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# Development of Ferroelectric Ceramics with High Dielectric Constant and Low Dissipation Factor for High-Voltage Capacitors

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**Abstract.** Both ferroelectric $BaTiO_3$-based and $SrTiO_3$-based dielectric ceramics with high dielectric constant and low dissipation factor have been successfully developed, and applied into mass production for high-voltage ceramic capacitors. Crystalline phases of the ceramics were identified by XRD. STEM study of the ceramics was also conducted. Based on the computer simulation of a shell-core and two-phase mixed structural model proposed, a novel processing method was employed to produce $SrTiO_3$-based ceramics with the following satisfactory dielectric properties: dielectric constant at room temperature $\varepsilon_{20'C} = 2000$, dissipation factor at room temperature $D_{20'C} = 0.003$, temperature coefficient of dielectric constant $\alpha_\varepsilon = -8\%$ ($-25$°C to 85°C), and, breakdown electric field $E_b = 10$ kV/mm (dc). Optional composition of $BaTiO_3$-based ceramics has been obtained through the orthogonal design experimentation: $BaTiO_3$—$x$$BaZrO_3$—$y$$BaSnO_3$, where $x = 8$ wt% and $y = 6$ wt%, with minor additions of $MnSiO_3$, $WO_3$, $CeO_2$, $Bi_2(SnO_3)_3$ and ZnO. Its major properties are as follows: Curie temperature $T_c = 21$°C, $\varepsilon_{20'C} = 18,000$, $D_{20'C} = 0.008$, $\alpha_\varepsilon = -80\%$ ($-25$°C $\sim +85$°C) and $E_b = 8$ kV/mm (dc).

**Keywords:** ferroelectric ceramics, computer simulation, ceramic capacitors, orthogonal design experimentation, XRD and STEM

## 1. Introduction

With the continuous trend of miniaturization of electronic devices and components, it is of key importance to develop high quality dielectric ceramics with high dielectric constant ($\varepsilon$) and low dissipation factor ($D$) for high-voltage capacitors, used in color TV, computer monitors, lasers and so on [1]. Naturally, ferroelectric ceramic materials are good candidates due to their high dielectric constants [2].

$BaTiO_3$-based ferroelectric ceramics are classic dielectric materials for ceramic capacitors [3]. It is well known that $BaTiO_3$ has the so-called perovskite $ABO_3$ cubic structure between 120°C and 1460°C, and, pseudo-cubic structure below 120°C [4]. At about 120°C there is a phase transition between paraelectric and ferroelectric phase, at the Curie point temperature, $T_c$. Within this temperature region, high $\varepsilon$ values can be obtained, but large $D$ and $\alpha_\varepsilon$ values are usually accompanied, which are not desired for ceramic capacitors. Moreover, high electric withstanding ability (breakdown electric field $E_b$) is desired for high-voltage ceramic capacitors. Therefore, $BaTiO_3$-based dielectric ceramics need to be improved, including the addition of chemicals that can shift the $T_c$ value to room temperature and to

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select carefully some kinds of reagents that can enhance $\varepsilon$ and minimize the values of $\alpha_\varepsilon$ and $D$.

However, $SrTiO_3$-based ceramics prepared by the conventional processing of electro-ceramics have the advantages of a lower $D$ value and higher $E_b$ value, but the disadvantage of larger $\alpha_\varepsilon$ value which arises from the ferroelectric–paraelectric transition. The problem can be solved if $\alpha_\varepsilon$ can be minimized within the working temperature range, for example, $-25°C$ to 85°C. This can be achieved when there are two or more Curie points, $T_c$, in the $\varepsilon - T$ curve, by the addition of other compositions with different values of $T_c$ in the basic composition [5,6]. This paper reports the successful results achieved to improve the properties of $BaTiO_3$-based and $SrTiO_3$-based ceramics for high-voltage capacitors.

## 2. Experiment

Though the co-precipitation (solution or wet) reaction method had also been tried in our laboratory, the solid-state reaction method was finally selected, so as to reduce product cost and be suitable for conventional production lines. Orthogonal design experimentation was used to optimize ceramic properties. Raw chemicals used are as follows: $BaCO_3$, $TiO_2$, $SrCO_3$, $CaCO_3$, $ZrO_2$, $SnO_2$, MnO2, $SiO_2$, $WO_3$, $CeO_2$, $Bi_2O_3$ and ZnO, with purity better than 98%. After being weighed according to the designed compositions, the chemicals were ball-milled and calcined at 1200°C for 1 h. Then they were ground, milled again with PVA (polyvinyl alcohol) solution binder and spray-dried for granulating. The dried powders were hydro-pressed into pellets and sintered at $1300 \pm 50°C$ for 2 h.

