Optimization of chemical parameters to develop lead-free piezoelectric films for energy harvesting applications

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Abstract

Piezoelectric material is one of the popular ways to harvest ambient mechanical energy in to electrical energy. The most widely used piezoelectric material is Lead Zirconate Titanate (PZT) as it possesses high electromechanical and piezoelectric properties in numerous applications but it not eco-friendly. In search of the lead-free piezoelectric material Sodium Bismuth Titanate (NBT) is one of the potential piezoelectric materials to give more piezoelectric constants compared to other lead-free materials. The present work is focused on to achieve pure stoichiometric Sodium Bismuth Titanate (NBT) phase in the film which is spin coated by NBT sol prepared by sol gel technique. The preparation of NBT sol and spin coating it on a substrate (platinized silica) involves many process parameters which affects the film thickness as well as its qualitative properties. Chemical parameters like rheology, pH & concentration of NBT sol change its viscosity which in turn changes the film properties. Spinning parameters like spin speed, spinning time and heating conditions also affects the final thickness of the film. NBT sol shows a linear relationship between shear rate and shear stress indicating it to be Newtonian fluid. Films with an approximate thickness of around 450 nm and film surfaces with an average roughness of about 40 nm are obtained by NBT sol with pH 2 without stoichiometric NBT phase in it. Films shows the presence of Bismuth Titanate ($Bi_2Ti_2O_7$) a pyrochlore phase which also possesses piezoelectric properties. Pure stoichiometric NBT phase with some amount of impurities is obtained in the powder samples of NBT.

Nomenclature

P	induced polarization
S	applied stress
E	applied electric field
ϵ	induced strain
D	piezoelectric coefficient linking these parameters
$[\eta_i]$	intrinsic viscosity or limiting viscosity number
M	molecular weight of polymer
K	empirically determined constants
a	solvent-polymer interaction parameter
$[\eta]$	Viscosity in the absence of the solute (solvent)
Ø	volume fraction of the solute in the solution
η	viscosity of the solution
$\eta_\circ$	viscosity of solvent
γ_{SV}	Specific energy of solid-vapor interface
γ_{SL}	Specific energy of solid-liquid interface
γ_{LV}	Specific energy of liquid-vapor interface
θ	contact angle

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Chapter 1

Introduction

2.1 Energy harvesting

There is abundant amount of energy available in our environment. The challenge is to convert that available ambient energy in to usable electrical energy to power an application i.e. energy harvesting. The process to extract small amount of energy from ambient available energy is known as energy harvesting. And the possible available sources of energy for harvesting are mostly ambient light (artificial or natural light), thermal energy sources, mechanical and ambient radio frequency. Technology is reaching a point where we can make practical useful systems down to the millivolts or even lower range, and in that range it is possible to harvest some energy from the environment. Using piezoelectric material is one of the popular ways to harvest ambient mechanical energy in to electrical energy. If an input vibration is applied on to the piezoelectric material it causes mechanical strain to develop in it which is converted to electrical charge which can be utilized for several applications.

2.2 Introduction to Piezoelectricity and Applications

Piezoelectric effect (the accumulation of electric charge on the surface of an element or material when it is mechanically strained) was first discovered by Curie brothers in 1880 in quartz crystal. Later on converse piezoelectric effect was also discovered as when a piezoelectric material is subjected an electric field in undergo deformation in nanoscale dimensions. There are numerous applications based on piezoelectric motion harvesting energy from the ambient available energy. Both direct as well as converse piezoelectric effects have been implemented for a wide range of sensors, actuators and transducer applications. High power and high temperature piezoelectric materials have been increased used and expanded significantly in past few years. Various applications exist where sensors,

actuators and transducers are operated at elevated temperature [1]. Piezoelectric materials have been used in various sectors such as medical, aerospace, nuclear and also in electronic industry as either tilt sensor or pressure sensor [2]. It can also be used to determine the aroma in the air simultaneously with sensor based application as electronic nose [3]. Bone is a naturally occurring piezoelectric material as it contains collagen which can act as a biological force sensor [4, 5]. Piezoelectric actuators have been used in controlling the small valves within the Diesel Fuel Injector, in piezoelectric motor, ultrasound cleaning, as stack actuators, stripe actuators. Vibrations from industrial machinery can also be harvested by piezoelectric materials to charge batteries for backup supplies or to power low-power microprocessors and wireless radios [6]. Atomic force microscopes and scanning tunneling microscopes employ converse piezoelectricity to keep the sensing needle close to the specimen [7].

2.3 Lead-based & lead-free piezoelectric materials

The most widely used piezoelectric material used so far is Lead Zirconate Titanate (PZT) as it has high electromechanical and piezoelectric properties. It has a very high Curie temperature which enables it to use in high temperature applications. It has a high dielectric constant i.e. it has high capacity to store electric charge in it [8]. But the presence of lead in PZT makes it harmful to use it in electrical and electronic applications as lead oxide is a toxic material and vaporizes in air and if inhaled by human while respiration is readily soluble in bloodstream which may cause deleterious effects on many important organs of the body including central nervous system and kidneys and if children are exposed to chronic lead it impairs the neurological and intellectual development [8, 9, 10, 11]. So due to the health risk posed by lead, it has been included in the Restriction of Hazardous Substances directive of European Union which limits the use of material containing lead in various electrical devices which are often encountered by human beings [12]. The directive calls for the substitution of this lead based material with environmentally-friendly alternatives. This directive call leads to considerable research in an attempt to find an alternative for this lead-based material [8, 13, 14]. In search of the lead-free piezoelectric material Sodium Bismuth Titanate (NBT) and Potassium Bismuth Titanate (KBT) are found to give more piezoelectric constants compared to other lead-free materials. The present work is focused on Sodium Bismuth Titanate (NBT) which is prepared by Sol gel technique and then this NBT sol is spin coated to give uniform thin film as this material shows the potential to be a good piezoelectric material [15, 16]. NBT thin film solutions are prepared

by Sol gel route as it offers a homogenous, inexpensive and allows low temperature processing compared to other routes to make a thin film. Depending on the operations that the sol gel process has been accompanied with various products can be made using the same solution. The homogenous solution so formed by sol gel route is then spin coated on a flat substrate which has many advantages over other sophisticated processes available to deposit a thin film.

2.4 Objective

To get stochiometric Sodium Bismuth Titanate ($Na_{0.5}Bi_{0.5}TiO_3$) NBT phase in the film formed by sol gel route via spin coating.

To optimize the chemical as well as spinning parameters to get a uniform NBT thin film for energy harvesting application.

The solution obtained from the sol gel route is affected by various other parameters involved in process. The type and quantity of metal precursor plays an important role in forming the metal chain in the sol. The choice of solvents in which the metal precursor is dissolved also plays an important role. The sol is greatly affected by the pH of the medium, as if the sol medium is acidic then it results in the formation of linear long metal chain in the sol and if the sol medium is basic then branched metal chain forms leading to increase the weight of the metal chain so formed thereby increasing the viscosity of the sol. Concentration of sol is related to the amount of metal precursor used to prepare the sol. High concentration sol requires more amount of metal precursor in it which in turns affects the viscosity of the sol. The viscosity of the sol is also an important parameter which affects the final thickness of the film formed by spin coating as if a viscous sol is spin coated keeping the other parameters constant it results in film with higher thickness and vice versa. When the sol is applied to the substrate for spin coating, the rheology that the sol exhibits will gives a broad idea to set the other process parameters. The rotation speed and the time for which the substrate is allowed to rotate greatly affect the thickness of the film. Heat treatment given to the coated substrate to dry and eventually evaporate the solvent from the coated film also has to be optimized. The annealing temperature greatly affects the crystallinity of the thin film so formed. Annealing is done to improve the grain size of NBT which also has to be optimized.

In this work, the very first aim is to get a stochiometric phase of Sodium Bismuth Titanate (NBT) in spin coated film after annealing. The stoichiometry of NBT is very complex, so it's very difficult to get a proper stochiometric phase of NBT in the film, and once stochiometric NBT phase forms in the film then the chemical and spinning parameters are to be optimized to get a desired thickness of the film for specific application.

Chapter 2

Literature Review

Sodium Bismuth Titanate (NBT) was first reported by Smolensk et. al. in the early decades after unusual ferroelectric and piezoelectric effect was observed in synthetic materials other than naturally occurring piezoelectric materials [17]. It is one of the several others lead-free materials which has received huge amount of attention in the recent past few decades. In 2002, Jones and Thomas found that NBT expresses rhombohedral crystal symmetry at room temperature which changes to tetragonal and then subsequently to cubic crystal symmetry during heating. The most commonly used piezoelectric materials were lead based e.g. lead zirconate titanate (PZT), lead magnesium niobate (PMN) etc. which shows high electromechanical and piezoelectric properties and has high Curie temperature. However, the toxicity posed by lead oxide during the sintering process which has a serious impact on human health as well as environment results in the development of low-lead or lead-free piezoelectric materials which has properties comparable to those lead-based materials. As a result many studies have been devoted in search of lead-free piezoelectric materials. NBT is one of the promising piezoelectric material which has a potential to replace all the lead-based compounds as it large polarization, high temperature dielectric constant and more importantly high Curie temperature which enables NBT to be used in high temperature applications [18, 19].

It has been proposed that Sodium Bismuth titanate (NBT) is a promising lead-free piezoelectric material which was synthesized by sol-gel technique and its thin films were deposited on a platinized (Pt/TiO2 /SiO2/Si) silica wafer by spin coating method where the piezoelectric response and microstructure of this thin films were studied which shows that the properties of these thin films were dependant on the process of fabrication of the films as well as the annealing temperature. Presence of NBT phase was reported in it. The dielectric constant and remnant polarization of the film increases with annealing

temperature and thickness of the NBT film. It reports that the electrical properties are strongly dependant on the thickness of the NBT film. The grain size is strongly affected by the annealing temperature as the size increases with annealing temperature [16, 20]. NBT has some high coercive field and high conductivity which causes problem while poling. So, to further improve the properties of NBT, it can be doped by other materials which enhances its several other properties as well. Morphotropic Phase Boundary (MPB) was reported when NBT was doped by slight amount Barium Titanate (BT) where exist an intimate coexistence of rhombohedral and tetragonal structures which reports significant enhancement in the dielectric permittivity and reported best ferroelectric responses in BNBT systems [21, 22]. MPB was also reported in potassium doped NBT prepared by sol gel technique and the spin coated thin films on platinized silica wafer with rapid thermal annealing. It reported that near MPB in this NKBT material, the film exhibit large grain size, high dielectric permittivity and a very large remnant polarization along with high electrostrictive properties [23, 24]. Sol gel is a wet chemical process for producing solid materials from small molecules which involves conversion of monomers in to colloidal solution known as sol that acts as a precursor for an integrated network (gel) of either discrete particles or network polymer. This sol is then coated on to the substrate by spin coating method which is one of the prominent methods to produce uniform thin film. There are several process parameters which affects the quality of the film produced via sol gel synthesis of the sol and spin coating method. The sol gel synthesis has a wide range of application as a number of useful products ranges from uniform small particles of nanosize to dense ceramic which can be derived from the same initial composition of the sol depending on the mechanical operation it has undergone. Various models have been developed in past keeping the process parameters that affect the film quality. The pioneer description of the flow of viscous fluid on rotating disk i.e. spin coating was given by Emslie et. al. where he simply modeled the spin coating process assuming the solution to be Newtonian (viscosity of the fluid remains constant) and all the solvent evaporates after spinning. It was reported that for a Newtonian fluid the solution of hydrodynamic equations leads to asymptotically to a uniform thickness layer of the coated fluid which in turns depends on the rotating speed, viscosity of fluid and time for which it was allowed to rotate. The thickness of the film was reported to decrease with spin speed and spin time as well [25]. In many cases, the coating material shows a Non-Newtonian behavior like the polymeric solution or paints and pitches where the sol is applied in the form of solution from which solvent evaporates. This evaporation of solvents was incorporated in model developed by Meyerhof where it was reported that the film thickness h was greatly affected

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by spin speed f, initial viscosity v_o and evaporation rate e of the solvent. The dependence was given by $h \propto f^{-2/3} vo^{1/3} e^{1/3}$ [26]. This model does not incorporate the solid concentration of the fluid and the shear stress that in turn develops above the rotating substrate and the ambient air. However the model proposed by Meyerhof includes the evaporation of the solvent at the later stages of the spin coating process suggesting that the fluid flow and the evaporation are decoupled stages. Yimsiri et. al. modified the model suggesting that the evaporation of the solvent is occurring simultaneously along the flow of the fluid during the spin off stage in spin coating. It was reported that the process conditions as well as the solution properties are the influencing factors to form a uniform film with the desired thickness of light emitting polymer (LEP) solution [27]. The model developed by Sahu et. al. elucidates the dominant mechanism in the film formation and establishes a relationship between film thickness and time including the evaporation of the solvent and the shear stress developed at the interface between the layer of the film and the surrounding air in extension of the Non-Newtonian fluid [28]. Britten et. al. developed a model for shear thinning fluid (Non-Newtonian) where it was reported that the non-uniformity of the spin coated multilayer films of silica/alumina for high reflector application depends on the rheology of the solution to be deposited. A model was developed considering the shear thinning behavior of the solution which shows the agreement of the experimental and the predicted thickness of the coated films to be uniform throughout the substrate except with non-uniformity at the center of the substrate [29]. A study on the silica xerogel by Huang et. al. reports that the sol of silica prepared by sol gel technique is affected by the medium of sol. The gelation point is dependent on the pH of the solution medium of silica which changes the rheology of the sol from Newtonian to Non-Newtonian. It was reported in the systematic study that there exists a process window between the aging time and the spin speed during coating to obtain uniform and defect free films. It was also reported that the viscosity of the silica sol and the initial concentration of the solid silica in the starting solution influences the quality of the film [30]. The effect of the initial concentration of the sol was studies by Holowacz et. al. which influences the thickness of the film [31].

Chapter 3

Methodology

4.1 Piezoelectricity

A material when subjected to a mechanical strain it produces a static electric charge on it, such material is called as piezoelectric material and the phenomena is called as piezoelectricity. And conversely when such material is subjected to an electric charge they undergo deformation, this phenomena is called as reverse or converse piezoelectricity. The direct piezoelectric effect can be described as:

where, σ is the applied stress,

$$P_i = d_{ijk} \sigma_{jk}$$

P is the induced polarization

and the reverse or converse piezoelectricity by:

$$\epsilon_{ij} = d_{ijk} E_k$$

where, E is the applied electric field,

ϵ is induced strain,

d is a piezoelectric coefficient linking these parameters

Piezoelectric materials have a unique ability to couple electrical and mechanical displacements, i.e., to change electrical polarization in response to an applied mechanical

stress or mechanically strain in response to an applied electric field. They are commonly used in sensor and actuator technologies, high voltage and power sources. Application of piezoelectric material ranges from buzzers to diesel engine fuel injector, nanopositioners in scanning microscopes, as a probe in atomic force microscopy, sonar, ultrasound, disc drives, inkjet printers, air bag sensor etc.

