

Ferroelectric-dielectric tunable composites

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The dielectric response of ferroelectric-dielectric composites is theoretically addressed. Dielectric permittivity, tunability (relative change of the permittivity driven by dc electric field), and loss tangent are evaluated for various composite models. The analytical results for small dielectric concentration and relative tunability are obtained in terms of the traditional electrostatic consideration. The results for large tunability are obtained numerically. A method is proposed for the evaluation of the tunability and loss at large concentrations of the dielectric. The basic idea of the method is to reformulate the effective medium approach in terms of electrical energies stored and dissipated in the composite. The important practical conclusion of the paper is that, for random ferroelectric-dielectric composite, the addition of small amounts of a linear dielectric into the tunable ferroelectric results in an increase of the tunability of the mixture. The loss tangent of such composites is shown to be virtually unaffected by the addition of moderate amounts of the low-loss dielectric. The experimental data for (Ba,Sr)TiO₃ based composites are analyzed in terms of the theory developed and shown to be in a reasonable agreement with the theoretical results. © 2006 American Institute of Physics. [DOI: 10.1063/1.2186004]

I. INTRODUCTION

Ferroelectrics have been studied for a long time. In particular, much attention has been paid to the “hysteresis-related” properties of these materials, while the nonlinear materials exhibiting no hysteresis behavior were less discussed in the past. However, these nonlinear materials are now attracting growing interest because of their high dielectric permittivity and relatively low loss, which allow the miniaturization of radio frequency and microwave components. Ferroelectrics in their paraelectric state satisfy the conditions of low loss, high dielectric permittivity, and nonhysteresis behavior. Such behavior is exhibited by incipient ferroelectrics such as SrTiO₃ or KTaO₃ at arbitrary temperatures and ferroelectrics such as Ba_xSr_{1-x}TiO₃ (Ref. 1) not too close to the temperature of the ferroelectric-paraelectric phase transition. The dielectric permittivity of such materials is a pronounced function of the electric field. This feature makes ferroelectrics one of the promising materials for developing functional (controllable) elements of electronics and especially microwave electronics, where ferroelectric varactors may compete with their semiconductor counterparts exhibiting lower loss at microwave frequencies.² It has been intuitively believed that the microwave performance of the ferroelectrics can be further improved by mixing them with linear low-loss dielectrics. That is why the attempts are being done in synthesizing such composite materials.^{3,4} The composite materials exhibiting relatively high tunability in combination with reduced dielectric permittivity, reasonable loss level and good temperature stability have been experimentally obtained.³

The theoretical aspect of the dielectric response of ferroelectric-dielectric composites has been recently addressed by different authors. The specifics of these systems are very strong contrast in the dielectric permittivity, dielectric nonlinearity, and loss tangent between the components. The theory of the linear dielectric response of such materials has been developed by Hudak *et al.*⁵ However, the dielectric nonlinearity of such composites has been treated only for the case of the simplest models where the components are distributed in layers oriented parallel or normal to the electric field.^{6,7} Thus, the available theoretical results do not suffice for a proper analysis of the dielectric properties of the ferroelectric-dielectric composites which are presently under intensive experimental consideration. The goal of this paper is to present a comprehensive (as possible) theoretical analysis of tunability and dielectric loss in these systems. Our analysis will be based on the available theoretical results on the dielectric nonlinearity of composites^{8,9} combined with our analytical and numerical results. For the case of the not small concentration of the dielectric, an approach is proposed for evaluation of the tunability and loss. The basic idea of the approach is to reformulate the effective medium approach^{9,10} in terms of electrical energies stored and dissipated in the composite. The important practical conclusion of this paper is that, for a random ferroelectric-dielectric composite, the addition of small amounts of the linear dielectric into the tunable ferroelectric results in an increase of the tunability of the mixture whereas the loss tangent of the composite is virtually unaffected by the addition of moderate amount of the low-loss dielectric. The available experimental data for (Ba,Sr)TiO₃ based composites are analyzed in terms of the theory developed and are found to be in a reasonable agreement with the theoretical results.

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The structure of the paper is as follows. In Sec. II we describe the relationships controlling the nonlinearity of ferroelectric being in the paraelectric state. Different models of space redistribution of the components in the composite are also introduced in this section. In Sec. III we derive the effective dielectric permittivity, effective tunability, and effective loss tangent of the composite as functions of the concentration and electric field for the introduced models. The results of this modeling are summarized and discussed in Sec. IV. The analysis of the available experimental data for (Ba,Sr)TiO₃ based composites in terms of the theory developed is given in Sec. V.

II. THE PROBLEM

A. Dielectric nonlinearity of a ferroelectric

In this paper we consider ferroelectrics in the paraelectric phase as dielectrically isotropic materials. This is fully justified for the case of ferroelectric ceramics. In the case of single crystals or textured thin films, some of the following results can be generalized. In the case, where the dielectric anisotropy is not strong, the obtained results are qualitatively applicable. The dielectric nonlinearity of a ferroelectric in the paraelectric phase is traditionally described in terms of the free energy expansion with respect to the macroscopic polarization. In this paper, we will use a modified version of this approach considering the expansion with respect to the ferroelectric (soft mode) contribution to the polarization \mathbf{P}_f , which provides an adequate description of the dielectric response also in the case where the background dielectric permittivity becomes essential.¹¹ Namely, we present the contribution of the ferroelectric subsystem to the free energy as

$$F = \frac{\alpha}{2} \mathbf{P}_f^2 + \frac{\beta}{4} \mathbf{P}_f^4 - \mathbf{P}_f \mathbf{E}, \quad (1)$$

where $\alpha = 1/(\varepsilon_0 \varepsilon_{f,0}) = (T - T_0)/(C \varepsilon_0)$, \mathbf{E} is the electric field, $\varepsilon_0 \approx 8.85$ pF/m, $\varepsilon_{f,0}$ is the soft-mode contribution to the permittivity of the ferroelectric measured at zero dc electric field, C is the Curie-Weiss constant, T_0 is the Curie-Weiss temperature, and β is the coefficient of the ferroelectric nonlinearity.

The condition of minimality $\partial F / \partial \mathbf{P}_f = 0$, leads to the equation of state of the ferroelectric,

$$\mathbf{E} = \alpha \mathbf{P}_f + \beta \mathbf{P}_f^3, \quad (2)$$

In terms of \mathbf{P}_f the displacement in the ferroelectric can be written as

$$\mathbf{D} = \varepsilon_0 \varepsilon_b \mathbf{E} + \mathbf{P}_f(\mathbf{E}), \quad (3)$$

where ε_b is a background dielectric permittivity of the ferroelectric, which is taken as a scalar because of the accepted isotropy of the material.

