure 7.23 The out_kctl with the resulting values providing the best χ^2 of the non-converged data.

Even though the out_kctl parameters did not result in a convergence, the resulting values can be found in the out_kctl and manually input into the NAME_in file as seen in A23 and A24. At this point, the kctl command can be re-run with the new parameters until a convergence is achieved. This process should be repeated until all of the parameters no longer change when the kctl command is run. Throughout this process continual

monitoring of the fit pattern as previously described and seen in A25. This should also be preformed to ensure that no unwanted peaks are appearing. This becomes more problematic when refining multiple sites. It should also be noted when refining multiple sites, to not open the same parameter on two different sites. In other words, do not open the isomer shift for MB site #1 and MB site #2. This can result in CONUSS providing results that fit the data but do not provide numbers that make scientific sense. Adding Mössbauer sites will be discussed later.

```

Appendix_in out_kctl in_kfit
(25) mode to run on hyperfine int. :: poly
*
@ &dist1 := 0.35
*
*****
*
*   defining MB site #1
*
(26.1.1) memo name for the site      :: iron
(26.1.2) number of MB atoms in the site :: 1
(26.1.3) ionization number          :: 0
(26.1.4) weight of the sublattice    :: 1
*
% (26.1.5) isomer shift              / mm/s      :: 0.15
*
% (26.1.6) magnetic hyperfine field / T          :: 46.65
(26.1.7) magnetic polar anisotropy              :: 0
(26.1.8) magnetic azimuthal anisotropy          :: 0
(26.1.9) magn.hyp.field dir. angle theta / deg  :: 90
(26.1.10) magn.hyp.field dir. angle phi / deg   :: 0
*
% (26.1.11) quadrupole splitting      / mm/s      :: 0
(26.1.12) asymmetry parameter         :: 0
(26.1.13) euler angle alpha for efg=>xtal /deg   :: 0
(26.1.14) euler angle beta  for efg=>xtal /deg   :: 0
(26.1.15) euler angle gamma for efg=>xtal /deg   :: 0
*
(26.1.16) name of the relaxation input file      ::
(26.1.17) name of the distribution input file :: <!
Target isomer shift
Make Gaussian 80 @&dist1
!
(26.1.18) texture coefficient / %              :: 0
*
(26.1.19) reserved for later versions ::
*
* (26.1.20 etc.) positions of the MB atoms of site #1
*
*
0 0 0
*

```

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Figure 7.24 The NAME_in file illustrating the values from the kctl_out file input into the NAME_in file for further fitting.

