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Ceramics International 38S (2012) S53–S56

CERAMICS INTERNATIONAL

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Dielectric tunable properties of high dielectric breakdown $Ba_{0.5}Sr_{0.5}TiO_3$–$Zn_2P_2O_7$ composite ceramics

Qiwei Zhang, Jiwei Zhai [*], Bo Shen, Xi Yao

Functional Materials Research Laboratory, Tongji University, Siping Road 1239, Shanghai 200092, People's Republic of China

Abstract

Dielectric properties of $Ba_{0.5}Sr_{0.5}TiO_3$–$xZn_2P_2O_7$ (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 °C) with increasing the content of $Zn_2P_2O_7$, and the dielectric constant were tuned effectively from 2020 to 107, while maintaining a relatively high tunability. $Zn_2P_2O_7$ additions remarkably inhibited the grain growth of $Ba_{0.5}Sr_{0.5}TiO_3$ phases, and improved the breakdown strength of samples up to 385 kV/cm. The sample with x = 10 wt% exhibited good dielectric properties ($\varepsilon_r = 290$, tg $\delta = 0.0006$, $T = 20.5\%$, BDS = 297 kV/cm). Meanwhile $Zn_2P_2O_7$ 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.

Keywords: A. Powders: solid state reaction; A. Grain growth; C. Strength; Tunability

1. Introduction

$Ba_xSr_{1-x}TiO_3$ (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 (≥1350 °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 (ε_r), and low loss tangent (tg δ). Therefore, microwave dielectric materials with low loss, low dielectric constant (e.g. MgO [4], Mg_2TiO_4 [5], $MgAl_2O_4$ [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 $Ba_xSr_{1-x}TiO_3$ ($0.4 \leq x \leq 0.6$) 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 $BaTiO_3$-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 $Zn_2P_2O_7$ ($\varepsilon_r = 7.5$, $Qxf = 50{,}000$) of microwave dielectric materials with lower sintered temperature (875 °C) was chosen as sintering additive and uniformly distributed into $Ba_{0.5}Sr_{0.5}TiO_3$ matrix [11]. The dielectric breakdown strength and dielectric properties of composite ceramics were investigated systematically.

2. Experimental

$BaTiO_3$ (99.9%), $SrTiO_3$ (99.9%), and ZnO (99%), $(NH_4)_2HPO_4$ (98%) were used as raw materials to synthesize pure $Ba_{0.5}Sr_{0.5}TiO_3$ and $Zn_2P_2O_7$ powders at 1100 °C and 650 °C via the conventional solid-state reaction, respectively. The calcined $Zn_2P_2O_7$ powders were added into $Ba_{0.5}Sr_{0.5}TiO_3$ 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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[*] Corresponding author. Tel.: +86 21 65980544; fax: +86 21 65985179.
E-mail address: apzhai@tongji.edu.cn (J. Zhai).

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doi:10.1016/j.ceramint.2011.04.048

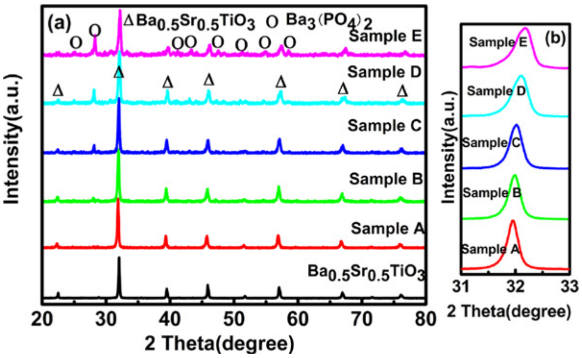

Fig. 1. (a) XRD patterns of $Ba_{0.5}Sr_{0.5}TiO_3$–$Zn_2P_2O_7$ composite ceramics and (b) the refined peaks near 32° for sample A, B, C, D and E.

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% $Zn_2P_2O_7$ content (marked as sample A, B, C, D, E) were sintered at 1200 °C for 4 h in air. Pure $Ba_{0.5}Sr_{0.5}TiO_3$ pellets were sintered at 1350 °C for 4 h.