Equation (2) corresponds to a nonlinear dependence of \mathbf{P}_f on the electric field

$$P_f = - \frac{\alpha \left(\frac{2}{3}\right)^{1/3}}{\sqrt{\beta(9E\sqrt{\beta} + \sqrt{3}\sqrt{4\alpha^3 + 27E^2\beta})^{1/3}}} + \frac{(9E_f\sqrt{\beta} + \sqrt{3}\sqrt{4\alpha^3 + 27E^2\beta})^{1/3}}{2^{1/3}3^{2/3}\sqrt{\beta}}. \quad (4)$$

In a nonzero bias field, the soft mode contribution to the differential dielectric permittivity becomes a tensor, $\varepsilon_{f,ij}$. Its inverse determined from Eq. (2) reads

$$(\varepsilon_f)_{ij}^{-1} = \frac{\partial^2 F}{\partial P_{f,i} \partial P_{f,j}} = \delta_{ij}(\alpha + \beta P_f^2) + 2\beta P_{f,i} P_{f,j}, \quad (5)$$

where δ_{ij} is the Kronecker symbol and the polarization \mathbf{P}_f comes from Eq. (4). For two cases of practical importance where the dc bias field is parallel and perpendicular to the ac measuring field, using the above relations one finds for the total permittivity,

$$\varepsilon_f^{\parallel}(E) = \frac{\varepsilon_{f,0}}{1 + 3\beta\varepsilon_0\varepsilon_{f,0}P_f^2(E)} + \varepsilon_b, \quad (6)$$

and

$$\varepsilon_f^{\perp}(E) = \frac{\varepsilon_{f,0}}{1 + \beta\varepsilon_0\varepsilon_{f,0}P_f^2(E)} + \varepsilon_b, \quad (7)$$

respectively. The value of the background dielectric permittivity, ε_b , entering these relations is typically much smaller than the soft-mode contribution to the permittivity $\varepsilon_{f,0}$. For perovskite ferroelectrics, a value of about 20 (a typical value of the permittivity in oxides without ferroelectric instabilities) can be taken as an estimate for ε_b . It can often be neglected, except, as we will see later, for situations where the depolarizing effects are essential.

In the case of weak tuning, where the relative change of the dielectric permittivity after applying a dc voltage is small, $|\varepsilon_{f,0} - \varepsilon_f(\mathbf{E})|/\varepsilon_{f,0} \ll 1$, Eqs. (6) and (7) can be simplified to the form

$$\varepsilon_f^{\parallel}(E) \approx \varepsilon_{f,0} + \mu_f E_f^2 + \varepsilon_b \quad (8)$$

and

$$\varepsilon_f^{\perp}(E) \approx \varepsilon_{f,0} + \frac{1}{3}\mu_f E_f^2 + \varepsilon_b, \quad (9)$$

where $\mu_f = -3\beta\varepsilon_0^3\varepsilon_{f,0}^4$ is the small-signal coefficient of dielectric nonlinearity.

To characterize the dielectric nonlinearity of materials, we will use two parameters—relative $n_r(E)$ and absolute $n(E)$ tunabilities defined as

$$n_r(E) = \frac{\varepsilon(0) - \varepsilon(E)}{\varepsilon(0)}, \quad (10)$$

$$n(E) = \frac{\varepsilon(0)}{\varepsilon(E)}, \quad (11)$$

where $\varepsilon(0)$ is the differential permittivity in the absence of dc bias field and $\varepsilon(E)$ is that in the presence of a bias field E but measured with an ac field which is parallel to the latter.

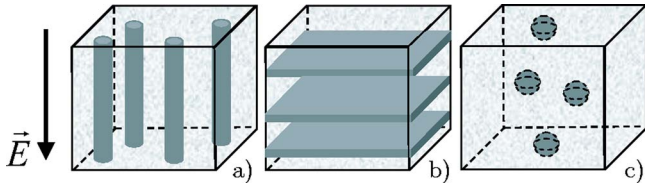


FIG. 1. Schematic representation of the (a) columnar composite model, (b) layered composite model, and (c) spherical inclusions model. The dark color corresponds to inclusions of the linear dielectric. Arrow shows the direction of the applied electric field.

For the situation, where the dielectric nonlinearity is controlled by Eq. (2) and the contribution of the background permittivity is negligible, the field E_n needed to achieve a given tunability n can be found from a relation which readily follows from Eqs. (2) and (6):

$$E_n = \frac{(2+n)\sqrt{n-1}}{\sqrt{27}\beta\epsilon_0^3\epsilon_{f,0}^3}. \quad (12)$$

For the situation where the dc and ac fields are perpendicular, the absolute, n^\perp , and relative, n_r^\perp , tunabilities, can be introduced in an analogous way. When the dielectric nonlinearity is controlled by Eq. (2) and the contribution of the background permittivity is negligible, n^\perp is linked to $n(E)$ by the relation

$$n^\perp(E) = \frac{n(E) + 2}{3}, \quad (13)$$

that can be obtained from Eqs. (6) and (7).

B. Composite models

In this paper, we consider the dielectric properties (focusing on the dielectric nonlinearity and loss) of two-component ferroelectric/dielectric composites. The permittivity and dielectric nonlinearity of the ferroelectric are described according to the relations from the previous subsection. The permittivity of the “dielectric” component is considered to be much smaller than that of the ferroelectric, whereas the dielectric nonlinearity of the dielectric component is neglected. The loss tangent of the dielectric is also considered to be negligible when compared to that of the ferroelectric. In our consideration, we assume that the impact of the chemical interaction between the components on its dielectric properties can be neglected so that the pure “composite” effect associated with the redistribution of the electric field due to the spatial inhomogeneity of the system is addressed.

We will discuss two models of the aforementioned composites, which enable exact analytical solutions for arbitrary concentration of the dielectric and arbitrary intensity of the dc bias field:⁶

- Columnar model, where the components are distributed with interfaces parallel to the electric field in the material [Fig. 1(a)].
- Layered model, where the components are distributed as layers with interfaces perpendicular to the electric field [Fig. 1(b)].

For the case of small concentrations of the dielectric, we consider the spherical inclusion model, where dielectric spheres are embedded into a ferroelectric matrix. The volume of the dielectric is much smaller than that of the ferroelectric [Fig. 1(c)]. Here, for the case of small relative tunability, we present analytical results obtained based on general relations from Ref. 8 and, for the case where the relative tunability of the material is not small compared to unity, the results of numerical analysis will be presented.

For the analysis of not small dielectric concentrations we will model the dielectric nonlinearity and loss in a random composite using our method based on Bruggeman effective medium approach (EMA). We will also present results for the loss tangent at not small concentrations obtained beyond the EMA approximation.

