BariumTitanate-Lead Titanate (BaTiO₃-PbTiO₃) Solid solution with B-site Cu-modification

M.Sc. Thesis

By Ananta Paul



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BariumTitanate-Lead Titanate (BaTiO₃-PbTiO₃) Solid solution with B-site Cu-modification

A THESIS

Submitted in partial fulfillment of the requirements for the award of the degree of Master of Science

> by ANANTA PAUL



DISCIPLINE OF PHYSICS INDIAN INSTITUTE OF TECHNOLOGY INDORE JUNE, 2020



INDIAN INSTITUTE OF TECHNOLOGY INDORE

CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled **BariumTitanate-Lead Titanate (BaTiO₃-PbTiO₃) Solid solution with B-site Cu-modification** in the partial fulfillment of the requirements for the award of the degree of **MASTER OF SCIENCE** and submitted in the **DISCIPLINE OF PHYSICS, Indian Institute of Technology Indore**, is an authentic record of my own work carried out during the time period from july 2019 to june, 2020 under the supervision of Dr. Somaditya sen, Associate Professor. 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.

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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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DEDICATED TO MY TEARCHS AND PARENTS

LIST OF PUBLICATIONS

1. Journal publications

- I. Synthesis, optical, and electrical properties of Cu_{1-x}Fe_xO.
 Ananta Paul, Ruhul Amin, Mohd Nasir, Bungkiu Kissinquinker and Somaditya Sen.
 (Submitted in JCR in April 30, 2020)
- II. Correlation of octahedral distortion with vibrational and electronic properties of LaFe_{1-x}Ti_xO₃ nanoparticles. E. G. Rini, Ananta Paul, Mohammad Nasir, Ruhul Amin and Somaditya Sen (Jelcom) https://doi.org/10.1016/j.jallcom.2020.154594

2. <u>Conference proceedings</u>

- I. "Investigation of Structural and Dielectric Characteristics of La₂Ni_{0.5}Al_{0.5}MnO₆ Double Perovskite Ceramics". Ananta Paul, Mohammad Nasir, Prashant Kumar Mishra, E. G. Rini and Somaditya Sen (AIP Conference Proceedings) DOI: 10.1063/5.0003085.
- II. "Investigation of Structural and Dielectric Characteristics of Dy₂NiMnO₆ Double Perovskite Ceramics". E. G. Rini, Ananta Paul, Mohammad Nasir, Bungkiu Kissinquinker, Prashant Kumar Mishra and Somaditya Sen (AIP Conference Proceedings) DOI: 10.1063/5.0002281.
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TABLE OF CONTENTS

CONTENTS		
Acknowledgements	i	
List of Publications	V	
List of Figures	Х	
List of Tables	xiii	
Abbreviations	XV	
Chapter 1: Introduction		
1.1 Introduction and Background		1-2
1.2 General definitions		2
1.2.1 Perovskite		2-3
1.2.1.1 Distorted Perovskite		3-4
1.2.2 Electroceramics properties		4-5
1.2.3 Dielectric properties		5-7
1.2.3.2 Ferroelectric to paraelectric phase	e transition	8-10
1.3 Literature survey: Barium Titanate Ba	TiO ₃ (BT)	10
1.3.1 Doped BaTiO ₃		11
1.3.2 Isovalent doping		11
1.3.3 Aliovalent doping		11-12
1.4 Motive of the present work		12-13
1.5 Outline of the thesis		13-14
1.6 References		14-18

Chapter 2: Synthesis and experimental details

2.1 Synthesis process	19-20
2.1.1 Sol-gel synthesis of Ba _{0.75} Pb _{0.25} Ti _{1-x} Cu _x O ₃	20-21
composition	
2.2 Characterizations techniques	21
2.2.1 Density measurement	21-22
2.2.2 X- Ray diffraction	22-25
2.2.3 Raman spectroscopy	25-28
2.2.4 Field emission scanning electron spectroscopy	28-31
2.2.5 Ultraviolet-visible absorption spectroscopy	31-32
2.2.6 Dielectric measurement	32-34
2.2.7 Ferroelectric measurement	34-35
2.3 References	35-36

Chapter 3: Modified A/B site by Pb and Cu Doping, Structural, microstructural and electronic studies of Ba_{0.75}Pb_{0.25}Ti_{1-x}Cu_xO₃ ceramics

3.1	Synthesis	37
3.2	Structural studies	37
3.3	Surface morphology study	37-38
3.4	X-ray diffraction analysis	38-42
3.5	Raman study	42-44
3.6	UV Vis spectroscopy analysis	44-45
3.7	I-V characteristics	45-46
3.8	Conclusions	46
3.9	References	46-48

Chapter 4: Structural, dielectric and ferroelectric studies of ceramic materials: Ba_{0.75}Ti_{0.25}Ti_{1-x}Cu_xO₃

4.1	Synthesis	49
4.2	Structural studies	49-52
4.3	Surface morphology study	52-53
3.4	Raman spectroscopy	53-55
3.5	Dielectric analysis	56-59
3.6	Ferroelectric measurements	59-60
3.7	Conclusions	60-61
4.8	References	61-64

Chapter 5: Conclusions and future research scope

5.1 Conclusions	65
5.2 Experiment performed at 950°C	65
5.2.1 Structural properties	65-66
5.2.2 Morphology analysis	67
5.2.3 U-V Vis spectroscopy analysis	67
5.3 Structural properties for BPTCO 1100°C Samples.	67
5.3.1 Structural properties	67-68
5.3.2 Dielectric properties	68
5.2.3 Ferroelectric properties	69
5.3 Major findings	69
5.4 Scope for future work	69

List of Figures

Figure 1.1: (a) Perovskite structure: octahedra enclosing the	3
A-site cation and (b) Perovskite (ABO ₃), CaTiO ₃ unit cell	C
structure (Cubic, Space group $Pm\overline{3}m$.	
Figure 1.2: Different contributing polarization mechanisms in	6
a dielectric material.	
Figure 1.3: The variation of of dielectric constant (ϵ_r) and loss	7
$(\tan \delta)$ with applied frequency.	
Figure 1.4: Relative permeability (ε_r) versus temperature	
behavior, where (a) Sharp phase and (b) diffuse phase	8
transition.	
Figure 1.5. In percessite structure the Aliovalent doping	12
effect. The resulting electrical dipole represent by red arrows	
eneet. The resulting electrical dipole represent by red arrows.	
Figure 2.1: A flowchart of the sample preparation using a sol-	21
gel method.	
Figure 2.2: A schematic representation of two-dimensional	
	23
diffraction of x-rays by crystals.	23
diffraction of x-rays by crystals. Figure 2.3: Quantum energy diagram for Raman scattering. A	23 26
diffraction of x-rays by crystals.Figure 2.3: Quantum energy diagram for Raman scattering. A Schematic diagram of photon interactions with the matter such	23 26
diffraction of x-rays by crystals. Figure 2.3: Quantum energy diagram for Raman scattering. A Schematic diagram of photon interactions with the matter such as Rayleigh scattering, Stokes and Anti-stokes scattering.	23 26
 diffraction of x-rays by crystals. Figure 2.3: Quantum energy diagram for Raman scattering. A Schematic diagram of photon interactions with the matter such as Rayleigh scattering, Stokes and Anti-stokes scattering. Figure 2.4: Schematic diagram of Raman spectrometer. 	23 26 27
 diffraction of x-rays by crystals. Figure 2.3: Quantum energy diagram for Raman scattering. A Schematic diagram of photon interactions with the matter such as Rayleigh scattering, Stokes and Anti-stokes scattering. Figure 2.4: Schematic diagram of Raman spectrometer. Figure 2.5: Schematic diagram of Field Emission Scanning 	23 26 27 30
 diffraction of x-rays by crystals. Figure 2.3: Quantum energy diagram for Raman scattering. A Schematic diagram of photon interactions with the matter such as Rayleigh scattering, Stokes and Anti-stokes scattering. Figure 2.4: Schematic diagram of Raman spectrometer. Figure 2.5: Schematic diagram of Field Emission Scanning Electron Microscope. 	23 26 27 30
 diffraction of x-rays by crystals. Figure 2.3: Quantum energy diagram for Raman scattering. A Schematic diagram of photon interactions with the matter such as Rayleigh scattering, Stokes and Anti-stokes scattering. Figure 2.4: Schematic diagram of Raman spectrometer. Figure 2.5: Schematic diagram of Field Emission Scanning Electron Microscope. Figure 2.6: Experimental set-up used for the field-effect 	23 26 27 30 30
 diffraction of x-rays by crystals. Figure 2.3: Quantum energy diagram for Raman scattering. A Schematic diagram of photon interactions with the matter such as Rayleigh scattering, Stokes and Anti-stokes scattering. Figure 2.4: Schematic diagram of Raman spectrometer. Figure 2.5: Schematic diagram of Field Emission Scanning Electron Microscope. Figure 2.6: Experimental set-up used for the field-effect scanning electron microscope equipped with the energy 	23 26 27 30 30
 diffraction of x-rays by crystals. Figure 2.3: Quantum energy diagram for Raman scattering. A Schematic diagram of photon interactions with the matter such as Rayleigh scattering, Stokes and Anti-stokes scattering. Figure 2.4: Schematic diagram of Raman spectrometer. Figure 2.5: Schematic diagram of Field Emission Scanning Electron Microscope. 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 	23 26 27 30 30
 diffraction of x-rays by crystals. Figure 2.3: Quantum energy diagram for Raman scattering. A Schematic diagram of photon interactions with the matter such as Rayleigh scattering, Stokes and Anti-stokes scattering. Figure 2.4: Schematic diagram of Raman spectrometer. Figure 2.5: Schematic diagram of Field Emission Scanning Electron Microscope. 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- 	23 26 27 30 30
 diffraction of x-rays by crystals. Figure 2.3: Quantum energy diagram for Raman scattering. A Schematic diagram of photon interactions with the matter such as Rayleigh scattering, Stokes and Anti-stokes scattering. Figure 2.4: Schematic diagram of Raman spectrometer. Figure 2.5: Schematic diagram of Field Emission Scanning Electron Microscope. 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. #4 It is a 	23 26 27 30 30

sample holder of the gold sputtering system.

Figure 2.7: A representation of circular pellet electrodes for33electrical measurements. The dielectric material issandwiched between the electrodes.

Figure 2.8: Marine India ferroelectric loop tracer35spectrometer the ferroelectric loop at ambient temperatures.

Figure 3.1: Surface morphology (a-d), (e) Crystalline size and(f) Particle size of $Ba_{0.75}Pb_{0.25}Ti_{(1-x)}Cu_xO_3$, (x=0%, x \leq 6.2%)powders with substitution.

Figure 3.2: (a) the XRD pattern of $Ba_{0.75}Pb_{0.25}Ti_{(1-x)}Cu_xO_3$ x=0%, 1.56%, 3.12%, and 6.25% and (b-c) the elongation of 38 two peaks at $2\theta = 31^{\circ}-32^{\circ}$ and $44^{\circ}-46^{\circ}$ respectively.

Figure 3.3: The Rietveld refinement of XRD data of $Ba_{0.75}Pb_{0.25}Ti_{(1-x)}Cu_xO_3x=0\%$ (a), 1.56% (b), 3.12% (c), and 6.25% (d).

Figure 3.4: (a) Lattice parameters ('a'='b' & 'c') and (b) the unit cell volume of $Ba_{0.75}Pb_{0.25}Ti_{(1-x)} Cu_xO_3 x=0\%$, 1.56%, 3.12%, & 6.25%.

