

# Development of hard high-temperature piezoelectric ceramics for actuator applications

Xiaolian Liu<sup>1</sup> · Guodong Wang<sup>1</sup> · Meiya Li<sup>2</sup> · Jianguo Chen<sup>3,4</sup> · Shuxiang Dong<sup>4</sup> · Zhongqiang Hu<sup>5</sup>

Received: 30 December 2014 / Accepted: 15 April 2015  
© Springer Science+Business Media New York 2015

**Abstract** Piezoelectric 0.365BiScO<sub>3</sub>–0.635PbTiO<sub>3</sub> (BSPT) ceramics are promising for high temperature actuator applications due to their high Curie temperature and high piezoelectric coefficient. However, relatively low mechanical quality factor ( $Q_m \approx 25$ ) and high dielectric loss ( $\tan \delta \approx 0.04$ ) would lead to self-heating and property degradation if BSPT ceramics are used in piezoelectric actuators that work at resonant frequency. In this work, Mn-doped BSPT ceramics were prepared by conventional solid state reaction to modify the electrical properties. Excellent hard piezoelectric properties of  $d_{33} \approx 200$  pC/N,  $Q_m \approx 210$ , and  $\tan \delta \approx 0.015$  were measured in the BSPT ceramics doped with 1.2 wt% of Mn. Further, Mn-doped BSPT ceramics showed a depoling temperature of 360 °C, about 100 °C higher than that of commercialized hard PZT ceramics. These results indicate that piezoelectric actuators fabricated with Mn-doped BSPT ceramics would exhibit enhanced thermal

stability and higher energy efficiency in a wide temperature range.

## 1 Introduction

Pb(Zr,Ti)O<sub>3</sub> (PZT) systems have been widely used in the fields of actuators, sensors as well as piezoelectric energy harvesting due to their excellent piezoelectric properties [1–4]. The most interesting aspect of piezoelectric ceramics is that the physical properties can be readily designed and modified for specific applications by means of doping or substitution of A/B site cations, or by changing the ratio of A/B site cation. For example, by doping with donors or acceptors in PZT, several types of piezoelectric ceramics have been developed and commercially available for specific applications, such as PZT4 hard ceramics (mechanical quality factor  $Q_m \approx 500$ , piezoelectric coefficient  $d_{33} \approx 300$  pC/N), PZT5 soft ceramics ( $Q_m \approx 80$ ,  $d_{33} \approx 600$  pC/N), and PZT8 ultra hard ceramics ( $Q_m \approx 1000$ ,  $d_{33} \approx 200$  pC/N) [2]. The hard piezoelectric ceramics have low dielectric loss and large mechanical quality factor, indicating that less heat will be generated by the mechanical vibration under resonant frequency, which are favorable to the fabrication of piezoelectric actuators working continuously under resonant frequency; however, the piezoelectric coefficient  $d_{33}$  for hard ceramics is relatively lower than soft piezoelectric ceramics. As a result, piezoelectric actuators fabricated by hard ceramics provide small driving force. On the contract, the soft piezoelectric ceramics with high  $d_{33}$  can provide larger driving force and displacement under electric field; however, the relatively high dielectric loss and small mechanical quality factor lead to severe self-heating and degradation of the device performance if working continuously. Consequently, various

---

✉ Shuxiang Dong  
sxdong@pku.edu.cn

✉ Zhongqiang Hu  
z.hu@neu.edu

<sup>1</sup> School of Electrical Engineering and Automation, Henan Polytechnic University, Jiaozuo 454000, China

<sup>2</sup> School of Physics and Technology, Wuhan University, Wuhan 430072, China

<sup>3</sup> Department of Materials Science and Engineering, Peking University, Beijing 100081, China

<sup>4</sup> School of Materials Science and Engineering, Shanghai University, Shangda Road No. 99, Shanghai 200072, China

<sup>5</sup> Department of Electrical and Computer Engineering, Northeastern University, Boston, MA 02115, USA

piezoelectric ceramics with specifically designed properties should be developed for different applications [2].

