

# Effect of DC biasing field on dielectric properties of ZrO<sub>2</sub>-doped barium strontium titanate

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**Abstract** Effect of DC biasing field on dielectric properties of (Ba<sub>0.6</sub>Sr<sub>0.4</sub>)TiO<sub>3</sub> and ZrO<sub>2</sub>-doped (Ba<sub>0.6</sub>Sr<sub>0.4</sub>)TiO<sub>3</sub> for application in phased array antennas have been characterized. The grain size is maximum for (Ba<sub>0.6</sub>Sr<sub>0.4</sub>)TiO<sub>3</sub> doped with 0.5 wt% ZrO<sub>2</sub> content. The real part of the relative dielectric constant of the specimens decrease with increasing applied DC biasing field. The tangent loss of the specimens is influenced much less by the DC biasing field than the real part of the relative dielectric constant. The tunability of the real part of the relative dielectric constant is about 45% for (Ba<sub>0.6</sub>Sr<sub>0.4</sub>)TiO<sub>3</sub> doped with 0.5 wt% ZrO<sub>2</sub> content.

## Introduction

Phased array antennas are currently constructed using ferrite phase-shifting elements. However, these are very costly, large, and heavy. In order to make these devices practical for commercial and military uses; better materials must be developed [1]. The desirable characteristics of the dielectric material for phased array applications would be a low dielectric constant, low dielectric loss factor and high dielectric tunability. The tunability of the specimen affects its properties through changes of the dielectric constant with applied electric field. The phase-shifting ability

is directly related to the tunability; therefore, higher tunability is desirable [2]. Reduction of the dielectric constant reduces the overall impedance mismatch. The loss tangent serves to dissipate or absorb the incident microwave energy; thus a low loss tangent serves to decrease the insertion loss [3]. Numerous studies on the dielectric properties of (Ba<sub>1-x</sub>Sr<sub>x</sub>)TiO<sub>3</sub> based ceramics using the conventional mixed oxide method have been carried out. The real part of the relative dielectric constant of Ba<sub>x</sub>Sr<sub>1-x</sub>TiO<sub>3</sub> ceramics varies from 200 to 900, and the loss factor of Ba<sub>x</sub>Sr<sub>1-x</sub>TiO<sub>3</sub> ceramics varies from 10<sup>-3</sup> to 10<sup>-2</sup> around 2 GHz [4]. The real part of the relative dielectric constant of samples doping with a small amount of phosphor sintered at 1,150 and 1,200 °C are 6,100 and 5,500, respectively [5]. Fe<sub>2</sub>O<sub>3</sub>-doped (Ba<sub>0.6</sub>Sr<sub>0.4</sub>)TiO<sub>3</sub> produced the smallest loss factor of all the dopants studied included Mn, Bi, Ga, Y, Nb and Fe [6]. BaTiO<sub>3</sub> with  $\epsilon_r \sim 1,000$ , and  $\tan \delta < \sim 0.04$  in the range of 1 KHz to 1 MHz was obtained by diffusion of externally placed Al during the sintering cycle [7]. However, there are few studies on the DC biasing field dependence of the dielectric properties.

For perovskite structures (ABO<sub>3</sub>), doping with small amounts of ions can greatly affect the dielectric properties [8–10]. The dielectric properties of (Ba<sub>0.6</sub>Sr<sub>0.4</sub>)TiO<sub>3</sub> doped with ZrO<sub>2</sub> have been found to be different from those of undoped (Ba<sub>0.6</sub>Sr<sub>0.4</sub>)TiO<sub>3</sub>. Further understanding of these different dielectric properties was achieved through X-ray diffraction measurements and observation of microstructures.

## Experimental procedure

The starting raw chemicals were high purity BaCO<sub>3</sub>, TiO<sub>2</sub>, SrCO<sub>3</sub> and ZrO<sub>2</sub> powders (Merck). The composition

