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Dielectric and Ferroelectric Properties of Ho₂O₃ Doped Barium Strontium Titanate Ceramics

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Abstract: The crystalline structure, surface morphology, dielectric and ferroelectric properties of 0~10wt% Ho₂O₃ doped (Ba_{0.75}Sr_{0.25}) TiO₃ ceramics prepared by conventional solid state method were studied using X-ray diffractometer, scanning electron microscopy, LCR measuring system and ferroelectric property test systems aiming for ceramic capacitor applications. It is found that proper amount of Ho₂O₃ can refine grains of the system. With the increase of Ho₂O₃ doping content, the average grain size of (Ba_{0.75}Sr_{0.25}) TiO₃ ceramics decreases. When Ho₂O₃>8 wt%, (Ba_{0.75}Sr_{0.25}) TiO₃ based ceramic samples are multi-phase compounds with typical perovskite structure accompanied by the appearance of cylindrical grains. The Ho³⁺ ions substitute the host A sites and B sites of (Ba_{0.75}Sr_{0.25}) TiO₃ perovskite lattice, resulting in the lattice distortion of the system and the change of the relative dielectric constant and dielectric loss at room temperature. With the increase of Ho₂O₃ doping content, the relative dielectric constant at room temperature of the system increases first and then decreases. The maximum of relative dielectric constant at room temperature can be found in the 1 wt% Ho₂O₃ doped (Ba_{0.75}Sr_{0.25}) TiO₃ ceramics. When Ho₂O₃>1 wt%, the maximum of relative dielectric constant ε_{rmax} decreases and the temperature corresponding to the maximum of relative dielectric constant T_m shifts toward lower temperature with the increase of Ho_2O_3 doping content. The $(Ba_{0.75}Sr_{0.25})$ TiO_3 ceramics with high Ho₂O₃ content show relaxor-like behavior which is characterized by the typical diffuse phase transition and frequency dispersion of dielectric constant. However, the (Ba_{0.75}Sr_{0.25}) TiO₃ ceramics with low Ho₂O₃ content do not exhibit permittivity frequency dispersion. According to the P-E hysteresis loops of Ho₂O₃ doped (Ba_{0.75}Sr_{0.25}) TiO₃ ceramics, the ferroelectricity was increased and then decreased with the increase of Ho₂O₃ doping content. With the increase of Ho₂O₃ doping content, the P-E relationships turn out to be straight lines, implying the paraelectric phase for (Ba_{0.75}Sr_{0.25}) TiO₃ ceramics with high Ho₂O₃ content.

Keywords: Barium Strontium Titanate, Perovskite, Relaxor Characteristic, Ferroelectric Properties

1. Introduction

Barium strontium titanate ((Ba_{1-x}Sr_x) TiO₃, BST), as an infinite solid solution of BaTiO₃ and SrTiO₃, maintains perovskite structure (ABO₃) similar to BaTiO₃, and has outstanding properties such as high dielectric constant, low dielectric loss and excellent ferroelectric properties [1-2]. In addition, its Curie temperature can be adjusted over a wide range of temperature by changing Ba/Sr ratio, making the BST systems become one of the basic ceramic materials for ceramic capacitors [3].

As an important component of electronic products, ceramic

capacitors require superior and more stable performance in smaller sizes. In order to meet the needs in different applications, people add metal oxides or their derivatives to BST systems to improve their comprehensive properties. The rare earth metal oxides play important roles in the property modification for dielectric materials, which has aroused great interest of many researchers [4-9]. D. C. Sinclair et al. studied the rare earth metal ions RE³⁺ doped barium titanate ceramics, and proposed that when the RE³⁺ ions enter the A site of the perovskite lattice, charge imbalance is created which must be compensated by either cation vacancies on the A or B site compensation), by (ionic or electrons

compensation) [10-11]. Three point defect reactions can be identified:

$$2RE_2O_3 + 3TiO_2 \rightarrow 4RE_{Ba}^{\bullet} + 3Ti_{Ti} + 12O_0 + V_{Ti}^{""}$$
 (1)

$$RE_2O_3 + 3TiO_2 \rightarrow 2RE_{Ba}^{\bullet} + 3Ti_{Ti} + 9O_0 + V_{Ba}^{"}$$
 (2)

$$2RE_{2}O_{3} + 4TiO_{2} \rightarrow 4RE_{Ba}^{\bullet} + 4Ti_{Ti} + 12O_{0} + O_{2} \uparrow + 4e'$$
 (3)

