Effect of Y_2O_3Doping on the Structure and Piezoelectric Properties of BCZT Ceramics

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Abstract. The $[50(Ba_{0.7}Ca_{0.3})TiO_3]-50[Ba(Zr_{0.2}Ti_{0.8})O_3]$ + *x*mol% Y_2O_3 lead-free ceramics(*x*=0,0.2,0.4,0.6,0.8 and 1.0) were fabricated successfully by the traditional solid-state reaction. And the microstructures, phase structure, ferroelectric and piezoelectric properties were investigated for the Y_2O_3-modified $[50(Ba_{0.7}Ca_{0.3})TiO_3]-50[Ba(Zr_{0.2}Ti_{0.8})O_3]$ lead-free piezoelectric ceramics. The appropriate dopant could reduce the pores in the specimens and enhance the ferroelectric properties. The optimal piezoelectric properties $d^*_{33}$of the lead free ceramic is 494pm/V.And the 50BCT-50BZT ceramics with 0.4mol% Y_2O_3possess the optimal ferroelectric properties,Pr=6.38μC/cm^2.

Introduction

Ferroelectric and piezoelectric materials are widely used in various devices such as sensors, actuators and memories.PZT is the dominant ferroelectric and piezoelectric materials. However, its toxicity can't be ignored during applying and casting aside. In recent years, the innovative environment friendly materials have attracted increasing attention for the substitution of Pb-based ceramics. There are several lead free ferroelectric materials, such as BT based ceramics, NBT and KNN based ceramics[1-4].

Since 2009, the lead-free [Ba(Zr0.2Ti0.8)O3]-x[(Ba0.7Ca0.3)TiO3] piezoelectric ceramic, BCZT, were designed by Ren and Liu, whichhas been attracted increasing attentions for its excellent piezoelectric property at morphotropic phase boundary MPB[5]. The maximum of piezoelectric coefficient reaches 620pC/N, which is regarded as the promising substitution of Pb-ceramic. Thus,there are a series of studies on BCT-BZT lead-free piezoceramics were published[8,14-16]. For instance, Ma et al. have prepared Sb2O3 modified (Ba0.85Ca0.15)(Ti0.9Zr0.1)O3 lead-free piezoelectric ceramics by conventional sintering and enhanced electric properties ofd33~556 pC/N,kp~52%, and Ɛr~3,895 was obtained for the BCZT-xSb ceramic with x=0.1%[6].Jiang et al. fabricated the Ba0.85Ca0.15Ti0.90Zr0.10O3+xmol% MnO2 lead-free ceramics by a conventional sintering method[7]. The 0.25 mol% MnO2addition promoted grain growth and improved the ferroelectricity of the ceramics. The ceramic specimens with x=0.25 exhibited the optimal piezoelectric properties (d*33=306pC/N andkp=42.2%,respectively).

In this work, Y element was added into BCZT lead-free piezoelectric ceramic to improve the ferroelectric and piezoelectric properties. And the effectsY2O3on the structure, piezoelectric and dielectric properties are investigated.

Experimental Procedure

50BCT-50BZT ceramic with xmol%Y2O3 (x=0.0,0.2,0.4,0.6,0.8and1.0)were prepared by traditional solid-state reaction. BaCO3(99 %, Sinopharm Chemical Reagent Co., Ltd,China), CaCO3(99 %, Sinopharm Chemical Reagent Co.,Ltd, China), TiO2(98 %, Sinopharm Chemical Reagent Co., Ltd, China), ZrO2(99 %, Sinopharm Chemical Reagent Co., Ltd, China), and Y2O3(99.99 %, Sinopharm Chemical Reagent Co., Ltd, China) were used as the raw materials. The

weighted powders of BCZT doped with x mol% Y2O3 were ball-mixed in ethanol for 24h and dried at 80°C.The obtained powders were calcined at 1200°C for 4h. The calcined powders were remixed by ball milling for 10h and then were dried. Then the obtain powders mixed with 8% PVA uniformly and were pressed into disks with 13 mm diameter and 1 mm thickness. The disks were sintered at 1400°C for 4h in air staying at 550°C for 2h to burn off PVA. The silver was coated on the sintered ceramic specimens as electrodes on the both side.

