

# A Novel Process For Preparing PZT Thick Films

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*Abstract:* A novel method for preparing PZT thick films has been developed, which integrated some advantages of common-used processes. Comparing with conventional methods, the present technology can prevent cracks, improve morphologies and properties in films, and increase an achievable thickness. The films show a dense structure and therefor uniform properties, that are comparable with those in bulk ceramics. PZT film of 3.5 $\mu$ m thickness has a large remanent polarization of 44 $\mu$ C/cm<sup>2</sup>, small coercive field of 50 kV/cm, large dielectric constant of 2000 and small dielectric loss tan $\delta$  of 0.04, respectively.

Key words: PZT; thick film; alkoxide; hydrolytic product

## INTRODUCTION

Ferroelectric films of thickness smaller than 1 $\mu$ m have been widely investigated due to their applications in capacitor, optical storage, memory, wave guide and so on.<sup>[1,2]</sup> There has been an increasing interest in thicker films for some potential applications such as microsensors and microactuators, which are cores of MEMS (Micro-Electro-Mechanical System), and many piezoelectric applications. In general, these applications are based on films of several microns to decades microns.<sup>[3]</sup>

Sol-Gel route has been considered to be the most important one for preparing thick films<sup>[4-6]</sup>. In this route thick films can be made either by multi-coating or by dispersing ceramic powders into a solution to form 0-3 composition<sup>[6]</sup>. However, both of them exist some disadvantages at present. For the former, thicker films can be set up by multi-coating steps and multi heating treatments. A longer period to finish a whole process is required. The ultimate thickness is also limited due to volume stress caused by multi interface between layers and multi heating impacts, which often causes cracks in films. Film thickness can be increased by increasing single layer thickness through using a more concentrated and viscous precursor, however, this process must be accompanied by a large volume shrinkage which is a main origin of cracking in films. For 0-3 composition, thicker films were prepared from a precursor made of sintered PZT powder and PZT solution with the same composition as powders. For the

system combined rigid PZT powders with PZT solution, holes are easy to form during the heating treatment. In addition, films made from this process exhibit a rough surface and need polishing for practical applications. It is difficult to obtain PZT films with dense homogeneous structure and uniform properties by using 0-3 composition. However, a high dense structure with negligible holes and uniform properties are required for all applications. In fact, properties of films made from 0-3 composition are somewhat poorer comparing to those of bulk ceramic.

In this paper, we put our attention on developing a novel process which absorbed some advantages from methods mentioned above and can avoid their disadvantages. Thick films with denser structure and uniform properties have been fabricated using this a new process. The results have proved that the method is favorable for making thick films with good structure and properties.

## EXPERIMENT

Lead acetate trihydrate [Pb(CH<sub>3</sub>COO)<sub>2</sub>·3H<sub>2</sub>O], zirconium i-propoxide Zr{O(C<sub>3</sub>H<sub>7</sub>)<sub>4</sub>}, titanium propoxide Ti{O(C<sub>3</sub>H<sub>7</sub>)<sub>4</sub>} were used as starting reagents. The lead acetate was completely dissolved in 2-methoxyethanol to form Pb solution. Titanium and zirconium alkoxides were mixed in the required stoichiometric (Zr/Ti=40/60) before the addition of the Pb solution. 5 mol % Pb excess was added into resulting solution. PZT solution was diluted in acetone with a suitable ratio of PZT/acetone. The diluted PZT solution was hydrolyzed by ammonia water. White precipitate was produced in the hydrolyzed solution by controlling a pH value of the solution. The precipitate was taken out from the solution, and dried at room temperature to form powder A. In order to study the influence of calcined powders on structure and properties of films, some of the precipitate was calcined at 600 °C to form powder B. Model HORIBA CAPA-700 was used to analyze particle size distribution. PZT precursor was formed by dispersing powder A into PZT solutions with the same composition as the powder. The resulting precursor was deposited on Pt/Ti/SiO<sub>2</sub>/Si substrates by spin coating. The thickness of every layer was determined by a ratio of the powder/solutions. Conventional heating treatment at various temperatures was used to dry and

