Dielectric tunability of $(Ba_{0.90}Ca_{0.10})(Ti_{0.75}Zr_{0.25})O_3$ ceramics

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We have performed a study on the dielectric properties of $(Ba_{0.90}Ca_{0.10})(Ti_{0.75}Zr_{0.25})O_3$ bulk ceramics prepared by a sol–gel technique in the cooling temperature range from 400 to 213 K. The ceramics are found to exhibit an interesting dielectric response under the presence of a dc bias field. The field dependence of dielectric constant is stronger at $T \approx T_m$ (T_m is the temperature of dielectric maximum) and the field-induced variation of dielectric constant $\Delta\varepsilon$ is nonzero for $T - T_m < 150$ K. One striking feature of these ceramics is that they possess a broad optimum value of figure of merit (as high as 200 at 30 kV/cm) between the temperature range from 295 and 330 K. At room temperature, the high tunability ($K = 60\%$), low-loss tangent (≈ 0.003), and large figure of merit (200), clearly indicate that these ceramics are suitable candidates for microwave applications. © *2004 American Institute of Physics*. [DOI: 10.1063/1.1781734]

Barium strontium titanate (BST) has attracted immense attention for their potential applications in dynamic random access memory and microwave devices.[1–3] The high dielectric constant made BST one of the important candidates for such applications. The solid solution nature of the $BaTi_{1-y}Zr_yO_3$ (BTZ) system has also been studied for their interesting dielectric behaviors.[4–9] For example, the dielectric measurement of the BTZ ceramics[4,5] in the region of $0 \leq y \leq 0.1$ has been reported to exhibit a typical ferroelectric behavior. For $0.1 \leq y \leq 0.26$, the material shows a diffuse transition, with a rounded transition and no frequency dispersion at the dielectric maximum ε_m. The ceramics are also found to exhibit diffuse transition with relaxorlike characteristics at the compositional range of $0.26 \leq y \leq 0.4$.[6] The transition temperature of the ceramics has been reported to depend strongly on Zr content and show a wide dielectric constant-temperature curve near T_C at $y > 0.08$.[7]

The related system of $(Ba_{1-x}Ca_x)(Ti_{1-y}Zr_y)O_3$ (BCTZ) bulk ceramics prepared in oxidizing atmosphere are reported to exhibit a broad dielectric constant-temperature curve near T_C, with values as high as $\varepsilon \sim 18\,000$.[10] While it is known that the dielectric constant of BCTZ bulk ceramics is high,[10] not much work has been performed on the electric-field dependence of dielectric constant on these ceramics. Though the effect of electric field on the dielectric constant of BCTZ has been explored in thin-film form,[11] the relevant study on bulk ceramics of BCTZ is still not available in literature. These motivate the present study in which the dielectric properties of $(Ba_{1-x}Ca_x)(Ti_{1-y}Zr_y)O_3$ bulk ceramics under a dc electric field are examined.

In this work, a sol–gel process has been used to prepare $(Ba_{0.90}Ca_{0.10})(Ti_{0.75}Zr_{0.25})O_3$ (BCTZ) ceramics.[12,13] The sol–gel process has many advantages. It is a relatively simple and low-cost process, and it is easy to control the stoichiometric compositions. In this study, a weighted amount of the appropriate proportions of high-purity barium acetate, calcium acetate, zirconium-*n*-propoxide, and titanium *n*-butoxide were used with acetic acid and 2-methoxyethanol as solvents. The

acetates and oxides were then dissolved in the acid and alcohol, respectively, to form a complex solution of BCTZ. By controlling the hydrolysis condition of the complex solution, the dry gel was annealed at 1100 °C for 2 h in an atmosphere to obtain the BCTZ powders. The annealed powders were then dried and pressed into disks form. After that, the pellets were sintered at 1350 °C for 5 h and cooled in a furnace. Fired-on silver paste was coated to form electrodes on both sides of the sintered ceramic specimens for dielectric measurement. We performed the measurement using a multifrequency LCR meter, Model SR720 of the Stanford Research System.

