

## High tunable dielectric response of $\text{Pb}_{0.87}\text{Ba}_{0.1}\text{La}_{0.02}(\text{Zr}_{0.6}\text{Sn}_{0.33}\text{Ti}_{0.07})\text{O}_3$ thin film

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### Abstract

The permittivity maximum of a sol-gel derived  $\text{Pb}_{0.87}\text{Ba}_{0.1}\text{La}_{0.02}(\text{Zr}_{0.6}\text{Sn}_{0.33}\text{Ti}_{0.07})\text{O}_3$  (PBLZST) thin film was observed to appear at  $T_m=70$  °C rather than at 40 °C as observed in the bulk ceramics with the same composition. Measurements of permittivity vs. electric field ( $E$ ) present two maximums at 60 (polarizing) and 25  $\text{kVcm}^{-1}$  (depolarizing), corresponding to antiferroelectric-ferroelectric and ferroelectric-antiferroelectric phase transitions, respectively. Calculations of tunability and Figure-of-Merit (FOM) display a maximum value of 75% at  $E = 350 \text{ kV cm}^{-1}$  and  $\sim 141$ , respectively. These high tunable dielectric responses imply that PBLZST thin films can be an attractive material for tunable device applications.

### Introduction

Nonlinear electric field-dependent dielectric constant characterizes ferroelectrics materials, which put them on the top of the best choices for microwave tunable devices. Among all the ferroelectrics films  $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$  has shown the highest tunability (92.7 % at 4 MV/cm) [1].  $\text{Pb}_x\text{Sr}_{1-x}\text{TiO}_3$  and  $\text{Ba}_x\text{Zr}_{1-x}\text{TiO}_3$  thin films have also been reported having very high tunabilities of 70% [2] and 84% [3], respectively. In addition to high tunability, low dielectric loss is also required for tunable microwave devices.

The (Pb,La)(Zr,Sn,Ti) system (PLZST) is known to develop antiferroelectric (AFE) phases with different symmetries (orthorhombic or tetragonal) [4]. Although antiferroelectric (AFE)-paraelectric (PE) phase transition occurs at high temperature ( $>150$  °C), PLZST compositions have attracted great attention as they may stabilize in a ferroelectric (FE) state by applying a small electric field,  $E$  [4-5], which is due to the small difference in free energy between the ferroelectric and antiferroelectric phases in the PLZST family of ceramics. Field-induced AFE-FE phase transition is known to bring about abrupt changes in macroscopic

properties, such as pyrocoefficient and charge release [6]. Liu *et al.* [7] have shown that the substitution of 10 at.% of barium in antiferroelectric PLZST bulk ceramic, forming  $\text{Pb}_{0.87}\text{Ba}_{0.1}\text{La}_{0.02}(\text{Zr}_{0.6}\text{Sn}_{0.4-x}\text{Ti}_x)\text{O}_3$  (PBLZST), permits decreasing AFE-PE phase transition down to room temperature. According to the phase diagram [7], PBLZST ceramics exhibit a tetragonal antiferroelectric phase for  $x \leq 0.07$ , with a ferroelectric relaxor rhombohedral phase being observed for  $x \geq 0.08$ . In particular, the  $\text{Pb}_{0.87}\text{Ba}_{0.1}\text{La}_{0.02}(\text{Zr}_{0.6}\text{Sn}_{0.33}\text{Ti}_{0.07})\text{O}_3$  composition has been reported [7] to exhibit large permittivity and the occurrence of AFE-PE phase transition at  $T_m = 40$  °C. Despite this,  $\text{Pb}_{0.87}\text{Ba}_{0.1}\text{La}_{0.02}(\text{Zr}_{0.6}\text{Sn}_{0.33}\text{Ti}_{0.07})\text{O}_3$  ceramics nevertheless undergo AFE-FE phase transition under an electric field as low as 9 kV/cm (at room temperature). There have been only a few studies addressing the effect of barium doping on the properties of PLZST ceramics [7-10], but none of them involving PLZST thin films. In this paper, we report dielectric properties of  $\text{Pb}_{0.87}\text{Ba}_{0.1}\text{La}_{0.02}(\text{Zr}_{0.6}\text{Sn}_{0.33}\text{Ti}_{0.07})\text{O}_3$  (PBLZST) thin film processed by a sol-gel method. AFE-PE phase transition is analyzed by using Curie-Weiss law. Furthermore, nonlinear dependence of permittivity with bias field ( $E$ ) at room temperature is also reported herein, and the applicability of PBLZST thin film for tunable devices discussed.

