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Effect of Zr^{4+} content on the T_C range and dielectric and ferroelectric properties of $BaZr_xTi_{1-x}O_3$ ceramics prepared by microwave sintering

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Abstract

Single phase and dense $BaZr_xTi_{1-x}O_3$ (BZT) ceramics ($x=0.05$, 0.1, 0.15, 0.2, 0.25) were obtained by microwave sintering and the powders of these ceramics were synthesized by conventional hydrothermal method. The microstructural, dielectric and ferroelectric properties of $BaZr_xTi_{1-x}O_3$ ceramics sintered at 1300°C were investigated. The XRD analysis revealed that the synthesized compound was formed with no second phase. As x was increased from 0.05 to 0.25, the average grain size was observed on the SEM micrographs to decrease from ~6 μm to ~3 μm. The dielectric constant as a function of temperature showed a decrease in Curie temperature (T_C) with an increasing x, while the maximum value of dielectric loss occurred (tan δ) at $x=0.1$. A ferroelectric-relaxor crossover was observed to take place with increasing x by using the modified Curie–Weiss law. The remnant polarization (P_r) decreased from 9.45 to 4.4 C/cm^2 with an increasing x, while the maximum value of $P_r=11.84$ also occurred at $x=0.1$. The breadth of T_C range increased rapidly when $x<0.15$, but no significant difference was observed with further doping of Zr^{4+}. The full width at half maximum (FWHM) was used to show the degree of the broadening in Curie peak.

Keywords: C. Dielectric properties; C. Ferroelectric properties; Barium zirconate titanate; Microwave sintering

1. Introduction

$BaZr_xTi_{1-x}O_3$ (BZT) system is one of the most used ferroelectrics in the microelectric industry [1,2], especially as dielectric material in multilayer ceramic capacitors (MLCC), piezoelectric actuators, electroluminescent panels, pyroelectric detectors, embeded capacitance in printed circuit boards, positive temperature coefficient of resistivity (PTCR) sensors, controllers and pulse generating devices [3–5]. The nature of phase transition temperature is known to change strongly with x. The dielectric constant near T_C is relative high compared with other parts, which prompted the authors to consider to broadening the T_C range so that the $BaZr_xTi_{1-x}O_3$ ceramics can have a high permittivity in a relative broad temperature range [6–8].

The solid state method is an universal way to prepare $Ba_xZr_{1-x}TiO_3$ ceramics, but it shows some disadvantages such as long processing time, low purity and nonuniform grain size (~10 μm), which always lead to poor dielectric properties. Hydrothermal method is a low-temperature process to synthesis high-purity, homogeneous and ultrafine powders under an environmentally friendly condition. Microwave sintering (MS) is an unique technique alternative to the conventional sintering by which the heat is generated internally within the material through microwave-material interaction instead of originating from external sources [9–11]. This sintering method is particularly suitable for the green bodies prepared by some wet chemistry methods such as hydrothermal and sol–gel, which exhibits smaller initial grain size. To obtain the $BaZr_xTi_{1-x}O_3$ ceramics with uniform grain size and broad T_C range, the powders were synthesized by conventional hydrothermal method and then sintered using microwave sintering method [12].

2. Experimental

$BaZr_xTi_{1-x}O_3$ ceramics were prepared from the mixture of $BaZrO_3$ and $BaTiO_3$ powders synthesized by conventional hydrothermal method. $BaCl_2 \cdot 2H_2O$ (aq) (AR, Sinopharm

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Chemical Reagent Co., Ltd., China), $ZrOCl_2 \cdot 8H_2O$ (aq) and $BaCl_2 \cdot 2H_2O$ (aq), $TiCl_4$(l) were mixed to synthesize $BaZrO_3$ and $BaTiO_3$ precursor respectively using NaOH to regulate $pH > 14$. Then the precursors were put into the heating-autoclave, followed by distilled water until the total volume reached to 20 ml, ~80% of the capacity of the autoclave. Typically, the hydrothermal reactions were carried out at 180 °C for 10 h. The resulting $BaTiO_3$ and $BaZrO_3$ powders were centrifuged and mixed according to their stoichiometric, and then washed with distilled water and finally oven dried at 80°C for 12 h. The powder mixtures were thoroughly ground in an agate mortar and passed through a sieve of 80 mesh and then admixed with polyvinyl alcohol (PVA) as binder. The mixture was pressed at 20 M Pa into disk shaped pellets and then calcined at 600 °C for 30 min to eliminate the water and organic. The calcined pellets were sintered in a microwave furnace at 1260 °C, 1280° C and 1300 °C respectively for 1 h. For electrical characterization, the ceramic pellets were polished, coated with silver paste, and fired at 600 °C for 10 min.