4.1.1 Fundamentals of Piezoelectricity

Piezoelectric materials undergo a small change in dimension when subjected to an external force such as an applied electric field, a mechanical stress or a change in temperature (applying heat). Such small change in dimension results in a change in the electric polarization depending on the material structure which gives rise to the occurrence of piezoelectric effects. Piezoelectric materials are single crystal or polycrystalline materials composed of crystallites which have a definite chemical composition, with the molecules made up of positive ions (atoms sharing a part of their valence electron with others) and negative ions (atoms receiving part of electron from others) occupying the lattice sites to constitutes a crystal structure lattice which implies that piezoelectric materials are polar in nature and are electrically ordered. The smallest repeating unit of the lattice is known as unit cell and the specific symmetry of the unit cell determines whether the crystal exhibits piezoelectric effects. There are in total 32 point groups which are classified on the basis of the symmetry elements of translational position and orientation. Fig. 1 shows the classification of crystals in three prominent classes with piezoelectric, pyroelectric and ferroelectric effects. Out of this 32 point groups, 11 classes (or point groups) are centrosymmetric and 21 classes are non-centrosymmetric. A centrosymmetric crystal is a crystal in which the movement of any point whose coordinates are defined as x, y, z with respect to the origin of the symmetry to a new point –x, -y, -z does not have any significant difference which implies that centrosymmetric crystals are non-polar in nature and does not possess a finite polarization or dipole moment. A non-centrosymmetric crystal does not possess any center of symmetry which is the only crystallographic requirement for a material to exhibit piezoelectricity. [35]

Only 20 non-centrosymmetric classes exhibit piezoelectric effect. Out of this 20 point groups, 10 classes exhibit electric polarization which can be induced due to mechanical stress whereas other 10 classes possess spontaneous electric polarization which means they are permanently polar in nature and thus can have both piezoelectric as well as pyroelectric effects. This 10 point groups have a subgroup known as 'Ferroelectric' which possesses

reversible spontaneous polarization [35]. This subgroup can exhibit all three effects namely
– piezoelectric, pyroelectric and ferroelectric.
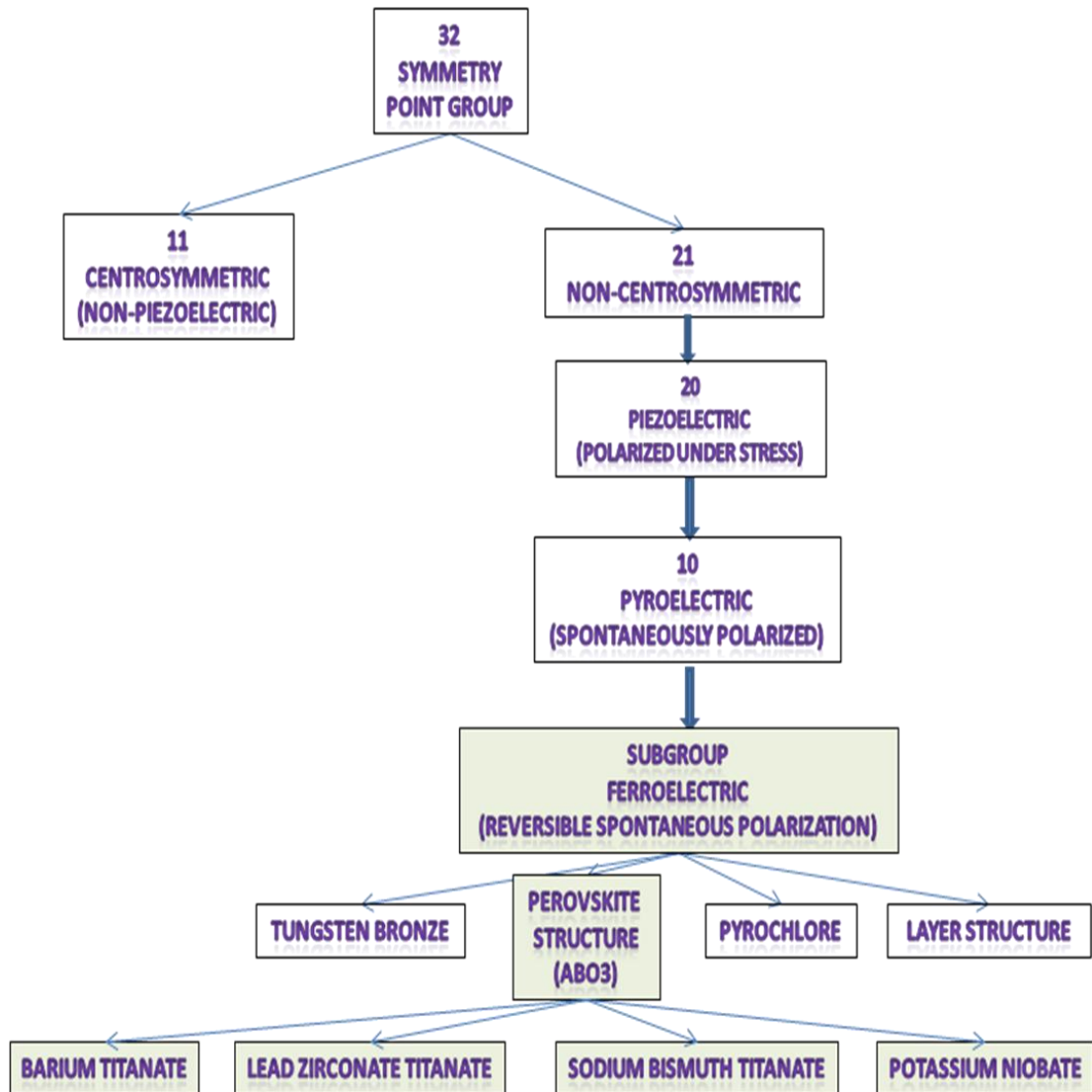
Figure 1: Classification of crystals showing the classes with piezoelectric, pyroelectric and ferroelectric effects

4.1.2 Ferroelectricity

Ferroelectric effect is empirical phenomenon distinct from piezoelectric and pyroelectric effects in that it exists with a reversible spontaneous polarization; ferroelectric material therefore shows a dielectric hysteresis loop.

Fig. 2 shows the ferroelectric hysteresis loop between applied electric field and polarization induced in the material. When an electric field is applied to a ferroelectric material the

domains (the regions of the crystal with uniformly oriented spontaneous polarization) starts to align in the direction in which the electric field is applied till saturation of polarization is reached. The saturation polarization (Ps) is reached when all the ferroelectric domains are aligned in the direction of applied field. When the intensity of the

Ferroelectric hysteresis diagram
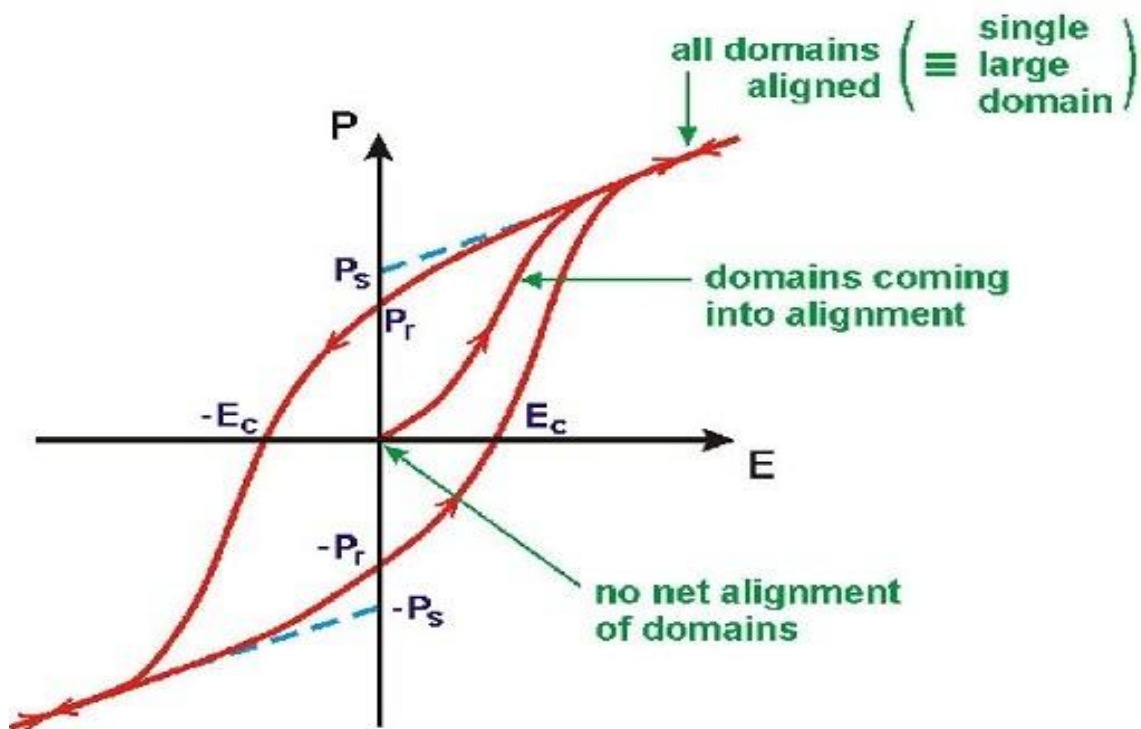
Figure 2: Ferroelectric (P-E) Hysteresis Loop

electric field is reduced till a point where no electric field is applied to the material; ferroelectric domains are still polarized and aligned. There exists some polarization when even the applied electric field is removed. Such remaining polarization is called as remnant

polarization (Pr). When the applied electric field is even more reduced i.e. applying electric field in opposite direction a point reaches where no net polarization is observed in the ferroelectric material. Such electric field where there is no net electric polarization is called as coercive field (Ec). When cooled, most perovskite structures undergo a transition from cubic crystal structure to a lower symmetry structure. This transition of crystal structure from one phase to other phase is known as Curie transition and the temperature at which it occurs is known as Curie temperature. Above this Curie temperature the ferroelectricity of the material vanishes as the crystal structure of the material is cubic which is highly symmetric. Below the Curie temperature, material exhibit ferroelectric properties.

In piezoelectric materials as discussed above, a spontaneous polarization exists due to the separation of negative and positive charge centers in the crystallographic unit cell. A characteristic example of a structure which exhibits spontaneous polarization is perovskite structure, ABO_3 where, A and B are cations of different sizes and O is an anion i.e., usually oxygen. In the idealized cubic unit cell of such a compound, 'A' atom sits at the corner of the cube, 'B' atom sits at the center of the cube and 'O' atom sits on the faces of the cubic unit cell. Such ideal cubic unit cell of compound of perovskite crystal structure is shown in fig. 3.
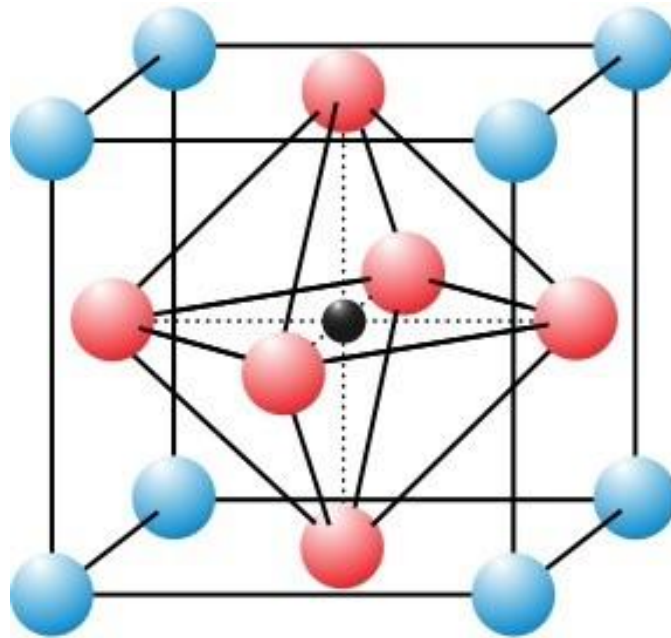

Figure 3: Ideal cubic structure of a unit cell of shows perovskite crystal structure ABO3

4.1.3 Lead Zirconate Titanate (PZT)

The most widely used piezoelectric ceramic till date is lead zirconate titanate (Pb [ZrxTi(1-x)]O3), or PZT because it has excellent electromechanical properties at room temperature. Lead zirconate titanate (PZT) has a perovskite crystal structure, ABO3 in which A site is constituted by Pb2+ ions, B site by Zr4+ and Ti4+ ions and O by O2- ions. PZT is a piezoelectric ceramic of Lead titanate which has a tetragonal crystal structure and Lead zirconate has orthorhombic crystal structure. There exists a boundary between the two crystal structure of Lead titanate and Lead zirconate at a specific composition of these two compounds. The ratio of the composition of the two compounds is Zirconium to Titanium is 52 to 48. At this specific composition of the two compounds there exists a morphotropic phase boundary (MPB) which is one of the main reasons PZT gives excellent piezoelectric properties. Compositions in the region of this particular morphotropic phase boundary are known to have enhanced the physical properties including higher piezoelectric coupling and dielectric constants.

There are two main reasons for PZT to give exceptional piezoelectric properties as presence of morphotropic phase boundary near Zr:Ti = 52:48 and high contribution to electromechanical properties from the motion of the ferroelectric domain walls. In this morphotropic phase boundary (MPB) of PZT, the ferroelectric polarization changes its crystallographic orientation from rhombohedral <111> to tetragonal <100> via an intermediate monoclinic phase. In the vicinity of MPB, ferroelectric domain changes their crystallographic orientation from rhombohedral to tetragonal and thus this MPB. This morphotropic phase boundary is independent of temperature and is only dependant of the composition of lead zirconate and lead titanate [32].

PZT have a very high Curie temperature of about 320° Celsius makes it suitable for applications over a wide range of ambient temperature. Though PZT is the piezoelectric material which has been used widely all over the world contains lead in oxide form which is toxic material and has a tendency to vaporize. Lead is harmful to human body in many aspects as if inhaled may cause respiratory problem and even can affect the central nervous system of the human body. So, as serious health risks caused by the use of lead, it has been included in Restriction of Hazardous Substances directive of the European Union, it limits the use of certain electronic and electrical equipments. So researchers are searching for an alternative for the lead based piezoelectric material which will match the potential of PZT

either by reducing the amount of lead conventionally used or by choosing some other potential material which will be lead-free but with considerable piezoelectric properties.

