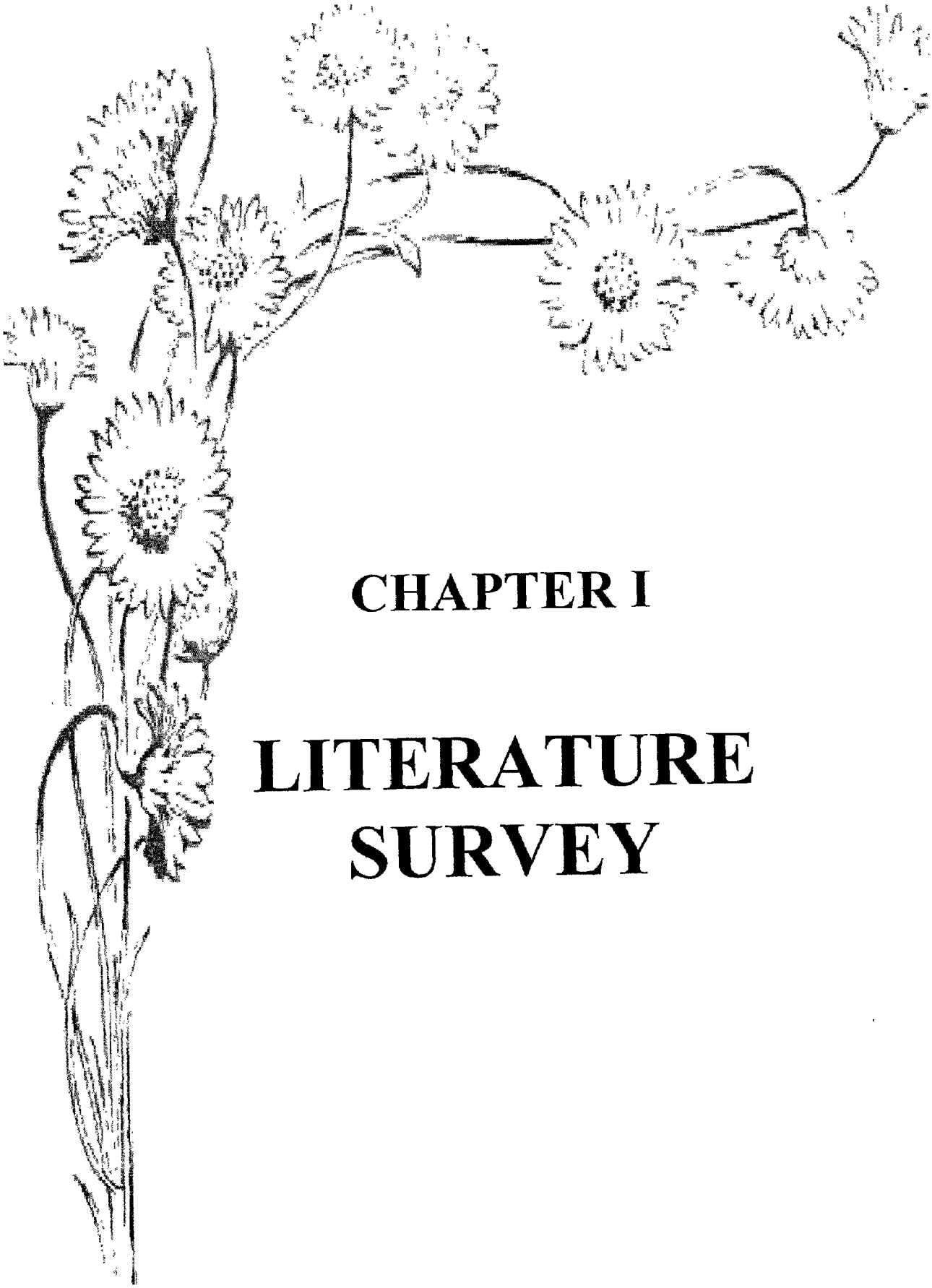

CHAPTER I

LITERATURE SURVEY

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LITERATURE SURVEY

I.1. Introduction

Materials technology has a profound impact on the evolution of human civilization that historians have defined distinct time periods by the materials that were dominant during these eras (e.g. the Stone Age, the Bronze Age, and the Iron Age). The current Synthesis Materials Age is identified by plastics, composites and other well designed, man –made engineering materials. In the more recent years, with the advancement of several emerging technologies, such as biotechnology, nanotechnology, and information technology, the dawn of the 21st Century will witness the emergence of the Smart Materials Age. "Smart " material is often defined as one that gives an unexpected response to an input **(Uchino, 2000)**. In the fields of mechanical and aerospace engineering, smart or active materials of interest are those which produce a mechanical response to an electrical, magnetic or thermal input can be used to replace existing servo mechanisms at lower size and weight or be used in applications where traditional actuators are either too bulky, in accurate or slow, such as active damping, ultrasonic, and microelectronic mechanical system (MEMS). A number of such materials exist including piezoelectric, magnetostrictors, and shape memory alloys **(Wells, 1977)**. Each of them can suit the specific potential requirements of the future smart

materials systems. For instance, piezoelectric materials, such as barium titanate, lead titanate, and lead zirconate titanate are ideal for applications requiring high frequency response, such as ultrasonic for medical imaging or sonar, or precise displacement, such as nanopositioning for fiber optic alignment or probe microscopy. These materials have the added advantages that they can be used as sensors as well as actuators allowing feedback control. In the present work, synthesis and characterization of barium titanate and lead titanate nanopowders by wet chemical methods will be focused on.

Barium titanate $BaTiO_3$ (BT) and lead titanate $PbTiO_3$ (PT) ferroelectrics ceramics materials are very important materials used for a wide range of applications. They used in microelectronics, telecommunications, energy storages and sensors. The applications of each barium titanate and lead titanate in details will be mentioned in later session [I.5.3]. Recent advances in microelectronics and communications have led to the further reduction of the grain size of the dielectric layer below the 1μn limit. To achieve this goal, powders with controlled stoichiometry, small and uniform size (of the order of 100 nm) are required.

Several techniques are available for synthesis of nanosized ferroelectric materials including co-precipitation, sol gel processing, hydrothermal, microemulsion, reaction in molten salts, polymeric and organic precursors **(Henning et al, 1987; Brinker et al, 1990; Yoo et al, 1997; Matsuda et al, 1998 and Gotar et al, 2003)**.

Now days the hydrothermal method has been utilized for the commercial production of ferroelectric powder (**Joshi, et al, 2006**). On the other hand, organic acid precursors technique involves the preparation of aqueous solution required cations, the chelating of cations in solution by addition of carboxylic acid and raising the temperature of the solution until formation the precursor. The precursor is calcined at high temperature to form the powder. The technique gives the formed powder in nano- size and improves the characterization of the powders.

In our present work, we aim to synthesis of nanosized barium titanate and lead titanate powders using hydrothermal and organic carboxylic acid precursor methods. Through the titanates nanoparticles formed, the change in phase identification, crystallite size, microstructure and detailed dielectric properties will be systematically studied.

I.2. Ferroelectric Materials

The term "ferroelectric" relates not to a relationship of the material to the element iron, but simply a similarity of the properties to those of ferromagnets: just as ferromagnets exhibit a spontaneous, reversible magnetization and an associated hysteresis behavior between magnetization and magnetic field. Ferroelectrics exhibit a spontaneous, reversible electrical polarization and an associated hysteresis behavior between polarization and electric field **(Megaw, 1957; Deri, 1969 and Jona et al, 1993)**. Likewise, much of the terminology associated with ferroelectrics is borrowed from ferromagnets. For instance, the transition temperature below which the material exhibits ferroelectric behavior is referred to as the Curie temperature. Other terminology is best introduced by examining the typical polarization-electric field hysteresis curve for a ferroelectric material, shown in Fig.1. The spontaneous polarization, Ps, is defined from this curve by the extrapolation of the linear region at saturation back to the polarization axis. The remaining polarization when the electric field returns to zero is known as the remnant polarization, Pr. Finally, the electric field at which the polarization returns to zero is known as the coercive field, Ec.

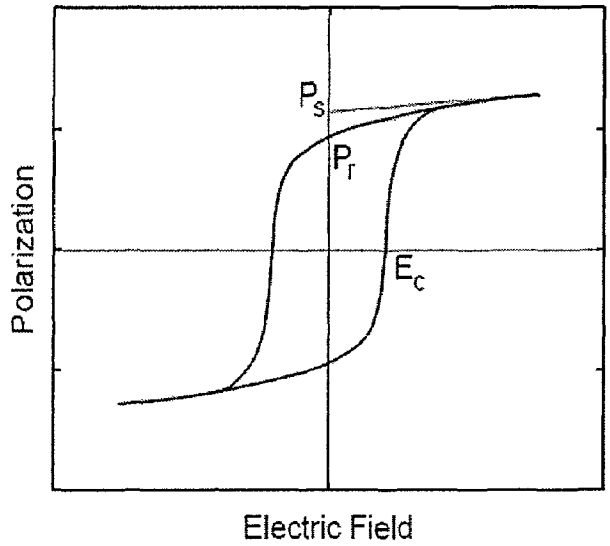


Fig.1: Polarization-electric field hysteresis for ferroelectric materials. The spontaneous Polarization (Ps), Remanent polarization (Pr), Coercive field (Ec)

Ferroelectrics materials are intensively studied in the last ten year for application in informatics (storage medium in dynamic access memory) as well as in microwave domain (dielectric resonators, substrates for microwave hybrid integrated circuits, planner antennas, etc). The specific application depends upon the properties of these materials which controlled by their structure. The ferroelectric phenomenon was first discovered in Rochelle salt ($NaKC_4H_4O_6.4H_2O$) in 1921 **(Xu, 1991; Moulson et al, 1992 and Solymar et al, 2004).**

Ferroelectric is a phenomenon that occurs when an electric field is applied to a dielectric, polarization occurs and dipoles become aligned with the field. When the field is removed, the polarization

generally vanishes. This occurs even when there are permanent dipoles since in the absent of the field they become randomly orientated. There are, however, ferroelectrics materials preserve the remaining polarization when the electric field returns to zero, this process called poling process **(Braithwaite et al 2000; Chiang et al, 1997 and Moulson et al 1992)**. The poling process is illustrated in Fig. 2.

