Percolative properties in ferroelectric-dielectric composite ceramics

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Percolative properties in dielectric (DE) tunability were observed in three ferroelectric (FE)-DE composite ceramics as follows: $xBa_{0.5}Sr_{0.5}TiO_3-MgO$, $xBa_{0.4}Sr_{0.6}TiO_3-Mg_2TiO_4$, and $xBa_{0.5}Sr_{0.5}TiO_3-Mg_3B_2O_6$. Dielectric constants of the composites increased monotonously with increasing volume fractions of FE component. Comparatively, their DE tunabilities exhibited a weak dependence on FE concentrations over a wide range. However, their tunabilities started to decrease substantially below a critical concentration of FE. The critical concentrations were 40 vol % for $Ba_{0.5}Sr_{0.5}TiO_3-MgO$, 38 vol % for $Ba_{0.4}Sr_{0.6}TiO_3-Mg_2TiO_4$, and 33 vol % for $Ba_{0.5}Sr_{0.5}TiO_3-Mg_3B_2O_6$. These results could be used as a guide to tailor the properties of FE-DE composites for tunable device applications. © *2010 American Institute of Physics.* [doi:10.1063/1.3514246]

$Ba_xSr_{1-x}TiO_3$ (BST, preferably with x=0.4–0.5) solid solutions are promising candidates for applications in microwave tunable devices, such as phase-shifters, antennas, oscillators, etc., owing to their highly nonlinear properties and relatively low losses.[1,2] For practical applications, tunable materials should have a dielectric (DE) constant of $30 < \varepsilon_r < 1500$, a DE loss of tan $\delta < 0.005$, and a tunability of T $> 10\%$.[3] In this respect, pure BST is not suitable for device applications and should be modified to have an appropriate value of DE constant and sufficiently low DE loss. It has been found that randomly mixing BST with nontunable (linear) DE materials, such as MgO (Ref. 3) and Mg_2TiO_4,[4,5] is an effective way to modify the DE properties of BST.

Meanwhile, DE properties of ferroelectric (FE)-DE composite materials also have been demonstrated theoretically. Based on the Bruggeman effective medium theory and the nonlinear model of FE materials,[6,7] the results by Sherman *et al.*[8] shows that additions of small amounts of DE components into BST matrix result in an increase in the tunability and no obvious reduction in tunability up to relatively high concentrations of DEs is suggested but DE loss almost remains unaffected. Jylhä *et al.*[9] reported that DE constant and tunability of $SrTiO_3$(ST)-poly tetra fluoro ethylene (PTFE) composite had a percolation threshold at ST volume fraction of 1/3. Similar theoretical results by Zhou *et al.*[10] were carried out in the FE($Ba_{0.6}Sr_{0.4}TiO_3$)-DE composites. However, to the best of our knowledge, these theoretical predictions of the presence of a threshold in FE-DE composites have not been validated by available experimental evidences.

Hence, the present study is aimed at not only systematically investigating the dependences of DE constant, loss and tunability on all volume fractions of FE inclusions but also searching for general characteristics of DE properties of FE-DE composites. The experiments are performed on ceramic samples of three composite systems. Such systems have three common characteristics closer to preconditions of the spherical inclusion model. (i) There are two pure phases

just the same as initial additives. (ii) Curie temperatures (T_C) have slight changes above the solubility limit of DEs. (iii) There is a big contrast in DE properties between FE and DE phases $[\varepsilon_r(FE) \gg \varepsilon_r(DE), T(FE) \gg T(DE), tg\delta(FE) \gg tg\delta(DE)]$.

The three composites are $xBa_{0.5}Sr_{0.5}TiO_3-MgO$ (BST50-MO), $xBa_{0.4}Sr_{0.6}TiO_3-Mg_2TiO_4$ (BST40-MT), and $xBa_{0.5}Sr_{0.5}TiO_3-Mg_3B_2O_6$ (BST50-MB), where x is the volume fraction of FEs from 0 to 100 vol %. BST40 and BST50 were synthesized at 1200 °C with starting materials of $BaTiO_3$ (99.9%) and $SrTiO_3$ (99.9%). Mg_2TiO_4 was derived from $(MgCO_3)_4 \cdot Mg(OH)_2 \cdot 5H_2O$ (99.9%) and TiO_2 (99.9%) at 1300 °C while $Mg_3B_2O_6$ was prepared at 1100 °C with MgO (99.9%) and H_3BO_3 (99.5%). Details of powder preparation, DE measurement and phase compositions can be found in Refs. 4 and 11. Samples of BST50-MO, BST40-MT, and BST50-MB were all prepared via the conventional solid-state reaction process. They were sintered for 4 h at 1450 °C, 1400 °C, and 1100 °C, respectively.

