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# Dielectric properties and tunability of $Ba(Zr_xTi_{1-x})O_3$ ceramics under high DC electric field

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## Abstract

$Ba(Zr_xTi_{1-x})O_3$ (BZT) ($x = 0.25$, 0. 3, 0.35, 0.4) ceramics were prepared by the traditional ceramic processing and their structural, surface morphological, dielectric properties, tunable properties as well as the mechanism of their nonlinear dielectric constant under DC electric field were systemically examined. The Zr ions substitution of Ti ions has a strong effect on the dielectric properties and the grain sizes. The results show $Ba(Zr_xTi_{1-x})O_3$ ($x = 0.25$, 0.3, 0.35) ceramics to be promising candidates for the DC electric field tunable materials for microwave electronics application, because they exhibit high tunability (27.6%, 26.3%, 19.4%, respectively) as the strength of electric field is up to 2 kV/mm, low dielectric loss (0.001–0.002, 0.001–0.002, 0.004–0.005, respectively) at 10 kHz at room temperature and low temperature coefficient of capacitance.

*Keywords:* A. Powders: solid state reaction; C. Dielectric properties; Electrical properties; D. $BaTiO_3$ and titanate

## 1. Introduction

Recently, there has been continued growth of interest in the use of $BaTiO_3$-based ceramics, because they are promising materials for tunable microwave device application such as electronically tunable mixers, delay lines, filters, capacitors, resonators and phase shifters [1–3]. Such applications demand the following characteristics: low dielectric constant ($\varepsilon_r$); large tunability ($(\varepsilon_{r(0)} - \varepsilon_{r(app)})/\varepsilon_{r(0)}$, where $\varepsilon_{r(0)}$ and $\varepsilon_{r(app)}$ are the dielectric constants under zero DC field and under the applied field, respectively); low loss tangent ($\tan\delta$); and good thermal stability. The tunability of materials affects their properties through the change of the dielectric constant with applied electric field. Higher tunability is desirable. The reduction of the dielectric constant decreases the overall impedance mismatch. The low loss tangent serves to decrease the insertion loss. Generally, high tunability leads to high loss and high dielectric constant; in order to get a balance among these parameters, some non-ferroelectric compounds are added to reduce the dielectric constant and loss while promising comparatively high tunability. Currently the most studied solid solutions are $(Ba, Sr)TiO_3$ with some additives such as MgO, $MgTiO_3$, or $Al_2O_3$ [4–6], but their reproducibility, as well as their stability need to be improved. So further exploration on new materials is desirable in developing tunable devices.

$Ba(Zr_xTi_{1-x})O_3$ (BZT) ceramic is obtained by substituting ions at the B site of $BaTiO_3$ with Zr ions. It is reported that BZT system has high dielectric constant and low loss tangent at room temperature. And for $x > 0.27$, there is only one broad peak of dielectric constant at $T_{max}$ with frequency dispersion for $T \ll T_{max}$ and an increase of $T_{max}$ when frequency increases, exhibiting a typical relaxor-like behavior [7,8]. Dielectric properties of BZT ceramics under a high alternative electric field were reported by Tsurumi et al. [9]. Zhi Yu et al. reported high tunability of $Ba(Zr_{0.3}Ti_{0.7})O_3$ ceramics [10]. Tang et al. reported phase transition and dielectric tunability of $Ba(Zr_xTi_{1-x})O_3$ ceramics, however these authors laid emphases on the diffuse phase transition and relaxor properties of $Ba(Zr_xTi_{1-x})O_3$ ceramics, and the behavior of BZT system under DC electric field was not studied carefully and systematically [11]. So it is necessary to study the behavior of BZT ceramics under DC electric field systemically and find the main factor of affecting its nonlinear properties. Generally, ferroelectrics with Curie temperature below the operating temperature are

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employed in practical device applications, because the paraelectric state of ferroelectric materials has lower dielectric loss owing to the disappearance of ferroelectric hysteresis. In this paper, we choose $Ba(Zr_xTi_{1-x})O_3$ ceramics ($x = 0.25, 0.3, 0.35, 0.4$) as research objective because they have low dielectric loss and study the DC electric field dependence of them systematically. The results show that $Ba(Zr_{0.25}Ti_{0.75})O_3$, $Ba(Zr_{0.3}Ti_{0.7})O_3$ and $Ba(Zr_{0.35}Ti_{0.65})O_3$ ceramics are promising candidates for the electric field tunable materials for microwave electronics application.