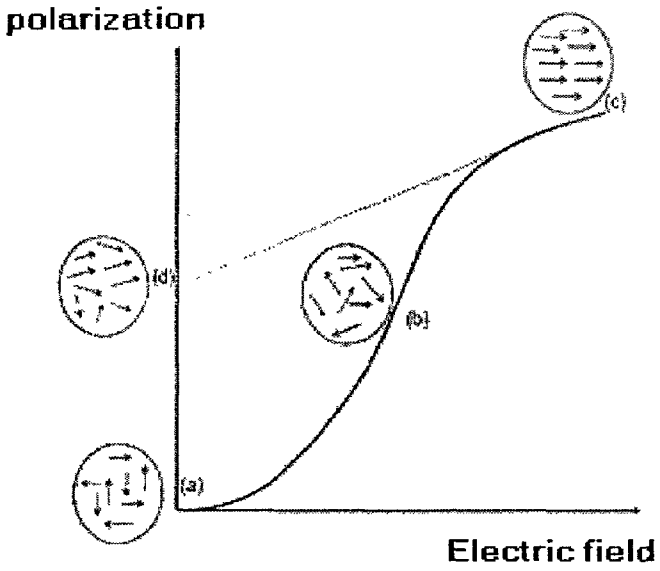


Fig.2: Poling process; (a) non-polar polycrystalline ferroelectric ceramic, (b) domains begin to align in the direction of external electric field (c) Fully polarized state (d) remnant polarization.

Most ferroelectrics materials undergo a structure phase transition from a high temperature non ferroelectric or (paraelectric) phase into a low temperature ferroelectric phase, of lower crystal symmetry. The phase transition temperature is usually called the Curie point (Tc) **(Cross, 1993)**. In most cases, the dielectric constant above this temperature obey the Curie- Weiss law and it is

said to be pyroelectric materials, which they exhibit a spontaneous ionic polarization changes with temperature. Above (Tc), the center of the positive and negative ions coincides with each other and cancels out the entire polarization. Ions coincide with each other and cancel out the entire polarization then the material is non-polarized. Below the Curie temperature, the positive and negative ions are off centered. Hence, the material stays polarized. The size dependence of Tc governs the ultimate size limit of ferroelectric non volatile memory and has been the subject of numerous investigations **(Junquera et al, 2003; Ahn etal, 2004 and Fong et al, 2004).**

I.2.1. Classification and Structure of Ferroelectric

Ferroelectric materials can be classified as the follows:-

- Ferroelectric of perovskite structure, **e.g.,** $BaTiO_3$, $PbTiO_3$.
- Ferroelectric of pyrochlore structures, **e.g.,** $Cd_2Nb_2O_7$, in this cases the Curie temperature are low.
- Ferroelectrics of potassium dihydrogen phosphate KH_2PO_4, (KDP) family including triglycine sulphate and cesium phosphate (CsH_2PO_4). The major applications of KDP family materials in the paraelectric prototypic form due to their Tc points (-150°C) **(Cross, 1984; Henning et al, 1987, and Jona et al, 1993)**

Table 1: Curie temperature and spontaneous polarization of some ferroelectric crystals **(Jona et al, 1993)**

Name and Chemical Formula	**Curie Temperature Tc (°C)**	**Spontaneous Polarization, P_S ($\mu C/cm^2$)**	**Year in which reported**
Rochelle Salt $NaKC_4H_4O_6.4H_2O$	23	0.25	1921
Potassium Dihydrogen Phosphate KH_2PO_4 (KDP)	-150	4	1935
Potassium Dihydrogen Arsenate KH_2AsO_4	-177	5	1938
Potassium Dideuterium Phosphate KD_2PO_4	-60	5.5	1942
Barium Titanate $BaTiO_3$	120	26	1945
Lead Titanate $PbTiO_3$	490	>50	1950
Potassium Niobate $KNbO_3$	415	30	1951
Lead Zirconate Titanate * $Pb(Zr_xTi_{1-x})O_3$	~350	>40	1952

* Polycrystalline ceramics

Perovskites ceramics materials are the main ferroelectrics due to many applications. Ideal perovskites have the general formula ABX_3, where the A-site cation is normally larger than the B-site cations and similar in size to the X-site anions **(Mitchell, 2002).** The X-anion can be oxygen (forming compounds of extensive applications), fluorine (i.e. halogen), e.g.$KMgF_3$, or a mixture of oxygen and nitrogen, e.g.$BaTaO_2N$. Those containing Li^+ and the alkaline earth cations adopt the inverse perovskite structure, i.e. BAX_3, e.g. $BaLiF_3$, with cations A and B exchanged their lattice positions. The halogen –based (or simply, halide) perovskites are usually non-cubic at room temperature due to the large ionic radii of the anions. The oxide – (or oxygen –based) perovskite, however, are the most studied family in the decades after the war since their extensive applications mainly in electronics and proton ionic conductors **(Bonanas, 1995)**. The oxides family include titanates of the simple compounds e.g. $BaTiO_3$, $CaTiO_3$, $SrTiO_3$, $PbTiO_3$ containing only two cations and one for each of the A- and B-sites; zirconium, of the simple compounds e.g. $BaZrO_3$. They become complex perovskites when contain two B-site cations, such as Pb $(Zr,Ti)O_3$, Ba $(Ti,Zr)O_3$, and Pb $(Sc,Ta)O_3$. In addition they can also contain two A-site cations, e.g. $(Pb,La)(Zr,Ti)O_3$ **(Heartling , 1999)**.The complex perovskites with a variety of chemical compositions exhibit useful electronic and dielectric properties have found extensive applications in the passive –component industries. One representative example is Pb $(Mg_{1/3}Nb_{2/3})O_3$ (acronym PMN), the so-called "relaxors" **(Rittenmyer, 1990)** in contrast to diffuse - phase - transition Ba (Ti, Zr)O_3, and normal

ferroelectrics ,e.g. $BaTiO_3$, $PbTiO_3$. Other examples of perovskite "relaxors" is PZN $(Pb(Ni_{1/3}Nb_{2/3})O_3$ **(Cross, 1994)**. Perovskite oxide structure with unconventional cations valences (I) or (V), e.g., $NaNbO_3$ and $KNbO_3$ is found **(Chiang et al, 1996)**. Most of these compounds are not cubic in symmetry at room temperature.

A simple crystal structure of perovskite type ABO_3 is cubic structure, show in Fig. 3 which consists of corner sharing oxygen octahedral (BO_6) arranged in three dimensions. Highly charged cations (B: Ti^{4+}, Zr^{4+}, Sn^{4+}, Nb^{5+}, Ta^{5+}, W^{6+}, etc.) is located in the middle of the octahedral, and lower charged cations (A: Na^+, K^+, Ca^{2+}, Ba^{2+}, Pb^{2+}, etc.) is located in between the octahedral, filling the interstices between octahedral in the larger 12- coordinated A sites. The A atoms sitting in the 12-fold interstice are coordinated with twelve O atoms i.e. with the coordinated number CN= 12, and the B atom locating in the octahedral interstice are coordination with six atoms, i.e. with CN=6. Because of the A and O are atoms form a close- packed array, they should be approximately the same ionic radii and the B atoms should be smaller and most perovskite-type ferroelectrics are compounds with either $A^{2+}B^{4+}O_3$ or $A^{1+}B^{5+}O_3$ type formula **(Kasap , 2000).**

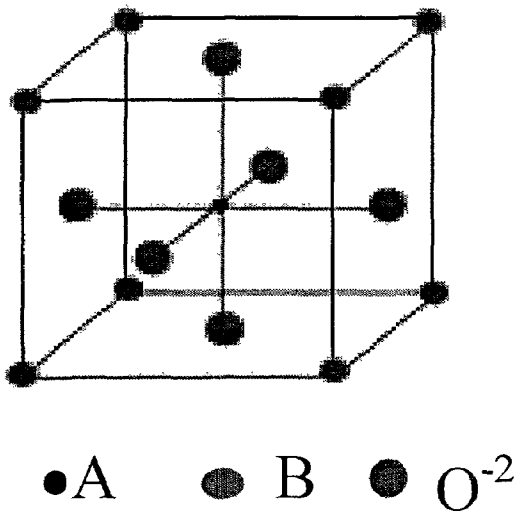


Fig. 3: Perovskite cubic structure ABO_3

I.3. Antiferroelectric Materials

In some perovskite ceramics, the instability that occurs at the Curie temperature is not ferroelectric but rather antiferroelectric. In antiferroelectric crystals the neighboring lines of ions are displaced in opposite polarization. Consequently, the net polarization is zero, and the dielectric constant does change at the transition temperature; examples of antiferroelectric crystals are WO_3, and $PbHfO_3$. In general, the difference in energies between the ferroelectric and antiferroelectric states is quite small (a few joules per mole). Consequently the phase transition between the two states occur readily and can be brought about by slight variations in composition or the application of strong electric fields **(Barsoum, 2003)**.

I.4. Piezoelectricity

All ferroelectric materials are potentially piezoelectric for a crystal classification. Piezoelectricity is the ability of certain crystalline materials to develop an electrical charge proportional to an applied mechanical stress (**Jaffe et al, 1971**). This phenomenon is direct piezoelectricity. Application of electric field to piezoelectric materials will result in a strain response directly proportional to the electric field. For a material to exhibit piezoelectric properties, it must have a permanent dipole and lack a center of symmetry on the atomic scale. The main examples of piezoelectric materials include quartz, lead titanate, lead zirconate titanate and barium titanate.

I.4.1. Piezoelectric Equations

The direct piezoelectric effect is defined as a linear relationship between stress and electric displacement or charge per unit area and indirect piezoelectric effect is defined as a linear relationship between strain and electric field. Equation (1) represented the direct and indirect piezoelectric effects respectively.

$$D = d\,\sigma \quad \& \quad \varepsilon = d\,E_e \qquad (1)$$

Where D is the electric displacement vector, σ is the stress tensor (direct piezoelectric effect), E_e is the electric field strength, ε is the strain tensor (indirect piezoelectric effect) and the piezoelectric constant d is numerically equal in both equations.

The units of measurement are however different. For the direct effect, d is measured in coulombs/ Newton while meters/volt is used for the indirect effect. The piezoelectric voltage constant g is also frequently used to describe the relationship between electric field produced by applying stress to a piezoelectric material. g is defined mathematically as in Equation (2) **(Nye,1985& Newnham, 2005)**.

$$E_e = g\,\sigma \tag{2}$$

Where units of g is volts m/N and it is related to the piezoelectric distortion constant d through permittivity ξ of the piezoelectric material by

$$g = d / \xi \tag{3}$$

For practical purposes, the electromechanical coupling factor, $\mathbf{k^2}$, perhaps offers the best measurement for the strength of a piezoelectric material. The electromechanical coupling factor measures the ability of a piezoelectric material to transform mechanical energy into electrical energy or transform electrical energy into mechanical energy. Mathematically, $\mathbf{k^2}$ is defined as

$$\mathbf{K^2} = \frac{\text{Mechanical energy converted to electrical energy}}{\text{In put mechanical energy}}$$

or

$$\mathbf{K^2} = \frac{\text{Electrical energy converted to mechanical energy}}{\text{Input electrical energy}} \tag{4}$$

k^2 values of piezoelectric materials depend on purity, microstructure and magnitude of electric polarization . Examples of k^2 values of some common piezoelectric materials are given in Table 2 **(Jaffe et al, 1971)**.

