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Investigation of dielectric and relaxor ferroelectric properties in $Ba(Zr_xTi_{1-x})O_3$ ceramics

J. W. Xiong · B. Zeng · W. Q. Cao

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Abstract Barium zirconate titanate $Ba(Zr_xTi_{1-x})O_3$ (BZT x= 0.1, 0.15, 0.2, 0.25) ceramics doped with Nb_2O_5 have been prepared by a traditional solid phase reaction. The temperature dependence of dielectric permittivity has been investigated. The results show that the phase transition temperature T_c is depressed and the diffuse phase transition behavior is enhanced with increasing Zr content. The Cole–Cole plot has been discussed and the cause of the deviation has been analyzed. The temperature dependence of inverse dielectric constants was investigated. A modified Curie–Weiss law can be used to describe the diffuseness of a phase transition, and diffusion factor increases with the Zr content.

Keywords BZT · Relaxor ferroelectrics · Dielectric

1 Introduction

Ceramics based on barium titanate ($BaTiO_3$) are frequently used to manufacture multilayer capacitors (MLCCs) and thermistors owing to their high dielectric constant. The nature of the ferroelectric phase transition at the transition temperature (T_m) in bulk ceramics is known to change strongly with Zr content. For Zr content above x=0.08, the $Ba(Zr_xTi_{1-x})O_3$ bulk ceramic shows a broad permitivity-temperature ($\varepsilon \sim T$) curve near T_m, which is caused by the inhomogeneous distribution of Zr ions on Ti sites and mechanical stress in the grain [1]. As the Zr content increases, the phase transition temperatures approach each other, until, at a Zr content of $x \sim 0.20$, only one phase transition exists [2]. The relaxor behavior disappears when Zr contents $x \leq 0.25$ in pure $Ba(Zr_xTi_{1-x})O_3$ [3] . In this work, lead-free $Ba(Zr_xTi_{1-x})O_3$ (x=0.1, 0.15, 0.2, 0.25) ceramics doped with Nb_2O_5 were prepared by a traditional solid phase reaction. The influence of Zr content on the dielectric properties of $Ba(Zr_xTi_{1-x})O_3$ ceramics with 0.1% Nb_2O_5 was examined, and the relaxor behavior is still observed even at a Zr content of x=0.1.

2 Experimental

The crystalline powder of $Ba(Zr_xTi_{1-x})O_3$ (with compositions x=0.1, 0.15, 0.2, 0.25; abbreviated as 0.1, 0.15, 0.2, and 0.25 BZT, respectively) was prepared from $BaCO_3$, ZrO_2, TiO_2 and 0.1% Nb_2O_5 using a traditional mixed oxide technique. The sample was calcined at 1,150 °C for 2 h and sintered at 1,230 °C for 2 h using a heating rate of 200 °C/h, respectively. The phase structure was confirmed by X-ray diffraction analysis. A HP4192A impedance analyzer in the frequency range from 20 Hz to 13 KHz was utilized to measure the temperature or frequency dependence of BZT samples on the dielectric properties.

3 Results and discussion

Figure 1 shows the diffraction peaks of BZT calcined powders and sintered compacts, compared with the standard cubic perovskite diffraction peaks of BZT, it is found that a pure perovskite phase was obtained, and no other impurity phases exist, it is indicated that the Nb ions enter the crystal lattices.

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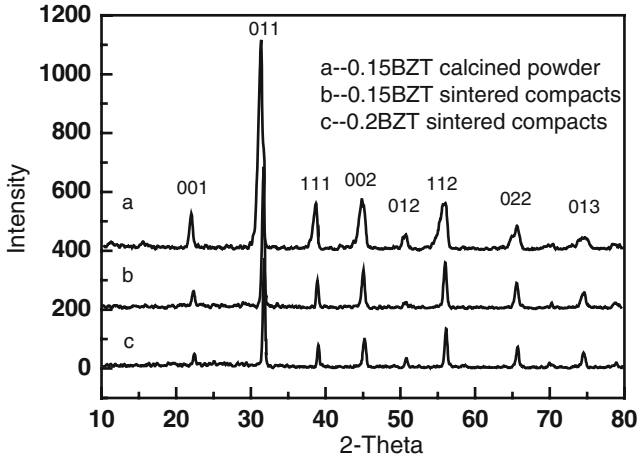

