

The model of electric field dependent dielectric properties for porous ceramics

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The electric field dependence on the dielectric properties of the porous ceramics was studied theoretically. The dielectric constant of the porous ceramics under certain direct current (dc) bias field and the real strength electric field in the porous ceramics were given quantitatively. As the pore can share the electric field, the tunability of the porous ceramics will be decreased when the porosity increases. The dielectric constant evolution of Ba_{0.6}Sr_{0.4}TiO₃-based porous ceramics with the dc bias electric field can be successfully explained by our theoretical results. Taking Ba_{0.6}Sr_{0.4}TiO₃-based porous ceramic samples, for example, there is good correspondence between the theoretical and the experimental results. © 2008 American Institute of Physics. [DOI: 10.1063/1.2937196]

I. INTRODUCTION

In recent years, no longer as much concerned with the properties of the best single-phase materials, many scientists search for the best compound of materials and the relationship between the microstructure and the physical properties.^{1,2} In most electronic devices, there are several phases involved and a number of material parameters to be optimized. Barium strontium titanate [Ba_{1-x}Sr_xTiO₃, (BST)] is an outstanding material due to its large field dependent dielectric constant. This property can be widely used in tunable devices, such as phase shifters, oscillators, filters, delay lines, and so on.^{3,4} Phase shifter, for example, requires a combination of properties such as high tunability [defined as $(C_0 - C_E)/C_0 \times 100\%$, where C_0 and C_E denote the capacitance without and with dc bias field, respectively], low dielectric constant, low dielectric loss tangent, and so on.⁵ As a matter of fact, the tunability of BST is relatively high, but the dielectric constant is also too large, which cannot satisfy the requirements of practical applications. Many approaches have been put forward to solve this problem. A number of groups of nonferroelectric additives such as MgO, MgTiO₃, Al₂O₃, and so on have been introduced to BST-based ceramics in order to dilute the dielectric constant and suppress the dielectric loss, but unfortunately the dielectric tunability is reduced as well.⁶⁻⁹ Up to now, there is little report fully satisfying all the requirements, and the general trend that indicates that the higher the dielectric constant, the higher the tunability generally holds in ferroelectric tunable materials.¹⁰ However, in our previous work, the BST-based porous ceramics showed an interesting “discrepancy,” which possessed low dielectric constant but still maintained the relatively high tunability.⁹ Therefore, we assume that there is

probably some principle behind the general trend, which would be very useful for the development of tunable materials.

Porous ferroelectric ceramics are of scientific interest because they are ideally suitable for verifying the theories advanced over approximately the past hundred years concerning the properties of multiphase materials.¹¹ Porous ferroelectric ceramics such as Pb(Zr,Ti)O₃ (PZT) have attracted much attention for many years. Moreover, the relationship between the dielectric constant and the porosity of this kind of materials at different conditions has been investigated by many research groups. Newnham *et al.*¹ discussed the importance of connectivity in piezoelectric composites about 30 years ago. Okazaki *et al.*^{12,13} used the depolarizing factor to express the permittivity-porosity relationship, which contains the influences of the pore size and pore shape. Banno¹⁴ described theoretical considerations of ceramics with closed pores based on the modified cube model. The effects of microstructure on the dielectric, piezoelectric, and mechanical constants of PZT ceramics have been systematically studied. Up to now, the correlation between the dielectric constant and the porosity of porous ceramics at different conditions was reported by some research groups, but there is still lack of studies about dielectric properties of the porous ceramics under dc electric field. Therefore, this communication is focused on developing a model to calculate the dielectric constant of porous ceramics with different porosities and under different dc bias field.