4.1.4 Sodium Bismuth Titanate (NBT)

Sodium bismuth titanate Na0.5Bi0.5TiO3 (NBT) with perovskite structure is the best known lead-free piezoelectric and ferroelectric material that promises a number of applications in sensors and actuators since the first report on its ferroelectricity by Smolenskii et al. [17]. It also has a distorted perovskite crystal structure ABO3, where A site occupied by Na+ and Bi3+, B site by Ti4+, and O by O2- with rhombohedral symmetry at room temperature. The standard ABO3 perovskite formula for NBT is (Na0.5Bi0.5)TiO3. An ABO3 perovskite structure can be considered in two ways, one way is to have bismuth and sodium cations at the corner of the unit cell, oxygen at the faces of the cube and titanium at the center of the oxygen octahedral that is formed. The other way is a three dimensional octahedra of the TiO6 with bismuth and sodium at the center of the cube formed by this octahedra.
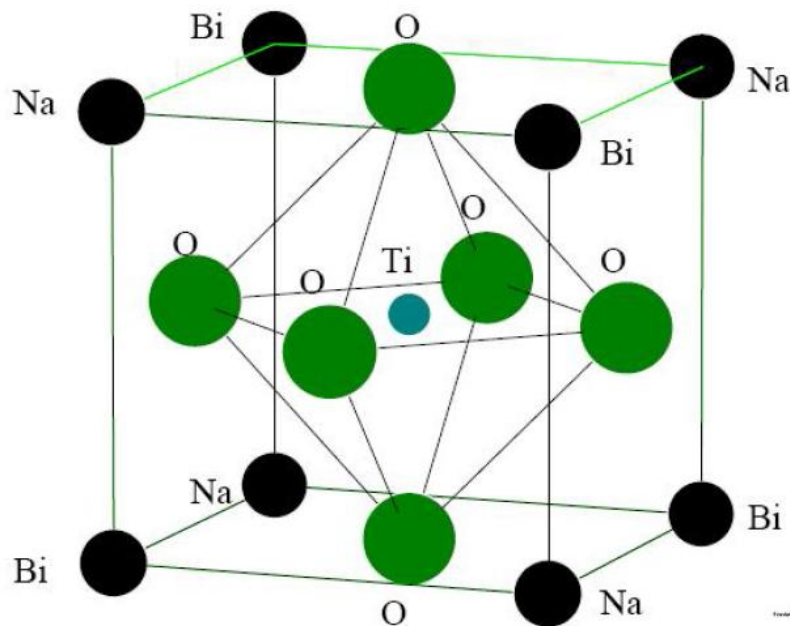
Figure 4: Perovskite crystal structure of Sodium Bismuth Titanate ($Na_{0.5}Bi_{0.5}TiO_3$)

Figure 4 represents a typical perovskite structure of cubic NBT in an ideal mixture. The figure shows that the sodium and bismuth are ordered on the A site, oxygen at the faces and titanium at the center of the cube. It is considered as one of the promising material of lead free piezoelectric ceramics because of the large remnant polarization at room temperature

[34]. The material does not have the piezoelectric properties like PZT and has many drawbacks. Some of the drawbacks are that it has a high coercive field and high conductivity which can be overcome by adding different dopants in NBT with increasing piezoelectric properties.

4.2 Process Description

4.2.1 Sol-gel Technique

Sol-gel technologies were developed during the last 40 years due to the need of new synthesis method in nuclear industry as well as an alternative for the preparation of glass and ceramics at considerably lower temperatures. Over the years, the sol gel sciences and technology have undergone impressive and informative developments with application widespread in every industrial sector which includes optical and photonic, electronic, thermal, mechanical, chemical and biomedical functions [35].

Sol-gel is a wet chemical process for producing solid materials from small molecules which involves conversion of monomers into a colloidal solution (sol) that acts as the precursor for an integrated network (gel) of either discrete particles or network polymers. The precursors for synthesizing the colloidal solution consist usually of a metal or metalloid element surrounded by various reactive ligands. The starting material is processed to form a dispersible oxide and forms a sol in contact with water or dilute acid. In this chemical procedure, the 'sol' or solution gradually evolves towards the formation of a gel-like biphasic system containing both a liquid phase and solid phase whose morphologies range from discrete particles to continuous polymer networks.
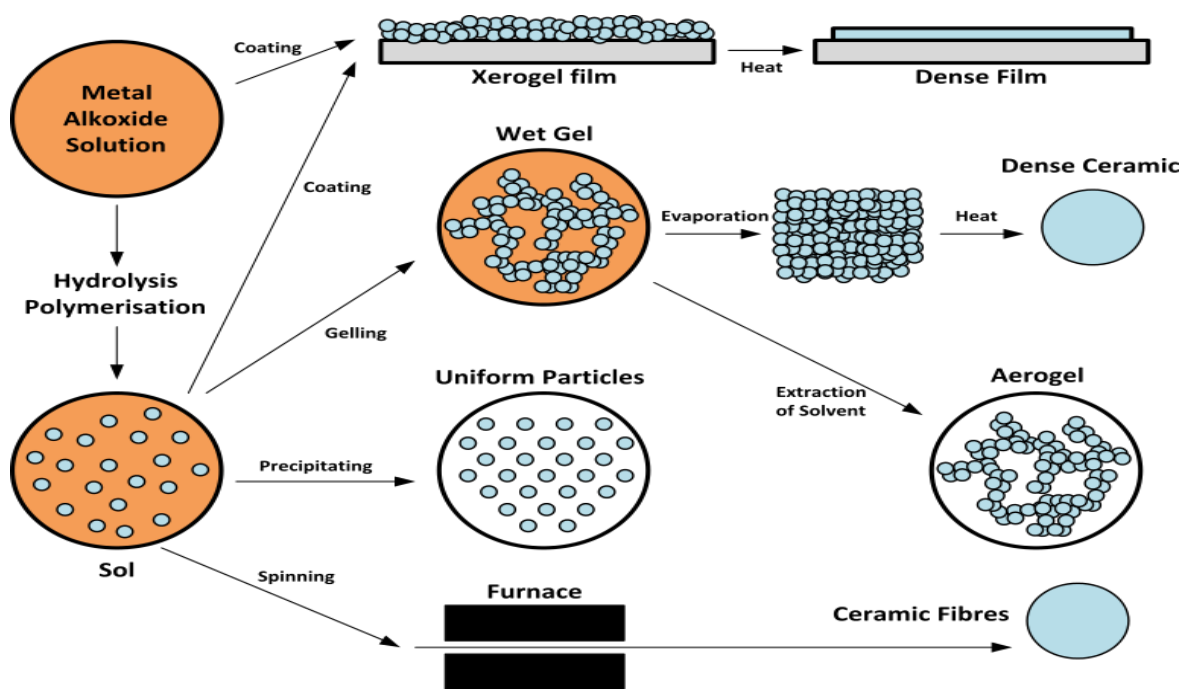
Figure 5: Schematic representation of different stages and routes of Sol-gel Technology

In fig. 5 a schematic representation is depicted showing different possible stages and routes of the sol gel technique to yield variety of products. Generally the chemical compounds which are normally in the sol gel technique are either organometallic or metal alkoxide based precursors. Metal alkoxide based precursor is more often used as it readily reacts with water and organic solvents. Fig. 3.2.1.1 depicts the processing of the sol which is formed by hydrolysis and condensation of metal alkoxide based precursor to various products. The sol so formed can be coated on a substrate to form a thin film over it which after heat treatment gives dense film. The sol can be allowed to age for some time so that the particles agglomerate and results in the form a wet gel, thereby evaporating the solvent and heat treatment yields in dense ceramic. The sol may either be allowed to precipitate to form uniform particles or can be treated in a furnace to yield ceramic fibers. The sol can be subjected to a series of operation like gelling, drying, pressing, casting, coating specific to the desired products which results in various structural and phase transformation which in turn permits formation of powders, fibers, coatings, ceramics, bulk monolithic products etc. from the same initial composition of sol.

Sol gel technique is peculiar in itself as it possibly controls the mechanism and the kinetics of the preceding chemical reactions. Each and every step of the sol gel technique can be

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controlled which may affect the structure of the material so formed by the chemical reaction of the precursors.

The sol-gel process can be characterized by a series of distinct steps.

Step 1: Formation of stable solutions of the alkoxide or solvated metal precursor known as Sol.

Step 2: Gelation resulting from the formation of an oxide or alcohol bridged network (the gel) by a poly-condensation reaction that results in a dramatic increase in the viscosity of the solution.

Step 3: Aging of the gel, during which the poly-condensation reactions continue until the gel transforms into a solid mass, accompanied by contraction of the gel network and expulsion of solvent from gel pores. Ostwald ripening (also referred to as coarsening, is the phenomenon by which smaller particles are consumed by larger particles during the growth process) and phase transformations may occur concurrently with aging. Sol-gel processing refers to the hydrolysis and condensation of metal alkoxide-based precursors.

The reactions involved in the sol-gel chemistry based on the hydrolysis and condensation of metal alkoxides M(OR)z can be described as follows:

$$MOR + H_2O \rightarrow MOH + ROH \text{ (hydrolysis)}$$

$$MOH + ROM \rightarrow M\text{-}O\text{-}M + ROH \text{ (condensation)}$$

Several process parameters involved in sol gel technique governs the quality of the product that is obtained by adopting different physical experimental techniques. The occurring hydrolysis and condensation steps in sol gel process depend on a series of parameters and successful synthesis depends on the component initial concentration in the mixture, medium pH, rheology of the resulting sol, solvent, temperature of the system etc. The effect of this process parameters are discussed in detail in following chapters. The idea behind sol-gel synthesis is to dissolve the compound in a liquid in order to bring it back as a solid in a controlled manner. Sol gel process ensures proper mixing at the atomic level of the multi component chemical compounds with a controlled stoichiometry which enables to form a stable homogeneous sol. It is one of the pioneer techniques which involve processing at lower temperatures.

4.2.2 Spin Coating

Spin coating is one of the most common techniques for applying thin films to substrates and is used in a wide variety of industries and technology sectors. It is the predominant technique employed to produce uniform thin film with the thickness of the order of several micrometers and nanometers of oxide layers and photosensitive organic materials.

The spin coating technique involves depositing a small puddle of fluid material in excess on to the center of the substrate (which is either rotating at low speed or in static position) and then it is rotated at a desired high speed with high acceleration in order to spread the fluid with centrifugal force. The rotation of the substrate is continued while the fluid spins off the edges of the substrate till the desired thickness of the film is achieved. Simultaneously evaporation of the solvent in the fluid material also takes place which again thin the film.

Fig. 6 shows the spin coating process that can be divided into four simple stages namely deposition, spin-up, spin-off and evaporation of solvents.

4.2.3 Deposition

The deposition of the fluid material on to the center of the surface of the substrate can be static or dynamic. Static dispense is simply depositing a small puddle of fluid in excess on or near the center of the substrate when it is not rotating. The quantity of the fluid material to dispense over the substrate depends up on the viscosity of the fluid and the size of the substrate to be coated. Higher viscosity and or larger substrates typically require a larger puddle to ensure full coverage of the substrate during the high speed spin step. Dynamic dispense is the process of dispensing fluid while the substrate is turning at low speed usually 500 rpm. Dynamic deposition is adopted when the fluid and substrate surface have poor wetting ability as it serves the fluid to spread over the substrate and result in less wastage of fluid material. This is the stage of delivering an excess of the liquid to be coated to the surface of the substrate a portion of which is immediately covered or "wetted". After the deposition of the fluid or coating material on the substrate, it is accelerated to the desired speed as a result the fluid spreads over the substrate due to centrifugal force acting radially outward.

4.2.4 Spin-up

In this stage the substrate is accelerated to its final, desired rotation speed. During this stage, the fluid material is expelled from the substrate surface by rotational motion. Spiral vortices may be present during this stage as due to the initial depth of the fluid on the substrate surface. This spiral vortices form due to the twisting motion caused by the inertial force that is exerted by the top layer of the fluid while the substrate below it rotates at high speed [28]. During spin-up, centrifugal force overwhelms the force of gravity,
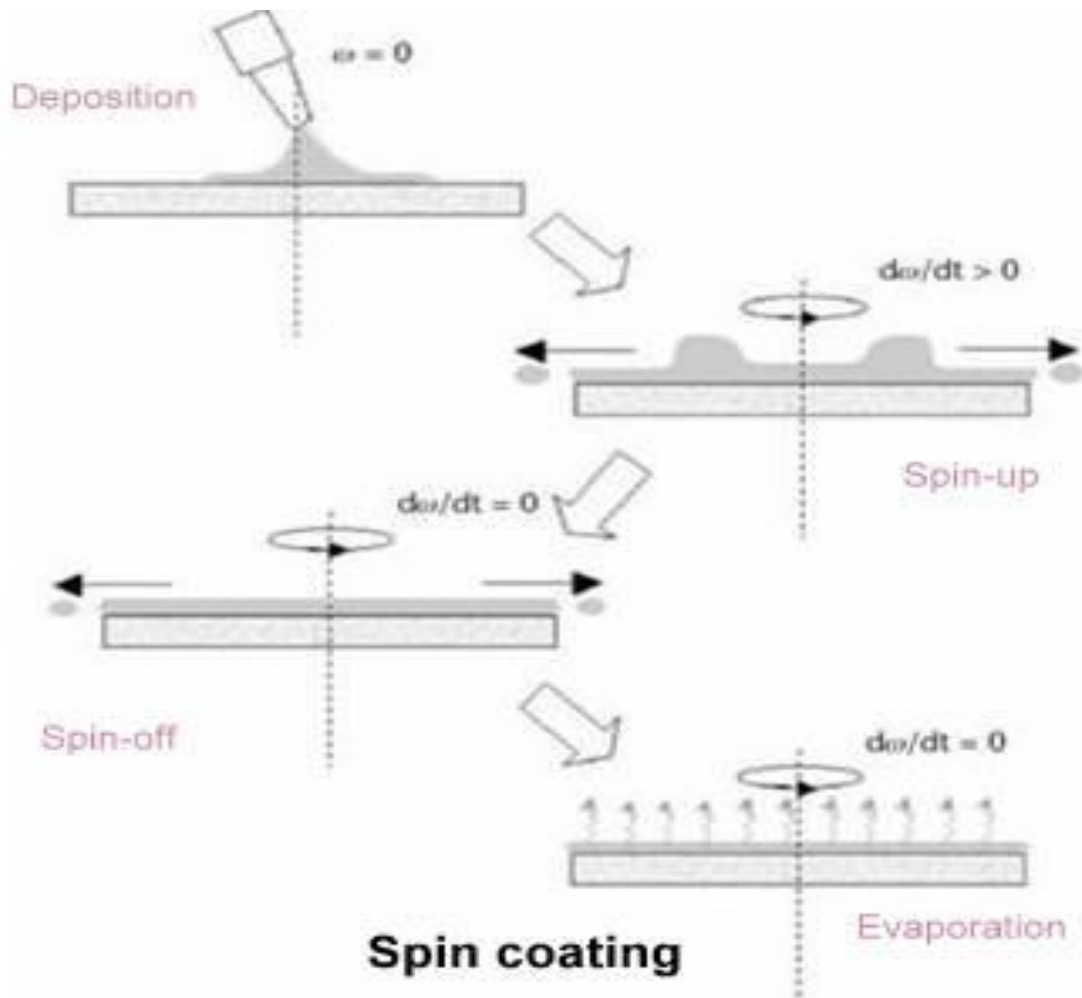

Figure 6: Typical stages of spin coating method

and rapid thinning quickly squelches all inertial forces other than centrifugal force. Eventually the substrate reaches its desired final speed as a result fluid thins enough to be

completely co-rotating with the substrate as the viscous shear drag exactly balances the rotational accelerations.

