THE DIFFUSE PHASE TRANSITION OF Ti-RICH (Ba\(_{0.75}\)Sr\(_{0.25}\))

\[ \text{Ti}_{1-x}\text{O}_{3+2} \]

DIELECTRIC CERAMICS

PREHOD DIFUZIVNE FAZE V DIELEKTRIČNE KERAMIKE,

BOGATE S Ti ((Ba\(_{0.75}\)Sr\(_{0.25}\), Ti\(_{1+x}\)O\(_{3+2}\))

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1 INTRODUCTION

Ferroelectric barium titanate (BaTiO\(_3\), BT) possesses a typical perovskite structure ABO\(_3\), which is used in many electronic devices, including high-permittivity multilayer ceramic capacitors (MLCC’s).\(^1\) The interest in BT stems from the high relative permittivity 10,000–12,000, observed at the ferro- to para-electric phase-transition temperature (about 130\(^\circ\)C), also known as the Curie temperature \(T_c\). Above \(T_c\), in the paraelectric state, the temperature dependence of the dielectric constant follows the Curie-Weiss law and around \(T_c\), a sharp Curie peak can always be found.

To meet the tolerances of the percentage change of capacitance \(\Delta C\) over a certain temperature range\(\Delta T\) for the different specifications of MLCCs, various dopants are often applied in BT dielectric ceramics.\(^3\),\(^5\) The majority of dopants added into BT cause a drop of \(T_c\), and some of them succeed in inducing the diffuse phase transition. For example, the substitution of Zr\(^{4+}\) with isovalent Ti\(^{4+}\) results in a solid solution from BT to Ba(Ti\(_{1-x}\)Zr\(_{x}\))O\(_3\) (BZT) and causes typical relaxor ferroelectric behavior characterized by the frequency dispersion of the relative permittivity maximum as well as a diffuse phase transition as \(x\) approaches 0.3.\(^6\),\(^7\) However, some of the dopants fail to modify the temperature stability of the capacitance, especially around the \(T_c\). For instance, the solid solution (Ba\(_{1-x}\)Sr\(_x\))TiO\(_3\) (BST) resulting from the substitution of Sr\(^{2+}\) with isovalent Ba\(^{2+}\) in BT still has a sharp Curie peak, even when \(x\) equals 0.4.\(^8\)

For practical capacitor applications, a further modification in BST ceramics is inevitable. Three common methods are employed: the addition of isovalent or aliovalent dopants such as Mg,\(^9\) Na,\(^10\) etc.; process controlling especially the calcination/sintering progress;\(^11\),\(^12\) and the usage of functionally graded materials (FGMs).\(^5\) Among the dopants, rare-earth elements (e.g., La\(^{3+}\), Dy\(^{3+}\), Sm\(^{3+}\)) are found to be effective in controlling the temperature dependency of the dielectric properties in stoichiometric BST ceramics.\(^13\)-\(^15\) The diffused ferroelectric-paraelectric phase transition accompanied by the comprehensive properties can be obtained in Ho\(_2\)O\(_3\) highly doped (Ba\(_{0.75}\)Sr\(_{0.25}\))TiO\(_3\) ceramics according to our previous study.\(^16\) The high unchanged dielectric constant with a slight decrease of loss tangent has been found in...
Ba-excessive Ba$_{0.71}$Sr$_{0.29}$TiO$_3$ ceramics$^{17}$ and adding deficient TiO$_2$ could bring about a diffuse phase transition in BST ceramics,$^{18}$ which provides us with the possibility to obtain fine dielectrics for ceramic capacitors by controlling the mole ratio of A-site ion to B-site ion ($n_A/n_B$) in BST ceramics. Furthermore, the dielectric temperature stability of the BST ceramics can be somehow improved by applying excessive TiO$_2$.\(^{19}$

Previous findings sparked our interest in finding out how the Ti-rich level influencing the dielectric properties and phase-transition behavior in non-stoichiometric BST ceramics modified with Ho$_2$O$_3$. Therefore, in this article we report a systematic study of the microstructure, dielectric properties and phase transition of non-stoichiometric (Ba$_{0.75}$Sr$_{0.25}$)Ti$_{1+n_{100}}$O$_{3+n_{100}}$ ($n_{100}$ = 0–0.02) based ceramics $^{[10]}$n$_A$:n$_B$ = (1+$n_{100}$).

