A research team led by users from Pennsylvania State University, in collaboration with the X-ray Microscopy Group at the Center for Nanoscale Materials and with the Center for Nanophase Materials Sciences, recently reported observation of novel monoclinic sub-phases in ferroelectric BaTiO3. These new low-symmetry intermediate phases are found to be locally stabilized near thermotropic phase boundaries in simple ferroelectrics and exhibit large enhancements in the existing nonlinear optical and piezoelectric property coefficients relative to the parent material. This discovery presents unique opportunities for the design of 'green' high-performance nanoscale energy materials. The findings reveal that phase transitions in ferroelectrics are intimately coupled to the underlying domain microstructure. Even in lead-free BaTiO3 and KNbO3, classic materials that have been known and studied for over 60 years, this new observation shows that domains can lend a thermotropic character to their otherwise well-known phase transitions. This leads to the emergence of intermediate monoclinic phases in a wide temperature range around the conventional inter-ferroelectric transitions. As this phenomenon arises due to the mechanical and dipolar interactions between competing ferroelectric-ferroelastic domains in a complex domain microstructure, advanced nanoscale-resolved multi-technique measurements in the same spatial location, such as those presented in this work, are required to properly reveal the underlying physics on a microscopic level. This work shows that in the stabilized intermediate phases, both the piezoelectric and the nonlinear optical properties can be strongly enhanced, and even newly induced. Since the mechanism of symmetry lowering through stresses and fields is in principle universal to all nontriclinic ferroelectric crystal systems, these results suggest a host of possibilities for the design of high-performance phases which can create unique nanoscale energy materials from simple lead-free ferroelectrics.

Reference:
“Thermotropic phase boundaries in classic ferroelectrics”
T. T. A. Lummen (PSU), Y. Gu (PSU), J. Wang (PSU, Beijing), S. Lei (PSU), F. Xue (PSU), A. Kumar (PSU, CNMS), A. T. Barnes (PSU), E. Barnes (PSU), S. Denev (PSU), A. Belianinov (CNMS), M. V. Holt (CNM), A. N. Morozovska (NAS Ukraine), S. V. Kalinin (CNMS), L.-Q. Chen (PSU), and V. Gopalan (PSU)
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