Synthesis and Characterization of Ferroelectric Polyvinylidieneflouride (PVDF)-$Bi_4Ti_3O_{12}$ nanocomposites

A dissertation submitted in the partial fulfillment of requirement for the award of the degree of

Master of Science
in
Physics

Submitted by
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July 2014

Dedicated

To

My Parents

CERTIFICATE

This is to certify that report entitled **"Synthesis and characterization of ferroelectric Polyvinylidieneflouride-$Bi_4Ti_3O_{12}$ nanocomposites"** being submitted by **Ms. Tamanna Vilacha (Roll no. 301204012),** in the partial fulfillment of the requirements for the award of the degree of Master of Science in Physics at **Thapar University, Patiala,** is an authentic work carried out by her under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to the any other University/Institute for the award of any degree or diploma.

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DECLARATION

I hereby declare that the project entitled **"Synthesis and characterization of ferroelectric Polyvinylidieneflouride-$Bi_4Ti_3O_{12}$ nanocomposites"** submitted to the Thapar University, Patiala, is a record of an original work done by me under the guidance of Dr. Dwijendra Pratap Singh, Assistant Professor, Thapar University and this project work has not performed on the basis for the award of any other degree or diploma/associate ship/fellowship and similar project if any.

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ABSTRACT

The composite of polymer polyvinyl-dieneflouride (PVDF) with ferroelectric ceramic $Bi_4Ti_3O_{12}$ was formed. Ceramic powder was prepared by Sol-Gel Combustion Route. The structural and morphological studies of ceramic and composite were done. X-ray analysis of $Bi_4Ti_3O_{12}$ results in the formation of single phase compound in orthorhombic crystal system with crystallite size ~19 nm. SEM studies of $Bi_4Ti_3O_{12}$ shows the good surface morphology.EDS studies gives us the stochiometric ratio equals to 1:5.The polymer composite of ferroelectric compound was prepared using PVDF as the polymer matrix by Solution Casting Method.SEM images of polymer/ceramic composites with different loading percentage of $Bi_4Ti_3O_{12}$ were taken which showed dense microstructure. The DSC studies showed that crystallinity increases with increase in weight percentage of $Bi_4Ti_3O_{12}$ in polymer matrix.

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CHAPTER 1

INTRODUCTION

1.1 Introduction

A ceramic is an earthy material usually of silicate nature and may be defined as a combination of one or more metals with a non-metallic element usually oxygen. The atoms in ceramic materials are held together by a chemical bond and the two most common chemical bonds for ceramic materials are covalent and ionic. Due to wide range of properties of ceramic materials, they are used for many applications. Most ceramics are hard, wear-resistant, brittle, refractory, thermal insulators, electrical insulators, nonmagnetic, oxidation resistant, prone to thermal shock, and chemically stable [1]. Nowadays, material scientists are involved in research and development of new multifunctional ceramic materials for many device applications such as multilayer capacitors, optical shutters and modulators, computer memory and display, microwave communication devices, piezoelectric detectors, ferroelectric random access memory (FRAM) etc [2]. Most commonly studied ceramics are ferroelectrics, which is a subgroup of dielectrics. Materials capable of storing electric energy are classified as dielectrics. A dielectric is an electrical insulator that can be polarized by the action of an applied electric field [3]. Dielectrics are broadly divided into two classes.

1. Polar dielectrics
2. Non-polar dielectrics

A dielectric having finite and permanent polarization even in the absence of electric field is known as polar dielectrics and the dielectrics where there is no such permanent polarization is called non-polar dielectrics.

1.2 Ferroelectric materials

There are large numbers of crystals existing in nature. Based on the crystal symmetry they all can be grouped into 32 point groups. Out of these 32 point groups 11 are centrosymmetric (i.e., the centre of the positive charge coincides with the centre of the negative charge) and 21 are non-centrosymmetric (i.e. the centre of the positive charge and the center of the negative charge does not coincide). Out of 21 non centrosymmetric points group, except one

point group all are piezoelectric. 10 out of the 20 point groups are called pyroelectric. They are also called polar crystals as they show the property of spontaneous polarization i.e. they exhibit electric dipole moment even in the absence of external electric field. Ferroelectric is a sub group of pyroelectric which is also a subgroup of piezoelectric.

Crystals are said to be ferroelectric if the magnitude and direction of spontaneous polarization can be reversed by application of an external electric field. The value of the spontaneous polarization depends upon the temperature. The spontaneous polarization decreases with increase in temperature. The variation of the spontaneous polarization with temperature for a ferroelectric crystal is shown in fig-1.

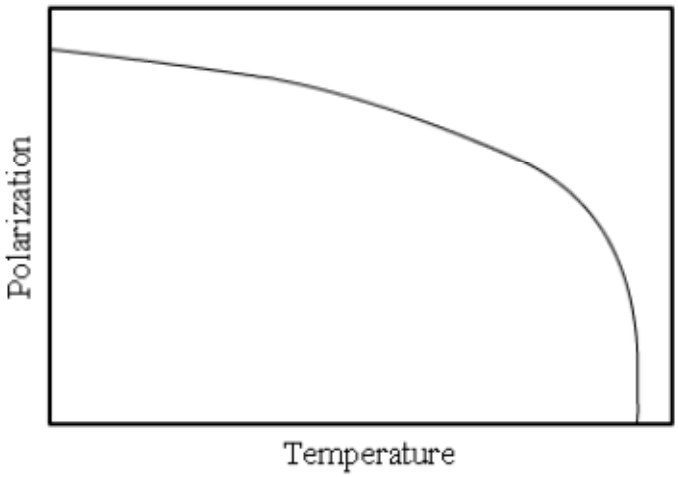


Fig.1. Temperature dependence of the spontaneous polarization

In Ferroelectric crystals there are regions with uniform polarization called ferroelectric domains where all the electric dipoles are aligned in the same direction. The most important characteristics of ferroelectric materials are the non linear relationship between the polarization and the field giving rise to a hysteresis.

The most important group of ferroelectric ceramic is the family of oxygen octahedral which can be further classified into four types. They are:

(1) Perovskite type

(2) Tungsten-Bronze type

(3) Spinel structure (Layered structure)

