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Journal of the European Ceramic Society 32 (2012) 517–520
www.elsevier.com/locate/jeurceramsoc

Short communication

Enhanced ferroelectric properties in $(Ba_{1-x}Ca_x)(Ti_{0.94}Sn_{0.06})O_3$ lead-free ceramics

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Received 15 July 2011; received in revised form 13 September 2011; accepted 19 September 2011
Available online 22 October 2011

Abstract

Lead-free $(Ba_{1-x}Ca_x)(Ti_{0.94}Sn_{0.06})O_3$ (BCST) ($x = 0.01$–0.04) ceramics were prepared using a solid-state reaction technique. The effects of Ca content on the phase structure and electrical properties of the BCST ceramics were investigated. High piezoelectric coefficient of $d_{33} = 440$ pC/N, planar electromechanical coupling factor of $k_p = 45\%$ and dielectric constant $\varepsilon_r = 6900$ were obtained for the samples at $x = 0.03$. At room temperature, a polymorphic phase transition (PPT) from orthorhombic phase to tetragonal phase was identified in the composition range of $0.02 < x < 0.04$.

Keywords: A. Sintering; C. Dielectric properties; C. Ferroelectric properties; C. Piezoelectric properties; Titanates

1. Introduction

Lead zirconate titanate (PZT) ceramics are the most widely used piezoelectric materials due to their superior piezoelectric properties close to the morphotropic phase boundary (MPB) between rhombohedral and tetragonal phases. Nevertheless, PZTs are not environmental friendly for their lead oxide toxicity. With the recent growing demand of global environmental protection, many researchers have greatly focused on lead-free ceramics to replace the lead-based ceramics.[1–3]

In lead-free ceramics, the enhanced piezoelectric properties are generally accompanied by the occurrence of polymorphic phase transition around room temperature,[3–7] and they are thus considered to be closely associated with the phenomenon of phase coexistence. However, these piezoelectric ceramics generally have inferior piezo-coefficients ($d_{33} < 300$ pC/N in most cases) compared to that of the most-desired PZTs ($d_{33} = 300$–600 pC/N).[1,8,9] Measures have been taken to improve the piezoelectric properties of lead-free ceramics.[10–12] Recently, high $d_{33} > 300$–600 pC/N in (Ca, Zr) co-doped $BaTiO_3$(BT)-based ceramics[7,13] was obtained successfully using a traditional solid-state reaction technique in optimal composition, suggesting that they might be promising candidates for lead-based piezoelectric materials. Besides being a high-piezoelectric coefficient material, BT-based ceramics have been used for Y5V-type multilayer ceramic capacitor (MLCC) due to their high dielectric constant and low loss.[14,15] Prior researches have shown that Sn doping not only results in lowering of the Curie temperature but also induces diffusion of the phase transition. Both these characteristics can be exploited in tailoring the dielectric response of ceramics suitable for MLCC.[16–18] However, the research of high piezoelectric properties in $(Ba_{1-x}Ca_x)(Ti_{0.94}Sn_{0.06})O_3$ ceramics with high dielectric constant has not been reported so far. In this paper, we report our achievement in $(Ba_{1-x}Ca_x)(Ti_{0.94}Sn_{0.06})O_3$ lead-free ceramics with enhanced piezoelectric properties and dielectric properties.

2. Experimental procedure

$(Ba_{1-x}Ca_x)(Ti_{0.94}Sn_{0.06})O_3$ (BCST) ceramics were prepared by conventional solid-state reaction technique. Raw materials of $BaCO_3$ (99.0%), $CaCO_3$ (99.0%), SnO_2 (99.0%) and TiO_2 (99.5%) were mixed with addition of alcohol, which were then dried and calcined at 1200 °C for 4 h. Thereafter, calcined powders were remixed and pressed into 12 mm-diameter pellets and sintered at 1500 °C for 4 h in air. Crystal structure was examined by using an X-ray diffraction meter with a Cu K_α radiation ($\lambda = 1.54178$ Å) (XRD, D8 Advance, Bruker Inc., Germany). Dielectric properties were measured by using the precision

