

# References

- [1] Su, J. & Zhang, J. Recent development on modification of synthesized barium titanate ( $\text{BaTiO}_3$ ) and polymer/ $\text{BaTiO}_3$  dielectric composites. *Journal of Materials Science: Materials in Electronics* **30**, 1957–1975 (2019).
- [2] Tsuda, K., Sano, R. & Tanaka, M. Nanoscale local structures of rhombohedral symmetry in the orthorhombic and tetragonal phases of  $\text{BaTiO}_3$  studied by convergent-beam electron diffraction. *Physical Review B* **86**, 214106 (2012).
- [3] Yang, S. *et al.* Large magnetostriction from morphotropic phase boundary in ferromagnets. *Physical Review Letters* **104**, 197201 (2010).
- [4] Li, F. *et al.* Piezoelectric activity in perovskite ferroelectric crystals. *IEEE transactions on ultrasonics, ferroelectrics, and frequency control* **62**, 18–32 (2015).
- [5] Anju Balaraman, A. & Dutta, S. Inorganic dielectric materials for energy storage applications: a review. *Journal of Physics D: Applied Physics* **55**, 183002 (2022).
- [6] Acosta, M. *et al.*  $\text{BaTiO}_3$ -based piezoelectrics: Fundamentals, current status, and perspectives. *Applied Physics Reviews* **4**, 041305 (2017).
- [7] Fu, D., Itoh, M., Koshihara, S.-y., Kosugi, T. & Tsuneyuki, S. Anomalous phase diagram of ferroelectric  $(\text{Ba,Ca})\text{TiO}_3$  single crystals with giant electromechanical response. *Physical Review Letters* **100**, 227601 (2008).
- [8] Yao, Y. *et al.* Large piezoelectricity and dielectric permittivity in  $\text{BaTiO}_3$ - $x\text{BaSnO}_3$  system: The role of phase coexisting. *EPL (Europhysics Letters)* **98**, 27008 (2012).
- [9] Shi, T., Xie, L., Gu, L. & Zhu, J. Why Sn doping significantly enhances the dielectric properties of  $\text{Ba}(\text{Ti}_{1-x}\text{Sn}_x)\text{O}_3$ . *Scientific Reports* **5**, 8606 (2015).
- [10] Akbarzadeh, A., Prosandeev, S., Walter, E. J., Al-Barakaty, A. & Bellaiche, L. Finite-temperature properties of  $\text{Ba}(\text{Zr,Ti})\text{O}_3$  relaxors from first principles. *Physical Review Letters* **108**, 257601 (2012).
- [11] Liu, W. & Ren, X. Large piezoelectric effect in Pb-free ceramics. *Physical Review Letters* **103**, 257602 (2009).
- [12] Yang, T., Ke, X. & Wang, Y. Mechanisms responsible for the large piezoelectricity at the tetragonal-orthorhombic phase boundary of  $(1-x)\text{Ba}(\text{Zr}_{0.20}\text{Ti}_{0.80})\text{O}_3$ - $x(\text{Ba}_{0.70}\text{Ca}_{0.30})\text{TiO}_3$  system. *Scientific Reports* **6**, 33392 (2016).

- [13] Xue, D. *et al.* Large piezoelectric effect in Pb-free Ba(Ti,Sn)O<sub>3-x</sub>(Ba,Ca)TiO<sub>3</sub> ceramics. *Applied Physics Letters* **99**, 122901 (2011).
- [14] Singh, A. K., Dubey, D. N., Gurvinderjit, S. & Tripathi, S. Tuning ferroelectricity by manipulating the global and local structure in a lead-free Sr-doped Ba(Ti<sub>1-x</sub>Sn<sub>x</sub>)O<sub>3</sub> ceramics. *EPL (Europhysics Letters)* **130**, 36002 (2020).
- [15] Bristowe, N., Varignon, J., Fontaine, D., Bousquet, E. & Ghosez, P. Ferromagnetism induced by entangled charge and orbital orderings in ferroelectric titanate perovskites. *Nature Communications* **6**, 6677 (2015).
- [16] Cohen, R. E. Origin of ferroelectricity in perovskite oxides. *Nature* **358**, 136 (1992).
- [17] Megaw, H. D. Origin of ferroelectricity in barium titanate and other perovskite-type crystals. *Acta Crystallographica* **5**, 739–749 (1952).
- [18] Salje, E. K. Ferroelastic materials. *Annual Review of Materials Research* **42**, 265–283 (2012).
- [19] Damjanovic, D. Ferroelectric, dielectric and piezoelectric properties of ferroelectric thin films and ceramics. *Reports on Progress in Physics* **61**, 1267 (1998).
- [20] Uchino, K. *Ferroelectric devices* (CRC press, 2018).
- [21] Lines, M. E. & Glass, A. M. *Principles and applications of ferroelectrics and related materials* (Oxford university press, 2001).
- [22] Damjanovic, D., Muralt, P. & Setter, N. Ferroelectric sensors. *IEEE sensors journal* **1**, 191–206 (2001).
- [23] Webber, K. G. *et al.* Review of the mechanical and fracture behavior of perovskite lead-free ferroelectrics for actuator applications. *Smart Materials and Structures* **26**, 063001 (2017).
- [24] Lu, H. *et al.* Mechanical writing of ferroelectric polarization. *Science* **336**, 59–61 (2012).
- [25] Bowen, C., Kim, H., Weaver, P. & Dunn, S. Piezoelectric and ferroelectric materials and structures for energy harvesting applications. *Energy & Environmental Science* **7**, 25–44 (2014).
- [26] Guo, R. *et al.* Non-volatile memory based on the ferroelectric photovoltaic effect. *Nature Communications* **4**, 1990 (2013).
- [27] Soares, M., Senos, A. & Mantas, P. Phase coexistence region and dielectric properties of PZT ceramics. *Journal of the European Ceramic Society* **20**, 321–334 (2000).
- [28] Ragini, Ranjan, R., Mishra, S. & Pandey, D. Room temperature structure of PbZr<sub>x</sub>Ti<sub>1-x</sub>O<sub>3</sub> around the morphotropic phase boundary region: A rietveld study. *Journal of Applied Physics* **92**, 3266–3274 (2002).

- [29] Pandey, D., Singh, A. K. & Baik, S. Stability of ferroic phases in the highly piezoelectric  $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$  ceramics. *Acta Crystallographica Section A: Foundations of Crystallography* **64**, 192–203 (2008).
- [30] Noheda, B. *et al.* Stability of the monoclinic phase in the ferroelectric perovskite  $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ . *Physical Review B* **63**, 014103 (2000).
- [31] Commission., E. Directive (EC) No. 2002/95/EC of the European Parliament and of the Council of 27 January 2003 on the restriction of the use of certain hazardous substances in electrical and electronic equipment. *Off J Eur Union L* **37**, 19 (2002).
- [32] Commission., E. Directive 2011/65/EU of the European Parliament and of the Council of 8 June 2011 on the restriction of the use of certain hazardous substances in electrical and electronic equipment (RoHS II). *Off J Eur Union L* **174**, 88 (2011).
- [33] Gordon, J., Taylor, A. & Bennett, P. Lead poisoning: case studies. *British Journal of Clinical Pharmacology* **53**, 451–458 (2002).
- [34] Cross, E. Lead-free at last. *Nature* **432**, 24–25 (2004).
- [35] Wu, J. Perovskite lead-free piezoelectric ceramics. *Journal of Applied Physics* **127**, 190901 (2020).
- [36] Jaffe, B., Cook, W. R. & Jaffe, H. *Piezoelectric ceramics* (Academic Press, London 1971).
- [37] Garcia, J. E. & Rubio-Marcos, F. Polymorphic phase boundary in piezoelectric oxides. *Journal of Applied Physics* **127**, 131102 (2020).
- [38] Damjanovic, D. A morphotropic phase boundary system based on polarization rotation and polarization extension. *Applied Physics Letters* **97**, 062906 (2010).
- [39] Cross, L. E. Relaxor ferroelectrics. *Ferroelectrics* **76**, 241–267 (1987).
- [40] Bokov, A. & Ye, Z.-G. Recent progress in relaxor ferroelectrics with perovskite structure. *Journal of Materials Science* **41**, 31–52 (2006).
- [41] Bokov, A. A. *et al.* Compositional disorder, polar nanoregions and dipole dynamics in  $\text{PbZn}_{1/3}\text{Nb}_{2/3}\text{O}_3$ -based relaxor ferroelectrics. *Z. Kristallogr.* **226**, 99–107 (2011).
- [42] Zhang, L. *et al.* Phase transitions and the piezoelectricity around morphotropic phase boundary in  $\text{Ba}(\text{Zr}_{0.20}\text{Ti}_{0.80})\text{O}_3-x(\text{Ba}_{0.70}\text{Ca}_{0.30})\text{TiO}_3$  lead-free solid solution. *Applied Physics Letters* **105**, 162908 (2014).
- [43] Li, W., Xu, Z., Chu, R., Fu, P. & Zang, G. Enhanced ferroelectric properties in  $(\text{Ba}_{1-x}\text{Ca}_x)(\text{Ti}_{0.94}\text{Sn}_{0.06})\text{O}_3$  lead-free ceramics. *Journal of the European Ceramic Society* **32**, 517–520 (2012).
- [44] Zhu, X. N., Zhang, W. & Chen, X. M. Enhanced dielectric and ferroelectric characteristics in Ca-modified  $\text{BaTiO}_3$  ceramics. *AIP Advances* **3**, 082125 (2013).