Figure 1 shows DE constants of the three composite systems as a function of volume fraction (vol %) of BST mea-
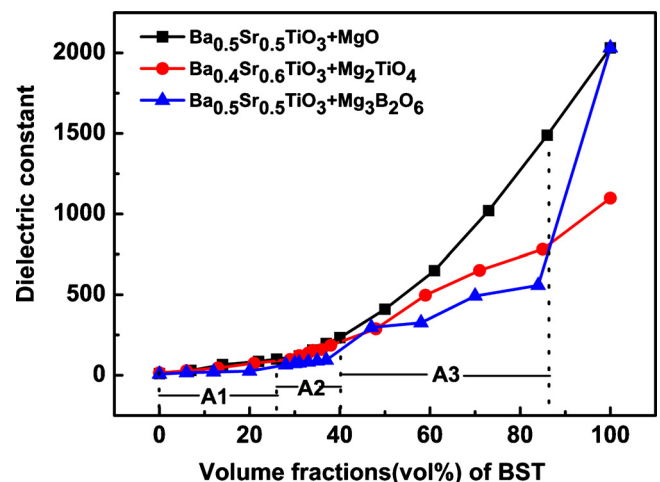

FIG. 1. (Color online) Dielectric constants of the composite ceramics as a function of BST volume fractions, measured at 10 kHz and RT.

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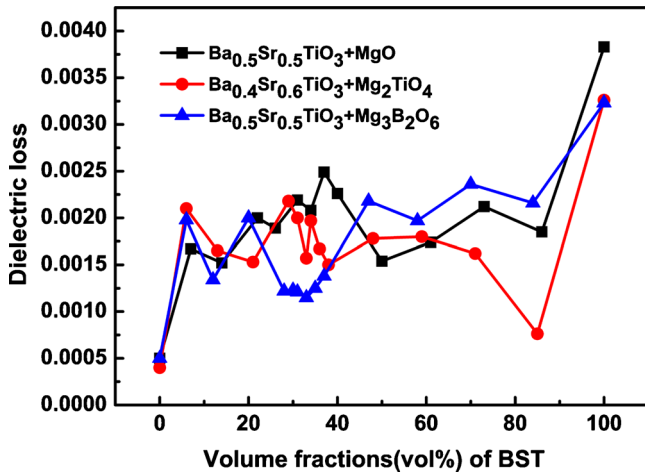
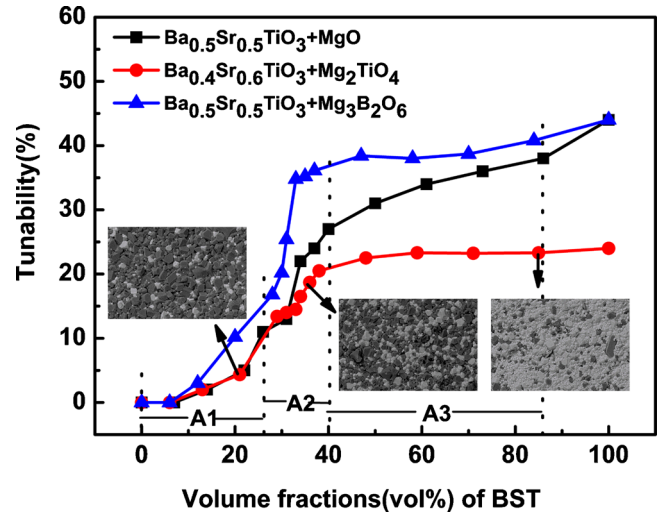FIG. 2. (Color online) Dielectric losses of the composite ceramics as a function of BST volume fractions.

FIG. 3. (Color online) Tunabilities of the composite ceramics as a function of BST volume fractions, measured at 60 kV/cm, 10 kHz, and RT. The insets are representative backscattered electron images of the $xBa_{0.4}Sr_{0.6}TiO_3-Mg_2TiO_4$ composite ceramics with different concentrations of BST40 (x=21,36,85 vol %) inclusions (gray).

sured at room temperature (RT) and 10 kHz. It is found that, DE constants of the samples increase almost linearly with increasing concentrations of BST below x=26 vol % (region A1). As x is increased into region A2 (26 vol % <x <40 vol %), their DE constant variations gradually deviate a linear behavior. In region A3, the variations in DE constant become linear again. In this region, DE constant increases more quickly than in region A1 with increasing BST volume fraction. Obviously, region A2 is the critical region, which can be explained by the percolative threshold reported by Jylhä *et al.*[9] and Zhou *et al.*[10] The dependences of DE constant of the samples, on the volume fraction of BST, are in a good agreement with the theoretical results.[9,10] Such a strong concentration dependence of DE constant is a typical composite effect.[8]