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0955-2219/$ – see front matter.
doi:10.1016/j.jeurceramsoc.2011.09.020

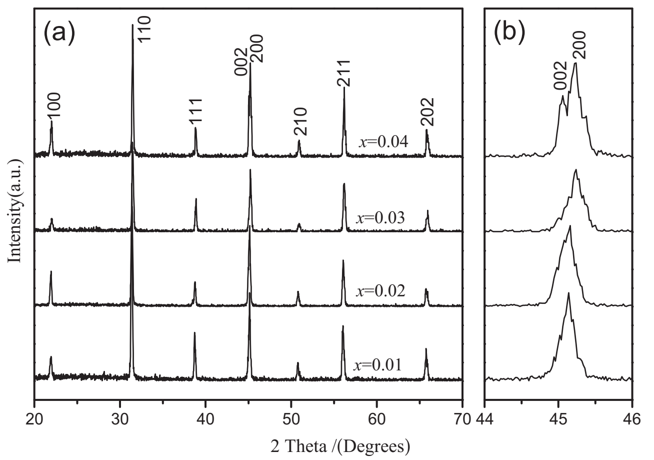

Fig. 1. X-ray diffraction patterns of the $(Ba_{1-x}Ca_x)(Ti_{0.94}Sn_{0.06})O_3$ ceramics at $x = 0.01$, 0.02, 0.03 and 0.04.

impedance analyzer (4294A Agilent Inc., Malaysia) at 100 kHz. Ferroelectric hysteresis loops were measured at room temperature by using an aix-ACCT TF2000FE-HV ferroelectric test unit (aix-ACCT Inc., Germany). The ceramics were poled under a dc field of 1–2 kV/mm at RT in a silicon oil bath for 20 min. Piezoelectric constant d_{33} was measured using a quasi-static d_{33} meter (YE2730 SINOCERA, China). Planar electromechanical coupling factor k_p was calculated following IEEE standards by using the impedance analyzer.

3. Results and discussion

Fig. 1 shows XRD patterns of the BCST ceramics with different Ca content. As can be seen, all the BCST ceramics show pure perovskite structure, suggesting that Ca and Sn diffuse into the $BaTiO_3$ lattice to form a solid solution. Orthorhombic phase[16–18] of BCST at room temperature is characterized by single peak at around 2θ of 46°, when $x = 0.01$ and 0.02. The BCST ceramics become tetragonal structures, featured with splitting of the (0 0 2)/(2 0 0) peaks at around 2θ of 46° with further increase of Ca content.[18,19] The BCST ceramics possess pure tetragonal phase, when $x = 0.04$. Therefore, it can be suggested that orthorhombic phase and tetragonal phase coexist in the composition range of $0.02 < x < 0.04$ for the BCST ceramics at room temperature. The changing of the lattice parameter with increasing of Sn content in BCST ceramics confirms the discussion above. Lattice parameters calculated from the diffraction data are presented in Table 1. Fig. 2 shows SEM micrographs of the BCST ceramics at $x = 0.01$, 0.02, 0.03 and 0.04, respectively. The microstructure of BCST ceramics at $x = 0.01$ is inhomogeneous and some pores exist in the grain boundary. For the samples at $x = 0.02$ and 0.03, the microstructure is homogeneous and no pore exists in the grain boundary, while the grain size is about 10 μm. For the sample at $x = 0.04$, the microstructure is inhomogeneous and the grain size becomes small (5 μm). The relative density are 96%, 98%, 99% and 97% for the BCST

Table 1
Lattice parameters obtained from the structural refinement using X-ray diffraction data at room temperature.

