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# Effect of sol composition on dielectric and ferroelectric properties of PZT composite films

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**Abstract**

Crack free calcium modified PZT composite films have been synthesized using modified sol–gel process by depositing the slurries prepared by mixing powder of composition $PbZr_{0.52}Ti_{0.48}O_3$ and sol of composition $Pb_{(1-x)}Ca_xZr_{0.52}Ti_{0.48}O_3$ (where $x = 0, 0.06, 0.1$) on Pt(1 1 1)/Ti/$SiO_2$/Si substrate. The infilteration process has also been employed which resulted in dense microstructure of the films. Thickness of the films as measured by SEM of cross section of the films was more than 25 μm. The XRD patterns of the resultant films consisted of pure perovskite phase and no peak related to either pyrochlore phase or Pt substrate was observed. The room temperature dielectric constant and loss were compared. The temperature dependence of dielectric constant revealed that $T_C$ of all the films was same, i.e., 351 °C, in spite of different compositions of the sol used. Well saturated PE-loops of the films show that the films were ferroelectric in nature.


*Keywords:* A. Sol–gel process, D. PZT; D. Perovskite; Infilteration process

## 1. Introduction

Thick PZT films are of great interest in actuation of active structures in MEMS [1–4]. Many applications use their sensor and actuation capabilities in various fields, e.g., medical, military, telecommunication, etc. The ferroelectric and piezoelectric properties of such films in the thickness range 5–100 μm make them suitable for integrated actuation applications. Thick film technology fills the technological gap between thin films and bulk ceramics because conventional thin film deposition processes can produce films with smaller thickness (a few microns) and bulk materials are hard to be manufactured with a thickness less than 100 μm. So, PZT ferroelectric thick films possess merits of both bulk materials and thin films. The density of the film also plays an important role in overall performance of the device. Therefore, preparing crack-free and dense thick films is of great significance. Recently, the tremendous growth of research on fabrication of PZT films has resulted in the development of many sophisticated PZT film synthesis techniques. Among these methods, sol–gel [5–8] is the most popular and widespread technique for its attractive advantages of simple set-up, low cost, low temperature processing conditions and good control over stoichiometry, hence excellent film properties. But the conventional sol–gel method suffers from serious drawbacks of cracking of films, hence considerable degradation of the properties and also low critical thickness [5,9,10]. Screen printing is one of the most commonly used processes for fabricating thick films with thickness larger than 10 μm. However, the films prepared by screen printing method have low density and require higher annealing temperatures (>800 °C). This high temperature processing results in damage of platinized silicon bottom electrode [11–13]. Therefore, modified sol–gel technique has been developed by Barrow et al. [14] in which annealed PZT powder is dispersed in sol–gel matrix to obtain paint like slurry which is when deposited on a substrate either by screen printing or by spin coating process results into thick films of thickness much greater than 1 μm. The resulting thick films are called 0–3 ceramic/ceramic composite films because the sol–gel matrix is connected in all the three directions and PZT powder is not connected in any direction. The main advantages of modified sol–gel method are:

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1. The film forms strongly bonded network, with a sol–gel film firmly bonded between ceramic particles, making it less likely that the film will crack during processing.
2. Due to the presence of significant amount of ceramic powder, the percentage of sol–gel in the film is decreased and less shrinkage occurs when the film is processed.
3. Comparatively thicker films can be obtained.
4. Properties are comparable to bulk material.
5. We are dealing with a two-phase system (sol and powder) and therefore have greater opportunity to tailor the properties of the final films because of many permutations and combinations possible with the two phases. Some of these may be:
   - Altering powder to sol ratio.
   - Altering quality/composition of the powder.
   - Using different sizes of the powder.
   - Using different compositions of the sol keeping the composition of the powder fixed, etc.

So, in order to use the films for specific applications, it is important to understand how the above factors influence the properties of the final films.

Nevertheless, there is one major drawback of the films prepared from modified sol–gel process that the films are highly porous. Therefore, to obtain dense thick films is still a challenging job. In the present work, the infiltration process has also been employed to reduce the porosity [15–18] wherein after the deposition of the slurry on the substrate, PZT precursor solution is deposited on the composite film to infiltrate and fill-up the pores.