Dielectric loss dependences of the composites on volume fractions of BST are shown in Fig. 2. The DE losses decrease considerably at higher volume fractions of BST mainly due to Mg^{2+} substitution. Such a substitution was also responsible for the shift in T_C and prevented the conversion of Ti^{4+} to Ti^{3+}.[12] However, DE loss does not always decrease with decreasing BST content but fluctuates slightly. According to the spherical inclusion model, $tg\delta_{eff}=tg\delta_f$, $\varepsilon_{eff} =\varepsilon_f(1-3/2q)$, where $tg\delta_{eff}$, $tg\delta_f$, and ε_{eff} and ε_f are DE loss and DE constant of composites and FEs, q is the volume fraction of DE inclusions.[8] In this case, DE loss is much less sensitive to the dilution effect of the "passive" components than DE constant. This implies that the dilution of DE materials cannot substantially lower the intrinsic loss of a composite material, as suggested by Sengupta.[3]

Calculated tunabilities of the composites, as a function of BST volume fraction, measured at 60 kV/cm, are shown in Fig. 3. As seen in Fig. 3, the composites with x below 14 vol % has very low tunability (T<2%). Once BST volume fractions are within the region of 14–40 vol % (regions A1 and A2), their tunability increases remarkably. This trend is similar to that of DE constants as shown in Fig. 1. In contrast, the variations in tunability become flattened with increasing volume fraction of BST as x values are above 40 vol % for BST50-MO, 38 vol % for BST40-MT, and 33 vol % for BST50-MB (region A3 of Fig. 3). For instance, tunability of the BST50-MB system varies weakly from 34.8% to 40% in this region, whereas DE constant increases

from 82 to 2031. Tunability below the threshold of 33 vol % drops substantially from 34.8% to 3.2%. Similar behaviors are also observed in BST40-MT and BST50-MO systems. Such a weak dependence of tunability on BST volume fraction in region A3 is consistent with the predictions reported by Sherman *et al.*[8] Nevertheless, these obvious changes in tunability between regions A2 and A3 in Fig. 3 have not been predicted by the spherical inclusion model, which also differs completely from the trend of DE constant as shown by region A3 in Fig. 1. According to the spherical inclusion model of FE-DE composites, the internal fields exerted to the BST phases contributed to tunability, especially, transverse-optical modes-induced DE interactions commonly occurred through the continuously connected Ti–O–Ti bonds in BST. Therefore, the connectivity levels among FE phases (depending on shapes, sizes of particles, and the ability to form clusters of particles)[13–15] may have more notable effect on the tunabiliy.[16] In FE-DE composites, FE phases diluted by the DE inclusions always exhibit a connectivity that may vary from 0–3 to 3–3 and to 3–0, with increasing volume fractions of the FE phases.[16,17] These connectivity levels have been observed in BST40-MT, which are represented by the backscattered images of the samples with different concentrations of BST that lay within regions A1, A2, and A3 in Fig. 3, where gray inclusions are BST40 phases. The region of 26–38 vol % BST should be the critical region, where BST phases are connected while MT phases are not (region A2 in Fig. 3). Such a region necessarily arouses inhomogeneous arrangements of electric field surrounding the BST phases, which consequently leads to a sharp increase in tunability from 13.4% to 20.5%. Such a strong dependence of tunability on connectivity and interactions between FE and DE phases was also justified experimentally by Irvin *et al.*[18] Comparing the region A3 in Fig. 1 and Fig. 3, DE constant decreases substantially while tunability maintains a relatively high level over 40–86 vol % of BST. In critical region of A2, tunability decreases more obviously than in others regions (A1 or A3) but correspondingly DE constant changes almost negligibly. The results could be used as a guide to tailor DE

properties and deeply understand physical behaviors of FE-DE composite systems.

In summary, DE properties of FE-DE composite ceramics were intensively investigated with volume fractions of BST. Percolative phenomena in DE tunability were observed. Near a critical concentration, relatively high tunabilities with a low DE constant can be realized in FE-DE composite ceramics, whereas the DE loss almost remains unaffected. Below a critical concentration, the tunability starts to decrease substantially. These critical concentrations are 40 vol % for BST50-MgO, 38 vol % for BST40-Mg_2TiO_4, and 33 vol % for BST50-$Mg_3B_2O_6$.

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