Large piezoelectric effect of $(Ba,Ca)TiO_3 - xBa(Sn,Ti)O_3$ lead-free ceramics

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ABSTRACT

$(Ba_{0.9}Ca_{0.1})TiO_3 - xBa(Sn_{0.2}Ti_{0.8})O_3$ ceramics (abbreviated as BCT-xBST) were obtained and the relationships among phase structure, energy barrier and piezoelectric properties were studied. Their phase structures are tetragonal (T)–orthorhombic (O) coexistence at $0.20 \leq x \leq 0.40$, rhombohedral (R)–O–T multiphase coexistence at $x = 0.45$ and R phase or R-cubic (C) two-phase coexistence at $0.50 \leq x \leq 0.60$, respectively. The energy barrier of polarization rotations and extension for R–O and O–T two-phase coexistence as well as R–O–T multiphase one was analyzed by the conservation law of energy and Landau–Devonshire theory. Because of extremely low energy barrier for polarization rotation and extension, high piezoelectric coefficients $d_{33} = 630$ pC/N, $k_p = 0.52$ and the lower $E_C = 0.81$ kV/cm were achieved at $x = 0.45$ which has R–O–T multiphase coexistence. These results confirm that the low energy barrier for polarization rotation and extension at R–O–T multiphase coexistence composition is beneficial to enhance the d_{33} value. The high piezoelectric property also indicates that BCT–xBST ceramics are a promising candidate for lead-free piezoelectric ceramics.

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1. Introduction

Lead-based piezoelectric materials, such as $Pb(Zr,TiO_3)$ (PZT), $Pb(Mg_{1/3}Nb_{2/3})O_3 - PbTiO_3$ (PMN-PT) and $Pb(Zr_{1/3}Nb_{2/3})O_3 - PbTiO_3$ (PZN-PT) systems, have been widely used in various types of sensors, actuators, buzzers, medical ultrasonic transducers and other electronic devices because of their excellent piezoelectric properties and good temperature stability [1,2]. However, these lead-based ceramics are facing global restrictions due to toxic Pb. It is urgent to develop lead-free alternative materials with comparable piezoelectric and electromechanical properties to their lead-based counterparts. A series of typical lead-free piezoelectric systems such as $BaTiO_3$ (BT), $(Bi_{0.5}Na_{0.5})TiO_3$ and $(K_{0.5}Na_{0.5})NbO_3$ based ceramics, have been highlighted to substitute for PZT [3–6]. Among them, BT-based ceramics with excellent electrical properties are considered as one of the most promising candidates for replacing the lead-based piezoelectric ceramics [7–9]. Recently, a group of BT-based piezoelectric ceramics with high piezoelectric constants of $d_{33} = 530$ pC/N, 550 pC/N, 620 pC/N, 670 pC/N and 570 pC/N were reported in $Ba(Sn_{0.12}Ti_{0.88})O_3 - 30(Ba_{0.7}Ca_{0.3})O_3$ [7], $Ba(Ti_{0.8}Hf_{0.2})O_3 - 50(Ba_{0.7}Ca_{0.3})TiO_3$ [8],

$Ba(Zr_{0.2}Ti_{0.8})O_3 - 50(Ba_{0.7}Ca_{0.3})TiO_3$ (BZT-50BCT) [9], $(Ba_{0.95}Ca_{0.05})(Ti_{0.89}Sn_{0.11})O_3$ [10] and $BaTiO_3 - 0.16(0.4CaTiO_3 - 0.6BaSnO_3)$ [11] systems, respectively. The $(Ba,Ca)(Ti,Sn)O_3$ system has been attracting significant attention in them because of its high piezoelectric property ($440 \sim 670$ pC/N) and complex phase structure [7,10–14]. However, many researches mainly focused on revealing the relationship between phase structure and piezoelectric property [10–14] as well as decreasing sintering temperatures for satisfying actual application [15–19] so far. Few work has been done toward understanding the origin of the high piezoelectric property of $(Ba,Ca)(Ti,Sn)O_3$ system.