The crystallography of the ceramics was characterized by XRD (X-ray Powder Diffractor, Rikagu Co., Japan). The microstructure of the ceramics was observed using SEM (Scanning Electron Microscope, Leica Co., England) and STEM (Scanning Transmission Electron Microscope, JEOL, Japan). After the ceramics were coated with silver paste and treated at 700°C for 20 min, the temperature dependences of dielectric constant and dissipation factor were measured by an HP-4284A meter with heating rate of 1°C per minute. The breakdown electric field $(E_b)$ was obtained by averaging 10 values of one batch of samples under a high-voltage breakdown tester.

However, based on a computer simulation result, a novel processing method has been applied to significantly minimize the $\alpha_\varepsilon$ value of $SrTiO_3$-based ceramics as follows. Commercially available chemicals were also employed. Two kinds of compositions, according to the formula of $(Sr_xPb_{1-x})TiO_3$ with $x$ values of 0.5 and 0.8, were milled and calcined, respectively, resulting in two kinds of calcined powders with different values of $T_c$. They were then mixed together using a certain weight percentage and with the addition of several additives, including $MnO_2$ and $SiO_2$. The mixtures were ball-milled, spray-dried, pressed and sintered in a similar way as the conventional processing.

## 3. Proposed Model and Computer Simulation

With the fast development of computer technology, the computer simulations in materials science become more and more helpful [7–9]. In order to find a possibility to effectively minimize the $\alpha_\varepsilon$ value of ceramics, a computer simulation of the temperature dependence of dielectric constant $(\varepsilon - T)$ has been conducted. Figure 1 shows the proposed shell-core and two-phase mixed structural model and its simplified equivalent electric circuits. In this way, the ceramic body may be taken as a composite system, consisting of ferroelectric grain-cores and paraelectric grain-shells, and/or ferroelectric grains and paraelectric grains. The Lichtenecker's logarithmic expression of mixture rule was used in the prediction of the total property of the resulting ceramics [10], as follows

$$\ln \varepsilon = V_1 \ln \varepsilon_1 + V_2 \ln \varepsilon_2$$

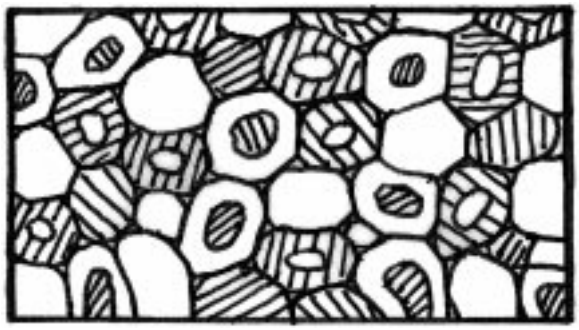

*Fig. 1.* The proposed shell-core and two-phase mixed structural model.

where $\varepsilon$, $\varepsilon_1$ and $\varepsilon_2$ are the dielectric constants of total system, phase 1 and phase 2, respectively; $V_1$ and $V_2$ are the volume fractions of the phase 1 and phase 2, respectively, and $V_1 + V_2 = 1$. In this paper, phase 1 and phase 2 corresponded to two different powders of calcined ceramics with different values of $T_c$, and, $V_1$ and $V_2$ are the volume fractions used. The values of $\varepsilon_1$ and $\varepsilon_2$ were the dielectric constants that were measured on the individual ceramics, which were separately sintered, curve A and E in Fig. 2, respectively.

The $\varepsilon - T$ curves calculated with different volume fractions of the powders (curves *B*, *C* and *D*) are shown in Fig. 2, which are the simulated results based on the experimental data (curves *A* and *E*) of two kinds of practical ceramics with different values of $T_c$. It can be seen that the $\alpha_\varepsilon$ value can obviously be minimized (curve *C*) by suitably selecting the volume fraction, which corresponded to different structural parameters such as the thicknesses of the grain-shell and grain-core, and/or volumes of ferroelectric grains and paraelectric grains in the ceramic system.

