Polymorphic phase transition and enhanced electrical properties of $(Ba_{0.91}Ca_{0.09-x}Sr_x)(Ti_{0.92}Sn_{0.08})O_3$ lead-free ceramics

Xiaofang Wang[a,b], Xiaolian Chao[a], Pengfei Liang[a], Lingling Wei[a], Zupei Yang[a,*]

[a]Key Laboratory for Macromolecular Science of Shaanxi Province, School of Materials Science and Engineering, Shaanxi Normal University, Xi'an, 710062, Shaanxi, People's Republic of China
[b]College of Chemistry and Chemical Engineering, Xianyang Normal University, Xianyang 712000, Shaanxi, People's Republic of China

Abstract

Lead-free $(Ba_{0.91}Ca_{0.09-x}Sr_x)(Ti_{0.92}Sn_{0.08})O_3$ ceramics were prepared by the solid state reaction method. Effects of Sr^{2+} content on the phase structure, electrical properties and temperature stabilities of the $(Ba_{0.91}Ca_{0.09-x}Sr_x)(Ti_{0.92}Sn_{0.08})O_3$ ceramics were investigated systematically. The polymorphic phase transition behavior from orthorhombic to tetragonal phase around room temperature was observed in the samples with $0.005 < x < 0.02$ according to XRD patterns. Owing to the coexistence of orthorhombic and tetragonal phases at room temperature, significantly enhanced electrical properties ($d_{33}=583$ pC/N, $k_p=40\%$, $P_r=8.73$ $\mu C/cm^2$, $E_c=0.07$ kV/cm and electrical strain$=0.20\%$) were obtained in $(Ba_{0.91}Ca_{0.08}Sr_{0.01})(Ti_{0.92}Sn_{0.08})O_3$ ceramics. Both d_{33} and k_p displayed excellent temperature stabilities in the range from -5 to 55 °C. These results demonstrated that $(Ba_{0.91}Ca_{0.08}Sr_{0.01})(Ti_{0.92}Sn_{0.08})O_3$ ceramics could be a promising candidate for lead-free piezoelectric material.
© 2014 Elsevier Ltd and Techna Group S.r.l. All rights reserved.

Keywords: Piezoelectric property; Lead-free ceramics; Polymorphic phase transition; Temperature stability

1. Introduction

It is well known that lead zirconate titanate (PZT) ceramics have been widely used owing to the excellent properties induced by morphotropic phase boundary (MPB) where rhombohedral and tetragonal phases coexist [1,2]. Nevertheless, they are not environment friendly for the lead oxide toxicity, and their industrial applications have been gradually prohibited in recent years [3,4]. Therefore, much attention has been paid to search for lead-free piezoelectric ceramics with high piezoelectric properties.

$BaTiO_3$ is considered to be an excellent candidate for lead-free piezoelectric ceramics [5]. However, the piezoelectric constant d_{33} of $BaTiO_3$ is relatively low (about 190 pC/N), and the pure $BaTiO_3$ undergoes a series of phase transformations with increasing temperature: rhombohedral to orthorhombic phase (R→O) at -80 °C, orthorhombic to tetragonal phase

(O→T) at 5 °C, and finally tetragonal to cubic phase (T→C) at 120 °C [6]. Some attempts have been conducted to shift the phase transitions to room temperature and improve d_{33} value through composition design. For example, the phase transformation temperature from tetragonal to orthorhombic (T_{T-O}) and orthorhombic to rhombohedral (T_{O-R}) can be shifted to room temperature by replacing Ti^{4+} with Zr^{4+} at the B-site in the $BaTiO_3$–$BaZrO_3$ system [7]. The A-site replacement of Ba^{2+} by Ca^{2+} can reduce the T_{T-O} and T_{O-R} in the $BaTiO_3$–$CaTiO_3$ system [8]. Recently, Liu and Ren [9] designed a ferroelectric system $(1-x)Ba(Zr_{0.2}Ti_{0.8})O_3–x(Ba_{0.7}Ca_{0.3})TiO_3$ (BZT–xBCT) composition to a triple point and observed a very high d_{33} value $\sim$620 pC/N. It was considered that BZT–xBCT showed a phase diagram similar to the Pb-based systems, with a MPB starting from a triple point of a paraelectric cubic phase, ferroelectric rhombohedral and tetragonal [10]. This triple point is shown to be a tricritical point, and thus the system exhibits very high piezoelectric performance. In addition, Li et al. reported (Ba,Ca) (Ti,Sn)O_3 ceramic system with a relatively high d_{33} of 530 pC/N owing to the formation of polymorphic phase transition (PPT)

