Low Sintering Temperature and High Piezoelectric Properties of Tb-doped ($Ba_{0.859}$ $Ca_{0.141}$) ($Zr_{0.106}$ $Ti_{0.894}$) O_3 Using $CaCl_2$ as Sintering Aid

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Abstract. Using $CaCl_2$ as sintering aid, the Tb-doped ($Ba_{0.859}$ $Ca_{0.141}$) ($Zr_{0.106}$ $Ti_{0.894}$) O_3 (BCZT) ceramics were fabricated by conventional solid-state reaction method. The sintering temperature of ceramics decreases from about 1450 ℃ down to about 1300 ℃. The SEM micrographs show that all ceramics sintered above 1300 ℃ are very dense and have clear grain boundaries. A piezoelectric coefficient of d_{33} 659 pm/V was obtained at 0.3 mol.% Tb-doped ($Ba_{0.859}$ $Ca_{0.141}$) ($Zr_{0.106}$ $Ti_{0.894}$) O_3 with $CaCl_2$ sintered at 1350 ℃ and residual polarization of that can reach 11.70 μC/cm^2. The results indicated that the excellent piezoelectric property could be a promising candidate for electronic industry purposes.

Introduction

$Pb(Zr_{1-x}Ti_x)O_3$ (PZT) ceramics with excellent piezoelectric properties are widely used in electronic industry for more than five decades [1,2]. However, the environmental concerns urgently require lead-free ceramics to substitute the PZT due to its Pb toxicity. In recent years, through the doping in A-site and B-site to improve the performance of ABO_3 structure lead-free ceramics, calcium barium zirconate titanate (BCZT) ferroelectric ceramics were considered as the most promising electro-ceramic materials. It has excellent electrical properties and high tenability [3-5]. At the proximity of the morphortropic phase boundary (MPB), high piezoelectric performance of the BCZT will be obtained and there is the multi-phase coexistence in BCZT. In this paper, the composition $47(Ba_{0.7}Ca_{0.3})TiO_3$-$0.53Ba$ $(Zr_{0.2}Ti_{0.8})O_3$ is near MPB at room temperature according to phase diagram [6]. And the rare earth elements are frequently employed in ceramics to obtain excellent electrical properties, such as Pr, Yd and Er [7-8]. In addition, the $CaCl_2$ as a sintering aid can decrease the sintering temperature without sacrificing the electric properties of $BaTiO_3$ lead-free ceramics, because its melting point is about 780 ℃, which below the sintering temperature of BCZT (about 1450 ℃). Meanwhile, there are no new impurities ions are introduced in it.

For this purpose, the high-piezoelectric coefficient BCZT as a host and the rare earth element Tb as an activator were used in this study to synthetize a multifunctional material. And using the CaCl2 as sintering aid to reduce the sintering temperature and form very dense ceramics.

Experiments

The 47(Ba0.7Ca0.3)TiO3-53(BaZr0.2Ti0.8)O3+ x mol % Tb ceramics (x=0, 0.2 ,0.3, 0.5) were prepared by the conventional solid-state reaction technique. To prepare BCTZ source powders, analytical-grade metal oxides or carbonate powders of BaCO3 (99.8%), TiO2 (99.48%), CaCO3 (99.5%) and ZrO2 (99.84%) were weighed according to the stoichiometric ratio and mixed by a ball grinder with a moderate number of zirconia balls and alcohol for 24 h. And the mixed powders were calcined at 1200 ℃ for 2 h. Then, the Tb4O7 (99.99%) according to different concentration was doped in calcined powders with remilled with appropriate polyvinyl alcohol (PVA) as the binder.

After that, the remixed powders were pressed into disks with 10 mm diameter and 1 mm thickness under 10 Mpa. The green pellets with different compositions were then sintered at 1450 ℃ for 4 h in air with 5 ℃/min heating rate. Finally, both the circular surfaces of part ceramics were polished and coated with silver as electrodes for dielectric properties testing. Moreover, the CaCl2 as sintering aid was added in optimal piezoelectric property BCZT which the x=0.3 before remilled source powders. And rests of the steps are repeated as above step before sintered. Subsequently, the pellets were sintered at 1300, 1350 and 1400 ℃ for 2 h in the air atmosphere.