The structure of sintered ceramic specimens was studied by an X-ray Diffraction meter(XRD, Bruker D8A25, Germany) with Cu Kα radiation. The microstructure of 50BCT-50BZT ceramic doped Y2O3 was examined by scanning electron microscopy (Quanta 200FEG, FEI, America). The dielectric performance of the ceramic specimens was investigated by using a precise impedance analyzer (4294A,Agilent, America). The piezoelectric response of the specimens was evaluated using a piezoelectric force microscope with a lock-in-amplifier at room temperature.

Results and Discussion

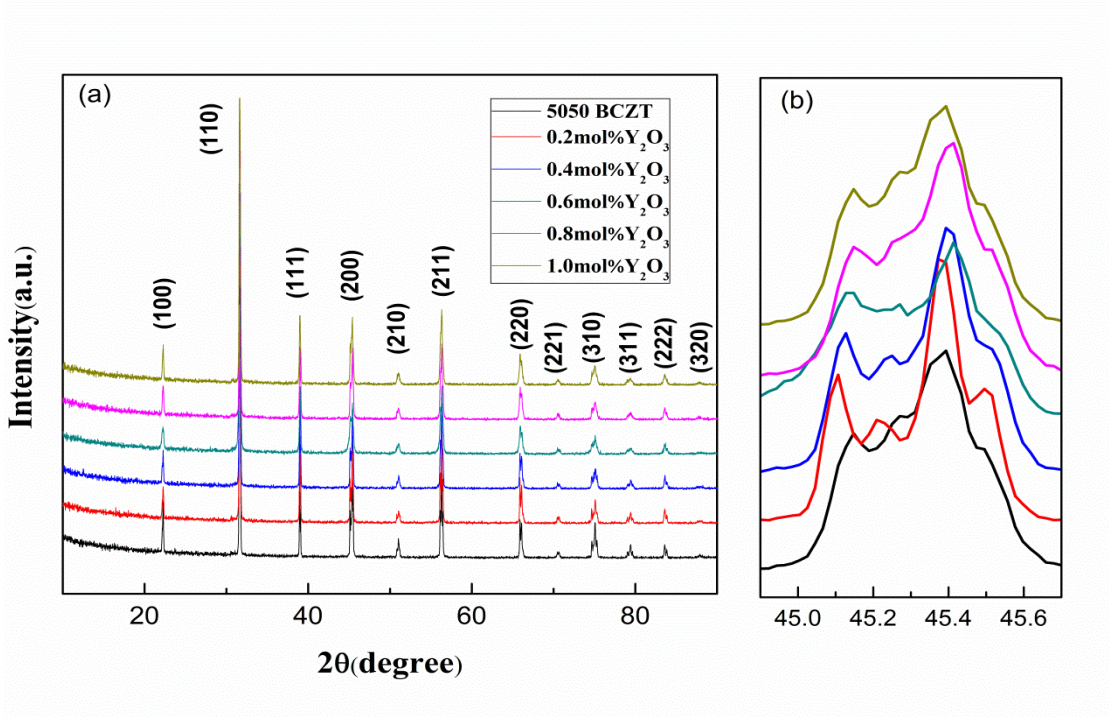

Figure 1. X-ray diffraction (XRD) patterns of 50BCT-50BZT-*x*mol% Y_2O_3 ceramics

XRD pattern of the BCZT-*x*mol%Y_2O_3 ceramic specimenswas shown in Figure 1.(a) sintered at 1400 °C for 4 h. The XRD pattern illustrates that the ceramic specimens exhibit pure perovikite phase and no other second phase, as shown in Figure 1.(a). It means that the Ca^{2+}ion and Zr^{4+} ion are distributed homogeneously in the $BaTiO_3$ crystal to form a solid solution. And the doping of Y_2O_3 doesn't influence the crystal structure of BCZT ceramic.