## 2. Experimental procedure

$Ba(Zr_xTi_{1-x})O_3$ ($x = 0.25, 0.3, 0.35, 0.4$) ceramics were prepared by traditional ceramic processing by mixing $BaCO_3$ (99.00%), $ZrO_2$ (99.13%), $TiO_2$ (99.08%) in chemical stoichiometric proportions and milled with alcohol and agate balls for 24 h. The dried powders were then calcined in air at 1250 °C for 2 h on recrystallised alumina crucibles. The calcined powders were again wet-grounded for 48 h. The dry calcined powders were mixed with polyvinyl alcohol (7 wt.%). The powders were then pressed into pellets of 13 mm in diameter and about 2 mm in thickness and sintered at 1400 °C for 2 h. After sintering, the disc samples were electroded with silver paint for electrical measurements.

For sintered sample phase characterization, X-ray diffraction pattern was obtained using an automated diffractometer (Rigaku RAX-10, Japan) with Cu K$\alpha_1$ radiation. The microstructure was analyzed by field emission scanning electron microscope (SEM) (JSM-6700F, JEOL, Japan). The dielectric constant of each sample was calculated from the measured capacitance and the dimensions of the specimen. The capacitance was measured with an LCR meter (HP4284A) at 10 kHz. For the tunable properties, a 1000 V DC power supply was connected to the LCR meter (PH2817) as the external DC bias electric field up to 2 kV/mm.

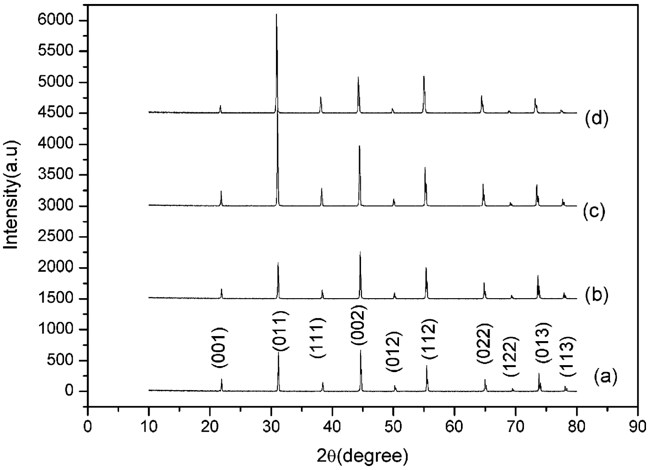

Fig. 1. XRD patterns of $Ba(Zr_xTi_{1-x})O_3$ ceramics: (a) $Ba(Zr_{0.25}Ti_{0.75})O_3$; (b) $Ba(Zr_{0.30}Ti_{0.70})O_3$; (c) $Ba(Zr_{0.35}Ti_{0.65})O_3$; (d) $Ba(Zr_{0.40}Ti_{0.60})O_3$.

## 3. Results and discussion

Fig. 1 shows XRD patterns of $Ba(Zr_xTi_{1-x})O_3$ ($x = 0.25, 0.3, 0.35, 0.4$) ceramics. All the samples show the typical XRD

