Large nonlinear dielectric behavior in BaTi$_{1-x}$Sn$_x$O$_3$

Pengrong Ren$^1$, Zicheng Liu$^1$, Qian Wang$^1$, Biaolin Peng$^2$, Shanming Ke$^3$, Huiqing Fan$^4$ & Gaoyang Zhao$^1$

BaTi$_{1-x}$Sn$_x$O$_3$ (BTSn, 0 $\leq$ x $\leq$ 0.30) ceramics were prepared by both the conventional sintering (CS) and sparking plasma sintering (SPS). Composition, temperature and grain size dependences of the nonlinear dielectric behaviors were systematically studied. BTSn was found to have especially large tunability ($>90\%$), which is larger than most other Pb-free systems, and is comparable to Pb-based relaxors. The high dielectric tunability in BTSn is attributed to its specific domain structures. Besides, temperature dependent tunability of BTSn presents a dispersed behavior and the dispersion is enhanced with the increase of Sn$^{4+}$ concentrations, which is explained by the compositional fluctuation model.

With the rapid development of tunable devices, nonlinear dielectric materials that have high tunability and low dielectric loss have been investigated extensively. Of the numerous perovskite-structured materials that exhibit variable permittivity under an external dc bias field, solid solutions, such as Ba$_{1-x}$Sr$_x$TiO$_3$ (BST) and BaTi$_{1-y}$Zr$_y$O$_3$ (BZT), have been widely studied. By adjusting the Sr and Zr ions concentrations in BST and BZT, respectively, for example, x = 0.6 or y = 0.35$^{14,15}$, the dielectric permittivity of the materials have been found to be highly tunable at the ambient temperature. In addition to normal ferroelectrics, some relaxor ferroelectric materials have also been reported to have abnormally large dielectric tunability, such as Pb$_{(1/3)_{1-x}}$Ni$_{x}$Ti$_{1/3}$O$_3$, Pb$_{(1/3)_{1-x}}$Nb$_{x}$Ti$_{1/3}$O$_3$, Pb$_{(1/3)_{1-x}}$Ta$_{x}$Ti$_{1/3}$O$_3$ and Pb$_{(1/3)_{1-x}}$Ba$_{x}$ZrO$_3$. The tunable dielectric properties of these relaxor ferroelectric ceramics are attributed to the presence of the “extrinsic” polar clusters as well as “intrinsic” lattice phonon polarization. The high dielectric tunability and low dielectric loss under dc electric field in relaxor ferroelectric ceramics is achieved by controlling the size of the polar clusters, which merged into polar nanoregions (PNRs)$^6$.

Recently, researchers have shown great interest in developing environmentally-friendly lead-free relaxors, in particular those based on BaTiO$_3$. The relaxor behavior in these kinds of materials has been in materials with a heterovalent cation substitution as well as in isovalently substituted-solid solutions such as BaTi$_{1-x}$Sn$_x$O$_3$ (BTSn). A systematic investigation of the Sn$^{4+}$-substitution on the phase transition behavior has been reported$^{16-19}$.

And tunable dielectric properties of BTSn were reported by Chen$^{14}$ and Lu$^{15}$. However, the majority of researches have focused on identifying the roles of dynamic/static PNRs on phase transition behavior$^{16-17}$. By contrast, research efforts towards the effects of domain structures (the morphology of domain, domain size, PNRs) on electric field-dependent nonlinear dielectric behaviors remain limited. Meanwhile, in addition to the contribution of PNRs, some researchers have argued that grain size has effects on the dielectric behavior of ferroelectric materials$^{16,19}$. However, the effect of grain size on the nonlinear dielectric behaviors remains controversial.

In the present work, BaTi$_{1-x}$Sn$_x$O$_3$ (BTSn, 0 $\leq$ x $\leq$ 0.30) solid solutions with a wide compositional range, from the normal ferroelectricity to the diffused phase transition (DPT) state, have been studied. The BTSn ceramics have grain size of 10–20 $\mu$m and 1 $\mu$m when prepared by the conventional sintering (CS) or sparking plasma sintering (SPS), respectively. The effects of domain structure and grain size on the nonlinear dielectric behavior in BTSn are investigated.