2 EXPERIMENTAL PART

The chemical compositions of the Ti-rich BST-based ceramics were given by the formula (Ba$_{0.75}$Sr$_{0.25}$)Ti$_{1+n_{100}}$O$_{3+n_{100}}$ + 3 at.% Ho$_2$O$_3$ ($\delta$ = 0, 0.005, 0.01, 0.015, 0.02) and symbolized as R0, R1, R2, R3, R4. High-purity BaCO$_3$ (>99.0 %), SrCO$_3$ (>99.0 %) and TiO$_2$ (>98.0 %) powders used as starting raw materials were weighed, ball-milled, dried and calcined at 1080 °C for 2 h. The calcined powders were mixed with Ho$_2$O$_3$ (>99.0 %), reground, dried and added with 5 % (w/%) polyvinyl alcohol (PVA) as a binder for granulation. The mixture was sieved through a 60-mesh screen and then pressed into pellets. Sintering was conducted in air at 1350–1480 °C for 1–6 h. For dielectric the measurements, both the flat surfaces of the specimens were coated with BQ-5311 silver paste after ultrasonic bath cleaning and then fired at 800 °C for 10 min.

The crystal structures of the specimens were confirmed by X-ray diffraction analysis (XRD, Rigaku D/max 2500v/pc) with Cu-$K_\alpha$ radiation. The surface morphologies of the as-sintered specimens were observed using the SEM (JSM-6480 ESEM). The temperature dependence of the dielectric constant and loss tangent was measured at 1 kHz, 10 kHz, 100 kHz and 500 kHz from −185 °C to 250 °C with a TZDM-200-300 automatic LCR measuring system. The percentage of permittivity variation at 1 kHz ($\Delta\varepsilon/\varepsilon_\alpha$) from −30 °C to 85 °C used for accessing the temperature stability of the relative dielectric constant is determined using the following Equation:

$$\frac{\Delta\varepsilon}{\varepsilon_\alpha} = \frac{\varepsilon_A - \varepsilon_{RT}}{\varepsilon_{RT}} \times 100\%$$

where $\varepsilon_{RT}$ is the relative dielectric constant at room temperature; $\varepsilon_\alpha$ is the relative dielectric constant at any other temperature. All the above microstructure analyses and dielectric measurements were conducted using the samples sintered at 1450 °C for 2 h.

3 RESULTS AND DISCUSSION

The X-ray diffraction patterns of the as sintered (Ba$_{0.75}$Sr$_{0.25}$)Ti$_{1+n_{100}}$O$_{3+n_{100}}$ bulk ceramics are shown in Figure 1. It appears that the stoichiometric ceramic (Ba$_{0.75}$Sr$_{0.25}$)TiO$_3$ and the non-stoichiometric (Ba$_{0.75}$Sr$_{0.25}$)Ti$_{1+n_{100}}$O$_{3+n_{100}}$ ceramics ($\delta$ = 0.005, 0.01, 0.015, 0.02) are single-phase solid solutions with a typical perovskite structure. No obvious secondary phase is detected, even for the (Ba$_{0.75}$Sr$_{0.25}$)Ti$_{1.02}$O$_{3.04}$ ceramics based on the X-ray diffraction patterns. According to the magnified view of the diffraction peaks presented in Figures 1b and 1c, the (002)/(200) and (202)/(220) diffraction peaks

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Figure 1: XRD patterns for (Ba$_{0.75}$Sr$_{0.25}$)Ti$_{1+n_{100}}$O$_{3+n_{100}}$ ceramics
can be seen in all the \((\text{Ba}_{0.75}\text{Sr}_{0.25})\text{Ti}_{1+\delta}\text{O}_{3+2}\) ceramics, indicating that the studied ceramics possess tetragonal perovskite structure (space group \(\text{P4}_3\text{mm}\)).