C. Parameters of the composite

We present results on dielectric nonlinearity and loss of the composite model introduced above. We will be interested in the effective differential permittivity of the system, at a given volume average of the electric field \bar{E} , defined as

$$\epsilon_{\text{eff},ij}(\bar{E}) = \frac{\partial \bar{D}_i}{\partial \bar{E}_j}, \quad (14)$$

where \bar{D} is the volume average of the electric displacement. Specifically, in the following consideration we will calculate the component of $\epsilon_{\text{eff},ij}(\bar{E})$ describing the nonlinearity in the situation where the bias dc and driving ac fields are parallel. We will denote this component as $\epsilon_{\text{eff}}(\bar{E})$. We will discuss the dielectric loss only in the absence of dc bias field. To characterize the loss in the composite we will use the effective loss tangent

$$\tan \delta_{\text{eff}} = \epsilon_{\text{eff}}'' / \epsilon_{\text{eff}}', \quad (15)$$

with ϵ_{eff}'' determined as

$$\epsilon_{\text{eff}}'' = \frac{2\dot{W}}{\omega \bar{E}^2}, \quad (16)$$

where \dot{W} is the rate of the energy dissipation per unit volume of the composite at the driving field having the volume averaged amplitude \bar{E} and frequency ω .

III. MODELING

A. Columnar composite [Fig. 1(a)]

We will start by discussing the case of columnar composite, which has the simplest structure from the point of view of modeling since in this case the electric field is homogeneous throughout the sample and equal $\bar{E} = U/h$, where U is the applied voltage and h is the distance between the electrodes.

For this case, one can easily get the field and concentration dependence of the effective dielectric permittivity, $\epsilon_{\text{eff}}(q, \bar{E})$, and concentration dependence of the effective loss

tangent, $\tan \delta_{\text{eff}}(q)$, of the composite by using an equivalent electrical circuit consisting of two lossy capacitors connected in parallel,⁶

$$\varepsilon_{\text{eff}}^{\text{col}}(q, \bar{E}) = (1-q)\varepsilon_f(\bar{E}) + q\varepsilon_d, \quad (17)$$

$$\tan \delta_{\text{eff}}^{\text{col}}(q) = \frac{(1-q)\tan \delta_f \varepsilon_f(0) + q \tan \delta_d \varepsilon_d}{(1-q)\varepsilon_f(0) + q\varepsilon_d}, \quad (18)$$

where q is the volume concentration of the linear dielectric, ε_d is the permittivity of the linear dielectric, $\varepsilon_f(\bar{E})$ is the field dependent dielectric permittivity of pure ferroelectric determined by Eqs. (4) and (6); $\tan \delta_f$ and $\tan \delta_d$ are the loss tangents of the ferroelectric and dielectric components, respectively.

Concerning these results, the following remark should be made. Because of the high ferroelectric/dielectric contrast of the permittivity, up to quite high concentrations of the dielectric, $1-q \gg \varepsilon_d/\varepsilon_f$, Eqs. (17) and (18) can be simplified to

$$\varepsilon_{\text{eff}}^{\text{col}}(q, \bar{E}) \approx (1-q)\varepsilon_f(\bar{E}), \quad (19)$$

$$\tan \delta_{\text{eff}}^{\text{col}}(q) \approx \tan \delta_f. \quad (20)$$

This implies that, in the case of columnar composite, in a wide range of the dielectric concentration, neither tunability nor loss tangent are affected by the dilution of the ferroelectric with the dielectric, the only result of the dilution being a reduction of the permittivity.

B. Layered composite [Fig. 1(b)]

The layered composite differs from the columnar one by the fact that in the former, the interfaces between the layers [see Fig. 1(b)] break the continuity of the electric field. At the same time, inside one component, the field is the same and homogeneous so that the problem can be obviously reduced to that of two capacitors connected in series. This leads to the effective dielectric permittivity of the composite,

$$\frac{1}{\varepsilon_{\text{eff}}^{\text{lay}}(q, \bar{E})} = \frac{1-q}{\varepsilon_f(E_f)} + \frac{q}{\varepsilon_d}, \quad (21)$$

where, the field in the ferroelectric should be calculated from the condition of continuity of electrical displacement

$$\varepsilon_0 \varepsilon_b E_f + P_f(E_f) = \varepsilon_0 \varepsilon_d E_d, \quad (22)$$

and the equation for the average field

$$(1-q)E_f + qE_d = \bar{E}, \quad (23)$$

solved together with Eqs. (2), (3), and (6). Here E_d and E_f are the electric fields in the dielectric and ferroelectric, respectively. The solution of the problem can be presented in the following form:⁶

$$\frac{1}{\varepsilon_{\text{eff}}^{\text{lay}}(q, \bar{E})} = \varepsilon_0 \alpha^* + 3\beta \varepsilon_0 |P_f(E_f^*)|^2 + \frac{q^2(\varepsilon_b - \varepsilon_d)}{\varepsilon_d[\varepsilon_b q + \varepsilon_d(1-q)]} - q\varepsilon_0(\alpha + 3\beta |P_0(E_f^*)|^2), \quad (24)$$

where $P_f(E_f^*)$ can be found from an equation similar to Eq. (2),

$$E_f^* = \alpha^* P_f + \beta P_f^3, \quad (25)$$

where

$$\alpha^* = \alpha + \frac{q}{\varepsilon_0 \varepsilon_b q + \varepsilon_0 \varepsilon_d (1-q)}, \quad (26)$$

$$E_f^* = \bar{E} \frac{\varepsilon_d}{\varepsilon_b q + \varepsilon_d (1-q)}. \quad (27)$$

A remarkable feature of this solution is that, in the case of small dielectric concentrations $q \ll 1$ and $q \ll \varepsilon_d/|\varepsilon_b - \varepsilon_d|$, the linear and nonlinear dielectric responses of the composite become identical to those of the pure ferroelectric with a reduced Curie-Weiss temperature,

$$T_0^* = T_0 - q \frac{C}{\varepsilon_d}. \quad (28)$$

This can be verified by taking into account that under the above conditions, the last two terms in Eq. (24) can be neglected as well as the difference between E_f^* and \bar{E} . With respect to the above result, two issues are worth mentioning. First, this result is actually a generalization to the nonlinear case of the classical result on the impact of the dielectric layer on the linear permittivity of the ferroelectric.¹² Second, as will be seen later, the tunability of the layered composite can remain appreciable only for small dielectric concentration. This means that, in this kind of composite in all cases of practical interest, the dilution effect on the dielectric response can be described by a shift of the Curie-Weiss temperature.

The effective loss tangent of this type of composite can be readily found in the form^{1,6}

$$\tan \delta_{\text{eff}}^{\text{lay}}(q) = \frac{\tan \delta_f \varepsilon_d (1-q) + \tan \delta_d \varepsilon_f(0) q}{\varepsilon_d (1-q) + \varepsilon_f(0) q}, \quad (29)$$

using an equivalent electrical circuit consisting of two lossy capacitors connected in series.

