# **Structure Correlated Ferroelectricity and Other Properties of Perovskite PbTiO<sub>3</sub>-Based Ceramics**

Ph.D. Thesis

By

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# DISCIPLINE OF METALLURGY ENGINEERING AND MATERIALS SCIENCE INDIAN INSTITUTE OF TECHNOLOGY INDORE

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# **Structure Correlated Ferroelectricity and Other Properties of Perovskite PbTiO<sub>3</sub>-Based Ceramics**

## A THESIS

Submitted in partial fulfillment of the requirements for the award of the degree of DOCTOR OF PHILOSOPHY

> by ARUN KUMAR YADAV



# DISCIPLINE OF METALLURGY ENGINEERING AND MATERIALS SCIENCE INDIAN INSTITUTE OF TECHNOLOGY INDORE September, 2018



# INDIAN INSTITUTE OF TECHNOLOGY INDORE

### **CANDIDATE'S DECLARATION**

I hereby certify that the work which is being presented in the thesis entitled "Structure Correlated Ferroelectricity and Other Properties of Perovskite PbTiO<sub>3</sub>-Based Ceramics" in the partial fulfillment of the requirements for the award of the degree of DOCTOR OF PHILOSOPHY and submitted in the DISCIPLINE OF METALLURGY ENGINEERING AND MATERIALS SCIENCE, Indian Institute of Technology Indore, is an authentic record of my own work carried out during the time period from July, 2014 to May 2018 under the supervision of Dr. Somaditya Sen, Associate professor, and Dr. Parasharam M. Shirage, Associate Professor, IIT Indore.

The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other institute.

## Signature of the student with date (Arun Kumar Yadav)

This is to certify that the above statement made by the candidate is correct to the best of my/our knowledge.

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ARUN KUMAR YADAV has suc	ccessfully given his Ph.D. Oral Exa	mination held on <b>06 September 2018</b> .	
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Signature of PSPC Member #1 Date:	Signature of PSPC Member #2 Date:	Signature of Convener, DPGC Date:	
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Arun Kumar Yadav

# DEDICATED TO MY PARENTS

#### LIST OF PUBLICATIONS

#### 1. From Thesis work: Journal Publications

- I. **A.K. Yadav**, P. Rajput, O. Alshammari, M. Khan, Anita, G. Kumar, S. Kumar, P.M. Shirage, S. Biring, S. Sen, Structural distortion, ferroelectricity and ferromagnetism in  $Pb(Ti_{1-x}Fe_x)O_3$ , Journal of Alloys and Compounds, 701 (2017) 619-625.
- II. A.K. Yadav, Anita, S. Kumar, V.R. Reddy, P.M. Shirage, S. Biring, S. Sen, Structural and dielectric properties of Pb<sub>(1-x)</sub>(Na<sub>0.5</sub>Sm<sub>0.5</sub>)<sub>x</sub>TiO<sub>3</sub> ceramics, Journal of Materials Science Materials in Electronics, 28 (2017) 10730-10738.
- III. A.K. Yadav, Anita, S. Kumar, A. Panchwanee, V.R. Reddy, P.M. Shirage, S. Biring, S. Sen, Structural and ferroelectric properties of perovskite Pb<sub>(1-x)</sub>(K<sub>0.5</sub>Sm<sub>0.5</sub>)<sub>x</sub>TiO<sub>3</sub> ceramics, RSC Advances, 7 (2017) 39434-39442.
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#### 2. From other work: Journal Publications

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- II. Anita Verma, A. K. Yadav, N. Khatun, S. Kumar, C.-M. Tseng, S. Biring, S. Sen, Size and strain dependent anatase to rutile phase transition in TiO<sub>2</sub> due to Si incorporation, Journal of Materials Science Materials in Electronics., 28 (2017) 19017-19024.
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- II. A. Verma, A. K. Yadav, S. Kumar, S. Sen, Lead free dielectric ceramic with stable relative permittivity of 0.90(Na<sub>0.50</sub>Bi<sub>0.50</sub>Ti)O<sub>3</sub>-0.10AgNbO<sub>3</sub>, AIP Conf. Proc., 1942 (2018) 030024.

- III. M. Kumar, A. K. Yadav, Anita Verma, S. Sen, S. Kumar, Lithium ion conduction in sol-gel synthesized LiZr<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> polymorphs, AIP Conf. Proc., 1942 (2018) 140026.
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- V. A. K. Yadav, Anita, Sunil Kumar, Parasharam M. Shirage, Somaditya Sen, "Structural and dielectric properties of A-site modified perovskite Pb<sub>(1-x)</sub>(Na<sub>0.5</sub>Sm<sub>0.5</sub>)<sub>x</sub>TiO<sub>3</sub>"International Conference on Technologically Advanced Materials and Asian Meeting on Ferroelectricity (ICTAM-AMF10\_7-11 Nov 2016), New Delhi, India, poster presentation.
- VI. A. K. Yadav, Anita Verma, Sunil Kumar, Velaga Srihari, Somaditya Sen, "Structural and ferroelectric property of (1x)PbTiO<sub>3</sub>-(x)LaAlO<sub>3</sub> ceramics" in 6<sup>th</sup> International symposium on Integrated Functionalities (ISIF-2017), held during 10-13 December, 2017 at Shangri-La's Eros, New Delhi, India, poster presentation.
- VII. A. K. Yadav, Anita Verma, Sunil Kumar, Somaditya Sen, "Structure, dielectric and ferroelectric properties of K/Sm modified perovskite PbTiO<sub>3</sub>" International Workshop on Advanced Nanoscience and Engineering 1<sup>st</sup> December 2017, IIT Indore, India, poster presentation.
- VIII. Anita Verma, A. K. Yadav, Sunil Kumar, Velaga Srihari, Somaditya Sen "Effect of grain size on dielectric property of Na<sub>0.47</sub>Bi<sub>0.47</sub>Ba<sub>0.06</sub>TiO<sub>3</sub> ceramic" International symposium on Integrated Functionalities (ISIF-2017), held during 10-13 December, 2017 at Shangri-La's Eros, New Delhi, India.

- IX. Anita Verma, A. K. Yadav, Nasima Khatun, Sunil Kumar, A.K. Sinha, Somaditya Sen, "Structural, dielectric and ferroelectric properties of lead-free piezoelectric 0.90(Na<sub>0.50</sub>Bi<sub>0.50</sub>Ti)O<sub>3</sub>-0.10AgNbO<sub>3</sub> ceramic" International symposium on Integrated Functionalities (ISIF-2017), held during 10-13 December, 2017 at Shangri-La's Eros, New Delhi, India.
- X. Anita Verma, A. K. Yadav, Nasima Khatun, Sunil Kumar, Somaditya Sen, "Study of structural, dielectric and ferroelectric properties of lead-free piezoelectric (Na<sub>0.50-x</sub>K<sub>x</sub>Bi<sub>0.50-x</sub>La<sub>x</sub>Ti)O<sub>3</sub> ceramics" International Workshop on Advanced Nanoscience and Engineering 1st December 2017, IIT Indore, India
- XI. Anita Verma, A. K. Yadav, Sunil Kumar, Parasharam M. Shirage, Somaditya Sen, "Influence of V<sup>5+</sup> doping on structure, microstructure and electrical properties of 0.94(Na<sub>0.5</sub>Bi<sub>0.5</sub>TiO<sub>3</sub>)-0.06(BaTiO<sub>3</sub>) lead-free ceramics" International Conference on Technologically Advanced Materials and Asian Meeting on Ferroelectricity (ICTAM-AMF10\_7-11 Nov 2016), New Delhi, India.

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# Abbreviations

Lead Titanate					PbTiO <sub>3</sub>
X-ray Diffract	XRD				
Synchrotron	Radiation	Source	Powder	X-ray	SRPXRD
Diffraction					
X-ray Absorpt	XANES				
Extended X-ra	EXAFS				
Tolerance Fac	t				
Field Emission	FESEM				
Energy Disper	EDS				
Dielectric Con	٤'				
Remnant Pola	$P_r$				
Coercive Field	$E_c$				
Oxygen Vaca	Vo				
Polarization ve	P-E				
Instantaneous	I-E				
Full Width Ha	FWHM				
$Pb_{(1-x)}(K_{0.5}Sm_{0.5})_xTiO_3$					PKST
$Pb_{(1-x)}(Na_{0.5}Sm_{0.5})_{x}TiO_{3}$					PNST
PbTi <sub>(1-x)</sub> Fe <sub>x</sub> TiC	PTFO				
$Pb_{(1-x)}La_{x}Ti_{(1-x)}$	PLTA				
$Pb_{(1-x)}Bi_xTi_{(1-x)}$	PBTM				
Volume	V				
Negative Ther	NTE				

## **Chapter 1**

### Introduction

#### **1.1 Introduction and Background**

Throughout history, technology has widely facilitated human development. Each technological innovation has marked an approach to change in human behavior and physical capabilities, which in turn, allowed for further technological innovations. Materials has technology too has exercised an intense impact on the evolution of human civilization. Historians have defined the various time periods in the human history distinctly as the Stone Age, Bronze Age, the Iron Age and Silicon or the Synthetic materials Age. Each era followed by another has been brought about by the invention of even better products. The beginning of the 21<sup>st</sup> century has already witnessed the emergence of the 'Smart Materials Age'. It has been categorized by a technological revolution that will exploit several emerging technologies such as materials science, biotechnology, biomimetic, nanotechnology, molecular electronics, and artificial intelligence. By developing state-of-the-art technologies in diverse fields of sciences, today's engineers, chemists, physicists and materials scientists are devising innovative inter-disciplinary techniques for synthesizing, analyzing, and manufacturing new generations of engineered materials. Smart materials systems are non-living systems that incorporate the utilities of actuation, sensing, logic, and monitor to respond adaptively to changes in their environment to which they are exposed, in a useful and usually repetitive manner. The smart materials are part of the smart system-functional materials for a variety of engineering applications. They possess both sensing and actuating functions. Many existing engineering materials can be engaged as sensor and actuator materials if they can be correctly designed. They include piezoelectric ceramics and polymers, shape memory alloys, optical fibers and conductive, etc. Each system can suit specific potential requirements of future smart materials systems. In this chapter, the general features of piezoelectric and ferroelectric materials are discussed. The chapter covers a brief historical introduction which includes the macroscopic and microscopic aspects of ferroelectricity/piezoelectricity.

#### **1.2 Perovskites**

 $CaTiO_3$  was discovered as a mineral in 1939 by Gustav Rose from the Ural Mountains. The structure of this mineral [Figure 1.1] was named after Russian mineralogist Lev Perovski as perovskite.



*Figure 1.1:* A schematic unit cell structure of  $CaTiO_3$  where Ca, Ti, and O representative is shown in the schematic figure.

Perovskite oxides, with chemical formula ABO<sub>3</sub>, are a wide range of compounds. It has a larger twelve-coordinated A cation and a smaller six-coordinated B cation. The structure is commonly represented by a cuboid unit cell with A cations at the corners, and Bcations at the centre, while the O anions are located around the central point of each face. This creates a BO<sub>6</sub> octahedron at the center of the unit cell. The distortion of this octahedron often leads to ferroelectricity. Tilting of the BO<sub>6</sub> octahedra reduces the coordination of an undersized A cation from 12 to as low as 8. Lattice distortions in perovskite crystals arise out of off-centered ionic displacements and order-disorder transitions which generate reversible spontaneous polarization [1]. Ferroelectric/piezoelectric materials are recognized as excellent sensors and actuators due to their cost-effectiveness and design flexibility with excellent functionalities [2, 3]. Industrial applications of piezoelectric are found in ultrasonic nondestructive devices, fuel injection valves, and piezoelectric motors, etc. Hence, they are essential components of civil, aerospace, mining, automotive industries, etc., [4]. Usage has increased exponentially in the last decade. With switchable spontaneous polarization, ferroelectrics are the soul of piezoelectric transducers and sensors. Ferroelectrics are also core parts of many energy conversion devices, such as ultrasonic medical diagnostic apparatus, ultrasonic nondestructive detectors, pyroelectric infrared sensors and magnetoelectric sensors. Amongst the various ferroelectrics, perovskites are technologically the most prominent due to their strong polarization, good response and multiple phases [5]. A-site cations can be monovalent (K, Na, Li, etc.), divalent (Pb, Ba, Sr, Ca, etc.), or trivalent (Bi, La, Sm/, etc.). B-sites can be trivalent (Fe, Mn, etc.), tetravalent (Ti, Ce, etc.), and pentavalent (V, W, Ta, Nb, etc.). Ideal perovskite is a cubic structure. Replacements or substitutions generates lattice strain and deviates from the cubic structure. This deviation from the ideal cubic structure is estimated by Goldschmidt tolerance factor [37, 38] (*t*):

$$t = \frac{(R_A + R_O)}{\sqrt{2}(R_B + R_O)}.$$
(1.1)

where,  $R_A$ ,  $R_B$ , and  $R_O$  are the ionic radii of A-site, B-site, and O ions respectively. For ideally closed cubic perovskite structure, tolerance factor is one. There are three main factors which lead to deviation from the ideal cubic structure: tilting of BO<sub>6</sub> octahedra, displacement of A/B-site cations from the centers of octahedra, and displacement of anion octahedra. Displacements of the cations and distortions of the octahedra are correlated and driven by electronic instabilities of cations. As tolerance factor decreases, the *A*-site becomes too small for the cuboctahedral site. When octahedron tilting occurs, it has the effect of reducing the volume and improving the stability of the structure. The room-temperature perovskite structure with 0.985 < t < 1.06 are expected to have untilted perovskite. Perovskites with 0.964 < t < 0.985 are usually tilted in anti-phase type and perovskites with t < 0.964 are predicted to show in-phase and anti-phase tilting. Tolerance factor continues to decrease, the stability of the perovskite phase decreases and eventually, perovskites will not form [6]. Perovskite structures can also be of other kinds:

- (a) Double perovskites  $(AA'B_2O_6)$  or  $(A_2BB'O_6)$
- (b) Layered perovskites which are of three types
  - (i) Dion Jacobson (A[A'<sub>n</sub>B<sub>n</sub>O<sub>3n+1</sub>])
  - (ii) Ruddlesden Popper ( $A_2[A_{n1}B_nO_{3n+1}][AO][ABO_3]n$ )
  - (iii) Aurivillius ([BiO<sub>2</sub>][A<sub>n-1</sub>MnO<sub>3n+1</sub>])

Practical benefits of a perovskite structure are that different cations can be substituted for both A and B-sites in ABO<sub>3</sub> perovskite structure without changing the complete structure. Complete solid solutions can be formed between many combinations of cations. Hence, manipulation of these materials leads to different functionalities including ferroelectric properties.

#### **1.3 Lead Titanate (PbTiO<sub>3</sub>)**

Pure PbTiO<sub>3</sub> belongs to a perovskite ABO<sub>3</sub> type family. At room-temperature, PbTiO<sub>3</sub> is a ferroelectric material with tetragonal structure  $C_{4v}^1$  (P4mm) space group as shown in Figure 1.2a. Pure PbTiO<sub>3</sub> is not commercially used as a piezoelectric material due to practical problems of making a sintered pellet or single crystal. However, it can be modified to form solid solutions with other elements for obtaining materials with excellent piezoelectric properties. PbTiO<sub>3</sub> undergoes structural first order phase transition at 763 K into cubic  $O_h^1$  (Pm3m) paraelectric structure as shown in Figure

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1.2 (a-b). The phase transition behavior is of displacive nature as the central Ti atom and the oxygen atoms are displaced from their centrosymmetric position of the cubic form [7]. One of the perovskites, BaTiO<sub>3</sub> is widely studied among ferroelectric materials. Although PbTiO<sub>3</sub> is isomorphous at room temperature with BaTiO<sub>3</sub> ceramic, there are important differences between these ferroelectric materials. The lattice constant of PbTiO<sub>3</sub> at room-temperature are a = b = 3.902Å and c = 4.156 Å. This gives a c/a ratio of 1.06 whereas, for BaTiO<sub>3</sub>, c/a ratio is 1.01. Hence, PbTiO<sub>3</sub> has more tetragonal distortion than BaTiO<sub>3</sub>. In tetragonal  $PbTiO_3$  phase, the position of the ions may be described by keeping the Pb ion at the origin (0, 0, 0), Ti ions (0.5, 0.5, 0.5)0.5+dz1), O1(0.5, 0.5, dz2), and O2(0.5, 0, 0.5+dz3) for Rietveld refinement. Displacement of Ti and O atoms from the ideal cubic position is denoted by dz. The shifting of Ti and O in the PbTiO<sub>3</sub> system is in the same direction whereas BaTiO<sub>3</sub> is in the opposite direction from the cubic system.



*Figure 1.2:* Schematic diagram of  $PbTiO_3$  structures, where (a) Tetragonal, and (b) Cubic structure is shown after phase transition at 763 K temperature.

The covalent character of Pb and its significant feature in ferroelectric/piezoelectric properties have been widely discussed in the literature of PbTiO<sub>3</sub> and based compounds. Cohen [5] has elaborated the difference in PbTiO<sub>3</sub> and lead-free perovskites (BaTiO<sub>3</sub>, KNbO<sub>3</sub>) properties. It has been shown that in PbTiO<sub>3</sub>, the hybridization between
*Ti-O* and *Pb-O* are important contributions towards ferroelectricity by weakening short-range repulsions. A weakening of this hybridization reduces the ferroelectricity in the PbTiO<sub>3</sub>.  $Pb(6s^2)$  states hybridize with the O(2p) and Ti(3d) to O(2p) states. This hybridization makes PbTiO<sub>3</sub>-based materials important as ferroelectrics. Since it is difficult to grow single crystals of PbTiO<sub>3</sub> of a size suitable for measurements; there have been relatively few attempts to systematically study dielectric, elastic, and piezoelectric properties of this crystal. A few complicated, experimental studies exhibit large conductivity, possibly related to high concentrations of Pb vacancies. The most relevant difference between PbTiO<sub>3</sub> and other perovskite ferroelectrics is a low anisotropy of permittivity and relatively low shear piezoelectric coefficients in PbTiO<sub>3</sub>. PbTiO<sub>3</sub> has many important technological applications in electronics and microelectronics due to its high spontaneous polarization, Curie temperature, and pyroelectric coefficient [8, 9]. Ferroelectric PbTiO<sub>3</sub> films deposited onto various substrates has proven advantageous in memory applications, field effect devices and pyroelectric detectors which have stimulated technological interest in this field of study.

### **1.4 Literature survey**

Lead titanate (PbTiO<sub>3</sub>) is widely known as a classical ferroelectric ceramic material which possesses excellent useful dielectric, pyroelectric, piezoelectric properties and belongs to the ABO<sub>3</sub> perovskite group. At room-temperature, PbTiO<sub>3</sub> has tetragonal structure. The PbTiO<sub>3</sub> perovskite structure when combined with other perovskites, forms many crystalline solutions such as Pb(Mg<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub>-Pb(Mg<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub>-xPbTiO<sub>3</sub>,Ba(Mg<sub>1/3</sub>-Nb<sub>2/3</sub>)O<sub>3</sub> $xPbTiO_3$ ,  $Ba(Zn_{1/3}Nb_{2/3})O_3 - xPbTiO_3$ ,  $Ba(Yb_{1/2}Nb_{1/2})O_3 - xPbTiO_3$ ,  $Ba(Sc_{1/2}Nb_{1/2})O_3 - xPbTiO_3$ ,  $BaSnO_3-xPbTiO_3$ , (1-x)PbTiO<sub>3</sub> $xBi(Zn_{1/2}Ti_{1/2})O_3$ ,  $(1-x)PbTiO_3 - xBi(Ni_{1/2}Ti_{1/2})O_3$ ,  $Pb(In_{1/2}-Nb_{1/2})O_3 - D_3$ Pb(Mg<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub>-PbTiO<sub>3</sub>, PbHfO<sub>3</sub>-Pb(Mg<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub>-PbTiO<sub>3</sub>, Pb(Sn,  $TiO_3-Pb(Mg_{1/3}Nb_{2/3})O_3-xPbTiO_3,$ Pb(Ho<sub>1/2</sub>Nb<sub>1/2</sub>)O<sub>3</sub>- Pb(Mg<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub>–PbTiO<sub>3</sub>, Pb(Y<sub>1/2</sub>Nb<sub>1/2</sub>)O<sub>3</sub>-Pb(Mg<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub>-PbTiO<sub>3</sub> and (1-x)PbTiO<sub>3</sub>-xBiFeO<sub>3</sub> etc., [10-17]. These PbTiO<sub>3</sub>-based materials are families of ferroelectric, paraelectric, anti-ferroelectric, and several other properties, etc. and have applications as capacitors, actuators, energy harvesting and sensors among several others. The physical properties of PbTiO<sub>3</sub> can be significantly modified with the help of substitution on the sites of Pb as well as Ti with suitable ionic radii and valency. The perovskite oxides have attracted significant attention due to their diverse physical properties and related practical applications in electronics. In the present time, a significant interest has emerged in the area of the ferroelectric/piezoelectric field due to dynamic random access memories (DRAMs), capacitors, non-volatile random access memories (RAMs), infrared sensors, piezoelectric actuators, shutters, optical modulators, colossal magneto-resistance, uncooled infrared detectors, microwave, magneto-optic and electrooptic devices, etc. PbTiO<sub>3</sub> perovskite structure has structural phase transition from ferroelectric to paraelectric phase at 763 K temperature. Suitable substitution at Pb or Ti site may shift the structural phase transition and consequently makes the materials necessary for device application at the desired temperature.

A.P. Barranco suggested [18] that *A*-site doping of PbTiO<sub>3</sub> reduces its remarkable tetragonality but yet can maintain ferroelectric properties for practical applications. It was found that rare earth doping of PbTiO<sub>3</sub> conserve electromechanical anisotropy and restores ferroelectric properties [19, 20]. The impressive range of structures and property interaction of perovskites endows them with outstanding potential for research in the fields of physics, materials science, and solid state chemistry, etc. Owing to the flexibility of the bond length and angles, myriad types of lattice distortion can occur in the different perovskite structure. A wide range of novel functional materials and device perceptions can be imagined through the fundamental understanding of the relationship between the structural, chemical, thermal, solid solubility, and lattice strain, etc. More explorations in these exciting fields also may not exhaust the different aspects of

perovskite materials. Ikegami et al. reported [21] that PbTiO<sub>3</sub> developed excellent piezoelectric properties by the combination of La and Mn substitution, and that ceramics are very good for resonator applications. Hiroshi et al. investigated electromechanical properties of modified PbTiO<sub>3</sub> ceramics with formula  $(Pb/R)(Ti/Mn)O_3$  where R =La, Pr, Nd, Sm, or Gd, were rare-earth elements [19]. In these systems,  $Mn^{3+}$  substituted  $Ti^{4+}$  (investigated with ESR studies), while  $R^{3+}$ substituted  $Pb^{2+}$ . These substitutions were intentionally prescribed to maintain electrical neutrality of the lattice. An electromechanical coupling factor was discussed between a thickness dilatational mode and planar extensional mode in this system. It was found that Sm substitution for Pb dramatically increases this electromechanical coupling factor. In the same group of samples some work was reported on surface acoustic-wave delay time [22-24]. Gurgel et al. [25] reported that Sm modified PbTiO<sub>3</sub> could be used to improve mechanical and electromechanical properties and also improve sintering capabilities. Structural characteristics are changed, due to incorporation of Sm in  $PbTiO_3$  and depend on Sm content. This also modifies lattice tetragonality and induces tetragonal to cubic phase transition and coercive field values. Paris *et al.* [26] correlated the O(2p) and Ti(3d)orbital behavior from density of states (DOS) calculations with the vibrational properties of (*Pb/Sm*)TiO<sub>3</sub>. Sun *et al.* have suggested [27] that, usually the spontaneous polarization decreases with doping Fe, Zr, Hf, etc. at Ti-site in PbTiO<sub>3</sub>. On the other hand, the effect of aliovalent  $Al^{3+}$  at the same *Ti*-site increases the spontaneous polarization. In Al-doped PbTiO<sub>3</sub> samples, the strong Pb6s-O2p hybridization was strengthened. Intensification of both the  $A_1$ transverse optical Raman modes and the stretching and bending vibration FTIR modes further signifies the increase of spontaneous polarization in the A and B-sites. Yilin Wang et al. has reported [28] NdFeO<sub>3</sub>-PbTiO<sub>3</sub> for x = 0.10 thin films prepared by sol-gel route. Thin films oriented along (100) direction show defect-dipoles induced cdomains at 150 °C, which is lesser than 345 °C (phase transition temperature from tetragonal to cubic phase). Such a phenomenon was ascertained by constant absence of (001) XRD peak at any temperature, hinting that *c*-domains are not triggered by lattice reorientation.

Solid solutions  $AB'_{1-x}B''_xO_3$  with perovskite structure represent a well-studied class of materials. Multiferroic properties were first observed within this class in the 1950s. A great number of ferroelectrics and substances with magnetic ordering have perovskitelike structure. Perovskite-like compounds (ABO<sub>3</sub>) typically have a large internal field which is necessary for appearance of ferroelectric state. At the same time, "cation B-oxygen-cation B" angle  $\simeq 180^{\circ}$ . This is an optimal condition for appearance of magnetic ordering in the *B* sub-lattice, owing to an indirect exchange interaction. Therefore in compounds of perovskite structures, one may expect coexistence of electric and magnetic ordering [29]. Stoupin *et al.* reported [30] substitution of *Ti* by *Mn* up to 20 mol % in PbTiO<sub>3</sub> without additional charge-compensation of A-site substituent. With the help of XANES spectra, a mixed phase of  $Mn^{3+}$  and  $Mn^{4+}$  charge states was observed. These samples were found to be weakly ferromagnetic below 50 K.

In the past, it was considered that the electrical properties are dependent on the particle size of the samples [31-33]. However, due to requirement of miniaturization of measurement devices, individual elements are required to be smaller and smaller. This is particularly important in electrical measurement systems related to ferroelectric properties. Particularly, for nano-sized grains, ferroelectric properties can be affected by many factors. As a result, the effect of grain size on ferroelectric properties has attracted considerable attention. Particle size effects on the ferroelectric phase transition behaviour were extensively investigated by theoretical as well as experimental studies. It is well known that small ferroelectric properties show different dielectric properties in case of thin film to that of bulk samples. This is due to the long-range Coulomb force [34]. Chattopadhyay et al.[35] revealed particle size dependence on phase transition behavior in PbTiO<sub>3</sub> ceramics. Tetragonal distortion in perovskite titanates is related to spontaneous polarization. This distortion decreases exponentially with particle size, *d*. With the reducing size of the particle, transition temperature gradually reduces. Thus, an increasingly diffuse type of phase transition below an average particle size is observed. For PbTiO<sub>3</sub> this particle size is  $d \le 80$  nm. Below  $d \sim 30$  nm, dielectric properties and DSC studies do not show structural transitions. Tetragonal distortion (*c*/*a* ratio) decreases exponentially with particle size and is unity at  $d \sim 5-7$  nm, which is the critical size for ferroelectricity in the samples [34, 36, 37]. Similarly other perovskite materials also reveal such phase transition behavior and ferroelectric properties [38, 39].

## **1.5 Motivation**

PbTiO<sub>3</sub>-based perovskite materials have many technological applications: capacitors, dielectric resonator, piezoelectric transducers, thin film resistor, hydrogen sensors, switch magnetic bubble memory, and electrostrictive actuators, etc. These types of properties operating in different environments are required for contemporary technology. So for these applications, PbTiO<sub>3</sub>-based materials can be modified to enhance functionalities by proper substitution with alkali, rare-earth, and transition materials. Even today in the age of bio-safety, these lead-based complex perovskite compounds and their solid solutions continue to be important and irreplaceable due to a variety of physical properties and a wide range of industrial applications.

Depending on ionic radii and ionic charges, ordering of cations may occur which gives rise to different structural and physical properties. Considerable amount of work has been carried out on *A*site, *B*-site, and *A*/*B*-site in ABO<sub>3</sub> type PbTiO<sub>3</sub> perovskite with different substituent. However, annealing processes are often accompanied with undesirable secondary phases such as oxides of substituent or non-ferroelectric pyrochlore phases. In recent years, hence a lot of attention is being focused at pure phase, *A*, *B*, and *A*/*B*site substitution in perovskite lattices.

There are no detailed study of a mixed A-site substitution of a rare earth and alkaline element such as  $(Na_{0.5}Sm_{0.5})$  and  $(K_{0.5}Sm_{0.5})$  at

the *Pb*-site with approximately the same ionic size and equal charge.  $Pb_{(1-x)}(K_{0.5}Sm_{0.5})_xTiO_3$  (x = 0, 0.06, 0.09, 0.12, 0.18, 0.25, 0.31, 0.37, and 0.50) and  $Pb_{(1-x)}(Na_{0.5}Sm_{0.5})_xTiO_3$  (x = 0, 0.10, 0.20, 0.30, 0.40, and 0.50) samples were prepared with sol-gel combustion method. A temperature-dependent structural and dielectric property study reveals correlation of structure and electrical properties. It also allows us to explore the variation in phase transition with changing substitution.

There are no systematic reports on PbTi<sub>1-x</sub>Fe<sub>x</sub>O<sub>3</sub> (x = 0, 0.03, 0.06, 0.09, 0.12, 0.18, 0.25, 0.31, 0.37, 0.43, and 0.50) with detailed study of structure associated with XANES/EXAFS, ferroelectric and ferromagnetic properties. Although some reports are available on the same compounds, they have secondary phases of pyrochlore, which is one of the big questions of magnetic properties. In our present study, we have used sol-gel combustion method. No secondary phase was found in any of the samples. These samples are multiferroics at room temperature.

There are many reports on La and Al modifications at A-site and *B*-site of PbTiO<sub>3</sub> ceramics separately. La is in  $La^{3+}$  state, while Al is in  $Al^{3+}$ . This creates charge imbalance in the lattice. However, very important functionalities are obtained by individual substitution of these two elements. Al at B-site helps increase tetragonality, while La at the A-site produces relaxor behavior. We wanted to check whether these properties are prevailing with simultaneous substitution at both sites. It should be noted that by substituting  $La^{3+}$  at the A-site and  $Al^{3+}$ at the B-site charge balance is maintained. To the best of our knowledge, there are no reports on La, and Al substituted in PbTiO<sub>3</sub> ceramics. Another A/B-site modification with Bi/Mn such as (Pb<sub>(1-</sub>  $_{x}Bi_{x}(Ti_{(1-x)}Mn_{x})O_{3}$  (x = 0, 0.06, 0.09, 0.12, 0.18, 0.25, 0.31, 0.34, 0.37, and 0.50) were similarly prepared. Independent Bi substitution results if very complex oxide structures may be due to volatility of both *Pb* and *Bi*. The charge of *Bi*, i.e.  $Bi^{3+}$  may be another good reason of incompetence. Mn-substituted PbTiO<sub>3</sub> bears the same problems. A solubility of ~20 % is observed in literature. Although not a room

temperature magnetic material, Mn substituted PbTiO<sub>3</sub> shows weak ferromagnetism at lower temperatures. On the other hand BiMnO<sub>3</sub> shows interesting physics at low temperatures. BiMnO<sub>3</sub> should be a type-II multiferroic, and ferromagnetic and ferroelectric orderings could coexist. However, by simultaneous substitution, we expected to take care of the charge imbalance in the lattice, as well as explore the chances of obtaining better multiferroic properties.

### **1.6 Ferroelectricity**

Ferroelectricity is an acronym to ferromagnetism, the former being related to electric polarization while the latter to magnetization. The word Ferro is derived from the word Ferum, which means iron in Latin. The term "Ferro" actually suits better to ferromagnetism than ferroelectricity because iron is associated to ferromagnetism due to the special type of spin arrangement of iron atoms but is in no way related to ferroelectricity. Similarities between ferroelectric and ferromagnetic materials are between a spontaneous polarization and a remnant magnetization for zero applied electric or magnetic fields below a phase transition temperature. Hence hysteresis loops and mechanical strains are generated with applied electric field. Nevertheless, ferroelectrics are different from ferromagnetic in their fundamental mechanism and also in some of their applications. Europe refers ferroelectrics as Seignette electrics. During the 17th century Pierre Seignette, of La Rochelle, France discovered Rochelle salt (potassiumsodium tartrate tetra hydrate), a colorless crystalline compound with an orthorhombic structure. This material was used as a laxative at that time. After 200 years, in 1921 Valasek [40], obtained hysteresis curves for Rochelle salt; same as the B-H curves of ferromagnetism, and also studied the piezoelectric response of the crystal. For the next 15 years, ferroelectricity was accepted as a very important property of Rochelle salt. After that, Busch and Scherrer discovered ferroelectricity in KH<sub>2</sub>PO<sub>4</sub> and its sister crystals in 1935. During World War II, abnormal dielectric properties were discovered in ceramics by Wainer and Solomon in the USA in 1992; by Ogawa in Japan in 1944; and by Wul

and Goldman in Russia in 1946. After that, many ferroelectrics have been investigated, and research has rapidly increased in this field. There are more than 1000 solid materials recognized at present that possess ferroelectric properties.

Ferroelectric materials are a sub-group of pyroelectric materials. In these materials, spontaneous polarization can be switched upon the application of an applied electric field (by changing the vector orientation of the electric dipole). We cannot determine whether a material will exhibit ferroelectric ordering by the knowledge of the crystal class alone. Switching off electrical polarization of the materials can be determined and plotted with a varying field to yield a hysteresis loop. After the application of an electric field, the individual dipoles of the material align with the electric field lines. This ensures spontaneous polarization to align in the direction of the electric field. After removal of the electric field, the spontaneous polarization does not disappear. This amount of polarization is called remnant polarization. Application of certain strength of electric field will reverse, to give net polarization.



*Figure 1.3:* (a) Ferroelectric polarization is shown in hysteresis loop,(b) Ferroelectric polarization hysteresis shape at different voltages.

Experimentally, we can examine the ferroelectric properties in the samples, with the help of applied *ac* electric fields that corresponds to polarization in the materials, taking the form of hysteresis loop as shown in Figure 1.3 (a-b). Starting at zero electric field (E = 0), polarization is zero. This is because, macroscopically, samples have multiple domains canceling each other. As the applied electric field increases, the polarization also increases simultaneously and reaches a saturation value. The ferroelectric domains being oriented along the applied electric field, on further increasing the electric field, a small increment in polarization happens due to the dielectric charging effect. If the electric field is decreased at this point, the curve does not follow the same path. The total polarization decreases with the decrease of electric field but is not zero at the zero electric field. The value of polarization at zero electric fields is called the remnant polarization  $(P_r)$ . Further increase of electric field in a negative direction will provide a similar saturation polarization but in a reverse direction. In between a zero remnant polarization is obtained for a particular field known as coercive field  $(E_c)$ . Similar process repeats again, when the electric field is reversed. Repeated cycles of the same process yield symmetric hysteresis loop. Ideally, saturation polarization should be equal to remnant polarization. But, saturation polarization is often higher than remnant polarization in polycrystalline materials. In polycrystalline materials formation of reverse domains happens during the reverse ramping of the electric field to zero. But in a perfect single crystal, the absence of single direction arrangement of unit cell and presence of domain boundaries between crystallites reverse domains are not observed [41, 42]. Figure 1.3b shows ferroelectric hysteresis loops at different voltages. Proper ferroelectric hysteresis loop is obtained at an optimum voltage at which all the domains will switch in the same direction. J. F. Scott has discussed in 'Ferroelectrics go bananas' about the proper ferroelectric loop and misleading ferroelectric loop in a sample [43]. A proper ferroelectric loop looks sharp and closed at the saturation point of the maximum applied field. Ferroelectric property is applicable for the creation of a 1/0 binary state, where each direction of spontaneous polarization represent either "ON" or "OFF" state. Application of a directional electric field can be used to switch between the states.