- [45] Li, W., Xu, Z., Chu, R., Fu, P. & Zang, G. Large piezoelectric coefficient in  $(\text{Ba}_{1-x}\text{Ca}_x)(\text{Ti}_{0.96}\text{Sn}_{0.04})\text{O}_3$  lead-free ceramics. *Journal of the American Ceramic Society* **94**, 4131–4133 (2011).
- [46] Maiti, T., Guo, R. & Bhalla, A. Structure-property phase diagram of  $\text{BaZr}_x\text{Ti}_{1-x}\text{O}_3$  system. *Journal of the American Ceramic Society* **91**, 1769–1780 (2008).
- [47] Lei, C., Bokov, A. A. & Ye, Z.-G. Ferroelectric to relaxor crossover and dielectric phase diagram in the  $\text{BaTiO}_3$ – $\text{BaSnO}_3$  system. *Journal of Applied Physics* **101**, 084105 (2007).
- [48] Kleemann, W., Miga, S., Xu, Z., Lu, S. & Dec, J. Non-linear permittivity study of the crossover from ferroelectric to relaxor and cluster glass in  $\text{BaTi}_{1-x}\text{Sn}_x\text{O}_3$  ( $x=0.175$ – $0.30$ ). *Applied Physics Letters* **104**, 182910 (2014).
- [49] Levin, I., Krayzman, V. & Woicik, J. C. Local-structure origins of the sustained curie temperature in  $(\text{Ba,Ca})\text{TiO}_3$  ferroelectrics. *Applied Physics Letters* **102**, 162906 (2013).
- [50] Troiler-McKinstry, S. Impact of ferroelectricity. *American Ceramic Society Bulletin* **99**, 22–23 (2020).
- [51] Bhalla, A. S. & Saxena, A. Ferroelectricity: 100 years on. *Physics World* **33**, 38 (2021).
- [52] Whatmore, R. W., You, Y.-M., Xiong, R.-G. & Eom, C.-B. 100 years of ferroelectricity—a celebration. *APL Materials* **9**, 070401 (2021).
- [53] Valasek, J. Piezo-electric and allied phenomena in rochelle salt. *Physical Review* **17**, 475 (1921).
- [54] Li, F. *et al.* Ultrahigh piezoelectricity in ferroelectric ceramics by design. *Nature Materials* **17**, 349–354 (2018).
- [55] Xu, Y. *Ferroelectric materials and their applications* (Elsevier, 2013).
- [56] Whatmore, R. Pyroelectric devices and materials. *Reports on progress in physics* **49**, 1335 (1986).
- [57] Hossain, A. & Rashid, M. H. Pyroelectric detectors and their applications. *IEEE Transactions on industry applications* **27**, 824–829 (1991).
- [58] Hunter, S. R., Lavrik, N. V., Mostafa, S., Rajic, S. & Datskos, P. G. Review of pyroelectric thermal energy harvesting and new mems-based resonant energy conversion techniques. *Energy Harvesting and Storage: Materials, Devices, and Applications III* **8377**, 77–90 (2012).
- [59] Bowen, C. R. *et al.* Pyroelectric materials and devices for energy harvesting applications. *Energy & Environmental Science* **7**, 3836–3856 (2014).
- [60] Sezer, N. & Koç, M. A comprehensive review on the state-of-the-art of piezoelectric energy harvesting. *Nano Energy* **80**, 105567 (2021).

- [61] Trolier-McKinstry, S., Zhang, S., Bell, A. J. & Tan, X. High-performance piezoelectric crystals, ceramics, and films. *Annual Review of Materials Research* **48**, 191–217 (2018).
- [62] Lay, R., Deijis, G. S. & Malmström, J. The intrinsic piezoelectric properties of materials—a review with a focus on biological materials. *RSC Advances* **11**, 30657–30673 (2021).
- [63] Damjanovic, D. Hysteresis in piezoelectric and ferroelectric materials. Tech. Rep., Academic Press (2006).
- [64] Kay, H. & Bailey, P. Structure and properties of  $\text{CaTiO}_3$ . *Acta Crystallographica* **10**, 219–226 (1957).
- [65] Johnsson, M. & Lemmens, P. Crystallography and chemistry of perovskites. *arXiv preprint cond-mat/0506606* (2005).
- [66] Tilley, R. J. *Perovskites: structure-property relationships* (John Wiley & Sons, 2016).
- [67] Ye, H.-Y. *et al.* Metal-free three-dimensional perovskite ferroelectrics. *Science* **361**, 151–155 (2018).
- [68] Howard, C. J. & Stokes, H. T. Structures and phase transitions in perovskites—a group-theoretical approach. *Acta Crystallographica Section A: Foundations of Crystallography* **61**, 93–111 (2005).
- [69] Stokes, H. T., Kisi, E. H., Hatch, D. M. & Howard, C. J. Group-theoretical analysis of octahedral tilting in ferroelectric perovskites. *Acta Crystallographica Section B: Structural Science* **58**, 934–938 (2002).
- [70] Knight, K. S. Parameterization of the crystal structures of centrosymmetric zone-boundary-tilted perovskites: an analysis in terms of symmetry-adapted basis-vectors of the cubic aristotype phase. *The Canadian Mineralogist* **47**, 381–400 (2009).
- [71] Glazer, A. M. The classification of tilted octahedra in perovskites. *Acta Crystallographica Section B: Structural Crystallography and Crystal Chemistry* **28**, 3384–3392 (1972).
- [72] Wang, D. & Angel, R. J. Octahedral tilts, symmetry-adapted displacive modes and polyhedral volume ratios in perovskite structures. *Acta Crystallographica Section B: Structural Science* **67**, 302–314 (2011).
- [73] Saha, S., Sinha, T. & Mookerjee, A. Electronic structure, chemical bonding, and optical properties of paraelectric  $\text{BaTiO}_3$ . *Physical Review B* **62**, 8828 (2000).
- [74] Bartel, C. J. *et al.* New tolerance factor to predict the stability of perovskite oxides and halides. *Science advances* **5**, eaav0693 (2019).
- [75] Li, C., Soh, K. C. K. & Wu, P. Formability of  $\text{ABO}_3$  perovskites. *Journal of Alloys and Compounds* **372**, 40–48 (2004).

- [76] Woodward, P. M. Octahedral tilting in perovskites. I. geometrical considerations. *Acta Crystallographica Section B: Structural Science* **53**, 32–43 (1997).
- [77] Randall, C., Bhalla, A., Shrout, T. & Cross, L. Classification and consequences of complex lead perovskite ferroelectrics with regard to B-site cation order. *Journal of Materials Research* **5**, 829–834 (1990).
- [78] Howard, C. J. & Stokes, H. T. Octahedral tilting in cation-ordered perovskites—a group-theoretical analysis. *Acta Crystallographica Section B: Structural Science* **60**, 674–684 (2004).
- [79] Singh, D. J., Ghita, M., Fornari, M. & Halilov, S. Role of A-site and B-site ions in perovskite ferroelectricity. *Ferroelectrics* **338**, 73–79 (2006).
- [80] Li, Z. *et al.* New mechanism for ferroelectricity in the perovskite  $\text{Ca}_{2-x}\text{Mn}_x\text{Ti}_2\text{O}_6$  synthesized by spark plasma sintering. *Journal of the American Chemical Society* **140**, 2214–2220 (2018).
- [81] Ghita, M., Fornari, M., Singh, D. J. & Halilov, S. Interplay between A-site and B-site driven instabilities in perovskites. *Physical Review B* **72**, 054114 (2005).
- [82] Yashima, M. & Ali, R. Structural phase transition and octahedral tilting in the calcium titanate perovskite  $\text{CaTiO}_3$ . *Solid State Ionics* **180**, 120–126 (2009).
- [83] Zhou, W. & Ariando, A. Review on ferroelectric/polar metals. *Japanese Journal of Applied Physics* **59**, S10802 (2020).
- [84] Sicron, N. *et al.* Nature of the ferroelectric phase transition in  $\text{PbTiO}_3$ . *Physical Review B* **50**, 13168 (1994).
- [85] Cohen, R. E. & Krakauer, H. Electronic structure studies of the differences in ferroelectric behavior of  $\text{BaTiO}_3$  and  $\text{PbTiO}_3$ . *Ferroelectrics* **136**, 65–83 (1992).
- [86] Van Aken, B. B., Palstra, T. T., Filippetti, A. & Spaldin, N. A. The origin of ferroelectricity in magnetoelectric  $\text{YMnO}_3$ . *Nature materials* **3**, 164–170 (2004).
- [87] Cohen, R. E. Theory of ferroelectrics: a vision for the next decade and beyond. *Journal of Physics and Chemistry of Solids* **61**, 139–146 (2000).
- [88] Shen, Y. *et al.* Role of lone-pairs in driving ferroelectricity of perovskite oxides: An orbital selective external potential study. *Advanced Theory and Simulations* **2**, 1900029 (2019).
- [89] Jan, J. *et al.* Direct experimental evidence of hybridization of Pb states with O 2 p states in ferroelectric perovskite oxides. *Applied Physics Letters* **87**, 012103 (2005).
- [90] Liu, Z. *et al.* High curie temperature bismuth-based piezo-/ferroelectric single crystals of complex perovskite structure: recent progress and perspectives. *Crys-tEngComm* (2021).
- [91] Kuroiwa, Y. *et al.* Evidence for Pb-O covalency in tetragonal  $\text{PbTiO}_3$ . *Physical Review Letters* **87**, 217601 (2001).

