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Ceramics International 39 (2013) S9–S13

CERAMICS INTERNATIONAL

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DC field effect on dielectric property of $Ba(Zr_xTi_{1-x})O_3$ ceramics

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Abstract

Barium zirconate titanate $Ba(Zr_xTi_{1-x})O_3$ (BZT) ceramics have been fabricated by conventional solid state route. The dielectric properties and ferroelectric relaxor behavior were investigated as a function of Zr content and DC bias field. It was found that the relaxor behavior of BZT is enhanced with the increase in Zr content. The temperature of maximum dielectric peak (T_m) of BZT ceramic is greatly increased with DC bias field (E) up to a certain threshold field E_t, below which T_m starts to increase gradually. This behavior could be associated with the size of domain. The relationship between temperature and dielectric tunability is also discussed in details.

Keywords: C. Dielectric properties; C. Ferroelectric properties; Relaxor behavior

1. Introduction

Barium zirconate titanate $Ba(Zr_xTi_{1-x})O_3$ (BZT) solid solution has recently received extensive attention due to its eminent dielectric performance. This system of BZT exhibits a pinched phase transition at $x \approx 0.15$ and a typical ferroelectric relaxor behavior at $x \approx 0.30$ with characteristics related to the substitution rate of Ti^{4+} ions for the Zr^{4+} [1,2]. In addition, BZT, as an important $BaTiO_3$-based ferroelectric material, presents a higher voltage resistance characteristic and a relatively large dielectric tunability under applied DC electric field [3–5]. It is a hopeful candidate for application in tunable ceramic capacitors and tunable microwave devices.

In addition, DC electric field dependence of dielectric behavior of the BZT systems have been reported, but concerning the electric field induced structure phase transition in a wide range of temperature, a systematic investigation is still lacking. In this present study, a systematic investigation on the dielectric response for $Ba(Zr_xTi_{1-x})O_3$ ($x=0.15$, 0.20, 0.25, 0.30, 0.35, 0.40) as a function of external electric field and temperature is presented, including the temperature dependence of the dielectric constant, tunability and the phase transition under higher electric fields.

2. Experimental processing

$Ba(Zr_xTi_{1-x})O_3$ ($x=0.15$, 0.20, 0.25, 0.30, 0.35, 0.40) powders were prepared by a conventional solid-state reaction method. The starting raw chemicals were $BaCO_3$(99.7%), ZrO_2(99.0%), TiO_2(99.9%) powders, which were weighed and mixed using alcohol and zirconia milling media for 24 h. After drying, the mixtures were calcined in an alumina

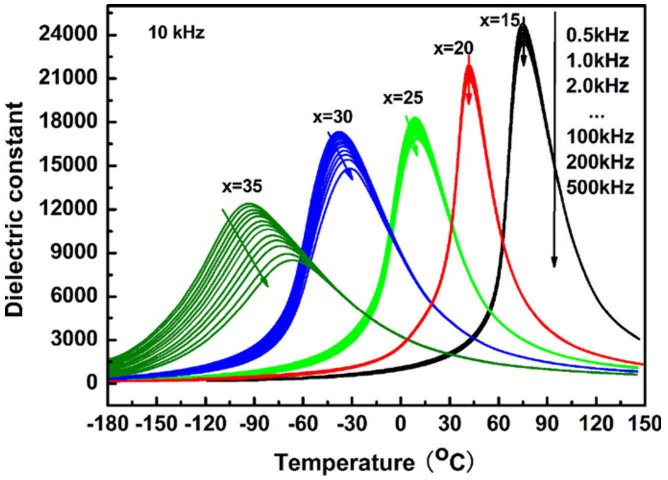

Fig. 1. Temperature dependence of dielectric constant of BZT ceramic samples with $x=0.15$, 0.20, 0.25, 0.30, 0.35 composition.

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http://dx.doi.org/10.1016/j.ceramint.2012.10.026

crucible at 1300 °C for 4 h in air, then re-milled and dried. The obtained powders with 8 wt% PVA binder were pressed into disc-shaped pellets of 10 mm in diameter at 100 MPa. The green pellets were sintered at 1500 °C for 4 h in air. In order to determine the dielectric properties of the samples, the two sides of the disc samples with thickness of ~0.20 mm were polished and electroded with silver paste and fired at 600 °C for 10 min.

