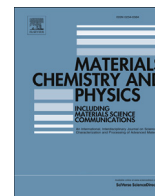




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## Characterisation of lead barium zirconate thin films for utilisation of the electrocaloric effect

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### HIGHLIGHTS

- Characterisation of sol-gel deposited Lead barium zirconate films.
- Absence of previously reported antiferroelectric phase.
- Identification of proposed non-PBZ phase.
- Anomalous increase in film capacitance with thickness interpreted.

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### ABSTRACT

Characterisation of a composition of Lead Barium Zirconate thin films deposited by a spin coating sol-gel process onto platinised silicon substrates has been undertaken to investigate a potential application utilising the reported electrocaloric properties of the material. Xray diffraction studies revealed that above 700 °C the presence of pyrochlore phase was replaced by ferroelectric phase but the identification of antiferroelectric phases previously reported could not be identified. Wet etching of the films produced an insoluble residue containing only evidence of zirconium out of the original three metals, which resembled a skeletal structure similar to the original rosette morphology of the annealed films. Elemental analysis of the annealed films using EDX indicated a non-target Pb:Ba:Zr ratio, which suggested a reduced Zr content of the films. "Solution-like" rather than "sol-like" nature of the spin coated sol and phase boundary proximity are proposed for reported observations, and a mechanism is proposed to account for the unusual observed trend in dielectric constant.

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### 1. Introduction

The electrocaloric effect is the adiabatic temperature change, or isothermal entropy change, caused by the polarisation change of a dielectric material when subjected to an external electric field. A recent review around potential electrocaloric materials [1] has highlighted the importance of ferroelectric materials, which demonstrate much larger electrocaloric effect (ECE) than traditional ceramic thin films, and which makes high performance solid-state cooling devices possible in the future. Measurements of ECE in

thin films are mostly based on field-induced polarisation measurements and Maxwell relations to derive  $\Delta S$  and  $\Delta T$  when an applied field is altered [2–12]. Very limited studies on a direct method of measuring the ECE have concentrated on using a high resolution calorimeter approach to measure the temperature change [13]. To address this issue and obtain accurate measurement of the ECE, development of a direct measurement method is a goal. One challenge is that the substrate under the film causes the fast heat dissipation, which increases the difficulty in measuring accurately the temperature change of the thin film caused by the application of an external electric field. Possibly, the formation of free standing or thin membrane supported ferroelectric materials can limit the heat loss/transfer mechanisms, both increasing the detectability of temperature change and simplifying the modelling of the structure. Published work by Saranaya [5] Mischenko [14] and Peng [15] represents some of the largest proposed  $\Delta T$  values

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reported for the ECE to date, with the later [15] claiming changes of 45 K at 60 kV/m for Lead Barium Zirconate (PBZ), and importantly near room temperature. This present study reports on further work carried out on the synthesis and characterisation of PBZ thin films based on the promising composition for electrocaloric applications looked at in the Peng et al. [15] study, and highlights some of the processing issues in scale up prior to the development of free standing membrane devices.

## 2. Material and methods

The target composition for finally annealed films was  $\text{Pb}_{0.8}\text{Ba}_{0.2}\text{ZrO}_3$  but a sol composition with 20% excess of lead based on this formula, was prepared to allow for lead loss during the film annealing. A 0.3 M sol with the main solvent components (glacial acetic acid:water:2-methoxyethanol(2 ME)) in a 1:1:1 vol ratio was prepared as follows.

First, 10.93 g of lead (II) acetate trihydrate (Sigma-Aldrich 99.5%) and 1.53 g of barium acetate (Acros Organics 99+%) were dissolved in a mixture 29.37 g of glacial acetic acid (Sigma-Aldrich 99%) and 26.45 g of water, by stirring in a covered beaker for 1 h at room temperature.

14.04 g of zirconium *n*-propoxide solution (Sigma Aldrich, 70% in 1-propanol) was mixed with 27.02 g of 2-methoxyethanol (Sigma-Aldrich 99.8%) in a 250 ml round bottom flask under nitrogen using a glove box (Bassaire Ltd, Manchester). The sealed flask was removed from the glove box and a preweighed 3.3 g (10% excess relative to Zr) of acetylacetone (Fluka 99.5%) was quickly added to the solution and swirled to stabilise the metal organic. The stabilised solution was then stirred for 30mins before combining with the Pb/Ba solution, and the combined "Sol" solution was stirred for 24 h at room temperature. The Sol was then filtered through a 0.45  $\mu\text{m}$  filter (Whatman Zap Cap™) and stored at room temperature before use. Particle size measurements were carried out using a Zetasizer™ (Model 3000, Malvern Ltd.), to investigate potential aging and potential shelf life of the "Sols".