The Curie temperatures ( $T_C$ ) of PZT ceramics are in the range of 180–386 °C varying with different compositions, and generally the operating temperatures have been limited to one half of the  $T_C$  ( $\leq 120$  °C) due to the depoling and the increase in leakage current at high temperature [5]. Recently, the automotive, petrochemical, and aerospace industries have shown their strong needs for actuating and sensing at high temperature. Specifically, in combustion engines, fuel injector controlled by ultrasonic motors has to work at  $\approx 150$  °C continually; In deep oil wells, sensors and transformers should work at about 120–200 °C; Converters and actuators in aircraft need to work at 150–300 °C [5–7]. Therefore, it is highly desired to search for novel high  $T_C$  piezoelectric materials with high performance.

In 2001, Eitel et al. [8, 9] reported new high temperature perovskite systems  $(100 - x)\text{BiScO}_3 - x\text{PbTiO}_3$  (BSPT $_x$ ). The BSPT64 system exhibits a high  $T_C$  of  $\approx 450$  °C near the morphotropic phase boundary (MPB) as well as a high piezoelectric coefficient  $d_{33}$  of  $\approx 460$  pC/N, showing promising potential for high temperature and high stability piezoelectric device applications [7–16]. However, the mechanical quality factor is too small ( $Q_m \approx 25$ ) and the dielectric loss is relatively high ( $\tan \delta \approx 0.04$ ), both of which are typical characteristics of soft piezoelectrics. To make it practically useful in the fields of piezoelectric actuators, transducers, sensors and ultrasonic motors, the BSPT system needs to be modified by doping, i.e., to improve the mechanical quality factor and decrease the dielectric loss while maintaining a piezoelectric coefficient  $d_{33}$  of  $>200$  pC/N.

In piezoelectric materials, acceptor dopants such as  $\text{Mn}^{2+,3+}$  play a hardening role by pinning domain wall motion and thus reducing internal loss and enhancing coercive field, but at the expense of decreasing dielectric and piezoelectric performance [17–20]. On the other hand, it is well known that piezoelectric ceramics near the MPB composition have anomalously high dielectric and piezoelectric properties as a result of enhanced polarizability arising from the coupling between two phases, allowing optimum domain reorientation during the poling process [11–16]. In order to achieve high values of  $Q_m$  while maintaining good dielectric and piezoelectric behavior in one material, the composition chosen for ion doping should be close to MPB. It was reported that the MPB composition in BSPT was near BSPT64 [9]. Zhang and Chen et al. reported the Mn-doped BSPT66 and BSPT64 ceramics and found that doping with Mn could increase the resistance and  $Q_m$  while decreasing the dielectric loss [7, 17–20]. Recently, a more detailed study showed that the best piezoelectric performance was in the composition of  $0.365\text{BiScO}_3 - 0.635\text{PbTiO}_3$  [10, 21]. However, there is no report on doping

of this composition in the literature. Therefore, in this work, we report on doping with acceptor dopants  $\text{MnO}_2$  in the composition of  $0.365\text{BiScO}_3 - 0.635\text{PbTiO}_3$ . The relationships between the content of  $\text{MnO}_2$  and the structural, ferroelectric, piezoelectric as well as the dielectric properties were studied. The mechanism of acceptor dopants modifying electrical properties of BSPT was also discussed.

