IRON INCORPORATION INTO FERROELECTRIC LEAD TITANATE

BY

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Approved __________________________
Advisor

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ABSTRACT

Incorporation of iron into ferroelectric lead titanate with ABO$_3$ perovskite structure is widely utilized to fabricate materials with ferroelectric and ferromagnetic order. These solid solutions exhibit room temperature ferromagnetic properties at iron concentration as low as 1 mole%. Iron (Fe$^{3+}$) is highly compatible with titanium (Ti$^{4+}$) in ionic radii and obviously incompatible in the valence state. Magnetoelectric coupling has been observed in 50 mole% Fe substituted lead titanate. The molecular mixing of precursor materials in wet chemical synthesis such as sol-gel has advantage over conventional solid state sintering in achieving higher solubility of the substituent.

A series of Pb(Fe$_x$Ti$_{1-x}$)O$_{3-\delta}$ solid solution in the composition range $x = 0$ to 1 has been synthesized using sol-get route, followed by a moderate temperature ($700 \, ^{\circ}\text{C}$) calcination. The structure and properties of samples were characterized using x-ray diffraction (XRD), x-ray absorption spectroscopy (XAS), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDX), dielectric spectroscopy, Raman spectroscopy, and magnetic measurements. SEM results indicated a gradual change in sample morphology, changing from individual particles to nano-aggregates with Fe concentration. EDX confirmed uniform distribution of dopants when Fe concentration $x \leq 0.3$ and Fe concentration close to nominal composition with possibility of lead loss. XRD results indicated a rapid reduction of tetragonal distortion upon Fe substitution, Fe solubility limit of 10 mole%, and PbFe$_{12}$O$_{19}$ impurity phase formation at compositions $x \geq 0.4$. XAS clearly indicated that Ti prefers a 6 coordinated distorted oxygen octahedra and Fe is surrounded by 5 oxygens situated at a similar distance. Other measurements suggested that ferroelectric and ferromagnetic ordering may arise in Ti-rich and Fe-rich phases, respectively. None of the samples below $x = 0.2$ was found to be ferromagnetic at room temperature.
1.1 Structure of Perovskites Oxides

The perovskite family of materials possess important physical and electrical properties desirable for numerous technological applications. [1-4] Properties such as pyro and piezo electricity, dielectric, superconductivity, linear and non-linear electro-optics effects differ from one perovskite to another, with no significant changes in crystal structure. [5] The ideal perovskite oxide structure can be represented by the general formula ABO$_3$ and has the structural arrangement of atoms depicted in Figure 1.1.

![Cubic ABO$_3$ perovskite unit cell with a = b ≠ c lattice parameters.](image)

Large-sized 12-coordinated A cations are close-packed in layers with oxygen anions. The smaller B metal ions are situated in octahedrally coordinated holes between
the close-packed layers. [6] Large-sized A and small-sized B cations are important for the formation of the perovskite structure. For example, the ilmenite (FeTiO$_3$) and ilmenite-related compounds have the same chemical formula as perovskite, ABO$_3$, but form a structure different from perovskite (trigonal rhombohedral) due to similar sized A and B cations. [7]

The ideal perovskite depicted in Figure 1.1 is a cubic lattice. Although a few compounds have this ideal cubic structure, many oxides form into distorted lower symmetry variants such as hexagonal or orthorhombic structure. A large number of perovskite oxides form a rhombohedral type lattice. Most perovskite oxides have a symmetry other than cubic at room temperature but turn into cubic symmetry at high temperatures. [8] [9] The electrostatic energy derived from arranging B cations in an array of corner sharing octahedra provides the stability to the perovskite structure. [9] [10] Additional stability is provided by accommodating large A cations within this BO$_3$ skeletal sub-array. [5] However, in many compounds a large amount of oxygen or cation deficiency has been observed. Owing to their large lattice energies, these compounds are still classified as perovskite oxides regardless of the defects. Various types of perovskite lattice distortions, especially those that stem from various defects, are strongly related to material properties. [11] [12] In particular, ferromagnetic and ferroelectric properties of these materials are strongly correlated with the defect structure. [13] [14]

### 1.2 Doping of Perovskites Oxides

The deviation from the ideal cubic perovskite structure upon doping can be monitored using ionic radii of the A and B site occupants. In the case of the ideal cubic structure, ABO$_3$, perovskite oxides are considered as purely ionic crystals in close-packing arrangement. Consequently, the following relationship (Equation 1.1) between the radii of the A, B and O ions holds true, where $r_A$, $r_B$ and $r_O$ are the
ionic radii of A cation, B cation and oxygen anion respectively, and $a$ is the lattice parameter. [15]

$$\frac{a}{2} = r_A + r_O = \sqrt{2}(r_B + r_O) \quad (1.1)$$

Therefore, any deviation from the ideal cubic structure known as the tolerance factor, $t$ is defined by Equation 1.2.

$$t = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)} \quad (1.2)$$

In general, the perovskite phase is favorable when the value of $t$ is approximately between 0.8 and 1.1. [5] When the tolerance factor is close to 1, the ideal cubic perovskite structure is formed. For example, both SrTiO$_3$ with $t = 1.00$ and BaZrO$_3$ with $t = 1.01$ form cubic structures at room temperature. On the other hand, the compounds SrZrO$_3$ and CaTiO$_3$ are orthorhombic with $t$ values of 0.94 and 0.97, respectively. If the tolerance factor is very far from unity, the perovskite structure is not formed, as evidenced by MgTiO$_3$ which has a $t$ value of 0.81, and adopts the ilmenite structure. [5, 15] In summary, when the tolerance factor deviates from unity, the perovskite cells are deformed into a lower symmetry structure.

The lowering of symmetry in perovskites is often accompanied by a tilting of the B octahedra. When the ionic radius of the A site is too small to occupy the volume available at a given temperature, octahedra may rotate to reduce the size of the interstices. The amount of tilting depends on the tolerance factor, temperature, and parameters associated with the composition. [16] Doping B sites with a different type of cation with similar ionic radius may not reduce the symmetry of the perovskite structure. Doping with cations that favor non-octahedral coordination may result in oxygen vacancies that drive octahedra away from corner-sharing towards edge-sharing or even face-sharing configurations, especially at higher dopant concentrations. [17]

Perovskite materials have the ability to accommodate more than one aliovalent
element in both A and B sites. The composition of the complex type perovskite compounds can be represented with the formula $A(B'_xB''_{1-x})O_3$, where $B'$ is the lower valence B-cation and $B''$ is the higher valence cation. Roy [18] has studied the possible multiple substitution in perovskites and categorized them into 5 groups:

1. $A(B'_{2/3}B''_{1/3})O_3$
2. $A(B'_{1/3}B''_{2/3})O_3$
3. $A(B'_{1/2}B''_{1/2})O_3$
4. Oxygen deficient phase $A(B'_xB''_{1-x})O_{3-\delta}$
5. Hexagonal perovskites of the type $A_nB_{n-1}O_{3n}$

A single property of a perovskite material can be tailored by selectively controlling the aliovalent dopants. [19] Continuing interest in perovskite materials is a consequence of the wide range of enhanced properties available in terms of A and B site substitutions. Among those improvements are the enhancement of piezoelectric properties in zirconium-substituted lead titanate, manipulation of ferroelectric transition temperature, dielectric constant, loss factor of materials, and improved material processing conditions. Additionally, peroskites may also be modified to have two or more properties, leading to new potential applications as multifunctional materials. [20] The flexibility in simultaneous manipulation of material properties as well as process conditions make perovskites a viable candidate for a wide range of technological applications.

1.3 Perovskites Transition Metal Oxides as Multiferroics

Multiferroics are single phase materials that simultaneously exhibit more than one of ferromagnetic, ferroelectric, and ferroelastic order parameters. [3] Similarly,
magnetoelectric materials display simultaneous ferromagnetic and ferroelectric ordering. However, due to the scarcity of magnetoelectric materials, the definition of magnetoelectric materials has been extended to include antiferromagnetic and antiferroelectric order. In this generalized group of magnetoelectric materials, coupling between the two order parameters may arise directly or indirectly via strain. Multi-phase materials are also considered multiferroic if the order parameters in separate phases are intimately connected via strain. A wide range of applications have been suggested for multiferroic materials including multi-state memory devices, magnetically switched electro-optic devices, and magnetically controlled piezoelectric transducers. The existence of the coupling between two order parameters such as in magnetoelectrics gives an additional degree of freedom in device design. For example, magnetoelectric storage devices, in theory, have the ability to write a data bit with a magnetic field while reading the stored information with an electric field, and vice-versa.

Considering the ability to retain structural integrity at large dopant concentrations, the incorporation of magnetic ions into perovskite oxides is a viable option for magnetoelectric materials synthesis. In materials with sufficient magnetic ion concentration, magnetic ordering could come to existence via double exchange or super exchange mechanisms. Therefore, sufficient concentration of magnetic dopants is essential to produce materials with strong magnetic response. Doping may also alter the properties of the host material. In particular, B site doping with 3d transition elements could alter the phase transition temperature, dielectric constant, hysteresis, and loss properties of ferroelectric materials. Additionally, a high level of magnetic ion substitution with the same element may produce relaxor-type ferroelectrics, some of which exhibit magnetoelectric properties.

Thermal disorder disrupts the ferromagnetic ordering which is manifested by
a transition to the paramagnetic state at a certain temperature. This critical temperature, at which the transition occurs, is known as the Curie temperature of the ferromagnetic materials, or Néel temperature for an antiferromagnetic compound. Above the critical temperature magnetic susceptibility obeys the Curie-Weiss law:

\[ \chi = \frac{C}{T - T_c} \]  

(1.3)

where \( C \) is the material specific Curie constant, \( T \) is the absolute temperature, and \( T_c \) is the Curie temperature. There is a divergence in the magnetic susceptibility at the Curie temperature where the magnetic moments are aligned by the exchange interactions even in the absence of an applied magnetic field.

A correlation is expected between the proximity of magnetic centers and the temperature at which they behave as isolated magnetic moments with random orientations. Therefore, the close proximity of magnetic centers, only achieved at high dopant concentrations, may be essential for high temperature magnetic ordering. The research on \((\text{PbTiO}_3)_{(1-x)} (\text{LaMnO}_3)_x\) and \((\text{PbTiO}_3)_{(1-2x)} (\text{PbMn}_{0.5} \text{Nb}_{0.5} \text{O}_3)_{2x}\) solid solutions by Havinga demonstrated that the substitution of 3d magnetic elements at higher concentrations increased the Curie temperature of the material. However, the improvement in magnetic properties is accompanied by undesirable suppression of ferroelectric properties.

The electric susceptibility of a ferroelectric material follows the Curie-Weiss law (equation 1.3) where \( T_c \) is the ferroelectric transition temperature. The existence or absence of ferroelectricity is determined by the delicate balance between the short-range repulsions and the long-range Coulomb forces. Consequently, ferroelectrics are highly sensitive to chemistry and the defect structure of the material. Short range repulsions prefer the non-polar cubic perovskite structure, which transforms to polar phase under dominating Coulomb forces below the transition temperature. The ferroelectric polarization results primarily from the displacement
of the B cation relative to the oxygen octahedron. Electronic structure calculations on PbTiO$_3$ and BaTiO$_3$ by Cohen and Krakauer [40] have shown that in both cases Ti 3d – O 2p hybridization is critical for the stabilization of the ferroelectric distortion. The hybridization between Pb 6s and O 2p orbitals results in large polarizability accompanied by strain which stabilizes PbTiO$_3$ and BaTiO$_3$ in tetragonal phase at room temperature. Both materials contain Ti$^{4+}$ B-site cation formally in a d$^0$ state, a noble gas shell configuration. Most other perovskite ferroelectrics with other types of B-site cations, such as Nb$^{5+}$, Zr$^{4+}$, Ta$^{5+}$ and W$^{6+}$ with different ionic radii, are also in d$^0$ configuration. Therefore, the existence of d electrons in the B-site cation, essential for magnetic ordering, may hinder the ferroelectric properties of perovskite oxides.

3d transition metal magnetic cations are often considered as B-site dopants owing the compatible ionic radii. Most ferroelectric materials do not contain trivalent B cations, which is favored by many magnetic 3d tradition metal ions. Therefore, when the dopant concentration is large, the charge compensation provided in terms of simultaneous A-site substitution is essential for the structural stability of perovskites. Otherwise, the limited ability of the host material to sustain oxygen vacancies may cause other forms of charge compensation, either by means of phase segregation or through structure transformations. For example, Mn incorporation into PbTiO$_3$ hosts was performed by Havinga [37] according to (PbTiO$_3$)$_{(1−x)}$ (LaMnO$_3$)$_x$, where equal amount of A-site Pb$^{2+}$ ions are also replaced by La$^{3+}$. While this fulfills the charge compensation requirement, large effects from changing the identity of the A-site cation may disrupt the ferroelectric order. The strain introduced by the A cation hybridization with O 2p orbitals is believed to be long range in nature and provides the long range forces that drives the phase transition. Consequently, the simultaneous substitution of B and A sites can adversely affect both properties indispensable for the existence of ferroelectricity, B cation displacement within the oxygen cage and the
long range ordering of the material.

Crystal size is known to alter the properties of ferroelectric ceramics. Fine grained ferroelectric perovskites showed an improvement in the dielectric constant below Curie temperature. Improved dielectric properties are often attributed to the increased stress in sub-micron grains or contributions from the enhanced domain wall structure. However, below a critical particle size, typically in the nano scale, a complete loss of ferroelectric properties has been observed. The paraelectric phase transformation of PbTiO$_3$ nano-crystals below 15nm has been reported. The loss of ferroelectric properties from ferroelectric tetragonal to paraelectric cubic structure is attributed to the loss of long range order. The transition is believed to be triggered by the loss of the delicate balance between short range forces favoring the cubic phase and long-range forces favoring the ferroelectric phase. Homogenous doping of A or B sites may have similar consequences for the ferroelectric crystal lattice. At dopant concentrations as low as 12.5%, one A or B lattice site of a 2×2×2 super cell is replaced by a dopant ion. The lattice disruptions caused by dopants could destroy the ferroelectric ordering of the material.

The competing conditions for ferroelectricity and magnetic ordering are rarely met. However, the wide availability of synthesis and characterization techniques and the demand for technological applications fuels the search for new multiferroics. Doped perovskites such as (Pb(Fe$_{2/3}$W$_{1/3}$)O$_3$)$_{(1-x)}$ (Pb(Mg$_{1/2}$W$_{1/2}$)O$_3$)$_x$ discovered as early as 1958 show multiferroic properties. Recent reports of multiferroic properties observed in chemically doped BiFeO$_3$ and PbTiO$_3$ remain unconfirmed.

### 1.4 Problem Formulation

Palkar and Malik reported the co-existence of ferroelectric and ferro-
magnetic properties at room temperature in Pb(Fe\textsubscript{x}Ti\textsubscript{1-x})O\textsubscript{3} samples. The samples were prepared using co-precipitation method for better chemical homogeneity and stoichiometry. The x-ray diffraction data of 50% iron substituted sample (x = 0.5) clearly show tetragonal splitting of peaks. A small amount of Pb\textsubscript{2}Ti\textsubscript{2}O\textsubscript{6} impurity phase was also present in the sample matrix. A significant reduction of the tetragonal lattice distortion (c/a) from 1.064 in pure PbTiO\textsubscript{3} to 1.028 at 50% iron substitution was reported. Substitution of B site Ti\textsuperscript{4+} by Fe\textsuperscript{3+} is feasible due to similar ionic radii. \textsuperscript{49} The reduction in tetragonal distortion is consistent with the behavior of 3d transition metal doped solid solutions. However, the reduction rate is significantly lower evidenced by the the presence of tetragonal distortion at 50 mole% dopant concentration. A-site doping of the PbTiO\textsubscript{3} host, a typical method for charge compensation, was not used, thus allowing the formation of oxygen vacancies in the lattice.

More recent work by Ren et al \textsuperscript{50} also reported room temperature ferromagnetism in Fe-doped PbTiO\textsubscript{3} nanocrystals. Their samples show clear signs of tetragonal distortion under x-ray diffraction. The maximum iron concentration of the samples is 4 mole% and appear to be phase pure. The magnetism of the nanocrystals developed from diamagnetism to ferromagnetism and paramagnetism when the nominal iron concentration was increased from 0 to 4 mole%. The improved room temperature ferromagnetic properties were attributed to oxygen vacancy (F-center) exchange interaction enhanced by planar-like, selfassembly via oriented aggregation of the crystals. However, the maximum concentration of iron used in this study is rather low (4 mole%) and does not provide insight to the crystal structure or the properties of Pb(Fe\textsubscript{x}Ti\textsubscript{1-x})O\textsubscript{3} at high Fe\textsuperscript{3+} concentrations.

The study discussed in this thesis is focused towards providing answers to some debatable questions about the Pb(Fe\textsubscript{x}Ti\textsubscript{1-x})O\textsubscript{3} solid solution series. It has been speculated that the lead titanate host material has sufficiently large tetragonal
distortion \((c/a = 1.064)\) which may retain the polarizability at large iron dopant concentrations. However, the solubility limit of iron in \(\text{PbTiO}_3\) host or structural transformations driven by doping, has not been yet established. Therefore this study is focused on:

1. Finding the limiting ability of \(\text{PbTiO}_3\) as a host material to sustain ferroelectricity upon \(\text{Fe}^{3+}\) doping and the solubility limit.
2. Investigating the crystal structure with both long-range and local probes and establish concentration dependent structural trends.
3. Investigating the \(\text{Fe}^{3+}\) concentration dependent ferromagnetic and ferroelectric properties of the solid solution.
4. Finding how oxygen vacancies manifest themselves in structural changes on the microscopic level and consequent effects on material properties.
5. Finding the \(\text{Fe}\) concentration dependent average local structure of \(\text{Ti}^{4+}\) and \(\text{Fe}^{3+}\).
6. Formation of impurity phases.
7. Answering the question of whether multiferroic behavior is truly associated with the perovskite structure or is it attributable to intimately mixed, perovskite and iron rich, oxygen deficient phases of different materials.

Over the course of this project a complete series of \(\text{Pb(Fe}_x\text{Ti}_{1-x})\text{O}_3-\delta\) was synthesized using sol-gel route in the \(x = 0\) to 1 range. The ability to incorporate dopants homogeneously using sol-gel technique allows for higher solubility limits compared to conventional solid state sintering. The series of solid solutions was characterized using X-ray Diffraction (XRD), thermal analysis, dielectric spectroscopy, Raman
spectroscopy, ferroelectric hysteresis measurements, magnetization measurements, and X-ray Absorption Spectroscopy (XAS) measurements.
CHAPTER 2
SAMPLE PREPARATION

2.1 Basic Concepts

Doping of ferroelectric perovskites with 3d magnetic elements and properties investigation has been a classical subject in material science over many decades. Some of these experiments are limited to small magnetic ion concentrations owing to challenges in material preparation. Materials prepared using conventional solid state sintering were subject to poor solubility, high amounts of impurity phases, inhomogeneities in dopant distribution, and required high processing temperatures. The advantages of wet chemical over solid state processing include: better homogeneity, high purity, significantly low processing temperatures, uniform phase distribution in multi-component systems, superior size and morphological control, the possibility of preparing new materials in both crystalline and non-crystalline phases, and the ability to make thin films and coatings, which is critical in both applications and material characterization.

Lead titanate (PbTiO$_3$) is a well studied displacive type ferroelectric with a tetragonal crystal lattice. The large difference in A and B site ionic radii (Pb$^{2+} = 1.63$ Å and Ti$^{4+} = 0.605$ Å) facilitates preferential doping of B site with 3d transition elements. Many electron paramagnetic resonance (EPR) studies have shown that 3d magnetic ions are indeed incorporated into the B-sublattice. The magnetic dopant chosen in this study, Fe$^{3+}$ with ionic radii of approximately 0.58 Å, is highly compatible with the B-site Ti$^{4+}$ ions. Typically, the charge compensation for partial oxygen vacancies created by Fe$^{3+}$ ions is carried out by La$^{3+}$ substitutions at A-sites. However, this study is focused on finding the limited ability of PbTiO$_3$ host to retain Fe$^{3+}$ ions, hence the A-site was not modified.
2.2 Choice of Method

Advanced material techniques facilitate the doping of PbTiO$_3$ at high concentrations required for magnetic interactions. The Pb(Fe$_{0.5}$Ti$_{0.5}$)$_3$O$_{3-\delta}$ sample in the study by Palkar and Malik [48] was prepared using co-precipitation and displayed both ferroelectric and ferromagnetic order. Sol-gel based techniques are also available for the preparation of pure and doped lead titanate ceramics. [61–63]

The important steps in sol-gel synthesis [64] are as follows: The hydrolysis starts with a mixture of a metal alkoxide and water in a solvent, typically alcohol at ambient or slightly elevated temperature. The next step, polymerization involves condensation of adjacent molecules wherein water and solvent are eliminated and links are formed. These polymeric networks grow to colloidal dimensions in the solution. In the gelation step, polymeric networks link to form a three dimensional tight network throughout the liquid (sol). At this step, the system becomes rigid and shows characteristics of a gel. A sufficiently aged gel is subsequently dried by removing water and solvent at a moderate temperature, forming a hydroxylated metal oxide with residual organic content. The next step, dehydration, is typically carried out at temperatures higher than 270 $^\circ$C. In this step organic constituents are either evaporated or decomposed, leaving the amorphous inorganic oxide. The final step known as densification is carried out at temperatures higher than 600 $^\circ$C, forming the dense crystalline metal oxide. For a powder sample, the particle size can be controlled by the densification temperature profile.

A simple sol-gel based technique with a single solvent [65], glacial acetic acid, was used for the preparation of iron doped lead titanates. All metallo-organic compounds used, lead subacetate Pb(C$_2$H$_3$O$_2$)$_2 \cdot$ 2Pb(OH)$_2$ (Sigma Aldrich, ACS reagent grade), iron (III) acetylacetonate Fe(C$_5$H$_7$O$_2$)$_3$ (Sigma-Aldrich, 99.9%) and titanium isopropoxide Ti(OCH(CH$_3$)$_2$)$_4$ (Sigma-Aldrich, 99.999%), have good solubility in
acetic acid (Themo-Fisher 98.5%).

2.3 Preparation Process

Stoichiometric solutions of specific Fe$^{3+}$ ion concentrations were prepared by dissolving measured amounts of the chemicals in acetic acid. Lead subacetate and iron acetylacetonate were dissolved separately, in 20 to 30 ml of glacial acetic acid with the aid of a magnetic stirrer. Beakers were covered with Parafilm$^{\text{R}}$M to minimize water absorption by the acetic acid. An excess amount of lead, typically 3%, was used to compensate for possible lead volatilization during thermal processing. When fully dissolved, the two solutions were mixed together and stirred for an additional 15-20 minutes before adding titanium isopropoxide. In this process, the order of adding metal alkoxides is important because of different hydrolysis/condensation reaction speeds. The higher reaction speed of titanium isopropoxide may form large titanium alkoxide chains leading to local inhomogeneities. Ultrasonication promotes better mixing of the solutions, aid gelation, and is known to prevent pyrochlore phase formation. Therefore, the solution was ultrasonicated for 2-3 hours. The viscosity of the solution was significantly increased during the sonication step. The amount of titanium isopropoxide used in the solution has to be reduced with increasing iron concentration. Longer gelation times associated with high iron concentration samples may result from the small amounts of gelation agent (titanium isopropoxide) used in the solution. The color of the solution varied from colorless-transparent to dark brown depending on iron concentration. Subsequently, samples were transferred into petri dishes and placed inside an approximately 75 °C oven for drying and aging. Actual drying time varied between 2 to 4 days depending on the dopant concentration. During this process, evaporation of acetic acid and the gradual increase in the viscosity were followed by the formation of transparent gels. A picture of an ultrasonicated sample and a dried gel is shown in Figure 2.1. Complete drying resulted in cracking
due to increasing stress. Wet gels are assumed to consist of pores that are filled with solvents. Crack or fractures in drying gels could occur when the capillary forces exerted by the pore liquid to the pore wall exceeds the strength of the gel network. Solutions with iron concentration less than 40% formed uniform gels with minimal or no precipitates. Solutions with higher iron concentrations yielded more precipitate areas that increased with the concentration.

