Journal of the European Ceramic Society xxx (2016) xxx–xxx

Contents lists available at www.sciencedirect.com

Journal of the European Ceramic Society

journal homepage: www.elsevier.com/locate/jeurceramsoc

Creating adjoining polymorphic phase transition (PPT) regions in ferroelectric (Ba,Sr)(Zr,Ti)O_3 ceramics

Yao Li[a,b], Hongbo Cheng[a,b], Menglin Liu[a,b], Yunxiang Zhang[a,b], Peng Yan[c], Chunming Wang[d], Jun Ouyang[a,b,e,*]

[a] Key Laboratory for Liquid-Solid Structure Evolution and Processing of Materials (Ministry of Education), School of Materials Science and Engineering, Shandong University, Jinan 250061, China
[b] Suzhou Institute of Shandong University, Suzhou 215123, China
[c] School of Mechanical Engineering, Shandong University, Jinan 250061, China
[d] School of Physics, Shandong University, Jinan 250010, China
[e] National Institute of Standards and Technology, Gaithersburg, MD 20899, USA[1]

ARTICLE INFO

Article history:
Received 4 August 2016
Received in revised form
14 November 2016
Accepted 16 November 2016
Available online xxx

Keywords:
Ferroelectric ceramics
Solid solution
Polymorphic phase transition
Piezoelectricity
Barium titanate

ABSTRACT

In this work, we report the polymorphic phase transitions(PPT) in ferroelectric $Ba_{0.95}Sr_{0.05}Zr_xTi_{(1-x)}O_3$ (BSZT, $x = 0.01–0.10$) ceramics synthesized by using a solid-state reaction method. The doping elements and composition ratios were selected to create adjoining PPT phase boundaries near room temperature, hence to achieve a broadened peak of piezoelectric performance with respect to composition. The temperature-composition phase diagram was constructed and the effects of PPT on the electromechanical and ferroelectric properties of the ceramics were investigated. It was revealed that the two adjacent PPT regions at room temperature showed different characteristics in property enhancement. However, due to the proximity of the phase boundaries, $Ba_{0.95}Sr_{0.05}Zr_xTi_{(1-x)}O_3$ ceramics in a fairly broad range of compositions ($0.02 \leq x \leq 0.07$) showed excellent piezoelectric properties, including a large piezoelectric constant ($312\ pC/N \leq d_{33} \leq 365\ pC/N$) and a high electromechanical coupling coefficient k_p ($0.42 \leq k_p \leq 0.49$).

1. Introduction

Electromechanical performance of ferroelectric ceramics has a close relationship with their phase structures [1–8]. The high d_{33} piezoelecteic coefficients in PZT ceramics are results of the effect of a morphotropic phase boundary(MPB) created by a proper Zr/Ti atomic ratio [9,10]. A MPB was initially defined as a vertical or near-vertical phase boundary in the temperature-composition (T-x) diagram which separates two polymorphic phases. It represents a very narrow composition region wherein two different phases coexist over a range of temperatures. On the other hand, for many other piezoelectric ceramics, the concept of polymorphic phase transition (PPT) instead of MPB has been used. For example, it is well known that a undoped $BaTiO_3$ (BT) ceramic have a rhombohedral-(R) → Orthorhombic (O) → Tetragonal(T) polymorphic phase transition sequence when it is heated from a low temperature to room temperature (RT) before it finally transforms into the paraelectric cubic phase above the Curie temperature T_C (~130 °C). This temperature sensitive polymorphism is associated with enhanced electromechanical properties in ferroelectric ceramics [6,11–13], i.e., when the temperatures are near the PPT temperatures (T_{PPT}), such as $T_{O\text{-}T}$ or $T_{R\text{-}O}$, the ferroelectric ceramics demonstrate performance peaks in their piezoelectric and dielectric responses.

L. E. Cross proposed five types of control in the engineering of ferroelectric phase transitions, including both MPB and PPT approaches, in his famous tutorial review on tailoring the properties of ferroelectric ceramics for specific applications [14]. He presented in the review the change of T_{PPT} and T_C in $BaTiO_3$-based ceramics with different doping elements. Adapted from Ref. [14], Fig. 1(a)–(c) describes the effects of a doping element on phase transition behavior of the BT ceramic in the case of a decreasing tolerance factor t. A single doping element will stabilize the lower symmetry phases of O and R near RT, if the curves of T_{PPT} vs. doping

---

* Corresponding author at: Key Laboratory for Liquid-Solid Structure Evolution and Processing of Materials (Ministry of Education), School of Materials Science and Engineering, Shandong University, Jinan 250061, China.

E-mail addresses: ouyangjun@sdu.edu.cn, jouyang2002@yahoo.com (J. Ouyang).

[1] Certain commercial equipment, instruments, or materials are identified in this paper to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

http://dx.doi.org/10.1016/j.jeurceramsoc.2016.11.030
0955-2219/© 2016 Elsevier Ltd. All rights reserved.

