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# Compositionally inhomogeneous Ti-excess barium strontium titanate ceramics with a robust dielectric temperature stability



Hanting Dong, Dengren Jin\*, Chaojun Xie, Jinrong Cheng, Lixin Zhou, Jianguo Chen

School of Materials Science and Engineering, Shanghai University, Shanghai 200072, China

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## ABSTRACT

Compositionally inhomogeneous barium strontium titanate (BST) ceramics with a robust dielectric temperature stability were synthesized by adding excessive TiO<sub>2</sub> into phase-mixed powders. Effects of excessive TiO<sub>2</sub> on microstructures, dielectric properties and tunabilities of these ceramics were investigated. Results show that the grain size is obviously decreased and the dielectric temperature stability is dramatically improved by adding excessive TiO<sub>2</sub>. Especially, almost little temperature dependence of dielectric constants for Ti-excess specimens is obtained from 25 °C to 70 °C. Meanwhile, their high tunabilities, more than 25% under the DC electric field of 10 kV/cm, are still retained. Such compositionally inhomogeneous Ti-excess BST ceramics with a weak dielectric temperature sensitivity and high tunability are potential materials for tunable microwave applications.

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## 1. Introduction

Barium strontium titanate (BST) ferroelectric materials have exhibited high dielectric non-linearity and low loss at room temperature and microwave frequencies, which allows them to have a great potentiality for tunable microwave applications, such as phase shifters, phased array antennas, resonators and capacitors [1]. Good dielectric temperature stability is required for these applications, because working temperature always changes due to the fluctuation of surrounding temperature and/or the heat caused by working devices, and the communication and information will break off if the dielectric temperature sensitivity of tunable materials is strong. The Curie temperature of uniform BST ceramics is always adjusted to around room temperature in order to obtain high tunability, but their dielectric constants and loss undergo a huge change through the Curie temperature, and have poor dielectric temperature stability. To overcome such shortcomings, a variety of methods were adopted to enhance the dielectric temperature stability. MgO [2], SrMoO<sub>4</sub> [3] or other linear dielectrics are usually introduced to form composites with paraelectric BST ceramics to suppress the Curie peaks, but their tunabilities are always reduced significantly. Doping ions always have similar effects on the dielectric temperature stability and tunability of BST ceramics [4]. Lubomirsky et al. [5] proposed a concept of intragrain concentration gradient ceramics. BST ceramics with intragrain concentration gradient synthesized

using sol–gel derived phase-mixed powders exhibit lower and wider Curie peaks, or better dielectric temperature stability than uniform BST ceramics do, and still keep sufficiently low loss and high tunability. The compositionally inhomogeneous BST ceramics can also be synthesized by using solid-state reaction powders [6], and the dielectric temperature stability can be further enhanced by adjusting the calcining temperature of phase-mixed powders [7].

In this paper, we have synthesized compositionally inhomogeneous BST ceramics by adding excessive TiO<sub>2</sub> into phase-mixed powders and much better dielectric temperature stabilities are obtained. Effects of Ti-excess adding on microstructures, dielectric properties were investigated.

## 2. Experimental

Barium titanate (BT), strontium titanate (ST), and Ti-excess BT and ST powders were prepared, respectively, by the conventional solid-state reaction. BaCO<sub>3</sub> (AR), SrCO<sub>3</sub> (AR) and TiO<sub>2</sub> (CP) powders were used as starting materials. The molar ratio of Ba/Ti in Ti-excess BT and Sr/Ti in Ti-excess ST is 1:1.04. BT and Ti-excess BT powders were calcined at 1100 °C for 2 h, while ST and Ti-excess ST powders were calcined, respectively, at 1200 °C for 2 h according to our previous work [7]. Three kinds of samples were prepared according to the two ways of introducing excessive TiO<sub>2</sub> or not. The mixture of BT and ST powders was named as BST. The mixture of BT, ST and excess-TiO<sub>2</sub> (4 mol% excess) powders, in which the excessive Ti ions were introduced independently in the form of TiO<sub>2</sub>, was defined as Mix-Ti, and the mixture of Ti-excess

\* Corresponding author. Tel.: +86 21 66137131.

E-mail address: [drjin@shu.edu.cn](mailto:drjin@shu.edu.cn) (D. Jin).

BT and Ti-excess ST, in which the excessive Ti ions were introduced during the calcination, was defined as Cal-Ti. The molar ratio of Ba/Sr in all samples was 3:1. The powder mixtures were mixed with polyvinyl alcohol and then compressed into pellets. All green compacts were heated at 700 °C to burn out the polyvinyl alcohol, and then were soaked in the BST precursor solution [6]. These sol-infiltrated green compacts were sintered at 1250–1350 °C for 4 h. The relative densities of all samples sintered at 1280–1350 °C respectively are above 91%. The details of preparing process can be found in reference [7].

The density of samples was measured by the Archimedes method. The phase structure was characterized by X-ray diffraction (DLMAX-2200). A Scanning Electron Microscope (HITACHI-S3400) was used to examine the microstructures of these ceramics. The dielectric properties were measured by an Agilent 4294A Impedance Analyzer. DC bias field dependence of the dielectric constants of samples is determined by the Agilent 4192A Impedance Analyzer combined with Trek 610D high voltage source.