When the RE³⁺ ions enter the B site of the perovskite lattice, charge imbalance is created which must be compensated by the oxygen vacancies [10]. The point defect reaction can be seen as follows:

$$2BaO + RE_2O_3 \rightarrow 2Ba_{Ba} + 2RE_{T_1}^{\bullet} + 5O_O + V_O^{\bullet \bullet}$$
 (4)

In general, the large size RE³⁺ ions tend to occupy the A site; The small size RE³⁺ ions tend to occupy the B site; The middle size RE³⁺ ions have the amphoteric behavior occupying both A and B site [12]. Y. Li et al. studied on the dielectric properties of Sm₂O₃ doped Ba_{0.68}Sr_{0.32}TiO₃ ceramics, and proposed that the substitution preference of Sm³⁺ in the lattice also depends on Sm₂O₃ doping content [13]. C. Zhao et al. prepared Y₂O₃ and Dy₂O₃ doped Ba_{0.7}Sr_{0.3}TiO₃ ceramics with comprehensive properties (ε_r =3.66×10³, $tan\delta$ =9.3×10⁻³, $\Delta\varepsilon_r/\varepsilon_r$ =14.1%) [14]. In addition, some researchers studied the effect of grain size on dielectric and ferroelectric properties of Ba_{0.80}Sr_{0.20}TiO₃ ceramics [15-16].

In our present work, $0\sim10$ wt% Ho_2O_3 doped $(Ba_{0.75}Sr_{0.25})$ TiO_3 ceramics were prepared by solid state reaction method. The effects of Ho_2O_3 doping content on crystalline structure, surface morphology, dielectric and ferroelectric properties of the system were investigated. The substitution characteristics of Ho^{3+} ions in $(Ba_{0.75}Sr_{0.25})$ TiO_3 perovskite lattice will be determined and the interrelationship between the macroscopic dielectric constant, dielectric loss, temperature-dependent properties and microscopic defect behavior will also be established.

2. Experimental

2.1. Sample Preparation

In this paper, high purity BaCO₃ (>99.0%), SrCO₃ (>99.0%) and TiO₂ (>98.0%) powders used as starting raw materials were proportionally weighed according to the formula (Ba_{0.75}Sr_{0.25}) TiO₃ and ball-milled for 24 h. After drying, the obtained powders were calcined at 1080°C for 2 h to form main crystalline phase. The calcined powders were mixed with 0.2 wt% MgO (\geq 98.5%), 0.2 wt% ZnO (\geq 99.0%) and 0~10 wt% Ho₂O₃(>99.0%), reground for 24 h, dried and added with 5 wt% polyvinyl alcohol (PVA) as a binder for granulation. The mixtures were sieved through 40-mesh screen and then pressed into pellets 10mm in diameter and 2~3 mm in thickness. Sintering was conducted in air at 1400°C for 2 h, and the sintering regime was illustrated on Figure 1. For dielectric properties measurement, both the flat

surfaces of the sintered samples were coated with BQ-5311 silver paste after ultrasonic bath cleaning and then fired at 800°C for 10 min.

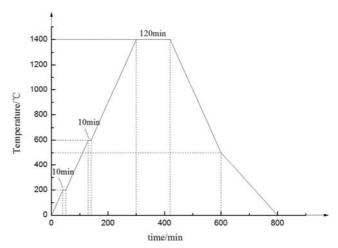


Figure 1. Sintering regime for the samples.