Samples	*a* (Å)	*b* (Å)	*c* (Å)
$x = 0.01$	4.01907	4.04534	4.01912
$x = 0.02$	4.01844	4.03279	4.01972
$x = 0.03$	4.01497	4.02121	4.01999
$x = 0.04$	4.01184	4.01184	4.02025

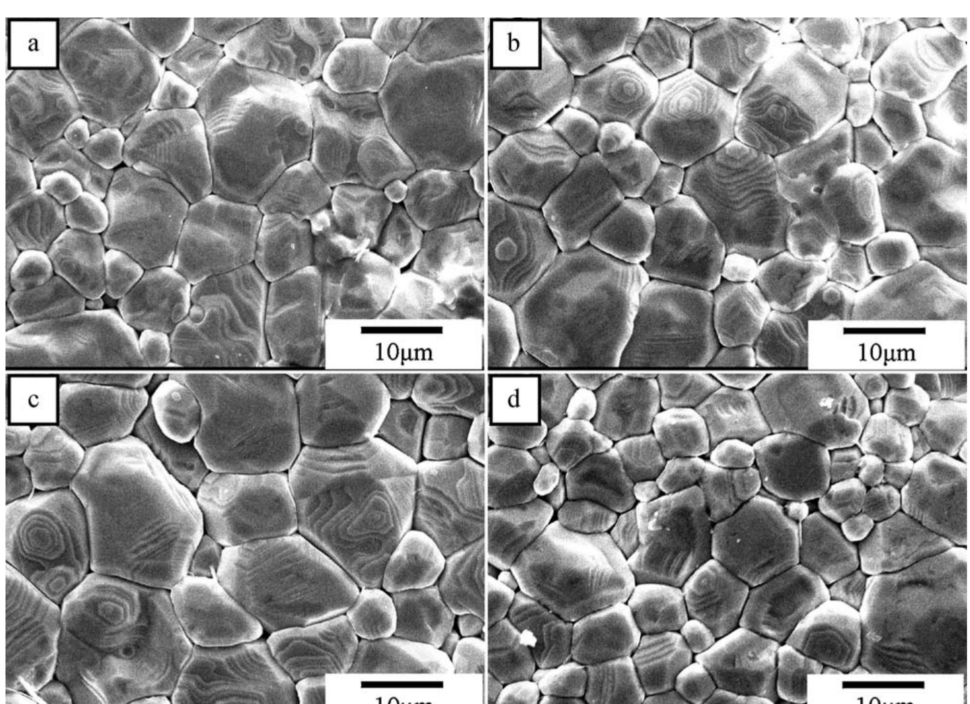

Fig. 2. SEM micrographs of the $(Ba_{1-x}Ca_x)(Ti_{0.94}Sn_{0.06})O_3$ ceramics sintered at 1500 °C: (a) $x = 0.01$, (b) $x = 0.02$, (c) $x = 0.03$ and (d) $x = 0.04$.

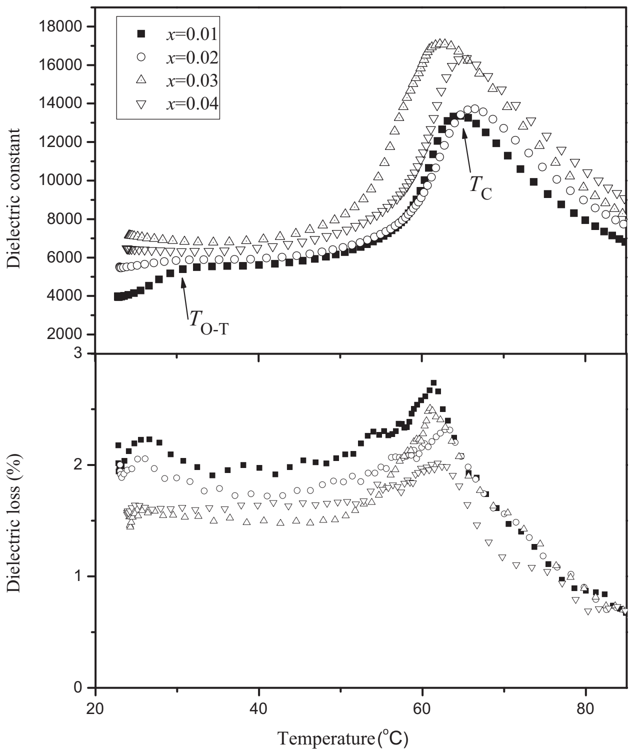

Fig. 3. Temperature dependence of dielectric constant and dielectric loss of the $(Ba_{1-x}Ca_x)(Ti_{0.94}Sn_{0.06})O_3$ ceramics at $x = 0.01$, 0.02, 0.03 and 0.04 measured at 100 kHz.

ceramics at $x = 0.01$, 0.02, 0.03 and 0.04, respectively. It is shown that clear grain boundary and uniformly distributed grain size could enhance the density of the BCST ceramics and may be advantageous to the electric properties.

