High-Permittivity and Bias-Voltage-Insensitive (Ba,Sr,Ca)TiO$_3$·0.03(Bi$_2$O$_3$·3TiO$_2$) Ceramics with Y5U Specification

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Abstract: Class II ceramics are a material with high permittivity but low reliability of their capacitance and bias voltage due to high the temperature sensitivity of their dielectric permittivity. In this work, a BST-based (Ba$_{0.9-x}$Sr$_x$Ca$_{0.1}$)TiO$_3$·0.03(Bi$_2$O$_3$·3TiO$_2$) ($x = 0.2, 0.25, 0.3, 0.35, 0.4$) composition with Y5U characteristics was investigated through compositional control to develop high-permittivity and voltage-stable ceramic compositions. Sr doping can increase the breakdown strength ($E_b$) but decreases the Curie temperature ($T_c$). The composition at $x = 0.3$ can obtain optimal comprehensive electrical properties, with high permittivity of 4206, low dielectric loss of ~0.009, and moderate breakdown strength ($E_b$) of 77.6 kV/cm, which meets Y5U specifications. Typically, a low bias-voltage dependence of capacitance is confirmed with a variation rate of 7.64% under 20 kV/cm. This strategy provides a promising candidate for high-permittivity Class II ceramic dielectrics that can be used in this field.

Keywords: lead-free ceramics; BST; dielectrics; Y5U

1. Introduction

In recent years, Ba$_{1-x}$Sr$_x$TiO$_3$ (BST) perovskite ceramics, as well as their derivatives, have been very widely investigated for energy storage, and BST ceramics are considered to be the most promising ceramic material for lead-free energy storage [1–3]. By doping and modifying BaTiO$_3$ with different amounts of Sr, a series of BST ceramics with continuously adjustable properties can be obtained [4–9]. They have been widely used in electronic devices such as high-voltage ceramic capacitors, multilayer ceramic capacitors (MLCCs), and ferroelectric thin-film memories. High-voltage ceramic capacitors are among the key components used in electronic devices, requiring high permittivity, high electrical endurance, relatively low dielectric loss, excellent temperature characteristics, and good bias stability [10]. Modified BaTiO$_3$ materials with high dielectric constants, good thermal shock resistance, and dielectric reliability are widely used in commercial MLCCs. According to the EIA standard, ceramic capacitors with high permittivity commonly have Y5V ($-30$–$85 \, ^\circ \text{C}$, $\Delta C = -82\%$–$22\%$) and Y5U ($-30$–$85 \, ^\circ \text{C}$, $\Delta C = -56\%$–$22\%$) characteristics belonging to Class II [11]. However, MLCCs that meet the Y5V characteristic are not good enough to be used in some systems because of their sensitive dielectric temperature behavior. Therefore, much attention has recently been paid to MLCCs satisfying the EIA Y5U specification. The dielectric constant–temperature curve of BaTiO$_3$-based materials can be purposely modified to be flat enough to meet these specifications by adjusting the composition. These ceramic materials typically possess high dielectric permittivity but bad reliability of their capacitance and bias voltage due to their temperature-sensitive dielectric properties. Therefore, it is of great practical significance to develop a material that
simultaneously possesses Y5U characteristics and has good bias stability. Yun et al. [12] investigated Ba$_{0.9}$Sr$_{0.1}$Ca$_{0.1}$TiO$_3$ ceramics sintered at 1280–1400 °C with a dielectric constant of about 2000 at room temperature and a breakdown strength of about 20 kV/cm. Lee et al. [13] studied Ba$_{0.3}$Sr$_{0.4}$Ca$_{0.1}$TiO$_3$ ceramics doped with 1.0 wt.% Al$_2$O$_3$ by sintering them at 1420 °C. The dielectric constant, dielectric loss, and bias stability of the samples under an electric field of 30 kV/cm were 829, 0.0039, and 12.94%, respectively. Li et al. [14] obtained Ba$_{0.3}$Sr$_{0.6}$Ca$_{0.1}$TiO$_3$ ceramics doped with 1.5–4.5 wt.% MgO by sintering them at 1340 °C, and the best performance, with a dielectric constant of 1821 and a breakdown strength of 194.3 kV/cm, was obtained at 2.0 wt.% MgO doping.