**Experimental procedure**

Samples of BaTi$_{1-x}$Sn$_x$O$_3$ with x = 0, 0.02, 0.04, 0.11, 0.15, 0.20 and 0.30 (labelled as BT, BTSn02, BTSn04, BTSn11, BTSn15, BTSn20 and BTSn30, respectively) were prepared by a solid state reaction using BaCO$_3$ (99.9%), TiO$_2$ (99.9%) and SnO$_2$ (99.9%) as starting reagents. The raw powders were dried at 180 °C, weighed according to the

---

1. Shaanxi Province Key Laboratory for Electrical Materials and Infiltration Technology, School of Materials Science and Engineering, Xi’an University of Technology, Xi’an, 710048, P.R. China. 2. School of Physical Science & Technology, Guangxi Key Laboratory for Relativistic Astrophysics, Guangxi University, Nanning, 530004, P.R. China. 3. College of Materials Science and Engineering, Shenzhen University, Shenzhen, 518060, P.R. China. 4. State Key Laboratory of Solidification Processing, School of Materials Science and Engineering, Northwestern Polytechnical University, Xi’an, 710072, P.R. China. Correspondence and requests for materials should be addressed to P.R. (email: renpengrong@126.com)
nominal stoichiometric ratio and then ball milled in ethyl alcohol using zirconia balls for 12 h. The resulting calcined powder was cold-isostatic-pressed under a pressure of 200 MPa to give a disk with a diameter of 10 mm and a thickness of 1 mm. The BTSn ceramics were then sintered at 1450 °C for 2 h under air. In order to study the effects of grain size on nonlinear dielectric behavior, BTSn15 ceramics were sintered by an SPS method at 1175 °C for 10 min. The phase structures of the BTSn ceramic powders were determined by X-ray powder diffraction (XRD; D/Max2550VB+PC, Rigaku, Tokyo, Japan) using Cu-Kα1 radiation and linear position-sensitive detector. Raman scattering experiments of the ceramics were performed using an instrument (LabRAM HR800, Horiba JobinYvon, Lyon, France) in a backward scattering geometry where the exciting source was a 514.5 nm line from an argon ion laser. The microstructure of the samples were observed using a scanning electron microscope (SEM, DSM 950, Zeiss, Oberkochen, Germany) operated at 15 kV. Transmission electron microscopy (TEM) samples were prepared by including grinding, cutting, dimpling, and ion milling. The dimpled disks were annealed at 200 °C for 2 h to minimize any artifacts that may have been introduced during mechanical thinning. A transmission electron microscope (Tecnai F30, FEI, Hillsboro, OR) at 200 kV accelerating voltage was used to analyze the disks.

A metal-insulator-metal (MIM) capacitor was formed in order to characterize the electric properties. To form this capacitor, the sintered pellets were polished, coated with silver electrodes and fired at 600 °C for 30 min. The dielectric properties of BTSn ceramics were investigated over the range of 200 °C to −100 °C (cooling rate 3 °C/min) using a precision LCR meter (E4294A, Agilent, Santa Clara, CA, USA) connected with a temperature controller (TP94, Linkam, Surrey, UK). Frequencies from 100 Hz to 1 MHz at a signal level of 0.5 V/mm were used for the measurement. The dielectric tunability properties were investigated at 25 °C by using an automatic component analyzer (TH2818, Tonghui, Changzhou, China) at 10 kHz. A blocking circuit was adopted to protect the analyzer from applied bias voltages. The external bias field was applied in steps of 1 kV/cm. And the temperature dependent tunability was measured by put a sample on a heater and the temperature is controlled from room temperature to 150 °C. Ferroelectric hysteresis loops were measured at room temperature using a ferroelectric tester (TF2000, aixACCT, Aachen, Germany).