C. Spherical inclusion model (analytical results)

In the case of the spherical inclusion model, analytical results can be obtained in the limits of small dielectric concentration and small relative tunability. In this case, the spheres are separated by distances much larger than their radius so that each sphere can be considered as imbedded in a homogeneous electric field.¹³ Thus, the electrostatic problem of redistribution of the electric field in the system consisting of n spherical inclusions with volume Ω introduced into a homogeneous media of volume V is equivalent to that consisting of one spherical inclusion having the volume $n\Omega$ introduced into the same volume V . In the case of weak tuning, the permittivity of the ferroelectric can be taken to be

in the form given by Eq. (8) and which corresponds to the expansion in terms of the square of the field containing only the two lowest terms. The same expansion can be applied to the effective permittivity of the composite,

$$\varepsilon_{\text{eff}}(q, \bar{\mathbf{E}}) = \varepsilon_{\text{eff},0}(q) + \mu_{\text{eff}}(q) \bar{\mathbf{E}}^2, \quad (30)$$

where $\varepsilon_{\text{eff},0}(q)$ is the effective differential dielectric permittivity of the composite at zero dc bias field and $\mu_{\text{eff}}(q)$ is the effective small-signal coefficient of dielectric nonlinearity. The coefficients $\varepsilon_{\text{eff},0}$ and μ_{eff} can be analytically found^{8,14} by applying the perturbation expansion method for calculating the electrical energy stored in the material. For the case where only the matrix is nonlinear, they can be expressed in terms of the fields in the matrix, $\mathbf{E}_{f,0}$, and in the inclusion, $\mathbf{E}_{d,0}$, calculated neglecting nonlinearity (i.e., $\mu_f=0$),

$$\varepsilon_{\text{eff},0} = \frac{1}{V\bar{\mathbf{E}}^2} \oint_{\Omega_f} \varepsilon_f(0) \mathbf{E}_{f,0}^2 dx^3 + \frac{1}{V\bar{\mathbf{E}}^2} \oint_{\Omega_d} \varepsilon_d \mathbf{E}_{d,0}^2 dx^3 \quad (31)$$

and

$$\mu_{\text{eff}} = \frac{1}{V\bar{\mathbf{E}}^4} \oint_{\Omega_f} \mu_f \mathbf{E}_{f,0}^4 dx^3, \quad (32)$$

where Ω_f and Ω_d are the volumes of the components of the composite, and $V = \Omega_f + \Omega_d$ is the total volume of the composite. Using the known solutions¹³ for the fields outside, $\mathbf{E}_{f,0}$, and inside, $\mathbf{E}_{d,0}$, the spherical inclusion, from Eqs. (31) and (32) one finds⁸

$$\varepsilon_{\text{eff},0}^{\text{sp}}(q) = \varepsilon_{f,0}(1 + 3qb) \quad (33)$$

and

$$\mu_{\text{eff}}^{\text{sp}}(q) = \mu_f \left[1 - q \left(1 - 4b - \frac{36}{5}b^2 - \frac{8}{5}b^3 - \frac{8}{5}b^4 \right) \right], \quad (34)$$

where $b = (\varepsilon_d - \varepsilon_{f,0}) / (\varepsilon_d + 2\varepsilon_{f,0})$. The imaginary part of the effective dielectric permittivity of the composite can readily be found⁶ using Eq. (16),

$$\varepsilon_{\text{eff}}^{\prime\prime\text{sp}}(q) = \frac{1}{V\bar{\mathbf{E}}^2} \oint_{\Omega_f} \varepsilon_f^{\prime\prime} \mathbf{E}_{f,0}^2 dx^3 + \frac{1}{V\bar{\mathbf{E}}^2} \oint_{\Omega_d} \varepsilon_d^{\prime\prime} \mathbf{E}_{d,0}^2 dx^3, \quad (35)$$

where $\varepsilon_f^{\prime\prime}$ and $\varepsilon_d^{\prime\prime}$ are the imaginary parts of the dielectric permittivity of the ferroelectric and dielectric components, respectively. Using the explicit form of the fields outside, $\mathbf{E}_{f,0}$, and inside, $\mathbf{E}_{d,0}$, the spherical inclusion, from Eqs. (35), (33), and (15) one finds the effective loss tangent of the composite,

$$\tan \delta_{\text{eff}}^{\text{sp}}(q) = \tan \delta_f \left[1 - q \frac{9\varepsilon_d \varepsilon_{f,0}}{(\varepsilon_d + 2\varepsilon_{f,0})^2} \right] + q \tan \delta_d \frac{9\varepsilon_d \varepsilon_{f,0}}{(\varepsilon_d + 2\varepsilon_{f,0})^2}. \quad (36)$$

In Eqs. (33), (34), and (36), only the terms linear in the dielectric concentration have been kept since the whole approach is valid only in the limit of small concentrations.

For realistic ferroelectric/dielectric composites where $\varepsilon_d \ll \varepsilon_{f,0}$ the obtained relations can be further simplified down to the forms,

$$\varepsilon_{\text{eff},0}^{\text{sp}}(q) = \varepsilon_{f,0}(1 - 1.5q), \quad (37)$$

$$\mu_{\text{eff}}^{\text{sp}}(q) = \mu_f(1 - 1.3q), \quad (38)$$

$$\tan \delta_{\text{eff}}^{\text{sp}}(q) = \tan \delta_f. \quad (39)$$

Relations (37) and (38) combined with (30) and (8) give a compact representation for the concentration and field dependence of the composite permittivity,

$$\varepsilon_{\text{eff}}(q, \bar{\mathbf{E}}) = \varepsilon_f(\bar{\mathbf{E}})(1 - 1.3q) - 0.2q\varepsilon_{f,0}. \quad (40)$$

Analyzing Eqs. (37)–(39), we see that in the limit of small concentration the spherical inclusion composite behaves qualitatively similar to the columnar one: the loss tangent is much less sensitive to the dilution than the permittivity.

