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Lead Zirconate Titanate (PZT) Synthesis and Its Applications

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ABSTRACT

Lead zirconate titanate (PZT) is a versatile material widely used in various applications due to its unique and excellent piezoelectric properties. While it has been employed in multiple forms, it is of utmost importance to develop an efficient manufacturing process for its nanoparticles that may be used to fabricate the other PZT elements. This review aims to compare different synthesis methods of PZT and evaluate their suitability and scalability for the large-scale production of PZT nanoparticles. Various synthesis techniques, including sol-gel, hydrothermal, and solid-state reactions, were analyzed for their processes, feasibility, advantages, and disadvantages. Factors such as cost-effectiveness, scalability, and resulting material purity are considered in determining an ideal synthesis method. While each method offers distinct benefits, no single method emerges as universally superior, and the choice of process depends on the specific requirements of the end product and its applications. This review aims to aid researchers and practitioners in selecting appropriate synthesis methods for PZT-based devices. Future research could focus on optimizing existing methods or exploring novel approaches to enhance the properties and performance of PZT materials for diverse applications.

Keywords: PZT, Piezoelectric materials, Synthesis, Manufacturing, Hydrothermal applications.

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INTRODUCTION

Multiple types of piezoelectric materials are employed in the manufacturing of devices with applications in most fields. These materials can be classified based on source (organic, inorganic/synthetic), polarization (ferroelectric, non-ferroelectric), and structure (polymers, single crystals, ceramics, composites). PZT or lead zirconate titanate ($Pb\,Zr_xTi_{1-x}\,O_3$) is a synthetic, lead-based ceramic with extensive applications, especially in the medical field, in MEMS and PMUTs.[1] Table 1 mentions the main types of piezoelectric materials along with their subtypes and states their respective features and applications. PZT is preferred over these materials for its superior efficiency, with high piezoelectric coefficients enabling effective energy conversion. It may be more cost-effective compared to single crystals, is durable with excellent mechanical strength, and is stable even in high-temperature environments due to its high Curie temperature. Despite environmental concerns over its lead content, its overall performance and cost advantages make it a preferred choice. PZT elements have multiple modes of vibration – powder, strip, plate, disc, ring, rod, cylinder, etc.[2] PZT and its nanoscale crystals are the most common ferroelectric inorganic compounds employed as piezoelectric materials with the highest coupling coefficient between the mechanical and electrical properties. It is evident that materials in the nanoscale possess a higher surface area to volume ratio compared to particles in microns and bigger scales and as a result, exhibit incredible and new chemical, physical, mechanical, optical, and electrical characteristics.[3] The other modes can also be manufactured using these nanoparticles by only applying different techniques based on shapes instead of having entirely separate manufacturing processes for each mode. This would aid in large-scale the manufacturing process of PZT elements and reduce the individual processing time and machinery costs. This is why developing a simple, streamlined, cost-effective, and faster process or concept to synthesize and manufacture PZT nanoparticles is essential and has become a topic of research interest.

Applications of PZT Elements

Piezoelectric (PZT) materials find widespread applications across various industries due to their versatile properties. In general, PZT elements are utilized in sensors for detecting

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Table 1: Types of piezoelectric materials with specific uses and features

Type	*Subtype*	*Examples*	*Applications*	*Pros*	*Cons*
Natural	Ceramics	Quartz, tourmaline, Rochelle salt	Frequency controllers, acoustic wave devices	High stability, low dielectric losses	Brittle, low piezoelectric coefficient (*d*)
	Biomaterials	Bone, wood, sugarcane	Biosensors, medical implants	Biocompatible, eco-friendly	Low *d* values, complex structure
Synthetic	Polymers	PLA, PVDF	Flexible sensors, wearable devices	Flexible, biocompatible, light-weight	Low *d* values, low-temperature stability
	Single Crystals	$LiTaO_3$, $GaPO_4$	High-precision sensors, optical devices	High stability, high *d* values, low dielectric losses	Expensive, and difficult to make large quantities
	Ceramics	PZT, $BaTiO_3$, $PbTiO_3$	Actuators, transducers, imaging	High *d* value, high Curie temperatures	Brittle, not biocompatible, toxic if lead-based
	Composites	PZT-PVDF, PZT-ZnO, $BaTiO_3$-epoxy	Flexible electronics, health monitoring	Tunable properties, benefits of ceramics and polymers	Complex manufacturing, potential adhesion, and compatibility problems
	Specialized Forms	Thin films, RFSCs	RF filters, precision positioning systems	Thin, light-weight, very high *d* values (RFSC)	Expensive, complex manufacturing, lead-based (RFSC), low *d* values (thin film)

pressure, acceleration, and force in automotive systems, industrial machinery, and consumer electronics. They are also utilized in actuators for precise positioning and vibration control in robotics and aerospace. Moreover, PZT's ability to generate electrical signals is employed in energy harvesting devices.

