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Ceramics International 39 (2013) 891–895

CERAMICS INTERNATIONAL

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Short communication

Dielectric and tunable properties of bulk columnar $Ba_{0.6}Sr_{0.4}TiO_3$/MgO composites

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Received 17 May 2012; received in revised form 19 June 2012; accepted 19 June 2012
Available online 26 June 2012

Abstract

$Ba_{0.6}Sr_{0.4}TiO_3$ (BST)/MgO columnar composites are fabricated via the spark plasma sintering (SPS) method. The microstructure, dielectric and tunable properties of columnar composites are investigated. The unmodified BST Curie temperatures with the increase of MgO addition indicate a sufficient suppression of ions interdiffusion between the two phases. The dielectric constant is decreased from 7000 to 3800 when MgO weight ratio is up to 15% while the tunability still stays at high level over 45%. The coefficient of the dielectric nonlinearity β shows a growing trend with increasing MgO content. The experimental results are in agreement with the theoretical prediction and confirm that if the composite is fabricated in columnar model, a reduction of dielectric constant without a deterioration of tunability could be achieved, which make them useful for potential tunable device applications in wireless communication system.

Keywords: B1. Composites; B2. Ferroelectric; Tunability

1. Introduction

Capacitors are essential building blocks of electrical radiofrequency circuits in numerous fields of applications, biology, nanotechnology, and electronics. Reconfigurable circuits whose electrical characteristics can be altered dynamically attract considerable attention for space and weight economy [1–3]. Electrically tunable capacitors, that is, varactors, are therefore in demand. The ferroelectric capacitor technology which involves the use of ferroelectric material as a tunable element is attractive for being a fast-response, low-noise competitive-loss level, but suffer from high permittivity for impedance matching [4–7]. The high permittivity is determined by the crystal structure and can be tuned by the external field. It is well known that the larger the initial permittivity, the larger the electrical field dependence of permittivity [2]. Consequently, two conflicting demands, namely low permittivity and high tunability, are required, which hinder the use of ferroelectric materials in reconfigurable high-frequency circuits. From the theoretical models proposed by Tagantsev et al., this problem can be solved by using tailed structures of ferroelectric materials with low-permittivity dielectric inclusions [2]. When ferroelectric and dielectric are connected in columnar type, the effective tunability of the composite can be kept (or even enhanced), while the effective permittivity is reduced. Nava Setter' group further fabricated amorphous $Ba_{0.3}Sr_{0.7}TiO_3$ and epitaxial $Ba_{0.3}Sr_{0.7}TiO_3$ columnar composite film capacitors [8]. Its tunability could be unchanged up to a volume fraction of 70% amorphous $Ba_{0.3}Sr_{0.7}TiO_3$. Additionally, they fabricated nanocolumnar perovskite $BaTiO_3$–fluorite (CeO_2) composite films [9]. The coefficient of the dielectric nonlinearity (β) of the nanocomposites increased up to 25 times compared to that of pure tunable ferroelectrics.

On the other hand a decrease of BST Curie temperature is observed for almost all compositions, which is attributed to the ion interdiffusion into the matrix lattice by conventional solid phase sintering [10,11]. The shift of Curie temperature reduces the performances of material at room temperature, in particular in terms of tunability that increases close to Curie temperature. A better control of

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0272-8842/$36.00
http://dx.doi.org/10.1016/j.ceramint.2012.06.058

both losses and interdiffusion between the ferroelectric and nonferroelectric phases was recently achieved by spark plasma sintering [12,13].

Based on the prediction of theoretical models proposed by Tagantsev et al. [2], in the present study we try to prepare bulk columnar composite by the SPS technique aiming at a reduction of dielectric constant without a deterioration of tunability.

2. Experimental procedure

In this communication, $Ba_{0.6}Sr_{0.4}TiO_3$ with low MgO content inclusion is fabricated by SPS sintering. BST powders are fabricated by the solid-state reaction method and MgO powders with mean particle size 50 nm are purchased from Aladdin.