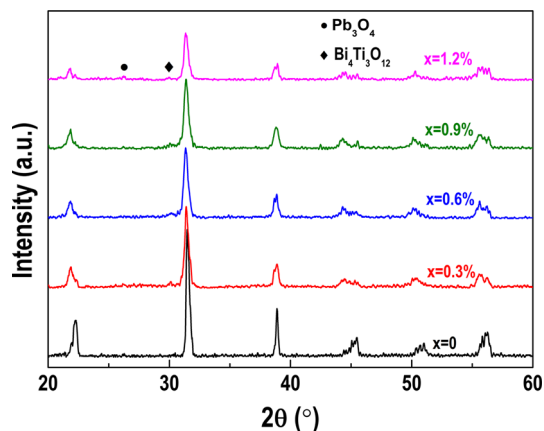
## 2 Experimental procedures

$0.365\text{BiScO}_3 - 0.635\text{PbTiO}_3 - x\text{MnO}_2$  ceramics (with  $\text{MnO}_2$  weight fraction  $x = 0, 0.3, 0.6, 0.9$  and  $1.2$  wt%) were prepared by the conventional solid-state reaction [16]. High purity ( $>99.9\%$ ) powders of  $\text{Bi}_2\text{O}_3$ ,  $\text{Sc}_2\text{O}_3$ ,  $\text{TiO}_2$  and  $\text{PbO}$  were weighed according to the stoichiometric compositions. Raw materials were milled and calcined for 3 h at 650 °C to obtain BSPT powders. Different contents of  $\text{MnO}_2$  were then added into the calcined powders, and ball milled for 24 h. The mixtures were then pressed into pellets and sintered at 1000 °C for 3 h. The sintered ceramic pellets have a density of  $>95\%$  of the theoretical value. With increasing Mn content, the color of the ceramics changed from light yellow to black.

Crystal structures of the ceramics were analyzed by X-ray diffraction (XRD, Bruker D8 Advance) with  $\text{Cu K}\alpha$  radiation. In order to measure the electrical properties, the ceramic pellets were carefully grounded down to  $\sim 1$  mm and electroded with silver paste on both sides. The ferroelectric hysteresis loops were characterised by a ferroelectric test system (Precision Premier Workstation, Radiant Technologies). The pellets were poled in a silicon oil bath under an electric field of 40 kV/cm at 125 °C for 15 min. After poling, the samples were aged for 24 h. The piezoelectric coefficient  $d_{33}$  was tested by Berlincourt-style  $d_{33}$  meter (ZJ-3A, IAAS). The dielectric properties at different temperatures were measured by an impedance analyzer (Agilent HP 4294 A) connected to a furnace.

## 3 Results and discussion

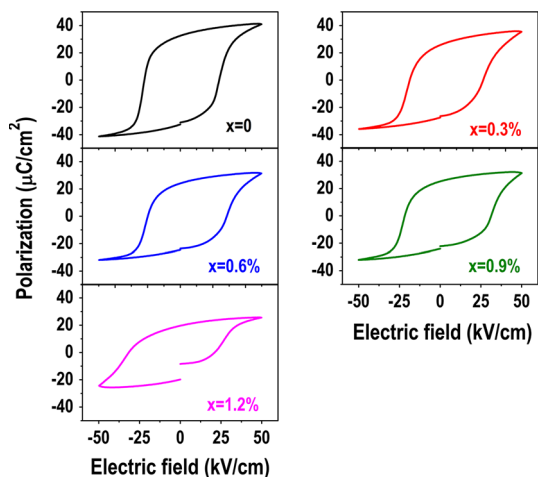
Figure 1 shows the XRD patterns of the Mn-doped BSPT Ceramics. Recently, the phase boundary near the composition of  $0.365\text{BiScO}_3 - 0.635\text{PbTiO}_3$  has been identified as a mixture of a tetragonal P4 mm phase and a monoclinic phase with space group Cm [20–22]. With the doping of Mn, the intensity of (001) peak increases while (100) peak decreases. This result implies that the tetragonal distortion  $c/a$  is reduced with Mn doping, which is consistent with earlier report [17, 18]. We can also see some extra peaks in the XRD patterns. The small peaks near 26° and 30° are probably from  $\text{Pb}_3\text{O}_4$  (PDF#41-1493) and  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$



**Fig. 1** XRD patterns of Mn-doped BSPT ceramics

(PDF#72-1019), respectively. These impurities may arise from the excess Pb and Bi that were used to compensate for the loss during the high temperature synthesis process.

