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Phase formation and electrical properties of $Ba(Zr_xTi_{1-x})O_3$ ceramics synthesized through a novel combustion technique

Phongthorn Julphunthong[a,b], Suphornpun Chootin[a,b], Theerachai Bongkarn[a,b,*]

[a]Department of Physics, Faculty of Science, Naresuan University, Phitsanulok 65000, Thailand
[b]Research Center for Academic Excellence in Petroleum, Petrochemicals and Advanced Materials, Naresuan University, Phitsanulok 65000, Thailand

Abstract

High quality $Ba(Zr_xTi_{1-x})O_3$ (BZT, $0.025 \leq x \leq 0.150$, step=0.025) ceramic has been prepared by the combustion technique. The raw materials were mixed with CH_4N_2O and calcined at 1000 °C and sintered at 1375 °C. For $Ba(Zr_xTi_{1-x})O_3$ with $x=0.025$, the ceramics exhibited orthorhombic structure at room temperature. The crystal structure was transformed to rhombohedral, tetragonal and cubic phase, respectively with increasing zirconium content. The effect of x on dielectric properties has been studied intensively. It is found that the phase formation, which was affected from zirconium substitution, strongly influences the dielectric behavior. The rhombohedral phase decreases the maximum dielectric constant while the tetragonal phase enhances it. An extrapolation studied revealed the phase transition peaks merged into one peak at $x \sim 0.094$. The highest diffuseness constant of 1.95 was observed in BZT with 0.075 mol% zirconium. This was caused by the broadest dielectric peak of ferroelectric phase transition and the imminent diffusion between ferroelectric phase transition peak and Curie phase transition peak. The ferroelectric properties were sensitive to the phase exhibited in BZT system.

Keywords: C. Dielectric properties; C. Ferroelectric properties; Barium zirconate titanate; Perovskite structure

1. Introduction

Barium titanate (BT) ceramics have been used extensively as electroceramics materials due to their high dielectric constant and low dielectric loss. The phase transformations of BT occur at 120 °C, 0 °C and −90 °C from cubic to tetragonal, tetragonal to orthorhombic and orthorhombic to rhombohedral, respectively [1]. The dropping in maximum dielectric constant is accompanied with the phase transformation at lower temperature.

$Ba(Zr_xTi_{1-x})O_3$ (BZT) system, one of the first $BaTiO_3$-based solid solution, has been chosen in the fabrications of ceramic capacitors because Zr^{4+} is chemically more stable than Ti^{4+}. Moreover, Zr-substitution at Ti-site has been found to be an effective way to decrease the Curie temperature and exhibits several interesting features in the dielectric behavior and phase formation of $BaTiO_3$ ceramics. The Zr-ion substitution affects an increase of rhombohedral to orthorhombic ($T_{r\text{–}o}$) and orthorhombic to tetragonal ($T_{o\text{–}t}$) phase transition temperature but decreases the tetragonal to cubic (T_c) phase transition temperature. The pinch phase transitions between three phase transitions merge into one peak where $x \leq 0.15$ [2,3]. Below 15 mol% zirconium, there are several difference reports about the effects of zirconium substituted on phase formation and dielectric properties of BZT. In term of structural phase, some researchers distinguished BZT belonging to tetragonal structure [3–5] and the tetragonality was decreased by increasing zirconium content [4,5] while several literatures reported that the amount of orthorhombic to rhombohedral phase transformation was increased with increasing zirconium [3,6,7]. In term of dielectric properties, Huang et al. [4] explained that maximum dielectric constant was enhanced by increasing the amount of zirconium. On the other hand, Chen et al. [5] reported that the maximum dielectric constant was depressed by the amount of zirconium substitution. Kuang

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[*]Corresponding author at: Naresuan University, Department of Physics, Faculty of Science, Phitsanulok 65000, Thailand.
Tel.: +66 5596 3528; fax: +66 5596 3501.
E-mail address: reseachcmu@yahoo.com (T. Bongkarn).

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et al. [6] represented the highest maximum dielectric exhibited in BZT with $x=0.08$. For BZT with x less than 0.08, maximum dielectric constant insignificantly relates to the amount of zirconium and in BZT with $x \geq 0.8$, it is observed that the maximum dielectric constant tended to increase with increasing zirconium content.

Due to the variation in reports, an accurate investigation of the zirconium content effects on phase formation and dielectric properties in BZT is topical. In addition, our previous work has demonstrated that high quality BZT ceramics such as nano-particles and high density can be produced via the combustion technique [8]. Therefore, this study aims to synthesize $Ba(Zr_xTi_{1-x})O_3$ (BZT, $0.025 \leq x \leq 0.150$, step$=0.025$) ceramics by the combustion technique. The effect of composition on phase formation, dielectric and ferroelectric properties of BZT was extensively investigated.