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prepared was  $(\text{Ba}_{1-x}\text{Sr}_x)\text{TiO}_3$  with  $x = 0.4$  being referred to as BSTO. Then the BSTO was doped with 0.5 wt%, 1.0 wt% and 1.5 wt%  $\text{ZrO}_2$ , these being referred to as, BSTO1, BSTO2 and BSTO3 respectively. The raw materials were weighed out in stoichiometric proportions, ball-milled in alcohol, dried and then calcined at  $1,150\text{ }^\circ\text{C}$  for 3 h. The obtained powders were then crushed to a fine powder and then through a 325-mesh screen. The powder then was axially pressed into pellets at  $20\text{ Kg/cm}^2$  with a diameter of 9.8 mm and thickness of 1.6 mm with no binder used. Then samples were sintered at  $1,450\text{ }^\circ\text{C}$  for 3 h. After sintering, the phases of the samples with a diameter about 8 mm and thickness about 1 mm were investigated with X-ray diffraction (Model Rigaku D/Max III.V) with  $\text{CuK } \alpha$  radiation and Ni-filter. The SEM was employed to examine the microstructures of the specimens. Then the average grain size was determined by the linear-intercept method from the microstructures of the specimens.

The indium-contained silver past (Du pont 4021) is painted as the electrode to provide ohmic contact. The dielectric properties of ceramic body were measured with HP4194 Impedance/Gain Phase Analyzer. The measurement temperature was  $25\text{ }^\circ\text{C}$ . With the capacitance of the sample measured, the real part of the relative dielectric constant  $\epsilon'_r$  was calculated as follows:

$$\epsilon'_r = \frac{Cd}{A\epsilon_0} \tag{1}$$

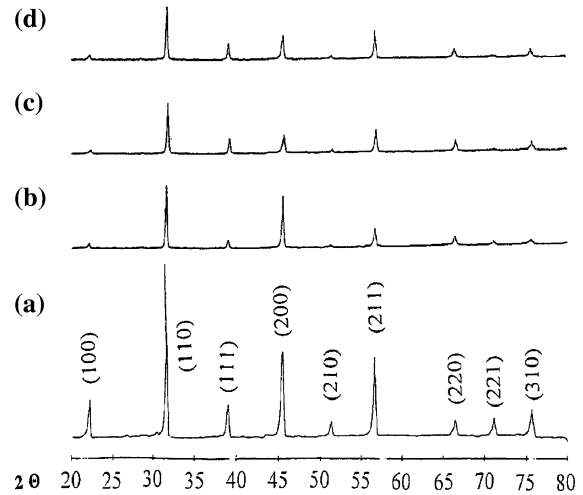
where  $C$  is the capacitance,  $d$  is the thickness,  $A$  is the area and  $\epsilon_0 = 8.8542 \times 10^{-12}\text{ F/m}$ . The %tunability is defined by the percentage of the real part of the relative dielectric constant with applied DC biasing field. The %tunability is determined using the following equation

$$\% \text{ tunability} = \{ \epsilon'_r(0) - \epsilon'_r(V_{\text{app}}) \} / \{ \epsilon'_r(0) \} \tag{2}$$

where  $\epsilon'_r(0)$  is the real part of the relative dielectric constant without DC biasing field and  $\epsilon'_r(V_{\text{app}})$  is the real part of the relative dielectric constant DC biasing field with  $V_{\text{app}}$ .

**Results and discussion**

For comparison, the X-ray diffraction patterns of all the specimens are shown in Fig. 1. As observed from the X-ray pattern, the peaks of BSTO (100), (110), (111), (200), (210), (211), (220), (221) and (310) are very distinct. BSTO exhibits a cubic-type crystal structure. Same spectral angle of X-ray diffraction peaks were observed were observed at various amount of  $\text{ZrO}_2$  additions. There is no second phase in the X-ray diffraction is observed for



**Fig. 1** X-ray diffraction of all samples; (a) BSTO, (b) BSTO1, (c) BSTO2 (d) BSTO3

$\text{ZrO}_2$ -doped BSTO. Microstructures of all the specimens are shown in Fig. 2. The grain sizes of the specimens were plotted as functions of  $\text{ZrO}_2$  doping contents as shown in Fig. 3. The grain sizes of the specimen increases with  $\leq 0.5\text{ wt}\%$   $\text{ZrO}_2$  contents and decreases with  $>0.5\text{ wt}\%$   $\text{ZrO}_2$  content.

