Tunable dielectric characteristics of $(Ba_{0.95}Ca_{0.05})(Ti_{1-y}Sn_y)O_3$ ferroelectric ceramics

H. H. Gu · X. M. Chen · N. Qin

Abstract In order to explore potential candidates for field tunable dielectric materials, the present work was focused on investigating the microstructure, dielectric and tunable dielectric properties of A- and B-site substituted barium titanate ceramics. Large tunability with lower dielectric loss was obtained in the present ceramics at a quite weak bias field. The excellent tunable characteristics were achieved for $y=0.15$ at room temperature (25 °C): tunability=26%, $\tan\delta<0.01$ at 10 kHz under a very weak bias DC electric field of 2.1 kV/cm.

Keywords Tunability · Solid solution · Phase transition · Dielectric properties · $(Ba_{0.95}Ca_{0.05})(Ti_{1-y}Sn_y)O_3$

1 Introduction

Recently, DC electric-field tunable dielectrics have attracted much scientific attention due to their important applications in the electric-field tunable devices such as voltage-controlled oscillators, tunable filters and phase shifters [1–5]. In these applications, the primary property requirements include the high tunability $(= [\varepsilon(0) - \varepsilon(E)]/\varepsilon(0))$, low dielectric loss and small temperature dependence. The currently most studied materials are $SrTiO_3$ [2], (Ba,Sr)TiO_3 [3, 4] and (Pb,Sr)TiO_3 [5], and some desired results have been obtained, especially in (Ba,Sr)TiO_3 thin films [6,7]. However, their higher dielectric loss ($\tan\delta>0.07$ at 10 kHz) and larger temperature coefficient are the essential

problems. Several groups have tried to search some new materials by B-site substitution in $BaTiO_3$ [8–10]. Moreover, the temperature stable dielectrics with tunable dielectric constant were obtained in Ca-substituted $BaTiO_3$ ceramics [11]. However, the higher dielectric loss is still a problem in the B-site substituted $BaTiO_3$, and the tunability of Ca-substituted $BaTiO_3$ is small. An interesting issue is to combine the merits of A- and B-site substituted $BaTiO_3$ to search temperature stable tunable dielectrics with high tunability and low dielectric loss.

In the present work, $(Ba_{0.95}Ca_{0.05})(Ti_{1-y}Sn_y)O_3$ ceramics are prepared, and the dielectric properties and their electric field dependence are characterized together with the microstructures. It is suggested that the present system is a promising candidate for the electric-field tunable materials.

2 Experimental

$(Ba_{0.95}Ca_{0.05})(Ti_{1-y}Sn_y)O_3$ ceramics ($y=0.05$, 0.1, 0.15, 0.2) were prepared by a solid state reaction process where the reagent grade $BaCO_3$ (99.95%), $CaCO_3$ (99.0%), SnO_2 (99.5%), and TiO_2 (99.5%) powders were adopted as the raw materials. The weighed raw materials were mixed by ball milling with zirconia media and were distilled water for 24 h, and then were calcined at 1200 °C in air for 3 h after drying. The calcined powders added with 8 wt% of PVA were pressed into discs and sintered at 1300 to 1375 °C in air for 3 h. After cooling from sintering temperature to 1100 °C at a rate of 2 °C min^{-1}, the ceramics were cooled with the furnace. All the samples were polished to 0.19–0.22 mm in thickness and gold-spray was used as the electrodes.

The crystalline phases of the sintered samples were identified by the X-ray powder diffraction pattern using

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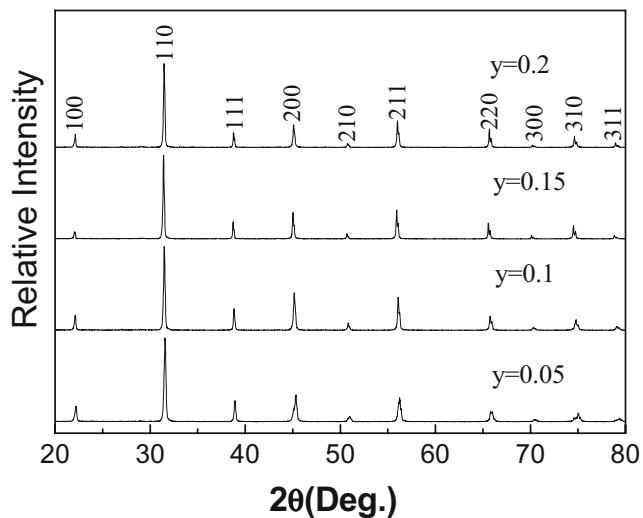e-mail: xmchen@cmsce.zju.edu.cn

Fig. 1 XRD patterns of $(Ba_{0.95}Ca_{0.05})(Ti_{1-y}Sn_y)O_3$ ceramics

CuK$_\alpha$ radiation. The temperature dependence of dielectric constant and the dielectric responses under bias voltage (0–40 V) were evaluated in the temperature range from −50 to 85 °C at 10 kHz by an LCR precise meter (HP4284A) equipped with a thermostat.

