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Structure, dielectric and electrical properties of cerium doped barium zirconium titanate ceramics

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ABSTRACT

Rare-earth doped barium zirconium titanate (BZT) ceramics, $Ba(Zr_{0.25}Ti_{0.75})O_3 + xCeO_2$, ($x = 0$–1.5 at%) were obtained by a solid state reaction route. Perovskite-like single-phase compounds were confirmed from X-ray diffraction data and the lattice parameters were refined by the Rietveld method. It is found that, integrating with the lattice parameters and the distortion of crystal lattice, there is an alternation of substitution preference of cerium ions for the host cations in perovskite lattice. Morphological analysis on sintered samples by scanning electron microscopy shows that the addition of rare-earth ions affects the growth of the grain and remarkably changes the grain morphology. The effect of rare-earth addition to BZT on dielectric and electrical properties is analyzed. High values of dielectric tunability are obtained for cerium doped BZT. Especially, the experimental results on the effect of the contents of rare-earth addition on the resistivity of BZT ceramics were investigated, demonstrating that the samples with $x = 0.4$ and $x = 0.6$ could be semiconducting in air atmosphere.

1. Introduction

$BaTiO_3$-based ceramics are widely used in the manufacture of thermistors and multiplayer ceramic capacitors owing to their high dielectric permittivity. Much effort has been expended to improve the dielectric properties by way of substitution for the host cations in perovskite lattice. Various $BaTiO_3$-based solid solutions have been developed, such as $Ba(TiZr)O_3$, $[Ba(Bi_{0.5}Na_{0.5})]TiO_3$, $(BaSr)TiO_3$ [1–3]. Among these solid solutions, the $Ba(Ti_{1-y}Zr_y)O_3$ material has attracted considerable attention because Zr^{4+} is chemically more stable than Ti^{4+} [4–10]. Furthermore, it was reported that BZT ceramics showed a broad dielectric peak near T_m owing to the inhomogeneous distribution of Zr ions on Ti sites and to mechanical stress in the grain [8]. In perovskites, the relaxor behavior occurs mainly in lead-based compositions with more than one type of ion occupying the equivalent six coordinated crystallographic sites [11,12]. Lead-free compositions can be of great interest for environmentally friendly applications such as actuators and dielectrics for capacitors.

It has been well documented that small amounts of impurity ions can dramatically modify the properties of BZT ceramics in general. The influence of rare-earth dopant on the dielectric properties of barium titanate has been widely researched. There are three different opinions about the substitution of rare-earth elements in $BaTiO_3$. Song reported that Y^{3+} entered into the A site (Ba^{2+}) acted as acceptor in $BaTiO_3$ [13]. On the contrary, Jing believed that substituted for the B site (Ti^{4+}) in $BaTiO_3$ [14]. Additionally, Watanabe reported that there are mainly three stages of substitution of rare-earth elements in $BaTiO_3$, in the first two stages, doping ions replaced the original ions located in the lattice on the A or B site, respectively. In the third stage, doping ions were over limit of substitution and a secondary phase appeared [15]. Thus, many researchers have reported that better dielectric properties of $BaTiO_3$-based ferroelectric ceramics have been obtained by substitution of some rare-earth ions. On the basis of the Ti-vacancy defect compensation model, Chou et al. reported that various amounts of rare-earth ions with different ionic radii were introduced to substitute for Ba^{2+} in the $BaZr_{0.8}Ti_{0.2}O_3$ ceramics according to the composition formula $(Ba_{1-x}Ln_x)Zr_{0.2}Ti_{0.8-x/4}O_3$ (Ln = La, Sm, Eu, Dy, Y) in order to study the effects of different ionic radius rare-earth elements on the dielectric properties and relaxor behavior of barium zirconate titanate ceramics. However, to the best of our knowledge, the effect of rare-earth addition to BZT on semiconducting phenomenon has never been reported.

