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Controllable-permittivity and high-tunability of $Ba_{0.5}Sr_{0.5}TiO_3$/MgO based ceramics by composite configuration

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$Ba_{0.5}Sr_{0.5}TiO_3$ (BST50)/MgO composites, with 2-2-type configurations, consisting of BST layers and MgO layers, were fabricated by using tape-casting and laminating technique. Microstructure, dielectric response, and tunable properties of the 2-2-type composites were investigated. An important feature of the 2-2 type composites is that DC fields can be effectively applied to the high-permittivity ferroelectric phase when the fields are applied in parallel direction to the inter-phase boundaries. As a result, with increasing volume fraction (q) of MgO, tunability of the composites remained almost unchanged, whereas their permittivity value could be reduced significantly. This behavior has not been observed in the conventional 3-0 type composites. © *2013 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4801777]

Ferroelectrics, exhibiting essential dielectric nonlinearity and moderate dielectric loss, have found applications in tunable microwave devices.[1] Among various ferroelectric materials, barium strontium titanate, $(Ba_{1-x}Sr_x)TiO_3$ (or BST), has been acknowledged to be the most promising candidate for such applications. However, BST generally has very high relative permittivity, which must be reduced to a certain value, due to the requirement of impedance matching, for practical applications in tunable microwave devices.[2,3] It has been demonstrated that the permittivity of BST can be readily lowered by incorporating with low-permittivity dielectric materials, such as MgO,[4,5] Mg_2TiO_4,[6] $BaMoO_4$ (Ref. 7) and so on.

When a tunable ferroelectric is mixed with a linear dielectric component, dielectric properties of the composite can be described by considering two effects: mutual doping and electrical field redistribution.[8,9] In this case, both composition and configuration could have significant influences on final dielectric properties of the composites. In terms of configuration, three basic models have been considered:[2,10] (i) layered structure with layers of the two components connected alternatively in series (2-2 model), (ii) parallel columnar structure of one phase embedded within the matrix of the other phase (1-3 model), and (iii) random distribution with one phase as spheres embedded into another as matrix (3-0 model). Theoretical studies indicated that dielectric tunability of the 1-3 type composites is almost unchanged with increasing concentration of the low-permittivity component, although their permittivity is significantly reduced. However, compared to 3-0 composites, 2-2 and 1-3 composites are rarely reported in the open literature. This is mainly because it is very difficult to fabricate 2-2 and 1-3 composites by using the conventional solid-state reaction process. There have been reports on dielectric properties of 2-2 and 1-3 composites prepared by using selective epitaxial growth process,[11] self-assembly techniques,[12] and dice-fill technique.[13,14] Obviously, these methods are not suitable for large-scale device fabrication.

In this Letter, we report on fabrication and characterization of $Ba_{0.5}Sr_{0.5}TiO_3$ (BST50)/MgO composites with 2-2-type configuration. BST50 was selected as ferroelectric phase due to its high dielectric tunability and low loss, whereas MgO was used as dielectric phase due to its low-permittivity of 7-10 and very high Q^*f value (113 600 GHz) (Ref. 15) at microwave frequencies. The 2-2-type BST50/MgO composites were fabricated by using tape-casting and laminating technique. According to the models of Astafiev *et al.*, the composites were taken as 2-2-type and 1-3-type when the external electric field $\boldsymbol{E}$ was perpendicular and parallel to the inter-phase boundaries, respectively.[10] In our present study, 2-2-⊥ and 2-2-// are used to represent the cases when the electric field is applied in perpendicular and parallel to the inter-phase boundaries, respectively. In other words, by maintaining the direction of the electric field unchanged but rotating the sample by 90°, 2-2-// type configuration is thus obtained, which is equal to the 1-3 model (shown in Fig. 1(d)). 3-0 type composites were also fabricated by using the conventional ball mill-mixing and solid-state reaction process for comparison.