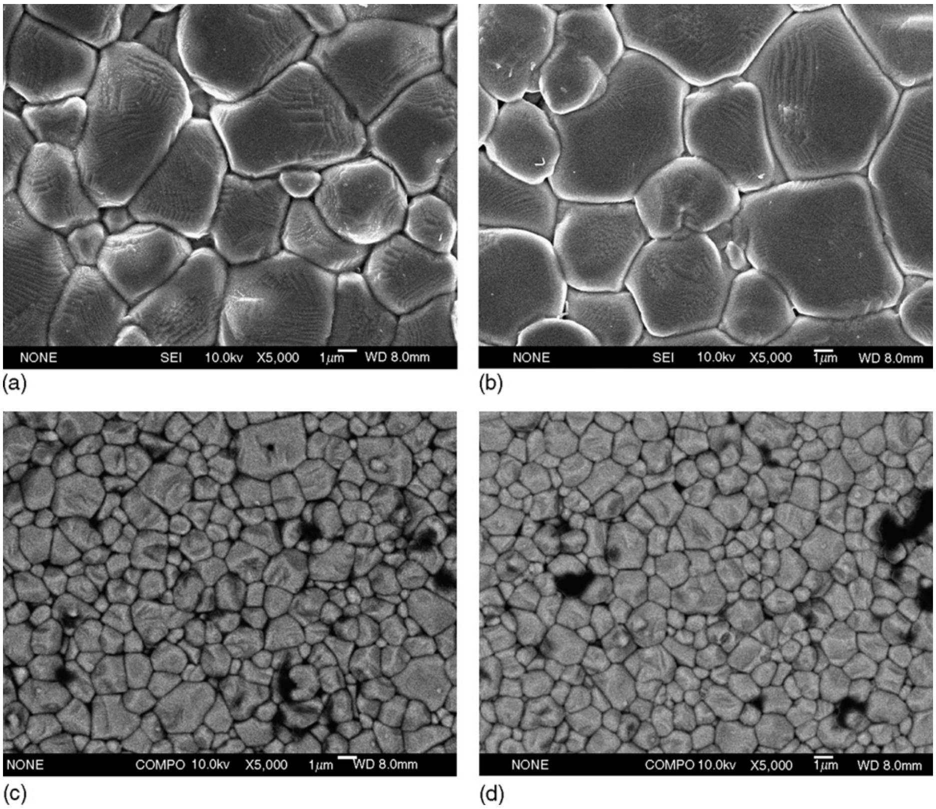

Fig. 2. SEM micrograph of (a) $Ba(Zr_{0.25}Ti_{0.75})O_3$; (b) $Ba(Zr_{0.30}Ti_{0.70})O_3$; (c) $Ba(Zr_{0.35}Ti_{0.65})O_3$; (d) $Ba(Zr_{0.40}Ti_{0.60})O_3$.

patterns of the perovskite structure and no secondary phase was observed.

The surface SEM micrographs of Ba(Zr$_x$Ti$_{1-x}$)O$_3$ ($x$ = 0.25, 0.3, 0.35, 0.4) ceramics are shown in Fig. 2. The grain sizes first increase a little and then decrease much with increasing Zr content. It implies the Zr ions substitution of Ti ions has a strong effect on the grain sizes. And the figure also presents a nonuniform distribution of the grain sizes.

Fig. 3 shows the dielectric properties of Ba(Zr$_x$Ti$_{1-x}$)O$_3$ ($x$ = 0.25, 0.3, 0.35, 0.4) as a function of temperature at 10 kHz. Due to the limitation of instrument, it was not possible to measure the dielectric constant and loss tangent at temperatures below −60 °C, so the $T_{\max}$ value of the samples is not shown in Fig. 3, and the diffuse phase transition and the relaxor-like behavior of BZT system that other researchers reported [7–9,12] cannot be also observed. However, it can indicate that $T_{\max}$ moves to lower temperature with higher Zr content and the dielectric constant decreases. This phenomenon is due to the substitution of Zr ions of Ti ions. The substitution might induce a 'break' of the cooperative vibration of Ti–O chains and bring about a decrease in the $c/a$ ratio. This 'break' is responsible for the lower $T_{\max}$ of BZT system. At room temperature, all samples have low dielectric loss (<0.005) and low temperature coefficient of capacitance (TCK) that are beneficial to the microwave application.