The microstructure morphologies were obtained by scanning electron microscopy (JEOL JSM-6390A JEOL Ltd. Tokyo), and the phase structure was analyzed by an X-ray diffraction (diffraction angle:15°–70°, anular step interval:0.02°, D/max 2200 pc, Rigaku, Tokyo, Japan) with CuKα radiation. The temperature dependence of dielectric properties was investigated with an LCR meter (HP4284A, Agilent, Palo Alto, CA). The polarization–electric field hysteresis loops were measured with a ferroelectric analyzer (Premier II, Radiant, USA).

3. Results and discussion

Fig. 1 shows the SEM micrographs of $BaZrO_3$ (a) and $BaTiO_3$ (b) powders synthesized by conventional hydrothermal method. Both crystals are well-grown and have uniform grain size. It can be seen that the $BaZrO_3$ microcrystal with a grain size of ~1 μm has a shape of rhombic-dodecahedron and the $BaTiO_3$ microcrystal with a grain size of ~0.1 μm has a shape of sphere.

The XRD patterns of the $BaZr_xTi_{1-x}O_3$ sintered at 1300 °C for 1 h are shown in Fig. 2. All the ceramics have pure perovskite structure and no second phases are detected. According to the Shannon ionic radius, the ionic radii of Ba^{2+}, Ti^{4+} and Zr^{4+} are 0.161 nm, 0.0605 nm and 0.072 nm respectively [13], suggesting that Zr^{4+} has been incorporated into the B site of BT lattices to form a solid solution. It is observed in the slow scan that the diffraction peaks shift towards the lower angle with increasing x.

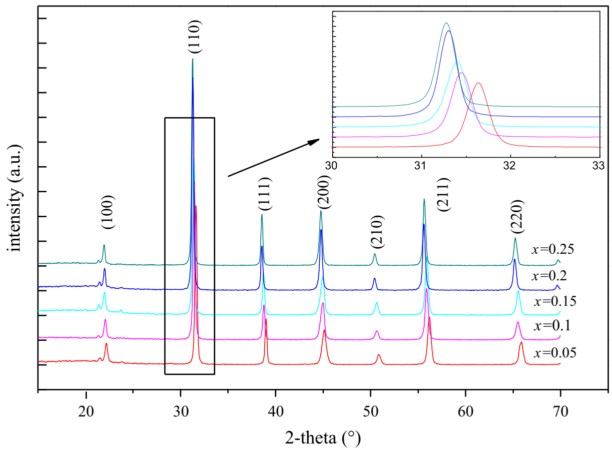

Fig. 2. X-ray patterns of $BaZr_xTi_{1-x}O_3$ ceramics sintered at 1300 °C for 1 h.

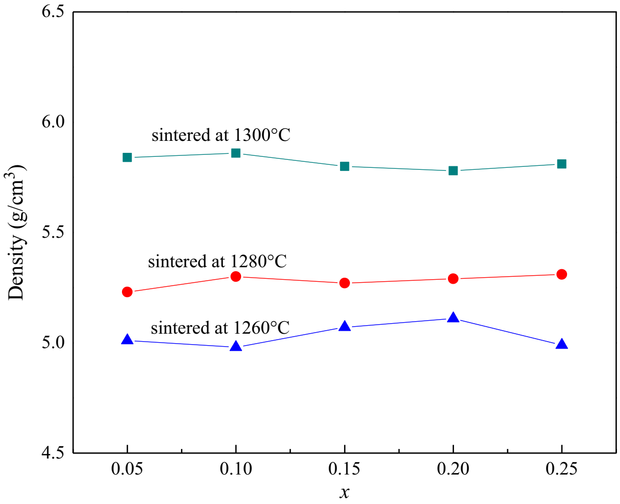

Fig. 3. Relative density of $BaZr_xTi_{1-x}O_3$ sintered at different temperatures as a function of x.

