Journal of Electroceramics, 11, 173–178, 2003

Dielectric Characteristics and Tunability of Barium Stannate Titanate Ceramics

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Submitted November 10, 2003; Revised January 16, 2004; Accepted January 19, 2004

Abstract. $Ba(Ti_{1-x}Sn_x)O_3$ solid solutions were prepared by a solid state reaction method, and their dielectric and tunable characteristics were investigated together with the microstructures and diffused phase transition behaviors. The dielectric relaxation behaviors were observed and became stronger with increasing x.The obvious field dependence of the present system was observed with high dielectric constant and low loss at relatively lower DC electric field. The excellent tunable dielectric characteristics were achieved for $x = 0.15$ at room temperature: tunability $\sim$ 56%, $\tan\delta \sim 0.003$ at 10 kHz under 7.6 kV/cm, indicating that it is a promising candidate for electric-field tunable dielectrics working at room temperature.

Keywords: tunability, solid solution, phase transition, dielectric properties, $Ba(Ti_{1-x}Sn_x)O_3$

1. Introduction

Recently, DC electric-field tunable dielectrics have been extensively studied due to their important applications in electric-field tunable devices such as voltage-controlled oscillators, tunable filters and phase shifters [1–5]. In these applications, both high tunability ($=[\varepsilon(0) - \varepsilon(E)]/\varepsilon(0)$) and low dielectric loss are required. The currently most studied materials are $SrTiO_3$ (denoted as ST) [2], $(Ba,Sr)TiO_3$ (denoted as BST) [3, 4] and $(Pb,Sr)TiO_3$ (denoted as PST) [5], and some desired results have been gained, especially in BST thin films [6, 7]. However, their reproductivity, dielectric loss, or stability of the materials need to be more improved. Therefore, further exploration on new materials is of great scientific and commercial value.

$Ba(Ti_{1-x}Sn_x)O_3$ (denoted as BTS) ceramics have received renewed attention because of their high dielectric performance, lead-free relaxor behaviors and sensor applications [8–11]. Especially, the system has high dielectric constant and low loss around room temperature. It is very interesting to investigate the DC electric-field dependence of dielectric constant and loss for the present ceramics.

In the present work, $Ba(Ti_{1-x}Sn_x)O_3$ solid solution ceramics ($x = 0.15, 0.17$, and 0.20) were prepared, and the dielectric properties and their electric field dependence were characterized together with the microstructures. It suggests that the present system is a promising candidate for the electric-field tunable materials.

2. Experimental

$Ba(Ti_{1-x}Sn_x)O_3$ ($x = 0.15, 0.17$ and 0.20) ceramics were prepared by a routine solid state reaction process where the reagent grade $BaCO_3$ (99.95%), SnO_2 (99.5%), and TiO_2 (99.5%) powders were adopted as the raw materials. The weighed raw materials were mixed by mall milling with zirconia media and distilled water for 24 h, and then calcined at 1100–1200°C in air for 3 h after drying. The calcined powders added with 8 wt% of PVA were pressed into discs and sintered at 1325 to 1350°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 polished to the 0.2–0.4 mm thickness (Table 1) and silver pasted was used as the electrodes.

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Table 1. Curve fitting results for Ba($Ti_{1-x}Sn_x$)O_3 ceramics.

Composition	T_m (°C)	ε_m	γ	Sample thickness (mm)
Ba($Ti_{0.85}Sn_{0.15}$)O_3	16	9800	1.615	0.26
Ba($Ti_{0.83}Sn_{0.17}$)O_3	−2	7700	1.645	0.28
Ba($Ti_{0.80}Sn_{0.20}$)O_3	−33	8500	1.675	0.33

The crystalline phases of the sintered samples were identified by the X-ray powder diffraction pattern using Cu K_α radiation. The temperature dependence of dielectric constant and the dielectric responses under bias voltage (0–35 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. The field dependence of dielectric characteristics at room temperature for all the samples were determined at 10 kHz by a precious impedance analyzer (HP4294A) with an extra voltage bias fixture (HP16065A, 0–200 V). Polarization hysteresis loops were also examined by a hysteresis meter (RT-6000HVS) at room temperature. Silver paste was used as the electrodes.