4.2.5 Spin-off

The spin-off stage is reached when the substrate starts spinning at a constant rate and fluid viscous force dominates the fluid thinning behavior. During this stage, excess of the fluid flows to the perimeter of the substrate surface and then leaves as a droplet. As the film thins, the rate of removal of excess fluid by spin-off slows down because the thinner the film, the greater is the resistance to flow. Fluid thinning is generally quite uniform, though with solutions containing volatile solvents; it is often possible to see interference colors while spinning off. The concentration of the non-volatile component in the film increases resulting in increase in its viscosity as the film becomes thin due to removal of excess fluid [36].

4.2.6 Evaporation

As the spin-off stage ends, it begins the drying of the film as evaporation takes over the primary mechanism of thinning. During this stage, the centrifugal outflow ceases completely and further shrinkage is due to solvent loss. Evaporation stage is reached when the substrate is rotating at constant rate and the fluid thinning is dominated by the evaporation of solvent which results in drastic increase in the viscosity. The rate of evaporation depends on the difference in the partial pressure of the solvent species between the free surface of the liquid layer and the bulk of the gas flowing around. During the evaporation the stage, the suspended or dissolved solids may become so concentrated that they form a solid thin layer.

The quality of the film coated by spin coating depend on several process parameters coupled together which involves spin speed, spinning time i.e. time for which the substrate is allowed to rotate which are discussed briefly in section 3.4.

4.3 Experimental Procedure

4.3.1 Preparation of Sol

Sodium Bismuth Titanate (NBT) sol was prepared by using the chemical compounds named as Sodium acetate, Bismuth nitrate, & Titanium iso-propoxide. Fig. 7 shows the flowchart of the preparation NBT sols. The solvents used to dissolve these chemical compounds were

Acetic acid and 2-Methoxyethanol. Sodium acetate and Bismuth nitrate were dissolved in Acetic acid and stirred continuously for 3 hours. Titanium iso-propoxide was dissolved in 2-metoxyethanol with continuous stirring for 3 hours. Continuous stirring is required so that the chemical compounds mix and react properly and it was achieved with the help of magnetic stirrer. Acetyl acetone was added to the titanium iso-propoxide solution in order to prevent the hydrolysis caused by moisture in the air to form a stable solution. Then this titanium iso-propoxide solution was added carefully drop-wise to the solution mixture of sodium-acetate and bismuth nitrate to produce a Na–Bi–Ti complex solution (sol). Then the resulting solution mixture (sol) is allowed to stir for 5 hours to produce long chain of the Na-Bi-Ti complex until a transparent and stable yellow precursor is obtained.

Three different concentrations of NBT sols were prepared namely 0.3M, 0.35M, 0.4M throughout the project and these sols were characterized to analysis for the rheology of the sols and also the same set of sols were then used for coating of the films.
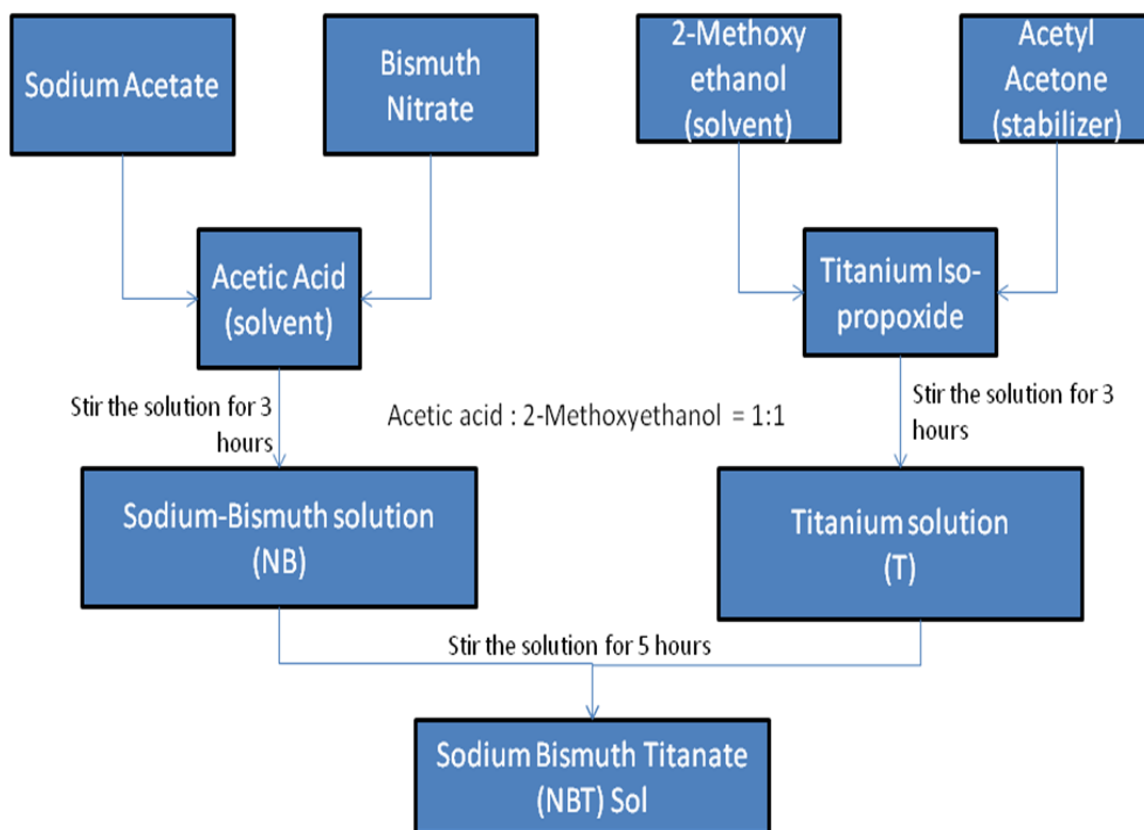

Figure 7: Flowchart for the preparation of Sodium Bismuth Titanate (NBT) sol

4.3.2 Spin coating of Sol

The sol so formed by sol-gel process is then spin coated on the substrate. The substrate is platinized silica Pt/Ti/SiO2/Si with (111) orientation. The orientation and the morphology of the film coated depends on the morphology and cleanliness of the surface of the substrate, therefore proper steps were employed to ensure that the substrate was cleaned properly. Substrate was first heated in synthesis acetone for 20 minutes at 90° C temperature. Then after that the substrate was sonicated twice with isopropyl alcohol and distilled water respectively. The substrate was then cleaned with nitrogen gas and kept on a hot plate for about 300 seconds at a temperature 200° C so that the traces of water droplets remaining on the substrate surface after sonicating with water are removed. After removing substrate from the hot plate, substrate was cooled with the nitrogen gas and then it was spin coated. The spin coater used for coatings and the remaining apparatus used for the coating of the film were washed and cleaned with the help of acetone so that not even a single minute dust particle falls on the substrate surface which spoils the morphology of the film. The sol was applied on the substrate surface with the help of micropipette and the quantity of the sol was taken as 56 μL and it was kept constant throughout the experiments. After applying sol to the substrate, it was rotated with high acceleration to the final spinning speed of 3000 rpm for 20 seconds and undergoes the four major stages of spin coating which results in uniform film formation on the substrate, after which the spin coated substrate was carefully taken out of the spin coater and was kept on the hot plate which was at 200° C temperature for 300 seconds for the drying of the film; thereafter keeping the coated substrate on another hot plate which was at 300° C temperature for 300 seconds so that the traces of solvent left in the film gets evaporated. Then the coated substrate is allowed to cool with the help of nitrogen gas. Each substrate was coated 5 times and was followed by the same procedure of coating the film, evaporating the solvents and subsequently cooling it. Then the coated substrate has a thin film of the NBT over it which is then annealed at high temperature.

The advantages of spin coating are the simplicity and relative ease with which a process can be set up coupled to obtain thin and uniform film coating. The advantages of this technique are we can get a 'homogeneous' thin film of 'uniform thickness' i.e. we can get a homogeneous lead-free piezoelectric thin film of uniform thickness. Moreover, this technique is very cost effective and fast operating; it doesn't require any other equipment other than a spin coater and can be used very fast and repitedly. And using this technique we can coat a thin film on a larger substrate i.e. coating of substrate having larger surface area

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is possible. There are several process parameters like spin speed and spinning time which affects the thickness of the thin film. The dependency of these parameters are discussed in the below sections.

4.3.3 Thermal annealing of the NBT thin films

Thermal annealing enhances the properties of the thin film by changing the microstructure and phases. The main purpose of post thermal annealing to any inorganic thin film is to improve its surface quality. During annealing under the presence of some suitable ambient or inert gas, the atoms start diffusing on the surface of the film in order to search for a better place to start nucleation. This nucleation of atoms at the suitable kink site enhances the grain size and crystallization of the thin film. Microscopically thermal annealing may relief the stress/strain caused due to lattice mismatch during film formation and also increases the crystallinity of the thin film. Annealing helps in increase in the grain size which in turns changes the surface morphology of the thin film as a result the surface roughness reduces.

Thermal annealing of the thin film so formed by spin coating the sol on the substrate was done in a tubular furnace in the presence of oxygen gas at 650° Celsius temperature for 30 minutes with the heating rate of 5° per minute. After annealing the films were allowed to cool and characterization of the film was done.

4.4 Factors affecting the thin film

4.4.1 Chemical parameters

4.4.2 Rheology of Sol

Rheology is the science of flow and deformation of matter (primarily in liquid states) and describes the inter-relation between force, deformation and time. The nature of this relation depends on the material of which the fluid is constituted. Rheological relationships help us to understand the fluids we are working with so that we can either know how they are behaving or force them to behave according to our needs when they are subjected to a shear. In, general, fluid rheology is used to describe the consistency of products, normally by two components viscosity and elasticity. By viscosity is usually meant resistance to fluid flow and by elasticity usually stickiness or structure. Rheology directly affects the product handling and flow characteristics in our case it may affect the piezoelectric thin film. The fluids are normally classified into three different groups Newtonian, non-Newtonian time

independent, non-Newtonian time dependent. One has to know what type of fluid or (sol) do we have to coat on the spin coater because every fluid has its own characteristic.

Flow behavior studies give us a direct assessment of process-ability. E.g. if the Sol is viscous in nature than to get a desired thickness of the thin one has to increase the rpm of the spin coater (i.e. shear) compared to that of sol having less viscous. So viscosity of sol (spin coating material) is a very important parameter that can influence the piezoelectric film thickness.

Viscosity is the measure of the internal friction of a fluid. This friction becomes apparent when a layer of fluid is made to move in relation to another layer (it happens when the spin coater starts rotating). The amount of force required to cause a movement to overcome friction is called shear. If friction between two layers of liquid or friction between liquid and solid is greater the greater is the amount of force required t overcome this friction. Shear force appears whenever the fluid is physically moved or distributed, as in pouring, spreading (spinning), spraying, mixing, etc. Highly viscous fluids, therefore, require more force to move than less viscous materials as mentioned earlier.

4.4.3 Concentration of Sol

A gel is a substance that contains a continuous solid skeleton enclosing a continuous liquid phase and these continuous solid three dimensional structures give elasticity to the gel. So, as gel is an integrated three dimensional network formed due to hydrolysis and condensation it may be considered as polymer which is made up of monomers. These monomer links together and for a network. The bigger the network, bigger will be its molecular weight which is related with the intrinsic viscosity by Mark Houwink Equation as,

$$[\eta_i] = KM^a$$

where, $[\eta_i]$ = intrinsic viscosity or limiting viscosity number (LVN), M = molecular weight of polymer, K are empirically determined constants a = solvent-polymer interaction parameter.

Intrinsic viscosity $[\eta_i]$ is a measure of a solute's contribution to the viscosity η of a solution and it is given by;

$$[\eta] = \lim_{\emptyset \to 0} \frac{\eta - \eta_o}{\eta_o \emptyset}$$

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Where, $[\eta]$ is the viscosity in the absence of the solute (solvent) and $\emptyset$ is the volume fraction of the solute in the solution.

So, the solution viscosity is related to the solvent viscosity and the mass concentration of polymer solution as,

$$\eta = \eta_\circ + \eta_\circ\{\eta_i e^{conc\text{-}1}\}$$

where, η & $\eta_\circ$ is the viscosity of the solution and solvent respectively, η_i is the intrinsic viscosity.

Rheology is the most sensitive method for material characterization (a process by which material's structure and properties are examined and measured) because flow behavior is responsive to properties such as molecular weight and molecular weight distribution.

4.4.4 pH of Sol

In chemistry, pH is a numeric scale used to specify the acidity or alkalinity of an aqueous solution. Solutions with a pH less than 7 are acidic and solutions with a pH greater than 7 are alkaline or basic. In our case, pH is generally maintained according to the ions that we have in the sol to reduce the gelling time i.e. to reduce the sol to gel transformation time which indirectly affects the thin film development. We will see how pH affects the thin film.

A sol is a colloidal suspension of solid particles in a liquid. These particles are so small that gravitational force is negligible and interactions are dominated by short range forces, such as van der Waals forces and surface charges. The inertia of these colloidal particles which are dispersed in the suspension is so small that it exhibits Brownian motion (a random walk driven by the momentum imparted due to the collision with molecules of surrounding media). As a result of these forces the particles will agglomerate and will settle down disturbing the colloidal suspension.

Agglomerations of small particles are due to van der Waals forces and a tendency to decrease the total surface energy. Van der Waals forces are weak, and extend only for a few nanometers. In order to counter the van der Waals interactions, repulsive forces must be established which may be accomplished by electrostatic repulsion.

In electrostatic repulsion the colloidal particles adsorbs a charged species on its surface by which they will repel each other and agglomeration will be prevented. Stabilization due to electrostatic repulsion is due to formation of a double layer on particle.

The surface of a particle is covered by ionic groups, which determines the surface potential. Counter ions in the solution will cover this layer, shielding the rest of the solution from the surface charges.

For hydroxides the surface potential will be determined by reactions with the ions

H^+ and OH^-. Thus, the surface potential is pH dependent.

$$M\text{-}OH + H^+ \rightarrow M\text{-}OH^{2+}$$

$$M\text{-}OH + OH^- \rightarrow M\text{-}O\text{-} + H2O$$
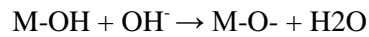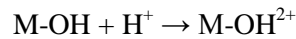
The pH where the particle is neutral is called PZC, point of zero charge (PZC). The size of the surface potential depends on the difference between pH and PZC. So during condensation reaction if the pH is maintained properly so that there are sufficient counter ions the gelling time can be reduced drastically. E.g. structural development of silica gels

Basic conditions

If the sol medium is basic then the particles may grow to sufficient size to become colloids, which are affected both by sedimentation and forces of gravity. Stabilized suspensions of such sub-micrometer spherical particles may eventually result in their self-assembly yielding highly ordered microstructures.