The crystal structure was examined by using an X-ray diffraction (XRD, X'pert, Philips, Holland) using CuKα (λ=1.5406 Å) radiation and the optical micrograph (OLYMPUS BX51) was employed to identify the microstructure of the materials. The electric-field-induced polarization (P–E) and strain (S–E) measurements were carried out using an Radiant Multiferroic ferroelectric tester produced in the United States (Radiant Multiferroic, USA). Then the piezoelectric coefficient (d33) could be calculated from S-E spectrum.

Results and Discussion

X-ray Diffraction Patterns

Figure 1 shows the X-ray diffraction patters of 0.3 mol % Tb-doped BCZT used 0.2 mol % $CaCl_2$ as sintering aid in different sintering temperature. The XRD pattern of BCZT shows sharp crystalline peaks at about 22 ° (100), 32° (110), 39° (111), 45° (200), 56° (211) and 65° (220), which indicates the BCZT possess the perovskite structure according to the crystallographic indexing [9, 10]. Even at 1300 ℃ sintering temperature, there is no second impurity phase in the solid solutions.

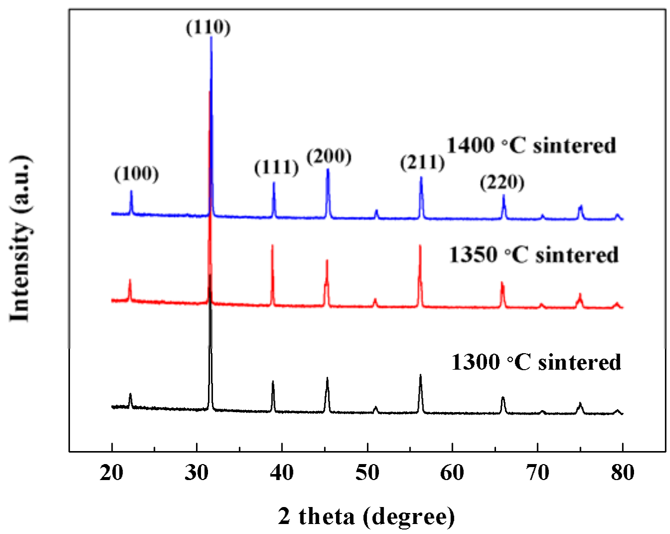


Figure 1. XRD patterns of BCZT/PVDF composite films with different sintering temperature

Surface Morphology

Figure 2 (a)-(c) show the SEM micrographs of the 0.3 mol % Tb doped BCTZ used 0.2 mol % $CaCl_2$ as sintering aid sintered at different temperature. The ceramics can be well sintered at a relatively low temperature range. All ceramics sintered above 1300 ℃ are very dense and have clear grain boundaries. Figure 2 (d) shows the 1450 ℃ sintered BCTZ without sintering aid. As can be seen in Figure, though the grain growth is well, the gap between grain boundaries is obvious. And there is liquid phase in Figure 2 (a)-(c), which can fill in the gap. Because $CaCl_2$ has a low melting point which is about 780 ℃ and it can form a liquid phase to lower the sintering temperature and make more dense ceramics.