D. Spherical inclusion model (numerical results)

We performed a numerical analysis of the dielectric nonlinearity of the spherical inclusion model at large tunabilities and dielectric concentrations up to 8%. The analysis was undertaken using the electrostatics package of the FEMLAB® software. The volume concentration of the dielectric (q) was controlled by the number of identical dielectric spheres (maximum number of spheres we used in the modeling corresponds to the volume concentration of the linear dielectric of 8%). The dielectric nonlinearity of the ferroelectric has been described by Eqs. (6) and (4) neglecting the background dielectric permittivity. First, the volume averaged electrical displacements $\bar{\mathbf{D}}$ have been calculated as the functions of the concentration of the dielectric at different values of the average electric field $\bar{\mathbf{E}}$ to obtain the effective integral dielectric permittivity of the composite defined as

$$\varepsilon_{\text{eff}}^{\text{int}}(\bar{\mathbf{E}}) = \frac{|\bar{\mathbf{D}}|}{|\bar{\mathbf{E}}|}. \quad (41)$$

Then, the sought differential susceptibility has been found by using the following evident relation:

$$\varepsilon(E) = \varepsilon^{\text{int}}(E) + \frac{\partial \varepsilon^{\text{int}}(E)}{\partial E} E. \quad (42)$$

First, we have treated such a structure supposing that the ferroelectric is a linear dielectric with the dielectric permittivity $\varepsilon_{f,0}$. This gave us an information on the effective dielectric permittivity of the linear composite, $\varepsilon_{\text{eff},0}(q)$, which was found to scale with the dielectric concentration according to the relation (37) up to 8% of the volume concentration of the dielectric. Then, for the nonlinear problem, increasing the field $\bar{\mathbf{E}}$ up to the level at which the relative tunability of the composite became equal 50%, the change of the effective dielectric permittivity of the composite has been calculated. This change normalized by that of the pure ferroelectric at the same electric field, $[\varepsilon_{\text{eff}}^{\text{int}}(q, \bar{\mathbf{E}}) - \varepsilon_{\text{eff},0}(q)] / [\varepsilon_f^{\text{int}}(\bar{\mathbf{E}}) - \varepsilon_{f,0}]$, is depicted in Fig. 2.

We have found that to within the accuracy of our calculations $[\varepsilon_{\text{eff}}^{\text{int}}(q, \bar{\mathbf{E}}) - \varepsilon_{\text{eff},0}(q)] / [\varepsilon_f^{\text{int}}(\bar{\mathbf{E}}) - \varepsilon_{f,0}]$ can be fitted to the dependence of $1 - 1.3q$ (dashed line in Fig. 2) at any

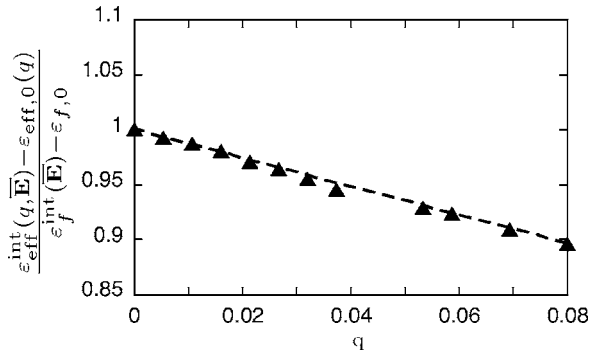


FIG. 2. FEMLAB® modeling of the change of the effective dielectric permittivity of the composite after the electric field had been applied to the composite normalized by that calculated for pure ferroelectric (triangles). The dashed line corresponds to the function $1 - 1.3q$. The parameters of the ferroelectric were chosen as following: $\epsilon_{f,0} = 1500$, $\beta = 10^{10} \text{ J C}^{-4} \text{ m}^5$, $\epsilon_d = 10$, volume concentration of one spherical inclusion, $\Omega/V = 0.005$, maximal number of spherical inclusions of linear dielectric, $N_d = 16$. The maximum field was chosen to obtain relative tunability of the ferroelectric of 50%.

values of the applied field corresponding to the relative tunability up to 50%. This fit can be translated into a relation for the calculated integral permittivity of the composite: $\epsilon_{\text{eff}}^{\text{int}}(q, \vec{E}) = \epsilon_f^{\text{int}}(\vec{E})(1 - 1.3q) - 0.2q\epsilon_{f,0}$. Using the relationship between the integral and the differential dielectric permittivities, Eq. (42), we arrive at the relation (40) obtained above for the spherical inclusion model in the limit of weak tuning and small dielectric concentration. Thus, we have found that, in the spherical inclusion model, the result for the field dependent permittivity obtained in the limit of small tunability and concentration, when written in the form of Eq. (40), approximately holds for dielectric concentration up to 8% and not weak tuning.

E. Not small dielectric concentrations and effective medium approximation

It is known that no analytical results can be obtained for the dielectric response of random binary composites with not small concentrations of one of the components. However, in the case of a ferroelectric/dielectric composite, due to a strong contrast of the real and imaginary parts of the permittivity between the components, one can find an important approximate relation for the composite loss tangent, specifically, it is expected to be weakly dependent on the dielectric content up to appreciable concentrations. To show this, one notices that Eqs. (31) and (35) for the real and imaginary parts of the permittivity hold for an arbitrary binary composite. If the aforementioned contrast is large, the last terms in these equations can be neglected as far as¹⁵

$$\overline{\mathbf{E}_{d,0}^2} / \overline{\mathbf{E}_{f,0}^2} \ll \epsilon_f / \epsilon_d. \quad (43)$$

With the last terms being neglected, Eqs. (31) and (35) evidently lead to loss tangent of the composite independent of the dielectric concentration. Except for the special kinds of composites containing “layers” of dielectric normal to the direction of the average electric field, one expects $\overline{\mathbf{E}_{d,0}^2}$ and $\overline{\mathbf{E}_{f,0}^2}$ to be of the same order of magnitude for appreciable concentration of the dielectric. This statement can be rationalized taking into account that for a dielectric sphere em-

bedded into a ferroelectric $\overline{\mathbf{E}_{d,0}^2} / \overline{\mathbf{E}_{f,0}^2} = 2.25$ (in the limit of large contrast of the permittivities). All the above arguments suggest that the dilution of a ferroelectric with low-permittivity dielectric should have a minor effect on the loss tangent up to appreciable dielectric concentrations (compared, e.g., to that on the permittivity).

Getting more results for the case of not small dielectric concentrations require the use of effective medium approximation (EMA) approaches. The most popular method used to model the properties of linear composites mixed with the arbitrary concentrations of the components is an EMA proposed by Bruggeman in 1935.^{10,16} Though this method is based on intuitively made statements, which are not mathematically justified, nowadays EMA is widely used to describe the electrical properties of arbitrary linear composites. There exist a few modifications of the effective medium approximation which allow the modeling of the properties of arbitrary nonlinear composites. The most popular of them is a combination of ordinary EMA with method of decoupling approximation.^{9,17} Unfortunately this method, being probably applicable at certain conditions, does not give results which agree with those obtained in the spherical inclusion approximation for small concentrations. Results of another method, introduced in Ref. 18 and called “unambiguous effective medium theory” do agree with the results obtained using the spherical inclusion approximation but only in the case of low concentration of linear dielectric ($q \ll 1$). At intermediate concentrations, this method yields an unphysical singularity whereas at high concentrations of the dielectric ($1 - q \ll 1$) it leads to a result contradicting to that of the spherical inclusion model.

We propose to reformulate the main ideas of EMA in the terms of energies stored or dissipated in the components of the composite to extend the ordinary EMA to the case of nonlinear composites.