Fig. 1 X-ray diffraction patterns of calcined BZT powders and sintered compacts

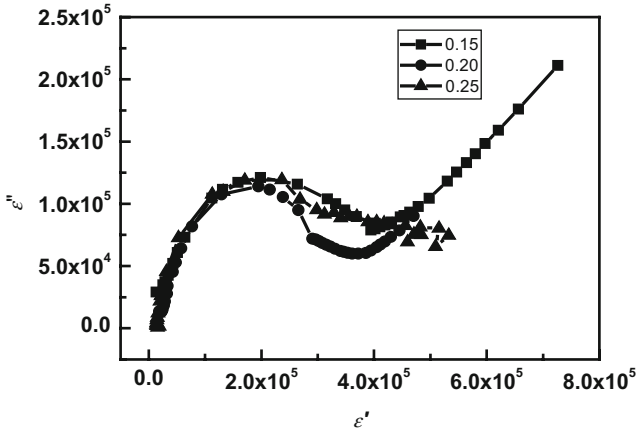

Fig. 3 Cole–Cole plot of BZT ceramics at room temperature

Figure 2 exhibits the frequency dependence of dielectric constant for the BZT samples at room temperature. The dielectric constants of 0.15 and 0.25 BZT samples are generally higher than those of the 0.1 and 0.2 BZT samples in lower frequency. So the 0.15 and 0.2 BZT ceramics can be selected as various materials for different requirement. For frequency $f>10$ kHz, the dielectric constant has comparative stabilization, the Zr content of $0.1<x<0.2$ is a reasonable range, in which the dielectric constant can be increased with increasing Zr content. For Zr content of $x>0.25$, it is possible that the Zr ion could diffuse into the grain boundaries, which result in the asymmetry increasing of the internal structure of BZT ceramics, and therefore the dielectric constant decreases.

Figure 3 shows the Cole–Cole plot of BZT ceramics at room temperature. The Cole–Cole plot of perfect single crystal is usually a semicircle, but in ceramics, the Cole–Cole plot is superposed by several semicircles, which may be attributed to a dissymmetrical distribution of several relaxor times induced by the asymmetrical internal structure of Nb doped BZT ceramics.

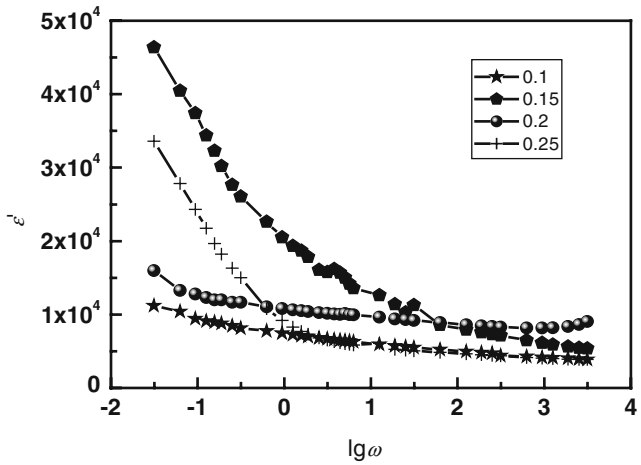

Fig. 2 Frequency dependence of dielectric constant ε of BZT ceramics at room temperature

