

High piezoelectricity by multiphase coexisting point: Barium titanate derivatives

Jinghui Gao¹, Xiaoqin Ke², Matias Acosta³, Julia Glaum⁴, Xiaobing Ren^{1,5*}

1. State Key Laboratory of Electrical Insulation and Power Equipment and Multi-disciplinary Materials Research Center, Frontier Institute of Science and Technology, Xi'an Jiaotong University, Xi'an, 710049, China
2. Frontier Institute of Science and Technology, and State Key Laboratory for Mechanical Behavior of Materials, Xi'an Jiaotong University, Xi'an, 710049, China
3. Institute of Materials Science, Technische Universität Darmstadt, Darmstadt 64287, Germany
4. Department of Materials Science and Engineering, NTNU - Norwegian University of Science and Technology, Sem Sælands vei 12, 7491 Trondheim, Norway
5. Center for Advanced Functional Materials, National Institute for Materials Science, Tsukuba, 305-0047, Ibaraki, Japan

Corresponding authors: a) ren.xiaobing@nims.go.jp

BaTiO₃(BT)-based lead-free piezoelectric materials have long been known as “a mediocre class of piezoelectric materials”. They have redrawn significant attention in recent years since the discovery of high piezoelectricity in Ba(Zr,Ti)O₃-(Ba,Ca)TiO₃ (BZT-BCT) and subsequently in its generic systems Ba(Sn,Ti)O₃-(Ba,Ca)TiO₃ (BST-BCT) and Ba(Hf,Ti)O₃-(Ba,Ca)TiO₃ (BHT-BCT). The unexpectedly high piezoelectricity in this class of BT-based materials calls for an explanation and thus has stimulated significant research activities. We present here a concise discussion on the notions leading to high piezoelectricity in BT-based systems. The possible role of a multi-phase-coexisting point (MCP) is highlighted.

Keywords: barium titanate, Pb-free, high-piezoelectric response, phase convergent point/region

Barium titanate (BaTiO_3 (BT)) was discovered in 1940's during World War II¹. Before the emergence of $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$ (PZT) in late 1950's, it had been the most important piezoelectric material due to its sizable piezoelectricity of $d_{33}=120\text{-}190\text{pC/N}$, which is significantly higher than that of older piezoelectric materials such as triglycine sulphate(TGS), KH_2PO_4 (KDP), quartz, etc. However, compared with PZT, which shows outstanding piezoelectricity with $d_{33}=350\text{-}700\text{pC/N}^2$, BT and BT-based materials appeared to be “mediocre” in terms of both piezoelectricity and T_c (about 130°C). Thus, they were soon replaced by PZT in piezoelectric applications³. It should be noted that although pure BT can show higher piezoelectricity in some special forms like single crystal^{4,5}, textured polycrystal⁶, or fine-grain/domain ceramic^{7,8}, it is challenging to achieve PZT-like, intrinsically high piezoelectricity in simple chemically-modified BT-based ceramics.

The Pb-free surge over the past 20 years has revived the research on the piezoelectricity of BT-based materials, in an attempt to discover a BT-based ceramic that can be comparable with PZT in piezoelectricity⁴⁻¹⁰. In 2009, Liu and Ren reported large piezoelectric response for the $\text{Ba}(\text{Zr}, \text{Ti})\text{O}_3$ - $(\text{Ba}, \text{Ca})\text{TiO}_3$ (BZT-BCT) ceramic system with a $d_{33} > 600\text{pC/N}$, which is comparable with soft PZT ceramics¹¹. These ceramics are made simply by standard solid-state reaction method, and their random polycrystalline feature suggested that the high piezoelectricity stems from its inherent effect. Further studies have shown that similar values of high piezoelectricity are also present in a generic class of BT-based materials including $\text{Ba}(\text{Sn}, \text{Ti})\text{O}_3$ - $(\text{Ba}, \text{Ca})\text{TiO}_3$ (BST-BCT) and $\text{Ba}(\text{Hf}, \text{Ti})\text{O}_3$ - $(\text{Ba}, \text{Ca})\text{TiO}_3$ (BHT-BZT)¹²⁻¹⁵. In contrast to the mediocre piezoelectricity of BT-based ceramics reported over the past 60 years, such soft-PZT-like piezoelectricity in BT-based ceramics is a surprise for the piezoelectric community and thus calls for an explanation. Significant efforts have been made towards this aim¹⁶⁻²⁶. In the following, we shall provide a brief review of the state-of-the-art of key results and current understanding. A more comprehensive review can be referred to reference²⁷.