In the ordinary EMA, first, the composite is substituted by a homogeneous effective medium with the sought dielectric permittivity of the composite. Then this medium is consequently replaced with spherical inclusions of the two components in the proportions corresponding to their volume fractions. Such replacements does not affect the composition of the material thus its overall properties should not change. In the classical Bruggeman approach one considers the overall polarization of the system and require that it should not change under such replacements. For the considered composite, this condition can be written as

$$\delta \mathbf{P}_d q + \delta \mathbf{P}_f (1 - q) = 0, \quad (44)$$

where $\delta \mathbf{P}_d$ and $\delta \mathbf{P}_f$ stand for the changes of the polarization induced by the insertion of spheres of dielectric and ferroelectric materials, respectively.¹⁶ (The insertion is performed at a fixed average electric field; the spheres are of the same radius.) In the classical EMA scheme, being interested in the linear dielectric response of the material, one readily solve Eq. (44) to find the sought dielectric permittivity of the composite. In principle, Eq. (44) might be used for evaluation of the nonlinear polarization response of the system, however, the resulting mathematical problem seems to be hardly trackable. We propose to apply the general concept of EMA to the

stored electrical energy and the rate of the energy dissipation (under the application of the ac electric field). We call this approach modified EMA (MEMA). The corresponding equation of constancy of the average values of these quantities with respect to the aforementioned substitution procedure can be written in the forms,

$$\delta W_d q + \delta W_f (1 - q) = 0, \quad (45)$$

$$\delta \dot{W}_d q + \delta \dot{W}_f (1 - q) = 0, \quad (46)$$

where δW_f and δW_d are the changes of the stored electrical energy induced by the insertion of the spheres whereas $\delta \dot{W}_f$ and $\delta \dot{W}_d$ are the corresponding changes of the volume average of rate of the energy dissipation.

In the case of weak tuning when the permittivity of the ferroelectric and composite can be taken in the forms Eqs. (8) and (30), condition Eqs. (45) yields

$$\varepsilon_{\text{eff}}^{\text{MEMA}}(q) = \frac{1}{4} [-\varepsilon_d + 3q\varepsilon_d + 2\varepsilon_{f,0} - 3q\varepsilon_{f,0} + \sqrt{8\varepsilon_d\varepsilon_{f,0} + (-\varepsilon_d + 3q\varepsilon_d + 2\varepsilon_{f,0} - 3q\varepsilon_{f,0})^2}], \quad (47)$$

$$\mu_{\text{eff}}^{\text{MEMA}}(q) = \frac{\mu_f c_f^4 (1 - q)}{1 - \left(\frac{36}{5} b_f^2 + \frac{8}{5} b_f^3 + \frac{8}{5} b_f^4 \right) (1 - q) - \left(\frac{36}{5} b_d^2 + \frac{8}{5} b_d^3 + \frac{8}{5} b_d^4 \right) q}, \quad (48)$$

where $c_f(q) = [3\varepsilon_{\text{eff}}(q)] / [\varepsilon_{f,0} + 2\varepsilon_{\text{eff}}(q)]$, $b_f(q) = [\varepsilon_{f,0} - \varepsilon_{\text{eff}}(q)] / [\varepsilon_{f,0} + 2\varepsilon_{\text{eff}}(q)]$, and $b_d(q) = [\varepsilon_d - \varepsilon_{\text{eff}}(q)] / [\varepsilon_d + 2\varepsilon_{\text{eff}}(q)]$.

Equation (46) being used for the calculation of the imaginary part of the composite permittivity, in combination with Eq. (47) yields for loss tangent of the composite,

$$\tan \delta_{\text{eff}}^{\text{MEMA}}(q) = \frac{1}{\varepsilon_{\text{eff},0}^{\text{MEMA}}(q)} \frac{q c_d^2 \varepsilon_d \tan \delta_d + (1 - q) c_f^2 \varepsilon_{f,0} \tan \delta_f}{1 - 2q b_d^2 - 2(1 - q) b_f^2}, \quad (49)$$

where $c_d = 3\varepsilon_{\text{eff}} / [\varepsilon_d + 2\varepsilon_{\text{eff}}]$. Here we skip the details of the calculations, which will be published elsewhere¹⁹ together with a discussion of different methods of evaluation of the dielectric nonlinearity of composites.

For the ε_{eff} and $\tan \delta_{\text{eff}}$ [Eqs. (47) and (49), respectively] this approximation reproduces the results of the ordinary effective medium theory. The result for the coefficient of small-signal dielectric nonlinearity μ_{eff} , Eqs. (48), in the limit of small concentrations ($q \ll 1$), is identical to that of the spherical inclusion model, Eq. (34). We have also checked that, at $1 - q \ll 1$, Eq. (48) is consistent with the result of the spherical inclusion model in the limit of small concentration of ferroelectric spheres in a dielectric matrix.

IV. RESULTS OF MODELING

Let us summarize and discuss the results of modeling presented in the previous sections. Figure 3 shows the concentration dependences for principle small-signal dielectric parameters of ferroelectric/dielectric composites evaluated for different types of composites and approximations discussed above in the paper. It is seen, that the spherical inclusion approximation, modified effective medium approximation and results of the numerical modeling are in a very good agreement between each other. The layered and columnar

models represent correspondingly lower and upper bounds for the real and imaginary parts of the effective dielectric permittivity as well as for the coefficient μ_{eff} . Though that the set of the results of modeling does not reliably cover the full concentration range, some conclusion could be drawn from these results.

The two models allowing the exact analytical treatment at any dielectric concentration exhibit very different features. In the layered model, the addition of the dielectric leads to a fast decrease of the permittivity, tunability, and the loss tangent of the material. For dielectric concentrations corresponding to a reasonable (not too small) relative tunability, the addition of the dielectric is equivalent to a downward shift of the Curie-Weiss temperature. One should stress that this is valid not only for the linear dielectric response (the issue fully understood in the past) but also for the nonlinear one. In the columnar model, only the permittivity of the material is affected by the addition of a dielectric whereas the tunability and loss tangent are virtually independent of the concentration of the dielectric up to very high level of the dilution.

An interesting issue to be mentioned is that the concentration dependence of the permittivity predicted for the small dielectric concentration in the spherical inclusion model, Eq. (37), holds up to appreciable concentrations as supported by the result of the EMA theory. Actually, for the case of a large contrast of the permittivity of the composite components, EMA yields Eq. (37) to within a very good accuracy up to $q \approx 0.66$.