Temperature dependence of dielectric constant and dielectric loss for the BCST ceramics is shown in Fig. 3. As can be seen, two obvious phase transitions above 20 °C corresponding to the orthorhombic–tetragonal ($T_{O–T}$) and tetragonal-cubic (T_C),[16–19] respectively, are observed for the samples of $x = 0.01$. The orthorhombic–tetragonal transition peaks, which become weak and broad, slightly shift towards lower temperature with increasing Ca content ($x = 0.02$ and 0.03). With further increasing of Ca content ($x = 0.04$), the orthorhombic to tetragonal phase transition cannot be observed above room temperature. It is interesting to note that phase transition temperature $T_{O–T}$ decrease obviously, and the Curie temperature T_C for each sample is above 60 °C. This result indicates that Ca addition does not strongly affect the T_C, but pushes the $T_{O–T}$ to lower temperatures in BCST system.[4,20] On the other hand, the dielectric constants are found to be on the order of 5200, 5800, 6900 and 6300 for BCST ceramics at $x = 0.01$, $x = 0.02$, $x = 0.03$ and $x = 0.04$, respectively. The dielectric loss is found to be on the order of 0.021, 0.018, 0.015 and 0.016 for the BCST ceramics at $x = 0.01$, $x = 0.02$, $x = 0.03$ and $x = 0.04$, respectively. The BCST ceramic at $x = 0.03$ is found to exhibit a high dielectric constant of 6900 and low dielectric loss of 0.015 at room temperature. The values show suitability of the composition for Y5V type of multilayer chip capacitors.

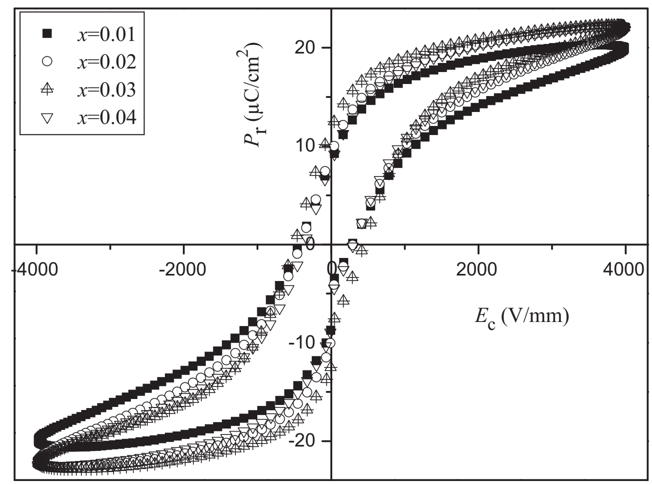

Fig. 4. Polarization versus electric field of the $(Ba_{1-x}Ca_x)(Ti_{0.94}Sn_{0.06})O_3$ ceramics at $x = 0.01$, 0.02, 0.03 and 0.04 at room temperature.

Hysteresis loops of polarization versus electric field for the BCST ceramics are shown in Fig. 4. Values of remnant polarization are 8.3, 9.8, 12.2 and 8.9 $\mu C/cm^2$ for the BCST ceramics at $x = 0.01$, $x = 0.02$, $x = 0.03$ and $x = 0.04$, respectively. It can be seen that with the increase of Ca content, remnant polarizations of the BCST ceramics increase to a maximum value 12.2 $\mu C/cm^2$ at $x = 0.03$ and then decrease. Fig. 5 shows piezoelectric coefficient and planar mode electromechanical coupling coefficient of the BCST ceramics as a function of Ca content. It can be observed that both the d_{33} and k_p curves possess a peak with increasing Ca content. At $x = 0.03$, the d_{33} and k_p of BCZT ceramics reach their maximum values of 440 pC/N and 45%, respectively. It is believed that the observed high piezoelectric properties should be ascribed to the phase coexistence, as case for other BT and KNN systems,[2,3,5–7,12,13] and polymorphic phase transition occurring near room temperature should be the origin of this phase coexistence. The orthorhombic–tetragonal phase coexistence causes instability of the polarization state, so that the polarization direction can be easily rotated by external stress or electric field, resulting in a high piezoelectricity.[21–23]