## 2. Experimental

### 2.1. Sol and slurry preparation

Calcium modified PZT precursor solutions with composition $Pb_xCa_{1-x}(Zr_{0.52}Ti_{0.48})O_3$ ($x = 0$, 0.06, 0.1) were prepared from lead acetate trihydrate ($Pb(CH_3COO)_2{\cdot}3H_2O$; >99%, Alfa Aesar), calcium acetate hydrate ($Ca(CH_3COO)_2{\cdot}H_2O$; 99%, Sigma Aldrich), zirconium propoxide ($Zr(OC_3H_7)_4$, 70 wt% in propanol; 99%, Aldrich) and titanium propoxide ($Ti(OC_3H_7)_4$; 98%, Aldrich). Glacial acetic acid and 2-methoxyethanol have been used as chelating agent and solvent respectively. The detail of sol preparation process is depicted in Fig. 1.

Calcined PZT powder of the composition $Pb(Zr_{0.52}Ti_{0.48})O_3$ prepared via conventional solid state reaction method was procured from CEL, India. Pure PZT powder was dispersed in unmodified and calcium modified PZT sols. Final slurries were prepared from powder loading level of 1.5 g:1 ml sol because this ratio resulted into the best quality films in terms of thickness and adhesion. The films obtained from powder loading level of 1 g:1 ml resulted into smaller film thickness of each layer and required more number of slurry layer deposition to get the desired film thickness. However, the powder loading level of 2.5 g:1 ml resulted into the films with poor adhesion to the surface of the substrate. Various dispersants were tried to make the slurries homogeneous but ESL 400 supplied by Electro Science Laboratories worked the best and hence was finally used.

### 2.2. Substrate cleaning

The substrate cleaning procedure used prior to film deposition greatly affects the adhesion of PZT films. The platinized silicon substrates (Pt(1 1 1)/Ti/$SiO_2$/Si) used in the present work were therefore methodically cleaned using following steps:

- Washed with soap solution using DI water.
- Completely immersed in trichloroethylene (works as de-greaser) and ultrasonicated for 15 min.
- Ultrasonication in high purity isopropanol (IPA) for further 15 min.

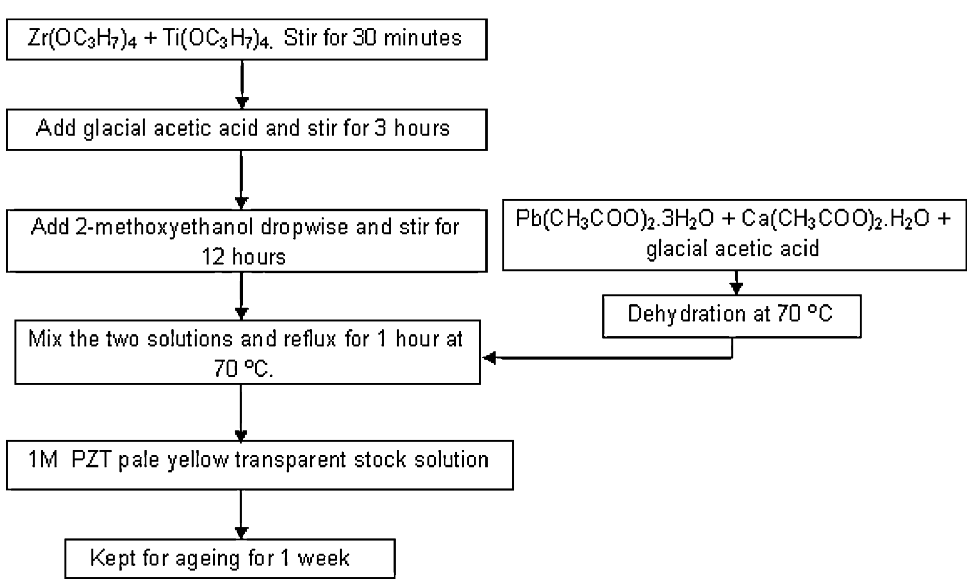


Fig. 1. Sol preparation process used in the present work.