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Synthesis $Ba_{0.6}Sr_{0.4}TiO_3$–$ZnNb_2O_6$ composite ceramics using chemical coating method

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ABSTRACT

A coating approach for preparing $0.8Ba_{0.6}Sr_{0.4}TiO_3$–$0.2ZnNb_2O_6$ (hereafter BSTZ) composite ceramics was investigated. The Al_2O_3-coated $Ba_{0.6}Sr_{0.4}TiO_3$ particles were prepared successfully by chemical coating method and used as raw materials to fabricate BSTZ composite ceramics. After BSTZ ceramic sintered at 1280 °C, the $BaNb_{3.6}O_{10}$ phase was suppressed, which should attributed to the separation of $Ba_{0.6}Sr_{0.4}TiO_3$ and $ZnNb_2O_6$ by the Al_2O_3 coating. The sintered BSTZ ceramics exhibited excellent dielectric temperature stability, with a moderate dielectric constant ($\varepsilon_r = 640.8$) and a low dielectric loss ($\tan\delta = 0.0078$) at 10 kHz. The dielectric constant change with temperature for BSTZ ceramics was less than ±5% over the temperature range of −55 °C to 125 °C, meeting the requirement of the X7R type capacitor specification. The tunability of the sample is 7.2% under a dc electric field of 3 kV/mm, which made it a promising candidate material used for the tunable ceramic capacitors and the phase shifters.

1. Introduction

$Ba_{1-x}Sr_xTiO_3$ (hereafter BSTO) ceramics are considered to be one of the most promising candidates for microwave elements because of their nonlinearity of dielectric constants under the applied electrical field, and the fact their Curie temperature can be controlled to meet the requirements of various applications by changing the strontium molar fraction. Especially, $Ba_{0.6}Sr_{0.4}TiO_3$ materials are the attractive candidates for phase shifters, tunable filters, phased array antennas, tunable ceramic capacitors, etc. [1–3]. However, the sintering temperature of BST prepared by conventional method is around 1400 °C [4]. Therefore, only palladium or silver-palladium can be used as internal electrodes for the LTCC process. These materials are usually expensive and their electrical performance is not satisfactory sometimes. In order to reduce the sintering temperature, the dielectric constant and the loss of BSTO, some research work has been performed. It is reported that CuO, V_2O_5, Bi_2O_3, ZnO additives were used to lower the sintering temperature of BSTO. MgO, Al_2O_3, ZrO_2, B_2O_3 additives were used to reduce the dielectric constant and the loss of BSTO [5–8]. Liang et al. [7] proposed that Al^{3+} behaved as a grain-growth supporter below a certain doping level and lower the dielectric constant. Both the dielectric loss and tunability were modified by the addition of Al_2O_3 at low doping content. What is more, the higher insertion loss and high dielectric constant of BSTO have restricted its application in phased array antennas [9]. The optimal dielectric parameters of the dielectric material for phased array antennas and phase shifter applications should be: moderate low dielectric constant at microwave frequencies ($30 < \varepsilon_r < 1500$), low dielectric loss tangents ($0.005 < \tan\delta < 0.01$), and high dielectric tunability ($T_u > 5\%$).

Recently, the BSTO-based composite ceramics were widely investigated, for examples, (Ba, Sr)TiO_3–Mg_2TiO_4 [10], $Ba_{0.7}SrO_{0.3}TiO_3$–Nb_2O_5 [11], etc. The composite ceramics had excellent dielectric properties and the characteristics of both the two original phases. However, the $\tan\delta$ of those composite ceramics was also high. What is more, (Ba, Sr)TiO_3–Mg_2TiO_4 composite ceramics were obtained only at a temperature range from 1350 °C to 1430 °C.