(4) Pyrochlore type

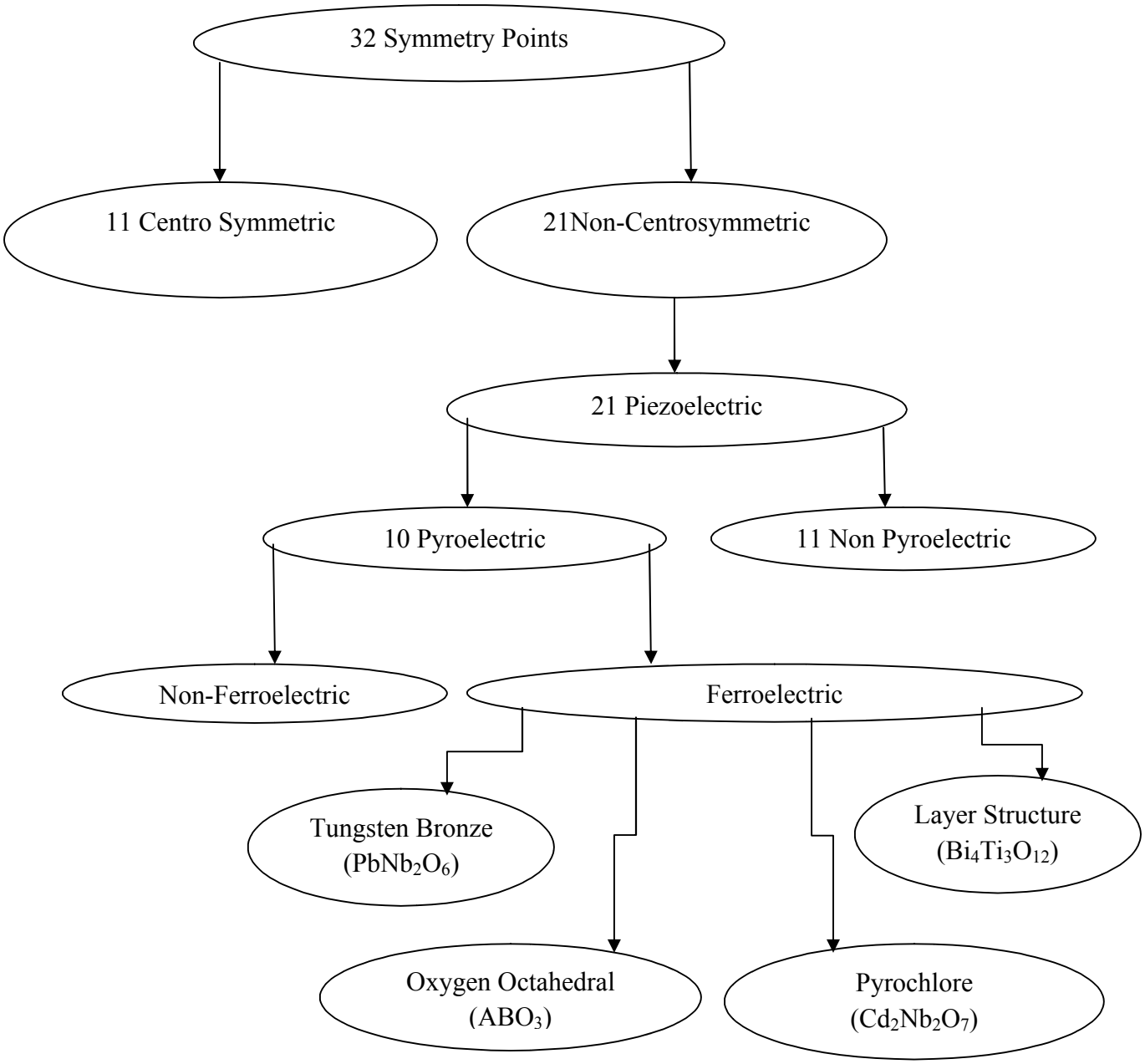


Fig2: Schematic representation of the classification of point group.

Most of the ferroelectric ceramics oxides with the perovskite structure include lead titanate ($PbTiO_3$), lead zirconate titanate (PZT), etc despite their excellent ferroelectric & piezoelectric properties these materials contain a large amount of lead (> 60 wt. %) which is toxic[4]. Therefore there is growing interest in developing lead free ferroelectric ceramics to replace lead based ferroelectric for environmental protection [5]. Among various lead free

perovskite systems, Bismuth Titanate and its Composites are expected to be the good candidates for lead free piezoelectric materials.

1.3 Bismuth Titanate

Bismuth titanate was discovered by Aurivillius in 1949 [6]. It is a ferroelectric material with the chemical formula $Bi_4Ti_3O_{12}$. It has been receiving attention because it can replace toxic ferroelectrics such as PZT and has applications in high temperature environments. It has a ferroelectric -to- paraelectric phase transition temperature of 675^oC, which makes it a good candidate for high temperature piezoelectric device. Above its Curie temperature it belongs to the tetragonal point group. Below T_c, it can be either the point group belonging to monoclinic or orthorhombic [7-8]. Some of the physical properties of $Bi_4Ti_3O_{12}$ ceramics are shown in table1.

TABLE 1: Electrical and Mechanical Properties of $Bi_4Ti_3O_{12}$ Powders [7]

Density ($x10^3$ kg/m^3)	6.55
T_C (^oC)	650
Mechanical Quality Factor QM	>600
Maximum Operating Temperature (^oC)	550
Dielectric Constant (1 kHz)	120
Planar Coupling k_p	0.03
Longitudinal Coupling k_{33}	0.09
Piezoelectric Coefficient d_{31} ($x10^{-12}$ m/V)	-2
Piezoelectric Coefficient d_{33} ($x10^{-12}$ m/V)	18

1.4 Structure of BIT

Bismuth titanate has a structure belonging to the Aurivillius or bismuth layer structure perovskites, having a pseudo-perovskite phase that is between $(Bi_2O_2)^{2+}$ layers. The empirical formula for BIT is ABO_3. $Bi_4Ti_3O_{12}$ is a material with a typical plate-like microstructure that has anisotropic properties, a low coercive field (E_c), small remnant polarization (P_s) excellent fatigue properties and retention time. The synthesis route has a strong influence on the structure and properties of BIT.

The structure of the Aurivillius phases can simply be described by the general formula $(Bi_2O_2)^{2+}(M_{n-1}R_nO_{3n+1})^{2-}$ where n can have the number 1 to 6. The $(M_{n-1}R_nO_{3n+1})^{2-}$ formula unit consists of n pseudo perovskite units which are sandwiched in between two $(Bi_2O_2)^{2+}$ layers. The M cation is a rather large mono-, di- or trivalent cation (e.g. Na^{+}, Pb^{2+}, Bi^{3+}) and the R cation is diamagnetic transition metal and smaller in size and either a tri-, tetra-, penta-or hexavalent cation (e.g. Fe^{3+}, Ti^{4+}, Ta^{5+}, W^{6+}) [9]. The structure of Aurivillius oxides consists of arrays of Bi_2O_2 and perovskite-like $(M_{n-1}R_nO_{3n+1})$ layers.

In fig. 3 a simplified crystal structure of $Bi_4Ti_3O_{12}$ is shown. The three pseudo perovskite units and bismuth oxide layers have been marked.

1.5. Polymer/Ceramic Composite:

A polymer is a large molecule whose structure is composed of multiple repeating units, which tells us about its high relative molecular mass and attendant properties. Nowdays ferroelectric polymer composite received attention as compared to ferroelectric ceramics because of their use in devices such as sensors, actuators, transducers etc [10]. Fabrication of composite materials means to combine two or more different materials having different properties to obtain the desirable material properties that often cannot be obtained in single-phase materials. Ceramics exhibit high stiffness and brittleness, which contributes to limited design flexibility.