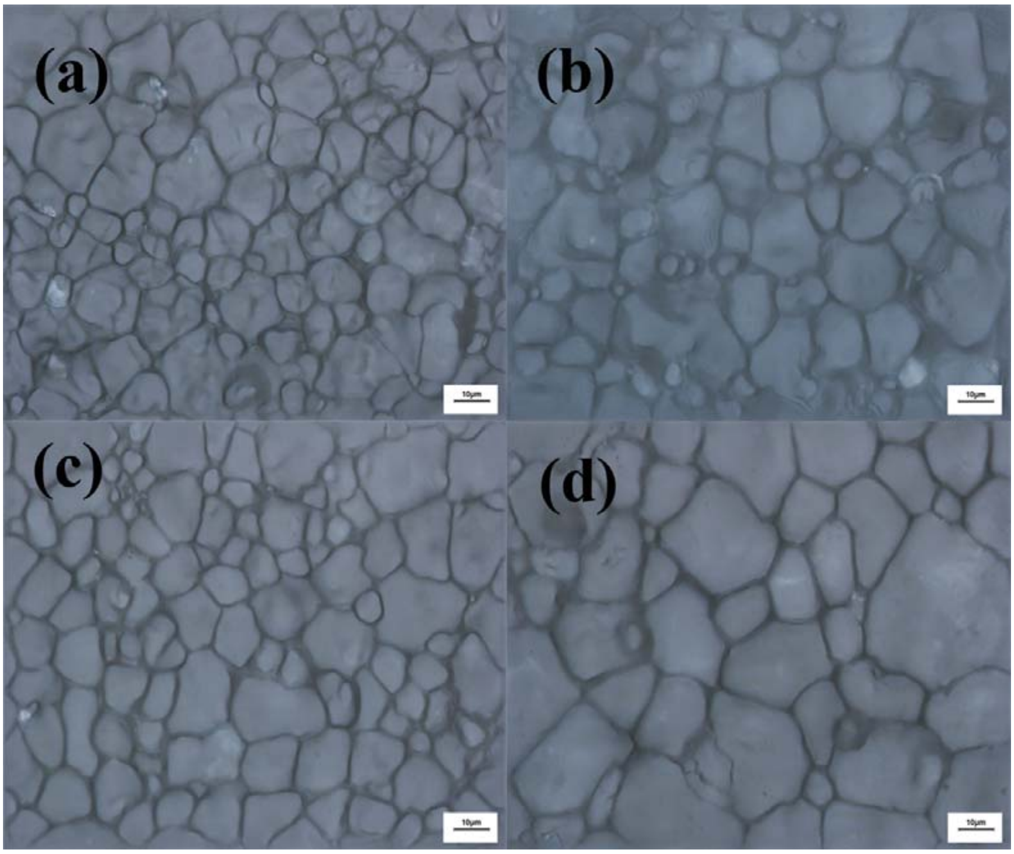
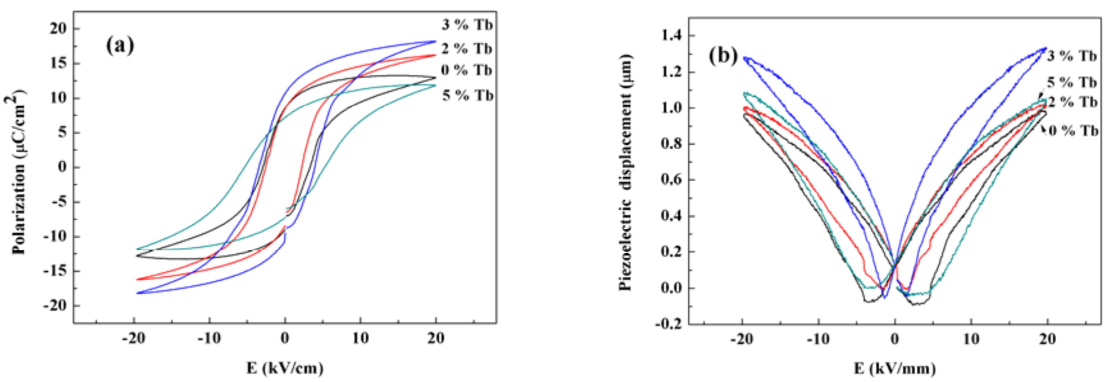


Figure 2. Surface morphologies of $CaCl_2$ as sintering aid (a) 1300 ℃ sintered Tb doped BCTZ (b) 1350 ℃ sintered Tb doped BCTZ (c) 1400 ℃ sintered Tb doped BCTZ and (d) 1450 ℃ sintered BCTZ without sintering aid

Ferroelectric and Piezoelectric Properties

Figure 3 (a)-(d) shows ferroelectric hysteresis loops (P-E loops) and electric field-induced strain (S-E loops) of ceramics measured at room temperature. All samples have well-saturated *P–E* hysteresis loops. And the piezoelectric coefficient was calculated base on S-E loops. As shown in Figure, with the Tb doped in BCZT, the P_r and d_{33} are gradually increased to S-E loops 10.49 μC/cm^2 and 627 pm/V before 0.3 mol % Tb-doped BCZT and then degrades with increasing Tb content at 1450 ℃. And $CaCl_2$ as sintering aid was doped in the optimal 0.3 mol % Tb BCZT. As can be seen in Table, the P_r and d_{33} of ceramics reaches the maximum value of 11.70 μC/cm^2, 659 pm/V at 1350 ℃, respectively. The $CaCl_2$ sintering aid not only improves the piezoelectric property of ceramics, but also reduced sintering temperature.