Zinc niobite ($ZnNb_2O_6$) ceramic is one of the candidates for low temperature sintering microwave dielectric material, with low sintering temperature (∼1150 °C) and promising microwave dielectric properties ($Q \times f = 87{,}300$ GHz, $\varepsilon_r = 25$ and $\tau_f = -56$ ppm/°C) [12,13]. Therefore, we fabricated the (Ba, Sr)TiO_3–$ZnNb_2O_6$ composite ceramics by combining $Ba_{0.6}Sr_{0.4}TiO_3$ (hereafter BST) and $ZnNb_2O_6$ ceramics. (Ba, Sr)TiO_3–$ZnNb_2O_6$ composite ceramics were prepared by the conventional solid-state reaction method. Besides the main phase of BST and $ZnNb_2O_6$, the new phase of $BaNb_{3.6}O_{10}$ has been detected. However, the formation of the new phase $BaNb_{3.6}O_{10}$ degraded the dielectric properties of the composite ceramics [6].

In this paper, a novel chemical coating route has been developed to solve these problems. $0.8Ba_{0.6}Sr_{0.4}TiO_3$–$0.2ZnNb_2O_6$ (hereafter

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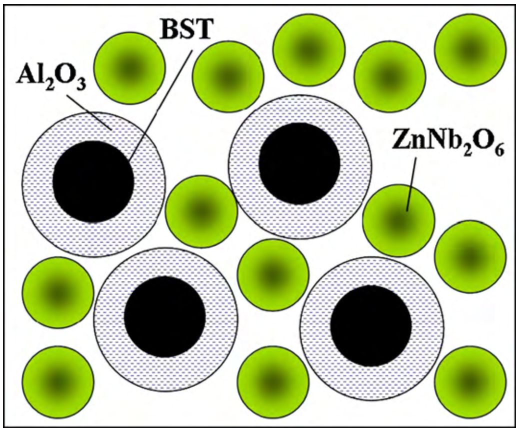

Fig. 1. Schematic of the Al_2O_3-coated BST particles mixed with $ZnNb_2O_6$ particles.

BSTZ) composite ceramics were fabricated by chemical coating method. In the first step, Al_2O_3-coated BST powder is prepared. In the second step, the Al_2O_3-coated BST powder is mixed with $ZnNb_2O_6$, as schematically illustrated in Fig. 1. The present method separates the reaction between the BST and $ZnNb_2O_6$ to prevent $BaNb_{3.6}O_{10}$ phase formation. The microstructure and dielectric properties of BSTZ composite ceramics are investigated.

2. Experimental

Reagent pure $BaCO_3$ (99.9%), $SrCO_3$ (99.9%), TiO_2 (99.9%), $ZnNb_2O_6$ (99.9%), and $AlCl_3$ (99.9%) were used as starting materials. An ammonium salt of poly (methacrylic acid) ($PMAA-NH_4$) (Darvan-C) with an average molecular weight of 5000 g/mol was used as the dispersant. The pH value was adjusted by adding HCl (analytically pure) and NH_4OH (analytically pure).

Firstly, $Ba_{0.6}Sr_{0.4}TiO_3$ (BST) powders were prepared by the conventional solid-state method. Stoichiometric mixtures of $BaCO_3$, $SrCO_3$, and TiO_2 were homogenized by ball-milled with ZrO_2 media in ethanol for 12 h and calcined at 1050 °C for 3 h. The Al_2O_3-coated BST powders were prepared as the following sequence. The precursor liquor was prepared by suspending 2 g of BST in 200 mL distilled water, followed by the addition of 0.8 wt% of $PMAA-NH_4$ to the precursor liquor. The mixture (pH 9) denoted as suspension I was then ultrasonicated and stirred for 20 min to break up the BST agglomerates. Then 0.01 mol of $AlCl_3$ was dissolved in 200 mL distilled water, which was denoted as suspension II. Then suspension I was added into suspension II drop by drop. After titration, the suspension II was aged for 30 min under stirring. Then the precipitate was filtrated and washed with distilled water. Subsequently, the washed precipitate was dried at 90 °C for 24 h. The Al_2O_3-coated BST powders were obtained by calcining at 800 °C for 4 h.