II. MODEL

To investigate the nonlinear field dependent dielectric properties of porous ceramics theoretically, we assume that the inclusion particles are spherical and uniform distribution, and ignore the strain induced preferred orientation and the little difference of the grain sizes. The porous material can be taken as a composite of two phases: the ceramics (phase 1) and the pores (phase 2). For this two-phase composite mate-

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rial, we aim at calculating the effective permittivity ε theoretically from the permittivity of its contents (ε_1 and $\varepsilon_2 = \varepsilon_0$ of the two components), the composition (their volume fractions Φ_1 and $\Phi_2 = 1 - \Phi_1$), the applied dc bias field (E), and so on. Suppose that the averages of electric field and electric displacement are unidirectional, pointing in the direction of the external dc electric field. The electric field strength and the electric displacement within the whole sample (E, D) and two phases (E_1, D_1, E_2, D_2) are assumed uniform. From basic electromagnetic principles, we can get the following equations:

$$\varepsilon = \frac{\partial D}{\partial E}, \quad (1)$$

$$\varepsilon_1 = \frac{\partial D_1}{\partial E_1}, \quad (2)$$

$$D_2 = \varepsilon_0 E_2. \quad (3)$$

For the tunable material, its permittivity varies with the electric field. Based on Devonshire's theory, Johnson gave the following equation that agreed well with experimental results:¹⁵

$$\varepsilon_1(E_1) = \frac{\partial D_1}{\partial E_1} = \varepsilon_1(0) / \{1 + B[\varepsilon_1(0)/\varepsilon_0]^3 E_1^2\}^{1/3}, \quad (4)$$

where $\varepsilon_1(0)$ and $\varepsilon_1(E_1)$ are the permittivity under zero dc bias field and under the applied dc bias field, respectively, and E_1 is the dc bias field in the ceramic part and B is the anharmonic coefficient, which are both temperature and grain size dependent.⁸

For the two-phase composite, as we have supposed that the averages of electric field and electric displacement are unidirectional, pointing in the direction of the external dc electric field, the electric field strength and the electric displacement obey the following relationships:

$$E = \Phi_1 E_1 + \Phi_2 E_2, \quad (5)$$

$$D = \Phi_1 D_1 + \Phi_2 D_2. \quad (6)$$

Now, consider a dielectric sphere (phase 1 or phase 2) surrounded by a matrix medium (the porous material) of permittivity ε , which is in a uniform external dc bias electric field E . Wong *et al.* theoretically developed the equation as follows:¹⁶

$$D_2 + 2\varepsilon(E_2 - E) = D, \quad (7)$$

$$D_1 + 2\varepsilon(E_1 - E) = D. \quad (8)$$

Thus, subtracting Eq. (8) from Eq. (7),

$$D_2 + 2\varepsilon(E_2 - E_1) = D_1. \quad (9)$$

Based on Eqs. (3), (5), and (9), the following can be obtained:

$$D_1 = (2\varepsilon + \varepsilon_0)E/\Phi_2 - (2\varepsilon + \varepsilon_0\Phi_1)E_1/\Phi_2. \quad (10)$$

When $\varepsilon \gg \varepsilon_0$, which always holds for the tunable BST ceramics, Eq. (10) is simplified to

$$D_1 = 2\varepsilon(E - E_1)/\Phi_2. \quad (11)$$

Combining Eqs. (3), (6), and (9), thus,

$$D = \Phi_1 D_1 + \Phi_2 \varepsilon_0 D_1 / (2\varepsilon + \varepsilon_0) + 2\Phi_2 \varepsilon_0 \varepsilon E_1 / (2\varepsilon + \varepsilon_0). \quad (12)$$

Also, since $\varepsilon \gg \varepsilon_0$ and taking $\Phi_1 > \Phi_2$ into consideration, the following can be achieved:

$$\Phi_1 D_1 > \Phi_2 D_1 \gg \Phi_2 \varepsilon_0 D_1 / 2\varepsilon > \Phi_2 \varepsilon_0 D_1 / (2\varepsilon + \varepsilon_0), \quad (13)$$

$$\Phi_1 D_1 \gg \Phi_2 \varepsilon_0 E. \quad (14)$$

Combining Eq. (12) with Eqs. (13) and (14), the following can be obtained:

$$D = \Phi_1 D_1. \quad (15)$$

Calculating the partial derivative of functions (11) and (15) and combining the results,

$$\varepsilon = \frac{\partial D}{\partial E} = \Phi_1 \varepsilon_1 \left(2\varepsilon + \frac{\Phi_2 D_1}{\varepsilon} \frac{\partial \varepsilon}{\partial E} \right) / (\Phi_2 \varepsilon_1 + 2\varepsilon). \quad (16)$$