Results and Discussions

Figure 1(a) shows XRD patterns of BTSn ceramics recorded at room temperature. The XRD patterns clearly show the formation of pure perovskite structure without any secondary phases. The split characteristic and the relative intensity of (002)/(200) peaks at about 45° indicates that at room temperature BTSn has a tetragonal phase with x ≤ 0.04, while it turns into a unique peak with x ≥ 0.11, suggesting a rhombohedral or cubic phase is obtained with x ≥ 0.11 at room temperature. The Raman spectra in Fig. 1(b) show similar results. The peak at 307 cm⁻¹,
which is a characteristic peak of tetragonal BaTiO$_3$, diminishes with increasing Sn content, and disappears when $x \geq 0.11$. The temperature dependence of the dielectric permittivity recorded at 10 kHz and 0.5 V during the cooling process from 200 to $-100 \, ^\circ\text{C}$ for the seven BTSn compositions is shown in Fig. 1(c). Three permittivity anomalies show that the samples undergo three phase transitions with decreasing temperature, i.e., cubic-tetragonal ($C$-$T$), tetragonal-orthorhombic ($T$-$O$) and orthorhombic-rhombohedral ($O$-$R$) for BT, BTSn0$_2$ and BTSn0$_4$. In contrast, BTSn1$_1$, BTSn1$_5$ and BTSn2$_0$ display only one phase transition from the cubic phase to rhombohedral phase at 42, 13 and $-36 \, ^\circ\text{C}$, respectively$^{12}$. The phase transition of BTSn3$_0$ occurs beyond the measured temperature range. For better illustration, a rough phase diagram of BTSn is shown in Fig. 1(d). The $C$-$T$, $T$-$O$ and $O$-$R$ phase transition lines gradually merge and the four phases eventually meet together, at a quasi-quadruple point around $42 \, ^\circ\text{C}$ with a composition of BTSn1$_1$. This is in agreement with the reported literature values$^{12}$. At room temperature (25 $^\circ\text{C}$), BTSn1$_1$ is in a ferroelectric state, while BTSn1$_5$ and BTSn2$_0$ are in a paraelectric state. As a result, each of them shows different dielectric behaviors, and each of these behaviors is studied in the following.

Figure 2(a–c) show the temperature dependences of the real ($\varepsilon'$) and imaginary parts ($\varepsilon''$) of the complex dielectric permittivities of BTSn1$_1$, BTSn1$_5$ and BTSn2$_0$ measured at different frequencies. With increasing Sn content, the peak of the dielectric permittivity becomes progressively more diffuse, but the peak position does not change. This behavior is denoted as DPT in order to differentiate it from relaxor behavior. Although DPT behavior has been observed in a number of systems, the interpretations of the nature of DPT behavior are complicated and controversial$^{21, 22}$. In BTSn ceramics, substitution of Ti$^{4+}$ by Sn$^{4+}$ results in the random breaking of Ti–O bonds because Sn$^{4+}$ does not go off-center. Since the ionic radius of Sn$^{4+}$ is larger than Ti$^{4+}$, Sn$^{4+}$ has less free space to shift within the oxygen octahedron. Spatial fluctuations of defective bonds lead to fluctuations of polar correlations, therefore precursor clusters are created and the Curie peak is broadened$^{10}$. The insets in Fig. 2(a–c) show the microstructure of BTSn1$_1$, BTSn1$_5$ and BTSn2$_0$, respectively. Each sample has a dense microstructure with grain sizes 10–20 $\mu\text{m}$.

In order to quantitatively describe the broad Curie peak, the temperature dependences of the dielectric permittivity were fit by using the Curie-Weiss and Lorenz law. Figure 2(d) shows the temperature dependence of the inverse dielectric permittivity as measured at $f = 10 \, \text{kHz}$ plotted against a reduced temperature scale. Evidently, within a certain temperature range above $T_{\text{m}}$, $1/\varepsilon'$ is not linear as is predicted by the Curie-Weiss law. Therefore, we adopted an empirical relationship to describe the temperature dependence of the dielectric permittivity$^{23, 24}$

$$1/\varepsilon' = 1/\varepsilon_{\text{max}}' + [(T - T_{\text{m}})/C]^\gamma$$

(1)

where $C$ and $\gamma$ are constants. The value of $\gamma$ is regarded as an indicator of the diffuseness of the phase transition. When $\gamma = 1$, Eq. (1) indicates a normal ferroelectric behavior and when $\gamma = 2$ it indicates a so-called DPT.
Traditional, in the ferroelectric state, the permittivity as a function of electric field can monotonously decrease. A very small E loop was obtained in BTSn20. There is also no obvious hysteresis phenomena for any of the prepared ceramics, including BTSn20. The observed peculiarities of the temperature-dependent behavior is in good agreement with the literature.

\[
\varepsilon' = \varepsilon_0 + \varepsilon_1 \left( \frac{\varepsilon_0}{\varepsilon_0 + \varepsilon_1} \right) \left( \frac{T}{T_m} \right) \left( \frac{T_m}{T} \right)
\]