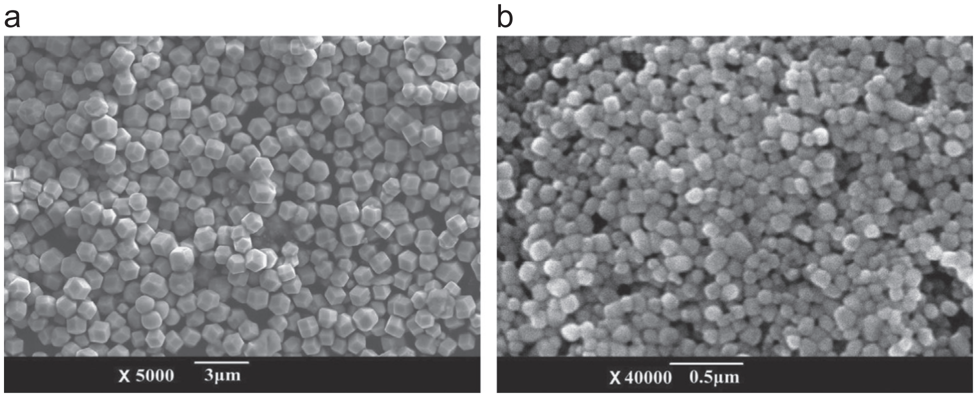

Fig. 1. SEM micrographs of $BaZrO_3$ (a) and $BaTiO_3$ (b) powders synthesized by conventional hydrothermal method.