![Figure 2.1. Transparent highly viscous gel formed by the 20% Fe solution.](image)

Dried gels were scraped off from the petri dishes and ground into a fine powder using an agate motor and pestle. Powders were then transferred into alumina combustion boats and heat treated at 300 °C for 5 hours according to the temperature profile shown in Figure 2.2. This preliminary heat treatment was used to decompose residual organics and remove water content, leaving the pure amorphous ceramic matrix. Thermo-Gravimetric Analysis (TGA) measurements show that this process is efficient above 300 °C. Percentage weight loss below 300 °C increased with the iron concentration, suggesting that the weight of organic constituents in dried powders in-
creases with iron concentration. (see Figure 2.3) Gels took a longer time to dry when the iron concentration was high. Therefore, the increase in percentage weight loss can be attributed to higher level of residual organic content due to iron (III) acetylacetone and wetness of the gels. A low temperature ramp rate was utilized to prevent possible dopant loss during organic decomposition. Initial crystallization occurs at temperatures higher than 400 °C. Therefore, no sharp diffraction peaks were observed in sample diffraction patterns taken after the preliminary firing. The resultant mate-

![Graph showing temperature vs. time for the preliminary firing profile of Pb(Fe\textsubscript{x}Ti\textsubscript{1-x})O\textsubscript{3} precursor materials. Possible lead loss during organic removal was minimized by the use of a 0.25 °C/min temperature ramp rate.](image)

Figure 2.2. Preliminary firing profile of Pb(Fe\textsubscript{x}Ti\textsubscript{1-x})O\textsubscript{3} precursor materials. Possible lead loss during organic removal was minimized by the use of a 0.25 °C/min temperature ramp rate.

rials were re-ground into a fine powder and sintered at 700 °C for 3 hours (See Figure 2.4) to form the crystalline ceramic. Both firing cycles were carried out under static air. A temperature of 700 °C is sufficient for effective crystallization of powders yet low enough to minimize material volatilization and related complications. Intermediate cubic phase and kinetically favorable stoichiometric pyrochlore phase (Pb\textsubscript{2}Ti\textsubscript{2}O\textsubscript{6})
are dominant at lower temperatures. [68] These phases can be transformed to tetragonal PbTiO$_3$ at higher temperatures. X-ray diffraction (XRD) analysis showed that the samples prepared at 700 °C are free of pyrochlore type impurities. The preparation of 100 % iron substituted end phase (Pb$_2$Fe$_2$O$_5$) and a possible impurity phase PbFe$_{12}$O$_{19}$ was attempted using 1:1 and 1:12 lead to iron molar ratio mixtures of lead subacetate and iron acetylacetonate. These samples were also subjected to similar drying and heat treatment as other samples. Pb$_2$Fe$_2$O$_5$ is known to be an incommensurate phase and thus hard to quantify using conventional diffraction methods. Simple peak match showed that this sample contains Pb$_2$Fe$_2$O$_5$, PbFe$_{12}$O$_{19}$, and PbO phases. The diffraction pattern of the attempted PbFe$_{12}$O$_{19}$ phase was noisy due to high amount of iron fluorescence produced by the Cu K$_\alpha$ radiation. While diffraction measurements of this sample showed no similarities with the published XRD spectra.
Figure 2.4. The secondary (calcination) firing profile of Pb(Fe\textsubscript{x}Ti\textsubscript{1-x})O\textsubscript{3} precursor materials. The samples were allowed to furnace-cool to room temperature.

of PbFe\textsubscript{12}O\textsubscript{19}, the local structure extracted from XAS agrees well with PbFe\textsubscript{12}O\textsubscript{19}.
CHAPTER 3

SCANNING ELECTRON MICROSCOPY AND ENERGY DISPERSIVE SPECTROSCOPY

3.1 Investigation of Microstructure

Properties of perovskite oxides, especially ferroelectric and dielectric properties are strongly correlated with the particle size. In the case of PbTiO$_3$, a systematic reduction in tetragonal distortion with the reduction of particle size has been reported. Smaller particles, approximately 15 nm in size, no longer show ferroelectric properties. Therefore, a qualitative investigation of the particle size was performed using Scanning Electron Microscopy (SEM) on a selected group of samples. SEM images of the Pb(Fe$_{x}$Ti$_{1-x}$)O$_{3-\delta}$ were captured using a JEOL JSM5900LV scanning electron microscope also capable of performing Energy Dispersive X-ray spectroscopy (EDX) measurements. Sample preparation for SEM measurements, particularly insulating powders such as perovskite ceramics, is challenging due to sample charging upon electron bombardment. Sample charging can move particles during measurements which could reduce the quality and resolution of the images by shadowing effects. Our samples were prepared by dispersing a thin layer of sample powder on a spectral grade, conductive carbon tape. Excess powder was carefully removed so that the prepared sample sufficiently represented the full range of particles available in the sample.

SEM images under different magnification conditions were captured to visualize the particle size distribution of the samples. Figure 3.1 shows the particle size distribution of Pb(Fe$_{0.025}$Ti$_{0.975}$)O$_{3-\delta}$ sample. Particle size distribution is broad with maximum particle size of approximately 100 $\mu$m. Particle shapes are highly irregular. At lower levels of iron doping, particles are well separated from each other as shown in Figure 3.1. Nano-aggregates can be observed in higher Fe concentrations. Figure 3.2 is an image of the Pb(Fe$_{0.6}$Ti$_{0.4}$)O$_{3-\delta}$ sample taken at $\times$1000 magnifica-
Figure 3.1. SEM image of $\text{Pb(Fe}_{0.025}\text{Ti}_{0.975})\text{O}_{3-\delta}$ sample at $\times 500$ magnification. Particles appear to be well separated. Images at a lower magnification indicate a maximum particle size of approximately 100 $\mu$m.

tion. The morphology of this sample is different from low iron doped samples. The maximum individual particle size is about 20 $\mu$m where as maximum nano-aggregate size is around 100 $\mu$m. Figure 3.3 is an image of the $\text{Pb(Fe}_{0.9}\text{Ti}_{0.1})\text{O}_{3-\delta}$ sample taken at $\times 2000$ magnification which clearly shows multiple nano-aggregates. The overall trend indicates a reduction in individual particle size and population along with nano-aggregates/nanoparticles that grow in population with the increasing iron concentration. When the amount of nano size particles increase the material properties significantly change. The lattice parameters or the amount of strain present in a nano scale sample maybe significantly different from the bulk. Having a broad range of particle sizes may have a negative impact on material characterization using techniques such as x-ray powder diffraction, thermogravimetric differential thermal analysis, differential thermal analysis, x-ray absorption spectroscopy and x-ray energy dispersive spectroscopy. These implications will be discussed in relevant chapters.
Figure 3.2. SEM image of Pb(Fe$_{0.6}$Ti$_{0.4}$)O$_{3-\delta}$ sample at $\times1000$ magnification. This sample consists of separate particles and nano-aggregates.

Figure 3.3. SEM image of Pb(Fe$_{0.9}$Ti$_{0.1}$)O$_{3-\delta}$ sample at $\times2000$ magnification. Particle on the bottom left corner of the image is an example for a nano-aggregate.
3.2 Distribution of the Dopants by Elemental Analysis

Scanning electron microscopes are equipped with optics capable of focusing an energetic electron beam down to a sub-nanometer size spot on the sample. [69] Most electron microscopes are capable of achieving sub micron size electron beams. Energetic electrons of a scanning electron microscope bombarding a sample can eject electrons from the inner shells of constituent atoms. These vacancies are immediately filled by electrons from higher energy levels, emitting x-rays characteristic of a particular atom. Intensities of these characteristic fluorescence lines can be used to measure the amount of atomic species in a particular sample. X-ray fluorescence lines from 1-3 microns below the surface can be detected revealing the chemical composition of micron sized volumes. [70] The ability to detect elemental concentrations depends on the ability to isolate a single characteristic fluorescence line with the aid of a detector with sufficient energy resolution. This technique is referred to as Energy Dispersive X-ray spectroscopy (EDX). In principle, all elements from atomic number 4 (Be) to 92 (U) can be detected. However, our instrument was not equipped with light element (atomic number less than 10) detection precluding quantification of oxygen. EDX is capable of providing data with atomic weight percentage accuracies below 1% with accurate instrument calibration. However, our samples consists of a wide range of particles size and texture that change with the dopant concentration. Under these conditions finding a true calibration standard with known atomic concentration was not possible, thus, measurements were carried out with the default calibration of the instrument. Nevertheless, relative atomic concentrations reveal valuable information about the dopant distribution and possible lead deficiencies as a function of the iron concentration.

Dopant distribution at various nominal Fe concentrations was investigated using EDX. A very small area of sample in the range 1 to 4 \( \mu m^2 \) was analyzed.
Table 3.1. Atomic fractions of Fe measured at various micro-regions by EDX

<table>
<thead>
<tr>
<th>Nominal x</th>
<th>Fe fraction by EDX</th>
<th>Nominal x</th>
<th>Fe fraction by EDX</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>0.017</td>
<td>0.4</td>
<td>0.379</td>
</tr>
<tr>
<td></td>
<td>0.012</td>
<td></td>
<td>0.409</td>
</tr>
<tr>
<td></td>
<td>0.011</td>
<td></td>
<td>0.388</td>
</tr>
<tr>
<td>0.025</td>
<td>0.027</td>
<td>0.5</td>
<td>0.617</td>
</tr>
<tr>
<td></td>
<td>0.067</td>
<td></td>
<td>0.555</td>
</tr>
<tr>
<td></td>
<td>0.031</td>
<td></td>
<td>0.616</td>
</tr>
<tr>
<td>0.05</td>
<td>0.046</td>
<td>0.6</td>
<td>0.674</td>
</tr>
<tr>
<td></td>
<td>0.057</td>
<td></td>
<td>0.635</td>
</tr>
<tr>
<td></td>
<td>0.045</td>
<td></td>
<td>0.575</td>
</tr>
<tr>
<td>0.1</td>
<td>0.097</td>
<td>0.7</td>
<td>0.739</td>
</tr>
<tr>
<td></td>
<td>0.096</td>
<td></td>
<td>0.751</td>
</tr>
<tr>
<td></td>
<td>0.091</td>
<td></td>
<td>0.810</td>
</tr>
<tr>
<td>0.15</td>
<td>0.144</td>
<td>0.8</td>
<td>0.826</td>
</tr>
<tr>
<td></td>
<td>0.284</td>
<td></td>
<td>0.740</td>
</tr>
<tr>
<td></td>
<td>0.151</td>
<td></td>
<td>0.853</td>
</tr>
<tr>
<td>0.2</td>
<td>0.232</td>
<td>0.9</td>
<td>0.943</td>
</tr>
<tr>
<td></td>
<td>0.182</td>
<td></td>
<td>0.939</td>
</tr>
<tr>
<td></td>
<td>0.187</td>
<td></td>
<td>0.923</td>
</tr>
<tr>
<td>0.3</td>
<td>0.317</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.254</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.331</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

A minimum of 3 measurements were taken per sample. Table 3.1 lists the micro-region iron concentrations of the Pb(Fe\(_x\)Ti\(_{1-x}\))O\(_{3-\delta}\) sample series. Results indicate distribution of the dopant is mostly homogenous throughout the sample series. The average composition of the samples was measured on a relatively large area, greater than 1000 \(\mu\)m\(^2\). The results are graphed in Figure 3.4 as a function of the nominal composition. The dashed line indicates the nominal composition. Measured and nominal dopant concentrations show excellent agreement when \(x = 0.2\) or less. At
concentrations higher than $x = 0.2$ the measured values are consistently higher than the nominal composition.

Absolute lead composition given by EDX was unrealistically low, possibly due to the instrument calibration. In order to understand the relative trends of lead composition, EDX data were first normalized by the total B site composition followed by the maximum value of the A-site occupation given by EDX. Pure lead titanate and the 50 mole% iron doped sample showed the minimum amount of lead vacancies as shown in Figure 3.5. Samples with nominal composition $x \leq 0.2$ have a maximum lead loss of 12 mole%. Lead loss shows an increase with the nominal composition up to $x = 0.4$. The trend continues after the anomaly at $x = 0.5$ which shows no lead loss. Higher amounts of lead loss might be indicating the formation of extra phases.
Figure 3.5. Average Pb composition calculated using EDX versus the nominal composition x.

with higher Fe:Pb ratios. Formation of Pb deficient impurity phases will be discussed in Chapters 4 and 7.

Elemental mapping of the samples is useful in identifying phase segregation. The ability to map large areas of the sample enables detection of segregated phases more effectively than multiple micro-region measurements. Elemental maps of Pb, Ti and Fe were captured using Pb M$_\alpha$, Ti K$_\alpha$ and Fe K$_\alpha$ fluorescence lines, respectively. Comparison of these elemental maps revealed that samples with iron concentrations x $\leq$ 0.3 show more homogenous distribution of all three elements. Samples with concentrations x $\geq$ 0.4 show areas of higher iron concentrations which are also deficient in lead. Figure 3.6 shows iron elemental maps for x = 0.3(a) and x = 0.6(b) samples. White arrows indicate iron rich, lead deficient areas which indicate the formation of impurity phases. Doping lead titanate B-site with iron above its solubility limit is known to form magnetic impurity phases such as PbFe$_{12}$O$_{19}$. [20]
The existence of impurity phases may have an adverse effect on dielectric properties of ferroelectric materials by increasing their electrical conductivity. SEM and EDX results indicate the formation of such phases, whose quantities increase rapidly when B-sites are doped beyond 50 mole% with iron.

SEM images indicated a change in sample morphology with the Fe concentration. The lower limit of the particles size is related to the existence of ferroelectricity. PbTiO$_3$ nano particles below 10 nm in size are cubic in structure, thus paraelectric. Low Fe concentration samples consisted of well separated particles. Nano-aggregates are only visible in high Fe concentration samples. EDX results showed a uniform distribution of dopants at low Fe concentrations. The measured Fe concentration was found to be very close to the nominal concentration. Lead loss was also indicated by EDX. However, more accurate determination constituent elements was precluded by the inability to perform a reliable instrument calibration. Clear indication of Fe-rich impurity phase formation was observed under elemental mapping when the Fe concentration $x \geq 0.4$. Below this concentration Fe appear to be uniformly distributed.
CHAPTER 4
X-RAY POWDER DIFFRACTION

4.1 Crystal Structure by Powder Diffraction

X-ray powder diffraction (XRPD) is routinely used to identify the crystal structure of materials and has the ability to recognize amorphous materials in partially crystalline mixtures. [71] In this study, XRPD has been utilized in the preparation process optimization, phase identification, and crystal structure determination of the samples. Samples prepared in this study were subjected to a preliminary firing cycle (depicted in Figure 2.1) to remove organic constituents. Resultant powders were investigated using XRPD. Figure 4.1 shows the diffraction pattern of PbTiO$_3$ precursor material after preliminary firing at 300 °C. Lack of sharp diffraction peaks indicates

![Diffraction pattern](image)

Figure 4.1. Diffraction pattern of the PbTiO$_3$ fired at 300 °C for 5 hours. The lack of sharp diffraction peaks indicates poor or no crystallization.

the lack of crystallinity in the sample after preliminary firing. Initial crystallization
was found to occur above 400 °C. At this temperature undesirable effects such as lead volatilization is minimal. However, at lower temperatures the formation of an intermediate cubic phase is more likely. The transformation from stoichiometric pyrochlore phase Pb$_2$Fe$_2$O$_6$ is kinetically more favorable than a direct transformation to the thermodynamically stable PbTiO$_3$ tetragonal perovskite phase. Crystalization was found to be efficient at temperatures around 700 °C. Our maximum process temperature is significantly lower than the temperatures used in the solid state sintering technique which is typically in excess of 1000 °C. The diffraction pattern of the post-annealed powder was indexed using PbTiO$_3$ $P4mm$ symmetry crystal reflections as shown in Figure 4.2. Iron doped samples prepared using similar processing conditions were found to be free from pyrochlore phases at least up x = 0.3. Diffractograms of the entire sample series are shown in Figure 4.3.

X-ray diffraction patterns of Pb(Fe$_x$Ti$_{1-x}$)O$_{3-\delta}$ solid solution series were col-

Figure 4.2. Diffraction pattern of the PbTiO$_3$ prepared using sol-gel route. Diffraction peaks are indexed with $P4mm$ tetragonal crystal structure.
Figure 4.3. Diffraction patterns of the Pb(Fe$_x$Ti$_{1-x}$)O$_{3-\delta}$ solid solution series. The evolution of the diffraction peaks clearly indicate the loss of tetragonal distortion at $x = 0.1$. The sample series was analyzed using Reitveld refinement up to $x = 0.3$. 
lected using a Bruker D2 Phaser diffractometer in Bragg-Brentano geometry using Cu-K\(_\alpha\) radiation. The Cu-K\(_\beta\) x-ray lines were removed employing a Ni filter. However, a small amount of Cu-K\(_\beta\) radiation leakage was present. Peaks resulting from K\(_\beta\) leakage were low in intensity thus only visible at the low theta base of the most prominent peak. (See Figure 4.2) Data collection was performed in the 2\(\theta\) range between 5\(^\circ\) and 130\(^\circ\) in 0.02\(^\circ\) steps. Diffracted intensity was measured using a LynxEye linear position sensitive detector with dwell time of 0.5 second per data point. Each diffraction pattern was compared with the reference spectra of possible phases which include PbFe\(_{12}\)O\(_{19}\), Pb\(_2\)Fe\(_2\)O\(_5\), lead oxides and iron oxides. Diffractograms of samples up to x = 0.3 were free from pyrochlore or impurity phases. Rapid reduction of the (001) – (100) tetragonal splitting can be observed up to x = 1 sample, where splitting is no longer visible. Diffraction patterns in the composition x = 0.1 and higher show increasing peak broadening and asymmetry. Samples with Fe concentrations x \(\geq\) 0.4 show minor reflections from the ferromagnetic magnetoplumbite phase, PbFe\(_{12}\)O\(_{19}\), which grows in intensity with increasing Fe concentration. A study on Pb[Zr\(_{0.6}\)Ti\(_{0.4}\)]O\(_3\) ceramics doped with Fe\(^{3+}\) ions reported PbFe\(_{12}\)O\(_{19}\) phase formation when doped beyond solubility limit (3 mole\%).\(^{[20]}\) Formation of PbFe\(_{12}\)O\(_{19}\) could be responsible for the room temperature ferromagnetism reported in 4 mole\% Fe-doped PbTiO\(_3\) nanocrystals.\(^{[50]}\) The diffraction pattern of the end phase x = 1 sample shows reflections from Pb\(_2\)Fe\(_2\)O\(_5\), PbFe\(_{12}\)O\(_{19}\), and PbO which confirms phase segregation at higher Fe-dopant concentrations.

4.2 Solubility Limit of Iron in Lead Titanate

Substitution of lead titanate B-sites beyond solubility limit may promote the formation of impurity phases. The solubility limit can be dependent on the preparation technique. Sol-gel based techniques typically report solubility limits superior to solid state sintering methods. In order to extract the iron solubility limit in the lead
titanate host ceramic and other structural parameters, sample diffraction patterns were evaluated using Reitveld refinement technique. [74] Diffractograms of samples up to \( x = 0.3 \) (\( x = 0, 0.005, 0.01, 0.025, 0.05, 0.075, 0.1, 0.125, 0.15, 0.175, 0.2, \) and 0.3) were evaluated using the program EXPGUI, [75] a graphical user interface to General Structure Analysis System (GSAS) and profile function 4. This profile function is equipped to better fit asymmetric profiles caused by variations in the sample height, detector height, and diffractometer diameter. It also takes into account instrumental broadening, Lorentzian crystallite size broadening, anisotropic crystallite size broadening, sample displacement, broadening due to stacking faults, sample transparency effects, pseudo-Voight mixing ratio, and anisotropic broadening as defined by the fitting model. \( \text{PbTiO}_3 \) \( P4mm \) (space group 99) was used as the starting model. Owing to similar x-ray scattering cross sections partial occupancies of iron and titanium were difficult to refine, and consequently set to nominal composition values. Attempts to refine site occupancies of lead or oxygen resulted in non-physical results or diverging fits, and were assumed to be unity. All structural parameters were refined. The atomic position z-coordinates were also refined. Lead atom coordinates were fixed at \((0 \ 0 \ 0)\) to define the origin. Isotropic displacement coefficients \((U_{iso})\) for all atoms were refined up to \( x = 0.2 \). In order to increase the stability, \( U_{iso} \) parameters of \( x = 0.3 \) sample were set to those of the \( x = 0.2 \) sample except \( \text{Pb}-U_{iso} \) which was refined in the fit. GSAS profile parameters such as sample displacement (shft) and all anisotropic strain broadening terms \((S_{hkl})\) were refined. The pseudo-Voight mixing ratio \((\eta)\) was refined except at \( x = 0.3 \), where line shape was set to purely Lorentzian \((\eta=1)\). The reflection \((hkl)\) dependent line shape broadening due to anisotropic strain in the tetragonal symmetry was modeled with four \( S_{hkl} \) parameters. A high level of correlation between crystallite size (Scherrer) broadening \((LX)\), \( S_{hkl} \), and \( \eta \) had a negative effect on the fit qualities and parameter accuracies at \( x = 0.05 \) and higher. Consequently, the \( LX \) values of samples \( x = 0.075 \) and beyond were
held constant at the value extracted from the $x = 0.05$ refinement. The background of the datasets was fitted using a 6-term shifted Chebyshev polynomial function.

Reitveld refinements yielded goodness-of-fit ($\chi^2$) values between 2.05 and 3.45. The profile residual ($R_p$) and the weighted profile residual ($R_{wp}$) values were in the ranges of $3.77 - 4.96$ % and $4.79 - 6.51$ %, respectively. Fits of samples with iron composition, $x \geq 0.0075$, showed significant correlation between parameters LX, $\eta$, and $S_{hkl}$. It was necessary to constrain LX parameter to improve the reliability of the fit results. The basis for implementing constraints is as follows.

The lineshapes of diffraction peaks changed from having more Gaussian character towards having more Lorentzian contribution with increasing Fe concentration. Consequently, $\eta$ was allowed to refine. Peak broadening and asymmetry could have contributions from many different origins. Three main contributions to the lineshape are considered to be instrumental broadening, crystalline size broadening, and strain broadening. Strain is a measure of lattice stress existing in the material as a result of crystal imperfections. [77] Low Fe-doped samples show tetragonal distortion at room temperature. Since these samples were sintered at 700 °C and cooled to room temperature through a cubic to tetragonal phase transition, the amount of residual stress is expected to be significant. Additionally, strain contributions that stem from oxygen vacancies, other forms of point defects, line defects, and place defects may also result in lineshape broadening. [78] Several models were tested in order to best fit datasets while refining a minimum number of parameters. The superior quality of microstrain-containing refinements over other fits provided strong evidence for the existence of strain induced lineshape broadening. The crystalline size distribution of these samples strongly depends on the sintering temperature and the soak time and is presumably less sensitive to small variations in iron composition. It was clear that constraining LX was more feasible than constraining $\eta$ or $S_{hkl}$. Therefore, LX
was held constant at the value extracted from the $x = 0.05$ fit for all the higher Fe concentration samples. Final fit residuals, $\chi^2$, and $\eta$ values at different compositions are listed in Table 1. Figures 4.4 and 4.5 show the Rietveld refinements of $x = 0$ and 0.1 samples.