40

Figure 3.5: The Raman spectra of Ba_{0.75}Pb_{0.25}Ti (1-x) Cu_xO₃ x=0%, 1.56%, 3.12% and 6.25%. 42 Figure 3.6: Raman fitted data of Ba_{0.75}Pb_{0.25}Ti (1-x) Cu_xO₃ x=0%, 1.56%, 3.12% and 6.25% composition at ambient 43 temperature. Figure. 3.7: (a) The band-edge from the UV-vis spectra (b) decrease of electronic band gap with substitution. 44 Figure 3.8: I-V characteristics of Ba_{0.75}Pb_{0.25}Ti (1-x) Cu_xO₃, $(x=0\%, x \le 6.2\%)$ ceramics. 45 Figure 4.1: (a) the XRD pattern of $Ba_{0.75}Pb_{0.25}Ti_{(1-x)}Cu_xO_3$, x=0%, 1.56%, 3.12%, and 6.25% and (b) the lattice 50 parameters.

Figure 4.2: The lattice parameters and volume of BPTCO samples.

Figure 4.3: Surface morphology of $Ba_{0.75}Pb_{0.25}Ti_{(1-x)}Cu_xO_3$,
(x=0%, x $\leq 6.2\%$) compositions. (a-d) x = 0, 0.0156, 0.0312
and 0.0625.52

Figure 4.4: Room Temperature Raman spectra of BPTCO samples in the range 100 to 800 cm-1

Figure 4.5: Room temperature dielectric constant and tan loss of the Ba_{0.75}Pb_{0.25}Ti (1-x) Cu_xO₃, (x=0%, x \leq 6.2%) range 56 samples, where (a) Relative permeability (ϵ r,) and (b) tangent loss (tan δ) with frequency.

Figure 4.6: Temperature dependent dielectric constant and tan loss of the Ba_{0.75}Pb_{0.25}Ti (1-x) Cu_xO₃, (x=0%, x \leq 6.2%) range samples, where (a,c,d,g) Relative permeability (ϵ r,) and 57 (b,d,f,h) tangent loss (tan δ) with temperature at some fixed frequency.

Figure 4.7: Modified Curie-Wiess law fitting $\left(ln\left(\frac{1}{\varepsilon}-\frac{1}{\varepsilon_m}\right)vs ln(T-T_m)\right)$ (a) S0, (b) , (c) BPTC2, (d) BPTC3.

Figure 4.8: Room temperature polarization versus electric field of (a) BPTO.

60

59

51

54

List of Tables

Table 3.1: Table 3.1: The lattice strain with compositions for	43
BPTCO samples.	
Table 5.1: Unit cell Parameters of BPTCO samples at 950°C.	65-66
Table 5.2: The lattice strain and crystalline size for BPTCO at	66
950°C.	
Table 5.3: Unit cell Parameters of BPTCO samples at 1100°C.	67-68
Table5.4: Dielectric constant with their temperature range for	68
BPTCO samples.	

Abbreviations

Barium Titanate	BaTiO ₃
Lead Titanate	PbTiO ₃
Barium-Lead Titanate	Ba _{0.75} Pb _{0.25} TiO ₃
X-ray Diffraction	XRD
	XRD
Powder X- ray Diffraction	PXRD
Tolerance Factor	Т
Field Emission Scanning Electron Microscopy	FESEM
Energy Dispersive Spectroscopy	EDS
Direct Current	DC
Electric Field	E
Dielectric Constant	Er
Dielectric Loss	Tanð
Polarization versus Electric Field	P-E
Instantaneous Current Versus Electric Field	I-E
Remnant Polarization	Pr
Maximum Polarization	P _{max}
Coercive Field	Ec
Room temperature	RT
$Ba_{0.75}Pb_{0.25}TiO_3$	ВРТО
$Ba_{0.75}Pb_{0.25}Ti_{(1-x)}Cu_{x}O_{3}$	BPTCO

Chapter 1

Introduction

1.1. Introduction and Background:

From precious stones to fundamental scientific interests, oxides have been a major part of research in the field of chemistry, physics, material science, electronics, electrical engineering, etc. Transition metal oxides show a wide range of exotic properties, which include high-TC superconductivity, ferromagnetism, gas sensing, magnetoresistance, and magneto-capacitance. Perovskite structures are a stable structure and hence can accommodate different transition metal ions, unravelling interesting physics and numerous functionalities and applications in the field of magnetism, ferroelectricity and electrical transport. Perovskites find many important technological applications. Keeping exotic features of simple and complex oxides in mind, we have focused on the study of perovskite oxides.

There are approximately more than 100 elements and every element has a unique electronic configuration, which is determined by its 3-D electron distribution, atomic number (Z) and energies. These elements can be categorized as metallic, gaseous, or nonmetallic solids. Therefore, each element is alloyed with other elements and forms new materials. These are classified as metals, semiconductors, ceramics and polymers. Each class has its distinct properties, i.e., in metals, delocalized electrons provide the force that holds the positive ions together and the bonding is metallic. In semiconductors, strong covalent bonds are formed between atoms (e.g. Si, Ge, GaAs, CdTe, and InP). Polymers consist of different organic atoms and molecules attached with very long C-based chains. Ceramics are solid compounds that are made by sintering. Due to their versatile properties, they are used widely in many applications, e.g., electronic and manufacturing industries [1], [2]. Ceramics are different from glasses and single crystals as they are composed of an aggregate of randomly oriented crystallites intimately bonded together to form a solid and have anisotropic character and are polycrystalline materials.

In the absence of an electric field, some materials show more than one orientation of polarization (i.e.spontenious polarization) and these materials can switch their polarization state from one state to another with an applied electric field (E), these materials are referred to as ferroelectric materials.

The area of interest in the present work is related to substituted barium titanate ferroelectric ceramics, which are a highly specialized class of materials, termed as electroceramics. Their properties are predominantly controlled by their composition, microstructure and processing methodology.

1.2 General definitions:

To understand the perovskite materials, a brief introduction on the structure, surface morphology, dielectric, ferroelectric and optoelectronic properties are given below.

1.2.1 Perovskite:

Perovskite word came into existence after the discovery of the mineral CaTiO3's structure by Gustav Rose in 1993 from the Ural Mountains. The structure of this mineral was named after Russian mineralogist Lev Perovski as perovskite [3], [4]. Perovskite oxides comprise of vast arrays of beneficial compounds with different functional properties. These are engineering materials used worldwide in devices due to their various properties such as optoelectronics, dielectric, superconductivity, piezoelectric, magnetism, ferroelectric, pyroelectric and electrostriction, etc. The typical crystal structure of perovskite oxides is adopted by a chemical formula of ABO3 [5]. In which, A-site (larger) cation has twelve co-ordinations, and B-site (smaller) cation has six co-ordinations.

In a perovskite, the oxidation state of A-site and B-site cations are +1 to +3 and +3 to +5, respectively [6]. Figure 1.1 shows that at the centre of the unit cell, a BO₆ octahedron is formed due to the atomic arrangement of atoms. In the perovskite cubic structure, with space group ($Pm\bar{3}m$) with the Ca⁺² situated at 8 corner A-site with coordinate (0 0 0), one Ti⁺⁴ placed at the centre, i.e., $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ on B-site and the centre of all faces contain 6 oxygen atoms with coordination $(0, \frac{1}{2}, \frac{1}{2})$; $(\frac{1}{2}, 0, \frac{1}{2})$; $(\frac{1}{2}, 0,$



Figure 1.1: (a) Perovskite structure: octahedra enclosing the A-site cation and (b) Perovskite (ABO₃), CaTiO₃ unit cell structure (Cubic, Space group $Pm\overline{3}m$.

1.2.1.1 Distorted perovskite:

The perovskite structure is flexible with the varying A and B ions; they lead to a wide range of known compounds with perovskite structures. Distortion in perovskite structure leads to piezo/ferroelectric properties [9]. The main reasons behind the distortion in the perovskite structure are:

- i. Size effect
- ii. Jahn-Teller effect
- iii. Deviation from the ideal chemical composition

For a certain compound, distortion in a perovskite can occur due to various reasons. A classic example of this complex BaTiO₃ shows four structural transitions with increasing temperature:

Rhombohedral with space group R3m (at -90 °C) to Orthorhombic with space group Amm2 (at 5 °C), Tetragonal with space group P4mm (at 120 °C) to Cubic with space group $Pm\overline{3}m$ [10].

i. **Size effect:** For a cubic unit cell, the axis 'a' is geometrically explained as the following equation:

$$a = \sqrt{2} \times (r_A + r_0).....(1.1)$$

$$a = 2 \times (r_B + r_0)....(1.2)$$

The Goldschmidt's tolerance factor (t) is the ratio of these above two expressions. It gives the degree of distortion. The tolerance factor for the compound with an ionic bonding is given by [11]:

Where A-site and B-site atomic radii are r_A and r_B , and r_O is the radius of O atom. The tolerance factor (t) is one for an ideal perovskite structure.

- ii. Jahn-Teller effect: Another type of distortion in some perovskites are explained by the Jahn-Teller effect. This arises due to the Bsite active ions. In LnMnO₃ (Ln = Nb, La, or Pr), the B-site cation Mn^{3+} ions in 3d⁴ electrons divide into 3t_g and 1e_g electrons. The [MnO₆] octahedra are distorted because, in the e_g orbital, the number of electrons is odd [12].
- iii. Modification from ABO₃ composition: In these types of perovskite materials, valence states are variable, resultant oxygen content varies between 2.5 3.0. For example, in SrFeO₃, Fe ion's valence state can change between '+3 and +4' by heating, and reducing/oxidizing environment. Due to oxygen vacancies, FeO₅ square pyramids are formed. This is an example of defect perovskite [13]. Another type of perovskite structure is also investigated in the literature, for example, layered perovskite, double perovskites, etc. [14].

1.2.2 Electroceramics properties:

Throughout the 20th century, ceramics were used in electronics for the gradual development of electronic devices. Electroceramics are

a special category of advanced ceramic materials that are used in various applications, e.g, optical, high resistivity, chemical stability, dielectric, piezo/ferroelectric, and magnetic. The motive of the present work is to explain various properties of BPTCO ceramics such as; structure, dielectric, ferroelectric and optoelectronic, which are briefly explained below.

1.2.3. Dielectric properties:

Dielectric materials behave as electrical insulators in an electric field (E). Under the applied electric field, both the positive and negative charges in the materials are slightly displaced/rearranged. As a result, electric dipoles are created.

The dipoles are oriented in the direction of the electric field, and each dipole has a dipole moment (p). This process is known as polarization. The magnitude of polarization (P) can be defined as the dipole moment per unit volume and this moment can be expressed as:

Dielectric polarization is described by various atomic mechanisms. Under the effect of the externally applied field, the material is polarized, and dipoles are created with a moment (p). This moment can be express by the formula:

The total polarizability (α) is the sum of four polarizing mechanisms given below [15]:

Polarizability (α) = Space charge (α_s) + Orientation (α_i) + Electronic (α_d) + Ionic (α_e)(1.5)

The contribution of each polarization also depends on the types of material. These polarization mechanisms are demonstrated in Figure 1.2. Brief discussions about these mechanisms explained below:

i. Space charge polarization (α_s): This is slightly different from other polarization mechanisms that are only related to the unbound charge. In this mechanism, electrons are mobile across the grain until they hit a defect like interfaces and grain boundary. As the

defect creates a potential barrier, space charge is accumulated across the interface and grain boundary. These charges are dominated only at low frequencies and high temperatures [16].

ii. Orientation/dipolar polarization (α_d): In this polarization mechanism, the applied electric field molecules reorient in the direction of the field. The total contribution of this polarization is higher than the atomic polarization [17]. The contribution of these molecular dipoles decreases as a function of frequency.



Figure 1.2: Different contributing polarization mechanisms in a dielectric material.

iii. Electronic/atomic polarization (α_e): In dielectric materials, this polarization comes from the relative displacement of the atoms' positively charged nucleus to the negatively charged electron cloud. This is a reversible phenomenon; after the removal of the electric field, the nucleus and electrons come to their original position. The contribution of α_e is present in all solids, as all of them are made up of atoms. The electronic polarization is one of the important contributions to the dielectric materials. The contribution of this polarization is less compared to other polarizations. It is affected by the temperature variations of the dielectric materials.

iv. **Ionic polarization** (α_i): The ionic polarization is originated due to relative displacements of the positive and negative ions in an ionic crystal. If a crystal or molecule consists of atoms of more than one kind, the distribution of charges around an atom in the crystal or molecule leans to positive or negative.