X-ray diffraction (XRD, Bruck, Germany) with a Cu K_α radiation was used to examine the phase structure. The domain structure of the samples was analyzed by transmission electron microscopy (Philips CM20). The temperature dependence of the dielectric constant was measured from −180 °C to 150 °C at frequencies of 0.5 kHz, 1 kHz, 2 kHz, 5 kHz, 10 kHz, 20 kHz, 50 kHz, 100 kHz, 200 kHz, and 500 kHz using a high-precision LCR meter (HP 4284A).

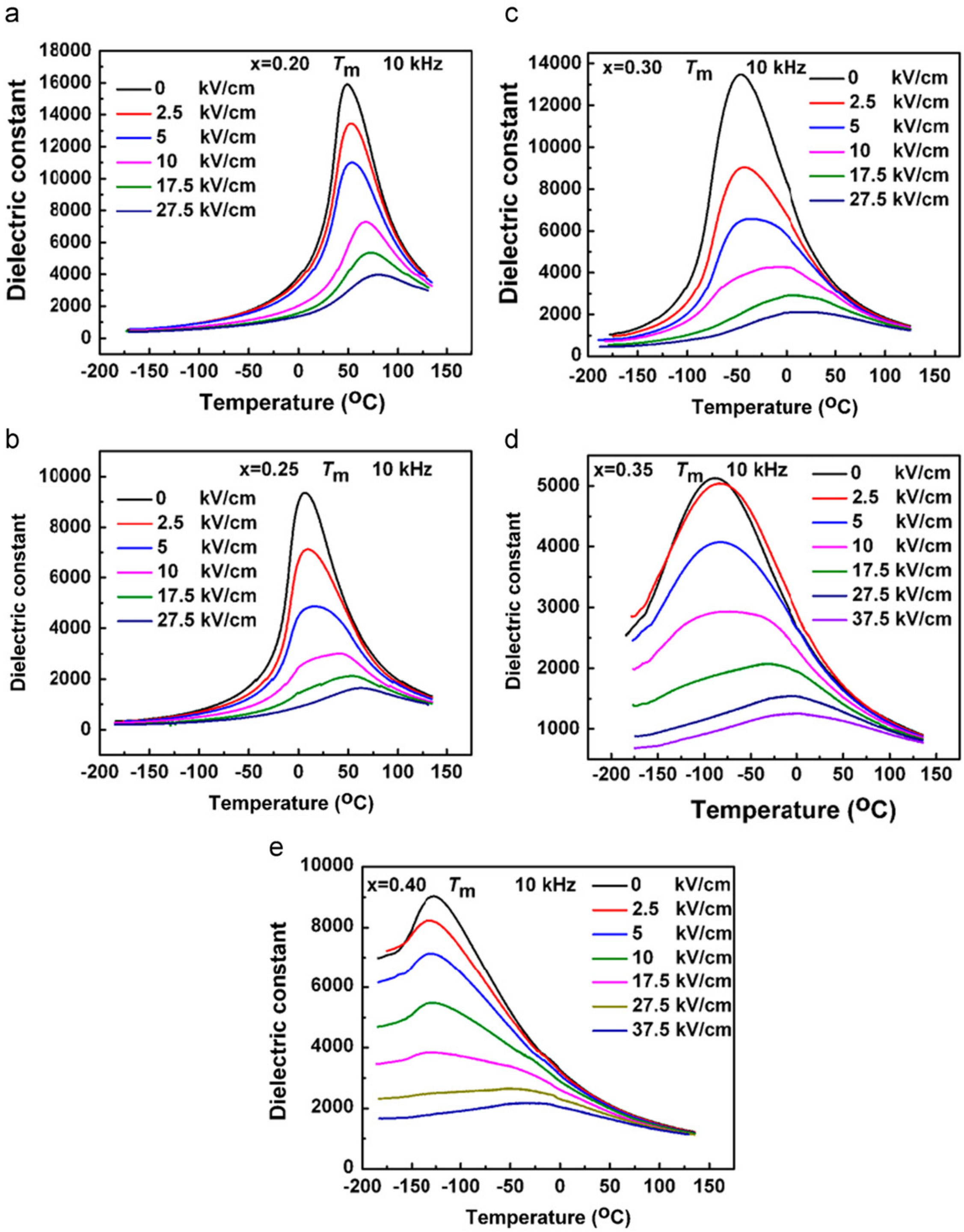

Fig. 2. Temperature dependence of dielectric constant for $Ba(Zr_xTi_{1-x})O_3$ ceramics at 10 kHz: (a) $x=0.20$, (b) $x=0.25$, (c) $x=0.30$, (d) $x=0.35$, (e) $x=0.40$.