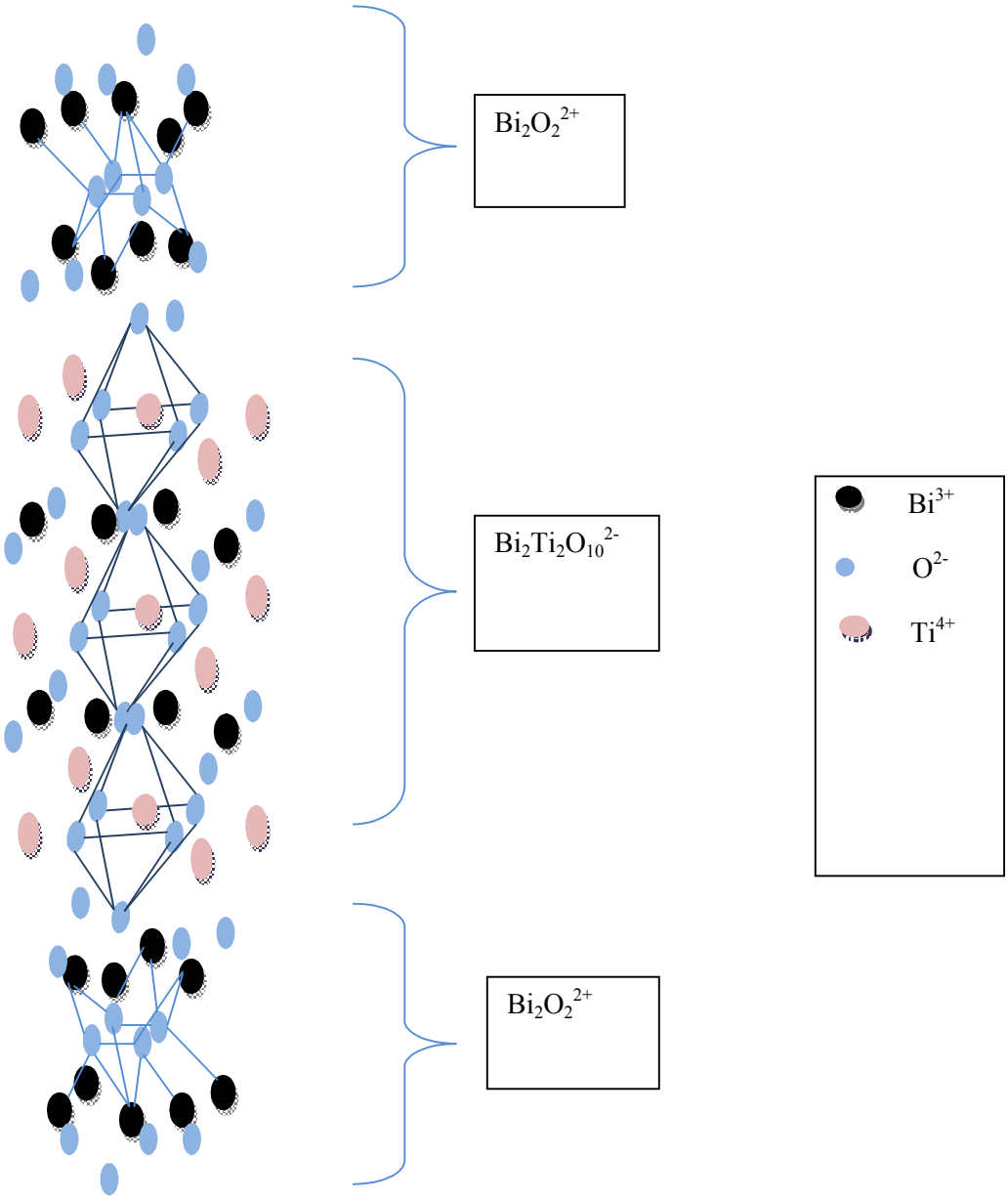


Fig. 3 Structure of $Bi_4Ti_3O_{12}$ showing the bismuth oxide layers and pseudo perovskite units.

Ferroelectric polymer such as PVDF exhibits piezoelectric and pyroelectric response and also their properties can be changed as per the requirement of the device. The best combination in properties can be obtained by the judicious combination of piezoelectric ceramics and polymers. Piezoelectric ceramic/polymer composites possess high electromechanical coupling and an intermediate dielectric constant. Also, composites are flexible, and cheap. For fabrication of a composite the important factors are properties of the components, amount of each phase present and their connectivity. Newnham et al., in 1978 and Tressler et al., in 1999 proposed the concept of connectivity. Generally, the host is a polymer in case of polymer composites. The 0-3 connectivity composites are easy to fabricate, which allows for commercial production of these composites in a cost effective manner.

1.6 Properties of Composites:

- Low density
- High stiffness and strength
- Corrosion Resistance
- High Thermal Conductivity
- High Electromagnetic Interference

1.7 Application of BIT composites:

The use of composites rather than metals has saved both cost and weight. Due to corrosion resistance and lightweight properties of composites is widely used in aerospace, defense, automotive, electronics, medical and sports. Composites are used to reduce transmitted mechanical noise from a ship or submarine to the surrounding water. Some examples are cascades for engines, curved fairing and fillets, replacements for welded metallic parts, cylinders, tubes, ducts, blade containment bands etc. Due to its high strength and transparency to electromagnetic waves, it is best choice for mobile phone base stations all over the world.

1.8 Literature Review

1. Giridharan *et al*., [11] found that crystallinity of the BTO film which is deposited on silicon and platinum coated silicon substrate, increases as the annealing temperature increases. Also the dielectric constant and dissipation factor at 1 KHz are 132 and 0.018 respectively. This BTO film show low leakage current density of the order of 10^{-7} A/cm^2.

2. Kong *et al*., [12] prepared thin films of $Bi_4Ti_3O_{12}$ by hybrid sol gel process. They showed that the phase transformation from Pyrochlore to $Bi_4Ti_3O_{12}$ takes place at temperature between 550^{o}C-600^{o}C.The dielectric constant at 1 kHz is ~105 and the thickness of the film formed is ~ 1 μm. Ferroelectric properties of the $Bi_4Ti_3O_{12}$ were discussed as a function of annealing temperature.

3. Nogueira *et al*., [13] synthesized Sillenite phase ($Bi_{12}TiO_{20}$) and Perovskite phase ($Bi_4Ti_3O_{12}$) by Oxidant Peroxide Method (OPM). By this method they conclude that Sillenite phase is formed first at low temperature and then $Bi_4Ti_3O_{12}$ is formed only at higher temperatures.

4. Hao *et al*., [14] found an effective low temperature method for the formation of nanobelts of Bismuth Titanate. They obtained hybrid nanobelts when calcined at low temperature and formation of single phase $Bi_4Ti_3O_{12}$ nanobelts when calcined at high temperature.

5. Subohi *et al*., [15] synthesized Bismuth titanate ($Bi_4Ti_3O_{12}$) by solution Combustion route with urea as fuel. They showed that phase transition from Ferroelectric to Paraelectric occurs at 660^{o}C. The dielectric constant decreases with increase in frequency. Also the remnant polarization and coercieve field are 0.012 μC/cm^2 and 3kV/cm respectively.

6. Li *et al.,* [16] fabricated binary PVDF/$BaTiO_3$ nanocomposites and ternary PVDF/$BaTiO_3$/GN hybrids by solution mixing and compressing molding. They showed that real part of permittivity (□') of PVDF/ $BaTiO_3$ nanocomposites increases with increase in $BaTiO_3$ concentration. They also concluded that dielectric constant and conductivity of the composites were dependent on temperature strongly.

7. Cwikiel *et al*., [17] fabricated $Bi_4Ti_3O_{12}$-PVC composites from ceramics powders and polymer powders by hot pressing method. They showed that for obtaining textured composites

nanopowders should be used. The reason behind the failure of their work was the excessive size of the grains of ceramic powder.

8. Zarycka *et al*., [18] synthesized the randomly oriented $Bi_4Ti_3O_{12}$ (BTO) thin films by modified hybrid sol-gel process. Silicon and Stainless Steel were used as substrate for the growth of thin films by sol-gel spin coating. The surface of the films was smooth, dense and crack free observed by scanning electron microscopy.

9. Stojanovic *et al*., [19] synthesized Bismuth Titanate ($Bi_4Ti_3O_{12}$) by two procedures: mechanically assisted synthesis and polymeric precursor method. The variation in microstructures, grain size, remnant polarization, coercitive field and properties of $Bi_4Ti_3O_{12}$ ceramics were observed. They concluded that mechanically assisted synthesis was more advantageous over polymeric precursor method because of its low cost and widely available oxides as starting materials.

10. Hincapie *et al*., [20] modeled the ferroelectric behavior of $Bi_4Ti_3O_{12}$ through Monte Carlo method. Hysteresis loop of BIT show the coercive field decreases with increase in temperature. They concluded that results obtained by model applied were good match with the experimental reports.

11. Cai *et al*., [21] investigated structure of Bismuth Titanate ($Bi_4Ti_3O_{12}$) by First Principles Method. The Monoclinic structure is more stable than the orthorhombic structure. The results show that refractive index in BTO is higher than in the filled valance band.

12. Osinska *et al*., [22] prepared $BiFeO_3/Bi_4Ti_3O_{12}$ ceramic-ceramic composites from $BiFeO_3$ and $Bi_4Ti_3O_{12}$ by free Sintering method. There was an abrupt increase in permittivity due to excess percolation threshold.

13. Du *et al*., [23] fabricated nanoplate like Bismuth Titanate ($Bi_4Ti_3O_{12}$) powder by modified sol-gel process. They conclude that with increase in temperature BIT grain rapidly grew and merge to adjacent grain. Also, they give much lower synthesis temperature than recorded earlier in literature.