In this works, the $Ba(Zr_{0.25}Ti_{0.75})O_3 + xCeO_2$ ceramics ($x = 0.05$, 0.1, 0.2, 0.4, 0.6, 0.9, 1.2 at%) in an ambient atmosphere using a conventional ceramics fabrication technique. The lattice parameters were calculated using XRD analysis. The influence of cerium

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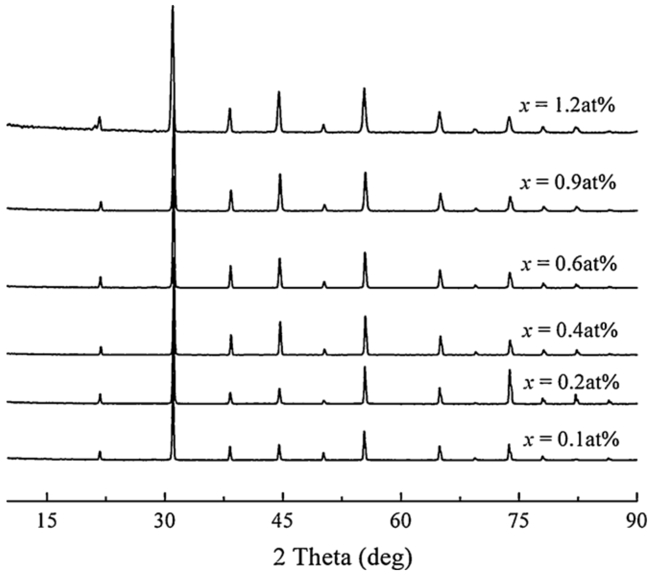

Fig. 1. XRD patterns of $Ba(Zr_{0.25}Ti_{0.75})O_3$ samples with CeO_2 doping sintered at 1290 °C for 2 h.

content on the dielectric and electrical properties of BZT ceramics was investigated.

2. Experimental procedure

$BaZr_xTi_{1-x}O_3$ ceramics has been widely investigated. In this experiment, $BaZr_{0.25}Ti_{0.75}O_3$ was chosen as the ground component. High purity (at least 99.5%) metal oxide and carbonate powder such as: ZrO_2, TiO_2, $BaCO_3$ and CeO_2 (Tianjin No. 3 chemical reagent factory), were used as the raw materials. The mixtures were milled in ethanol with nylon balls for 4 h. After drying, the mixed powder was calcined at 1050 °C for 2 h. The cerium element was added to the BZT precursor by means of CeO_2. The content of dopant was designed to be 0 to 1.2 at%. The powder was then ground by ball mill in ethanol, for a further 6 h. The dried powder was uniaxially pressed into discs at 1000 kg cm^{-2}. The samples were sintered at 1270–1320 °C for 2 h. The sintered samples were cleaned using an ultrasonic bath, then dried. Both sides of the specimens for dielectric property measurements were screened electrode paste composing mainly of Ag_2O some fluxes and binders, then fired at 530 °C for 10 min.

Table 1
Lattice parameters of $Ba(Zr_{0.25}Ti_{0.75})O_3$ samples with CeO_2 doping.

x (at%)	a (nm)	c/a
0.1	0.40620	1.00857
0.2	0.40561	1.00434
0.4	0.40508	1.00277
0.6	0.40509	1.00247
0.9	0.40607	1.00426
1.2	0.40631	1.00611

The microstructures of the well-sintered samples were observed with ESEM (Philip XL 30 ESEM). The XRD pattern was obtained with X-ray diffraction-meter (Rigaku D/Max 2500V/PL). After supersonic cleaning, fired on silver paste was used as the electrodes for purposes of measuring dielectric properties with an Automatic LCR Meter (Automatic LCR Meter 4425, Tianjin) at 1 kHz. Temperature dependences of permittivity was drawn with an automated dielectric system at 1 kHz, which consisted of the Automatic LCR Meter and a temperature-control unit.