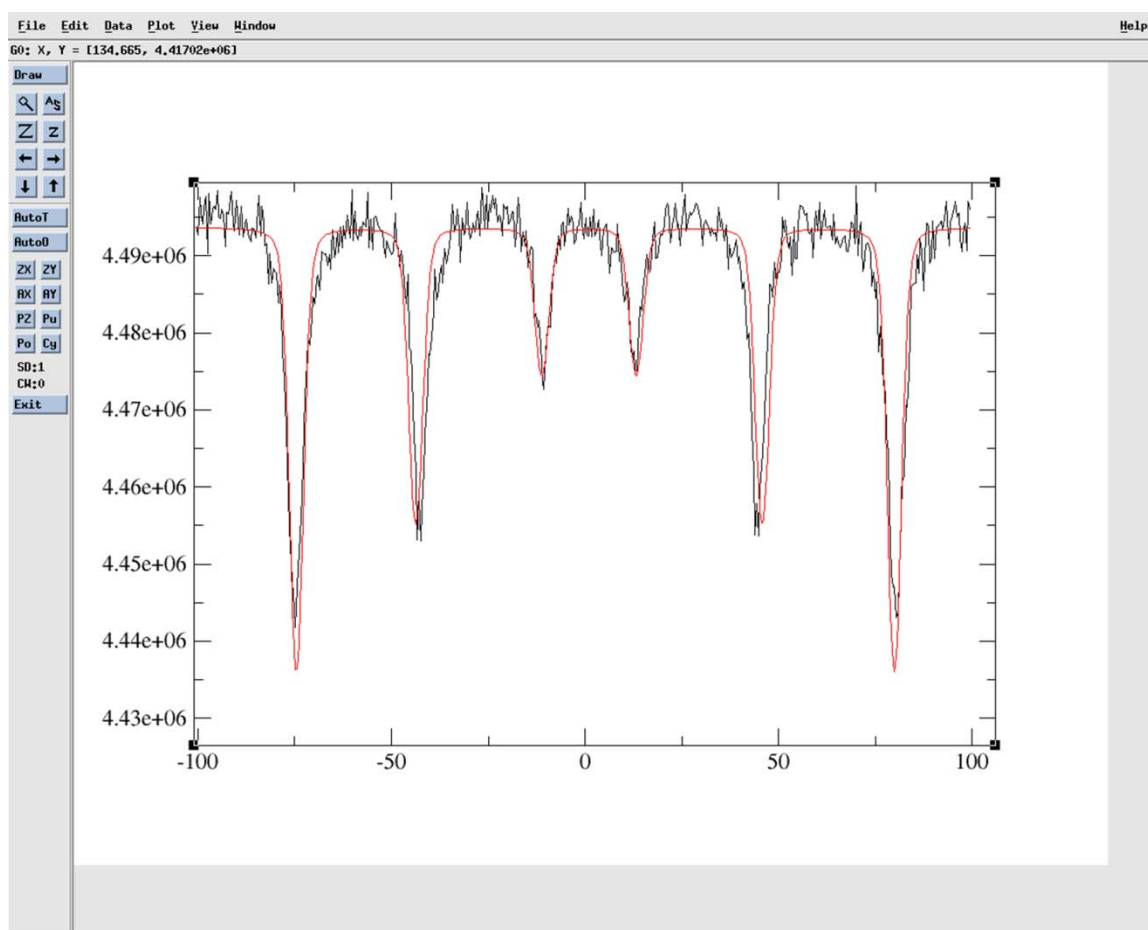
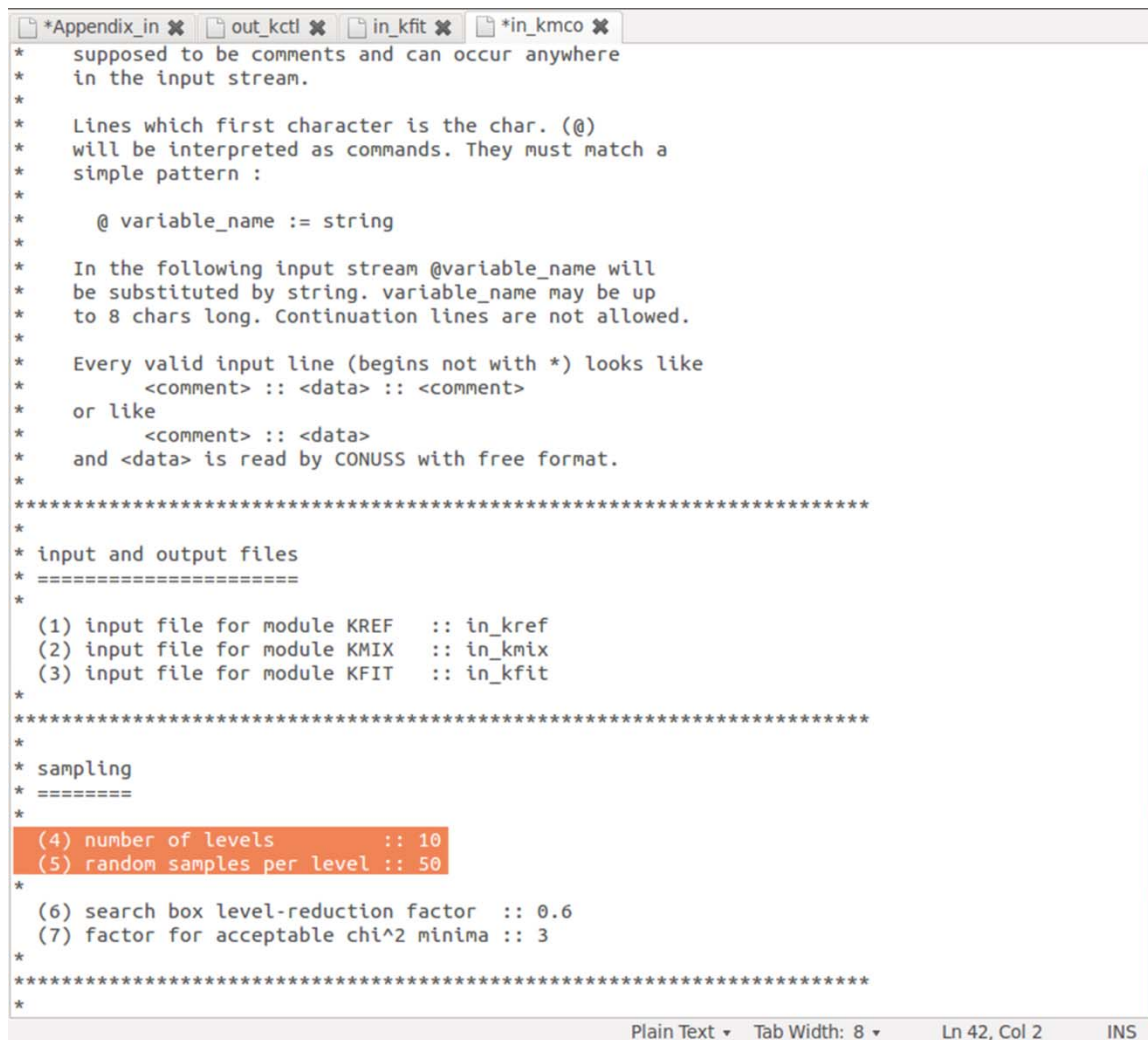


Figure 7.25 The resulting spectrum of a non-converged kctl command with the isomer shift, magnetic hyperfine field, and quadrupole splitting parameters open.

The kmco command, which uses a Monte Carlo-like method, can potentially be one of the most useful starting commands when performing a Mössbauer fit. The starting point again begins with refining the background as previously discussed. When the background has been established, similar to the procedure of the kctl command, the user will be performing most of the work in the NAME_in file, but first, the sampling levels and number of samples per level must be adjusted to the operator's specifications. The more

samples per level and the more levels that are specified the longer the operation will take, therefore, taking the time to decide on reasonable criteria for this can save time in the end. As seen in A26, the number of levels is 10 and samples per level is 50, this will provide information that will allow the operator to narrow the parameters.



```

*Appendix_in ✕ out_kctf ✕ in_kfit ✕ in_kmco ✕
* supposed to be comments and can occur anywhere
* in the input stream.
*
* Lines which first character is the char. (@)
* will be interpreted as commands. They must match a
* simple pattern :
*
* @ variable_name := string
*
* In the following input stream @variable_name will
* be substituted by string. variable_name may be up
* to 8 chars long. Continuation lines are not allowed.
*
* Every valid input line (begins not with *) looks like
* <comment> :: <data> :: <comment>
* or like
* <comment> :: <data>
* and <data> is read by CONUSS with free format.
*
*****
*
* input and output files
* =====
*
* (1) input file for module KREF :: in_kref
* (2) input file for module KMIX :: in_kmix
* (3) input file for module KFIT :: in_kfit
*
*****
*
* sampling
* =====
*
* (4) number of levels :: 10
* (5) random samples per level :: 50
*
* (6) search box level-reduction factor :: 0.6
* (7) factor for acceptable chi^2 minima :: 3
*
*****
*

```

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Figure 7.26 The in_kmco with highlighted number of levels and samples per level.