Figure 1.3: The variation of dielectric constant (ε_r) and loss $(tan\delta)$ with applied frequency.

The relative permeability or Dielectric constant (ε_r) and dielectric loss tan δ with applied frequency are shown in Figure 1.3. In dielectric materials, the total polarization is the sum of the ionic polarization, space charge polarization, orientation polarization, and electronic polarization. All these polarizations are strongly dependent on the applied electric field [18]. At low frequency, the space charge polarization contributes more and decreases sharply with higher frequency. Similarly, there is another important property called relaxor polarization [19], which occurs at specific critical frequencies. Possibly these are the reasons behind the decrease of ε_r and tan δ with applied frequency.

2.4. Ferroelectric to a paraelectric phase transition:

The complete description of ferroelectrics was described by the Landau theory of phase transition, which explains thermodynamic phenomenological aspects leading to macroscopic symmetry breaking. These properties are significantly affected by structural changes such as symmetry change from one space group to another space group. Every ferroelectric material has a critical temperature, known as Curie temperature (Tc) at this temperature a structural phase transition occurs [20, p. 3]. For temperature T < T_c, these materials exhibit ferroelectric ordering, while for T > T_c, the ferroelectric nature disappears, which is known as a paraelectric phase [21]. All the thermodynamic properties such as dielectric, elastic and optical have unusual nature near the phase transition temperature. Above Curie (Tc), the net spontaneous polarization (ferroelectricity) disappears. Two types of phase transition behaviours are observed in these materials, first (sharp) and second (diffused) order phase transitions.



Figure 1.4: Relative permeability (ε_r) versus temperature behaviour, where (a) Sharp phase and (b) diffuse phase transition.

The electrical susceptibility (χ) of the materials can be expressed as the Curie-Weiss law, above the sharp phase transition temperature T_c[22].

Where, 'T' = Absolute temperature and 'C' = Curie constant.

At the phase transition temperature the dielectric constant shows highest (i.e. sharp transition) [Figure 1.4a]. The nature of these types of phase transition known as a first-order phase transition. For perfect crystalline materials, the dielectric constant shows a sharp transition at T_c . The dielectric properties are affected by some factors such as porosity, inhomogeneity, secondary phases, and material conductivity, grain size and grain boundary, etc.

The diffused phase transition behaviour was discovered in the early 1950s [23, p. 3]. The diffused phase transition behaviour is a fascinating area of research now. In this, the materials have unique physical properties such as thermally stable dielectric constant, which is used in various practical applications. The diffused phase transition is due to the disordered lattice [24]. The disorder arises from the random distribution of heterovalent ions at the same lattice site in a unit cell [25]. This often leads to many chemical combinations, and therefore microregions of different site cations have a locally varying phase transition temperature. A diffused phase transition occurs in these ceramics due to the multiple relaxations. This is the second type of phase transition behaviour [Figure 1.4b].

Diffused transition behaviour can be explained by modified Curie-Weiss law [26]:

Where γ is the degree of diffuseness, which varies between $(1 \le \gamma \le 2)$. For ideal sharp phase transition, $\gamma = 1$, while, for diffused phase transition $\gamma = 2$. From a linear fitting plot between $ln\left(\frac{1}{\varepsilon'} - \frac{1}{\varepsilon'_m}\right)$ versus $ln(T - T_m)$ curve, the value of γ was estimated. The significant characteristics of the diffused phase transition are listed below:

- i. Diffuse/broad maxima in ε_r versus T curve.
- ii. Reduction of the spontaneous/remnant polarization with increasing temperature.

- iii. Relaxation behaviour of the dielectric properties in the transition region.
- iv. Non-coincidence of transition temperatures achieved by different probes.

1.3. Literature survey: Barium Titanate BaTiO₃ (BT):

BT is a famous ferroelectric material that was discovered in the 1940s and studied in different forms (i.e., powder, thin, bulk and films) [27]. Due to the high permittivity (ε_r), piezoelectricity and stable ferroelectric properties BT uses in technical applications. BT also has a perovskite structure (i.e., ABO₃). Where the Ba⁺² situated at 8 corner A-site with coordinate (0 0 0), one Ti⁺⁴ placed at the body centre i.e. ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$) on B-site and six oxygen atoms are situated at the 6 face centre with coordination (0, $\frac{1}{2}$, $\frac{1}{2}$); ($\frac{1}{2}$, 0, $\frac{1}{2}$); ($\frac{1}{2}$, 0, $\frac{1}{2}$)].

BT shows a series of different phase transitions at different temperatures. [29], [30]. Out of all the phases of BT, the cubic phase has not shown ferroelectric, but other phase having lower symmetry than the cubic phase possess ferroelectricity [31]. In BT, the tolerance factor is greater than one (i.e., t >1). Therefore, the off-centering of the Ti⁴⁺ ion gives rise to the spontaneous polarization.

The phase transition temperature T_c (i.e., Curie temperature) is a very important parameter in perovskite materials. The Tc decides whether the material is polar or non-polar. BT shows ferroelectric properties below T_c (i.e., non-centrosymmetric and polar), but it has shown paraelectric properties above T_c (centrosymmetric and nonpolar). The permittivity has a maximum value at Curie temperature Tc "where the spontaneous polarization is zero.". In BT, due to the displacement of the Ti ion form its centrosymmetry position in the BO₆ octahedra, a ferroelectric state occurs. It is also known that at very high temperatures (i.e., above 1460 °C), BT shows a hexagonal structure and it is paraelectric nature.

1.3.1. Doped BaTiO₃:

BT has a wide variety of industrial applications. To improvise the structural, morphological, electrical and optical properties of BT, many dopants are added to the parent material [32, p. 3], [33, p. 3], [34]. In BT, the doping is possible in three cationic sites, i.e., Ba, Ti, or both. The dopants are categorized as isovalent and aliovalent based on their charge. The Ba2+ atom having a higher ionic radius in comparison to the Ti4+ atom occupies the A-site. The Ti4+ having lower ionic radius occupies the B-site [35], [36]. As an impurity is doped to BT, the ionic radius and the charge state decides whether it will occupy A or B- site [37] [38], [39], [40, p. 3], [41]. However, due to the incorporation of various ionic radius ions, different properties (i.e., relative permeability (ε_r), density, grain size, lattice parameter, volume and conductivity) in BT are enhanced.

1.3.2. Isovalent doping:

The isovalent doping can be expressed as the substitution of the same ionic charge on a host ion. The isovalent doping produces an effect on BT material; as a result, the Tc decreases and goes towards room temperature. Due to the lower doping of isovalent atoms i.e. Zr^{4+} [42]and Sn^{4+} [43] by replacement of Ti^{4+} , the Tc decreases while small incorporation of isovalent substitution Sr^{2+} [44], Ca^{2+} [45] replaced by Ba^{2+} shift T_c to higher temperatures. However, it is interesting to know that the incorporation of Pb²⁺ shows an opposing feature, i.e., Tc increasing.

From the literature review, a sharp phase transition is observed for lower dopant of Zr^{4+} and Sn^{4+} , while for higher dopant of Zr^{4+} and $Sn^{4+}a$ diffused type phase transition is observed [46, p. 3], [47].

1.3.3. Aliovalent doping:

The aliovalent doping can be expressed as the substitution of different ionic charges on a host ion. Depending on the valence state, the dopants are categorized as donor and acceptor dopants. When valence state greater than or less than the host ion, they are recognized as a donor or acceptor dopant, respectively. In BT, at the A-site, the doping of A^{3+} is known as a donor and A^{+1} ion doping is

known as acceptor, respectively.

In a cubic perovskite structure [Fig 1.5.] shows the two kinds of dopants.



Figure 1.5: The Aliovalent doping effect in the perovskite structure. The resulting electrical dipole is represented by red arrows.

The significant effect has been observed with the incorporation of aliovalent dopants (i.e. RE^{3+} ions) which shows the effect on decreasing of Curie temperature Tc [48].

With incorporation of La³⁺ and Nd³⁺ ions at the Ba-site, the Tc decreased by 25 °C/mol% [49], [50] while for small substitution Ho³⁺ in place of Ti ions the T_c decreases by 20 °C/mol% [51, p. 17].

1.4 Motive of the present work:

The present study is aimed at exploring the possibilities to enhance different functional properties in BPTCO ceramics. The dopants are substituted at A, B, or A/B-site. A detailed investigation is performed to observe the role of different dopants and overcome the drawbacks of BPTCO along with attaining improvements in thermally stable dielectric properties and energy storage properties. The research plan is as follows:

i. For the improvement in dielectric, ferroelectric properties:

In the present study to improve the various electrical properties, two different ways were chosen. These are explained below:

a. **Donor doping:** In BPTO materials, deviation from the ideal chemical composition originates from the volatility of Ba and

Pb. As a result, oxygen vacancies are created, which raises leakage current and coercive field. Donor doping with a higher charge than Ti⁴⁺ reduces oxygen vacancies in BPTO perovskite oxides. Hence, Ti⁴⁺ was replaced by Cu²⁺ (a donor) in Ba_{0.75}Pb_{0.25}Ti_{1-x}CuxO₃ (x=0%, $x \le 6.2\%$ (hereafter referred to as BPTCO) ceramics. Ionic radii of Cu²⁺ (0.73 Å) are comparable to Ti⁴⁺(0.605 Å). A complete study concerning the effects of Cu doping on the structural, morphologic, vibrational, dielectric, ferroelectric properties polycrystalline ceramics BPTCO was performed. The XRD result promotes the tetragonal phase. Due to larger ionic radii of Cu compared to Ti, it promotes the tetrahedral phase; hence the modified materials can be used for high-temperature piezoelectric applications compared to parent one.

The precise objectives of this research work are categorised as follows:

- i. Fabrication of A, B, or A/B-site substituted BPTCO ceramics materials *via* a modified sol-gel method.
- To investigate the effect of Cu incorporation on the lattice dynamics of BPTO as a function of substitution. For the detailed structural study, the XRD data was refined by Rietveld Refinement and lattice parameters were obtained.
- iii. To explore the substitution effect on microstructure, dielectric, ferroelectric and optoelectronic properties.
- iv. The structural and electric properties correlations are also examined.

1.5 Outline of the thesis:

Greatly encouraged by the above background, the work attempts to explore the crystal structural, surface morphological, vibrational, dielectric, ferroelectric, and optoelectronic properties of BPTCO based samples.

The present study divided into four chapters including a brief introduction to the problem, detailing the synthesis and characterization techniques, reporting the results supported by structure-electrical property correlation, and finalized by a conclusion and future scope of the BPTCO based ceramic materials.

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Chapter 2 Synthesis and experimental details

This chapter discusses, in brief, the synthesis and the detailed characterization techniques for Ba_{0.75}Pb_{0.25}TiO₃-based ceramics. Sample synthesis using a sol-gel process followed by calcination and high-temperature sintering. Investigation of material properties was performed by employing selected characterization techniques: For phase purity and crystal structure were studied using powder X-ray diffraction (Bruker D2 Phaser x-ray diffractometer). The vibrational modes were investigated using the Raman spectroscopy (LABRAM-HR visible). The surface morphology, average grain size and elemental mapping were studied using FESEM (Supra 55). To study the temperaturedependent dielectric properties in 100°C to 350°C temperature and 100Hz to 1MHz frequency range, Newton's 4th Ltd. PSM 1735 phasesensitive LCR-meter was used. The ferroelectric loop of the prepared samples we observed using the Marine India ferroelectric loop tracer spectrometer ferroelectric loop tracer. This chapter gives a brief idea about the history of the subject and the prepared materials.

