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## Review on Different Preparation Techniques of Lead Zirconate Titanate

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### Abstract

Lead zirconatetitanate (PZT), one of the best piezoelectric material, possess prominent dielectric and ferroelectric properties. It is widely used in several applications such as transistors, ferroelectric memories, sensors, etc. After discovering the existence of ferroelectricity in PZT, various synthesis techniques have been developed to produce PZT in various forms. In this paper, we report an extensive review on different preparation methods of PZT. The analysis has been done on the basis of literature which was collected from different sources. On the basis of cost effectiveness, PZT can be prepared in ceramic and film forms using solid state synthesis and sol-gel methods respectively. This review also include other synthesis techniques such as co-precipitation method, hydrothermal assisted process, spray pyrolysis, pulsed laser deposition (PLD), chemical solution deposition (CSD), etc. Also, this paper report the kind of properties that have been investigated, under different methods.

**Keywords:** PZT; Thin Film; Solid State Synthesis; Sol-Gel;

### 1.Introduction

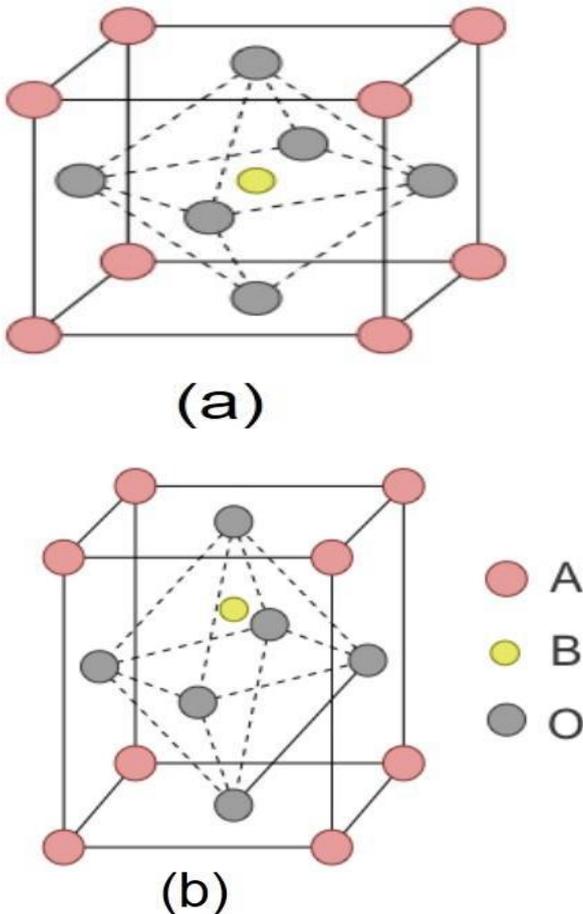
Material has got the utmost importance in several industries like mechanical, electrical, chemical, etc. In 20<sup>th</sup> and 21<sup>st</sup> century, materials have become the part of engineering and technology. In line with the semiconductor technology, ceramic engineering, processing and technology also got the huge importance in research and development. So, various ceramic materials such as lead zirconatetitanate, lead titanate, bismuth ferrite, calcium titanate, etc. have been developed for the electrical, chemical, mechanical and electronic applications. Since last decade, an extensive and intensifying research is being carried on the perovskite ceramics. Apart from the ceramics, new processes have been developed for the development of thin films. Because the thin films are found to have better integration with the devices, than bulk ceramics. Several synthesis

techniques were invented to optimize the properties of both ceramics and thin films. Among the complex and composite perovskite materials, ABC<sub>3</sub> perovskites are the most widely investigated materials.

Perovskite is a material that has a chemical formula of ABC<sub>3</sub>. A, B are the two different cations and C is an anion. In the physics of solid state materials, understanding the physical and chemical properties of perovskite oxides is crucial. The general formula of perovskite oxide is ABO<sub>3</sub> where A, B are different sized cations and O is anion [1]. The structure of perovskite is stable only when tolerance factor (t) is between 0.89 and 1.06. Its structure is cubic when t = 1, and TRO (Tetragonal, Rhombohedral, and Orthorhombic) when t < 1. The cations should possess the valency of +1/+2/+3 at A site and +3/+4/+5 at B site.

Lead zirconatetitanate (PZT), is material that belongs to ABO<sub>3</sub> perovskite (as shown in figure 1

(a) family [2]. It is used extensively in sensors, memories, MEMS, actuators, etc. The structure possess  $\text{Pb}^{+2}$  ions at A-site,  $\text{Zr}^{+4}$  and  $\text{Ti}^{+4}$  ions (together) at B-site.  $\text{O}^{2-}$  ions occupy the faces of the unit cell [3]. The structural phase of PZT is usually tetragonal (as shown in figure 1 (b)), when the amount of  $\text{Ti}^{+4}$  is more [2].