Generic phase diagram

The common feature of these high-performance BaTiO_3 -based systems (BZT-BCT, BST-BCT, BHT-BCT) is that they exhibit similar phase diagrams, as depicted in **Figure 1a-c**¹¹⁻¹³. They all exhibit a PZT-like phase diagram characterized by a morphotropic phase boundary (MPB) separating two ferroelectric phases (tetragonal (T) and rhombohedral (R))^{11,28-31}. As highlighted in **Figure 1a-c**, the most important feature of the phase diagrams in this generic class of materials is that MPB starts from a multi-phase coexisting point (MCP) in the phase diagrams, where cubic (C), T, R, and O phases meet. We shall show later that MCP will result in important consequences that account for the high piezoelectricity of

this new class of BT-based materials.

More detailed recent investigations suggest the existence of a bridging orthorhombic (O) phase in BZT-BCT between the T and R phases at MPB so that the MPB is no longer a line but becomes an extended O phase³²⁻³⁵ (**Figure 1d**). It is likely that the bridging O phase also exists in BST-BCT and BHT-BCT systems and further studies need to check this speculation.

Interestingly, the research development in BZT-BCT is similar to that of PZT, where MPB was initially reported to be a line separating R and T phases, but later turned out to be a bridging monoclinic phase³⁶. The existence of bridging O phase at MPB suggests that the MCP is not a C-T-R triple point but a C-T-O-R multi-phase coexisting point. It is noted that there is an issue about concerning the MCP being described as a point or an extended region^{37,38}. Further research is needed to clarify this issue.

Properties in relation to MPB and MCP

Figure 2 depicts an example that ferroelectricity, dielectric permittivity, and more importantly piezoelectricity shows maximum values around the MPB composition in BZT-BCT¹¹, and similar results have been found in BST-BCT and BHT-BCT^{12,13}. In these systems, the optimal d_{33} at the MPB can reach 500-620pC/N, comparable with that of soft PZT. It is also found that the permittivity peaks at the MCP, showing $\epsilon_r \sim 25,000$, which is much higher than that of the pure BT ceramic ($\sim 10,000$)^{11,39}. This suggests that the MCP is the most field-susceptible location in the phase diagram.

Given that BT and normal BT-based ceramics do not show high piezoelectricity, the anomalously high piezoelectricity in BZT-BCT generic systems needs an explanation. Much effort has been made in the attempt to answer this important question¹⁶⁻²⁶. Factors such as elastic softening^{37, 38,40-42}, high domain wall mobility^{16,17}, phase instability^{18,43} and degree of poling^{19,38} have been considered but no single factor is considered deterministic. The role of these factors in improving the piezoelectric performance can be referred to recent review papers^{27,28}. In the following, we shall show that the high piezoelectricity of the BZT-BCT generic systems stems from the MCP in the system, and this explains why normal BT and other BT-based systems do not show impressive piezoelectricity (in random polycrystalline form).

Tricriticality and microstructural anomaly at the MCP

Figure 3a presents that the MCP is not merely a point where C, T, R, and O phases meet; it is a tricritical point, i.e., a point where 1st-order transition crossovers into a 2nd order transition, as characterized by vanishing transition hysteresis and latent heat^{11,44}. This means that at the MCP there exists no energy barrier among the four phases and thus this corresponds to a completely flat or frying-pan-shaped free energy landscape¹¹ as provided in **Figure 3b1, b2**. This can make a difference between

the BZT-BCT generic systems and other BT-based systems and thus provides an explanation for the unexpectedly high piezoelectricity.