Figure 4 demonstrates the temperature dependence of the dielectric constant for the BZT samples at 0.1 k, 1 k, 10 k, 100 kHz. The results show that the transition temperature T_m decreases from 90 °C of 0.1 BZT to 0 °C of 0.25 BZT with increasing Zr content, implying that the Zr^{4+} substitution for Ti^{4+} in $BaTiO_3$ influences the transition temperature T_m. The results of the dielectric response of the four samples exhibit a diffuse phase transition around the transition temperature T_m. First, a frequency dispersion and the depressed dielectric maximum ε m are observed. The Tm moves toward higher temperatures with increasing of frequency. The low-temperature frequency dispersion of the dielectric maximum $\varepsilon_m(T)$ clearly demonstrates a relaxation nature, i.e. a relaxor-type diffused permittivity for 0.1, 0.15, 0.2, and 0.25 BZT ceramics is observed, respectively. Second, the diffusion transition behavior is enhanced with increasing Zr content, indicating a composition-induced diffuse transition; and the BZT ceramics exhibit a strong relaxor behavior for higher Zr content. Tang [3] reported that there is no relaxor behavior exist in the pure BZT ceramics with Zr content $x\leq 0.25$. Obviously a typical relaxor behavior is observed 0.1 BZT ceramics doped with Nb in Fig. 4, which can be induced by a microscopic composition fluctuation, it is illustrated that Nb doping and increasing Zr content can enhance the relaxor behavior as influencing the asymmetrical internal structure of BZT ceramics.

A diffuse phase transition is generally characterized by : (a) Broadening in the dielectric constant; (b) frequency dispersion of both ε and tan δ in the transition region ; (c) a deviation from Curie–Weiss law in the vicinity of T_m. The former two characters can be observed straightly in Fig. 4. It is know that the dielectric permittivity of a normal ferroelectric above the Curie temperature follows the

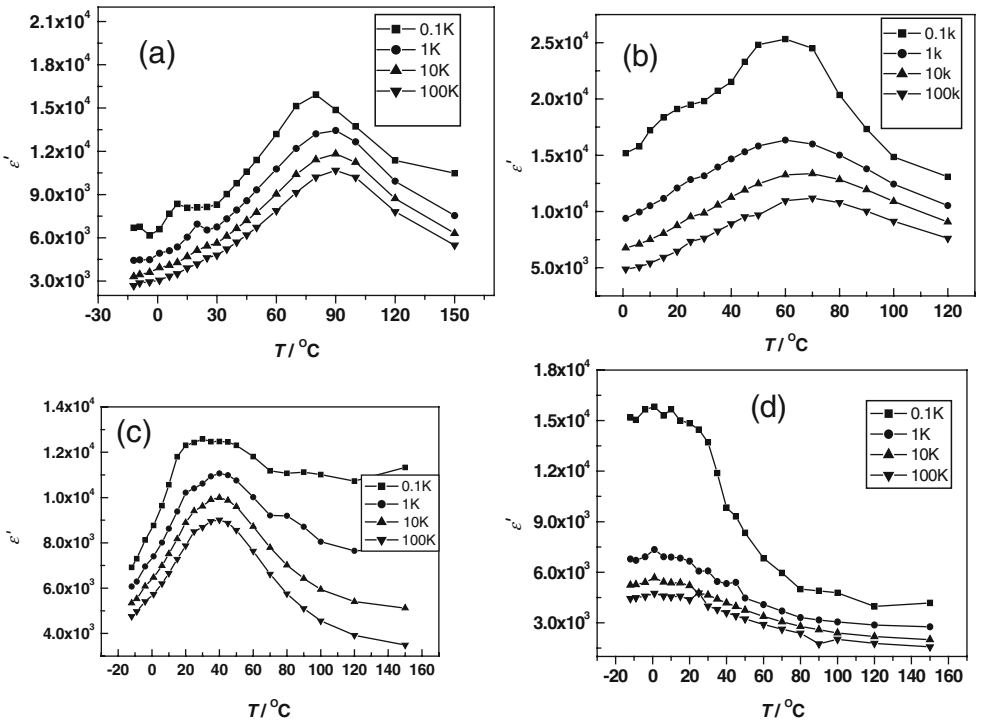

Fig. 4 Temperature dependence of dielectric constant ε of (**a**) 0.1 BZT; (**b**) 0.15 BZT; (**c**) 0.2 BZT; (**d**) 0.25 BZT ceramics

Curie–Weiss law described by $1/\varepsilon = (T - T_0)/C$, $(T > T_c)$, where T_0 is the Curie–Weiss temperature and C is the Curie–Weiss constant. A T_0 of 383 K and C of 1.56×10^5 K have been obtained for a pure $BaTiO_3$ crystal [4]. Figure 5 shows the plots of inverse dielectric constant (at 10 kHz) versus temperature for the BZT ceramics. A modified Curie–Weiss law [5, 6] has been proposed to describe the diffuseness of a phase transition

$$1/\varepsilon - 1/\varepsilon_m = (T - T_m)^\gamma / C' \quad (1)$$

where γ and C' are assumed to be constant. The parameter γ gives information on the character of the phase transition: for γ=1, a normal Curie–Weiss law, γ=2, a complete diffuse phase transition [7, 8].