Here, we make an approximation by neglecting $(\Phi_2 D_1 / \varepsilon)(\partial \varepsilon / \partial E)$. For the approximation, the larger the ε , the lesser the mismatch. Then, Eq. (16) can be simplified to

$$\varepsilon = \left(\Phi_1 - \frac{\Phi_2}{2} \right) \varepsilon_1 = \left(1 - \frac{3}{2} \Phi_2 \right) \varepsilon_1. \quad (17)$$

If we already know ε_1 at a certain electric field E_1 , we can have ε , but the corresponding electric field E on the sample is unequal to E_1 . The following equation can be derived from Eqs. (11) and (17):

$$E = E_1 + \frac{D_1}{\varepsilon_1(2/\Phi_2 - 3)}. \quad (18)$$

If the relationship between the dielectric constant and dc bias field of the dense ceramic is known, we can get B from Eq. (4) and then D_1 can be obtained. Finally, from Eqs. (17) and (18), the numerical value of ε at certain E for different porosities Φ_2 can be obtained.

III. EXPERIMENTAL RESULTS

Porous $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$ (BST60) fixing experiments are performed to evaluate the predictions of the model experimentally. The BST-based porous ceramic samples were prepared by adding poly(methyl methacrylate) (PMMA) as a pore former. The diameter of the PMMA is about 10 μm . The designed compositions of mixed powders were BST60 + a PMMA, where $a=0, 4, 8, 12$ wt %. The specimens were sintered at 1330 °C. All the samples have the typical x-ray diffraction pattern of the perovskite structure, and with the increase of the porosity, the samples have a little preferred (110) orientation. More details were described in our previous work.⁹ The SEM micrographs of the samples are shown in Fig. 1. Generally, the pore sizes are similar to the initial size of the PMMA, 10 μm . With increasing porosity, the grain size is also observed to become a little smaller and much more uniform. Variations in dielectric constant and loss tangent of BST60 specimens as a function of tempera-

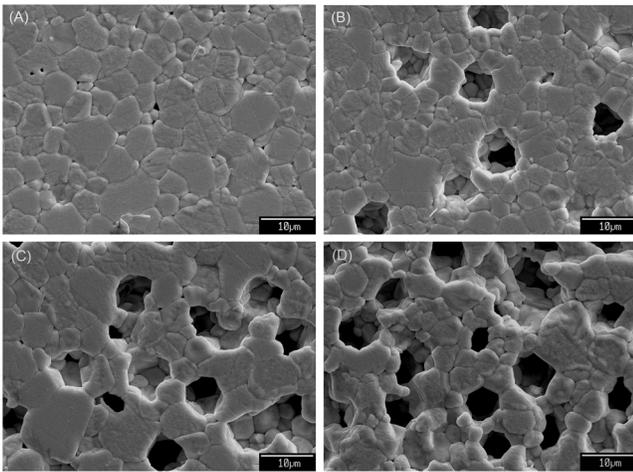


FIG. 1. (Color online) SEM micrograph of the BST60 ceramics with different contents of PMMA: (A) BST60, (B) BST60+4 wt % PMMA, (C) BST60+8 wt % PMMA, and (D) BST60+12 wt % PMMA.

TABLE I. Variation of porosity (both tested and calculated) with the content of the pore former PMMA. BST60: $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$.

| Sample | P_t | $P_{\text{calc.}}$ |
|--------------------|-------|--------------------|
| BST60 | 4.1% | 0 |
| BST60+4 wt % PMMA | 19.9% | 16.5% |
| BST60+8 wt % PMMA | 27.8% | 24.7% |
| BST60+12 wt % PMMA | 34.3% | 31.5% |

ture and porosity have also been measured, as shown in Fig. 2. The Curie temperature T_C is about -8°C , which changes little for BST60 with different porosities. As can be seen, the dielectric constant shows large changes, while the dielectric loss tangent changes a little. In the case of 10 kHz and 18°C , for example, the dielectric constant is decreased more than 45% from $\epsilon_{r(0)} \sim 4425$ (the density BST60) to $\epsilon_{r(0)} \sim 2400$ (porosity 34.3% BST60), but the dielectric loss tangent is both about 0.3%.