2.2. Equipment and Characterization

The crystal structures of the samples were confirmed by X-ray diffraction analysis (XRD, Rigaku D/max 2500v/pc) with Cu K α radiation; The phase and plane index (hkl) were obtained by search/match using Jade 6.0. The surface morphologies of the gold-sprayed ceramic samples were observed using the SEM (JSM-6480 ESEM). The capacitance quantity (C) and dissipation factor (D) were measured with TZDM-200-300B testing system. The relative dielectric constant (ε_r) and dielectric loss ($tan\delta$) were calculated by the following Equations:

$$\varepsilon_r = \frac{14.4Ch}{\Phi^2} \tag{5}$$

$$tan\delta = D \tag{6}$$

where C is the capacitance quantity (pF); h is the thickness (cm); Φ is the diameter of the electrode (cm); D is the dissipation factor. The temperature dependence of dielectric parameters was measured at $1\sim100$ kHz from -150 to 150°C. The P-E hysteresis loops of Ho_2O_3 doped ($Ba_{0.75}Sr_{0.25}$) TiO_3 ceramics at room temperature was obtained using the ferroelectric property test system.

3. Results and Discussion

3.1. XRD Analysis

The XRD patterns of Ho_2O_3 doped $(Ba_{0.75}Sr_{0.25})$ TiO_3 ceramics are shown in Figure 2. It appears that all samples are single phase solid solutions with typical perovskite structure. No obvious secondary phase is found even for the 10 wt% Ho_2O_3 doped $(Ba_{0.75}Sr_{0.25})$ TiO_3 ceramics based on the XRD patterns.

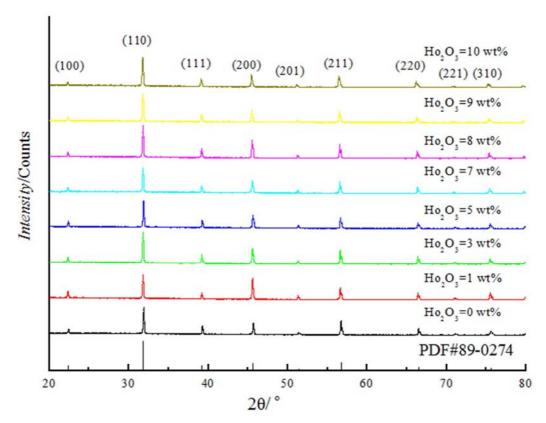


Figure 2. XRD patterns of Ho₂O₃ doped (Ba_{0.75}Sr_{0.25}) TiO₃ ceramics.

3.2. SEM Analysis

Figure 3 shows the SEM images of Ho_2O_3 doped $(Ba_{0.75}Sr_{0.25})$ TiO_3 ceramics. It appears that all samples exhibit dense microstructures and possess uniform grain size. With the increase of Ho_2O_3 doping content, the average grain size of $(Ba_{0.75}Sr_{0.25})$ TiO_3 ceramics decreases. The reason is

that $\mathrm{Ho^{3^+}}$ ions are easily segregated near the grain boundary, which hinders the further grain growth [17]. However, the cylindrical grains indicating the appearance of secondary phase (marked using red circles in Figure 3 (g) and (h)) which is not detected by XRD due to its small amount exist in the 9 and 10 wt% $\mathrm{Ho_2O_3}$ doped ($\mathrm{Ba_{0.75}Sr_{0.25}}$) $\mathrm{TiO_3}$ ceramics.

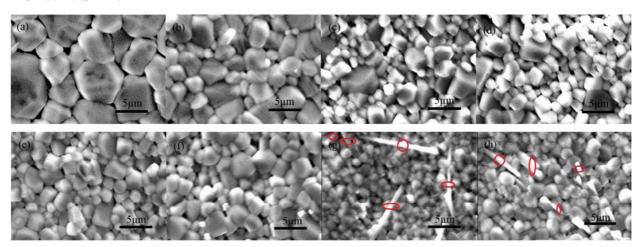


Figure 3. SEM images of Ho_2O_3 doped $(Ba_{0.75}Sr_{0.25})$ TiO_3 ceramics: (a) $Ho_2O_3=0$ wt%; (b) $Ho_2O_3=1$ wt%; (c) $Ho_2O_3=3$ wt%; (d) $Ho_2O_3=5$ wt%; (e) $Ho_2O_3=5$ wt%; (f) $Ho_2O_3=5$ wt%; (g) $Ho_2O_3=6$ wt%; (h) $Ho_2O_3=6$ wt%.