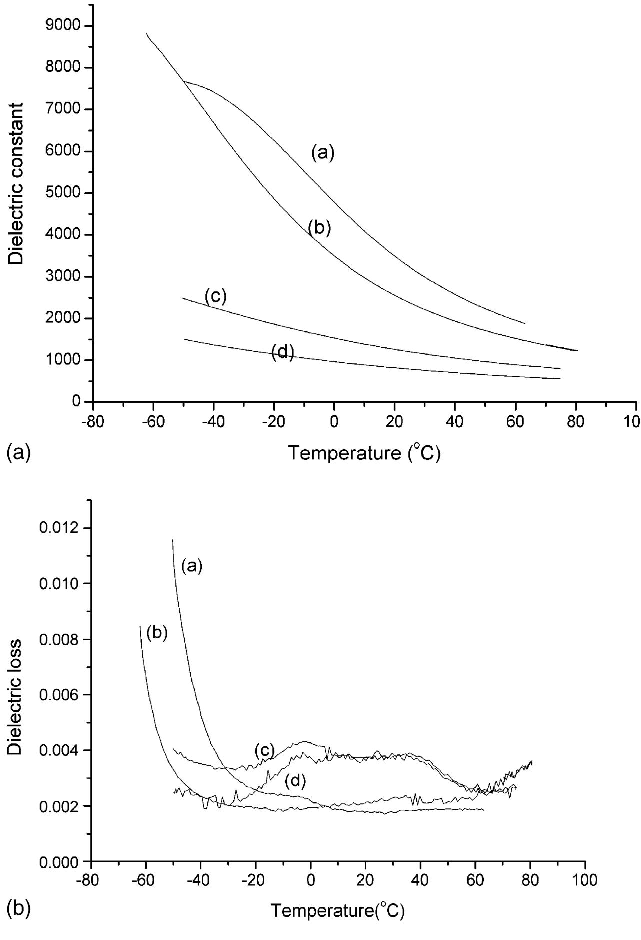

Fig. 3. Temperature dependence of the dielectric constant and loss tangent measured at 10 kHz: (a) Ba(Zr$_{0.25}$Ti$_{0.75}$)O$_3$; (b) Ba(Zr$_{0.30}$Ti$_{0.70}$)O$_3$; (c) Ba(Zr$_{0.35}$Ti$_{0.65}$)O$_3$; (d) Ba(Zr$_{0.40}$Ti$_{0.60}$)O$_3$.

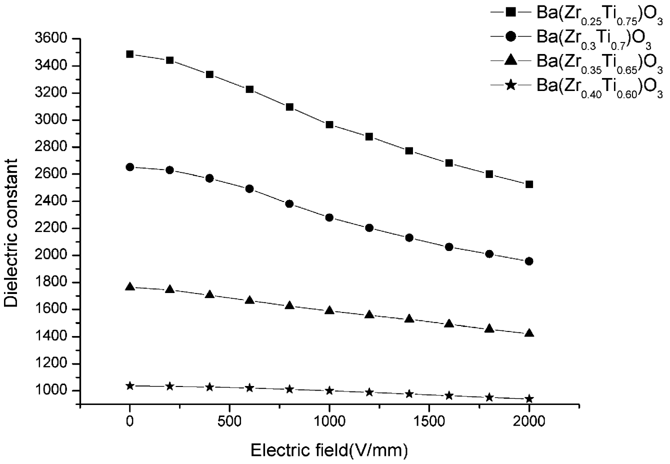

Fig. 4. DC field dependence of the dielectric constant for all the specimens at 10 kHz at room temperature: (■) Ba(Zr$_{0.25}$Ti$_{0.75}$)O$_3$; (●) Ba(Zr$_{0.30}$Ti$_{0.70}$)O$_3$; (▲) Ba(Zr$_{0.35}$Ti$_{0.65}$)O$_3$; (★) Ba(Zr$_{0.40}$Ti$_{0.60}$)O$_3$.