Figure 4 shows that the tricriticality of the MCP yields interesting microstructural features^{39,44-47} unseen in standard BT-based materials. At the MCP (the tricritical point), mottled nanodomains appear with blurred boundaries^{39,44}, contrasting with large hierarchical domains in the off-MCP compositions. The isotropic nanodomains at the MCP are consistent with the vanishing polarization anisotropy or vanishing energy barriers⁴⁴. The off-MCP compositions show a hierarchical domain structure at the MPB in BZT-BCT^{30,31,48-52}, which indicates low but non-vanishing polarization anisotropy¹¹ (as indicated in **Figure 3c1, c2**). Therefore, the high piezoelectric performance at MPB seems to stem from the vanishing polarization anisotropy at MCP.

Modelling

Effort has been made to understand the observed experimental phenomena using Landau-Devonshire-type phenomenological models⁵³⁻⁵⁵. However, so far there is no predictive theory that can explain why the BZT-BCT generic systems show a tricritical MCP and high piezoelectricity whereas normal BT-based materials do not. This is at the heart of the problem and awaits future theoretical efforts.

Summary

In conclusion, we give a brief review of the phase diagrams, piezoelectric property, microstructure, and theoretical modelling for BZT-BCT-type generic systems. The role of the multi-phase coexisting point (MCP) and the MPB region starting from a MCP in enhancing the piezoelectric performance is highlighted. The understanding of high piezoelectricity in the hitherto “mediocre” BT-based piezoelectric materials may be transferable to understanding and developing high-performance Pb-free piezoelectric materials in other systems^{56,57}.

Acknowledgements

The authors thank Yan Wang, Yongbin Liu and Zhixin He for helpful discussion, and gratefully acknowledge the support of National Basic Research Program of China (Grant No. 2012CB619401), the National Natural Science Foundation of China (Grant Nos. 51571156, 51321003, 51302209, 51431007, and 51320105014), and Program for Changjiang Scholars and Innovative Research Team in University (IRT13034). J. G acknowledges the Fundamental Research Funds for the Central Universities for financial support.