synthesize wet films, and then the films were annealed in oxygen atmosphere to realize phase transformation from an amorphous to a perovskite phase. X-ray diffraction (XRD) was used to identify the phase structure of films. Scanning electron microscopy (SEM) was used to examine morphologies of powders and films. The thickness of films was estimated from a cross-sectional view taken from SEM. Gold electrodes of  $2.5 \times 10^{-4} \text{ cm}^2$  were deposited on the surface of the film for measurement of electrical properties. P-E hysteresis loops were observed by a RT66A ferroelectric tester. The dielectric permittivity  $\epsilon$  and dielectric loss factor  $\tan\delta$  were measured by a HP4192A impedance analyzer.

## RESULTS AND DISCUSSION

1. Chemical and physical properties, such as composition, structure and charged state, are quite different in powder A and powder B, even these powders are derived from a same PZT solution. White powder A is product from Pb, Zr and Ti complex alkoxides by hydrolysis. Chemical and physical properties of powder A are close to that of PZT solution. The powder A can be conversely dissolved into 2-methoxyethanol at a suitable temperature. In principle, the powder A is not PZT solid solution because the powder did not undergo a complete reaction process caused by calcining. While yellow powder B made of the precipitate calcined at  $600^\circ\text{C}$  is PZT powder. Because powder B was undergone nucleation, crystallization, particle growth and aggregation process during the heating treatment route. The phase structures of powder A and powder B from XRD analysis are shown in Fig.1. It can be found that powder A exhibits a non-crystallized state and powder B shows a pure perovskite structure. The specific surface area of powder ( $S_w$ ) was used to evaluate size of these powders.  $S_w$  ( $\text{m}^2/\text{g}$ ) of A and B are 2.307 and 2.020, respectively. It is clear that the size of powder A is smaller than that of powder B. The calcined powder B are of an aggregated nature, an undesirable property for sintering to high dense structure of film. The higher calcined temperature, the larger powder size.

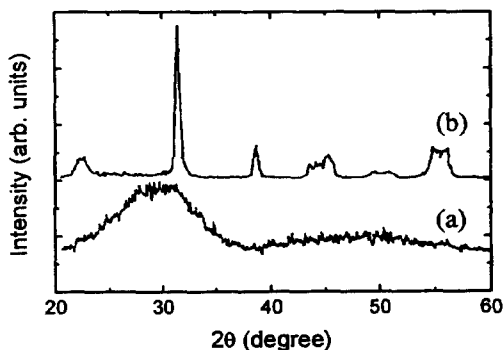


Fig.1. XRD profiles of (a) without calcined powder A and (b) powder B (PZT).

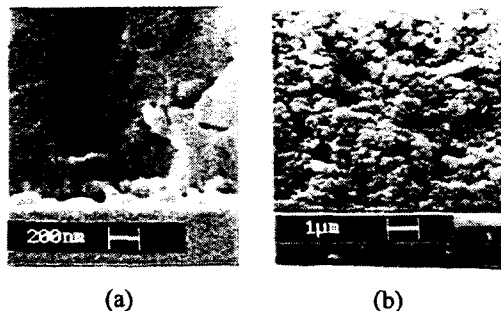


Fig.2. SEM cross-section images of (a) FA and (b) FB.