Fig. 4 shows the applied DC field dependence of the dielectric constant for all specimens at room temperature at 10 kHz. It indicates that the dielectric constant of all specimens decreases with increasing applied DC field. The fact that the dielectric constant nonlinearly decreases with increasing applied DC field at the paraelectric state in perovskite-like structure can be explained by the phenomenological theory of Devonshire [13,14]. On the basis of the framework, Johnson proposed an expression for the dielectric constant under the DC field as follows[15]:

$$\frac{\varepsilon_{\mathrm{r(app)}}}{\varepsilon_{\mathrm{r(0)}}} = \frac{1}{[1+\alpha\varepsilon_{\mathrm{r(0)}}^{3}E^{2}]^{1/3}} \tag{1}$$

where $\varepsilon_{\mathrm{r(0)}}$ and $\varepsilon_{\mathrm{r(app)}}$ are the dielectric constants under zero DC field and under the applied field, respectively, and $\alpha$ is the anharmonic coefficient. The anharmonic coefficient is assumed to be an order parameter of the anharmonic interactions. For the perovskite structure materials, the DC field ($E$) effect in the paraelectric state is originated from the anharmonic interactions of Ti$^{4+}$ ions. And for Ba$_{1-x}$Sr$_x$TiO$_3$ (BST) ceramics, Johnson's expression fits experimental data well when they are in paraelectric state.

Because Ba(Zr$_x$Ti$_{1-x}$)O$_3$ ($x$ = 0.25, 0.3, 0.35, 0.4) ceramics show the typical perovskite structure (shown in Fig. 1) and their $T_{\max}$ are all below room temperature (shown in Fig. 3), we tried to apply Johnson's expression to explain this phenomenon. To make Johnson's expression Eq. (1) more simple, we get Eq. (2):

$$y = 1 + bx \tag{2}$$

where $y = (\varepsilon_{\mathrm{r(0)}}/\varepsilon_{\mathrm{r(app)}})^3$, $x = E^2$, $b = a\varepsilon_{\mathrm{r(0)}}^3$, and from this definition, if Johnson's expression can be applied to BZT system, the experimental data can be linearized by Eq. (2), and the ordinate intercept of the line is "1".

On the basis of Eq. (2), Fig. 5 presents a linearized plot of the experimental data of the Ba(Zr$_x$Ti$_{1-x}$)O$_3$ ($x$ = 0.25, 0.3, 0.35,

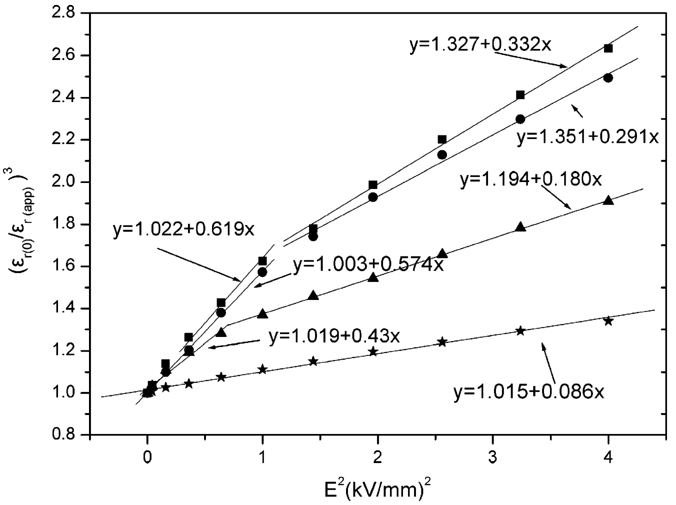

Fig. 5. Linearized plot of the electric-field dependence of the coefficient $(\varepsilon_{r(0)}/\varepsilon_{r(app)})^3$ of $Ba(Zr_xTi_{1-x})O_3$ ceramics: (■) $Ba(Zr_{0.25}Ti_{0.75})O_3$; (●) $Ba(Zr_{0.30}Ti_{0.70})O_3$; (▲) $Ba(Zr_{0.35}Ti_{0.65})O_3$; (★) $Ba(Zr_{0.40}Ti_{0.60})O_3$.

