Finite Element Modeling of Dielectric-Paraelectric Composite Materials

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Abstract: Finite Element analysis is used to model 2-D and 3-D paraelectric-dielectric composites (BaTiO3 spherical fillers randomly distributed in constant dielectric matrix). The effective dielectric response and tunability are studied under different filler sizes and different volume fractions. The results are consistent with previous theoretical and experimental results: with the increasing of filler size and volume fraction, the dielectric response and dielectric tunability are also increasing. Meanwhile, by making composite material, the dielectric response can be reduced greatly compared to pure BST material, while still keeping a high tunability.

Keywords: Dielectric, Paraelectric, Composite, Tunability

1. Introduction

Ferroelectric (FE) materials are important for their nonlinear nature. With high and tunable permittivity, they are used to make capacitors with high tunable capacitance, and small in size. The spontaneous polarization of ferroelectric materials implies a hysteresis effect which can be used in the field of telecommunications and to make ferroelectric RAM for computers. [1-3] However, the dielectric losses for ferroelectric materials are pretty high (typically the dielectric losses and tunability are proportional to the dielectric permittivity [2]). Here are ways of getting around of this problem.

1.1 Ferroelectric Material in Paraelectric State

Barium strontium titanate ($Ba_xSr_{1-x}TiO_3$ or BST) is one of the most promising materials systems for tunable devices owing to its high dielectric response and its tunability near the ferroelectric phase transformation temperature T_C. For bulk BST 60/40 ($Ba_{0.60}Sr_{0.40}TiO_3$), T_C is below room temperature (–30°C) and this can be controlled by adjusting the composition. Ideally, BST is employed in its paraelectric (PE) state to reduce losses associated with the hysteresis due to polarization switching. Several compositions of BST thin films have been studied in great detail for use in tunable microwave devices using a variety of different fabrication methods and substrates [3] and indicating that high dielectric tunability and relatively low losses accompanied by a minimal dispersion in dielectric properties over a large temperature interval can be achieved in FE heterostructures and graded multilayers [4].

1.2 Creating Composite Material

Another way of further reducing the loss tangent is by creating a composite material consisting of a low-loss linear dielectric and a non-linear dielectric material, preferably a FE in its PE state. The determination of the dielectric properties of composite materials is a classical problem in electromagnetism that has been investigated using the effective medium theory (EMT). [5] Recently, Tagantsev and co-workers have used a modified EMT that takes into account the non-linear dielectric response of the FE material in a FE-dielectric composite. [6,7] The dielectric response, and its electric field dependence, of the FE is provided through a Landau potential that is then coupled with the EMT to establish electrostatic interactions between the FE matrix and the dielectric filler. The analysis shows that addition of a small amount of linear dielectric to a FE matrix actually improves the dielectric tunability but the loss tangent of the composite remains unaffected.

In this report, we analyze the dielectric response of a composite consisting of a linear, low-loss dielectric matrix with uniformly sized, randomly distributed PE BST 60/40 particles as functions of the fraction and size of the particles in 2-D and 3-D situations.

2. Thermodynamic Model

We first start off with the description of the electric field dependence of the dielectric response of the PE BST 60/40. BST 60/40 has the prototypical cubic perovskite lattice in its PE state above T_C = –30°C and transforms to a tetragonal FE phase below this temperature. The phase transformation characteristics can be described via a Landau potential given by

$$F(P,T,E) = F_0 + \frac{1}{2}aP^2 + \frac{1}{4}bP^4 + \frac{1}{6}cP^6 - EP \quad (1)$$

where P is the polarization, T is the temperature, E is the applied electric field, F_0 is the energy in the PE state, and a, b, and c are the dielectric stiffness coefficients. The temperature dependence of a is given by the Curie-Weiss law, $a = (T - T_C)/\varepsilon_0 C$, where C is the Curie-Weiss constant and ε_0 is the permittivity of free space. We shall assume that the BST inclusions are embedded in a compliant linear dielectric matrix and are stress free. The electric field dependence of the polarization follows from the equation of state such that:

$$\frac{\partial F(P,T,E)}{\partial P} = 0 = aP_0 + bP_0^3 + cP_0^5 - E \quad (2)$$

where $P_0(E)$ is the equilibrium polarization at a given field E. The relative dielectric response parallel to the applied electric field and its tunability are given by:

$$\varepsilon(E) = \left(\varepsilon_0 \frac{\partial^2 F(P,T,E)}{\partial P^2}\right)^{-1} = \frac{1}{\varepsilon_0[a + 3bP_0^2 + 5cP_0^2]}$$

$$\eta(E) = \frac{\varepsilon(E=0) - \varepsilon(E)}{\varepsilon(E=0)} \quad (3)\&\ (4)$$

For BST 60/40, the relevant Curie temperature, the Curie-Weiss constant, and the higher order Landau dielectric coefficients in SI units are: T_C = –30°C, C = 1.34×10^5, b = $8.64\times10^6\times(T-175)+3.36\times10^9$, and c = 2.38×10^9 [complied from Refs. 8,9]. Using Eqs. (2) and (3), the dielectric response and its electric field dependence can be calculated. At RT (=25°C), this results in the well known bell-shaped curve typical for a FE material in its PE state, as shown in Fig. 1.

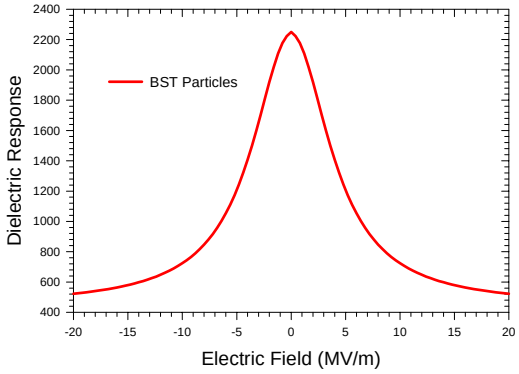


Fig. 1. Change of dielectric response for BST fillers as a function of electric field

3. Model Description and Results

A 2-D schematic depicting the model is shown in Figure 1a. The system is a composite thin film of dimensions L and L' consisting of randomly distributed PE BST 60/40 spherical particles of diameter D embedded in a linear dielectric matrix with a relative dielectric constant of 25 sandwiched between metallic electrodes. Three different particle sizes were analyze d with D=20, 50, and 80 nm whereas L and L' were fixed at 250 nm and 500 nm, respectively. (The 3-D model has similar schematic, with size L', L' and L).

For numerical modeling we use the nonlinear, time dependent Laplace equation realized in the COMSOL Multiphysics ™ finite element toolbox. To construct the composite material, randomly positioned circles of diameter D representing BST particles are inserted into a rectangular dielectric matrix of dimensions L and L'. To calculate the effective dielectric response for the composite material, the built-in electrostatic module of COMSOL is employed which utilizes a two-dimensional Laplace relation given by $\nabla[\varepsilon_0\varepsilon_r\nabla V(x,y)]=0$ to determine the local potential $V(x,y)$ within a single mesh.

3.1 Two Dimensional Model

The model is first run for the 2-D geometry as illustrated in Figure 2a. Direct Time Dependent Solver in the COMSOL package is then used to

obtain a transient analysis, with tested time steps and tolerances. Figure 2b shows the electric field contour plot for an applied electric field *E* and a corresponding potential *V*. Due to the abrupt change of dielectric response at the boundary between the BST particles and the matrix, the electric field and polarization vary greatly. In Figure 2c, the electric field is plotted along a section denoted AA'. From the straightforward application of the relevant Maxwell equations and the boundary condition corresponding to the continuity of the dielectric displacement at the dielectric/PE interface, one can conclude that due to the large difference between the dielectric response of the particles and the matrix, the electric field inside BST particles will be much lower than outside. The same result is demonstrated in Figure 2d where the polarization profile along AA' is plotted.