2.1 Synthesis process:

For the past few decades, ceramic materials are a major component in the area of materials science, with significant implications on human life [1], [2]. A prime focus is the synthesis of new ceramic materials to improve different functional properties for practical applications. There are several synthesis routes for the fabrication of ceramic materials e.g. the hydrothermal, co-precipitation, a sol-gel, and solid-state route, etc. In the present study, Ba_{0.75}Pb_{0.25}TiO₃ and its derivatives were synthesized by the sol-gel process because, among all the above, this method yields excellent control of chemical homogeneity and precursor stoichiometry, eases the incorporation of a wide range of elements, has comparatively low annealing time, good nanoparticle size control and low-temperature crystallization, simple and economical

processing equipment [3], [4]. However, sometimes in this method, metal-organic precursors are used, which are usually more costly.

2.1.1 Sol-gel synthesis of Ba_{0.75}Pb_{0.25}Ti_{1-x}Cu_xO₃ composition:

Polycrystalline powders of $Ba_{0.75}Pb_{0.25}Ti_{(1-x)}Cu_{(x)}O_3$ (hereafter called BPTCO) were prepared (Pechini sol-gel method). The expression x=n/64 with n=0, 1, 2, 4. The individual samples will be called S0, S1, S2 and S4, for n= 0, 1, 2 and 4, respectively.

All precursors were obtained from Alfa Aesar. $Ba(NO_3)_2$ of purity 99.999%, $Pb(NO_3)_2$ with purity 99.999% Copper (II) oxide (99.7%, Alfa Aesar, metal basis, CuO with purity 99.7% and Dihydroxybis (Ammonium Lactate) Titanium (IV) of 50% w/w aqueous solution were used.

All the precursors except CuO were soluble in deionized water (DIW). The CuO was soluble in dilute HNO₃. Each solution was prepared in separate beakers. The Ba and Pb solutions were mixed and stirred vigorously for 30 minutes. Similarly, the Cu and Ti solutions were mixed in another beaker separately and stirred for 30minutes. The latter solution was next added to the first solution and stirred for 30 minutes again to attain homogeneity in the distribution of the contributing ions. In another beaker C₆H₈O₇ (citric acid) and C₂H₆O₂ (ethylene glycol) were mixed and heated at 60°C for 30 minutes. This combination forms a polymeric solution which is used to arrest the ions in a homogeneous distribution. This polymeric solution was poured into the solution containing the precursor ions while stirring. Stirring continued for the next few hours with continuous heating. The water content gradually evaporated leaving a gel behind. After removal of the magnetic stirrers, the gels were burnt in open to allow oxygen to react with the dry gels. Powders containing the un-reacted precursor ions along with some un-burnt carbonaceous and nitrogenated complexes were formed. De-nitrification and partial de-carbonization were carried out by heating these powders at 450 °C for 12 hours. An entire decarbonization was performed at 600 °C for 6 hours. This ensured the complete reaction between the precursors and complete elimination of the unwanted chemicals. The desired phase of the desired chemical composition was not obtained at these temperatures. Next, these powders were ground thoroughly. The finely ground powders were then heated at 950 °C for 6 hours. Finally, sub-micron grains of the desired phase were obtained. The physical properties of these final powders will be discussed in this study. After obtaining the powder, the powder were pressed in a mechanical pelletizer and pellets were formed having a dimension of ~ 10 mm diameter and ~ 1.5 mm thickness. Thereafter, the pellets were sintered at different temperatures in the range of 1350°C to 1100°C depending upon the percentage of Cu in the respective samples to achieve proper densification.



Figure 2.1: A flowchart of the sample preparation using a sol-gel method.

2.2. Characterizations techniques:

The details of the theory, and the working principles of all the characterization techniques used in this work are discussed in this section.

2.2.1 Density measurement:

In most of the electrical applications, sintered ceramics are required to have maximum density i.e. least porosity. From the application point of view, properties reach their optimum values at the highest density, while porosity over of 25-30% allows the ingress/entrance of moisture leading to many serious problems. However, there are cases where porosity is desirable: for example, in humidity and gas sensors and where thermal shock resistance is of overriding importance. Keeping in view the application potential of these materials for electrical devices, the compositions developed in this work have been optimized to obtain a maximum density.

The Bulk densities (ρ_B) of the ceramics was calculated in air and density of sintered ceramics was calculated by the given formula:

Where:

M = Mass of the ceramic pellet,

d = Diameter of the ceramic pellet,

h =Thickness of the ceramic pellet.

The relative density of sintered pellets are calculated as the ratio of the theoretical density (ρ_T) to the ratio of the Bulk density (ρ_B)

2.2.2 X-Ray diffraction:

XRD (X-ray diffraction) is a nondestructive analytical tool to identify and investigate the crystal structure, phase purity, and atomic spacing of crystalline materials. The crystallinity of materials plays an essential role in the physical properties like optical, mechanical, electrical, and magnetic, etc. To investigate these properties, it's very important to understand the structural details.

A German physicist W. C. Roentgen was discovered X-rays in late 1895. X-rays are electromagnetic waves of wavelength in the range of 0.01-10 nm, i.e., (frequency range 3 x 10^{16} - 3 x 10^{19} Hz, and energy range 10 eV-100 keV). The wavelengths of x-rays are comparable to the atomic size and separation and therefore be used to estimate dimensions of atomic size like interatomic bond lengths and unit cell parameters of the crystalline materials. Elastic scattering takes place when an electromagnetic wave (x-rays) interacts with atoms. The interaction of the x-rays with the electron clouds and charge centres of the atoms executes the scattering. For randomly arranged atoms with irregular structure, a pattern is not possible. When x-ray interacts with periodically arranged atoms, a constructive and destructive superposition occurs. A bright spot occurs when constructive superposition happens and also obeys the Bragg's law.

In 1913, the law was proposed by the Lawrence Bragg and William Henry Bragg. An incident wave diffracted by the family of lattice planes generates bright and dark regions, which given the correlation between incident x-ray wavelength (λ) and angle (θ) with the interplanar spacing (d).



Figure 2.2: A schematic representation of two-dimensional diffraction of x-rays by crystals.

The scattered waves from the first plane will be in phase and angle of reflection is " θ ", equal to the angle of incidence. The path difference between the waves reflected from the first and second lattice plane is = 2dsin θ . For constructive interface, path difference should be equal to "n λ ", where "n" diffraction order.

$$n\lambda = 2d\sin\theta$$
.....(2.2)

For a cubic system, the inter planar distance (d) is given by;

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2} \dots \dots \dots \dots \dots (2.3)$$

Chapter 2

Combining the above two equations we get a relation, which predicts the diffraction angle for any set of planes, For any set of planes, for a given ' λ ' if the following condition is satisfied, we can calculate the hkl values for at different Sin θ and find out the unit cell parameter.

$$\sin^2\theta = \frac{\lambda^2}{4a^2}(h^2 + k^2 + l^2).....(2.4)$$

Similarly, the relation for a tetragonal and orthorhombic system

$$\sin^2 \theta = \frac{\lambda^2}{4} \left(\frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2} \right)....(2.5)$$
$$\sin^2 \theta = \frac{\lambda^2}{4} \left(\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \right)....(2.6)$$

Scherrer calculated the average crystallite size, *D*, from the XRD data by using an equation:

$$D = k\lambda/\beta cos\theta \dots (2.7)$$

In this equation, he assumed that for spherical symmetry, $k \sim 0.9$, a constant. $\lambda_{Cu} K\alpha = 1.5418$ Å. The only variables were the diffraction angle, θ_{s} and the full-width half maxima (FWHM), β , of the most intense peak. The lattice strain was determined from the XRD data using EVA software (Williamson-Hall equation).

System specifications:

is

Model: Bruker D2 Phaser x-ray diffractometer Max Power: 3 kW X-ray target: Cu anode (Kα =1.5406 Å) Operating voltage: 30 kV Optics: Bragg Brentano, Parallel beam

Analysis using Rietveld refinement:

Rietveld refinement was performed to quantitatively analyze various physical parameters from the Powder XRD data. Diffraction patterns obtained were compared with the standard CIF files. Rietveld analysis of XRD data was carried for phase analysis using FullProf suite software [5]. It was named after a scientist Hugo Rietveld who developed this method. This is the least-square fit method and takes care of variable influencing the diffraction peaks [6]. The observed diffraction pattern consists of individual reflection planes. Each plane is defined by peak position, peak breadth, and peak intensity which decreases gradually with the distance. Rietveld technique is a very powerful tool for the refinement of powder diffraction data and consequently, detailed structural information of the sample is extracted. Though the principle involved in the Rietveld profile refinement are rather straightforward, it requires some expertise. The presence of bad starting XRD data points and default instrument parameters may cause to diverge the refinement at early stages. This procedure is only structural refinement and not a structure determination method. The refinement is carried out using the proposed model for the crystal structure, instrumental broadening, diffraction optics effects, and other sample properties (e.g. strain, anisotropy) as per the requirement and can be modelled. After refinement, the final crystallographic information files (CIF) can be used as an input file to the Vesta software to get respective bond angles and bond length of constituent elements in the compound.

2.2.3 Raman spectroscopy:

In 1928, Indian physicist C. V. Raman and K. S. Krishnan discovered the Raman Effect [7]. When monochromatic light is incident on a material, scattering of radiation happens in all directions; a very small fraction of the scattered radiation is inelastically scattered in comparison to a majority elastic scattered radiation. The change in wavelength concerning incident radiation happens due to the exchange of momentum with the vibrating molecules, i.e., phonons. Hence, this change in wavelength is dependent on the nature and structure of the molecules present in the samples. Thus, to investigate the vibrational properties of the solid, liquid, and gaseous samples Raman spectroscopy is used and thereby characterize the materials according to their identity.

When an incident photon of monochromatic light of energy hv_0 is incident on the sample, the energy quantum is absorbed and the molecule's energy state is promoted to higher virtual energy states [Figure 2.3]. These states are unstable and the molecule returns to the

more stable original state. However, there may be other real states available with energy $hv_{0\pm}hv_{\text{vib}}$ lesser or more than the original energy State. These return energy distributions can be categorized as the Rayleigh (elastic), Stokes ($< hv_0$) and Anti-Stokes ($> hv_0$) phenomena in Figure 2.3.



Figure 2.3: Quantum energy diagram for Raman scattering. A Schematic diagram of photon interactions with the matter such as Rayleigh scattering, Stokes and Anti-stokes scattering

An infinitesimal amount of inelastic Raman scattered light is produced. This is an electromagnetic wave in which direction of propagation of the wave, electric and magnetic component are mutually perpendicular to each other. Polarization of incident monochromatic light is changed due to interaction with matter. The vibration of two coupled atoms is explained by a harmonic oscillator. The resultant frequency is changed due to the interatomic force constant (k) and reduced mass (m) of the atoms and is presented by the formula: $\omega =$

 $2\pi f = \sqrt{\frac{k}{m}}$. A Raman spectrum generally consists of many sharp peaks.

The Vibrational properties of the lattice were studied a Horiba made LabRAM HR Evolution Raman spectrometer was used to derive the Raman spectra of the samples. A 632.8 nm laser (He-Ne) was the excitation source. The spectral resolution was 0.9 cm⁻¹. A pure Si single crystal shows a transverse optical mode at 520.7 cm⁻¹ [ref: <u>https://www.nature.com/articles/s41598-018-22503-6</u>]. This Si-line was used to calibrate the spectra.



Figure 2.4. Schematic diagram of Raman spectrometer.

The basic components of Raman spectrometer are the following:

Excitation source (Laser): a good laser should consist of narrow linewidth and extremely stable output.

Sample lighting system and light gathering optics: First, a laser beam (UV, Visible, NIR) is normally illuminated on the sample, then the scattered rays collected using lens are passed through spectrophotometer to get the desired Raman profile of the sample.