Table 4.1. Values of the fit parameters and pseudo-Voight mixing ratios at different Fe concentrations.

<table>
<thead>
<tr>
<th>$x$</th>
<th>$\chi^2$</th>
<th>$R_p$ (%)</th>
<th>$R_{wp}$ (%)</th>
<th>$\eta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.05</td>
<td>4.20</td>
<td>5.38</td>
<td>0.62</td>
</tr>
<tr>
<td>0.005</td>
<td>2.64</td>
<td>4.46</td>
<td>5.72</td>
<td>0.64</td>
</tr>
<tr>
<td>0.01</td>
<td>2.85</td>
<td>4.70</td>
<td>6.07</td>
<td>0.66</td>
</tr>
<tr>
<td>0.025</td>
<td>3.37</td>
<td>4.89</td>
<td>6.42</td>
<td>0.57</td>
</tr>
<tr>
<td>0.05</td>
<td>3.45</td>
<td>4.96</td>
<td>6.51</td>
<td>0.52</td>
</tr>
<tr>
<td>0.075</td>
<td>2.70</td>
<td>4.70</td>
<td>5.90</td>
<td>0.65</td>
</tr>
<tr>
<td>0.1</td>
<td>2.52</td>
<td>4.41</td>
<td>5.50</td>
<td>0.71</td>
</tr>
<tr>
<td>0.125</td>
<td>2.26</td>
<td>4.26</td>
<td>5.34</td>
<td>0.71</td>
</tr>
<tr>
<td>0.15</td>
<td>2.42</td>
<td>4.22</td>
<td>5.29</td>
<td>0.68</td>
</tr>
<tr>
<td>0.175</td>
<td>2.42</td>
<td>4.26</td>
<td>5.38</td>
<td>0.81</td>
</tr>
<tr>
<td>0.2</td>
<td>2.09</td>
<td>3.77</td>
<td>4.79</td>
<td>0.91</td>
</tr>
<tr>
<td>0.3</td>
<td>3.04</td>
<td>4.21</td>
<td>5.50</td>
<td>1.00</td>
</tr>
</tbody>
</table>

The tetragonal distortion ($c/a$) ratio of 1.056 extracted from the PbTiO$_3$ sample is lower than the value 1.066 reported in the literature. [25] The linear variation observed in both $a$ and $c$ lattice parameters, following Vegard’s law [79], is a strong indication that B-site doping is homogenous. Elemental analysis, discussed in section 3.2 also agrees with this result. The sol-gel preparation technique is known to produce samples with high purity and homogeneously distributed dopants at significantly lower processing temperatures compared to traditional solid state sintering. Consequently, the solubility limit of iron in the lead titanate matrix is improved.

Figure 4.6 illustrates the variation of lattice parameters versus iron concen-
Figure 4.4. Diffraction pattern of the PbTiO$_3$ (red markers) and the fit (green curve). Diffraction peaks are indexed with P4mm tetragonal crystal structure (black markers). Fit residual is indicated by the purple curve.
Figure 4.5. Diffraction pattern of the Pb(Fe$_{0.1}$Ti$_{0.9}$)O$_{3-\delta}$ (red markers) and the fit (green curve). Diffraction peaks are indexed with P4mm tetragonal crystal structure (black markers). Fit residual is represented by the purple curve.
The linear variation of these parameters ends at $x = 0.1$, which indicates the solubility limit of iron in lead titanate (using our sol-gel preparation technique) is approximately 10 mole%. Least square fits to lattice parameters are given by $a = 0.34(2)x + 3.9069(9)$ and $c = -1.44(9)x + 4.125(5)$. Figures 4.7 and 4.8 illustrate the variations in tetragonal distortion versus Fe concentration and the unit cell volume versus Fe concentration. When lead titanate is doped above its solubility limit impurity phases are formed. Nevertheless, this series of samples are free from impurity phases up to 30 mole% B-site doping. Table 4.2 lists the data used in these graphs with associated errors.

![Graph of lattice parameters a and c as a function of Fe concentration.](image)

**Figure 4.6.** Graphs of lattice parameters a and c as a function of Fe concentration. Both parameters behave as a linear function of the Fe concentration up to $x=0.1$.

### 4.3 Oxygen Vacancies by Microstrain

The tetragonally distorted lead titanate structure consists of an off-center shifted Ti$^{4+}$ ion encapsulated by an octahedron of oxygen atoms. The oxygen octahedra are elongated along the [0 0 1] direction. Due to the similar ionic radii of
Figure 4.7. Tetragonal distortion versus B-site Fe concentration.

Figure 4.8. The unit cell volume versus B-site Fe concentration.
Table 4.2. Refined lattice constants of Pb(Fe<sub>x</sub> Ti<sub>1−x</sub>)O<sub>3−δ</sub> samples.

<table>
<thead>
<tr>
<th>x</th>
<th>a</th>
<th>c</th>
<th>Volume</th>
<th>c/a</th>
<th>P(nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3.90817(8)</td>
<td>4.12688(15)</td>
<td>63.033(4)</td>
<td>1.05596(4)</td>
<td>230.0</td>
</tr>
<tr>
<td>0.005</td>
<td>3.90766(8)</td>
<td>4.12275(14)</td>
<td>62.954(4)</td>
<td>1.05504(4)</td>
<td>268.3</td>
</tr>
<tr>
<td>0.01</td>
<td>3.90956(9)</td>
<td>4.11122(16)</td>
<td>62.839(4)</td>
<td>1.05158(5)</td>
<td>215.8</td>
</tr>
<tr>
<td>0.025</td>
<td>3.91610(13)</td>
<td>4.07929(22)</td>
<td>62.559(6)</td>
<td>1.04167(6)</td>
<td>123.9</td>
</tr>
<tr>
<td>0.05</td>
<td>3.92151(14)</td>
<td>4.06004(23)</td>
<td>62.436(6)</td>
<td>1.03533(7)</td>
<td>120.8</td>
</tr>
<tr>
<td>0.075</td>
<td>3.93420(22)</td>
<td>4.00519(38)</td>
<td>61.992(10)</td>
<td>1.01805(11)</td>
<td>120.8*</td>
</tr>
<tr>
<td>0.1</td>
<td>3.93984(23)</td>
<td>3.98908(44)</td>
<td>61.920(9)</td>
<td>1.01250(13)</td>
<td>120.8*</td>
</tr>
<tr>
<td>0.125</td>
<td>3.94260(24)</td>
<td>3.98828(45)</td>
<td>61.994(8)</td>
<td>1.01159(13)</td>
<td>120.8*</td>
</tr>
<tr>
<td>0.15</td>
<td>3.94215(21)</td>
<td>3.99234(39)</td>
<td>62.043(8)</td>
<td>1.01273(11)</td>
<td>120.8*</td>
</tr>
<tr>
<td>0.175</td>
<td>3.94676(29)</td>
<td>3.97449(54)</td>
<td>61.910(8)</td>
<td>1.00703(16)</td>
<td>120.8*</td>
</tr>
<tr>
<td>0.2</td>
<td>3.94817(28)</td>
<td>3.96826(53)</td>
<td>61.857(7)</td>
<td>1.00509(15)</td>
<td>120.8*</td>
</tr>
<tr>
<td>0.3</td>
<td>3.94827(36)</td>
<td>3.96182(57)</td>
<td>61.760(10)</td>
<td>1.00343(17)</td>
<td>120.8*</td>
</tr>
</tbody>
</table>

* Held constant during refinement.

Ti<sup>4+</sup> and Fe<sup>3+</sup> ions, doped Fe<sup>3+</sup> ions are preferentially substituted at the B-site. However, at high Fe concentrations, greater than the solubility limit, the probability to substitute at the A-site increases. The phase Pb<sub>2</sub>Fe<sub>2</sub>O<sub>5</sub> has its A-equivalent sites partially substituted by Fe ions. [80]

Substitution of Ti<sup>4+</sup> by Fe<sup>3+</sup> gives rise to new charge compensation requirements which necessitates formation of oxygen vacancies. The site at which oxygen vacancies forms depends on the energy minimization. Density Functional Theory (DFT) calculations have been performed by Meštrić et. al. [49] on Fe doping and oxygen vacancy formation in lead titanate host material. Calculations performed on 2×2×2 PbTiO<sub>3</sub> unit cells have shown that formation of oxygen vacancies along the c direction are energetically more favorable than in other directions. The effect of spin polarization on energy was found to be insignificant. Two oxygen atoms in the c direction have dissimilar bond length with the B-site cation (Ti<sup>4+</sup>). Formation of an
oxygen vacancy at the c-direction oxygen site furthest from the B-cation was favored compared to the closer sites. When an oxygen vacancy is created, the cations nearest to the vacant site move away from the vacancy, resulting in a shorter metal oxygen bond distance. With homogeneously distributed dopants, composition \( x = 0.125 \) corresponds to one \( \text{Fe}^{3+} \) ion substitution at B-site and nominally one half oxygen created in each \( 2 \times 2 \times 2 \) super cell. The oxygen vacancy may distress the structure of the entire super cell, resulting in shorter bond lengths which preferentially lowers the c lattice parameter and the tetragonal distortion.

To explain the modification of the lead titanate B-sites by \( \text{Fe}^{3+} \) we utilize the symbolism by Kröger and Vink. This substitution is known to create \((\text{Fe}^{'}_{T_i} - V_{o}^{**})^\bullet\) defect dipoles with partially charge compensating oxygen vacancies. In this notation \( \text{Fe}^{'}_{T_i} \) represents the negative charge created by replacing \( \text{Ti}^{4+} \) ion with \( \text{Fe}^{3+} \) in an otherwise neutral crystal structure. Similarly \( V_{o}^{**} \) represents the doubly positive charge resulting from \( \text{O}^{2-} \) vacancy. Ideally, one oxygen vacancy site should be capable of neutralizing two \( \text{Fe}^{'}_{T_i} \) charges in the crystal lattice. \((\text{Fe}^{'}_{T_i} - V_{o}^{**})^\bullet\) defect dipoles are energetically favored to form along the polarization direction of the crystal [0 0 1]. \((\text{Fe}^{'}_{T_i} - V_{o}^{**})^\bullet\) defect dipoles can be incorporated into the refinement in terms of oxygen occupation numbers based on partial fractions of \( \text{Fe}^{3+} \) ions. This change only improved the fit quality by a negligible amount. Consequently, oxygen site occupancies were held constant at unity.

We have found that both size-type and anisotropic microstrain-type peak broadenings are present in diffraction patterns. The instrument broadening effect has been parametrized using NIST SRM 660a LaB\(_6\) standard. Anisotropic microstrain was observed to be a dominant contributor to the line broadening, especially at high Fe concentrations. The evolution of the size of coherently diffracting domains was refined up to the \( x = 0.3 \) sample. The size of coherently diffracting domains
(assumed to be spherical) was evaluated using the Scherrer formula

\[ P(nm) = \frac{1800K\lambda}{\pi(LX - X_{\text{inst}})} \] (4.1)

where \( K = 0.9 \) is the Scherrer constant, \( \lambda \) is the x-ray wave length, \( X_{\text{inst}} \) is the instrumental broadening, and \( LX \) is the refined Lorentzian coefficient for size type broadening. \[83\] Particle sizes calculated using this formula are listed in Table \[4.2\].

The anisotropic strain broadening has been modeled using the description of Stephens. \[83\] Microstrain-type broadening in this model is considered a manifestation of the distribution of reciprocal lattice parameters. This distribution can originate from crystalline defects such as oxygen vacancies or local inhomogeneities in the chemical composition. The microstrain along the direction \([hkl]\) has been calculated according to the formula \[83\]

\[ \frac{\delta d_{hkl}}{d_{hkl}} = \frac{\pi(\sigma(M_{hkl}))^\frac{1}{2}}{18000M_{hkl}} \] (4.2)

where \( M_{hkl} = 1/d_{hkl}^2 \) and \( \sigma^2(M_{hkl}) \) is the variance of \( M_{hkl} \). Complete description of the model can be found elsewhere. \[83\] In tetragonal symmetry, the strain broadening contribution to the width of the diffraction peak \((hkl)\) is parametrized by \[75, 83\]

\[ \sigma^2(M_{hkl}) = S_{400}(h^4 + k^4) + S_{004}l^4 + 3S_{220}(h^2k^2) + 3S_{202}(h^2l^2 + k^2l^2) \] (4.3)

GSAS profile function 4 has been utilized to refine \( S_{hkl} \) coefficients, \( S_{400}, S_{004}, S_{220}, S_{202} \). The values of \( S_{400} \) and \( S_{202} \) are significantly different from the others, which suggests crystallite strain is indeed anisotropic. The \( S_{202} \) parameter values are negative, thus variation of \( a \) and \( c \) lattice parameters have a negative correlation.

Anisotropic strain contains useful information about “soft” crystal direction with respect to composition changes. Formation of \((\text{Fe}^{+}_T - V_{\text{o}^{\bullet\bullet}})^*\) defect dipoles upon iron doping could build up extra forces that elevate the level of strain. In addition, structural defects such as dislocations or stacking faults could contribute to the strain
anisotropy. Figure 4.9 illustrates the variation of lattice strain along different crystal directions calculated according to

\[ S_{hkl} = \frac{\pi d^2}{180} \sqrt{\sum_{hkl} \sigma^2(M_{hkl})} \% \]  (4.4)

where \( S_{hkl} \) is the percentage strain along the [hkl] direction. The magnitude of the strain increases with iron concentration which suggests a direct relationship between the two parameters. Since the number of oxygen vacancies formed mainly depends on the Fe concentration, strain can be linked to the preferred direction of vacancy formation. The approximately linear trend between strain in the [110] direction and the Fe concentration is consistent with the theoretical prediction that oxygen vacancies displace cations (inducing strain) away from the vacancy site. Since \((\text{Fe}_T - \text{V}_{o}^\bullet)\bullet\) defect dipole is singly positive, simple electrostatic stability conditions require the
closest oxygen ions to move towards each other, causing strain. Other mechanisms such as an electron \((e')\) trapped in the vacancy site could potentially satisfy the charge compensation requirements with different potential strain. Oxygen vacancy centered oxygen-oxygen and B-site cation-cation displacements induce strain within the crystal planes. Deviation from the linear trend observed around the solubility limit may originate from other forms of structural defects such as dislocations and stacking faults contributing to the microstrain. In addition, dissimilar ionic radii, \(\text{Fe}^{3+}\) being 0.025 Å smaller than \(\text{Ti}^{4+}\), could play a role in increasing microstrain proportional to the Fe concentration. Similar anomalous behavior of microstrain is observed in [100], [001], and [111] directions as shown in Figure 4.9. Strain in the [111] direction is small compared to other directions. The (111) reflections are unaffected by the tetragonal distortion, possibly resulting a low level of strain in the [111] direction. The oxygen vacancies are energetically favorable to form in the [001] direction at the oxygen site furthest from the B-site cation. Therefore, the significantly large microstrain values in the [001] direction as compared to the [100] direction may result from the oxygen defect-induced forces. In conclusion, the solubility limit of Fe in lead titanate was found to be 10 mole%. The crystal structure remains tetragonally distorted even at \(x = 0.3\), suggesting the existence of spontaneous polarization. The relationship between microstrain and Fe concentration extracted using XRD also suggest formation of oxygen vacancies in the c direction, in agreement with the theoretical predication by Meštric et. al. on the formation of \((\text{Fe}^{3+} - \text{V}_o^\bullet\bullet)\) defect dipoles. [49]

### 4.4 Structural Changes and Ferroelectric Properties

Oxygen ions in the c direction and the B-site cation share similar a, b coordinates. The oxygen vacancies arising from iron substitutions are formed at the site furthest from the B-site, which further reduces the bond length of the short bond length oxygen ion. [49] Figure 4.10 illustrates the changes in the short bond length
between B-site cation and c direction oxygen ions versus Fe concentration. The overall trend, where short bond length further decreases with increasing Fe concentration agrees with the theoretical predications. In PbTiO$_3$, four oxygen atoms in the a and b faces have z coordinates slightly offset from the Ti$^{4+}$ ion. Fe substitution forces the B-site cation to a more centro-symmetric position in the oxygen octahedra. Consequently, the four oxygens on the a, b faces move closer to the z-plane of the B-cation. Figure 4.11 shows the z coordinate difference between these oxygens and the B-site cation as a function of Fe concentration. The difference decreases with increasing x, apart from the anomaly at the x = 0.3 composition. This qualitative trend subjected to error bars indicates the tendency towards having a center of symmetry increase with Fe concentration. Nevertheless, at compositions x ≤ 0.3 the B-site cation remains shifted off-center. The distance to c direction oxygens from the B-site remains significantly different. Therefore, samples with Fe concentrations as high as x = 0.3 may still possess displacive type ferroelectric properties. Ferroelectric properties measurements and related complexities will be discussed in Chapters 5.
Figure 4.11. The average z-coordinate offset between B and O2 versus Fe concentration.

The anomaly at x = 0.3 is suggestive of the incipient failure of the tetragonal model. A large number of oxygen vacancies could force oxygen octahedra to shift from corner-sharing to edge-sharing or even face-sharing configurations, where a tetragonal model would no longer apply. Phase segregation could break the long range order in crystalline materials. High Fe concentration samples may consist of Fe-rich and Ti-rich segregated phases, which could produce a sample without true long range order. Unlike XRD, X-ray Absorption Spectroscopy (XAS) does not require long-range order and is capable of probing the average local structure about different atomic species. XRD is not sensitive to atom identities of Fe and Ti due to similar scattering cross sections. The long range sensitivity of XRD limits its ability to determine true structural changes. The average structure determined by XRD is common to both Ti and Fe atoms may not be true for either of the elements. Since spontaneous polarization tends to depend on the long range order, ferroelectric properties predicted by XRD results based on the existence of tetragonal distortion, are not conclusive. The collapse of the host matrix due to an excessive number of oxygen vacancies or tilting
of oxygen polyhedra resulting short B–B cation distances are difficult to accurately determine using XRD. However, employing XAS is particularly useful in determining the average structure about Pb, Fe, and Ti atoms at all Fe concentrations. A detailed discussion on the XAS technique and the results can be found in Chapter 7.

The isotropic displacement coefficients ($U_{iso}$) were constrained such that all oxygens have the same value. Similarly Ti and Fe ion $U_{iso}$ parameters were constrained and refined in the fit. The behavior of $U_{iso}$ parameters were tested against different particle size broadening models and the trends were verified to be similar. Figure 4.12 shows the refined $U_{iso}$ parameters versus Fe concentration. $U_{iso}$ parameters of lead systematically increase with Fe concentration. This trend may have dominant non-thermal contributions from elevated disorder or lead loss. Elemental analysis of Pb concentration indicates a general trend (with a few exceptions at lower Fe concentration) that Pb loss increases with up to $x = 0.3$ Fe concentration (See
Figure 3.5. The B-site $U_{iso}$ parameter increases at lower concentrations ($x < 0.05$) and decreases at higher concentrations. Any increase in $U_{iso}$ of B-site cations or oxygen anions may have significant partial contributions from disorder. At higher Fe concentrations B-site ions are more tightly bound to oxygen anions as evidenced by the decreasing B-O bond length. Reduction in the unit cell volume and more tightly bound atoms may result in lower $U_{iso}$ values. Furthermore, the oxygen octahedron encapsulating the B-site cation is clearly asymmetric, thus treating thermal factors as isotropic is likely to be an invalid approximation, particularly at higher Fe-concentrations. In addition, the number of oxygen vacancies (increasing with the Fe concentration) was ignored in the refinement, and may contribute to the anomalous behavior (beyond the solubility limit) of the oxygen $U_{iso}$ parameter.

The solubility limit of iron in the lead titanate host matrix using our sol-gel synthesis technique was found to be 10 mole%. Substitutions beyond the solubility limit are known to produce impurity phases. However, XRD patterns of our sample series is free from impurity phases up to $x = 0.3$. A rapid reduction of the tetragonal distortion with the Fe concentration has been observed up to $x = 0.1$. Samples up to $x = 0.3$ show tetragonal distortion, indicating possible existence of ferroelectric properties. However, XRD is a long range probe and incapable of identifying Fe and Ti atoms separately. Long range order is essential for ferroelectric properties in lead titanate, which can be broken easily by incorporating iron centers. Consequently, XRD results alone do not provide conclusive evidence on the existence of ferroelectricity.
5.1 Sample Pellet Preparation

Preparation of sample pellets with parallel sides was necessary for the dielectric and ferroelectric measurements. Producing pellets requires prior determination of the melting point of the sample materials. Iron doping at the B-site is expected to reduce the melting point of lead titanate. Impurity phase formation above $x = 0.4$ and wide distribution of particle sizes may adversely affect the determination of the sample melting point. [84]

Preparation of dense pellets required for dielectric measurements typically involve sample pellet pressing followed by sintering at temperatures preferably below the melting point. A solid solution sample heated above its melting point may show phase segregation. [85] If the phase diagram has a region where liquid and solid phases can coexist, the sample inevitably passes through this region upon cooling. Ti-rich compositions of the $\text{Pb(Fe}_x\text{Ti}_{1-x})\text{O}_{3-\delta}$ series samples are expected to have higher melting temperatures than Fe-rich compositions. Therefore, nucleation of Ti-rich phases may create a solid-liquid state where the liquid phase is different from the solid phase. Limited ionic diffusion rates within the solid phase further promote phase segregation. Properties of a phase segregated pellet sample could have different properties from the initial powder sample. If the phases are connected via a medium such as lattice stress, there is a possibility of having both ferromagnetic and ferroelectric properties with coupled order parameters.

A series of $\text{Pb(Fe}_x\text{Ti}_{1-x})\text{O}_{3-\delta}$ sample pellets were prepared by sintering at 1000 °C for 2 hours. Both firing temperature and time duration were similar to pellet preparation conditions used in Palkar’s study. [48] Sample powders of approximately 550 to 750 mg were mixed with a few drops of binder (5 wt% polyvinyl alcohol) using
an agate mortar and a pestle. The resultant mix with the consistency of molding clay was cold pressed inside a 13 mm die (Specac). A load of 8 tons was applied using a hydraulic press to which formed a lamination free pellet.

Cold pressed pellets were first fired at 550 °C for 5 hours, a temperature, and time sufficient for complete decomposition of the organic binder. The firing profile of the pellets is shown in Figure 5.1. Since the melting point is dependent on the composition x, pellets prepared at a constant sintering temperature of 1000 °C may have different densities. Consequently, it would be difficult to perform a comparison of dielectric measurement throughout the sample series. Nevertheless, measurements can reveal information on dielectric, loss properties, and ferroelectric properties, which is sufficient for fingerprinting magnetoelectric behavior.

![Figure 5.1](image_url)

Figure 5.1. The temperature profile used in Pb(Fe\textsubscript{x}Ti\textsubscript{1−x})O\textsubscript{3−δ} pellet processing. Samples were free cooled down to room temperature. Some samples were sintered at 850 °C using the same ramp soak conditions.

Sintering was performed at 1000 °C using a muffle furnace. The sample pellet
was placed inside an alumina crucible and covered with an alumina lid. This crucible was then placed inside a larger alumina crucible containing PbO powder, which was covered with another alumina lid to provide additional PbO vapor pressure. The lead oxide volatilization during sintering can be countered by providing additional lead oxide vapor pressure. Volatilization of lead oxide increases at temperatures above 800 °C. Lead loss causes a change in stoichiometric composition of lead titanate based ceramics which may also change their properties. However, sintering for two hours may not cause a heavy lead loss. Lead titanate and low Fe concentration Pb(FeₓTi₁₋ₓ)O₃₋δ samples (x ≤ 0.05) show significant tetragonal distortion below ferroelectric transition temperature. Pellets of these samples are hard to make in fully dense form due to lead volatilization and brittleness caused by residual stress buildup in pellets when cooled below the ferroelectric phase transition temperature. High Fe concentration pellets deformed and shrunk in diameter. Significant porosity was observed in low Fe-concentration samples. Consequently, no attempt has been made to calculate the density of these pellets through physical dimension measurements.