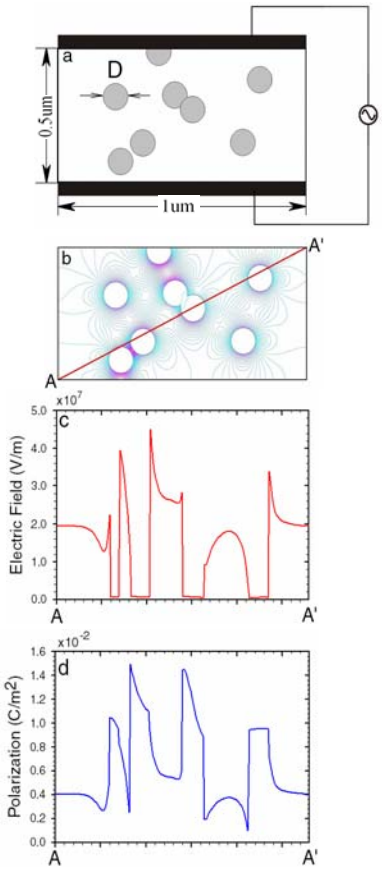


Fig. 2. **(a)** Schematic of composite made of BST particles and the linear dielectric matrix, **(b)** electric field distribution within the composite shown in **(a)**, **(c)** electric field distribution, and **(d)** electric polarization distribution along section AA' in **(b)**.

To examine the effect of the size of the PE particles on the overall dielectric response and tunability, we simulated three series of composites with particle diameters *D*=20, 50, and 80 nm. The effective small-signal dielectric response is calculated from the total energy of the system, i.e., the numerical integration of the local dielectric displacements and electrical fields. Figure 2 shows the result of composite relative dielectric response as a function of BST volume fraction and particle size. When the volume fraction is below the percolation threshold, all three of these composites show a linear dielectric response; above the percolation threshold, the response increases sharply and nonlinearly in each case. The percolation limits for the composites with 20, 50, and 80 nm particles were determined from Figure 3 to be 45%, 37%, and 27% BST, respectively. These findings are in excellent agreement with theoretical results based on Monte Carlo methods for hard spherical and semi-penetrating particles. [10,11] When the particles are small, the probability for them to overlap is smaller than larger particles and as such, composites with larger particles have a smaller percolation threshold, as shown in Figure 3. Furthermore, for the same BST volume fraction, composites with larger particles have a higher dielectric response as it is easier to form a percolation path with larger particles. These results are also consistent with the findings of Jylhä and Sihvola. [12] Using a similar approach wherein a Bruggeman EMT is employed together with a non-linear thermodynamic model for the incipient FE $SrTiO_3$ (STO) based on Vendik and Zubko [13], the dielectric tunability of a composite consisting of STO particles embedded in a linear dielectric matrix was simulated. The theoretical model shows that once the percolation limit for STO particles is reached at around 30 volume percent, the dielectric tunability increases continuously with increasing volume fraction of STO.

In Figure 4, dielectric tunability is calculated as a function of volume fraction and particle size between zero electric field and 12 kV/mm. It shows, as expected, a similar trend to the dielectric response shown in Figure 3. Below the percolation thresholds the tunabilities for the three series of composites are very small. As the volume fraction is increased, the tunabilities increase exponentially and composites with

larger BST particles have a larger tunability at the same volume fraction. We use the model of *D*=80nm to compare the tunability between monolithic unclamped, stress-free BST and the composite material. At a volume fraction of 45% BST, the relative small-signal dielectric response of the composite is 360 and the tunability is about 58% at an applied field of 12 kV/mm. However, for monolithic BST, the relative dielectric response is 2300 and tunability is around 70% at 12 kV/mm. This means that by employing a composite material such as the one described in this analysis, one can reduce the effective permittivity greatly while still maintaining a very high tunability.