## 4. Experimental Results and Discussion

### *4.1. $BaTiO_3$-Based Ceramics*

Both $BaSnO_3$ and $BaZrO_3$ were added into the $BaTiO_3$ matrix at a ratio of 8 mol% and 6 mol%, respectively, since they not only are totally soluble in $BaTiO_3$, but also can lower $T_c$ as the Ti ion can be partially replaced by Sn and Zr ions. Experiment results (Fig. 3) show that they can remarkably enhance the dielectric constant in addition to decreasing the *D* value of the ceramics within the working temperature region. This may be due to the superposition of multiple peaks in the $\varepsilon - T$ plot as the result of different transition points in different micro-regions. On the other hand, paraelectric $BaSnO_3$ and $BaZrO_3$ dispersed in the $BaTiO_3$ matrix could also ease local ferroelectricity, thus acting as a ''dielectric dilutant'', and supply larger free space for reorientation of electric domains and development of new domains [5].

In addition, $Bi_2(SnO_3)_3$ had also been added which could effectively smooth the $\varepsilon - T$ curve of the ceramics. It may be due to the disappear of ferroelectricity in certain micro-regions, where the Ba ion has been replaced by Bi in the *A* position of the perovskite $ABO_3$ structure. Since the radius of the Bi ion is equal to 0.12 nm which is smaller than that of the Ba ion (0.16 nm), the octahedral space formed by both the Bi ion and O ions closed-occupied face-center cube is too small for Ti to move. Consequently, there is no spontaneous polarization in such micro-regions, and, a smoothing effect was achieved. It is noteworthy that Bi will obviously decrease the $\varepsilon$ value at the same time as smoothing the $\varepsilon - T$ curve. So, the additional amount of $Bi_2(SnO_3)_2$ is usually limited to within 1 wt%.

Minor additions, such as $WO_3$, $CeO_2$, $MnSiO_3$ and ZnO, also have effect on decreasing D. These additions may form second phases on grain boundaries, and lower the resistant force for the reorientation of electric domains in grains.

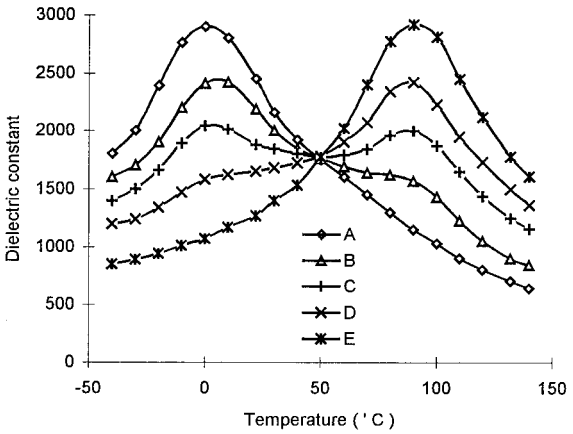


*Fig. 2.* The temperature dependence of dielectric constant simulated.

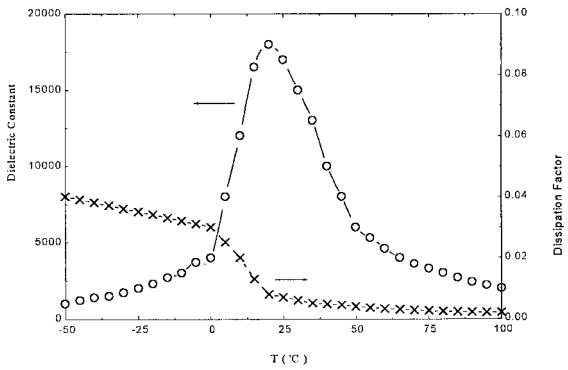


*Fig. 3.* The temperature dependence of dielectric constant of $BaTiO_3$-based ceramics.

The orthogonal design experimentation had been applied to optimize the composition and processing parameters for optimal dielectric properties of the ceramics. The factor-level table $L_9(3^4)$ of the orthogonal design was selected [11]. The values used for the table are shown in Table 1, which is an example of the experiment to optimize the sintering temperature $(T_s)$, and amounts of ZnO, $WO_3$ and $MnSiO_3$. The data of 9 prepared compositions are presented in Table 2, in addition to the base constituent: $BaTiO_3$—$x$BaZrO$_3$—$y$BaSnO$_3$, where $x = 8$ wt% and $y = 6$ wt%. The experimental results are shown in Fig. 4, which was treated by the polar-difference analysis. It can be seen [Fig. 4(a)] that $\varepsilon$ increase first and then decreases with increasing sintering temperature; whereas, $D$ showed little change during this temperature range. Therefore, $T_s = 1330$°C was the optional value. Figure 4(b) show that $\varepsilon$ decreases a little with the increase of ZnO, and $D$ decreases obviously in the same time. Thus, 0.2 wt% of ZnO is better. However, $\varepsilon$ increases