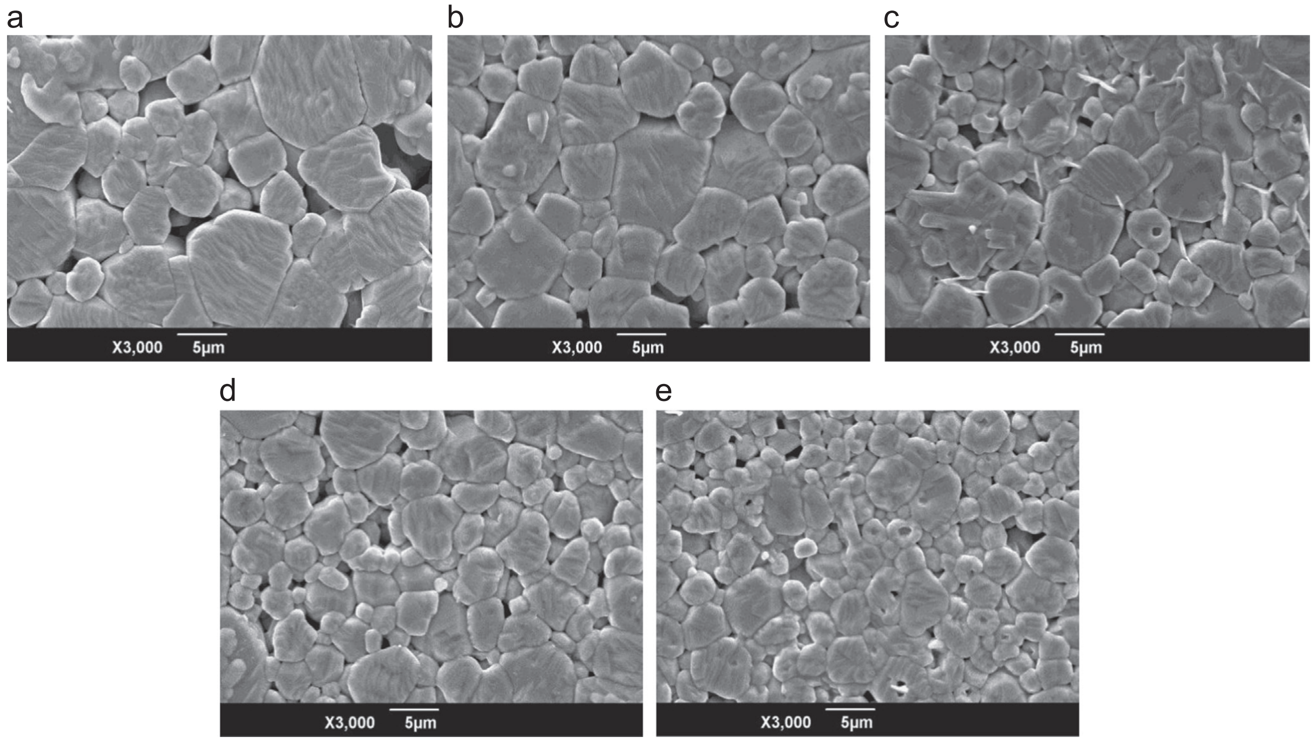

Fig. 4. SEM micrographs of the $BaZr_xTi_{1-x}O_3$ ceramics sintered at 1300°C. (a) $x=0.05$; (b) $x=0.1$; (c) $x=0.15$; (d) $x=0.2$; and (e) $x=0.25$.

This is possibly due to the fact that the ionic radius of the Ti^{4+} is shorter than that of Zr^{4+}. With the substitution of Zr^{4+}, the lattice spacing d increases, the 2θ decreases which are agreed with the equation $2d \sin\theta = n\lambda$.

All the ceramics are well-sintered at 1300 °C for 1 h and Fig. 3 shows the densities of the studied samples measured by the Archimedes principle sintered at different temperatures. The theoretical density of $BaZr_xTi_{1-x}O_3$ ceramics was calculated to be 6.02 g/cm^3, and the measured density increased with increasing the sintering temperature. The SEM micrographs of the $BaZr_xTi_{1-x}O_3$ ceramics with $x=0.05$–0.25 are shown in Fig. 4. It can be seen obviously that the grain size is greatly influenced by the concentration of Zr^{4+}. The average grain size is observed to decrease from ~6 μm to ~3 μm with x increased from 0.05 to 0.25. The increasing Zr^{4+} amount acts as an inhibitor of the grain growth during sintering process [14], so that a reduction of the average grain size of the BZT ceramics sintered at 1300 °C is obtained for higher x. The decreasing grain size with increasing x is associated with the lower grain-growth rate caused by the slow diffusion of the Zr^{4+} [15], which had a larger ionic radius than Ti^{4+}. Smaller ions always lead to fast diffusion and grain growth. The $BaTiO_3$ powders prepared by conventional hydrothermal method seen in Fig. 1 (b) adhere together, which contributes to the growth of grain size of ceramics during microwave sintering. The doping of Zr^{4+} helps to prevent this behavior and lead to a smaller grain size.

Fig. 5 shows the dielectric constant of $BaZr_xTi_{1-x}O_3$ ceramics sintered at 1300 °C for 1 h as a function of temperature at 0.1–1000 kHz. From Fig. 5 it is observed that T_C reduces from 110.7 °C for $x=0.05$ to 47.4 °C for $x=0.20$,

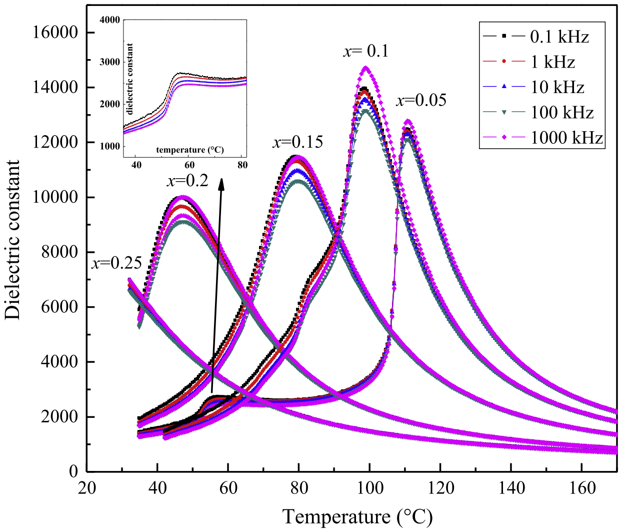

Fig. 5. Temperature dependences of dielectric constant of $BaZr_xTi_{1-x}O3$ sintered at 1300 °C.