Differential thermogravimetric (TG) measurements were performed to evaluate weight loss due to possible lead volatilization. The Mettler Toledo TGA/SDTA851e instrument is capable of simultaneously measuring differential thermal analysis (DTA) curves which is useful in monitoring phase transitions and melting points. This instrument is only equipped with a single sample holder thus the reference standard temperature is calculated rather than directly measured. Consequently, the instrument was first calibrated with the aid of high purity metal standards, namely indium, lead, aluminum, and gold. The melting point range of the metal standards was sufficient to calibrate the instrument at different temperature ramp rates under nitrogen atmosphere within the temperature range 100 °C to 1100 °C. Instrument calibration was verified to be accurate using calcium oxalate monohydrate (CaC₂O₄·H₂O) thermal decomposition TG/DTA curves. Proper densification of
the samples depends on correct stoichiometric composition and sintering temperature. The B-site doping of lead titanate may result in lower melting points that depend on the dopant concentration. Consequently, samples with an iron concentration higher than the solubility limit may have much lower melting points compared to lead titanate. Figure 5.2 depicts the DTA curves of Pb(Fe$_x$Ti$_{1-x}$)O$_{3-\delta}$ samples at x = 0.2, 0.4 and 0.6 compositions. Sample powders weighing 100 - 200 mg were packed inside an alumina crucible and placed on the measuring arm of the instrument. All measurements were performed in nitrogen atmosphere at a temperature ramp rate of 10 °C/min. The melting temperature of pure lead titanate is 1250 °C, so the melting point of the x = 0.2 sample might be outside the maximum temperature (1100 °C) of the instrument. Observation of samples after TGA measurements revealed that partial melting had occurred. Both samples x = 0.4 and 0.6 powders showed good melting behavior. However, DTA curves of these samples do not show
sharp endothermic peaks typically associated with the melting point. The broad endothermic features situated between 900 to 1100 °C provide an approximate range for the melting point. Therefore, sintering of \( x \geq 0.4 \) sample pellets at 1000 °C may result in phase segregation as discussed above. Nevertheless, phase segregated samples may still display coupled magnetoelectric properties available in separate yet connected phases. There is additional evidence provided by Palkar [48] that \( x = 0.5 \) sample sintered at 1000 °C is magnetoelectric.

The ferroelectric phase transition temperature of pure lead titanate occurs at 490 °C. [92] Our lead titanate sample under TGA shows a small endothermic peak (not shown) with an onset approximately at 475 °C. The phase transition temperature depends on the particle size. Crystals that are a few nano meters in size are already in the cubic phase at room temperature. The broad particle distribution of our lead titanate sample and low temperature resolution at 10 °C/min temperature ramp rate may have contributed to the discrepancy in the ferroelectric transition temperature. Lead titanate powders are less dense compared to sintered dense pellets. Therefore, a 15 °C difference in ferroelectric phase transition temperature is not significant. The DTA spectra of other samples such as \( x = 0.1 \) and 0.2 were free of sharp endothermic peaks related to ferroelectric transition between 50 to 600 °C. Figure 5.2 shows DTA curves of \( x = 0.2, 0.4 \) and 0.6 composition samples, with no endothermic peaks between 300 to 500 °C. Low temperature resolution, high sensitivity DTA measurements at 20 °C/min provided similar results. The absence of phase transition endothermic peaks might be the result of multiple factors such as, a broad particle size distribution which diffuses the peak or low instrument sensitivity due to small sample quantity used (100–200 mg limited by the instrument). Doping ferroelectric materials has been known to produce relaxors (relaxor ferroelectrics) with a diffuse phase transition. One of the distinctive features of relaxors is the ferroelectric phase transition occurring in a wide temperature range.
The weight loss behavior was studied using TGA curves. Figure 5.3 illustrates the sample weight loss at 10 °C/min heating rate. Weight loss appears to start between 800–900 °C. However, the total loss may not be significant for a sintering time duration of 2 hours. The overall weight loss behavior appears to be dependent on Fe concentration, possibly due to lowering of the melting temperature. Changes in the stoichiometric composition as a result of lead loss are more conducive for lead deficient phase formation. One such phase is PbFe_{12}O_{19} which has good ferromagnetic properties. Providing additional Pb partial pressure using PbO may hinder the formation of Pb deficient phases and result the formation of dense pellets. Consequently, a series of pellets was prepared according to the procedure discussed above sintering at 1000 °C with the temperature profile depicted in Figure 5.1.
pellets were also prepared at sintering temperatures of 850 °C (below the approximate melting temperature of 930 °C) and 750 °C for comparison with Palker’s sample made at 1000 °C.

Diffraction patterns of the sample pellets sintered at 1000 °C were collected using the Bruker D2 Phaser instrument. Additional detail on the diffraction measurements are given in section 4.1. The peak positions of the powder diffraction patterns in reflection geometry are sensitive to height changes in the sample position. Sample pellets of different thicknesses may result in sample height changes which could make the diffraction spectra difficult to compare. Typical powder samples cover a circular area of approximately 25 mm in diameter. Our sample pellets were approximately 13 mm thus x-ray over spill may contribute to complex background shapes or additional diffraction peaks. Consequently, negative effects were minimized by mounting sample pellets on a 25 mm diameter Si zero background substrate. Sample pellets were secured on the substrate using a small piece of double sided tape (Scotch® brand). The zero background substrate was then mounted inside a Poly methyl methacrylate (PMMA) sample holder with a cylindrical hole, with the aid of 3 small pieces of modeling clay. The sample pellet surface was leveled with the PMMA sample holder by gently applying pressure using a flat glass slide.

Collected pellet diffraction patterns were compared with the powder patterns of similar composition. Sample pellets were first prepared by sintering at 1000 °C using sample powders with Fe concentration x ≤ 0.6. Diffraction patterns of powder samples up to 30 mole% B-site doping were free from impurity phases. Powders with higher Fe concentrations contained a small amount of PbFe$_{12}$O$_{19}$ phase. The diffraction pattern of the lead titanate pellet was similar to the powder diffraction pattern. The tetragonal distortion of the lead titanate pellet was slightly larger than that of the powder. This might be the result of small particles combining
and transforming into larger particles with larger tetragonal distortion. The lead titanate pellet was not fully dense and contained small voids which were visible under an optical microscope. This result is not surprising since densification of pure lead titanate is known to be difficult due to high melting temperature, lead loss at high temperatures, and brittleness resulting from the cubic to tetragonal phase transition when cooled below the Curie temperature. Compared to the powder sample, the peak shape broadening of the pellet diffractogram was large, possibly due to higher levels of residual stress build up during the ferroelectric phase transition. Other pellets at low composition such as $x = 0.05$ showed similar behavior.

The diffraction pattern of the powder sample at the solubility limit, $x = 0.1$, showed no peak splitting at lower angles. Figure 5.4 shows diffraction patterns of the pellet and powder sample at the solubility limit. Vertical dashed lines mark significant peak feature changes in the diffraction patterns. The diffraction pattern
of the pellet sample shows tetragonal distortion in the first peak ((001) – (100)). Phase segregation can be ruled out due to small Fe concentration at the solubility limit, and the absence of Fe-rich type impurity phases. Consequently, a higher level of densification achieved by high temperature sintering may be responsible for the observed peak splitting. The diffraction pattern of \(x = 0.2\) pellet (see Figure 5.5) shows a similar trend. The absence of impurity phases suggests that the melting point of the \(x = 0.2\) sample is sufficiently greater than the sintering temperature of 1000 °C.

The powder sample where 30 mole% of the Ti B-site were substituted with Fe ions is free from impurity phases. Figure 5.6 shows diffraction patterns of \(x = 0.3\) powder and pellet samples. Surprisingly, the \(x = 0.3\) pellet sample sintered at 1000 °C is also free from additional diffraction peaks due to impurity phases. The absence of a lead deficient phase suggests that the additional vapor pressure provided by lead oxide

Figure 5.5. Diffraction patterns of \(\text{Pb(Fe}_{0.2}\text{Ti}_{0.8})\text{O}_{3-\delta}\) powder and pellet samples.
inside the outer alumina crucible is effectively minimizing the expected lead loss behavior at high temperatures. Moreover, the absence of impurity phases demonstrates the ability of the lead titanate host to accommodate Fe ions at its B-sites well above the solubility limit. However, the significant broadening and amplitude reduction of the peaks may be indicative of possible phase segregation behavior. The ability of the lead titanate host material to maintain lattice integrity with charge compensating oxygen vacancies is limited. Extra Fe doping beyond this limit would create additional oxygen vacancies that may induce structural transformations such as tilting or rotating oxygen polyhedra. The Fe-centered oxygen cage may transform from corner-sharing to edge or face sharing configurations depending on the Fe concentration. Phase segregation can create an array of Fe-rich phases. All pellets made from $x = 0.4$ to $0.7$ composition powders at $1000 \, ^\circ\text{C}$ sintering show additional peaks resulting from Fe-rich and Ti-rich phases. Figure 5.7 shows an example. The intensities of
diffraction peaks vary, showing no correlation with the Fe concentration, possibly due
to different melting points. All pellets show reflections from PbFe$_{12}$O$_{19}$ magnetopo-
plumbite phase ($P6_3/mmc$) with edge-sharing and face-sharing octahedra. Line-
shape broadening prevented quantitative analysis on sintered pellets. Peak matching
performed using the PDF-2 database revealed additional plausible phases, Pb$_2$Fe$_2$O$_5$,
PbFe$_2$O$_4$, Pb$_2$Fe$_{16}$O$_{17}$, and PbFe$_6$O$_{10}$, which are consistent with phase segregation.

Figure 5.7 shows the diffraction patterns of PbTiO$_3$ powder, Pb(Fe$_{0.5}$Ti$_{0.5}$)O$_{3-\delta}$
powder and pellet samples. Black circles indicate the distinct reflections from the
magnetoplumbite, PbFe$_{12}$O$_{19}$ phase. Vertical lines indicate peaks similar to PbTiO$_3$
reflections. Possible diffraction peak intensity modifications due to effects such as
texture and preferred orientation further complicate phase identification. Neverthe-
less, diffraction peaks of the Pb(Fe$_{0.5}$Ti$_{0.5}$)O$_{3-\delta}$ pellet sample clearly indicate the
presence of Ti-rich PbTiO$_3$ and Fe-rich PbFe$_{12}$O$_{19}$ phases, consistent with phase segregation discussed in section 5.1. Therefore, the Fe concentration limit, below which the lead titanate host is able to retain it’s structural integrity is less than 40 mole%. However, with the aid of additional charge compensation methods such as La$^{3+}$ ion substitutions at A-sites, lead titanate host structure might be stable at higher Fe concentrations.

The effect of sintering temperature on densification and phase segregation was studied by preparing Pb(Fe$_{0.5}$Ti$_{0.5}$)O$_3$ pellets at 750 °C and 850 °C. The level of densification achieved after 2 hours soak time at 750 °C was not sufficient to hold the pellet together. The pellet sintered at 850 °C appeared to be dense, similar to the 1000 °C sintered pellet. Figure 5.8 shows the diffraction patterns of Pb(Fe$_{0.5}$Ti$_{0.5}$)O$_{3-\delta}$ powder and pellets prepared at temperatures 850 °C and 1000 °C. Both pellets show

![Diffraction patterns](image)

Figure 5.8. Diffraction patterns of Pb(Fe$_{0.5}$Ti$_{0.5}$)O$_{3-\delta}$ powder and pellet prepared at different sintering temperatures. Black circles indicate reflections from the PbFe$_{12}$O$_{19}$ phase.
phase segregation but the level of segregation is lower in 850 °C sintered sample. As suggested by the peak intensities, the amount of PbFe_{12}O_{19} (marked by black circles) appears to be small. Neither of these pellet diffraction patterns matches with Palkar’s Pb(Fe_{0.5}Ti_{0.5})O_{3-δ} pellet (sintered at 1000 °C) diffraction patterns for reasons to be discussed below.

We were unable to reproduce Palkar’s diffraction results by processing our Pb(Fe_{0.5}Ti_{0.5})O_{3-δ} samples pellets under similar processing conditions. However, the diffraction pattern of the pellet processed at lower sintering temperature has better resemblance with Palkar’s pattern. Lowering process temperature and sintering time may produce sample pellets with diffraction patterns similar to Palkar’s. Loss of tetragonal splitting at x = 0.1 Fe concentration, lowering of melting point as a result of Fe doping, and peak splitting observed in pellets processed under different sintering temperatures suggest that Palkar’s sample may consist of segregated Ti-rich and Fe-rich phases.

5.2 Pellet Dielectric Measurements

The capacitance of a parallel plate capacitor in vacuum is given by the equation:

\[ C_0 = \epsilon_0 \frac{A}{d} \]  \hspace{1cm} (5.1)

where \( \epsilon_0 = 8.854 \times 10^{-12} \text{Fm}^{-1} \) is the electric permittivity of vacuum, A is the surface area of the capacitor plates, and d is the plate separation. When the space between capacitor plates is filled with a dielectric material, the capacitance is increased by a factor of the dielectric constant. Therefore, the dielectric constant of the material can be calculated as the ratio:

\[ \epsilon = \frac{C}{C_0} \]  \hspace{1cm} (5.2)

Various loss effects in the dielectric media can be modeled as a circuit containing an
ideal capacitor $C_p$ connected parallel with a resistor $R_p$, which represents loss effects of the system. Dissipation factor (Df) of a capacitor is the fraction of power lost due to heat dissipation in the dielectric material. This parameter is also known as the loss tangent represented by

$$\tan \delta = \frac{I_{\text{conduction}}}{I_{\text{displacement}}} \quad (5.3)$$

where, $I_{\text{conduction}}$ is the current through the resistor (also known as the leakage current), $I_{\text{displacement}}$ is the current through the capacitor, and $\delta$ is the loss angle. [96]

The loss tangent for a parallel capacitor resistor configuration is given by

$$\tan \delta = \frac{1}{2\pi f R_p C_p} \quad (5.4)$$

where $f$ is the frequency. [96]

Careful pellet preparation is necessary for comparing loss effects of pellets in a wide range of Fe concentrations. Pellets should be compatible with dielectric measurements as well as ferroelectric hysteresis measurements. The maximum voltage of the ferroelectric loop tracer was limited to 4 kV, which required thin pellets with thickness around 0.5 mm. Post-sintered pellets were slightly deformed. In order to meet the thickness and parallel sides requirement, the pellets were polished using an Inland lapidary lapping and polishing apparatus equipped with a 1200 grit diamond wheel. Samples were first mounted on a South Bay Technology micrometer controlled lapping fixture with a special mounting resin. The mounting resin has a melting point of about 80 °C, and is soluble in acetone. The lapping fixture was useful in making two sides of the pellet parallel, in a controlled manner in the thickness range of 0.25 to 0.4 mm. Polished pellets were first sonicated for 10 minutes using acetone followed by BUEHLER ultramet® sonic cleaning solution diluted by 1:20 with distilled water to clean and remove any metal contamination. Finally, pellets were sonicated for 15 minutes in distilled water to remove the residual cleaning solution and completely dried in a furnace at 125 °C. Copper electrodes were deposited on the pellets using a
Denton vacuum bell jar thermal evaporator system at a base pressure of $5 \times 10^{-5}$ Torr. One side of the pellet was completely covered using a copper mask, leaving a small margin around the edge. Seven electrodes of 2 mm in diameter were deposited on the other side of the pellet, leaving a 1 mm margin between the electrodes. Dielectric media extending beyond the diameter of the electrodes is helpful in minimizing possible arcing at high electric fields. Having multiple electrodes on a single pellet is useful in the event of possible dielectric breakdown during measurements. Multiple measurements performed at different electrodes can be used as a measure of the dielectric inhomogeneity in sintered pellets.

Dielectric measurements were performed using an Agilent E4980A precision LCR meter. Ferroelectric hysteresis measurements were performed using a RADIANT Technologies Precision Premier II, equipped with a 4 kV scannable power supply. The pellets were placed on the instrument apparatus and electrical contacts were made as shown in Figure 5.9.

X-ray diffraction results predict that low Fe concentration samples should have better dielectric properties. However, the level of porosity in pellets can significantly reduce the effective pellet thickness. Pellets fired at 1000 °C have become dense with the Fe concentration due to decreasing melting point. Figure 5.10 depicts the behavior of the dielectric constant versus frequency for different concentration sample pellets. Dielectric constants of $x = 0.4$ and 0.6 samples were expected to be inferior to low Fe concentration samples. These pellets were investigated using an optical microscope and showed fewer and smaller sized pores compared to low Fe concentration pellets. Therefore, the observed high dielectric constants of these pellets may be the result of better quality dense pellets. High concentration of pores in a ceramic material typically results in high dielectric losses. Lead zirconate titanate materials with high level of porosity reported higher dissipation factors. [97] The dissipation factor of our
pellets shows an increase with the Fe concentration as shown in Figure 5.11. Since the pellets become denser with increasing Fe concentration, the amount of pores should also decrease, lowering the dissipation factor. Opposite behavior is observed in our sample pellets. Therefore, the dominant contribution to high dissipation factors can be attributed to conductivity that increases with the Fe dopant concentration. Phase segregation at high Fe concentrations and possible ordering of oxygen vacancies may modify the electronic properties of the material, which is different from its powder form. A detailed investigation of such parameters is outside of the scope of this study.

Bias voltage-dependent dielectric property measurement is useful for studying dissipation behavior and widely used to fingerprint ferroelectric materials. All voltage sweeps were carried out at a frequency of 10 kHz, between -40 and +40 Volts. Capac-

Figure 5.9. The dielectric measurement setup for sintered pellets. Electrode A is attached to a Cu strip in good electrical contact with the bottom electrode. Electrode B is in contact with a top electrode. The pellet and electrode quality and possible burn marks due to dielectric breakdown can be monitored using the low power optical microscope mounted above the sample.
Figure 5.10. Frequency dependent dielectric constant of different Fe concentration pellets sintered at 1000 °C.

The lowest value of the curves was around 0 V and increased with the magnitude of the applied bias voltage. This behavior more closely resembles a semiconducting material rather than a ferroelectric material. The magnitude of the capacitance (or permittivity) was highest at x = 0.4 and 0.5, and can be interpreted using pellet density and porosity conditions as with the frequency dependent measurements. Large voltage-dependent dissipation factors (Figure 5.13) associated with high Fe concentration samples can be attributed to conductive phase formation due to phase segregation. Residual carbon from organic constituents could also contribute towards high leakage currents, thus large dissipation factors. Ferroelectric hysteresis measurements performed at 2 kHz confirmed that pellets sintered at 1000 °C do not possess ferroelectric properties. This result contradicts the XRD prediction that x = 0.05.
pellets should exhibit ferroelectric behavior. Close inspection of the sample revealed that the pellet is highly porous and brittle. Therefore, inability to see ferroelectric hysteresis at low Fe concentrations is attributed to low density of the pellets. High density samples with low Fe concentrations may display ferroelectric properties as predicted by XRD results.

5.3 Thin Film Dielectric Measurements

Pellet samples sintered at 1000 °C were porous at low Fe concentration and show phase segregation at high Fe concentration. None of the pellets showed good ferroelectric properties. Nevertheless, structure refinement using XRD shows tetragonal distortion up to $x = 0.3$ Fe concentration, hence the possibility of good ferroelectric properties. Sol gel synthesis is useful in preparing dense thin films at lower sintering
temperatures. Two sol-gel precursor solutions with $x = 0.1$ and 0.2 compositions were prepared using the procedure described in section 2.3. The addition of excess lead is known to produce better quality lead lanthanum zirconate titanate and lead zirconate titanate thin films. [98] Excess lead promotes perovskite phase formation and produces dense, transparent thin films with superior electrical properties. [98, 99] Consequently, 0.5 M sol-gel solutions with 12% excess lead were prepared. Precursor solutions were aged for 2 days before depositing thin films. Thin film annealing is typically carried out at rapid anneal rates and shorter times compared to powder synthesis. Mismatch in thermal expansion coefficients may cause film cracking or weaken the adhesion with the substrate. Direct deposition of the precursor solution on to a substrate such as Si or Ni may produce other impurity phases. In order to overcome these problems, our films were deposited on a Si substrate with SiO$_2$ (500 nm), Ti (50 nm), and Pt (200 nm) overlayers. The substrate dimensions are $10 \times 10 \times 0.5$ mm
Figure 5.13. Bias voltage dependent dissipation factors of different Fe concentration pellets sintered at 1000 °C. The frequency was held constant at 10kHz.

with a terminating platinum surface roughness less than 5 Å.

The substrate was mounted on a 4 inch Si wafer with double-sided tape, which was subsequently mounted on the vacuum chuck of a spin coater (Laurell Technologies, WS-400). The substrate was centered on the vacuum chuck and cleaned using dry nitrogen and ethanol. The substrate surface was completely dried by flowing dry nitrogen. The precursor solution was first filtered using a syringe and a 0.02 µm filter. A few drops of the filtered solution were placed on the substrate and spin coated at 3000 rpm for 30 seconds. Figure 5.14 shows the Pb(Fe₀.₁Ti₀.₉)O₃₋δ film after different processing stages. The freshly coated sample with a light green color (5.14-a) was subsequently dried inside a 125 °C furnace for 5 to 10 minutes. The completely dried sample was first placed inside an alumina combustion boat then inserted into a 1 inch diameter tube furnace and heated to 300 °C. After 5 minutes of firing, the sample was removed from the furnace and allowed to cool down to room
temperature. Preliminary firing changed the sample color from light green to bright purple (5.14-b). After cleaning the sample surface with ethanol and dry nitrogen, it was placed inside a furnace heated to 650 °C and annealed for 3 minutes. The color of the film after this step was a bright golden yellow (5.14-c). Lead lanthanum zirconate titanate samples prepared using 0.5 M solutions under similar conditions were bright golden yellow at a film thickness of approximately 115 nm and deep golden yellow at approximately 120 nm. Films with thickness greater than 120 nm were red or green in color. Therefore, it is reasonable to assume that a single layer of our sample is approximately 115 nm in thickness. X-ray reflectivity measurements can be utilized to accurately measure the thin film thickness and the density. This study was limited to qualitative fingerprinting of ferroelectric properties, thus no X-ray reflectivity measurements were performed. An additional 2 layers (total of 3 layers, approximately 345 nm) were deposited using the procedure described above. To improve the film quality and homogeneity, the final annealing step was carried out for total of 6 minutes.

Both samples (x = 0.1 and 0.2) were investigated using XRD and found to have diffraction patterns similar to the powder samples, free from any impurity phases. Thin films were then prepared for dielectric measurements by depositing 250 µm
diameter Pt electrodes on the surface. Dielectric and ferroelectric hysteresis measurements were carried out as described in Section 5.2 in the apparatus shown in Figure 5.9.

Frequency dependent capacitance and corresponding dissipation factors are shown in Figure 5.15. Both films showed good capacitance and low loss factors comparable to lead titanate materials. Thin films with higher Fe concentration, $x = 0.2$ had higher dissipation loss compared to the $x = 0.1$ thin film, which is consistent with the pellet measurement results. Frequency dependent capacitance values are similar for both samples. The thickness of the two thin films are presumably similar. Therefore, having similar capacitance indicates that the lead titanate host material is capable of maintaining its tetragonal distortion and structural integrity at Fe concentrations as high as 20 mole% of the B-sites. This result is consistent with XRD analysis. Unlike pellet samples where dissipation loss slowly increased with the fre-
quency, the dissipation loss of thin films showed a rapid increase with the frequency. This behavior may not be desirable for potential applications of these materials which require a constant frequency response.