3.3. Dielectric Properties at Room Temperature

In the ABO₃ type perovskite structure, the coordination numbers of A and B site are 12 and 6, respectively. The radius of Ho³⁺ ion (1.23 Å, in 12 coordination) is smaller than that of

 Ba^{2^+} ion (1.61 Å, in 12 coordination) and Sr^{2^+} ion (1.44 Å, in 12 coordination); The radius of Ho^{3^+} ion (0.90 Å, in 6 coordination) is bigger than that of Ti^{4^+} ion (0.61 Å, in 6 coordination) [18]. Therefore, Ho^{3^+} ion can substitute the A or B site of ($\mathrm{Ba}_{0.75}\mathrm{Sr}_{0.25}$) TiO_3 perovskite lattice. When Ho^{3^+} ion

substitutes the A site, the point defect reaction is as follows:

$$2\text{Ho}_2\text{O}_3 + 4\text{TiO}_2 \rightarrow 4\text{Ho}_{p_0}^{\bullet} + 4\text{Ti}_{T_1} + 12\text{O}_0 + \text{O}_2 \uparrow + 4\text{e}'$$
 (7)

When Ho³⁺ ion begins to substitute the B site, the point defect reaction can be expressed as follows:

$$2BaO + Ho_2O_3 \rightarrow 2Ba_{Ba} + 2Ho_{-}^{\bullet} + 5O_O + V_O^{\bullet \bullet}$$
 (8)

Figure 4 shows the relative dielectric constant and dielectric loss of (Ba_{0.75}Sr_{0.25}) TiO₃ ceramics at room temperature with variation of Ho₂O₃ content. It is obvious that all ceramics

possess high relative dielectric constant ($\varepsilon_r \ge 1.69 \times 10^3$) and low dielectric loss ($tan\delta \le 6.4 \times 10^{-3}$) at room temperature. With the increase of Ho₂O₃ doping content, the relative dielectric constant of the system increases first and then decreases. The maximum of relative dielectric constant at room temperature can be found in the 1 wt% Ho₂O₃ doped (Ba_{0.75}Sr_{0.25}) TiO₃ ceramics. The dielectric loss of the system increases first, then decreases, and finally increases with the increase of Ho₂O₃ doping content.

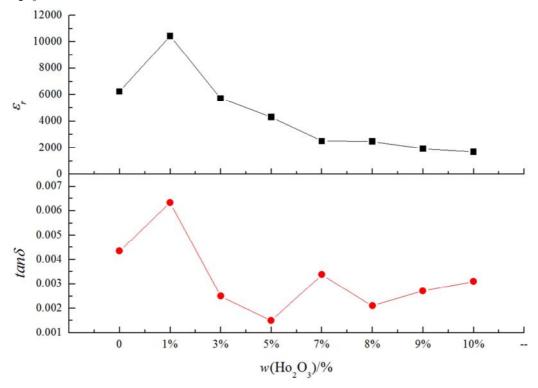


Figure 4. ε_r and $\tan\delta$ of Ho_2O_3 doped $(Ba_{0.75}Sr_{0.25})$ TiO_3 ceramics at room temperature.