*Corresponding author. Tel.: +86 29 81530 718; fax: +86 29 81530 702.
E-mail addresses: yangzp@snnu.edu.cn, chaoxl@snnu.edu.cn (Z. Yang).

from orthorhombic to tetragonal phase [11]. It is known that the MPB or PPT plays a very important role in piezoelectric ceramics because dielectric and piezoelectric properties show maximum values around MPB and PPT [12]. However, the MPB or PPT in $BaTiO_3$-based system is very different from that in PZT-based ceramics. The piezoelectric constant shows very strong temperature dependence in $BaTiO_3$-based system, which is often undesirable for practical application in any device [13,14]. $SrTiO_3$ is an effective additive being widely used in many perovskite piezoelectric ceramics to tailor the electrical performances [15]. As well known, the radius of Sr^{2+} is 1.12 Å, Ca^{2+} is 0.99 Å, and Ba^{2+} is 1.34 Å. In view of the radius, it is possible for Sr^{2+} to enter into the A-site of $(Ba,Ca)(Ti,Sn)O_3$ ceramics system and affect the phase structure and electrical properties. Thus, a question can be proposed whether the electrical performance and temperature stability have been improved by modified phase transition behavior using the Sr^{2+} ion substitution.

In this work, based on the modified phase transition behavior with ion doping, we designed a lead-free piezoelectric $(Ba_{0.91}Ca_{0.09-x}Sr_x)(Ti_{0.92}Sn_{0.08})O_3$ system. The conventional solid state reaction method was employed to prepare designed $(Ba_{0.91}Ca_{0.09-x}Sr_x)(Ti_{0.92}Sn_{0.08})O_3$ ceramics, and the effects of Sr^{2+} content on the phase transition, electrical properties and temperature stability were investigated in detail. Especially, the correlation between the phase structure and piezoelectric properties was explored and discussed.

2. Experimental

The $(Ba_{0.91}Ca_{0.09-x}Sr_x)(Ti_{0.92}Sn_{0.08})O_3$ (x=0.00, 0.005, 0.01, 0.02 and 0.03) lead-free ceramics were prepared by the conventional solid-state reaction method. High purity raw materials, $BaCO_3$ (99.99%), $CaCO_3$ (99.99%), TiO_2 (99.99%), SnO_2 (99.50%), $SrCO_3$ (99.00%), were weighed according to the stoichiometric ratio and then ball-milled in ethanol using zirconia balls for 16 h in air. Subsequently, the mixtures were dried and calcined at 1200 °C for 6 h. After calcinations, the powder was mixed with 5 wt% polyvinyl alcohol (PVA) solution and then uniaxially pressed into disk specimens with a diameter of 15 mm under 100 MPa. After burning out PVA at 500 °C, the disks were sintered at 1450 °C for 6 h in air with a heating rate of 3 °C/min.