Table 1
Physical and electrical properties of $BaZr_xTi_{1-x}O_3$ ceramics.

x	T_C (°C)	$T_{O\text{–}T}$ (°C)	ε_m	P_r	ρ	FWHM (°C)
0.05	120	59.1	12,781	9.45	5.84	21.9
0.1	98.9	–	14,713	11.84	5.86	29.2
0.15	79.7	–	11,464	6.4	5.8	37.9
0.2	47.4	–	10,045	5.9	5.78	39.7
0.25	–	–	–	4.4	5.81	–

and these values are shown in Table 1. That is possibly due to the weak bonding force between the Ti^{4+} and the oxygen ion of the ABO_3 perovskite structure. As the Zr–O bond (776.1 kJ/mol) is stronger than Ti–O bond (672.4 kJ/mol), hence the Zr^{4+} ions can be substituted at lower temperature for cubic-tetragonal phase transition [16]. The $BaZr_{0.05}Ti_{0.95}O_3$ ceramics displays another obviously phase transitions temperature at 59.1 °C, which is marked with arrow in Fig. 5, corresponding to the orthorhombic to tetragonal ($T_{O–T}$). The peak of $T_{O–T}$ can only be observed in $BaZr_xTi_{1-x}O_3$ ceramics with lower Zr^{4+} content for it will move and be overlapped by the Curie peak with higher Zr^{4+} content (< 0.06) [17]. With increasing x, the T_C range becomes broader and the ceramics exhibits relaxor property with a diffuse ferro-para phase transition and dispersion in the polar phase ($T < T_C$). It is probably due to the fact that ceramics with higher x have smaller grain size which diffuse the ferroelectric phase area, and smaller ferroelectric domains always turn during a relative broad temperature range. The T_C range of these $BaZr_xTi_{1-x}O_3$ ceramics are broader ($\sim$100 °C, seen from Fig. 5) compared with those prepared by solid state method.

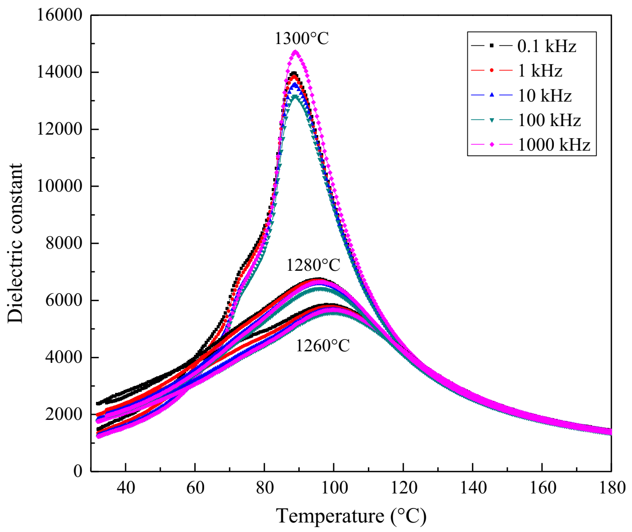

Fig. 6. Temperature dependence of dielectric constant of $BaZr_xTi_{1-x}O3$ sintered at different temperatures.

Fig. 6 shows the temperature dependences of dielectric constant of $BaZr_{0.1}Ti_{0.9}O_3$ ceramics sintered at different temperatures at 0.1–1000 kHz. It can be observed that the samples sintered at 1300 °C show a relative high permittivity near T_C compared to those sintered at 1260 °C and 1280 °C. That is probably because ceramics sintered at higher temperature always show larger grain size and the increasing average grain size makes the domain wall move easier at the higher sintering temperature, which results in an increasing dielectric constant. Meanwhile, higher temperature contributes to the dispersion of Zr^{4+} and more grain boundaries. As the grain boundaries have high resistance and capacitance as compared to the bulk, it results in a high interfacial polarization leading to the increase in dielectric constant.