Acidic conditions

Under acidic condition, the inter-particle forces have sufficient strength to cause considerable agglomeration of particles prior to their growth resulting in sedimentation of the particles.

4.4.5 Adhesion between the coating material and substrate surface

When two dissimilar materials are brought into intimate contact, a new interface is formed at the expense of the two free surfaces in air. Such an interface is formed between the coating material and the surface of the substrate. The interaction between the substrate and the coating determines the strength of the bond between them which is greatly determined by the wet ability between the substrate and the coating material.

Wetting is the intimate contact between the substrate and coating. Wetting is a necessary criterion for adhesion. Mechanisms of adhesion are only operational if and only if, effective wetting is present between the coating and the substrate. The coating material applied onto a substrate surface must be adequately spread or smeared consistently before the solvent evaporates off during spinning of the coater. The surface tension of the coating material which is in liquid state and the surface energetic of both the substrate and coating or solid coating (already coated) are important parameters that can influence the strength of the interfacial bond and adhesion development.

The degree to which coating material wets a substrate surface is measured by the contact angle between them. The contact angle is the angle, conventionally measured through the liquid, where a liquid/vapor interface meets a solid surface. It quantifies the wet ability of a solid surface by a liquid via the Young equation.

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} * \cos\theta$$

where,

γ_{SV} = Specific energy of solid-vapor interface, γSL = Specific energy of solid-liquid interface,

γ_{LV} = Specific energy of liquid-vapor interface, θ = contact angle

If the contact angle is 0 then the liquid molecules are strongly attracted to the solid molecules then the liquid drop will completely spread out on the solid surface. Such liquid whose contact angle is zero with the solid surface is called spreading liquid and the solid will be covered with the liquid film.

Table 1: Showing the wettability of the liquid with the solid surface

Contact Angle	Degree of wettability
Θ = 0°	Perfect wetting
0 < θ < 90°	High wettability
90° <= θ <180°	Low wettability
Θ = 180°	Perfectly non-wetting

Table 1shows range of the contact angle from which a broad idea is obtained about the wetting ability of liquid with the solid surface; if the liquid's contact angle is smaller than 90° with the solid surface, the solid surface is considered hydrophilic and if the liquid's contact angle is larger than 90°, the solid surface is considered hydrophobic. So surface tension of coating material also affects the film formation as it influences the adhesion development on the substrate surface and also the strength of the interfacial bond.

4.4.6 Spinning parameters

4.4.7 Spin speed

Spin speed is one of the most important factors in spin coating which directly affects the thin film. Spin speed accounts the degree of radial (centrifugal) force that acts on the sol when the substrate is subjected to spinning. The greater the spin speed of the substrate, the greater will be the shear force acting on the sol towards the edge of the substrate. So, high spin speeds generally result in thin films. Acceleration of the substrate towards the final spin speed also affects the coated film properties as it provides the twisting force to the sol which aids in the dispersal of the sol uniformly such as sol covers the whole substrate surface. Film thickness is largely a balance between the shear that is acting on the sol and the drying rate

which affects the viscosity of the sol. Fig. 8 shows the dependence of the film thickness with the spin speed keeping rest of the process parameters constant.
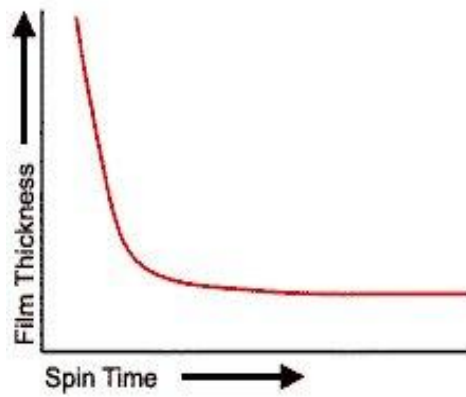

Figure 8: Effect of spin speed on the film thickness

4.4.8 Spin time

It is the time for which the substrate is allowed to rotate. It is one of the parameter which affects the thin film as when the substrate starts rotating most of the sol is flung away from its edge and a very small amount of sol is utilized for film formation, this small amount of sol spreads over the substrate surface uniformly and excess of solvent in dried during to spin-off stage and later on in evaporation stage.

The film thins during the two stages of spin coating as mentioned in chapter 4, so if the substrate is allowed to spin for longer duration of time which results in more uniform thin film. Generally, if all other process parameters of the spin coating are held constant then with high spin speed the film tends to become more uniform and thin as shown in fig 9.
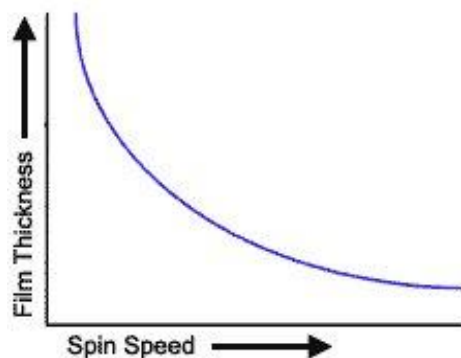
Figure 9: Effect of spin time on the film thickness

The drying rate of the sol during the spin process is defined by the nature of the sol itself (volatility of the solvent used to prepare sol) as well as the air surrounding the substrate during the spin process. The temperature and humidity of the surrounding air above the substrate during spin coating process affects the drying rate of film and hence properties of the film.

Chapter 4

Results and Discussion

5.1 Characterization of NBT Sol

5.1.1 Newtonian Rheology of NBT Sol

Three different concentrations of Sodium Bismuth Titanate (NBT) sol namely 0.3M, 0.35M and 0.4M were prepared by sol-gel technique whose rheology characterization was done using a cup and plate rheometer for three different days. This set of sols were allowed to age for 10 days and rheological characterization was done on 0th, 5th and 10th day.
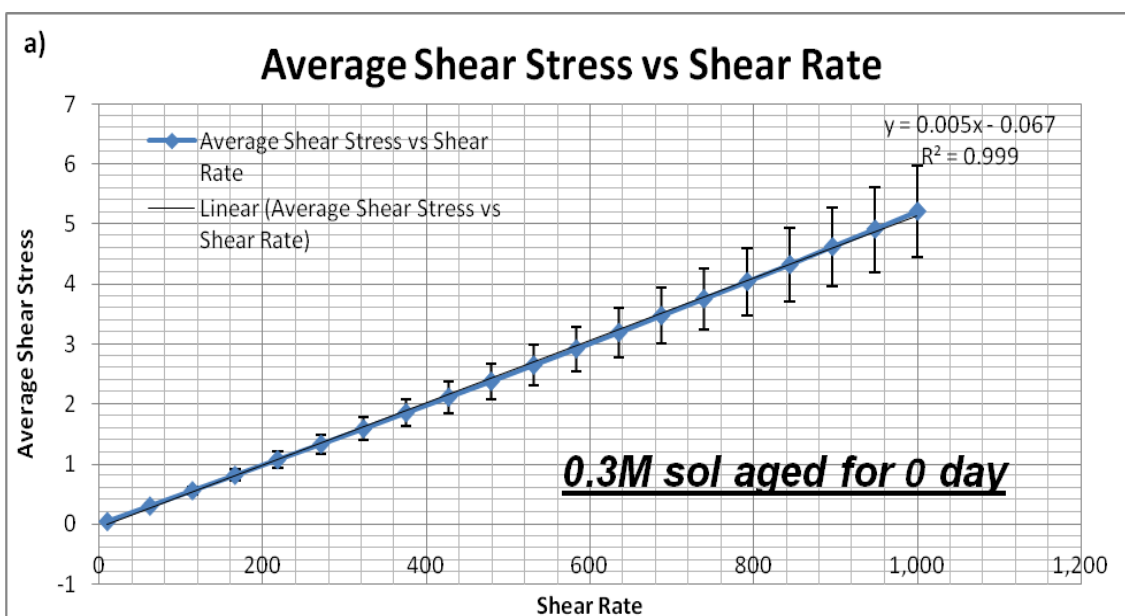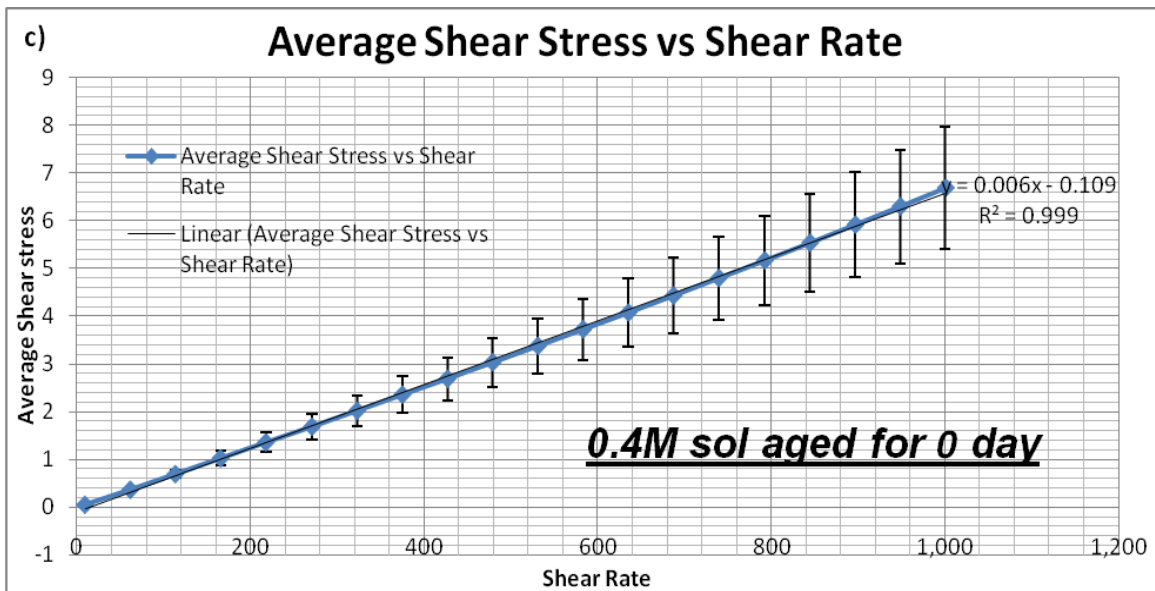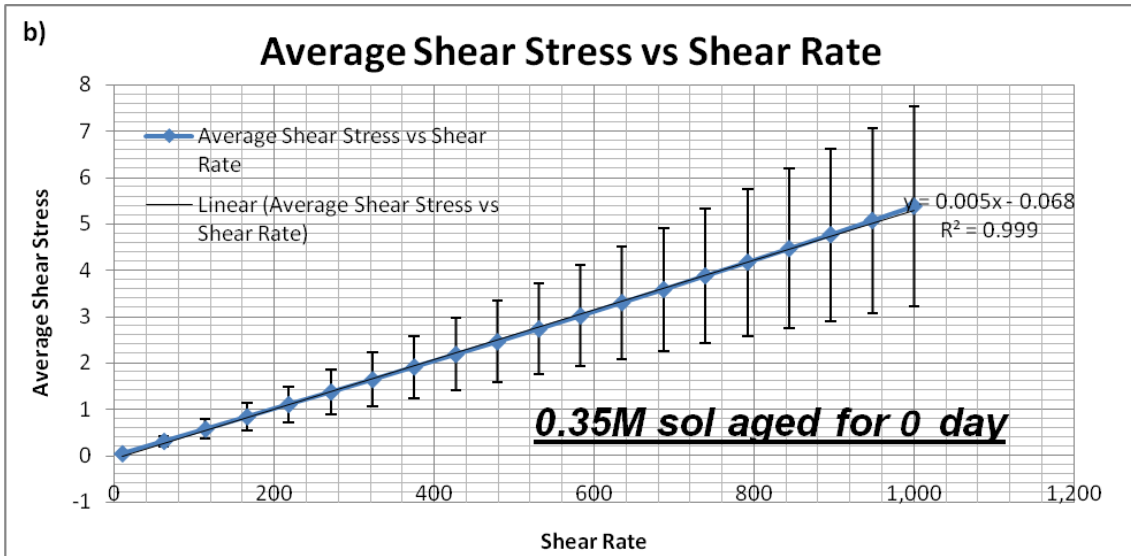
Figure 10: a, b & c Relationship between shear rate and shear stress for freshly prepared NBT sols i.e. aged for 0 day