Table 2: Electromechanical coupling factors of some piezoelectric materials

MATERIALS	k^2
Quartz	0.01
Barium titanate ceramic	0.16
Lead zirconate titanate	0.25-0.49
Rochelle salts	0.81

I.5. Barium Titanate ($BaTiO_3$) and Lead Titanate

Barium titanate and lead titanate materials are the main principal commercial piezoelectric and ferroelectric ceramics. They are used in manufacturing of electronic components for electronic devices. Barium titanate and lead titanate are popular not only because of their attractive dielectric, ferroelectric, piezoelectric properties but also because it is mechanically and chemically stable **(Heartling, 1999)**. Even more interesting is the amenability of the structure to different compositional changes which is useful in tailoring electrical properties of the ceramic. For example, substitution of some Ba^{2+} ions with Pb^{2+} leads to stabilization of the abnormally high dielectric constant of $BaTiO_3$ at the Curie temperature **(Mostaghaci et al, 1986)**. Improved synthesis techniques have also enabled production of $BaTiO_3$ and $PbTiO_3$ powders with high purity and adjustable physical and chemical properties (**Park et al, 1999**).

Barium titanate material exhibits four crystal phases, namely, cubic, tetragonal, orthorhombic and rhombohedral. At high temperature, it has a cubic perovskite structure. When cubic $BaTiO_3$ cooled below 120°C, it transforms into the ferroelectric tetragonal structure by elongating along an edge. The tetragonal phase is stable until 5°C where it transforms into the orthorhombic phase then to the rhombohedral phase at -90°C, shown in Fig.4. The transition temperature is depending mainly on grain size, particle size, and chemical composition. (**Hench et al, 1990; Noma et al, 1996 and Shi et al, 1997**)

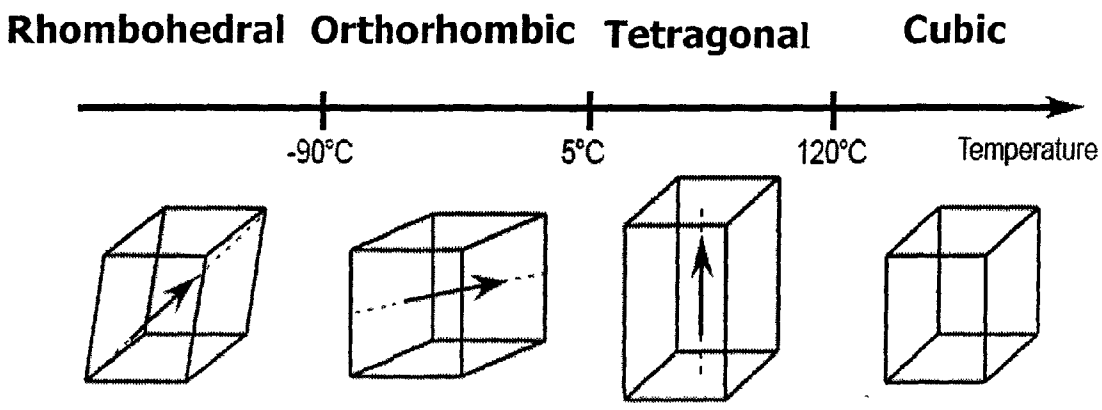


Fig.4: Phases structure of barium titanate

I.5.1. Synthesis of Barium Titanate and Lead Titanate

Synthesis of barium titanate and lead titanate can be divided to main methods:

1. Solid State Method (Conventional method)
2. Wet Chemical Methods : These are including on

i. Co-precipitation method

ii. Sol- gel method

iii. Microemulsion method

iV. Organic carboxylic acid precursor method

V. Hydrothermal method

The two main methods are discussed in details and the comparisons between them are summarized in Table 3.

I.5.1.1.Solid State Method

The most direct method of making mixed – oxides is reacting a mixture of metal oxides, hydroxide or carbonate in the solid state. Conventional processing to prepare multicomponent mixed- oxide ceramic powders involves three consecutive steps of mixing, solid state reaction and milling. Particles can be formed either in a structured fashion or randomly. Then the multicomponent is formed via solid state reaction. Consequently, these solid state reactions typically result in the formation of aggregates (hard agglomerations) that required a comminuting process to reduce the particle size to the micrometer level. Milling to particle size < 1μm is technically difficult for some hard materials and contaminates the product and is energy intensive **(Bauger et al ,1983 ; Chu et al ,1995 ; Phule et al ,1990 ; López ,1999 ; Su et al ,2001 and Stankus et al ,2004).**

The solid state reaction occurs by solid state diffusion with a relatively slow diffusion rate. Therefore, small diffusion distances or high calcination temperatures are necessary to complete the reaction. Since, however, high calcination temperature will result in coarse- grained powders having unsuitable sintering properties, the diffusion distance must be minimized. This can be achieved by intimate mixing or milling procedures (dry or wet using water, alcohol, etc) of the ingredients. Mixing or milling times are also limited because long of times lead to increasing impurity concentrations by mechanical abrasion of the milling equipment.

The powder preparation usually proceeds due to the principal facts just mentioned, as follows:

1-Weighing of the raw materials

2- Intimate mixing or milling (dry or wet) for time from 1 to 10 hrs using porcelain, SiO_2, or Al_2O_3 materials for equipment.

3- Calcination the powders for calcination time 1- 10 hrs at temperatures from1050 – 1200 °C according to the following equations:-

$$BaCO_3+TiO_2 \longrightarrow BaTiO_3 + CO_3 \quad (1050 \text{ to} 1200\ ^\circ C) \quad (5)$$

$$PbO + TiO_2 \longrightarrow PbTiO_3 + CO_3 \quad (800 \text{ to } 900\ ^\circ C) \quad (6)$$

4- Sintering the formed powders at high temperature up to 1300°C and finally machining to different geometry (**Amin et al, 1983**).

The disadvantages of synthesis of barium titanate and lead titanate nanopowders are include high calcination temperature, necessity of milling and mixing of raw materials for long periods about 10 hrs. The possibility of contaminate during milling and formation of other phases, such as Ba_2TiO_4, $BaTiO_9$, and $BaTi_2O_5$ for barium titanate and in case of lead titanate Pb_2TiO_4, $PbTiO_9$ and $PbTi_2O_5$ **(Ananta et al, 1999; López et al, 1999, and Ananta et al, 2000).**

Stojanvic et al, 2005 and **Simon –Seveyrat, et al 2007,** improved the synthesis of barium titanate by solid state method according to the flow sheet diagram given in Fig.5. Although other phases of Ba_2TiO_4 and barium carbonate after calcination are still formed.

Udomporn et al, 2004, tried to avoid the formation of other phases during synthesis of lead titanate powders by mixing PbO and TiO_2 using ball milling then calcined at temperature 550°C for time 4 hrs. The crystallite size of the produced $PbTiO_3$ powders was in the range between 75-385 nm. Other phases of $PbTi_3O_7$ with TiO_2 with minor were also formed.

Wongmaneerung et al, 2006, synthesized lead titanate (PT) by solid state reaction via a rapid vibro-milling technique. The resulting PT powders have a range of particle size, depending on milling time. Production of a single phase PT powder can be successfully achieved at 25 hrs of vibro-milling after which a higher degree of particle agglomeration was observed by milling to 35 hrs.

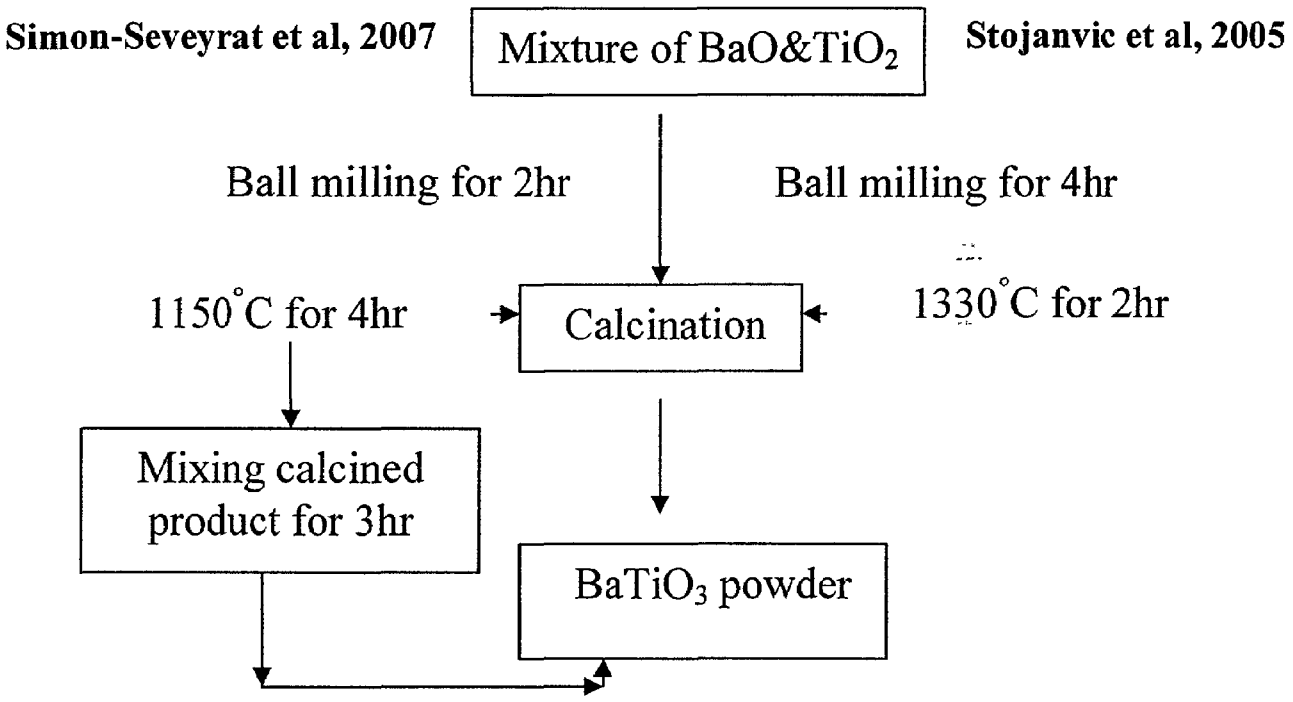


Fig.5: Block flow-sheet diagram of formation of barium titanate through solid state method according to **Simon-Seveyrate et al, 2007** and **Stojanvic et al, 2005**

I.5.1.2. Wet Chemical Method

Wet chemical method affords modern means for achieving high homogenization on the atomic scale during calcination of the different elements that form the perovskite compounds. Moreover, this method includes the possibility of producing very pure materials. The wet chemical method including *Co-precipitation from solution, Sol- gel, Microemulsion method, Organic carboxylic acid precursor techniques and Hydrothermal method* **(Potdar, 1999 & Kim et al, 1996).**

i. *Co-precipitation Method*

Co-precipitation from solution is one of the oldest wet chemical techniques for the preparation of mixed oxides. It consists of preparation of an aqueous solution which contains the precipitation agent. The precipitated products is separated from the liquid by filtration, dried and thermally decomposed to the desired compound. Several parameters, such as pH, mixing rates time, temperature and concentration have to be controlled to produce satisfactory results. The composition control, purity and morphology of the resulting products are good. However, different rates of precipitation of each individual compound may lead to microscopic in homogeneity and agglomerates are generally formed during calcination, as with other solution techniques. By controlling the synthesis conditions, this method can produce stoichiometric electroceramic powders of high purity and is currently applied widely to make electroceramic powders in

industry **(Phule et al, 1990; lee et al, 2003 and Tartaj et al 2001).** The block flow sheet diagram for preparation of barium titanate or lead titanate is shown in Fig. 6.