- [92] Glazer, A. Simple ways of determining perovskite structures. *Acta Crystallographica Section A: Crystal Physics, Diffraction, Theoretical and General Crystallography* **31**, 756–762 (1975).
- [93] Howard, C. J. & Carpenter, M. A. Octahedral tilting in cation-ordered jahn–teller distorted perovskites—a group-theoretical analysis. *Acta Crystallographica Section B: Structural Science* **66**, 40–50 (2010).
- [94] Perez-Mato, J., Orobengoa, D. & Aroyo, M. Mode crystallography of distorted structures. *Acta Crystallographica Section A: Foundations of Crystallography* **66**, 558–590 (2010).
- [95] Hafiz, H. *et al.* A high-throughput data analysis and materials discovery tool for strongly correlated materials. *npj Computational Materials* **4**, 63 (2018).
- [96] Dixon, C. A. *et al.* Thermal evolution of the crystal structure of the orthorhombic perovskite LaFeO<sub>3</sub>. *Journal of Solid State Chemistry* **230**, 337–342 (2015).
- [97] Dubey, D. N., Singh, G., Singh, A. K. & Tripathi, S. Role of  $\Gamma_4^-$  phonon mode in the enhancement of ferroelectric polarization in a perovskite-based eco-friendly functional material. *Europhysics Letters* **140**, 26003 (2022).
- [98] Busmann-Holder, A. The polarizability model for ferroelectricity in perovskite oxides. *Journal of Physics: Condensed Matter* **24**, 273202 (2012).
- [99] Kwei, G., Lawson, A., Billinge, S. & Cheong, S. Structures of the ferroelectric phases of barium titanate. *The Journal of Physical Chemistry* **97**, 2368–2377 (1993).
- [100] Cochran, W. Crystal stability and the theory of ferroelectricity. *Advances in Physics* **9**, 387–423 (1960).
- [101] Shirane, G., Frazer, B., Minkiewicz, V., Leake, J. & Linz, A. Soft optic modes in barium titanate. *Physical Review Letters* **19**, 234 (1967).
- [102] Harada, J., Axe, J. & Shirane, G. Neutron-scattering study of soft modes in cubic BaTiO<sub>3</sub>. *Physical Review B* **4**, 155 (1971).
- [103] Comes, R., Lambert, M. & Guinier, A. The chain structure of BaTiO<sub>3</sub> and KNbO<sub>3</sub>. *Solid State Communications* **6**, 715–719 (1968).
- [104] Zalar, B., Laguta, V. V. & Blinc, R. NMR evidence for the coexistence of order-disorder and displacive components in barium titanate. *Physical Review Letters* **90**, 037601 (2003).
- [105] Zalar, B. *et al.* NMR study of disorder in BaTiO<sub>3</sub> and SrTiO<sub>3</sub>. *Physical Review B* **71**, 064107 (2005).
- [106] Völkel, G. & Müller, K. Order-disorder phenomena in the low-temperature phase of BaTiO<sub>3</sub>. *Physical Review B* **76**, 094105 (2007).
- [107] Ravel, B., Stern, E., Vedrinskii, R. & Kraizman, V. Local structure and the phase transitions of BaTiO<sub>3</sub>. *Ferroelectrics* **206**, 407–430 (1998).

- [108] Pugachev, A. *et al.* Broken local symmetry in paraelectric BaTiO<sub>3</sub> proved by second harmonic generation. *Physical Review Letters* **108**, 247601 (2012).
- [109] Zhong, W., Vanderbilt, D. & Rabe, K. Phase transitions in BaTiO<sub>3</sub> from first principles. *Physical Review Letters* **73**, 1861 (1994).
- [110] Chaves, A., Barreto, F. S., Nogueira, R. & Zeks, B. Thermodynamics of an eight-site order-disorder model for ferroelectrics. *Physical Review B* **13**, 207 (1976).
- [111] Qi, Y., Liu, S., Grinberg, I. & Rappe, A. M. Atomistic description for temperature-driven phase transitions in BaTiO<sub>3</sub>. *Physical Review B* **94**, 134308 (2016).
- [112] Kamba, S. Soft-mode spectroscopy of ferroelectrics and multiferroics: A review. *APL Materials* **9**, 020704 (2021).
- [113] Buscaglia, M. T. *et al.* High dielectric constant and frozen macroscopic polarization in dense nanocrystalline BaTiO<sub>3</sub> ceramics. *Physical Review B* **73**, 064114 (2006).
- [114] Tsunoda, N., Kumagai, Y. & Oba, F. Stabilization of small polarons in BaTiO<sub>3</sub> by local distortions. *Physical Review Materials* **3**, 114602 (2019).
- [115] Porta, M. & Lookman, T. Effects of tricritical points and morphotropic phase boundaries on the piezoelectric properties of ferroelectrics. *Physical Review B* **83**, 174108 (2011).
- [116] Wu, Z. & Cohen, R. E. Pressure-induced anomalous phase transitions and colossal enhancement of piezoelectricity in PbTiO<sub>3</sub>. *Physical Review Letters* **95**, 037601 (2005).
- [117] Noheda, B. *et al.* A monoclinic ferroelectric phase in the Pb(Zr<sub>x</sub>Ti<sub>1-x</sub>)O<sub>3</sub> solid solution. *Applied Physics Letters* **74**, 2059–2061 (1999).
- [118] Sato, Y., Hirayama, T. & Ikuhara, Y. Monoclinic nanodomains in morphotropic phase boundary Pb(Mg<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub>-PbTiO<sub>3</sub>. *Applied Physics Letters* **104**, 082905 (2014).
- [119] Singh, A. K. & Pandey, D. Evidence for M<sub>B</sub> and M<sub>C</sub> phases in the morphotropic phase boundary region of (1-x)[Pb(Mg<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub>]-x PbTiO<sub>3</sub>: A Rietveld study. *Physical Review B* **67**, 064102 (2003).
- [120] Kuwata, J., Uchino, K. & Nomura, S. Phase transitions in the Pb(Zn<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub>-PbTiO<sub>3</sub> system. *Ferroelectrics* **37**, 579–582 (1981).
- [121] Kiat, J.-M. *et al.* Monoclinic structure of unpoled morphotropic high piezoelectric PMN-PT and PZN-PT compounds. *Physical Review B* **65**, 064106 (2002).
- [122] Glazer, A., Thomas, P., Baba-Kishi, K., Pang, G. & Tai, C. Influence of short-range and long-range order on the evolution of the morphotropic phase boundary in Pb(Zr<sub>1-x</sub>Ti<sub>x</sub>)O<sub>3</sub>. *Physical Review B* **70**, 184123 (2004).
- [123] Vanderbilt, D. & Cohen, M. H. Monoclinic and triclinic phases in higher-order devonshire theory. *Physical Review B* **63**, 094108 (2001).