The maximum shear rate was set as 1000 s-1 and corresponding stress was plotted. The graph plotted between shear rate and shear stress for all concentration of sols. The graphs so plotted show a linear relationship for each concentration thus in turn indicating that the sols exhibit Newtonian behavior. The slope of the graph gives the viscosity of the sol for corresponding concentration. Fig. 10: a, b & c shows the relationship between shear rate and shear stress for freshly prepared sol and the corresponding slope indicates the viscosity of the sols.
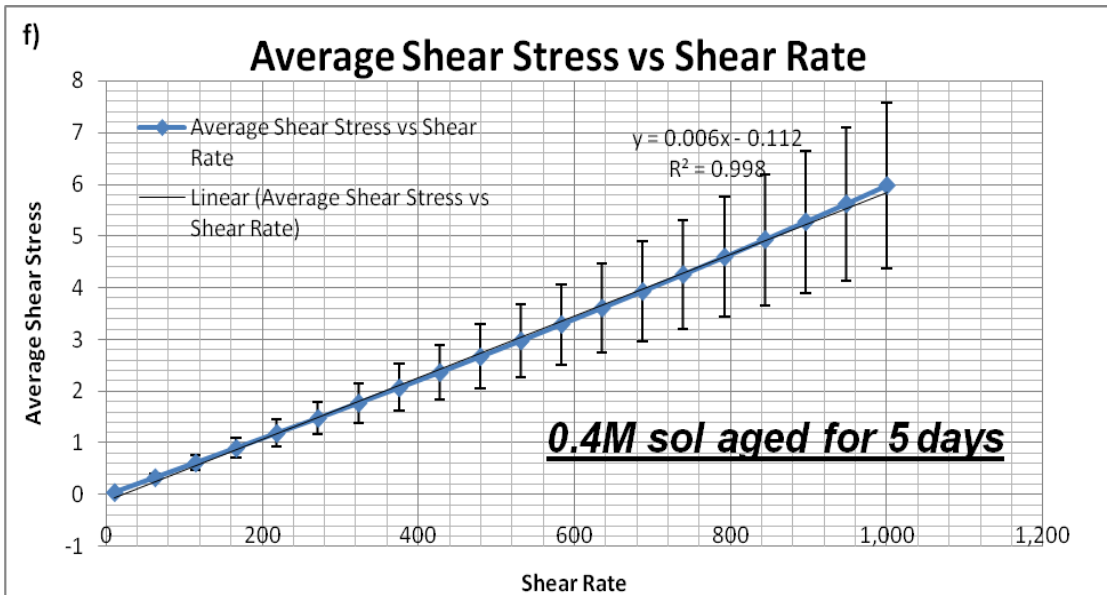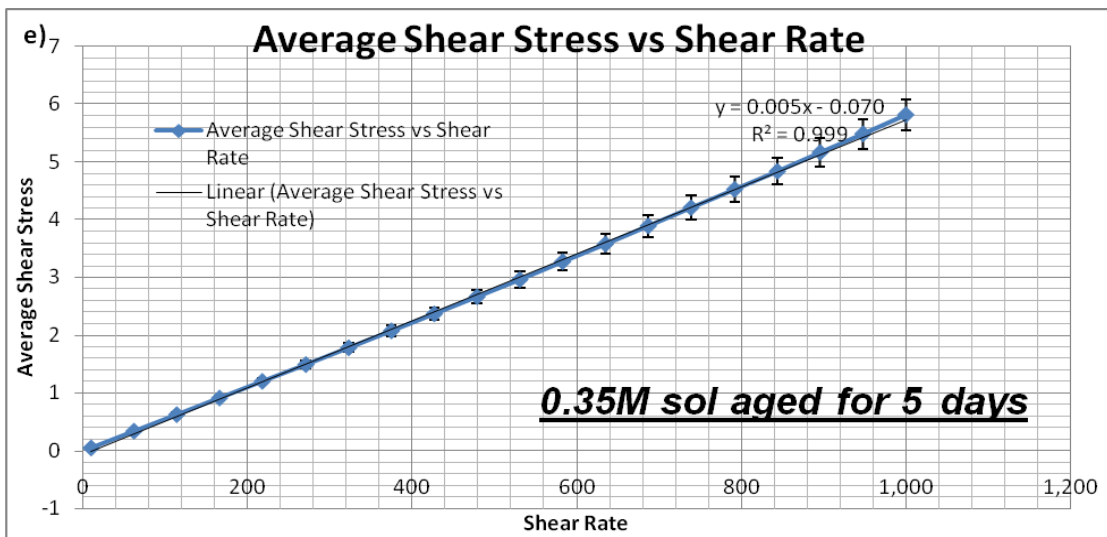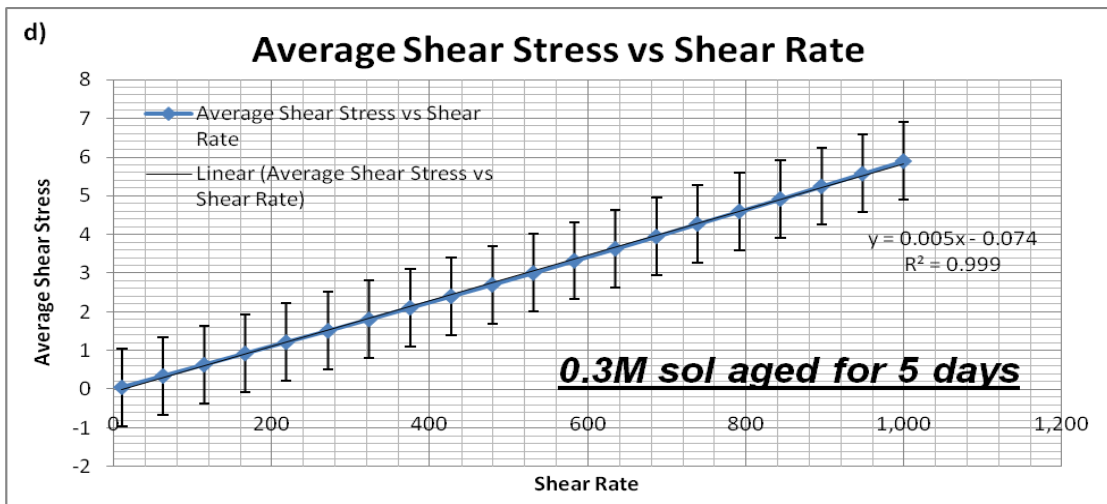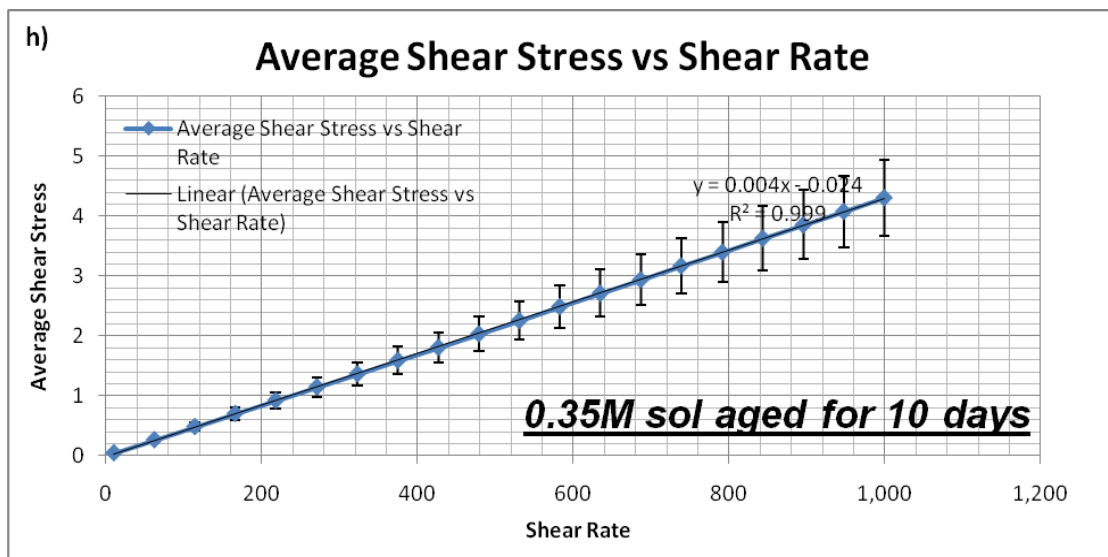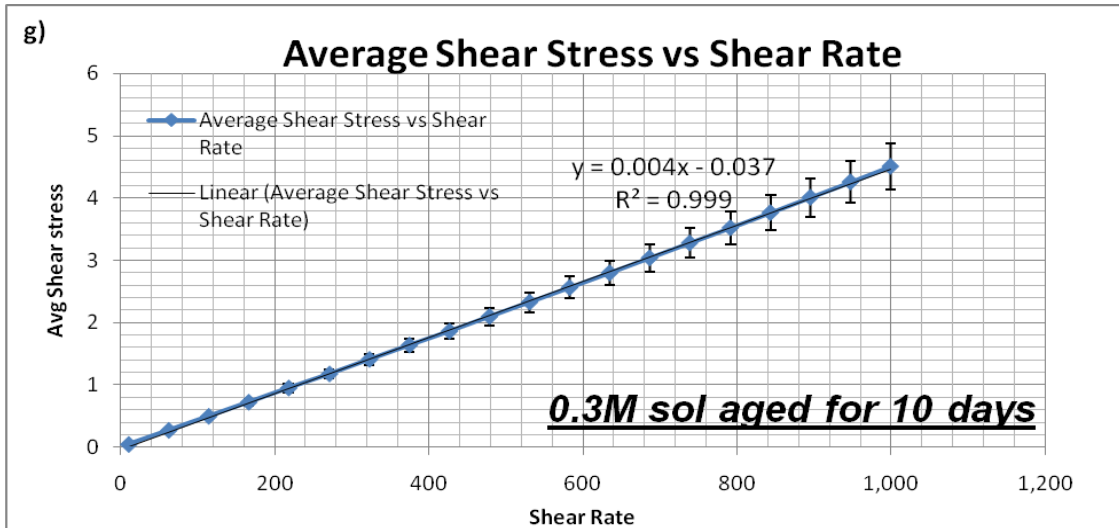
Figure 11: d, e & f Relationship of shear rate and shear stress for NBT sols of 0.3M, 0.35M and 0.4M concentration aged for 5 days

Fig. 11:d e, & f shows a linear relationship between the shear rate and shear stress for three different concentrations of sol aged for 5 days where the slope of the graphs indicates the viscosity of the fluid. There is no significant change in the viscosities of the sols aged till 5 days.

The sols were allowed to age for 10 days and then again rheology characterization was done to test whether there is any change in rheology of the sol. It was found that the rheology of sol was not changed as the relationship between shear rate and shear stress shows linear behavior. Whereas the viscosities of the sol of concentration 0.3M, 0.35M and 0.4M has decreased on the 10th day. From fig 12 g, h & i, it is clear that the NBT sols exhibit Newtonian behavior even after 10 days of aging.
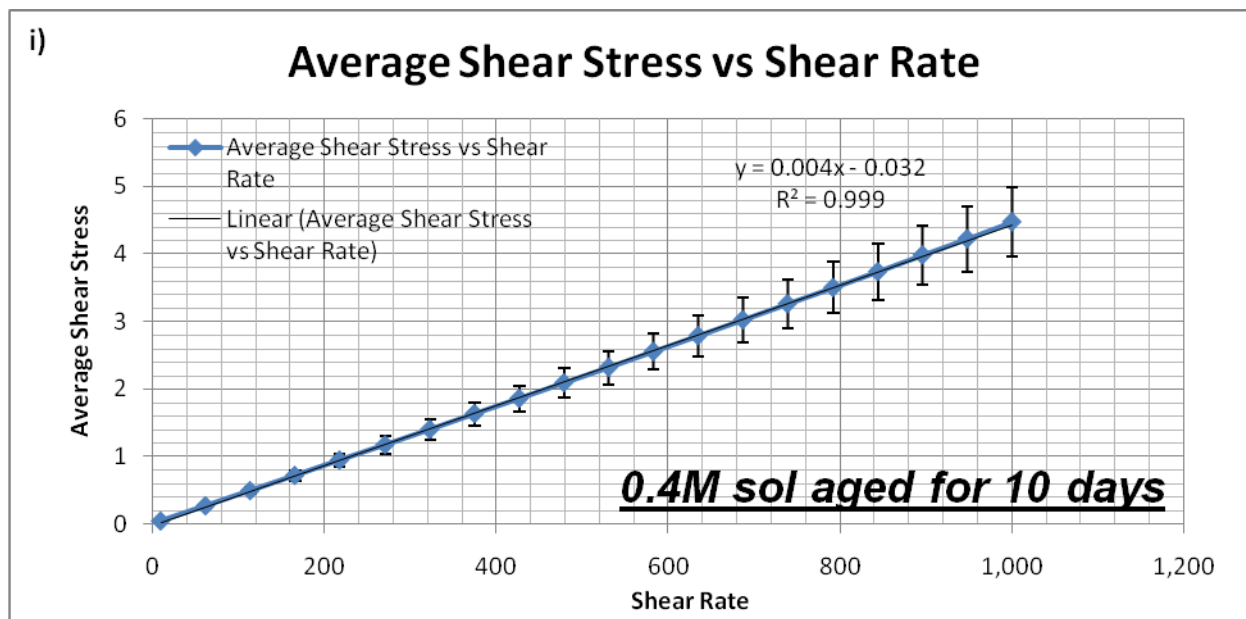

Figure 12: g, h & i Relationship of shear rate and shear stress for NBT sols of 0.3M, 0.35M and 0.4M concentration aged for 5 days

Table 2: Viscosities of 0.3M, 0.35M and 0.4M NBT sols aged for 0, 5 and 10 days

Concentration of Sol/ Aging of Sol	0.3M	0.35M	0.4M
0th day	5 centipoise	5 centipoise	6 centipoise
5th day	5 centipoise	5 centipoise	6 centipoise
10th day	4 centipoise	4 centipoise	4 centipoise

Table 2 shows the comparison of viscosity change for three different concentrations of NBT sol allowed to age for 0, 5 and 10 days. From the table it can be inferred that the viscosities of sols does not change when the sol is allowed to age for 5 days. The viscosities of sol are same on the 0th and 5th day. The viscosities of the sols after 10 days of aging are decreased slightly. This may be because.

5.1.2 Perfect Wettability of Sol on the Substrate Surface

The wettability of the sol with the surface of the substrate was characterized by goniometer. This characterization was done for all three concentrations of sol aged for different time. The contact angle between the liquid sol and the surface of the substrate was found to be between 0° to 10° for all the three concentration aged for different times which infer that the liquid sol completely wets the substrate surface. The liquid sol completely wets the substrate surface which ensures that no part of the substrate surface is left uncoated from the
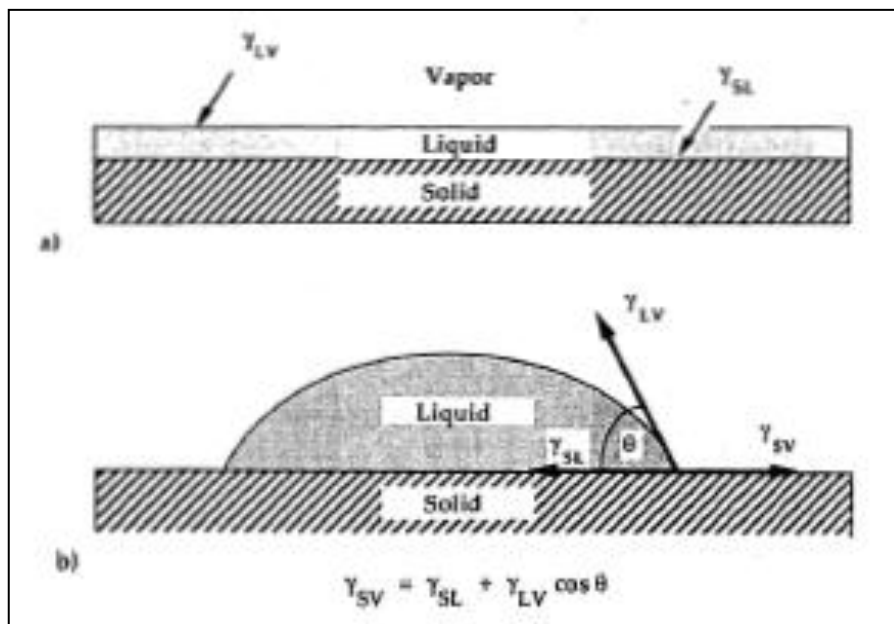

Figure 13: Contact angle between NBT Sol and the substrate surface

liquid sol. But as the sol's viscosity is less and it completely smears the substrate surface the evaporation of solvent starts at the early stages during spin coating. Aging does not affect the contact angle and thus the wettability of the liquid sol to the substrate surface. Fig 13 shows that the NBT sol completely wets the substrate surface as the contact angle between the NBT sols and substrate surface is very negligible.

