The abnormal increase of tunability in ferroelectric-dielectric composite ceramics and its origin

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ABSTRACT

The ternary ferroelectric—dielectric composite ceramics $Ba_{0.45}Sr_{0.55}TiO_3$—MgO—Mg_2TiO_4 were prepared by solid-stated method and the dielectric tunable properties of composite ceramics were investigated. The abnormal increased tunability in the ternary ferroelectric-dielectric composite ceramics was observed, which shows further that the abnormal increase of tunability exists universally in ferroelectric-dielectric composite. A simple 3D Finite Element Method model was constructed to simulate the dielectric response and explore the origin of abnormal increase of tunability in ferroelectric-dielectric composite. The simulation results of tunability show the same trend as the experimental data. Further analysis of the electric field distribution in ferroelectric-dielectric composites indicated that the abnormal increase of tunability originates from the enhancement of the electric field on a fraction of the ferroelectrics around dielectrics.

1. Introduction

Barium strontium titanate (BST) is a excellent material to fabricate tunable microwave devices, such as tunable capacitors, phase shifters, delay lines, etc., due to its DC electric field-dependent relative permittivity [1—5]. However, pure BST with high loss tangent and high relative permittivity restricts its application in microwave devices [6]. Generally, adding linear dielectric materials, such as MgO, Mg_2TiO_4, Mg_2SiO_4, etc., to form composite material, is an efficient way to decrease loss tangent and relative permittivity and to keep tunability at a quite high level [3—19]. However, increasing linear dielectric concentration generally resulted in the decrease of tunability due to the dilution of ferroelectricity [5,12,14,15], which is disadvantageous to tunable microwave applications. For example, Sengupta et al. [5] reported that increasing MgO content from 10 wt% to 60 wt%, the dielectric constant of $Ba_{0.6}Sr_{0.4}TiO_3$—MgO decreases from 1431 to 118, and the tunability at 2 kV/mm decreases from 16.6% to 10%. Chou et al. [14] reported the dielectric tunable properties of $Ba_{0.5}Sr_{0.5}TiO_3$-Mg_2TiO_4 composite ceramics. With increasing Mg_2TiO_4 content from 50 wt% to 80 wt%, the dielectric constant of the ceramics at 10 kHz

decreases from 335 to 35 and the corresponding tunability at 3 kV/mm decreases from 18.4% to 10.8%. In recent years, Kozyrev et al. [20] and Nenasheva et al. [21] observed abnormal increase of tunability in binary ferroelectric-dielectric BST-Mg_2TiO_4 composites: with increasing Mg_2TiO_4 content from 8.3 wt% to 44.4 wt%, the tunability of BST—Mg_2TiO_4 composite at 4 kV/mm increases from ~19% to ~30% [20]. We studied systemically the dielectric tunable properties of BST-Mg_2TiO_4 and speculated that the abnormal increase of tunability exists universally in ferroelectric-dielectric composite [22]. There was no doubt that the abnormal increase of tunability is beneficial for tunable microwave application. The advantage of ternary ferroelectric-dielectric composites over binary ferroelectric-dielectric composites is the ease on the adjustment of dielectric properties [10,13]. However, whether the abnormal increase of tunability exists in ternary ferroelectric-dielectric composites is an open question. Therefore, the aim of this article is to explore whether abnormal increased tunability can be found in $Ba_{0.45}Sr_{0.55}TiO_3$—MgO—Mg_2TiO_4 composite ceramics.

The dielectric response of ferroelectric—dielectric composites was theoretically addressed by Sherman et al. [23]. They reported that the addition of small amounts of a linear dielectric into the tunable ferroelectric results in an increase of the tunability of the mixture due to a redistribution of the electric field in the material. On the other hand, stimulated results on ferroelectric-dielectric composites using finite element method (FEM) was reported by