SEM images of the 2-2 multilayer and 3-0 random BST50/MgO composites, with same MgO volume fraction (q = 0.45), are shown in Figs. 1(a) and 1(b). By adjusting the MgO volume fraction q, permittivity and tunability of the 2-2 and 3-0 composites can be tailored to meet the requirements of different applications. As shown in Fig. 1(c), dense, sharp, and well defined interfaces between BST50 and MgO were formed in the 2-2 composites. In the 3-0 composite, the dark gray MgO particles are randomly dispersed in the white BST50 matrix. Dielectric properties and tunability were measured by using a high precision Agilent 4284A LCR meter. The tunability was measured at 10 kHz with a bias voltage source. To avoid the effect of preparation process, all samples were prepared under same conditions, including properties of raw materials, pressures of sample fabrication

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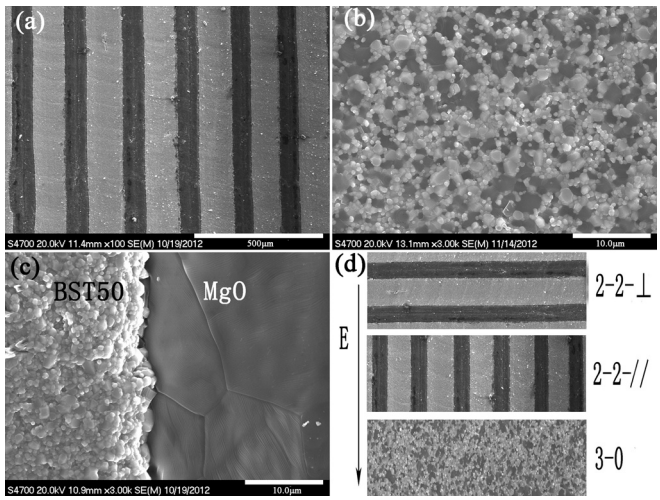

FIG. 1. SEM images of the BST50-MgO composite ceramics with (a) 2-2 configuration (q = 0.45), (b) 3-0 configuration (q = 0.45), (c) interfaces between BST50 and MgO, and (d) schematic of the three configurations.

(20 MPa vertical suppress and then 200 MPa isostatic pressing), debinding (550 °C, 24 h), sintering (sinter temperature of 1350 °C and soaking time of 4 h), and electrode (600 °C, 30 min). The sample configuration was sandwich structure with planar silver electrode. Samples for low frequency dielectric measurement are about 4 mm in diameter and 1 mm in thickness.

Fig. 2 shows temperature dependent permittivity of the three composites with MgO volume fraction of q = 0.23, measured at 10 kHz. There is a significant difference in dielectric response between pure BST and the composites. Also, configuration has an obvious effect on dielectric properties of the composites. At 20 °C, permittivity values of pure BST50, 2-2-⊥, 3-0, and 2-2-// samples are 2000, 1460, 1044, and 88, respectively. Transition peak of the 2-2-⊥ type composite is largely reduced and diffused.

Dielectric properties of ferroelectric-dielectric bi-component composites have been well studied theoretically, by using the Bruggeman effective medium theory and the

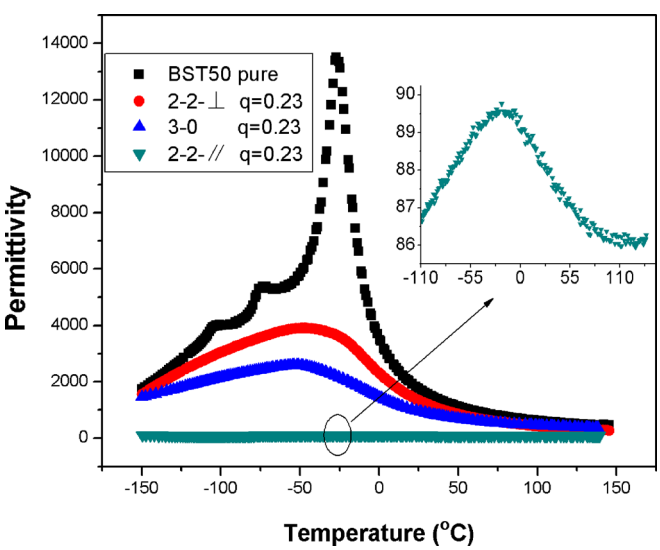

FIG. 2. Temperature dependent permittivity of the BST50, 2-2, and 3-0 composites at 10 kHz.

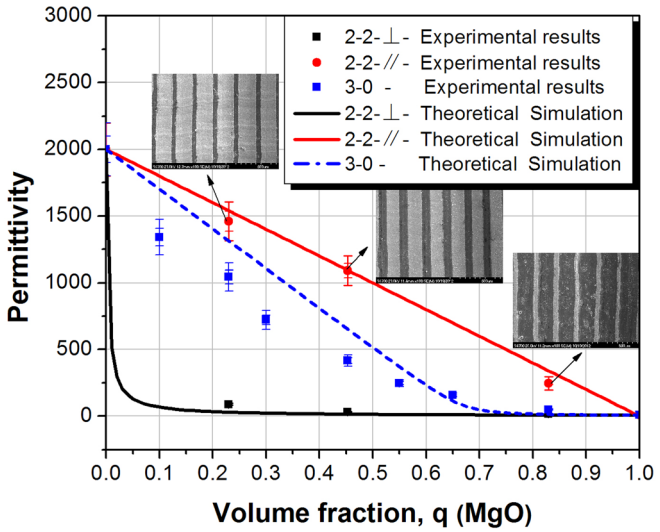

FIG. 3. Theoretical and experimental permittivity values (at 20 °C and 10 kHz) of the three composites.