- [124] Singh, A. K. & Pandey, D. Structure and the location of the morphotropic phase boundary region in  $(1-x)[\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3]-x\text{PbTiO}_3$ . *Journal of Physics: Condensed Matter* **13**, L931 (2001).
- [125] Zhang, N. *et al.* The missing boundary in the phase diagram of  $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ . *Nature Communications* **5**, 5231 (2014).
- [126] Zhang, N. *et al.* Local-scale structures across the morphotropic phase boundary in  $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ . *IUCrJ* **5**, 73–81 (2018).
- [127] Budimir, M., Damjanovic, D. & Setter, N. Piezoelectric response and free-energy instability in the perovskite crystals  $\text{BaTiO}_3$ ,  $\text{PbTiO}_3$ , and  $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$ . *Physical Review B* **73**, 174106 (2006).
- [128] Damjanovic, D. Contributions to the piezoelectric effect in ferroelectric single crystals and ceramics. *Journal of the American Ceramic Society* **88**, 2663–2676 (2005).
- [129] Xu, F. *et al.* Domain wall motion and its contribution to the dielectric and piezoelectric properties of lead zirconate titanate films. *Journal of Applied Physics* **89**, 1336–1348 (2001).
- [130] Li, F., Zhang, S., Damjanovic, D., Chen, L.-Q. & Shrout, T. R. Local structural heterogeneity and electromechanical responses of ferroelectrics: learning from relaxor ferroelectrics. *Advanced Functional Materials* **28**, 1801504 (2018).
- [131] Hirota, K. Phase transitions in relaxor ferroelectricity. *Ferroelectrics* **354**, 136–144 (2007).
- [132] Zhang, L.-L. & Huang, Y.-N. Theory of relaxor-ferroelectricity. *Scientific Reports* **10**, 5060 (2020).
- [133] Bokov, A. & Ye, Z.-G. Recent progress in relaxor ferroelectrics with perovskite structure. *Progress in Advanced Dielectrics* 105–164 (2020).
- [134] Phelan, D. *et al.* Role of random electric fields in relaxors. *Proceedings of the National Academy of Sciences* **111**, 1754–1759 (2014).
- [135] Ahn, C. W. *et al.* A brief review on relaxor ferroelectrics and selected issues in lead-free relaxors. *Journal of the Korean Physical Society* **68**, 1481–1494 (2016).
- [136] Bokov, A. Recent advances in diffuse ferroelectric phase transitions. *Ferroelectrics* **131**, 49–55 (1992).
- [137] Bokov, A. A. & Ye, Z.-G. Dielectric relaxation in relaxor ferroelectrics. *Journal of Advanced dielectrics* **2**, 1241010 (2012).
- [138] Burns, G. & Dacol, F. Crystalline ferroelectrics with glassy polarization behavior. *Physical Review B* **28**, 2527 (1983).
- [139] Dul'kin, E., Roth, M., Janolin, P.-E. & Dkhil, B. Acoustic emission study of phase transitions and polar nanoregions in relaxor-based systems: Application to the  $\text{PbZn}_{1/3}\text{Nb}_{2/3}\text{O}_3$  family of single crystals. *Physical Review B* **73**, 012102 (2006).

- [140] Toulouse, J., Jiang, F., Svitelskiy, O., Chen, W. & Ye, Z.-G. Temperature evolution of the relaxor dynamics in  $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ : A critical raman analysis. *Physical Review B* **72**, 184106 (2005).
- [141] Dkhil, B. *et al.* Intermediate temperature scale  $T^*$  in lead-based relaxor systems. *Physical Review B* **80**, 064103 (2009).
- [142] Viehland, D., Li, J., Jang, S., Cross, L. E. & Wuttig, M. Dipolar-glass model for lead magnesium niobate. *Physical Review B* **43**, 8316 (1991).
- [143] Uchino, K. & Nomura, S. Critical exponents of the dielectric constants in diffused-phase-transition crystals. *Ferroelectrics* **44**, 55–61 (1982).
- [144] Du, H. *et al.* High  $T_m$  lead-free relaxor ferroelectrics with broad temperature usage range:  $0.04\text{BiScO}_3\text{-}0.96(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3$ . *Journal of Applied Physics* **104**, 044104 (2008).
- [145] Maiti, T., Guo, R. & Bhalla, A. The evolution of relaxor behavior in  $\text{Ti}^{4+}$  doped  $\text{BaZrO}_3$  ceramics. *Journal of Applied Physics* **100**, 114109 (2006).
- [146] Shvartsman, V. V. & Lupascu, D. C. Lead-free relaxor ferroelectrics. *Journal of the American Ceramic Society* **95**, 1–26 (2012).
- [147] Peláiz-Barranco, A., Calderón-Piñar, F., García-Zaldívar, O. & González-Abreu, Y. Relaxor behaviour in ferroelectric ceramics. *Advances in Ferroelectrics* 85–107 (2012).
- [148] Maiti, T., Guo, R. & Bhalla, A. Evaluation of experimental resume of  $\text{BaZr}_x\text{Ti}_{1-x}\text{O}_3$  with perspective to ferroelectric relaxor family: an overview. *Ferroelectrics* **425**, 4–26 (2011).
- [149] Smolenskii, G. A. Physical phenomena in ferroelectrics with diffused phase transition. *Journal of the Physical Society of Japan* **28**, 26–37 (1970).
- [150] Viehland, D., Jang, S., Cross, L. E. & Wuttig, M. Freezing of the polarization fluctuations in lead magnesium niobate relaxors. *Journal of Applied Physics* **68**, 2916–2921 (1990).
- [151] Glazounov, A. & Tagantsev, A. A “breathing” model for the polarization response of relaxor ferroelectrics. *Ferroelectrics* **221**, 57–66 (1999).
- [152] Westphal, V., Kleemann, W. & Glinchuk, M. Diffuse phase transitions and random-field-induced domain states of the “relaxor” ferroelectric  $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ . *Physical Review Letters* **68**, 847 (1992).
- [153] Glinchuk, M. & Farhi, R. A random field theory based model for ferroelectric relaxors. *Journal of Physics: Condensed Matter* **8**, 6985 (1996).
- [154] Pirc, R. & Blinc, R. Spherical random-bond–random-field model of relaxor ferroelectrics. *Physical Review B* **60**, 13470 (1999).
- [155] Cheng, Z.-Y., Katiyar, R., Yao, X. & Guo, A. Dielectric behavior of lead magnesium niobate relaxors. *Physical Review B* **55**, 8165 (1997).

- [156] Haeni, J. *et al.* Room-temperature ferroelectricity in strained SrTiO<sub>3</sub>. *Nature* **430**, 758–761 (2004).
- [157] Choi, K. J. *et al.* Enhancement of ferroelectricity in strained BaTiO<sub>3</sub> thin films. *Science* **306**, 1005–1009 (2004).
- [158] Haislmaier, R. C. *et al.* Large tetragonality and room temperature ferroelectricity in compressively strained CaTiO<sub>3</sub> thin films. *APL Materials* **7**, 051104 (2019).
- [159] Fu, D., Itoh, M. & Koshihara, S.-y. Invariant lattice strain and polarization in BaTiO<sub>3</sub>–CaTiO<sub>3</sub> ferroelectric alloys. *Journal of Physics: Condensed Matter* **22**, 052204 (2010).
- [160] Shu, C., Reed, D. & Button, T. W. A phase diagram of Ba<sub>1-x</sub>Ca<sub>x</sub>TiO<sub>3</sub> ( $x=0-0.30$ ) piezoceramics by raman spectroscopy. *Journal of the American Ceramic Society* **101**, 2589–2593 (2018).
- [161] Kalyani, A. K., Krishnan, H., Sen, A., Senyshyn, A. & Ranjan, R. Polarization switching and high piezoelectric response in Sn-modified BaTiO<sub>3</sub>. *Physical Review B* **91**, 024101 (2015).
- [162] Phelan, D. *et al.* Structural properties of barium stannate. *Journal of Solid State Chemistry* **262**, 142–148 (2018).
- [163] Horchidan, N. *et al.* Multiscale study of ferroelectric–relaxor crossover in BaSn<sub>x</sub>Ti<sub>1-x</sub>O<sub>3</sub> ceramics. *Journal of the European Ceramic Society* **34**, 3661–3674 (2014).
- [164] Deluca, M. *et al.* High-field dielectric properties and raman spectroscopic investigation of the ferroelectric-to-relaxor crossover in BaSn<sub>x</sub>Ti<sub>1-x</sub>O<sub>3</sub> ceramics. *Journal of Applied Physics* **111**, 084102 (2012).
- [165] Veselinović, L. *et al.* The effect of Sn for Ti substitution on the average and local crystal structure of BaTi<sub>1-x</sub>Sn<sub>x</sub>O<sub>3</sub> ( $0 \leq x \leq 0.20$ ). *Journal of Applied Crystallography* **47**, 999–1007 (2014).
- [166] Veselinović, L., Mitrić, M., Avdeev, M., Marković, S. & Uskoković, D. New insights into BaTi<sub>1-x</sub>Sn<sub>x</sub>O<sub>3</sub> ( $0 \leq x \leq 0.20$ ) phase diagram from neutron diffraction data. *Journal of Applied Crystallography* **49**, 1726–1733 (2016).
- [167] Ke, X. *et al.* Existence of a quadruple point in a binary ferroelectric phase diagram. *Physical Review B* **103**, 085132 (2021).
- [168] Ren, P. *et al.* Large nonlinear dielectric behavior in BaTi<sub>1-x</sub>Sn<sub>x</sub>O<sub>3</sub>. *Scientific Reports* **7**, 6693 (2017).
- [169] Surampalli, A., Egli, R., Prajapat, D., Meneghini, C. & Reddy, V. R. Reentrant phenomenon in the diffuse ferroelectric BaSn<sub>0.15</sub>Ti<sub>0.85</sub>O<sub>3</sub>: Local structural insights and first-order reversal curves study. *Physical Review B* **104**, 184114 (2021).
- [170] Xie, L. *et al.* Static and dynamic polar nanoregions in relaxor ferroelectric BaTi<sub>1-x</sub>Sn<sub>x</sub>O<sub>3</sub> system at high temperature. *Physical Review B* **85**, 014118 (2012).