**Fig.1. (a) Cubic Structure, (b) Tetragonal Structure**

Density and uniformity of the polycrystalline material, is crucial for convenient usage in applications. Production of uniform and dense tetragonal PZT (T-PZT) ceramics, is quite not an easy thing. Because, T-PZT exhibit the mechanical strain due to the phase transition i.e. from cubic to tetragonal. Further, the strain creates internal mechanical stress and hence, the ceramic may broke easily. Therefore, T-PZT is less widely investigated. For more in-depth understanding on PZT as a material and its properties, bibliography can be referred.

## 2. Discussion and Analysis

Various methods such as solid state synthesis, sol-gel, co-precipitation method, hydrothermal assisted process, spray pyrolysis, pulsed laser deposition (PLD), chemical solution deposition (CSD), etc. are available for the preparation of various types of materials. But in this work, review on only solid state synthesis and sol-gel has been focused.

### 2.1 Solid State Synthesis

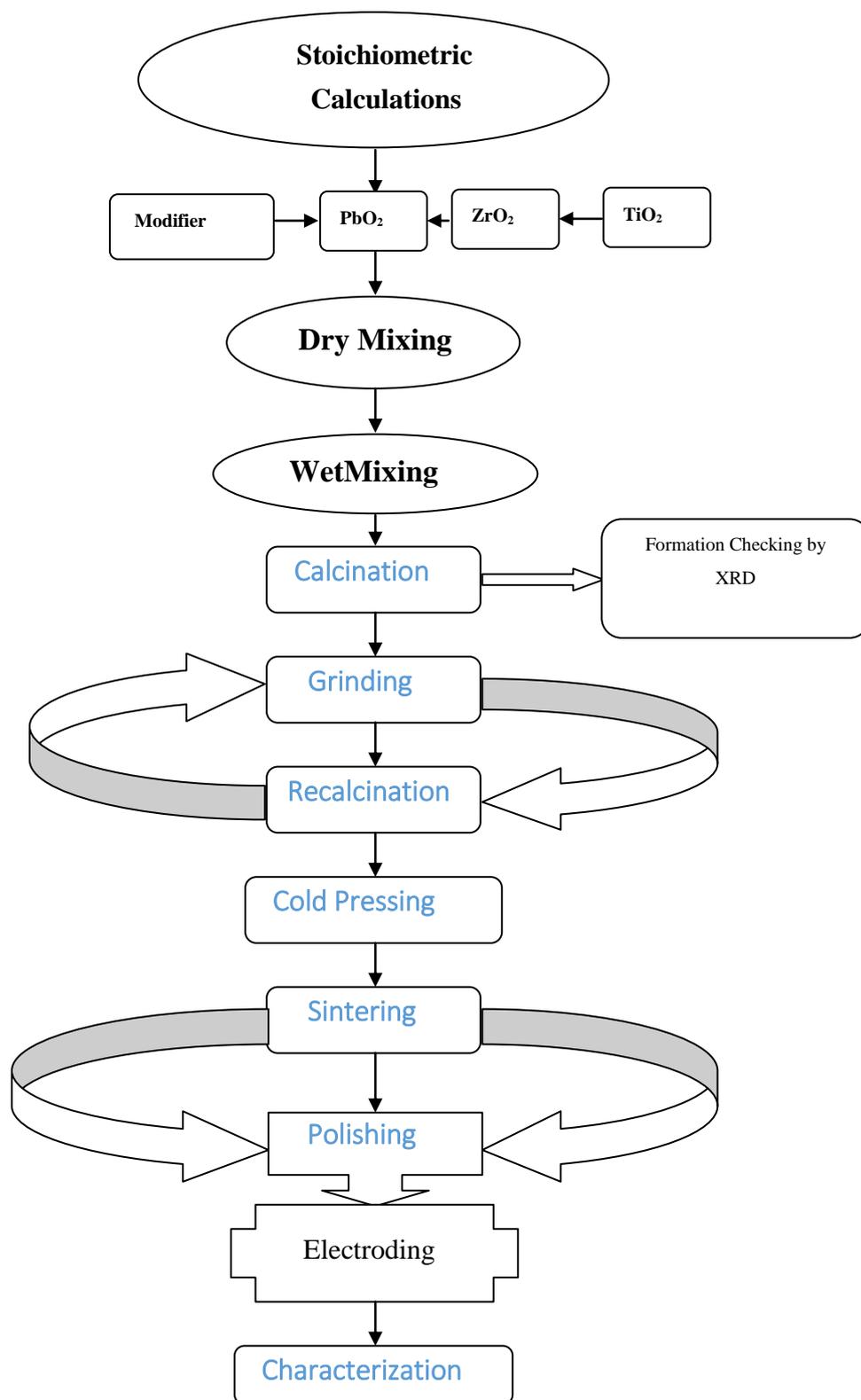
Majority of the ceramic materials are usually processed through solid state synthesis. This is due to the following reasons:

- It involves low cost processing
- Method require less experimental facilities
- Takes less amount of time
- High purity chemicals can be mixed

The method involves the following disadvantages:

- Composition of the materials cannot be controlled
- The reactivity of the chemicals could be low
- Low reproducibility of the same kind of material
- It involves high temperature calcinations
- Uncontrolled microstructure growth

Solid state synthesis involve a series of steps as follows: stoichiometric calculations → grinding → calcination → checking of phase formation → pellet making → sintering → polishing → electroding → characterization (flow chart is given in figure 2). Stoichiometry should be chosen as per the desire or with specific aim. All the chemicals of high purity should be weighed accordingly and then mixed. Mixing of chemical powders can be done in two ways: one is dry grinding i.e. mixing the powders in open air and the other is wet grinding i.e. mixing the powders in alcohol like acetone, methanol, etc. Then the powders should be subjected to very high temperatures (below their melting point) i.e. calcining of powders. Structure of the calcined samples can be checked through x-ray diffraction technique. If the desired structure is confirmed/formed, then the powders would be cold pressed using conventional hydraulic press.



