

# Dielectric tunable properties of high dielectric breakdown $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3\text{-Zn}_2\text{P}_2\text{O}_7$ composite ceramics

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## Abstract

Dielectric properties of  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3\text{-}x\text{Zn}_2\text{P}_2\text{O}_7$  ( $x = 1, 3, 5, 10, 15$  wt%) composite ceramics, which were prepared by solid-state reaction process, were intensively investigated. The results showed that the Curie temperature ( $T_c$ ) of composites gradually shifted to lower temperature ( $-140^\circ\text{C}$ ) with increasing the content of  $\text{Zn}_2\text{P}_2\text{O}_7$ , and the dielectric constant were tuned effectively from 2020 to 107, while maintaining a relatively high tunability.  $\text{Zn}_2\text{P}_2\text{O}_7$  additions remarkably inhibited the grain growth of  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$  phases, and improved the breakdown strength of samples up to 385 kV/cm. The sample with  $x = 10$  wt% exhibited good dielectric properties ( $\epsilon_r = 290$ ,  $\text{tg } \delta = 0.0006$ ,  $T = 20.5\%$ , BDS = 297 kV/cm). Meanwhile  $\text{Zn}_2\text{P}_2\text{O}_7$  addition also made the  $T_c$  far away from the room temperature, which reduced the sensitivity of the dielectric constant to temperature change and simultaneously improved the stability of materials.

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## 1. Introduction

$\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$  (BST) solid solutions are widely studied due to their potential applications in tunable devices, such as the phase shifters, delay lines, voltage controlled oscillators, and tunable capacitors [1,2]. However, high permittivity and sintering temperature ( $\geq 1350^\circ\text{C}$ ) of pure BST ceramics restrict its applications [3]. Therefore, the optimal trade-off of the correlated dielectric parameters of BST is very critical, namely keeping tunability ( $T$ ) as high as possible with low dielectric constant ( $\epsilon_r$ ), and low loss tangent ( $\text{tg } \delta$ ). Therefore, microwave dielectric materials with low loss, low dielectric constant (e.g.  $\text{MgO}$  [4],  $\text{Mg}_2\text{TiO}_4$  [5],  $\text{MgAl}_2\text{O}_4$  [6], etc.) are always deliberately introduced to BST matrix in order to overcome the drawbacks mentioned above. Such a method effectively tailors dielectric properties of pure BST. Besides, low DC breakdown strength (BDS < 60 kV/cm) of pure  $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$  ( $0.4 \leq x \leq 0.6$ ) ceramics in air restricts the stability of materials under high applied electric field. The risk of dielectric breakdown results in the irreversible degradation of ferroelectric materials or mechanical failure [7].

Although it was reported that some glasses [8,9] or other sintering aids [10] can improve the breakdown strength (BDS) of  $\text{BaTiO}_3$ -based ceramics prepared by the solid-state reaction, the tunability smartly degraded. Therefore, optimization of the correlated parameters and improvement of the stability of materials (e.g. the breakdown strength and temperature stability) while keeping an acceptable tunability have become important issues in the field of tunable devices.

In this paper, the  $\text{Zn}_2\text{P}_2\text{O}_7$  ( $\epsilon_r = 7.5$ ,  $Qxf = 50,000$ ) of microwave dielectric materials with lower sintered temperature ( $875^\circ\text{C}$ ) was chosen as sintering additive and uniformly distributed into  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$  matrix [11]. The dielectric breakdown strength and dielectric properties of composite ceramics were investigated systematically.

## 2. Experimental

$\text{BaTiO}_3$  (99.9%),  $\text{SrTiO}_3$  (99.9%), and  $\text{ZnO}$  (99%),  $(\text{NH}_4)_2\text{HPO}_4$  (98%) were used as raw materials to synthesize pure  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$  and  $\text{Zn}_2\text{P}_2\text{O}_7$  powders at  $1100^\circ\text{C}$  and  $650^\circ\text{C}$  via the conventional solid-state reaction, respectively. The calcined  $\text{Zn}_2\text{P}_2\text{O}_7$  powders were added into  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$  powders in a proper weight fractions (1, 3, 5, 10, 15 wt%). The mixed powders were ball-milled using the alcohol and zirconia

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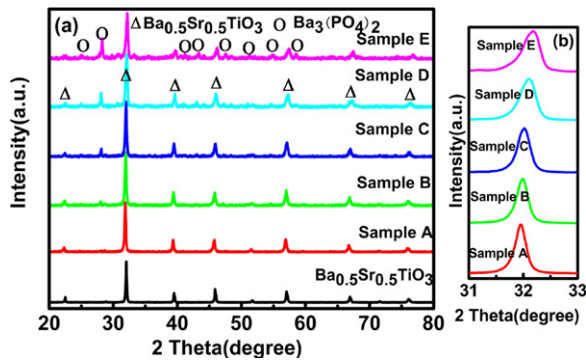


Fig. 1. (a) XRD patterns of  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3\text{-Zn}_2\text{P}_2\text{O}_7$  composite ceramics and (b) the refined peaks near  $32^\circ$  for sample A, B, C, D and E.

balls grinding media for 24 h. And then, the dried powers, which were added with 8 wt% polyvinyl alcohol binder, were uniaxially pressed into disk-shaped pellets with 10 mm diameter and 1 mm thickness for dielectric measurements. At last, the green pellets with 1, 3, 5, 10, 15 wt%  $\text{Zn}_2\text{P}_2\text{O}_7$  content (marked as sample A, B, C, D, E) were sintered at  $1200^\circ\text{C}$  for 4 h in air. Pure  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$  pellets were sintered at  $1350^\circ\text{C}$  for 4 h.