According to the tolerance factor[9], the doping ions, of which the ionic radius is smaller than 0.087nm, will occupy B site. The large ions (r(RVI3+)≥0.094nm) will occupy A site. The intermediate ions could occupy the A site or B site. Because the ionic radius of Ba2+(0.135nm) and Ca2+(0.1nm) are both larger than that of Y3+(0.09nm), the lattice constants decrease when the Y3+ as donor dopant occupies A site, leading to the position of the X-ray diffraction peak moving to the high angles. Similarly, the ionic radii of Ti4+ and Zr4+are respectively 0.0605nm and 0.072nm and the lattice constants increase when the Y3+ as acceptor dopant occupies B site, leading to the position of the X-ray diffraction peak moving to the low angles. It matches the appearance from

Figure 1.(b). It can be observed that the X-ray diffraction peak moves to low angles and then high angles with Y3+ dopant increasing in Figure 1.(b)[10-13].

It can be seen that fracture occurs in the grain interior, without obvious dissociation surface in Figure 2. The quantities of the pores in theceramics decrease, and thenthey increase with doping. As shown in Figure 3,the temperature dependent dielectric permittivity diagram (Ɛ-T) of the BCZT-xmol%Y2O3 ceramic specimens from -65°C to 200°C at 1kHz. For x=0.0, x=0.2 and x=0.4, the Ɛ max peaks of the specimens are slim and deep and reach the maximum at 100°C, 100°C and 96°C , respectively. For the specimens of x=0.0 and x=0.2, there is an obvious peak near the room temperature. But, for the specimens of the other components, the peaks have been broadened because of the diffuse phase transition(DPT). It illustrates that the dielectric performance of the ceramic specimens increases with the Y3+ ion increasing. Similarly, the Ɛ max peaks(TC) become broadened and move shifts to the low temperature with Y3+ion increasing.