3. Results and Discussion

Figure 1 shows the X-ray powder diffraction (XRD) patterns of Ba($Ti_{1-x}Sn_x$)O_3 ($x = 0.15, 0.17,$ and 0.20) dense ceramics. Except for the peaks' shift little, the diffraction peaks and their intensities are very similar for the investigated compositions, which indicates the formation of solid solution. All peaks can be assigned to Ba(Ti,Sn)O_3 with cubic perovskite structure, and the result is similar to the previous work [12].

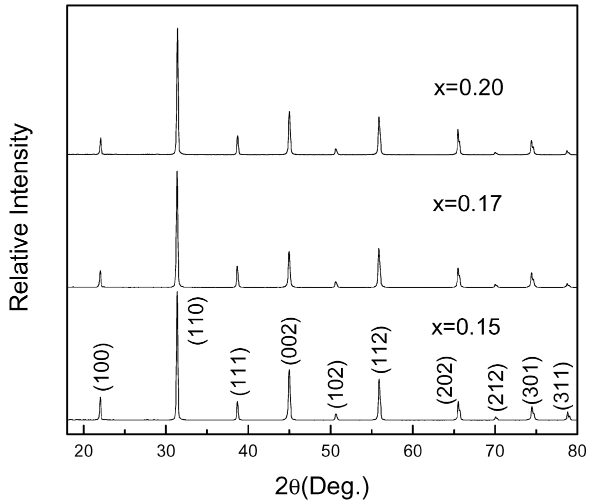

Fig. 1. XRD patterns of Ba($Ti_{1-x}Sn_x$)O_3 dense ceramics.

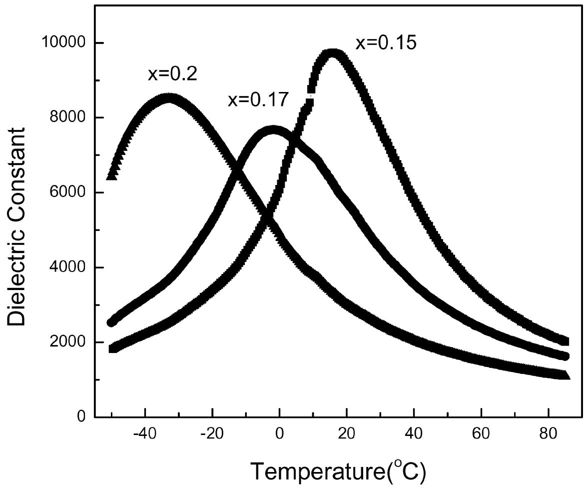

Fig. 2. Temperature dependence of dielectric constant of Ba($Ti_{1-x}Sn_x$)O_3 dense ceramics at 10 kHz.

The temperature dependence of dielectric constant for Ba($Ti_{1-x}Sn_x$)O_3 solid solutions at 10 kHz is shown in Fig. 2. Dielectric peaks are observed in the temperature range of –50 to 85°C, and it is noted that the maximum of the dielectric constant (ε_m) reaches reasonably high value in BaTiO_3-based solid solutions, especially, $\varepsilon_m = 9{,}800$ at 10 kHz for $x = 0.15$ with $T_m = 16$°C. With increasing Sn content, the temperature with the maximum dielectric constant (T_m) decreases almost linearly, as well as the ε_m (see Table 1). It is noted that the ε_m value of $x = 0.17$ is less than that of $x = 0.2$. This is because the dielectric constant decreases with decreasing thickness and the sample thickness of $x = 0.17$ is less than that of $x = 0.20$. At the same time, dielectric peaks for all samples show notable diffused phase transition behaviors (DPT) and the full width of half maximum (FWHM) extends to more wide range with increasing x. Martirena [13] and Uchino [14] proposed the following empirical relation for the temperature variation of ε for DPT:

$$\frac{1}{\varepsilon} = \frac{1}{\varepsilon_m} + \frac{(T - T_m)^\gamma}{C'} \qquad (1)$$

where γ is the critical exponent and C' is the Curie-Weiss-like constant. It is believed that the power factor

γ close to 1 suggests normal ferroelectrics, while close to 2 suggests relaxor ferroelectrics. The experimental dielectric constant data was fitted to Eq. (1) very well and the obtained γ values are shown in Table 1. The results suggest that BTS solid solutions within the investigated composition range exhibit reasonable relaxor behaviors and the relaxor tendency grows stronger with increasing Sn content, which also are proved partly by the P-E behavior. As shown in Fig. 3, the polarization hysteresis loops were obtained for all the samples at room temperature, and gradually became smaller and weaker with increasing Sn content.