3. Results and discussion

XRD patterns of various amounts of CeO_2 doped barium zirconium titanate ceramic samples are shown in Fig. 1. As can be known from these figures, perovskite structure is observed and no obvious secondary phase is found for all samples. The variation of lattice parameters obtained from XRD analysis is plotted in Table 1. The lattice constant (a) and the molar ratio of c/a decrease with the increase of x at the beginning ($x < 0.6$ at%), and when the content of cerium is beyond 0.6 at%, a and c/a rise with the increase of x ($x > 0.6$ at%). For the enlarged part of Fig. 1, it can be seen that the patterns are same at around $2\theta = 31.2°$ and 44.5° (see Fig. 2). The diffraction peaks (0 1 1) and (0 0 2)/(2 0 0) of samples are shifted to the higher angle side with the increase of rare-earth ionic doping concentration (see Fig. 2). All rare-earth substituted ionic radii are smaller than that of Ba^{2+} (0.161 nm) and larger than that of Zr^{4+} (0.084 nm) and Ti^{4+} (0.061 nm). These shifts demonstrate that the lattice parameter of $Ba(Zr_{0.25}Ti_{0.75})O_3 + xCeO_2$ ceramics is

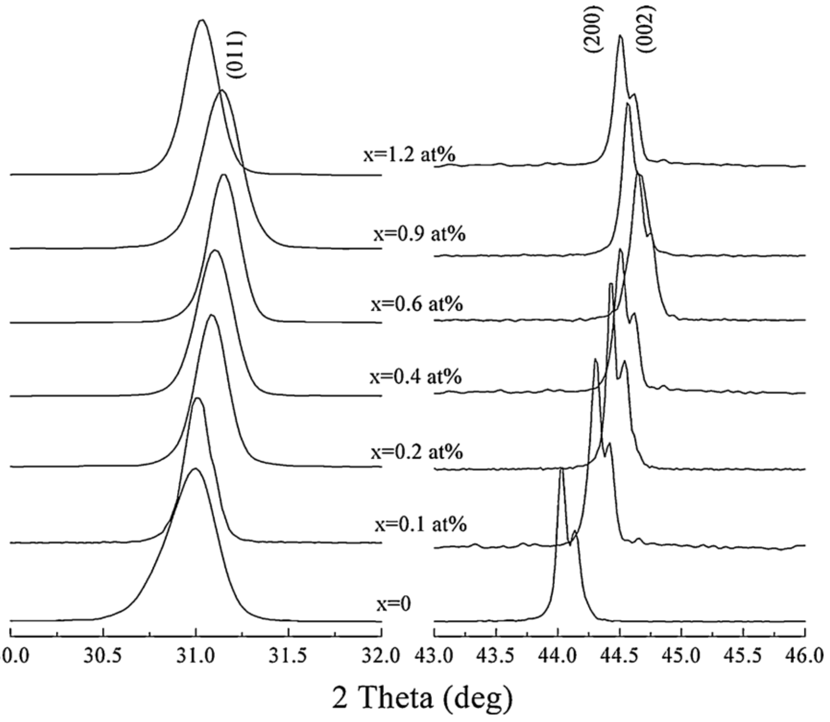

Fig. 2. XRD evolution of $Ba(Zr_{0.25}Ti_{0.75})O_3$ samples with CeO_2 doping at 2θ between 30–32° and 43–46°.