Voltage dependent capacitance and dissipation loss measurements were performed and are shown in Figures 5.16 and 5.17. Measurements were carried out at a frequency of 10 kHz. Both samples show capacitance curves characteristic of ferroelectric materials. The dissipation loss values of the thin films stay constant with the bias voltage, which is completely different from the pellet samples where loss effects increase with the voltage. These results indicate that both thin films possess good ferroelectric properties.

Polar materials are materials that possess an effective electric dipole moment in the absence of an external field. Typically, the individual dipoles are randomly oriented in the space. Ferroelectrics such as lead titanate are a special case of polar materials where spontaneous polarization ($P_S$) may have at least two equilibrium states. The orientation of the polarization vector can be manipulated between the two equilibrium states using an electric field. The spontaneous polarization in ferroelectric crystals or grains in a polycrystalline ferroelectric film is typically not aligned throughout the material. For example, lead titanate in its high temperature, non-polar cubic phase is symmetric along a and c axes, in both positive and negative directions. When cooled below the Curie temperature, polarization may arise along any one of six equally probable directions. The regions with uniformly oriented, spontaneous polarization are called domains. The onset of spontaneous polarization below the paraelectric-ferroelectric phase transition temperature leads to formation of surface charges. The accumulation of surface charge results in an electric field known as the depolarization field ($E_d$), which is oriented opposite to ($P_S$). The depolarizing field will form whenever there is a non-homogeneous distribution of spontaneous po-
Figure 5.16. Capacitance and dissipation loss of Pb(Fe$_{0.1}$Ti$_{0.9}$)O$_3$ thin film versus the bias voltage. The measurements were carried out at a frequency of 10 kHz.

Figure 5.17. Capacitance and dissipation loss of Pb(Fe$_{0.2}$Ti$_{0.8}$)O$_3$ thin film versus the bias voltage. The measurements were carried out at a frequency of 10 kHz.
Figure 5.18. Ferroelectric (P-E) hysteresis loop of Pb(Fe$_x$Ti$_{1-x}$)O$_3$ thin films. The thin film with Fe concentration $x = 0.2$ shows higher coercive field compared to $x = 0.1$ thin film, when poled by a similar electric field. Graph inset shows the negative offsets at starring points.

Polarization which then drives the formation of domains to minimize the electrostatic energy of the field.

Polarization reversal by an electric field, otherwise known as poling, is only possible in ferroelectric materials. This property is defining and the most important characteristic of ferroelectric materials. One consequence of domain-wall switching in ferroelectric materials is the occurrence of ferroelectric hysteresis loop. Places where the hysteresis loop cuts the polarization is known as the remanent polarization ($P_R$) and where it intercepts with the field axis is the coercive field ($E_c$).
ideal hysteresis loop is symmetrical with both $P_R$ positive and negative as well as $E_c$ positive and negative values being equal. However, the coercive field, spontaneous and remnant polarization, and the shape of the hysteresis loop may be affected by many factors including the thickness of the sample, the preparation conditions, the presence of charged defects, mechanical stress, and thermal treatment. [102]

Figure 5.18 shows the hysteresis loops of thin film samples taken at different electric fields. The thin film with Fe concentration $x = 0.2$ experienced dielectric breakdown at higher fields possibly due to higher leakage current. All hysteresis loops show negative polarization at the starting point, possibly due to poling from previous measurements, but are symmetric in both polarization and electric field axes. Both samples are ferroelectric and show significantly different hysteresis loops. The sample with Fe concentration $x = 0.2$ is easily polarized, and displayed a higher coercive field compared to the $x = 0.1$ sample, when polarized with a similar strength electric field. The scope of this study is limited to identifying the ferroelectric behavior of the doped materials, thus further analysis of the data has not been performed.

In conclusion, thin film samples $x = 0.1$ and 0.2 showed ferroelectric properties in agreement with XRD results. Pellets prepared using conventional pellet pressing and sintering did not show good ferroelectric properties. Pellets $x = 0.1$ and higher sintered at 1000 °C showed signs of phase segregation under XRD analysis. A high level of porosity and the consequent reduction in effective thickness maybe responsible for the poor ferroelectric performance of pellets. A technique capable of detecting ferroelectricity, such as Raman spectroscopy can be utilized to fingerprint ferroelectric behavior of powder samples.
6.1 Raman Scattering

Raman scattering is a general term for inelastic scattering of electromagnetic radiation by a molecule, essentially independent collection of molecules in a gas or liquid, or by a solid material. Raman spectroscopy is widely used to study vibrational, rotational, and other low-frequency modes in a system. A typical Raman instrument is designed to detect Raman scattering of monochromatic light, typically from an intense laser source, operating in the near infrared to near ultraviolet frequency regime. The electromagnetic radiation from the laser interacts with molecular vibrations in the system, resulting the laser frequency being shifted up or down. This shift in frequency is designated as a Stokes shift, if the frequency is lower than the incident electromagnetic radiation. A shift to a higher frequency is designated as an anti-Stokes shift.

As the electromagnetic wave interacts with the matter, the electron system within the constituent molecules is perturbed periodically with the same frequency as the electric field of the incident wave. The oscillatory perturbations of the electron cloud result in a periodic separation of charge within the molecules known as an induced dipole moment. The oscillating induced dipole moment acts as a source of electromagnetic radiation, resulting in scattered electromagnetic radiation. The frequency of the scattered radiation depends on the polarizability ($\alpha$) of the medium.

The strength of the dipole moment induced by external electromagnetic radiation is given by

$$P = \alpha \bar{E}$$

where $\alpha$ is the polarizability and $\bar{E}$ is the electric field. The polarizability is a material specific property that depends on the nature of the bonds and the molecular
structure. $\vec{E}$ can be expressed as

$$\vec{E} = E_0 \cos(2\pi\nu_0 t) \quad (6.2)$$

where $\nu_0$ is the frequency of the incident electromagnetic wave and $t$ is time. Combining Equation [6.1] and [6.2] yields the time-dependent induced dipole moment.

$$P = \alpha E_0 \cos(2\pi\nu_0 t) \quad (6.3)$$

The ability to perturb the local electron cloud of a molecule depends on the nature of the bonds and the relative location of the individual atoms. In the simplest case, the polarizability is a function of the instantaneous position of the constituent atoms. Since atoms in any molecular bond are confined to quantized vibrational modes, the vibration energy of a particular mode, under harmonic oscillator approximation, is expressed by

$$E_{vib} = (j + \frac{1}{2})h\nu_{vib} \quad (6.4)$$

where $j$ ($j=0, 1, 2, \ldots$) is the vibrational quantum number, $\nu_{vib}$ is the frequency of the vibrational mode, and $h$ is the Planck’s constant. An atom is displaced to a position $Q$ from the equilibrium position due to a particular vibrational mode. This physical displacement, $dQ$, can be expressed as

$$dQ = Q_0 \cos(2\pi\nu_{vib} t) \quad (6.5)$$

where $Q_0$ is the maximum displacement about the equilibrium position due to bond restrictions. For a diatomic molecule such as $N_2$, the maximum displacement could be as much as 10% of the bond length (much lower for solids). Under the small displacement assumption, the polarizability may be approximated by a first order Taylor series expansion,

$$\alpha = \alpha_0 + \frac{\partial \alpha}{\partial Q} dQ \quad (6.6)$$
where $\alpha_0$ is the polarizability at the equilibrium position. Combining equations 6.3, 6.5, and 6.6 gives,

$$P = \alpha_0 E_0\cos(2\pi\nu_0t) + \frac{\partial \alpha}{\partial Q} Q_0 E_0 \cos(2\pi\nu_0t) \cos(2\pi\nu_{vib}t) \quad (6.7)$$

After mathematical manipulation, the above equation takes the form

$$P = \alpha_0 E_0\cos(2\pi\nu_0t) + \left(\frac{\partial \alpha}{\partial Q} Q_0 E_0\right) \{\cos[2\pi(\nu_0 - \nu_{vib})t] + \cos[2\pi(\nu_0 + \nu_{vib})t]\} \quad (6.8)$$

Examination of equation 6.7 reveals that induced dipole moments can be created at three distinct frequencies, $\nu_0$, $(\nu_0 - \nu_{vib})$, and $(\nu_0 + \nu_{vib})$, which results in scattered radiation at the same frequencies. The frequency $\nu_0$ corresponds to the incident frequency, hence elastic scattering also known as Rayleigh scattering. Frequencies $(\nu_0 - \nu_{vib})$ and $(\nu_0 + \nu_{vib})$ where the wavelength is upward or downward shifted, are referred to as Raman scattering. As mentioned above, frequency down-shift is known as Stokes scattering while up-shift is referred to as anti-Stokes scattering. In this study Raman scattering is used to study phonons. However, other excitations such as molecular rotational excitations, free-carrier excitations, or magnetic excitations may also give rise to Raman scattering.

6.2 Ferroelectricity and the Soft Mode Concept

The first report of the soft mode concept was in a paper by Raman and Nedungadi, where they first mentioned a soft phonon at the $\alpha - \beta$ transition in quartz, in 1940. Later, in 1959, Cochran pointed out that the second order ferroelectric transition, where the dielectric constant diverges, is associated with a transverse optical mode that approaches zero. This suggestion was a great stimulus in ferroelectric theory and research. The soft-mode concept enables characterization of ferroelectrics without being affected by the possible complexity of a particular crystal structure, and is often used to fingerprint the existence of ferroelectricity.
Lead titanate is a classic example of the soft-mode atomic displacement which breaks the inversion symmetry of the high temperature cubic phase to a lower symmetry tetragonal phase below the transition temperature. Typical soft-mode vibrational frequencies are less than 100 cm$^{-1}$ in wavenumber, thus difficult to measure. Nevertheless, the ability to identify the existence of ferroelectricity in powder, pellet, and thin film samples using soft mode behavior (with Raman spectroscopy) is particularly useful in this study.

Raman spectroscopy measurements were performed using a Renishaw inVia Raman spectrometer equipped with a 633 nm wavelength laser and an edge filter for Rayleigh scattering rejection. The sharp cut of the edge filter designed for 633 nm wavelength excitation allowed the measurements of soft modes to as low as 40 cm$^{-1}$. Burns et. al. [112] discussed the lattice modes in ferroelectric perovskites including lead titanate in detail. Figure 6.1 shows the Raman spectrum of pure PbTiO$_3$ powder with labeled Raman-active modes. Our Raman spectrum shows all Raman-active modes expected for lead titanate. [112] Terms TO and LO represent transverse optical and longitudinal optical modes. A detail discussion on PbTiO$_3$ mode labeling can be found elsewhere. [112] The existence of the soft mode E(1TO) is a prerequisite for the existence of spontaneous polarization through long range interaction. [113] Therefore, the E(1TO) mode can be utilized to fingerprint the existence of ferroelectricity in Fe-doped samples. This method is unaffected by the presence of minor conductive impurities such as carbon or the condition of the sample. For example, conventional hysteresis measurements require the powder samples to be pelletized, densified by sintering at high temperature, and must satisfy electrical conductivity requirements. Our sintered pellets especially those with high Fe concentration showed significant structural modifications evidenced by XRD measurements. None of the samples including low Fe concentration pellets showed good ferroelectric response due to porosity and possible conductivity issues. Nevertheless, Raman measurements...
Figure 6.1. Raman spectrum of the powder PbTiO$_3$ sample synthesized using sol-gel technique, calcined at 700 °C.

can be performed on powder, pellet or thin film samples thus a good technique for detecting the existence of ferroelectricity.

Raman measurements were performed on a series of Pb(Fe$_x$Ti$_{1-x}$)O$_3$–δ powder and pellet samples. Figure 6.2 shows the Raman spectra of powder samples. All samples except x = 0.5 show the E(1TO) soft mode, indicating the samples are indeed ferroelectric. The iron doped samples have significantly broader lineshapes, which are shifted to lower wavenumbers compared to PbTiO$_3$. The sample with Fe concentration x = 0.5 does not show significant Raman peaks suggesting a high level of disorder. The E(1TO) peak position of x = 0.1 (69 cm$^{-1}$) and x = 0.2 (68 cm$^{-1}$) samples are significantly lower than that of PbTiO$_3$ (our sample = 84 cm$^{-1}$, Literature [112] = 89 cm$^{-1}$). XRD measurements revealed that powder samples with x ≥ 0.4 contain a PbFe$_{12}$O$_{19}$ magnetoplumbite phase with edge-sharing and face-sharing Fe octahedra. However, XRD measurements depend on long range order,
Figure 6.2. Raman spectra of the Pb(Fe\textsubscript{x}Ti\textsubscript{1-x})O\textsubscript{3-δ} powder samples synthesized using sol-gel technique, calcined at 700 °C.

thus local structure level tilting of Fe octahedra (driven by oxygen vacancies) may occur at much lower x values. The formation of oxygen vacancies and tilting of oxygen octahedra may disrupt long range order, a requirement for the spontaneous polarization below critical temperature. The E(1TO) mode broadening and shift towards lower wave number (x = 0.1 and 0.2) and complete disappearance at x = 0.5 are attributable to the formation of such defects.

Figures 6.3, 6.4, and 6.5 show Raman spectra of powder and pellet samples at compositions of x = 0.1, 0.2, and 0.5 for comparison. The Raman spectra of the pellets samples have much narrower and better defined peaks compared to those of the powder samples.

The Raman spectra of the pellets samples with x = 0.1 and 0.2 show all the features of the PbTiO\textsubscript{3} spectrum. The peak position of the E(1TO) mode is slightly
shifted towards that of PbTiO$_3$. The observation of a strong E(1TO) Raman mode in these pellets confirms the existence of ferroelectricity, which we failed to observe through dielectric and ferroelectric measurements. An improved Raman response of pellets, which better resembles the Raman spectrum of PbTiO$_3$ confirms the phase segregation observed in XRD measurements. Segregation into a Ti-rich phases could produce a Raman response similar to that of PbTiO$_3$, subject to broadening by the defect structure.

The Raman spectrum of the x = 0.5 powder sample has no intense peaks compared to the lower Fe composition samples. However, the Raman spectrum of the pellet (x = 0.5) sintered at 1000 °C shows multiple peaks and shoulders, similar to PbTiO$_3$. The structure of the x = 0.5 sintered pellet must be significantly different from the powder sample. The broad E(1TO) peak is stronger in the pellet.
Figure 6.4. Raman spectra of the Pb(Fe\(_{0.2}\)Ti\(_{0.8}\))O\(_{3−\delta}\) powder calcined at 700 °C and pellet sintered at 1000 °C.

Figure 6.5. Raman spectra of the Pb(Fe\(_{0.5}\)Ti\(_{0.5}\))O\(_{3−\delta}\) powder calcined at 700 °C and pellet sintered at 1000 °C.
sample, which implies possible ferroelectric properties. The XRD results in Section 5.1 indicated that the x = 0.5 pellet contains segregated Ti-rich and Fe-rich phases, which is consistent with the Raman results. Therefore, the ferroelectricity in Pb(Fe$_{0.5}$Ti$_{0.5}$)O$_{3-\delta}$, 1000 °C sintered pellet may be associated with Ti-rich phases, separate from the ferromagnetic Fe-rich phases.

In summary, Raman spectroscopy has been successfully utilized to detect ferroelectric properties of iron substituted lead titanates. Powders below x = 0.3 showed the E(1TO) peak, indicating the samples are ferroelectric, in agreement with XRD predictions. The ferroelectric nature of x = 0.1 and 0.2 samples were confirmed under ferroelectric hysteresis measurements. The pellets of composition x = 0.1, 0.2, and 0.3 showed enhanced ferroelectric properties, possibly due to phase segregation. The phase segregation in pellets was also suggested by XRD results. Raman spectra of x = 0.5 powder and pellet samples did not indicate good ferroelectric properties. The improvement of the peak intensity observed in x = 0.5 pellets compared to the powder sample is also attributed to phase segregation, and was clearly evidenced by XRD.
7.1 Fundamentals of X-ray Absorption Spectroscopy

X-ray Absorption Spectroscopy (XAS) refers to the measurement of the x-ray absorption coefficient at energies near (X-ray Absorption Near Edge Structure or XANES) and above (Extended X-ray Absorption Fine Structure or EXAFS) the core-level binding energies of an atom. The electronic and local geometric structure of the absorbing atom significantly affects the XAS spectra. The XANES region extends from the edge to about 50 eV above, and is determined by the scattering of the final state photoelectron by the neighboring atoms (multiple-scattering effects). Consequently, XANES is highly sensitive both to the coordination chemistry and the oxidation state of the absorbing atom. For crystalline materials, this region contains information about structural organization up to 10 Å. Quantitative description of the near edge spectra is complicated due to multiple-scattering processes and difficult to analyze compared to EXAFS.

The EXAFS region, extending from 50 eV up to approximately 1000 eV contains information about the atomic structure around the absorbing atom. This region contains information about near-neighbor atoms such as coordination of the absorbing atom, bond length, and disorder. Nevertheless, EXAFS has a long history as an analytical tool for material characterization. Unlike x-ray or neutron diffraction, XAS does not require long range order, can be tuned to a chemical element to obtain element-specific local structure, and is sensitive to very small concentrations. Consequently, employing XAS is advantageous in studying the micro- and nano-crystalline and disordered multicomponent materials such as ceramics, clays, and glasses as well as complex fluids and solutions.

The linear absorption coefficient ($\mu$) represents the absorption properties of a
When a collimated monochromatic x-ray beam propagates through a sample, the attenuation \( dI \) in the beam intensity is given by the equation,

\[
dI = -\mu I dx
\]  

(7.1)

where \( dx \) is a small thickness of the material. Integration of Equation 7.1 gives the Beer-Lambert law,

\[
I = I_0 e^{-\mu x}
\]  

(7.2)

where \( I_0 \) is the incident x-ray intensity, \( x \) is the sample thickness, and \( I \) is the transmitted intensity of the x-ray beam. Variation of the x-ray absorption coefficient is a smooth function of energy \( E \), which behaves according to:

\[
\mu \simeq \frac{\rho Z^4}{AE^3}
\]  

(7.3)

where \( \rho \) is the density of the sample, \( A \) is the atomic mass, and \( Z \) is the atomic number. When the x-ray energy is sufficiently large, an electron from a bound quantum level can be excited through absorption of an x-ray photon, which causes a sharp rise in the absorption spectrum known as an absorption edge. The energy of the excited photoelectron is given by the difference between the photon energy and the binding energy of the core level electron. When the difference is in the range of -10–50 eV, one probes the XANES region which allows accurate determination of the oxidation state with the aid of known reference materials based on the shift in the absorption edge energy. As the x-ray energy is increased, the EXAFS range of the XAS spectra can be measured.

EXAFS refers to the measurement of the oscillatory variations of the x-ray absorption coefficient, \( \mu \), as a function of photon energy. In a transmission experiment, \( \mu \) or \( \mu x \) is calculated by a modified version of Equation 7.2 given by

\[
\mu x = \log \frac{I_0}{I}.
\]  

(7.4)
The oscillatory variations are strongest immediately after the absorption edge and can be significant up to about 1000 eV above the edge. These oscillations are the result of the final state interference effect which involves the liberated photoelectron scattered from the neighboring atoms. The probability of an x-ray photon being absorbed is given by “Fermi’s golden rule” depends on the initial and final states of the system. [117] The initial state is a localized core level of an atom which determines the absorption edge. In a first approximation, final state can be represented by a superposition of spherical waves which corresponds to the liberated photoelectron wave function and the components of the wave function scattered by neighboring atoms. Constructive or destructive interference of these waves governed by the phase shift (depends on the type of neighboring atoms and interatomic distance) modulates the absorption probability resulting in an oscillatory variation of the x-ray attenuation. [120] Oscillations of the absorption coefficient can be determined by measuring the incident intensity and the transmitted intensity of the x-ray beam impinging on the sample according to Equation 7.4. X-ray fluorescence intensity is also proportional to the amount of incident radiation absorbed by the sample, [122] thus modulation of the absorption coefficient in fluorescence mode is given by

$$\mu = \frac{I_f}{I_0}$$  \hspace{1cm} (7.5)

where $I_f$ is the fluorescence intensity. [123]

7.2 EXAFS equation

A simple way of thinking about EXAFS is to consider it to be the interference between the excited photoelectron propagating outward and the backscattered waves due to potential fields of the neighboring atoms. Then the liberated photoelectron will travel as a spherical wave with the wave number given by,

$$k = \sqrt{\frac{2m}{\hbar}(E - E_0)}$$  \hspace{1cm} (7.6)
where \( m \) is the electron mass and \( E_0 \) is the absorption edge energy. For EXAFS, the interest is in the oscillatory part well above the absorption edge which is given by,

\[
\chi(E) = \frac{\mu(E) - \mu_0(E)}{\mu_0(E)}
\]  

(7.7)

where \( \mu \) is the measured absorption coefficient and \( \mu_0 \) is the so called “bare atom background” of an isolated atom. EXAFS is best understood treating the liberated photoelectron as a wave, thus the above expression is typically converted into wave number relationship \( \chi(k) \) using the relationship given in equation 7.6. EXAFS oscillations typically decay rapidly with the wave number. Therefore, \( \chi(k) \) is often multiplied by a power of \( k \), typically \( k^2 \) or \( k^3 \) to emphasize oscillations.

When the energies are sufficiently large, typically greater than 50 eV above the absorption edge, \( \chi(k) \) can be analytically related to structural parameters. This relationship known as the EXAFS equation is given by,

\[
\chi(k) = \sum_i N_i S_0^2 F_i(k) e^{-2\sigma_i^2 k^2} e^{-2r_i/\lambda(k)} \sin \left[ 2kr_i + \phi_i(k) \right] \frac{k r_i^2}{\lambda^2(k)}
\]  

(7.8)

where \( F_i(k) \) is the backscattering amplitude from each \( N_i \) neighboring atoms of \( i \) type, \( \sigma_i^2 \) is the so called “EXAFS Debye-Waller factor” which accounts for both static and thermal type disorder; \( r_i \) is the absorber-scatterer inter atomic distance, and \( \phi_i(k) \) is the total phase shift experienced by the photoelectron. The exponential term \( e^{-2r_i/\lambda(k)} \) accounts for the losses in the scattering process, where \( \lambda(k) \) is the wavenumber-dependent mean free path. The factor represented by \( S_0^2 \) known as the amplitude reduction factor approximates the losses due to multiple excitations at the absorbing atom. The origin of this loss mechanism is the excess energy \( (E - E_0) \) in the photoionization process that can excite or ionize (shake up/shake off) the outer or valence electrons of the absorbing atom. The \( S_0^2 \) parameter is completely correlated with the path degeneracy, thus accurate determination is critical for the accurate calculation of coordination numbers \( N_i \) using EXAFS.
The structural information of a sample can be extracted by comparing a theoretical EXAFS spectrum with the measured. Equation 7.8 shows that the total EXAFS is the sum of all possible backscattering events. The effective scattering amplitude $F_i(k)$ that depends only on the type of the backscatterer, is calculated using multiple scattering theory. Other parameters calculated similarly are the effective phase shift $(\phi_i)$ and the mean free path. Unlike $F_i(k)$, $\phi_i(k)$ contains contributions from both the absorbing atom and the backscatterer. In the case of ordered materials, the scattering atoms arranged in a group (determined by the real space resolution of EXAFS) are referred to as a coordination shell. Most materials have a strongly ordered first coordination shell, which is readily apparent in the EXAFS spectrum. The number of atoms in a coordination shell is represented by the parameter $N_i$. The amplitude of the EXAFS oscillations is damped by the gaussian term $e^{-2\sigma_i^2 k^2}$, where $\sigma^2$ is the square sum of static distortions ($\sigma_{\text{stat}}^2$) and vibrational disorder ($\sigma_{\text{vib}}^2$) of a particular shell. This parameter is different from the Debye-Waller factor (DWF) yet in the context of EXAFS often referred to as the DWF. If the sample material is free from structural transformations within a temperature range, multiple temperature dependent EXAFS measurements can be utilized to estimate the amount of static disorder since only thermal disorder depends on the temperature.