## Experimental

$\text{Pb}_{0.87}\text{Ba}_{0.1}\text{La}_{0.02}(\text{Zr}_{0.6}\text{Sn}_{0.33}\text{Ti}_{0.07})\text{O}_3$  thin film was fabricated by a sol-gel method.  $\text{Pb}(\text{OA})_2 \cdot 3\text{H}_2\text{O}$ ,  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{Ti}(\text{O}^n\text{Bu})_4$ ,  $\text{Zr}(\text{O}^n\text{Pr})_4 \cdot \text{Pr}^n\text{OH}$  and  $\text{Sn}(\text{OCH}(\text{CH}_3)\text{CH}_2\text{OCH}_3)_4$  were used as starting materials and dissolved in acetic acid, 2-methoxyethanol and deionised water, thereby forming a stable sol with a concentration of 0.4 M. PBLZST sol was spin-coated at 3000 rpm for 30 s onto a Pt(111)/Ti/TiO<sub>2</sub>/SiO<sub>2</sub>/Si substrate. The layer obtained was pyrolysed at 350 °C for 1 min. and subsequently annealed at 650 °C for 5 min. The above-mentioned procedure was repeated several times until the total thickness of the film was 200 nm. The structure of the films was monitored by X-ray diffraction (XRD) on a Siemens XS D5005 diffractometer, using Cu K $\alpha$  radiation. Permittivity measurements were carried out using a Wayne Kerr impedance analyzer at  $V_{\text{a.c.}} = 100$  mV. Temperature was controlled with the aid of a Peltier element.

## Results

XRD pattern of  $\text{Pb}_{0.87}\text{Ba}_{0.1}\text{La}_{0.02}(\text{Zr}_{0.6}\text{Sn}_{0.33}\text{Ti}_{0.07})\text{O}_3$  (PBLZST) thin film is illustrated in Fig. 1. Single phased and (111)-orientated perovskite film was achieved. A doublet of (111) and (-111) (see inset of Fig. 1) indicates that PBLZST thin film crystallizes in a rhombohedral

phase, which does not corroborate with the tetragonal phase found in  $\text{Pb}_{0.87}\text{Ba}_{0.1}\text{La}_{0.02}(\text{Zr}_{0.6}\text{Sn}_{0.33}\text{Ti}_{0.07})\text{O}_3$  ceramics [7]. This may be due to the existence of interfacial stress due to the lattice mismatch between PBLZST film and (111)-orientated platinised substrate. Lattice parameter of PBLZST film ( $a = b = c$ ) was determined to be  $a \sim 0.412$  nm as lattice parameter of Pt(111) is  $a \sim 0.392$  nm. By using Scherrer's formula, with (111) peak as reference, crystallite size of PBLZST film was calculated to be  $\sim 37.5$  nm.

Temperature dependence of relative permittivity ( $\epsilon'$ ) and dielectric loss ( $\tan \delta$ ) observed in PBLZST thin film, at 1.5, 5, 10, 50 and 100 kHz, is shown in Fig. 2. Although the values of permittivity are higher ( $\epsilon'_m \sim 937$ ) compared with those found in PZT-based compositions, it is rather lower than obtained for corresponding sintered bulk PBLZST ceramics with the same composition ( $\epsilon'_m \sim 4200$ ) [7]. This difference has been attributed to small grain size in thin film compared with similar bulk ceramics. Likewise, the maximum value of permittivity is observed at 70 °C ( $T_m$ ), rather than at 40 °C reported in PBLZST bulk material [7]. Moreover, the relaxation observed by the frequency- dependent permittivity indicates the existence of defects which, in addition to the small thickness of the film, clamping by the substrate and low annealing temperature, may contribute to decreasing of permittivity and the shift of  $T_m$  comparing with bulk ceramics.

In order to analyze the corresponding phase transition observed at  $T_m$ , permittivity data were fitted in accordance with the Curie-Weiss law as follows:

$$\frac{1}{\epsilon'} = \frac{(T - T_C)}{C} \quad (1)$$

where  $T_C$  and  $C$  are the Curie temperature and constant, respectively. Fig. 3 illustrates the fitting of Eq. (1) to the reciprocal permittivity ( $\epsilon'^{-1}$ ) data obtained above  $T_m$ . Negative  $T_C$  (-1472 °C) is found from the fitting to  $T > T_m$  data which is recognized to be due to a paraelectric-antiferroelectric phase transition occurring at  $T_m$ . Therefore, at zero-field conditions, PBLZST thin film is stabilized in an antiferroelectric state at  $T < T_m$ , in agreement with results obtained in PBLZST ceramics by Liu *et al.* [7].