Figure 2 shows ferroelectric hysteresis loops of BSPT ceramics with different MnO<sub>2</sub> contents. Pure BSPT ceramics have a typical rectangular-like *P-E* loop with a remanent polarization of 32.5 μC/cm<sup>2</sup> and a coercive field of 23 kV/cm. As the MnO<sub>2</sub> content increases, the value of remanent polarization decreases gradually while the coercive field increases. It is known that after sintered at 1000 °C, Mn cations turn into divalent and trivalent ions (Mn<sup>2+</sup> and Mn<sup>3+</sup>), which will be incorporated into the B-site of the perovskite structure to replace the Sc<sup>3+</sup> and Ti<sup>4</sup> as acceptors [18]. To maintain the charge neutrality, positively charged oxygen vacancies are created with the addition of acceptor dopants. Oxygen vacancies combined with negatively charged acceptor sites (such as Mn<sup>′</sup><sub>Ti</sub> or Mn<sup>″</sup><sub>Ti</sub>) form oriented defect dipoles, which would pin the



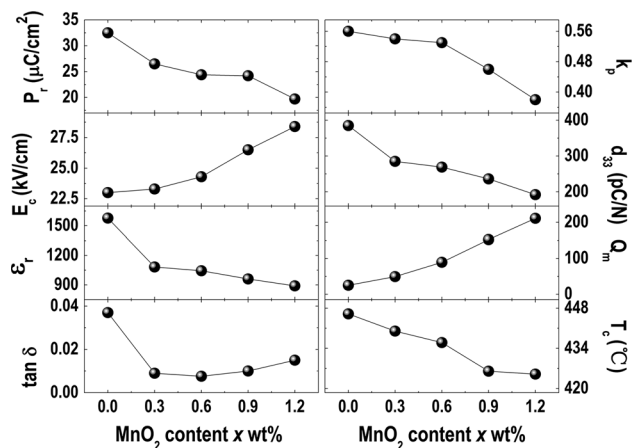
**Fig. 2** Ferroelectric hysteresis loops of BSPT ceramics with different MnO<sub>2</sub> contents

ferroelectric domain walls and increase the mechanical quality factor as well as the coercive field of piezoelectrics [2, 23–25]. When the doping content is as high as 1.2 wt%, the hysteresis loop is asymmetric, as shown in Fig. 2. This is because the content of MnO<sub>2</sub> has exceeded the solid solubility. The extra Mn ions accumulate at the grain boundaries, thereby influence the polarization switching [2].

Figure 3 shows the ferroelectric, dielectric, and piezoelectric properties of BSPT ceramics at room temperature as functions of MnO<sub>2</sub> content. It is found that as the MnO<sub>2</sub> content increases, electromechanical coupling factor *k<sub>p</sub>*, piezoelectric coefficient *d<sub>33</sub>*, dielectric constant  $\epsilon_r$ , dielectric loss *tan δ* as well as Curie temperature *T<sub>c</sub>* decrease and mechanical quality factor *Q<sub>m</sub>* increases. These changes of electrical properties are due to the hardening effect of Mn additive. When *x* ≥ 0.9 wt%, *tan δ* increases gradually which is probably caused by the accumulation of Mn ions around grain boundaries [25, 26].