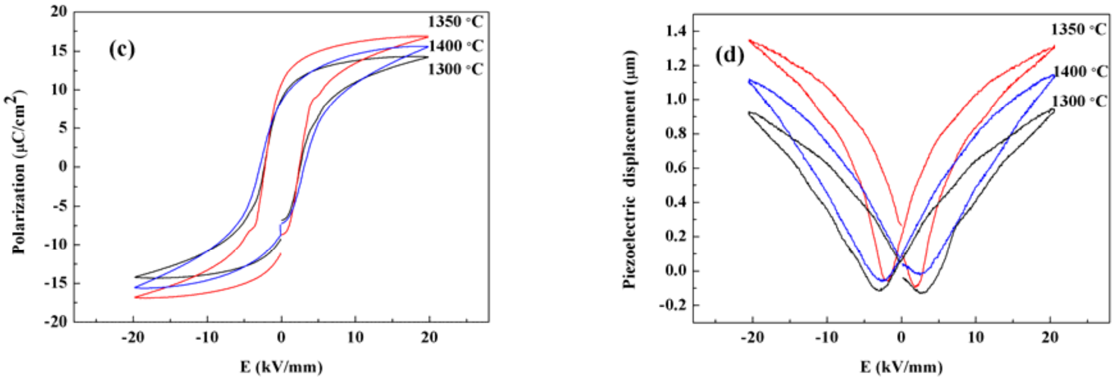


Figure 3. (a) P-E loops of Tb-doped BCZT ceramics,(b) S-E loops of Tb-doped BCZT ceramics,(c) P-E loops of 0.3 mol % Tb-doped BCZT ceramic with $CaCl_2$ sintering aid sintered at different temperature,(d) S-E loops of 0.3 mol % Tb-doped BCZT ceramic with $CaCl_2$ sintering aid sintered at different temperature

On the one hand, the melting point of $CaCl_2$ is about 780 ℃ and existence of liquid phase will make the ceramics with high density to high piezoelectric response in BCZT. Base on the ceramics sintering theory, the doping elements or sintering aids are usually located in the surfaces of grains at the initial state, and then continuously diffuse into the lattice of grain as the sintering temperature increases. That can result in the grain growth and make ceramics become more density [11, 12]. On the other hand, it may be related to the oxygen vacancies in BCZT. In this case, the Tb ions may be mainly confirmed to occupy the B-site of BCZT with the valence of +3, +4 to form a solid solution. It results in lattice deformation because of the formation of oxygen vacancies for charge compensation and combines with the oxygen vacancies to form the defect dipole which may enhance electric properties of BCZT ceramics [13-14].

Conclusions

The structure and electrical properties of BCZT lead-free piezoelectric ceramics prepared at different concentration Tb doped (0.2, 0.3 and 0.5 mol. %) and sintering temperatures (1300, 1350 and 1400 ℃) used $CaCl_2$ as sintering aid have been studied. The SEM micrographs show that after used $CaCl_2$ as sintering aid, there is liquid phase in BCZT above 1300 ℃sintering. And the 0.3 mol. % Tb-doped BCZT ceramics with $CaCl_2$ as sintering aid sintered at 1350 ℃ exhibit optimum properties, P_r and d_{33} are11.70 μC/cm^2 and 659 pm/V,which is better than that of BCZT sintered at 1450 ℃ (8.56 μC/cm^2 and 491 pm/V). The enhanced piezoelectric property and lower sintering temperature are obtained by doping Tb and $CaCl_2$ as sintering aid, which may be a potential applications in industry.

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