References

1. F. Jona, G. Shirane, *Ferroelectric Crystals* (Pergamon Press, Oxford, UK, 1962).
2. T.R. Shrout, S.J. Zhang, *J. Electroceram.* **19** 113 (2007).
3. B. Jaffe, W. R. Cook, H. Jaffe, *Piezoelectric Ceramics* (Academic Press, New York, 1971).
4. T. Sluka, A.K. Tagantsev, D. Damjanovic, M. Gureev, N. Setter, *Nat. Commun.* **3** 748 (2012)
5. S. Wada, K. Yako, H. Kakemoto, T. Tsurumi, T. Kiguchi, *J. Appl. Phys.* **98** 014109 (2005)
6. S. Wada, K. Takeda, T. Muraishi, H. Kakemoto, T. Tsurumi, T. Kimura, *Ferroelectrics.* **373** 11 (2008)
7. T. Karaki, K. Yan, T. Miyamoto, M. Adachi, *Jpn. J. Appl. Phys.* **46** 97 (2007)
8. Z.Y. Shen, J.F. Li, *J. Ceram. Soc. Jpn.* **118** 940 (2010)
9. X. Ren, *Nat. Mater.* **3** 91 (2004)
10. M. Budimir, D. Damjanovic, N. Setter, *Phys. Rev. B.* **72** 064107 (2005)
11. W. Liu, X. Ren, *Phys. Rev. Lett.* **103** 257602 (2009)
12. D. Xue, Y. Zhou, H. Bao, J. Gao, C. Zhou, X. Ren, *Appl. Phys. Lett.* **99** 122901 (2011)
13. C. Zhou, W. Liu, D. Xue, X. Ren, H. Bao, J. Gao, L. Zhang, *Appl. Phys. Lett.* **100** 222910 (2012)
14. L. Zhao, B.P. Zhang, P.F. Zhou, L.F. Zhu, J.F. Li, *J. Eur. Ceram. Soc.* **35** 533 (2015).
15. L.F. Zhu, B.P. Zhang, X.K. Zhao, L. Zhao, F.Z. Yao, X. Han, P.F. Zhou, J.F. Li, *Appl. Phys. Lett.* **103** 072905 (2013).
16. J. Gao, X. Hu, L. Zhang, F. Li, L. Zhang, Y. Wang, Y. Hao, L. Zhong, X. Ren, *Appl. Phys. Lett.* **104** 252909 (2014)
17. G. Tutuncu, B. Li, K. Bowman, J.L. Jones, *J. Appl. Phys.* **115** 144104 (2014)
18. W. Wang, L.D. Wang, W.L. Li, D. Xu, Y.F. Hou, W.P. Cao, Y. Feng, W.D. Fei, *Ceram. Int.* **40** 14907 (2014)
19. M.C. Ehmke, J. Glaum, M. Hoffman, J.E. Blendell, K.J. Bowman, *J. Am. Ceram. Soc.* **96** 9 (2013)
20. M. Acosta, N. Novak, G.A. Rossetti, J. Rodel, *Appl. Phys. Lett.* **107** 142906 (2015)
21. M.C. Ehmke, N.H. Khansur, J.E. Daniels, J.E. Blendell, K.J. Bowman, *Acta Mater.* **66** 340 (2014)
22. F. Li, L. Jin, R. Guo, *Appl. Phys. Lett.* **105** 232903 (2014)
23. M. Acosta, L.A. Schmitt, C. Cazorla, A. Studer, A. Zintler, J. Glaum, H.J. Kleebe, W. Donner, M. Hoffman, J. Rodel, M. Hinterstein. *Sci. Rep-UK.* **6** 28742 (2016)
24. V. Rojas, J. Koruza, E.A. Patterson, M. Acosta, X. Jiang, N. Liu, C. Dietz, J. Rodel, *J. Am. Ceram. Soc.* **100** 4699 (2017)
25. H.I. Humburg, M. Acosta, W. Jo, K.G. Webber, J. Rodel, *J. Eur. Ceram. Soc.* **35** 1209 (2015)
26. L. Zhao, X. Ke, W. Wang, L. Zhang, C. Zhou, Z. Zhou, L. Zhang, X. Ren, *Phys. Rev. B.* **95** 020101 (2017)
27. M. Acosta, N. Novak, V. Rojas, S. Patel, R. Vaish, J. Koruza, G.A. Rossetti Jr., J. Rodel, *Appl. Phys. Rev.* **4** 041305 (2017)
28. M.C. Ehmke, S.N. Ehrlich, J.E. Blendell, K.J. Bowman, *J. Appl. Phys.* **111** 124110 (2012)
29. A.B. Haugen, J.S. Forrester, D. Damjanovic, B. Li, K.J. Bowman, J.L. Jones, *J. Appl. Phys.* **113** 014103 (2013)
30. J. Gao, D. Xue, Y. Wang, D. Wang, L. Zhang, H. Wu, S. Guo, H. Bao, C. Zhou, W. Liu, *Appl. Phys. Lett.* **99** 092901 (2011)
31. J. Gao, L. Zhang, D. Xue, T. Kimoto, M. Song, L. Zhong, X. Ren, *J. Appl. Phys.* **115** 054108 (2014)
32. D.S. Keeble, F. Benabdallah, P.A. Thomas, M. Maglione, J. Kreisel, *Appl. Phys. Lett.*, **102** 092903 (2013)