The temperature dependence of dielectric loss (tan δ) for the $BaZr_xTi_{1-x}O_3$ ceramics with different x sintered at 1300 °C are shown in Fig. 7. All the samples exhibit a dielectric loss < 0.1 at lower temperature and a strong increase of tan δ occurred at $T > 120$ °C, which is probably due to a thermally activated space

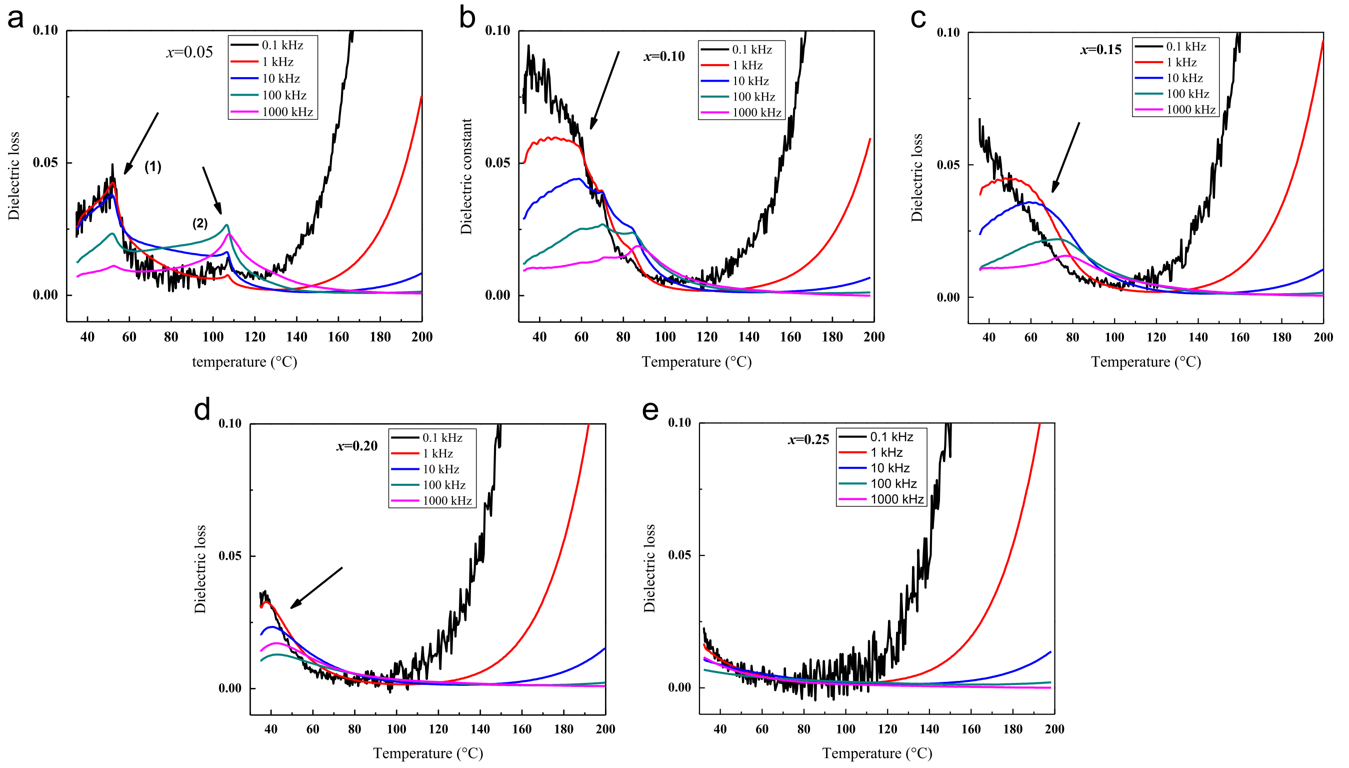

Fig. 7. Temperature dependence of tan δ for the $BaZr_xTi_{1-x}O_3$ ceramics sintered at 1300°C. (a) $x=0.05$; (b) $x=0.1$; (c) $x=0.15$; (d) $x=0.2$; and (e) $x=0.25$.