When $\text{Ho}_2\text{O}_3\leq 1$ wt%, Ho^{3^+} ions tend to substitute the A site ions of the perovskite lattice. The difference of the ionic radius causes the shrinkage deformation of the perovskite unit cells and the increase of the internal stress which result in the increase of relative dielectric constant [19]. When $\text{Ho}_2\text{O}_3=1\sim 8$ wt%, Ho^{3^+} ions gradually enter the B site. The bigger Ho^{3^+} ions in the B site restrict the activity of B site ions and thus weaken the spontaneous polarization, which causes the relative dielectric constant decrease significantly with the increase of Ho_2O_3 doping content. When $\text{Ho}_2\text{O}_3>8$ wt%, non-ferroelectric secondary phase induced by the excessive Ho_2O_3 addition dilutes the ferroelectric phase, which makes the relative dielectric constant further decrease with the increase of Ho_2O_3 doping content [20].

As for the dielectric loss, When Ho³⁺ ions enter the A site of the perovskite lattice, the electrons as shown in Equation (7) are trapped by Ti⁴⁺ to form Ti³⁺, leading to the increase of the dielectric loss gradually [21]. When Ho₂O₃=1~5 wt%, the weakened spontaneous polarization results in the decrease of

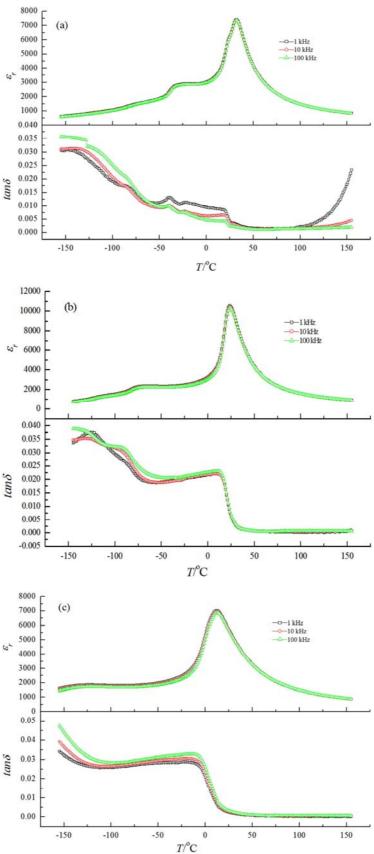
the dielectric loss significantly with the increase of Ho_2O_3 doping content. On the other hand, the oxygen vacancies as shown in Equation (8) have pinning effect on the ferroelectric domains, which also causes the decrease of dielectric loss [22-24].

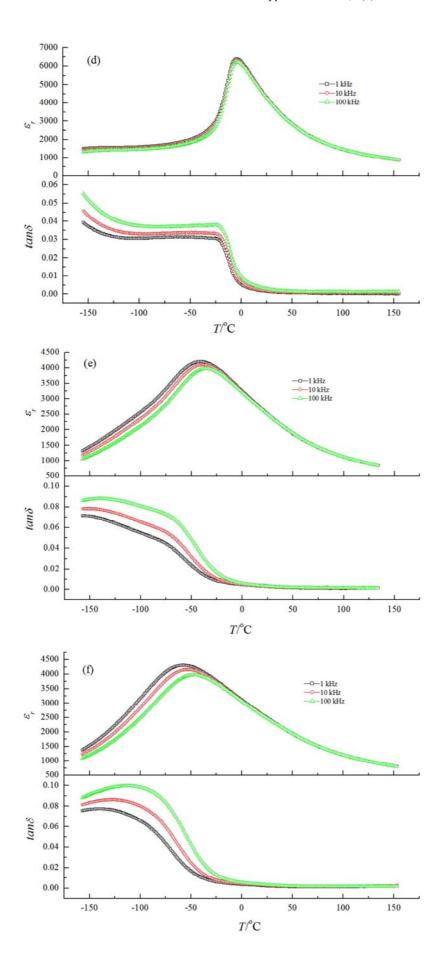
3.4. Temperature Dependence of the Relative Dielectric Constant and Dielectric Loss at Various Frequencies