Secondly, $0.8Ba_{0.6}Sr_{0.4}TiO_3$–$0.2ZnNb_2O_6$ (BSTZ) ceramics were fabricated. Al_2O_3-coated BST powders and $ZnNb_2O_6$ were weighed and ball-milled for 4 h. The mixed powder was pressed into two types of samples at 100 MPa. One was a disk with 12.0 mm in diameter and 1.0 mm thick, the other sample for measuring microwave dielectric properties was a strip with 25.0 mm long, 15.0 mm wide, and 1.0 mm thick. The pellets were heated in air at 5 °C/min to 500 °C, held for 7 h to remove the PVA binder, and sintered at 1280 °C for 2 h. The sintered samples were polished and pasted with silver on both surfaces.

The microstructure of the powders and BSTZ ceramics were examined by a scanning electron microscopy (SEM) (Model JSM EMP-800, JEOL, Tokyo, Japan), and transmission electron microscope (TEM) (Model Tecnai F30, FEI, Holand). The crystal structures were analyzed by X-ray diffraction (XRD) (Model D/Max-IIIC, Rigaku, Tokyo, Japan, CuKα, $\lambda = 1.54178$ Å). XPS analysis was carried out on a VG ESCALB spectrometer equipped with Mg Kα X-ray source, operating at 300 W. For all the samples, the spectra of Ba3d, Sr3d, Ti2p, O1s, C1s, and Al2p were recorded. The binding energies were referred to the C1s binding energy at 284.5 eV. The surface potentials of the particles were measured using a zeta potential meter (Malvern Zetasize 2000). The dependence of the dielectric constant and loss on temperature was measured using a high precision LCR meter (HP 4284A, Agilent, Palo Alto, CA), from −50 °C to 125 °C. The tunability was measured at 10 kHz by a tunability testing system combined with a Keithley Model 6517A Electrometer and LCR meter. The dielectric constant and loss at microwave frequencies were analyzed using the Hakki-Coleman dielectric resonator method by the network analyzer (E8363B, Agilent) combining a resonating cavity.

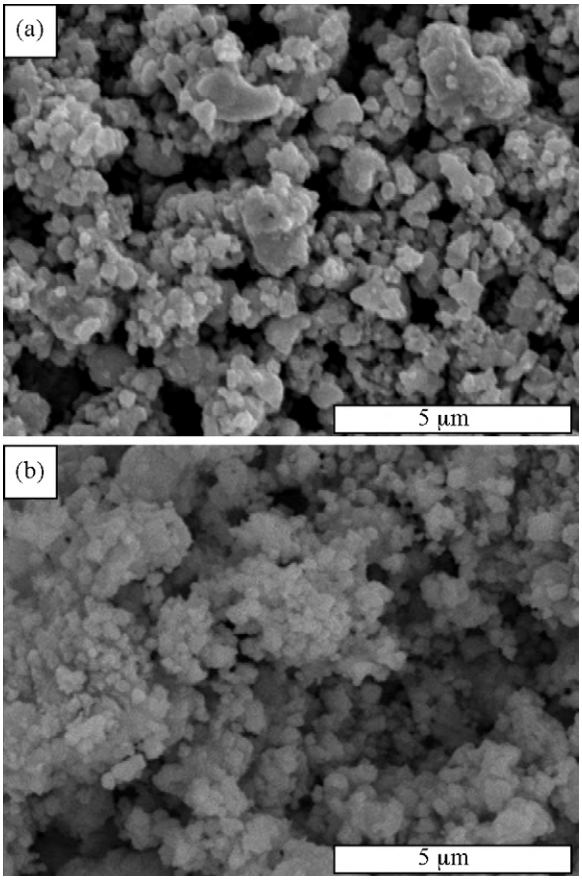

Fig. 2. SEM image of BST powders (a) uncoated BST powder; (b) Al_2O_3-coated BST powders.

3. Results and discussion

3.1. Microstruture and characteristic of Al_2O_3-coated BST powders

Fig. 2 shows the SEM images of uncoated and Al_2O_3-coated BST powders, respectively. It is observed that the surface of BST powder was distinctly changed after Al_2O_3 coating. The uncoated BST powders have relative smooth surfaces; while continuous and dense alumina coating layers covered on the surfaces of the BST powders and the alumina aggregated together, as shown in Fig. 2(b).