The addition of CaTiO$_3$ as a broadening agent in traditional BST-based ceramics can make the Curie peak smoother, increase the temperature stability of the material, and slightly enhance the dielectric constant with moderate doping [15–19]. However, the increasing trend is not significant, and when the amount exceeds 0.1, the dielectric constant slightly decreases [20]. A small substitution of Ba$^{2+}$ (0.143 nm) by Ca$^{2+}$ (0.106 nm) at the A site can enhance the activity of Ti$^{4+}$ ions and lead to a slight increase in the dielectric constant. However, a large amount of CaTiO$_3$ can make Ti$^{4+}$ ions difficult to move and lead to spontaneous polarization, resulting in a decrease in the dielectric constant [19]. The breakdown strength ($E_b$) increases with Ca addition, facilitating the improvement in breakdown strength and the reduction in dielectric loss. Additionally, it has been reported that when the Ca$^{2+}$/Ti$^{4+}$ ratio is greater than 1, Ca$^{2+}$ occupies the B-site to substitute for Ti$^{4+}$, and even a small amount of Ca$^{2+}$ can have a significant effect [21–24].

The addition of the sintering aid Bi$_2$O$_3$·3TiO$_2$ can reduce the sintering temperature due to its lower melting point (870 °C) and induce the formation of a liquid phase during the sintering process, which promotes the mass-transfer process, and thus, sintering. The presence of a suitable liquid phase greatly facilitates particle rearrangement and mass transport processes, which occur at the grain boundaries. Meanwhile, a small amount of Bi$_2$O$_3$·3TiO$_2$ (1.0–7.0%) can enhance the relaxation characteristics and significantly increase the dielectric constant of the material [25]. In this work, the (Ba$_{0.9-x}$Sr$_x$Ca$_{0.1}$)TiO$_3$·0.03(Bi$_2$O$_3$·3TiO$_2$) (x = 0.2, 0.25, 0.3, 0.35, and 0.4) compositions were selected to develop high-permittivity but bias-stable Class II-type dielectrics with Y5U specifications.

2. Experimental Section

A series of (Ba$_{0.9-x}$Sr$_x$Ca$_{0.1}$)TiO$_3$·0.03(Bi$_2$O$_3$·3TiO$_2$) (x = 0.2, 0.25, 0.3, 0.35, 0.4) ceramics were fabricated via solid-state synthesis. The analytically pure chemicals were selected, including BaCO$_3$ (≥99.0%), SrCO$_3$ (≥99.0%), and Bi$_2$O$_3$ (≥98.0%), and CaCO$_3$ (≥99.0%). All of the raw materials used here were produced by Sinopharm Chemical Reagent Co. Ltd. The powders were milled with absolute ethyl alcohol for 24 h with using zirconia balls, with a horizontal ball mill (GMS3-4) speed of 120 t/min. The size and mass ratio of the zirconia balls used was 3mm:5mm:7mm = 3:4:3. The mixed Bi$_2$O$_3$ and TiO$_2$ powders in a molar ratio of 1:3 were sintered at 800 °C for 2 h to form a Bi$_2$O$_3$·3TiO$_2$ phase. Similarly, the (Ba$_{0.9-x}$Sr$_x$Ca$_{0.1}$)TiO$_3$ compositions were synthesized at 1100 °C for 2 h to form solid solutions. The final ceramic compositions were designed via the combination of Bi$_2$O$_3$·3TiO$_2$ and (Ba$_{0.9-x}$Sr$_x$Ca$_{0.1}$)TiO$_3$ to be mixed via ball milling. The dried powders were calcined at 1150 °C for 2 h. The powders were mixed with PVA solutions and pressed into disc pellets at 150 MPa. The specimens were debindered at 600 °C for 2 h, and then, sintered at 1280 °C for 2 h. The ceramic pellets were covered with the final powders to avoid Bi volatilization. Finally, the ceramics were ground and polished to ~0.5 mm in thickness and coated with Ag electrodes with a diameter of nearly 6 mm.