In the NAME_in file, as seen in A27, the isomer shift, magnetic hyperfine field, and quadrupole splitting are open to refinement with the "%" symbol. The important aspect at

this point is following the initial guess of the specific parameter another number is inserted. For example, the isomer shift initial guess in A27 is 0.25 which is followed by a space then the number 0.5. This is directing CONUSS, under the kmco command, to select a random number within an equal range totaling to 0.5 of the guess. This number, 0.5, covers the entire region around 0.25, therefore the sample region is from 0.0-0.75. Another example to clarify, is with the quadrupole splitting, the initial guess is 0 and the range is 3, therefore CONUSS, under the kmco command, will randomly select numbers between -1.5 and +1.5.

```

*Appendix_in  out_kctl  in_kfit
(25) mode to run on hyperfine int. :: poly
*
@ &dist1 := 0.35
*
*****
*
*   defining MB site #1
*
(26.1.1) memo name for the site      :: iron
(26.1.2) number of MB atoms in the site :: 1
(26.1.3) ionization number          :: 0
(26.1.4) weight of the sublattice    :: 1
*
% (26.1.5) isomer shift              / mm/s      :: 0.25 0.5
*
% (26.1.6) magnetic hyperfine field / T          :: 50 100
(26.1.7) magnetic polar anisotropy              :: 0
(26.1.8) magnetic azimuthal anisotropy          :: 0
(26.1.9) magn.hyp.field dir. angle theta / deg  :: 90
(26.1.10) magn.hyp.field dir. angle phi  / deg  :: 0
*
% (26.1.11) quadrupole splitting      / mm/s      :: 0 3
(26.1.12) asymmetry parameter         :: 0
(26.1.13) euler angle alpha for efg=>xtal /deg  :: 0
(26.1.14) euler angle beta  for efg=>xtal /deg  :: 0
(26.1.15) euler angle gamma for efg=>xtal /deg  :: 0
*
(26.1.16) name of the relaxation input file  ::
(26.1.17) name of the distribution input file :: <!
Target isomer shift
Make Gaussian 80 @&dist1
!
(26.1.18) texture coefficient / %          :: 0
*
(26.1.19) reserved for later versions  ::
*
* (26.1.20 etc.) positions of the MB atoms of site #1
*
*
0 0 0
*

```

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Figure 7.27 The kmco set up in the NAME_in file.

After the initial guesses and ranges have been appropriately established, the kmco command can be input into the terminal for execution. At this point, the terminal will randomly select points around the initial guess within the region established by the user and calculate the respective χ^2 for these values. If the point provides a lower χ^2 value over the previously established, the terminal will report it. When the random samples per level is reached, (in this case it is fifty), the next sample level will be entered. This level's

starting point will be the previous level best sampling, at which point, again random points are selected similar to the first level. This process continues until the number of levels and random samples per level previously input by the user has finished. This is unlike the kctl command which stops upon convergence. If it were to happen that the best point was selected immediately by the kmco command, the process would continue until finished. Upon completion of the kmco command, similar to the kctl command, an output file will be produced as seen in A29. The best sampling as a result of the kmco command are toward the bottom of this file as seen in A30. These values should be inserted into the NAME_in respective parameters as seen in A31. At this point kmco can be ran again until or if the operator is satisfied with the parameters provided, the kctl command should be performed as previously described until the fit is ideal.

```
shaun@ubuntu: ~/Desktop/Thesis
File Edit View Search Terminal Help
reading file : in_kfit
total number of lines : 121
      valid lines : 17

Estimated success probabilities vs. level:
  Individual sampling: 6.67E-07 3.09E-06 1.43E-05 6.62E-05 3.06E-04 1.42E-03 6
.56E-03 3.04E-02 1.41E-01 6.51E-01
  All samplings:      3.33E-05 1.54E-04 7.14E-04 3.30E-03 1.52E-02 6.85E-02 2
.81E-01 7.86E-01 9.99E-01 1.00E+00
  Number of samplings: 501

Best samplings:
  49.67 2.50E-01 5.00E+01 0.00E+00 -1.59E+07
  41.73 9.78E-02 -4.74E+01 -2.53E+00 -1.59E+07
  29.91 2.25E-01 -4.35E+01 -1.71E+00 -1.59E+07
  29.05 6.77E-01 1.21E+02 1.42E+00 -1.59E+07
  27.59 -8.52E-02 1.46E+02 2.70E+00 -1.59E+07
  26.37 2.25E-01 7.79E+01 -7.43E-01 -1.59E+07

Entering nesting level 2; using 48 search area(s)
  23.17 6.97E-02 8.08E+01 1.41E+00 -1.59E+07

Entering nesting level 3; using 38 search area(s)
  9.21 1.32E-01 -4.63E+01 -8.09E-01 -1.59E+07

Entering nesting level 4; using 1 search area(s)
  6.13 1.24E-01 -4.70E+01 -2.89E-01 -1.59E+07

Entering nesting level 5; using 1 search area(s)
  4.59 1.33E-01 -4.62E+01 -2.84E-01 -1.59E+07

Entering nesting level 6; using 1 search area(s)
  4.56 1.45E-01 -4.63E+01 -1.65E-01 -1.59E+07

Entering nesting level 7; using 5 search area(s)

Entering nesting level 8; using 9 search area(s)
  4.14 1.38E-01 -4.66E+01 -3.64E-01 -1.59E+07
  3.98 1.53E-01 -4.66E+01 -2.87E-01 -1.59E+07

Entering nesting level 9; using 4 search area(s)

Entering nesting level 10; using 5 search area(s)
  3.89 1.32E-01 -4.65E+01 -3.74E-01 -1.59E+07
  3.88 1.50E-01 -4.65E+01 -2.73E-01 -1.59E+07

-- CPU time : user 104.65 s system 0.24 s
-- CONUSS module KMCO finished

shaun@ubuntu:~/Desktop/Thesis$
```

Figure 7.28 The terminal illustration of output from the kmco command.