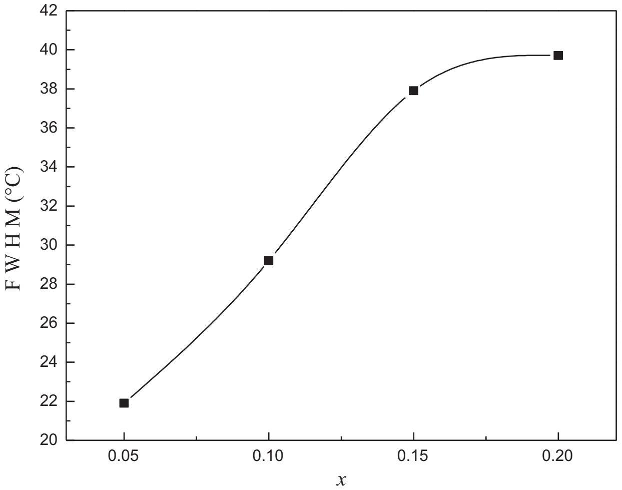

Fig. 8. Relationship between x and FWHM.

charge contribution (Maxwell–Wagner type). That is commonly presented in systems with local compositional and electrical inhomogeneity. $\mathrm{BaZr}_x\mathrm{Ti}_{1-x}\mathrm{O}_3$ with $x=0.1$ has a maximum value in dielectric loss and then the dielectric loss decreases with higher x. That is because at lower x, the defect chemical reaction of Zr^{4+} substitution for Ti^{4+} is represented as [18]:

$$\mathrm{Zr}^{4+} \rightarrow \mathrm{Zr}^{*}_{\mathrm{Ti}} + 2\mathrm{O}^{*}_{\mathrm{O}}$$

$$\mathrm{Ti}^{4+} + \mathrm{e}' \rightarrow \mathrm{Ti}^{3+}$$

Ti^{4+} reduces to Ti^{3+} at the higher sintering temperature, and the electron hopping between Ti^{4+} and Ti^{3+} ions leads to a higher dielectric loss. When $x>0.20$, the ceramics become more densified with lower porosity for their smaller grain size which exhibited low tan δ. Both of the two features result in a maximum value in dielectric loss at $x=0.1$. Some peaks marked with arrows can be observed in Fig. 7, which are corresponding to phase transition temperature in Fig. 5. But the peaks in Fig. 7 shift towards the left 3–5 °C compared with Fig. 5 in each sample. That is due to the fact that dipoles take some time to orientate, and this behavior leads to relaxation polarization loss. Frequency dispersion can be observed in all the samples, indicating a dielectric relaxation.

The full width at half maximum (FWHM) is used to characterize the broadening of Curie peak, and the relationship between x and the FWHM is shown in Fig. 8. It can be observed that the FWHM increased rapidly when $x<0.15$, but no significant differences are observed with further doping of Zr^{4+}. That is probably due to the fact that the Zr^{4+} has a saturated degree of dispersion when x was increased to 2.0, more doping of Zr^{4+} had less effect on refining the grain size and broadening T_C range. BaZrO_3 is an electric material nonferroelectric properties and can form solid solution with BT in any proportion. The micro-dopant of Zr^{4+} can both decrease the permittivity at TC and broaden the TC range while the further doping can only decrease the permittivity without broadening the TC range.

It is concluded in Fig. 5 that the ceramics have broader Curie peak with increasing x, indicating the ferro-para phase transition becomes more diffusive with increasing x. A modified Curie–Weiss law is proposed to describe the diffuseness of a phase transition.

$$1/\varepsilon - 1/\varepsilon_\mathrm{m} = (T - T_\mathrm{m})\gamma / C$$

where ε_m is the maximum value of relative permittivity at the phase transition temperature T_C (T_m), γ is the degree of diffusion and C is the Curie-like constant. The γ has a value ranging from 1 for a normal ferroelectric to 2 for an ideal relaxor ferroelectric [18]. The plots of ln $(1/\varepsilon - 1/\varepsilon_\mathrm{m})$ as a function of ln $(T - T_\mathrm{m})$ for the different Zr^{4+} contents are shown in Fig. 9. The γ was determined by least-squared fitting the experimental data to the modified Curie–Weiss law. The γ increased from 1.40 to 1.81