Measurements of permittivity and dielectric loss as a function of bias field ( $E$ ) were carried out at 10 kHz at room temperature, and the results are shown in Fig. 4. The butterfly-shaped  $\epsilon'$  and  $\tan \delta$  curves against electric field indicate a nonlinear field dependence.

Both permittivity and dielectric loss increase with  $E$  up to 60  $\text{kVcm}^{-1}$ , and decrease rapidly at  $E > 60$   $\text{kVcm}^{-1}$ , which indicates that an AFE-FE phase transition takes place. Fig. 4 shows electrical hysteresis in the  $E$  range of 0-300  $\text{kV cm}^{-1}$  which is associated with ferroelectric domain walls displacement [11] and the coexistence of FE and AFE domains.

Antipolar (AFE) to polar (FE) state transition (or vice versa) is known to accompany abrupt changes in macroscopic properties, and its effect on PBLZST thin film dielectric tunability is herein demonstrated. Dielectric tunability is defined as:

$$Tunability(\%) = \frac{\varepsilon'(0) - \varepsilon'(E)}{\varepsilon'(0)} \times 100 \quad (2)$$

The field dependence of tunability for both polarizing and depolarizing curves was estimated, by using Eq. (2). It was found that the tunability increases with  $E$  and the large values of 73% (polarizing approach) and 75% (depolarizing branch) are obtained at  $E = 350 \text{ kVcm}^{-1}$ . Nonetheless, the competence of a dielectric for tunable device applications requires not only high value of tunability but also low dielectric loss. Figure-of-Merit (FOM) of dielectric tunability is defined as:

$$FOM = \frac{Tunability}{\tan \delta} \quad (3)$$

FOM obtained in PBLZST thin film can be seen in Fig. 5. Similar to tunability, FOM also increases with  $E$  and a maximum value of 141 was found in both polarizing and depolarizing branches. FOM values observed in PBLZST thin film are high and therefore PBLZST thin film can be a very promising material for dielectric tunable device applications.

## Conclusions

Single phased and (111)-orientated  $\text{Pb}_{0.87}\text{Ba}_{0.1}\text{La}_{0.02}(\text{Zr}_{0.6}\text{Sn}_{0.33}\text{Ti}_{0.07})\text{O}_3$  thin film was fabricated by sol-gel method. Relative permittivity reaches a maximum value ( $\varepsilon'_m \sim 939$ ) at  $T_m = 70 \text{ }^\circ\text{C}$ , which is lower than that found in PBLZST ceramics ( $\varepsilon'_m \sim 4200$ ) with the same composition. The reasons for such a low value may be associated with a combination of several factors such as small grain size, substrate clamping, thinner thickness and the existence of defects. Curie-Weiss analysis indicates a second-order PE-AFE phase transition at  $T_m = 70 \text{ }^\circ\text{C}$ .  $\varepsilon'$ - $E$  curves suggest that AFE-FE phase transition occurs when  $E = 60 \text{ kV cm}^{-1}$  is applied and that said phase transition results in large nonlinear field dependence of permittivity and dielectric loss. Electrical hysteresis is observed and FE-AFE phase transition occurs at  $25 \text{ kV cm}^{-1}$ . Field-induced AFE-FE phase transition (and vice-versa) results in an abrupt change in permittivity. Hence high values of tunability are found for both polarizing (73%) and depolarizing (75%) approaches at  $350 \text{ kV cm}^{-1}$ . FOM is reported to increase by increasing  $E$ , and high value as 141 was determined for both depolarizing and polarizing curves. Such values of FOM are the highest ever reported. Consequently,  $\text{Pb}_{0.87}\text{Ba}_{0.1}\text{La}_{0.02}(\text{Zr}_{0.6}\text{Sn}_{0.33}\text{Ti}_{0.07})\text{O}_3$  thin film can be a promising candidate for tunable device applications.

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**Figure captions:**

Fig. 1 XRD pattern of  $\text{Pb}_{0.87}\text{Ba}_{0.1}\text{La}_{0.02}(\text{Zr}_{0.6}\text{Sn}_{0.33}\text{Ti}_{0.07})\text{O}_3$  thin film.

Fig. 2 Temperature dependence of relative permittivity ( $\epsilon'$ ) and dielectric loss ( $\tan \delta$ ) at different frequencies: 1.5, 5, 10, 50 and 100 kHz.

Fig. 3 Reciprocal permittivity as a function of temperature obtained at 10 kHz (open marker) at  $T > T_m$ . Curie-Weiss fitting (dashed line).

Fig. 4 Relative permittivity ( $\epsilon'$ ) and dielectric loss ( $\tan \delta$ ) vs. bias field,  $E$ , at 10 kHz.

Fig. 5 Field ( $E$ ) dependence of tunability and FOM.