Advantages of Co-precipitation method:

1- Low cost compared by other techniques
2- High degree of homogeneity
3- Mass production

Disadvantages of Co-precipitation method

- Wide particle size distribution

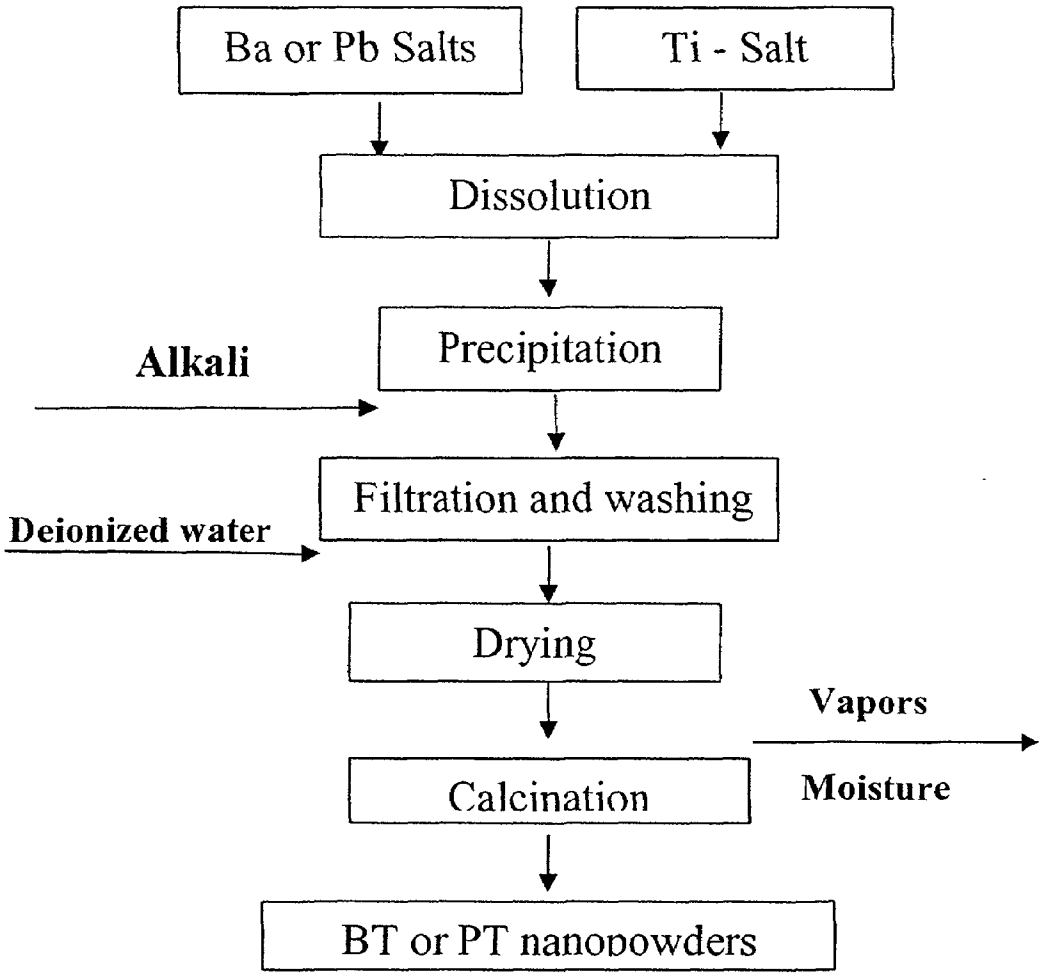


Fig. 6: Block flow sheet diagram for the production of $BaTiO_3$ or $PbTiO_3$ nanopowders by Co-precipitation method

ii. *Sol- Gel Method*

Sol gel process involves the transition of a solution system from a liquid "sol" (mostly colloidal) into a solid "gel" phase. The basic principle of the sol gel is formation a solution of the elements of the desired compound in an organic solvent and, polymerizes the solution to form a gel and dry and fire this gel to displace the organic compounds and form a final inorganic oxide (**Brinker et al, 1990; Lan et al, 1995 and Bersani et al, 1996**).

Sol gel processing comprises the following stages

1- Sol production
2- Gel formation
3- Gel aging
4- Gel drying

Sol production and Gel formation

In the sol gel processing, the precursor (starting compounds of the alkoxides) for preparation of a colloid consists of a metal or metalloid element surrounded by various ligands. Metal alkoxides are popular precursors because they react readily with water. The reaction is called hydrolysis because a hydroxyl ion becomes attached to the metal atom. The hydrolysis step replaces an alkoxide with a hydroxyl group from water and a free alcohol is formed as in the following reaction in the presence of acid or base catalyzed materials (**Kim et al, 1999**).

$$Ti(OR)_4 + H_2O \longrightarrow Ti(OH)_4 + 4ROH \qquad (7)$$

Gel aging

Gelation is a spectacular event, when a solution suddenly losses its fluidity and takes an appearance of an elastic solid. The gel point represents the moment when last link is formed in the chain bonds that constitutes the spanning cluster. The processes of change during aging after gelation rate are categorized as polymerization is the increase connectivity of the net work produced by condensation.

Gel drying

In this step, the solvent is removed from the pores of the gel. The remaining rigid monolithic shape consists of covalently bonded, nanometer-size particle that are arranged in a 3- dimensional network. Supercritical drying (aerogel formation) is a tool to drive off the solvent from the alcogel without shrinkage of the gel network. The alcogel is put in an autoclave and the container is filled with alcohol and the temperature is raised to the supercritical points of the used alcohol. The drying process of the porous materials under ambient pressure can yield what is called xerogel. **(Beck et al, 2001)**. Fig.7 illustrates the stages for synthesis of barium titanate and lead titanate nanopowders via sol gel method

Advantages of Sol- gel method

1-Products of superior high purity can be fabricated

2- High degree of homogeneity of the product can be obtained

3- Low temperature technique

4- Environmentally friendly

5- Improved properties of formed oxides by microstructure

6- Unlimited applications

Disadvantages of sol- gel method

1- High cost materials

2- Aerogel need control

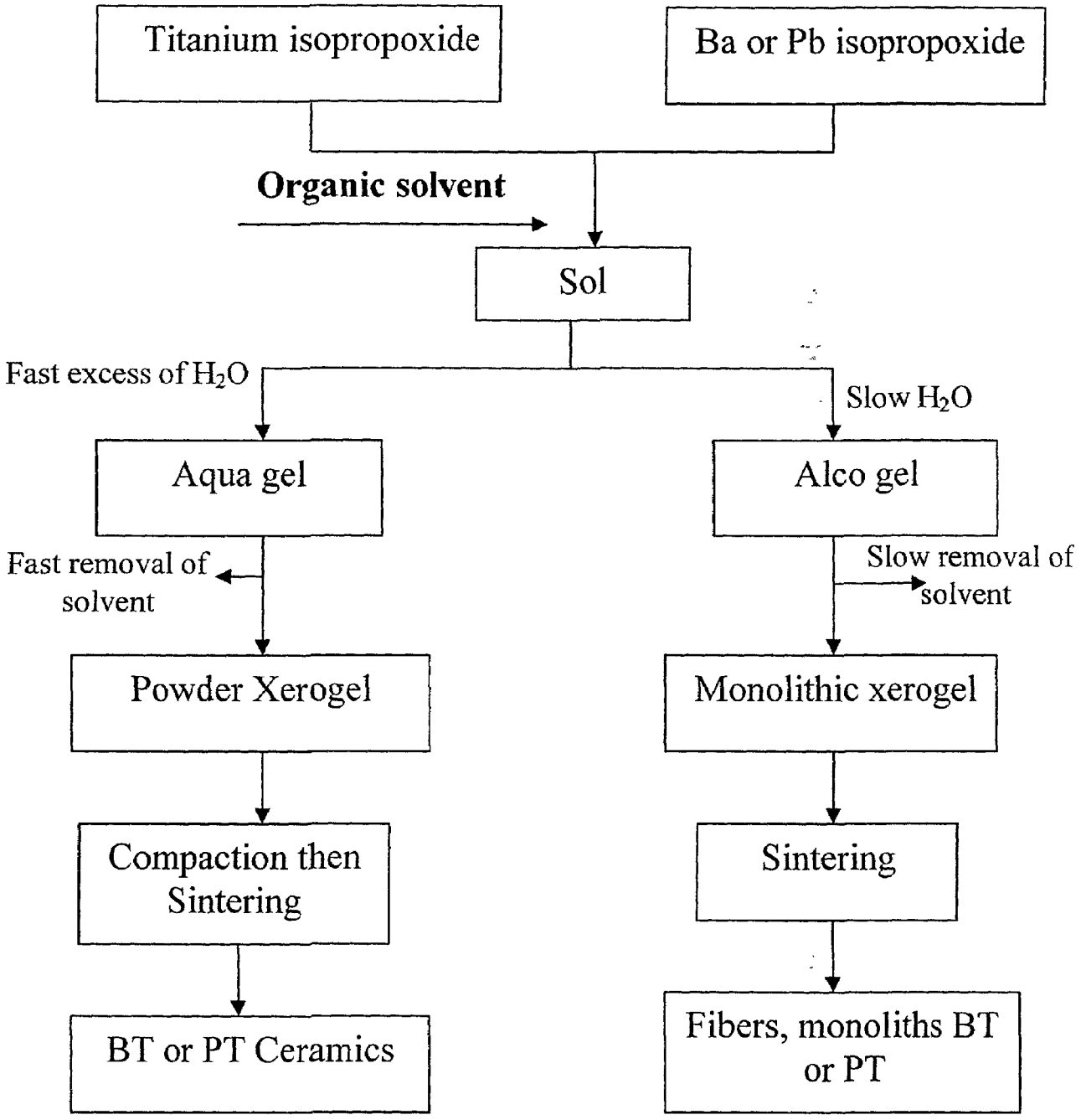


Fig.7: Flow sheet diagram for the production of $BaTiO_3$ or $PbTiO_3$ nanopowders by sol-gel method

iii. Microemulsion Method

Microemulsions are colloidal of oil in water or water in oil stabilized by a surfactant film. These thermodynamically stable dispersions can be considered as truly nanoreactors which can be used to carry out chemical reactions and, in particular, to synthesize nanomaterials. The main idea behind this technique is that by appropriate control of the synthesis parameter, one can use these nanoreactors to produce tailor-made products down to nanoscale level with new and special properties. Fig. 8 shows the block flow sheet of barium titanate and lead titanate by microemulsion method **(Loez-Quintela, 2003)**.Surfactants reduce the surface tension of liquids, or reduce interfacial tension between two liquids or a liquid and a solid. Short-chain alcohol and fatty acids with less than eight carbon atoms in a chain are not typically emulsifiers. Surfactants with 10-18 carbon atoms in a chain have the best emulsifying ability. Surfactants are an organic compound consisting of two parts

1- a non-polar (lipophilic) portion usually including a long hydrocarbon chain.