### **1.7 Piezoelectricity**

In piezoelectricity, the prefix piezo- is derived from the Greek word piezein, meaning pressure. Piezoelectric are materials in which electricity can be generated by an application of mechanical stress. The reverse is also true. Mechanical stress can also be produced by an applied electric field. This convertible behavior (electric to mechanical stress vice versa) was first discovered by Pierre and Jacques Curie in 1880 in some crystals, such as quartz, tourmaline, and Rochelle salt. The word piezoelectricity has been used by the scientists since 1881 to discriminate the piezoelectric phenomena from electrostriction. The direct piezoelectric effect is known as the ability to convert mechanical to electrical energy also known as generator or transducer effect while the converse piezoelectric effect describes the ability to transform electrical to mechanical energy known as motor/actuator effect [44] According to the description of 'direct piezoelectric effect', when a mechanical strain is applied to piezoelectric material by an external stress, an electric charge occurs on the surface(s) of the piezoelectric material and the polarity of this observed electric charge on the surface(s) can be reversed by reversing the direction of the mechanical strain applied as shown in Figure 1.4 (a-c). On the other hand, according to the explanation of 'converse piezoelectric effect,' when an electric field is applied to a piezoelectric material subjected to an electric field, a mechanical deformation on the surface is observed which is seen as a change in dimensions of the piezoelectric material. The direction of mechanical strain can also be changed by changing the applied electric field and vice-versa.





**Figure 1.4:** A schematic diagram of piezoelectric effect where (a) Piezoelectric material, (b) Energy generation under tensile stress, and (c) Energy generation under compressive strain.

The phenomenon of piezoelectricity can also be described as the motion of ions inside certain crystalline structures, leading to a variation of dipolar moment. In presence of a centre of symmetry, no dipoles are present, and thus no piezoelectricity can be found. The applied stress to a polar crystal will contribute to already existing spontaneous piezoelectric polarization. In polar-neutral crystals, with the exception of 432 groups, the effect of external mechanical stress is to generate a single polar direction. A graphical example is given in Figure 1.5.



# *Figure 1.5: Piezoelectric effect in polar-neutral symmetries explained with a simple molecular mode.*

According to the converse piezoelectric effect, the strain is linearly proportional to the applied electric field when the piezoelectric

coefficient is constant. When the electric field is parallel to the polarization, strain increases with increase of electric field strength and the maximum strain occurs at maximum electric field. However, polarization switching in ferroelectrics subjected to an electric field leads to electromechanical hysteresis, as shown in Figure 1.6. The loop shows piezoelectric response as well as polarization switching under a bipolar electric field. The sign of strain depends on the relative directions of the polarization and the electric field. When the field and polarization are parallel, the lattice expands, and the strain is positive. When the field and polarization directions are antiparallel, the lattice contracts and the strain is negative. An abrupt change in the strain axis occurs due to polarization switching. The electromechanical response is in general reversible. The piezoelectric coefficients can be calculated from the slope of linear regions of the loop.



**Figure 1.6:** A schematic diagram of strain versus electric field of piezoelectric material. The piezoelectric coefficient is determined from the slope of the straight lines.

Human beings have known piezoelectricity for a long time. It is understood that human beings used flint, a type of quartz, to produce fire by applying mechanical stress. In reality, flint was a core material during "Stone Age" because of its worthy cutting properties that were useful to construct tools and arms. The "lighter" was an accidental discovery during the process of manufacturing tools. Later on, and before the invention of matches, these materials continued to be used like a lighter, creating fire spark by when knocked against iron. A piezoelectric material reveals a type of lattice where the central cation is at the center of the lattice (centrosymmetry of the lattice) due to cubic nature of lattice. A small offset from this position of the central cation (non-centrosymmetry) leads to an electric dipole, which can switch between two available symmetric positions.

mathematically This property was constructed from fundamental thermodynamic principles by Lippmann in 1881[45]. It was confirmed experimentally by the Curies who foregrounded the existence of the converse effect and also found quantitative proofs of reversibility of electro-elastomechanical deformation the in piezoelectric materials. The first use of a piezoelectric material was in ultrasonic submarine detector during World War-I. This was the beginning of development of SONAR (Sound Navigation and **R**anging). This opens up areas of applications of piezoelectric devices such as microphones, ultrasonic transducers, and signal filters. The continued development of piezoelectric materials has directed to more extensive market products extending from the everyday products to scientific and military applications. Also, during the Second World War in the United States, Japan and the Soviet Union, research groups working on capacitor materials explored that polycrystalline anisotropy showed a high dielectric constant (Roughly 100 times higher than cut crystals) in barium titanate polycrystalline ceramic. Before 1946, scientists thought that polycrystalline materials are only ferroelectric not piezoelectric. Effect of an electric field (a process called poling) was investigated to understand that polycrystalline ferroelectric ceramics could be converted into piezoelectric materials. This investigation enhanced development of piezoelectric devices.

### **1.8 Crystal structure for ferroelectricity**

The crystal structure is the primary governing point for ferroelectric/piezoelectric properties. Structures of different Bravais lattices govern the crystal symmetry. Crystal structures in nature can be described in 230 space groups based on symmetry elements [46]. There are 32 point groups [47], and in that 21 are noncentrosymmetric, i.e., they do not show an inversion symmetry with respect to the centre of the unit cell [Figure 1.7]. In the 21 noncentrosymmetric; 20 are piezoelectric, i.e., they exhibit accumulation of charge when mechanical stress is applied and one non-piezoelectric material. Among these 20 piezoelectrics, 10 carry a unique polar axis and possess spontaneous polarization. These are the pyroelectric. Similar to pyroelectric materials, ferroelectrics possess spontaneous polarization, but the magnitude and direction of the polarization can be reversed by an external electric field.



# *Figure 1.7: Symmetry relationships of piezoelectricity, pyroelectricity and ferroelectricity and some ferroelectric materials.*

Crystalline materials are distinguished into seven different crystal structures [Table 1.1]. These crystal structures are easily identified by constraints on the unit cell parameters.

Crystal system	Cell parameters		Centro- symmetric	Non- centro- symmetric
Cubic	a = b = c	$\alpha = \beta = \gamma =$ 90°	<i>m</i> 3, <i>m</i> 3 <i>m</i>	$23, \overline{4}3m,$ $432$
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^{\circ}$	4/m, 4/mmm	$4, \overline{4}, 442, $ $4mm, \overline{4}2m$
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^{\circ}, \gamma$ $= 120^{\circ}$	6/m, 6/mmm	$6, \overline{6}, 622, 6mm, \overline{6}m2$
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^{\circ}$	mmm	222, mm2
Rhombohedral	a = b = c	$\alpha = \beta = \gamma \neq$ 90°	$\overline{3}, \overline{3}m$	3, 32, 3 <i>m</i>
Monoclinic	$a \neq b \neq c$	$\alpha = \overline{\gamma = 90^{\circ}, \beta}$ $\neq 90^{\circ}$	2/m	2, <i>m</i>
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^{\circ}$	Ī	1

**Table:** 1.1 Seven crystal systems with their crystal constraints, centrosymmetric and non-centrosymmetric point groups in crystals with different symmetries.

A three-dimensional lattice may be constructed for each of these crystal systems. In crystallography and solid state physics, the minimum volume cell (a unit cell) corresponding to a single lattice point of a structure with discrete translational symmetry is called a primitive cell. A lattice can be characterized by the geometry of its primitive cell. Non-primitive unit cells contain additional lattice points, either on a face of the unit cell or within the unit cell, and so have more than one lattice point per unit cell. The structure and symmetries of the materials, entirely affect its overall physical properties. According to the Neumann's principles [48], "if the structure of a material is invariant with respect to certain symmetry elements, any of its physical properties is also invariant with respect to the same symmetry

elements." Hence, if the materials do not change, the structure also exhibits the same physical properties.

Ferroelectric materials are a subgroup of crystalline dielectric materials. Figure 1.8 graphically indicates the family of ferroelectric as a subgroup of pyroelectric, piezoelectric and dielectric crystals, hence exhibiting pyroelectricity, piezoelectricity, and dielectric permittivity.



*Figure 1.8:* A schematic venn diagram demonstrating the four classes of the polar dielectric.

As seen in Fig 1.8 ferroelectrics are very small subgroup of the entire family of dielectrics. But being a subgroup of each subgroup, one expects all the other properties in ferroelectrics and hence in this contemporary world of technological advancement this group of materials is extremely important.

## **1.9** Ferroelectric to paraelectric phase transition

A complete understanding of ferroelectrics was provided by Landau theory of ferroelectric phase transitions which tells about thermodynamic phenomenological aspects leading to macroscopic symmetry breaking [49]. Properties modify when materials undergo structural phase transitions from one space group to another. Ferroelectricity/piezoelectricity is greatly affected by structural phase transition temperature called Curie point ( $T_c$ ) [Figure 1.9]. At a temperature  $T < T_c$ , the crystal exhibits ferroelectricity, while for  $T > T_c$  ferroelectric ordering vanishes (paraelectric state). At or near the structural phase transition temperature, thermodynamic properties including dielectric constant, elastic, optical, etc. show anomalous behavior. The net spontaneous polarization (ferroelectricity) disappears above the Curie point. Sharp phase transition behavior follows the Curie-Weiss law [50, 51]:

Dielectric constant = 
$$\frac{c}{T-\theta}$$
,  $T \ge \theta$  ..... (1.2)

where, *C* is the Curie constant and the Curie-Weiss temperature. Usually,  $T_c$  and  $\theta$  differ only a few degrees. Hence, the dielectric constant shows high values and tends to infinity [Figure 1.9]. This is represents a first order phase transition behavior.



*Figure 1.9:* Dielectric constant versus temperature of a PbTiO<sub>3</sub>-based ferroelectric material.

Thus, for all perfect crystalline materials, we can expect a sharp maximum for dielectric constant at transition temperature. Sample porosity, secondary phases, inhomogeneity, grain size and material conductivity, etc. directly affect dielectric properties.

# 1.10 Diffuse phase transition

A diffused phase transition feature is an interesting area of research due to their unique physical properties and wide practical application. A sharp transition of perfect crystals of normal ferroelectric materials is absent and the transition temperature is smeared over a large temperature range showing a broad peak [Figure 1.10]. When different types of ions randomly occupy equivalent lattice sites, crystals become imperfect and ferroelectric phase transition is diffused. This is the most widely accepted model. Hence, diffused phase transition behavior is a result of composition fluctuations on a microscopic scale caused by disorder of the ions. If the Curie point temperature depends on composition, the phase transition temperature in different micro-regions takes place at different temperatures [52]. This is a second-order phase transition.



*Figure 1.10: Diffuse type of phase transition behavior of sodium bismuth titanate sample.* 

Diffuse type of phase transition behavior does not follow the Curie – Weiss law. It follows the modified Curie – Weiss law [53]:

where, *C* is Curie-Weiss constant, and  $\gamma$  ( $1 \le \gamma \le 2$ ) gives the degree of diffuseness. A sharp transition is achieved for  $\gamma = 1$ , while  $\gamma = 2$  is an ideal diffuse phase transition. The degree of diffuseness was calculated by the least square linear fitting of  $\ln \left(\frac{1}{\varepsilon'} - \frac{1}{\varepsilon'_m}\right)$  versus  $\ln (T-T_m)$  curves. In ferroelectrics, diffuse type of phase transitions was first discovered in the literature in early 1950's.

Some significant characteristics of the diffuse phase transitions include:

- Broadened maxima in dielectric constant versus temperature curve
- Decrease of spontaneous/remnant polarizations with increase in temperature
- Relaxation character of the dielectric properties in transition region
- Non-coincidence of transition temperatures obtained by different probes
- Absence of Curie-Weiss behavior

Diffuseness of the phase transition is due to two kinds of fluctuations: compositional and polarization (structural) fluctuations. Ferroelectric solid-solutions with multiple elements show compositional fluctuation from thermodynamic point of view. On the other hand, polarization fluctuation is due to small energy difference or fluctuation during the ferroelectric to paraelectric phase transition.

# **1.11 Domain structures**

As discussed above, ferroelectric materials possess a finite electric polarization even in the absence of an electric field. This polarization must exist in at least two stable states. These stable states must have the capability to be reversibly switched by the application of an applied electric field to one state to other. The energy versus polarization graph is a symmetric single well potential in case of a symmetric structure [Figure 1.11]. With a structural distortion of the unit cell the number of local minima will increase. The general situation is a double-well potential where polarization can happen in two opposite directions. With the increase of temperature the distortion reduces reducing the well-depths until at the transition temperature, the distortion equals to zero, and structure is symmetric, resulting in a single well nature of the energy.



*Figure 1.11: Free energy versus polarization for ferroelectric materials.* 

The entire sample does not need to be in the same polarized state. There may be domains of differentially polarized states separated by domain walls. Two kinds of domain walls can be found in tetragonal perovskites: 90° domain wall (polarizations of the neighboring regions are perpendicular), and 180° domain wall (polarizations of the neighbor regions are opposite). Across the domain walls, the polarization changes continuously but sharply. These ferroelectric domains allow minimizing of the electrostatic energy of depolarization field and the elastic energy accumulated during the structural paraelectric to ferroelectric phase transition. The polarization of the material. This charge generates electric fields which are oriented oppositely to the polarization. The opposite electric fields can be strong ~ MV/m. To minimize these electric fields in the ferroelectric samples, different domains with opposite polarization will form. Let us

assume that the cubic cell of a perovskite above the Curie temperature is compressed along one of the polarized direction. To minimize the elastic energy, the long axis of the tetragonal cell will develop along a direction perpendicular to the stress direction, while other unstressed areas will remain parallel to the stress. The combination of electrical and elastic boundary conditions acting during the ferroelectric phase transition determines the domain structure as shown in Figure 1.12. Only 90° domains minimize the elastic energy. Both 180° and 90° domain walls contribute to the reduction of electrostatic energy. They are called ferroelectric domain wall because they differ in orientation concerning the spontaneous polarization. Only the 90° minimize the elastic energy. This kind of wall is also called ferroelastic because the orientation differs from the spontaneous strain tensor [54].

For reasons related to energy distribution in the material, the domains are arbitrarily distributed in the unpolarized state. With the application of field these domain walls move in a way which supports the growth of certain domains already polarized in the direction of the applied field. Hence, as the field increases the aligned domains grow in size and results in maximum polarization of the material. However with increase of temperature the thermal energy disturbs this alignment and destroys the polarization. The phase transition temperature denotes that specific thermal energy which is required to destroy the entire polarization. This transforms the material to a cubic phase [55].



*Figure 1.12:* Formation of 90° and 180° domain wall in a tetragonal perovskite[54].

In  $PbTiO_3$ -based compounds of mostly tetragonal structure, by cooling a perovskite structure through Curie temperature, the ion in the centre of the octahedra shifts towards one of the oxygen. There are six possible directions and are all equal.

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# Chapter 2 Synthesis and experimental details

In this chapter, the synthesis route of the prepared samples will be discussed. A series of techniques used to characterize and analyse the materials will also be elaborated. All the studied samples have been synthesized using sol-gel combustion method. To analyse these materials we have employed: (1) High resolution Synchrotron-based powder x-ray diffraction to confirm the crystal structure and phase purity, (2) Raman spectroscopic technique to study compositional dependence of the vibrational modes, (3) Field emission scanning electron microscopy equipped with energy dispersive spectroscopy to see the surface morphology and elemental distribution, (4) Dielectric properties to study the phase transition temperature and conduction mechanism, (5) XANES/EXAFS used to confirm the charge state and local environment of constituent elements, (6) Ferroelectric loop tracing to study the spontaneous polarization properties, and (7) PPMS magnetometry to analyse the ferromagnetic properties in the materials. This chapter also attempts to provide a brief history of the subject as well as the materials in discussion.

### 2.1 Synthesis process

Ceramic materials are significant components in the field of Materials Science, with direct/indirect implications in human life. Synthesis of new ceramic materials plays a key role in the field of Materials Science. There are several methods of preparation of the ceramic materials such as solid-state route, sol-gel method, hydrothermal synthesis, and co-precipitation method, etc. In the present investigation, PbTiO<sub>3</sub> and based compounds were prepared using sol-gel combustion method.

### 2.1.1 Sol-gel method

Nanocrystalline powders of PbTiO<sub>3</sub> were synthesized using standard modified sol-gel process followed by high temperature annealing of the samples to study the temperature dependent structural properties of the solid solution [Figure 2.1]. High purity precursors, Lead (II) nitrate (99.99 %, Alfa Aesar, Puratronic) and Dihydroxybis (ammonium lactate) titanium (IV), 50% w/w aqua solution (Alfa Aesar) were used to synthesize these materials. The choice of such precursors was made due to their solubility in doubly deionized water. Solutions of each element were prepared with doubly deionized water of low conductivity ~ 0.055 microsiemens / cm. The lead solution was added to the titanium solution. A solution of citric acid and ethylene glycol was prepared in a separate beaker to serve as gel former and was thereafter added after vigorous stirring and heating for one hour.

$$Pb(NO_{3})_{2} + C_{6}H_{18}N_{2}O_{8}Ti + C_{6}H_{8}O_{7} + HOCH_{2}CH_{2}OH \rightarrow$$

$$---- (C_{2}H_{5}-O-Pb-O-C_{2}H_{5}-O-Ti-O-C_{2}H_{5})_{n} -----$$

$$\rightarrow PbTiO_{3} + H_{2}O + N_{2} + CO_{2} + CO$$

This solution then started to get heated up gradually and started to dehydrate as the stirring on the hot plate around 80 °C continued. The process resulted in a black powder and some yellow powder in the beaker on the hot plate. The resultant powders were properly grounded in the mortar and pestle and kept at 450 °C for 12 h to decarbonize and denitrify the sample. We obtained a yellow powder of PbTiO<sub>3</sub>. These powders were further calcined at 700 °C for 12 h. For structural studies of this sample at high temperature, we prepared pellets and heated in a muffle furnace and covered them with the same sample to reduce the volatization effect of the *Pb*.

Chapter 2



*Figure 2.1:* Schematic diagram of sol-gel combustion synthesis method.

# 2.2 Substituted sample preparations

For all substituted samples, the procedure is the same as discussed in **section 2.1.1.** We measured the stoichiometric precursors for all the samples and mixed them in a similar fashion as previously discussed. For all doped samples the gels were burnt, decarbonized and denitrified similar to the process discussed in **section 2.1.1**. The processes of obtaining these solutions are documented in detail in the following sections.

# i. (K<sub>0.5</sub>Sm<sub>0.5</sub>) substituted PbTiO<sub>3</sub> synthesis:

Samples  $Pb_{(1-x)}(K_{0.5}Sm_{0.5})_xTiO_3$  were synthesized for x = 0, 0.06, 0.09, 0.12, 0.18, 0.25, 0.37, and 0.50 compositions. Solgel processed polycrystalline  $Pb_{(1-x)}(K_{0.5}Sm_{0.5})_xTiO_3$  ( $0 \le x \le$ 0.5) ceramics were prepared using Lead (II) nitrate ( $Pb(NO_3)_2$ ), Potassium nitrate ( $KNO_3$ ), Samarium oxide, and Dihydroxy bis (ammonium lactate) titanium (IV), 50 % w/w aqua (TALH) solution as precursors with purity > 99.99 % (Alfa Aesar, Puratronic grade). Sm<sub>2</sub>O<sub>3</sub> was dissolved in dilute HNO<sub>3</sub>. TALH, Pb( $NO_3$ )<sub>2</sub> and KNO<sub>3</sub> were dissolved in DDW. *Sm* and Ti solutions were mixed, and after that, the K solution was added to form a mixed solution of Sm, Ti, and K and stirred for a while. The *Pb* solution was added to this combined solution.

 $Sm_2O_3 + 6HNO_3 \rightarrow 2Sm(NO_3)_3 + 3H_2O$ Pb(NO\_3)\_2 + C\_6H\_18N\_2O\_8Ti + Sm(NO\_3)\_3 + KNO\_3 + C\_6H\_8O\_7 + HOCH\_2CH\_2OH →

 $(C_2H_5-O-Pb-O-C_2H_5-O-Ti-O-C_2H_5-O-Sm-O-C_2H_5-O-K-O-C_2H_5)_{n} \rightarrow Pb_{(1-x)}(K_{0.5}Sm_{0.5})_xTiO_3 + H_2O + N_2 \uparrow + CO_2 \uparrow$ 

A solution of citric acid and ethylene glycol of 1:1 molar ratio was prepared in a separate beaker as gel former and was subsequently added to the mixture. The resultant sols were vigorously stirred and heated at ~ 80 °C on a hot plate to form gels. The gels were burnt to form black powders. To de-carbonate and de-nitrate, these powders were heated at 500 °C for 12 h. Pellets (diameter ~10 mm; thickness ~ 1.5 mm) were prepared by uni-axially pressing carefully grinded powders mixed with a binder polyvinyl alcohol (PVA) with 5 % weight solution. These pellets were sintered at 600 °C for 6 h to burn the binder followed by another heating at 1050 °C for 6 h to form mechanically dense pellets.

### ii. (Na<sub>0.5</sub>Sm<sub>0.5</sub>) substituted PbTiO<sub>3</sub> synthesis

Polycrystalline samples of  $Pb_{(1-x)}(Na_{0.5}Sm_{0.5})_xTiO_3$  for x = 0, 0.10, 0.20, 0.30, 0.40, and 0.50 compositions were taken. Samples were prepared using sol-gel combustion process and precursors were used to synthesize these materials: Lead (II) nitrate (99.99 %, Alfa Aesar), Samarium oxide (99.99 %, Alfa Aesar), Sodium nitrate and Dihydroxybis (ammonium lactate) titanium (IV) and 50 % w/w aqua solution (Alfa Aesar). A solution of citric acid and ethylene glycol of 1:1 molar ratio was prepared in a separate beaker as gel former and was thereafter added after vigorous stirring and heating (~ 80 °C) on the hot plate. The solution was continuously stirred and heated (~ 80 °C) on hot plate to form gel. The complete equation for the process is given below: 
$$\begin{split} & Sm_2O_3+6HNO_3 \ \ \, \bigstar \ \, 2Sm(NO_3)_3+3H_2O\\ & Pb(NO_3)_2+C_6H_{18}N_2O_8Ti\,+\,Sm(NO_3)_3\,+\,NaNO_3\,+\,C_6H_8O_7\,+\\ & HOCH_2CH_2OH \ \ \, \bigstar \end{split}$$

 $----- (C_2H_5\text{-}O\text{-}Pb\text{-}O\text{-}C_2H_5\text{-}O\text{-}Ti\text{-}O\text{-}C_2H_5\text{-}O\text{-}Sm\text{-}O\text{-}C_2H_5\text{-}O\text{-}Sm\text{-}O\text{-}C_2H_5\text{-}O\text{-}Sm\text{-}O\text{-}C_2H_5\text{-}O\text{-}Sm\text{-}O\text{-}C_2H_5\text{-}O\text{-}Sm\text{-}O\text{-}C_2H_5\text{-}O\text{-}Sm\text{-}O\text{-}C_2H_5\text{-}O\text{-}Sm\text{-}O\text{-}C_2H_5\text{-}O\text{-}Sm\text{-}O\text{-}C_2H_5\text{-}O\text{-}Sm\text{-}O\text{-}C_2H_5\text{-}O\text{-}Sm\text{-}O\text{-}C_2H_5\text{-}O\text{-}Sm\text{-}O\text{-}C_2H_5\text{-}O\text{-}Sm\text{-}O\text{-}C_2H_5\text{-}O\text{-}Sm\text{-}O\text{-}C_2H_5\text{-}O\text{-}Sm\text{-}O\text{-}C_2H_5\text{-}O\text{-}Sm\text{-}O\text{-}C_2H_5\text{-}O\text{-}Sm\text{-}O\text{-}Sm\text{-}O\text{-}C_2H_5\text{-}O\text{-}Sm\text$ 

→  $Pb_{(1-x)}(Na_{0.5}Sm_{0.5})_xTiO_3 + H_2O + N_2 + CO_2$ After that, gels were burnt into a big beaker of two liters inside a fume hood. Burnt powders were heated at 450 °C for 12 h as a denitrification of powders. Carefully grinding of these powders were mixed with 5 weight % PVA solution as a binder and uniaxially pressed into discs of 13 mm diameter and 1.5 mm thickness. These pellets were sintered at 600 °C for 6 h to burn out the binder continued with 1050 °C for 4 h.

### iii. Fe substituted PbTiO<sub>3</sub> synthesis

Nanocrystalline powders of PbTi<sub>(1-x)</sub>Fe<sub>(x)</sub>O<sub>3</sub> for x = 0, 0.03, 0.06, 0.09, 0.12, 0.18, 0.25, 0.31, 0.37, 0.43, and 0.50 compositions were synthesized using standard, modified sol-gel process followed by high temperature annealing of samples to study the temperature-dependent structural properties of the solid solution. High purity precursors, Lead (II) nitrate (99.99 %, Alfa Aesar), Iron (III) nitrate nonahydrate (98 %, Alfa Aesar) and Dihydroxybis (ammonium lactate) titanium(IV) and 50 % w/w aqua solution (Alfa Aesar) were used to synthesize these materials. The choice of such precursors was made due to their solubility in doubly deionized water. Solutions of each element were prepared with doubly deionized water of low conductivity ~ 0.055 microsiemens / cm. The iron solution was added to the titanium solution followed by the addition of the lead solution.

Pb(NO<sub>3</sub>)<sub>2</sub> + C<sub>6</sub>H<sub>18</sub>N<sub>2</sub>O<sub>8</sub>Ti + Fe(NO<sub>3</sub>)<sub>3</sub> .9H<sub>2</sub>O + C<sub>6</sub>H<sub>8</sub>O<sub>7</sub> + HOCH<sub>2</sub>CH<sub>2</sub>OH →

 $\longrightarrow PbTi_{(1-x)}Fe_xO_3 + H_2O + N_2 + CO_2 + CO_2$ 

A solution of citric acid and ethylene glycol was prepared in a

separate beaker to serve as gel former and was added after vigorous stirring and heating for one hour. The solution was heated to form gels which were burnt to produce colored powders followed by further heating at 450 °C for 6 h. Colours of powders gradually changed from white as in undoped PbTiO<sub>3</sub> to yellowish brown with an increase of substitution. Powders heated at 450 °C have been treated as starting materials of this work. Samples were further heated at 600 °C, 700 °C, 800 °C and finally at 1000 °C / 6 h in the form of pellets.

### iv. *La* and *Al* substituted PbTiO<sub>3</sub> synthesis:

 $Pb_{(1-x)}La_xTi_{(1-x)}Al_xO_3$  for x = 0, 0.03, 0.06, 0.09, 0.12, 0.18, and 0.25 compositions were prepared using the sol-gel combustion process. Precursors used to synthesize these materials were lead (II) nitrate, lanthanum nitrate, aluminium nitrate, and dihydroxy bis (ammonium lactate) titanium (IV) (50% w/w aqua solution). All the precursors were Puratronic grade (purity >99.99 from Alfa Aesar). The precursors were selected on the basis of solubility in doubly deionized water (DDI). Stoichiometric solutions of each precursor were prepared with DDW in separate glass beakers. Lanthanum solution was added to titanium solution. Aluminium and lead solutions were added to mixture subsequently. 5 % excess lead nitrate was used accounting for the volatile nature of *Pb* during sintering at high temperatures. The mixed solution was stirred at normal temperature for 30 minutes to ensure proper homogeneity in the composition. A gel former was prepared in a separate beaker by using a solution of citric acid and ethylene glycol in 1:1 molar ratio.

 $Pb(NO_{3})_{2} + C_{6}H_{18}N_{2}O_{8}Ti + La(NO_{3})_{3} + Al(NO_{3})_{3} + C_{6}H_{8}O_{7} + HOCH_{2}CH_{2}OH \rightarrow$ -(C<sub>2</sub>H<sub>5</sub>-O-Pb-O-C<sub>2</sub>H<sub>5</sub>-O-La-O-C<sub>2</sub>H<sub>5</sub>-O-Ti-O-C<sub>2</sub>H<sub>5</sub>-O-Al-O-C<sub>2</sub>H<sub>5</sub>)<sub>n</sub> → (Pb<sub>(1-x)</sub>La<sub>x</sub>)(Ti<sub>(1-x)</sub>Al<sub>x</sub>)O<sub>3</sub> + H<sub>2</sub>O + N<sub>2</sub> ↑ + CO<sub>2</sub> ↑

The homogeneous solution containing the requisite ions were poured in the gel former and vigorous stirring and heating (~80 °C) followed on the hot plate continuously until a gel was formed. Gels were burnt in the open air inside a fume hood. Burnt powders were ground and thereafter heated at 500 °C for 12 h to get rid of trapped polymers and nitrates. Resultant powders were grounded with mortar pestle and re-heated at 700 °C for 12 h. After that, powders were mixed with five weight % PVA solution (a binder) and pressed into pellet form of 10 mm diameter and 1.5 mm thickness using a uniaxial press. These pellets were sintered first at 600 °C for 6 h (to burn out binder) and continuous 1150 °C for 6 h. Note that, we had covered pellets with powders of the same composition to reduce Pb loss. Mechanically strong pellets were formed at this optimum temperature. However, it has been reported that Pb evaporates from pellet surface layers during sintering up to 200 - 250 nm deep, we have removed a similar amount from pellets before performing any characterization. One of pellets of each composition was ground for structural characterization using an XRD Bruker D2 Phaser [*Cu*  $k\alpha = 1.5418$  Å wavelength] at initial stage. We have done synchrotron-based XRD to see actual lattice dynamics in samples.

## v. Bi and Mn substituted PbTiO<sub>3</sub> synthesis

Polycrystalline  $(Pb_{1-x}Bi_x)(Ti_{1-x}Mn_x)O_3$  ( $0 \le x \le 0.50$ ) powders were synthesized using sol-gel combustion process. Precursors selected to synthesize these materials were Puratronic grade lead (II) nitrate, manganese nitrate (50 % w/w aqua solution), bismuth nitrate, and dihydroxy bis (ammonium lactate) titanium (IV) (50 % w/w aqua solution). Precursors were selected on the basis of solubility in doubly de-ionized water. Stoichiometric solutions of each precursor were prepared with DDW water in separate glass beakers. Manganese solution was added to titanium solution. Bismuth and lead solutions were added to mixture subsequently. 5 % excess lead nitrate was used accounting for the volatile nature of *Pb* during sintering at high temperatures. The mixed solution was stirred for one hour to ensure proper homogeneity in the solution at normal temperature.

$$Pb(NO_3)_2 + C_6H_{18}N_2O_8Ti + Bi(NO_3)_3 .5H_2O + Mn(NO_3)_3 + C_6H_8O_7 + HOCH_2CH_2OH \rightarrow$$

$$\rightarrow (Pb_{(1-x)}Bi_x)(Ti_{(1-x)}Mn_x)O_3 + H_2O + N_2 \uparrow + CO_2 \uparrow \downarrow$$

A gel former was prepared in a separate beaker by mixing citric acid and ethylene glycol in 1:1 molar ratio in solution. This gel former solution was added to the homogeneous precursor solution. This solution containing constituent ions was vigorously stirred and heated (~80 °C) on a magnetic stirrer hotplate until a gel was formed. Gels were burnt inside a fume hood. Burnt powders were ground carefully in a mortar and pestle. After that powders were heated at 500 °C for 12 h to get rid of the trapped nitrates and polymers. These resultant powders were grounded again in mortar/pestle and re-heated at 700 °C for 12 h. After that, powders were mixed with 5 % PVA solution and pressed into pellets of 13 mm diameter and 1.5 mm thickness using a uniaxial hydraulic press. These pellets were heated first at 600 °C for 6 h to burn out binders and thereafter sintered continuously at 1000 °C for 6 h to form the dense pellets. Pellets were covered with powders of the same composition during heating to reduce Pb loss.

# 2.3 Fabrication of ceramics

Phase purity of the powder samples was examined with the xray diffraction (XRD) method. After that, XRD data was analysed using the Fullprof software. After finding the single phase of the powder samples, it was noted that for electrical measurements, pellets with high density (i.e., low porosity) are required. To further enhance the intimate bonding between crystallites, we started to mix with the PVA (Polyvinyl alcohol) binder in the powder with the help of mortar and pestle and pressed them into the circular pellet with the help of hydraulic press and die set. 5 weight % PVA solution binder was used
because since the circular ages of the pellet were not sharp enough for the use but with the use of the binder, a regular shape of the circular pellet was obtained. These pellets were heated at different temperatures to get the highly dense ceramics. The final temperature of the pellet was much higher compared to the calcination and was below the melting point. This post-calcination and with the temperature below the melting point helps in (i) improving the crystal quality, (ii) enhancing grain growth, and (iii) attaining the maximum possible density. We reached the final temperature in a two-step processes: first at 600 °C for 6 h to burn out the binder (PVA) that continued with the final sintering temperature. It was a trial method to get the dense ceramic structure. Final temperatures for each sample are provided in the corresponding chapters. Also, a significant observation to be noted is that during sintering, the pellet was covered with the similar powder samples to reduce the volatization of the Pb element from the sample. Even then, after annealing, we polished the top surface around 200 to 300 nm on each side before conducting any measurement.

#### **2.4 Characterizations techniques**

Structural characterization techniques are briefly discussed below.

# 2.4.1 X-ray diffraction

Crystallinity determines the physical properties of materials, such as electrical, magnetic, and optical, etc. Hence, understanding the structural details, such as the shape and symmetry of the unit cell, surrounding and positions of the ions, nature and distances of the bonds becomes extremely important. The bond lengths vary from fractions of an Angstrom to a few Angstrom. X-rays have wavelength  $\sim 0.01 - 10$  nm (corresponding frequencies 3 x  $10^{16}$  to 3 x  $10^{19}$  Hz and energies 100 eV to 100 keV) compatible with the bond lengths and unit cell parameters of the crystalline materials. Lattice constants, bond lengths, bond angles, crystallite size, lattice strain etc. can be calculated from the position and profile of the x-ray diffraction peaks. Most importantly, XRD tells us about the phase of the materials. Elastic scattering of the electromagnetic wave takes place when x-rays

interact with atoms. The scattering takes place due to the charge centers and electron clouds of the atoms. This scattering does not follow a pattern if the atoms are arbitrarily arranged. However, a collection of periodically arranged atoms can interact with these xrays, leading to a constructive and destructive superposition of the scattered waves. The direction at which a constructive superposition happens sees a bright spot fulfilling the Bragg's law. The lower the wavelength of the light, i.e. the higher the energy, better is the resolution of the XRD data.



**Figure 2.2:** (a) Diffraction of x-rays through lattice/atomic planes of a crystal, the diffracted x-rays exhibit the constructive interference between the differ of path difference (CBD)of two incident x-ray by an integer number of wavelength, (b) basic set-up of Bragg Brentano Diffractometer.