Figure 4 describes the dielectric responses of Ba(Ti$_{1-x}$Sn$_x$)O$_3$ solid solutions ($x = 0.15$, 0.17, and 0.20) under various DC bias electric-field. With increasing the external DC bias electric-field, the dielectric constant for all compositions decreases apparently, as well as the dielectric loss with the low values. The suppression of dielectric constant at relatively low electric-field ($E \sim 1$ kV/cm) are 12.1% for $x = 0.15$ when $E = 1.34$ kV/cm and $T = 25°$C, 13.4% for $x = 0.17$ when $E = 1.25$ kV/cm and $T = 10°$C, and 11.6% for $x = 0.20$ when $E = 0.909$ kV/cm and $T = -20°$C. With increasing the temperature ($T > T_m$), suppressions of dielectric constant and loss become weak, especially when T is far beyond T_m. All these results can be explained by virtue of DPT behavior of BTS. As mentioned above, around the phase transition temperature range, BTS exhibits more DPT and relaxor behaviors with increasing x. This means, when the temperature is slightly above T_m, BTS ceramics still exhibits considerable nonlinear behaviors even in the paralectric state, hence the dielectric properties responses for external DC bias electric-field appear sensitive and notable. As the temperature increases far beyond the corresponding T_m, the BTS ceramics deviate from the DPT and relaxor state and exhibit more paraelectric state behaviors. This can be proved by the BTS polarization hysteresis loops at room temperature shown in Fig. 3. At room temperature, suppression of dielectric constant and loss decrease dramatically with increasing x.

Under very small external DC electric-field (<1.5 kV/cm), obvious field dependence of dielectric properties of BTS solid solutions have been observed, indicating that the BTS system is a promising candidate for the electric-field tunable dielectrics, especially for electric field tunable applications operating at room temperature. It is necessary to further investigate the dielectric responses of BTS under higher field.