In the medical field, one common application of PZT is in medical imaging technologies like ultrasound machines. PZT elements generate and receive ultrasound waves, enabling imaging of internal body structures for diagnostics and monitoring. They are also used in medical devices such as nebulizers for drug delivery, where they create ultrasonic vibrations to aerosolize medications for inhalation therapy. They also provide precise control when used in surgical tools due to their ability to deliver controlled vibrations. They are also employed in microfluidic systems for precise fluid manipulation for diagnostics, sensors in wearable devices to monitor vitals, and PZT-based bone conduction devices in hearing aids and cochlear implants.

Important Parameters Concerning Applications

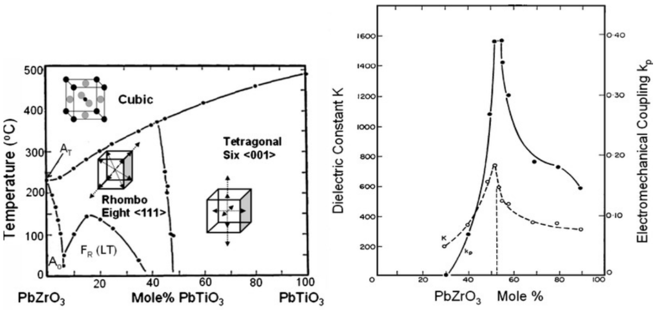
In medical applications, parameters such as piezoelectric strain coefficients (d_{31}, d_{33}), dielectric loss factor, and electric permittivity are crucial determinants of PZT element performance. The d_{31} and d_{33} coefficients impact the efficiency of ultrasound generation and reception in imaging technologies, affecting image clarity and resolution. Moreover, the dielectric loss factor and electric permittivity influence PZT element performance in devices like nebulizers and therapeutic tools. High dielectric loss may lead to energy dissipation, diminishing energy conversion efficiency, while electric permittivity affects sensitivity in sensing and actuation. Usually, PZT exhibits high piezoelectric coefficients and typically has low dielectric loss factors and high electric permittivity, but the specific performance of PZT can vary depending on factors such as composition, processing, and manufacturing quality. Thus, optimizing these parameters enhances the reliability, precision, and effectiveness of medical devices employing PZT elements, ultimately improving healthcare outcomes. The table below Table 2 gives a list of parameters and properties of PZT.[4]

Synthesis Methods

The morphotropic phase boundary (MPB) refers to the boundary in the phase diagram of a material system where there is a transition between different crystallographic phases. For PZT, it is an essential parameter to be considered because in this region tetragonal and rhombohedral phases coexist, and consequently, the properties of the material are significantly improved.[5] PZT ceramics lie near a morphotropic phase boundary at ~x=0.48 PT, shown below in Fig. 1.[6] Thus, the most efficient composition of PZT consists of 52% lead zirconate ($PbZrO_3$) and 48% lead titanate ($PbTiO_3$). Ceramic properties are strongly influenced by the density and microstructure which depend upon the procedure of synthesis and the powder processing.[5] PZT may be fabricated using both top-down and bottom-up methods. There are three commonly used methods to synthesize PZT particles and thin films – solid-state, sol-gel, and hydrothermal or coprecipitation. While solid-state synthesis is a widely used top-down technique, the other two are more advanced bottom-up techniques. Each synthesis

Table 2: Properties of PZT

Property	*Values for PZT*
Piezoelectric constant (C/m^2)	$e_{31} = -6.5$; $e_{33} = 23.4$
Piezoelectric coefficient (pm/V)	$d_{31} = -125$ to -170; $d_{33} = 60$ to 130
Electromechanical coupling coefficient	0.57 to 0.68
Resistivity (Ω cm)	1×10^9



a

b

Fig. 1 (a,b): MPB phases of PZT

method offers distinct advantages and is chosen based on the desired characteristics of the final product.