X-ray diffraction of samples were measured with Bragg-Brentano geometry [Figure 2.2a] [1]. In this geometry, the sample-to-source and sample-to-detector distances are kept constant. X-ray falls at an incidence angle and gets diffracted by sets of atomic planes of the

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crystal lattice. The angle of incidence and angle of reflection both are same ~  $\theta$ , thereby creating a deflection of  $2\theta$  [Figure 2.2b]. A conventional way of plotting XRD data is by plotting intensity as a function of the angle of deviation. The path difference between x-rays scattered by planes 1 and 2 is CB+BD =  $d.\sin\theta + d.\sin\theta = 2d.\sin\theta$ . For constructive interference, the path difference must be equal to an integer number of wavelength ( $\lambda$ ) of the x-ray radiation. Thus,  $2d.\sin\theta$ =  $n\lambda$  (n is the order of scattering ~1, 2,...) is a requirement for constructive interference and is known as Bragg's law. Note that in this equation, the value of  $\lambda$  is proportionate to *d*, the inter-planar distance. Hence the smaller the  $\lambda$ , the smaller planar spacing can be investigated. Calculating the *d*-spacing, the crystal structure of the samples can be estimated by choosing an appropriate model obeying a definite space group.

For regular studies, the samples phase and structure were analyzed using x-ray diffraction data from a Bruker D2 Phaser X-ray Diffractometer with Cu Ka radiation ( $\lambda = 1.5418$ ) for  $2\theta \sim 10^{\circ} - 100^{\circ}$ (step size ~  $0.01^{\circ}$ ). However, as mentioned earlier a better resolution was intended with lower wavelengths. Hence, the structural investigation was ultimately carried out at the synchrotron-based powder angle dispersive x-ray diffraction (ADXRD) measurement facility. ADXRD was carried out at the Extreme Conditions Angle Dispersive/Energy dispersive x-ray diffraction (EC-AD/ED-XRD) beamline (BL-11) at Indus-2 synchrotron source, Raja Ramanna Centre for Advanced Technology (RRCAT), India. Measurements were carried out in capillary mode. The crushed powders were filled in the capillary of 0.2 mm diameters. The diameter of the capillary tube was selected taking into account of the linear absorption coefficient of the sample and 25% packing density of material in the capillary. The capillary was rotated at ~150 rpm to reduce the orientation effects. From the white light of the bending magnet, a wavelength was selected using a Si (111) channel-cut monochromator and then focused with a Kirkpatrick-Baez mirror or K-B mirror for ADXRD measurements. A MAR345 image plate detector (which is an area detector) was used to

collect two-dimensional diffraction data. The sample to detector distance and the wavelength (0.4457 Å, 0.5034 Å) of the beam were calibrated using NIST standards LaB<sub>6</sub> and CeO<sub>2</sub>. Calibration and conversion/integration of 2D diffraction data to 1D, intensity versus 2theta, was carried out using FIT2D software [2]. Temperature-dependent XRD studies were performed for some selected samples using STOE high-temperature attachment as shown in Figure 2.3.



Figure 2.3: Temperature-dependent x-ray diffraction set up using STOE high-temperature attachment at BL-11 RRCAT, Indore, India. The figure has been taken from the website of RRCAT with due permission.

The temperature control of the diffractometer [Figure 2.3] is automatically software-controlled. The accuracy of the temperature of this system is 0.1 °C. In this system, a sample filled capillary is kept and rotated with the 150 rpm to reduce the orientation effect in the polycrystalline samples. The samples were kept at a constant temperature for 10 minutes to ascertain temperature stability in the sample because ceramic samples have less conductivity and require more time to reach the equilibrium temperature. Wavelengths and other details related to the samples are provided in the corresponding chapter.



*Figure 2.4: Temperature-dependent x-ray diffraction set up at BL-12 RRCAT, Indore, India. The figure has been taken from the website of RRCAT with due permission.* 

For some samples, Indus-2 BL-12 synchrotron-source was used at the Raja Ramanna Centre for Advanced Technology (RRCAT), India to study the temperature-dependent XRD study with wavelength ~ 0.8016 Å. The temperature-dependent XRD set up was shown in Figure 2.4. The sample holder set-up is shown for high-temperature XRD measurement. An automatic temperature control system with 2 to 3 °C temperature error bar was available for the measurements. Samples were kept on a quartz glass plate and then on the heater [Figure 2.4]. Using the Miller indices each diffraction peak (Bragg peak) can be represented as a vector *hkl* defined in the reciprocal space lattice.

# 2.4.2 Raman spectroscopy

Usually, when a radiation passes through a transparent medium, the present species in the samples scatter a fraction of radiation in all directions. In 1928, physicist C. V. Raman and K. S. Krishnan from India discovered that wavelengths of a small fraction of the scattered radiation differ from that of the incident beam. He further noted that

the shift in the wavelength depends on the structure of the molecules responsible for the scattering. Raman spectroscopy is a vibrational spectroscopic technique which provides informations on molecular vibrations (energy  $\sim$  hv) and crystal structures. It uses a monochromatic light source (often a laser) to irradiate a sample. An infinitesimal amount of inelastic Raman scattered light is generated. Light being an electromagnetic wave consists of electric and magnetic fields oscillating perpendicular to each other and also perpendicular to the direction of propagation. A change in the polarizability in the materials due to the incidence of the monochromatic light is responsible for the phenomena. The motion of two coupled atoms can be described by a harmonic oscillator. The exact frequency is governed by the interatomic force constant k and the reduced mass m of the participating atoms. In the case of a monoatomic chain composed of an identical atom, it can be described with the  $\omega = 2\pi f = \sqrt{\frac{k}{m}}$  formula. Atoms in a crystal are strongly coupled, and thus correlated motions around the equilibrium positions of the crystal obey symmetric restrictions. The incident light interacts with the molecule and distorts the cloud of electrons. This forms a unstable "virtual state". The photon is immediately re-radiated as scattered light. In a typical Raman spectrum, three types of radiations are observed: Stokes  $(hv_0 - hv)$ , Anti-Stokes  $(hv_0+hv)$  and Rayleigh  $(hv_0)$  scatterings. Stokes and Anti-Stokes scatterings are inelastic scattering and are called Raman

scatterings [Figure 2.5]. In Rayleigh scattering an excited electron returns to the same ground level after excitation and energy is conserved. Rayleigh scattering is the dominant process. Raman scattering is an extremely weak process. Only one in every  $10^6 - 10^8$  photons are inelastically scattered. Rayleigh scattered light is rejected using different types of filters, such as notch filters, edge filters and band-pass filters, etc..

Stokes Raman scattering is a process in which an electron is excited from the ground level to a virtual state and falls to a vibrational level with higher energy level than the ground state, which means the scattered light has less energy (longer wavelength) than incident light. Another scenario is of an electron being excited to a virtual state from the same vibration state. This electron if it gets back to the ground state contributes to an anti-Stokes Raman scattering process.

The infinitesimal amount of inelastic scattered light is detected by a CCD camera as a spectrum. This spectrum contains characteristic fingerprints of a sample. Identification of polymorphs of substances and evaluation of local crystallinity, orientation and stress is possible using Raman spectroscopy. Raman frequencies can correspond either to rotational, vibrational or electronic frequencies.

Population of the ground and excited states of the molecule determine the Stokes to anti-Stokes signal ratio. Population in an excited vibrational level is smaller than that of the ground level at room temperature. Hence, Stokes lines are more intense than anti-Stokes Raman lines. As temperature increases the ratio of Stokes to anti-Stokes signal decreases. Hence, this ratio is informative of the temperature of a sample.



**Figure 2.5:** Schematic diagram of photon interactions with the matter (left side): with Infrared absorption, the photon energy corresponds to the energy difference between two allowed vibrational states, Rayleigh scattering, excitation to a virtual electronic state (dashed line) from which the system recovers immediately. The incident and the scattered light have the same energy, Raman scattering, the vibrational state after the photon-phonon interaction is either higher or lower than the

initial state. The scattered phonon energy is decreased (Stokes) or increased (anti-Stokes) compared to the initial photon energy [3].

Chemical bonds, crystallographic orientation and symmetry of the structure can be assessed using Raman spectroscopy due to the unique vibration properties (phonon modes) of the molecule depending on its chemical composition. Raman spectroscopy is very sensitive and an excellent tool for qualitatively assessing retention of domain structure, defect, and structural distortion and thereby understanding deformations and lattice strains associated with substitutions/dopant in the samples. In the present investigation, Raman spectroscopy is carried out to see the change of modes with the substitution and examine the phase of the samples with the substitutions. The samples were analysed with the powder form as well as in pellet form. The high-resolution Raman spectrometer is an Integrated Raman System that includes a confocal microscope, a large focal length (~ 800 mm) Czerny-Turner type achromatic spectrograph with a spectral resolution of 0.4 cm<sup>-1</sup>/pixel operating at the spectral range of 200–1050 nm and the source of excitation- a 632.8 nm, air-cooled He-Ne laser. The position of the peak was analysed using the origin software with the multi-peak fit option. Lorentzian line shape is mostly observed in the obtained Raman spectra.

## 2.4.3 Field Emission Scanning Electron Microscopy (FESEM)

Due to diffraction limit of light, optical microscopes have limited spatial resolution, and higher resolution is needed to see nm or even sub nm objects. Field Emission Scanning Electron Microscopy (FESEM) is a powerful and widely known tool for imaging the topology of surfaces of almost any materials. FESEM gives better and less distorted images with spatial resolution ~1 nm which is very high compared to conventional SEM and optical microscope. Associated with a FESEM, Energy Dispersive X-ray Photoelectron Spectroscopy (EDS), gives thus information on composition and chemical uniformity of the samples with very high resolution. It produces high quality and low voltages images with negligible electrical charging in the samples. The field emission process is the emission of electrons induced by an electrostatic field. This enables to extract narrower probing beams at low as well as high electron energy. Improved spatial resolution and minimized sample charging/damage can be achieved using a field emission source. In the present investigation, the FESEM micrographs were collected on pellet surfaces as well as fracture cross sections of the samples. The model used was Supra55 Carl Zeiss FESEM [Figure 2.6]. For non-conductive samples, ~ 5 nm gold was sputtered on the samples to establish charge drainage routes to avoid charging. As PbTiO<sub>3</sub> based materials are ferroelectric and hence nonconductive, therefore charging effect is pronounced. Hence, these samples needed the charge drainage metallic deposition on the surface.



Figure 2.6: Experimental set-up used for the field effect scanning electron microscope equipped with the energy dispersive x-ray

spectroscopy. 1. Complete arrangement of the FESEM. 2. Connected computer system running user-friendly software. 3. EDX measurement system Marked point 4 is a complete set of the gold sputtering. 5. Enlarged part of the sample holder for gold sputtering system.

Interactions of highly energetic beam of electrons on the samples generate secondary electron, back-scattered electron, and x-rays. High-speed electrons that strike the sample surface are called the primary electron. They transfer the kinetic energy to electrons on the surface of the sample. With this sufficient energy the surface electron overcomes the strong attractive force of the nuclei and escapes from the sample. These electrons are called secondary electrons. Hence these are very sensitive to the surface characteristics of the sample. It is suitable for all materials. The surface morphology of the samples with a large depth of field can be obtained with the secondary electrons. Images obtained from secondary electrons need low acceleration potentials (< 5 kV). These are mostly recommended for working with sensitive samples in which effect of charging is more.

An incident electron from the incoming beam is deflected by the electrostatic field of the positive nucleus. Some electrons get scattered elastically by the positive nucleus at high angles. These electrons are called backscattered electrons. A backscattered electron is sensitive to the atomic number of the elements present in the samples. Therefore, such electrons are used to analyse changes in chemical compositions of the sample.

The incident electron beam generates x-ray photons too. These x-rays are generated, when the electron beam removes an inner shell electron from the sample; causing a higher-energy electron to fill the shell and release energy. These x-ray photons emerging from the specimen have energies specific to the elements in the specimen. These are characteristics x-rays that provide analytical capabilities and the technique is known as EDS. The x-rays we analyze usually have energies between 0.1 and 20 keV. Apart from the determination of the composition 2-diemnsional EDS scans can assess the homogeneity of elements in the sample.

# 2.4.4 Dielectric spectroscopy analysis

A dielectric material is a poor conductor of electricity with low dielectric loss. Dielectric materials belong to a broad family of materials. When placing a dielectric material in an electric field, positive and negative molecules orient themselves along the electric field lines. This effect is known as polarization (dipole moment per unit volume) [4]. The polarization properties arise from their atomic structure. The positive and negative charge centers separate with the application of electric field, forming electric dipoles. Electric field not only influences electronic polarization, but also displaces anions and cations in ionic crystals (ionic polarizations). It can further realign permanent molecular dipoles (orientation polarizations). There is no free movement of electrons from molecule to molecule. Hence, they do not have a net change in molecular charge and tend instead to just stretch and rotate. Dielectric permittivity is the electrical response of a material to an applied electric potential and is dependent on frequency. Ideal dielectrics have zero DC conductivity. For a homogeneous, isotropic, source-free, free of charges and time-invariant material this effect of polarization is well behaved. Before the external electric field is applied, the molecules of the dielectric are typically in random orientations. So there should be no net electric field in the dielectric, even though on a molecular level there are many individual electrical dipoles moments. When an external field is applied to the dielectric molecules, it will change the balanced condition in a manner that depends on both the electric field and also the internal dipole moments. In the case of an externally applied electric field, different frequencies applied provoke different response depending on the externally applied electric field- on the collective response of the dipole moments at those frequencies.

In the present investigation, electrical properties such as dielectric and ferroelectric properties were measured for the circular disk type pellet, electroded with silver paste on both sides as shown in Figure 2.7 below.

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**Figure 2.7:** Schematic diagram of circular pellet electrodes for electrical measurements. Line between electrodes is representing the thickness of dielectric material.

Electrodes were prepared using high-temperature silver paste on both sides of sintered pellets. The silver pasted pellets on either side were cured at 550 °C for 15 minutes to establish pellet-electrode contact. Before measurements, samples were heated at 200 °C for 15 minutes to get rid of the surface moisture. The dielectric response was measured using a Newton's 4<sup>th</sup> Ltd. PSM 1735 phase sensitive LCR meter with the signal strength of ~1V<sub>rms</sub>. All the samples were prepared accordingly, keeping in mind the parallel plate capacitor type.

Permittivity,  $\varepsilon_r$ , is a complex number containing both real ( $\varepsilon'$ ) and imaginary part ( $\varepsilon''$ ). The relation is given by:  $\varepsilon_r = \varepsilon' + \varepsilon''$ . Dielectric constant,  $\varepsilon'$ , is the real part of permittivity which determines the energy is stored in the material. The imaginary part ( $\varepsilon''$ ) represents the amount of the energy lost. The capacitance of a pellet can be represented as  $C = \varepsilon' \varepsilon_o \frac{A}{d}$ ; where C is known as capacitance, A area of the pellet, d thickness of the pellet, and  $\varepsilon_o$  is the permittivity of free space (8.854 \* 10<sup>-14</sup> F/cm). A/d is also known as the geometric factor. The dielectric loss or loss tangent,  $tan\delta$ , can be written as a relation  $tan(\delta) = \frac{\varepsilon''}{\varepsilon'}$ . The variations of dielectric constant ( $\varepsilon'$ ) and  $\varepsilon''$  as a function frequency is shown in Figure 2.8.

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*Figure 2.8:* Schematic diagram of dielectric constant and loss as a function of frequency.

It is observed that dielectric constant decreases with increasing frequency. At lower frequency, all the contributions such as space charge, ionic, orientation, and electronic are present in the dielectric constant. As the frequency increases, the different components stop contributing to the dielectric constant, and at high frequency (>  $10^{11}$ Hz), only the electronic part contributes. Also, dielectric losses increase in the same region where the contributions drop out, because, switching the direction of the field, the direction of polarization also switches to align with the new electric field direction. This process cannot occur instantaneously, as some time is needed for the movement of charges, i.e. rotation of dipoles. If the electric field is switched, there is a characteristic time that polarization takes to adjust in that direction, called the relaxation time. Typical relaxation times are  $\sim 10^{-11}$  s. Hence, if the electric field switches direction at a frequency higher than  $\sim 10^{11}$  Hz, the dipole orientation cannot keep up with the alternating field. The polarization is unable to remain aligned with the field, and this polarization mechanism ceases to contribute to the polarization of the dielectric constant. Dielectric loss is exceptionally high near the resonance frequencies of the polarization mechanisms as the polarization lags behind the applied filed, causing an interaction between the field and the dielectric's polarization that results in heating as shown in Figure 2.8.

# 2.4.4.1 Impedance spectroscopy

Complex Impedance Spectroscopy (CIS) is a powerful tool to investigate the electrical properties of the complex perovskite oxides. The main advantages of this technique are: (1) it involves relatively simple electrical measurements that can readily be automated (2) measurements can be executed by using arbitrary electrodes (3) results correlate with properties such can often as composition, microstructure, defects, dielectric properties, chemical reactions, etc. of the sample (4) resistance of the grain boundaries and that of grains can be easily separated in most of the polycrystalline sample. ACmeasurements are often made with a Wheatstone Bridge type apparatus in which the resistance (R) and capacitance (C) of the sample are measured and balanced against variable resistors and capacitors. The impedance |Z| and the phase difference ( $\theta$ ) between the voltage and current are measured as a function of frequency for the given sample, and the technique is called impedance spectroscopy. Analysis of data is carried out by plotting the imaginary part of the impedance  $|Z|\sin\theta$  against the real part  $|Z|\cos\theta$  on a complex plane called the impedance plot. An impedance plot with a linear scale is used to analyze the equivalent circuit as follows. Impedance plot of the pure resistor is a point on the real axis, and that of the pure capacitor is a straight line coinciding with the imaginary axis. The impedance of a parallel *RC* combination is expressed by the following relation:

 $Z^* = Z' - jZ'' = R/(1 + j\omega RC)$  .....(2.4)

After simplification, one gets

$$\left(Z' - \frac{R}{2}\right)^2 + Z''^2 = \left(\frac{R}{2}\right)^2$$
 .....(2.5)

which represents the equation of a circle with radius R/2 and centre at (R/2,0). Thus, a plot of Z' versus Z'' (as the parametric function of  $\omega$ ) will result in a circle as shown in Figure 2.10 of radius R/2.



*Figure 2.9*: (a) *The impedance plot for a circuit of a resistor and capacitor in parallel and (b) the corresponding equivalent circuit [5].* 

This plot is often called a Nyquist plot. The time constant of the simple circuit is defined as  $\tau = RC = 1/\omega_0$ . This corresponds to the relaxation time of the sample, and characteristic frequency lies at the peak of the semi-circle. In an ideal polycrystalline sample, the impedance plot exhibits an arc at high frequency, which corresponds to the grain, grain boundary, and the electrode effect at the lowest frequency. Figure 2.10 shows a typical impedance plot for a polycrystalline sample and equivalent circuits. In the present work, impedance measurements have been performed using the Newtons 4<sup>th</sup> Ltd phase sensitive impedance analyzer in the frequency range of 1Hz to 1 MHz at different temperatures.

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*Figure 2.10*: Equivalent circuits for the complex impedance and Cole diagram for grain, grain boundary, and electrode effect [6].

# 2.4.5 Poling and aging:

A polycrystalline ferroelectric ceramic may have a zero net polarization due to the random orientation of its domains. Random orientation of domains cancels out the piezoelectric effect in the polycrystalline ceramics. To develop piezoelectricity in the polycrystalline ferroelectric materials, their domains have to be aligned with ferroelectric domains in a polar state. This procedure is known as the poling process, in which we apply a high continuous DC electric field in the material, which changes with DC voltage, temperature, and time. We apply 20-100 kV/cm electric fields (this depends on the thickness of the samples) at some temperature near the Curie point of the ferroelectric material and both the temperature and the electric field are expected to accelerate domain wall movement in the direction of electric field. One of the best ways to pole the samples is to heat the samples at more than  $T_C$  and apply the maximum electric field that can sustain the material and then start cooling the samples with that electric field. Electric dipoles in artificial piezoelectric materials are randomly oriented as shown in Figure 2.11a; hence these materials do not exhibit the piezoelectric effect. Electric dipoles are oriented in the direction of applied external DC electric fields as shown in Figure 2.11b. The orientation is dependent on the applied external DC electric field which is known as the poling effect. Once the electric field is applied, the dipoles maintain their orientation, and the material then exhibits the piezoelectric effect, so that an electrical voltage can be recovered along any surface of the material when the material is subjected to mechanical stress [7]. However, the alignment of electric dipole moments may not be perfect [Figure 2.11c], since before the field was applied, the orientation of the polarization of domains may have been random.



**Figure 2.11:** A schematic orientation of dipoles due to the application of an electric field, (a) Random orientation of polar domains, (b) Application of high DC electric field, (c) Remnant polarization after the DC electric field is removed.

In this way, all ferroelectric domains will orient in the same direction. Temperatures higher than  $T_C$  (Curie point) affect the tetragonal structure. During cooling in the presence of an electric field, materials transform in the ferroelectric phase (non-centrosymmetric structure). At the beginning of the para - ferro phase transition, the permanent dipoles start to orient in the direction of the applied field. Gradually, all the domains orient in the direction of the applied field. Such high electric field in the air medium is not possible, as it starts to spark, and a short-circuit occurs. To avoid such circumstances, we apply such high DC electric field in a silicon oil bath. In this bath chamber, we can apply the required DC electric field in the samples.

However, for the second temperature, there are some limitations. However, as the boiling point of silicon oil is  $\sim 180$  °C, we are unable to process the same technique in case of materials with Curie point higher than 180 °C. Also, it is important to reach the highest macroscopic polarization avoiding breakdown of the ferroelectric materials. It usually occurs due to the dielectric breakdown of the materials itself; through cracks, moisture, discharge, defects, bubbles, and moisture. Mostly, dielectric strength is increased along with the increase of the thickness of the samples but this is not always the case. However, we optimize the high temperatures with the maximum electric field that it is possible to apply to the samples and give more time so that the probability of switching the domains is maximized. However, we cannot align all of the domains in the applied electric field direction. Depending on the many factors such as structure, synthesis method, etc., we can reach ~ 86 % for the rhombohedra phase, ~ 83 % for the tetragonal phase, and ~ 91 % for the orthorhombic phase compared to single crystals [8]. After the poling process in the sample, the polarization induced in the ferroelectric samples start to decrease as a function of time. This process is called the aging process. Although, many theories have been proposed to understand the mechanism of the aging process, till now there is no clear understanding of the process to degrade the poling process with time. Also, at this time stage, the major cause of the aging to reduce the poling process with time is minimizing the electrostatic energy. Hence, from a thermodynamic point of view, the necessity to obtain the lowest energy level with the reduction is in the poling process. Also, defect dipole reorientation model appears to apply to elaborate the de-poling behaviour with time as a function of vacancy concentration. A mobile charged defect can assess the spontaneous polarization in two ways: orientation of defect electric dipoles along the spontaneous polarization and the movement of free charges along the perimeter of the crystal grain boundary that reduces the effective polarization response.

#### 2.4.6 X-ray absorption spectroscopy (XAS)

X-ray absorption spectroscopy (XAS), is a widely used method to determine atomic local structure as well as electronic states. These experiments are mostly performed at synchrotron-radiation source, which provides high resolution and tunable x-ray beam. The wavelength of x-rays ranges from 25~0.25 Å. Therefore, the energy of X-rays ranges from 500 eV~500 keV. The wide range of x-ray energy enables x-rays to eject electrons from different levels of an atom, including the core level. X-ray strikes an atom and excites a core electron that can either be promoted to an unoccupied level or ejected from the atom. Both of these processes create a core hole. The electrons that are excited are typically from the 1s or 2p shell [Figure 2.10], so the energies are on the order of thousands of electron volts since it requires high-energy x-ray excitation, which is possible at the synchrotron radiation source. When energy is absorbed from 1s or 2pshell, an abrupt increase in absorption cross-section gives rise to an absorption edge in the absorption versus photon energy. The edges for an atom can be named according to the principle quantum number of the electron that is, K for n = 1, L for n = 2, M for n = 3, etc. The abbreviation XAS covers both x-ray absorption near edge structure (XANES) and extended x-ray absorption fine structure (EXAFS) spectroscopies. X-ray absorption near the edge structure can be used to determine the valence state and coordination geometry, while EXAFS can be used to determine the local environment. An atom contains a dense nucleus of positively charged protons and uncharged neutrons surrounded by negatively charged electrons. The atomic number Zassociated with an element in the periodic table corresponds to the number of protons, and a neutral atom has an equal number of protons and electrons. There are two groups of electrons associated with an atom. The loosely bound electrons, known as valence electrons occupy the outermost orbitals and participate in chemical bonding, and the tightly bound core electrons occupy the innermost orbitals that are an essential part of an atom. Different oxidation states of the atom are determined by charge imbalances caused by the removal of the

outermost electrons. For example, Cr(0), Cr(III), and Cr(VI) have lost zero, three, and six electrons, respectively, and Cr(VI) is in a higher oxidation state than Cr(III) or Cr(0).



**Figure 2.12:** A schematic diagram of the absorption of x-ray by an atom promoting a core-level electron K into the continuum [9]. The inset shows the schematic for x-ray absorption measurements: An incident monochromatic beam of intensity  $I_1$  passes through a sample thickness  $\Delta d$  and transmitted beam has intensity  $I_2$ .

The scattering of an incident wave by the local arrangement of elements results in a complex interference pattern in the extended range of x-ray energies beyond the edge. The full implications of this process are that when applied to the molecules, liquids, and solids, it gives rise to XAFS. When discussing x-ray absorption, we are primarily concerned with the absorption coefficient  $\mu$ , which allows for the probability that x-rays will be absorbed according to Beer's Law [10, 11]:

$$I_2 = I_1 e^{-\mu\Delta d}$$
 .....(2.6)

where  $I_1$  is the x-ray intensity incident on the sample,  $\Delta d$  is the sample thickness, and  $I_2$  is the intensity transmitted through the sample, as shown in the inset of Figure 2.12. X-ray intensity is proportional to the number of x-ray photons. The absorption coefficient  $\mu$  is a smooth function of energy, with a value that depends on the sample density  $\rho$ , the atomic number *Z*, atomic mass *A*, and the x-ray energy *E* roughly as:

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The strong dependence of  $\mu$  on both *Z* and *E* is a fundamental property of x-rays and is the key to why x-ray absorption is useful for different applications.

Whenever the incident x-ray energy equals that of the binding energy of the core-level electron, an x-ray has been absorbed. This absorption looks like a step. This is called absorption edge and has the properties of being linear and smooth below the absorption edge, increasing rapidly at the edge and then oscillating above the edge. The main sharp edge is the absorption edge, due to the excitation of the photoelectron into the continuum. An extended x-ray absorption fine structure (EXAFS) is the normalized oscillatory part of the absorption coefficient above the absorption edge to approximately 1000 eV or higher. It measures the energy dependence of  $\mu$  at and above the binding energy of a known core level of a known atomic species. Every atom has core-level electrons with the well-defined binding energies, and x-rays can be tuned according to the absorption edge of a selected species. Roughly, the edge energy varies with the atomic number of the element. In Figure 2.12, an electron of k-shell has been excited, and a core hole is created. To fill the core-shell within femtoseconds, the excited state will eventually decay of the absorption event. The decay does not affect the absorption process.





*Figure 2.13*: The decay of an excited state: (a) X-ray fluorescence and (b) The Augur effect [12]. In each of the case, the probability of emission is directly proportional to the absorption probability.

There are additional mechanisms for the decay of electrons, one being fluorescence, as shown in Figure 2.13 a. When a sample is illuminated with high energy x-ray photons, particles such as x-ray photons and electrons with sufficient energy are ejected from the atoms. This generates a 'hole' in one shell, resulting in the conversion of the atom into an unstable ion. To restore a (more) stable state, the holes in inner shells are filled by transforming electrons from outer orbitals. Since outer shells have higher energy than inner shells; such electron transitions are accompanied by energy emission in the form of secondary x-ray photons, which is referred to as fluorescence [13]. In x-ray fluorescence, a higher energy core-level electron fills the deeper core hole, ejecting an x-ray of well-defined energy. The fluorescence energies emitted in this way are characteristic of the atom and can be used to identify the atoms in a system and to quantify their concentrations. For example, an L or M shell electron dropping into the K level yields the K fluorescence line. The second effect is known as the Augur effect, in which an electron drops from a higher electron level and a second electron is emitted into the continuum (and possibly even out of the sample) as shown in Figure 2.13 b. In the hard x-ray region (> 2 KeV), x-ray fluorescence is more likely to occur than Auger emission, but for lower energy x-ray absorption, Auger processes dominate. Either of these processes can be used to measure the absorption coefficient  $\mu$ , though the use of fluorescence is more common. XANES/ EXAFS measurement can be carried out either in transmission or fluorescence mode as shown in Figure 2.13. The geometry for Augur measurement is also the same as the fluorescence geometries, except that the position of the detector, as in the fluorescent mode, it is the right angle to the incident beam as shown in Figure 2.14, whereas in transmission mode, the detector is in line with the beam.





Overall, the energy dependence of the absorption coefficient  $\mu(E)$  can be measured in transmission as

$$\mu(E) = \log(\frac{I_2}{I_1})$$
 (2.8)

and in x-ray fluorescence mode as

where,  $I_f$  is the monitored intensity of a fluorescence line associated with absorption process. In the present work, XANES and EXAFS were measured of the  $PbTi_{(1-x)}Fe_xO_3$  series, where *Pb*  $L_3$  edge is measured in the transmission mode. *Ti K* edge, and *Fe K*–edges are carried out in the fluorescence mode. XANES measurement is used to see the charge state whereas EXAFS is used to understand the local environment of the element.

# 2.4.7 Ferroelectric and piezoelectric measurement

This is one of the most potent tools to confirm that the material is a ferroelectric material. The set-up of the equipment is shown in Figure 2.15 and block diagram is shown in Figure 2.16. P-E hysteresis measurement of bulk samples was carried out using the Radiant Technologies ferroelectric test system. The ferroelectric test modes systems are virtual ground and Sawyer-Tower modes. In the Sawyer-Tower technique, the capacitive voltage of the bulk samples would be used, and it comprises of the test sample and a sensing capacitor. The generated voltage across the sense capacitor is proportional to the charge stored in the sample. In the virtual ground mode, the stored charge of the ferroelectric sample would be measured by integrating the current required to maintain the sample at zero volts, hence it is known as virtual ground. By eliminating the external sense capacitor, this circuit drastically reduces the effects of parasitic elements. A very high precision capacitor used as the feedback element in the current integrator is a key element in obtaining high accuracy with this technique. In Figure 2.15, Ferroelectric/piezoelectric set up has been shown with the mark of 1 to 5 numbers. Number 1 indicates the three elements kept on one by one that is Ferroelectric circuit systems. Number 2 indicates the ferroelectric measurement sample holder connected with two high voltage wires. Number 3 is indicates the computer system with relevant software combined with systems, and numbers 4 and 5 show the piezoelectric measurement and sample holder respectively, that is also connected to the same computer with labeled as number 3. In this piezoelectric system, we measure the indirect piezoelectric coefficient, since we apply the electric field and measuring strain generated in the samples. Both unipolar and bipolar measurements are possible with this system. In Figure 2.16, the block diagram is shown one by one to confirm the working of a principle of the ferroelectric measurement systems.



Figure 2.15: Radiant-technology set-up to measure the ferroelectric loop and additional set up joint to measure the piezoelectric butterfly loop.



*Figure 2.16:* Block diagram of the Radiant technology *P*-*E* loop tracer set-up.

Using the radiant-technology set up for the ferroelectric loop measurement, all samples are performed to see the ferroelectric properties. It is an automatic system and user-friendly software. In the beginning, we applied the small electric field at some fixed frequency. Moreover, we increased the electric field to see the hysteresis curve of the sample. At the maximum applied field, we kept varying the different frequencies to see the nature of hysteretic nature of the ferroelectric material. It is to be noted here that during the ferroelectric measurement the samples were immersed in the silicon oil bath to prevent electric arcing at high voltages. Such a high voltage in the air is not possible because it will result in a short circuit. Also, we measured the bipolar strain with the applied electric field. This is commonly known as indirect piezoelectric measurement. In the present work, ferroelectric measurement of bulk form was performed in the polarization versus electric field loop (P-E) tracer (from M/s Radiant Instruments, USA) in UGC-DAE Indore India.

#### 2.4.8 Magnetic measurement

In the present work, magnetic measurement was performed with the Magnetic field dependent magnetization of the samples and was examined using a Quantum Design Physical Property Measurement System (PPMS) equipped with a 9T magnet. The working principle of PPMS is briefly described below. PPMS system is available in a truly cryogen-free package. It is He-based gas flow control system that provides the rapid temperature cycling and accurate temperature control. Temperatures can vary from 1.8 K to 400 K and the magnetic field can be 9T, 12T or 14T. Its operation is fully automated. To confirm the magnetic property in the samples, measurement was carried out at a fixed temperature as a function of the applied magnetic field. We have measured it at different fixed temperature. This measurement gives information about the magnetic state and hysteresis behaviour in high fields.

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## 2.5 Rietveld refinement techniques

Rietveld refinement method was carried out to quantitative analysis of powder x-ray diffraction data. Using a crystal structure model, Rietveld quantitative analysis involves calculating diffraction patterns of individual components of a mixture. The observed pattern is fit by the resultant simulated pattern by varying the parameters of the model. The Rietveld refinement method is one of the very powerful techniques that provide information regarding the samples such as unit cell parameters, atomic occupancies, position parameters, etc. Most of XRD instruments manufactures in the current time offer some form of Rietveld refinement in their XRD software packages. In the present samples studied, we have performed Rietveld refinement of the highresolution powder x-ray diffraction pattern data. Improvements were carried out using the Fullprof software packages.

The Rietveld refinement method is used to refine a calculated line pattern to evaluate potential matches with the experimental pattern. This method aims to minimize the difference between the experimental and calculated patterns by least-squares refinement. It does this by making small incremental changes to the model using a series of changeable parameters. This special technique was originally developed by the Rietveld for nuclear and magnetic structural refinements but has subsequently been adapted to allow for different peak profiles found in XRD patterns [14].

There are two approaches to allocating with the background in an x-ray powder diffraction pattern. It can be estimated by plotting a series of data points between peaks and subsequently subtracting them, or can be modelled by a function containing several refinable parameters. Both models have their positive and negative points corresponding to the XRD data. For a simple pattern where most of the peaks are resolved to the base-line data, both methods work well, and the refinement fit is easily verified. In many complex patterns, the reflection of peaks is not well resolved with a high degree of reflection overlap (some time say as noisy background). This type of background is more difficult in refining the data. In such cases, if background subtraction method is used, the background has to be re-estimated and re-subtracted several times during a refinement. Similarly, there can be issues with the refinable background, as the initial polynomial is unable to describe the experimental data, and more complex mathematical functions also proves insufficient. Thus, it becomes impossible to fit regardless of how many refinement iterations are carried out. In such a situation, both these methods should be used beginning with the simple function of complex polynomial function carried out step by step.

Before refining the actual structural parameters, the initial shape of the peaks in the powder x-ray diffraction data is needed. The refinement will be in an appalling shape if the peak shape does not match well. Hence, peak shape analysis is a major contribution to the Rietveld refinement analysis. Contributing parameters to the peak shape analysis arise from both structural defects and instrument characteristics (radiation source, slit sizes, geometry) and they vary as a function of angle. Most of the researchers use a linear combination of Lorentzian and Gaussian profiles, which is known as a pseudo-Voigt function [15].