33. L. Zhang, M. Zhang, L. Wang, C. Zhou, Z. Zhang, Y. Yao, L. Zhang, D. Xue, X. Lou, X. Ren, *Appl. Phys. Lett.* **105** 162908 (2014)
34. D. Damjanovic, A. Biancoli, L. Batooli, A. Vahabzadeh, J. Trodahl, *Appl. Phys. Lett.* **100** 192907 (2012)
35. S. Zhukov, M. Acosta, Y.A. Genenko, H.V. Seggern, *J. Appl. Phys.* **118** 134104 (2015)
36. B. Noheda, D.E. Cox, G. Shirane, *Appl. Phys. Lett.* **74** 2059 (1999)
37. M. Acosta, N. Novak, W. Jo, J. Rodel, *Acta Mater.* **80** 48 (2014)
38. M. Acosta, N. Khakpash, T. Someya, N. Novak, W. Jo, H. Nagata, G.A. Rossetti, J. Rödel, *Phys. Rev. B.* **91** 104108 (2015)
39. J.H. Gao, X.H. Hu, Y. Wang, Y.B. Liu, L.X. Zhang, X.Q. Ke, L.S. Zhong, H. Zhao, X.B Ren, *Acta Mater.* **125** 177 (2017)
40. F. Benabdallah, A. Simon, H. Khemakhem, C. Elissalde, M. Maglione, *J. Appl. Phys.* **109** 124116 (2011)
41. D. Xue, Y. Zhou, H. Bao, J. Gao, C. Zhou, X. Ren, *J. Appl. Phys.* **109** 054110 (2011)
42. D. Xue, J. Gao, Y. Zhou, X. Ding, J. Sun, T. Lookman, X. Ren, *J. Appl. Phys.* **117** 124107 (2015)
43. D. R. J. Brandt, M. Acosta, J. Koruza, K. G. Webber, *J. Appl. Phys.* **115** 204107 (2014)
44. J. Gao, D. Ye, X.H. Hu, X.Q. Ke, L.S. Zhong, S.T. Li, L.X. Zhang, Yu. W, D. Wang, Y. Wang, Y.B. Liu, *Eur. Phys. Lett.*, **115** 37001 (2016).
45. J. Gao, D. Xue, W. Liu, C. Zhou, X. Ren, *actuators* **6** 3 (2017)
46. J. Gao, Y. Wang, Y. Liu, X. Hu, X. Ke, L. Zhong, Y. He, X. Ren, *Sci. Rep-UK.* **7** 40916 (2017).
47. J. Gao, Y. Liu, Y. Wang, X. Hu, W. Yan, X. Ke, L. Zhong, Y. He, X. Ren, *J. Phys. Chem. C*, **121** 13106 (2017).
48. H. Guo, C. Zhou, X. Ren, and X. Tan, *Phys. Rev. B* **89** 100104 (2014).
49. H. Guo, B. K. Voas, S. Zhang, C. Zhou, X. Ren, S. P. Beckman, and X.Tan, *Phys. Rev. B* **90** 014103 (2014).
50. M. Zakhosheva, L. A. Schmitt, M. Acosta, W. Jo, J. Rödel, and H.-J. Kleebe, *Appl. Phys. Lett.* **105**, 112904 (2014).
51. M. Zakhosheva, L. A. Schmitt, M. Acosta, H. Guo, W. Jo, R. Schierholz, H. J. Kleebe, and X. Tan, *Phys. Rev. Appl.* **3** 064018 (2015).
52. D. Xue, Y. Zhou, J. Gao, X. Ding, X. Ren, *Eur. Phys. Lett.* **100** 17010 (2012)
53. M. Porta, T. Lookman. *Phys. Rev. B*, **83** 174108 (2011).
54. A.A. Heitmann, G.A. Rossetti, *J. Am. Ceram. Soc.*, **97** 1661 (2014).
55. T. Yang, X. Ke, Y. Wang. *Sci. Rep-UK.* **6** 33392 (2016).
56. J. Gao, Y. Hao, S. Ren, T. Kimoto, M. Fang, H. Li, Y. Wang, L. Zhong, S. Li, X. Ren, *J. Appl. Phys.* **117** 084106 (2015).
57. J. Gao, S. Ren, L. Zhang, Y. Hao, M. Fang, M. Zhang, Y. Dai, X. Hu, D. Wang, L. Zhong, S. Li, *Appl. Phys. Lett.* **107** 032902 (2015).