Wavelength selector (Filter or Spectrophotometer) is used to separate the incident light spatially according to the wavelength.

Detector (**Photodiode array, CCD or PMT**): Detector is a key component of the Raman spectrometer. A wide selection of detector is available depending upon the excitation laser being used. A standard CCD is used for visible excitation, a photomultiplier tube (PMT) is utilized for UV excitation, and an indium gallium arsenide (InGaAs) array is well suited for NIR excitation [8], [9].

System specifications:

Make: Jobin Yvon Horibra Model: LABRAM-HR visible (400–1100 nm) Spectral Range: 50–4000 cm⁻¹ Excitation Laser Sources: He-Ne laser with wavelength -632.8 nm Detector: CCD detector Spectral: ~1 cm⁻¹ Optics: High stability confocal Microscope.

2.2.4 Field emission scanning electron spectroscopy:

The FE-SEM (Field emission scanning electron microscopy) utilizes a low energy electron beam from a field emission gun to produce the surface image of the sample. This technique is quite useful to measure delicate samples with low melting temperature such as ceramic. Standard scanning electron microscopy is unable to provide reliable information on such samples. An optical microscope is based on diffraction of light, and also it has a moderate spatial resolution ~ few μ m. To image objects in the scale of nanometers, one needs higher resolution in the range of a few nm, which further requires light of a wavelength in nm. The fine electron beam spot as compared to visible light spot is advantageous to obtain much better spatial resolution. The FESEM provides better and less distorted images with high spatial resolution ~1 nm, which is superior to conventional optical microscope and SEM.

The collision between the energetically electron and materials results produced Auger electrons, secondary electrons (SEs), backscattered electrons (BSEs), and X-rays etc. FESEM uses SEs and BSEs for construction of images, x-rays for elemental/composition analysis [Figure 2.5]

 Secondary electrons (surface morphology): Secondary electrons are used for imaging of the surface of the samples. These originate from near-surface regions (~ 10 nm) of the sample. The mechanism behind the generation of these electrons is by the inelastic collision between the energetically primary electron and the material. Secondary electrons are very helpful for the investigation of the morphology of the sample's surface.

- ii. **Back-scattered electrons:** Back-scattered electrons are generated from a wide region within the interaction volume. During elastic collisions of electrons and atoms, these Back-scattered electrons are generated. Which leads to a change in the electrons' trajectory. This phenomenon is called "billiard-ball" model, in this model, tiny particles (electrons) collide with larger particles (atoms). The number of the backscattered electrons reaching the detector is directly proportional to their 'Z' number and it helps to discriminate between different phases. It provides imaging that conveys information about the sample's composition.
 - a. Energy-dispersive X-ray spectroscopy:

To study the elemental analysis, energy dispersive X-ray spectroscopy (EDS, EDX, and EDXS) technique were used. It can detect the relative amount of each element and map the distribution of the element. EDX is an integrated part of FESEM. In FESEM the X-ray generated in a two-step.

First step: An electron beam strikes on the sample and transfers its energy to the atoms of the sample. As a result, the electrons could jump to higher energy shell or knocked-off from the atom. After this transition, holes are created.

Second step: Higher energy shell electrons recombine with lower energy shell holes. The difference in energy of these two shells released in the form of x-rays. The generated x-ray is related to the atomic number and also a unique property of each element. The energy of these transitions is used to identify the elements.

Chapter 2



Figure 2.5: Schematic diagram of Field Emission Scanning Electron Microscope.

In the present study, FESEM micrographs were recorded on pellet surfaces of the samples. A Supra55 Carl Zeiss FESEM was used for recording these images. As $Ba_{0.75}Pb_{0.25}TiO_3$ -based materials are ferroelectric and highly insulating/nonconductive, therefore a charging effect is prominent. Hence, to avoid the charging effect, a metallic gold deposition (~ 5 nm) by sputtering techniques was required for charge drainage from the surface. The image of FESEM setup is shown in Figure 2.5.



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. #4 It is a complete set of the gold sputtering. #5 Enlarged part of the sample holder of the gold sputtering system.

> System specifications: Make: Zeiss Model: Supra 55 Operating voltage: 0.02–30 kV Working distance: up to 100 nA Variable pressure mode: up to 133 Pa

2.2.5 Ultraviolet-visible absorption spectroscopy:

In the case of atoms or molecules, electron excitation from lower energy level to higher energy levels is accompanied by the absorption of visible and ultraviolet light. Since all the atoms or molecules have quantized energy levels, only light with the exact amount of energy can cause a transition from one level to another and will be absorbed. So to absorb light in the spectroscopic range from 200-800 nm, the molecule should possess an σ bond or atoms with non-bonding orbitals (lone pair of electrons).

When electromagnetic radiation is illuminated on material, various physical phenomena are observed such as reflectance, absorbance, scattering, and fluorescence. Ultraviolet–visible (UV–vis) spectroscopy studies the interaction of UV–vis light with the specimen. This causes an electronic transition of an electron from the filled orbital to the vacant or partially filled orbital when sample absorbs light of a particular wavelength. This fixed wavelength of light reveals information about the energy bandgap. The absorption of a material at a given wavelength is defined using Beer-Lambert law [10] as:

$$A = -\log(I/I0) \tag{2.9}$$

Where I and IO are the intensities of the radiation incident and transmitted through the sample. The absorption (A) is directly

proportional to the concentration of absorbing species (c) and the distance travelled by the light through the sample (l).

Kubelka-Munk [11] $F(R\infty)$ represented in the equation can be written in terms of absorption

$$F(R\infty) \propto \alpha \propto (h\nu - Eg)^{1/n} / h\nu \dots (2.10)$$

$$(F(R\infty)*h\nu)^n = A(h\nu - Eg)....(2.11)$$

In the present work room temperature, optical absorption was studied in the range 200–800 nm using a Research India UV–Vis spectrophotometer. The Tauc plots were obtain using Kubelka-Munk [12], [13] technique from the reflectivity data: $\alpha h\nu = A(h\nu - Eg)^n$; where, α = the absorption coefficient, A= a constant, $h\nu$ = the energy of the incident light and n = constant. For direct bandgap, n=1/2 and indirect bandgap, n=2. The bandgaps were estimated from the intercepts of the extrapolated linear parts of the (α h\nu)^{1/n} vs h\nu plots for both cases.

2.2.6 Dielectric measurement:

Dielectric materials are generally insulators or poor conductors with low dielectric loss. There are a wide variety of these materials. An effect of the applied external electric field, the dielectric materials are polarized i.e. the positive and negative centers are separated, and electric dipoles are formed. The polarizations defined as dipole moment per unit volume. This property originates from the structural noncentrosymmetry.

Dielectric permittivity of a sample is defined as the ability of how much electrical potential energy stored of material under the influence of an electric field. It is dependent on the applied frequency and temperature.

32



Figure 2.7: A representation of circular pellet electrodes for electrical measurements. The dielectric material is sandwiched between the electrodes.

In the present study, electric properties (dielectric and ferroelectric) properties were measured on circular disk-like pellets. On both sides of well-sintered pellets, Silver paste electrodes were prepared [Figure 2.7]. The electrodes were cured at ~ 520 °C for 30 minutes. This enables better adhesion of the electrodes to the pellets and ensures proper contact.

As moisture can play a derogative role in electrical properties, these samples so to remove of the surface moisture the sample heated at ~200 °C for 10 minutes before any electrical measurements. Newton's 4^{th} Ltd. PSM 1735 phase-sensitive LCR-meter was used to measure the dielectric response with signal strength ~ 1 V_{rms}. The basic accuracy of this device is 0.1 % and the temperature variation in the furnace used for high-temperature dielectric measurement is \pm 3 °C. Dielectric measurement was carried out in parallel plate capacitance mode.

Dielectric constant or relative permittivity, ε_r , is a complex quantity, containing real (ε') and imaginary (ε'') parts: $\varepsilon_r = \varepsilon' + \varepsilon''$. Dielectric constant, the real part of ε_r (ε'), quantifies the stored energy and imaginary part (ε'') gives the dielectric loss factor, which is the electric energy loss due to the movement of atoms/molecules in continuously changing applied field. The dielectric loss tangent is represented by the formula $tan\delta = \frac{\varepsilon''}{\varepsilon'}$. This component also gives rise to a phase difference between the field function and the resulting polarization. Both components are frequency dependent. The capacitance of pellets was estimated as $C = \varepsilon' \varepsilon_0 \frac{A}{d}$; where 'C' is capacitance, 'A' cross-sectional area of the pelleted, 'd' separation between the pellets and ' $\varepsilon_0 \sim 8.854 * 10^{-12}$ F/m' is the permittivity of the free space.

2.2.7 Ferroelectric measurement:

In the present work, Marine India ferroelectric loop tracer spectrometer was used to measure the room temperature ferroelectric (P-E hysteresis loop) of the silver pasted pellets. At very high voltage sparks are generated to avoid the spark all samples/Pellets were immersed in silicone oil. The applied externally electric voltage frequency was 50 Hz. In this experiment, the applied field range varies from 0 to 50kV/cm depending on the samples.

The ferroelectric measurement set up can be compartmented in four units [Figure 2.8]:

#1 Three separate ferroelectric circuit systems kept individually

#2 Ferroelectric measurement sample holder connected with two high voltage wires.

#3 Computers had user-friendly software for driving the measurement system.

#4 Self-made ferroelectric measurement sample holder set-up poured in silicon oil for high-temperature measurements with a heater heating the oil with an automated recording of temperature; connected to two high voltage wires.

34



Figure 2.8: Marine India ferroelectric loop tracer spectrometer the ferroelectric loop at ambient temperatures.

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Chapter 3

Modified A/B site by Pb and Cu Doping, Structural, microstructural and electronic studies of Ba_{0.75}Pb_{0.25}Ti₁₋ _xCu_xO₃ceramics

The polycrystalline $Ba_{0.75}Pb_{0.25}Ti_{1-x}Cu_xO_3$ (for x = 0%, 1.5%, 3.1% & 6.2%) are synthesized by modified sol-gel process. The aim of this chapter is a detailed study of crystal structural, surface morphology, vibrational and optoelectronic properties of Cu²⁺ doped $Ba_{0.75}Pb_{0.25}TiO_3$ ceramics. All the samples are prepared at 950°C-6h to observe the different properties of materials.

In BPTCO lattice, due to the volatile nature of Pb ions, oxygen vacancies are very prone to be created in all the samples. To overcome these drawbacks donor doping is known to improve the structural and optical properties which lead to development in various application.

3.1 Synthesis:

Sol-gel processed polycrystalline Ba_{0.75}Pb_{0.25}Ti_{1-x}Cu_xO3 (for x = 0% 1.5%, 3.1% and 6.2% composition) [named as BPTCO] ceramics were prepared using barium nitrate (99.9 %), lead nitrate (99.9 %), Copper (II) oxide (99.7%), Coper Oxide (CuO) and Dihydroxybis (Ammonium Lactate) Titanium (IV) of 50% w/w aqueous solution precursors . All the precursors are from Alfa Aesar. Details are given in chapter 2.

3.2 Structural studies:

3.3 Surface morphology study:

The BPTC powders were in the form of spherical agglomerates [Figure 3.1(a,b,c,d)]. Image J software was used to analyses the average grain size from the FESEM images of the powders. The average grain size overall increased with the increase of Cu^{2+} substitution up to sample

S3 and negligible changes for S4 ample. [Figure 3.1 (f)]



Figure 3.1: Surface morphology (a-d), (e) Crystalline size and (f) Particle size of $Ba_{0.75}Pb_{0.25}Ti_{(1-x)}$ CuxO3, (x=0, x ≤ 0.062) powders with substitution.

Therefore, due to the incorporation of Cu doping the average grain size increases with the increase substitution.

3.4 X-ray diffraction analysis:

The PXRD (powder X-ray diffraction) patterns of BPTCO samples are shown in Figure 3.2.