2. Experimental procedure

$Ba(Zr_xTi_{1-x})O_3$ or (BZT100x) ceramics were prepared via the combustion technique using urea as fuel. The starting materials barium carbonate ($BaCO_3$), zirconium dioxide (ZrO_2) and titanium dioxide (TiO_2) were weighed based on the stoichiometric compositions of $Ba(Zr_xTi_{1-x})$ O_3(BZT100x, $0.025 \leq x \leq 0.150$, step$=0.025$). The weighed raw materials were mixed by ball milling with zirconia media in ethanol for 24 h, and then were dried and the powders were ground using an agate mortar and sieved into a fine powder. The mixed powders and urea (CH_4N_2O) were mixed with a ratio of 1:2 in an agate mortar. All compositions were calcined at 1000 °C for 5 h [8]. The calcined ones were again ball-milled in the mixture medium absolute ethanol for 24 h. Disc-shaped specimens with 15 mm in diameter were fabricated using a hydraulic pressing and then the green body were sintered at 1375 °C with soaking time at 2 h [8]. The phase formation behavior and the lattice refinement of all compositions were studied by XRD analytical technique. The bulk densities of the sintered samples were measured by the Archimedes method. The temperature dependence of relative permittivity and dielectric loss of BZT specimens was investigated using LCR meter. The measurement of ferroelectric hysteresis loops was conducted at room temperature by using a ferroelectric tester.

3. Results and discussion

The phase formation of BZT ceramics were studied using XRD patterns as shown in Fig. 1 and the results showed that pure perovskite phase was found in all sintered samples (Fig. 1(a)). To determine the phase formation behavior of BZT with the increasing zirconium content, the XRD patterns which measured from 72 to 77° at a very low scanning rate (step size 0.00116°, time/θ 7.42 s, scan speed 0.05152°/s) were investigated (Fig. 1(b)). It can be seen that the diffraction angle also decreases as the zirconium content is raised. This can be explained by the ionic radius of Zr^{4+} (0.072 nm) being larger than Ti^{4+}(0.061 nm), so more substitution of Zr^{4+} will increase the d spacing of BZT and cause the diffraction peaks to shift toward a lower angle [4]. At room temperature, the splitting of (133) and (311) diffraction peaks of BZT2.5 ceramics confirms the orthorhombic phase (Refer to ICCD No.01-0812196). When zirconium content was increased to 5 mol%, the two diffraction peaks gradually merged into one peak which was indicated by the rhombohedral phase which was initially diffused and influenced the phase system (Refer to ICCD no. 01-0850368). The diffraction peak exhibited a sharper curve and a nearly symmetric shape, lightly skewed to the left side in BZT7.5. This implies that the tetragonal phase was occurred and slightly diffused in rhombohedral phase of BZT system (Refer to ICCD no. 00-0030725). When zirconium content was increased to 10 mol%, the distinct non-symmetry (skewed to the right side) of the diffraction peak can be explained by the BZT showing a tetragonal phase. Moreover, when zirconium content was higher than 10 mol%, the diffraction peak changed from non-symmetry to near symmetry illustrated the cubic phase influence on BZT system (Refer to ICCD no. 01-0741961). The XRD analysis indicates that a slight change of zirconium content highly influences on the crystal structure of BZT ceramics. The accurate interpretation is derived from high quality samples which were produced via the combustion technique.

The measured density with a variation in zirconium content of BZT is listed in Table 1. The density of the ceramics was in the range of 5.61–5.86 g/cm^3 and the densities insignificantly changed with zirconium content modification. The highest density exhibited in BZT12.5 was 97% of the theoretical density and was higher than the samples which were prepared via the solid-state reaction method [3] and the wet chemical reaction method [7].

The temperature dependence of the dielectric constant of BZT ceramics with various stoichiometric percentage of zirconium is shown in Fig. 2. It was found that as zirconium increased from 2.5 to 5.0 mol%, maximum dielectric constant tended to increase. The reduction of maximum dielectric constant appeared in BZT with 7.5 mol% zirconium. Thereafter, more zirconium doping induced the increasing of maximum dielectric constant again. The increasing of maximum dielectric constant reached maximum value in BZT12.5 thereafter, it decreased in BZT15. The maximum dielectric constant and the loss tangent at Curie point were listed in Table 1. The value of density and maximum dielectric constant of BZT in all compositions in this study were higher when compared to previous works [3,5,7,9] which indicated that high quality BZT ceramics could be prepared via the combustion technique.