2. In order to comparing this new method with the common 0-3 composition, two kinds of precursor were prepared by dispersing powder A and powder B into PZT solution, respectively. Same coating steps (2000 rpm for 2 minutes) and same heating treatments (baked at  $350^\circ\text{C}$  and annealed at  $680^\circ\text{C}$ ) were employed for preparing film A (FA) and film B (FB). In fact, FA is made from the new way and the FB is made from the commonly used 0-3 composition route. Films were examined by SEM as shown in Fig.2. The structures of films are depending on natures of powders. FA shows a dense structure while FB is porosity. It is due to similarity of powder A to PZT solution in chemical and physical states. Strong networks and bonds are formed between powder A and PZT solution through hydroxyl and functional groups existed on surfaces of the powder and in the solution. There are a good affinity between powder A and PZT solution, so the powder A can be dispersed into the PZT solution uniformly. Organic solvents in the powders and the solution are removed during heating treatment process synchronously. A homogenization process in the co-existing system of powder A and PZT solution can occur by diffusion between uncalcined powder and solution with similar state during the sintering process. It is clear that such process is effective for increasing packing density of films. In addition, the size of powder A is smaller, so that a dense structure is easy to be obtained. For FB prepared from 0-3 composition way, reaction speed and volume shrinkage for rigid sintered powder B and PZT solution are different, holes are easily formed and film structure is not dense as that in FA. XRD is used to research crystalline phase development in the films as shown in Fig.3. Both of FA and FB exhibit pure perovskite structure.

3. In this new method, there are mass hydrolytic products existence in wet films therefor volume shrinkage of films is decreased when the films is processed. It is useful for increasing thickness of a single layer and avoiding cracking in films. This is similar to 0-3 composition system. However, the thickness of a single layer is thinner than that of the films obtained from 0-3 composition, this is because of the small size and loose structure of hydrolytic products comparing with that of rigid sintered powders.

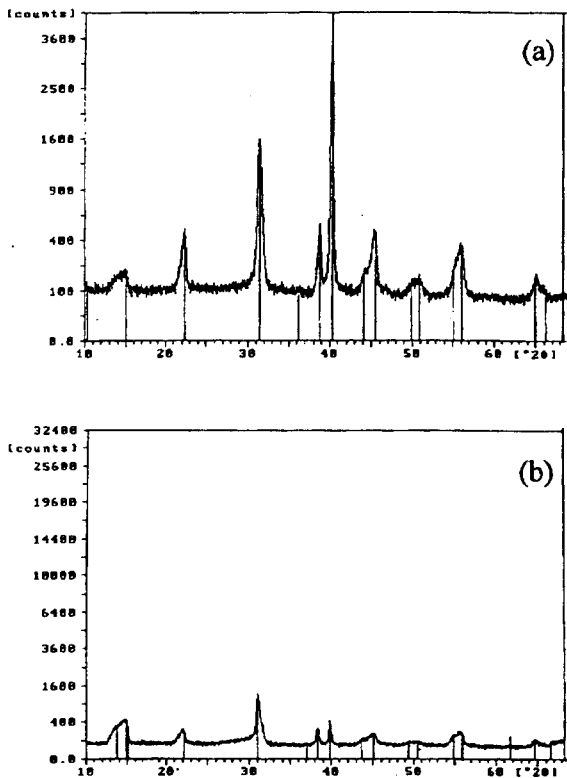


Fig.3. XRD profiles of (a) FA and (b) FB.

4. The electric properties of films are related to microstructure seriously. Ferroelectric properties are characterized by P-E hysteresis loop. Fig.4 shows hystereses of FA and FB. FA exhibits larger  $P_r$  and smaller  $E_c$  comparing to that in FB. This is due to the

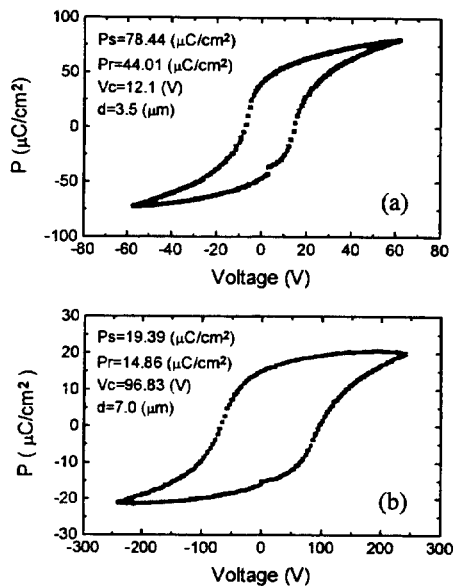


Fig.4. P-E hysteresis loops for (a) FA and (b) FB.