Figure 3.2: (*a*) the XRD pattern of $Ba_{0.75}Pb_{0.25}Ti_{(1-x)}Cu_{(x)}O_3$ x=0%, 1.56%, 3.12%, and 6.25% and (b-c) the zoomed view of two peaks at $2\theta = 31^{\circ}-32^{\circ}$ and $44^{\circ}-46^{\circ}$ respectively.

The data was recorded in the range $2\theta = 20^{\circ}$ to 80° for 950° C heated samples. Characteristic peaks in the XRD data are observed around $2\theta \sim 31.6^{\circ}$ for (101)/(110) reflections, $\sim 45^{\circ}$ or (002)/(200) reflections, $\sim 52^{\circ}$ for (102)/(210) reflections and $\sim 65.9^{\circ}$ for (202)/(220) reflections. These pairs are split for the S0 sample. These split peaks are signatures of a *P4mm* tetragonal phase common to both BaTiO₃ and PbTiO₃. This ensures the formation of a homogeneous solid solution of the two titanates for all the samples. The amount of splitting for the (001)/(100), (101)/(110) and (202)/(220) peaks reduces with Cusubstitution [Figure 3.2 inset] in S1 and S2 and is nominal for the S4. As the splitting is a sign of a tetragonal phase [4], [5] it may be logical to infer that the tetragonality decreases with Cu-incorporation. A more cubic structure is attained with Cu-incorporation. However, the existence of splitting even for the highest Cu-content ensures the absence of a cubic phase in the materials. These variations need a proper Rietveld refinement to specify the detailed structural modifications. Figure 3.3 shows the Rietveld refinement data which was fitted with a BaTiO₃ P4mm CIF file.



Figure 3.3: The Rietveld refinement of XRD data of $Ba_{0.75}Pb_{0.25}Ti_{(1-x)}Cu_{(x)}O_3 = 0\%$ (a), 1.5% (b), 3.1% (c), and 6.2% (d).

Ionic radius of Pb²⁺ (1.49 Å) at the A-site is lesser than Ba²⁺ (1.61Å) [<u>https://www.unf.edu/~michael.lufaso/spuds/radii-size.pdf</u>]. On the other hand, Ti⁴⁺ (VI) (0.605 Å) is lower radii comparable to Cu²⁺ (VI) (0.73 Å) at the B-site. The tolerance factor, *t*, is a measure of tetragonality of the structure: t = RA-RO/(RB-RO). For a cubic phase, one expects t = 1. The tolerance factor reduces continuously from 1.087 to 1.0815 from S0 to S4.

The lattice parameters are measured from Rietveld refinement data. It is obtaining that the lattice parameter 'a' is first decreases for x=1.56% and thereafter continuously increases up to x=6.25% and on the other hand the lattice parameter 'c' continuously increases with increasing Cu incorporation. The overall unit cell volume increased with substitution. This is most probably due to the larger size of the Cu²⁺ ion. This indicates that the bond lengths are affected by Cu incorporation.



Figure 3.4: (a) Lattice parameters ('a'='b' & 'c') and (b) the unit cell volume of $Ba_{0.75}Pb_{0.25}Ti_{(1-x)}Cu_{(x)}O_3 x=0\%$, 1.56%, 3.12%, & 6.25%.

Although a major tetragonal P4mm phase is dominant, traces of Ba2TiO4 phase were present in all the samples. Minor peaks (~3.3% intensity of 101 of P4mm phase) revealed this phase in the range, $2\theta \sim 27-29^{\circ}$. Such a negligible derivative phase may have formed due to lack of Ti and excess of Ba proportions at the starting resulting out of the hygroscopic nature of the Ti precursor.

From the FESEM results, the particle sizes were observed to be >1 micron for all samples. Hence, the XRD peak widths should be very sharp and invariant with composition as all were in the bulk regime.

However, the XRD peak FWHMs show modifications from 0.216° (S0) to 0.193° (S1), 0.389° (S2) and 0.408° (S4). These FWHMs correspond to crystallite sizes in the nano and not in the bulk regime. Also, in the bulk regime, it is unlikely to expect variations in the FWHM for comparable particles. Hence, the modifying nature of these FWHMs with composition reflects the possibility that the crystallite sizes are not in the bulk regime. With Cu incorporation, the average crystallite size shows an irregular composition dependence. It increases from 28.76 nm (S0) to 44.7 nm (S1) and thereafter gradually decreases to ~22.15 nm (S2) and more or less remains invariant at 21.1 nm for S4 [Figure 3.1.(e)]. Hence, the particle sizes observed from the FESEM images may originate due to an agglomeration of multiple crystallites. On a closer observation stacking layers are observed in the FESEM images which may be the reason for such smaller sizes of the crystallites. However, a detailed HRTEM analysis is due to this aspect of the investigation of these materials.

The strain in the samples first decreased from 0.0046 (S0) to 0.003 (S1) and thereafter increased to 0.0061 (S2) and 0.0064 (S4) [Table 3.1]. This initial decrease in strain may be related to the incorporation of Cu^{2+} in place of Ti^{4+} which may be a possible reason for the formation of some O-vacancies thereby reducing the effective volume of the unit cell. The increase of strain with further doping can be related to the continuous increase of distortion on account of the larger size of Cu^{2+} . And associated O-loss from the lattice.

 Table 3.1: The lattice strain with compositions for BPTCO samples.

Samples name	Lattice strain
SO	0.0046

Chapter 3

S1	0.003
S2	0.0061
S4	0.0064

3.5 Raman study:

The Raman spectrum in dependence of the composition of BPTCO samples at 950°C for a wide range of frequency 100-800 cm-1 and carried out at room temperature shown in Figure 3.5.



Figure 3.5: The Raman spectra of $Ba_{0.75}Pb_{0.25}Ti_{(1-x)}Cu_{(x)}O_3$ x=0%, 1.56%, 3.12% and 6.25%.

A broad feature appears at lower frequencies due to the overlap of several Raman modes. These Raman modes are considerably broad (FWHM ~ cm⁻¹ individually. This may be a consequence of considerable disorder in the BPTCO lattice. BT shows different phase transition when continuously heating from -190°C to 230°C such as rhombohedral to orthorhombic, orthorhombic to tetragonal, and tetragonal to cubic. As temperature increases, Raman peaks are shifted and some peaks disappear.

From the literature survey, it was found that in cubic phase all Raman modes are disappeared [6, p. 3].

The A (TO) Raman mode in the rhombohedral phase will be shifted towards lower frequency and the peak is very sharp [7]. The Raman modes corresponding E (LO), A (TO) will appear with increasing temperature [8, p. 2]. Now farther increasing temperature the orthorhombic phase changes to tetragonal phase and the Raman modes A(TO) and E(LO), A(TO) will disappear but some picks are broader. The Raman modes corresponding to the B1, E(TO+LO) at 305 cm⁻¹ will be sharper and it is the characteristic modes of tetragonal phase [9, p. 3].





All the Raman modes can be related to BPTCO phonons are shown in Figure 3.5(a-d). Here, the broad asymmetry mode occurs at frequency 175 cm⁻¹. Due to the vibration of Ti- O_6 octahedral several modes are originate in the frequency range 450-600 cm⁻¹. Few other modes are observed due to overlapping of two bands [A_1 (LO) & E (LO)] above 700 cm⁻¹ [10, p. 3]. However, the symmetry mode A_1 originating due to the vibration of Ti-*O bond* vibrations and this mode is related to the structural phase transition of the system [11]. Figure 3.5 shows the fitted spectra of BPTCO phonons. In this work with Cu incorporation, an overall redshift was observed for all compositions due to the higher mass of Cu compared to titanium atom, since $f = 2\pi \sqrt{(k/m)}$ may be one of the possible reason for such changes.

3.6 UV Vis spectroscopy analysis:

The bandgap energy is one of the fundamental characteristics, particularly, when the optical devices are invented. Most of the perovskite oxides generally shows a wide bandgap energy i.e. BaTiO₃, PbTiO₃ and PZT have bandgaps Eg=3.3 eV, 3.2 eV and 3.63 eV respectively [12, p. 3], [13, p. 3], [14]. The optical properties of BPTCO samples are examined from 200 nm to 800 nm by UV-Vis spectroscopy [Figure3.7].



Figure. 3.7: (*a*) *The band-edge from the UV-vis spectra* (*b*) *decrease of electronic band gap with substitution.*

The Tauc equation [15] : $(\alpha h\nu)^{1/n} = A'(h\nu - Eg)$, is used to calculate electronic bandgap energy. Where, Absorption coefficient = α , A' = independent photon energy constant, $h\nu$ = energy of incoming photon, Eg = energy of electronic bandgap, and n = dimensionless parameter .for direct bandgap n = 1/2 and for n=2 for indirect band [16], [17]. The direct bandgap energy is estimated by plotting hv in abscissa

and $(\alpha hv)^2$ in ordinate. The extrapolation of the linear part of the graph on the $(\alpha hv)^2$ axis provides the bandgap [18], [19]. The bandgap seems to decrease 3.27-2.93 eV for x=0% to x = 3.1%, and after that increase up to 2.96 eV with further increase in x. As Cu²⁺ replaces Ti⁴⁺, this effect creates an impurity energy band in the samples which are created due to the creation of the impurity levels inside the gap. This type of variation in band gap also shown in different samples e.g, in KNbO₃xBaNi_{1/2}Nb_{1/2}O_{2.75} (KN-xBNN) the bandgap energy changes in the range 3.8 eV for x = 0 to x=1.39 eV for x = 0.1 [20] and in ferroelectric perovskite PbTiO_{3x}Bi(Co₂₃Nb₁₃)O₃ the bandgap energy decreased in the range 3.2-2.6 eV for x = 0 to x = 0.1[21].

3.7 I-V characteristics:

The current-voltage characteristics measured with an applied DC voltage from -20 to +20 volts in capacitor mode. With Cu substitution. The electrical conductive property degrades as is observed from the reduced current in the BPTC samples. The conductivity was 2.433x 10-7 S/m for x=0.0% and it was drastically decreased to 9.561x10-9 S/m for x=1.5%. However, for further doping, the conductivity changes nominally. The conductivity for x=3.1% was 9.45x10-9 S/m and 8.58x10-9 S/m for x=6.2%.



Figure 3.8: *I-V* characteristics of $Ba_{0.75}Pb_{0.25}Ti_{(1-x)}$ Cu (x)O₃ ($0 \le x \le 0.0625$) ceramics.

3.8 Conclusions:

single-phase Polycrystalline of In summary, powder Ba_{0.75}Pb_{0.25}Ti_{1-x}Cu_xO₃ (x=0%, x \leq 6.2%) ceramics synthesized by modified sol-gel self-combustion process. To study Powder X-ray diffraction data of all the samples it was confirmed that all the compositions belong to the tetragonal crystal structure to the P4mm space group. There is a structural change in the samples with composition, the phase was changed from tetragonal to cubic for Cu incorporation at x=6.2% Lattice parameter 'a' firstly decreases and then increases and 'c' increase continuously, with an increase in Cu content and increase the volume with substitution. All the compositions show a dense and homogeneous microstructure, the average grain size overall increased with the increase of Cu²⁺ substitution up to sample S3 and negligible changes for S4 ample. The shift in phonon energy reveals distortion of BO6 octahedra. The phonon mode at 302.99 Cm-1 indicates a tetragonal phase of all samples. But this mode is reducing its intensity with the incorporation of Cu, which reduced the tetragonality of the samples. The electronic bandgap energy and also the conductivity continuously decreases with increasing substitution.