The BST and MgO powders were weighed according to different weight ratios, namely 5, 10, and 15 wt% MgO (termed as samples A, B, and C). All samples were sintered using a Dr Sinter 2040 SPS apparatus (SPS Syntex Inc., Tokyo, Japan). The BST and MgO powders(without any sintering aids) were in turn loaded into a 10 mm inner diameter cylindrical die. The applied uniaxial pressure was 50 MPa. The temperature was raised to 600 °C at a heating rate of 150 °C/min, over a period of 3–4 min. and from this point it was monitored and regulated by an optical pyrometer focused on a small hole located at the surface of the die. A heating rate of 100 °C/min was used to reach 900 °C and then reached the final temperature 1100 °C at a slower rate of 60 °C/min. The highest temperature held for 3 min, obtaining a density close to 97%.

Scanning electron microscope (SEM) micrographs of the fracture surface of the sintered ceramics were recorded using a JSM-6700F JEOL. Dielectric measurements were performed on electrode disk samples using Hewlett Packard LCR meter. In addition, the electric field dependence of permittivity was characterized using our self-assembly equipment.

3. Results and discussion

Fig. 1 shows the SEM micrograph of the fracture of sample A. By energy dispersive analysis, the light gray area marked as "A" is revealed to be $Ba_{0.6}Sr_{0.4}TiO_3$ phase and the dark area marked as "B" is MgO phase. There was a particularly sharp and well-defined interface between the two components, owing to the SPS technique. In the SPS process, the combination of high pressure, pulsed electrical current, and plasma generation lead to efficient heat transfer. Consequently, very high heating rate was reached. Thus, the interdiffusion of cations between different layers is limited, allowing the preservation of clean interfaces, which is evidenced by Fig. 1.

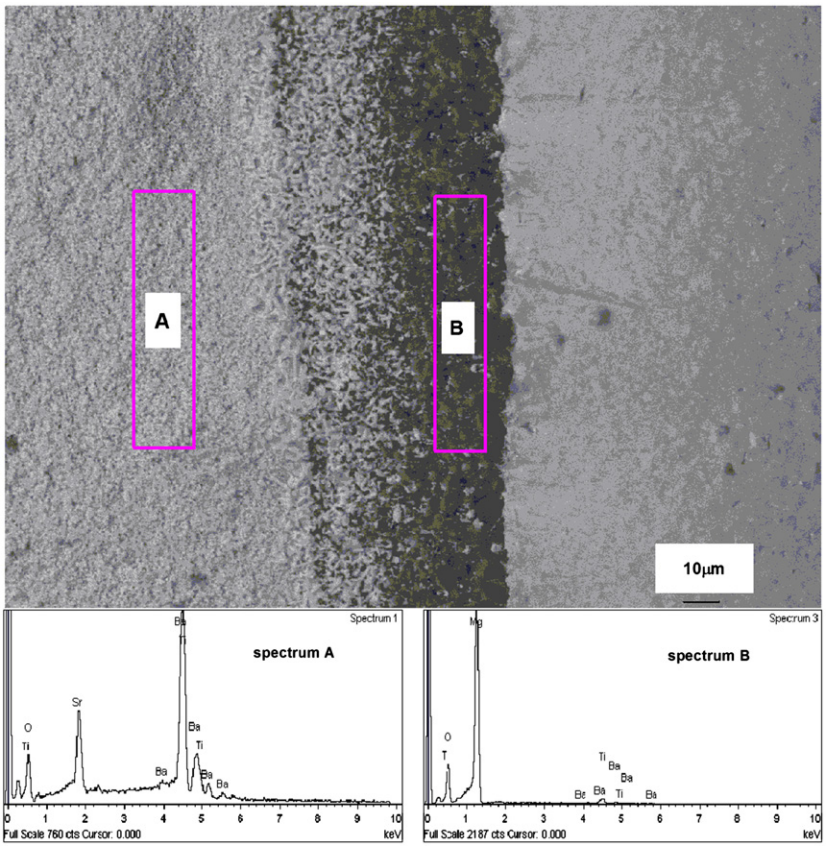

Fig. 1. Scanning electron microscope micrograph of the fracture surface of columnar BST/MgO/BST ceramic sintered by spark plasma sintering. The light gray grains marked as "A" are $Ba_{0.6}Sr_{0.4}TiO_3$ and the dark grains marked with "B" are MgO.