The dielectric constant as a function of the temperature and DC bias field was measured by a Keithley Model 6517A Electrometer coupled with a TH2613A LCR meter.

3. Results and discussion

XRD revealed that all samples are of single perovskite structure of ABO_3 (data is not shown here). The temperature dependence of dielectric constant of $Ba(Zr_xTi_{1-x})O_3$ ($x=0.15$, 0.20, 0.25, 0.30, 0.35) with different frequencies is given in Fig. 1. It can be seen from Fig. 1 that the crossover of normal ferroelectric to relaxor behavior in BZT can be obviously observed. When the values x are beyond 0.15 for $Ba(Zr_xTi_{1-x})O_3$, the phase transitions from tetragonal to orthorhombic (T_2) and orthorhombic to rhombohedral (T_1) disappear, only the phase transition from tetragonal to cubic (T_c) exists. Typical relaxor behavior with increasing frequency occurs in the samples with $x \geq 0.25$. The temperature T_m, corresponds to the dielectric constant maximum, is shifted to a higher temperature, and the maximum value of the dielectric constant is decreased with increasing frequencies, as expected for typical relaxor ferroelectric. This phenomenon indicates that the BZT with a higher Zr content shows typical ferroelectric relaxor behavior. These results are basically in agreement with the recent data in terms of structure phase transition temperature [6,7].

Fig. 2 displays the temperature dependence of dielectric constant for $Ba(Zr_xTi_{1-x})O_3$ ($x=0.20$, 0.25, 0.30, 0.35, 0.40) samples measured at 10 kHz under different DC electric fields. The applied DC electric fields to the samples are from 0 kV/cm to 37.5 kV/cm. As shown in Fig. 2, it is found that the dielectric constant is gradually decreased with increasing electric field, and the Curie peaks, corresponding to the maximum dielectric constant, are suppressed and broadened. At the same time, The Curie temperature (T_m) shifts towards higher temperature under higher electric field. In particular, in the case of $x=0.35$ and 0.40 compositions, the shift of T_m with increasing electric field becomes more and more pronounced. Another obvious characteristic is observed from the Fig. 2, the value of T_m shifts slightly to higher temperature as the DC electric field is below ~5 kV/cm. However, in the vicinity of a certain threshold field, T_m depends strongly on the electric field.

From the temperature dependence of dielectric constant in Fig. 2, it is worth noting that the T_m shifts to higher temperature with increasing electric field. The relationship between T_m and external electric field under various DC bias field for BZT ceramics is shown in Fig. 3. For instance, Fig. 3(d) shows the variation of T_m with DC bias levels of 0 kV/cm, 2.5 kV/cm, 5 kV/cm, 10 kV/cm, 17.5 kV/cm, 27.5 kV/cm, and 37.5 kV/cm (measured at 10 kHz), respectively. It can be seen that the transition temperature for paraelectric (PE) phase to ferroelectric (FE) phase occurs at about −88.8 °C under zero DC bias. The phase transition temperature T_m shifts to a higher temperature and the dielectric peak value decreases and becomes broader with increasing of DC bias field. For example, under a DC bias field of 17.5 kV/cm, the phase transition temperature T_m is shifted to about −32 °C. When the DC bias field reaches 27.5 kV/cm, the T_m increases to about −6 °C.