Equation (4) is used to fit the permittivity data. The parameters \(\varepsilon_0\), \(\varepsilon_1\), \(T_m\), and \(T\) are fixed to the values obtained from fitting the dielectric response data. The values of \(\varepsilon_0\) and \(\varepsilon_1\) are in an order of magnitude for BTSn11, BTSn15 and BTSn20, respectively, which are in agreement with the results of Bi-doped SrTiO\(_3\) (2.9 \(\times\) 10\(^{10}\) V m\(^{-1}\) C\(^{-1}\)) and Ba\(_0.6\)Sr\(_{0.4}\)TiO\(_3\) (2.9 \(\times\) 10\(^{10}\) V m\(^{-1}\) C\(^{-1}\))\(^{27}\). Polar clusters of BTSn11, BTSn15 and BTSn20 were measured at 32 \(^\circ\)C and 10 Hz and are shown in Fig. 2(f). At 32 \(^\circ\)C, BTSn11 is in a ferroelectric state, while BTSn15 and BTSn20 are in a paraelectric state. However, the samples show E loops. As Sn concentration is increased in BTSn, the saturated polarization and remnant polarization change. A very small E loop was obtained in BTSn20. There is also no obvious hysteresis phenomena for any of the prepared ceramics, including BTSn20. The observed peculiarities of the temperature-dependent behavior is in good agreement with the literature.

Table 1. The parameters obtained from fitting by Eqs (1) and (2).

| Samples   | f (kHz) | \(T_m/\^\circ\)C | \(T_m\) | \(\varepsilon_{\infty}\) | \(\gamma\) | \(T_m/\^\circ\)C | \(\varepsilon_\infty\) | \(\delta\) |
|-----------|---------|----------------|--------|----------------|----------|--------|----------------|----------|
| BTSn11    | 10      | 42             | 25355  | 1.46(1)        | 38.8(2)  | 24882(9)  | 12.1(2)        |
| BTSn15    | 10      | 13             | 19302  | 1.80(1)        | 10.0(4)  | 19000(8)  | 17.3(3)        |
| BTSn20    | 10      | -36            | 14844  | 2.04(1)        | -40.1(3) | 14778(8)  | 21.5(2)        |

Figure 3 illustrates permittivity as a function of dc electric field from bias electric field measurement taken at 10 kHz and room temperature. The measurements were made by stepwise increasing bias electric field from 0 to 30 kV/cm. With the electric field increasing, the permittivities of BTSn11, BTSn15 and BTSn20 monotonously increase. Excellent fits are achieved above \(T_m\) but the nonlinearity with \(E\) loops. As Sn concentration is increased in BTSn, the saturated polarization and remnant polarization change. A very small E loop was obtained in BTSn20. There is also no obvious hysteresis phenomena for any of the prepared ceramics, including BTSn20. The observed peculiarities of the temperature-dependent behavior is in good agreement with the literature.

\[
\varepsilon'(E) = \varepsilon_0(0)/\{1 + \lambda[\varepsilon_0\varepsilon_\infty(0)^2E^3]\}^{1/3}
\]

Equation (3) is used to fit the permittivity data. The parameters \(\varepsilon_0\), \(\varepsilon_\infty\), \(\lambda\), and \(E\) are fixed to the values obtained from fitting the dielectric response data. The values of \(\lambda\) are in an order of magnitude for BTSn11, BTSn15 and BTSn20, respectively, which are in agreement with the results of Bi-doped SrTiO\(_3\) (6.0 \(\times\) 10\(^{10}\) V m\(^{-1}\) C\(^{-1}\))\(^{26}\) and Ba\(_0.6\)Sr\(_{0.4}\)TiO\(_3\) (2.9 \(\times\) 10\(^{10}\) V m\(^{-1}\) C\(^{-1}\))\(^{27}\). Polar clusters of BTSn11, BTSn15 and BTSn20 are 67(1), 93(1) and 41(1) nm in size, respectively. Besides, \(P_s\) are 4.1(1), 2.8(1) and 0.50(1) \(\mu\)C cm\(^{-2}\) for BTSn11, BTSn15 and BTSn20, respectively. These polarizations are close to the remnant polarizations obtained from the aforementioned E- loops, as shown in Fig. 2(f).

Tunability (\(\eta\)) is usually calculated by using the following expression:

\[
\eta = \frac{\varepsilon'(0) - \varepsilon'(E)}{\varepsilon(0)} \times 100%
\]

where \(\varepsilon'(0)\) and \(\varepsilon'(E)\) represent the dielectric permittivity at zero and a certain electric field, respectively. The insets in Fig. 3 show the tunability of BTSn11, BTSn15 and BTSn20 as a function of electric field measured at 10 kHz.
32 °C and 50 °C, with $f = 10 \text{kHz}$ and with the maximum electric field of 30 kV/cm. At 32 °C, BTSn15 exhibits the maximum tunability (90.5%), which is larger than most Pb-free systems, for example, BST and BZT, and even comparable with the Pb-based relaxors, such as Pb(Mg1/3Nb2/3)O3 and Pb0.8Ba0.2ZrO3. BTSn15 has larger tunability at 50 °C, which is up to 92.6%.