For PBZ crystallization studies, electroded silicon wafers were prepared as substrates to allow subsequent electrical characterisation. Silicon wafers (Orientation:  $\langle 100 \rangle$ . Resist: 10–30ohm-cm: Doping: P-type) with a thermal oxide coating were used supplied from Mi-Net Technology Ltd. (UK). Titanium/platinum (Ti/Pt) coatings were deposited by physical vapour deposition (PVD) using a Nordiko™ Ltd. sputtering system. This PVD approached used Rf (Titanium) and DC(Platinum) (300 W) water cooled, magnetron sputtering to deposit the bottom Ti/Pt electrodes using Argon gas at 5 mT and without substrate heating to achieve the target thicknesses of 10 nm/100 nm respectively.

Fig. 1 shows the deposition cycle used to deposit and build up film thickness of PBZ films as reported in the literature [15]. Pieces of Ti/Pt coated wafers ( $\sim 2 \times 2 \text{ cm}^2$ ) were first dried on a hotplate at 100 °C. To aid wetting of the Pt surface by the sol, it was found that spin rinsing with distilled water and blow drying with nitrogen immediately before deposition of the first layer greatly improved the qualitative appearance of the deposited layer and subsequent film. The sol was applied using a syringe fitted with a 0.2  $\mu\text{m}$  filter (Whatman™) to help reduce defects from particulate impurities. Following static sol application, a layer was coated using a spin coater (Electronic Micro Systems Ltd.) with an acceleration speed of  $\sim 2000\text{rpm}$ , and then annealed using two hotplates (CEE 1100 Brewer Science, and Sawatec HP 160/700 Sawatzki Technology) respectively. This was repeated for a total of 8 layers, and then a single furnace crystallisation carried out. A small Carbolite™ tube furnace (Model: MTF 10/25/130) was initially used to try to replicate results obtained from the referenced work [15], but samples were also prepared in a Carbolite™ box furnace (Model: ELF 11/6) to

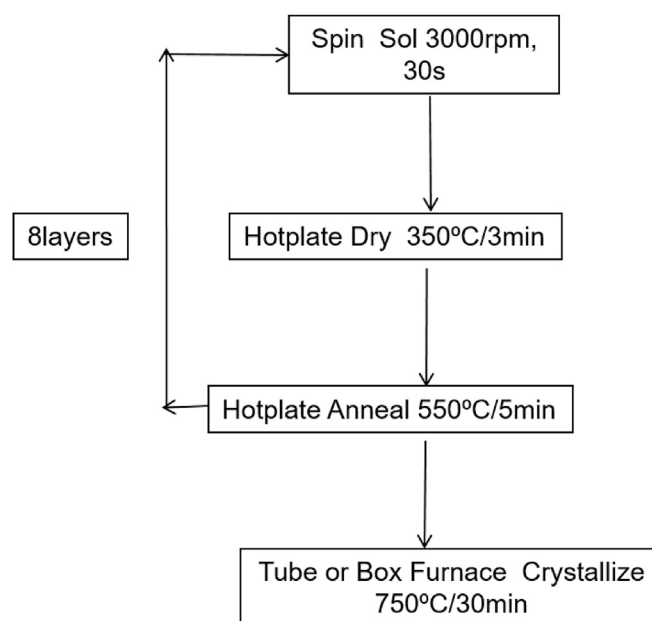


Fig. 1. Sol-gel spin coating deposition cycle. Primary PBZ film deposition conditions based on previous study [15].

accommodate the necessary scale up required to process a full wafer. A target thickness of  $\sim 380 \text{ nm}$  was expected for such an 8 layer film. Additional samples, looking at variations of the annealing and crystallization times were also made to try to help to solve some of the processing issues encountered. Film characterisation was carried out on annealed and part annealed samples using a Polyvar microscope (Reichert Jung), for optical studies, an X-Ray Diffraction system (Model: D500. Siemens Ltd.) for crystallisation investigation and scanning electron microscopy (FEI XL30 SFE) with EDX to complement optical studies and look for compositional variation. Dielectric measurements were also made using an impedance analyser (Wayne kerr Electronics Ltd. Model 3245)) for the purposes of this study to provide comparison with published values. Hysteresis measurements were collected from a RT66A (Radiant Technology Ltd.)

## 3. Results

Based on qualitative visual studies, the prepared PBZ sols were green solutions with good clarity even after 6 months. In initial work, a fine precipitate had been observed after trying to stabilize the Zirconium alkoxide using a 1:1 Zr/acetylacetone ratio, which was believed to be zirconium oxide, and due to incomplete transfer of all the acetylacetone. The subsequent addition of the 10% excess amount subsequently ensured at least an equimolar transfer, and the resultant clear "sols". Consequently, with no evidence of precipitation within these prepared sols, there is high confidence that the target composition of reactants was being deposited. Particle sizing results carried out on diluted samples of the sol over a 6 month period gave consistent values of  $12 \pm 6 \text{ nm}$ . However, it is worth noting that the zetasizer indicated relatively low sampling counts suggesting that the measurement was operating in the "noise" region of the machine, and the evidence of the low counts is potentially an indication of a solution rather than a "sol" nature to the prepared sols.

Fig. 2 shows the initial XRD analysis on 4 layer samples crystallised with varying temperature, and clearly shows the removal of the broad pyrochlore phase peak centred at  $29.84^\circ$ , above  $650^\circ\text{C}$ , as

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