Figure Captions

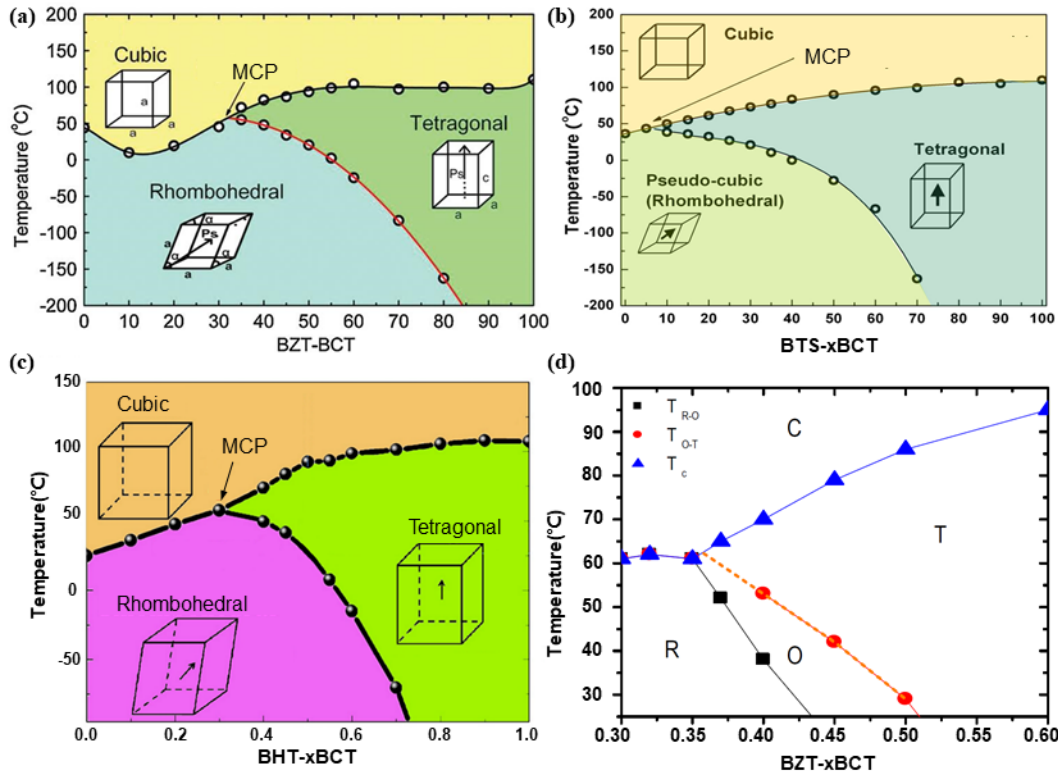


Figure 1. (a) The phase diagram of Ba(Zr,Ti)O₃-(Ba,Ca)TiO₃ (BZT-BCT) by Liu and Ren¹¹. The phase diagram of generic systems (b) Ba(Sn,Ti)O₃-(Ba,Ca)TiO₃ (BTS-BCT) by D. Xue et al.¹² and (c) Ba(Hf,Ti)O₃-(Ba,Ca)TiO₃ (BHT-BCT) by C. Zhou et al.¹³ (d) Modified phase diagram of BZT-BCT (M. Acosta et al.³⁷) which amends Liu-Ren phase diagram by adding an intermediate orthorhombic phase.