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5.2 Characterization of synthesized thin film prepared by NBT sol

5.2.1 Absence of stochiometric NBT phase in the XRD diffraction pattern of films coated with two pH of NBT sol

The three different concentrations Sodium Bismuth Titanate (NBT) sols were prepared by sol gel technique. These sols were then utilized to coat NBT film by spin coating. All the three NBT sols of different concentration so obtained were more acidic in nature whose pH was around 2, NBT sol's medium was changed to less acidic with pH 5 by adding Sodium hydroxide in it. Films were coated by both more acidic as well as less acidic medium NBT sols for the prepared set of concentration. The films were coated by spin coating with two steps in the process with 500 rpm for 30 seconds in first step and 4000 rpm for 90 seconds in the second step followed by drying at 250° on a hot plate. Films with more acidic sol were coated 5 times with the above mentioned steps whereas the films with less acidic sol were coated only 3 times as the film surface became rough after 3 coatings. These films were then characterized to confirm that the stochiometric NBT phase has formed in it or not.
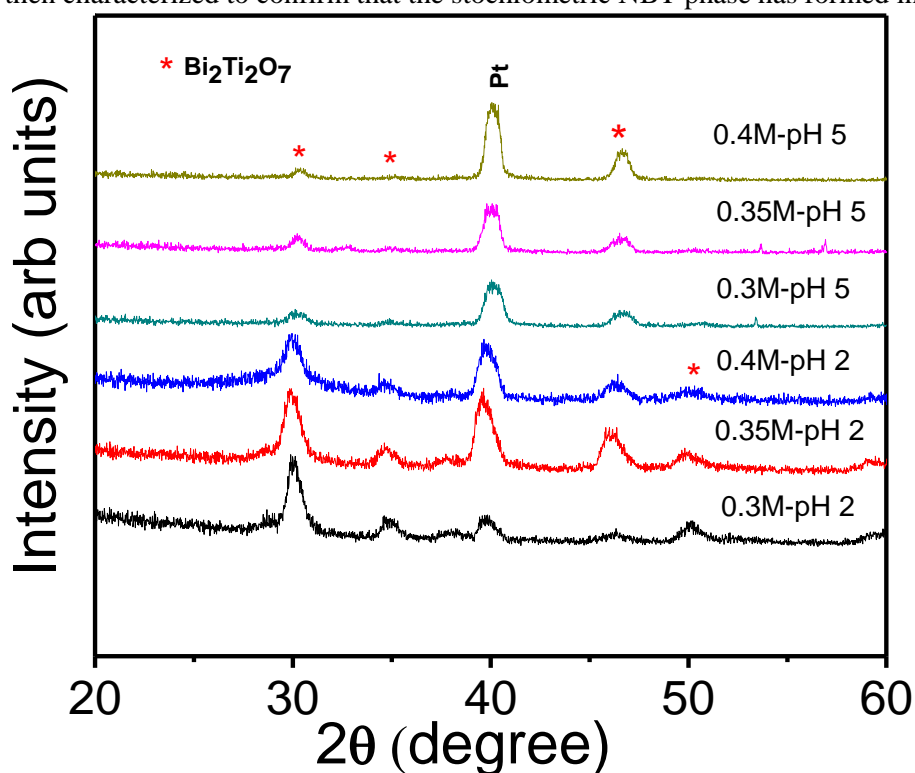

Figure 14: X-ray diffraction pattern of synthesized thin films with three different molarities having two different pH annealed at 700 °C for 30 minutes

Fig. 14 shows the X-ray diffraction pattern of the synthesized thin films by NBT sols with different molarities with two different pH values which were annealed at 700° C for 30

minutes in a tubular furnace in oxygen gas ambience. It is clear from the figure that films lack the presence of stochiometric NBT phase; instead shows the presence of another pyrochlore (Bismuth Titanate) compound in the films.

5.2.2 Cross sectional and surface morphology characterization of the films by FESEM

Fig. 15 a, b c, d, e & f shows the cross sectional images of the film coated by 0.4M, 0.35M & 0.3M NBT sols with two different pH medium. The thicknesses of the film coated by both more acidic and less acidic sols of NBT are indicated in the figures. These cross sectional images were taken by FESEM with 60 KX magnifications. The thickness of the films coated by NBT sol with pH 2 was found to be greater than with pH 5 with smoother surfaces.
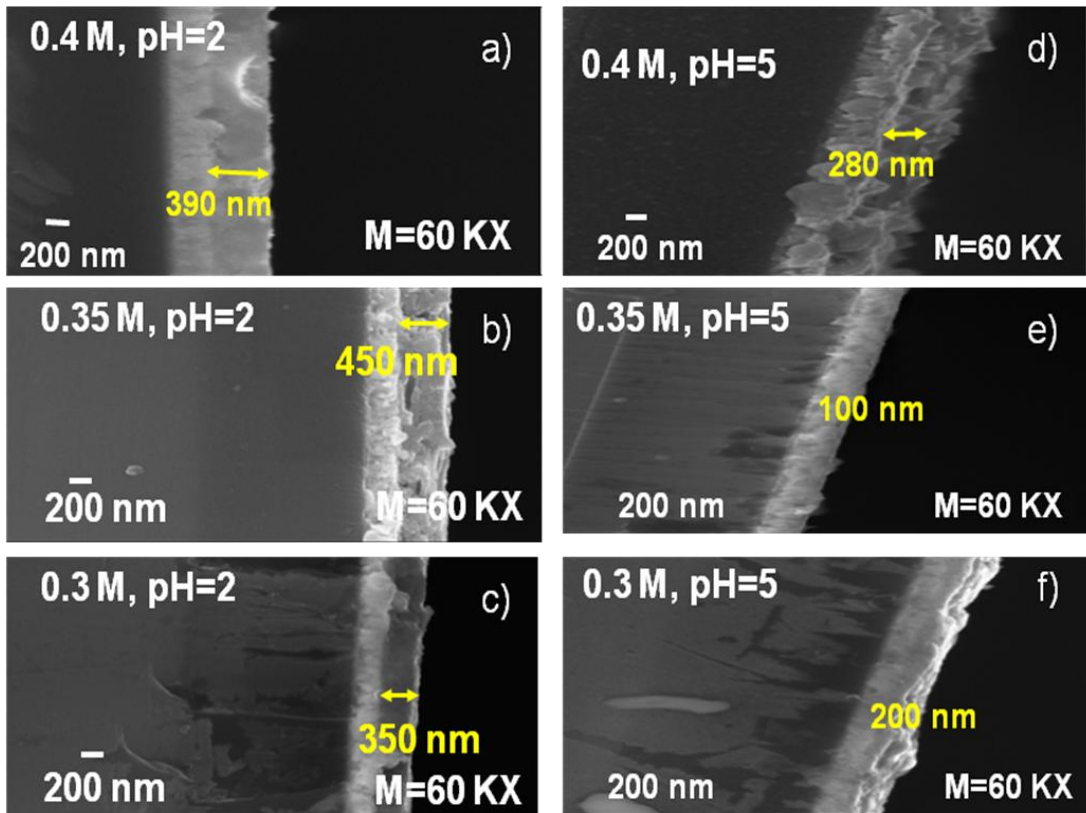

Figure 15: a, b & c: Cross sectional image of films with pH 2 of molarities 0.4M, 0.35M & 0.3M NBT sol resp.; d, e & f: Cross sectional image of films with pH 5 of molarities 0.4M, 0.35M & 0.3M NBT sol respectively.
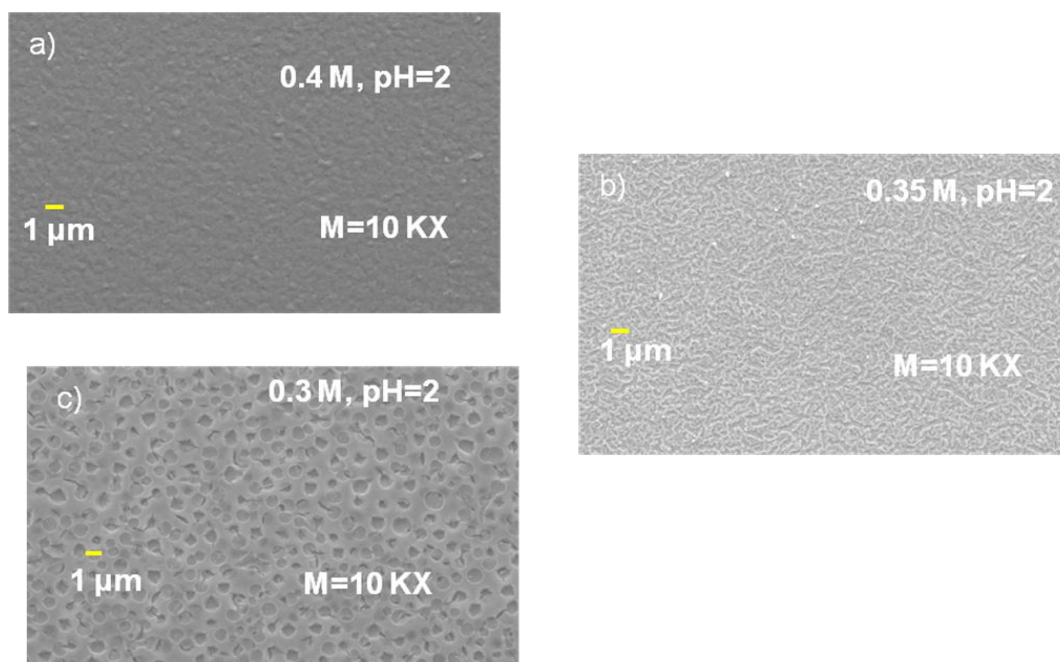
Figure 16: a, b & c: Surface images of the film coated by 0.4M, 0.35M & 0.3M NBT sol with pH 2 respectively.

Gold coating was applied on the films by RF sputtering for the surface characterization of films by Field Emission Surface Electron Microscopy (FESEM). Fig. 16 a, b & c shows the surface morphology of the films coated by NBT sols of molarities 0.4M, 0.35M & 0.4M with pH 2 resp. It can be inferred that the film coated by 0.4M of NBT sol are smooth whereas films with cracked surfaces are obtained coated by 0.35M NBT sol.

5.2.3 Absence of stochiometric NBT phase in the XRD diffraction pattern of films coated by NBT sol with pH 2

NBT sol were prepared with pH 2 and films were coated by spin coating method as a one step process with 3000 rpm for 20 seconds followed by drying at 200° on a hot plate for 300 seconds and pyrolysing the coated film at 350°C for 300 seconds. The above step was repeated for 5 times and then the films were annealed at 650°C for 30 minutes. Fig. 17 shows the XRD pattern of the synthesized thin films by NBT sols with pH 2 of different molarities and indicates that stochiometric NBT phase is absent in the film. The XRD pattern of the film so obtained was carefully analyzed and presence of Bismuth Titanate (pyrochlore) can be inferred in it.
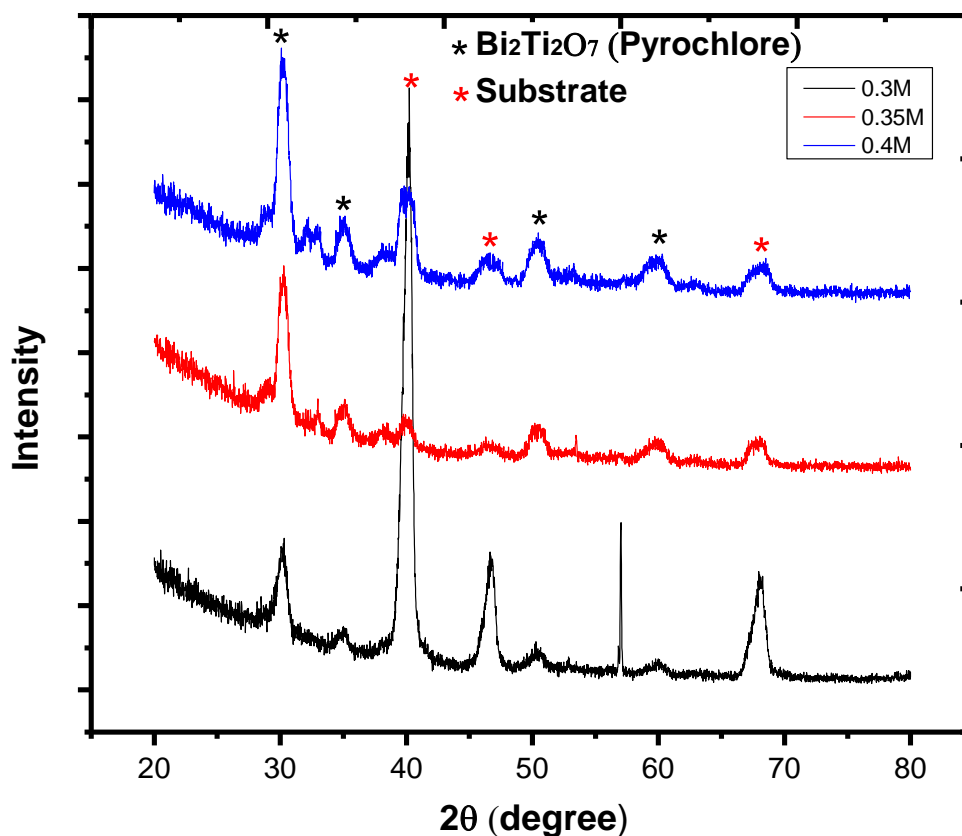

Figure 17: X-ray diffraction pattern of synthesized thin films with three different molarities having pH as 2 annealed at 650°C for 30 minutes

5.2.4 Cross sectional and surface morphology characterization of the films by SEM and AFM

Fig. 18 shows the cross sectional images of the films coated with one step process during spin coating after annealing the films at 650°C for 30 minutes. The cross sectional images were taken by SEM and shows the average thickness of the film coated by three different concentrations NBT sol. The average thickness of the film coated by 0.3M, 0.35M & 0.4M NBT sol was found to be 420 nm, 440 nm & 450 nm respectively.
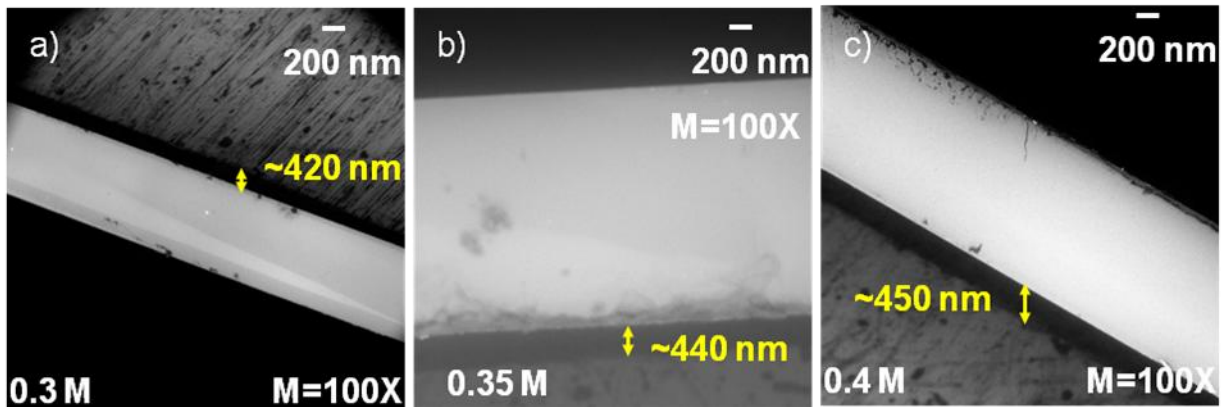

Figure 18: a, b & c Cross sectional images of films of coated by NBT sols with pH 2 of molarities 0.3M, 0.35M & 0.4M resp.