To find the peak parameters reliably from the experimental equivalent peaks, one method described below is efficient. In this case, we should first try structure free approaches like Le-Bail method, in which the intensities of the peaks are only adjusted to fit the observed ones to obtain initial values for the profile parameters without accounting the atom positions. After finding these values, well-adjusted starting values for the Rietveld refinement parameters can be defined. To the observer, in the progress of the refinement, the two useful parameters are profile fit and the nature of fit parameters shift (oscillation, convergence, and divergence). The Rietveld refinement and calculated pattern. Numerically, the goodness of fit factor  $\chi^2$  (equation 2.12) can be an indication. Generally, its value not exceeds ~10.

Difference profile plot is one of the best ways to guide a

Rietveld refinement as the fit, difference in calculated and observed data can also be calculated and expressed as a series of numerical coefficients. Weight profile factor is one of such coefficient  $R_{wp}$  defined as

where  $y_i(obs)$  is observed (experimental) intensity,  $y_i(calc)$  the intensity from the calculated model, and  $w_i$  the weight. When the background is refined,  $y_i(obs)$  and  $y_i(calc)$  will include the background. In an ideal scenario, the final  $R_{wp}$  should approach the statically expected R value,  $R_{exp}$ ,

where N is defined as the number of observations and P as the number of parameters.  $R_{exp}$  reflects the quality of the data before refinement, and after that when compared to  $R_{wp}$ , gives an overall view of the quality of Rietveld refinement. The ratio of the two between the  $R_{wp}$ and  $R_{exp}$  provides an excellent fit. This is a good indicator of the overall quality of both experimental and calculated profile data.

Overall, the judging criteria of Rietveld refinement are: fit of the experimental and calculated a pattern data and position of the structural model with a sensible set of chemical compositions.

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# **Chapter 3**

# **Part-A**

# Structural and ferroelectric properties of perovskite Pb<sub>(1-x)</sub>(K<sub>0.5</sub>Sm<sub>0.5</sub>)<sub>x</sub>TiO<sub>3</sub> ceramics

This chapter aims at studying numerous physical properties of A-site modified PbTiO<sub>3</sub> with approximately equal ionic radii and charge state. This chapter covers sample preparation followed by characterizations to see properties of materials. We prepared samples using a modified sol-gel combustion process followed by solid-state sintering for crystallization of these samples. After synthesis samples were characterized by synchrotron-based XRD using rotating capillary mode to reduce orientation effects. Such a strong source and probe was used to ensure phase purity and detailed crystal structure of these samples. Vibrational studies were verified by observing variations in phonon modes in Raman spectra of these materials. Temperature-dependent dielectric studies were carried out to perceive variations of phase transition temperature with composition. Impedance studies were investigated to analyze grain and grain boundary contributions in these samples. Polarisation versus electric field measurements was performed to confirm ferroelectric properties. Rietveld refinement was carried out to estimate structural variations with compositions.

# **3A.1** Synthesis

Sol-gel processed polycrystalline  $Pb_{(1-x)}(K_{0.5}Sm_{0.5})_xTiO_3$  ( $0 \le x \le 0.50$ ) (*PKST*) ceramics were prepared using hydrated Lead (II) nitrate (*Pb*(*NO*<sub>3</sub>)<sub>2</sub>), Potassium nitrate (*KNO*<sub>3</sub>), Samarium oxide and Titanium(IV) bis(ammonium lactato) dihydroxide (*TALH*) solution as

precursors with purity > 99.99 % (Alfa Aesar, Puratronic grade).  $Sm_2O_3$  was dissolved in dilute *HNO*<sub>3</sub>. Details are given in chapter 2.

# **3A.2 Structural properties**

Synchrotron-based x-ray powder diffraction (SRPXRD) pattern in rotating capillary mode of  $Pb_{(1-x)}(K_{0.5}Sm_{0.5})_xTiO_3$  ( $0 \le x \le 0.50$ ) powders with  $0 \le x \le 0.50$  range, were analyzed after crushing pellets sintered at 1050 °C for 6 h with mortar and pestle. Wavelength ( $\lambda$ ) was calibrated 0.44573 Å for XRD measurement. SRPXRD patterns are shown in Figure 3A.1. All peaks correspond to pure PbTiO<sub>3</sub> structure. Hence, in all samples, there are no secondary phases observed.



*Figure 3A.1:* Synchrotron-radiation source powder x-ray diffraction patterns of  $Pb_{(1-x)}(K_{0.5}Sm_{0.5})_xTiO_3$  ( $0 \le x \le 0.50$ ) range samples.

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**Figure 3A.2:** Enlarge part of SRPXRD patters of  $Pb_{(1-x)}(K_{0.5}Sm_{0.5})_xTiO_3$  ( $0 \le x \le 0.50$ ) range samples to see variations in the peak shape and positions with increasing compositions.

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**Figure 3A.3:** Goodness of SRPXRD data fittings for  $Pb_{(1-x)}(K_{0.5}Sm_{0.5})_xTiO_3$  ( $0 \le x \le 0.50$ ) samples, where (a) x = 0,(b) x = 0.06, (c) x = 0.09, (d) x = 0.12, (e) x = 0.18, (f) x = 0.25, (g) x = 0.37, and (h) x = 0.50 compositions. To visualize the fitting and change in peak

shape with increasing composition, inset figures are high lighted at lower angles for all compositions.

With increase in substitution peaks merge and system tends to transform gradually from tetragonal to cubic structure [Figure 3A.2]. Tetragonal (001) and (100) peaks merge into cubic (100) while (101) and (110) merge to cubic (110) peaks [Figure 3A.2(a-b)]. Similar peak merging is observed for other parts of SRPXRD data [Figure 3A.2c]. To understand quantitative and qualitative analysis of SRPXRD data and transformation from tetragonal to cubic system, Rietveld refinement of all SRPXRD data was performed. Excellent fitting parameters for  $0 \le x \le 0.37$  compositions were obtained with tetragonal *P4mm* space group. Only for x = 0.50, a cubic *Pm3m* space group was required. Refinements were performed keeping Pb/K/Sm positions fixed at (000). Variations in crystal structure and lattice dynamics in PbTiO<sub>3</sub>-based tetragonal and cubic systems are widely investigated using such a model [1, 2]. Background estimation was performed with linear interpolation and Bragg peaks with Pseudo-Voigt function, using axial divergence asymmetry function.

Shape and asymmetry parameters were refined with excellent goodness of fit. Scale factor, lattice parameters (*a*, *c*), half width parameters (*U*, *V*, *W*) and positional coordinates (*x*, *y*, *z*) of various lattice sites were also refined. Refinement started with pure PbTiO<sub>3</sub> SRPXRD data. For a higher substituted composition, the preceding lower substituted composition was considered as a starting model for refinement of structural parameters. Rietveld refinement patterns with fitted data are shown in Figure 3A.3(a-h). Hollow black circles are observed data points; red lines are the simulated data; dark yellow lines are the differences of observed and calculated data points, and vertical green line bars are Bragg positions related to fitted space group. Rietveld refinement parameters such as *R*-factors ( $R_p$ ,  $R_{wp}$ , and  $R_{exp}$ ) and  $\chi^2$  were in acceptable range for all samples [Table 3A.1].
**Table 3A.1:** Parameters related to goodness of fitting (*R*-factors and  $\chi^2$ ) from Rietveld refinement of XRD data of  $Pb_{(1-x)}(K_{0.5}Sm_{0.5})_xTiO_3$  samples

Compositions	$R_p$	$R_{wp}$	R <sub>exp</sub>	$\chi^2$
x = 0	7.48	8.51	5.97	2.03
<i>x</i> = 0.06	7.29	6.75	6.51	1.07
x = 0.09	7.02	7.65	5.13	2.22
<i>x</i> = 0.12	7.90	8.53	7.38	1.34
<i>x</i> = 0.18	10.4	11.8	7.43	2.51
<i>x</i> = 0.25	9.61	10.3	10.01	1.07
<i>x</i> = 0.37	8.81	8.13	7.81	1.08
x = 0.50	7.65	7.82	6.44	1.47

Refined position parameters for all samples are provided in table 3A.2. The *z*-parameters of *Ti*, *O1* and *O2* are found to decrease with increase in substitution. Other positions are invariant for all the samples. For x = 0.50 composition, system is centrosymmetric and all the positions are invariant.

**Table 3A.2:** Rietveld refined position parameters of  $Pb_{(1-x)}(K_{0.5}Sm_{0.5})_xTiO_3$  ( $0 \le x \le 0.50$ ) samples after final cycle.

Atoms	Coordin	<b>Compositions</b> ( <i>x</i> )				
	ates	0.00	0.06	0.09	0.12	
Pb/Sm/	x	0	0	0	0	
Κ	У	0	0	0	0	
	Z.	0	0	0	0	
Ti	x	0.5	0.5	0.5	0.5	
	у	0.5	0.5	0.5	0.5	
	Z.	0.53816	0.53813	0.53781	0.53695	
		(1)	(1)	(1)	(1)	
01	x	0.5	0.5	0.5	0.5	
	у	0.5	0.5	0.5	0.5	
	Z.	0.1086	0.10844	0.10329	0.09688	
		(267)	(1)	(1)	(1)	
O2	x	0.5	0.5	0.5	0.5	
	У	0	0	0	0	
	Z.	0.60843	0.60615	0.60479	0.60285	
		(157)	(0)	(1)	(1)	

Atoms	Coordin	Compositions (x)				
	ates	0.18	0.25	0.37	0.50	
Pb/Sm/	x	0	0	0	0	
Κ	у	0	0	0	0	
	Z.	0	0	0	0	
Ti	x	0.5	0.5	0.5	0.5	
	У	0.5	0.5	0.5	0.5	
	Z.	0.5366	0.53562(	0.52142(1	0.5	
		(1)	1)	78)		
01	x	0.5	0.5	0.5	0.5	
	у	0.5	0.5	0.5	0.5	
	Z.	0.08053	0.05957(	0.05896(3	0	
		(1)	1)	25)		
02	x	0.5	0.50	0.5	0.5	
	у	0	0	0	0	
	Z.	0.58873	0.57327(	0.56704(1	0.5	
		(1)	1)	87)		

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Lattice parameter 'c' decreases with increasing composition x, while 'a' is almost constant [Figure 3A.4]. Hence, c/a ratio decreases to ~1 for x = 0.5 as shown in Figure 3A.4. Variation of lattice parameters with composition is also a signature of proper substitution of Pb by K/Sm.  $Pb^{2+}(XII)$  has a crystal radii of 1.62 Å. On the other hand, crystal radii of  $K^+(XII)$  is ~1.78 Å and that of  $Sm^{3+}(XII)$  is ~1.38 Å. An average of these two is ~1.58 Å which is slightly smaller but comparable to the parent  $Pb^{2+}(XII)$ . This small decrease of effective ionic radii may have led to decrease in lattice parameters. Overall tetragonal lattice strain, estimated from c/a ratio decreases (c/a = 1 for x = 0.50 composition) with increase in substitution.



Figure 3A.4: Calculated lattice parameters and c/a ratio of  $Pb_{(1-x)}(K_{0.5}Sm_{0.5})_xTiO_3$  ( $0 \le x \le 0.50$ ) samples.

In perovskite ABO<sub>3</sub> samples, tolerance factor is a quantitative measure of mismatch between bonding requirements of *A* and *B*-site cations and subsequently reflects structural distortions such as rotation/tilt of *B*-octahedral. Lattice stability and distortion of crystal structures are related to this mismatch [3] and hence can be estimated from tolerance factor (t), given by,

$$t = \frac{(R_A + R_O)}{\sqrt{2}(R_B + R_O)}$$
 .....(3A.1)

where,  $R_A$ ,  $R_B$  and  $R_O$  are radii of A and B-site ions and O ions, respectively. Since average A-site ionic radii of substituent are lesser compared to Pb, tilt as well as non-centrosymmetric distortion will reduce. Merging peaks in SRPXRD data indicate a transformation from non-centrosymmetric to centrosymmetric structure [4, 5]. The tolerance factor of the  $Pb_{(1-x)}(K_{0.5}Sm_{0.5})_xTiO_3$  samples decreases from 1.019 as in x = 0 to 0.988 for x = 0.5, also lattice strain decreases with increasing substitution.

Room-temperature Raman spectroscopy was done to qualitatively assess retention of domain structure, defects and structural distortions and thereby understand deformations and lattice strains associated with substitution in  $Pb_{(1-x)}(K_{0.5}Sm_{0.5})_xTiO_3$  samples.

Raman spectra for samples are shown in Figure 3A.5. All observed modes belong to pure PbTiO<sub>3</sub> having tetragonal space group symmetry  $(C_{4v}^1)$  with 12 optical modes attributed to three  $A_1$ -symmetry modes, eight *E*-symmetry modes (Four degenerate pairs) and a  $B_1$ -symmetry mode [6-8].



**Figure 3A.5:** Room temperature Raman spectra of  $Pb_{(1-x)}(K_{0.5}Sm_{0.5})_xTiO_3$   $0 \le x \le 0.5$  range samples. Peaks reduce in intensity with increasing substitution, hinting at changing structure from tetragonal to pseudo cubic structure.



*Figure 3A.6:* Graphical representation of zone-center normal modes of vibrations for  $PbTiO_3$  with atoms projected on xy basal plane. The corner atoms are Pb and the shaded atoms are Ti. The oxygen atoms are shown by large open circles [6].

Intensity of  $A_1(1TO)$ ,  $A_1(2TO)$  and  $A_1(3TO)$  reduces with increasing substitution. Among  $A_1$  modes, the most intense mode is  $A_1(1TO)$ . This mode merges with E(1TO) mode to form  $T_{1u}$  mode in cubic form. The  $A_{l}(1TO)$  mode is due to oscillations of Ti-octahedra (i.e. Ti and O together) relative to Pb ions [9]. This mode does not soften much but nearly vanishes after x = 0.09 composition.  $A_1(2TO)$  mode is due to oscillations of Ti ion relative to O and Pb ions. This mode softens nominally until x = 0.09 but thereafter drastically softens to merge with E(2TO) mode in x = 0.5 composition. A similar but less drastic trend is observed for  $A_1(3TO)$  mode, in which Ti ions and the apical O ions together form a chain and vibrates along c-axis with respect to Pb and other O atoms. From all these three modes it is understood that relative motion between Pb, Ti and O ions reduces along c-axis with substitution. In Figure 3A.6, we have shown a pictorial representation of all vibrational modes of  $PbTiO_3$ . The corner gray ions represent Pbwhile central blue ones represent Ti ions. Smaller green spheres represent oxygen ions. All ions lie on the xy basal plane. The plus sign represents ions vibrating out of plane of paper while minus represents opposite direction. Directions, in-plane vibrations are shown by arrows.

Tetragonal PbTiO<sub>3</sub> is a strained lattice. The strain originates from a very strong hybridization between  $Pb(6s^2)$ -O(2p) and also due to a moderate Ti(3d)-O(2p) hybridization [10, 11]. As a result of substitution of Pb by K/Sm, we expect a reduction of strong  $Pb(6s^2)$ -O(2p) bond. This reduction in strength of the bond reduces energy of vibration which is reflected in softening of  $A_1(2TO)$  mode. Such a reduction in energy in  $A_1(1TO)$  mode is not observed as in this mode; A-site is freely oscillating with respect to Ti-O octahedron. However lesser number of oscillators reduce the intensity of  $A_1(1TO)$  and  $A_1(2TO)$ . Note that E(3TO) mode gains energy with substitution. Lower mass of K/Sm compared to Pb may be a reason for the same.

The most noticeable significance of Raman measurement is that even at x = 0.50 we observe all modes where from XRD  $c/a \sim 1$ . Such an observation hints at fact that a remnant strain which may or may not be related to tetragonal structure is retained in high *x* samples. In cubic mode, pure *PbTiO*<sub>3</sub> does not have any Raman mode, as all  $A_1(TO)$  and E(TO) modes merge and vanish gradually at phase transition [6].

Microstructure analysis of  $Pb_{(1-x)}(K_{0.5}Sm_{0.5})_xTiO_3$  ( $0 \le x \le 0.50$ ) ceramic samples are recorded in  $0.06 \le x \le 0.50$  range using Field emission scanning electron micrograph. Surface microstructures are shown for all samples in Figure 3A.7. Grains are closely packed in all samples. Average grain size was calculated using Image J software [12]. Average grain size was found to decrease from  $1.19 \pm 0.53 \mu m$ for composition with x = 0.06 which decreases to  $0.98 \pm 0.37 \mu m$  for x = 0.50 composition. Average grain size seems to decrease nominally with increasing *K/Sm* substitution. This behavior could be attributed to the lower diffusivity of rare earth during sintering. Similar behavior has been observed in other rare earth doped perovskites and layered perovskites [13, 14].

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Figure 3A.7: Surface microstructure analysis of  $Pb_{(1-x)}(K_{0.5}Sm_{0.5})_xTiO_3$ samples, where (a) x = 0.06, (b) x = 0.09, (c) x = 0.12, (d) x = 0.18, (e) x = 0.25, (f) x = 0.37, and (g) x = 0.50 compositions.



**Figure 3A.8:** Microstructure analysis of fractured surface of  $Pb_{(1-x)}(K_{0.5}Sm_{0.5})_xTiO_3$  samples annealed at 1150 °C for 6 hours, where (a) x = 0.06, (b) x = 0.09, (c) x = 0.12, (d) x = 0.18, (e) x = 0.25, (f) x = 0.37, and (g) x = 0.50 compositions.

To see inside grain morphology, we have captured micrographs of fractured pellets. These micrographs of fracture surface [Figure 3A.8] reveals compact grains in the samples. The good compact poreless nature of the bulk of these pellets reduces chances of silver paste to percolate through the surface while making electrodes for electrical measurements.

Densities of sintered  $Pb_{(1-x)}(K_{0.5}Sm_{0.5})_xTiO_3$  pellets were measured by the Archimedes method using double distilled water (density = 1 g/cm<sup>3</sup>) as immersing liquid. Theoretical densities were also estimated using formula weight and volume of unit cells calculated from refinement of XRD data. Relative density (= Measured density/Theoretical density) was calculated to be ~ 93 %, 94 %, 95 %, 95 %, 95 %, 92 %, and 91 % for x = 0.06, 0.09, 0.12, 0.18, 0.25, 0.37, and 0.50 respectively.

## **3A.3 Dielectric properties**

To explore electrical properties of  $Pb_{(1-x)}(K_{0.5}Sm_{0.5})_xTiO_3$  pellet samples, electrodes were prepared using high-temperature silver paste, painted on both sides of sintered pellets. Silver coated pellets on either side were cured at 550 °C for 15 minutes to improve pellet electrode adhesion. Before doing the measurement, we heated samples at 200 °C for 10 minutes to get rid of any adhered surface moisture. A dielectric response was measured using a Newton's 4<sup>th</sup> Ltd PSM 1735 phase sensitive LCR meter with signal strength of ~1V.

Room temperature dielectric properties were measured as a function of frequency for PKST ( $0.06 \le x \le 0.50$ ) range samples as shown in Figure 3A.9a. Dielectric constant ( $\varepsilon$ ) and loss (tan $\delta$ ) (Figure 3A.11a) decreases at low frequency range (100 Hz to 10 kHz) and remains almost constant in high frequency region.

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**Figure 3A.9:** (a) Room temperature dielectric constant versus frequency for  $Pb_{(1-x)}(K_{0.5}Sm_{0.5})_xTiO_3$   $0.06 \le x \le 0.50$  range samples, and (b) Compositional dependence of dielectric constant at specific frequencies.

There are contributions in dielectric constant and loss at lower frequency region such as space charge, ionic, orientation, and electronic polarization. With increase in frequency, contribution sources continuously reduce and filter out at specific frequencies. We observe that with increasing substitution, value of  $\varepsilon'$  of PKST ceramics increases exponentially as shown in Figure 3A.9b. This behavior of  $\varepsilon'$  at room temperature and similar trend in  $tan\delta$  can be attributed to higher dipolar polarizability of *K/Sm* than *Pb* [15, 16]. For x = 0.50 composition,  $\varepsilon'$  increases rapidly probably due to its near room temperature phase transition.

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*Figure 3A.10: Temperature-dependent dielectric constant was* measured at some specific frequency, where (a) x = 0.06, (b) x = 0.09, (c) x = 0.12, (d) x = 0.18, (e) x = 0.25, (f) x = 0.37, (g) x = 0.50compositions, and (h) Phase transition temperature with compositions.

To study phase transition temperature in PKST and other dielectric properties, capacitance and dielectric loss factor were measured over temperature range of 300 K – 773 K at various frequencies in 1 kHz –1 MHz range for  $0 \le x \le 0.37$  range samples. For x = 0.5 composition, temperature range was 80 K to 355 K. It was quite difficult to fabricate a pure phase, sufficiently dense and mechanically robust *PbTiO*<sub>3</sub> pellet. Hence, dielectric properties of *PbTiO*<sub>3</sub> phase were not investigated.

Pure *PbTiO*<sub>3</sub> undergoes a sharp ferroelectric to paraelectric transition accompanied by a structural transition from polar tetragonal to non-polar cubic phase [17]. In such ferroelectrics, we observe maxima in  $\varepsilon'$ -*T* data, associated with this phase transition. For *PbTiO*<sub>3</sub> reported phase transition temperature is around 763 K (Curie temperature). In PKST samples this phase transition temperature (*T<sub>m</sub>*) varies from 680 K for x = 0.06 to 341 K as in x = 0.50 composition

shown in Figure 3A.10(a-g). Note that transition temperature is not frequency dependent; thereby samples are not relaxor.



**Figure 3A.11:** (a) Room temperature dielectric loss  $(tan\delta)$  versus frequency and inset figure is showing the dielectric loss  $(tan\delta)$  at high frequencies. Temperature-dependent dielectric loss  $(tan\delta)$  was measured at some specific frequencies, where (b) x = 0.06, (c) x = 0.09, (d) x = 0.12, (e) x = 0.18, (f) x = 0.25, (g) x = 0.37, and (h) x = 0.50 compositions.

Phase transition temperature approximately decreases linearly with substitution as shown in Figure 3A.10h. *Pb*  $6s^2$  lone pair helps in stabilizing tetragonal strain (~ 6 %) in *PbTiO*<sub>3</sub> [18]. We have shown from our SRPXRD and Raman analysis that with increasing substitutions, tetragonal strain is relieved in PKST samples. Reduction of tetragonal distortion reduces with substitution thereby requiring lesser thermal energy to achieve centrosymmetric cubic structure. Therefore, with increase in composition, phase transition temperature decreases. Similar trend has been observed in other perovskite-related ferroelectrics [19]. Similar phase transition behavior is also observed in temperature-dependent loss (tan $\delta$ ) for all samples as shown in Figure 3A .11(b-h).

A diffuse type of phase transition temperature was observed with increasing composition in temperature dependent dielectric studies. For better understanding the diffesed nature normalized dielectric constant versus  $T-T_m$  plots are shown in figure 3A.12 (a).

Investigation of possessing diffuse type phase transitions is of great interest because they have unique physical properties and wide practical applications. Diffuse phase transition is usually observed in perovskites with random distribution of different types of ions on structurally identical sites in lattice.



**Figure 3A.12:** (a) Normalize dielectric constant( $\varepsilon'/\varepsilon_m$ ) versus  $T-T_m$  for all the compositions at 1MHz frequency. Linear fitting of  $ln[(1/\varepsilon')-(1/\varepsilon'_m)]$  verses  $ln(T-T_m)$  of temperature–dependent dielectric constant at 1MHz frequency, where (b) x = 0.06, (c) x = 0.09, (d) x = 0.12, (e) x = 0.18, (f) x = 0.25, (g) x = 0.37, and (h) x = 0.50 compositions. Solid lines representing the fitted data and black symbols are observed data. (i) The calculated degree of diffuseness with the compositions for all the samples.

It must be noted that diffuse phase transition exhibit a broad change of structure and properties at Curie point compared to a sharp peak in normal ferroelectric materials [20-22]; consequently, phase transition characteristics of such materials are known to diverge from characteristic of Curie-Weiss behavior and can be described by a modified Curie-Weiss formula [23, 24].

$$\frac{1}{\varepsilon'} - \frac{1}{\varepsilon'_m} = C^{-1} (T - T_m)^{\gamma} \qquad (3A.2)$$

Where, *C* is Curie-Weiss constant and  $\gamma$   $(1 \le \gamma \le 2)$  gives degree of diffuseness. A value of  $\gamma = 2$  describes an ideal diffuse phase transition. Degree of diffuseness was calculated by the least-square linear fitting of  $\ln(\frac{1}{\epsilon'} - \frac{1}{\epsilon''_m})$  versus  $\ln(T - T_m)$  curves at a frequency of 1 MHz of PKST ceramics [Figure 3A.12(a-g)]. Slope of the linear fit, was found to increase from  $1.136 \pm 0.007$  for x = 0.06 to  $1.693 \pm 0.019$ for x = 0.50 indicating a significant increase in diffuseness of phase transition in doped samples as shown in Figure 3A.12h. Compositional disorder arising due to random distribution of  $K^+$  and  $Sm^{3+}$  seems to be responsible for observed diffuse phase transition in PKST ceramics.

Impedance spectroscopy enables to determine the various contributions to dielectric constant, such as grain, grain boundaries, and electrode effect [25]. Impedance of such type of system can be described by the Cole-Cole equation [26]

$$Z^*(\omega) = \frac{R_1}{1 + (j\omega\tau)^{1-\alpha}}$$
 ..... (3A.3)

The real (Z') and imaginary (Z'') parts of impedance can be written in the following manner:

with Cole-Cole parameter,  $\alpha = 2\theta/\pi$  being a measure of distribution of relaxation time,  $\tau = R_1 C$ , related to the resistance  $R_1$  and capacitance C associated with grain.



**Figure 3A.13:** (a-b) Nyquist plots of  $Pb_{(1-x)}(K_{0.5}Sm_{0.5})_xTiO_3$  ( $0 \le x \le 0.5$ ) range samples at 743K, (c) Resistance and time constant ( $\tau$ ), extracted from fitting of Nyquist-plots by Cole-Cole equation for all the samples.

The imaginary, -Z'' (capacitive) and real, Z' (resistive) impedances are plotted in Figure 3A.13(a-b). Capacitance due to grain boundary contribution is generally much higher than that of grain [25]. This may be due to grains having less resistance than grain boundary. In Nyquist plot, these effects are generally observed as three semicircles; first smaller one belonging to grain, second grain boundary followed by electrode contribution. Our results show only one semicircle. This contribution seems to be from grain as the semicircle starts from origin (high-frequency regime) and at highfrequency we have observed a steady dielectric constant. Note that, it may be possible due to less resistance at grain boundary, its effect suppresses and merge with grain effect. Also note that resistance of sample has increased with substitution as shown in Figure 3A.13. The increasing resistance is an indication of better charge retention properties, enhancing capability of being a polarizable material. Time constant or relaxation time ( $\tau$ ) is multiplication of resistant and capacitance. Accordingly, increase in resistance and capacitance increases time constant with increase in *x*. In addition, increase in temperature decreases the relaxation time for all compositions as shown in Figure 3A.13c.

## **3A.4 Ferroelectric properties**

Room temperature electric polarization (ferroelectric properties) was investigated for all compositions by studying field dependent polarization (P-E loops) at 1Hz frequency. There are two origins of ferroelectricity, spontaneous polarization, and domain switching. For  $0.06 \le x \le 0.37$ , the structure is elongated tetragonal type and a strained lattice is expected result in spontaneous polarization. It is to be noted that tetragonality decreases with substitution until x = 0.5 where phase is pseudo cubic-like. This hints at reducing ferroelectricity with substitution. Also, Raman modes broaden with increasing substitution hinting at dispersed vibrational motion of the phonons.  $A_{l}(1TO)$  mode is related to the vibration and distortion of Ti - O bonds and thereby to ferroelectricity. Mode sustains for all samples although getting diminished with substitution. Dielectric properties show shifting of phase transition towards lower temperatures with increasing substitution, suggesting existence of ferroelectricity at room temperature.



**Figure 3A.14:** Polarization and instantaneous current versus electric field of  $Pb_{(1-x)}(K_{0.5}Sm_{0.5})_xTiO_3$  samples, where (a) x = 0.06, (b) x = 0.12, (c) x = 0.18, (d) x = 0.25, (e) x = 0.37, and (f) x = 0.50 compositions.

Electric field dependent polarization (P-E hysteresis) and instantaneous current (I-E hysteresis) at 1 Hz frequency have been reported for all compositions as shown in Figure 3A.14(a-f). For  $0.06 \leq$  $x \le 0.12$ , *P*-*E* hysteresis loops [Figure 3A.14(a-b)] appears to be lossy dielectric type [27, 28] rather than typical ferroelectric. Also, no signature of domain switching is observed in *I*-*E* data for  $x \le 0.12$ samples [Figure 3A.14(a-b)]. Leaky, lossy nature may be due to comparatively lower resistances of lesser modified samples (observed from impedance studies). For x > 0.12, leaky nature decreases and proper hysteresis *P*-*E* loops were observed. For x = 0.5, it is expected a non-ferroelectric sample due to its cubic-like structure. However, we find a slim *P*-*E* loop with a weak *I*-*E* data. This hints at a nearly cubic structure for x = 0.5 composition. For a maximum applied electric field of 60 kV/cm sample with x = 0.25 shows highest apparent remnant polarization of 15.9  $\mu C/cm^2$  and a coercive field of 27.2 kV/cm. These values reduce with substitution to  $2.97 \mu C/cm^2$  and 6.91 kV/cmrespectively in x = 0.5 composition. A comparison of ferroelectric properties and phase transition temperature for a few PbTiO<sub>3</sub>-based compositions with compound Pb<sub>0.750</sub>Na<sub>0.125</sub>Sm<sub>0.125</sub>TiO<sub>3</sub> (studied in present investigation) is provided in Table 3A.3.

Table 3A.3: Remnant polarization,	coercive field, and phase transition
temperature for few selected PbTiO	3-based compounds:

			-	
Composition	Remnant polarization ( <i>P<sub>r</sub></i> )	Coercive field ( <i>E<sub>c</sub></i> )	Applied electric field at room temperatu re (E)	Phase transition temperature $(T_c)$
PbTiO <sub>3</sub> single crystal (001) oriented [29]	$\sim$ 57 $\mu$ C/cm <sup>2</sup>		± 20 kV/cm	~ 490 °C
Pb(Ho <sub>1/2</sub> Nb <sub>1/2</sub> )O <sub>3</sub> - Pb(Mg <sub>1/3</sub> Nb <sub>2/3</sub> )O <sub>3</sub> -PbTiO <sub>3</sub> single crystal (001) oriented [30]	~24.5 µC/cm <sup>2</sup>	~3.22 kV/cm	±7.5 kV/cm	~ 140 °C
Pb(Mg <sub>1/3</sub> Nb <sub>2/3</sub> )O <sub>3</sub> -PbTiO <sub>3</sub> (011)- oriented single crystal [31]	~28.9 µC/cm <sup>2</sup>	~1.2 kV/cm	±8 kV/cm	
PLT8 thin film ( $Pb_{1-x}La_xTi_{1-x/4}O_3$ for x=0.08) [32]	~18.5 µC/cm <sup>2</sup>	~144 kV/cm		~ 330 °C
Pb(Zr <sub>0.532</sub> Ti <sub>0.468</sub> )O 3 ceramics [33]	$\sim 26.2$ $\mu C/cm^2$	~18.4 kV/cm		~ 359 °C
$     Pb_{1-}     xLa_x(Zr_{0.52}Ti_{0.48})O      3 for x=0.05     ceramic [34]   $	8.99 µC/cm <sup>2</sup>	6 kV/cm		~ 105 °C
$     Pb_{1-}     x(K_{0.5}Sm_{0.5})xTiO_3     for x=0.25     ceramic     $	15.9 µC/cm <sup>2</sup>	27.2 µC/cm <sup>2</sup>	±60 kV/cm	~ 286 °C

Improvement of ferroelectric properties at room temperature in PKST samples results from increase of resistive and capacitive properties. In  $PbTiO_3$ , Pb and O vacancies are a common feature and results in non-stoichiometric samples mostly originating due to high volatility of Pb and subsequent O-vacancies due to missing Pb ions. By K/Sm substitution, Pb content is less, thereby evaporation of

volatile matter is reduced. Therefore, Pb vacancies and resultant oxygen vacancies are reduced resulting in more stoichiometric samples. Although *K* is also volatile, charge of *K* ion is lesser than the *Pb* ion and hence *O* vacancies will be lesser. Vacancies play a very important role and enhance the conductivity of materials [35-37]. The defect structure can be represented by the Kröger–Vink notation [38]:

$$Pb_{Pb}^{\times} + O_o^{\times} \leftrightarrow PbO(\uparrow) + V_{Pb}^{\prime\prime} + V_o^{\circ} \qquad \dots \dots \dots \dots \dots (3A.6)$$

$$2K_{K}^{\times} + O_{o}^{\times} \leftrightarrow \mathrm{K}_{2}\mathrm{O}(\uparrow) + 2V_{K}' + V_{o}^{\cdots} \qquad (3\mathrm{A}.7)$$

Oxygen vacancies in perovskites can contribute to transport by migration from one site to another along the direction of applied high electric field increasing mobility and accumulate in the places with low free energy, such as domain walls and interfaces with electrodes. Accumulation of these oxygen vacancies at the domain boundary causes domain pinning. This restricts polarization switching [39].

### **3A.5** Conclusions

substituted  $PbTiO_3$  ceramic  $(K_{0.5}Sm_{0.5})$ samples were synthesized by modified sol-gel process. Synchrotron-based powder xray diffraction confirmed a tetragonal *P4mm* phase for  $0 \le x \le 0.37$ samples while pseudo-cubic like behavior for x = 0.5 composition. Lattice parameter 'c' decreases with increasing composition x, while 'a' is almost constant. Raman spectroscopy shows changes in intensity and energy of phonon modes related to tetragonal-cubic phase transformations and lattice strain with ferroelectric property. The lower mass of K/Sm compared to Pb may be a reason for such changes. However, in spite of the tetragonal-near cubic transformation the existence of Raman modes even for x = 0.50 hints at the fact that either some local tetragonality is retained or some other phenomenon apart from a tetragonal structure generates strain which can be attributed to remnant polarization for x = 0.5 sample. High-temperature dielectric

study clearly indicates a dielectric phase transition which moves towards lower temperature with increasing substitution. Diffuseness of phase transition increases with substitution due to compositional disorder arising due to the random distribution of  $K^+/Sm^{3+}$ . As a result, we find changes in ferroelectric property which is for lower substitutions not much of significance due to the leaky nature but with increasing resistance becomes more effective and promising as a ferroelectric. However, remnant polarization decreases with substitution probably due to reduction in tetragonality.