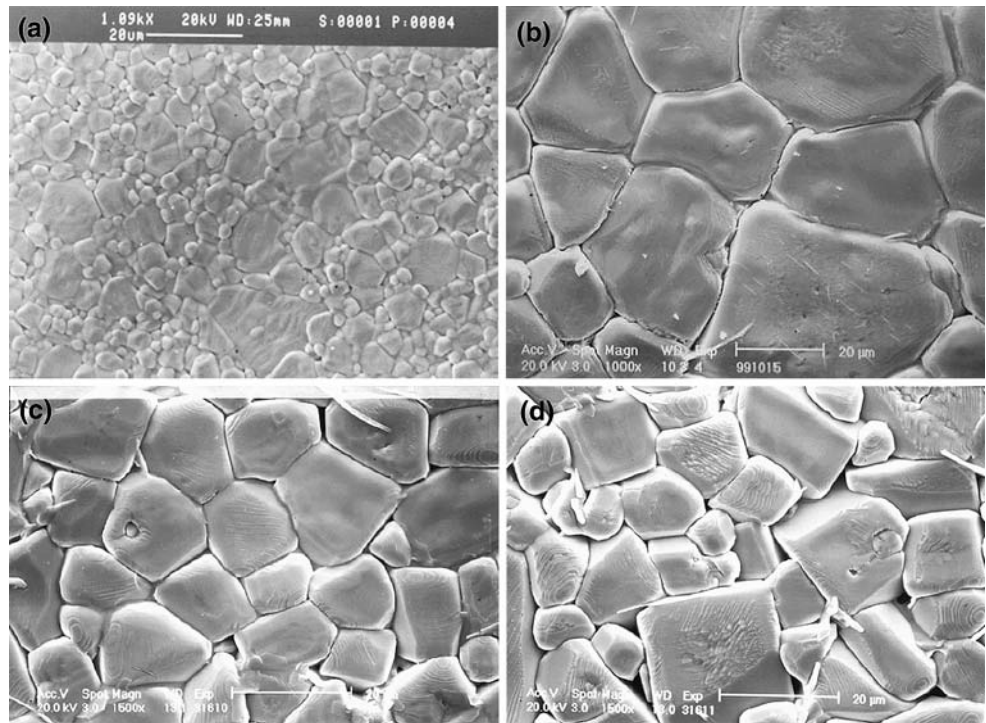
The solid line in Fig. 4 is the real part of the relative dielectric constant of the samples with respect to DC biasing field measured at different frequencies. From the results of Fig. 4, it is evident that the real part of the relative dielectric constant of the samples decreases with increasing the DC biasing field. The nonlinearity of the real part of the relative dielectric constant with the DC biasing field results from the anharmonic interaction of Ti ions in the perovskite cubic structure. This can be explained by Johnson’s theory [11]. The real part of the relative dielectric constant  $\epsilon'_r$  was represented as

$$\frac{\epsilon'_r}{\epsilon'_{r0}} = \frac{1}{(1 + a\epsilon'^3_{r0}E^2)^{1/3}}, \tag{3}$$

$\epsilon'_{r0}$  and  $\epsilon'_r$  are the real part of the relative dielectric constant under zero DC biasing field and under DC biasing field  $E$ , respectively; and  $a$  is the phenomenological coefficient. The real part of the relative dielectric constant of the samples decreases with the increasing of the DC biasing field.

The DC biasing field of loss factor measured at different frequencies is illustrated as a dotted line in Fig. 4. As shown in Fig. 4, the tangent loss of the samples influenced by the biasing DC field is slight. This is due to the fact that with the capacitor circuit model, there are two loss mechanisms for the dielectric loss with biasing DC field. The tangent loss  $\tan \delta$  can be expressed as [12]:

**Fig. 2** Microstructures of all samples; (a) BSTO, (b) BSTO1, (c) BSTO2, (d) BSTO3

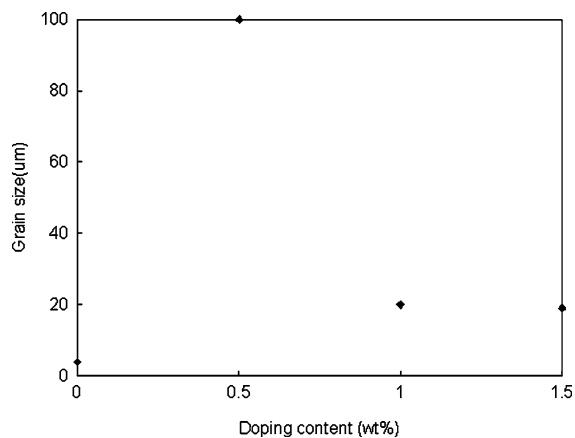


$$\tan \delta = \tan \delta_C + \tan \delta_R \quad (4)$$

$\tan \delta_C$  and  $\tan \delta_R$  are the intrinsic tangent loss and conduction tangent loss, respectively.