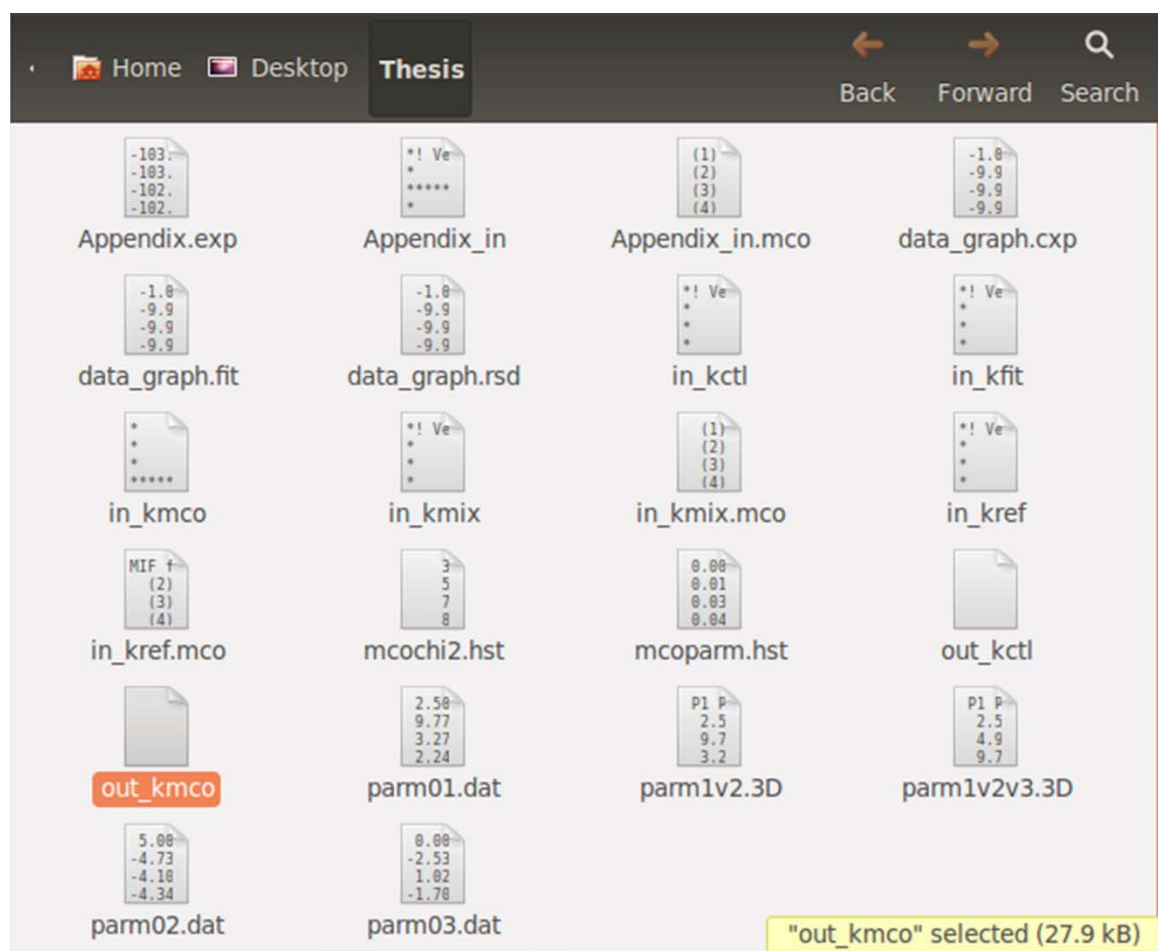


Figure 7.29 The highlighted output file as result from the kmco command.

```

Appendix_in  out_kctf  in_kfit  in_kmco  *out_kmco
1 | (26.1.5) isomer shift | 1 |
2 | (26.1.6) magnetic hyperfine field | 1 |
3 | (26.1.11) quadrupole splitting | 1 |
4 | (10) background | 1 |
-----
Estimated success probabilities vs. level:
Individual sampling: 6.67E-07 3.09E-06 1.43E-05 6.62E-05 3.06E-04 1.42E-03 6.56E-03
3.04E-02 1.41E-01 6.51E-01
All samplings: 3.33E-05 1.54E-04 7.14E-04 3.30E-03 1.52E-02 6.85E-02 2.81E-01
7.86E-01 9.99E-01 1.00E+00
Number of samplings: 501

Best sampling:
3.88 1.50E-01 4.65E+01 2.73E-01 1.59E+07

List of all 501 samplings:
49.67 2.50E-01 5.00E+01 0.00E+00 -1.59E+07
41.73 9.78E-02 -4.74E+01 -2.53E+00 -1.59E+07
57.86 3.27E-01 -4.10E+01 1.02E+00 -1.59E+07
29.91 2.25E-01 -4.35E+01 -1.71E+00 -1.59E+07
74.84 -2.36E-01 9.66E+00 1.72E+00 -1.59E+07
124.69 5.26E-01 -7.39E-01 7.27E-01 -1.59E+07
76.61 5.08E-01 -1.12E+01 -2.54E+00 -1.59E+07
67.27 2.08E-01 -9.67E+00 -5.59E-01 -1.59E+07
40.61 1.82E-01 1.03E+02 2.26E+00 -1.59E+07
43.63 2.19E-02 7.14E+01 3.11E-01 -1.59E+07
63.94 2.93E-01 1.95E+01 -2.37E+00 -1.59E+07
45.82 -2.34E-01 -4.36E+01 -8.33E-01 -1.59E+07
70.92 -1.17E-01 5.69E+01 -5.04E-01 -1.59E+07
29.05 6.77E-01 1.21E+02 1.42E+00 -1.59E+07
69.24 -6.08E-02 3.40E+01 6.27E-01 -1.59E+07
65.27 -1.12E-01 -2.60E+01 2.28E+00 -1.59E+07
77.89 6.20E-01 1.41E+01 2.08E+00 -1.59E+07
67.04 -1.10E-01 2.54E+01 2.77E+00 -1.59E+07
40.57 2.39E-01 9.89E+01 1.56E+00 -1.59E+07
30.56 4.86E-02 1.33E+02 2.32E+00 -1.59E+07
43.98 4.75E-03 6.42E+01 -1.58E+00 -1.59E+07
27.59 -8.52E-02 1.46E+02 2.70E+00 -1.59E+07
67.40 2.08E-01 3.50E+01 0.13E-01 -1.59E+07