In this study, the dielectric properties of the samples were measured from 100 Hz to 100 kHz in the cooling temperature range from 400 to 213 K, at a rate of -1 K/min. Figure 1 shows the dielectric constant of BCTZ ceramics as a function of frequency and temperature under different field strengths. The temperature dependences of dielectric constant $\varepsilon(T,0)$ show a strong dispersion maximum [$\varepsilon_m(T_m,0))$, T_m is the temperature of dielectric maximum] at the temperature $T \leq T_m$ (see Fig. 1), with T_m increasing from 231 K at 100 Hz to 244 K at 100 kHz. The dielectric constant is suppressed with increasing dc bias field, as depicted in Fig. 1. Note that the dielectric dispersion becomes very weak under a dc field of 15 kV/cm and disappears at 30 kV/cm. In the presence of a dc field, the dielectric peak ε_m is broadened
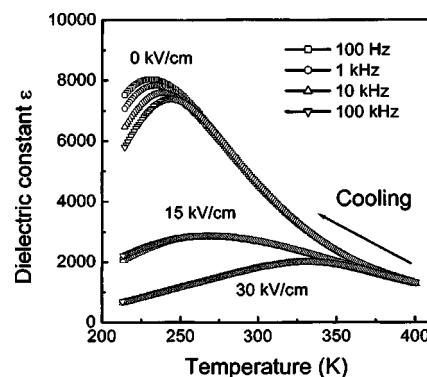

FIG. 1. Temperature and frequency dependence of dielectric constant for BCTZ ceramics under different dc electric fields.

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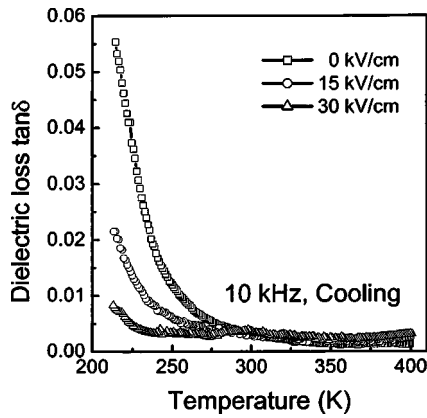[b)]Electronic mail: apahlcha@polyu.edu.hk

FIG. 2. Temperature dependence of dielectric loss tan δ for BCTZ ceramics.

and T_m of the dielectric constant maximum ε_m is shifted toward higher temperatures.

We now look at the temperature dependences of the dielectric loss in BCTZ ceramics. Unless otherwise specified, the results shown are for frequency $f = 10$ kHz. Figure 2 depicts the loss tan δ as a function of temperature for the ceramics. In general, the dielectric loss decreases with increasing temperature. The loss decreases sharply in the region near T_m and maintains values below 0.005 at a temperature above 275 K. It is also observed that the dielectric loss is smaller in the presence of a dc bias field. It is interesting to note that the dissipation factor for the ceramics at room temperature is as low as ~0.003.

One of the important properties for a material to be used in tunable microwave devices is electric-field dependence in the dielectric constant. As the ceramics are found to possess a low-loss tan δ, particularly at $T > T_m$, the analysis on the field dependence of dielectric constant is now focused on this temperature region $T > T_m$. Let us define the field-induced variation of dielectric constant as