3 Results and discussion

Dense $(Ba_{0.95}Ca_{0.05})(Ti_{1-y}Sn_y)O_3$ ceramics with the maximum density of about 95% are obtained by sintering at

Table 1 Comparison of lattice parameters (a and c), unit cell volume (V) in $(Ba_{0.95}Ca_{0.05})(Ti_{1-y}Sn_y)O_3$ ceramic (y=0.05, 0.1, 0.15, 0.2).

y	a (Å)	c (Å)	V (Å^3)	c/a
0.05	3.9987	4.0063	64.04	1.0020
0.10	4.0109	4.0151	64.59	1.0010
0.15	4.0238	4.0224	65.13	0.9997
0.20	4.0183	4.0177	64.87	0.9998

1300–1350 °C. Figure 1 shows the X-ray powder diffraction (XRD) patterns of the present ceramics. All the peaks can be assigned to $(Ba,Ca)(Ti,Sn)O_3$ solid solution with tetragonal perovskite structure (JCPDS Card No. 75-2121) and no secondary phase peaks is detected. The detailed diffraction (XRD) patterns of $(Ba_{0.95}Ca_{0.05})(Ti_{1-y}Sn_y)O_3$ are shown in Fig. 2, it is interesting to view that, the peaks of different y values show lattice characteristic. The reflection peaks of y=0.05, 0.10, 0.15 move toward left linearly, but the peak of y=0.20 move toward right compared with y=0.15. The value of lattice parameters a, c and the unit cell volume V increase with increasing Sn concentration (seen in Table 1). When y=0.20, the value of the lattice parameter a and the unit cell volume V decrease, indicating some shrinkage of the lattice.

The temperature dependence of dielectric constant in $(Ba_{0.95}Ca_{0.05})(Ti_{1-y}Sn_y)O_3$ ceramics is plotted in Fig. 3 for various frequencies. The temperature with the maximum dielectric constant (T_m) for $(Ba_{0.95}Ca_{0.05})TiO_3$ is about

Fig. 2 Detailed XRD patterns for individual diffraction peaks of $(Ba_{0.95}Ca_{0.05})(Ti_{1-y}Sn_y)O_3$ ceramics
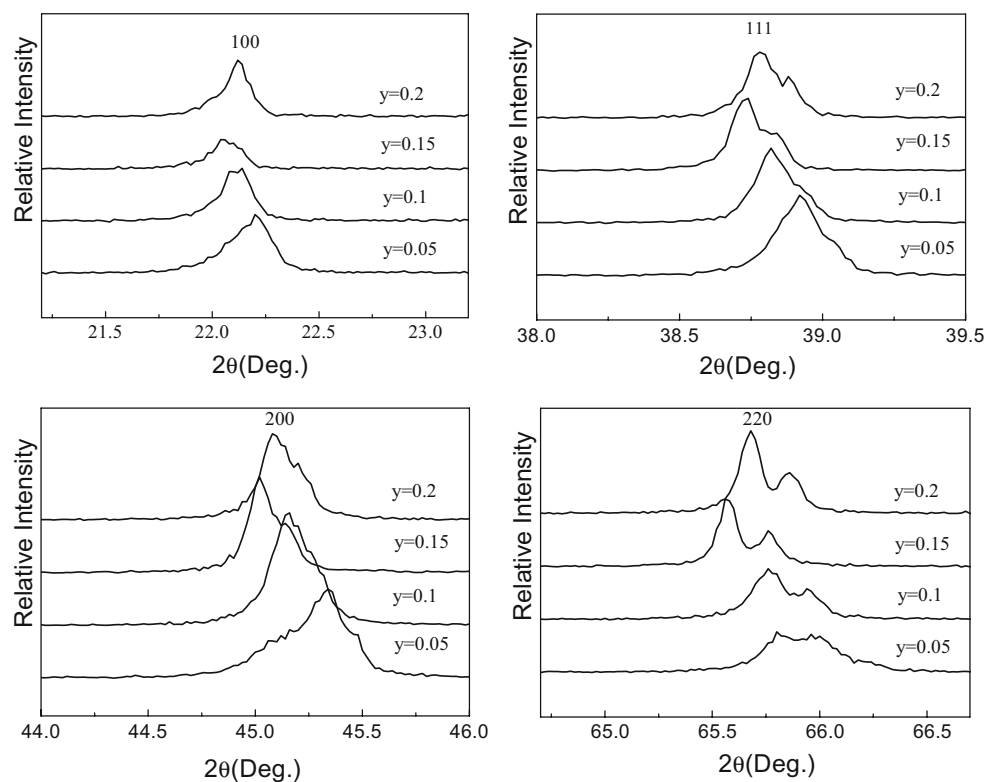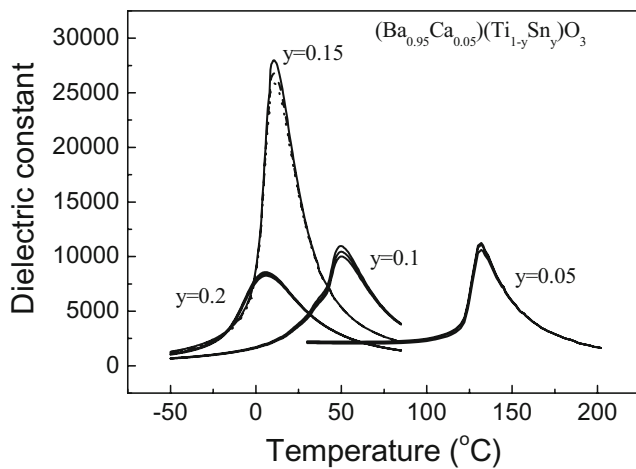
Fig. 3 Temperature dependence of dielectric constant of $(Ba_{0.95}Ca_{0.05})(Ti_{1-y}Sn_y)O_3$ ceramics at 10 kHz, 100 kHz, and 1 MHz: y=0.05, y=0.1, y=0.15 and y=0.2