nonlinear model.[2,16,17] Experimental and theoretical results are shown in Figs. 3 and 4. According to previous theoretical studies,[10,18] the 2-2-⊥ sample is a capacitor consisting of capacitors corresponding to the two types of layers in the composite in-series connection. Electrically, it is equivalent to a capacitor of two capacitors (BST50 and MgO) in-series connection. Therefore, its effective dielectric permittivity and loss can given by

$$1/\varepsilon_{mix}^{\perp} = (1-q)/\varepsilon_f + q/\varepsilon_d, \tag{1}$$

$$\tan\delta_{mix}^{\perp} = \frac{(1-q)\tan\delta_f\varepsilon_d + q\tan\delta_d\varepsilon_f}{(1-q)\varepsilon_f + q\varepsilon_d}. \tag{2}$$

The 2-2-// configuration is equivalent to a capacitor with the two capacitors connected in parallel, whose dielectric properties can be presented by

$$\varepsilon_{mix}^{//} = \varepsilon_f(1-q) + \varepsilon_d q, \tag{3}$$

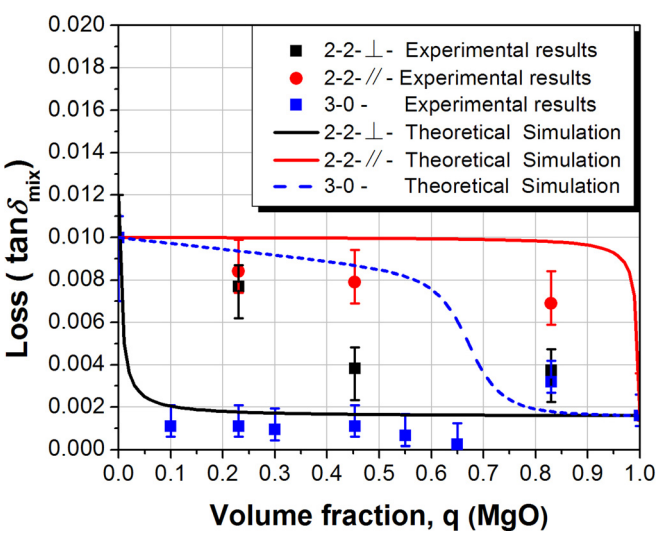

FIG. 4. Theoretical and experimental dielectric loss (at 20 °C and 10 kHz) of the three composites.

$$\tan\delta_{mix}^{//} = \frac{(1-q)\tan\delta_f\varepsilon_f + q\tan\delta_d\varepsilon_d}{(1-q)\varepsilon_f + q\varepsilon_d}. \quad (4)$$

The random sample (3-0) is complicated, which can be simulated by using a modified effective medium approximation (MEMA) as[18]

$$\varepsilon_{mix}^{sp} = 0.25\Big[3q\varepsilon_d - \varepsilon_d + 2\varepsilon_f - 3q\varepsilon_f + \sqrt{8\varepsilon_d\varepsilon_f + (3q\varepsilon_d - \varepsilon_d + 2\varepsilon_f - 3q\varepsilon_f)^2}\Big], \quad (5)$$

$$\tan\delta_{mix}^{sp} = \frac{1}{\varepsilon_{mix}^{sp}}\frac{qc_d^2\varepsilon_d\tan\delta_d + (1-q)c_f^2\tan\delta_f}{1-2qb_d^2-2(1-q)b_f^2}, \quad (6)$$

where q is volume concentration of MgO in the composites, ε_{mix}, ε_f, and ε_d are permittivity of the composites, pure ferroelectric (BST50), and linear dielectric (MgO), respectively.

