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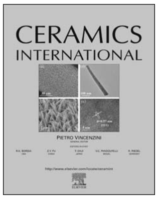

Multiphase coexistence and enhanced electrical properties in (1-x-y) $BaTiO_3$-$x$$CaTiO_3$-$y$$BaZrO_3$ lead-free ceramics

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ABSTRACT

In this work, the multiphase coexistence of rhombohedral-orthorhombic and orthorhombic-tetragonal (R-O/O-T) was constructed in (1-x-y)$BaTiO_3$-$x$$CaTiO_3$-$y$$BaZrO_3$ ceramics with $0.14 \le x \le 0.16$ and $0.10 \le y \le 0.12$, and thus a large piezoelectric constant (d_{33}) of 600 pC/N was attained in the ternary (1-x-y)$BaTiO_3$-$x$$CaTiO_3$-$y$$BaZrO_3$ ceramics using the optimization of x and y. The R-O/O-T multiphase coexistence as well as the enhancement of dielectric and ferroelectric properties can be responsible for the high d_{33} of this work. In addition, a high strain of 0.15% was observed in the multiphase coexistence. As a result, electrical properties of $BaTiO_3$ can be optimized by the construction of multiphase coexistence through the co-doping of $CaTiO_3$ and $BaZrO_3$.

1. Introduction

Piezoelectric ceramics were widely used for some electronic devices, such as buzzers, actuators, piezoelectric energy harvesting, etc [1,2]. Since then, Pb(Zr,Ti)O_3 (PZT) piezoelectric ceramics have exhibited the outstanding performance and dominated the piezoelectric markets [1–4]. However, the involved toxic lead is damaging our environment during their fabrication and waste disposal process. Until now, several kinds of lead-free piezoceramics have been extensively studied to replace PZT, including potassium sodium niobate (K,Na)NbO_3 (KNN), bismuth sodium titanate (Bi,Na)TiO_3 (BNT), and barium titanate $BaTiO_3$ (BT) [3,5–9]. However, their electrical properties are still far from satisfactory, which were unable to fully take the place of PZT [3,5–9]. Therefore, it's an urgent task to develop the lead-free piezoceramics with high performance.

Recently, $BaTiO_3$ ceramics have been extensively studied due to the construction of phase boundaries [10,11]. As we known, there are three kinds of phase transitions in a pure $BaTiO_3$, including rhombohedral-orthorhombic (R-O) phase transition, orthorhombic-tetragonal (O-T) phase transition, and tetragonal-cubic (T-C) phase transition. Therefore, it is highly expected to construct the phase boundaries of $BaTiO_3$ ceramics by modifying their phase transition temperatures ($T_{R\text{-}O}$ and $T_{O\text{-}T}$) using chemical components, finally resulting in the enhancement of piezoelectric properties [12,13]. Some breakthroughs have taken placed in the lead-free $0.5(BaZr_{0.2}Ti_{0.8}O_3)$–$0.5(Ba_{0.7}Ca_{0.3}TiO_3)$ [$BZ_{0.2}T$-$x$$BC_{0.3}T$] ceramics [10], possessing a high piezoelectric coefficient of 620 pC/N. It was thought that the extraordinary piezoelectricity stems from a tricritical triple point where R, T and C phases meet [10]. In addition, further studies on $BZ_{0.2}T$-$x$$BC_{0.3}T$ system have affirmatively confirmed the relationship between enhanced electrical properties and multiphase boundaries [14–22].