The intrinsic tangent loss  $\tan \delta_C$  can be expressed as [11]:

$$\frac{\tan \delta_C}{\tan \delta_{CO}} = \frac{1}{[1 + a \tan \delta_{CO}^3 E^2]^{1/3}} \quad (5)$$

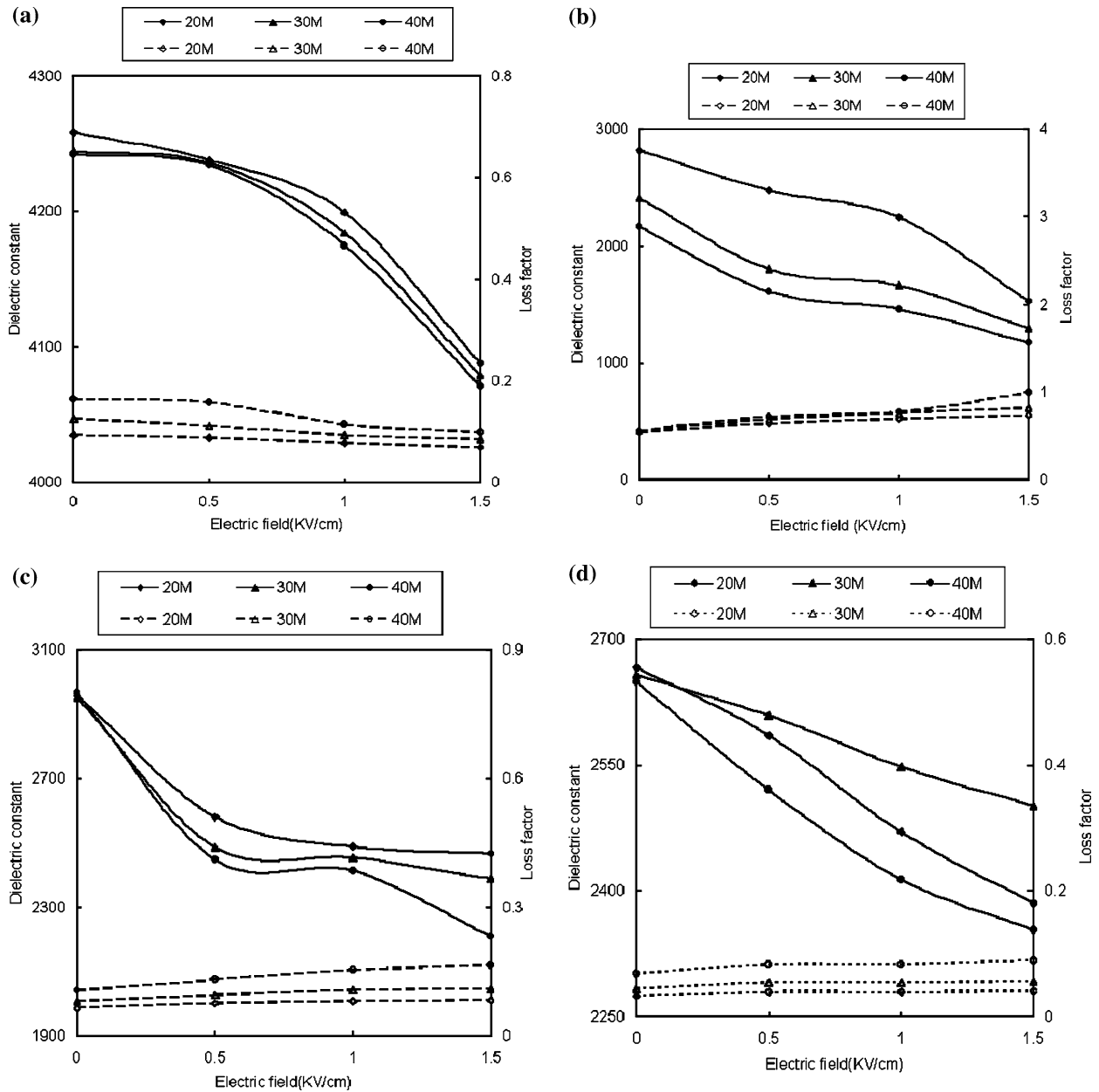


**Fig. 3** Grain size of the specimens as a function of ZrO<sub>2</sub> doping content

This intrinsic tangent loss is decreased by applying the biasing DC field.  $\tan \delta_{CO}$  is the intrinsic dielectric tangent loss with zero DC biasing field and  $a$  is the phenomenological coefficient. The other term  $\tan \delta_R$  is the conduction tangent loss can be expressed as [12, 13]:

$$\tan \delta_R = \frac{1}{\omega RC_0} \quad (6)$$

$R$  is the resistance and  $C_0$  is the geometrical capacitance of the specimen. The resistance decreases with increasing the DC biasing field and the conduction tangent loss increases with increasing the DC biasing field. The intrinsic tangent loss is reduced by the DC biasing field as expressed in Eq. 5 which dominates at temperatures below “behavior transformation” temperature  $T_b$ . So the tangent loss decreases with increasing biasing DC field for the temperatures lower than  $T_b$ . As the temperature increases, the DC biasing field effect on the intrinsic tangent loss is suppressed due to the reason that the decreasing of  $a \epsilon_{r0}^3$  [11, 14]. The conduction tangent loss increases due to the fact that both the real part of the relative dielectric constant and the resistance decrease [12, 13]. So the tangent loss increases with biasing DC field above “behavior transformation” temperature and is not influenced by the DC biasing field at “behavior transformation” temperature. From the results of Fig. 4, the tangent loss of the samples under the influence of biasing DC fields are slight. It is



**Fig. 4** (a) The real part of the relative dielectric constant and loss factor of BSTO2 versus DC field at 20, 30, 40 MHz. (b) The real part of the relative dielectric constant and loss factor of BSTO1 versus DC field at 20, 30, 40 MHz. (c) The real part of the relative dielectric

constant and loss factor of BSTO2 versus DC field at 20, 30, 40 MHz. (d) The real part of the relative dielectric constant and loss factor of BSTO3 versus DC field at 20, 30, 40 MHz

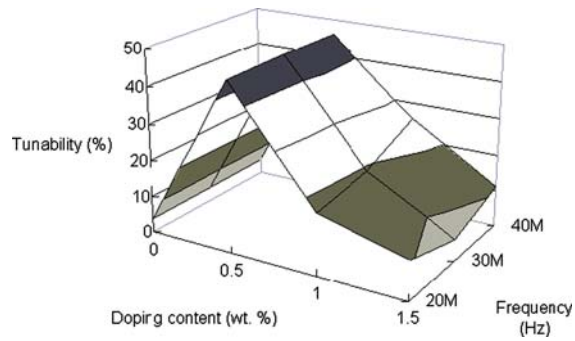
inferred that the  $T_b$  of the samples is around the measurement temperature (25 °C).

The tunability is defined as the changing percentage of the real part of the relative dielectric constant. Variation of tunability with ZrO<sub>2</sub> contents measured at different frequencies is illustrated in Fig. 5. The tunability is about 45% for (Ba<sub>0.6</sub>Sr<sub>0.4</sub>)TiO<sub>3</sub> doped with 0.5 wt% ZrO<sub>2</sub> content. The tunability and grain size have similar trends as a function of ZrO<sub>2</sub> contents. This is due to the fact that Johnson’s theory assumes a stress-free condition. However there is internal stress among grains that affect the

dielectric properties. The internal stress decreases with the increase of the grain size. As a result of the grain size of BSTO1 being the largest and the internal stress effect on BSTO1 would be smallest, BSTO1 has maximum tunability. The sample with larger grains has larger tunability.

**Conclusions**

Pure BSTO and composites BSTO and ZrO<sub>2</sub> were fabricated and characterized. The composites have adjustable



**Fig. 5** Variation of tunability with  $\text{ZrO}_2$  content measuring at different frequencies

dielectric properties. The real part of the relative dielectric constant decreases with increasing applied biasing DC field and the tangent loss influenced by biasing DC field is slighter. The nonlinearity of the real part of the relative dielectric constant with the DC biasing field can be explained by Johnson's theory. The lighter of the tangent loss influenced by the DC biasing field is due to there are two loss mechanisms for the dielectric loss in the capacitor circuit model. The tunability and grain size have similar trends as a function of  $\text{ZrO}_2$  contents. It is inferred that the tunability of the specimens is affected by the grain size. The  $\text{ZrO}_2$ -doped BSTO materials exhibit high tenability

behavior which reminds them suitable for use in phase array antennas.

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