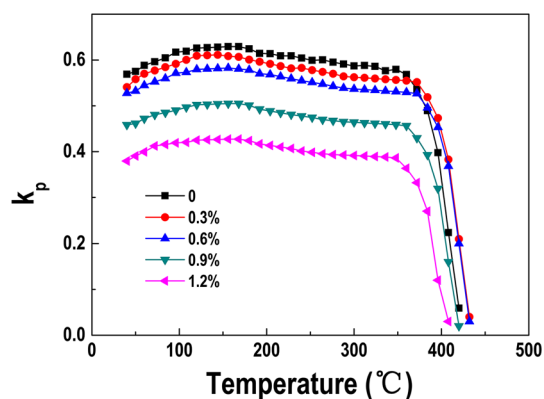
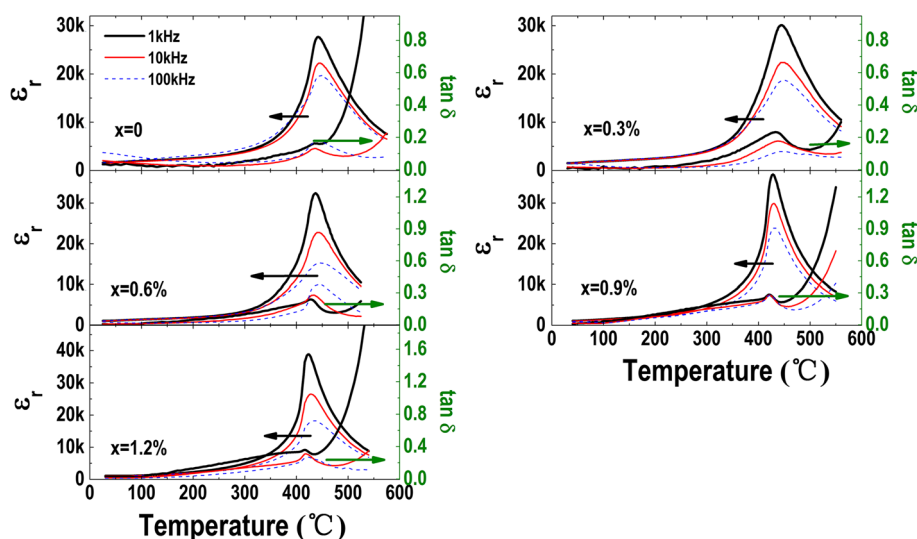
Figure 4 presents the dielectric constant and dielectric loss as functions of temperature and frequency for BSPT ceramics. *T<sub>c</sub>* is determined by the temperature corresponding to the dielectric peak. Multiple frequency dielectric measurements show no variation of *T<sub>c</sub>* with frequency (1, 10, and 100 kHz). The *T<sub>c</sub>* of pure BSPT ceramics is 446 °C, which decreases rapidly with increasing Mn content, in good agreement with previous reports [18–20]. When *x* ≥ 0.9 wt%, *T<sub>c</sub>* decreases slightly.

Figure 5 shows the temperature dependence of electromechanical coupling factor *k<sub>p</sub>* of MnO<sub>2</sub> -doped BSPT ceramics. As the temperature increases from room temperature to ~200 °C, *k<sub>p</sub>* increases slightly (<10 %) at first due to the increase in thermal energy of domains. In this situation, a relatively low excitation energy is enough to make domains switch, thus the external polarization



**Fig. 3** Electrical properties of BSPT ceramics at room temperature as functions of MnO<sub>2</sub> content

**Fig. 4** Dielectric constant and dielectric loss as functions of temperature and frequency for Mn-doped BSPT ceramics



**Fig. 5** Temperature dependence of  $k_p$  for Mn-doped BSPT ceramics

increases with the temperature [14, 15, 27]. When the temperature is lower than 360 °C, the value of  $k_p$  has little change with the temperature. At high temperature (>360 °C), the dramatic decrease of  $k_p$  is caused by thermal de-poling [2]. Therefore, it is observed that Mn-doped BSPT ceramics exhibit excellent thermal stability.

#### 4 Conclusions

In summary, Mn-doped  $0.365\text{BiScO}_3\text{-}0.635\text{PbTiO}_3$  high-temperature piezoelectric ceramics were prepared by conventional solid state reaction. The structural, ferroelectric, dielectric, and piezoelectric properties of these ceramics were studied. XRD results showed that rhombohedral and tetragonal structures were coexistent in Mn-modified BSPT piezoelectric ceramics without impurity phase. The hardening effect of Mn additive considerably decreased the dielectric loss and increased the mechanical quality factor. High  $Q_m \approx 210$  with  $d_{33} = 200$  pC/N were obtained in

BSPT ceramics doped with 1.2 wt% of Mn. Besides, the de-poling temperature of BSPT ceramics was 360 °C and revealed excellent thermal stability. These results indicated that hard BSPT piezoelectric ceramics are promising for high-temperature actuator applications.

**Acknowledgments** This work was supported by the National Natural Science Foundation of China (Grant Nos. U1304608, 51372174, 51132001, 51072003, and 51302163).