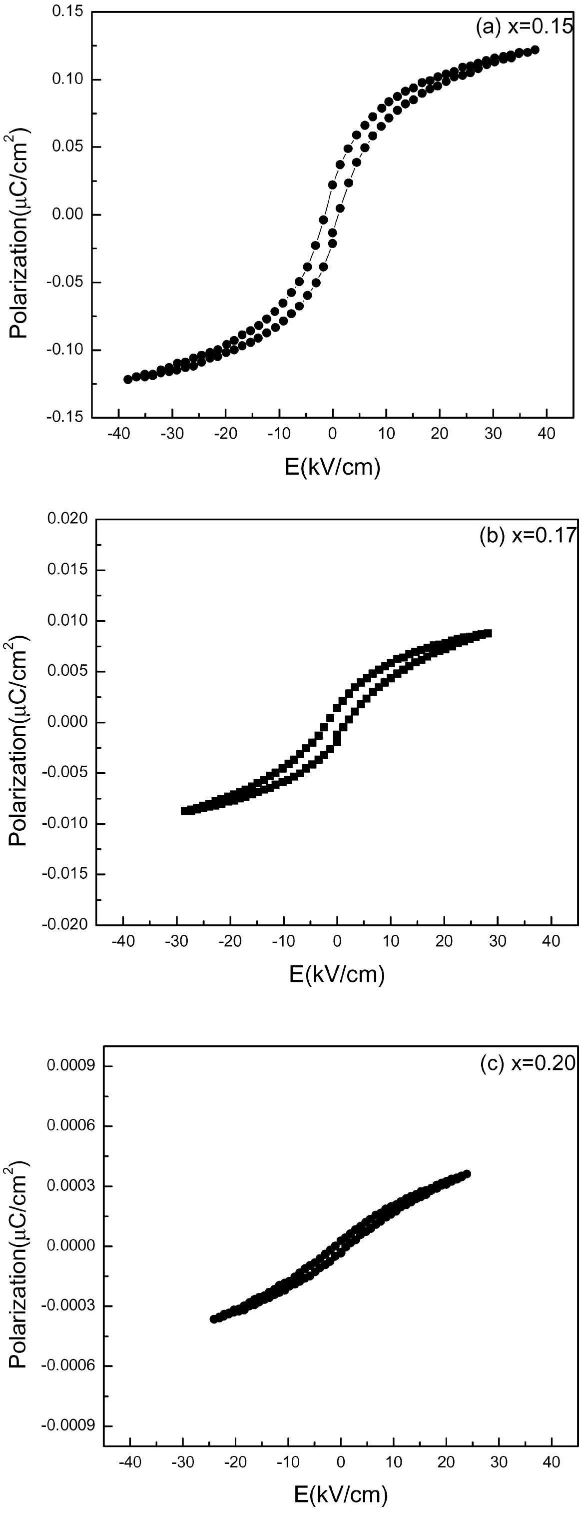

Fig. 3. Polarization hysteresis Loops of Ba(Ti$_{1-x}$Sn$_x$)O$_3$ dense ceramics at room temperature.