Fig. 5 Room temperature tunability of dielectric constant of $(Ba_{0.95}Ca_{0.05})(Ti_{1-y}Sn_y)O_3$ ceramics as functions of composition at 10 kHz under various DC bias filed

130 °C, where the dielectric constant (ε_m) is about 11,200 at 10 kHz [12]. The dielectric properties of $(Ba_{0.95}Ca_{0.05})(Ti_{1-y}Sn_y)O_3$ ceramics get more sensitive with increasing Sn content, and the T_m decreases almost linearly (from 125 to 5 °C). The ε_m generally increases with increasing y, and reaches the maximum at y=0.15, and then turns to decrease. These results are similar with the situation in $Ba(Ti_{1-x}Sn_x)O_3$ ceramics [8]. Assuming a rigid ion model, large "rattling" space is expected for the smaller B-site ions in the disordered structure because the larger B-site ions prop
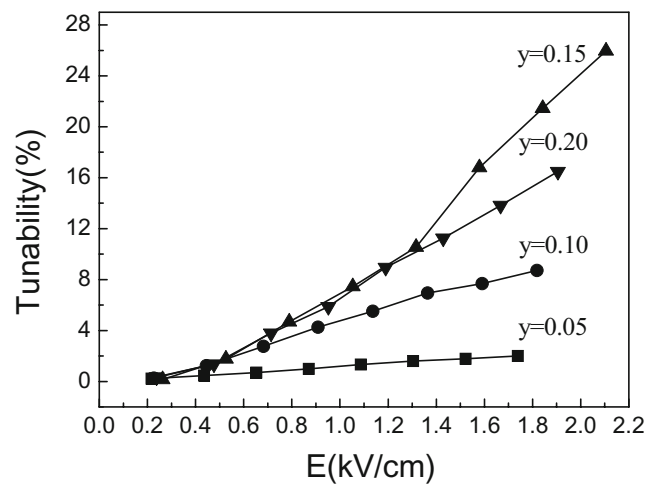
open the lattice framework. When an electric field is applied to a disordered perovskite, the B-site ions with a large rattling space can shift easily without distorting the oxygen framework. Larger dielectric constants can be expected because of the larger polarization [13]. With increasing Sn content, the perovskite turns into order structure in short range with a small rattling space, the B-site ions can not move easily without distorting the octahedron, and subsequently a smaller dielectric constant