The overall tunability can be ascribed to the contribution of the Johnson term ($t_J$) and Langevin term ($t_L$), which are quantified by Eq. (6) and (7), respectively:

$$t_j = \frac{\varepsilon_j(0) - \varepsilon_j(E)}{\varepsilon(0) - \varepsilon(E)} \times 100\%$$  \hspace{1cm} (6)

$$t_L = \frac{\varepsilon_L(0) - \varepsilon_L(E)}{\varepsilon(0) - \varepsilon(E)} \times 100\%$$  \hspace{1cm} (7)

$\varepsilon_j(0)$, $\varepsilon_j(E)$, $\varepsilon_L(0)$ and $\varepsilon_L(E)$ are dielectric permittivity of the simulated Johnson term and Langevin term at zero and a certain electric field, respectively. The calculated $t_j$ and $t_L$ are listed in Table 2. As shown in Table 2, BTSn15

| Samples      | $\lambda$/V m$^{-1}$ C$^{-1}$ | $L$/nm | $P_0$/μC cm$^{-2}$ | $t_J$/% | $t_L$/% | $\eta$/% |
|--------------|-------------------------------|--------|-------------------|---------|---------|----------|
| BTSn11*      | $(9.2(1) \times 10^{10})$     | 6.7(1) | $4.1(1)$          | 28.42   | 71.58   | 92.6     |
| BTSn15       | $(7.5(1) \times 10^{10})$     | 9.3(1) | $2.8(1)$          | 21.27   | 78.73   | 90.5     |
| BTSn20       | $(2.1(1) \times 10^{10})$     | 4.1(1) | $0.50(1)$         | 49.72   | 50.28   | 72.3     |
| BTSn15-SPS   | $(9.7(1) \times 10^{10})$     | 5.5(1) | $4.1(1)$          | 35.74   | 64.26   | 78.1     |

Table 2. The fitting parameters by using Eq. (4): anharmonic coefficient ($\lambda$), cluster size ($L$) and effective polarization ($P_0$), the contribution of the Johnson term ($t_j$) and Langevin term ($t_L$), the overall tunability ($\eta$) of BTSn ceramics. 

*Parameters of BTSn11 are obtained based on the dielectric tunability data measured at 50 °C. Parameters of other samples are obtained based on the dielectric tunability data measured at 32 °C.

32 °C and 50 °C, with $f = 10 \text{kHz}$ and with the maximum electric field of 30 kV/cm. At 32 °C, BTSn15 exhibits the maximum tunability (90.5%), which is larger than most Pb-free systems, for example, BST, and even comparable with the Pb-based relaxors, such as Pb(Mg1/3Nb2/3)O3 and Pb0.8Ba0.2ZrO3. BTSn11 has larger tunability at 50 °C, which is up to 92.6%.

The overall tunability can be ascribed to the contribution of the Johnson term ($t_j$) and Langevin term ($t_L$), which are quantified by Eq. (6) and (7), respectively:
has the maximum Langevin contribution (78.73%), which suggests that the “extrinsic” polarization plays a major role on its nonlinear dielectric behavior. For normal ferroelectrics such as PbTi$_{1-x}$Zr$_x$O$_3$ (PZT) and BaTiO$_3$ (BT), the “extrinsic” polarization is usually derived from the rotation of domain and domain-wall motion. However, for relaxors such as Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ (PMN) and BaTi$_{1-x}$Zr$_x$O$_3$ (BZT) the “extrinsic” polarization is mainly from the contribution of nanometer polar clusters. BTSn$_{15}$ is located at an intermediate state between “normal” ferroelectric and relaxor. Therefore, it is probable that the rotation of domain, domain-wall motion as well as polar clusters co-contribute on its nonlinear dielectric behavior.