Phase structure was evaluated via XRD analysis with a PANalytical type (PANalytical B.V., Almelo, Netherlands). The cell parameters were fitted via the Rietveld method using MDI jade 6.5 software (Livermore, CA, USA). A Quanta 450FEG-type SEM (FEI Corporation, Hillsboro, OR, USA) was employed to characterize the microstructures. The silver paste was printed on both sides of the ceramic sample for the measurement of electrical properties. An E4980A LCR analyzer was introduced to measure the dielectric constant–temperature properties.
characteristic from −40 °C to 120 °C with frequency. The bias-voltage characteristic was tested using a Concept 80 broadband dielectric spectrometer with a high-voltage module (Novocontrol GmbH, Montabaur, Germany). A PKCPE1701 ferroelectric testing system (PolyK Technologies, Philipsburg, PA, USA) was employed to measure ferroelectric P–E loops and cyclic fatigue performance.

3. Results and Discussion

Figure 1 depicts the XRD patterns of the (Ba$_{0.9-x}$Sr$_x$Ca$_{0.1}$)TiO$_3$·0.03(Bi$_2$O$_3$·3TiO$_2$) ceramics. As shown, both the (110) and (200) peaks exhibit single peaks without splitting, indicating that the ceramic samples show a typical pseudocubic phase. Moreover, the (110) and (200) diffraction peaks gradually shift towards higher angles due to the difference in the ionic radius between the Ba ion (0.135 nm) and Sr ion (0.113 nm). The cell parameters for $x = 0.2$, $x = 0.25$, $x = 0.3$, $x = 0.35$, and $x = 0.4$ are 3.9225 Å, 3.9006 Å, 3.8997 Å, 3.8994 Å, and 3.8856 Å, respectively.

![Figure 1. (a) XRD spectra of (Ba$_{0.9-x}$Sr$_x$Ca$_{0.1}$)TiO$_3$·0.03(Bi$_2$O$_3$·3TiO$_2$) ceramics; (b) locally enlarged (110) peak; (c) locally enlarged (200) peak. The arrow means that the diffraction peaks shift to high angle due to Sr doping.](image)

Figure 2 shows the microstructure of the (Ba$_{0.9-x}$Sr$_x$Ca$_{0.1}$)TiO$_3$·0.03(Bi$_2$O$_3$·3TiO$_2$) ceramic samples obtained via sintering at 1280 °C. The samples were subjected to cross-sectional thermal etching before testing, with a temperature 100 °C lower than the sintering temperature and a holding time of ten minutes. From the Figure, it can be seen that the (Ba$_{0.9-x}$Sr$_x$Ca$_{0.1}$)TiO$_3$·0.03(Bi$_2$O$_3$·3TiO$_2$) ceramics with different Sr element contents exhibit a uniform and dense microstructure, with clear grain boundaries and almost no pores. The average grain size and grain size distribution of the ceramics were calculated via the linear intercept method, as shown in Figure 2f. With increasing Sr content, the average grain size gradually decreases. The average grain sizes at $x = 0.2$, 0.25, 0.3, 0.35, and 0.4 are 0.79 µm, 0.75 µm, 0.69 µm, 0.63 µm, and 0.62 µm, respectively. This is because the substitution of smaller Ca$^{2+}$ and Sr$^{2+}$ ions for larger Ba$^{2+}$ ions leads to a decrease in the interplanar spacing, resulting in lattice contraction and grain refinement in the ceramics [26–28]. This observation is consistent with the XRD analysis.