14. Brochin *et al*., [24] observed finite size effects on transport properties of polycrystalline Bismuth (Bi) with different grain sizes. They extracted Band parameters and concluded that

grain boundaries scattering affects the band parameters and causes characteristics deviations from bulk single-crystal behavior.

15. Pookmanee *et al*., [25] fabricated Bismuth Titanate ($Bi_4Ti_3O_{12}$) by Modified Co-precipitation Method. Results of SEM showed that with increase in calcination temperature average parameter size increases. Single phase orthorhombic structure of BIT was obtained after calcination at 1000^oC for 2 hours.

16. Ling *et al*., [26] synthesized Bismuth Titanate ($Bi_4Ti_3O_{12}$) by Metal Organic Decomposition. X-ray diffraction studies revealed that BTO nanocrystal are orthorhombic and has an average size of ~60 nm. Raman and IR data investigated an inactive mode for octahedral which can be explained by a large distortion appearing in BTO.

1.9 Motivation and Objectives

Various investigations mentioned in literature survey are emphasing the importance of polymer-ferroelectric nanocomposites for various electronic applications. Moreover lead free ceramic ferroelectric materials are essential and environment friendly. Therefore, the investigation of this dissertation is aimed at:

- To synthesize $Bi_4Ti_3O_{12}$ nanoparticles.
- To synthesize PVDF- $Bi_4Ti_3O_{12}$ nanocomposite.
- To characterize it by XRD, SEM and DSC.
- Also to confirm the ferroelectricity in $Bi_4Ti_3O_{12}$ by polymerization vs electric field loop.

CHAPTER 2

SYNTHESIS & CHARACTERIZATION TECHNIQUES

2.1 Synthesis

Nowadays ceramic materials are very important for various industrial applications. Ceramic processing is a sequence of operations that systematically changes the chemical and physical aspects of the structure which ultimately affect the physical properties of the material. The aim of the science behind ceramic processing is to identify the important properties and to understand the effect of processing parameters on the structural and physical properties of the materials. There are different methods for the fabrication of different forms of ferroelectric materials as shown in Table. 2

TABLE 2: Different methods for fabrication of ferroelectric materials:

Methods to diff. form of material	Different Routes
Nano	Sol Gel route, hydrothermal synthesis, solvothermal method, Sol Gel Combustion Method etc.
Bulk	Solid state route, Sol Gel method etc.
Thin film	Sol-Gel, Chemical Solution Deposition(CSD), Sputtering , Pulsed Laser deposition and Metal Organic Chemical Vapour Deposition (MOCVD) etc.

2.2 Fabrication of Bismuth Titanate Ceramic:

Out of all above mentioned methods, sol-gel combustion method has many advantages over other methods**.** Therefore we choose it for our dissertation.

2.2.1 Sol-Gel Combustion

It is a new and different method with a combination of two processes i.e., chemical sol-gel process and the combustion process. Nowadays, the sol–gel auto-combustion technique has emerged as an attractive method for the production of high-purity, homogeneous and crystalline oxide powders using inexpensive raw materials. This method involves exothermic and self-sustaining reaction, which is obtained from aqueous solution containing desired metal salts (oxidizer) and organic complexant (reductant) [27]. Proportions between reductant and salts are usually calculated according to the valences of the reacting elements in order to supply the relation of oxidizer/reductant equal to 1[28]. The nitrate salts are favoured as precursors, because they serve as water-soluble low temperature oxidant source for synthesis. In some cases, metal nitrates and reductant are directly mixed together by stirring and heating without adding water. Metal nitrates have the ability to attract and hold water molecules from the surrounding environment; therefore, they easily absorb moisture and become slurry.
The process can be explained by following steps:

- The first step consists of the formation of the sol. A sol is a dispersion of the solid particles (~ 0.1-1 μm) in a liquid where only the Brownian motions suspend the particles.
- An aqueous solution (sol) containing the desired metal salts and organic fuel forms a gel through a sol–gel process.
- The third step is the aging of the gel, in which the gel transforms into a solid mass, accompanied by contraction of the gel network and expulsion of solvent from gel pores.
- The fourth step is drying of the gel, when water and other volatile liquids are removed from the gel network. This process is complicated due to fundamental changes in the structure of the gel.
- Thereafter, the gel is ignited to combust, yielding a voluminous and fluffy product with large surface area.
- After that thermal treatment like calcinations and sintering are given.

2.2.2 Advantages of Sol-Gel Combustion

- The reactants are well-dispersed, providing a homogeneous reaction mixture.
- Reactants are in a much higher reactive state than in the corresponding solid-state reaction precursors.
- The reaction requires less energy, and the initial reaction threshold temperature can be lowered.
- Distribution of the components in mixed solids is more uniform and random because of the homogeneous starting mixture.

2.2.3 Calcination

Calcination is a chemical and physical change in the nature of ceramic produced by heating to high temperatures. Thus calcination means driving out of volatiles. Significant mass loss and a corresponding decrease in density occur in ceramics during the calcination process. The ceramic powder is taken in crucible and calcined in POT furnace at particular temperatures according to sample. Temperature of calcination must be less than the temperature of melting of the materials, which differs from materials to materials. Greater calcinations temperature means that final product is highly homogeneous and can be heated to a greater extent.

2.2.4 Preparation of Sample

Following steps takes place for the preparation of sample:

- Solution-I is prepared by adding Acetic acid in Bismuth nitrate in ratio 30:1. The solution is constantly stirred by magnetic stirrer at $40^{o}C$ for 30 min.
- In this solutions, distilled water is added in ratio H_2O: Bi $(NO_3)_3.5H_2O$ for 6:1.
- Solution-II is prepared by mixing Titanate (IV) Isoproxide in 2-methoxyethanol in ratio 30:1 and stirred by magnetic stirring at $40^{o}C$ for 30 min.
- After that both solution (first and second) are mixed and stirred for 30 min until we get a transparent solution.

- To increase the stability of solution we add 10 ml Acetyl acetone. After adding acetyl acetone the color of the solution gets changed. This solution was remained as it is for 18 hours at room temperature.
- After that it was heated at 40^{o}C on magnetic stirrer along with stirring and after desirable time gel is formed. Gel is dried and Combustion takes place which gives us powder.
- Then we grind the powder and bring it more fine form with help of Mortar Pestle.
- Then it was Calcined at 500^{o}C for 14 hours.