Fig. 3 shows that experimental permittivity of the 2-2 composite agrees well with theoretical prediction. However, there is an obvious deviation in the 3-0 composite. This is because the theoretical simulation for 3-0 composite had an assumption that the impact of chemical interactions between the components on dielectric properties of the composite could be neglected. In fact, chemical interactions and inter-phase diffusion effects cannot be avoided due to the use of the high sintering temperature. In the composites with a 3-0 configuration, the grains of MgO/BST50 are randomly distributed in BST50/MgO matrix. Therefore, the 3-0 composite has much more inter-phase boundaries of BST50/MgO than the 2-2 sample. Moreover, dielectric response of a composite is also closely related to grain size.[19] The presence of MgO suppressed the grain growth of the BST50. This is the reason why Mg doping or MgO addition could be used to reduce permittivity and losses of BST ceramics and thin films.[5,20,21] It means that inter-phase interaction and/or chemical doping should have played important roles in determining dielectric properties of the 3-0 composite. Although loss of all three samples is pretty low (less than 0.0084), the experimental results do not comply with the theoretical simulation, as shown in Fig. 4. Since $\varepsilon_f \gg \varepsilon_d$, Eqs. (2) and (4) would mainly depend on $\tan\delta_d\varepsilon_f$ for the 2-2-⊥ model and $\tan\delta_d\varepsilon_f$ for the 2-2-// model. The inter-phase doping could lead to a reduced $\tan\delta_f$ for BST50 and an increased $\tan\delta_d$ for MgO. This can be used to explain the deviation of the experimental data from the theoretical predictions for the 2-2 model. For the 3-0 model, MgO might precipitate out and thus probably segregate at the grain boundaries of BST50, which ''diluted'' its permittivity and hindered abnormal grain growth. This could help to minimize the domain-wall contribution to the dielectric losses.[20] It has been reported that dielectric loss was decreased gradually with increasing content of Mg. There are two types of effects, i.e., "doping" and "composite," responsible for the difference in dielectric properties of a composite between experiment and theoretical simulation.

The theoretical curves and experimental data for dielectric tunability of the composites measured at 30 kV/cm are shown in Fig. 5. The tunability is defined as

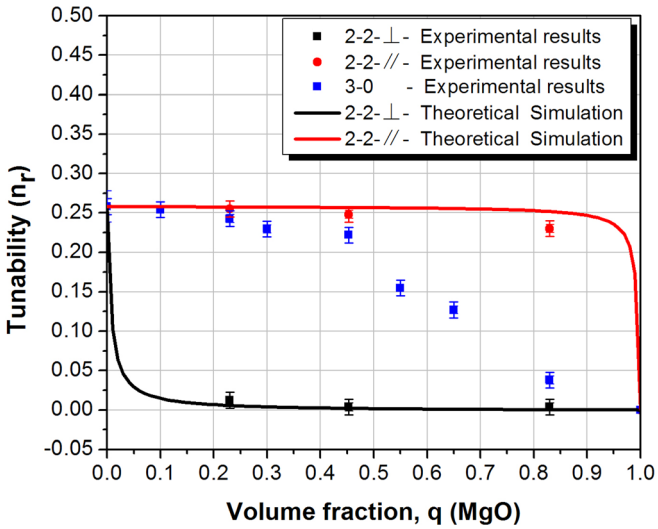

FIG. 5. Theoretical and experimental tunability (at 20 °C and 30 kV/cm) of the three composites.

$$n_r = [\varepsilon_{mix}(0) - \varepsilon_{mix}(E)]/\varepsilon_{mix}(0), \quad (7)$$

where $\varepsilon_{mix}(0)$ and $\varepsilon_{mix}(E)$ are the permittivity at zero and an applied electric field, respectively. Unfortunately, the MEMA for 3-0 model is only applicable for $q \ll 1$ or $(1\text{-}q) \ll 1$.[2,18,22] Therefore, no simulation result is included for 0-3 composite in Fig. 5. Tunability of the 3-0 composite is reduced from 0.258 to 0.039 as q is increased from 0 to 0.83. In contrast, tunability of the 2-2-// sample is only slightly decreased from 0.25 to 0.23. Although there is no significant decrease in tunability, permittivity of the 2-2-// composite can be easily adjusted from 2000 to 247. This is a great advantage for practical applications as discussed earlier.

In summary, BST50/MgO composites with 2-2-type (2-2-// and 2-2-⊥) configurations can be readily fabricated by using tape-casting and laminating technique. The experimental results of the 2-2 (2-2-// and 2-2-⊥) composites were in a good agreement with the theoretical predictions. Specifically, for the 2-2-// type composites, permittivity could be adjusted from 2000 to 247, while high dielectric tunability could be retained. This makes the 2-2-// type composites to be very good candidates for tunable microwave devices.

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