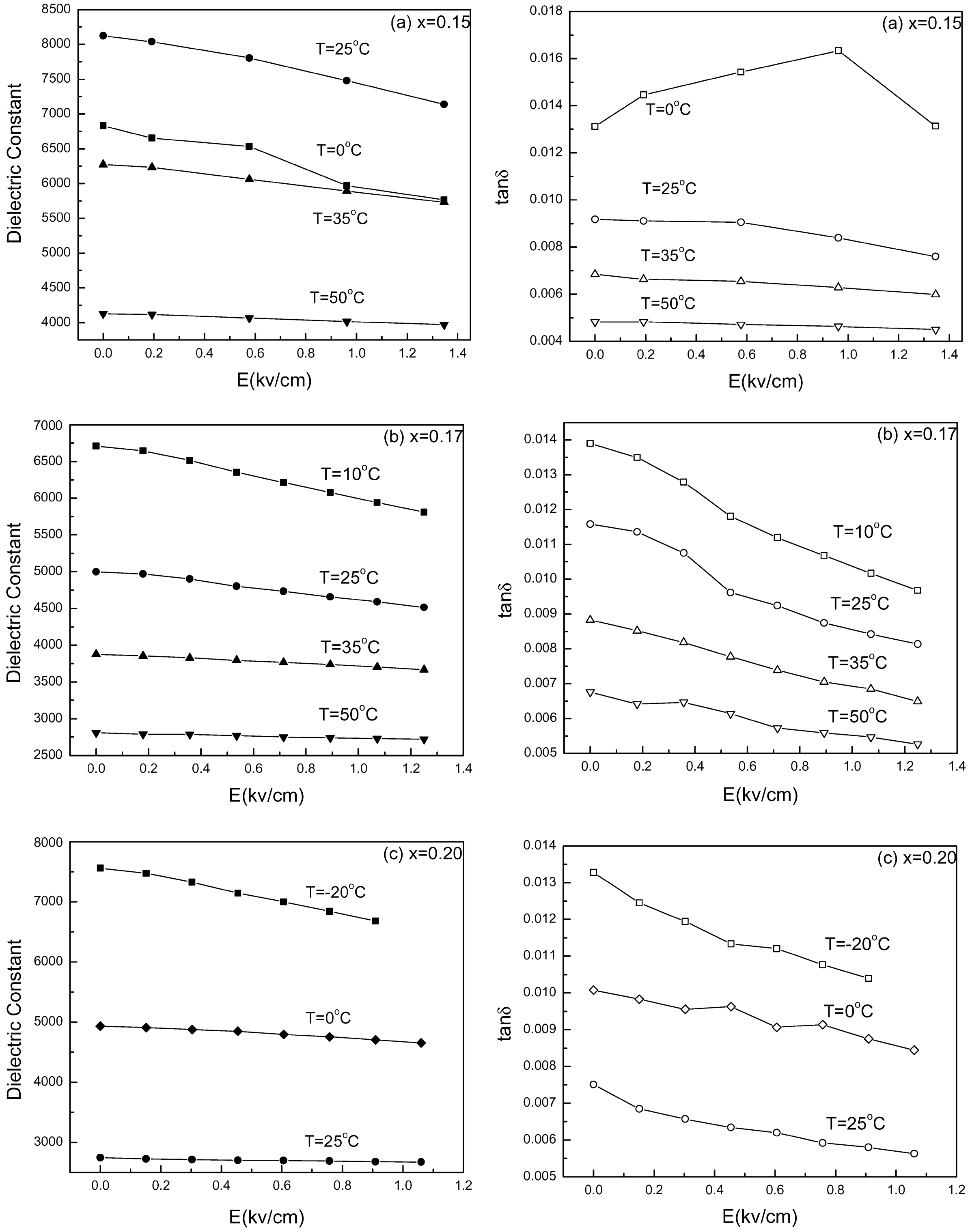

Fig. 4. Dielectric responses of $Ba(Ti_{1-x}Sn_x)O_3$ ceramics at 10 kHz for applied electric dc bias field.

Fig. 5 shows field dependence of dielectric constant of Ba(Ti$_{1-x}$Sn$_x$)O$_3$ solid solutions ($x = 0.15$, 0.17, and 0.20) at 10 kHz and room temperature with the external voltage up to 200 V. The electric field is applied in the following steps (1) increasing from zero to 200 V, (2) decreasing from 200 V to zero. The field dependence of dielectric constant increases a lot when the external voltage increases further. For example, tunability for $x = 0.20$ varies from 2.7% under 1 kV/cm to 13.6% under 6 kV/cm. With decreasing Sn content, field dependence of Ba(Ti$_{1-x}$Sn$_x$)O$_3$ solid solutions at room temperature increases apparently. When $x = 0.15$, tunability reaches to 56% under 7.7 kV/cm, the highest value in the investigated compostions. So, field dependence of dielectric properties of Ba(Ti$_{0.85}$Sn$_{0.15}$)O$_3$ ceramic is characterized particularly and thoroughly, shown in Fig. 6. The electric field was applied in the following steps (1) increasing from zero to 200 V, (2) decreasing from 200 V to zero, (3)increasing from zero to –200 V, and (4) decreasing from –200 V to zero. It can be seen that the external electric-field tunable behavior of Ba(Ti$_{0.85}$Sn$_{0.15}$)O$_3$ is symmetrical and stable and tunability at 7.7 kV/cm, 10 kHz and room temperature have already reached to 56% with $\varepsilon \sim 3800$ and $\tan\delta \sim 3 \times 10^{-3}$, competitive to all the currently studied tunable dielectrics. In addition, the present DC bias electric field (7.7 kV/cm) is still very low, and tunability should increase further under higher external E. On the other hand, high dielectric constant permits much space in dielectric and tunable properties improvement. In particular, dielectric loss can be reduced by adding