2.2.5 Experimental Flowchart

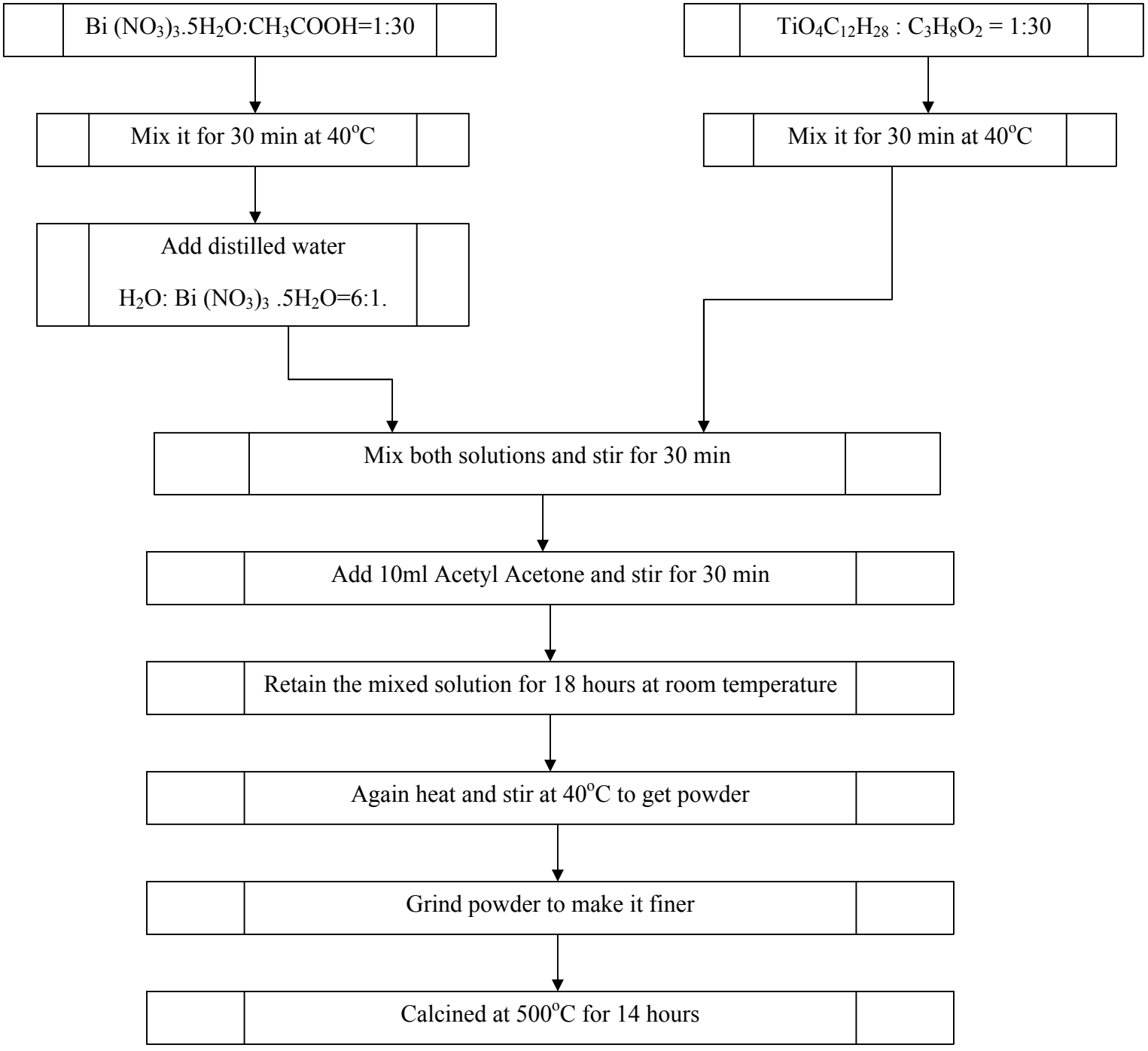


Fig.4: Flow chart for the preparation of BIT by sol-gel combustion method.

2.3 Synthesis of Ceramic/Polymer Composite

Fabrication of composite materials is accomplished by a wide variety of techniques, such as: Advanced fiber placement (Automated fiber placement), Tailored fiber placement, Fiberglass spray lay-up process, Filament winding, Lanxide process, Tufting, Z-pinning, Solution Casting Method and Hot Pressing Method. Composite fabrication usually involves wetting, mixing or saturating the reinforcement with the matrix, and then causing the matrix to bind together (with heat or a chemical reaction) into a rigid structure. The operation is usually done in an open or closed forming mold, but the order and ways of introducing the ingredients varies considerably.

2.3.1 Solution Casting Method

Solution Casting method is one of the most traditional and simple method for the Casting polymer/ceramic composite films. In this method, polymer and ceramic are mixed in the adequate amount of solvent according to wt%. The thickness of the film formed can be in µm or nm.

2.3.2 Preparation of composite

Process of formation of composite can be explained as under:

- Add polymer (PVDF) to solvent Dimethylformamide (DMF) and heat it at 70^{o}C until the solution become viscous on the magnetic stirrer.
- Now add Bismuth Titanate with weight percentage ratio and continue heating on magnetic stirrer at 70^{o}C for 30 min.
- After that pour the solution in petri-dish and remain it at room temperature for casting.
- After sometime put the petri-dish on hot plate and heat it at 70^{o}C.
- This will give us crack free thin film of thickness of µm or nm.

2.3.3 Experimental Flow Chart

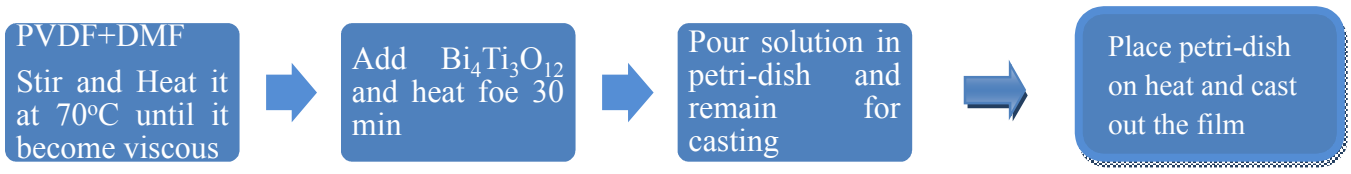


Fig 5: Flowchart for the preparation of thin film composite

2.4 Characterization Techniques

Characterization refers to the use of external techniques to probe into the internal structure and properties of a material. Characterization can take the form of actual materials testing, or analysis, for example in some form of microscope. Analysis techniques are used simply to magnify the specimen, to visualize its internal structure, and to gain knowledge as to the distribution of elements within the specimen and their interactions. For this we use various techniques such as Scanning Electron Microscope (SEM), Transmission Electron Microscope (TEM), X-Ray Diffraction (XRD), Energy dispersive Spectroscopy (EDS), Differential Scanning Caloriemetry (DSC), Let us discuss some of them.

2.4.1 X-Ray Diffraction (XRD)

The X-ray diffraction technique is used to determine the atomic arrangements (i.e., crystal structure) of the materials because the interplanar spacing (d-spacing) of the diffracting planes is of the order of X-ray wavelength. For a crystal of given d-spacing and wavelength λ, the various orders n of reflection occurs only at the precise values of angle θ which satisfies the Bragg condition

$$2d \sin\theta = n\lambda$$

Fig.6: **XRD apparatus.**

About 95% of all solid materials can be described as crystalline. When X-rays interact with a crystalline substance (Phase), one gets a diffraction pattern. The X-ray diffraction pattern of a pure substance is, like a fingerprint of the substance. The powder diffraction method is thus ideally suited for characterization and identification of polycrystalline phases. The main use of powder diffraction is to identify components in a sample by a search/match procedure. Furthermore, the areas under the peak are related to the amount of each phase present in the sample. The most common use of powder (polycrystalline) diffraction is chemical analysis. This can include phase identification (search/match), investigation of high/low temperature phases, solid solutions and determinations of unit cell parameters of new materials. The accurate determination of interplanar spacing, lattice parameters etc. provides an important basis in understanding of various physical properties of materials.

For structural characterization of the material, the X-ray diffraction (XRD) patterns of all the compounds have been recorded at room temperature (25^0C) using X-ray powder diffractometer (Philips X-ray diffractometer) with Cukα radiation (λ = 1.5405 Å) in a wide 2θ (Bragg angle) range ($20^0 \leq 2\theta \leq 80^0$).

2.4.2 Scanning Electron Microscopy (SEM)

The scanning electron microscope (SEM) is one of the most versatile instruments available for the examination and analysis of the microstructure morphology and chemical composition characterizations. The combination of high resolution, an extensive magnification range, and high depth of field makes the SEM uniquely suited for the study of surfaces. SEM micrograph was taken on the fractured surface of the sample using scanning electron microscope (SEM: JSM-6510LV scanning microscope JEOL).The samples were made conducting by coating a thin layer of platinum using a sputter coater.

Fig 7: Apparatus of Scanning Electron microscope.

2.4.3 Energy Dispersion Spectroscopy (EDS)

Energy-dispersive spectrometers (EDSs) employ pulse height analysis: a detector giving output pulses proportional in height to the X-ray photon. A solid state detector is used because of its better energy resolution. Incident X-ray photons cause ionization in the detector, producing an electrical charge, which is amplified by a sensitive preamplifier located close to the detector. Both detector and preamplifier are cooled with liquid nitrogen to minimize electronic noise. EDS makes use of the X-ray spectrum emitted by a solid sample bombarded with a focused beam of electrons to obtain a localized chemical analysis. All elements from atomic number 4 (Be) to 92 (U) can be detected in principle, though not all instruments are equipped for 'light' elements ($Z < 10$). Qualitative analysis involves the identification of the lines in the spectrum and is fairly straightforward owing to the simplicity of X-ray spectra.