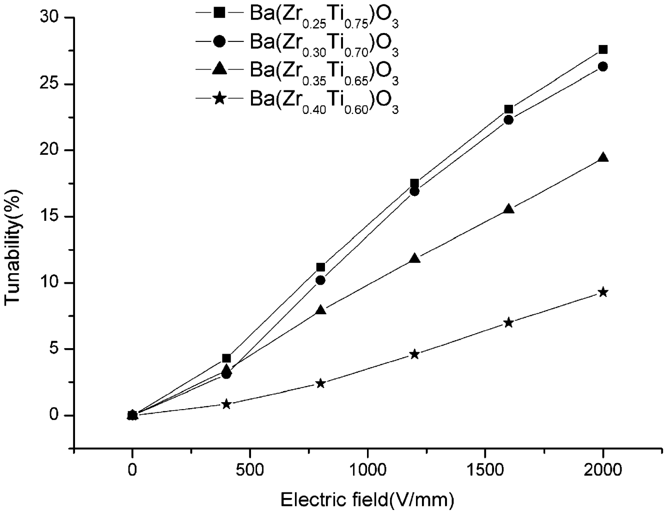

Fig. 6. Tunability of $Ba(Zr_xTi_{1-x})O_3$ ceramics as function of the strength of the external field at 10 kHz at room temperature.

0.4) ceramics. In this figure, two different linear regions with different slopes can be seen in $Ba(Zr_{0.25}Ti_{0.75})O_3$, $Ba(Zr_{0.30}Ti_{0.70})O_3$ and $Ba(Zr_{0.35}Ti_{0.65})O_3$. And for $Ba(Zr_{0.40}Ti_{0.60}O_3)$ there is one linear region predicted by Eq. (2). The deviation of $Ba(Zr_xTi_{1-x})O_3$ ($x = 0.25$, 0.3, 0.35) ceramics from the behavior predicted by Eq. (2) may be attributed to polar microregions (PMRs) in which randomly oriented dipoles are fluctuating[9]. Although the operating temperature is above $T_{max}$, dipoles still exist in PMRs, which is the character of the relaxor-like ferroelectrics. Under high DC electric field, dipoles in PMRs freeze and domain-wall motion's contribution to $\varepsilon$ decreases, so the dielectric constant decreases. To be precise, in $Ba(Zr_xTi_{1-x})O_3$ ($x = 0.25$, 0.3, 0.35) ceramics, there are two main reasons contributing to the nonlinear dielectric constant under DC electric field: one is the the anharmonic interactions of $Ti^{4+}$ ions proposed by Devonshire, which is embodied in Eq. (1); another is the freezing of the dipoles in PMRs; and the latter explains the deviation from the behavior predicted by Eq. (2). With the increase of the DC electric field strength, the contribution of the PMRs to the nonlinear dielectric constant decreases [8], and this explains why the slope of the second line is lower than the first line. For $BaZr_{0.40}Ti_{0.60}O_3$ ceramic, $T_{max}$ is far below the operating temperature, the effect of the dipoles in PMRs can be neglected so its behavior under DC field can be linearized by Eq. (2). The slight deviation of the ordinate intercept of these lines from "1" can be attributed to the nonuniform dielectric constant of the specimens and instrumental errors.

The tunability of $Ba(Zr_xTi_{1-x})O_3$ ($x = 0.25$, 0.3, 0.35, 0.40) ceramics as a function of the strength of the external field at 10 kHz at room temperature is shown in Fig. 6. From the Eq. (1), we can see generally, the higher the dielectric constant, the higher the tenability, which also can be applied to BZT system. When the strength of electric field is up to 2 kV/mm, for $x = 0.25$ ($\varepsilon_{r(0)} \approx 3500$), $x = 0.30$ ($\varepsilon_{r(0)} \approx 2650$), $x = 0.35$ ($\varepsilon_{r(0)} \approx 1760$), $x = 0.4$ ($\varepsilon_{r(0)} \approx 1000$) ceramics, their tunability are 27.6%, 26.3%, 19.4% and 9.3%, respectively. For comparatively equal dielectric constant, BST system and BZT system have nearly the same tunability [16].