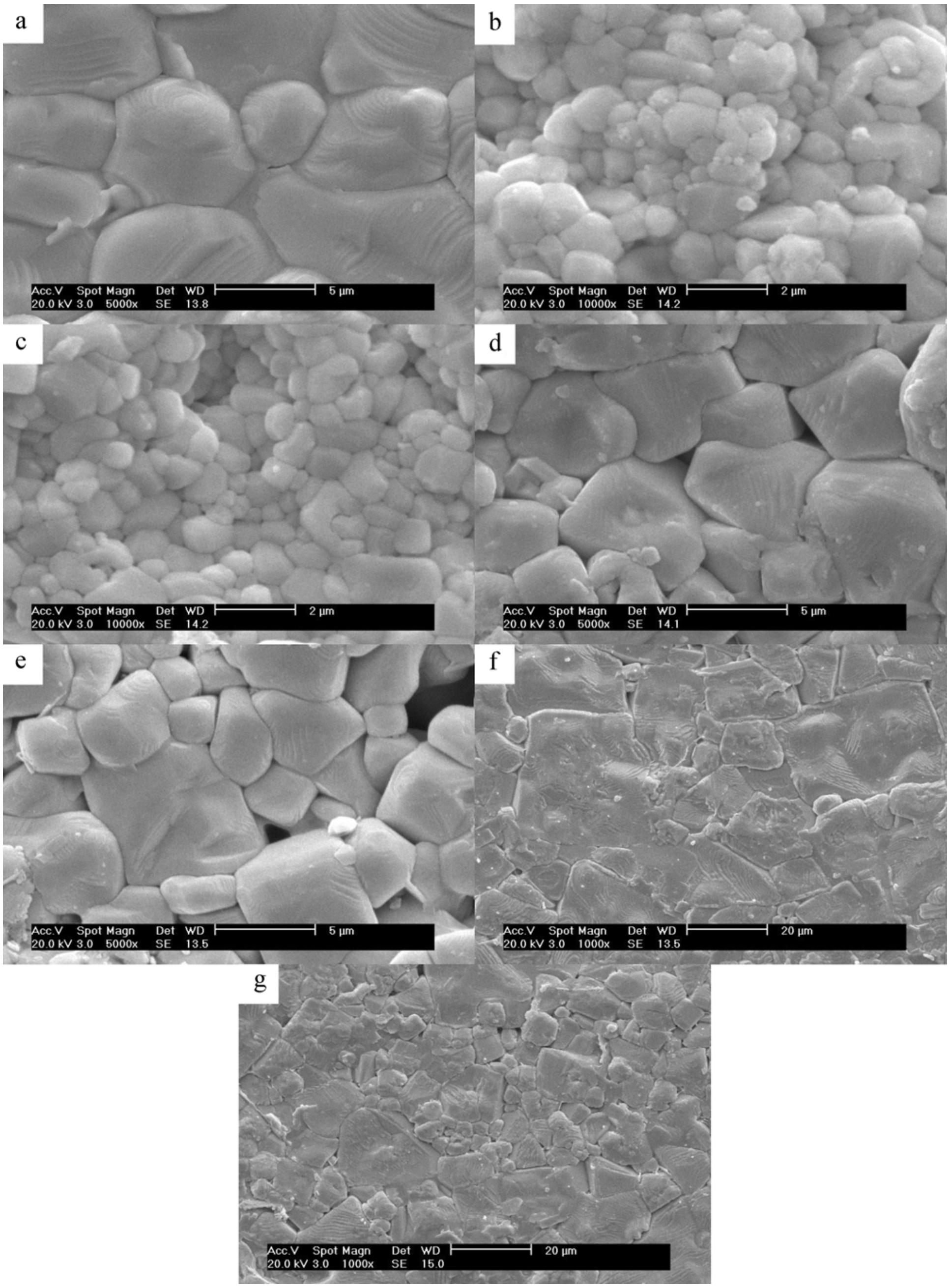

Fig. 3. SEM images of $Ba(Zr_{0.25}Ti_{0.75})O_3 + xCeO_2$ doping sintered at 1290 °C for 2 h. (a) $x = 0$ at%; (b) $x = 0.1$ at%; (c) $x = 0.2$ at%; (d) $x = 0.4$ at%; (e) $x = 0.6$ at%; (f) $x = 0.9$ at%; (g) $x = 1.2$ at%.

decreased with the increase of rare-earth ion doping content. It can be explained that all the doped rare-earth ions enter the unit cell of $Ba(Zr_{0.25}Ti_{0.75})O_3$ lattice maintaining the perovskite structure of solid solution.