*Table 1.* The values for the factor-level table $L_9(3^4)$ of the orthogonal design

| | Factor A T (°C) | Factor B ZnO (wt%) | Factor C $WO_3$ (wt%) | Factor D $MnSiO_3$ (wt%) |
|---|---|---|---|---|
| Level 1 | 1310 | 0.1 | 0.3 | 0.1 |
| Level 2 | 1330 | 0.2 | 0.4 | 0.15 |
| Level 3 | 1350 | 0.4 | 0.5 | 0.2 |

*Table 2.* Data of 9 compositions of the table $L_9(3^4)$

| Compositions No. | T (°C) | ZnO (wt%) | $WO_3$ (wt%) | $MnSiO_3$ (wt%) |
|---|---|---|---|---|
| 1 | 1310 | 0.1 | 0.3 | 0.1 |
| 2 | 1310 | 0.2 | 0.4 | 0.15 |
| 3 | 1310 | 0.4 | 0.5 | 0.2 |
| 4 | 1330 | 0.1 | 0.4 | 0.2 |
| 5 | 1330 | 0.2 | 0.5 | 0.1 |
| 6 | 1330 | 0.4 | 0.3 | 0.15 |
| 7 | 1350 | 0.1 | 0.5 | 0.15 |
| 8 | 1350 | 0.2 | 0.3 | 0.2 |
| 9 | 1350 | 0.4 | 0.4 | 0.1 |

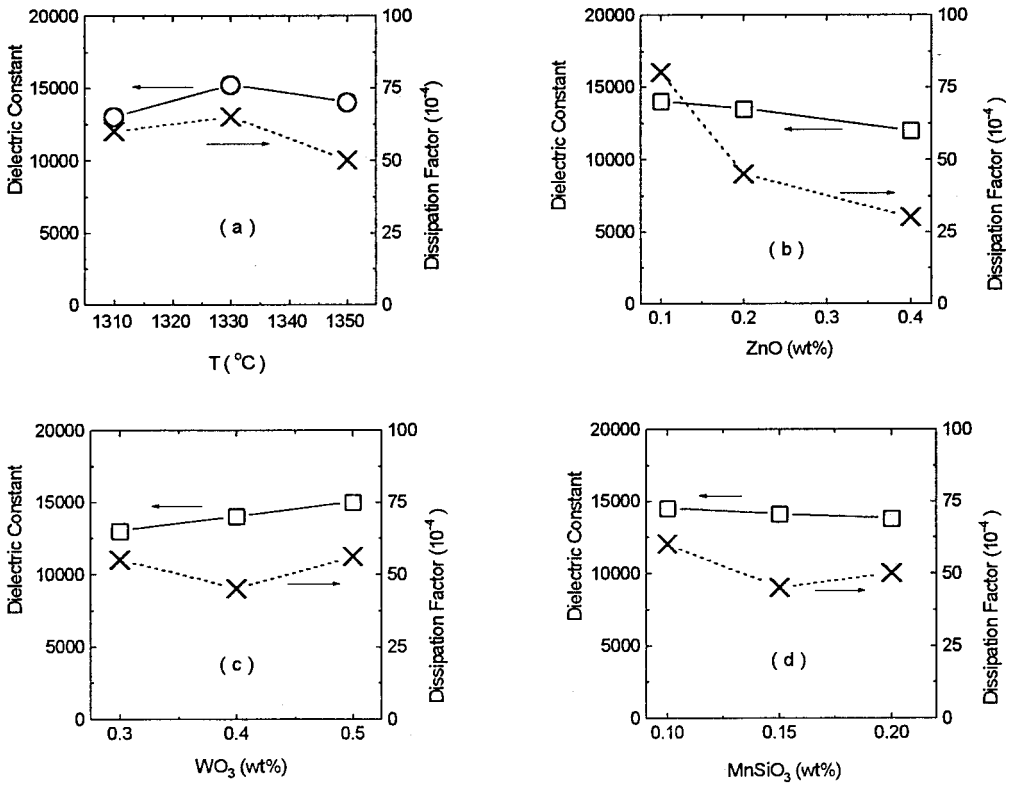


*Fig. 4.* The results of orthogonal design experimentation of $BaTiO_3$-based ceramics.