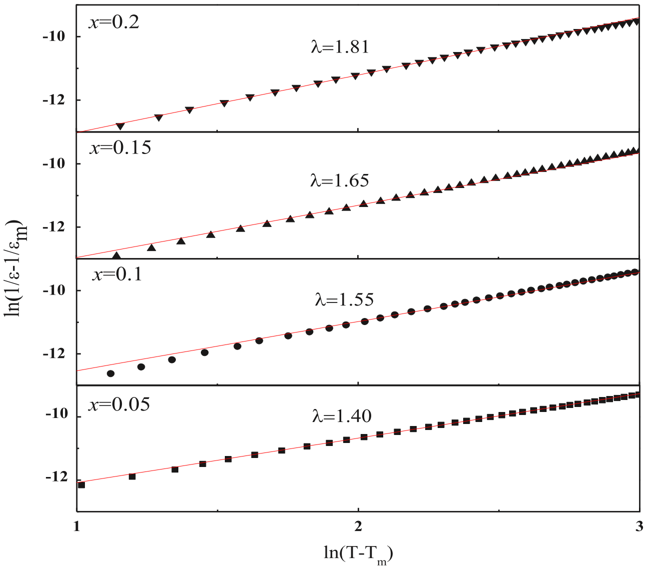

Fig. 9. The plots of ln $(1/\varepsilon - 1/\varepsilon_\mathrm{m})$ as a function of ln $(T - T_\mathrm{m})$ for the $\mathrm{BaZr}_x\mathrm{Ti}_{1-x}\mathrm{O}_3$ ceramics sintered at 1300 °C.

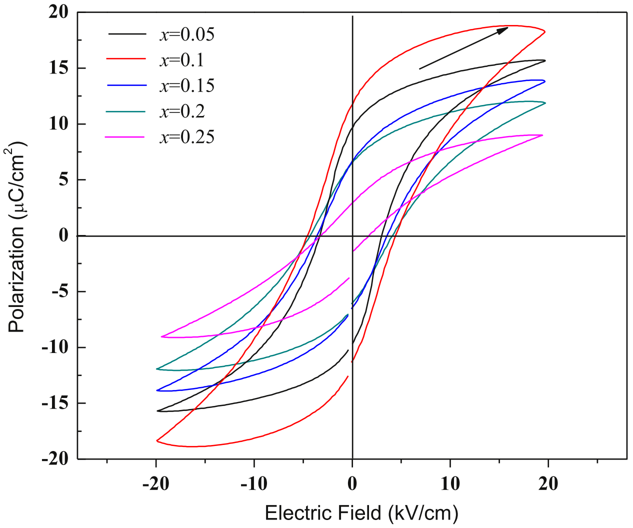

Fig. 10. P–E loops of the $\mathrm{BaZr}_x\mathrm{Ti}_{1-x}\mathrm{O}_3$ ceramics with different Zr^{4+} contents.

when the x is increased from 0.05 to 0.20. These results suggest that the addition of Zr^{4+} make the BZT ceramics more relaxor.

The P–E loops of the $BaZr_xTi_{1-x}O_3$ ceramics tested at room temperature are shown in Fig. 10 and these results display the most prominent features, which obviously change with increasing x. The P_r values of $Ba_xZrTi_{1-x}O_3$ ceramics are shown in Table 1. These samples have a maximum value of P_r at $x=0.1$, exhibiting an unsaturated P–E loop, and the loops become gradually flattened and slanted with further doping level of Zr^{4+}. It also can be observed in $BaZr_{0.1}Ti_{0.9}O_3$ ceramics that the maximum value of polarization marked with arrow is not corresponding to the maximum value of electric field. That is probably due to the fact that the relaxation polarization occurred with some doping of Zr^{4+} during electric field inversion, resulting in a poor ferroelectric characterization. The decrease in P_r with further Zr^{4+} content may be attributed to the change in the grain size as it is shown in Fig. 4.

4. Conclusions

$Ba_xZr_{1-x}TiO_3$ ceramics with different x were prepared by powders synthesized using conventional hydrothermal method. By increasing the x, the grain size decreased from ~ 6 μm to ~ 3 μm, leading to a decrease in the T_C and broadening the T_C range in the temperature dependences of permittivity and a ferroelectric-relaxor crossover. The $\tan\delta$ and P_r decreased when the x was increased from 0.05 to 0.25 while they both show a maximum value at $x=0.1$. The Curie peak broadened rapidly when x increased from 0.05 to 0.15, but no significant differences were observed with further doping for the Zr^{4+} had a saturated degree of dispersion with higher x.

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