```

Figure 7.30 The best sampling as a result of the kmco command highlighted in the out_kmco file.

```

*Appendix_in  out_kctf  in_kfit  in_kmco  *out_kmco
(25) mode to run on hyperfine int. :: poly
*
@ &dist1 := 0.35
*
*****
*
*   defining MB site #1
*
(26.1.1) memo name for the site      :: iron
(26.1.2) number of MB atoms in the site :: 1
(26.1.3) ionization number          :: 0
(26.1.4) weight of the sublattice    :: 1
*
% (26.1.5) isomer shift              / mm/s      :: 0.15
*
% (26.1.6) magnetic hyperfine field / T          :: 46.5
(26.1.7) magnetic polar anisotropy              :: 0
(26.1.8) magnetic azimuthal anisotropy          :: 0
(26.1.9) magn.hyp.field dir. angle theta / deg  :: 90
(26.1.10) magn.hyp.field dir. angle phi / deg   :: 0
*
% (26.1.11) quadrupole splitting      / mm/s      :: 0.273
(26.1.12) asymmetry parameter         :: 0
(26.1.13) euler angle alpha for efg=>xtal /deg  :: 0
(26.1.14) euler angle beta  for efg=>xtal /deg  :: 0
(26.1.15) euler angle gamma for efg=>xtal /deg  :: 0
*
(26.1.16) name of the relaxation input file  ::
(26.1.17) name of the distribution input file :: <!
Target isomer shift
Make Gaussian 80 @&dist1
!
(26.1.18) texture coefficient / %          :: 0
*
(26.1.19) reserved for later versions  ::
*
* (26.1.20 etc.) positions of the MB atoms of site #1
*
*
0 0 0
*

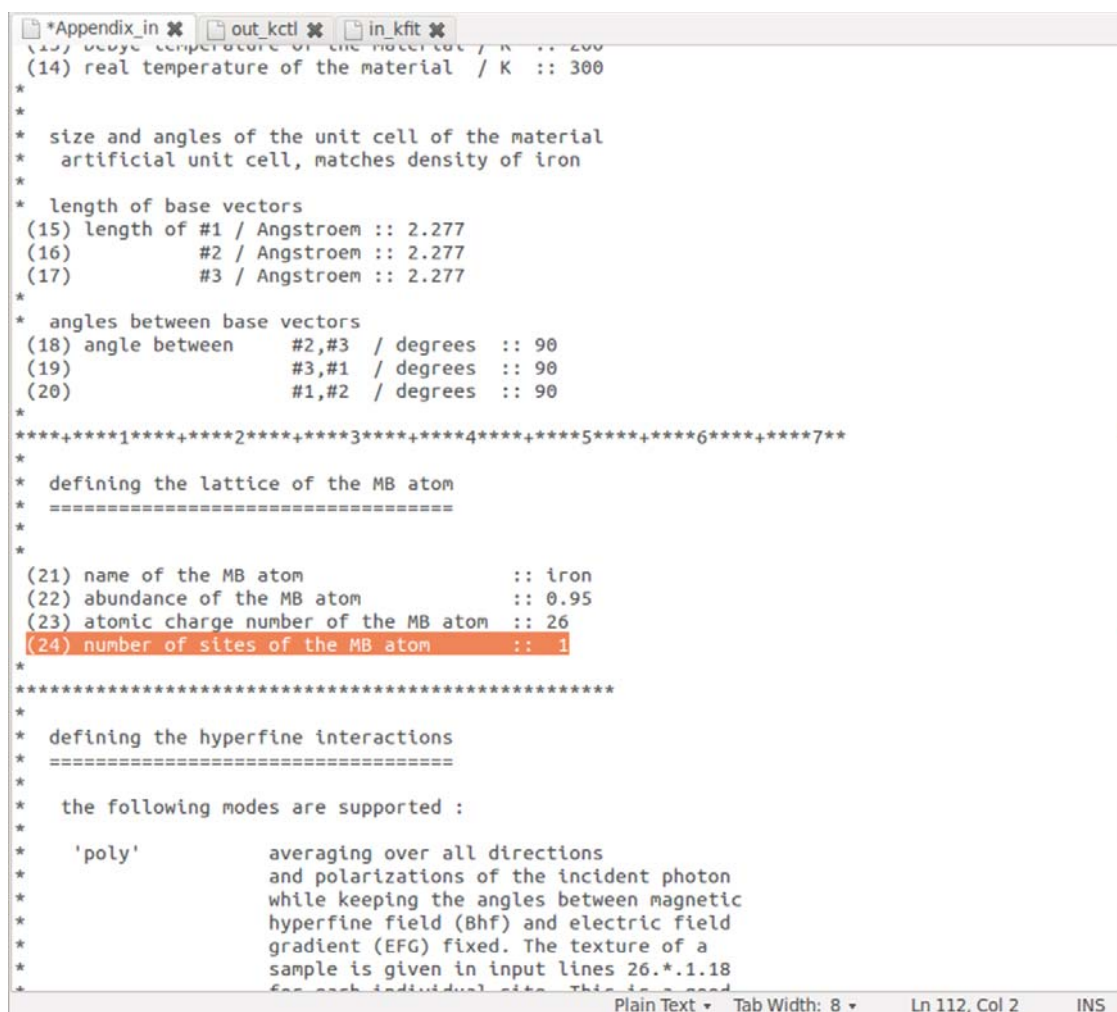
```

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Figure 7.31 The best sampling values input into the NAME_in file for further refinement.