Figure 3 illustrates the dielectric constant–temperature-dependence of the (Ba$_{0.9-x}$Sr$_x$Ca$_{0.1}$)TiO$_3$·0.03(Bi$_2$O$_3$·3TiO$_2$) ceramics with frequencies from 100 Hz to 1 MHz. It can be observed that the samples exhibit typical relaxor ferroelectric characteristics with significant frequency dispersion. As the frequency increases, the Curie peak shifts towards high temperatures. Moreover, this phenomenon becomes more pronounced with increasing Sr$^{2+}$ content [9,12,16]. This can be attributed to the fact that the Curie temperature of BaTiO$_3$ is around 120 °C, while that of SrTiO$_3$ is approximately −250 °C. Therefore, the Curie temperature of the ceramics can be adjusted by adding Sr$^{2+}$. The main mechanism for this adjustment is as follows: the radius of Sr$^{2+}$ (0.113 nm) is smaller than that of Ba$^{2+}$ (0.135 nm). When a portion of the larger Ba$^{2+}$ ions is replaced by smaller Sr$^{2+}$ ions, it leads to a contraction in the unit cell volume. This reduces the mobility of Ti$^{4+}$ ions in
the oxygen octahedra, resulting in weaker activity of Ti$^{4+}$ ions towards the oxygen atoms at lower temperatures. This leads to spontaneous polarization and a decrease in Curie temperature [8,9,28–30]. The efficiency of Curie temperature shifting in pure Ba$_x$Sr$_{1-x}$TiO$_3$ can be calculated using the following formula:

$$\eta = \frac{t_{CB} - t_{CA}}{100}$$

(1)

Figure 2. SEM images of (Ba$_{0.9-x}$Sr$_x$Ca$_{0.1}$)TiO$_3$·0.03(Bi$_2$O$_3$·3TiO$_2$) bulk ceramics: (a) $x = 0.2$; (b) $x = 0.25$; (c) $x = 0.3$; (d) $x = 0.35$; (e) $x = 0.4$; (f) variation in the average grain size.

Figure 3. Dielectric constant–temperature spectra of the (Ba$_{0.9-x}$Sr$_x$Ca$_{0.1}$)TiO$_3$·0.03(Bi$_2$O$_3$·3TiO$_2$) ceramics with various frequencies: (a) $x = 0.2$; (b) $x = 0.25$; (c) $x = 0.3$; (d) $x = 0.35$; (e) $x = 0.4$; (f) the variation in Curie temperature with Sr element content.

In this formula, $\eta$ represents the mobility in degrees Celsius per mole of Curie temperature shift, indicating the change in Curie temperature for each mole or 1% substitution of A-site or B-site ions. $t_{CA}$ is the Curie temperature of the matrix material, and $t_{CB}$ is the Curie temperature of the substituting material. Upon calculating the formula, $\eta$(SrTiO$_3$) is $-3.7$ ($^\circ$C/mol%), which means that adding 1% (molar fraction) of SrTiO$_3$ to BaTiO$_3$ can decrease its Curie temperature by 3.7 $^\circ$C. As shown in Figure 3f, the Curie temperatures at $x = 0.2$, 0.25, 0.3, 0.35, and 0.4 are 53.62 $^\circ$C, 31.35 $^\circ$C, 9.17 $^\circ$C, $-0.41$ $^\circ$C, and $-24.03$ $^\circ$C, respectively. The phase structure gradually transfers from a ferroelectric to a paraelectric state near room temperature due to compositional modulation [12,26,31–34].

According to the Electronic Industries Association (EIA) standard, the temperature characteristics of capacitors are typically characterized by the ratio of the capacitance under bias voltage, and the change rate of capacitance is only 7.64%, indicating good bias stability of the sample.
change ΔC/C. It can be observed in Figure 4 that the sample at x = 0.3 exhibits Y5U-type temperature characteristics.

![Figure 4](image)

**Figure 4.** The capacitance–temperature variation rate curve for \((\text{Ba}_{0.9-x}\text{Sr}_x\text{Ca}_{0.1})\text{TiO}_3\cdot0.03(\text{Bi}_2\text{O}_3\cdot3\text{TiO}_2)\) ceramics.

The phenomenon of a decrease in actual capacitance when a DC voltage is applied to a capacitor is called the DC bias characteristic of the capacitor. This characteristic mainly occurs in ceramic capacitor materials with high dielectric constants, such as barium titanate-based ferroelectric ceramics. For ferroelectrics, bias voltage can induce switching of the ferroelectric dipole along the electric field. For a given ceramic capacitor, it can always be used in an external electric field, which can easily impact the stability of the capacitance. Figure 5 shows the voltage dependence of the dielectric constant of \((\text{Ba}_{0.9-x}\text{Sr}_x\text{Ca}_{0.1})\text{TiO}_3\cdot0.03(\text{Bi}_2\text{O}_3\cdot3\text{TiO}_2)\) ceramics. As seen, the dielectric constant decreases under bias voltage, and the change rate of capacitance is only 7.64%, indicating good bias stability of the sample.