Phase structure of the samples was identified by X-ray diffraction (XRD, Bruker D8 Advanced, Germany) with 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 ± 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 ≈ 1.44 mm^2, electrode thickness ≈ 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 °C to −100 °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 $Ba_{0.5}Sr_{0.5}TiO_3$. But a new phase $Ba_3(PO_4)_2$ is observed obviously with increasing the content of $Zn_2P_2O_7$ except for BST phase, and the peaks around 32° 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 Zn^{2+} (0.90 Å) ions dominantly enter into Ba^{2+} (1.610 Å) site in BST lattice because of formation of $Ba_3(PO_4)_2$ phase. Meanwhile, the new phase may restrain the P^{5+} (0.38 Å) ions substitution for 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 (~0.5 μm) of composites is far smaller than that of pure BST ceramic (~5.0 μm). With increasing of the $Zn_2P_2O_7$ content, the second phase [$Ba_3(PO_4)_2$] gives rise to appearance of liquid-phase at higher temperature (1200 °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 °C to −140.1 °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 Zn^{2+} ions increasingly enter into divalent 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, $Zn_2P_2O_7$ addition

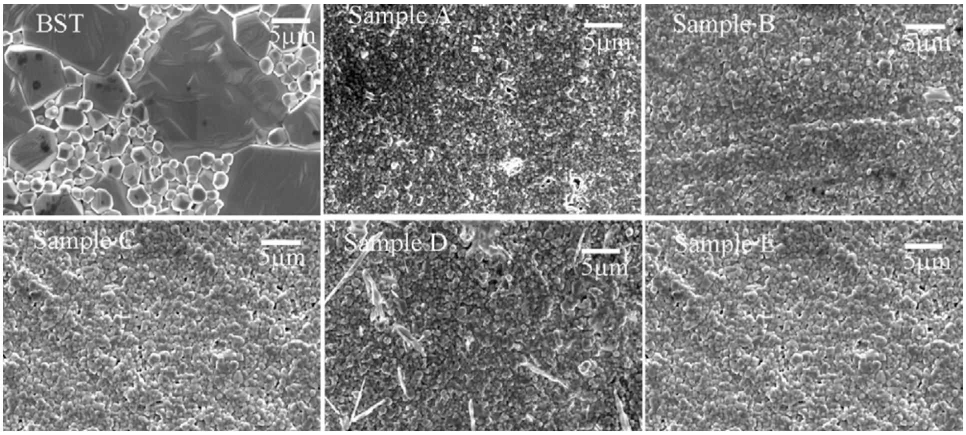

Fig. 2. SEM images of $Ba_{0.5}Sr_{0.5}TiO_3$–$Zn_2P_2O_7$ composite ceramics.

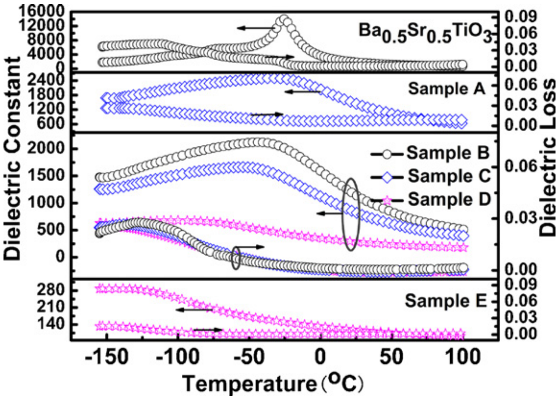

Fig. 3. Dielectric constant and loss as a function of temperature for sample A, B, C, D, E and pure $Ba_{0.5}Sr_{0.5}TiO_3$ measured at 10 kHz.

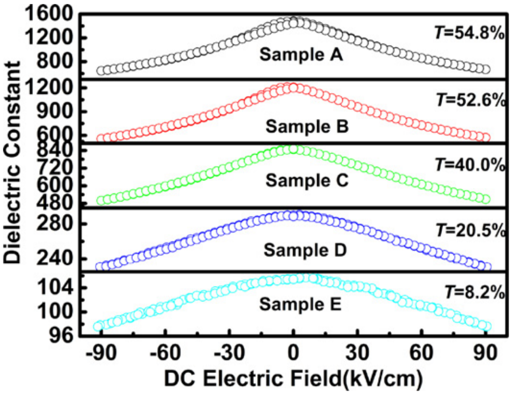

Fig. 4. DC electric field dependent dielectric constant for sample A, B, C, D and E at 10 kHz and 20 °C.

Table 1
Dielectric properties of $Ba_{0.5}Sr_{0.5}TiO_3$–$Zn_2P_2O_7$ composite ceramics.

Samples	Dielectric properties at 10 kHz				BDS at 20 °C
	T_c (°C)	ε_r (20 °C)	tg δ (20 °C)	T (90 kV/cm)	Breakdown strength (BDS) (kV/cm)
$Ba_{0.5}Sr_{0.5}TiO_3$	−23.5	2020	0.0013	–	85
Sample A	−36.6	1473	0.0043	54.8%	186
Sample B	−46.3	1210	0.0019	52.6%	198
Sample C	−57.4	850	0.0031	40.0%	240
Sample D	−99.2	290	0.0006	20.5%	297
Sample E	−140.1	107	0.0013	8.2%	385

makes the T_c far away from the room temperature and reduces the sensitivity of the dielectric constant on temperature changes.