The temperature dependent dielectric constant and loss tangent for pure $Ba_{0.6}Sr_{0.4}TiO_3$ and columnar composite are given in Figs. 2 and 3. The Curie temperatures of columnar composites are nearly unchanged compared with pure BST. This unmodified Curie temperature is attributed to the SPS technique which fully restraints the chemical reactivity of the interface between BST and MgO. If the composite is prepared by conventional solid sintering, there is a nearly 30 °C downshift even with only 1 wt%MgO doping concentration [10]. So the Curie temperature of the composite can be controlled by the structure design and sintering technique. The dielectric anomalous peaks of ferroelectric–paraelectric phase transition for the composites are suppressed and broadened with increasing MgO content from 5 to 15 wt%. All composites' dielectric loss tangents at room temperature are below 0.5%.The dielectric constant is decreased from 7000 to 3800 when MgO weight ratio is up to 15% at 10 kHz at room temperature. According to theoretical models proposed by Tagantsev et al., the columnar ferroelectric/dielectric composite structure is equivalent to the parallel connection of two capacitors corresponding to the two components of the mixture. The effective dielectric permittivity of such composite can be presented as

$$\varepsilon_{mix}(q) = \varepsilon_f(1-q) + \varepsilon_d q \quad (1)$$

where q is the volume concentration of the dielectric phase in the composite. ε_{mix}, ε_f, ε_d are the dielectric constants of the composite, ferroelectric and dielectric, respectively. Considering the dielectric constant of ferroelectric is much higher than that of dielectric, Eq. (1) indicates that the higher the volume concentration of dielectric phase, the lower the dielectric constant of the composite. Therefore,

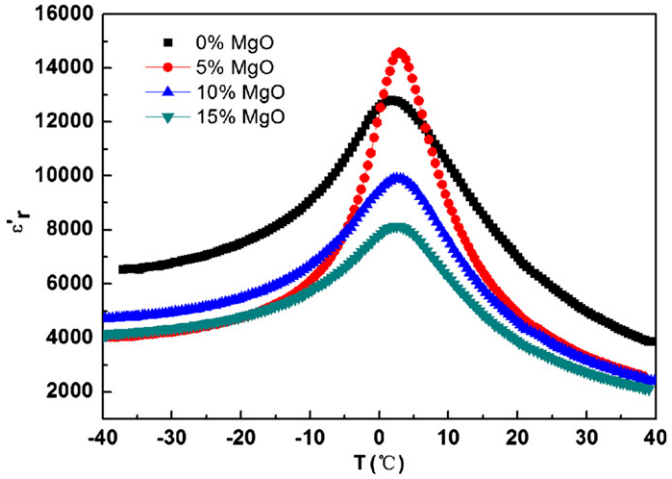

Fig. 2. Temperature dependent dielectric constant for pure $Ba_{0.6}Sr_{0.4}TiO_3$ and composite ceramics measured at 10 kHz.