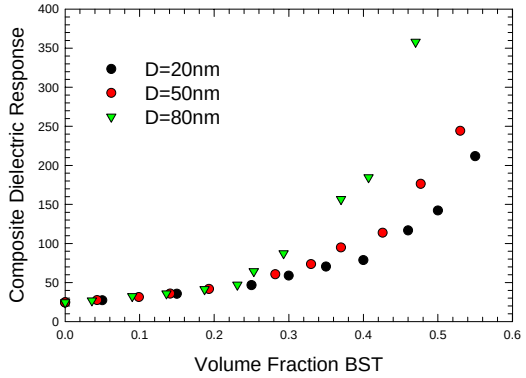


Fig. 3. Change of the composite dielectric response as functions of volume fraction and particle size

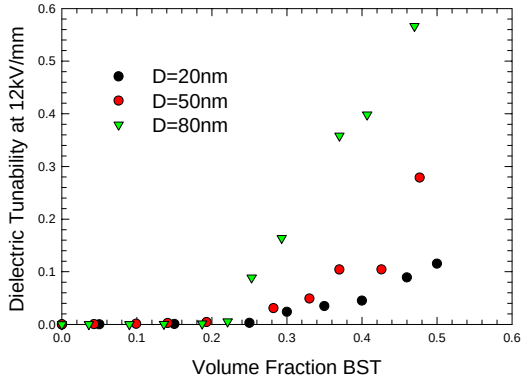


Fig. 4. Change of dielectric tunability at 1.2 kV/mm as function of volume fraction and particles size.

3.1 Three Dimensional Model

The 3-D has model has similar configuration as the 2-D model. PE sphere BST particles are randomly distributed in dielectric matrix. By contacting each other, PE percolation path can be formed in the dielectric matrix, as shown in Figure 5.

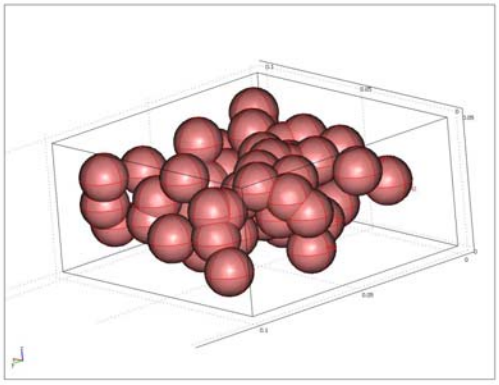
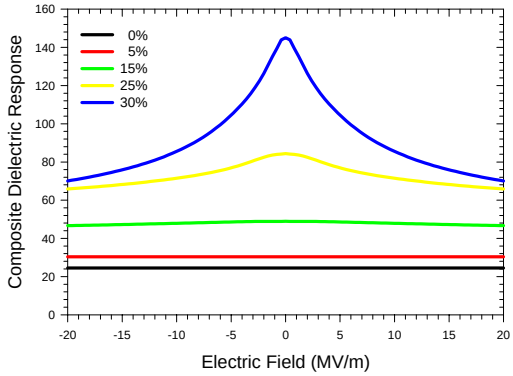


Fig. 5. Change of the composite dielectric response as functions of volume fraction and particle size

To examine the effect of volume fraction of the PE particles on the overall dielectric response, 50nm particles are inserted into the rectangular dielectric matrix and electric field dependent composite dielectric responses are calculated under different volume fractions. As seen in Fig. 6, with the increasing of volume fraction, the dielectric response is increasing. Also, when the volume fraction is below 20 percent, all the composite dielectric responses are nearly flat as a function of electric field; once the volume fraction exceeds above 20 percent, there are peaks coming out around small electric field and the composite dielectric response is getting similar to the bell-shaped curve in Fig. 1.



4. Conclusions

As discussed above, we have configured Comsol to research paraelectric and dielectric composite

materials theoretically. However, to make the model more approaching the real experimental results, chemical interactions between BST particles and the matrix, and their modification of the polarizability at the interfaces need to be taken into account explicitly. And we need to work on 3-D model with more particles with different sizes and surfaces, to examine the effect cause by space charge rough surfaces.

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