Solid-state reaction method

Top-down methods are more commonly used due to their simpler processes. They involve calcination and milling of PZT raw materials (usually zirconium and titanium oxides in powder form). In the solid-state technique, a proper molar ratio of oxides is mixed and then undergoes a solid-state reaction by a calcination process. The initial mixing of the zirconium and titanium oxides is typically carried out using mechanical methods to ensure a uniform distribution of the raw materials. The calcination processes the oxides under around 650°C for 2 to 3 hours, which results in an intermediate phase that is then held under around 850°C to allow recrystallization and formation of the desired PZT phase. This step is critical as it ensures the development of the correct crystalline structure necessary for the material's piezoelectric properties. After calcination, the resultant PZT ceramic is coarse and requires further processing to achieve the desired particle size and morphology. The final product is milled down to the desired particle size.[7] This typically involves the use of high-energy ball mills or other grinding equipment. The milling process also helps to break up any agglomerates, ensuring a fine and uniform powder. Fig. 2 is a flowchart representing the solid-state synthesis process in short.[8]

Sol-gel synthesis method

This technique involves the transition of a solution into a gel phase, which is then dried and heat-treated to form ceramic particles. To say briefly, it uses a polymerization reaction of soluble precursor compounds to create three-dimensional structures and form gel.[7] It begins with preparing a solution of lead, zirconium, and titanium alkoxides, which undergoes hydrolysis and polycondensation to form a gel. The sol transforms into a gel by controlling the pH to 4 to 5 and temperature to 60 to 80°C. The gel is dried at 100 to 150°C, then calcined at 500 to 700°C for 1 to 3 hours to remove organic components and induce crystallization. The temperature and duration of calcination are critical in determining the final crystalline structure and properties of the PZT powder. Thus, it may vary depending on the equipment, time, and following processes.

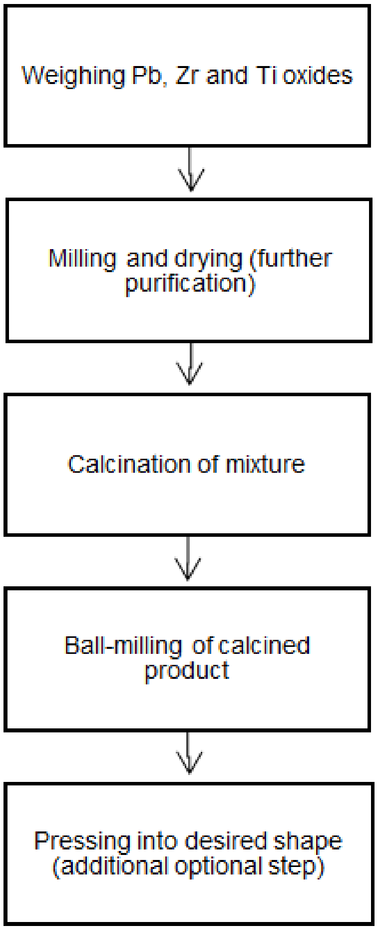


Fig. 2: Flowchart depicting the solid-state reaction process

Hydrothermal or coprecipitation method

This is a process in which temperature, duration, or mineralizer concentrations are optimized to produce PZT nanoparticles with controlled size and distribution. It involves chemical reactions in aqueous solutions at elevated temperatures and pressures, facilitating the growth of crystalline structures with high purity and controlled morphology. Typically, it involves mixing PZT precursors, such as lead acetate, zirconium nitrate, and titanium isopropoxide, in a solution under controlled conditions of temperature, pressure, pH, mineralizer concentration, and heating or cooling rates. The precursor solution is then sealed in a pressure vessel and heated to temperatures typically ranging from 100 to 250°C under elevated pressures ranging from tens to hundreds of atmospheres. This hydrothermal environment promotes the hydrolysis and condensation reactions of the precursors, leading to the nucleation and growth of PZT nanoparticles. The reaction time can vary from several hours to a day or more, depending on the desired particle size and properties. After synthesis, the PZT nanoparticles may undergo post-processing steps such as washing, drying, and calcination to remove impurities, like excess lead in some cases, and enhance crystallinity.