Also, a slight shift of the diffraction peaks to higher two-theta values with the increasing \(\delta\) value is observed, which indicates that the unit-cell volumes of the \((\text{Ba}_{0.75}\text{Sr}_{0.25})\text{Ti}_{1+\delta}\text{O}_{3+2}\) ceramics decrease as the non-stoichiometric level of the Ti ions present in the ABO\(_3\) perovskite structure increases. Similar phenomena have been previously reported in Ca-substituted BST ceramics\(^{20}\) and in our previous work for Ti deficient \((\text{Ba}_{0.75}\text{Sr}_{0.25})\text{Ti}_{1-\delta}\text{O}_{3-2}\) ceramics.\(^{21}\)

Initially, the A-site vacancies \(V'_A\) and oxygen vacancies \(V''_O\) remain in the un-doped \((\text{Ba}_{0.75}\text{Sr}_{0.25})\text{Ti}_{1+\delta}\text{O}_{3+2}\) calcined powders according to the following point-defect reaction equation:

\[
\text{(Ba}_{0.75}\text{Sr}_{0.25})\text{Ti}_{1+\delta}\text{O}_{3+2} \rightarrow 0.75\text{Ba}^{2+}_A + 0.25\text{Sr}^{2+}_A + (1+\delta)\text{Ti}^{4+} + (3+2\delta)\text{O}_2 \quad (2)
\]

After \(\text{Ho}_2\text{O}_3\) doping, the A-site vacancies \(V'_A\) are partially filled up by \(\text{Ho}^{3+}\) ions forming the point defects \(\text{Ho}^{3+}_A\) and the leftover A-site vacancies \(\delta V'_A\) taking the negative charge remain there to compensate the positive charge of \(\text{Ho}^{3+}_A\). After that, the \(\text{Ho}^{3+}\) ions begin to substitute the host ions (including both the A-site ion and B-site ion) because the concentration of \(\text{Ho}^{3+}\) doping ions (6 at.%) is much more than that of the A-site vacancies (less than or equal to 2 at.%). And the other two point defect reactions happen:

\[
\text{Ho}_2\text{O}_3 \rightarrow 2\text{Ho}^{3+} + 3\text{O}_2 \quad (3)
\]

\[
\text{Ho}_2\text{O}_3 \rightarrow 2\text{Ho}^{3+} + 3\text{O}_2 \quad (4)
\]

Therefore, there are totally four kinds of point defects \(\text{Ho}^{3+}_A\), \(\text{Ho}^{3+}_B\), \(V'_A\) and \(V''_O\) in the \(\text{Ho}_2\text{O}_3\) doped \((\text{Ba}_{0.75}\text{Sr}_{0.25})\text{Ti}_{1+\delta}\text{O}_{3+2}\) ceramics. With the increase of \(\delta\), the amount of \(\text{Ho}^{3+}\) ion occupying the A-site increases, while that in the B-site decreases due to the fixed concentration of \(\text{Ho}^{3+}\) ions. The radii of the host \(\text{Ba}^{2+}\) and \(\text{Sr}^{2+}\) ions are 0.161 nm (in 12 coordination) and 0.144 nm (in 12 coordination), respectively, while the radius of the host \(\text{Ti}^{4+}\) ion is 0.061 nm (in 6 coordination). The \(\text{Ho}^{3+}\) doping ion with a moderate radius of 0.0901 nm can cause the shrinkage of the unit cell by entering the A-site or the unit-cell expansion by getting into the B-site due to the radius difference between the \(\text{Ho}^{3+}\) ion and the host ion. Apparently, the obtained shrinkage of the unit-cell volume with the increase of \(\delta\) in \((\text{Ba}_{0.75}\text{Sr}_{0.25})\text{Ti}_{1+\delta}\text{O}_{3+2}\) ceramics is exactly attributed to the above-mentioned difference of the \(\text{Ho}^{3+}\) distribution in the host lattice site when increasing \(\delta\).