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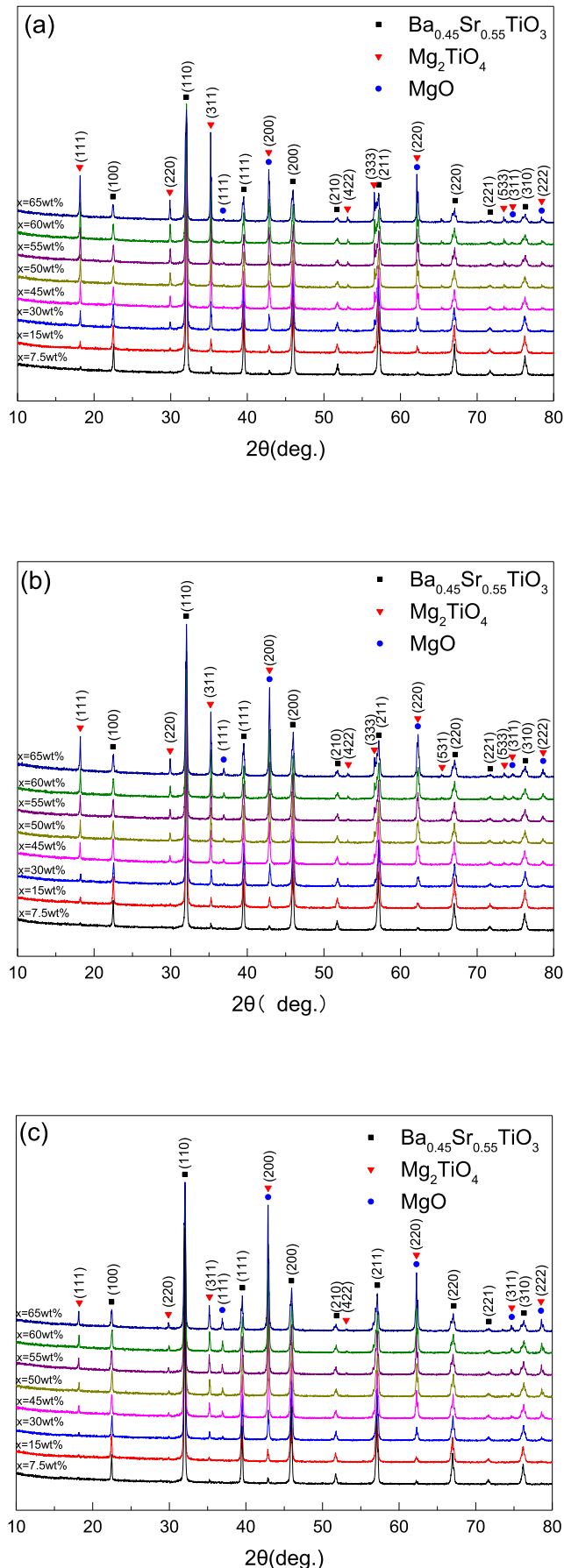
some authors [24,25]. Zhou et al. used the 2D FEM to simulate the dielectric response of a composite consisting of a linear, low-loss dielectric matrix with uniformly sized, randomly distributed $Ba_{0.6}Sr_{0.4}TiO_3$ particles [24]. They found that increasing BST concentration from 0 to 50 vol%, the tunability of composite increases monotonically. The above simulation cannot provide abnormal increase of tunability, let alone the origin. Up to now, no literature states clearly how the redistribution of the electric field results in the abnormal increase of the tunability in ferroelectric-dielectric composite ceramics.

In this article, the microstructures and dielectric tunable properties of $Ba_{0.45}Sr_{0.55}TiO_3$−MgO−Mg_2TiO_4 composite ceramics were investigated. The abnormal increase of tunability was observed in ternary ferroelectric-dielectric composites. A three-dimensional FEM model was established to explore the origin for the abnormal increase of tunability in ferroelectric-dielectric composites. The results show that it is the enhancement of the electric field on a fraction of the ferroelectrics around dielectrics contributes to the abnormal increase of tunability.

2. Experimental procedure

(1−x) $Ba_{0.45}Sr_{0.55}TiO_3$+x[(1-y)Mg_2TiO_4+ yMgO] (x = 0.075, 0.15, 0.30, 0.45, 0.50, 0.55, 0.60 and 0.65; y = 0.20, 0.50 and 0.80.) ceramics were prepared by conventional solid-state reaction method. The raw chemicals $BaCO_3$, $SrCO_3$ and TiO_2 were mixed in appropriate proportion and ball-milled in deionized water using agate media for 6 h. Then the dried mixtures were calcined at 1100 °C for 4 h to get $Ba_{0.45}Sr_{0.55}TiO_3$. The calcined $Ba_{0.45}Sr_{0.55}TiO_3$ powder mixed with the raw Mg_2TiO_4 and MgO in proportion according to the formula (1−x) $Ba_{0.45}Sr_{0.55}TiO_3$+x[(1-y)Mg_2TiO_4+ yMgO] and milled in deionized water with agate media for 6 h. Afterwards, the composite powders, adding the binder (5% polyvinyl alcohol solution), were pressed uniaxially into disk-shaped pellets at a pressure of 150 MPa and subsequently sintered at 1400 °C for 3 h. Silver paste was coated to form electrodes on both sides of the sintered ceramic samples for dielectric measurements.

Phase identification on the sintered ceramics was conducted by using powder X-ray diffraction (XRD) using CuK_α radiation (X'Pert PRO; PANalytical B.V., Almelo, The Netherlands). The diffractometer operated at a voltage of 40 kV and current of 40 mA. An environmental scanning electron microscopy (Quanta 200; FEI, Netherlands) was used to characterize the microstructures and chemical component elements. The relative permittivity and loss tangent were measured using Agilent 4294A precision impedance analyzer (Agilent Technologies, Santa Clara, CA). The tunability for all the composite bulk ceramics was measured at 10 kHz with a LCR meter (TH2816A, Changzhou, China) at biases up to 1500 V DC via an external power supply.

3. Results and discussion

Fig. 1 shows the XRD patterns of (Ba, Sr)TiO_3-Mg_2TiO_4-MgO composite ceramics. All the XRD patterns show three phases: a cubic perovskite structure paraelectric BST, a face centered-cubic structure Mg_2TiO_4 and a cubic MgO without other phases being detected for the composite ceramics. The shift of diffraction peaks is not obviously observed, let alone phase transition. In BST-MgO [3,6,19] or BST-Mg_2TiO_4 [14−16,22] composite ceramics, no phase transition was observed. Therefore, our results are consistent with

Fig. 1. The XRD patterns of (Ba, Sr)TiO_3−Mg_2TiO_4−MgO composite ceramics. (a) (1−x) $Ba_{0.45}Sr_{0.55}TiO_3$+x(0.8Mg_2TiO_4+0.2MgO), (b) (1−x)$Ba_{0.45}Sr_{0.55}TiO_3$+x(0.5Mg_2TiO_4+0.5MgO), (c) (1−x)$Ba_{0.45}Sr_{0.55}TiO_3$+x(0.2Mg_2TiO_4+0.8MgO).