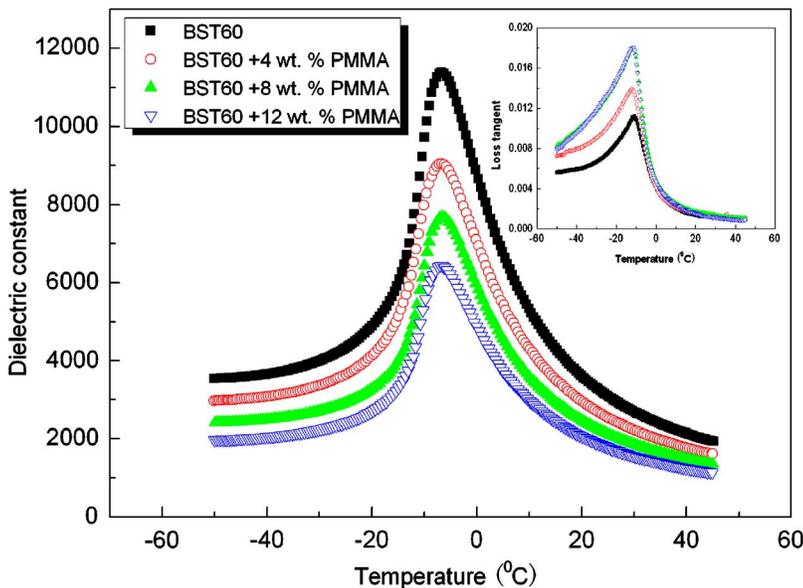


FIG. 2. (Color online) Temperature dependence of the dielectric constant of BST60-based porous ceramics measured at 10 kHz. Inset: Temperature dependence of the dielectric loss tangent.

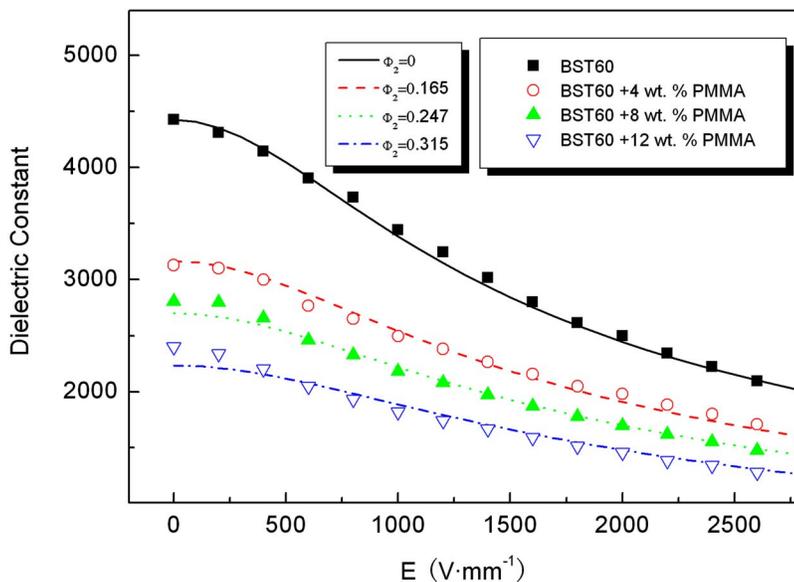


FIG. 3. (Color online) Comparison between the experimental and theoretical results of the dielectric constant of BST60-based porous ceramics with different porosities (the solid and dashed lines are the fitted results and the symbols are the experimental results).