2.4.4 Differential scanning calorimetry (DSC)

Fig 8: Apparatus of Differential Scanning Calorimetry

In the differential scanning calorimetry (DSC), heat is supplied by using the electrical energy to the reference material or the sample to maintain both the substances at the same temperature. The rate of heat flow is measured as a function of temperature. In DSC, the measuring principle is to compare the rate of heat flow to the sample and to the reference material which are heated or cooled at the same rate. The phase transitions in the sample which are associated with absorption or evolution of heat cause a change in the differential heat flow which is then recorded as a peak. The area under the peak is directly proportional to the enthalpic change and its direction indicates whether the thermal event is endothermic or exothermic. The DSC measurements of the films were carried out at 10^0C/min in the temperature range of 30 to 250^0C and 10 mg of the samples were used.

CHAPTER 3

RESULTS AND DISCUSSION

The structural, morphological and elemental analysis of ceramic is carried out by using XRD, SEM, EDS and DSC respectively. The thermal study of Nano composite has also been done.The Results of these experimental investigations are discussed in the subsequent subsection.

3.1 XRD Analysis of Bismuth Titanate Ceramic:

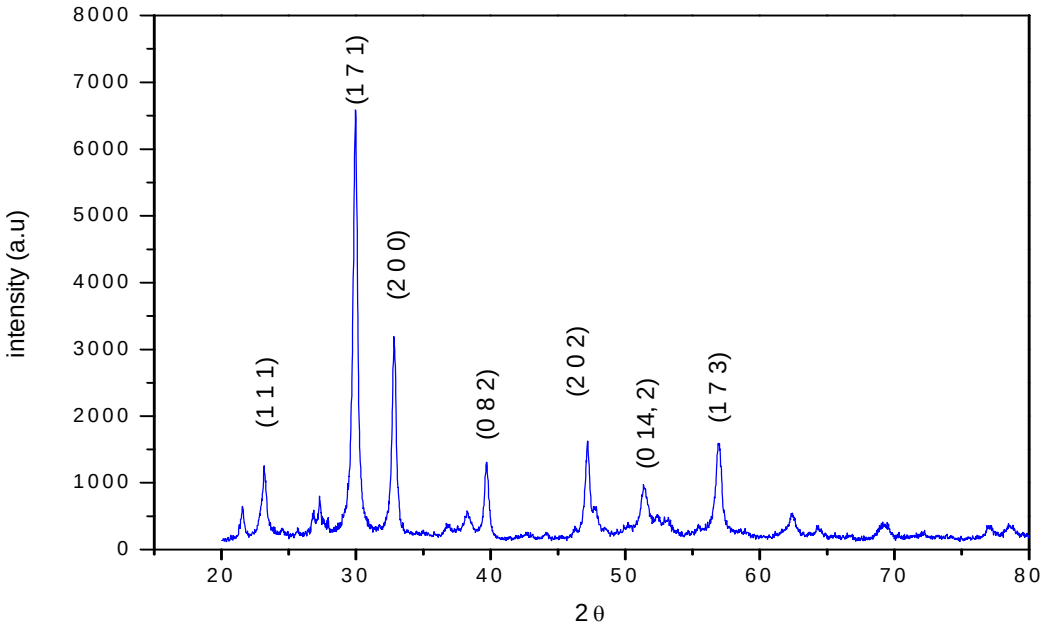


Fig 9: XRD Pattern of Bismuth Titanate Ceramic

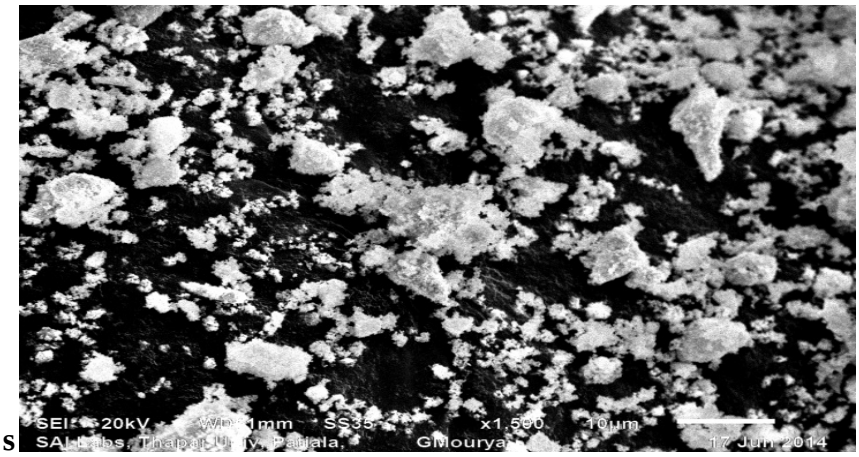
The as derived BIT powder was amorphous but transform to crystalline BIT after calcination at 500^{o}C for 14 hours. Fig 9 show the XRD analysis of nanoparticle where all the peaks are indexed and well matched to the orthorhombic structure. The lattice parameter of calcined BIT obtained

from XRD analysis are a = c = 5.4489Å, b= 32.8156Å (File name xrd2288). The crystallite size of BIT nanoparticles was found to be □ 19nm which was calculated by Scherrer's formula

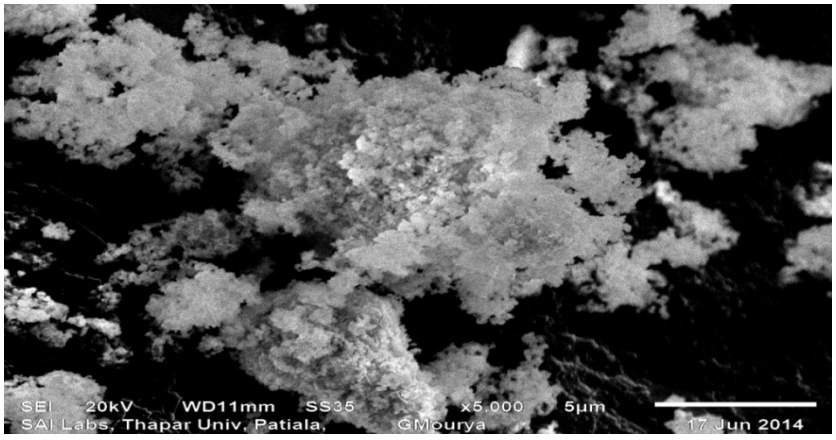
$$d = \frac{k\lambda}{\beta cos\theta}$$

where k is the shape factor (k = 0.94), λ is the x-ray wavelength, β is the line broadening at half the maximum intensity (FWHM) in radians, and θ is the Bragg's angle, d is the crystallite size.

3.2 SEM Analysis of Bismuth Titanate:



(A)



(B)

Fig 10: SEM micrograph of BIT at different magnifications.

SEM micrograph of Calcined powder of Bismuth Titanate with different magnification is shown in the fig.10. Sample shows good surface morphology with particle size □19 nm. Bismuth Titanate is formed in fine powder form with no clustering.