The final important aspect of Mössbauer fitting using CONUSS is refining data with multiple sites. It is common for materials or compounds to have multiple sites and this is performed by the addition of another site into the NAME_in file. This can easily be performed by changing a few parameters. In the NAME_in file the first step should be changing the number of sites of the MB from 1 to 2, or 2 to 3, etc, as seen in A32 and

A33. From there, simple copying and pasting of the @ &dist1 then changing the 1 to 2 should be performed. The next step is copying all of the information from defining MB site #1 to 0 0 0 toward the bottom of the file, as seen at the bottom of A31 and pasting it below the 0 0 0. At this point, all of the numbers that were previously 1 such as defining MB site #1, the @ &dist1, or (26.1.4) need to be changed to 2 as in defining MB site #2, @ &dist2, and 26.2.4 respectively as seen in A33-A36.



```

*Appendix_in  out_kctf  in_kfit
(13) Debye temperature of the material / K :: 200
(14) real temperature of the material / K :: 300
*
*
* size and angles of the unit cell of the material
* artificial unit cell, matches density of iron
*
* length of base vectors
(15) length of #1 / Angstroem :: 2.277
(16)          #2 / Angstroem :: 2.277
(17)          #3 / Angstroem :: 2.277
*
* angles between base vectors
(18) angle between #2,#3 / degrees :: 90
(19)          #3,#1 / degrees :: 90
(20)          #1,#2 / degrees :: 90
*
****+****1****+****2****+****3****+****4****+****5****+****6****+****7**
*
* defining the lattice of the MB atom
* =====
*
(21) name of the MB atom          :: iron
(22) abundance of the MB atom     :: 0.95
(23) atomic charge number of the MB atom :: 26
(24) number of sites of the MB atom :: 1
*
*****
*
* defining the hyperfine interactions
* =====
*
* the following modes are supported :
*
* 'poly'          averaging over all directions
*                  and polarizations of the incident photon
*                  while keeping the angles between magnetic
*                  hyperfine field (Bhf) and electric field
*                  gradient (EFG) fixed. The texture of a
*                  sample is given in input lines 26.*.1.18
*                  for each individual site. This is a good

```

Figure 7.32 Number of sites of the MB atom highlighted in the NAME_in file with 1 site.

```

*Appendix_in  out_kctf  in_kfit
(13) Debye temperature of the material / K :: 200
(14) real temperature of the material / K :: 300
*
*
* size and angles of the unit cell of the material
* artificial unit cell, matches density of iron
*
* length of base vectors
(15) length of #1 / Angstroem :: 2.277
(16)          #2 / Angstroem :: 2.277
(17)          #3 / Angstroem :: 2.277
*
* angles between base vectors
(18) angle between #2,#3 / degrees :: 90
(19)          #3,#1 / degrees :: 90
(20)          #1,#2 / degrees :: 90
*
*****1*****2*****3*****4*****5*****6*****7**
*
* defining the lattice of the MB atom
* =====
*
*
(21) name of the MB atom          :: iron
(22) abundance of the MB atom     :: 0.95
(23) atomic charge number of the MB atom :: 26
(24) number of sites of the MB atom :: 2
*
*****
*
* defining the hyperfine interactions
* =====
*
* the following modes are supported :
*
* 'poly'          averaging over all directions
*                  and polarizations of the incident photon
*                  while keeping the angles between magnetic
*                  hyperfine field (Bhf) and electric field
*                  gradient (EFG) fixed. The texture of a
*                  sample is given in input lines 26.*.1.18
*                  for each individual site. This is a good

```

Figure 7.33 Number of sites of the MB atom highlighted in the NAME_in file with the changed number of sites from 1 to 2.

```

*Appendix_in  out_kctl  in_kfit
*
@ &dist1 := 0.35
@ &dist2 := 0.35
*
*****
*
*   defining MB site #1
*
(26.1.1) memo name for the site      :: iron
(26.1.2) number of MB atoms in the site :: 1
(26.1.3) ionization number          :: 0
(26.1.4) weight of the sublattice    :: 1
*
(26.1.5) isomer shift                / mm/s      :: 0.141
*
(26.1.6) magnetic hyperfine field / T          :: 46.46
(26.1.7) magnetic polar anisotropy             :: 0
(26.1.8) magnetic azimuthal anisotropy         :: 0
(26.1.9) magn.hyp.field dir. angle theta / deg :: 90
(26.1.10) magn.hyp.field dir. angle phi  / deg :: 0
*
(26.1.11) quadrupole splitting      / mm/s      :: -0.321
(26.1.12) asymmetry parameter       :: 0
(26.1.13) euler angle alpha for efg=>xtal /deg  :: 0
(26.1.14) euler angle beta  for efg=>xtal /deg  :: 0
(26.1.15) euler angle gamma for efg=>xtal /deg  :: 0
*
(26.1.16) name of the relaxation input file  ::
(26.1.17) name of the distribution input file :: <!
Target isomer shift
Make Gaussian 80 @&dist1
!
(26.1.18) texture coefficient / %          :: 0
*
(26.1.19) reserved for later versions  ::
*
* (26.1.20 etc.) positions of the MB atoms of site #1
*
*
0 0 0
*