A noticeable result of modeling is an increase of the tunability with the dilution of the ferroelectric. For small relative tunability and dielectric concentration, the spherical inclusion model yields [cf. Eqs. (37) and (40)] this trend in an analytical form,

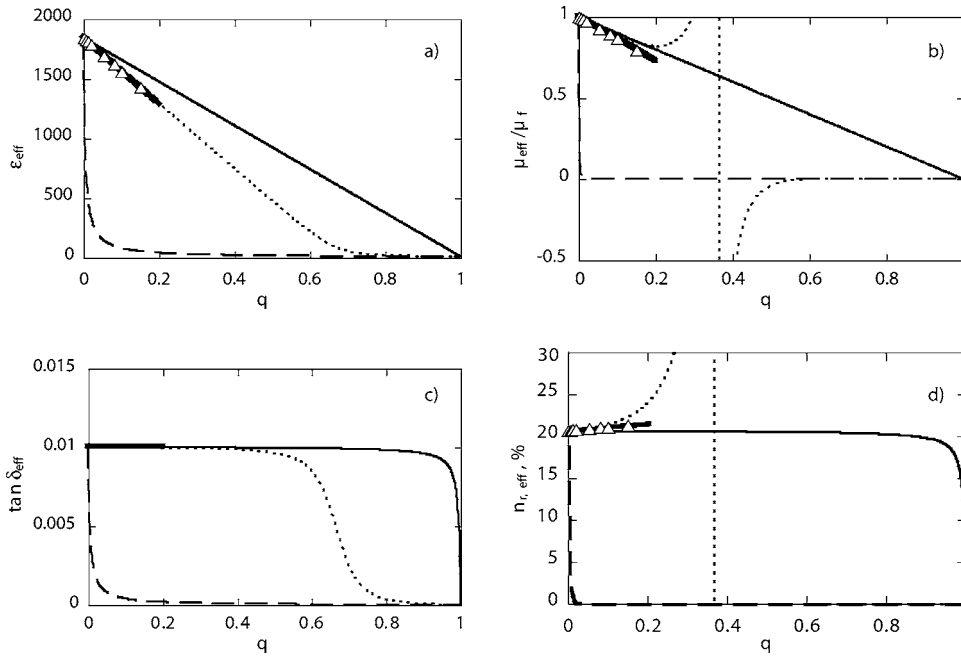


FIG. 3. The concentration dependences for principle small-signal dielectric parameters of ferroelectric/dielectric composites: (a) effective dielectric permittivity, (b) coefficient of small-signal nonlinearity of the effective dielectric permittivity, (c) loss tangent, and (d) relative tunability. Thin solid lines correspond to the columnar model, thick solid lines—to the spherical inclusion model, dotted lines correspond to the modified effective medium approximation, dashed lines correspond to the layered model, and triangles correspond to the results of the finite element method analysis. The evaluation has been done for typical values of dielectric parameters of the composite components: $\epsilon_{f,0}=1800$, $\mu_f=-1.6 \times 10^{-11} \text{ m}^2/\text{V}^2$, $\epsilon_d=10$, $\tan \delta_f=0.01$, $\tan \delta_d=0$, $n_{r,f}=-\mu_f|\mathbf{E}|^2/\epsilon_f=0.2$, $|\mathbf{E}|=5 \times 10^6 \text{ V/m}$.

$$n_{r,\text{eff}}(q, \bar{\mathbf{E}}) = \frac{\epsilon_{\text{eff},0}(q) - \epsilon_{\text{eff}}(q, \bar{\mathbf{E}})}{\epsilon_{\text{eff},0}} \approx n_{r,f}(\bar{\mathbf{E}})(1 + 0.2q). \quad (50)$$

This unexpected result can still be rationalized. The big contrast in the values of dielectric permittivities of the spherical inclusion (ϵ_d) and the ferroelectric (ϵ_f) affects the redistribution of the electric field around the inclusion. The dielectric permittivity of the ferroelectric under applied electric field becomes in-homogeneously distributed over the volume of the ferroelectric. The overall tunability of the composite, thus changes. Two competitive phenomena affect the tunable properties of the ferroelectric when it is diluted with a dielectric. First, the reduction of the volume of ferroelectric, which is responsible for tuning, will cause suppression of the tunability of the material. Second, the redistribution of the electric field surrounding the inclusion will affect the local tuning of the ferroelectric. Depending on the shape of the inclusion and on the dielectric permittivities of the components, the impact of each of these two effects on the composite tunability is different and the second effect may be stronger. This is the case in the considered model. On the lines of this argument, one suggests that the tunable performance of such composites might be further improved by changing the shape or dielectric permittivity of the inclusions.

The numerical modeling confirms (to within the accuracy of the calculations) that the relation (50) can be applicable up to 50% of relative tunability and $q=0.08$. The result of MEMA for μ_{eff} suggests a further increase of the tunability of the composite with the dilution, however, it is not clear up to what dielectric concentrations it can be trusted because of unphysical singularity in the concentration dependence of μ_{eff} . Equation (48) yields such singularity when the contrast of the permittivity between the components of the composite exceeds a factor of 10. Similar divergence has been discussed in Ref. 18. It is clear from the above discussion that

$n_{r,\text{eff}}$ should pass through a maximum as a function of q . Though the position and height of this maximum cannot be determined from existing theories, the presented results suggest that in real composites one should not expect an appreciable reduction of tunability up to relatively high concentrations of the dielectric, say 40%–50%.

Another remarkable feature of the above analysis is that the spherical inclusion model and the MEMA suggest that the loss tangent of the random dielectric/ferroelectric composite is virtually independent of the dielectric concentration up to appreciable concentrations. This result is also confirmed by model-free arguments for the Sec. III E.

All in all, the concentration dependences of the main dielectric parameters of a ferroelectric diluted with a dielectric, Eqs. (37), (50), and (39), which were initially derived for the spherical inclusion model, are expected to be a reasonable approximation up to appreciable dielectric concentrations in random ferroelectric/dielectric composite and at not small relative tunabilities.

Thus, the general conclusion of the theoretical analysis is that diluting the ferroelectric with the linear low-loss dielectric should primarily influence the permittivity (decrease) of the material while virtually no decrease of the tunability and loss tangent may be expected up to appreciable concentration of the dielectric. One may even expect some increase of the tunability, however, the strength of this effect cannot be presently evaluated.

V. COMPARISON TO EXPERIMENT

An experimental study of the electrical properties of the tunable ferroelectric based composite ceramics has been carried out. A set of samples made of $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ and $\text{Ba}_{0.55}\text{Sr}_{0.45}\text{TiO}_3$ mixed with MgO powder in different proportions and having cylindrical shapes with diameter 2 mm and thicknesses varying from 0.25 to 1 mm have been used. The samples were electroded on parallel sides so that they were effectively parallel plate capacitors at radio fre-

quencies (1 kHz–1 MHz) and the dielectric resonators at microwave frequencies. The capacitance of such varactors has been measured at 10 kHz under normal conditions by the HP4284A impedance analyzer. The change of the capacitance under dc electric field—tunability—has been investigated by applying a high dc voltage (up to 4 kV) to the parallel plate electrodes through a dc blocking circuit. The microwave measurements have been carried out by a resonant method.^{1,20} A specially designed sample holder that allows the excitation of TM_{mm0} resonance modes in the cylindrical sample has been used. The measured resonance frequency of the lowest TM_{mm0} mode and its unloaded quality factor were used to extract the dielectric permittivity and the loss tangent of the ceramics. Because the resonance frequency of the dielectric resonator depends on the dielectric permittivity of the ceramics, the loss tangent of different samples has been measured at different frequencies (from 5 to 8 GHz). The linear frequency dispersion of the loss tangent has been assumed to interpolate the measured values of the loss tangent to the unique frequency of 10 GHz.