3.3 EDS of Bismuth Titanate Ceramic:

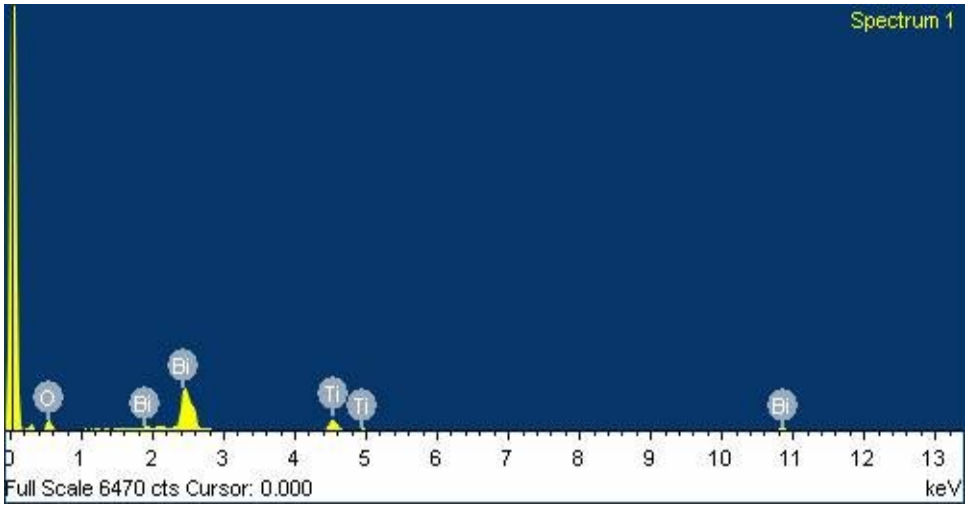


Fig 11: EDS Spectrum of BIT.

To find the elements present in the sample fabricated, EDS (Energy-dispersive spectroscopy) was performed on the samples along with SEM analysis.

Fig 11 shows the EDS spectrum of BIT.

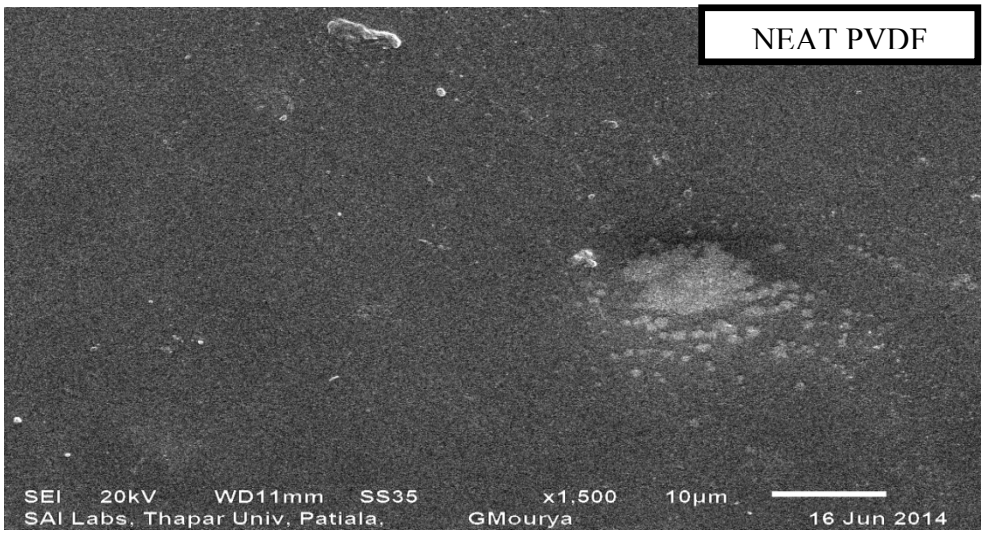
TABLE 3: Stochiometric composition of Bismuth, Titanium and Oxygen

Element	Atomic%
Oxygen	76.40
Titanium	10.18
Bismuth	13.41

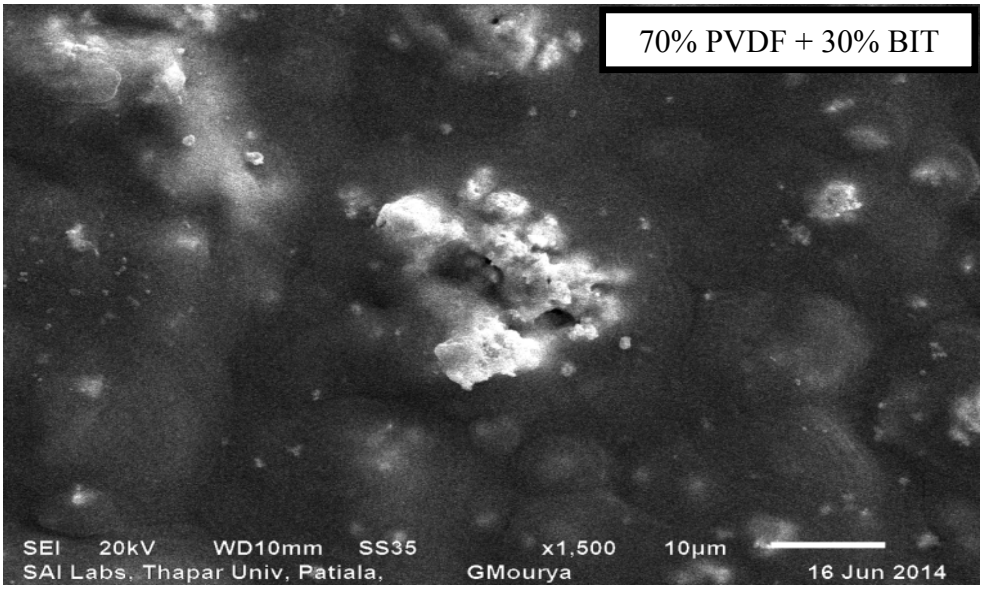
TABLE 4: Stochiometric ratio of Bismuth, Titanium and Oxygen

Composition	Ratio of Bi/Ti	Ratio of Bi/O
$Bi_4Ti_3O_{12}$	1.3	5.6

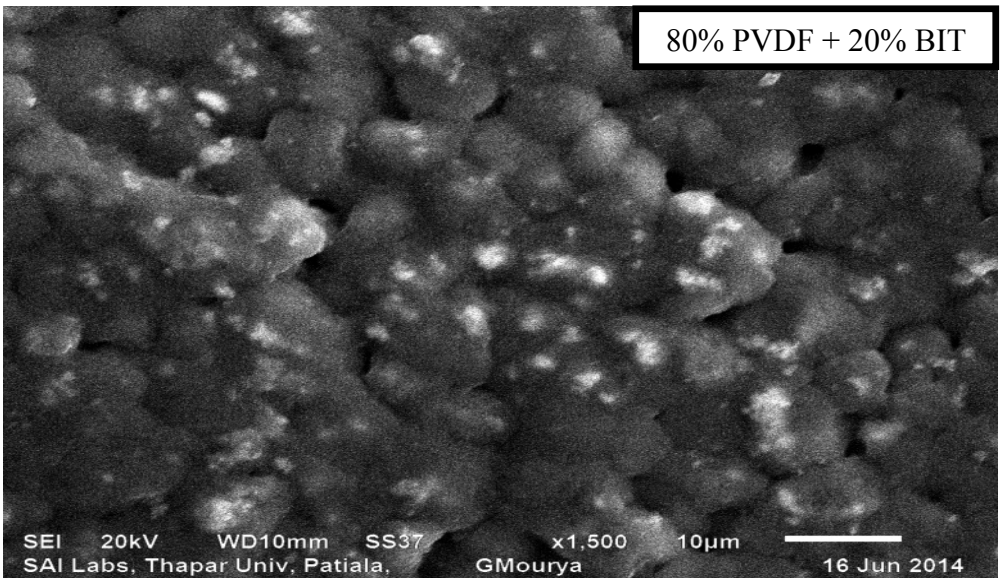
3.4 SEM of BIT/PVDF Composite:



(A)



(B)



(C)

Fig 12: SEM micrograph of (A) Pure PVDF and (B) 70%of PVDF + 30% BIT nanocomposite (C) 80% of PVDF + 20% of BIT nanocomposite

The SEM Morphology of prepared powder are presented in fig 12. It can be seen that nanoparticles are embedded in the PVDF matrix. As the weight % of BIT increases in PVDF matrix, the connectivity of the particle within matrix decreases. Properly dispersed nanoparticles in PVDF matrix has been synthesized and confirmed from the SEM analysis. The lighter region shows ceramic BIT and the darker region represents polymer matrix.