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Chapter 4

Structural, dielectric and ferroelectric studies of ceramic materials: Ba_{0.75}Ti_{0.25}Ti_{1-x}Cu_xO₃

Actuators, sensors, and ultrasonic transducers have been targeted for advance developments in ferroelectric (FE) ceramics [1], [2]. The Ba_{0.75}Pb_{0.25}Ti_{1-x}Cu_xO₃, has anomalous dielectric and ferroelectric response due to the morphotropic phase boundary like PZT [3], [4] and NBT [5]. This chapter aims to investigate the structural, microstructure, thermally stable dielectric properties and ferroelectric properties for Ba_{0.75}Pb_{0.25}Ti_{1-x}Cu_xO₃ (x=0%, $x \le 6.2\%$) ceramics fabricated via a modified sol-gel method. The doping of Cu at the Ti-site affects the T_c which decreases with increasing Cu content. In addition to this, it also improves dielectric and ferroelectric properties [6, p. 3]. Structural analysis of XRD data was carried out to check the phase purity and structural changes as a function of composition. High-temperature and room temperature dielectric measurement have been done to investigate the effect of Cu substitution in BPTO. These types of materials, with the high stable dielectric constant (ε_r) and low loss (tan δ), have a vast scope in the field of the thermally stable dielectric constant materials and energy storage applications.

4.1 Synthesis

A series of polycrystalline $Ba_{0.75}Pb_{0.25}Ti_{I-x}Cu_xO_3$, (for x = 0%, 1.2%, 3.1%, & 6.2%) powder was prepared using barium nitrate, lead nitrate, copper oxide, and dihydroxybis (ammonium lactato) titanium, potassium nitrate for Alfa Asear. Details are given in chapter 2.

4.2 Structural analysis

The powder X-ray diffraction (PXRD) provides all the

information about the crystallographic structure of the materials [7]. Powder X-ray diffraction pattern of Ba_{0.75}Pb_{0.25}Ti_{1-x}Cu_xO₃ where x=0%, 1.5%, 3.1%, and 6.2% with pure tetragonal phase (space group *P4mm*) were recorded in the 20 range from 20° to 80° are shown in [Fig.4.1].



Fig.4.1: (a) the XRD pattern of $Ba_{0.75}Pb_{0.25}Ti_{1-x}Cu_xO_3 = 0\%$, 1.5%, 3.1%, and 6.2% and (b) the lattice parameters.

Characteristic peaks in the XRD data are observed around $2\theta \sim 31.6^{\circ}$ for (101)/(110) reflections, $\sim 45^{\circ}$ or (002)/(200) reflections, $\sim 52^{\circ}$ for (102)/(210) reflections and $\sim 65.9^{\circ}$ for (202)/(220) reflections. These pairs are splitted for the S0 sample. These splitted peaks are sign of a *P4mm* tetragonal phase common in both BaTiO₃ and PbTiO₃. This ensures the formation of a homogeneous solid solution of the two titanates for all the samples. The amount of splitting for the (001)/(100), (101)/(110) and (202)/(220) peaks reduces with Cu-substitution in S1 and S2 and is nominal for the S4 sample. As the splitting is a sign of a tetragonal phase [8], [9] it may be logical to infer that the c/a continuously decreases with Cu-incorporation [Fig.4.2]. The lattice parameters were calculated by Reitveld refinement using Fullprof
software. Fig 2 shows that the (c/a) continuously decreases with increasing Cu incorporation i.e. the lattice structure changes from tetragonal (*P4mm*) to cubic (Pm-3m). This is due to the contraction of the c-axis and elongation along a-axis. The volume of the samples decreases for $x \le 3.1\%$ but for x = 6.2% the volume increases.



Figure 4.2: The lattice parameters and volume of BPTCO

samples.

Average crystallite size is determined using Debye Scherrer equation [7], [10] for all composition;

$$\langle D \rangle = \frac{\lambda k}{\beta}$$
.....(4.1)

with the help of most intense peaks.

Where β = FWHM from Gaussian fitting (degree), k α wavelength = λ , θ = Bragg's angle of diffraction, k = 0.9 a constant [11].

Average crystallite size continuously decreases with an increase in Cu doping. Since the crystallite size is small the peak broadening can be observed in the XRD. So, it is difficult to confirm whether the dominant phase is tetragonal or cubic. However, it is known that the tetragonal distortion in BT decreases as the grain size is less than 1um. Because it is possible that on the surface of the grain a non-ferroelectric grain boundary layer is present. However, we observed a splitting of (200) peak in (200) and (002) signifying the stabilization of the tetragonal phase of BPTCO.

4.3 Surface morphology:

The FESEM analysis reveals spherical agglomerates shown in [Fig 4.5(a-d)]. Image J software was used to analyse the grain size from the Obtained FESEM images. The average grain size of the agglomerates increase from 0.972 μ m to 9.63 for S0 to S2 respectively and after that, it decreased 2.158 μ m for S4.

The increase in average grain size with the increase in copper substitution might be related to a rise of oxygen vacancies contribution [12], [13, p. 3]. In BPTCO oxygen vacancies are created by the charge compensation.



Figure 4.3: Surface morphology of $Ba_{0.75}Pb_{0.25}Ti_{1-x}Cu_xO_3$ (x=0%, x \leq 6.2%) compositions. (a-d) x = 0%, 1.5%, 3.1% and 6.2%.

The Theoretical density (ρ_t) can be measured from PXRD refined data, and the experimental density (ρ_e) was calculated from Archimedes' methods. The Relative density ($\rho_R = 100 \times \rho_e / \rho_t$), continuously increases form ~ 80.5 % to ~ 91.2 % with increasing Cu doping.

3.4 Raman spectroscopy

To study the effect of Cu-doping on phonons or lattice vibrations, Raman spectroscopic studies were performed. Phonon modes are extremely sensitive to structural distortion. The phonons are also dependent on the motion of the oxygen sublattice in complicated systems like perovskites [14]. The scattered light for incoming polarization can be classified as a combination of a longitudinal optical (LO) and transverse optical (TO) modes. Two other overlaid sub-lattices apart from the oxygen sub-lattice constitute the perovskite ABO₃ structure. Since a single unit cell of BaTiO₃ contains 5 atoms so its degrees of freedom is15 [15, p. 3]. Cubic symmetry 4F1u+1F2u represent the symmetry of the vibrational modes of BaTiO₃. Out of this only F1u represent an acoustical branch and the remaining 3F1u+1F2u represent an optical branch. However, it is also known that in C_{4v} symmetry or tetragonal structure the vibrational modes (Raman active modes) are [three {A1 (TO) +A1 (LO)} one B1 and four {E (TO+LO)}] having wavenumbers 250, 307, 515, 715 cm⁻¹ respectively. There are also several modes present along with the above modes [16]. The Raman active modes (optical and acoustical) are absent or inactive in cubic symmetry but both modes are present/ active in the tetragonal symmetry.

The F1u vibrational mode in a cubic structure is divided into two modes i.e. A1+E and the F2u mode is also divided into B1+ E modes. The vibrational mode A1, represents the vibrations of lattice along the c-axis while the mode E modes represent the lattice vibration along the a/b axes. The ionic properties of the lattice are altered due to the longrange electrostatic force due to this effect; the Raman active A1 and E modes further split a pair of transverse optical mode (TO) and longitudinal optical mode (LO) [17], [18].

The Raman spectroscopy of all the samples were recorded at room temperature in the frequency range of 50-800 cm-1. A broad feature appears at lower frequencies due to the overlap of several Raman modes. These Raman modes are considerably broad (FWHM ~ cm⁻ 1) individually. This may be a consequence of considerable disorder in the BPTCO lattice. For BPTC0, the phonon modes were observed for $A_1(LO_1)$) (~103.3 cm⁻¹), $A_1(TO_2)$ (~132.55 cm-1), [E(TO_1), $A_1(LO_1)$] (~165.41), [$A_1(TO_1)+E(LO_1)$] (~191.45cm⁻¹), [E(TO_3+LO_2)+B_1] (~302.99 cm⁻¹), [$A_1(LO_2)$, E(LO_3)] (~492.61 cm⁻¹), [$A_1(LO_2)$, E(TO_3)] (516.01 cm⁻¹), [$A_1(TO_2),E[(TO_3)]$ (~547.8 cm⁻¹), [$E(LO_4)$, $A_1(LO_3)$] (~715.33 cm⁻¹).



Figure 4.4: *Room Temperature Raman spectra of BPTCO* samples in the range 50 to 800 cm⁻¹

All Raman active modes in BPTCO sample (x=0) are well-match with our previous report [20]. Literature survey it was found that the phonon mode at 108^{-1} consists A₁ (TO), A₁ (LO₁), E (LO₁) and E

 (TO_2) modes which are very close to each other. In powder samples, it is difficult to resolve these peaks properly. It was also observed that these modes are combined a pair of [E (TO₂), A₁ (LO₁)] and [A₁(TO), E(LO₁)] respectively. However, in a single crystal with the help of polarized Raman spectroscopy, these vibrational modes are distinguishable [21].

The asymmetry vibration mode $[A_1 (TO_2), E(LO_1)]$ at 191.45 cm⁻¹ which is a combination of two Vibrational modes shows a blue shift. The origin of this mode due to the asymmetric stretching of Ti–O bonds. Such blue shifts can be observed in the samples due to the change in Ti-O bond strengths.

It was observed that the Raman active $[A_1(LO_2), E(TO_3)]$ mode around 516.01 cm⁻¹ firstly shifted toward higher wavenumber 521.05 cm-1 shows a blue shift and then sharply decrease to the lower frequency at the same position (516.01 cm⁻¹) shows redshift. The origin of this mode is the symmetric stretching O–Ti–O.

In BaTiO₃ the tetragonal phase confirmation Raman active mode is [E (TO₃+LO₂) +B₁] around 307 cm-1[22]–[24]. Which is known as the signature mode of tetragonality. In this work, this mode is observed near about wavenumber 299.83 cm-1. The origin of this mode is the asymmetry of TiO₆ octahedral. This mode confirms that all the compositions are in the tetragonal phase which is also correlated the XRD data.

It was observed that the vibration around wavenumber 715.33 cm^{-1} consists of two modes E (LO₄) and A1(LO₃) coexist. According to *suchainciz et al.* at high frequency originates oxygen atom vibration and oxygen vacancy.

4.5 Dielectric Study:

To study the phase transition of materials, room temperature and temperature dependent-dielectric properties were studied. The room temperature relative permittivity (ϵ_r) and dielectric loss (tan δ) for

BPTCO samples with frequency were measured from 100Hz - 1MHz. It is interesting to note that the ε_r and tan δ are shown a similar trend with increasing frequency for all compositions Figure 4.7(a-b)]. In dielectric materials, the Polarization depends on electronic, ionic, orientation, and space polarization. Since all the four polarization is frequencydependent so with applied frequency all these polarizations are changes accordingly. For lower frequency, all these polarization are contributed easily, but with higher frequencies, different polarizations will filter out. The possible reason behind this is that with the applied *ac*-electric field (increasing frequency) the number of responding dipoles are reduced [25, p. 3].



Figure 4.5: Room temperature dielectric constant and tan loss of the $Ba_{0.75}Pb_{0.25}Ti_{1-x}Cu_xO_3$ (x=0%, $x \le 6.2\%$) range samples, where (a) Relative permeability ($\varepsilon_{r,}$) and (b) tangent loss (tan δ) with frequency.

However, the ε_r and tan δ are shown opposite trend with the increasing substitution for all compositions i.e. Relative dielectric constant ε_r increases for increasing substitution and the dielectric loss decrease with increasing substitution. The relative permeability depends on electronic polarizability (α_D) and it depends on phase transition. The net polarizability parent Ba/Pb ions are lower compare to the substituent Cu ion. So with increasing substitution, the increase of ε_r might be due to the increase in net polarizability.

High-temperature dielectric measurement has been done for BPTCO samples to investigate the effect of the composition. For this study, the dielectric constant ε_r and tan loss tan δ were measured in the



range of temperature (100-300 °C) with different frequencies Figure 4.6].

Figure 4.6: Temperature dependent dielectric constant and tan loss of the Ba_{0.75}Pb_{0.25}Ti_{1-x}Cu_xO₃ (x=0%, $x \le 6.2\%$) range samples, where (a,c,d,g) Relative permeability (ε_r ,) and (b,d,f,h) tangent loss (tan δ) with temperature at some fixed frequency.