Figure 4 is typical TEM image of BTSn$_{11}$, BTSn$_{15}$ and BTSn$_{20}$ at room temperature. In BTSn$_{11}$, lamellar-like domains are observed. The width between two domain boundaries is about 150 nm. However, in BTSn$_{15}$, lamellar-like but slim domains that are ~50 nm in size appear, meanwhile PNRs with a size of 10 nm are present and coexist with the lamellar-like domains, as shown in Fig. 4(b). BTSn$_{20}$ does not exhibit lamellar-like domains, while PNRs with a size of 10 nm are observed. As the domain size is proportional to the square root of domain wall energy, slim domains with reduced domain wall energy can easily respond to external excitations (e.g., mechanical force or electric field). For this reason, BTSn$_{15}$ can be easily excited by electric field and its permittivity suddenly decreases when applied a small electric field, as shown in Fig. 3(c). Therefore BTSn$_{15}$ has the maximum Langevin contribution and has a large tunability at room temperature. Such a phenomenon was also validated in both lead-based and lead-free piezoceramics. Zhang reported that nanodomains (50 ± 2 nm) could be assembled into domain stripes after poling, thus benefit the high piezoelectric properties.

From the above results, it can be found that the nonlinear dielectric behavior of BTSn is highly related to its domain structures. Figure 5 gives a schematic evolution of domain structures with increasing Sn$^{4+}$ concentrations at the measured temperature $T$: (a) BTSn$_{11}$, (b) BTSn$_{15}$ and (c) BTSn$_{20}$.

Figure 4. TEM images of (a) BTSn$_{11}$, (b) BTSn$_{15}$ and (c) BTSn$_{20}$ at room temperature.

Figure 5. Schematic evolution of domain structures with the increasing of tin concentrations at the measured temperature $T$: (a) BTSn$_{11}$, (b) BTSn$_{15}$ and (c) BTSn$_{20}$.
Figure 6. (a–c) Dielectric permittivity as a function of dc electric field of BTSn11, BTSn15 and BTSn20 from bias electric field measurement taken at 10 kHz and at different temperatures; (d) dielectric tunability of BTSn11, BTSn15 and BTSn20 at different temperatures.

Figure 6 (a–c) shows dielectric permittivity as a function of dc electric field of BTSn11, BTSn15 and BTSn20 at 10 kHz and at different temperatures. And the tunability of BTSn11, BTSn15 and BTSn20 at different temperatures is summarized in Fig. 6(d). Tunability of BTSn11 first increases and reaches a maximum value around $T_c$, and then gradually decreases. Tunability of BTSn15 and BTSn20 gradually decreases with temperature increasing. Temperature dependent tunability of BTSn also presents a dispersed behavior. In order to evaluate the dispersion of tunability, temperature dependent tunability was also fitted by a Lorenz-type formula:

$$\eta_{\text{fit}}/\eta = 1 + (T - T_c)^2/2\delta^2$$

where $\eta_{\text{fit}}$ is a constant and $\delta$ is the diffuseness of the tunability as a function of the temperature. The fitted $\delta$ for BTSn11, BTSn15 and BTSn20 are 25.7(1), 40.7(1) and 49.2(1), respectively. The variance of $\delta$, with the temperature has a similar trend with $\delta$, indicating that tunability is also affected by the concentration of Sn ions. Large concentration of Sn ions not only leads to the depression of the dielectric peak at $T_c$, tunability is also dispersed due to compositional fluctuation at a local region.

Besides temperature, the grain size also has some effects on the nonlinear dielectric behavior of BTSn ceramics. BTSn15 ceramics were prepared by an SPS method (labeled as BTSn15-SPS) with a relative density of 98%. Figure 7(a) shows the temperature-dependent real and imaginary dielectric permittivity of BTSn15-SPS. The inset in Fig. 7(a) shows the SEM image of BTSn15-SPS with a grain size less than 1 $\mu$m. Dielectric permittivity of BTSn15-SPS is slightly lower than BTSn15 prepared by CS. dc bias dependent dielectric permittivity of BTSn15-SPS is also investigated and is shown in Fig. 7(b). The data were also fitted by Eq. (4). The results suggest that the contribution of the Langevin term of BTSn15-SPS is slightly lower than that of BTSn15 prepared by CS. And $L$ and $P_0$ are 5.5(1) nm and 4.1(1) $\mu$C/cm$^2$. The increase of the polarization might be due to the enhancement of the density of sample. The inset of Fig. 7(b) illustrates the tunability of BTSn15-SPS as a function of the electric field. The maximum tunability is 78.1% at the electric field of 30 kV/cm, which is smaller than that of conventional-sintered BTSn15. The reason is speculated that because BTSn15-SPS has smaller grain size, the rotation of the micro-domain might be hindered by the grain boundary, and ultimately leading to the decrease in tunability and the contribution of Langevin term. This will be studied in detail and the corresponding evidence will be provided in our follow-up work.