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# **Chapter 3**

# Part B

# Structural and dielectric properties of Pb<sub>(1-x)</sub>(Na<sub>0.5</sub>Sm<sub>0.5</sub>)<sub>x</sub>TiO<sub>3</sub> ceramics

This chapter aims at studying physical properties of A-site modified PbTiO<sub>3</sub>. A combination of Na/Sm was chosen to effectively achieve ionic radii and charge state approximately comparable to the host Pb ion. This chapter covers sample preparation, followed by property characterization of the materials. Samples were prepared by modified sol-gel combustion process followed by solid-state sintering for crystallization of samples. Crystal structure and phase purity of the samples were investigated by synchrotron-based powder x-ray diffraction using rotating capillary mode to reduce orientation effects. Rietveld refinement using Fullprof software reveals variation in structure. Raman spectroscopy was performed to verify compositional dependence of phonon modes. Phase transitions of these materials were investigated by studying temperature-dependent dielectric properties. Polarizations versus electric field measurements were performed to study ferroelectric properties and energy storage density of these samples.

# **3B.1** Synthesis

Polycrystalline powders of  $Pb_{(1-x)}(Na_{0.5}Sm_{0.5})_xTiO_3$  ( $0 \le x \le 0.50$ ) (named as PNST-*x*) ceramics were prepared using modified sol-gel process. Precursors were used to synthesizing these materials, Lead (II) nitrate (99.99 %, Alfa Aesar), Samarium oxide (99.99 %, Alfa Aesar), Sodium nitrate and Dihydroxybis (ammonium lactate) titanium (IV), 50 % w/w aqua solution (Alfa Aesar). The stoichiometric solutions of each precursor were prepared with double distilled water in a separate beaker. Samarium oxide is soluble in dilute nitric acid, and it was added to the titanium solution followed by addition of the sodium and lead solution. Details are given in chapter 2.

## **3B.2** Results and discussion

#### **3B.2.1** Structural studies

Synchrotron-based x-ray powder diffraction (wavelength = 0.5034 Å) patterns (SRPXRD) of PNST-*x* powders, ( $0 \le x \le 0.50$ ), reveal peaks related to pure PbTiO<sub>3</sub> structure [Figure 3B.1a]. A tetragonal phase *P4mm* is detected for compositions x = 0, 0.10, 0.20, 0.30 and 0.40, and cubic *Pm3m* phase for x = 0.50 compositions. Peaks belonging to tetragonal symmetry continuously merge to a cubic symmetry with increasing substitution. Two regions have been highlighted to demonstrate such merging [Figure 3B.1a]. Tetragonal (001) and (100) peaks merge into cubic (100) while (101) and (110) merge to cubic (110) peaks [Figure 3B.1(b-c)]. Rietveld refinement of SRPXRD data has been carried out using Fullprof software [1] to observe variation in lattice dynamics.



**Figure 3B.1:** (a) Synchrotron-based x-ray powder diffraction patterns of  $Pb_{(1-x)}(Na_{0.5}Sm_{0.5})_xTiO_3$  ( $0 \le x \le 0.50$ ) range samples, (b) Enlarge

part of the (001) and (100) peaks, and (c) Highlighted part of max intense peak (101) and (110) peaks. Merging of (001) and (110) into (100) and (101) with increasing substitution hints at a structural transformation from tetragonal to cubic type.

Rietveld refinement was performed with A-site element fixed at origin, while refining positions of *Ti* and both planar/apical *O* along *z*-axis only. Voigt axial divergence asymmetry function was used to model Bragg peaks. Background was estimated by linear interpolation between selected background points. Scale parameter, lattice parameters (*a*, *b*, *c*), half-width parameters (*U*, *V*, *W*), position parameters of various lattice sites (*x*, *y*, *z*) were refined one by one. A goodness of refinement is obtained after refining preferred orientation and asymmetric parameters. Acceptable *R*-factors,  $R_{wp}$ , and  $R_{exp}$  were obtained for all compositions. Rietveld refinement of samples with *x* = 0, 0.10, 0.20, 0.30, 0.40 and 0.50 compositions along with *R*-factors of fit are shown in Figure 3B.2(a-f).

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**Figure 3B.2:** Goodness of Rietveld refinement fitting of SRPXRD data for  $Pb_{(1-x)}(Na_{0.5}Sm_{0.5})_xTiO_3$  ( $0 \le x \le 0.50$ ) samples with their R-factors, where (a) x = 0, (b) x = 0.10, (c) x = 0.20, (d) x = 0.30, (e) x = 0.40, and (f) x = 0.50 compositions. Lower angles are highlighted to visualize the fitting and shape of the peaks with increasing compositions.

Also, refined position parameters for all the samples, after final cycle

of refinement are provided in table 3B.1. Here, we observed that there is no variation in the position of x and y parameters of any of the atoms, whereas z-parameters of Ti, apical, and planar oxygen position are varying continuously with the substitution. It was found that position parameters of Ti and oxygen's are decreasing with increase in substitution and constant at x = 0.50 samples. This is also the direct conclusion of structural transition with substitution from tetragonal to cubic structure.

**Table 3B.1**: Refined position parameters of  $Pb_{(1-x)}(Na_{0.5}Sm_{0.5})_xTiO_3$  (0  $\leq x \leq 0.50$ ) samples

	Coordi	Composition ( <i>x</i> )					
Atoms	nates	0.00	0.10	0.20	0.30	0.40	0.50
Pb/Na/	x	0	0	0	0	0	0
Sm	у	0	0	0	0	0	0
	z	0	0	0	0	0	0
Ti	x	0.5	0.5	0.5	0.5	0.5	0.5
	у	0.5	0.5	0.5	0.5	0.5	0.5
	z	0.5381	0.53396	0.53147	0.5263	0.50549	0.5
		6(1)	(1)	(207)	2 (248)	(1)	
01	x	0.5	0.5	0.5	0.5	0.5	0.5
	у	0.5	0.5	0.5	0.5	0.5	0.5
	z	0.1086	0.10823	0.09515	0.0741	0.03142	0
		(267)	(1)	(3)1)	0(111)	(1)	
O2	x	0.5	0.5	0.5	0.5	0.5	0.5
	у	0	0	0	0	0	0
	z	0.6084	0.60084	0.58996	0.5654	0.54073	0.5
		3	(0)	(280)	2 (173)	(1)	
		(157)					

Calculated lattice parameters and volumes of all samples are shown in Figure 3B.3(a-b). Lattice parameter 'a' was almost invariant, whereas 'c' decreased remarkably with increasing substitution resulting in continuous volume contraction in substituted compounds. This hints at *Pb* being substituted by *Na/Sm*.





**Figure 3B.3:** (a) Calculated lattice parameters of  $Pb_{(1-x)}(Na_{0.5}Sm_{0.5})_xTiO_3$  ( $0 \le x \le 0.50$ ) samples and average ionic radii at A-site, (b) Calculated volume of the samples. Decrease of lattice parameter 'c' and change in average ionic radii at A-site with composition is almost similar.

The average ionic radii of *A*-site substituents are calculated using the relation [2]:

$$r_A = [(1-x)r_{Pb^{2+}}] + [\frac{x}{2}(r_{Sm^{3+}} + r_{Na^+})] \quad \dots \dots \quad (3B.1)$$

where, Shannon's radii values are given as,  $r_{Pb^{2+}} = 1.49$  Å,  $r_{Sm^{3+}} = 1.24$  Å, and  $r_{Na^+} = 1.39$  Å. Note that  $r_A$  decreases linearly with substitution as shown in Figure 3B.3a. This decrease may be proportionately determining changes in c-axis. Tolerance factor (*t*) is related to ionic radii, as,

$$t = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)}$$
 ..... (3B.2)

where,  $r_A$ ,  $r_B$  and  $r_O$  are the effective radii of the A-site cation, B-site cation and the oxygen ion respectively. Tolerance factor is a quantitative measure of the mismatch between the bonding requirements of the *A*-site and *B*-site cations in the perovskite ABO<sub>3</sub> and subsequently reflects the structural distortion such as rotation and tilt of the octahedral. Since the substituent at *A*-site ionic radii are lesser compare to *Pb* so tilt as well as non-centrosymmetric distortion

will reduce. It is also reflected with merging of peaks in SRPXRD data that indicate from non-centrosymmetric to centrosymmetric structure. Again we need to mention that for tolerance factor ~ 1, a perovskite phase is expected [3, 4]. The tolerance factor of the PNST-*x* samples decreases from 1.019 as in x = 0 to 0.988 for x = 0.5 [table 3B.2]. Hence, the general tendency of these structures is to be in the perovskite phase as  $t \sim 1$ . Also notice a strong similarity between the natures of decrement of *c*-axis with the reduction in effective ionic radius of the A-site although *a*-axis is invariant. This indicates that *Na/Sm* substitution does not influence the *a*-axis but varies proportionately the *c*-axis.



**Figure 3B.4:** (a) Temperature-dependent SRPXRD patterns of  $Pb_{(1-x)}(Na_{0.5}Sm_{0.5})_xTiO_3$  for x = 0.30 sample, (b) Enlarge view of (101) and (110) peaks, (c) Calculated lattice parameters and volumes at different temperatures.

High-temperature structural studies were performed on a selected

composition (x = 0.30). Temperature-dependent SRPXRD data at different temperatures from 353 K to 673 K are shown in Figure 3B.4a. With increase in temperature, similar merging of tetragonal peaks to cubic phase peaks is observed [Figure 3B.4b]. As mentioned before, such merging of peaks is a clear indication of structural phase transition in sample but this time dependent on temperature. A similar tetragonal to cubic structural analysis has been carried out by performing Rietveld refinement with Fullprof software on the temperature-dependent SRPXRD data. Lattice parameters 'a' increase while 'c' decrease with increase in temperature. The structure become cubic, i.e. 'a = c' at 543 K [Figure 3B.4c], the Curie point for x = 0.30. This is in agreement with observations from temperature-dependent dielectric studies, to be discussed later in this chapter. A negative thermal expansion coefficient is observed from volume contraction with increasing temperature in the tetragonal phase [5] [Figure 3B.4c]. After phase transition at T = 543K, in the cubic phase a positive expansion coefficient is observed.

There is a subtle balance between the long-range Coulomb interaction and short-range forces in materials. Domain structure and defect determine the long-range Coulomb interaction which in turn makes the ferroelectric transitions highly sensitive. Such changes lead to the splitting of longitudinal optical (LO) and transverse optical (TO) phonons [6, 7]. Hence Raman spectroscopy is an excellent tool in qualitatively assessing retention of domain structure, defects, and structural distortions thereby understand deformations and lattice strains associated with substitution in ferroelectrics like in PNST-x.

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**Figure 3B.5:** (a) HR Raman spectroscopic measurement of the compounds  $Pb_{(1-x)}(Na_{0.5}Sm_{0.5})_xTiO_3$   $0 \le x \le 0.5$  range samples (b) Variations of phonon modes after fitting the Raman data.

The Raman spectra of PNST-x are shown in Figure 3B.5a. All the phonon vibrations of these compounds correspond to known vibrational modes of pure PbTiO<sub>3</sub>. Intensities decreased, peak widths increased and positions varied for different modes with substitution. The cubic paraelectric phase of pure PbTiO<sub>3</sub> belongs to the space group with 12 optic modes at the point of the Brillouin zone in the  $3T_{1u}+T_{2u}$  representation of the  $O_h$  point group. The  $3T_{1u}$  modes are Raman inactive but infrared active while  $T_{2u}$  modes (silent modes) are both Raman and infrared inactive. Therefore the cubic phase has no Raman active modes [8-10]. Although in SRPXRD we see that the lattice is becoming cubic, the very fact that in our samples Raman modes are visible up to x = 0.50, hints at retention of ferroelectricity until x = 0.50. After fitting the Raman data, energy variations of the phonon modes with composition are observed as shown in Figure 3B.5b. Except  $A_1(3LO)$ , E(3TO) and E(2TO) which are blue shifted, all other modes are red shifted.

The  $A_1(1TO)$  transverse optical mode relates to the relatively opposite vibrations of the *O-B-O* chains to the *Pb* sub lattice along *c*axis in the *ABO*<sub>3</sub> perovskite structure. It is also dependent on the displacement of the  $BO_6$  octahedron relative to Pb atoms [11-13]. It has a direct relation to the order parameter.  $A_1(1TO)$  is generally called "soft mode" due to losing energy as the sample undergoes a tetragonal to cubic phase transition [14, 15]. In PNST-x,  $A_1(1TO)$  mode loses intensity and energy with increasing substitution indicating a direct relation to our SRPXRD results. Reduction in the energy is a direct consequence of the reduction in the *c*-axis in spite of reduction of effective mass of the A-site. Such a reduction may be due to increase of lattice distortions due to Na/Sm introduction. Please note that the energy of  $A_{l}(3TO)$  reduces while E(3TO) modes marginally increases to merge in x = 0.4 sample. The relative vibrational motion of the *Ti* atoms with respect to the oxygen atoms along the O-Ti-O chains along *c*-axis result in  $A_1(3TO)$  soft modes. As TO modes vibrate along the direction of the spontaneous polarization (c-axis) in PbTiO<sub>3</sub>, the  $A_1(3TO)$  mode is very important. The E(3TO) mode is one of the modes which has gained energy. This mode is a result of vibrations of Ti and planar O ions with respect to each other along the 'a' and 'b' axes. Please note, in parent PbTiO<sub>3</sub>, the displaced off-centered Ti ion is at a strained bonding with the planar oxygen. With the reduction in tetragonality, these Ti ions will be nearer to the O-plane and the structure will become more centro-symmetric. Thereby the strain in the *O-Ti-O* bond will be reduced, and the ions will be capable of vibrating more energetically. In congruence with our, SRPXRD results the reduction of tetragonality is also reflected in our Raman results.

### **3B.2.2 Dielectric properties**

Dielectric measurement is a powerful tool to study the effect of *Na/Sm* substitution on the phase transition of the PNST-*x* ceramics. A phase pure, sufficiently dense and mechanically robust PbTiO<sub>3</sub> pellet was extremely difficult to fabricate and hence dielectric property of PbTiO<sub>3</sub> phase was not investigated. With substitution preparation of pellets, appropriate for dielectric measurements, became easier and dielectric properties including dielectric constant, impedance, capacitance and dielectric loss factor were measured in the temperature

range 300-750 K for various frequencies in 1 kHz – 1 MHz range. Here we will concentrate on the dielectric constant and loss ( $tan \delta$ ) to discuss a probable ferroelectric to paraelectric phase transition of these materials.



**Figure 3B.6:** (a) Room temperature dielectric study of the  $Pb_{(1-x)}(Na_{0.5}Sm_{0.5})_xTiO_3$   $0.1 \le x \le 0.5$  range samples, where (a) dielectric constant versus frequency, and (b) Dielectric loss (tan $\delta$ ) versus frequency for all samples.

Room temperature frequency (100 Hz  $\leq$  f  $\leq$  1 MHz) dependent dielectric constant and loss was measured for all samples [Figure 3B.6(a-b)]. Dielectric constant ( $\varepsilon$ ) of PNST-*x* ceramics gradually increases with increasing *x* in the range 0.10  $\leq$  *x*  $\leq$  0.40 and thereafter decreases for *x* = 0.5 (Table 3B.2). Dielectric loss (*tan* $\delta$ ) is also increasing with increase in substitution at low frequency but almost constant at high frequency for all samples. This behavior of increase of dielectric constant can be attributed to the higher polarizability of *Na* and *Sm* than *Pb* [16]. The decrease in  $\varepsilon'$  in *x* = 0.5 is due to the paraelectric phase of the sample at room temperature whereas the other samples are in ferroelectric phase.

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**Figure 3B.7:** Temperature-dependent dielectric constant of  $Pb_{(1-x)}(Na_{0.5}Sm_{0.5})_xTiO_3$  compositions, where (a) x = 0.10, (b) x = 0.20, (c) x = 0.30, (d) x = 0.40, (e) x = 0.50, and (f) Dielectric constant versus temperature at 100 kHz for  $0.10 \le x \le 0.50$  compositions.

Temperature-dependent dielectric constant [Fig. 3B.7(a-e)] for different fixed frequencies as a function of temperature for PNST-*x* ceramics shows peaks above room temperature for all samples except for x = 0.50 composition. The temperature of dielectric maximum,  $T_m$ , decreases with increasing substitution from ~ 677 K in x = 0.1 to ~ 338 K in x = 0.4 for all frequencies. At 1 kHz,  $\varepsilon$ '-*T* peak around 670 K seems to be overshadowed by some other phenomenon. This may be a space-charge polarization effect. Values of dielectric constant at  $T_m$  for x = 0.1 show no significant frequency dispersion. The x = 0.5 sample shows a gradually decreasing  $\varepsilon'$  with increase in temperature in the entire range suggesting  $T_m$  below room temperature. It can be further noticed that the frequency dispersion in dielectric constant around  $T_m$  decreases with increasing *Na/Sm* content. Such frequency dispersion trend can be explained by the incidence of space charge polarization which becomes significant at low frequencies and high temperatures [17]. Temperature-dependent losses (*tan* $\delta$ ) at the same frequency (measured dielectric constant) are shown in Figure 3B.8(a-e). Similar phase transition behaviour was observed. Increases in losses (*tan* $\delta$ ) are comparably much less as compared to dielectric constant.



**Figure 3B.8:** Temperature-dependent  $tan\delta$  versus temperature at some fixed frequencies for  $Pb_{(1-x)}(Na_{0.5}Sm_{0.5})_xTiO_3$  samples, where (a) x = 0.10, (b) x = 0.20, (c) x = 0.30, (d) x = 0.40, and (e) x = 0.50 compositions.

Pure  $PbTiO_3$  is known to have a sharp ferroelectric to paraelectric transition around 763 K (Curie temperature) accompanied by a
structural transition from polar tetragonal to non-polar cubic phase [18]. This structural phase transition manifests as a sharp and frequency independent peak in dielectric permittivity versus temperature plot. Figure 3B.7f shows,  $\varepsilon'$  as a function of temperature measured at 100 kHz for various PNST-x samples. It can be clearly seen that the temperature of dielectric maximum decreases linearly with increasing x.  $Pb6s^2$  lone pair electrons help in stabilizing the large tetragonal strain (~ 6 %) in PbTiO<sub>3</sub>. Our SRPXRD analysis confirmed that  $Na^+/Sm^{3+}$  substitution at  $Pb^{2+}$  (with  $6s^2$  lone pair) site modifies the tetragonal strain in PbTiO<sub>3</sub> and finally for x = 0.5 exhibits a '*cubic*' structure. Note that such a structural change is also reflected in phase transition temperature, Na/Sm substitution requiring lesser thermal energy for the ferroelectric-paraelectric phase transition. Similar trend has been observed in other perovskite related ferroelectrics [2, 19]. For better understanding, normalized dielectric constant ( $\varepsilon'/\varepsilon_m$ ) versus (T- $T_m$ ) plot is shown in the Figure 3B.9 for all the compositions at 100 kHz. It is observed that the peak shape is becoming broad with increasing compositions. This is the clear indication of diffuse type of phase transition behavior with increasing compositions.



**Figure 3B.9:** Plot between  $\varepsilon'/\varepsilon_m$  verses T- $T_m$  for all compositions of the compound PNST-x at 100 kHz, where  $\varepsilon_m$  and  $T_m$  denotes the maximum dielectric constant and phase transition temperature respectively. Broadness at the maxima with compositions are indicating diffuse type of behavior.

The diffuse phase transition is usually observed in perovskites with random distribution of different types of ions on structurally identical sites in lattice [20, 21].



**Figure 3B.10:** Plot between  $ln\left(\frac{1}{\varepsilon'} - \frac{1}{\varepsilon'_m}\right)$  verses  $ln\left(T-T_m\right)$  with linear fitting of the compound PNST-x at 100 kHz, where solid lines are representing the fitted data and symbols experimental data.

It must be noted that diffuse phase transition exhibit a broad instead of a sharp change of structure and properties at the Curie point in normal ferroelectric materials [22, 23]; consequently, the phase transition characteristics of such materials are known to diverge from the characteristic Curie-Weiss behavior and can be described by a modified Curie-Weiss formula [24, 25].

$$\frac{1}{\varepsilon'} - \frac{1}{\varepsilon'_m} = \mathcal{C}^{-1} (T - T_m)^{\gamma} \quad \dots \dots \quad (3B.3)$$

where, *C* is Curie-Weiss constant and the degree of diffuseness,  $\gamma$  (1  $\leq \gamma \leq 2$ ; where  $\gamma = 1$  gives a sharp change while an ideal diffuse phase transition gives  $\gamma = 2$ ). An apparent increase in diffuseness of peak in  $\varepsilon$ -*T* plots is reflected in the least-square linear fitting of ln ( $\frac{1}{\varepsilon'} - \frac{1}{\varepsilon'_m}$ )

versus ln  $(T - T_m)$  curves as shown in Figure 3B.10, at a frequency of 100 kHz of PNST-*x* ceramics. A reasonably good fit is observed for all compositions. The degree of diffuseness,  $\gamma$  was calculated from the slope of linear fit.  $\gamma$  was found to increase from  $1.15 \pm 0.02$  for x = 0.1 to  $1.69 \pm 0.01$  for x = 0.50 indicating a significant increase in diffuseness of phase transition in doped samples. Compositional disorder arising due to the random distribution of  $Na^+/Sm^{3+}$  seems to be responsible for observed diffuse phase transition in PNST-*x* ceramics [23].

**Table. 3B.2:** Room temperature dielectric constant and loss  $(Tan\delta)$ , average grain size, tolerance factor, phase transition temperature, apparent remnant polarization and coercive field for the compounds *PNST-x*.

Substi	°3	Tanδ	Average	Toler	T <sub>m</sub>	2P <sub>r</sub>	2E <sub>C</sub>
tution	(100	(100	grain size	ance	(K)	( <i>µC/cm</i> )	( <i>kV</i> /
<i>(x)</i>	kHz	kHz)	(~µm)	factor			cm)
	)			(t)			
0.10	178	0.012	$1.03\pm0.36$	1.019	677	0.43	14.8
							2
0.20	236	0.017	$0.88\pm0.25$	1.013	584	2.14	25.8
							4
0.30	397	0.026	$0.67\pm0.24$	1.007	486	47.65	43.2
							5
0.40	122	0.038	$0.60\pm0.25$	1.001	338	18.56	16.9
	5						9
0.50	364	0.073	$0.60\pm0.17$	0.995			

#### **3B.2.3 Ferroelectric properties**

To confirm the ferroelectricity in PNST-*x*, polarization versus electric field (*P*-*E*) hysteresis loop measurements were carried out for all the compositions as shown in Figure 3B.11. The hysteresis loops were measured at a frequency of 1 Hz at room temperature. For composition with x = 0.10, [Figure 3B.11a], *P*-*E* hysteresis loops are not typical ferroelectric loops but are more like those usually obtained for lossy dielectric materials [26]. Observed apparent remnant

polarization and coercive field values at an applied electric field ~ 50 kV/cm for all the samples are given in Table 3B.2. *P*-*E* hysteresis loops obtained for compositions with x = 0.20, 0.30, and 0.40 are typical hysteresis loops obtained for ferroelectric ceramics while an almost linear relation between *P* and *E* is observed for composition with x = 0.50. This suggests that sample with x = 0.50 is macroscopically in paraelectric state at room temperature and it is expected as corroborated by the SRPXRD, Raman and dielectric studies. Sample with composition x = 0.30 shows the highest apparent remnant polarization of 23.82  $\mu C/cm^2$  and a coercive field of 21.62 kV/cm at an applied electric field of 50 kV/cm. Also, a comparision of remnant polarization, coercive field, and phase transition temperatures of some selected samples in table 3B.3 are provided.



*Figure 3B.11: P*-*E* loop measurement of the samples PNST-x, (*a*) x = 0.10, (*b*) x = 0.20, (*c*) x = 0.30, (*d*) x = 0.40, and (*e*) x = 0.50 samples.

From the structural point of view, composition with x = 0.10 is expected to be ferroelectric. However, at applied electric fields up to 50-60 *kV/cm*, no signature of domain switching (or ferroelectric ordering) is apparent in *P-E* hysteresis loops. It was not possible to apply more voltage due to high leakage current in this composition [27, 28].

Drastic improvement in room temperature ferroelectric properties in *Na/Sm* doped samples can be attributed to the cumulative

effect of improved density, reduced volatilization of *Pb*, associated oxygen vacancies, increased dielectric constant and reduced tetragonal strain. It is well known that oxygen vacancies are created due to *Pb* loss during high-temperature sintering of PbTiO<sub>3</sub> based perovskite ceramics and are expressed by following Kröger-Wink equation [29]:

$$Pb_{Pb}^{\times} + O_o^{\times} \leftrightarrow \text{PbO}(\uparrow) + V_{Pb}^{\prime\prime} + V_o^{\circ}$$
 .....(3B.4)

These oxygen vacancies can hop easily due to their high mobility in applied high electric field and accumulate in the places with low free energy, such as domain walls and grain boundaries. Accumulation of these oxygen vacancies at the domain boundary causes domain pinning which restricts polarization switching [30, 31].

*Table.* 3B.3: Remnant polarization, coercive field, applied electricfield, and phase transition temperature of some selected compounds.

Compositions	Remnant polarization (P <sub>r</sub> )	Coercive field (E <sub>c</sub> )	Applied electric field at room	Phase transition temperature	
			temperature	-	
$Pb_{1-x}La_x(Zr_{0.5})$	~ 8.99	~ 6		~ 378 K	
$_{2}\text{Ti}_{0.48})\text{O}_{3}$ for	$\mu$ C/cm <sup>2</sup>	kV/cm			
x = 0.05					
ceramic [32]					
0.57(Bi,La)Fe	$\sim 20 \ \mu C/cm^2$	~ 100	± 120 kV/cm		
O <sub>3</sub> -		kV/cm			
0.43PbTiO <sub>3</sub>					
(BLF-PT)					
Thin film [33]					
PbTiO <sub>3</sub> single	~ 57 $\mu$ C/cm <sup>2</sup>		$\pm$ 20 kV/cm	~ 763 K	
crystal (001)					
oriented[34]					
$Pb_{0.6}Sr_{0.4}TiO_3$	~ 15 $\mu$ C/cm <sup>2</sup>	~ 12	$\pm$ 50 kV/cm		
Ceramic [35]		kV/cm			
$0.19Pb(In_{1/2}N)$	~ 27.1	~ 5.5	$\pm$ 12 kV/cm	~ 463 K	
b <sub>1/2</sub> )O <sub>3</sub>	$\mu C/cm^2$	kV/cm			
0.46Pb(Mg <sub>1/3</sub>					
Nb <sub>2/3</sub> )O <sub>3</sub>					
0.35PbTiO <sub>3</sub>					
Single crystal					
[36]					

Ba <sub>0.99</sub> Al <sub>0.01</sub> Ti	~ 11.4	~ 4	$\pm$ 16 kV/cm	386 K
O <sub>3</sub> ceramic	$\mu$ C/cm <sup>2</sup>	kV/cm		
[37]				
Pb <sub>(1-</sub>	~ 23.82	~ 21.62	$\pm$ 50 kv/cm	~ 486 K
$_{x)}(Na_{0.50}Sm_{0.50}$	$\mu C/cm^2$	kV/cm		
) <sub>x</sub> TiO <sub>3</sub>				
for $x = 0.30$				
ceramic				
Pb <sub>(1-</sub>	~ 10.92	~8.54	$\pm$ 60 kV/cm	~ 338 K
$_{x)}(Na_{0.50}Sm_{0.50}$	$\mu C/cm^2$	kV/cm		
) <sub>x</sub> TiO <sub>3</sub>				
for $x = 0.40$				
ceramic				

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Spontaneous polarizations versus electric field curves become slimmer with substitution. These low coercive field and high polarization materials can be used as energy storage properties. The energy storage efficiency was calculated using,  $\eta = \frac{W_{stored}}{W_{supplied}} * 100 \%$  [38, 39]for  $x = 0.20, 0.30, 0.40, \text{ and } 0.50 \text{ samples. } \eta = 45.6 \%, 5.8 \%, 40.2 \%, \text{ and } 96.5 \%$  for  $x = 0.20, 0.30, 0.40, \text{ and } 0.50 \text{ samples respectively. Hence, energy storage efficiency is maximum for <math>x = 0.50$  and can be used as energy storage capacitor material.

#### **3B.3** Conclusions

Sodium (*Na*) and samarium (*Sm*) doped PbTiO<sub>3</sub> ceramic samples, Pb<sub>(1-x)</sub>(Na<sub>0.5</sub>Sm<sub>0.5</sub>)<sub>x</sub>TiO<sub>3</sub> ( $0 \le x \le 0.50$ ), (PNST-x) have been successfully synthesized by modified Pechini sol-gel process. Phase confirmation and crystal structure were investigated from SRPXRD studies. Rietveld refinement confirmed a tetragonal phase for  $x \le 0.40$ but a cubic phase for x = 0.50 composition at ambient temperature. HR Raman spectroscopy at room temperature revealed remnant ferroelectric property-related PbTiO<sub>3</sub>-type vibrational modes in highly substituted PNST-x samples. Composition dependence of phase transition was studied using high temperature dielectric study as a probe. Phase transition temperature decreased with substitution. This is due to replacement of *Pb* ( $6s^2$ ) by effectively smaller *Na/Sm* combination. Diffuse type phase transition behavior was observed and fitted with modified Curie-Weiss law. The diffuse nature comes from a random distribution of *Na/Sm* at the *Pb* site. Actual structural phase transition temperature was estimated using temperature-dependent SRPXRD measurement of one selected sample (x = 0.30). Transition temperatures obtained from both probes are in agreement with each other within error bars. Samples with x > 0.10 show proper ferroelectric loops. P-E loops are slimmer for higher substitution. Energy storage efficiency rises with substitution and is maximum 96.5 % for x = 0.50. Thus, these ferroelectric materials are important for energy storage and other technical applications.

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## **Chapter 4**

# Structural distortion, ferroelectricity and ferromagnetism in $Pb(Ti_{1-x}Fe_x)O_3$ ceramics

This chapter aims at studying various physical properties of Fe modified PbTiO<sub>3</sub>. Sample preparation is followed by characterization of the materials. Samples were prepared by modified sol-gel process followed by solid-state sintering for crystallization of samples. Samples were characterized using XRD, Raman spectroscopy, and XANES/EXAFS. Magnetization and electric field dependent ferroelectric polarisation properties were examined. Profile matching technique was used to estimate lattice parameters using Fullprof software. Charge states of component elements and their local environment were analyzed using XANES/EXAFS spectroscopy. Fe modified PbTiO<sub>3</sub> samples are multiferroic.

#### 4.1 Synthesis

Nanocrystalline powders of  $PbTi_{(1-x)}Fe_{(x)}O_3$  were synthesized using standard modified sol-gel process followed by high-temperature annealing of samples to study the temperature-dependent structural properties of a solid solution. High purity precursors, Lead (II) nitrate (99.99 %, Alfa Aesar, Puratronic), Iron (III) nitratenonahydrate (98 %, Alfa Aesar) and Dihydroxybis (ammonium lactate) titanium (IV), 50 % w/w aqua solution (Alfa Aesar) were used to synthesize these materials. Detail procedure is given in chapter 2.

#### 4.2 Results and discussion

#### 4.2.1 Structural studies

X-ray diffraction was performed on all samples using a Bruker D2Phaser X-ray Diffractometer to investigate compositional dependence of phase and structure of samples. XRD analysis of initial burnt powders yielded spurious peaks not commensurate with PbTiO<sub>3</sub> phases. After these powders were heated at 450 °C, XRD was done; an extra phase corresponding to PbO was present. This is in fact presumed as we had intentionally put excess Pb precursor to take care of the volatile nature of Pb based oxides which often results in Pb-deficit in the samples leading to creation of unwanted extra phases of Ti and Fe oxides. As we are interested in magnetism, hence to avoid unwanted magnetic phases from Fe oxides we introduced excess Pb because Pb oxides are not magnetic, but Fe oxides are magnetic. Thus the extra Pb accounts for volatile losses and non-formation of undesired phases of Ti and Fe oxides. Samples were treated at higher temperatures at 600 °C, 700 °C, 800 °C and 1000 °C. XRD data confirmed reduction of extra PbO with increasing temperature. X-ray diffraction spectra of  $PbTi_{(1-x)}Fe_{(x)}O_{(3-\delta)}$  in  $0 \le x \le 0.50$  range are shown in Figure 4.1a. Tetragonality of altered PbTiO<sub>3</sub> reduces with increasing substitution to a nearly cubic form. This is evident from merging of similar indexed peaks in Figure 4.1(b-e).



**Figure 4.1:** (a) X-ray diffraction pattern of  $PbTi_{(1-x)}Fe_{(x)}O_{(3-\delta)}$  in the regime  $0 \le x \le 0.50$ , (b-e) Highlighted XRD peaks to see the converging peaks, implying changes in lattice structure from a distorted tetragonal to a less distorted form.

Tetragonal peaks in XRD data of samples reduces with increasing substitution. Fullprof software was used to estimate lattice

parameters of samples adopting profile matching technique [1]. Lattice parameters are shown in Figure 4.2a. Lattice contracts along 'c' axis and elongates along 'a' axis with increase in substitution.



**Figure 4.2:** (a) Lattice parameters of  $PbTi_{(1-x)}Fe_{(x)}O_{(3-\delta)}$  in the regime  $0 \le x \le 0.50$ . The lattice expands exponentially along the 'a' and 'b' axes but contracts exponentially along the elongated 'c'-axis. (b) The c/a ratio which is an estimate of the tetragonal distortion of the lattice also follows an exponential decrease, and (c) Volume reduces while density increases exponentially with increasing substitution.

Ferroelectricity in perovskite ABO<sub>3</sub> structures arises due to structural distortion related to tetragonality which is determined by '*c/a*' ratio [Figure 4.2b]. It was observed that c/a > 1 from lattice parameters estimated by profile matching technique. This indicates that these materials have retained their tetragonal distortion and hence their ferroelectric properties in spite of *Fe* substitution. We also calculated volume and density of the materials from molecular weights and lattice parameters. We observe a reduction of volume and a subsequent increase of density with increase in substitution as shown in Figure 4.2c. A comparison is done of '*r/R*' ratios where '*r*' represents ionic radius of metal ions (i.e., either *Ti* or *Fe*) and 'R' that of ligands (in this case, oxygen ion (~1.4 Å)).  $Ti^{4+}$ (VI) ion has a radius of ~0.604 Å. Hence, r/R ratio > 0.414, which determines octahedral nature of crystal field [2].

Ionic properties of constituent ions were investigated using xray absorption near edge structure (XANES) while their local environments were investigated using extended x-ray absorption fine structure (EXAFS). These investigations were carried out at the Scanning EXAFS Beamline (BL-09) of Indus-2, RRCAT, Indore, India. The beamline consists of a *Rh/Pt* coated meridional cylindrical mirror for collimation, a Si(111) based double crystal monochromator to select excitation energy and a post-mirror (*Pt/Rh*) for vertical focusing.

However, it is not straightforward to determine charge state of Fe ions. X-ray diffraction studies reveal that lattice distortion reduces. However, distortion does not become zero and main structure is invariant. Hence, *Fe* site should be tentatively similar to *Ti* site. In transition metal oxides, transition metals have unoccupied *d*-electron states which are inaccessible to dipole excitations of *s*-electrons [3]. Lattice distortions are correlated to departure from centrosymmetry. These types of distortions are associated with displacements of transition metal ions along a specific direction which sometimes provide an enhanced polarization. This displacement is a result of hybridization of oxygen 2p-electron with lead 6s-electrons and transition metal 3d-electrons [4-7].