Figure 2 shows the surface morphologies of the as-sintered \((\text{Ba}_{0.75}\text{Sr}_{0.25})\text{Ti}_{1+\delta}\text{O}_{3+2}\) ceramics. All the \((\text{Ba}_{0.75}\text{Sr}_{0.25})\text{Ti}_{1+\delta}\text{O}_{3+2}\) samples possess dense microstructures and a fine grain size distribution can be found in

![Figure 2: SEM micrographs of \((\text{Ba}_{0.75}\text{Sr}_{0.25})\text{Ti}_{1+\delta}\text{O}_{3+2}\) ceramics: a) \(\delta = 0\), b) \(\delta = 0.005\), c) \(\delta = 0.01\), d) \(\delta = 0.015\), e) \(\delta = 0.02\)](image-url)
Figure 3: Temperature dependence of the relative dielectric constant and loss tangent for (Ba$_{0.75}$Sr$_{0.25}$)Ti$_{1+\delta}$O$_{3+2\delta}$ ceramics at different frequencies: a) $\delta = 0$, b) $\delta = 0.005$, c) $\delta = 0.01$, d) $\delta = 0.015$, e) $\delta = 0.02$
ceramics with a small $\delta$ value. However, with the increase of $\delta$, the abnormal grain growth becomes distinct, as shown in Figures 2c, 2d and 2e. The average grain size of the (Ba$_{0.75}$Sr$_{0.25}$)Ti$_{1+}$O$_{3+2}$ ceramics analyzed using the Nano Measurer software is collected in Table 1. It is obvious that the average grain size of the (Ba$_{0.75}$Sr$_{0.25}$)Ti$_{1+}$O$_{3+2}$ ceramics increases with the increasing $\delta$ value.

Table 1: Average grain size of (Ba$_{0.75}$Sr$_{0.25}$)Ti$_{1+}$O$_{3+2}$ ceramics

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>R0</th>
<th>R1</th>
<th>R2</th>
<th>R3</th>
<th>R4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grain size($\mu$m)</td>
<td>2.1</td>
<td>2.6</td>
<td>2.8</td>
<td>2.9</td>
<td>3.1</td>
</tr>
</tbody>
</table>