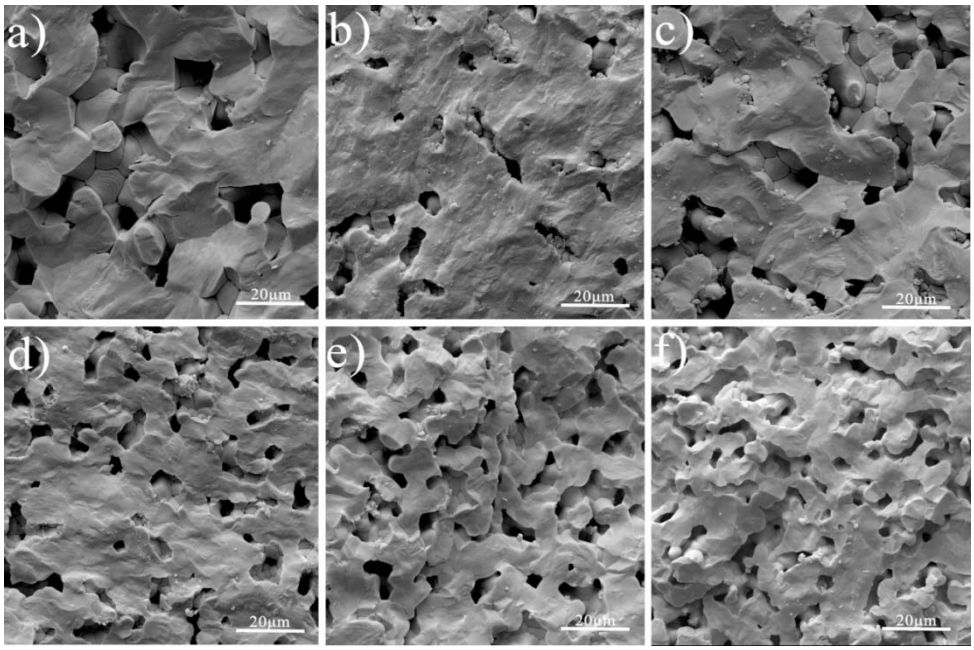

Figure 2.The SEM images of the cross section for BCZT-*x* mol% Y_2O_3 ceramic specimens: a:*x*=0.0,b: *x*=0.2,c:*x*=0.4, d: *x*=0.6, e: *x*=0.8, f: *x*=1.0.

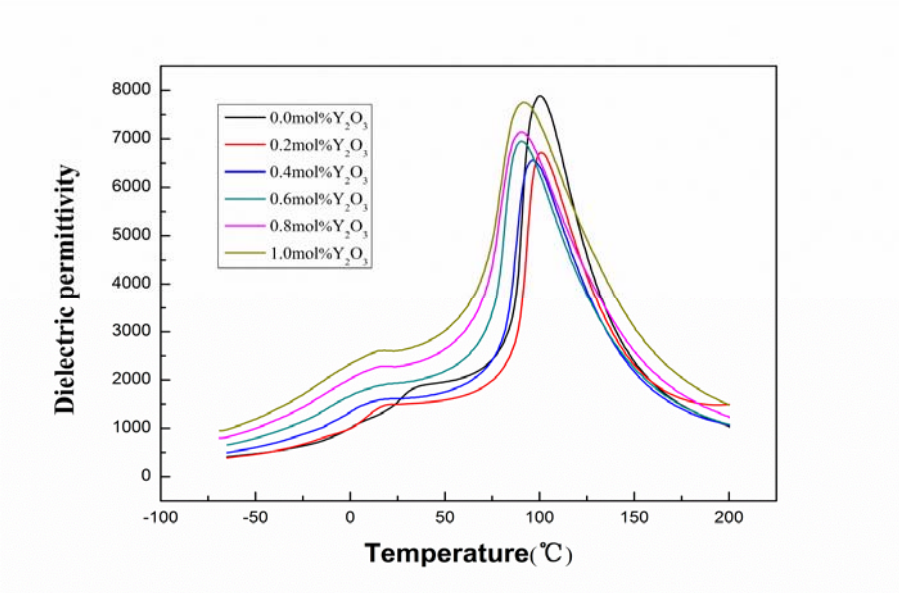

Figure 3. Temperature dependence of dielectric permittivity for the BCZT-*x*mol% Y_2O_3 ceramic specimens measured at 1kHz.

The hysteresis loops of BCZT ceramic specimens doping of various *x*mol%Y_2O_3were measured under 25 kV/cm and 10 Hz, which were shown in Figure 4. All ceramic specimens exhibit a typical P–E loop.The remain polarizationP_r increases and then decreases with doping,the maximum value is 6.38μc/cm^2 at x=0.4. The values of remain polarization P_r and coercive field for all ceramic specimens were shown in Table 1 and Figure 5.

Table 1. Related parameters of 50BCT-50BZT-*x*mol% Y_2O_3 ceramics

*x*mol%	0	0.2	0.4	0.6	0.8	1.0
T_m(°C)	100	100	96	90	90	90
P_r(μC/cm^2)	4.65	5.51	6.38	5.74	5.09	4.98
E_c(kV/cm)	3.52	4.87	4.65	4.17	4.57	4.58
d_{33}^*(pm/V)	437	494	459	408	375	367