Fig. 3 shows the TEM image of Al_2O_3-coated BST powders. It is obviously that the core-shell structure was obtained with Al_2O_3 distributed around the BST powders in a flocculating form. It is confirmed that the continuous and dense alumina coating layers formed on the surface of BST.

Fig. 4 shows the XRD patterns of BST powders. Either the XRD pattern of Al_2O_3-coated BST sample or that of uncoated powder shows the diffraction peaks of BST (PDF#34-0411). There is no crystal alumina oxide detected in Al_2O_3-coated BST powders by XRD analysis, which means that alumina existed in amorphous hydrated alumina under the present experimental conditions. Zhang et al. [14] reported that the alumina nanofilms that existed in amorphous hydrated alumina phase were anchored at the surfaces of TiO_2. Our experimental result is in consistence with their reported research before.

Fig. 5 shows the XPS survey spectra of uncoated and Al_2O_3-coated BST powder. Table 1 shows the element content (%) on the surface of BST powder. It is clearly to see that the Al2p peak appeared in the XPS pattern of Al_2O_3-coated BST powder, and the

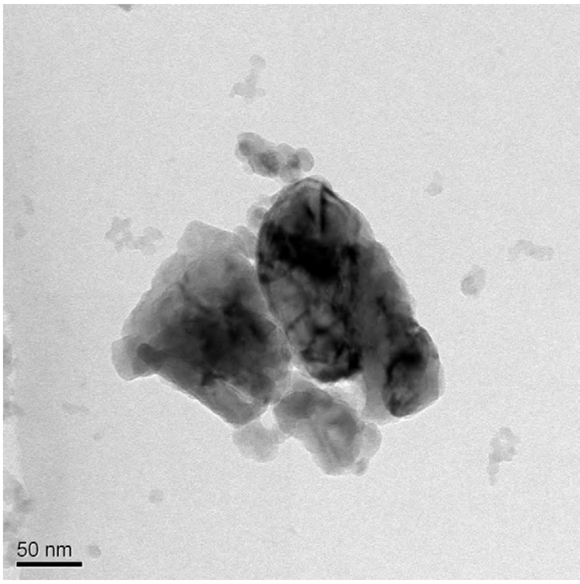

Fig. 3. TEM image of Al_2O_3-coated BST powders.

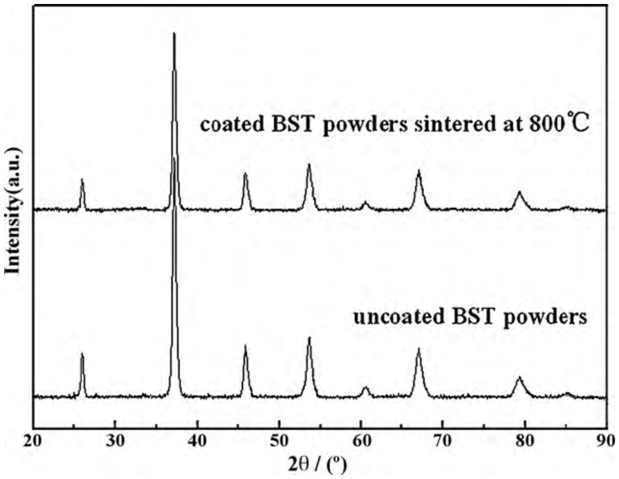

Fig. 4. XRD patterns of uncoated and Al_2O_3-coated BST powder.

amount of alumina reached 19.54%. Shen et al. [15] reported that the binding energy of Al2p of amorphous aluminum hydroxide was 74.2 eV. The binding energy of Al2p of the Al_2O_3-coated BST sample was 74.16 eV (Fig. 4), in consistence with the reported data. Combined with the XRD analyses, it is concluded that the Al_2O_3 nanofilms existed in amorphous hydrated alumina phase and were anchored at the surfaces of BST particle.

Fig. 6 shows the Zeta potential for coated and uncoated BST powders. The isoelectric point (IEP) of the uncoated BST particles is around pH 3.2, and that of the alumina-coated BST particles is around pH 8. The IEP shifts to higher pH values, and the Zeta potential of the Al_2O_3-coated BST particles approaches the one of Al_2O_3 particles, indicating that the BST particles were coated with Al_2O_3 particles. The result shows that Al_2O_3-coated BST powder can be prepared successfully by chemical coating method.