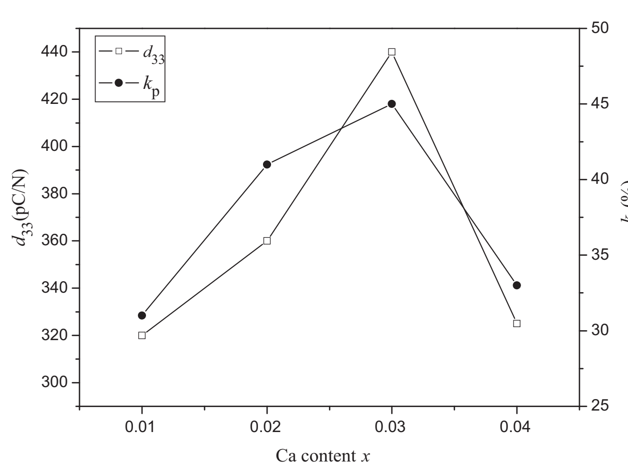

Fig. 5. Piezoelectric coefficient and planar mode electromechanical coupling coefficient of the $(Ba_{1-x}Ca_x)(Ti_{0.94}Sn_{0.06})O_3$ ceramics as a function of x.

4. Conclusion

A PPT from orthorhombic to tetragonal phase around room temperature was identified in the $(Ba_{1-x}Ca_x)(Ti_{0.94}Sn_{0.06})O_3$ ceramics at $0.02 < x < 0.04$. BCST ceramics at PPT composition exhibit extremely high piezoelectric coefficient of $d_{33} = 440$ pC/N and dielectric constants of $\varepsilon_r = 6900$. Our work provides a new way for designing lead-free materials with both of high piezoelectric properties and dielectric properties.

Acknowledgements

This work was supported by the Natural Science Foundation of Shandong Province of China (No. ZR2011EMQ015) and the Research Foundation for Excellent Young and Middle-aged Scientists of Shandong Province of China (No. BS2010CL010).