The transition temperature from orthorhombic to tetragonal structure (T_{o-t}) is obviously observed in BZT2.5, BZT5.0 and BZT7.5 ceramics. The dielectric peak at T_{o-t} appeared broader with increasing zirconium content. From literature surveyed, by increasing x, T_{r-o} and T_{o-t} peaks were shifted to higher temperatures. However, the shifted rate of T_{r-o} peak is

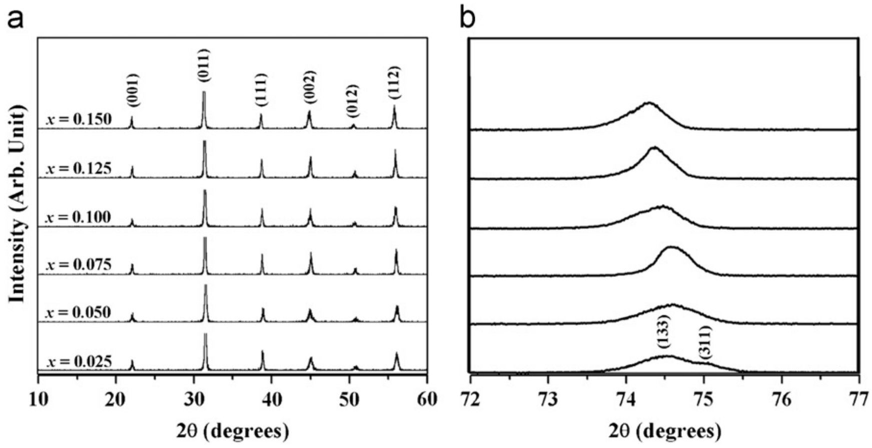

Fig. 1. XRD patterns of $Ba(Zr_xTi_{1-x})O_3$ ceramics where $0.025 \leq x \leq 0.150$.

Table 1
The density, T_{o-t}, T_c, maximum dielectric constant (ε_r) and dielectric loss (tanδ) at T_c, γ, P_r and E_c of $Ba(Zr_xTi_{1-x})O_3$ ceramics.

x	Density (g/cm^3)	T_{o-t} (°C)	T_c (°C)	ε_r at T_c	tanδ at T_c	γ	P_r (μC/cm^2)	E_c (kV/cm)
0.025	5.69	39	108	11,380	0.004	1.32	8.31	2.42
0.050	5.64	50	100	13,770	0.006	1.85	8.36	4.51
0.075	5.61	71	94	9930	0.009	1.95	3.61	2.17
0.100	5.78	–	84	16,540	0.013	1.72	7.27	2.34
0.125	5.86	–	73	19,600	0.015	1.76	6.33	2.11
0.150	5.75	–	66	16,600	0.017	1.90	3.12	1.79

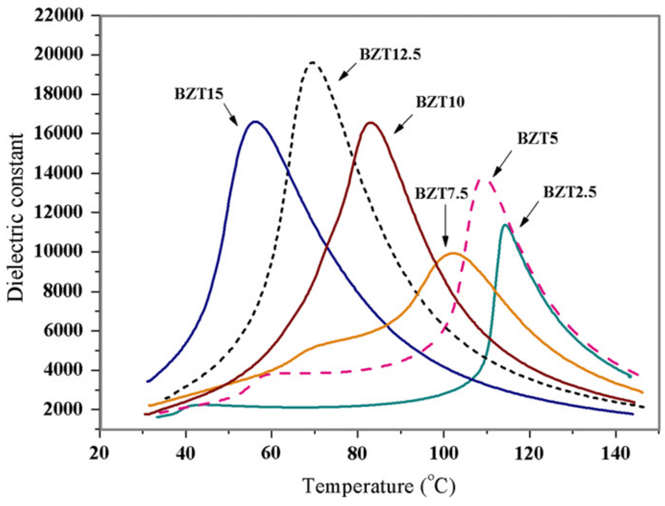

Fig. 2. Temperature dependences of dielectric constant of BZT100x ceramics where $0.025 \leq x \leq 0.150$.

higher than that of T_{o-t} peak and two peaks were nearly merged at around x of 0.08 [3]. Therefore, the broadening of dielectric curve at T_{o-t} is caused from higher diffusive T_{r-o} peak by increased amount of zirconium.