The EXAFS equation (Equation 7.8) clearly shows that EXAFS is a combination of different frequency waves. Each frequency corresponds to a different distance between the absorber selected by the edge energy and the scatterers, typically organized in coordination shells. Longer scattering paths corresponds to higher frequency waves. The Fourier transform of $\chi(k)$ can be utilized to produce a spectrum that closely resembles a radial distribution function where the coordination shells are shifted by a phase $\phi(k)$. As a result of attenuation from terms $1/r_i$ and exponential dampening $e^{-2r_i/\lambda(k)}$, the amplitude of the radial distribution is significantly reduced.
at distances exceeding 6 Å. Low temperature can be useful in recovering intensity at high \( r_i \) values, as it minimizes the broadening due to thermal vibrations. [134]

These parameters define the distance range accessible to the technique which renders EXAFS a local probe.

So far we have considered single-scattering contributions to the EXAFS theory. However, multiple scattering from three or more atoms (including the absorber) can also cause significant oscillations in the EXAFS spectrum. [117] Depending on the arrangement of atoms, the outgoing photoelectron may be strongly forward-scattered by the intervening atoms, thus enhancing the scattering amplitudes. Multiple scattering processes with large amplitude can be accounted for by including effective single scattering paths in the EXAFS equation. These paths behave as an oscillation \( \sin[2kr_{\text{eff}}] \), where \( r_{\text{eff}} \) is the total multiple scattering path length. [120] In comparison with single scattering contributions, these oscillations in many cases become relatively unimportant due to their large effective path lengths. Consequently, in most cases good agreement with the experimental spectra can be achieved by considering a small number of terms in the EXAFS equation.

In the XANES region where the photoelectron has a lower energy, it can effectively undergo many more scattering processes due to a longer, energy dependent, mean free path. Therefore, theoretical calculation of XANES requires a large number of multiple scattering paths for a relatively large cluster of atoms. [135] [136] The requirement of a “full multiple scattering approach” in calculations renders quantitative analysis of XANES more difficult. Nevertheless, qualitative results of XANES and quantitative results of EXAFS are complementary and effectively used in local structure investigations. [137] Both techniques were effectively used to study the structural properties driven by iron incorporation into lead titanate host material.
7.3 Experimental

X-ray data collection was performed at the Advanced Photon Source, Argonne National Laboratory. The data at absorption edges Pb L\textsubscript{III} (13035 eV) and Fe K (7112 eV) were collected at the Materials Research Collaborative Access Team (MRCAT) 10 ID beamline. All XAS data collection at the Ti K edge (4966 eV) was carried out at the MRCAT 10 BM beamline. A series of iron doped lead titanate samples Pb(Fe\textsubscript{x}Ti\textsubscript{1-x})O\textsubscript{3-δ} up to x=1 was measured on all three edges. Iron and lead edge EXAFS of a sample prepared in 1:12 Pb:Fe ratio was also measured. These measurements are useful in studying the local environment of the possible impurity phase PbFe\textsubscript{12}O\textsubscript{19}.

The powder samples were first ground into a fine powder and then evenly spread on kapton tape. The crystal structure of lead titanate materials changes from tetragonal to cubic at very low particle sizes, approximately 15 nm. [44] The average particle size of our synthesized materials was greater than 100 nm. Mild grinding using an agate mortar and a pestle does not reduce the size below 15 nm as evidenced by XRD analysis. Most samples had high concentration of lead as well as titanium or iron. The XAS spectra of concentrated materials can exhibit distortions caused by the thickness effects. [138] These undesirable effects decrease with the particle size. [139] Our sample spectra were carefully observed throughout the measurements and found to have minimal distortions from thickness effects. The high concentration of lead in the samples is believed to be responsible for the minimum thickness effects at the low energy titanium (4966 eV) and iron (7112 eV) absorption edges. The linear absorption coefficient depends on \(Z^4\), hence high atomic number (\(Z=82\)) could prevent the radiation from penetrating deeper into large particles, hence eliminating XAS spectral distortions. The particle sizes are small enough at the lead L\textsubscript{III} edge (13035 eV) to prevent significant amplitude loss caused by thickness effects. The
pellets (0.5–1 mm thick) prepared by pressing and sintering at high temperatures were also measured. XAS spectra were collected using pellets encapsulated in kapton tape. These spectra were also free from undesirable thickness effects.

X-ray absorption measurements can be performed by many different methods. Among those, transmission mode and fluorescence mode are frequently used. When permitted by experimental conditions, transmission mode XAS measurements are easiest to perform and analyze. In this mode, the incident and transmitted intensity of the x-ray beam is recorded and the absorption coefficient is calculated using the relationship given in Equation 7.4. However, a homogenous, pinhole free transmission mode sample with appropriate thickness is essential in performing XAS measurements in transmission mode. In cases where measuring the transmitted intensity becomes impossible or the attenuation from the absorber is insufficient, fluorescence mode can be utilized. Ideally, the fluorescence intensity is proportional to the absorption coefficient of the sample material. Consequently, oscillatory variations in the absorption coefficient can be calculated by normalizing the fluorescence intensity by the intensity of the incident beam (Equation 7.6). A wide variety of samples, sometimes with no or little preparation can be measured in fluorescence mode. However, detector performance limitations, lack of linearity between incident beam and fluorescence mode detectors, and sample limitations such as self absorption effects may adversely affect fluorescence mode XAS measurements. The XAS experimental setup typically allows simultaneous measurements to be performed in both transmission and fluorescence modes. The transmission mode XAS spectra were measured using ionization chambers. The fluorescence intensity was measured using a Vortex Si drift x-ray detector at the titanium edge. The fluorescence intensity of the samples with Fe concentration greater than 5 % was measured using a three-grid Lytle ionization chamber detector filled with Ar gas and a Vortex Si drift x-ray detector was utilized at lower concentrations.
Transmission mode XAS measurements of pellet samples were clearly impossible due to zero transmitted beam intensity. However, there was more flexibility in the sample preparation of powder samples. The choice of data collection mode was determined by the absorption properties of the material being studied. The total absorption coefficient of the material is defined by the concentrations of constituent chemical elements and their absorption cross sections. The total absorption cross section \( \mu_{\text{tot}} \) of a material can be expressed by,

\[
\mu_{\text{tot}} \approx \rho \sum_i \frac{m_i}{M} \sigma_i
\]  

(7.9)

where \( \rho \) is the density of the material, \( m_i/M \) and \( \sigma_i \) are the mass fraction and the absorption cross section of the \( i \)th element, respectively. The choice of data collection mode depends on the fraction of the absorption given by a constituent element. Calculations performed using Equation 7.9 showed that lead is responsible for over 90\% of the total absorption. Therefore, the obvious choice for measuring powder samples at Pb L\text{III} edge energy was transmission mode. Considering approximately 10\% fraction of total absorption shared by titanium and iron, along with variations in their concentration from zero to 100\%, the transmission mode was chosen for XAS measurements at their respective edges.

The Pb L\text{III} edge data was collected in the transmission mode with samples prepared using the powder on tape method described above. This method is more convenient than pressing pellets, which requires accurate sample quantities as well as a low absorption cross section material to increase the volume (Boron nitride, graphite, and sugar are commonly used). The ability to approximately double the absorption length by folding the tape is convenient in XAS measurements. From a purely statistical viewpoint, where better signal to noise ratio is desired, the optimum \( \mu_{\text{tot}} x = 2.6 \) samples are preferred. Under experimental considerations, XAS spectra of a \( \mu_{\text{tot}} x = 2.6 \) sample would suffer significant amplitude loss due to thickness effects.
Stern suggested that a $\mu_{\text{tot}}x$ value of 1.6 is proper to avoid thickness effects in concentrated samples. Therefore, multiple layers of our samples were used to achieve a $\mu_{\text{tot}}x$ of approximately unity. Additional beamline related information is discussed in Appendix C.

XAS measurements at the Ti K-edge were performed using samples oriented 45 degrees with respect to the incident x-ray beam. This apparatus allows for simultaneous measurements in both transmission and fluorescence mode. The ability to measure a reference foil (Ti foil) using the transmitted beam intensity allows corrections for possible energy shift during measurements. Fe K-edge measurements were carried out in a similar manner at the Ti K-edge. For both edges, fluorescence mode data was superior to transmission mode data and was free from significant amplitude loss due to self absorption effects. Consequently, fluorescence mode data at Ti K and Fe K-edges were used in the final analysis.

All XAS data sets were processed and analyzed using Athena-Artemis software suite, a front end to FEFF and IFEFFIT. The subtracted background was calculated using AUTOBK algorithm implemented in the software. The bare atom background function, $\mu_0(E)$ is represented by spline with maximum number of spline knots defined by:

\begin{equation}
N_{\text{knots}} = \frac{2R_{\text{bkg}}\Delta k}{\pi + 1}
\end{equation}

where $\Delta k$ is the useful k-range of the data, $R_{\text{bkg}}$ is the upper limit of low-R regions over which the background was fit. As a rule-of-thumb $R_{\text{bkg}}$ is about half the distance of the first shell peak. Minimization of R components higher than $R_{\text{bkg}}$ in the background is performed by setting equally spaced spline knots in k space. Therefore, $R_{\text{bkg}}$ can be thought as a frequency above which no signal can be measured (Nyquist frequency). In this XAS analysis $R_{\text{bkg}}$ values of Ti and Fe edges were set to 0.8 Å and
1.0 Å respectively. An $R_{bbg}$ value of 1.6 Å was used for processing Pb data.

### 7.4 Analysis of Ti K-edge data

Figure 7.1 shows the XANES region of the Ti K-edge XAS spectra for powder samples with various nominal iron concentrations. At low concentrations the XANES spectra look identical with only slight increase in broadening with the increasing Fe concentration. Significant changes in the spectra appear when $x$ is greater than 0.5. This is a clear indication that the Ti$^{4+}$ ion has a strong preference to its local environment which will be discussed in detail. The shape of the XANES pre-edge features at low Fe concentrations are similar to that of rutile (TiO$_2$). In this region three peaks A1, A2, and A3, marked with dashed lines, are visible. The assignment of these peaks in the literature is as follows: the A1 peak is due to a weak quadrupole $1s \rightarrow 3d$ transition whereas the A2 and A3 peaks are the results of dipole $1s \rightarrow 3d/2p$ transitions to states that are mainly $t_{2g}$ in character. These dipole transitions promoted to $3d/2p$ orbital are forbidden in a centrosymmetric environment such as a regular octahedron (Laporte’s rule). A review of the literature indicates that the intensity of the dominant A2 peak decreases and its energy increases as a result of reduced $p-d$ mixing caused by an increase in the level of centrosymmetry. The A2 peak becomes more intense and moves towards lower energy as the coordination number of titanium changes from six-fold $\rightarrow$ five-fold $\rightarrow$ four-fold. Our XANES spectra show an increase in the A2 peak intensity as well as shift towards lower energy, but only at concentrations greater than $x=0.5$. This observation suggests that the titanium coordination could be moving from six-fold towards five-fold coordination. The XANES absorption edge energy difference between five-fold and six-fold coordination reported in literature is approximately 1 eV, yet our samples only show a maximum A1 energy shift of about 0.5 eV. The A3 peak feature on the high energy side of the XANES spectra can be attributed to the
off-center distortion of the TiO$_6$ octahedron in ferroelectric PbTiO$_3$ (similar to rutile). The resultant tetragonal symmetry of the crystal field leads to splitting of orbitals into two levels, A2 with lower energy and A3 with higher energy. Consequently, the existence and the shape of the A3 peak provides sensitive information on the degree of distortion of the TiO$_6$ octahedron. Our samples show a gradual reduction in the A3 feature with increasing Fe concentration until it almost disappears at the highest values. In summary, our results indicate that Ti ions strongly prefer six coordinate environment at all Fe concentrations. However, iron dopants may cause a reduction in the off-center distortion of the TiO$_6$ octahedron significant beyond x=0.5.

Figure 7.2 shows the XANES region of the Ti K edge XAS spectra for pellet samples with various nominal iron concentrations. All pellet samples analyzed using XAS were prepared by sintering at 1000 °C. Unlike powder samples, pre-edge features of high Fe concentration samples look similar to those of rutile or PbTiO$_3$. This observation supports the phase segregation behavior discussed in Section 5.1. Sintering at 1000 °C may cause Ti-rich phases to form, where the TiO$_6$ octahedron are similar to those of low Fe concentration.

The Ti-edge EXAFS data in k-space for powder and pellet samples are shown in Figures 7.3 and 7.4 respectively. During data collection multiple data scans were collected for each sample. Comparing these individual scans against their average gives an idea about the noise level and the reliability of the data. The data sets of low Fe concentration samples were reliable up to k=12 Å$^{-1}$, whereas higher concentration samples produced good data up to k=11 Å$^{-1}$. We observed that none of the EXAFS spectra were affected by significant self absorption effects. Therefore, the k-range 2.5 to 11 Å$^{-1}$ was used for EXAFS analysis.

The Ti EXAFS data was Fourier transformed and used for data fitting in the Artemis program using FEFF6 theoretical standards. Ti K-edge R-space
Figure 7.1. Normalized Ti K-edge XANES data for Pb(Fe$_x$Ti$_{1-x}$)$_3$O$_{3-\delta}$ powder samples synthesized using sol-gel technique, calcined at 700 °C. The spectra are labeled with the nominal iron composition. The A1 dashed line denotes the weak quadrupole 1s $\rightarrow$ 3d transition whereas the A2 and A3 dashed lines represent the dipole 1s $\rightarrow$ 3d/2p transitions.
Figure 7.2. Normalized Ti K-edge XANES data for Pb(Fe$_x$Ti$_{1-x}$)O$_{3-\delta}$ pellet samples synthesized by sintering at 1000 °C. The spectra are labeled with the nominal iron composition. The A1 dashed line denotes the weak quadrupole $1s \rightarrow 3d$ transition whereas the A2 and A3 dashed lines represent the dipole $1s \rightarrow 3d/2p$ transitions.
Figure 7.3. Ti K-edge EXAFS data for Pb(Fe$_x$Ti$_{1-x}$)O$_{3-\delta}$ powder samples synthesized by firing at 700 °C. The spectra are labeled with the nominal iron composition.
Figure 7.4. Ti K-edge EXAFS data for Pb(Fe$_x$Ti$_{1-x}$)O$_{3-\delta}$ pellet samples synthesized by sintering at 1000 ºC. The spectra are labeled with the nominal iron composition.
transforms of powder and pellet samples are shown in Figures 7.5 and 7.6, respectively. The standard scattering paths are calculated using the positions and type of atoms around the Ti absorber. Atomic xyz coordinates were generated using ATOMS code [150] integrated in the Artemis program. [141] Well known crystallographic parameters of the PbTiO$_3$ structure at 300 K [151] were used in the proper input format with the Ti atom defined as the absorber.

The crystal structure of PbTiO$_3$ contains 3 different Ti–O subshells (1.77, 1.98, and 2.39 Å) in the first coordination shell. [152] The path lengths of all three subshells have a greater separation (0.21 and 0.41 Å) compared to typical EXAFS resolution (0.14 Å) given by $\Delta R = \pi/2k_{\text{max}}$, [153] where $k_{\text{max}}$ is the maximum energy of the photoelectron, at a $k_{\text{max}} = 11$ Å$^{-1}$. However, parameterization of all possible variables including coordination number, path length and Extended X-ray Absorption Fine Structure Spectroscopy Debye–Waller Factor (EXAFS DWF) is impossible due to limitations in the available independent parameters. All interatomic distances were varied in the model. Only 2 EXAFS DWFs were used in the first shell. Paths along the direction of the tetragonal distortion (2 paths, along c–direction) were assigned one EXAFS DWF, while other 4 scattering paths along a and b directions were assigned another. As a result of the crystal geometry, some multiple scattering contributions were found to be significant. These paths were parametrized using first shell variables, which significantly improved the stability of the fits. Other scattering paths were also parametrized as permitted by the availability of free parameters and constrained in some cases with known information, preserving a physically realistic model. Details of the Ti-K edge EXAFS paths and fit parameters are listed in Table C.1. The degeneracies of all the fitting paths in the fitting range 0.8–4.38 Å were kept at their original values given by the PbTiO$_3$ structure. The amplitude reduction factor was extracted using the spectra of PbTiO$_3$ since the structure is well known. [151] [152] The reliability of the fits was checked against small changes in the k-range and the
Figure 7.5. Fourier transformed Ti K-edge EXAFS data for Pb(Fe$_x$Ti$_{1-x}$)O$_{3-\delta}$ powder samples synthesized by firing at 700 °C. The spectra are labeled with the nominal iron composition.
Figure 7.6. Fourier transformed Ti K-edge EXAFS data for Pb(Fe$_x$Ti$_{1-x}$)O$_{3-\delta}$ pellet samples synthesized by sintering at 1000 °C. The spectra are labeled with the nominal iron composition.
fitting range and was found to be stable.

Titanium K-edge EXAFS data sets were multiplied by k, k^2, and k^3 weights and fit simultaneously for each Fe concentration. Simultaneous fitting of multiple k-weighted spectra reduces the correlations between variable parameters which often limit EXAFS data analysis. For example, correlations between EXAFS DWF and the amplitude, scattering path length and the edge energy are often high. Furthermore, multiple datasets were grouped according to composition and simultaneously fit in a single Artemis project file. This approach reduces the number of fitting parameters, for example, by using a common E_0 for all datasets. Another advantage is the ability to extract trends in parameters, which might be affected by correlations. This method is suitable for consistent data sets such as a temperature series of a single sample or a series of samples with gradually changing composition dependent structure.

Prior knowledge about the system under study can be incorporated into EXAFS fits in terms of set parameters (not varied during fit) or parameter constraints implemented by means of a penalty added to the statistical quality of the fit. This approach was used to constrain The EXAFS DWFs of the shortest bond length (O_{sh}) and the longest bond length (O_{lo}) of oxygen, which are identical considering adjacent unit cells of PbTiO_3(c-direction). Therefore, these two scattering paths were combined with an EXAFS DWF, \( \sigma_c \). Four oxygen atoms on a and b faces (O_{ab}) were grouped with one disorder parameter, \( \sigma_{ab} \). The parameter \( \sigma_c \) was constrained to be greater than 0.003. Two Pb scattering paths tend to be out of phase, and thus hard to fit without implementing constraints. Such constraints are essential above a concentration of x=0.3. Lead loss tends to be significant at higher Fe concentrations, confirmed by the formation of the lead deficient PbFe_{12}O_{19} described in Chapter . However, this effect was not parametrized in the fitting model for better stability.
Due to strong correlation between the amplitude and the EXAFS DWF, any lead loss is accounted for in the Pb EXAFS DWF $\sigma_{Pb}$. The EXAFS DWF of Ti paths $\sigma_{Ti}$ was constrained to be greater than 0.003. Similar models were used to fit both the powder and pellet Ti K-edge EXAFS data sets. Grouping of different Pb(Fe$_x$Ti$_{1-x}$)O$_{3-\delta}$ samples and their “goodness of fit” parameters can be found under Appendix C Tables C.1 and C.2.

The first shell Ti-O interatomic distances of powder and pellet samples are shown in Figures 7.7 and 7.8 respectively. The results indicate that the Ti ion has a highly preferential environment even at very high Fe concentrations. This result agrees with the XANES predictions but does not explain the loss of A3 peak at very high Fe concentrations. Figures 7.9 and 7.10 depict the behavior of EXAFS DWFs in the first coordination shell.

![Figure 7.7. Ti–O interatomic distances of Pb(Fe$_x$Ti$_{1-x}$)O$_{3-\delta}$ powder samples.](image-url)
Figure 7.8. Ti–O interatomic distances of Pb(Fe\(_x\)Ti\(_{1-x}\))O\(_{3-\delta}\) pellet samples.

Figure 7.9. Ti–O EXAFS DWFs of Pb(Fe\(_x\)Ti\(_{1-x}\))O\(_{3-\delta}\) powder samples.
Figure 7.10. Ti–O EXAFS DWFs of Pb(Fe$_x$Ti$_{1-x}$)O$_{3-\delta}$ pellet samples.

Figure 7.11. Ti–Pb and Ti–Ti/Fe EXAFS DWFs of Pb(Fe$_x$Ti$_{1-x}$)O$_{3-\delta}$ powder samples.
Figure 7.12. Ti–Pb and Ti–Ti/Fe EXAFS DWFs of Pb(Fe\textsubscript{x}Ti\textsubscript{1−x})O\textsubscript{3−δ} pellet samples.

Figure 7.13. Ti–Pb and Ti–Ti/Fe interatomic distances of Pb(Fe\textsubscript{x}Ti\textsubscript{1−x})O\textsubscript{3−δ} powder samples.
Figure 7.14. Ti–Pb and Ti–Ti/Fe interatomic distances of Pb(Fe$_x$Ti$_{1-x}$)O$_{3-\delta}$ pellet samples.

Ti–O EXAFS DWFs increase with Fe concentration below the solubility limit. This increase may be attributed to the preferential loss of c-direction oxygen as a result of Fe doping. However, the error bars associated with these parameters are large and prevents an absolute determination. The pellet samples show a similar but smoother trend, possibly due to Ti rich phase formation as a result of high temperature sintering. The powder samples with high Fe concentrations are also believed to have Ti-rich phases, as evidenced by similar Ti–O distances observed in samples with $x \geq 0.3$. EXAFS DWFs of higher order scattering paths show clear evidence of lead loss, hence the formation of PbFe$_{12}$O$_{19}$ impurity phase, which are shown in Figures 7.11 and 7.12 for powder and pellet samples, respectively. Ti–Pb and Ti–Ti/Fe scattering path lengths are shown in Figures 7.13 and 7.14.

7.5 Analysis of Fe K-edge data

All Fe K-edge data sets were processed similarly to Ti K-edge data. Pre-edge
features in Fe K-edge data sets were weak and not considered in the analysis. Observation of the Fe composition-dependent edge position revealed that the broadening and shifting towards lower energies suggested that Fe exists in mixed valence states, both Fe$^{3+}$ and Fe$^{2+}$. The edge positions of samples up to $x = 0.2$ look similar in edge energy. (See Figure 7.15). Spectra of intermediate compositions are not shown for clarity. Samples with iron concentration $x \geq 0.3$ show significant shift and broadening that increase with $x$, as shown in Figure 7.15.

![Figure 7.15. Derivative of Fe K-edge XAS data for Pb(Fe$_x$Ti$_{1-x}$)O$_{3-\delta}$ powder samples synthesized by firing at 700 °C.](image)

Fe K-edge EXAFS data sets of powder and pellet samples are shown in Figures 7.16 and 7.17 respectively. These data sets were Fourier-transformed in the k-range from 2 to 11 Å$^{-1}$. Beyond this limit the data quality was significantly affected by
noise. Fourier transformed Fe K-edge data sets of powder and pellet samples are shown in Figures 7.18 and 7.19 respectively. Direct qualitative comparison of Fourier transformed Fe K-edge spectra showed the first coordination shell does not change with the composition, suggested that the oxygen polyhedra around Fe ions remain similar regardless of the Fe concentrations. However, the formation of a new second coordination shell with a relatively short Fe-Fe distance, approximately at 2.5 uncorrected Å, can be observed in samples with Fe concentration $x \geq 0.3$. The formation of this coordination shell is consistent with the formation of PbFe$_{12}$O$_{19}$, magneto-plumbite phase with edge-sharing and face-sharing iron polyhedra.