Dielectric constant vs. DC electric field is presented in Fig. 4, and calculated tunability properties (T) are listed in Table 1. The tg δ vs. electric field also gives similar curve to tuning one (not shown here). It is found that, all composite samples are subjected to the higher DC electric field (90 kV/cm) without breakdown in air than that of pure $Ba_{0.5}Sr_{0.5}TiO_3$ ceramic. With low levels of additives (≤5 wt%), the tunability is well enhanced and the values keep more than 40%. With increasing the content of $Zn_2P_2O_7$ up to 15 wt%, the Curie temperature (T_c) moves far away from the room temperature, subsequently the tunability strongly reduced to 8.2%.

The average breakdown strengths of all samples, tested in silicon oil, are summarized in Table 1. The dielectric constant as a function of average breakdown strength is shown in Fig. 5. The average breakdown strength for each composition is obtained from eight samples. At the DC electric field of 85 kV/cm, pure $Ba_{0.5}Sr_{0.5}TiO_3$ ceramic undergoes a breakdown, whereas sample A (186 kV/cm), B (198 kV/cm), C (240 kV/cm), D (297 kV/cm), E (385 kV/cm) can undergo higher electric field than pure BST. Such an obvious improvement in BDS can be well interpreted according to the relation [17]: $E_{bds} \propto G^{-a}$, where E_{bds} is the breakdown strength, G is the grain size, and a is a constant. As the grain size decreases, the BDS clearly increases. Nevertheless, as the content of $Zn_2P_2O_7$ gradually increased from 1 to 15 wt%, it is found that the grain size of BST changes slightly from the SEM images above, but the breakdown strength monotonously increases. More recently, McPherson and co-workers give the universal relationship between dielectric breakdown and dielectric constant as follows [18,19]:

$E_{bds} \propto (\varepsilon_r)^{-1/2}$, wherein E_{bds} and ε_r are the breakdown strength and the dielectric constant, respectively. The breakdown strength shows an inverse square-root correlation of the dielectric constant. In order to determine whether the BDS and ε_r of sample A, B, C, D and E follow this trend, the experimental data of ε_r or $(\varepsilon_r)^{-1/2}$ vs. E_{bds} at 20 °C are fitted using this equation above as the solid lines. As shown in Fig. 5, all samples have been found to exhibit the expected trend for BDS dependence on dielectric constant. The experimental data can be well fitted, and the correlated coefficient of fitting is 0.989. Consequently, this is sufficiently suggested that so higher BDS

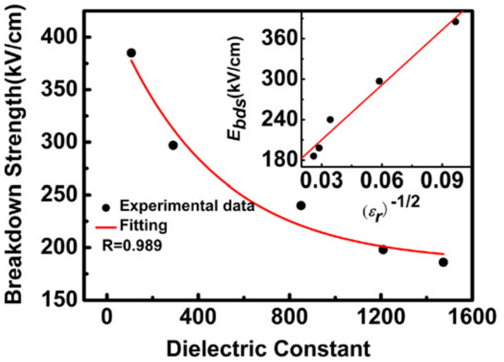

Fig. 5. Breakdown strength dependent dielectric constant for samples A, B, C, D and E at 20 °C. The experimental data are fitted by the equation $E_{bd} \propto (\varepsilon_r)^{-1/2}$ as solid lines. The inset shows the breakdown strength (E_{bds}) vs. the dielectric constant $(\varepsilon_r)^{-1/2}$.

is primarily attributed to the reduction of grain size, formation of the second phase, and the substitutions among ions.

4. Conclusions

$Ba_{0.5}Sr_{0.5}TiO_3$–$Zn_2P_2O_7$ composite ceramics are fabricated via the solid-state reaction at only 1200 °C. With the increase of $Zn_2P_2O_7$ content, the dielectric constant of composites is effectively reduced to 107, and the tunability still keeps more than 8%. The tunability of optimum composition with 10 wt% $Zn_2P_2O_7$ is up to 20.5% at 90 kV/cm, together with higher BDS (297 kV/cm), relatively low sintering temperature (1200 °C) and an appropriate value of dielectric constant (290), which should be a suitable candidate for tunable microwave device applications.

Acknowledgements

This research was supported by the Ministry of Sciences and Technology of China through 973-project under grant 2009CB623302, the Cultivation Fund of the Key Scientific and Technical Innovation Project, Ministry of Education of China (No. 707024).

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