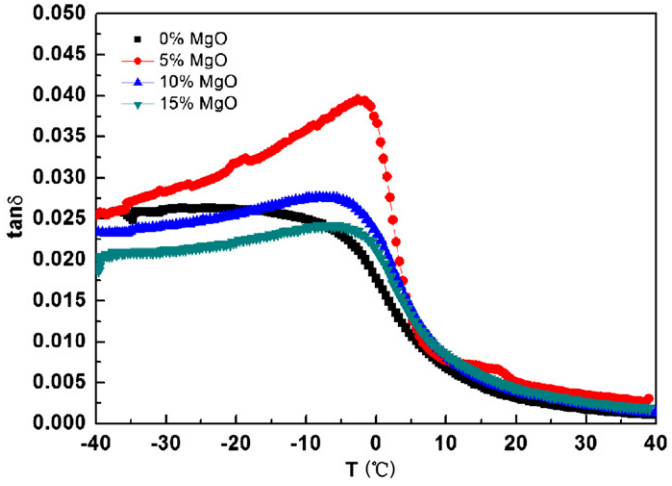

Fig. 3. Temperature dependence loss for $Ba_{0.6}Sr_{0.4}TiO_3$ and composite ceramics measured at 10 kHz.

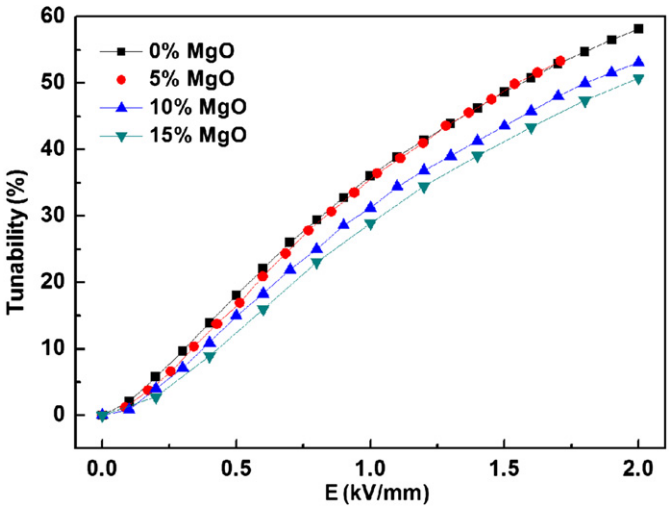

Fig. 4. DC electric field dependence dielectric constant for pure $Ba_{0.6}Sr_{0.4}TiO_3$ and composite ceramics at 10 kHz and room temperature.

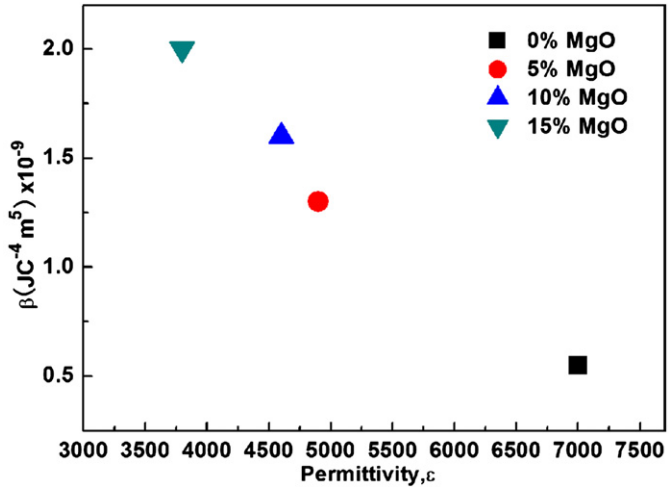

Fig. 5. Coefficient of dielectric nonlinearity for $Ba_{0.6}Sr_{0.4}TiO_3$–MgO columnar composites, estimated at field levels between $E=0$ and 1.7 kV/mm, with respect to the permittivity($E=0$). The value for pure $Ba_{0.6}Sr_{0.4}TiO_3$ is also plotted for comparison.

Table 1
Dielectric properties of pure $Ba_{0.6}Sr_{0.4}TiO_3$ and composite ceramics.