**Fig.2. Flow Chart of Solid State Synthesis**

The press can be done at different pressures, depending on the strength of the machine. Through the process of cold pressing, the powders will be

transformed into the pellets in the form of discs of different diameters. Depending on usage, the thickness of the pellets would vary large in

magnitude. Then the pellets will be made ready for electrical characterization, after polishing and electroding. Polishing means the reduction of roughness of surface of material, by using air drying silver paste or others. It is worth to note that the processing conditions vary with the type and nature of material that is being processed. Lots of work has been reported by lots of researchers, on the solid state synthesized PZT ceramics. In one of the work [4], PZT of 52/48 ratio has been prepared by modifying it with cerium. It was observed that the relative permittivity of the PZT has been enhanced. In another work [1], it was observed that the impedance of PZT of 35/65 ratio, synthesized through solid state mixing only, has been altered with the substitution of cerium. In PZT of 35/65 ratio, it is identified from the scanning electron micrographs that the grains of the material are uniformly distributed on the surface [3]. It is concluded that the interesting electrical properties can be induced by PZT, when it is synthesized through solid state mixing of powders. For more understanding on this method, bibliography can be referred [1-11].

## 2.2 Sol-Gel Synthesis

Majority of thin film materials are produced by synthesizing them through the sol-gel technique. Due to the versatile nature in behavior and properties of films, they can be integrated easily into the system of devices, than bulk ceramics. One of the technique to prepare easily the films, is identified as sol-gel. It has gone through various developments to become easy, reliable and robust preparation technique. Advantages of this process are as follows:

- Microstructure growth can be controlled
- Composition of material can be maintained
- Reactivity of chemicals can be high compared solid state method
- Possibility of using high purity chemicals

Some of the disadvantages of this method are as follows:

- Like solid state method, it also involves the high temperature processing
- Unlike solid state method, the cost ranges from medium to high

- Within stipulated time, the processing of samples should be completed

In one of the recent work of synthesis of PZT through sol-gel [12], 20% extra lead was added to sample to compensate the loss of lead. Usually, extra amount of lead source (i.e. 2% - 10%) will be added to the samples while synthesizing through solid state reaction. But for sol-gel precursors, the amount of extra lead added is a bit more than solid state powders. The properties of the film is summarized in table 1.

S.No.	Property	Value
1.	Dielectric Constant	1224.25
2.	Remanant Polarization	20.25 $\mu\text{C}/\text{cm}^2$
3.	Coercive Field	54 kV/cm
4.	Current Density	$4.57 \times 10^{-7}$ A/cm <sup>2</sup>

$\text{Pb}(\text{Zr}_{0.53}\text{Ti}_{0.47})_{0.90}\text{Sc}_{0.10}\text{O}_3$  is an epitaxial thin film with {100} orientation grown on MgO substrate. Due to the high dielectric constant (5700) and large dielectric breakdown strength (1.82 MV/cm) along with high energy storage characteristics, the aforementioned films are suggested for ferroelectric based capacitors [13]. For more understanding on this sol-gel method, bibliography can be referred [14-17].

The thin film of PZT has been realized as an energy harvester of both mechanical vibrations and magnetic energy [18]. The material (PZT/Ni) has been prepared by the deposition of the film on the Ni cantilever surface through pulsed laser deposition (PLD) method. The film was deposited at oxygen pressures (P) of 13 Pa, 26 Pa and 40 Pa. It is identified from the literature that deposition condition of PZT has been optimized in one of the work [19-20]. The details are as follows: 10 Hz is the repetition of rate of laser, 2.5 J/cm<sup>2</sup> is the magnitude of energy storage density, 10 Pa is the oxygen pressure, and 600 °C is the temperature of substrate.

Other methods such as co-precipitation method, hydrothermal assisted process, spray pyrolysis, etc. can be referred in bibliography [21-23].

## Conclusions

In this paper, a review has been made to provide basic understanding on the synthesis methods of lead zirconatetitanate. From the review, it has been

identified solid state is the simpler and easy employable method, to prepare the samples of bulk ceramics. Sol-gel is little bit difficult to handle than solid state method. For the effective finding on the effect of solid state synthesis, it is recommended to investigate a single sample under different processing conditions. For instance, one sample can be subjected to different calcinations/sintering temperatures, and also a sample grinding should be done with the instruments not by hands. Composition, morphology and reactivity of material can be well controlled through sol-gel, than solid state method of preparation.

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