Figure 5 shows the temperature dependence of the relative dielectric constant and dielectric loss at $1 \text{kHz} \sim 100 \text{kHz}$ for Ho_2O_3 doped ($\text{Ba}_{0.75}\text{Sr}_{0.25}$) TiO_3 ceramics. When Ho_2O_3 content is higher than 5 wt%, the temperature corresponding to the maximum of relative dielectric constant (T_m) for ($\text{Ba}_{0.75}\text{Sr}_{0.25}$) TiO_3 ceramics shifts toward higher temperature obviously and the relative dielectric constant (in the $T < T_m$ range) decreases with the increase of test frequency, which is known as the frequency dispersion [25]. However, as indicated in Figure 5 (a) \sim (d), the ($\text{Ba}_{0.75}\text{Sr}_{0.25}$) TiO_3 ceramics with low Ho_2O_3 content do not exhibit permittivity frequency

dispersion. As shown in Figure 5 (c)~(h), the $tan\delta$ increases significantly with the increase of test frequency at low temperature; the $tan\delta$ is almost unaffected by the test frequency at high temperature, and the $tan\delta$ remains at a low

value over a wide temperature range (room temperature~150°C), indicating that Ho_2O_3 doped ($Ba_{0.75}Sr_{0.25}$) TiO_3 ceramics are promising for the application in capacitors as low dielectric loss dielectrics.





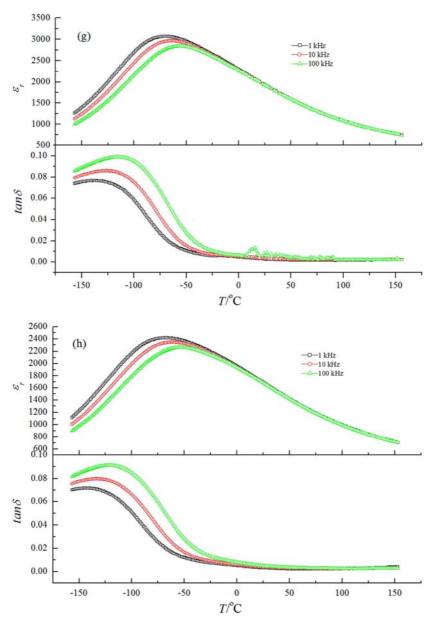


Figure 5. Temperature dependence of the relative dielectric constant and dielectric loss of Ho_2O_3 doped $(Ba_{0.75}Sr_{0.25})$ TiO_3 ceramics: (a) $Ho_2O_3=0$ wt%; (b) $Ho_2O_3=1$ wt%; (c) $Ho_2O_3=3$ wt%; (d) $Ho_2O_3=5$ wt%; (e) $Ho_2O_3=7$ wt%; (f) $Ho_2O_3=8$ wt%; (g) $Ho_2O_3=9$ wt%; (h) $Ho_2O_3=10$ wt%.

The maximum of relative dielectric constant (ε_{rmax}) and the temperature corresponding to this maximum (T_m) of (Ba_{0.75}Sr_{0.25}) TiO₃ ceramics with variation of Ho₂O₃ content are shown in Figure 6. When Ho₂O₃>1 wt%, the T_m shifts toward lower temperature and the ε_{rmax} decreases with the increase of Ho₂O₃ doping content. The local deformation caused by Ho₂O₃ doping gives rise to the reduction of T_m . On the other hand, the non-ferroelectric layer in grain boundary of ferroelectric ceramics makes the ferroelectricity decrease, which causes T_m and ε_{rmax} decrease. As mentioned previously, the average grain size of Ho₂O₃ doped (Ba_{0.75}Sr_{0.25}) TiO₃ ceramics decreases with the increase of Ho₂O₃ doping content, which means that the grain boundary effect [26] is enhanced with the increase of Ho₂O₃ doping content and consequently makes the T_m and ε_{rmax} decrease.

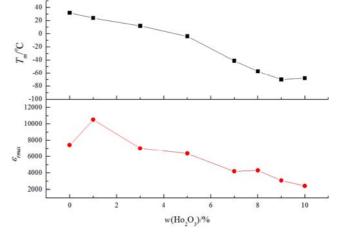


Figure 6. T_m and ε_{rmax} of Ho_2O_3 doped ($Ba_{0.75}Sr_{0.25}$) TiO_3 ceramics.