linearly with increase of $WO_3$ and at the same time $D$ is almost unchanged [Fig. 4(c)], then, 0.5 wt% of $WO_3$ is suitable. With the increase of $MnSiO_3$, $\varepsilon$ decrease slowly and $D$ changes little [Fig. 4(d)], 0.1 wt% of $MnSiO_3$ is the optional one. In this manner, we obtained the best dielectric properties of the ceramics as follows: $T_c = 21°C$, $\varepsilon_{20'C} = 18{,}000 \pm 1{,}500$, $D_{20'C} = 0.0080 \pm 0.0005$, $\alpha_\varepsilon = -(80 \pm 3)\%(-25 \text{ to } +85\,°C)$, $E_b(\text{dc}) = 8.0 \pm 0.5$ kV/mm, $E_b(\text{ac}) = 3.0 \pm 0.2$ kV/mm.

### 4.2. $SrTiO_3$-*Based Ceramics*

The temperature dependencies of the dielectric constant of the $SrTiO_3$-based ceramics are presented in Fig. 5. Curves $A$ and $E$ were obtained from different ceramic samples with only one, different value of $T_c$ processed by the conventional method. Curves $B$, $C$ and $D$ correspond to three ceramic samples, displaying two $T_c$ peaks. They were mixed with different weight percentages of the two calcined powders according to the formula of $(Sr_xPb_{1-x})TiO_3$ with $x$ values of 0.5 and 0.8, i.e., sample $B$, $C$ and $D$ consisted of 75 wt%, 50 wt% and 25 wt% of the calcined powder with $x$ value of 0.5, respectively. Sample $C$ shows a smooth $\varepsilon - T$ relationship, which was optimized for both chemical composition and processing parameters, and exhibits the satisfactory dielectric properties of: $\varepsilon_{20'C} = 2000 \pm 130$, $D_{20'C} = 0.0030 \pm 0.0002$, $\alpha_\varepsilon = -(8 \pm 1)\%(-25°C$ to $85°C)$, $E_b(\text{dc}) = 10 \pm 0.5$ kV/mm, and $E_b(\text{ac}) = 4.0 \pm 0.3$ kV/mm.

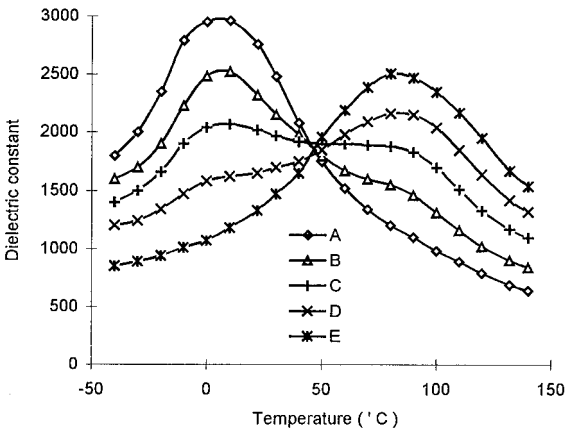


*Fig. 5.* The temperature dependence of dielectric constant of $SrTiO^3$-based ceramics.

Figure 6 shows X-ray diffraction spectra of the $SrTiO_3$-based ceramics with one value of $T_c$ (sample $A$) and two values of $T_c$ (sample $C$), respectively. The peaks of the ceramics with two values of $T_c$ are rather low, but are broadened, which may be due to an inhomogeneously distributed chemical composition, as will be demonstrated by the results obtained using electron microscopy below.

The analytical results obtained using STEM (Scanning Transmission Electron Microscope) equipped with EDAX is shown in Fig. 7, whilst Fig. 8 shows the corresponding sampling points. It can be seen that the relative contents of elements change in the different sampling points, especially for the ceramics with two values of $T_c$ near to the grain boundaries. These results show that there is an inhomogeneously distributed chemical composition in the ceramics.