Figure 4.3: (a) XANES Pb L3-edge spectra of  $PbTi_{(1-x)}Fe_{(x)}O_{(3-\delta)}$  for 0

 $\leq x \leq 0.50$ , shows predominantly  $Pb^{2+}$  state with very subtle difference between the pure and the substituted samples; (b) The Ti K-edge remains unchanged upon substitution ensuring a Ti<sup>4+</sup> state. The preedge feature which is a signature of the tetragonal distortion shows a gradual decrease of intensity (Figure 4.3b inset) with increasing substitution showing reduction in distortion at the Ti site. (c) The Fe K-edge confirms a Fe<sup>3+</sup> state with the pre-edge feature increasing with increased substitution (Figure 4.3c inset) pointing out the presence and enhancement of electric field by the Fe site.

A transition from s-states to these states appears as a pre-edge feature in XANES spectrum [8, 9]. In absence of this displacement, this pre-edge peak is tiny or absent. Ravel. et al. [10] derived from perturbation theory that area of this pre-edge peak is proportional to ensemble average of dot product of net polarization and this displacement vector. Hence this area will be negligible or zero when displacement is perpendicular to polarization. XANES studies of our samples at *Pb L3*-edge [Figure 4.3a], correspond strongly to  $Pb^{2+}$ valence states with no pre-edge feature. This nulls the possibility of any  $Pb^{4+}$  state and hence charge disproportion at Pb site. On the other hand, Ti-edges (as shown in Figure 4.3b) are preceded by strong preedge features which may be attributed to transition from 1s to  $3d_{xy}$  and  $3d_{z}$  [11] energy levels. These transitions are forbidden in dipole approximation. However, they become allowed by mixing with oxygen *p*-state orbitals due to *Ti* atom distortions from oxygen octahedral centres. Presence of a pre-edge feature for any amount of substitution confirms that Ti sites are distorted even after substitutions with x = 0.5. XANES analysis of Fe K-edge confirms a predominantly  $Fe^{3+}$  ionic state for all substituted samples as shown in Figure 4.3c. Pre-edge features of Fe K-edges are much weaker implying that displacements of Fe ions are either zero or perpendicular to direction of polarization. Dipole transitions to final *p*-states are related to main *Fe K*-edge. On the other hand, pre-edge features are related to final 3d-state transitions via quadruple and p/d-hybridization [8].



**Figure 4.4:** (a) EXAFS plots of  $PbTi_{(1-x)}Fe_{(x)}O_{(3-\delta)}$  shows similarities in the local environment of the Ti and Fe ions ensuring proper substitution of Ti by Fe. (b) The Pb environment remains modified but unchanged for all  $PbTi_{(1-x)}Fe_{(x)}O_{(3-\delta)}$  for  $0 \le x \le 0.50$  ensuring the structural similarity in the samples.

A careful scrutiny of EXAFS data reveals similarities between local environments of  $Ti^{4+}$  (VI) and  $Fe^{3+}$  (VI) ions as shown in Figure 4.4a. To be noted is that Fe ion local environment does not match with any reported iron oxide EXAFS pattern [12]. This strongly suggests that Fe is not present in impure iron oxide forms. Similarity with EXAFS patterns of octahedral Ti sites, as in parent PbTiO<sub>3</sub>, supports substitution claims. Local environments around  $Pb^{2+}$  (XII) ions remain unaltered to notable extent agreeing with a PbTiO<sub>3</sub> like structure [Figure 4.4b]. Any deviation would have hinted at phase segregation. Hence, such possibilities of multiple phase materials can be ruled out from EXAFS studies. Ti local environment is subject to negligibly small modification. This similarity in Ti environment conforms to XANES pre-edge findings, that distorted nature of PbTiO<sub>3</sub> unit cell is unaltered with substitution by Fe. However, some nominal changes in bond-lengths may be observed for *Ti-O* bonds from slight differences in shell outlines of radial distribution of EXAFS data. Changes in lattice parameters will then be more dependent on Pb-O and Fe-O bond-lengths. We observe some changes in local environment of Pb and Fe sites.  $Fe^{3+}$  ion has a reduced charge than  $Ti^{4+}$  ion. Hence a different crystal field will be created on  $Fe^{3+}$  addition. EXAFS patterns of *Fe* edges reflect these changes in terms of fluctuations in positions of first and second major shells. Hence, local environments of *Fe* sites are dependent on amount of substitutions. Similarity of *Fe*-edge and *Ti*-edge shell-shapes ensure  $Fe^{3+}$  replacing  $Ti^{4+}$ .

Due to lesser ionic charge of  $Fe^{3+}$  state, oxygen deficiencies are likely to be created. As a result the chemical formula of modified materials can be represented by  $PbTi_{(1-x)}Fe_{(x)}O_{(3-\delta)}$ , where ' $\delta$ '  $\rightarrow$  net oxygen deficiency in the composition. Vacancies may arise due to *Pb* volatilization and  $Ti^{4+}$ - $Fe^{3+}$  charge imbalance. Both account for  $\delta$  and is given by Kröger Vink equations [13]:

 $\operatorname{Fe}_{2}\operatorname{O}_{3} \xrightarrow{2TiO_{2}} 2Fe_{Ti}^{'} + 3O_{o}^{\times} + V_{o}^{''} \qquad (4.1)$ 

A  $Fe^{3+}$  at B-site will tend to create oxygen vacancies in its vicinity. However, one oxygen vacancy will require two  $Fe^{3+}$  ions in PbTiO<sub>3</sub> lattice. A most likely configuration is sharing either an apical or a planar oxygen vacancy in between two neighbouring unit cells containing *B*-site  $Fe^{3+}$  ions to. We observe similar symptoms from xray diffraction studies, *Ti* pre-edge feature from XANES, and local environment of *Fe*-sites and *Ti*-sites from EXAFS studies. *Pb* environment also is invariant providing an enormous support to perovskite-like units. This perovskite-like model associated with a structural modification is a strong support of ferroelectricity retained in these samples.

Out of the two possibilities discussed above, in the first case, an apical oxygen position will be vacated between two units in contact along 'c' axis creating two square pyramidal structures pointed in opposite directions. The second option is a planar oxygen loss between two unit cells lying side by side. Note that in both cases coordination of  $Fe^{3+}$  ion will be five. According to theoretical calculations, a

triangular bi-pyramid structure is more stable than a square pyramidal structure [14]. Hence, most probably an oxygen vacancy will be shared between two subsequently placed unit cells in one plane. As a result, such a change will be visible when viewed along c-axis as modifications. Such an observation was reported [15] in a previous sample using a similar chemical route although heat treatments were different in previous cases. However, more direct proof of how this oxygen deficiency is accommodated is a matter of investigation and requires neutron diffraction techniques which require further investigations.

 $Ti^{4+}$  in perovskites usually is in octahedral coordination [16]. There is a possibility of  $Fe^{3+}$  having coordination number lesser than six in presence of a large number of ordered oxygen vacancies resulting in further lowering of symmetry and formation of a supercell. Also, a possibility of an anti-site disorder ( $Fe^{3+}$  occupying an empty Asite) could have potentially increased effective coordination number of  $Fe^{3+}$ . However, dissimilarities in local environments of Fe and Pb edges of EXAFS data suggest that such a possibility may be ruled out. High spin  $Fe^{3+}$  (VI) case is also less likely, because r/R < 0.414 which does not support an octahedral field. Hence,  $Fe^{3+}$  may not be six coordinated. However, to claim this strong experimental evidence is needed which needs further investigation. Taking all the above logics into account there is a fair probability that Fe sites experience a tetrahedral-like crystal field. However, this will mean strong structural disorders which may lead to a different phase. We inform that beyond x = 0.5, structure is actually modified. However, as a future work, we will not discuss it in this thesis.

Let us now consider chances of  $Fe^{3+}$  (VI) in an octahedral field. This will require charge compensation by presence of some  $Pb^{4+}$  ions replacing some  $Pb^{2+}$  ions. But, XANES data confirms presence of  $Pb^{2+}$  valence state, thereby weakening possibilities of a  $Fe^{3+}$ octahedral state. Also,  $Fe^{3+}$  (VI) have either a much lesser ionic radii (~0.55 Å) for a high spin state or larger ionic radius (~0.64 Å) for low spin state. We can rule out a low spin state as it will result in an increase of volume which is contrary to our observations. A reducing nature of volume with substitution further strengthens the fact that ionic radii of substituent ions are lesser than  $Ti^{4+}$  ions. This is commensurate with  $Fe^{3+}$  (V) ionic size (~ 0.58 Å).

Distortions at Fe sites are low in trigonal bi-pyramidal crystal field. However, it is not possible at this stage to comment on how displacement direction is oriented with respect to polarization, as it can only be determined for a single crystal. Our future research plans will be aimed towards this end.

Raman spectroscopy measurement was done at UGC-DAE, Indore, India, using a micro-Raman system from Jobin Yvon Horiba LABRAM-HR visible (400-1100 nm) spectrometer and an Argon 488 nm laser. Raman spectra for PbTi<sub>(1-x)</sub>Fe<sub>(x)</sub>O<sub>(3- $\delta$ )</sub> (0 ≤ *x* ≤ 0.5) are shown in Figure 4.5a. All observed modes of these samples corresponded to known Raman modes of pure PbTiO<sub>3</sub>. With increasing substitution, we see a decrease in intensity, along with increased peak width while positions vary for different modes [Figure 5(b-c)].



**Figure 4.5:** (a) Raman spectra of  $PbTi_{(1-x)}Fe_{(x)}O_{(3-\delta)}$ , for  $0 \le x \le 0.50$ showing reducing intensity and broadening of characteristic vibrational modes of  $PbTiO_3$ , (b) Compositional dependence of  $A_1(TO)$ , (c-d) E(LO) and other vibrational modes showing mostly an exponential nature of decay of the vibrational energy.

Even for higher substituted samples, some phonon modes are visible. It is being emphasized at this point that in a cubic phase all

Raman modes disappear. Cubic paraelectric phase of pure PbTiO<sub>3</sub> belongs to O<sub>h</sub><sup>1</sup> space group with 12 optic modes at point of Brillouin zone in  $3T_{1u}+T_{2u}$  representation of  $O_h$  point group.  $3T_{1u}$  modes are Raman inactive but infrared active while  $T_{2u}$  modes (silent modes) are both Raman and infrared inactive. Cubic phase, therefore, has no Raman active modes. Hence, very fact that in our samples Raman modes are visible implies that ferroelectric properties are sustained in these samples and they are not paraelectric [17, 18].

In our samples,  $A_1(1TO)$  transverse optical mode weakens in intensity but shifts towards higher frequencies with increasing substitution.  $A_1(1TO)$  is generally called "soft mode" since it tends to move towards zero or lower frequency as sample undergoes a tetragonal to cubic phase transition irrespective of factor (temperature, pressure, chemical substitution) which causes transition.  $A_1(1TO)$ mode relates to relatively opposite vibrations of O-B-O chains along c-axis of  $BO_6$  octahedra with Pb sub lattice along c-axis. This also includes a relative vibration of BO<sub>6</sub> octahedra with respect to *Pb*-cage. This has a direct relation to order parameter [19]. Hence this increment in energy not only nulls chances of a cubic structure but also indicates towards an enhanced order in lattice due to Fe incorporation which may be magnetic in nature. Loss of intensity may happen due to presence of defect dipoles created by  $Fe^{3+}$  substitutions at B-site in place of  $Ti^{4+}$ . Loss of ferroelectricity in such a situation will require these dipoles to have a moment opposite to spontaneous polarization. However,  $A_1(2TO)$  and  $A_1(3TO)$  modes soften with substitution exponentially.  $A_1(2TO)$  and  $A_1(3TO)$  modes consist of displacements of Ti ion relative to planar oxygen and Pb ions, while Ti ions with apical oxygen vibrate along *c*-axis [20, 21].

This indicates that certain O-B-O chains loses energy and gradually becomes weak compared to original PbTiO<sub>3</sub> lattice. As ferroelectricity is related to displacement of Ti ions along this direction, such changes will imply weakened ferroelectricity but, as discussed before, presence of these modes confirm some remaining

ferroelectric component in these materials with either tetragonal, orthorhombic or even more distorted phases. In distorted tetragonal ferroelectric phase, space group is  $C_{4\nu}^1$  (*P4mm*). In this phase triply degenerate  $T_{1u}$  modes split into two modes transforming as A<sub>1</sub>+E irreducible representations of C<sub>4v</sub> point group.  $T_{2u}$  mode splits into B<sub>1</sub>+ E modes which are Raman active but are indistinguishable from each other. A<sub>1</sub>+E modes are complicated and each has optic modes which have transverse optical (TO) and longitudinal optical (LO) modes relative to direction of propagation of light [21-23]. E and B<sub>1</sub> modes are overlapped and resultant remains strong at ~ 289 cm<sup>-1</sup> which is also an indication of a non-cubic structure.

E(2TO) mode (*Pb/O* sub-lattice vibrating out of phase with *Ti* sub-lattice in *a-b* plane) initially softens until  $x \sim 0.2$  and then hardens linearly with further substitution. This trend of softening indicates a tendency towards a cubic symmetry. However, these modes move to higher frequencies, implying that structure returns to a more noncentrosymmetric type. This may occur since net polarization is a sum of spontaneous polarization and polarization from defect dipoles interacting with their modified environment. Since these dipole moments can be even larger than spontaneous polarization, we expect that at some level of substitution net polarization may tend to zero due to opposite direction of constituent polarizations. However, different modes behave differently in terms of softening and hardening indicating a complex interaction between electric and magnetic dipoles of constituent ions. Although our x-ray diffraction studies reveal a tendency towards a structurally cubic system, Raman studies and distortion of structure hint at a complex interdependence of magnetoelectric coupling between magnetic and ferroelectric dipoles.

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**Figure 4.6:** (a) Ferromagnetic hysteresis loops of  $PbTi_{(1-x)}Fe_{(x)}O_{(3-\delta)}$ , for  $0 \le x \le 0.50$  samples showing increasing residual and saturation magnetization along with coercive field. (b) Coercive and saturation field increases and then stabilizes after x = 0.25 while,(c) Remnant and saturation magnetization increases steadily with increasing composition.

#### 4.2.2 Magnetic study

Magnetic field dependent magnetizations of these samples were examined using a Quantum Design Physical Property Measurement System (PPMS) equipped with a 9 Tesla magnet at Miami University USA. Samples appear ferromagnetic in nature at room temperature for substitution of  $x \ge 0.0937$  as shown in Figure 4.6; below which a paramagnetic nature is observed. Remnant magnetization and saturation magnetization linearly increases with substitution indicating stronger ferromagnetic exchange interaction between  $Fe^{3+}$  ions for x >0.093. However, coercive field and field required to saturate magnetization (hereby called saturation field), increases in regime  $0.093 \le x \le 0.25$ . For x > 0.25 there is a tendency towards saturation. Fe-O-Fe interaction between two substituent Fe ions is a source of

ferromagnetism in samples but such results need more intricate study and analysis. A probable twisting of Fe-O trigonal bipyramids with respect to parent lattice may be responsible for saturation of coercive field beyond x = 0.25. On the other hand, increasing remnant magnetization is indicative of increasing number of Fe-O-Fe units. This trend of gradually changing parameters in magnetization with substitution of Fe is further a proof that magnetization is not due to some impurity phase of iron oxides or metallic clusters of Fe but is due to proper substitution. It is strongly suggested to note that reported results of hysteresis patterns in iron oxides [24], including Fe<sub>2</sub>O<sub>3</sub>, FeO and Fe<sub>3</sub>O<sub>4</sub> do not agree to trend of hysteresis at room temperature of these samples. Thus any doubt about the origin of magnetism from impurity phase may be ruled out. This is strongly supported by the fact that EXAFS studies too, do not support an impurity phase. Also to be noted is that the nature of increase of both saturation field and coercive field is similar to the nature of change of lattice parameters and tetragonal lattice distortion. As tetragonal distortion decreases, we observe an increase of ferromagnetism.

#### 4.2.3 Ferroelectric properties

Ferroelectric (P-E) loop measurements were carried out using a ferroelectric loop (*P-E*) tracer of *M/s* Radiant Instruments, USA. During ferroelectric measurements, samples were immersed in silicone oil to prevent electric arcing. Polarization versus electric field of PbTi<sub>(1-x)</sub>Fe<sub>(x)</sub>O<sub>(3-\delta)</sub> samples is shown in Figure 4.7 (a-f).





**Figure 4.7:** Polarization versus electric field hysteresis loops measured at room temperature for different composition of the  $PbTi_{(1-x)}Fe_{(x)}O_{(3-\delta)}$  samples, where (a) x = 0.03, (b) x = 0.06, (c) x = 0.09, (d) x = 0.12, (e) x = 0.18, and (f) x = 0.50 compositions.

Ratios of lattice constants, c/a, reflect strength of coercive field which is further related to domain switching. Often c/a is reduced by substitution in substituted PbTiO<sub>3</sub> ceramics. Ferroelectric domain switching becomes easier and contributes positively to ferroelectricity [25] in such a scenario. As discussed in literature, in PbTiO<sub>3</sub>, orbital hybridization ( $Pb6s^2$  with O2p and Ti3d) leads to non-centrosymmetric distortion giving rise to ferroelectric polarization. In  $PbTi_{(1-x)}Fe_{(x)}O_{(3-\delta)}$ , c/a value decreases exponentially with substitution. System appears to transform to a cubic paraelectric phase for x > 0.31, as  $c/a \rightarrow 1$ . However, keeping in view that tetragonal distortion was observed in Ti-pre-edge XANES studies for all of samples, we continue to expect some remaining ferroelectricity in these materials. To confirm ferroelectricity in samples, P-E loop measurements were performed on all samples at room temperature with 50 Hz frequency. All samples revealed ferroelectric loops. We could not demonstrate saturation of polarization in all samples due to high leakage current resulting out of highly conductive nature of some samples probably because of enhanced oxygen vacancies [26].

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**Figure 4.8:** Current density versus electric field for two selected samples of  $PbTi_{(1-x)}Fe_{(x)}O_{(3-\delta)}$  for x=0.37 and 0.50 compositions.

We have performed conductivity measurement [Figure 4.8] of two selected samples to see current density of samples, keeping in mind leakage factors in ferroelectric measurements. Current density, *J*, at 6 kV/cm for x = 0.50 composition is ~ 1.55 e<sup>-6</sup>A/cm<sup>2</sup>. Comparatively for x = 0.37, *J* is much lesser ~ 8.58 e<sup>-9</sup> A/cm<sup>2</sup>. Hence, it is confirmed, with an increase in substitution, conductivity increases. However, it is evident from Figure 4.7(a-f) that samples are ferroelectric. Coexistence of ferroelectric and ferromagnetic hysteresis at room temperature makes these materials competent as functional room temperature ambient multiferroic.

#### **4.3 Conclusions**

Overall in this chapter, we have carried out structural and electronic properties of  $PbTi_{(1-x)}Fe_{(x)}O_{(3-\delta)}$  in regime  $0 \le x \le 0.50$  range. Tetragonal distortion of lattice and hence crystal field reduces exponentially with substitution due to reduced ionic radius of substituent  $Fe^{3+}$  compared to substituted  $Ti^{4+}$  ion. Charge reduction at B-site may generate some oxygen deficiency. *Ti*-site remains unaltered and distorted as evident from XANES pre-edge studies. A similar distortion is also evident at the  $Fe^{3+}$  site providing evidence of an electric field and a remnant ferroelectric polarization. Coexistence of lattice distortion, as well as ferromagnetism, makes this material an important functional material as a multiferroic at room temperature.

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## **Chapter 5**

# Investigation of *La* and *Al* substitution on the spontaneous polarization and lattice dynamics of the $Pb_{(1-x)}La_xTi_{(1-x)}Al_xO_3$ ceramics

In the previous chapter we discussed either A-site or B-site substitutions in PbTiO<sub>3</sub>. This chapter aims at studying various properties of simultaneous A and B-site modified PbTiO<sub>3</sub>. Pb at A-site is modified with La while Ti at B-site is modified by Al. Sample preparation and characterisation with a target of understanding physical properties of the materials is the motive of this chapter. Samples were prepared by modified sol-gel process followed by solidstate sintering for crystallization of samples. After that these samples were characterized by synchrotron-based XRD using rotating capillary mode, Raman spectroscopy, room temperature as well as temperaturedependent dielectric study to see variation of phase transition temperature with composition, impedance study, and polarisation versus electric field techniques. Rietveld refinement was carried out using Fullprof software to investigate variations in structure with composition. These modified materials are very good ferroelectric/piezoelectric materials.

#### **5.1 Preparation of the samples**

 $Pb_{(1-x)}La_xTi_{(1-x)}Al_xO_3$  ( $0 \le x \le 0.25$ ) range polycrystalline powders were prepared using sol-gel process. Precursors used to synthesize these materials were lead (II) nitrate, lanthanum nitrate, aluminium nitrate and dihydroxy bis (ammonium lactate) titanium (IV) (50 % w/w aqua solution). All precursors were Puratronic grade (purity > 99.99 from Alfa Aesar). Precursors were selected on basis of solubility in doubly deionized (DDI) water. Details are given in chapter 2 experimental section.

#### 5.2 Results and discussion

#### **5.2.1 Structural studies**

Synchrotron-based high-resolution powder x-ray diffraction in capillary mode (SRPXRD) was performed for all samples at room temperature to investigate phase purity and crystal structure of samples with composition. All SRPXRD patterns are shown in Figure 5.1a. These SRPXRD pattern reveal that  $Pb_{(1-x)}La_xTi_{(1-x)}Al_xO_3$  ( $0 \le x \le 0.25$ ) crystallographic structure resembles pure PbTiO<sub>3</sub> structure. There were no other peaks related to any other phase in samples. To investigate merging of the peaks, we have highlighted two of lower angles peaks in Figure 5.1(b-c). SRPXRD peaks are merging with increase in composition. Peak intensity of (001) and (110) reduced followed by a merger with (100) and (101) respectively as shown in Figure 5.1(b-c). Other peaks also related to a tetragonal phase merged to cubic structure too. However, beyond x = 0.18 there was no splitting in peaks, and a near cubic phase was evident.



**Figure 5.1:** Synchrotron-based x-ray powder diffraction patterns for  $Pb_{(1-x)}La_xTi_{(1-x)}Al_xO_3 \ 0 \le x \le 0.25$  compositions, (b) Merging of peak position of (001) to (100), and (c) Merging of peak position of (101) to (110).

To investigate variation of peak and lattice dynamics in

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samples with composition, we have performed Rietveld refinement of synchrotron-based x-ray powder diffraction of PLTA data using Fullprof software [1]. The initial structural model corresponds to pure PbTiO<sub>3</sub> with atomic positions being given in non-centrosymmetric space group *P4mm* (No. 99) with *Pb/La* at the origin (0, 0, 0) [2, 3]. PbTiO<sub>3</sub> tetragonal space group (*P4mm*) was fitted for  $0 \le x \le 0.18$  compositions whereas, for x = 0.25 composition was cubic space group (*Pm3m*). After background estimation, Bragg peaks were modeled with Pseudo-Voigt function, using axial divergence asymmetry function. Significant improvement in goodness of fit was attained with shape and asymmetry parameters refinement. Scale factor, lattice parameters (*a*, *c*), half width parameters (*U*, *V*, *W*) and positional coordinates (*x*, *y*, *z*) of various lattice sites were also refined.

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**Figure 5.2:** Goodness of fitting after Rietveld refinement are shown for the  $Pb_{(1-x)}La_xTi_{(1-x)}Al_xO_3$  samples, where (a) x=0, (b) x=0.03, (c) x=0.06, (d) x=0.09,(e) x=0.12, (f) x=0.18, and (g) x=0.25 compositions.

Starting from pure PbTiO<sub>3</sub>, XRD data for increasing substitutions were refined one by one using final refined structural parameters of lower

substituted composition as starting model for next higher substituted composition. This was done to achieve a trend and a logical structural correlation between samples [4].

Observed and calculated patterns show an excellent match with low values of the goodness of fit obtained for all samples. The fitted plots of refined XRD data for all samples are shown in Figure 5.2(a-g). There are two sample peaks are indexed with their corresponding (hkl) parameters one with tetragonal for x = 0 composition and another one for x = 0.25 composition with cubic phase. The fitting *R*-factors were in acceptable range for all samples and shown in Table 5.1.

**Table 5.1:** Rietveld refinement of  $Pb_{(1-x)}La_xTi_{(1-x)}Al_xO_3$  ( $0 \le x \le 0.25$ ) compositions, *R*-parameters for all the samples.

Compositions	R <sub>p</sub>	$\mathbf{R}_{wp}$	R <sub>exp</sub>	$\chi^2$
x = 0	7.15	8.08	6.07	1.77
<i>x</i> = 0.03	12.03	10.5	9.47	0.758
<i>x</i> = 0.06	9.37	10.1	6.67	2.3
<i>x</i> = 0.09	9.02	9.66	5.9	2.68
<i>x</i> = 0.12	9.37	8.63	6.46	1.78
<i>x</i> = 0.18	7.95	8.05	5.29	2.32
<i>x</i> = 0.25	7.69	7.77	6.03	1.66

Refined position parameters of all samples were obtained after final cycle of Rietveld refinement. *B*-site atom (*Ti/Al*) and *O*-position are continuously decreasing with increase in composition. At x = 0.25 composition, systems tend to cubic (centrosymmetric) system, and after that, there is no variation in position parameters.

**Table 5.2:** Refined position parameters of the  $Pb_{(1-x)}La_xTi_{(1-x)}Al_xO_3 0 \le x \le 0.25$  range samples with their co-ordinates.

Atoms	Coor	<b>Composition</b> ( <i>x</i> )						
	dinat	0.00	0.03	0.06	0.09	0.12	0.18	0.25
	es							
Pb/La	x	0	0	0	0	0	0	0
	у	0	0	0	0	0	0	0
	z	0	0	0	0	0	0	0.5
Ti/Al	x	0.5	0.5	0.5	0.5	0.5	0.5	0.5

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	у	0.5	0.5	0.5	0.5	0.5	0.5	0.5
	z	0.53907	0.536	0.5207	0.5186	0.50698	0.5038	0.5
		(1)	89 (2)	0(1)	(1)	(1)	0(1)	
01	x	0.5	0.5	0.5	0.5	0.5	0.5	0.5
	у	0.5	0.5	0.5	0.5	0.5	0.5	0.5
	z	0.10499	0.094	0.0854	0.0756	0.06661	0.0608	0
		(1)	45 (1)	0(1)	(1)	(2)	5 (1)	
02	x	0.5	0.5	0.5	0.5	0.5	0.5	0.50
	у	0	0	0	0	0	0	0
	z	0.6117	0.592	0.5804	0.5702	0.55981	0.5312	0.5
		(1)	90 (1)	6(1)	(1)	(21)	8 (1)	



*Figure 5.3: Tetragonal displacement of Ti, apical, and planar oxygen position with compositions.* 

Average tetragonal displacement of *B*-site from centrosymmetry (Ti/Al position obtained from z-values of refinement) is found to decrease with substitution, implying a decrease in tetragonal strain as shown in Figure 5.3. Similar observations are made for the *O*-ions too.



**Figure 5.4:** Variation of lattice parameters and unit cell volume of  $Pb_{(1-x)}La_xTi_{(1-x)}Al_xO_3 \ 0 \le x \le 0.25$  compositions.

Variation of calculated lattice parameters with increase in dopant concentration (x) is shown in Figure 5.4. Lattice parameters 'a' slightly increases while 'c' decreases with increase in substitution. Variations in lattice parameters are observed because of smaller ionic radii of substituted elements compare to parent elements. Also, decrease of volume with increase of substitution hints of substitution of *Pb/Ti* by *La/Al*.

High-temperature structural studies were performed for x = 0.09 composition with synchrotron-based source (wavelength ~ 0.80165 Å) at BL-12, Indus-2 Beamline in RRCAT Indore, India. Temperature-dependent XRD patterns are shown in the Figure 5.5a, from 300 K to 613 K temperatures. Variations of peak intensity for (001) and (100) are shown in the Figure 5.5b, a large splitting of these peaks at lower temperatures, indicating a tetragonal phase. With increasing temperature, peaks merge gradually into a single peak at 573 K, i.e., transform to a cubic phase [5-7].
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**Figure 5.5**: Synchrotron-based temperature dependent XRD for x = 0.09 composition where (a) X-ray spectra at different temperatures (b) merging of (100) and (001) peaks with rising temperature implying tetragonal to cubic phase transition (c) Temperature dependence of lattice parameters.

Likewise, other peaks related to tetragonal to cubic phase show a similar trend (As we have also highlighted in Figure 5.5a). Temperature variation of lattice parameters was calculated by refinement of temperature-dependent XRD data. A profile matching technique (using Fullprof software) was adopted to calculate the lattice parameters. Lattice parameters with temperature are shown in the Figure 5.5c. Lattice parameter 'a' increases gradually while 'c' decreases considerably with an increase of temperature. Both parameters become equal ~573 K, indicating the cubic phase of this sample. Hence, we can confirm that x = 0.09 sample has structural phase transition from tetragonal to the cubic system at 573 K temperature.

Lattice mismatch was calculated using Goldschmidt tolerance factor, t [8].

$$t = \frac{(R_A + R_O)}{\sqrt{2}(R_B + R_O)}$$
 (5.1)

Where  $R_A$  and  $R_B$  are the average ionic radii of A and B-site ions, respectively, while  $R_O$ , that of oxygen ion. Average ionic radii of ions  $Pb^{2+}(XII)$ ,  $La^{3+}(XII)$ ,  $Ti^{4+}(VI)$ ,  $Al^{3+}(VI)$ ,  $O^{2-}(VI)$  are 1.490, 1.360, 0.605, 0.535, and 1.40 Å respectively. Stable perovskite phase will form if *t* is close to one [7, 9-11]. Untilted perovskites have 0.985 < *t* < 1.06 range. Tolerance factor will decrease with decrease of *A*-site ion size. For 0.964 < *t* < 0.985 range, a tilted anti-phase is expected while t < 0.964 in-phase and anti-phase tilting may occur. If *t* continues decreases, stability of perovskite phase will decrease, and eventually, perovskite structure will not form [12]. Tolerance factor for PLTA samples was calculated and found to decrease linearly from 1.019 for *x* = 0 to 1.016 for *x* = 0.25 composition. Note that tolerance factor of PLTA samples indicates an untilted stable perovskite structure.

Paraelectric and ferroelectric phases are stabilized by short and long-range forces, respectively. There is a delicate balance between these two types of forces, and ferroelectric phase transition occurs as a result of this balance. Long-range Coulomb interaction is affected by defects and domain structure and leads to splitting of longitudinal (LO) and transverse (TO) optical phonons. Near phase transition temperature, short-range and long-range forces compensate each other in such a way that frequency of optical phonon approaches zero. [13, 14] Hence, Raman spectroscopy is a sensitive and excellent tool in qualitatively assessing retention of domain structure, defect, and structural distortion, thereby understand deformations and lattice strains associated with substitution in ferroelectric like PLTA samples.

HR Raman spectroscopy was done with Czerny-Turner type achromatic spectrograph with spectral resolution of 0.4 cm<sup>-1</sup>/pixel. Wavelength of excitation source was 632.8 nm. Room temperature Raman spectroscopy was performed for all PLTA samples. Raman spectra of PLTA samples are shown in Figure 5.6. All observed modes belong to a pure PbTiO<sub>3</sub> structure. For pure PbTiO<sub>3</sub> ferroelectric tetragonal phase ( $C_{4v}^1$ , (*P4mm*) space group) transform to paraelectric cubic phase ( $O_h^1$  (*Pm3m*) space group) at 763 K. At the  $\Gamma$  point in Brillouin zone, the 12 optical phonon modes transform as  $3T_{1u}+T_{2u}$ irreducible representation.  $T_{1u}$  modes were infrared active, and  $T_{2u}$ 



mode was silent, neither infrared nor Raman active.

*Figure 5.6:* Room temperature Raman spectroscopy spectra of  $Pb_{(1-x)}La_xTi_{(1-x)}Al_xO_3$  ( $0 \le x \le 0.25$ ) compositions.

Below phase transition temperature, tetragonal phase is called ferroelectric phase and corresponds to  $C_{4v}^1$  (*P4mm*) space group.  $T_{1u}$ mode becomes the  $A_I + E$  mode, whereas  $T_{2u}$  mode transforms to  $B_I + E$ mode. All these modes were active in both Raman and infrared region. As in cubic phase, long-range electrostatic forces split  $A_I + E$  modes into *TO* (transverse optical) and *LO* (longitudinal optical) components. Splitting of  $B_I + E$  modes was also allowed, but this had not been observed.  $B_I + E$  modes were designated as "silent" modes. Triply degenerate modes of E(TO) (denoted as E(1TO), E(2TO), and E(3TO)), along with 3E(LO),  $3A_I(TO)$ , and  $3A_I(LO)$  modes are prominent detectable modes of PbTiO<sub>3</sub> [15, 16]. Transverse optical modes of  $A_I$ symmetry are important for  $PbTiO_3$  based materials because *TO* modes are oscillations along the *c*-axis, i.e., along direction of spontaneous polarization.  $A_I(1TO)$  mode is due to vibrations of *B*-site octahedra relative to *A*-site cage.  $A_I(2TO)$  and  $A_I(3TO)$  soft modes consist of

displacements along c-axis of the B-site ion relative to oxygen and Asite ions. It was observed that  $A_1(1TO)$ ,  $A_1(2TO)$ , and  $A_1(3TO)$  modes soften with increasing substitution [Figure 5.5] due to tetragonal to cubic structural transformation. Such was also observed in A/B- site doped  $PbTiO_3$  systems like  $Pb_{(1-x)}(Na_{0.5}Sm_{0.5})_xTiO_3$ ,  $PbTi_{1-x}Fe_xO_3$ , and  $PbZr_{1-x}Ti_xO_3$  [17-20] where c/a ratio reduced. In pure PbTiO<sub>3</sub>, tetragonal strain originates from hybridization between  $Pb(6s^2)$ -O(2p)and O(2p)-Ti(3d) hybridization [21]. While substituting Pb/Ti by La/Al, hybridization becomes softer as La and Al do not hybridize strongly with O atoms. Due to this decrease of hybridization strength, system tends to transform from tetragonal to a cubic structure. Contrary to other modes,  $A_1(3LO)$  mode hardens with substitution. A relative vibration between Ti and planar oxygen ion along a and baxes, this mode becomes more energetic due to an increase in a and baxes with the increase in substitution. Hence, XRD and Raman analyses confirm that tetragonal strain is relieved with increase in La and Al incorporation.

Microstructure and grain size of sintered pellets were investigated by Supra55 Carl Zeiss field emission scanning electron microscope. Field effect scanning electron micrographs of PLTA samples sintered at 1150  $^{\circ}$ C for 6 h are shown in Figure 5.7.



**Figure 5.7:** FESEM microstructure analysis of  $Pb_{(1-x)}La_xTi_{(1-x)}Al_xO_3$ samples, where (a) x = 0.03, (b) x = 0.06, (c) x = 0.09, (d) x = 0.12, (e) x = 0.18, and (f) x = 0.25 compositions.