- [171] Shvartsman, V. *et al.* Crossover from ferroelectric to relaxor behavior in  $\text{BaTi}_{1-x}\text{Sn}_x\text{O}_3$  solid solutions. *Phase Transitions* **81**, 1013–1021 (2008).
- [172] Shvartsman, V., Kleemann, W., Dec, J., Xu, Z. & Lu, S. Diffuse phase transition in  $\text{BaTi}_{1-x}\text{Sn}_x\text{O}_3$  ceramics: An intermediate state between ferroelectric and relaxor behavior. *Journal of Applied Physics* **99**, 124111 (2006).
- [173] Lu, S., Xu, Z. & Chen, H. Tunability and relaxor properties of ferroelectric barium stannate titanate ceramics. *Applied Physics Letters* **85**, 5319–5321 (2004).
- [174] Lei, C., Bokov, A. & Ye, Z.-G. Relaxor behavior in  $\text{Ba}(\text{Ti}_{0.72}\text{Sn}_{0.28})\text{O}_3$  solid solution. *Ferroelectrics* **339**, 129–136 (2006).
- [175] Akbarzadeh, A., Kornev, I., Malibert, C., Bellaiche, L. & Kiat, J.-M. Combined theoretical and experimental study of the low-temperature properties of bazro 3. *Physical Review B* **72**, 205104 (2005).
- [176] Nuzhnyy, D. *et al.* Broadband dielectric response of  $\text{Ba}(\text{Zr,Ti})\text{O}_3$  ceramics: from incipient via relaxor and diffuse up to classical ferroelectric behavior. *Physical Review B* **86**, 014106 (2012).
- [177] Geneste, G. & Kiat, J.-M. Ground state of Ca-doped strontium titanate: Ferroelectricity versus polar nanoregions. *Physical Review B* **77**, 174101 (2008).
- [178] Tripathi, A., Dubey, D. N., Kumar, H. & Tripathi, S. Stabilizing ferroelectricity in alkaline-earth-metal-based perovskites ( $\text{ABO}_3$ ) via  $A-(\text{Ca}^{2+}/\text{Sr}^{2+}/\text{Ba}^{2+})$  and  $B$ -site ( $\text{Ti}^{4+}$ ) cationic radius ratio ( $R_A/R_B$ ). *Journal of Applied Crystallography* **55**, 1446 (2022).
- [179] Curecheriu, L. P., Ciomaga, C. E. & Mitoseriu, L. Temperature-dependent tunability in the paraelectric state of  $\text{BaTiO}_3$ -based solid solutions. *Ferroelectrics* **391**, 83–90 (2009).
- [180] Peng, J. *et al.* A thermodynamic potential for barium zirconate titanate solid solutions. *npj Computational Materials* **4**, 66 (2018).
- [181] Kalyani, A. K., Senyshyn, A. & Ranjan, R. Polymorphic phase boundaries and enhanced piezoelectric response in extended composition range in the lead free ferroelectric  $\text{BaTi}_{1-x}\text{Zr}_x\text{O}_3$ . *Journal of Applied Physics* **114**, 014102 (2013).
- [182] Paściak, M., Welberry, T., Kulda, J., Leoni, S. & Hlinka, J. Dynamic displacement disorder of cubic  $\text{BaTiO}_3$ . *Physical Review Letters* **120**, 167601 (2018).
- [183] Neilson, J. R. & McQueen, T. M. Representational analysis of extended disorder in atomistic ensembles derived from total scattering data. *Journal of Applied Crystallography* **48**, 1560–1572 (2015).
- [184] Farhi, R., El Marssi, M., Simon, A. & Ravez, J. A raman and dielectric study of ferroelectric ceramics. *The European Physical Journal B-Condensed Matter and Complex Systems* **9**, 599–604 (1999).

- [185] Karan, N., Katiyar, R., Maiti, T., Guo, R. & Bhalla, A. Raman spectral studies of  $Zr^{4+}$ -rich  $BaZr_xTi_{1-x}O_3$  ( $0.5 \leq x \leq 1.00$ ) phase diagram. *Journal of Raman Spectroscopy* **40**, 370–375 (2009).
- [186] Laulhé, C. *et al.* EXAFS study of lead-free relaxor ferroelectric  $BaZr_xTi_{1-x}O_3$  at the Zr K edge. *Physical Review B* **74**, 014106 (2006).
- [187] Levin, I. *et al.* Local structure of  $Ba(Ti,Zr)O_3$  perovskite-like solid solutions and its relation to the band-gap behavior. *Physical Review B* **83**, 094122 (2011).
- [188] Laulhé, C., Hippert, F., Bellissent, R., Simon, A. & Cuello, G. Local structure in  $Ba(Ti_{1-x}Zr_x)O_3$  relaxors from neutron pair distribution function analysis. *Physical Review B* **79**, 064104 (2009).
- [189] Buscaglia, V. *et al.* Average and local atomic-scale structure in  $BaZr_xTi_{1-x}O_3$  ( $x=0.10, 0.20, 0.40$ ) ceramics by high-energy x-ray diffraction and raman spectroscopy. *Journal of Physics: Condensed Matter* **26**, 065901 (2014).
- [190] Pramanick, A. *et al.* Stabilization of polar nanoregions in Pb-free ferroelectrics. *Physical Review Letters* **120**, 207603 (2018).
- [191] Laulhé, C., Pasturel, A., Hippert, F. & Kreisel, J. Random local strain effects in homovalent-substituted relaxor ferroelectrics: a first-principles study of  $BaTi_{0.74}Zr_{0.26}O_3$ . *Physical Review B* **82**, 132102 (2010).
- [192] Jeong, I.-K., Park, C., Ahn, J., Park, S. & Kim, D. Ferroelectric-relaxor crossover in  $Ba(Ti_{1-x}Zr_x)O_3$  studied using neutron total scattering measurements and reverse monte carlo modeling. *Physical Review B* **81**, 214119 (2010).
- [193] Brajesh, K., Tanwar, K., Abebe, M. & Ranjan, R. Relaxor ferroelectricity and electric-field-driven structural transformation in the giant lead-free piezoelectric  $(Ba,Ca)(Zr,Ti)O_3$ . *Physical Review B* **92**, 224112 (2015).
- [194] Brajesh, K., Abebe, M. & Ranjan, R. Structural transformations in morphotropic-phase-boundary composition of the lead-free piezoelectric system  $Ba(Ti_{0.80}Zr_{0.20})O_3-(Ba_{0.70}Ca_{0.30})TiO_3$ . *Physical Review B* **94**, 104108 (2016).
- [195] Gao, J. *et al.* Microstructure basis for strong piezoelectricity in Pb-free  $Ba(Zr_{0.20}Ti_{0.80})O_3-x(Ba_{0.70}Ca_{0.30})TiO_3$  ceramics. *Applied Physics Letters* **99**, 092901 (2011).
- [196] Guo, H. *et al.* Polarization alignment, phase transition, and piezoelectricity development in polycrystalline  $0.5Ba(Zr_{0.20}Ti_{0.80})O_3-0.5(Ba_{0.70}Ca_{0.30})TiO_3$ . *Physical Review B* **90**, 014103 (2014).
- [197] Tutuncu, G., Li, B., Bowman, K. & Jones, J. L. Domain wall motion and electromechanical strain in lead-free piezoelectrics: Insight from the model system  $(1-x)Ba(Zr_{0.20}Ti_{0.80})O_3-x(Ba_{0.70}Ca_{0.30})TiO_3$  using in situ high-energy x-ray diffraction during application of electric fields. *Journal of Applied Physics* **115**, 144104 (2014).