2- a polar (hydrophilic) portion which renders the compound sufficiently soluble or dispersible in water or another polar solvent.

Reaction in microemulsion

In water- oil microemulsions, a necessary step prior to their chemical reaction is the exchange of reactants by the coalescence of two droplets. The aqueous droplets continuously collide, coalesce and break apart resulting in a continuous exchange of solute content. The collision process depends upon the diffusion of the aqueous droplets in the continuous media, i.e. oil, while the exchange process depends on the attractive interactions between the surfactant tails and the rigidity of the interface, as the aqueous droplets approach close to each other when the chemical reaction is fast, the overall reaction rate is likely to be controlled by the rate of coalescence of droplets. There, properties of the interface such as interfacial rigidity are of major importance. Relatively rigid interface decreases the rate of coalescence, and hence leads to a low precipitation rate. On the other hand, a substantially of hid interface in the microemulsion enhances the rate of precipitation. Thus by controlling the structure of the interface, one can change the reaction kinetics in microemulsions by an order of magnitude **(Pillai et al, 1995 and Wang et al, 1999)**.

Advantages of microemulsion method

1- High degree of homogeneity of the product can be obtained
2- It minimized agglomeration of the final products
3- It relatively moderate cost
4- The ability to precisely control the size and shape of the particles formed

Disadvantages of microemulsion method

1- High cost materials

2 - Need control

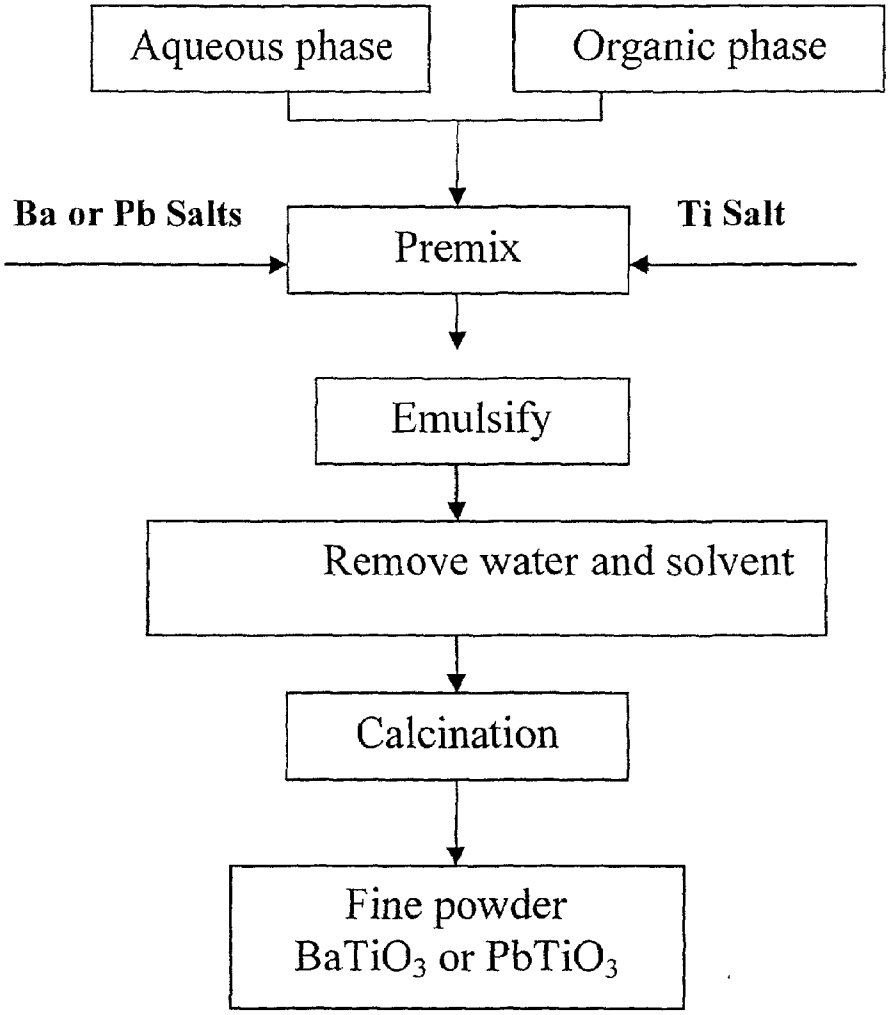


Fig.8: Flow sheet diagram for the production of $BaTiO_3$ or $PbTiO_3$ nanopowders by microemulsion method.

IV. *Organic Carboxylic Acid Precursor Method*

The organic carboxylic acid precursor technique involves the preparation of aqueous solution required cation, the chelation of cations in solution by addition of carboxylic acid than, raising the temperature of solution until formation the precursor. The precursor is calcinated at high temperature to form the powder where the quasi-atomic dispersion of constituent components in liquid precursors which facilitates synthesis of the crystallized powder **(Potdar et al, 1996; Poth et al, 2000; Anuradha et al, 2001; Arya et al, 2003 and Malghe et al, 2004)**.

The function of carboxylic acid was used as an organic fuel, i.e. it can form stable complexes with Ti and Ba or Pb ions and also a rich fuel. The precipitation of Ba, Pb and Ti cations occurred simultaneously. Titanium is precipitated as titanyl oxalate or titanyl citrate.... etc and barium or lead precipitated as barium or lead oxalate, citrate, tartarate ...etc. Fig.9 shows the block flow sheet diagram of barium titanate and lead titanate using organic carboxylic acid precursor method (**Guiffard et al, 1998 and Jha et al, 2003**).

Preparation of barium titanate by organic carboxylic acid method

Cho et al, 1998, using citric acid as source of organic acid, barium carbonate and titanium isopropoxide as sources of Ba and Ti at mole ratio Ba/ Ti equal 1. These materials were polymerized in mixed solution of citric acid, ethylene glycol at mole ratio 1 / 4, then heating the mixed solution at 90°C and continued heating at 200°C for 5 h to form dark brown resin which was used as a precursor. Heating the resin at 400°C for 2 h in electric furnace then thermally treated again the polymeric precursor in static air furnace at 500-900°C for 5 hrs. The first appearance of $BaTiO_3$ as a cubic single phase was detected for the sample heated at 600°C. The Raman spectrum suggested that tetragonal structure might be slightly sustained in the ultrafine $BaTiO_3$ particles. The complete transformation of the precursor into tetragonal $BaTiO_3$ was achieved after 8 h at 900°C.

Potdar et al, 1999, synthesized barium titanate using oxalic acid with alcoholic solutions of butyl titanate at molar ratio 1:1 which formed titanyl oxalate. When titanyl oxalate reacted with sodium oxalate solution at molar ratio of Ti /oxalic 1:2, it converted into soluble sodium titanyl oxalate. The produced soluble reacted with a solution of barium acetate to form mixed oxalate [BaC_2O_4+ TiO (C_2O_4) (H_2O)$_2$] as precursor at 200°C. The precursor was transformed to $BaTiO_3$ powders after calcination 560-960°C for 5 hrs. In other study, **Potdar et al, 2001**, synthesized barium titanate by calcination of BTO (Barium titanyl oxalate) which was formed by reacting of alcoholic solution of titanium tetrabutoxide with

oxalic acid to form titanyl oxalate ($TiOC_2O_2$) which convert to ammonium titanyl oxalate by ammonium oxalate and react with barium salt, "BTO" was calcinated at 700°C for 5 hrs to obtain Ba_2TiO_4 & $BaTi_3O_7$.

Duran et al, 2001, prepared barium titanate using citric acid as source of organic acid. The titanium tetrabutoxide dissolved in ethylene glycol and nitric acid solution. A certain amount of citric was added to the solution, and then barium titanate was added. The mixture was heated to180°C until convert the pale yellow solution to brown viscous. BT nanopowders were formed by calcining the precursor at 750°C for 2 hrs.

Khollam et al, 2002 , were synthesized barium titanate using oxalic acid as source of organic acid and titanium tetrabutoxide with isopropanol give oxalotitanic acid $[H_2TiO(C_2O_4)_2]$ (HTO) which reacts with barium hydroxide to give barium titanyl oxalate (BTO) as precursor with yield ≥ 99%. The controlled pyrolysis of BTO at 750°C for 4hrs in air- produced agglomerated cubic $BaTiO_3$ powders having spherical particles with size about 100 nm.

Simon-Seveyrat et al, 2005, using barium acetate and butyl titanate as source of barium and titanium in the presence of oxalic acid to form barium titanate after calcination the formed precursor at 650°C for 10 hrs.

Lee et al, 2005, prepared barium titanate using citric acid as source of organic acid, barium carbonate and titanium tetra-isopropoxide as source of Ba^{2+} and Ti^{4+}, respectively. Tetragonal $BaTiO_3$ phase was formed after calcination at 1050°C for 3 hrs.

Hwu et al, 2005, synthesized barium titanate using oxalic acid, barium chloride and titanium tetrachloride $TiCl_4$ as source of barium and titanium at mole ratio Ba / Ti=1.05. The mole ratio of oxalic acid to titanium tetrachloride was 2.2. The precipitated oxalate precursor was filtered and washed in distilled water several times and dried at 80°C for 24 hrs to form barium titanyl oxalate BTO $[BaTiO(C_2O_4)_2.4H_2O]$. The Barium titanate phase can be obtained by calcination barium titanyl oxalate precursor at 800°C for 6 hrs.