Grains are spherical type in shape and are compactly packed in all samples. The average grain size was calculated using Image J software, and it was found to decrease from  $12.39 \pm 3.70 \,\mu\text{m}$  for x = 0.03 to 0.67  $\pm 0.27 \ \mu m$  for x = 0.25 composition. The decrease of grain size could be endorsed to lower diffusivity of rare earth element (here La element) during sintering. Analogous results are also observed in other rare earth doped perovskite and layered perovskite materials [22-24]. Also, the decrease of average grain size could be related to a reduction of oxygen vacancy contribution. Oxygen vacancies are produced in Pb based ceramics by the charge compensation due to the evaporation of volatile  $Pb^{2+}$  during the sintering process. Because, the sintering involved the material flow, and in dense ceramics, ionic vacancies are the available sites through which ions can move. Hence oxygen vacancies are first ionic sites to flow the materials in the dense ceramics [25, 26]. Hence, these are the possible reason for the decrease of grain size in the PLTA samples with composition.

Bulk densities of sintered PLTA pellets were measured by the Archimedes method using double distilled water (density =  $1 \text{ g/cm}^3$ ) as immersing liquid. Theoretical densities were also estimated using formula weight and volume of unit cells calculated from the refinement of XRD. Relative density (= Measured density/Theoretical density) was calculated to be ~ 0.92, 0.93, 0.94, 0.95, 0.95, and 0.94 for x = 0.03, 0.06, 0.09, 0.12, 0.18, and 0.25, respectively.

For x = 0.03, intra-grain cracks were observed, highlighted with orange arrows as shown in Figure 5.7a. These fractures occurred due to high tetragonal lattice strain. Different from other samples, the x = 0.03has a high tetragonal strain. Due to limitations in the cooling process of the furnace, an abrupt anisotropic phase transition from cubic  $(T > T_m)$ to tetragonal  $(T < T_m)$  generates cracks, which degrade the ferroelectric properties of the sample. In other substituted samples such inter-grain cracks are not observed, possibly due to lowered tetragonal strain.

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**Figure 5.8:** (a) FESEM-EDS elemental mapping of  $Pb_{(1-x)}La_xTi_{(1-x)}Al_xO_3$  for x = 0.125 composition where (a) secondary electron image and analogous elemental mapping of the element (b) Pb, (c) Ti, (d) La, (e) Al, (f) O elements, (g) Area EDS spectrum and right table for the atomic and weight percentage of various elements.

Elemental mapping by energy dispersive x-ray spectrometry (FESEM/EDS) was performed for all the samples. Obtained compositions from EDS analysis of individual samples were compared to the corresponding targeted chemical phase. The obtained compositions matched well within the typical errors related to EDS analysis. A representative EDS spectrum, and elemental mapping along with the secondary electron micrograph for the x = 0.125 are shown in Figure 5.8(a-g). Spot EDS was carried out on different grains to confirm chemical compositions. Elemental analysis for area EDS was performed to verify the homogeneity of the samples Figure 5.8(b-f)]. An integrated area spectrum is shown in Figure 5.8g and tabulated with atomic and the weight percentage of constituent elements. Hence, all the elements present in the samples are homogeneously distributed across the samples.

#### **5.2.2 Dielectric Properties**

Electrical properties of PLTA samples were investigated by painting electrodes on both sides of sintered dense pellets using high-temperature silver paste. The silver coats were cured at 550 °C for 15 minutes to ensure proper electrode adhesion to the pellet. Before each measurement, we heated the samples at 200 °C for 10 minutes to get rid of any adhered surface moisture. Dielectric response was measured using a Newton's 4<sup>th</sup> Ltd PSM 1735 phase sensitive LCR meter with signal strength of ~1V.

Frequency dependent dielectric properties were measured at room temperature for samples with compositions, x = 0.03 to 0.25 and are shown in Figure 5.9(a-b).



**Figure 5.9:** (a) Room temperature dielectric constant versus frequency for  $Pb_{(1-x)}La_xTi_{(1-x)}Al_xO_3$  samples, and (b) Room temperature  $tan\delta$ versus frequency for  $Pb_{(1-x)}La_xTi_{(1-x)}Al_xO_3$  samples.

As discussed in introduction chapter it is difficult to fabricate pure PbTiO<sub>3</sub> (x = 0) ceramic pellet. Hence, its dielectric and ferroelectric properties are not investigated in the present work. Dielectric constant ( $\varepsilon'$ ) and loss (tan $\delta$ ) are slightly decreasing with increase in frequency for all samples [Figure 5.9(a-b)]. This is in agreement with similar reports on other perovskite titanates [22, 27,

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28]. Room temperature  $\varepsilon'$  increases notably while  $tan\delta$  slightly increases with increasing *x* in the range  $0.03 \le x \le 0.18$  samples. This can be correlated with higher electronic polarizability of *La* than *Pb [29]*. Also, decrease of the phase transition temperature with the increase in the composition may be the reason of high dielectric constant with increase in substitution. A very high dielectric constant and low loss (tan $\delta$ ) for the *x* = 0.18 composition, making the material usable for the capacitor applications etc. However, for *x* = 0.25,  $\varepsilon'$ suddenly reduces. As paraelectric samples have low dielectric constant than ferroelectric materials [22], this decrease may be due to the paraelectric behavior of *x* = 0.25. Note that, except *x* = 0.25, all other samples are in ferroelectric phase at room temperature, as revealed from XRD and Raman spectroscopic results.

Temperature-dependent  $\varepsilon'$  and  $tan\delta$ , frequencies in 1 kHz – 1 MHz range, were measured in the temperature range, 300-773 K, to study phase transition temperature of samples with  $0.03 \le x \le 0.18$  as shown in Figure 5.10(a-e).



**Figure 5.10:** Temperature dependent dielectric constant at different frequencies showing phase transition for  $Pb_{(1-x)}La_xTi_{(1-x)}Al_xO_3$  samples where (a) x=0.03, (Inset figure is showing an anomalies ~ 500 K at low frequencies whereas at high frequency, there is no change) (b) x =0.06, (c) x = 0.09, (d) x = 0.12, (e) x = 0.18, and (f) x = 0.25compositions.



**Figure 5.11:** Temperature dependent  $Tan\delta$  of the  $Pb_{(1-x)}La_xTi_{(1-x)}Al_xO_3$ samples at different frequencies where (a) x = 0.03, (b) x = 0.06, (c) x = 0.09, (d) x = 0.12, (e) x = 0.18, and (f) x = 0.25 compositions.

For x = 0.25, same was measured in the range 80-450 K as shown in the Figure 5.9f. Temperature-dependent  $tan\delta$  curves are shown in Figure 5.11. A ferroelectric to paraelectric phase transition is generally associated with a  $\varepsilon'$  maximum at  $T_m$ , due to dielectric catastrophic behavior. Pure PbTiO<sub>3</sub> undergoes a sharp ferroelectric to paraelectric phase transition around 763 K (Curie temperature) accompanied by a structural transition from polar tetragonal to non-polar cubic phase [30]. Also, same tetragonal to cubic phase transition was obtained for pure PbTiO<sub>3</sub> at 11.2 GPa at room temperature [31]. In PLTA samples,  $T_m$  linearly decreases gradually from 680 K (for x = 0.03) to ~175 K (for x = 0.25) with an increase of La and Al substitutions. In  $tan\delta$ versus temperature also same decrease type of anomaly, was confirming the actual phase transition of the PLTA samples at the respective temperature. For  $0.03 \le x \le 0.18$  composition, the  $\varepsilon'$  maxima are frequency independent. For x = 0.03, a dielectric anomaly around 500 K is observed in  $\varepsilon'$ -T curve, for lower frequencies as shown in inset Figure 5.10a. At higher frequencies this is absent. This anomaly is related to relaxation process involving oxygen vacancies [32, 33]. Note that with increased substitution this relaxation is not observed. This is direct evidence that oxygen defects reduce with increasing xvalues.

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**Figure 5.12:** Normalized dielectric constant  $(\varepsilon'/\varepsilon_m)$  versus  $T-T_m$  for  $Pb_{(1-x)}La_xTi_{(1-x)}Al_xO_3$  (0.03  $\leq x \leq 0.25$ ) range samples, where  $\varepsilon_m$  and  $T_m$  represents the maximum dielectric constant and phase transition temperature of these corresponding samples.

In temperature-dependent dielectric constant measurement, diffuse type of dielectric maxima was observed with increasing substitutions. Normalized dielectric constant versus  $T-T_m$  plots are plotted for all the samples at 1MHz frequency in Figure 5.12 for better understanding.

The diffuseness of  $\varepsilon'$ -T maxima was observed for all PLTA samples. A modified Curie-Weiss model describes the diffused type phase transition [34, 35],

$$\frac{1}{\varepsilon'} - \frac{1}{\varepsilon'_m} = C^{-1} (T - T_m)^{\gamma} \tag{5.2}$$

where *C* is Curie-Weiss constant and  $\gamma$  ( $1 \le \gamma \le 2$ ) gives the degree of diffuseness. A sharp transition is achieved for  $\gamma = 1$ , while  $\gamma = 2$  is an ideal diffuse phase transition. The degree of diffuseness was calculated by the least square linear fitting of  $\ln \left(\frac{1}{\varepsilon'} - \frac{1}{\varepsilon'_m}\right)$  versus  $\ln (T - T_m)$  curves at a frequency of 1 MHz of all the PLTA ceramic samples. A linear fitted data are shown in Figure 5.13.



**Figure 5.13:** Modified Curie Weiss law was modeled for the  $Pb_{(1-x)}La_xTi_{(1-x)}Al_xO_3$  samples of  $ln1/\varepsilon'-1/\varepsilon'_m$  versus  $ln(T-T_m)K$  curves (a) x = 0.03, (b) x = 0.06, (c) x = 0.09, (d) x = 0.12, (e) x = 0.18, and (f) x = 0.25 compositions. Symbols are representing the experimental data whereas red line fitted data.

The constant  $\gamma$ , obtained from the slope of linear fits was found to increase with the increase in *La/Al* incorporation. The  $\gamma$  was found from 1.084 ± 0.011 to 1.922 ± 0.002 for x = 0.03 to 0.25 composition. This increase of diffuseness indicates compositional disorder originating from the random distribution of *La* and *Al*. Broadening of the maxima instead of sharp transition relates to nature of structural changes at Curie point. This is usually observed in perovskites with a random distribution of ions on structurally identical sites in lattice [36, 37].

Hence, from XRD, Raman and dielectric properties, with increasing *La* and *Al* incorporation, it can be inferred that tetragonal strain is relieved on account of the random distribution of *La* and *Al*, thereby decreasing  $T_m$ , and affecting relaxation properties.

## **5.2.3 Ferroelectric properties**

Ferroelectric (P-E) loop measurements were carried on sintered high density pellets with electrodes coated with cured silver paste immersed in silicone oil (to prevent electric arcing at high voltages) using a ferroelectric loop (P-E) tracer of M/s Radiant Instruments, USA. Ferroelectric materials were categorized by measuring their

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spontaneous polarization as a function of applied ac electric field. Ferroelectric responses from the samples were strongly nonlinear in behavior; hence, as a result of domain wall motion variation of polarization with ac electric field was hysteretic. At a low electric field, a linear relationship was observed between polarizations with applied electric field, since energy obtained from the electric field was not sufficient to switch ferroelectric domains. Hence, materials behave like linear dielectric. As the applied electric field is increased, ferroelectric domains start switching along the direction of the field. Polarization increases rapidly until all domains had switched and attains saturation. This saturated polarization is known as spontaneous polarization [38]. Polarization versus electric field (P-E) hysteresis loop measurement was done of all PLTA compositions. A strongly nonlinear hysteretic polarization as a function of applied ac electric field (E), at room temperature, was observed for  $0.03 \le x \le 0.18$ composition. The hysteresis loops were measured at a frequency of 1 Hz. Proper ferroelectric saturated loops are obtained for  $0.06 \le x \le$ 0.18 compositions as shown in Figure 5.14(a-e). This is most probably due to switching of domains under the influence of electric field [39]. We can also see that for  $0.06 \le x \le 0.18$  compositions, instantaneous current versus electric field was showing corresponding peaks related to domain switching behavior in these compounds. These peaks were confirming the proper ferroelectric nature of these compounds.



Figure 5.14. Polarization and instantaneous current versus electric

field at room temperature of  $Pb_{(1-x)}La_xTi_{(1-x)}Al_xO_3$  samples, where (a) x = 0.03, (b) x = 0.06, (c) x = 0.09, (d) x = 0.12, (e) x = 0.18, and (f) x = 0.25 compositions.

However, for x = 0.25, absolute linear polarization was observed suggesting paraelectric nature at room temperature. This is in agreement with SRPXRD, Raman and dielectric analyses. There was no signature of domain switching for x = 0.25 composition. It has phase transition temperature from tetragonal to cubic at below the room temperature.

As for composition x = 0.03 [Figure 5.14a], we did not obtain the proper saturation ferroelectric polarization loop. Also, there was no signature of domain switching because we did not get any response peak in instantaneous versus electric field for this composition. Although it has high non-centrosymmetric tetragonal strain compare to other substituted samples. From the structure point of view, composition x = 0.03 should be strong ferroelectric, but we know that ferroelectric is a long-range ordering phenomena. It is not only depending on the tetragonal with non-centrosymmetric structure in PbTiO<sub>3</sub> based compound. In high *Pb* containing materials, there is a serious problem of *Pb* loss due to its extreme volatile nature during sintering at elevated temperatures. It is widely known that the ionization of oxygen vacancy will create [40].

 $O_0 = V_0 + \frac{1}{2}O_2$  .....(5.3)

Conduction of electrons created by the ionization of oxygen vacancies could be described using the Kröger–Vink notation of defects [41, 42].

$$V_0 = V_0' + e'$$
 .....(5.4)

$$V_0 = V_0' + e'$$
 (5.5)

where  $V_0^{\cdot}$ ,  $V_0^{\cdot}$  were single-ionized and doubly-ionized oxygen vacancies respectively. The ionization of oxygen vacancies will create electrons. These electrons might be loosely bonded to the  $Pb^{2+}$  or  $Ti^{4+}$ 

ions, and their exact location depends on many factors [43, 44]. The overall reactions could be described as:

Oxygen vacancies formed to maintain the charge neutrality in PLTA ceramics are known as extrinsic vacancies [40]. These oxygen vacancies can hop easily due to their high mobility in the applied high electric field and accumulate in the places with low free energy, such as domain walls and interfaces with electrodes. Accumulating of these oxygen vacancies at the domain boundary causes domain pinning which restricts polarization switching.[41, 45] Due to larger proportions of *Pb* in x = 0.03, *O*-vacancies are more probable, large free charges restricting to apply electric field more than the coercive field.

Spontaneous polarization and coercive field versus compositions at 60 *kV/cm* applied electric field are shown in Figure 5.15. For x = 0.09 composition, spontaneous polarization is maximum  $(2P_r = 20.841 \mu \text{m/cm}^2)$  whereas coercive field is low  $(2E_c = 48.708 kV/cm)$ . Also, the continuous decrease of the coercive field may be the reason of decrease of the grain size with increase in composition.



**Figure 5.15:** Spontaneous polarization and coercive field versus compositions for  $Pb_{(1-x)}La_xTi_{(1-x)}Al_xO_3$  samples.

Piezoelectric materials are certain crystalline materials, with

non-centrosymmetry, which has a direct relation between force and electricity. A piezoelectric material can generate proportional electricity upon application of a mechanical stress, known as a direct effect. However, in inverse piezoelectric effect, a mechanical strain can be generated proportional to an applied electric field.



**Figure 5.16:** Bipolar strain versus electric field of  $Pb_{(1-x)}La_xTi_{(1-x)}Al_xO_3$ for x = 0.06, 0.09, 0.12, and 0.18 compositions.

Bipolar strain versus electric-field curves of PLTA ceramics measured at room temperature under an applied maximum electric field 60 kV/cm is shown in Figure 5.16. Typical butterfly-shaped loops, for  $0.06 \le x \le 0.12$  compositions, confirm piezoelectric nature of the samples. A piezoelectric strain was found to decrease with substitution. Similar behavior is also observed in other perovskites [46, 47]. For x > 0.18 composition, we did not obtain any piezoelectric nature in the samples.



Figure 5.17: (a) Schematic illustration of energy storage

characteristics of a ferroelectric loop, (b) Energy storage efficiency versus composition of the  $Pb_{(1-x)}La_xTi_{(1-x)}Al_xO_3$  samples.

Energy storage density for a polarizable material is given by, W  $=\int_{P_i}^{P_f} EdP$ , where, W represents the electrical energy density, E refers to the applied external electric field,  $P_i$  and  $P_f$  are the initial and final polarization respectively [48-50]. In a ferroelectric material, the charging and discharging process corresponds to the total energy supplied,  $W_{supplied}$ , and stored,  $W_{stored}$ , respectively. These are actually the areas under the E-P diagrams for charging and discharging plots as shown in the schematic diagram of Figure 5.17a. The area enclosed by the ferroelectric loop, therefore, corresponds to the energy lost,  $W_{lost}$ . A relation between these energy densities is given by,  $W_{supplied} = W_{stored}$ +  $W_{lost}$ . The storage efficiency,  $\eta$ , can be estimated by,  $\eta = \frac{W_{stored}}{W_{supplied}}$ . For PLTA samples, an area of loops gradually decreases with increasing substitution. Hence, the energy loss is less. Therefore, the storage efficiency,  $\eta$ , increases with La/Al addition as shown in Figure 5.17b. As a result, ferroelectric materials in the paraelectric region can have high storage efficiency. In case of x = 0.25, this was calculated to be 96 % and can be used as an energy storage material. On the other hand, for  $0.06 \le x \le 0.18$  samples are in ferroelectric phase with nonlinear hysteresis curve at room temperature. Thereby, losses are more and cannot be used as energy storage materials, but can be used in ferroelectric RAM, sensors, etc. We have plotted the composition dependence of energy storage density and observe that for the initial doping of  $x \le 0.12$  the efficiency is less and rising nominally, whereas, for  $x \ge 0.18$  it rises drastically.

#### **5.3 Conclusions**

In this chapter,  $Pb_{(1-x)}La_xTi_{(1-x)}Al_xO_3$  ( $0 \le x \le 0.25$ ) ceramics were fabricated form the powders synthesize successfully using the sol-gel process. Rietveld refinement of SRPXRD data was performed for all samples to investigate the effect of *La/Al* doping on the crystal structure. Analysis confirmed the tetragonal *P4mm* phase for the  $0 \le x$  $\leq 0.18$  composition whereas x = 0.25 composition was found to be in cubic structure with Pm3m space group. Lattice parameters 'c' decreased while 'a' increased with the increase in substitution (x). Raman spectroscopy shows variations in intensity and energy of phonons modes related to tetragonal to cubic phase transformation. A temperature-dependent dielectric study confirmed the phase transition from tetragonal to the cubic structure. The decrease in the temperature of phase transition with increased substitution was correlated with the SRPXRD and Raman spectroscopy. Temperature-dependent x-ray diffraction study co-relates the exact structural phase transition from tetragonal to the cubic structure. The degree of diffuseness of the dielectric peak was found to increases with increase in substitution. We have obtained good ferroelectric/piezoelectric loops for the samples with  $0.06 \le x \le 0.18$ . Energy storage density was calculated for all the samples and sample with composition x = 0.25 showed the highest energy density of 96.5 %.

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# Chapter 6 $(Pb_{1-x}Bi_x)(Ti_{1-x}Mn_x)O_3$ : Competing mechanism of Tetragonal-Cubic phase on *A/B* site modifications

This chapter covers various physical properties of *Bi/Mn* modified PbTiO<sub>3</sub>. Chapter starts with sample preparation and followed with characterizations. Samples were prepared by modified sol-gel process followed by the solid-state sintering for the crystallization of samples. After that these samples were characterised by Synchrotron-based XRD, Raman spectroscopy, FESEM/elemental mappings and dielectric properties. Temperature-dependent XRD was carried out to investigate the lattice change with temperature. Rietveld refinement using Fullprof software was adopted to estimate changes in structure as a function of composition and temperature.

## 6.1 Synthesis

 $(Pb_{1-x}Bi_x)(Ti_{1-x}Mn_x)O_3 \ (0 \le x \le 0.50)$  polycrystalline powders were synthesized using Puratronic grade lead (II) nitrate, manganese nitrate (50 % w/w aqua solution), bismuth nitrate, and dihydroxy bis (ammonium lactate) titanium (IV) (50 % w/w aqua solution). Detailed synthesis method is in chapter 2.

# 6.2 Results and discussion

#### 6.2.1 Structural studies

Ambient synchrotron-based powder x-ray diffraction (named as SRPXRD) patterns for  $0 \le x \le 0.50$  are shown in Figure 6.1a. SRPXRD patterns, of samples with  $x \le 0.37$ , belong to a pure tetragonal phase with *P4mm* space group, whereas for x = 0.50 composition diffraction peaks corresponding to cubic *Pm3m* space group. Variations of peak intensity with the composition (x) in  $0 \le x \le$ 

0.50 range are shown in the Figure 6.1b, highlighted part of Figure 6.1a. To confirm the actual changes in structure as well as the phase purity of the sample, we have performed the Rietveld refinement on the SRPXRD data.



**Figure 6.1:** (a) SRPXRD of  $(Pb_{1-x}Bi_x)(Ti_{1-x}Mn_x)O_3$  ( $0 \le x \le 0.50$ ) range, calculated unit cell volume as a function of compositions are shown in inset fig. 6.1a., (b) Highlighted part x-ray spectra (c) Calculated lattice parameters and c/a ratio as a function of compositions, inset figure is showing the zoom part of the c/a ratio mark with arrow.

The initial structural model for Rietveld refinement was taken as pure PbTiO<sub>3</sub> with the atomic positions being given in the noncentrosymmetric space group *P4mm* (No. 99) with *Pb/Bi* at the origin (0, 0, 0) [1, 2]. Background estimation was performed using linear interpolation between a set of background points and profile function was chosen as axial divergence asymmetric Pseudo-Voigt function. Parameters such as scale factor, lattice parameters, profile parameters (*U*, *V*, *W*) and position parameters (*x*, *y*, *z*) were refined one after the other. After successive refinement of these parameters, calculated and observed patterns show excellent match with the reasonable goodness of fit parameters ( $\chi^2$ ,  $R_p$ ,  $R_{wp}$ ,  $R_{exp}$ ). Representative plot with the goodness of fit parameter for all samples are shown in the Figure 6.2 & 6.3.



**Figure 6.2:** Rietveld refinement goodness of fitting for  $Pb_{(1-x)}Bi_xTi_{(1-x)}Mn_xO_3$  samples where (a) x = 0, (b) x = 0.06, (c) x = 0.09, (d) x = 0.12, and (d) x = 0.18 compositions. Fitting parameters are provided in the corresponding figure. The hollow black symbols are observed data, red solid line calculated data, below dark yellow solid line difference of observed and calculated data, and vertical blue bar lines are Bragg positions with the corresponding P4mm space group.



**Figure 6.3:** Rietveld refinement goodness of fitting for  $Pb_{(1-x)}Bi_xTi_{(1-x)}Mn_xO_3$  samples where (a) x = 0.25, (b) x = 0.31, (c) x = 0.34, (d) x = 0.37, and (e) x = 0.50 compositions. Fitting parameters are provided in the corresponding figure. The hollow black symbols are observed data, red solid line calculated data, below dark yellow solid line difference of observed and calculated data, and vertical blue bar lines are Bragg positions with the corresponding space group.

**Table 6.1:** Position parameters of the  $Pb_{(1-x)}Bi_xTi_{(1-x)}Mn_xO_3$  ( $0 \le x \le 0.50$ ) range samples after the Rietveld refinement of SRPXRD data.

Atoms	Coo	<b>Composition</b> ( <i>x</i> )				
	rdi	0.00	0.06	0.09	0.12	0.18
	nate					
	S					
Pb/Bi	x	0	0	0	0	0
	у	0	0	0	0	0
	z	0	0	0	0	0
Ti/Mn	x	0.5	0.5	0.5	0.5	0.5

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		-	-	-		<b>T</b>	
	у	0.5	0.5	0.5	0.5	0.5	
	Z.	0.538	0.54018	0.53986	0.54217	0.54204	
		16(1)	(1)	(1)	(75)	(1)	
01	x	0.5	0.5	0.5	0.5	0.5	
	у	0.5	0.5	0.5	0.5	0.5	
	Z.	0.108	0.10844	0.10902	0.10477	0.1180	
		61 (1)	(1)	(1)	(207)	(1)	
O2	x	0.5	0.5	0.5	0.5	0.5	
	у	0	0	0	0	0	
	Z.	0.608	0.60615	0.60778	0.60728	0.60445	
		43 (1)	(0)	(1)	(126)	(1)	
Atoms	Coo	Composition (x)					
	rdin	0.25	0.31	0.34	0.37	0.50	
	ates						
Pb/Bi	x	0	0	0	0	0	
	у	0	0	0	0	0	
	Z.	0	0	0	0	0	
Ti/Mn	x	0.5	0.5	0.5	0.5	0.5	
	у	0.5	0.5	0.5	0.5	0.5	
	Z.	0.5429	0.54419	0.54363(	0.53907(	0.5	
		1(1)		1)	1)		
01	x	0.5	0.5	0.5	0.5	0.5	
	у	0.5	0.5	0.5	0.5	0.5	
	Z.	0.1194	0.10646	0.10311(	0.09403(	0	
		5(1)		1)	1)		
O2	x	0.50	0.5	0.5	0.5	0.5	
	у	0	0	0	0	0	
	Z.	0.6056	0.59988(	0.59978(	0.59481(	0.5	
		6(1)	1)	1)	1)		

The fitting *R*-factors are in acceptable range for all samples as shown in Figure 6.2 & 6.3. A schematic representation of unit cell is shown in Figure 4 for x = 0 and x = 0.50 compositions with the help of VESTA software [3]. Position parameters for all the samples obtained from Rietveld refinements are provided in the Table 6.1.



**Figure 6.4:** Unit cell structure after Rietveld refinement (a) Pure  $PbTiO_3$  with tetragonal structure, (b)  $Pb_{(1-x)}Bi_xTi_{(1-x)}Mn_xO_3$  for x = 0.50 composition with cubic structure. Mark of Pb with 1 and 2 is just for explanation.

The calculated lattice parameters (a, c) with c/a ratio as a function of composition are shown in Figure1c. Lattice parameters 'a' slightly decreases while 'c' increases up to x = 0.12 composition. Hence, tetragonality (c/a ratio) nominally increased initially in the range  $0 \le x \le 0.12$  from 1.064 to ~1.066, thereafter decreasing continuously in the range  $0.12 \le x \le 0.50$  to 1, for x = 0.50 (c/a = 1). At A-site, crystal radii of  $Bi^{3+}(XII)$  (~1.58 Å) is lesser than  $Pb^{2+}(XII)$ (1.63 Å) while for B-site  $Mn^{3+}$ (VI) (0.72 Å for low spin) and  $Mn^{4+}$ (VI) (0.67 Å) are less than  $Ti^{4+}(VI)$  (0.745 Å). Only  $Mn^{3+}(VI)$  (0.785 Å for high spin) is larger than the  $Ti^{4+}$  ion [4]. Though, the crystal radii of substituent ions were smaller than the host ions, the observed unusual decrease in a and increase in c parameter at low concentration of x can only be explained with the chemistry associated with Bi-ion lone pair.  $Bi(6s^2)$  lone pair is more prominent than the  $Pb(6s^2)$ , hence hybridization between  $Bi(6s^2)$  and O(2p) is more strong than  $Pb(6s^2)$ and O(2p). Upto a critical concentration of the *Bi*-ion in the system such as in this case  $x \leq 0.12$ , the ionic size effect is not only the controlling factor in the structural distortion. After that decrease of the lattice parameters are controlled by the ionic size effect at A and B-site [5]. However, the overall unit cell volume decreased with increase in substitution as shown in inset of Figure 6.1a.

Temperature-dependent SRPXRD (HT-SRPXRD) ( $\lambda = 0.5036$ Å) was performed, in same geometry, to study phase transition temperature and lattice dynamics on selected samples (x = 0, 0.06, 0.09compositions). Thermal equilibrium of samples was obtained by keeping the temperature constant for 10 min at the desired temperature, before start of experiment at each temperature. Non-centrosymmetric tetragonal to centrosymmetric cubic phase transformation is observed [Figure 6.5 (a-c) and Figure 6.6a] from merging of tetragonal peaks [Figure 6.5 (b-d) and Figure 6.6b] in the SRPXRD plots with the increase in temperature. Temperature-dependence of lattice parameters was estimated by refinement of HT-SRPXRD data. By using Le Bail profile fitting technique as implemented in Fullprof software to estimate lattice parameters of HT-SRPXRD data. Calculated lattice parameters for x = 0, 0.06, and 0.09 samples are shown in Figure 6.6c as a function of temperature. Lattice parameters 'a' is increasing while 'c' is decreasing with increase in temperature. All three lattice parameters become equal after tetragonal to cubic phase transition ( $T_C$ ~763 K) for x = 0, and 0.06 composition. However, for x = 0.09,  $T_C$ increased to ~773 K, in agreement with c/a ratio. Variation of unit cell volume as a function of temperature for x = 0, 0.06 and 0.09 is shown in Figure 6.6d. The volume was found to decrease with increase in temperature for all measured three samples upto Curie point  $(T_C)$ .

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**Figure 6.5:** Temperature-dependent SRPXRD data of  $(Pb_{1-x}Bi_x)(Ti_{1-x}Mn_x)O_3$  for x = 0 and 0.06 composition, where (a) SRPXRD spectra at different temperatures for x = 0 composition, (b) Highlighted spectra of most intense x-ray peak, (c) x-ray spectra at different temperature for x = 0.06 composition, and (d) Highlighted spectra of most intense peak.



Figure 6.6: Temperature-dependent SRPXRD data of  $(Pb_{1-x}Bi_x)(Ti_{1-x}Bi_x)$ 

 $_xMn_x)O_3$  for x = 0.09 composition, where (a) SRPXRD spectra at different temperatures, (b) Highlighted spectra of most intense x-ray peak, (c) Calculated lattice parameters as a function of temperatures for x = 0, 0.06, 0.09 compositions, and (d) Calculated unit cell volume as a function of temperatures for x = 0, 0.06, 0.09 compositions.

Below  $T_C$ , thermal expansion coefficient,  $\alpha(T)$ , was negative, i.e., unit cell volume contracted with temperature [Figure 6.6d] for all three samples. The decrease in unit cell volume increased as  $T \rightarrow T_C$ . After phase transition temperature, a positive thermal expansion was observed. Hence, structural transition from ferroelectric to paraelectric can be related to the nature of thermal expansivity of these materials. Thus, tetragonal distortion of ferroelectric phase must be related to negative thermal expansion coefficient. All samples are tetragonal at room temperature, except for x = 0.50. Hence, it can also be expected that for higher *Bi/Mn* modified PbTiO<sub>3</sub> systems with  $0.09 \le x < 0.37$ , will have negative thermal expansion behavior similar to x = 0, 0.06and 0.09 until phase transition temperature. The negative thermal expansion coefficient was calculated from the observed reduction in the volume data as a function of temperature using equation:  $\frac{\Delta V}{V_{e}} = \alpha_{v}$  $\Delta T$ , where  $V_0$  is the volume of the unit cell at 373 K, V volume of the unit cell as a function of temperature,  $\alpha_{\nu}$  thermal expansion coefficient,  $\Delta T$  temperature difference, and  $\Delta V$  are change in volume. Thermal expansion coefficient was estimated to be  $-1.571*10^{-5}$  /K, - $2.44*10^{-5}$  /K, and  $-5.025*10^{-6}$  /K for x = 0, 0.06, and 0.09 samples respectively by fitting the estimated volume data as a function of temperature [6, 7].

Correlation between negative thermal expansion and tetragonality of PbTiO<sub>3</sub> related structures can be associated to the nature of TiO<sub>6</sub> and PbO<sub>12</sub> polyhedra. In cubic PbTiO<sub>3</sub> ( $T > T_C$ , i.e. 763 K) the TiO<sub>6</sub> and PbO<sub>12</sub> polyhedra are perfectly symmetric. The symmetry in cubic phase is due to equal bond strengths of *Pb*1-*O*2 and *Pb*2-*O*2 bonds (atoms nomenclature are shown in Fig. S3). As the

sample is cooled down from  $T_c$ , the symmetry of the polyhedra are destroyed as lattice parameters 'c' become larger than 'a' or 'b'. This happens due to the strong hybridization of *Pb*6s-*O*2p electrons. This should have resulted in the contraction of the c-axis if both Pb1 and Pb2 would have bonded equivalently to O2. However, the presence of TiO<sub>6</sub> octahedra does not allow such contraction and results in O2 being asymmetrically shared between Pb1 and Pb2. Hence, in the tetragonal phase, bond strength of Pb1-O2 is much stronger than Pb2-O2. On the other hand, this powerful Pb1-O2 bond also creates an asymmetry in the TiO<sub>6</sub> octahedral, elongating TiO<sub>6</sub> octahedra along the *c*-axis and moving the O-cage upwards. Ti is also displaced due to changes in the position of O2 and O1. Hence, below  $T_C$  both polyhedra are distorted. It is interesting to notice that during cooling below  $T_C$ , rate of increase of 'c' lattice parameter is much more  $(2 \sim 10 \text{ times})$  than that of 'a or b' parameters. This ratio increases with increasing temperature and is strongest near  $T_C$ . This may be responsible for the negative thermal expansion of these materials. Above  $T_C$ , thermal energy supplied to the lattice further enlarges all bonds, thereby increasing lattice parameters. Hence, it is interesting to envisage that the same Pb2-O2 bond which was decreasing below  $T_C$ , increases beyond  $T_C$ . BiMnO<sub>3</sub> modified PbTiO<sub>3</sub> are tetragonal up to x = 0.37 [Figure 6.1a]. Although hightemperature structural studies could not be investigated for all samples, it may be expected that similar behavior may exist for all sample with *x* < 0.37 [6, 8-10].

Raman spectroscopy is an excellent tool to assess lattice vibrations, structural distortion and lattice strains associated with the substitution in PBTM samples. Twelve optic modes  $(3T_{1u} + T_{2u})$  are observed in the cubic phase, where triply degenerate  $T_{1u}$  modes are infrared active and  $T_{2u}$  are silent modes which are neither Raman nor infrared active [11]. Tetragonal phase exhibits fifteen Raman active modes. The irreducible representation can be written as  $\Gamma_{Raman} = 3A_1(TO) + 3A_1(LO) + B_1 + 4E(TO) + 4E(LO)$ .

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**Figure 6.7:** (a and b) Un-polarised room temperature Raman spectra of  $(Pb_{1-x}Bi_x)(Ti_{1-x}Mn_x)O_3$  (x = 0, 0.06, 0.09, 0.12, 0.18, 0.25, 0.31, 0.34, 0.37 and 0.50) system. Inset of (a) show the substitution evolution of soft mode S1.

It is evident from the recorded spectra that there are total 12 distinct modes of vibration for pure PbTiO<sub>3</sub> system in the spectral range of 20-950 cm<sup>-1</sup> (S1 to S12). The observed feature of Raman spectra confirms the tetragonal structure of PbTiO<sub>3</sub> under ambient condition [12]. With increasing substitution, a tetragonal to cubic-like phase transformation is witnessed. These modes remain consistent in all compositions with  $x \le 0.12$  (Figure 6.7a) and exhibit some changes in mode frequency. However, for 0.18 < x < 0.50, few modes get merged and disappear from the spectra (Figure 6.7b). All the observed phonon modes in Raman spectra for  $(Pb_{1-x}Bi_x)(Ti_{1-x}Mn_x)O_3$  are tabulated in Table 6.2.