Table 3: Effects of excess lead concentrations on PZT particle synthesis

Excess lead (% wt)	*Particle size (nm)*	*Observations*		
		Larger particle size (µm) and agglomeration	*Degree and size (µm) of aggregation*	*Amount of amorphous*
0	200–400	Few particles ~1	High >10	Large
10	200–400	Few particles ~1	High 1–10	Some
20	300–500	Few particles ~10	Lower 1–6	Little
40	450–850	Most particles agglomerate ~1	Low 1–2	None
80	600–1000	Particles and agglomerates ~1	Very low 1–2	None

Advantages and Disadvantages of PZT Synthesis Methods

Solid-state reaction technique

It is extensively used to manufacture PZT on a large scale because it mostly requires ball mills and calcination furnaces, both readily available in varying sizes and modifications. Additionally, it allows to precisely control stoichiometry by controlling the raw materials put into the ball mill and initial mixture. Although the typical resulting PZT particle size is around 1-µm, the problems faced are contamination and non-uniform morphology, leading to lower purity of PZT particles compared to the other two methods.[7] The entire process is also very time and energy-consuming due to the long calcination process that also uses very high and damaging sintering temperatures.

Sol-gel process

It allows for the uniform distribution of precursors (that can be purified before being processed to ensure high purity) at the molecular level, resulting in homogeneous materials. Thus, it creates PZT with high purity and high density.[7] Since the process enables the use of various substrates, the produced PZT can be of various forms/modes and can also be easily integrated into designs. It also utilizes a high temperature that is lower than the sintering temperature used in the above process, thus saving more energy. Although the sol-gel process provides many benefits for fabricating PZT thin films, limitations also exist for this promising technique. Usually, metals including gold (Au) and platinum (Pt) with a thin layer of titanium (Ti) or chromium (Cr) are used as the electrodes (the thin layer of Ti or Cr is applied to improve the adhesion between electrode and substrate), but these metals are quite unstable at 600°C during the high-temperature sintering process, which can result in porosity that could further impair the electric conductivities of the electrodes.[9] However, research by Q.Q. Zhang *et al.* showed a technique that entails a modified sol-gel process with vacuum filling of PZT precursor solution.[10] It significantly reduced cracks and porosity. Moreover, the sol-gel technique uses advanced technology and concepts involving gel formation. As a result, the fabrication process can be very expensive in terms of both materials and equipment. This process still includes grounding and may lead to the same problems—contamination and non-uniform morphology—as the solid-state technique. Although the process and its prospects have gained much attention, it is still under research and is not used to manufacture PZT in bulk due to its high firing temperature and other mentioned factors.

Hydrothermal process

It also creates PZT particles with high purity and high density (lower density compared to the sol-gel process). It involves complex machinery that may not be readily available or require modifications, but it is less expensive than the sol-gel technique. It uses lower temperatures compared to the other two methods and usually involves ramping and cooling rates.[11] Similar to the sol-gel process, the shape, morphology, and purity of the resultant PZT particles can be controlled, but in this process, the important parameters affecting these factors are the pH of the solution, mineralizer concentration (2–5 M), mixing rate (1–3 hours), ratio of the oxides (50–50, 52–48), and temperature, processing time (1–5 hours), ramping (5, 10, 20°C/min) and cooling rates (1.5–5°C/min), and amount of lead (0–80%).[7,11] This process offers the most feasible flexibility in tuning the properties of PZT nanoparticles to reduce porosity, increase crystallinity, control size, reduce agglomeration, and reduce overall production time and energy consumption.

DISCUSSION AND CONCLUSION

While the solid-state process is widely used, it may involve a longer process that also uses a temperature that is not as suitable for manufacturing for continuous longer periods and does not yield the purest product compared to the other two methods. On the other hand, the sol-gel process has almost comparable purity of PZT synthesized by the hydrothermal process, but it is much more expensive and requires the most maintenance due to the high working temperature and advanced technology. When comparing cost-effectiveness and end-product along with the time and energy consumption of the three methods, the hydrothermal/coprecipitation process is an ideal technique to fabricate PZT. According to research by Hsien-Lin Huang that used variations of these factors to determine the most optimal production parameters, highly pure PZT nanoparticles of 300 to 600 nm size (1–2 μm aggregates) can be produced with 50% lead excess, 2.5 to 3.5 M concentration of KOH (used as mineralizer), 3 hours processing time, 5°C/min cooling rate, and a 20°C/min ramping rate.[7] Table 3 from the same paper shows how these changes in the amount of excess lead affected crystallinity and agglomeration, thus enabling manufacture according to requirements.

Sufficient research on the processes and parameters makes it possible to compare the three processes and understand their features and techniques. A problem noticed during research was that most research papers used similar foundational concepts but different techniques. Even if the same techniques were used, the difference in times caused a difference in the parameters and fabrication conditions. Thus, more research needs to be done on the feasibility of these specific processes and possible future applications to produce PZT nanoparticles in bulk using these more efficient processes that have worked and shown favorable results theoretically or on a small-scale basis.

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