Among these doping components, $CaTiO_3$ or $BaZrO_3$ was often used to modify the $BaTiO_3$, and some new phase boundaries can be formed [17,23,24]. According to the previous references and our experiments, we chose $CaTiO_3$ or $BaZrO_3$ to modify the $BaTiO_3$, that is, (1-z)$BaTiO_3$-$z$$CaTiO_3$ and (1-w)$BaTiO_3$-$w$$BaZrO_3$. One can observe from Fig. 1(a) that the addition of $CaTiO_3$ can shift both $T_{O\text{-}T}$ and $T_{R\text{-}O}$ to the lower temperature [25], resulting in the formation of tetragonal phase at room temperature. In addition, both $T_{O\text{-}T}$ and $T_{R\text{-}O}$ moved forward to a higher temperature by introducing $BaZrO_3$ [26], resulting in the construction of O-T phase boundary. However, O-T and T phases in (1-z)$BaTiO_3$-$z$$CaTiO_3$ and (1-w)$BaTiO_3$-$w$$BaZrO_3$ can't achieve a satisfied d_{33} value, that is, a low d_{33} of < 250 pC/N can be observed [Fig. 1(c) and (d)]. To realize high piezoelectric constant, the ternary material system of (1-x-y)$BaTiO_3$-$x$$CaTiO_3$-$y$$BaZrO_3$ [BT–xCT–yBZ, $x = 0$–0.25 ($y = 0.10$), $y = 0$–0.20 ($x = 0.16$)] was designed, and then effects of $CaTiO_3$ and $BaZrO_3$ contents on phase structure and electrical properties of $BaTiO_3$ ceramics were investigated. By optimizing the compositions, multiphase coexistence (R-O/O-T) can be realized, and then the enhancement of electrical properties can be attained. In addition, the mechanism researches of large piezoelectric constant near the multiphase coexistence were also discussed.

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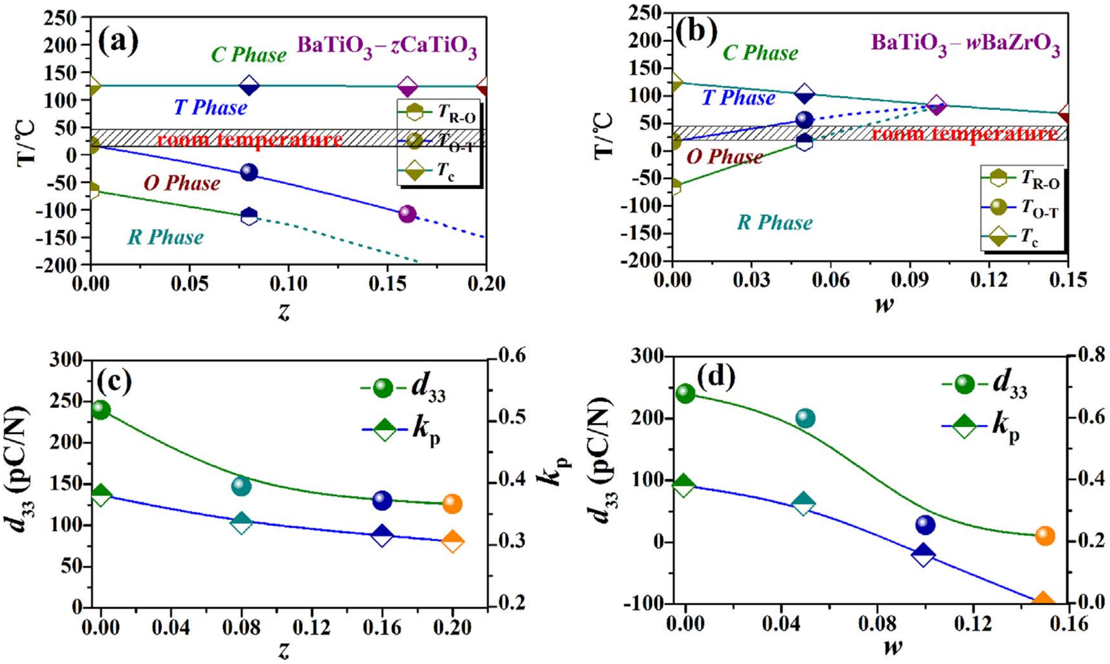

Fig. 1. Phase diagrams of (a) (1-*x*)$BaTiO_3$-*z*$CaTiO_3$ and (b) (1-*w*)$BaTiO_3$-*w*$BaZrO_3$ ceramics. (c) and (d) are their corresponding d_{33} and k_p values.