References

1. Saito Y, Takao H, Tani T, Nonoyama T, Takatori K, Homma1 T, et al. Lead free piezoceramics. *Nature* 2004;**432**:84–7.
2. Hollenstein E, Damjanovic D, Setter N. Temperature stability of the piezoelectric properties of Li-modified KNN ceramics. *J Eur Ceram Soc* 2007;**27**:4093–7.
3. Zhang SJ, Xia R, Shrout TR. Piezoelectric properties in perovskite $0.948(K_{0.5}Na_{0.5})NbO_3$–$0.052LiSbO_3$ lead-free ceramics. *J Appl Phys* 2006;**100**:104108.
4. Jaffe B, Cook WR, Jaffe H. *Piezoelectric ceramics*. London: Academic; 1971.
5. Zhang JL, Zong XJ, Wu L, Gao Y, Zheng P, Shao SF. Polymorphic phase transition and excellent piezoelectric performance of $(K_{0.55}Na_{0.45})_{0.965}Li_{0.035}Nb_{0.80}Ta_{0.20}O_3$ lead-free ceramics. *Appl Phys Lett* 2009;**95**:022909.
6. Wu L, Xiao DQ, Wu JG, Sun Y, Lin DM, Zhu JG, et al. Good temperature stability of $K_{0.5}Na_{0.5}NbO_3$ based lead-free ceramics and their applications in buzzers. *J Eur Ceram Soc* 2008;**28**:2963–8.
7. Li W, Xu ZJ, Chu RQ, Fu P, Zang GZ. Piezoelectric and dielectric properties of $(Ba_{1-x}Ca_x)(Ti_{0.95}Zr_{0.05})O_3$ lead-free ceramics. *J Am Ceram Soc* 2010;**93**:2942–4.
8. Halder S, Gerber P, Schneller T, Waser R. Electromechanical properties of $Ba(Ti_{1-x}Zr_x)O_3$ thin films. *Appl Phys A* 2005;**81**:11–3.
9. Maiti T, Guo R, Bhalla AS. Electric field dependent dielectric properties and high tenability of $BaZr_xTi_{1-x}O_3$ relaxor ferroelectrics. *Appl Phys Lett* 2006;**89**:122909.
10. Rubio-Marcos F, Ochoa P, Fernandez JF. Sintering and properties of lead-free $(K,Na,Li)(Nb,Ta,Sb)O_3$ ceramics. *J Eur Ceram Soc* 2007;**27**:4125–9.
11. Takahashi H, Numamoto Y, Tani J, Tsurekawa S. Piezoelectric properties of $BaTiO_3$ ceramics with high performance fabricated by microwave sintering. *Jpn J Appl Phys* 2006;**45**:7405–8.
12. Wang K, Li JF. Domain engineering of lead-free Li-modified $(K,Na)NbO_3$ polycrystals with highly enhanced piezoelectricity. *Adv Funct Mater* 2010;**20**:1924–9.
13. Liu WF, Ren XB. Large piezoelectric effect in Pb-free ceramics. *Phys Rev Lett* 2009;**103**:257602.
14. Maurya D, Ahn CW, Zhang SJ, Priya S. High dielectric composition in the system Sn-modified $(1-x)BaTiO_3$–$xBa(Cu_{1/3}Nb_{2/3})O_3$, $x = 0.025$ for multilayer ceramic capacitors. *J Am Ceram Soc* 2010;**93**:1225–8.
15. Zhang SW, Zhang HL, Zhang BP, Zhao GL. Dielectric and piezoelectric properties of $(Ba_{0.95}Ca_{0.05})(Ti_{0.88}Zr_{0.12})O_3$ ceramics sintered in a protective atmosphere. *J Eur Ceram Soc* 2009;**29**:3235–42.
16. Markovic S, Mitric M, Cvjeticanin N, Uskokovic D. Preparation and properties of $BaTi_{1-x}Sn_xO_3$ multilayered ceramics. *J Eur Ceram Soc* 2007;**27**:505–9.
17. Lei C, Bokov AA, Ye ZG. Ferroelectric to relaxor crossover and dielectric phase diagram in the $BaTiO_3$–$BaSnO_3$ system. *J Appl Phys* 2007;**101**:084105.
18. Singh KC, Nath AK, Laishram R, Thakur OP. Structural, electrical and piezoelectric properties of nanocrystalline tin-substituted barium titanate ceramics. *J Alloy Compd* 2011;**509**:2597–601.
19. Lu SG, Xu ZK, Chen H. Tunability and relaxor properties of ferroelectric barium stannate titanate ceramics. *Appl Phys Lett* 2004;**85**:5319–21.
20. Zhang PZ, Shen MR, Fang L, Zheng FG, Wu XL, Shen JC, et al. Pr^{3+} photoluminescence in ferroelectric $(Ba_{0.77}Ca_{0.23})TiO_3$ ceramics: sensitive to polarization and phase transitions. *Appl Phys Lett* 2008;**92**:222908.
21. Zhang SJ, Xia R, Shrout TR. Modified $(K_{0.5}Na_{0.5})NbO_3$ based lead-free piezoelectrics with broad temperature usage range. *Appl Phys Lett* 2007;**91**:132913.
22. Fu HX, Cohen RE. Polarization rotation mechanism for ultrahigh electromechanical response in single-crystal piezoelectrics. *Nat Mater* 2000;**403**:281–3.
23. Damjanovic D. Contributions to the piezoelectric effect in ferroelectric single crystals and ceramics. *J Am Ceram Soc* 2005;**88**:2663–76.