- [198] Jiang, X., Dietz, C., Liu, N., Rojas, V. & Stark, R. W. Ferroelectric domain evolution in a  $\text{Ba}(\text{Zr}_{0.20}\text{Ti}_{0.80})\text{O}_3\text{-}0.5(\text{Ba}_{0.70}\text{Ca}_{0.30})\text{TiO}_3$  piezoceramic studied using piezoresponse force microscopy. *Applied Physics Letters* **118**, 262902 (2021).
- [199] Ji, X. *et al.* Structure and electrical properties of BCZT ceramics derived from microwave-assisted sol–gel-hydrothermal synthesized powders. *Scientific Reports* **10**, 20352 (2020).
- [200] Keeble, D. S., Benabdallah, F., Thomas, P. A., Maglione, M. & Kreisel, J. Revised structural phase diagram of  $(\text{Ba}_{0.70}\text{Ca}_{0.30})\text{TiO}_3\text{-Ba}(\text{Zr}_{0.20}\text{Ti}_{0.80})\text{O}_3$ . *Applied Physics Letters* **102**, 092903 (2013).
- [201] Akbarzadeh, A. *et al.* Quantum-fluctuation-stabilized orthorhombic ferroelectric ground state in lead-free piezoelectric  $(\text{Ba,Ca})(\text{Zr,Ti})\text{O}_3$ . *Physical Review B* **98**, 104101 (2018).
- [202] Zhu, L.-F. *et al.* Enhanced piezoelectric properties of  $(\text{Ba}_{1-x}\text{Ca}_x)(\text{Ti}_{0.92}\text{Sn}_{0.08})\text{O}_3$  lead-free ceramics. *Journal of the American Ceramic Society* **96**, 241–245 (2013).
- [203] Chen, M. *et al.* Enhanced piezoelectricity in broad composition range and the temperature dependence research of  $(\text{Ba}_{1-x}\text{Ca}_x)(\text{Ti}_{0.95}\text{Sn}_{0.05})\text{O}_3$  piezoceramics. *Physica B: Condensed Matter* **433**, 43–47 (2014).
- [204] Zhu, L.-F., Zhang, B.-P., Zhao, L. & Li, J.-F. High piezoelectricity of  $\text{BaTiO}_3\text{-CaTiO}_3\text{-BaSnO}_3$  lead-free ceramics. *Journal of Materials Chemistry C* **2**, 4764–4771 (2014).
- [205] Zhu, L.-F. *et al.* Large piezoelectric effect of  $(\text{Ba,Ca})\text{TiO}_3\text{-}x\text{Ba}(\text{Sn,Ti})\text{O}_3$  lead-free ceramics. *Journal of the European Ceramic Society* **36**, 1017–1024 (2016).
- [206] Zhu, L.-F. *et al.* Phase transition and high piezoelectricity in  $(\text{Ba,Ca})(\text{Sn}_x\text{Ti}_{1-x})\text{O}_3$  lead-free ceramics. *Applied Physics Letters* **103**, 072905 (2013).
- [207] Kim, H.-T., Ji, J.-H., Kim, B. S. & Koh, J.-H. Strain related curie temperature and improved piezoelectric properties of lead-free  $(1-x)\text{Ba}(\text{Sn,Ti})\text{O}_3\text{-}x(\text{Ba,Ca})\text{TiO}_3$  ceramics. *Ceramics International* **46**, 25050–25057 (2020).
- [208] Abebe, M., Brajesh, K., Mishra, A., Senyshyn, A. & Ranjan, R. Structural perspective on the anomalous weak-field piezoelectric response at the polymorphic phase boundaries of  $(\text{Ba,Ca})(\text{Ti,M})\text{O}_3$  lead-free piezoelectrics ( $\text{M}=\text{Zr,Sn,Hf}$ ). *Physical Review B* **96**, 014113 (2017).
- [209] Goutam, S., Omar, N., Van Den Bossche, P. & Van Mierlo, J. Review of nanotechnology for anode materials in batteries. *Emerging Nanotechnologies in Rechargeable Energy Storage Systems* 45–82 (2017).
- [210] Cullity, B. D. *Elements of X-ray Diffraction* (Addison-Wesley Publishing, 1956).
- [211] Ladd, M. F. C., Palmer, R. A. & Palmer, R. A. *Structure determination by X-ray crystallography* (Springer, 1977).

- [212] Ameh, E. A review of basic crystallography and x-ray diffraction applications. *The international journal of advanced manufacturing technology* **105**, 3289–3302 (2019).
- [213] Rodrigues-Carvajal, J. refinement. *FULLPROF: A Rietveld Refinement and Pattern Matching Analysis Program (Laboratoire Léon Brillouin (CEA-CNRS), France (2000))*.
- [214] Djerdj, I. *Rietveld Refinement in the Characterization of Crystalline Materials* (MDPI, 2019).
- [215] Noheda, B. *et al.* Tetragonal-to-monoclinic phase transition in a ferroelectric perovskite: The structure of  $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ . *Physical Review B* **61**, 8687 (2000).
- [216] McCusker, L., Von Dreele, R., Cox, D., Louër, D. & Scardi, P. Rietveld refinement guidelines. *Journal of Applied Crystallography* **32**, 36–50 (1999).
- [217] Toby, B. H. R factors in rietveld analysis: How good is good enough? *Powder diffraction* **21**, 67–70 (2006).
- [218] Zhang, H. *et al.* A review on the development of lead-free ferroelectric energy-storage ceramics and multilayer capacitors. *Journal of Materials Chemistry C* **8**, 16648–16667 (2020).
- [219] Yang, Z., Du, H., Jin, L. & Poelman, D. High-performance lead-free bulk ceramics for electrical energy storage applications: design strategies and challenges. *Journal of Materials Chemistry A* **9**, 18026–18085 (2021).
- [220] Pezzotti, G. Raman spectroscopy of piezoelectrics. *Journal of Applied Physics* **113**, 211301 (2013).
- [221] Jones, R. R., Hooper, D. C., Zhang, L., Wolverson, D. & Valev, V. K. Raman techniques: fundamentals and frontiers. *Nanoscale Research Letters* **14**, 1–34 (2019).
- [222] Tuschel, D. Raman crystallography in theory and in practice. *Spectroscopy* **27**, 22–27 (2012).
- [223] Mishra, S. *et al.* Phonon dynamics and inelastic neutron scattering of sodium niobate. *Physical Review B* **89**, 184303 (2014).
- [224] Krishna, P., Mishra, S., Shinde, A., Kesari, S. & Rao, R. Raman spectroscopy of lithium modified sodium niobate at elevated temperature. *Ferroelectrics* **510**, 34–42 (2017).
- [225] Yang, Y. *et al.* Morphotropic relaxor boundary in a relaxor system showing enhancement of electrostrain and dielectric permittivity. *Physical Review Letters* **123**, 137601 (2019).
- [226] Maurya, D. *et al.* Local structure and piezoelectric instability in lead-free  $(1-x)\text{BaTiO}_3-x\text{A}(\text{Cu}_{1/3}\text{Nb}_{2/3})\text{O}_3$  (A=Sr,Ca,Ba) solid solutions. *RSC Advances* **4**, 1283–1292 (2014).

- [227] Janbua, W., Bongkarn, T., Kolodiazny, T. & Vittayakorn, N. High piezoelectric response and polymorphic phase region in the lead-free piezoelectric BaTiO<sub>3</sub>-CaTiO<sub>3</sub>-BaSnO<sub>3</sub> ternary system. *RSC Advances* **7**, 30166–30176 (2017).
- [228] Li, X. & Wang, J. Effect of grain size on the domain structures and electromechanical responses of ferroelectric polycrystal. *Smart Materials and Structures* **26**, 015013 (2016).
- [229] Bednyakov, P. S., Sluka, T., Tagantsev, A. K., Damjanovic, D. & Setter, N. Formation of charged ferroelectric domain walls with controlled periodicity. *Scientific Reports* **5**, 15819 (2015).
- [230] Liu, G., Zhang, S., Jiang, W. & Cao, W. Losses in ferroelectric materials. *Materials Science and Engineering: R: Reports* **89**, 1–48 (2015).
- [231] Senn, M., Keen, D., Lucas, T., Hriljac, J. & Goodwin, A. Emergence of long-range order in BaTiO<sub>3</sub> from local symmetry-breaking distortions. *Physical Review Letters* **116**, 207602 (2016).
- [232] Xiaoyong, W., Yujun, F. & Xi, Y. Dielectric relaxation behavior in barium stannate titanate ferroelectric ceramics with diffused phase transition. *Applied Physics Letters* **83**, 2031–2033 (2003).
- [233] Mitsui, T. & Westphal, W. B. Dielectric and x-ray studies of Ca<sub>x</sub>Ba<sub>1-x</sub>TiO<sub>3</sub> and Ca<sub>x</sub>Sr<sub>1-x</sub>TiO<sub>3</sub>. *Physical Review* **124**, 1354 (1961).
- [234] Puli, V. S., Pradhan, D. K., Riggs, B. C., Chrisey, D. B. & Katiyar, R. S. Investigations on structure, ferroelectric, piezoelectric and energy storage properties of barium calcium titanate (BCT) ceramics. *Journal of Alloys and Compounds* **584**, 369–373 (2014).
- [235] Hou, Y., Yang, L., Qian, X., Zhang, T. & Zhang, Q. Electrocaloric response near room temperature in Zr- and Sn-doped BaTiO<sub>3</sub> systems. *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences* **374**, 20160055 (2016).
- [236] Mao, C. *et al.* Microscopic region effect on the dielectric property of the diffused phase transition ferroelectrics: a reasonable and effective diffuseness characterizing parameter. *Journal of the American Ceramic Society* **93**, 4011–4014 (2010).
- [237] Chen, C. *et al.* Effect of Ca substitution sites on dielectric properties and relaxor behavior of Ca doped barium strontium titanate ceramics. *Journal of Materials Science: Materials in Electronics* **26**, 2486–2492 (2015).
- [238] Kumar, A., Rivera, I. & Katiyar, R. Investigation of local structure of lead-free relaxor Ba(Ti<sub>0.70</sub>Sn<sub>0.30</sub>)O<sub>3</sub> by raman spectroscopy. *Journal of Raman Spectroscopy* **40**, 459–462 (2009).
- [239] Deluca, M. *et al.* Raman spectroscopic study of phase transitions in undoped morphotropic PbZr<sub>1-x</sub>Ti<sub>x</sub>O<sub>3</sub>. *Journal of Raman Spectroscopy* **42**, 488–495 (2011).