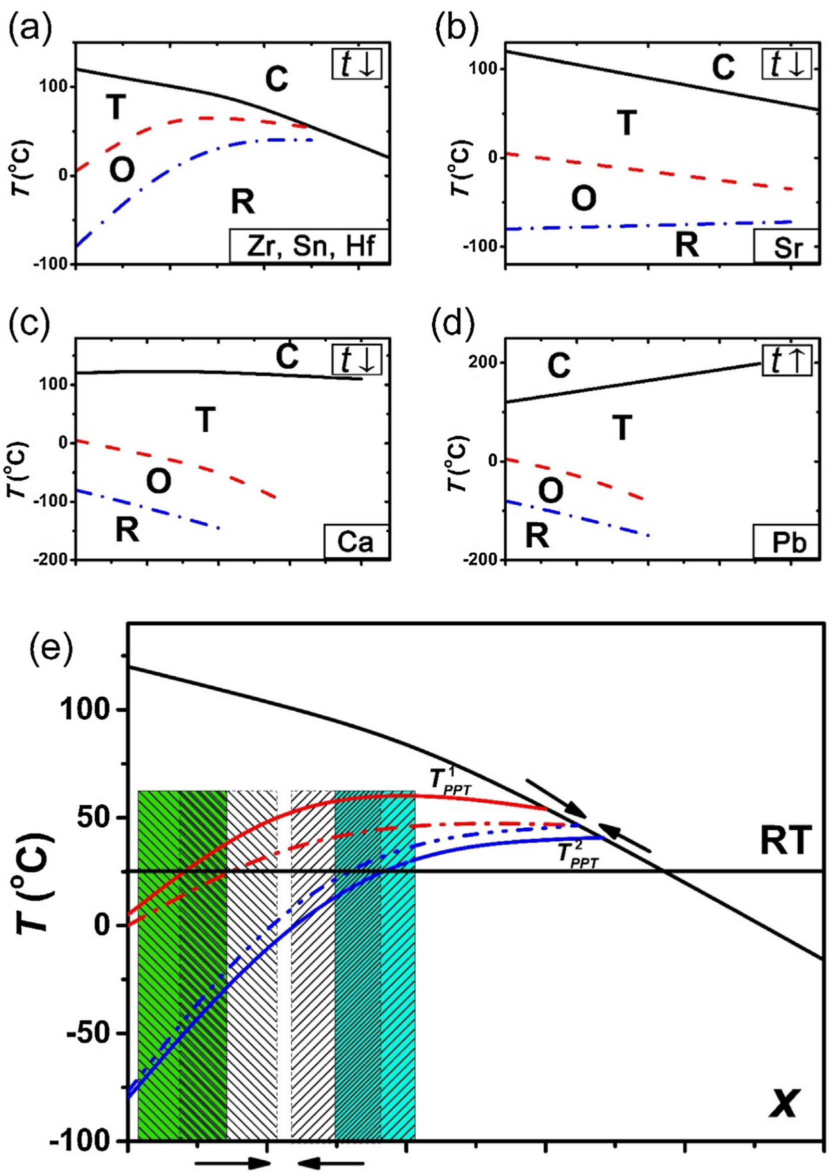

Fig. 1. The phase transition behavior of BT ceramics doped with: (a) a larger B-site ions, such as Zr, Sn and Hf, (b) a slightly smaller A-site ion, such as Sr, (c) a much smaller A-site ion, such as Ca, (d) a larger A-site ion, such as Pb; (e) the effect of co-doping with a larger B-site ion and a slightly smaller A-site ion on bringing together the two polymorphic phase transition regions. ((a)-(d) adapted from Ref. 14.).

concentration are sloping up (Fig. 1a), leading to the formation of a "pinch-off" region between the two T_{PPT} curves and a sloping-down T_C curve (Fig. 1a). This type of phase transition behavior takes place in some doping elements including Zr, Sn and Hf [4,14], all of which substituting the B-site Ti ions with larger ionic radius. Fig. 1(b) and (c) shows another type of commonly observed phase transition behavior: both the T_C curve and the T_{PPT} curves slope down but with different slopes. Fig. 1(b) shows a much slower ramping-down of the T_{PPT} with the doping concentration as compared with that of T_C, while Fig. 1(c) illustrates the opposite scenario with a much slower decreasing T_C. Sr and Ca are representative elements of the two scenarios of phase transition behavior with doping elements, respectively. Sr^{2+} ions have the smallest radius difference among di-valence cations that can replace Ba^{2+} in BT, therefore it produces the smallest perturbation on the stability of the low symmetry phases, especially on that of the R phase which is induced by a rotation of the oxygen octahedral, a lattice distortion sensitive to the stacking density (hence ionic radii) of the perovskite structure [1,15]. On the other hand, Ca^{2+} ions have a much larger size difference with Ba^{2+}, therefore the stabilities of low symmetry phases are perturbed more prominently, as shown in Fig. 1(c). For an increasing tolerance factor *t* due to doping with larger A-site ions, Fig. 1(d) illustrates the composition-dependent T_{PPT} and T_C. It is noted that the three phase transition behaviors demonstrated in Fig. 1b through 1d correspond to stabilization of high symmetry phases (either C or T phases) near RT instead of low symmetry ones.

In recent years, a lot of research efforts have been made to construct rhombohedral–orthorhombic(R–O), orthorhombic–tetragonal(O–T) and tetragonal- rhombohedral (T-R) phase boundaries near room temperature in $BaTiO_3$- and (K, Na)NbO_3- based ceramics [3–5,7,16–18]. These efforts are mostly concentrated in obtaining discrete PPT or MPB regions near RT in the *T*- *x* diagram. This goal has been achieved by taking advantage of the phase transition behavior shown in Fig. 1a for single-element doped BT ceramics [4,16], where the O-T and R-O PPT regions are usually well defined and separated by a sizable composition difference. Moreover, by constructing a complex phase diagram with multiple doping elements differing in the induced phase

Please cite this article in press as: Y. Li, et al., Creating adjoining polymorphic phase transition (PPT) regions in ferroelectric (Ba,Sr)(Zr,Ti)O_3 ceramics, *J Eur Ceram Soc* (2016), http://dx.doi.org/10.1016/j.jeurceramsoc.2016.11.030