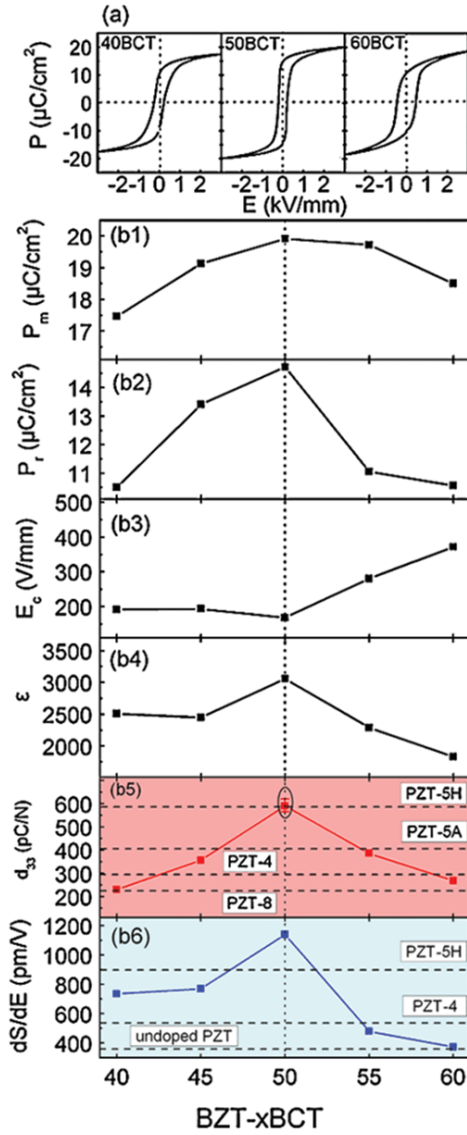


Figure 2. Ferroelectricity, dielectric permittivity, and piezoelectricity of $(1-x\%)\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3-x\%(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$ (abbreviated as BZT- x BCT) around MPB composition¹⁰. (a) Hysteresis loops of BZT-40BCT, BZT-50BCT, and BZT-60BCT. (b1) Saturation polarization P_m , (b2) Remnant polarization P_r , (b3) coercive field E_c , (b4) permittivity ϵ_r , (b5) piezoelectric coefficients d_{33} , and (b6) converse piezoelectric coefficient dS/dE .¹¹

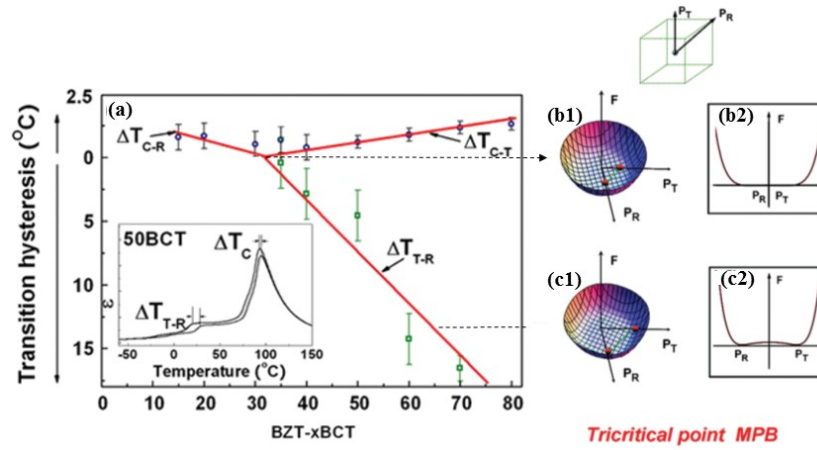


Figure 3.(a) Thermal hysteresis of the three transitions (C-T, C-R, and T-R) for BZT-xBCT ceramic approaching MCP. (b1),(b2) MCP tricritical point showing flat free energy landscape. (c1),(c2) MPB composition at room temperature showing low but non-vanishing free energy landscape.¹¹