Vinothini et al, 2005, applied the technique used mentioned before by **Cho, 1998** and they showed that the complete transformation of the precursor into tetragonal BT was finally achieved after 8 hrs calcination time at 900°C.

Ghosh, et al, 2007, synthesized barium titanate using barium nitrate and titanyl oxalate solutions dissolved in 2N nitric acid. Tartaric acid 0.6 M was used as source of organic acid. The solution was heated at temperature 130°C for 30 min until dried precursor formed then the precursor was calcined at 900°C for 2 hrs to get a conversion of BT nanopowders with 90 % yield.

Preparation of lead titanate by organic carboxylic acid method

Paris et al, 1998, synthesized lead titanate using citric acid as sources of organic acid and lead acetate with titanium isopropoxide as source of Pb^{2+} and Ti^{4+} at mole ratio Pb/Ti ≈ 1 the mole ratio of Ti (IV) to citric acid 1:3 with ethylene glycol then heating the solution at 250°C for 3 h then continuous heating at 300°C for 1h to form precursor. PT phase is formed after calcination at 300-600°C for 1 or 2 h

Pontes et al, 2000, applied the similar method by **Paris et al, 1998**. The different is heating the solution at 80-90°C, until become more viscous then dried at 150°C for 20 min and heating at 350°C for 2 h to formed precursor. PT phase is formed after calcination at 500°C for 4 h.

Jha et al, 2003, synthesized lead zirconate titanate after formation the dark yellow citrate precursor at 300°C for 2 hrs. The formed precursor was calcined at 500°C for 2 hrs and then calcinated at 800°C for 8 hrs to form PZT nanopowders.

Advantages of organic carboxylic acid precursor method

1- The technique gives nanosized powders.
2- Chemical homogeneity of the produced powders
3- High purity
4- Low cost (use of inexpensive inorganic salt precursors improve the cost – effectiveness of the powder production.

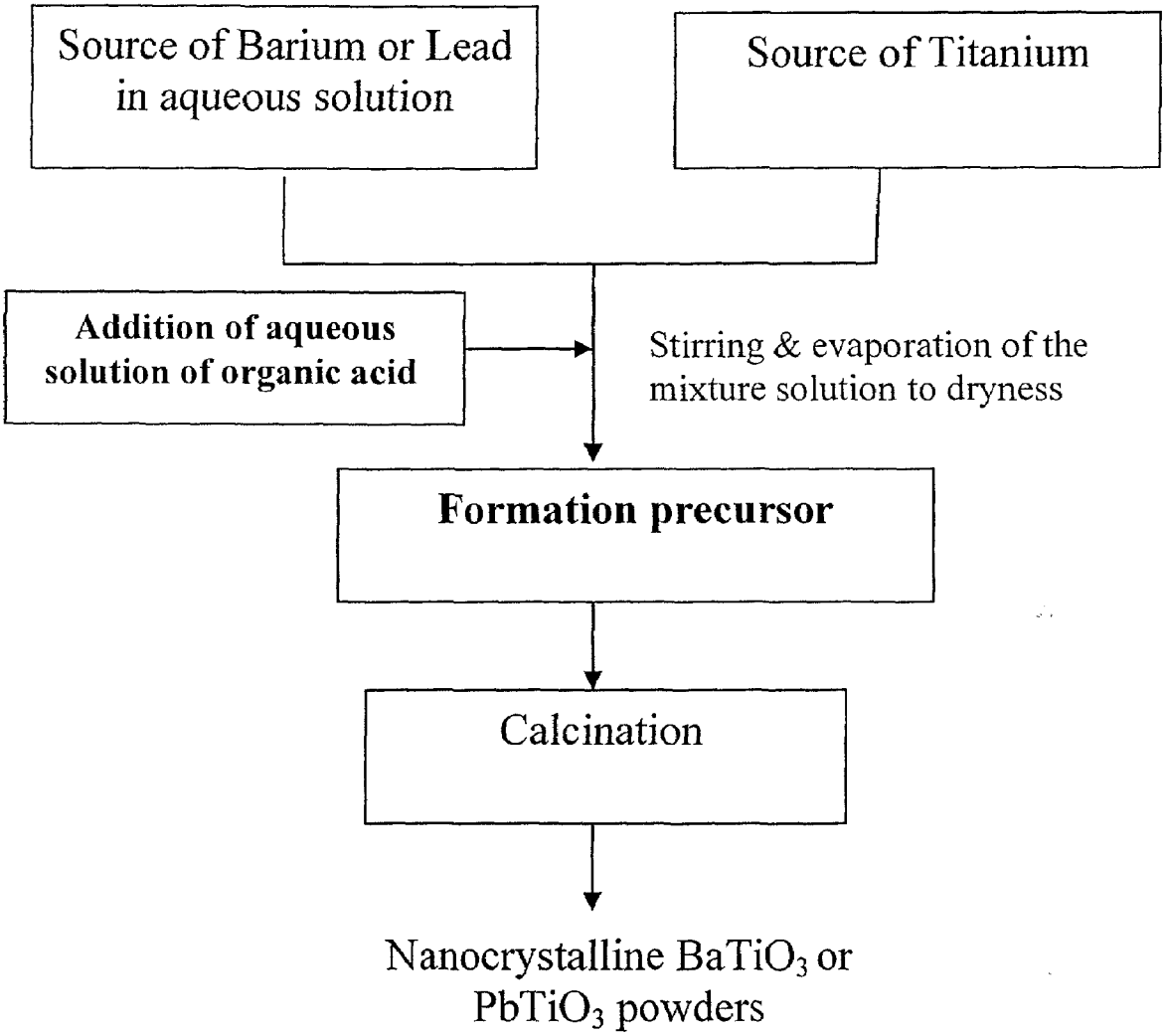


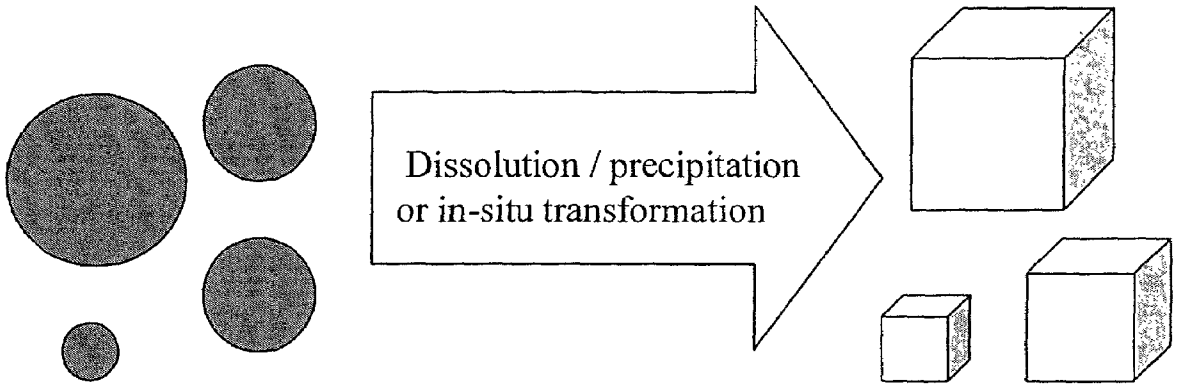
Fig. 9: Flow sheet diagram for the production of $BaTiO_3$ or $PbTiO_3$ nanopowders by organic carboxylic acid precursor method

V. Hydrothermal method

Hydrothermal method means treatment of aqueous solution or suspension of precursors at elevated temperature in pressurized vessels. It is an aqueous chemical route for preparation of crystalline, anhydrous ceramic powders and can be easily differentiated from other process, such as the sol-gel and co-precipitation processes, by the temperature and pressure used in the synthesis reactions. Typically, the pressure ranges up to 15MPa. The specific conditions employed should be capable of maintaining a solution phase that provides a labile mass transport path promoting rapid phase transformation kinetics. The combined effect of pressure and temperature can also reduce free energies for various equilibrium- stablising phases that might not be stable at atmospheric conditions (**Phule ,1990 ; Lencka ,1993 ; Begg et al ,1994; Xia et al ,1996; Cho et al ,1996 and Chen et al ,2004; Rujiwatra et al, 2006**).

The basic mechanism for the hydrothermal formation of ceramic oxide particles is described as a dissolution / precipitation and / or in – situ transformation process which showed in Fig.10. The dissolution / precipitation mechanism is operative when the suspended reactant particles, normally oxides, hydroxides, can dissolve into solution, supersaturate the solution phase, and eventually precipitate out product particles. The driving force in these reactions is the difference in solubility between the oxides phase and the least soluble precursor or intermediate. In many cases, however, the suspended solids are not soluble enough in

aqueous solution, and hence, either mineralizes such as bases have to be added, or ceramic particles are formed via another in-situ transformation mechanism in which the suspended particles undergo a polymorphic or chemical phase transformation. In some cases, both mechanisms might be in operation on the synthesis conditions. **(Lencka et al, 1994 & Pinceloup et al, 1999)** Thus; it is particularly suitable for preparation of electroceramic powders such as barium titanate and lead titanate.



Poorly Ordered Precursor
(Coprecipitated Mixture)

Crystalline Hydrothermal
Ceramic powder

Fig.10: Hydrothermal dissolution / precipitation and / or in – situ transformation process (after **Dawson et al, 1988**)

Preparation of Barium Titanate by Hydrothermal Method

Urek et al, 1998, synthesized barium titanate nanopowders using tetramethyl ammonium hydroxide as precipitating agent and barium hydroxide or barium acetate as sources of barium. When using barium hydroxide added dilute nitric acid to reduce barium carbonate impurity level. When using of barium acetate lead to formation of single phase of barium titanate.

Lu et al, 2000, synthesized barium titanate ($BaTiO_3$) nanocrystals in presence of polyoxyethylene as polymeric surface. The mean particle size produced was 77.8±23.5 nm by TEM and 83±19 nm by laser- scattering particle size analyzer. The nanocrystals were identified as metastable cubic phase.

Xu et al, 2002, synthesized tetragonal barium titanate powder with an average particle size of 80 nm. Effect of reactants concentration of titanium ions on the crystallite size of barium titanate was studied. When the concentration of Ti^{4+} decreased and NaOH excess concentration increased, the average particle size increased. **Dutta et al, 1992** have reported that increasing the pH first increasing the average particle size and the average particle size decreased as the OH^- concentration increased to > 4.0 M.

Viviani et al, 2002, studied the effect of barium ions on reaction kinetics, particle size and crystallite size. At low concentration of Ba^{2+} ~0.12 Mol L^{-1}, the fine powders of barium titanate with 30 nm

size was obtained. When concentration of barium ions increased, the submicron barium titanate (100-300 nm) was produced.

Xu et al, 2003, synthesized nanocrystalline tetragonal- $BaTiO_3$ powder with average particle size 70 nm. The average crystallite of barium titanate increased with increased pH and it decreased by increased titanium source concentration.