Conclusions

BaTi$_{1-x}$Sn$_x$O$_3$ (BTSn, $0 \leq x \leq 0.30$) ceramics that have a wide compositional range, from normal ferroelectricity to the DPT state, were prepared by both the conventional sintering and sparking plasma sintering. BTSn15 was
found to have the maximum tunability at the room temperature, which is up to 90.5%. The nonlinear dielectric behavior of BTSn ceramics was analyzed by the multipolarization-mechanism model. The enhanced dielectric tunability is attributed to the presence of micro-domains that coexist with polar nanoregions. This work could provide new insights into the nonlinear dielectric behavior of Pb-free dielectrics.

References
1. Joshi, P. C. & Cole, M. W. Mg doped thin films for tunable microwave applications. Appl. Phys. Lett. 77, 289–291 (2000).
2. Tang, X. G., Chew, K.-H. & Chan, H. L. W. Diffuse phase transition and dielectric tunability of Ba(Zr, Ti, x)O, relaxor ferroelectric ceramics. Acta Mater. 52, 5177–5183 (2004).
3. Zhang, J. J. et al. Microwave and infrared dielectric response of tunable Ba1-xSrTi3O7 ceramics. Acta Mater. 57, 4491–4499 (2009).
4. Chou, X. J., Zhao, J. W. & Yao, X. Relaxor Behavior and Dielectric Properties of MgTiO3-Doped BaZr0.2Ti0.8O3, Composite Ceramics for Tunable Applications. J. Am. Ceram. Soc. 90, 2799–2801 (2007).
5. Peng, B. L., Fan, H. Q. & Zhang, Q. The Contribution of the "Extrinsic" Polarizations to the Dielectric Tunability of Pb(Mg1/3Nb2/3)1-xTiO3 Relaxor Ferroelectrics. J. Am. Ceram. Soc. 95, 1651–1655 (2012).
6. Peng, B. L., Fan, H. Q. & Zhang, Q. Dielectric tunability properties of the Pb[(Mg0.5Nb0.5)x(Zr0.5Ti0.5)1-x]O3 ceramics. J. Alloys. Compd. 549, 283–287 (2013).
7. Peng, B. L., Fan, H. Q. & Zhang, Q. High tunability in (111)-oriented relaxor Pb0.8Ba0.2ZrO3 thin film with antiferroelectric and ferroelectric two-phase coexistence. J. Am. Ceram. Soc. 96, 1852–1856 (2013).
8. Xu, Q. et al. Evolution of dielectric properties in BaZr1-xTixO3 ceramics: effect of polar nanoregions. Acta Mater. 61, 4481–4489 (2013).
9. Smolensky, G. A. & Isupov, V. A. Ferroelectric characteristics of solid solutions of barium stannate in barium titanate. Soviet J. Tech. Phys. 24, 1375–1386 (1954).
10. Shvartsman, V. V., Kleemann, W. & Dec, J. Diffuse phase transition in BaTi1-xSnxO3 ceramics: An intermediate state between ferroelectric and relaxor behavior. J. Appl. Phys. 99, 124111 (2006).
11. Lei, C., Bokov, A. A. & Ye, Z.-G. Ferroelectric to relaxor crossover and dielectric phase diagram in the BaTiO3–BaSnO3 system. J. Appl. Phys. 101, 084105 (2007).
12. Yao, Y. G. et al. Large piezoelectricity and dielectric permittivity in BaTiO3-xBaSnO3 system: The role of phase coexisting. EPL. 98, 27008 (2012).
13. Horchidan, N. et al. Multiscale study of ferroelectric–relaxor crossover in BaSn1-xTi1-xO3 ceramics. J. Eur. Ceram. Soc. 34, 3661–3674 (2014).
14. Wang, T., Chen, X. M. & Zheng, X. H. Dielectric characteristics and tunability of barium stannate titanate ceramics. J. Electroceram. 11, 173–178 (2003).
15. Lu, S. G., Xu, Z. K. & Chen, H. Tunability and relaxor properties of ferroelectric barium stannate titanate ceramics. Appl. Phys. Lett. 85, 5319–5321 (2004).
16. Kleemann, W., Miga, S. X., Xu, Z. K., Lu, S. G. & Dec, J. Non-linear permittivity study of the crossover from ferroelectric to relaxor and cluster glass in BaTi1-xSnxO3 (x=0.175–0.30). Appl. Phys. Lett. 104, 182910 (2014).
17. Zhang, L., Hao, H., Liu, H., Cao, M. & Yao, Z. Dielectric response of 0.85 Ba(Ti0.96Zr0.04)O3–0.15 Bi(Mg0.5Ti0.5)O3 relaxor ferroelectrics under electric field: evolution of PNRs. J. Mater. Sci.: Mater. Electr. 26, 1–6 (2015).