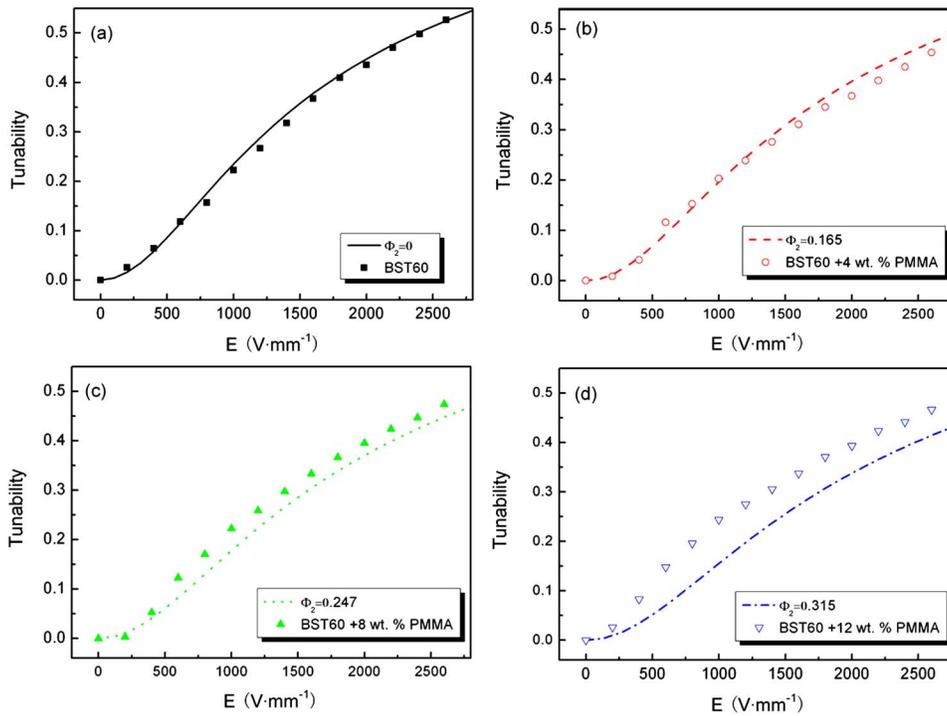


FIG. 4. (Color online) Comparison between the experimental and theoretical results of the tunability of BST60-based porous ceramics with different porosities (the solid and dashed lines are the fitted results and the symbols are the experimental results).

From the viewpoint of simulation, Eq. (4) is an important part of our base. The precondition is that it is usually used for a relative dense material, which should be the BST60 ceramic sample without PMMA at 4.1% porosity in our case. Therefore, the porosities of BST-based porous ceramics had to be corrected by taking the samples with 0% PMMA (4.1% porosity) as 100% density and using the following formula:

$$P_t = (1 - P_{\text{calc}}) \times 4.1\% + P_{\text{calc}}, \quad (19)$$

where P_t is the tested porosity and P_{calc} is the porosity used in the theoretical calculation. The calculated results are shown in Table I. Table I shows the values of P_t and P_{calc} of the ceramics with the pore former content and P_{calc} is equal to Φ_2 .

Figure 3 shows the comparison between the experimental and theoretical results of the dielectric constant. From the dielectric property of the compact BST60 ceramic sample under dc bias field at 18 °C, the values of B can be obtained, $1.42 \times 10^{-17} (\text{m/V})^2$. Then, the approximation, $2\varepsilon \gg (\Phi_2 D_1 / \varepsilon)(\partial\varepsilon / \partial E)$, can be proved right at different porosities, which indicates that the simulation results are reasonable. From Fig. 3, it can be seen that dielectric constant decreases with increasing porosity, and our predictions are in good agreement with the experimental values. To know clearly about the mechanism of the nonlinear field dependent dielectric properties of porous BST60 ceramics, the tunability of the porous materials with different pores' volume fractions Φ_2 under external dc bias field E is shown in Fig. 4. From the simulation results, it can be seen that the tunability decreases with increasing porosity. It is mainly due to the fact that the strength of the electric field on the tunable material BST60 is smaller than the strength of the external electric field, which can be explained in Eq. (17). As shown, the simulation and experimental results fit less well with increas-

ing porosity. This may be attributed to the fact that our model does not consider the effect of the change of grain size, a little preferred orientation, and distribution of the pores, whereas there will be a departure as the pore increases.^{14,17,18} Further work will be done to improve the model in the future.

IV. CONCLUSIONS

In conclusion, the effects of the pores and the electric field on the dielectric properties were studied theoretically. The dielectric constant can be given at a certain external electric field and certain porosity if the dielectric properties of the initial dense phase are known, which can be expressed as $\varepsilon = (1 - \frac{3}{2}\Phi_2)\varepsilon_1$, $E = E_1 + [D_1 / \varepsilon_1(2/\Phi_2 - 3)]$. Since the pore can share the electric field, the tunability of the porous ceramics will be smaller than the dense ceramics. Taking porous $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$ ceramic samples, for example, the obtained dielectric constants and tunability fit well with the theoretical results.

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