- [240] Tenne, D. *et al.* Lattice dynamics in  $\text{Ba}_x\text{Ca}_{1-x}\text{TiO}_3$  single crystals: A raman study. *Physical Review B* **70**, 174302 (2004).
- [241] Raddaoui, Z. *et al.* Correlation of crystal structure and optical properties of  $\text{Ba}_{0.97}\text{Nd}_{0.0267}\text{Ti}_{1-x}\text{W}_x\text{O}_3$  perovskite. *RSC Advances* **8**, 27870–27880 (2018).
- [242] Kreisel, J., Bouvier, P., Maglione, M., Dkhil, B. & Simon, A. High-pressure raman investigation of the Pb-free relaxor  $\text{BaTi}_{0.65}\text{Zr}_{0.35}\text{O}_3$ . *Physical Review B* **69**, 092104 (2004).
- [243] Frantti, J., Lantto, V., Nishio, S. & Kakihana, M. Effect of a-and b-cation substitutions on the phase stability of  $\text{BaTiO}_3$  ceramics. *Physical Review B* **59**, 12 (1999).
- [244] Mahajan, A. *et al.* Structure and ferroelectric studies of  $(\text{Ba}_{0.85}\text{Ca}_{0.15})(\text{Ti}_{0.90}\text{Zr}_{0.10})\text{O}_3$  piezoelectric ceramics. *Materials Research Bulletin* **48**, 4395–4401 (2013).
- [245] Souza, A. E. *et al.* Photoluminescence activity of  $\text{Ba}_{1-x}\text{Ca}_x\text{TiO}_3$ : dependence on particle size and morphology. *Journal of Materials Chemistry C* **2**, 7056–7070 (2014).
- [246] Ghosh, S., Ganguly, M., Rout, S. & Sinha, T. Order-disorder correlation on local structure and photo-electrical properties of  $\text{La}^{3+}$  ion modified BZT ceramics. *The European Physical Journal Plus* **130**, 68 (2015).
- [247] Mendez-González, Y., Peláiz-Barranco, A., Curcio, A., Rodrigues, A. & Guerra, J. Raman spectroscopy study of the La-modified  $(\text{Bi}_{0.5}\text{Na}_{0.5})_{0.92}\text{Ba}_{0.08}\text{TiO}_3$  lead-free ceramic system. *Journal of Raman Spectroscopy* **50**, 1044–1050 (2019).
- [248] Puli, V. S. *et al.* Barium zirconate-titanate/barium calcium-titanate ceramics via sol-gel process: novel high-energy-density capacitors. *Journal of Physics D: Applied Physics* **44**, 395403 (2011).
- [249] Margaritescu, I., Datta, K., Chen, J. & Mihailova, B. Distinct temperature behavior of the local structure of  $(1-x)\text{PbTiO}_3-x\text{BiNi}_{0.5}\text{Ti}_{0.5}\text{O}_3$  at the morphotropic phase boundary. *Journal of Raman Spectroscopy* **51**, 1200–1209 (2020).
- [250] Cowley, R., Gvasaliya, S., Lushnikov, S., Roessli, B. & Rotaru, G. Relaxing with relaxors: a review of relaxor ferroelectrics. *Advances in Physics* **60**, 229–327 (2011).
- [251] Li, F., Jin, L., Xu, Z. & Zhang, S. Electrostrictive effect in ferroelectrics: An alternative approach to improve piezoelectricity. *Applied Physics Reviews* **1**, 011103 (2014).
- [252] Uchino, K., Nomura, S., Cross, L. E., Newnham, R. E. & Jang, S. J. Electrostrictive effect in perovskites and its transducer applications. *Journal of Materials science* **16**, 569–578 (1981).

- [253] Kuwata, J., Uchino, K. & Nomura, S. Dielectric and piezoelectric properties of  $0.91\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-}0.09\text{PbTiO}_3$  single crystals. *Japanese Journal of Applied Physics* **21**, 1298 (1982).
- [254] Park, S.-E. & Shrout, T. R. Ultrahigh strain and piezoelectric behavior in relaxor based ferroelectric single crystals. *Journal of Applied Physics* **82**, 1804–1811 (1997).
- [255] Li, F., Jin, L., Xu, Z., Wang, D. & Zhang, S. Electrostrictive effect in  $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-}x\text{PbTiO}_3$  crystals. *Applied Physics Letters* **102**, 152910 (2013).
- [256] Cross, L., Jang, S., Newnham, R., Nomura, S. & Uchino, K. Large electrostrictive effects in relaxor ferroelectrics. *Ferroelectrics* **23**, 187–191 (1980).
- [257] Dubey, D. N., Singh, G. & Tripathi, S. Relaxor ferroelectricity driven by ‘A’ and ‘B’ site off-centered displacements in cubic phase with  $Pm\bar{3}m$  space group. *Journal of Physics D: Applied Physics* **54**, 365304 (2021).
- [258] Jauhari, M., Mishra, S., Mittal, R., Sastry, P. & Chaplot, S. Effect of chemical pressure on competition and cooperation between polar and antiferrodistortive distortions in sodium niobate. *Physical Review Materials* **1**, 074411 (2017).
- [259] Wu, B. *et al.* Superior electrostrictive effect in relaxor potassium sodium niobate based ferroelectrics. *ACS applied materials & interfaces* **12**, 25050–25057 (2020).
- [260] Damjanovic, D. & Newnham, R. Electrostrictive and piezoelectric materials for actuator applications. *Journal of intelligent material systems and structures* **3**, 190–208 (1992).
- [261] Margaritescu, I., Datta, K. & Mihailova, B. Multistep coupling of preexisting local ferroic distortions in  $\text{PbTiO}_3$  above the curie temperature. *Journal of Physics: Condensed Matter* **30**, 435401 (2018).
- [262] Sati, A. *et al.* Origin of ferroelectricity in cubic phase of Hf substituted  $\text{BaTiO}_3$ . *Journal of Physics: Condensed Matter* **33**, 165403 (2021).
- [263] Keswani, B. C. *et al.* Role of A-site Ca and B-site Zr substitution in  $\text{BaTiO}_3$  lead-free compounds: Combined experimental and first principles density functional theoretical studies. *Journal of Applied Physics* **123**, 204104 (2018).
- [264] Deluca, M. *et al.* Investigation of the composition-dependent properties of  $\text{BaTi}_{1-x}\text{Zr}_x\text{O}_3$  ceramics prepared by the modified pechini method. *Journal of the European Ceramic Society* **32**, 3551–3566 (2012).
- [265] Aroyo, M. I., Kirov, A., Capillas, C., Perez-Mato, J. & Wondratschek, H. Bilbao crystallographic server. II. representations of crystallographic point groups and space groups. *Acta Crystallographica Section A: Foundations of Crystallography* **62**, 115–128 (2006).
- [266] Orobengoa, D., Capillas, C., Aroyo, M. I. & Perez-Mato, J. M. AMPLIMODES: symmetry-mode analysis on the bilbao crystallographic server. *Journal of Applied Crystallography* **42**, 820–833 (2009).

- [267] Ansari, M. A. & Sreenivas, K. Effects of disorder activated scattering and defect-induced phase on the ferroelectric properties of  $\text{BaSn}_x\text{Ti}_{1-x}\text{O}_3$  ( $0 \leq x \leq 0.28$ ) ceramics. *Ceramics International* **45**, 20738–20749 (2019).
- [268] Singh, G., Upadhaya, A., Sinha, A. & Tiwari, V. Investigation of orthorhombic–tetragonal structural crossover in  $(\text{Ba}_{0.92}\text{Ca}_{0.08})(\text{Zr}_{0.05}\text{Ti}_{0.95})\text{O}_3$ . *Journal of Applied Crystallography* **47**, 1647–1650 (2014).
- [269] Singh, G., Tiwari, V. & Gupta, P. Evaluating the polymorphic phase transition in calcium-doped  $\text{Ba}(\text{Zr}_{0.05}\text{Ti}_{0.95})\text{O}_3$ : a lead-free piezoelectric ceramic. *Journal of Applied Crystallography* **46**, 324–331 (2013).
- [270] Zhang, W. *et al.* High pressure raman studies of dense nanocrystalline  $\text{BaTiO}_3$  ceramic. *Journal of Electroceramics* **21**, 859–862 (2008).
- [271] Venkataraman, G. Soft modes and structural phase transitions. *Bulletin of Materials Science* **1**, 129–170 (1979).
- [272] Wesselinowa, J. M. *et al.* Hardening and softening of soft phonon modes in ferroelectric thin films. *Physical Review B* **75**, 045411 (2007).
- [273] Cowley, R. Soft modes and structural phase transitions. *Integrated Ferroelectrics* **133**, 109–117 (2012).
- [274] Stokes, H. T., Hatch, D. M., Campbell, B. J. & Tanner, D. E. ISODISPLACE: a web-based tool for exploring structural distortions. *Journal of Applied Crystallography* **39**, 607–614 (2006).
- [275] Stokes, H., Hatch, D. & Campbell, B. Isotropy software suite, iso. byu. edu. *ISOSUBGROUP, ISOTROPY Software Suite, iso.byu.edu* (2007).
- [276] Kumar, H., Singh, A., Martinez, J. L., Alonso, J. A. & Tripathi, S. Unexplored signatures of magnetoelastic and isosymmetric metal-insulator phase transition in a rare-earth nickelate via mode crystallography. *Physical Review B* **106**, 214103 (2022).
- [277] Kroumova, E., Perez-Mato, J. & Aroyo, M. WYCKSPLIT: a computer program for determination of the relations of wyckoff positions for a group-subgroup pair. *Journal of Applied Crystallography* **31**, 646–646 (1998).
- [278] Capillas, C. *et al.* SYMMODES: a software package for group-theoretical analysis of structural phase transitions. *Journal of Applied Crystallography* **36**, 953–954 (2003).
- [279] Stokes, H. T., Orden, S. V. & Campbell, B. J. ISOSUBGROUP: an internet tool for generating isotropy subgroups of crystallographic space groups. *Journal of Applied Crystallography* **49**, 1849–1853 (2016).
- [280] Guo, R. *et al.* Origin of the high piezoelectric response in  $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ . *Physical Review Letters* **84**, 5423 (2000).