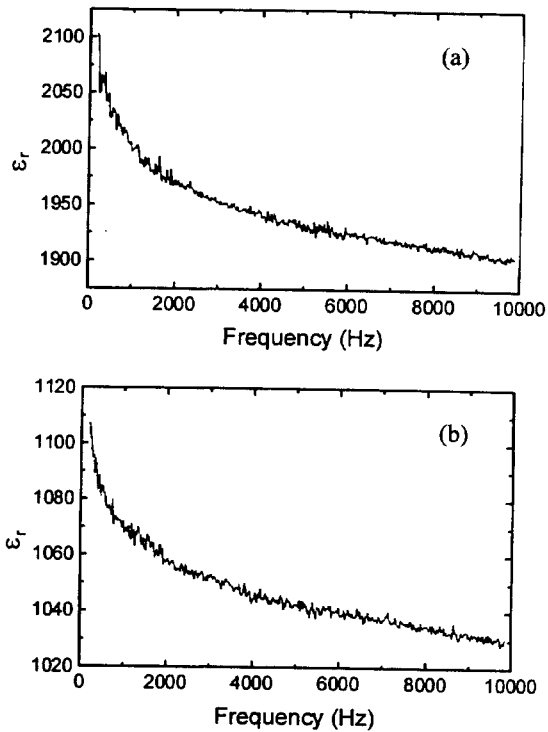


Fig.5. Change of dielectric constant with frequency for (a) FA and (b) FB.

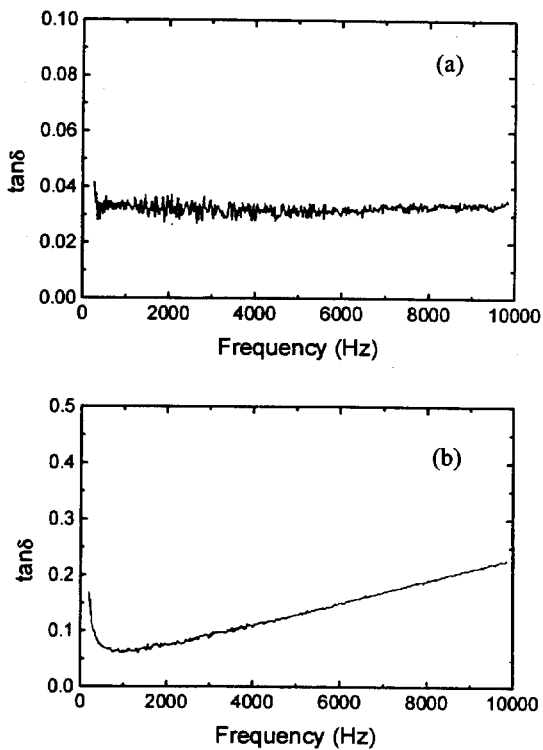


Fig.6. Change of  $\tan \delta$  with frequency for (a) FA and (b) FB.

dense structure and ferroelectric phase can be existed continually in FA. Contrary, the existence of rigid PZT powders in films prevents forming continual ferroelectric phase. Dielectric properties are also studied. The results are shown in Fig.5 and Fig.6, respectively. The dielectric constant of the film from powder A is much larger and dielectric loss  $\tan\delta$  is smaller than that in the film from 0-3 composition. It is obvious that large permittivity is attributed to a great volume of grain boundary and smaller dielectric loss is related to dense structure in FA.

#### SUMMARY

A new method for preparing PZT thick films has been established. The key in the process is to prepare a new precursor formed from the hydrolytic products of complex alkoxides and PZT solution. It must be emphasized that the hydrolytic products are undergone synthesis, nucleation, crystallization and phase development together with PZT solution synchronously during whole reaction process, because of the similarity in chemical and physical states between the hydrolytic products of complex alkoxides and PZT solution. Using this technology, crack-free PZT thick films with uniform structure and excellent properties, which are comparable with those of bulk ceramics, have been prepared. Results point that the new technology is a most favorable one for preparing thick films.

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