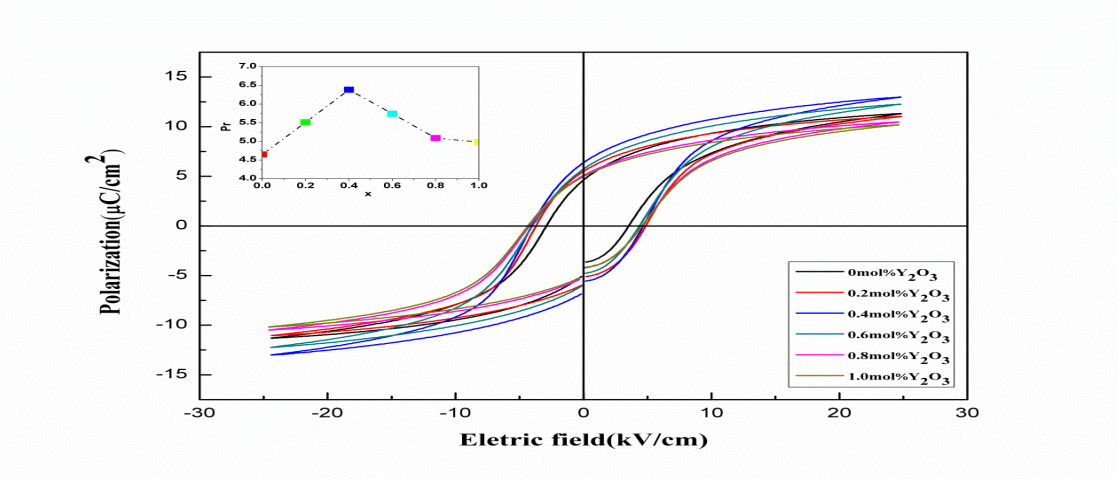

Figure 4.Temperature dependent of dielectric permittivity for 50BCT-50BZT-*x*mol% Y_2O_3 ceramics measured at 1kHz,10kHz and 100kHz.

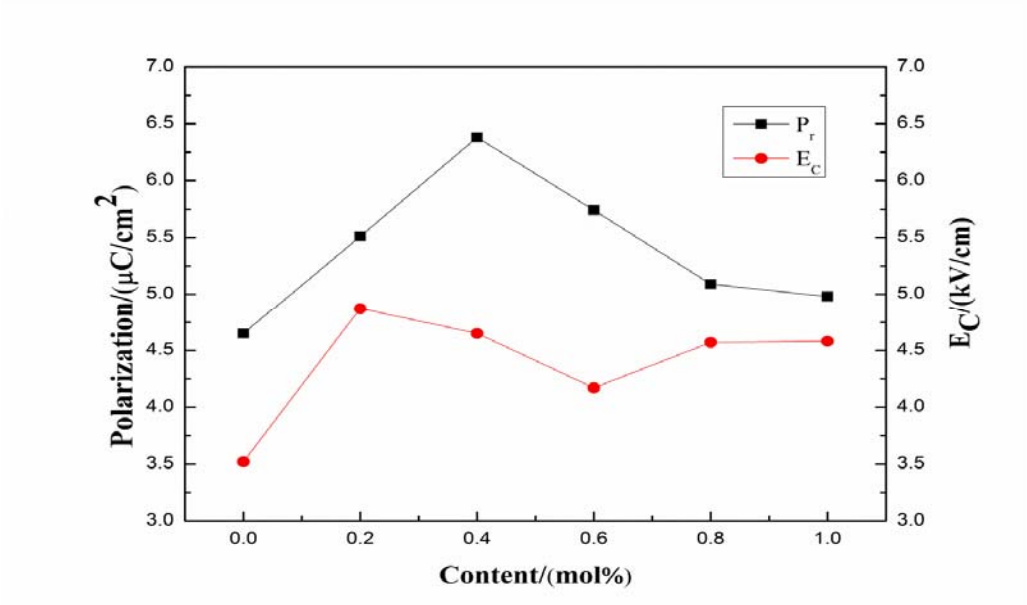

Figure 5. Remain polarization value and Coercive field of 50BCT-50BZT-*x*mol% Y_2O_3 ceramics.