The phase transition temperature T_{o-t} (exhibited at lower temperature) and T_c (exhibited at higher temperature) were observed from dielectric loss peak and are listed in Table 1. To investigate the pinch phase transition characteristic, the phase transition temperature T_{o-t} and T_c as function of zirconium doping content were plotted (Fig. 3). It is found that the increase of T_{o-t} and decrease of T_c showed nonlinear function with increasing zirconium content. The intersection of T_{o-t} and T_c phase transitions temperature was observed at around 9.4 mol% of zirconium which displays the two phase transition is pinched into one dielectric peak due to the increased Zr content. Moreover, the function plotted revealed that the interval

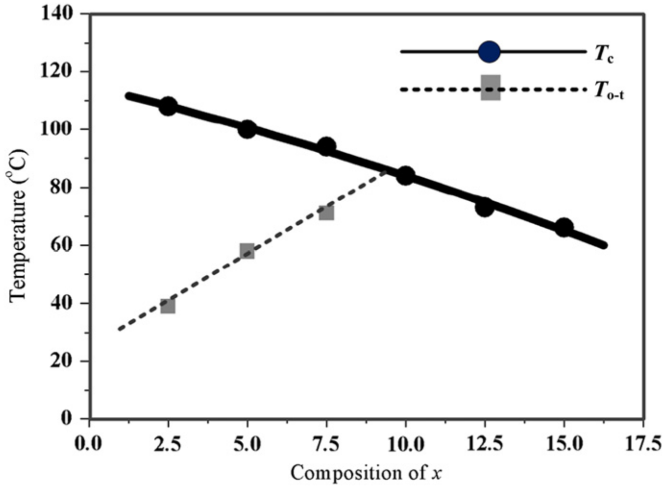

Fig. 3. Phase transition temperature T_c and T_{o-t} as function of zirconium content x for $Ba(Zr_xTi_{1-x})O_3$ ceramics.

between $T_{\mathrm{o-t}}$ and T_{c} tended to decrease by increasing zirconium content.

The study of phase transition characteristic exposed the increase and decrease of maximum dielectric constant and broadening of dielectric curve in dielectric result. In this study, BZT with zirconium $0.025 \leq x \leq 0.075$ showed lower maximum dielectric constant compared with BZT with zirconium $0.1 \leq x \leq 0.15$. This can be related to the orthorhombic phase influences on dielectric constant. In case of BZT with 7.5 mol% zirconium, the lowest of maximum dielectric constant with broadest dielectric curve was exhibited. This may be attributed to the rhombohedral phase being the highest diffused as exhibited in the XRD result. Maximum dielectric constant was enhanced immediately again in the BZT sample with zirconium content 10 mol% and reached the highest in BZT with 12.5 mol% zirconium. This demonstrated that tetragonal phase induces increasing dielectric constant. The reduction of BZT with 15 mol% zirconium could be speculated by the cubic phase affected.

A diffuse phase transition is generally characterized by the diffuseness of phase transition (γ) which was calculated from a modified Curie–Weiss law [8]. The γ values of the BZT prepared via the combustion technique are in the range of 1.32 to 1.95 up on zirconium content as listed in Table 1. The diffuseness was increased when zirconium content increased and reached its highest diffuseness of 1.95 on BZT7.5. This result was supported by two reasons. The first one is the diffusion between $T_{\mathrm{r-o}}$ and $T_{\mathrm{o-t}}$ arouse dielectric curve to broader. Another one reason is the reducing of the interval between $T_{\mathrm{o-t}}$ and T_{c} which indicated the phase transition at $T_{\mathrm{o-t}}$ and T_{c} more easily diffused. After reaching the highest value, the diffuseness decreased in BZT10 and increased again in BZT12.5 and BZT15. The increment of the γ with increasing zirconium content can be explained by the diffusive phase transition between ferroelectric to paraelectric phase. This result is consistent with the XRD result and the report in literature [5,10,11].

Fig. 4 shows the polarization-electric field characteristics of BZT ceramics at room temperature. It is found that well-behaved hysteresis loops can be observed in all compositions of BZT. The hysteresis loop increasingly swelled with increasing amount of zirconium from BZT2.5 to BZT5. In BZT7.5, the altitude of *P–E* loop was decreased and appears slimmer as shown in Fig. 4(a). The loop altitude was raised again in BZT10, and thereafter the altitude and the slope were decreased with increasing zirconium content (Fig. 4(b)). The remanant polarization (P_{r}) and the coercive field (E_{c}) of BZT for all compositions were listed in Table 1. The value of P_{r} tended to increase as the amount of zirconium then depreciated for BZT7.5. The remanant polarization was raised again in BZT10 thereafter the P_{r} was found to decrease with increasing zirconium content. The reduction of P_{r} in BZT7.5 may be due to the diminution of domain wall mobility caused from the mixing phase of rhombohedral and orthorhombic phase. In the case of BZT5, although the diffusion of rhombedral phase did not cause P_{r} to reduce, it affected the value of E_{c} which showed the highest. For BZT with $x \geq 10$, remanent polarization tended to decrease with increasing zirconium content. This can be explained by the difference of the radius of Zr^{4+} and Ti^{4+} [5]. Moreover, the procrastination of Curie temperature approaching to room temperature may cause the decrease of the ferroelectric characteristic [3].