Since the diffuse phase transition is generally characterized by broadening in the dielectric constant (ε) versus temperature (T) curve, the full-width of half-maximum (FWHW) of ε_r -T curve is here calculated and listed in Table 1. It is notable that the FWHW increases from 31°C to 222.8°C when Ho₂O₃ content increases from 1wt% to 10wt%. In other words, the Curie peaks of high Ho₂O₃ concentration ceramics

are more diffused and broadened than that of low Ho_2O_3 concentration ones. Since the typical diffuse phase transition and frequency dispersion of dielectric constant occurred in the $(Ba_{0.75}Sr_{0.25})$ TiO_3 ceramics with high Ho_2O_3 content, it can be concluded that with the increase of Ho_2O_3 doping content, $(Ba_{0.75}Sr_{0.25})$ TiO_3 ceramics are transformed into a relaxor-like ferroelectrics.

Table 1. The FWHW of Ho_2O_3 doped ($Ba_{0.75}Sr_{0.25}$) TiO_3 ceramics.

W (Ho ₂ O ₃)/%	0	1	3	5	7	8	9	10
FWHW/°C	41.1	31	56.1	65.9	159	166.9	197.8	222.8

3.5. Ferroelectric Properties

Figure 7 shows the *P-E* hysteresis loops of $(Ba_{0.75}Sr_{0.25})$ TiO_3 ceramics with different Ho_2O_3 doping content measured at room temperature. The typical P-E hysteresis loops can be found for undoped and 1 wt% Ho_2O_3 doped $(Ba_{0.75}Sr_{0.25})$ TiO_3 ceramics. Especially, compared with the undoped $(Ba_{0.75}Sr_{0.25})$ TiO_3 ceramics, the ferroelectricity of the 1 wt% Ho_2O_3 doped $(Ba_{0.75}Sr_{0.25})$ TiO_3 ceramics is enhanced, which exactly explains that the ε_{rmax} of the 1 wt% Ho_2O_3 doped $(Ba_{0.75}Sr_{0.25})$ TiO_3 ceramics achieve the maximum as shown in Figure 6. With the increase of Ho_2O_3 doping content, the P-E relationships turn out to be straight lines, implying the paraelectric phase for $(Ba_{0.75}Sr_{0.25})$ TiO_3 ceramics with high Ho_2O_3 content.

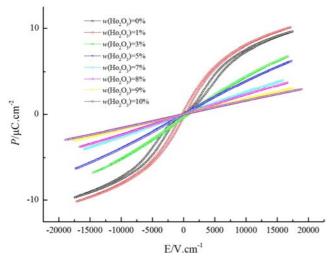


Figure 7. P-E hysteresis loops of Ho₂O₃ doped (Ba_{0.75}Sr_{0.25}) TiO₃ ceramics.

4. Conclusions

The Ho₂O₃ doped (Ba_{0.75}Sr_{0.25}) TiO₃ ceramics were prepared by solid state reaction method and their crystalline structure, surface morphology, dielectric and ferroelectric properties were investigated. The results show that:

- (1) The proper Ho₂O₃ doping content is beneficial to obtaining fine grain structure. When Ho₂O₃>8 wt%, ceramic samples are multi-phase compounds with typical perovskite structure.
- (2) Ho³⁺ ions enter the A and B site of perovskite lattice, causing lattice distortion of the system and affecting

- the relative dielectric constant and dielectric loss at room temperature. In addition, the electrons and oxygen vacancies produced in the substitution process also have a certain effect on the dielectric loss.
- (3) The diffuse phase transition and frequency dispersion of dielectric constant reveal a relaxor characteristic of high Ho₂O₃ doped (Ba_{0.75}Sr_{0.25}) TiO₃ ceramics.
- (4) According to the *P-E* hysteresis loops, the ferroelectricity is increased and then decreased with the increase of Ho₂O₃ doping content.

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