```

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Figure 7.34 The @ &dist2 parameter highlighted after it was copied from the @ &dist1 parameter and the 1 changed to 2.

```

*Appendix_in  out_kctf  in_kfit
make Gaussian 80 @autst1
!
(26.1.18) texture coefficient / %      :: 0
(26.1.19) reserved for later versions ::
*
* (26.1.20 etc.) positions of the MB atoms of site #1
*
*
* 0 0 0
*
* defining MB site #2
*
(26.1.1) memo name for the site      :: iron
(26.1.2) number of MB atoms in the site :: 1
(26.1.3) ionization number          :: 0
(26.2.4) weight of the sublattice    :: 1
*
(26.2.5) isomer shift                / mm/s      :: 0.141
*
(26.2.6) magnetic hyperfine field / T          :: 46.46
(26.1.7) magnetic polar anisotropy             :: 0
(26.1.8) magnetic azimuthal anisotropy         :: 0
(26.1.9) magn.hyp.field dir. angle theta / deg :: 90
(26.1.10) magn.hyp.field dir. angle phi / deg  :: 0
*
(26.2.11) quadrupole splitting / mm/s          :: -0.321
(26.1.12) asymmetry parameter                 :: 0
(26.1.13) euler angle alpha for efg=>xtal /deg :: 0
(26.1.14) euler angle beta for efg=>xtal /deg  :: 0
(26.1.15) euler angle gamma for efg=>xtal /deg :: 0
*
(26.1.16) name of the relaxation input file    ::
(26.1.17) name of the distribution input file :: <!
Target isomer shift
Make Gaussian 80 @&dist2
!
(26.1.18) texture coefficient / %      :: 0
(26.1.19) reserved for later versions ::
*
* (26.1.20 etc.) positions of the MB atoms of site #1

```

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Figure 7.35 The NAME_in file with defining MB site #2 highlighted after the 1 was changed to 2 and the entire section of defining MB site #1 was copied and pasted beneath the 0 0 0 at the bottom of defining MB site #1.

```

*Appendix_in  out_kctf  in_kfit
(26.1.2) number of MB atoms in the site :: 1
(26.1.3) ionization number           :: 0
(26.2.4) weight of the sublattice    :: 1
*
(26.2.5) isomer shift                / mm/s      :: 0.141
*
(26.2.6) magnetic hyperfine field / T          :: 46.46
(26.1.7) magnetic polar anisotropy           :: 0
(26.1.8) magnetic azimuthal anisotropy       :: 0
(26.1.9) magn.hyp.field dir. angle theta / deg :: 90
(26.1.10) magn.hyp.field dir. angle phi  / deg :: 0
*
(26.2.11) quadrupole splitting      / mm/s      :: -0.321
(26.1.12) asymmetry parameter       :: 0
(26.1.13) euler angle alpha for efg=>xtal /deg :: 0
(26.1.14) euler angle beta  for efg=>xtal /deg :: 0
(26.1.15) euler angle gamma for efg=>xtal /deg :: 0
*
(26.1.16) name of the relaxation input file  ::
(26.1.17) name of the distribution input file :: <!
Target isomer shift
Make Gaussian 80 @&dist2
!
(26.1.18) texture coefficient / %          :: 0
(26.1.19) reserved for later versions  ::
*
* (26.1.20 etc.) positions of the MB atoms of site #1
*
*
0 0 0
*
*****1*****2*****3*****4*****5*****6*****7**
*
* defining the lattices of the non MB atoms
* =====
*
(27) number of lattices of non MB atoms :: 0
*
*****1*****2*****3*****4*****5*****6*****7**
*

```

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Figure 7.36 The final paramater to be renamed, Make Gaussian 80 @&dist2, is highlighted after all of the parameters have been changed in the defining MB site #2.

Now that all of the names of the parameters have been changed accordingly from 1 to 2 or 2 to 3 depending on how many sites have been added, the final parameter to be aware of is the weight of the sublattice parameter. Previously, this parameter was not necessary due to only 1 site being responsible for the entirety of the sample. With multiple sites, each site will have a weighted effect on the peak intensities, widths, splitting etc.