Figure 3 shows the temperature dependence of the relative dielectric constant and dielectric loss for the (Ba$_{0.75}$Sr$_{0.25}$)Ti$_{1+}$O$_{3+2}$ ceramics at 1 kHz, 10 kHz, 100 kHz and 500 kHz. The dielectric constant peaks corresponding to the ferroelectric-paraelectric phase transition can be observed for all the (Ba$_{0.75}$Sr$_{0.25}$)Ti$_{1+}$O$_{3+2}$ ceramics. The relative dielectric constant at room temperature (25 °C) $\varepsilon_{RT}$, the loss tangent at room temperature (25 °C) $\tan\delta_{RT}$, the maximum of dielectric permittivity $\varepsilon_m$ at 1 kHz and the temperature corresponding to this permittivity maximum $T_m$ are collected in Table 2. The $\varepsilon_{RT}$, $\tan\delta_{RT}$ and $\varepsilon_m$ increase with the increasing $\delta$ value, in general. The (Ba$_{0.75}$Sr$_{0.25}$)Ti$_{1+}$O$_{3+2}$ ceramics with low $\delta$ value, such as R1 and R2, possess a high relative dielectric constant (>6000) and a low dielectric loss (<0.004) at room temperature. With the increase of $\delta$ value, the $T_m$ increase from $-1$ °C for R0 to 6 °C for R2 and then to 12 °C for R4. The rise of $T_m$ is also found in samarium-doped Ba$_{0.68}$Sr$_{0.32}$TiO$_3$ ceramics. The charged vacancies, such as A-site vacancies $V_A$ and oxygen vacancies $V_O$, in (Ba$_{0.75}$Sr$_{0.25}$)Ti$_{1+}$O$_{3+2}$ ceramics, as mentioned previously, give rise to the distortion of the ABO$_3$ perovskite unit cells and thus a stronger deviation of the B-site ion from the center of the oxygen octahedron. It is exactly this stronger deviation that explains the enhancement of the spontaneous polarization, in other words, the increased $\varepsilon_m$ with increasing $\delta$. The increase of $\varepsilon_{RT}$ and $\varepsilon_m$ with increasing $\delta$ is also attributed to the strengthened spontaneous polarization. It has been reported that the smaller grains in ferroelectric ceramics inhibit the formation of large ferroelectric domains and thus reduce the effective contribution to the total polarization. Furthermore, the (Ba$_{0.75}$Sr$_{0.25}$)Ti$_{1+}$O$_{3+2}$ ferroelectric ceramics with a smaller grain size contain more non-ferroelectric grain boundaries but relatively fewer ferroelectric grains than those with a larger grain size. Therefore, the increased average grain size gives another reason for the increase of $\varepsilon_{RT}$ and $\varepsilon_m$ with increasing $\delta$. The $\Delta\varepsilon/\varepsilon_m$ at 1 kHz from $-30$ °C to 85 °C for the (Ba$_{0.75}$Sr$_{0.25}$)Ti$_{1+}$O$_{3+2}$ ceramics is shown in Table 2. The $\Delta\varepsilon/\varepsilon_m$ of R4 sample (+20.0 % -- -68.7 %) satisfies the Y5V standard ($\Delta\varepsilon/\varepsilon_m$ $\leq +22$ % -- -82 % from $-30$ °C to 85 °C) according to the ceramic capacitor classification of the Electronic Industries Association (EIA). The low temperature ($T < T_m$) frequency dispersion of the relative dielectric constant can be found in (Ba$_{0.75}$Sr$_{0.25}$)Ti$_{1+}$O$_{3+2}$ ceramics. The dielectric loss of (Ba$_{0.75}$Sr$_{0.25}$)Ti$_{1+}$O$_{3+2}$ ceramics shows the strong frequency dependence across the whole temperature range.

Table 2: Dielectric parameters for (Ba$_{0.75}$Sr$_{0.25}$)Ti$_{1+}$O$_{3+2}$ ceramics at 1 kHz

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>$\delta$</th>
<th>$\varepsilon_{RT}$</th>
<th>$\tan\delta_{RT}$</th>
<th>$\varepsilon_m$</th>
<th>$\Delta\varepsilon/\varepsilon_m$ (%, $T_m$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R0</td>
<td>0</td>
<td>4469</td>
<td>0.0017</td>
<td>6565</td>
<td>+46.9-- -60.8</td>
</tr>
<tr>
<td>R1</td>
<td>0.005</td>
<td>6159</td>
<td>0.0022</td>
<td>8123</td>
<td>+31.9-- -67.1</td>
</tr>
<tr>
<td>R2</td>
<td>0.015</td>
<td>6478</td>
<td>0.0039</td>
<td>8330</td>
<td>+28.6-- -66.6</td>
</tr>
<tr>
<td>R3</td>
<td>0.015</td>
<td>6172</td>
<td>0.0122</td>
<td>7842</td>
<td>+27.1-- -70.5</td>
</tr>
<tr>
<td>R4</td>
<td>0.02</td>
<td>8119</td>
<td>0.0220</td>
<td>9742</td>
<td>+20.0-- -68.7</td>
</tr>
</tbody>
</table>