Fig. 3 shows the morphologies of $Ba(Zr_{0.25}Ti_{0.75})O_3 + xCeO_2$ ceramics. The grain size of $Ba(Zr_{0.25}Ti_{0.75})O_3$ sample without cerium doping was around 5 μm, however, the grain size of the BZT samples with a trace amount of cerium (0.1 and 0.2 at%) decreased significantly to about 1 μm. Interestingly, the grain size of the BZT samples with a trace amount of cerium (0.4 and 0.6 at%) increased significantly to about 5 μm. For the samples ($x = 0.4$ and 0.6 at%), it is obvious to occur a gap among these grains and there is very different for the morphologies from ellipse-like ($x = 0.1$ and 0.2 at%) to polyhedron-like ($x = 0.4$ and 0.6 at%) structure. With increase of the content of cerium ($x = 0.9$ and 1.2 at%), the grain size increased up to 20 μm and the gap between grains with unordered structure and unhomogeneous distribution of grains has already disappeared.

The variation of dielectric properties with x in $Ba(Zr_{0.25}Ti_{0.75})O_3 + xCeO_2$ samples is plotted in Fig. 4. Compared to that of BZT sample, the dielectric constant of the BZT samples with a small amount of cerium (0.1 and 0.2 at%) is decreased from 8796 to around 2790 while there is no obvious changes for the loss tangent. With increase of x to 0.4 at%, the dielectric constant and the loss tangent reach the maximum. While both decrease greatly when x is over 0.6 at%. Thus, the trace amount of Ce^{4+} doping could affect the dielectric properties remarkably. Based on the observations, Ce doping changes not only the intrinsic dielectric constant of BZT but also the grain size of BZT as shown in Fig. 3. Even though BZT samples have the same chemical composition, the dielectric constant of BZT should be changed

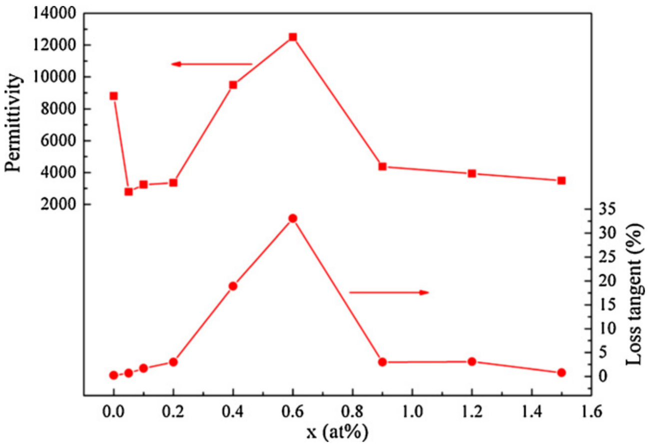

Fig. 4. Content dependence of dielectric properties at a frequency of 1 kHz for $\mathrm{Ba(Zr_{0.25}Ti_{0.75})O_3}$ samples with $\mathrm{CeO_2}$ doping.

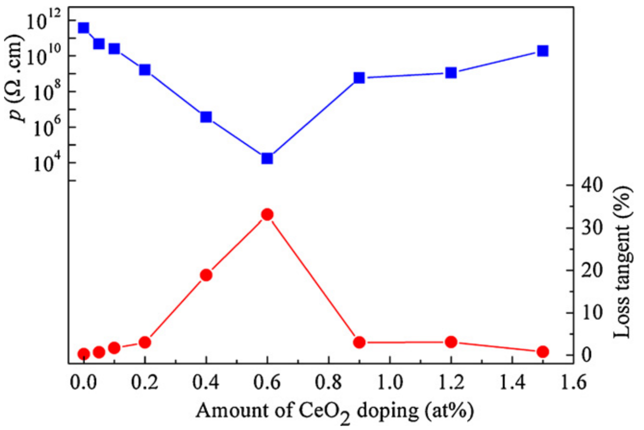

Fig. 6. $\mathrm{CeO_2}$ content dependence of resistivity and loss tangent for $\mathrm{Ba(Zr_{0.25}Ti_{0.75})O_3}$ samples with $\mathrm{CeO_2}$ doping.