From the temperature-dependent dielectric measurement, it can be observed that for all samples the dielectric constant (ε_r) increases with increasing at a certain temperature T_m and after that, ε_r decreases with increasing temperature above T_m . Thus T_m called the maximum dielectric constant temperature and it is the characteristic temperature of AFE to FE phase transition [Figure 4.6] [26]. From measurement, it is found that the T_m (maximum dielectric constant temperature) decrease with increasing substitution. Similar type of results found different systems such as: (0.935-x)Bi_{0.5}Na_{0.5}TiO₃-0.065BaTiO₃xSrTiO₃[27],0.95[0.94(Bi_{0.5}Na_{0.5-x}Li_x)TiO₃-0.06BaTiO₃]-0.05CaTiO₃ [28], etc. the possible reasons of decreasing T_m might be due to the reduced the unit cell distortion with increasing Cu substitution which is confirmed by PXRD data. From literature, it was found that both the Curie temperature and unit cell distortion are connected. The variation T_m is also correlated with the structural data. These reductions of T_m can also be correlated with the partial substitution of Pb^{2+} in Ba^{2+} ions and the lone pair of Cu²⁺. From literature, it was found that Pb doping at Ba place improves dielectric and ferroelectric properties (for x < 0.15) [29, p. 3]. In perovskite system, the diffuse type of phase transition is observed instead of a sharp phase transition due to the random distribution of heterovalent ions at A/B-site of (A'A")(B'B")O₃ type unit cell. However, in a certain domain large no of polycrystal are containing and leads to many chemical combinations and therefore micro-regions of different A/B-site cations with the locally varying phase transition temperature. These might be responsible for a diffuse type of phase transition. In Ba_{0.75}Pb_{0.25}Ti_{1-x}Cu_xO₃ samples, Ba²⁺/Pb²⁺ ions occupy the A-site and Cu²⁺ occupied B site of ABO₃ and shows diffused phase transition. As a result of these materials used in high-temperature stable capacitor applications.

A well-known very sharp ferroelectric (tetragonal) to paraelectric (cubic) phase transitions observed for both pure BT and PT Perovskite. It is observed that the diffuse phase transition exhibits a broad change of structure and properties at the phase transition temperature while sharp peaks are observed in normal ferroelectric materials. The diffused nature of phase transition can be explained by modified Curie-Weiss law [30], [31] $(1/\epsilon - 1/\epsilon_m) = [T-T_m]^{\gamma}/C$.

Where, ε_m = maximum relative permeability at T_m, C = Curie-Weiss constant and the degree of diffuseness define by γ (1 $\leq \gamma \leq 2$). $\gamma = 1$ for purely ferroelectric material, and $\gamma = 2$ for relaxor type. A linear fit of $\ln\left(\frac{1}{\varepsilon} - \frac{1}{\varepsilon_m}\right) vs \ln(T - T_m)$ plot at 10 kHz frequency (Fig. 6) shows the value of γ For S0, $\gamma \sim 1.28$ implying a diffuse ferroelectric phase while $\gamma \sim 1.11$ for S1 and decreases up to $\gamma \sim 1.03$ for S4 which also suggests that BPTCO is a good ferroelectric material.



Fig. 4.7: Modified Curie-Wiess law fitting $\left(\ln\left(\frac{1}{\varepsilon} - \frac{1}{\varepsilon_m}\right) vs \ln(T - T_m)\right)$ (a) S0, (b) S1, (c) S2, (d) S4

In polycrystalline materials, the distribution of different atoms are random and shows a phase transition in a wide range of temperature. Hence, as a result, wide range (i.e. diffused nature) of the dielectric constant observed. So in this ceramics, both the Ba^{2+} and Pb^{2+} atoms are homogeneously distributed over the entire region.

4.6 Ferroelectric measurements

The variation of Polarization (P) with an applied electric field (E) was measured at room temperature with an applied voltage frequency 50Hz.



Figure.4.8: *Room temperature polarization versus electric field of (a) BPTO.*

The coercive field and remnant polarization of the BPTCO samples is $(2E_c) = 2.73$ (kV/cm) and $(2P_r) = 3.56$ (μ C/cm2) respectively.

4.7 Conclusions

In summary, single-phase Polycrystalline powder of Ba_{0.75}Pb_{0.25}Ti_{1-x}Cu_xO₃ (x=0%, x \leq 6.2%) ceramics were successfully synthesized by modified sol-gel autocombustion process. The powder X-ray diffraction of all samples confirmed that the compositions are in tetragonal phase (P4mm). There is a structural change in the samples with composition, the phase was changed from tetragonal to cubic for Cu incorporation at x=6.2%. The c/a decreases with increase in Cu doping, while the volume increases with an increase in Cu substitution. All the compositions show a dense and homogeneous microstructure, the average grain size firstly increases up to 3.1% and then decreases for 6.1% incorporation of Cu^{2+} . The shift in phonon energy reveals distortion of BO₆ octahedra. The phonon mode at 302.99 Cm-1 indicates a tetragonal phase of all samples. But the decrease in the intensity of this mode with increase in Cu incorporation of tetragonality with an increase in Cu doping. The result shows that this material has a vast scope in high-temperature applications. At room temperature (RT), ferroelectric properties improved for x = 0.0 composition, $2P_r \sim 3.56 \ \mu\text{C/cm}^2$ increased and $2E_c \sim 2.73 \ \text{kV/cm}$. As a result, it can be said that BPTCO materials can be used as excellent dielectric, ferroelectric and piezoelectric applications.

4.8 References

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Chapter 5

Conclusions and future research scope

5.1 Conclusions

ABO₃ type Ba_{0.75}Pb_{0.25}TiO₃-based ferroelectric materials were synthesized *via* a sol-gel method followed by sequential hightemperature sintering. The Ba_{0.75}Pb_{0.25}TiO₃ ceramic was modified at the B-site by Cu2+ substitution in the range x=0, x \leq 6.2%. These chemical modifications were significantly helpful in the improvement of the various functional properties of the parent compound. In this work, all the characteristics are investigated into two different temperatures (1) at 950°C and other (2) at 1100°C. The structure, morphology, vibrational, dielectric and ferroelectric properties were investigated. A brief resultsbased summary and future scope are provided below:

5.2 Experiment performed at 950°C

5.2.1 Structural properties:

Detailed structural properties for all the above-mentioned samples were investigated as a function of composition. To investigate the structure properties, Rietveld refinement was carried out by power XRD data of all samples. Structural analysis revealed a change in lattice dynamics as a function of composition. All compositions at 950°C are tetragonal phase (*P4mm*). The details of the structural components are enlisted in Table 7.1.

Tab	ole 5.1:	Unit cell	Parameters	of BPTCC) samples a	t 950°C
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Sample name	Lattice parameters		Volume	c/a
	a=b (Å)	c (Å)		
S 0	3.99366	4.03106	64.29283	1.00937

Chapter 5

S1	3.96716	4.03893	63.56608	1.01809
S2	3.9774	4.04286	63.9568	1.01646
S4	3.98966	4.04222	64.34164	1.01317

The tetragonal unit cell distortion phase decreases continuously with increases in Cu doping. For all compositions series, the tetragonal phase decreases as a function of composition [see respective chapters]. The unit cell distortion tetragonal phase's decreases as a function of increasing substitution. The variation of crystalline size and strain are shown in Table 7.2.

Table 5.2. The lattice strain and crystalline size for BPTCO at950°C.

Sample name	(hkl)	20 (°)	FWHM(β)(°)	Crystalline size(nm)	Lattice strain
SO	111	31.620	0.216	39.94	0.0033
S1	111	31.556	0.193	44.69	0.0030
S2	111	31.059	0.389	22.15	0.0061
S4	111	31.204	0.408	21.12	0.0064

5.2.2 Morphology analysis

The BPTC powders were in the form of spherical agglomerates. With Cu incorporation, the average grain size of the agglomerates increased with substitution.

5.2.3 U-V Vis spectroscopy analysis

From U-V Vis spectroscopy measurements the bandgap decreases from 3.27-2.93 eV for S0 to S2, and thereafter increases to 2.96 eV with further increase in x. As Cu^{2+} replaces Ti^{4+} , this effect creates an impurity energy band in the samples which are created due to creation of energy level due to the presence of Cu^{2+} .

5.3 Structural properties for BPTCO 1100°C Samples.

5.3.1 Structural properties

The powder X-ray diffraction (PXRD) provides all the information about the crystallographic structure of the materials. Powder X-ray diffraction pattern of Ba_{0.75}Pb_{0.25}Ti_{1-x}Cu_xO₃ where x=0%, 1.56%, 3.12%, and 6.25% with pure tetragonal phase (space group *P4mm*) were recorded in the 2 θ range from 20° to 80°.

Rietveld refinement confirms that all compositions are tetragonal phase having space group (P4mm). The details of the structural components are enlisted in Table 7.3.

 Table 5.3: Unit cell Parameters of BPTCO samples at 1100°C.

Sample name	Lattice parameters		Volume	c/a
	a=b (Å)	c (Å)		
S0	3.9755	4.0494	63.99915	1.01859

Chapter 5

S1	3.97604	4.04607	63.96389	1.01761
S2	3.97645	4.04192	63.91146	1.01646
S4	3.98129	4.03881	64.01784	1.01445

5.3.2 Dielectric properties

Temperature-dependent dielectric properties for some fixed frequency range were measured for all BPTCO at 1100°C. The frequency-dependent dielectric constant was found to increase as a function of substitution at ambient temperature. The temperaturedependent dielectric measurement revealed a single high-temperature dielectric anomaly at a Curie temperature, T_m . The feature of the anomaly becomes more diffused with increasing substitution.

The Curie temperature, T_m was decreased with an increasing substitution for all the substituted samples. It decreased from ~ 236 °C for x = 0% to 194°C for (x = 6.2%).

The dielectric anomalies become more diffused with increasing substitution. As a result, a steady thermally-stable dielectric constant was obtained in samples, which are shown in the given below [Table 7.4].

Table 5.4: Dielectric constant with their temperature range for BPTCO samples.

Samples	Thermally stable dielectric constant (ε _r)	Temperature range (°C)
BPTO (<i>x</i> = 0%)	1972 ± 5 %	243-230
BPTCO (<i>x</i> = 1.5%)	5265 ± 5 %	230-340
BPTCO (<i>x</i> = 3.1%)	2406 ± 5 %	220-233
BPTCO($x = 6.2\%$)	4500 ± 5 %	190-198

5.2.3 Ferroelectric properties

BPTO material is a good ferroelectric (Tetragonal *P4mm* phase) material at room temperature. It has a high E_c , which restrict to use of this material in practical application. In the present study, the room temperature FE are measured with the applied field. The coercive field and remnant polarization of all the BPTCO samples with external applied electric field are (2E_c) = 2.73 (kV/cm) and (2P_r) = 3.56 (μ C/cm2) respectively.

5.3 Major findings

The major findings of all series are listed below:

- For BPTCO the sintering temperature decrees to 1100 °C sample. In Pure BaTiO₃ it is near ~1250 °C. It was a big achievement to decrease sintering temperature.
- Decrease the phase transition temperature from 220 °C to 194 °C.
- For BPTO all compositions, the ε_r are increases and tand decreases with the incorporation of Cu substitution.
- Thermally stable ε_r ~ 4500 ± 5 % (190-198 °C), and ~ 5265 ± 5 % at (230-340 °C) for x = 0.0625 and 0.0156 samples was obtained, respectively.

5.4 Scope for future work

- Thin films and single crystals of these materials might provide more interesting results to understand the mechanism and sophisticated application point of view.
- Pyroelectric measurements are to be performed for all the samples from the application point of view.
- Polymer composite should be prepared to make the transparent capacitor materials.