It is well known that the morphotropic phase boundary (MPB) separating rhombohedral (R) phase and tetragonal (T) one plays an important role in enhancing piezoelectric properties of the PZT piezoelectric family. The mechanism of the property enhancement near the MPB is associated with easy path for polarization rotation in anisotropically flattened free energy profile [20–23]. Similar to MPB behavior in PZT system, the high piezoelectric properties $d_{33} = 530$ pC/N, 550 pC/N, 620 pC/N for $Ba(Sn_{0.12}Ti_{0.88})O_3 - x(Ba_{0.7}Ca_{0.3})O_3$ [7], $Ba(Ti_{0.8}Hf_{0.2})O_3 - x(Ba_{0.7}Ca_{0.3})TiO_3$ [8] and BZT–xBCT [9] systems are also attributed to MPB which is close to a tricritical triple point in the phase diagram and has the low energy barrier of polarization rotation and extension or even vanishing polarization

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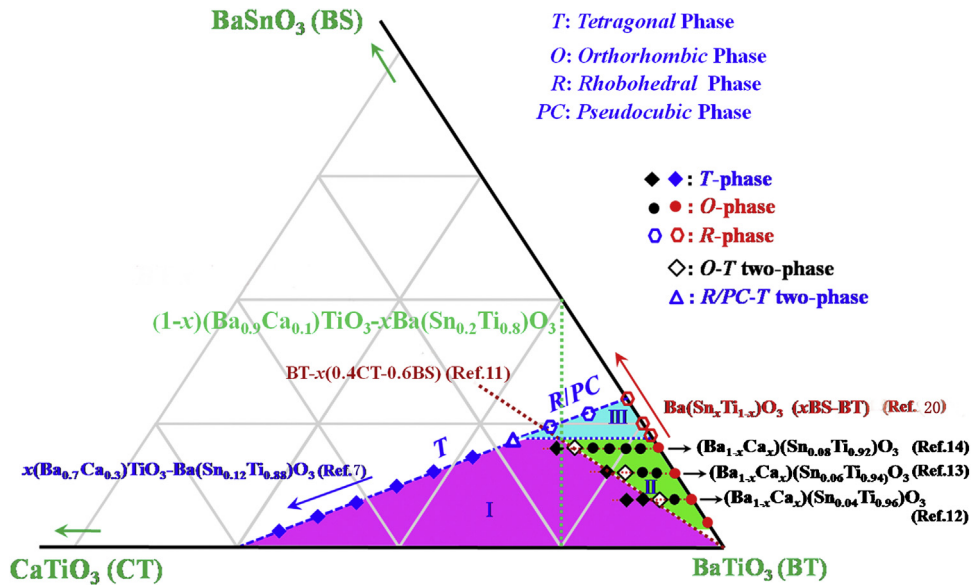 *E-mail address:* bpzhang@ustb.edu.cn (B.-P. Zhang).

Fig. 1. Phase diagram of BT–CT–BS ternary system near BT-rich corner. (For interpretation of the references to colour in the text, the reader is referred to the web version of this article.)

anisotropy between $(001)_T$ and $(111)_R$ [7–9,24]. Further, no energy barrier for polarization rotation and extension in a quasi-quadruple point where four phases (*Cubic–T–Orthorhombic–R*) nearly coexist together exhibiting double MPBs in the temperature-composition phase diagram was reported in $BaTiO_3–xBaSnO_3$ system [25], which exhibits an ultrahigh relative dielectric constant 75,000 and piezoelectric coefficient $d_{33} = 697$ pC/N at $x = 0.11$. Therefore, it is a good choice to design two-phase or multiphase coexistence near room temperature which has the low energy barrier of polarization rotation and extension to enhance the piezoelectric properties. Our previous studies have pointed out that the $BaTiO_3–x(0.4CaTiO_3–0.6BaSnO_3)$ ceramics has $O–T$ two phases and $R–O–T$ multiphase coexistence depending on x content. Because of $R–O–T$ multiphase coexistence, a high converse piezoelectric coeffcient of $d_{33}{}^* = 1444$ pm/V and strain of 0.070% were achieved at $x = 0.16$ [11]. However, the relationship between phase structure, energy barrier and d_{33} has not been well studied yet in the $(Ba,Ca)(Ti,Sn)O_3$ system, especially the energy barrier of polarization rotation for $R–O–T$ multiphase composition.