Table 1
Element content (%) on the surface of uncoated and Al_2O_3-coated BST powder.

Element	Ba	Sr	Ti	O	C	Al
Uncoated BST powder	3.24	3.51	7.45	32.68	53.12	0
Al_2O_3-coated BST powder	2.20	1.51	3.99	53.45	19.31	19.54

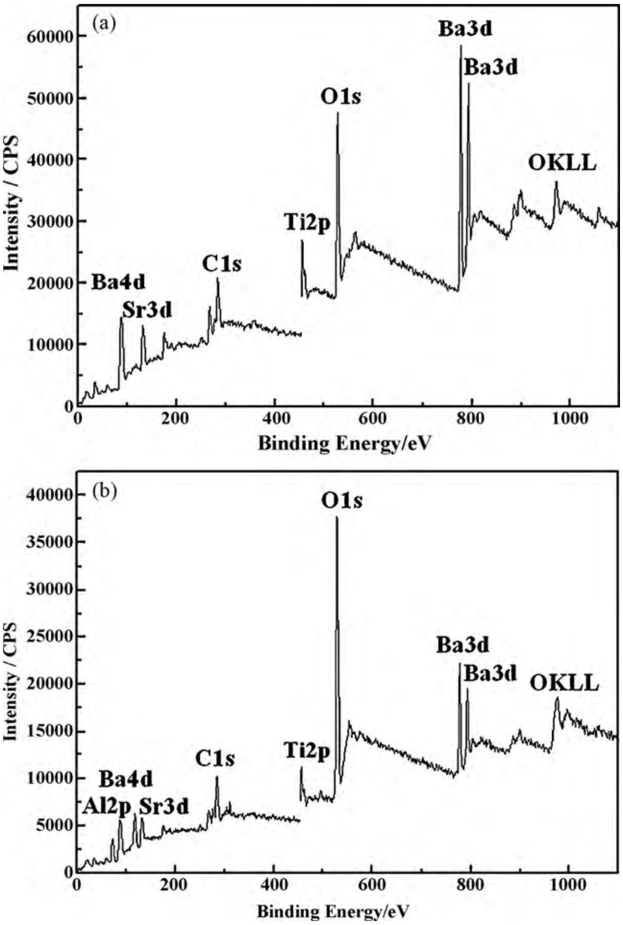

Fig. 5. XPS survey spectra of BST powders (a) uncoated BST powder; (b) Al_2O_3-coated BST powder.

3.2. Microstructure and dielectric properties of BSTZ ceramics

Fig. 7 shows the XRD patterns of BSTZ ceramics prepared by conventional solid-state reaction method (hereafter CM), and by chemical coating method (hereafter CCM) sintered at 1280 °C for 2 h. The main phases are $Ba_{0.6}Sr_{0.4}TiO_3$ and $ZnNb_2O_6$. And as expected $BaNb_{3.6}O_{10}$ phase is restrained in the samples prepared by CCM. It indicates that the coating of Al_2O_3 on BST prevents the reaction between BST and $ZnNb_2O_6$, and reduces the formation of

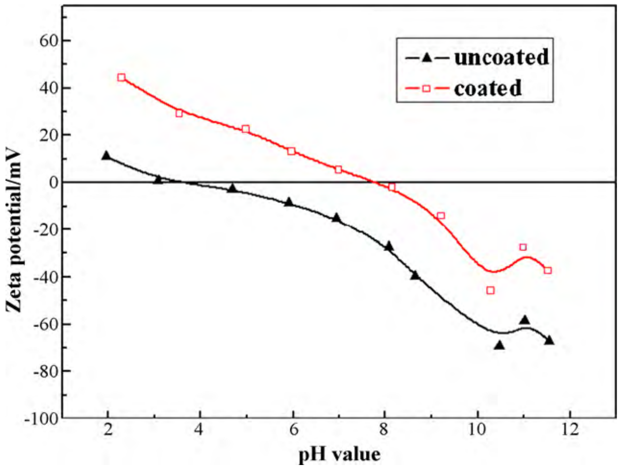

Fig. 6. Zeta potential versus pH value for uncoated and coated powders.