Qi et al, 2004, synthesized of tetragonal sub-micron barium titanate particles through a low temperature solvothermal method with treatment in dehydrated dimethyl formamide (DMF) as solvent. The average size obtained of $BaTiO_3$ was 240 nm

Tripathy et al, 2005, used ethanol as solvent for solvothermal of BT synthesis and barium titanate $BaTiO_3$ powders of size 50~100 nm was formed. The particle sizes depend mainly on the feed stock concentration where at higher concentration, the larger particle size is formed.

Hirasawa et al, 2005, synthesized cubic $BaTiO_3$ powders using hydrothermal soft chemical process in the presence of (n-hexa decyltrimethyl ammonium hydroxide HTMM-OH as cationic surfactant. The surfactant plays an important role in changing particle morphology. The cubic $BaTiO_3$ phase was obtained in the low temperature range below 150°C and the tetragonal $BaTiO_3$ phase was obtained in the high- temperature range over 250°C.

Xu et al, 2006, synthesized barium titanate powders after preparation of barium titanyl oxalate tetrhydrate [$BaTiO(C_2O_4)$-$4H_2O$] as precursor and the formed precursor is hydrothermally treated at 200°C for 72 h.

Joshi, et al, 2006, synthesized barium titanate nanowires via surfactant – free hydrothermal process. Using barium hydroxide and titanium oxide as source of barium and titanium and the ethanol was used as a solvent. The pH adjusted above 13 and the solution hydrothermally treated at a constant temperature (170°C) for 3 days. The SEM and TEM micrographs showed that the BT nanowire was formed.

Preparation of Lead Titanate by Hydrothermal Method

Yao et al, 1993, synthesized lead titanate (PT) using lead acetate and titanium dioxide as starting materials. The reaction temperature affected on produced lead titanate powders. When the temperature increased up to 200°C, the well crystalline PT phase was formed. Mole ratio, concentration of KOH and also pH effects on the phase formation. Other parameters including mole ratio, KOH concentration and pH played importance role for synthesis of pure PT phase.

Cho et al, 2003, synthesized of lead titanate ($PbTiO_3$) phase using tetramethyl ammonium hydroxide penthydrate $C_4H_{12}NOH.5H_2O$ as precipitating agent. The lead titanate PT phase and microstructure mainly on the pH, concentration of TMAH and Pb/Ti mole ratio. Cubic PT phase was formed at Pb:Ti mole ratio 1 and platelet phase at Pb:Ti mole ratio 1.25.

Rujiwatra et al ,2005, synthesized lead titanate using lead nitrate and titanium dioxide as source of lead and titanium at respectively mole ratio Pb/Ti=1. The lead titanate phase formation and morphology depend on reaction temperature, time, concentration and type of alkali reagent., the results showed a narrower size distribution and smaller average grain size of lead titanate compared to the case of KOH at pH 14 and temperature lower than 250°C

Chen et al, 2005 synthesized lead titanate powders using lead oxide and titanium dioxide as source of lead and titanium at different mole ratio of Pb/Ti. After increasing mole ratio Pb/Ti to 1.7, the intensity of lead titanate peaks increased.

Pan et al, 2007, synthesized lead zirconate titanate (PZT) powders using lead acetate, zirconium nitrate and titanium isopropoxide were used as starting materials. Potassium hydroxide was used as to adjust the pH of the mixture. The final solution was transferred into autoclave and first at 180°C for 12 hrs, and then heated at 210°C for 10 hrs.

Advantages of hydrothermal method

The advantages of hydrothermal processing as applied to ferroelectric ceramic powders are summarized as follows (**Wu et al, 1999**)

1- Reactants, which are normally volatile at the required reaction temperatures, tend to condense during the hydrothermal process maintaining the reaction stoichiometry, and so high purity multi component ferroelectric powders can be obtained.

2- Synthesis is accomplished in a closed system from which different chemicals can recover and recycled. That makes it an environmentally benign process.

3- It is a low temperature process. With many effects achievable even below 300°C. The relatively low temperature can break down stable precursors under pressure, which avoids the extensive agglomerations that the solid – state reaction usually cause at high temperature.

4- The process is able to produce solid – solution particles with controlled particle size distribution morphology and complex chemical compositions; multi- doped perovskite ABO_3 ceramic powders, for example, can be grown to submicron- or even nano-meter size by control of the nucleation and growth processes.

5- The powders synthesized by the hydrothermal process are more reactive toward sintering and often no calcination stages are needed. This feature is particularly important for synthesizing high quality and relative PT powder because PbO is appreciably volatile (above 800°C) and hence even more so the temperature necessary for conventional calcination and sintering. The block flow sheet for synthesis of BT or PT by hydrothermal method is summarized in Fig. 11

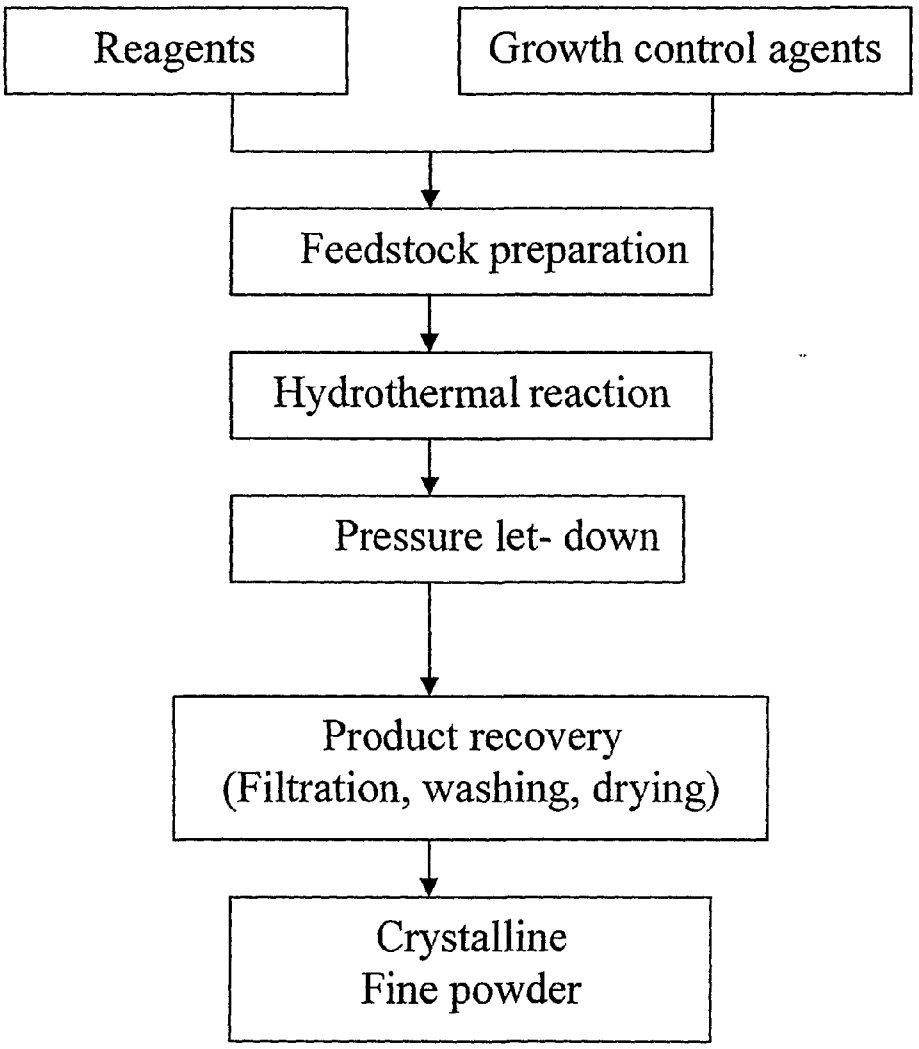


Fig.11: Flow sheet diagram of hydrothermal method

Table 3: General comparison of the synthesis of BT & PT powders by different routes **(Bauger et al ,1983** and **Potdar, 1999)**

Synthesis Method	**Solid-state reaction**	**Co-precipitation**	**Sol-gel**	**Micro-emulsion synthesis**	**Organic carboxylic Acid precursor**	**Hydrothermal**
State of development	Commercial	Commercial	R&D	Demonstration	Demonstration	Demonstration
Composition control	poor	good	excellent	excellent	excellent	excellent
Powder reactivity	poor	good	good	good	good	good
Crystal size (nm)	>1000	>100	<100	<100	<100	<100
Purity (%)	>99.5	>99.5	>99.9	>99.9	>99.9	>99.9
Agglomeration	Moderate	High	Moderate	low	low	low
Calcination step	Yes	Yes	Yes	Yes	Yes	No
Milling step	Yes	Yes	Yes	Yes	No	No
Costs	Low-moderate	moderate	Moderate high	Moderate	Cheaper	Moderate

I.5.2. Properties of Barium Titanate and Lead Titanate

i. High permittivity

Permittivity is the product of permittivity of free space and dielectric constant **(Jona et al, 1993).**

$$\varepsilon = \varepsilon_0 \varepsilon_e$$

ε: absolute permittivity

ε_0: permittivity of free space has a value of 8.85×10^{-12}

ε_e: relative permittivity or dielectric const.

ii. Dielectric constant

Relative permittivity or dielectric constant is defined as the ratio of the permittivity of the materials to the permittivity of the free space. **This** is measure of how well a materials will store an electrical charge when the materials is going to be used as an insulator, then a low dielectric constant is needed. When the materials are going to be used in condenser application, a high dielectric constant is needed. It is the ratio of the capacity of a condenser made with a plastic. The dielectric constant can be calculated from the measured values of capacitance and physical dimension of the specimen.

$$C = \varepsilon A / d$$

Where C: Capacitance, the unit of capacitance (F) and measure at 1KHZ

A: The plate area

The separation **d** of the plates and the medium between them,

Where $\varepsilon_0 \varepsilon_e = Cd/A \quad \therefore \varepsilon_e = Cd / \varepsilon_0 A$

Relative permittivity merely stating the factor that must be used to multiply the permittivity of free space in order to obtain the permittivity of some materials for vacuum the relative permittivity is 1. For plastics it is between about 2 and 3 and for glass between 5 and10 **(Neelakanta, 1995 & Devaraju et al 2005).**

In real materials, there is a response time for polarization which acts as internal resistance causing a phase logs δ of the charging current results in input powder dissipated as heat. The dielectric loss factor (dissipation factor) is a measure of the amount electrical energy which is lost through conduction when voltage is applied across piezoelectric materials and it measure directly using impedance bridge. Dielectric constant and dissipation factor (dielectric loss constant) of some piezoelectric materials are shown in Table 4.