The phase structures of the sintered specimens were identified by X-ray power diffraction (XRD, D/max-2550/PC, Rigaku, Japan) with Cu Kα radiation. To measure the electrical properties, silver paste was coated on both sides of the sintered pellets and fired at 840 °C for 30 min to form electrodes. Temperature-dependent dielectric constant was obtained with an LCR meter (Agilent, E4980A) connected to a computer-controlled temperature chamber by measuring the capacitance at 10 kHz. The polarization (P) and strain (S) hysteresis as a function of external electric field (E) were measured at 1 Hz with a 50 kV/cm using a high voltage amplifier (Model 610E, Trek, USA) for the electrical loading. The piezoelectric coefficient d_{33} was measured by a quasistatic piezoelectric meter (ZJ-3d, Institute of Acoustic Academic Sinica, Beijing, China). The electromechanical coupling

coefficient k_p was determined by the resonance and anti-resonance techniques using an impedance analyzer (HP/Agilent 4294A).

3. Results and discussion

Fig. 1(a) shows the XRD patterns of the $(Ba_{0.91}Ca_{0.09-x}Sr_x)(Ti_{0.92}Sn_{0.08})O_3$ ceramics as a function of Sr^{2+} contents. It can be seen that all samples show pure perovskite phase structure. And there is no trace of second phase, implying that Sr^{2+} can diffuse into the $(Ba,Ca)(Ti,Sn)O_3$ lattice to form a solid solution. In order to further analyze the effect of Sr^{2+} content on the phase structure, Fig. 1(b) plots the fine scanning XRD patterns in the 2θ range from 44° to 46° for all samples. An orthorhombic phase (PDF#81-2200) has been demonstrated in the ceramics with $0.00 \leq x \leq 0.005$, which is characterized by the (0 2 2)/(2 0 0) peaks at around 2θ of 45°. The tetragonal phase (PDF#79-2264) is observed in the samples with $0.02 \leq x \leq 0.03$, featured with the (0 0 2)/(2 0 0) peaks at around 2θ of 45°. The peaks characteristic near 45° in sample with x=0.01 show a mixture-phase behavior of both orthorhombic and tetragonal phases. Furthermore, it is noted that with increase of x from 0.00 to 0.02, the diffraction peak shifts to lower angle. When x=0.03, the diffraction peak shifts slightly to higher angle. In consideration of the ionic radius (Sr^{2+} is 1.12 Å, Ca^{2+} is 0.99 Å, and Ba^{2+} is 1.34 Å), the above phenomena may be attributed to the lattice deformation caused by Sr^{2+} occupying the position of Ba^{2+} or Ca^{2+} partly. Similar peak shifting behavior induced by the partial substitution of a higher-ionic-radius element for a lower-ionic-radius element was also observed in Zr-modified $BaTiO_3$ ceramics [16].

To further confirm the effect of Sr^{2+} content on the crystal lattice, the lattice parameters a, b and c were calculated using the least square method from XRD data, which are displayed in Fig. 2. The lattice parameters of sample with orthorhombic symmetry are a=4.006 Å, b=4.003 Å, c=4.000 Å at x=0.00. The lattice parameters of tetragonal phase are a=b=4.874 Å, c=3.834 Å at x=0.02. As shown in Fig. 2, the values of lattice parameters a, b and c varied continuously in the range of $0.00 \leq x \leq 0.005$ and $0.01 \leq x \leq 0.03$. The distinctly discontinuous change is observed around x=0.01, suggesting
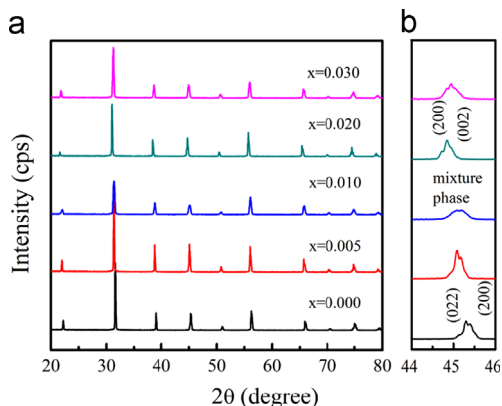

Fig. 1. XRD patterns of $(Ba_{0.91}Ca_{0.09-x}Sr_x)(Ti_{0.92}Sn_{0.08})O_3$ ceramics with different x between the 2θ range of 20°–80° (a) and 44°–46° (b).