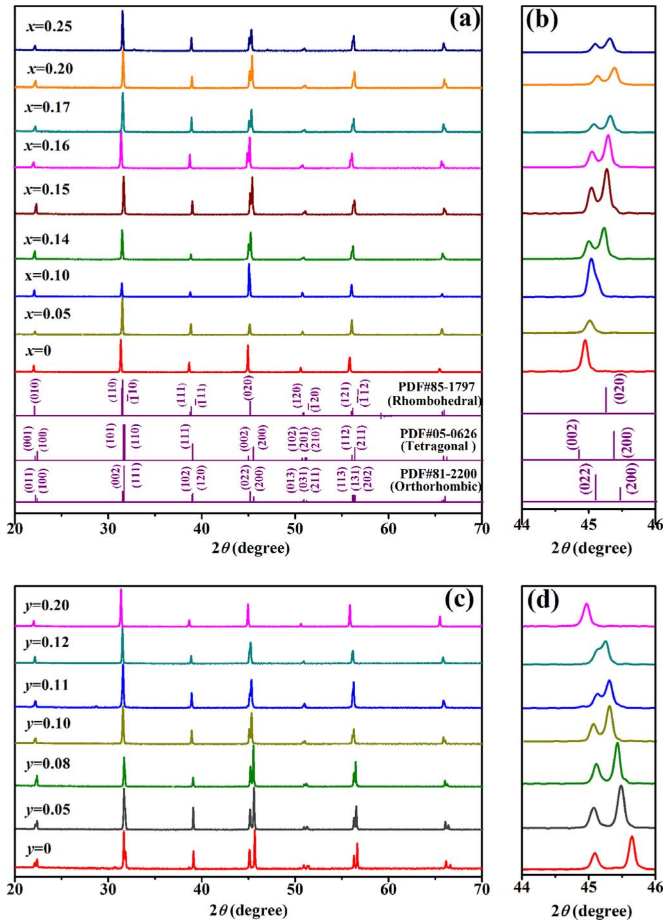

Fig. 2. XRD patterns of (1-*x*-*y*)$BaTiO_3$-*x*$CaTiO_3$-*y*$BaZrO_3$ ceramics with (a) *x* (*y* = 0.10) and (c) *y* (*x* = 0.16). (b) and (d) are their corresponding XRD patterns at 2*θ* = 44–46°.

2. Experimental procedure

Lead-free (1-*x*-*y*)$BaTiO_3$-*x*$CaTiO_3$-*y*$BaZrO_3$ [*x* = 0–0.25 (*y* = 0.10), *y* = 0–0.20 (*x* = 0.16)] ceramics were synthesized by the conventional solid-state sintering method. Barium carbonate ($BaCO_3$, 99%), calcium carbonate ($CaCO_3$, 99%), titanium dioxide (TiO_2, 98%), and barium zirconate ($BaZrO_3$, 99%) were used as raw materials. All the raw materials were weighted and ball milled for 24 h with alcohol. After that, the mixing slurries were dried and calcined at 1260 °C for 3 h and were mixed with a binder of 8 wt% polyvinyl alcohol (PVA). The calcined powders were pressed into the disks with a diameter of 10 mm and a thickness of 1 mm under a pressure of 10 MPa. After PVA was burned off, the pellets were sintered at 1450 °C for 3 h in air. The sintered samples were pasted with silver and then fired at 600 °C for 10 min. At last, the direct current electric field of 2 kV/mm was applied to pole each sample in a silicon oil bath for 30 min.

The phase structure of the as-sintered ceramics was analyzed by X-ray diffraction with a CuK_α radiation (λ = 1.5406 Å) (XRD, Bruker D8 Advanced XRD, Bruker AXS, Inc., Madison, WI). Field emission scanning electron microscopy (FE-SEM) (JSM-7500, Japan) was used to investigate surface morphologies of the sintered samples. Raman spectroscopic studies were carried out by a Horiba Aramis spectrometer (Horiba Scientific) with excitation sources of 473 nm. The spectra were recorded in the temperature range from −150 to 140 °C using a connected temperature controller. The temperature dependence of dielectric properties was examined using an *LCR* meter (TH2816A, China) at 10 kHz under the temperature range of −150 to 150 °C. The relative permittivity and dielectric loss of the samples were measured using an LCR meter (HP 4980, Agilent, U.S.A) in the poled state. Ferroelectric properties (polarization-electric field loops) were measured using a Radiant Precise Workstation (Radiant Technologies, Medina NY) with a frequency of 10 Hz. Measurement of longitudinal piezoelectric coefficient (d_{33}) was characterized using a piezoelectric coefficient d_{33} testing meter (ZJ-3A, China), and the planar electromechanical coupling coefficient k_p was measured using an impedance analyzer (HP 4299A). The strain-electric field (*S*–*E*) curves were measured by a strain analyzer (aixACCF TF Analyzer 1000, Germany).