The experimentally measured dielectric permittivity, relative tunability, and loss tangent of $(1-q)Ba_{0.55}Sr_{0.45}TiO_3 + qMgO$ and $(1-q)Ba_{0.7}Sr_{0.3}TiO_3 + qMgO$ composites are plotted versus volume concentration of MgO, q , in the range of 0–30 volume percents, in Fig. 4. The interpretation of the experimental data requires taking into account that the dilution of the ferroelectric with oxide results in two effects: (i) chemical doping of the ferroelectric and (ii) mechanical mixing of the ferroelectric with the dielectric. The first effect results primarily in a shift and smearing of the temperature anomaly of the permittivity. This effect takes place at low concentrations comparable with the solubility limit of the addition. The second effect leads to a redistribution of the electric field in the material. It is this effect that we are dealing in the paper. In the presented experimental data, the first effect is clearly seen at first 3–5 vol % MgO. Here the temperature shift of the transition temperature manifests itself in rapid variation of all parameters of the system with doping. For higher concentrations, the set of the experimental data appears to be in a reasonable agreement with Eqs. (37), (50), and (39) which were initially derived for the spherical inclusion model and shown to hold approximately up to moderate concentration of random composite. This conclusion agrees with that of a similar analysis of the experimental data on a ferroelectric/dielectric composite reported earlier.¹

VI. CONCLUSION

The effect of dilution of tunable ferroelectric with linear materials has been theoretically addressed. This impact of the dilution on the main dielectric parameters of the material has been shown to be very sensitive to the composite type. In the layered model for the case of practical interest with not too small relative tunability, the addition of the dielectric has an impact identical to a downward shift of the Curie-Weiss temperature leading to a fast decrease of the permittivity,

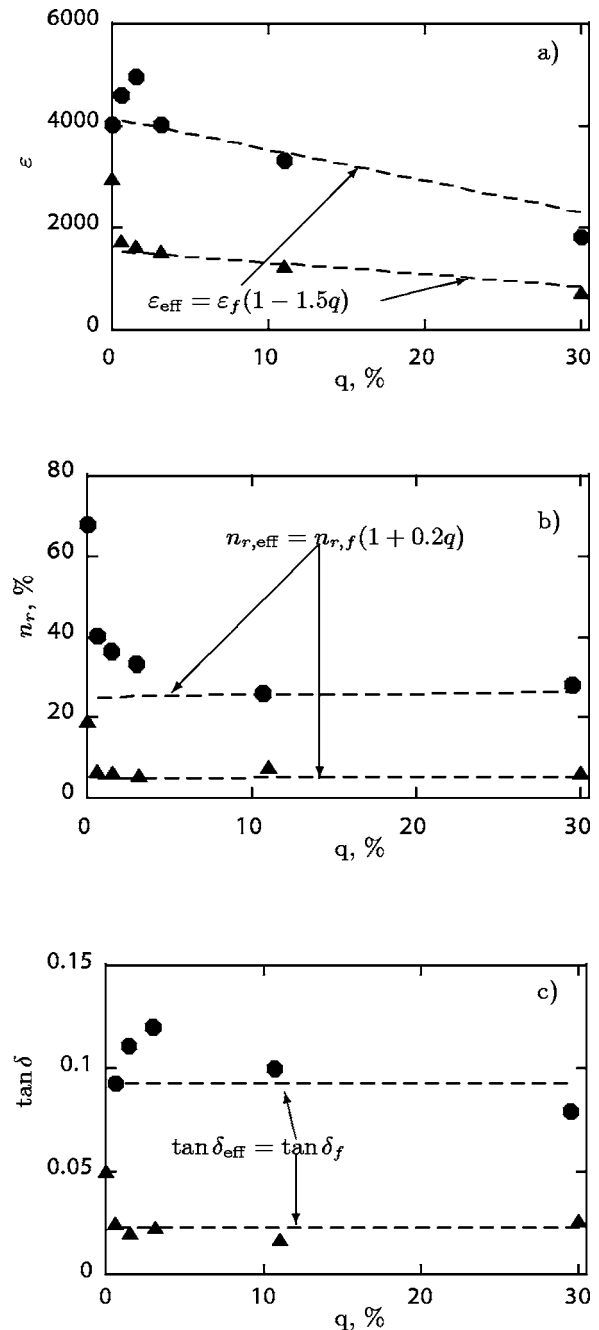


FIG. 4. Dielectric permittivity (a), relative tunability at $E=20$ kV/cm (b), and loss tangent at frequency 10 GHz (c) of the BST70/30 (circles) and BST55/45 (triangles) mixed with MgO as the functions of volume concentration of latter. The dashed lines correspond to the theoretically predicted trends for concentration dependencies of the permittivity, tunability, and loss tangent.

tunability and the loss tangent of the material. In the columnar model, only the permittivity of the material is affected by addition of a dielectric whereas the tunability and loss tangent are virtually independent of the concentration of the dielectric up to very high dilution level.

It has been shown that the concentration dependences of the main dielectric parameters of a ferroelectric diluted with a dielectric, Eqs. (37), (50), and (39), which were initially derived for the spherical inclusion model, are expected to be a reasonable approximation up to appreciable dielectric concentrations in random ferroelectric/dielectric composite. This

prediction has been shown to be in agreement with the experimental data on $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ and $\text{Ba}_{0.55}\text{Sr}_{0.45}\text{TiO}_3$ ceramics diluted with MgO .

The general conclusion of the paper is that the main impact of the dilution [considering three-dimensional (3D) random composites] of a ferroelectric with low-permittivity, low-loss dielectric is a reduction of the overall permittivity whereas the dilution induced variations of the loss tangent and tunability are much weaker up to appreciable concentration of the dielectric. Noticeably, no reduction of the loss tangent is expected up to quite strong dilution level. As for the tunability, it may even slightly increase with the dilution. Applying these conclusions to real materials, one should, however, bear in mind that the effect of the dilution-driven field redistribution in the material, which is addressed in the paper, may not be the only manifestation of addition of the dielectric into ferroelectrics. This addition can also influence the chemistry and microstructure of the material, which in turn can affect the dielectric parameters of the material. Thus, the sum of the effects discussed in the paper and those related to the chemistry and microstructure of the material should be taken into account when analyzing the impact of the dielectric addition on the tunable behavior of a ferroelectric composite.

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