## 5. Concluding Remarks

In attempting to achieve enhanced $\varepsilon$ values, shifting of the $T_c$ point and smoothing of the $\varepsilon - T$ curve, a new

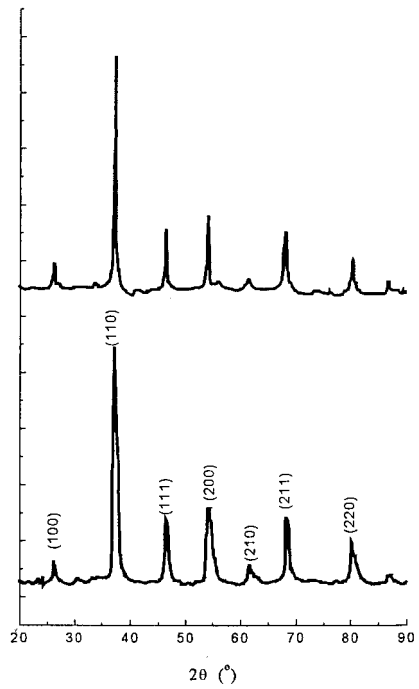


*Fig. 6.* X-ray diffraction spectra of $SrTiO_3$-based ceramics with: (a) one value of $T_c$ (sample A) and (b) two values of $T_c$ (sample C) respectively.

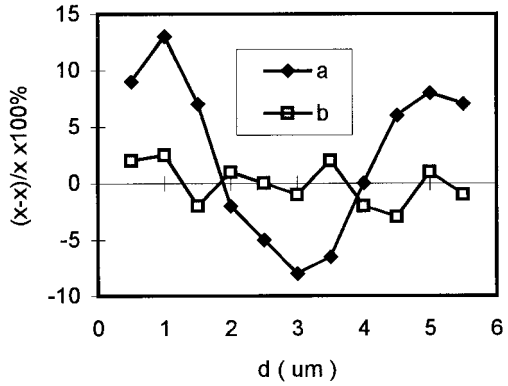


*Fig. 7.* The relative contents of element Sr vs. sampling positions of the ceramics with: (a) one value of $T_c$ (sample A) and (b) two value of $T_c$ (sample C).

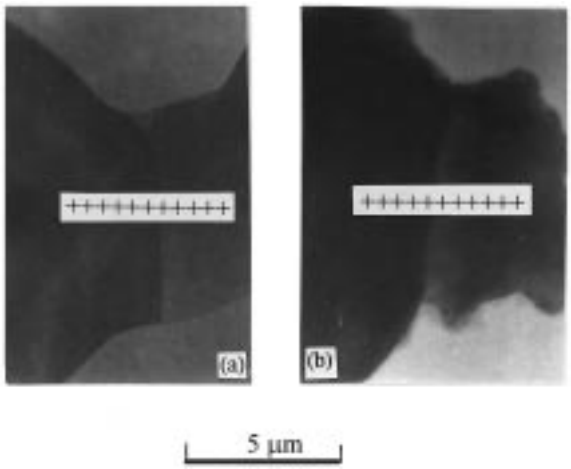


*Fig. 8.* The STEM images of the ceramics with sampling positions indicated: (a) one value of $T_c$ (sample A) and (b) two value of $T_c$ (sample C).

type of ferroelectric $BaTiO_3$-based dielectric ceramic with high dielectric constant and low dissipation factor has been successfully developed and applied into batch production for high-voltage ceramic capacitors. Optional compositions have been obtained through orthogonal design experimentation: $BaTiO_3$—$x$$BaZrO_3$—$y$$BaSnO_3$, where $x = 8$ wt% and $y = 6$ wt%, with minor additions of $MnSiO_3$, $WO_3$, $CeO_2$, $Bi_2(SnO_3)_3$ and ZnO. Major properties are as follows: $T_c = 21°C$, $\varepsilon_{20'C} = 18{,}000 \pm 1{,}500$, $D_{20'C} = 0.0080 \pm 0.0005$, $\alpha_\varepsilon = -(80 \pm 3)\%(-25$ to $+85°C)$, $E_b(\mathrm{dc}) = 8.0 \pm 0.5$ kV/mm, $E_b(\mathrm{ac}) = 3.0 \pm 0.2$ kV/mm.

Based on the computer simulation of a shell-core and two-phase mixed structural model proposed, a novel processing method was employed to produce $SrTiO_3$-based ceramics with the following satisfactory dielectric properties: $\varepsilon_{20'C} = 2000 \pm 130$, $D_{20'C} = 0.0030 \pm 0.0002$, $\alpha_\varepsilon = -(8 \pm 1)\%(-25°C$ to $85°C)$, $E_b(dc) = 10 \pm 0.5$ kV/mm, and $E_b(\mathrm{ac}) = 4.0 \pm 0.3$ kV/mm, which has also been applied for mass production for high quality ceramic capacitors.

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