Fig 19 a, c, e shows the 2-D images of the surfaces of the synthesized film coated by 0.4M, 0.35M & 0.3M NBT sol and b, d, & f shows 3-D images resp. The films coated by spin coating method were found to be rougher with average roughness of 19.5 nm, 51.6 nm and 37.3 nm for 0.4M, 0.35M & 0.3M NBT sol
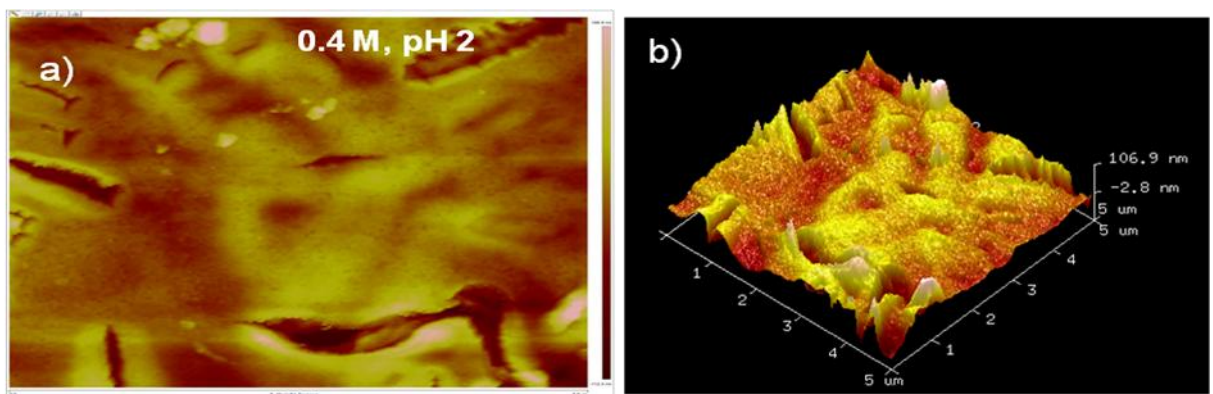

Image Surface Area 26.6 µm²
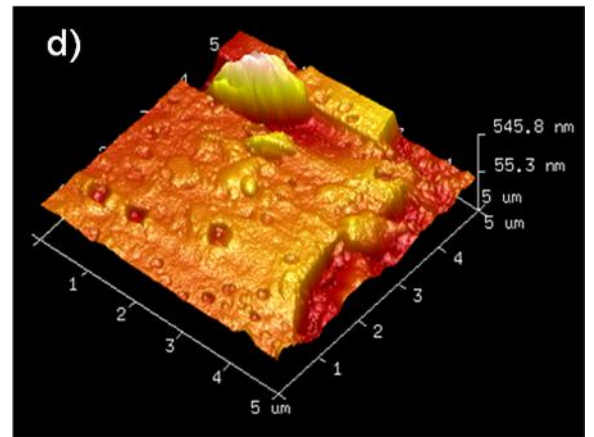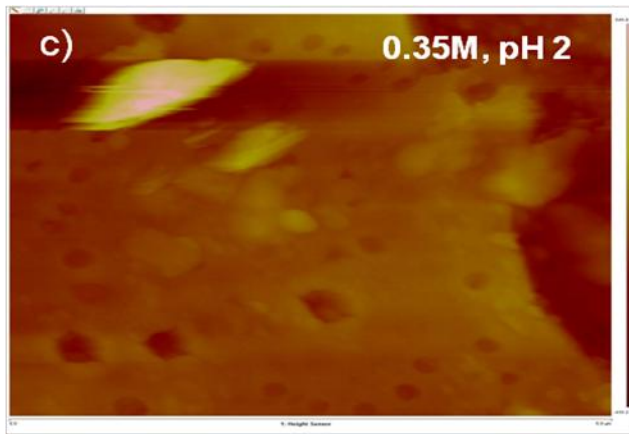Image Projected Surface Area 25.0µm²
Roughness average 19.5 nm

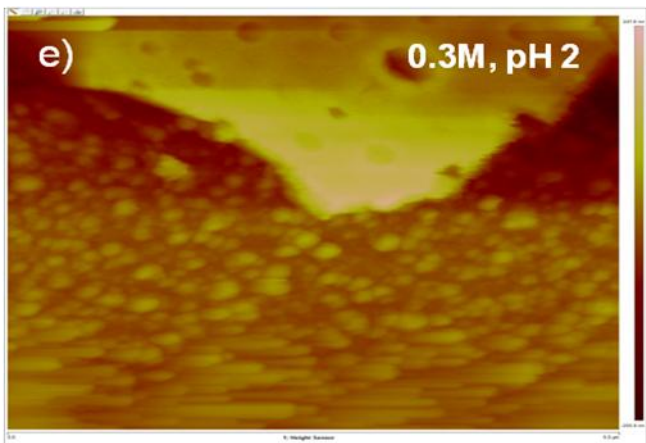Image Surface Area 28.9 µm²
Image Projected Surface Area 25.0µm²
Roughness average 51.6 nm
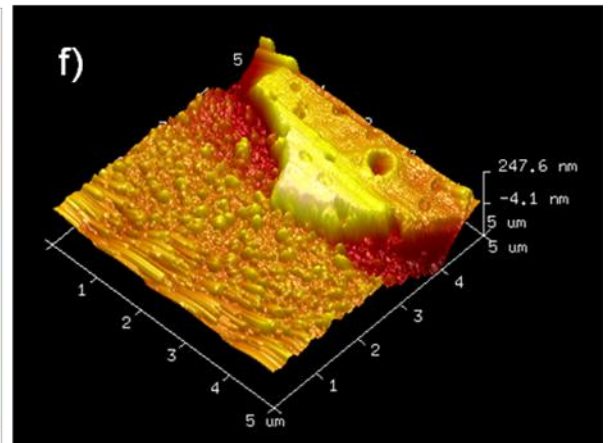
Surface Area 27.6 µm²
Projected Surface Area 25.0 µm²
Roughness average 37.3 nm

Figure 19: a, c & e 2-D surface images of the films; b, d & f 3-D surface images of the films coated by 0.4M, 0.35M & 0.3M NBT sol with pH 2

5.2.5 Annealing film at different temperature shows absence of stochiometric NBT

XRD diffraction pattern of NBT powder samples shows presence of pure stochiometric NBT phase formation without any impurities prepared from 0.35M NBT sol. The powder samples were annealed at 800°C temperature for 3 hours which is higher than the film annealing temperature. Films were coated with 0.35M NBT sol with one step spin coating process with 3000 rpm for 20 seconds followed by drying at 200° on a hot plate for 300 seconds and pyrolysing the coated film at 450°C for 300 seconds. The above step was repeated for 5 times and films were annealed at three different temperatures to study the effect of annealing temperature on NBT phase formation. Fig. 20 shows the XRD pattern of the films coated by 0.35M NBT sol annealed at three different temperatures namely 550°C, 650°C and 700°C. Figure indicates the absence on NBT phase in the film and presence of Bismuth Titanate (pyrochlore) in it. It can also be inferred from the figure that annealing temperature seems no reason for the presence of NBT phase in our study.
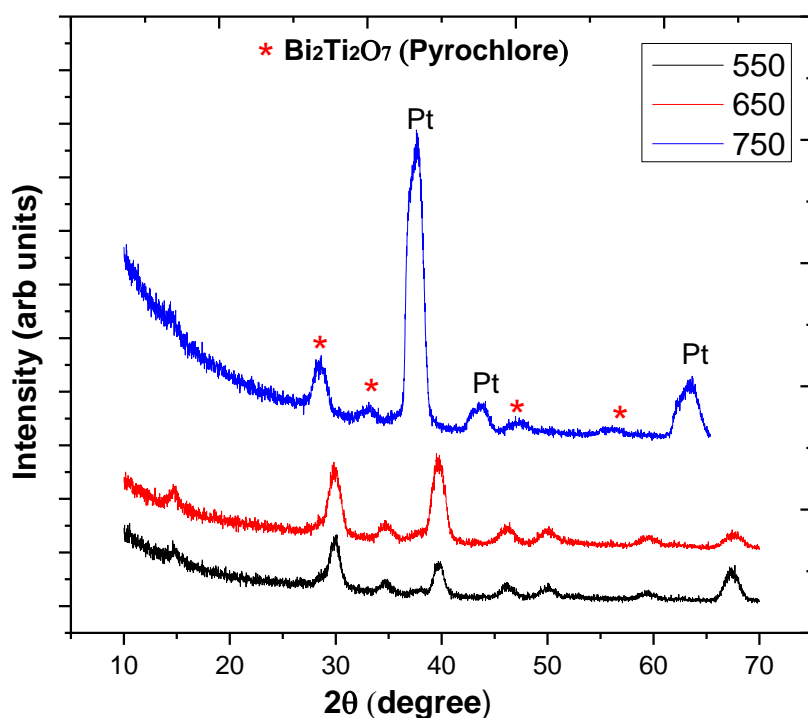
Figure 20: X-ray diffraction pattern of synthesized thin films with three different molarities having pH as 2 annealed at 650°C for 30 minutes

The absence of stoichiometric NBT phase in the synthesized films may be stated because of improper intermixing of the cations while annealing them. This may be due the formation of pyramids of TiO_2 or distortion in the crystal structure of TiO_2 to tetragonal structure (one of the layer in our substrate) while annealing at around 650 temp which in turn hinders the mobility of ions while annealing.

5.3 Characterization of NBT powder

4.3.1 Presence of stochiometric NBT phase with some impurities in NBT powder

NBT powder samples were obtained by evaporating the solvent present in the NBT sols which were prepared by sol gel technique. The three NBT sols of 0.4M, 0.35M & 0.3M concentration were heated at 90°C till the solvent evaporates completely to obtain NBT powder samples. These NBT powder samples of different molarities were then sintered at 800°C for 3 hours. These sintered powder NBT samples were then subjected to characterization. Fig. 21 shows the XRD pattern of powder NBT samples sintered at 800°C for 3 hours which indicates the presence of pure stochiometric NBT phase in 0.35M NBT powder samples and along with presence of impurities Bismuth Titanate (pyrochlore) in 0.4M & 0.3M NBT powder samples. The presence of impurity in 0.4M & 0.3M NBT powder sample may be because the NBT sols undergone aging for several days from which this powder samples were obtained whereas 0.35M NBT sol was freshly prepared.
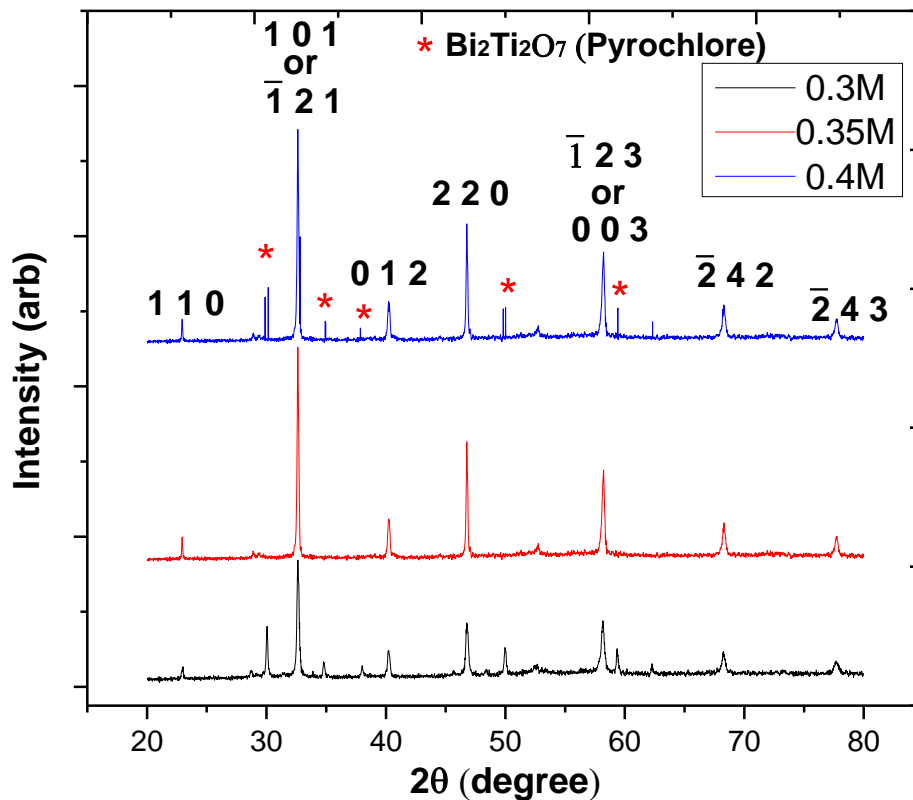

Figure 21: X-ray diffraction pattern of $Na_{0.5}Bi_{0.5}TiO_3$ powder samples with different molarities

Chapter 5

Conclusion and Future Work

NBT sol prepared by sol gel technique shows a linear behavior between shear stress and shear strain indicating it to be a Newtonian fluid (at high shear rate). The contact angle between the substrate surface (platinized silica) and NBT sol is very negligible thus it completely wets the substrate surface which proves to be very beneficial for the drying of the film during spin coating stages. Films synthesized from the NBT sols with pH 2 shows higher thickness and smoother surfaces compared to films coated from NBT sols with pH 5. Films with rough surfaces having considerable thicknesses were obtained with pyrochlore phase formed in it. Stoichiometric Sodium Bismuth Titanate (NBT) phase formed in powder samples. Annealing temperature does not seem to be the reason for the absence of NBT in synthesized films.

Till now the films coated by NBT sol prepared by sol gel technique were annealing at high temperature for 30 minutes. As bismuth has high vapor pressure and sodium with low atomic weight, annealing the films at high temperature for 30 minutes may leads to deficiency of this cations in the films while annealing. It have been reported in the literature that annealing temperature and annealing time plays a major role in defining formation of perovskite structure of the material and also affects the final grain size and hence, piezoelectric as well as ferroelectric properties of the films. It is clear from the result that pure NBT perovskite structure is absent in the film annealed for 30 minutes. Now, the films will be subjected to Rapid Thermal Annealing (RTP) i.e. coating the film then evaporating the solvents followed by anneal the films for 3 minutes and repeating the above steps for subsequent coatings.

A careful study on the effect of viscosity of the sol on the film thickness will be accomplished along with the study of aging effect on the rheology of the sol as sol will be allowed to age for longer duration of time. Further study will be done on the effect of

rotation speed (rpm) of the substrate and rotation time while spin coating to obtain film with high thicknesses.

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