The diffuse phase transition is always characterized by a deviation from the Curie-Weiss law in the vicinity of the Curie temperature ($T_c$). It is known that the dielectric permittivity of a normal ferroelectric above the Curie temperature follows the Curie-Weiss law described by the following Equation (5):

$$\frac{1}{\varepsilon} = \frac{T-T_0}{C}$$

where $T_0$ is the Curie-Weiss temperature and $C$ is the Curie-Weiss constant. Figure 4 shows the inverse relative dielectric constant for (Ba$_{0.75}$Sr$_{0.25}$)Ti$_{1+}$O$_{3+2}$ ceramics as a function of temperature at 1 kHz. The plots (for the $T > T_m$ part) are fitted linearly according to Equation (5) and the Curie-Weiss temperature $T_0$ obtained from the fittings is listed in Table 3.

Obviously, the dielectric behavior of the (Ba$_{0.75}$Sr$_{0.25}$)Ti$_{1+}$O$_{3+2}$ ceramics with a low $\delta$ value shows a deviation from the Curie-Weiss law at temperatures above the $T_m$.

Figure 4: Temperature dependence of the inverse relative dielectric constant for (Ba$_{0.75}$Sr$_{0.25}$)Ti$_{1+}$O$_{3+2}$ ceramics at 1 kHz (The symbols: experimental data; the solid line: fitting to the Curie-Weiss law.)
Then the parameter $\Delta T_m$, often used to characterize the degree of the deviation from the Curie-Weiss law and defined as follows, is calculated (Table 3):

$$\Delta T_m = T_m - T_w$$

where $T_w$ denotes the temperature from which the dielectric permittivity starts to deviate from the Curie-Weiss law and $T_m$ represents the temperature of the dielectric constant maximum. With the increase of the $\delta$ value, $\Delta T_m$ decreases from 79 °C (for R0 sample) to 1 °C (for R4 samples), which indicates that the diffuse transition behavior is suppressed with an increasing $\delta$ value, and the diffuse phase-transition behavior of (Ba0.75Sr0.25)Ti1+O3+2 ceramics even vanishes at $\delta = 0.02$.

Table 3: Temperature parameters for (Ba0.75Sr0.25)Ti1+O3+2 ceramics at 1 kHz

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>$\delta$</th>
<th>$T_o$ (°C)</th>
<th>$T_w$ (°C)</th>
<th>$T_m$ (°C)</th>
<th>$\Delta T_m$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R0</td>
<td>0</td>
<td>21</td>
<td>78</td>
<td>-1</td>
<td>79</td>
</tr>
<tr>
<td>R1</td>
<td>0.005</td>
<td>16</td>
<td>59</td>
<td>7</td>
<td>52</td>
</tr>
<tr>
<td>R2</td>
<td>0.01</td>
<td>4</td>
<td>37</td>
<td>6</td>
<td>31</td>
</tr>
<tr>
<td>R3</td>
<td>0.015</td>
<td>-16</td>
<td>18</td>
<td>8</td>
<td>10</td>
</tr>
<tr>
<td>R4</td>
<td>0.02</td>
<td>-37</td>
<td>11</td>
<td>12</td>
<td>1</td>
</tr>
</tbody>
</table>

A modified Curie-Weiss law has been proposed to describe the diffuseness of the ferroelectric phase transition:

$$\frac{1}{\varepsilon_r} - \frac{1}{\varepsilon_m} = \frac{(T-T_m)^\gamma}{C}$$

where $\gamma$ and $C$ are assumed to be constant. The parameter $\gamma$ reveals the characteristic of the phase transition: for $\gamma = 1$, a normal Curie-Weiss law is obtained; for $\gamma = 2$, a complete diffuse phase transition is described. The parameters $\gamma$ can be obtained by a linear fitting of the data through $\ln(1/\varepsilon_r - 1/\varepsilon_m) \sim \ln(T-T_m)$. The plots of

$$\ln(1/\varepsilon_r - 1/\varepsilon_m)$$

as a function of $\ln(T-T_m)$ for (Ba0.75Sr0.25)Ti1+O3+2 ceramics are shown in Figure 5. The $\gamma$ values for R0, R2, R3 and R4 ceramics are $1.47026$, $1.46651$, $1.30255$ and $1.03711$, respectively.