The plots of $\ln(1/\varepsilon - 1/\varepsilon_m)$ as a function of $\ln(T - T_m)$ for the four samples are shown in Fig. 6. A linear relationship is observed for the four samples. The slope of the fitting curves is used to determine the value of γ, listed in Table 1.

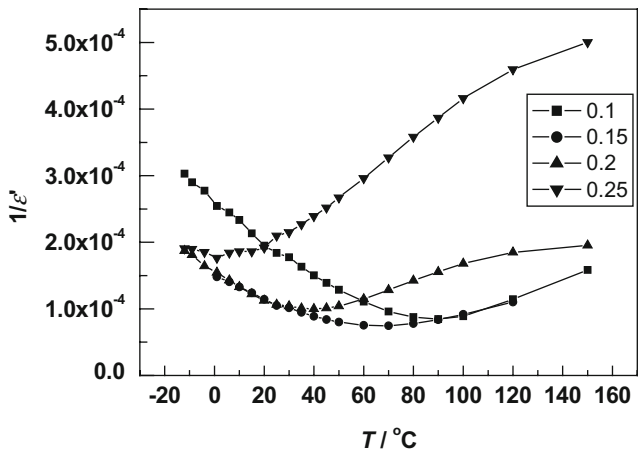

Fig. 5 The inverse dielectric constant $(1/\varepsilon)$ as a function of temperature at 10 KHz for the four samples

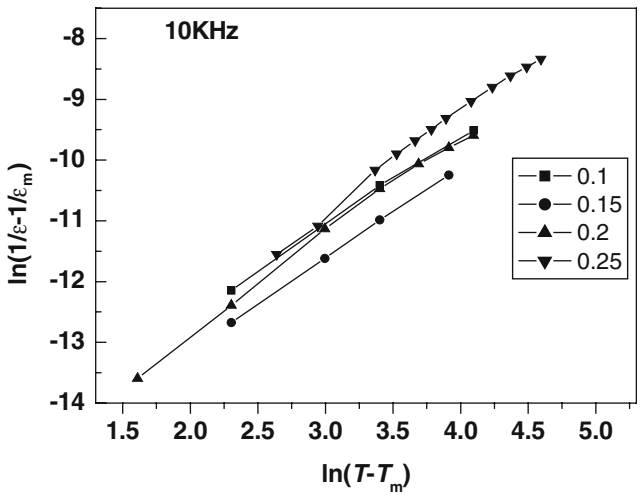

Fig. 6 Plot of $\ln(1/\varepsilon - 1/\varepsilon_m)$ as a function of $\ln(T - T_m)$ for the four samples

Table 1 The temperature of dielectric constant maximum (T_m), dielectric constant maximum (ε_m), and diffuseness constant (γ) for the four samples at 10 kHz.

Sample	0.1 BZT	0.15 BZT	0.2 BZT	0.25 BZT
T_m(°C)	90	70	40	0
ε_m	11,821.78	13,364.04	9,995.642	5,664.911
γ	1.48038	1.51185	1.63554	1.66071

4 Conclusion

The effects of the Zr content on the dielectric constant of the Nb_2O_5 doped BZT ceramics have been investigated. The Zr substitution for Ti in $BaTiO_3$ affects the transition temperature T_m by shifting T_m to a lower temperature region. The diffuse phase transition behaviors of the ceramics become more remarkable at higher Zr content, implying a composition-induced diffuse transition. The relaxor behavior is still observed even at a Zr content of x=0.1, which illustrates that Nb doping can enhance the relaxor behavior resulting from the asymmetrical internal structure of BZT ceramics. A modified Curie–Weiss law $1/\varepsilon - 1/\varepsilon_m = (T - T_m)^\gamma / C'$ has been proposed to describe the diffuseness of a phase transition, γ is a critical exponent.

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