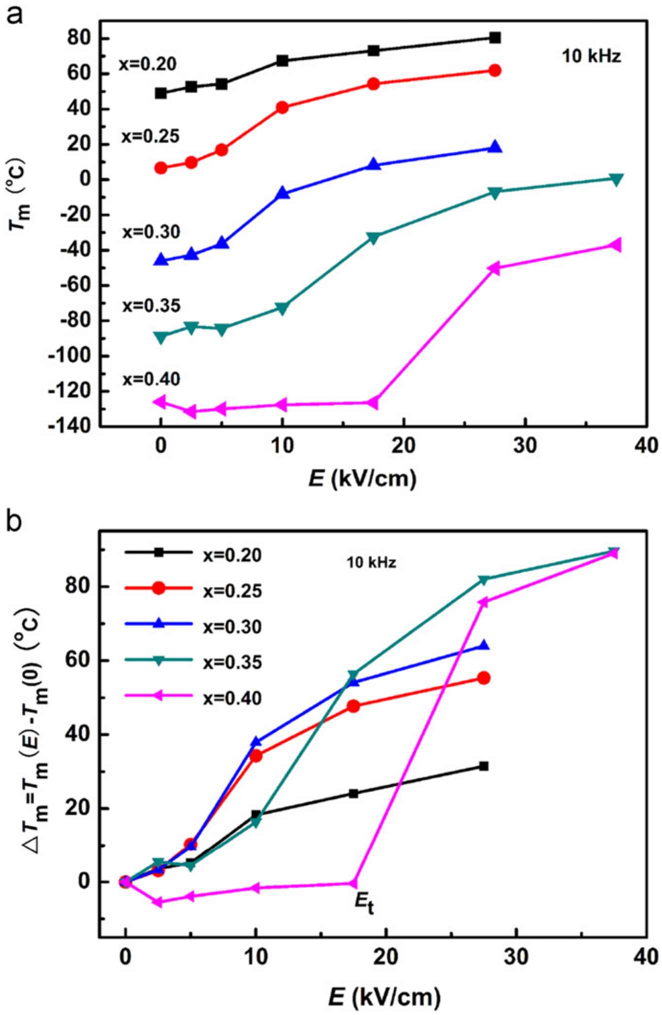

Fig. 3. T_m and ΔT_m dependence of electric field, E under various DC bias fields for $Ba(Zr_xTi_{1-x})O_3$ ceramics.

These results show that the enhancement of long-range force by a DC bias field tends to stabilize the low temperature ferroelectric phase, and extends its thermal stability region to higher temperatures. The T_m is shifted to higher temperatures and becomes increasingly broaden with the increase of DC bias field. This result is consistent with that found in (Pb, La)(Zr, Ti)O_3 ceramics [8]. This behavior could be attributed to the presence of a diffuse phase transition in $Ba(Zr_xTi_{1-x})O_3$ ceramics and the character of diffuse phase transition is more obvious with the increase of DC bias field.

For comparison purposes, we define $\Delta T_m = T_m(E) - T_m(0)$, wherein $T_m(E)$ is the Curie temperature at DC bias field E.

In contrast to normal ferroelectrics, where ΔT_m monotonically increases with a DC bias field E in $Ba(Zr_xTi_{1-x})O_3$ ceramics. ΔT_m was observed to increase slowly with DC bias field up to a certain threshold field E_t; above E_t, ΔT_m increases strongly. The similar result was also reported by Raevski [9]. In addition, with the increase of Zr content, the threshold field E_t increases and the temperature range for T_m shift enlarges.

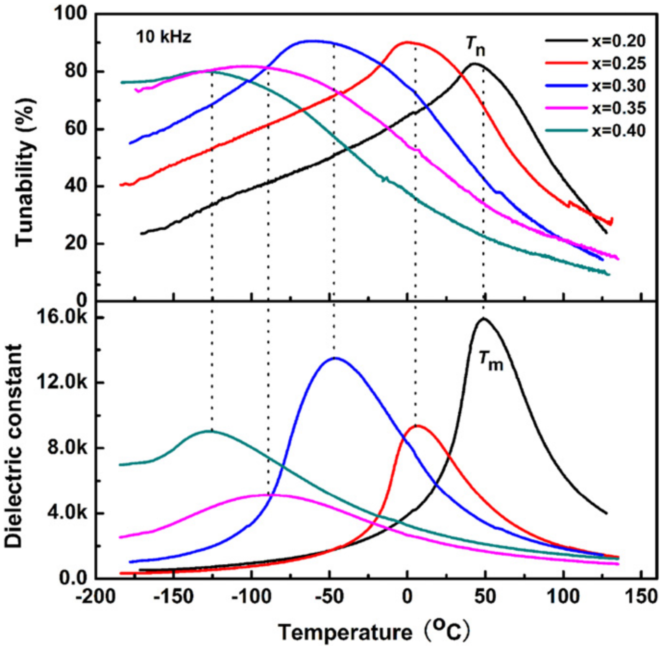

Fig. 4. Temperature dependence of the tunability for $Ba(Zr_xTi_{1-x})O_3$ ceramics at 10 kHz.

Table 1
The dielectric properties of $Ba(Zr_xTi_{1-x})O_3$ ceramics.