**Table 6.2:** The observed phonon modes and their assignment for  $(Pb_{1-x}Bi_x)(Ti_{1-x}Mn_x)O_3$  (x = 0, 0.06, 0.09, 0.12, 0.18, 0.25, 0.31, 0.34, 0.37 and 0.50) system. The mode frequencies are in cm<sup>-1</sup>.

Phonon	PTBM	PTBM	PTBM	PTBM	PTBM	Mode
Modes	(x = 0)	(x= <b>0.06</b> )	(x=0.09)	( <i>x</i> =0.12)	( <i>x</i> = <b>0.18</b> )	Assignment
S1	84.2	82.5	80.5	76.4	75.4	E (1TO)
S2	110.9	107.7	104.4	98.1	-	E (1LO)
\$3	149.2	151.5	152.2	149.9	158.6	A <sub>1</sub> (1TO)

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S4	213	224.2	226.1	226.8	233.7	E (2TO)
S5	287.9	284.9	283.3	282.9	274.3	B <sub>1</sub> +E
\$6	346.3	348.8	345.5	322.4	323.5	A <sub>1</sub> (2TO)
S7	446.2	446.1	446.1	442.5	-	E (2LO)+
						A1 (2LO)
S8	503.7	509.5	508.9	506.4	507.3	E (3TO)
<b>S</b> 9	587.6	584.4	581.4	-	-	
S10	626.8	623.3	607.1	579.9	595.7	A <sub>1</sub> (3TO)
S11	724.7	699.7	691.9	676.4	680.9	E (3LO)
S12	763.8	757.7	745.5	734.6	752.8	A <sub>1</sub> (3LO)
Phonon	РТВМ	РТВМ	РТВМ	РТВМ	РТВМ	Mode
Modes	( <i>x</i> =0.25)	(x=0.31)	( <i>x</i> = <b>0.34</b> )	(x= <b>0.37</b> )	( <i>x</i> =0.50)	Assignment
S1	75.8	73.7	-	-	-	E (1TO)
\$2	-	-	-	-	-	E (1LO)
S3	163.3	-	-	-	-	A <sub>1</sub> (1TO)
S4	237.1	-	-	-	-	E (2TO)
S5	274	271.4	272.7	271.9	273.6	B <sub>1</sub> +E
\$6	320.1	315.9	313.4	311	309.2	A <sub>1</sub> (2TO)
S7	-	-	-	-	-	Е
						(2LO)+
						A1
						(2LO)
S8	496.3	492.4	489.2	487.3	482.6	E (3TO)
S9	-	-	-	-	-	
S10	590.8	569.9	551.2	559.2	545.9	A <sub>1</sub> (3TO)
S11	672.3	665.1	651.9	647.7	648.4	E (3LO)
S12	7515	752.8	753.1	750.7	748.3	A <sub>1</sub> (3LO)

Phonon modes below 150 cm<sup>-1</sup> i.e., E(1TO) (~ 84 cm<sup>-1</sup>) and  $A_{I}(TO)$  (~150 cm<sup>-1</sup>) are considered as soft phonon modes originating from the  $T_{Iu}$  (TO) mode of the cubic phase mainly arises due to the vibration of Pb-ion with respect to TiO<sub>6</sub> octahedra [13, 14]. A weak E(1LO) i.e., S2 mode vanishes after x = 0.12. For x > 0.34 all soft modes vanish. All three soft modes are a signature of A-site ordering in the ABO<sub>3</sub> structure [15]. Gradual loss of these modes hints at loss of order at the A-site in substituted samples.



**Figure 6.8:** Substitution dependence of mode frequency, FWHM and normalized intensity for modes S1, S3, S4 and S5 of  $(Pb_{1-x}Bi_x)(Ti_{1-x}Mn_x)O_3$  (x = 0, 0.06, 0.09, 0.12, 0.18, 0.25, 0.31, 0.34, 0.37 and 0.50). Shaded region show that maximum changes in the phonon self-energy parameters and integrated intensity are observed till x = 0.12 of substitution. Dotted vertical line shows that dominating phase beyond ~ 37 % of substitution is cubic as all the parameters are nearly invariant of substitution.

Figure 6.8 shows variation of mode frequency, full-width at half maximum (FWHM)/damping coefficient and intensity of phonon

modes (S1, S3, S4, and S5). Following observations follows: (i) S1: frequency sharply decreases (~9.3 %) for  $x \le 0.12$ , marginally decreases (~2.1 %) upto x = 0.31; thereafter disappears for x > 0.31 (ii) mode S3 and S4 shows large increase in mode frequency ~ 8 % and 14 %, respectively, with substitution up to x = 0.25 and on further increase in x concentration mode S3 disappear and mode S4 merge with mode S5; (iii) frequency of mode S5 shows continues decrease upto x =0.12, and on further increase in substitution, it shows mode softening by ~ 3.04 % at x = 0.18 and thereafter it remains almost constant; (iv) damping coefficient of modes (S1, S3, S4, and S5) shows large increase (as large as 400 %) with increase in concentration clearly suggesting that disorders are increasing linearly with the substitution. As the damping coefficient is inversely proportional to the life time of a phonon mode, a large increase in damping coefficient with increase in substitution suggests that phonon life time decreasing sharply, indirectly reflecting the presence of disorder in the system (v) the intensity of modes (S1, S3, S4, and S5) shows sharp drop on the increase in substitution up to x = 0.12 and remain almost constant on further increase in x concentration.



Figure 6.9: Substitution dependence of mode frequency, FWHM and
normalized intensity for modes S6, S8, S10 and S11 of  $(Pb_{1-x}Bi_x)(Ti_{1-x}Mn_x)O_3$  (x = 0, 0.06, 0.09, 0.12, 0.18, 0.25, 0.31, 0.34, 0.37 and 0.50). Shaded region show that maximum changes in the phonon self-energy parameters and integrated intensity are observed till x = 0.12 of substitution. Dotted vertical line shows that dominating phase beyond ~ 37 % of substitution is cubic as all the parameters are nearly invariant of substitution.

Based on studies on S6, S8, S10, and S11 (Figure 6.9), following observation can be made: (i) frequency of mode S6 remain nearly constant upto x = 0.09 and shows mode softening (~6.7 %) at x = 0.12, and decreases on further increase in x concentration upto x = 0.31, and after that it remains almost constant; (ii) frequency of mode S8 shows slight increase upto x = 0.12 and decreases on further increase in x concentration; (iii) modes S10 and S11 shows a large decrease in mode frequency upto x = 0.34 and thereafter remain nearly constant with increase upto x = 0.34 and remain constant after that, on the other hand damping coefficient of mode S8 and S10 shows increase upto x = 0.12 and thereafter it remains almost constant. The intensity of mode S6, S8, S10 and S11 shows a large decrease (~80 %) till x = 0.31 and after that remains constant.

It is evident from the above observation that there is a systematic structural distortion in  $(Pb_{1-x}Bi_x)(Ti_{1-x}Mn_x)O_3$  with an increase in substitution. The crystal radius of  $Pb^{2+}(XII)$  (~1.63 Å) is smaller than  $Bi^{3+}(XII)$  (~1.59 Å). On the other hand, the crystal radius of  $Mn^{3+}(VI)$  (~0.72 Å for low spin and ~0.785 Å for high spin) is either smaller or larger compared to  $Ti^{4+}(VI)$  (~0.745 Å) depending on the bond strength of Mn with O ions. As Bi is already smaller than Pb, it is most likely that Mn-O bonds will be longer. Hence, the chance of smaller crystal radius of Mn is lesser than the larger version, thereby resulting in a high spin state. Presence of all phonon modes associated with tetragonality of ABO<sub>3</sub> structure confirms a tetragonal (Pb<sub>1-x</sub>Bi<sub>x</sub>)(Ti<sub>1-x</sub>Mn<sub>x</sub>)O<sub>3</sub> phase for  $x \leq 0.12$ . Further substitution shows renormalization of phonon modes self-energy parameters, i.e. mode

frequency and damping coefficient; reflecting indications of clear structural distortion. A morphotropic phase boundary in these samples, with co-existent tetragonal and pseudo-cubic phases, [16] may be responsible for such structural distortions. Soft modes in these systems are extremely sensitive to any perturbation, e.g., pressure (external as well as internal), temperature, etc. Such a perturbation in form of substitution is reflected in PBTM samples. With increasing substitution, broadening, merging and finally, the disappearance of phonon modes hint at a tetragonal-cubic phase transition. The tetragonal phase for lower substitution ( $x \le 0.12$ ), followed by a gradual appearance of cubic phase is evident from Fig. 6.4 and 6.5, ultimately changing to a cubic phase after ~ 34 % substitution.



**Figure 6.10:** Surface microstructural analyses of  $(Pb_{1-x}Bi_x)(Ti_{1-x}Mn_x)O_3$  samples where (a) x = 0.06, (b) x = 0.09, (c) x = 0.12, (d) x = 0.18, (e) x = 0.25, (f) x = 0.31, (g) x = 0.34, (h) x = 0.37, and (i) x = 0.50 compositions.

Microstructure analyses of the PBTM samples were performed with FESEM study. Gold-sputtered pellets were used to see the Micrographs of the PBTM samples. Micrographs were collected in the secondary electron mode. Images of all the PBTM samples are shown in Figure 6.10(a-i). Grains are compactly packed in all the samples. Average grain size, estimated using Image J software, decreases from 14.55  $\pm$  4.82 µm for x = 0.06 to 11.53  $\pm$  4.32 µm for x = 0.50 and can be related to reduction in the diffusion coefficient of *Bi/Mn* substitution elements [5, 17].



**Figure 6.11:** FESEM-EDS elemental mapping of  $(Pb_{1-x}Bi_x)(Ti_{1-x}Mn_x)O_3$  for x = 0.125 composition where (a) secondary electron image and corresponding elemental mapping of the element (b) Pb, (c) Bi, (d) O, (e) Ti, (f) Mn elements, (g) Area EDS spectrum and right table for the atomic and weight percentage of various elements.

To understand the surface morphology of the PBTM samples, The FESEM image and elemental mappings for all the elements are performed. A representative EDS spectrum and elemental mappings along with the secondary electron micrograph for x = 0.12 composition are shown in Figure 6.11(a-g). Spot EDS was performed on grain and grain boundary regions to confirm chemical composition and homogeneity of the sample. Chemical homogeneity of *Pb*, *Ti*, *Bi*, *Mn*, and *O* was also confirmed using area EDS elemental analysis [18, 19]. A combined graph of area spectra [Figure 6.11g] provides atomic and the weight percentage of constituent elements [Table in Figure 11]. The obtained atomic and weight percentage of the composition is well matched with the target sample (Pb<sub>0.88</sub>Bi<sub>0.12</sub>Ti<sub>0.88</sub>Mn<sub>0.12</sub>O<sub>3</sub>) within the



errors related to EDS analysis. Hence, there is no secondary phase perceived in the sample, and all the elements are homogeneously distributed across the sample.

**Figure 6.12:** Temperature-dependent dielectric constant and  $\tan \delta$  of the  $(Pb_{1-x}Bi_x)(Ti_{1-x}Mn_x)O_3$  samples where (a) x = 0.06, (b) x = 0.09, (c) x = 0.12, (d) x = 0.18, and (e) x = 0.25 compositions.

#### **6.2.2 Dielectric properties**

To explore the physical properties of the PBTM samples, temperature-dependent dielectric constant and loss (tan $\delta$ ) measurements were carried out at various frequencies. Dielectric constant and tan $\delta$  versus temperature for  $0.06 \le x \le 0.25$  compositions are shown in the Figure 6.12(a-e). For  $0.06 \le x \le 0.18$ , a single dielectric catastrophic anomaly is observed at a certain temperature (Curie point,  $T_c$ ) corresponding to a structural phase transition from polar tetragonal to the centrosymmetric cubic phase of a perovskite structure [20, 21]. PbTiO<sub>3</sub> has a sharp transition at  $T_C \sim 763$  K for ferroelectric to paraelectric phase [22]. For x = 0.06 composition,  $T_C$  is invariant ~763 K. However,  $T_C$  increased to ~773 K for x = 0.09composition which is 10 K temperature more than the pure PbTiO<sub>3</sub> system.  $T_C$  for x = 0, 0.06, and 0.09 was also confirmed from temperature-dependent SRPXRD (Figure 6.5 (a-c) and Figure 6.6a).  $T_C$ reduces to lower temperatures for  $x \ge 0.12$  [Figure 6.12(c-e)]. For x =0.25 composition, the negative dielectric constant was observed after ~600 K, a phenomenon not possible in capacitive materials. Negative  $\varepsilon_r$  may be due to the conductive nature of the material. However, the dielectric anomaly is still evident at  $T_C \sim 700$  K. In these samples with higher substitution, the dielectric anomaly was not observed.

In the ABO<sub>3</sub> structure of PbTiO<sub>3</sub>, the *Pb*1-*O*2 bond strength is a determining factor as has been discussed before. Substitution of *Pb* by *Bi* introduces stronger *Bi*-*O*2 bonds for the lower amount of substitutions, due to the smaller size of *Bi* compared to *Pb* [23]. These stronger *Bi*-*O*2 bonds create larger distortion along *c*-axis and are supported by a larger size  $Mn^{3+}$ . This results in an increase of *c/a* ratio. However, this size effect cannot extend indefinitely. The proximity of *Mn* and *O*1 ions will soon reach a minimum and after that elongation will be restricted. After that, arrangements of ions happen by enlarging along '*a* or *b*' axes. This restructures electronic clouds around *Pb/Bi* ions and thereby bonding with *O*2 is modified reducing *c*-axis. It is observed that *c/a* increases until *x* = 0.12 and after that decreases.

#### **6.3 Conclusions**

Polycrystalline powders of  $(Pb_{1-x}Bi_x)(Ti_{1-x}Mn_x)O_3$  ( $0 \le x \le 0.50$ ) were successfully prepared via the sol-gel method. Structural properties were investigated with Rietveld refinement of the SRPXRD data and Raman spectroscopy. Tetragonal phase (*P4mm*) was identified for  $0 \le x \le 0.37$  samples whereas cubic phase (*Pm3m*) for x = 0.50 sample. Lattice parameters '*a*' slightly decreases while '*c*' increases upto x = 0.12 composition. Hence, tetragonality (*c/a* ratio)

nominally increased initially in the range  $0 \le x \le 0.12$  from 1.064 to ~1.066, thereafter decreasing continuously in the range  $0.12 \le x \le 0.50$ to 1, for x = 0.5 (c/a = 1). A Ferro-para phase transition in these materials can be related to tetragonal to cubic phase transition using composition dependent dielectric studies of the materials. Synchrotronbased temperature-dependent SRPXRD was carried out for x = 0, 0.06, and 0.09 samples to study the lattice dynamics of the phase transition temperature. Lattice parameters 'c' decreased while 'a' increased with increase in temperature. The phase transition temperature,  $T_{C}$ , increased from 763 K in  $x \le 0.06$  to 773 K in x = 0.09 samples. Thermal expansion coefficient was obtained to be  $-1.571*10^{-5}$  /K, - $2.44*10^{-5}$  /K, and  $-5.025*10^{-6}$  /K for x = 0, 0.06, and 0.09 samples respectively by fitting the estimated volume data as a function of temperature. Dielectric properties also reveal same phase transition temperature. Unit cell volume was found to decrease with increase in temperature until  $T_C$ , showing negative thermal expansion.

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# **Chapter 7**

# Conclusions and Future Research Scope

#### 7.1 Conclusions

Structure, dielectric, and ferroelectric properties of modified sol-gel prepared lead titanate perovskite ceramics have been investigated. Samples are in single phase. Lead titanate was modified at A-site with  $(K_{0.5}Sm_{0.5})$ ,  $(Na_{0.5}Sm_{0.5})$ , *B*-site with *Fe*, *A/B*-site with *La/Al* and *Bi/Mn* elements. A concise results-based summary and future scope is provided here.

(K<sub>0.5</sub>Sm<sub>0.5</sub>) or (Na<sub>0.5</sub>Sm<sub>0.5</sub>) modified PbTiO<sub>3</sub>: The influence of A-site modified PbTiO<sub>3</sub> with  $(K_{0.5}Sm_{0.5})$  and  $(Na_{0.5}Sm_{0.5})$  on structural and electrical properties were investigated. Samples were prepared by sol-gel combustion method and followed by solid-state sintering. Synchrotron-based high-resolution powder x-ray diffraction in capillary mode was carried out to examine the lattice dynamics with compositions at ambient temperature. There were no secondary phases observed in all the samples. Rietveld refinement was performed for all the XRD data to evaluate structural variation with substitutions. With (K<sub>0.5</sub>Sm<sub>0.5</sub>) or (Na<sub>0.5</sub>Sm<sub>0.5</sub>) modification, a reduction in tetragonal structure (P4mm space group) was observed. There is a tendency of formation of a more ordered pseudo-cubic structure (Pm3m space group). In both series, lattice parameter, 'c', decreases, while 'a' is almost constant. Lattice became pseudo cubic for x = 0.50 of both series, as lattice parameters a = c composition. Ti position was found to decrease in the z-direction while apical, and planner oxygen's increase with substitution. Tetragonal lattices are ferroelectric material whereas cubic structure is paraelectric in nature. Raman spectroscopy shows changes in intensity and energy of phonon modes related to tetragonal-cubic structure phase transformations and lattice strain with ferroelectric properties. The lower mass of Na/Sm or K/Sm compared

to Pb may be a reason for such changes. Average grain size was found from FESEM micrographs. Average grain size decreases from 1.03  $\pm$ 0.36 µm as in x = 0.10 to 0.60 ± 0.17 µm for x = 0.50 for Na/Sm series and  $1.19 \pm 0.53 \ \mu\text{m}$  as in x = 0.06 to  $0.98 \pm 0.37 \ \mu\text{m}$  for x = 0.50 for K/Sm series. The decrease of grain size in samples with increase in substitution is due to lower diffusivity of rare earth elements. A temperature-dependent dielectric study was performed to observe the phase transition temperature with compositions. In both of the cases, the phase transition-temperature from tetragonal to cubic phase was found to decrease with increase in compositions. The nature of phase transition temperature became diffused with increase in substitution. Diffusivity was calculated using modified Curie-Weiss law. The diffusivity is due to random distribution of K/Sm or Na/Sm at the Pb site. The decrease in the temperature of phase transition with increased substitution was correlated with the hybridization of  $Pb(6s^2)$  to O(2p)and Ti(3d). The phase transition temperature was verified from temperature-dependent high-resolution powder x-ray diffraction. Changes in unit cell structure, especially at the tetragonal to cubic phase transition temperature gave a clear indication of the exact transition temperature. Impedance measurement of K/Sm substituted samples showed only one semicircle starting from the origin of realimaginary plane of permittivity. Thus a complete grain contribution in the system was observed. Resistivity increases with increase in substitution. An increase of resistivity with substitution was orchestrated by reduction of lead loss at high temperature in substituted samples. AC-electric field dependent polarization was performed for all the samples at 1 Hz frequencies. Samples with lower substitution of both series did not show proper ferroelectric loop due to leaky nature. increasing substitution, But with resistance increases and ferroelectricity becomes pronounced.

*Fe* modified PbTiO<sub>3</sub>: Structural and electronic properties of PbTi<sub>(1-x)</sub>Fe<sub>(x)</sub>O<sub>(3- $\delta$ )</sub> in regime  $0 \le x \le 0.50$  range has been carried out. Tetragonal distortion of lattice and hence crystal field reduces exponentially with substitution due to reduced ionic radius of

substituent  $Fe^{3+}$  compared to substituted  $Ti^{4+}$  ion. Charge reduction at *B*-site may generate some oxygen deficiency. *Ti*-site remains unaltered and distorted as evident from XANES pre-edge studies. A similar distortion is also evident at  $Fe^{3+}$  site providing evidence of an electric field and a remnant ferroelectric polarization. Coexistence of lattice distortion, as well as ferromagnetism, makes this material an important functional material as a multiferroic at room temperature. This is detailed below.

The samples  $PbTi_{(1-x)}Fe_xO_3$  ( $0 \le x \le 0.50$ ) were synthesized by sol-gel combustion methods. XRD patterns show that crystal structures gradually approach higher symmetry (pseudo-cubic) with incorporation of Fe at the Ti-site. Tetragonal distortion of the lattice and hence the crystal field reduces exponentially with substitution due to reduced ionic radius of the substituent  $Fe^{3+}$  compared to the substituted  $Ti^{4+}$  ion. Raman spectroscopy showed the reduction in intensity and energy of phonon modes related to change in structure from non-centrosymmetric tetragonal to centrosymmetric pseudo-cubic type. Charge states and local environments were investigated with high-resolution synchrotron-based XANES/EXAFS data. The XANES spectra confirm that Ti, Fe, Pb are in 4+, 3+ and 2+ respectively in all the samples. The Ti-edge is preceded by a strong pre-edge feature which is attributed to the transition from 1s to  $3d_{xy}$  and  $3d_z$  energy levels. These transitions are forbidden generally in the dipole approximation but are allowed by mixing with oxygen *p*-state orbitals due to the distortion of *Ti* atoms from the oxygen octahedron. The presence of a pre-edge feature for any amount of substitution confirms that *Ti*-sites are distorted even after substitutions with x = 0.50. Also, EXAFS data reveals similarities between the local environment of  $Ti^{4+}$ (VI) and  $Fe^{3+}$ (VI) ions. Hence, it confirms that Fe is substituting the Ti in PbTiO<sub>3</sub> ceramics. The field dependent magnetization measurement of the PbTi<sub>(1-x)</sub>Fe<sub>x</sub>O<sub>3</sub> ( $0 \le x \le 0.50$ ) samples confirms ferromagnetic nature at room temperature for samples with a substitution of  $x \le 0.09$ . Below  $x \le 0.09$  we observe a paramagnetic nature. The Fe - O - Feinteraction between two substituent Fe ions is a source of ferromagnetism in these samples. Polarization versus electric field measurement was performed to confirm ferroelectric nature in the materials. Ferroelectricity in the samples was measured in all the samples, but spontaneous saturation was not obtained for all samples due to the leaky nature of some samples. Leaky nature in samples was observed due to the enhanced oxygen vacancies. These oxygen vacancies pins down the domains and restrict domain switching. Oxygen vacancies are created due to lead loss during high-temperature sintering of samples and also due to  $Fe^{3+}$  being of lesser charge as compared to  $Ti^{4+}$ . Coexistence of ferroelectric and magnetic hysteresis at room temperature makes these materials competent as enhanced functional multiferroic materials.

La/Al modified PbTiO<sub>3</sub>:  $(Pb_{(1-x)}La_x)(Ti_{(1-x)}Al_x)O_3$   $(0 \le x \le x \le x)$ 0.25) powders were obtained using sol-gel combustion process. These were later pelletized and annealed to form ceramics. High-resolution powder x-ray diffraction in rotating capillary mode was carried out to investigate the crystal structure and phase purity of the samples. There was no secondary phase observed in any of the samples. To confirm the actual crystal structure and variations with composition, Rietveld refinement of synchrotron XRD data was performed for all samples in the range  $\sim 0 \le x \le 0.25$ . The analysis confirmed a tetragonal phase of space group *P4mm* for the  $0 \le x \le 0.18$ . For x = 0.25 pseudo-cubic structure with Pm3m space group was found. Lattice parameters 'c' decreased while 'a' increased with the increase in substitution (x). Rietveld refinement confirmed reduction in tetragonal displacement. Structure tends to more ordered pseudo-cubic structure with increase in substitution. Raman spectroscopy shows variations in intensity and energy of phonons modes related to tetragonal to pseudo-cubic phase transformation. Tetragonal structures of PbTiO<sub>3</sub>-based materials are Raman active whereas cubic phase is Raman inactive. Field effect scanning electron microscopy equipped with the energy dispersive xray diffraction was carried out on all the samples to confirm the grain size distribution and elemental homogeneity in the samples. Average grain size was found to decrease from  $12.3 \pm 3.7 \ \mu m$  for x = 0.03 to

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 $0.67 \pm 0.27$  µm for x = 0.25. The decrease in the average grain size could be endorsed to lower diffusivity of the rare earth element (here, La element) during sintering. Elemental homogeneity of the samples was confirmed by elemental mapping using energy dispersive x-ray spectrometry (FESEM/EDS). The atomic/weight composition matched well with the target composition within error bar. A temperaturedependent dielectric study confirmed the phase transition from tetragonal to the cubic structure. The hybridization of  $Pb(6s^2)$  to O(2p)and Ti(3d) makes these materials potent for the high phase transition temperature of  $PbTiO_3$ . Since La is substituting Pb and does not have the  $6s^2$  lone pair hence there is no hybridization bond. It may be the possible reason for the decrease of the phase transition temperature that also correlated to the XRD and Raman spectroscopy results. Temperature-dependent high-resolution powder x-ray diffraction study co-relates the exact structural phase transition from tetragonal to a pseudo-cubic structure. The degree of diffuseness of dielectric peak was found to increase with an increase in substitution. It was calculated with the modified Curie-Weiss law. Polarization versus electric field was measured for all samples at room temperature. We have obtained proper ferroelectric loops for samples with  $0.06 \le x \le 0.18$ . Electric field dependent strain yielded prominent butterfly loops for  $0.06 \le x \le$ 0.18. For x = 0.25, the structure is cubic. The phase transition temperature is below room temperature. Also, for x = 0.03 a proper ferroelectric/piezoelectric loop was not obtained, may be due to excess lead evaporation during sintering at high temperature. Oxygen vacancies related to this hinders the switching of the ferroelectric domains. A relaxation due to oxygen vacancies was also observed in temperature-dependent dielectric constant measurement. Energy storage density was calculated for all samples. The x = 0.25 sample showed the highest energy density of 96.5 %.

**Bi/Mn modified PbTiO<sub>3</sub>:** Polycrystalline powders of (Pb<sub>1-</sub> <sub>x</sub>Bi<sub>x</sub>)(Ti<sub>1-x</sub>Mn<sub>x</sub>)O<sub>3</sub> ( $0 \le x \le 0.50$ ) range samples were successfully prepared via the sol-gel combustion method. Structural properties were investigated with the Rietveld refinement of the high-resolution powder x-ray diffraction data. Tetragonal phase (space group P4mm) was identified for  $0 \le x \le 0.37$  samples whereas pseudo-cubic phase (space group Pm3m) for x = 0.50 sample. Lattice parameters 'a' slightly decreases while 'c' increases up to x = 0.12 composition. Hence, tetragonality (c/a ratio) nominally increased initially in the range  $0 \le x \le 0.12$  from 1.064 to ~1.066, thereafter decreasing continuously in the range  $0.12 \le x \le 0.50$  to 1, for x = 0.5 (c/a = 1). Raman spectroscopy was carried out for all the samples at ambient temperatures to see the variations of the vibrational modes with compositions. Microstructural analysis of the pellet surface was carried out with FESEM equipped with energy dispersive x-ray analysis. All the samples were compact and dense, and the average grain size was found to decrease from  $14.55 \pm 4.82 \ \mu m$  for x = 0.06 to  $11.53 \pm 4.32$  $\mu$ m for x = 0.50 samples respectively. Homogeneity of elements in samples was ensured from elemental mapping techniques. A ferro para electric phase transition in these materials can be related tetragonal to cubic phase transition using composition dependent dielectric studies of the materials. For x = 0.06 and 0.09, phase transition temperature, was found to be 763 K and 773 K respectively. We want to notify that x = 0 also has 763 K temperature from tetragonal to cubic phase transition. Hence, Bi/Mn substitutions increase the phase transition temperature up to certain limit such as  $x \leq x$ 0.09 compositions. For compositions  $x \ge 0.12$ , the phase transition temperature was found to decrease up to x = 0.25 composition. For  $x \ge 1000$ 0.31 compositions, samples showed inductive effect in the temperature-dependent dielectric response. Synchrotron-based temperature-dependent XRD was carried out for x = 0, 0.06, and 0.09 samples. Lattice parameters 'c' decreased while 'a' increased with increase in temperature. The phase transition temperature,  $T_{C}$ , increased from 763 K in  $x \le 0.06$  to 773 K in x = 0.09 samples in agreement with the temperature-dependent dielectric studies. In temperature-dependent XRD analysis of the unit cell structure, we have observed that the unit cell volume decreases with increase of temperature up to the phase transition temperature. Thermal expansion

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coefficient was calculated to be negative ~  $-1.571*10^{-5}$  /K,  $-2.44*10^{-5}$  /K, and  $-5.025*10^{-6}$  /K for x = 0, 0.06, and 0.09 samples respectively. Beyond the phase transition temperature, the unit cell volume increases with temperature rise. Hence, these materials have negative thermal expansion coefficient in the tetragonal ferroelectric phase while positive thermal expansion behavior in the cubic paraelectric phase. Hence, these materials are useful for designing the sophisticated instruments.

A comparative study: The samples of different series of PbTiO<sub>3</sub>based ceramics have been compared in this section [Figure 7.1]. From the lattice parameter studies it seems that the *c*-axis is contracting with substituting for all samples. The only exception is the PBTM series for which the *c*-axis initially increases and thereafter starts to decrease. The c/a ratio, which determines the tetragonality of the lattice, also follows the same trend. However, even in the trend of reducing tetragonality, there is a variation. The PKST and the PNST series demonstrate a linearly proportional decrement with substitution. However, in PBTM it is delayed while for both PTFO and PLTA the decrement happens drastically. This is reflected in the phase transition temperature as well. Note that for PBTM the  $T_C$  is higher for all the low doped samples. However, one problem of these samples is that they become lossy at very low doping. Hence, in spite of having a retained tetragonal structure dielectric PBTM is not a good ferroelectric. Also note that with substitution every series shows an increase of dielectric constant with substitution. However, for every series there is an optimum substitution for which the dielectric constant was maximum, beyond which dielectric constant decreases. This nature is observed both for low and high frequencies. The coercive field of all samples decreases with substitution for all series. The remnant polarization on the other hand shows a maximum for a certain substitution.

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**Figure 7.1:** A brief comparisons of (a) Lattice parameters 'a', (b) Lattice parameters 'c', (c) Tetragonality *c/a* ratio with compositions, (d) Phase transition temperatures with compositions of the corresponding series, (e) Dielectric constant with composition at 1 MHz, (f) Dielectric constant with composition at 100 Hz, (g) Remnant polarizations, and (h) Coercive field with compositions.

## 7.2 Scope for the future work

- Thin films and single crystals are to be prepared and studied for better understanding. Sophisticated application point of view can open up from these studies.
- Piezoelectric and pyroelectric measurements are to be performed for all the samples from application point of view.
   Few other doping combinations can be tried to enhance the piezoelectricity in the system with suitable substitution.
- Domain configuration in the samples should be seen with the HRTEM studies to observe the degree of order. It will be more helpful in understanding the ferroelectric properties.
- Polymer composite should be prepared to make the transparent capacitor materials of high dielectric constant materials.

# Appendix



### HRTEM study of some selected samples:

*Figure S1: HRTEM image of PTO with SAED and FFT patterns, showing crystallographic resemblance to XRD analysis.* 



*Figure S2: HRTEM image of PLTA18 with SAED and FFT patterns, showing crystallographic resemblance to XRD analysis.* 

High Resolution Transmission Electron Microscopy (HRTEM) was performed on micron sized PbTiO<sub>3</sub> (PTO) and Pb<sub>(1-x)</sub>La<sub>x</sub>Ti<sub>(1-x)</sub>Al<sub>x</sub>O<sub>3</sub> for x =0.18 (PLTA18) samples as shown in Figure S1 and Figure S2 respectively, with HRTEM JEOL JEM-2100 LaB<sub>6</sub>, operated at voltage of 200 kV. HRTEM and Selected Area Electron Diffraction (SAED) images were obtained at different focal length and magnifications. The samples for HRTEM were prepared by gently grinding the micron sized powder samples in high purity ethyl alcohol, without introducing strain in the lattice. The solution containing the particles was dropped on holy carbon grids and dried in air under a heating bulb. The average size of the samples as observed by the microscope after grinding was still in the range of a few microns. The sharp edges of the broken crystallites were investigated to understand the crystallinity and the structure of the powders. The SAED patterns have been indexed and correspond to a P4mm space group in agreement with the XRD and Raman results. The HRTEM images show highly regular crystalline nature of the constituent atoms. Fast Fourier Transform (FFT) of these atomic distributions reveals the structural arrangement belonging to the same space group. Hence, it may be concluded that the local as well as the global structure of a crystallite matches with each other. The resemblance with the structure of XRD analysis and a global similarity of atomic distribution ensures a homogeneous sample.

Note that the pure PTO sample has d-spacing corresponding to (001) plane of ~4.1 Å, which corresponds to the calculated lattice parameter 'c' from Rietveld analysis. Similarly, there is a similar correspondence between the 'a' or 'b' lattice parameters and the (010) d-spacing. A similar observation is noteworthy in the PLTA18 sample also. Similar observations are there for other series and do not bear extra information. However, a more detailed study can be done on poled and unpoled samples for the entire four series discussed in the thesis.

Band gap study of some selected samples:



*Figure S3:* (a) UV measurement spectra of  $Pb_{1-x}(Na_{0.5}Sm_{0.5})_xTiO_3$  ( $0 \le x \le 0.50$ ) range samples. (b) Calculated band gap with substitutions.



**Figure S4**: (a) UV-visible spectroscopy of  $PbTi_{(1-x)}Fe_{(x)}O_{3-\delta}$  ( $0 \le x \le 0.50$ ) shows gradually shifting absorption edge from higher to lower energies with increasing substitution. (b) Bandgap calculated from the UV-vis spectra shows an exponential nature commensurate with the exponential decrease of tetragonality.

UV-vis spectroscopy was performed using a Shimadzu UV-2600 spectrophotometer to determine the bandgap of all the samples. In case of  $PbTi_{(1-x)}Fe_{(x)}O_{3-\delta}$  (PTFO), bandgap decreases with increasing substitution

for all temperatures [Figure S4]. The smaller ionic radius of the  $Fe^{3+}$  ion and the expansion of 'a' and 'b' axes might be a signature of reduction in the bond strength. A reducing bandgap is a signatory of a reducing crystal field. As the amount of  $Fe^{3+}$  increases, the lattice uniformly enlarges in the 'a' and 'b' axes seeing a further reduction in the band gap. It is to be noted that the composition dependence of the c/a ratio and the bandgap both decreases exponentially with substitution. The tetragonality is a signature of the distortion in the lattice which in turn increases the crystal field splitting.

In the PNST similar results are observed for tetragonal and pseudocubic structure as shown in Figure S3. However, as the structure changes to pure cubic structure, we see a higher bandgap than the pseudo cubic structure. Yet the bandgap is lower than a tetragonal structure. A more detailed investigation needs to be carried out supported by a theoretical DFT study.



**Figure S5:** (a) UV-vis spectra of  $Pb_{1-x}(K_{0.5}Sm_{0.5})_xTiO_3$  (0.06  $\leq x \leq 0.50$ ) samples, and (b) UV-vis spectra of  $Pb_{1-x}La_xTi_{1-x}Al_xO_3$  (0.03  $\leq x \leq 0.25$ ) samples.

More investigations need to be done on PKST and PLTA samples as a proper trend was not obtained as shown in Figure S5 (a-b).