In this work, we designed the $(1 - x)(Ba_{0.9}Ca_{0.1})TiO_3–xBa(Sn_{0.2}Ti_{0.8})O_3$ (BCT–xBST) system, which passes through the $R–O–T$ multiphase point proved by previous results of us [11] as shown by a green dotted line in Fig. 1. The energy barrier of polarization rotations for $R–O$ and $O–T$ two-phase coexistence or $R–O–T$ multiphase one were analyzed by the laws of thermodynamics and combining Landau-Devonshire theory. The results indicate that energy barrier of polarization rotation and extension for $R–O–T$ multiphase coexistence is lower than that of $O–T$ or $R–O$ ones. Because of the extremely low energy barrier for polarization rotation and extension in the $R–O–T$ multiphase coexistence composition, high piezoelectric coefficients $d_{33} = 630$ pC/N and $k_p = 0.52$ were achieved in BCT–xBST system at $x = 0.45$. These results provide clues that the $R–O–T$ multiphase coexistence also has an extremely low energy barrier of polarization rotation and extension, which is beneficial to enhance the d_{33} value.

2. Experimental

Barium carbonate ($BaCO_3$, 99.0%), calcium carbonate ($CaCO_3$, 99%), stannic oxide (SnO_2, 99.5%) and titanium dioxide (TiO_2, 99.0%) were used as raw materials. These powders were weighed accord-
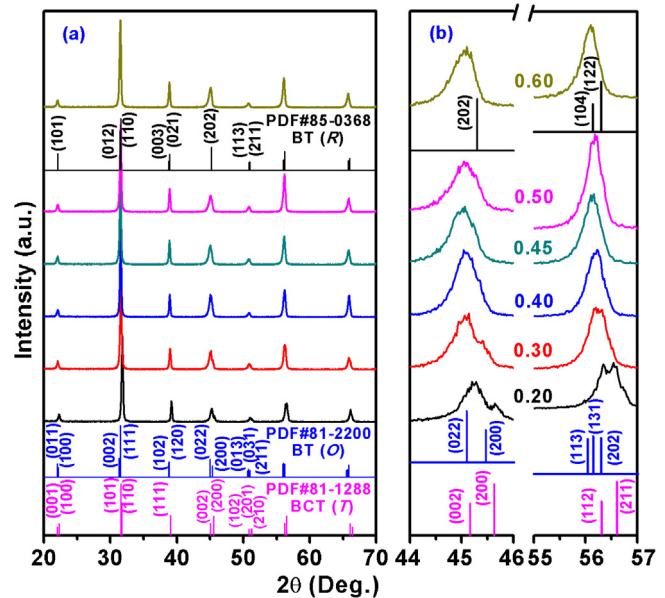

Fig. 2. X-ray diffraction patterns between the 2θ range of $20°$–$70°$ (a) enlarged ranges of $44°$–$46°$ and $55°$–$57°$ (b) for the BCT–xBST ceramics.

ing to the compositions of $(1 - x)(Ba_{0.9}Ca_{0.1})TiO_3–xBa(Sn_{0.2}Ti_{0.8})O_3$ (abbreviated as BCT–xBST, $x = 0.20, 0.30, 0.40, 0.45, 0.50, 0.60$) and mixed with alcohol. After drying the slurry and calcining at $1300\,°C$ for 4 h, the resultant powders were remixed and pressed into disks of 10 mm in diameter and 1.5 mm in thickness under 80 MPa using 2 wt% polyvinyl alcohol (PVA) as the binder, followed by burning the binder at $650\,°C$ by $5\,°C$/min and for 1 h. The samples were cooled to room temperature and then rose directly to $1480\,°C$ by $5\,°C$/min and held for 4 h. The sintered specimen was coated with silver paint on the upper and bottom surfaces and fired at $600\,°C$ for 30 min for electrical measurements. The poling was performed under a dc field of 4 kV/mm at room temperature for 30 min in a silicone oil bath.

The crystal structure was studied by using XRD with a Cu $K\alpha$ radiation ($\lambda = 1.5406$ Å) filtered through a Ni foil (Rigaku; RAD-B system, Tokyo, Japan). The microstructure of the sintered samples was observed by field emission scanning electron microscopy