Fe K-edge data reduction and fitting were carried out following standard EXAFS analysis procedures. The initial crystallographic model for Fe doped compounds was prepared by substituting the titanium atom in the PbTiO$_3$ structure [151] by an iron atom. Ti and Fe ions have similar scattering cross sections [156] so are not expected to show a significant difference especially in the higher order shells. Consequently, the second shell Fe and Ti scattering paths were treated as Fe–Fe scattering paths. All path degeneracies were fixed at the values obtained from the hypothetical PbFeO$_3$ structure, except in the first coordination shell. The peak corresponding to the first shell (Fe–O) was sharp and required a single scattering path to fit. The coordination number was allowed to change during the fit to account for possible oxygen vacancy formation. The amplitude reduction factor, $S_0^2$, was determined to be 0.75 by simultaneously fitting the low Fe concentration data sets. Fourier-transformed spectra were fit in the range of 1–4.2 Å with all the possible scattering paths included. Fe K-edge EXAFS model is listed in Appendix C Table C.4. The inclusion of 3 multiple scattering paths was essential at all compositions to achieve good quality fits.

EXAFS DWFs of Fe–Fe/Ti and Fe–Pb from the PbFeO$_3$ structure were constrained to improve the stability. An additional low Fe–Fe scattering path (3.0449 Å) generated from PbFe$_{12}$O$_{19}$ structure was used to fit the data sets of the higher $(x \geq 0.3)$
concentration samples. The coordination number of this path was optimized during the fit while keeping the EXAFS DWF restrained (see Table C.4). Coordination shells beyond this path were fit similarly to the low Fe concentrations samples.

The first shell fit parameters versus composition are shown in Figures 7.20, 7.21, and 7.22. The results confirm that oxygen vacancies are formed even at very low Fe concentrations and persist throughout the series, in both powder and pellet samples. Interatomic distances do not show significant changes. Both powder and pellet samples show similar EXAFS DWFs throughout the composition range. The values subjected to error bars suggests that the level of static disorder in the first (Fe–O) shell is not strongly dependent on the Fe concentration. Exact values of static disorder can be extracted using the Einstein model at 300 K, since the Einstein temperature for iron oxide is known. However, the large error bars associated with EXAFS DWFs, precluded further analysis. The persistence of Fe ions towards a symmetric first coordination shell may explain the rapid reduction of the tetragonal distortion with increasing Fe concentration. Unit cells with an iron center may break the long range order required for spontaneous polarization due to dissimilar coordination preferences of Ti and Fe centers. XAS results showed that titanium atoms indeed prefer a first coordination environment significantly different from that of iron. This could induce strain in the crystal structure. XRD technique is long range sensitive, thus captures the increase in micro strain with concentration as shown in Figure 4.9.

XRD Reitveld refinements using the PbTiO$_3$ tetragonal model failed beyond Fe concentration of x = 0.3. Samples with x $\geq$ 0.4 show evidence of PbFe$_{12}$O$_{19}$, hence the existence of edge-sharing and face-sharing Fe polyhedra. Fe K-edge EXAFS results confirm the existence of short Fe–Fe scattering paths, a sign of tilted oxygen polyhedra in an edge-sharing configuration. Doping Ti sites with Fe creates oxygen vacancies and the perovskite crystal lattice may have a limited ability to maintain its structural
integrity while supporting these oxygen vacancies. It is clear that below the solubility limit \( x=0.1 \), established by XRD, the structural integrity remains intact. Fe K-edge EXAFS results of both powder and pellet samples confirm that the \( x=0.2 \) sample is the last sample free from the short distance Fe–Fe scattering path. Consequently, the limiting ability of the \( \text{PbTiO}_3 \) host to maintain structural integrity against Fe substitution is approximately 20%. The coordination number and Fe–Fe short path distance versus composition are shown in Figures 7.23 and 7.24 respectively.

The diffraction pattern of \( \text{PbFe}_{12}\text{O}_{19} \) prepared in our study did not match with the published patterns in PDF-4+ 2010 ICDD database. The XAS measurement performed on this sample was somewhat affected by self absorption. Low Pb content due to high Fe concentration may have contributed to self absorption. Self absorption compensation was performed using Athena and its implementation of the correction developed originally by Booth and Bridges. EXAFS data in the \( k \)-range \( 2 – 11 \, \text{Å}^{-1} \) was Fourier transformed and fit in the range \( 1 – 3.6 \, \text{Å} \). Fitting paths were generated using crystallographic data for \( \text{PbFe}_{12}\text{O}_{19} \). The data was analyzed by simultaneously fitting in \( k \), \( k^2 \), and \( k^3 \) weights, using the original scattering paths and coordination numbers. Refinements to the original path parameters from the fit were small. Data and the fit in \( k \) and \( R \) spaces are shown in Figures 7.25 and 7.26 respectively. This result confirms the ability to form \( \text{PbFe}_{12}\text{O}_{19} \)-like clusters, which are not identified using long range sensitive probes such as XRD.

### 7.6 Analysis of Pb L\(_{\text{III}}\)-edge data

Pb L\(_{\text{III}}\) XAS data collection was limited to low Fe concentration powder samples. EXAFS spectra of Pb edge is comparatively difficult to analyze since there is no clear separation between coordination shells. The Pb L\(_{\text{III}}\) XANES edge energies of \( \text{Pb}_(\text{Fe}_{x}\text{Ti}_{1-x})\text{O}_{3-\delta} \) powder samples were found to be consistent with the expected Pb\(^{2+}\) state. These data sets were collected in transmission mode and have good re-
liability at higher k values. Pb L\textit{III}-edge EXAFS data sets of powder samples are shown in Figure 7.27. The data sets were Fourier transformed in the range 2.5 to 11 Å\textsuperscript{−1}. The resultant spectra are shown in Figure 7.28.

An attempt to fit these data sets was made using the model discussed by Sicron, [160] where the bulk crystallographic properties of PbTiO\textsubscript{3} have been utilized to parametrize an EXAFS model. In this model the bond lengths are parametrized using lattice parameters a and c. Such a model can be useful in monitoring tetragonal distortion and off-center displacements of atoms relative to the center of symmetry against parameters such as temperature or applied voltage. A similar model was used by Stoupin [28] for the parameterization of manganese doped PbTiO\textsubscript{3} samples. This model was used to fit EXAFS data in the composition range x=0 to 0.2, between 1.4 to 5 Å, in k-weights 1,2, and 3 simultaneously. The model and the parametrization of scattering paths are listed in Tables C.7 and C.8 respectively. Goddness-of-fit parameters are listed in Table C.9. The results indicate a reduction in the lattice parameter c at low Fe concentrations, which remains unchanged at higher concentrations. No significant change in a lattice parameter can be observed. (See Figure 7.29) Variation of the parameters representing off center displacements of titanium and oxygen atoms were statistically nonsignificant. The model is clearly insufficient for large Fe concentrations, since the Pb sublattices around Ti and Fe might be significantly different. However, the decreasing quality of the fit with increasing Fe concentration is a qualitative test for the deviation of the Pb local environment of Pb(Fe\textsubscript{x}Ti\textsubscript{1−x})O\textsubscript{3−δ} from that of pristine PbTiO\textsubscript{3}.

In summary, we found that Ti and Fe have highly specific first coordination shell preferences. Ti ions are encapsulated by a 6-coordinated, distorted oxygen octahedron. Fe ion is 5-coordinated and the oxygens are situated similar distances away from the central iron. Both Fe and Ti do not change their first shell coordination
preference with Fe concentration. At concentrations $x \geq 0.3$, formation of a short Fe–Fe coordination shell was observed. This represents the tilting of Fe–O polyhedra towards an edge sharing configuration. However, the observed Fe–Fe scattering path length is not consistent with full edge-sharing or face-sharing Fe polyhedra formation. Furthermore, tilted Fe polyhedra denote that a long range tetragonal crystal structure no longer exists at compositions $x \geq 0.3$. 
Figure 7.16. Fe K-edge EXAFS data for Pb(Fe\(_x\)Ti\(_{1-x}\))O\(_{3-\delta}\) powder samples synthesized by firing at 700 °C. The spectra are offset and labeled with the nominal iron composition.
Figure 7.17. Fe K-edge EXAFS data for Pb(Fe<sub>x</sub>Ti<sub>1−x</sub>)O<sub>3−δ</sub> pellet samples synthesized by sintering at 1000 °C. The spectra are offset and labeled with the nominal iron composition.
Figure 7.18. Fourier transformed Fe K-edge EXAFS data for Pb(Fe$_x$Ti$_{1-x}$)O$_{3-\delta}$ powder samples synthesized by firing at 700 °C. The spectra are offset and labeled with the nominal iron composition.
Figure 7.19. Fourier transformed Fe K-edge EXAFS data for Pb(Fe$_x$Ti$_{1-x}$)O$_{3-\delta}$ pellet samples synthesized by sintering at 1000 °C. The spectra are offset and labeled with the nominal iron composition.
Figure 7.20. Fe–O coordination numbers of Pb(Fe$_x$Ti$_{1-x}$)O$_{3-\delta}$ powder and pellet samples. Powder samples were synthesized by firing at 700 °C. Pellets samples were sintered at 1000 °C.
Figure 7.21. Fe–O bond lengths of Pb(Fe$_x$Ti$_{1-x}$)O$_{3-\delta}$ powder and pellet samples. Powder samples were synthesized by firing at 700 °C. Pellets samples were sintered at 1000 °C.
Figure 7.22. Fe–O EXAFS DWFs of Pb(Fe$_x$Ti$_{1-x}$)O$_{3-\delta}$ powder and pellet samples. Powder samples were synthesized by firing at 700 °C. Pellets samples were sintered at 1000 °C.
Figure 7.23. Fe–Fe$_{\text{short}}$ coordination numbers of Pb(Fe$_x$Ti$_{1-x}$)O$_{3-\delta}$ powder and pellet samples. Powder samples were synthesized by firing at 700 °C. Pellets samples were sintered at 1000 °C.
Figure 7.24. Fe–Fe$_{\text{short}}$ path lengths of Pb(Fe$_x$Ti$_{1-x}$)$_3$O$_{3-\delta}$ powder and pellet samples. Powder samples were synthesized by firing at 700 °C. Pellets samples were sintered at 1000 °C.
Figure 7.25. Fe K-edge EXAFS data and the fit for PbFe\textsubscript{12}O\textsubscript{19} powder samples synthesized by firing at 700 °C.

Figure 7.26. Fourier transformed Fe K-edge EXAFS data and the fit for PbFe\textsubscript{12}O\textsubscript{19} powder samples synthesized by firing at 700 °C.
Figure 7.27. Pb L₃-edge EXAFS data for Pb(FeₓTi₁₋ₓ)O₃₋δ powder samples synthesized by firing at 700 °C. Spectra are offset and labeled with the nominal iron composition.
Figure 7.28. Fourier transformed Pb L₃-edge EXAFS data for Pb(FeₓTi₁₋ₓ)O₃₋δ powder samples synthesized by firing at 700 °C. The spectra are offset and labeled with the nominal iron composition.
Figure 7.29. Lattice parameters of Pb(Fe<sub>x</sub>Ti<sub>1-x</sub>)O<sub>3-δ</sub> powder samples.
8.1 Magnetic properties of powders

Magnetic measurements of the powder samples were carried out using a Quantum Design PPMS 6000 extraction magnetometer. A small amount of sample powders, typically 20–240 mg, was placed inside a teflon capsule and secured using an end cap. The design of the end cap prevents any relative motion of the powder against the teflon capsule during measurements. Pellet samples prepared in this study were not compatible with the magnetometer design due to their large diameter. Magnetic response is dependent on the geometric properties of the sample. Consequently, preparation of small pelletized samples with identical shape was essential for accurate measurement of magnetic properties. However, structural investigations described above using XRD and XAS demonstrated phase segregation and Fe-rich phase formation when sintering at high temperatures. To avoid these uncertainties, magnetic measurements were limited only to powder samples.

Powder samples under XRD showed peaks belonging to magnetic impurity phases when the Fe concentration \( x \geq 0.4 \). However, local structure investigations using XAS revealed that edge-sharing Fe polyhedra allowing direct magnetic interaction between Fe ions may form at concentrations as low as \( x = 0.3 \). One of the objectives of this research was to investigate the validity of the claims that room temperature ferromagnetic properties in \( \text{Pb(Fe}_x\text{Ti}_{1-x})\text{O}_3-\delta \) series may exist at Fe concentrations as low as \( x = 0.01 \). The F-center exchange mechanism (FCE) has been used to explain the magnetic coupling believed to occur at low Fe concentrations. Another report showed evidence for room temperature ferromagnetic properties in the \( \text{Pb(Fe}_{0.5}\text{Ti}_{0.5})\text{O}_3-\delta \) sample. In an attempt to verify the accuracy of these experiments, temperature dependent magnetic measurements were carried out on a
selected set of samples. Ferromagnetic hysteresis measurement were also performed.

**Figure 8.1.** Magnetization versus temperature graphs Pb(Fe\(_x\)Ti\(_{1-x}\))O\(_{3-\delta}\) powder samples.

Magnetization versus temperature measurements are shown in Figures 8.1 and 8.2. All samples were subjected to a constant magnetic field of 1000 Oe. Samples \(x = 0.05\) and 0.1 samples graphs indicate paramagnetic behavior. Room temperature hysteresis measurement of the \(x = 0.05\) sample was linear and did not indicate any sign of ferromagnetic order. Therefore, our results do not support the previous report that room temperature ferromagnetism may exist even at very low Fe dopant concentrations.\(^{[50, 163, 164]}\) The magnetic response of the \(x = 0.2\) sample with temperature is significantly different from those of \(x = 0.05\) and 0.01 samples. The difference may be due to increased Fe–Fe ion interactions that occurs as a result of the high Fe concentration. XAS results are averaged over all Fe atoms and thus do not rule out the existence of small number of edge-sharing Fe polyhedra that allows direct Fe–Fe coupling. Samples with Fe concentration \(x \geq 0.4\) show clear signs of ferromagnetic
properties in both magnetization versus temperature and ferromagnetic hysteresis measurements. However, these samples \((x = 0.4, 0.5, 0.6, 0.7)\) do contain magneto-plumbite, implying that the magnetic properties observed in Fe doped samples maybe the result of magnetic impurities. Clearly, more accurate measurements are necessary to determine the lowest Fe dopant level necessary for ferromagnetic interaction. Our measurements confirm that the \(\text{Pb(Fe}_{0.5}\text{Ti}_{0.5})\text{O}_{3-\delta}\) sample is ferromagnetic. However, the structural investigations provided evidence that ferromagnetic and ferroelectric properties may exist in separate phases. The strain arising from the different preferred environments of Ti and Fe atoms may serve as the coupling mechanism between two order parameters.

![Magnetization vs temperature graph](image)

**Figure 8.2.** Magnetization versus temperature graphs \(\text{Pb(Fe}_x\text{Ti}_{1-x})\text{O}_{3-\delta}\) powder samples.
Figure 8.3. Magnetization versus temperature graph of Pb(Fe$_{0.5}$Ti$_{0.5}$)O$_{3-\delta}$ powder samples.
CHAPTER 9
SUMMARY AND FUTURE WORK

9.1 Iron Incorporation

Work presented herein is an experimental investigation of the model system, a ferroelectric PbTiO$_3$ with ABO$_3$ perovskite structure where iron is incorporated in various concentrations at the B-site. Additional charge compensation was not performed in order to maintain the compatibility with existing investigations. These reports highlight the ferromagnetic properties observed in samples doped at various concentrations from 1% up to 50%. Charge compensation substitutions, at the A-site in particular, are known to disrupt desirable ferroelectric properties. The methodology adopted in this study is suitable for providing direct answers to questions about both structural and associated properties variations without suffering complications from additional parameters.

The level of compatibility with the B-site is essential in 3d transition metal doping process. Iron (Fe$^{3+}$) is a good match with titanium (Ti$^{4+}$) in terms of the ionic radii yet incompatible with the valence state. In addition, iron or any 3d transition metal in a d$^n$ state violates the established condition, d$^0$-ness (absence of d electrons), [165] for the existence of ferroelectricity. Other complications such as high level of strain and structural instabilities due to oxygen vacancies may arise due to oxygen near-neighbor preferences of two different atoms, titanium and iron. The solubility limit of Fe in the PbTiO$_3$ host matrix may depend on the synthesis technique used. Typically, wet chemical synthesis techniques such as sol-gel have better solubility limits and uniform distribution of dopants compared to its solid state sintering counterpart. [55] Structural instabilities may result from either reaching the solubility limit or reaching the limiting conditions of the host matrix to retain charge compensating oxygen vacancies. At some Fe concentrations both factors could play a vital
role in structural deformations as well as impurity phase formation.

The structure and related properties of the system under study may have another dimension in the parameter space with varied processing temperatures. The physical form (powder, pellet, thin film) and excess materials used to compensate loss may have a large impact on observed properties. High levels of atomic mobility provided by high temperatures enable phase segregation where similar type of atoms with similar near-neighbor environment separate, thereby eliminating the excess lattice energy induced by strain.

A series of Pb(Fe\textsubscript{x}Ti\textsubscript{1-x})O\textsubscript{3-δ} samples in the composition range x = 0 to 1 was prepared and characterized using XRD. Results indicated a linear reduction in lattice parameter up to x = 0.1, hence the solubility limit of iron in the PbTiO\textsubscript{3} host using our sol-gel preparation technique is approximately 10 mole\%. Growth in microstrain with the Fe concentration observed under XRD was primarily attributed to the formation of charge compensating oxygen vacancies and associated structural changes. The EXAFS results revealed that Ti and Fe ions prefer different coordination environments, which could potentially contribute to the microstrain, especially below the solubility limit. Impurity phase formation is expected when the host material is doped beyond its solubility limit. However, the formation of the magnetoplumbite (PbFe\textsubscript{12}O\textsubscript{19}) phase is not clearly evident in XRD data until the iron concentration is 40 mole\%. Ti-rich and Fe-rich phase segregation has been observed in high temperature sintered (1000 °C) pellet samples using XRD. Pellet samples show better “softmode” behavior under Raman spectroscopy compared to powder samples, which further supports the formation of Ti-rich phase(s).

X-ray absorption spectroscopy revealed site specific structural information. Analysis of Ti K-edge XANES and EXAFS show that Ti prefers a distorted oxygen octahedra independent of Fe concentration. Major changes in the Ti environment are
observed below \( x = 0.2 \) for both powder and pellet samples. Beyond this limit the site preference remains unchanged possibly due to phase segregation.

Unlike Ti, Fe ions prefer a symmetric polyhedron with an average coordination number of 5, which agrees with the formation of charge compensating oxygen vacancies. The error bars associated with the coordination number remain large, possibly due to large correlation between EXAFS DWF and the coordination number. The formation of face-sharing oxygen polyhedra encapsulating Fe ions at \( x \geq 0.3 \) concentrations denotes the collapse of the host matrix as a result of oxygen vacancies. Therefore, the upper limit of oxygen vacancies supported by the host matrix while maintaining the structural integrity is about 20 mole\%. Extraction of both local and long-range structural information was made possible by using EXAFS and XRD as complementary techniques.

### 9.2 Feasibility of Room Temperature Magnetoelectrics

The observation of magnetoelectric properties in \( \text{Pb(Fe}_{0.5}\text{Ti}_{0.5})\text{O}_3-\delta \) with coupled magnetic and ferroelectric order parameters is a promising start to the preparation of magnetoelectrics. Doping of the B-site of \( \text{PbTiO}_3 \) is easy to perform using sol-gel synthesis. However, this method faces a few fundamental difficulties. Magnetic ions situated at close proximity promote magnetic interaction. This is often achieved by doping the host matrix above the solubility limit, which may result in impurity phases. Consequently, room temperature ferromagnetism in single phase, 1 % Fe doped \( \text{PbTiO}_3 \) is far from feasible. Nevertheless, there are multiple reports on room temperature ferromagnetism observed in Fe doped \( \text{PbTiO}_3 \), with concentrations less than 5 mole\%. The conditions for ferroelectric and ferromagnetic properties are mutually exclusive. [35] This raises the question of whether or not these properties exist in a single phase or two phases, one ferromagnetic and one ferroelectric, coupled through a mechanism such as strain. The loss of tetragonal distortion and
ferroelectric properties in PbTiO$_3$ nano-particles has been observed. Doping of either A or B site of PbTiO$_3$ has been known to rapidly reduce the tetragonal distortion. This behavior provides evidence that spontaneous polarization requires long range order, which tends to break upon homogenous doping.

XRD analysis of our Pb(Fe$_x$Ti$_{1-x}$)O$_{3-\delta}$ powder samples indicated a rapid reduction in ferroelectric properties due to loss of tetragonal distortion. Raman spectroscopy provided complementary evidence. Conducting losses were also increased. The structural integrity was compromised when the dopant concentration was greater than 20 mole%, which also indicated the formation of non-perovskite-like local structure. Furthermore, the high temperature sintered sample pellets show phase segregation into Ti-rich and Fe-rich compounds. All evidence suggests that magnetic and ferroelectric properties observed in Pb(Fe$_x$Ti$_{1-x}$)O$_{3-\delta}$ samples may exist in two or more different phases. The strain due to the different coordination preferences of Fe and Ti ions may act as a coupling force between magnetic and ferroelectric properties since the phases are intimately connected. Other research work also supports this notion. For example, Havinga noted that a seemingly ferrimagnetic behavior exhibited by (Ba$_{6-2x}$R$_{2x}$)(Nb$_{9-x}$Fe$_{1+x}$)O$_{30}$ was due to minute amounts of BaFe$_{12}$O$_{19}$. Small amounts of a secondary phase could easily go undetected in XRD experiments. Kleebe also reported the formation of PbFe$_{12}$O$_{19}$ magnetic grains when PbZr$_{0.6}$Ti$_{0.4}$O$_3$ ceramic is doped with 3 mole% Fe$^{3+}$ ions (solubility was reported as approximately 1 mole%). In their experiment Transmission Electron Microscopy (TEM) was utilized for the detection of PbFe$_{12}$O$_{19}$ phase. Therefore, the formation of the PbFe$_{12}$O$_{19}$ phase can contribute to ferromagnetic properties. We do not rule out the possibility of magnetic contributions through phases such as Pb$_2$Fe$_2$O$_5$.

9.3 Future Work

The material preparation technique and characterization techniques utilized
in this thesis are adequate for the thesis objective. More sophisticated techniques such as TEM can be used for better sensitivity and accuracy. The sol-gel techniques can be adopted to prepare high quality thin films of these materials which are useful for dielectric and ferroelectric measurements. Quantification of the impurity phases which was not a part of this thesis may be valuable to establish the relationship between Fe concentration and the percentage amounts of impurity phases.

Basic material properties such as conductivity, melting point, ferroelectric transition temperature are critical for understanding material properties. A detailed study on these properties as well as the temperature dependence of dielectric and ferroelectric properties would strengthen the understanding between the structure and the material properties. More detailed study of the ferroelectric and ferromagnetic properties will be essential for discovering a possible coupled behavior of the ferroelectric and ferromagnetic properties. Such coupling is one of the key parameters in potential device applications.