with grain size. Therefore, the reasons of the dielectric constant change of $\mathrm{Ba(Zr_{0.25}Ti_{0.75})O_3} + x\mathrm{CeO_2}$ samples can be ascribed to the function of Ce concentration and the function of grain size.

The temperature dependence of the relative permittivity for $\mathrm{Ce^{4+}}$ doped BZT ceramics sintered at 1290 °C is illustrated in Fig. 5. The variation of dielectric properties of the $\mathrm{Ba(Zr_{0.25}Ti_{0.75})O_3} + x\mathrm{CeO_2}$ samples is same with the observations (see Fig. 4). However, there is a similar phenomenon that the curves become so smooth. It is hard to obtain the position of the Curie temperature under the same condition [16,17].

In order to investigate the effect of the contents of rare-earth addition on the resistivity of BZT ceramics, the resistivities were presented in Fig. 6. With increase of x to 0.4 and 0.6 at%, the resistivities significantly deceased. Especially, the sample ($x = 0.6$ at%) reached the minimum. These samples could be semiconducting in air atmosphere. It has been reported that aliovalent cations incorporated in perovskite lattice served as donors or acceptors, which could affect the electrical characteristics greatly, even though the solubility remained at trace level [18]. Watanabe reported that there were mainly three stages of substitution of rare-earth elements in $\mathrm{BaTiO_3}$. In the first two stages, doping ions replaced the original ions located in the lattice on the A or B site, respectively. The third stage was over limit of substitution and a secondary phase appeared [15]. In this work, $\mathrm{CeO_2}$ maybe shows the double effects. The mechanism for the effect of $\mathrm{CeO_2}$ is very complicate. Ce ion possibly exists in the BZT structure in two valence states: $\mathrm{Ce^{4+}}$ in radius of 0.094 nm and $\mathrm{Ce^{3+}}$ in radius of 0.118 nm. The result, hence, may concern with their simultaneous effect as its effect on $\mathrm{Pb(Zr,Ti)O_3}$ ceramics [19]. In view of the radius, it is obvious that there are two cases for cerium ions occupy into A or B site of BZT. One is that $\mathrm{Ce^{3+}}$ goes to $\mathrm{Ba^{2+}}$ site in BZT when the concentration of rare-earth addition is relatively low ($x < 0.6$ at%). $\mathrm{Ba^{2+}}$ ions are replaced by $\mathrm{Ce^{3+}}$ ions in the this stage, which has a smaller ionic radius, and consequently, lattice constant (a) decreases while the replacement of $\mathrm{Ba^{2+}}$ by $\mathrm{Ce^{3+}}$ almost does not cause the deformation in BZT lattice to make an evident contribution to enhance the domain movement. Maybe, the reaction happened below:

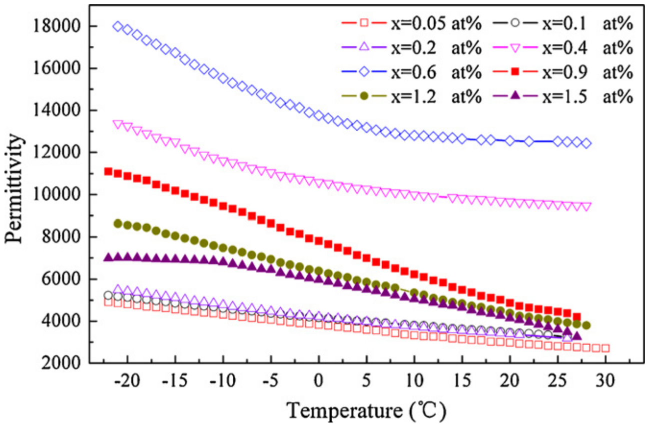

Fig. 5. Temperature dependence of permittivity at a frequency of 1 kHz for $\mathrm{Ba(Zr_{0.25}Ti_{0.75})O_3}$ samples with $\mathrm{CeO_2}$ doping.