#### References

1. B. Jaffe, W.R. Cook, H. Jaffe, *Piezoelectric Ceramics* (Academic Press, London, 1971)
2. K. Uchino, *Piezoelectric Actuators and Ultrasonic Motors* (Kluwer Academic Publishers, Boston, 1997)
3. S. Dong, J.F. Li, D. Viehland, *Appl. Phys. Lett.* **85**(12), 2307 (2004)
4. S. Dong, J. Zhai, J.F. Li, D. Viehland, S. Priya, *Appl. Phys. Lett.* **93**(10), 103511 (2008)
5. R.C. Turner, P.A. Fueierer, R.E. Newnham, T.R. Shorout, *Appl. Acoust.* **41**(4), 299–324 (1994)
6. A. Sehrioglu, A. Sayir, F. Dynys, *J. Appl. Phys.* **106**(1), 014102 (2009)
7. S. Zhang, R.E. Eitel, C.A. Randall, T.R. Shrou, E.F. Alberta, *Appl. Phys. Lett.* **86**(26), 262904 (2005)
8. R.E. Eitel, C.A. Randall, T.R. Shrou, P.W. Rehrig, W. Hackenberger, S.-E. Park, *Jpn. J. Appl. Phys.* **40**(10), 5999–6002 (2001)
9. R.E. Eitel, C.A. Randall, T.R. Shrou, S.-E. Park, *Jpn. J. Appl. Phys.* **41**(Part 1, No. 4A), 2099–2104 (2002)
10. T. Zou, X. Wang, H. Wang, C. Zhong, L. Li, I.W. Chen, *Appl. Phys. Lett.* **93**(19), 192913 (2008)
11. S. Zhang, R. Xia, C.A. Randall, T.R. Shrou, R. Duan, R.F. Speyer, *J. Mater. Res.* **20**(8), 2067–2071 (2005)
12. J. Cheng, R. Eitel, N. Li, L.E. Cross, *J. Appl. Phys.* **94**(1), 605 (2003)
13. C.A. Randall, R.E. Eitel, B. Jones, T.R. Shrou, *J. Appl. Phys.* **95**(7), 3633 (2004)
14. I. Sterianou, D.C. Sinclair, I.M. Reaney, T.P. Comyn, A.J. Bell, *J. Appl. Phys.* **106**(8), 084107 (2009)

15. A. Sehirlioglu, A. Sayir, F. Dynys, *J. Am. Ceram. Soc.* **93**(6), 1718–1724 (2010)
16. Z. Hu, J. Chen, M. Li, X. Li, G. Liu, S. Dong, *J. Appl. Phys.* **110**(6), 064102 (2011)
17. S. Zhang, E.F. Alberta, R.E. Eitel, C.A. Randall, T.R. Shrout, *IEEE Trans. Ultrason. Ferroelectr. Freq. Control* **52**(11), 2131–2139 (2005)
18. J. Chen, Z. Hu, H. Shi, M. Li, S. Dong, *J. Phys. D Appl. Phys.* **45**, 465303 (2012)
19. J. Chen, Z. Chen, X. Li, S. Dong, *Appl. Phys. Lett.* **102**, 052902 (2013)
20. J. Chen, J. Cheng, S. Dong, *J. Adv. Dielectr.* **04**, 1430002 (2014)
21. S. Zhang, X. Wang, L. Li, *Ferroelectrics* **450**(1), 28–34 (2013)
22. K. Datta, D. Walker, P.A. Thomas, *Phys. Rev. B* **82**, 144108 (2010)
23. M.D. Drahos, P. Jakes, E. Erdem, S. Schaab, J. Chen, M. Ozerov, S. Zvyagin, R.-A. Eichel, *Phys. Rev. B* **84**(6), 064113 (2011)
24. T. Kamiya, T. Suzuki, T. Tsurumi, M. Daimon, *Jpn. J. Appl. Phys.* **31**, 3058–3060 (1992)
25. H.-Y. Park, C.-H. Nam, I.-T. Seo, J.-H. Choi, S. Nahm, H.-G. Lee, K.-J. Kim, S.-M. Jeong, *J. Am. Ceram. Soc.* **93**(9), 2537–2540 (2010)
26. Y. Hou, M. Zhu, F. Gao, H. Wang, B. Wang, H. Yan, C. Tian, *J. Am. Ceram. Soc.* **87**(5), 847–850 (2004)
27. Q. Zhang, Z. Li, F. Li, Z. Xu, X. Yao, *J. Am. Ceram. Soc.* **93**(10), 3330–3334 (2010)