The tunability in (Ba, Sr)TiO$_3$–Mg$_2$TiO$_4$ system

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Abstract

(Ba, Sr)TiO$_3$–Mg$_2$TiO$_4$ composite ceramics were fabricated via solid-state reaction method. X-ray diffraction, scanning electron microscopy and Raman spectroscopy were used to characterize the phase compositions and microstructures. The dielectric characteristics and tunability of composite ceramics were investigated. Depending on the tunability, the composition of (Ba, Sr)TiO$_3$–Mg$_2$TiO$_4$ can be divided into three regions: initial decreasing region, unusual increasing region and final decreasing region. This unusual increased tunability is due to electric field redistribution caused by composite effect, that is proved by the simulation result. Moreover, the change of Curie temperature also has a great impact on the tunability in this region.
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1. Introduction

In recent years, Ba$_x$Sr$_{1-x}$TiO$_3$ (BST) has become a superior candidate for manufacturing tunable microwave devices, such as tunable filters, phase shifters, delay lines, etc., due to its high dielectric nonlinear properties [1–3]. In general, the requirements of the materials for tunable microwave devices are relatively low dielectric constant, low loss tangents and high dielectric tunability [4]. However, the high inherent material loss and high dielectric constant of pure BST has restricted its application in the field of tunable microwave devices.

Generally, adding linear dielectrics with low dielectric constant, such as MgO and Mg$_2$TiO$_4$, into ferroelectric material is an effective method to decrease its dielectric constant and loss tangent and keep the tunability at a sufficiently high level [4–10]. However, increasing dielectric content also leads to the decrease of tunability due to the dilution of ferroelectrics [1]. For example, increasing MgO content from 10 to 60 wt%, the tunability of Ba$_{0.6}$Sr$_{0.4}$TiO$_3$– MgO at 2 kV/mm was suppressed from 16.6% to 10% [5].

In Ba$_{0.5}$Sr$_{0.5}$TiO$_3$–Mg$_2$TiO$_4$ system, with increasing Mg$_2$TiO$_4$ content from 50 to 80 wt%, the tunability at 3 kV/mm declined from 18.4% to 10.8% [7]. However, Kozyrev et al. [11] and Nenasheva et al. [12] observed an opposite trend: with increasing Mg$_2$TiO$_4$ content in BST–Mg$_2$TiO$_4$ composite ceramics from 8.3 to 44.4 wt%, the tunability was increased anomalously. The result that the tunability is improved with increasing Mg$_2$TiO$_4$ content is contrary to the experimental data in most ferroelectric–dielectric composites and is beneficial for tunable microwave applications [4–8]. Up to now, no researcher has tried to explain this apparent contradiction. Furthermore, it is unclear what condition could cause the anomaly and whether or not the anomaly can be observed in other ferroelectric–dielectric systems.

In this article, the dielectric tunable properties of Ba$_x$Sr$_{1-x}$-TiO$_3$ (x=0.45 and 0.5)–Mg$_2$TiO$_4$ composite ceramics are investigated. Increasing Mg$_2$TiO$_4$ content from 7.5 wt% to 50 wt% causes the rise of tunability anomalously. However, increasing Mg$_2$TiO$_4$ content further, the tunability starts to decrease. The seemingly contradictory results between Refs. [7] and [11] could be attributed to the different Mg$_2$TiO$_4$ content range. Far more important is that, according to the tunability, the composition of (Ba, Sr)TiO$_3$–Mg$_2$TiO$_4$ can be

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divided into three regions: initial decreasing region, unusual increasing region and final decreasing region. The unusual increasing region is due to the electric field redistribution caused by composite effect, that is proved by our simulation result. Moreover, the change of Curie temperature also has a great impact on the tunability in this region.

2. Experimental procedure

The raw chemicals are high-purity powders of $BaCO_3$, $SrCO_3$, TiO_2 and Mg_2TiO_4. $BaCO_3$, $SrCO_3$ and TiO_2 powders were mixed and ball-milled in deionized water using agate media for 6 h. Then the powder was calcined at 1100 °C for 4 h after drying to achieve $Ba_{0.45}Sr_{0.45}TiO_3$ and $Ba_{0.5}Sr_{0.5}TiO_3$. The $Ba_{0.45}Sr_{0.45}TiO_3$ or $Ba_{0.5}Sr_{0.5}TiO_3$ powders were mixed with Mg_2TiO_4 according to the formula $(1-x)Ba_{0.45}Sr_{0.45}TiO_3-xMg_2TiO_4$ and $(1-x)Ba_{0.5}Sr_{0.5}TiO_3-xMg_2TiO_4$ and milled with agate balls for 6 h. After that, the composite powders, which were mixed with the binder (5% polyvinyl alcohol solution), were pressed into pellets at a pressure of 150 MPa and sintered at 1340–1400 °C for 3 h. Lastly, the sintered ceramic samples were coated with silver paste to form electrodes.

Phase compositions of the sintered samples were determined by powder X-ray diffraction (XRD) using CuKα radiation (Empyrean; PANalytical B.V., Netherlands) after crushing and grinding. An environmental scanning electron microscopy (Quanta 200; FEI, Netherlands) and a field emission scanning electron microscopy (Nova NanoSEM 450; FEI, Netherlands) were used to characterize the microstructures and chemical component elements. Raman spectra of the composite ceramics were measured by Raman spectrometer (LabRAM HR800; Horiba JobinYvon, France) with the light source of 532 nm laser. The dielectric constant and loss tangent were measured by using TH2816A precision LCR meter (Tonghui Electronics, China). The tunability was also measured at 10 kHz via an external DC power supply.