18. Li, C. H., Zhang, X. Q., Cheng, Z. H. & Sun, Y. Room temperature giant dielectric tunability effect in bulk LuFe2O4. Appl. Phys. Lett. 92, 182903 (2008).
19. Iles, D. C. & Atheron, D. L. Theory of ferromagnetic hysteresis. J. Magn. Magn. Mater. 61, 48–60 (1986).
20. Ren, P. R., Fan, H. Q., Wang, X. & Dong, G. Z. Phase transition, high figure of merit and polar nano-regions in dielectric tunable lanthanum substituted barium titanate. J. Alloys. Compd. 617, 337–344 (2014).
21. Mueller, V., Beige, H. & Abicht, H. P. Non-Debye dielectric dispersion of barium titanate thin film and tunable microwave applications. Appl. Phys. Lett. 84, 1341 (2004).
22. Wei, X. Y., Feng, Y. J. & Yao, X. Dielectric relaxation behavior in barium stannate titanate ferroelectric ceramics with diffused phase transition. Appl. Phys. Lett. 83, 2031 (2003).
23. Uchino, K. & Nomura, S. Critical exponents of the dielectric constants in diffused-phase transition crystals. Ferroelectrics 44, 55–61 (1982).
24. Santos, I. A. & Eiras, J. A. Phenomenological description of the diffuse phase transition in ferroelectrics. J. Phys.: Condens. Matter 13, 11733 (2001).
25. Bokov, A. A. et al. Empirical scaling of the dielectric permittivity peak in relaxor ferroelectrics. Phys. Rev. B 68, 052102 (2003).
26. Ang, C. & Yu, Z. dielectric-field dependence of the dielectric constant in polar dielectrics: Multipolarization mechanism model. Phys. Rev. B 69, 174109 (2004).
27. Tsurumi, T. et al. Ultrawide range dielectric spectroscopy of BaTiO$_3$-based perovskite dielectrics. Appl. Phys. Lett. 91, 182905 (2007).
28. Curecheriu, L. P., Mitoseriu, L. & Ianculescu, A. Tunability properties of the Pb(Mg$_{1/3}$Nb$_{2/3}$O$_3$) relaxors and theoretical description. J. Alloys. Compd. 485, 1–5 (2009).
29. Rossetti, G. A., Khachatryan, A. G., Akcay, G. & Ni, Y. Ferroelectric solid solutions with morphotropic boundaries: vanishing polarization anisotropy, adaptive, polar glass, and two-phase states. J. Appl. Phys. 103, 134113 (2008).
30. Qin, Y. L., Zhang, J. L., Yao, W. Z., Lu, C. J. & Zhang, S. J. Domain configuration and thermal stability of (K$_{0.48}$Na$_{0.52}$)(Nb$_{0.96}$Sb$_{0.04}$)O$_3$-Bi$_{0.50}$(Na$_{0.82}$K$_{0.18}$)$_{0.50}$ZrO$_3$ piezoceramics with high $d_{33}$ coefficient. ACS Appl. Mater. Interfaces 8, 7257–7265 (2016).

Acknowledgements
This work was financially supported by the National Natural Science Foundation of China (No. 51402234, No. 51402196), the China Postdoctoral Science Foundation (2014M552229, 2015T80915), Natural Science Basic Research Plan (No. 2015JQ158, 2015JQ5142), Postdoctoral Scientific Research Project and Young Talent fund of University Association for Science and Technology (20150106) in Shaanxi, China, the doctoral starting fund (No. 101-211408) and New-Star of science and technology (101-256101511) of Xi’an University of Technology.

Author Contributions
R.P.R., F.H.Q. and Z.G.Y. wrote the main manuscript text. R.P.R. prepared Figures 1–6. W.Q. prepared samples and measured dielectric properties. L.Z.C. prepared TEM samples. P.B.L. and K.S.M. carried out TEM analysis. All authors reviewed the manuscript.

Additional Information
Competing Interests: The authors declare that they have no competing interests.

Publisher’s note: Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made. The images or other third party material in this article are included in the article’s Creative Commons license, unless indicated otherwise in a credit line to the material. If material is not included in the article’s Creative Commons license and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this license, visit http://creativecommons.org/licenses/by/4.0/.

© The Author(s) 2017