### 3. Results and discussions

The XRD patterns of green compacts and sintered ceramics are shown in Fig. 1. It is found that the major phase of all samples is the typical perovskite structure. There is no second phase detected in Mix-Ti green compact, but a second phase formed after sintering. On the contrary, there is another second phase observed in Cal-Ti green compact, but the second phase disappeared after sintering. These second phases probably are some kinds of Ti-rich phases, as reported that a Ti-rich phase is formed during cooling at the boundary of barium titanate ceramics [8,9]. Therefore, the different ways of introducing TiO<sub>2</sub> will lead to different phase compositions. Such difference can be attributed to the different solubility of TiO<sub>2</sub> in BT and ST solid solutions. As reported, BaTiO<sub>3</sub> ceramics with a small excess of TiO<sub>2</sub> (Ba/Ti=0.999) showed a second phase [8], while there was no second phase detected by XRD analysis even when the ratio of Sr/Ti was 0.997 in SrTiO<sub>3</sub> ceramics [10]. For Cal-Ti green compacts, the second phase comes from Ti-excess BT, due to the low solubility of TiO<sub>2</sub> in BT. After sintering, the original second phase on the BT particles will decompose and diffuse into the Sr<sup>2+</sup>-rich BST region due to their small size. But for the Mix-Ti ceramics, the second phase appears

probably because excess-TiO<sub>2</sub> with larger grain size cannot thoroughly solute in the Sr<sup>2+</sup>-rich region, and more excess-TiO<sub>2</sub> dissolve into the Ba<sup>2+</sup>-rich BST region during the sintering but segregate and form the second phase during the cooling.

Table 1 shows the diffraction angles ( $2\theta$ ) of crystal plane (1 1 1) of sintered specimens and their full width at half-maximum (FWHM). It is seen that the FWHM values of (1 1 1) plane of the BST ceramics decrease obviously as the sintering temperatures increase from 1250 °C to 1320 °C. This phenomenon indicates that the compositional homogenization degree of the BST ceramics becomes higher as the sintering temperatures increase. It is also found that the compositional homogenization degree is decreased significantly by adding excessive TiO<sub>2</sub> when comparing the FWHM values of BST, Mix-Ti and Cal-Ti ceramics sintered at 1280 °C. BST ceramics exhibit a typical ABO<sub>3</sub>-type perovskite structure: A-site is occupied by Ba<sup>2+</sup> ions or Sr<sup>2+</sup> ions and B-site is occupied by Ti<sup>4+</sup> ions. Adding excessive TiO<sub>2</sub> leads to creating more A-site vacancies, and decreasing the concentration of A-site ions in ABO<sub>3</sub>-type structure. It is believed that decreasing the concentration gradient of A-site ions is the main reason for mitigating the A-site ions interdiffusion by excessive TiO<sub>2</sub>. Further studies are still to go to clarify the mechanism of mitigating the ions interdiffusion by excessive TiO<sub>2</sub>.

It is found from the SEM images (Fig. 2) that all samples exhibit a quite dense microstructure, which agrees with the results of relative density measurement. It can also be seen that the grain growth of BST ceramics is remarkably inhibited by adding excessive TiO<sub>2</sub>, but the way of introducing excessive TiO<sub>2</sub> exerts little effects on the grain growth. Adding excessive TiO<sub>2</sub> makes the grain size reduced from 2–4 μm to 1–2 μm when sintered at 1280 °C and reduced from 3–6 μm to 2–5 μm as sintered at 1320 °C. The inhibiting of the grain growth can be attributed to the mitigating

**Table 1**  
Diffraction angles ( $2\theta$ ) of (1 1 1) plane of sintered ceramics and their FWHM values.

Sample	BST/1250 °C	BST/1280 °C	BST/1320 °C	Mix-Ti/1280 °C	Cal-Ti/1280 °C
$2\theta_{(111)}$	39.200	39.179	39.061	39.181	39.300
FWHM	0.331	0.241	0.196	0.322	0.300

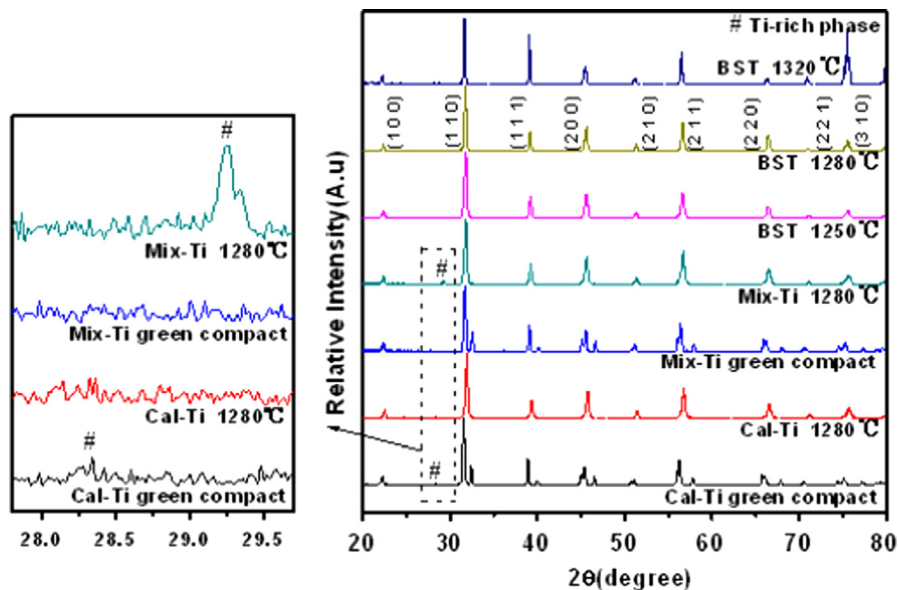


Fig. 1. XRD patterns of green compacts and sintered ceramics.

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