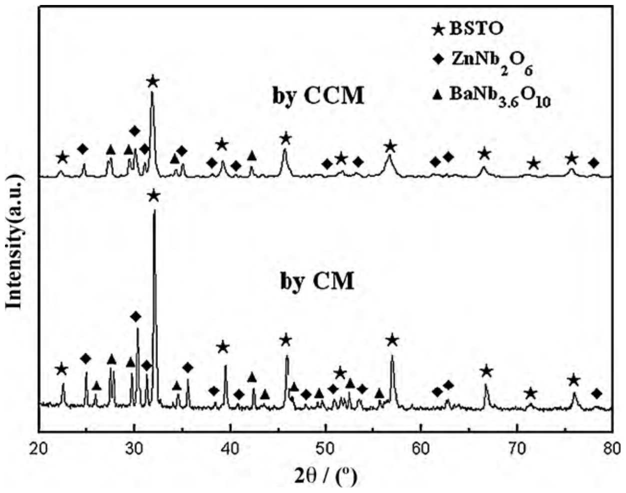

Fig. 7. XRD patterns of BSTZ composite ceramics prepared by two methods.

$BaNb_{3.6}O_{10}$ phase. However, the Al_2O_3 coating layers are not dense enough to eliminate the $BaNb_{3.6}O_{10}$ phase.

The microstructures of the BSTZ ceramics prepared by two methods are shown in Fig. 8. It is observed that the grain boundaries of the BSTZ ceramics prepared by CM are very clear. However, the microstructures of the composite by CCM are more dense with fewer pores than that of the CM. The sample prepared by CM method contains three kinds of grains, the first one is an equiaxial grain corresponding to BST, the second one is a columnar $ZnNb_2O_6$ grain, and the last is an acicular grain resulting from $BaNb_{3.6}O_{10}$, respectively. While there are only equiaxial and columnar grain coexisting in the BSTZ ceramics prepared by CCM. All of these results indicate that the Al_2O_3 coating layers prevent the reaction between BST and $ZnNb_2O_6$.

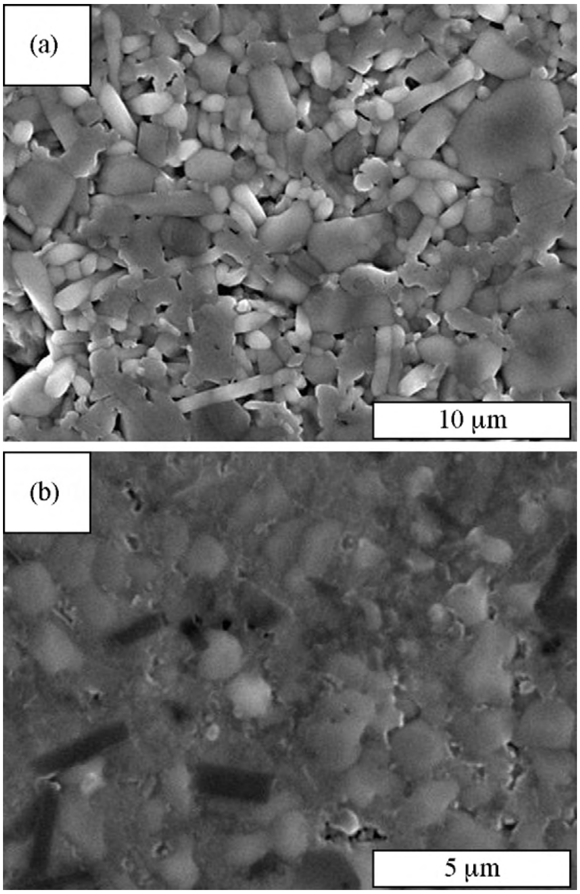

Fig. 8. SEM image of BSTZ composite ceramics (a) conventional method; (b) chemical coating method.