Phase structure of the samples was identified by X-ray diffraction (XRD, Bruker D8 Advanced, Germany) with  $\text{Cu K}\alpha$  radiation. The microstructure was characterized by scanning electron microscope (SEM, JSM EMP-800, JEOL, Tokyo, Japan). The samples were polished and sputtered with gold electrodes on both sides for dielectric property measurements. All samples for the DC breakdown measurements were uniformly polished to  $0.1 \pm 0.01$  mm in thickness and tested in silicon oil in order to prevent arcing. Some circular gold electrodes with around 1.2 mm in diameter (area  $\approx 1.44$  mm<sup>2</sup>, electrode thickness  $\approx 50$  nm) were sputtered on the top face. The dielectric constant and loss versus temperature was measured using E4980A LCR meter (Agilent, Palo Alto, CA) at 10 kHz and temperature range from  $-150^\circ\text{C}$  to  $-100^\circ\text{C}$ . The dielectric constant dependence on the biasing electric field (0–90 kV/cm) was tested in air by a Keithley 2410 (Cleveland, OH) high voltage source and TH2816A LCR (TongHui Electronics, China) analyzer.

### 3. Results and discussion

Fig. 1(a) shows the XRD patterns of the sintered composite ceramics. Sample A exhibits a single phase of  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ . But a new phase  $\text{Ba}_3(\text{PO}_4)_2$  is observed obviously with increasing the content of  $\text{Zn}_2\text{P}_2\text{O}_7$  except for BST phase, and the peaks around  $32^\circ$  move to large angles (in Fig. 1(b)). It indicates that the interdiffusion between two phases notably appears during the sintering. It is founded that  $\text{Zn}^{2+}$  (0.90 Å) ions dominantly enter into  $\text{Ba}^{2+}$  (1.610 Å) site in BST lattice because of formation of  $\text{Ba}_3(\text{PO}_4)_2$  phase. Meanwhile, the new phase may restrain the  $\text{P}^{5+}$  (0.38 Å) ions substitution for  $\text{Ti}^{4+}$  (0.605 Å) at the B site [12]. Such a substitution will lead to the decrease of BST lattice constant. It should display a shift of the diffraction peaks to the large angle in XRD patterns, which is well proved from Fig. 1(b).

The microstructure of sintered sample A, B, C, D, E, and pure BST are presented in Fig. 2. The grain growth of composite samples is dramatically inhibited compared to that of the pure BST ceramic. The average grain size ( $\sim 0.5$  μm) of composites is far smaller than that of pure BST ceramic ( $\sim 5.0$  μm). With increasing of the  $\text{Zn}_2\text{P}_2\text{O}_7$  content, the second phase [ $\text{Ba}_3(\text{PO}_4)_2$ ] gives rise to appearance of liquid-phase at higher temperature ( $1200^\circ\text{C}$ ), which acts as compressive phase to restricts the grain growth, and lowers the sintering temperature [13,14].

Dielectric constant and loss dependences on temperature at 10 kHz are shown in Fig. 3. In comparison with pure BST, the Curie peaks of sample A, B, C, D, and E are obviously suppressed and broadened. The Curie temperature ( $T_c$ ) is continuously shifted to the lower temperature from  $-23.5^\circ\text{C}$  to  $-140.1^\circ\text{C}$ . The obvious shifts of  $T_c$  also well adjust the dielectric constants of samples at room temperature from 2020 to 107, and the dielectric loss is also effectively reduced ( $\text{tg } \delta < 0.5\%$ ). Generally, the small grain size results in large internal stress, and then causes the shift of  $T_c$  to low temperature [15]. On the other hand, divalent  $\text{Zn}^{2+}$  ions increasingly enter into divalent  $\text{Ba}^{2+}$  position in BST lattice. The lattice constant of BST is deformed due to crystal cell shrunk, as demonstrated above in Fig. 1(b). The deformed crystal cells greatly bring the modification of  $T_c$  [16]. Most importantly,  $\text{Zn}_2\text{P}_2\text{O}_7$  addition

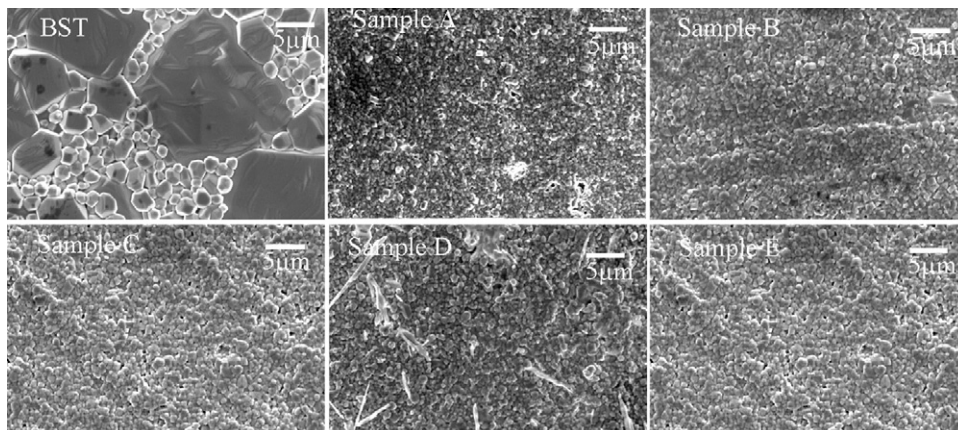


Fig. 2. SEM images of  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3\text{-Zn}_2\text{P}_2\text{O}_7$  composite ceramics.

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