$Ba(Zr_xTi_{1-x})O_3$	**Dielectric properties (10 kHz)**		
	T_m (°C)	Max. tunability (%)	T_n (°C)
$x=0.20$	49.0	82.7@27.5 kV/cm	43.2
$x=0.25$	6.6	90.1@27.5 kV/cm	0.6
$x=0.30$	−46.0	90.6@27.5 kV/cm	−59.5
$x=0.35$	−88.8	81.8@37.5 kV/cm	−104.6
$x=0.40$	−126.6	80.1@37.5 kV/cm	−126.6

The temperature dependence of the tunability of samples with applied DC electric field of 27.5 kV/cm ($x=0.20$, 0.25, 0.30) and 37.5 kV/cm ($x=0.35$, 0.40) is presented in Fig. 4. From Fig. 4, it is evidently seen that the maximum tunability (T_n) of BZT samples occurs in the vicinity of ferroelectric–paraelectric transition [$T_m(0)$] at every fixed electric fields. For instance, the samples with $x=0.20$, 0.25 and 0.30 under DC field of 7.5 kV/cm and 10 kHz, show the maximum tunability of ~82.7% at 43.2 °C, ~90.1% at 0.6 °C, and ~90.6% at −59.5 °C, respectively. The detailed results are listed in Table 1. From Table 1, we found that the value of T_n under the electric fields is generally lower than $T_m(0)$. Similar behavior was observed in other systems reported by others [10].

Fig. 5 presents the TEM images of $Ba(Zr_{0.20}Ti_{0.80})O_3$ and $Ba(Zr_{0.40}Ti_{0.60})O_3$ ceramics, respectively. It is noticed that domains in $Ba(Zr_{0.40}Ti_{0.60})O_3$ are much finer than that in the $Ba(Zr_{0.20}Ti_{0.80})O_3$ sample. It is clearly seen that the nano-sized domains in the $Ba(Zr_xTi_{1-x})O_3$ samples actually consist of much finer irregular domain structure of the size down to 20 nm. The distribution of the domain in $Ba(Zr_xTi_{1-x})O_3$ samples shown in Fig. 5 has an obviously difference. Under DC electric field, the nano-domains will incorporate into micro-domain and results in the phase transition. With the increase of Zr content, the DC electric field incorporated nano-domain into micro-domain is decreased.

4. Conclusions

In summary, the dielectric properties of $Ba(Zr_xTi_{1-x})O_3$ ($x=0.15$, 0.20, 0.25, 0.30, 0.35, 0.40) samples fabricated by the conventional solid-state reaction method were investigated systematically under different DC electric fields. The results suggest that both the dielectric constant and the peak of ferroelectric–paraelectric phase transition are gradually suppressed with the increase of the electric fields, and the phase transition peaks are regularly broadened and diffused. The degree of diffused peaks is enhanced with electric field, and the Curie temperature (T_m) is strongly shifted to higher temperature above a certain threshold field E_t. The maximum tunability of samples all occurs in the vicinity of ferroelectric–paraelectric transition.

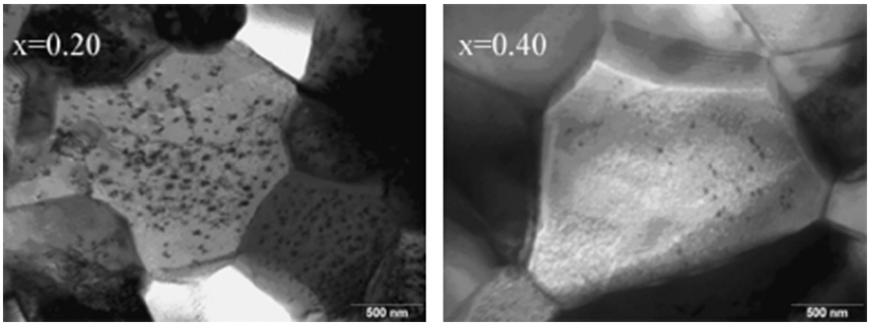

Fig. 5. The TEM image of $Ba(Zr_xTi_{1-x})O_3$ ceramics with $x=0.20$ and $x=0.40$.

With increasing Zr content, the DC electric field incorporated nano-domain into micro-domain is decreased.

Acknowledgments

This work was supported by the Ministry of Sciences and Technology of China through 973-project under grant 2009-CB623302. It was also partially supported by the Research Grants Council of the Hong Kong Special Administrative Region, China (CityU No. 103307).

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