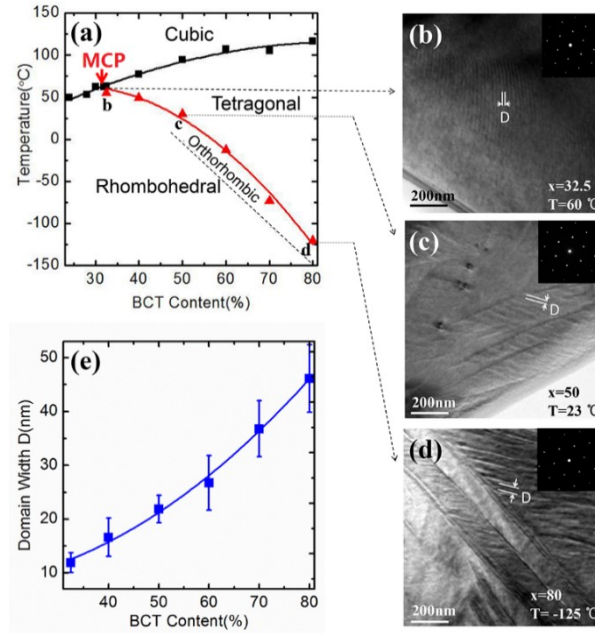


Figure 4. TEM observation for domain structures of BZT-xBCT on MPB line approaching to MCP tricritical point⁴⁴. (a) Phase diagram for BZT-BCT showing the locations for TEM observations; (b) At MCP tricritical point, mottled nanodomains appear with blurred boundaries. (c)-(d) Off-MCP compositions show hierarchical domain structure at MPB in BZT-xBCT. (e) Domain width decreases on approaching MCP.

Author biographies



Dr. Jinghui Gao (Xi'an Jiaotong University, No. 28, Xianning West Road, Xi'an 710049 China; Email: gaojinghui@mail.xjtu.edu.cn), is an associate professor in the State Key Laboratory of Electrical Insulation and Power Equipment at Xi'an Jiaotong University. He received his PhD from Xi'an Jiaotong University in 2012. During the period of 2009~2012, he worked at National Institute for Materials Science (Japan) for a joint program. His current research interests focus on functional dielectric materials and the correlated microstructure characterization. He has published more than 50 papers in peer-reviewed journals (over 1100 citations).



Dr. Xiaoqin Ke (Xi'an Jiaotong University, No. 28, Xianning West Road, Xi'an 710049 China, Phone:+86 02983395126; Fax: +86 02983395126; Email: kexiaoqin@xjtu.edu.cn), is currently a lecturer at the frontier institute of science and technology in Xi'an Jiaotong University. She received her PhD degree from the department of materials science and engineering at the Ohio State University in 2014. Her research interests mainly focus on modelling and designing of ferroelectric and ferromagnetic materials and she has published about 20 papers in this field.



Dr. Matias Acosta is a Feodor Lynen Fellow at the University of Cambridge (ma771@cam.ac.uk, 27 Charles Babbage Road, Cambridge CB3 0FS). His interests include synthesis and characterization of piezoelectric and ionic conductor ceramics and thin films. As Global Shaper, he works on projects at the interface between science and policy. M. Acosta received his engineering degree from Sabato Institute (Argentina, 2011) and doctoral degree with honors (summa cum laude) from the Technical University of Darmstadt (Germany, 2015). He published more than 30 articles (>900 citations), 2 pending patents, and 1 book.



Dr. Julia Glaum (Norwegian University of Science and Technology, Trondheim, Norway, Julia.glaum@ntnu.no), is an Adjunct Associate Professor in the Department of Materials Science and Engineering at NTNU. She received her PhD at TU Darmstadt, Germany in 2010 and conducted a Postdoc at UNSW Australia holding a Discovery Early Career Researcher Award. In 2015, she was awarded a Marie-Curie Fellowship by the European Research Council. Her research focusses on functional biomedical materials and fundamental switching phenomena in relaxor-ferroelectrics. She has published more than 50 papers being cited over 1000 times.



Prof. Xiaobing Ren

Professor, Frontier Institute for Science and Technology, Xi'an Jiaotong University, and Managing Researcher, National Institute for Materials Science. His research interest is centered on a wide range of ferroic materials, from ferroelectric/piezoelectric materials, shape memory alloys, to magnetostrictive materials. He has published more than 200 papers in peer-reviewed journals, including Nature, Science, Nature Materials, Physical Review Letters, etc. His papers have been cited for more than 11000 times and his research has made an impact on both academia and industry. He received Outstanding Young Researcher Award of Japan Institute of Metals and Materials (1998), and Tsukuba Outstanding Young Scientist Prize (2005), and Meritorious Award of Japan Institute of Metals and Materials (2011), and National Natural Science Prize of China (2016).