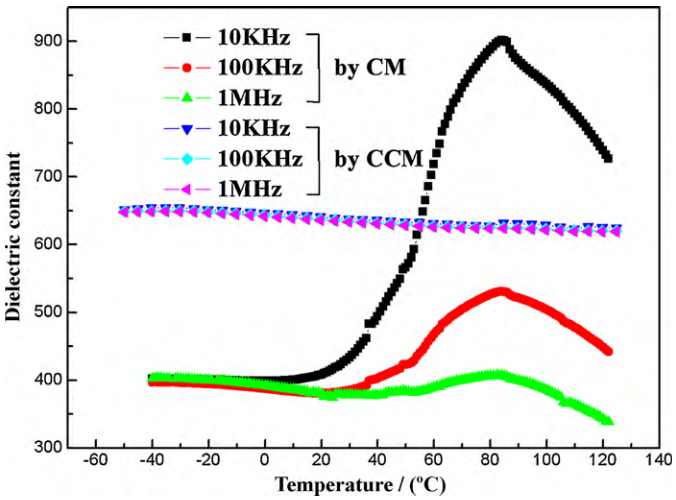

Fig. 9. Temperature dependence of dielectric constant of BSTZ composite ceramics prepared by two methods.

The temperature dependence of dielectric constant is shown in Fig. 9 for BSTZ ceramics prepared by two methods at 10 kHz, 100 kHz and 1 MHz. The permittivity peak, corresponding to the ferroelectric to paraelectric phase transition, appears in the plots of BSTZ ceramics prepared by CM. Compared with pure BST sintered at 1400 °C for 1 h [4], the dielectric constant of BSTZ ceramics prepared by CM decreased, which attributed to the low dielectric constant of $ZnNb_2O_6$ ($\varepsilon_r = 25$). It is commonly recognized that several possible factors including defects, oxygen vacancies, high strain, interfacial layers, and nonstoichiometry are the main reasons. These factors result in lower ε_{max} [16]. A strong frequency dispersion of the dielectric constant is clearly seen for the BSTZ composite ceramics prepared by CM, the maximum of dielectric constant decreases as the measurement frequency increases. The results reveal that the dipoles would contribute to the polarization of BSTZ composite ceramics under lower applied frequency. As the applied frequency increases, more polarizations could not be set up and more dipoles could not be reversed, so the dielectric constant and $\tan\delta$ will decrease [17]. While the dielectric constant of the BSTZ composite ceramics prepared by CCM shows no change with frequency. At the same time, there is no noticeable corresponding dielectric constant peak observed in the plots of BSTZ ceramics prepared by CCM. The dielectric constant of the sample prepared by CCM is higher than that of CM at room temperature. The plots of the temperature dependence of dielectric constant of CCM are all flatter than those of CM, which should be attributed to the nonferroelectric material Al_2O_3 coated on the ferroelectric material BST.

What is more, Electronic Industries Association (EIA) has set down many detailed criteria to clarify the ceramic capacitors. In X7R typed ceramic capacitors, the capacitance change from +15% to −15% is allowed with temperature from −55 °C to +125 °C [18]. As shown in Fig. 9, the dielectric constant change with temperature for BSTZ ceramics prepared by chemical coating method is less than ±5% over the temperature range of −55 °C to 125 °C, meeting the requirement of the Electronics Industries Association (EIA) X7R specification, which made it a promising candidate material used for tunable X7R typed ceramic capacitors.

The dielectric properties of BSTZ ceramics prepared by two methods at room temperature are shown in Table 2. The results

Table 2
The dielectric properties of BSTZ composite ceramics prepared by two methods.