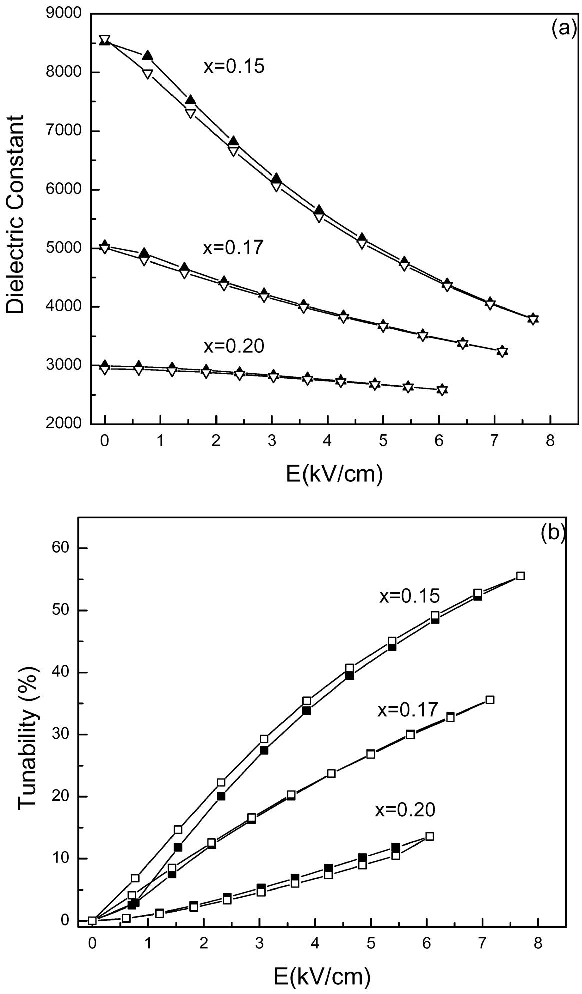

Fig. 5. Field dependence of Ba(Ti$_{1-x}$Sn$_x$)O$_3$ dense ceramics at room temperature and 10 kHz (solid symbol, bias E increasing; hollow symbol, bias E descending).

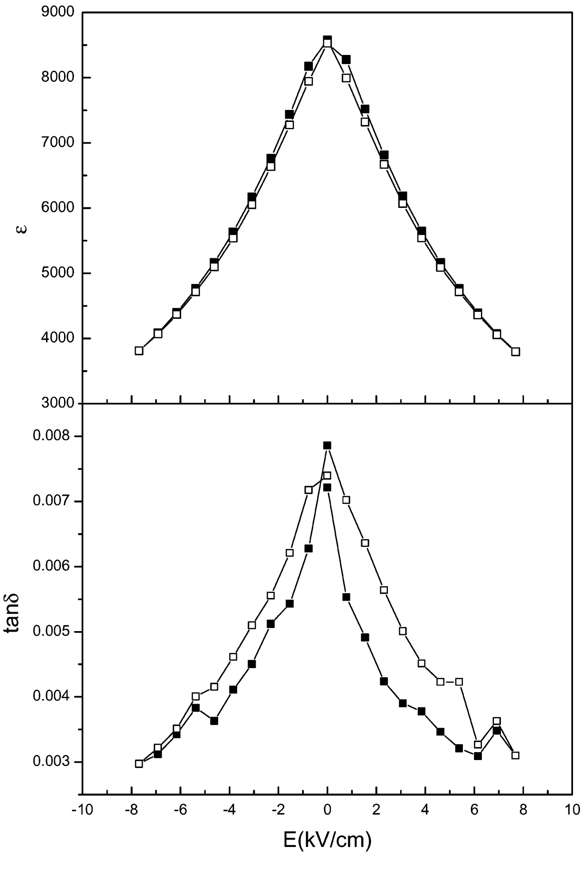

Fig. 6. Field dependence of dielectric properties of Ba(Ti$_{0.85}$Sn$_{0.15}$)O$_3$ ceramics at room temperature and 10 kHz (solid symbol, bias E increasing; hollow symbol, bias E descending).

additives to BTS solid solutions and dielectric constant can be tailored to the suitable values for practical applications.

4. Conclusion

Ba(Ti$_{1-x}$Sn$_x$)O$_3$ ceramics ($x = 0.15$, 0.17, and 0.20) were prepared by a solid state reaction method, and the dielectric characteristics and their tunability were investigated with microstructures and diffused phase transition behaviors. With increasing Sn content, the T_m of BTS solid solutions decreases almost linearly and BTS shows more DPT and relaxor behaviors.

Obvious DC bias electric-field dependence of dielectric properties of BTS is observed, especially close to the phase transition temperature. The tunability increases with increasing external electric-field, while it drops sharply when the temperature is above Tm. With increasing Sn content, tunability of the studied ceramics at room temperature drops sharply due to Tm decreasing gradually. In the present work, Ba(Ti$_{0.85}$Sn$_{0.15}$)O$_3$ ceramics exhibits high tunability (∼56%) and low loss ($\tan\delta \sim 0.003$) at relatively low electric-field, indicating that it is a promising candidate for electric-field tunable dielectrics working at room temperature.

Acknowledgment

This work was financially supported by National Science Foundation for Distinguished Yong Scholar under grant number 50025205, the Primary Projects of National Science Foundation of China under grant number 50332030 and Chinese National Key Project for Fundamental Researches under grant number 2002CB613302. Thanks are due to Prof. Z.Y. Meng in Shanghai Univ., China for the help during field dependence characterizations.

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