Table 4: Dielectric constant and dissipation factor of some piezoelectric materials **(Barsoum, 2003)**

Piezoelectric materials	**Dielectric constant**	**Dissipation factors, %**
$Ba_4Ti_4O_9$	40	0.03- 0.01
$BaTiO_3$	14,000	0.01- 0.05
$BT+BaZrO_3$	5700-700	< 3
$Ba,Sr,Ca,ZrTiO_3$	11.500-14.000	< 3
$Ba(TiZr)O_3$ [BZT]	10.000	< 3
$Pb(Mg_{1/3}\ Nb_{2/3})O_3$ - $PbTiO_3$ [PMN-PT]	20.000-28.000	< 3

iii. High spontaneous polarization

In crystalline ferroelectrics, this initial rapid rise in spontaneous polarization is due to the elementary dipoles in the material interacting with each other, producing an initial field which lines up the dipoles, eventually yielding saturation of the spontaneous polarization. It is observed that the temperature dependence of the spontaneous polarization. Barium titanate and lead titanate have high polarization due to the fact that the small Ti^{4+} ions in the center of the cubic cell have relatively more space within the oxygen octahedral that formed TiO_6-octahedra **(Perambur, 1995 & Philip et al, 2002)**. Ferroelectric properties of BT and (1-x) PZT are shown in Table 5.

Table 5: Ferroelectric properties of BT & (1-x) PZT ceramics **(Devaraju et al, 2005)**

Composition	**Ferroelectric properties**		
	Pr(μC/cm^2) Saturation polarization	**Ps (μC/cm^2)** Remanent polarization	**Ec (v/cm^2)** Coercive force
0.5PZT-0.5 BT	3.673	6.996	11.68
0.3PZT-0.7 BT	3.988	7.597	11.79
BT	7.775	18.41	4.626

iV. High resistivity

Resistivity **ρ** is a measure of the electrical resistance of a material and is defined the following Equation:

$$\rho = RA / L$$

Where **R**: Resistance of a length, **L** is the length of a material of cross- sectional area the unit of resistivity is the Ohm meter (Ω m). **Resistance** referred to the extent to insulator prevents the flow of electric charges through it. An ideal insulator has a bulk resistance of infinity with zero current flowing through it. In practice, insulation resistance can be divided into volume resistance and surface resistance (**Jackson, 1998**& **(Purcell, 1985**). Volume resistance refers to bulk resistance offered by the whole body of the insulating medium and surface resistance refers to the resistance offered by the surface of insulating materials to the sheet of surface current on it. In case of ceramic materials (barium titanate and lead titanate) the resistivity is about $10^{10}\Omega$ m or high. The addition of a small amount (0.1-0.3 %) of La_2O_3 or Sm_2O_3 drops to resistivity exhibits a pronounced increase at the Curie point of pure $BaTiO_3$.The resistivity decreased with increasing temperature.

V. *Curie temperature*

In ferroelectrics the domain state spontaneous polarization is decreased as the function of temperature, going to zero at a phase transition temperature Tc, which is called the **Curie point (Solymar et al 2004& Kasap, 2002)**. Above Tc a number of ferroelectrics exhibited very high that when an electric field is applied. The ions moved to give distorted crystal structure and this persisted when the field is removed thus resulting in a permanent electric dipole. The distortion increased as the temperature increased until at certain temperature. The distortion is a maximum, above that temperature the distortion rapidly vanishes as the structure assumes the undistorted crystalline form. Curie temperature is the point at which certain materials losses the behavior of ferroelectric or we can be described. The dielectric constant of a ferroelectric when plotted against temperature shows a maximum and transition into the ferroelectric state. In the Paraelectric, non polar state, the change in dielectric constant with temperature and we can calculated by curie- Weiss law **(Newenham, 2005).**

$$\acute{\eta} = C / T - Tc \quad \text{or} \quad \varepsilon = \varepsilon_{\infty} + A / T - Tc$$

Where

$\acute{\eta}$: Dielectric susceptibility

C or A: Curie constant which is constant characteristic for a given materials

Tc: Curie temperature

T : Temperature

Cubic barium titanate ($BaTiO_3$), the Curie point Tc (about120°C) due to Ti^{4+} ions in the center of the oxygen octahedron is stable. Below Tc the Ti^{4+} ions occupy off- center position Tc results in a series of important physical consequences that the crystal structure change from cubic to tetragonal, orthorhombic, rhombohedra at the same time of spontaneous polarization ($26\mu c/cm^2$) at room temperature depend on the Curie point. Fig.12 described the dielectric constant of $BaTiO_3$ at room temperature is about 3000 while at this temperature (Tc) is about dielectric constant of 10.000 to 15.000. $BaTiO_3$ if substitution of $\mathbf{Ba^{2+}}$ with $\mathbf{Sr^{2+}}$ or $\mathbf{Ti^{4+}}$ with $\mathbf{Zr^{4+}}$ below of Tc But if substitution of $\mathbf{Ba^{2+}}$ with $\mathbf{Pb^{2+}}$ ions increase of Tc linearly up to **490 °C (Neelakanta , 1995).**

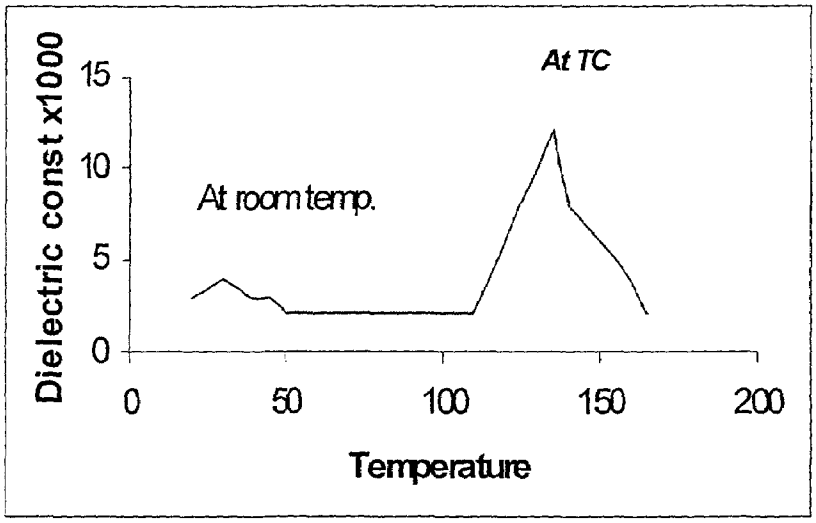


Fig.12: Relation between dielectric constant and temperature in barium titanate

I.5.3.Applications of Barium Titanate and Lead Titanate

Barium titanate and lead titanate are insulators because of its large band gap of Eg. 2.9 ~ 3.05 ev. They used in wide application in such parts as multilayer ceramic capacitors (MLCC), positive temperature coefficient thermistor (PTC), dynamic random access memory capacitor (DRAM) where allow more charge storage per unit area, Electro- optic devices, ultrasonic transducers, micro electro mechanical systems (MEMS), chemical sensors, infrared detector, colour filters, capacitance in printed circuit boards, thermistors, micro positioning devices, active damping, phonograph pickups, Infrared detectors , pigment and piezoelectric devices (**Venigalla, 1999**).

For instance, multilayer capacitors show in Fig.13, consist of ceramic layer of BT. The layer thickness is less than 2-3 **μm** to increase the number of layers and consequently the capacitance.

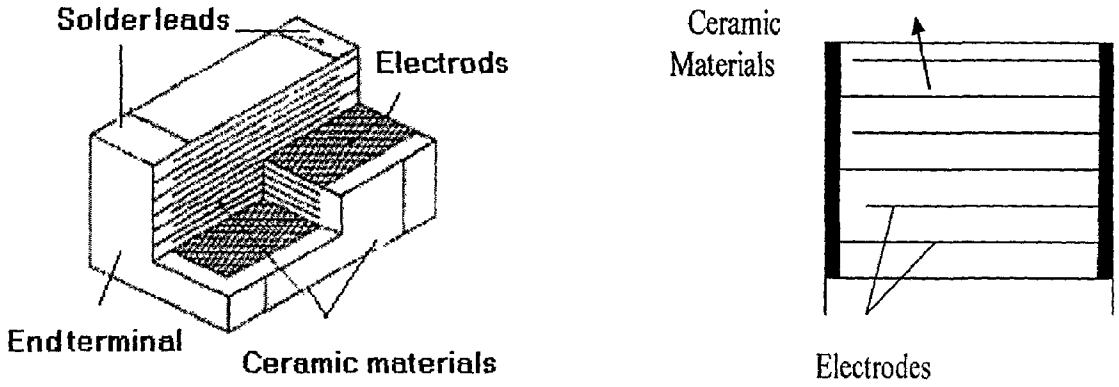


Fig.13: Structure of multi-layer capacitor

Multi-layer capacitor involves forming the dielectric powder into a slip with an organic binder and firing it to form a continuous strip. The electrode pattern is then screen printed onto the surface, the electrode sheets then stacked and consolidated under pressure. Heating is then used to remove the organic binder and the structure then fired. Higher capacitance in smaller case sizes requires is reduction of the thickness of the ceramic layers below **2-3 μm** and the increase of the number of layers (**Aburatani et al, 1994& Im et al, 2000**).

For PTC thermistors and PTC heaters are made of polycrystalline ceramic on a base of barium titanate by doping a small amount of rare earth elements. Semi conduction and thus low resistance are achieved by doping a small amount of rare elements (Y, La, etc).The types for PTC thermistors.

-Elements .... Disk, plate, cylinder etc
-Lead, dip type .... Painted, non- painted
-Case type ..... Plastic/ ceramic case
-Assembly type .... Unit product

PTC thermistors are **used for** current limiter elements, isothermal heaters, motor starter and temperature sensors. PTC elements are flat "stone" with the thickness varying with the operating voltage. Standard stone thickness is shown in the table below.
Typical application include: air heaters, enclosure heaters, small appliances and fuel oil heaters (**Chantterjee et al 2001 & Huybrechts et al, 1995**).

Table 6: Relation between thickness PTC heaters and voltage

Voltage, V	**Minimum thickness, mm**
12-27	1.1
120	1.4
240	1.8

AIM OF THE WORK

The present study aims at synthesis of barium titanate and lead titanate nanopowders via organic acid precursor and hydrothermal methods. All the parameters affecting the synthesis conditions are systematically studied and the optimum conditions are determined.

The formed powders are characterized by X-ray diffraction analysis (XRD), Fourier Transformer Infrared (FT-IR), Scanning electron microscope (SEM) and transmission electron microscope (TEM). The detailed dielectric properties of the formed powders are also measured. The effect of Zr^{4+} ions addition on the crystal structure, microstructure and dielectric properties of barium titanate and lead titanate synthesized by these techniques is also discussed in details.