Samples	ε_r			$\tan\delta$		
	1 kHz	10 kHz	100 kHz	1 kHz	10 kHz	100 kHz
CM	524.4	404.1	368.9	0.2581	0.1095	0.0376
CCM	644.9	640.8	637.8	0.0661	0.0199	0.0078

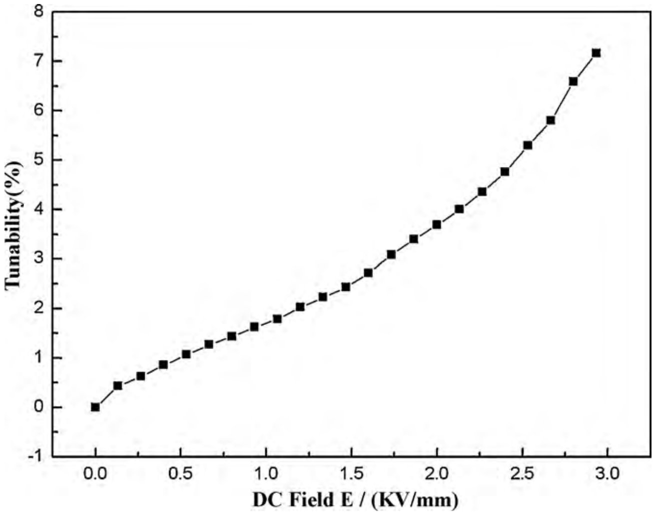

Fig. 10. Tunability of BSTZ composite ceramics prepared by chemical coating methods at 10 kH.

show substantial decrease of the dielectric loss from 0.0376 (CM) to 0.0078 (CCM) at 100 kHz, respectively. The chemical coating method also optimizes the microwave (9.4 GHz) dielectric properties of BSTZ ceramics. Comparing to the dielectric loss (0.202) of BSTZ prepared by CM, a low dielectric loss (0.07) was obtained at 9.4 GHz by CCM. The significant decrease of the dielectric loss means $ZnNb_2O_6$ contributes much more to the dielectric properties by CCM than that by CM.

Fig. 10 illustrates the tunability of BSTZ composite ceramics prepared by chemical coating method at 10 kHz and room temperature. According to Devonshire's theory, there is a functional relationship between the dielectric constant and the voltage for a ferroelectric [19]. The equation can be written as follow:

$$\frac{\varepsilon_r}{\varepsilon_0} \approx [1+\alpha\varepsilon_0^3E^2]^{-1/3} \tag{1}$$

$$\alpha = \frac{12B}{(4\pi)^3} \tag{2}$$

$$\varepsilon_0 = \frac{1}{2}A(T-T_C) \tag{3}$$

where T is the temperature, T_C is the Curie temperature.

The dielectric tunability (T_u), which is defined as the percentage of change of the dielectric constant under a specific dc field can be expressed as:

$$T_u = \frac{\varepsilon(0)-\varepsilon(E_0)}{\varepsilon(0)} \times 100\% \tag{4}$$

where $\varepsilon(0)$ is the dielectric constant at zero electric field, and $\varepsilon(E_0)$ is the dielectric constant on the applied bias electric field E_0. The tunability of the sample prepared by CM is 7.2% under a dc electric field of 3 kV/mm. Thus, it is found that a high dielectric constant of the material is really essential to its tunable behavior. The electrical breakdown property is also improved by chemical coating method from 1.6 kV/mm (CM) to 3 kV/mm (CCM).

4. Conclusions

The BSTZ composite ceramics were fabricated by using chemical coating method. In the first step, the alumina-coated BST powders were prepared successfully. The results indicated that the alumina nanofilms existed in amorphous hydrated alumina phase and were anchored at the surfaces of $Ba_{0.6}Sr_{0.4}TiO_3$ particle. The IEP of $Ba_{0.6}Sr_{0.4}TiO_3$ particle shifted from pH 3.2 to pH 8. The coating of Al_2O_3 on BST prevented the reaction between BST and $ZnNb_2O_6$ at sintering stage and reduced the formation of $BaNb_{3.6}O_{10}$ phase. The chemical coating method improved the dielectric properties of the sintered BSTZ composite ceramics. The ceramics prepared by chemical coating method exhibited excellent dielectric temperature stability, with a moderate dielectric constant ($\varepsilon_r = 640.8$) and a low dielectric loss ($\tan\delta = 0.0078$) at room temperature. The tunability of BSTZ composite ceramics was 7.2% under a dc electric field of 3 kV/mm. The chemical coating method could also improve the electrical breakdown voltage of BSTZ ceramics. It is a kind of promising materials used for tunable ceramic capacitors and phase shifter.

Acknowledgements

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