- [281] Dai, Y.-J., Zhang, X.-W. & Chen, K.-P. Morphotropic phase boundary and electrical properties of  $K_xNa_{1-x}NbO_3$  lead-free ceramics. *Applied Physics Letters* **94**, 042905 (2009).
- [282] Singh, A. K., Dubey, D. N., Singh, G. & Tripathi, S. Unambiguous evidence of three coexisting ferroelectric phases in a lead-free  $Li_xNa_{1-x}NbO_3$  system. *Applied Physics Letters* **116**, 232902 (2020).
- [283] Iwata, M. & Ishibashi, Y. Theory of morphotropic phase boundary in solid solution systems of perovskite-type oxide ferroelectrics: PE hysteresis loop. *Japanese journal of Applied Physics* **38**, 5670 (1999).
- [284] Lemanov, V., Smirnova, E., Syrnikov, P. & Tarakanov, E. Phase transitions and glasslike behavior in  $Sr_{1-x}Ba_xTiO_3$ . *Physical Review B* **54**, 3151 (1996).
- [285] Surampalli, A. *et al.* Evidence of structural modifications in the region around the broad dielectric maxima in the 30% Sn-doped barium titanate relaxor. *Physical Review B* **100**, 134104 (2019).
- [286] Prosandeev, S., Wang, D., Akbarzadeh, A. & Bellaiche, L. First-principles-based effective hamiltonian simulations of bulks and films made of lead-free  $Ba(Zr,Ti)O_3$  relaxor ferroelectrics. *Journal of Physics: Condensed Matter* **27**, 223202 (2015).
- [287] Osman, R. A. *et al.* Ferroelectric and relaxor ferroelectric to paraelectric transition based on lead magnesium niobate (PMN) materials. In *Advanced Materials Research*, vol. 795, 658–663 (Trans Tech Publ, 2013).
- [288] Uchino, K. Piezoelectric ceramics for transducers. *Ultrasonic Transducers* 70–116 (2012).
- [289] Yasuda, N., Ohwa, H. & Asano, S. Dielectric properties and phase transitions of  $Ba(Ti_{1-x}Sn_x)O_3$  solid solution. *Japanese Journal of Applied Physics* **35**, 5099 (1996).
- [290] Singh, A., Moriyoshi, C., Kuroiwa, Y. & Pandey, D. Evidence for diffuse ferroelectric phase transition and cooperative tricritical freezing of random-site dipoles due to off-centered  $Bi^{3+}$  ions in the average cubic lattice of  $(Ba_{1-x}Bi_x)(Ti_{1-x}Fe_x)O_3$ . *Phys. Rev. B* **85**, 064116 (2012).
- [291] Pramanick, A. *et al.* Dynamical origins of weakly coupled relaxor behavior in Sn-doped  $(Ba,Ca)TiO_3$ - $BiScO_3$ . *Physical Review B* **103**, 214105 (2021).
- [292] Zhuang, J. *et al.* Impact of quenched random fields on the ferroelectric-to-relaxor crossover in the solid solution  $(1-x)BaTiO_3$ - $xDyFeO_3$ . *Physical Review B* **98**, 174104 (2018).
- [293] Ke, S., Fan, H., Huang, H. & Chan, H. Lorentz-type relationship of the temperature dependent dielectric permittivity in ferroelectrics with diffuse phase transition. *Applied Physics Letters* **93**, 112906 (2008).
- [294] Tang, X., Chew, K.-H. & Chan, H. Diffuse phase transition and dielectric tunability of  $Ba(Zr_yTi_{1-y})O_3$  relaxor ferroelectric ceramics. *Acta Materialia* **52**, 5177–5183 (2004).

- 
- [295] Kleemann, W. Random fields in relaxor ferroelectrics—a jubilee review. *Journal of Advanced Dielectrics* **2**, 1241001 (2012).

## List of Publications

1. **Digvijay Nath Dubey**, Gurvinderjit Singh, and Saurabh Tripathi, Relaxor ferroelectricity driven by ‘A’ and ‘B’ site off-centered displacements in cubic phase with  $Pm\bar{3}m$  space group, Journal of Physics D: Applied Physics **54**, 365304 (2021).
2. **Digvijay Nath Dubey**, Gurvinderjit Singh, Akhilesh Kumar Singh, and Saurabh Tripathi, Role of  $\Gamma_4^-$  phonon mode in the enhancement of ferroelectric polarization in a perovskite-based eco-friendly functional material, EPL (Europhysics Letters) **140**, 26003 (2022).
3. Anuvrat Tripathi, **Digvijay Nath Dubey**, Harsh Kumar, and Saurabh Tripathi, Stabilising ferroelectricity in alkaline-earth-metal-based perovskites ( $ABO_3$ ) via  $A-(Ca^{2+}/Sr^{2+}/Ba^{2+})$  and  $B$ -site ( $Ti^{4+}$ ) cationic radius ratio ( $R_A/R_B$ ), Journal of Applied Crystallography **55**, 1446 (2022).
4. Abhinav Kumar Singh, **Digvijay Nath Dubey**, Gurvinderjit Singh, and Saurabh Tripathi, Tuning ferroelectricity by manipulating the global and local structure in a lead-free Sr doped  $Ba(Ti_{1-x}Sn_x)O_3$  ceramics, EPL (Europhysics Letters) **130**, 36002 (2020).
5. Abhinav Kumar Singh, **Digvijay Nath Dubey**, Gurvinderjit Singh, and Saurabh Tripathi, Unambiguous evidence of three coexisting ferroelectric phases in a lead-free  $Li_xNa_{1-x}NbO_3$  system, Applied Physics Letters **116**, 232902 (2020).

## Conferences/Schools

1. Gave an oral presentation on “Dielectrics 2022” organised by “IOP Institute of Physics” during 27/04/2022 to 29/04/2022.  
Paper title: Relaxor ferroelectricity in an average cubic ( $Pm\bar{3}m$ ) phase of a lead-free

smart material.

Authors: **Digvijay Nath Dubey**, Gurvinderjit Singh, and Saurabh Tripathi.

2. Attended “Rigaku School for Practical Crystallography”, organised by Rigaku Japan, January 10-21, 2022.

3. Poster presentation at “IUCr 2021- XXV General Assembly and Congress of the International Union of Crystallography”, organised by Czech and Slovak Crystallographic Association, Ostricová 668/5, Stodulky, 155 00 Praha 5 Czech Republic, during 14-22 Aug, 2021.

Paper Title: Ferroelectricity driven by ‘A’ and ‘B’ site off-centered displacements in cubic phase with  $Pm\bar{3}m$  space group.

Authors: **Digvijay Nath Dubey**, Gurvinderjit Singh, and Saurabh Tripathi.

4. Gave an oral presentation at “4<sup>th</sup> International Conference on Science and Engineering of materials”, organised by School of Basic Sciences and Research, Department of Physics, Sharda University, during July 19-22, 2021.

Paper Title: Ferroelectricity driven by ‘A’ and ‘B’ site off-centered displacements in cubic phase with  $Pm\bar{3}m$  space group.

Authors: **Digvijay Nath Dubey**, Gurvinderjit Singh, and Saurabh Tripathi.

5. Attended “International Conference on Recent Advances in Material Science”, organized By Department of Physics HNB Garhwal University, Srinagar Uttarakhand-India, during May 15-17, 2021.

6. Attended “International Conference on Functional Materials and Applied Physics”, organised by Sardar Vallabhbhai National Institute of Technology, Surat, during May 14-15, 2021.