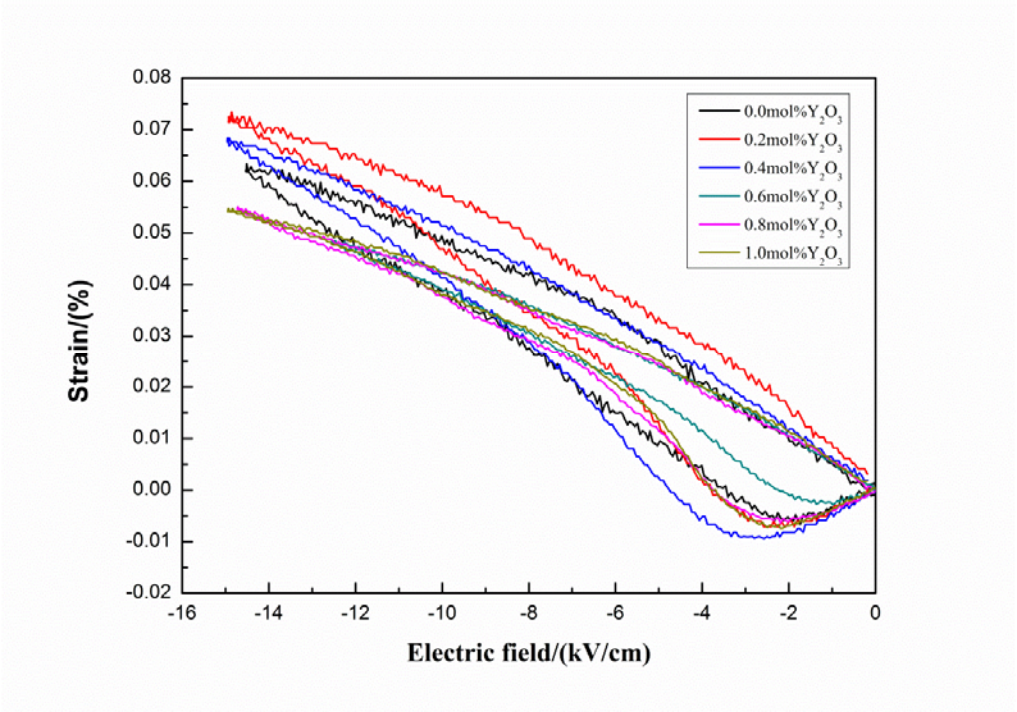

Figure 6.Piezoelectric graph of 50BCT-50BZT-*x*mol%Y_2O_3ceramic.

It can be seen inFigure 6 that the ceramic specimens of all amounts exhibit the characteristic "butterfly" shape measured at 15 kV/cm and room temperature. The $d^*_{33}$of ceramic specimens for *x*=0, *x*=0.2,*x*=0.4,*x*=0.6,*x*=0.8 and *x*=1.0is 437pm/V, 494pm/V, 459pm/V, 408pm/V, 375pm/V and 367pm/V, respectively. And the d^*_{33} reaches the maximum value 494pm/V for *x*=0.2, which means that Y_2O_3 doped could improve the piezoelectric performance of BCZT ceramics.

Conclusions

The [50(Ba0.7Ca0.3)TiO3]-50[Ba(Zr0.2Ti0.8)O3] + xmol% Y2O3 lead-free ceramics(x=0, x=0.2,x=0.4,x=0.6,x=0.8 and x=1.0) were fabricated successfully by a traditional solid-state reaction. It is illustrated that the specimens exhibit pure perovikite phase and no other second phase. The Y3+ dopant is dissolved into the crystal lattice and forms a stable solid solution. And the introduction of Y3+ icon is effective for the ferroelectric performance. For the ceramic with 0.4mol% Y2O3 doping, the ferroelectric properties becomes the optimum, withPr=6.38μC/cm2. And the d*33was enhanced to 494pm/V for the ceramic with 0.2mol% Y2O3 doping.

Acknowledgements

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