3.5 DSC of BIT/PVDF Composite:

The differential thermal analysis of the prepared films with different compositions is shown in fig 13. Crystallinity has been calculated by the formula

$$X= \Delta H/\Delta H^0$$

where ΔH^0 is the Heat of Fusion for the 100% crystalline PVDF and its value is 104.6 J/g. The Composites samples are heated in liquid Argon atmosphere from temperature ranging from 30 to 250^0C. With the increase of weight percentage crystallinity is found to increase. Percentage crystallinity of composite is given by 80.86% for weight percentage ratio of PVDF: BIT equals to 7: 3 and 50.2%for 8: 2.

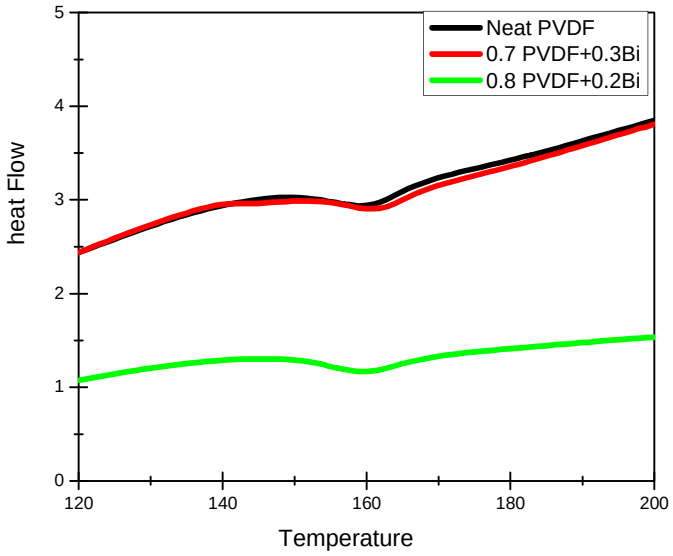


Fig 13: DSC curves of BIT/PVDF naocomposite.

CHAPTER 4

CONCLUSION & FUTURE SCOPE

The conclusions of characterization and synthesis are follows:

4.1 Conclusion

The discussed results in earlier chapter can be concluded as follows.

- The BIT powder has been successfully synthesized by Sol Gel Combustion method.
- The XRD studies has confined the BIT crystallizes into single orthorhombic phase with lattice parameter a = c = 5.4489Å, b= 32.8156Å.
- The crystalline size is calculated by using Debye Scherer's formula and it is found to be ~19 nm.
- The SEM studies show the good morphology with fine nanoparticles.
- The EDS studies of BIT show the stochiometric ratio is given by 1:5.
- The BIT/PVDF Composite has been synthesized by Solution Casting Method.
- The SEM studies shows nanoparticles are embedded in the PVDF matrix. Connectivity decreases with increase in weight % of BIT in PVDF matrix.
- The DSC studies shows change in Heat flow with change in temperature. Crystallinity inecreases with increase in weight % of BIT in PVDF.
- % crystallinity for 0.7 PVDF+0.3 BIT is 80.86% and for 0.8 PVDF+0.2 BIT is 50.2%.

4.2 FUTURE SCOPE

Ferroelectric $Bi_4Ti_3O_{12}$ is a widely studied composition and its composites with polymer have good electronics application. The studies present in my thesis are very preliminary in nature. Therefore, some valuable and applicable investigation of BIT and its composites with polymers are required. The following are the suggestion for the future scope of studies:

- The curie temperature of $Bi_4Ti_3O_{12}$ is very high. Hence its composite with polymer could be investigated for high energy capacitors.
- The dielectric relaxation phenomenon of PVDF- $Bi_4Ti_3O_{12}$ nanocomposites could be informative for enriching the physics.

REFRENCES

1. V. G. Sukumaran and N. Bharadwaj, *Trends* in *Biomaterials* & *Artificial Organs*, **20**, 7 (2006).
2. G. H. Haertling, *Journal of the American Ceramic Society*, **82**, 797 (1999).
3. Charles Kittel, *Introduction to Solid State Physics*, Wiley India Edition, (2008).
4. T. Takenaka, K. Maruyama, K. Sakata, *Japanese journal of Applied Physics*, **30**, 2236 (1991).
5. T.Takanaka, H. Nagata, *Journal of the European* Ceramic Society, **25**, 2693 (2005).
6. B. Aurivilius, *Arkiv Kemi,* **1,** 494 (1949).
7. Z. Lazarevic, B. D. Stojanovic, J. A. Varela*, Science of Sintering*, **37**,199 (2005).
8. E. Cummins, L. E. Cross, *Journal of Applied Physics,* **39,** 2268 (1968).
9. M. Villegas, C. Moure, J. F. Fernandez, P. Duran, *Ceramics* International **22**, 15 (1996).
10. R. E. Newnham, L. J. Bowen, K. A. Klicker, L. E. Cross, *Materials in engineering*, **2,** 93 (1980).
11. N. V. Giridharan, S. Madeswaran, R. Jayavel, *Journal of Crystal Growth,* **237,** 468 (2002).
12. L. B. Kong, J. Ma, *Thin Solid Films*, **379**, 89 (2000).
13. A. E. Nogueira, E. Longo, E. R. Leite , E. R. Camargo, *Journal of Colloid and Interface Science* ,**415**, 89 (2014).
14. P. Hao, Z. Zhao, J. Tian, Y. Sang, G. Yu , H. Liu , S. Chen , W. Zhou., *Acta Materialia,* **62**, 258 (2014).
15. O. Subohi, G. S. Kumar, M. M. Malika, R. Kurchania., *Optik,* **125**, 820 (2014).
16. Y. C. Li, S. C. Tjong, R. K. Y. Li, *eXPRESS Polymer Letters.,* **5,** 526 (2011).
17. E. N. Ćwikiel, H. Bernard, *Condensed Matter Physics*, **16**, 31705 (2013).
18. A. Zarycka, A. L. Czekaj, J. Czuber, T. Orkisz, J. Ilczuk, D. Czekaj, *Journal of Materials* Science , **23**, 1 (2005).
19. B. D. Stojanovic, A. Z. Simoes, C. O. P. Santos, C. Quinelato, E. Longo, J. A. Varela, *Ceramic International,* **32**, 707 (2006).

20. C. M. B. Hincapie, E. R. Parra, J. C. R. Rojas, J. J. O. Flores, J. E. Alfonso, *Computational Materials Science,* **62**, 131 (2012).
21. M. Q. Cai, Z. Yin, M. S. Zhang, Y. Z. Li, *Chemical Physics Letter,* **401**, 405 (2005).
22. K. Osinska, A. L. Czekaj, H. Bernard, J. Dzik, M. Adamczyk, D. Czekaj, *Archieves of Metallurgy and Materials,* **56,** 1093 (2011).
23. X. Du, Y. Xu, H. Ma, J. Wang, and X. Li, *Journal of the American Ceramic Society*, **91**, 2079 (2008).
24. F. Brochin, B. Lenoir, C. Bellouard, and H. Scherrer., *Physical Review B*, **63,** 073106 (2001).
25. P. Pookmaneea, S. Phanichphant, *Journal of Ceramic Processing Research*, **10,** 448 (2009).
26. Z. C. Ling , H. R. Xia , W. L. Liu, H. Hand, X. Q. Wang , S. Q. Sun, D. G. Ran, L. L. Yu., *Materials Science and Engineering B,* **128,** 156 (2006).
27. M. Airimioaei, C. E. Ciomaga, N. Apostolescu, *Journal of Alloys and Compounds*, **31**, 8065 (2011).
28. A. C. F. M. Costa, M. R. Morelli, R. H. G. A. Kiminami, *Journal of Materials Synthesis and Processing*, **9,** 347 (2001).