The solubility limit of Fe$^{3+}$ in the PbTiO$_3$ host matrix may have a significant temperature dependence. Furthermore, incorporation of a charge-compensation mechanism may strengthen the structural integrity at high dopant concentrations. Further investigation of the end phase Pb$_2$Fe$_2$O$_5$ is necessary by first overcoming the challenges in synthesis. A recent study [168] of single phase multiferroic with magnetoelectric coupling: (PbZr$_{0.53}$Ti$_{0.47}$O$_3$)$_{1-x}$(PbFe$_{0.5}$Ta$_{0.5}$O$_3$)$_x$ provide additional encouragement for pursuing new possibilities for magnetoelectrics. These new studies [168, 169] however should use sensitive techniques such as TEM or XAS to explore the true mechanism responsible for such properties.
APPENDIX A

XRD FITS USING GSAS
X-ray diffraction patterns of Pb(Fe\textsubscript{x}Ti\textsubscript{1-x})O\textsubscript{3-δ} samples were analyzed using Rietveld refinement. Following figures show the data, fit, and the fit residuals.
Figure A.1. Diffraction pattern of the PbTiO$_3$ (red markers) and the fit (green curve). Diffraction peaks are indexed with P4mm tetragonal crystal structure (black markers). Fit residual is indicated by the purple curve.
Figure A.2. Diffraction pattern of the Pb(Fe_{0.005}Ti_{0.995})O_3-δ (red markers) and the fit (green curve). Diffraction peaks are indexed with P4mm tetragonal crystal structure (black markers). Fit residual is indicated by the purple curve.
Figure A.3. Diffraction pattern of the Pb(Fe$_{0.01}$Ti$_{0.9}$)O$_{3-\delta}$ (red markers) and the fit (green curve). Diffraction peaks are indexed with P4mm tetragonal crystal structure (black markers). Fit residual is indicated by the purple curve.
Figure A.4. Diffraction pattern of the Pb(Fe\textsubscript{0.75}Ti\textsubscript{0.25})O\textsubscript{3-δ} (red markers) and the fit (green curve). Diffraction peaks are indexed with P4\textsubscript{mm} tetragonal crystal structure (black markers). Fit residual is indicated by the purple curve.
Figure A.5. Diffraction pattern of the Pb(Fe$_{0.05}$Ti$_{0.95}$)O$_{3-\delta}$ (red markers) and the fit (green curve). Diffraction peaks are indexed with P4mm tetragonal crystal structure (black markers). Fit residual is indicated by the purple curve.
Figure A.6. Diffraction pattern of the \( \text{Pb}(\text{Fe}_{0.075}\text{Ti}_{0.925})\text{O}_3-\delta \) (red markers) and the fit (green curve). Diffraction peaks are indexed with P4mm tetragonal crystal structure (black markers). Fit residual is indicated by the purple curve.
Figure A.7. Diffraction pattern of the Pb(Fe$_{0.1}$Ti$_{0.9}$)O$_{3-\delta}$ (red markers) and the fit (green curve). Diffraction peaks are indexed with P4mm tetragonal crystal structure (black markers). Fit residual is indicated by the purple curve.
Figure A.8. Diffraction pattern of the Pb(Fe_{0.125}Ti_{0.875})O_{3-δ} (red markers) and the fit (green curve). Diffraction peaks are indexed with P4mm tetragonal crystal structure (black markers). Fit residual is indicated by the purple curve.
Figure A.9. Diffraction pattern of the Pb(Fe_{0.15}Ti_{0.85})O_{3-\delta} (red markers) and the fit (green curve). Diffraction peaks are indexed with P4mm tetragonal crystal structure (black markers). Fit residual is indicated by the purple curve.
Figure A.10. Diffraction pattern of the Pb(Fe$_{0.2}$Ti$_{0.8}$)$_3O_3$−δ (red markers) and the fit (green curve). Diffraction peaks are indexed with P4mm tetragonal crystal structure (black markers). Fit residual is indicated by the purple curve.
Figure A.11. Diffraction pattern of the Pb(Fe$_{0.3}$Ti$_{0.7}$)O$_3$−δ (red markers) and the fit (green curve). Diffraction peaks are indexed with P4mm tetragonal crystal structure (black markers). Fit residual is indicated by the purple curve.
APPENDIX B

CALIBRATION OF THE METTLER TOLEDO TGA/SDTA851E INSTRUMENT
The positions of important TG or DTA curves may be shifted due to differences in heat capacities, thermal conductivities, heating rate, type of gas used and the flow rate of the gas. The instrument used in this study was only equipped with a single sample position, thus the reference temperature is calculated rather than directly measured. Therefore, the instrument calibration is essential for acquiring accurate temperature measurements of endothermic or exothermic processes and onset temperatures of material loss.

Calibration of the entire temperature range of the instrument was necessary since the expected organic loss, ferroelectric transition temperatures, and melting points of iron doped lead titanate samples are believed to spread in a range of temperatures. Melting points of pure lead titanate as well as low Fe doped samples may exceed the maximum capability of the instrument, which is 1100 °C.

Therefore, the instrument calibration has been performed using materials listed in Table B.1 at different heating rates under nitrogen gas flow. Using materials with known melting points which are also good heat conductors allow for accurate measurement of melting point shifts with the heating rate. A minimum of 4 standards are necessary for acquiring all the parameters necessary for building the calibration curves, which accurately calculates the temperature at a heating rate of 0 °C/min and the reference temperature. The entire calibration procedure was carried out according to the procedures prescribed in the instrument manual. Accuracy of the calibration was verified using the melting points of Pb and Au. TG measurement accuracy of the instrument was tested using calcium oxalate monohydrate (CaC$_2$O$_4$·H$_2$O) with well known thermal decomposition.
Table B.1. Melting points of chemical elements used in the calibration of Mettler Toledo TGA/SDTA851e TG/DTA instrument.

<table>
<thead>
<tr>
<th>Element</th>
<th>Melting point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>In</td>
<td>156.6</td>
</tr>
<tr>
<td>Pb</td>
<td>327.5</td>
</tr>
<tr>
<td>Al</td>
<td>660.4</td>
</tr>
<tr>
<td>Au</td>
<td>1064</td>
</tr>
</tbody>
</table>
APPENDIX C
X-RAY ABSORPTION SPECTROSCOPY-ADDITIONAL INFORMATION
The EXAFS measurements were performed at the Advanced Photon Source (APS), using Materials Collaborative Access Team undulator (MRCAT, 10-ID), and bending magnet (MRCAT, 10-BM) beamlines. Fe K-edge and Pb-L_{III} edge measurements were performed at the 10-ID beam line. Ti K-edge measurements were performed at the 10-BM beam line. XAS measurements at Ti edge (4966 eV) is difficult due to multiple reasons. Even Kapton tape, typically used in XAS measurements have a high absorption cross section at lower energies. A thick layer of Kapton can absorb as much as 50% of the incident beam intensity. Therefore, a thin Kapton tape with acrylic adhesive was used to encapsulate samples measured at the Ti-edge. Acrylic adhesive appears to have a low absorption cross section compared to typical silicone adhesive commonly found on Kapton tapes. Nitrogen and argon constituents of air can significantly attenuate the incident beam intensity, thus air in the beam was minimized. Ion chambers I_{0} and I_{t} were filled with He/N_{2} and N_{2} gas mixes to absorb approximately 10 % and 70 % of the beam intensity, respectively. Fluorescence data was collected using a Vortex® silicon drift detector with regions of interest set using TiO_{2} standard. This region was later fine tuned using a low Ti concentration Pb(Fe_{x}Ti_{1-x})O_{3-δ} sample.

Higher order harmonics of the beam were removed by detuning the second crystal of the monochromator by 50 % of the rocking curve peak intensity. Energy calibration was performed using a thin Ti foil energy spectrum in transmission mode. The sample were mounted 45 degrees from the incident beam to achieve good fluorescence intensity. The detector position was manipulated to have similar number of counts in all 4 channels of the detector while maintaining the detector dead time to below 20 %. The horizontal beam size does not affect the energy resolution, thus horizontal beam size manipulation was also used for achieving best data quality. The repeatability of the monochromator at MARCAT 10-BM line was found to be satisfactory during the experiment. The transmitted beam intensity was too low for
measuring a reference spectrum due to high absorption from the samples. Therefore, the titanium foil scans were performed after measuring the samples as a verification of monochromator repeatability.

Fe-K edge (7112 eV) fluorescence measurements were performed at the MRCAT-10ID beam line using a Lytle detector. Harmonic rejection was performed using a Pd coated mirror or a glass mirror. Ion chambers $I_0$ and $I_t$ were filled with He/N$_2$ and N$_2$/Ar gas mixes to absorb approximately 10 % and 70 % of the beam intensity, respectively. Approximate beam size was 1x1 mm. Energy calibration was performed using the XAS spectra of a thin Fe foil.

Pb L$_{III}$-edge measurements were performed in transmission mode using detectors filled with a gas mixture of N$_2$ and Ar. Gas mix of the transmission ion chamber was kept below the widely used 70 % absorption due to dynamic range limitations of the current amplifiers used. Energy calibration was performed using a thin Pb foil, which served as a reference standard during sample data collection.
Table C.1. Ti K-edge powder and pellet EXAFS fit model. Paths denoted by * were not used in compositions x ≥ 0.3. Fitting parameters ssO1 (0.003 – 0.015 Å²), delrPb (-0.1 – 0.1 Å), and ssPb (0.003 – 0.025 Å²) were restrained in the limits given in parenthesis. It should be noted that, for doped samples, Ti symbol also represents Fe backscatterers.

<table>
<thead>
<tr>
<th>Path</th>
<th>length(R) Å</th>
<th>Degeneracy</th>
<th>ΔR</th>
<th>EXAFS DWF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti–O1</td>
<td>1.7671</td>
<td>1</td>
<td>delrO1</td>
<td>ssO1</td>
</tr>
<tr>
<td>Ti–O2</td>
<td>1.9792</td>
<td>4</td>
<td>delrO2</td>
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</tr>
<tr>
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<td>delrO3</td>
<td>ssO1</td>
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<tr>
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<td>4</td>
<td>delrPb</td>
<td>ssPb</td>
</tr>
<tr>
<td>Ti–Pb2</td>
<td>3.5556</td>
<td>4</td>
<td>delrPb</td>
<td>ssPb</td>
</tr>
<tr>
<td>Ti–Ti1</td>
<td>3.9050</td>
<td>4</td>
<td>delrTi</td>
<td>ssTi</td>
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<tr>
<td>Ti–Ti1–O2</td>
<td>3.9317</td>
<td>8</td>
<td>delrO2+delrTi</td>
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<tr>
<td>Ti–O2–O2</td>
<td>3.9583</td>
<td>4</td>
<td>delrO2+delrTi</td>
<td>ssO2+ssTi</td>
</tr>
<tr>
<td>Ti–Ti1–O2</td>
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<td>4</td>
<td>delrO2+delrTi</td>
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<tr>
<td>Ti–Ti2</td>
<td>4.1560</td>
<td>2</td>
<td>delrTi</td>
<td>ssTi</td>
</tr>
<tr>
<td>* Ti–Ti2–O1</td>
<td>4.1560</td>
<td>2</td>
<td>delrO1+delrTi</td>
<td>ssO1+ssTi</td>
</tr>
<tr>
<td>* Ti–O1–Ti–O1</td>
<td>4.1560</td>
<td>2</td>
<td>delrO3+delrTi</td>
<td>ssO2+ssTi</td>
</tr>
<tr>
<td>* Ti–O1–Ti2–O1</td>
<td>4.1560</td>
<td>1</td>
<td>delrO1+delrTi</td>
<td>ssO1+ssTi</td>
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<tr>
<td>* Ti–O1–Ti2–O1</td>
<td>4.1560</td>
<td>1</td>
<td>delrO3+delrTi</td>
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<tr>
<td>Ti–O1L</td>
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<td>Ofar</td>
<td>ssOfar</td>
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<tr>
<td>Ti–O2L</td>
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<td>Ofar</td>
<td>ssOfar</td>
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<tr>
<td>Ti–O2L</td>
<td>4.3779</td>
<td>8</td>
<td>Ofar</td>
<td>ssOfar</td>
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</table>

Table C.2. Ti K-edge powder EXAFS fit parameters. Fe concentration (Fe x), the number of multiple scattering paths included in the fit (MSP) and goodness of fit parameters are listed in the table.

<table>
<thead>
<tr>
<th>Fe x</th>
<th>MSP</th>
<th>R-factor</th>
<th>Reduced χ²</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 – 0.05</td>
<td>8</td>
<td>0.026</td>
<td>213</td>
</tr>
<tr>
<td>0.075 – 0.2</td>
<td>8</td>
<td>0.021</td>
<td>374</td>
</tr>
<tr>
<td>0.3 – 0.6</td>
<td>3</td>
<td>0.018</td>
<td>492</td>
</tr>
<tr>
<td>0.7 – 0.9</td>
<td>3</td>
<td>0.024</td>
<td>174</td>
</tr>
</tbody>
</table>
Table C.3. Ti K-edge pellet EXAFS fit parameters. Fe concentration (Fe x), the number of multiple scattering paths included in the fit (MSP) and goodness of fit parameters are listed in the table.

<table>
<thead>
<tr>
<th>Fe x</th>
<th>MSP</th>
<th>R-factor</th>
<th>Reduced $\chi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0 – 0.05</td>
<td>8</td>
<td>0.020</td>
<td>639</td>
</tr>
<tr>
<td>0.075 – 0.2</td>
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<td>0.013</td>
<td>688</td>
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<tr>
<td>0.3 – 0.7</td>
<td>3</td>
<td>0.014</td>
<td>585</td>
</tr>
</tbody>
</table>

Table C.4. Fe K-edge powder and pellet EXAFS fit model. Following parameter restraints were used: (0.005 $\geq$ ssPb $\geq$ 0.007), (1 $\geq$ cdnPb $\geq$ 0.7), (0.01 $\geq$ ssFeShort $\geq$ 0.01), and (0.1 $\geq$ delrFe2 $\geq$ -0.1). Path denoted by $^*$ was only used in compositions x $\geq$ 0.3. It should be noted that, for doped samples, Fe symbol also represents Ti backscatterers.

<table>
<thead>
<tr>
<th>Path</th>
<th>length(R) Å</th>
<th>Degeneracy</th>
<th>$\Delta R$</th>
<th>EXAFS DWF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe–O</td>
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<td>cdnO</td>
<td>delrO</td>
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<td>Fe–Pb1</td>
<td>3.3608</td>
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<tr>
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<td>3.5556</td>
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</tr>
<tr>
<td>* Fe–FeShort</td>
<td>3.0449</td>
<td>cdnFeShort</td>
<td>delrFeShort</td>
<td>ssFeShort</td>
</tr>
<tr>
<td>Fe–Fe1</td>
<td>3.9050</td>
<td>4 - cdnFeShort</td>
<td>delrFe1</td>
<td>ssFe</td>
</tr>
<tr>
<td>Fe–Fe1</td>
<td>4.1560</td>
<td>4</td>
<td>delrFe2</td>
<td>ssFe</td>
</tr>
<tr>
<td>Fe–Fe1–O</td>
<td>3.9317</td>
<td>8</td>
<td>delrO+delrFe1</td>
<td>ssO+ssFe</td>
</tr>
<tr>
<td>Fe–O–Fe–O</td>
<td>3.9583</td>
<td>8</td>
<td>2 x delrO</td>
<td>2 x ssO</td>
</tr>
<tr>
<td>Fe–O–Fe1–O</td>
<td>3.9583</td>
<td>8</td>
<td>2 x delrO</td>
<td>2 x ssO</td>
</tr>
</tbody>
</table>

Table C.5. Fe K-edge powder EXAFS fit parameters. Fe concentration (Fe x), the number of multiple scattering paths included in the fit (MSP) and goodness of fit parameters are listed in the table.

<table>
<thead>
<tr>
<th>Fe x</th>
<th>MSP</th>
<th>R-factor</th>
<th>Reduced $\chi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.025 – 0.2</td>
<td>3</td>
<td>0.012</td>
<td>120</td>
</tr>
<tr>
<td>0.3 –0.5</td>
<td>3</td>
<td>0.021</td>
<td>1784</td>
</tr>
<tr>
<td>0.6 – 1</td>
<td>3</td>
<td>0.009</td>
<td>1239</td>
</tr>
</tbody>
</table>
Table C.6. Fe K-edge pellet EXAFS fit parameters. Fe concentration (Fe x), the number of multiple scattering paths included in the fit (MSP) and goodness of fit parameters are listed in the table.

<table>
<thead>
<tr>
<th>Fe x</th>
<th>MSP</th>
<th>R-factor</th>
<th>Reduced $\chi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.075 – 0.2</td>
<td>3</td>
<td>0.025</td>
<td>668</td>
</tr>
<tr>
<td>0.3 – 0.5</td>
<td>3</td>
<td>0.023</td>
<td>1954</td>
</tr>
<tr>
<td>0.6 – 1</td>
<td>3</td>
<td>0.018</td>
<td>1683</td>
</tr>
</tbody>
</table>
Table C.7. Pb L$_3$-edge EXAFS model parameters used in Artemis.

<table>
<thead>
<tr>
<th>Parameter type</th>
<th>Parameter name</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>set</td>
<td>a0</td>
<td>3.906</td>
</tr>
<tr>
<td>set</td>
<td>c0</td>
<td>4.133</td>
</tr>
<tr>
<td>guess</td>
<td>dti</td>
<td>0.39</td>
</tr>
<tr>
<td>guess</td>
<td>do1</td>
<td>0.1139</td>
</tr>
<tr>
<td>guess</td>
<td>do2</td>
<td>0.1169</td>
</tr>
<tr>
<td>set</td>
<td>amp</td>
<td>0.847</td>
</tr>
<tr>
<td>set</td>
<td>temp</td>
<td>300</td>
</tr>
<tr>
<td>set</td>
<td>theta_pb_sh</td>
<td>227</td>
</tr>
<tr>
<td>set</td>
<td>theta_pb_lo</td>
<td>204</td>
</tr>
<tr>
<td>def</td>
<td>dwf_pb_ti_sh</td>
<td>eins(temp,theta_pb_sh)</td>
</tr>
<tr>
<td>def</td>
<td>dwf_pb_ti_lo</td>
<td>eins(temp,theta_pb_lo)</td>
</tr>
<tr>
<td>set</td>
<td>dwf_pb_pb</td>
<td>0.018</td>
</tr>
<tr>
<td>guess</td>
<td>dwf_pb_o</td>
<td>0.01</td>
</tr>
<tr>
<td>guess</td>
<td>dwf_pb_ofar</td>
<td>0.01</td>
</tr>
<tr>
<td>guess</td>
<td>e0_pb_o</td>
<td>0</td>
</tr>
<tr>
<td>guess</td>
<td>e0_pb_ti</td>
<td>0</td>
</tr>
<tr>
<td>def</td>
<td>e0_pb_pb</td>
<td>e0_pb_ti</td>
</tr>
<tr>
<td>def</td>
<td>rpbo1</td>
<td>sqrt(0.5<em>a^2+(c</em>do1)^2)</td>
</tr>
<tr>
<td>def</td>
<td>rpbo2_sh</td>
<td>sqrt(c^2*(0.5-abs(do2))^2+(0.5*a)^2)</td>
</tr>
<tr>
<td>def</td>
<td>rpbo2_lo</td>
<td>sqrt(c^2*(0.5+abs(do2))^2+(0.5*a)^2)</td>
</tr>
<tr>
<td>def</td>
<td>rtipb_sh</td>
<td>sqrt(0.5<em>a^2+c^2</em>(0.5-dti)^2)</td>
</tr>
<tr>
<td>def</td>
<td>rtipb_lo</td>
<td>sqrt(0.5<em>a^2+c^2</em>(0.5+dti)^2)</td>
</tr>
<tr>
<td>def</td>
<td>ro12_sh</td>
<td>sqrt(c^2*(1-do1)^2+0.5*a^2)</td>
</tr>
<tr>
<td>def</td>
<td>ro12_lo</td>
<td>sqrt(c^2*(1+do1)^2+0.5*a^2)</td>
</tr>
<tr>
<td>def</td>
<td>ro22_sh</td>
<td>sqrt(c^2*(0.5-do2)^2+1.25*a^2)</td>
</tr>
<tr>
<td>def</td>
<td>ro22_lo</td>
<td>sqrt(c^2*(0.5+do2)^2+1.25*a^2)</td>
</tr>
</tbody>
</table>
Table C.8. Pb L₃-edge EXAFS fit model. An amplitude reduction factor ($S_0^2$) of 0.9 was used.

<table>
<thead>
<tr>
<th>Path</th>
<th>length(R) Å</th>
<th>Degeneracy</th>
<th>ΔR</th>
<th>EXAFS DWF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb–O1</td>
<td>2.5194</td>
<td>4</td>
<td>rpbo₂_sh-reff</td>
<td>abs(dwf_pb_o)</td>
</tr>
<tr>
<td>Pb–O2</td>
<td>2.8015</td>
<td>4</td>
<td>rpbo₁-reff</td>
<td>abs(dwf_pb_o)</td>
</tr>
<tr>
<td>Pb–O3</td>
<td>3.2227</td>
<td>4</td>
<td>rtipb_sh-reff</td>
<td>abs(dwf_pb_o)</td>
</tr>
<tr>
<td>Pb–Ti₁</td>
<td>3.3608</td>
<td>4</td>
<td>rpbo₂_sh-reff</td>
<td>abs(dwf_ti_pb_sh)</td>
</tr>
<tr>
<td>Pb–Ti₂</td>
<td>3.5556</td>
<td>4</td>
<td>rtipb_lo-reff</td>
<td>abs(dwf_ti_pb_lo)</td>
</tr>
<tr>
<td>Pb–Pb₁</td>
<td>3.9050</td>
<td>4</td>
<td>a-reff</td>
<td>abs(dwf_Pb_Pb)</td>
</tr>
<tr>
<td>Pb–Pb₂</td>
<td>4.1560</td>
<td>4</td>
<td>c-reff</td>
<td>abs(dwf_Pb_Pb)</td>
</tr>
<tr>
<td>Pb–O₁far</td>
<td>4.6032</td>
<td>4</td>
<td>ro₁₂_sh-reff</td>
<td>abs(dwf_Pb_ofar)</td>
</tr>
<tr>
<td>Pb–O₂far</td>
<td>4.6472</td>
<td>8</td>
<td>ro₂₂_sh-reff</td>
<td>abs(dwf_Pb_ofar)</td>
</tr>
<tr>
<td>Pb–O₃far</td>
<td>5.0631</td>
<td>8</td>
<td>ro₂₂_lo-reff</td>
<td>abs(dwf_Pb_ofar)</td>
</tr>
</tbody>
</table>

Table C.9. Pb L₃-edge powder EXAFS fit parameters. Fe concentration (Fe x), the number of multiple scattering paths included in the fit (MSP) and goodness of fit parameters are listed in the table.

<table>
<thead>
<tr>
<th>Fe x</th>
<th>MSP</th>
<th>R-factor</th>
<th>Reduced χ²</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0.021</td>
<td>8084</td>
</tr>
<tr>
<td>0.01</td>
<td>0</td>
<td>0.022</td>
<td>10205</td>
</tr>
<tr>
<td>0.025</td>
<td>0</td>
<td>0.025</td>
<td>10734</td>
</tr>
<tr>
<td>0.05</td>
<td>0</td>
<td>0.028</td>
<td>11054</td>
</tr>
<tr>
<td>0.075</td>
<td>0</td>
<td>0.029</td>
<td>9948</td>
</tr>
<tr>
<td>0.1</td>
<td>0</td>
<td>0.033</td>
<td>9883</td>
</tr>
<tr>
<td>0.125</td>
<td>0</td>
<td>0.033</td>
<td>10394</td>
</tr>
<tr>
<td>0.15</td>
<td>0</td>
<td>0.031</td>
<td>7724</td>
</tr>
<tr>
<td>0.2</td>
<td>0</td>
<td>0.035</td>
<td>10333</td>
</tr>
</tbody>
</table>
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