Therefore, changing the weight of the sublattice value will increase the effect those parameters have on the fitting of the Mössbauer spectra. As illustrated by A37 and A38, the values were both decreased to 0.5. This parameter should also be opened for refinement.

```

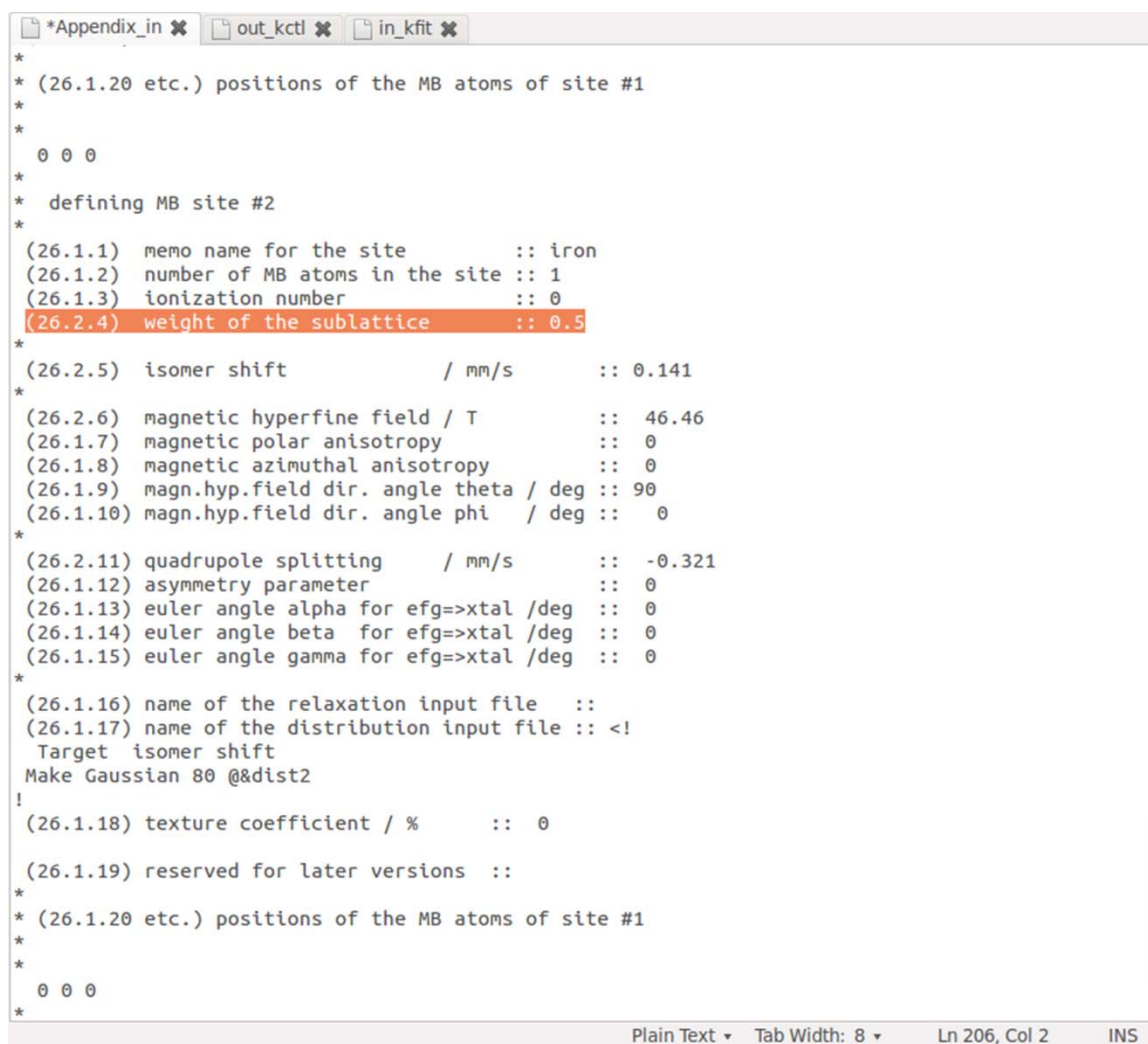
*Appendix_in  out_kctf  in_kfit
(25) mode to run on hyperfine int. :: poly
*
@ &dist1 := 0.35
@ &dist2 := 0.35
*
*****
*
*   defining MB site #1
*
(26.1.1) memo name for the site      :: iron
(26.1.2) number of MB atoms in the site :: 1
(26.1.3) ionization number          :: 0
(26.1.4) weight of the sublattice    :: 0.5
*
(26.1.5) isomer shift                / mm/s      :: 0.141
*
(26.1.6) magnetic hyperfine field / T          :: 46.46
(26.1.7) magnetic polar anisotropy             :: 0
(26.1.8) magnetic azimuthal anisotropy         :: 0
(26.1.9) magn.hyp.field dir. angle theta / deg :: 90
(26.1.10) magn.hyp.field dir. angle phi  / deg :: 0
*
(26.1.11) quadrupole splitting      / mm/s      :: -0.321
(26.1.12) asymmetry parameter       :: 0
(26.1.13) euler angle alpha for efg=>xtal /deg  :: 0
(26.1.14) euler angle beta  for efg=>xtal /deg  :: 0
(26.1.15) euler angle gamma for efg=>xtal /deg  :: 0
*
(26.1.16) name of the relaxation input file  ::
(26.1.17) name of the distribution input file :: <!
Target isomer shift
Make Gaussian 80 @&dist1
!
(26.1.18) texture coefficient / %          :: 0
*
(26.1.19) reserved for later versions  ::
*
* (26.1.20 etc.) positions of the MB atoms of site #1
*
*

```

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Figure 7.37 The weight of sublattice parameter for site 1 within the NAME_in file is highlighted illustrating its change from 1 to 0.5 due to the addition of the second site.

When performing a fit refinement with multiple sites, it is strongly suggested to initially start with one site and refine the site as far as possible before adding a second site. After the addition of the second site, refine only the second site until the fit no longer improves. At this point, opening different parameters with both sites may improve the fit. When it has been determined the addition of a third site is required, again, only focus on the new site before opening parameters of the previously refined sites.



```

*Appendix_in  out_kct1  in_kfit
*
* (26.1.20 etc.) positions of the MB atoms of site #1
*
* 0 0 0
*
* defining MB site #2
*
(26.1.1) memo name for the site      :: iron
(26.1.2) number of MB atoms in the site :: 1
(26.1.3) ionization number          :: 0
(26.2.4) weight of the sublattice    :: 0.5
*
(26.2.5) isomer shift                / mm/s      :: 0.141
*
(26.2.6) magnetic hyperfine field / T          :: 46.46
(26.1.7) magnetic polar anisotropy            :: 0
(26.1.8) magnetic azimuthal anisotropy        :: 0
(26.1.9) magn.hyp.field dir. angle theta / deg :: 90
(26.1.10) magn.hyp.field dir. angle phi  / deg :: 0
*
(26.2.11) quadrupole splitting      / mm/s      :: -0.321
(26.1.12) asymmetry parameter      :: 0
(26.1.13) euler angle alpha for efg=>xtal /deg :: 0
(26.1.14) euler angle beta  for efg=>xtal /deg :: 0
(26.1.15) euler angle gamma for efg=>xtal /deg :: 0
*
(26.1.16) name of the relaxation input file  ::
(26.1.17) name of the distribution input file :: <!
Target isomer shift
Make Gaussian 80 @&dist2
!
(26.1.18) texture coefficient / %          :: 0
*
(26.1.19) reserved for later versions  ::
*
* (26.1.20 etc.) positions of the MB atoms of site #1
*
* 0 0 0
*

```

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Figure 7.38 The weight of sublattice parameter for site 2 within the NAME_in file is highlighted illustrating its change from 1 to 0.5 due to the addition of the second site.

At this point, a general understanding of how to operate CONUSS should have been achieved. Parameters that were not discussed within were not used in laboratory Mössbauer spectroscopy but were used in synchrotron Mössbauer spectroscopy.

REFERENCES

REFERENCES

- [1] W. Sturhahn, *Hyperfine Interact.* 125 (2000) 149.