$$\Delta\varepsilon = \varepsilon_m(T_m,0) - \varepsilon(T,E), \qquad (1)$$

where $\varepsilon_m(T_m,0)$ is the zero-field dielectric peak and $\varepsilon(T,E)$ represents the field-dependent dielectric constant. Figure 3 shows the $\Delta\varepsilon$ versus $T - T_m$ curves for two different dc field strengths. The value of $\Delta\varepsilon$ is larger under a higher bias field. It is shown that the field-induced dielectric constant becomes larger as the temperature of the ceramic is close to T_m, implying a strong field dependence in the dielectric constant as $T \approx T_m$. An interesting behavior observed from Fig. 3 is that the temperature region with $\Delta\varepsilon \neq 0$ for this ceramics is well
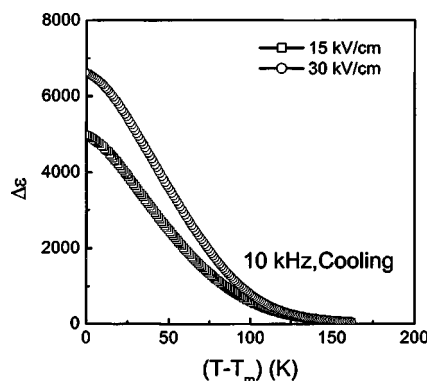
defined by $T - T_m < 150$ K. No change of $\Delta\varepsilon$ is found for $T - T_m > 150$ K, indicating the dielectric constant is independent of dc bias field at $T - T_m > 150$ K.

Since the ceramic exhibits a strong field dependence of dielectric constant and low loss at $T > T_m$, it is worthwhile to look at the tunability of these ceramics at $T > T_m$. The tunability is expressed as

$$K = \frac{\varepsilon(T,0) - \varepsilon(T,E)}{\varepsilon(T,0)}, \qquad (2)$$

where $\varepsilon(T,0)$ and $\varepsilon(T,E)$ denote the zero-field and field-dependent dielectric constant. The tunability as a function of temperature is shown in Fig. 4. With decreasing temperature, the tunability is enhanced and reaches a maximum at $T \approx T_m$. This is because the field-induced dielectric constant is larger for T in the regime near T_m of the ceramics, as shown in Fig. 3. Higher tunability is achieved as the dc field increases. For example, at $T \approx 210$ K, the value of tunability is 68% for $E = 15$ kV/cm, whereas the K value is as larger as 90% under the dc electric field of 30 kV/cm.

Figure 5 shows the figure of merit (FOM) versus temperature for the BTCZ ceramics. The FOM is calculated based on the expression below:[14]
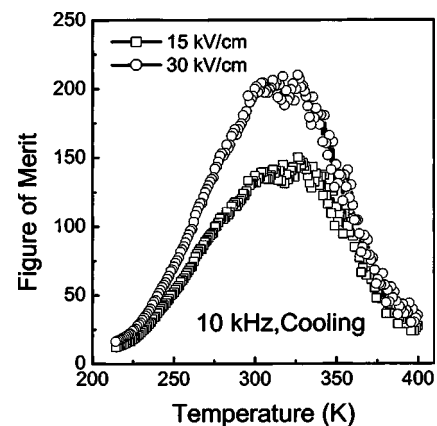

FIG. 4. Tunability as a function of temperature for BCTZ ceramics under different dc electric fields.

FIG. 3. $\Delta\varepsilon$ as a function of $(T\text{-}T_m)$ for BCTZ ceramics.

FIG. 5. FOM as a function of temperature for BCTZ ceramics under different dc electric fields.

$$FOM = \frac{1}{\tan \delta} K, \tag{3}$$

where K is as expressed in Eq. (2). The FOM as a function of temperature shows an interesting Gaussian shape characteristics with an optimum value of 140 and 200 for 15 kV/cm and 30 kV/cm, respectively. One of the striking features is that the optimum value of FOM is located in the temperature range between 295 and 330 K, encompassing the room temperature.

In conclusion, we have studied the dielectric properties of BCTZ ceramics measured from 100 Hz to 100 kHz in the cooling temperature range from 400 to 213 K. The ceramics is found to exhibit a diffuse phase transition characteristic with a strong dispersion of $\varepsilon(T,0)$ at $T \leqslant T_m$. The field dependence of dielectric constant is larger for $T \approx T_m$ and the value of $\Delta\varepsilon$ is nonzero for temperature $T - T_m < 150$ K. At room temperature 300 K, the high tunability ($K = 60\%$), low-loss tangent (≈ 0.003), and large FOM (200), clearly imply that these ceramics are promising materials for tunable microwave device applications.

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