3. Results and discussion

Fig. 1 shows the XRD patterns of (Ba, Sr)TiO_3–Mg_2TiO_4 composite ceramics. In both groups of (Ba, Sr)TiO_3 composites, a cubic perovskite structure (Ba, Sr)TiO_3 and a face-centered-cubic structure Mg_2TiO_4 are observed without other phases being detected. With the increase of Mg_2TiO_4 content, the diffraction peaks of (Ba, Sr)TiO_3 decrease and the diffraction peaks of Mg_2TiO_4 increase. These patterns exhibit that the (Ba, Sr)TiO_3 and Mg_2TiO_4 are distributed as individual phases in the final composite bulk ceramics.

Fig. 2 shows SEM images of (Ba, Sr)TiO_3–Mg_2TiO_4 composite ceramics. SEM images and the energy dispersive spectrometer (EDS) spectra of $55Ba_{0.45}Sr_{0.45}TiO_3$–$45Mg_2TiO_4$ and $55Ba_{0.5}Sr_{0.5}TiO_3$–$45Mg_2TiO_4$ samples are shown in Fig. 3. The small particles marked A and C are (Ba, Sr)TiO_3 and the large particles with sharp edges marked B and D are Mg_2TiO_4. It should be noted that Mg element is observed in the spectra A and C, which implies that Mg^{2+} ions have entered the lattice structure
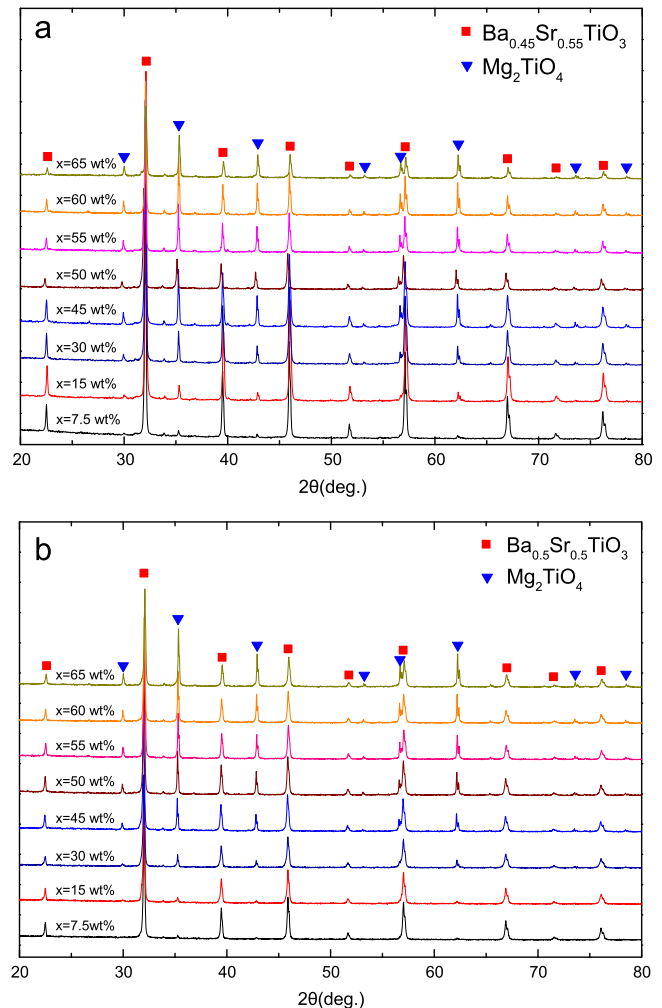

Fig. 1. XRD patterns of (Ba, Sr)TiO_3–Mg_2TiO_4 composite ceramics. (a) $(1-x)Ba_{0.45}Sr_{0.55}TiO_3-xMg_2TiO_4$, (b) $(1-x)Ba_{0.5}Sr_{0.5}TiO_3-xMg_2TiO_4$.

of (Ba, Sr)TiO_3. The SEM and EDS observations are consistent with the XRD results.

Fig. 4 shows the Raman spectra of (Ba, Sr)TiO_3–Mg_2TiO_4 composite ceramics measured at room temperature. Seven peaks are observed at $\sim$182, 231, 337, 393, 516, 581 and 738 cm^{-1}. The peaks at $\sim$182, 231 and 581 cm^{-1} are related to BST while the other four peaks are related to Mg_2TiO_4. The peaks at 182 cm^{-1} and 231 cm^{-1} are due to the rotations of oxygen cage and B-site ordering, which are considered to be the $A_1(TO_1)$ and $A_1(TO_2)$ phonon modes of the BST [13]. The 581 cm^{-1} peak is the E(TO) phonon mode of the BST which is related to the stretching of the TiO_6 octahedron [13]. For Mg_2TiO_4, three kinds of phonon modes are Raman active: E_g, T_{2g} and A_{1g}. The peaks at $\sim$337, 393, 516 and 738 cm^{-1} are T_{2g}^3, E_g, T_{2g}^2 and A_{1g} mode of Mg_2TiO_4, respectively [14,15]. With increasing Mg_2TiO_4 content, the peaks at $\sim$337, 393, 516 and 738 cm^{-1} become stronger, which also proves that these peaks are related to the Mg_2TiO_4 component.

The dielectric constant and loss tangent of (Ba, Sr)TiO_3–Mg_2TiO_4 ceramics measured at 10 kHz are shown in Fig. 5. We can see that the dielectric constant was suppressed by increasing Mg_2TiO_4 content: increasing Mg_2TiO_4 content from 7.5 wt% to