Figure 3 also provides the dielectric response of the (Ba0.75Sr0.25)Ti1+O3+2 ceramics at various frequencies. The relative dielectric constant (in the $T$-$T_m$ range) decreases with the increase of the test frequency. The $\varepsilon_m$ and $T_m$ of the (Ba0.75Sr0.25)Ti1+O3+2 ceramics at 1 kHz, 10 kHz, 100 kHz and 500 kHz are shown in Table 4. The $T_m$ for the R1, R2, R3, and R4 samples shifts only 1 °C towards higher temperature with increasing frequency. For the R0 sample, there is no shift in $T_m$ at all. The $\varepsilon_m$ for all the (Ba0.75Sr0.25)Ti1+O3+2 ceramics shows an obvious frequency dispersion.

Table 4: $\varepsilon_m$ and $T_m$ for (Ba0.75Sr0.25)Ti1+O3+2 ceramics at different frequencies

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>$\delta$</th>
<th>$\varepsilon_m$ (1 kHz)</th>
<th>$\varepsilon_m$ (10 kHz)</th>
<th>$\varepsilon_m$ (100 kHz)</th>
<th>$\varepsilon_m$ (500 kHz)</th>
<th>$T_m$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R0</td>
<td>0</td>
<td>6565</td>
<td>6494</td>
<td>6414</td>
<td>6383</td>
<td>-1</td>
</tr>
<tr>
<td>R1</td>
<td>0.005</td>
<td>8123</td>
<td>8021</td>
<td>7901</td>
<td>7912</td>
<td>7</td>
</tr>
<tr>
<td>R2</td>
<td>0.01</td>
<td>8330</td>
<td>8215</td>
<td>8077</td>
<td>7964</td>
<td>6</td>
</tr>
<tr>
<td>R3</td>
<td>0.015</td>
<td>7842</td>
<td>7695</td>
<td>7528</td>
<td>7396</td>
<td>8</td>
</tr>
<tr>
<td>R4</td>
<td>0.02</td>
<td>9742</td>
<td>9469</td>
<td>9152</td>
<td>8870</td>
<td>12</td>
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4 CONCLUSIONS

Ti-rich (Ba0.75Sr0.25)Ti1+O3+2 ceramics for low-frequency capacitor applications were prepared by a conventional solid-state method. The microstructures, dielectric properties and ferroelectric-paraelectric phase transition were investigated with a non-stoichiometric level by SEM, XRD and an LCR measuring system. The following was observed:

1) All the (Ba0.75Sr0.25)Ti1+O3+2 ceramics ($\delta = 0.005, 0.01, 0.015, 0.02$) are single-phase solid solutions with a typical tetragonal perovskite structure.

2) With the increasing $\delta$ value, the abnormal grain growth occurs and the average grain size of the (Ba0.75Sr0.25)Ti1+O3+2 ceramics increases.

3) The enhanced spontaneous polarization takes the main responsibility for the increase of the transition...
temperature $T_m$ as well as the increase of the dielectric constant $\varepsilon_{RT}$ and $\varepsilon_{2m}$ when $\delta$ increases.

4) The low-temperature ($T \leq T_m$) frequency dispersion of the relative dielectric constant can be found and the diffuse phase-transition behavior is suppressed with an increasing $\delta$ value in the (Ba$_{0.75}$Sr$_{0.25}$)Ti$_{1-x}$O$_{3+2\delta}$ ceramics.

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5 REFERENCES