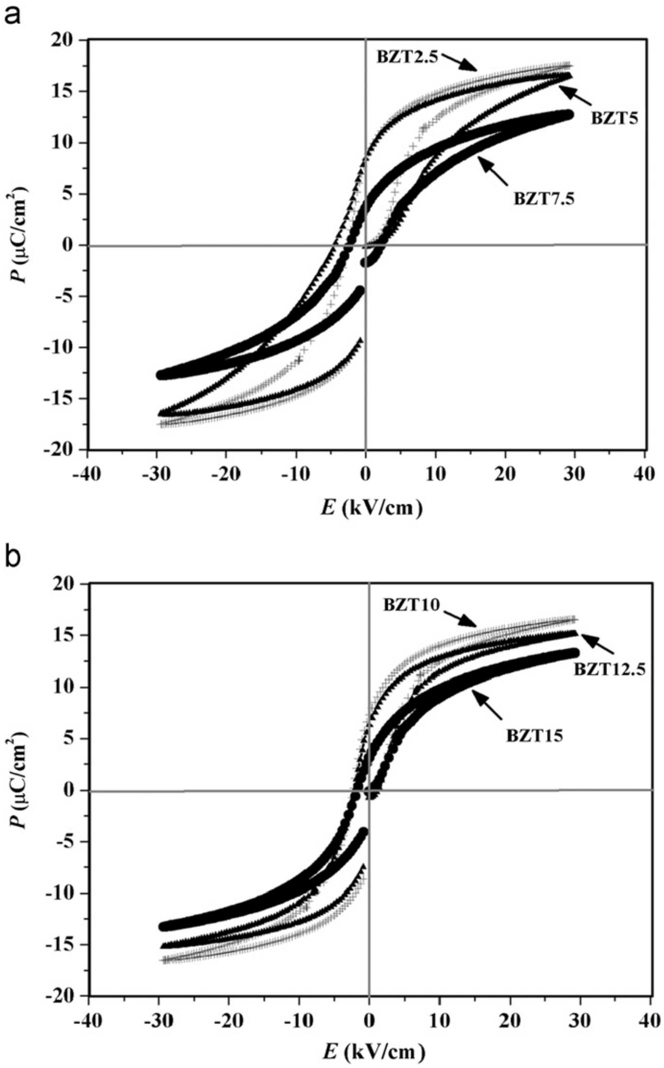

Fig. 4. *P–E* hysteresis loop of BZT100x ceramics (a) $0.025 \leq x \leq 0.075$ and (b) $0.10 \leq x \leq 0.150$.

4. Conclusions

The phase formation, dielectric behavior and ferroelectric properties of $\mathrm{Ba(Zr_xTi_{1-x})O_3}$ ceramics with $0.025 \leq x \leq 0.150$ prepared via the combustion technique were investigated. The X-ray diffraction patterns clearly indicated that the transformation from orthorhombic to rhombohedral, tetragonal or cubic phase is dependent on zirconium content. The dielectric measurement indicated that, by increasing the amount of zirconium substituted, $T_{\mathrm{r-o}}$, $T_{\mathrm{o-t}}$ and T_{c} phase transition peaks were shifted and the pinched phase transition occurred in BZT with zirconium content

$\sim$9.4 mol%. The lowest and the highest maximum dielectric constant were 9930 and 19,600 which were exhibited in BZT with $x=0.075$ and 0.125, respectively. The diffusion of rhombohedral and tetragonal phase influenced on the decrease and increase of maximum dielectric constant, respectively. In addition, the diffusion of $T_{\mathrm{r-o}}$ to $T_{\mathrm{o-t}}$ dielectric peak and $T_{\mathrm{o-t}}$ to T_{c} dielectric peak also caused the reduction in maximum dielectric constant of BZT7.5. Ferroelectric properties were decreased by the diffusion of rhombohedral into orthorhombic phase. The result from XRD investigation, the dielectric behavior analysis and the ferroelectric results were consistent with each other, and hence this work demonstrates the potential for the combustion technique in preparing BZT ceramics.

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