Fig. 4 Temperature dependence of dielectric loss of $(Ba_{0.95}Ca_{0.05})(Ti_{1-y}Sn_y)O_3$ ceramics at 10, 100 and 1 MHz: (a) y=0.05, (b) y=0.1, (c) y=0.15 and (d) y=0.2
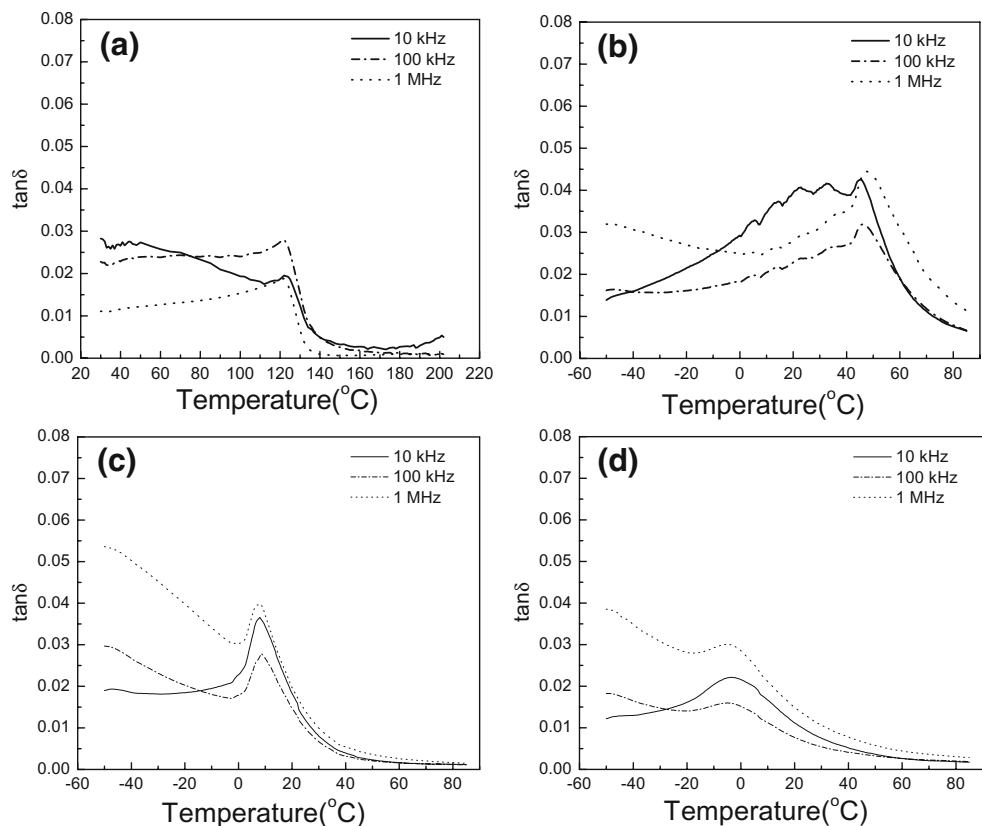
can be expected. Figure 4 shows the temperature dependence of dielectric loss (tanδ) of $(Ba_{0.95}Ca_{0.05})(Ti_{1-y}Sn_y)O_3$ ceramics with different y values. No obvious frequency dispersion is observed in dielectric constant and dielectric loss. This suggests that $(Ba_{0.95}Ca_{0.05})(Ti_{1-y}Sn_y)O_3$ ceramics are normal ferroelectric. The full width at half maximum extends wider when $y=0.2$, which indicates the features of diffuse phase transition. The temperature with the maximum loss for all compositions is 3–10 °C lower than the corresponding T_m. The dielectric loss of $(Ba_{0.95}Ca_{0.05})(Ti_{1-y}Sn_y)O_3$ ceramics at various temperatures decreases with increasing y, and it is obviously lower than that in $Ba(Ti, Sn)O_3$ ceramics [8]. A low dielectric loss (tanδ<0.01 at 1 MHz and 25 °C) is observed for $y \geq 0.15$.

Under low DC bias, obvious field dependence of dielectric properties of $(Ba_{0.95}Ca_{0.05})(Ti_{1-y}Sn_y)O_3$ ceramics has been observed at room temperature, indicating that $(Ba_{0.95}Ca_{0.05})(Ti_{1-y}Sn_y)O_3$ is a promising candidate for the tunable dielectrics. Figure 5 shows the dielectric tunability of $(Ba_{0.95}Ca_{0.05})(Ti_{1-y}Sn_y)O_3$ ceramics as functions of composition and bias field. With increasing Sn content, the tunability increases apparently until $y=0.15$ where the maximum tunability of 26% is obtained under 2.1 kV/cm. For the composition of $y=0.2$, a lower tunability is obtained than that of $y=0.15$ under the bias field greater 1.2 kV/cm.

4 Conclusion

$(Ba_{0.95}Ca_{0.05})(Ti_{1-y}Sn_y)O_3$ ceramics were prepared by a solid state reaction method, and the dielectric characteristics and the tunability was investigated. $(Ba_{0.95}Ca_{0.05})(Ti_{1-y}Sn_y)$ O_3 ceramics indicated a high tunability (up to 26% under a weak bias field of 2.1 kV/cm) combined with a low dielectric loss (tanδ<0.01 at 10 kHz and 25 °C) when $y \geq$ 0.15. These ceramics are promising materials for tunable dielectrics working at room temperature.

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