![Figure 5](image)

**Figure 5.** Voltage dependence of dielectric constant and capacitance of the \((\text{Ba}_{0.6}\text{Sr}_{0.3}\text{Ca}_{0.1})\text{TiO}_3\cdot0.03(\text{Bi}_2\text{O}_3\cdot3\text{TiO}_2)\) ceramics.

Temperature stability is an important parameter for measuring ceramic dielectric materials. Ceramic dielectric materials need to be used at different temperatures, so they need to have good temperature stability. Figure 6 depicts the temperature dependence and cyclic dependence of ferroelectric polarization of the \((\text{Ba}_{0.9-x}\text{Sr}_x\text{Ca}_{0.1})\text{TiO}_3\cdot0.03(\text{Bi}_2\text{O}_3\cdot3\text{TiO}_2)\) ceramics. It can be observed that as the temperature increases, the maximum polarization \(P_m\) of the ceramics gradually decreases, while the residual polarization \(P_r\) remains unchanged. This is consistent with the dielectric constant–temperature characteristic. The cyclic stability of ceramics can evaluate their long-term stability and enable us to assess whether performance degradation occurs during cycling. Figure 6c,d show the changes in the P-E loops
and ferroelectric polarization of the ceramics before and after $10^5$ cycles. It can be observed that ferroelectric polarization of the ceramic shows no significant changes after $10^5$ cycles. The maximum polarization ($P_m$) of the ceramic slightly increases from 27.06 $\mu$C/cm$^2$ to 28.19 $\mu$C/cm$^2$, and the remnant polarization ($P_r$) slightly increases from 5.06 $\mu$C/cm$^2$ to 6.27 $\mu$C/cm$^2$, respectively. This indicates that the (Ba$_{0.9-x}$Sr$_x$Ca$_{0.1}$)TiO$_3$·0.03(Bi$_2$O$_3$·3TiO$_2$) ceramic exhibits excellent cyclic reliability in long-term use.

**Figure 5.** Voltage dependence of dielectric constant and capacitance of the (Ba$_{0.9-x}$Sr$_x$Ca$_{0.1}$)TiO$_3$·0.03(Bi$_2$O$_3$·3TiO$_2$) ceramics.

**Figure 6.** (a) Temperature-dependent P-E loops, (b) temperature-dependent ferroelectric polarization, (c) P-E loops for 100 k cycles, and (d) ferroelectric polarization of the (Ba$_{0.6}$Sr$_{0.3}$Ca$_{0.1}$)TiO$_3$·0.03(Bi$_2$O$_3$·3TiO$_2$) ceramics after 100 k cycles.

**4. Conclusions**

In this study, a series of (Ba$_{0.9-x}$Sr$_x$Ca$_{0.1}$)TiO$_3$·0.03(Bi$_2$O$_3$·3TiO$_2$) ceramics ($x$ = 0.2, 0.25, 0.3, 0.35, 0.4) with Y5U characteristics were prepared using the solid-state method. The XRD test results indicated that all samples exhibited the typical perovskite structure. The SEM results revealed that the samples displayed a dense microstructure. The dielectric property test results showed that with an increase in Sr content, the Curie temperatures of the samples shifted towards lower temperatures. The samples transformed from the ferroelectric phase to the paraelectric phase. At $x$ = 0.3, they were in a phase transition phase (morphotropic phase boundary) and achieved optimal performance. The optimal electrical properties can be achieved with a high dielectric constant $\varepsilon_r$ of 4206, low dielectric loss $\tan\delta$ of 0.009, and high breakdown strength $E_b$ of 77.6 kV/cm, which meets the Y5U specification. Additionally, the capacitance variation rate is only 7.64% under a high bias voltage of 20 kV/cm, which is indicative of good bias-voltage stability. It can be concluded that the ceramics exhibit high capacitance, good cyclic stability, and bias-voltage stability suitable for potential use in Y5U-type ceramic capacitors.

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