Fig. 7 shows the DC field dependence of the loss tangent for all the specimens. As shown from these curves, the influence of the DC field on the loss factor of the samples is minor. This may be attributed to the fact that there are two loss mechanisms for the dielectric loss [17] under the DC field: a conduction loss factor ($\tan\delta_R$) and an intrinsic loss ($\tan\delta_c$); $\tan\delta$ can be expressed as follows:

$$\tan\delta = \tan\delta_c + \tan\delta_R \tag{3}$$

and $\tan\delta_c$ can be expressed as follows [15]:

$$\frac{\tan\delta_c}{\tan\delta_{c0}} = \frac{1}{[1+\eta\varepsilon_{(0)}^3 E^2]^{2/3}} \tag{4}$$

$$\eta = \alpha t^2 \tag{5}$$

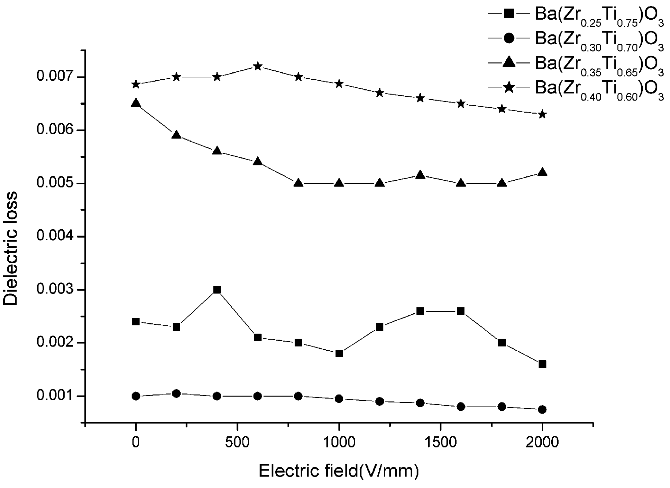

Fig. 7. DC field dependence of the loss tangent of $Ba(Zr_xTi_{1-x})O_3$ ceramics at room temperature.

where $\alpha$ is anharmonic coefficient, which is shown in Eq. (1) and $t$ is thickness of material. The intrinsic loss factor is decreased by applying the DC field. The term $\tan\delta_{c0}$ is the intrinsic loss under the zero field bias. The other term $\tan\delta_{R}$ is the conduction loss factor and can be expressed as follows:

$$\tan\delta_{R} = \frac{1}{\varepsilon_{(\mathrm{app})} wRC_0} \tag{6}$$

where $R$ is the resistance, $w$ is the measuring frequency and $C_0$ is the geometrical capacitance of the specimen. The intrinsic loss ($\tan\delta_c$) is reduced by the DC field, as shown in Eq. (4), while the conduction loss increases with the electric field strength. Since the influence of the DC field on the loss factor of the samples is minor, which is shown in Fig. 7, it indicates that the effect of the intrinsic loss should counteract the effect of the conduction loss.

## 4. Conclusions

(1) The Zr ions substitution of Ti ions has a strong effect on the dielectric properties and the grain sizes. With the increase of Zr ions content, $T_{\max}$ moves to lower temperature and the grain sizes increase a little at first and then decrease much.

(2) The behavior of $Ba(Zr_{0.4}Ti_{0.6})O_3$ under DC electric field can be explained by the phenomenological theory of Devonshire. For $Ba(Zr_xTi_{1-x})O_3$ ($x = 0.25, 0.3, 0.35$), there are two main reasons contributing to the nonlinear dielectric constant: one is the anharmonic interactions of $Ti^{4+}$ ions proposed by Devonshire; another is the freezing of the dipoles in PMRs.

(3) The influence of the DC field on the loss factor of $Ba(Zr_xTi_{1-x})O_3$ ($x = 0.25, 0.3, 0.35, 0.40$) ceramics is minor at room temperatue because the effect of the intrinsic loss should counteract the effect of the conduction loss.

(4) $Ba(Zr_xTi_{1-x})O_3$ ($x = 0.25, 0.3, 0.35$) ceramics are promising candidates for the electric field tunable materials for microwave electronics application, because they exibit high tunability (27.6%, 26.3%, 19.4%, respectively) as the strength of electric field is up to 2 kV/mm, low dielectric loss (0.001–0.002, 0.001–0.002, 0.004–0.005, respectively) at 10 kHz at room temperature. However their dielectric constants are high for impedance match, so further work is to reduce dielectric constant while promising high tunability and low dielectric loss.

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