$$\mathrm{BaMO_3} + x\mathrm{Ce}^{3+} \rightarrow \mathrm{Ba}^{2+}_{1-x}\mathrm{Ce}^{3+}_{x}(\mathrm{M}^{4+}_{1-x}(\mathrm{M}^{3+})_{x})\mathrm{O}_3^{2-} + x\mathrm{Ba}^{2+} \qquad (1)$$

Moreover, aliovalent substitutions cause a distortion of lattice, as shown in Fig. 2. Thus, $\mathrm{Ce^{3+}}$ functions as a donor leading to some vacancies of A site in the lattice, which facilitates the movement of domain wall so as to improve the dielectric properties significantly. In contrast with $\mathrm{Ce^{3+}}$, $\mathrm{Ce^{4+}}$ has smaller radius and may occupy the $\mathrm{Ti^{4+}}$ site when the concentration of rare-earth addition is relatively low ($x > 0.6$ at%). The occupation of $\mathrm{Ce^{4+}}$ in $\mathrm{Ti^{4+}}$ site may change the space charges to suppress the domain movement, resulting in a decrease in the dissipation factor. Maybe, the reaction happened below.

$$\mathrm{BaMO_3} + x\mathrm{Ce}^{3+} \rightarrow \mathrm{Ba}^{2+}_{1-(1/2)x}\mathrm{Ce}^{3+}_{(1/2)x}(\mathrm{M}^{4+}_{1-(1/2)x}\mathrm{Ce}^{3+}_{(1/2)x})\mathrm{O}_3^{2-} + \frac{1}{2}x\mathrm{Ba}^{2+} + \frac{1}{2}x\mathrm{M}^{4+} \qquad (2)$$

The experimental results on the effect of the contents of rare-earth addition on the resistivity of BZT ceramics demonstrated that the samples with $x = 0.4$ and $x = 0.6$ could be semiconducting in air atmosphere. The mechanism of this abnormal phenomenon is proposed. The samples with high dielectric constant and loss tangent could be semiconducting, which may result from the formation of the insulated boundary layer among the grains of the $\mathrm{Ba(Zr_{0.25}Ti_{0.75})O_3} + x\mathrm{CeO_2}$ samples. Therefore, the reason of the semiconducting phenomenon is the charge and diacharge of the samples with high dielectric constant under AC field rather than the increase number of carrier.

4. Conclusions

Rare-earth doped barium zirconium titanate (BZT) ceramics, $\mathrm{Ba(Zr_{0.25}Ti_{0.75})O_3} + x\mathrm{CeO_2}$ ($x = 0$–1.5 at%) were obtained by a solid state reaction route. Perovskite-like single-phase compounds were confirmed from X-ray diffraction data and the lattice parameters were refined by the Rietveld method. It is found that, integrating with the lattice parameters and the distortion of crystal lattice, there is an alternation of substitution preference of Ce^{3+} ion for the host cations in perovskite lattice. Morphological analysis on sintered samples by scanning electron microscopy shows that the addition of rare-earth ions affects the growth of the grain and remarkably changes the grain morphology. The effect of rare-earth addition to BZT on dielectric and electrical properties is analyzed. High values of dielectric tunability are obtained for cerium doped BZT. Especially, the experimental results on the effect of the contents of rare-earth addition on the resistivity of BZT ceramics were investigated, demonstrating that the samples with $x = 0.4$ and $x = 0.6$ could be semiconducting in air atmosphere.

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