Ceramic samples	Dielectric properties(at 10 kHz)				
	T_c(°C)	At about 20 °C			β(109 J C^{-4} m^5)
		ε_r	tan δ	T (% at 1.7 kV/mm)	
$Ba_{0.6}Sr_{0.4}TiO_3$	1.84	7000	0.0031	53	0.55
Sample A	2.88	4900	0.0050	53	1.3
Sample B	2.5	4600	0.0039	48	1.6
Sample C	2.5	3800	0.0042	45	2.0

the dielectric constant of the columnar BST/MgO composite decreased with increasing MgO amount.

It is very interesting to note that at Curie temperature the permittivity of sample A is even higher than pure SPS sintered BST. It is maybe attributed to the interface effect. The interface between BST and MgO phase could induce the appearance of internal stress, defects, space charge etc, which have a profound effect on the polarization and hence on the dielectric properties [14–16].

As expected, the permittivity measured at 10 kHz decreased significantly under an applied dc bias (Fig. 4). We compare the dependence of the dielectric permittivity on dc bias electric field E through the parameter T which is defined as $T(\%)=100\times[\varepsilon(E)-\varepsilon(0)]/\varepsilon(0)$, where $\varepsilon(E)$ and $\varepsilon(0)$ are the permittivities under and without an applied electric field, respectively. Their dielectric properties and calculated tunability are summarized in Table 1. Compared to the data of pure BST measured under the same conditions, sample A has kept tunability at the high level (53% at 1.7 kV/mm) while decreasing the dielectric constant from 7000 to 4900. With increasing the addition amount of MgO, the dielectric constant decreases dramatically, while the tunability declined a little from 53% to 45%. The conventional Landau theory explains the dielectric response controlled by the lattice dynamics of the ferroelectrics. In the limit of weak nonlinearity, the tunability can be expressed as [2]

$$n_r=\frac{\varepsilon(0)}{\varepsilon(E)}\approx 1+3\beta(\varepsilon(0)\varepsilon_0)^3E^2 \quad (2)$$

where ε_0 is the vacuum permittivity, $\varepsilon(0)$ is the permittivity at zero bias, $\varepsilon(E)$ is the permittivity at E. E is the external dc bias field, β is the phenomenological coefficient of the fourth powder of polarization. From the equation above, the relative tunability is a function of β, $\varepsilon(0)$ and E. At a given application electric field, n_r is both controlled by β and $\varepsilon(0)$. Considering that a given material has their distinctive β and $\varepsilon(0)$, we should take into account the comprehensive effects of the two parameters rather than anyone of them separately. The effectiveness of the composite structures of this study is expressed best in terms of the coefficient of the dielectric nonlinearity β in the relation $E=\alpha P_{dc}+\beta {P_{dc}}^3$, where $\alpha=1/[\varepsilon_0\varepsilon(0)]$. As can be seen in Fig. 5, the coefficient Beta (β) of columnar composite shows a growing trend with increasing MgO content. Beta (β) of BST-15% MgO composite is up to 4 times larger than that of pure BST. Although the permittivity is decreased with increasing MgO amount, the coefficient Beta (β) increases, so a reduction of dielectric constant without a distinct deterioration of tunability could be achieved if the composite is prepared in columnar structure by the SPS technique. Our experimental results agree well with the theoretical prediction.

4. Conclusion

In summary, bulk columnar perovskite $Ba_{0.6}Sr_{0.4}TiO_3$–dielectric MgO composites were fabricated by spark plasma sintering. The unmodified BST Curie temperatures with the increase of MgO addition indicate a sufficient suppression of ions interdiffusion between the two phases. The columnar composite exhibits remarkably declined permittivity from 7000 to 3800 at room temperature while the tunability still stays at high level over 45%. The coefficient Beta (β) of columnar composite shows a growing trend with increasing MgO content. The experiment results indicate if the composite is prepared in columnar structure,a reduction of dielectric constant without a distinct deterioration of tunability could be achieved This columnar composite with declined dielectric constant, relatively high tunability, and low dielectric loss could be very promising for tunable device applications.

Acknowledgments

This work was supported by Joint Funds of National Natural Science Foundation (NSFC) of China (U0937603) and NSFC project of China (50902141).

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